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LA THÈSE A ÉTÉ
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TABLE OF CONTENTS

ABSTRACT

The electrophilic addition of areneselenyl and arenesulfenyl halides to alkyl substituted allenes was investigated.

It was found that both species attack the allenic moiety in a 1 : 1 fashion giving rise to addition products of E and Z stereochemistry where attack of the Seleno or Thio moiety had occured exclusively on the central allenic carbon atom.

In the case of 2-Nitroarenesulfenyl chlorides, there is no evidence for a special ortho-Nitro group effect involving a spirosulfurane type intermediate.

For benzeneselenation, preferential formation of the Z-alkenes was observed in contrast to the Sulfur version which favors E-alkenes.

The mechanism of these additions was investigated by following their kinetics by means of the stopped-flow technique. It was found that different intermediates are involved in areneselenation and arenesulfenation of allenes. In the case of PhSeCl a mechanism is suggested wherein the electrophile and allene approach each other so as to form an alkylideneepiselenurane-like species during the rate determining step.

For the Sulfur analogue there is evidence for an S_N2 type mechanism. In this case the allenic π-orbitals are considered as nucleophiles and the halogen atom as the leaving group. This involves the eventual formation of alkylidenethiiranium ions.

A separate investigation was concerned with the first observation of axial dissymmetry induced magnetic nonequivalence in the Carbon-13 NMR of allenes.

Finally, the electrophilic addition of PhSeCl, PhSCl and Iodine to α-allenic alcohols was applied to the synthesis of 2,5-dihydrofuran derivatives. A consequence of this work was a recognition of the stereospecificity of the electrophilic addition of PhSeCl and PhSCl to the allenic system.

INTRODUCTION

PART A: SYNTHETIC APPROACHES TO ALLENES

I- ALLENES

1- General introduction

Substances which contain the $\rangle C(=C)_n=C\langle$ grouping are knownas cumulenes. A subset of these,having only two cumulated double bonds, are known as allenes.

Cumulenes first appeared in the literature as early as 1864, when Reboul[1] suggested that valerylen contained a propadiene unit. Eventhough this was later shown to be only a mixture of C_5 hydrocarbons he was the first one to advance the formula of an allene.

The trivial name "allene" originates from the work of Henry[2] in 1875 and is now widely used for propadiene derivatives. The earliest authentic synthesis of allenes were reported nearly 80 years ago[3]. Methods of preparation were tedious and allenes were thought to be relatively unstable. Because of this precedent these novel compounds became chemical curiosities rather then useful synthetic tools,mainly of interest for their unusual stereochemistry which Van't Hoff predicted as long ago as 1875[4].

In 1921, Brand[5] accidently obtained the next higher homologue of allene, namely a butatriene and it took another 17 years to extend the series of cumulenes still further[6].

In the last 20 years this situation has entirely changed. Several convenient methods have been devised for the synthesis of allenes, and an evergrowing volume of publications is unfolding their interesting properties. They have found use in industry as dyes , antioxidants , polymers , copolymers and heat-

or corrosion-resistant materials.

Proof that natural organisms produce compounds containing the allene bond system was first obtained in 1952 when Celmer and Solomons[7] showed that the highly unstable antibiotic, mycomycin (1) contains an allenic grouping to which it owes its optical activity.

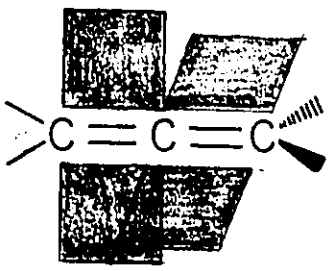
$$HC{\equiv}CC{\equiv}CCH{=}C{=}CHCH{=}CHCH{=}CHCH_2COOH$$

(1)

Recently development has been achieved in the study of cumulenes mainly because of progress realized in the field of acetylenic chemistry.

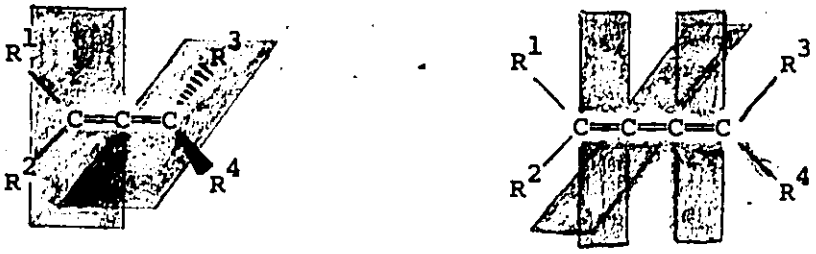
2- Physical properties:

Allenes boil at higher temperatures than paraffins with the same carbon skeleton and have higher refractive indices than the corresponding acetylenes. On the basis of molecular orbital theory, no conjugation or delocalization of electrons occurs between the two π bonds, which are mutually perpendicular.



Heats of hydrogenation and combustion suggest that allenes are less stable than the isomeric species having isolated double bonds. The bond energy[8] of the allenic double bonds amounts to 133.97 Kcal/mole.

One of the most striking physical properties of adequatly substituted allenes is their optical activity. According to Van't Hoff's theory, cumulenes with an even number of doubles bonds have their four substituents arranged in two perpendicular planes, whereas in the case of an odd number of doubles bonds, the substituents must be in the same plane.



This implies that members of the former type (allenes) must occur in optically active forms if $R^1 \neq R^2$ and $R^3 \neq R^4$. On the other hand, cumulenes with an odd number of double bonds will occur as cis and trans isomers.

3- Nuclear magnetic resonance spectra:

Proton nmr spectra of allenes are of considerable interest. Allenes of the type

$$H_a - \overset{|}{C} = C = \overset{|}{C} - H_b$$

show exceptionally large coupling constants between the protons H_a and H_b (6-7 Hz), in spite of their separation by four bonds. This is one of the largest J^4 so far observed. The large coupling is attributed to σ-π interaction between the electrons of the C-H bond and the double bond furthest from it. (The rigid nature of the allene bond also minimizes steric hindrance of resonance).

The vinyl protons in allenes resonate at higher field than in simple olefins due to shielding of the terminal protons by the central sp-hybridized carbon atom.

The ^{13}C resonance spectra of allenes also present interesting features. The central allenic carbon resonates at 200-215 ppm downfield from tetramethylsilane.

Magnetic nonequivalence has been observed in the pmr spectra of allenic ethers of the type:

$$PhCH{=}C{=}CR{-}O{-}CH_2CH_3 \qquad (R = Me,\ i\text{-}Pr)$$

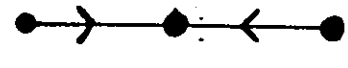
Their molecular asymetry is revealed by the observation of ABX_3 patterns for the methylene hydrogens of the ethyl group.

In the course of this work, axial dissymmetry induced magnetic nonequivalence of isopropyl methyl carbon resonances in appropriately substituted allenes, was observed for the first time.

4- Infrared spectra:

To a first approximation, a symmetric allenic system may be considered as a triatomic linear vibrator, for which three vibrational frequencies are to be considered:

(ν_1, asymmetric streching)



(ν_2, symmetric streching)

(ν_3, bending)

For identification of allenes two bands are of special interest. In the 1970 cm^{-1} region, ν_1 (due to the antisymmetric C=C=C streching vibration) and ν_2 (due to torsional motion of an allenic terminal methylene) in the 850 cm^{-1} region. The band at 850 cm^{-1} is only apparent for terminal allenes. The increase in substitution about the allene by alkyl or aryl groups decreases the intensity of ν_1.

II- SYNTHETIC ROUTES TO ALLENES:

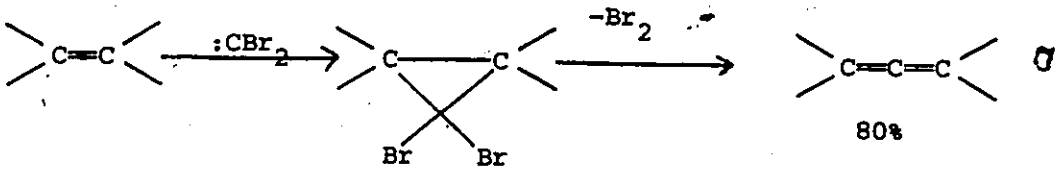
1- Introduction:

Many of the earlier syntheses were based on the well-established methods for introducing carbon-carbon double bonds into organic molecules. These methods soon proved to be very laborious and yields were usually very low. Fortunately the growing interest in allenic chemistry has motivated the development of new techniques specific to allene synthesis such as dehalogenation of gem-dihalocyclopropanes, rearrangement of acetylenes and 1,4 addition to vinylacetylenes.

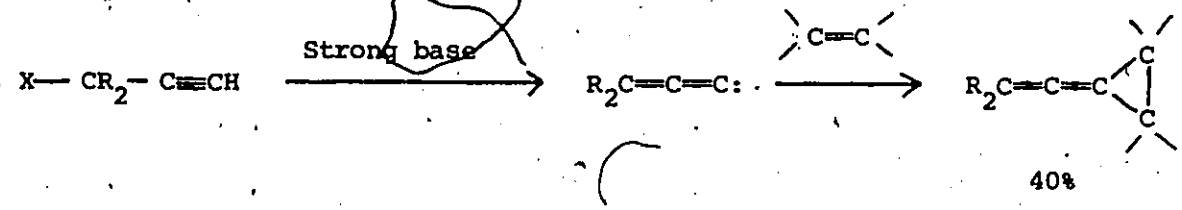
In scheme I are summarized various synthetic routes to allenes.

SCHEME I

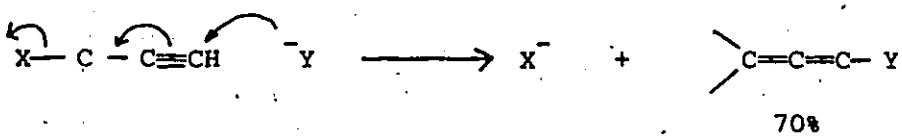
a. Dehalogenation of gem-dihalocyclopropanes[9]:



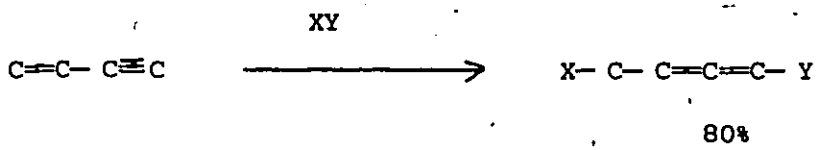
b. Dehydrohalogenation of propargyl halides[10]:



c. Propargyl rearrangement[11]:



d. Addition to vinylacetylenes[12]:



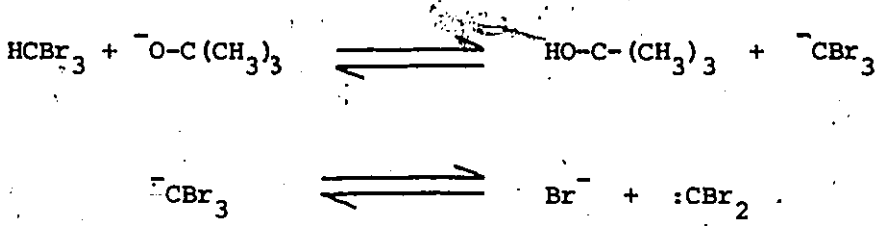
For this work was needed a variety of allenes possessing different structural features. When planning on the synthesis of a large quantity of a class of compounds, one must choose a convenient and versatile route that will provide the pure desired product in fair yield in a relatively small period of time. One must also consider availability and cost of starting materials. For these reasons, all allenes were synthesized by mainly two routes: dehalogenation of gem-dibromocyclopropanes and nucleophilic displacement on propargyl alcohol esters by organocuprate derivatives.

The first method proved interesting due to availability of a variety of branched olefins. The second one is more versatile and very interesting due to extremely low cost of starting materials.

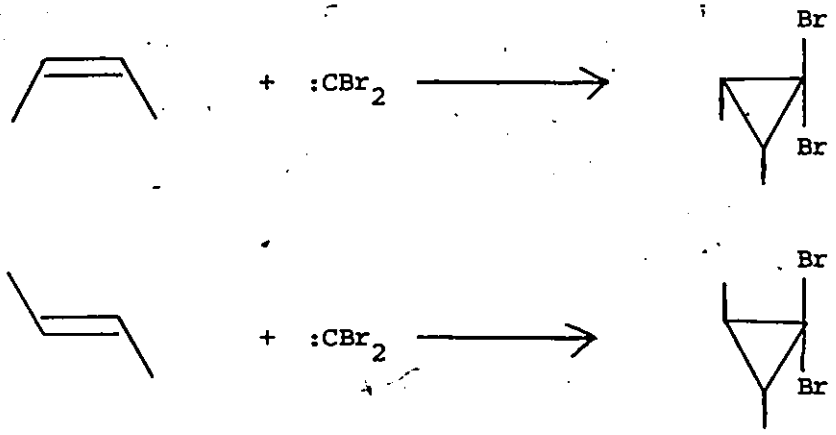
2- MECHANISM OF THE FORMATION OF ALLENES BY DEHALOGENATION OF GEM-DIBROMOCYCLOPROPANES:

The first step in the preparation of a 1,1-dibromocyclopropane is the generation of dibromocarbene from bromoform in strongly basic medium. The best results are obtained with a slurry of freshly prepared alcohol-free potassium t-butoxide in pentane according to scheme II

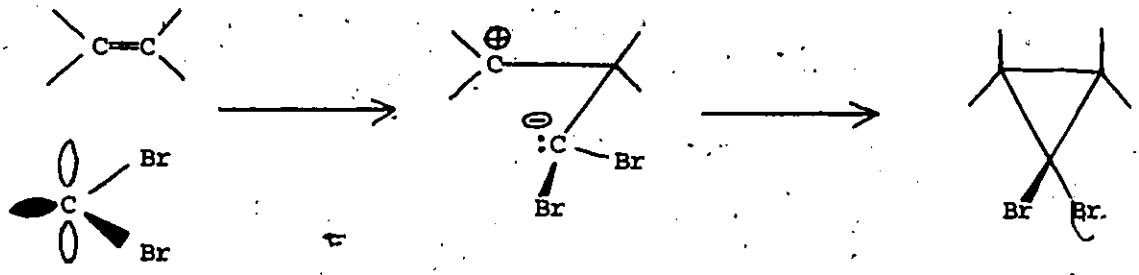
SCHEME II



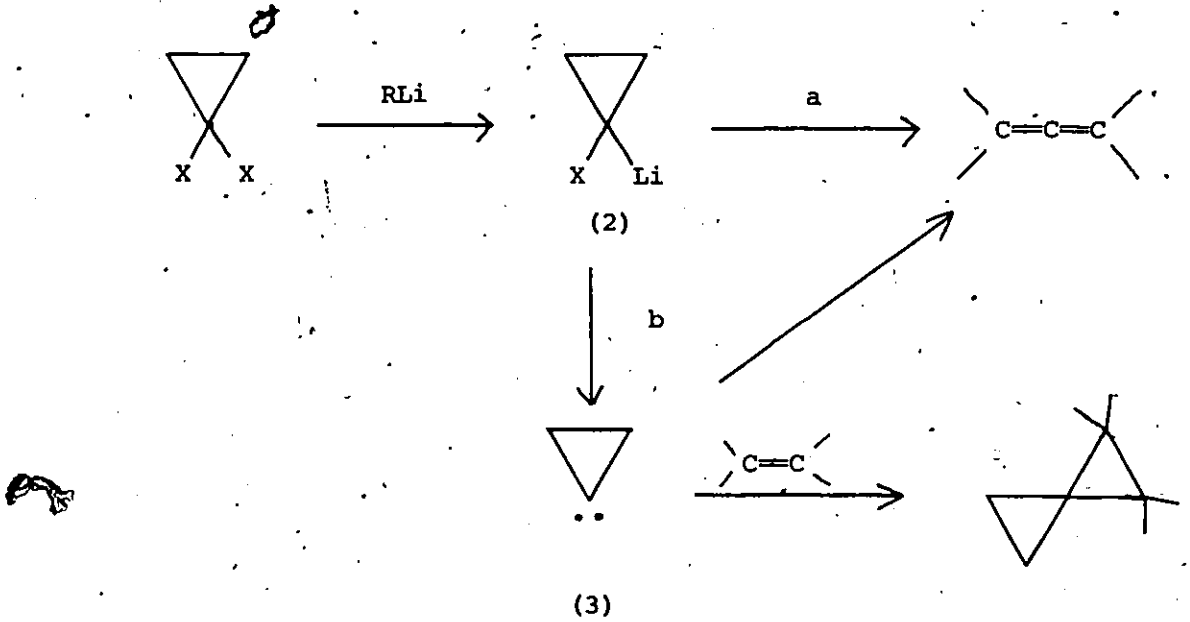
The reaction of dibromocarbene with E- or Z-alkenes is stereospecific[13] and produces the E- or Z-1,1-dibromocyclopropanes respectively.



