EXPLORING THE SYNTHETIC UTILITY OF VINYLDICHLOROSILANES AND VINYLARYLSILANES

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ABSTRACT

The addition of electrophiles to styrylsilanes when electronegative chloride ligands replaced electron-donating ligands on silicon has been investigated. These addition reactions were shown to be advantageous over the normal electrophilic substitution reactions found in the literature, in that the retained silicon may subsequently direct the regiochemistry and stereochemistry of further synthetic reactions. In addition, the retained silicon offers the advantage of being replaced by other useful functional groups, in a controllable manner, as we have demonstrated by an oxidative cleavage reaction. Our results showed that allylsilanes, unlike vinyl silanes, perhaps due to their inherently higher reactivity (relative to vinylsilanes), are not prone to electrophilic addition when electron-withdrawing ligands are placed on silicon. Our experimental results also suggest that the success of these addition reactions depends on the stability of the intermediate adduct cations formed; addition products are typically obtained for the more stable cations.

Carbocationic organosilicon chemistry has been dominated by the ability of silicon to electronically stabilize positive charges in the β-position, thereby influencing the reactivity of species that pass through such stabilized intermediates. However, steric influences on reactivity are not so well documented. Therefore, the reactivity of arylsilylstyrenes when the silylaryl group is sterically crowded with methyl substituents was investigated. The ability of silicon to effect electrophilic substitution on the silylaryl

substituent of (*E*)-β-(dimethylmesitylsilyl)styrene rather than on the silylstyryl substituent, even though substitution on the arene required destroying aromaticity, is reported. This anomaly has been rationalized as being primarily due to steric factors.

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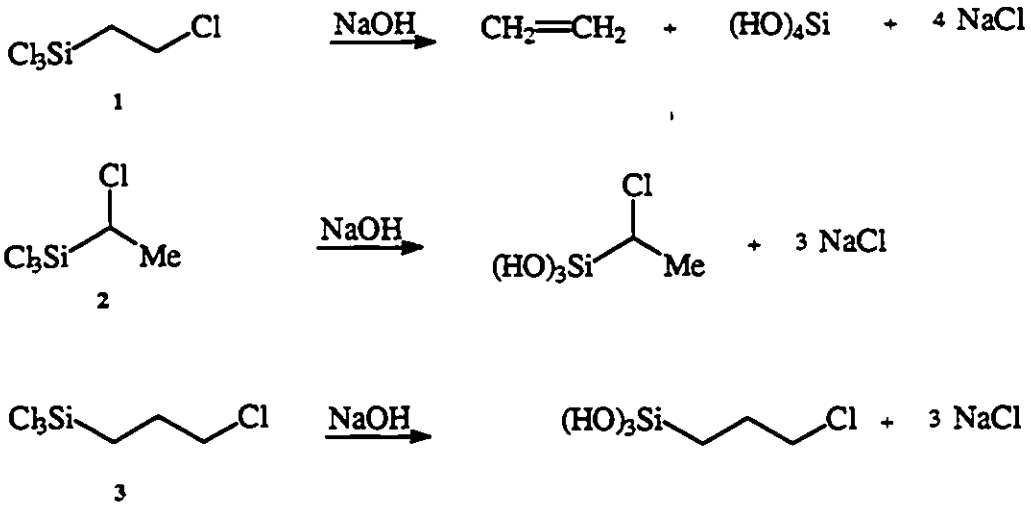
CHAPTER 1

INTRODUCTION

1.1) The nature of the β-silicon interaction with carbocations

The discovery of the β-effect has been credited to the work of Ushakov and Itenberg.[1] The following fifty years saw much mechanistic, theoretical and synthetic work that clarified and utilized the interaction of silicon with β-carbocations. The nature of the β-silicon interaction with carbocations has been the subject of much controversy. Sommer, Whitmore and coworkers reported the high reactivity of β-chlorosilane **1** in comparison to α-chlorosilane **2** and γ-chlorosilane **3** (Scheme 1.1).[2]

Scheme 1.1



Sommer initially favored rate determining Si-C cleavage to a silylium ion and a carbanion, followed by loss of Cl^- (E_{1cb} mechanism).[2] A concerted *syn*-elimination of Me_3Si/Cl was briefly favored by Eabern for the analogous compound $Me_3SiCH_2CH_2Cl$.[3] Other possible mechanisms included rate determining attack of solvent or base on the C-Cl bond (S_N2), and rate determining attack by solvent or base on silicon (E_2).[4] Rate determining cleavage of the C-Cl bond to form a carbocation (E_1) was also proposed.[4] The majority of evidence today favors the latter (E_1) mechanism.

One of the earliest mechanistic studies involved the solvolysis of $Me_3SiCH_2CH_2Cl$ in aqueous ethanol and formic acid.[5] This study established that the reaction rate was dependent upon the ionizing power of the solvent, while independent of solvent nucleophilicity. Other solvolysis studies carried out with *erythro*-1,2-dibromopropyltrimethylsilane supported the observation that reaction rate accelerated with increasing ionization power of the solvent.[6] Sommer[5] and Jarvie[6] independently carried out these solvolysis studies, and were able to conclude separately from their observations that the rate determining step could not be the concerted *syn*-elimination route. A concerted mechanism would show little or no dependency on solvent ionizing power. Because of the independence of the reaction rate with solvents of varying nucleophilicity, mechanisms involving attack by solvent or base in the rate determining step were also rejected.[5,6] Sommer and coworkers[5] concluded that, "strong participation of electron release from silicon in the rate controlling transition state occurs without simultaneous

nucleophilic attack by the solvent on the silicon atom". Thus, a β-silicon cation was implicated in the solvolysis (E_1) of compounds having a β-silicon leaving group.

The E_1 mechanism was also probed with the help of deuterium isotope studies. The compound $Me_3SiCH_2CD_2Br$ **4** was prepared and its solvolysis rate in aqueous ethanol (Equation 1.1) determined and compared with that for the non-deuterated compound.[6] The isotope effect obtained ($k_H/k_D = 1.10$), is expected (i.e., $k_H/k_D > 1.0$) when there is a change in hybridization from sp^3 to sp^2 at the α-carbon to which the leaving group (bromide) is attached, as is the case for the E_1 mechanism.[6]

Equation 1.1

$$\underset{\mathbf{4}}{Me_3SiCH_2CD_2Br} + ROH \longrightarrow Me_3SiOR + CH_2CD_2 + HBr$$

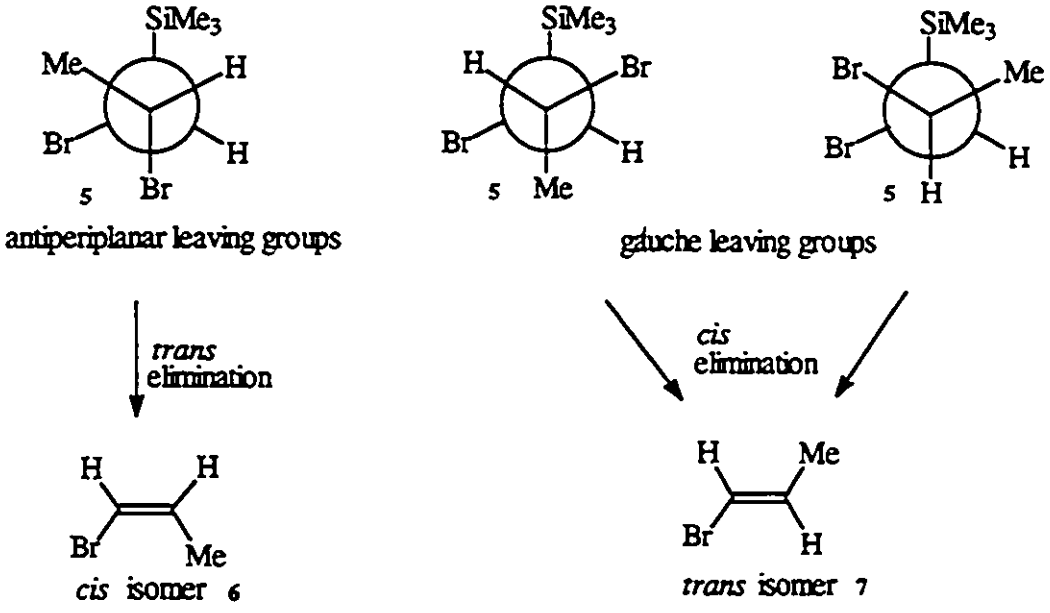
E_2 reactions have values of k_H/k_D much closer to unity than E_1 reactions on account of the increased crowding or coordination expansion in the transition state of the carbon α to the leaving group.[6]

Isotope studies were also carried out for $Me_3SiCHDCH_2Br$, which has deuterium adjacent to silicon, and the undeuterated analogue. A small difference in the rates of solvolysis ($k_H/k_D = 1.02$) was observed for these two compounds.[6] The lack of any significant isotope effect here suggests very little Si-C bond breakage in the rate determining step.[6] A normal isotope effect in the direction $k_H/k_D > 1$ would be expected if

the atoms CHD and CHH, adjacent to silicon in the deuterated and undeuterated analogues, were in the same plane owing to the partial detachment of the Me_3Si group.

The stereochemistry of solvolysis was elucidated by Jarvie, Holt and Thompson.[7] The solvolysis of *erythro*-$Me_3SiCHBrCHBrCH_3$ **5** led predominantly to *cis*-1-bromopropene **6** (Scheme 1.2).[7] This stereochemical outcome is possible when the leaving groups (Br and Me_3Si) are antiperiplanar to each other (Si-C-C-Br dihedral angle 180°, Scheme 1.2).[7] Synperiplanar (Si-C-C-Br dihedral angle 0°) or gauche (Si-C-C-Br dihedral angle 60°) arrangements would lead to the *trans* isomer **7**, which was not observed (Scheme 1.2).

Scheme 1.2

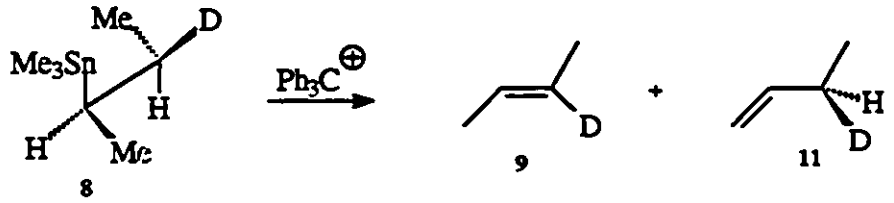


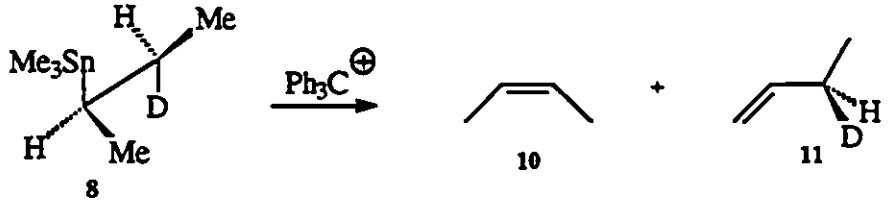
The *anti*-elimination products, reported by Jarvie and coworkers (Scheme 1.2),[7] may also be explained by a concerted E_2 mechanism, i.e., synchronous, *anti*-elimination of Br and Me_3Si. However, the high correlation between reaction rate and solvent ionizing power suggested considerable charge development in the transition state, such as would be expected from an E_1 mechanism, involving rate determining C-Br ionization.[4] The antiperiplanar geometric preference for elimination was further consolidated by the work of Hudrlik and Peterson.[8]

Similar stereochemical findings were reported by Traylor and coworkers for the dehydrometalation of organotin compounds (Scheme 1.3).[9] Thus, *threo*-3-deuterio-2-(trimethylstannyl)butane **8** reacted with trityl tetrafluoroborate to yield *trans*-2-deuterio-2-butene **9**, *cis*-2-butene **10**, and 3-deuterio-1-butene **11** (Scheme 1.3).[9] The results indicated that elimination took place *via* the antiperiplanar geometry in preference to a *syn*-elimination mechanism.

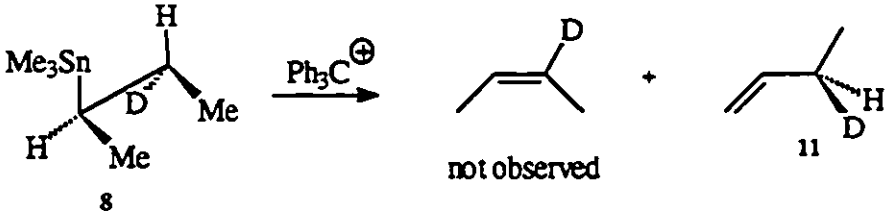
Scheme 1.3

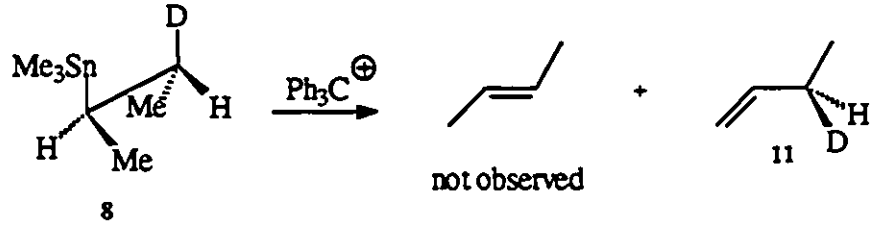
Antiperiplanar leaving groups





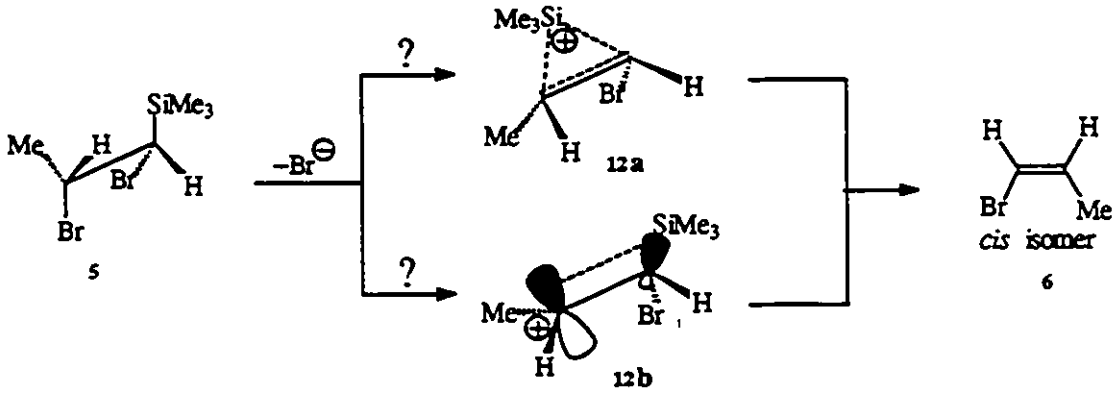
Synperiplanar leaving groups





During the 1960s, the major issue in need of clarification was whether the interaction of silicon occurred entirely by hyperconjugation **12b** (also called vertical stabilization and defined as a process without significant movement of the Si-C bond in the transition state or intermediate), or by internal neighboring group participation (referred to as anchimeric assistance or non-vertical stabilization) to form a three-membered ring (eg., silacyclopropane cation **12a**, Scheme 1.4). Jarvie[7] favored the cyclic (non-vertical stabilization) intermediate **12a**, having strong kinetic assistance from the inductive release by silicon.

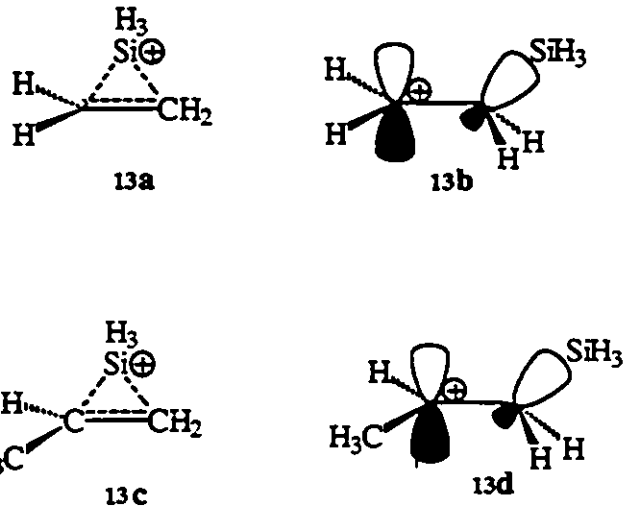
Scheme 1.4



Jorgensen's calculations found the bridged cation **13a** to be about 2.4 kcal/mole more stable than the open cation **13b** for primary carbons, and the open form was not an energy minimum (Figure 1.1).[10] In the secondary carbocation, however, the open form **13d** was

found to be about 4 kcal/mol more stable than the bridged form **13c**, and the bridged form was not an energy minimum (Figure 1.1).[10]

Figure 1.1



Thus, direct calculations did not provide a clear answer as to which form of the cation is more stable.[11] Moreover, theory addresses only the fully developed carbocation, whereas the actual transition state has only a partial positive charge and a weakly bonded leaving group.

Treatment of $Me_3SiCH_2CD_2OH$ **14** (Equation 1.2) with PBr_3 gave equal amounts of the directly substituted bromide **15**, together with the rearranged substituted bromide **16**.[6]

Equation 1.2

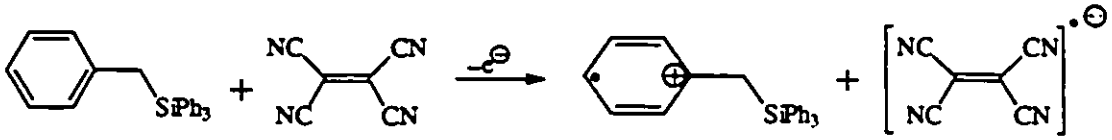
$$\underset{\textbf{14}}{Me_3SiCH_2CD_2OH} + PBr_3 \longrightarrow \underset{\textbf{15}}{Me_3SiCH_2CD_2Br} + \underset{\textbf{16}}{Me_3SiCD_2CH_2Br}$$

A similar rearrangement was observed by Eaborn and coworkers.[12] Jarvie[6] and Eaborn[12] proposed that the scrambling was consistent with either a symmetrical silacyclopropyl cation or the open cation. For the open cation, a rapid 1,2 shift of the Me_3Si group ($Me_3SiCH_2CD_2^+ \rightleftharpoons Me_3SiCD_2CH_2^+$) was proposed to explain the rearrangement.[6,12] The absence of the species $Me_3SiCHDCHDBr$ was regarded as an indication that hydrogen or deuterium rearrangement did not contribute significantly to the observed rearrangement.[6,12]

Traylor and coworkers provided the first set of evidence that tilted the balance in favor of a vertical or hyperconjugation process, called the β-effect.[13,14,15,16,17] One way of deciding whether a group acts to stabilize a positive charge by either a non-vertical or a vertical process is to study the effect of that group on an established vertical process. Such a vertical process, for example charge-transfer absorption, occurs too rapidly to allow the nuclear movement which accompanies non-vertical stabilization.[17] Therefore, the energy of a vertical process cannot be lowered by internal nucleophilic displacement (non-vertical movement of silicon), since this requires considerable movement by the stabilizing group.[17] Traylor and coworkers, measured the ionization potentials from

charge-transfer absorptions and were able to show that Me_3SiCH_2 does exert a significant stabilizing effect on this vertical process.[13-17] The charge-transfer complexes used involved a π-donor (benzene derivative **17**) and a π-acceptor (tetracyanoethylene **18**, Scheme 1.5). The magnitude of the stabilization obtained from the charge-transfer complexes (σ^+_p-Me_3SiCH_2) was comparable with that measured for other reactions such as solvolysis which places the positive charge in a similar position β to silicon.[13-17]

Scheme 1.5



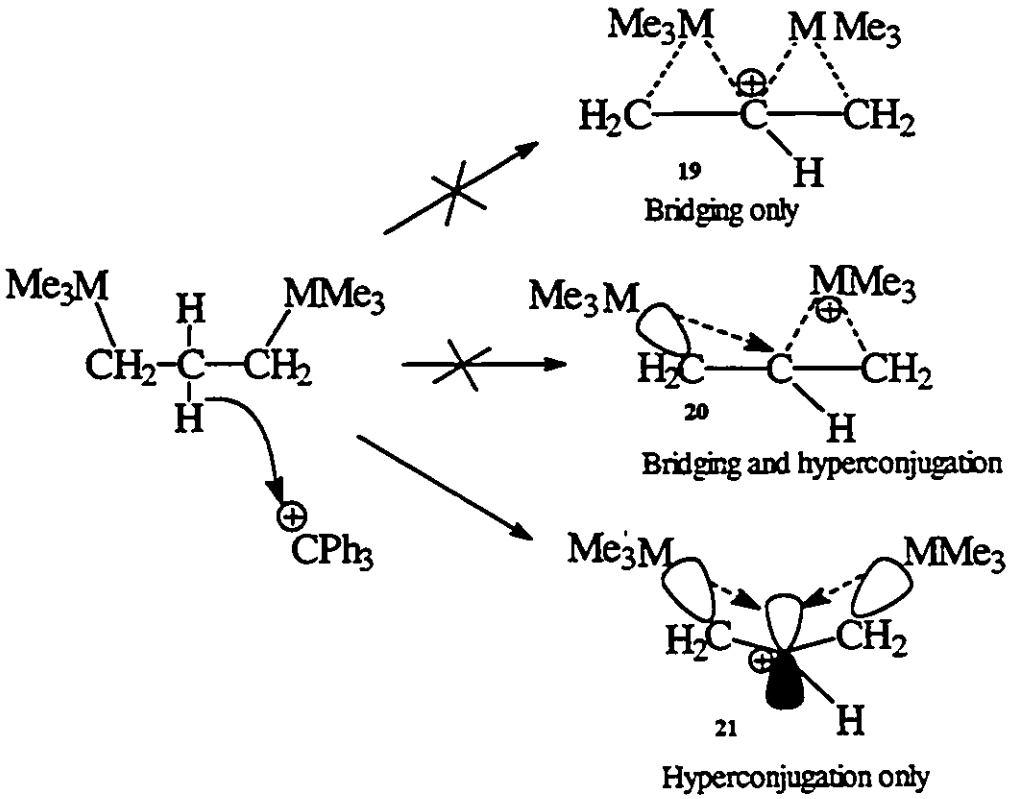
17 **18**

Traylor and coworkers therefore concluded that these different reactions (charge-transfer absorption and solvolysis), having similar magnitude for the β-Si stabilization, all occurred *via* transition states that do not require nuclear movement.

Having established that dehydrometalation reactions proceeded with *anti* stereochemistry, Traylor and Koerner proposed that the most effective way for two Group 14 elements to participate in the stabilization of a common carbocation β to both elements was by both elements being *anti* to the leaving group (Scheme 1.6).[17] Since Me_3M (M equals C, Si, Ge, Sn, Pb) groups are large, they were expected to engender

considerable steric repulsion, and thus small rate acceleration, if both groups participated as a bridged intermediate **19** (Scheme 1.6).[17]

Scheme 1.6



The two potentially stabilizing bridging groups (MMe_3) would be in competition with each other, instead of simultaneously augmenting the stabilization of each other.[17] A combination of $(\sigma\text{-p})\pi$ hyperconjugation and a bridged intermediate **20** (Scheme 1.6), would also be expected to generate considerable steric repulsion, and thus small rate

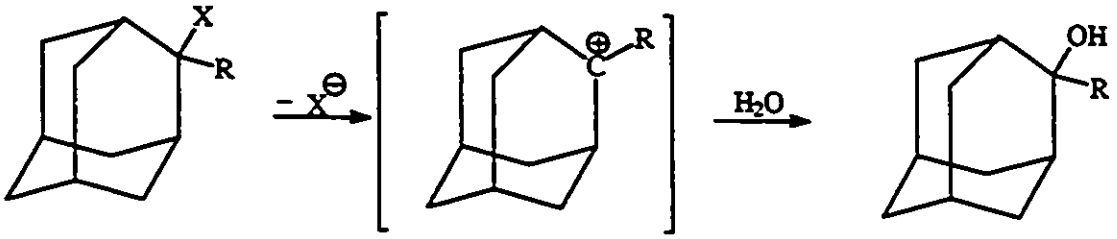
acceleration, between one stabilizing Group 14 element and the other.[17] This hypothesis, regarding small rate acceleration accompanying bridging, was established in a related reaction where an increase in the rate by a factor of less than two was observed for bridging by two phenyl groups relative to bridging by one phenyl group.[17] On the other hand, simultaneous hyperconjugation by two Group 14 elements as shown in **21** (Scheme 1.6) should not generate considerable steric repulsion since significant movement by the elements towards each other does not take place.[17] The lack of steric repulsion between the two Group 14 elements should therefore lead to each group augmenting the stabilization provided by the other, resulting in substantial rate acceleration. It was observed that the stabilization of the transition state provided by both MMe_3 group was additive and therefore quite substantial, leading to an increase by orders of magnitude in the reaction rate. For these reasons, dehydrometalation reactions were thought to occur with hyperconjugative $(\sigma\text{-p})\pi$ stabilization.[17] The accumulative hyperconjugation stabilization in **21** provided by the two Group 14 elements was obtained from the Hammett-type relationship, $\log k_2 = \rho\Sigma\sigma^+ + \text{constant}$ where $\Sigma\sigma^+$ is the sum of $\sigma^+CH_2MMe_3$ for both metals.

Recently, ^{13}C and ^{29}Si NMR spectroscopic studies and photochemical studies have been used to confirm the existence of β-Si carbocations.[18,19,20]

1.1.1) A question of silicon inductive interactions with carbocations

Ibrahim and Jorgensen used theoretical calculations to provide an upper limit for β-Si inductive stabilization; their calculations did not show any inductive stabilization of a primary cation by a β-SiH_3 group.[10,21] Calculations by Lambert and coworkers indicated a β-$SiMe_3$ inductive acceleration of the reaction rate of magnitude (k_{Si}/k_H) 10^2; insufficient to explain the large rate acceleration (k_{Si}/k_H 10^{12}) observed experimentally.[11,22,23,24,25,26,27] The upper limit for the β-Si inductive contribution to the stabilization of carbocations may be gleaned by looking at the magnitude of the α-Si inductive effect. It has been well established that an α-Me substituent provides a large stabilization to carbenium ions. For instance, the calculated stabilization energy of the classical ethyl cation (34 kcal/mol at the MP3 level) is in good agreement with the experiment value (36.4 kcal/mol).[10] Theoretically, however, the α-SiH_3 group (17.8 kcal/mol at the MP3 level) is much less effective than a methyl group in stabilizing the primary carbocation, inspite of silicon being more electropositive than carbon.[10] *Ab initio* calculations also indicate that α-SiH_3 substituted carbenium ions are less stable than their α-CH_3 substituted counterparts by approximately 18, 14 and 19 kcal/mol for primary, secondary and tertiary cations, respectively.[28] Theory is consistent with experimental observations. Thus, Apeloig and Stanger reported that the α-$SiMe_3$ group in 2-adamantyl derivative **24**, stabilized the carbenium ion center 12-14 kcal/mol more than hydrogen **22** and 6-8 kcal/mol less than the α-CH_3 group **23**.[28]

Scheme 1.7



X = *p*-$O_2NC_6H_4COO$

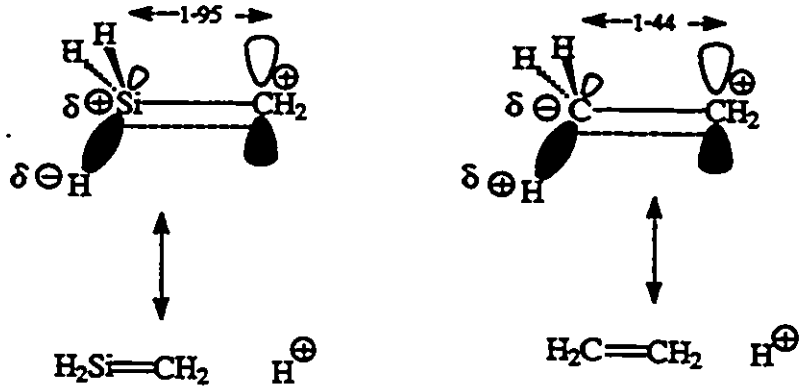
R = H, 22
CH_3, 23
$SiMe_3$, 24

Further experimental evidence for the relatively weak α-Si stabilization was demonstrated by additional solvolysis data. For example, no detectable reaction of Me_3SiCH_2X (X = Br, Cl) was observed in aqueous solvents at 70 °C.[29] $PhCMe(SiMe_3)Br$ also solvolyses slower than $PhCMe_2Br$, while Me_3SiCMe_2Br solvolyses 3800 times slower than Me_3CCMe_2Br.[29]

The smaller stabilization of a carbocation by the α-silyl group compared to the α-methyl group is due to several reasons. For example, the longer Si-C^+ bond length (Si-C^+ 1.95 Å, compared to C-C^+ 1.44 Å) is thought to contribute to poor hyperconjugative overlap (i.e., between Si-H and the empty p-orbital on carbon, Figure 1.2).[10] Pitt estimates an approximately 50% decrease in σ-π-orbital overlap on increasing bond length from 1.54 Å to 1.87 Å.[32] The longer Si-C^+ bond distance also reduces inductive donation by silicon.[10,15,32] Furthermore, hyperconjugation results in a canonical structure having

Si-C double bonds, which are weaker than C-C double bonds on account of the poorer π-orbital overlap between orbitals of different sizes (Figure 1.2).

Figure 1.2



As a result of the small stabilization afforded a carbenium ion by an α-Si group, β-Si stabilization was not considered to be primarily an inductive effect; inductive release is known to be more pronounced over shorter distances. Therefore, β-Si inductive contribution to stabilization should be even less effective than α-Si inductive stabilization. Furthermore, the inductive effect is a through-bond effect and should be independent of the dihedral angle of the Si-C-C-X fragment. We shall see in the next section that β-Si stabilization is indeed angular dependent.

