REACTIONS OF VINYLSILANES AND ALLYLSILANES

by

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ABSTRACT

Ph.D. Patrick Wan-Kit Lau Chemistry

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The electrophilic substitution reactions of trisubstituted vinylsilanes with various electrophiles were found to be stereospecific. The vinylsilanes were converted stereoselectively into various vinyl halides and α,β-unsaturated ketones and aldehydes of defined stereochemistry.

The cleavage of the silicon-carbon bond of triorganosilyloxiranes by fluoride ion was described. The cleavage rate was comparable to the cleavage of the silicon-alkynyl carbon bond. The stereochemistry of substitution at the oxiranyl carbon was determined.

The regioselectivity of the reactions of 1-trimethylsilylallyl carbanion with carbonyl compounds was controlled by the addition of magnesium bromide to give predominately the α-addition alcohols. This provided a path for the conversion of carbonyl compounds into 1,3-dienes by the subsequent elimination of R_3SiO^-.

Allylsilyloxy carbanion, from metalation of allyloxysilane, existed in equilibrium with its rearranged oxyanion. The product ratio of their reactions with various electrophiles was dependent on the nature of the electrophiles. Finally, some reactions of α-siloxyallylsilane with acid chlorides were examined.

RESUME

Ph.D. Patrick Wan-Kit Lau Chimie

LES REACTIONS DES VINYLSILANES ET ALLYLSILANES

On a montré que les réactions électrophiles des vinylsilanes trisubstitués avec divers électrophiles sont stéréospécifiques. Les vinylsilanes sont convertis stéréosélectivement en divers halogenures de vinyle, en cétones α,β-insaturées, et en aldehydes de stéréochimie définie.

La rupture de la liaison silicium-carbone des triorganosilyloxiranes par l'ion fluorure est décrite. La vitesse de rupture est comparable à celle de la liaison silicium-carbone d'un groupe alcynyle. La stéréochimie de la substitution au niveau du carbone de l'oxiranyle a été déterminée.

La régiosélectivité des réactions du carbanion du triméthylsilyl-1-allyle avec des composés carbonylés est controlée par l'addition de bromure de magnésium pour donner d'une façon prédominante les alcools de l'addition α. Ceci permet la conversion des composés carbonylés en dienes-1,3 après l'élimination de R_3SiO^-.

Le carbanion de l'allylsilyloxyde, provenant de la métallation de l'allyloxysilane, existe en équilibre avec son oxyanion transposé. Le rapport des produits de leurs réactions avec divers électrophiles est dépendant de la nature de ces derniers.

Finallement, quelques réactions de l'α-silyloxyallylsilane avec des chlorures d'acide sont étudiées.

To my parents

and to my wife Carme

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Professor T.H. Chan without whose patience and encouragement this work would not have been completed.

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TABLE OF CONTENTS

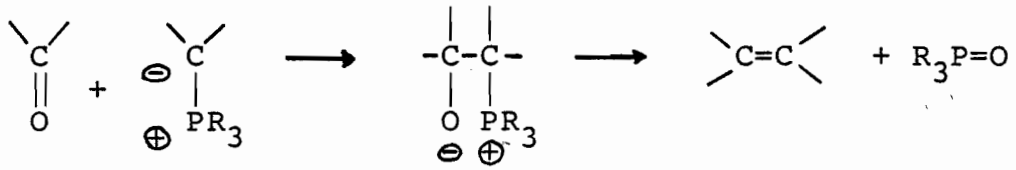
LIST OF TABLES

CHAPTER 1

INTRODUCTION

(a) VINYLSILANES

One important reaction in synthetic organic chemistry is the formation of carbon-carbon double bonds. Of the methods developed for this purpose, the Wittig reaction is the most often employed[1,2,3]. The principle for this alkene synthesis is the olefination of a carbonyl compound. It can be represented by the following equation.

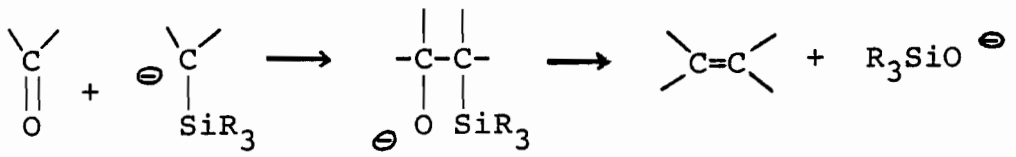


It is based on the role of phosphorus in the carbanion formation as well as the elimination step. A phosphorus ylid is generated from the phosphonium salt formed by an alkyl halide and triphenylphosphine. The phosphorus ylid is then reacted with a carbonyl compound, the addition followed by elimination of the phosphine oxide to give the alkene. The driving force of this reaction is the formation of the strong phosphorus-oxygen bond. Modifications in the structure of the organophosphorus compound often improve this reaction. For example, the Horner modification[4] using a phosphinylalkyl metal compound (i.e. using $R_2P(O)$ instead of R_3P) is of

definite advantage over the Wittig reaction. Other modifications of the Wittig reaction using different phosphorus substituted carbanions[5,6] have been used.

These olefination reactions are not unique to organophosphorus compounds. Corey's olefin synthesis using sulfinamide derivative ($-SONR_2$)[7] is an example. The use of other sulfur derivatives such as sulfides[8], sulfoxides[9], sulfoximides[10] and sulfones[11] have also been reported in the olefination of carbonyl compounds.

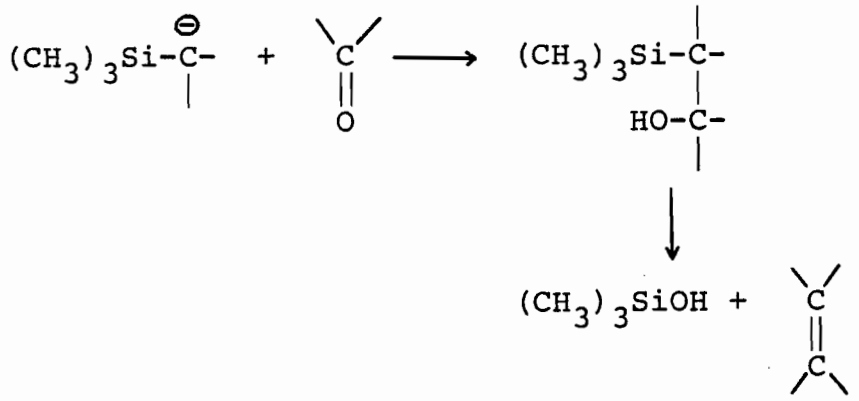
The olefination of carbonyl compounds has also been extended to the use of organosilicon compounds. The recognition that β-functional organosilanes can undergo elimination to give carbon-carbon double bond underlines the basis of the new alkene synthesis.



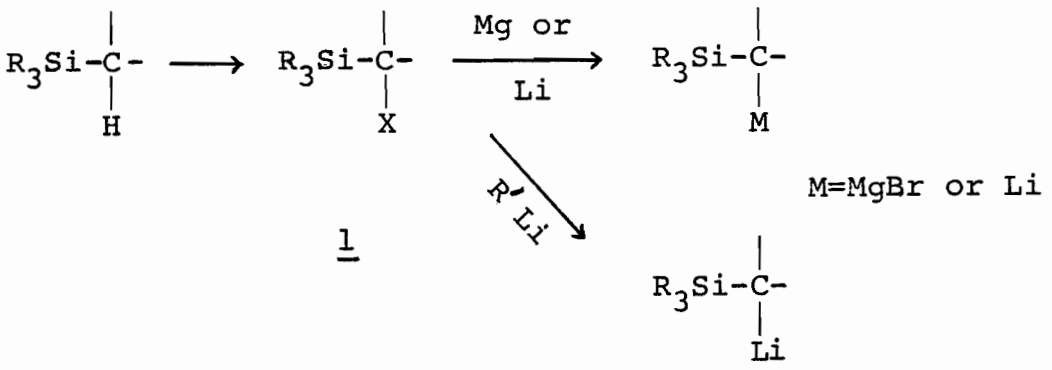
It involves the addition of carbonyl compounds to α-silyl carbanions, followed by elimination of the R_3SiO^- moiety. This, of course, bears similarity to the Wittig reaction[12] and its many modifications[3]. However, this method is competitive with the Wittig reaction. Using this method, strained alkenes such as allene oxides[13,14,15], cyclopropenes[16] and bridgehead alkenes[17] which would have been difficult to prepare otherwise

are generated. Hetero-substituted alkenes[18,19,20] can also be synthesized using this silicon method.

Peterson[21] was the first to demonstrate the alkene synthesis using the reaction between α-silyl carbanion and carbonyl compounds. An α-trimethylsilyl substituted carbanion is used to react with different carbonyl compounds, which include aromatic and aliphatic ketones and aldehydes, to give β-hydroxysilanes. These β-hydroxysilanes undergo elimination of trimethylsilanol to give the alkenes in good yields under both basic and acidic conditions.

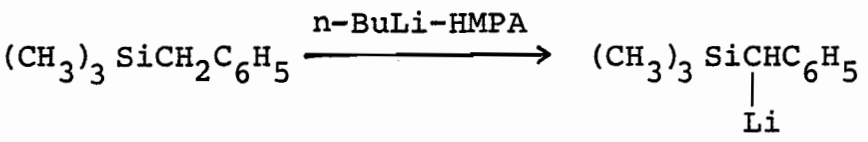


In order to proceed with the alkene synthesis, methods of generating the α-silyl carbanions must be found. Two methods involving α-halosilanes can be employed. One reaction would be a Grignard reaction between the α-halosilanes and magnesium[22,23] or lithium. The other method is the metal-halogen exchange reaction between the α-halosilanes and alkyllithium, thus giving the carbanions[24]. However, these methods are limited by the availability of the α-halosilanes 1 which are normally derived by the free radical halogenation of alkylsilanes[24].



1

Other methods where the precursors are more readily available have been developed. Direct metalation by alkyllithium in hexamethylphosphoramide of benzyltrimethylsilane is used by Chan to generate the carbanion[25]. This gives a useful method for the preparation of α-silylalkyllithium compounds when the alkyl group is activated, for example in this case, by a phenyl group.



A limitation to this method is that it cannot be applied to generate carbanions on simple long chain alkyl carbon moieties. For example, metalation of n-butyltrimethylsilane with n-butyllithium-TMEDA occurs mainly on the methyl carbon[26].

An alternative method of generating α-silylalkyllithium compounds is making use of the fact that organolithium reagents can add across the double bond of triorganovinylsilanes[27,28,29].

$$R_3SiCH{=}CH_2 \;+\; R'Li \longrightarrow R_3SiCH(Li)\text{-}CH_2R'$$

Both triphenylvinylsilane[26] and trimethylvinylsilane[30] can be used in the reaction. This marks one of the first times where reactions involving vinylsilanes are employed for alkene synthesis. The carbanion can be generated by the reaction of equimolar quantities of the alkyllithium and the triorganovinylsilane in ether.

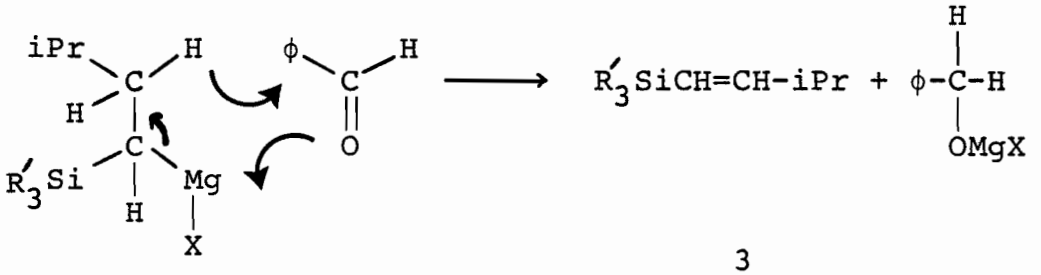
Buell[31] has found that this method can be extended to the use of Grignard reagent instead of the alkyllithium compounds. Grignard reagents can add to activated vinylsilanes as follows:

$$(CH_3)_2Si(OC_2H_5)\text{-}CH{=}CH_2 \;+\; RMgX \longrightarrow (CH_3)_2Si(OC_2H_5)\text{-}CH(MgX)\text{-}CH_2R$$

2

However, unlike the cases of the alkyllithium compounds, the Grignard reagents formed do not add to carbonyl compounds. There is no trace of product which can be identified as due to the addition of the carbonyl compound to the Grignard reagent 2. For example, if R=i-Pr[29], isopropylmagnesium chloride is added to dimethylvinylethoxysilane to give 2, then benzaldehyde is added to the reaction mixture and quenched

with acetyl chloride, the products are found to be benzyl acetate and compound 3. The formation of benzyl acetate can be explained from the hydride transfer mechanism[29].



3

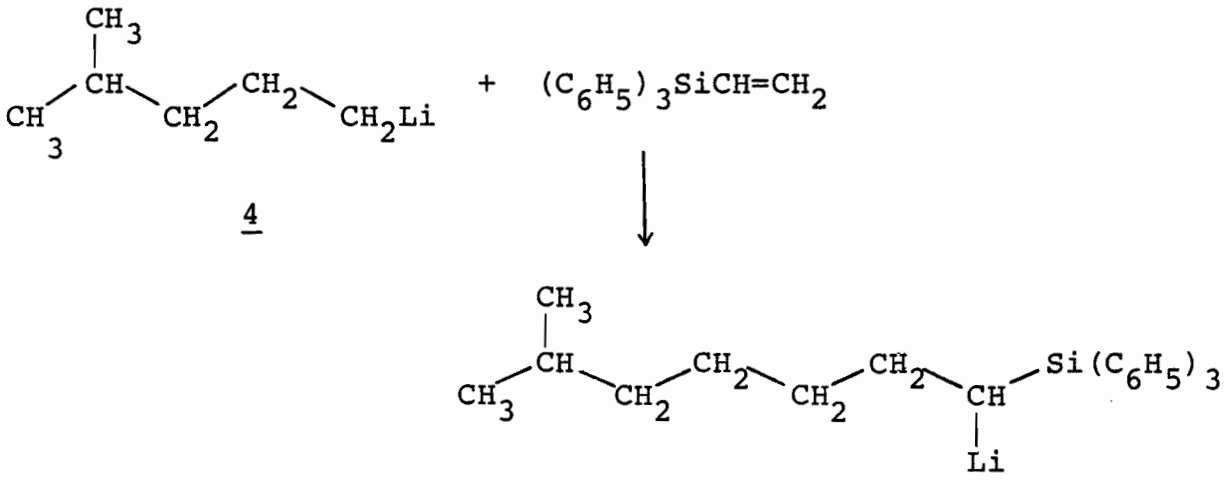
Using other carbonyl compounds, for example, acetophenone and 2-methylhept-2-en-6-one, also gives the same kind of results[29].

The use of the reaction of vinylsilanes with alkyllithium to generate the α-silyl carbanion and its subsequent reaction with carbonyl compounds to give the corresponding alkenes has been demonstrated by Chan[29] in the synthesis of the sex pheromone of the Gypsy moth (disparlure). The structure of the pheromone has been identified as cis-7,8-epoxy-2-methyl-octadecane 7[32].

The α-silyl carbanion 5 is generated by reaction of triphenylvinylsilane and 4-methylpentyllithium 4, prepared in situ from the corresponding chloro compound.

Reaction with undecanal gives both geometric isomers of 2-methyl-7-octadecene 6 (E:Z=1:1). This is followed by epoxidation using m-chloroperbenzoic acid to give the cor-

responding epoxide 7 in quantitative yield. The epoxides are found to be a 1:1 mixture of the cis and trans isomers. They are identical in all respect with the authentic mixture.



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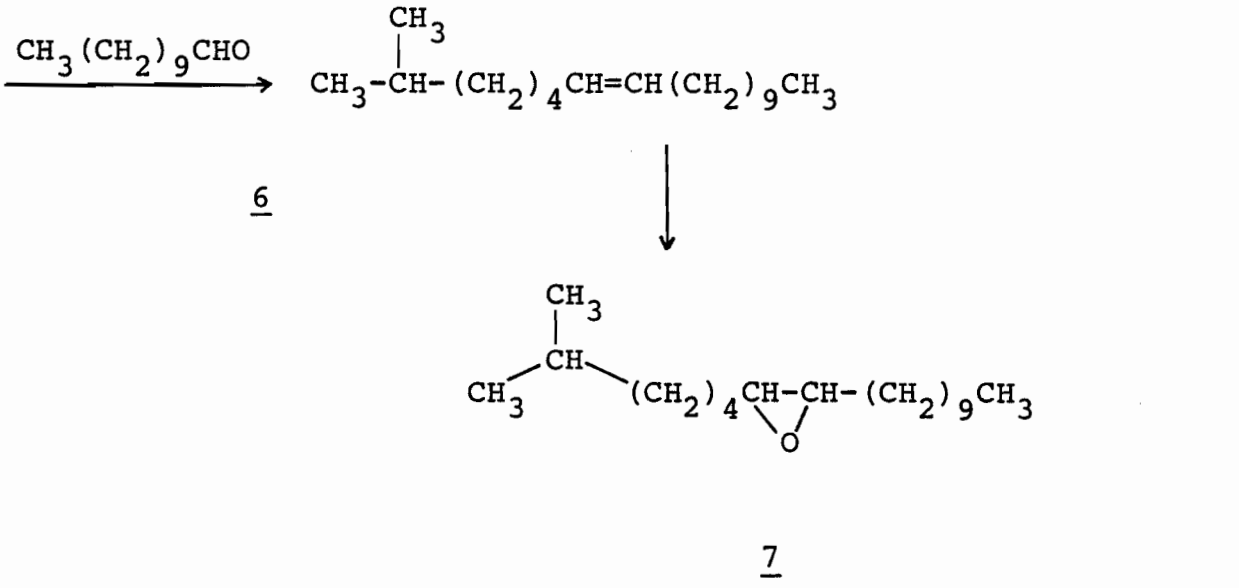

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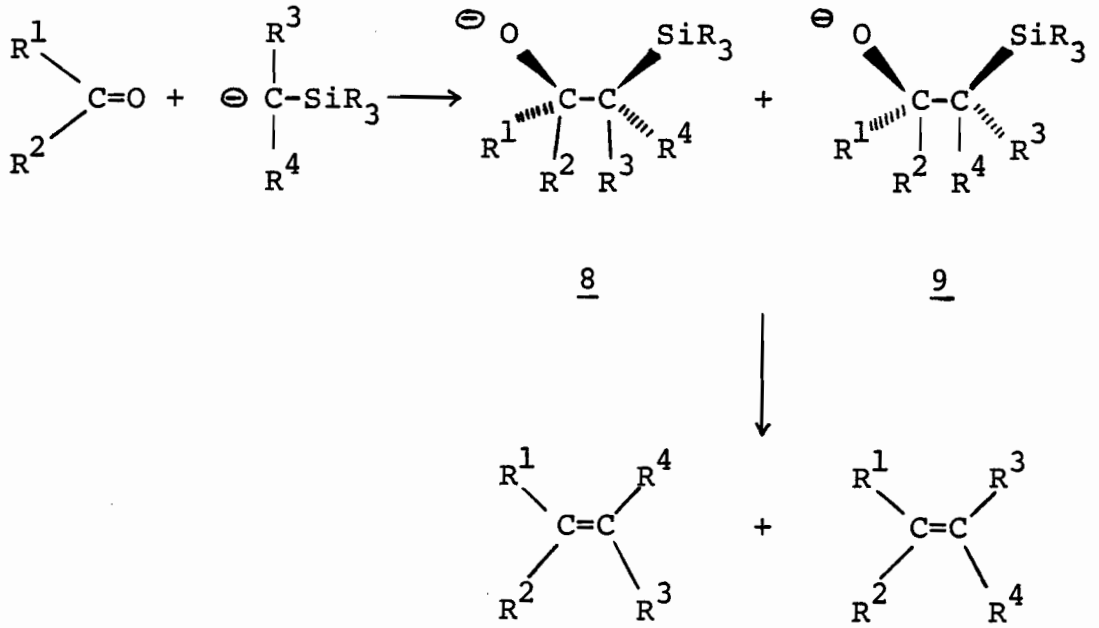
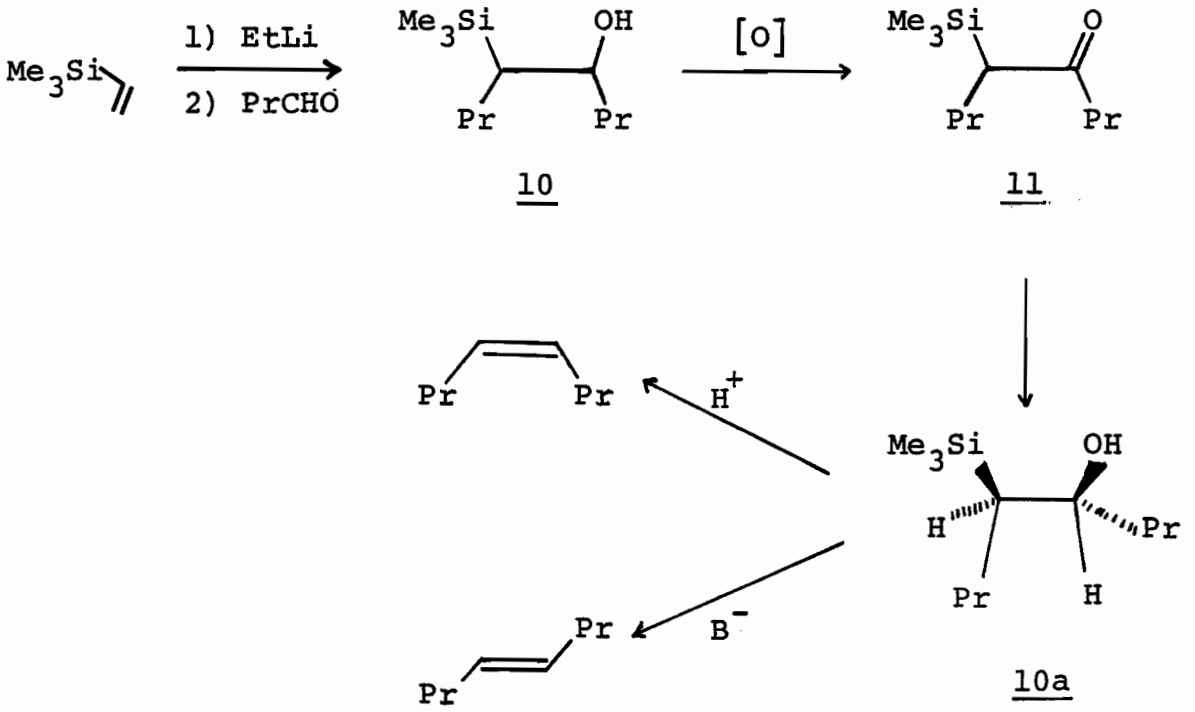
The condensation of α-silyl carbanion with a carbonyl compound to give an alkene has become a very useful procedure. However, there is one drawback. As can be seen in the above example of the synthesis of the sex pheromone of the Gypsy moth, the alkene 6 synthesized can display geometric isomerism, and the product obtained is a mixture of the E and Z isomers in equal proportions. This lack of stereoselectivity, of course, diminishes the synthetic utility of the reaction.

The lack of stereoselectivity can be explained by the non-selective addition of the α-silyl carbanion to the carbonyl compound to give the two diastereomers 8 and 9. Each diastereomer can eliminate stereospecifically to give only one isomer of the alkene.



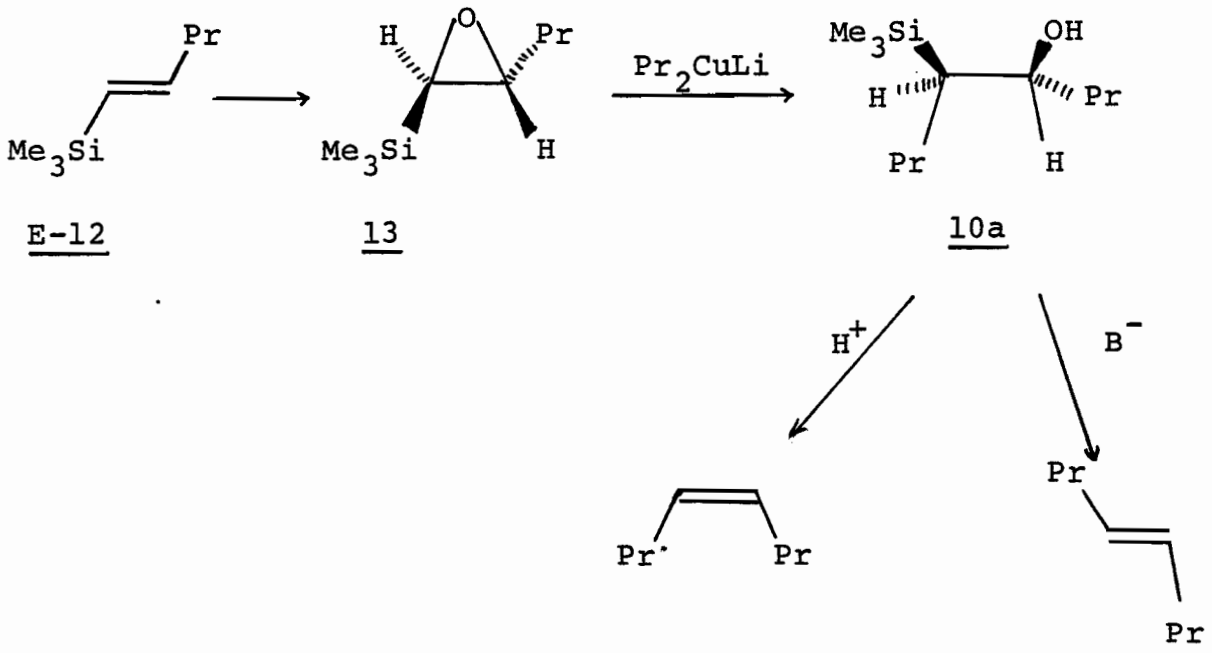
Methods for the stereoselective synthesis of alkenes have been developed. However, many of these methods[33,34,35] can only give stereoselectively one isomer while the other geometric isomer cannot be obtained by the same method. Thus, a general method for stereoselectively synthesizing both the E and Z isomers is desired.

Vinylsilanes have been used by Hudrlik[36,37] in the stereoselective synthesis of E and Z disubstituted alkenes. Trimethylvinylsilane is reacted with an alkyllithium, followed by addition of an aldehyde to give a β-hydroxyalkylsilane 10. Then the β-hydroxyalkylsilane is oxidized to a β-ketosilane 11. The β-ketosilane is then selectively reduced by diisobutylaluminum hydride (DIBAL) back to only one diastereomer of the threo β-hydroxysilane 10a, which then, depending on the reaction conditions, gives either the E or Z isomer on elimination (Scheme 1).



SCHEME 1

Another method of generating one diastereomer of the β-hydroxysilane 10 is also demonstrated by Hudrlik[37]. The starting material used is a vinylsilane of defined stereochemistry. Epoxidation of the vinylsilane E-12 gives an α,β-epoxysilane 13. The epoxysilane is then treated with an organocopper lithium reagent. This reaction is stereoselective, and only one diastereomer of the β-hydroxylsilane 10a is formed. Once again, depending on the reaction conditions of the elimination step, either the E or Z isomer of the alkene will be obtained in >98% stereochemical purity (Scheme 2).



E-12 13 10a

SCHEME 2

There is, however, one drawback about this method. This reaction is dependent on using geometrically pure vinylsilane as the starting material which is sometimes quite difficult to obtain.

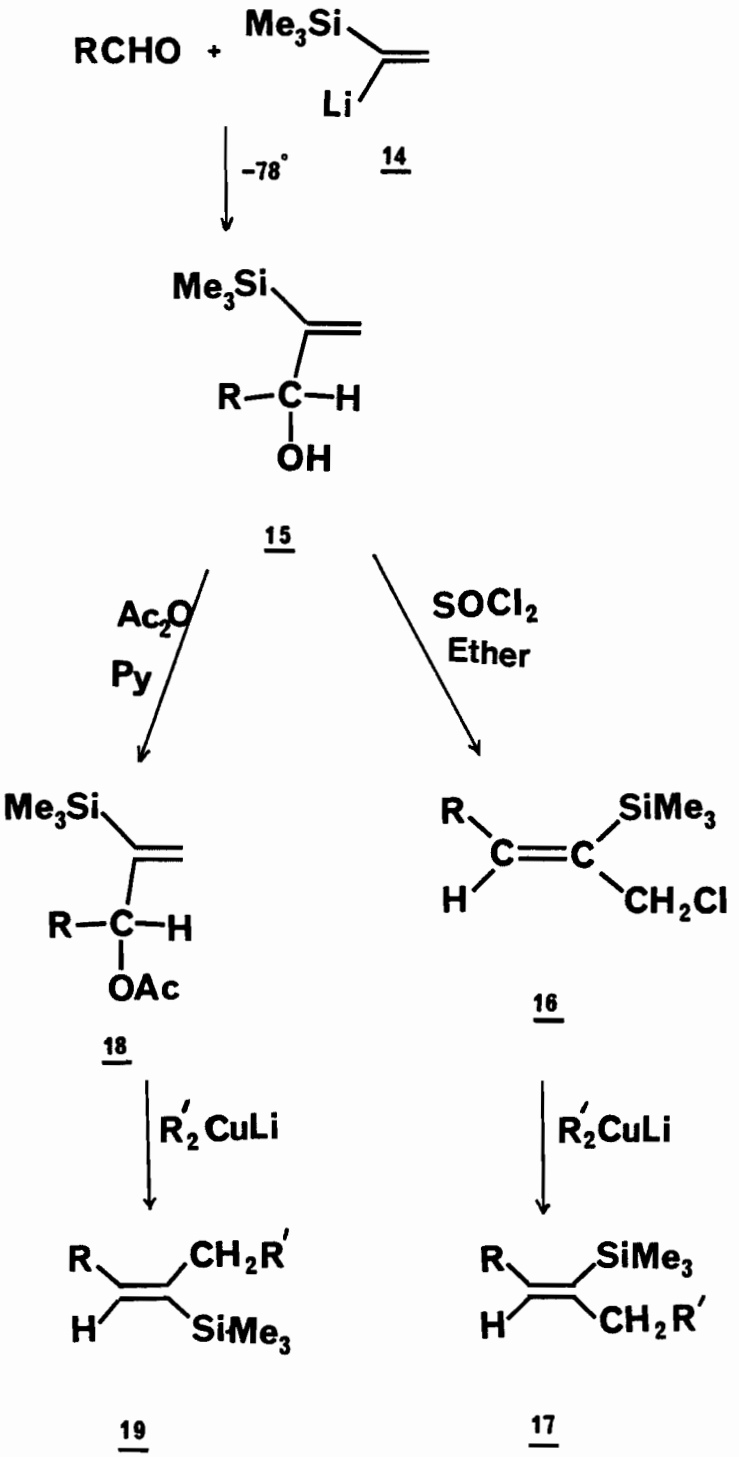
Since it has been demonstrated that vinylsilanes have great potential in alkene synthesis, if methods for the stereoselective synthesis of the geometric isomers of the vinylsilanes from readily available starting materials are developed, the utility of vinylsilanes as synthetic intermediates will be greatly enhanced.

Recently, Chan[38] has reported on the stereoselective synthesis of trisubstituted vinylsilanes. These vinylsilanes can serve as useful precursors for the stereoselective synthesis of trisubstituted alkenes[33,38], which are of particular interest because of the widespread occurrence of this structure in nature.

Reaction of aldehydes with α-trimethylsilylvinyllithium 14[24,39,40], prepared from α-bromovinyltrimethylsilane and t-butyllithium at -78°C gives the alcohols 15 in good yields[41]. From then on, depending on the reaction conditions used, either the E or the Z isomer of the trisubstituted vinylsilanes can be prepared[38] (Scheme 3).

The alcohols 15 can be converted stereoselectively into predominantly the Z isomer of the allylic chlorides 16 by reaction with 20% excess thionyl chloride in ether[41]. Reaction with organocopper lithium reagents at room temperature gives

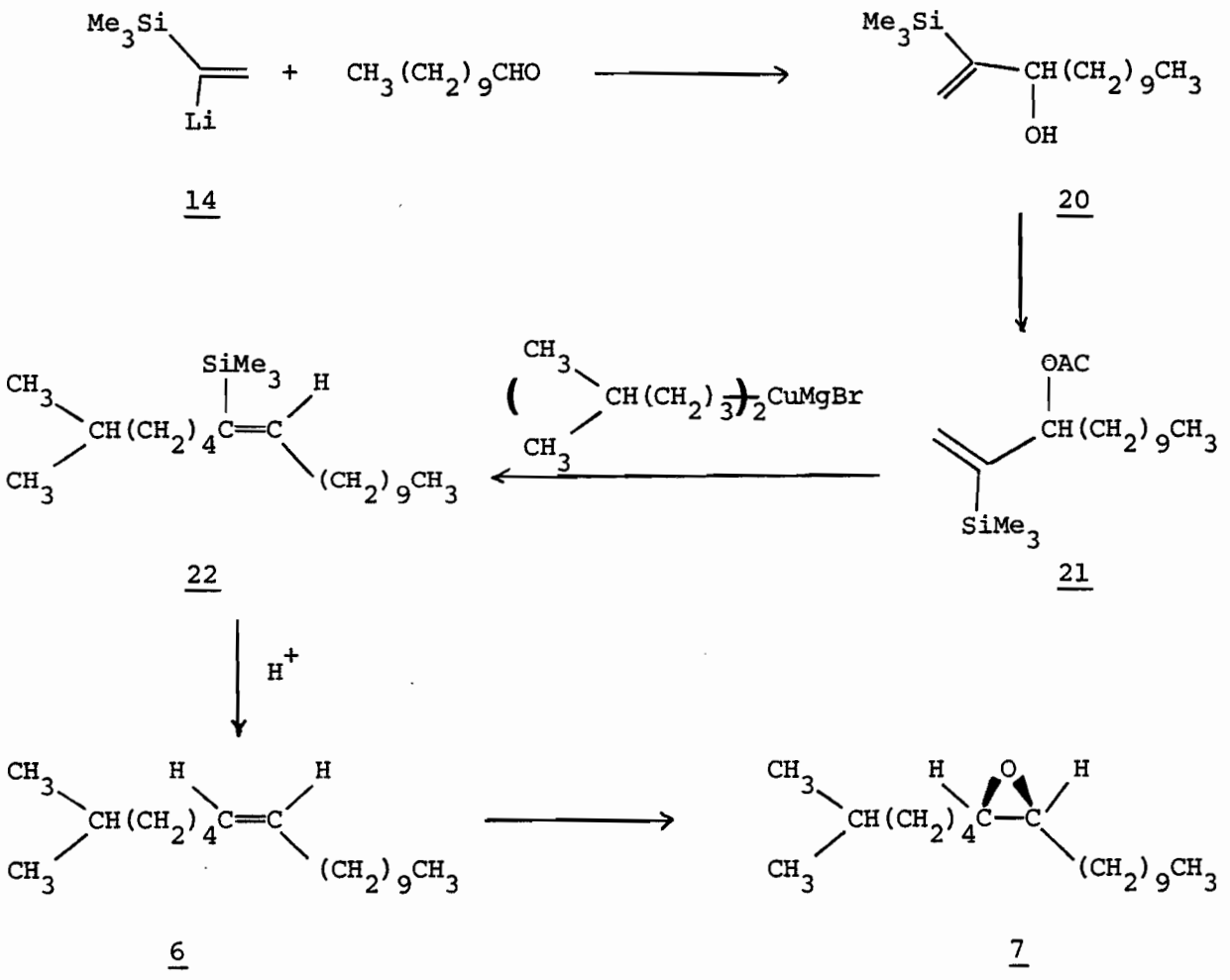
the Z isomer vinylsilanes 17 in high yields with the same stereochemical purity as the allylic chloride 16[42].



Scheme 3

However, if the alcohols 15 are refluxed with acetic anhydride in pyridine, the corresponding acetates 18 are formed. Reactions of 18 with organocopper lithium reagents at low temperature can give stereoselectively the E isomer of the vinylsilanes 19[35]. This reaction, however, is very sensitive to the size of the alkyl group, the temperature of the reaction and the choice of the copper reagent[38].

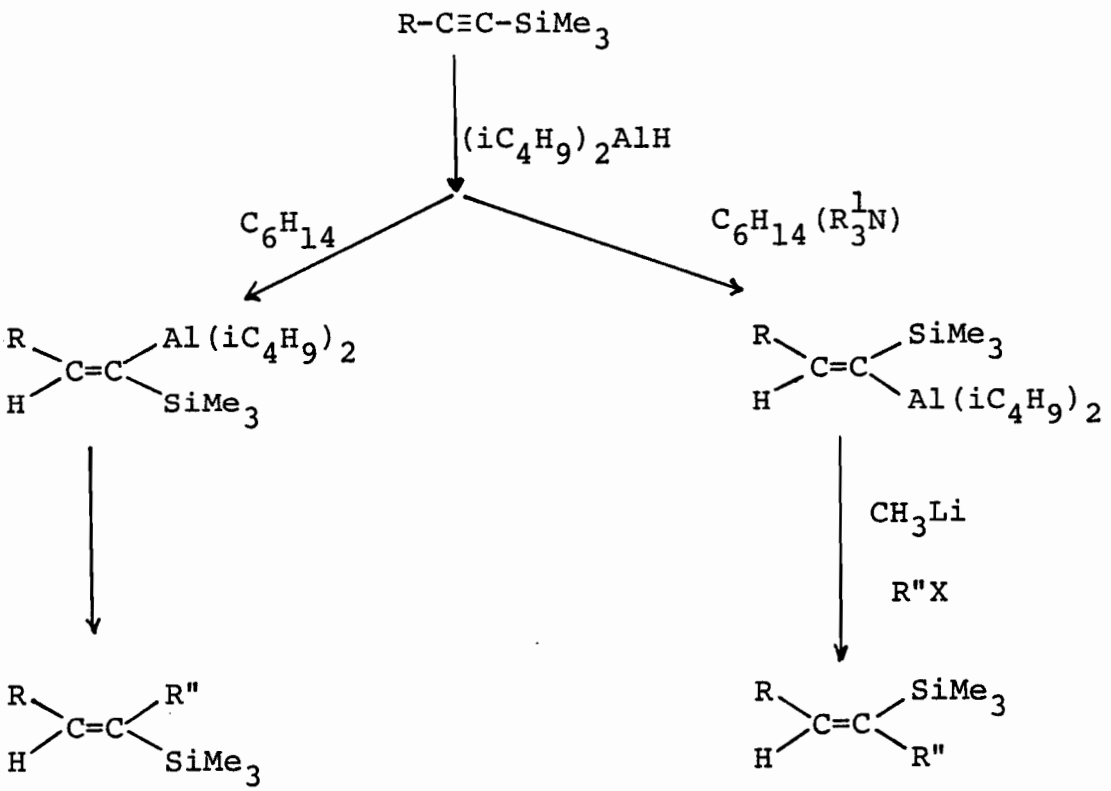
The utility of vinylsilanes in organic synthesis has been demonstrated by Chan[38] in a new stereoselective synthesis of the sex pheromone of Gypsy moth disparlure 7 (Scheme 4).



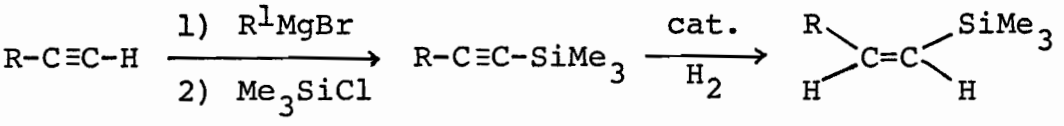
SCHEME 4

The alcohol 20 is prepared from reaction of 14 with undecanal, followed by acetylation to give the acetate 21. Low temperature reaction of 21 with organocopper magnesium bromide gives the E isomer vinylsilane 22. The vinylsilane is then converted to the Z alkene 6 by the action of 57% hydriodic acid at room temperature. Epoxidation[29] of alkene 6 gives the sex pheromone 7 in overall yield of 65% (E:Z=13:87)[38].

Other methods of stereoselective synthesis of both isomers of vinylsilanes have been developed. Both Eisch[43] and Utimoto[44] have reported stereoselective synthesis of trisubstituted vinylsilanes starting with acetylenic compounds.

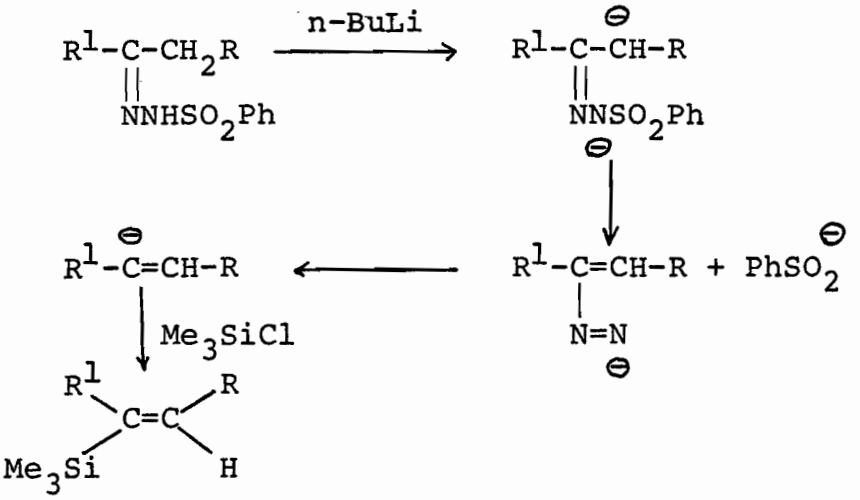


The use of acetylenic compounds as starting material for vinylsilane synthesis has been performed by other groups[45,46,47] before. However, they only give disubstituted vinylsilanes.

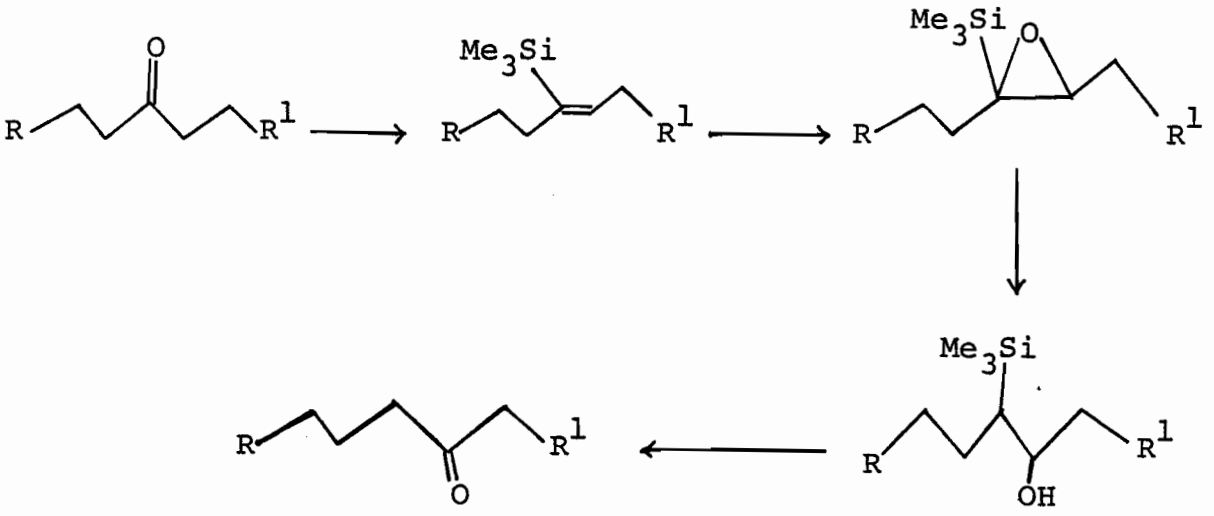


Other methods developed by Seebach[40], Sakurai[48], Brook[39] and Cunico[49] give various kinds of vinylsilanes, some with other functionalities, e.g. carbonyl groups, halides. However, only one geometric isomer of the vinylsilanes can be obtained by these methods, or if both isomers can be synthesized by these methods there is no stereoselectivity in the products obtained.

Chan[50] has also reported a method of vinylsilane synthesis from benzenesulfonylhydrazones. This reaction is clean and gives stereoselectively the Z isomer. The same method has also been developed by Paquette[51].



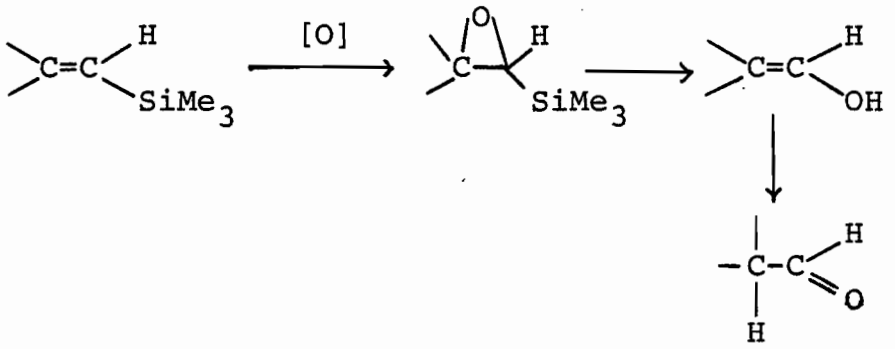
One synthetic application of this particular vinylsilane synthesis is in the 1,2-migration of the carbonyl group of ketones using the vinylsilanes as intermediates[52]. Using a ketone as starting material, it can be transformed into vinylsilane via benzenesulfonylhydrazone using the above method. The vinylsilane can be epoxidized to the epoxysilane. Hydride reduction followed by chromic acid oxidation will give the ketone with the carbonyl group having migrated (Scheme 5).



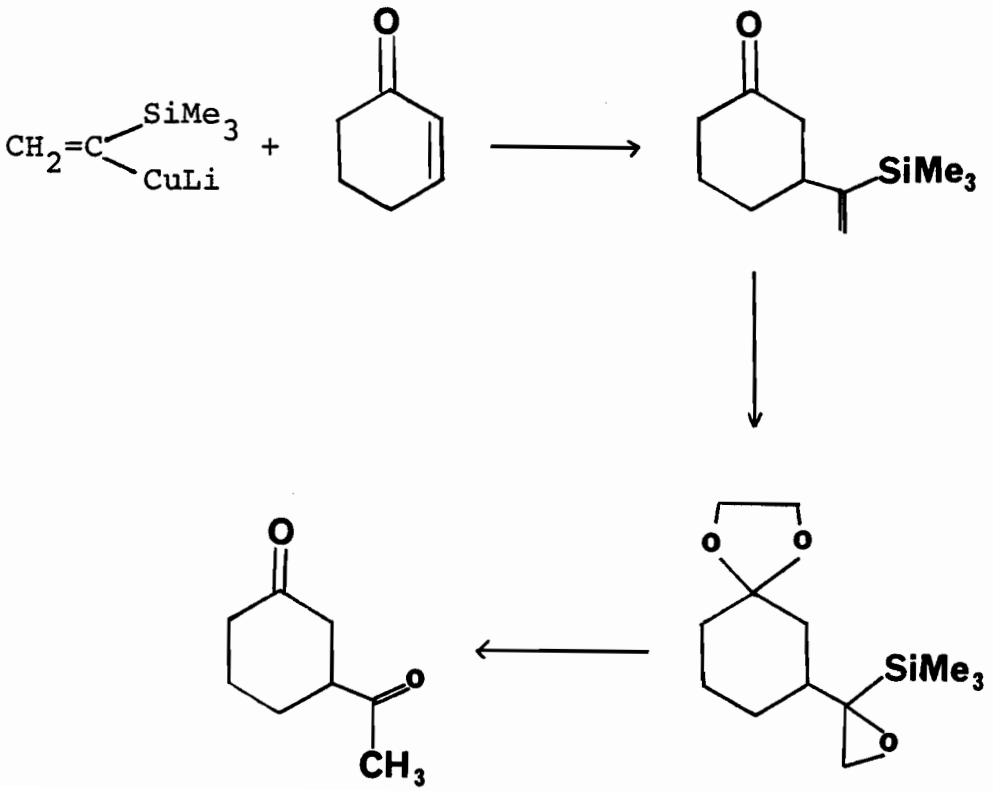
SCHEME 5

Thus, many methods have been developed for the synthesis of vinylsilanes, but only a few are stereoselective. Both the Eisch[43] and the Utimoto[44] methods have the drawback that the reductive alkylation of the vinylaluminum intermediates does not work very well for simple alkyl halides. Only a low yield results. Thus the stereoselective synthesis of vinylsilanes reported by Chan[38] is more advantageous because of its readily available starting materials, its high stereoselectivity and the overall high yields of products.

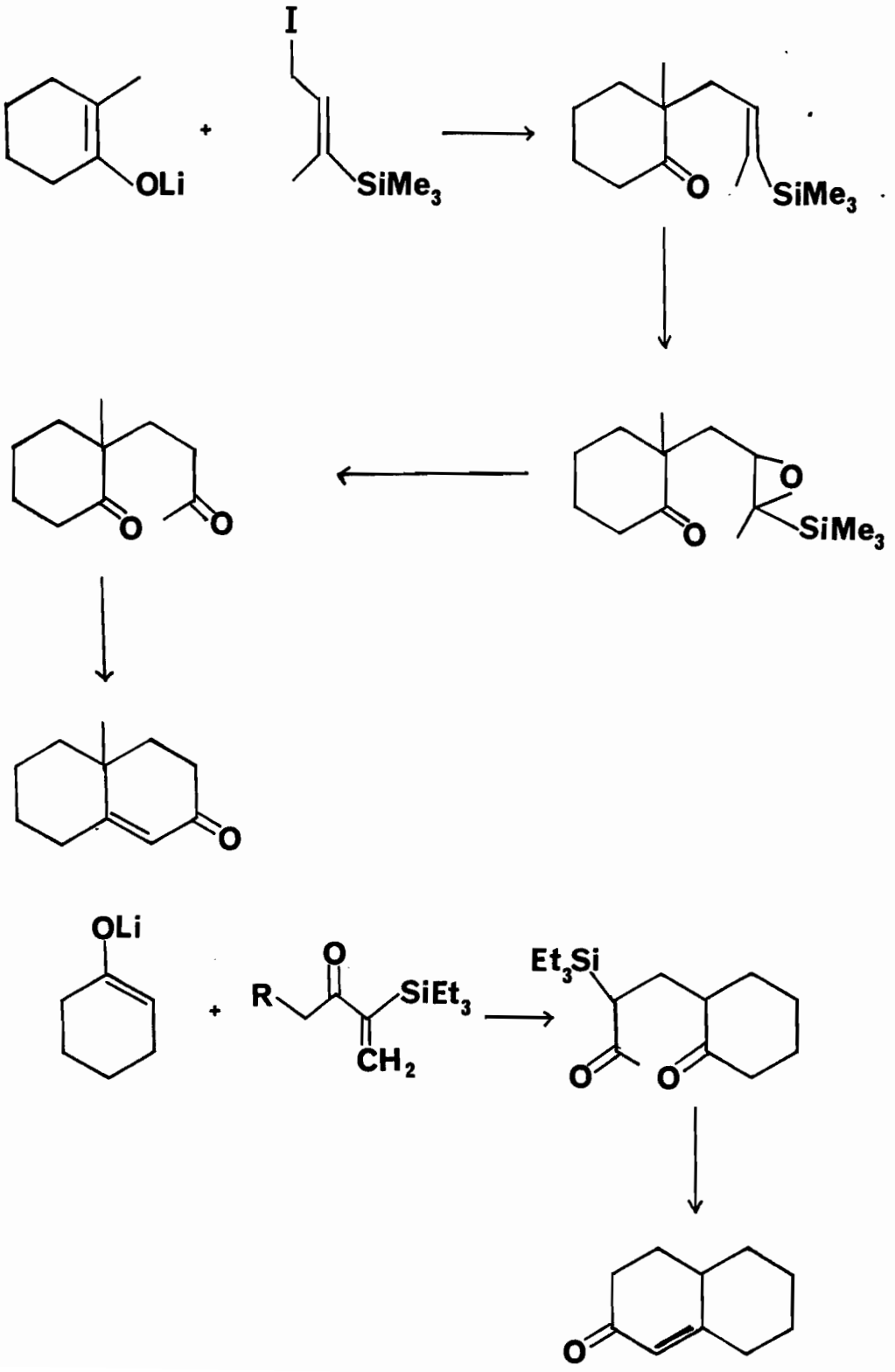
Vinylsilanes can be protodesilylated[53] into substituted alkenes. But other than alkene synthesis, vinylsilanes are important precursors to many difficult functional groups in organic synthesis. Stork[46] has reported the following transformation of vinylsilanes into aldehydes.



This method has been extended by other people in the synthesis[40] of methyl ketones and dicarbonyl compounds[54].

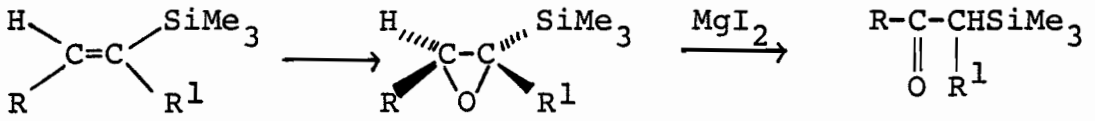


Stork[55,56] has also reported the use of vinylsilanes in the annelation reaction of ketones to give fused polycyclic systems.

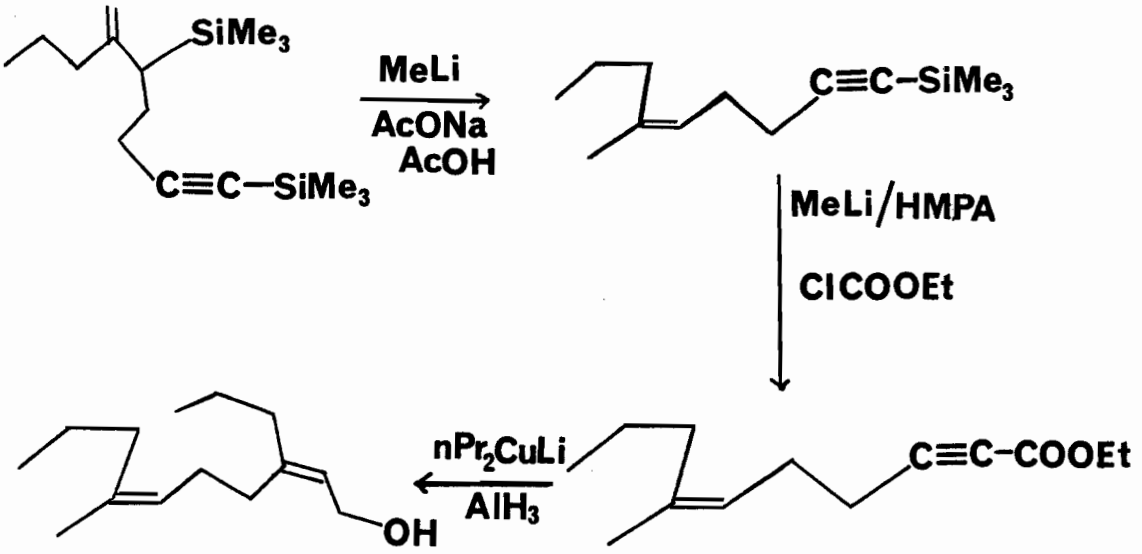


As demonstrated above by Stork[46,56] and by Boeckman[54], α,β-epoxysilanes, prepared by epoxidation of vinylsilanes, are efficient precursors of carbonyl compounds under acidic conditions. However, these epoxysilanes can be very useful synthetic precursors under other conditions.

α,β-Epoxysilanes, formed by epoxidation of trisubstituted vinylsilanes, can rearrange in the presence of magnesium iodide in ether to give the β-ketosilanes[57,58].



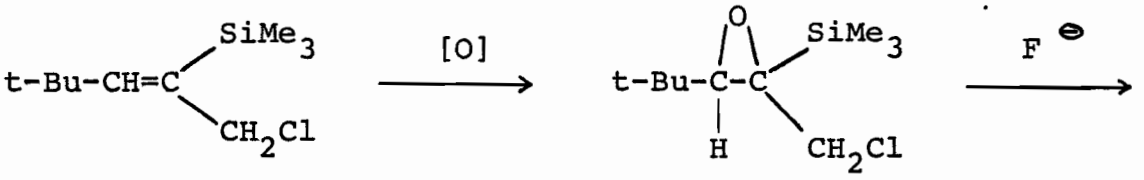
The use of this β-ketosilane from vinylsilane can be demonstrated[59] in the synthesis of 7-methyl-3-propyl-2(Z), 6(Z)-decadien-1-ol[60], a tetrahomoterpene alcohol obtained from the codling moth (Scheme 6).



Scheme 6

The synthesis of allene oxides[13,14,15] from epoxysilanes is another example. Allene oxides, except for a few highly hindered ones, have been difficult to isolate because of the ease of the opening of the epoxide ring under acidic conditions during the peracid epoxidation. Because of the difficulties for the allene oxides' preparation, the use of allene oxides as synthetic intermediates has been limited. However, Chan[13,14,15] has developed a method of synthesizing allene oxides from vinylsilanes, making use of the fact that fluoride ion has high affinity for silicon. β-Functionalized vinylsilanes can be epoxidized to give the corresponding α,β-epoxysilanes. These epoxysilanes can undergo β-elimination to give allene oxides on treatment with fluoride ion.

For example[14], epoxidation of the β-functional vinylsilane 23 (mixture of E and Z isomers) gives the α,β-epoxysilane 24. Reaction of 24 with cesium fluoride in triglyme generated the 1-t-butylallene oxide 25 by β-elimination of the chlorotrimethylsilane.



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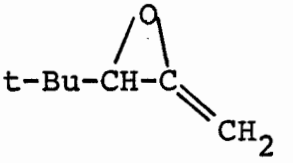
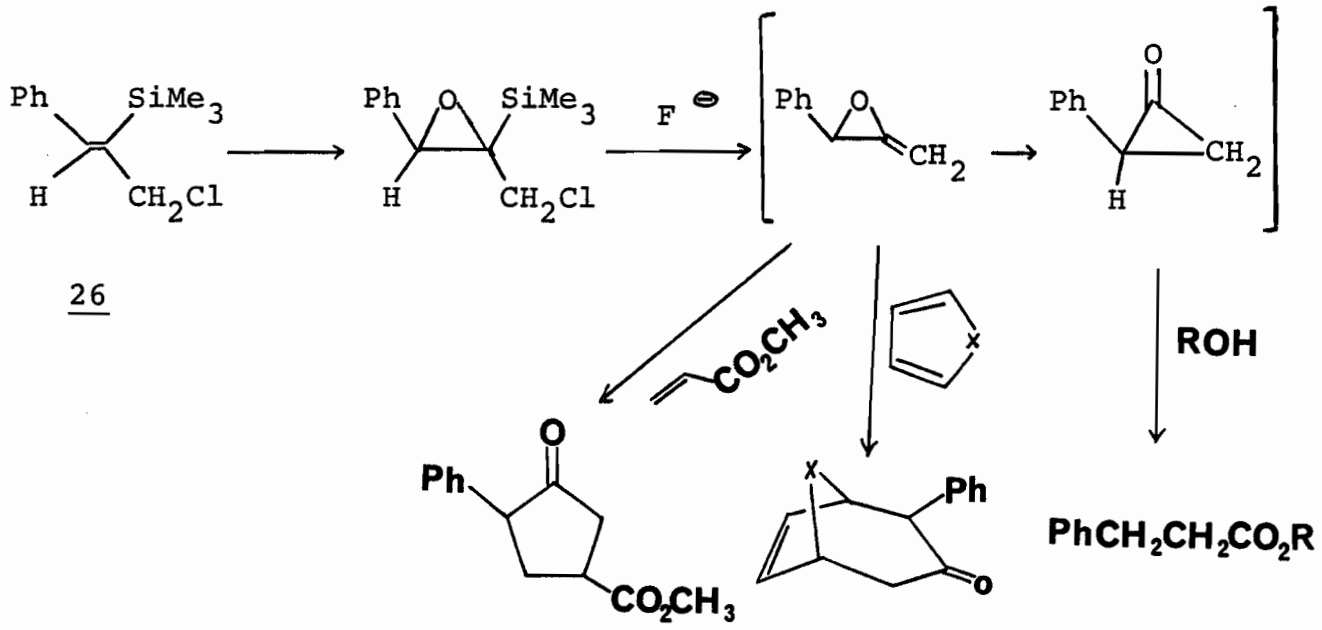


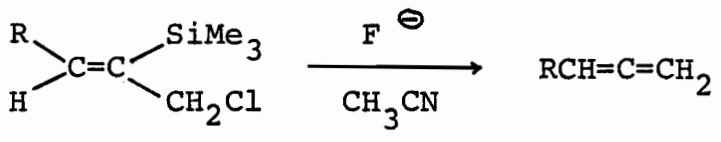
25

Using the same method, other allene oxides have been generated and characterized by trapping with various nucleophiles[13,14,15] and dienes[13]. The usefulness of allene oxides as synthetic intermediates can be demonstrated by the following transformation from vinylsilane 26.



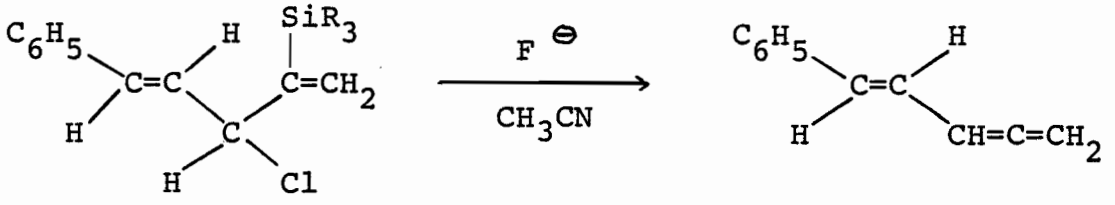
26

However, even without epoxidation, the β-functionalized vinylsilanes of the general structure 27 can undergo similar kind of β-elimination of chlorotrimethylsilane when treated with fluoride ion to give quantitatively the allene 28[61,62].



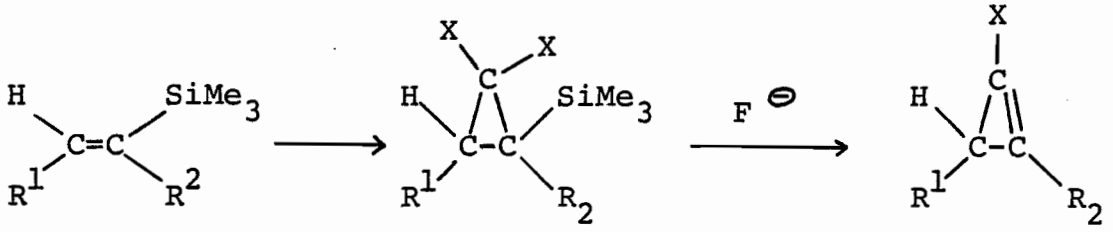
27 28

There is one advantage of this allene synthesis from vinylsilanes. No contamination by the isomeric alkynes of products is obtained which often occurs in other methods of allene synthesis under strongly basic conditions. Also, a double bond elsewhere in the molecule is not affected by this transformation. For example[61], the β-functionalized vinylsilane 29 can undergo β-elimination to give the allene 30 while the other double bond in the vinylsilane 29 is not touched.



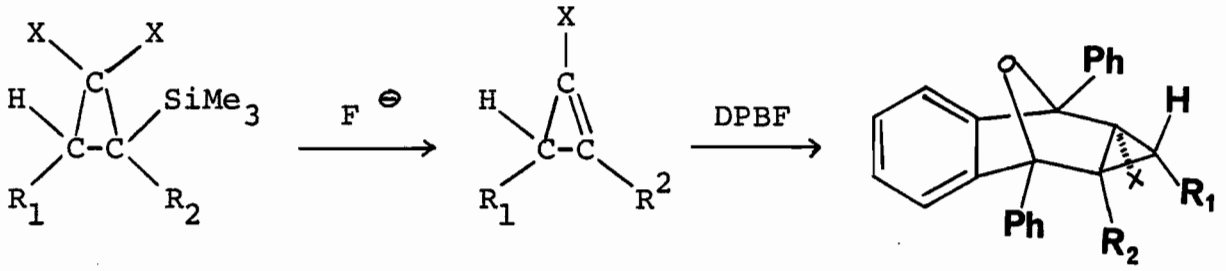
29 30

The use of fluoride ion to promote β-dehalosilylation has been extended to the generation of cyclopropenes[16] and bicyclo bridgehead alkenes[17] from vinylsilanes.