It is proposed that the intermediate complex in carbene-olefin reactions is a partially-formed cyclopropane with carbonium ion character developped on one of the carbons of the double bond[13]:



The second step is dehalogenation of the gem-dibromocyclopropane and conversion into the corresponding allene. The first approach to this problem was given by Doering and LaFlamme[14] and was later revised by Skattebol who suggested the use of alkyllithiums as dehalogenating agents[9]. The first step can be depicted as a halogen-lithium interconversion with formation of a 1-lithio-1-halocyclopropane intermediate (2) :



(2)

(3)

It is expected that intermediate (2) readily eliminates lithium halide. This may occur by two different mechanisms:

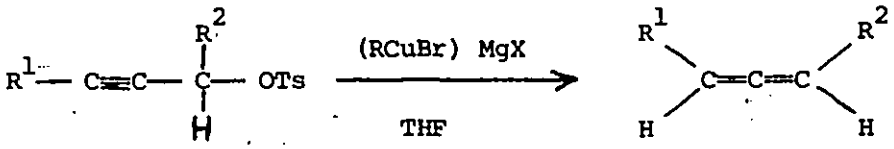
a- Concerted elimination and ring opening to an allene

b- α-elimination to carbene intermediate (3)

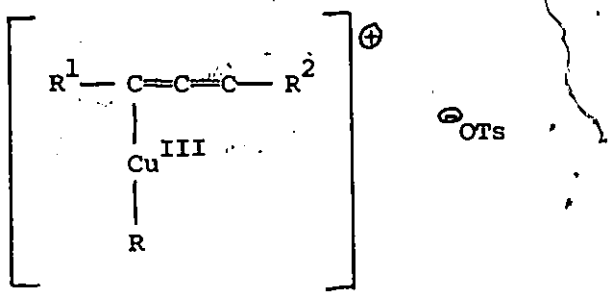
Path a- is most likely to be the correct one eventhough non-allenic isomers have been reported in some reactions. This method was successfully applied to relatively unstrain mono-, di-, and trisubstituted olefins.

3- ALLENES VIA PROPARGYL REARRANGEMENT:

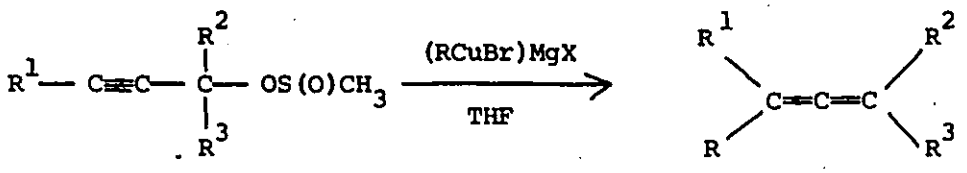
The most widely used method for the synthesis of allenes is probably that using gem-dibromocyclopropanes; however, alkenes are often expensive and yields are very low in the case of sterically hindered olefins. In 1975 was reported an efficient synthesis of allenic hydrocarbons from 2-propynyl tosylates and organocopper (I) reagents in tetrahydrofuran[15].



This reaction is thought to occur via Cu(III) intermediates such as



The main disadvantage of this method is that tosylates are not very stable and very difficult to obtain pure in the case of tertiary alcohols. With this problem in mind, Vermeer showed that the more readily available sulfinate esters can be substituted very satisfactorily by organocopper(I) reagents[16]. When carried out in THF, alkylheterocuprates (RCuBr)MgX convert 2-propynyl esters (4) into allenes (5).



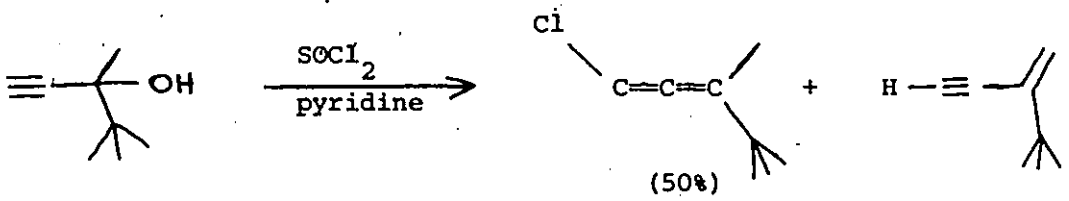
(4) (5)

(yields: 90%)

We have applied successfully this method to R, R^1, R^2, R^3 = H, alkyl or aryl. Here again, the reaction is thought to proceed through Cu^{III} intermediates.

4- 1-CHLOROALLENES FROM PROP-2-YN-1-OLS[17]:

Tertiary acetylenic carbinols react with thionyl chloride to give 1-chloroallenes and alkenynes, whereas secondary and primary acetylenic carbinols give mainly acetylenic chlorides. Good yields of chloroallenes are obtained from sterically hindered tertiary acetylenic carbinols.



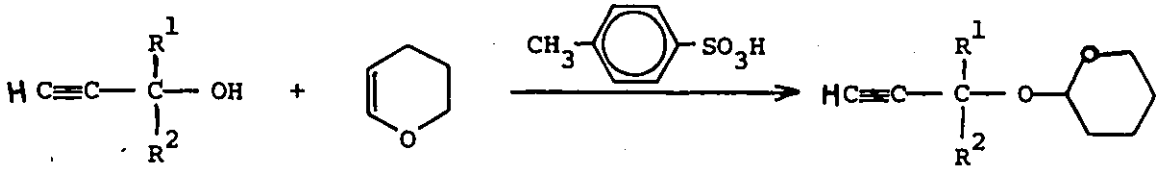
5-α-ALLENIC ALCOHOLS:

The occurence of the α-allenic alcohol moiety in naturally occuring substances has promoted active research in this field. α-allenic alcohols are synthesized by four major routes:

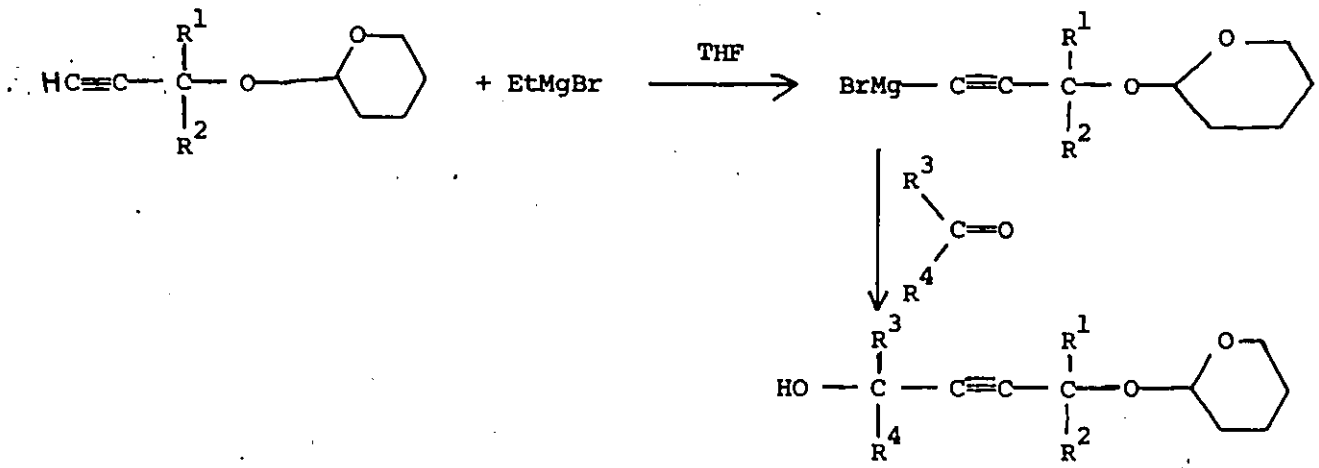
- Propargylic transposition
- Synthesis from α-allenic ketones
- Addition to 1,4-vinylacetylenes
- Synthesis involving gem-dibromocyclopropanes

Only the first route will be discussed as it is the most widely used due to versatility and availability of starting materials. The other routes are discussed in the excellent review article by M. Huche[18]

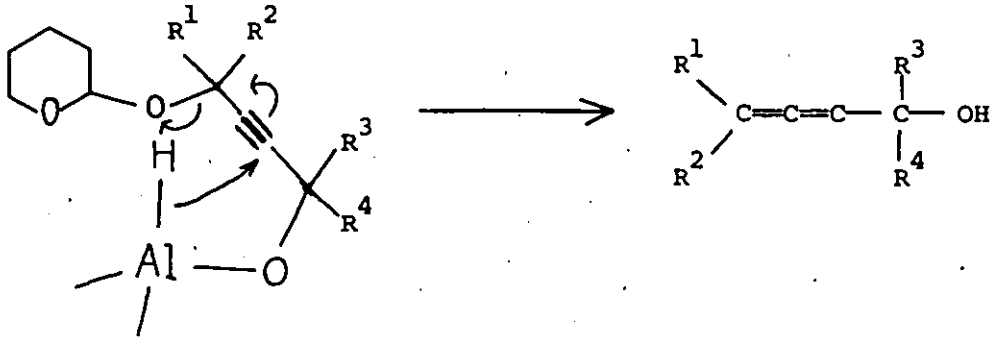
The first step is the conversion of an α-acetylenic alcohol to a pyranyl ether[19].



This intermediate is then condensed with a ketone or aldehyde via a Grignard reaction:



The alcohol is reduced with lithium aluminum hydride, yielding the α-allenic alcohol in approximately 70% yield.

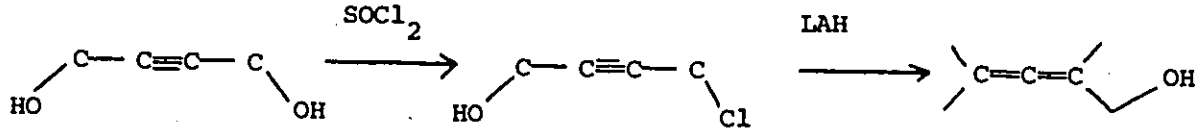


This method is applicable to the three classes of alcohols, to ene-allenols (R^3 = —C=CR^{5}R^6) and to the synthesis of β-allenic alcohols. For the latter, symmetrical epoxides are condensed with the Grignard instead of carbonyl compounds. α-allenic alcohols are useful synthetic intermediates. They can be converted to the corresponding ketone, aldehyde or amide[20] or cyclized to unsaturated, functionalized ethers as demonstrated in this work.

Note that α-allenic alcohols synthesized in this way always contain a hydrogen in the α-position on the allene.

Other leaving groups such as chloride[21] or triethylamine[22] can be used as substitute for the pyranyl ether.

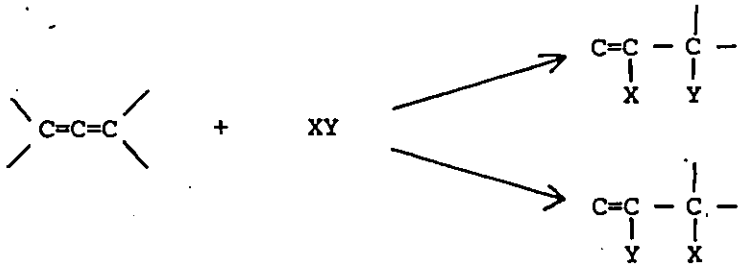
For instance:



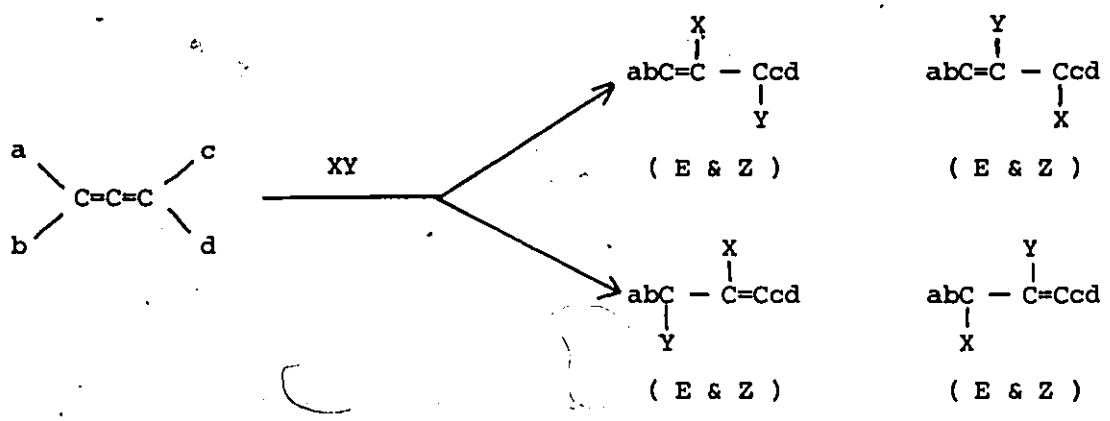
PART B: ELECTROPHILIC ADDITION REACTIONS OF ALLENES

1- General information

A relatively high degree of unsaturation and a readily accessible π-bond system makes allenic compounds particularly reactive towards electrophilic additions. Because of the geometry and polarizability of the π-bond, groups attached to the cumulene bond will strongly affect orientation of attack by electrophiles. Attack of an allene by an unsymmetrical reagent XY can lead to two different products depending on whether the electrophile attacks at the central carbon or at a terminal position:



If the two π-bonds are differently substituted, their reactivity is likely to be different and the reagent may therefore be expected to show some selectivity between them, as well as between the two carbons of a given bond. Also, when the substituents at one terminus are different, two directions of approach of a reagent are possible and this leads to E and Z isomerism. In total there are eight possible products of addition of XY to an unsymmetrically substituted allene.



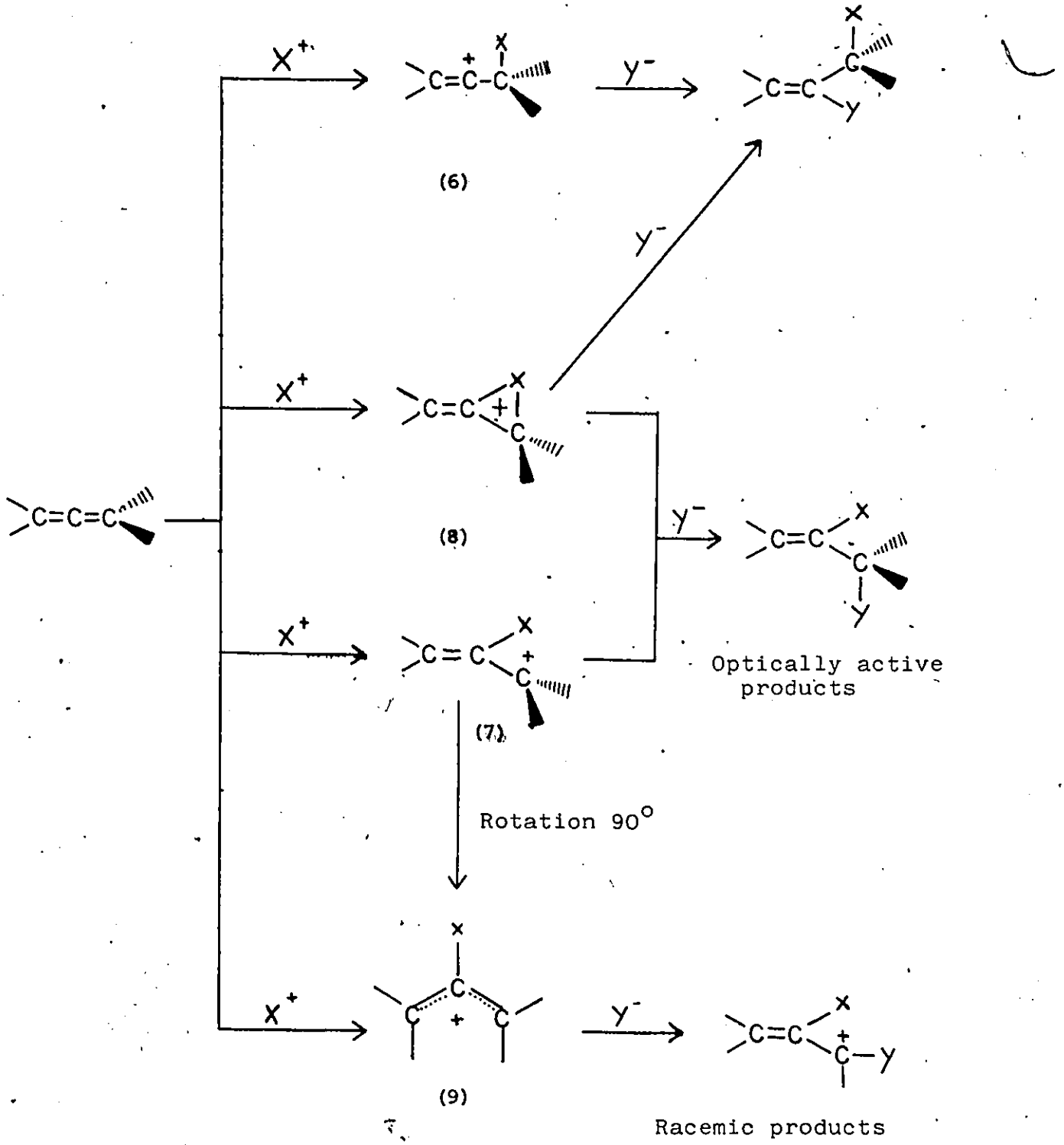
Distribution of products resulting from electrophilic addition of XY to an allene will depend on the structure of the reaction intermediate as shown in scheme III.