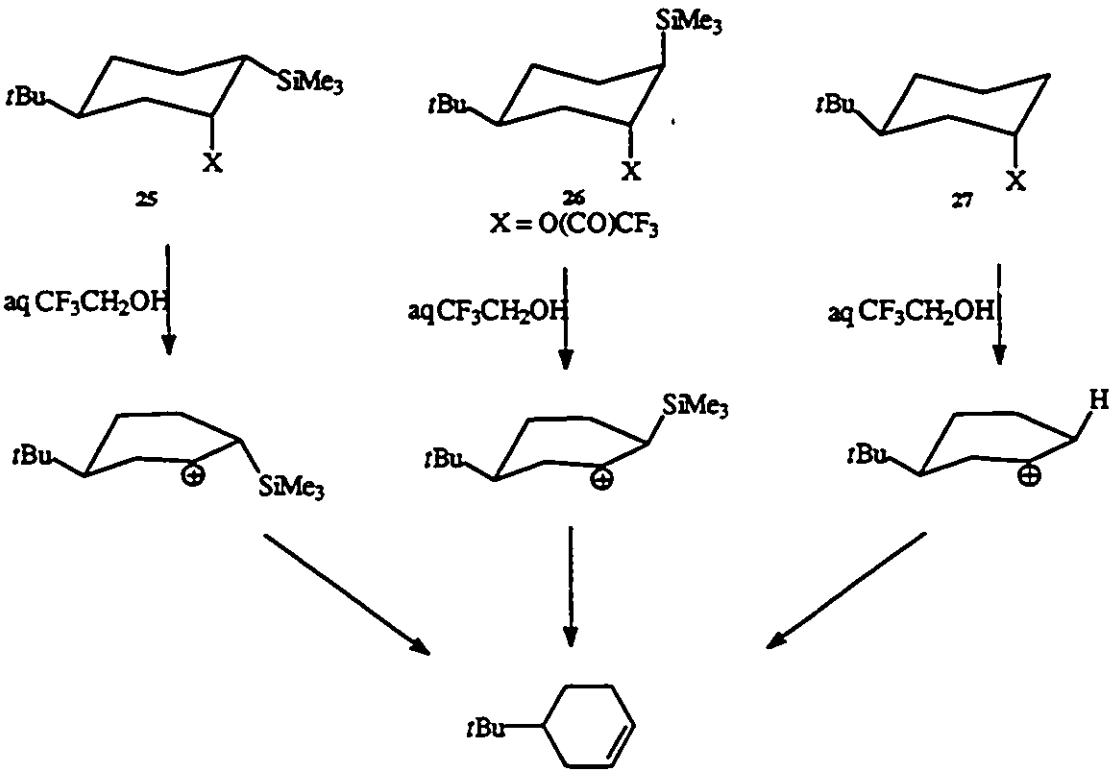
1.1.2) Geometric dependence of the β-effect

We have seen from the earlier solvolysis studies of Sommer,[5] Jarvie,[6] and Hurdlik[8] that there is a preference for *anti*-alignment of the Si-C σ-bond with the developing empty p-orbital of the carbocation. This geometric dependence of the β-effect has been observed in many elegant studies carried out by Lambert and coworkers.[11,22-27] Non-vertical stabilization *via* the silacyclopropyl cation should take place primarily in the antiperiplanar geometry where there is an Si-C-C-X dihedral angle of about 180° (X is the leaving group).[11] At dihedral angles smaller than 180°, a rapid decrease in the reaction rate is expected for non-vertical (bridging) stabilization.[11] Below 90° (especially at Si-C-C-X dihedral angle 0°), severe steric interaction between silicon and the leaving group should inhibit internal nucleophilic assistance by silicon.[11] Thus, at 0° Si-C-C-X dihedral no β-Si stabilization should be possible for non-vertical stabilization.[11] On the other hand, hyperconjugative (vertical) stabilization by silicon should show a dependence of the reaction rate on the cosine square of the dihedral angle.[11] Thus, for vertical stabilization, rate acceleration maxima would be expected at Si-C-C-X dihedral angles of 180° and 0°.[11]

In an attempt to establish the nature of β-Si involvement with carbocations, Lambert and coworkers synthesized several compounds with varying Si-C-C-X dihedral angles. Solvolysis studies were conducted on the compounds 5-*tert*-butyl-*trans*-2-(trimethylsilyl)cyclohexyl-*trans*-trifluoroacetate **25** and 5-*tert*-butyl-*cis*-2-(trimethylsilyl) cyclohexyl-*trans*-trifluoroacetate **26**, in 97% aqueous trifluoroethanol (Scheme 1.8).[23]

The *trans*-diaxial molecule **26** reacted 10^{12} (k_S/k_H) times faster than cyclohexyltrifluoroacetate **27**, under similar conditions.[23]

Scheme 1.8

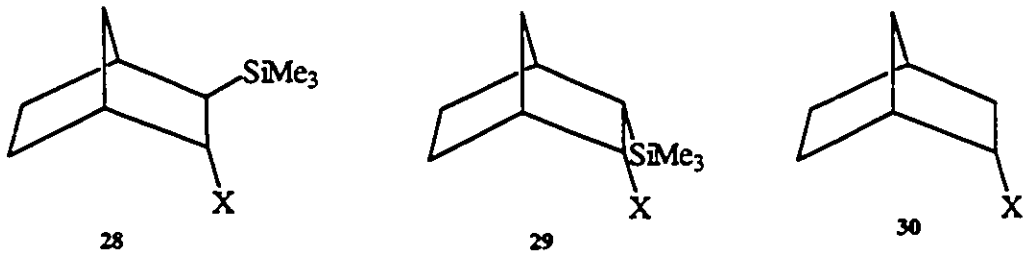


This conformationally rigid molecule **26**, which has the trimethylsilyl and leaving groups "frozen" into the antiperiplanar relationship (Si-C bond has a dihedral angle 180° with respect to the C-X bond), gave the largest experimental rate acceleration in solution observed so far. The rate acceleration was much less for the equatorial-axial

cyclohexylderivative **25** ($k_S/k_H = 4 \times 10^4$), where the Si-C bond makes a dihedral angle of 60° with the C-X bond.[23]

Solvolysis studies were also effected on *exo*-3-(trimethylsilyl)-*endo*-2-norbornyltrifluoroacetate **28** and *endo*-3-(trimethylsilyl)-*endo*-2-norbornyltrifluoroacetate **29** in aqueous trifluoroethanol (Figure 1.3).[11] *Endo*-3-(Trimethylsilyl)-*endo*-2-norbornyltrifluoroacetate **29** which has an Si-C-C-X dihedral angle of 0°, gave a significant rate enhancement ($k_S/k_H = 10^5$) relative to *endo*-2-norbornyltrifluoroacetate **30**, which lacks the trimethylsilyl group.[11] While, *exo*-3-(trimethylsilyl)-*endo*-2-norbornyltrifluoroacetate **28** which has an Si-C-C-X dihedral angle of 120°, gave a rate enhancement (k_S/k_H) of 1.7×10^5.[11]

Figure 1.3



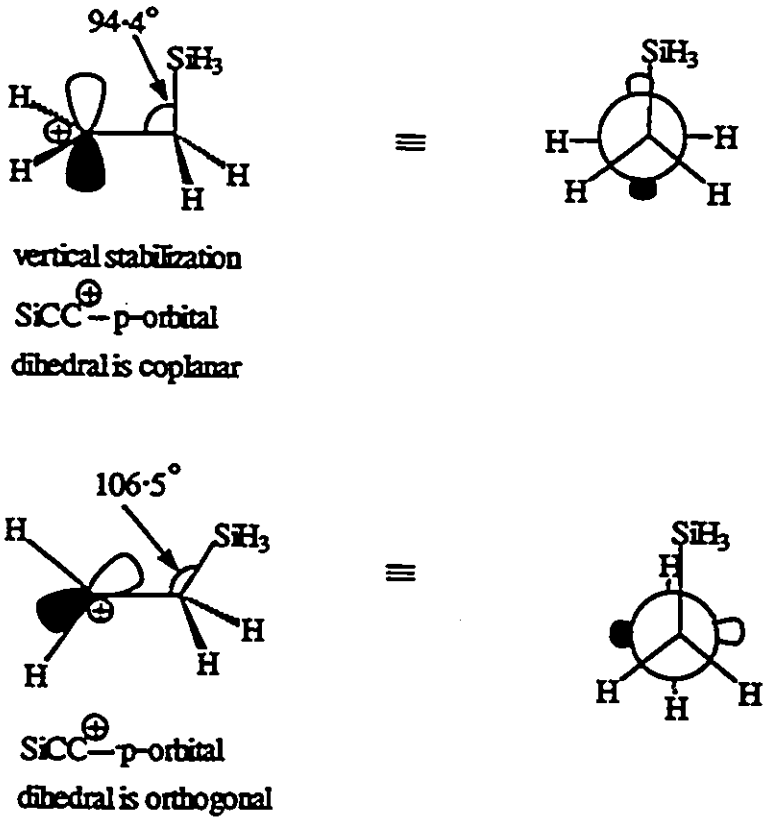
28 **29** **30**

X = O(CO)CF$_3$

As was pointed out earlier, vertical or hyperconjugative stabilization by silicon was expected to be significant for both the antiperiplanar and synperiplanar geometries.[11]

Theory has supported the superiority of the antiperiplanar overlap over the synperiplanar overlap. One explanation given is that there is greater steric inhibition to orbital overlap in the synperiplanar stereochemistry.[11] Calculations by Jorgenson[10] and Lambert[24,25] on primary alkyl cations have indicated that the so-called vertical transition state actually involves considerable movement of the silicon atom (Si-C-C$^+$ angle 94.4°, Figure 1.4), away from the normal tetrahedral geometry towards an optimized geometry for overlap.

Figure 1.4

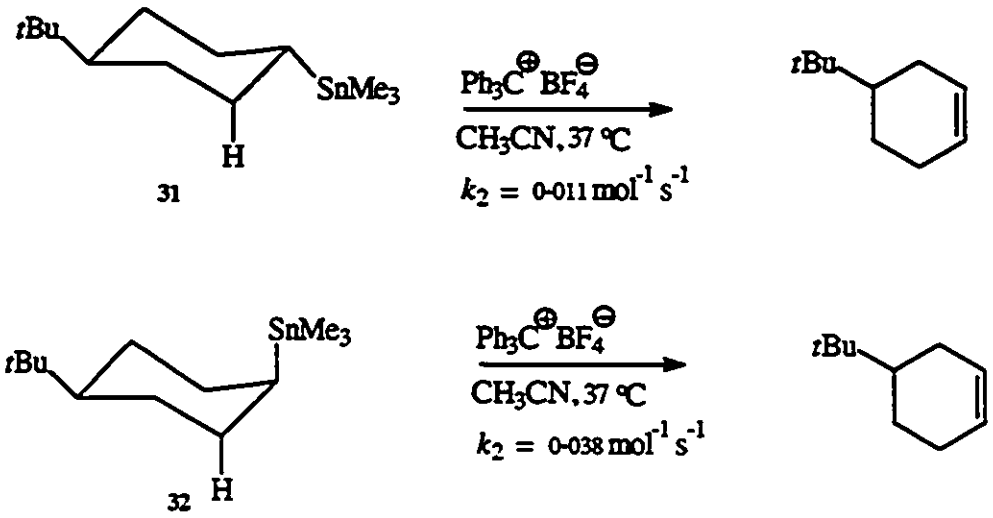


Hyperconjugative interaction will be optimum when the Si-C-C bond and the vacant orbital are parallel and the Si-C-C$^+$ angle is 90°.[32] Significant movement towards this optimized geometry brings silicon closer to the leaving group when silicon is *syn* to the leaving group, sterically inhibiting (σ-p)π-orbital overlap.[11] For this reason the β-effect is smaller in the *syn*-alignment relative to the *anti*-alignment.

The geometric dependence of the β-effect has also been corroborated by theoretical calculations. Thus, Lambert and coworkers calculated a 15.8 kcal/mol increase in stabilization for the silyl substituted cyclopentyl cation relative to the unsubstituted cyclopentyl cation when the β-silyl group was in the pseudoaxial geometry.[25] A much smaller increase was calculated when the β-silyl group was in the pseudoequatorial position.[25]

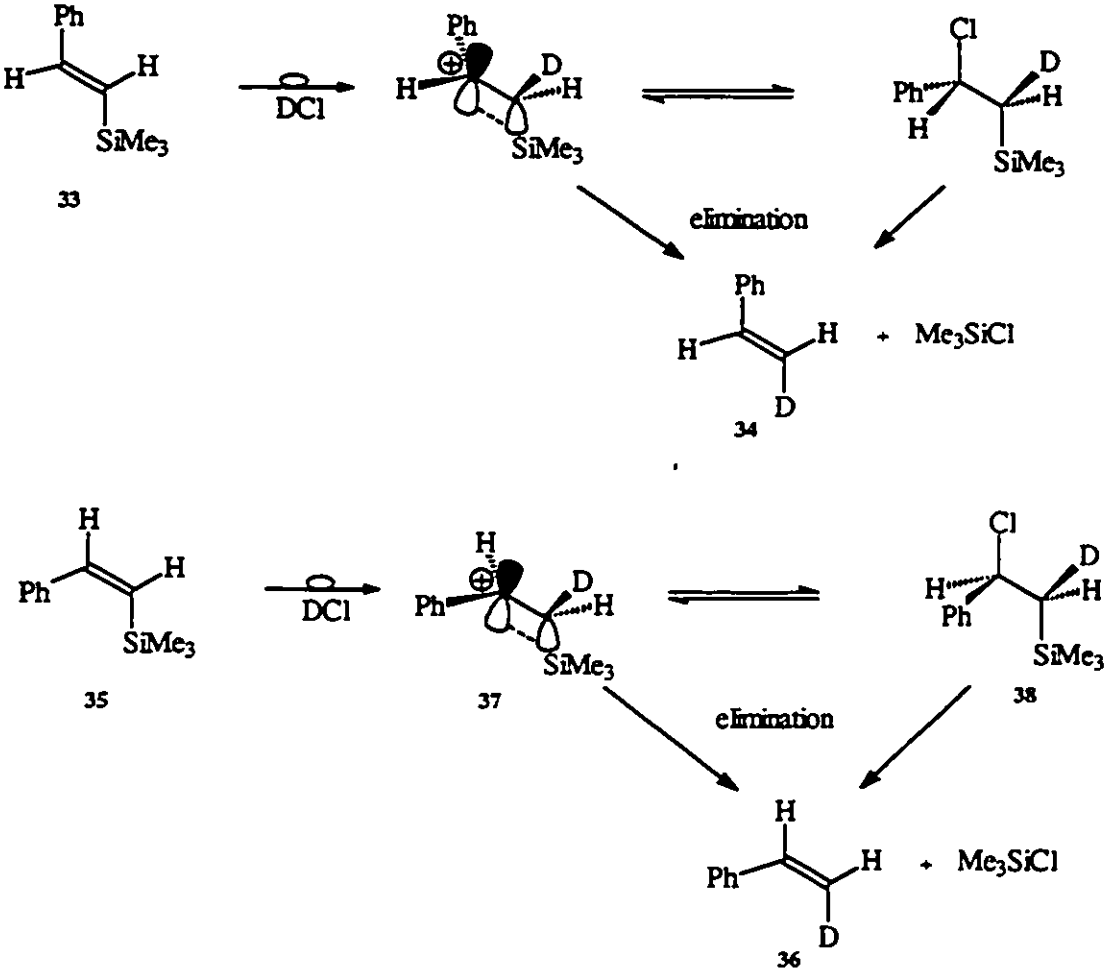
Traylor and others have similarly demonstrated a preference for the antiperiplanar alignment between silicon and the departing group in dehydrometalation reactions. For example, the abstraction of hydride from cyclohexyltin derivatives was much more facile for **32**, where the leaving group and trimethyltin group were *trans*-diaxial to each.[16] The rate was slower for **31**, where the leaving group and trimethyltin group have an axial-equatorial arrangement (dihedral angle 60°, Scheme 1.9).[16]

Scheme 1.9


tBu
SnMe3
H
31
Ph3C⊕BF4⊖
CH3CN, 37 °C
k2 = 0-011 mol-1 s-1
tBu
SnMe3
tBu
H
32
Ph3C⊕BF4⊖
CH3CN, 37 °C
k2 = 0-038 mol-1 s-1
tBu

The reaction of deuterium chloride with (*E*)-β-trimethylsilyl styrene **33** also proceeds with stereochemical dependence (Scheme 1.10). Formation of (*E*)-β-deuteriostyrene **34**, as the only product, indicated a preference for coplanar geometry between the Si-C σ-bond and the empty p-orbital.[38]

Scheme 1.10



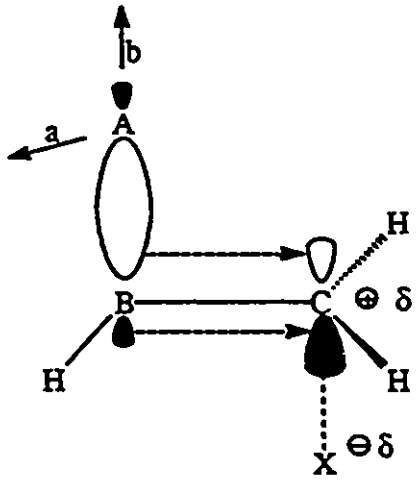
Similarly, (*Z*)-β-trimethylsilylstyrene **35** yields equally pure (*Z*)-β-deuteriostyrene **36** upon reaction with deuterium chloride.[38] Koenig and Weber proposed a mechanism to explain these results.[38] This mechanism involved deuteron addition to the double bond occurring simultaneously with rotation about the developing C-C single bond in the direction that permitted continuous hyperconjugative overlap between Si-C and the developing p-orbital of the transition state.[38] The β-stabilized cationic intermediate **37** could also be in equilibrium with the adduct **38** resulting from *cis*-addition of DCl to the vinyl silane.[38] Subsequent *anti*-elimination of $SiMe_3$/Cl gave products **34** and **36** in which the original stereochemistry of the reactant vinylsilanes **33** and **35** was retained.[38]

1.1.3) Vertical stabilization of carbocations by β-silicon: general considerations

For the hypothetical model compound shown in Figure 1.5, the stabilization provided to the transition state arises from delocalizing the AB σ-bond and from the formation of $B{=}CH_2$ π-bond. Thus, we expect this hyperconjugation to be enhanced by any structural change which makes the AB σ-bond more delocalizable or polarizable or increases the strength of the $B{=}CH_2$ π-bond. Since the sp^3 hybrid orbitals of B have to overlap with the developing p-orbital of C, the extent of this overlap will be dependent upon the electronegativity[15,42-50] and position[10,15] of A. For instance, the σ-orbital of B will overlap less with A and more with C if A, by some geometrical constraint, is forced away from the normal equilibrium position.[15] Either bending (direction a, Figure 1.5) or

stretching (direction b) the A-B bond should have this effect. In addition, lowering the electronegativity of A decreases the probability that the electrons will be near A and this should result in better B-C (σ-p)π-bonding. Finally, changing B or C to atoms having a strong π-bond would also be expected to strengthen (σ-p)π hyperconjugation.

Figure 1.5



1.1.4) The effect of varying Group 14 elements on β-carbocations

As we proceed down Group 14, the stabilization afforded by the elements increases. Lambert, for instance, found that the acceleration provided by Ge (k_{Ge}/k_H) exceeded that for Si (k_{Si}/k_H) by a factor of 10, for analogous molecules with the same dihedral angle (Scheme 1.11, Table 1.1).[26] The acceleration afforded by Sn (k_{Sn}/k_H) exceeded that for Si by several orders of magnitude. Thus, the stabilization afforded a carbocation by β-positioned Group 14 element increases as the element becomes more electropositive, and as hyperconjugation increases.

Scheme 1.11

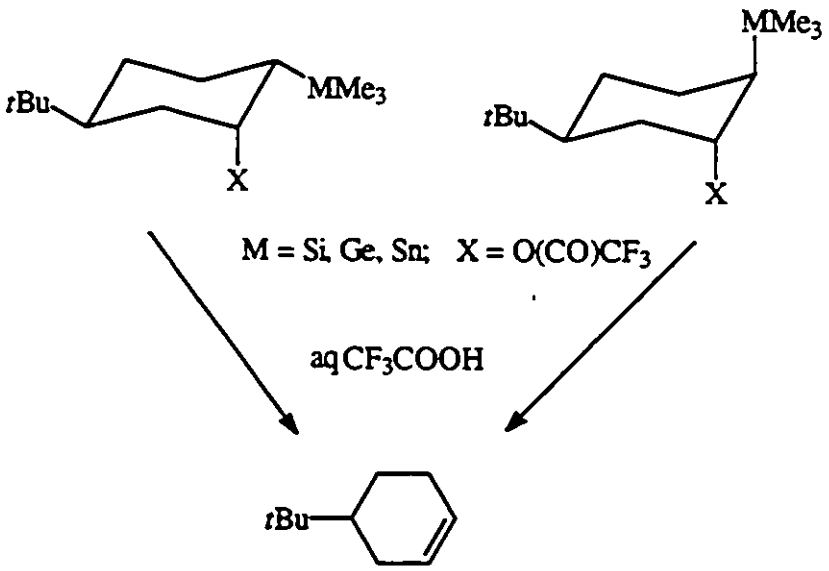


Table 1.1: Variation of reaction rates with Group 14 elements[26]

Group 14	Rate (k_M/k_H)	
	dihedral angle	
	60°	180°
Si	10^4	10^{12}
Ge	10^5	10^{13}
Sn	10^{11}	$>>10^{14}$

Charge-transfer spectra of $ArCR_2MPh_3$ systems (see Scheme 1.5) have also been used to study the effect of varying Group 14 elements on β-carbocations.[16]

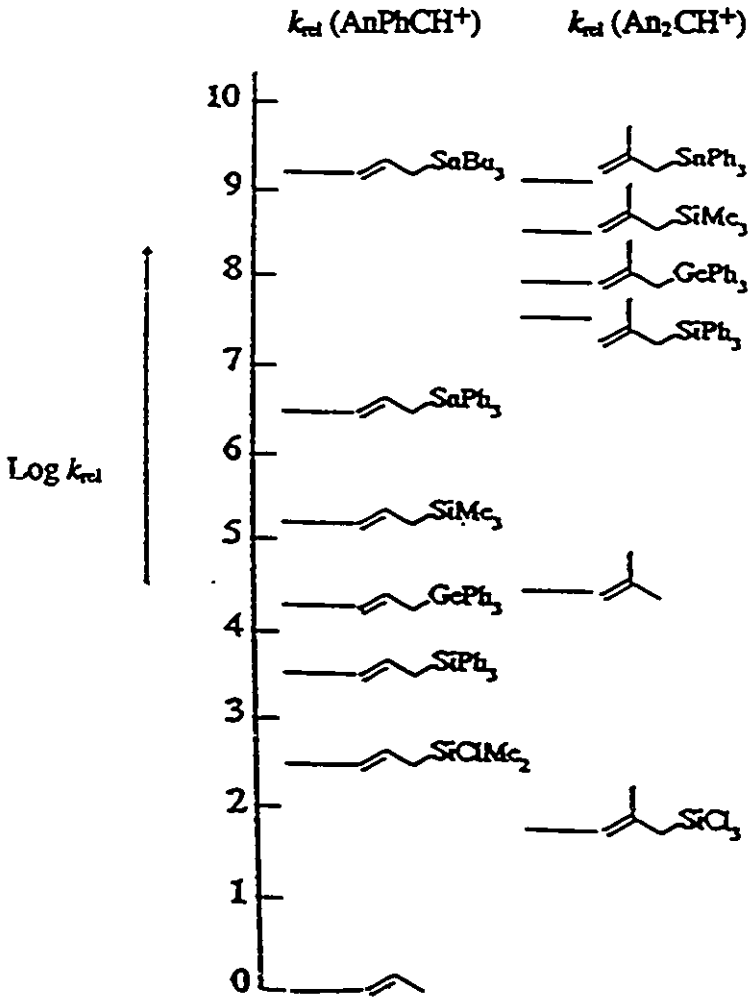
Table 1.2 lists the charge-transfer frequencies for the interaction of the aryl π-donor with the tetracyanoethylene π-acceptor (Scheme 1.5).[16] The data indicates that as we proceed down Group 14, the charge-transfer absorption requires less energy, as shown by the decrease in the charge-transfer frequencies.[16] This decrease in the charge-transfer frequencies is attributed to increasing stabilization of the intermediate as the element becomes more electropositive. The σ_y^+ values quantity the stabilization afforded by the varying Group 14 elements; increasing stabilization is associated with a greater negative value.

Table 1.2: Charge-transfer frequencies for the complex PhY/tetracyanoethylene[16]

Ph-Y	ν (cm^{-1})	σ_y^+
Ph-H	25840	0.0
$Ph\text{-}CH_2CPh_3$	23700	-0.20
$Ph\text{-}CH_2SiPh_3$	22220	-0.42
$Ph\text{-}CH_2GePh_3$	20660	-0.60
$Ph\text{-}CH_2SnPh_3$	18760	-0.81
$Ph\text{-}CH_2PbPh_3$	17060	-1.0

A similar trend of increasing stabilization of β-cations, as we proceed down Group 14, has been observed for the reaction of $H_2C{=}CHCH_2MPh_3$ with diarylcarbenium ions.[42,44] Thus, the reactivity of $H_2C{=}CHCH_2SnPh_3$ ($k_{Sn}/k_H \sim 10^6$) was higher than that of $H_2C{=}CHCH_2GePh_3$ ($k_{Ge}/k_H \sim 10^4$), which in turn was higher than $H_2C{=}CHCH_2SiPh_3$ ($k_{Si}/k_H \sim 10^3$, Figure 1.6).[42,44]

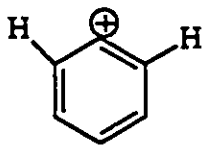
Figure 1.6: Nucleophilicities of allylsilanes, allylgermanes, and allylstannanes towards $AnPhCH^+$ and An_2CH^+, relative to propene (left) and isobutene (right)[42,44]



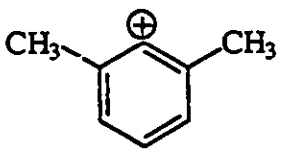
1.1.5) Magnitude of the β-effect

Jorgensen and coworkers have calculated the β-effect to be about 38 kcal/mol for primary carbocations.[10,21] This value corresponds well with experimental studies. For example, Hajdasz and Squires found the β-effect to be 39 kcal/mol for the primary cation $Me_3SiCH_2CH_2^+$ by mass spectrometric studies.[33] Secondary systems in solution gave β-stabilization of 18 kcal/mol,[23] compared to the value of 22 kcal/mol calculated by Jorgenson,[10,21] and 28 kcal/mol observed by Li and Stone[34] for secondary systems in the gas phase. Jorgensen calculated a comparatively smaller value (16 kcal/mol) for tertiary systems.[10,21] *Ab initio* calculations predicted that **40** is more stable than **39** by 10 kcal/mol at the 3-21G level, while **41** is more stable than **40** by 15 kcal/mol.[28,34,40] This large stabilization provided by silicon has been used to generate the first aryl cation in solution by the solvolysis of aryl triflates.[57]

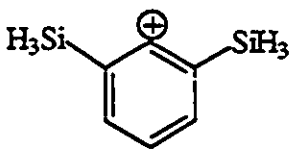
Figure 1.7



39



40

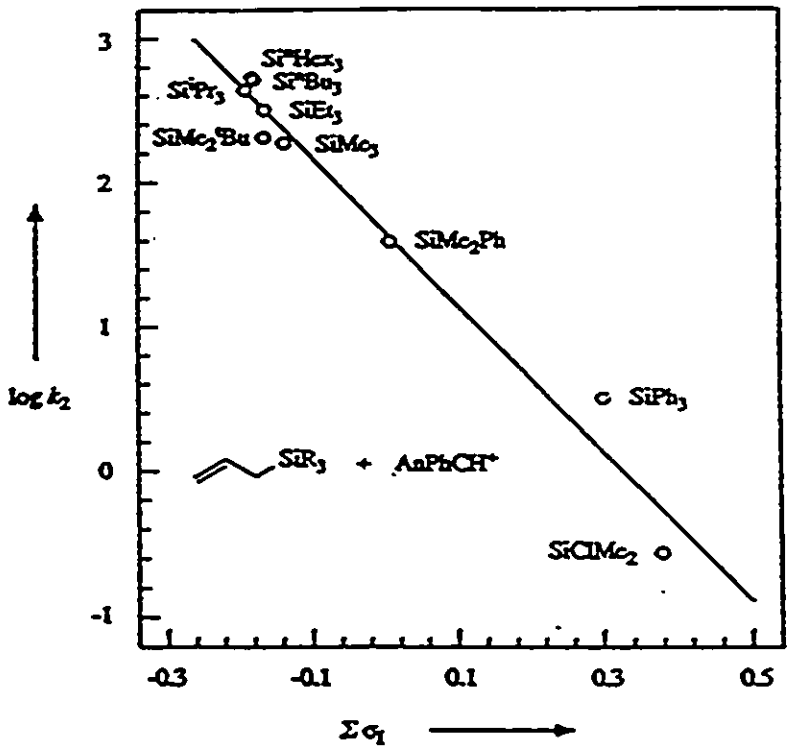


41

1.1.6) Substituent effect

A comprehensive quantitative study on the degree of activation of C-C π-bonds of silylallyl compounds having varying ligands on silicon was carried out by Mayr, Panek and coworkers.[42,44,48] In general, the replacement of methyl substituents on silicon by larger alkyl groups (branched or unbranched) led to a slight increase in the reactivity of allylsilanes.[42,44] The replacement of a methyl ligand on silicon by a phenyl substituent reduced the reactivity of the allylsilane (Figure 1.6).[42,44,48] Reduction of reactivity was observed when methyl groups were replaced by chloride ligands (Figure 1.6).[42,44] The inductive, electron-withdrawing effect of the chloride ligand accumulated in allyltrichlorosilane.[42,44] This compound, in contrast to propene, did not react with *p*-anisylphenyl carbenium ion indicating a deactivation of the double bond by the trichlorosilyl group.[42,44] Mayr found that the reactivities of allylsilanes towards *p*-anisylphenylcarbenium ion gave a linear correlation with the sum of Taft's inductive substituent constants for the three ligands on silicon (i.e., $\log k_2 = \rho\Sigma\sigma +$ constant, Figure 1.8).[42,44]

Figure 1.8: Correlation of the reactivities of allylsilanes towards *p*-anisylphenylcarbenium ion (CH_2Cl_2, -70 °C) with Taft's inductive substituent constants for the substituents at silicon[42,44]



. Brook and coworkers have also demonstrated that the magnitude of the β-effect is directly related to the electron-withdrawing or electron-donating ability of the ligands on silicon.[50,58] Thus, the reaction of (*E*)-β-silylstyrene derivatives with bromine could give either (*E*)-β-bromostyrene or (*Z*)-β-bromostyrene, depending on the magnitude of the β-effect exerted by silicon (Scheme 1.12). This magnitude, in turn, was affected by electron-donating or electron-withdrawing groups on silicon. For example, the reaction of bromine with (*E*)-β-trimethylsilylstyrene **42** (XYZ equal Me_3, Table 1.3, Scheme 1.12) or (*E*)-β-chlorodimethylsilylstyrene **43** (XYZ equal Me_2Cl, Table 1.3, Scheme 1.12) yielded exclusively (*E*)-β-bromostyrene.[50,58] The stereoselectivity of these reactions has been rationalized in terms of the *syn*-addition of bromine across the styrene double bond when the β-effect is strong for relatively electron rich Me_3 and Me_2Cl ligands on silicon.[50,58] The dibromoadduct resulting from the *syn*-addition of Br_2, then undergoes fluoride assisted *trans*- or *anti*-elimination to form (*E*)-β-bromostyrene (Scheme 1.12).[50,58]

Scheme 1.12

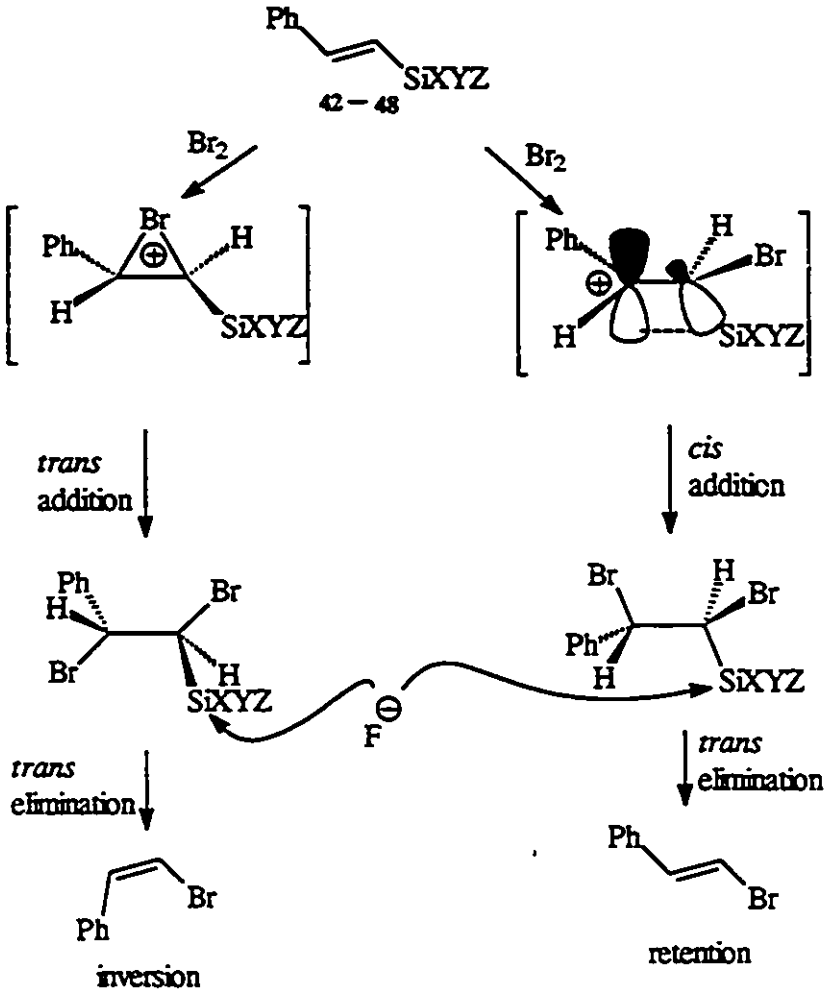

Ph
SiXYZ
42 – 48
Br2
Br2
Br
Ph
H
H
SiXYZ
Ph
H
Br
H
SiXYZ
trans
addition
cis
addition
Ph
H
Br
Br
H
SiXYZ
Br
H
Br
Ph
H
SiXYZ
F
trans
elimination
trans
elimination
Ph
Br
Ph
inversion
Ph
Br
retention

Table 1.3: Comparison of the ratio of *syn*-addition/*anti*-addition of Br_2 to (*E*)-β-silylstyrene **42-48** *versus* silyl group electronegativity[50,58]

compounds in Scheme 1.12	ligands XYZ on Si	*syn*/*anti* ratio	silyl group electronegativity
42	Me_3	100/0	2.06
43	Me_2Cl	100/0	2.12
44	Me_2F	85/15	2.18
45	$MeCl_2$	75/25	2.19
46	Cl_3	55/45	2.26
47	MeF_2	40/60	2.32
48	F_3	15/85	2.47

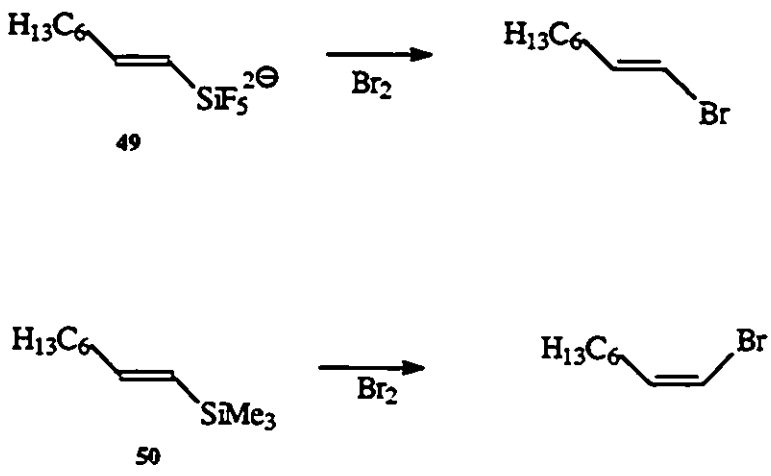
It has been proposed that *syn*-addition of Br_2 occurs when the intermediate is an open cation, due to the closer proximity of the bromine nucleophile to the *cis* face of the intermediate.[50] In addition, *trans*-addition of bromine might be sterically hindered by the bulky Si XYZ groups.[51]

As the silyl ligands (**42-48**, Table 1.3) become more electronegative, the degree of *anti*-addition of bromine increases. The reduced β-effect, associated with the more electronegative ligands on silicon, is compensated by increased bridging to form a bromonium ion. This bridging effectively hinders *cis*-addition of Br_2, instead allowing the more usual *anti*-addition of Br_2 to take place.[50] Subsequent fluoride assisted *anti*-

elimination of SiXYZ and Br was effected to produce (*Z*)-β-bromostyrene from (*E*)-β-silylstyrenes, which is inversion of the olefin geometry..