31 32 33

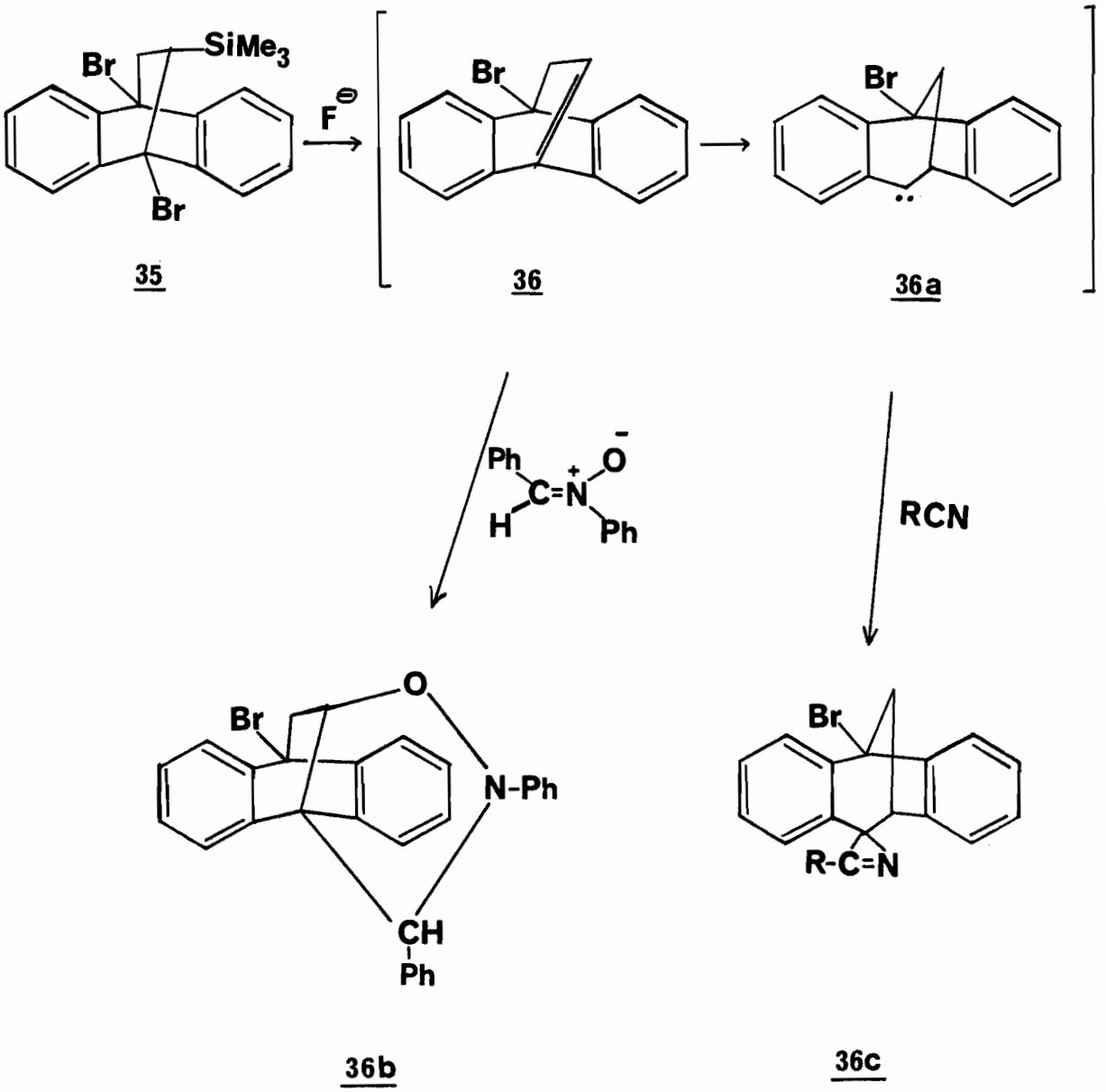
Vinylsilane 31 can undergo dihalocyclopropanation to give the 1,1-dihalo-2-trimethylsilyl-cyclopropane 32. Treatment of 32 with fluoride ion gives the cyclopropene 33 as product. This fluoride ion promoted dehalosilylation has been used to prepare a number of bicycloalkenes. In all cases, these strained cyclopropenes have been trapped as the Diels-Alder adducts 34 of 1,3-diphenylisobenzofuran[16] (DPBF).



32 33 34

The use of vinylsilanes for the synthesis of strained alkenes via β-elimination using fluoride ion has been used by Chan[17] in the study of the nature of the double bond of bicyclo bridgehead alkenes. Compound 35, formed by the Diels-Alder reaction of trimethylvinylsilane with 9,10-dibromoanthracene, is reacted with fluoride ion under a variety of conditions. In all cases debromosilylation occurs[17].

From the product 36c formed, it is believed that a carbene species is involved as an intermediate. The carbene intermediate can only be formed from the rearrangement of the bridgehead alkene 36. Evidence of 36 is deducted by trapping



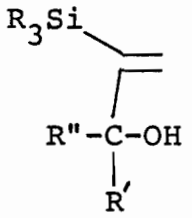
35 36 36a

36b 36c

it with a 1,3-dipolar compound to give the cycloadduct 36b. To account for the product 36b obtained, it seems that the double bond in 36 must possess some polar character[17].

The use of vinylsilanes as important synthetic intermediates has been demonstrated in the above reactions. The fact that β-functionalized vinylsilanes and epoxysilanes can react with fluoride ions to give allenes and allene oxides

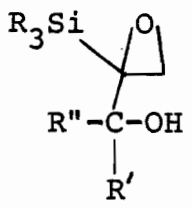
via β-elimination of chlorotrimethylsilane has opened up new routes of synthesis of compounds otherwise difficult to obtain under mild conditions. However, if the β-functional group is a hydroxy group, as in structure 37, reactions with fluoride



37

ion do not give the β-elimination. Efforts to convert the β-hydroxy vinylsilanes 37 into allenes by β-elimination under a variety of conditions are unsuccessful[63]. This is in great contrast to the ease of elimination associated with other β-functionalized (e.g. chloride or acetate) alkylsilanes.

Reactions of β-hydroxy epoxysilanes 38 with fluoride ions have also been studied[64].



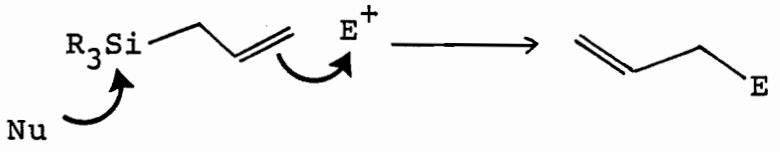
38

Likewise, no β-eliminations occur in these reactions. These reactions of epoxysilanes with fluoride ions and other related reactions will be discussed in more details in this thesis.

From the various vinylsilane reactions mentioned and with the development of different methods of stereoselective synthesis of trisulbstituted vinylsilanes, vinylsilanes have become more and more important synthetic intermediates. The fact that the trialkylsilyl group of the vinylsilanes can be replaced easily by a variety of electrophiles under mild conditions has made vinylsilanes even more versatile synthetic intermediates. To demonstrate this, the stereoselective conversion[65] of these trisubstituted vinylsilanes into substituted alkenes with different functionalities (e.g. halides, carbonyl groups) by electrophilic substitution reactions and the stereochemistry of the products are discussed in detail in this thesis.

(b) ALLYLSILANES

Like vinylsilanes, allylsilanes 39 are becoming very useful synthetic intermediates. Because of the highly nucleophilic double bond, the allylsilanes can react with a variety of electrophiles in the way shown.



39

The electrophile E will attack at the γ carbon, and the double bond will move to the α,β-position. The high reactivity of the trialkylallylsilanes towards electrophilic reagents can be explained by the strong inductive effect of the R_3SiCH_2-group.

Compared with carbon, silicon is more electropositive. Thus, it would be expected that a trialkylsilyl group R_3Si- would have a greater inductive effect than the comparable carbon group R_3C-. However, if the silicon atom is attached directly to an atom with lone pair electrons or an unsaturated group, the inductive effect will be opposed by the (p-d)π bonding. But in the case of trialkylallylsilanes, there is a methylene group in between the silicon and the functional group, so the strong inductive effect of the R_3Si group can be observed.

An example to show the electron donating effect of the trimethylsilylmethyl group has been done by Eaborn[66]. The rates of hydrogen exchange for a series of [1-^{3}H] acetylenic compounds $XC{\equiv}C\text{-}^3H$ is used to evaluate the substituent effect of the R_3SiCH_2-groups. These exchange rates are increased by electron withdrawing groups and retarded by electron donation. It is found that the trialkylsilylmethyl compounds $R_3SiCH_2C{\equiv}C\text{-}^3H$ react at about half the rate of their carbon analogs. This shows that the R_3SiCH_2-group donates electrons more effectively than the comparable carbon compound.

Another explanation of the high reactivity of the tri-

alkylallylsilanes is hyperconjugation as suggested by a Russian group[67]. They seem to favour the σ-π conjugation between the electrons of the silicon-carbon bond and the π electrons of the multiple bond β to it. However, there is no chemical evidence to support that this is the reason responsible for the high reactivity of the trialkylallylsilanes towards electrophiles. On the basis of chemical evidence available at the present time, the high reactivity of the trialkylallylsilanes towards electrophiles can be explained merely by the high inductive effect of the R_3SiCH_2- group.

Trialkylallylsilanes react very actively in electrophilic addition reactions. They are very active towards reagents such as bromine, thiocyanogen and hydrogen halides (chloride, bromide and iodide) etc. in electrophilic addition reactions.

In the case of bromination, β-elimination occurs after the addition[68]. Iodine reacts in the same way with alkyltrimethylsilane while chlorine adds to the double bond without cleavage[68].

$$R_3SiCH_2CH{=}CH_2 + Br_2 \longrightarrow R_3SiCH_2CHBrCH_2Br \longrightarrow R_3SiBr + CH_2{=}CHCH_2Br$$

On the other hand, the addition of thiocyanogen gives the

dithiocyano alkyl products which are stable and do not undergo β-elimination[67].

$$R_3SiCH_2CH{=}CH_2 + (SCN)_2 \longrightarrow R_3SiCH_2\underset{SCN}{CH}\text{-}\underset{SCN}{CH_2}$$

Even in the presence of peroxides, the addition of hydrogen bromide to trialkylallylsilanes occurs in a Markownikoff way. This again shows the high reactivity of the trialkylallylsilanes in ionic addition reactions because these reactions occur so rapidly that the free radical reactions just cannot compete with them.

$$Me_3SiCH_2CH{=}CH_2 + HBr \longrightarrow Me_3SiCH_2CHBrCH_3$$

This high reactivity, as mentioned previously, is attributed to the strong electron donating effect of the trimethylsilylmethyl group. The following reaction is used to demonstrate the magnitude of this effect. The addition of hydrogen bromide to a 1,1-dimethyl-substituted allylsilane takes place in an anti-Markownikoff way.

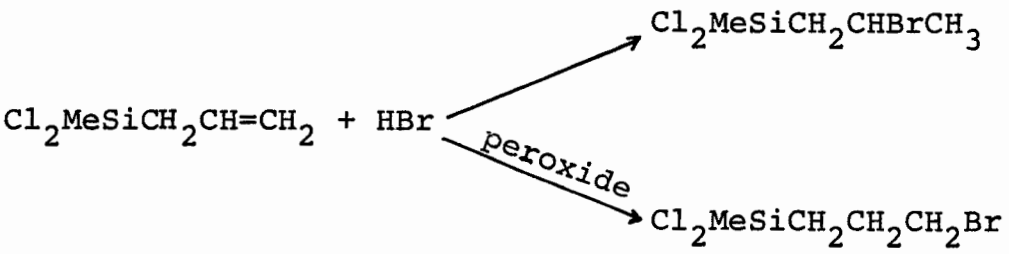
$$Me_3SiCH_2CH{=}CMe_2 + HBr \longrightarrow Me_3SiCH_2CHBrCHMe_2$$

First of all, it is unlikely that this is a radical reaction in a system where the double bond has such high

electron density. Thus, the orientation of the addition shows that the trimethylsilylmethyl group is more effective in stabilizing a carbonium ion.

Replacing the alkyl group on the silicon atom by electronegative chlorine substituents decreases the reactivity of the allylsilanes in ionic addition reactions. For example, the addition of bromine, chlorine or hydrogen bromide to allyltrichlorosilane proceeds slowly at room temperature whereas these reagents react rapidly with trialkylallylsilane even at -70°C[68].

Furthermore, it is found that addition of HBr to allylmethyldichlorosilane goes in the Markownikoff way in the absence of peroxides, but anti-Markownikoff in the presence of peroxide.



In the case of allyltrichlorosilane, HBr adds in an anti-Markownikoff way even in the absence of peroxide.

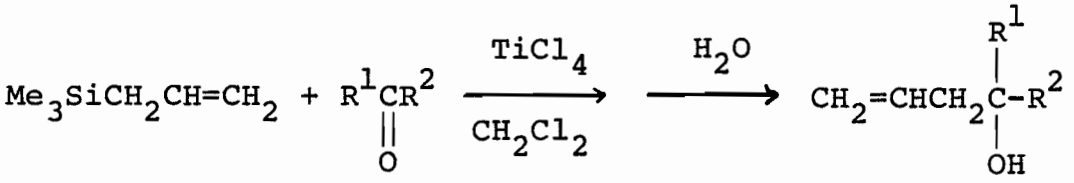
$$Cl_3SiCH_2CH{=}CH_2 + HBr \longrightarrow Cl_3SiCH_2CH_2CH_2Br$$

All these reactions indicate that on replacing the alkyl

groups on silicon by the electronegative chlorine substituents the ionic addition is suppressed and the radical addition takes over. This decrease in the reactivity in ionic addition can arise only from the decrease in the inductive effect of the R_3SiCH_2-group because of the replacement by chlorine.

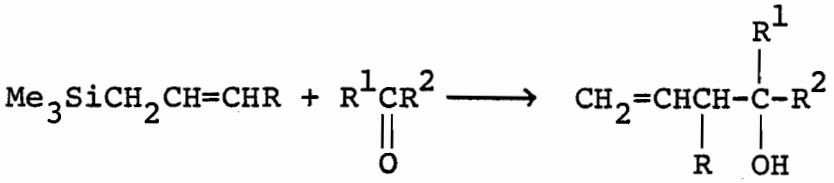
Trialkylallylsilanes do not react readily with nucleophiles in addition reactions. It is found that trialkylallylsilanes are quite inert towards phenyl- and butyllithium. Unlike the case of vinylsilanes, no addition products are formed with allylsilanes[27]. However, nucleophiles cleave allylsilanes more readily than vinylsilanes presumably because the cleavage of the silicon-carbon bond in the allylsilane system will be facilitated by the resonance stabilization of the carbanion[69].

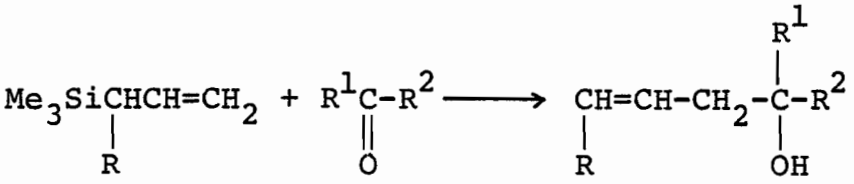
Recently, allyltrimethylsilane has been found to be a good reagent for allylation of carbonyl compounds or acyl halides in the presence of a Lewis acid, e.g. aluminum chloride or titanium tetrachloride. This allyl transfer reaction is found to be very general and smooth. It is found that a wide variety of aliphatic, alicyclic and aromatic carbonyl compounds when activated with titanium tetrachloride can react with the allylsilane, and the transposition of the allylic part is regiospecific[70]. γ,δ-Unsaturated alcohols 40 can be synthesized from the allylsilane and carbonyl compounds in the presence of titanium tetrachloride. This type of reaction



40

is not confined to allyltrimethylsilane. Other allylsilanes can be used in the reactions. However, the carbon-carbon bond formation occurs exclusively at the γ-carbon of the allylsilanes.

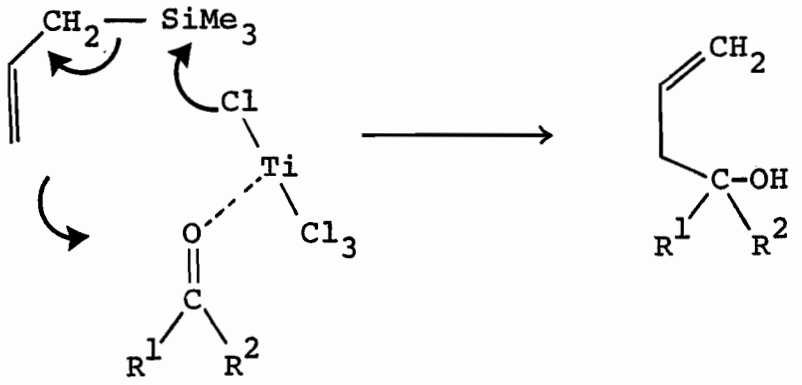




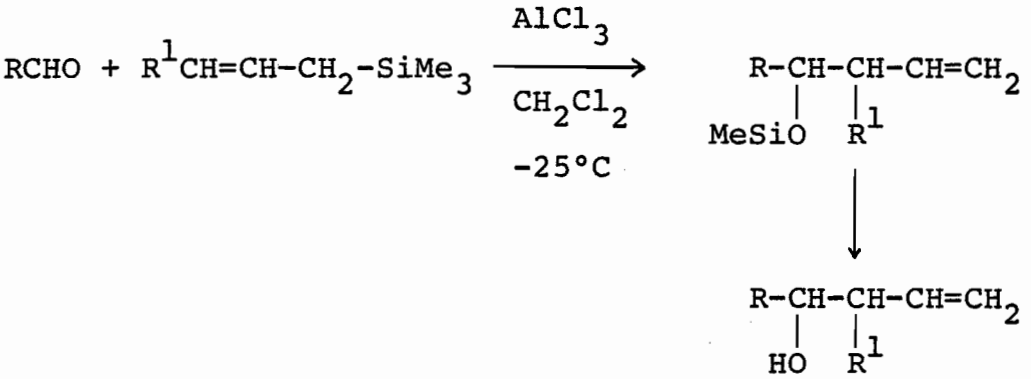
This regiospecific addition of the allylic group to a carbonyl function enhances the synthetic utility of this reaction. This allyl transfer reaction is a very rapid reaction. Prolonged reaction time leads to less satisfactory results due to polymerization. Also, other Lewis acids such as $AlCl_3$, $SnCl_4$, can be used as substitute for $TiCl_4$, but the yield is less satisfactory.

The authors propose a mechanism of cyclic process[71] involving a nucleophilic attack of the allylsilane on the

carbonyl carbon polarized[72] partially by the titanium tetrachloride, thus giving the regiospecificity observed.



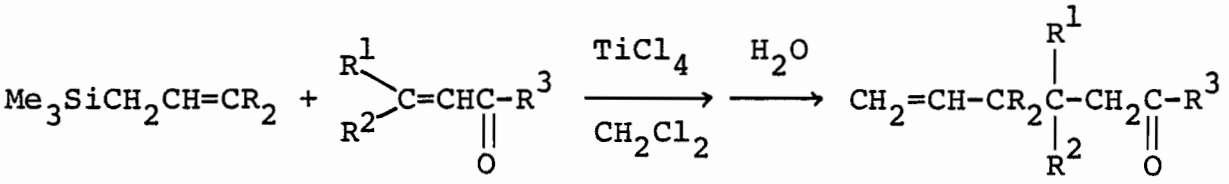
At about the same time, Calas[73] reported the same kind of allylsilane reactions with aldehydes in the presence of aluminum chloride.



Later Sakurai[74] made use of this method in the preparation of allyl-substituted hydroquinones. Allyltrimethylsilane is reacted with various substituted p-quinones at low temperatures in the presence of titanium tetrachloride, giving the alkyl-substituted hydroquinones. This method of allylation

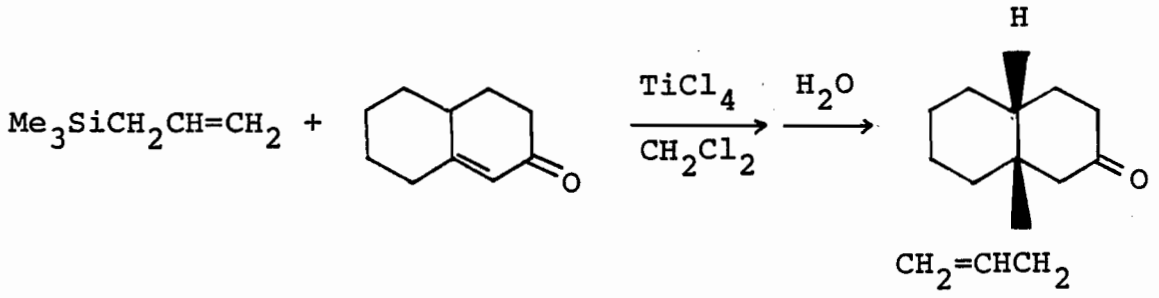
of quinones can be a simple but important reaction in the preparation of isoprenoid quinones which are of importance in biological processes.

This allylation reaction is not restricted to simple carbonyl compounds. Allylsilanes can react with α,β-unsaturated carbonyl compounds, e.g. α,β-enones 41, in the presence of titanium tetrachloride to give δ,ε-enones 42 via a Michael addition type of reaction[75].



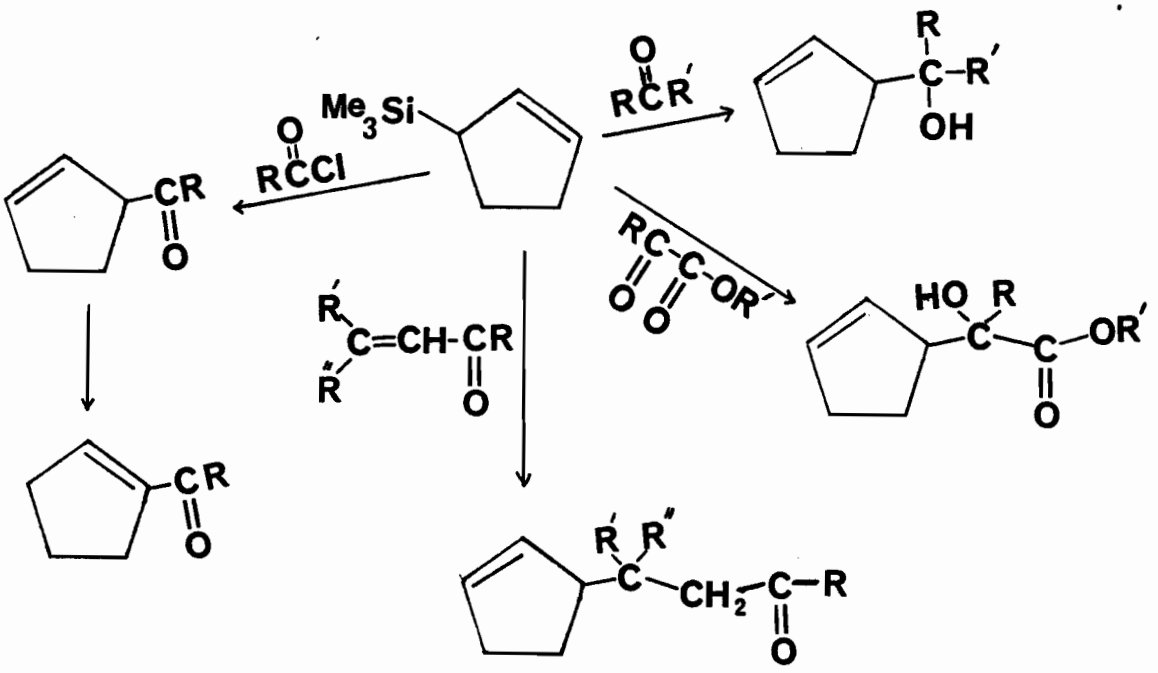
41 42

This reaction can be of important synthetic utility. For example, it can provide a stereoselective, direct introduction of the allyl group to a fused cyclic α,β-enone 43[75]. The introduction of functional substituents in fused cyclic compounds is generally an important step for synthesis.



43

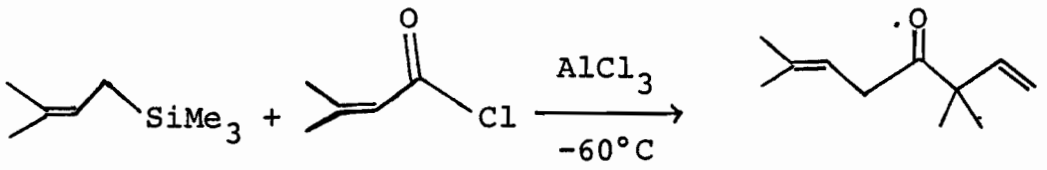
Cyclic allylsilanes can also react with various carbonyl compounds. For example, the cyclic allylsilane 3-trimethylsilyl cyclopent-1-ene is highly reactive at low temperature towards carbonyl compounds such as aldehydes, ketones, α,β-unsaturated ketones, α-keto esters and acyl halides in the presence of Lewis acid[76].



Using this method, the cyclic allylsilane 3-trimethylsilyl cyclopent-1-ene becomes a useful new reagent for the regiospecific introduction of cyclopentene in organic synthesis.

As mentioned before, allylsilanes can also react with

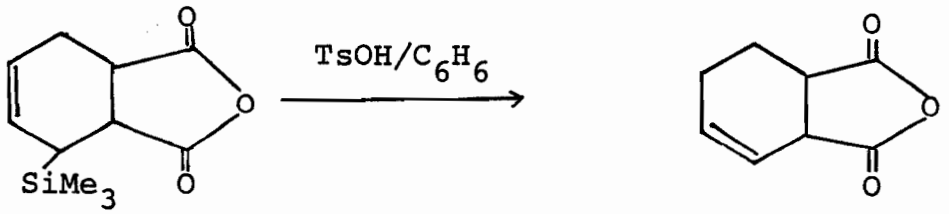
acid chlorides. One example is by Calas[77] in the synthesis of the naturally occurring Artemisia ketone 44 using a substituted allylsilane and an acid chloride in the presence of aluminum chloride.



44

This is an efficient method for the synthesis of ketone 44 compared with other previously reported syntheses[78].

Other than allyl transfer reactions, allylsilanes have also been used as intermediates in other organic syntheses[79]. For example, allylsilane 45, prepared from the Diels-Alder reaction[80] of maleic anhydride with 1-trimethylsilyl butadiene, can be protodesilylated to give the anhydride 46.

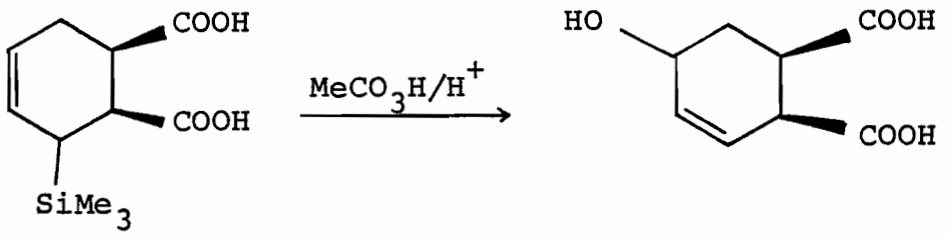


45 46

The main feature of this reaction is the ability to shift the double bond in this Diels-Alder adduct. This can be useful in the design of organic syntheses.

Dicarboxylic acid 47, derived from 45, can react with

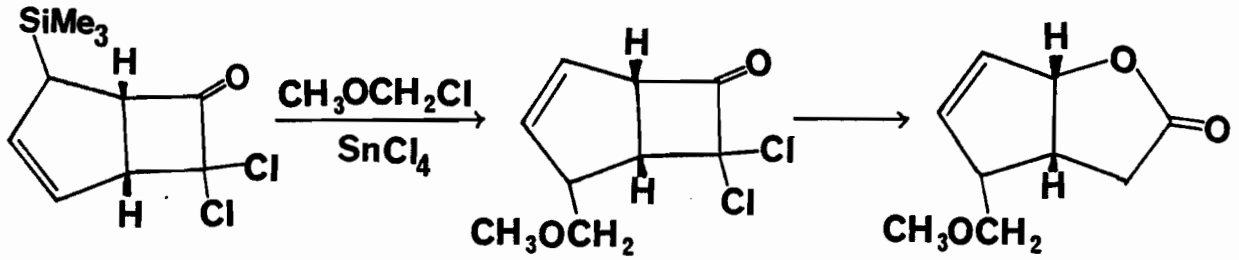
peracid, thus giving the allylic alcohol 48[79].



47 48

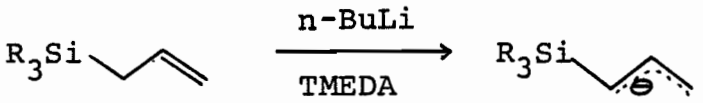
Allyl alcohols are versatile intermediates in organic synthesis, and they are very easily made from allylsilanes by this method. One advantage of using allylsilanes in this type of electrophilic substitution is that the [1,3]-allylic rearrangement is slow with allylsilanes at ordinary reaction temperature[81]. Thus, there is little risk that the allylsilanes may isomerize like other allyl metal compounds[82].

Allylsilane is also involved as intermediate in other syntheses of natural products[83,84]. In one case, allylsilane 49, obtained from reaction of dichloroketene and trimethylsilylcyclopentadiene[83], can react with methoxy methyl chloride in the presence of stannic chloride to give an intermediate 50, which can be converted into the lactone 51, which has been used as intermediate for prostaglandin synthesis[85].



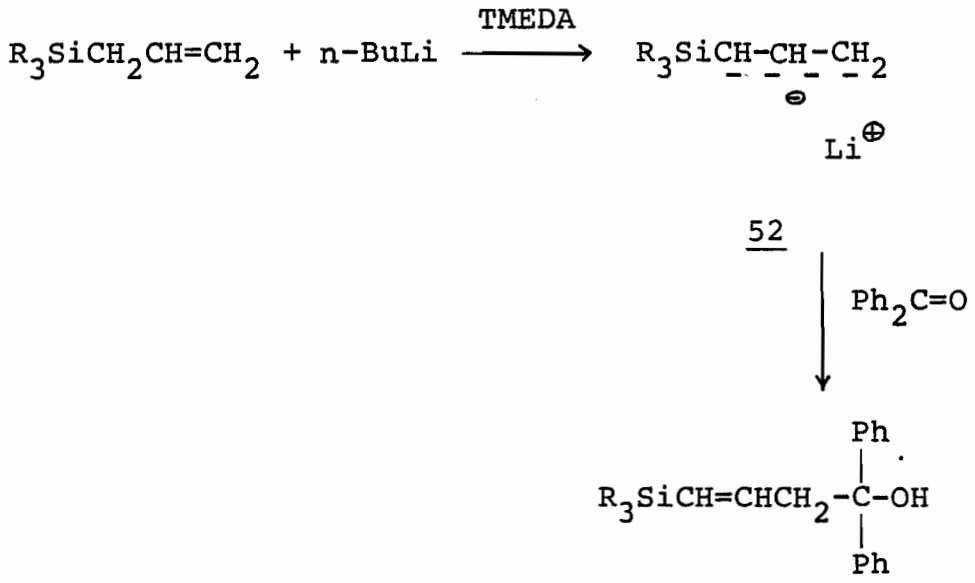
49 50 51

α-Silylallyl carbanions 52 can be obtained from reaction of butyllithium with allylsilanes in ether or tetrahydrofuran in the presence of tetramethylethylenediamine, and their reactions with various organic reagents have been studied[86,87].



52

It is found that 52 reacts with carbonyl compounds, e.g. benzophenone to give exclusively the γ-product 53[87].



53

The α-silylallyl carbanion also reacts with chlorotrimethylsilane to give the γ-addition product 54[87].

$$R_3SiCH\text{-}CH\text{-}CH_2 \xrightarrow{Me_3SiCl} R_3SiCH{=}CHCH_2SiMe_3$$

(⊖ on the carbanion)

53 54

Allylsilanes can react with N-bromosuccinimide (NBS) to give the bromo compound 55, which then can be transformed into the α-silylallyl magnesium bromide 56 by reaction with magnesium[87].

$$R_3SiCH_2CH{=}CH_2 + NBS \longrightarrow R_3SiCH{=}CHCH_2Br$$

55

↓ Mg

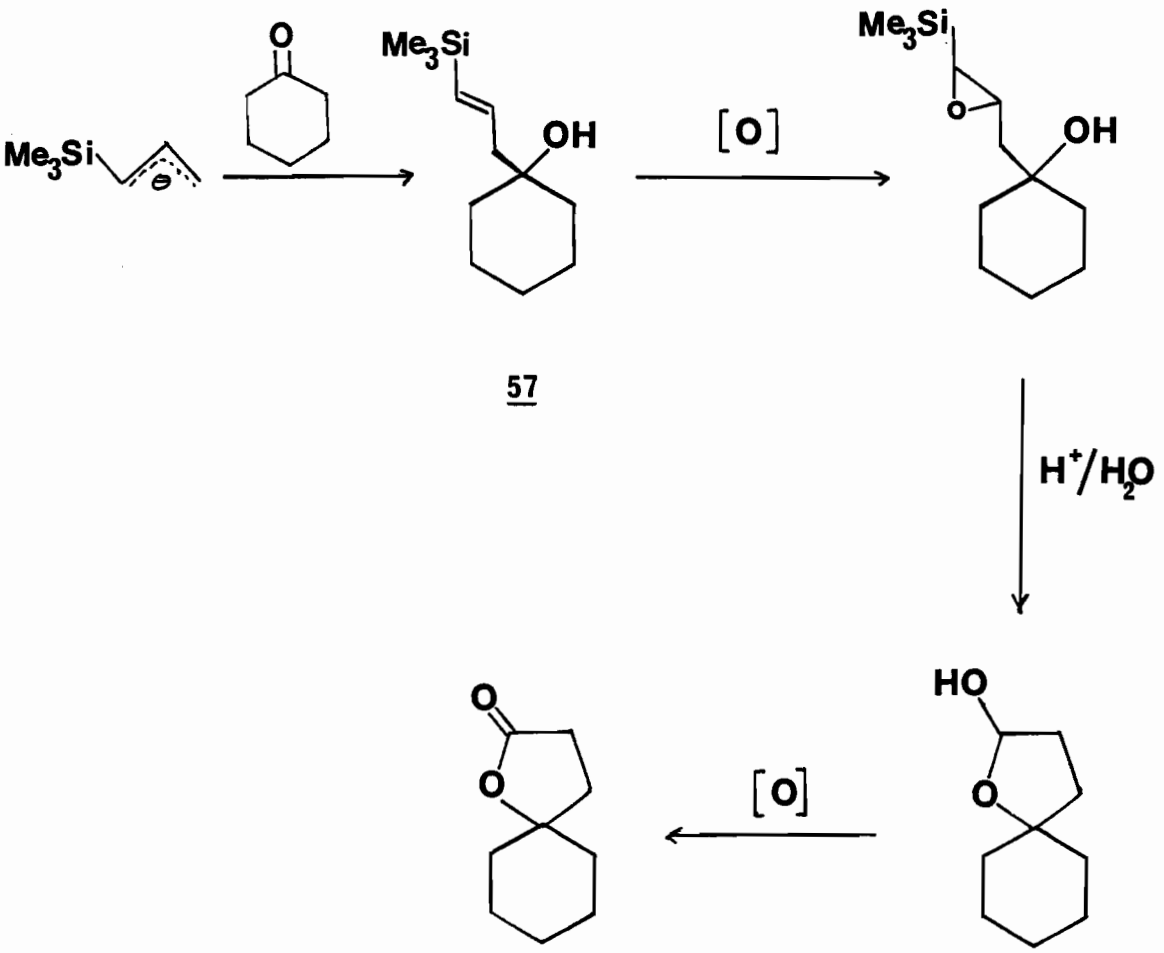
$$R_3SiCH{=}CHCH_2MgBr$$

56

Compound 56 reacts with carbonyl compounds or chlorotrimethylsilane to give the same kind of results as with the α-silylallyl carbanions. Thus, silicon containing allyl carbanions can be obtained from allylsilanes by two different procedures.

The reactions of α-silylallyl carbanions with various organic reagents are found to be very useful in the synthesis of various carbon functional organosilanes[86,87,88]. However,

this reaction is also useful in the synthesis of other organic compounds as demonstrated by Magnus[89]. Using this method of generating α-silylallyl carbanion, δ-hydroxy vinylsilanes 57 can be prepared. They, in turn, can be readily converted into γ-lactols 58 and γ-lactones 59.

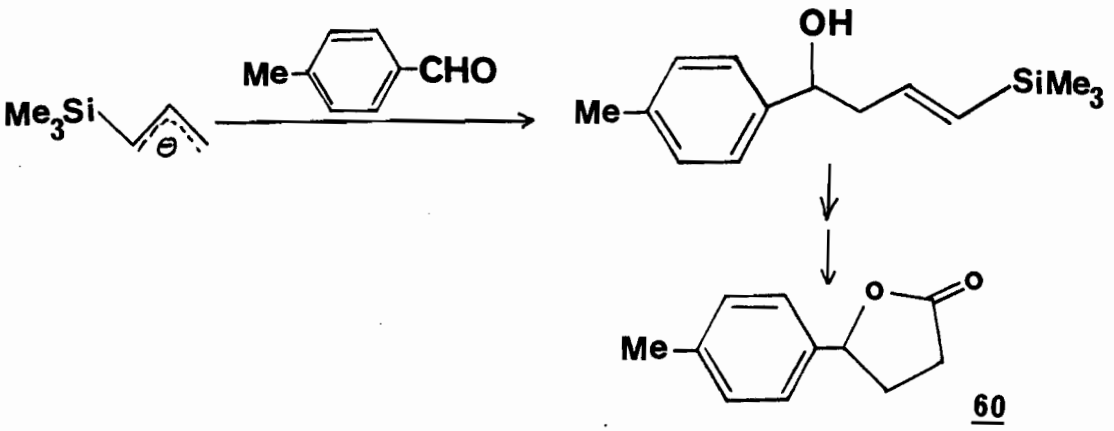


57

59

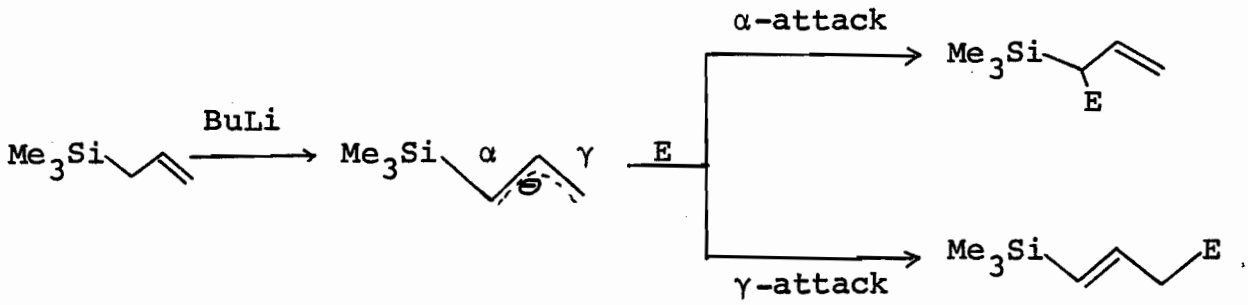
58

Similarly, α-silylallyl carbanion can react with p-tolualdehyde, and further reactions give the lactone 60.



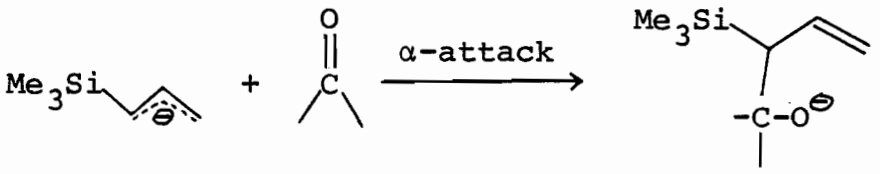
60

As demonstrated by the above examples, α-silylallyl carbanion 52 can react with various carbonyl compounds to give only the γ-addition products. However, both the α and γ-positions of 52 can participate in the electrophilic addition reaction.



Efforts are to be made so that the carbonyl compounds and other organic reagents can add to the α position of the α-silylallyl carbanions as well. This problem of regioselectivity will be discussed in the latter part of this thesis.

The α-addition products of the α-silylallyl carbanions with carbonyl compounds can be of synthetic interest. As can be seen, this α-addition product 61 has a functional group β to the trimethylsilyl group.

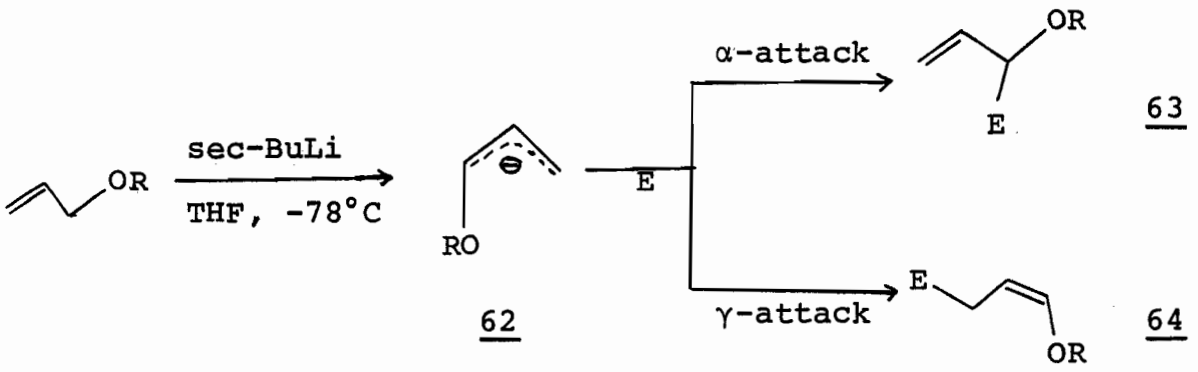


52 61

This has interesting synthetic potentials, as we have already demonstrated that β-functionalized organosilanes can undergo elimination to give alkenes.

The study of the reaction between α-silylallyl carbanions with carbonyl compounds and the control of the regioselectivity of this type of reactions has led us to look at another similar type of allyl carbanion, the allyloxysilyl carbanion, which is formed by metalation of the allyloxysilane.

It has been shown that simple allylic ethers can be metalated at low temperature to give allyloxy carbanions 62[90,91].



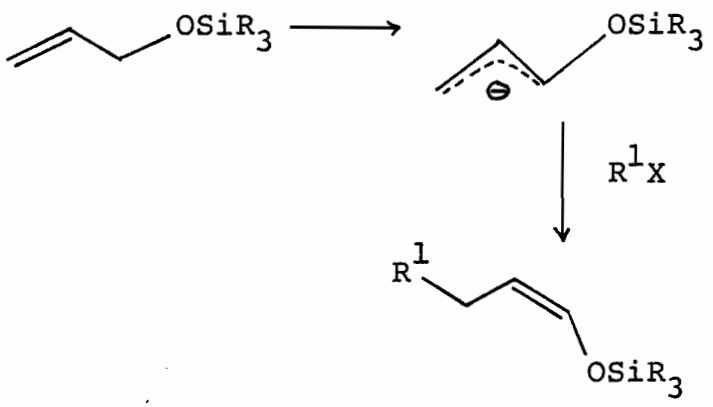
As in the previous case of α-silylallyl carbanions, these allyloxy carbanions can react with electrophiles in two positions, via α-substitution to give the allylic ethers 63 or via γ-substitution to give the enol ethers 64. It is found

that in alkylation reactions of allyloxy carbanions 62 with alkyl halides the product ratio of γ:α is determined by the oxygen ligand R rather than by other reaction conditions such as solvent or temperature. However, in most cases the γ-addition products predominate [90]. This is not the case in the reaction of 62 with carbonyl compounds, though. The α product seems to be more favoured. However, exceptions occur in some cases. For example, if R is ethyl or methyl, the reactions with cyclohexanone give the γ:α ratio of 70:30 and 72:28 respectively.

Also, the ratio of the γ:α product is highly counter ion dependent[90]. It has been found that the allyl zinc reagent, prepared by adding one equivalent of zinc chloride to 62, reacts with carbonyl compounds giving exclusively the α product. For example, when R is methyl or ethyl, reactions with cyclohexanone in the presence of zinc chloride give exclusively the α product in both cases. Thus, with simple allylic ethers, the allyloxy carbanions formed react regioselectively in the γ position in alkylation reactions, but no selectivity is seen in reactions with carbonyl compounds. However, the addition of zinc chloride causes regioselective addition, giving exclusively the α product[90].

In the cases where R is a trialkylsilyl group, i.e. in allyloxysilanes, the allyloxysilyl carbanions react with alkyl halides the way the simple allyloxy carbanions do. The γ products predominate, i.e. the terminally alkylated enol

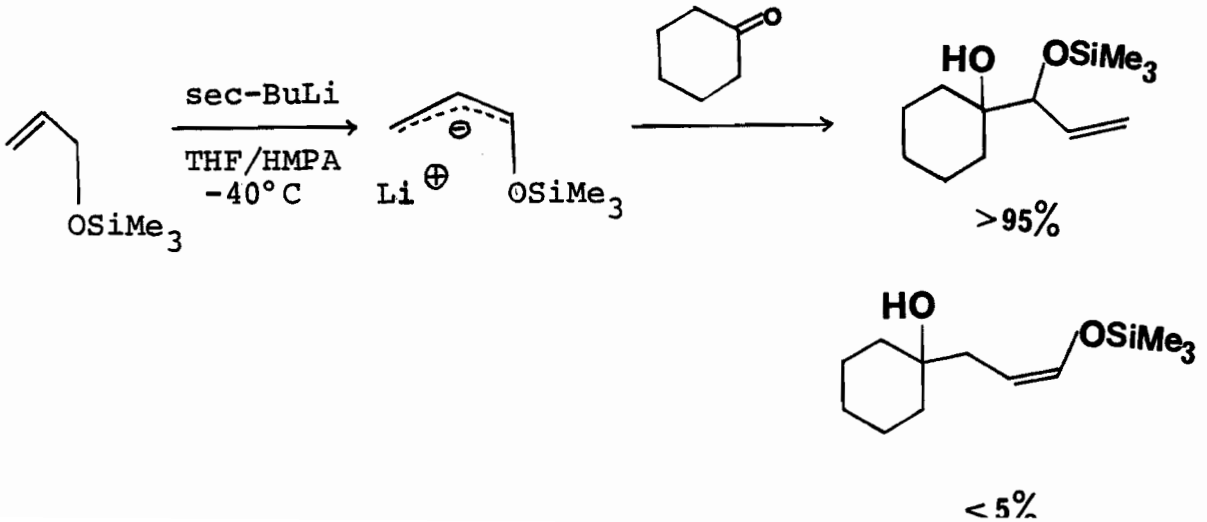
ether 65 is the product[91].



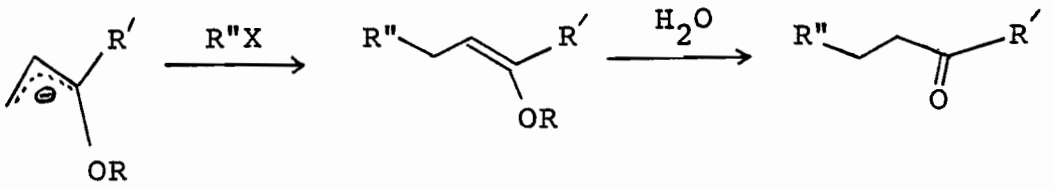
65

Attempts have been made to increase the proportion of the terminally alkylated enol ether 65 by varying the silyl group substituent. In one case, the anion of triethylallyloxysilane is terminally alkylated (γ addition) by methyl iodide in more than 92% yield[91].

In the reactions with carbonyl compounds however, the trimethylsilylallyloxy carbanion in THF-HMPA reacts regioselectively to give the α addition product[92].

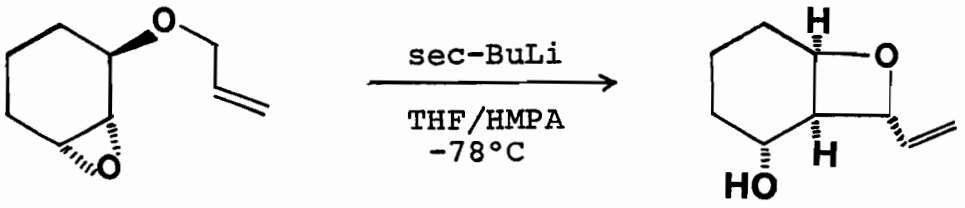


Since allylic ether deprotonation is extremely fast to give the stable allyloxy carbanions, these allyloxy carbanions can be useful in organic synthesis. For example, carbanion 66 can react with alkyl halides to give the γ addition enol ether 67 which can lead to the β-alkylated aldehyde or ketone 68[91].



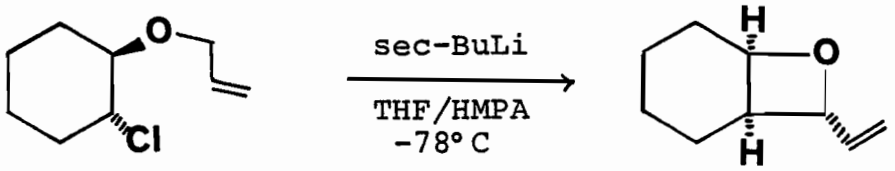
66 67 68

Another example of synthetic utility is the allyloxy carbanion cyclization[93] leading to the vinyl oxetane 69.



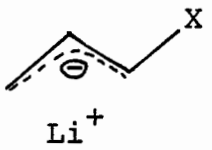
69

The allyloxy carbanion cyclizations are not limited to epoxides. Chloro allylic ether also cyclizes to give the vinyl oxetane 70.



70

In general it is found that allyllithium compounds 71 terminally substituted by anion-destabilizing groups



71

(where X=OR[90-92] or NR_2[94]) react with alkyl halides at the γ position and with carbonyl compounds at the α position, while allyllithium compounds with anion-stabilizing group such as -SR[95] behave in the opposite way, i.e. the alkyl halides add α and carbonyl compounds add γ.

However, this rule holds only for the compounds in which the allyl anion and the lithium cation are associated. The situation may well be changed if the reaction conditions are changed. Addition of co-solvents[96] may produce free allylic anions. Free allylic anions may behave differently. Also if the association between the allylic anion and the counter ion is weak, e.g. the allylic anion has a strong anion-stabil-

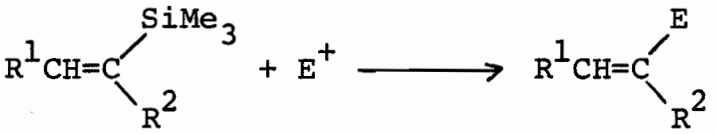
izing group attached, the electron density at the α position will be higher, and the proportion of carbonyl attack at the α position will be increased[97].

CHAPTER 2

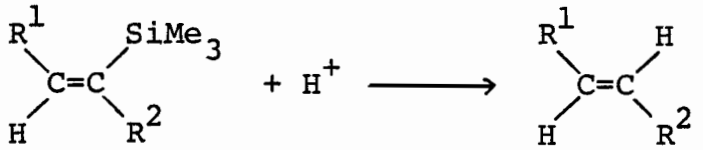
ELECTROPHILIC SUBSTITUTION REACTIONS OF TRISUBSTITUTED VINYLSILANES

(a) GENERAL CONSIDERATIONS

With the development of the stereoselective synthesis of trisubstituted vinylsilanes[38,43,44], vinylsilanes have become more important as synthetic intermediates. Examples given in the previous chapter have already demonstrated this fact. However, one other type of interesting reaction in terms of synthetic utility is the electrophilic substitution reactions of vinylsilanes. This is based on the fact that the silyl group can be replaced with ease by a variety of electrophiles[47,48], giving substituted alkenes of defined stereochemistry[65,99].



Indeed, this electrophilic substitution reaction has been used in the traditional method of differentiation of geometric isomers of trisubstituted vinylsilanes. The usual way is to convert the isomeric vinylsilanes by protodesilylation[38,53] to the disubstituted alkenes. For example,



The assignment of stereochemistry is based on:

i) the difference in the coupling constants of the vinyl protons and also the 900 cm^{-1} region of the IR spectra of the geometric isomers of the alkene products.

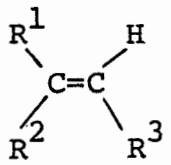
ii) the substitution of the silyl group by proton proceeds with retention of configuration[53].

Another method of differentiating the geometric isomers of trisubstituted vinylsilanes is a physical method based on the difference of the ^{1}H and ^{13}C NMR spectra as well as the GLC retention times of pairs of geometric isomers of the vinylsilanes[100].

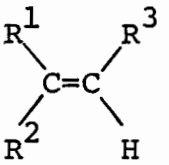
With the stereochemistry of the geometric isomers of the trisubstituted vinylsilanes determined, electrophilic substitution reactions are carried out to convert these vinylsilanes into trisubstituted alkenes with different functionalities, and the stereochemistry of these trisubstituted alkenes is determined by chemical methods and also by the chemical shifts of the vinyl protons of the substituted alkene isomers. The chemical shifts of vinyl protons in substituted alkenes can be predicted reasonably well by using the following empirical formula[101]:

$$\delta_{C=C\diagdown H} = 5.25 + \Sigma Z$$

where the Z-factors are the substituent shielding coefficients.



72E



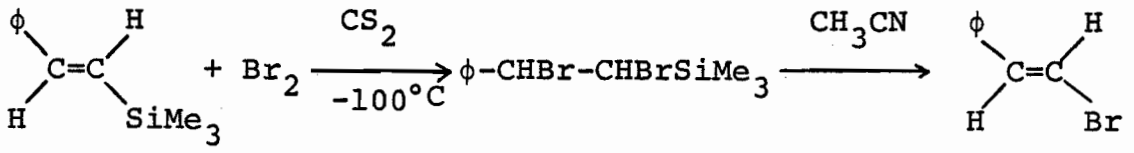
72Z

For the isomers 72E and 72Z, depending on the positions of the substituents R^1, R^2 and R^3 with respect to the vinyl proton (the R groups can be in cis, trans or gem position), each substituent will have a different shielding effect on the vinyl proton. Thus each will have a different shielding coefficient Z. It is found that in all cases, the vinyl protons of the E isomers of the trisubstituted alkenes should appear at lower field than their corresponding Z isomer alkenes. Using this prediction, the stereochemistry of the geometric isomers of the trisubstituted alkenes from the electrophilic substitution reactions is assigned. To further prove that the assignment of the stereochemistry is correct, other chemical methods are used to transform these alkenes to other compounds whose stereochemistries are known.

(b) BROMODESILYLATION

The reactions of bromine with disubstituted vinylsilanes have been reported. Weber[102] has reported that trans-β-trimethylsilylstyrene 73 reacts with bromine in CS_2 at -100°C to give a dibromo adduct. This dibromo adduct is stable for

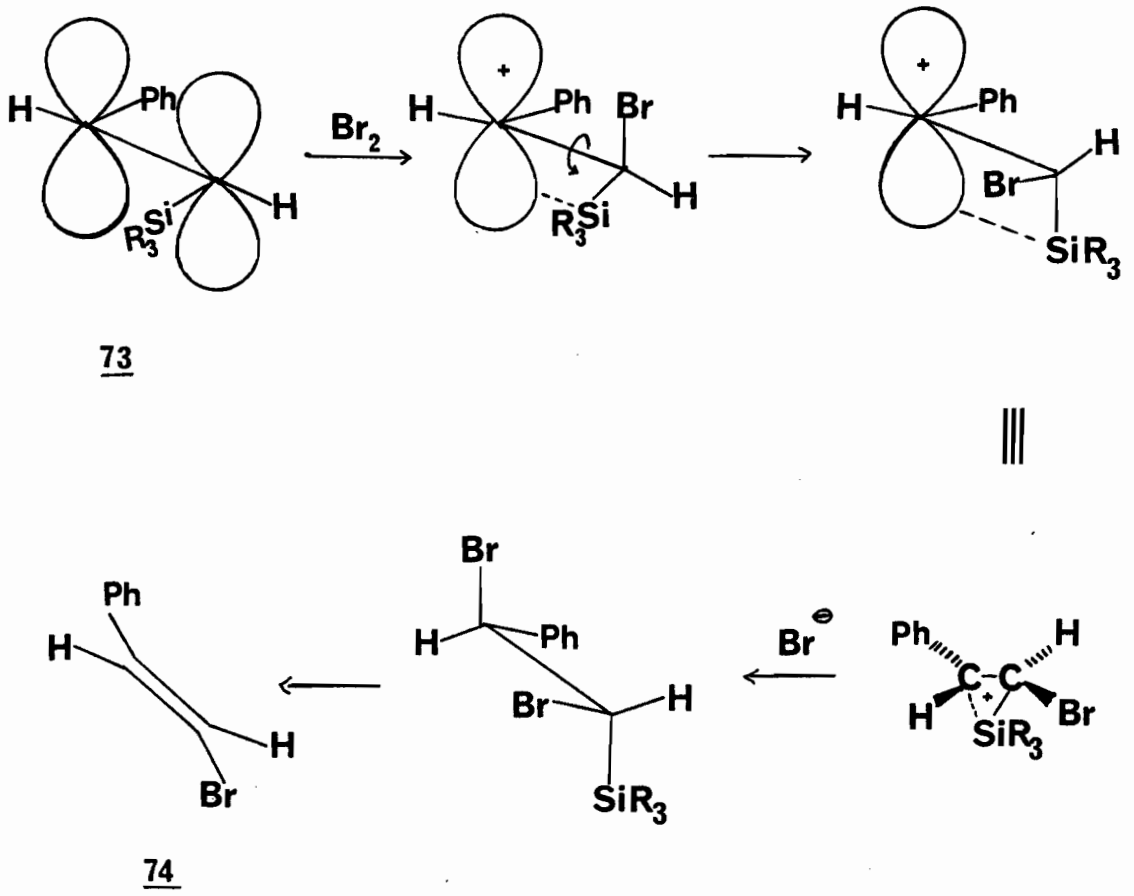
several hours even when warmed up to room temperature. However, addition of acetonitrile to the dibromo adduct causes an elimination reaction to occur, and the products are trimethylbromosilane and trans-β-bromostyrene 74[103].



73 74

To explain the retention of configuration, the following mechanism is proposed. As the bromine attacks on the double bond, the developing carbon-carbon single bond rotates in such a direction to permit the trimethylsilyl group to continuously stabilize the forming benzylic carbonium ion by hyperconjugation[104a] or by bridging[104b]. Rotation in the opposite direction will not permit stabilization of the carbonium ion by the silyl group, because the trimethylsilyl group will be in the nodal plane of the developing carbonium ion centre. It is well known that a trimethylsilyl group is able to stabilize a carbonium ion β to it[105].

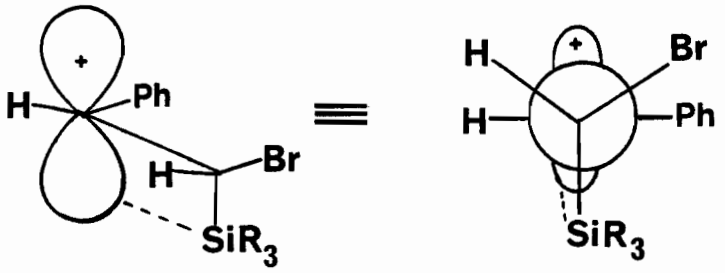
The attack of the nucleophilic bromide anion can only occur from the top side because the bridging of the trimethylsilyl group blocks the attack from the bottom side. Thus, a



cis-addition of the bromine occurs to give the dibromide adduct. A trans-elimination[106] of trimethylbromosilane will give the product 74.

Cis-β-trimethylsilylstyrene also reacts with bromine at -100°C in CS_2 to give a dibromo adduct which is stable. Addition of acetonitrile to the adduct results in an elimination reaction to give trimethylbromosilane and mostly cis-β-bromostyrene contaminated by a little trans-β-bromostyrene. The presence of the trans-β-bromostyrene can be explained in two ways. First, cis-β-bromostyrene can

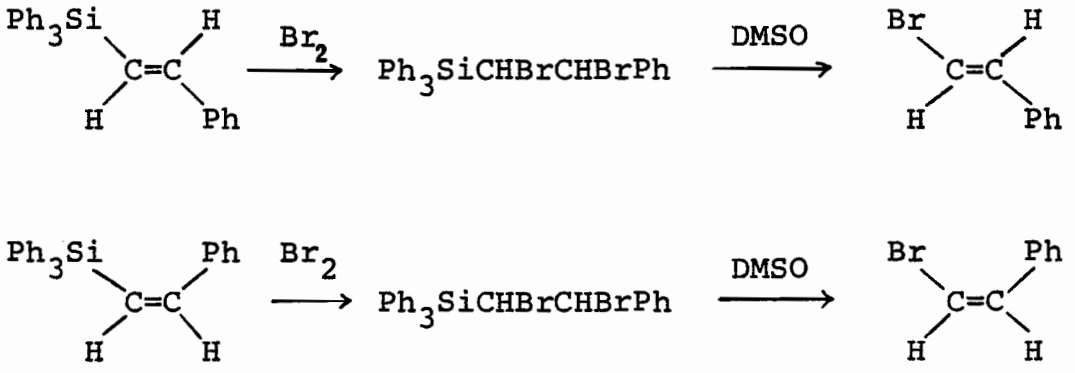
isomerize to the thermodynamically more stable trans isomer very easily. Secondly, in the formation of the dibromo adduct, the participation of the trimethylsilyl group leads to an ion which can have gauche interaction between the bromine and the phenyl group.



This gauche interaction can destabilize the silyl bridged benzylic carbonium ion. An open benzylic carbonium ion may result to give to the small amount of trans-β-bromostyrene observed.

Brook[99] has also studied the bromination of vinylsilanes and the debromosilylation of their dibromides using the trans- and cis-triphenylsilylstyrenes. It is found that the bromination of trans-triphenylsilylstyrene in dichloromethane at -78°C gives a single stable dibromide characterized by the NMR spectrum of the cold reaction mixture. Under the same conditions, a different single isomer is characterized and isolated from the bromination of the cis-triphenylsilylstyrene. Treatment of the dibromide from the trans isomer with dimethyl sulfoxide at 25°C gives the pure trans-β-bromostyrene. In contrast, the dibromide from the cis-silylstyrene

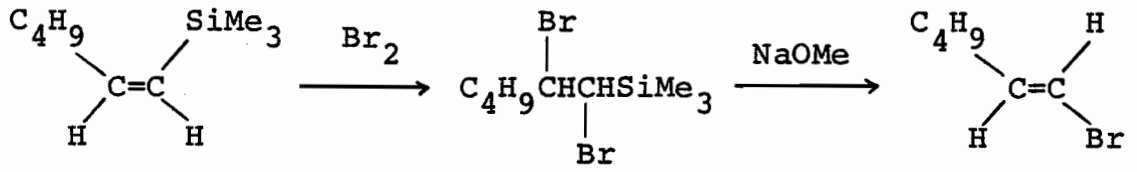
eliminates in dimethyl sulfoxide at 25° C to give the pure cis-β-bromostyrene.



The retention of configuration is the same as that obtained by Weber using the trimethylsilyl styrenes. The crystal structure of the dibromide formed by the bromination of trans-triphenylsilylstyrene is determined by X-ray diffraction technique. It is found that the dibromide is of the threo configuration, arising from the cis-addition of bromine to the double bond. Based on this finding and the stereochemistry of the final vinylbromide, the dibromosilylation reaction has to occur in a trans fashion. This argument is, of course, in complete agreement with the proposals of Weber[102].

In the case of alkenylsilanes, the results are completely different. Miller[47] has found that the bromination of cis-vinylsilane gives a trans-vinyl bromide. Bromination of cis-1-trimethylsilyl-1-hexene 75 with one equivalent of bromine at -23°C gives a dibromide in 98% yield. The dibromosilylation is carried out by reaction with methanolic sodium

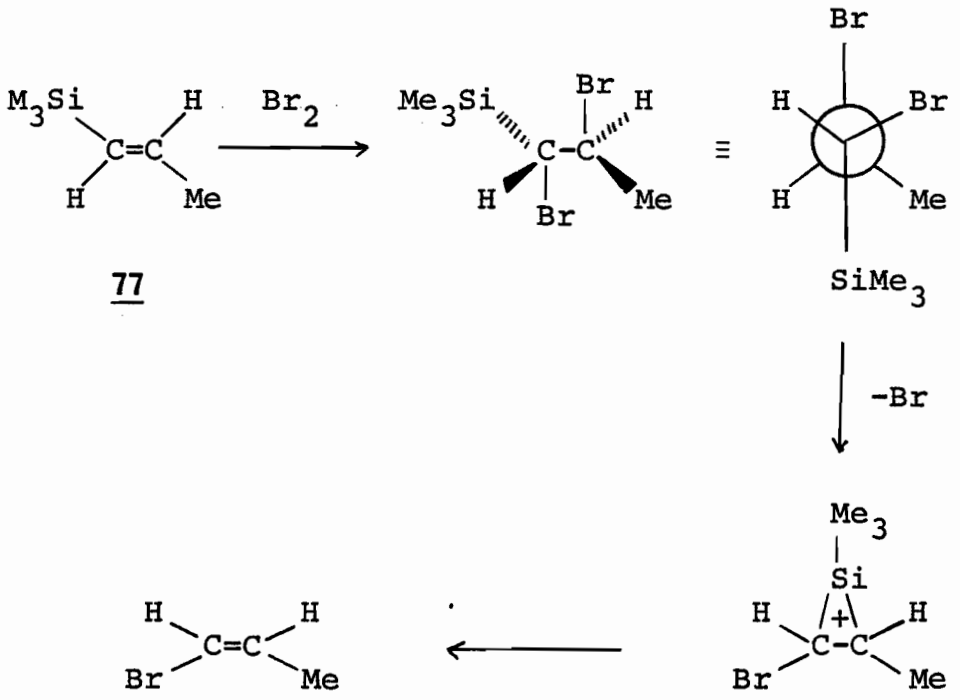
methoxide at room temperature. The stereochemistry of the product, trans-1-bromo-1-hexene 76 is assigned by comparison with authentic samples of the cis- and trans-vinyl bromides.



