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THE SYNTHESIS OF ALKENES

THE SYNTHESIS OF ALKENES FROM CARBONYL COMPOUNDS AND CARBANIONS ALPHA TO SILICON

by

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ABSTRACT

A general and facile synthetic method to terminal allenes was developed, utilizing α-silylvinyl carbanions and carbonyl compounds. Fluoride ion was found to effect cleavage of silicon-carbon vinyl bonds if a beta-functionality were present. The products obtained were dependent on the functionalities beta to the silicon. A stereoselective conversion of RCHO into E-RCH = $CHCH_2Cl$ has been developed utilizing organosilicon intermediates. A stereoselective synthesis of E and Z dialkylsubstituted vinylsilanes has been developed using organocopper reagents. This reaction was extended to the stereoselective synthesis of E and Z disubstituted alkenes. The gypsy moth sex pheromone, disparlure, was stereoselectively synthesized using organosilicon intermediates.

RESUME

Une méthode de synthèse générale et facile d'allènes terminaux a été développée, utilisant des carbanions α-vinylsilylés et des composés carbonylés. On a trouvé que l'ion fluorure peut effectuer un clivage de la liaison carbone-silicium si une fonction est présente en position β. Le produit obtenu dépend de la fonction en β du silicium. Une conversion stéréosélective de RCHO en R-RCH = $CHCH_2Cl$ a été developpée au moyen d'intermédiaires organosilanes. Une synthèse stéréosélective de vinylsilanes disubstitués par des groupes alkyles a été mise au point au moyen de derivés organiques du cuivre. Cette réaction a été étendue à la synthèse stéréosélective d'alcènes disubstitués E et Z. La phéromone sexuelle de la mite gypsy (disparlure) a été synthétisée stéréospécifiquement à partir d'intermédiaires organosilylés.

ACKNOWLEDGEMENTS

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

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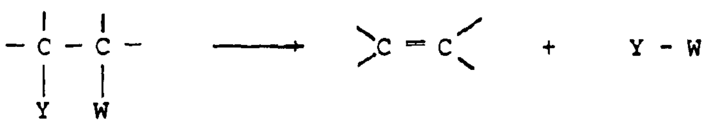
CHAPTER I

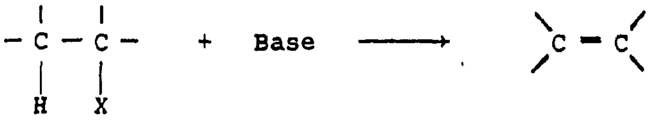
INTRODUCTION

In the synthesis of organic molecules, both complex as well as simple, in many cases the crucial step of the synthesis is the introduction of a carbon-carbon double bond into the structure. The carbon-carbon double bond can be generated from a wide variety of functionalized organic molecules. General methods of alkene synthesis can be found in many organic texts[1,2] as well as in specific books on synthetic methods[3,4] or alkenes[5].

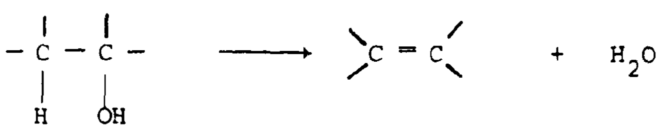
(a) General Methods of Alkene Synthesis

One of the most widely used methods of alkene formation is via an elimination reaction. The variety of functionalities employed in these reactions is extremely large. Dehydrohalogenation of an alkyl halide in the presence of base is one such reaction. Different combinations of base/solvent pairs have been employed in this reaction with varied success depending on the alkyl halide used[4].



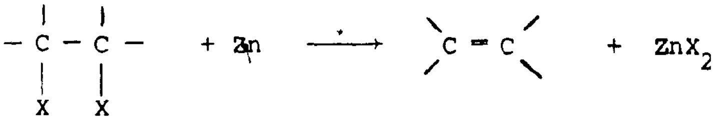


Dehydration of an alcohol can be used as a second method. This reaction is normally performed with the aid of a strong acid,



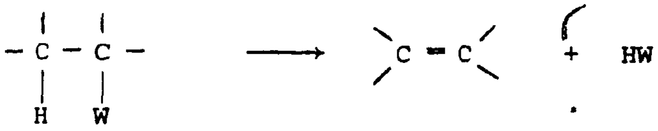
but recently a number of modified, less harsh reaction conditions have been developed. These usually involve the conversion of the alcohol to a labile ester followed by the elimination of the ester, to give an olefin[4].

Olefin formation can be accomplished via dehalogenation of vicinal dihalides. Zinc is but one of the reagents which has been



employed to effect this transformation. A wide variety of other reagents also can be used[4].

A number of other functionalized organic molecules also undergo elimination to yield olefins. Where W is an acid (W = COOH),

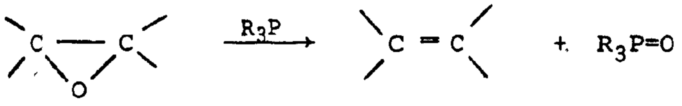


a decarboxylation reaction yields an olefin. This is generally accomplished at elevated temperatures and in the presence of a catalyst[4]. Acid halides, as well as anhydrides, also undergo a similar reaction to give alkenes[4]. Amides undergo elimination of H-NHCOR to give alkenes in certain molecules[4]. Amines, where W = NRR', also give olefins via a number of pathways, either by formation of an ammonium salt followed by elimination, or via an N-oxide species followed by elimination[4].

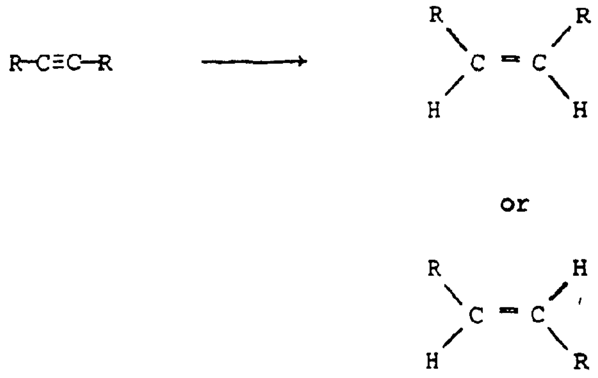
When W = -OC(O)R, an ester, a number of pathways is available to give alkenes. One is via a pyrolytic cis elimination, the second is transformation of the ester to an alcohol, followed by dehydration of the alcohol[4].

Ether can be converted into olefins (W = OR) under certain conditions via treatment with acid, alkyllithium or a number of other specific reagents[4].

Epoxides undergo deoxygenation with a number of reagents to give alkenes, the best known reagent being phosphines.

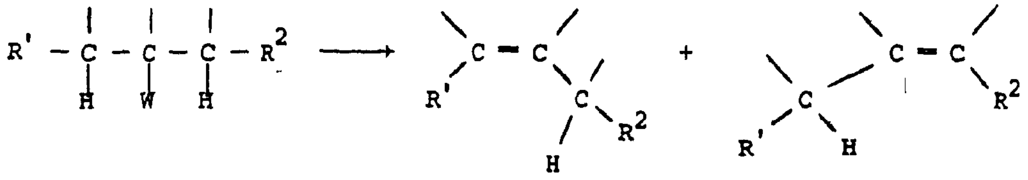


One of the drawbacks of these methods of olefin synthesis is the non-stereoselectivity of the reactions. If geometric isomers are possible a mixture of isomers usually results. One method of overcoming this shortcoming is the reduction of alkynes. This reaction can be

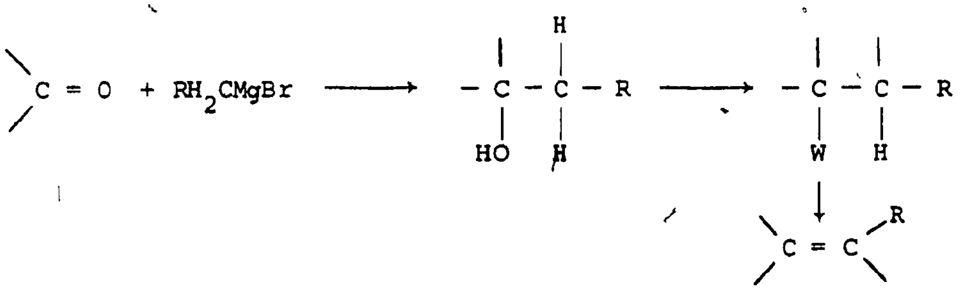


controlled to give, stereospecifically, the E or Z disubstituted alkenes[3].

Although a wide variety of methods has been mentioned for generation of a carbon-carbon double bond, when one is looking for a method of introducing an unsaturation into a molecule, none of these methods is very attractive. A number of shortcomings of these methods exists. Firstly, in the elimination reactions the first step of the reaction is the formation of a carbon-carbon bond which, in most of these cases, can be accomplished by using the Grignard reaction. Secondly, the elimination itself is normally non-regiospecific; that is, when two paths are open for elimination to occur, a mixture of products results.



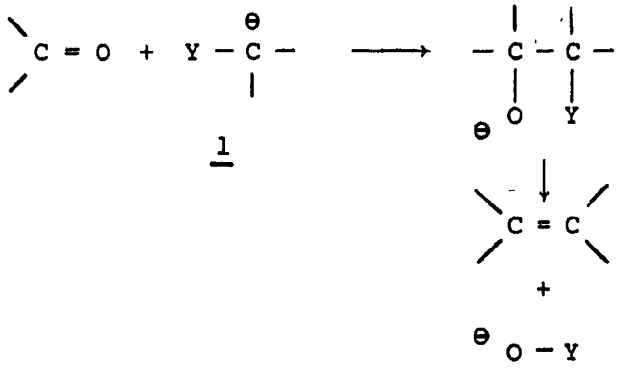
Many of these elimination reactions involve a series of reactions, starting from carbon-carbon single bond formation, followed by transformation to a specific functionality, followed finally by elimination, in some cases under harsh reaction conditions. A more



attractive sequence would be one in which both bonds of the alkene are formed in one reaction under mild conditions and with regiospecificity.

(b) <u>The Wittig Reaction</u>

The method of choice for the formation of a carbon-carbon double bond is via the olefination of a carbonyl compound. Of the methods available, the Wittig reaction, is by far the most often employed (Y = $P^{+}R_{3}$)[6,7,8].



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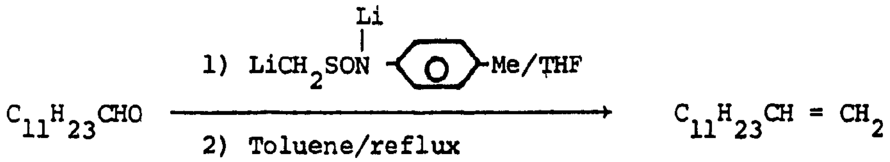
In the Wittig reaction, a phosphorus ylid (1) is used to effect the conversion. The phosphorus ylid itself is generated from the phosphonium salt formed by an alkyl halide and triphenylphosphine. The Wittig reaction has been found to be a general method of converting carbonyl compounds to a wide variety of olefins. However, a number of reports recently have shown that modifications in the structure of the organophosphorus compound can offer improvements to this reaction in the synthesis of certain beta-functionalized olefins. For example, the Horner modification, using a phosphinylalkyl metal compound ($Y = R_2P(O)-$), has been shown to have advantages in certain cases over the Wittig reaction[9]. Similarly, Wadsworth and Emmons have used phosphonate carbanions ($Y = (RO)_2 P(O)-$) which show certain advantages over the normal Wittig reaction[10]. The Wittig reaction has been extended to other phosphorus-substituted carbanions, such as alpha-lithiophosphoric acid bisamides ($Y = (RR'N)_2P(O)-$)[11] and O,O'-dialkyl alpha-lithiophosphoronothionate esters ($Y = (RO)_2P(S)-$)[12].

There are two main reasons for an improved reaction with these modifications in the structure of the phosphorus reagent (1). The first is that the Wittig reaction uses an ylid as the reagent. If an electron-withdrawing beta-functionality is attached in addition to the carbanion carbon, then the ylid can become too unreactive and may not react with the carbonyl compound. In the modifications mentioned, the attacking carbon atom is a carbanion carrying a full negative charge and thus a higher reactivity. The second advantage is an easier workup procedure. Triphenylphosphine oxide, formed in the Wittig reaction, is at times difficult to separate from the olefin formed.

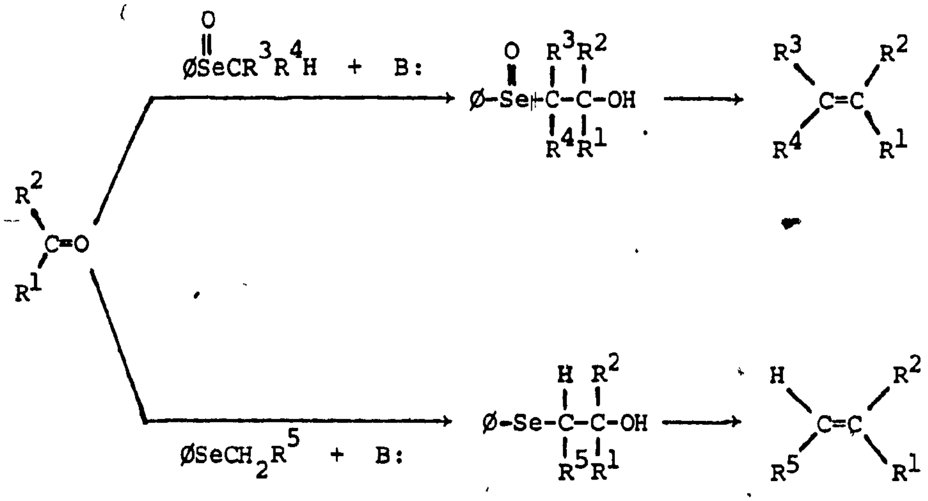
For example, in the Wadsworth and Emmons modification ($Y = (RO)_2P(O)-$) the phosphate salt formed ($RO_2P(O)OM$) can be removed from the organic solution easily. The starting phosphorus reagents are often also less expensive than triphenylphosphine used in the Wittig reaction.

A number of groups has recently found that these olefination reactions are not unique to organophosphorus compounds. Corey has reported the use of sulfinamide derivatives to convert carbonyl compounds to olefins[13,14]. In addition to this reaction, sulphides[15,16],

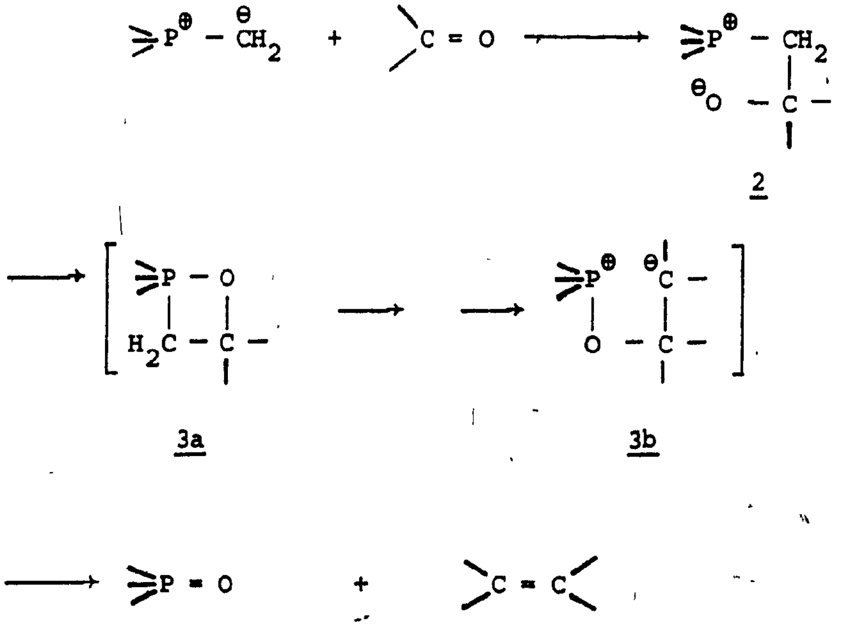


sulfoxides[17], sulfoximides[18] and sulphones[19] have been used to effect olefination of carbonyl compounds.

The olefination of carbonyl compounds has also been extended with the use of organoselenium compounds[20,21,22]. This method of olefination has the advantage over the Wittig reaction of being applicable to the synthesis of tetrasubstituted olefins, for which the Wittig reaction usually fails.



The Wittig olefination reaction, as well as its many modifications, can be generalized as shown in Scheme 1. The important features of this reaction are the formation of the betaine 2 and the



Scheme 1

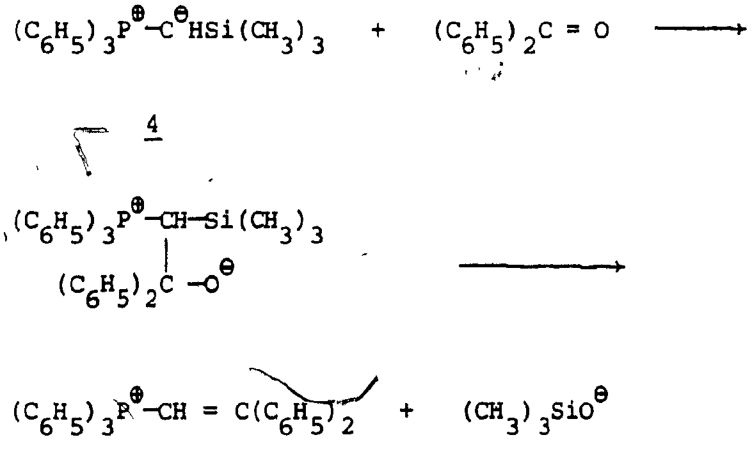
subsequent attack of the alkoxide on the phosphorus atom to form a pentacovalent intermediate 3a[23] or possibly 3b where the alpha-carbon atom carries some negative charge[2,3]. The final step of the reaction is the elimination of the phosphine oxide and the formation of the olefin. The driving force of the reaction is then the formation of the very strong phosphorus-oxygen bond.

The criteria necessary for the olefination reaction in the phosphorus case are the following:

(a) alkoxide attacks phosphorus readily,
(b) oxygen and phosphorus form a very strong bond,
(c) the d-orbitals of phosphorus can conceivably allow it to form a pentacovalent species, and
(d) the phosphoryl moiety is a good leaving group.

If one takes into consideration the above information, it is conceivable to extend this olefination reaction to organosilicon compounds, since like phosphorus, silicon fulfills all the above requirements.

There exists additional information in the literature to support this postulation. In 1962 Gilman and Tomasi[24] reported that they were able to synthesize tetraphenylallene from benzophenone and the ylid 4, $(C_6H_5)_3\overset{\oplus}{P}-\overset{\ominus}{C}HSi(CH_3)_3$. The explanation for the reaction is shown in Scheme 2. The first part of the reaction sequence was, in fact, an olefination reaction using an organosilicon intermediate.



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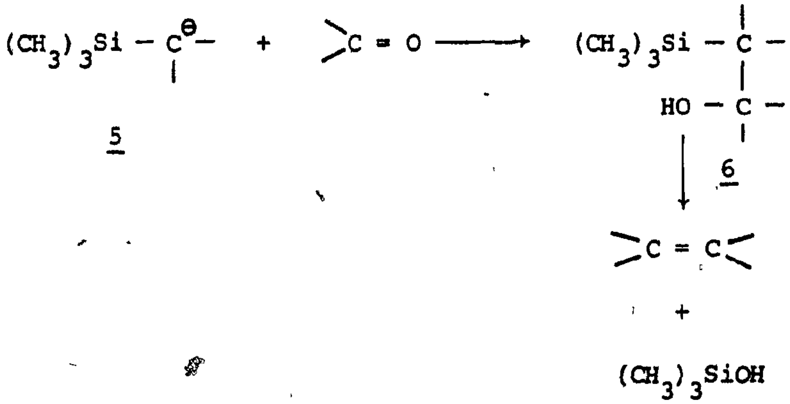
$$(C_6H_5)_3P^{\oplus}-C^{\ominus}HSi(CH_3)_3 + (C_6H_5)_2C=O \longrightarrow (C_6H_5)_3P^{\oplus}-\underset{\displaystyle (C_6H_5)_2C-O^{\ominus}}{CH}-Si(CH_3)_3 \longrightarrow (C_6H_5)_3P^{\oplus}-CH=C(C_6H_5)_2 + (CH_3)_3SiO^{\ominus}$$

Scheme 2

(c) The Silicon Method

Peterson was the first to show that olefination of carbonyl compounds with organosilanes could be extended to a general method of alkene synthesis[25,29]. Peterson employed an α-silylsubstituted carbanion (5) which reacted with the carbonyl to give a β-hydroxysilane (6). Using either base or dilute acid, these β-hydroxysilanes undergo



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elimination of silanol to give alkenes. Peterson found that both aromatic and aliphatic ketones and aldehydes react readily with the α-silyl carbanions to give the alkenes in good yields (50-90%).

This reaction was, however, limited in the types of olefins obtainable, due to the limited number of alpha-silylcarbanions then available. Peterson employed two methods of generating the carbanions. The first was via a Grignard reaction on an alpha-halosilane. This was

$$\underset{\underline{7}}{(CH_3)_3SiCH_2X} + Mg \longrightarrow (CH_3)_3SiCH_2MgX$$

limited in that the starting alpha-halo compounds (7) were not readily available with other substituents on the alpha-carbon. The second method for carbanion formation utilized was via metalation of silanes.

$$(CH_3)_3SiCH_2R' + RLi \longrightarrow (CH_3)_3SiCHLiR'$$

$R' = (C_6H_5)_2P$

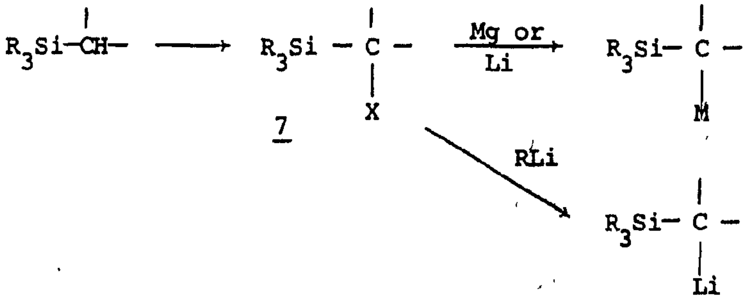
$= CH_3S$

$= C_6H_5$

Several examples were used.

Although this increased the number of alkenes obtainable via this reaction, it was still restricted to specific cases. Peterson also found that the final elimination of silanol was at times sluggish, requiring long reaction times. Thus, to make this reaction a viable method for forming carbon-carbon double bonds, a more general method for generating carbanions alpha to silicon must exist, and methods of effecting elimination of the siloxy group readily had to be developed.

Chan et al. subsequently reported the extension of this reaction[26,27]. They found that many different methods could be utilized to generate carbanions alpha to silicon. As reported by Peterson, alpha-halosilanes react with magnesium or lithium to generate the carbanion. This reaction became of synthetic utility by the fact that alpha-halosilanes (7) could in turn be prepared by free radical halogenation of alkylsilanes[28]. Metal-halogen exchange reactions between alpha-halosilanes and alkyllithiums also lead to alpha-silylalkyllithium compounds (8)[28].



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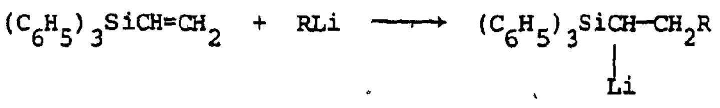
A second method employed by Chan et al. for the generation of the carbanion was direct metalation by alkyllithium in hexamethylphosphoramide (HMPA) of benzyltrimethylsilane[26,27]. This method is

$$(CH_3)_3SiCH_2C_6H_5 \xrightarrow{\text{n-BuLi/HMPA}} (CH_3)_3SiCHLiC_6H_5$$

only applicable in the synthesis of carbanions with activating groups such as phenyl. For the generation of carbanions on simple alkyl chains a different method had to be developed.

Cason and Brook reported that alkyllithiums add across the double bond of triphenylvinylsilane to give metalated silanes (9)[30].

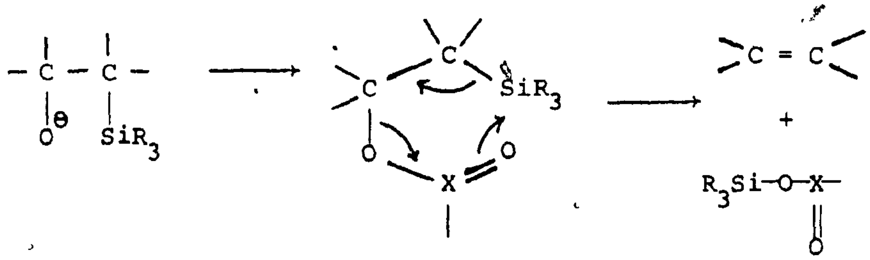


$$(C_6H_5)_3SiCH{=}CH_2 + RLi \longrightarrow (C_6H_5)_3Si\underset{\displaystyle Li}{\underset{|}{C}}H{-}CH_2R$$

9

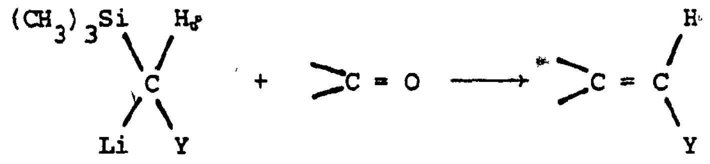
Chan et al. showed that by choosing the appropriate methods cited above, alpha-silyl carbanions (9) of diverse structures could be synthesized[26,27].

Peterson found that elimination of trimethylsilanol from the beta-hydroxysilyl adduct was at times sluggish[25]. Chan found that elimination occurs spontaneously when the alkene formed is non-terminal. When the alkene is terminal, as in most of Peterson's examples[25], neither the lithium nor the magnesium salt of the beta-hydroxysilane (6) undergoes elimination. Acid treatment, as employed by Peterson[25], does give alkene but the resultant alkene may isomerize in acid and thus this could not be considered a good synthetic method. Chan found that treatment of the intermediate beta-alkoxysilane with either thionyl chloride or acetyl chloride gave alkenes in good yield with no double bond isomerization. Yields of products, in comparison with other methods of synthesis of specific alkenes, are similar or higher.



Subsequent to these initial reports of the olefination of carbonyl compounds by carbanions alpha to silicon, many other reports have appeared. Most of them deal with new methods of generating different functionalized alpha-silylcarbanions. Suggestion has been made in the literature to name this as the Peterson olefination reaction.

Carey has reported the use of alpha-silylcarbanions in the synthesis of hetero-substituted alkenes (10)[31,32,33].



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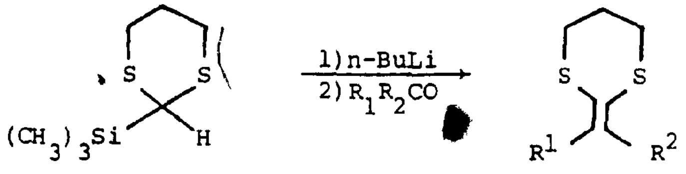
$Y = P(O)(OEt)_2$

= SPh

= S(O)Ph

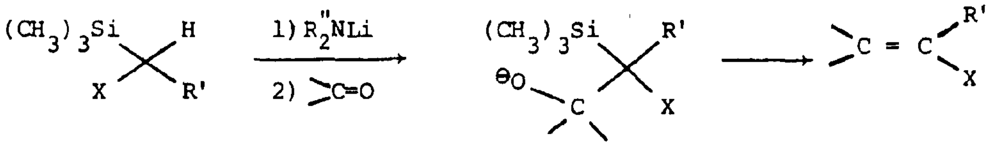
Carey[32], Lappert[34], as well as Seebach[35] have also used organosilicon intermediates in the synthesis of ketene thioacetals (11).



11

This method of synthesis appears to be superior to that of the Wittig reaction[36] for these synthetically useful intermediates[37,38].

The Peterson olefination reaction of carbonyl compounds has also been extended to the synthesis of α,β-unsaturated esters[39,40] and nitriles[41]. The method of choice previously for the synthesis of



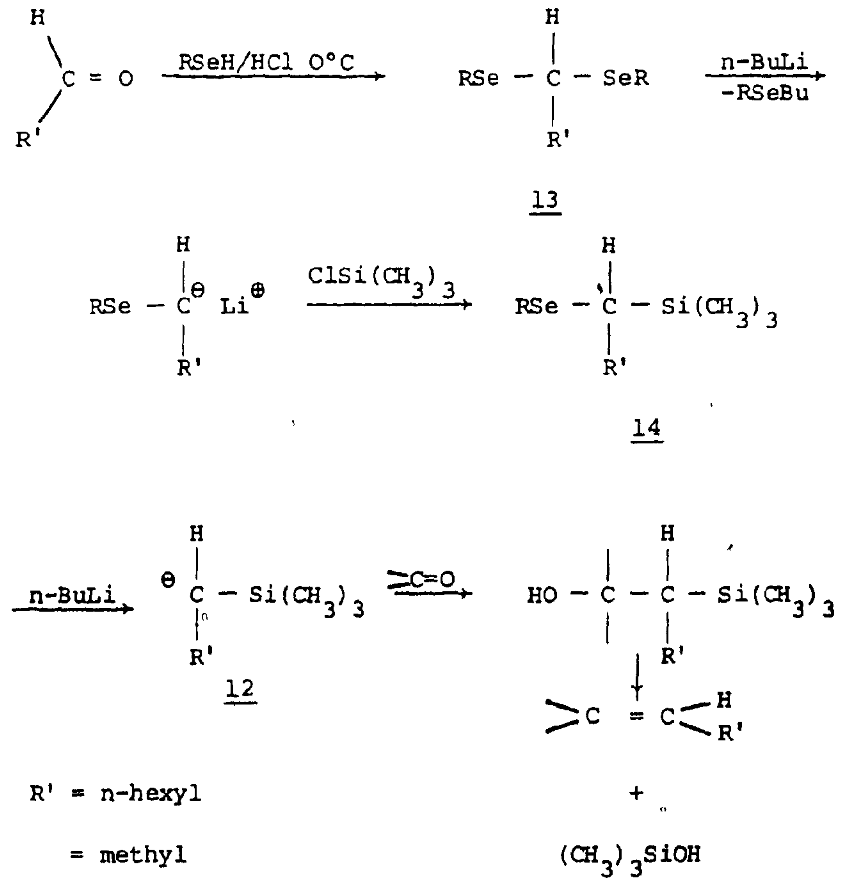
X = CN

= COOR

α,β-unsaturated esters and nitriles had been via the Wadsworth-Emmons-Horner modificaiton of the Wittig reaction (i.e., via phosphonate carbanions)[10]. However, the use of the α-silyl carbanions appears to have certain advantages over the Wadsworth-Emmons-Horner method[10].

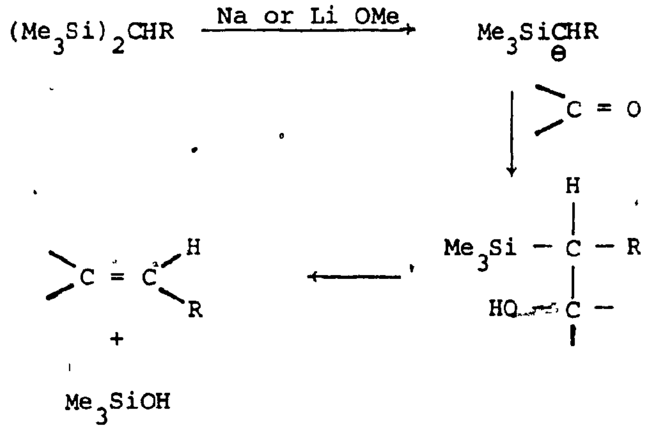
The silyl method uses milder conditions to effect this conversion. In addition, for readily enolizable ketones, with the phosphonate carbanions proton transfer reactions may occur faster than carbonyl addition together with the risk of enolate condensation reactions[42,43,44]. These side reactions do not seem to occur with the use of silyl compounds and one obtains, in good yields, α,β-unsaturated esters and nitriles.

Recently, a new method for generating α-silyl carbanions has been reported. Dumont and Krief[45] have reported the synthesis of mono-substituted α-silyl carbanions (12) using organoselenium precursors (13).



The α-silylmethylselenides (14) can easily be prepared[46,47] with a wide variety of alkyl substituents, and thus a wide variety of α-silyl carbanions, otherwise not available, can be generated. This method at present is limited to the generation of mono-substituted α-silyl carbanions.

Sakurai[48] has also developed an alternative method of α-silyl carbanion generation. Here, the carbanion is obtained by the alkaline cleavage of a silicon-carbon bond. This method has not been studied



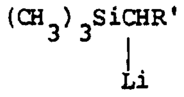
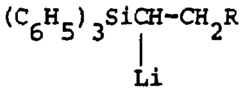
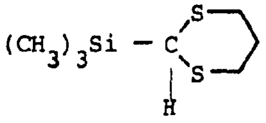
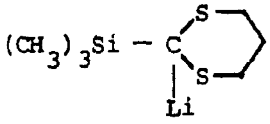
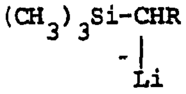
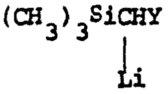
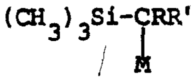
in any great detail however, and therefore its general applicability is yet to be explored.

The Peterson olefination reaction has, in the past nine years, been developed into a viable alternative to the Wittig reaction. The availability of the α-silyl carbanions has made this reaction of considerable use in organic synthesis (Table I). Yields of the alkenes range from 35-90%, the low yield reactions usually result from unstable products. Most of the α-silyl carbanions react with a range of ketones and aldehydes with ease, to give β-hydroxysilanes which subsequently undergo elimination of silanol quite readily, under a wide range of reaction conditions, to give alkenes.

On examination of the types of carbanions - alpha to silicon - employed in the Peterson olefination reaction, it is apparent that of all the cases studied (Table I) only carbanions on saturated carbon atoms have been utilized. This thesis deals with the chemistry of α-silylvinyl carbanions and the chemistry of the adducts of these vinyl carbanions with carbonyl compounds.

TABLE I

Alpha-silyl Carbanions

Precursor	α-Silyl carbanions
$(CH_3)_3SiCHRX$ + Mg R = H = alkyl	$(CH_3)_3SiCHRMgX$
$(CH_3)_3SiCH_2R'$ R' = $(C_6H_5)_2P$ = CH_3S = C_6H_5 = $P(O)(OEt)_2$ = SC_6H_5 = $S(O)C_6H_5$	 $(CH_3)_3Si\underset{\mathrm{Li}}{\underset{\vert}{C}}HR'$
$(C_6H_5)_3SiCH{=}CH_2$ + RLi R = alkyl	 $(C_6H_5)_3Si\underset{\mathrm{Li}}{\underset{\vert}{C}}H{-}CH_2R$
 + n-BuLi	
$(CH_3)_3Si{-}CHR{-}SeR'$ + n-BuLi R = alkyl R'= alkyl	 $(CH_3)_3Si{-}\underset{\mathrm{Li}}{\underset{\vert}{C}}HR$
$(CH_3)_3SiCH_2Y$ + $LiN(iPr)_2$ Y = CN = COOR	 $(CH_3)_3Si\underset{\mathrm{Li}}{\underset{\vert}{C}}HY$
$[(CH_3)_3Si]_2CR'R$ + Na or LiOMe R,R' = H, C_6H_5, t-Bu, $Si(CH_3)_3$	 $(CH_3)_3Si{-}\underset{\mathrm{M}}{\underset{\vert}{C}}RR'$

CHAPTER II

ALLENES

(a) Allene Synthesis

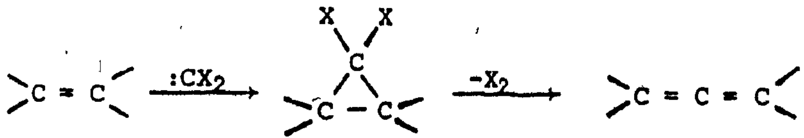
Although allenes have been known for some time little work has been performed on them. The discovery that these compounds have industrial uses and occur in nature has prompted increased interest in this system in the last 30 years[49,50].

To introduce the second double bond into an alkene to give an allene, many of the methods for forming carbon-carbon double bonds can be used.

Dehalogenation has been used for allene formation. Dihaloalkenes undergo loss of a molecule halogen to give allenes in good

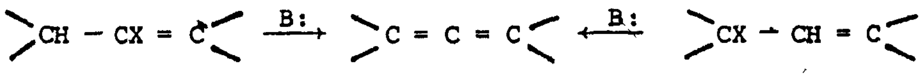
$$RR'CX - CX = CH_2 \xrightarrow[-X_2]{} RR'C = C = CH_2$$

yields[49,50]. The method used most often for allene formation involves the conversion of an alkene to allene via a dihalocyclopropane. Dichloro or dibromocarbene is added across the double bond to give the



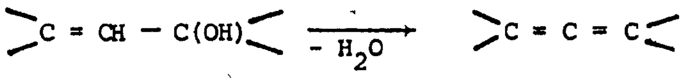
dihalocyclopropane. Treatment of this by organolithium reagents results in the loss of X_2 and the rearrangement to allene[49,50]. The yields are excellent in this method and the reactions are quite easily carried out. The drawbacks are that (i) other double bonds elsewhere in the starting olefinic molecule may interfere with the reaction, and (ii) due to the fact that strong base is employed, isomerization to acetylenic compounds commonly occurs[49,50].

Dehydrohalogenation, as in alkene formation, is also utilized for allene synthesis. As was already mentioned however, since base is



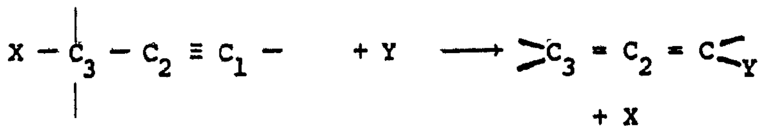
employed isomerization of the allene product may occur if this method is used[49,50].

Dehydration of α,β-unsaturated alcohols has a very limited use in the synthesis of allenes. The product normally is the



conjugated diene, except in cases where it is forced to give allene[49,50].

An alternative method of allene formation which can be employed is that of propargyl rearrangement. The first type of rearrangement

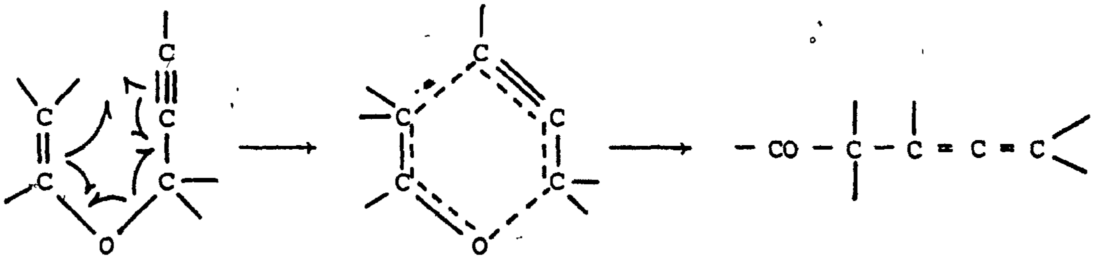


$$X - C_3 - C_2 \equiv C_1 - \quad + Y \longrightarrow {>}C_3 = C_2 = C{<}_{Y} \quad + X$$

is prototropic (i.e., X=Y=H). Here, base is employed to effect the rearrangement under controlled conditions. This reaction cannot be employed for terminal allenes due to polymerization in most cases[49,50].

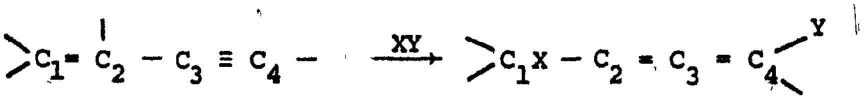
Anionotropic rearrangements also occur, normally to generate α-haloallenes (X=Y=anion)[49,50]. If the incoming anion is different (X≠Y), then the rearrangement can be considered a displacement[49,50]. The leaving group in this reaction is normally a halide or hydroxide, and the entering anion either hydride, halide, or a carbanion, although other groups have been used[49,50].

Intramolecular rearrangements also can be classified according to this set of reactions. The Claisen rearrangement of propargyl vinyl ethers is such a process[49,50]. These are normally thermal reactions



which are carried out at 140-250°C.

An alternative method of allene synthesis is via addition to vinylacetylenes. This is accomplished by 1,4-addition across the



$$>C_1=\overset{|}{C_2}-C_3\equiv C_4- \xrightarrow{XY} >C_1X-C_2=C_3=C_4\overset{Y}{<}$$

15

conjugated system of the 1,3-alkenyne system (15). However, normally 1,2- and 3,4-additions accompany this 1,4-addition and mixtures of isomers result.

The Wittig synthesis of olefins has also been extended to allenes.

$$R_2C = C = PPh_3 + R'_2C = O \longrightarrow R_2C = C = CR'_2$$

$$\geqslant P = CR_2 + {>}C = C = O \longrightarrow {>}C = C = CR_2$$

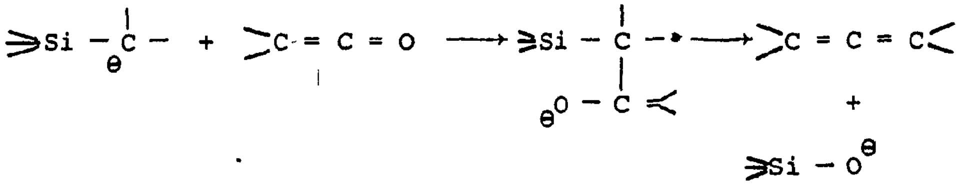
$$Ph_3P = CMeCO_2Et + C_5H_{11}CH_2COCl \longrightarrow C_5H_{11}CH = C = CMeCO_2Et$$

A number of pathways exist to effect this conversion, starting from ketones[24], ketenes[51] or acylhalides[52]. Wadsworth and Emmons have demonstrated that phosphonate carbanions react with ketenes to give allenes[10].

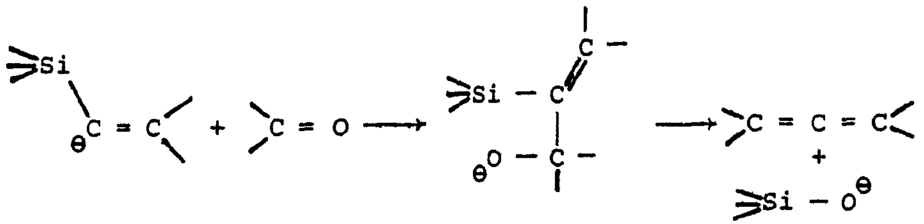
(b) Allene Synthesis Using The Silicon Method

The last methods of allene synthesis mentioned dealt with the Wittig reaction or its modifications. Peterson's olefination reaction has been shown to be an alternative method of alkene synthesis to the Wittig method. It is thus of interest to extend this silicon method to the allene systems as well.

Two approaches exist for this problem. The first is to employ, as the Wittig reaction had[51], ketenes in place of ketones or

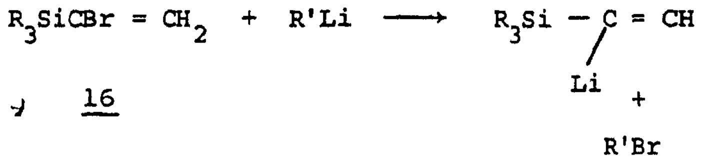


aldehydes in the reaction. However, this method is unattractive due to the general unavailability of the ketenes and their instability. The second approach is to employ a vinyl carbanion alpha to silicon in the reaction and use ketones or aldehydes as the precursors.



The Triphenylsilyl Adducts

Although, as was mentioned in Chapter I, vinyl cabanions alpha to silicon had not been employed in the Peterson olefination reactions,this was not due to their unavailability. Both Brook[28,53] as well as Seebach[54] have shown that vinyl carbanions alpha to silicon could readily be generated via a metal-halogen exchange reaction between alpha-bromovinylsilanes (16) and alkyllithiums.



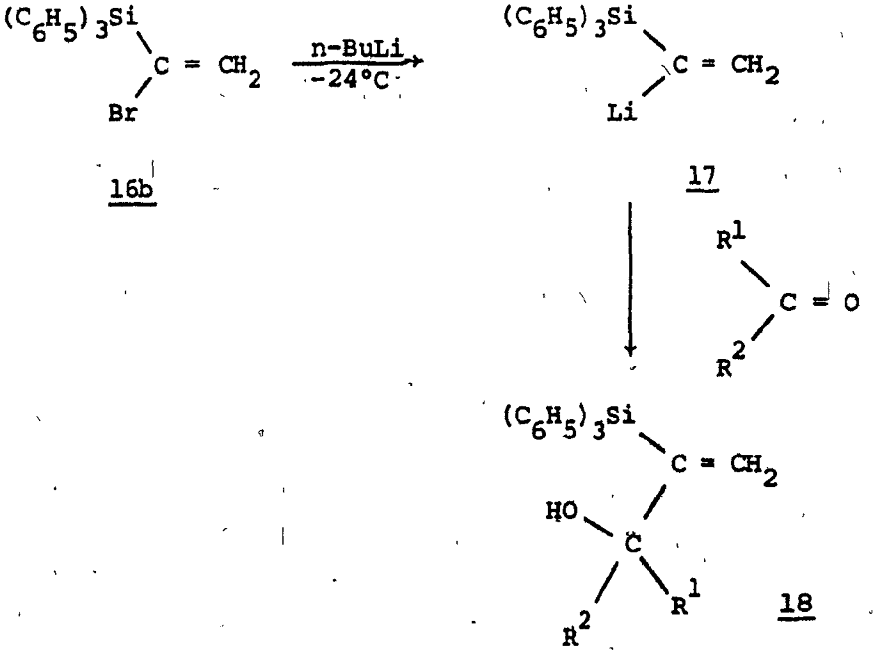
$$R_3SiCBr = CH_2 + R'Li \longrightarrow R_3Si - C(Li) = CH + R'Br$$

16

a) R = Me, R' = t - Bu (-78°C)

b) R = C_6H_5, R' = n - Bu (-24°C)

The starting alpha-bromovinylsilanes (16) were readily available from published procedures. In the case of alpha-bromovinyltriphenylsilane (16b), vinyltriphenylsilane is first prepared by the reaction of phenylmagnesium bromide with vinyltrichlorosilane[55]. Bromination of triphenylvinylsilane under a sunlamp, followed by dehydrobromination[28] in refluxing pyridine, afforded in high yield (75%) alpha-bromovinyltriphenylsilane. Treatment of alpha-bromovinyltriphenylsilane with n-BuLi in diethyl ether at -24°C for one-and-a-half hours gives alpha-lithiovinyltriphenylsilane (17)[28]. The vinylcarbanion reacted readily with a wide variety of carbonyl compounds to give in good yields the beta-hydroxysilanes (18) (Table II).