Studies by Tamao, Kumada and others have also evaluated the electronic role of ligands on the extent of β-Si stabilization.[54] These workers also found the stereochemistry of halogenolysis of vinyl silanes to be greatly dependent upon the nature of the silyl ligands, including the coordination state of silicon.[54] Thus, bromine cleavage of (*E*)-1-octenylpentafluorosilicate **49** proceeded with retention of configuration, in sharp contrast to (*E*)-1-octenyltrimethylsilane **50** which proceeded with inversion (Scheme 1.13).[54]

Scheme 1.13



For the pentafluorosilicate derivative **49**, it was proposed that increased β-Si stabilization of the carbonium ion intermediate resulted from the high concentration of

negative charge surrounding silicon. This increased β-Si stabilization gave rise to an open cation to which *syn*-addition of Br_2 took place.[54] The reasons for *syn*-addition are, perhaps, similar to those previously proposed by Weber[51] (i.e., steric inhibition by Si to *anti*-addition) or Brook[49,50] (the proximity of Br^- to the *syn* face of the cation) as described above. Subsequent *anti*-elimination gave products with overall retention of geometry.[54] In contrast, Br_2 addition to (*E*)-1-octenyltrimethylsilane **50** proceeded with overall inversion of geometry as a result of *anti*-addition of bromine followed by *anti*-elimination of Me_3Si/Br.[54] Similar to the styryl system, the *anti*-addition process is thought to occur with **50** *via* bromonium ion bridge formation when the β-effect is reduced (i.e., reduced in **50** compared to **49**).[54]

1.2) Arylsilanes

It is now widely accepted that the β-effect features quite prominently in the electrophilic aromatic substitution of $ArMR_3$ compounds (M equals Si, Ge, Sn, Pb). Many of the studies done to elucidate the mechanism of electrophilic aromatic substitution of $ArMR_3$ have been carried out by Eaborn and coworkers. We will now look at the mechanistic evidence, including isotope effects and stereochemical evidence, that is consistent with the β-effect being the mechanism involved in electrophilic aromatic substitution of $ArMR_3$.

The cleavage of Ar-MR_3 bonds (called demetalation) by electrophilic reagents, is closely related to conventional electrophilic aromatic substitution involving Ar-H bond cleavage. For instance, the direction of bond polarization is the same; the Ar-H bond is polarized and cleaved in the direction $C^{\delta-}$-$H^{\delta+}$, while in demetalations the bond is polarized and broken in the direction $C^{\delta-}$-$MR_3{}^{\delta+}$. Another closely related feature involves the carbocation intermediate. Both conventional electrophilic aromatic substitution (Ar-H cleavage) and demetalation are thought to involve Wheland intermediates or σ-complexes **51** and **52**, respectively (Figure 1.9).

Figure 1.9

51 **52**

E = electrophile M = Si, Ge, Sn, Pb

1.2.1) Deuterium isotope studies

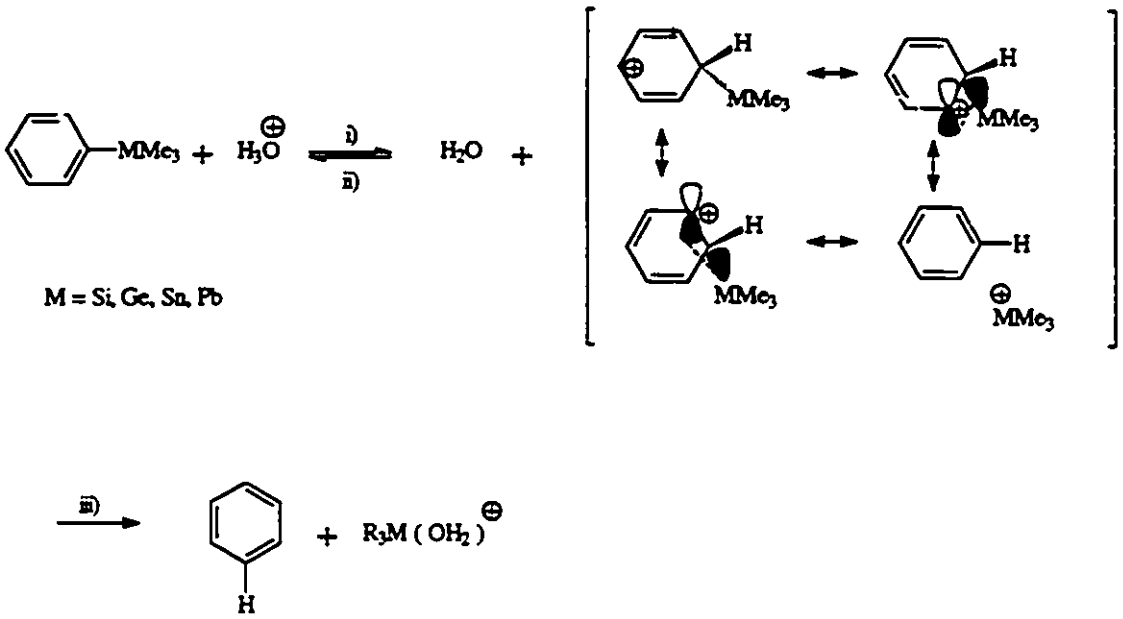
The attachment of a proton is the rate determining step for protiodemetalation of $ArMR_3$ compounds. The rate determining step was established by two studies involving solvent isotope effects. The first study examined the cleavage of compounds *p*-$XC_6H_4MR_3$ by hydrochloric acid in aqueous dioxane medium (M equals Si, Ge, Sn, Pb).[59] In all cases the reaction was slower when deuterium oxide replaced protium oxide (Table 1.4).[59]

Table 1.4: Cleavage of *p*-$XC_5H_4MR_3$ compounds at 50 °C in dioxane containing hydrogen chloride and 25 mole % water[59]

R_3M	X	k_{H_2O}/k_{D_2O}
Me_3Si	*p*-OMe	1.55
Et_3Ge	*p*-OMe	1.71
Et_3Ge	*p*-CH_2SiMe_3	1.60
Et_3Sn	H	2.45
Et_3Pb	H	3.05

The simplest mechanism consistent with the kinetic isotope effect observed is shown in Scheme 1.14.[59]

Scheme 1.14



The second study involved the cleavage of $XC_6H_4SiMe_3$ and $XC_6H_4SnMe_3$ compounds in trifluoroacetic acid and acetic acid media, respectively (Table 1.5).[60] Once again, product isotope ratios obtained from competitive cleavage in a 1:1 mixture of ordinary acid/*O*-deuterated acid showed that proton transfer was faster than deuteron transfer. This result is consistent with rate determining proton (or deuteron) transfer.

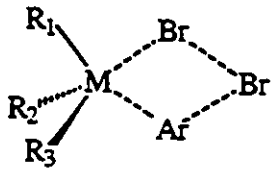
Table 1.5: Isotope effects in the acid cleavage of $XC_6H_4MMe_3$[60]

M	X	Acid	Product isotope effect
Sn	*p*-OMe	Acetic	5.9
Sn	*p*-Me	Acetic	5.2
Sn	H	Acetic	5.2
Sn	*m*-CF_3	Acetic	5.0
Sn	*p*-Cl	Acetic	4.9
Si	*p*-OMe	Trifluoroacetic	6.1
Si	*p*-Me	Trifluoroacetic	6.5
Si	H	Trifluoroacetic	6.5
Si	*p*-Cl	Trifluoroacetic	6.0

1.2.2) Stereochemical studies

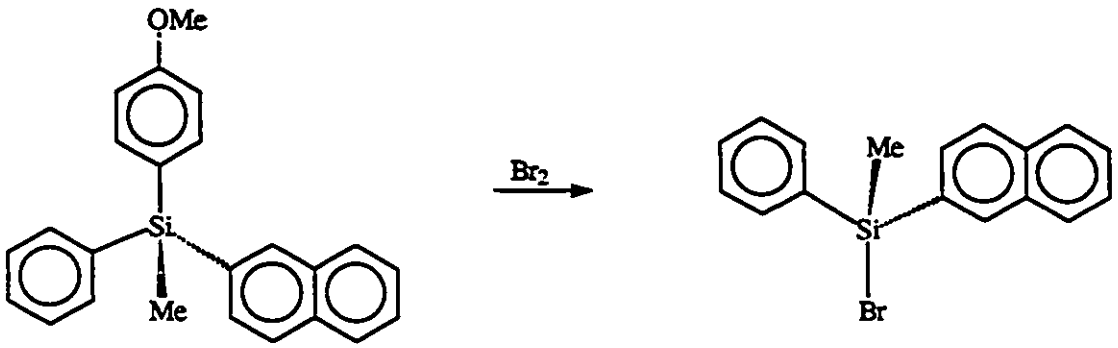
It was previously thought that the electrophilic aromatic substitution of $ArMR_3$ could involve a concerted four-center intermediate (M equals Si, Ge, Sn, Pb, Figure 1.10).[59,62]

Figure 1.10



However, there was compelling evidence against such a mechanism for the bromodesilylation of optically active *p*-methoxyphenylmethyl-2-naphthylphenylsilane **53** in non-polar media (benzene or carbon tetrachloride, Scheme 1.15).[63,64] This reaction proceeded with the inversion of configuration at silicon, which was attributed to back-side attack on silicon in the Wheland intermediate **55** (Figure 1.11). Front-side attack would involve the retention of the configuration of silicon.[63,64] A concerted process was expected in non-polar media since ionic processes are generally not advantageous to non-ionic processes under these conditions.[65]

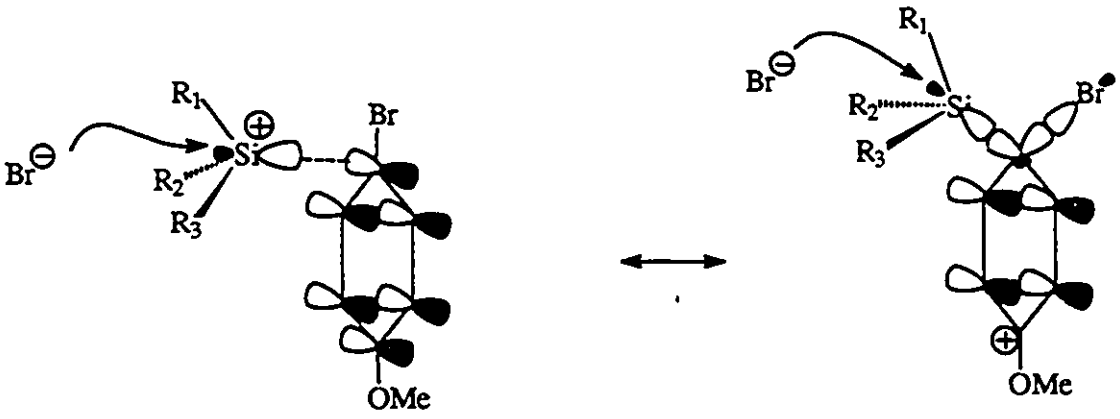
Scheme 1.15



53

This stereochemical finding did not rule out the possibility that C-Si bond breakage may occur to form a π-complex **54** between the π-electrons of the ring and a silylium ion, analogous to the π-complex proposed by Reed[70] (Figure 1.11).[64]

Figure 1.11



54 55

π-complex σ-complex

The silylium ion could then be exclusively removed by back-side nucleophilic attack (S_N2) with inversion, accounting for the stereochemistry observed.[64] However, the well known kinetic instability of silylium ions in the condensed phase would undermine such a mechanistic interpretation.

1.2.3) The effect of varying M (in $ArMR_3$) on electrophilic aromatic substitution

The rates of cleavage of $PhMEt_3$ compounds by aqueous methanolic perchloric acid increases in the sequence Si < Ge << Sn << Pb. The relative reactivities (k_M/k_H) of $PhMEt_3$ are approximately Si, 1; Ge, 36; Sn, 3.5×10^5; Pb, 2.0×10^8.[36] The increasing reactivity of $PhMEt_3$ as one goes down Group 14 has been attributed to increasing hyperconjugative stabilization of the Wheland-type intermediate.[36] Hyperconjugative stabilization was also used to explain why Ph-$SiMe_3$ reacts 4×10^4 times faster than Ph-H in aqueous sulphuric acid.[36,59,65]

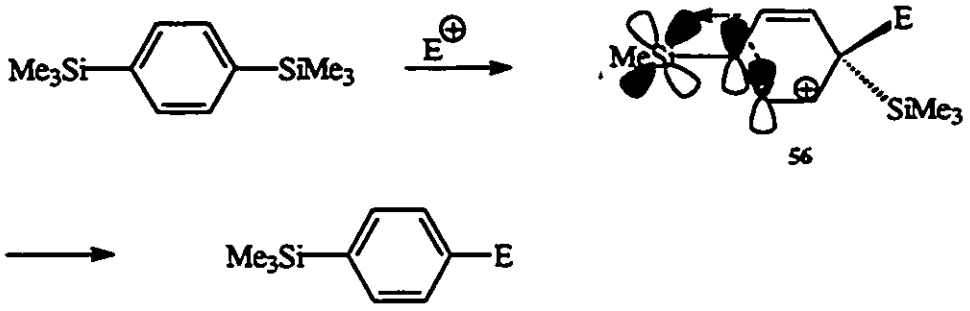
1.2.4) The effect of varying R (in $ArSiR_3$) on electrophilic aromatic substitution

The effect of varying the ligands on silicon on the rate of electrophilic aromatic substitution of $ArSiR_3$ has been systematically studied for acid induced reactions.[68,75] The results showed that increasing electron release toward Si from the R group increased the rate of reaction. This trend is expected for a reaction in which the formation of a β-Si stabilized Wheland intermediate is formed in the rate determining step.[68] It has been found, however, that steric effects can outweigh the electronic influence.[65] For instance, **Ar**-Si^{i}Pr$_3$ compounds were cleaved less readily by electrophiles than **Ar**-SiMe$_3$ compounds even though there is a greater inductive release of electrons from the isopropyl ligands relative to the methyl ligands.[65] In addition, the low reactivity of $ArSiPh_3$ compounds relative to $ArSiMe_3$ has been attributed to a combination of steric and electronic factors.[68] Electronically, the sp^2 hybridization of the phenyl ligand makes it more inductively electron-withdrawing relative to the sp^3 hybridized alkyl ligand. As would be expected, **Ar**-SiX$_3$ (X = halogen) bonds are cleaved less readily than **Ar**-SiMe$_3$ bonds. **Ar**-Si(OEt)$_3$ is also cleaved by perchloric acid 30 times slower than $ArSiMe_3$ for similar reasons.[65]

1.2.5) The effect of varying X (in $XC_6H_4MR_3$) on electrophilic aromatic substitution

The change in the reactivity of $R_3SiC_6H_4X$ compounds as X is varied has been extensively covered in the literature.[65,69,71-73] The values for the rates (k_M/k_H) of acid and bromine induced cleavages of $XC_6H_4MR_3$ (M equals Si, Ge, Sn), relative to the $C_6H_5MR_3$ compounds, can be interpreted in terms of standard substituent constants (σ) for the substituent X.[65,69] As is usually observed with conventional electrophilic aromatic substitution (Ar-H cleavage), electron-releasing substituents accelerate and electron-withdrawing substituents retard the rate of demetalation. For example, *para*-alkyl substituents activate the ring to desilylation in accordance with the hyperconjugative order *p*-Me > *p*-Et> *p*-^{i}Pr > *p*-^{t}Bu.[69] Studies have shown that the rates of desilylation of *meta* substituted compounds also vary in a regular manner, and are completely predictable on the basis of the inductive effect of the *meta* substituent (eg., *m*-^{t}Bu > *m*-^{i}Pr > *m*-Et > *m*-Me).[76] Similar substituent effects have been observed for protiodegermylation,[80] protiodestannylation,[74] and protiodeplumbylation[81] reactions. The activating effects of *m*-$SiMe_3$ ($\sigma^+_{m\text{-}Me_3Si}$ = -0.05) and *p*-$SiMe_3$ ($\sigma^+_{p\text{-}Me_3Si}$ = -0.03), however, are quite small.[69,77] In fact, the activating effect of *p*-$SiMe_3$ is considerably smaller than *p*-Me ($\sigma^+_{p\text{-}Me}$ = -0.14). The smaller value for *p*-$SiMe_3$ has been rationalized in terms of resonance withdrawal of electrons from the p-orbital of the ring into the d-orbitals of silicon as shown in **56** (Figure 1.12).[77]

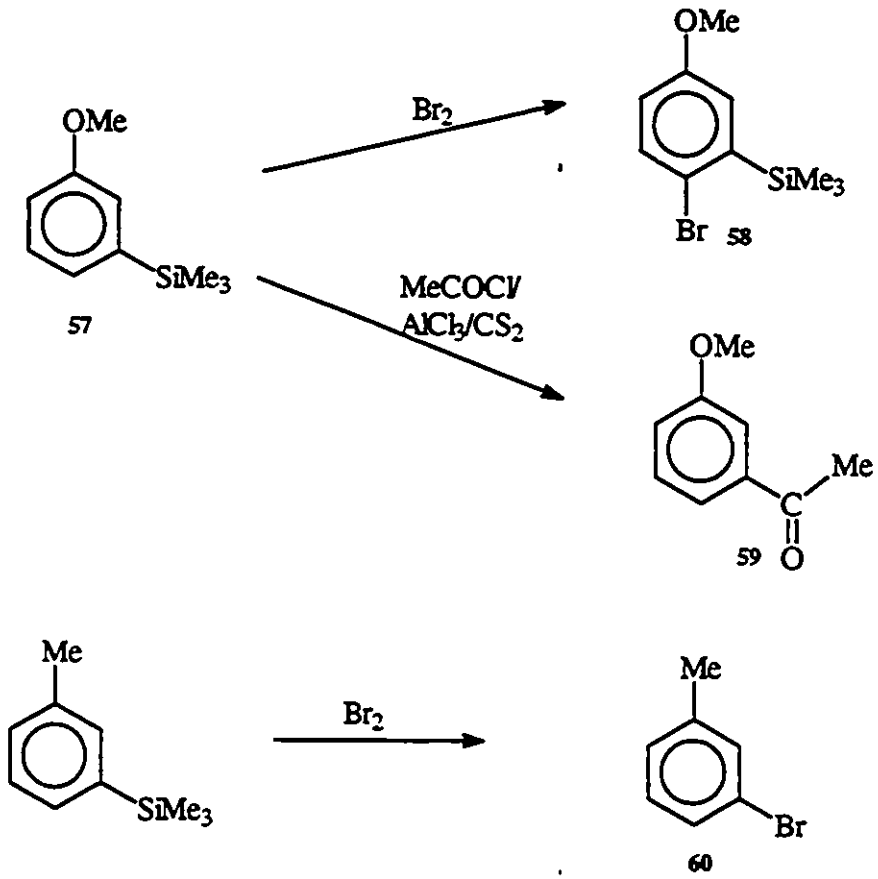
Figure 1.12



When multiple substituents including a silyl group are present on the aromatic ring, the degree of Si-C cleavage compared to C-H cleavage will depend upon the relative abilities of the silyl group and the other activating group to stabilize the intermediate. In general, amino and dimethylamino groups are more powerful *ortho*-, *para*-directors than Me_3Si is an *ipso*-director. However, the activating influence of *ortho, meta* or *para* substituted methyl groups is less powerful than the *ipso* activating ability of the $SiMe_3$ group as seen from the production of **60** (Scheme 1.16).[29] It should be noted, however, that the relative ability of the silyl group to direct *ipso*-substitution in competition with other groups also depends on the nature of the electrophile. Thus, we see that *m*-$MeOC_6H_4SiMe_3$ **57** undergoes *ipso*-silicon substitution and desilylation in acetyl chloride to give **59**, but this same substrate undergoes Ar-H bond cleavage more readily than Ar-Si cleavage in bromine to give **58** (Scheme 1.16). Other bromination reactions do lead to

Ar-Si cleavage products, eg. **60**, in contrast to the above mentioned (Scheme 1.16).[29] Nitration also presents a special case where the Ar-H bond is sometimes cleaved more readily than the Ar-Si bond, for no obvious reason.[29]

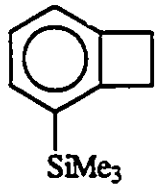
Scheme 1.16



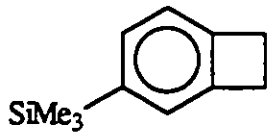
1.2.6) Applications of aryl demetalation reactions

The demetalation reactions have been shown to be of synthetic and mechanistic utility due to the high reactivity of $ArMR_3$ compared with ArH. For example, electrophilic aromatic substitutions involving $XC_6H_4SiMe_3$ compounds have been of benefit in that they gave quantitative information about the effects of powerful deactivating substituents such as, NO_2, NMe_3^+, CF_3 and CO_2R. $ArMR_3$ compounds have also been used to carry out electrophilic aromatic substitution under relatively mild conditions. The ability to carry out a reaction under mild conditions is especially important if the rest of the molecule would not survive the more vigorous conditions required for the conventional aromatic substitutions (Ar-H cleavage). For example, in aqueous perchloric acid, 1,2-dihydro-3-trimethylsilylbenzocyclobutane **61** and 1,2-dihydro-4-trimethylsilylbenzocyclobutane **62** undergo electrophilic aromatic substitution at silicon (protiodesilylation) without opening the four-membered ring (Figure 1.13).[82]

Figure 1.13



61



62

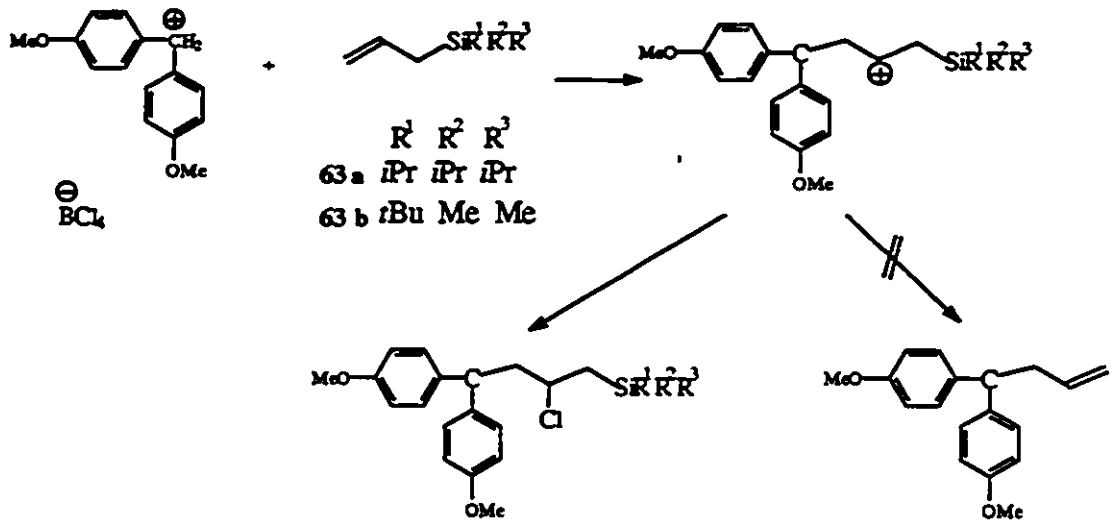
Competitive ring opening frequently complicates the reaction of 1,2-dihydro-benzocyclobutene with electrophilic reagents.[82] In addition, studies of the effect of the C≡CH substituent on the reactivity of the benzene ring have been made possible using *para* and *meta* substituted $HC{\equiv}C\text{-}C_6H_4SnMe_3$ compounds.[83-85] Conventional electrophilic aromatic substitution cannot be carried out with HC≡C-Ph because electrophiles attack the triple bond more readily than the phenyl ring.[83] Aromatic demetalations are of further value because of the single isomer they produce. Sometimes, these reactions provide isomers that are otherwise formed only in small quantities during conventional electrophilic aromatic substitution (Ar-H cleavage). For example, *m*-$MeOPhSiMe_3$ **57** undergoes electrophilic substitution at silicon (*meta* to the methoxy group) to form **59**, irrespective that the methoxy group is a powerful *ortho-*, *para*-director (Scheme 1.16).[29] In this case, the Me_3Si group is a greater *ipso*-director than MeO is an *ortho-*, *para*-director. As a result of the powerful *ipso*-silicon activating influence of the trimethylsilyl group, aromatic compounds with $SiMe_3$ substituents have found a special use in determining and controlling the reactivity of the aromatic ring at any specific ring position.

1.3) The addition of electrophiles to organosilyl π-nucleophiles

The ability of silicon to direct regioselective electrophilic substitution reactions involving vinylsilanes, allylsilanes and arylsilanes was previously discussed.[42,44,55] Regiocontrol in these reactions has been attributed to the electronic steering influence of the β-Si group in the β-Si stabilized carbocation intermediates. The stereocontrol that silicon affords vinylsilanes during the course of electrophilic substitution has also been discussed.[55] This stereoselectivity (retention *versus* inversion of olefin geometry) results from the geometrical requirements for optimum β-Si stabilization. These electrophilic reactions usually terminate with the loss of silicon.

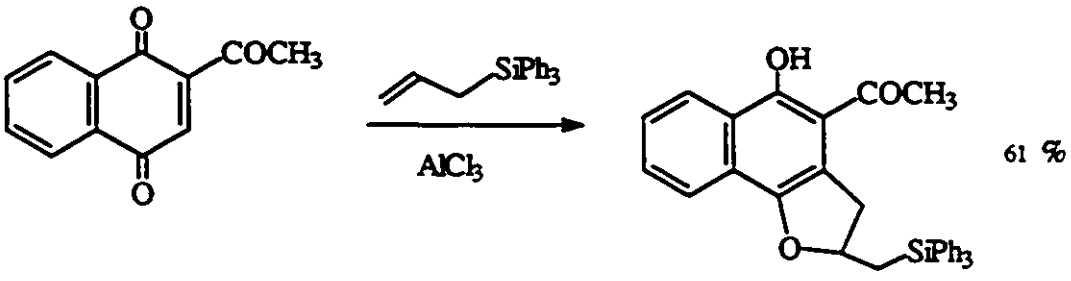
There are, however, a few reported instances of electrophilic addition reactions where silicon is retained. One such reaction occurs when bulky ligands are placed on silicon. For example, Mayr reported exclusive addition products **64a** and **64b** for reactions of diarylcarbenium ions with allylsilanes containing bulky triisopropyl ligands **63a** and *tert*-butyldimethyl ligands **63b** on silicon (Scheme 1.17). This result contrasts with the exclusive substitution reactions observed for allylsilanes containing smaller silyl groups (eg., $R^1R^2R^3$ = Me, Scheme 1.17).[44]

Scheme 1.17



Some addition product **65** was also observed for allyltriphenylsilane (Scheme 1.18).[44] In addition reactions, the elimination of silicon was perhaps thwarted by the inability of nucleophilic counterions to get sufficiently close to silicon to initiate bimolecular desilylation.[55] The retention of silicon has also been observed in systems where the hyperconjugative stabilization cannot be optimized because of inappropriate geometry,[88] for instance, when conformational constraints place the Si-C σ-orbital and the empty p-orbital close to a 90° dihedral angle.[55]

Scheme 1.18

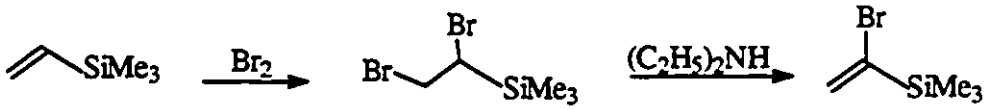


61 %

65

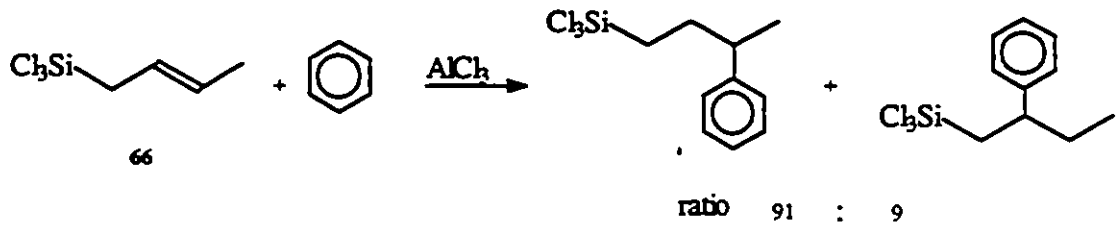
There has also been a tendency towards deprotonation rather than desilylation, where reactions were carried out in basic medium (Scheme 1.19).[89]

Scheme 1.19



Other examples of silicon retention involve electron deficient alkenylsilanes. In the early 1950s and 1960s Bailey[90] and Andrianov,[91] respectively, observed that trichlorovinylsilanes undergo electrophilic addition reactions with benzene in the presence of aluminum chloride. Similar results were obtained by Tamao[86] and Mayr[42] for trichlorocrotylsilane **66** (Scheme 1.20) and trichloroallylsilane, respectively.

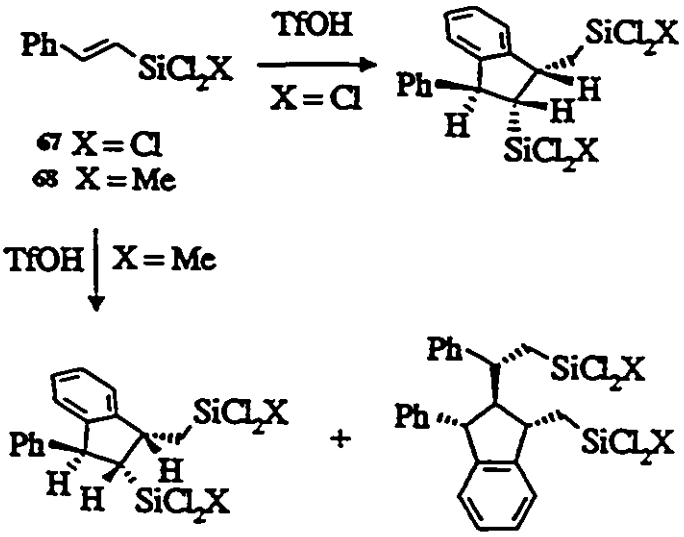
Scheme 1.20



Here the silicon was precluded from leaving due to the reduced β-stabilization afforded by the electron-withdrawing trichlorosilyl groups. We have already discussed why the leaving group ability for trihalosilyl species is much lower than that for trialkylsilyl groups.[49,50,54] The reduced β-stabilization for trihalosilyl species means that a coplanar arrangement between the Si-C σ-orbital and the empty p-orbital, required for elimination, is not an energy minimum.[58] More recently, Brook and coworkers showed that (*E*)-β-(trichlorosilyl)styrene **67** and (*E*)-β-(dichloromethylsilyl)styrene **68** can undergo

diastereoselective dimerization, in the presence of trifluoromethanesulfonic acid, with retention of the silyl group (Scheme 1.21).[92]

Scheme 1.21



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CHAPTER 2

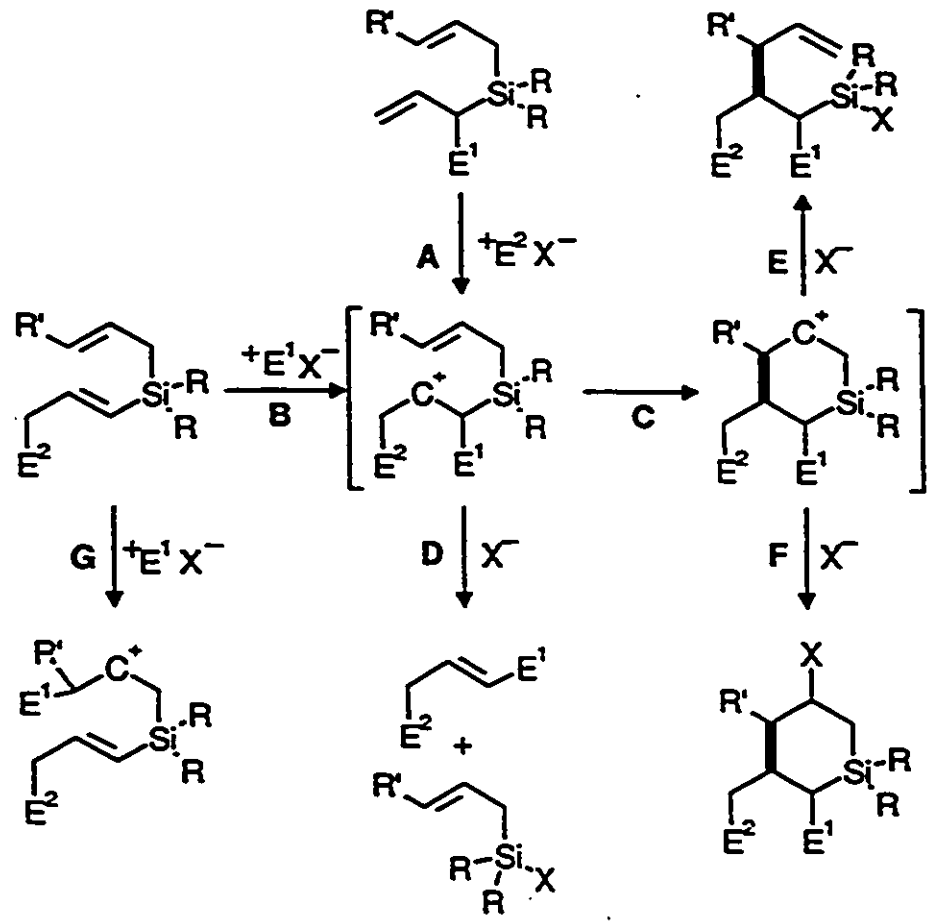
GOALS AND STRATEGY OF STUDY

Given the regioselectivity and stereoselectivity afforded by silicon to reactions that take place *via* β-carbocations, a greater synthetic advantage would arise should the silicon remain in the molecule. A retained silicon could, in theory, effect further regiocontrol and stereocontrol before ultimately being excised from the molecule. For this reason, we have sought to carry out reactions involving electrophilic attack on vinylsilanes that would terminate with the retention of silicon. That is, addition rather than substitution reactions. Furthermore, we hoped that these reactions would lead to the formation of diastereomers.