75 76

This inversion of configuration of the vinylbromide is in agreement with the report by Jarvie[106] on the bromination reaction with trans-propenyl-trimethylsilane 77 giving the cis-1-bromopropene 78 as product. Bromination of trans-propenyl-trimethylsilane gives the erythro-1,2-dibromo-propyltrimethylsilane. The addition of bromine to the olefin is accepted to proceed in a trans-manner through a bromonium ion, thus giving only one isomer of the dibromide. The bromo-desilylation proceeds in an E1 fashion similar to that proposed by Cram[107] to explain trans stereospecificity in E1 reactions. It is suggested that the initial step in the reaction is the cleavage of the carbon-halogen bond assisted by the participation of the silicon with the developing positive charge on the carbon atom, and trans-elimination follows to give the cis-1-bromopropene 78.

Thus in the case of disubstituted vinylsilanes, the bromination reactions appear to be mainly retention of

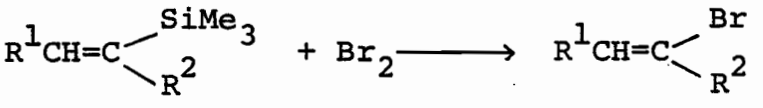


77

78

configuration[99,102] in the case of β-silylstyrenes and mainly inversion of configuration in the case of alkenylsilanes[47,106].

The reactions of bromine with the trisubstituted vinylsilanes have been studied. The geometric isomers of these trisubstituted vinylsilanes are prepared according to the stereoselective synthesis of trisubstituted vinylsilanes proposed by Chan[38] (Table 1).



79 80

a) $R^1 = C\text{-}C_6H_{11}$; $R^2 = C_2H_5$

b) R^1 = i-Pr; $R^2 = n\text{-}C_5H_{11}$

c) $R^1 = n\text{-}C_{10}H_{21}$; $R^1 = n\text{-}C_5H_{11}$

TABLE 1: SYNTHESIS OF TRISUBSTITUTED VINYLSILANES[38] 79

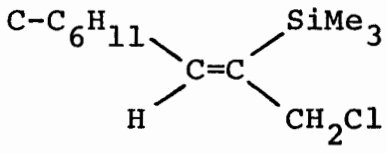
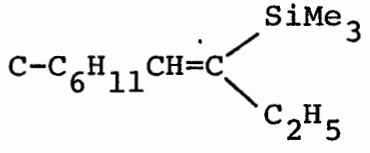
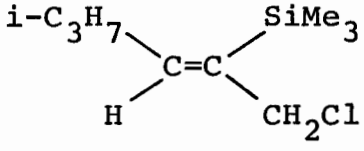
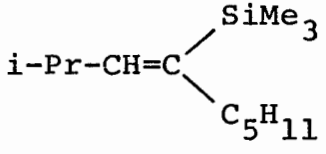
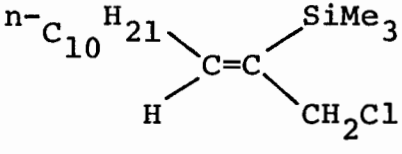
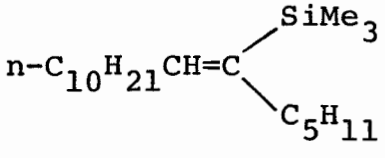
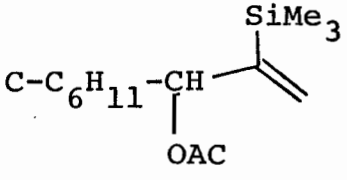
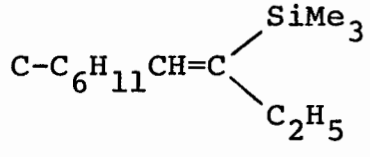
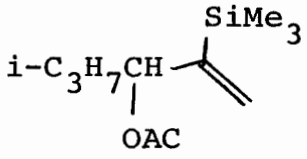
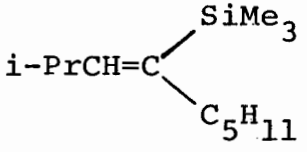
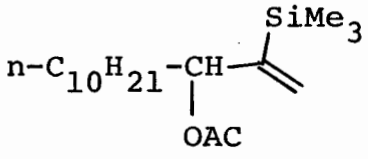
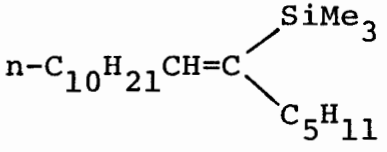
Precursor	Reagent	Temp.°C	Product[a]	Yield[b](E:Z)
	$(CH_3)_2CuLi$	r.t.		80 (15:85)
	$(n\text{-}C_4H_9)_2CuLi$	r.t.		80 (10:90)
	$(n\text{-}C_4H_9)_2CuLi$	r.t.		80 (11:89)
	$(CH_3)_2CuLi$	-78°C		78 (94:6)

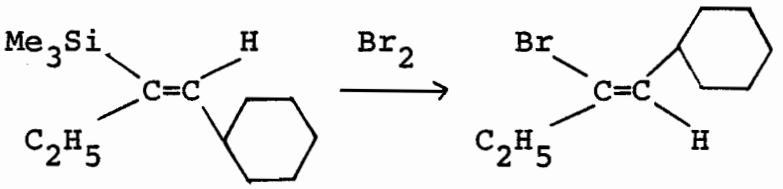
TABLE 1: continued

Precursor	Reagent	Temp.°C	Product[a]	Yield[b] (E:Z)
	$(n\text{-}C_4H_9)_2CuLi$	-78°C		79 (92:8)
	$(n\text{-}C_4H_9)_2CuMgBr$	-78°C		80 (86:14)

a) Purified by column chromatography or by distillation

b) Isolated yield

The E isomers of vinylsilanes 79 react rapidly with bromine in methylene chloride at -78° C. The reaction mixture is worked up and the product is purified by thin layer chromatography on silica gel with hexane as eluent to give clearly the Z isomers of 80. The isolated yield is in the range of 65-87%. The typical physical data are: IR = 1655 cm^{-1}; NMR: δ = 5.4 (d); and m/e at 216, 218 for the vinyl bromide Z-80a.

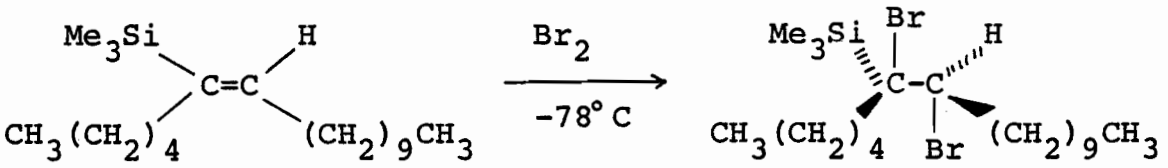


E-79a Z-80a

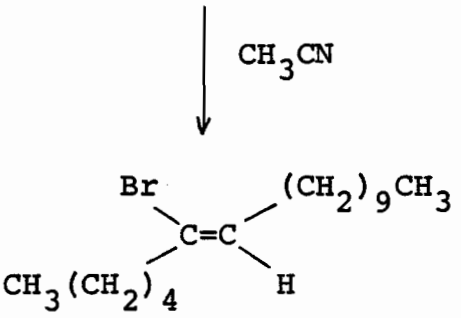
The inversion of stereochemistry observed is presumably due to anti-addition of bromine across the double bond to give the dibromide adduct followed by anti-elimination of bromosilane as suggested by Jarvie[106]. In both the cases of E-79a and E-79b, the bromination reactions proceed rapidly giving cleanly the Z isomers of 80a and 80b. However, the intermediate dibromide is detected in the case of E-79c where R^1 and R^2 are long chain alkyl groups.

E-79c reacts rapidly with bromine in methylene chloride at -78°C. On work up, a light yellowish liquid is obtained. ^1H NMR of this crude material shows the trimethylsilyl group is still present. The vinyl proton signal of the starting

material has disappeared, while a new signal at $\delta = 4.3$ is found. This can be the signal of the $-\underset{\underset{Br}{|}}{\overset{|}{C}}-\underline{H}$ proton after the addition of bromine to the double bond. Furthermore, from the IR spectrum the signal at 1610 cm^{-1} has disappeared. This indicates the double bond is no longer present.



E-79c



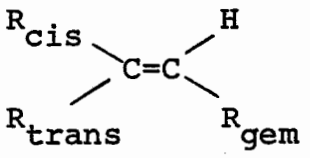
Z-80c

However, after the crude material is stirred with dry acetonitrile for 5 hours at room temperature the NMR spectrum shows that the signal for the trimethylsilyl group has disappeared as well as the signal at $\delta = 4.3$. A new signal appears at $\delta = 5.6$ indicating the presence of, once again, a vinyl proton. The IR spectrum also shows a peak at 1650 cm^{-1} indicating the presence of the carbon-carbon double bond. The product Z-80c is isolated by preparative thin layer chromatography using hexane as eluent. Z-80c is characterized by

δ = 5.6 in NMR and 1650 cm^{-1} in IR spectra. The mass spectrum has m/e at 316 and 318, almost equivalent in abundance. This shows the presence of the molecular ion (316) and its isotope (M+2). The isotopic abundance of these two fragments indicates the presence of bromine in the molecule. All these data indicate the presence of a vinyl bromide as product.

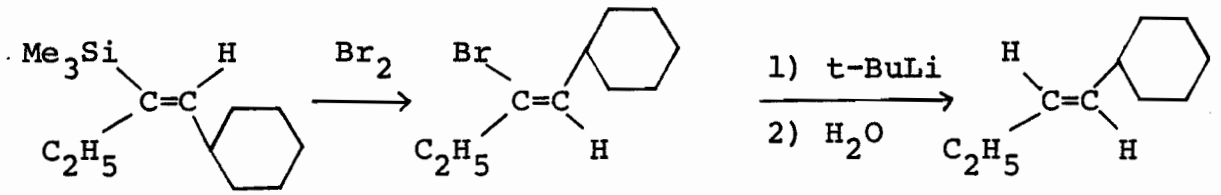
The assignment of Z configuration for the vinyl bromide is based on the chemical shift of the vinyl proton. Using the empirical formula[101], the Z vinyl bromide should have the vinyl proton at higher field than the corresponding E vinyl bromide.

$$\delta_{C=C\diagdown H} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$



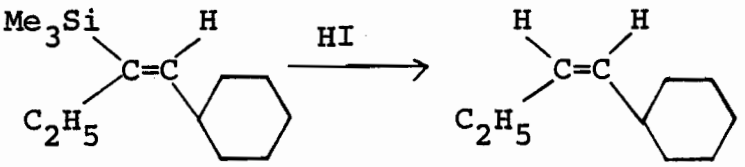
Further proof of the configuration is demonstrated by converting the supposed Z vinyl bromide into olefin by lithiation reaction which is known to proceed with retention of configuration[108], then comparing this olefin with olefins prepared from protodesilylation of vinylsilanes of known geometries. Protodesilylation, of course, proceeds with retention of configuration[38,53].

Take the bromination of vinylsilane E-79a as an example. E-79a reacts with bromine rapidly to give, presumably Z-80a on work up. Reaction of the vinyl bromide Z-80a with t-butyllithium at -78°C for 1½ hour followed by quenching with water gives the olefin 81.

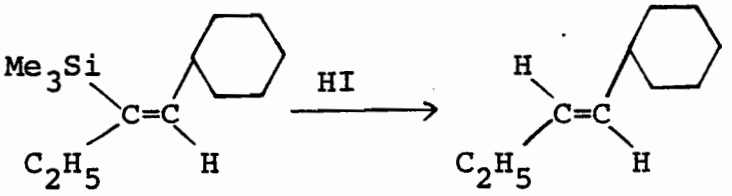


E-79a Z-80a 81

Protodesilylation is carried out on the E and Z isomers of 79a. 57% Hydriodic acid is added separately in two reactions to E-79a and Z-79a in methylene chloride at room temperature. After stirring for 30 minutes and work up, two olefins 82 and 83 are obtained respectively from the two reactions.



E-79a 82



Z-79a 83

Comparing 82 and 83 with 81, it is found that 81 and 83 are identical in IR and NMR. Both 81 and 83 have the vinyl protons at $\delta = 5.3$ in NMR and a signal at 970 cm^{-1} in IR spectrum, while 82 has $\delta = 5.2$ and no 970 cm^{-1} in IR.

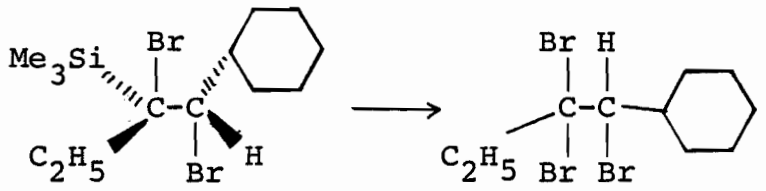
Since the protodesilylation of Z-79a proceeds with retention of configuration, and the geometry of Z-79a is known, compound 83 obtained has E-configuration. This indicates that compound 81 also has E-configuration. Also, since lithiation reaction goes with retention of configuration, in order to obtain compound 81 as the E isomer the starting vinyl bromide must have the Z-configuration as in Z-80a. This proves, chemically, that bromination of E-79a giving Z-80a as the product vinyl bromide goes with inversion of configuration.

Reactions of the Z-isomers of the vinylsilanes 79 with bromine are not as smooth as those of the E isomers. Bromination of the Z-isomers at -78° C gives a complicated mixture of products, among which are the dibromide adducts. Taking the vinylsilane Z-79a as an example, Z-79a reacts rapidly with bromine at -78° C. On work up, the NMR of the crude material obtained shows no vinyl proton signal. However, the trimethylsilyl signal is still present, and two new doublets are seen at δ = 4.1 and 4.3. Gas chromatography shows two major peaks. Preparative thin layer chromatography of the crude material using hexane as eluent gives two major fractions. The first fraction isolated has the NMR signal at δ = 5.6, indicating the presence of vinyl proton. This signal is not present in the crude material before TLC. No trimethylsilyl signal is seen in this fraction. The other NMR data bear similarities in pattern to those of the vinyl bromide Z-80a obtained from the bromination of the E-vinylsilane E-79a.

IR shows 1640 cm^{-1}, indicating carbon-carbon double bond. Mass spectrum of this fraction has m/e at 216 and 218 in almost equivalent abundance. This gives the molecular ion (216) of the vinyl bromide. Isotopic abundance of m/e 216 and 218 indicates the presence of bromine in the molecule. This vinyl bromide obtained is different from Z-80a because the chemical shift of the vinyl proton is at lower field of $\delta = 5.6$. Thus, this vinyl bromide obtained is the E isomer vinyl bromide E-80a. From the empirical formula, it is predicted that the chemical shift of the E vinyl bromides should appear at lower field than the corresponding Z isomers.

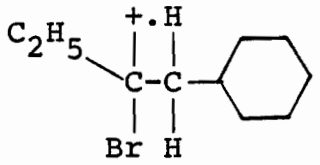
It is believed that this E vinyl bromide is derived from the decomposition of the dibromide adduct on the silica gel during TLC development, because no vinyl proton signal is observed before plating. Also the trimethylsilyl signal and the signal at $\delta = 4.3$ have disappeared after plating. Neither of these signals is observed in the second major fraction obtained by TLC.

NMR of the second fraction has signals for the cyclohexyl protons and the ethyl protons. However, the signal at $\delta = 4.1$, a doublet, is also present. This signal is the same as that on the crude material before TLC. The ratio of protons of this signal to the other proton signals is 1:16. This side product appears to be the tri-bromide 84 formed by the addition of bromine to the double bond followed by further replacement of the silyl group with bromine.



84

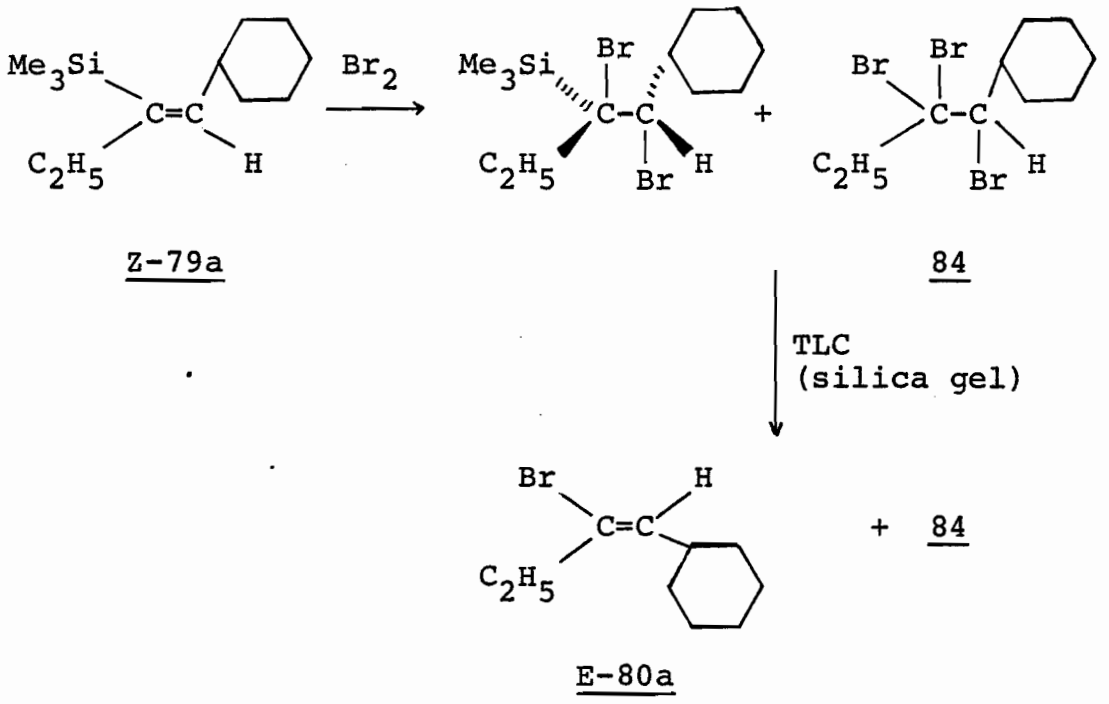
Mass spectrum of this fraction has m/e at 217 and 219. They are almost equivalent in abundance. This indicates the presence of one bromine in the fragment $(217)^{+\cdot}$. Fragment $(217)^{+\cdot}$ can be obtained if 84 loses two bromine atoms and gains a proton (374-158+1=217), giving this fragment 85.



85

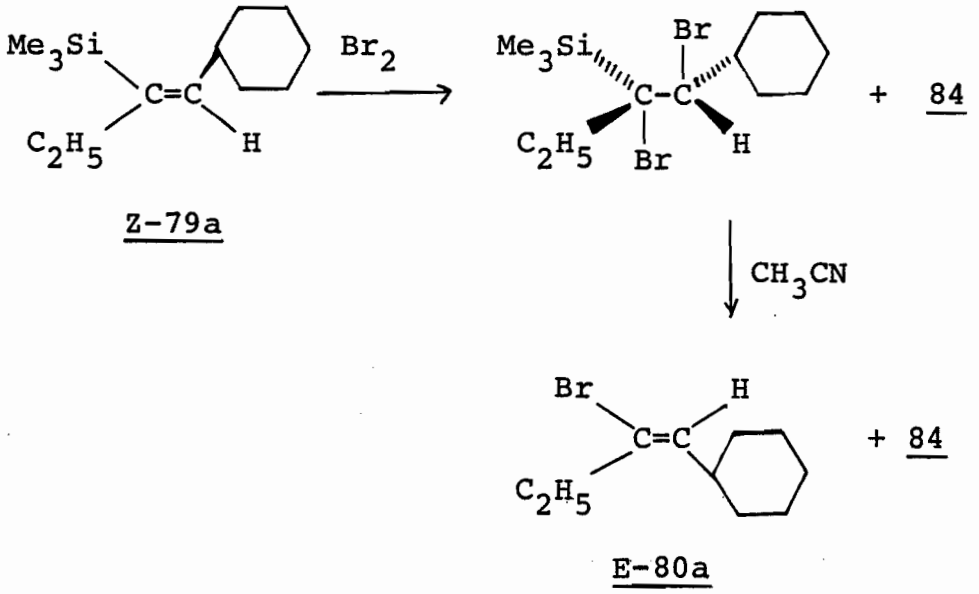
Another fragment m/e 137 is also present. This indicates a further loss of HBr from 85 (217-80=137). However, other than looking at the NMR which gives a proton at δ = 4.1 (a doublet) and the mass spectrum, no other reactions are performed to further prove the structure of 84.

The same kind of results can be obtained if the crude product mixture obtained from the bromination of Z-79a is stirred in acetonitrile at room temperature for 5 hours. NMR of the crude material obtained shows δ = 4.1 and 5.6. Preparative TLC using hexane as eluent gives two major fractions.



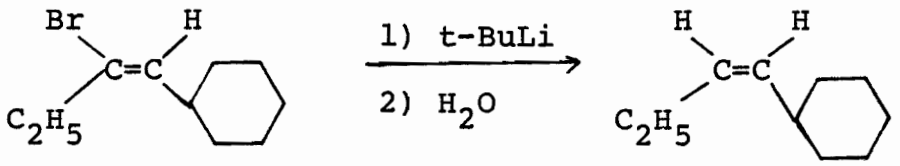
Z-79a

The first fraction is identical to the vinyl bromide E-80a obtained previously by direct TLC of the dibromide adduct product mixture. Physical data for this vinyl bromide are: NMR: δ = 5.6 (d); IR: 1640 cm^{-1}; mass spectrum m/e 216, 218. Fraction two has the NMR spectrum identical to compound 84.



Z-79a

The assignment of E-configuration to the product of bromination reaction of Z-79a can be proved chemically by treating E-80a with t-butyllithium at -78°C for 1½ hour followed by quenching with water to give the Z olefin 86. Comparing 86 with compounds 82 and 83 obtained by protodesilylation of the two geometric isomers of 79, it is found that 86 is identical to 82 in spectral data.



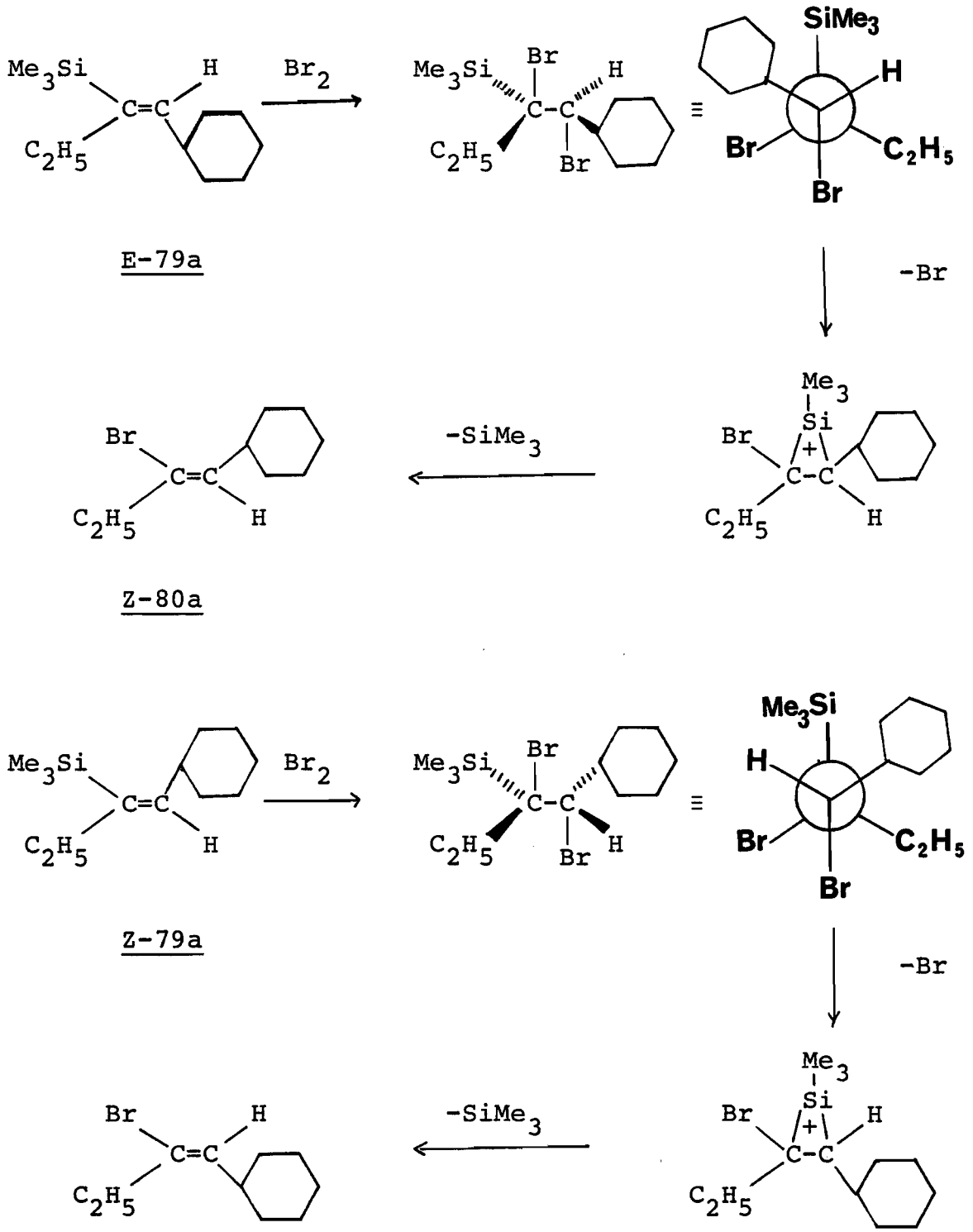
E-80a 86

Compound 82 has Z-configuration. This means 86 also has Z-configuration. Thus its precursor E-80a must have E-configuration. Therefore, bromination of Z-79a gives the vinyl bromide E-80a with inversion of configuration. Similar bromination reactions are carried out for vinylsilanes Z-79b and Z-79c. The same kind of results are obtained as in reaction with Z-79a, a dibromide adduct is formed in each case. Vinyl bromides E-79b and E-79c are obtained as products respectively after stirring with acetonitrile at room temperature for a few hours. The chemical shift of the vinyl protons of these E-vinyl bromides are at lower field compared with their corresponding Z isomers. This is in agreement with the prediction made previously about the chemical shifts of the vinyl protons of substituted alkenes.

Thus, for both geometric isomers of the trisubstituted vinylsilanes 79, bromination proceeds through the formation of the dibromide adducts, and the final products vinyl bromides have opposite configuration from the starting material, i.e. inversion of configurations has taken place. The mechanism of the bromodesilylation reactions for both geometric isomers is likely to proceed through anti-addition of bromine across the double bond, followed by anti-elimination of the bromosilane which proceeds in two parts via an E1 mechanism. The first step in the elimination involves the cleavage of the carbon-bromine bond with the help of the silyl group, and then trans-elimination of the trimethylsilyl group (Scheme 7).

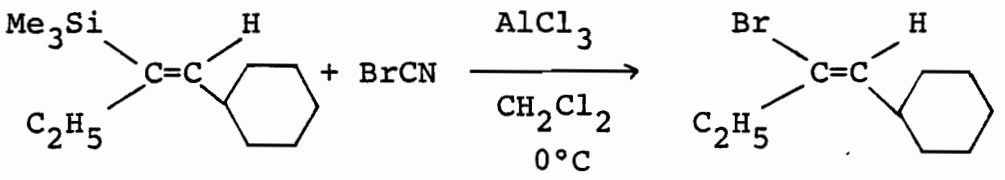
Thus, trisubstituted vinylsilanes can act as precursors for the stereoselective synthesis of the geometric isomers of vinyl bromide. However, there is one drawback. While the conversion of the E-vinylsilanes is smooth and clean to give the Z-vinyl bromides with reasonable yields (65-87% isolated yield), the conversion of the Z-vinylsilanes to E-vinyl bromides is not as good. The yield is low (the isolated yields range from 10-56%), and side products are present. This can hardly be considered as a good synthetic route to E-vinyl bromides.

Fortunately, a convenient method for preparing the E-vinyl bromides is discovered when we find that reactions of the vinylsilanes E-79 with cyanogen bromide in the presence of aluminum chloride in methylene chloride proceed cleanly to give the desired vinyl bromides E-80 with retention of stereochemistry. For example, vinylsilane E-79a reacts with


Me3Si
H
C=C
C2H5
Br2
Br
C-C
SiMe3
Br
C2H5
-Br
Me3
Si
+
-SiMe3
E-79a
Z-80a
Z-79a
E-80a

SCHEME 7

cyanogen bromide in the presence of aluminum chloride at 0°C to give cleanly the E-vinyl bromide E-80a. NMR of the crude material shows no side product is present. Preparative TLC using hexane as eluent gives E-80a in 73% isolated yield. (NMR: δ = 5.6 (d); IR: 1640 cm^{-1}).

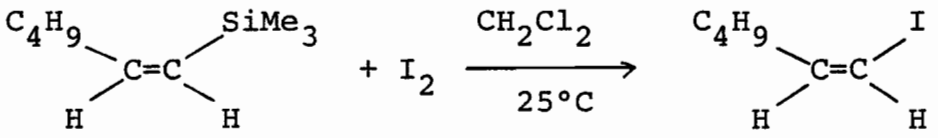


E-79a E-80a

Similar reactions of cyanogen bromide with other trisubstituted vinylsilanes E-79b and E-79c proceed cleanly to give E-80b and E-80c respectively with retention of stereochemistry. The presence of aluminum chloride is important, because no reaction is observed between cyanogen bromide and the vinylsilanes in the absence of aluminum chloride with other reaction conditions identical. Thus with appropriate reagents, it is possible to obtain either isomer of the vinyl bromide 80 starting from the same isomer of vinylsilane E-79. The difference in stereochemical results suggests strongly that a different mechanism is operative in the bromodesilylation reaction with cyanogen bromide.

(c) IODODESILYLATION

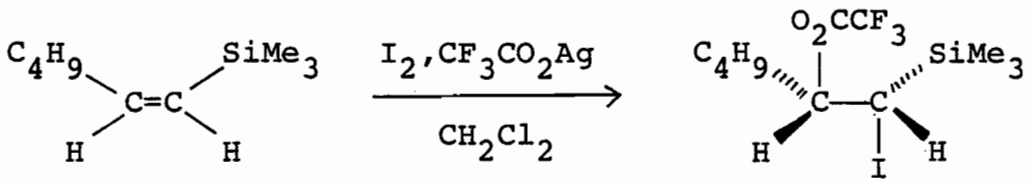
Reactions of disubstituted vinylsilanes with iodine go with retention of configuration[47]. For example,



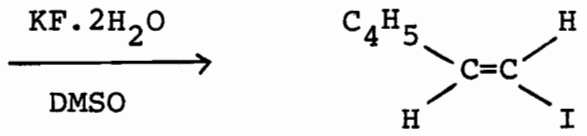
75 87

Cis-1-trimethylsilyl-1-hexene 75 reacts with iodine in methylene chloride at room temperature to give cis-1-iodo-1-hexene 87.

However, the trans-iodide can also be obtained from cis-1-trimethylsilyl-1-hexene 75. Reaction of 75 with a mixture of iodine and silver trifluoroacetate in dichloromethane gives an adduct 88. Reaction of 88 with potassium fluoride dihydrate[109] in dimethyl sulfoxide gives the trans-1-iodo-1-hexene 89.



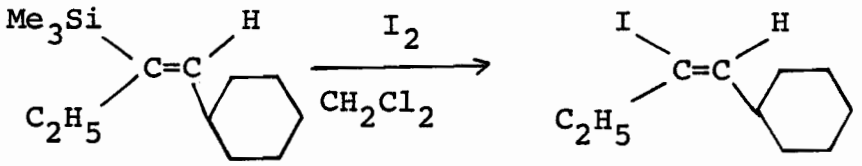
75 88



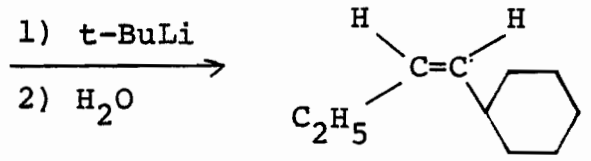
89

Unlike the reactions of bromine, the reactions of iodine with the trisubstituted vinylsilanes 79 are straight forward

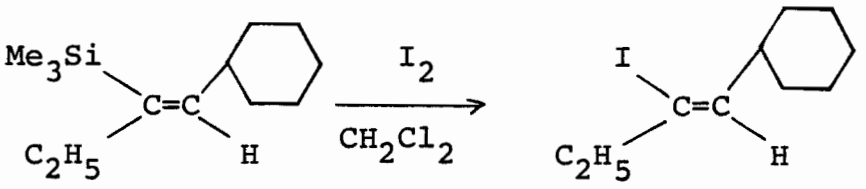
and give the corresponding vinyl iodides 90 with high stereospecificity and retention of configuration. For example, vinylsilane E-79a reacts with iodine in methylene chloride at room temperature to give a brownish liquid on work up. No diiodide adduct is obtained. NMR of the crude material obtained shows the signals for the vinyl iodide. The trimethylsilyl signal has disappeared. No other side product signals are seen. The product is purified by preparative TLC (silica gel) using benzene:hexane (5:1) as eluent. The isolated yield of the product E-90a is 60%. Physical data: IR: 1625 cm^{-1}; NMR: δ =6.0 (d); mass spectrum m/e at 264. Similarly the corresponding Z isomer vinylsilane Z-79a reacts with iodine to give the Z-vinyl iodide Z-90a on work up. Physical data for Z-90a: IR: 1640 cm^{-1}; NMR: δ = 5.2 (d); mass spectrum m/e at 264. The assignment of the stereochemistry can be based on the chemical shift of the vinyl protons of the vinyl iodides. The Z-isomer vinyl proton is at higher field compared to the corresponding E-isomer (δ = 5.2 compared to δ =6.0).



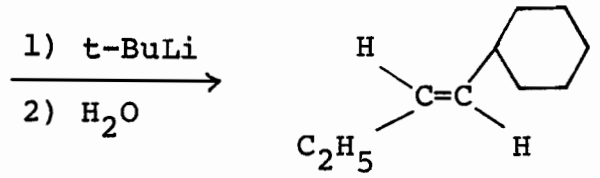
E-79a E-90a



82



Z-79a Z-90a

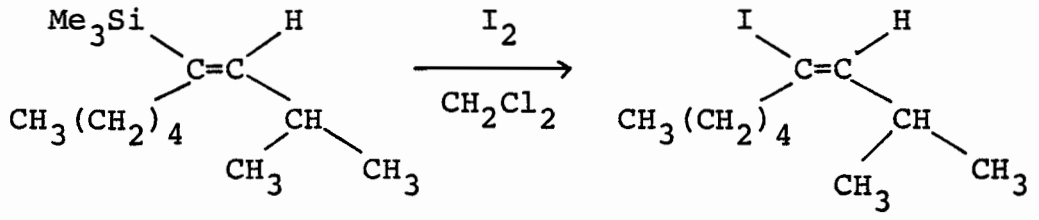


83

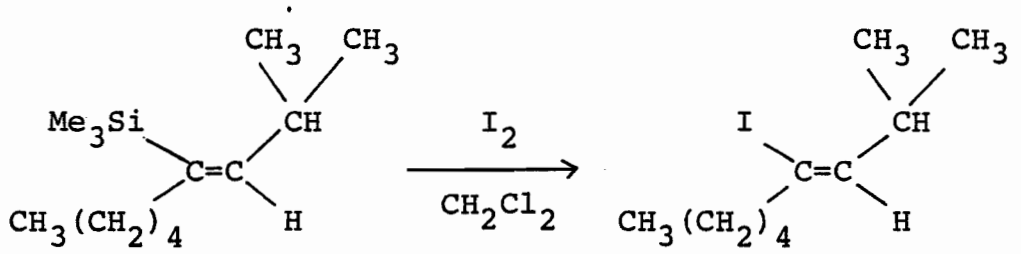
The assignment of stereochemistry can be confirmed by chemical means as in vinyl bromide. E-90a reacts with t-butyllithium at -78°C and when quenched with water gives a disubstituted alkene identical to alkene 82. Similarly Z-90a can be transformed to an alkene identical to 83. These prove that the configuration for E-90a is E and Z-90a is Z, because these reactions do not involve a change in configuration[108].

Similar iododesilylation reactions are carried out with vinylsilanes E-79b and Z-79b. In both cases, the corresponding vinyl iodides E-90b and Z-90b are obtained respectively with retention of configuration. As before, the assignment of stereochemistry is by looking at the vinyl protons of the product vinyl iodides. The vinyl proton of Z-90b obtained from Z-79a is at higher field than that of E-90b and is assigned to have Z-configuration. As in the cases of 79a, the reactions of iodine with 79b are clean. Only the vinyl iodides 90b are formed. No other side products are found. Isolated

yields by preparative TLC are 75% from E-90b and 81% for Z-90b.



E-79b E-90b

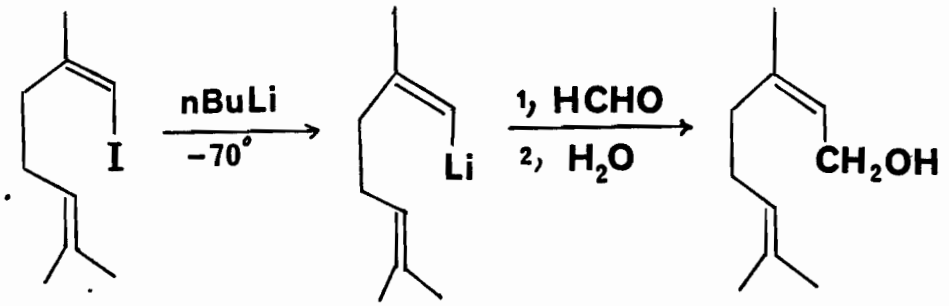


Z-79b Z-90b

Thus, trisubstituted vinylsilanes are found to be useful precursors for the stereoselective synthesis for vinyl halides. Since vinyl bromides and vinyl iodides can be converted easily to other trisubstituted alkenes either via lithiation[108] or by reaction with organocopper compounds[42], the vinylsilane route to these vinyl halides represents a reaction of considerable synthetic utility.

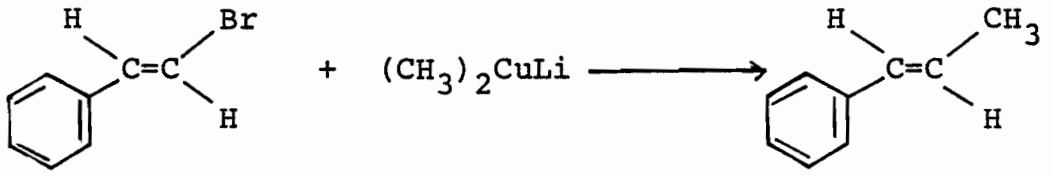
The transformation of vinyl iodide into another trisubstituted alkene via lithiation has been demonstrated in the synthesis of nerol 91 by Normant[108]. Vinyl iodide 92 is allowed to react with n-butyllithium at -70°C to give the alkenyllithium compound 93. Reaction of 93 with formaldehyde followed

by aqueous work up gives the product 91.



92 93 91

Reactions of vinyl bromide and organocopper lithium compounds have been demonstrated by Corey[110] to give substituted alkenes. For example, trans-β-bromostyrene reacts with lithium dimethyl cuprate with retention of configuration.



Thus, these vinyl halides, themselves, are very useful intermediates in organic synthesis, because they can be transformed to other substituted alkenes with different functionalities.

The ^{13}C NMR of a number of geometric isomers of the vinyl halides are examined. In all cases, it is found that:

i) the difference in chemical shifts between the two olefinic carbons (C_d-C_c) is always larger in the E isomers than in the corresponding Z isomers.

TABLE 2: SYNTHESIS OF VINYL HALIDES FROM VINYLSILANES

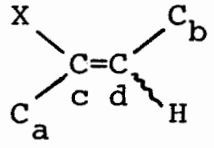
Vinylsilane	Reaction Condition	Product	Isolated Yield [a], %	Physical Data[b]
E-79a	Br_2, -78°C	Z-80a	87	IR: 1655; NMR: 5.4 (d)
E-79b	Br_2, -78°C	Z-80b	65	IR: 1655; NMR: 5.4 (d)
E-79c	Br_2, -78°C	Z-80c	65	IR: 1655; NMR: 5.6 (t)
Z-79a	Br_2, -78°C	E-80a	21	IR: 1640; NMR: 5.6 (d)
Z-79b	Br_2, -78°C	E-80b	10[c]	IR: 1640; NMR: 5.6 (d)
Z-79c	Br_2, -78°C	E-80c	56	IR: 1640; NMR: 5.8 (t)
E-79a	BrCN/$AlCl_3$/0°C	E-80a	73	
E-79b	BrCN/$AlCl_3$/0°C	E-80b	53	
E-79c	BrCN/$AlCl_3$/0°C	E-80c	60	
E-79a	I_2/r.t.	E-90a	58	IR: 1625; NMR: 6.0 (d)
E-79b	I_2/r.t.	E-90b	75	IR: 1625; NMR: 6.0 (d)
Z-79a	I_2/r.t.	Z-90a	71	IR: 1640; NMR: 5.2 (d)
Z-79b	I_2/r.t.	Z-90b	81	IR: 1640; NMR: 5.2 (d)

a) Isolated yield after TLC purification unless otherwise specified

b) All compounds have consistent spectroscopic data with purity and molecular weight confirmed by GC-MS. Infrared (IR) spectra in neat reported in cm^{-1}. Proton NMR determined in CCl_4, with vinyl proton reported in ppm

c) Yield estimated by NMR

TABLE 3: ^{13}CNMR DATA FOR THE VINYL HALIDES



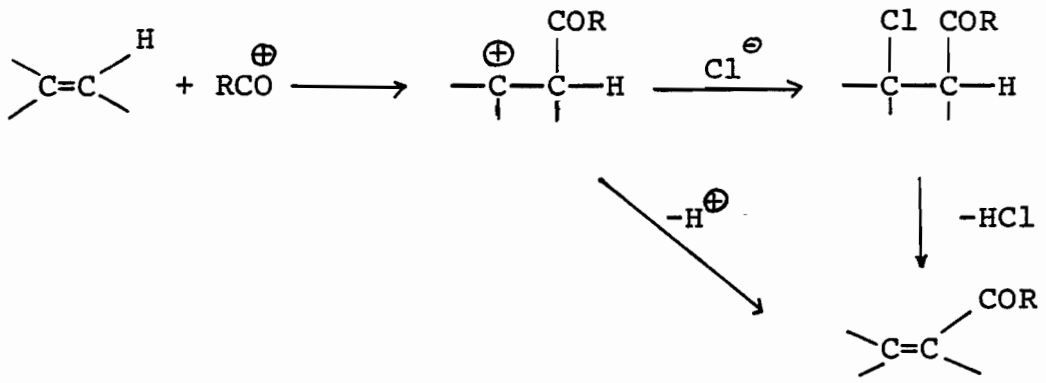
		C_a	C_b	C_c	C_d	C_d-C_c (in ppm)
X = Br	E-80a	29.48	39.10	126.8	137.3	10.5
	Z-80a	35.13	40.39	128.0	132.8	4.8
	E-80b	30.90	35.69	124.7	139.5	14.8
	Z-80b	31.03	41.47	126.2	135.4	9.2
X = I	E-90a	32.63	40.27	104.4	146.3	41.9
	Z=90a	38.92	45.31	108.8	138.8	30.0
	E-90b	30.68	38.67	102.2	148.3	46.1
	Z-90b	36.08	45.10	106.9	141.4	34.5

ii) the two carbons (C_a and C_b) α to the olefinic carbons always appear at higher fields in the E isomers than in the corresponding Z isomers.

These findings may be helpful in the differentiation of the geometric isomers of substituted vinyl halides.

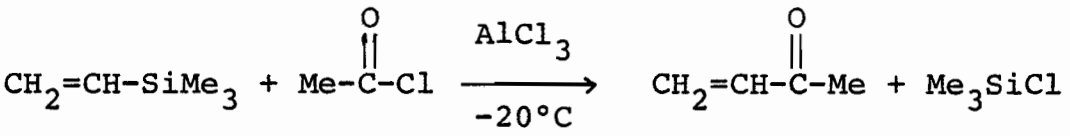
(d) FRIEDEL-CRAFTS ACYLATION

Olefins can be acylated at an aliphatic carbon[111] under Friedel-Crafts conditions. The product may be obtained by two paths. The initial attack is by the acyl cation RCO^+ or by the acyl halide, free or complexed, on the olefin to give a carbonium ion. Then the carbonium ion can lose a proton to give the product, an unsaturated ketone, via the SE1 mechanism, or the carbonium ion can combine with the chloride ion to give a β-halo ketone, which then under the conditions of the reaction loses HCl to give the unsaturated ketone.

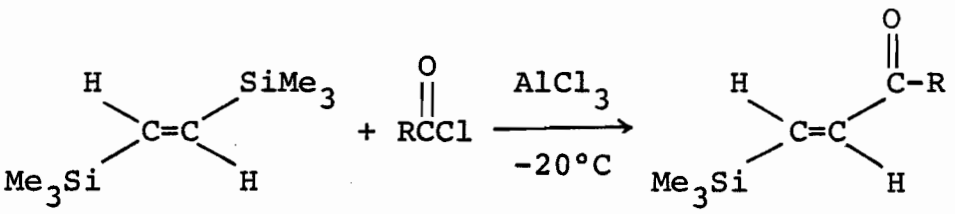


This type of acylation reaction is not limited to olefins; simple vinylsilanes have also been acylated. For example[112],

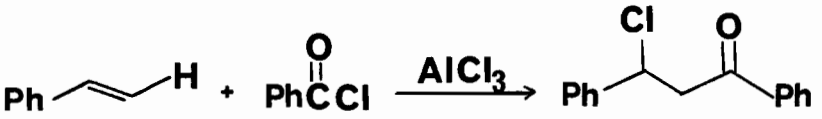
vinyltrimethylsilane reacts with acetyl chloride at -20°C in the presence of aluminum chloride to give methyl vinyl ketone.



Disubstituted vinylsilanes also undergo Friedel-Craft acylation reactions with different acid chlorides in the presence of aluminum chloride. For example[113], trans-bis(trimethylsilyl)-1,2-ethene can react with different acid chlorides to give α,β-unsaturated ketones.

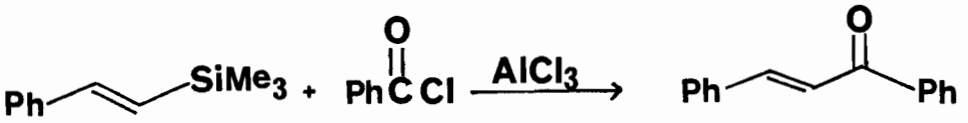


Thus, vinylsilanes can participate in aliphatic Friedel-Crafts acylation to give substitution products. The acylation reaction is site-selective[98]: acylation takes place at the carbon atom carrying the trimethylsilyl group. This site-selective property is very important in organic synthesis. The aliphatic Friedel-Crafts reaction is not as often used as its aromatic counterpart, because it does not always give the simple substitution products. However, a suitably placed trimethylsilyl group encourages the formation of simple substitution products. For example, styrene reacts with benzoyl chloride and aluminum chloride to give the addition product 94,



94

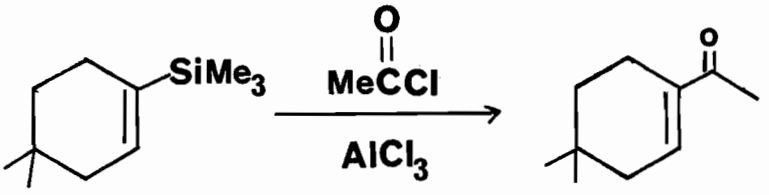
while trans-β-trimethylsilylstyrene reacts with benzoyl chloride and aluminum chloride to give the substitution product 95.



95

A relatively symmetrical olefin, e.g. 4,4-dimethylcyclohexene, may pose a problem in Friedel-Crafts acylation. Acylation of this compound can be expected to give mixtures of products resulting from electrophilic attack on either carbon atom of the double bond. However, this problem can be solved by the presence of a trimethylsilyl group.

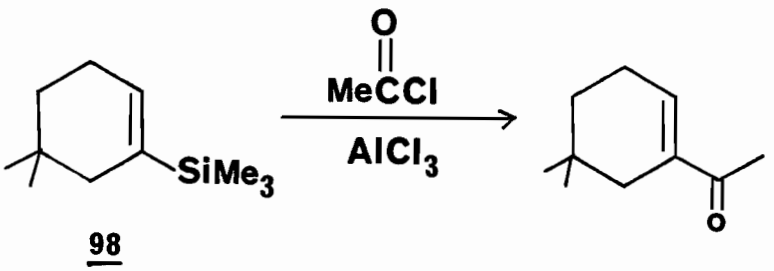
Vinylsilane 96, available from the corresponding vinyl chloride, reacts with acetyl chloride and aluminum chloride to give the substitution product 97 in high yield. No product resulting from attack at the other end of the double bond is obtained.



96 97

Vinylsilane 98 also gives the substitution product on reaction with acetyl chloride and aluminum chloride while

once again no product from attack at the other end of the double bond is obtained.



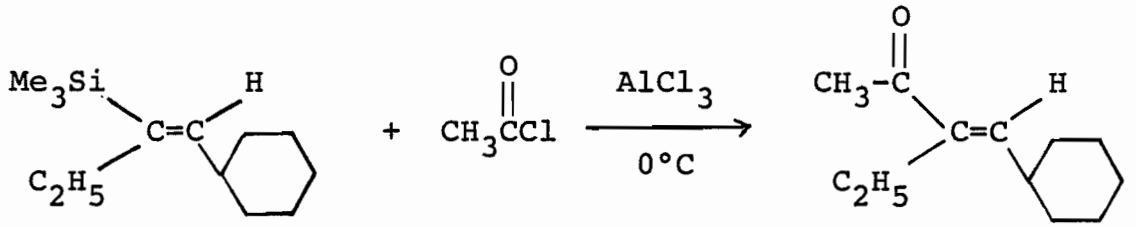
98

Thus, the presence of the trimethylsilyl group determines the site of attack of the acyl group on the double bond. This can be useful in times when selective substitution is preferred. The trimethylsilyl group can produce this effect partly because it is easily cleaved from a carbon atom next to a carbonium ion, and partly by the stabilisation it gives to such a β carbonium ion[114].

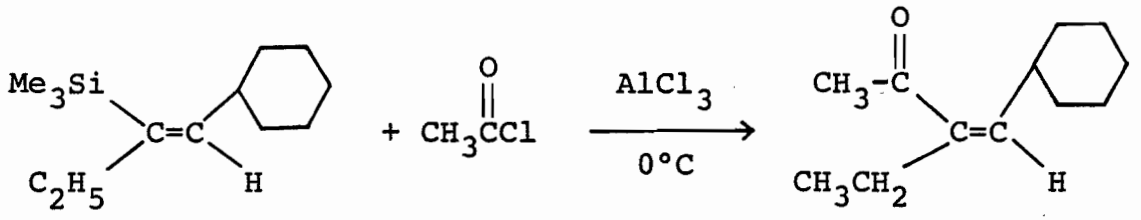
Friedel-Crafts acylations of trisubstituted vinylsilanes are also studied. Vinylsilane E-79a reacts with acetyl chloride and aluminum chloride in methylene chloride at 0°C to give the corresponding α,β-unsaturated ketone E-99a. Preparative TLC (silica gel) with benzene: methylene chloride (5:1) as eluent gives the isolated yield at 70%. The reaction is clean and stereospecific. Only one geometric isomer of the ketone is obtained. E-99a: 1665 cm^{-1}, δ = 6.21 (d); m/e at 180.

The geometric isomer vinylsilane Z-79a also reacts with acetyl chloride and aluminum chloride to give an α,β-unsaturated ketone Z-99a in high yield. Z-99a: 1690 cm^{-1}, δ = 5.2 (t,d); m/e at 180. The ketone E-99a obtained from E-79a is assigned

to have the E-configuration while Z-99a has the Z-configuration. The stereochemistries of the isomeric ketones 99a are evident from the carbonyl absorption in the infrared spectra and the chemical shifts as well as the allylic coupling of the vinyl protons in the NMR spectra. The vinyl proton of the E isomer is at lower field in NMR.



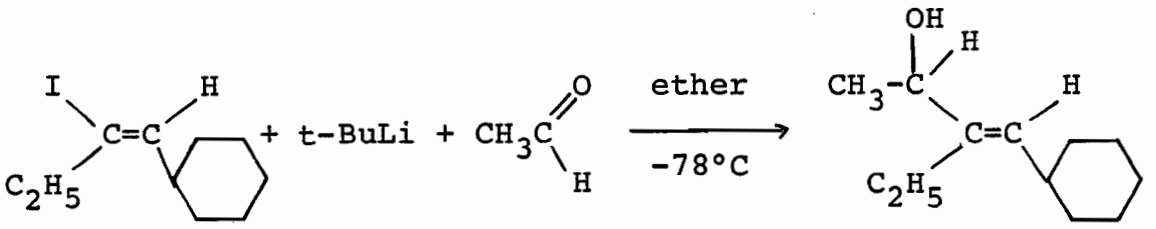
E-79a E-99a



Z-79a Z-99a

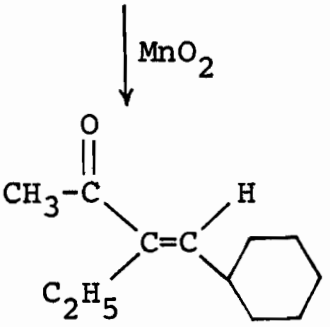
Thus, retention of stereochemistry is found in the Friedel-Crafts acylations of vinylsilanes 79a. Chemical correlation of stereochemistries can also be demonstrated. Taking the vinyl iodide E-90a obtained from the vinylsilane E-79a as the starting material, the configuration of E-90a is established to be E. Reaction of E-90a with t-butyllithium at -78°C for 2 hours followed by the addition of acetaldehyde gives the allylic alcohol 100 on aqueous work up[108]. The configuration

of 100 is not changed from that of E-90a because lithiation reaction does not involve a change in configuration. Thus 100 has E-configuration. The allylic alcohol 100 can be oxidized to the unsaturated ketone by stirring with freshly prepared manganese dioxide[115] in petroleum ether at room temperature for 1 hour. The ketone obtained from this oxidation has the same configuration as the allylic alcohol because there is no change in configuration involved in oxidation. Comparing the spectral data of this ketone with those of E-99a, they are found to be identical. Thus, E-99a has the same configuration as the ketone obtained from oxidation of the allylic alcohol 100, which is E in configuration. Starting from the E configuration E-79a, Friedel-Crafts acylation gives E-99a as product with no change in configuration. Retention of stereochemistry is seen. This is in agreement with the assignment based on the chemical shifts of the vinyl protons of the substituted alkene products.



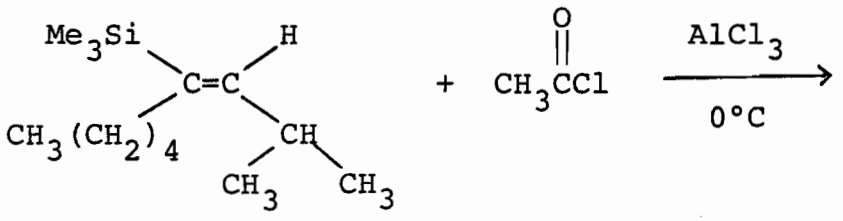
E-90a

100

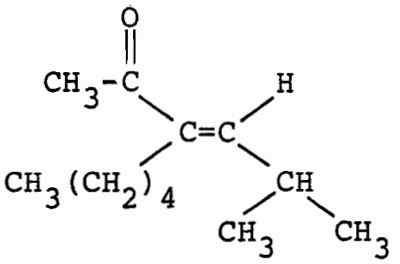


E-99a

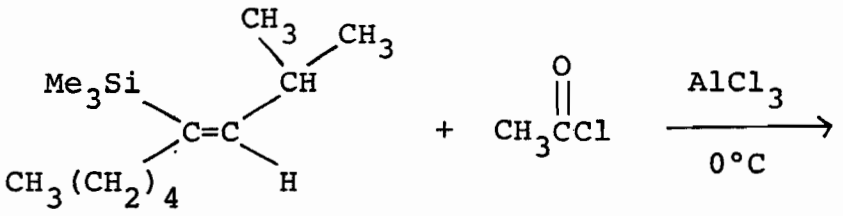
Vinylsilanes E-79b and Z-79b are also subjected to Friedel-Crafts acylation. In both cases, the results are the same as in the previous vinylsilane acylations. The reactions are stereospecific and retention of stereochemistry is observed.



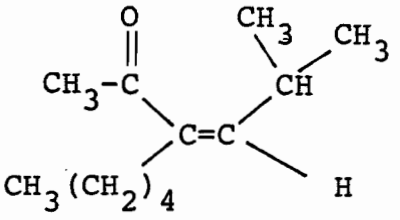
E-79b



E-99b



Z-79b

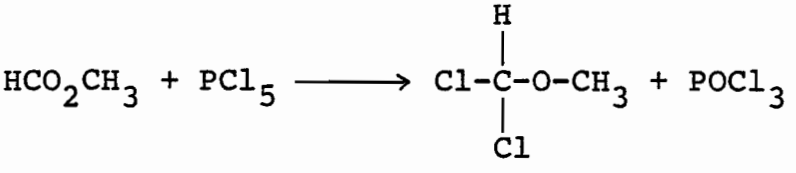


Z-99b

Thus, vinylsilanes react with electrophiles in the same way as the corresponding olefins in Friedel-Crafts acylation. But unlike the oliphatic Friedel-Crafts acylation of olefin, no addition product is formed for the vinylsilanes. The formation of the substitution products may be due to the ease of cleavage of the trimethylsilyl-to-carbon bond after the formation of the β carbonium ion. In conclusion, Friedel-Crafts acylation of vinylsilanes represents a method for the direct stereoselective synthesis of α,β-unsaturated ketones. The main feature of this acylation is the reaction's being site-selective and stereospecific.

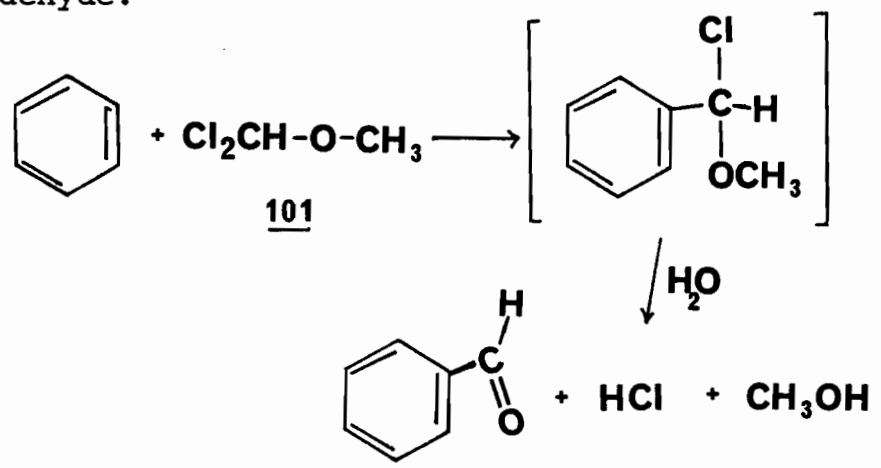
(e) FRIEDEL-CRAFTS FORMYLATION

Since vinylsilanes behave in the same way as olefins in the Friedel-Crafts acylation, it will be interesting to see how they react in Friedel-Crafts formylation. The compound used in the formylation reaction is dichloromethyl methyl ether 101 which can be prepared[116] by stirring methyl formate and phosphorus pentachloride at room temperature under nitrogen atmosphere for one hour. The reaction mixture is then distilled. The distillate, dichloromethyl methyl ether 101, is collected at 87°C as a colourless liquid (NMR at δ = 3.6 (s) and 7.1 (s)).

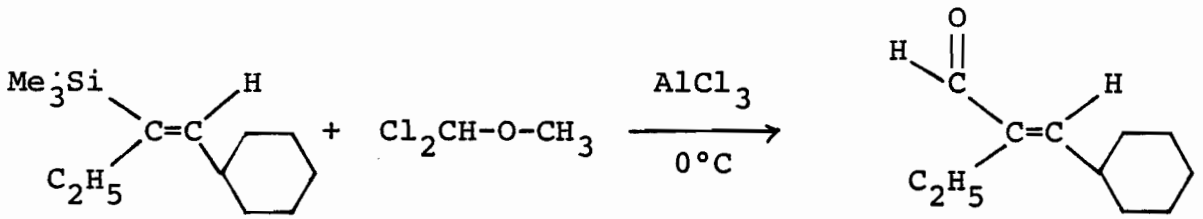


101

Dichloromethyl methyl ether 101 has been known to react with various aromatic hydrocarbons in the presence of catalyst in the Friedel-Crafts formylation to give aromatic aldehydes[117]. For example, the ether 101 can react with benzene to give benzaldehyde.



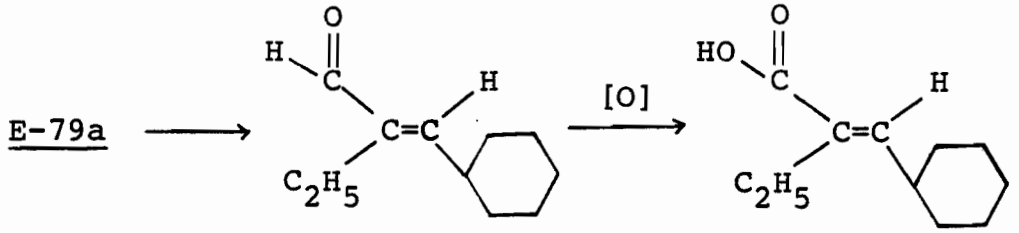
Formylation of vinylsilanes is not as straight forward as the acylation reaction. Reaction of vinylsilane E-79a with 101 and aluminum chloride in methylene chloride at 0° gives the conjugated aldehyde E-102a in good yield. The spectral data of E-102a are: IR: 2700, 1690, 1640 cm^{-1}; NMR at δ = 6.1 (d), 9.2 (s); mass spectrum m/e 165 (P-1).



E-79a 101 E-102a

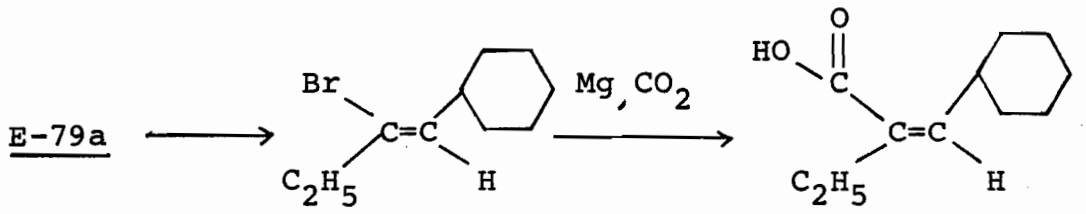
The stereochemistry of E-102a is established to be E by chemical method. Compound E-102a can be oxidized by chromic acid to corresponding conjugated carboxylic acid 103. The

carboxylic acid 103 should have the same configuration as the precursor E-102a because the oxidation does not involve a change in configuration.



E-102a 103

At the same time, Z-80a, obtained from bromination of E-79a, is allowed to react with magnesium to give the vinyl magnesium bromide. Quenching the vinyl magnesium bromide with carbon dioxide followed by aqueous work up will give the corresponding conjugated carboxylic acid 104. Since Z-80a has Z-configuration, the carboxylic acid 104 also has Z-configuration since such transformation does not change the configuration.