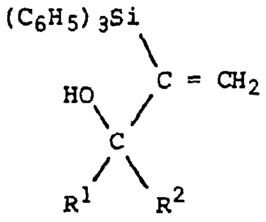
16b

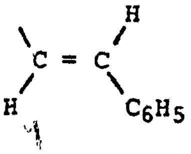
17

18

TABLE II

Synthesis of 18



	R^1	R^2	Yield	m.p.
a	H	C_6H_5	75	84-85°
b	C_6H_5	C_6H_5	80	108.5-109.5°
c	H	n-$C_{10}H_{21}$	~75^a	-
d	CH_3	$-(CH_2)_2CH = C(CH_3)_2$	~75^a	-
e	cyclo ——	C_5H_{10}	~75^a	-
f	H		~80^a	-
g	H	CH_3	~75^a	-
h	H	H	65^a	-

a) crude yield of oil

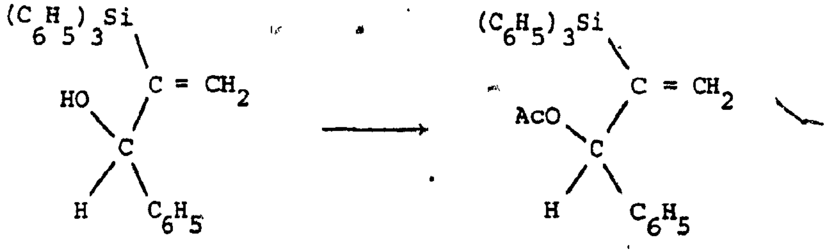
The reaction of the vinyl carbanion with the carbonyl compounds is, in general, quite clean; however, complications could arise. After the addition of the carbonyl compound to the carbanion, the mixture should be stirred from 5 - 8 hours at -24°C. Otherwise, in cases where the mixture was allowed to warm up quickly (within one hour), an unwanted side product arose. The side product appeared to be the result of the decomposition of the vinyl carbanion (17). The exact structure of this product was not established but it did appear to be a dimer with m.p. ~200°C. Little, if any, of this product resulted if the reaction mixture is allowed to cool for an extended period and much higher yields of beta-hydroxysilanes (18) were obtained. The same observation, decomposition of the carbanion, was noted on preparing the carbanion by Brook's method[53].

A further complication arises in this reaction when the ketones used are easily enolizable, such as examples <u>18d</u> and <u>e</u>, Table II. In these cases the reaction is complicated by proton transfer reactions between the carbonyl and the carbanion. However, this is a minor factor and can be almost completely eliminated by using shorter cooling times after addition of the carbonyl compound. In these cases the decomposition of the vinyl carbanion (17) does not occur to any appreciable extent and the yield of beta-hydroxyvinylsilane (18) is good.

Attempted Elimination

In view of the propensity of beta-functionalized organosilicon compounds to undergo elimination to give alkenes[56,57], it was thought that these beta-hydroxyvinylsilanes (18) should lead to allenes with little difficulty. Surprisingly though this was not the case.

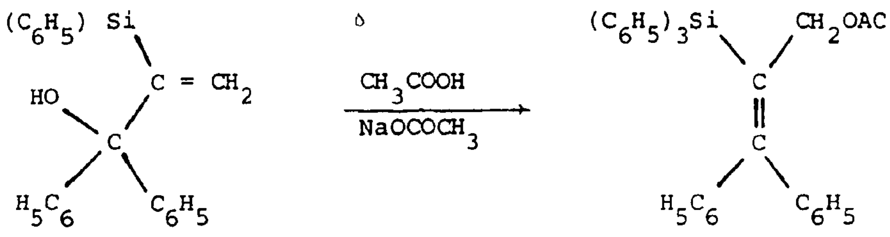
The methods utilized initially by Peterson[25] to effect elimination of beta-hydroxysilanes was to treat them with either dilute acid or base. However, the beta-hydroxyvinylsilanes (18) were found to be quite resistant to both. The compound 18a when treated with either dilute acid, HCl or H_2SO_4[58], or sodium hydride[27], was recovered unchanged from the reaction mixture on work-up. An alternative method of effecting elimination in beta-hydroxysilanes was to go through an acetate intermediate[27,58]. The formation of the acetate could be accomplished via a number of routes. Treatment of the beta-hydroxyvinylsilane 18a anion with acetyl chloride gave the acetate 19a in quantitative yield. The beta-hydroxyvinylsilane 18a itself, when treated with acetic acid/sodium acetate or acetic anhydride/pyridine, was converted, in quantitative yield, to the acetate 19a. If, however,



18a

19a

the beta-hydroxyvinylsilane <u>18b</u> is employed in these acetylations, a rearranged acetate <u>19b</u> results.

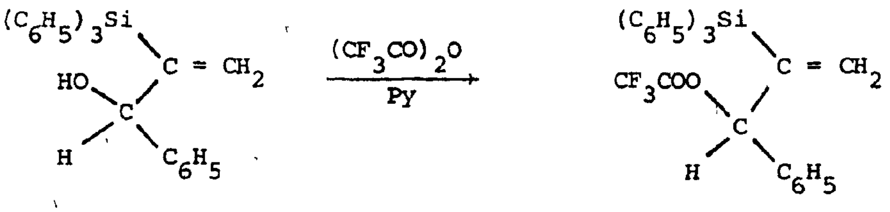


<u>18b</u>

<u>19b</u>

The acetates <u>19</u> were found to be unusually stable and did not undergo elimination to give allene even on heating to 200°C or on dilute acid treatment. One modification which can be attempted is to introduce a better leaving group, beta to silicon. To investigate this possibility a trifluoroacetate functionality seemed to be appropriate. The trifluoroacetate, being a better leaving group than the acetate, might facilitate the allene formation.

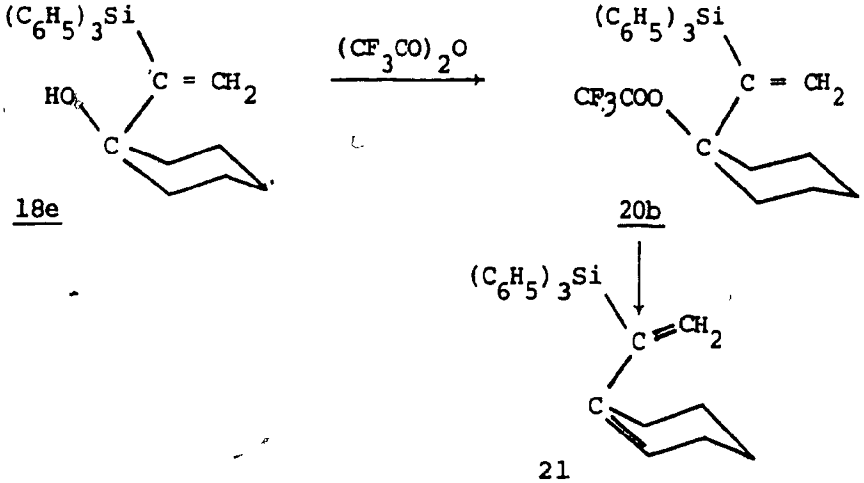
The trifluoroacetate <u>20a</u> was formed, in quantitative yield, by treatment of the beta-hydroxyvinylsilane (18a) with trifluoroacetic anhydride/pyridine. Again, however, no allene formation was observed



<u>18a</u>

<u>20a</u>

on heating or dilute acid treatment. The trifluoroacetate (21a) does, however, hydrolyse quite readily, giving back the starting beta-hydroxyvinylsilane (18a). The trifluoroacetates, in some cases <u>20b</u>, undergo elimination of trifluoroacetic acid spontaneously at room temperature to give a diene <u>21</u>. This result is identical to the findings of Carey[59]. Carey found that esters of beta-hydroxysilanes

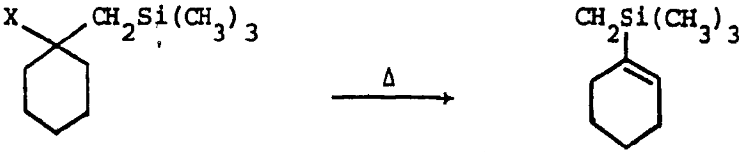


<u>18e</u>

<u>20b</u>

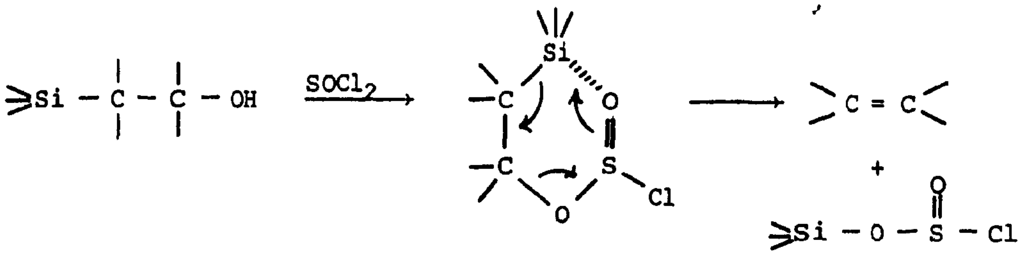
<u>21</u>

eliminate the acid if a beta-hydrogen is available.



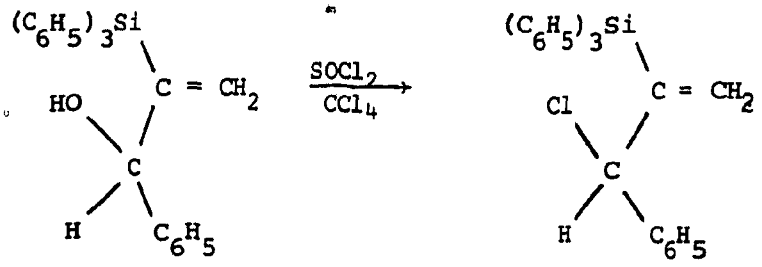
X = CO(O)NHPh

An alternative method for effecting the elimination of silanol from beta-hydroxysilanes has been by the use of thionyl chloride[27]. A six-membered ring transition state 22 is postulated to be in operation.



22

Treatment of the beta-hydroxyvinylsilane (18a) with thionyl chloride in carbon tetrachloride gave the corresponding chloride 23 in quantitative yield. The chloride formed in this reaction was found

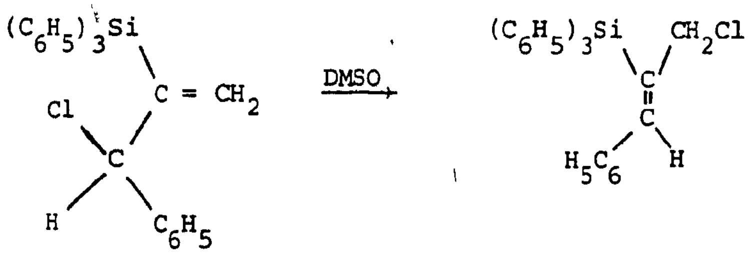


18a

23

to be resistant to elimination, as were the alcohols and esters. Heating to 175°C or treatment with alcoholic silver nitrate gave no allene. This particular isomer of the chloride 23 however, was found to be unstable.

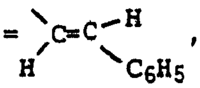
On dissolving in polar solvent such as dimethyl sulfoxide, an allylic rearrangement occurs (See Chapter IV).



23 24a

Investigation of other beta-hydroxyvinylsilanes (18b,c,f) in reaction with thionyl chloride showed that 18a is the only case which gives un-rearranged chloride 23, which can be isolated and characterized. In all other cases a mixture of both rearranged 24 and un-rearranged chlorides resulted in the reaction in CCl_4. In all cases the predominant product was the rearranged chloride 24. If instead of a non-polar solvent such as CCl_4, a more polar solvent is employed, for example diethyl ether, only rearranged chloride 24 results when a dilute solution is used (1 gram (18) in 25 ml ether). The mechanistic aspects of this

18 24

a) $R' = C_6H_5$, $R'' = H$
b) $R' = R'' = C_6H_5$
c) $R' = n\text{-}C_{10}H_{21}$, $R'' = H$
f) R' = , R" = H

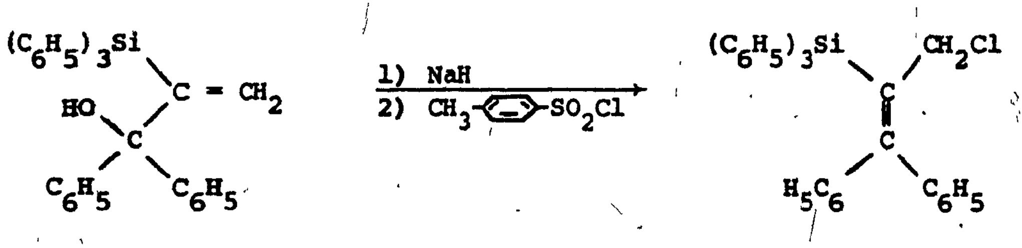
reaction and the stereochemistry of the products obtained will be discussed in Chapter IV of this thesis.

The chlorination reaction was found to be applicable only to beta-hydroxyvinylsilanes derived from aldehydes or ketones without β-hydrogens. No chloride resulted on chlorination of beta-hydroxyvinylsilane derived from aliphatic ketones. Reaction did occur; however, the product was a diene formed by elimination of HCl, similar to the trifluoroacetate case (20b-21).

A number of other methods were attempted to promote elimination of silanol from the beta-hydroxyvinylsilanes (18). Treatment of the beta-hydroxyvinylsilanes (18a and b) with boron trifluoride etherate in benzene gave a new product but no sign of allene. The product of this reaction was not identified.

Treatment of 18a with phosphorus pentafluoride again gave no trace of allene. The product of this reaction, from examination of the infrared spectrum, appeared to be identical to that obtained from the boron trifluoride etherate reaction.

The introduction of a para-toluenesulfonate group beta to the silicon atom might be an effective method of effecting elimination. However, when the anion of 18b was treated with para-toluenesulfonyl chloride the expected sulfonate ester did not arise. Instead, the product was identical to that formed from the reaction of 18b with thiony chloride (24b).



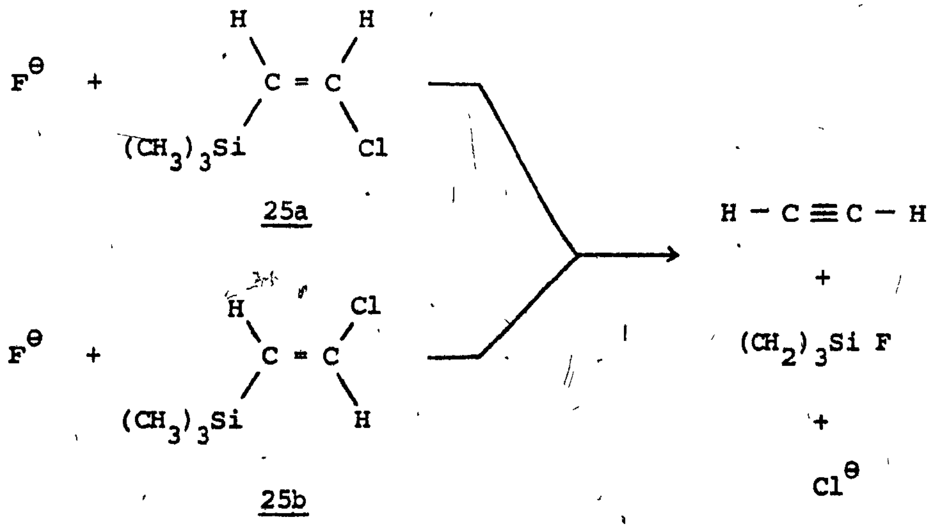
18b

24b

The Fluoride Ion Promoted Elimination

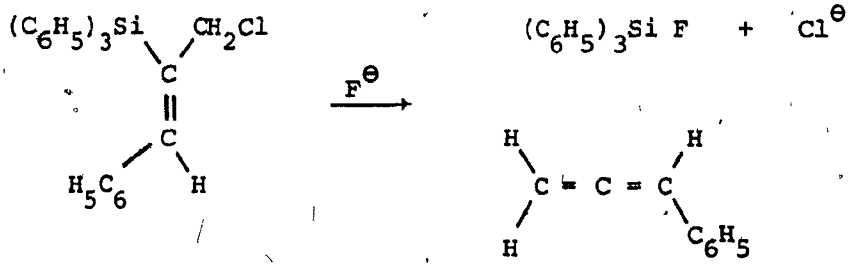
The extension of the Peterson olefination reaction to allenes thus seems to have come to an impasse. All conventional methods of effecting elimination of beta-hydroxysilanes failed to generate the allenes from the beta-hydroxyvinylsilanes (18). The beta-hydroxyvinylsilanes (18) appear to be much more resistant to elimination than the corresponding saturated system. Indeed, cleavage of silicon-vinyl carbon bonds is generally rare[57]. The product allene, being a strained molecule, presumably requires more energy for its formation.

In the course of searching for a method of effecting elimination in these beta-functionalized unsaturated silanes, a report appeared in the literature on the elimination of $(CH_3)_3SiCl$ from a beta-chlorosilane (25) with fluoride ion[60]. This approach appeared to provide a possible solution to the problem at hand.



In the elimination process the driving force of this reaction is presumably the formation of the silicon-fluoride bond. It is recognized that the bond energy of Si-F bond is higher than that of the Si-O bond[61]. The additional energy provided might be sufficient to effect the formation of allene.

To test this possibility the beta-chlorovinylsilane 24a derived from 18a was dissolved in DMSO-d_6 and anhydrous potassium fluoride added. The reaction was monitored by pmr. Over a period of ten hours, a slow change in the spectrum occurred. The singlet of the methylene protons ($-CH_2Cl$) slowly disappeared and a new set of doublets and triplets appeared. These new peaks, when compared to the spectrum of an authentic sample of phenylallene, proved to be identical. On work-up in ether and water, phenylallene was isolated in quantitative yield, based on the chloride 24a.

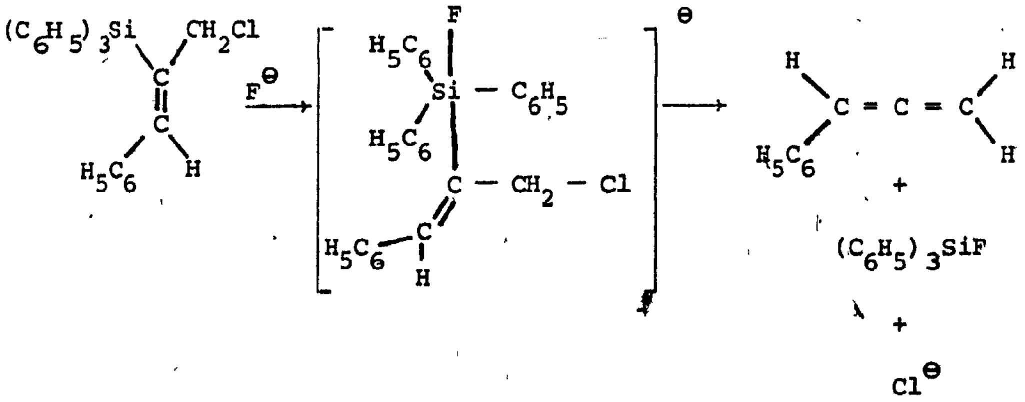


This, then, appeared to be a solution to the problem of effecting elimination of the beta-hydroxyvinylsilanes (18) to give allene. However, there was one drawback to this reaction as it now stood - that was the fairly long reaction time (10 hours). Although the conditions were milder than used in most other methods of allene synthesis[49,50], the time required to effect complete reaction was quite long. Allenes dimerize quite readily and therefore this long reaction time might prove to be a problem in the synthesis of highly reactive allenes.

The slowness of the reaction is due mainly to the low solubility of KF in DMSO (8 mg/100 g DMSO)[60]. To overcome this problem a more soluble source of fluoride ion was necessary. A solution to this problem was to employ tetraethylammonium fluoride in either DMSO or CH_3CN[62]. This reagent dissolves readily in either solvent. Thus, when the beta-chlorovinylsilane 24a was dissolved in either DMSO or CH_3CN and anhydrous Et_4NF added, the formation of allene was complete within one hour.

Other fluorides also gave the same product. For example, both cesium and tetramethylammonium fluoride effected the elimination; however, reaction times in either case were longer than with Et_4NF but shorter than with KF.

The mechanism of this reaction is thought to occur via attack of the fluoride ion on silicon to form the penta-coordinate intermediate 26 which subsequently eliminates $(CH_3)_3SiF$ and $Cl^{\ominus}$ to give allene[68,69].



Although triphenylfluorosilane is produced according to this mechanism, none is isolated on work-up. This is believed to be due to its hydrolysis in water, during work-up, giving a mixture of triphenylsilanol and hexaphenyldisiloxane which have indeed been isolated[63].

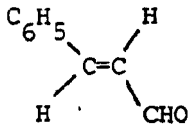
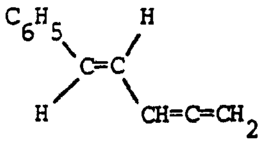
The generality of this reaction sequence can be shown in that a number of carbonyl compounds can be converted to the terminal allenes (Table III).

The isolated yields reported are lower than the crude yield, presumably due to loss in the purification step of the reaction. Allenes on heating are known to dimerize and polymerize quite readily[49,50], therefore loss due to heating on distillation of the allene is expected. Since both the chlorination of the beta-hydroxyvinylsilane and the subsequent elimination of triphenylchlorosilane were found to proceed in quantitative yield, the crude overall yield of allene should be, and indeed was found to be identical to the yield of the first step of the sequence, the reaction of the carbonyl with alpha-lithiovinyltriphenylsilane (75-80%)(Table II).

The advantage of this method of synthesis of allenes over the other methods available[49,50] lies in the fact that the starting material, the carbonyl compounds, is readily available and the conditions employed to generate allene are much milder than those normally required to synthesize allenes. The other methods available for the synthesis of allene, discussed at the beginning of this chapter, usually suffer in that a strong base must be employed to effect the synthesis of allene. In the

TABLE III

Preparation of 1,2-Alkadienes

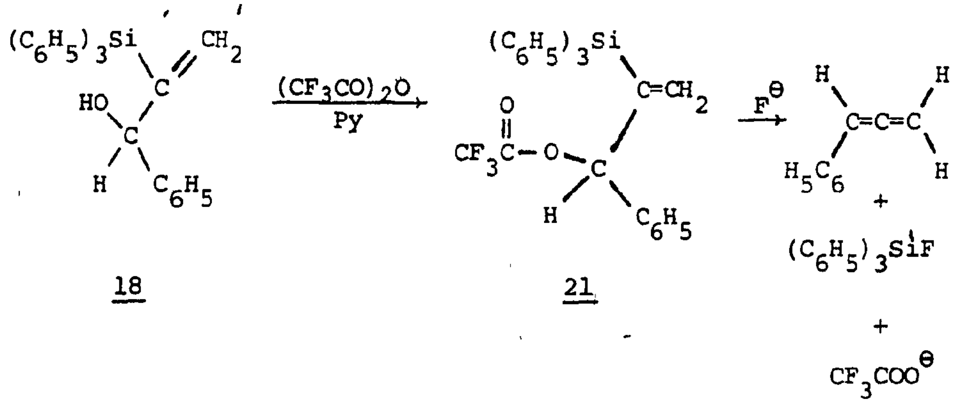
	Starting Carbonyl	Product	b.p.	Isolated Yield %
a)	C_6H_5CHO	$C_6H_5CH{=}C{=}CH_2$	83-85/24 mm[62]	59
b)	$(C_6H_5)_2CO$	$(C_6H_5)_2C{=}C{=}CH_2$	100°/.025 mm[63]	45[a]
c)	$CH_3(CH_2)_9CHO$	$n\text{-}C_{10}H_{21}CH{=}C{=}CH_2$	63-4/.1 mm	44
d)			70-75/.075 mm	35

a) Purified by preparative layer chromatography on silica gel.

presence of base, allenes isomerize to acetylenes. The most widely utilized method for synthesizing allenes, the reaction of a dihalocyclopropane with alkyl lithium, results in acetylenic impurities in the product. Such was indeed observed when an authentic sample of phenylallene was synthesized[64,65]. No such problem exists by utilizing the silicon method of synthesizing allenes, since strong base is not employed in the final step.

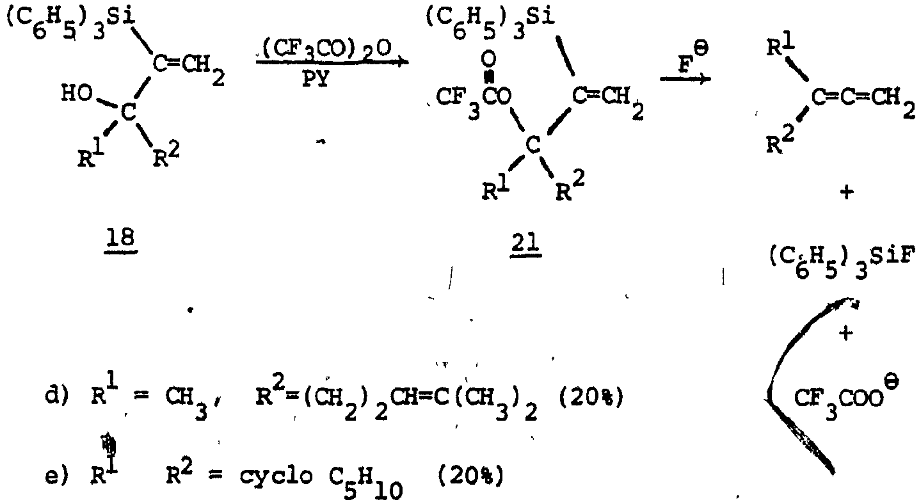
The silicon method of allene synthesis has the advantage over most of the other methods[49,50] in that conjugated allenes can be synthesized and can be obtained pure, with no isomerization (e.g., item d, Table III). Normally, if a conjugated allene is to be synthesized, it is obtained via isomerization of a conjugated acetylene and mixtures of isomers result[49,50]. The addition of dihalocarbene to an alkene, followed by carbene generation to give allene, cannot be employed if a second carbon-carbon double bond is present.

The allene synthesis reaction using organosilicon intermediates, however, does suffer two limitations. The first is that only terminal allenes have so far been synthesized. However, non-terminal allenes could presumably be synthesized if substituted alpha-bromovinylsilanes were employed. A more serious shortcoming of the reaction at the moment is that only aldehydes or aromatic ketones can be converted to allenes. As the reaction stands, the beta-hydroxyvinylsilane (18) must first be converted to the beta-chlorovinylsilanes (24). This, however, as was mentioned previously, cannot be accomplished for beta-hydroxyvinylsilanes (18), where the alcohol is tertiary and possesses a β-hydrogen. This limitation, however, can be overcome. If instead of the chloride (24), the trifluoroacetate (21) is used in the reaction, it is found that elimination occurs just as well, with Et$_4$NF, to give allene in quantitative yield within one hour.



18 21

This, then, gives an alternative route to allene from the beta-hydroxyvinylsilanes. Using this modification, it is possible to extend the allene synthesis to aliphatic ketones. This reaction,



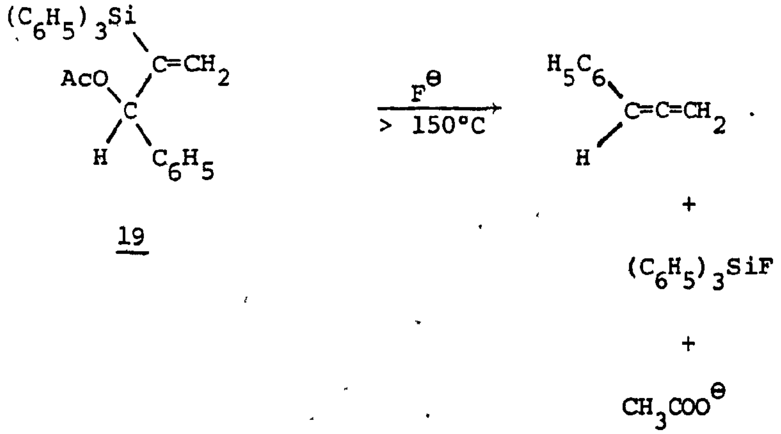
18 21

d) $R^1 = CH_3$, $R^2 = (CH_2)_2CH=C(CH_3)_2$ (20%)

e) R^1 R^2 = cyclo C_5H_{10} (20%)

however, is complicated by the fact that the esters (21) undergo loss of trifluoroacetic acid to give silyldiene. Due to this, yields of allene are low (~20%). Using anhydrous Et_4NF and carrying out the elimination as soon as possible after the formation of the ester (21), it should be possible to improve the yield.

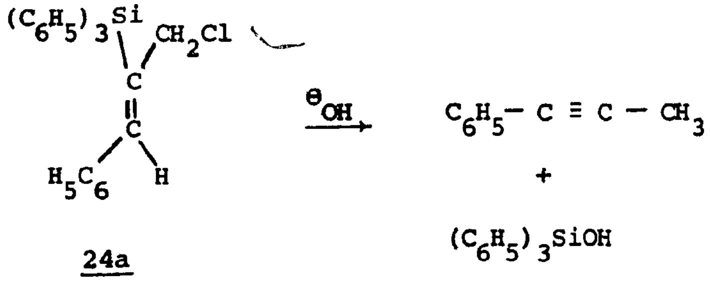
Since the trifluoroacetate (21) undergoes elimination in the presence of fluoride ion to give allene, the acetate (19) itself might also give allene. However, unlike the trifluoroacetate <u>21a</u> the acetate <u>19a</u> was quite stable in DMSO in the presence of fluoride. Only on heating to 150°C did elimination occur to give allene. This could not be used as an alternative method of generating allene however, due to the high temperature used. Loss of product due to dimerization and polymerization would cause low yields. The difference in reactivity



can be attributed to the leaving group ability of the two esters.

The trifluoroacetate is the more labile group and has been used extensively as a leaving group in many reactions.

The beta-chlorovinylsilane 24a also undergoes elimination of triphenylchlorosilane, on treatment with hydroxide. The use of alkoxide to effect cleavage of silicon-carbon bonds with beta-functionalities is well documented[56]. However, the product of this reaction was not allene but instead 1-phenylpropyne. This is readily understood since allenes


24a

are known to isomerize to acetylenes in the presence of base[49,50].

The cleavage of the silicon-carbon bond by fluoride ion is postulated to be due to the high bond energy associated with the formation of the silicon-fluorine bond. If this is so, then no other halide ion should cause elimination in the beta-chlorovinylsilanes (18). Treatment of the chloride 24a with tetraalkylammonium chloride, bromide or iodide, even for prolonged reaction times (5 days), gave no allene and the starting materials were recovered in quantitative yield. Thus, fluoride ion is unique in its ability to effect elimination in these systems.*

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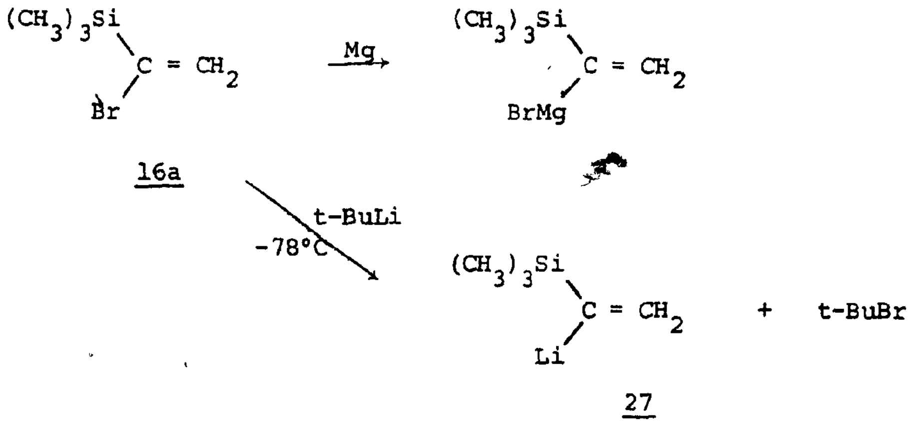
* This work has been published:
T.H. Chan and W. Mychajlowskij, Tetrahedron Letters, 171 (1974).

Trimethylsilyl Adducts

During the course of this work, a number of reports appeared on the synthesis of beta-hydroxyunsaturated silanes[54,66]. The only difference in the products which were reported in these papers and the results given in this thesis is that instead of triphenylsilyl derivatives these groups had employed trialkylsilyl derivatives. It was of interest to extend the allene synthesis reaction to the trialkylsilyl series for a number of reasons. When the allene synthesis is carried out on the triphenylsilyl adducts (18), one of the problems lies in the separation of the allene from the triphenylsilanol. If the trimethylsilyl adducts were employed, the trimethylsilyl fluoride produced is a gas and thus only allene should be left on work-up.

Alpha-bromovinyltrimethylsilane[67] 16a can readily be converted to the vinyl carbanion via either treatment with magnesium to give the Grignard, or with t-BuLi at -78°C to give the lithio carbanion 27[28,53,54].



The metal-halogen exchange reaction with t-BuLi at -78°C was found to be the method of choice. This carbanion 27 reacted with a wide variety of carbonyl compounds to give beta-hydroxyvinyltrimethylsilanes 28 in good yields (Table IV).

The beta-hydroxyvinylsilanes (28a,b,c) can then be converted, in quantitative yield, to the chlorides 29 by treatment with thionyl chloride. The details of this reaction, the allylic rearrangement and its stereochemical consequences, will be discussed later. Elimination of trimethylchlorosilane to give allene could be accomplished by the use of Et_4NF. Allenes were obtained in yields very similar to those obtained from the triphenylsilyl adducts (Table V).

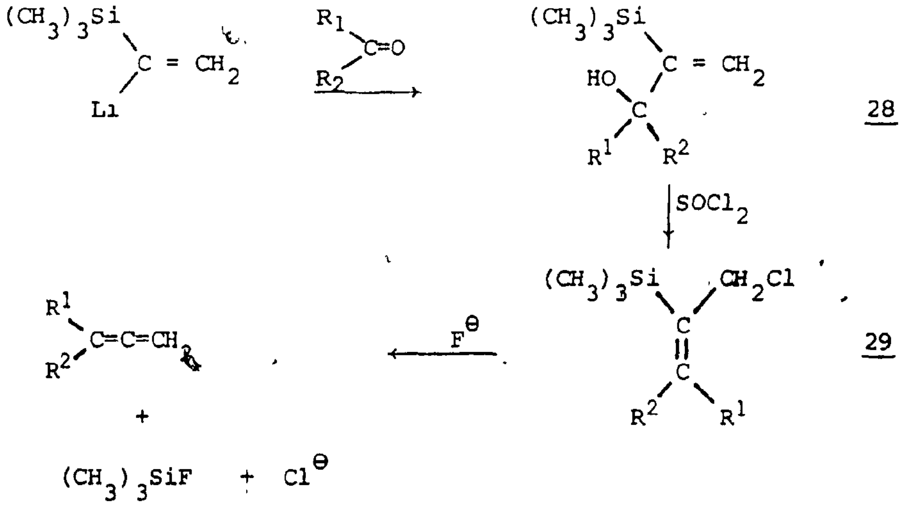
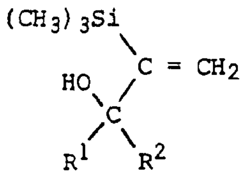
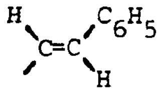


TABLE IV

Preparation of



(28)

	R^1	R^2	Yield %	b.p. (°C/mHg)
a	H	C_6H_5	80	82-84/0.9
b	C_6H_5	C_6H_5	80	(a)
c	H	n-$C_{10}H_{21}$	75	118-9/0.03
d	H	cyclo C_6H_{11}	75	64-66/0.025
e	H	$-CH(CH_3)_2$	76	82-84/16
f	H	H	65	71-73/28
g	CH_3	$-(CH_2)_2CH=C(CH_3)_2$	80	120-122/9
h	cyclo C_5H_{10}		75	(a)
i	H		75	(a)
j	H	CH_3	65	69-71/21
k	H	$C(CH_2)_3$	79	69-71/5

(a) not distilled

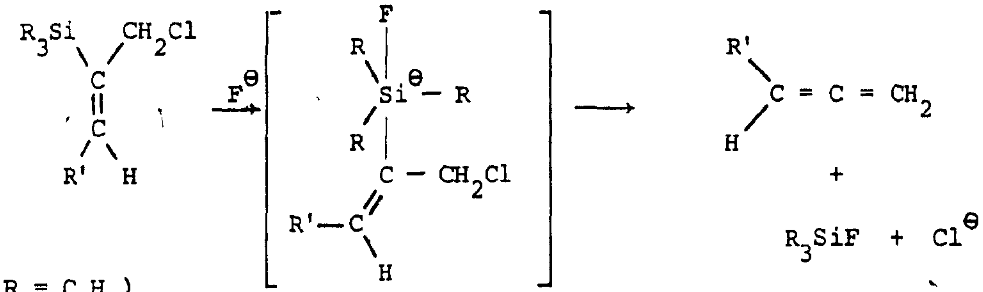
TABLE V

Preparation of 1,2 Alkadienes

	Starting Carbonyl	Product	Yield %(a)
a	C_6H_5CHO	$C_6H_5CH{=}C{=}CH_2$	60
b	$(C_6H_5)_2CO$	$(C_6H_5)_2C{=}C{=}CH_2$	50
c	$CH_3(CH_2)_9CHO$	$n\text{-}C_{10}H_{21}CH{=}C{=}CH_2$	48

(a) distilled

Thus, allene synthesis could be accomplished using the trimethylsilyl adducts. However, a difference does exist. The rates of elimination of $(CH_3)_3SiCl$ and $(C_6H_5)_3SiCl$ are quite different. Under standard conditions, the triphenylsilyl adducts <u>24</u> undergo elimination within one hour, whereas the trimethylsilyl adducts <u>29</u> require five hours for the completion of the reaction if Et_4NF is employed. The difference in reactivity can be explained by taking into account the mechanism of the reaction and the different stereoelectronic effect of the methyl group as opposed to the phenyl. Methyl is considered to be electron-donating and one would therefore expect the silicon of a trimethylsilyl group to be less electrophilic than the silicon of the triphenylsilyl group. If it is assumed that the elimination occurs via the attack of the fluoride ion on the silicon, producing a penta-coordinated intermediate 30 as the rate determining step[68,69], the phenyl groups would stabilize this intermediate much more than the methyl group.



24 (R = C_6H_5)

29 (R = CH_3)

30

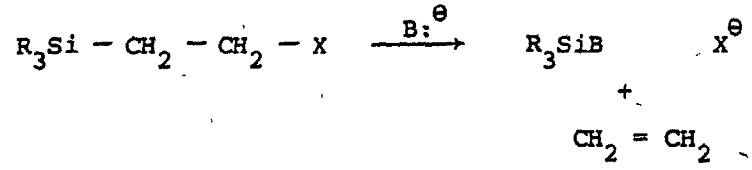
CHAPTER III

CLEAVAGE OF SILICON-CARBON BONDS BY FLUORIDE ION

(a) Nucleophilic Cleavage of Silicon-Carbon Bonds

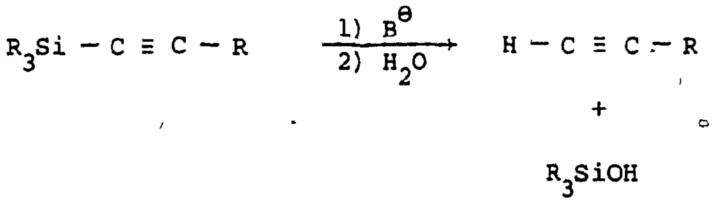
In considering the nucleophilic cleavage of the silicon-carbon bond, an examination of the nature of this bond is warranted. Based strictly on bond energy considerations it is expected that the silicon-carbon bond (78 Kcal/mole)[61] would be almost as stable as a simple carbon-carbon bond (82.6 Kcal/mole)[61]. However, the difference in electronegativities must also be taken into consideration. Silicon is more electropositive than carbon (in Pauling's scale: Si=1.8, C=2.5, H=2.1), the silicon-carbon bond is presumably more ionic (12% ionic character) even than a C-Cl bond (6% ionic character)[61]. This high degree of ionic character in the Si-C bond renders cleavage of it much more facile than cleavage of a C-C bond.

The most common nucleophilic cleavage reaction which occurs on the Si-C bond is by strong base such as hydroxide, amides and alkoxides[57,63]. This cleavage reaction has normally been utilized on beta-functionalized silanes.



$$R_3Si-CH_2-CH_2-X \xrightarrow{B:^{\ominus}} R_3SiB \quad X^{\ominus} + CH_2=CH_2$$

The cleavage of silicon-alkynyl carbon bonds can also be accomplished by a host of nucleophiles including hydroxide[70] as well as fluoride ions[71]. However the corresponding cleavage of silicon-

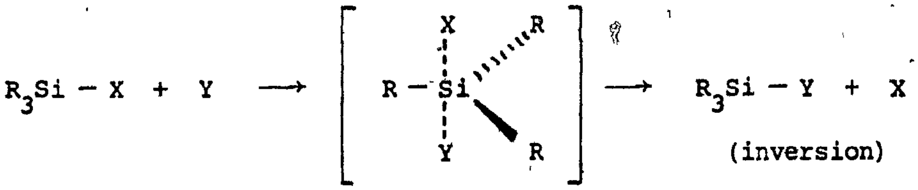


$$R_3Si-C\equiv C-R \xrightarrow[2)\ H_2O]{1)\ B^{\ominus}} H-C\equiv C-R \;+\; R_3SiOH$$

vinyl carbon bonds is extremely rare[57]. For example, vinyltrimethylsilane is stable towards KF in refluxing ethanol[71] and the compound $CH_3CH = CHSiH_3$ is not cleaved by hot aqueous alkali[72].

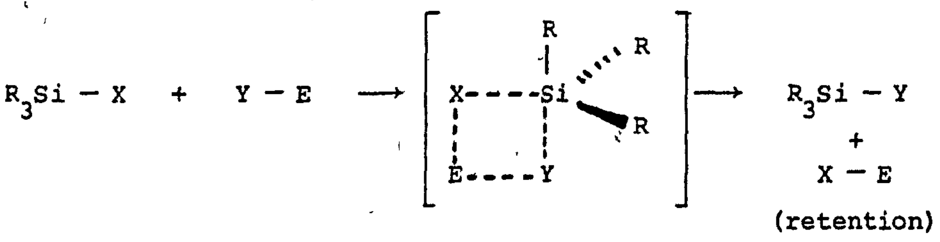
Mechanistic studies of nucleophilic substitution reactions on silicon have been quite extensive, the majority of the studies being those carried out by Sommer and his collaborators[68,69]. Two mechanisms have been proposed for nucleophilic substitution reactions on silicon. They are classified as S_N2-Si and S_Ni-Si.

The S_N2-Si mechanism is similar to its carbon analogue except that here the 3d orbitals of the silicon are believed to participate



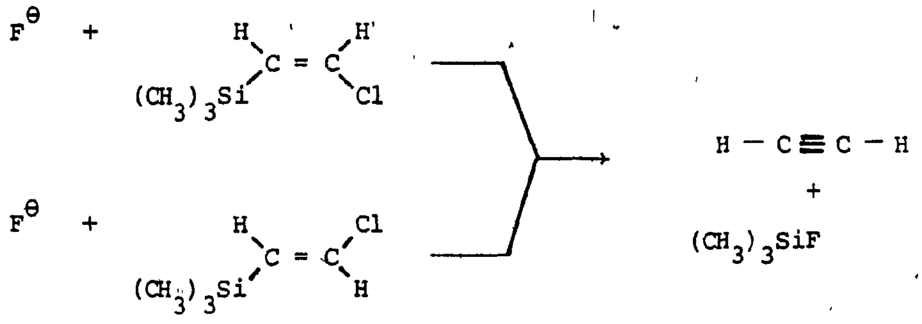
in a significant and special way in forming the pentacovalent transition state or intermediate with the entering nucleophile and the departing leaving group occupying the apical positions. The stereochemical consequence of the S_N2-Si mechanism is an inversion of configuration at silicon.

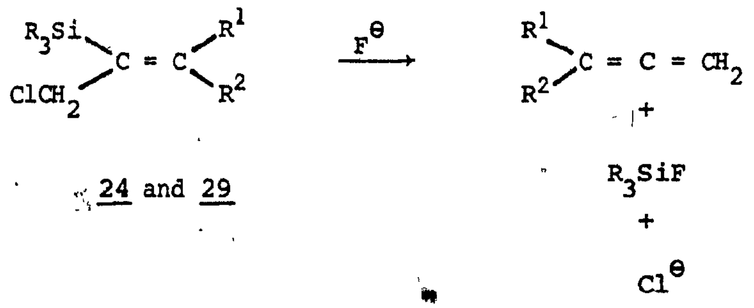
The other mechanism which is involved in some cases is the S_Ni-Si. This involves same side attack rather than backside attack by the nucleophile. Again a pentacovalent transition state or intermediate is postulated, and usually the counter ion, E, coordinates between the entering nucleophile and the leaving group in a cyclic manner. The stereochemical consequence of the S_Ni-Si mechanism is retention of configuration at silicon. The mechanism at work in any particular nucleophilic substitution reaction at silicon is dependent on a number of factors such as the nature of the reagent, the basicity of the leaving group, the polarity of the solvent and the nature of the counter ion.