We intended to pursue two strategies in our attempts to effect addition reactions. The retention of silicon in electrophilic addition reactions of vinylsilanes using either bulky or electronegative silyl ligands appealed to us since these two strategies appeared to be applicable to a wider range of reactions. We recognised, however, if our methods were to be made generally available for the synthesis of non-silicon target molecules, that it was equally important for us to demonstrate that an initially retained silicon could be subsequently cleaved. In this respect, the use of bulky ligands was somewhat daunting since this would require careful choice of ligands that will protect silicon from the electrophile's counterion, but must somehow allow the silicon to be subsequently cleaved. Furthermore, the use of alkyl groups as bulky ligands was considered disadvantageous

since the desired molecular fragment could be cleaved under the harsh conditions required to sever the Si-alkyl bond. For these reasons, we initially chose to use electron-withdrawing silyl ligands to reduce the leaving group ability of silicon. To prevent a reaction leading to dimers and trimers (Scheme 1.21), we modified the ligands on silicon to include two π-nucleophiles. That is, we selected a molecular system in which electrophilic addition to one π-nucleophile may be followed by intramolecular trapping of the carbocation initially formed by another π-nucleophile (Scheme 2.1C). Such a reaction might facilitate the addition process, in that *intra*molecular nucleophilic attack upon the carbocation by a silyl π-nucleophile (Scheme 2.1C) might occur more rapidly than *inter*molecular attack at silicon by a halide counterion (Scheme 2.1D). Furthermore, the formation of a cyclic transition state or intermediate (Scheme 2.1C) might lead to control of the stereochemistry. Thus, we hoped that in addition to retaining silicon in the molecule, the diastereoselectivity shown in Scheme 1.21 would be observed in our system.

Scheme 2.1



CHAPTER 3

THE SYNTHESIS AND EVALUATION OF SUBSTRATES FOR ELECTROPHILIC ADDITION

3.1) Proton addition to organosilane π-nucleophiles

This chapter describes our search to find suitable silyl substrates to carry out electrophilic addition reactions. We proposed that compounds bearing electronegative ligands on silicon would not be prone to protiodesilylation. We synthesized several dichloroorganosilane π-nucleophiles and diphenyldiallylsilane **70** and reacted them with a common electrophile, triflic acid (TfOH), in an attempt to determine if they would undergo addition reactions. The type of reaction, addition *versus* substitution, and the mechanistic interpretation given to the results are described below.

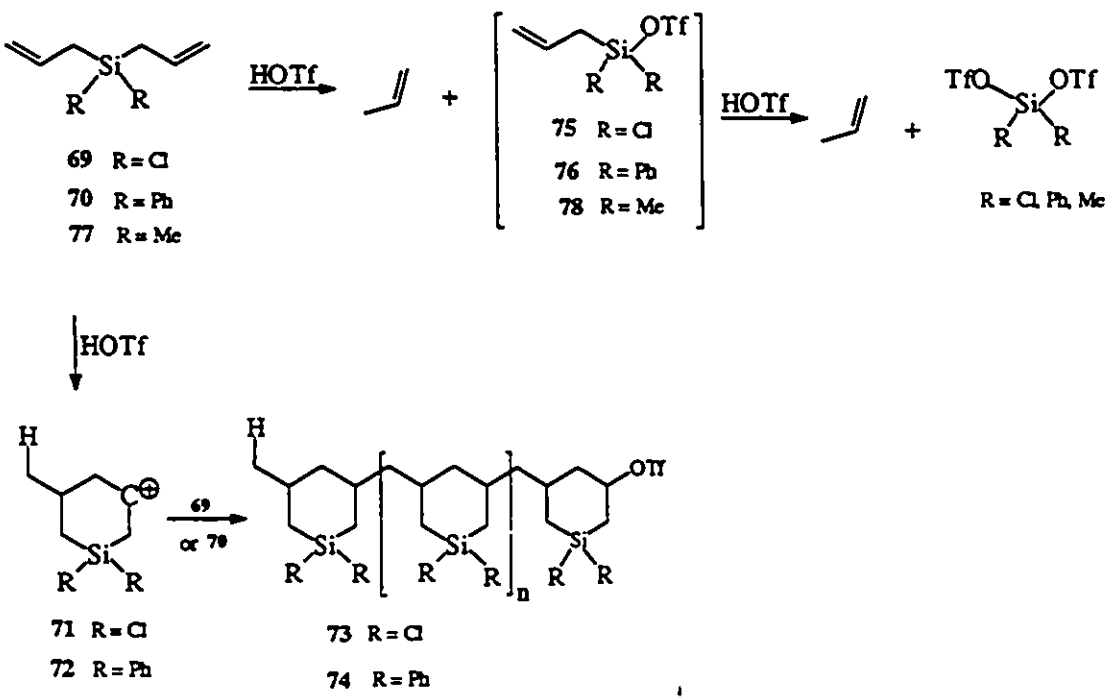
3.1.1) The reactions of diallylsilanes

Our initial attempts at electrophilic addition were with diallylsilanes. The reaction of diallyldimethylsilane **77** with triflic acid, as expected for a trialkylsilyl leaving group,[1,2] resulted in the loss of propene and formation of allyldimethylsilyl triflate **78**.

For our first attempt at reactions in which silicon would not be cleaved, we synthesized and reacted diallyldichlorosilane **69** and diphenyldiallylsilane **70** with triflic

acid. In contrast to diallyldimethylsilane **77**, simple protiodesilylation to give **75** and **76**, respectively, did not predominate the reaction mixture. Rather, a mixture containing oligomeric products was obtained. In addition to protiodesilylation, species such as **71** and **72** could act as electrophiles in the reaction leading to oligomers of type **73** and **74** respectively (Scheme 3.1).[3]

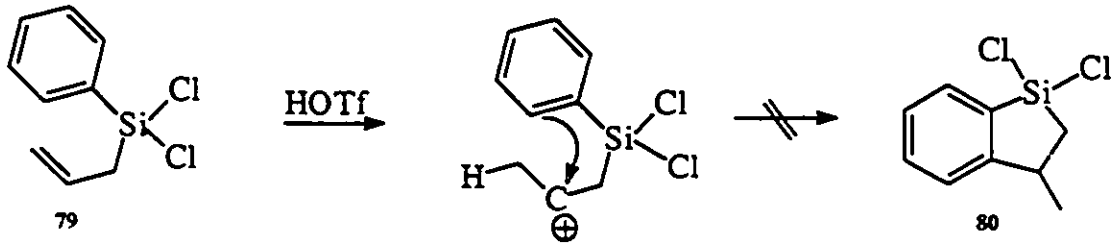
Scheme 3.1



3.1.2) The reactions of phenylallylsilane and vinylallylsilane

We next turned our attention to allyldichlorophenylsilane **79**. This species could form a 5-membered ring *via* a Friedel-Crafts alkylation. Thus, the reaction of triflic acid with allyldichlorophenylsilane **79** was expected to give compound **80**. However, the loss of propene occurred and a mixture was formed for which no evidence for **80** (Scheme 3.2) could be found, although analogous reactions forming carbocycles are known. The cyclization leading to a 5-ring transition state or intermediate might be hampered by the greater ring strain arising from the fact that Si-C bonds are much longer than C-C bonds.[5]

Scheme 3.2

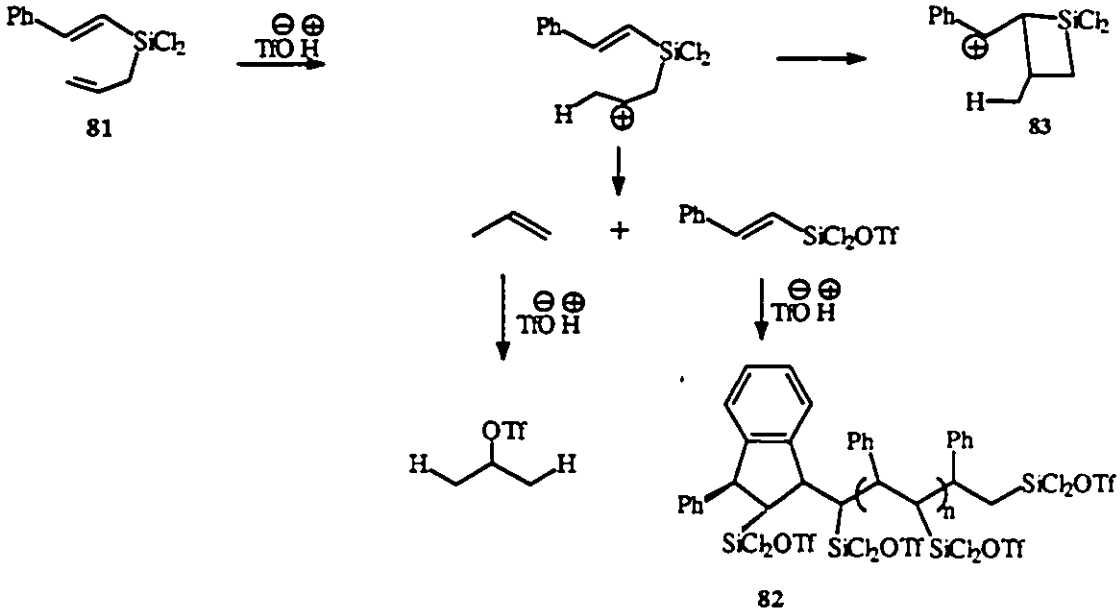


79 **80**

In order to examine if ring strain was indeed important, we decided to attempt a cyclization involving vinylallylsilanes, which involved the formation of a 6-membered ring analogous to the diallylsystems (see Scheme 2.1 for vinylallylsilane and diallylsilane cyclizations). The addition of triflic acid to (*E*)-β-(allyldichlorosilyl)styrene **81** led to

elimination of the allyl group and, additionally, oligomeric species **82** reminiscent of those derived from trichlorosilylstyrene (Scheme 3.3).[4] The desired reaction path leading to a 6-membered ring was not achieved because the allyl moiety, rather than the vinyl moiety, reacted first with the proton. Ring closure of the intermediate could lead to a 4-membered ring **83**. It seems likely that elimination would be the preferred pathway rather than the higher energy 4-membered ring.

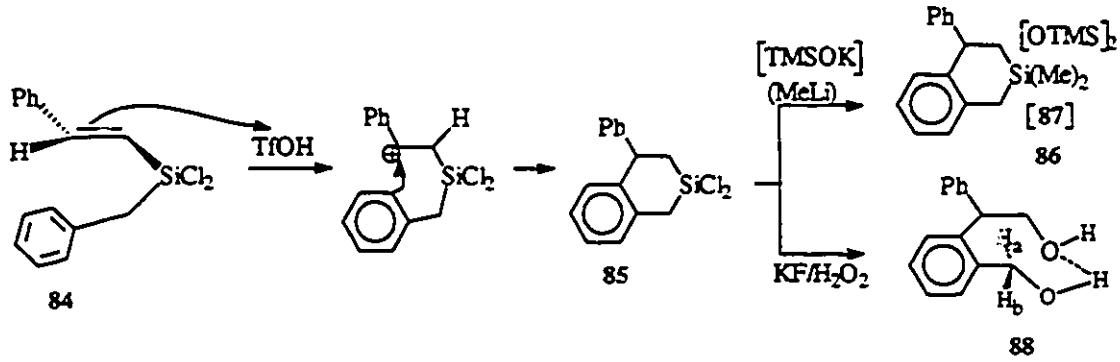
Scheme 3.3



3.1.3) The reaction of vinylbenzylsilane

As a result of the elimination of the allyl moiety when **81** reacted with triflic acid we turned to a less reactive allylsilane. A benzylsilane serves as an allylsilane of lower π-nucleophilicity than a vinylsilane. We therefore prepared and reacted (*E*)-β-(dichlorobenzylsilyl)styrene **84** with triflic acid. The reaction gave the cyclization product, 3,3-dichloro-1-phenyl-3-sila-tetrahydronaphthalene **85**, *via* the β-silyl cation (Scheme 3.4).

Scheme 3.4



84 85 86 [87] 88

^{1}H NMR suggested the quantitative formation of **85**. The isolated yield after distillation (65%) was determined after conversion of dichlorosilyl group **85** to the more stable dimethyl derivative **86**. Alternatively, **85** was converted to the more stable

bis(trimethylsiloxy) derivative **87** using commercially available Me_3SiOK. Compound **87** can be chromatographically separated on silica gel and, in principle, subsequently reconverted to the dichlorosilane **85** by the use of redistribution reactions with $SiCl_4$,[8] or otherwise functionalized. Thus, we were able to demonstrate that, with a suitable organosilyl π-nucleophile, electrophilic addition giving synthetically useful Si-C bonds can be achieved in preference to substitution.

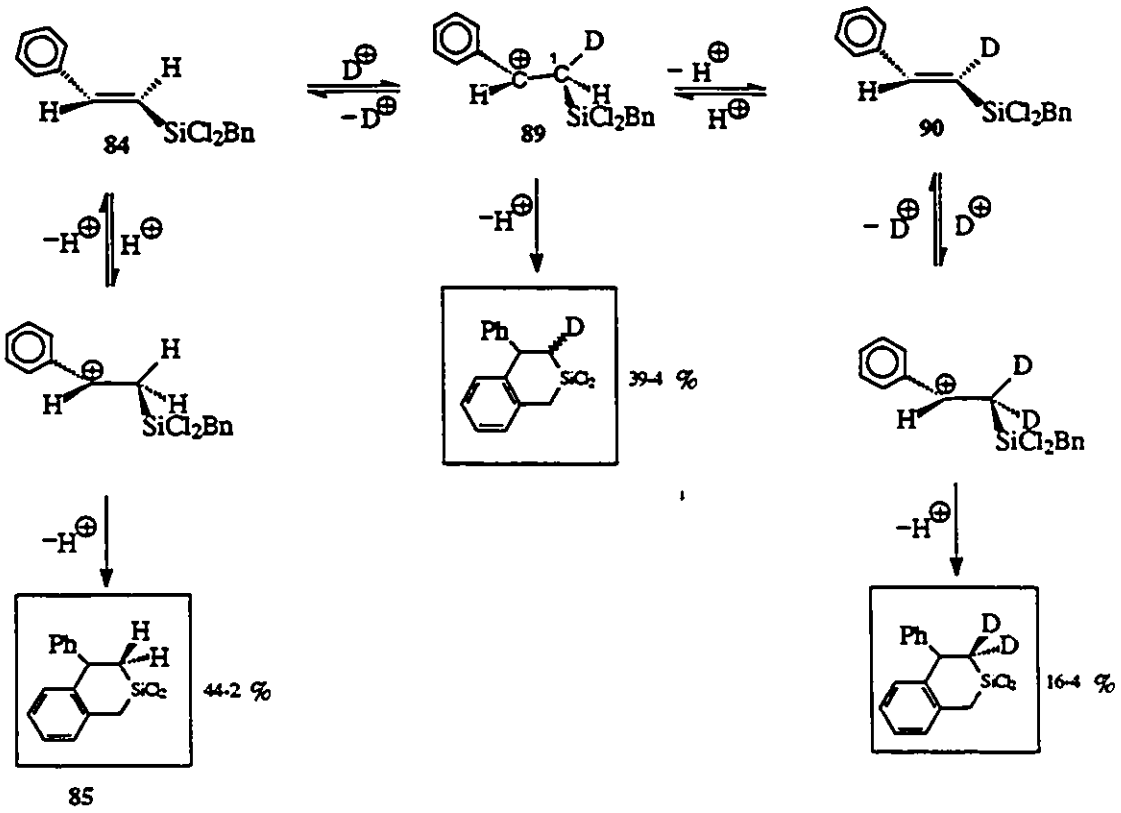
To broaden the utility of this synthetic strategy, we sought to demonstrate that the silicon could be subsequently removed from the carbon skeleton. Accordingly, the Si-C bonds of 3,3-dichloro-1-phenyl-3-sila-tetrahydronaphthalene **85** were oxidized using KF and H_2O_2 to yield the diol **88**.[8] The benzylic methylene protons (H_a and H_b) of this diol **88** appeared as a doublet of doublets in the proton NMR spectrum. The observed diastereotopicity of the methylene protons was attributed to the chiral centre and manifested by intramolecular H-bonding, which would restrict bond rotation thereby giving different electronic environments for these protons.

3.1.4) The results of deuterium isotope studies

In an attempt to probe the reaction mechanism, we also examined deuteration. The reaction of (*E*)-β-(dichlorobenzylsilyl)styrene **84** with deuterated triflic acid (TfOD) led to the formation of mono- (~39%, 1:1 diastereomeric ratio by ^2H NMR) and dideuterated (~16%) 3,3-dichloro-1-phenyl-3-sila-tetrahydronaphthalene, along with

nondeuterated 3,3-dichloro-1-phenyl-3-sila-tetrahydronaphthalene **85** (~44%, Scheme 3.5). The presence of the dideuterated compound showed that the initial protonation was reversible. At the beginning of the reaction, when the concentration of deuterated triflic acid is high, a second deuteration can occur. The absence of diastereoselectivity in the deuteration process could arise from equal amounts of *syn*-addition and *anti*-addition of the proton/benzyl group to the styryl double bond of (*E*)-β-(dichlorobenzylsilyl)styrene **84**. Alternatively, the absence of diastereoselectivity could result from a loss of stereochemical integrity during the reversible protonation. To speculate about this somewhat, the addition of protons or deuterons could lead to a cationic intermediate **89** which freely rotates about the ^{+}C-^{1}C bond (Scheme 3.5) on account of the reduced β-stabilization. This free rotation might allow, in the reversible step, the loss of a proton (or deuteron) to yield equal amounts of (*Z*)-β-(dichlorobenzylsilyl)styrene and (*E*)-β-(dichlorobenzylsilyl)styrene. One isomer might then undergo completely stereoselective *syn*-addition while the other undergoes completely stereoselective *trans*-addition of the proton/benzyl group to the styryl double bond, although we have no proof for this. This reaction course would lead to the experimentally observed equal amounts of monodeuterated diastereomers.

Scheme 3.5



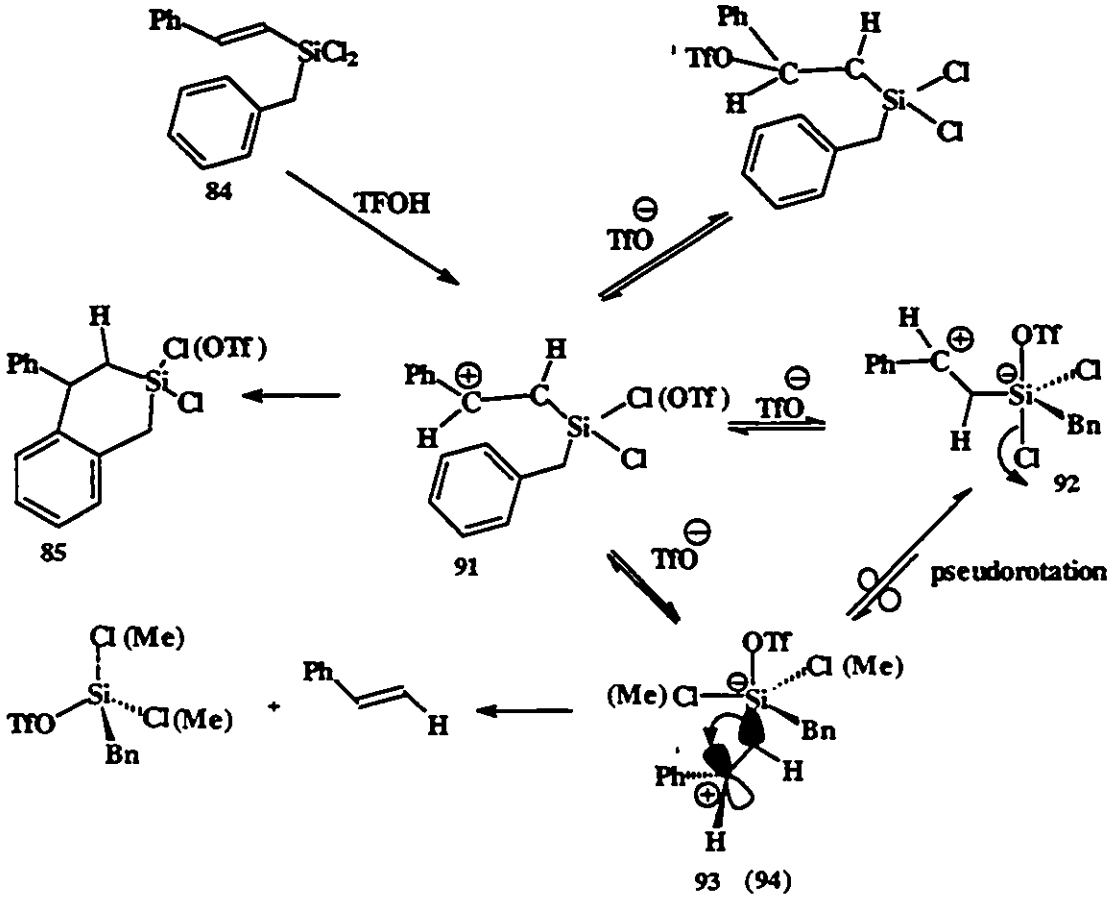
3.1.5) Mechanistic implications

The replacement of the usual electron-donating alkyl groups on silicon with electronegative groups such as chloride dramatically affected the chemical outcome of the reactions of the styryl π-systems bonded to silicon because of changes in the leaving group ability of the silyl moiety.[19]

The leaving group ability of the alkyldichlorosilyl group was attenuated when compared with trialkylsilyl group. The poor leaving group ability of the alkyldichlorosilyl group could be most clearly seen from the deuteration studies. The production of dideuterated 3,3-dichloro-1-phenyl-3-sila-tetrahydronaphthalene showed that **90** was formed reversibly from **89**; proton loss occurred more efficiently than the formal loss of "$^{+}SiCl_2CH_2Ph$". Protons eliminated in this manner, or from the cyclization/ rearomatization process, reacted with (*E*)-β-(dichlorobenzylsilyl)styrene **84** to form nondeuterated species **85** (Scheme 3.5).

The preferential loss of protons over the silyl group arises from mechanistic features at both silicon and carbon. We will deal with both of these in turn. With respect to silicon, nucleophilic substitution reactions at silicon are normally bimolecular in nature, with attack by the nucleophile the requisite first step.[9] Silicon can expand its coordination beyond tetrahedral to form stable pentacoordinate intermediates. Following addition of the electrophile to **84** giving **91**, subsequent nucleophilic attack may give pentacoordinate intermediates **92** and **93** (Scheme 3.6).

Scheme 3.6

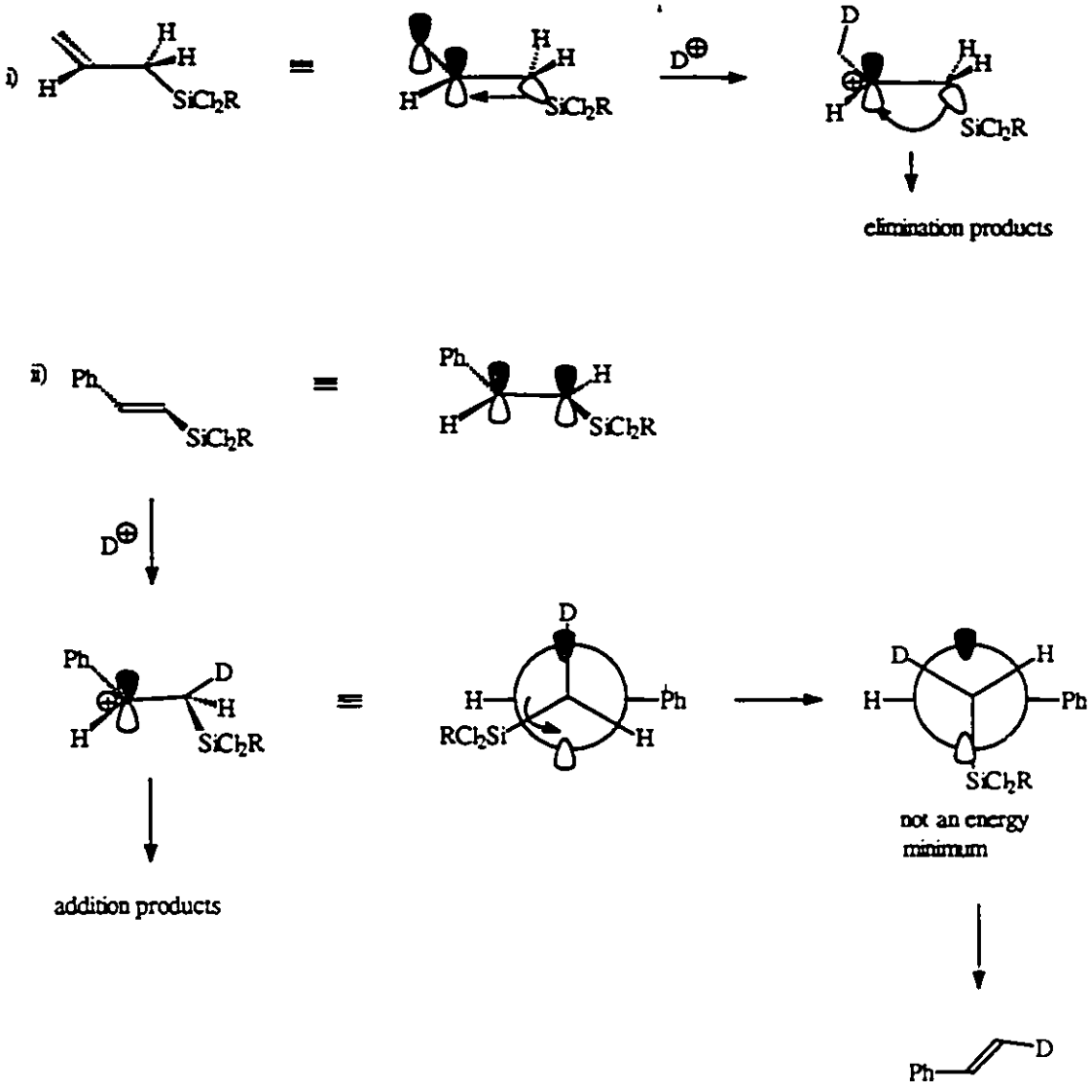


If the chloride has a higher apicophilicity[10] than the carbenium ion, then production of **92** will be favored over **93** (there will be an energy barrier between **92** and **93**, Scheme 3.6).[11] Loss of the apical Cl^- or TfO^- group leading to **92** will be followed by attack of a nucleophile at carbon giving **85**. In contrast, upon replacing both Cl ligands with Me ligands **94** the alkyl carbenium ion becomes the most apicophilic ligand on silicon and will

occupy, preferentially, the leaving or axial position. This axial orientation of the carbenium ion is conducive for elimination of the alkyl carbenium fragment from rest of the molecule.

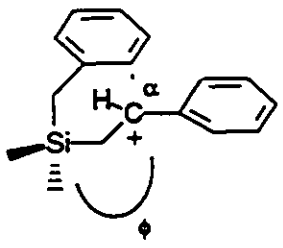
The mechanistic features at carbon might explain the difference in reactivity between (*E*)-β-(dichlorobenzylsilyl) styrene **84** and the allylsilanes. The coplanar arrangement of the Si-C bond relative to the empty p-orbital, required for optimum β-stabilization of the intermediate cation, is also highly conducive to silyl group elimination. Allylsilanes are normally more reactive than the corresponding vinylsilanes towards electrophiles because there is little or no steric interaction between the incoming electrophile and the silyl group. More important, however, the higher reactivity of allylsilanes is also attributed to the coplanar arrangement of the Si-C bond and the filled π-orbital, prior to electrophile attack (Scheme 3.7 i).[12] Thus, the silyl group in an allylsilane is more susceptible to elimination since no molecular movement is required for the β-Si stabilization of the developing cation (Scheme 3.7 i). For vinylsilanes on the other hand, the electrophile must add to the carbon bearing the silyl group engendering a steric interaction. Furthermore, molecular rotation is required for the β-effect to manifest itself (Scheme 3.7 ii). We therefore observe that although the dichloroalkylsilyl group has a lower leaving group ability than trialkylsilyl groups, β-elimination of the dichloroalkylsilyl group nevertheless occurred with allylsilanes.

Scheme 3.7

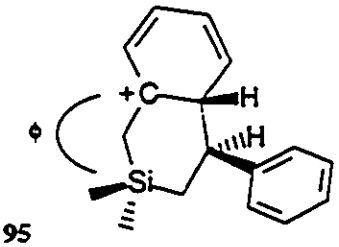

i)
SiCl2R
D⊕
elimination products
ii)
Ph
SiCl2R
addition products
not an energy minimum

To further examine the reasons for retention of the silyl group in the case of **84**, we studied the cyclization reaction of **84** using molecular mechanics calculations to determine possible orientational parameters of the reaction. When the distance α in **86a** was held at 2.5 Å to mimic the approach in the bond forming process between these two centers, the resultant angle (ϕ) between the Si-C bond and the empty p-orbital in the minimized structure was 84° (Figure 3.1). This result implies no β-effect for the cation in this conformation and may be one reason why no elimination occurred; the appropriate geometry was not obtained.

Figure 3.1: 86a: Intramolecular approach, minimized with constraint α = 2.5 Å (resultant angle ϕ Si-C-C-p-orbital = 84°), **95:** Fully cyclized structure (resultant angle ϕ Si-C-C-p-orbital = 26°)



86a



95

In contrast, following cyclization to **95**, the angle between the C-Si σ-orbital and the pentadienyl cation was found to be 26°. Little β-Si stabilization is expected here, however, on account of reduced orbital interaction between the empty p-orbital and the electron deficient Si-C σ bond (electron deficient due to electron-withdrawal by the two chloride ligands). Thus, even when the process of cyclization forces the Si-C bond into a

conformation where elimination is possible, the presence of electronegative ligands on silicon thwarts desilylation.

3.2) Experimental procedures

3.2.1) General procedures and instrumentation

The ^{1}H-NMR spectra were recorded on a Varian EM-390 (90-MHz) spectrometer and Bruker AM-500 (500-MHz) spectrometer or Bruker AC-200 (200 MHz) spectrometer. ^{2}H, ^{13}C and ^{29}Si-NMR were performed on a Bruker AC-300 (at 300 MHz for protons) and Bruker WM-250 (at 250 MHz for protons). Chemical shifts are reported with respect to tetramethylsilane as standard, set to 0 ppm. Coupling constants (J) are recorded in Hertz (Hz). The abbreviations s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, are used in reporting the spectra.

Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of ~ 200 °C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. High resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the EI method.

Infrared spectra were run on a Perkin Elmer 283 spectrometer and a BIO RAD FTS-40 spectrometer, as neat films.

The purity of new compounds was confirmed, after distillation, by chromatography on a HP-5890A Gas Chromatograph; glass capillary column, SPB-1, 30 meters, 0.075 mm ID.

All solvents were thoroughly dried before use. Dichloromethane was distilled over P_2O_5. Diethyl ether, THF and hexane were distilled over Na/benzophenone. NEt_3 was dried by refluxing with NaOH and distilling over BaO.

Diallyldimethylsilane **77**, diphenyldichlorosilane and allyldichlorophenylsilane **79** were obtained from Hüls America. Deuterated triflic acid (TfOD) was purchased from Aldrich. Diallyldiphenylsilane[13] **70** was prepared by the reaction in Et_2O of diphenyldichlorosilane with allylmagnesium bromide (1M in Et_2O). (*E*)-β-(Trichlorosilyl)styrene was prepared by the H_2PtCl_6 catalyzed hydrosilation of phenylacetylene with $HSiCl_3$ in THF.[14]

Due to the tendency of halo groups on silicon to hydrolyze easily, all reactions were carried out in dry apparatus under a nitrogen atmosphere with the use of septa and syringes for the transfer of reagents.