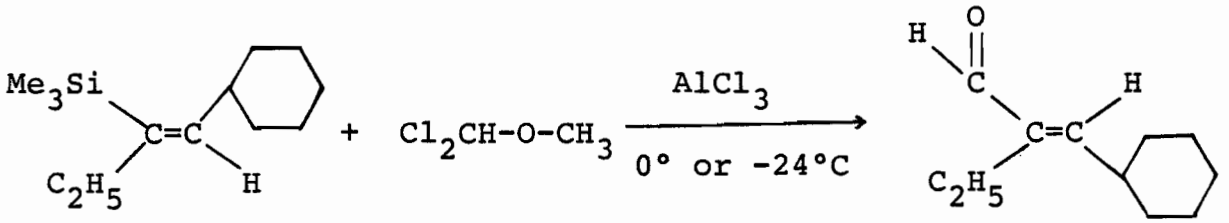


Z-80a 104

Comparing this carboxylic acid 104 with 103 which is formed by the oxidation of E-102a, they are different from each other. These two carboxylic acids must be geometric isomers because they both are derived from the same starting

material E-79a. Since 104 has Z-configuration, carboxylic acid 103 must then have E-configuration. This indicates that the conjugated aldehyde E-102a has E-configuration also. Thus, Friedel-Crafts formylation of vinylsilane E-79a goes with retention of configuration to give the conjugated aldehyde E-102a.

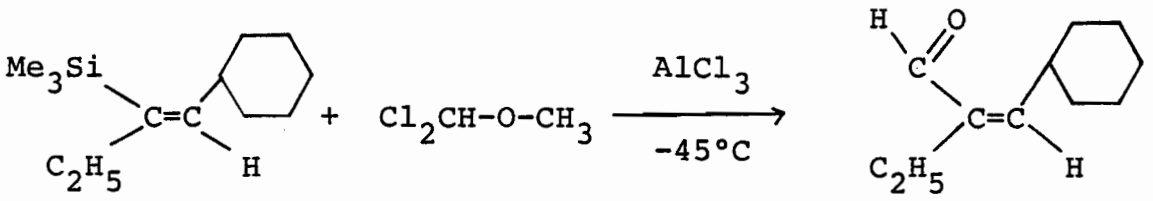
However, the Friedel-Crafts formylation of the geometric isomer vinylsilane Z-79a gives quite unexpected results. Z-79a reacts with 101 and aluminum chloride in methylene chloride at 0°C to give also the conjugated aldehyde E-102a. The same result is obtained if the reaction is carried out at -24°C. Only the aldehyde E-102a is obtained.



Z-79a 101 E-102a

Then if the reaction temperature is lowered to -45°C and the reaction time is shortened, the NMR of the crude material obtained from the formylation of Z-79a consists of a mixture of products, the E-102a and its geometric isomer Z-102a as well as a deconjugated isomer 105 in the ratio of 1:2:1. Upon warming or on longer reaction time the mixture eventually transforms into E-102a only. It is likely, therefore, that the formylation proceeds with retention of stereochemistry

but under the reaction conditions, the less stable Z-102a isomerizes to the more stable E-isomer via 105. Physical data of Z-102a: IR: 2700, 1690, 1610 cm^{-1}; NMR at δ = 5.7 (d), 10.1 (s). For compound 105: IR: 1725 cm^{-1}; NMR at δ = 5.5 (d), 9.4 (d). The IR signal at 1725 cm^{-1} indicates a normal (not conjugated) carbonyl group. NMR of the reaction product at still lower reaction temperature, e.g. -78°C shows more of the compound Z-102a, some of 105 and little of the compound E-102a. However, it is not possible to prevent the isomerization even when the reaction is carried out at -100°C.



Z-79a 101 Z-102a

E-102a 105

GC of the crude mixture shows three peaks. One peak corresponds to the retention time of E-102a. Another peak is more prominent in lower temperature reactions, while the peak corresponding to E-102a diminishes. GC-ms shows these two

TABLE 4: FRIEDEL-CRAFTS REACTIONS OF VINYLSILANES

Precursor	Reaction Condition	Product	Isolated Yield [a], %	Physical Data[b]
E-79a	$CH_3COCl/AlCl_3/0°$	E-99a	70	IR: 1665, 1630; NMR: 6.2 (d)
E-79b	$CH_3COCl/AlCl_3/0°$	E-99b	60	IR: 1665, 1630; NMR: 6.2 (d)
Z-79a	$CH_3COCl/AlCl_3/0°$	Z-99a	65	IR: 1690, 1620; NMR: 5.2 (d)
Z-79b	$CH_3COCl/AlCl_3/0°$	Z-99b	58	IR: 1690, 1620; NMR: 5.2 (d)
E-79a or Z-79a	$Cl_2CHOCH_3/AlCl_3/0°$	E 102a	90[c]	IR: 2700, 1690, 1640; NMR: 6.1 (d), 9.2 (s)
Z-79a	$Cl_2CHOCH_3/AlCl_3/-45°$	E-102a: Z-102a: 105 (1:2:1)	90[d]	Z-102a: IR: 2700, 1690, 1610 NMR: 5.7 (d), 10.1 (s) 105: IR: 1725; NMR: 5.5 (d), 9.4 (d)
E-79b or Z-79b	$ClCHOCH_3/AlCl_3/0°$	E-102b	90[c]	IR: 2700, 1690, 1640 NMR: 6.1 (d), 9.2 (s)

a) Isolated by TLC unless otherwise specified

b) All compounds have consistent spectroscopic data with purity and molecular weight confirmed by GC-MS. Infrared (IR) spectra in neat reported in cm^{-1}. Proton NMR with the vinyl and the aldehyde protons reported in ppm

c) Crude yield only

d) Crude yield of the mixture

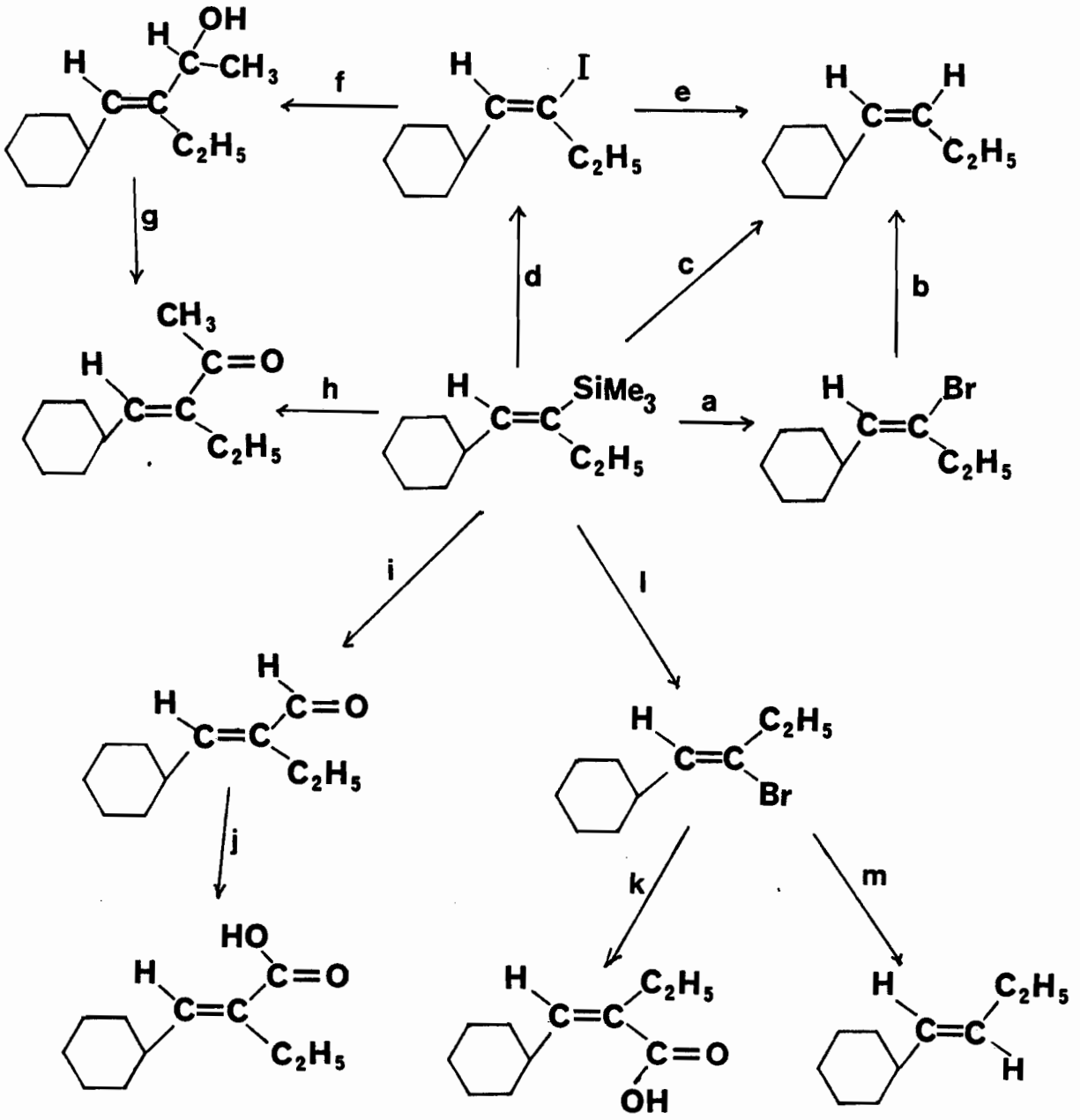
components have identical mass spectra. They are geometric isomers, E-102a and Z-102a. The third peak also has a similar mass fragmentation pattern. It has m/e at 165 which is $(M-1)^+$.

Similar results are obtained for the formylation reaction of vinylsilanes E-79b and Z-79b. Only the E-configuration conjugated aldehyde E-102b is obtained when the reactions are carried out at 0°C. Thus, like the acylation reactions, vinylsilanes undergo Friedel-Crafts formylation with retention of stereochemistry to give α,β-unsaturated aldehydes. However the aldehydes are more reactive, and the Z-isomers tend to isomerize to the more stable E-isomers even at low temperatures.

(f) CHEMICAL CORRELATIONS AND MECHANISM

Electrophilic substitution reactions of trisubstituted vinylsilanes are seen to be stereospecific. For these aliphatic trisubstituted vinylsilanes, the reactions go with retention of stereochemistries except for the bromodesilylation reaction using bromine as electrophile. Chemical correlation of stereochemistries has also been demonstrated by using compound E-79a (Scheme 8). Scheme 8 also seems to show the versatility of vinylsilanes as synthetic precursors.

The mechanism proposed by Weber[53a] for the protodesilylation can be modified to account for the stereochemical outcome of the electrophilic substitution of vinylsilanes. The initial step involves the attack of the electrophile on the double bond. The developing carbon-carbon single bond rotates in a direction to



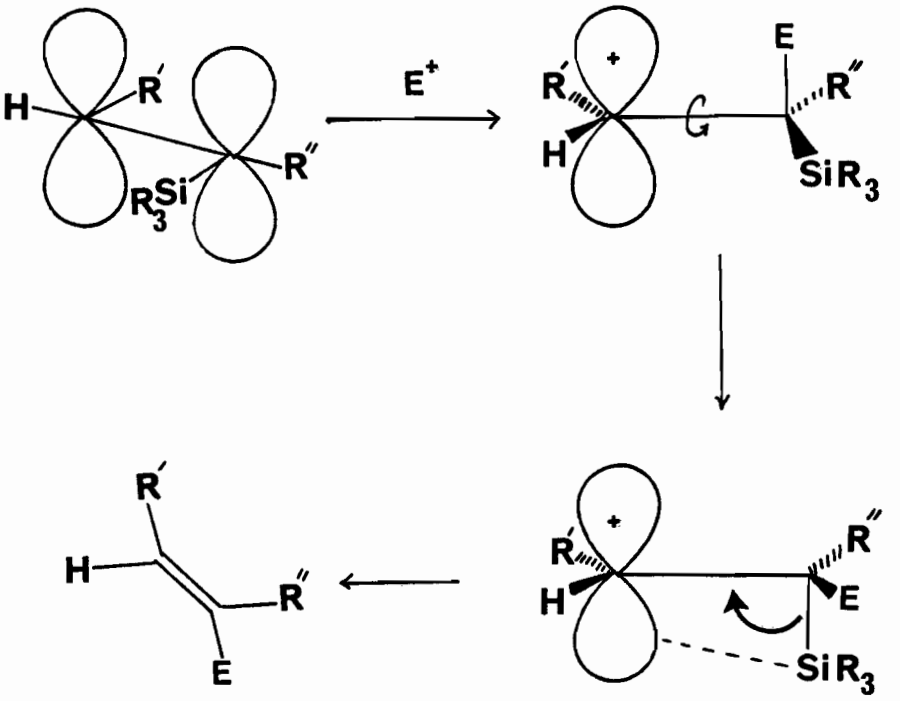
SCHEME 8: CHEMICAL CORRELATION OF STEREOCHEMISTRIES OF SOME TRISUBSTITUTED ALKENES

a) $BrCN/AlCl_3$; b) t-BuLi, H_2O; c) HI; d) I_2;
e) t-BuLi, H_2O; f) t-BuLi, CH_3CHO; g) MnO_2;
h) $CH_3COCl/AlCl_3$; i) $Cl_2CHO\text{-}CH_3/AlCl_3$; j) $HCrO_4$;
k) Mg, CO_2; l) Br_2; m) t-BuLi, H_2O

permit the trimethylsilyl group to stabilize the forming carbonium ion. Retention of stereochemistry results whenever the counter ion of the electrophile is complexed, e.g. in the cases of Friedel-Crafts acylation or formylation reaction when the counter ion, the chloride ion, is complexed with aluminum chloride, the addition of the counter ion to the carbonium ion is slowed by this complexing. In the reaction with cyanogen bromide, the presence of aluminum chloride is essential. The mechanism of this bromodesilylation has not been established. However, a Friedel-Crafts type mechanism may be possible because in the absence of aluminum chloride the reaction does not proceed. The counter ion of the bromine electrophile may be complexed with the aluminum chloride, thus rendering the addition to the carbonium ion more difficult. Retention of stereochemistry occurs in the same manner as the other Friedel-Crafts acylation or formylation reactions because the addition to the incipient carbonium ion is kinetically not competitive with the elimination of the trimethylsilyl moiety.

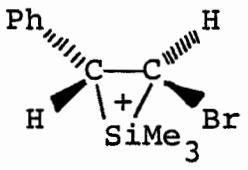
In the case of iododesilylation, the iodide anion may be too bulky thus, once again, the addition is not competitive with the elimination of the trimethylsilyl group. This is why no stable diiodide has even been isolated in these cases. Another example for this argument of bulky counter ion is the reaction of trifluoromethanesulfonic acid with trans-β-trimethylsilylstyrene to give styrene. The inability of the trifluoromethanesulfonate anion to function as a nucleophile to carbon precludes the addition to the carbonium ion. However, the

elimination reaction by the trifluoromethanesulfonate anion attacking silicon leading to the formation of trimethylsilyl trifluoromethanesulfonate can occur. Thus, retention of stereochemistry occurs whenever the counter ion is either complexed or sterically too bulky so that the addition to the incipient carbonium ion is kinetically not competitive with the elimination of the trimethylsylyl moiety.



However, if an adduct is formed as in the case of bromodesilylation where a dibromide is actually obtained first, the stereochemical outcome will depend on the mode of addition. In general, bromination of alkenes is a trans addition process

involving a bromonium ion intermediate, i.e. a trans addition of bromine across the double bond to give a trans dibromide. This is the case in the bromodesilylation of alkenylsilanes. In all cases of bromodesilylation of di- and trisubstituted vinylsilanes where the substituents are alkyl groups, trans additions to give the dibromides occur followed by trans elimination of bromotrimethylsilane in an E1 mechanism with the help of the trimethylsilyl group. However when the substituents are aromatic groups, i.e. in silylstyrenes, cis addition is favoured. This is explained by the fact that the trimethylsilyl group can stabilize the forming benzylic carbonium ion by hyperconjugation or bridging. Thus bromination can proceed via a silicon-stabilized cationic species.



Addition of the bromine anion can only occur on the same side as the electrophile, thus giving the cis dibromide. Trans elimination occurs in the debromosilylation step. However, because of the different modes of addition in the bromination step, different stereochemical outcomes result.

CHAPTER 3

CLEAVAGE OF THE SILICON-CARBON BOND BY FLUORIDE ION IN TRIORGANOSILYLOXIRANES

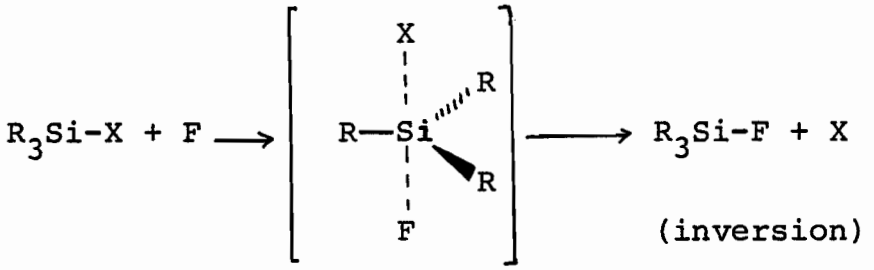
(a) CLEAVAGE OF SILICON-CARBON BONDS

The potential of vinylsilanes as synthetic intermediates has been demonstrated in the previous two chapters. The transformation of these intermediates into various organic compounds involves the cleavage of the silicon-carbon bond. The bond energy[118] for the silicon-carbon bond is 320 Kjoule/mole while that of a simple carbon-carbon bond is 347 Kjoule/mole. Also silicon is more electropositive than carbon. These two factors render the cleavage of the silicon-carbon bond much more facile than the cleavage of carbon-carbon bond. This has already been demonstrated as a factor for the site-selectivity of Friedel-Crafts acylation in Chapter 2.

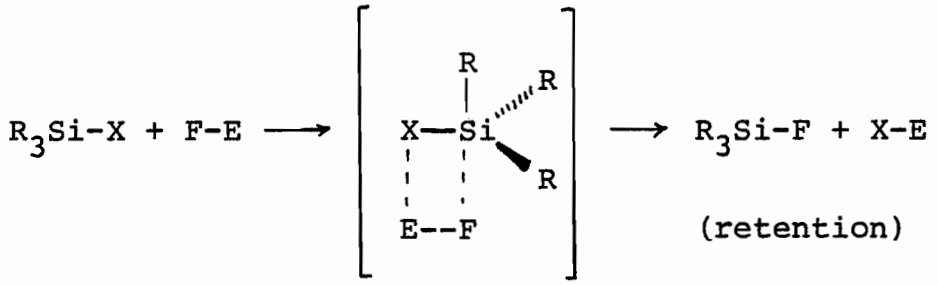
One of the most common nucleophilic cleavage reactions involving the silicon-carbon bond is the reaction by fluoride ion with β-functionalized silanes. Examples are the synthesis of allene oxide 25, allene 30 and bridgehead alkenes 33 in Chapter 1. Mechanistic studies of the nucleophilic substitution reactions on silicon have been quite extensive[119], and two mechanisms have been proposed.

The first one is the S_N2-Si mechanism. It is similar to its carbon analog. However, the 3d orbitals of the silicon are believed to participate in order to form the pentacovalent

transition state with both the entering nucleophile and the leaving group occupying the apical positions. The stereochemistry of the S_N2-Si mechanism is an inversion of configuration at silicon.



The second mechanism is the S_Ni-Si mechanism. It involves the front side attack by the nucleophile. A pentacovalent transition state is also postulated. The counter ion E of the nucleophile also participates in forming a cyclic complex with the leaving group. The stereochemistry of the S_Ni-Si mechanism is retention of configuration at silicon.



Which mechanism will be involved in any particular nucleophilic substitution reaction at silicon depends on many factors such as the nature of the reagent, the leaving group, the counter ion and the polarity of the solvent.

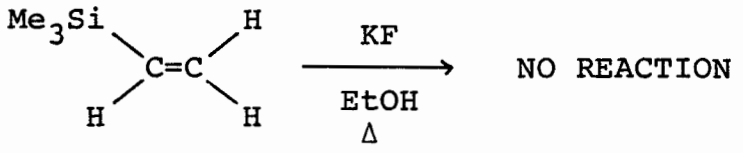
The affinity of fluoride ion for silicon has made fluoride ion a reagent of choice for the cleavage of silicon-carbon bond.

In fact, the silicon-fluorine bond has the highest single-bond energy among elements (142 Kcal/mole). However, fluoride ions do not cleave every kind of silicon-carbon bond. It is, therefore, of interest to study the limitations of fluoride ion cleavage reactions.

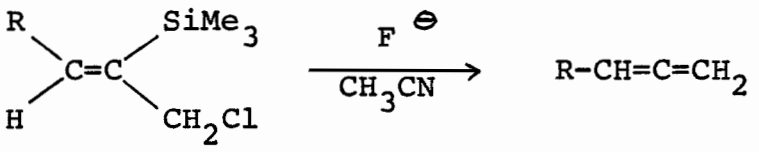
The cleavage of the silicon-alkynyl carbon bond can be achieved easily by hydroxides[120] and fluoride ions[121]. However, the cleavage of the silicon-vinyl carbon bond is difficult[69].

$$R_3Si\text{-}C{\equiv}C\text{-}R^1 \xrightarrow[2)\ H_2O]{1)\ F^{\ominus}} H\text{-}C{\equiv}C\text{-}R^1 + R_3SiF + {}^{\ominus}OH$$

For example, vinyltrimethylsilane is stable towards potassium fluoride in refluxing ethanol[121] and the compound $CH_3CH{=}CHSiCH_3$ is not cleaved by hot aqueous alkali[122]. This is attributed in part to the ability of the alkynyl anion to act as a better leaving group in what is probably an S_N2-Si reaction[119].

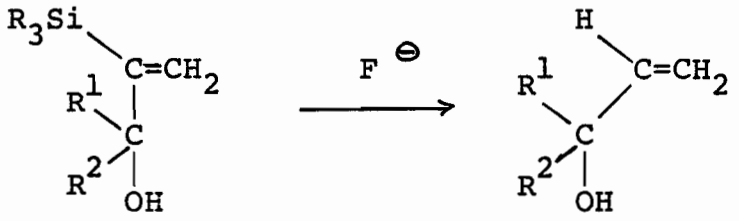


Fluoride ion, however, has been found to cleave the silicon-vinyl carbon bond of β-functionalized silyl compounds. An example is the cleavage of the silicon-vinyl bond of the β-chlorovinylsilane 27 to yield the allene 28 in Chapter 1.



27 28

Similar β-elimination occurs when the chloro group in the beta position is replaced by a trifluoroacetate group[63]. If there is a β-hydroxy group present as in 37, cleavage of the silicon-vinyl carbon bond by fluoride ion also occurs, but unlike the chlorides which undergo β-elimination to give allenes, the β-hydroxy-vinylsilanes give allylic alcohols 106 with no elimination of the β-hydrogen group.



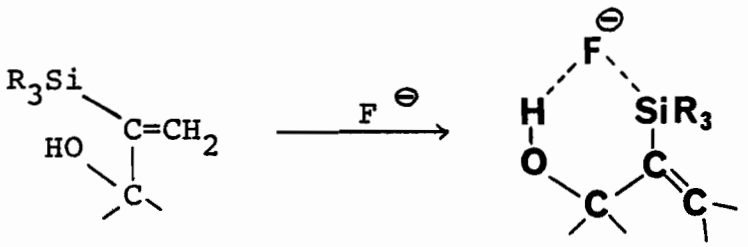
37 106

Under similar reaction conditions (using Et_4NF and CH_3CN), the rate of the β-elimination of the chloro compound to give an allene and the rate of reaction to give the allylic alcohol from 37 where R = C_6H_5 (i.e. the triphenylvinylsilane) are approximately the same. However, the β-hydroxytrimethylvinylsilanes need more drastic reaction conditions. The cleavage occurs only on refluxing in CH_3CN[63].

The difference in reactivity can be attributed to the

fact that the methyl group is electron-donating. Therefore, the silicon of a trimethylsilyl group will be less electrophilic than the silicon of a triphenylsilyl group. Thus, fluoride ion will attack the triphenylsilyl compound more readily than the corresponding trimethylsilyl compound.

A β-hydroxy effect is proposed to account for the result obtained from the reaction of fluoride ion and β-hydroxyvinylsilane[63]. To account for the course of the reaction, a cyclic transition state 107 is postulated. The mechanism proposed is the S_Ni-Si type.



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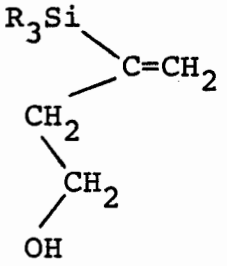
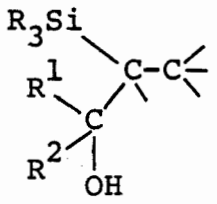
Such a cyclic transition state is favoured because of the following factors: (i) the strong hydrogen bond between hydroxy groups and the fluoride ion, (ii) the favourable entropy of the six-membered ring, (iii) the affinity of the fluoride ion for silicon, and (iv) the vinyl carbanion as the leaving group.

The specific role of the β-hydroxy group in this cleavage reaction can be further demonstrated by the fact that if the hydroxy group is moved from the β-position to the γ-position, as in the γ-hydroxy vinylsilane 108, no cleavage reaction occurs even under drastic reaction conditions (KF/DMSO/150°). Of



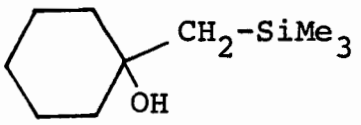
108

course, it has been mentioned previously that in the absence of the hydroxy group, no reaction will occur either. However, the mere presence of a β-hydroxy group does not always lead to the cleavage reaction. If the double bond is saturated as in structure 109, the cleavage of the silicon-alkyl carbon bond by fluoride ion does not occur even with the presence of a β-hydroxy group.



109

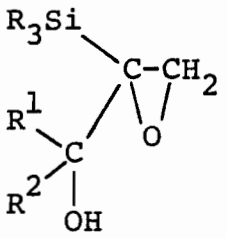
For example, compound 110 does not react with fluoride ion even at a temperature of 120°C.



110

These results show that cleavage of the silicon-vinyl carbon bond by fluoride ion occurs when a β-functionality exists. The β-functional group can act as a leaving group (in the case of chloride) or as a proton source (in the case of hydroxy group). A change in the nature of the functionality will alter the course or the rate of the reactions.

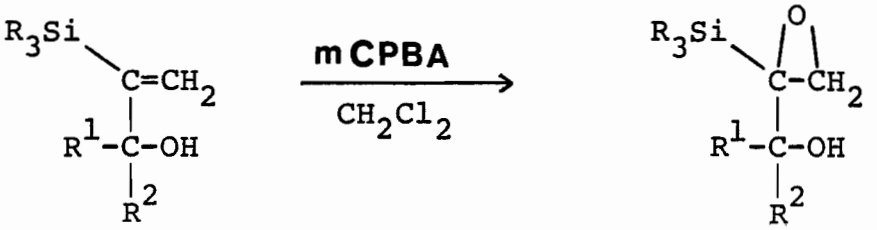
Fluoride ions also cleave silicon-carbon bonds of other systems. An example from Chapter 1 shows the cleavage of the silicon-carbon bond in β-chloro epoxysilanes to give allene oxides. Thus, the β-chlorovinylsilanes and their epoxysilanes react in the same manner with fluoride ions. β-Eliminations occur in which the chlorides act as leaving groups. By changing the β-functionality from a chloride to a hydroxy group, the reaction course is completely changed. β-Hydroxyvinylsilanes react with fluoride ions to give allylic alcohols. In view of the increasing interest of silyloxiranes in organic synthesis[13,46,54] and the expectation that the oxiranyl anion may be somewhere in between the vinyl anion and the alkyl anion in terms of basicity[123], we examine the cleavage of the silicon-carbon bond of the β-hydroxysilyloxiranes 111 by fluoride ions.



111

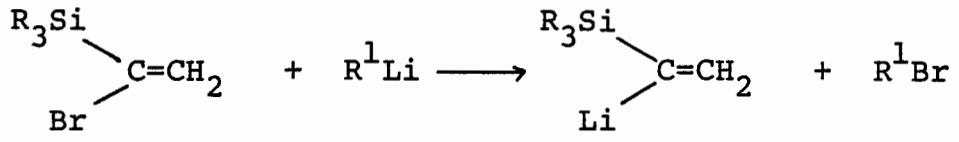
(b) PREPARATION OF THE β-HYDROXYSILYLOXIRANES

β-Hydroxysilyloxiranes 111 are obtained by epoxidation of the corresponding β-hydroxyvinylsilanes 37 with m-chloroperbenzoic acid in methylene chloride at room temperature.



37 111

In order to obtain the silyloxiranes 111 the β-hydroxyvinylsilanes 37 must be synthesized first. The starting materials for the synthesis of 37 are α-bromovinylsilanes 112. Depending on whether the R groups attached to silicon in 37 are phenyl or methyl groups, the starting material used will be α-bromovinyltriphenylsilane 112a or α-bromovinyltrimethylsilane 112b. It is found that[24,39,40] under low temperature a metal-halogen exchange reaction between α-bromovinylsilane and alkyllithium can occur to generate a vinyl carbanion α to silicon.



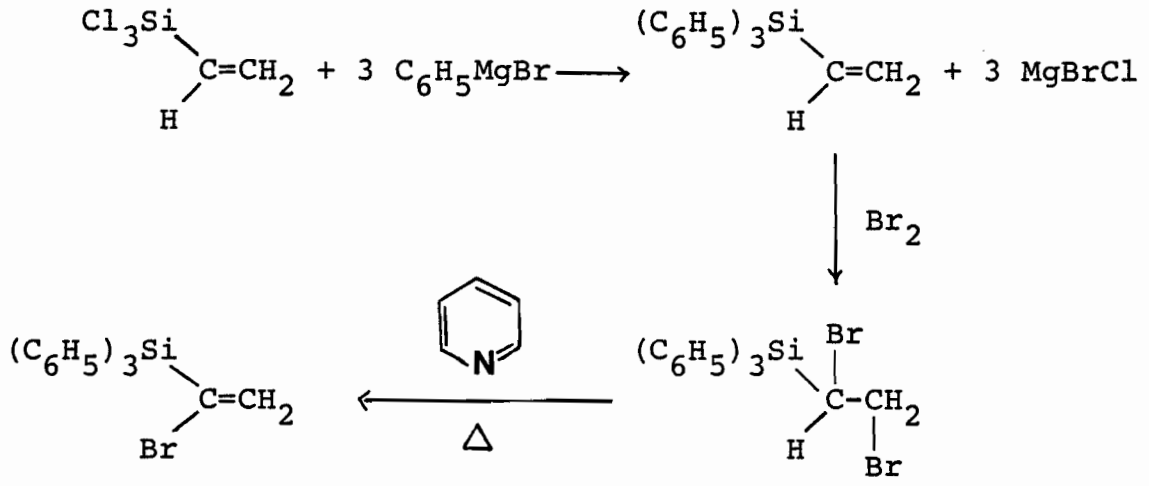
112

a) R = C_6H_5; R^1 = n-Bu (-24°C)

b) R = CH_3; R^1 = t-Bu (-78°C)

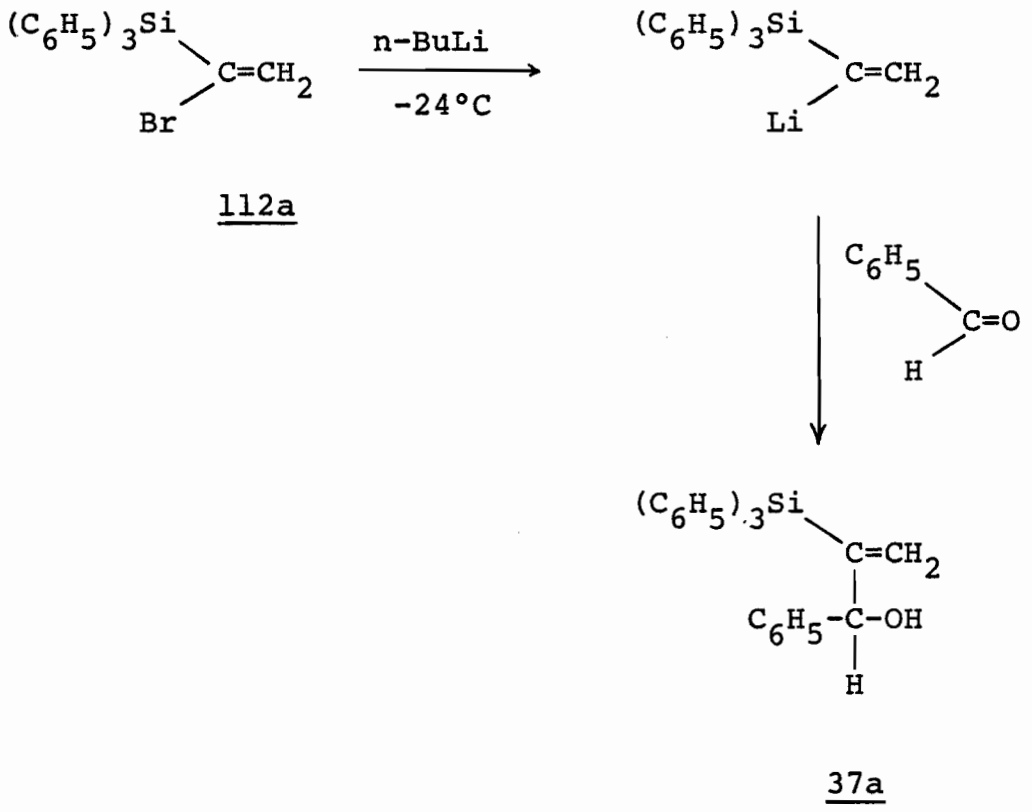
The vinyl carbanion reacts readily with a wide variety of carbonyl compounds to give the β-hydroxyvinylsilanes 37 in good yields.

In the case of β-hydroxyvinyltriphenylsilanes (R = C_6H_5), the starting material will be σ-bromovinyltriphenylsilane 112a. First of all, phenyl magnesium bromide is reacted with vinyltrichlorosilane[124] to give vinyltriphenylsilane. Bromination of the vinyltriphenylsilane followed by dehydrobromination[24] by refluxing pyridine gives the compound 112a.



112a

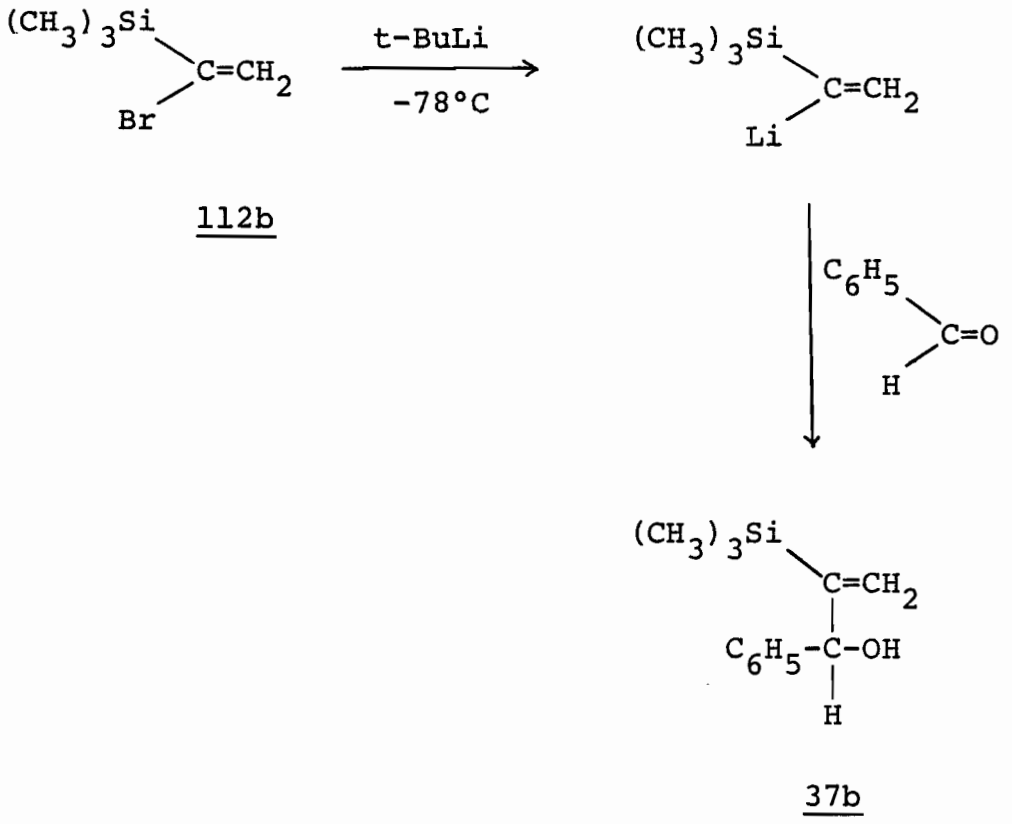
Treatment of 112a with n-butyllithium in diethyl ether at -24°C for two hours will give the vinyl carbanion. Quenching the reaction mixture with a carbonyl compound, e.g. benzaldehyde, followed by aqueous work up will give the β-hydroxyvinyltriphenylsilane 37a in good yield (75% after recrystallization). Compound 37a is a white crystalline solid and has a melting point of 84-85°C.



112a

37a

In the case when R=CH_3, the starting material α-bromovinyltrimethylsilane 112b is also prepared from vinyltrichlorosilane. Bromination of vinyltrichlorosilane followed by reaction with quinoline gives α-bromovinyltrichlorosilane. Treatment of α-bromovinyltrichlorosilane with methyl magnesium iodide will give the compound α-bromovinyltrimethylsilane 112b. Compound 112b reacts with t-butyllithium in diethyl ether at -78°C to give the vinyl carbanion. Quenching this reaction with a carbonyl compound, e.g. benzaldehyde, followed by aqueous work up will give the β-hydroxyvinyltrimethylsilane 37b in 80% yield. 37b is a colourless liquid and has a boiling point of 100-104°C at 4 mm Hg.



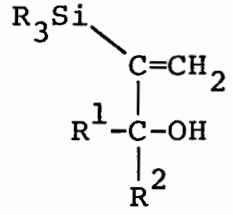
112b

37b

Some of the β-hydroxyvinylsilanes 37 prepared by these methods are listed in Table 5.

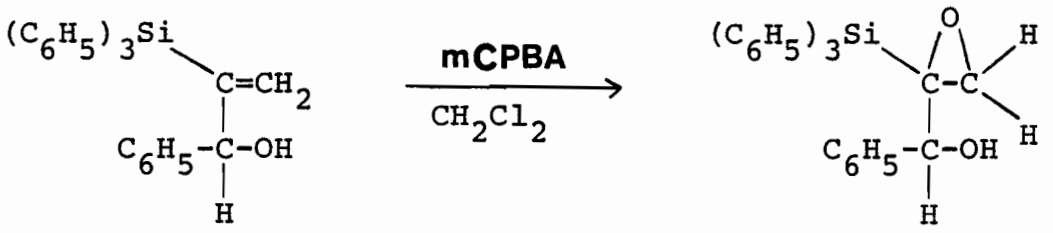
Once the β-hydroxyvinylsilanes 37 are synthesized, the epoxidation reaction proceeds smoothly to give corresponding β-hydroxysilyloxiranes 111. For example, in the preparation of 111a, 37a is stirred with 10% excess of the m-chloroperbenzoic acid in methylene chloride at room temperature for two hours. A white precipitate is formed. NMR of the reaction mixture shows no signals of the vinyl protons. Furthermore, new signals appear at δ = 2.7 and 3.1. Both signals are doublets. After work up and recrystallization, white crystals of 111a are obtained. Compound 111a has a melting point of

TABLE 5: SYNTHESIS OF 37



	R	R^1	R^2	Yield %	m.p.(°C) or b.p.(°C/mm Hg)
a)	C_6H_5	H	C_6H_5	75	84-85
b)	CH_3	H	C_6H_5	80	100-104/4
c)	C_6H_5	H	CH_3	75	61-64
d)	CH_3	-cyclo C_5H_{10}-		75	67-69/0.9
e)	C_6H_5	C_6H_5	C_6H_5	80	106-108

105-106°C. NMR data of 111a: δ = 7.3 (m, 20H), 5.1 (s, 1H), 3.1 (d, 1H), 2.7 (d, 1H), 2.6 (b, 1H). On addition of D_2O, the signal at δ = 2.6 disappears. This indicates that δ = 2.6 is a hydroxy group.

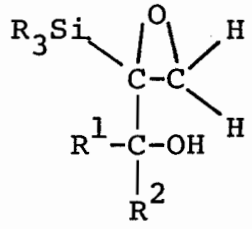


37a 111a

Similar epoxidation can be applied to β-hydroxyvinyl-trimethylsilanes, e.g. to compound 37b. However, the epoxidation of these trimethylsilyl compounds proceeds faster than the corresponding triphenylsilyl compound. NMR shows that the epoxidation of 37b takes only 30 minutes to complete. Work up of the reaction gives a light yellow liquid. 111b Has a boiling point of 147-150°C at 6 mm Hg. NMR data for compound 111b: δ = 7.5 (m, 5H), 4.9 (s, 1H), 3.2 (d, 1H), 2.7 (d, 1H), 3.0 (b, 1H), 0.0 (s, 9H).

Olefins can be epoxidized by a number of peracids, of which m-chloroperbenzoic acid is the most often used. The reaction has wide utility[125]. Conditions of the reaction are mild and yields are high. Also the presence of other groups like alkyl, aryl or hydroxy groups do not affect the reaction. All these facts are demonstrated in the above epoxidation reactions of the β-hydroxyvinylsilanes. Electron-donating groups increase the rate of the reaction because they make

TABLE 6: SYNTHESIS OF COMPOUNDS 111

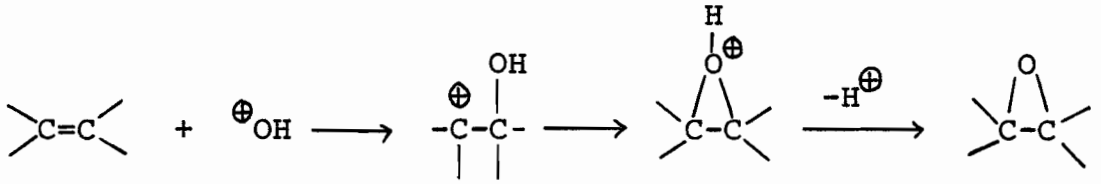


	R	R^1	R^2	Yield %	m.p.(°C) or b.p.(°C/mm Hg)
a)	C_6H_5	H	C_6H_5	80	105-106
b)	CH_3	H	C_6H_5	74	147-150/6
c)	C_6H_5	H	CH_3	72	127-129
d)	CH_3	-cyclo C_5H_{10}-		94[a]	

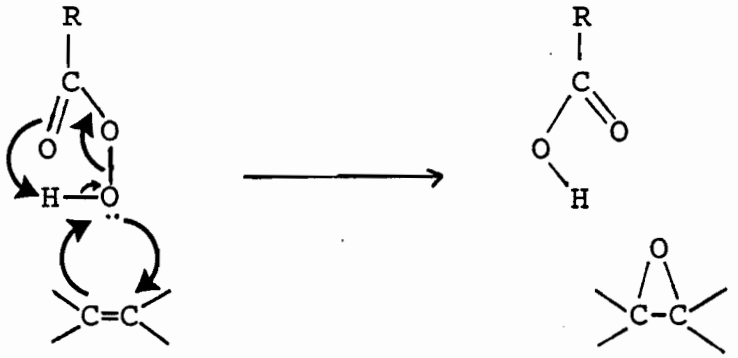
a) Crude yield of colourless liquid

the double bond more nucleophilic. This may be one of the reasons why the trimethylsilyl compound 37b epoxidizes faster than the triphenylsilyl compound 37a. Methyl group is considered to be electron-donating. Thus, the silicon of the trimethylsilyl group should be less electrophilic than the silicon of the triphenylsilyl group. Another reason for the difference in reactivity may be because the triphenylsilyl group is more bulky than the trimethylsilyl group. This will hinder the epoxidation reaction. Thus, it is easier to epoxidize compound 37b than compound 37a.

Several mechanisms have been proposed for the epoxidation reaction. One mechanism proposed for the reaction involves attack by OH^+, formed by ionization of the peracid[126].



However, another mechanism which has won greater acceptance involves the simultaneous forming and breaking of all the bonds involved.



Evidence for this mechanism[127] is: (i) The reaction is second order. If ionization of the peracid is the rate determining step, it would be first order in peracid. (ii) The reaction takes place readily in non polar solvents. This is not favourable if the formation of ion is involved. (iii) The addition is stereospecific. That is, a trans olefin gives a trans epoxide, and a cis olefin gives a cis epoxide.

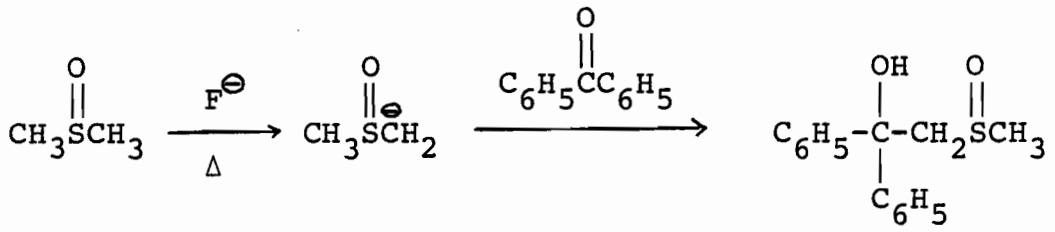
(c) REACTION OF FLUORIDE ION WITH BETA-HYDROXYSILYLOXIRANES

Once the silyloxiranes are synthesized, their reactions with fluoride ion can be studied. Different fluoride salts can be used in the cleavage reactions. However, inorganic fluorides such as potassium fluoride and cesium fluoride are not very soluble in common organic solvents. Reactions tend to proceed more slowly because of this drawback. Tetraethylammonium fluoride seems to be the best choice for the cleavage reactions.

The reagent, tetraethylammonium fluoride is commercially available. However, it can be prepared from tetraethylammonium bromide and silver fluoride in aqueous solution[128]. The solution is concentrated in vacuo. Acetonitrile is then added and removed again in vacuo to eliminate traces of water. The reagent can also be prepared by titration of tetraethylammonium hydroxide with Hydrofluoric acid. This titration method is adopted by our laboratory for the preparation of tetraethylammonium fluoride.

Acetonitrile and dimethylsulfoxide are good solvents for

the reagent, tetraethylammonium fluoride. However, DMSO reacts slowly with the fluoride at slightly elevated temperature. The hydroxysulfoxide 113 is isolated from the mixture of the fluoride and DMSO after treatment with benzophenone. This proves the formation of the methylsulfinyl carbanion 114[129].



114 113

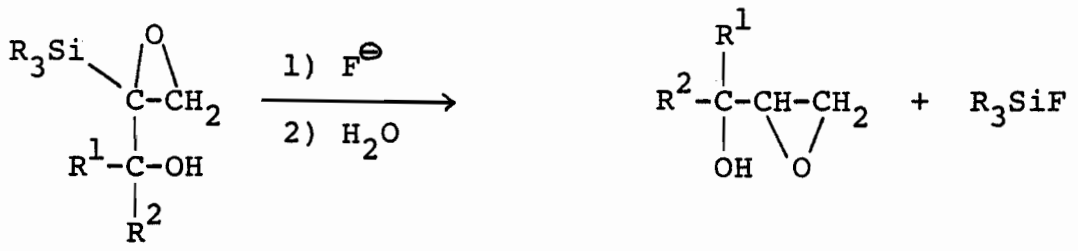
In solution or in solid state, decomposition of tetraethylammonium fluoride can occur when heated over 80°C. Ethylene, triethylamine and hydrogen fluoride are the products identified[130]. Also the fluoride compound is liable to lose its reactivity if the reaction mixture is contaminated with water.

Tetraethylammonium fluoride can effect the α-elimination of hydrogen halide from haloform producing dihalonorcarane in the presence of cyclohexene[128]. This example of proton abstraction by fluoride ion shows definitely the ability of the fluoride ion to act as a base in aprotic solvents.

A mixture of the compound 111 and tetraethylammonium fluoride (1.1 equivalent) in acetonitrile is stirred at room temperature. TLC or NMR is used to follow the reaction.

After two hours the reaction mixture is quenched with

water and extracted with ether. Compound 115 is then formed.



111 115

a) $R = R^2 = C_6H_5$, $R^1 = H$ a) $R^1 = H$, $R^2 = C_6H_5$

b) $R = CH_3$, $R^1 = H$, $R^2 = C_6H_5$

c) $R = C_6H_5$, $R^1 = H$, $R^2 = CH_3$ c) $R^1 = H$, $R^2 = CH_3$

d) $R = CH_3$, $R^1R^2 = $ -cyclo-$(CH_2)_5$- d) $R^1R^2 = $ -cyclo$(CH_2)_5$-

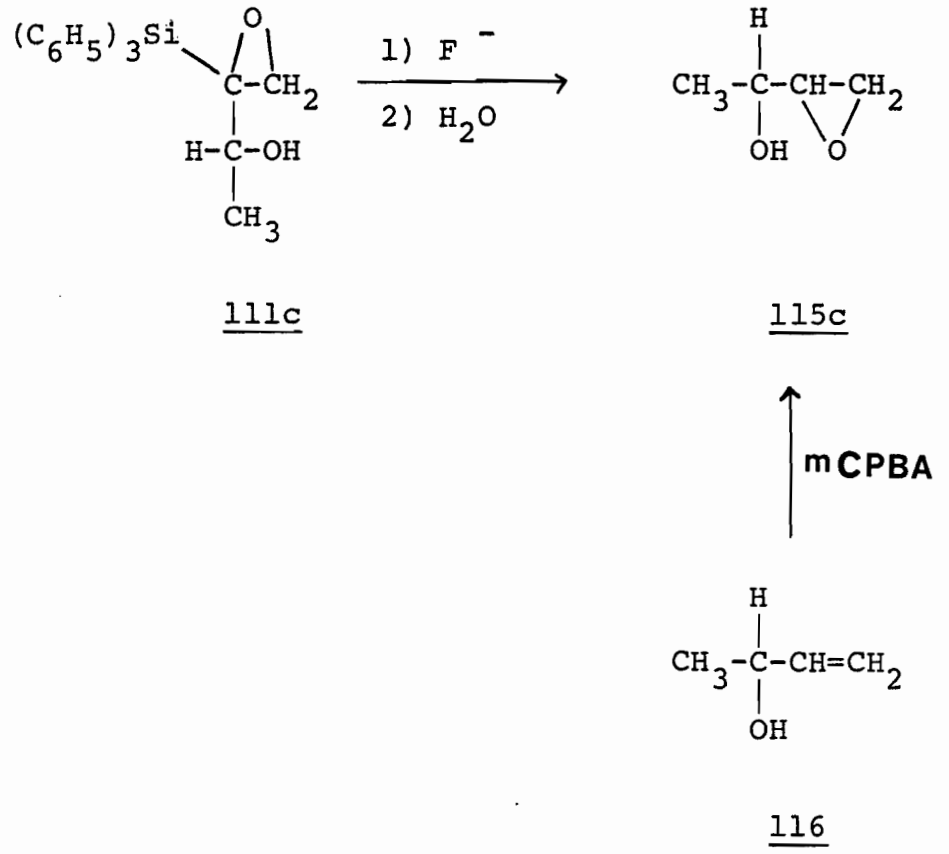
Using the above conditions the replacement of the silyl groups of all the β-hydroxysilyloxiranes by proton can indeed be achieved with relative ease. For example in the case of 111a, the reaction with 1.1 equivalent of tetraethylammonium fluoride in acetonitrile is followed by TLC. A white precipitate forms after stirring for a few minutes. After stirring for two hours, TLC shows that no more starting material is present. Work up of the reaction followed by isolation using preparative TLC gives the product 115a, a colourless oil, in good yield. NMR data for 115a: δ = 7.3 (s, 5H), 4.8 (d, 1H), 3.2 (q, 1H), 2.8 (two q, 2H), 2.4 (b, 1H). The signal at 1430 cm^{-1} in the IR of the starting material 111a indicating the presence of the silicon-phenyl bond has disappeared in the

IR of the product 115a, confirming the cleavage of the silicon-carbon bond. Two other products are isolated from the preparative TLC. Both of them are colourless crystals. One melts at 135-138°C and has NMR identical to triphenylsilanol. The other solid melts at 220-222°C and is identical to hexaphenyldisiloxane.

The cleavage reaction is also carried out for compound 111b. TLC shows that the reaction is completed after stirring at room temperature for one hour. Purification after the work up gives the product 115a. It has identical NMR spectral data with the product from the cleavage reaction of 111a. One interesting note is that the cleavage of these two β-hydroxysilyloxiranes 111a and 111b is very fast. This is quite different from the cleavage reaction of their precursors, the β-hydroxyvinylsilanes 37a and 37b. In that case the cleavage reaction of the trimethylsilyl compound 37b is much slower than the reaction with the triphenylsilyl compound 37a. Also when comparing the two trimethylsilyl compounds 37b and 111b, the cleavage reaction of β-hydroxysilyloxirane 111b is much faster than the reaction with β-hydroxyvinylsilane 37b.

The identities of compounds 115 are secured by standard spectroscopic means as well as by comparison with authentic compounds prepared by epoxidation of the corresponding allylic alcohols. For example in the cleavage reaction of compound 111c, TLC shows that the reaction is finished after two hours. The product 115c is isolated. NMR data for 115c: δ = 1.2 (d, 3H). 2.6 (two d, 2H), 2.8 (m, 1H), 3.2 (b, 1H), 3.6 (m, 1H).

However, compound 115c can also be prepared by the epoxidation of the commercially available 3-buten-2-ol 116.



111c

115c

116

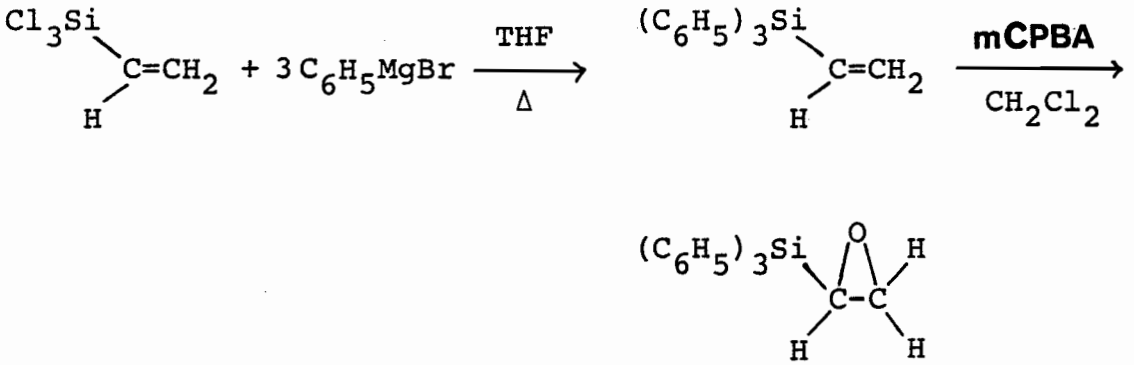
Indeed, a white precipitate of m-chlorobenzoic acid is formed after the mixture of 116 and 1.1 equivalent of m-chloroperbenzoic acid is stirred at room temperature for one hour. Stirring is continued for another two hours before work up. The product distills at 131°C as a colourless liquid. It is identical in all respects in spectral data (NMR and IR) with the product of the cleavage reaction of compound 111c by fluoride ion.

Similar cleavage reaction by fluoride ion can be carried out smoothly on compound 111d to give the product 115d at

room temperature in good yield. NMR data for compound 115d: δ = 1.6 (b, 10H), 2.5 to 2.9 (m, 3H), 3.0 (b, 1H).

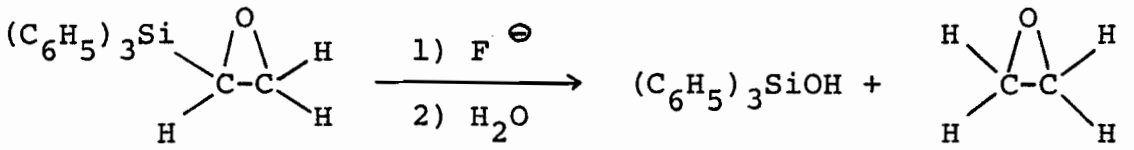
(d) REACTION OF FLUORIDE ION WITH SIMPLE SILYLOXIRANES

Comparison of the relative rates of reaction with fluoride ion shows that it is easier to cleave the silicon-carbon bond in β-hydroxysilyloxiranes 111 than in β-hydroxy-vinylsilanes 37. In both cases the β-functionality is present. This leads us to investigate the reaction of simple triorgano-silyloxiranes with fluoride ion. The first simple silyloxirane studied is triphenylsilyloxirane 117. Triphenylsilyloxirane 117 can be prepared from the readily available vinyltrichloro-silane. Reaction of the Grignard reagent phenyl magnesium bromide with vinyltrichlorosilane in refluxing tetrahydrofuran gives vinyltriphenylsilane in good yield. Epoxidation of vinyltriphenylsilane by m-chloroperbenzoic acid in methylene chloride gives the compound triphenylsilyloxirane (isolated yield: 83%; m.p. 70-71°C).



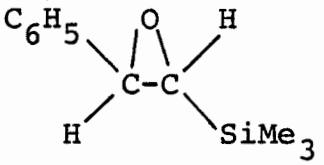
117

The reaction of triphenylsilyloxirane with tetraethylammonium fluoride in acetonitrile at room temperature is followed by TLC. The reaction is finished in two hours. Work up of the reaction mixture gives a crude solid. Preparative TLC gives a white solid of melting point 136-138°C. NMR indicates the solid is triphenylsilanol. This is the only product obtained. Once the reaction conditions are established, an effort is made to isolate ethylene oxide, the other low boiling product (b.p. $\sim$ 15°C). Fortunately, the ethylene oxide can be isolated in a cold trap (-78°C) containing carbon tetrachloride by constantly passing nitrogen gas slowly through the reaction mixture during the reaction. In this particular reaction dimethylsulfoxide is used as solvent instead of acetonitrile, because DMSO has a higher boiling point than acetonitrile. The solvent will be less easily flushed out by the nitrogen gas. NMR of the distillate collected in the cold trap has only one signal, a singlet at $\delta = 2.6$. This is the signal of the protons of ethylene oxide. To further prove this, a drop of authentic ethylene oxide is added to the distillate. NMR shows one signal only at $\delta = 2.6$. This signal is more intense than it was before adding the authentic ethylene oxide. No other signals are present. This shows that the compound collected in the cold trap is ethylene oxide from the cleavage reaction of triphenylsilyloxirane by fluoride ion. Work up of the reaction mixture gives, once again, white crystals of triphenylsilanol.



117

Another silyloxirane used in the reaction with fluoride ion is trans-1-phenyl-2-trimethylsilyloxirane 118.

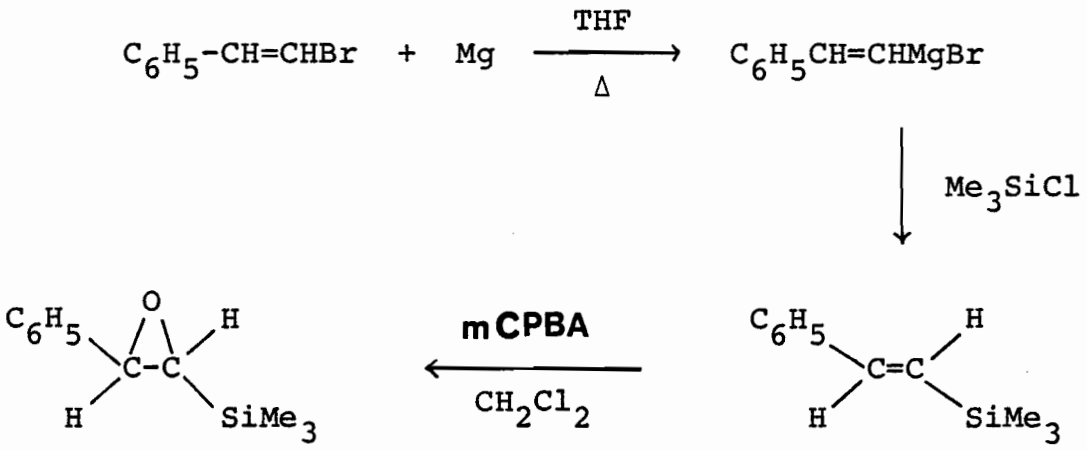


118

Compound 118 is prepared by the epoxidation of trans-β-styryltrimethylsilane 119. Compound 119 is synthesized according to the method of Seyferth[103]. Freshly distilled commercially available β-bromostyrene is reacted with magnesium in refluxing THF to give the corresponding magnesium bromide. Reaction of this Grignard reagent with trimethylchlorosilane gives the compound 119 in 65% yield. Compound 119 is a colourless liquid with a boiling point of 80-82°C at 2.5 mm Hg. NMR of 119 shows the coupling constant of the vinyl protons to be 18 HZ, indicating trans configuration.

The epoxidation reaction of compound 119 is carried out smoothly using m-chloroperbenzoic acid. A vigorous reaction occurs about half a minute after addition of the peracid to 119, and a white precipitate is formed. NMR taken after half

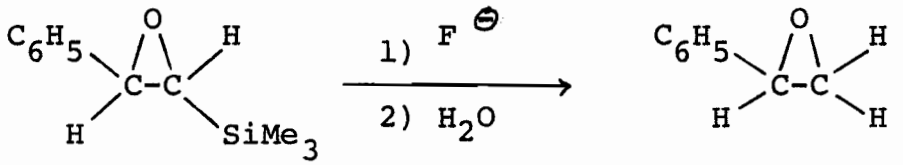
an hour of reaction time shows that the vinyl protons are gone. Work up of the reaction gives the crude epoxide. Compound 118 is purified by distillation. It is collected as a colourless liquid at a boiling point of 83-85°C at 0.7 mm Hg. NMR for 118: δ = 0.4 (s, 9H), 2.4 (d, 1H), 3.8 (d, 1H), 7.3 (s, 5H).



118 119

Different types of fluoride salts in different solvents have been used in the cleavage reaction of compound 118. However, tetraethylammonium fluoride is by far the best, possibly, because of its high solubility in the solvent. Either acetonitrile or dimethylsulfoxide can be used as solvent. For example, trans-1-phenyl-2-trimethylsilyloxirane 118 on treatment with 1.1 equivalent of tetraethylammonium fluoride in dimethylsulfoxide at room temperature followed by quenching with water gives styrene oxide 120 in good yield. The product is compared with authentic styrene oxide.

They are identical in NMR data. NMR for product 120 is: δ = 2.7 (m, 1H), 3.1 (m, 1H), 3.8 (m, 1H), 7.3 (s, 5H). The chemical shifts of the protons found in the styrene oxide product 120 are in agreement with those assigned by Reilly[131].



118 120

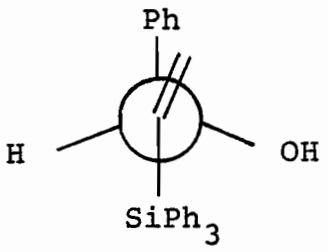
Thus, both the simple and β-substituted silyloxiranes react smoothly with fluoride ions to give the corresponding oxiranes in which the triorganosilyl group is replaced by a proton. The reaction behaves the same way as the cleavage reaction of fluoride ion on β-hydroxyvinylsilanes. However, the rate of the cleavage reaction is very much faster in the cases of the silyloxiranes.

(e) STEREOCHEMISTRY OF SUBSTITUTION AT THE OXIRANYL CARBON

The products of the cleavage reaction with fluoride ion have been identified. However, the stereochemistry of substitution at the oxiranyl carbon has not been established. This problem has been examined on the basis of the following experiments.

Epoxidation of compound 37a occurs in a stereoselective manner to give the epoxy compound 111a as one diastereomer. While the stereochemistry of compound 111a has not been

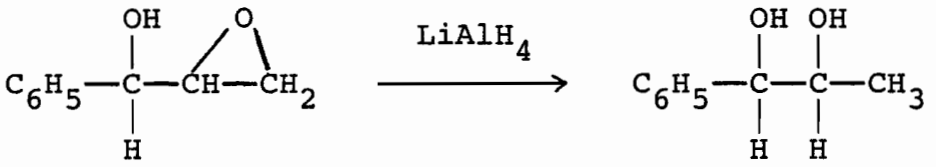
established with certainty, it is argued that the preferred conformation of 37a is likely to have the vinyl group eclipsed with the phenyl group. Eclipsed conformation has been found to be general for alkenes[132]. Epoxidation of 37a occurs on



37a

the same side as the hydroxy group. Whitham[133], in his studies of epoxidation of allylic alcohols with peroxy-acids, concludes that in epoxidation the allylic alcohol assumes a certain preferred geometry. The peroxy-acid is considered to be positioned on the face of the double bond proximate to the hydroxy group. Hydrogen bonding between the hydroxy group of the allylic alcohol and the peroxy-acid is possible. Epoxidation, thus, occurs on the same side as the hydroxy group because of this arrangement.

The stereochemistry of compound 115a can be deduced definitely by lithium aluminum hydride reduction. The reduction product is identified to be erythro-1-phenylpropane-1,2-diol 121 by NMR[134] and its melting point[135].