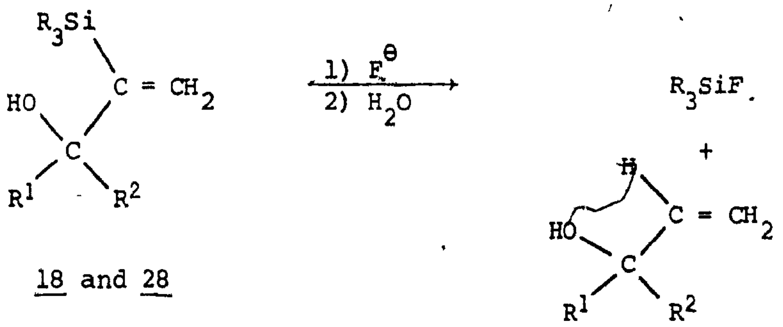
(b) Experimental Observations

Fluoride ion has been found to cleave the silicon-vinyl carbon bond of beta-chlorosilyl compounds to yield acetylenes. Indeed, fluoride ion also cleaves silicon-vinyl carbon bonds of the beta-chlorovinylsilanes (24 and 29) to yield allenes. Similar elimination reactions occur when a trifluoroacetate or acetate functionality replaces the chloro group in the beta position. It seems therefore of interest to us to attempt the reaction of fluoride ion with the beta-hydroxyvinylsilanes (18 and 28) themselves.





On treatment of the compounds 18 or 28 with fluoride ion, an unexpected reaction was observed. Unlike the chlorides 24 and 29 which undergo formation of allene, the beta-hydroxyvinylsilanes (18 and 28) yielded allylic alcohol 31.



18 and 28

18 R = C_6H_5

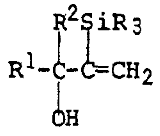
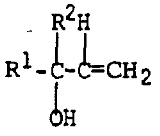
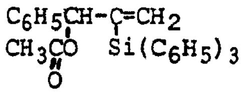
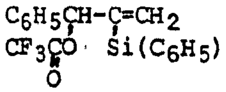
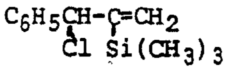
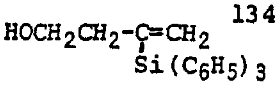
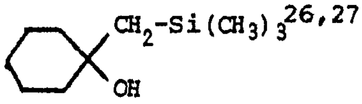
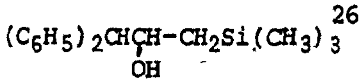
28 R = CH_3

31

The reaction conditions are similar to those used for allene synthesis. Either DMSO or CH_3CN can be employed as solvent, and either Et_4NF, KF, CsF or Me_4NF[26,27] can be utilized as the reagent. In the case of 18, the rate of reaction is approximately the same as that with the beta-chloro derivatives 24. The reaction is usually complete within one hour using Et_4NF in CH_3CN. However, for the beta-hydroxyvinylsilanes 28, more drastic conditions are required. The cleavage occurred only on refluxing the solvent, CH_3CN, to give the allylic alcohols 31. Yields of allylic alcohols 31 appear to be quantitative prior to purification (Table VI).

TABLE VI

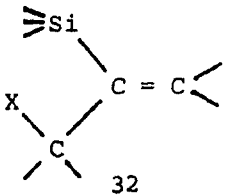
Reaction of Organosilicon Compounds with Fluoride Ion

Starting Material	Reaction conditions reagent/solvent/temp./time	Products (% isolated yield)
 18,28		 31
18a: R=R^1=C_6H_5, R^2=H	Me_4NF/CH_3CN/r.t./2h	31a: R^1=C_6H_5, R^2=H (80)
18b: R^1=R=R^2=C_6H_5	Et_4NF/DMSO/r.t./2h	31b: R^1=R^2=C_6H_5 (65)
18c: R=C_6H_5, R^1=n-$C_{10}H_{21}$ R^2=H	Et_4NF/DMSO/r.t./2h	31c: R^1=n-$C_{10}H_{21}$, R^2=H (68)
28d: R=CH_3, R^1=C_6H_5, R^2=H	Me_4NF/CH_3CN/80°/3h	31a: R^1=C_6H_5, R^2=H (65)
28: R=CH_3, R^1=R^2=H	KF/DMSO/15°/2h	31: R^1=R =H^2(> 90) (a)
28: R=CH_3, R^1=CH_3, R^2=-$(CH_2)_2$-CH=$C(CH_3)_2$	Et_4NF/CH_3CN/80°/2h	31: R^1=CH_3 (52) R^2=-$(CH_2)_2$CH=$C(CH_3)_2$
28: R=CH_3, R^1,R^2=$(CH_2)_5$	Et_4NF/CH_3CN/80°/2h	31: R^1,R^2=$(CH_2)_5$ (69)
19a:  $C_6H_5\underset{\underset{O}{\overset{\|}{CH_3CO}}}{CH}-\underset{Si(C_6H_5)_3}{C}=CH_2$	KF/DMSO/100°/2h	no reaction
	KF/DMSO/150°/2h	$C_6H_5CH=C=CH_2$ (b)
21a:  $C_6H_5\underset{\underset{O}{\overset{\|}{CF_3CO}}}{CH}-\underset{Si(C_6H_5)}{C}=CH_2$	Et_4NF/CH_3CN/r.t/2h	$C_6H_5CH=C=CH_2$ (60)
29c:  $C_6H_5\underset{Cl}{CH}-\underset{Si(CH_3)_3}{C}=CH_2$	KF/DMSO/r.t/10h	$C_6H_5CH=C=CH_2$ (60)
34 :  $HOCH_2CH_2-\underset{Si(C_6H_5)_3}{C}=CH_2$ [134]	KF/DMSO/150°/2h	no reaction
33:  [26,27]	KF/DMSO/120°/2h	no reaction
33a:  $(C_6H_5)_2CH\underset{OH}{CH}-CH_2Si(CH_3)_3$ [26,27]	KF/DMSO/150°/2h	no reaction

(a) Determined by nmr with internal standard.

(b) Yield not determined.

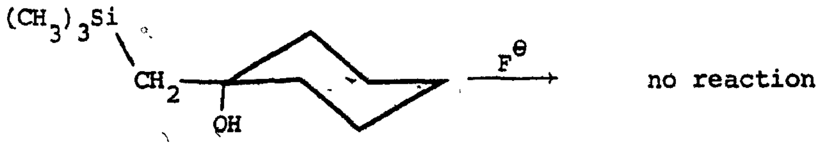
From these results it appears that cleavage of the silicon-vinyl carbon bond occurs when a beta-functionality exists (32). The



32

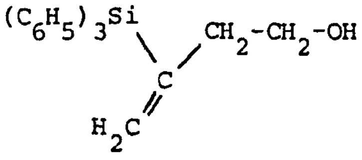
β-functional group can act either as a leaving group (chloride or ester), or as a proton source (hydroxy). Since it is known that fluoride does not effect cleavage in simple vinylsilanes (e.g., trimethylvinylsilane), it is of interest to study the limitations of fluoride ion cleavage reactions and the effect of altering the structural features of the substrate 32.

Obviously, removal of the beta-functionality of 32 causes the cleavage reaction to stop. Both trimethyl and triphenylvinylsilane are quite stable to fluoride ion even at temperatures of 150°C for long periods of time. The starting materials were recovered quantitatively from the reaction mixtures. If, instead of removing the beta-functionality, the double bond is saturated 33, there is again no reaction in the presence



33

of fluoride ion even up to a temperature of 120°C. Retaining the unsaturation but moving the hydroxy group to a gamma position 34, also proved to be a sufficient change to prevent cleavage of the silicon-vinyl carbon bond by fluoride ion.



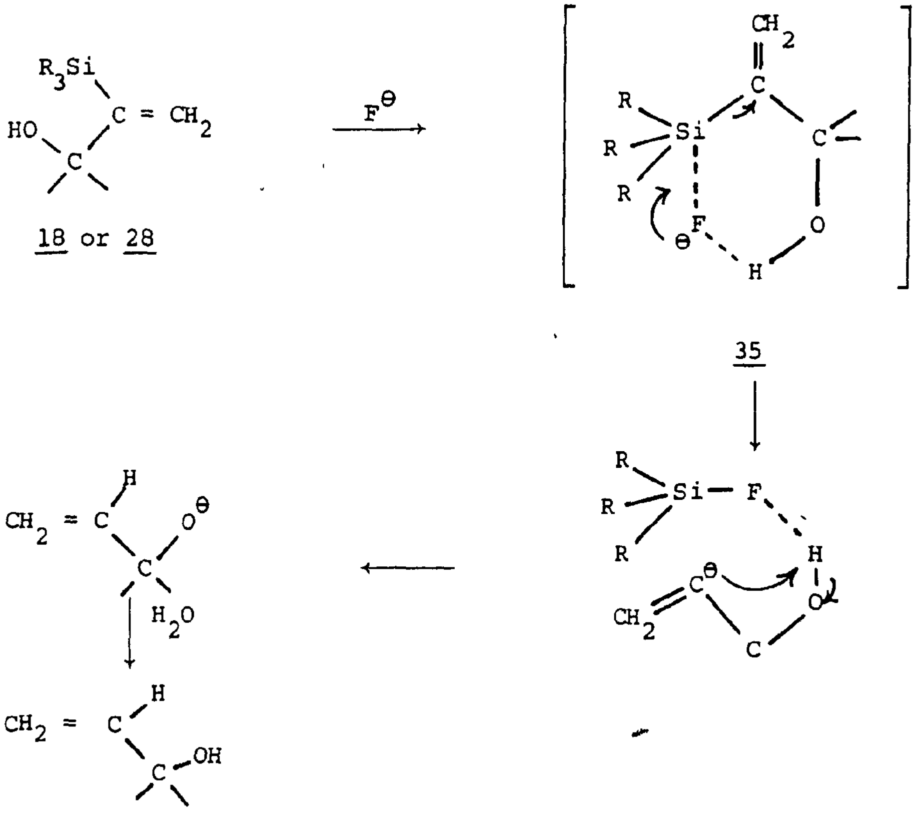
34

Changes in the nature of the functionality have already been demonstrated to alter the course or the rate of reaction, (e.g., X=Cl, $CH_3C(O)O$, $CF_3C(O)O$, OH) (Table VI).

(c) The Beta-Hydroxy Effect

In view of the results which have been obtained, a statement on the mechanism of the cleavage of silicon-carbon bonds by fluoride ion can be made.

It appears, that for the cleavage of the silicon-carbon bond to occur, some specific structural features must exist. At present, the mechanism which appears to be compatible with all the findings is one in which a cyclic transition state 35 is postulated. The occurrence of the cleavage reaction depends then on the cooperative effect 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.



18 or 28

35

31

A combination of all these factors leads to cleavage of the silicon-vinyl carbon bond in the beta-hydroxyvinylsilanes (18 and 28), and the absence of any one of them alters the pathway of the reaction or prevents cleavage completely. The mechanism proposed can be considered as similar to the S_Ni-Si type.*

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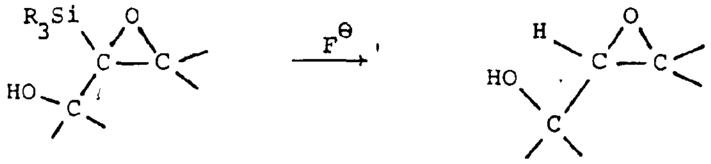
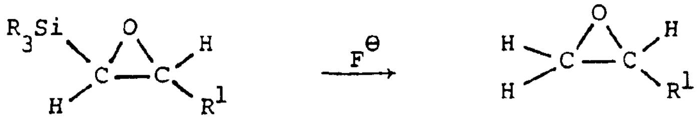
* This work has been published, T.H. Chan and W. Mychajlowskij, Tetrahedron Letters, 3479 (1974).

A recent observation from this laboratory by Chan et al.[73] has found that replacement of the double bond of the substrate 32 by an oxirane does not alter the course of reaction. Indeed the rate of



reaction is greatly increased and occurs even in the absence of the beta-hydroxy group. The difference in reactivity of these systems



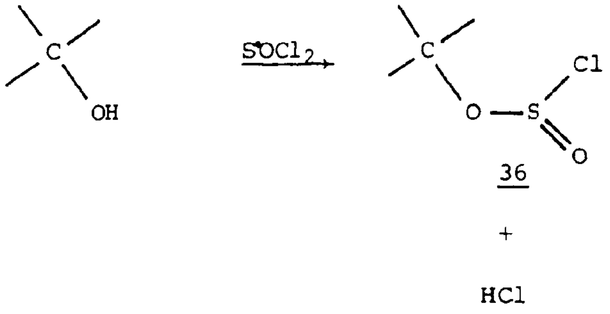
as opposed to the unsaturated system has been attributed to the oxiranyl anion being a better leaving group than the vinyl carbanion.

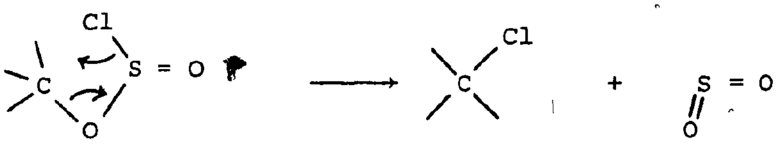
CHAPTER IV

THE STEREOSELECTIVE CONVERSION OF RCHO TO E-RCH=CHCH$_2$Cl

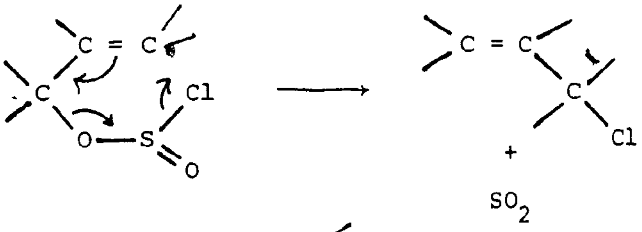
(a) Introduction to Allylic Rearrangement

The reaction of thionyl chloride with allylic alcohols has been well studied[2,74-78]. The chlorination reaction can be generally classified as being a nucleophilic-substitution reaction. The first step of all reactions of an alcohol with thionyl chloride is the formation of an alkylchlorosulfite 36. For most alkylchlorosulfites, they normally undergo an internal-nucleophilic substitution reaction (S$_N$i) to give the alkyl chlorides. In support of this mechanism, the chloride obtained from an optically active alcohol under these conditions



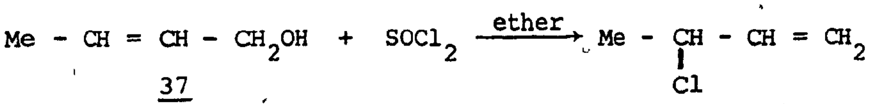


has been found to have the same configuration as the precursor alcohol[2]. However, for allylic chlorosulfites it is possible that the nucleophile will attack the gamma position instead of the alpha position. This has been referred to as the S_Ni' mechanism and, in fact, is a much more favourable reaction pathway.



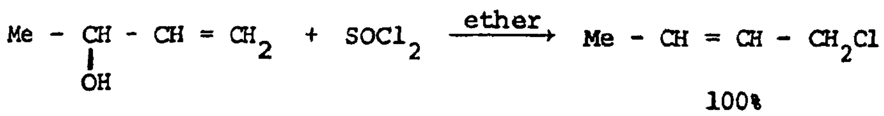
The reaction of thionyl chloride with alcohols produces HCl and this HCl is partially ionized. In the presence of $Cl^{\ominus}$ the chlorosulfites may conceivably react by as many as five mechanisms: S_N1, S_N2, S_N2', S_Ni and S_Ni'. In non-polar solvent the dry HCl produced may remain unionized and the first three mechanisms would then be unimportant in the reaction sequence.

In dry diethyl ether it is expected that the predominant mechanism for the reaction of an allylic alcohol with thionyl chloride would be the S_Ni' mechanism[75,76]. Thus, only rearranged chloride is expected in the reaction. This was indeed the case. When the allylic alcohols 37 and 38 were treated with thionyl chloride in dry diethyl ether



$$\underset{\underline{37}}{Me - CH = CH - CH_2OH} + SOCl_2 \xrightarrow{\text{ether}} Me - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH = CH_2$$

100%

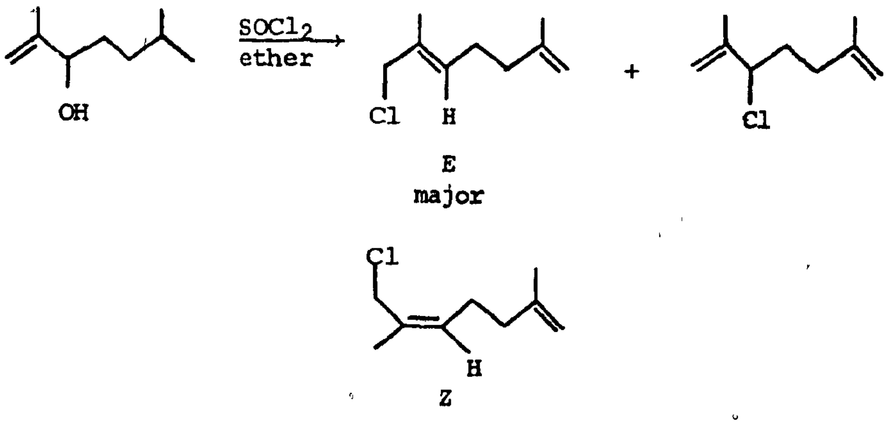


$$\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{Me-CH}}\mathrm{-CH=CH_2} + \mathrm{SOCl_2} \xrightarrow{\text{ether}} \underset{100\%}{\mathrm{Me-CH=CH-CH_2Cl}}$$

38

only rearranged chlorides resulted[78]. Extensive studies on the effect of different solvent systems on the course of reaction showed that dry diethyl ether is the best if the S_Ni' product is desired. For most other solvents, the reaction gives mixtures of direct and allylic substitution products[75,76,78].

A further and very useful feature of the allylic rearrangement is that if geometric isomers were possible in the product one would be formed preferentially. The reaction was stereoselective[76]. It was

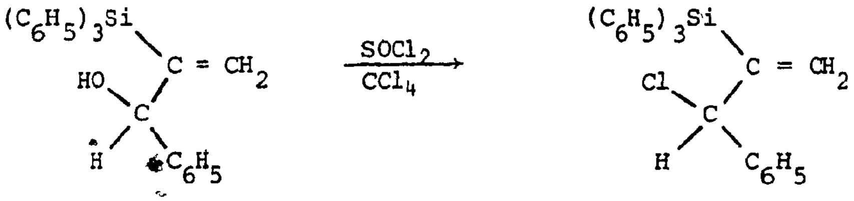


found that for the trisubstituted systems the E isomer was formed predominantly (~ 85-90%) with little, if any, Z isomer and trace amount of the direct substitution product[76].

(b) Allylic Rearrangements Involving a Silicon Atom

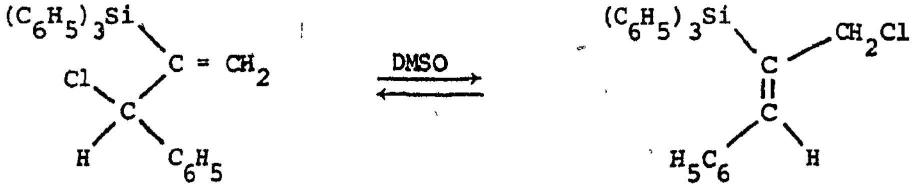
When this information about allylic rearrangement in chlorination of alcohols is taken into consideration it is expected that treatment of the beta-hydroxyvinylsilanes (18 and 28) with thionyl chloride should follow a similar pathway.

Treatment of the beta-hydroxyvinylsilane 18a with thionyl chloride in carbon tetrachloride gave, in quantitative yield, a non-rearranged chloride 23 by an S_Ni mechanism. The product was crystalline and could be recrystallized from ethanol. It gave spectral (ir, pmr, ms) and elemental analysis in compliance with this structure. However, when this chloride 23 was dissolved in dimethyl sulfoxide, an allylic rearrangement occurred giving the chloride 24a. The rearrangement can be



18a

23

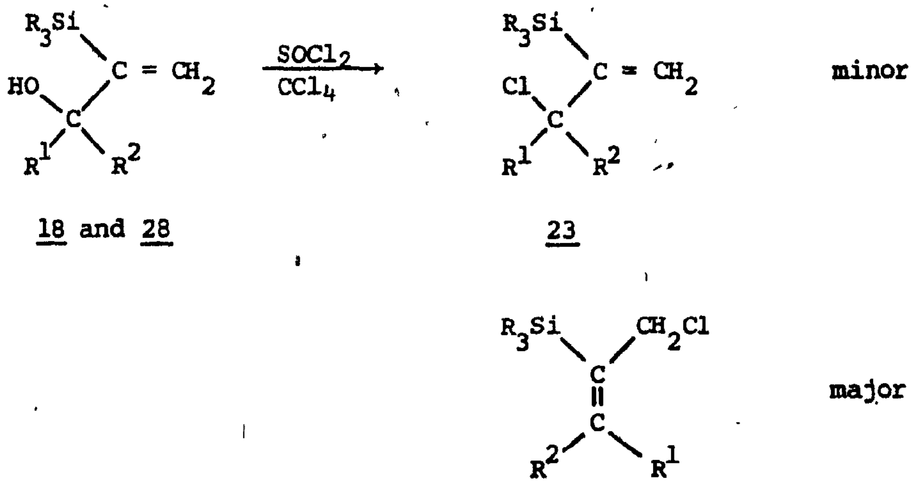


23

24a

readily understood since a more stable product is formed. According to Claisen[79], olefin stability increases with increasing alkyl substitution. Also, it is known that if the double bond in one isomer can be in conjugation with an aromatic ring, then that isomer is more stable and will predominate at equilibrium[80,81]. Therefore, in the equilibrium between <u>23</u> and <u>24a</u> the more stable product <u>24a</u> is formed.

This chemical behaviour is, however, not general. If any other beta-hydroxyvinylsilane (18 or 28) were treated with thionyl chloride in carbon tetrachloride a mixture of rearranged and non-rearranged products result. The major isomers are found to be the



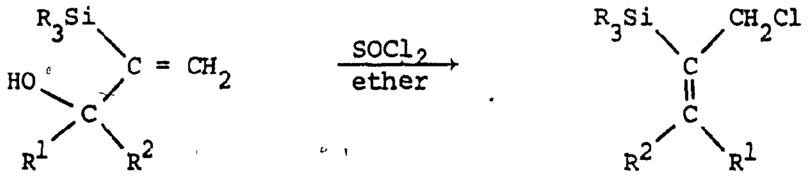
<u>18</u> and <u>28</u>

<u>23</u>

<u>24</u> and <u>29</u>

rearranged chlorides <u>24</u> and <u>29</u> in approximately 70-80%.

When this reaction was carried out in anhydrous diethyl ether, only rearranged chloride (24 and 29) resulted. Yields of the chlorides were very good (see Table VII).

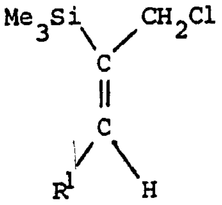


18 and 28 → 24 and 29

We have already mentioned that when the product can exhibit geometric isomers in the allylic rearrangement, normally one isomer is formed preferentially[76]. This is also the case for these silyl derivatives (24 and 29). On examination of the pmr spectra of these chlorides (spectra 1-3) it is observed that the methylene peak ($-CH_2-Cl$) appears as one major peak with only a small second peak. In the trimethylsilyl compounds 29, the trimethylsilyl peak in the pmr spectra also appears as one major peak. From these spectral observations it is postulated that the chlorination reaction is not only regioselective, but also stereoselective. From the pmr spectra the stereoselectivity appears to be of the order of 85-90%. However, the geometry of the major isomer was yet unknown. The assignment of the stereochemistry of the double bond is based on the following transformation.

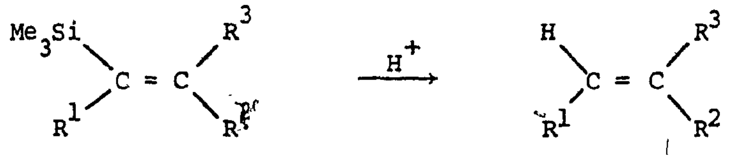
A number of reports have stated that vinylsilanes on treatment with acid undergo stereospecific replacement of the Me_3Si - group by a proton. The reaction has been shown to proceed with retention of

TABLE VII

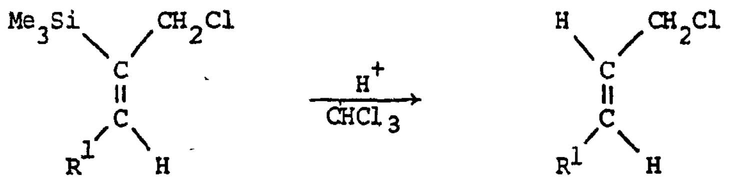
Preparation of  29

	R^1	b.p. (°C/mmHg)	Yield
c	n-$C_{10}H_{21}$	99-100/0.05	79
d	cyclo - C_6H_{11}	66-67/0.35	75
e	- $CH(CH_3)_2$	73-75/12	88
a	C_6H_5	89-90/1.5	79

configuration about the double bond[82,83].



The chlorides 29a,c,d,e, when treated with either dry HCl, HBr or 48% HI in a chloroform solution, underwent hydrodesilylation in quantitative yield to give the corresponding olefins 39. The



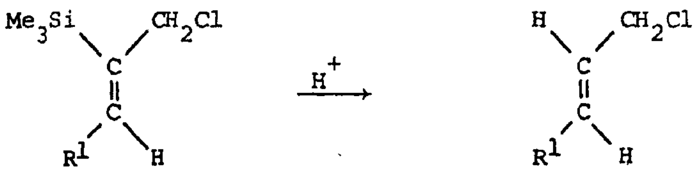
29 39

stereochemistry of the resultant olefins can be deduced from their pmr and ir spectra.

The pmr spectra should give the coupling constants between the two olefinic protons. The differences between E and Z coupling constants in disubstituted olefins are sufficiently great that this should prove to be a method of stereochemical assignment. Unfortunately, the 60 as well as the 100 MHz pmr spectra were much too complex for simple interpretation (spectra 4-6). However, the 220 MHz spectra proved to be of great help (spectra 4c-6c). The two olefinic protons now were well separated and coupling constants could be assigned with little difficulty. The coupling constants ranged from 15 to 19 Hz (Table VIII) which are very characteristic of disubstituted olefins with the E geometry. Furthermore, the coupling constants are large enough not to be mistaken for those of the Z geometry.

This interpretation is further supported by ir spectra of the olefins. The four chlorides 39 (a,c,d,e) all have a strong peak at 960 cm^{-1}, very characteristic of the E isomer of disubstituted olefins.

From this information it is thus possible to assign the geometry of the olefin 39 as E and therefore the precursor vinylsilane 29 as Z.



29

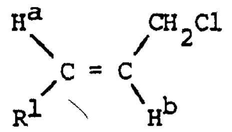
Z

39

E

Thus, this set of reactions can be used to transform an aldehyde RCHO into an allylic chloride of the E configuration, $E - R^1HC = CHCH_2Cl$ stereoselectively. From the 220 MHz pmr spectra it was also possible to deduce the extent of stereoselectivity. The methylenic ($-CH_2-Cl$) protons of the E and Z isomers are separated enough in the 220 MHz pmr to permit integration of the two sets of peaks. Thus a ratio of E/Z isomers can be obtained (Table VIII). One example

TABLE VIII

Preparation of  39

	R^1	b.p. (°C/mmHg)	Yield	J^{ab} (Hz)	E/Z
a	C_6H_5	(i)	90^{iv}	(i)	$100/0^{v}$
b	n-$C_{10}H_{21}$	76-77/0.06	$74(66)^{ii}$	15	85/15
d	cyclo-C_6H_{11}	53/1.3	$65(62)^{ii}$	18.8	85/15
e	i-Pr	58-60/89	$75(45)^{iii}$	15.3	90/10

i) Compound compared with authentic sample.

ii) Yield determined by vpc with isolated yield in parenthesis.

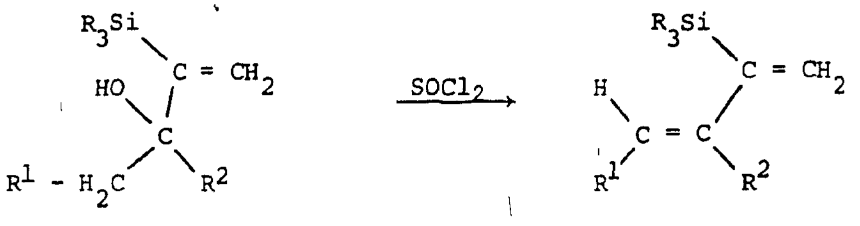
iii) Lower isolated yield was due to loss in distillation because of the relatively low boiling point of the compound.

iv) pmr showed that (a) was the only compound in the product.

v) Any Z isomer, if formed, may have isomerized to the E isomer under the reaction conditions.

cited 39a gave stereospeficically 100% E. This is likely to be due to the fact that the Z isomer, under the reaction conditions (acidic), would rearrange to the more stable E isomer.

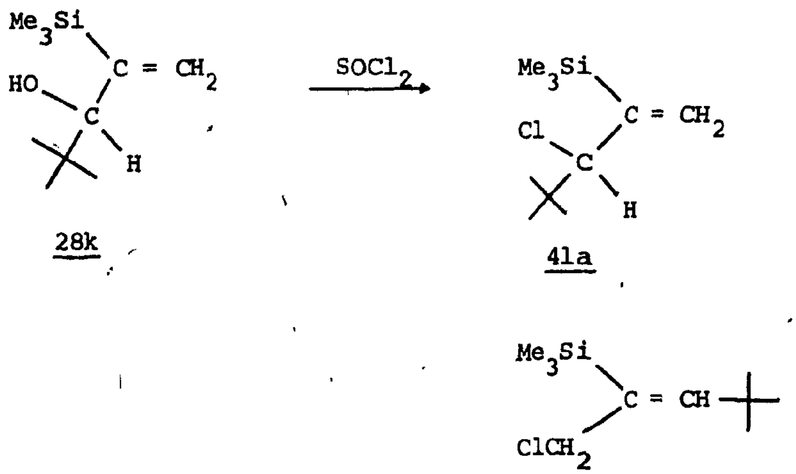
This synthesis of Z-beta-chlorovinylsilanes (24 and 29) and subsequently E-allylic chlorides 39 by this route has its limitations. It has already been pointed out that only aliphatic aldehydes could be used as starting materials. The beta-hydroxyvinylsilanes (18 and 28) produced from aliphatic ketones could not be chlorinated by thionyl chloride, but instead underwent elimination to give a diene 40.



18 or 28

40

A special case of this rearrangement reaction studied, was that of the beta-hydroxyvinylsilane 28k, obtained from pivalaldehyde. This compound, due to the steric interactions of the t-butyl group with the Me_3Si group, gave different results. When the beta-hydroxyvinylsilane 28k was treated with thionyl chloride in ether, chlorination did occur; however, three chlorides were produced. They are the three possible isomers, 41a, b and c, in a ratio of 13:52:35



28k

41a

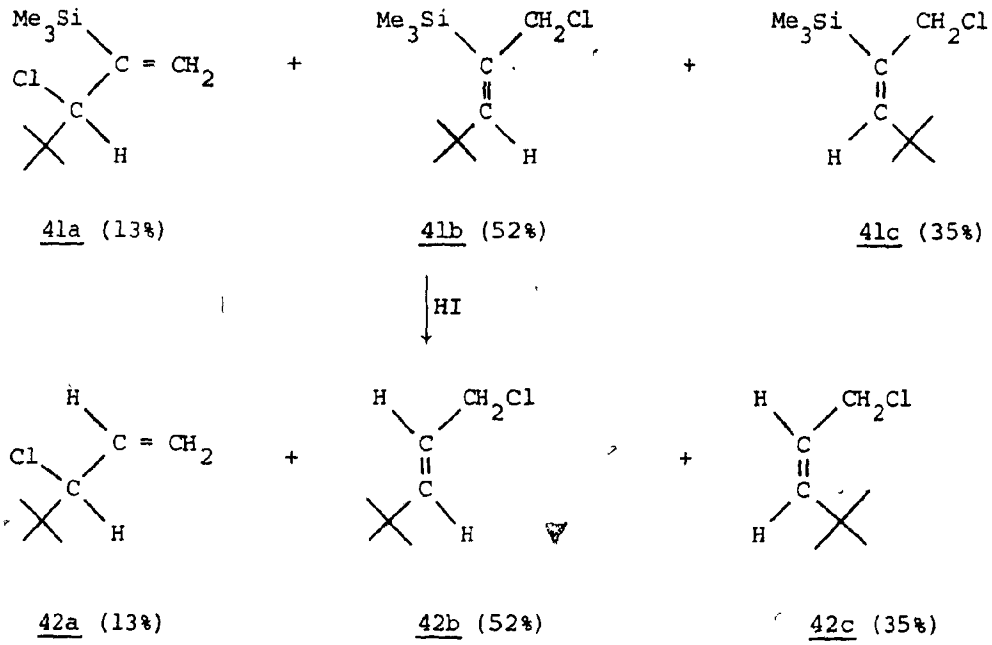
41b Z

41c E

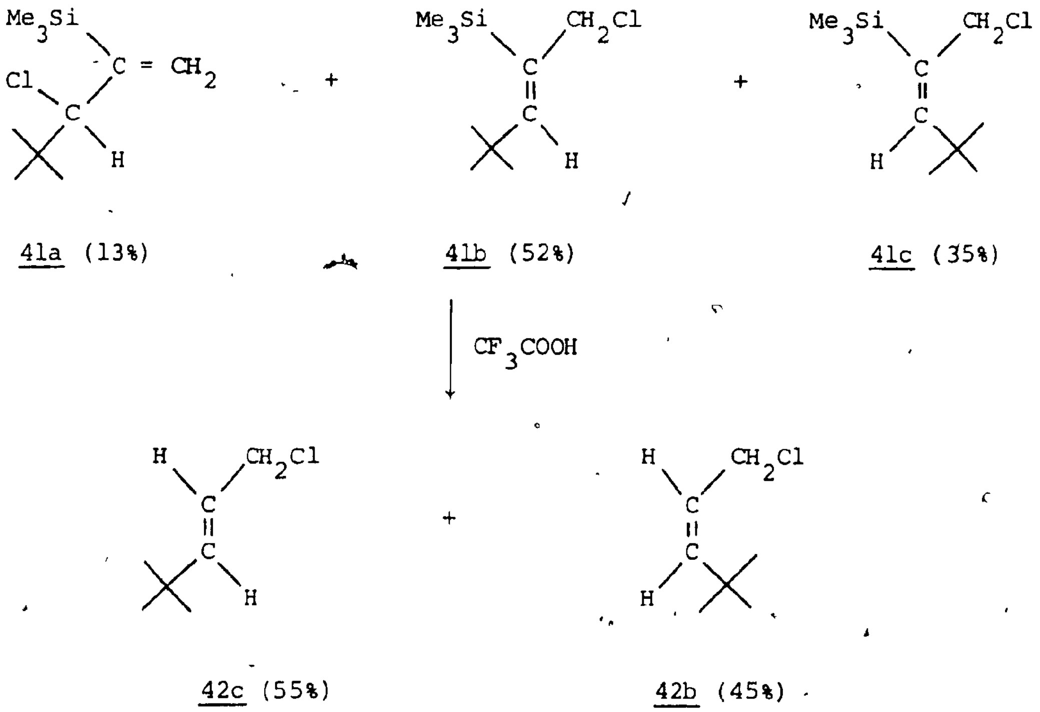
according to pmr and vpc analysis (spectrum 7). It is clear that in this case the steric interaction of the trimethylsilyl group with the tert-butyl group modifies somewhat the course of the reaction.

The isomeric mixture of vinylsilanes 41 was not thermally stable. On heating the reaction mixture neat to 150°C for a period of three hours, a change in the isomeric ratio occurred according to the pmr spectrum and vpc (spectrum 8). The isomer 41b, the Z isomer, disappeared while the non-rearranged isomer 41a increased. The proportion of the E isomer 41c seemed to remain the same. The ratio of isomers at this point is a:b:c = 62:0:38 by pmr and vpc. No further change of isomeric ratio was observed even on prolonged heating.

Treatment of the original mixture of isomers (i.e., 41a:b:c = 13:52:35) with 48% HI afforded a mixture of three olefins 42a,b,c in a ratio identical to that of the starting vinylsilane 41.



Treatment of this same isomeric mixture (i.e., 41a:b:c = 13:52:35) with trifluoroacetic acid, produced olefins 42 also. However, according to the pmr of the products, it appears that only the rearranged isomers 41b and c undergo hydrodesilylation. The unrearranged chloride 41a is stable to trifluoroacetic acid, under these conditions. The terminal vinylsilane 41a is apparently more resistant to acid than the non-terminal ones (41 b and c). However, on further standing in TFA, this isomer did disappear, but not to the corresponding olefin 42a. Instead it appeared to rearrange slowly to 41c which then underwent hydrodesilylation. The final mixture of olefins was E:Z = 55:45 (spectrum 9).



An interesting possibility is suggested by these results. It would seem that it is possible to produce stereoselectively the Z isomer 42b, under these conditions, even though the Z isomer is expected to be the one most sterically hindered. This is indeed supported by the following results. On treating the heated mixture (i.e., 41a:c = 62:38), with TFA essentially only one olefin resulted, 42b (spectrum 10)*.

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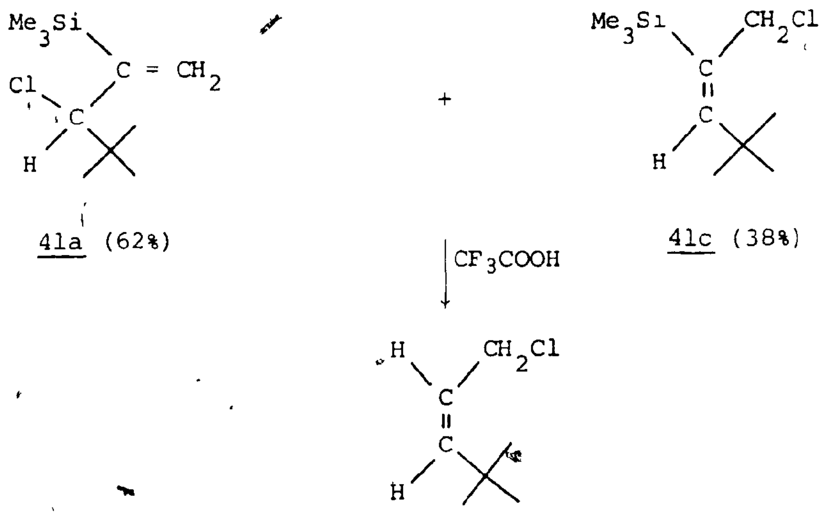
* 42c and 42b identified by comparison of ir and pmr spectra with literature[135].



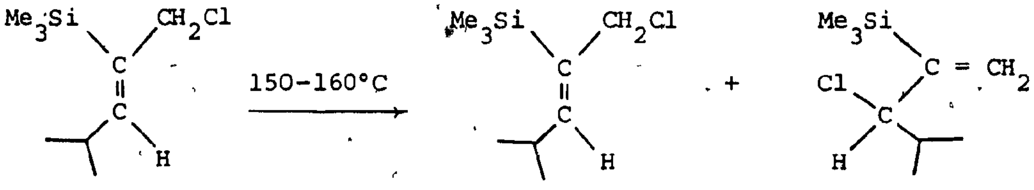
41a (62%)

41c (38%)

42b·

From these results it would seem that a more careful examination of the chemistry of the other beta-chlorovinylsilanes (29) is warranted.

When the beta-chlorovinylsilane 29c was heated to 150-160°C, a slow change in the pmr spectrum was observed. The allylic chloride 29c underwent rearrangement to the terminal olefin 43. However, the rate of isomerization appeared to be much slower than the case of 41.

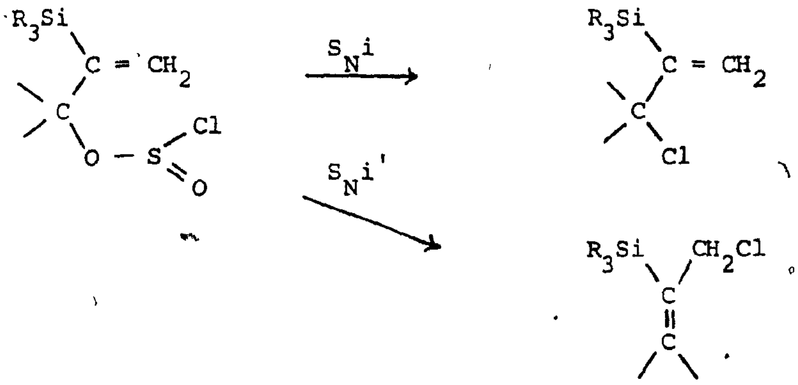


29c

43

Even on prolonged heating, only a small amount of rearranged product 43 was observed. The rate of reaction appears therefore to be dependent on the steric interaction between the trimethylsilyl group and the alkyl substituent. This thermal rearrangement poses problems in distilling high-boiling beta-chlorovinylsilanes, for example 29c. In this case it is possible to obtain substantial amounts of terminal olefin (20%) if distillation is carried out at high temperatures, and thus lowers the stereochemical purity of the olefin 39.

A few comments can be made concerning the mechanism of the chlorination even though it is not the aim of this thesis to deal with the mechanisms of reactions. As was mentioned, the chlorination of allylic alcohols with thionyl chloride can proceed in two directions. Several mechanisms can be in operation. The S_Ni and S_Ni' mechanisms both go through an intermediate chlorosulfite 36[84-86]. The difference



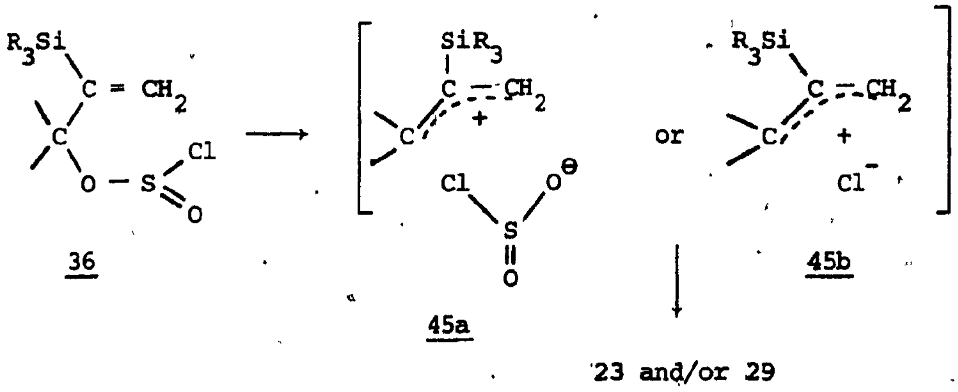
23

29

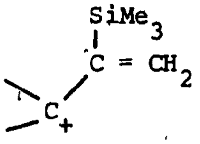
arises in the eventual position of chlorination. The S_Ni pathway gives rise to an alpha substitution product 23 while the S_Ni' pathway gives a gamma-chlorination product 29 via an allylic rearrangement.

Two modes of the breakdown of the chlorosulfite exist. One is the concerted decomposition with internal substitution[86b] of the chloride ion at α-carbon (for S_Ni) or at γ-carbon (for S_Ni') of the allylic system. This is presumed to be in operation in non-polar solvents such as carbon tetrachloride. The S_Ni' mechanism appears to be the predominant pathway.

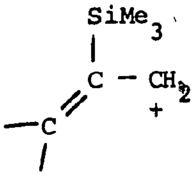
The second mode of decomposition is via an ionic mechanism involving the breakdown of 36 to what is probably an intimate carbonium chlorosulfite 45a[87] or carbonium chloride 45b[88] ion pair. Subsequent attack of the chloride ion of 45a or 45b on α-carbon or γ-carbon of the allyl cation of 45 leads respectively to chlorides 23 and 29. This mode of decomposition appears to be in operation in the more polar



solvents such as diethyl ether. In this solvent a rapid formation of what is probably an intimate ion pair 45a or 45b takes place. The rate-determining step of the reaction was then the union of the chloride ion and the allyl cation of the ion pair. The two resonance structures 46a and 46b are both contributing to the hybride.



46a



46b

The course of the union of the chloride ion and the allyl cation is consequently controlled by the relative thermodynamic stabilities of the products. The more stable 29 is therefore produced preferentially.*

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* This work has been published: T.H. Chan, W. Mychajlowskij, B.S. Ong and D.N. Harpp, J. Organomet. Chem., 107, C1-C4 (1976).

CHAPTER V

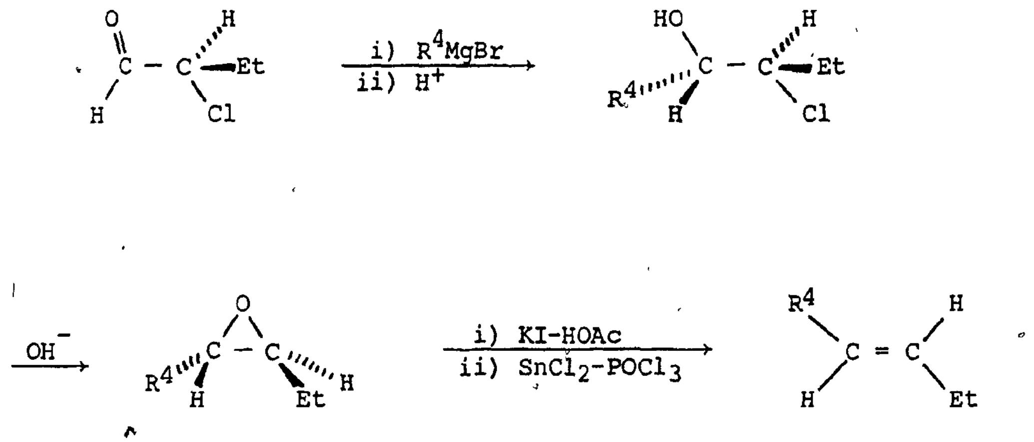
THE STEREOSELECTIVE SYNTHESIS OF
E AND Z DISUBSTITUTED ALKENES

(a) Stereoselective Synthesis of Alkenes

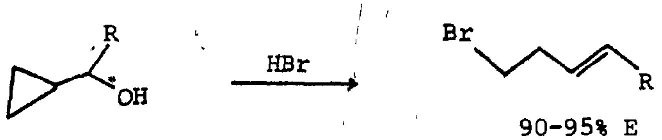
The introduction of this thesis dealt with the synthesis of carbon-carbon double bonds. When the olefin which is produced can exhibit geometric isomers, many of the methods mentioned suffer the problem that they yield mixtures of isomers in a nonselective manner. In cases where it is crucial to produce only one isomer, several methods have been developed for the stereoselective synthesis of alkenes[90,91].