It should be mentioned that reaction conditions were not optimised so that the reactions might have been completed before the times given.

3.2.2) Synthesis

3.2.2a) Synthesis of diallyldichlorosilane 69

To a solution of tetrachlorosilane (25.9 g, 152.4 mmol) in diethyl ether (240 mL) was slowly added allylmagnesium bromide (305 mL, 1.0 M in Et_2O, 30.5 mmol) at -100 ° C. After stirring for 16 h at -100 °C, the reaction mixture was warmed to room temperature. Following filtration and evaporation of solvents, ^1H NMR showed diallyldichlorosilane **69** (4.1 g, 75%), allyltrichlorosilane (0.3 g, 8%), triallylchlorosilane (0.48 g, 9.6%) and tetraallylsilane (0.42 g, 7.4%) and excess tetrachlorosilane. Kugelrohr distillation gave diallyldichlorosilane **69** (oven temperature 26 °C, 30 mmHg, 2.2 g, 40%).

Diallyldichlorosilane 69:

^1H NMR ($CDCl_3$, 90 MHz): δ(ppm) 2.09-2.11 (m, 4H), 5.07-5.11 (m, 4H), 5.72-5.81 (m, 2H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 129.2, 117.9, 26.6;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) 23.2;

MS (EI, m/z): 180 (16), 165 (8), 152 (12), 139 (100) 117 (25), 103 (22), 63 (65);

HRMS (m/z, M^+): calc. for $C_6H_{10}Cl_2Si$ 179.9928; found 179.9939;

IR (neat): ν(cm^{-1}) 3083, 2978, 2925, 2888, 1633, 1433, 1400, 1169, 1090, 1030, 991, 908, 792, 598, 550. 468.

3.2.2b) Synthesis of diallyldiphenylsilane 70

To a solution of diphenyldichlorosilane (5.0 g, 19.74 mmol) in diethyl ether (100 mL) was slowly added allylmagnesium bromide (43.4 mL, 1.0 M in Et_2O, 43.4 mmol) at ambient temperature. The reaction was followed to completion by thin layer chromatography (TLC). Following filtration and evaporation of solvents, radial chromatography using hexane as eluent gave (4.5 g, 90%) diallyldiphenylsilane **70**.

Diallyldiphenylsilane 70:

^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 2.12-2.14 (m, 4H), 4.87-4.95 (m, 4H), 5.76-5.84 (m, 2H), 7.24-7.63 (m, 10H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 134.9, 133.6, 129.4, 127.7, 114.6, 19.9;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) -11.6;

MS (EI, m/z): $M^+ - C_3H_5$ 223 (90), 183 (85), 161 (100), 146 (42), 117 (39), 105 (72), 77 (26);

IR (neat): ν(cm^{-1}) 3071, 3051, 2973, 2917, 2882, 1630, 1487, 1427, 1391, 1261, 1192, 1155, 1112, 1030, 994, 930, 898, 836, 790, 736, 700, 605, 577, 477.

3.2.2c) Synthesis of (*E*)-β-(allyldichlorosilyl)styrene 81

To a solution of (*E*)-β-trichlorosilylstyrene (48.0 g, 204 mmol) in diethyl ether (250 mL) was added allylmagnesium bromide (102.0 mL, 1.0 M in Et_2O, 102.0 mmol) at -10 °C. After stirring for 4 d at -10 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Following filtration and evaporation of solvents, Kugelrohr distillation (oven temperature 100 °C, 0.4 mmHg) gave (*E*)-β-(allyldichlorosilyl)styrene **81** (22.5 g, 93%).

(*E*)-β-(Allyldichlorosilyl)styrene 81:

^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 2.27-2.28 (m, 2H), 5.18-5.21 (m, 2H), 5.85-5.93 (m, 1H), 6.46 (d, 1H, J=18.9 Hz), 7.34 (d, 1H, J=18.9 Hz), 7.37-7.54 (m, 5H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 150.2, 136.2, 129.7, 129.2, 128.7, 127.0, 119.3, 118.0, 27.6;

^{29}Si NMR ($CDCl_3$, 49.69MHz): δ(ppm) 12.9;

MS (EI, m/z): 242 (15), 201 (40), 175 (12), 165 (100), 129 (30), 103 (20), 84 (56), 77 (15), 63 (12);

HRMS (m/z, M^+): calc. for $C_{11}H_{12}Cl_2Si$ 242.0085; found 242.0088;

IR (neat): ν(cm^{-1}) 3081, 3062, 3026, 2978, 2888, 1632, 1603, 1574, 1494, 1448, 1417, 1388, 1336, 1219, 1196, 1172, 1032, 988, 911, 834, 816, 733, 688, 609, 552, 474.

3.2.2d) Synthesis of (*E*)-β-(dichlorobenzylsilyl)styrene 84

To a solution of (*E*)-β-(trichlorosilyl) styrene (48.1 g, 204 mmol) was added benzylmagnesium chloride (102 mL, 1M in Et_2O, 102 mmol). After stirring overnight at -50 °C, the reaction mixture was allowed to warm to ambient temperature (20 °C) and stirred at that temperature for 1 h. A yield of 28 g (95 %, with reference to BzMgCl) was obtained after removing excess trichlorosilylstyrene at 97 °C, 5 mmHg followed by distillation of (*E*)-β-(dichlorobenzylsilyl)styrene **84** (b.p. 170 °C, 0.1 mmHg).

(*E*)-β-(Dichlorobenzylsilyl)styrene 84:

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) 2.63 (s, 2H), 6.19 (d, 1H, J = 18.0 Hz), 7.11 (d, 1H, J = 18.0 Hz), 7.05-7.23 (m, 10H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 150.4, 136.1, 133.8, 129.7, 128.9, 128.4, 128.3, 127.2, 125.7, 118.8, 30.2;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) 15.7;

MS (EI, m/z): 292 (10), 257 (12), 201 (55), 165 (100), 91 (38), 77 (20), 63 (15), 51 (10);

HRMS (m/z, M^+): calc. 292.0206; found 292.0224;

IR (neat): ν(cm^{-1}) 3027, 2895, 1602, 1493, 1450, 1396, 1210, 1175, 11 00, 1058, 1029, 989, 908, 833, 803, 764, 733, 697, 591, 500, 459.

3.2.3) Reactions with triflic acid: general procedure

To a solution of the silane in methylene chloride was added triflic acid at reduced temperature under a N_2 atmosphere. After a period of time, the solution was allowed to warm to rt. Following ^{1}H NMR of the crude mixture, workup was performed.

3.2.3a) Reaction of diallyldimethylsilane 77 with triflic acid

Diallyldimethylsilane **77** (0.2 mL, 1.0 mmol); $CDCl_3$ (4 mL); triflic acid (0.08 mL, 0.95 mmol). After 5 min, the solution was allowed to warm to rt. ^{1}H NMR indicated about 85% conversion to a new allylsilane, presumably allyldimethylsilyl triflate. This conclusion was reinforced after hydrolysis of the crude mixture led to the formation of diallyltetramethyldisiloxane.[15,16] The remainder was dimethylsilyl ditriflate.[17]

Allyldimethylsilyl triflate 78: **^{1}H NMR** ($CDCl_3$, 200 MHz): δ(ppm) 0.49 (s, 6H), 1.92 (d, 2H, J = 8.2 Hz), 5.05 (m, 2H), 5.76 (apparent sextet, 1H, J = 8.2 Hz).

Dimethylsilyl ditriflate: **^{1}H NMR** ($CDCl_3$, 200 MHz): δ(ppm) 0.87 (s, 6H).

3.2.3b) Reactions of diallyldichlorosilane 69, diallyldiphenylsilane 70 and (*E*)-β-(allyldichlorosilyl)styrene 81 with triflic acid

The reactions of each of these compounds with triflic acid led to loss in the ^1H NMR of all vinyl signals and, after workup with MeMgBr, to the formation of complex oligomeric mixtures. A typical proton NMR is that shown for the products formed from protonation of diallyldiphenylsilane **70** **^1H NMR** ($CDCl_3$, 90 MHz): δ(ppm) 0.8-0.9 (broad m, 9H), 1.15-1.3 (broad m, 2H), 7.3 (m, 10H).

3.2.3c) Reactions of (*E*)-β-(dichlorobenzylsilyl)styrene 84 with triflic acid

(*E*)-β-(Dichlorobenzylsilyl)styrene **84** (5.7 g, 19.7 mmol) was added to triflic acid (1.7 mL, 19.7 mmol) in CH_2Cl_2 (500 mL) at -82 °C. The mixture was stirred at -82 °C for 4 d, quenched with NEt_3 (4.1 mL, 29.5 mmol), and warmed to rt. Following removal of CH_2Cl_2 under reduced pressure and replacement with diethyl ether (300 mL), methylation was effected using MeMgBr (66 mL, 3.0 M in Et_2O, 197 mmol).

Workup A); conversion to 3,3-dimethyl-1-phenyl-3-sila-tetrahydronaphthalene **86**: Methylmagnesium bromide (66 mL, 3.0 M solution in diethyl ether, 197.0 mmol) was added slowly to the reaction vessel, at 0 °C and stirred overnight at ambient temperature

(20 °C). The product was purified by Kugelrohr distillation (oven temperature 150 °C, 1.0 mmHg). Yield 3.2 g, 65%.

3,3-Dimethyl-1-phenyl-3-sila-tetrahydronaphthalene 86:

^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 0.10 (s, 3H), 0.29 (s, 3H), 1.29 (dd, 1H, J = 4.6, J = -14.2 Hz), 1.34 (dd, 1H, J = 10.4, J = -14.2 Hz), 2.12 (d, 1H, J = -14.5 Hz), 2.18 (d, 1H, J = -14.6 Hz), 4.26 (dd, 1H, J = 4.6, 10.4 Hz), 6.77-7.48 (m, 9H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 145.1, 144.8, 138.6, 130.4, 129.8, 128.9, 127.7, 126.9, 126.8, 125.4, 45.3, 21.8, 18.8, -1.2;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) 0.5;

MS (EI, m/z): 252 (100), 237 (41), 224 (7.5), 209 (7.5), 191 (7.5), 178 (41), 161(64), 141 (48), 133 (40), 121 (26), 114 (20), 105 (21)), 91 (14), 59 (21), 43 (13);

MS (CI, m/z): $M^+ + NH_4$ 270 (100), 252, 237 (18), 207 (15), 180 (40), 152 (18), 91 (10), 76 (15);

HRMS (m/z, M^+): calc. 252.1334, found 252.1340;

IR (neat) ν(cm^{-1}): 3002, 2800, 1590, 1470, 1430, 1225, 1190, 1140, 1030, 820, 770, 730, 675;

Anal. calc. for $C_{17}H_{20}Si$: C 80.97, H 8.00; found: C 80.71, H 8.06.

Workup B); conversion to 3,3-bis(trimethylsiloxy)-1-phenyl-3-sila-tetrahydronaphthalene **87**: To a solution of **85** (0.20 g, 0.68 mmol) in CH_2Cl_2 (50 mL) was slowly added

Me_3SiOK (3.0 g, 18 mmol, in CH_2Cl_2 (30 mL)). The mixture was allowed to warm to room temperature and stirred for 16 h. Ammonium chloride (50 mL, satd. soln.) was added to quench the excess Me_3SiOK and the product was extracted with Et_2O, dried over Na_2SO_4 and purified by radial chromatography. Yield 0.23 g, 85%.

3,3-Bis(trimethylsiloxy)-1-phenyl-3-sila-tetrahydronaphthalene 87:

^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 0.10 (s, 9H), 0.23 (s, 9H), 1.31 (dd, 1H, J = 4.4 Hz, J = -14.5 Hz), 1.32 (dd, 1H, J = 10.40 Hz, J = -14.5 Hz), 2.21 (d, 2H, J = -14.8 Hz), 4.40 (dd, 1H, J = 4.5 Hz, J = 10.4 Hz), 6.77-7.49 (m, 9H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 144.2, 143.9, 136.9, 130.6, 128.4, 128.3, 127.4, 126.3, 126.2, 125.0, 45.0, 22.9, 18.6, 1.8, 1.6;

MS (EI, m/z): 400 (28), 386 (5), 371 (8), 309 (25), 297 (30), 281 (50), 207 (100), 149 (40), 84 (94);

HRMS (m/z, M^+): calc. 400.1710; found 400.1704.

IR (neat): ν(cm^{-1}) 2950, 1600, 1490, 1450, 1250, 1210, 1160, 1050, 835, 750, 690;

Workup C; oxidation to 2(2-hydroxymethylphenyl)-2-phenylethanol **88**: To a solution of 1-phenyl-3,3-(dichlorosila)tetrahydronaphthalene **85** in CH_2Cl_2 prepared as above at half scale (prior to methylation), NEt_3 (2.0 mL, 14.8 mmol) was added to neutralize the acid present. KF (14 g, 250 mmol, 25 equiv.) was then added to the reaction mixture at ambient temperature (20 °C) and stirred for 2 h. Dimethylformamide (10 mL), water (10

mL), and hydrogen peroxide (27 mL, 236 mmol, 24 equiv., 30% in H_2O) were added and the ensuing solution heateded for 7 h at 60 °C. The reaction mixture was quenched with sodium bisulphite prior to extraction with Et_2O, removal of solvents under reduced pressure and purification by radial chromatography. Yield 0.49 g, 22% with reference to (*E*)-β-dichlorobenzylsilyl)styrene **84**.

2(2-Hydroxymethylphenyl)-2-phenylethanol 88:

^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 2.17 (broad s, 2H, OH), 4.07 (dd, 1H, J = 8.9 Hz, J = -10.4 Hz), 4.15 (dd, 1H, J = 6.2 Hz, J = -10.4 Hz), 4.48 (d, 1H, J = -12.4 Hz), 4.9 (dd, 1H, J = 6.2 Hz, J = 8.9 Hz), 4.77 (d, 1H, J = -12.3 Hz), 7.12-7.29 (m, 9H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 141.5, 140.5, 139.2, 129.6, 128.7, 128.1, 127.7, 126.9, 126.8, 66.2, 63.4, 47.8;

MS (EI, m/z): M^+-H_2O 210 (15), 192 (30), 179 (100), 165 (23), 152 (8), 119 (32), 91 (50), 77 (10), 65 (8);

MS (CI, m/z): $M^+ + NH_4$ 246 (95), 228 (100), 209 (20), 193 (38), 180 (20), 119 (10), 91 (5);

HRMS (m/z, M^+-H_2O): calc. 210.1041; found 210.1045;

IR (neat): ν(cm^{-1}) 3359, 3082, 3026, 2897, 1600, 1493, 1451, 1400, 1261, 1070, 909, 759, 699.

Deuteration of (*E*)-β-dichlorobenzylsilylstyrene **84**: (*E*)-β-Dichlorobenzylsilylstyrene **84** (1.0 g, 3.4 mmol) was added dropwise to deuterated triflic acid (0.3 mL, 3.4 mmol) in $CDCl_3$ (35 mL) at -50 °C. Immediately after the addition, the mixture was allowed to warm to -2 °C over 3.5 h and was then quenched by the addition of NEt_3 (5.0 mL, 34 mmol). The solvents were removed under reduced pressure and MeMgBr (33 mL, 3.0 M in Et_2O) was added to effect methylation. ^1H NMR and ^2H NMR indicated mono- and di-deuteration at the position adjacent to silicon. The monodeuteration occurred at both diastereotopic positions in equal proportions. **^2H NMR** ($CDCl_3$) δ(ppm) 0.97, 1.05.

Analysis of the mass spectrum[18] indicated 44.18% of the nondeuterated, 39.44% monodeuterated, and 16.38% dideuterated species. **MS** [EI, m/z, M^+]: 251 (9), 252 (88), 253 (100), 254 (58), 255 (17); compare with the natural abundance distribution MS [EI, m/z, M^+]: 251 (12), 252 (100), 253 (28), 254 (8), 255 (1).

3.2.4) Molecular mechanics calculations

Molecular mechanics calculations were done with PC-Model (Serena Software, Bloomington, Indiana) using the supplied MMX force constants. As appropriate force constants are not available for Cl-Si bonds, the intermediates **86a** and **95** were modelled with Si-Me groups instead. For compound **86a** the distance α was constrained to 2.5 Å in order to mimic the approach towards the transition state for bond formation between these

two centers. The Si-C-C-p-orbital angles in the minimized structures of **86a** and **95** were found to be 84° and 26°, respectively.

3.3) References and notes

1) Colvin, E.W. *Silicon in Organic Synthesis*, Butterworths, London (1981); Weber, W.P. *Silicon Reagents in Organic Synthesis*, Springer, Berlin (1983).

2) Hagen, G.; Mayr, H. *J. Chem. Soc., Chem. Commun.* 91 (1989); Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* 113, 4954 (1991).

3) Noll, W. *Chemistry and Technology of Silicones* Academic Press, New York, p. 141 (1968).

4) Brook, M. A.; Hülser, P.; Sebastian, T. *Macromolecules* 22, 3816 (1989); Brook, M. A.; Modi, P.; Dickson, J. M. *Macromolecules* 26, 2624 (1993).

5) One possibility which does exist is that indeed the cyclization took place, but was followed by protiodesilylation at the propyl group from the silicon. We have, however, no evidence to support this conclusion.

6) For example, see Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Organometallics* 7, 1165 (1988).

7) Eaborn, C. *Organosilicon Compounds*, Butterworths, London, Chap. 8 (1960).

8) Tamao, K.; Hayashi, T.; Ito, Y. in *Frontiers of Organosilicon Chemistry*, Bassindale, A. R.; Gaspar, P. P. eds., Royal Society of Chemistry, Cambridge, p. 197 (1989); Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc, Chem. Commun.* 29 (1984).

9) See, however, the most recent report of silylium ion formation: Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* 383 (1993); Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* 262, 402 (1993).

10) Corriu, R. J. P. *J. Organomet. Chem.* 400, 81 (1990).

11) Bassindale, A. R.; Taylor, P.G. in *The Chemistry of Organic Silicon Chemistry*, Patai, S.; Rappoport, Z.; eds., Wiley-Interscience, Chichester, Vol. 2, Chap. 13 (1989).

12) In β-functionalized silanes, this effect is sufficiently strong that even in the ground state it manifests itself in the lengthening of the β-C-leaving group bond: White, J. M.; Robertson, G. B. *J. Org. Chem.* 57, 4638 (1992). Theoretical and spectral studies also support an unexpected raising of the magnitude of the π-HOMO in allylsilanes in the ground state that has been attributed to Si-C hyperconjugative interaction with the filled π-HOMO: Weidner, U.; Schweig, A. *Angew. Chem. Int. Ed. Engl.* 11, 146 (1972); Brown, R. S.; Eaton, D. F.; Hosomi, A.; Traylor, T. G.; Wright, J. M. *J. Organomet. Chem.* 66, 249 (1974).

13) Cragg, R. H.; Jones, R. G.; Swain, A. C.; *Eur. Polym. J.* 27, 785 (1991).

14) Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics* 1, 355 (1982).

15) The ^1H NMR spectrum of the disiloxane was identical to that reported in the literature for the product of hydrolysis of the commercially available product $ClMe_2SiCH_2CH{=}CH_2$ obtained from Aldrich.

16) Forbes, M. D. E.; Patton, J. T.; Myers, T. L.; Maynard, H. D.; Smith, D. W., Jr.; Schulz, G. R.; Wagener, K. B. *J. Am. Chem. Soc.* 114, 10978 (1992).

17) Brook, M. A.; Jiang, J.; Dickson, J.M. *Heteroatom Chem.* in press.

18) Werstiuk, N. H.; Banerjee, S. *J. Org. Chem.* 46, 470 (1981).

19) The reaction of (*E*)-β-(chlorodibenzylsilyl)styrene, which compared to (*E*)-β-(dichlorobenzylsilyl)styrene **84** has an increased statistical probability of trapping the cation formed from proton addition across the styryl group, nevertheless proceeded by elimination. This elimination reaction is due to the increased electron-releasing ability of the dibenzylchlorosilyl moiety over the dichlorobenzylsilyl moiety.

CHAPTER 4

EVALUATION OF THE REACTIONS OF CARBON ELECTROPHILES WITH AN ORGANOSILICON π-NUCLEOPHILE

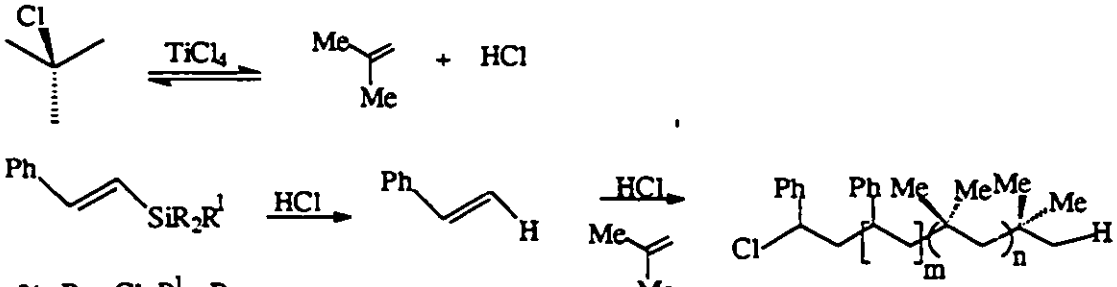
4.1) The addition of carbon electrophiles to (*E*)-β-(dichlorobenzylsilyl)styrene

The ability of (*E*)-β-(dichlorobenzylsilyl)styrene to undergo proton addition without loss of silicon (protiodesilylation) has been previously described. Replacement of the usual electron-donating alkyl groups on silicon with electronegative chloride ligands, changes the mechanism and outcome of the reaction from substitution to addition. Our next task was to find out whether carbon electrophiles could also be successfully used to perform electrophilic additions to dichloroorganosilanes. Carbon-carbon bond formation has several advantages over carbon-proton bond formation. The former may be used to assemble large molecules and, moreover, could lead to the formation of a new chiral center. For these reasons we reacted the substrate that was successful with proton addition, (*E*)-β-(dichlorobenzylsilyl)styrene **84**, with a series of carbon electrophiles of varying electrophilicity.

4.1.1) Results

The reaction of *tert*-butyl chloride with (*E*)-β-(dichlorobenzylsilyl)styrene **84** in the presence of titanium tetrachloride led exclusively to the formation of an intractable polymeric mixture (Scheme 4.1). Examination of the crude ^{1}H NMR allowed us to conclude that a polymer containing primarily polystyryl units, with inclusion of small amounts of isobutylene groups, was the major constituent of the reaction products. These polymers, perhaps of the type **97** shown in Scheme 4.1, contained no silicon groups.[1,2]

Scheme 4.1



The loss of silicon when *tert*-butyl chloride was used as an electrophile was probably due to protiodesilylation initiated by protons produced through elimination of tertiary butyl cations. The protiodesilylation step was likely facilitated by the high concentration of relatively nucleophilic chloride anion. Such anions might promote desilylation of (*E*)-β-

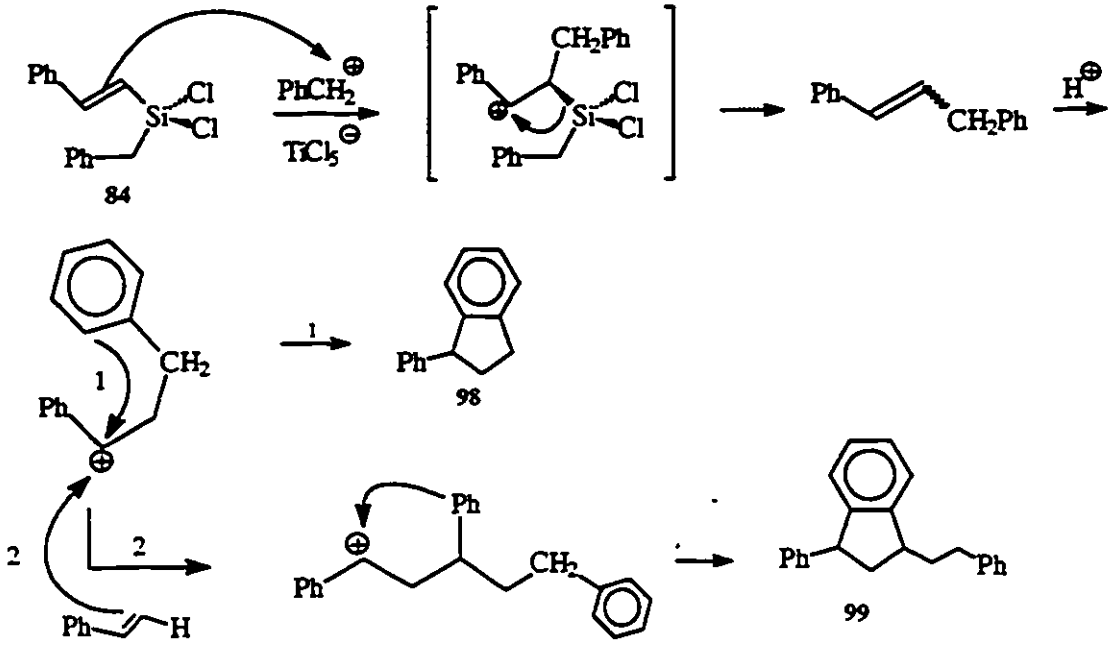
(dichlorobenzylsilyl)styrene **84** to give styrene which then polymerized with incorporation of some isobutylene (Scheme 4.1). This process, of protiodesilylation followed by polymerization of styrene, is analogous to the process observed for trimethylsilylstyrene **96** (Scheme 4.1).[1]

Upon exposure of (*E*)-β-(dichlorobenzylsilyl)styrene **84** to the trityl cation (Ph_3C^+), no reaction was observed irrespective of the nature of the counterion (BF_4^-, $SbCl_6^-$).

The addition of $^tBu^+$ and Ph_3C^+ to silylstyrene **84** should, in theory, be extremely slow because of the steric interaction. Steric interaction could account for the absence of reaction when Ph_3C^+ was used as the electrophile. In addition, steric interaction could explain why elimination of protons from $^tBu^+$ occured instead of addition of $^tBu^+$ to the silylstyrene **84**; proton elimination may have a lower energy pathway. Mayr has similarly proposed that steric hindrance accounts for the absence of reactivity of trityl chloride with isobutene, α-methylstyrene and styrene.[3] Mayr found that α-methoxybenzyl chloride, which forms an even more electronically stabilized carbenium ion, reacts readily with these alkenes. Mayr therefore concluded that resonance stabilization of the trityl cation could not account for its inactivity.[3]

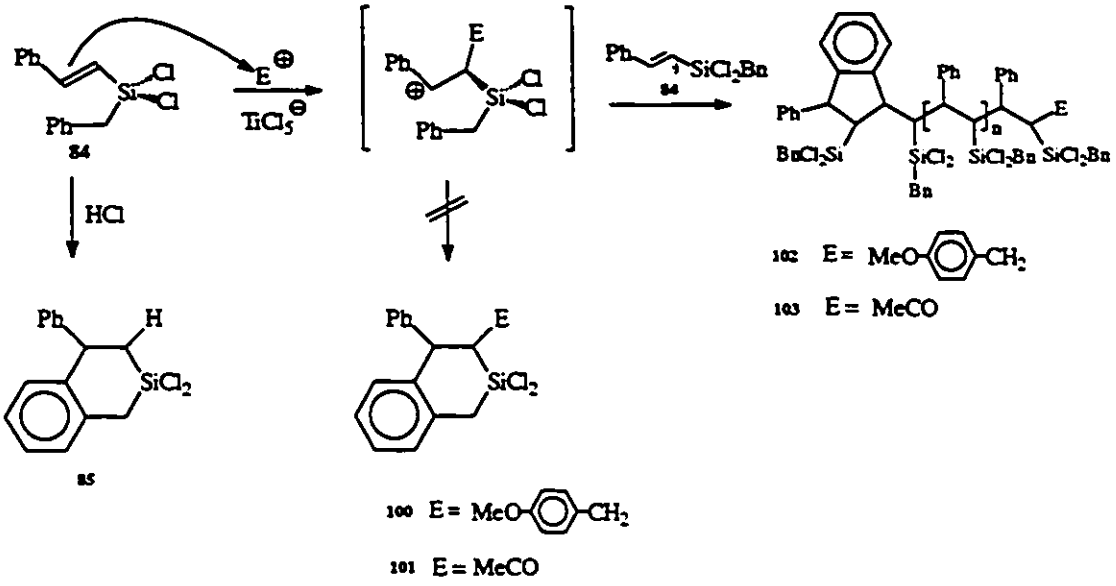
Benzyl cations added to (*E*)-β-(dichlorobenzylsilyl)styrene **84** to give an oligomeric mixture in which most of the silicon groups had disappeared (> 70%). The primary product appeared to be an adduct between the benzyl cation and styrene **98** or a styrene dimer **99** (Scheme 4.2).

Scheme 4.2



p-Methoxybenzyl cation reacted with (*E*)-β-(dichlorobenzylsilyl)styrene **84** to give 20% of 3,3-dichloro-1-phenyl-3-silatetrahydronaphthalene **85** and 60% of the oligomer **102** in which most of the silyl groups were retained (Scheme 4.3). There was no evidence for the expected silatetrahydronaphthalene derivative **100** (Scheme 4.3).

Scheme 4.3



The addition of acyl cations to (*E*)-β-(dichlorobenzylsilyl)styrene **84** also led to the formation of **85** (10%) and oligo(benzyldichlorosilyl)styrene **103** in which 90% of the silyl group had been retained but less than 5% of the acetyl groups had been incorporated. Once again, there was no evidence for the desired cyclized compound **101** (Scheme 4.3). This result contrasted with the results obtained by Fleming for the reaction of trimethylsilylstyrene with phenylacetyl chloride in the presence of Lewis acids. Fleming's reaction produced desilylated materials exclusively.[4]

The formation of 3,3-dichloro-1-phenyl-3-silatetrahydronaphthalene **85** was the result of proton addition to (*E*)-β-(dichlorobenzylsilyl)styrene **84**.[5] Presumably, once the educt cations *p*-$MeOPhCH_2^+$ and $MeCO^+$ initiated the reaction, polymerization occurred

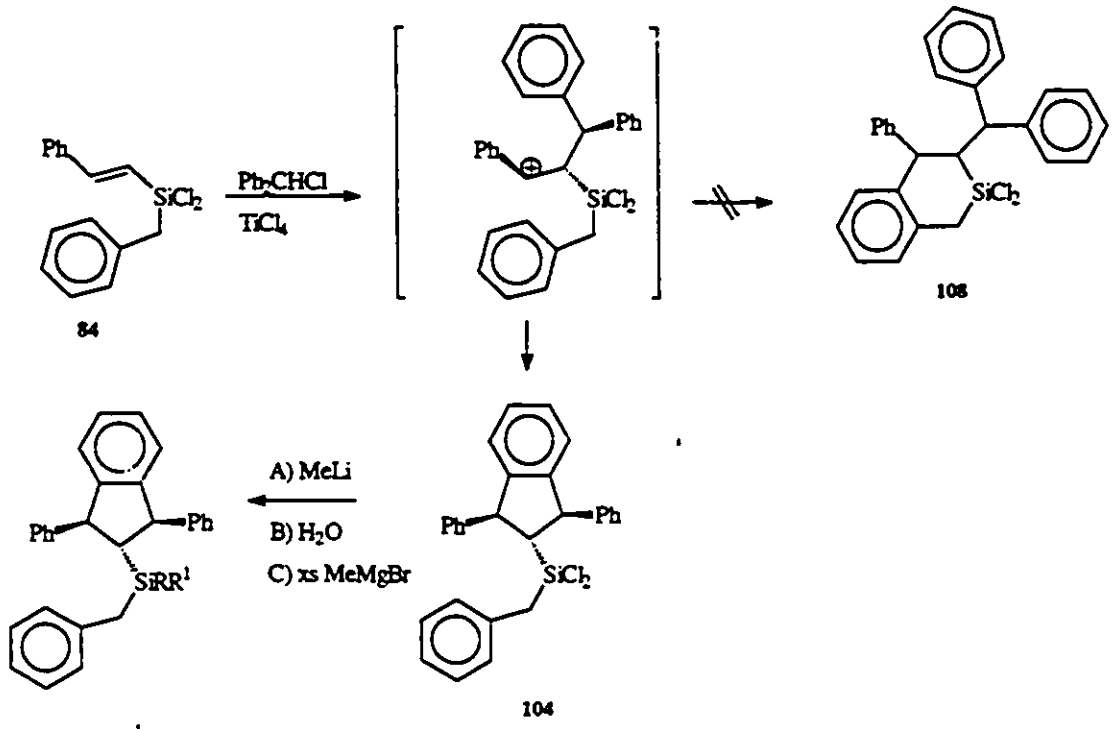
which terminated with Friedel-Crafts ring closure (**102** and **103**, Scheme 4.3). Ring closure produced protons that could compete with the educt cations for the silylstyrene **84**. This type of competitive addition has previously been reported. Melloni, for example, detected HCl adducts of alkenes and alkynes formed during cyclization reactions of these π-nucleophiles with chlorodiphenylmethane in the presence of Lewis acids.[6]

The most rewarding carbon electrophile was Ph_2CH^+. Thus, the reaction of chlorodiphenylmethane with (*E*)-β-(dichlorobenzylsilyl)styrene **84** in the presence of $TiCl_4$ gave 73% of the 1:1 cyclized adduct 1,3-diphenyl-2-(dichlorobenzylsilyl)indane **104** after chromatography (Scheme 4.4). The ^1H NMR spectrum of the crude mixture, after removal of solvents, revealed that only a single *trans/trans* meso indane **104** was produced at 42 °C and -35 °C, respectively. This *trans/trans* diastereoselectivity is consistent with the observed stereochemistry for the addition of diarylcarbenium ions to *Z*- and *E*-alkenes.[7] These reactions occur stereoselectively to form *trans/trans*-1,2,3-trisubstituted indanes as a result of a transition state or intermediate that is less crowded than that through which the *cis/cis* or *trans/cis*-1,2,3-trisubstituted indanes would arise.[7]

The structural elucidation of **104** was accomplished after converting it to the methylhydroxysilyl derivative **105**. The reaction of **104** with 2 equivalents of methyl lithium resulted only in monomethylation giving **105**; steric congestion of the silicon by the indane moiety effectively prevented methylation of the second chloride ligand. This chloride was, however, susceptible to hydrolysis upon quenching the reaction mixture with water. Complete methylation to **107** was possible only after a huge excess of MeMgBr

was allowed to react with **104** over an extended period of time. Direct hydrolysis of **104** gave the diol **106**. Again, there was no evidence for the 6-membered ring **108**.