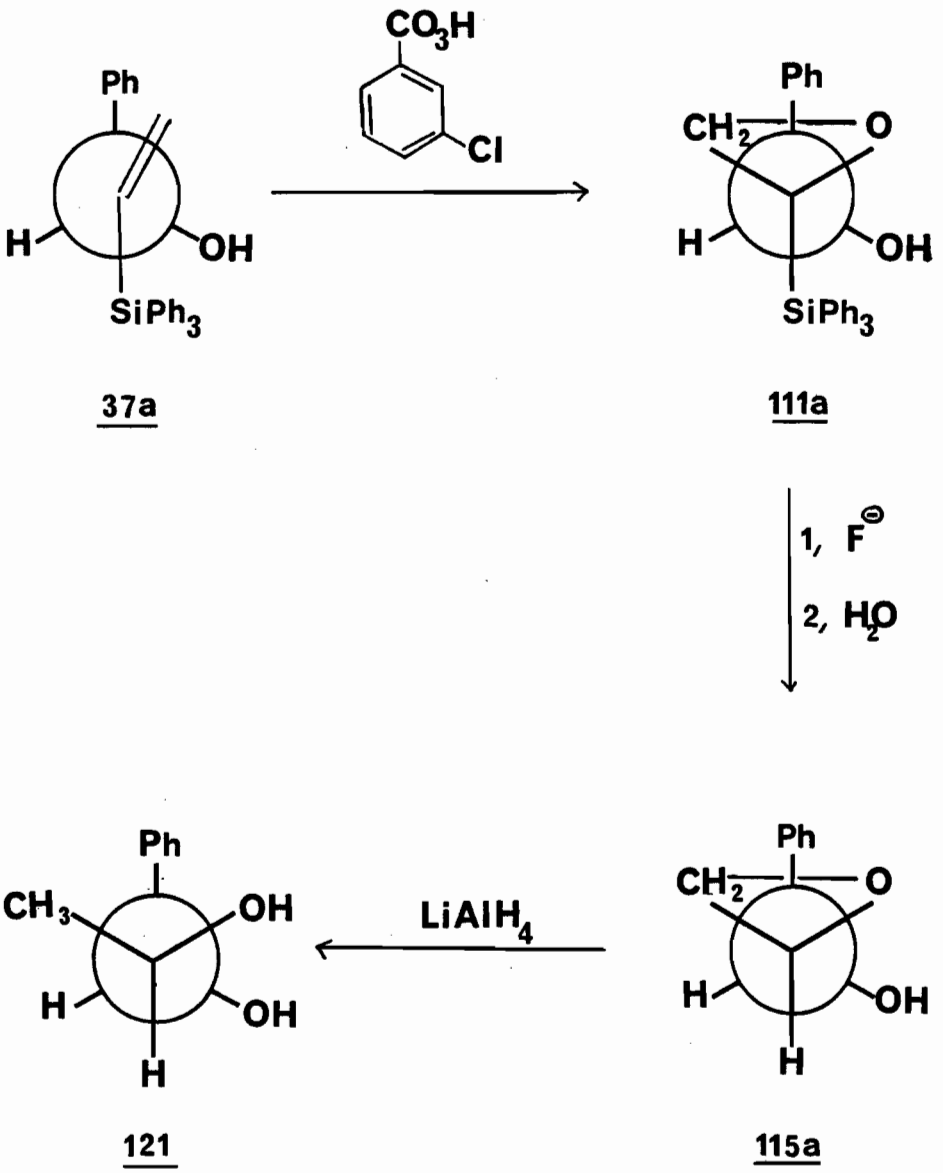


115a 121

The reduction reaction is carried out as follows. Compound 115a is stirred with an equivalent amount of lithium aluminum hydride in ether at room temperature overnight. Work up of the reaction mixture with water and a little sulfuric acid gives the crude diol. The diol is recrystallized using petroleum ether and carbon tetrachloride. The colourless crystals obtained have a melting point of 90-91°C. The literature[135] melting point for the erythro isomer is 92-93°C, while for the threo isomer the melting point is 54-55°C. NMR for the obtained compound 121 is: δ = 1.1 (d, 3H), 2.2 to 2.7 (b, 2H), 4.0 (m, 1H), 4.7 (d, 1H), 7.2 (s, 5H). On additon of D_2O the broad signal at δ = 2.2 to 2.7 disappears. This indicates the presence of hydroxy group. The IR of 121 shows signals at 3240 cm^{-1} and 3380 cm^{-1}. This indicates the presence of two hydroxy groups. The chemical shift of the methyl group in the NMR is at δ = 1.1. This is in agreement with the finding by Schmid[134]. He has reported that the methyl signal of the erythro isomer appears at a lower magnetic field than the corresponding threo isomer. This is because the methyl protons of the erythro isomer are less shielded by the aromatic ring. Chemical shift for the methyl protons of the threo isomer is

δ = 1.02.

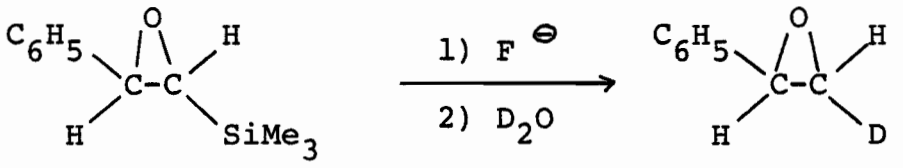
The identification of the reduction product 121 to be the erythro isomer helps to establish the stereochemistry of its precursor, the compound 115a. The reduction of epoxides with lithium aluminum hydride alone involves the attack of hydride at the least substituted carbon[136] giving the terminal methyl group. In order to obtain the erythro isomer, the stereochemistry of 115a must be that shown in Scheme 9.



SCHEME 9

In Scheme 9 the hydride will add to the least substituted carbon, i.e. to the methylene carbon. Thus, the epoxide will open in such a way that the two hydroxy groups are on the same side of the molecule, giving the erythro isomer 121. Since the preferred conformation of 37a is likely to have the vinyl group eclipsing the phenyl group and the epoxidation of 37a occurs on the same side as the hydroxy group, the stereochemistry of 111a is likely to be that shown in Scheme 9. Thus, the stereochemistries of both 111a and 115a are established in Scheme 9. Looking at the cleavage reaction by fluoride ion in Scheme 9, the transformation of 111a to 115a involves the replacement of the triphenylsilyl group by a proton with no change in the stereochemistry. Thus the cleavage reaction of the silicon-carbon bond by fluoride ion goes with retention of configuration at the oxiranyl carbon. Similar stereospecific transformations are obtained for the sequence 37b → 111b → 115a. The replacement of the silyl group by proton occurs with retention of configuration at carbon.

Retention of configuration at the oxiranyl carbon can be definitely demonstrated in the conversion of trans-1-phenyl-2-trimethylsilyloxirane 118 to the partly deuterated styrene oxide 122.



118 122

A solution of 118 and tetraethylammonium fluoride in 1 ml of DMSO-d_6 is stirred for one minute at room temperature. The reaction mixture is then poured into 20 ml D_2O. The styrene oxide is isolated in good yield and is found by mass spectrometry to have approximately 33% deuterium incorporation.

This approximate calculation is based on the abundance of the molecular ion M^+ and its isotope peak $(M+1)^+$ in the mass spectra of the standard styrene oxide and the partly deuterated styrene oxide product 122. Under the same conditions, the mass spectra of both compounds are obtained. From the mass spectrum of the standard styrene oxide, signals at m/e 120 and 121 indicate the presence of the molecular ion M^+ and its isotope peak $(M+1)^+$. The ratio of the abundance of m/e 120 to 121 is 100:12.5. For compound 122, the mass spectrum shows signals at m/e 120 and 121. The ratio of abundance of M:M+1 is 100:66. Therefore, the difference in abundance at m/e 121 between the two spectra is due to deuterium incorporation, i.e. this 53.5 unit of $(M+1)^+$ is from deuteration of the styrene oxide.

Therefore, the ratio of M:M+1 after deuteration is 100:53.5. The amount of deuteration is:

$$\frac{53.5}{100+53.5} \times 100\% = \sim 33\%$$

The NMR of compound 122 also shows deuterium incorporation with all the deuterium confined to the trans position. Both the 60 MZ and the 100 MZ NMR integrations give the relative

ratios of the trans-proton, the cis-proton and the benzylic proton as 0.67/1.00/1.00. This shows a 33% deuterium incorporation exclusively at the trans-position. The modest deuterium incorporation is due in part to the trace of water inevitably present in the tetraethylammonium fluoride. However, the exclusive deuteration at the trans-position shows retention of configuration at the oxiranyl carbon during the cleavage reaction by fluoride ion.

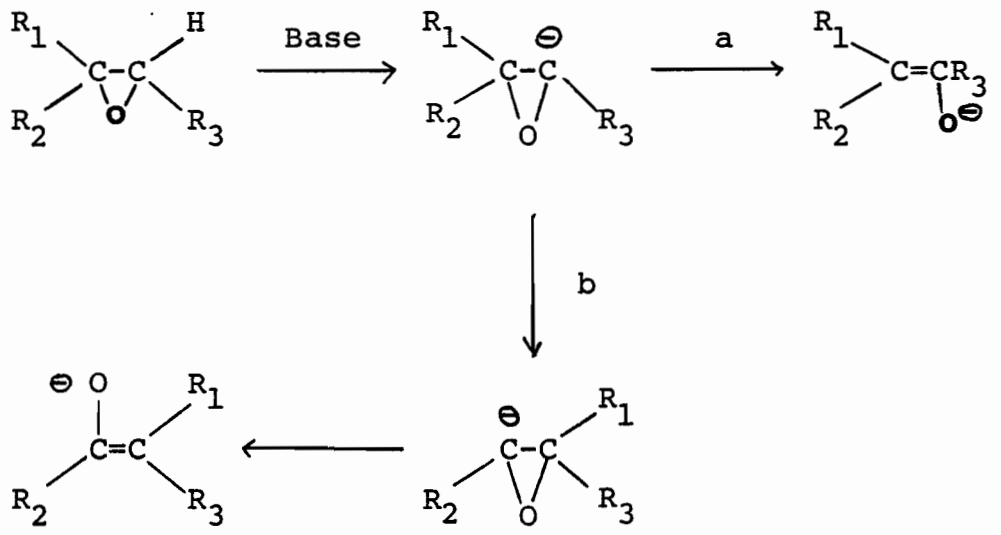
(f) MECHANISM OF THE CLEAVAGE REACTION

Two mechanisms can be considered to account for the observed retention of configuration in these cleavage reactions. The first one involves a frontside electrophilic substitution at the oxiranyl carbon[137]. The silicon-carbon bond cleavage occurs in the same transition state that involves the carbon-hydrogen bond formation on the same side. No carbanion is involved because the forming and breaking of bonds occur simultaneously. This mechanism, however, is considered less likely in view of the relative order of reactivity of alkynyl > vinyl > alkyl. The rate of the cleavage reaction of silyloxiranes by fluoride ion is comparable to the rate of the cleavage of silicon-alkynyl to carbon bond, and it is certainly faster than the rate of the cleavage of the silicon-vinyl carbon bond. Thus, silyloxiranes can be placed in between silicon-alkynyl and silicon-vinyl in relative order of reactivity. In both the alkynyl and vinyl cases, cleavage reactions

involve the formation of anions. Thus, some carbanionic character must have developed at the carbon centre in the cleavage reactions of silyloxiranes.

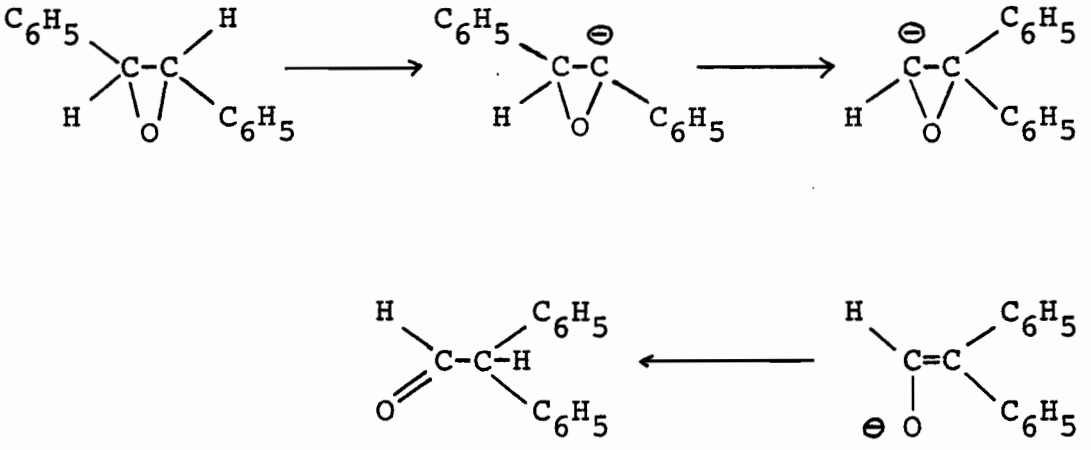
In the case of the second mechanism, an oxiranyl anion is postulated as the intermediate. Oxiranyl anion has previously been implicated in the base catalyst rearrangement of epoxides[138]. Cope has studied the reaction of a number of phenyl substituted ethylene oxides with the base lithium diethylamide. Trans-stilbene oxide reacts with the base to give diphenylacetaldehyde while 1,1-diphenyl-2-p-totyl-ethylene oxide yields benzhydryl-p-totyl ketone. However, tetraphenylethylene oxide does not react with the base. To account for these results, a mechanism is proposed based on the abstraction of a proton from the oxirane ring by the base followed by ring opening or rearrangement.

The first step would be the removal of a proton from the oxiranyl ring by the diethylamide ion to give an oxiranyl anion. Accordingly the fully substituted tetraphenylethylene oxide does not react with the base because there is no proton to be abstracted. Once the proton has been removed for the other compounds involved, ring opening can occur directly to give the anion of a carbonyl compound (path a) or rearrangement can occur (path b) to give another isomeric product (See Scheme 10).



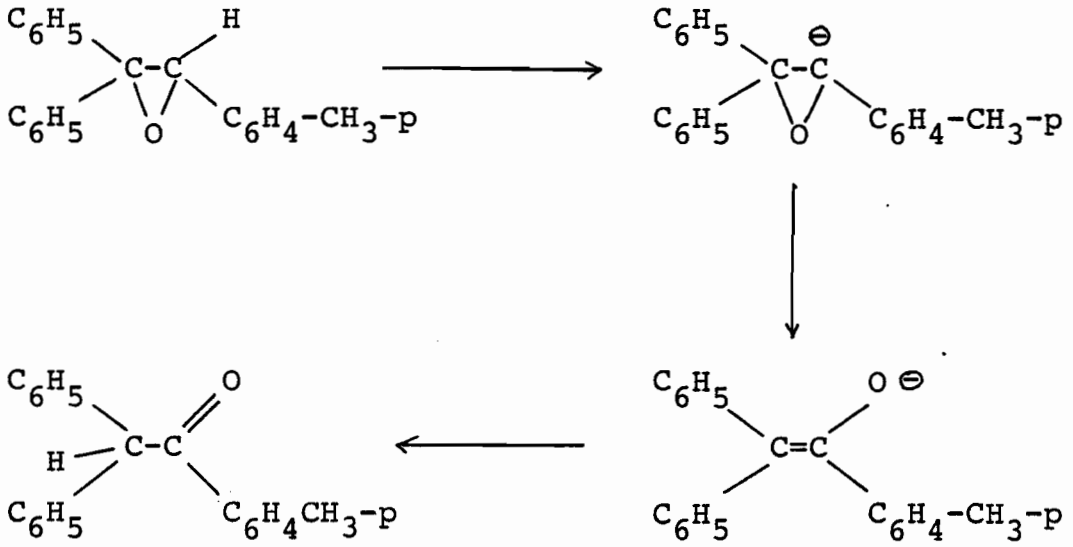
SCHEME 10

With trans-stilbene oxide the product of the reaction shows that a phenyl group has migrated (path b) to give the rearranged diphenylacetaldehyde.



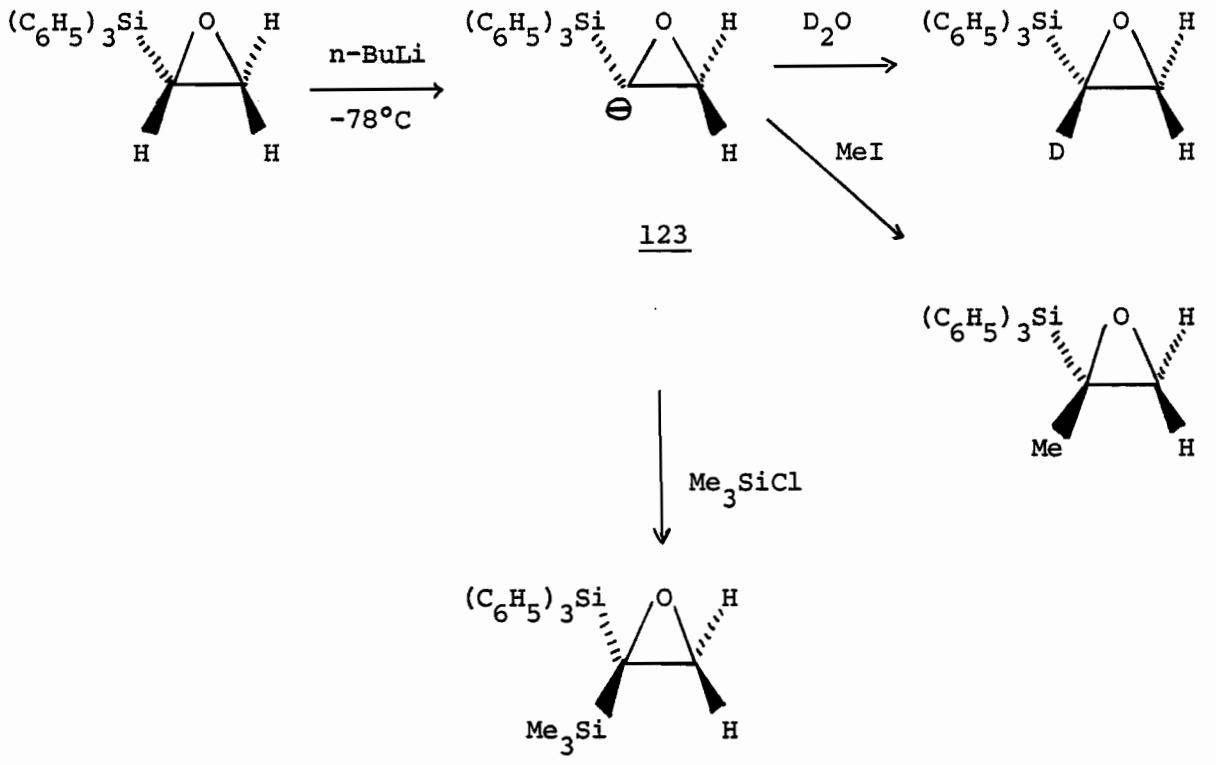
In the case of 1,1-diphenyl-2-p-totylethylene oxide, the structure of the product shows no migration of an aryl

group occurred in this case, i.e. path (a) is followed.



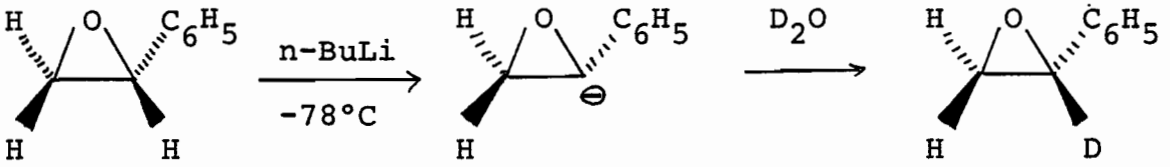
No matter what reaction path is followed in these reactions, oxiranyl anions are postulated as intermediates.

Concurrent with our work, evidence for the existence of oxiranyl anions as intermediates has been found during a study of the reactions of organolithium reagents with epoxyalkylsilanes[139]. It has been found[140] that n-butyllithium in tetrahydrofuran is able to metalate triphenylsilyloxirane 117 at -78°C in high yield and exclusively on the oxiranyl carbon α to silicon. The resulting oxiranyl carbanion 123 is found to retain its stereochemical and structural integrity at this temperature, and it can be quenched with various reagents to give derivatives in high yields with retention of configuration at the carbon centre involved (Scheme 11).



SCHEME 11

The metalation of epoxides does not require the presence of an α-substituted silyl group. For example, styrene oxide can be metalated exclusively at the carbon α to the phenyl group to give an oxiranyl anion 124 by either n-butyl or t-butyllithium in THF at -78°C or -95°C respectively. Quenching this reaction mixture with D_2O gives only 50% α-deuterated product while 50% of the starting material is recovered. This shows that the metalation is not as complete as in the cases of silyloxiranes. However, it indicates that the oxiranyl anion is formed by metalation as the intermediate of the reaction.



The presence of sulfur or phosphorus groups at the α position does not affect the metalation of epoxides[141]. Examples of oxiranyl anions with sulfur or phosphorus groups have been formed. Like other oxiranyl anions, they can be quenched with various reagents to give derivatives with retention of configuration at the carbon centre.

All these examples indicate that an oxiranyl anion is involved as a reaction intermediate. It is very likely that the cleavage of the silicon-carbon bond of silyloxiranes by fluoride ions also involves oxiranyl anions as intermediates. Another feature that favours the formation of an oxiranyl anion as an intermediate is the stability of the oxiranyl anion formed. When the carbanionic carbon is next to oxygen as in the case of oxiranyl anion, there is inductive stabilization. The electron withdrawing inductive effect stabilizes the carbanion further since the more electronegative oxygen is better capable than carbon of bearing a negative charge. Thus the stability of the ion is even greater because of induction.

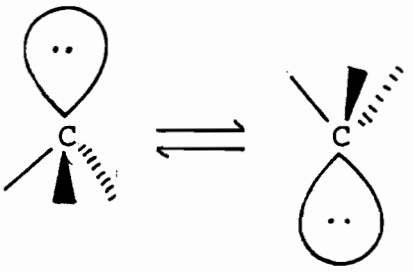
Inasmuch as the present reaction gives an indication of the nature of carbanionic character at the carbon centre, the results also suggest that:

i) Oxiranyl anion is comparable to alkynyl anion as a leaving group. As seen from the different types of cleavage

reactions, the cleavage of the silicon-carbon bond in silyloxiranes (both with and without the beta functionalities) is faster than the cleavage of the silicon-carbon bond in β-hydroxyvinylsilanes. Actually the rate of the cleavage of the silicon-carbon bond in silyloxiranes is comparable to the cleavage of the silicon-alkynyl carbon bond. Thus, the oxiranyl anion has the ability to be a very good leaving group.

ii) The rate of inversion of the oxiranyl anion is sufficiently slow with respect to proton transfer that the stereochemical integrity at the oxiranyl carbon is maintained.

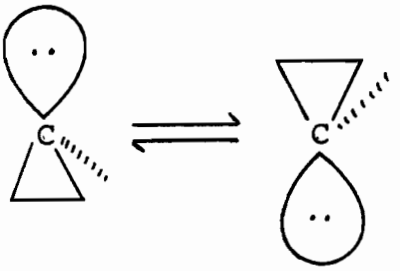
The structure of a simple carbanion is likely to have the central carbon being sp^3 hybridized with the unshared pair of electrons occupying one apex of the tetrahedron. Carbanions would thus have pyramidal structures, similar to those of amines. Like amines, the unshared pair and the central carbon of the carbanion oscillate rapidly from one side of the plane to the other, i.e. the pyramidal inversion of carbanions and amines are very fast.



FAST INVERSION

The energy barrier to pyramidal inversion of tercovalent nitrogen is greatly increased by ring strain when nitrogen is in a three-membered ring[142]. Inversion is more difficult

because it is not easy to go through the planar transition state in a strained ring. The presence of an adjacent hetero-atom will further increase the energy barrier for inversion due to the repulsion between unshared electron pairs of the nitrogen and those of the adjacent hetero-atom. Therefore oxaziridines have very high energy barriers for inversion[143]. Similarly the energy barrier to pyramidal inversion for carbon is very high because of ring strain in cyclopropyl carbanions. Inversion is slow because it is not easy to invert through the planar transition state.



SLOW INVERSION

By putting a hetero-atom into the cyclopropyl ring as in the case of oxiranyl carbanions, the inversion energy barrier is even higher just as in the cases of oxaziridines because of repulsion of the electron pairs. Thus, the pyramidal inversion rate is very slow at the carbon centre for oxiranyl anion. Thus, the stereochemical integrity at the oxiranyl carbon is maintained because of the extremely slow inversion rate.

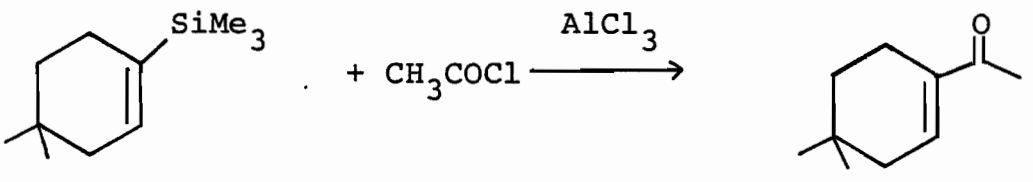
CHAPTER 4

ALLYLSILANES IN ORGANIC SYNTHESIS

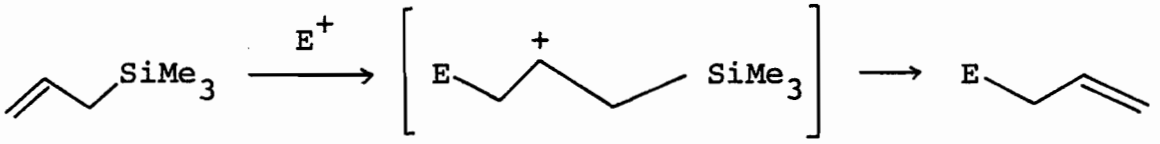
(a) DIRECTING EFFECT OF SILICON SUBSTITUENTS

In the introductory chapter some reactions involving allylsilanes were described. They give some ideas of the use of allylsilanes in organic synthesis. Like vinylsilanes, allylsilanes react readily with electrophiles. However, nucleophiles can cleave allylsilanes more readily than vinylsilanes presumably because the carbanion formed by the cleavage reaction will be stabilized by resonance. This is why allylsilanes can be induced to transfer the allyl group to suitable electrophiles[76,77].

One important feature, however, which exists in both vinylsilanes and allylsilanes is the directing effect of the silicon substituents in these silanes. In vinylsilanes the orientation of electrophilic attack on the double bond is controlled by the presence of the silyl group. This has been shown in the electrophilic substitution reactions of vinylsilanes. For example, in the Friedel-Crafts acylation of vinylsilanes the acyl group replaces the trimethylsilyl group on the same carbon atom only.

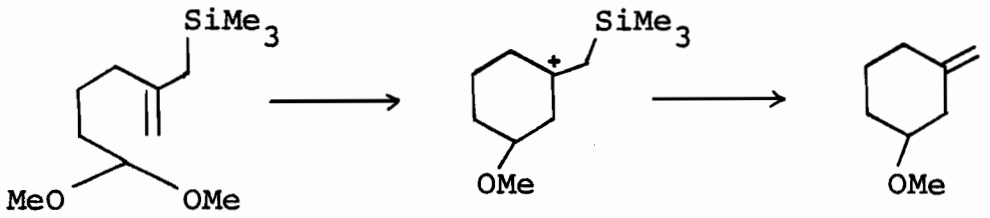


Allylsilanes, as homologues of vinylsilanes, also undergo regiospecific electrophilic attack in which the electrophile bonds to the γ-carbon atom. This results in a net shift of the position of the double bond (Scheme 12).



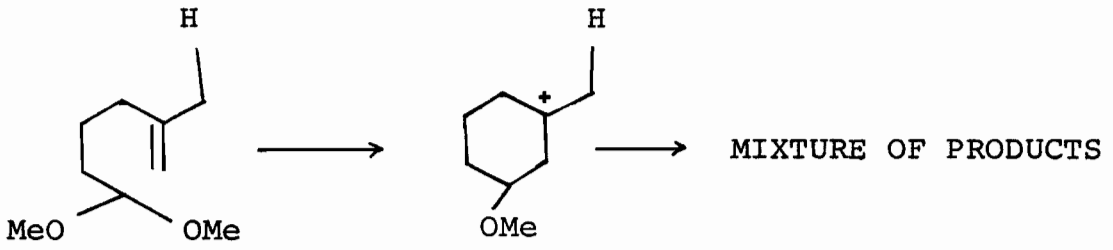
SCHEME 12

The formation of the carbonium ion in Scheme 12 is favourable because the trimethylsilyl group is known to stabilize a carbonium ion β to it[104]. The following example shows the powerful directing effect of silicon in allylsilanes[144]. Compound 124 reacts with stannic chloride in carbon tetrachloride to give the olefin 125 in which the double bond is formed by loss of the trimethylsilyl group.



124 125

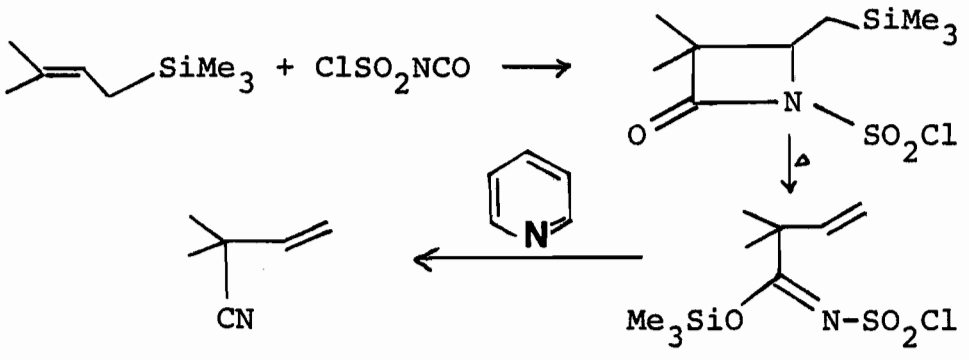
In contrast, compound 126, where the trimethylsilyl group is replaced by a proton, will give a variety of compounds as products.



126

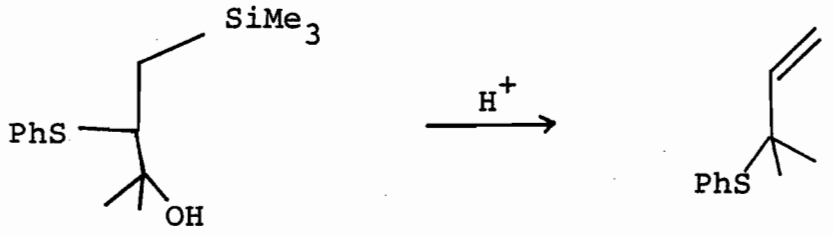
Thus, the presence of the trimethylsilyl group is important in the way that it controls the outcome of a carbonium ion reaction. A carbonium ion is a useful intermediate in organic synthesis only if the product to be obtained from it is easily predictable and when it is the desired product. However, many reactions involving carbonium ions tend to give a mixture of products, both wanted and unwanted. Thus, the above example shows that a carbonium ion can be made to give a single product if a trimethylsilyl group is placed in a proper place in the starting material.

Allylsilanes also react regiospecifically with chlorosulfonyl isocyanate to give intermediate β-lactams, which can be rearranged thermally to silyl ethers 127. On treatment with pyridine[145], compound 127 can be converted into a nitrile.



127

In the thermal rearrangement step the β-lactam ring is opened and the trimethylsilyl group is lost to give a new double bond. This bears similarity to the previous example in which a carbonium ion β to silicon is formed, followed by the loss of the trimethylsilyl group to give a new double bond. This directing effect of the silicon substituents is not restricted only to vinylsilanes and allylsilanes. Other silanes, e.g. alkylsilanes, also exhibit this effect. An example would be the acid catalysed rearrangement of β-hydroxy alkyl phenyl sulfide to give alkyl sulfides by phenylthio migration[146].

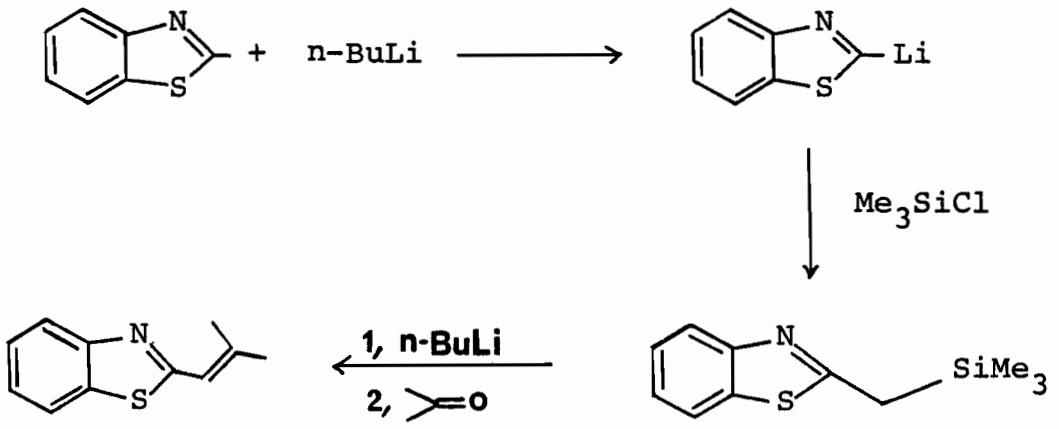


Besides this directing effect, vinylsilanes and alkylsilanes have other common features. For example, they both react with butyllithium at low temperature to give α-silyl carbanions which can react with carbonyls and other compounds.

(b) REACTIONS INVOLVING α-SILYL CARBANIONS

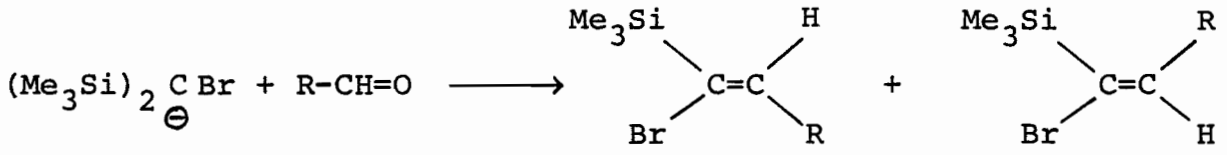
The reaction of α-silyl carbanions with aldehydes or ketones to give alkenes has been developed into a useful synthesis[147,148] of substituted olefins since Peterson[21] first reported the carbonyl olefination reaction using silyl-

substituted organometallic compounds. Stereochemical control of the reaction can now be achieved with some degree of certainty. This control of stereochemistry has been shown by the various stereoselective syntheses of the geometric isomers of the alkenes by different research groups[36,38,53b,65]. Various functionalized carbanions can be used in this olefination reaction. For example, Corey[149] has been able to convert carbonyl compounds to vinyl benzothiazoles 128 using the carbanion formed from metalation of 2-methyl benzothiazole. These vinyl benzothiazoles can then be used for other organic syntheses, e.g. to synthesize complex cyclic molecules[150].

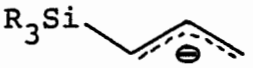


128

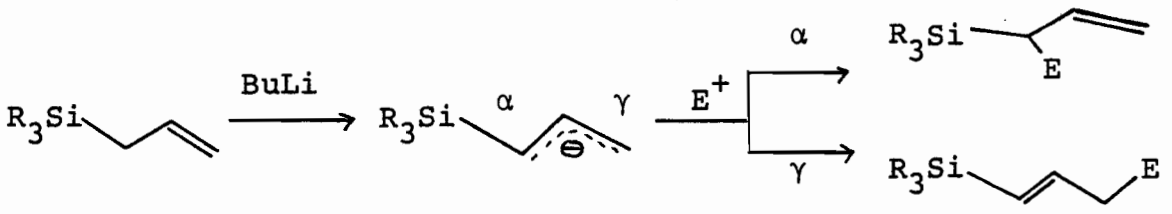
Another example[151] of the use of functionalized carbanions is the reaction of bis-(trimethylsilyl)bromomethyl carbanion with aldehydes to give the two isomers of α-bromovinyltrimethylsilanes.



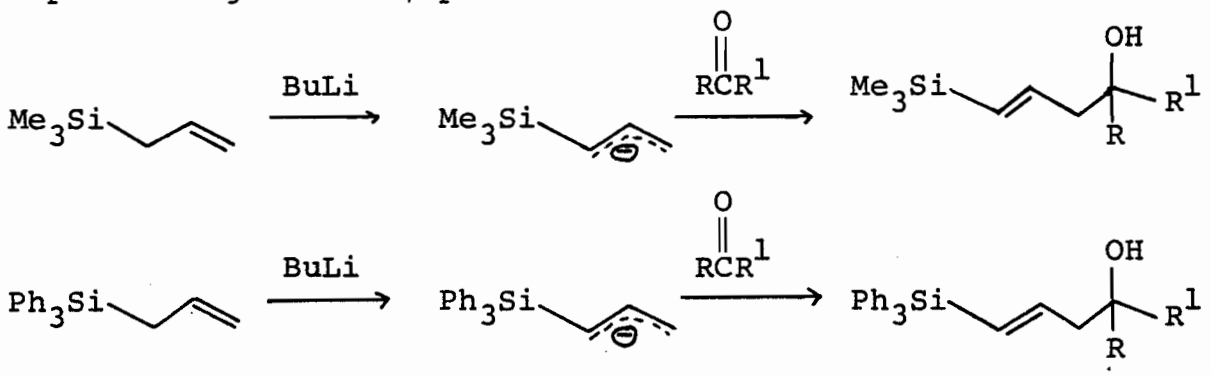
All these examples show that the reaction between α-silyl carbanions and carbonyl compounds proceed well to give the desired alkene products. However, it is quite different in the cases when α-silylallyl carbanion is involved. Like other α-silyl carbanions, α-silylallyl carbanion can be prepared by reaction with butyl lithium at low temperatures. But unlike the α-silyl carbanion formed from alkylsilanes or vinylsilanes where the negative charge is on the carbon α to silicon, the negative charge of the α-silylallyl carbanion can be delocalized among three carbon atoms. Because of this,



electrophiles can add to the α-silylallyl carbanion at either the α or the γ position with respect to the silicon atom. This problem of regioselectivity in reactions does not exist with other α-silyl carbanions.



The control of regioselectivity in the reactions of α-silylallyl carbanions with aldehydes and ketones has not been resolved. It has been found by several groups[87,88,89] that α-silylallyl carbanions react with carbonyl compounds to give exclusively the γ products. The regioselectivity does not appear to be affected by the substituents on silicon[86] because both the α-trimethylsilylallyl carbanion and the α-triphenylsilylallyl carbanion react with the carbonyl compound to give the γ-products.



Neither is the regioselectivity affected by the counter ion, the solvent, nor for that matter, the carbonyl compounds. Changing of the counter ion, e.g. by the addition of zinc chloride or cadmium iodide to the α-silylallyl carbanion to give an organozinc[90] or organocadmium compound before the reaction with carbonyl compounds does not change the course of the reaction. Once again, only the γ product is obtained. Changing to different solvent systems does not help to change the course of the reaction either. The use of different carbonyl compounds, both aldehydes and ketones, alkyl or aryl, also has no effect on the course of the reaction. Only the

γ product is obtained in each case.

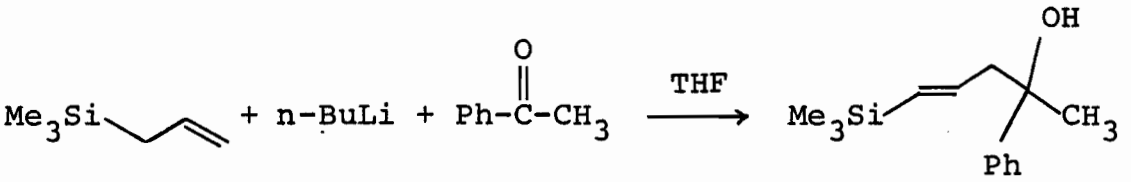
A great deal of effort has been spent to try to control the regioselectivity of this reaction, i.e. to change the course of the reaction so that the carbonyl compounds can add to the α position of the α-silylallyl carbanion. Such α addition would be of great synthetic interest. This is because the α addition product between the carbonyl compound and α-silylalkyl carbanion will have a functionality β to the silyl group. Such an arrangement is the basis for the general synthesis of substituted alkenes using the organosilicon method.

(c) REGIOSELECTIVITY IN THE REACTIONS OF 1-TRIMETHYLSILYLALLYL CARBANION

To study the control of regioselectivity in the reactions of α-silylallyl carbanions with aldehydes and ketones, α-trimethylsilylallyl carbanion from allyltrimethylsilane is reacted with acetophenone and benzaldehyde under different reaction conditions.

First, allyltrimethylsilane is reacted with n-butyllithium in tetrahydrofuran at room temperature to give the α-trimethylsilylallyl carbanion. Reaction of this carbanion with acetophenone gives the γ product 129. Compound 129 is isolated by preparative thin layer chromatography as a light yellow liquid. Physical data for compound 129: NMR: δ = -0.1 (s, 9H), 1.4 (s, 3H), 1.7 (b, 1H), 2.5 (m, 2H), 5.7 to 5.9 (m, 2H), 7.4 (m, 5H); IR: 3400, 2920, 1615 and 1245 cm^{-1}; mass spectrum at m/e 219, 121, 77 and 73.

The proton distribution in the NMR spectrum of 129 indicates that there are only two olefinic protons present. This excludes the possibility that 129 is the α addition product because this compound would have three vinyl protons. However, the proton distribution is correct for the γ product. From the coupling constant of the two olefinic protons (J = 18 Hz), compound 129 is of the trans-geometry. The IR at 3400 cm^{-1} indicates the presence of a hydroxy group. The mass spectrum has a fragment at m/e 219 which indicates the loss of mass unit 15 from the molecular ion (234), i.e. the molecular ion loses a methyl group. The most abundant fragment, m/e 121, indicates the presence of $Ph-\overset{+}{C}(OH)-CH_3$, while the fragments m/e 77 and 73 indicate the presence of a phenyl group and a trimethylsilyl group respectively.

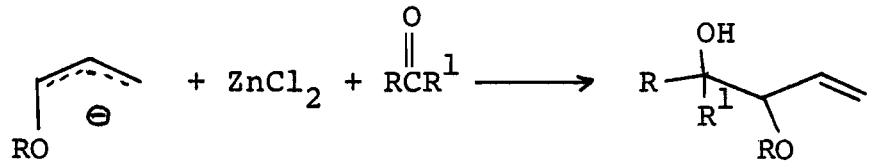


129

The addition of tetramethylethylenediamine (TMEDA) to the α-trimethylsilylallyl carbanion to activate the carbanion before quenching with acetophenone does not affect the course of the reaction. Only the compound 129 is formed.

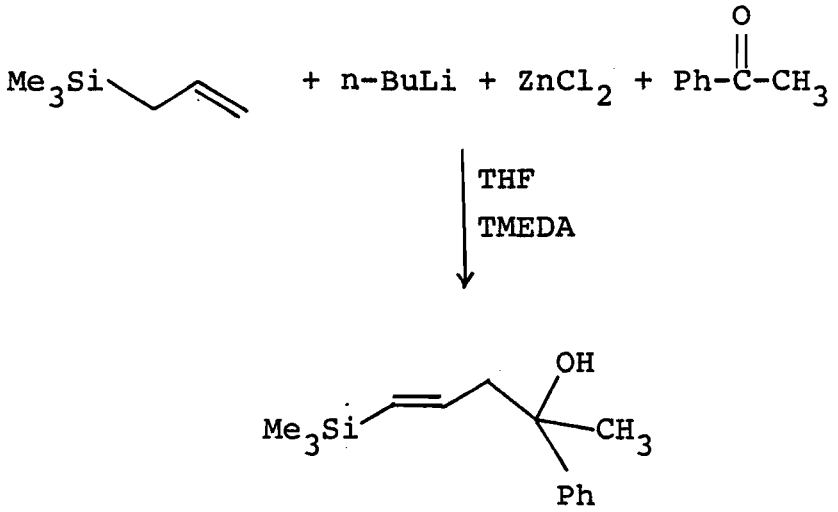
Evans[90] has found that in the reactions of the oxyallylic anion 62 with carbonyl electrophiles the product ratio is

counter ion dependent. The organozinc reagent, prepared by the addition of one equivalent of zinc chloride to 62, reacts with aldehydes and ketones exclusively α to oxygen.



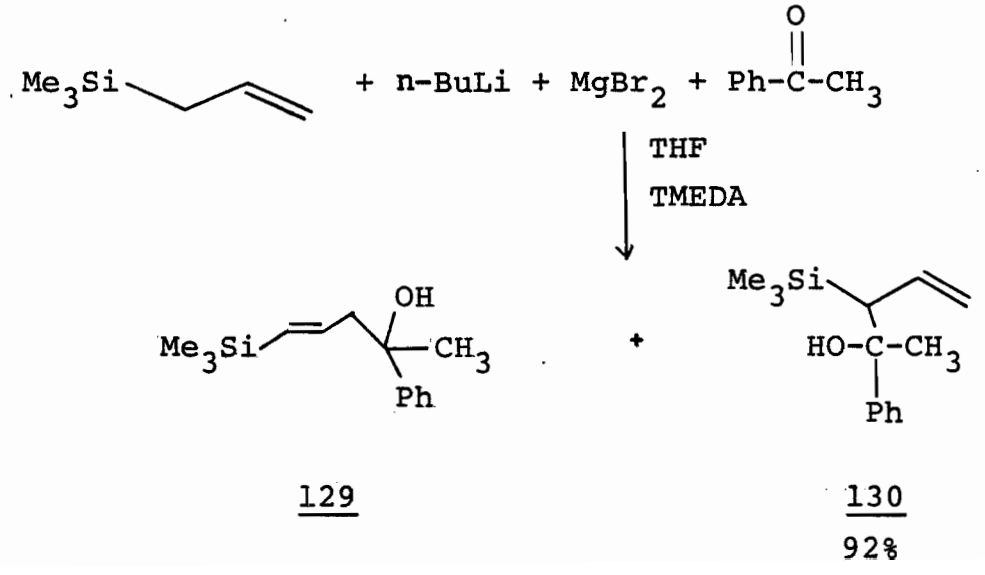
62

This counter ion effect is tried on the reaction of allyltrimethylsilane with acetophenone. The α-trimethylsilyl-allyl carbanion is prepared from allyltrimethylsilane and n-butyllithium. Then a solution of zinc chloride in tetra-hydrofuran is added to the carbanion to give the organozinc reagent. This reagent is allowed to react with acetophenone. On work up, only compound 129 is formed. No α addition product is detected. Neither is the regioselectivity affected if cadmium iodide is used instead of zinc chloride. The reaction is not counter ion dependent.



129

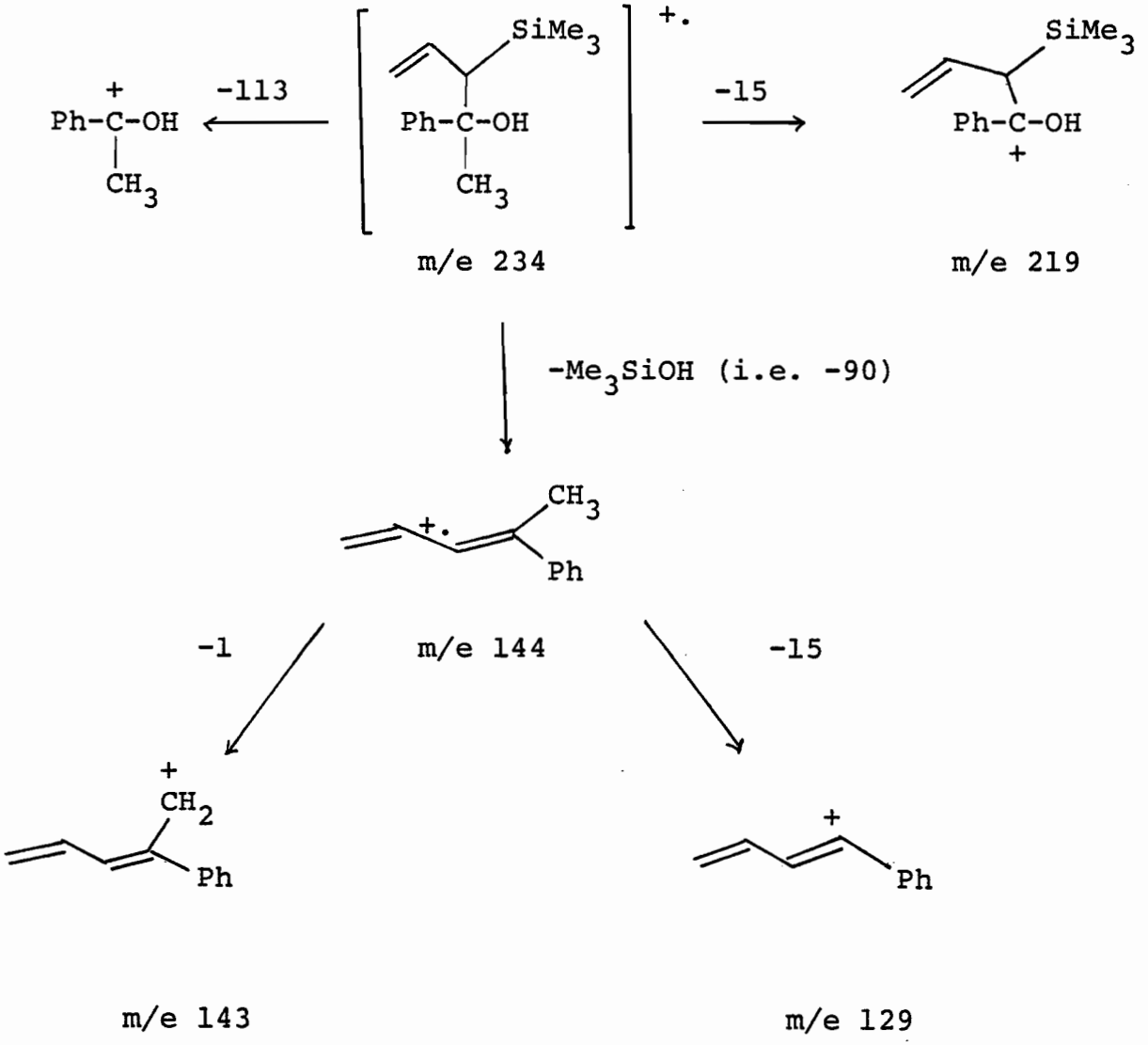
It is, therefore, surprising when we find that the α-trimethylsilylallyl carbanion reacts with aldehydes and ketones in the presence of magnesium bromide to give regioselectively the α product. Thus, an equimolar amount of n-butyllithium is added to a stirred solution of allyltrimethylsilane in tetrahydrofuran. This is followed by the addition of tetramethylethylenediamine. The solution is then stirred for a few hours before it is cooled to -78°C. Then, a solution of freshly prepared magnesium bromide etherate[152] is added and stirred for another hour before a solution of acetophenone in tetrahydrofuran is added. Under these conditions, the products obtained are a mixture of the γ product 129 and the α product 130 with the compound 130 predominating. The relative amount of γ to α is 8:92% (crude estimate from the NMR spectrum). Preparative thin layer chromatography is used to isolate compound 130 as a light yellow liquid. Physical data for 130: NMR: δ = -0.2 (s, 9H), 1.5 (s, 3H), 1.6 (b, 1H), 2.1 (d, 1H), 4.8 to 5.2 (m, 2H), 5.7 to 6.3 (m, 1H), 7.4 (m, 5H); IR: 3500, 3040, 2940, 1625, 1600 and 1245 cm^{-1}; mass spectrum at m/e 219, 144, 143, 129, 121, 77 and 73.



129 130

92%

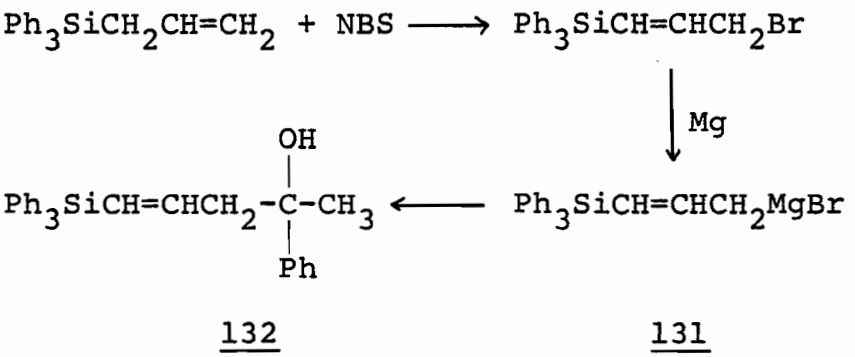
From the NMR of compound 130, there are three vinyl protons. This is different from the NMR of compound 129. The mass spectrum of 130 is also different from that of 129. Extra fragments at m/e 144, 143 and 129 can only appear from the α addition product. For example, m/e at 144 arises from the loss of a molecule of trimethylsilanol from the molecular ion. This can only happen in the case when the hydroxy group is β to the trimethylsilyl group as in compound 130 (Scheme 13).



SCHEME 13: FRAGMENTATION PATTERN OF COMPOUND 130

The reaction is repeated using the same conditions except that no tetramethylethylenediamine is added. The NMR of the crude material on work up shows also that a mixture of the α and γ products is obtained with the α compound predominating. The relative amount of compound 129 to 130 is 14:86%. This reaction shows that TMEDA has no significant effect in the change of regioselectivity of the reaction.

The role of magnesium bromide[153] is critical in moderating the regioselectivity of the reaction. Other metal halides, e.g. zinc chloride[90] or cadmium iodide[154], are found not to be effective. The change in regioselectivity does not appear to be due to the formation of the α-silylallyl magnesium bromide 131, because the Grignard reagent, generated independently from the bromo precursor, reacts with acetophenone to give only the γ product 132[87].

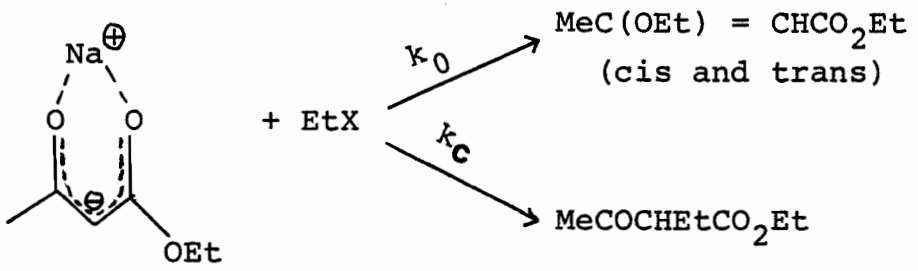


132 131

The bromo compound is obtained by refluxing allyltriphenylsilane and N-bromosuccinimide in carbon tetrachloride in the presence of a small amount of benzoyl peroxide. Compound 131 is then obtained from reaction of the bromo

compound with excess magnesium in ether. Reaction of the α-triphenylsilylallyl magnesium bromide 131 with acetophenone gives the γ product 132 only.

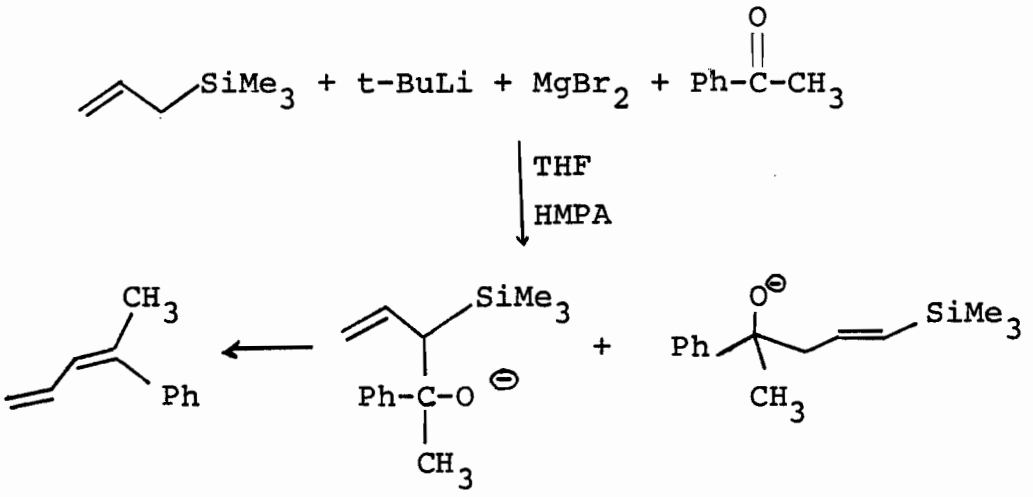
The explanation we favour at the moment is that magnesium bromide complexes with the carbonyl compound thus rendering it a more reactive electrophile. It is well known that in the reactions of ambident anions, the regioselectivity depends on the reactivity of the electrophile[155]. An example is the alkylation reaction of sodium enolate of ethyl acetoacetate with different electrophiles in dimethoxyethane. Whether the C- or O-alkylation product is formed in the reaction will be dependent on the reactivity of the electrophile EtX (e.g. EtI, EtBr, TsOEt etc.).



In support of this explanation, that the regioselectivity depends on the reactivity of the electrophile, the reaction is carried out in a different way. Magnesium bromide etherate is pre-mixed with acetophenone. This mixture is then added dropwise to a solution of α-trimethylsilylallyl carbanion in tetrahydrofuran. On work up, the same regioselectivity is obtained in which the α compound 130 predominates. This reaction shows that the formation of the Grignard reagent is

not necessary to obtain the α product 130.

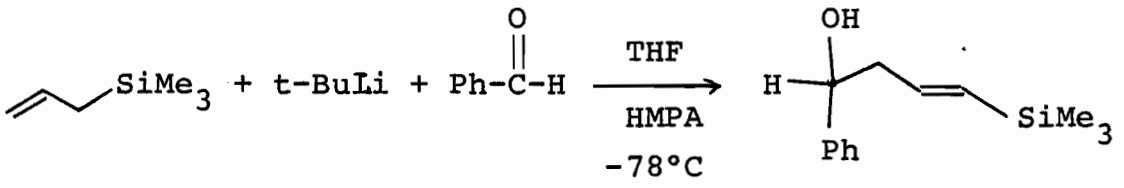
The α-trimethylsilylallyl carbanion can also be obtained from the reaction of the allyltrimethylsilane with t-butyllithium at -78°C. This carbanion can then be mixed with magnesium bromide and the mixture reacted with acetophenone to give predominately the α addition product. The relative amount of the γ product is about 5%. However, NMR of the crude material shows that the α addition product obtained is in the form of the conjugated diene 133 obtained by the elimination of trimethylsilanol from the α-alcohol 130.



133 < 5%

The same kind of regioselectivity can be obtained if the magnesium bromide is pre-mixed with acetophenone and this mixture is added to the α-trimethylsilylallyl carbanion prepared from t-butyl lithium and allyltrimethylsilane. Once again, the α product is obtained as the diene 133 instead of the α alcohol 130.

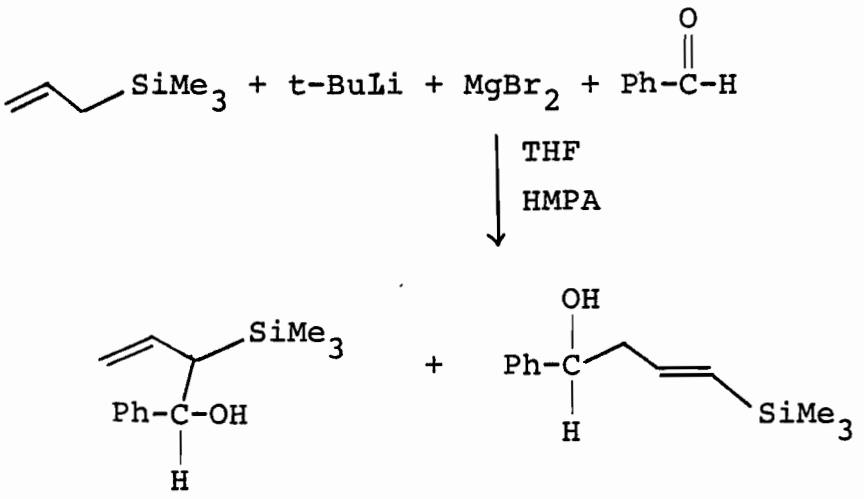
To study the generality of such reactions we turn our attention to the reaction with aldehydes. Benzaldehyde is chosen for the reaction. The α-trimethylsilylallyl carbanion is prepared from the reaction of allyltrimethylsilane with t-butyllithium at -78°C. Hexamethylphosphoramide (HMPA) is added to activate the carbanion. However, in the absence of magnesium bromide, the reaction of the carbanion with benzaldehyde gives only the γ product 134. From the coupling constant of the olefinic protons (J = 18 Hz), the compound 134 is of the trans-geometry. Physical data for 134: NMR: δ = 0.1 (s, 9H), 2.6 (t, 2H), 2.7 (b, 1H), 4.7 (t, 1H), 5.7 (d, 1H, J = 18 Hz), 6.2 (d of t, 1H), 7.3 (m, 5H); IR: 3380, 3050, 1620 and 1450 cm^{-1}; mass spectrum at m/e 205, 107, 77 and 73.



134

The NMR is correct for the γ product because there are only two olefinic protons present. M/e at 205 in the mass spectrum indicates a loss of mass unit 15 from the molecular ion, i.e. loss of a methyl group from the trimethylsilyl group. M/e at 107 is the most abundant fragment ion. This indicates the presence of $Ph-\overset{+}{\underset{OH}{C}}-H$, while m/e at 77 and 73 indicate the presence of a phenyl group and a trimethylsilyl group respectively.

In the presence of magnesium bromide etherate, the α-trimethylsilylallyl carbanion reacts with benzaldehyde to give a mixture of the α and the γ products. The relative amount of the α product 135 to γ product 134 is 60:40%.

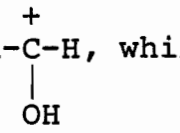


135 134

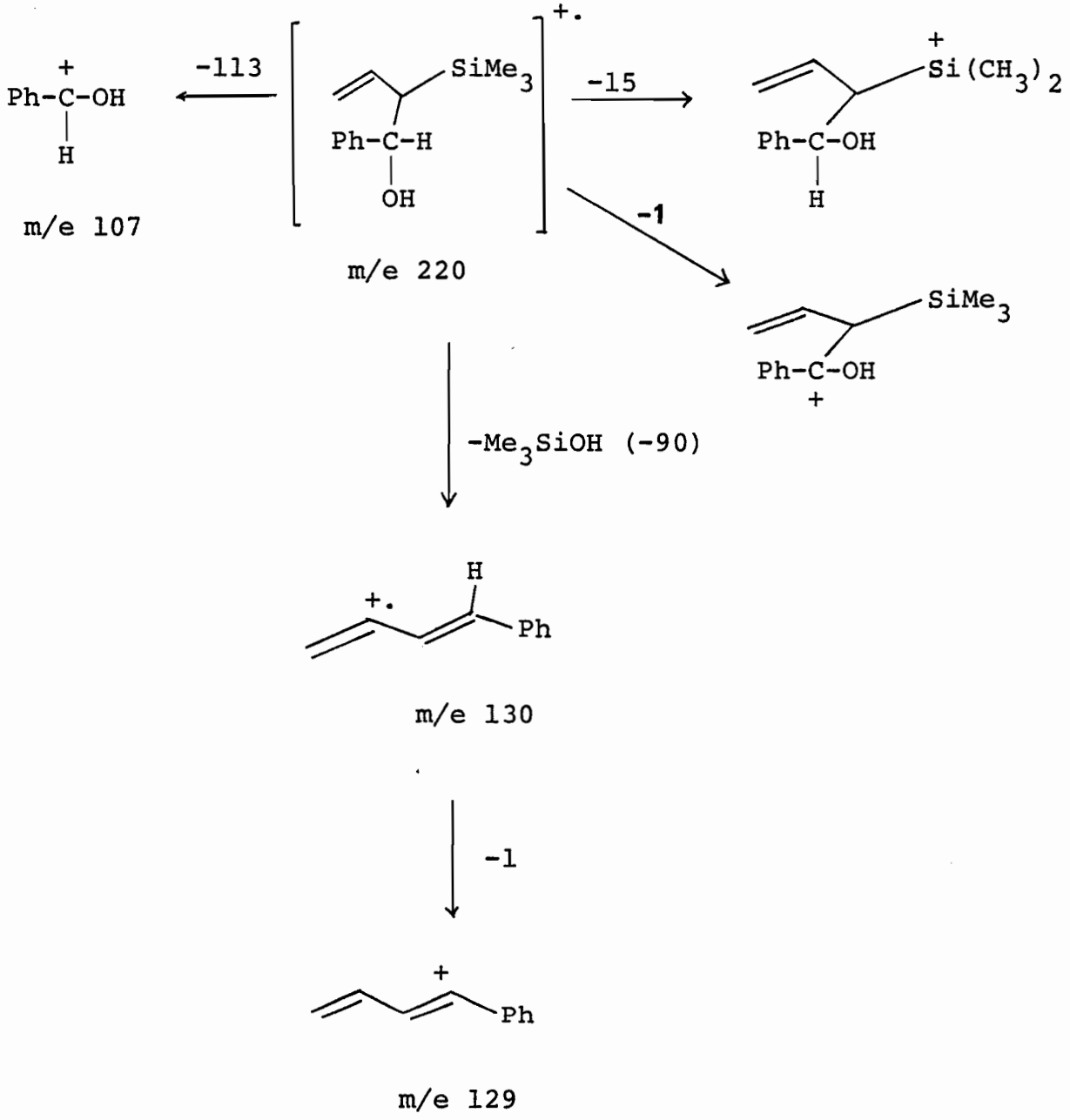
Preparative thin layer chromatography is tried to separate the two compounds. However, their Rf values are very similar to each other. There is no separation. NMR shows the presence of both compounds after TLC. The NMR data of compound 135 can be deduced from the NMR of the mixture because the chemical shifts of the protons of compound 134 are known. NMR data for compound 135 is roughly as follows: δ = 0.0 (s, 9H), 2.0 (b, 1H), 2.1 (t, 1H), 4.9 (d, 1H), 5.0 (m, 2H), 5.9 to 6.3 (m, 1H), 7.3 (m, 5H).