Acetylenes have already been shown to give stereospecifically one alkene isomer on reduction. Catalytic reduction of acetylenes generally affords the Z-olefins, while reduction by sodium in liquid ammonia in the presence of a hydrogen donor gives the E-olefins[90,91].

Cornforth showed that an α-chlorocarbonyl compound in reaction with a Grignard reagent gave stereoselectively one isomer due to steric hindrance in the addition of the Grignard to the carbonyl[92]. The stereoselectivity was of the order of 70%. Johnson[93] later increased the stereoselectivity to over 90% by simply lowering the temperature of the reaction.

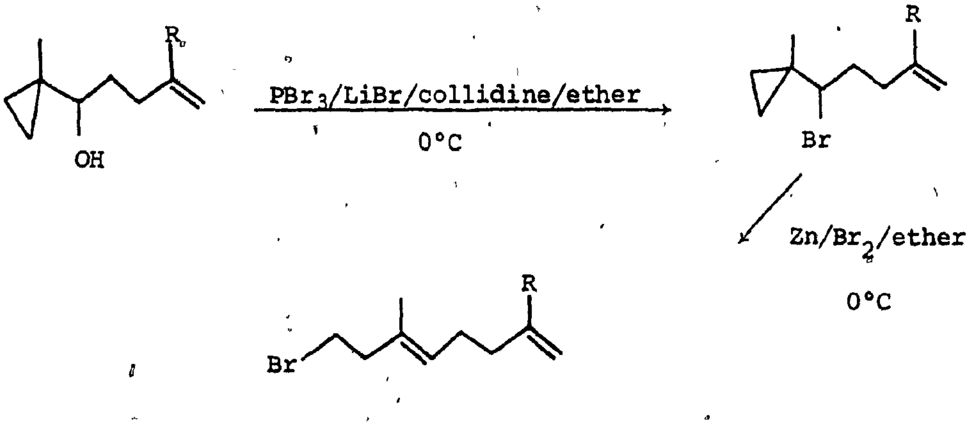


Many rearrangement reactions have been found to yield stereoselectively one olefinic isomer[90,91]. For example, α-cyclopropylcarbinols when treated with acid, undergo cleavage to give stereoselectively the E-alkenes[94]. Johnson extended this reaction to the



90-95% E

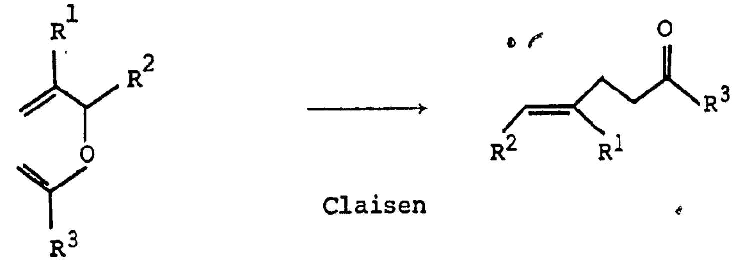
synthesis of trisubstituted olefins by a modified procedure[93].



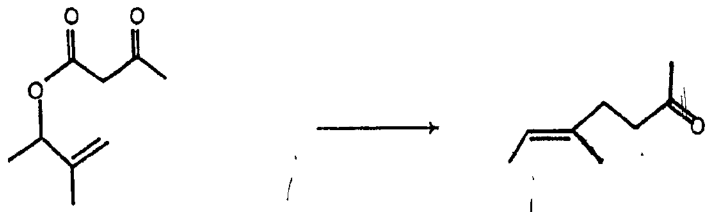
85-90% yield

(2-4% Z)

Intramolecular rearrangement reactions such as the Claisen and the Carroll rearrangement have been employed extensively in the stereoselective synthesis of trisubstituted olefins[90,91].

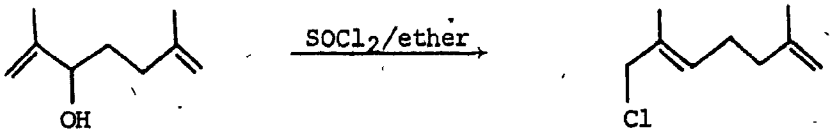


Claisen

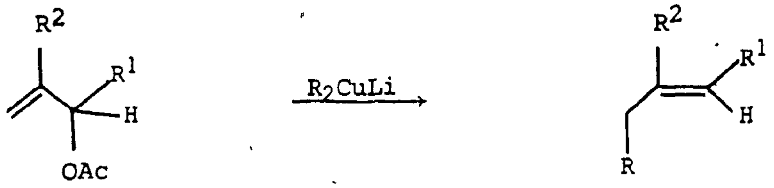


Carroll

Allylic rearrangements can also result in stereoselective synthesis of olefins[90,91]. It has already been mentioned in Chapter IV that allylic alcohols are converted to E-trisubstituted chlorides with thionyl chloride[76,77,95].



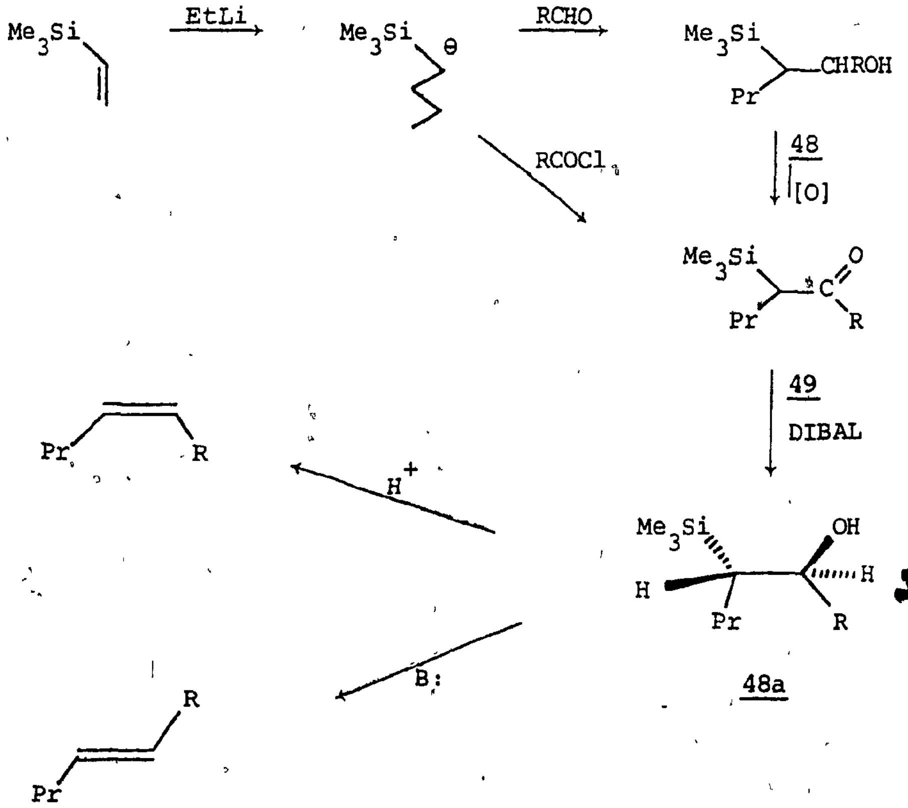
Allylic acetates undergo reaction with organocopper lithium reagents to give stereoselectively (~90%) E-trisubstituted olefins[96].



Many of these methods of stereoselective olefin synthesis have been developed for trisubstituted olefins and produce one isomer selectively. A general method for synthesizing both E and Z isomers is preferred. In its original form, the Wittig reaction had little stereoselectivity in its products. However, subsequent investigations have shown that by altering the conditions under which the reaction is carried out, stereoselectivity can be achieved[90,91]. The Wittig reaction is limited to disubstituted olefin synthesis; both tri- and tetrasubstituted olefins are produced in low yield and lower selectivity. The various modified Wittig reactions also show selectivity, usually to give predominantly the E-isomer[90,91].

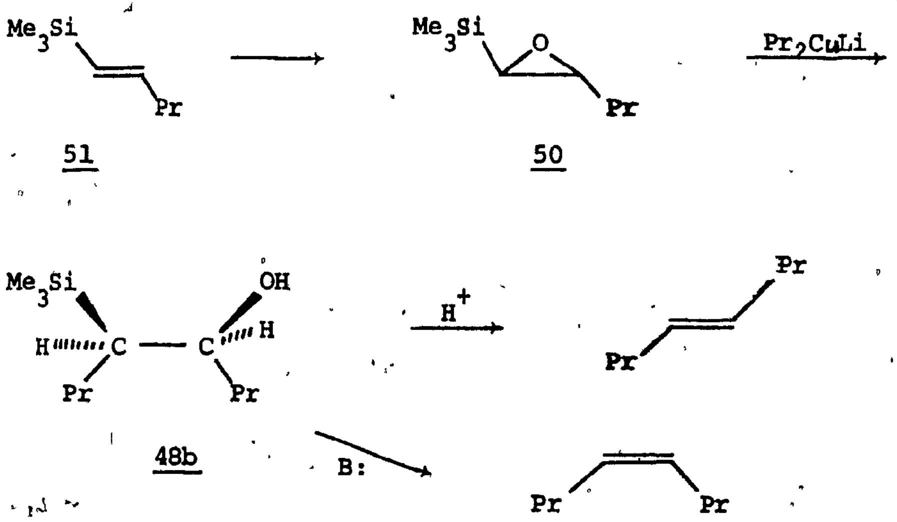
Unfortunately, this same stereoselectivity is absent in the olefin synthesis using α-silylcarbanions. The alkenes obtained by this reaction have been found to be usually mixtures of E and Z isomers in nearly equal proportions[27,39-41].

Attempts to introduce stereoselectivity into this reaction have been made. Hudrlik[97,98] found that E and Z disubstituted alkenes could be stereoselectively synthesized from β-hydroxysilanes. This was accomplished by preparing only one diastereomer of the β-hydroxysilane (48) and then effecting the subsequent elimination under controlled conditions. The key step of the reaction is the choice of a selective reducing agent to convert the β-ketosilane 49 to the (threo)-β-hydroxysilane 48a.



Hudrlik found that diisobutylaluminum hydride (DIBAL) accomplished this very well. The reduction afforded one diastereomer in accordance with Cram's rule for reduction[99,100]. The subsequent elimination of trimethylsilanol could be controlled to give either E or Z isomer depending on whether acid or base were used to effect elimination. The stereoselectivity of the reaction was > 95%. So far the methodology has been demonstrated only with 4-octene and it is not clear whether the reaction is general. The drawback in this method is that only disubstituted olefins can be formed and the stereoselectivity might drop significantly if a different group other than propyl were used alpha to silicon. That is, if the size of the substituent on the α-carbon (in this case the propyl group) is bulkier, Cram's rule may not hold so strictly and a lower selectivity would result.

Hudrlik[101] has found an alternative method of synthesizing one diastereomer of the beta-hydroxysilane (48). In this reaction



the starting material is the vinylsilane 51 of specific stereochemistry. Epoxidation of it gives an α,β-epoxysilane 50. On treatment of 50 with an organocopperlithium reagent, it was found that only one diastereomer of β-hydroxysilane 48b was formed. Elimination with acid or base gave E or Z isomers in > 98% stereochemical purity.

This second method of stereoselective olefin synthesis appears to be an attractive route and more generally applicable. However, one major problem exists; that is, this reaction is dependent on starting with geometrically pure vinylsilanes which are at present difficult to obtain. It is also not clear how this reaction can be applied to the olefination of carbonyl compounds.

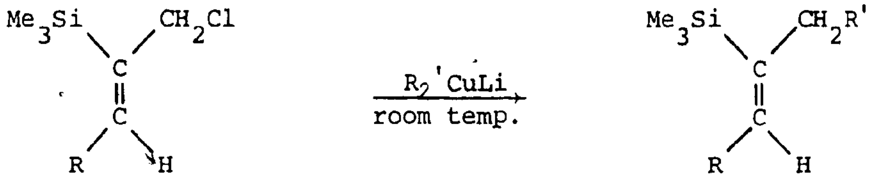
We wish to report here on the stereoselective synthesis of E and Z disubstituted olefins from carbonyl compounds and carbanions alpha to silicon.

(b) Stereoselective Synthesis of E-Alkenes

A method for converting aldehydes (RCHO) to allylic chlorides (E-$RCH=CHCH_2Cl$) stereoselectively has already been described in Chapter IV. One of the features of this transformation is that a functionality exists in the molecule (i.e., a chloride). This has the advantage that further modification of the structure is possible.

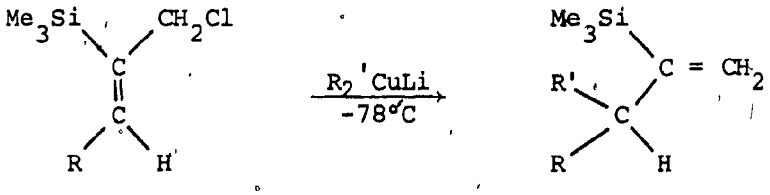
One such transformation is the conversion of the chloro group into an alkyl chain. The method of choice for effecting such a conversion is by reaction with organocopperlithium reagents[102,103]. It has been found that these reagents alkylate or arylate a wide variety of halides with ease and in mild conditions. In the present case, compounds <u>29</u> were treated with a number of organocopperlithium reagents at room temperature. In all cases, vinylsilanes <u>52</u> were obtained in high yields

(Table IX). The stereochemical purity of the product vinylsilane is



29 52

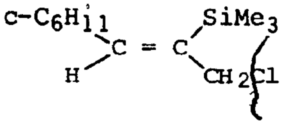
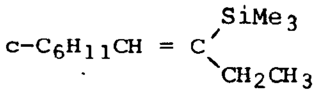
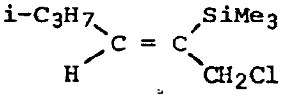
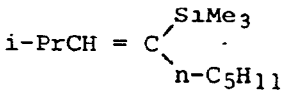
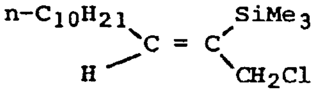
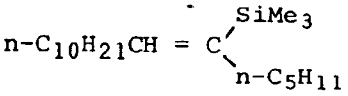
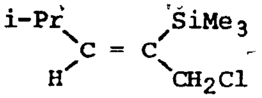
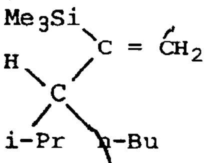
identical to that of the starting chloride 29 (see pmr spectra 11-13). The course of the reaction depends rather critically on the reaction temperature. At room temperature the organocopperlithium reagents displace the chloride directly. However, if the reaction temperature is lowered to -78°C the direct displacement reaction is no longer in effect; instead, an allylic substitution reaction occurs. From this reaction the terminal vinylsilane 53 was obtained in high yield (~ 80%).



29 53

At a temperature between -78°C and room temperature a mixture of products 52 and 53 resulted. It seems therefore that as long as the reaction temperature is controlled properly, conversion of 29 to 52 can be

TABLE IX - Synthesis of Z-Vinylsilane (52)

Precursor	Reagent	Temp °C	Product	Yield[a] (E:Z)
(a) 	$(CH_3)_2CuLi$	22		80(15:85)
(b) 	$(n\text{-}C_4H_9)_2CuLi$	22		80(10:90)
(c) 	$(n\text{-}C_4H_9)_2CuLi$	22		80[b](11:89)
(d) 	$(n\text{-}C_4H_9)_2CuLi$	-78		d

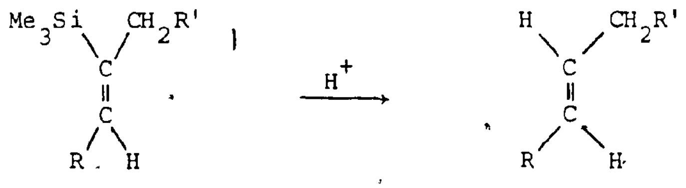
a Isolated yield.

b Contains <5% terminal isomer.

c Purified by column chromatography over silica gel/hexane.

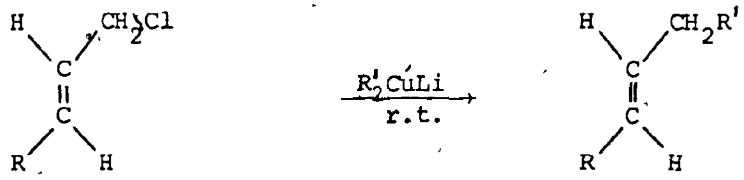
d Yield not determined (estimated to be ~80%).

accomplished cleanly and in high yield. These vinylsilanes 52 can be hydrodesilylated to the E-olefin 54 by treatment with acid, in



52

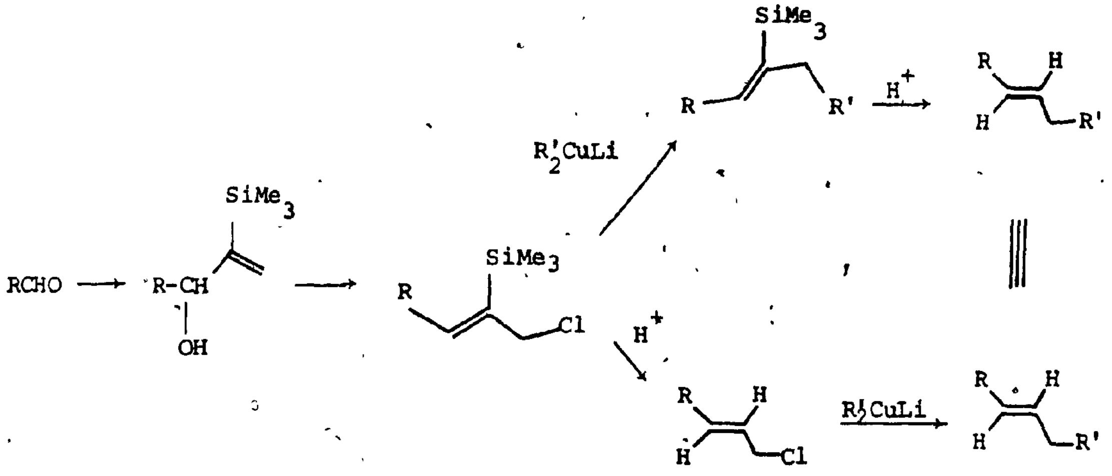
quantitative yield. The exchange of the Me_3Si group for hydrogen has been shown to be stereospecific, with retention of configuration about the double bond[82,83]. The stereochemistry of the resultant olefin was verified by comparison of its spectral properties (ir, pmr, vpc) with those of a sample prepared by alkylation of the allylic chloride 39 itself. The two samples were identical in all respects.



39

54

We have therefore two routes leading from the aldehyde stereoselectivity to the E alkene. The overall transformations can be summarized by Scheme 3.

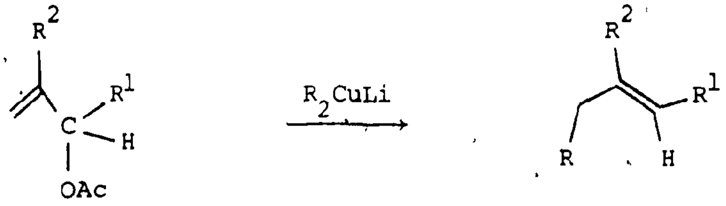


Scheme 3

This method is able to synthesize olefins of the E-geometry and vinylsilanes with Z-geometry in good yields and high (85-90%) stereoselectivity. It still remains to develop a method for the synthesis of Z-olefins and E-vinylsilanes.

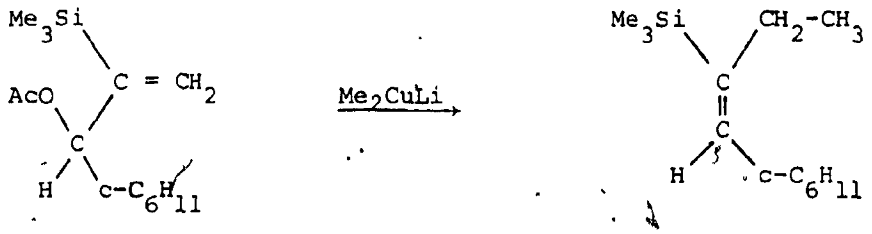
(c) Stereoselective Synthesis of Z-Alkenes

The stereoselective synthesis of the thermodynamically less stable Z-alkene is a more difficult problem in general. Other than by way of semihydrogenation of acetylenes, most reactions give the E-alkenes selectively. A relevant example is the reaction of organocopperlithium reagents with allylic acetates[90,96,102].



It has been found that reaction of organocopperlithium reagents with allylic acetates produce olefins of the E-geometry in high stereoselectivity (> 90%) and in high yields (~80%). The stereoselectivity is apparently controlled by the relative steric sizes of R^2 versus the entering R group. High stereoselectivity is obtained when R^2 is hydrogen or smaller in size than the R group of the copper reagent. It seems to us that it may be possible to reverse the stereoselectivity of the reaction if one were to use a bulky R^2 which can, however, be eventually replaced. The trimethylsilyl group can fulfill this role. It is expected to be bulky sterically and it can be replaced readily by a number of electrophiles, e.g., proton.

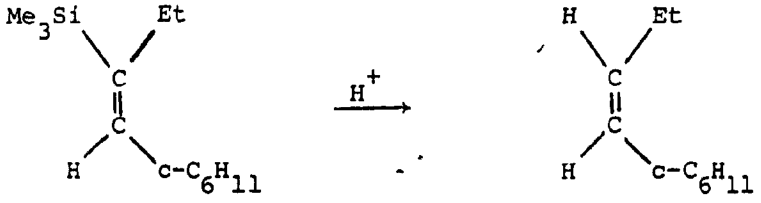
When the allyl acetate 55a was treated with dimethylcopperlithium at -78°C in diethyl ether, it underwent a clean reaction to yield the vinylsilane 56a in approximately 80% yield. The pmr spectrum (spectrum 14) of the product indicated that the reaction was indeed highly stereoelective. This statement is based on the fact that the trimethylsilyl signals in the pmr spectrum are essentially one major peak with only a small second peak (~8%). By comparison of the pmr spectrum (# 14) of 56a with that of



55a 56a

52a (spectrum #11) which is known to be the Z-isomer, a marked difference was observed (Table XI). This indicates that the major isomer obtained in this reaction has the E-geometry.

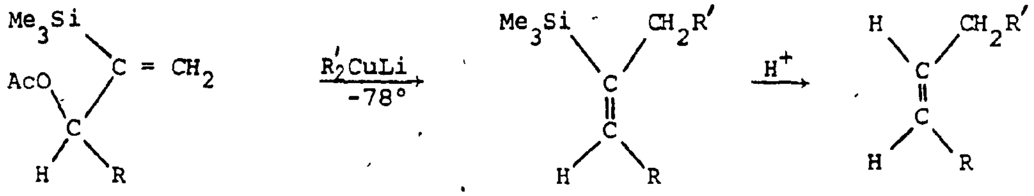
Acid cleavage of the vinylsilane 56a yielded the olefin 57a in quantitative yield. Comparison of the pmr and ir spectra of this olefin 57a (spectrum #15) with those obtained from the E-olefin 54a (spectrum #16) again proves that the products are different. The vinyl protons of 57a have a different chemical shift and give a different splitting pattern from the corresponding olefin 54a. Also, the



56a 57a

E-olefin 54a exhibits a strong peak at 960 cm^{-1} in the ir, characteristic of E-disubstituted olefins; however, this peak is very weak in the ir spectrum of olefin 57a. From these results it can be concluded that olefin 57a is of the Z-geometry and therefore the vinylsilane 56a is E.

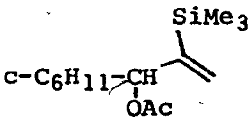
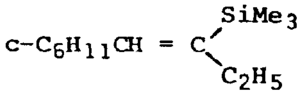
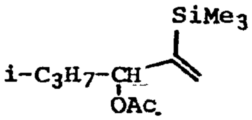
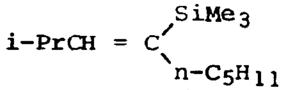
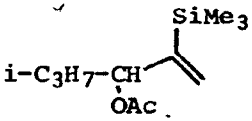
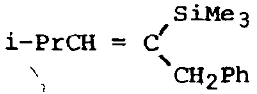
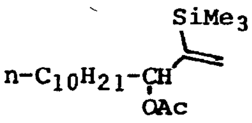
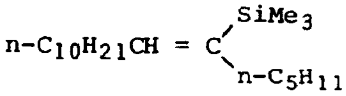
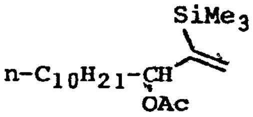
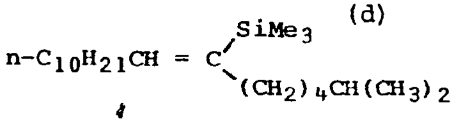
This reaction can be applied in general to a number of systems to give E-vinylsilanes and subsequently Z-olefins in high yield and high stereoselectivity (Table X). However, the reaction has been found to be very sensitive to the size of the alkyl group R, the temperature of the reaction as well as choice of copper reagent.



55 56 57

When the alkyl group R was isopropyl (55b) or cyclohexyl (55a), the reaction proceeded at -78°C to give vinylsilanes 56 in good yield (~80%) and high stereoselectivity (>90%). The same reaction, if carried out at higher temperatures, gave mixtures of products containing the E and Z isomers (52 and 56) as well as the terminal vinyl silane 53. The latter product was evidently produced by the direct displacement of the acetate by the alkyl group R'. When the alkyl group R was n-$C_{10}H_{21}$ the reaction of the acetate 55d with dialkylcopperlithium, even at -100°C, gave little stereoselectivity and an equal mixture of E and Z isomers resulted. It seems therefore that the stereoselectivity of this reaction

TABLE X - Synthesis of E-Vinylsilanes (56)

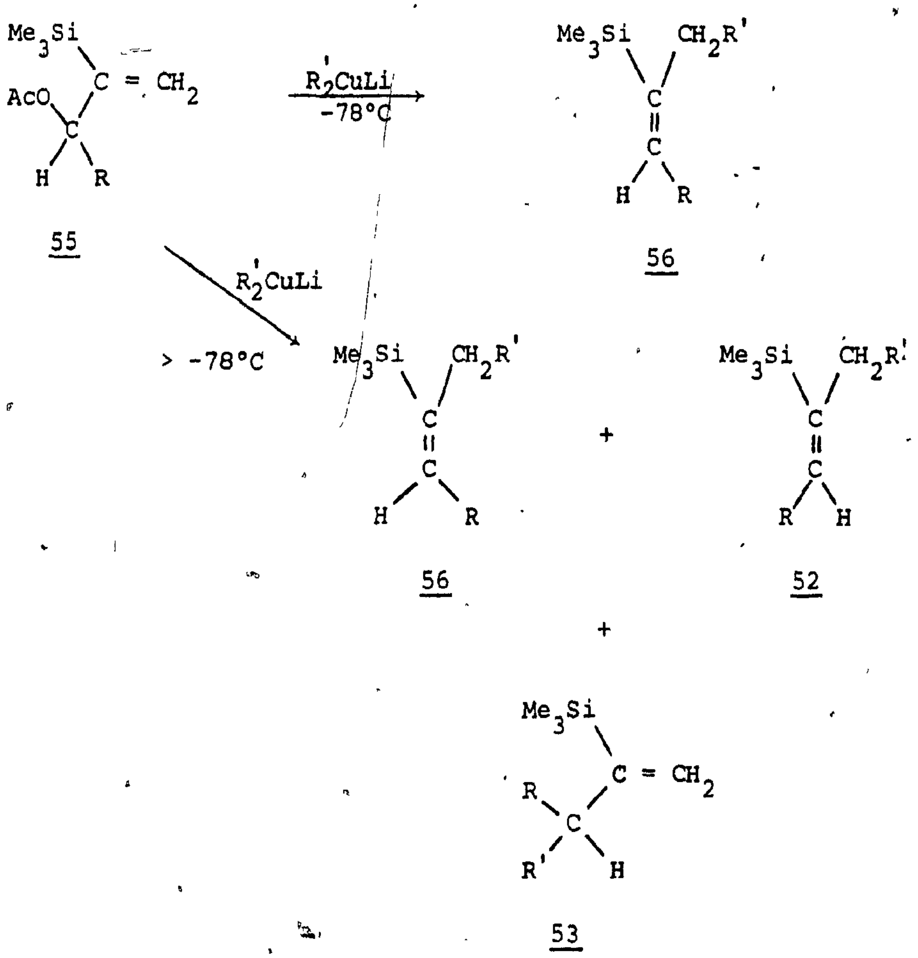
Precursor	Reagent	Temp °C	Product	Yield(a) (E:Z)
(a) 	$(CH_3)_2CuLi$	-78	 $c\text{-}C_6H_{11}CH=C(SiMe_3)(C_2H_5)$ b.p.67-69/1 mm	78[b](94:6)
(b) 	$(n\text{-}C_4H_9)_2CuLi$	-78	 $i\text{-}PrCH=C(SiMe_3)(n\text{-}C_5H_{11})$ b.p. 78-80°/5mm	78[b](92:8)
(c) 	Ph_2CuLi	-78	 $i\text{-}PrCH=C(SiMe_3)(CH_2Ph)$ b.p.67-69/0.25 mm	61(100:0)
(d) 	$(n\text{-}C_4H_9)_2CuLi$	0	 $n\text{-}C_{10}H_{21}CH=C(SiMe_3)(n\text{-}C_5H_{11})$ (d)	—[c] (30:70)
		-78 -100		—[c] (53:47)
	$(n\text{-}C_4H_9)_2CuMgBr$	-78		80 (86:14)
(e) 	$[(CH_3)_2CH(CH_2)_3]_2CuMgBr$	-78	 $n\text{-}C_{10}H_{21}CH=C(SiMe_3)((CH_2)_4CH(CH_3)_2)$ (d)	82(87:13)

a Isolated yield.

b Contains < 5% terminal isomer.

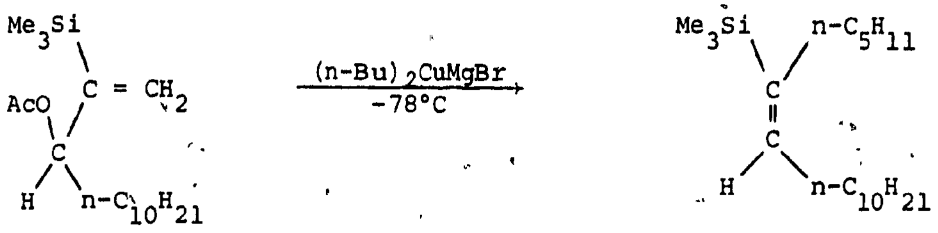
c Yield not determined.

d Purified by column chromatography over silica gel/hexane.



is governed by the steric interaction of the R group and the trimethylsilyl group. When the R group is less sterically encumbered, lower stereoselectivity results.

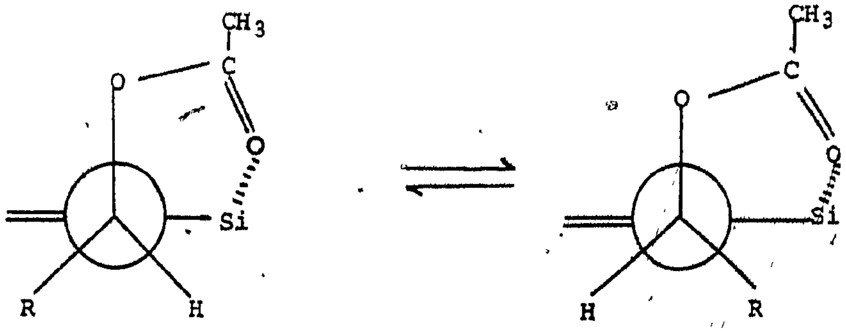
However, when the acetate 56d was treated with di-n-butylcoppermagnesium bromide, a stereoselective reaction occurred once again. The less reactive organocopper Grignard reagent gave the vinylsilane 56d



55d 56d

in good yield (80%) and the stereoselectivity although lower than in the previous cases, was still high (86%-E).

On examination of molecular models of the acetates 55, it is probable that there is hindered rotation about the $>C \circlearrowright C = C$ bond of 55. At room temperature rotation is free. However, on cooling the isomer 55, rotation becomes more difficult and one conformation 58 predominates over the other 59. The steric interaction of the



58 59

alkyl group R (58, 59) with the trimethylsilyl group is much greater in 59 than in 58, and therefore 58 is expected to predominate. Allylic substitution with the copper reagent would occur preferentially with 58 thus giving the E-vinylsilane 56. In the case of R being n-$C_{10}H_{21}$, the steric interaction is much less than that produced from R = i-Pr or c-C_6H_{11} and thus the barrier for interconversion of 58 ⇄ 59 is somewhat less. With organocopperlithium reagents, it seems that this reagent is too reactive, the transition states leading to both E and Z isomers do not differ in energy, i.e., lack of stereoselectivity. However, with the organocopper Grignard reagent which is less reactive, the transition states have still an energy difference even though somewhat diminished and thus reintroduce stereoselectivity into the reaction.

These vinylsilanes can all be converted to Z-olefins by simple acid treatment in quantitative yield[82,83].

Thus, methods have now been developed for the conversion stereoselectively, of an aldehyde to, first E or Z vinylsilanes (56 or 52) and subsequently to E or Z olefins (54 or 57) in good yield.*

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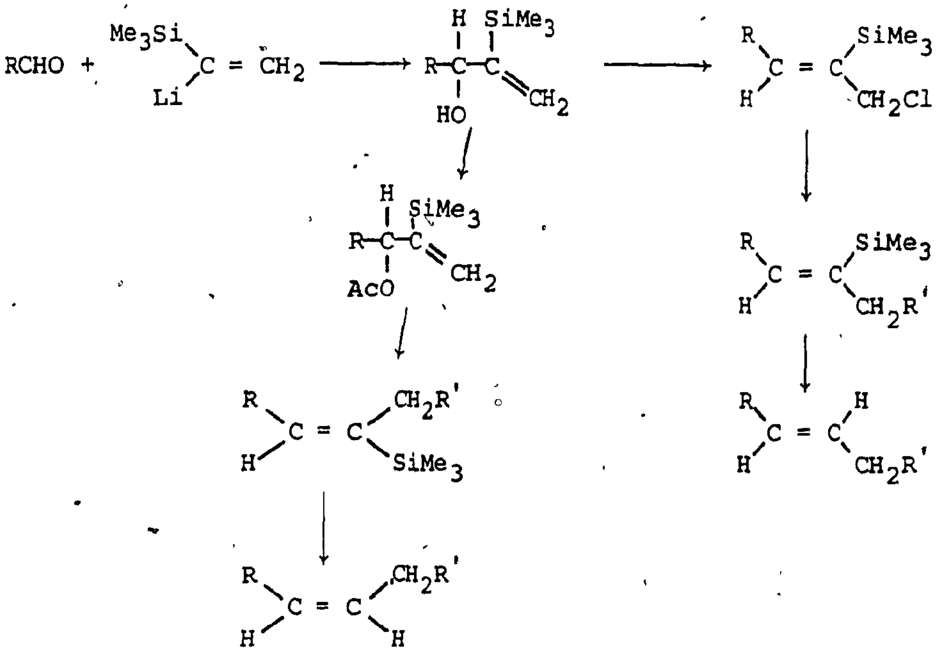
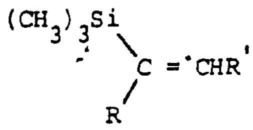
* This work has been published: W. Mychajlowskij and T.H. Chan, Tetrahedron Letters 4439 (1976).



One of the methods used to distinguish the E and Z vinylsilanes was their pmr spectra. Indeed, it was found that the geometry of the vinylsilanes could be assigned on the basis of chemical shift of the trimethylsilyl peak as well as the vinyl peak in both pmr and cmr spectra (Table XI). The trimethylsilyl peak in the pmr and cmr of the E-isomer was consistently at higher field than the Z-isomer peak. In the cmr, in fact, the E-isomer was at higher field than TMS while the Z-isomer was at lower field than TMS. The same shift is observed for the vinyl protons in the pmr spectra.

TABLE XI

Nuclear Magnetic Resonance Spectral Data of Vinylsilanes



Vinylsilane		^1H-NMR (CCl_4) δ [ppm]	^{13}C-NMR ($CDCl_3$) δ [ppm]
R = C_2H_5	(E)	0.05 (s, 9H)	- 1.08
R' = c-C_6H_{11}		5.52 (d, 1H)	
R = n-C_5H_{11}	(E)	0.05 (s, 9H)	- 1.035
R' = i-C_3H_7		5.51 (d, 1H)	
R = n-C_5H_{11}	(E)	0.05 (s, 9H)	- 1.035
R' = n-$C_{10}H_{21}$		5.53 (t, 1H)	
R = $(CH_2)_4CH(CH_3)_2$	(E)	0.05 (s, 9H)	- 1.035
R' = n-$C_{10}H_{11}$		5.53 (t, 1H)	
R = C_2H_5	(Z)	0.13 (s, 9H)	0.56
R' = c-C_6H_{11}		5.71 (d, 1H)	
R = n-C_5H_{11}	(Z)	0.13 (s, 9H)	0.604
R' = i-C_3H_7		5.80 (d, 1H)	
R = n-C_5H_{11}	(Z)	0.13 (s, 9H)	0.431
R' = n-$C_{10}H_{21}$		5.83 (t, 1H)	
R = $(CH_2)_4CH(CH_3)_2$	(Z)	0.13 (s, 9H)	0.431
R' = n-$C_{10}H_{21}$		5.83 (t, 1H)	
R = $C_6H_5CH_2$	(Z)	- 0.08 (s, 9H)	- 1.078
R' = i-C_3H_7		5.80 (d, 1H)	

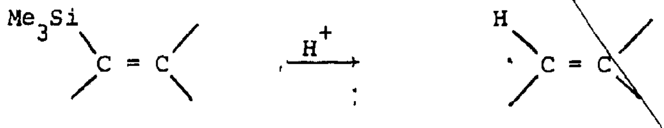
TABLE XI continued

Vinylsilane		^{1}H-NMR (CCl_4) δ [ppm]		^{13}C-NMR ($CDCl_3$) δ [ppm]
R = $CH(i\text{-}C_3H_7)(CH_2\ {}_3CH_3$ R' = H		0.10 (s, 9H) 5.66 (m, 2H)		- 0.43
R = CH_3 R' = $n\text{-}C_6H_{13}$	(E)	0.03 (s, 9H) 5.62 (q, 1H)	[a]	-
R = CH_3 R' = $n\text{-}C_6H_{13}$	(Z)	0.10 (s, 9H) 5.92 (q, 1H)	[a]	-
R = $CH_2CH = CH_2$ R' = $n\text{-}C_6H_{13}$	(Z)	0.12 (s, 9H) 5.97 (t, 1H)	[a]	-
R = $CH_2\text{-}C(CH_3) = CH_2$ R' = $n\text{-}C_6H_{13}$	(Z)	0.10 (s, 9H) 5.90 (t, 1H)	[a]	-
R = $CH_2\text{-}CCl = CH_2$ R' = $n\text{-}C_6H_{13}$	(Z)	0.14 (s, 9H) 5.99 (t, 1H)	[a]	-
R = CH_2Cl R' = $i\text{-}C_3H_7$	(Z)	0.22 (s, 9H) 6.08 (d, 1H)		-
R = CH_2Cl R' = $n\text{-}C_{10}H_{21}$	(Z)	0.22 (s, 9H) 6.28 (t, 1H)		-
R = CH_2Cl R' = $c\text{-}C_6H_{11}$	(Z)	0.22 (s, 9H) 6.08 (d, 1H)		-
R = CH_2Cl R' = $i\text{-}C_3H_7$	(E)	0.14 (s, 9H) 5.78 (d, 1H)		-
R = CH_2Cl R' = $c\text{-}C_6H_{11}$	(E)	0.14 (s, 9H) 5.78 (d, 1H)		-

[a] see ref. 122.

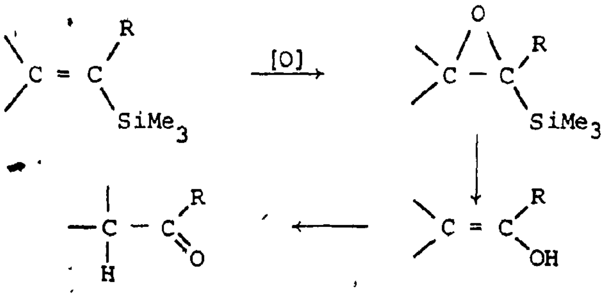
(d) Synthesis of Vinylsilanes and their Applications

The synthesis of vinylsilanes is of interest not only with respect to alkene synthesis as reported in the previous chapter. Vinylsilanes have recently been found to have considerable importance



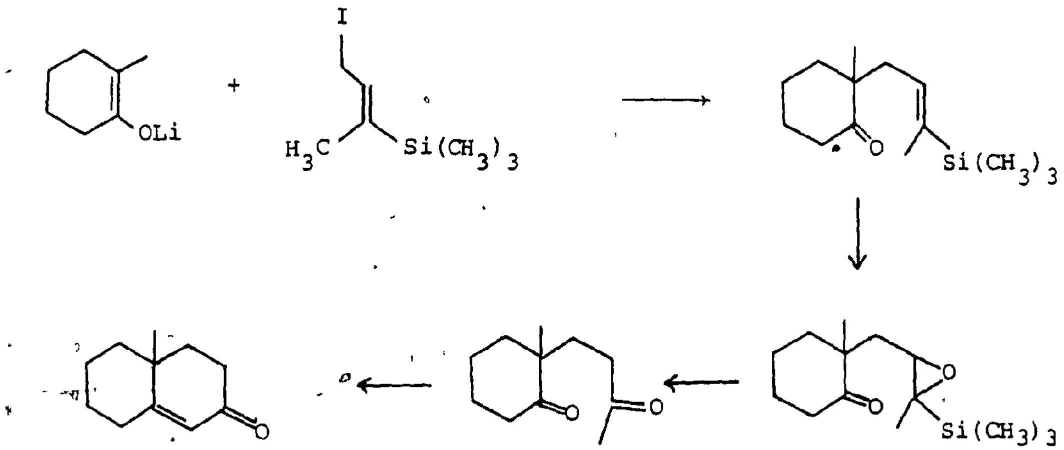
as precursors to many different functional groups in organic synthesis.

Stork[104] has reported that vinylsilanes could be transformed into aldehydes quite readily (R = H). This is accomplished by first

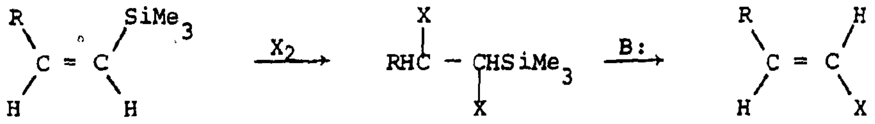


epoxidizing the vinylsilane to the α,β-epoxysilane, which on treatment with acid gives the aldehyde in good yield. Seebach[54] has extended this reaction to include the synthesis of methyl ketones (R = CH_3). This reaction has also recently been applied to the synthesis of dicarbonyl compounds[105].

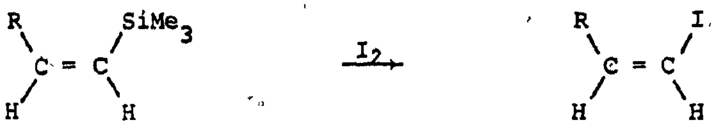
Stork[106,107] has subsequently demonstrated the usefulness of this carbonyl forming reaction by employing it in an annelation reaction.



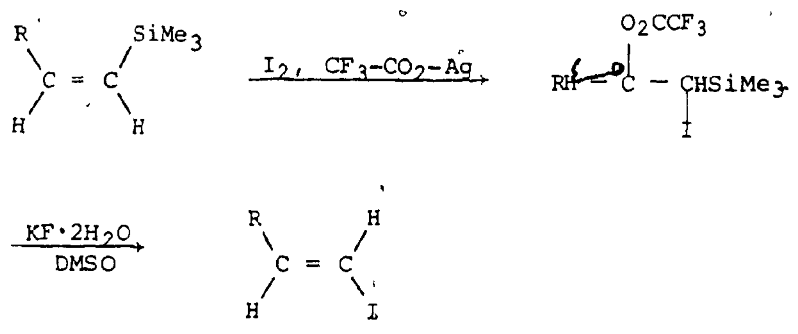
Vinylsilanes have also been converted to vinylhalides stereospecifically[89,108,109]. Mono-substituted vinylsilanes on reaction with chlorine or bromine are converted first to the dihalides[109]. The



dihalides undergo dehalosilylation with base to give vinyl halides of opposite stereochemistry to that of the starting vinylsilanes. In the case of iodine, however, the dihalide has not been isolated but instead vinyliodide is obtained directly, with retention of stereochemistry

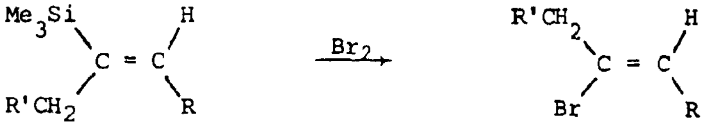


about the double bond. Inversion of stereochemistry can occur, however, if a modified procedure is employed. These reactions have



only been applied to monosubstituted vinylsilanes. No examples of the halodesilylation of di- and tri-substituted vinylsilanes had been reported as yet.