Attachement of the electrophile X^+ to a terminal carbon probably involves vinylic cation (6) intermediates. On the other hand, attack at the central carbon indicates that allylic cations (7) may be formed. An alternative to non-planar ions (7) are bridged ions (8) in which the locus of initial attack has lost some of its meaning. Bridged ions (bromonium, episulfonium ions) are thought to be involved in stereospecific trans-addition of halogens, sulfenyl chlorides and mercuric salts to alkenes. It remains uncertain whether electrophilic attack at the central carbon of an allenic system will involve resonance stabilized allylic intermediates (9) or non-planar allylic intermediates (7) or (8). Occurence of a particular intermediate will clearly depend on the structure of the allene and the nature of the electrophile.

2- Reactivity of 1,2-propadiene:

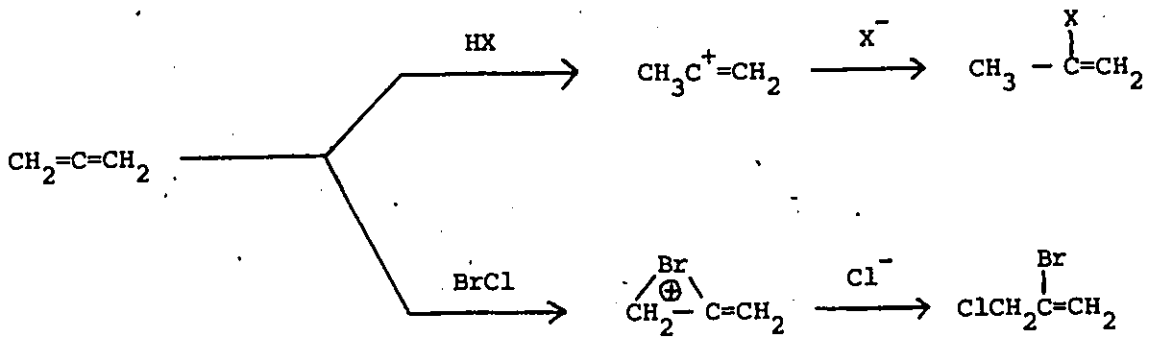
The dependence of product formation on structure of both allene substrate and attacking electrophile is clearly demonstrated in the case of 1,2-propadiene itself.

SCHEME III

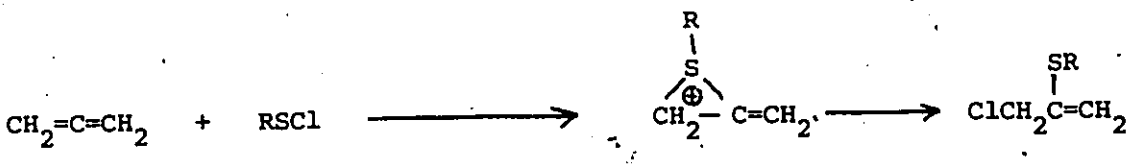

X+
Y-
(6)
(8)
(7)
Rotation 90°
Optically active products
Racemic products

- Methoxymercuration and hydrogen halide addition give electrophilic attack at the terminal carbon[23].
- Addition of sulfenyl halides and halogens on the other hand result in the opposite orientation[24].

In the case of alkenes, addition of electrophiles such as halogens and sulfenyl halides occurs via bridged ion intermediates[25]. However, electrophilic additions to allenes seem to follow one of two paths depending on the nature of the reactant. Hydrogen halides add with the formation of a vinylic carbonium ion intermediate whereas interhalogen compounds attack (e.g. BrCl), involves formation of a bromonium ion and subsequent nucleophilic attack of the chloride ion on the terminal sp^3 carbon.



A similar episulfonium ion intermediate (10) can a priori be considered for the sulfenyl chloride addition to allene:

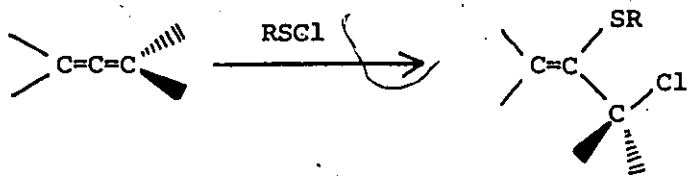


(10)

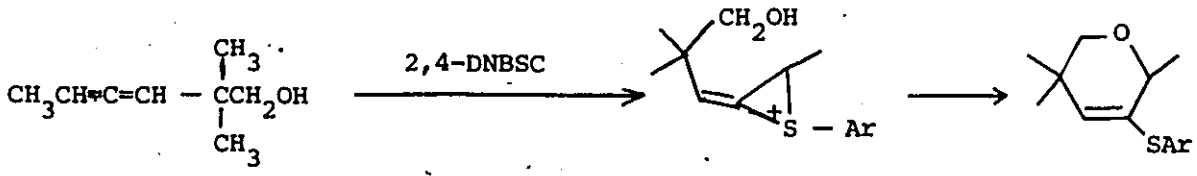
3- Reactivity of substituted allenes

If one considers more highly substituted allenes, the situation may be entirely different. For example, addition of HCl to 1,3-disubstituted allenes appears to proceed largely by way of central electrophilic attack[26,27]. In the case of oxymercuration, on increasing methyl substitution there is a clear change in orientation from exclusive terminal electrophilic attack on allene to exclusive central attack[23].

Sulfenyl chloride additions to allenes are reported to orient the sulfenyl group to the central allenic carbon and the chloride to a terminal position.

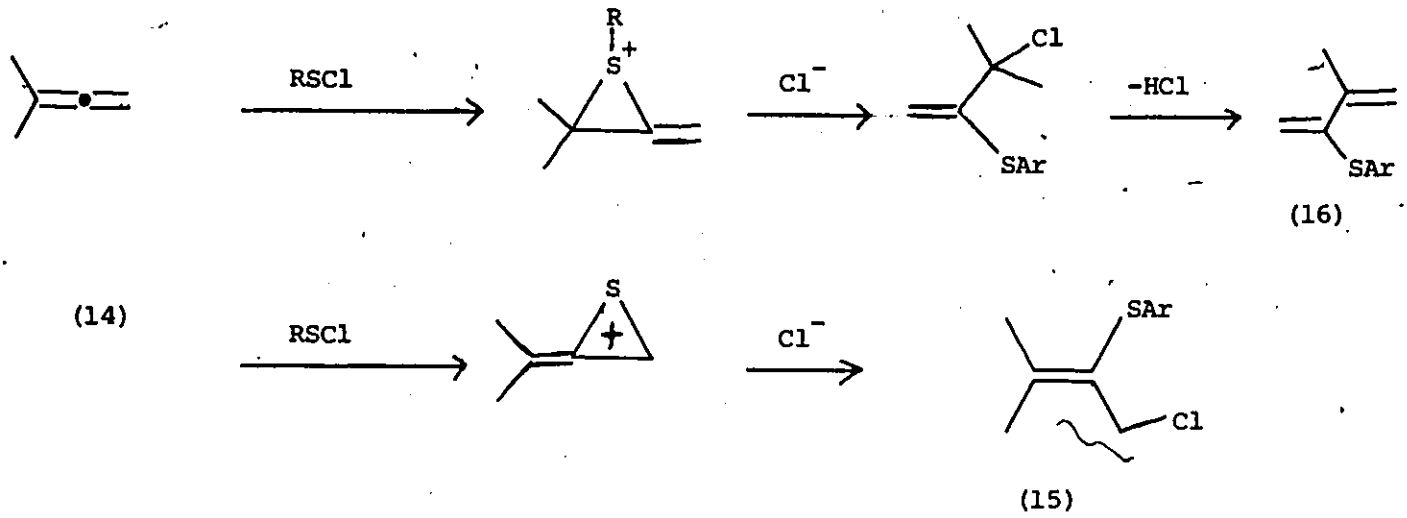


Jacobs[28] has obtained evidence that a dissymmetric intermediate such as the vinylic episulfonium ion (11) must be involved in the addition of 2,4-dinitrobenzenesulfenyl chloride (2,4-DNBSC), to optically active 2,2-dimethyl-3,4-hexadien-1-ol (12) since the cyclic adduct (13) was obtained optically active.

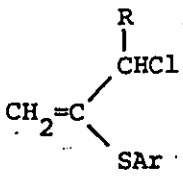


(12) (11) (13)

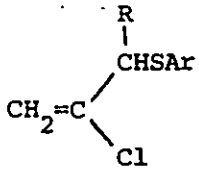
Allenes in which the cumulated double bonds are differently substituted offer two different sites for attack by sulfenium ions.



One might anticipate that the more highly substituted double bond would be attacked preferentially. However, the addition of 2,4-DNBSC to 1,1-dimethyl allene (14) gives the primary chloride (15) rather then the isomeric tertiary allylic chloride[29] although approximately 60% of the overall product mixture is the diene[30] (16). More recently, Jacobs and Kammerer[31] reported that the major adduct of 2,4-DNBSC with various monosubstituted allenes is that of type A rather than that of type B structure.

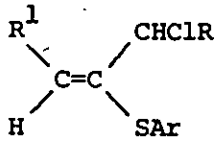


A

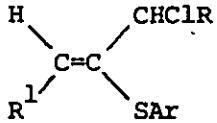


B

It was reported in the same article that 1,3-disubstituted allenes give mixtures of adducts of type A and B. We have found that attack by sulfur occurs exclusively at the central allenic carbon[32] yielding mixtures of E and Z isomers



(E)



(Z)

The case of halogenation resembles that of oxymercuration in that the electrophile enters at the central carbon and the nucleophile at the more highly substituted carbon. The bromination of 2,2-dimethyl-3,4-hexadien-1-ol is thought to be non-stereospecific[28] whereas that of 1,3-dimethyl allene is reported to retain configuration[33].

4- The effect of methyl substitution

The influence of methyl substituents is due to a balance between steric and electronic effects. It is related to the fact that carbonium ion stability increases with methyl substitution. The change in orientation from terminal to central electrophilic attack with increasing methyl substitution reflects the increase in stability of secondary and tertiary carbonium ions relative to primary and vinyl carbonium ions. The preference for attack at the more highly substituted of two cumulated bonds is also related to such factors. This becomes of less importance in bridged ion intermediates where the position of attack becomes obscure. The transition state nevertheless has carbonium ion character and will be stabilized by electron donating substituents such as alkyl groups.

Steric effects are more ambiguous. A reagent approaching one double bond is coplánar with the substituents at the terminal of the other double bond, and this in principle could lead to unfavorable steric interactions. Steric effects of this type do not appear to be a dominating influence as evidenced by the fact that the major products of halogenation and oxymercuration are the Z-alkenes. G.Schmid and al.[34] have studied the rates and products of addition of benzenesulfenyl chloride to allene and its five methyl-substituted derivatives. Substituting the hydrogens on allene by methyl groups has a large effect on the rate of addition. The rates of addition to 2,3-pentadiene and 3-methyl-1,2-butadiene

are almost identical, indicating that the effect of a methyl group is transmitted across both double bonds.

RESULTS AND DISCUSSION

INTRODUCTION:

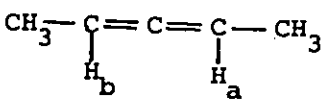
The allenes used in the present investigation were synthesized according to literature methods described previously in the introduction.

Overall yields were low due to azeotroping of the allene by residual amounts of solvent. However, Nuclear Magnetic Resonance revealed a purity greater than 90% in most cases. Impurities were identified as residual solvent (THF) or unreacted sulfinate ester that could not be separated by simple distillation. However they did not interfere when the allene was subjected to electrophilic addition conditions. The allenes were fully characterized by IR (band at 1975 cm^{-1}), ^{1}H NMR and ^{13}C NMR spectroscopy.

As a representative example, the IR spectrum of 1,2-cyclotridecadiene is shown in figure 1. The C=C=C strech is easily discernable at 1970 cm^{-1}.

The ^{1}H NMR spectra of allenes are characterized by two main features:

- the allenic protons resonate at a high chemical shift ranging from 5.0 to 5.4 ppm downfield from TMS, and are strongly coupled.
- The spectra are always complex due to the importance of the ^{5}J coupling constant between allenic protons and aliphatic substituents.



This is exemplified in figure 2 which is the 60 MHz ^{1}H NMR spectrum of 2,3-pentadiene. The methyl group appears as a triplet because of the coupling with both H_a and H_b protons. It is interesting to note that $^{3}J_{Me-H_a} \simeq {}^{5}J_{Me-H_b}$.