GC of the mixture shows two peaks. The GC-MS for the smaller peak has a mass spectral pattern similar to that obtained for compound 134. Thus, it is the γ product. GC-MS for the

larger peak has a mass spectrum of m/e at 219, 205, 130, 129, 107, 77 and 73. All these fragment ions combine to support that this compound 135 is the α addition product.

The molecular ion of 135 is at m/e 220. Fragment ion at m/e 219 indicates a loss of a proton. M/e at 205 indicates a loss of a methyl group from the trimethylsilyl group. M/e at 130 indicates a loss of a molecule of trimethylsilanol (mass unit 90). This can only happen when the hydroxy group is at a β position to the trimethylsilyl group as in the case of the α alcohol 135. M/e at 129 indicates a further loss of a proton from fragment in 130. M/e at 107 indicates the presence of  , while m/e at 77 and 73 indicate the presence of a phenyl group and a trimethylsilyl group respectively (Scheme 14).

The most abundant fragment ion is m/e 129. It is derived from the further loss of a proton after the elimination of a molecule of trimethylsilanol from the molecular ion. The loss of trimethylsilanol is already a good indication that compound 135 is the α addition product because the γ addition product 134 does not have a hydroxy group β to the trimethylsilyl group. As a result, the mass spectrum of 134 does not have significant fragments at m/e 130 and 129. Thus, in general, in order to identify the α from the γ alcohol product the presence of a significant fragment ion in the mass spectrum at m/e (m-90), where m is the molecular ion, will indicate that it is the α addition product.



SCHEME 14: FRAGMENTATION PATTERN OF COMPOUND 135

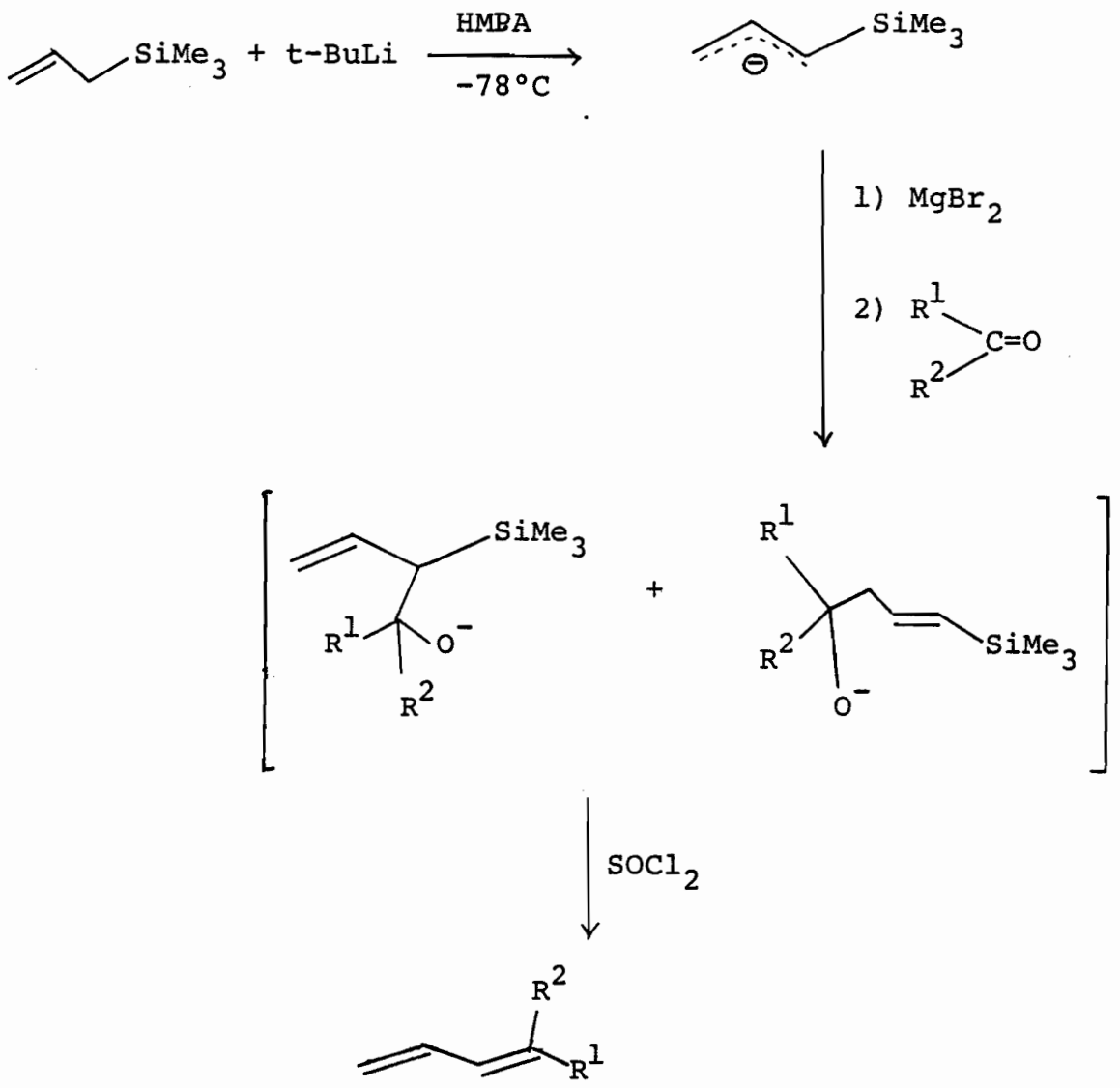
This reaction is repeated again. However, this time the magnesium bromide is pre-mixed with benzaldehyde in tetrahydrofuran. This mixture is then added to the α-trimethylsilylallyl carbanion. On work up, the same regioselectivity is obtained where the relative amount of the α:γ products is 60:40%. This, once again, proves that no Grignard reagent is involved in the control of regioselectivity in the reaction of α-silylallyl carbanion with carbonyl compounds. A summary of the regioselectivity in the reaction of α-trimethylsilylallyl carbanion with acetophenone and benzaldehyde is given in Table 7.

With the introduction of a functionality at the β position to the trimethylsilyl group in the reaction between α-silylallyl carbanion and carbonyl compounds, other organic syntheses can be carried out based on the principle that β-functionalized organosilanes can be easily induced to eliminate.

(d) SYNTHESIS OF 1,3-DIENES

Once the regioselectivity of the reactions between α-silylallyl carbanion and carbonyl compounds can be controlled, the conversion of aldehydes and ketones into 1,3-dienes can be achieved easily. However, it has been shown that the α-alcohols 130 and 135, prepared from reaction with acetophenone and benzaldehyde respectively, do not eliminate consistently to give dienes. β-Elimination is dependent on the reaction conditions. To facilitate the β-elimination the crude mixture

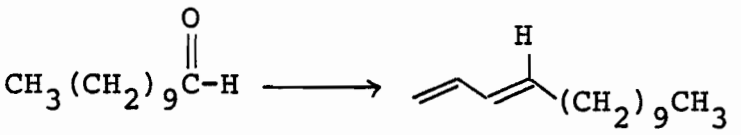
of the alkoxides obtained is quenched with thionyl chloride[148] before work up. The 1,3-diene can be purified by distillation or preparative TLC, in an overall isolated yield of ~ 50%.



This 1,3-diene synthesis from carbonyl compounds is found to be a very general method. It is applicable to both aliphatic and aromatic aldehydes and ketones. The

general synthesis is as follows. Allyltrimethylsilane is reacted with t-butyllithium at -78°C to give the α-trimethylsilylallyl carbanion. This is followed by the addition of HMPA and then magnesium bromide etherate. Different carbonyl compounds can then be added to the reaction mixture, followed by quenching with thionyl chloride. The different dienes can be obtained on work up.

For example, undecanal, an aliphatic aldehyde, can react with the α-silylallyl carbanion to give a long chain aliphatic diene 136.

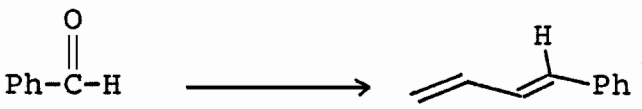


136

Compound 136 is isolated as a light yellow liquid by preparative TLC. Physical data for 136: NMR: δ = 0.9 (t, 3H), 1.4 (b, 16H), 2.1 (m, 2H), 4.8 to 5.4 (m, 2H), 5.8 to 6.5 (m, 3H); IR: 2930, 2860, 1600 and 1465 cm^{-1}; mass spectrum at m/e 194, 123, 109, 95, 81 and 67. The mass spectrum shows the molecular ion at m/e 194. The mass spectral pattern also shows the loss of mass unit 14 in each fragment ion from m/e 123 to 67. This indicates the presence of a long chain alkyl group as the product. GC-MS of 136 shows this product to be one pure isomer.

Aromatic aldehydes can also be converted to 1,3-dienes

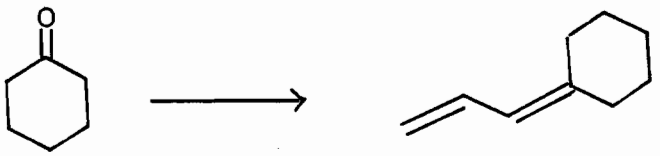
smoothly. For example, benzaldehyde reacts with α-silylallyl carbanion to give the diene 137.



137

Physical data for 137: NMR: δ = 4.9 to 5.4 (m, 2H), 6.1 to 6.7 (m, 3H), 7.0 to 7.4 (m, 5H); IR: 1630, 1600 and 945 cm^{-1}; mass spectrum at m/e 130, 129 and 77. GC shows one isomer only. The mass spectrum has the molecular ion at m/e 130. The most abundant fragment ion is at m/e 129. This is obtained by the loss of a proton for the molecular ion.

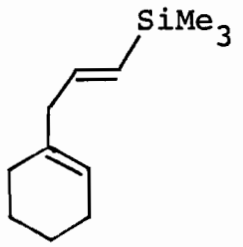
In the reactions with the ketones, cyclohexanone reacts with the α-silylallyl carbanion to give the diene 138.



138

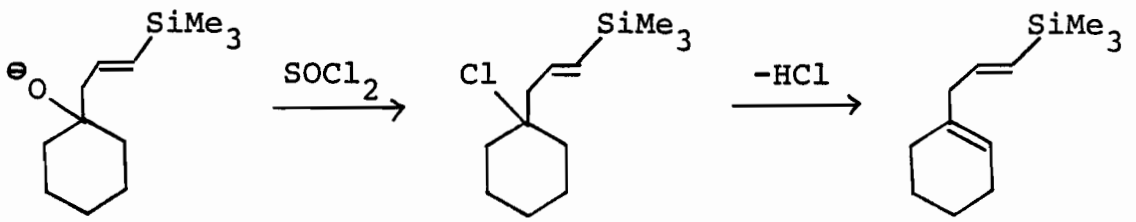
Compound 138 is isolated by preparative TLC as a light yellow liquid. Physical data for 138: NMR: δ = 1.7 (m, 6H), 1.9 to 2.4 (m, 4H), 4.8 to 5.2 (m, 2H), 5.4 to 5.9 (m, 1H), 6.2 to 6.8 (m, 1H); IR: 2900, 2830, 1610 and 1440 cm^{-1}; mass spectrum at m/e 122 and 79. Once again, the mass spectrum shows the molecular ion (122).

However, there is one minor side product isolated by TLC in this particular reaction (yield ∿ 10%). The structure of the side product 139 is assigned according to its NMR and mass spectrum.



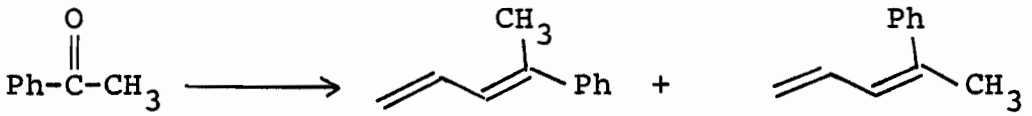
139

The NMR of 139 shows δ = 0.1 (s, 9H), 1.6 to 2.2 (broad m, 8H), 2.8 (d, 2H), 5.5 (broad m, 1H), 5.8 to 6.3 (m, 2H). The mass spectrum of 139 has signals at m/e 194, 179 and 73. The ion at m/e 194 would be the molecular ion of compound 139. The ion at m/e 179 indicates a loss of mass unit 15 from the molecular ion, i.e. a loss of a methyl group, probably from the trimethylsilyl group. The presence of a trimethylsilyl group is indicated by the ion at m/e 73. Compound 139 can be derived from the γ-addition product. The γ chloride, compound 140, obtained from the reaction of thionyl chloride with the alkoxide mixture, can lose a molecule of HCl to give the compound 139.



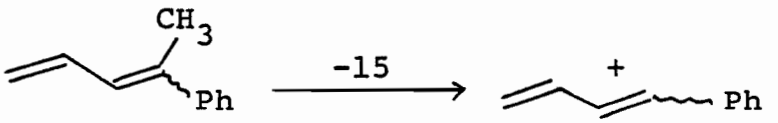
140 139

Aromatic ketones also react with α-silylallyl carbanion to give dienes. In the case of acetophenone, two geometric isomers of the diene 141 are formed as products.



141a 141b

The two isomers of the diene 141 are obtained by distillation. They distil as one fraction at 80-83°C/ 5mm Hg. GC of 141 shows two equal peaks with close retention times. GC-MS of the two peaks show that they have identical mass spectra. The two compounds are geometric isomers. The mass spectrum has ions at m/e 144, 129, 128 and 77. The ion at m/e 144 is the molecular ion, while m/e at 129 indicates a loss of a methyl group from the molecular ion.



m/e 144 m/e 129

The NMR of the distillate has a signal at δ = 2.1 which is a singlet split at the top. This indicates the presence of the two methyl groups of the two isomers. Other signals are at δ = 4.8 to 5.5 (m, 2H), 6.0 to 6.9 (m, 2H), 7.1 to 7.4 (m, 5H). The two isomers of the diene 141 are of equal proportion in the

TABLE 7: REGIOSELECTIVITY IN THE REACTION OF α-TRIMETHYLSILYLALLYL CARBANION WITH ACETOPHENONE AND BENZALDEHYDE

	Compound	Reaction Condition	Relative Amount (%)	
			γ	α
a)	Acetophenone	n-Butyllithium	100	
		n-BuLi/TMEDA/$ZnCl_2$	100	
		n-BuLi/TMEDA/CdI_2	100	
		n-BuLi/TMEDA/$MgBr_2$	8	92[a]
		n-BuLi/$MgBr_2$	14	86[a]
		n-BuLi/TMEDA/$MgBr_2$ premixed with carbonyl compound	43	57[a]
		t-BuLi/HMPA/$MgBr_2$	< 5	>95[b]
		t-BuLi/HMPA/$MgBr_2$ premixed	~20	~80[b]
b)	Benzaldehyde	t-BuLi/HMPA	100	
		t-BuLi/HMPA/$MgBr_2$	40	60[c]
		t-BuLi/HMPA/$MgBr_2$ premixed	40	60[c]

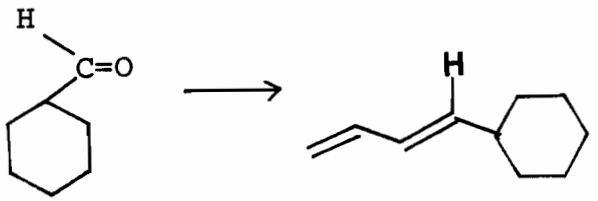
a) Two diastereomers are formed in the ratio of 2:1 according to NMR

b) Obtained as diene

c) One diastereomer is formed according to NMR

distillate. IR data: 1630, 1600, 1495 and 1445 cm^{-1}.

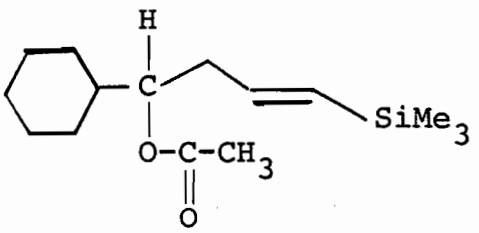
Alternatively, instead of quenching the reaction mixture with thionyl chloride, the diene can be generated by quenching the reaction mixture with acetyl chloride and the resultant acetates treated with tetraethylammonium fluoride in acetonitrile[61]. Cyclohexane carboxaldehyde is converted into diene 142 by using this method.



142

Preparative TLC is used to isolate the diene 142. Compound 142 is a light yellow liquid. Physical data for 142: NMR: δ = 1.0 to 2.1 (m, 11H), 4.9 to 5.4 (m, 2H), 5.6 to 6.7 (m, 3H); IR: 2930, 2860, 1600 and 1450 cm^{-1}; mass spectrum at m/e 136 and 67. The ion at m/e 136 is the molecular ion. GC shows only one isomer is present.

Another minor product is also isolated by TLC. From its NMR, this compound 143 is assigned to be the γ-acetate product. NMR: δ = 0.1 (s, 9H), 1.0 to 1.9 (m, 11H), 2.0 (s, 3H), 2.4 (m, 2H), 4.7 (m, 1H), 5.4 to 6.2 (m, 2H).



143

With the control of regioselectivity of the reaction of α-silylallyl carbanion with carbonyl compounds, these carbonyl compounds can be converted into 1,3-dienes by quenching with thionyl chloride or by quenching with acetyl chloride followed by tetraethylammonium fluoride. A summary of the 1,3-diene synthesis can be found in Table 8.

TABLE 8: DIENE SYNTHESIS FROM CARBONYL COMPOUNDS AND α-TRIMETHYLSILYLALLYL CARBANION

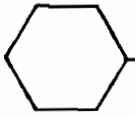
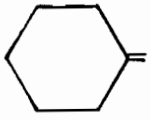
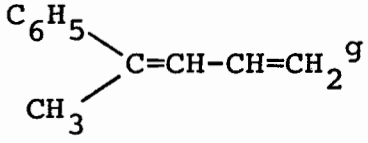
Product	Reaction Condition	Isolated Yield [b], %	^{1}H NMR[c]; IR[d] and M.S. data[e]
$CH_3(CH_2)_9CH=CH-CH=CH_2$ [a]	A	54	0.9 (t,3H), 1.4 (b,16H), 2.1 (m,2H), 4.8 to 5.4 (m,2H), 5.8 to 6.5 (m,3H); 2930, 2860, 1465, 1600; 194 (12), 67 (100).
 $CH=CH-CH=CH_2$ [a]	B	42	1.0 to 2.1 (m,11H), 4.9 to 5.4 (m,2H), 5.6 to 6.7 (m,3H); 2930, 2860, 1600, 1450; 136 (63), 67 (100).
$C_6H_5-CH=CH-CH=CH_2$ [a]	A	50	[f] 4.9 to 5.4 (m,2H), 6.1 to 6.7 (m,3H), 7.0 to 7.4 (m,5H); 1630, 1600, 945; 130 (83), 129 (100).
 $=CH-CH=CH_2$ [a]	A	49	[f] 1.7 (m,6H), 1.9 to 2.4 (m,4H), 4.8 to 5.2 (m,2H), 5.4 to 5.9 (m, 1H), 6.2 to 6.8 (m,1H); 2900, 2830, 1610, 1440; 122 (29), 79 (100).

TABLE 8: continued

Product	Reaction Condition	Isolated Yield [b], %	^{1}H NMR[c]; IR[d] and M.S. data[e]
 [g]	A	43	2.1 (br,s,3H), 4.8 to 5.5 (m,2H), 6.0 to 6.9 (m,2H), 7.1 to 7.4 (m,5H); 1630, 1600, 1495, 1445; 144 (22), 129 (100).

Reaction conditions: Method A: The crude mixture is quenched with thionyl chloride.

Method B: The crude mixture is quenched with acetyl chloride followed with tetraethylammonium fluoride.

a) GC-MS shows the product to be one pure isomer

b) Isolated yield of products by distillation or preparative TLC

c) ^{1}H NMR are reported in δ ppm in CCl_4 solution

d) IR spectra are reported in cm^{-1} as neat

e) MS data are in m/e (% abundance)

f) Identical NMR and IR data as obtained by Corey in Reference 156

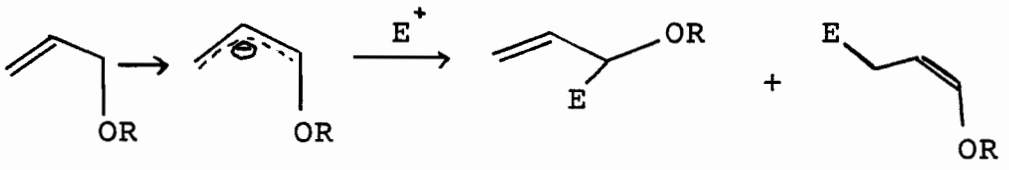
g) Two isomers in ratio of about 1:1 was detected by GC-MS after purification by distillation

CHAPTER 5

REACTIONS OF ALLYLOXYSILANES

(a) ALLYLOXY CARBANIONS

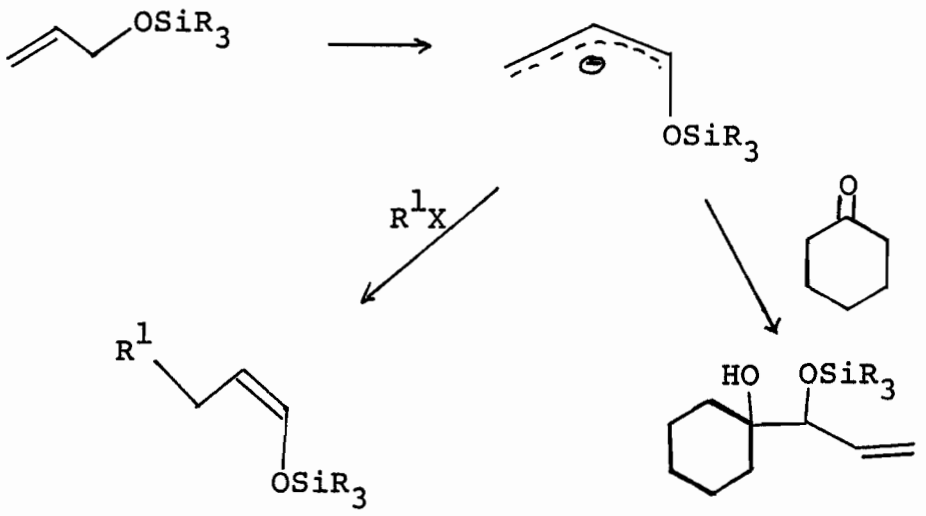
In the introductory chapter it was shown that simple allylic ethers can be metalated at low temperature to give allylic carbanions 62[90,91]. These allyloxy carbanions can



62 63 64

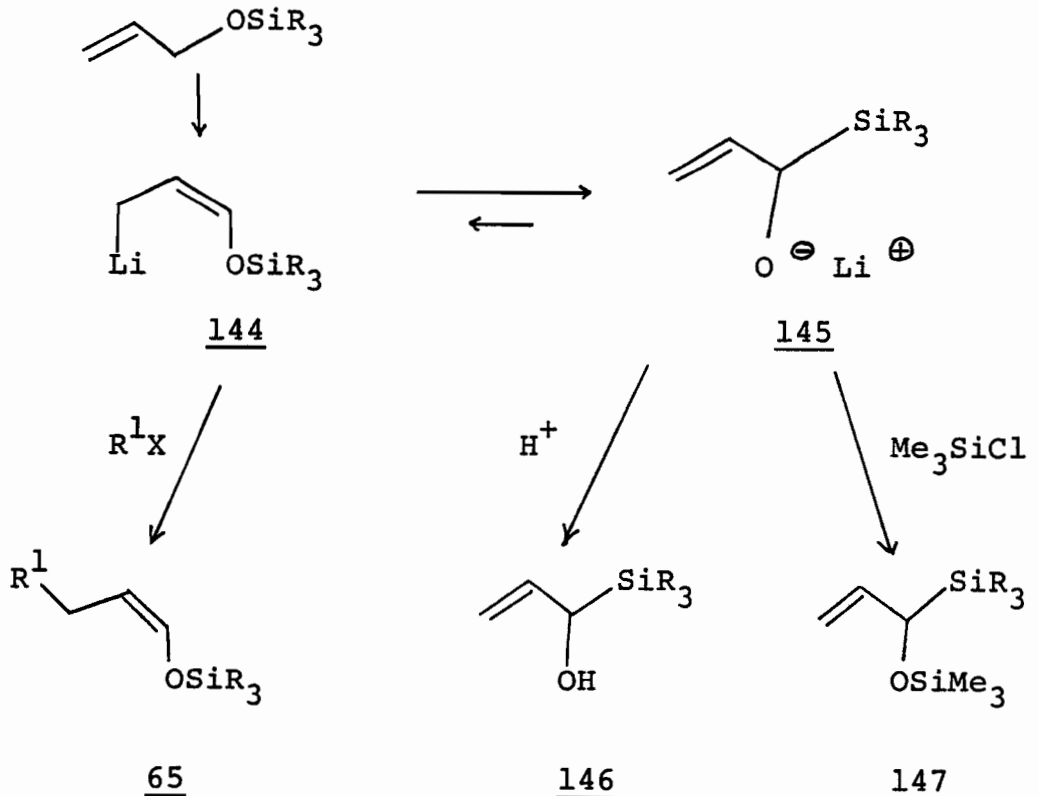
react with electrophiles in two positions, via α-substitution or γ-substitution to give the allylic ether 63 or the enol ether 64. Usually a mixture of the two is formed. The ratio of the two products is determined by the substituent on the allylic anion. This ratio is also counter ion dependent[90] as in the cases of simple allylic ethers.

In the cases where R is a trialkylsilyl group, i.e. in allyloxysilanes, the allyloxysilyl carbanions react with alkyl halides to give predominately the γ products, i.e. giving the terminally alkylated enol ethers 65 as the products[91]. In the reactions with carbonyl compounds, e.g. with cyclohexanone, the trimethylsilylallyloxy carbanion in THF-HMPA reacts regioselectively to give the α-addition product[92].



65 > 99%

Unlike other simple allyloxy carbanions, the allylsilyloxy carbanions 144 derived from allyloxysilanes are in rapid equilibrium with the corresponding silyl alkoxides 145. These species may be alkylated on carbon to give 65 or they may be protonated or silylated on oxygen to give compounds 146 or 147[157].

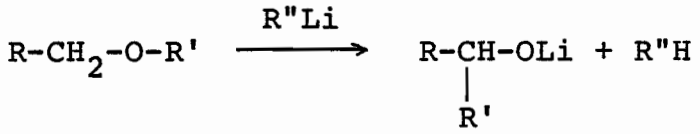


144 145

65 146 147

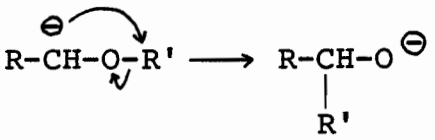
(b) WITTIG REARRANGEMENT AND THE 1,2-ANIONIC REARRANGEMENT OF ALKOXYSILANES

The rearrangement of carbanion 144 to the silyl alkoxide 145 is analogous to the Wittig rearrangement. Many organic ethers may be converted to isomeric alcohols in the presence of excess organolithium reagent by the Wittig rearrangement[158].

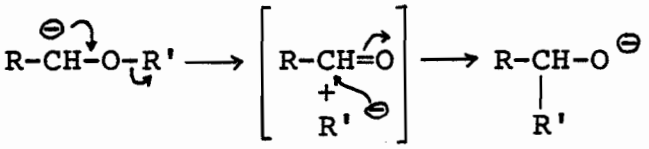


R and R' may be alkyl or aryl. Also, one of the hydrogens in the ether may be replaced by an alkyl or aryl group. In such case the product is the tertiary alkoxide. Two mechanisms are suggested for the Wittig rearrangement.

Mechanism (a):



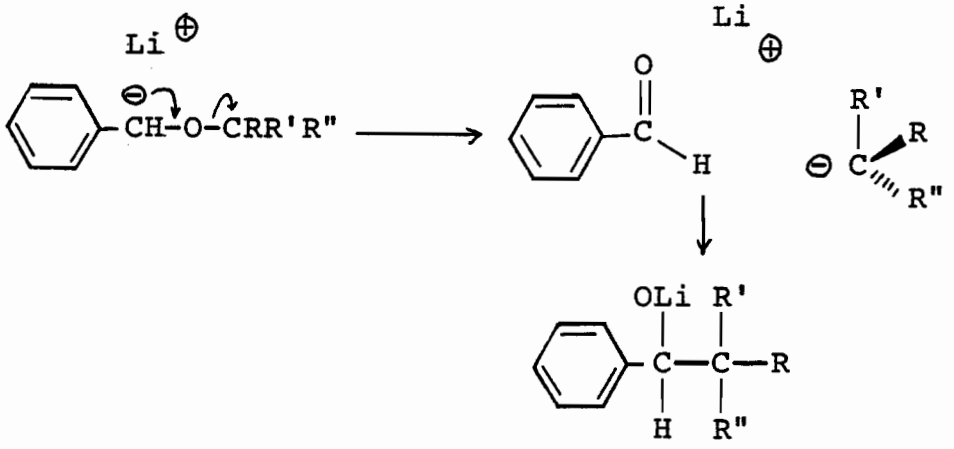
Mechanism (b):



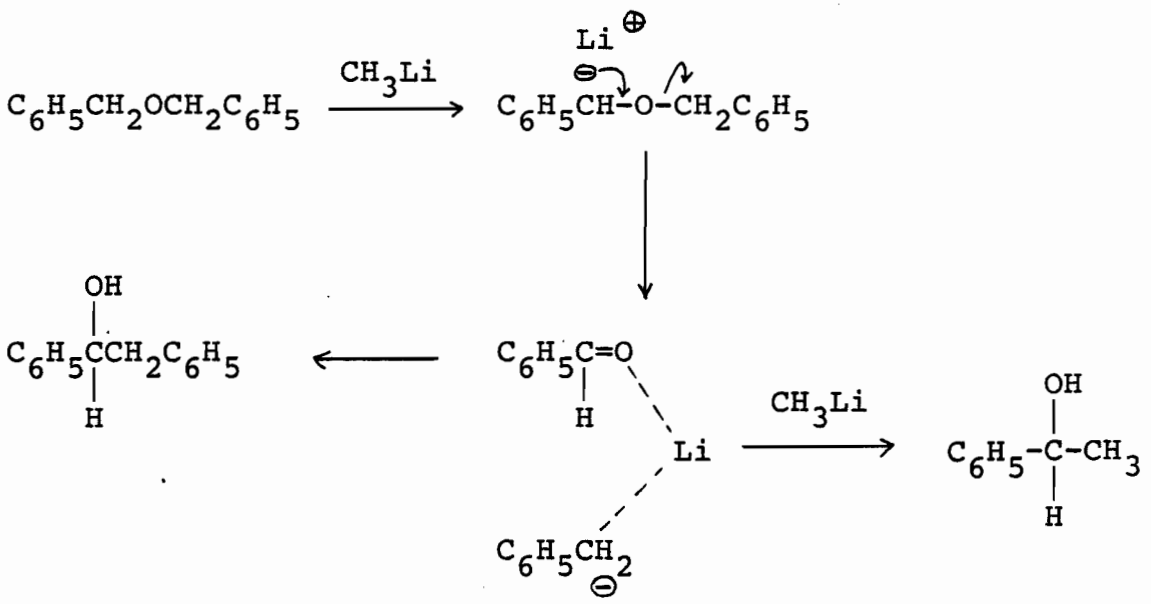
The migratory order is allyl, benzyl > methyl, ethyl > phenyl[159]. This migratory order favours the mechanism (a) since this is the order of carbonium ion stability. However, there are a number of facts supporting the mechanism (b):

i) aldehydes are formed as side products[160].

ii) partial racemization of R' has been observed[161]. Schollkopf observed that partial racemization occurred in the rearrangement of optically active benzyl 2-butyl ether. This can be explained by a cleavage-recombination reaction involving the initial cleavage of the migrating group as a carbanion. Thus partial racemization can occur because of the possible inversion of the carbanion.

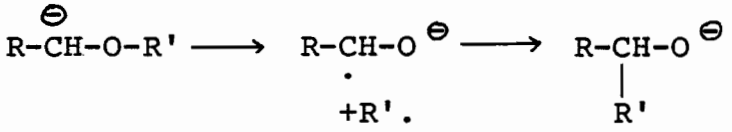


iii) crossover products have also been detected[162]. This cannot have happened with mechanism (a). Lansbury and Pattison were able to detect crossover products during the methyllithium induced rearrangement of benzyl ether. Methyl phenyl carbinol 148 is obtained as one of the products other than the desired rearranged alcohol 149.



149 148

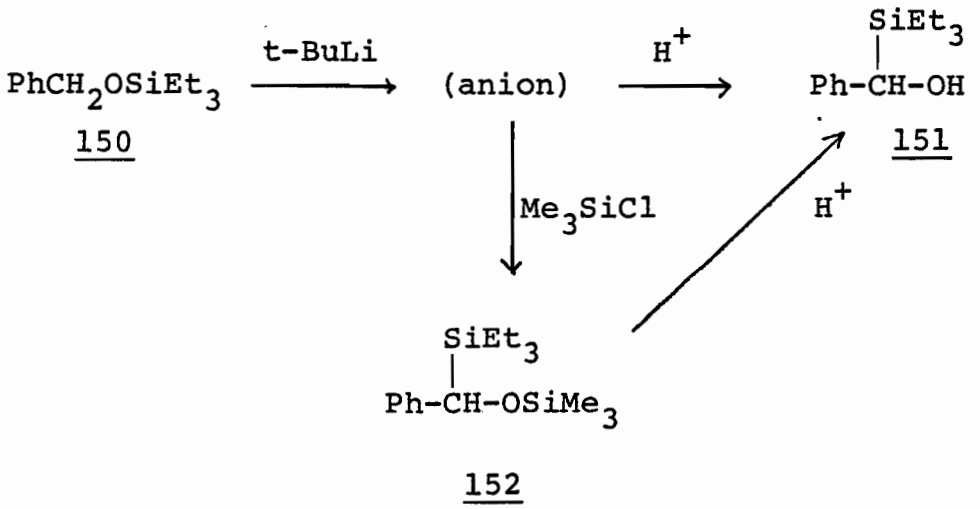
A third mechanism has also been proposed which is similar to mechanism (b) except that the cleavage gives a pair of radicals[163].



The 1,2-anionic rearrangement of alkoxysilanes to α-silylcarbinol is analogous to the Wittig rearrangement. The alkoxysilane rearrangement probably proceeds by an intramolecular mechanism involving a pentacoordinate silicon intermediate, whereas many Wittig rearrangements apparently proceed by cleavage-recombination reactions. The first example of the Wittig type rearrangement of an alkoxysilane to give the

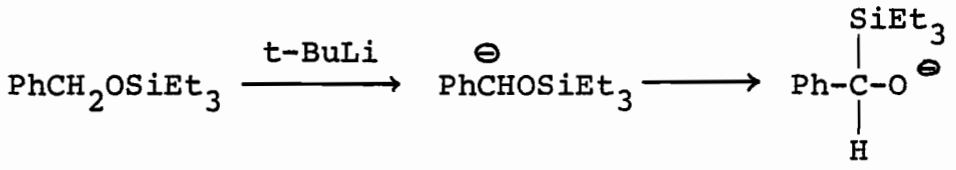
isomeric α-silylcarbinol was reported by West[164]. This rearrangement is expected to be quite general provided that a proton on the carbon attached to oxygen in the alkoxysilane can be selectively metalated by an alkyllithium reagent. This is because the reaction may be limited by competing metalation at methyl groups attached to silicon. For example, benzyloxytrimethylsilane cannot be used in the rearrangement reaction because metalation of the silylmethyl protons occurs[165].

Benzyloxytriethylsilane 150 is used to demonstrate the anionic rearrangement. Compound 150 is treated with a slight excess of t-butyllithium in pentane at room temperature, and the mixture is subsequently neutralized with aqueous acid, the rearranged compound 151 is produced in high yield.



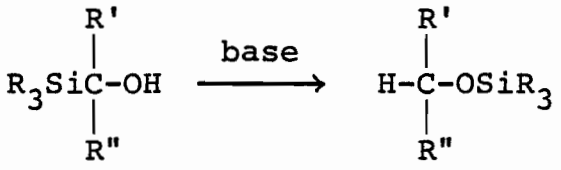
When the metalation is repeated and the reaction mixture is quenched with trimethylchlorosilane, compound 152 is formed. Hydrolysis of 152 gives the compound 151. This indicates

that compound 152 has the structure Ph-CH-($SiEt_3$)$OSiMe_3$. The result of the reactions also suggests that the anion 153 has already rearranged to the form of 154 at the instant of reaction with water or trimethylchlorosilane.



150 153 154

The reverse rearrangement in which a silylcarbinol rearranges to an alkoxysilane is also a well known reaction due to the work by Brook[166]. This "anti-Wittig" rearrangement takes place by an intramolecular anionic mechanism, catalyzed by a small amount of base.



"Anti-Wittig" rearrangement also takes place for compound 151. Treatment of 151 in anhydrous ether with sodium-potassium alloy gives 100% of compound 150 after two minutes without observable evolution of hydrogen or attack on the alkali metal. The reaction, carried out in pentane, requires 40 minutes for completion. Since this "anti-Wittig" rearrangement is still much faster than the anionic rearrangement of alkoxysilanes, it is of interest to add sodium-potassium alloy to the anion

of the silyl-Wittig rearrangement known to give only the silylcarbinol 151 upon neutralization to see if compound 150 would still form. However, no compound 150 is observed after 24 hours treatment of the anion solution with sodium-potassium alloy.

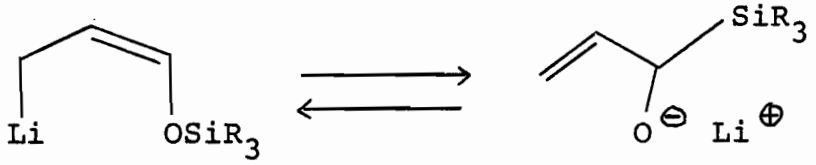
Thus, with sodium-potassium alloy, compound 151 is the preferred product when anions are equilibrated, and compound 150 is the preferred product when neutral species are equilibrated. In other words, the equilibrium shifts completely to the rearranged anion 154 on metalation of the alkosysilane 150.

Rearrangement of silylcarbinols to alkoxysilanes (i.e. the anti-Wittig rearrangement) has been explained as proceeding in the observed direction because of the stability of the Si-O bond in the product. This explanation is valid when neutral species are equilibrated, as with sodium-potassium alloy. However, in the rearrangement of alkoxysilane to silylcarbinol the anions are equilibrated. The rearrangement takes place because the greater stability of the oxyanion vs the carbanion outweighs the energy difference between the Si-O and the C-O bond.

(c) REACTIONS OF ALLYLOXYSILYL CARBANION WITH ELECTROPHILES

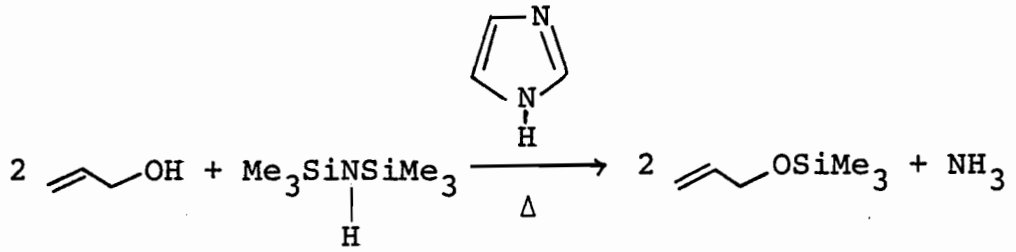
In general it is found that allyloxysilyl carbanion reacts with alkyl halides via γ-substitution to give enol ethers while the reaction with carbonyl compounds, e.g. ketones, proceeds

mainly by α-attack. It has also been found that the allyloxysilyl carbanions 144 are in rapid equilibrium with the corresponding silyl alkoxides 145. This is demonstrated in the silylation reactions of the alkoxysilanes with trimethylchlorosilane. Here we study the extent of such rearrangement of carbanion 144 to oxyanion 145 in different reactions.



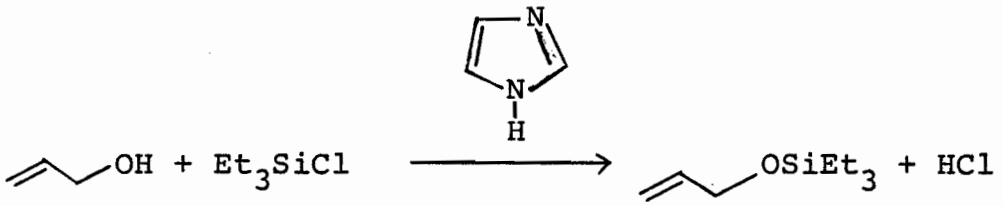
144 145

Trimethylallyloxysilane 155 and triethylallyloxysilane 156 are used as the allyloxysilanes in the study. Trimethylallyloxysilane 155 is prepared by refluxing allyl alcohol with hexamethyldisilazane in the presence of imidazole as in the method described by Glass[167]. The reaction proceeds via N-trimethylsilylimidazole, which then reacts with the allyl alcohol to give the product trimethylallyloxysilane 155. The reaction is driven to completion because ammonia is formed as one of the products.



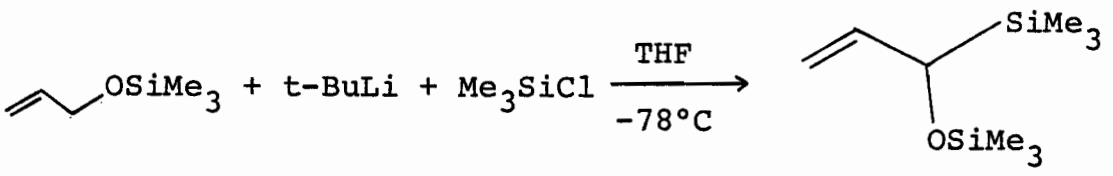
155

Triethylallyloxysilane 156 is prepared by the reaction of allyl alcohol with triethylchlorosilane in the presence of imidazole in dimethylformamide according to the method by Corey[168]. This reaction is also believed to proceed via the intermediate N-triethylsilylimidazole.



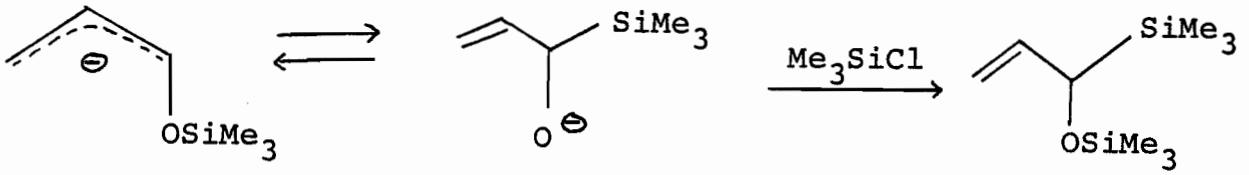
156

Trimethylsilylallyloxy carbanion 157, prepared by the reaction of trimethylallyloxysilane 155 with t-butyllithium at-78°C, reacts with trimethylchlorosilane to give only one product. GC shows only one peak. The structure of this product 158 is determined by standard spectral data. Physical data for compound 158: NMR: δ = 0.0 (s, 9H), 0.1 (s, 9H), 4.0 (m, 1H), 4.8 to 5.2 (m, 2H), 5.6 to 6.2 (m, 1H); IR: 3090, 2960, 2900, 1630, 1250 and 1040 cm^{-1}; mass spectrum at m/e 202, 187 and 73. The fragment ion at m/e 202 gives the molecular weight of the compound 158, thus confirming the structure of the compound.

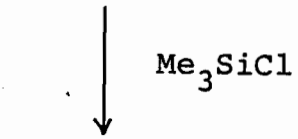


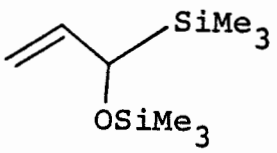
158

Since the substituents on the two silicon atoms are all methyl groups, there is no way of telling if the formation of compound 158 is from the silylation of the rearranged oxyanion 159 or from direct silylation of the trimethylsilyl-allyloxy carbanion 160.



160 159 158

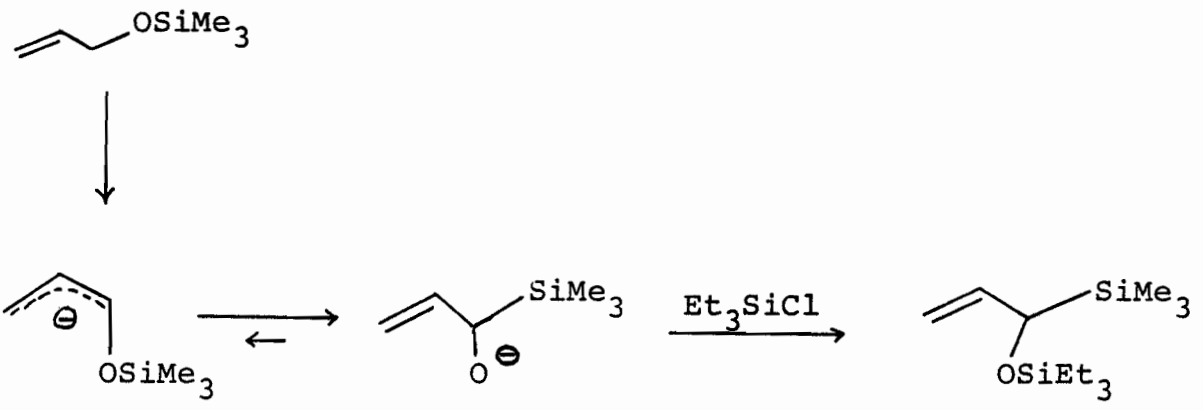




158

Two reactions are performed to clarify the situation. The first reaction involves, once again, the reaction of the trimethylallyloxysilane with t-butyllithium at -78°C. Then, instead of quenching the reaction mixture with trimethylchlorosilane, triethylchlorosilane is used to quench the reaction mixture. An α-siloxyallylsilane 161 is obtained. Looking at the NMR spectrum of 161 the signal of the trimethyl-

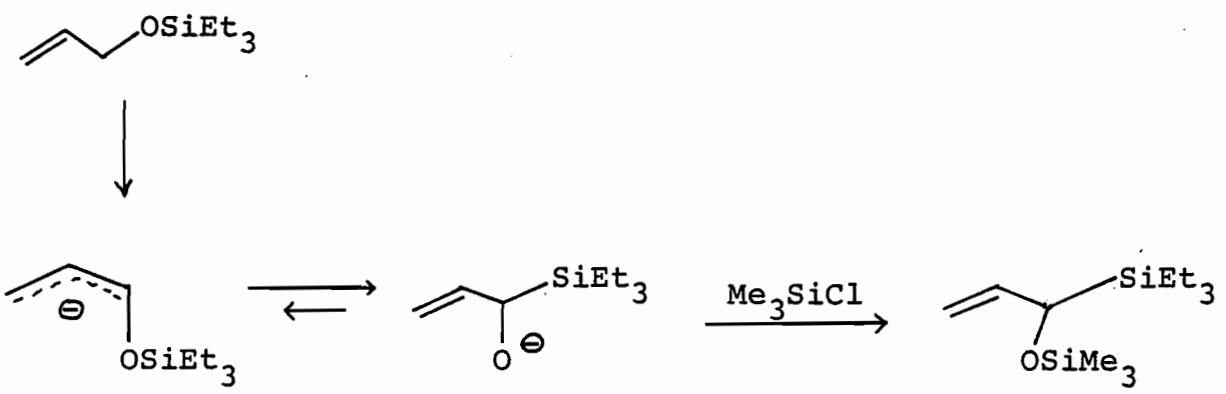
silyl group appears at a higher field compared to the trimethylsilyl signal of the starting material, trimethylallyloxysilane. It is known that the methyl protons signal of C-$SiMe_3$ appears at higher field than the methyl protons of O-$SiMe_3$ group[157]. The NMR of 161 indicates that the trimethylsilyl group is attached to a carbon atom instead of to an oxygen as in the starting material. This accounts for the upfield shift of the signal. This can only happen if the carbanion is rearranged to the oxyanion 159 before silylation.



160 159 161

The above speculation is further proved by the following reaction. Triethylsilylallyloxy carbanion, prepared from the reaction of triethylallyloxysilane and t-butyllithium at -78°C, is reacted with trimethylchlorosilane to give the α-siloxyallylsilane 162. The NMR of 162 shows that the trimethylsilyl signal is at lower field compared to the trimethylsilyl signal of 161. For compound 162, the trimethylsilyl group is likely to be attached to an oxygen, i.e. the O-$SiMe_3$ group. A

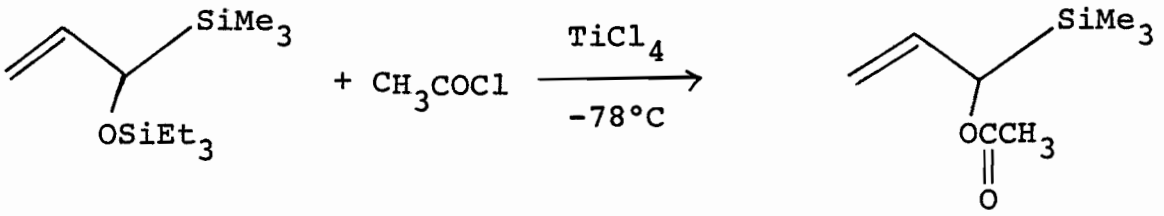
comparison of the NMR of 162 with that of trimethylallyloxysilane shows that both trimethylsilyl groups appear at the same position, δ = 0.1. Thus, compound 162 is obtained from the silylation of the rearranged oxyanion.



162

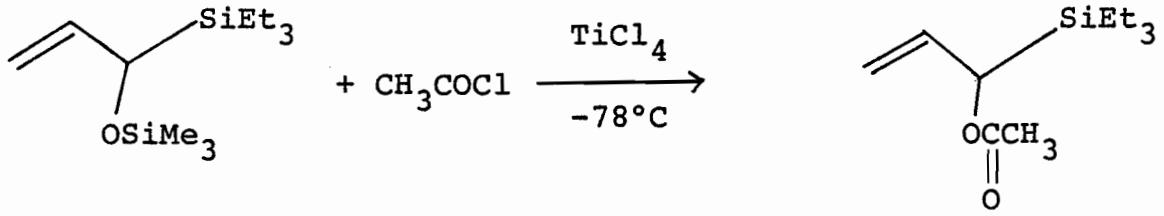
Compounds 161 and 162 have very similar NMR data except for the positions for the trimethylsilyl signals. (δ = 0.0 for compound 161 and δ = 0.1 for compound 162). The structures of 161 and 162 are further proven to be correct by the following transformations.

Compound 161 reacts with acetyl chloride in the presence of titanium tetrachloride in methylene chloride at -78°C to give the acetate 163 with the trimethylsilyl signal remaining at δ = 0.0. NMR for 163: δ = 0.0 (s, 9H), 2.0 (s, 3H), 4.0 (m, 1H), 4.8 to 5.2 (m, 2H), 5.6 to 6.2 (m, 1H). Under such conditions the O-silyl group is very easily cleaved.



161 163

Compound 162 also reacts with acetyl chloride in the presence of titanium tetrachloride at -78°C to give an acetate 164. However, NMR of 164 shows that no trimethylsilyl signal is present. This is reasonable because the Si-O bond is cleaved in the reaction and the trimethylsilyl group is lost in the reaction.

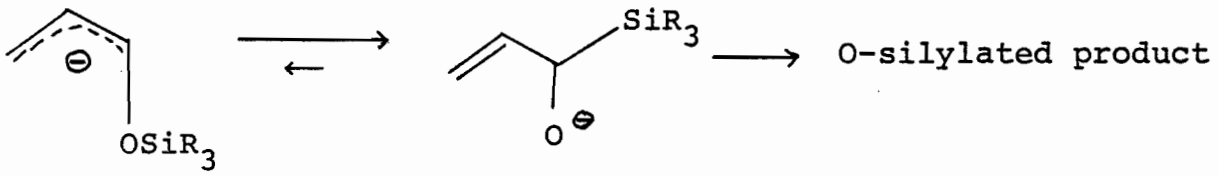


162 164

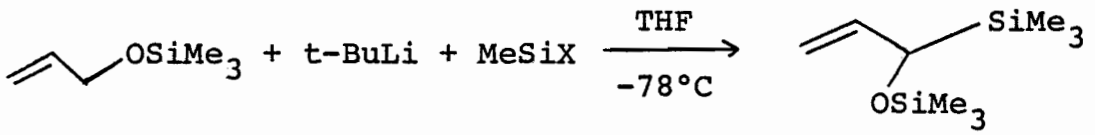
The reactions of α-siloxyallylsilanes with acid chlorides will be discussed in detail later in this chapter.

From the silylation products of the allyloxysilanes, it can be seen that the carbanion from the allyloxysilane goes through the 1,2-anionic rearrangement to give the oxyanion before it reacts with the silyl chloride. The fact that only one product is seen in every silylation reaction indicates

that the equilibrium is shifted favourably to the rearranged oxyanion in the silylation reaction. In other words, the O-silylation reaction is favoured.



From the results obtained, it is deduced that compound 158 is also obtained from the rearranged oxyanion 159. A series of silylating reagents is tried in the silylation of trimethylallyloxysilane. However, compound 158 is the only product obtained in the silylation reactions.



X = F, Cl, Br and I

158

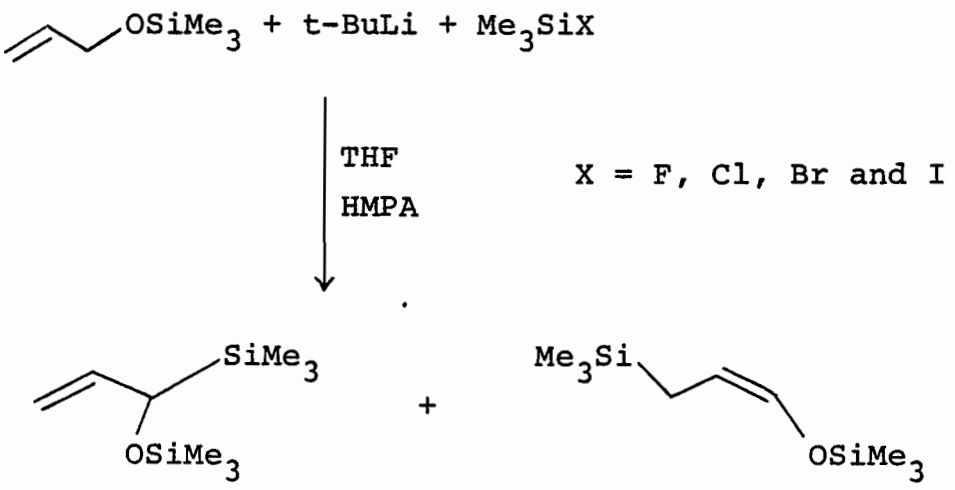
Since the O-silylation reaction is favoured in the reaction with trimethylchlorosilane to give the rearranged product from the oxyanion 159 and the silylation reactions using a series of trimethylsilyl halides under the same reaction conditions gives also only compound 158, it strongly suggests that compound 158 is also from the rearranged oxyanion 159, i.e. through the same kind of reaction mechanism as the reaction with trimethylchlorosilane. That no γ-addition product

is formed shows that the different silylating reagents have no effect on the equilibrium between the anions. The different silylating reagents do not affect the rate of C- or O-silylation.

The position of equilibrium between the carbanion and oxyanion has been demonstrated by West[164] to favour the oxyanion. The fact that only the O-silylated product is present in the silylation reaction and only the C-alkylated product is formed in the alkylation reaction of allyloxysilane suggests that the two anions are in rapid equilibrium with each other even though the oxyanion is the favoured species.

The situation, however, is changed if a little HMPA is added to the allyloxysilyl carbanion before quenching with the silylating reagent. In this case, two products are obtained after work up. NMR of the crude material obtained shows that one of the products is 158 while the other product 165 is identified to be the direct silylation product of the allyloxysilyl carbanion 160 without rearrangement. GC-MS shows that one of the products has identical mass spectral data with the compound 158. Mass spectrum of the other product has the parent ion at m/e 202 which is identical to the molecular weight of the silylated product of the allyloxysilyl carbanion 160. However, attempts to isolate both compounds from the crude material by preparative TLC fail. Only compound 158 can be isolated from the plates. The other

product 165, being a vinyl silyl ether, has probably decomposed in the TLC development



158 165

The ratio of the two products depends on the silylating reagents used (See Table 9). For example, the reaction with trimethylchlorosilane gives the two products 158 and 165 in the ratio of 1:1 (calculated from GC and the integrations of the olefinic protons in NMR). From the NMR of the crude material obtained, the NMR data for 165 is: δ = 0.0 (s, 9H), 0.1 (s, 9H), 1.4 (d of d, 2H), 4.4 (d of t, 1H) and 6.2 (m, 1H). Mass spectral data of 165 from GC-MS has fragment ions at m/e 202, 187 and 73.

The formation of product 165 has to be due to the presence of HMPA because all other reaction conditions are identical. However, it is unlikely that HMPA has any significant effect on the rate of equilibrium between the two anions because

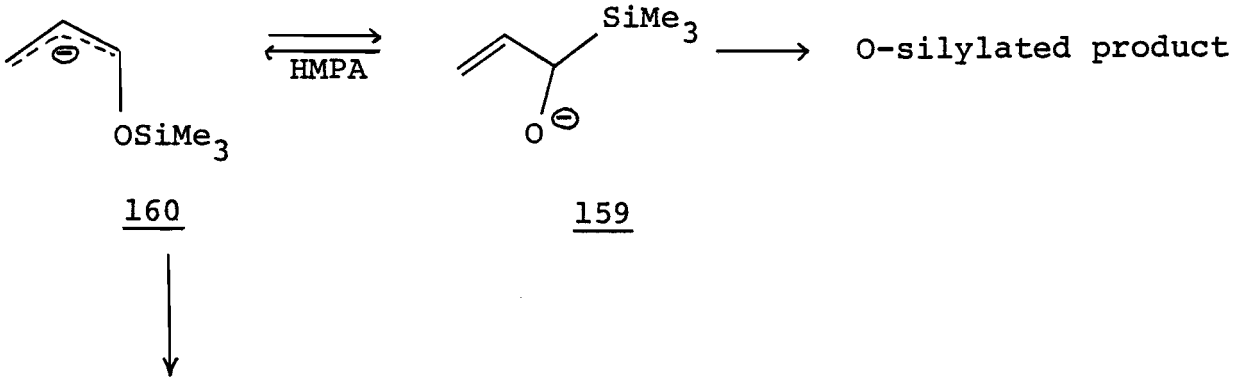
TABLE 9: SILYLATION OF TRIMETHYLALLYLOXYSILANE IN THE PRESENCE OF HMPA

Me_3SiX	Products %	
	158	165
X = F	35	65
Cl	50	50
Br	75	25
I	85	15

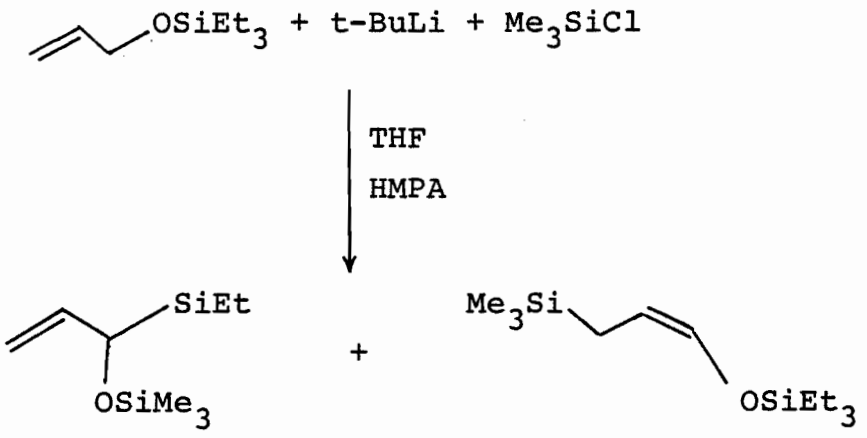
the equilibrium is rapid or on the extent of equilibrium. Most likely the presence of HMPA favours the C-silylation reaction, i.e. increases the rate of C-silylation. The competition between the two kinds of silylation gives a mixture of compounds as products. The ratio of the product shows the C-silylation is also a fast reaction because, even though the carbanion 160 is not the dominant species in the reaction mixture, in each case quite a large percentage of C-silylated product is formed.

The change in product ratio with different silylating reagents can be explained by the difference in "hardness" of the nucleophiles involved[169,170]. The oxyanion 159 is a harder nucleophile compared with the carbanion 160. Thus, it is not surprising for it to bind more favourably with

trimethyliodosilane than trimethylfluorosilane because the silicon in R_3Si-I is a harder electrophile than the silicon in R_3Si-F. Likewise, the carbanion 160 being a softer nucleophile tends to bind more favourably with trimethylfluorosilane, which is softer in the sense of an acid compared to trimethyliodosilane. Thus, more C-silylation occurs in the reaction with trimethylfluorosilane while more O-silylation occurs for the reaction with trimethyliodosilane



The effect of HMPA on silylation reaction of allyloxysilanes seems to be very general. For example, instead of trimethylallyloxysilane, triethylallyloxysilane also reacts with t-butyllithium and trimethylchlorosilane at -78°C in the presence of HMPA to give a mixture of two products. The ratio of the products is 1:1 according to GC and also NMR integrations of the olefinic protons.

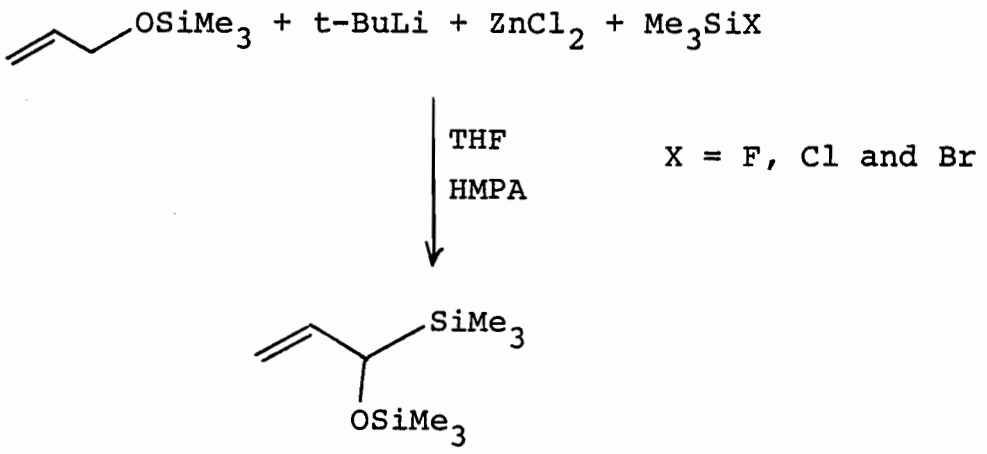


162 166

The NMR of the crude material obtained shows that one of the products is compound 162. This is then confirmed by GC-MS. Mass spectrum of one of the products has identical mass spectral data to compound 162. The other product 166 has signals of the vinyl silyl ether obtained directly from the C-silylation of the allyloxysilyl carbanion without rearrangement. NMR for compound 162: δ = 0.1 (s, 9H), 0.5 to 1.3 (m, 15H), 4.1 (m, 1H), 4.8 to 5.2 (m, 2H), 5.7 to 6.2 (m, 1H); mass spectrum of 162 has fragment ions at m/e 244, 229, 215, 115, 87 and 73. For compound 166, NMR data has δ = 0.0 (s, 9H), 0.5 to 1.3 (m, 15H), 1.4 (d of d, 2H), 4.4 (d of t, 1H), 6.0 (m, 1H). The mass spectrum from GC-MS for compound 166 has fragment ions at m/e 244, 229, 215, 115, 87 and 73. The ion at m/e 244 is the parent ion. This gives the correct molecular weight of compound 166 as speculated.