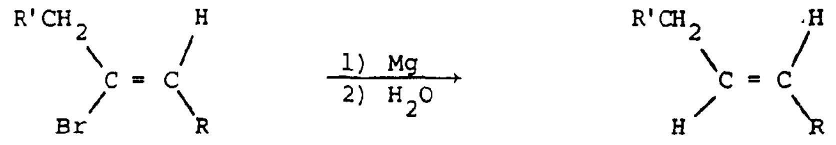
We found that treatment of the vinylsilane 56 with bromine in methylene chloride at -78°C gave the vinylbromide 60 in quantitative yield. The configuration of the bromide 60 was deduced by converting



56 60

R' = CH_3, R = c-C_6H_{11} , R' = n-Bu, R = i-Pr

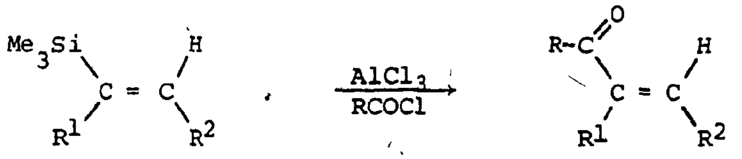
it to the olefin 54 through the Grignard reaction. It has been

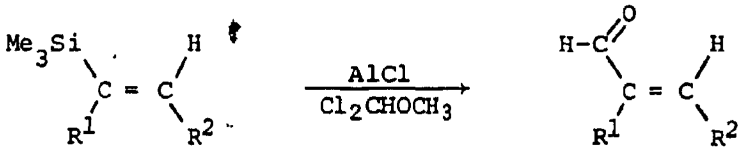


60 54

well documented in the literature that such conversion does not change the stereochemistry. The conversion of the vinylsilane 56 to the vinylbromide 60 thus proceeded with inversion of configuration, in agreement with literature examples. However, when 52 was treated with bromine, under identical conditions, no vinylbromide was ever isolated and a complicated mixture of products resulted. At the moment, the structures of the products have not been fully established. The reasons for the failure of the Z-isomer to undergo clean bromodesilylation is therefore at present unknown and further work is warranted.

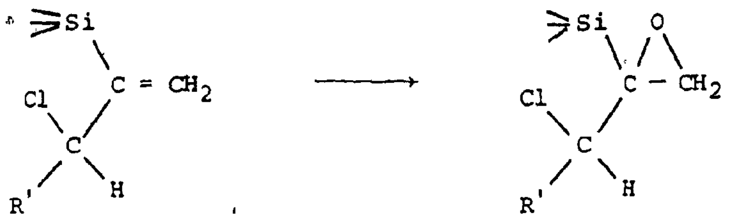
Vinylsilanes have been found to undergo Friedel-Crafts acylation reactions to give α,β-unsaturated ketones[110,111] and aldehydes[111]. The



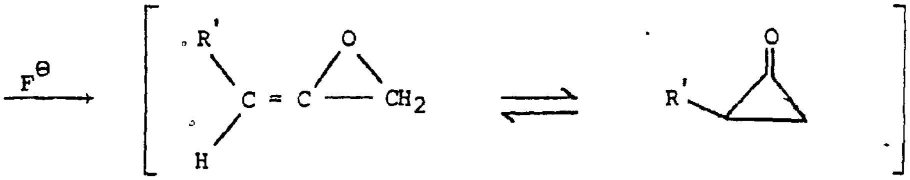


reactions are very fast and a good yield of product arises (~60-70%). The reactions appear to proceed with retention of configuration about the double bond .

Vinylsilanes on epoxidation yield α,β-epoxysilanes. It has already been shown that acid treatment of these yields carbonyl compounds. Furthermore, β-functionalized vinylsilanes 61 can also be epoxidized to give the corresponding epoxides 62. These epoxides 62 on treatment with



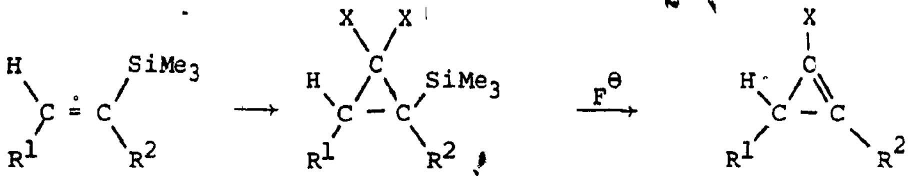
61 62



63a 63b

fluoride ion undergo β-elimination of chlorotrimethylsilane to give allene oxides 63[112-114].

A recent reaction, developed by Chan and Massuda[115], is that vinylsilanes can be converted to cyclopropenes 64. This is accomplished by dihalocyclopropanation of the vinylsilane (65) to give the dihalocyclopropane 66. Reaction of 66 with fluoride leads to the generation

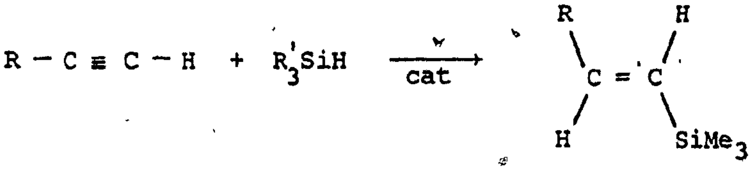


65 66 64

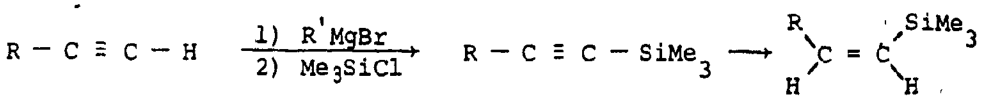
of cyclopropene 64.

It thus appears that vinylsilanes have considerable potential as synthetic intermediates. This fact has prompted many groups to study ways of synthesizing vinylsilanes and particularly methods of stereoselective synthesis.

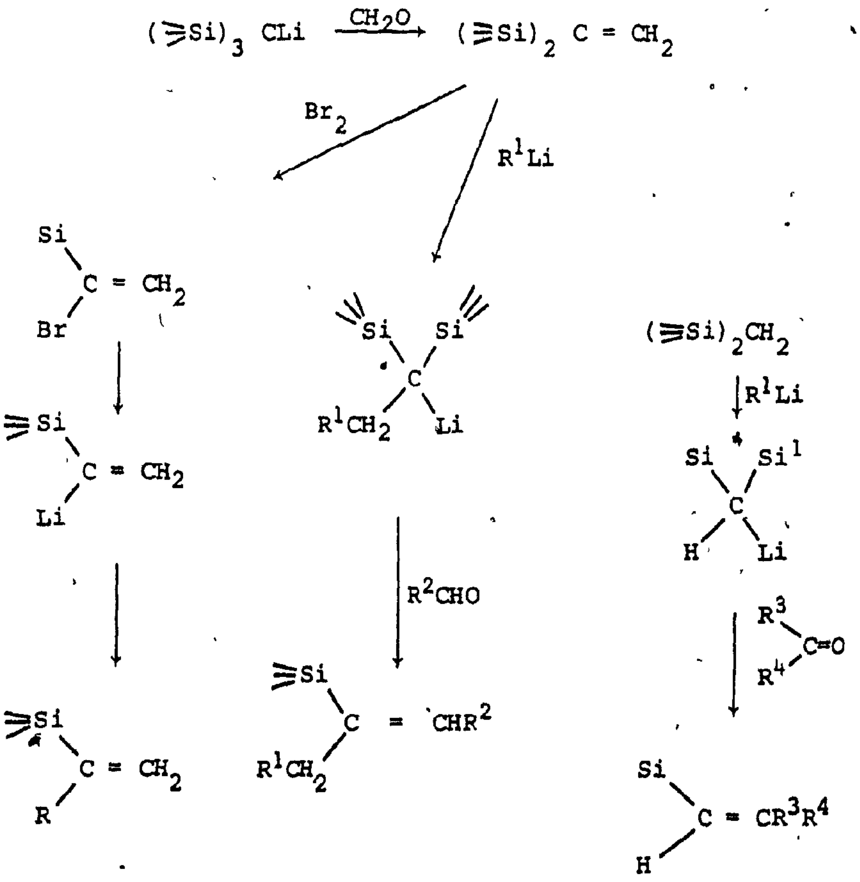
The methods developed initially for the synthesis of vinylsilanes all started with alkyl or arylacetylenes. The addition of trialkylsilane to a terminal acetylene, with the aid of a catalyst, has been used[116]. Alternatively, a terminal acetylene is first transformed into a



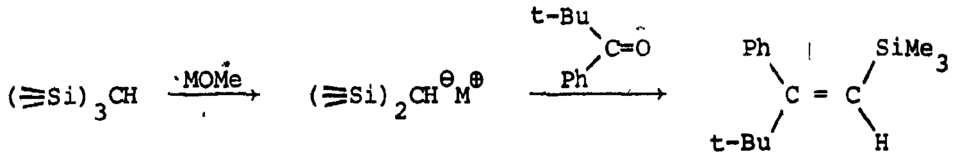
trialkylsilylacetylene which is then semihydrogenated to give the Z-vinylsilane[104,108].



These methods, while useful, are limited to the synthesis of monosubstituted vinylsilanes. Seebach[54] has developed a method for the synthesis of mono- and disubstituted vinylsilanes in good yield. The method is apparently applicable to a wide variety of systems. The drawback of this method is that there is no stereoselectivity in the products.



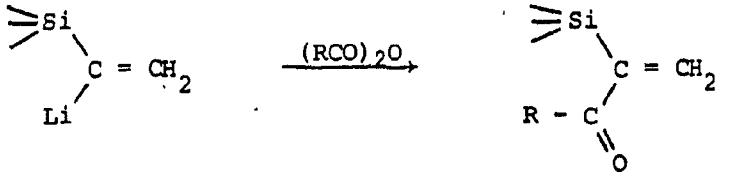
Sakurai et al.[48] have developed a method similar to that of Seebach[54]. When this was applied to the synthesis of 67, the authors



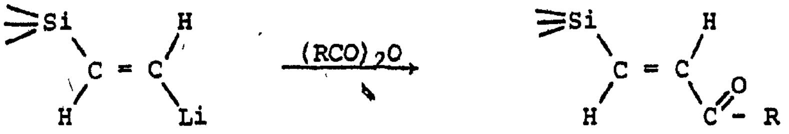
67

reported that they obtained only one geometric isomer. This is, however, likely to be due to the choice of ketone employed and not necessarily applicable in general to other carbonyl compounds. It would be expected to be a non-stereoselective synthesis of vinylsilanes as is Seebach's[54] method.

Brook[53] has described the synthesis of silylsubstituted α,β-unsaturated ketones (68 and 69). Cunico[117] has extended this work

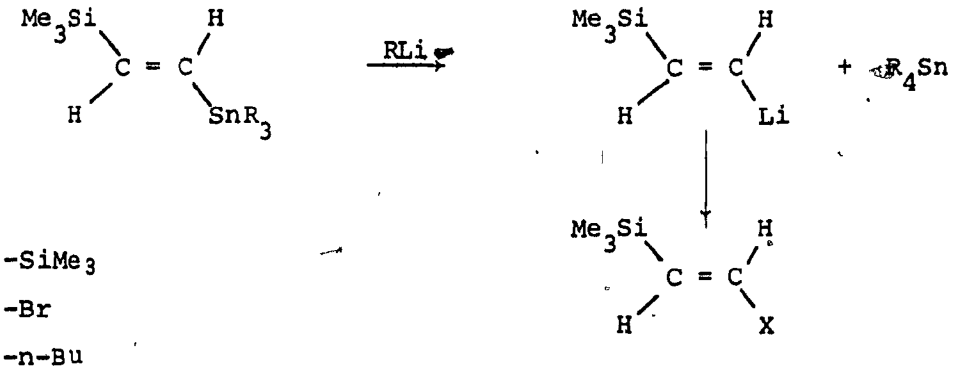


68



69

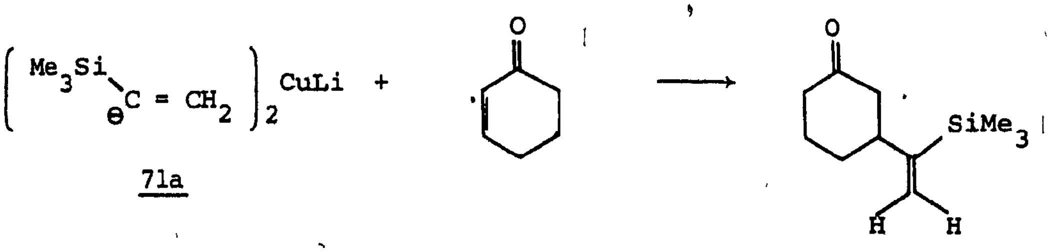
and found he could make also a number of other functionalized compounds of that general structure 70.



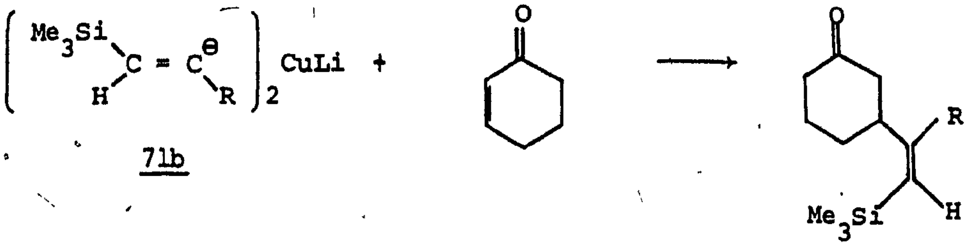
X = $-SiMe_3$
= $-Br$
= $-n-Bu$
= $-CO_2H$

70

Vinylsilanes have also been generated from α,β-unsaturated ketones[105]. Here, the vinylsilane is formed by conjugate addition of bis-trimethylsilylvinylcopper lithium reagent (71) to an α,β-unsaturated ketone. The vinylsilane has subsequently been epoxidized and treated with acid to give a dicarbonyl product.

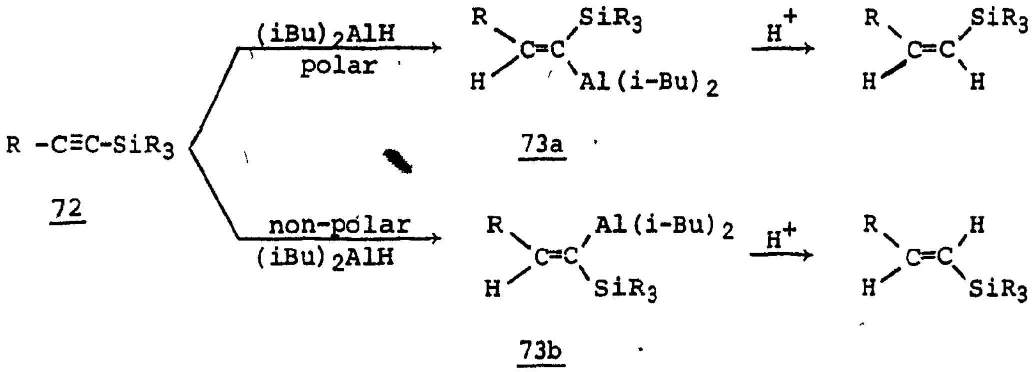


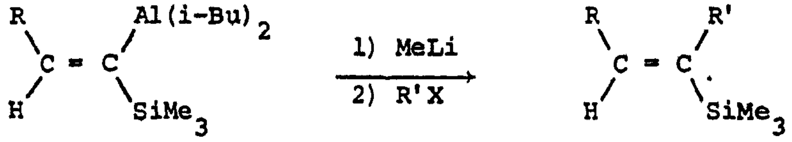
71a



71b

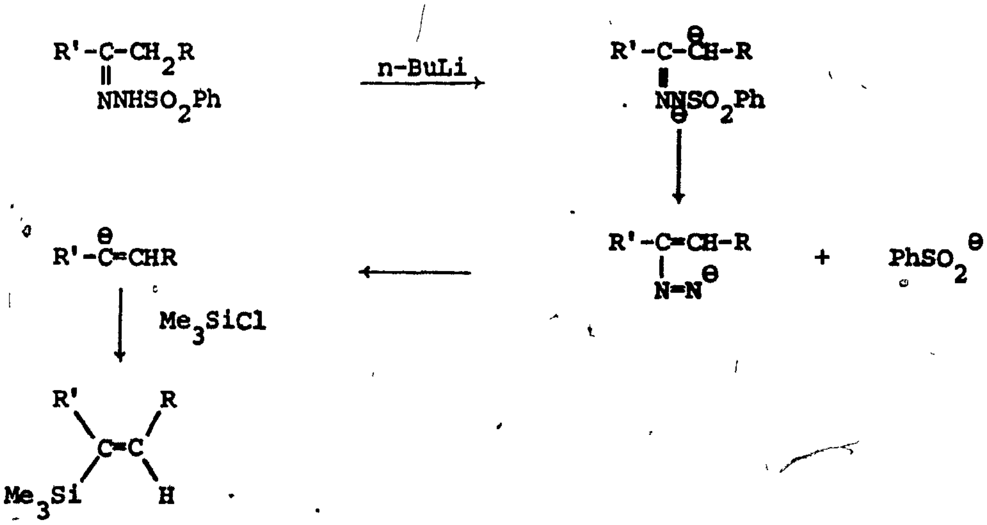
For the stereoselective synthesis of vinylsilanes, one of the methods involved[104-108] hydroalumination of the silylacetylenes 72 to give the vinylaluminum compounds 73, which on treatment with water or dilute acid yielded monosubstituted vinylsilanes[118-120]. The advantage of this method of semihydrogenation is that both cis and trans addition products can be obtained stereospecifically by simply changing solvents. Subsequently, two groups, Eisch[121] and Utimoto[122], have reported the reductive alkylation of trialkylsilylacetylenes using this hydralumination reaction. Both groups found that the hydralumination product 73 could be readily alkylated by treatment first with an alkyllithium, followed by an alkyl or arylhalide. This reaction yields vinylsilanes of high stereochemical purity (> 95%) of either E or Z isomer.





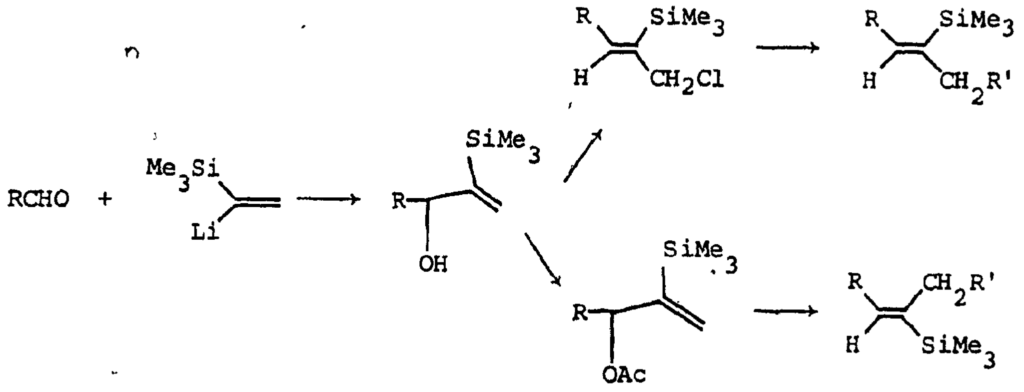
The reaction would then seem to be a very useful method of stereoselective synthesis of disubstituted vinylsilanes. However, there is a shortcoming. Both Eisch[121] and Utimoto[122] mentioned that the reductive alkylation of the vinylaluminum 73 occurs readily only for allylic or aromatic halides. In the case of simple alkyl halides the reaction is poor and low yields result.

Chan et al. have reported a method of synthesizing vinylsilanes from benzenesulfonylhydrazones[123]. This reaction appears to be clean



and simple and gives stereoselectively (> 90%) the Z-isomer. The same method has been developed independently by Paquett and his group[136].

The method developed in section (b) of this chapter thus offers another stereoselective synthesis of disubstituted vinylsilanes.



This method has the advantages of (1) using readily available starting materials (aldehydes), (2) high stereoselectivity (85-100%), and (3) high overall yields (65-70% based on aldehyde) of vinylsilanes. Also, there appears to be few restrictions on the type of alkyl or aryl substituents on the vinylsilane.

CHAPTER VI

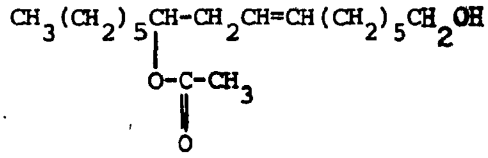
STEREOSELECTIVE SYNTHESIS OF THE SEX PHEROMONE OF THE GYPSY MOTH (DISPARLURE)

(a) Sex Pheromone of the Gypsy Moth

The gypsy moth, Porthetria dispar (L.), is a serious despoiler of forest, fruit and shade trees in the northeastern United States. The gypsy moth was introduced into the U.S.A. about a century ago by a French naturalist who wanted to use the insect to start a silk-producing industry in New England. Some species of the insect escaped from his laboratory and a plea to local authorities to eradicate the pest went unheeded. Since that time the gypsy moth has become a serious pest, affecting large areas with serious consequences. In more recent times, DDT has been used as a very effective control; however, environmental considerations have deemed DDT to be unattractive.

A more attractive method of control has been developed more recently. The male moth is attracted to the virgin female by means of a substance secreted from her abdominal glands. The use of traps baited with crude extracts of these glands is the best known means of detecting infestations by the insect. Control measures are then applied in specific areas of high concentrations of gypsy moths thus preventing defoliation and migration to new territory. Insecticide is applied only to areas as needed, therefore residues are kept to a minimum[124]. Indeed, use of the pheromone itself as a biological control can be developed thus eliminating insecticides completely.

For over thirty years research has been underway to isolate and identify the sex attractant of the gypsy moth. In 1960 Jacobson et al.[125] isolated and identified the gypsy moth sex pheromone as cis-7-hexadecene-1,10-diol 10-acetate (gyptol) (74). Synthetic samples of 74 and its homolog, gyplure (cis-9-octadecene-1,12-diol 12-acetate), were found to be highly active as gypsy moth sex pheromone.



$$CH_3(CH_2)_5\underset{O-\underset{\underset{O}{\|}}{C}-CH_3}{\underset{|}{CH}}-CH_2CH=CH(CH_2)_5CH_2OH$$

74

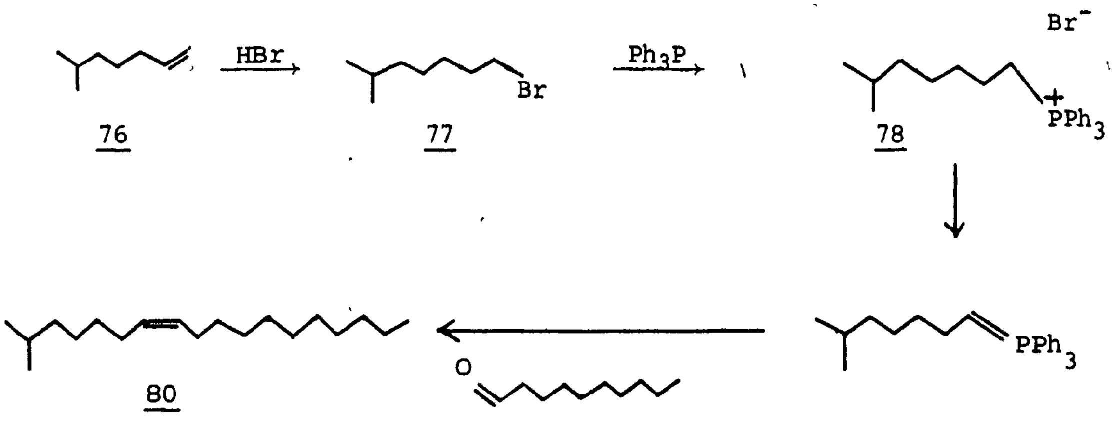
However, another preparation of these compounds by a second group[126] was found to be inactive. On re-investigation of the problem by Jacobson[127], these findings were confirmed and the reason for activity of the original gyptol preparation was attributed to the presence of trace amounts of another substance with extraordinarily high biological activity.

The problem was eventually resolved by Bierl and Beroza. They identified the gypsy moth sex pheromone as being cis-7,8-epoxy-2-methyloctadecane (disparlure) 75[128].

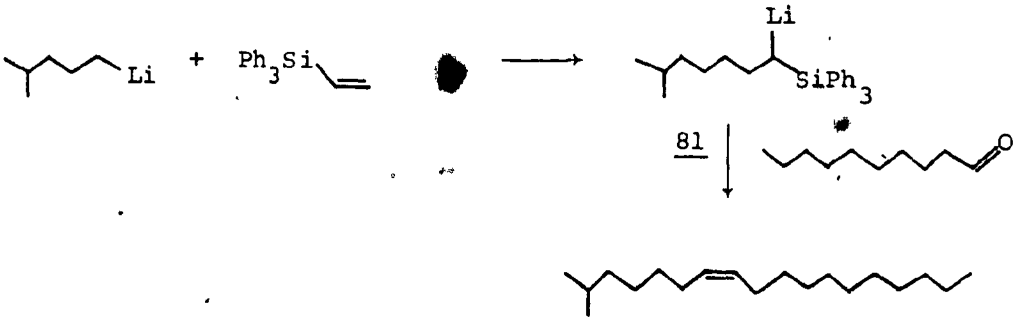
75

(b) Previous Methods of Synthesis of Gypsy Moth Sex Pheromone (Disparlure)

The original synthesis of the gypsy moth sex pheromone, disparlure, was via the Wittig reaction. Hydrogen bromide was added in an anti-Markownikoff fashion to 6-methyl-1-heptene 76 in the presence of benzoyl peroxide, to give 1-bromo-6-methylheptane 77. Reaction of 77 with triphenylphosphine in refluxing acetonitrile gave the phosphonium salt 78. The salt was converted to the ylid 79 by n-butyllithium in dry dimethylsulfoxide. The ylid 79, on reaction with undecanal, gave 2-methyl-7-octadecene 80 in an overall yield of 35%. The product was found to be 85% Z and 15% E. Epoxidation of the olefin gives disparlure 75. The reaction was later improved to give yields of 50-60% and isomeric purity of Z:E ≐ 94:6[129].



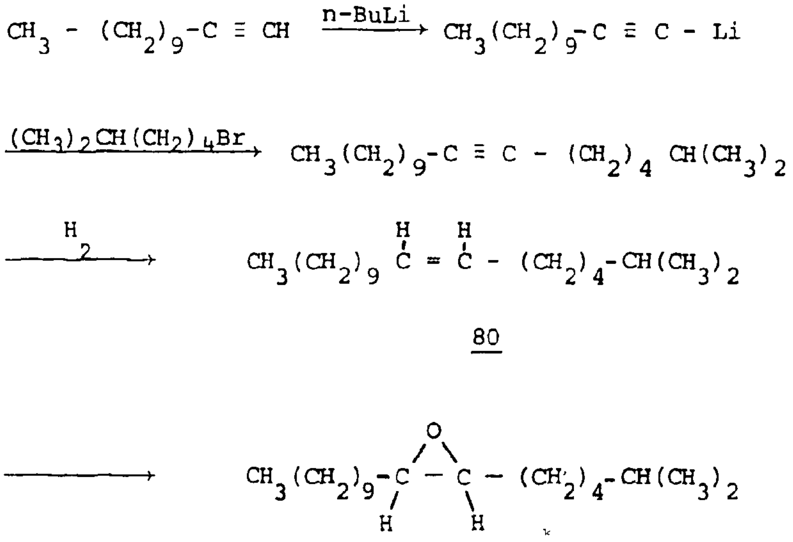
The silicon method of olefin synthesis has also been utilized to synthesize disparlure (75)[27]. In this case 4-methylpentyllithium reacted with triphenylvinylsilane to give the lithium salt 81.



80

Undecanal was then added to the mixture and on workup 80, 2-methyl-7-octadecene was isolated in 50% yield. Epoxidation of 80 gave disparlure 75. However, the product was a 50:50 mixture of cis and trans isomers. No stereoselectivity was obtained in the alkene forming step. Biological activity was, however, reasonably high even if the E isomer was present which has been found not to block the action of the Z isomer.

A further synthesis was developed which involved semi-hydrogenation of an acetylene[130,131]. Yields are good and the isomeric purity is high with Z:E = 96:4.



$$CH_3 - (CH_2)_9-C \equiv CH \xrightarrow{n\text{-BuLi}} CH_3(CH_2)_9-C \equiv C - Li$$

$$\xrightarrow{(CH_3)_2CH(CH_2)_4Br} CH_3(CH_2)_9-C \equiv C - (CH_2)_4\ CH(CH_3)_2$$

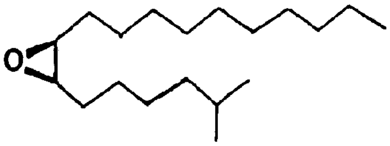
$$\xrightarrow{H_2} CH_3(CH_2)_9\ \overset{H}{C} = \overset{H}{C} - (CH_2)_4-CH(CH_3)_2$$

80

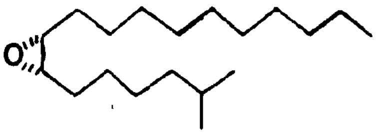
$$\longrightarrow CH_3(CH_2)_9-\overbrace{\underset{H}{C} - \underset{H}{C}}^{O} - (CH_2)_4-CH(CH_3)_2$$

75

The sex pheromone, disparlure, is expected to be optically active and indeed this is the case. Two groups have now reported on the synthesis of the two enantiomers of disparlure (82,83).[132,133].



82 (7R, 8S)
+

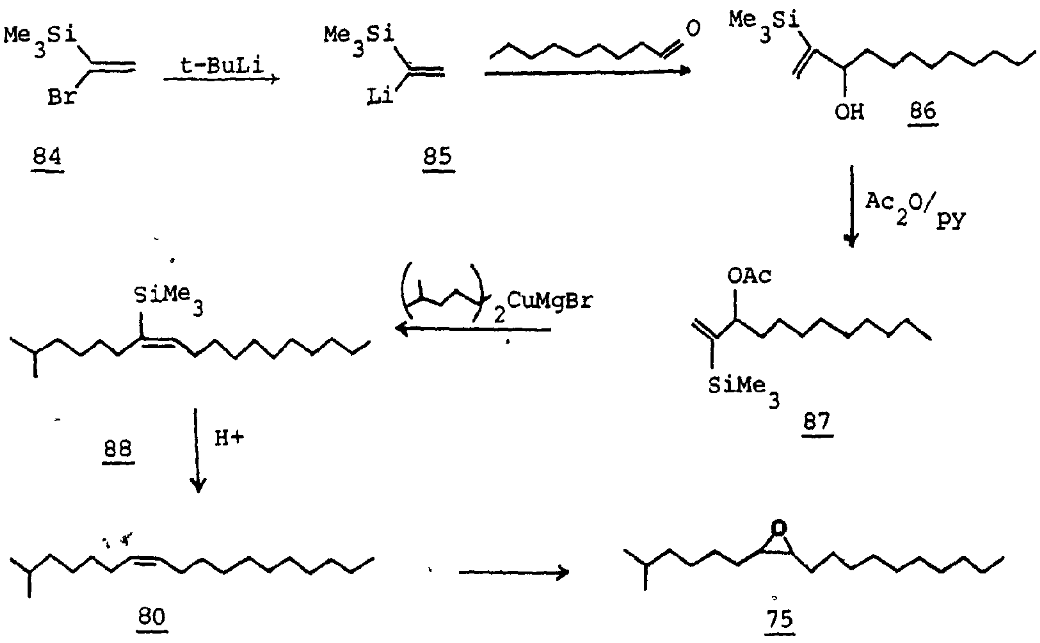


83 (7S, 8R)
-

It has been found that the 7R, 8S - enantiomer is much more effective as an attractant of the male gypsy moth than the 7S, 8R - enantiomer. Mixing the enantiomers to give the racemic mixture lowers the biological activity.

(c) The Present Synthesis

The method reported in Chapter V can now be applied to the stereoselective synthesis of disparlure. Thus, reaction of alpha-bromovinyltrimethylsilane (84) with t-butyllithium at -78°C afforded alpha-lithiovinyltrimethylsilane (85). Addition of undecanal to 85 gave in 80% yield the alcohol 86. Acetylation of 86 with acetic anhydride/pyridine gave 87 in quantitative yield. To a solution of 2-methylpentylmagnesium bromide in ether at 0°C, was added half-equivalent cuprous iodide. The mixture was warmed up to room temperature for 15 min. and then cooled to -78°C. To this mixture was added the



acetate 87 slowly. The mixture was allowed to warm to room temperature slowly with stirring for 16 hours. On workup, there was obtained in 82% yield the vinylsilane 88 (E:Z = 87:13), after purification by column chromatography on silica gel (hexane). Treatment of 88 with hydroiodic acid gave the olefin 80 in quantitative yield. Epoxidation of 80 gave disparlure in quantitative yield. The identity of the product was confirmed by comparison with the spectral data of an authentic sample kindly provided by Dr. Beroza. The isomeric purity of disparlure synthesized by this method has been found to be Z:E = 87:13, by both pmr and vpc analyses.

This new method of stereoselective synthesis of disparlure offers some attractive advantages to other methods which have been developed. Yields are higher by this method than those previously obtained from other pathways, starting materials are readily available and also inexpensive. The simplicity of operations makes this route attractive as a method of synthesis of disparlure, the sex pheromone of the gypsy moth.*

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* This work has been published: W. Mychajlowskij and T.H. Chan, Tetrahedron Letters, 4439 (1976).

CHAPTER VII

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 are uncorrected.

Infrared spectra were recorded on Perkin-Elmer Model 257 or Unicam SP1000 grating infrared spectrometers. Spectra were calibrated with the 1601 cm^{-1} band of a polystyrene film.

Nuclear magnetic resonance spectra (pmr) were recorded on Varian Associates T-60 or HA-100 or HR-220 spectrometers as indicated. Cmr spectra were recorded on a Bruker WH-90 spectrometer, at 22.628 MHz.

Mass spectra were recorded on an AE1-MS-902 Mass spectrometer. The operating conditons were a 70-ev electron energy, resolution of 1000 and 8 Kv accelerating voltage.

Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

Gas chromatographic (vpc) analyses were performed on an F & M Model 5751-A Research Chromatograph. Two 6' x $^1/_8$" stainless steel columns were used: 10% SE-30 Ultraphase on Chromosorb W A/W-DMCS, or 10% Apiezon-L on Chromosorb W A/W-DMCS.

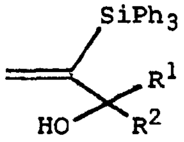
α-Bromovinyltriphenylsilane

The title compound was prepared according to the reported procedure[28,55] as follows:

To a solution of PhMgBr in 1.5 liter anhydrous ether (prepared from 1.65 mol PhBr and 1.7 mol Mg in 1.5 liter anhydrous ether) was added dropwise a solution of 0.5 mol of trichlorovinylsilane in 600 ml anhydrous ether over a period of 2 hrs. After the addition, the reaction was heated under reflux for another 40 hrs. The reaction mixture was hydrolysed with water and then dried with anhydrous $MgSO_4$. Removal of the solvent from the reaction mixture, followed by recrystallization from EtOH gave the desired vinyltriphenylsilane in 91% yield (m.p. = 70-72; lit[55] m.p. = 72).

To an ice-cooled solution of 0.45 mol vinyltriphenylsilane in 500 ml CCl_4, irradiated with a uv sun lamp, was added dropwise a solution of 0.45 mol Br_2 in 100 ml CCl_4, over a period of 1 - 2 hrs. After the addition, the mixture was stirred for 1/4 hr and the solvent was then removed. The resulting solid was added to 0.65 mol pyridine and the reaction mixture was heated under reflux for 2 hrs. The reaction mixture was poured into ice water. A ppt. formed which was filtered, washed with water and then recrystallized from EtOH to give α-bromovinyltriphenylsilane in 90% yield (m.p. = 132-134; lit[28] m.p. = 128-129).

1-Substituted-2-triphenylsilyl-2-propen-1-ols



The titled alcohols were prepared from the reaction of α-silylvinyl carbanions with appropriate carbonyl compounds. The carbanion was generated by the metal-halogen exchange reaction[28] of α-bromovinyltriphenylsilane with n-butyllithium in dried ether at low temperature. Following is an illustrative procedure.

To a solution of 0.025 mol α-bromovinyltriphenylsilane in 60 ml anhydrous ether at -24° (dry ice - CCl_4 bath) under a N_2 atmosphere was added slowly, by means of a syringe, a solution of 0.025 mol n-butyllithium. The resulting mixture was kept stirred at the same temperature for 1-$^1/_2$ hrs. A solution of 0.025 mol carbonyl compound in 10 ml dried ether was added. The reaction mixture was stirred at -24°C for 5 hrs then stirring was continued overnight at room temperature. The reaction mixture was poured into 50 ml 10% HCl, and the organic phase was extracted, dried and evaporated to give the desired alcohol in good yield.

a) 1-Phenyl-2-triphenylsilyl-2-propen-1-ol (18a, R^1=H, R^2=C_6H_5):

(recrystallized from pet. ether 30-60°) m.p. 84-5°; 75% yield.

ir (KBr) 3580, 1435, 1115, 700 cm^{-1};

pmr ($CDCl_3$) δ 1.8 (s, 1H), 5.5 (t, 1H), 5.8 (t, 1H), 6.2 (t, 1H), 7.2-7.8 (m, 20H);

Ms, m/e (intensity): 392(0.5), 375(2), 374(5), 315(17), 314(37), 313(52), 260(17), 259(70), 208(9), 200(20), 199(100), 183(11), 182(16), 181(24), 180(7), 116(15), 115(12), 107(12), 105(19), 80(12), 79(10), 78(14).

Anal. Calcd. for $SiC_{27}H_{24}O$: C, 82.62; H, 6.16

found: C, 82.60; H, 6.22.

b) 1,1-Diphenyl-2-triphenylsilyl-2-propen-1-ol (18b, $R^1=R^2=C_6H_5$):

(recrystallized - pet. ether 30-60°) m.p. 108.5-109.5°; 80% yield.

ir (KBr) 3580, 1435, 1115, 700 cm^{-1};

pmr ($CDCl_3$) δ 2.6 (s, 1H), 5.7 (d, 1H), 5.9 (d, 1H), 7.2-7.8 (m, 25H);

Ms, m/e (intensity): 468(1), 392(18), 393(43), 314(5), 313(7), 286(18), 260(6.5), 259(27), 200(20), 199(100), 192(18), 191(12), 184(14), 183(80), 182(11), 181(20), 115(10), 105(72), 78(11), 77(37).

Anal. Calcd. for $SiC_{33}H_{23}O$: C, 84.57; H, 6.02

found: C, 84.54; H, 6.06.

c) 2-Triphenylsilyl-1-tridecen-3-ol (18c, $R^1=H$, $R^2=n-C_{10}H_{21}$):

Cooled only 1 hr instead of 5 hrs after adding carbonyl compound.

Not recrystallized; 75% yield.

ir (CCl_4) 3580, 1435, 1115, 700 cm^{-1};

pmr (CCl_4) δ 0.9-1.6 (m, 22H), 4.2 (m, 1H), 5.5 (m, 1H), 6.2 (m, 1H), 7.2-7.8 (m, 15H);

Ms, m/e (intensity): 456(0.7), 439(7), 438(13), 380(3), 379(10), 378(4), 377(4), 276(6), 259(100), 237(20), 200(20), 199(100), 183(30), 181(20).

Exact mass; calcd. for $SiC_{31}H_{40}O$: 456.285

found: 456.280.

d) 3,7-Dimethyl-2-triphenyl-1,6-octadien-3-ol (18d, R^1=CH_3, R^2= $-(CH_2)_2CH{=}C(CH_3)_2$):

Cooled only 1 hr after adding carbonyl compound rather than 5 hrs.

Not recrystallized; 75% yield.

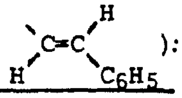
pmr (CCl_4) δ 0.9-2.5 (m, 14H), 5.0 (m, 1H), 5.6 (d, 1H), 6.0 (d, 1H), 7.2-7.8 (m, 15H).

e) 1-Hydroxycychohexyl-1-triphenylsilylethylene (18c, R^1,R^2= c-C_5H_{10}):

Cooled only 1 hr after adding carbonyl compound rather than 5 hrs.

Not recrystallized; 75% yield.

pmr (CCl_4) δ 0.9-2.4 (m, 1H), 5.5 (d, 1H), 6.00 (d, 1H), 7.2-7.8 (m, 15H).

f) E-1-Phenyl-4-triphenylsilyl-1,4-pentadien-3-ol (18f, R^1=H, R^2= ):

Not recrystallized; 80% yield.

ir (CCl_4) 3580, 1435, 1115, 700 cm^{-1};

pmr (CCl_4) δ 5.0 (m, 1H), 5.7-6.5 (m, 4H), 7.2-7.8 (m, 20H);

Ms, m/e (intensity): 418(2), 417(5), 416(4), 260(30), 259(100), 199(20), 183(12), 181(16), 105(20).

Exact mass: calcd. for $SiC_{29}H_{26}O$: 418.175

found: 418.174

g) 2-Triphenylsilyl-1-buten-3-ol (18g, R^1=H, R^2=CH_3):

Not recrystallized; 75% yield.

pmr (CCl_4) δ 1.05 (d, J=6Hz, 3H), 1.9 (s, 1H), 4.4 (q, J=6Hz, 1H), 5.5 (d, 1H), 6.1 (d, 1H), 7.2-7.8 (m, 15H).

h) 2-Triphenylsilyl-1-propen-3-ol (18h, R^1=R^2=H):

Recrystallized from EtOH, m.p. 98-104°, 73% yield.

pmr ($CDCl_3$) δ 1.5 (s, 1H), 4.25 (m, 2H), 5.55 (m, 1H), 6.15 (m, 1H), 7.2-7.8 (m, 15H).

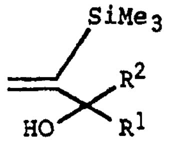
α-Bromovinyltrichlorosilane

The title compound was prepared according to the reported procedure[95] as follows:

To a solution of 0.5 mol trichlorovinylsilane in 500 ml CCl_4 irradiated with a daylight lamp was added dropwise a solution of 0.5 mol Br_2 in 100 ml CCl_4 over a period of 1 - 2 hours. Occasional cooling was necessary as the reaction was highly exothermic. After the addition, the mixture was stirred for an hour, and the solvent was then removed. To the solvent-free mixture was added slowly 0.65 mol quinoline, and the reaction mixture was distilled at reduced pressure to give α-bromovinyltrichlorosilane in 82% yield (b_{53}=70-1°; lit[95] b_{749}=145.5°).

To a solution of CH_3MgI in 1.5 liter anhydrous ether (prepared from 1.5 mol CH_3I and 37 g Mg in 1.5 liter anhydrous ether) was added dropwise a solution of 0.4 mol of α-bromovinyltrichlorosilane in 500 ml anhydrous ether over a period of 2 hrs. After the addition, the reaction mixture was heated under reflux for another 5 hrs. The reaction mixture was hydrolysed with water, and then dried with anhydrous $MgSO_4$. Removal of the solvent from the reaction mixture, followed by fractional distillation at reduced pressure, gave the desired α-bromovinyltrichlorosilane in 70% yield (b_{67}=56-7°; lit[95] b_{41}=47-8°).

1-Substituted-2-trimethylsilyl-2-propen-1-ols



The titled alcohols were prepared from the reaction of α-trimethylsilylvinyl carbanion with appropriate carbonyl compounds. The carbanion was generated by metal-halogen exchange reaction[28,53,54] of α-bromovinyltrimethylsilane with tert-butyllithium in anhydrous ether at low temperature. Following is an illustrative procedure.

To a solution of 0.05 mol α-bromovinyltrimethylsilane in 150 ml anhdrous ether at -78° under a N_2 atmosphere, was added slowly by means of a syringe a solution of 0.052 mol tert-butyllithium in pentane. The resulting mixture was kept well stirred at the same temperature for 2 hours. A solution of 0.05 mol carbonyl compound in 10 ml anhydrous ether was added. The reaction mixture was stirred at -78° for another hour and was then allowed to warm up to room temperature by itself. After hydrolysis (50 ml water) and drying with anhydrous $MgSO_4$, the reaction mixture was reduced in volume in vacuo and fractionally distilled at low pressure to give the desired alcohol in good yield.

a) 1-Phenyl-2-trimethylsilyl-2-propen-1-ol (28a, R^1=H, R^2=C_6H_5):

b.p. 82-84/0.9 mm; 80% yield.

pmr (CCl_4) δ 0.15 (s, 9H), 3.7 (s, 1H), 5.5 (m, 1H), 6.0 (AB, 2H), 7.6 (s, 5H).

b) 1,1-Diphenyl-2-trimethylsilyl-2-propen-1-ol (28b, R^1=R^2=C_6H_5):

Not distilled; 80% yield.

pmr (CCl_4) δ 0.2 (s, 9H), 3.0 (s, 1H), 5.5 (AB, 2H), 7.4 (s, 10H).

c) 2-Trimethylsilyl-1-tridecen-3-ol (28c, R^1=H, R^2-n-$C_{10}H_{21}$):

b.p. 118-9°/0.03 mm; 75% yield.

ir (neat) 3450, 2950, 1250, 850 cm^{-1};

pmr (CCl_4) δ 0.1 (s, 9H), 0.7-1.7 (m, 21H), 1.9 (s, 1H), 4.15 (t, J=6Hz, 1H), 5.5 (AB, 2H);

Ms, m/e (intensity): 270(3), 241(4), 201(6), 179(2), 157(21), 144(45), 129(13), 113(34), 96(7), 95(5), 85(7), 83(5), 82(6), 81(8), 75(100), 73(90), 73(90), 55(14), 54(16), 43(18), 41(19).