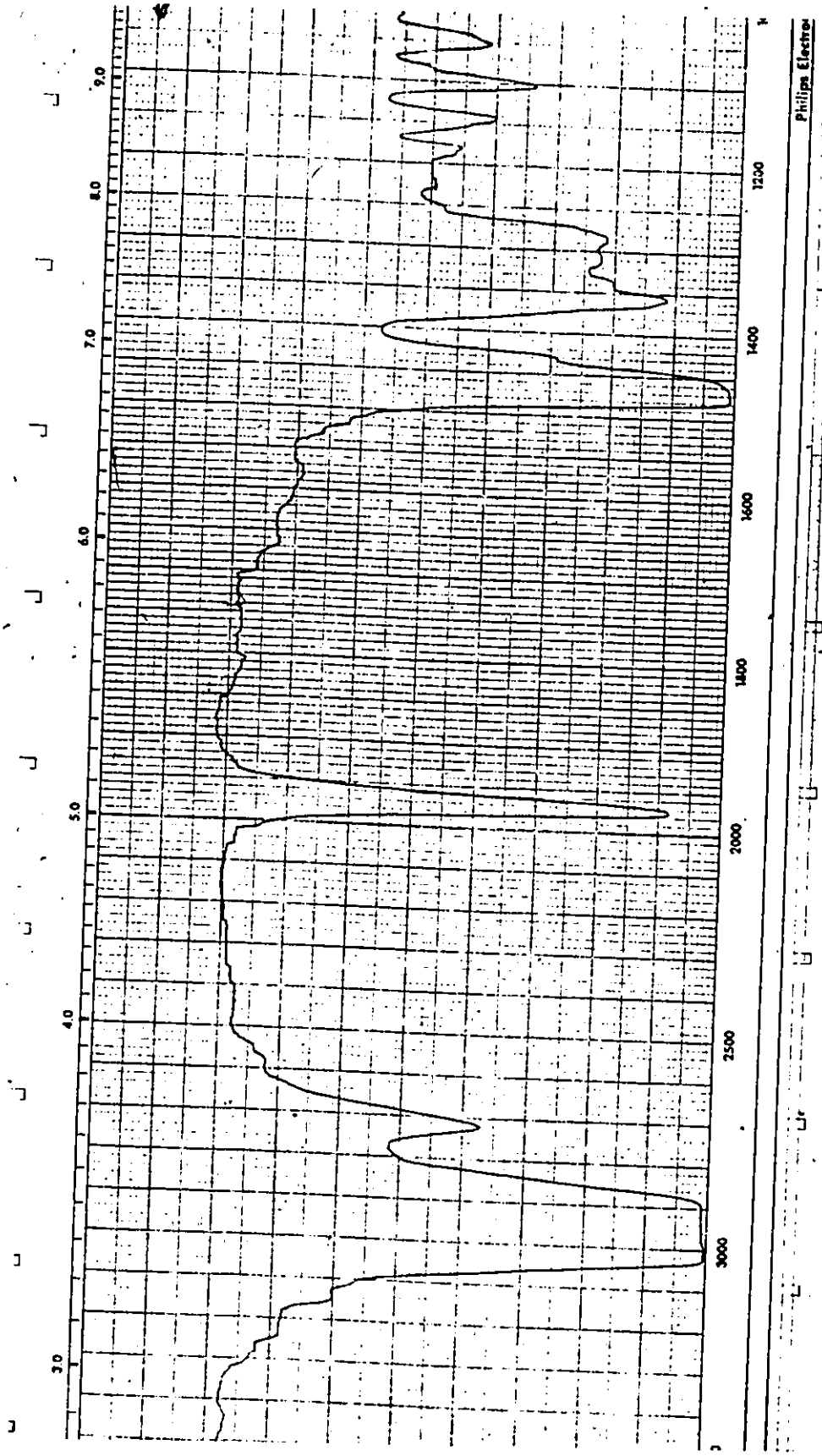


figure 1 Infra Red spectrum of 1-2-cyclotridecadiene

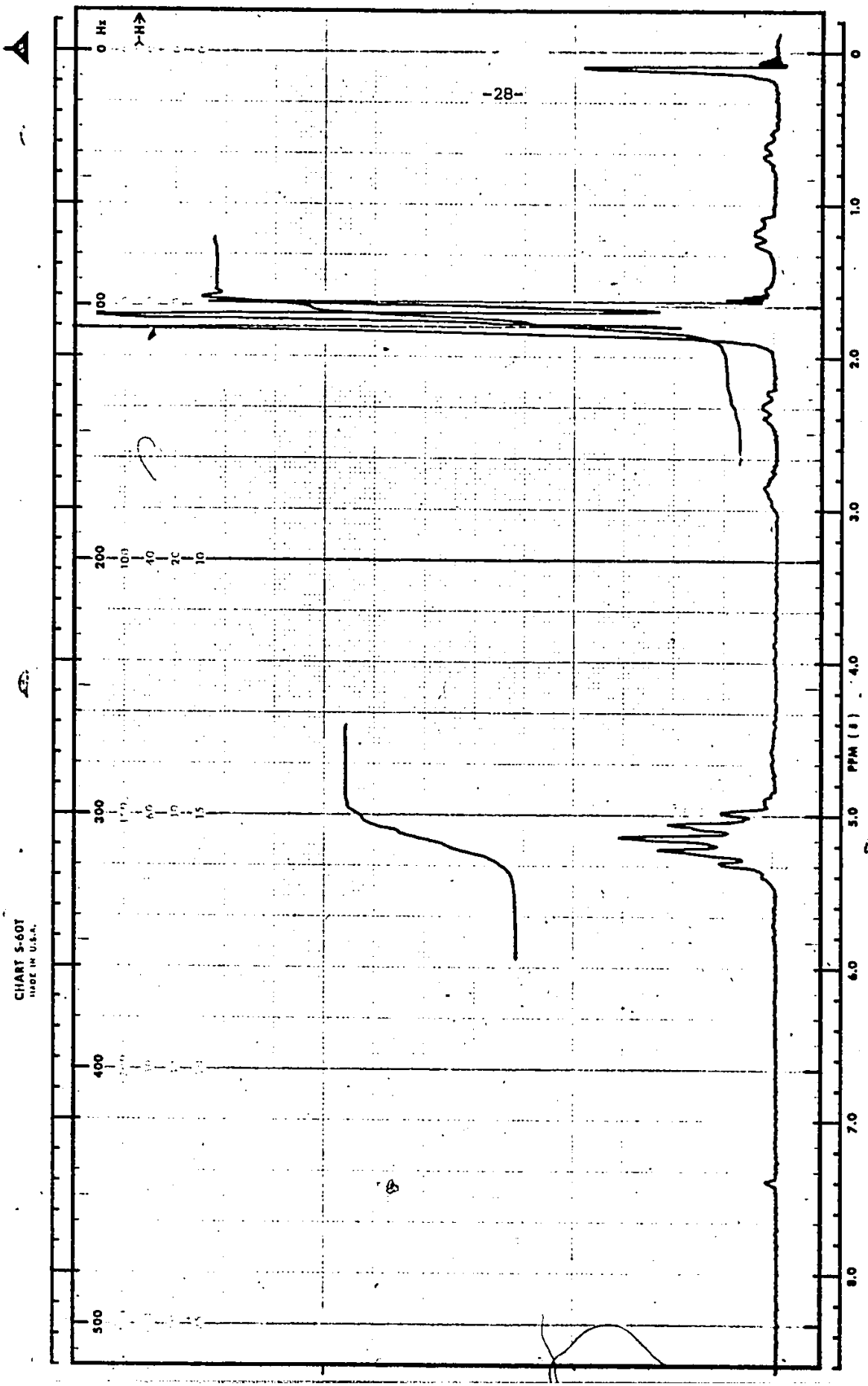


figure 2 proton NMR spectrum of 2-3-pentadiene

The ^{1}H NMR spectral parameters (chemical shifts and coupling constants) of all allenes synthesized in this work are tabulated in Appendix I.

Carbon-13 NMR spectroscopy also allows unequivocal identification of the allenic moiety due to the very lowfield resonance of the central allenic carbon[52,53] (about 200 ppm downfield from TMS at 20 MHz).

In the case of tetrasubstituted allenes, Carbon-13 NMR was the only reliable identification tool as the IR allenic absorption was too weak to be observable and there were no allenic protons present.

The central allenic carbon being quaternary its intensity is very weak and it was found necessary to use concentrated samples of the allene (approximately 30% in $CDCl_3$). This increased the signal to noise ratio to an extent that the characteristic carbon resonance was easily distinguishable from the background.

The Carbon-13 NMR spectral parameters of allenes used in this work are tabulated in Appendix II.

PART I

AXIAL DISSYMMETRY INDUCED MAGNETIC NONEQUIVALENCE IN THE CARBON-13 NMR SPECTRA OF ALLENES

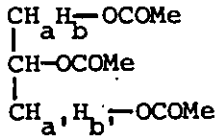
1- INTRODUCTION :

It is generally assumed that two identical atoms or groups attached to a common atom (eg., the protons of a CH_2 group), are indistinguishable due to free rotation about a single bond.

Often, one has to consider the 3-dimensional molecular structure in order to understand unexpected nonequivalence.

Two atoms are defined as magnetically equivalent if they are isochronous and if their coupling constants to any other atoms are identical. Unfortunately such factors as Accidental Magnetic Equivalence often complicate the picture.

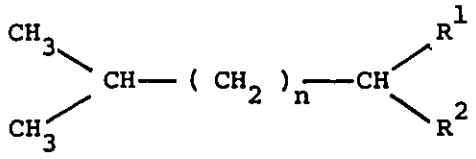
Magnetic nonequivalence occurs even when there is no chiral center present in the molecule. This is a result of the fact that some atoms are diastereotopic. This is exemplified in the complexity of the ^1H NMR spectrum of the triglyceride, Triacetin.



TRIACETIN

Magnetic nonequivalence is not restricted to proton NMR spectroscopy. Carbon-13 NMR chemical shifts can be influenced by molecular asymmetry.

The effect of molecular asymmetry on the resonance of methyl carbons in isopropyl groups in compounds of the type

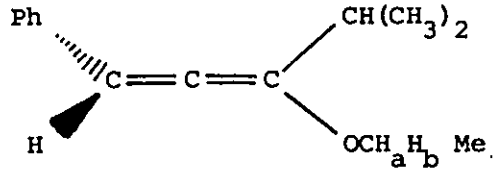


was reported by Roberts et al.[55]

Carbon-13 NMR spectroscopy is a very useful tool in the study of magnetic non-equivalence because the effect of conformational change on ^{13}C chemical shifts is quite significant.

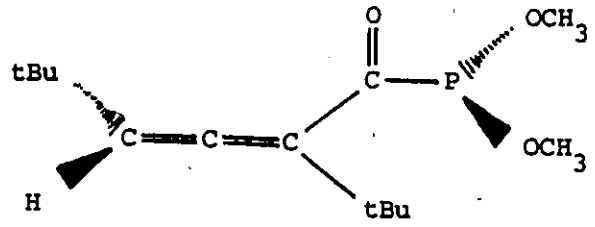
Magnetic nonequivalence is not restricted to molecules having a potential-asymmetric center. The chirality may be induced by an axis of dissymmetry such as in allenes or biphenyls.

The methylene protons of the ethyl group in the allene depicted below are not equivalent due to the axis of dissymmetry inherent of the allenic moiety :



The corresponding effect in carbon-13 spectroscopy has not been investigated to a significant extent. The only two examples that have appeared in the literature are not as clear cut as one would like.

G.A.Krudy and R.S.Macomber[53] have reported the nonequivalence of the two methoxy groups in the following phosphonic ester :



However, only an averaged chemical shift was reported.

Isopropyl methyl carbons in trisubstituted allenes have also been reported to be nonequivalent but the difference was small and in one allene out of three studied, accidental coincidence was observed.

Because of the availability of a large number of allenes prepared for view during this mechanistic study, we undertook an extensive, systematic investigation of the NMR properties of the allenes. We present unequivocal evidence for the axial dissymmetry induced magnetic nonequivalence of isopropyl methyl carbon resonances in appropriatly substituted allenes.

2- OBSERVATIONS :

The Carbon-13 NMR spectra were recorded using a VARIAN ASSOCIATES FT-80 spectrometer with a broad band probe operating at 20.000 MHz, using 16K memory. Initial proton-decoupled spectra were run with a spectral width of 2000 to 2809 Hz dependent upon fold-back problems.
A pulse width of 5 microseconds corresponding to a flip angle of approximately 21.5° was employed. Chemical shifts are reported δ ppm downfield from an internal TMS standard $\pm$ 0.02 ppm.

The carbon-13 NMR spectral parameters of allenes are reported in Appendix II. In table1 are reported the ^{13}C chemical shifts of the methyl carbons of isopropyl groups in appropriatly substituted allenes.

The degree of magnetic nonequivalence is defined as the difference in chemical shifts of methyl groups a and b.

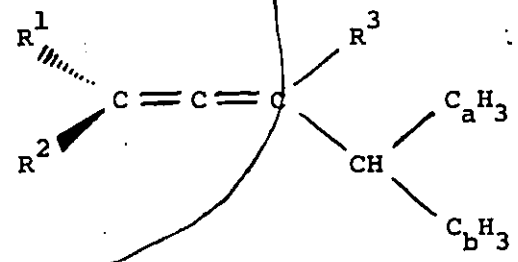
$$\Delta = \delta_a - \delta_b$$

(the designations as a and b are arbitrary)

The magnitude of Δ is seen to be very dependent on the substitution pattern, varying from 0.00 to 0.83 ppm.

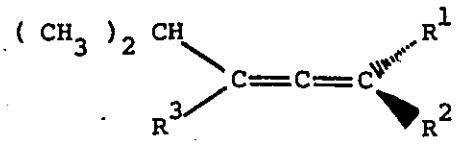
TABLE XI

THE OBSERVED CARBON-13 NMR CHEMICAL SHIFTS OF DIASTEREOTOPIC ISOPROPYL METHYL CARBONS IN ALLENES



R^3	R^1	R^2	δ_a	δ_b	$\Delta = \delta_a - \delta_b$ (± 0.02 ppm)
H	Me	H	22.63	22.60	0.03
H	Et	H	22.45	22.40	0.05
H	iPr	H	22.61	22.44	0.17
H	tBu	H	22.59	22.41	0.18
H	Me	Et	22.63	22.53	0.10
H	Me	iPr	22.75	22.57	0.18
H	Me	tBu	22.65	22.47	0.18
H	Et	tBu	22.59	22.59	0.00
H	iPr	tBu	22.54	22.51	0.03
Me	Me	H	21.60	21.44	0.16
Me	Et	H	21.70	21.55	0.15
Me	iPr	H	21.69	21.54	0.15
Me	C_6H_{11}	H	21.74	21.57	0.17
Me	tBu	H	21.70	21.55	0.15
Me	Me	tBu	21.64	21.50	0.14
Me	Et	tBu	21.72	21.72	0.00
Me	iPr	tBu	21.96	21.64	0.32
Et	Me	tBu	21.99	21.99	0.00
iPr	Me	H	22.50	22.21	0.29
iPr	Et	H	22.57	22.31	0.26
iPr	iPr	H	22.73	22.39	0.34
iPr	tBu	H	22.73	22.35	0.38
iPr	iPr	tBu	21.83	21.26	0.57
tBu	Me	H	24.85	24.31	0.54
tBu	Et	H	24.94	24.39	0.55
tBu	iPr	H	24.87	24.21	0.66
tBu	tBu	H	25.17	24.34	0.83
tBu	Me	Et	24.95	24.95	0.00
tBu	Me	iPr	25.11	24.82	0.29
tBu	Me	tBu	24.98	24.77	0.21

One can analyse the data by considering the effect of increasing steric bulk of the substituents using the following model :



Group R^3 seems to have the greatest influence on Δ, independently of groups R^1 and R^2. This is seen by keeping R^3 constant and varying the substituents away from the isopropyl group (R^1 and R^2).

When R^3 = H	Δ	varies	from	0.03 to 0.18 ppm
When R^3 = Me	Δ	"	"	0.14 to 0.32 ppm
When R^3 = iPr	Δ	"	"	0.26 to 0.38 ppm
When R^3 = tBu	Δ	"	"	0.21 to 0.83 ppm

Therefore, the bulk of the substituent geminal to the isopropyl group seems to be the dominant influence governing the magnitude of the difference in chemical shift of the two isopropyl methyl groups. The larger the steric bulk of the geminal substituent, the larger the difference in chemical shift.

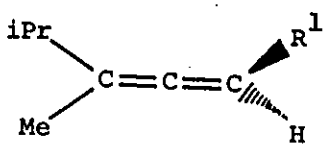
The influence of group R^3 can also be viewed in a different way. Consider for example the 1,3-disubstituted allenes :

iPr–CH=C=CH–R

As the group R is varied from Methyl to Tert-Butyl there is a drastic change in the value of Δ.

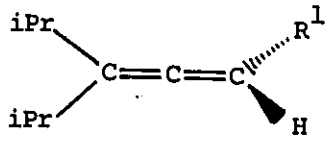
R	Δ (ppm)	
Me	0.03	
Et	0.05	
iPr	0.17	Variation = 500%
tBu	0.18	

On the other hand, if one looks at the value of Δ for 1-methyl-1-isopropyl-3-substituted allenes, the difference is not significant on varying the remote substituent from Methyl to tert-Butyl



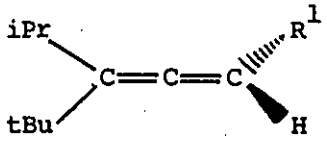
R^1	Δ(ppm)	
Me	0.16	
Et	0.15	
iPr	0.15	Variation = 13%
tBu	0.15	
C_6H_{11}	0.17	

A similar trend is observed for 1,1-diisopropyl-3-substituted allenes :



R^1	Δ(ppm)	
Me	0.29	
Et	0.26	Variation = 30%
iPr	0.34	
tBu	0.38	

Similarly :



R^1	(ppm)	
Me	0.54	
Et	0.55	Variation = 54%
iPr	0.66	
tBu	0.83	

Summarizing these preliminary results we consider the effect of varying the group remote from the isopropyl moiety.