Scheme 4.4



A) R = Me, R^1 = OH **105**

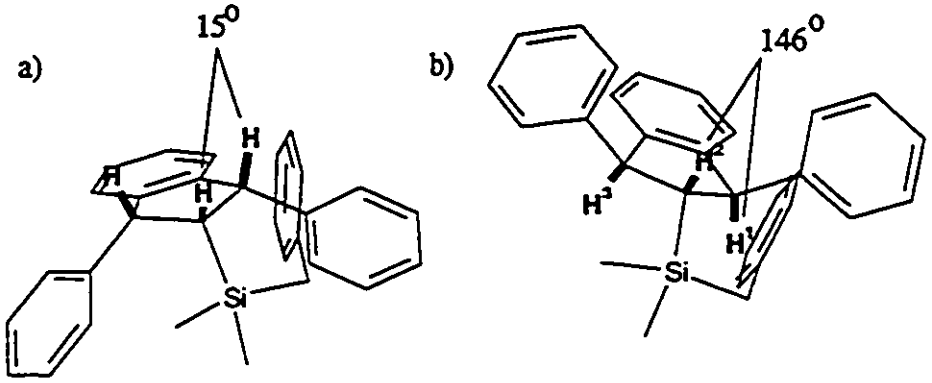
B) R, R^1 = OH **106**

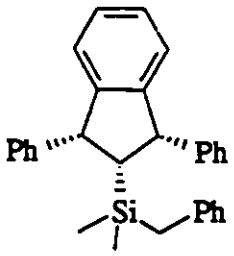
C) R, R^1 = Me **107**

The structure was assigned the *trans/trans* geometry based on nOe (nuclear Overhauser effect) measurements, as well as by the ^1H-^1H scalar coupling constants and molecular mechanics calculations. A coupling constant $J(H^1\text{-}H^2)$ of 11.8 Hz correlates

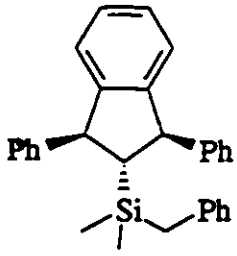
better with a 180° dihedral angle (*trans* geometry) on the Karplus scale, than to a 0° dihedral angle (*cis* geometry). Molecular mechanics calculations indicated that a dihedral angle of 146° for H^2-C-C-H^1 or H^2-C-C-H^3 in **107** when the hydrogens H^1, H^2 and H^3 are *trans* diaxial, corresponded to a low energy (Figure 4.1b).

Figure 4.1: Molecular mechanics (MM2) minimized structure of a) the *cis-cis* isomer **109**; steric energy 49.9 kcal/mol and, b) the *trans-trans* isomer **107**; steric energy 26.4 kcal/mol.





109



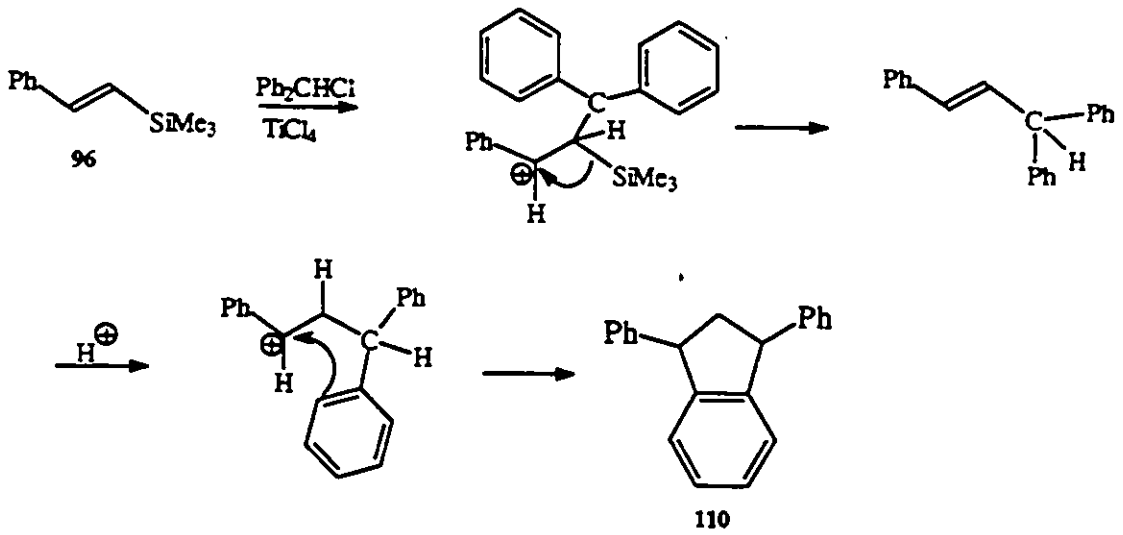
107

In contrast, structure **109** which has a dihedral angle of 15° for the hydrogens that are *cis* to each other was of a higher energy perhaps due to the torsional strain resulting from gauche bulky phenyl and silyl groups (Figure 4.1a).

4.1.2) β-Silyl group leaving group ability

The elimination of silicon from the carbon skeleton requires bimolecular nucleophilic substitution reaction at silicon, with attack by the nucleophile as the requisite first step.[5] Thus, attack by the counterion Cl^- favors a pentacoordinate intermediate which has the most electronegative ligands (Cl) in the apical position.[8,9] We have explained in the previous chapter that the apicophilicity of the chloride might explain the decreased leaving group ability of the $BnCl_2Si$ group when compared to the $SiMe_3$ group. For instance, for the substrate (*E*)-β-(dichlorobenzylsilyl)styrene **84** which has a $BnCl_2Si$ group,[10] the 1:1 addition product **104** was obtained for the electrophile Ph_2CH^+ (Scheme 4.4). In contrast, for the analogous substrate **96** which has a $SiMe_3$ group, the elimination product **110** was formed exclusively using the same electrophile (Scheme 4.5).[11]

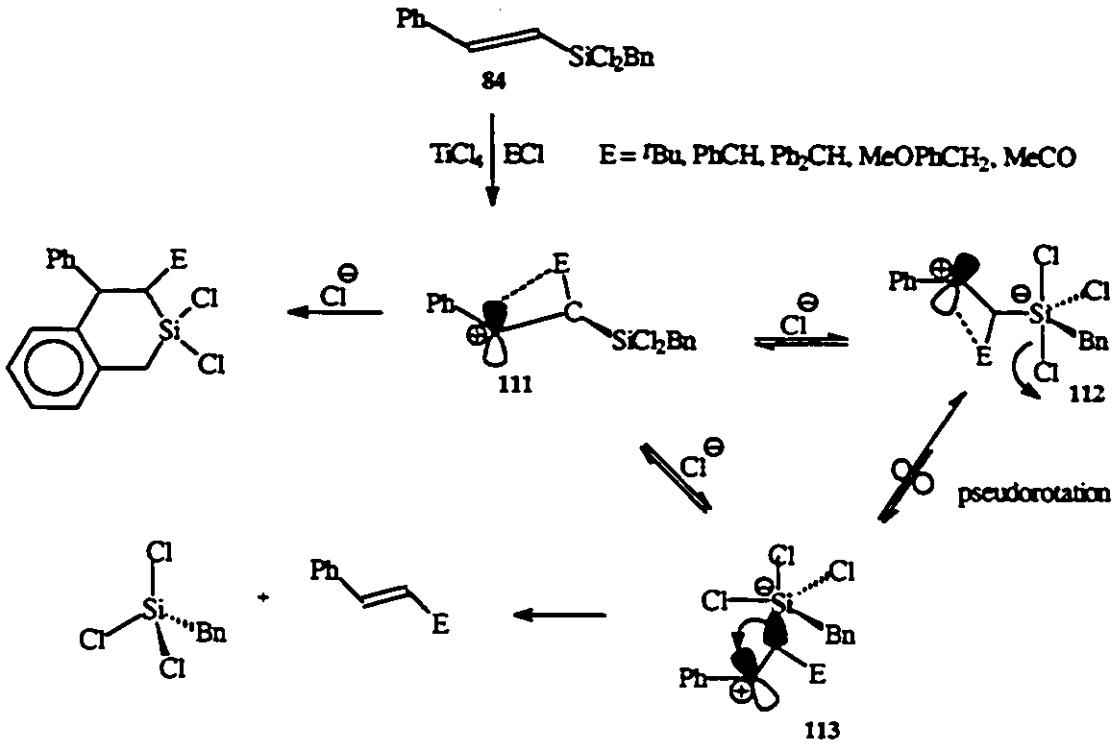
Scheme 4.5



The question we need now to address is why the loss of a silyl group was observed for some reactions and not for others given that all the reactions involve the same substrate **84**. We know that the relative electronegativities of ligands determine which ligands occupy the apical or leaving group position; greater apicophilicity or leaving group ability is associated with very electronegative groups.[9] Therefore, we need to examine how the different carbon electrophiles might affect the relative electronegativity of the alkyl carbenium ion fragment on silicon, and in so doing influence the ability of this fragment to be cleaved from silicon.

The electronegativity, and therefore apicophilicity, of the alkyl carbenium ion fragment of intermediate **111** decreases relative to chloride as the stability of the adduct carbenium ion increases (Scheme 4.6). The stability of the adduct ion **111** is in turn dependent on increased through-space electron-donation from the π electrons on **E** (where the electrophiles are aryl carbenium ions) or lone pairs of **E** (in the case of the acylium ion) to the positive charge (Scheme 4.6).

Scheme 4.6



Thus, as the ligands of the educt electrophiles $PhCH_2^+$, *p*-$MeOPhCH_2^+$, CH_3CO^+ and Ph_2CH^+ become more electron rich, as characterized by greater stability of the cations, there will be increasing electron-donation from E to the positive charge of the adduct **111**.[12] This electron-donation in **111** leads to a less electronegative and therefore less apicophilic alkyl carbenium ion fragment **112** which is less likely to undergo desilylation. That is, the pentacordinate intermediate **112** is favored over intermediate **113**. The correlation between educt ion stability and silyl group retention is then readily seen from

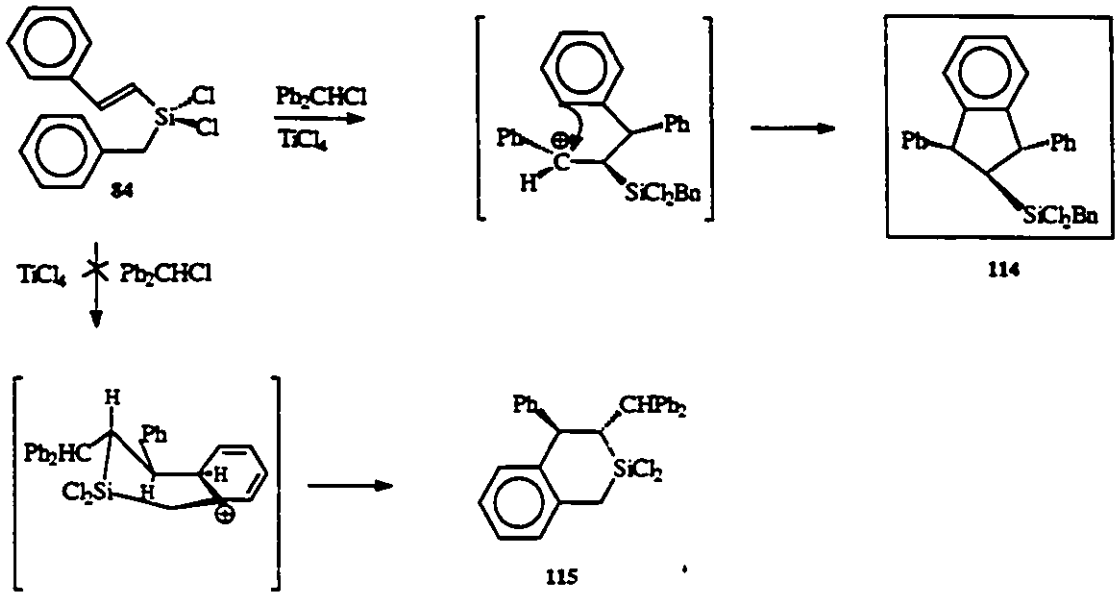
the relationship between educt carbenium ion and % silyl group retention; $PhCH_2^+$ (30%) < *p*-$MeOPhCH_2^+$ (60%) < CH_3CO^+ (90%) < Ph_2CH^+ (100%). Thus, desilylation is reduced as the educt carbenium ion becomes increasingly stable.

The degree of silyl group retention for the *t*-Bu system is not included since, as mentioned above, the reaction mechanism is thought to proceed exclusively by protiodesilylation.

4.1.3) The reaction with Ph_2CH^+: 6-membered ring *versus* 5-membered ring formation

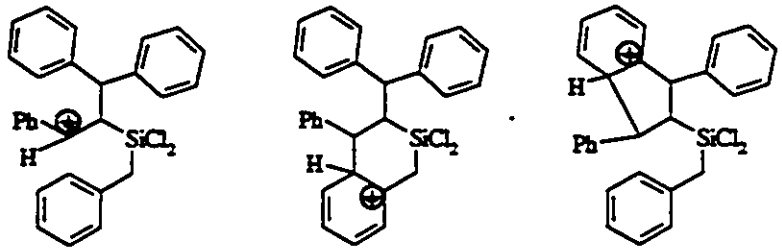
Initially, we anticipated that in analogy to 3,3-dichloro-1-phenyl-3-silatetrahydro naphthalene **85** (Scheme 4.3) a 6-membered ring **115** would be formed upon addition of Ph_2CH^+ to (*E*)-β-(dichlorobenzylsilyl)styrene **84** (Scheme 4.7). However, the 5-membered ring indane derivative **114** was exclusively formed (Scheme 4.7). There is a statistical advantage for the formation of the 5-membered ring **114** in preference to the 6-membered ring **115**. That is, two aryl rings are present which can cyclize giving the 5-membered ring, while only one aryl ring that can cyclize to give the 6-membered ring.

Scheme 4.7



In order to determine what additional factors influenced the formation of the 5-membered indane **114** we calculated the relative stability of three cations, namely the open cation **116**, the 6-membered ring cation **117**, and the 5-membered ring cation **118** (Figure 4.2). The open cation **116** was found to have a heat of formation of 181.6 kcal/mol, whereas the 6-membered ring **117** and 5-membered ring **118** were found to have heats of formation 188.0 and 180.9 kcal/mol, respectively. Thus, on thermodynamic grounds, the formation of 5-membered ring **118** is favored over 6-membered ring **117**.

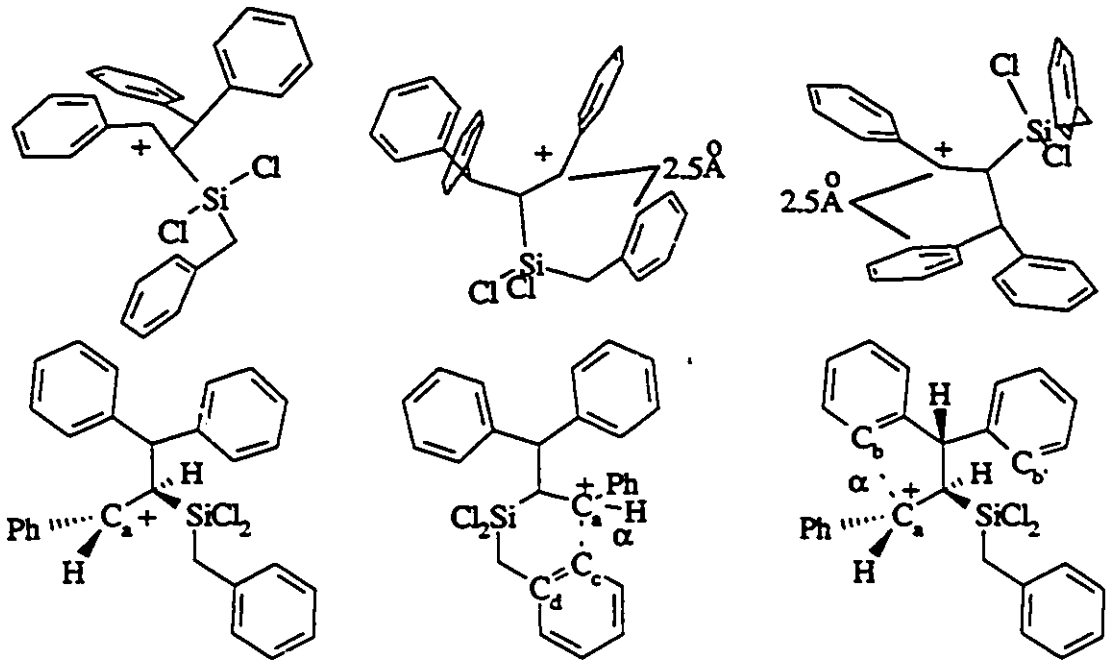
Figure 4.2: Proposed intermediates for the reactions shown in Scheme 4.7



116 **117** **118**

To examine the relative degree of steric resistance that might be incurred in going from the open cation **116** to the 6-membered ring cation **117** or the 5-membered ring cation **118** (Figure 4.2), we looked at the conformational energy on the path to the transition state using molecular mechanics calculations. The distances between the benzylic carbon ($^{+}C_a$) and the aromatic carbons (C_c in **119** and C_b in **120**, respectively) were fixed at 2.5Å (Figure 4.3). The results after structure minimization suggested that a greater energy barrier would be encountered during formation of the 6-membered ring **119** (steric energy 79.10 kcal/mol) compared to formation of the 5-membered ring **120** (steric energy 65.05 kcal/mol). The open cation **116** with steric energy 58.00 kcal/mol was the least sterically hindered.

Figure 4.3: MMX calculated structures **116**, **119** and **120** on the transition paths for the formation of 6-membered **115** and 5-membered **114** rings ($\alpha = 2.5$Å)



116 **119** **120**

These results suggest that formation of the indane **114** may also be favored over the silatetrahydronaphthalene derivative on kinetic grounds (Scheme 4.7).

The Si-C-C$^+$-p-orbital dihedral angle in the minimized structure **120** was found to be 172°. This dihedral angle could have led to significant β-Si stabilization and thus desilylation, had it not been for the electronegative chloride ligands on silicon.

4.2) Experimental procedures

4.2.1) General procedures and instrumentation

The ^{1}H-NMR spectra were recorded on a Varian EM-390 (90-MHz) spectrometer and the Bruker AM-500 (500-MHz) spectrometer, Bruker AC-300 (300 MHz) spectrometer or Bruker AC-200 (200 MHz) spectrometer. ^{13}C and ^{29}Si-NMR were performed on a Bruker AC-200 (at 200 MHz for protons), and a Bruker AC-300 (at 300 MHz for protons), respectively. Chemical shifts are reported with respect to tetramethylsilane as standard, set to 0 ppm. Coupling constants (J) are recorded in Hertz (Hz). The abbreviations s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, are used in reporting the spectra.

Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of ~ 200 °C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. High resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the EI method. Infrared spectra were run on a Perkin Elmer 283 spectrometer and a BIO RAD FTS-40 spectrometer, as a neat film.

The purity of new volatile compounds was confirmed by chromatography on a HP-5890A Gas Chromatograph; glass capillary column, SPB-1, 30 meters, 0.075 mm ID after distillation.

All solvents were thoroughly dried before use. Dichloromethane was distilled over P_2O_5. Diethyl ether, THF and hexane were distilled over Na/benzophenone. NEt_3 was dried by refluxing with NaOH and distilling over BaO.

Due to the tendency of halo groups on silicon to hydrolyse easily, all reactions were carried out in dry apparatus under a nitrogen atmosphere with the use of septa and syringes for the transfer of reagents.

The standard work-up procedure for all reaction products, unless otherwise indicated, was extraction with diethyl ether, washing with distilled water, removal of solvent under reduced pressure and purification by radial chromatography and/or distillation or Kugelrohr distillation. Reaction conditions were not optimised so that reactions might have been completed within the reaction times given.

4.2.2) Reactions of (*E*)-β-(dichlorobenzylsilyl)styrene 84 with carbon electrophiles

4.2.2a) *tert*-Butyl cation as electrophile

(*E*)-β-(Dichlorobenzylsilyl)styrene **84** (4.64 g, 15.8 mmol) was added to a mixture of titanium tetrachloride (2.0 mL, 17.4 mmol), and *tert*-butyl chloride (1.61 mL, 17.4 mmol) in dichloromethane (400 mL) at -40 °C. The reaction mixture was stirred at -40 ° C (20 h), -10 °C (1 h) and 0 °C (2 h) followed by the removal of dichloromethane under

reduced pressure at ambient temperature (22-25 °C). Alkylation was effected using MeMgBr (53 mL, 3.0 M in diethyl ether, 159 mmol) and stirring for 16 h at ambient temperature. The reaction yielded a complex oligo/polymeric mixure, primarily polystyrene with some isobutylene (~10%).

Crude material; ^{1}H NMR ($CDCl_3$ 90 MHz): δ(ppm) 1.2 (broad s, ~ 0.6 H), 1.5-2.3 (m, 3H), 7.3-7.6 (m, 5H).

4.2.2b) Benzyl cation as electrophile

(*E*)-β-(Dichlorobenzylsilyl)styrene **84** (2.0 g, 6.8 mmol) was added to a mixture of titanium tetrachloride (3.4 mL, 29.6 mmol) and benzyl chloride (0.78 mL, 6.8 mmol) in dichloromethane (140 mL) under reflux. The reaction mixture was stirred under reflux for 48 h followed by removal of dichloromethane under reduced pressure at ambient temperature (22-25 °C). Alkylation was effected using MeMgBr (90 mL, 3.0 M in diethyl ether, 270 mmol) and stirring for 16 h at ambient temperature. The crude ^{1}H NMR showed the presence of ~ 30% Me_2Si groups. Otherwise, the oligomeric mixture [^{1}H NMR ($CDCl_3$, 90 MHz): δ(ppm) 0.1-0.35 (m, < 30% based on aryl protons, $SiMe_2$), 1.4-1.7 (m, 6H), 2.1-2.3 (m, 1H), 3.5-4.2 (m, 1 H), 7.3-7.6 (m, 14 H)] contained primarily styryl monomers and dimers (dimer formation could be initiated by benzyl cations, Scheme 4.2).

4.2.2c) *para*-Methoxybenzyl cation as electrophile

(*E*)-β-(Dichlorobenzylsilyl)styrene **84** (2.0 g, 6.8 mmol) was added to a mixture of titanium tetrachloride (3.4 mL, 29.6 mmol) and *p*-methoxybenzyl chloride (0.92 mL, 6.8 mmol) in dichloromethane (140 mL) under reflux. The reaction mixture was stirred under reflux for 48 h followed by removal of dichloromethane under reduced pressure at ambient temperature (22-25 °C). Alkylation was effected using MeMgBr (90 mL, 3.0 M in diethyl ether, 270 mmol) and stirring for 16 h at ambient temperature. The reaction yielded 3,3-dimethyl-1-phenyl-3-silatetrahydronaphthalene **86** (0.34 g, 20%), along with oligomeric material.

3,3-Dimethyl-1-phenyl-3-silatetrahydronaphthalene 86:

^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 0.10 (s, 3H), 0.29 (s, 3H), 1.29 (dd, 1H, J = 4.6, J = -14.2 Hz), 1.34 (dd, 1H, J = 10.4, J = -14.2 Hz), 2.12 (d, 1H, J = -14.5 Hz), 2.18 (d, 1H, J = -14.5 Hz), 4.26 (dd, 1H, J = 4.6, J = 10.4 Hz), 6.77-7.48 (m, 9H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 145.1, 144.82, 138.6, 130.4, 129.8, 128.9, 127.7, 126.9, 126.8, 125.4, 45.3, 21.8, 18.8, -1.2;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) 0.5;

MS (EI, m/z): 252 (100), 237 (41), 224 (7.5), 209 (7.5), 191 (7.5), 178 (41), 161 (64), 141 (48), 133 (40), 121 (26), 114 (20), 105 (21)), 91 (14), 59 (21), 43 (13);

MS (CI, m/z): $M^+ + NH_4$ 270 (100), 252 (35), 237 (18), 207 (15), 180 (40), 152 (18), 91 (10), 76 (15);

HRMS (m/z, M^+): calc. for $C_{17}H_{20}Si$ 252.1334, found 252.1340;

IR (neat): ν(cm^{-1}) 3002, 2800, 1590, 1470, 1430, 1225, 1190, 1140, 1030, 820, 770, 730, 675;

Anal. calc. for $C_{17}H_{20}Si$: C 80.97, H 8.00; found: C 80.71, H 8.06.

4.2.2d) Acylium ion as electrophile

(*E*)-β-(Dichlorobenzylsilyl)styrene **84** (1.0 g, 3.4 mmol) was added to a mixture of titanium tetrachloride (1.65 mL, 14.4 mmol) and acetyl chloride (0.29 g, 3.7 mmol) in dichloromethane (70 mL) at ambient temperature (22-25 °C). The reaction mixture was stirred while refluxing for 20 h. Following removal of dichloromethane under reduced pressure at ambient temperature and replacing with 30 mL diethyl ether, alkylation was effected using MeLi (46 mL, 1.5 M in diethyl ether, 69 mmol). After addition of the lithium reagent, the reaction mixture was stirred for 16 h at ambient temperature. The reaction yielded 3,3-dimethyl-1-phenyl-3-silatetrahydronaphthalene **86** (0.85 g, 10%), in addition to an intractable mixture of oligomeric species. There was no evidence for acyl groups or the Me_3COH groups expected to be produced upon methylation with MeLi. Crude material: ^{1}**H NMR** ($CDCl_3$, 90 MHz): δ(ppm) 0.1-0.4 (m, 5.5 H), 1.5-2.3 (m, 2H), 2.5 (broad s, 2H), 7.3-7.6 (m, 10H).

4.2.2e) Diphenylcarbenium ion as electrophile: synthesis of 1,3-diphenyl-2-(dimethylbenzylsilyl)indane 107

(*E*)-β-(Dichlorobenzylsilyl)styrene **84** (5.0 g, 17.2 mmol) was added to a mixture of titanium tetrachloride (8.5 mL, 74.2 mmol) and chlorodiphenylmethane (3.4 mL, 17.2 mmol) in dichloromethane (250 mL) under reflux. The reaction mixture was stirred under reflux for 24 h. Following removal of dichloromethane under reduced pressure at ambient temperature (22-25 °C), alkylation was effected using MeMgBr (186 mL, 3.0 M in diethyl ether). After addition of the Grignard reagent, the reaction mixture was stirred for 1 week at ambient temperature. The result after radial chromatography and distillation was 1,3-diphenyl-2-(dimethylbenzylsilyl)indane **107** (yield 5.25 g, 73%; b.p. 220 °C, 2.0 mmHg).

1,3-Diphenyl-2-(dimethylbenzylsilyl)indane 107:

^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) -0.15 (s, 6H), 1.94 (s, 2H), 2.22 (t, 1H, J = 11.1 Hz), 4.38, (d, 2H, J = 11.1 Hz), 6.78-7.41 (m, 19H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 148.0, 145.1, 139.5, 128.9, 128.4, 128.1, 127.9, 126.6, 126.5, 124.2, 123.8, 53.3, 45.6, 24.7, -3.7;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) 3.1;

MS (EI, m/z): 418 (20), 403 (15), 327 (30), 267 (100), 191 (30), 165 (16), 149 (30), 135 (80), 91 (15), 59 (20);

HRMS (m/z, M^+): calc. for $C_{30}H_{30}Si$ 418.2156, found 418.2136;

IR (neat): $\nu(cm^{-1})$ 3061, 3025, 2955, 2892, 1599, 1494, 1453, 1251, 1206, 1157, 1076, 1029, 908, 831, 754, 700.

4.2.2f) Diphenylcarbenium ion as electrophile: synthesis of 1,3-diphenyl-2-(dihydroxybenzylsilyl)indane 106 and 1,3-diphenyl-2-(methylhydroxybenzylsilyl)indane 105

A similar reaction to that above was used, with less Grignard reagent: (*E*)-β-(dichlorobenzylsilyl)styrene **84** (1.1 g, 3.7 mmol); $TiCl_4$ (1.7 mL, 14.8 mmol); chlorodiphenylmethane (0.74 mL, 3.7 mmol); in CH_2Cl_2 (70 mL). After 17 h, the acids were neutralized with triethylamine (37 mmol) followed by removal of dichloromethane under reduced pressure at ambient temperature (22-25 °C). Alkylation was effected using MeMgBr (14.8 mL, 3.0 M in diethyl ether), with stirring for 17 h at ambient temperature. The reaction yielded 1,3-diphenyl-2-(dihydroxybenzylsilyl)indane **106** (0.27 g, 17%), 1,3-diphenyl-2-(methylhydroxybenzylsilyl)indane **105** (0.33 g, 21%) and 2% 1,3-diphenyl-2-(dimethylbenzylsilyl)indane **107**.

1,3-Diphenyl-2-(dihydroxybenzylsilyl)indane 106:

^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 2.0 (s, 2H), 2.10 (t, 1H, J = 11.4 Hz), 2.73 (broad s, 2H, OH), 4.55 (d, 2H, J = 11.4 Hz), 6.86-7.44 (m, 19H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 148.2, 145.2, 137.7, 129.4, 129.3, 129.1, 128.8, 127.4, 127.4, 125.1, 124.9, 52.8, 25.4, 5.6;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) -10.9;

MS (EI, m/z): 422 (75), 404 (10), 331 (28), 268 (40), 191 (40), 153 (65), 139 (60), 91 (100), 63 (32);

HRMS (m/z, M^+): calc. for $C_{28}H_{26}SiO_2$ 422.1702, found 422.1702;

IR (neat): ν(cm^{-1}) 3603, 3387, 3081, 3026, 2795, 1600, 1594, 1452, 1400, 1261, 1210, 1167, 1076, 1030, 992, 909, 842, 817, 735, 700;

Anal. calc. for $C_{28}H_{26}O_2Si$: C 79.59%, H 6.21%; found: C 79.33%, H 6.01%.

1,3-Diphenyl-2-(methylhydroxybenzylsilyl)indane 105:

^{1}H NMR ($CDCl_3$, 500 MHz): δ(ppm) 0.07 (s, 3H), 1.4 (broad s, 1H, OH), 1.9 (d, 1H, J = -14.0 Hz), 1.95 (d, 1H, J = -14.0 Hz), 2.12 (t, 1H, J = 11.3 Hz), 4.33 (d, 1H, J = 11.3 Hz), 4.38 (d, 1H, J = 11.3 Hz), 6.77-7.37 (m, 19 H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 147.8, 144.8, 138.3, 128.8, 128.7, 128.3, 126.7, 124.3, 52.7, 52.6, 47.5, 26.2, -2.4;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) -21.9;

MS (EI, m/z): 420 (20), 402 (5), 329 (16), 267 (22), 191 (10), 151 (20), 137 (55), 84 (100), 61 (37), 49 (20);

HRMS (m/z, M^+): calc. for $C_{29}H_{28}SiO$ 420.1874, found 420.1876;

IR (neat): ν(cm^{-1}) 3364, 2896, 2797, 2248, 1599, 1493, 1452, 1258, 1206, 1157, 1008, 909, 820, 733, 700.

^{1}H NMR NOE experiments : Irradiation of **105** at δ 0.07 (CH_3) produced enhancement at δ 4.38 (22%, ring benzylic CH), compared with the smaller enhancement at δ 2.12 (11%, ring α-silyl CH). The results after energy minimization of the *trans/trans* and *cis/cis* structures indicated that only in the *trans/trans* structure are the CH_3 protons closer to the ring benzylic CH proton than to the ring α-silyl CH proton.

4.2.3) Results of AMPAC calculations

AM1 calculations on the proposed intermediate cations **116, 117** and **118** were performed with AMPAC version 2.1 ported to an IBM RS/6000 computer. The heats of formation of the three intermediates were calculated to be 181.6, 188.0 and 180.9 kcal/mol for compounds **116, 117** and **118**, respectively.