Anal. Calcd. for $SiC_{16}H_{34}O$: C, 71.03; H, 12.67

found: C, 71.11; H, 12.78.

d) 1-Cyclohexyl-2-trimethylsilyl-2-propen-1-ol (28d, R^1=H, R^2=c-C_6H_{11}):

b.p. 64-6°/0.025 mm; 75% yield.

ir (neat) 3400, 2920, 2850, 1450, 1250, 850 cm^{-1};

pmr (CCl_4) δ 0.2 (s, 9H), 0.8-2.5 (m, 12H), 3.85 (d, J=5Hz, 1H), 5.45 (AB, 2H).

e) 4-Methyl-2-trimethylsilyl-1-penten-3-ol (28e, R^1=H, R^2= -CH$(CH_3)_2$):

b.p. 82-4°/16 mm; 76% yield.

ir (neat) 3420, 2950, 1250, 850 cm^{-1};

pmr (CCl_4) δ 0.1 (s, 9H), 0.9 (d, J=7Hz, 6H), 1.5-2.0 (m, 2H), 3.85 (d, J=7Hz, 1H), 5.55 (AB, 2H).

f) 2-Trimethylsilyl-2-propen-1-ol (28f, R^1=R^2=H):

b.p. 74-5°/30 mm; 65% yield.

pmr (CCl_4) δ 0.0 (s, 9H), 3.95 (s, 1H), 4.1 (m, 2H), 5.5 (AB, 2H).

Anal. Calcd. for $SiC_6H_{14}O$: C, 55.32; H, 10.83

found: C, 55.44; H, 10.92.

g) 3,7-Dimethyl-2-trimethylsilyl-1,6-octadien-3-ol (28g, R^1=CH_3, R^2= -$(CH_2)_2$CH=C$(CH_3)_2$):

b.p. 120-2°/9 mm; 80% yield.

ir (neat) 3460, 2950, 1250, 850 cm^{-1};

pmr (CCl_4) δ 0.15 (s, 9H), 1.2 (s, 3H), 1.2-2.1 (m, 11H), 5.0 (m, 1H), 5.4 (AB, 2H).

Ms, m/e (intensity): 226(6), 208(9), 193(5), 155(10), 152(7), 128(16), 127(79), 111(14), 93(22), 75(75), 73(100), 69(40).

Exact mass - Calcd. for $SiC_{13}H_{26}O$: 226.1753

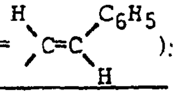
found: 226.1749

(±.0004)

h) 1-Hydroxycyclohexyl-1-trimethylsilylethylene (28h, R^1R^2=cyclo-C_5H_{10}):

Not distilled; 75% yield.

pmr (CCl_4) δ 0.15 (s, 9H), 1.2-2.4 (m, 12H), 5.4 (AB, 2H).

i) E-1-Phenyl-4-trimethylsilyl-1,4-pentadien-3-ol (28i, R^1=H, R^2=  $\overset{H}{\diagdown}\!C{=}C\!\overset{C_6H_5}{\diagup}$ $\underset{\diagup}{}\quad\underset{H}{\diagdown}$):

Not distilled; 75% yield.

pmr (CCl_4) δ 0.2 (s, 9H), 4.85 (m, 1H), 5.6 (AB, 2H), 6.15 (AB, 2H), 7.0-7.3 (m, 5H).

j) 3-Trimethylsilyl-3-buten-2-ol (28j, R^1=H, R^2=CH_3):

b.p. 69-71°/21 mm; 65% yield.

ir (neat) 3220, 2940, 1250, 840 cm^{-1};

pmr (CCl_4) δ 0.1 (s, 9H), 1.15 (d, J=7Hz, 3H), 3.0 (s, 1H), 4.3 (q, J=7Hz, 1H), 5.45 (AB, 2H).

Anal. Calcd. for $SiC_7H_{16}O$: C, 58.83; H, 11.18

found: C, 58.69; H, 11.03.

k) 4,4-Dimethyl-2-trimethylsilyl-1-penten-3-ol (28k, R^1=H, R^2= $-C(CH_3)_3$):

b.p. 69-71°/5 mm; 79% yield.

pmr (CCl_4) δ 1.5 (s, 9H), 0.8 (s, 9H), 3.8 (s, 1H), 5.45 (AB, 2H).

Reaction of 1-Substituted-2-triphenylsilyl-2-propen-1-ols with Thionyl Chloride in Carbon Tetrachloride

To a solution of 50 mmol of alcohol 18 in 40 ml CCl_4 at room temperature was added dropwise a solution of 7.1 g of $SOCl_2$ (20% excess) in 20 ml CCl_4. The reaction was exothermic, and an ice bath was used occasionally to cool down the reaction mixture to below room temperature. Although the reaction was completed in ca. half-an-hour, the reaction mixture was generally kept well stirred for another two hours before workup. The solvent was evaporated under vacuo to give an oil. Alcohol 18a gave the chloride 23, all other alcohols 18b, c and d gave mixtures of 23 and 24, 24 being the major isomer. All reactions appeared to give quantitative yield of products.

a) 1-Chloro-1-phenyl-2-triphenylsilyl-2-propene (23):

(Recrystallized from diethyl ether). m.p. 148-149°.

ir (KBr) 3080, 1435, 1115, 700 cm^{-1};

pmr ($CDCl_3$) δ 5.85 (AB, 2H), 6.7 (t, J=1.5 Hz, 1H), 7.1 (s, 5H), 7.1-7.8 (m, 15H).

Anal. Calcd. for $SiC_{27}H_{23}Cl$: C, 78.91; H, 5.64

found: C, 78.54; H, 5.68.

b) 3-Chloro-1-phenyl-2-triphenylsilyl-1-propene (24a R^1=H, R^2=C_6H_5):

(Recrystallized from diethyl ether). m.p. 148-149°.

pmr ($CDCl_3$) δ 4.25 (s, 2H), 6.6 (m, 1H), 7.0-7.8 (m, 20H).

Ms, m/e (intensity): 410(6), 343(6), 332(10), 296(6), 260(39), 259(100), 227(14), 220(11), 219(35), 218(18), 217(83), 208(11), 193(11), 192(20), 183(22), 182(25), 181(55), 180(18), 155(14), 154(11), 135(14), 121(11), 120(16), 116(27), 115(27), 107(11), 100(11), 105(42).

Anal. Calcd. for $SiC_{27}H_{23}Cl$: C, 78.91; H, 5.64

found: C, 78.63; H, 5.60.

c) 3-Chloro-1,1-diphenyl-2-triphenylsilyl-1-propene (24b, R^1=R^2=C_6H_5):

m.p. 147-148°.

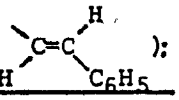
ir (KBr) 3080, 1435, 1115, 700 cm^{-1};

pmr (CCl_4) δ 4.2 (s, 2H), 6.6-7.8 (m, 25H).

d) 1-Chloro-2-triphenylsilyl-2-tridecene (24c, R^1=H, R^2=n-$C_{10}H_{21}$):

(Not recrystallized).

pmr (CCl_4) δ 0.9-2.1 (m, 21H), 4.15 (s, 2H), 6.85 (t, J=8 Hz, 1H), 7.2-7.8 (m, 15H).

e) 5-Chloro-1-phenyl-4-triphenylsilyl-1,3-pentadiene (24f, R^1=H, R^2=  $-CH=CH-C_6H_5$):

(Not recrystallized.)

pmr (CCl_4) δ 4.19 (s, 2H), 6.4-7.8 (m, 23H).

Reaction of 1-Substituted-2-trimethylsilyl-2-propen-1-ols with Thionyl Chloride in Ether

To a solution of 50 mmol of the alcohol 28 in 40 ml Et_2O at room temperature was added dropwise a solution of 7.1 g of $SOCl_2$ (20% excess) in 20 ml Et_2O. The reaction was exothermic, and an ice bath was used occasionally to cool the reaction mixture to below room temperature. The reaction mixture was kept well-stirred for two hours. Analysis of the reaction mixture by pmr spectroscopy revealed virtually one chloride 29 with allylic rearrangement. The reaction mixture was fractionally distilled at reduced pressure to give the chloride 29 in good yield.

a) 3-Chloro-1-phenyl-2-trimethylsilyl-1-propene (29a, $R^1=C_6H_5$):

b.p. 89-90°/1.5 mm; 79% yield.

pmr (CCl_4) δ 0.2 (s, 9H), 4.2 (s, 2H), 6.8 (s, 1H), 7.0-7.4 (m, 5H).

Anal. Calcd. for $SiC_{12}H_{17}Cl$: C, 64.11; H, 7.62

found: C, 63.95; H, 7.54.

b) 1-Chloro-2-trimethylsilyl-2-tridecene (29c, $R^1=n\text{-}C_{10}H_{21}$):

b.p. 90-100°/0.05 mm; 79% yield.

pmr spectrum #1

pmr (CCl_4) δ 0.22 (s, 9H), 0.7-2.3 (m, 21H), 3.9 (s, 2H), 6.28 (t, J=8Hz, 1H).

Anal. Calcd. for $SiC_{16}H_{33}Cl$: C, 66.50, H, 11.51

found: C, 66.84, H, 11.58.

c) 3-Chloro-1-cyclohexyl-2-trimethylsilyl-1-propene (29d, R^1=cyclo-C_6H_{11}):

b.p. 66-7°/0.35 mm; 75% yield.

ir (neat) 2920, 2840, 1610, 1450, 1250, 850 cm^{-1};

pmr spectrum #2

pmr (CCl_4) δ 0.22 (s, 9H), 0.7-2.3 (m, 1H), 4.0 (s, 2H), 6.08 (d, J=10Hz, 1H).

Anal. Calcd. for $SiC_{12}H_{23}Cl$: C, 62.43; H, 10.04

found: C, 62.31; H, 10.01.

d) 1-Chloro-4-methyl-2-trimethylsilyl-2-pentene (29e, R^1= $-CH(CH_3)_2$):

b.p. 73-5°/12 mm; 88% yield.

pmr spectrum #3

pmr (CCl_4) δ 0.22 (s, 9H), 1.05 (d, J=7Hz, 6H), 2.6 (m, 1H), 4.05 (s, 2H), 6.08 (d, J=10Hz, 1H).

Anal. Calcd. for $SiC_9H_{19}Cl$: C, 56.66; H, 10.04

found: C, 56.81; H, 10.13.

e) Reaction of 4,4-Dimethyl-2-trimethylsilyl-1-penten-3-ol with thionyl chloride in ether, gave a mixture of chlorides 41a, b and c in ratio of 13:52:35%.

b.p. 89-91°/14 mm; 80% yield.

ir (neat) 2850-3000, 1600, 1250, 850 cm^{-1};

pmr - see spectrum #7

Reaction of 1-Substituted-2-silyl-2-propen-1-ols with Acetic Anhydride/Pyridine

To a solution of 50 mmol of the alcohol 18 or 28 in 10 ml of pyridine at room temperature was added dropwise 5.0 g of acetic anhydride (10% excess). The reaction was exothermic. The mixture was heated under reflux for 2 hrs, cooled, and poured into 20 ml of water. The reaction mixture was extracted with 2 x 20 ml of ether. The ether solution was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give the corresponding acetates in quantitative yields.

Reaction of 1-Substituted-2-silyl-2-propen-1-ol Anions with Acetyl Chloride

The procedure outlined for the preparation of the alcohols is followed except prior to work-up 5.0 g of acetyl chloride (10% excess) are added and stirred 30 min. Work-up is identical to that of the alcohols. Yields identical to alcohol yield.

a) 3-Acetoxy-3-phenyl-2-triphenylsilyl-1-propene (19a):

(Recrystallized from hexane) m.p. 90-91°

ir (KBr) 1750 cm^{-1};

pmr (CCl_4) δ 2.1 (s, 3H), 5.75 (m, 1H), 6.1 (m, 1H), 6.45 (m, 1H), 7.15 (s, 5H), 7.15-7.8 (m, 15H).

b) 3-Acetoxy-3-cyclohexyl-2-trimethylsilyl-1-propene (55a):

b.p. 76-78°/0.1 mm;

ir (neat) 2920, 2840, 1740, 1250, 850 cm^{-1};

pmr (CCl_4) δ 0.18 (s, 9H), 0.9-1.9 (m, 11H), 1.95 (s, 3H), 5.05 (d, J=6Hz, 1H), 5.5 (AB, 2H).

Ms, m/e (intensity): 254(<1), 194(10), 179(22), 171(3), 151(3), 133(4), 131(5), 130(5), 129(6), 120(13), 117(100), 114(24), 75(24), 73(35).

c) 3-Acetoxy-4-methyl-2-trimethylsilyl-1-pentene:

b.p. 54-6°/0.75 mm.

pmr (CCl_4) δ 0.18 (s, 9H), 0.88 (d, J=7Hz, 6H), 1.85 (m, 1H), 2.05 (s, 3H), 5.1 (d, J=7Hz, 1H), 5.6 (AB, 2H).

d) 3-Acetoxy-2-trimethylsilyl-1-tridecene:

b.p. 104-106°/0.1 mm;

ir (neat) 2920, 2840, 1740, 1245, 845 cm^{-1};

pmr (CCl_4) δ 0.18 (s, 9H), 0.7-2.3 (m, 21H), 2.0 (s, 3H), 5.35 (m, 1H), 5.55 (AB, 2H).

Reaction of 1,1-Diphenyl-2-triphenylsilyl-2-propen-1-ol with Acetic acid/Sodium Acetate

A solution of 0.33 g of 18b in 10 ml of acetic acid saturated with sodium acetate was heated to 90°C for a half-hour. The reaction mixture was poured into 20 ml of water, extracted with 2 x 10 ml ether, dried with anhydrous $MgSO_4$ and evaporated in vacuo to give a solid 19b. It was recrystallized from EtOH to give 3-Acetoxy-1,1-diphenyl-2-triphenylsilyl-1-propene, m.p. 164-167°.

ir (KBr) 3050, 1750, 1435, 1250, 1115, 1040, 700 cm^{-1};

pmr ($CDCl_3$) δ 1.6 (s, 3H), 4.80 (s, 2H), 6.6-7.8 (m, 25H).

Anal. Calcd. for $SiC_{35}H_{30}O_2$: C, 82.28; H, 5.92

found: C, 82.27; H, 5.93

Reaction of 1-Substituted-2-silyl-2-propen-1-ols with Trifluoroacetic Anhydride/Pyridine

To a solution of 50 mmol of the alcohol 18 or 28 in 10 ml pyridine at 0° were added dropwise 12 g of trifluoroacetic anhydride (10% excess). The reaction mixture was stirred at room temperature for 2 hrs, poured into 20 ml of water and extracted with 2 x 20 ml of ether. The organic solution was drived over anhydrous $MgSO_4$ and evaporated in vacuo to give the corresponding acetates in quantitative yield. No further purification of these compounds was undertaken.

a) 1-Trifluoroacetoxy-1-phenyl-2-triphenylsilyl-2-propene (20a):

ir (CCl_4) 1780 cm^{-1};

pmr (CCl_4) δ 5.95 (m, 1H), 6.35 (m, 1H), 6.55 (m, 1H), 7.2-7.8 (m, 20H).

b) 1-(α-Trifluoroacetoxycyclohexyl)-1-Triphenylsilylethylene (20b):

ir (CCl_4) 1785 cm^{-1};

pmr (CCl_4) 0.9-2.5 (m, 11H), 5.85 (AB, 2H), 7.2-7.8 (m, 15H).

When the product 20b was dissolved in DMSO, heated on a steam bath to aid dissolving, a ppt. formed. The mixture was poured into water and extracted with ether. The ether solution was dried over $MgSO_4$ and evaporated in vacuo. Recrystallization of the residue from EtOH gave a solid 21, m.p. 89-93°. Possibly 1-Cyclohexenyl-1-Triphenylsilylethylene (21):

ir (KBr) 2920, 1435, 1115, 700 cm^{-1};

pmr ($CDCl_3$) 1-2.5 (m, 6H), 5.4 (d, J=2.5 Hz, 1H), 5.76 (m, 1H), 6.08 (d, J=2.5 Hz, 1H), 7.2-7.8 (m, 15H).

c) 3-Trifluoroacetoxy-3,7-dimethyl-2-triphenylsilyl-1,6-octadiene:

ir (CCl_4) 1760 cm^{-1};

pmr (CCl_4) δ 1.2-2.3 (m, 13H), 4.8 (m, 1H), 5.9 (AB, 2H), 7.2-7.8 (m, 15H).

Reaction of 1-Phenyl-2-triphenylsilyl-2-propen-1-ol with $BF_3 \cdot OEt_2$:

To a solution of 0.2 g of 18a in 5 ml of benzene was added one drop of $BF_3 \cdot OEt_2$. The mixture was stirred one hour, poured into 5 ml of 2N HCl, washed with 10 ml of water and dried over anhydrous $MgSO_4$. The mixture on evaporation in vacuo gave a solid, m.p. 170-175°. No allene formation was observed, according to the spectroscopic data of the product.

Reaction of 1-Phenyl-2-triphenylsilyl-2-propen-1-ol with PF_5:

To a solution of 0.2 g of 18a at -78°C was added via a bubbler, PF_5 for 2 mins. The reaction was stirred one hour at room temperature, poured into 5 ml water, dried over anhydrous $MgSO_4$ and evaporated in vacuo to give a solid. No allene formation was observed. The solid was identical to the product from the $BF_3 \cdot OEt$ reaction.

Reaction of 1,1-Diphenyl-2-triphenylsilyl-2-propen-1-ol (18b) with Para-toluenesulfonyl chloride:

To a suspension of 0.013 g NaH (excess) in 5 ml of ether was added 0.08 g of 18b. The mixture was stirred under reflux for 30 min. Para-Toluenesulfonyl chloride, 0.05 g (excess), was added. The mixture was stirred for 30 mins., poured into 10 ml water, washed with 5 ml of 10% $MaHCO_3$ solution and dried over anhydrous $MgSO_4$. After being evaporated in vacuo, the product was identified to be the chloride 24b.

Reaction of 3-Chloro-1-phenyl-2-triphenylsilyl-1-propene (24a) with KOH:

To a solution of 0.3 g of 24a in 5 ml DMSO was added 0.1 g KOH in 1 ml of H_2O. The mixture was stirred for 3 hrs., poured into 5 ml of water and extracted with 2 x 5 ml ether. The ether solution dried with anhydrous $MgSO_4$, evaporated under vacuo to give 1-phenylpropyne, identical in all respects to an authentic sample.

Fluoride Ion Promoted Elimination of Beta-functionalized Vinyl Silanes:

General Procedure:

To a solution of 0.02 mol of silane in 15-20 ml of solvent was added 0.025 mol of inorganic fluoride. The reaction mixture was stirred for the required length of time (Table VI), poured into 20 ml water, washed with 2 x 10 ml water, dried over anhydrous $MgSO_4$ and evaporated in vacuo. The product was subsequently purified by distillation under reduced pressure. All yields prior to purification appeared to be quantitative.

Synthesis of 1,2-Alkadienes from Carbonyl Compounds:

The carbonyl compounds were reacted with α-silylvinyl carbanions to give the alcohols 18 and 28 as previously described. The alcohols were used without purification for chlorination or trifluoroacylation, using procedures as described. Again, the products were not purified. Elimination with fluoride ion was carried out as outlined.

Typical procedure followed:

Synthesis of 1,2-tridecadiene:

To a solution of 8.8 g (0.024 m) of α-bromovinyltriphenylsilane in 60 ml anhydrous ether at -24°, an equal mole of n-butyl lithium was added slowly and stirred for 1-$^1/2$ hrs. An equal mole of undecanal in 10 ml ether was added slowly and the reaction mixture was stirred at -24° for one hour. The stirring was continued at room temperature overnight. The reaction mixture was poured into 50 ml of 10% HCl, and the organic phase was extracted and washed with 1 x 50 ml of water, dried over anhydrous

$MgSO_4$ and evaporated in vacuo to give the crude product <u>18c</u>. The crude alcohol was dissolved in 25 ml of CCl_4 and a 25% excess of thionyl chloride was added. The reaction was stirred for two hours and then evaporated in vacuo to give the crude chloride <u>24c</u>. The crude chloride was dissolved in DMSO (25 ml per gram Et_4NF) and Et_4NF was added (10% excess). The mixture was stirred for two hours at room temperature. The reaction mixture was portioned between 25 ml of ether and 25 ml of water. The ether phase was dried over $MgSO_4$ and evaporated in vacuo to give crude product. The crude product was treated with 10 ml of hexane and cooled. Filtration gave triphenylsilanol. Distillation of the filtrate gave 1,2-tridecadiene, b.p. 63-64°/0.1 mm Hg in 44% yield. Similar procedures were followed for the other allenes. For the trimethylsilyl adducts no hexane was used to ppt out trimethylsilanol.

Physical properties and yields reported in Tables III and V:

a) <u>Phenylpropadiene:</u>

Identical in all respects to authentic sample prepared, according to reported procedures[62].

b) <u>1,1-Diphenylpropadiene</u>

Identical in all respects to authentic sample prepared[63].

c) <u>1,2-Tridecadiene:</u>

ir(neat) 2950, 2880, 1960, 1475, 840 cm^{-1},

pmr (CCl_4) δ 0.75-2.25 (m, 21H), 4.6 (m, 2H), 5.05 (m, 1H).

d) E-1-Phenyl-1,3,4-pentatriene:

ir (neat) 3040, 1960, 1615, 1510, 970, 860, 760, 700 cm^{-1};

pmr (CCl_4) δ 4.9 (d, J=7Hz, 2H), 5.65-6.8 (ABC, 3H), 7.1-7.6 (m, 5H).

e) Vinylidenecyclohexane:

Prepared from trifluoroacetate (20b); 20% yield.

ir (neat) 2900, 2825, 1955, 1445, 850 cm^{-1};

pmr (CCl_4) δ 1.1-2.3 (m, 10H), 4.4 (m, 2H).

f) 3,7-Dimethyl-1,2,6-octatriene:

Prepared from trifluoroacetate; 20% yield.

ir (neat) 2900, 1955, 1445, 850, 760 cm^{-1};

pmr (CCl_4) δ 1.5 (s, 3H), 1.6 (s, 3H), 1.5-2.3 (m, 7H), 4.4 (m, 2H), 4.95 (m, 1H).

Cleavage of Vinyl-carbon-silicon bond by Fluoride Ion: Allylic Alcohols (31) formed following described procedure.

Yields and conditions used given in Table VI.

a) 1-Phenyl-2-propen-1-ol:

Identical in all respects to sample prepared from reaction of benzaldehyde with vinylmagnesium bromide; b.p. 89-90°/8 mm.

b) 1,1-Diphenyl-2-propen-1-ol:

Identical in all respects to sample prepared from reaction of benzophenone with vinylmagnesium bromide; b.p. 109-111°/0.25 mm.

c) 1-Tridecen-3-ol:

b.p. 88-90°/0.075 mm.

ir (neat) 3400, 2955, 2840, 1460, 990, 920 cm^{-1};

pmr (CCl_4) δ 0.75-1.75 (m, 21H), 3.5-4.15 (m, 2H), 5.1 (m, 2H) 5.8 (m, 1H).

d) 2-Propen-1-ol:

Identical in all respects to authentic sample.

e) 3,7-Dimethyl-1,6-octadien-3-ol:

Identical in all respects to sample prepared from reaction of 6-Methyl-5-hepten-2-one with vinylmagnesium bromide; b.p. 103-105°/ 30 mm.

pmr (CCl_4) δ 1.2 (s, 3H), 1.2-2.35 (m, 11H), 5.02 (m, 3H), 5.85 (m, 1H).

f) 1-Ethylenecyclohexanol:

Identical in all respects to sample prepared from reaction of cyclohexanone with vinylmagnesium bromide; b.p. 84-85°/30 mm.

pmr (CCl_4) δ 1-2.4 (m, 10H), 2.15 (s, 1H), 5.05 (m, 2H), 5.95 (m, 1H).

Reaction of 1-Substituted-3-chloro-2-trimethylsilyl-1-propene 24 and 29 with Gaseous HCl:

Dried gaseous HCl was bubbled into a solution of 24 or 29 (1 g) in 10 ml of chloroform for ca. 5 min. The mixture was stirred at room temperature for 2 - 5 days. The reaction mixture was subjected to GLPC analysis which revealed formation of the desilylated product, γ-substituted allylic chloride <u>39</u> in good yield. The pure product was obtained by distillation at reduced pressure. Listed in Table VIII are the yields and physical data of the chlorides obtained.

a) <u>1-Chloro-4-methyl-2-pentene (39e, R^1=$CH(CH_3)_2$):</u>

ir (neat) 2960, 2870, 1670, 1470, 1250, 965 cm^{-1};

pmr spectrum #6

Exact mass - Calcd. for $C_6H_{11}{}^{35}Cl$: 118.0549

found: 118.0504

b) <u>1-Chloro-2-tridecene (39b, R^1=n-$C_{10}H_{21}$):</u>

ir (neat) 2920, 2840, 1665, 1470, 1250, 965 cm^{-1};

pmr spectrum #4

Exact mass - Calcd. for $C_{13}H_{25}{}^{35}Cl$: 216.1645

found: 216.1653

c) <u>3-Chloro-1-cyclohexyl-1-propene (39d, R^1=c-C_6H_{11}):</u>

ir (neat) 2920, 2850, 1665, 1450, 1250, 960 cm^{-1};

pmr spectrum #5

Exact mass - Calcd. for $C_9H_{15}{}^{35}Cl$: 158.0863

found: 158.0848

d) <u>3-Chloro-1-phenyl-1-propene (39a, R^1=C_6H_5):</u>

Identical to authentic sample in all respects.

Reaction of 1-Chloro-4,4-dimethyl-2-trimethylsilyl-2-pentene and 3-Chloro-4,4-dimethyl-2-trimethylsilyl-1-pentene with Trifluoroacetic acid

To a solution of 0.2 g, 41a, b and c mixture in 5 ml of $CHCl_3$ was added 0.2 g (excess) trifluoroacetic acid and stirred at room temperature for two days. The reaction mixture was poured into 10 ml water, washed with 10 ml of 10% $NaHCO_3$, dried over anhydrous $MgSO_4$ and evaporated under vacuo to give the allylic chlorides 42. The allylic chlorides 42 had spectroscopic properties identical to those reported in the literature[135].

a) Product from reaction of 41a:b:c = 13:52:35 was 42c:b = 55:45, from analysis of pmr spectrum #9.

b) Product from reaction of 41a:b:c = 62:0:38 was 42b.

42, b.p. 75-77°/100 mm;

ir 42c:b = 55:45 (neat) 2950, 1370, 1260, 970, 780 cm^{-1};

pmr see spectrum #9

ir 42b (neat) 2950, 1370, 1260, 780 cm^{-1};

pmr see spectrum #10

Synthesis of Lithium Organocuprates[102,103,137]

Cuprous Iodide

Cuprous iodide as purchased from Alfa Chemical Co. or Fisher Scientific Co. was a brown or black powder. A sample (10 g) was stirred with a solution of potassium iodide (98 g) in water (75 ml). After addition of decolorizing carbon (0.25 g) the solution was filtered into water (250 ml). The suspension was allowed to settle, decanted and washed well with water, absolute ethanol and hexanes. The cuprous iodide (a white powder) was dried under vacuum.

Lithium Organocuprates

Purified cuprous iodide (1.9 g, 10 mmol) was placed in a three-necked flask, fitted with two dropping funnels with equilibrating side arms, and a magnetic stirrer. The apparatus was flame-dried under a stream of prepurified nitrogen. Anhydrous ether (10 ml) was added, and the stirred suspension was cooled to the required temperature. The alkyl or aryl lithium was then added dropwise.

Lithium Dimethylcuprate

This compound was prepared at or below 0°. On addition of the first drops of methyl lithium an intense yellow coloration (methyl copper) was produced; then as further addition of methyl lithium was continued a colorless or light tan solution was produced (after addition of 20 mmol). This end point could be titrated easily with methyl lithium.

Lithium di-n-butylcuprate

The preparation was carried out at or below -30°. The initial bright yellow color lasted until about half the butyl lithium was added; this changed to a bright blue solution which turned red at the end point.

Lithium Diphenylcuprate

This was prepared at or below 0°. The suspension initially turned bright yellow, then a red brown color until one equivalent of the phenyl lithium had been added. The solution then started turning green. After addition of two equivalents of phenyl lithium a dark green or black solution was obtained.

Lithium di-4-methylpentylcuprate

This compound was prepared at or below -30°. After addition of two equivalents of 4-methylpentyl lithium prepared from 4-methylpentyl bromide and powdered lithium, a black solution resulted. This end point was very difficult to detect.

Bis-4-methylpentylcoppermagnesium bromide

4-Methylpentylmagnesium bromide was prepared from 4-methylpentylbromide and magnesium in ether. To this solution was added cuprous iodide at 0°. The reaction mixture was warmed up to room temperature for 15 min. A black-brown solution resulted.

Bis-n-butylcoppermagnesium bromide

Prepared as outlined above for bis-4-methylpentylcoppermagnesium bromide.

Reaction of Lithium Organocuprates with Vinylsilanes 29 and 55

The vinylsilane (10 mmol) in anhydrous ether (40 ml) was added dropwise to the organocopper reagent under a stream of prepurified nitrogen. The temperature of addition is given in Tables IX and X. The mixture was then stirred overnight at room temperature. The mixture was then hydrolyzed with saturated ammonium chloride solution (50 ml). After stirring 15 min. at room temperature, the mixture was filtered and both copper salts and the aqueous layer were washed well with ether. The organic extracts were dried ($MgSO_4$) and evaporated to give an oil. The oil was purified by distillation or column chromatography (Tables IX and X).

Yield and Isomeric purity of vinylsilanes given in Tables IX and X.

a) 1-Cyclohexyl-2-trimethylsilyl-1-butene:

b.p. 67-69°/1 mm

(52a) Z isomer see pmr spectrum #11

(56a) E isomer see pmr spectrum #14

E and Z: ir (neat) 2955, 2840, 1610, 1450, 1250, 930, 840, 760 cm^{-1};

E: Ms, m/e (intensity): 210(12), 195(7), 153(4), 137(7), 136(52), 113(28), 107(11), 99(5), 85(8), 83(11), 81(9), 79(8), 75(25), 73(100), 59(31), 55(17).

b) 2-Methyl-4-trimethylsilyl-3-nonene:

b.p. 78-80°/5 mm

(52b) Z isomer see pmr spectrum #12

(56b) E isomer see pmr spectrum #17

c) 6-Trimethylsilyl-6-heptadecene:

(52c) Z isomer see pmr spectrum #13

(56d) E isomer see pmr spectrum #18

d) 3-(2-Methylpropyl)-2-trimethylsilyl-1-heptene:

see pmr spectrum #19

e) 4-Methyl-1-phenyl-2-trimethylsilyl-2-pentene (56c):

b.p. 67-69°/0.25 mm
E-isomer
pmr (CCl_4) δ -0.08 (s, 9H), 1.0 (d, J= 7Hz, 6H), 2.6 (m, 1H), 3.6 (s, 2H), 5.80 (d, J=9Hz, 1H), 7.15 (s, 5H).

f) 2-Methyl-8-trimethyl-8-nonadecene (88c):

see pmr spectrum #20

Reaction of Vinylsilanes with HI:

To a solution of 0.002 mol of vinylsilane in 5 ml CH_2Cl_2 were added four drops of 48% HI. Analysis by vpc showed reaction was complete in ~15 min. Mixture was poured into 10 ml water. The organic phase was washed with 10 ml - 10% $NaHCO_3$, dried over anhydrous $MgSO_4$ and evaporated in vacuo to give in quantitative yield the olefin.

a) Reaction of 41a:b:c = 13:52:35 gave 42a:b:c = 13:52:35, from analysis of pmr spectrum. Products spectroscopically identical to literature[135].

b) 1-Cyclohexyl-1-butene (54a and 57a):

b.p. 59-59.5°/12 mm

(57a) Z - ir (neat) 2910, 2840, 1450, 890 cm^{-1};

(54a) E - ir (neat) 2910, 2840, 1450, 940, 890 cm^{-1};

57a (Z) pmr see spectrum #15

54a (E) pmr see spectrum #16

c) 2-Methyl-8-nonadecene (80): (Z)

ir (neat) 2910, 2840, 1465, 1325 cm^{-1};

pmr (CCl_4) δ 0.85 (d, J=6Hz, 6H), 0.9-2.2 (m, 30H), 5.15 (AB, 2H)

Identical in all respects to sample obtained by T.H. Chan and E. Chang[27].

d) 2-Methyl-3-nonene:

Z - ir (neat) 2950, 2860, 1465 cm^{-1};

E - ir (neat) 2950, 2860, 1465, 970 cm^{-1};

Z - pmr (CCl_4) δ 0.95 (d, J=7Hz, 6H), 0.9-2.2 (m, 11H), 2.55 (m, 1H), 5.05 (AB, 2H).

E - pmr (CCl_4) δ 0.95 (d, J=7Hz, 6H), 0.9-2.2 (m, 11H), 2.55 (m, 1H), 5.2 (AB, 2H).

Reaction of Vinylsilanes 56 and 52 with Bromine:

To a solution of 0.001 mol vinylsilane in 5 ml CH_2Cl_2 at -78° was added 0.160 g Br_2 in 2 ml CH_2Cl_2. The reaction was stirred for 30 min and then the solvent evaporated under vacuo to give the product.

a) For reaction of 56a the product was 60a, 2-bromo-1-cyclohexyl-1-butene:
b.p. 66-68°/1.3 mm, > 90%.
ir (neat) 2920, 2840, 1660, 1450, 970, 900 cm^{-1};
pmr (CCl_4) δ 0.6-2.0 (m, 14H), 2.4 (9, J=7Hz, 2H), 5.35 (d, J=8Hz, 1H).

b) For reaction of 56b the product was 60b, 4-Bromo-2-methyl-3-nonene:
ir (neat) 2950, 2860, 1655, 1470, 1260 cm^{-1};
pmr (CCl_4) δ 1.15 (d, J=7Hz, 6H), 0.9-2.0 (m, 9H), 2.45 (m, 2H), 2.85 (m, 1H), 5.45 (d, J=8Hz, 1H).

c) Reaction with 52a and b produced a mixture of products which were not further purified.

Synthesis of the Sex Pheromone of the Gypsy Moth, Disparlure

To a solution of 0.05 moles of α-bromovinyltrimethylsilane in 80 ml of ether, under a N_2 atmosphere, at -78° was added with stirring 30 ml of 1.6N t-BuLi in hexane. The reaction mixture was stirred at -78°C for 1-^{1}/2 hrs. A solution of 0.05 mole of undecanal in 15 ml of ether was added dropwise over one hour. The reaction mixture was allowed to warm up to room temperature slowly and stirred overnight. To the reaction mixture were added 10 ml of CH_3COCl in 15 ml of ether. The solution was stirred for half-an-hour, poured into water, and washed with 2 x 50 ml of water. The organic solution was dried over $MgSO_4$ and evaporated to give 87. Distillation (b.p. 103-106°/0.1 mm) gave 87 in 75% yield.

To a solution of 0.015 mol 4-methylpentylmagnesium bromide, in 20 ml of ether, prepared from 0.015 mol of 4-methylpentylbromide and 0.015 mol magnesium, under a stream of purified N_2, was added 0.0075 mol of CuI at 0°. The reaction was warmed up to room temperature for 15 min. then cooled to -78°C. The acetate <u>87</u> (0.006 mol) in 10 ml of ether, was added dropwise over a 20 min. period. The reaction was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into 25 ml of saturated NH_4Cl, stirred 15 min. and filtered. The solid and the aqueous layer were washed with 2 x 20 ml ether. The combined ether solution was dried over $MgSO_4$ and evaporated in vacuo to give the vinylsilane <u>88</u>. The product was purified on a silica gel column eluted with hexane. Yield, 82%.

The vinylsilane <u>88</u> was dissolved in 10 ml of CH_2Cl_2 and four drops of 48% HI added. The reaction mixture was stirred for half-an-hour, poured into 10 ml of water. The organic phase was washed with 5 ml of 10% $NaHCO_3$ solution, dried over $MgSO_4$ and evaporated in vacuo to give the olefin <u>80</u> in quantitative yield. Purification by column chromatography on silica gel with hexane as eluent gave pure <u>80</u>.

To <u>80</u> in 10 ml benzene was added 1.0 g of m-chloroperbenzoic acid ($m\text{-}ClC_6H_4COOOH$). The reaction mixture was stirred for 4-^{1}/2 hrs. The precipitate, $m\text{-}ClC_6H_4COOH$, was filtered. The filtrate was washed with 10 ml dil. aq. $NaHCO_3$ solution and with 10 ml water, dried over $MgSO_4$ and evaporated in vacuo to give 7,8-epoxy-2-methyloctadecane in quantitative yield. Purification by column chromatography on silica gel/hexane gave disparlure Z:E = 87:13 in overall yield based on undecanal of

62%. The product was identical in all respects to an authentic sample of disparlure (E:Z = 85:15).*

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* Authentic sample obtained from Dr. Beroza.

CHAPTER VIII

CLAIMS TO ORIGINAL RESEARCH

1. Carbonyl compounds were converted to terminal allenes using organosilicon intermediates under mild conditions.

2. Fluoride ion cleaved the silicon-carbon vinyl bond in 1-substituted-2-silyl-2-propen-1-ols to give allylic alcohols, demonstrating an unexpected β-hydroxy effect.

3. Aldehydes (RCHO) were converted to E-RCH = $CHCH_2Cl$ stereoselectively employing an organosilicon intermediate.

4. A stereoselective synthesis of E and Z dialkylsubstituted vinylsilanes was developed using an organocopper reagent. This reaction could be extended to the stereoselective synthesis of E and Z disubstituted alkenes.

5. A new stereoselective synthesis of the gypsy moth sex pheromone was developed using an organosilicon intermediate and an organocopper-magnesium halide reagent.

6. Thionyl chloride reacted with 1-substituted-2-silyl-2-propen-1-ols to give stereoselectively Z-3-chloro-1-substituted-2-silyl-1-propenes.

7. Organocopper reagents reacted with 1-acetoxy-1-substituted-2-silyl-2-propenes to give stereoselectively E-dialkyl-substituted vinylsilanes.

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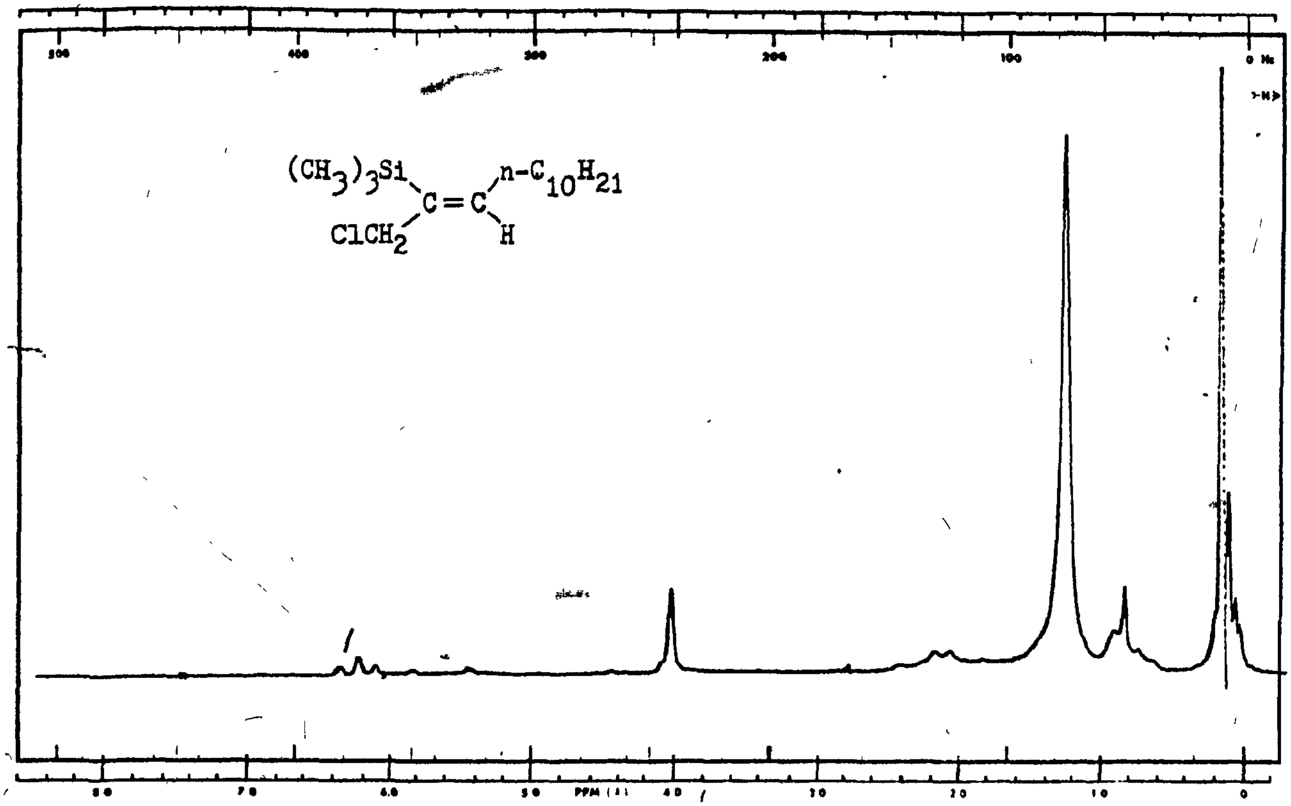

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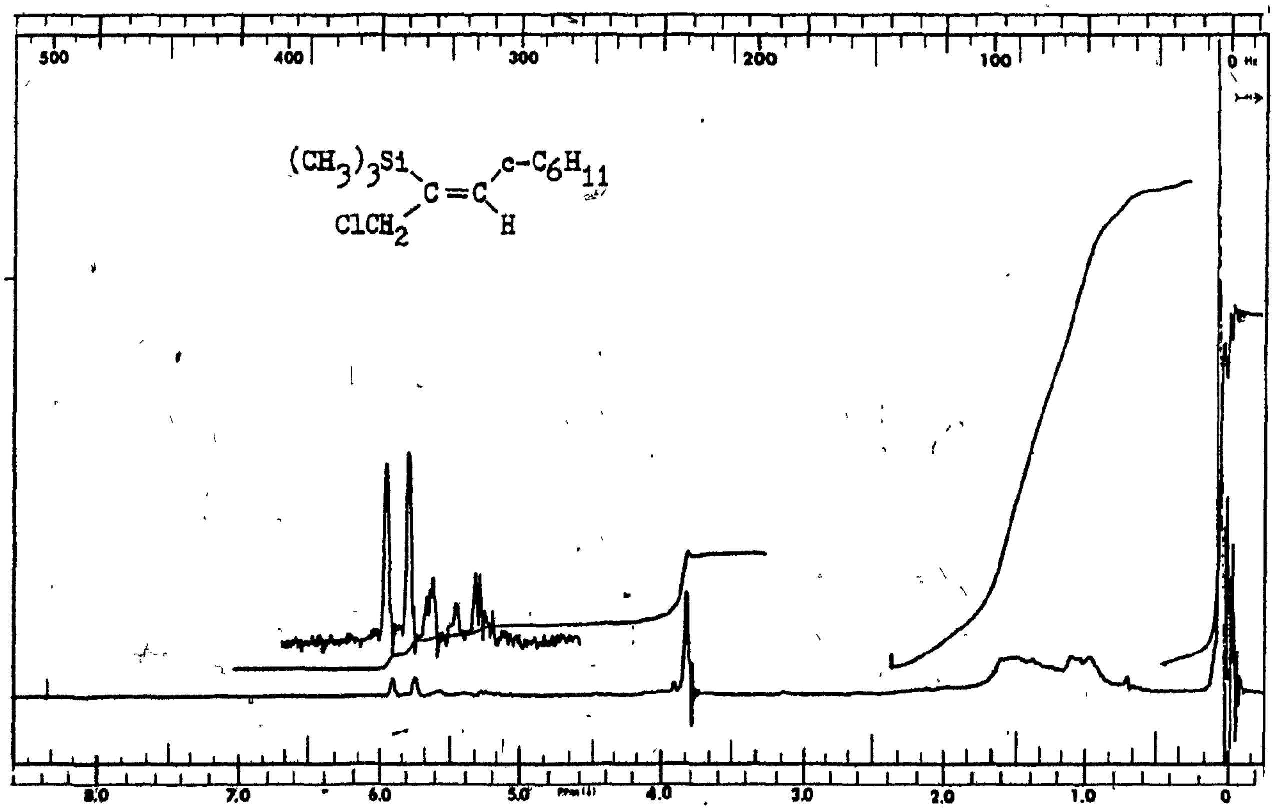