R^3	Δ % when R^1 = Me...Et...iPr...tBu
H	500
Me	13
iPr	30
tBu	54

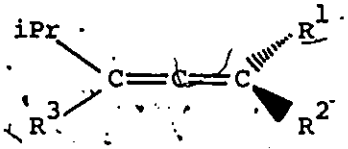
There is a tremendous difference between the series where R^3 is Hydrogen and the others. The fact that the substituents away from the isopropyl group has little influence on the magnitude of Δ is depicted in the next table.

iPr R^3—C=C=CH–R^1

R^1	Value of Δ for R^3 = H	Me	iPr	tBu
Me	0.03	0.16	0.29	0.54
Et	0.05	0.15	0.26	0.55
iPr	0.17	0.15	0.34	0.66
tBu	0.18	0.15	0.38	0.83

It can be seen that whatever the substituent away from the isopropyl group (R^1), there is a similar trend (Δ increases), when changing R^3 from Hydrogen to tert-Butyl (i.e., down a column)

So far, we have only examined the case of trisubstituted allenes. Consider tetrasubstituted allenes where all four groups are different. These allenes vary only in the spatial arrangement of the various substituents



R^1	R^2	R^3	Δ
Et	tBu	Me	0.00
Me	tBu	Et	0.00
Me	Et	tBu	0.00

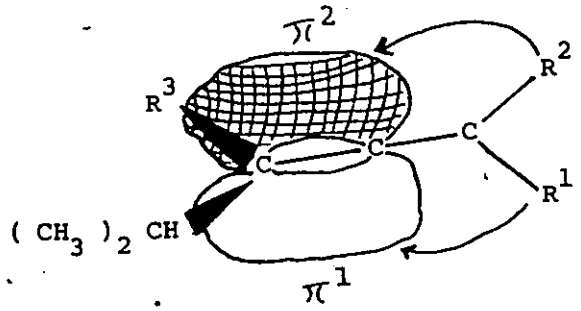
In these cases, accidental coincidence of the methyl carbon resonances of the isopropyl groups is observed.

3- DISCUSSION :

Rationalization for the existence and magnitude of Δ can be made on the grounds of conformational effects. This is due to the fact that the substituents in the 1 and 3 positions of an allene are sufficiently remote from one another that there can be no steric interaction between them.

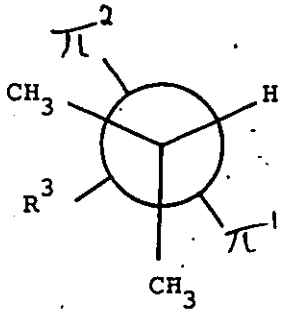
i.e., the steric bulk of a substituent on one side of the allene moiety does not influence the spatial conformation of a substituent on the other side.

It was mentioned in the introduction that the allene moiety contains 2 π-systems which are mutually perpendicular. If substituent effects are observed accross this system, it must arise from perturbation of the π-orbitals as shown below.

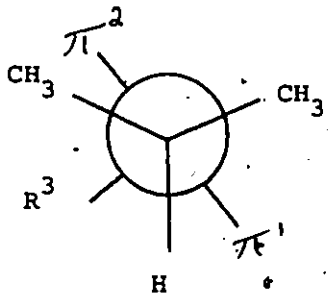


Pertubations of the collinear π orbitals, π^1 and π^2 by the substituents R^1 and R^2 may affect the conformations of the isopropyl and the R^3 group on the other side of the allenic system. The magnitude of this perturbation will depend on the steric and electronic properties of the groups R^1 and R^2. This can be envisioned a lot better by considering Newman projections of the allenes along the bond joining the isopropyl group to the propadiene system.

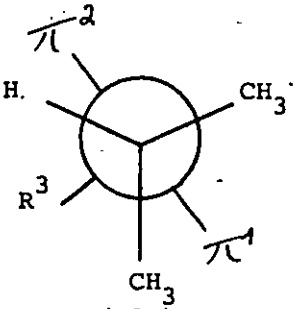
There are three possible staggered conformations to be considered as they are the most stable and reflect best the ground state.



(1)



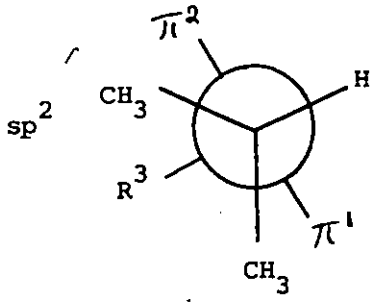
(2)



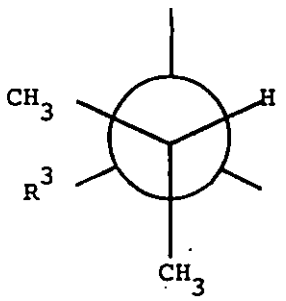
(3)

NOTE : In the case of allenes, the staggered conformations are different from those of an isopropyl group bonded to an sp^3 center. This is due to the fact that the R^3 group is oriented perpendicular to the two π orbitals.

(vs 109° in the sp^3 case)



(A)



(B)

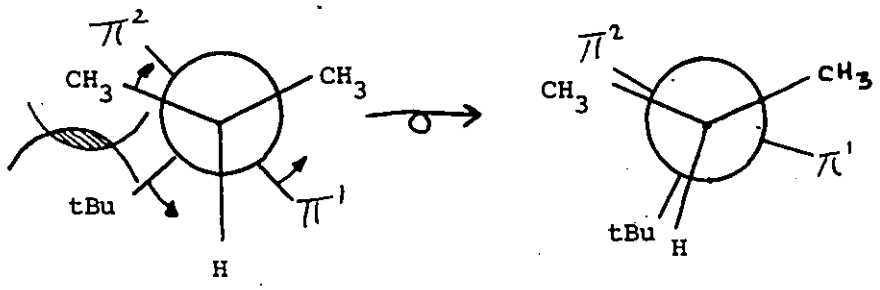
sp^3

As it can be seen, the gauche interaction of the isopropyl methyl groups with the π orbitals in A are greater than the analogous interaction of the isopropyl methyl groups with vicinal substituents in the case of B.

A rationale for the small magnitude of Δ is the attenuation of the substituent effects with transmission of the dissymmetry over the two bonds of the allenic system. On observation of conformers (1), (2) and (3), it is obvious that the R^3 group will have a greater effect on the isopropyl methyls than the two remote substituents R^1 and R^2, as is observed experimentally.

The steric bulk of R^3 will determine the importance of the conformers relative to one another.

e.g., if R^3 is very large (tert-Butyl), conformers (2) and (3) should predominate over the first one, providing the two methyl groups with very different environments, Therefore, resulting in a large Δ. However, if the R....Me interaction is still significant, there will be a deviation from the perfectly staggered conformations which will tend to eclipse the two methyl groups with the π-orbitals as demonstrated below :



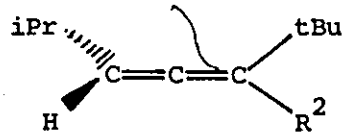
If such is the case, the magnitude of Δ should become small unless R^1 and R^2 have a different ability to perturb their respective π -orbitals. This last factor may be the explanation to abnormal behavior observed in table (11).

When R^1 = H and R^2 varies from methyl to tert-Butyl, normal behavior is observed.

i.e., Δ increases with the ability of the remote substituent to perturb the π - system. The ability is governed by both steric bulk and electron donating power.

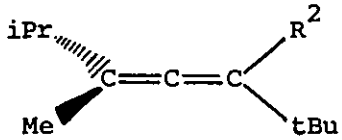
On the other hand, deviations are observed when $R^1 \neq R^2 \neq H$

e.g.,



R^2	Δ
H	0.18
Me	0.18
Et	0.00
iPr	0.03

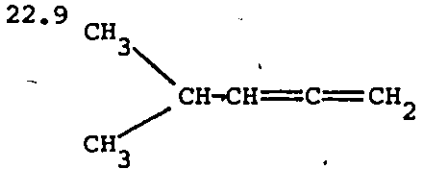
Similarly :

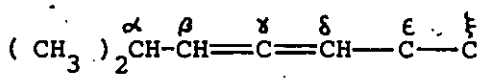


R^2	Δ
Me	0.14
Et	0.00
iPr	0.32

In the two previous examples, the value of Δ does not increase linearly with the ability of the remote substituent to perturb the π-orbitals. On the contrary, the value of Δ goes through a minimum (magnetic equivalence). However this is observed only when R^1 =.tert-Butyl and as will be seen later, anomalous behavior often occurs when allenes are substituted with tert-Butyl groups.

It is not yet possible to correlate carbon-13 chemical shifts with stereochemical factors but one can say that the methyl carbons of the isopropyl group experience both a ϵ- and a ξ-substituent effect of the order of 0.3 ppm and 0.2 ppm respectively (both to higher field).

22.9 



With the data available at present, it is not yet possible to state whether Δ is due to conformer populations only or if it reflects intrinsic diastereomerism of the averaged environments of the isopropyl methyl carbons as well[54].

$$\Delta = \Delta_{cp} + \Delta_{ID}$$

The contribution of intrinsic diastereomerism to the magnetic nonequivalence of the diastereotopic carbons is determinable only in these cases where the individual conformers are observable. This could not be achieved in the scope of this work.

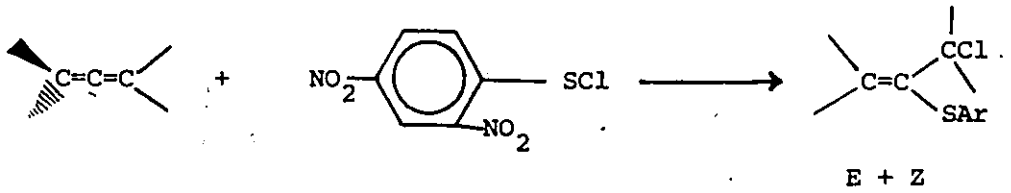
PART II

CONCERNING THE ORTHO-NITRO GROUP EFFECT IN THE REACTION OF ARENESULFENYL CHLORIDES WITH 1,3-DISUBSTITUTED ALLENES

1- INTRODUCTION :

Our work on electrophilic additions to allenes was initiated about a year ago when the reaction of 2,4-dinitrobenzenesulfenyl chloride (2,4-DNBSC), with various 1,3-disubstituted allenes was reexamined[56].

As mentioned previously in the introduction, substituted allenes can give rise to eight possible addition products with unsymmetrical electrophiles. However, we observed that allenes reacted with 2,4-DNBSC in a 1:1 fashion to give adducts where attack of sulfur had occured exclusively at the central allenic carbon giving products of E and Z configuration.



E + Z

Because of our interest in elucidating the factors influencing the nature of the product determining step in the reaction of arenesulfenyl chlorides with allenes we extended our work by examining the reaction of twelve different arenesulfenyl chlorides with a series of ten 1,3-disubstituted allenes.

As previously observed, the sulfenyl chlorides were found to add to the allene moiety in a 1:1 fashion with exclusive attack of sulfur on the central allenic carbon.

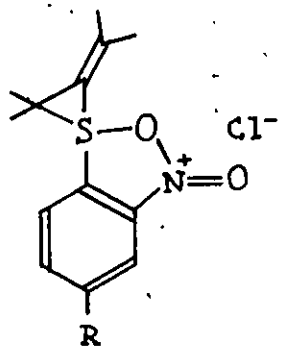
Products of double addition of the sulfenyl chloride on both double bonds of the allenes was not observed and adducts did not eliminate HCl as had been observed previously[57].

The mechanism of addition of 2,4-DNBSC to allenes is not yet very clear but there is evidence for Ad_E2 type behavior[58]. Possible pathways are shown below in SCHEME IV

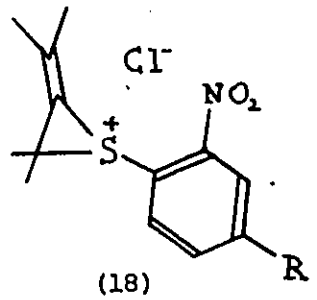
In this case, the results were interpreted in terms of steric approach control[59] leading to the formation of a series of alkylidenethiiranium ions or alkylideneepisulfuranes[60].

In order to confirm these predictions we underwent an extensive study of additions of sulfenyl chlorides to allenes where the steric requirements and aptitude to stabilize development of charge on sulfur would be varied.
In addition to present some evidence for an Ad_E2 type mechanism, the effect of an ortho-Nitro group on the sulfenyl chloride was also analyzed.

It has been postulated[61] that an ortho-Nitro group in a 2-Nitrobenzene-sulfenyl chloride may stabilize a positive charge on sulfur by delocalization into the adjacent Nitro group. Compare for example the spirosulfurane intermediate (17) and the commonly accepted thiiranium ion (18)

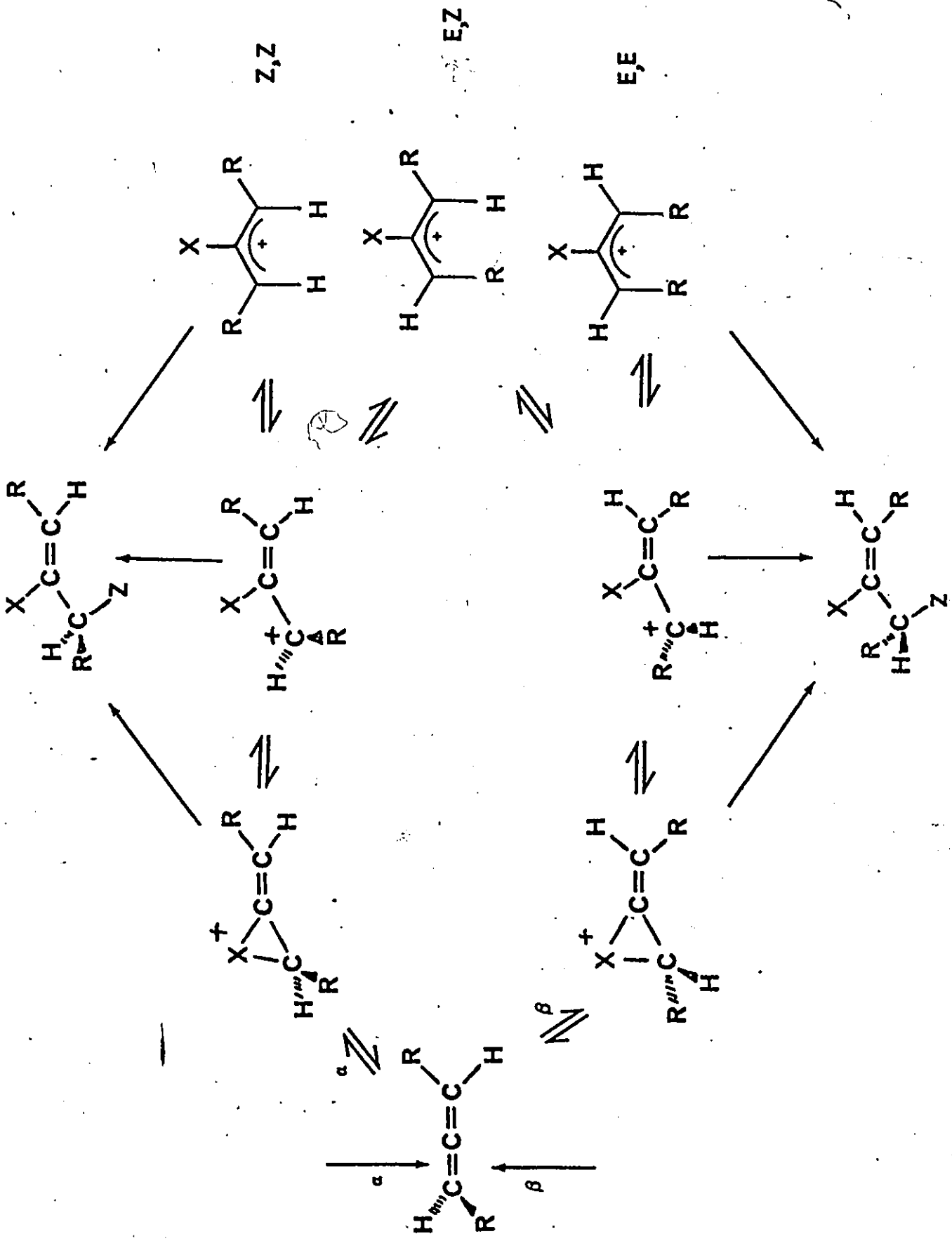


(17)



(18)

SCHEME IV



If such is the case, arenesulfenyl chlorides containing an ortho-Nitro group would be expected to react quite differently from other simple alkyl-substituted arenesulfenyl chlorides[61 (e,f)].