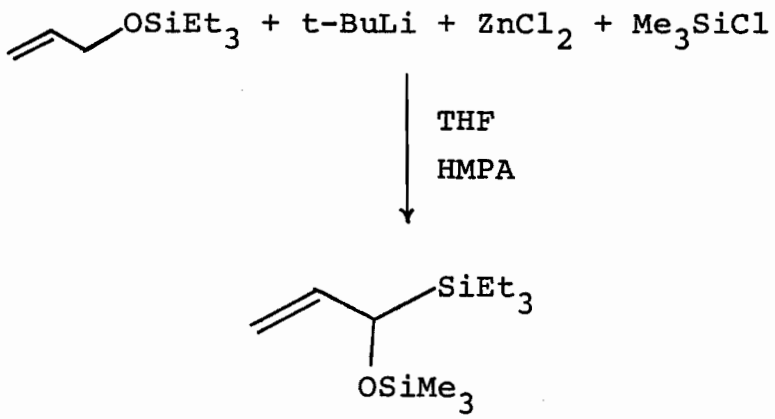
The addition of zinc chloride to the silylation reaction alters the nature of products obtained. Once again compound

158 is obtained as the sole product in the silylation reaction of trimethylallyloxysilane with a series of silylating reagents.



158

The reaction of triethylallyloxysilane with trimethylchlorosilane in the presence of molar equivalent of zinc chloride gives only one product. The product is identified to be compound 162, which is the same product derived from the silylation of the rearranged oxyanion.

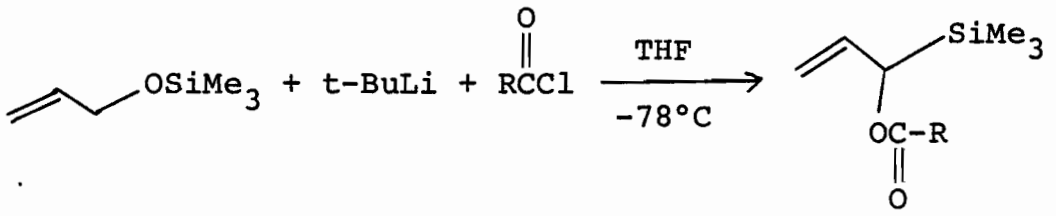


162

The result of this particular silylation implies that the counter ion effect[90] that is used to explain the product ratio in the reactions of simple allylic ethers with electrophiles may not give a satisfactory answer for the product obtained. In simple allylic ethers, the addition of the electrophiles is exclusively α to oxygen in the presence of zinc chloride, However, in the silylation of allyloxysilanes only the rearranged product is obtained. It is certain that zinc chloride has an effect on the silylation reaction but it is not clear exactly how. Is it the allylic zinc reagent that is formed in the reaction or merely the presence of zinc chloride that favours the equilibrium to shift to the oxyanion that leads to the rearranged product? Or is it the presence of zinc chloride that reduces the effect of HMPA in the reaction, and thus reduces the rate of the C-silylation reaction? More work has to be done in this area in order to clarify the role of zinc chloride in the silylation reaction.

It has been reported by Still[92] that allyloxysilyl carbanion reacts with carbonyl compounds, e.g. ketones, to give mainly the α-addition products. However, this does not hold true for reactions with other carbonyl compounds. For example, we find the trimethylallyloxysilane reacts with different acid chlorides or chloroformates to give only the rearranged products. These reactions are similar to the silylation reactions. The products are isolated by preparative TLC. The structures of the products are identified by the upfield shift of the chemical shifts of the protons of

the trimethylsilyl group in NMR, by the carbonyl absorption of the IR spectra and by mass spectral data. In some cases the structures are identified by comparing with authentic compounds prepared by other means.



163 R = CH_3-

167 R = C_6H_5-

168 R = CH_3O-

169 R = C_2H_5O-

The reaction is carried out in similar fashion to the silylation reactions. However instead of quenching the trimethylsilylallyloxy carbanion with silyl halides, the carbanion is reacted with different carbonyl compounds. For example, trimethylallyloxysilane reacts with acetyl chloride to give a compound with identical spectral data to compound 163 prepared from the reaction of α-siloxyallylsilane 161 with acetyl chloride in the presence of titanium tetrachloride. The chemical shift of the trimethylsilyl group is shifted upfield from δ = 0.1 to 0.0. An extra singlet at δ = 2.0 indicates the presence of a methyl group shifted downfield because of the adjacent carbonyl group. IR for 163 has signals at 3090, 2960, 1740, 1630 and 1250 cm^{-1}. The signal

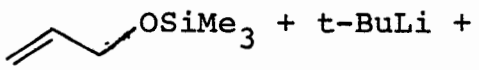
at 1740 cm^{-1} indicates the presence of an ester instead of a ketone. Also the NMR signal of the trimethylsilyl group indicates the presence of a C-$SiMe_3$ group rather than an O-$SiMe_3$ group. Both these indicate the structure of the product is the rearranged compound, a substituted allylsilane. This can only happen if the rearrangement of the allyloxysilyl carbanion 160 to the oxyanion 159 has taken place after metalation. The mass spectrum of 163 gives the parent ion at m/e 172. This gives the molecular weight of the compound. The fact that only one product is obtained also indicates the complete rearrangement to the oxyanion.

If the reaction mixture is quenched with benzoyl chloride instead of acetyl chloride, compound 167 is obtained. The spectral data of 167 indicates that it is also formed from the rearranged oxyanion. Once again $\delta = 0.0$ indicates a C-$SiMe_3$ group. The IR signal at 1720 cm^{-1} indicates the presence of an aromatic ester and not a ketone, while the mass spectrum has the parent ion at m/e 234, indicating the molecular weight of the compound.

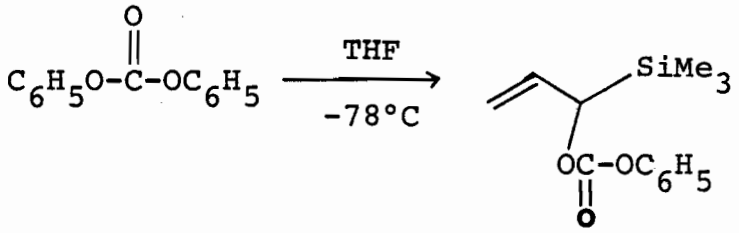
The reactions with chloroformates also give the same kind of results. Reactions with methyl chloroformate and ethyl chloroformate give the compounds 168 and 169 respectively. The mass spectra give the molecular weight of the two compounds by the presence of the parent ions (m/e 188 for compound 168 and m/e 202 for compound 169). Both compounds have the chemical shifts of the trimethylsilyl

groups at δ = 0.0, indicating the presence of C-$SiMe_3$ groups. The IR spectra of both 168 and 169 have signals at 1750 cm^{-1}. This is an indication of the presence of a carbonate group. All these information indicate, once again, the rearranged oxyanion 159 is involved in the reactions. This is not surprising because the reaction of oxyanion with α-chloro carbonyl compounds to give an ester is a favourable reaction. Besides, the reaction is fast due to the fact that the chloride ion is a good leaving group which facilitates the reaction. This, together with the fact that the anion exists mostly in the form of the oxyanion 159 favours the formation of the rearranged product.

The effect of the nature of leaving group can be shown by the reaction of allyloxysilane with carbonates. For example, trimethylallyloxysilane reacts with diphenyl carbonate in the same way as the reaction with acid chloride. Only the rearranged carbonate 170 is obtained. This is probably because the phenoxide ion is a good leaving group.

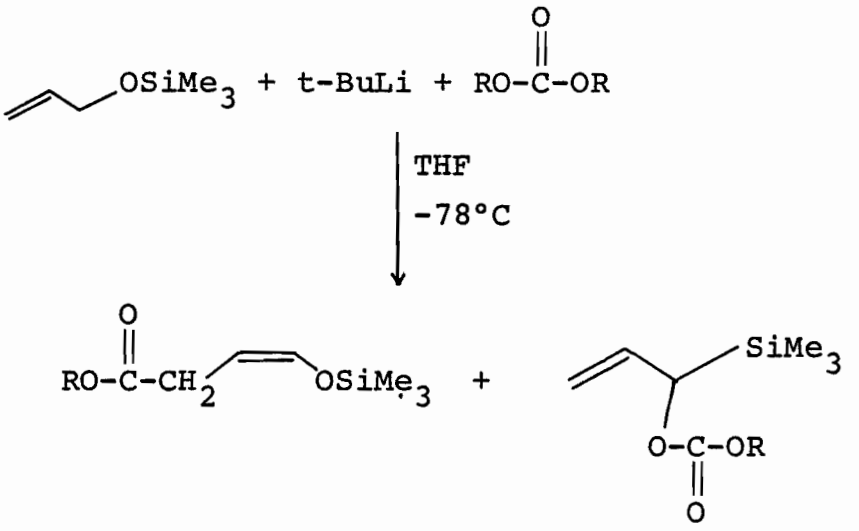


+ t-BuLi +



170

Trimethylallyloxysilane, however, reacts with dimethyl or diethyl carbonate to give two products.



171	R = CH_3-	168	R = CH_3-
172	R = C_2H_5-	169	R = C_2H_5-

The rearranged product in each case from the reaction with dialkyl carbonate has identical spectral data to compound 168 or 169, which is formed from the reaction of trimethylallyloxysilane with methyl chloroformate or ethyl chloroformate. In the reaction with dimethyl carbonate, the ratio of the products 171 to 168 is ∿ 2:1, estimated from the NMR of the crude materials obtained. The NMR data for 171 can be obtained from the crude material obtained. δ = 0.1 (s, 9H), 3.0 (d of d, 2H), 3.6 (s, 3H), 4.5 (m, 1H), 6.2 (m, 1H). GC-MS gives the mass spectrum of 171 as follows: m/e 188, 173, 129, 89, 73 and 59. The fragment ion at m/e 188 is the parent ion which gives the correct molecular weight of

171. However, compound 171 cannot be isolated by preparative TLC. The compound is a vinylsilyl ether and is probably unstable on TLC plates. Only compound 168 is isolated.

In the reaction with diethyl carbonate, the ratio of the products 172 to 169 is 1.2 to 1, estimated from the NMR of the crude material obtained. Compound 172 is unstable on preparative TLC. Only compound 169 is isolated. However, from GC-MS the mass spectrum of 172 is obtained. The fragment ion at m/e 202 gives the correct molecular weight of compound 172. Other fragments obtained are at m/e 187, 159, 157, 129, 73, 41 and 29. From the crude product, the NMR data for 172 is also observed at δ = 0.2 (s, 9H), 1.2 (t, 3H), 3.0 (d of d, 2H), 4.2 (q, 2H), 4.7 (m, 1H), 6.2 (m, 1H).

The reactions with dimethyl carbonate and diethyl carbonate are slower because methoxy and ethoxy anions are not as good leaving groups when compared to the phenoxy anion or chloride ion. If the reaction is slow, the presence of the two anions in equilibrium can lead to the formation of two products even though one of the anions predominates in the reaction mixture. The fact that more of the non rearranged product is formed indicates that the carbanion 160 is a better nucleophile than the oxyanion 159 in the reaction with the carbonyl carbon of the dialkyl carbonate.

The addition of HMPA to the reaction mixture does not affect the product ratio as in the case of silylation reaction. For example, reactions of trimethylallyloxysilane

with acid chlorides in the presence of HMPA give also only one product as in the cases when HMPA is absent. However, other side reactions occur. The yield of the rearranged product is low and it is accompanied by many unidentified side products.

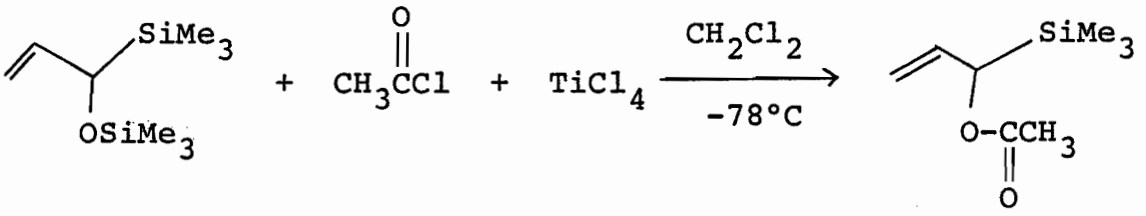
In general, metalation of allyloxysilane gives a carbanion which is in rapid equilibrium with the rearranged oxyanion. The products obtained from the reactions of these anions with electrophiles depend on the kind of electrophiles and the reaction conditions involved.

(d) REACTION OF α-SILOXYALLYLSILANE WITH ACID CHLORIDE

The synthetic utility of allylsilanes has been demonstrated in their reactions with various carbonyl compounds in the presence of a Lewis acid as discussed in the introductory chapter. One example, by Calas[77], is the synthesis of the naturally occurring Artemisia ketone 44 using a substituted allylsilane and an acid chloride in the presence of aluminum chloride.

With the synthesis of α-siloxyallylsilane 158, the reactions of this compound with various acid chlorides are investigated. Reaction of 158 with acetyl chloride at -78°C in methylene chloride in the presence of titanium tetrachloride[171] gives cleanly one product, the ester 163. The reaction is followed by GC and is found to be very fast. The reaction mixture turns brown 5 minutes after the addition of the

α-siloxyallylsilane 158. GC shows that no starting material 158 is left.



158 163

Since only the O-$SiMe_3$ group reacts with the acetyl chloride and the C-$SiMe_3$ group is untouched, the reaction is repeated using two equivalents (molar quantities) of both the acetyl chloride and titanium tetrachloride with respect to the α-siloxyallylsilane 158. However, the result is not changed. Only the compound 163 is obtained as product. Neither the use of a different Lewis acid like aluminum chloride nor the change in reaction temperature has any effect on the outcome of the reaction. However if the reaction temperature is raised from -78°C to -24°C or higher, less of the product 163 is obtained. Side reactions also occur leading to unidentified decomposition products.

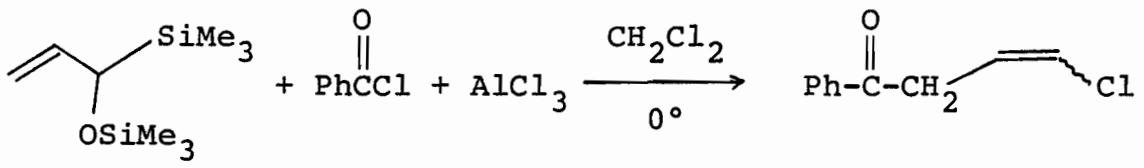
α-Siloxyallylsilane 158 is allowed to react with various other acid chlorides in the presence of a Lewis acid. However, at -78°C the reaction is very slow in each case, only some of the ester is formed while a large amount of the acid chloride is recovered. No other product is found. In the cases where

molar equivalents of the allylsilane and acid chloride are used, raising the reaction temperature from -78°C to 0°C does help as more of the corresponding esters are formed. Observation from the NMR of the crude material obtained in each case shows that the ester is the major product formed. Prolonging reaction time does not help very much as other unidentified products are observed from the NMR. Thus, in each case it is seen that in compound 158, the O-$SiMe_3$ group is more reactive than the C-$SiMe_3$ group in the same molecule.

If the reaction is carried out at a temperature higher than -78°C, e.g. at 0°C, using two molar equivalents each of the acid chloride and Lewis acid with respect to the α-siloxyallylsilane, very little if any, of the corresponding ester is obtained. However, other interesting reaction products are observed. A few of the reactions of α-siloxyallylsilane with different acid chloride are discussed.

In the reaction of α-siloxyallylsilane 158 with two equivalents each of benzoyl chloride and aluminum chloride in methylene chloride at 0°C, GC of the crude material obtained shows two peaks of equal magnitude with very close retention times. The NMR of the crude material shows no trimethylsilyl signal is present. Preparative TLC, however, cannot separate the two major components. One major fraction is isolated by preparative TLC. However, GC of this fraction consists of the same two peaks of equal magnitude. GC-MS shows the two components have identical mass spectra, indicating the two

components are geometric isomers of each other.



158 173 cis and trans

The structure of the product 173 is deduced from various spectral data. The NMR of 173 (see Figure 1, internal $CHCl_3$ standard) indicates the presence of a methylene group, two olefinic protons and five aromatic protons at δ = 3.6 to 3.9, 6.0 to 6.4 and 7.4 to 8.1 respectively. The IR has a signal at $\sim$ 1690 cm^{-1} indicating an aromatic ketone is present. The two identical mass spectra (Figures 2 and 3) have fragment ion at m/e 180 which corresponds to the molecular weight of 173. A small peak at m/e 182 which is about 33% in intensity compared to the parent ion, indicates the presence of chlorine. From the computer print out, the abundance of fragment 180 is 0.6% while fragment 182 is 0.2% compared to the base peak at m/e 105. Other major fragments are m/e 144, 105 and 77. Fragment at m/e 144 is P-36, indicating a loss of a molecule of HCl from the compound. This also indicates the presence of chlorine in the molecule. The isolated yield of compound 173 is $\sim$ 84.5%.

To further prove the presence of chlorine, a chemical test is performed to compound 173. The Beilstein test[172] for halogen is found to be positive. That the flame test

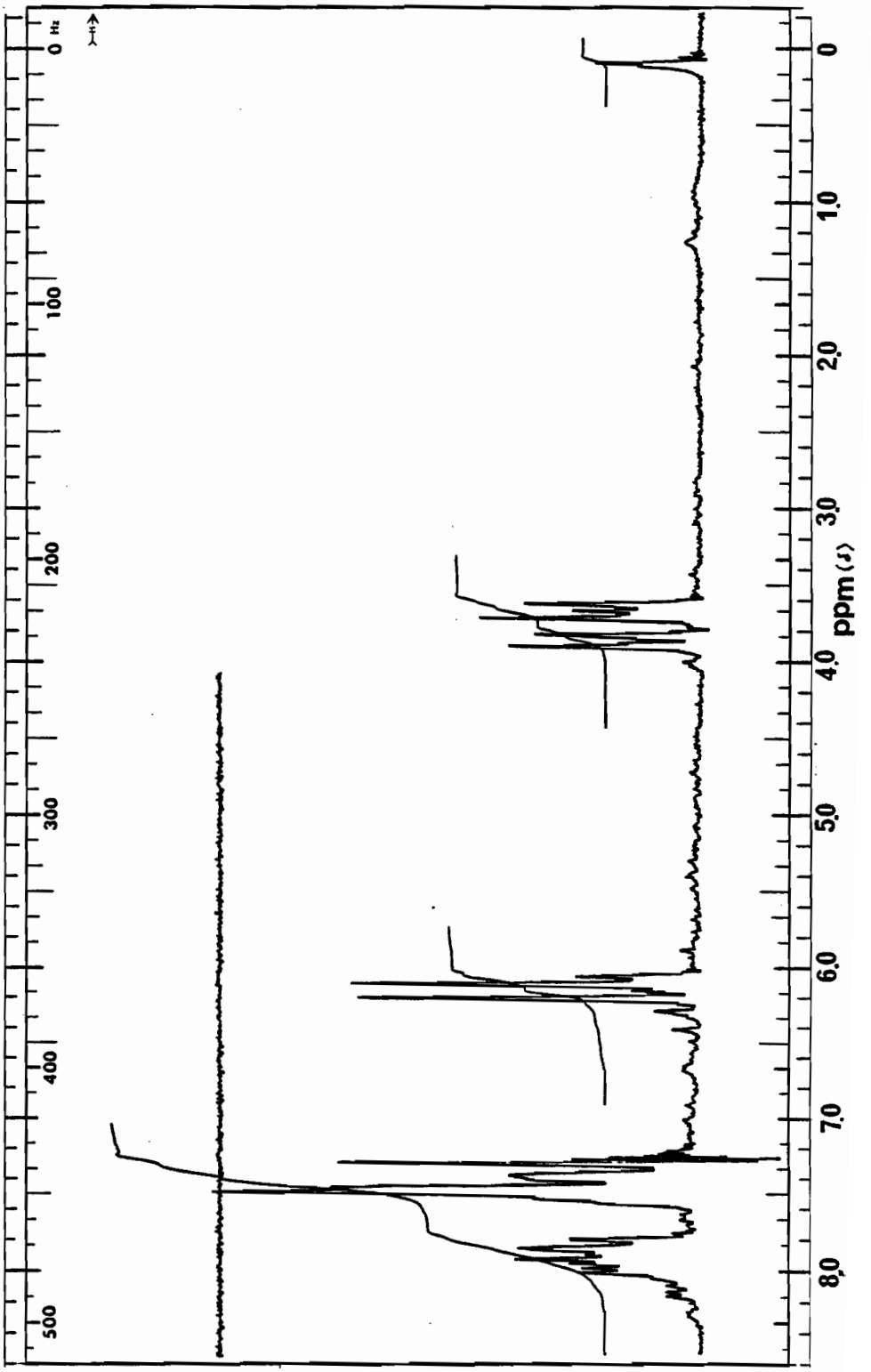
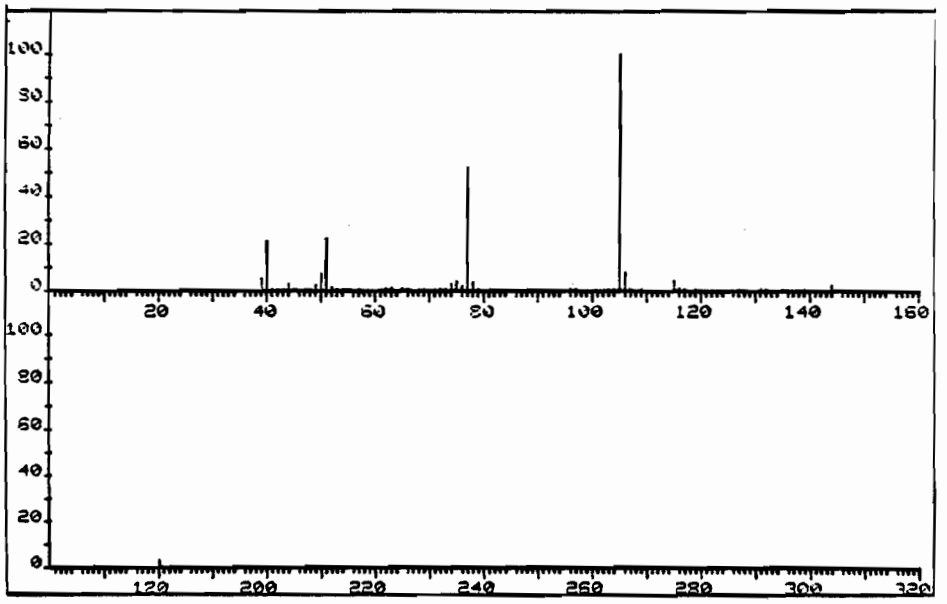
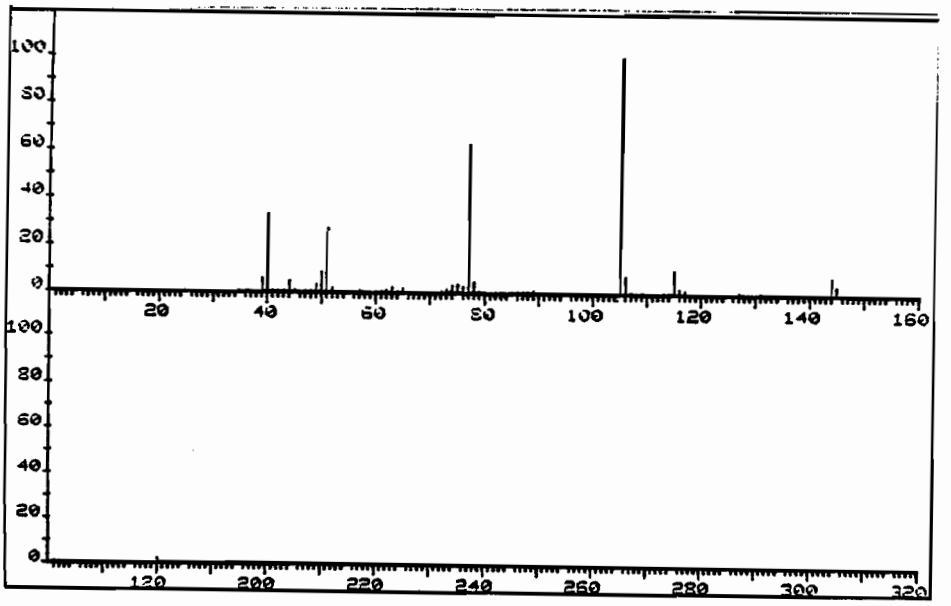


FIGURE 1: NMR OF COMPOUND 173 ($CHCl_3$ internal standard)

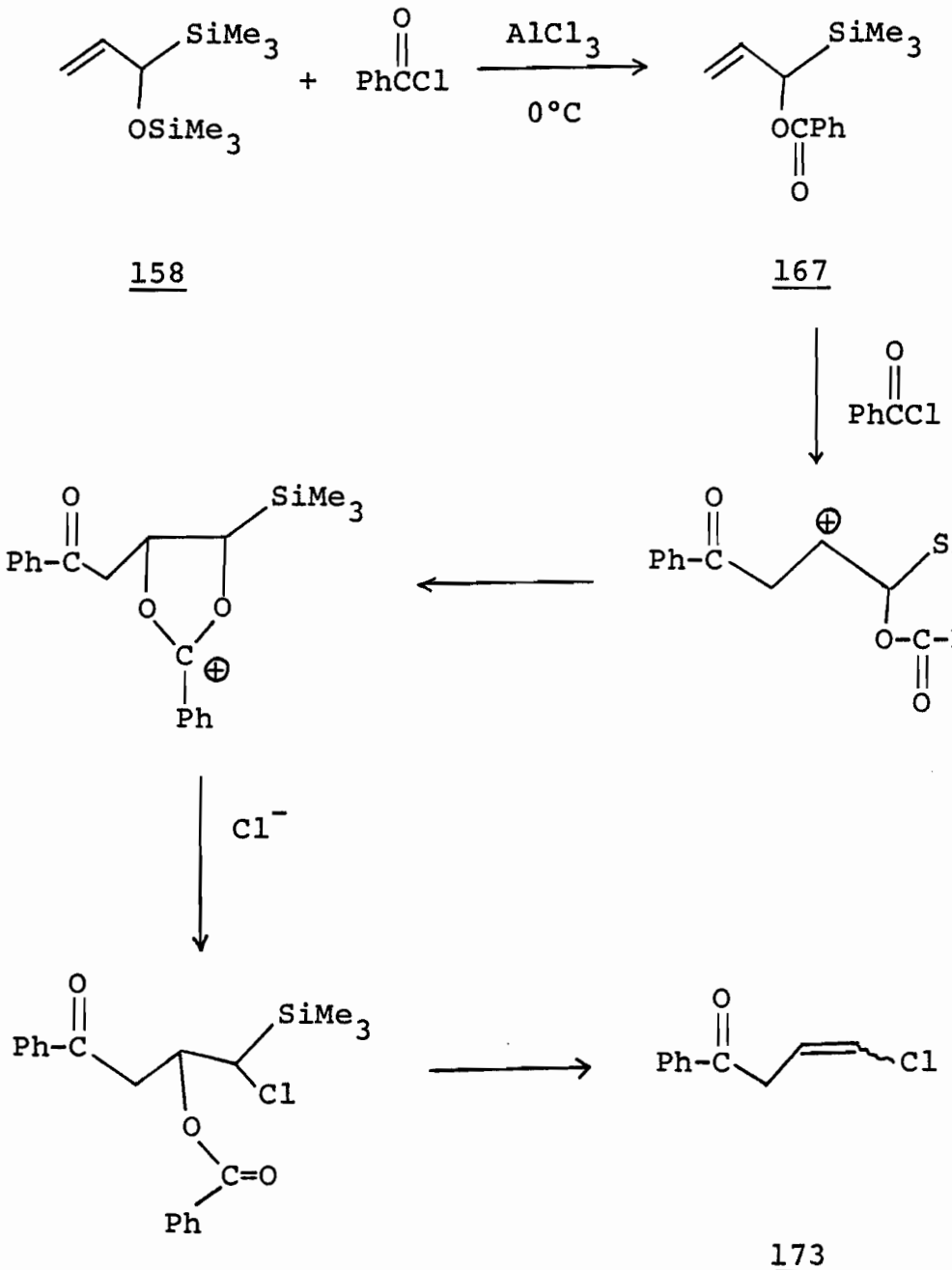




FIGURES 2 and 3: MASS SPECTRA OF GEOMETRIC ISOMERS OF COMPOUND 173

for 173 gives a greenish colour indicates the presence of halogen, which is chlorine in this case.

To determine how compound 173 is formed from the reaction between 158 and benzoyl chloride, a mechanism involving the ester 167 as intermediate is proposed (Scheme 15).



SCHEME 15

The reaction of α-siloxyallylsilane 158 with p-anisoyl chloride (p-methoxy benzoyl chloride) in the presence of aluminum chloride is carried out at 0°C. However, the reaction is slow. The reaction is repeated at room temperature. On work up, three major compounds are detected by GC. Preparative TLC gives two major fractions. The GC of one fraction gives two peaks of equal magnitude with very close retention times. GC-MS shows the two components have identical mass spectra. Once again these two components are geometric isomers. Like compound 173, the products from this fraction are the vinyl chloride 174. The mass spectrum of 174 has parent ion at m/e 210 which is the molecular weight of the vinyl chloride. A smaller peak at m/e 212 indicates the presence of (M+2) ion. The abundance of m/e 210 and 212 are 1.6 and 0.6% with respect to the base peak at m/e 135. The relative abundance of the (M+2) fragment to the parent ion is about 1:3. This indicates the presence of a chlorine atom in the molecule. The IR of 174 has a signal at 1675 cm^{-1}, indicating the presence of an aromatic ketone. The NMR of compound 174 (Figure 4, internal CH_2Cl_2 standard) also gives the correct ratio of the different types of protons of the vinyl chloride 174. The isolated yield of 174 by preparative TLC is ∿ 55.9%.

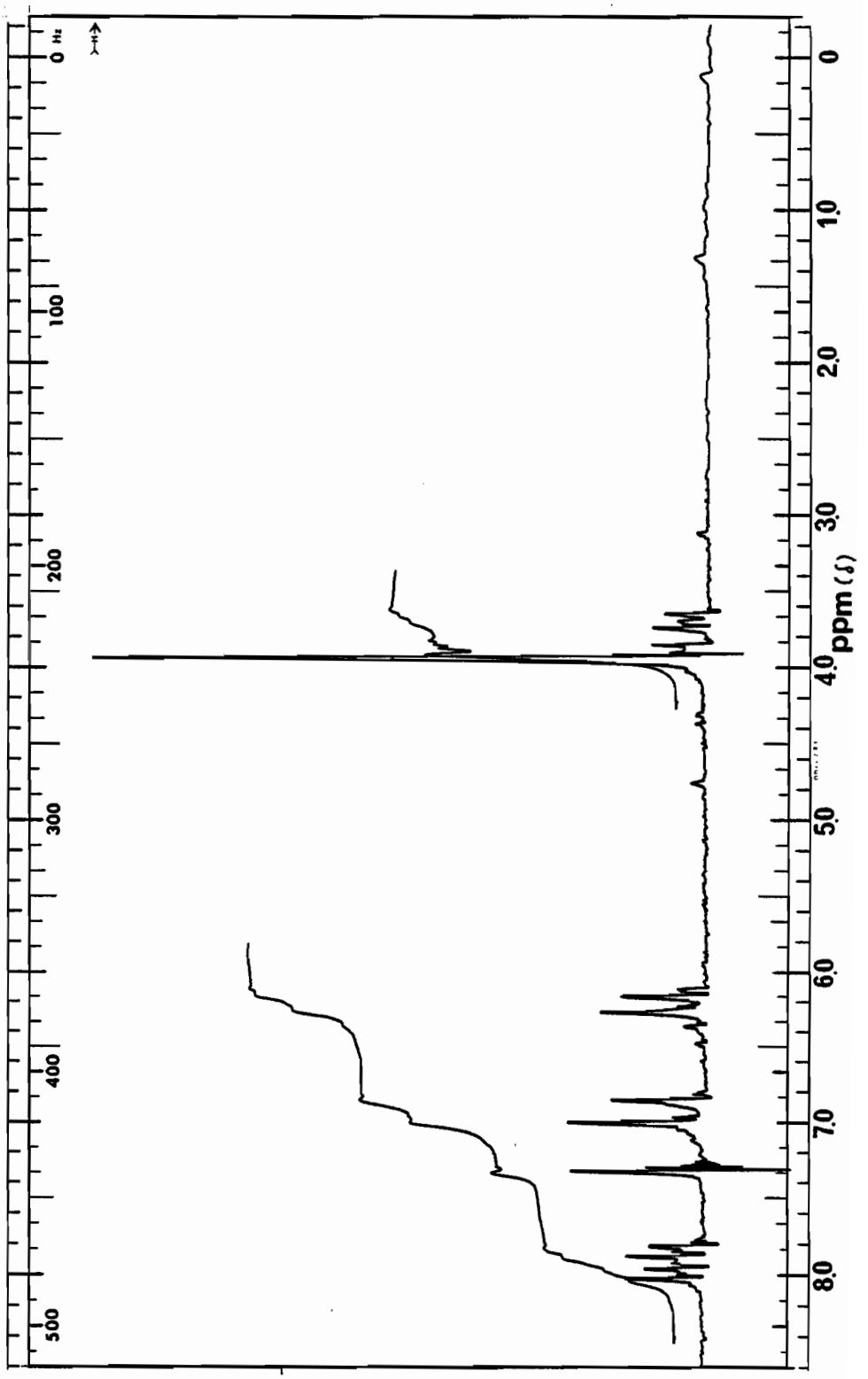
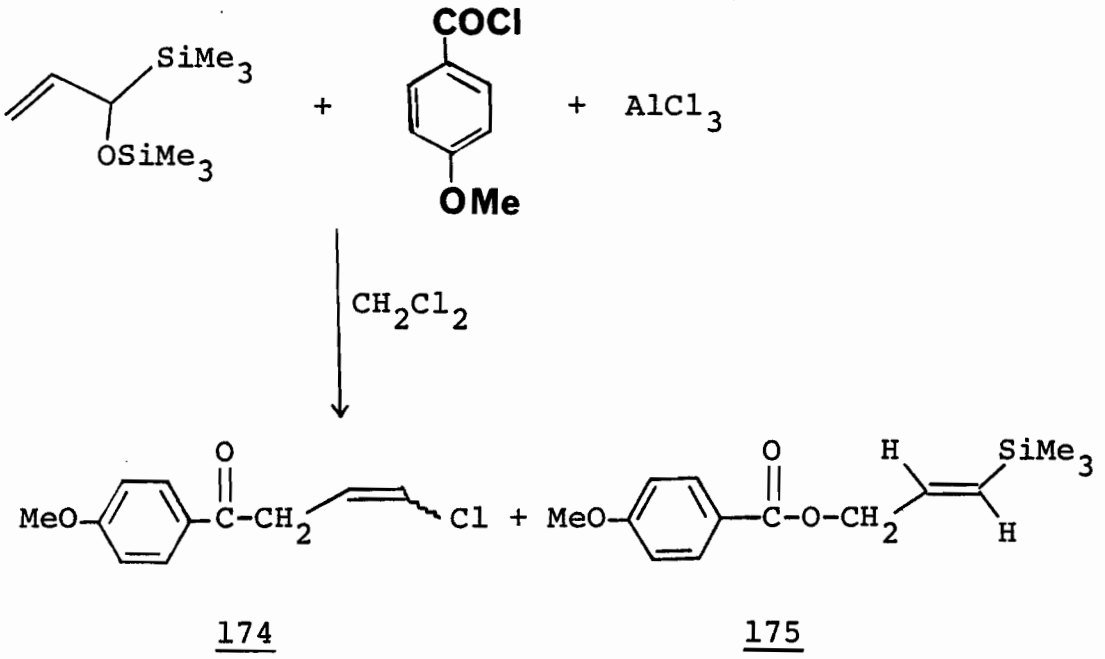


FIGURE 4: NMR OF COMPOUND 174 ($CHCl_3$ internal standard)



174 175

The other fraction isolated from preparative TLC consists of only one compound (GC analysis). The IR signal at 1710 cm^{-1} is too high for an aromatic ketone but can be that of an aromatic ester. The structure of 175 is based on its NMR (Figure 5, internal $CHCl_3$ standard). The chemical shift at δ = 0.1 (s, 9H) indicates the presence of a trimethylsilyl group. δ = 3.8 (s, 3H) is the methoxy group. δ = 4.7 (d, 2H) is a methylene group, downfield because of deshielding. The multiplet at δ = 5.6 to 6.1 has two olefinic protons, while the symmetrical signals at δ = 6.8 and 7.9 are the four aromatic protons of the disubstituted benzene ring. The geometry of the vinylsilane 175 is determined by the HA-100 MHz NMR to be trans because the coupling constant of the olefinic protons is $\sim$ 18 Hz (see Figure 6). The mass spectrum of 175 has fragment ions at m/e 264, 165, 135, 107, 92, 77 and 73.

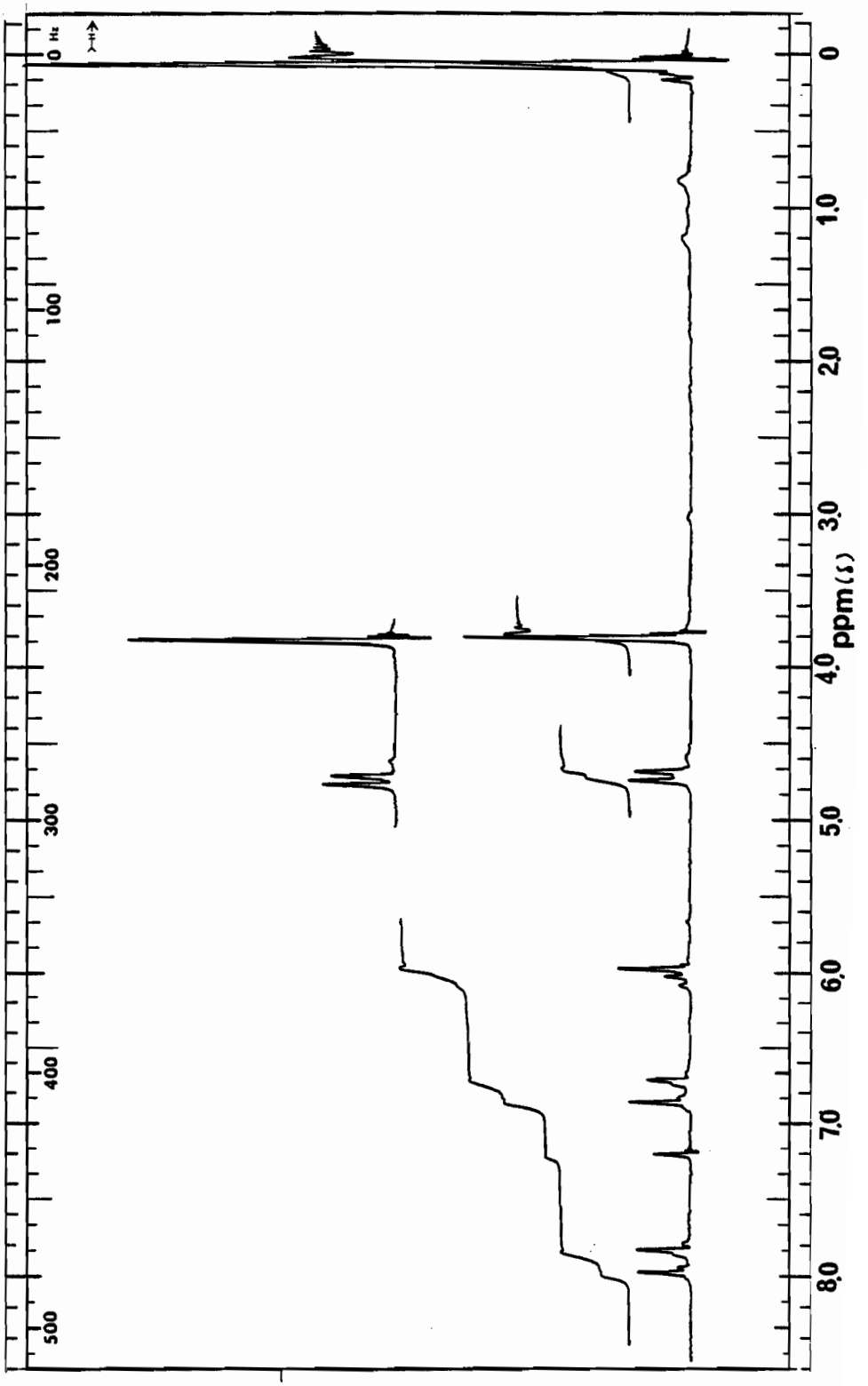


FIGURE 5: NMR OF COMPOUND 175 ($CHCl_3$ internal standard)

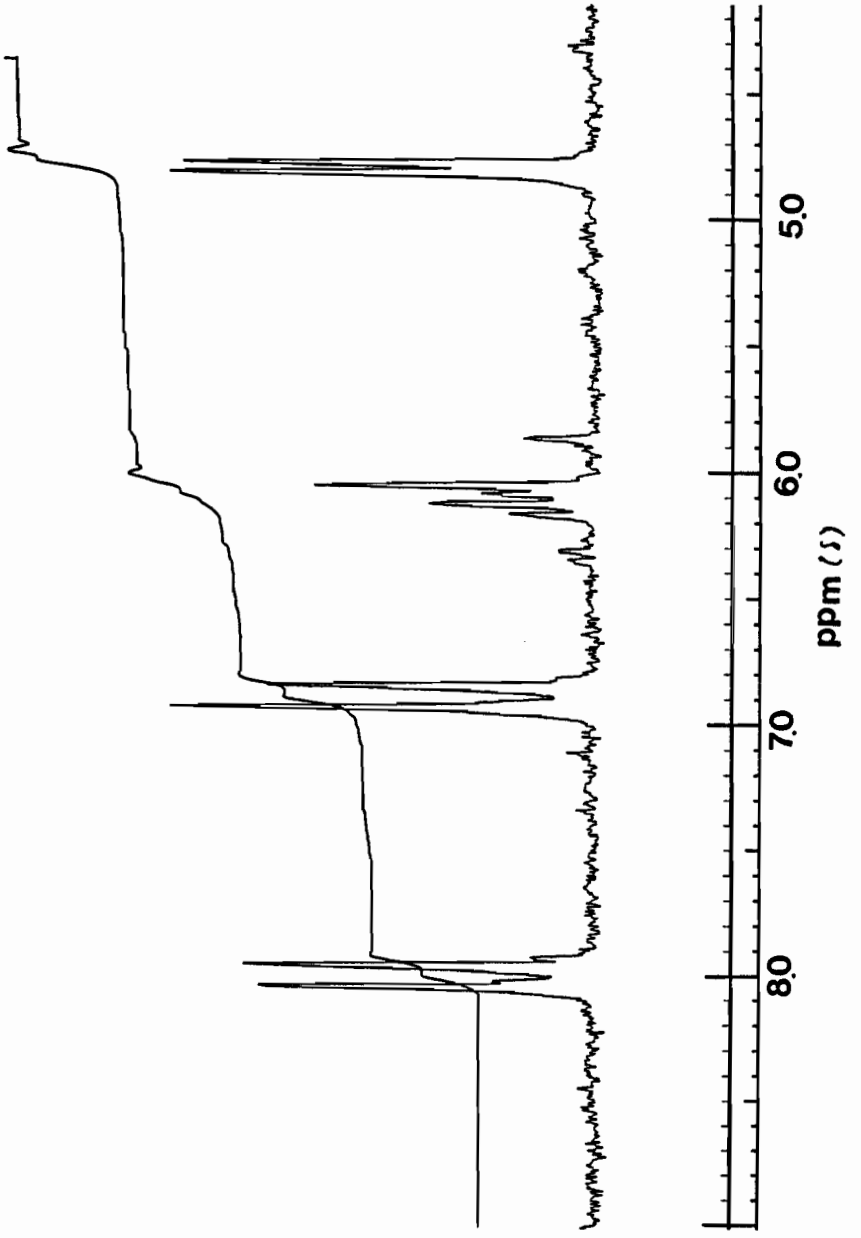
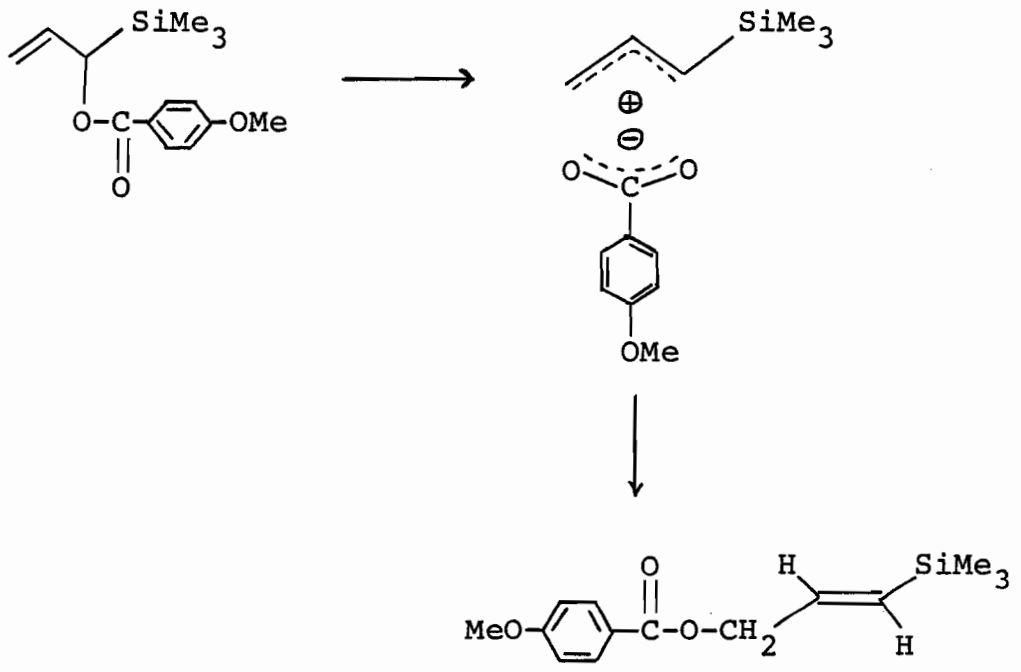


FIGURE 6: COUPLING CONSTANTS OF THE OLEFINIC PROTONS OF COMPOUND 175 FROM 100 MHz NMR

The parent ion at m/e 264 gives the molecular weight of compound 175. The isolated yield of 175 is ∿ 24.4%.

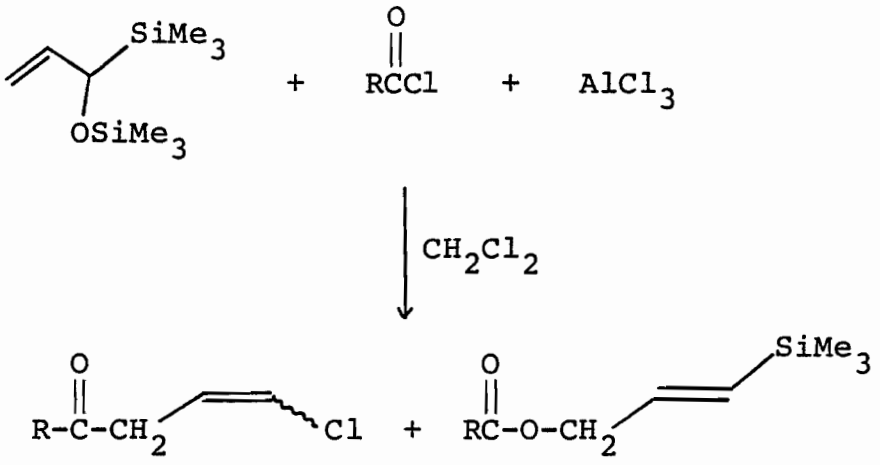
The formation of 175 can be explained by "internal return" rearrangement. The corresponding ester is first formed as an intermediate. Then the ester group is dissociated with the help of the Lewis acid to form an intimate ion pair with the carbonium ion, and is then preferentially recaptured in the rearranged product to give 175.



175

α-Siloxyallylsilane 158 reacts with other acid chlorides to give the same kind of results. The corresponding vinyl chloride isomers and vinylsilanes are obtained. These prod-

ucts are, once again, identified by their spectral data as in the cases of benzoyl chloride and p-anisoyl chloride (See Figures 7 to 10).



R = CH_3-C$_6$H$_4$- 176 (∿ 52.0% isolated) 177 (22.0% isolated)

R = C_5H_{11}- 178 (∿ 55.9%) 179 (22.0%)

In general, α-siloxyallylsilane reacts with two equivalents of acid chloride to give three products, the two vinyl chloride isomers and a minor product, the rearranged trans-vinylsilane. The acid chloride tends to react with the O-$SiMe_3$ group. In order that the α-siloxyallylsilane can be used in allylation reactions in the same way as the simple allylsilanes, something must be done to stop the reaction between the acid chloride and the O-silyl group. Most recently, Sakurai[173] has published some reactions of α-siloxyallylsilanes with acid chlorides in which the O-silyl group is a very bulky O-t-butyl-dimethylsilyl group. In such cases the acid chlorides react

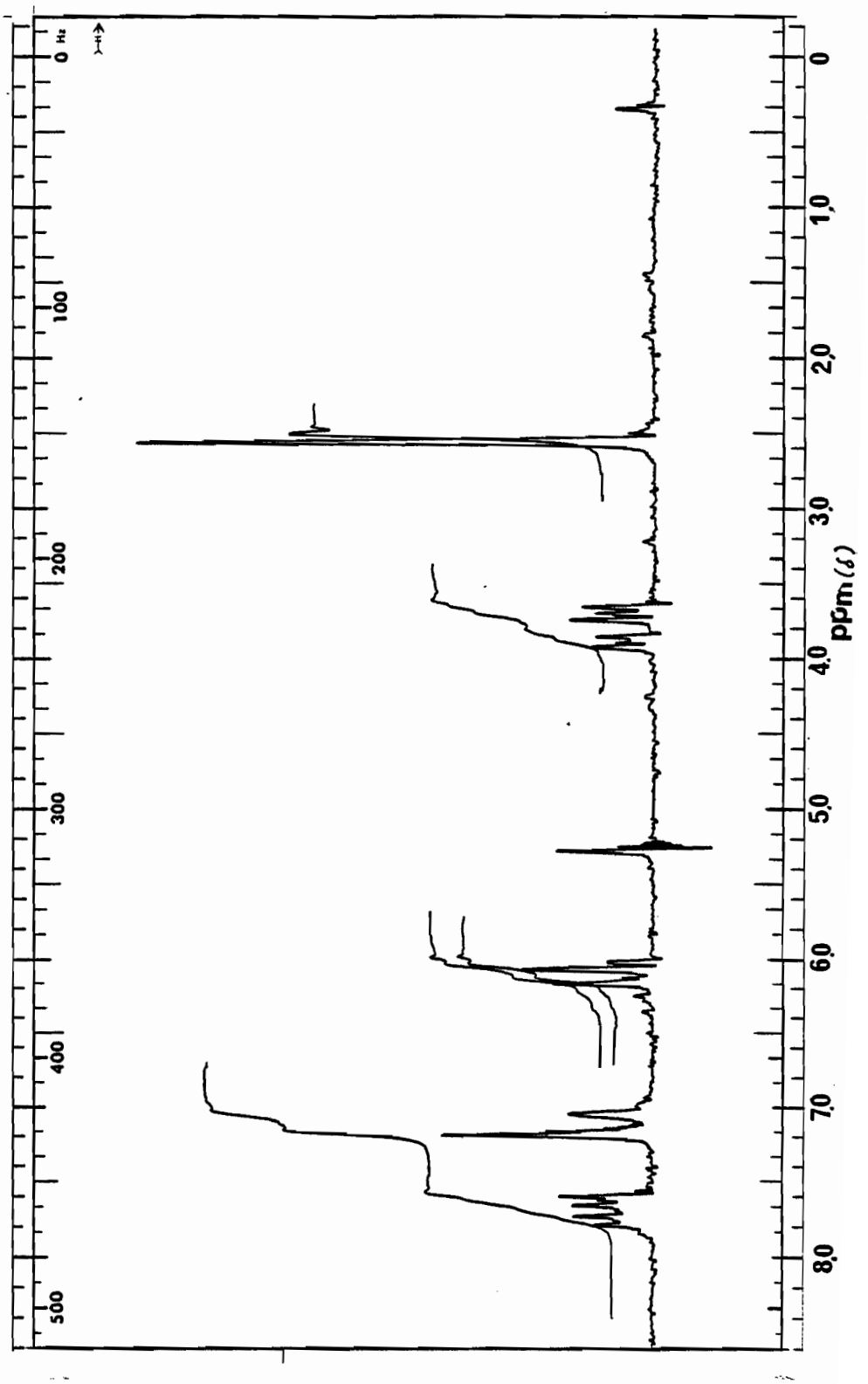


FIGURE 7: NMR OF COMPOUND 176 (CH_2Cl_2 internal standard)

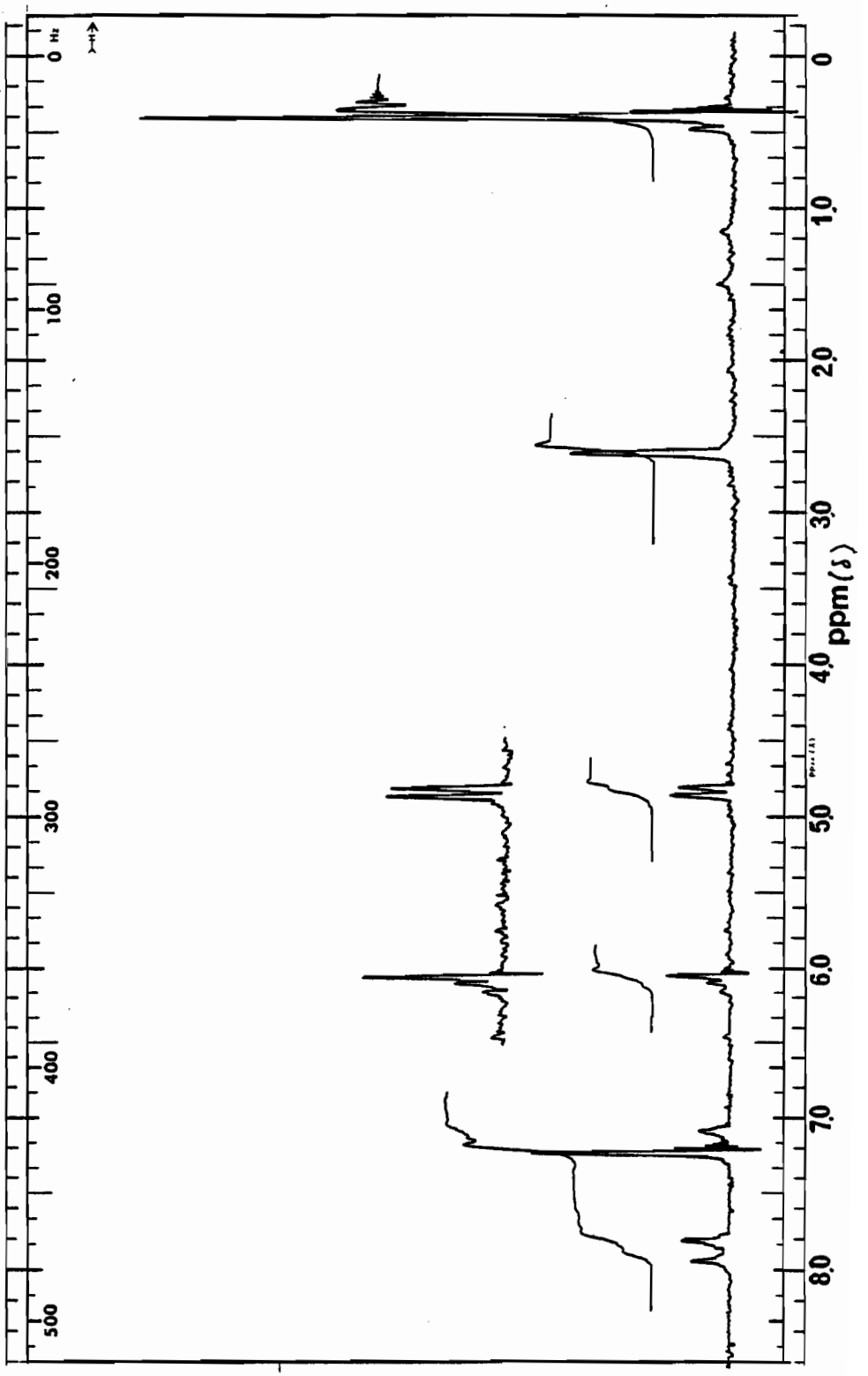


FIGURE 8: NMR OF COMPOUND 177 ($CHCl_3$ internal standard)

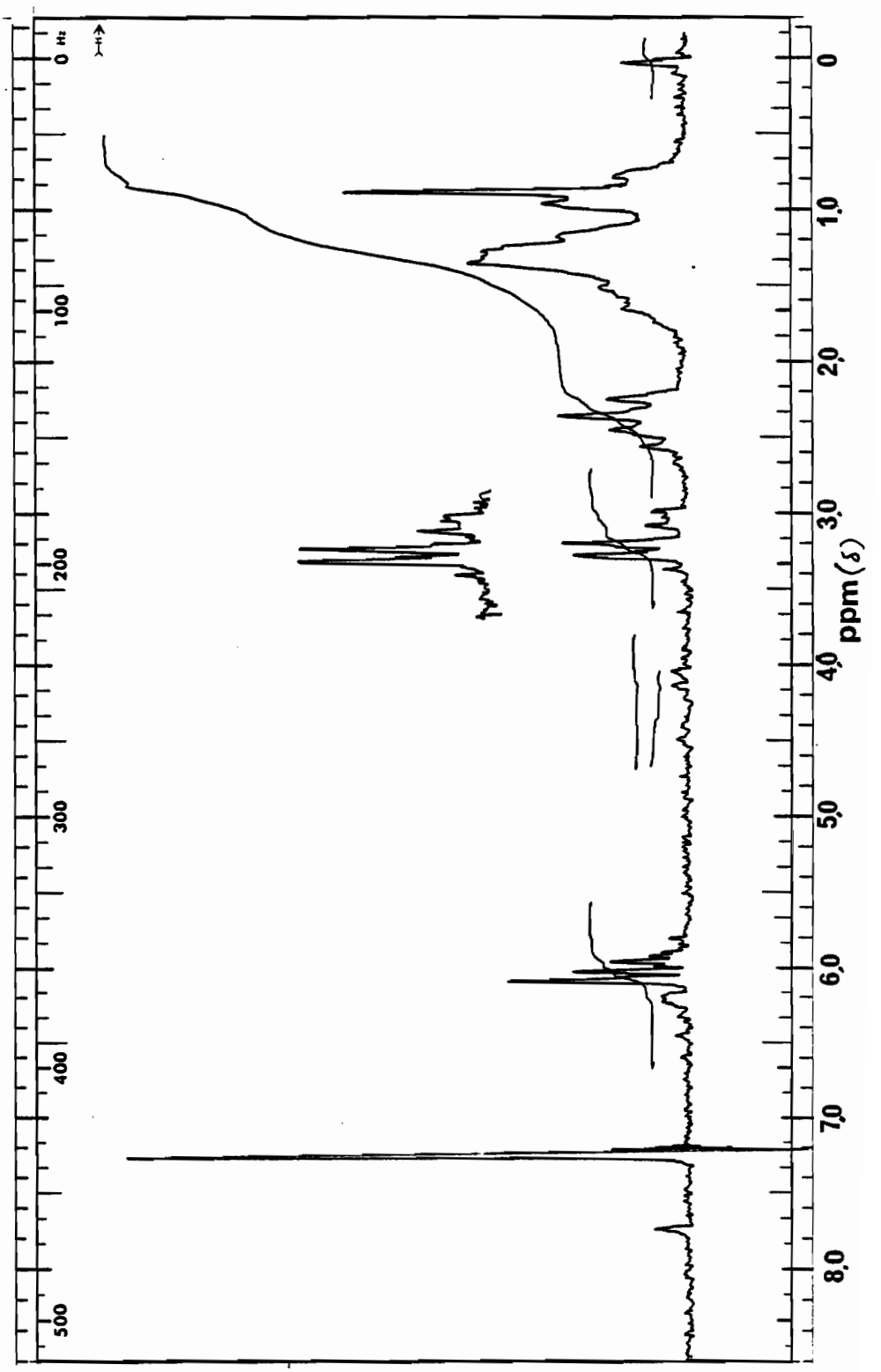


FIGURE 9: NMR OF COMPOUND 178 ($CHCl_3$ internal standard)

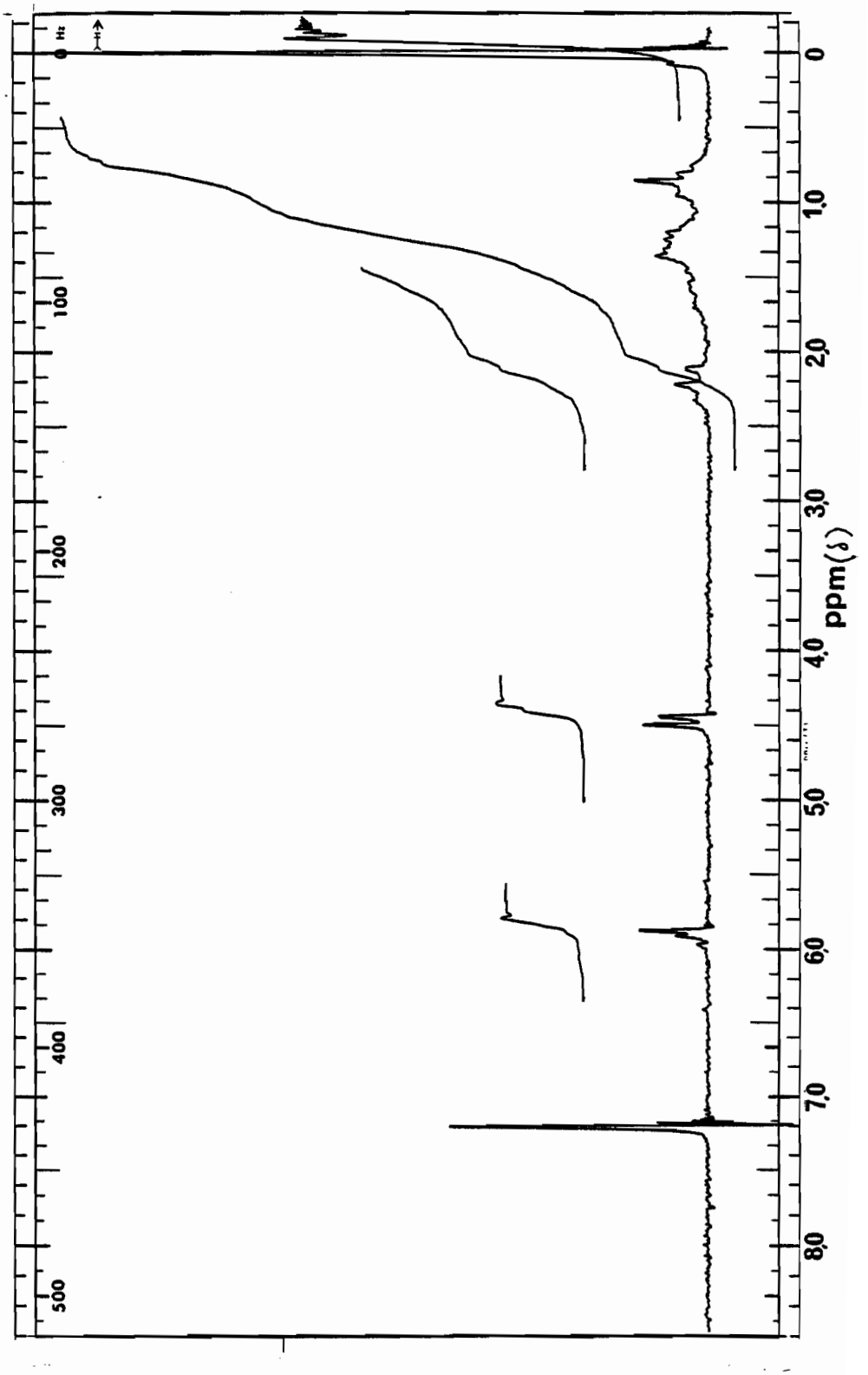


FIGURE 10: NMR OF COMPOUND 179 ($CHCl_3$ internal standard)

preferentially with the C-$SiMe_3$ group to give various γ-keto aldehydes.