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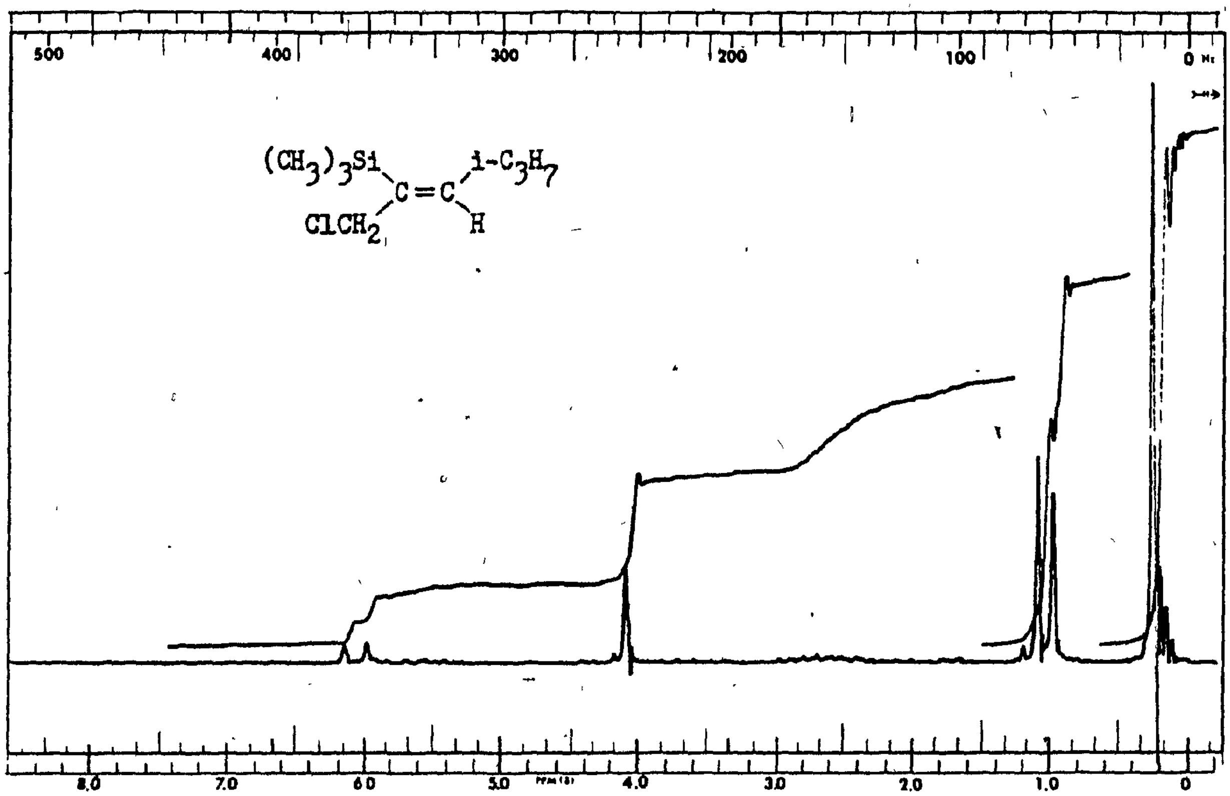

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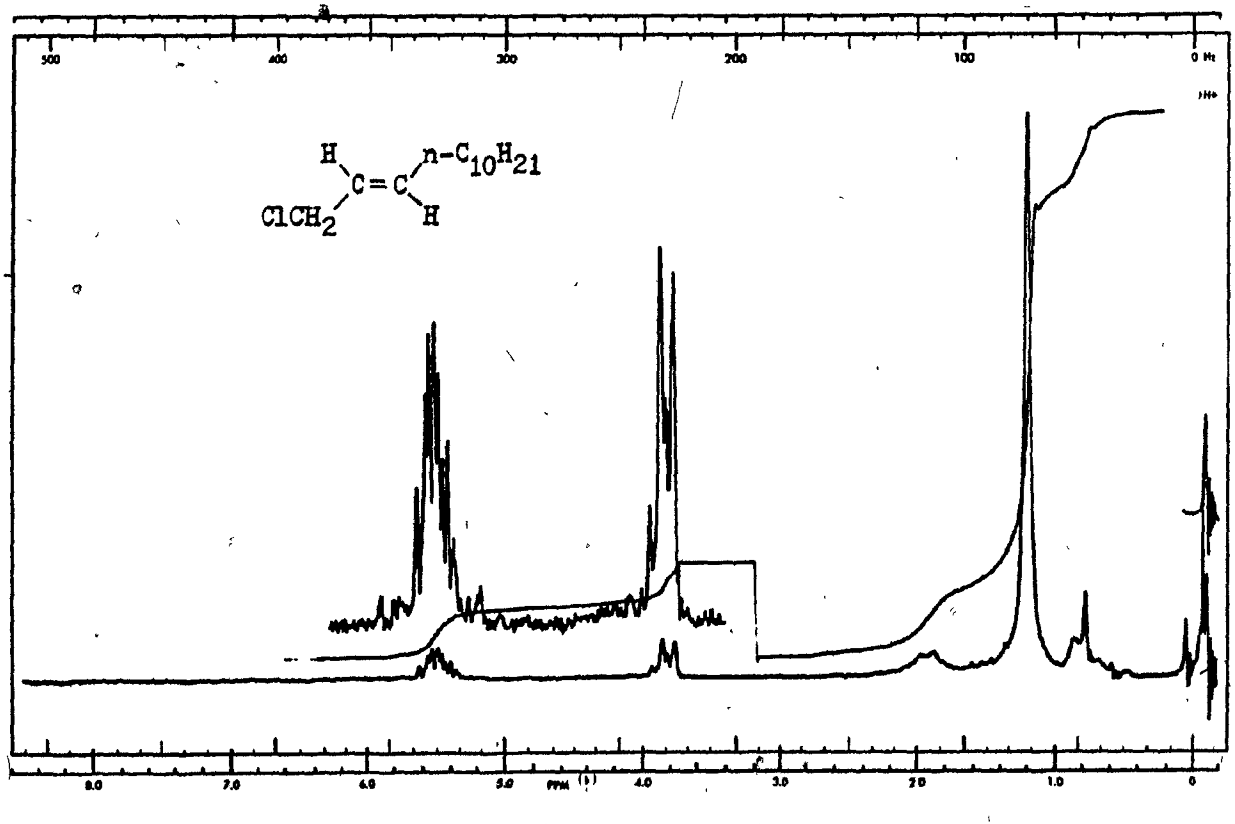

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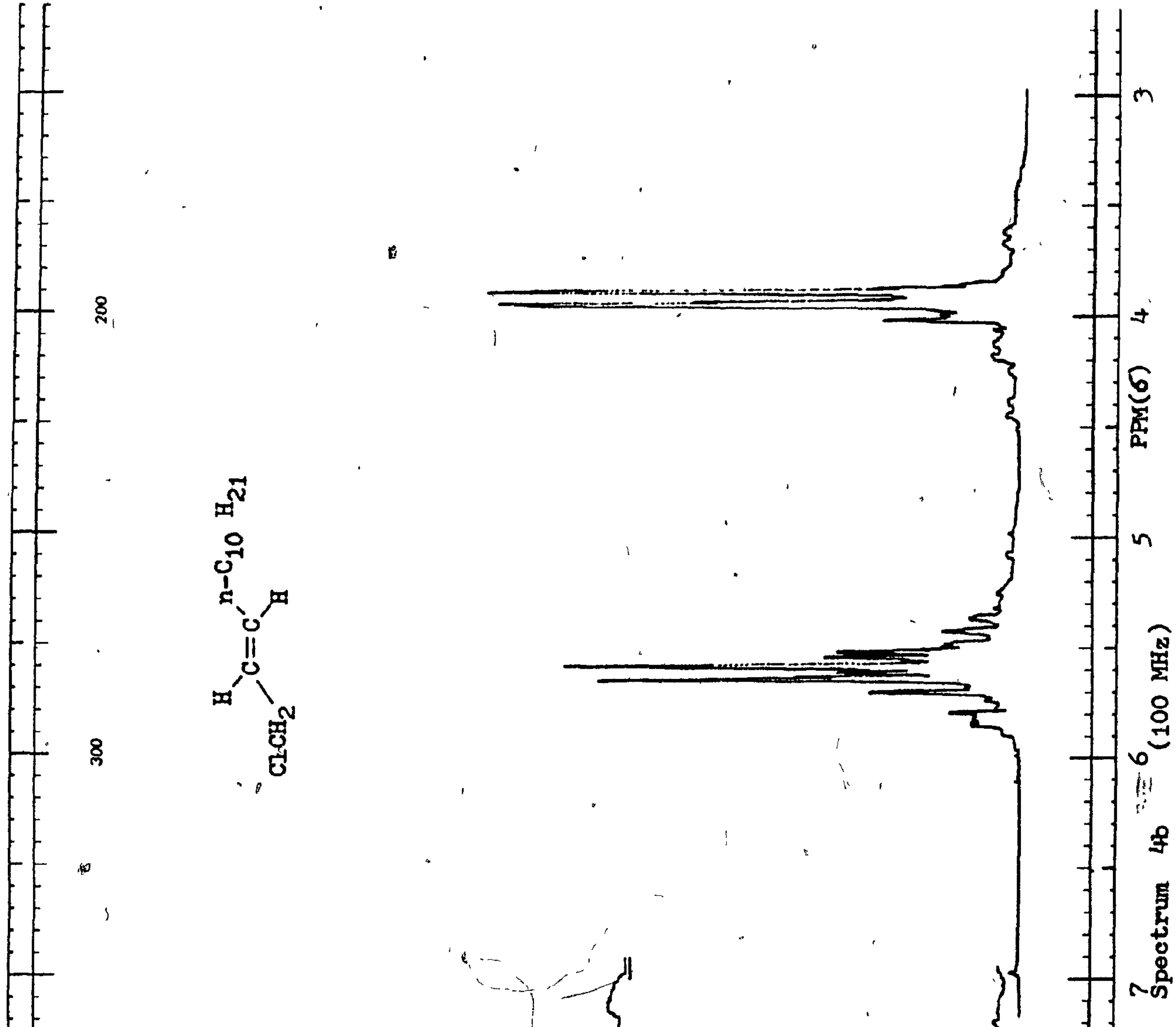

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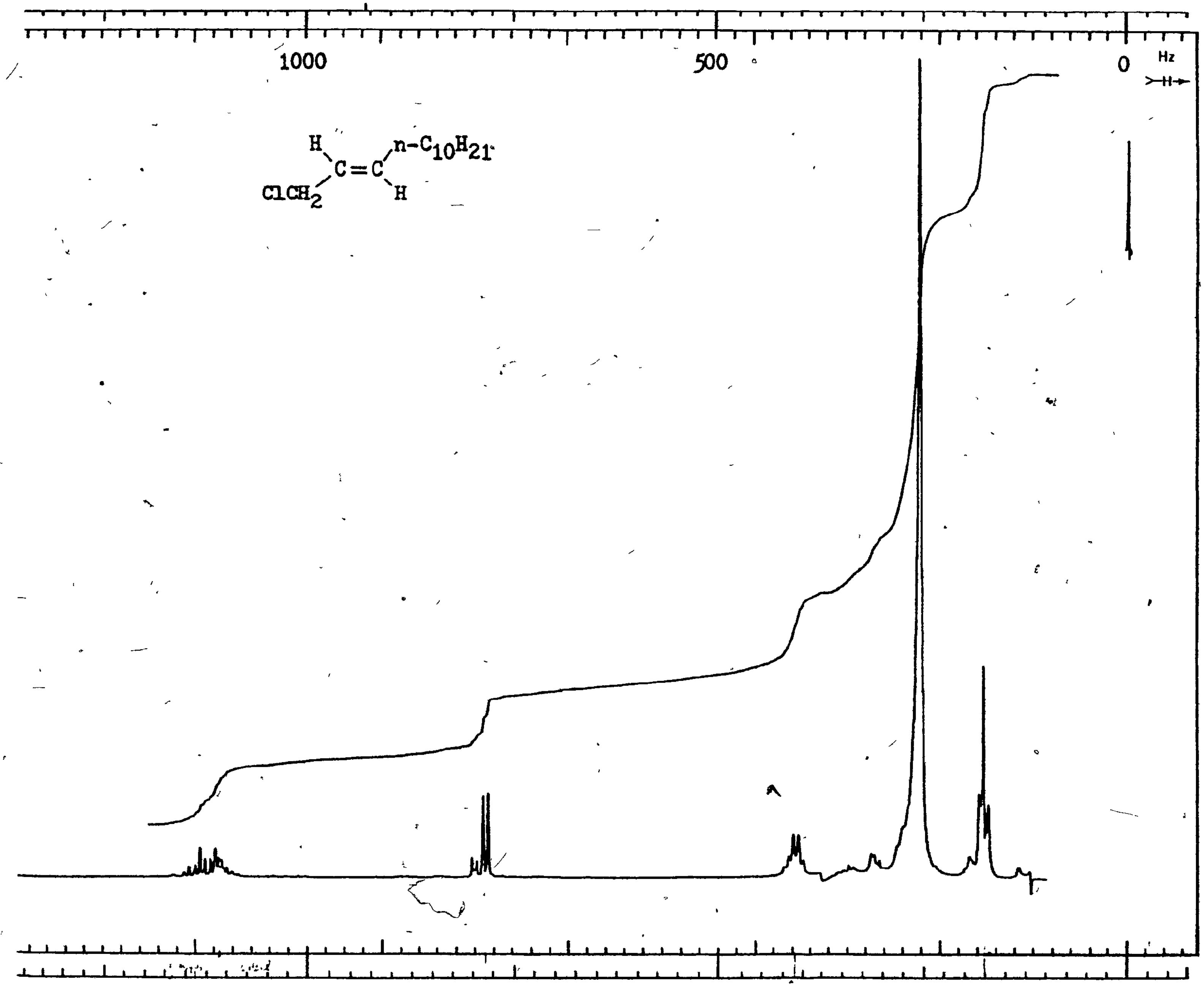
200
300
400
1000
500
250
100
50
4X
3
4
5
6
7
PPM(δ)
(100 MHz)

Spectrum 4b



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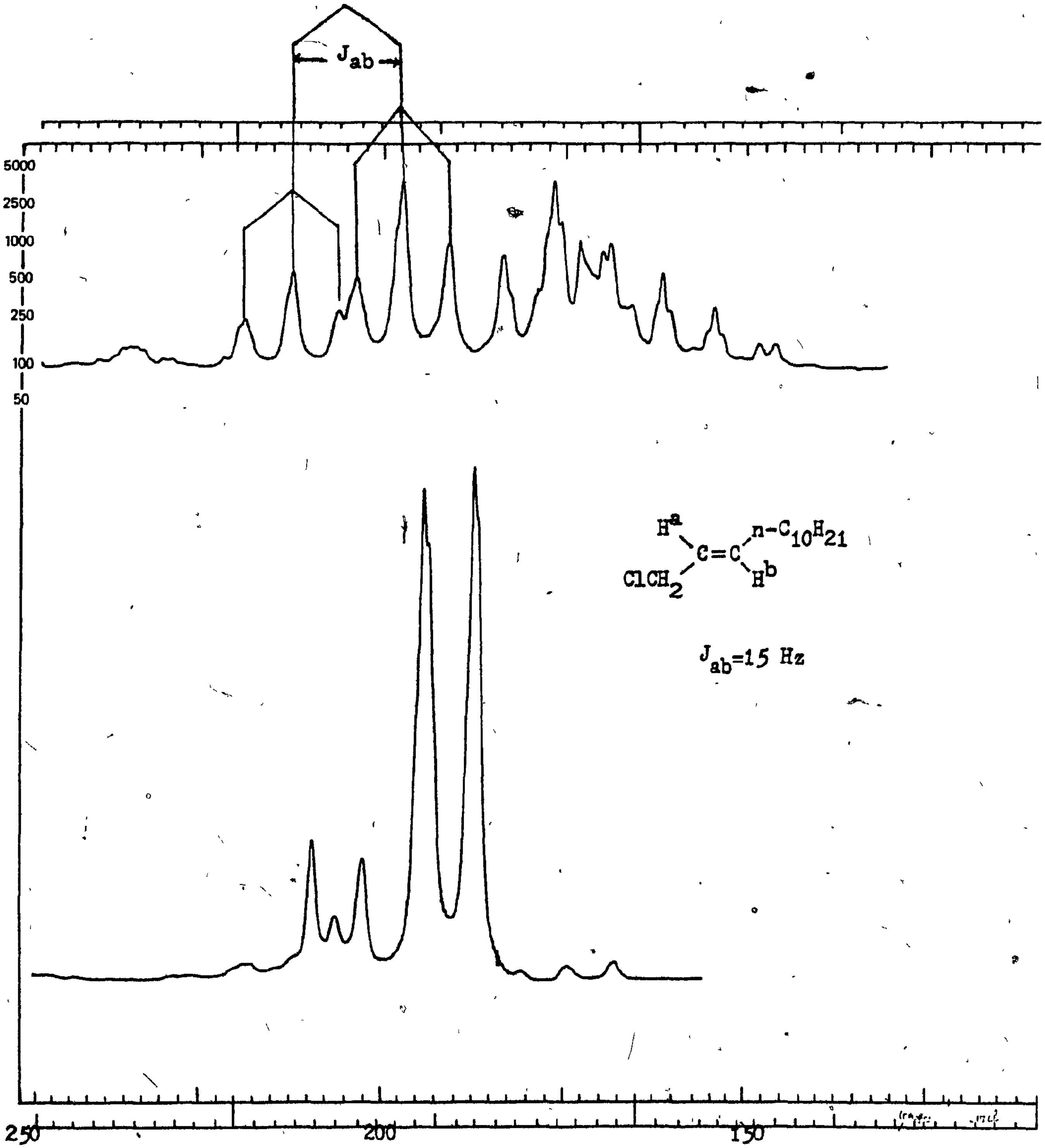
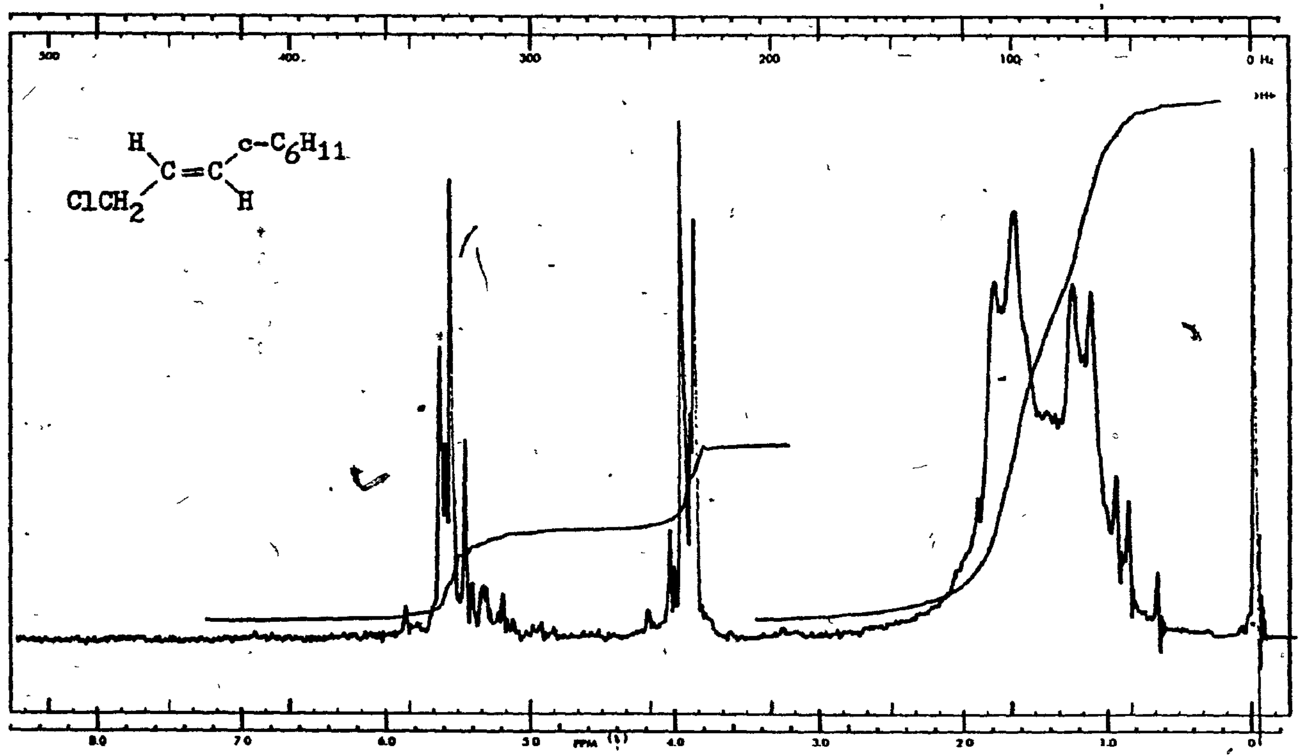
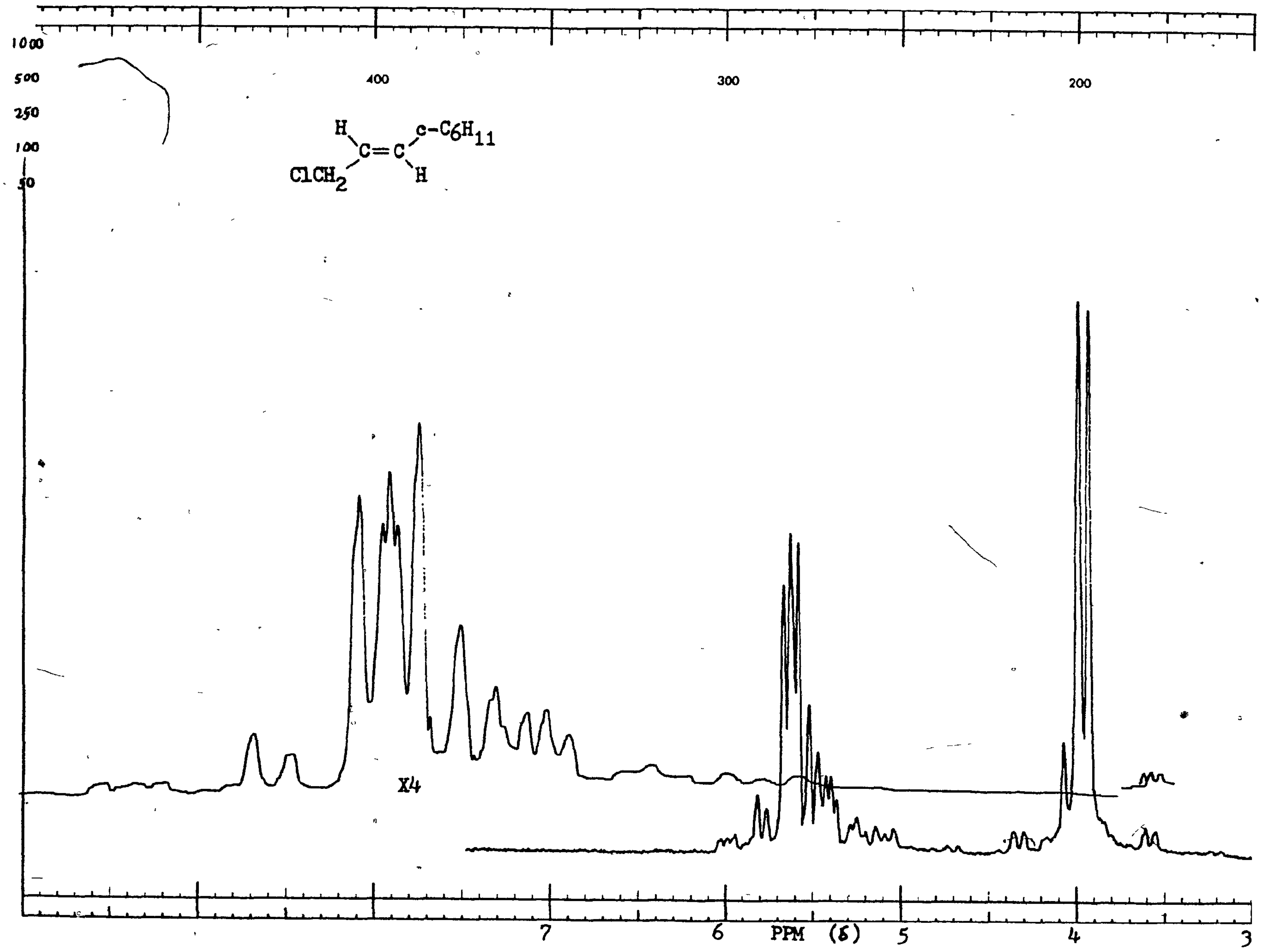


Spectrum 4c X10 (220 MHz)



Spectrum 5a (60 MHz)



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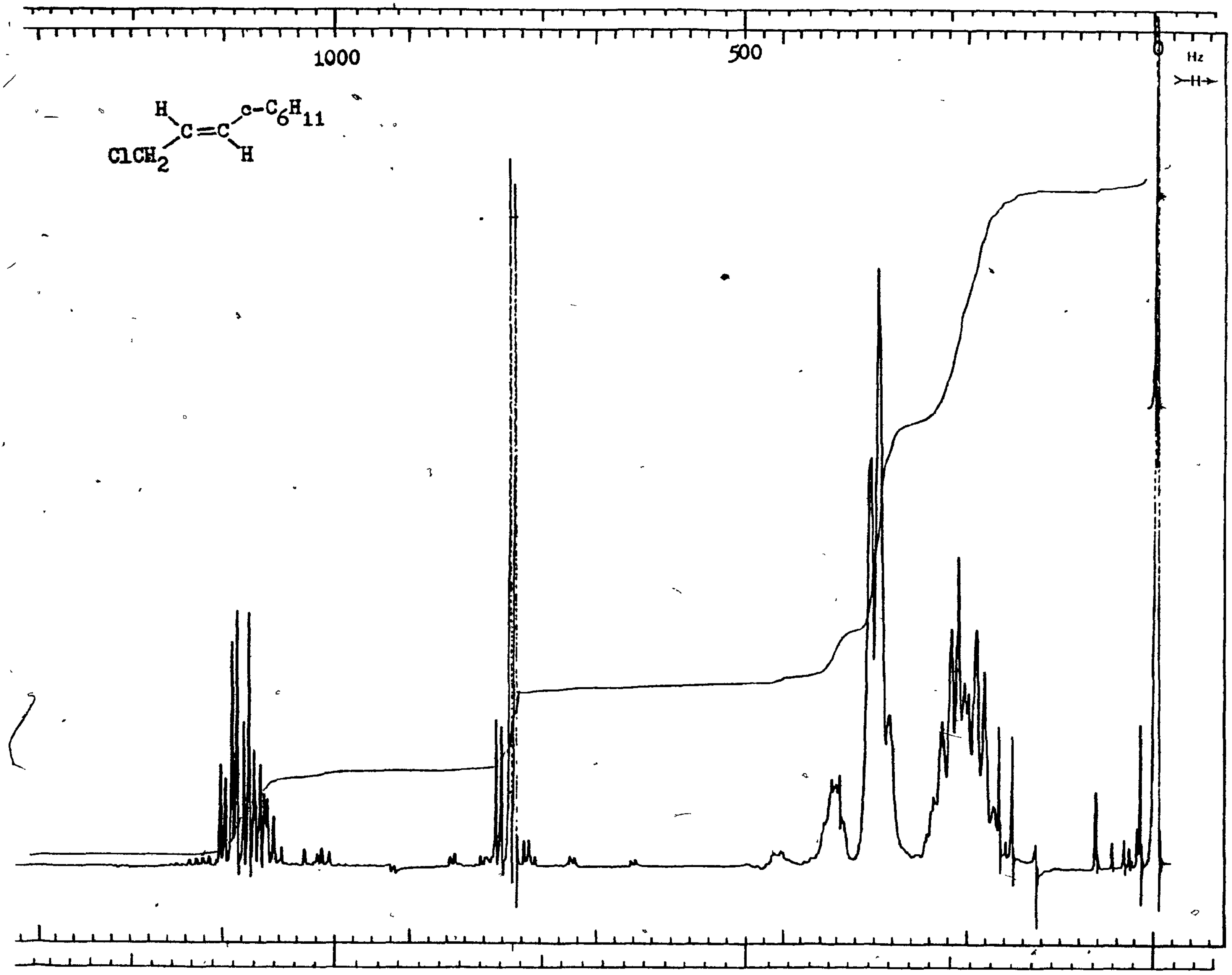

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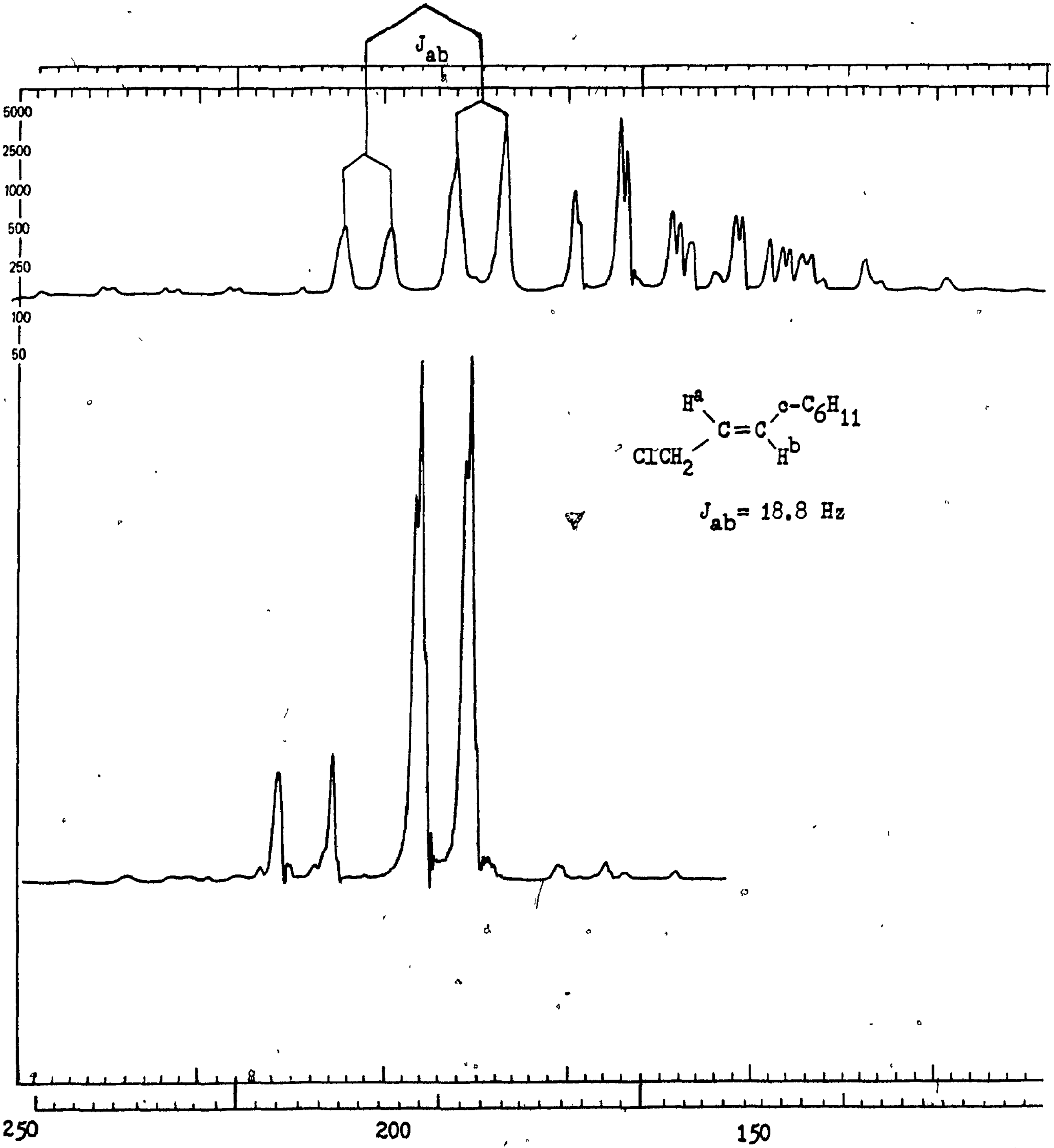

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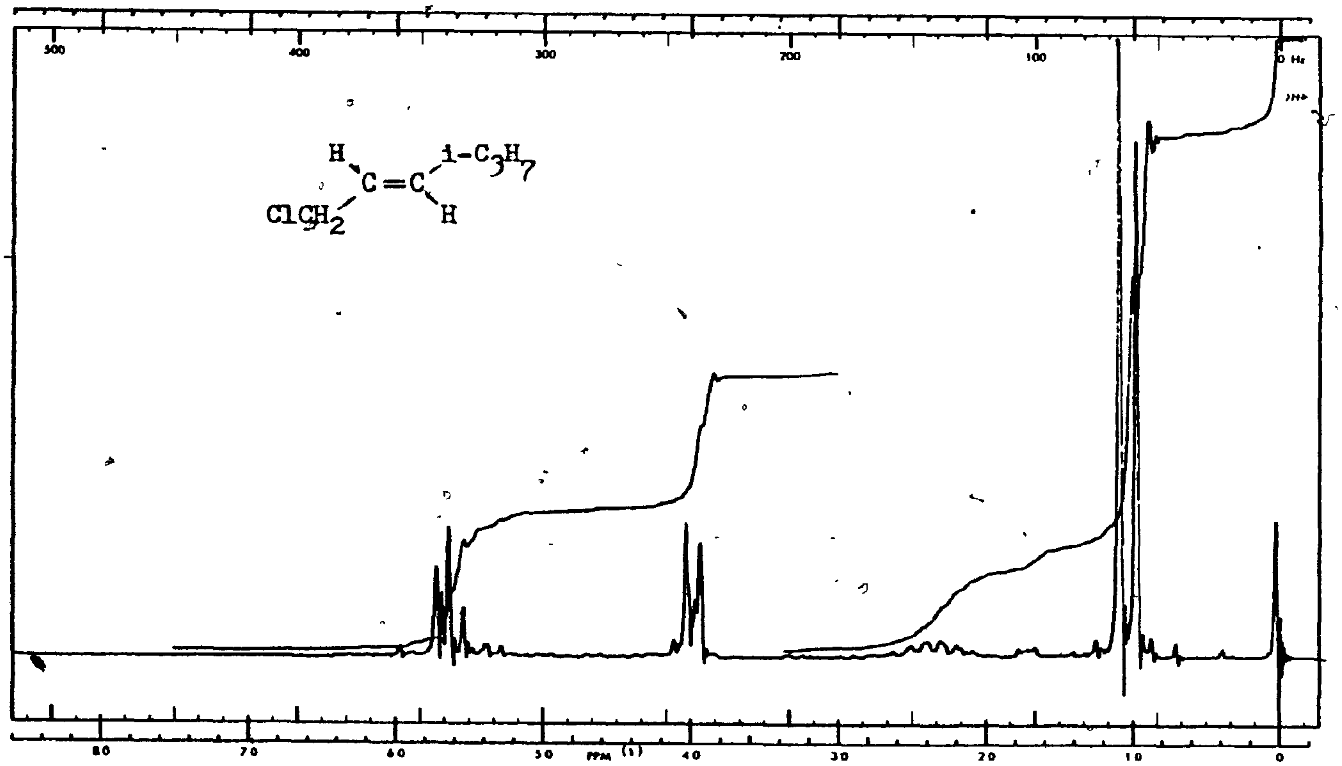

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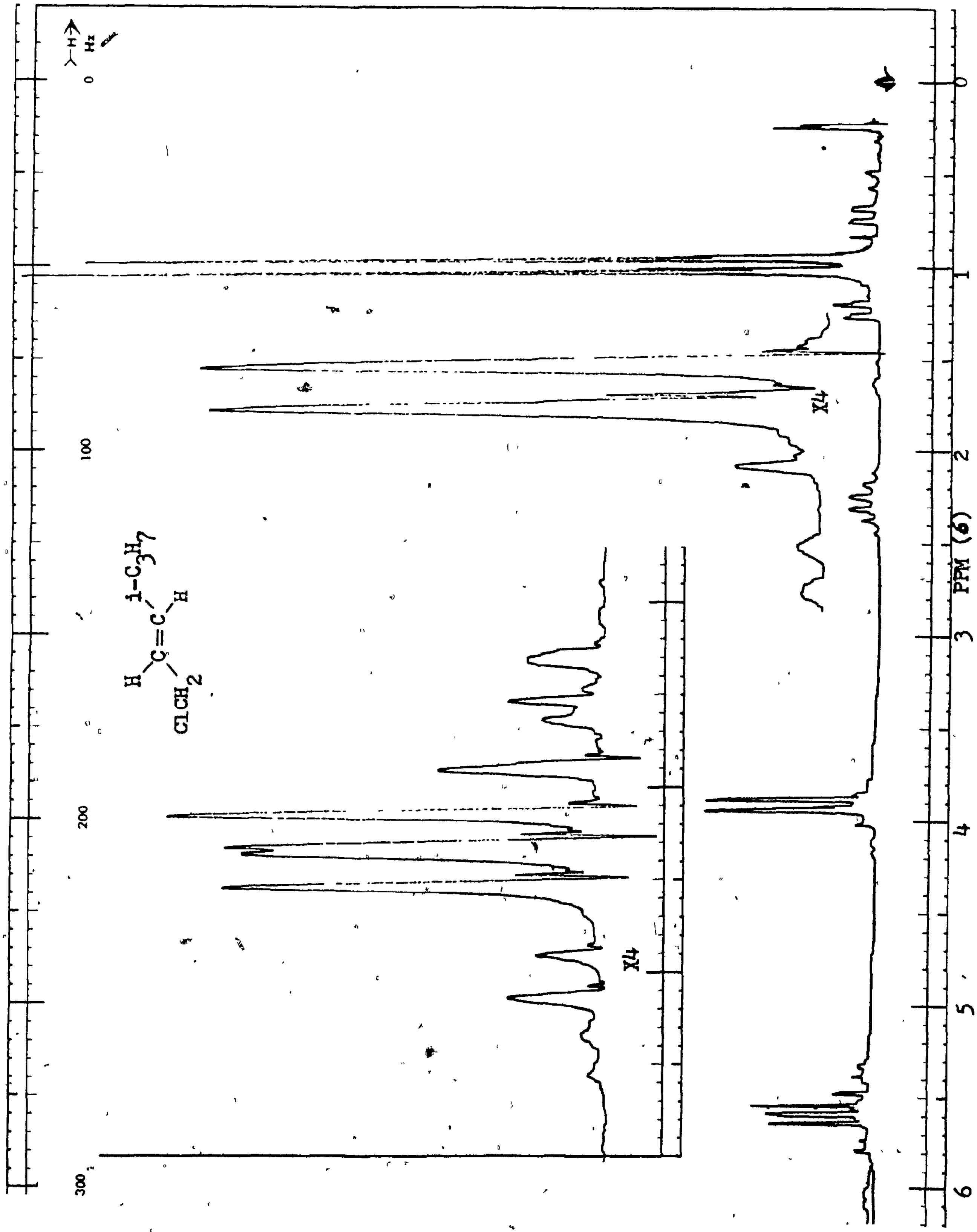

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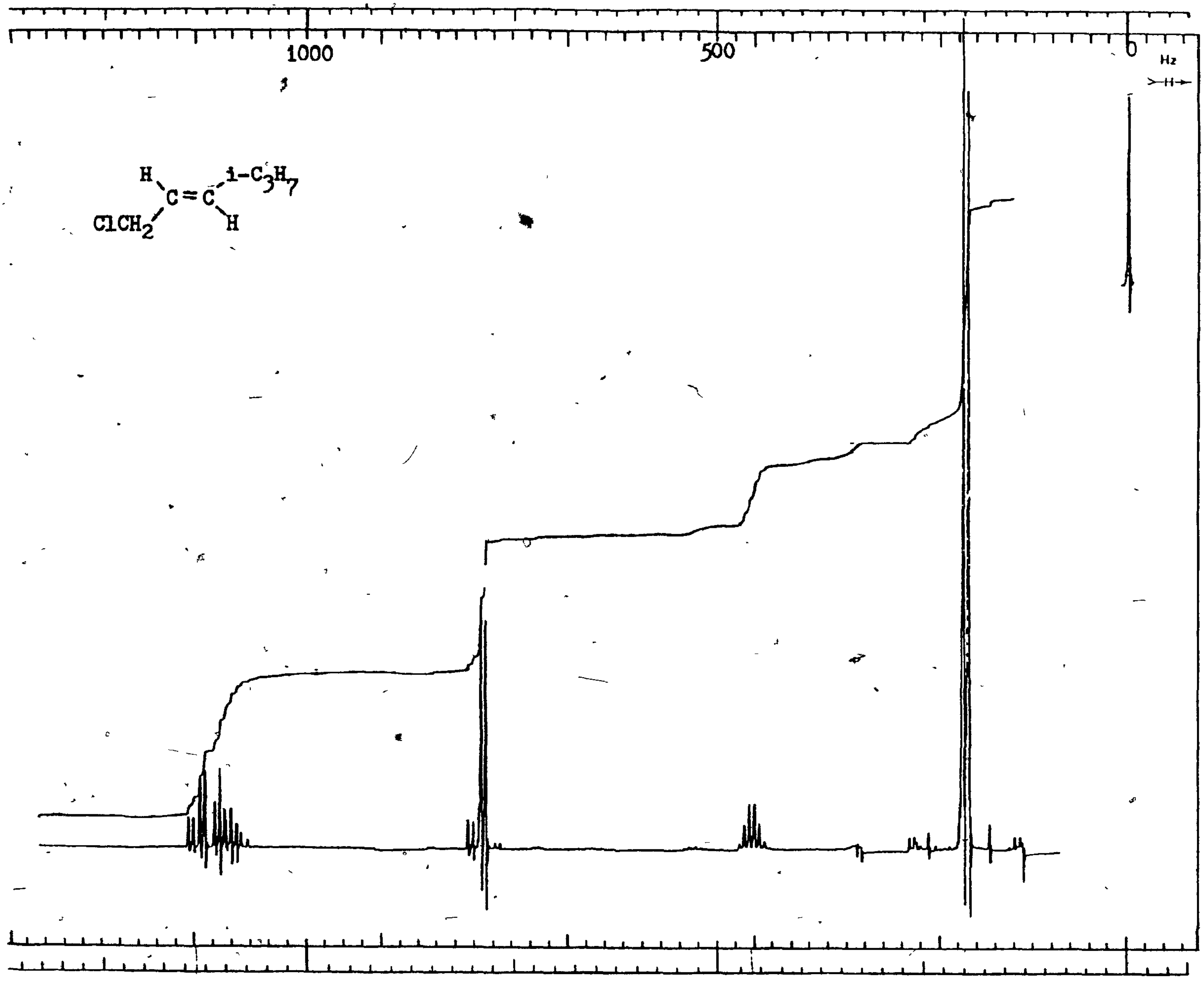

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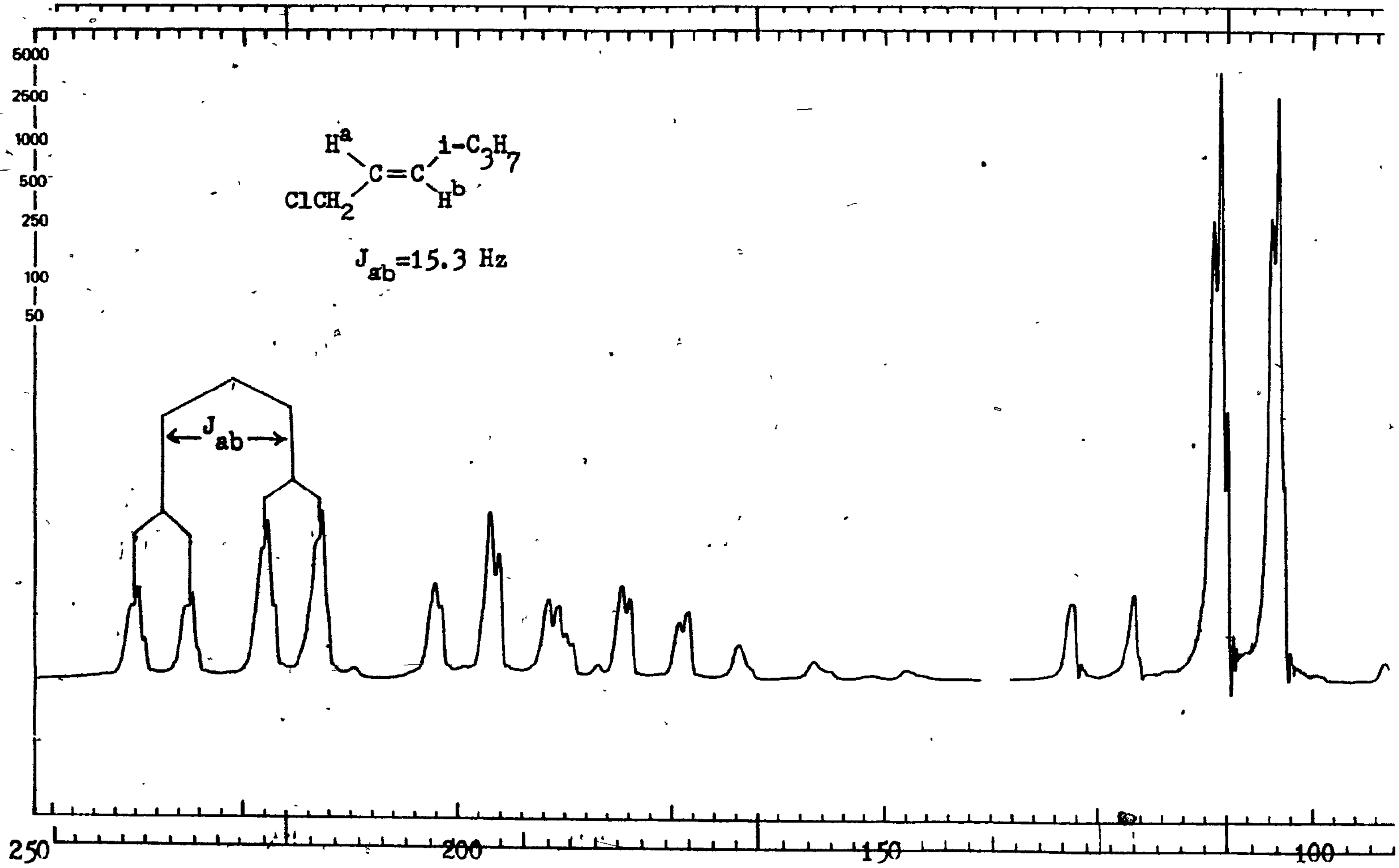