Due to its nature, the Nitro group in a 2-Nitroarenesulfenyl chloride may also influence the course of an electrophilic addition to a double bond through destabilization by inductive electron withdrawal, and/or steric effect.

2- ADDITION OF ARENESULFENYL CHLORIDES TO 1,3-DISUBSTITUTED ALLENES :

In order to gain information on the effect of the ortho-Nitro group and the degree of involvment of steric and electronic factors we investigated the reaction of 1,3-disubstituted allenes with a series of 12 arenesulfenyl chlorides shown below.

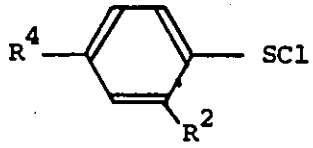
1,3-DISUBSTITUTED ALLENES

RCH=C=CHR'

R	R'
Me	Me
Et	Et
iPr	iPr
tBu	tBu
Me	Et
Me	iPr
Me	tBu
Et	iPr
Et	tBu
iPr	tBu

PARASUBSTITUTED ARENESULFENYL CHLORIDES

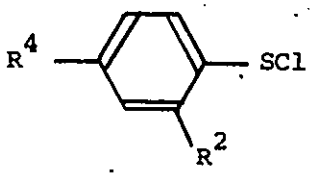
(SERIES A)



Entries	R^2	R^4
I	H	NO_2
II	H	CF_3
III	H	Cl
IV	H	H
V	H	CH_3
VI	H	OCH_3

ORTHO-NITRO-PARASUBSTITUTED ARENESULFENYL CHLORIDES

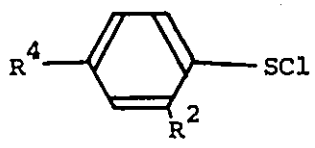
(SERIES B)



Entries	R^2	R^4
VII	NO_2	NO_2
VIII	"	Cl
IX	"	H
X	"	CH_3
XI	"	OCH_3

ORTHO-SUBSTITUTED ARENESULFENYL CHLORIDES

(SERIES C)



Entries	R^2	R^4
XII	CH_3	H
XIII	CF_3	H

Series A and B will provide evidence for or against the ortho-Nitro group effect, while series C will serve to demonstrate specific steric and electronic effects.

Depending on the nature of the sulfenyl chlorides, additions were carried out either in CH_2Cl_2 at room temperature or as NMR tube reactions in $CDCl_3$ at 0°C.

Reaction end-points were determined by the disappearance of the S-Cl chromophore (λ_{max} = 392 nm), or a negative starch-iodide test[62].
The mixtures of adducts were analyzed immediatly by ^1H NMR analysis in order to obtain the kinetically controlled distribution of products.

Arenesulfenyl chlorides containing a Nitro group in the 2-position were found to react many orders of magnitude slower than the others (half-life of the order of 3 days at 0.05 M vs a few milliseconds).
Consequently, isomerization of products was found to be negligible over a period of time much longer then that required for analysis of initially formed products.
In these cases, the reactions were run at room temperature in dichloromethane.

On the other hand, all sulfenyl chlorides lacking the 2-Nitro substituent were found to be more reactive; isomerization of products occuring within a few hours or minutes even at low temperature. Consequently, these reactions were run at 0°C in NMR tubes and analyzed immediatly.

In some cases, it was not possible to obtain the kinetically controlled product distribution due to fast isomerization, E$\rightleftharpoons$Z, at ambient temperature. (sulfenyl chlorides V, VI, XII).

The relative reactivity of the 4-substituted-2-Nitrobenzenesulfenyl chlorides (series B) was observed to follow the order.

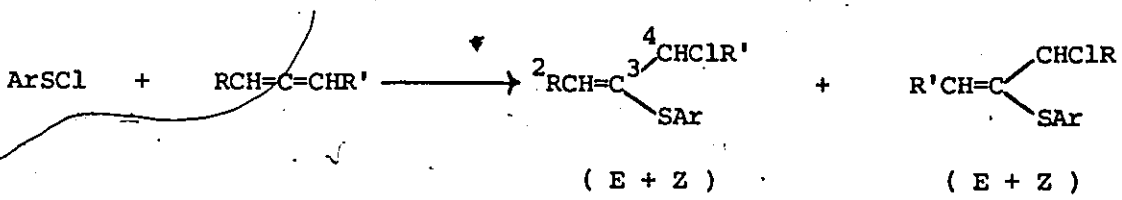
$$XI > X > IX > VIII > VII$$

in accord with the rate measurements of Brown and Hogg[63]. This reflects the charge stabilization ability of the 4-substituent.

3- ANALYSIS OF ADDUCT MIXTURES :

Analysis was performed by ^{1}H NMR, ^{13}C NMR spectra and Mass Spectral Fragmentation patterns according to criteria previously established[56]. These will now be summarized.

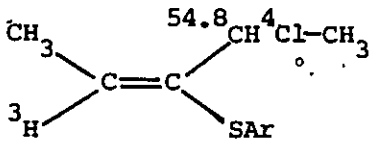
The reactions were found to be regiospecific with exclusive attack of sulfur on the central allenic carbon



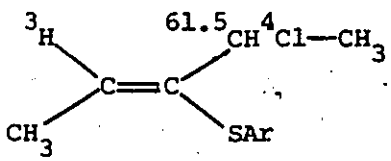
(E + Z) (E + Z)

Spectral parameters for adducts of these types are reported in APPENDIX III

Evidence for regiospecificity is given by the Carbon-13 chemical shift of the carbon bearing the chlorine atom.



(19)



(20)

Based on the electronegativity of the two substituents,

S = 2.48

Cl = 2.99

one expects a carbon bearing a sulfur atom to resonate at a higher field with respect to one attached to a chlorine atom.

The observed Carbon-13 chemical shifts are consistent with the presence of allylic chlorines.

C=*CCH SAr exhibits a ^{13}C resonance at 45.4 ppm

C=*CCH $ClCH_3$ " " " 56.9 ppm

(G.H.Schmid, S.Yeroshalmy, and D.G.Garratt, J.Org.Chem., in press)

Furthermore the one bond coupling constant $J_{3,3}$ is in the range expected for a carbon directly bonded to a halogen.

(151.6 vs 148.7 ppm for CH_3Cl - See table 13, APPENDIX III)

Further indication for regiospecificity is found in the Mass Spectral Pattern of the adducts. They all exhibit α-cleavage with loss of CHClR from the molecular ion. No radical or cationic species of the type CHSAr could be detected as would have been expected from an adduct resulting from attack of chlorine at the central allenic carbon.

The assignement of configuration as E and Z follows from several criteria based on ^1H and ^{13}C NMR chemical shifts and coupling constants. If one considers the two adducts (19) and (20), proton H_3 is shielded in the E isomer relative to that of the corresponding Z isomer (20). H_4 on the other hand is deshielded in the E isomer relative to that of the corresponding Z isomer[64].

The allylic proton-proton coupling constant $^4J_{HC=CCH}$(cis) is larger than $^4J_{HC=CCH}$(trans) thus allowing (20) to be assigned the Z configuration. Vicinal carbon-proton coupling constants of the type $^3J_{CC=CH}$ are more reliable. The valuesfor $^3J_{CC=CH}$(cis) and $^3J_{CC=CH}$(trans) are normally very different (trans is larger than cis).

An examination of table 13 of APPENDIX III is in accord with this configurational assignement.

Carbon-13 chemical shifts may also confirm our assignements as they are very dependent on stereochemistry. Using γ -gauche interaction effects, one expects the methine carbon bonded to chlorine (C_3 in table 14) to be shielded in the E isomer relative to the Z isomer.

All observations described above were found to be consistent throughout the series of arenesulfenyl chlorides. Figures 3-6 provide examples of spectra obtained from adducts of symmetrically and unsymmetrically 1,3-disubstituted allenes.

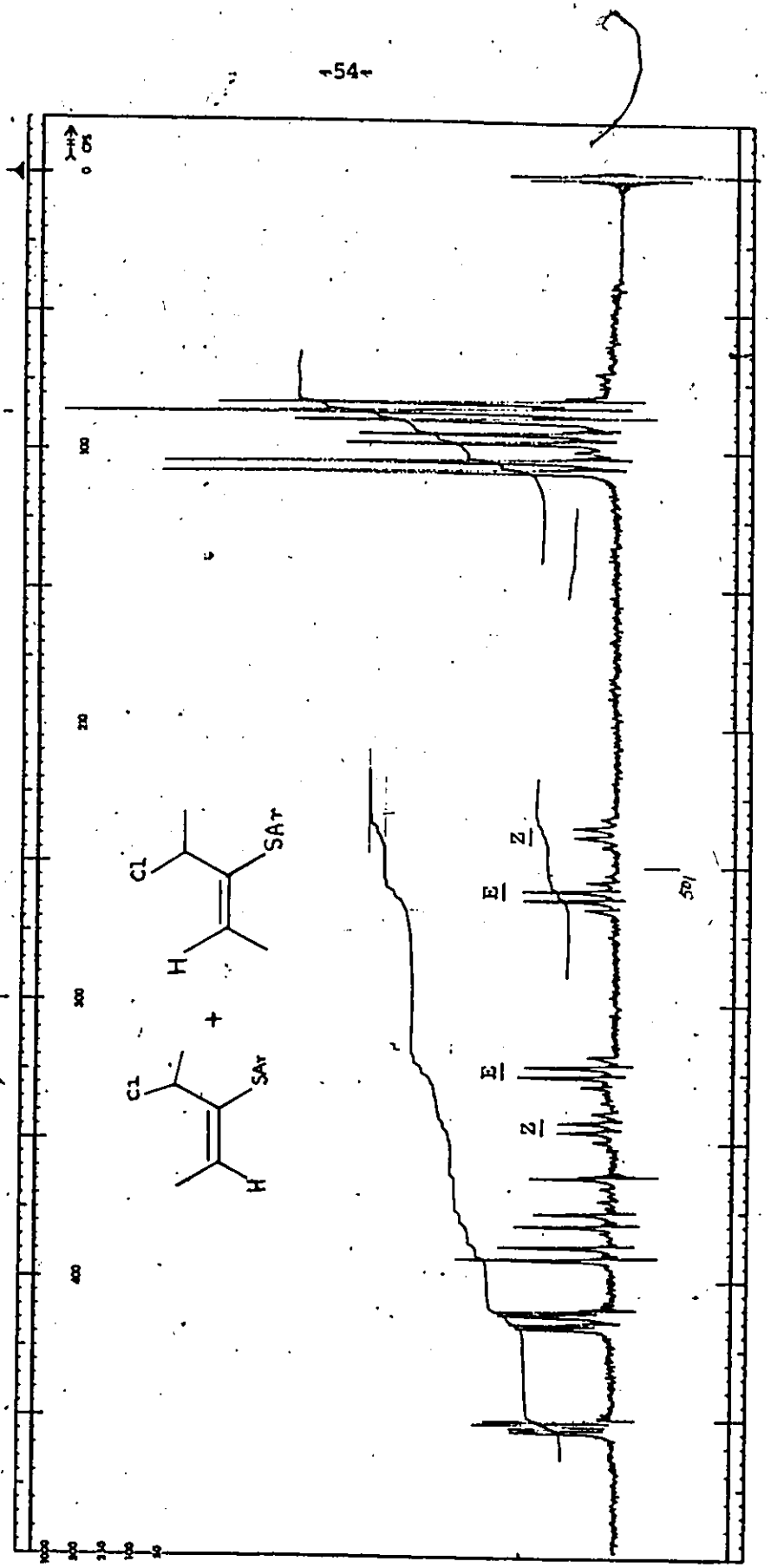


Figure 3: 100MHz nmr spectrum of 2-3, pentadiene adduct.

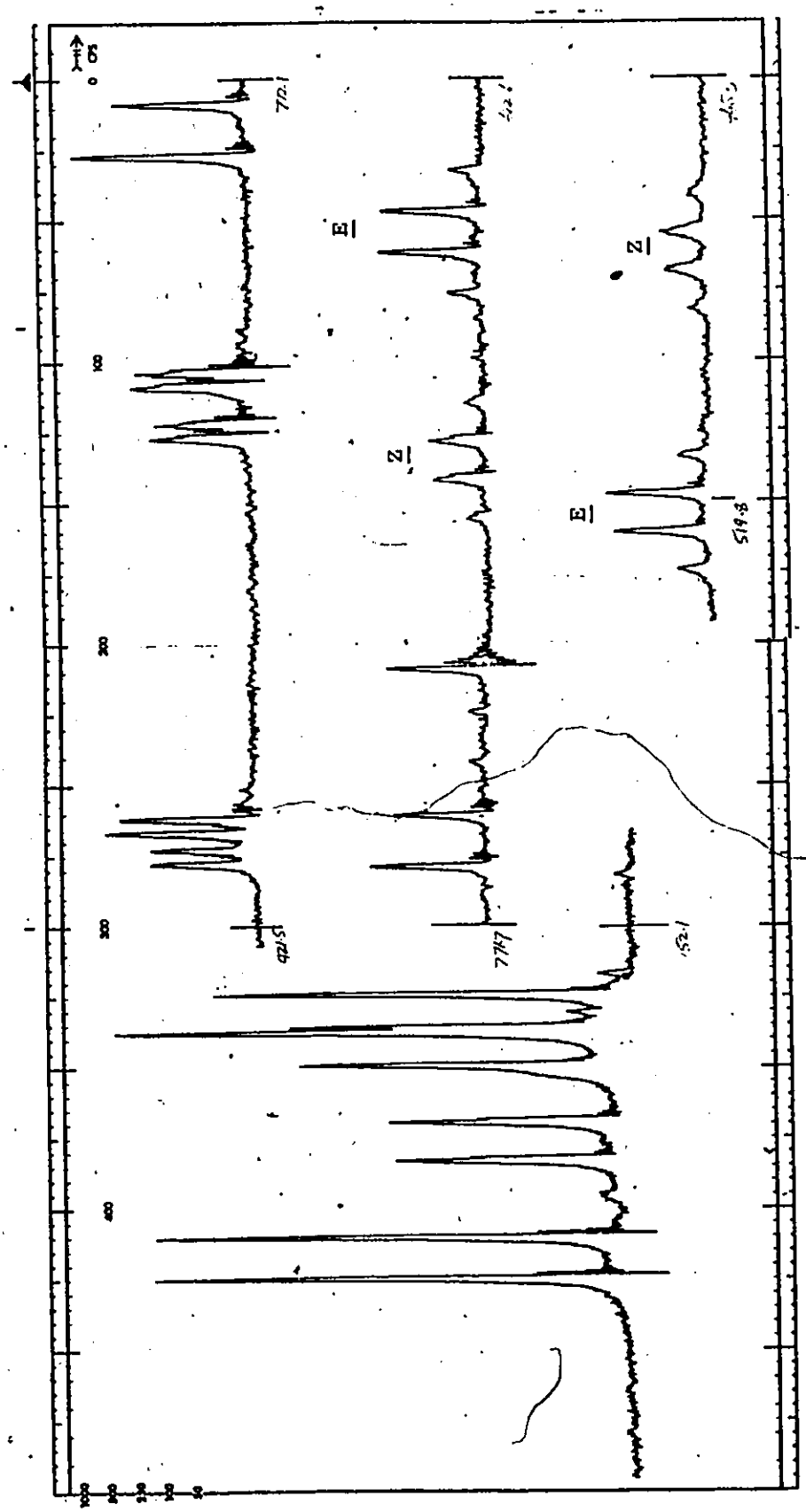


Figure 3: 100MHz nmr spectrum of 2,3-pentadiene adduct (expansion).