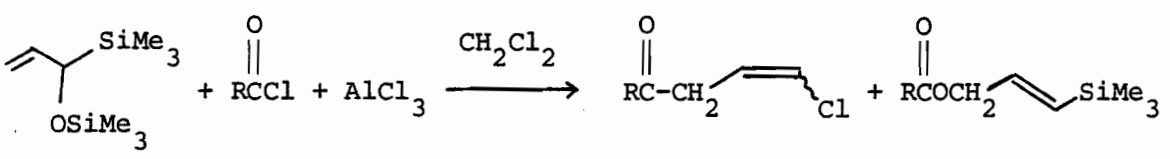
CHAPTER 6

CLAIMS TO ORIGINAL RESEARCH

1. The electrophilic substitution reactions of trisubstituted vinylsilanes with various electrophiles are found to be stereospecific.
2. Geometric isomers of different trisubstituted alkenes are stereoselectively synthesized from trisubstituted vinylsilanes. Various alkenes synthesized include trisubstituted vinyl halides and α,β-unsaturated carbonyl compounds.
3. Fluoride ion cleaves the silicon-carbon bond in silyloxiranes (both simple and β-hydroxysilyloxiranes) very easily to give oxiranes. This cleavage is faster than the cleavage of the silicon-carbon bond in β-hydroxyvinylsilanes which is promoted by the β-hydroxy effect.
4. An oxiranyl anion is involved in the cleavage reactions with fluoride ions. Retention of configuration is observed at the oxiranyl carbon in these cleavage reactions. This shows that the rate of inversion of the oxiranyl anion is sufficiently slow with respect to proton transfer that the stereochemical integrity at the oxiranyl carbon is maintained.
5. The rate of cleavage of the silicon-carbon bond in silyloxiranes is comparable to the cleavage of the silicon-

alkynyl carbon bond. Thus, the oxiranyl anion is comparable to the alkynyl anion as a leaving group.

6. The regioselectivity in the reactions of α-silylallyl carbanions with aldehyde and ketones can be controlled to give mainly the α-addition alcohols by the addition of magnesium bromide etherate to the reaction mixtures.
7. The control of regioselectivity to give the α-addition products provides a path for the conversion of carbonyl compounds into 1,3-dienes by the subsequent elimination of the R_3SiO^- moiety.
8. The rearrangement of allylsilyloxy carbanion into oxyanion gives two anions in rapid equilibrium with each other. This equilibrium leads to the competition between the two anions in reactions with carbonyl compounds such as acid chlorides, chloroformates and organic carbonates. The product ratio of these reactions is dependent on the nature of the leaving group of the carbonyl compounds.
9. Reactions of α-trimethylsiloxyallylsilane with different acid chlorides in the presence of Lewis acid give three products: the geometric isomers of a vinyl chloride and a rearranged trans-vinylsilane.



cis and trans

CHAPTER 7

EXPERIMENTAL SECTION

Common chemicals were obtained from commercial sources and were purified as necessary. Melting points were obtained on a Gallenkamp melting point apparatus and were uncorrected. Likewise, boiling points obtained were uncorrected.

Nuclear magnetic resonance spectra (NMR) were recorded on Varian Associates T-60 or T-60A or HA-100 spectrometers. ^{13}CMR spectra were recorded on a Brucker WH-90 spectrometer at 22.628 MHz.

Infrared spectra were recorded on Perkin-Elmer Model 257 or Model 297 or Unicam SP 1000 grating infrared spectrometers. Spectra were calibrated with the 1601 cm^{-1} band of polystyrene film.

Mass spectra were recorded on an AEI-MS-902 mass spectrometer. The operating conditions were a 70 ev electron energy, resolution of 1000 and 8 kv accelerating voltage. GC-MS were recorded on a HP 5984A gas chromatograph-mass spectrometer unit using a 2m column of 5% OV-101 on chromosorb 750 programmed from 100° to 300°C at 16°C rise per minute. Ion source energy was 70 ev at a temperature of 230°C.

Gas chromatograms were performed on a F & M Model 5751A Research Chromatograph. Two 6'xl/8" stainless steel columns were used: 5% OV-101 on chromosorb 750, or 10% SE-30 ultraphase on chromosorb W A/W DMCS.

Preparative thin layer chromatography was carried out on silica gel HF 254+366 supplied by Merck. The particular developing solvent used is described in the procedure.

The starting materials, the geometric isomers of trisubstituted vinylsilanes 79, were prepared[38] by my colleague, Dr. W. Mychajlowskij, to whom I express my sincere gratitude.

REACTION OF VINYLSILANES 79 WITH BROMINE

Typical procedure for the E-vinylsilane reaction: a solution of bromine (1 mmole) in 5 ml methylene chloride was added dropwise to a solution of vinylsilane E-79 (1 mmole) in 10 ml methylene chloride at -78°C. Decolourization occurred immediately. After 15 minutes, the solvent was removed by evaporation. The product was purified by preparative TLC on silica gel using hexane as eluent.

a) E-1-Cyclohexyl-2-trimethylsilyl-1-butene (E-79a)

Product: Z-2-Bromo-1-cyclohexyl-1-butene (Z-80a), yield 87%
NMR (CCl_4) δ 1.2 (t, 3H), 1.2 to 1.9 (b, 11H), 2.4 (q, 2H), 5.4 (d, 1H). IR (neat) 2910, 2840, 1655 and 1445 cm^{-1}. MS, m/e (intensity): 218 (8), 216 (8), 137 (20), 95 (37), 82 (100), 81 (60), 67 (88). ^{13}CMR ($CDCl_3$) 13.7, 25.8, 32.1, 35.1, 40.4, 128.0 and 132.8 ppm.

b) E-2-Methyl-4-trimethylsilyl-3-nonene (E-79b)

Product: Z-4-Bromo-2-methyl-3-nonene (Z-80b), yield 65%.
NMR (CCl_4) δ 1.0 (d, 6H), 1.0 to 1.6 (b, 9H), 2.4 (bt, 2H), 2.8 (m, 1H), 5.4 (d, 1H). IR (neat) 2950, 2920, 2860, 1655

and 1460 cm^{-1}. MS, m/e (intensity): 220 (5), 218 (5), 139 (7), 83 (57), 69 (100), 55 (50). ^{13}CMR ($CDCl_3$) 14.0, 21.9, 22.4, 27.9, 30.6, 31.0, 41.5, 126.15 and 135.4 ppm.

c) E-6-Trimethylsilyl-6-heptadecene (E-79c)

The crude material obtained after evaporation of the solvent was stirred at room temperature with 5 ml dry acetonitrile before purification by preparative TLC. Product: Z-6-Bromo-6-heptadecene (Z-80c), yield 65%. NMR (CCl_4) δ 1.0 (b, 6H), 1.4 (b, 22H), 2.0 to 2.7 (b, 4H), 5.6 (t, 1H). IR (neat) 2940, 2910, 2840, 1655 and 1465 cm^{-1}. MS, m/e (intensity): 318 (7), 316 (7), 237 (3), 125 (16), 111 (33), 97 (77), 83 (71), 69 (81), 55 (100) and 41 (93).

For the bromodesilylation reactions of the Z-vinylsilanes, the procedures were similar to the reactions with the E-vinylsilanes except that the crude materials obtained after evaporation of the solvents were stirred with dry acetonitrile for a few hours at room temperature before isolation by preparative TLC.

d) Z-1-Cyclohexyl-2-trimethylsilyl-1-butene (Z-79a)

Product: E-2-Bromo-1-cyclohexyl-1-butene (E-80a), yield 21%. NMR (CCl_4) δ 1.2 (t, 3H), 1.2 to 1.9 (b, 11H), 2.5 (q, 2H), 5.6 (d, 1H). IR (neat) 2910, 2840, 1640 and 1450 cm^{-1}. MS, m/e (intensity): 218 (8), 216 (8), 137 (18), 95 (39), 82 (100), 81 (64), 67 (94). ^{13}CMR ($CDCl_3$) 13.7, 25.9, 29.5, 33.1, 39.1, 126.8 and 137.3 ppm.

e) Z-2-Methyl-4-trimethylsilyl-3-nonene (Z-79b)

Product: E-4-Bromo-2-methyl-3-nonene (E-80b), yield 10%. NMR (CCl_4) δ 1.0 (d, 6H), 1.0 to 1.6 (b, 9H), 2.2 to 2.7 (m, 3H), 5.6 (d, 1H). IR (neat) 2940, 2910, 2860, 1640 and 1465 cm^{-1}. MS, m/e (intensity): 220 (5), 218 (5), 139 (6), 83 (57), 69 (100), 55 (55). ^{13}CMR ($CDCl_3$) 14.0, 22.6, 22.8, 28.0, 29.6, 30.9, 36.0, 124.7 and 139.5 ppm.

f) Z-6-Trimethylsilyl-6-heptadecene (Z-79c)

Product E-6-Bromo-6-heptadecene (E-80c), yield 56%. NMR (CCl_4) δ 1.0 (b, 6H), 1.4 (b, 22H), 2.0 to 2.7 (b, 4H), 5.8 (t, 1H). IR (neat) 2940, 2910, 2840 1640 and 1465 cm^{-1}. MS, m/e (intensity): 318 (6), 316 (6), 237 (3), 125 (17), 111 (35), 97 (77), 83 (71), 69 (81), 55 (100), 41 (93).

REACTION OF E-VINYLSILANES WITH CYANOGEN BROMIDE

Typical procedure: 1 mmole aluminum chloride in 5 ml dry methylene chloride was placed in a 25 ml flask. 1 mmole of cyanogen bromide in 1 ml dry methylene chloride was added and the flask was cooled to 0°C before 1 mmole of the E-vinylsilane in 1 ml methylene chloride was added and stirred for 10 minutes. The reaction mixture was worked up by quenching with saturated aqueous ammonium chloride and extraction with ether. The organic layer was then washed with 10% sodium carbonate solution and water. After drying and evaporation of the solvent, the product was isolated by preparative TLC using hexane as eluent.

Products obtained: E-80a 73%

E-80b 53%

E-80c 60%

REACTION OF VINYLSILANES 79 WITH IODINE

Typical procedure: a solution of iodine (1 mmole) in 5 ml methylene chloride was added to a solution of vinylsilane (1 mmole) in 5 ml methylene chloride at room temperature. The reaction mixture was stirred for 1 hour. The solvent was then removed by evaporation and ether was added. The solution was then washed with 10% aqueous sodium thiosulfate solution and then with water. After the solution was dried the solvent was evaporated. Preparative TLC using benzene:hexane (5:1) as eluent was used to isolate the product.

a) E-1-Cyclohexyl-2-trimethylsilyl-1-butene (E-79a)

Product: E-1-Cyclohexyl-2-iodo-1-butene (E-90a), yield 58%. NMR (CCl_4) δ 1.1 (t, 3H), 1.1 to 2.0 (b, 11H), 2.4 (q, 2H), 6.0 (d, 1H). IR (neat) 2950, 2910, 2840, 1625 and 1445 cm^{-1}. MS, m/e (intensity): 264 (25), 137 (33), 95 (97), 81 (100), 67 (85). ^{13}CMR ($CDCl_3$) 14.9, 25.8, 32.6, 33.0, 40.3, 104.4 and 146.3 ppm.

b) E-2-Methyl-4-trimethylsilyl-3-nonene (E-79b)

Product: E-4-Iodo-2-methyl-3-nonene (E-90b), yield 75%. NMR ($CDCl_4$) δ 1.0 (d, 6H), 1.0 to 1.6 (b, 9H), 2.3 to 2.9 (m, 3H), 6.0 (d, 1H). IR (neat) 2950, 2920, 2860, 1625 and 1460 cm^{-1}.

MS, m/e (intensity): 266 (11), 83 (55), 69 (100), 55 (72). ^{13}CMR ($CDCl_3$) 13.9, 22.5, 22.7, 29.1, 30.7, 38.7, 102.2 and 148.3 ppm.

c) Z-1-Cyclohexyl-2-trimethylsilyl-1-butene (Z-79a)

Product: Z-1-Cyclohexyl-2-iodo-1-butene (Z-90a), yield 71%. NMR (CCl_4) δ 1.2 (t, 3H), 1.2 to 2.0 (b, 11H), 2.5 (q, 2H), 5.2 (d, 1H). IR (neat) 2950, 2910, 2840, 1640 and 1445 cm^{-1}. MS, m/e (intensity): 264 (27), 137 (38), 95 (95), 81 (100), 67 (85). ^{13}CMR ($CDCl_3$) 15.0, 25.7, 26.0, 31.8, 32.9, 38.9, 45.3, 108.8 and 138.8 ppm.

d) Z-2-Methyl-4-trimethylsilyl-3-nonene (Z-79b)

Product: Z-4-Iodo-2-methyl-3-nonene (Z-90b), yield 81%. NMR (CCl_4) δ 1.0 (d, 6H), 1.0 to 1.7 (b, 9H), 2.2 to 2.8 (m, 3H), 5.2 (d, 1H). IR (neat) 2940, 2910, 2850, 1640 and 1460 cm^{-1}. MS, m/e (intensity): 266 (14), 83 (63), 69 (100), 55 (71). ^{13}CMR ($CDCl_3$) 13.9, 21.7, 22.7, 29.0, 30.4, 30.7, 36.1, 45.1, 106.9 and 141.4 ppm.

FRIEDEL-CRAFTS ACYLATION OF VINYLSILANES 79

Typical procedure: to a mixture of acetyl chloride (1 mmole) and aluminum chloride (1 mmole) in 10 ml methylene chloride was added the vinylsilane 79 (1 mmole). The reaction mixture was stirred for 20 minutes at 0°C and then quenched with saturated aqueous ammonium chloride solution and extracted with ether. The organic layer was then washed with 10% aqueous sodium bicarbonate solution and then by

water. After the solution was dried with anhydrous magnesium sulfate, the solvent was removed. The product was purified by preparative TLC using benzene:methylene chloride (5:1) as eluent.

a) E-1-Cyclohexyl-2-trimethylsilyl-1-butene (E-79a)

Product: E-1-Cyclohexyl-2-ethyl-1-buten-3-one (E-99a), yield 70%. NMR (CCl_4) δ 1.0 (t, 3H), 1.2 to 2.0 (b, 11H), 2.3 (s, 3H), 2.4 (q, 2H), 6.2 (d, 1H). IR (neat) 2910, 2840, 1665, 1630 and 1445 cm^{-1}. MS, m/e (intensity): 180 (30), 165 (40), 137 (25), 95 (30), 81 (45), 67 (35), 43 (100).

b) E-2-Methyl-4-trimethylsilyl-3-nonene (E-79b)

Product: E-5-Methyl-3-pentyl-3-hexen-2-one (E-99b), yield 60%. NMR (CCl_4) δ 1.0 (d, 6H), 1.0 to 1.6 (b, 9H), 2.1 (bt, 2H), 2.2 (s, 3H), 2.8 (m, 1H), 6.2 (d, 1H). IR (neat) 2940, 2910, 2840, 1665, 1630 and 1460 cm^{-1}. MS, m/e (intensity): 182 (22), 167 (40), 139 (8), 83 (52), 69 (70), 55 (50), 43 (100).

c) Z-1-Cyclohexyl-2-trimethylsilyl-1-butene (Z-79a)

Product: Z-1-Cyclohexyl-2-ethyl-1-buten-3-one (Z-99a), yield 65%. NMR (CCl_4) δ 1.1 (t, 3H), 1.2 to 1.9 (b, 11H), 2.3 (s, 3H), 2.4 (q, 2H), 5.2 (d, 1H). IR (neat) 2920, 2840, 1690, 1620 and 1450 cm^{-1}. MS, m/e (intensity): 180 (30), 165 (40), 137 (28), 95 (32), 81 (48), 67 (30), 43 (100).

d) Z-2-Methyl-4-trimethylsilyl-3-nonene (Z79b)

Product: Z-5-Methyl-3-pentyl-3-hexen-2-one (Z-99b), yield 65%. NMR (CCl_4) δ 1.1 (d, 6H), 1.0 to 1.6 (b, 9H), 2.1 (bt, 2H),

2.2 (s, 3H), 2.8 (m, 1H), 5.2 (d, 1H). IR (neat) 2940, 2910, 2840, 1690, 1620 and 1460 cm^{-1}. MS, m/e (intensity): 182 (20), 167 (40), 139 (10), 83 (50), 69 (68), 55 (52), 43 (100).

PREPARATION OF DICHLOROMETHYL METHYL ETHER

Dichloromethyl methyl ether was prepared according to the procedure in the literature[116].

Yield: 75%, b.p. 87-89°C (lit.[116] b.p. 85-87°C).

FRIEDEL-CRAFTS FORMYLATION OF VINYLSILANES 79

Typical procedure: to a mixture of dichloromethyl methyl ether (1 mmole) and aluminum chloride in 10 ml methylene chloride at -24°C, the vinylsilane 79 (1 mmole) in 2 ml methylene chloride was added and stirred. The reaction was followed by GC. The reaction mixture was then worked up after 4 hours the same way as in the acylation reaction. However, the product was not purified.

a) For either isomer of vinylsilane 79a

(E and Z-1-Cyclohexyl-2-trimethylsilyl-1-butene)

Product: E-3-Cyclohexyl-2-ethyl-2-propenal (E-102a), yield 90%. NMR (CCl_4) δ 1.0 (t, 3H), 1.1 to 2.0 (b, 11H), 2.3 (q, 2H), 6.1 (d, 1H), 9.2 (s, 1H). IR (neat) 2910, 2840, 2700, 1690, 1640 and 1450 cm^{-1}. MS, m/e (intensity): 166 (10), 137 (7), 95 (50), 81 (50), 67 (50), 57 (100), 43 (25).

b) For either isomer of vinylsilane 79b

(E and Z-2-Methyl-4-trimethylsilyl-3-nonene)

Product: E-4-Methyl-2-pentyl-2-pentenal (E-102b), yield 90%.

NMR (CCl_4) δ 1.1 (d, 6H), 1.1 to 1.7 (b, 9H), 2.2 (bt, 2H), 2.8 (m, 1H), 6.1 (d, 1H), 9.2 (s, 1H). IR (neat) 2940, 2910, 2840, 2700, 1690, 1640 and 1460 cm^{-1}. MS, m/e (intensity): 166 (8), 137 (5), 95 (46), 81 (55), 67 (45), 57 (100), 43 (20).

c) Formylation reaction of Z-1-Cyclohexyl-2-trimethylsilyl-1-butene (Z-79a) at -45°C

The procedure was the same as above except the reaction temperature was lowered to -45°C (acetonitrile in dry ice bath), and the reaction time was shortened to 1/2 hour. Products: E-102a spectral data same as above. Z-102a: NMR (CCl_4) δ 1.0 (t, 3H), 1.0 to 2.0 (b, 11H), 2.3 (q, 2H), 5.7 (d, 1H), 10.1 (s, 1H). IR (neat) 2910, 2840, 2700, 1690, 1610 and 1450 cm^{-1}. 105: NMR (CCl_4) δ 1.0 (t, 3H), 1.0 to 2.0 (b, 10H), 2.3 (q, 2H), 3.2 (m, 1H), 5.5 (d, 1H), 9.4 (d, 1H). IR (neat) 2910, 2840, 2700 and 1725 cm^{-1}.

REACTION OF VINYLSILANES WITH HI

To a solution of 1 mmole of vinylsilane 79 in 5 ml methylene chloride was added two drops of 48% HI. GC showed that the reaction was completed in 15 minutes. The mixture was poured into water and ether. The organic phase was washed with 10 ml aqueous sodium bicarbonate solution, dried over anhydrous magnesium sulfate and evaporated in vacuo to give the olefin in quantitative yield.

a) E-1-Cyclohexyl-2-trimethylsilyl-1-butene (E-79a)

Product: Z-1-Cyclohexyl-1-butene 82. NMR (CCl_4) δ 1.0 (t, 3H),

1.0 to 1.8 (b, 11H), 2.0 (m, 2H), 5.0 to 5.4 (m, 2H). IR (neat) 2910, 2840, 1450 and 890 cm^{-1}.

b) Z-1-Cyclohexyl-2-trimethylsilyl-1-butene (Z-79a)

Product: E-1-Cyclohexyl-1-butene 83. NMR (CCl_4), δ 1.0 (t, 3H), 1.0 to 2.3 (b, 13H), 5.0 to 5.6 (m, 2H). IR (neat) 2910, 2840, 1450, 940 and 890 cm^{-1}.

The identities of 82 and 83 were also established by the following experiment.

REACTION OF VINYLHALIDES WITH t-BUTYLLITHIUM

To a solution of 1 mmole of vinyl halide in 5 ml dry tetrahydrofuran at -78°C was added t-butyllithium in n-pentane (1.1 mmole). The reaction mixture was stirred for one hour before quenching with water. The organic phase was then washed with saturated salt solution, dried over anhydrous magnesium sulfate and evaporated in vacuo to give the olefin.

a) Vinyl bromide E-80a and vinyl iodide E-90a

Product: 82 spectral data same as before.

b) Vinyl bromide Z-80a and vinyl iodide Z-90a

Product: 83 spectral data same as before.

PREPARATION OF 1-CYCLOHEXYL-2-ETHYL-1-BUTEN-3-OL (100)

To a solution of 1 mmole of vinyl iodide E-90a in 5 ml anhydrous ether at -78°C was added 1.1 mmole of t-butyllithium in n-pentane. The reaction mixture was stirred for 2 hours at -78°C before 1 mmole of acetaldehyde was added.

Stirring was continued for 1/2 hour at -78°C before the cooling bath was removed. The reaction mixture was allowed to warm to room temperature before work up.

The reaction mixture was poured into a separatory funnel containing ether and aqueous ammonium chloride solution. The organic phase was washed with water and then dried with anhydrous magnesium sulfate. The solvent was then evaporated in vacuo to give the alcohol 100. Yield 74%. NMR (CCl_4) δ 1.1 (t, 3H), 1.2 (d, 3H), 1.0 to 1.9 (b, 12H), 2.2 (q, 2H), 4.0 (q, 1H), 5.1 (d, 1H). IR (neat) 3400, 2940, 2910, 2840, 1650 and 1450 cm^{-1}.

OXIDATION OF ALLYL ALCOHOL 100 BY MANGANESE DIOXIDE[115]

To a solution of the alcohol 100 (0.4 mmole) in 10 ml of petroleum ether (30°C to 60°C range) was added 4 mmole active manganese dioxide prepared according to the procedure in the literature[115]. The reaction mixture was stirred for one hour at room temperature. It was then filtered, and the residue was washed a few times with petroleum ether. The total filtrate was evaporated in vacuo to give the ketone, E-1-cyclohexyl-2-ethyl-1-buten-3-one (E-99a) (yield 68%), identical in all respects with E-99a prepared from the acylation reaction of E-1-Cyclohexyl-2-trimethylsilyl-1-butene E-79a.

α-BROMOVINYLTRIPHENYLSILANE 112a

The title compound was prepared according to the reported procedure[24,124]. The yield obtained was 90%

(m.p. 129-130°C; lit.[24] m.p. 128-129°C).

1-SUBSTITUTED-2-TRIPHENYLSILYL-2-PROPEN-1-OLS (37)

Typical procedure: to a solution of 25 mmole α-bromovinyltriphenylsilane 112a in 60 ml anhydrous ether at -24°C (dry ice-CCl_4 bath) under nitrogen atmosphere was added slowly a solution of 25 mmole n-butyllithium. The reaction mixture was stirred at -24°C for 1 1/2 hours. A solution of 25 mmole carbonyl compound in 10 ml anhydrous ether was added and stirred for another 5 hours at -24°C. Stirring was continued overnight at room temperature. The reaction mixture was poured into 50 ml 10% HCl, and the organic phase was extracted with ether, dried and evaporated to give the alcohol in good yield[62] (See Table 5).

a) 1-Phenyl-2-triphenylsilyl-2-propen-1-ol (37a)

Recrystallized from 30-60°C petroleum ether, m.p. 84-85°C, yield 75%. NMR ($CDCl_3$) δ 1.8 (s, 1H), 5.5 (t, 1H), 5.8 (t, 1H), 6.2 (t, 1H), 7.2 to 7.8 (m, 20H). IR (KBr) 3580, 1435, 1115 and 700 cm^{-1}.

b) 2-Triphenylsilyl-1-buten-3-ol (37c)

Purified by column chromatography using Silica Gel 60 (70-230 mesh ASTM, supplied by Merck). Benzene was used as eluent. M.p. 61-64°C, yield 75%. NMR (CCl_4) δ 1.1 (d, 3H), 1.9 (s, 1H), 4.4 (q, 1H), 5.5 (d, 1H), 6.1 (d, 1H), 7.2 to 7.8 (m, 15H).

c) 1,1-Diphenyl-2-triphenylsilyl-2-propen-1-ol (37e)

Recrystallized from petroleum ether 30°C to 60°C range. M.p. 106-108°C, yield 80%. NMR ($CDCl_3$) δ 2.6 (s, 1H), 5.7 (d, 1H), 5.9 (d, 1H), 7.2 to 7.8 (m, 25H). IR (KBr) 3580, 1435, 1115 and 700 cm^{-1}.

α-BROMOVINYLTRIMETHYLSILANE (112b)

The title compound was prepared according to the procedure reported in the literature[174]. The yield obtained was 82%, $b.p._{53}$ 70-1°C (lit.[174] $b.p._{749}$ 140°C).

1-SUBSTITUTED-2-TRIMETHYLSILYL-2-PROPEN-1-OLS (37)

To a solution of 50 mmole α-bromovinyltrimethylsilane 112b in 150 ml anhydrous ether at -78°C under nitrogen atmosphere was added slowly, by means of a syringe, a solution of 52 mmole t-butyllithium in n-pentane. The reaction mixture was stirred at -78°C for 2 hours. Then a solution of 50 mmole carbonyl compound in 10 ml anhydrous ether was added and stirred for another hour at -78°C. The reaction mixture was allowed to warm to room temperature. After hydrolysis with water (50 ml) and drying with anhydrous magnesium sulfate, the reaction mixture was evaporated in vacuo and fractionally distilled at reduced pressure to give the alcohol in good yield (See Table 5).

a) 1-Phenyl-2-trimethylsilyl-2-propen-1-ol (37b)

B.p. 100-104°C/4 mm, yield 80%. NMR (CCl_4) δ 0.1 (s, 9H). 3.7 (s, 1H), 5.5 (m, 1H), 5.8 (m, 1H), 6.0 (m, 1H), 7.6 (s, 5H).

IR (neat) 3350, 3040, 3010, 2940, 1630 and 1250 cm^{-1}.

b) 1-Hydroxycyclohexyl-1-trimethylsilylethylene 37d

B.p. 67-69°C/0.9 mm, yield 75%. NMR (CCl_4) δ 0.1 (s, 9H), 1.2 to 1.8 (b, 12H), 5.2 (d, 1H), 5.5 (d, 1H). IR (neat) 3400, 2920, 2840, 1450 and 1250 cm^{-1}.

SYNTHESIS OF 3-HYDROXY-3-SUBSTITUTED-2-TRISUBSTITUTEDSILYL-PROPYLENE 1,2-OXIDE (111)

Compounds 111 were prepared by the epoxidation of their corresponding β-hydroxyvinylsilane 37 using a 10% excess of m-chloroperbenzoic acid in methylene chloride at room temperature. The reaction was followed by NMR. It was found that the epoxidation of β-hydroxytrimethylvinylsilanes took place faster than the corresponding β-hydroxytriphenylvinylsilanes. Following is a typical experimental procedure.

To a solution of 15 mmole of β-hydroxyvinylsilane 37 in 15 ml dry methylene chloride at room temperature was added in small portions 16.5 mmole of m-chloroperbenzoic acid. The acid dissolved in the reaction mixture and a colourless solution was formed. The reaction was then followed by NMR. White precipitate formed after stirring at room temperature for about 1/2 hour. The reaction was finished when the NMR spectrum showed no sign of vinyl protons.

The mixture was filtered to remove the m-chlorobenzoic acid formed, and the filtrate was washed with 10% aqueous sodium sulfite solution (2 x 15 ml) to remove the excess

m-chloroperbenzoic acid. The mixture was then washed with 10% sodium bicarbonate solution (3 x 10 ml). The organic layer was then washed with water and then dried with anhydrous magnesium sulfate. The solvent was then removed in vacuo to give the crude silyloxirane which could be purified by recrystallization or by distillation depending on the physical state of the silyloxirane (See Table 6).

a) 3-Hydroxy-3-phenyl-2-triphenylsilyl-propylene 1,2-oxide(111a)

Recrystallized from petroleum ether (30°C to 60°C range); m.p. 105-106°C, yield 80%. NMR ($CDCl_3$) δ 2.5 (b, 1H), 2.6 (d, 1H), 3.0 (d, 1H), 5.0 (s, 1H), 7.0 to 7.6 (m, 20H). δ 2.5 disappeared on addition of D_2O. IR (KBr) 3400, 3040, 2980, 2860, 1580, 1490, 1430, 1190 and 1110 cm^{-1}.

b) 3-Hydroxy-3-phenyl-trimethylsilyl-propylene 1,2-oxide(111b)

B.p. 147-150°C/6 mm; yield 74%. NMR (CCl_4) δ 0.1 (s, 9H), 2.8 (d, 1H), 3.1 (b, 1H), 3.3 (d, 1H), 5.0 (s, 1H), 7.6 (s, 5H). δ 3.1 disappeared on addition of D_2O. IR (neat) 3400, 3020, 2940, 2880, 1490, 1450 and 1250 cm^{-1}.

c) 3-Hydroxy-3-methyl-triphenylsilyl-propylene 1,2-oxide(111c)

Recrystallized from petroleum ether (30°C to 60°C range); m.p. 127-129°C, yield 72%. NMR ($CDCl_3$) δ 1.0 (d, 3H), 2.0 (b, 1H), 2.7 (d, 1H), 3.1 (d, 1H), 4.3 (q, 1H), 7.2 to 7.8

(m, 15H). δ 2.0 disappeared on addition of D_2O. IR (KBr) 3490, 3040, 2970, 2860, 1580, 1490, 1430 and 1110 cm^{-1}.

d) 1-Hydroxycyclohexyl-1-trimethylsilyl ethylene oxide (111d)

Not distilled, yield 94%. NMR (CCl_4) δ 0.1 (s, 9H), 1.2 to 1.8 (b, 10M), 1.9 (b, 1H), 2.4 (d, 1H), 2.8 (d, 1H). δ 1.9 disappeared on addition of D_2O. IR (neat) 3460, 2940, 2860, 1450, 1380 and 1250 cm^{-1}.

REACTION OF β-HYDROXYSILYLOXIRANES 111 WITH FLUORIDE ION

Typical procedure: to a solution of 2 mmole of β-hydroxysilyloxirane 111 in 10 ml acetonitrile was added 2.2 mmole tetraethylammonium fluoride. The reaction mixture was stirred at room temperature and the fluoride dissolved. A light yellow solution was formed. The reaction was followed by TLC or NMR. A white precipitate was formed after stirring for a few minutes in the cases involving β-hydroxytriphenylsilyloxirane (111a and 111c). After stirring for two hours at room temperature, TLC showed no more starting material was present. The reaction mixture was quenched with water and extracted with with ether. The organic layer was then washed with saturated salt solution and dried with anhydrous magnesium sulfate. After filtering off the sulfate, the solvent was evaporated in vacuo to give the oxirane 115 as a light yellow oil.

a) Reaction with silyloxirane (111a)

Product: 3-Hydroxy-3-phenyl propylene 1,2-oxide (115a). Purified by preparative TLC using chloroform as eluent, yield 72%.

NMR (CCl_4) δ 2.4 (b, 1H), 2.8 (two q, 2H), 3.2 (m, 1H), 4.8 (d, 1H), 7.3 (s, 5H). δ 2.4 disappeared on addition of D_2O. IR (neat) 3400, 3040, 2980, 2870, 1590, 1490 and 1450 cm^{-1}. MS, m/e (intensity): 150 (20), 149 (18), 121 (10), 107 (100), 77 (35).

b) Reaction with silyloxirane (111b)

Product: 3-Hydroxy-3-phenyl propylene 1,2-oxide (115a). Purified by preparative TLC using chloroform as eluent, yield 70%. Spectral data same as before.

c) Reaction with silyloxirane (111c)

Product: 3-Hydroxy butylene 1,2-oxide (115c). Not purified. NMR (CCl_4) δ 1.2 (d, 3H), 2.6 (m, 2H), 2.8 (m, 1H), 3.2 (b, 1H), 3.6 (m, 1H). δ 3.2 disappeared on addition of D_2O. IR (neat) 3400, 2980, 2920, 2890 and 1380 cm^{-1}. MS, m/e (intensity): 88 (35), 87 (15), 45 (100).

d) Reaction with silyloxirane (111d)

Product: 1-Hydroxycyclohexylethylene oxide (115d). Purified by preparative TLC using chloroform as eluent, yield 85%. NMR (CCl_4) δ 1.4 to 1.9 (b, 10H), 2.5 to 2.9 (m, 3H), 3.0 (b, 1H). δ 3.0 disappeared on addition of D_2O. IR (neat) 3420, 2930, 2860 and 1450 cm^{-1}. MS, m/e (intensity): 142 (20), 141 (15), 99 (100).

EPOXIDATION OF 3-BUTEN-2-OL (116)

3-Buten-2-ol (75 mmole was epoxidized with m-chloroperbenzoic acid (83 mmole) using the method described before.

Product: 3-Hydroxy butylene 1,2-oxide (115c), b.p. 131°C, yield 75%. Spectral data same as before.

PREPARATION OF TRIPHENYLSILYLOXIRANE (117)

Triphenylsilyloxirane could be prepared from the readily available vinyltrichlorosilane. To a solution of phenyl magnesium bromide in 400 ml dry tetrahydrofuran (prepared from 0.4 mole bromobenzene and 0.4 gm-atom magnesium) was added dropwise a solution of 0.13 mole vinyltrichlorosilane in 200 ml tetrahydrofuran. After the addition the reaction mixture was refluxed for 40 hours. It was then hydrolysed with water and then dried with anhydrous magnesium sulfate. Removal of the solvent, followed by recrystallization from ethanol gave the compound vinyltriphenylsilane in 90% yield (m.p. 57-59°C).

Epoxidation of vinyltriphenylsilane (10 mmole) with m-chloroperbenzoic acid (11 mmole) using the previously described method gave the compound triphenylsilyloxirane 117. The product was recrystallyzed from petroleum ether (30°C to 60°C range). Yield 83%, m.p. 70-71°C. NMR (CCl_4) δ 2.6 (m, 1H), 3.0 (m, 2H), 7.3 to 7.7 (m, 15H).

REACTION OF TRIPHENYLSILYLOXIRANE 117 WITH FLUORIDE ION

To a solution of 5 mmole triphenylsilyloxirane 117 in 5 ml dimethyl sulfoxide at room temperature was added 5.5 mmole of tetraethylammonium fluoride and the mixture was stirred. Any gaseous product could be isolated in a cold trap (-78°C) containing carbon tetrachloride by constantly

passing nitrogen gas slowly through the reaction mixture during the reaction. After stirring the reaction mixture for 4 hours, it was poured into ether and water. The organic layer was then washed with water to remove any DMSO left. After drying the organic layer with anhydrous magnesium sulfate, the solvent was removed. The solid product obtained was purified by preparative TLC using benzene as eluent and identified to be triphenylsilanol. (m.p. 136-138°C, white solid). NMR ($CDCl_3$) δ 4.5 (b,1H), 7.2 to 7.8 (m, 15H). δ 4.5 disappeared on addition of D_2O. The product isolated in the cold trap was found to be ethylene oxide with NMR (CCl_4) δ 2.6 (s).

To prove that the product was ethylene oxide, a drop of authentic ethylene oxide was added to the distillate collected in the cold trap. NMR showed one signal only. The signal was more intense than it was before adding the authentic ethylene oxide. The compound collected was not DMSO because when one drop of DMSO was added, the NMR showed two signals (singlets at δ 2.5 and 2.6).

PREPARATION OF TRANS-β-STYRYLTRIMETHYLSILANE 119

Compound 119 was prepared according to the procedure in the literature[103].

Yield 65%, b.p. 80-82°C/2.5 mm; lit.[103] b.p. 80-83°C/3mm.

PREPARATION OF TRANS-1-PHENYL-2-TRIMETHYLSILYLOXIRANE 118

Epoxidation of 119 (11 mmole) with m-chloroperbenzoic acid (13 mmole) in methylene chloride at room temperature

using the previously described method gave the product trans-1-phenyl-2-trimethylsilyloxirane 118. The product was purified by distillation. Yield 85%, b.p. 83-85°C/0.7 mm. NMR (CCl_4) δ 0.4 (s, 9H), 2.4 (d, 1H), 3.8 (d, 1H), 7.3 (s, 5H). IR (neat) 3020, 2950, 2890, 1600, 1455, 1400 and 1250 cm^{-1}.

CLEAVAGE REACTION OF COMPOUND 118 WITH FLUORIDE ION

To a solution of trans-1-phenyl-2-trimethylsilyloxirane 118 (1 mmole) in 1 ml of DMSO-d_6 at room temperature was added 1.1 mmole tetraethylammonium fluoride. The reaction mixture was stirred for one minute. NMR of the reaction mixture showed that the reaction was complete. The reaction mixture was poured into water and ether. The organic layer was washed with water to remove any DMSO. The organic layer was then dried with anhydrous magnesium sulfate, and the solvent was evaporated in vacuo to give the product styrene oxide 120 in quantitative yield. The NMR data was identical to that of the authentic styrene oxide. NMR (CCl_4) δ 2.7 (m, 1H), 3.1 (m, 1H), 3.8 (m, 1H), 7.3 (s, 5H). MS, m/e (intensity): 121 (7), 120 (50), 119 (45), 91 (100), 77 (15).

The cleavage reaction of compound 118 with tetraethylammonium fluoride was repeated using the same reaction conditions except that the reaction mixture was quenched with D_2O first. The usual work up was then followed to give the same product styrene oxide. The NMR data obtained was the same as before. However, the ratio of the integration of the signals at δ 2.7: 3.1: 3.8 was 1: 0.67: 1. This indicated a 33% deu-

terium incorporation at the position trans to the phenyl group, i.e. at δ 3.1. The mass spectrum of this particular styrene oxide gave the following data: m/e (intensity): 121 (33), 120 (50), 119 (48), 91 (100), 77 (17).

REACTION OF 3-HYDROXY-3-PHENYL PROPYLENE 1,2-OXIDE (115a) WITH LITHIUM ALUMINUM HYDRIDE

To a suspension of 1.3 mmole lithium aluminum hydride in 10 ml anhydrous ether at room temperature was added slowly 1.3 mmole of 3-hydroxy-3-phenyl propylene 1,2-oxide 115a in 10 ml anhydrous ether. The reaction mixture was stirred at room temperature overnight.

After stirring overnight, 1 ml of ethyl acetate was added and stirred for a few minutes to destroy the excess LAH. The reaction mixture was then hydrolysed with ice water and a little dilute sulfuric acid. The reaction mixture was then extracted with ether (5 x 20 ml). The combined ether extract was then washed with 20 ml 10% sodium bicarbonate solution, followed by 20 ml water. The organic layer was then dried by anhydrous magnesium sulfate. Evaporation of the solvent gave the product erythro-1-phenyl propane-1,2-diol 121.

Compound 121 was isolated as a gummy material by preparative TLC using chloroform as eluent. Recrystallization using carbon tetrachloride and petroleum ether gave the diol as colourless crystals. Yield 62%, m.p. 90-91°C; lit.[135] m.p. 92-93°C. NMR (CCl_4) δ 1.1 (d, 3H), 2.2 to 2.7 (b, 2H),

4.0 (m, 1H), 4.7 (d, 1H), 7.2 (s, 5H). δ 2.2 to 2.7 disappeared on addition of D_2O. IR (KBr) 3380, 3240, 3020, 2960, 2920, 2880, 1500, 1450, 1390, 1350, 1135, 1090 and 1020 cm^{-1}.

REACTION OF 1-TRIMETHYLSILYLALLYL CARBANION WITH CARBONYL COMPOUNDS

To a solution of 2 mmole allyltrimethylsilane in 10 ml tetrahydrofuran at room temperature was added 2.2 mmole n-butyllithium. The yellow solution formed was stirred for two hours before a solution of 2 mmole carbonyl compound in 2 ml tetrahydrofuran was added. The reaction mixture turned colourless and then light yellow. The reaction mixture was stirred for another hour before being poured into aqueous ammonium chloride solution and ether. The organic layer was washed with water and then dried with anhydrous magnesium sulfate. The solvent was then evaporated in vacuo. The γ-alcohol product was purified by preparative TLC using methylene chloride as eluent.

The reaction was repeated under different conditions, e.g. by the addition of tetramethylethylenediamine (TMEDA) to the carbanion before adding the carbonyl compound or by the addition of zinc chloride. However, only the γ-alcohol was obtained as product. The reaction was also carried out using t-butyllithium at -78°C instead of using n-butyllithium at 0°C. But, once again, only the γ-alcohol was formed as product (See Table 7).

a) t-1-Trimethylsilyl-4-phenyl-1-penten-4-ol 129

from acetophenone

NMR (CCl_4) δ -0.1 (s, 9H), 1.4 (s, 3H), 1.7 (b, 1H), 2.5 (m, 2H), 5.7 to 5.9 (m, 2H; J = 18 Hz), 7.4 (m, 5H). IR (neat) 3400, 3020, 2980, 2920, 2860, 1615, 1490, 1445 and 1245 cm^{-1}. MS, m/e (intensity): 219 (3), 121 (100), 77 (9), 73 (13).

b) t-1-Phenyl-4-trimethylsilyl-3-buten-1-ol 134

NMR (CCl_4) δ 0.1 (s, 9H), 2.6 (t, 2H), 2.7 (b, 1H), 4.7 (t, 1H), 5.7 (d, 1H; J = 18 Hz), 6.2 (d of t, 1H), 7.3 (m, 5H). IR (neat) 3380, 3050, 3010, 2930, 2880, 1620, 1490, 1450 and 1245 cm^{-1}. MS, m/e (intensity): 205 (0.3), 107 (100), 77 (41), 73 (30).

REACTION OF 1-TRIMETHYLSILYL CARBANION WITH CARBONYL COMPOUNDS (IN THE PRESENCE OF $MgBr_2$)

To a solution of 2 mmole allyltrimethylsilane in 10 ml tetrahydrofuran at -78°C was added a solution of t-butyllithium (2.1 mmole, 1.8 M in n-pentane). This was followed by the addition of 0.5 ml hexamethylphosphoramide (HMPA) and the reaction mixture was stirred at -78°C for 2 hours. To the mixture, a solution of freshly prepared magnesium bromide (4 mmole, in 30 ml ether and 10 ml benzene)[152] was added at -78°C. Decolourization occurred and a cloudy mixture was formed. After 3/4 hour, a solution of the carbonyl compound (2 mmole) in 2 ml tetrahydrofuran was added and the mixture

was stirred for another hour. The reaction mixture was allowed to warm to room temperature and then poured into aqueous ammonium chloride solution and ether. The organic layer was washed with water and then dried with anhydrous magnesium sulfate. The solvent was then evaporated in vacuo to give a mixture of α and γ-alcohols with the α-alcohol predominating.

The reaction could also be carried out by using n-butyllithium and TMEDA at room temperature instead of using t-butyllithium and HMPA. The reaction was also repeated by premixing the magnesium bromide etherate with the carbonyl compound before addition to the 1-trimethylsilylallyl carbonyl. The outcome, however, was the same with the α-alcohol predominating.

a) Compounds 129 and 130 from acetophenone

Compound 129: spectral data same as before.

Compound 130: NMR (CCl_4) δ -0.2 (s, 9H), 1.5 (s, 3H), 1.6 (b, 1H), 2.1 (d, 1H), 4.8 to 5.2 (m, 2H), 5.7 to 6.3 (m, 1H), 7.4 (m, 5H). IR (neat) 3500, 3040, 2940, 2900, 2880, 1625, 1600, 1490, 1445 and 1245 cm^{-1}. MS, m/e (intensity): 219 (3), 144 (21), 143 (11), 129 (100), 128 (17), 121 (30), 77 (13), 73 (59).

b) Compounds 134 and 135 from benzaldehyde

Compound 134: spectral data same as before.

Compound 135: NMR (CCl_4) δ 0.0 (s, 9H), 2.0 (b, 1H), 2.1

(t, 1H), 4.9 (d, 1H), 5.0 (m, 2H), 5.9 to 6.3 (m, 1H), 7.3 (m, 5H). IR (neat) 3400, 3040, 3000, 2930, 2870, 1620, 1490, 1450 and 1245 cm^{-1}. MS, m/e (intensity): 219 (1), 205 (1), 130 (99), 129 (100), 107 (21), 77 (35), 73 (65).

SYNTHESIS OF 1,3-DIENES FROM CARBONYL COMPOUNDS AND 1-TRIMETHYLSILYLALLYL CARBANION

To a solution of 2 mmole allyltrimethylsilane in 10 ml tetrahydrofuran at -78°C was added a solution of t-butyllithium (2.1 mmole). This was followed by the addition of 0.5 ml hexamethylphosphoramide, and the reaction mixture was stirred at -78°C for 2 hours. To the mixture was added a freshly prepared solution of magnesium bromide etherate (4 mmole). Decolourization occurred. The reaction mixture was stirred for another hour. Then 2 mmole of the carbonyl compound in 2 ml of tetrahydrofuran was added and stirred for another hour. The reaction mixture was warmed up to 0°C. Then 2 mmole of thionyl chloride was added and stirred for 1/2 hour before it was allowed to warm to room temperature.

The reaction mixture was poured into aqueous ammonium chloride solution and ether. The organic layer was then washed with aqueous sodium bicarbonate solution, water and then dried with anhydrous magnesium sulfate. The solvent was then evaporated in vacuo to give the crude product. The diene was purified by preparative TLC using chloroform as eluent or was purified by distillation.

a) From undecanal

Product: 1,3-Tetradecadiene 136, purified by preparative TLC, yield 54%. NMC (CCl_4) δ 0.9 (t, 3H), 1.4 (b, 16H), 2.1 (m, 2H), 4.8 to 5.4 (m, 2H), 5.8 to 6.5 (m, 3H). IR (neat) 3020, 2960, 2930, 2860, 1600 and 1465 cm^{-1}. MS, m/e (intensity): 194 (12), 123 (10), 109 (33), 96 (53), 95 (60), 82 (82), 81 (79), 68 (84), 67 (100).

b) From benzaldehyde

Product: 1-Phenyl-1,3-butadiene 137, b.p. 78-80°C/6 mm, yield 50%. NMR (CCl_4) δ 4.9 to 5.4 (m, 2H), 6.1 to 6.7 (m, 3H), 7.0 to 7.4 (m, 5H). IR (neat) 3080, 3060, 3030, 2970, 1630, 1600, 1480, 1450, 1000 and 945 cm^{-1}. MS, m/e (intensity): 130 (83), 129 (100), 128 (64), 127 (28), 115 (62), 77 (13).

c) From cyclohexanone

Product: Allylidene cyclohexane 138, purified by preparative TLC, yield 49%. NMR (CCl_4) δ 1.7 (m, 6H), 1.9 to 2.4 (m, 4H), 4.8 to 5.2 (m, 2H), 5.4 to 5.9 (m, 1H), 6.2 to 6.8 (m, 1H). IR (neat) 3050, 2900, 2820, 1610, 1440 and 1340 cm^{-1}. MS, m/e (intensity): 122 (29), 107 (28), 93 (24), 79 (100).

d) From acetophenone

Product: 4-Phenyl-1,3-pentadiene 141, b.p. 80-83°C/5 mm, two isomers present at 1:1 ratio, yield 43%. NMR (CCl_4) δ 2.1 (bs, 3H), 4.8 to 5.5 (m, 2H), 6.0 to 6.9 (m, 2H), 7.1 to 7.4

(m, 5H). IR (neat) 3080, 3040, 2970, 2920, 1630, 1600, 1495 and 1445 cm^{-1}. MS, m/e (intensity): 144 (22), 143 (11) 129 (100), 128 (66), 115 (22), 77 (22).

e) From cyclohexane carboxaldehyde

In this particular reaction, after the addition of the carbonyl compound and stirring at -78°C for one hour, the reaction mixture was quenched with 2 mmole of acetyl chloride instead of thionyl chloride. The work up was carried out in the same way as before. A yellow liquid was obtained on work up. To the yellow liquid obtained from the work up was added 5 ml acetonitrile. Then 1.5 mmole of tetraethylammonium fluoride was added and stirred for 5 minutes. GC showed that the reaction was completed.

The reaction mixture was poured into water and ether. The organic layer was then washed once with water and then with saturated salt solution. The organic layer was then dried with anhydrous magnesium sulfate. The solvent was then evaporated in vacuo to give the diene 142.
Product: 1-Cyclohexyl-1,3-butadiene 142, purified by preparative TLC, yield 42%. NMR (CCl_4) δ 1.0 to 2.1 (m, 11H), 4.9 to 5.4 (m, 2H), 5.6 to 6.7 (m, 3H). IR (neat) 3090, 3040, 2930, 2860, 1650, 1600 and 1450 cm^{-1}. MS, m/e (intensity): 136 (63), 107 (33), 93 (22), 82 (67), 81 (77), 67 (100).

PREPARATION OF TRIMETHYLALLYLOXYSILANE 155

Allyl alcohol (0.5 mole) was added slowly to a 250 ml flask containing 0.6 mole of hexamethyldisilazane. Then 4 mmole of imidazole was added and stirred. The reaction mixture was stirred and heated at 110°C (oil bath temperature) overnight. The reaction mixture was fractionally distilled to give the product 155. Yield 87%, b.p. 98-99°C. NMR (CCl_4) δ 0.0 (s, 9H), 4.0 (m, 2H), 4.8 to 5.3 (m, 2H), 5.5 to 6.0 (m, 1H). IR (neat) 2940, 2840, 1420 and 1250 cm^{-1}.

PREPARATION OF TRIETHYLALLYLOXYSILANE 156

To a solution of 50 mmole allyl alcohol in 20 ml N,N-dimethylformamide was added at room temperature 60 mmole triethylchlorosilane. Then 120 mmole imidazole was added and stirred for 6 hours. The reaction mixture was then poured into ether and water. The organic layer was washed with water and then dried with anhydrous magnesium sulfate. The solvent was evaporated to give the product which was purified by distillation. Yield 95%, b.p. 79-81°C/30 mm. NMR (CCl_4) δ 0.5 to 1.2 (m, 15H), 4.2 (m, 2H), 4.9 to 5.4 (m, 2H), 5.6 to 6.2 (m, 1H). IR (neat) 3020, 2960, 2920, 2880, 1650, 1460, 1470, 1380 and 1240 cm^{-1}. MS, m/e (intensity): 172 (1), 143 (100), 115 (96), 87 (79), 59 (76), 57 (20).

REACTION OF TRIMETHYLALLYLOXYSILANE WITH SILYL HALIDES

To a solution of 25 mmole trimethylallyloxysilane in 40 ml tetrahydrofuran at -78°C was added slowly 27.6 mmole

t-butyllithium in n-pentane. A yellow solution was formed. The reaction mixture was stirred at -78°C for 1 1/2 hour before 25 mmole of the silyl halide in 2 ml tetrahydrofuran was added. A colourless solution was obtained. Stirring was continued for another 1/2 hour before the cooling bath was removed. The reaction mixture was allowed to warm to room temperature before work up.

The reaction mixture was poured into water and ether. The organic layer was washed with aqueous sodium bicarbonate solution and then with water. The organic layer was then dried with anhydrous magnesium sulfate. The solvent was evaporated in vacuo to give the product. The product was purified by distillation or by preparative TLC. (∿ 75%).

a) From trimethylsilyl halides Me_3SiX where X = F, Cl, Br and I

Product: α-Trimethylsiloxyallylsilane 158, b.p. 70-71°C/35 mm. NMR (CCl_4) δ 0.0 (s, 9H), 0.1 (s, 9H), 4.0 (m, 1H), 4.8 to 5.2 (m, 2H), 5.6 to 6.2 (m, 1H). IR (neat) 3080, 3040, 2940, 2880, 1640, 1420, 1320 and 1250 cm^{-1}. MS, m/e (intensity): 202 (3), 187 (2), 129 (4), 73 (100).

b) From triethylchlorosilane

Product: α-Triethylsiloxyallylsilane 161, purified by preparative TLC using chloroform as eluent. NMR (CCl_4) δ 0.0 (s, 9H), 0.5 to 1.2 (m, 15H), 4.0 (m, 1H), 4.8 to 5.2 (m, 2H), 5.6 to 6.2 (m, 1H). IR (neat) 3070, 2950, 2910, 2880, 2820, 1630,

1460, 1420 and 1250 cm^{-1}. MS, m/e (intensity): 244 (1), 215 (20), 115 (59), 87 (77), 73 (100).

The reaction was repeated with the addition of 0.5 ml HMPA after the addition of the t-butyllithium at -78°C. The rest of the procedure remained the same as before. Work up gave a mixture of two products.

From trimethylsilyl halides Me_3SiX

Products: α-Trimethylsiloxyallylsilane 158, spectral data same as before. γ-Addition product 165. NMR (CCl_4) δ 0.0 (s, 9H), 0.1 (s, 9H), 1.4 (d of d, 2H), 4.4 (d of t, 1H), 6.2 (m, 1H). MS, m/e (intensity): 202 (5), 187 (2), 73 (100).

The reaction was repeated with the addition of a solution of molar equivalent of zinc chloride in tetrahydrofuran after the addition of HMPA at -78°C. The rest of the procedure remained the same as before. Work up gave only the rearranged product 158 from the trimethylsilyl halides.

REACTION OF TRIETHYLALLYLOXYSILANE WITH TRIMETHYLCHLOROSILANE

The procedure was the same as in the reaction of trimethylallyloxysilane with trimethylchlorosilane.

Product: α-Trimethylsiloxyallylsilane 162. NMR (CCl_4) δ δ 0.1 (s, 9H), 0.5 to 1.3 (m, 15H), 4.1 (m, 1H), 4.8 to 5.2 (m, 2H), 5.7 to 6.2 (m, 1H). IR (neat) 3080, 2950, 2910, 2880, 1630, 1455, 1410 and 1250 cm^{-1}. MS, m/e (intensity):

244 (3), 299 (1), 215 (26), 115 (35), 87 (100), 73 (57), 59 (62).

The reaction was repeated with the addition of 0.5 ml HMPA after the addition of the t-butyllithium at -78°C. Products: α-Trimethylsiloxyallylsilane 162, spectral data same as before. γ-Addition product 166. NMR (CCl_4) δ 0.0 (s, 9H), 0.5 to 1.3 (m, 15H), 1.4 (d of d, 2H), 4.4 d of t, 1H), 6.0 (m, 1H). MS, m/e (intensity): 244 (16), 229 (1), 215 (29), 115 (36), 87 (100), 73 (78), 59 (59).

The reaction was repeated with the addition of a solution of molar equivalent of zinc chloride in tetrahydrofuran after the addition of HMPA at -78°C. The rest of the procedure remained the same as before. Work up gave only compound 162 as product.

REACTIONS OF TRIMETHYLALLYLOSYSILANE
WITH CARBONYL ELECTROPHILES

The reaction was carried out in similar fashion to the silylation reactions of trimethylallyloxysilane with silyl halides. However instead of reacting the trimethylsilyl-allyloxy carbanion with silyl halides, the carbanion is reacted with equal molar quantities of different carbonyl compounds.

a) With acetyl chloride

Product: Ester 163, purified by preparative TLC using chloroform as eluent, yield 73.6%. NMR (CCl_4) δ 0.0 (s, 9H),

2.0 (s, 3H), 4.7 to 5.1 (m, 3H), 5.5 to 6.0 (m, 1H). IR (neat) 3080, 3010, 2960, 2910, 2860, 1740, 1630, 1410, 1370 and 1250 cm^{-1}. MS, m/e (intensity): 172 (2), 129 (25), 73 (100), 45 (14), 43 (33).

b) With benzoyl chloride

Product: Ester 167, purified by preparative TLC using methylene chloride as eluent, yield 75%. NMR (CCl_4) δ 0.0 (s, 9H), 4.8 to 5.2 (m, 2H), 5.4 (m, 1H), 5.6 to 6.2 (m, 1H), 7.2 to 8.0 (m, 5H). IR (neat) 3060, 3040, 2940, 2880, 1720, 1630, 1600, 1450, 1360, 1310 and 1255 cm^{-1}. MS, m/e (intensity): 234 (1), 219 (7), 129 (13), 105 (100), 77 (36), 73 (66).

c) With methyl chloroformate

Product: carbonate 168, purified by preparative TLC using methylene chloride as eluent, yield 68%. NMR (CCl_4) δ 0.0 (s, 9H), 3.7 (s, 3H), 4.8 to 5.2 (m, 3H), 5.5 to 6.1 (m, 1H). IR (neat) 3100, 3030, 2960, 2900, 2850, 1750, 1640, 1440 and 1250 cm^{-1}. MS, m/e (intensity): 188 (1), 173 (1), 129 (15), 89 (10), 73 (100), 59 (26), 45 (18).

d) With ethyl chloroformate

Product: carbonate 169, purified by preparative TLC using methylene chloride as eluent, yield 74%. NMR (CCl_4) δ 0.0 (s, 9H), 1.2 (t, 3H), 4.1 (q, 2H), 4.8 to 5.1 (m, 3H), 5.6 to 6.1 (m, 1H). IR (neat) 3070, 2970, 2950, 2880, 1745, 1630, 1470, 1370 and 1250 cm^{-1}. MS, m/e (intensity): 202 (1), 187

(2), 129 (15), 73 (100), 45 (16), 29 (19).

e) With diphenyl carbonate

Product: Carbonate 170, purified by preparative TLC using chloroform as eluent, yield 45%. NMR (CCl_4) δ 0.0 (s, 9H), 4.9 to 5.2 (m, 3H), 5.5 to 6.2 (m, 1H), 7.2 (m, 5H). IR (neat) 3040, 3000, 2940, 2880, 1755, 1630, 1590, 1490 and 1250 cm^{-1}. MS, m/e (intensity): 129 (11), 77 (22), 73 (100).

f) With dimethyl carbonate

Products: carbonate 168, spectral data same as before. Vinylsilyl ether 171. NMR (CCl_4) δ 0.1 (s, 9H), 3.0 (d of d, 2H), 3.6 (s, 3H), 4.5 (m, 1H), 6.2 (m, 1H). MS, m/e (intensity): 188 (10), 173 (9), 129 (72), 89 (47), 73 (100), 59 (18).

g) With diethyl carbonate

Products: carbonate 169, spectral data same as before. Vinylsilyl ether 172. NMR (CCl_4) δ 0.2 (s, 9H), 1.2 (t, 3H), 3.0 (d of d, 2H), 4.2 (q, 2H), 4.7 (m, 1H), 6.2 (m, 1H). MS, m/e (intensity): 202 (9), 187 (1), 159 (6), 157 (2), 129 (85), 73 (100), 45 (24), 29 (25).

REACTION OF α-TRIMETHYLSILOXYTRIMETHYLALLYLSILANE 158 WITH ACETYL CHLORIDE

To a solution of 2 mmole titanium tetrachloride in 10 ml dry methylene chloride was added at -78°C 2 mmole of acetyl chloride in 2 ml methylene chloride. The reaction mixture was stirred for 5 minutes at -78°C. Then 1 mmole

of compound 158 in 2 ml methylene chloride was added slowly. The reaction mixture was stirred at -78°C. GC showed that no starting material 158 was left after stirring for 5 minutes at -78°C.

The reaction mixture was poured into ether and aqueous sodium bicarbonate solution. The organic layer was washed with water and then with saturated salt solution. After drying with anhydrous magnesium sulfate, the solvent was evaporated in vacuo to give the product 163. The product 163 was purified by preparative TLC using chloroform as eluent, yield 70%.

The spectral data for 163 was identical to those obtained before

REACTION OF α-TRIMETHYLSILOXYTRIETHYLALLYLSILANE 162 WITH ACETYL CHLORIDE

The procedure was the same as for the reaction of 158 with acetyl chloride, yield 65%. Product: Ester 164. NMR δ 0.5 to 1.3 (m, 15H), 2.0 (s, 3H), 4.8 to 5.3 (m, 3H), 5.5 to 6.0 (m, 1H). IR (neat) 2960, 2910, 2880, 1730, 1630, 1460, 1430 and 1375 cm^{-1}. MS, m/e (intensity): 214 (1), 185 (7), 171 (21), 115 (48), 87 (100), 59 (48), 43 (28).

REACTION OF α-TRIMETHYLSILOXYTRIMETHYLALLYLSILANE 158 WITH OTHER ACID CHLORIDES

To a mixture of 2 mmole aluminum chloride in 10 ml methylene chloride at 0°C (or room temperature depending on the particular acid chloride) was added a solution of

2 mmole of the acid chloride in 2 ml methylene chloride. The reaction mixture was stirred for 1/2 hour during which a homogeneous pale yellow solution was formed. Then 1 mmole of the compound 158 in 2 ml methylene chloride was added slowly. The reaction was followed by GC.

When no more starting material was present, the reaction mixture was poured into ether and aqueous ammonium chloride solution. The organic layer was washed with aqueous sodium bicarbonate solution (2 x 10 ml) and then with water. The organic layer was dried with anhydrous magnesium sulfate. The solvent was evaporated in vacuo. The products were isolated by preparative TLC using methylene chloride as eluent.

a) With benzoyl chloride

The reaction was carried out at 0°C.

Products: Cis and trans-isomers vinyl chloride 173, yield 84.5%. NMR (CCl_4) δ 3.6 to 3.9 (m, 2H), 6.0 to 6.4 (m, 2H), 7.4 to 8.1 (m, 5H). IR (neat) 3060, 3020, 2880, 1690, 1640, 1610, 1450, 1410, 1340 and 1220 cm^{-1}. MS, m/e (intensity): 182 (0.2), 180 (0.6), 144 (3), 105 (100), 77 (52).

b) With p-anisoyl chloride

The reaction was carried out at room temperature.

Products: (i) Isomers of vinyl chloride 174, yield 55.9%. NMR (CCl_4) δ 3.6 to 3.9 (m, 2H), 3.9 (s, 3H), 6.2 (m, 2H), 6.9 (m, 2H), 7.9 (m, 2H). IR (neat) 3050, 2990, 2940, 2920, 2830, 1675, 1600, 1575, 1520, 1450, 1340 and 1310 cm^{-1}.

MS, m/e (intensity): 212 (0.6), 210 (1.6), 174 (3), 135 (100), 107 (9), 92 (11), 77 (15).

(ii) t-Vinylsilane 175, yield 24.4%. NMR (CCl_4) δ 0.1 (s, 9H), 3.9 (s, 3H), 4.7 (d, 2H), 5.7 to 6.1 (m, 2H, J = 18 Hz), 6.8 (d, 2H), 7.9 (d, 2H). IR (neat) 3050, 2980, 2940, 2820, 1710, 1600, 1575, 1515, 1450, 1410, 1360, 1310 and 1250 cm^{-1}. MS, m/e (intensity): 264 (20), 249 (20), 165 (21), 135 (85), 107 (39), 92 (57), 77 (80), 73 (100), 59 (57).

c) With p-toluoyl chloride

The reaction was carried out at room temperature.

Products: (i) Isomers of vinyl chloride 176, yield 52%. NMR (CCl_4) δ 2.6 (s, 3H), 3.6 to 3.9 (m, 2H), 6.0 to 6.3 (m, 2H), 7.1 (m, 2H), 7.7 (m, 2H). IR (neat) 3020, 2940, 2910, 1675, 1625, 1600, 1570, 1410, 1340 and 1180 cm^{-1}. MS, m/e (intensity): 158 (16), 119 (100), 91 (40), 65 (16).

(ii) t-Vinylsilane 177, yield 22%. NMR (CCl_4) δ 0.4 (s, 9H), 2.6 (s, 3H), 4.8 (d, 2H), 6.1 (m, 2H), 7.2 (d, 2H), 7.9 (d, 2H). IR (neat) 3020, 2940, 2910, 1720, 1610, 1435, 1405, 1370, 1305 and 1250 cm^{-1}. MS, m/e (intensity): 248 (6), 233 (20), 177 (31), 119 (44), 91 (97), 73 (100), 59 (45).

d) With hexanoyl chloride

The reaction was carried out at 0°C.

Products: (i) Isomers of vinyl chloride 178, yield 56%. NMR (CCl_4) δ 0.9 (t, 3H), 1.0 to 1.7 (b, 6H), 2.4 (t, 2H), 3.2 (m, 2H), 5.8 to 6.3 (m, 2H). IR (neat) 2940, 2910, 2850,

1710, 1625, 1535, 1460, 1400 and 1335 cm^{-1}. MS, m/e (intensity): 138 (0.3), 99 (57), 77 (6), 75 (16), 71 (48), 43 (100), 39 (25).

(ii) t-Vinylsilane 179, yield 22%. NMR (CCl_4) δ 0.1 (s, 9H), 0.9 (t, 3H), 1.1 to 1.7 (b, 6H), 2.2 (t, 2H), 4.5 (d, 2H), 5.9 (m, 2H). IR (neat) 2940, 2920, 2850, 1730, 1620, 1450, 1375 and 1250 cm^{-1}. MS, m/e (intensity): 228 (0.6), 213 (2), 185 (14), 157 (26), 129 (89), 115 (61), 99 (62), 73 (100), 71 (47), 43 (73).

BEILSTEIN TEST FOR HALOGEN

The test on compound 173 was performed according to the procedure on page 319 of reference 172.

The flame test for compound 173 gave a blue-greenish colour indicating the presence of halogen.

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