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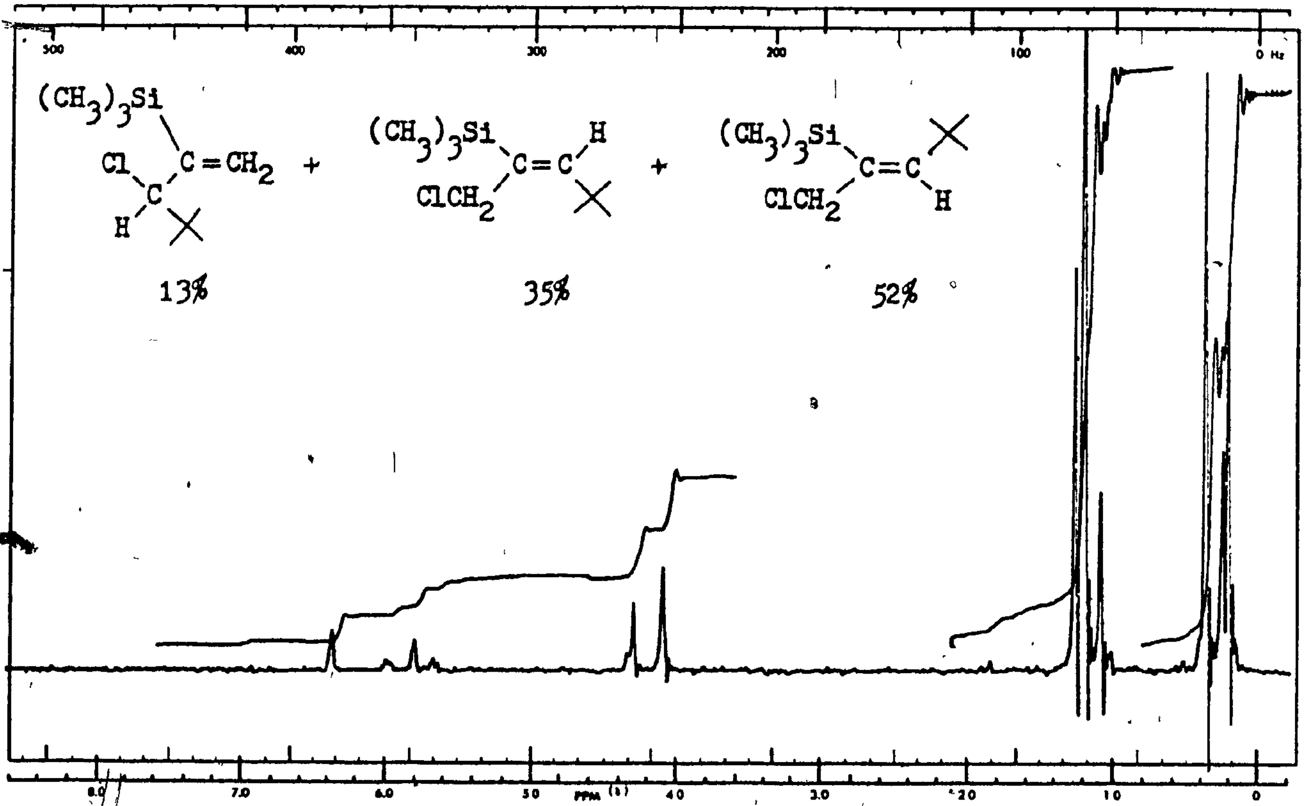

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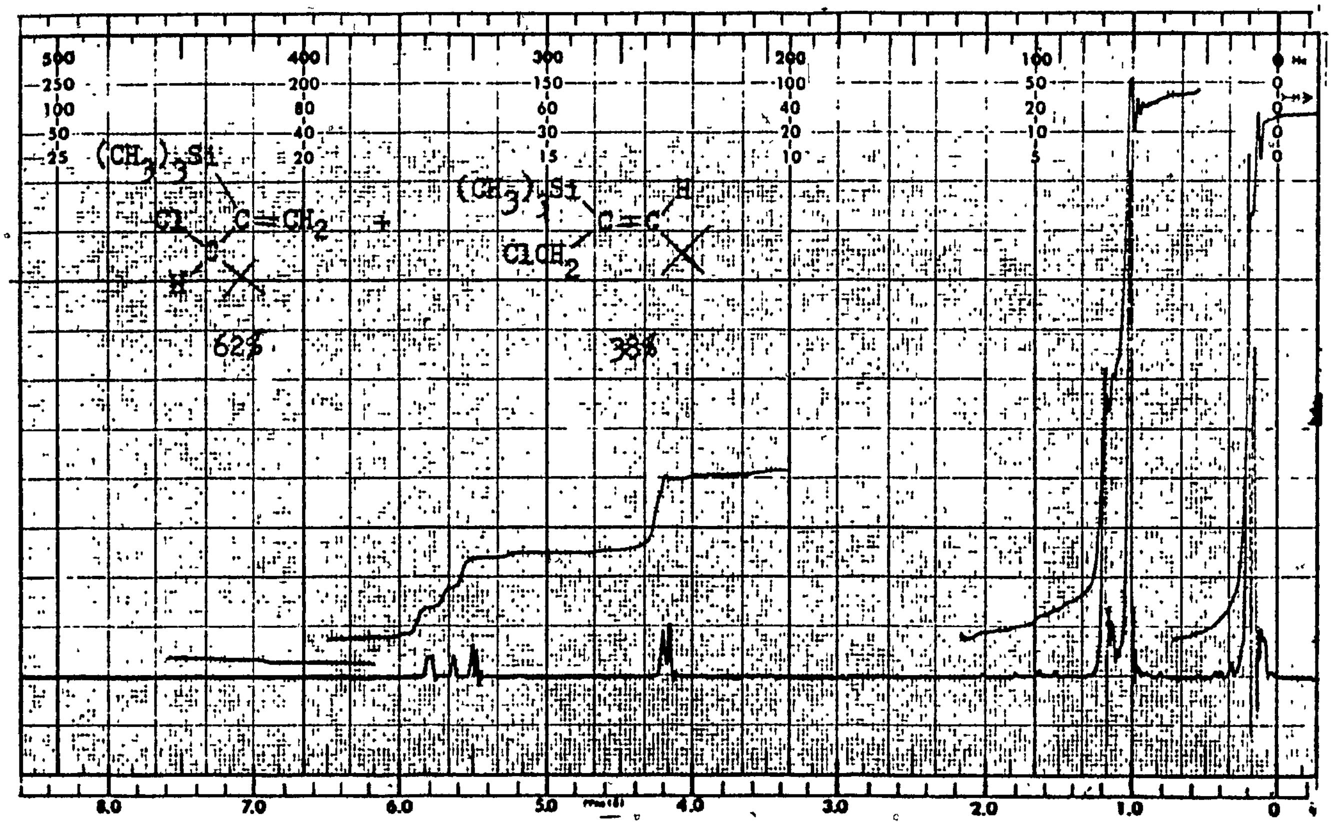

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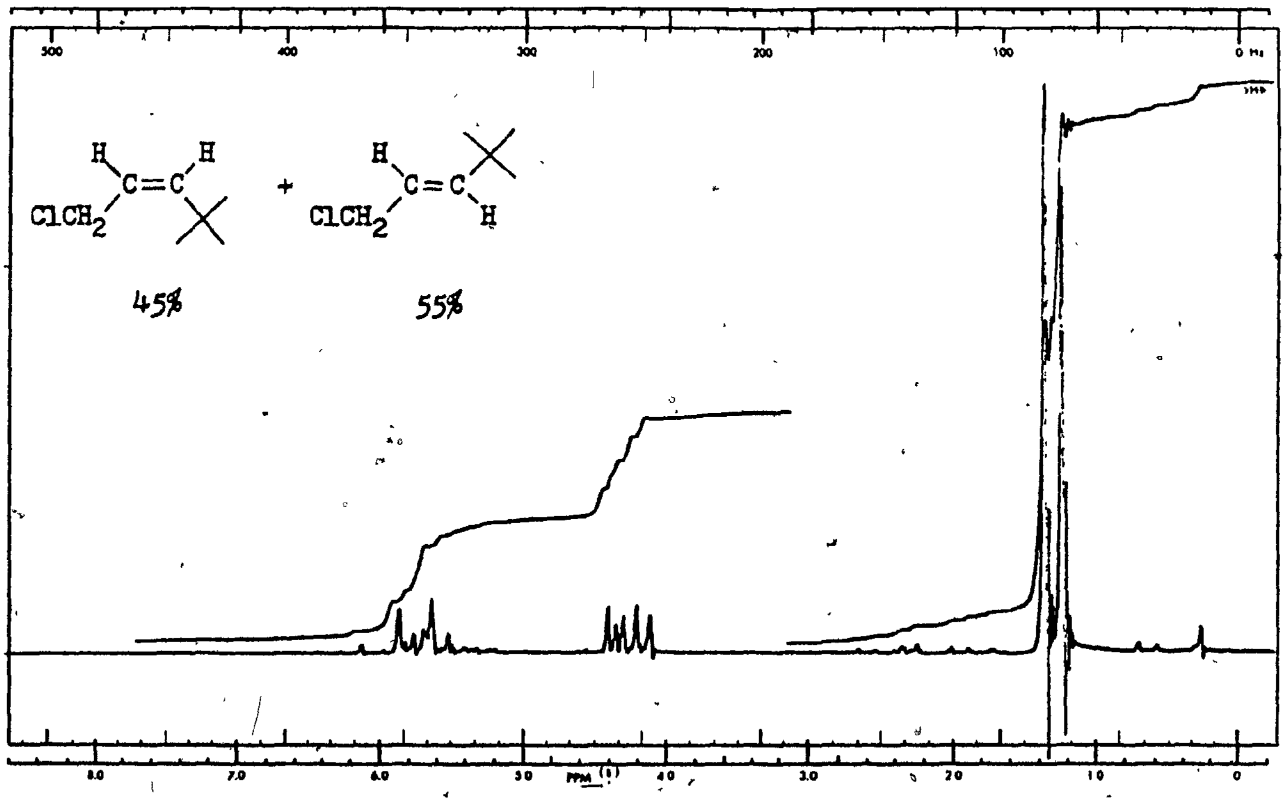

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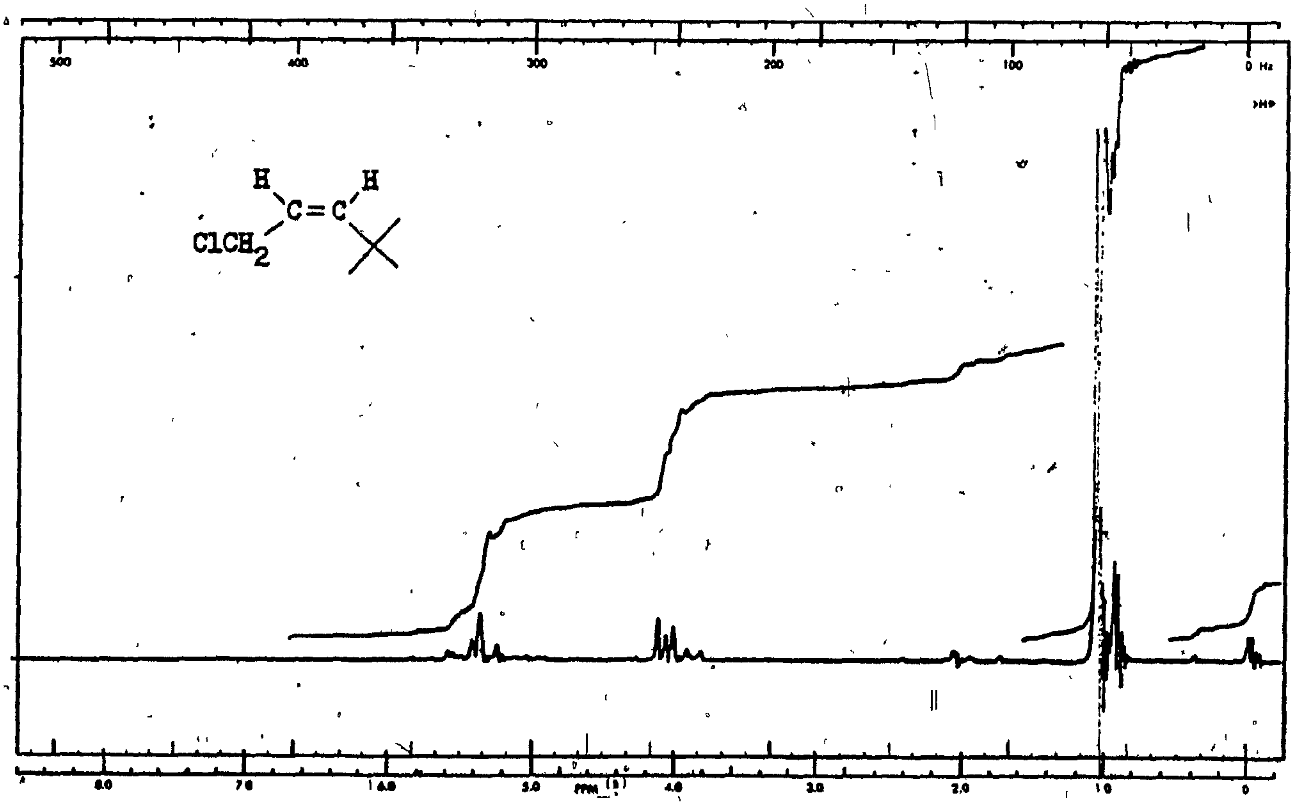

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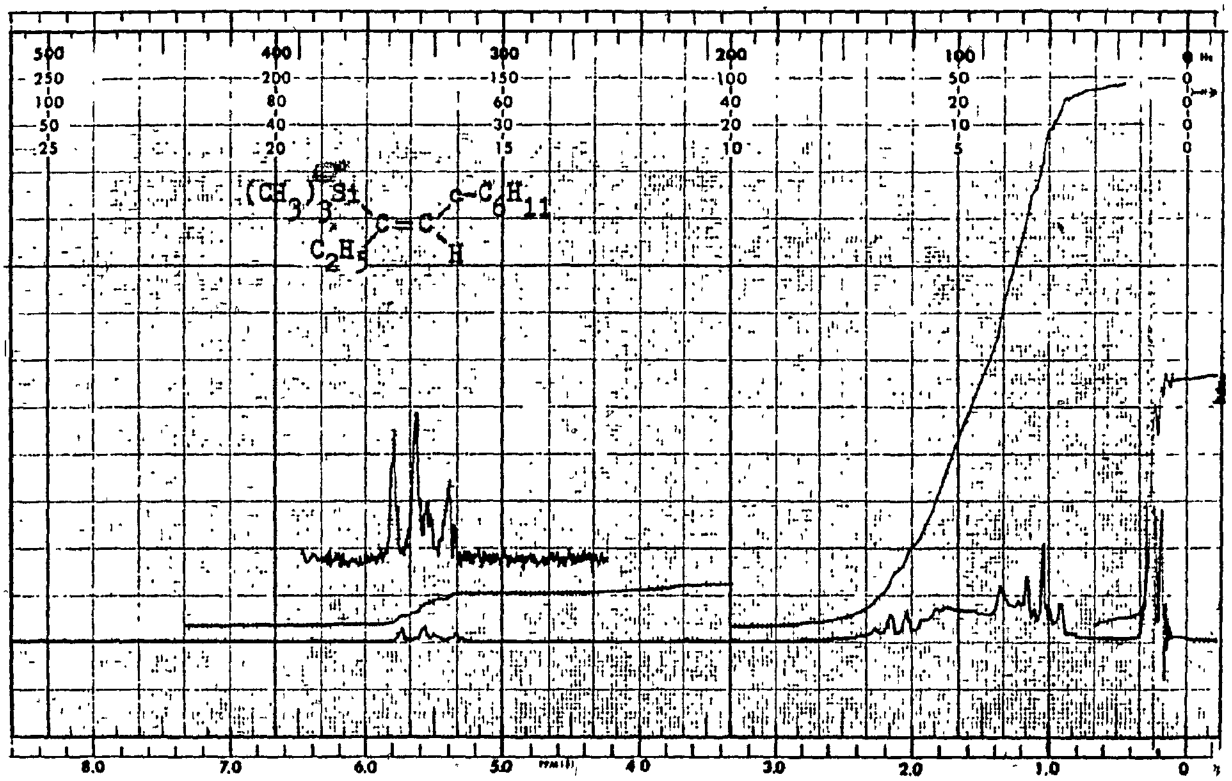

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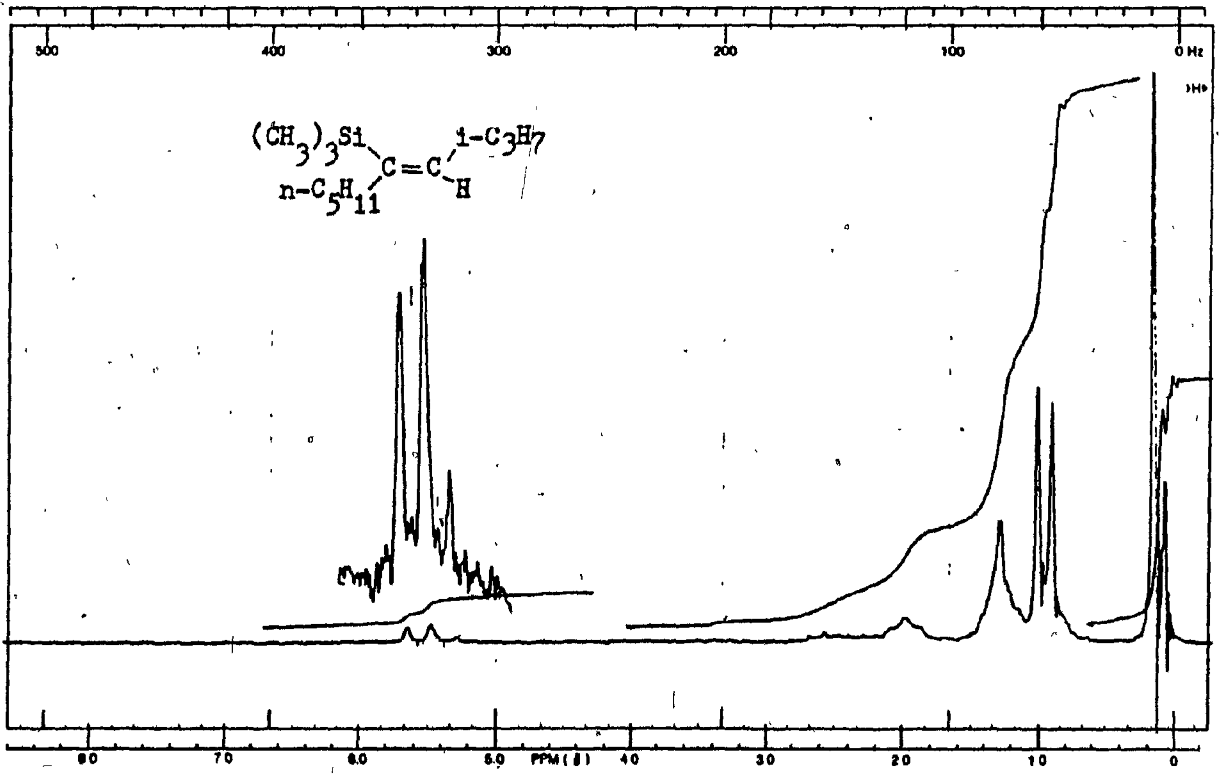

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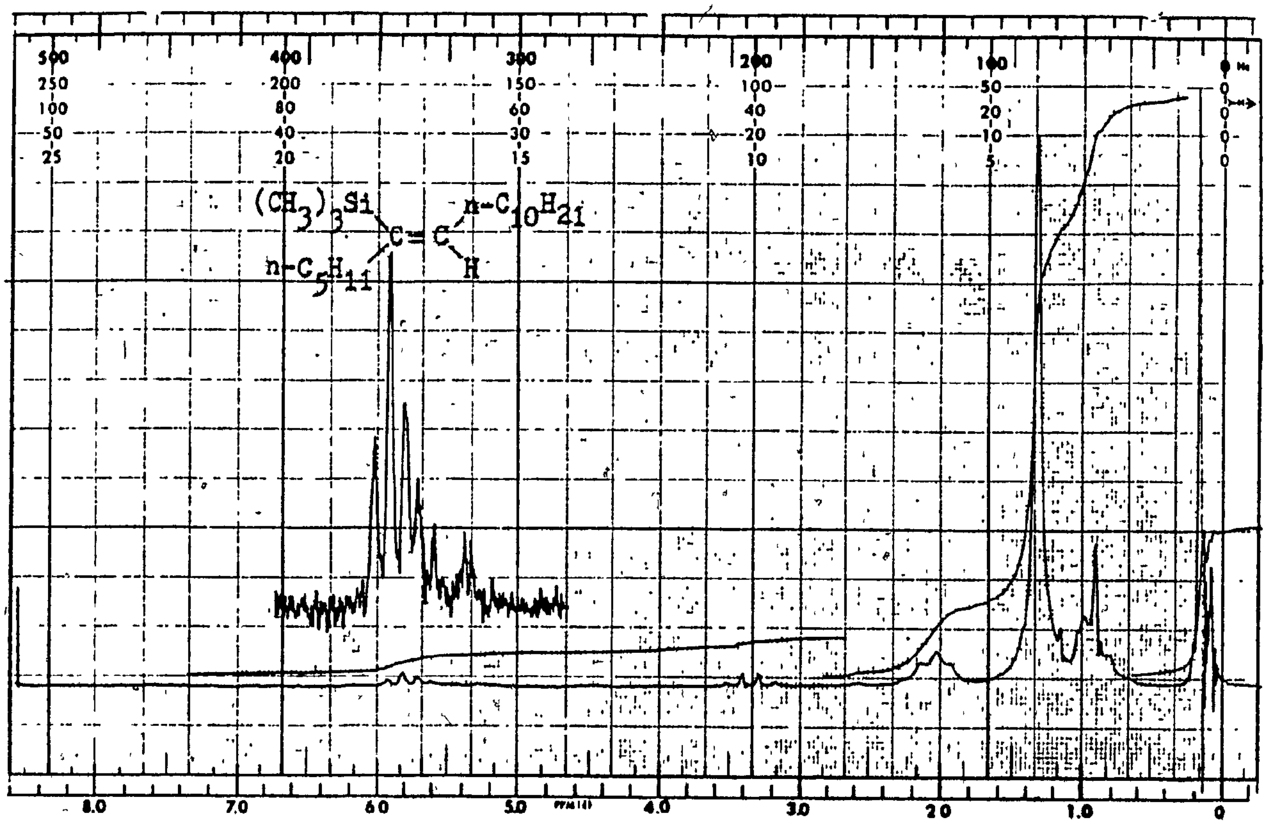

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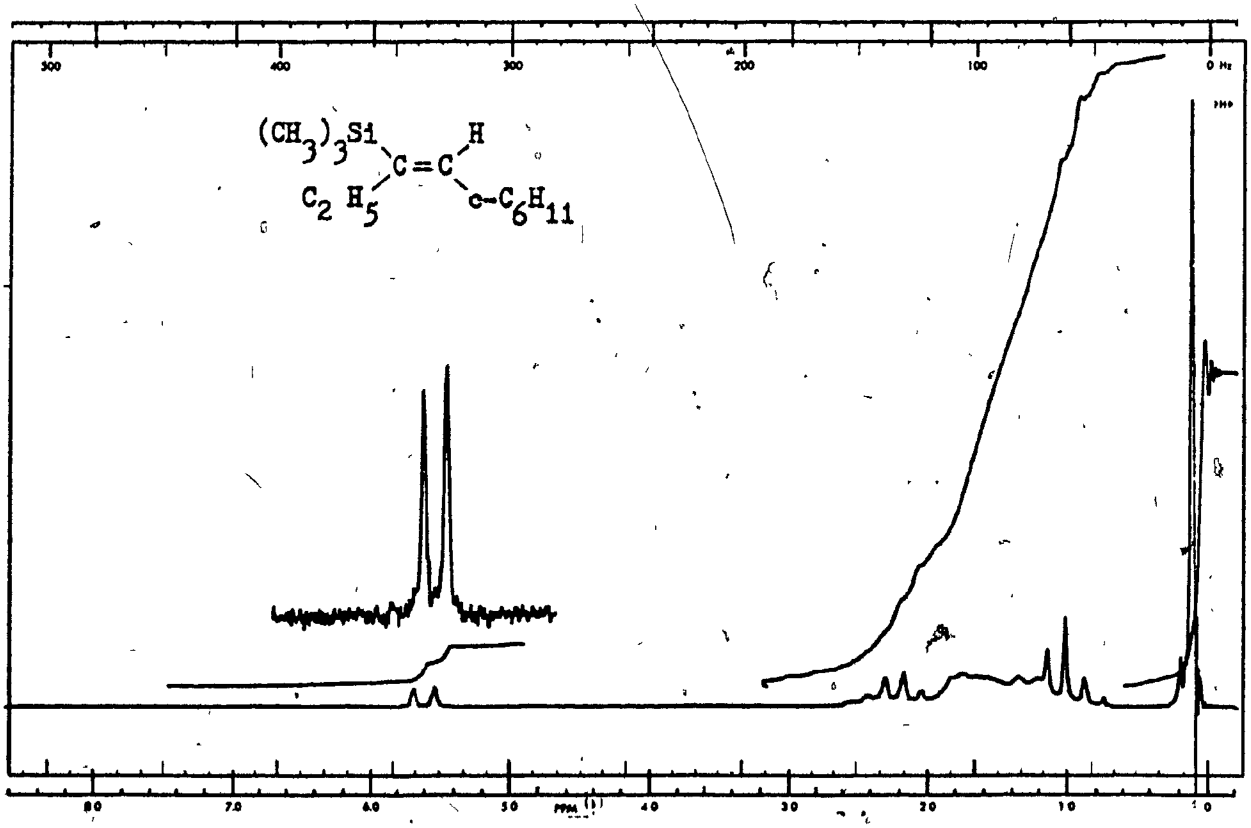

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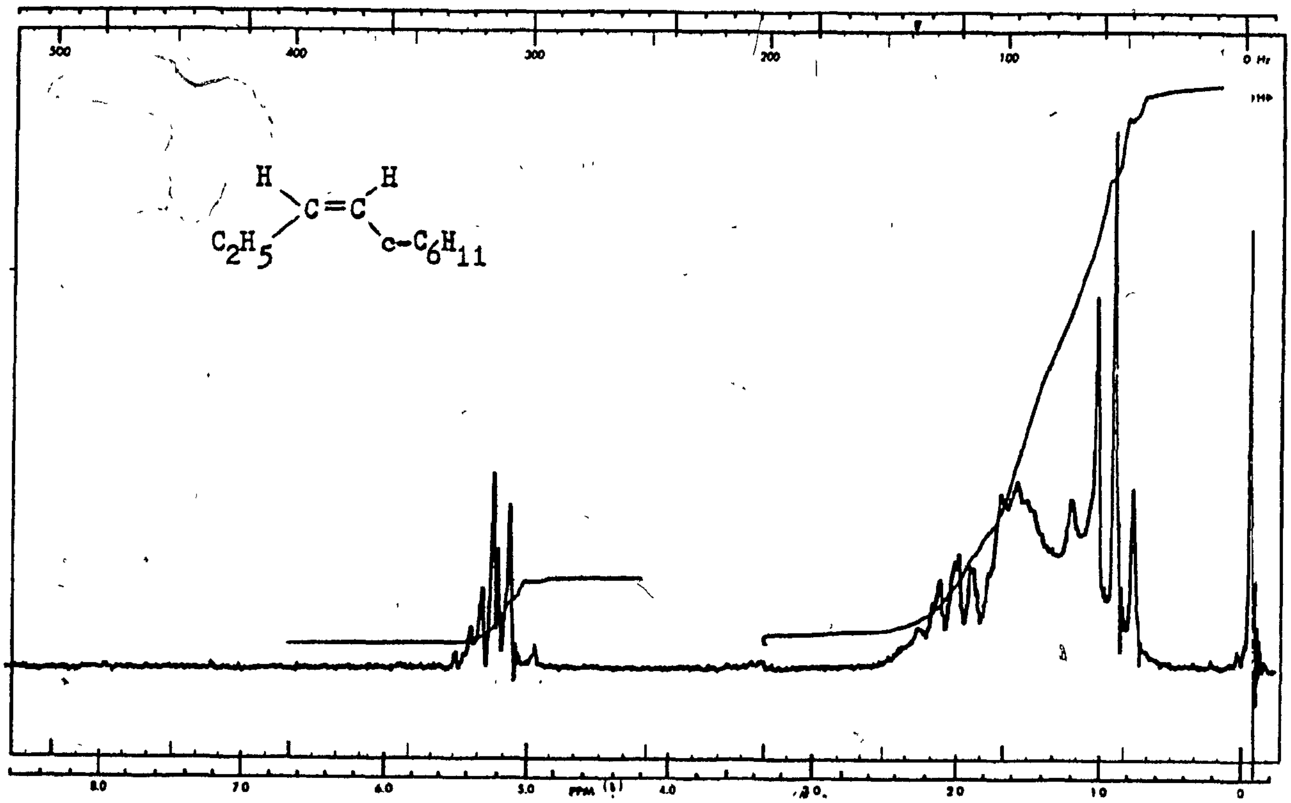

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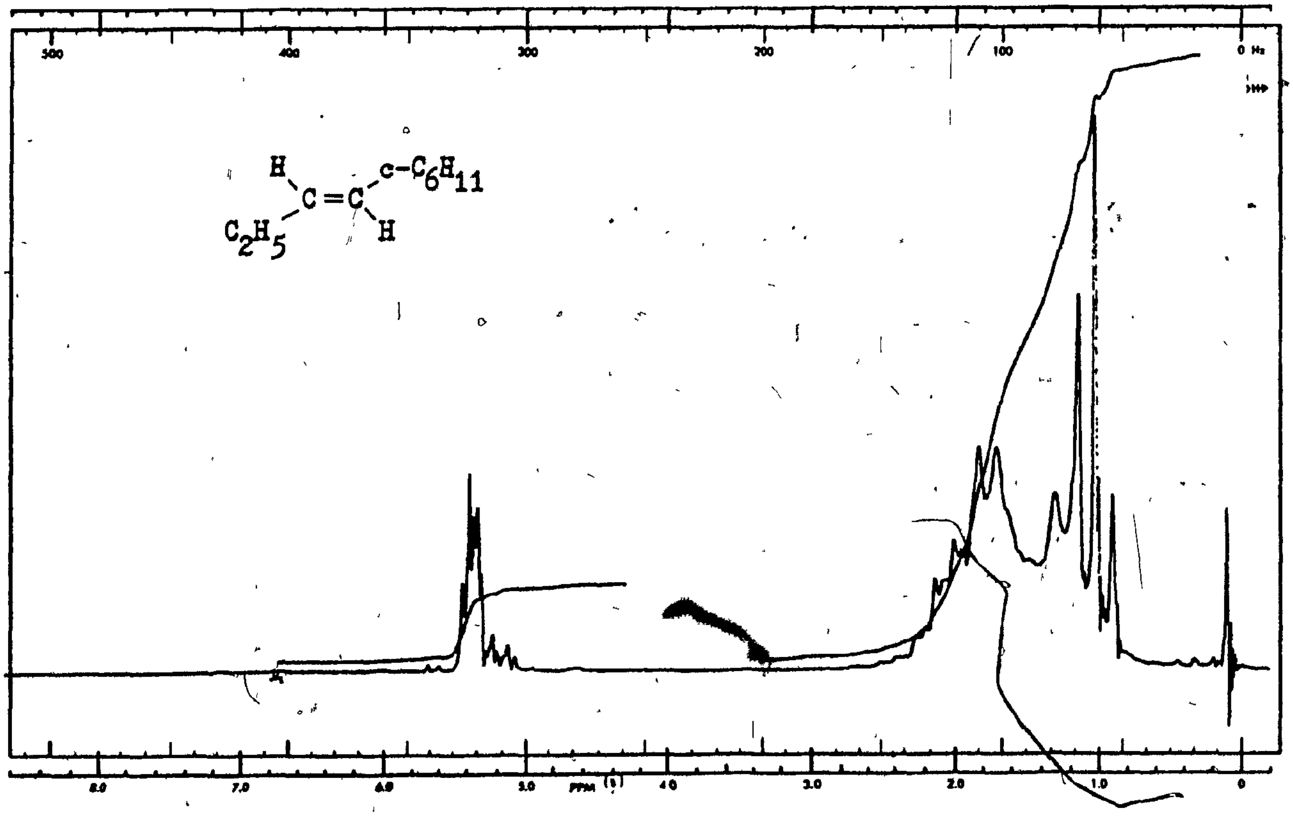

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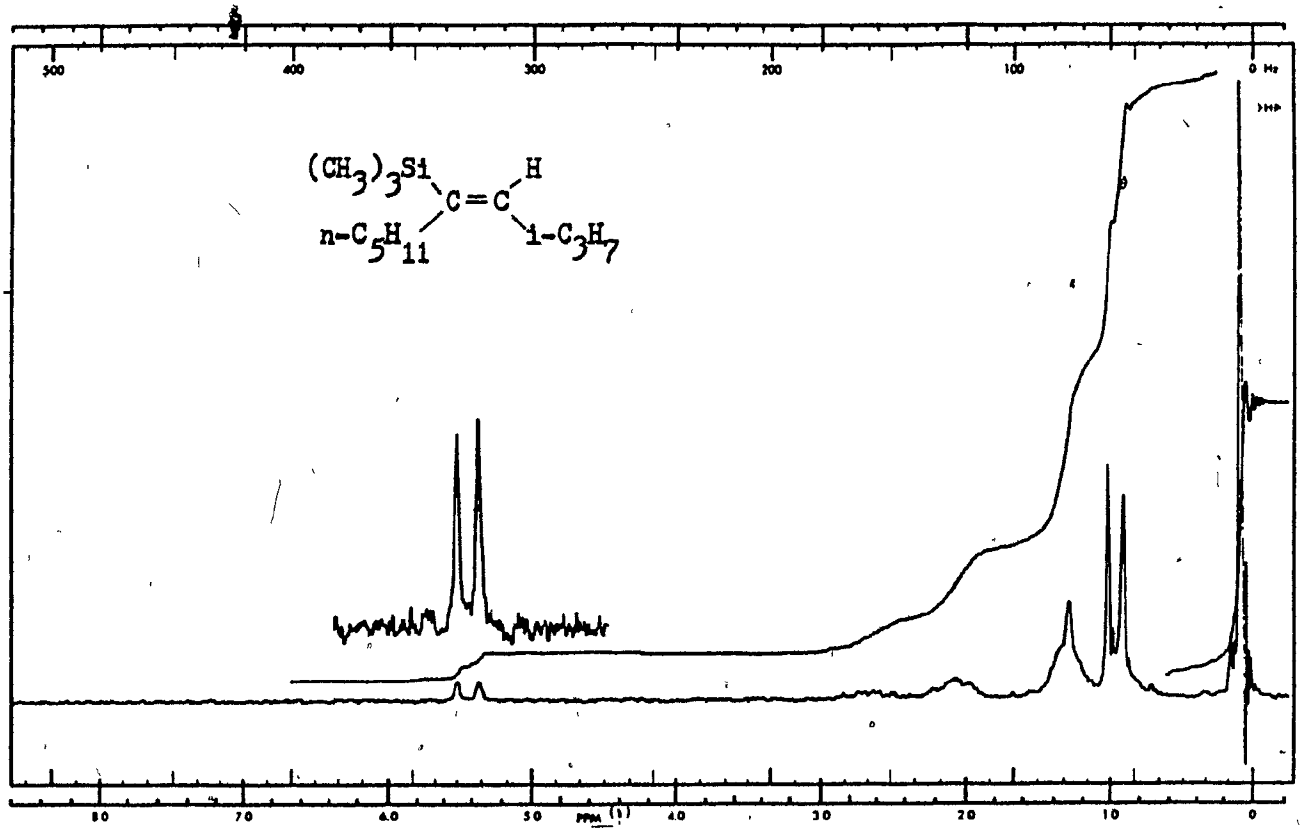

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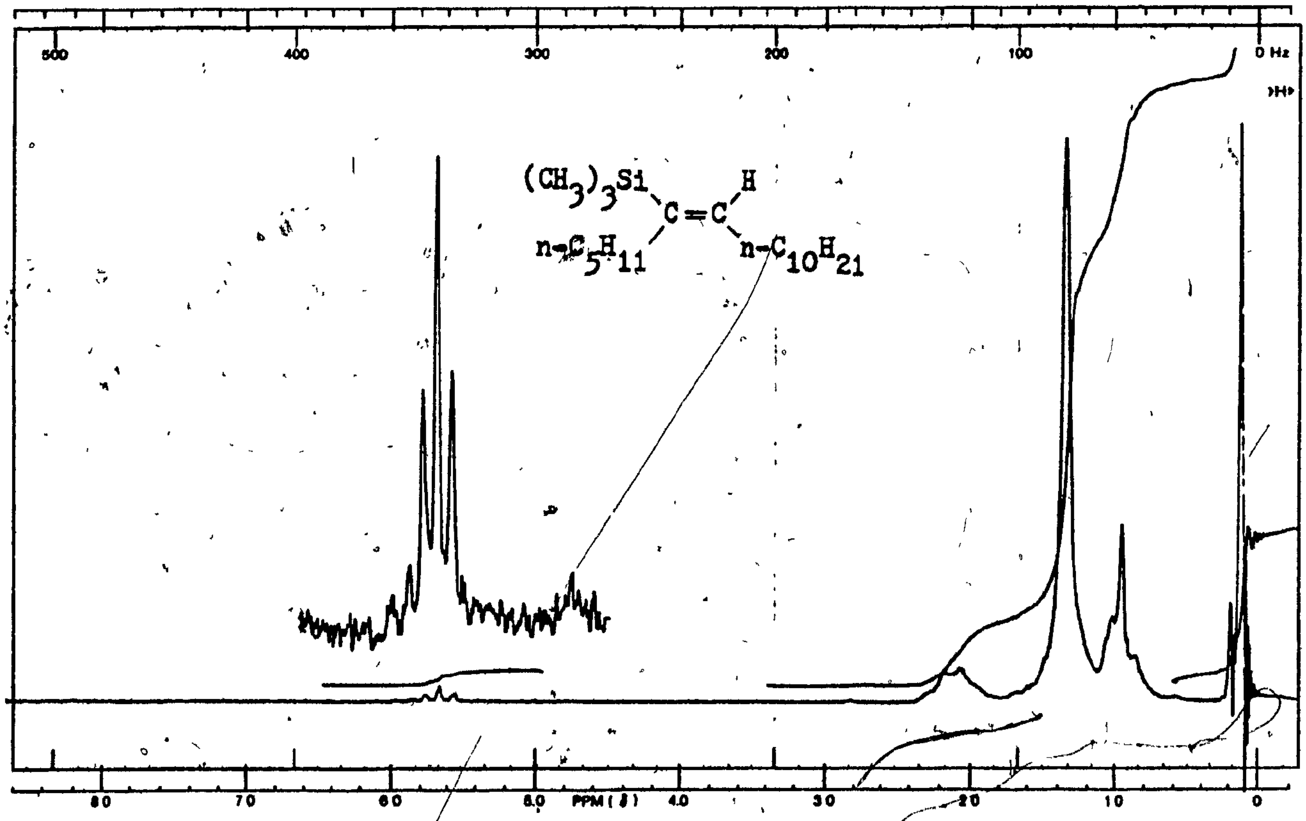

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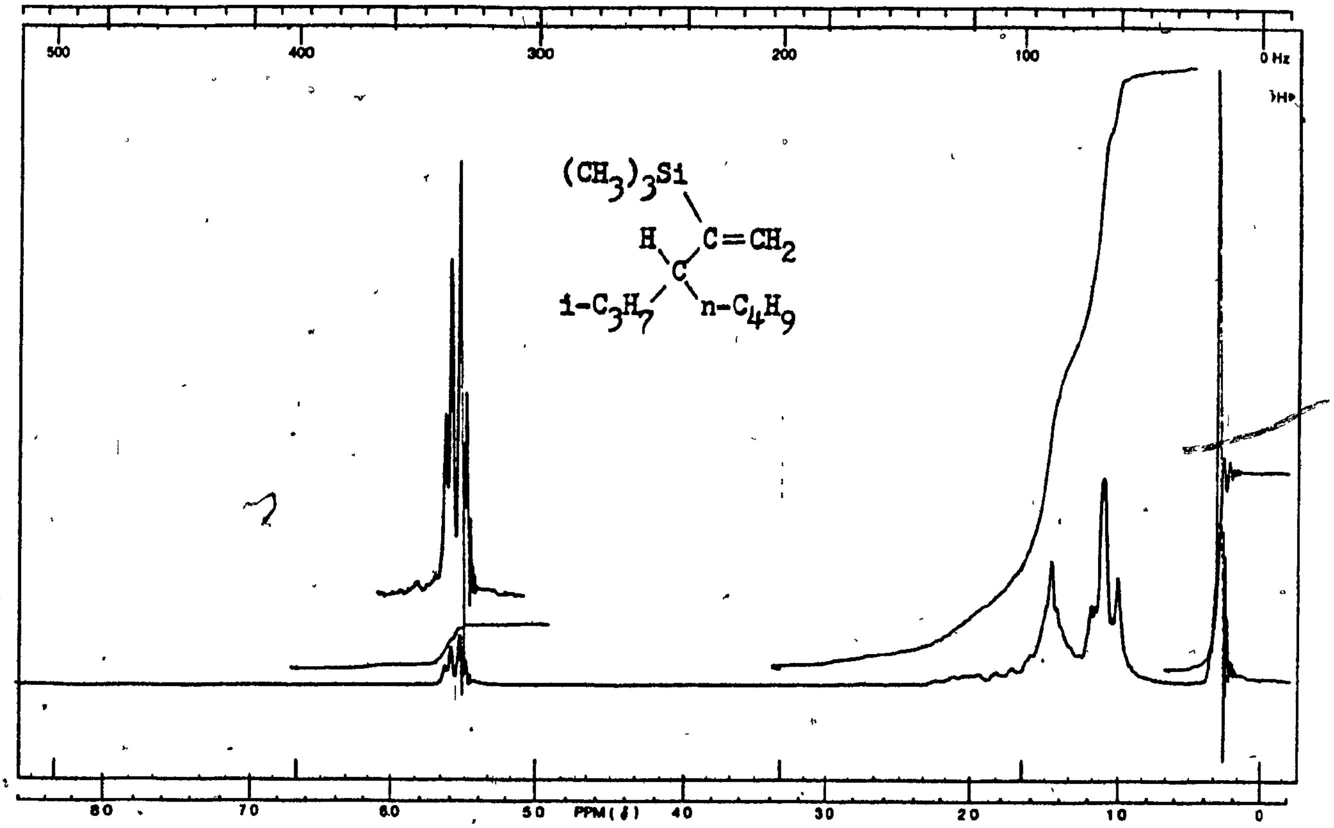

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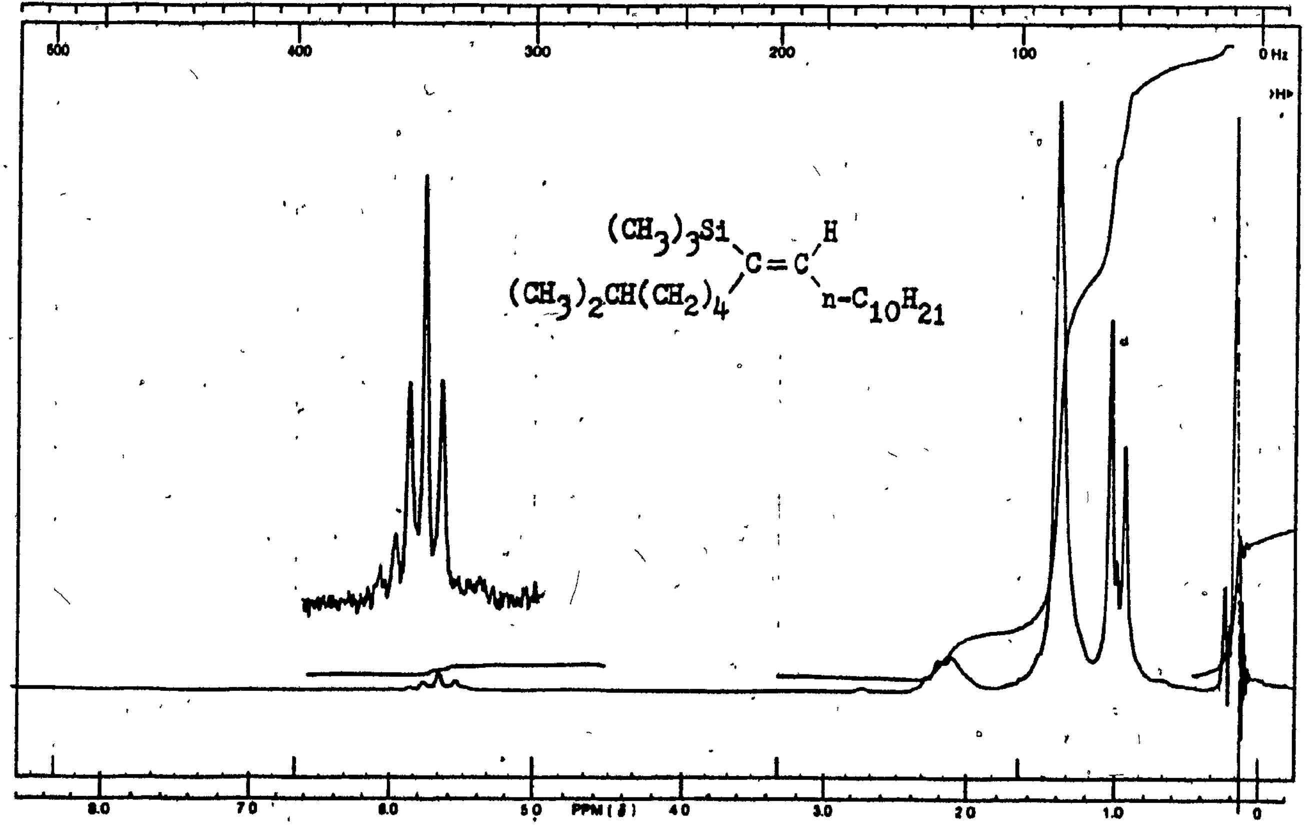

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