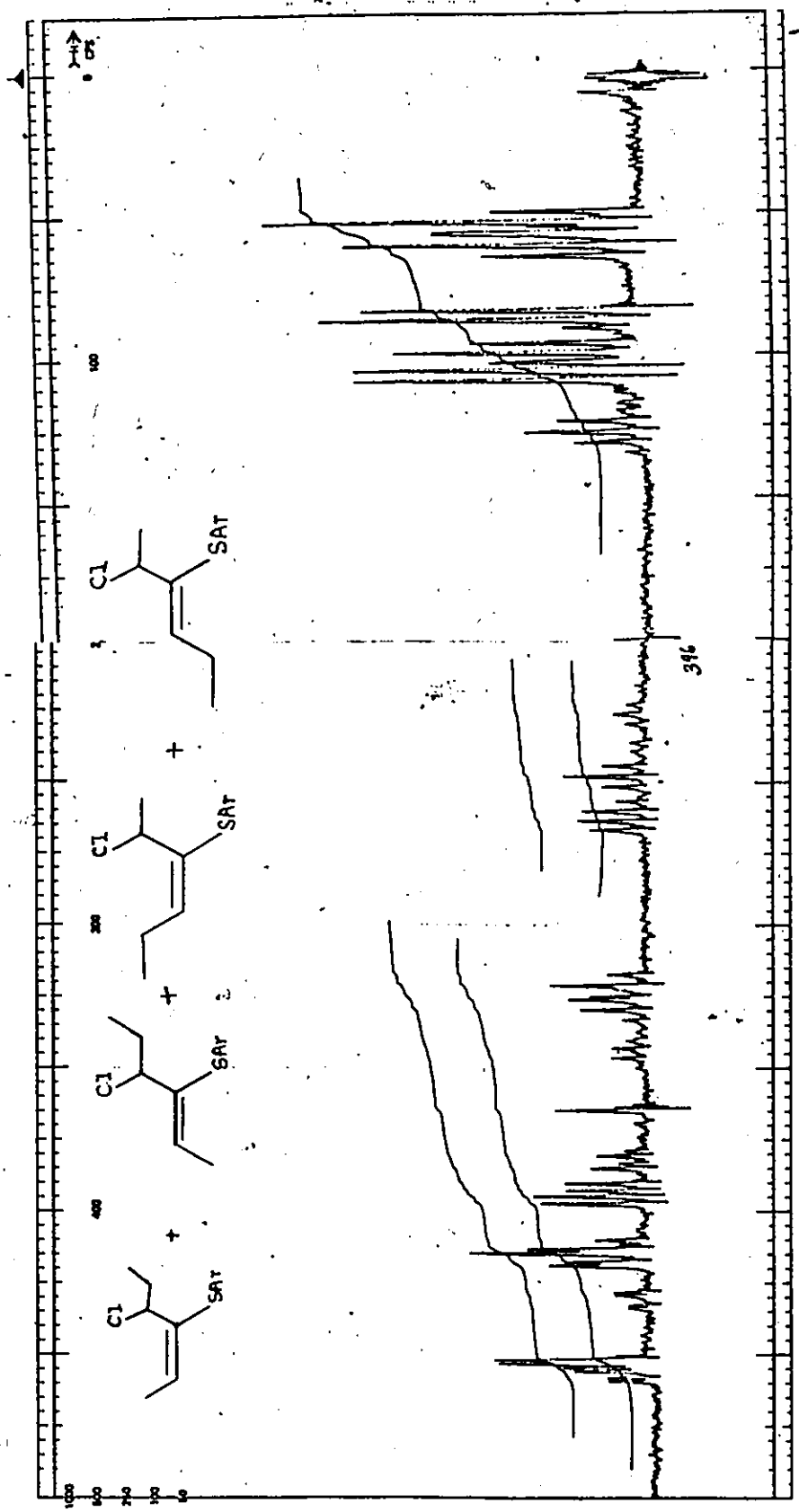


Figure 4: 100MHz ^{1}H nmr spectrum of the 2-3,-hexadiene adduct.

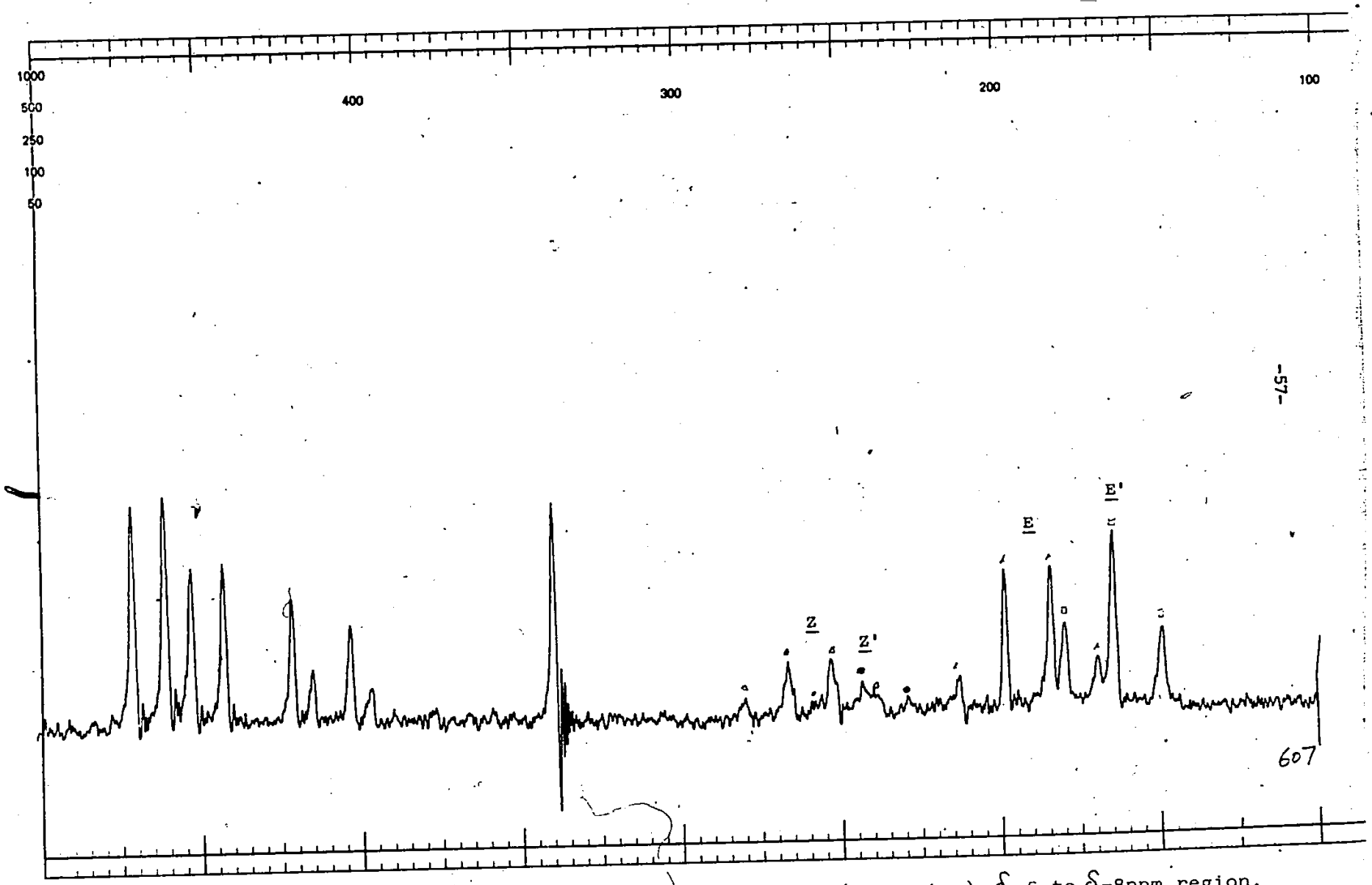


Figure 4: 100MHz ^1H nmr spectrum of the 2,3-hexadiene adduct (expansion): δ=6 to δ=8ppm region.

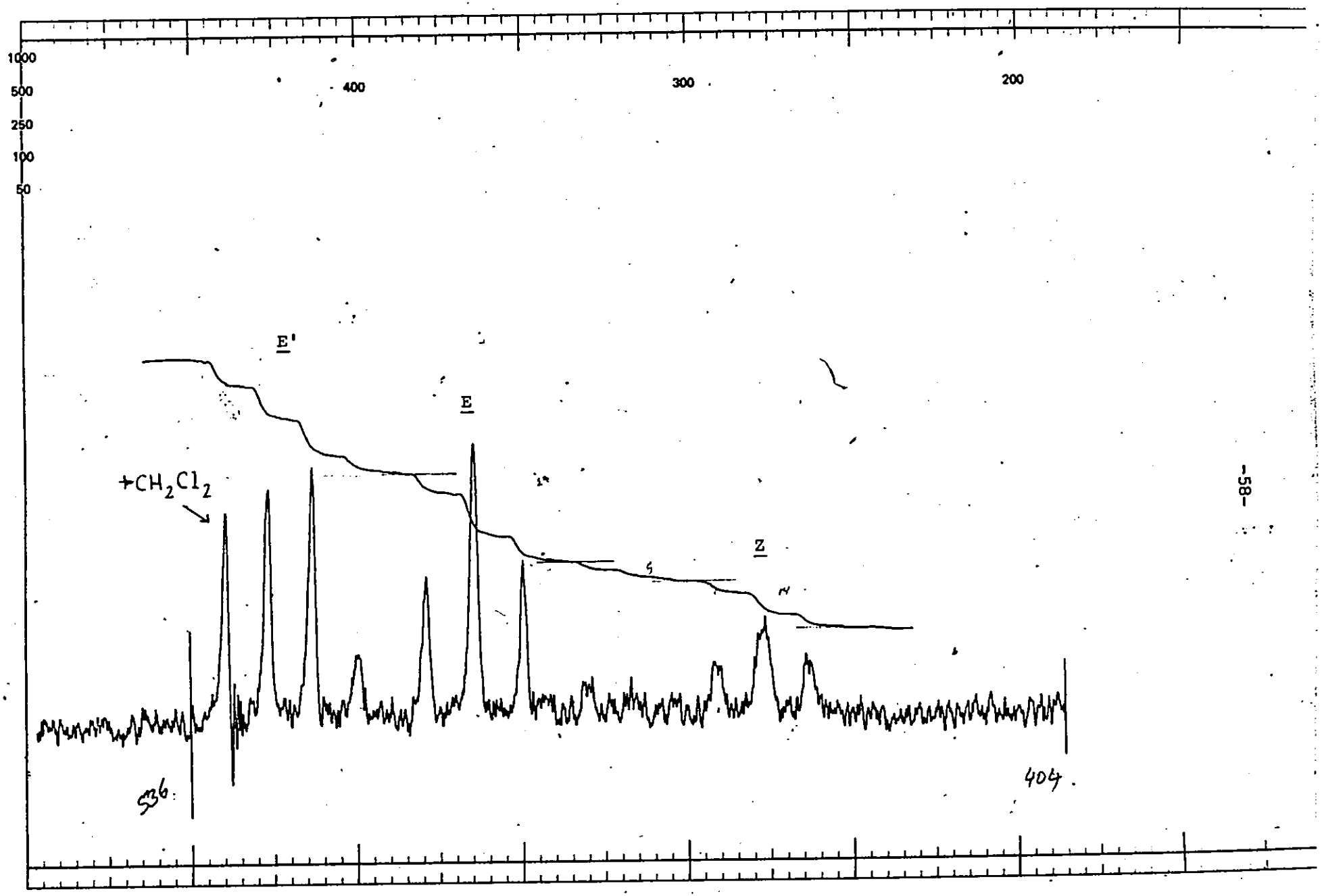


Figure 4: 100MHz ^{1}H nmr spectrum of the 2,3-hexadiene adduct (expansion) δ =4 to δ =6ppm region.

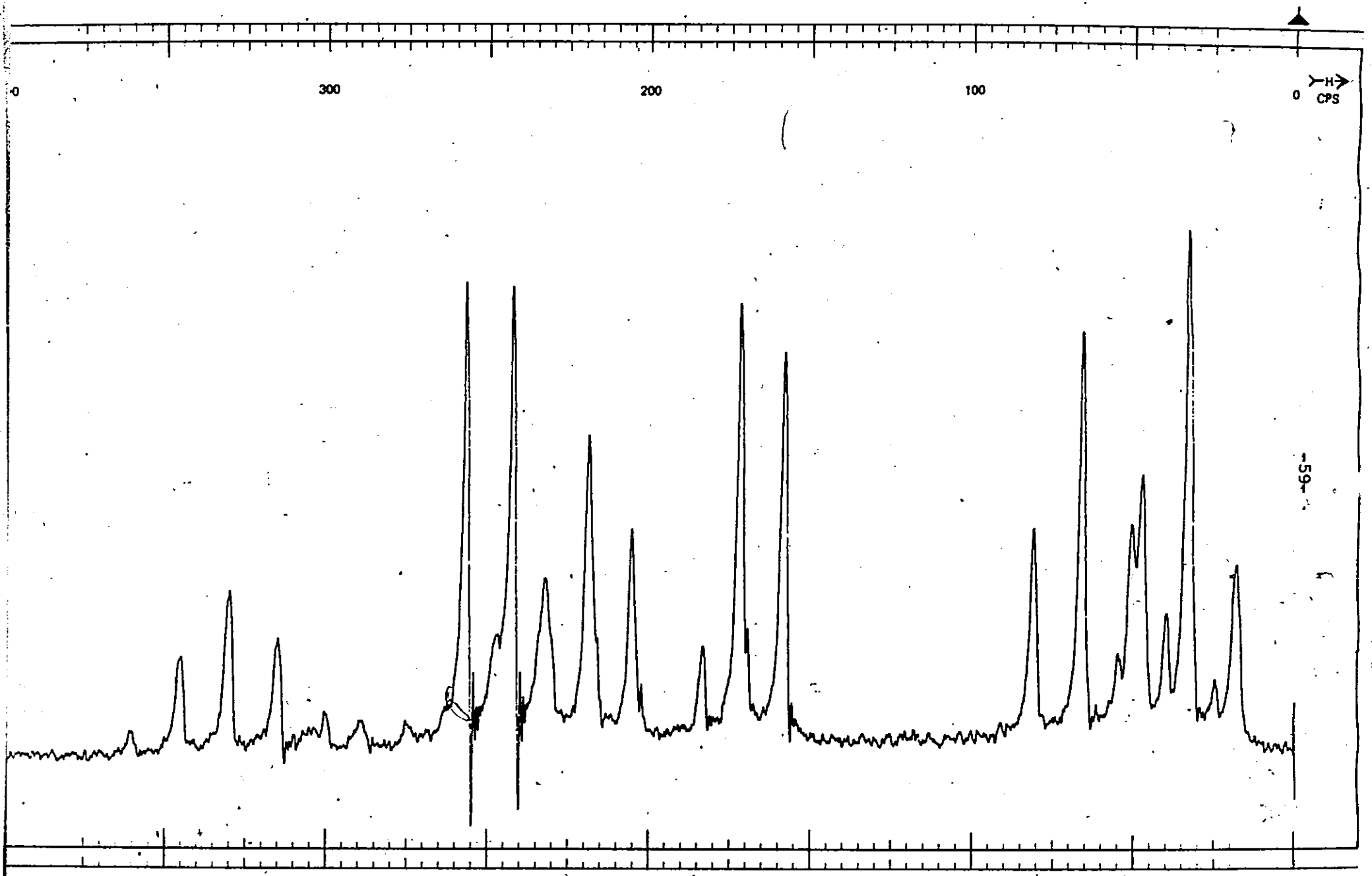
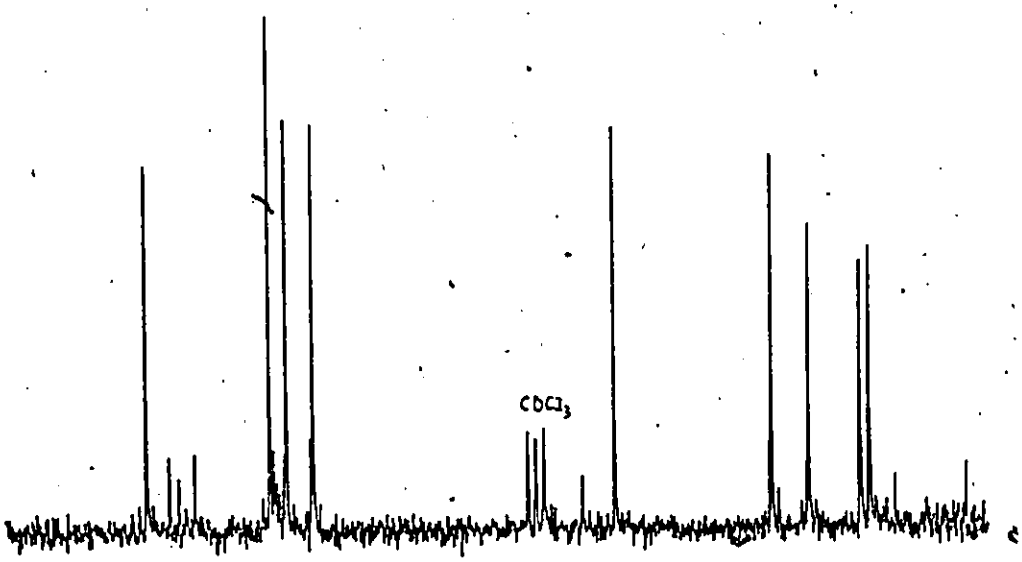
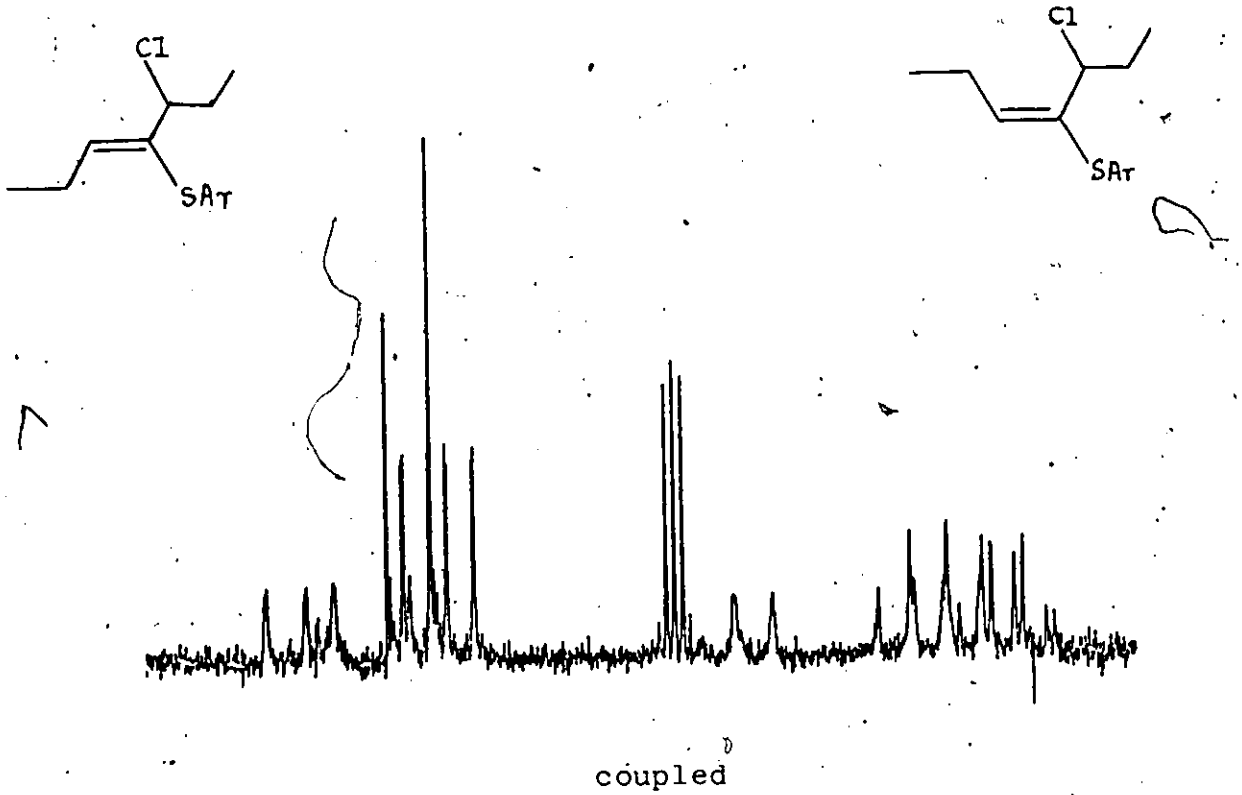