4.2.4) Molecular mechanics calculations

Molecular mechanics calculations were done using PC-Model (Serena Software, Bloomington, Indiana) using the supplied MM2 force constants. As appropriate force constants are not available for Cl-Si bonds, the intermediates **116, 119** and **120** were modeled with Si-Me groups instead. The C_a-C_b distance in **120** and C_a-C_c distance in **119**

were constrained to 2.5 Å in order to mimic the transition state for bond formation between these two centers. The energy of **116**, **119** and **120** was minimized using the MMX parameter set which has preliminary parameters for carbenium ions.

4.3) References

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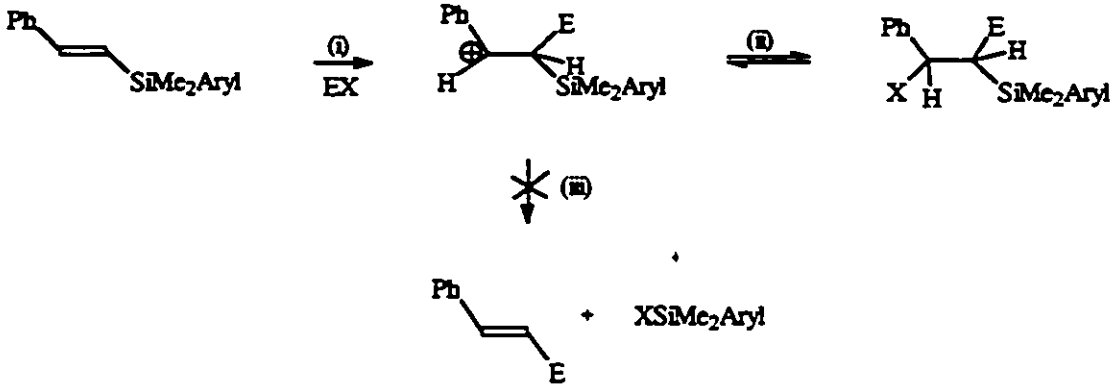
CHAPTER 5

THE USE OF BULKY ARYL LIGANDS ON SILYLSTYRENE DERIVATIVES

5.1) The anomalous reactivity of (*E*)-β-(mesityldimethylsilyl)styrene with acid chlorides

In the two previous chapters the use of electron poor silanes as a means of effecting electrophilic addition to vinylsilanes was discussed. In the introduction, it was also noted that the use of bulky ligands on silicon might be an alternative strategy for retaining silicon. As indicated there, the use of bulky alkyl groups is disadvantageous in that harsh conditions are usually required to cleave the Si-alkyl bonds. As a result, bulky alkyl ligands on silicon are generally not compatible with further synthetic manipulations. For this reason we chose to examine bulky aryl groups on silicon since these are easily removed under milder electrophilic conditions than bulky alkyl groups.[1] Our hope was that the styryl fragment would preferentially attack the electrophile while the aromatic moiety remains unreacted (Scheme 5.1 ii).

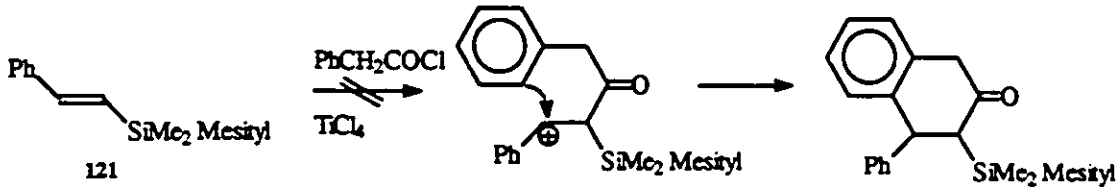
Scheme 5.1


Ph
SiMe2Aryl
(i)
EX
Ph
E
H
H
SiMe2Aryl
(ii)
Ph
E
H
X
H
SiMe2Aryl
(iii)
Ph
E
+
XSiMe2Aryl

5.1.1) Results

As a prototypical bulky aryl group, we began our studies with mesityl substituted styrylsilanes. Initial attempts to acylate the styryl group of (*E*)-β-(mesityldimethylsilyl)styrene **121** (Scheme 5.2) led instead to electrophilic substitution occurring on the mesityl ring (Scheme 5.3). The silylmesityl part of the molecule, instead of the silylstyrene fraction, reacted with the acid chloride irrespective of the fact that styrene is more reactive than mesitylene towards electrophilic substitutions.[2]

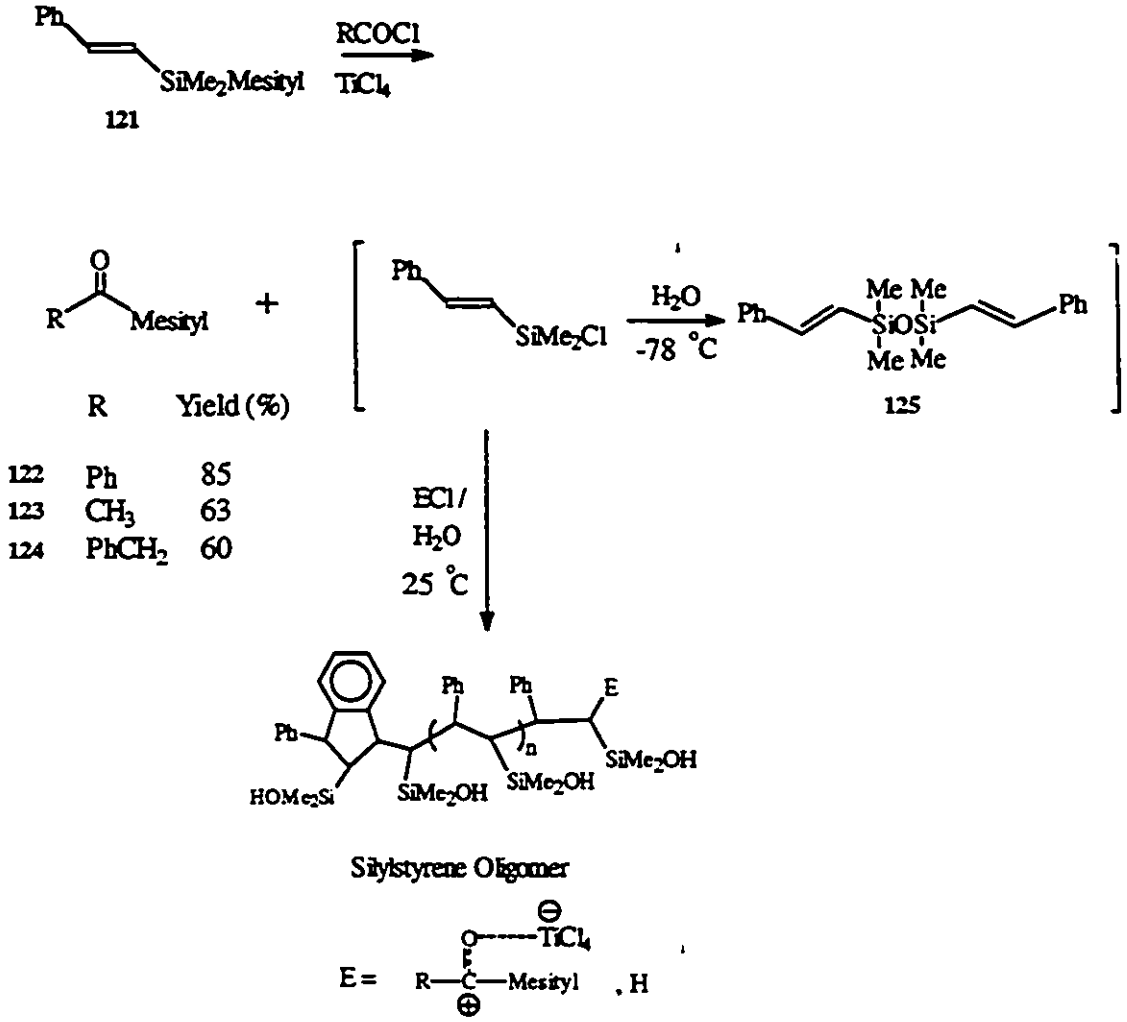
Scheme 5.2



The reaction of phenylacetyl chloride in titanium tetrachloride with (*E*)-β-(mesityldimethylsilyl)styrene **121** yielded benzyl mesityl ketone **124** and dimethylsilylstyrene oligomer (Scheme 5.3). ^{1}H and ^{29}Si NMR established that the phenyl and $SiMe_2$ moieties were intact in the oligomer (see silylstyrene oligomer, Scheme 5.3). Quenching the reaction mixture at low temperature (-78 °C) with aqueous K_2CO_3 produced 1,3-distyryltetramethyldisiloxane **125** in addition to the ketone and smaller

amounts of oligomer (Scheme 5.3). The compound **125** was thought to arise from the hydrolysis (*E*)-β-(chlorodimethylsilyl)styrene; chlorosilanes are known to hydrolyze readily, forming disiloxanes.[3] The presence of **125** after quenching the reaction mixture at -78 °C indicated to us that (*E*)-β-(chlorodimethylsilyl)styrene was perhaps the precursor to the oligomer (Scheme 5.3). Presumably, oligomerization of (*E*)-β-(chlorodimethylsilyl)styrene was initiated by the ketone (**122-124**). Alternatively, oligomerization could be initiated by HCl formed upon quenching the reaction mixture containing $TiCl_4$ with H_2O. Similar results were observed for the reactions of benzoyl and acetyl chloride in titanium tetrachloride with (*E*)-β-(mesityldimethylsilyl)styrene **121**; phenyl mesityl ketone **122** and acetyl mesityl ketone **123** were obtained, respectively (Scheme 5.3). Elimination products resulting from initial acylation of the styryl double bond were not observed in any of these cases (Scheme 5.1 iii).

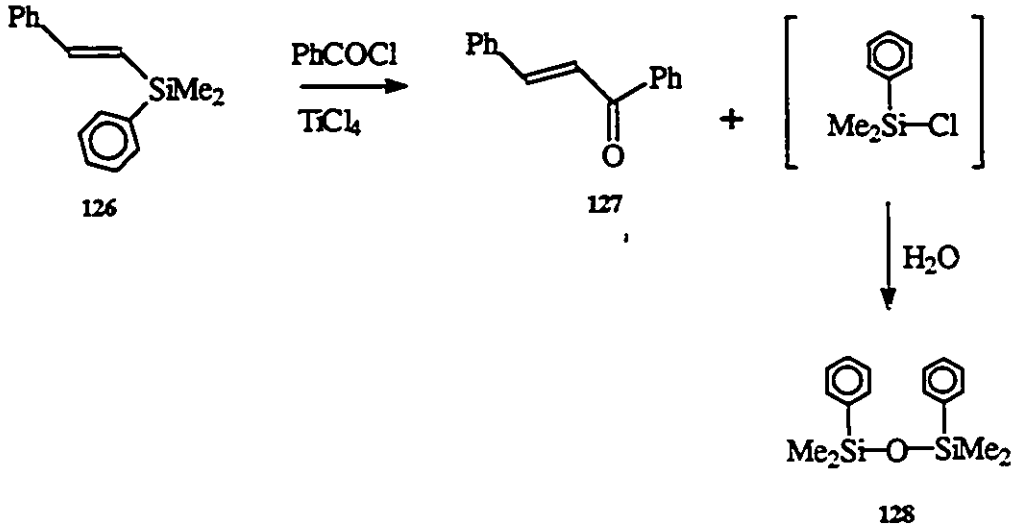
Scheme 5.3



In order to explore the reasons why the styryl group had not participated in the reaction, we systematically varied the steric bulk of the aryl group. We therefore prepared and reacted (*E*)-β-(phenyldimethylsilyl)styrene **126** with benzoyl chloride in titanium

tetrachloride. Benzylidene acetophenone **127** and 1,3-diphenyltetramethyldisiloxane **128** were obtained (Scheme 5.4).

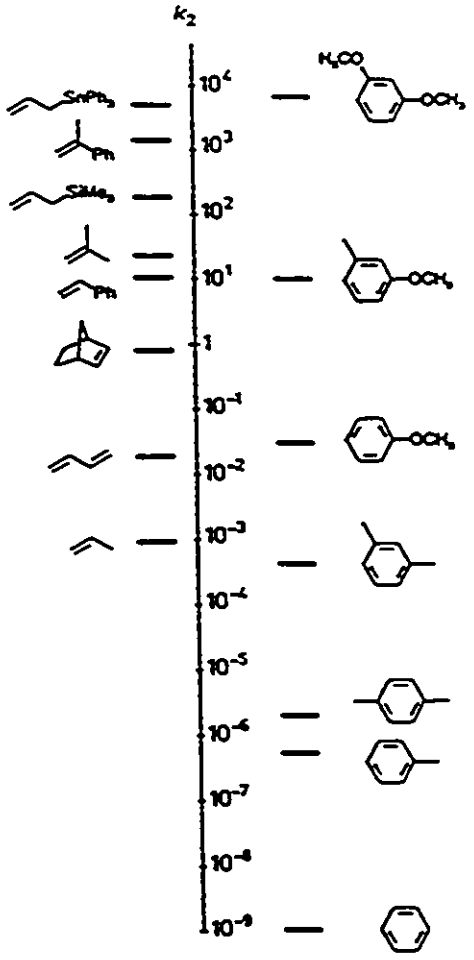
Scheme 5.4



126 127 128

These are the predicted products based upon the relative nucleophilicities of benzene and styrene (Figure 5.1).[2] Here the silylstyrene moiety, rather than the silylphenyl fraction, reacts preferentially with the acid chloride. In this case, benzophenone, which could be obtained from reaction of the phenyl ligand of the phenyldimethylsilyl moiety with benzoyl chloride, was not detected in the reaction products.

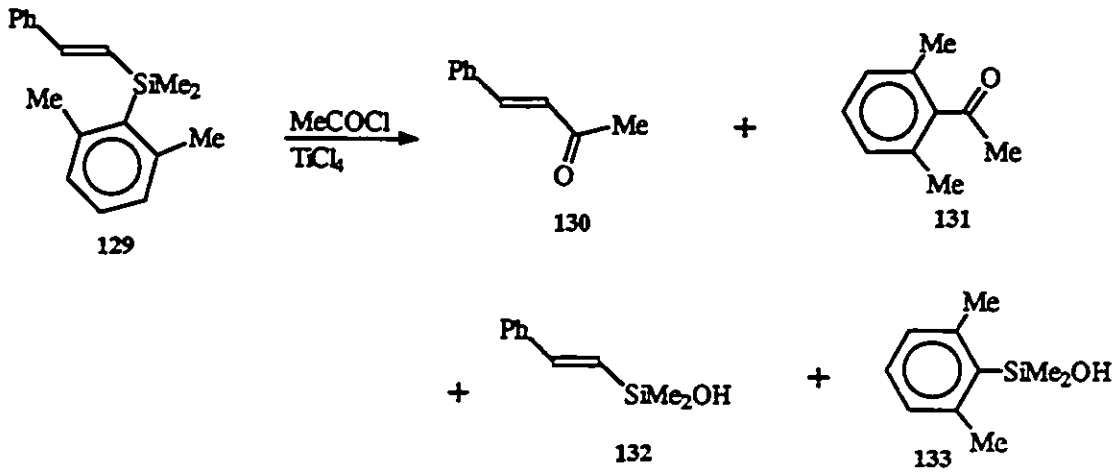
Figure 5.1: Comparison of the nucleophilicities of alkene and arenes towards *p*-methoxy substituted diphenylcarbenium ion (-70 °C)[2]



We further prepared and reacted (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **129** with acetyl chloride. This reaction yielded an intractable mixture when carried out under conditions that were successful for the silylstyrenes **121** and **126**. However, when **129** reacted acetyl chloride at -78 °C over a shorter period (2-4 min), GC/MS analysis revealed four products **130-133**, along with unreacted starting material **129** (Scheme 5.5). Notably, a 2:1 mixture of *trans*-4-phenyl-3-buten-2-one (benzylidene acetone) **130** and

2,6-dimethylacetophenone **131** were obtained. This result was intermediate between those obtained for (*E*)-β-(mesityldimethylsilyl)styrene **121** and (*E*)-β-(phenyldimethylsilyl) styrene **126** in that both the styryl and 2,6-dimethylphenyl moieties of (*E*)-β-[(2,6-dimethylphenyl)dimethyl silyl]styrene **129** reacted with the acid chloride.

Scheme 5.5



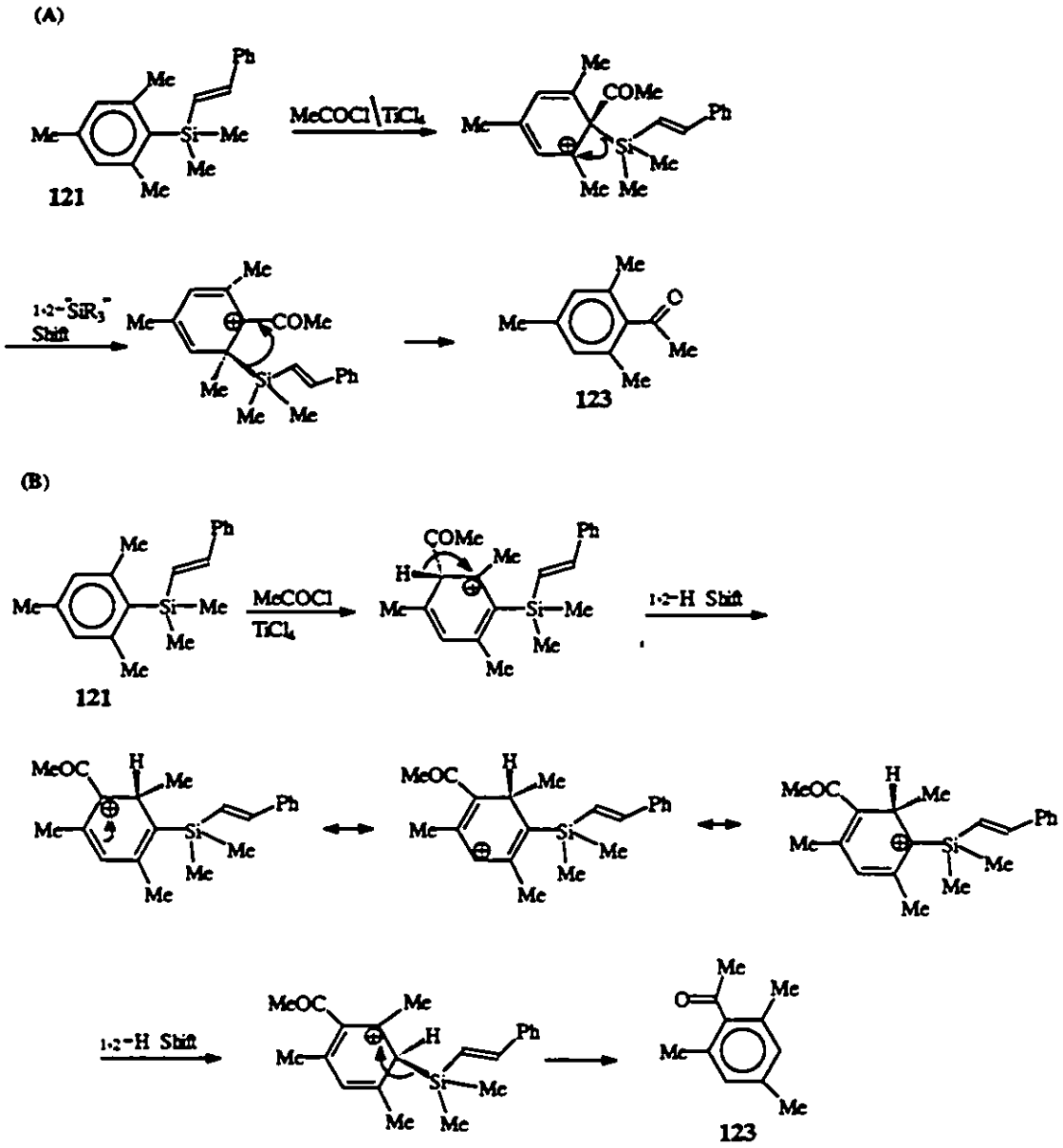
5.1.2) Mechanistic considerations

The products obtained might arise mechanistically in several different ways. For example, the production of mesityl ketones could occur by a 1,2-hydride or 1,2-silicon shift (Scheme 5.6). Another possible mechanism could involve a circuitous route requiring conventional electrophilic aromatic substitution (C-H cleavage) *meta* to silicon, followed by HCl induced desilylation (Scheme 5.7B). In theory, this might be the preferred reaction course if *ipso*-silicon attack by the electrophile is sterically prevented by contiguous, bulky silicon and methyl substituents. Yet another mechanism could involve direct *ipso*-silicon substitution by the acid chloride (Scheme 5.8). Each of these mechanistic processes will be discussed in turn.

5.1.2a) 1,2-Hydride shifts and 1,2-SiR_3 rearrangements

1,2-Migration of the trimethylsilyl group (Scheme 5.6A) or a 1,2-hydride shift (Scheme 5.6B) can be readily discarded on the basis that they both involve energetically uphill shifts; the pentadienyl cation shifts from inductively donating α-methyl to electron-withdrawing α-carbonyl substituents.

Scheme 5.6


(A)
MeCOCl\TiCl4
121
1,2-SiR3 Shift
123
(B)
MeCOCl
TiCl4
121
1,2-H Shift
1,2-H Shift
123

The migration of trimethylsilyl groups has been reported in the literature under conditions which prolong the life of the cation. For example, *ortho*-bis(trimethylsilyl)benzene was converted into the *meta* isomer by treatment with a small quantity of trifluoroacetic acid in benzene.[4,6] This rearrangement was possible because the low concentration and low nucleophilicity of anions (CF_3COO^-) in solution extended the life of the pentadienyl cation, allowing migration to occur.[4] Given the large amounts of $TiCl_4$ (4.0 equivalents) and acid chloride (1.0 equivalent) used for our experiments, it would seem likely that the cationic Wheland intermediate formed should easily collapse as a result of desilylation initiated by chloride anions. Therefore the migration of $SiMe_2$Styryl is not expected under the reaction conditions we used.

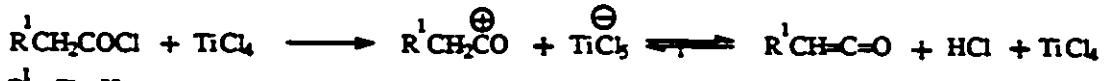
Eaborn and co-workers demonstrated that deuterium shifts do not occur for arylstannanes in the presence of large amounts (1.0 equivalent) of a relatively weak acid CF_3COOD.[4] Therefore, we surmised that hydrogen shifts do not readily occur in arylsilanes except for special reaction conditions such as in superacids and when nucleophile concentrations are low. The mechanisms shown in Scheme 5.6A and Scheme 5.6B involving silicon and hydride migrations, were discounted based on these criteria.

5.1.2b) HCl participation

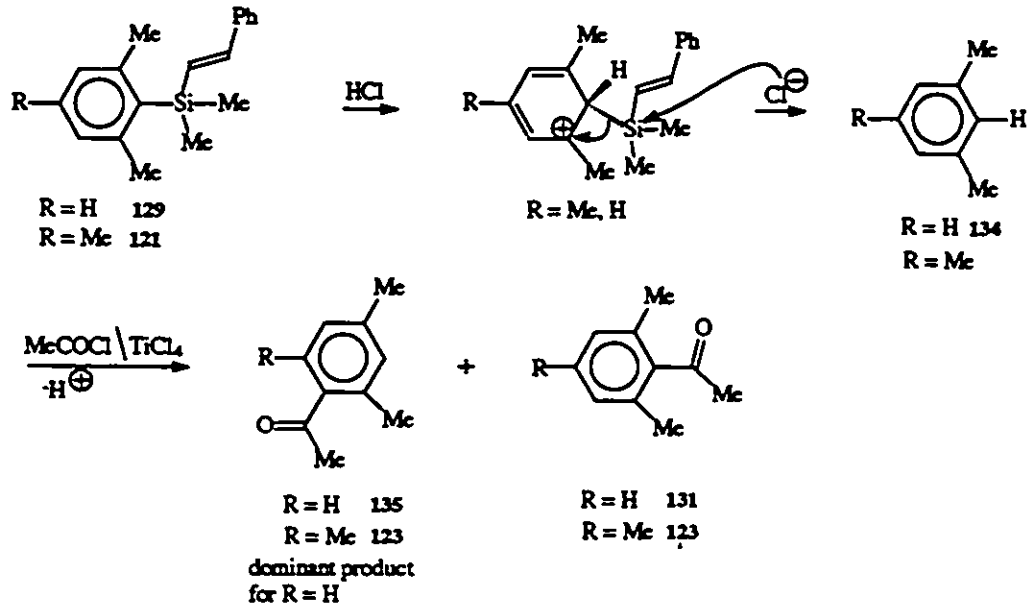
The presence of 2,6-dimethylacetophenone **131** as the only isomeric *m*-xylyl methyl ketone in the reaction between (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **129** and acetyl chloride allowed us to conclude that HCl was not substantially involved in the mechanistic process (Scheme 5.7). To establish this, let us closely examine what effects HCl would be expected to have on product formation.

We have already established in the introduction that attack by protons on arylsilanes produces protiodesilylated products.[10,13,14,20-26] Thus, proton attack on **129**, in theory, is expected to produce *m*-xylene **134** (Scheme 5.7A). *M*-xylene **134**, so produced, should undergo conventional electrophilic aromatic substitution (C-H cleavage) predominantly at the electronically favored positions *ortho*/*para* to the Me group,[7,8,9] yielding 2,4-dimethylacetophenone **135** as the major isomer (Scheme 5.7A). This product was not observed when we carried out the reaction, as shown by comparison of the reaction products with pure commercially obtained 2,4-dimethylacetophenone.

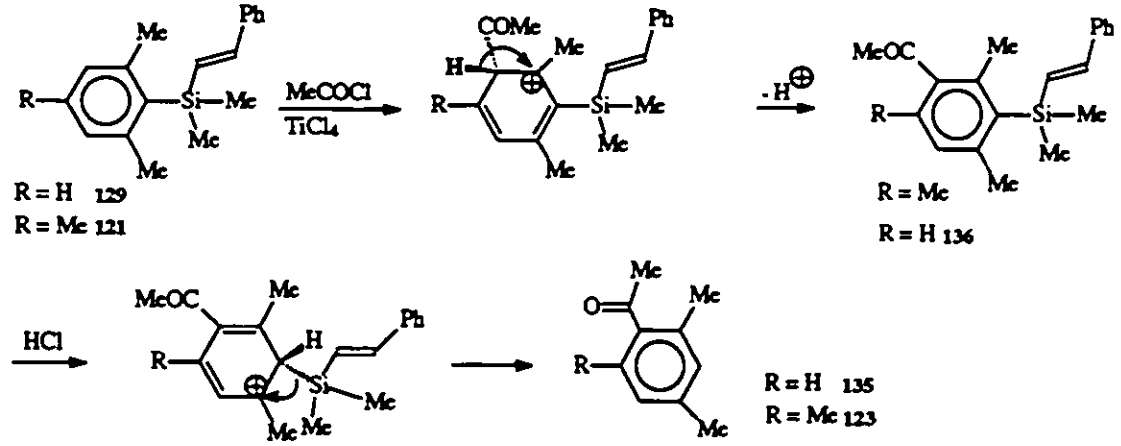
Scheme 5.7


R¹CH₂COCl + TiCl₄
R¹CH₂CO⊕ + TiCl₅⊖
R¹CH=C=O + HCl + TiCl₄
R¹= Ph, H

(A)


HCl
R = H 129
R = Me 121
R = Me, H
R = H 134
R = Me
MeCOCl / TiCl₄
-H⊕
R = H 135
R = Me 123
dominant product for R = H
R = H 131
R = Me 123

(B)

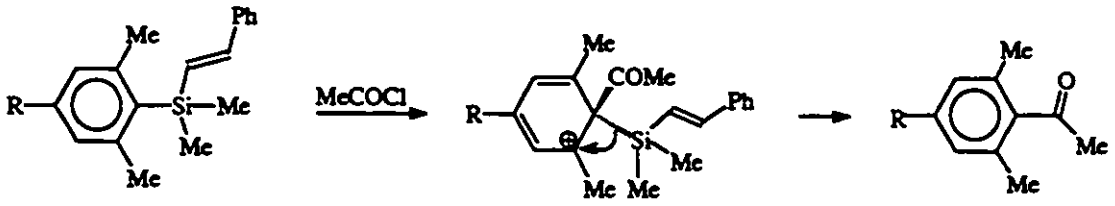

MeCOCl
TiCl₄
-H⊕
R = H 129
R = Me 121
R = Me
R = H 136
HCl
R = H 135
R = Me 123

A circuitous route, requiring conventional electrophilic aromatic substitution (C-H cleavage) on **129** *meta* to silicon, followed by HCl induced desilylation, was also expected to yield 2,4-dimethylacetophenone **135** as the only compound (Scheme 5.7B). The absence of **135** in the product mixture is therefore inconsistent with a mechanism involving protons. Conventional electrophilic substitution initiated by the acid chloride attacking the aryl ring of **129** at the position *meta* to the silyl group is further precluded because it should have led to **136** (Scheme 5.7B). Such silylated products were not observed.

5.1.2c) *ipso*-substitution

The presence of 2,6-dimethylacetophenone **131** as the only isomeric *m*-xylyl methyl ketone in the reaction between (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **129** and acetyl chloride allowed us to conclude that the mechanism involves direct *ipso*-silicon substitution by the acetyl group (Scheme 5.8). Abundant studies in the literature support the two step mechanistic process involving *ipso*-silicon substitution. Such a mechanism is known to occur irrespective of the fact that silicon is flanked by bulky *ortho* substituents on the aromatic ring (Scheme 5.8).[10-15] In fact, studies have shown that *ipso*-silicon substitution actually becomes more facile as the bulk of substituents *ortho* to silicon increases.[10-15] This result contrasts that observed for conventional electrophilic aromatic substitution (C-H cleavage) where it is difficult to effect substitution between two methyl substituents *meta* to each other.[7-9]

Scheme 5.8



121 R = Me
129 R = H

123 R = Me
131 R = H

5.1.3) Reactivity

Having established that *ipso*-silicon substitution was the likely mechanistic process, we can now attempt to account for the reactivity pattern observed for the reactions of (*E*)-β-(aryldimethylsilyl)styrenes (aryl = mesityl **121**, phenyl **126**, and 2,6-dimethylphenyl **129**) with acid chlorides. Why, for instance, did we observe exclusive reactivity by the mesityl group of **121**, while it was the silylstyrene moiety that singularly reacted for **126**? What can be said about the intermediate reactivity of **129**, whereby both the styryl and the 2,6-dimethylphenyl groups reacted to give their respective ketones? A look at the comparative nucleophilicities of alkenes and arenes towards *p*-methoxy substituted diphenyl carbenium ions shows that styrene is approximately 10^{10} (k_{rel}) more reactive than benzene (Figure 5.1).[2] Thus, the sole ketone, *trans*-chalcone **127**, obtained when **126** reacted with benzoyl chloride in titanium tetrachloride, correlates well with the

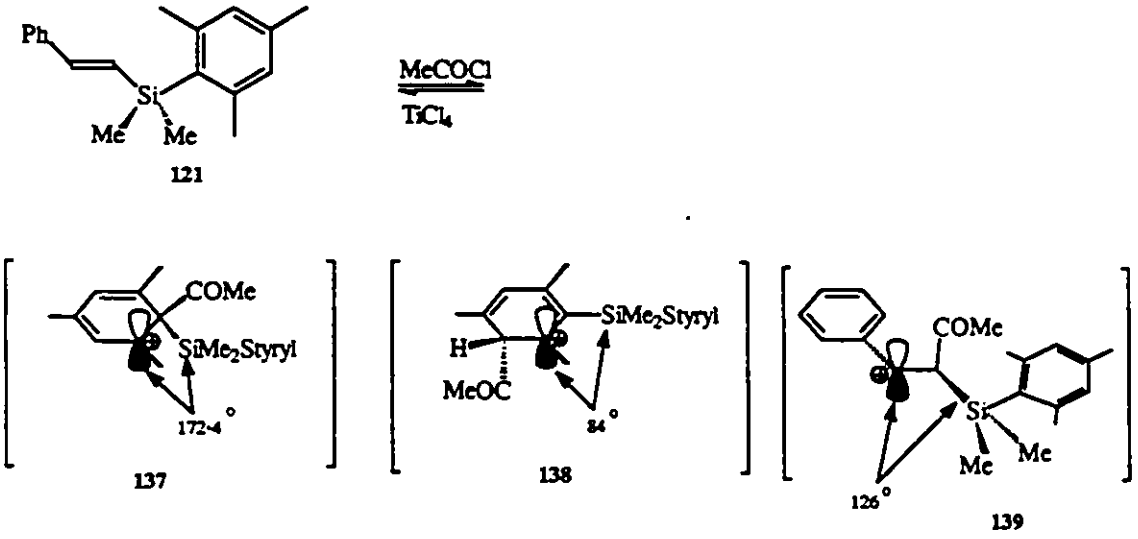
relative reactivities of styrene relative to benzene. On the other hand, styrene is 10^4 times more reactive than *m*-xylene[2] which would lead us to expect, once again, exclusive reaction of the styryl moiety. Yet we observe substantial reaction by the 2,6-dimethylphenyl group implying a rate ratio of only 2:1 based on product ratio under conditions of kinetic control. Although styrene is 10-10^2 more reactive than mesitylene,[2] we observe a reversal in the reactivity rates of the silylstyryl and silylmesityl groups of 121; the silylmesityl is more reactive. Thus, like the 2,6-dimethylphenylsilyl moiety, there is an enhancement in the reactivity rate of the silylmesityl species or a retardation in the reactivity of the silylstyryl species.

There are several factors which can influence the reactivity of organic compounds; solvent effects, induction, resonance, and steric factors, are a few. We believe that resonance and steric factors are primarily responsible for the abnormalities observed for the relative reactivities mentioned above. We will look at the role these two factors have on the reactivity of the styrylarylsilanes.

5.1.3a) Resonance impact on reactivity

The enhanced reactivity observed for mesityl and 2,6-dimethylphenyl groups of (*E*)-β-(mesityldimethylsilyl)styrene **121** and (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **129**, respectively, may be due in part to β-Si hyperconjugative stabilization of the Wheland intermediate. Molecular mechanics calculation of the proposed Wheland intermediate **137**, formed during *ipso*-silicon acylation, shows that the dihedral angle between the Si-C bond and the empty p-orbital of the ring carbon is 172.4° (Scheme 5.9).

Scheme 5.9

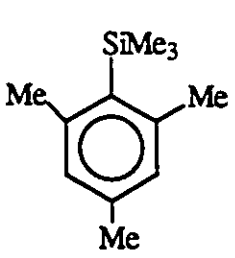


This dihedral angle can provide an enhanced hyperconjugative stabilization energy to the intermediate cation by as much as 15 kcal/mol (β-Si stabilization relative to β-hydrogen).[16-19] While electrophilic attack at the ring position *meta* to silicon also results in a cation β to silicon, the dihedral angle between the Si-C bond and the empty p-orbital of carbon is close to 90° (**138** Scheme 5.9). As a consequence, there is no overlap between the Si-C σ-bond and the empty p-orbital of carbon, therefore β-Si hyperconjugative stabilization of that Wheland intermediate **138** does not occur. Finally, acylation of the silylstyrene π-bond would also give a secondary β-Si stabilized cation **139**. However, our models predict that the dihedral angle between the Si-C bond and the empty *p*-orbital of carbon is 126° (Scheme 5.9). This dihedral angle corresponds to a maximum β-Si stabilization of approximately 6 kcal/mol.[16-19] Therefore, it appears for the Wheland intemediate **137**, formed from *ipso*-silicon substitution on the mesityl or 2,6-dimethylphenyl moieties, that the degree of β-Si hyperconjugative stabilization is more effective than a similar stabilization of the styryl intermediate **139** (Scheme 5.9). Apparently, steric congestion of the Wheland intermediate by the adjacent dimethyl substituents constrains the Si-C σ-orbital to occupy a geometry that engenders significant β-Si stabilization to the intermediate. This geometry, it seems, is partly responsible for the increased reactivity rates observed for the mesityl or 2,6-dimethylphenyl moieties relative to styryl moiety.

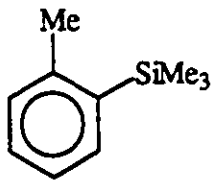
5.1.3b) Steric impact on reactivity

One special feature associated with ring substituents in demetalation reactions is the steric acceleration which arises when the $SiMe_3$ group is crowded by a neighbouring group.[10,13,14,20] For example, 1-trimethylsilyl-2,6-dimethylbenzene **140** and 1-trimethylsilyl-2,4,6-trimethylbenzene **141** react much faster with acid than would be expected based on simple additivity of the electronic effects of the separate *ortho*- and *para*-Me groups.[10,13,14,20] A single *ortho*-Me substituent activates to the same extent as a single *para*- Me substituent so that 1-trimethylsilyl-2-methylbenzene **142** and 1-trimethylsilyl-4-methylbenzene **143** are cleaved at similar rates (Figure 5.2). However, **140** with two flanking Me substituents *ortho* to silicon is activated markedly more than 1-trimethylsilyl-2,4-dimethylbenzene **144** which has one Me *ortho* to silicon and another *para* to silicon, on the same ring (Figure 5.3).

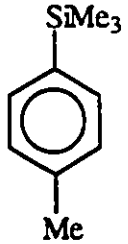
Figure 5.2



141

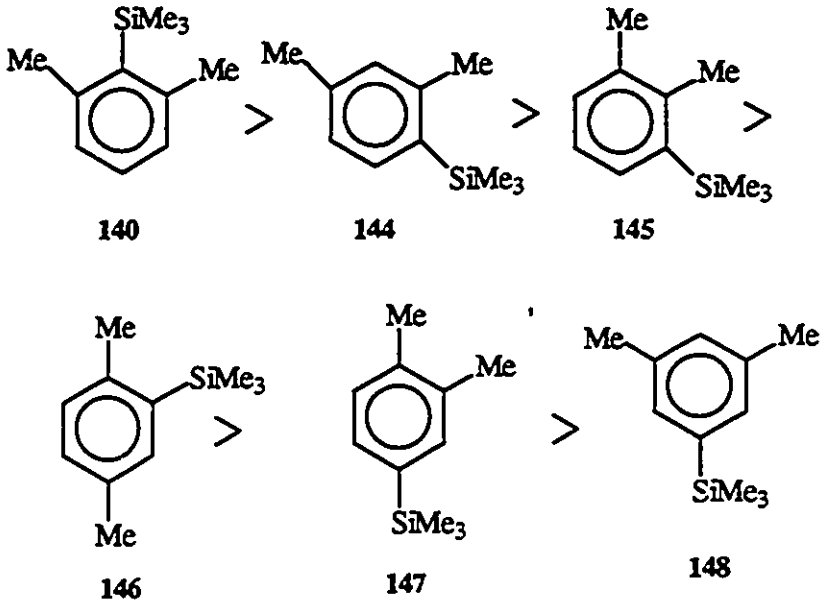


142



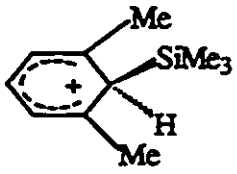
143

Figure 5.3: Reactivity order for the reaction of arylsilanes with protons or halogens[10]



Thus, compound **140** is 12 times more reactive than **144** towards electrophiles (Figure 5.3).[10] The greater acceleration of **140** is ascribed to steric factors, there being release of steric strain when the structure **140** passes into the protonated intermediate **149** or int a transition state close to **149** in structure (Figure 5.4).[10] Such an intermediate or transition state like **149** places the bulky silyl group out of the plane of the ring, reducing congestion between silicon and the *ortho* methyl substituents.

Figure 5.4

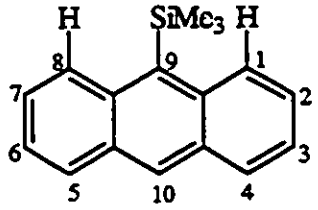


149

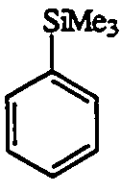
This steric effect on reactivity was also observed for halogenation reactions involving arylsilanes, in contrast to halogenation reactions involving non-silylated arenes. 1-Trimethylsilyl-3,4-dimethylbenzene **147** cleaved less rapidly than 1-trimethylsilyl-2,5-dimethylbenzene **146** (Figure 5.3).[14] This enhanced reactivity of **146** over **147** was attributed by Benkeser and Krysaik to a steric effect.[14] Steric rate enhancement was attributed to relief of congestion by the methyl group *ortho* to silicon in **146** in the transition state or intermediate, as previously described. Similar steric arguments have been used to account for the fact that 1-trimethylsilyl-2,3-dimethylbenzene **145** cleaved more rapidly than 1-trimethylsilyl-3,4-dimethylbenzene **147**,[14] even though the rate of bromination at the 3-position in non-silylated *ortho*-xylene is slower than at the 4-position (Scheme 5.3).[28]

Another example of such steric acceleration is thought to occur with 9-trimethylsilylanthracene **150** where there is interference between the trimethylsilyl group and 1-H and 8-H on the ring accounting for 9-trimethylsilyl anthracene **150** being 10^5 times more reactive than phenyltrimethylsilane **151** (Figure 5.5).[20]

Figure 5.5



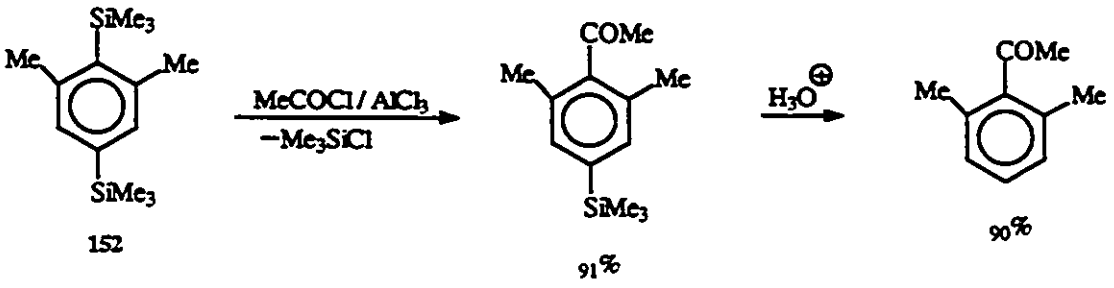
150



151

Accelerated protonation and halogenation reactions for arylsilanes, when silicon is buttressed by adjacent methyl substuents, have been discussed above. Not surprisingly, accelerated acylation reactions have also been observed for arylsilanes in which the silicon is flanked by methyl substituents.[11] For example, Calas and co-workers found that 1,4-bis (trimethylsilyl)-2,6-dimethylbenzene **152** reacted exclusively at the 1-position when treated with one equivalent of acetyl chloride (Scheme 5.10).[11]

Scheme 5.10



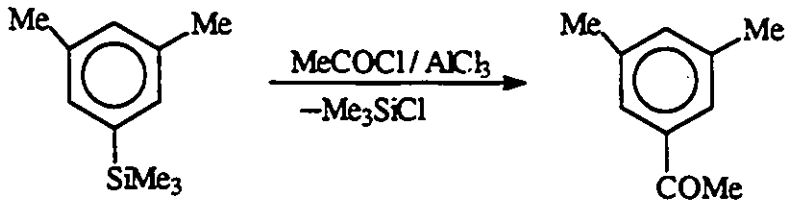
152

91%

90%

Once again, preferential acetyl substitution at the 1-position of **152**, rather than the 4-position, is thought to be derived from buttressing of the $SiMe_3$ group at the 1-position by adjacent methyl substituents. Acetylation *meta* to the two Me groups (4-position of **152**) does occur when there is no $SiMe_3$ group sandwiched by Me groups (1-position of **152**), as shown for the reaction of **148** (Scheme 5.11).[11]

Scheme 5.11



148

88 %

A look at our substrates, (*E*)-β-(mesityldimethylsilyl)styrene **121** and (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **129**, shows that buttressing of the bulkier $SiMe_2$styryl group (bulkier relative to $SiMe_3$) by the adjacent methyl substituents, should be even more pronounced. This buttressing should lead to greater steric acceleration of reactions involving these substrates with acid chlorides, on account of the greater steric stress that would be relieved in the transition state or intermediate.

The greater reactivity observed for the mesityl ligand in (*E*)-β-(mesityldimethylsilyl)styrene **121**, compared to the 2,6-dimethylphenyl ligand in (*E*)-β-[(2,6-dimethyl phenyl)dimethylsilyl]styrene **129**, may be rationalized on electronic grounds. While the electronic influence of hydrogen or *para* $SiMe_3$ is small ($\sigma^+_H = 0.0$ and $\sigma^+_{p\text{-}Me_3Si} = -0.03$), that for *para* Me is substantial ($\sigma^+_{p\text{-}Me} = -0.14$). Therefore, the greater inductive release of electrons by *para* Me, relative to hydrogen, accounts for the greater reactivity of mesityl ligand in **121** over 2,6-dimethylphenyl ligand in **129**.

5.2) Experimental

5.2.1) General procedures and instrumentation

The ^{1}H-NMR spectra were recorded on a Varian EM-390 (90-MHz) spectrometer and the Bruker AM-500 (500-MHz) spectrometer, Bruker AC-300 (300 MHz) spectrometer or Bruker AC-200 (200 MHz) spectrometer. ^{13}C and ^{29}Si-NMR were performed on a Bruker AC-200 (at 200 MHz for protons) and Bruker AC-300 (at 300 MHz for protons), respectively. Chemical shifts are reported with respect to tetramethylsilane as standard, set to 0 ppm. Coupling constants (J) are recorded in Hertz (Hz). The abbreviations s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, are used in reporting the spectra.

Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of ~ 200 °C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system. High resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the EI method.

Infrared spectra were run on a Perkin Elmer 283 spectrometer and a BIO RAD FTS-40 spectrometer, as a neat film.

The purity of new compounds was confirmed by chromatography on a HP-5890A Gas Chromatograph/TCD detector; glass capillary column, SPB-1, 30 meters long, 0.075 mm inner diameter.

GC/MS was carried out at oven temperature 80 °C (initial temperature) to 150 °C (final temperature) with an incremental increase of 10 °C/min. Injection and detector temperatures were set at 250 °C. Injection volume 1.0 μL, sample concentration 100 ng/μL.

All solvents were thoroughly dried before use. Dichloromethane (CH_2Cl) was distilled over phosphorus pentaoxide (P_2O_5). Diethyl ether (Et_2O), tetrahydrofuran (THF) and hexanes were distilled under nitrogen, over Na/benzophenone.

2,4-Dimethylacetophenone **135**, purchased from Aldrich, was used as a standard for comparison with 2,6-dimethylacetophenone **131** obtained from the reaction of (*E*)-β-[(2,6-Dimethylphenyl)dimethylsilyl]styrene **129** with acetyl chloride. **131**, obtained from the reaction of 2,6-dimethylphenyl-1-magnesium bromide with acetyl chloride, was used as another standard. The retention time obtained from the GC/MS of 2,4-dimethylacetophenone **135** was 16.31 min. Retention times of 14.97 min and 14.95 min were obtained from the GC/MS of 2,6-dimethylacetophenone **131** produced upon reacting acetyl chloride with **129** and 2,6-dimethylphenyl-1-magnesium bromide, respectively. For comparison, the mass spectrum of the commercially obtained 2,4-dimethylacetophenone was recorded under identical conditions used to record the mass spectrum of 2,6-dimethylacetophenone **131**. 2,4-Dimethylacetophenone **135** MS (EI, m/z): 148 (26), 133 (100), 105 (55), 77 (35), 63 (13), 51 (14).

Reaction conditions were not optimised so that reactions might have been completed before the reaction times given.

5.2.2) Synthesis

5.2.2a) Synthesis of (*E*)-β-(mesityldimethylsilyl)styrene 121

Mesityl magnesium bromide (115 mL in diethyl ether, 1.0 M, 1.1 eq) was added slowly to (*E*)-β-(trichlorosilyl)styrene (24.81 g, 104.4 mmol) in 100 mL tetrahydrofuran at ambient temperature. The mixture was heateded at 50 °C overnight (16 h). Diethyl ether (120 mL) was removed from the reaction flask by distillation, followed by addition of methyl lithium (153 mL, 1.5 M in diethyl ether, 2.2 equiv.) at ambient temperature (22 °C). After stirring at this temperature for 1 h, the reaction mixture was once more heateded at 50 °C overnight (16 h). Upon distillation, the reaction yielded (*E*)-β-(trimethylsilyl)styrene (b.p. 52 °C, 2.0 mmHg, 3.3 g, 18%) and (*E*)-β-(mesityldimethylsilyl)styrene **121** (b.p. 160 °C, 2.0 mmHg, 15 g, 51%).

(*E*)-β-(Mesityldimethylsilyl)styrene 121:

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) 0.52 (s, 6H), 2.24 (s, 3H), 2.42 (s, 6H), 6.62-7.41 (m, 9H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 144.6, 142.8, 138.8, 138.5, 131.3, 130.6, 129.1, 128.5, 128.1, 127.9, 126.5, 126.4, 25.0, 20.9, 2.2;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) -11.8;

MS (EI, m/z): 280 (30), 265 (20), 219 (10), 189 (40), 161 (100) 145 (90), 135 (60), 115 (20), 105 (25), 91 (27), 59 (25);

HRMS (m/z, M^+): calc. 280.1667; found 280.1669;

IR (neat): ν(cm^{-1}) 3024, 2956, 2732, 1604, 1573, 1493, 1448, 1410, 1252, 1065, 1029, 990, 845, 776, 735, 689.

5.2.2b) Synthesis of (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene 129

2,6-Dimethylphenyl-1-magnesium bromide [prepared by reacting 2,6-dimethyl-1-bromobenzene (6.2 mL, 46.5 mmol) with magnesium (4.7 g, 85 mmol) in tetrahydrofuran, for 4 h at ambient temperature] was added to (*E*)-β-(trichlorosilyl)styrene (10 mL, 42.5 mmol) in 100 mL tetrahydrofuran at 0 °C. The mixture was stirred for 1 h, followed by heating at 50 °C over the weekend (~ 3 d). Methyl magnesium bromide (63 mL, 3.0 M in diethyl ether) was added slowly at ambient temperature and the contents of the reaction flask further heated at 50 °C overnight (16 h). Upon distillation, the reaction yielded (*E*)-β-(trimethylsilyl)styrene (1.6 g, 21%) as the distillate (b.p. 30 °C, 0.1-0.5 mmHg) and (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **129** (^{1}H NMR) as the residue. Subsequent clean-up of the residue **129** by radial chromatography yielded pure (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl] styrene **129** (8.9 g, 70%).

(*E*)-β-(2,6-Dimethylphenyl)dimethylsilyl]styrene 129:

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) 0.58 (s, 6H), 2.49 (s, 6H), 6.68-7.45 (m, 10H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 144.4, 143.0, 138.4, 134.9, 130.4, 129.0, 128.4, 128.1, 127.9, 126.3, 25.1, 2.1;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) -12.6;

MS (EI, m/z): 266 (32), 251 (40), 175 (35), 162 (50), 147 (100), 135 (50), 121 (15), 105 (11), 91 (10), 59 (20), 43 (12);

HRMS (m/z, M^+): calc. 266.1491; found 266.1497;

IR (neat): ν(cm^{-1}) 3023, 2957, 1602, 1573, 1493, 1446, 1252, 1130, 1028, 990, 845, 833, 771, 689.

5.2.2c) Synthesis of (*E*)-β-(phenyldimethylsilyl)styrene 126

Phenylacetylene (20 mL, 182.2 mmol) and chlorodimethylsilane (33 mL, 297.2 mmol) were mixed together and hexachloroplatinic acid (0.5 mL, 0.02 M in ethanol) added to the mixture at -15 °C. The reaction mixture was stirred at this temperature for 4 h. The temperature was raised to 25 °C and the mixture stirred for 2 d. Diethyl ether (200 mL) and phenylmagnesium bromide (60.7 mL, 3.0 M in diethyl ether) were added to the reaction mixture and refluxed overnight. Distillation yielded (*E*)-β-(phenyldimethylsilyl)styrene **126** (28 g, 65%, b.p. 106-108 °C, 0.05 mmHg).

(*E*)-β-(Phenyldimethylsilyl)styrene 126:

^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 0.56 (s, 6H), 6.68-6.74 (d, 1H, J = 19.2 Hz), 7.04-7.10 (d, 1H, J = 19.2 Hz), 7.35-7.71 (m, 10H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 145.0, 138.3, 137.9, 133.6, 128.7, 128.2, 127.9, 127.5, 126.8, 126.2, 125.9, -2.8;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) -11.1;

MS (EI, m/z): 238 (82), 223 (100), 145 (85),135 (28), 121 (30), 86 (15);

HRMS (m/z, M^+): calc. 238.1178; found 238.1188;

IR (neat): ν(cm^{-1}) 3067, 3023, 2957, 2899, 1953, 1884, 1819, 1604, 1573, 1493, 1427, 1334, 1251, 1115, 1068, 990, 911, 846, 730, 698, 646.

5.2.3) Reaction with acid chlorides

5.2.3a) Reaction of (*E*)-β-(mesityldimethylsilyl)styrene 121 with acetyl chloride

(*E*)-β-(Mesityldimethylsilyl)styrene **121** (0.9 g, 3.15 mmol) was added to a solution of methylene chloride (15 mL) containing acetyl chloride (0.25 g, 3.15 mmol), and titanium tetrachloride 1.5 mL, 12.6 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h, warmed slowly to -50 °C for 30 min, then the temperature was finally raised to 25 °C for a further 30 min. The reaction mixture was quenched by adding

saturated potassium carbonate (150 mL). Extraction with diethyl ether (2 X 100 mL), and radial chromatography yielded 2,4,6-trimethylacetophenone **123** (0.32 g, 63%), and an oligomer of chlorodimethylsilylstyrene.

Mesityl methyl ketone (2,4,6-trimethylacetophenone) 123:

^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 1.98 (s, 6H), 2.04, (s, 3H), 2.20 (s, 3H), 6.60 (s, 2H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 207.8, 139.6, 137.8, 131.8, 128.1, 31.7, 20.6, 18.7;

MS (EI, m/z): 162 (25), 147 (100), 119 (50), 91 (20), 77 (15);

MS (CI, m/z): $M^+ + NH_4$ 180 (8), 163 (100), 147 (20);

IR (neat): ν(cm^{-1}) 2957, 2921, 1699, 1611, 1453, 1425, 1353, 1252, 1164, 1060, 965, 851, 803, 702, 671, 595, 528.

5.2.3b) Reaction of (*E*)-β-(mesityldimethylsilyl)styrene 121 with benzoyl chloride

(*E*)-β-(Mesityldimethylsilyl)styrene **121** (0.9 g, 3.15 mmol) was added to a solution of methylene chloride (15 mL) containing benzoyl chloride (0.36 mL, 3.15 mmol), and titanium tetrachloride (1.5 mL, 12.6 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h, warmed slowly to -50 °C for 30 min, then the temperature

was finally raised to 25 °C for a further 30 min. The reaction mixture was quenched by adding saturated potassium carbonate (150 mL). Extraction with diethyl ether (2 X 100 mL), and radial chromatography yielded 2,4,6-trimethylbenzophenone **122** (0.60 g, 85%) along with an oligomer of chlorodimethylsilylstyrene.

Phenyl mesityl ketone (2,4,6-trimethylbenzophenone) 122:

^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 1.88 (s, 6H), 2.10 (s, 3H), 6.68 (s, 2H), 7.14-7.63 (m, 5H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 200.0, 138.0, 137.0, 136.6, 133.7, 133.1, 128.9, 128.4, 128.0, 20.7, 19.0;

MS (EI, m/z): 224 (84), 223 (100), 209 (30), 147 (70) 119 (75), 105 (58), 91 (15), 77 (25);

IR (neat): ν(cm^{-1}) 2953, 2920, 2861, 1672, 1611, 1448, 1379, 1312, 1268, 1170, 1072, 1027, 958, 910, 851, 801, 748, 711, 609.

The reaction procedure described above for 2,4,6-trimethylbenzophenone **122** was modified so that reactants stirred at -78 °C for 1.0-1.5 h were quenched at this temperature with saturated potassium carbonate. The procedure led to 2,4,6-trimethylbenzophenone **122** (60-70%, 0.42 g -0.49 g) as well as (*E*)-β-distyryltetramethyl disiloxane **125** (0.125 g, 12%) and an oligomer of chlorodimethylsilylstyrene.

(*E*)-β-Distyryltetramethyl disiloxane 125:

^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 0.02 (s, 12H), 6.19-6.25 (d, 2H, J = 19.2 Hz), 6.70-6.76 (d 2H, J = 19.2 Hz), 7.02-7.21 (m, 10H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 143.7, 138.0, 127.9, 127.5, 125.9, 0.2;

^{29} Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) -2.2;

MS (EI, m/z): 338(20), 247 (45), 219 (100), 193 (40), 145 (30), 73 (20);

IR (neat): ν(cm^{-1}) 3024, 2958, 1605, 1574, 1494, 1447, 1255, 1043, 990, 849, 797, 689, 559, 450.

5.2.3c) Reaction of (*E*)-β-(mesityldimethylsilyl)styrene 121 with phenylacetyl chloride

(*E*)-β-(Mesityldimethylsilyl)styrene **121** (1.68 g, 6.0 mmol) was added to a solution of methylene chloride (150 mL) containing phenylacetyl chloride (0.927 g, 6.0 mmol), and titanium tetrachloride 4.6 g, 24 mmol) at -78 °C. The reaction mixture was

stirred at -81 °C for 2.5 h, warmed slowly to -45 °C overnight (16 h), then the temperature was finally raised to 25 °C for a further 30 min. The reaction mixture was quenched by adding saturated potassium carbonate (150 mL). Extraction with diethyl ether (3 X 100 mL), and radial chromatography yielded benzyl mesityl ketone **124** (0.85 g, 60%) along with an oligomer of chlorodimethylsilylstyrene.

Benzyl mesityl ketone 124:

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) 2.26 (s, 6H), 2.39 (s, 3H), 4.10 (s, 2H), 6.94 (s, 2H), 7.36-7.39 (m, 5H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 206.8, 138.8, 138.0, 133.0, 132.3, 129.5, 128.1, 126.6 , 51.3, 20.6, 18.8;

MS (EI, m/z): 147 (100), 119 (20), 91 (15);

MS (CI, m/z): $M^+ + NH_4$ 256 (15), 239 (20), 147 (100), 119 (5), 91 (10);

IR (neat): ν(cm^{-1}) 3025, 2961, 2923, 2740, 1950, 1880, 1701, 1611, 1501, 1450, 1380, 1311, 1250, 1070, 1030, 985, 850, 720, 690.

5.2.3d) Reaction of (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene 129 with acetyl chloride

(*E*)-β-[(2,6-Dimethylphenyl)dimethylsilyl]styrene **129** (0.45 g, 1.69 mmol) was added to a solution of methylene chloride (60 mL), acetyl chloride (0.133 g, 1.69 mmol), and titanium tetrachloride (0.4 mL, 3.40 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 2-4 min, then quenched by adding saturated potassium carbonate (150 mL). GC/MS analysis of the crude organic mixture indicated a 2:1 ratio of *trans*-4-phenyl-3-buten-2-one **130** [MS (EI, m/z): 146 (28), 131 (83), 103 (100), 77 (60), 63 (14), 51 (28)] to 2,6-dimethylacetophenone **131** [MS (EI, m/z): 148 (27), 133 (100), 105 (77), 77 (40), 63 (15), 51 (15)], as well as (*E*)-β-(dimethylhydroxysilyl)styrene **132** [MS (EI, m/z): 178 (22), 163 (60), 145 (100), 137 (22), 115 (10), 103 (15), 91 (10), 77 (34), 61 (26), 51 (15), 45 (37)], and 2,6-(dimethylphenyl)hydroxydimethylsilane **133** [MS (EI, m/z): 180 (26), 165 (100)]. Unreacted (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **129** (0.40 g, 89%) was recovered after separation by radial chromatography.

5.2.3e) Reaction of 2,6-dimethylphenyl-1-magnesium bromide with acetyl chloride

The structure of **131** was proved by an independent synthesis and comparison of spectral data, including the retention times mentioned in section **5.2.1.** 2,6-Dimethylphenyl-1-magnesium bromide (2.96 g, 20.0 mmol) [prepared by reacting 2,6-dimethylphenylbromide (3.0 mL, 20.0 mmol) with magnesium (0.6 g, 24.0 mmol) in 50 mL tetrahydrofuran for 16 h at 55 °C] was added to a solution of tetrahydrofuran (50 mL) and acetyl chloride (2.84 mL, 40.0 mmol) at ambient temperature. The reaction mixture was stirred at ambient temperature (22 °C) for 3 d, then quenched by adding saturated potassium carbonate (250 mL), and extracted with diethyl ether (2 X 300 mL). The reaction yielded 2,6-dimethylacetophenone **131** (0.24 g, 8%) after separation by radial chromatography.

2,6-Dimethylacetophenone 131:

^{1}H NMR ($CDCl_3$, 200 MHz): δ(ppm) 2.25 (s, 6H), 2.48 (s, 3H), 7.00-7.04 (m, 3H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 208.4, 142.5, 132.1, 128.5, 127.7, 32.0, 19.1;

MS (EI, m/z): 148 (25), 133 (100), 105 (75), 77 (37), 63 (14), 51 (14);

IR (neat): ν(cm^{-1}) 2925, 2859, 1699, 1596, 1460, 1352, 1256, 1057, 773, 700.

5.2.3f) Reaction of (*E*)-β-(phenyldimethylsilyl)styrene 126 with benzoyl chloride

Titanium tetrachloride (1.6 mL, 13.4 mmol) was added to benzoyl chloride (0.78 mL, 6.7 mmol) in methylene chloride (20 mL) at -78 °C. (*E*)-β-(Phenyldimethylsilyl)styrene **126** (1.6 g, 6.7 mmol) in methylene chloride (10 mL) was added dropwise and the reaction stirred for 1 h at -78 °C. The reaction mixture was warmed to ambient temperature (22 °C) then quenched with saturated aqueous potassium carbonate (200 mL) and extracted with diethyl ether (2 X 300 mL). Radial chromatography yielded *trans*-chalcone **127** (0.86 g, 62%), and 1,3-diphenyltetramethyldisiloxane **128** (1.1 g, 57%).

Benzylideneacetophenone (*trans*-chalcone) 127:

^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 7.52-7.57 (d, 1H, J = 15.7 Hz), 7.81-7.86 (d, 1H, J = 15.7 Hz), 7.26-8.05 (m, 10H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 190.4, 144.7, 138.1, 134.8, 132.7, 130.4, 128.9, 128.5, 128.4, 128.3, 122.0;

MS (EI, m/z): 208 (100), 179 (20), 165 (12), 131 (30), 105 (25), 77 (31);

MS (CI, m/z): M^+ + H 209 (100), 131 (10);

IR (neat): ν(cm^{-1}) 3082, 3060, 3028, 1961, 1903, 1664, 1605, 1576, 1495, 1449, 1336, 1286, 1215, 1178, 1073, 1036, 1017, 980, 860, 787, 747, 689, 566, 526, 485.

1,3-Diphenyltetramethyldisiloxane 128:

^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 0.48 (s, 12H), 7.46-7.71 (m, 10H);

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ(ppm) 139.8, 133.0, 129.2, 127.7, 0.9;

^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ(ppm) -1.2;

MS (EI, m/z): 286 (10), 271 (100), 193 (60), 135 (25);

IR (neat): ν(cm^{-1}) 3136, 3069, 3051, 3012, 2958, 2900, 1591, 1487, 1428, 1255, 1119, 1060, 832, 792, 739, 700, 649.

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CHAPTER 6

CONCLUSION

The most important observation for our study, involving electronegative ligands on silicon, was that the leaving group ability of the alkyldichlorosilyl groups was attenuated when compared with trialkylsilyl groups. The replacement of trialkylsilyl with dichloroalkylsilyl groups on an olefin reduced the leaving group ability of silicon. Sequential C-H/C-C and C-C/C-C bonds formed without significant loss of silicon, for cyclization reactions initiated by proton and carbon electrophiles, respectively. Desilylation was suppressed because of the reduced β-Si stabilization, and reduced apicophilicity of the intermediate alkyl carbenium ion fragment on silicon. The utilization of electron poor dichlorosilanes requires a sensible choice of carbon electrophiles. The electrophiles must not place extreme steric demands on the alkenylsilane, must be relatively stable carbenium ions, and must have weakly nucleophilic counterions. Thus, one can design reactions in which silicon provides a controlling influence for more than one bond formation and may be subsequently excised from the molecule in a synthetically useful way.

Our studies involving arylsilylstyrenes revealed that bulky alkyl substituted aromatic rings were inadequate for steering electrophilic addition reactions towards the

vinylic moiety, due to the high reactivity of these silylarenes. However, we have determined that arylvinylsilanes, having bulky aryl groups, could be potentially advantageous in synthetic applications where electrophilic aromatic substitution is desired over electrophilic attack on the vinyl group. Additionally, 1-SiR_3-2,6-dimethylbenzene derivatives such as **121**, **129**, and **140**, serve as important regiospecific precursors for 1-functional-2,6-dimethylbenzene derivatives. 1-Functional-2,6-dimethylbenzene derivatives are difficult to prepare from 2,6-dimethylbenzene by conventional electrophilic aromatic substitution (C-H cleavage); here, electronically (*ortho/para*) favored 1-substituted-2,4-dimethylbenzene derivatives are usually obtained instead. Finally, (*E*)-β-(mesityldimethylsilyl) styrene **121** and (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **129** can serve as models from which other β-[(2,6-disubstitutedphenyl)silyl]alkenes may be prepared. From these, the relative nucleophilicity of the arenes and olefins could be determined, and a scale of olefin/arene nucleophilicity prepared. The olefin/arene nucleophilicity scale (Figure 5.1) prepared by Mayr has the disadvantage of not including electrophilic substitution at a position on the ring that allows the electrophile to be flanked by bulky substitutions. The presence of silicon on the aromatic ring allows the reactivity of any ring position to be determined without contributions to the reactivity from competing reactions at other ring positions.