Figure4": 100MHz ^{1}H nmr spectrum of the 2,3-hexadiene adduct (expansion) δ =0 to δ =3ppm region.



fully uncoupled



coupled

Figure 5.: ^{13}C nmr spectrum of the 3,4-hexadiene adduct

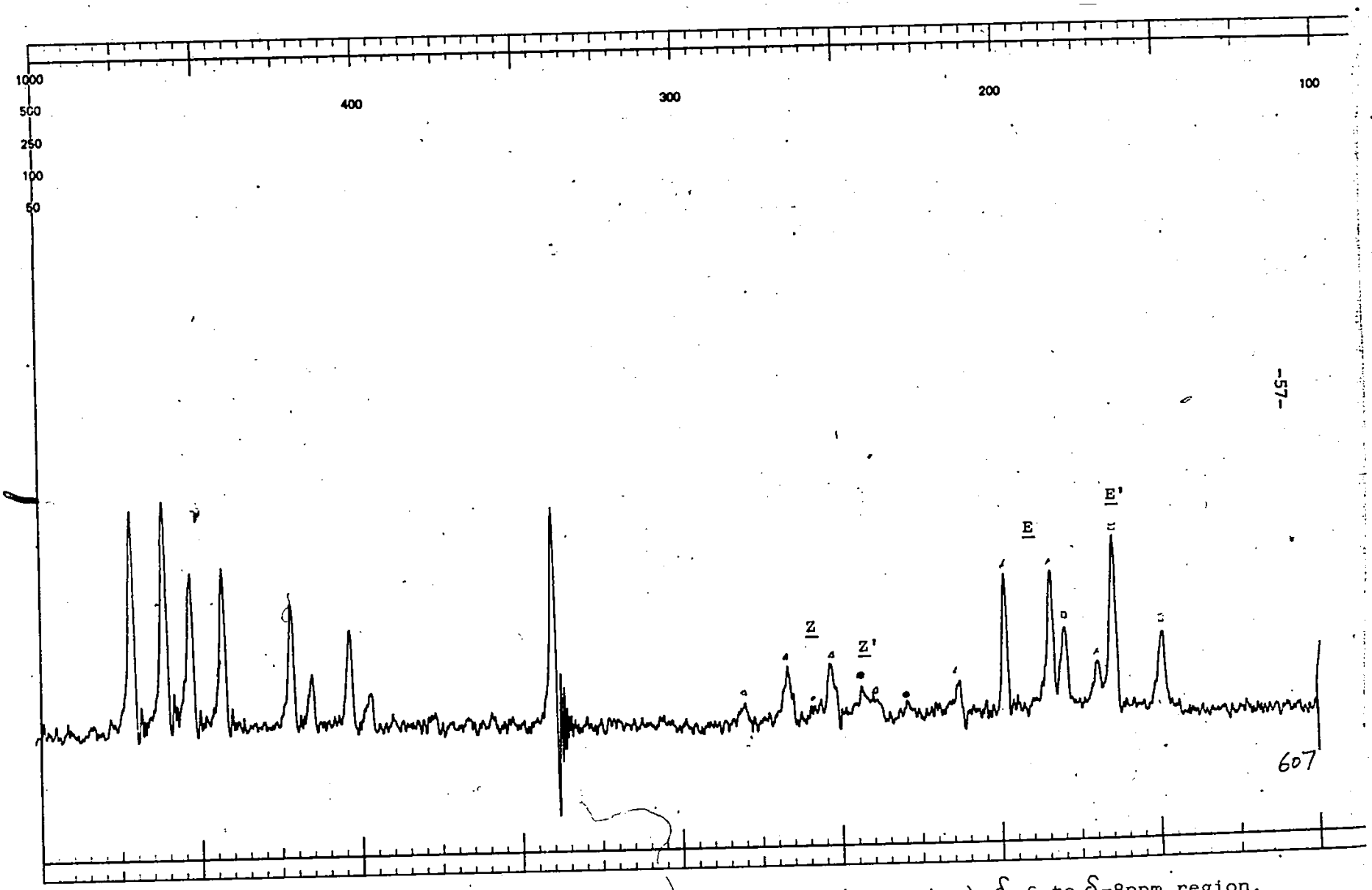


Figure 4: 100MHz 1H nmr spectrum of the 2,3-hexadiene adduct (expansion): δ=6 to δ=8ppm region.

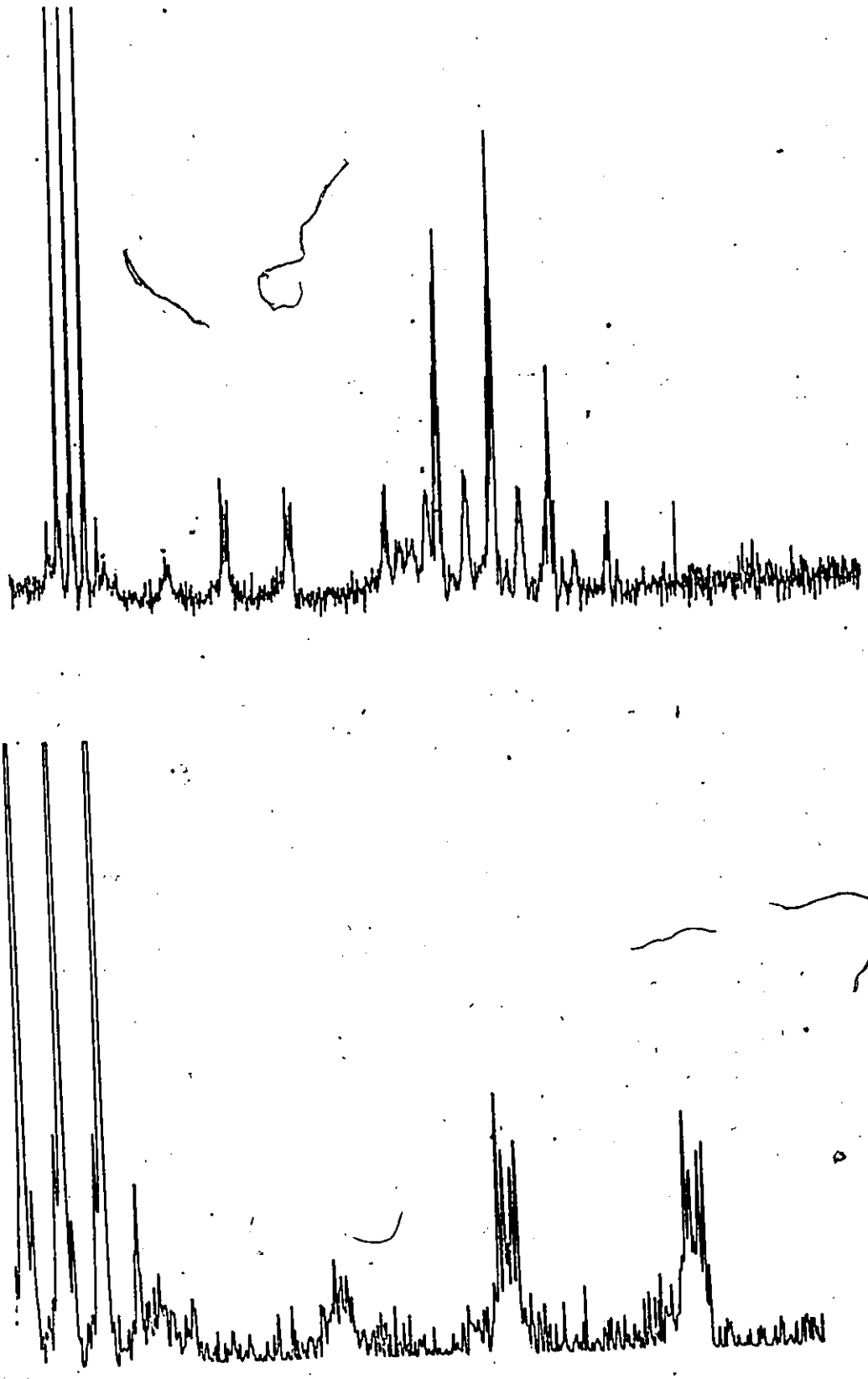


Figure 5" : ^{13}C nmr spectrum of the 5,5-dimethyl -2,3-hexadiene adduct

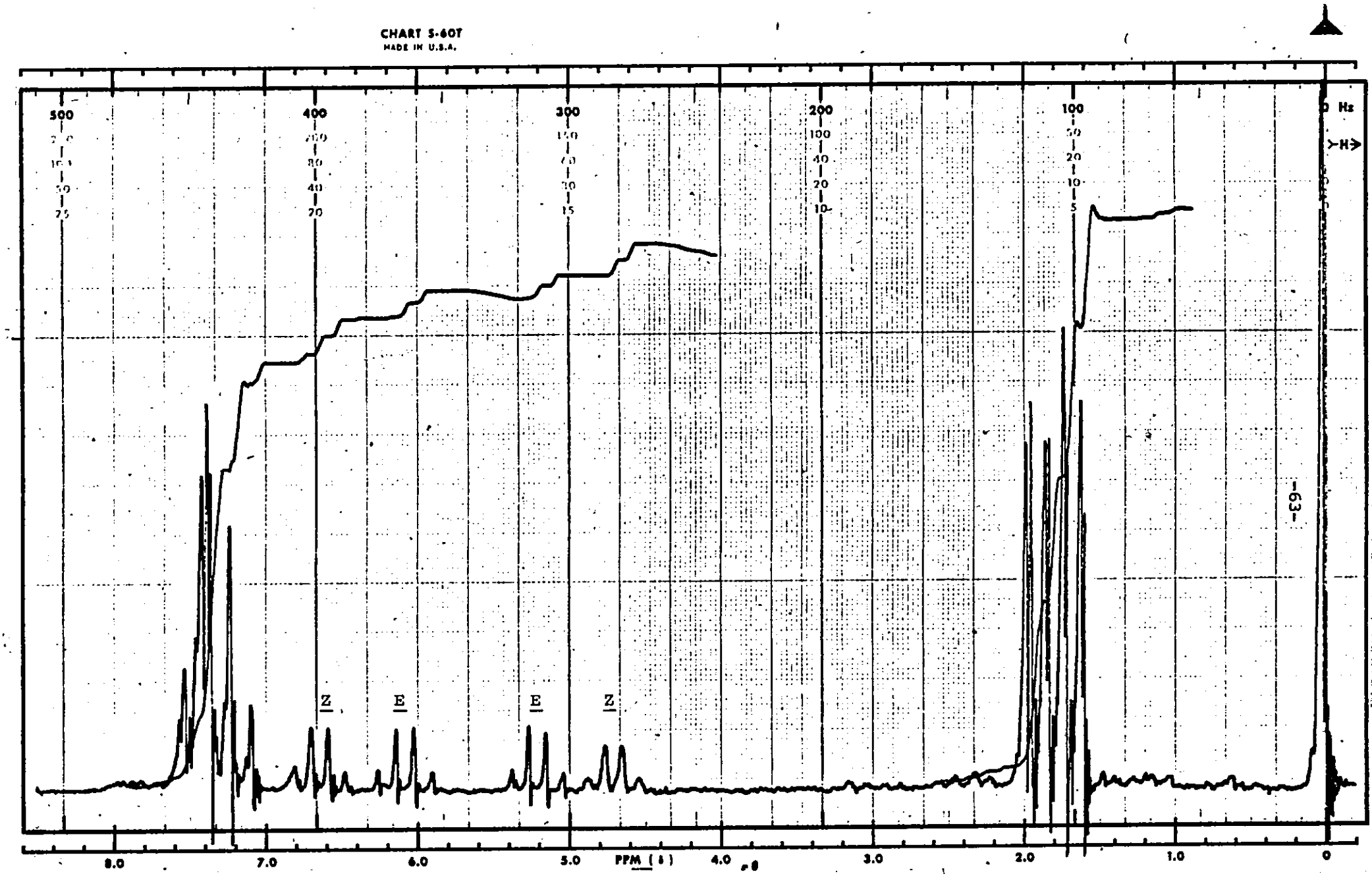


figure 6 adduct of 2-3-pentadiene with 4-bromo-benzene-sulfenyl chloride

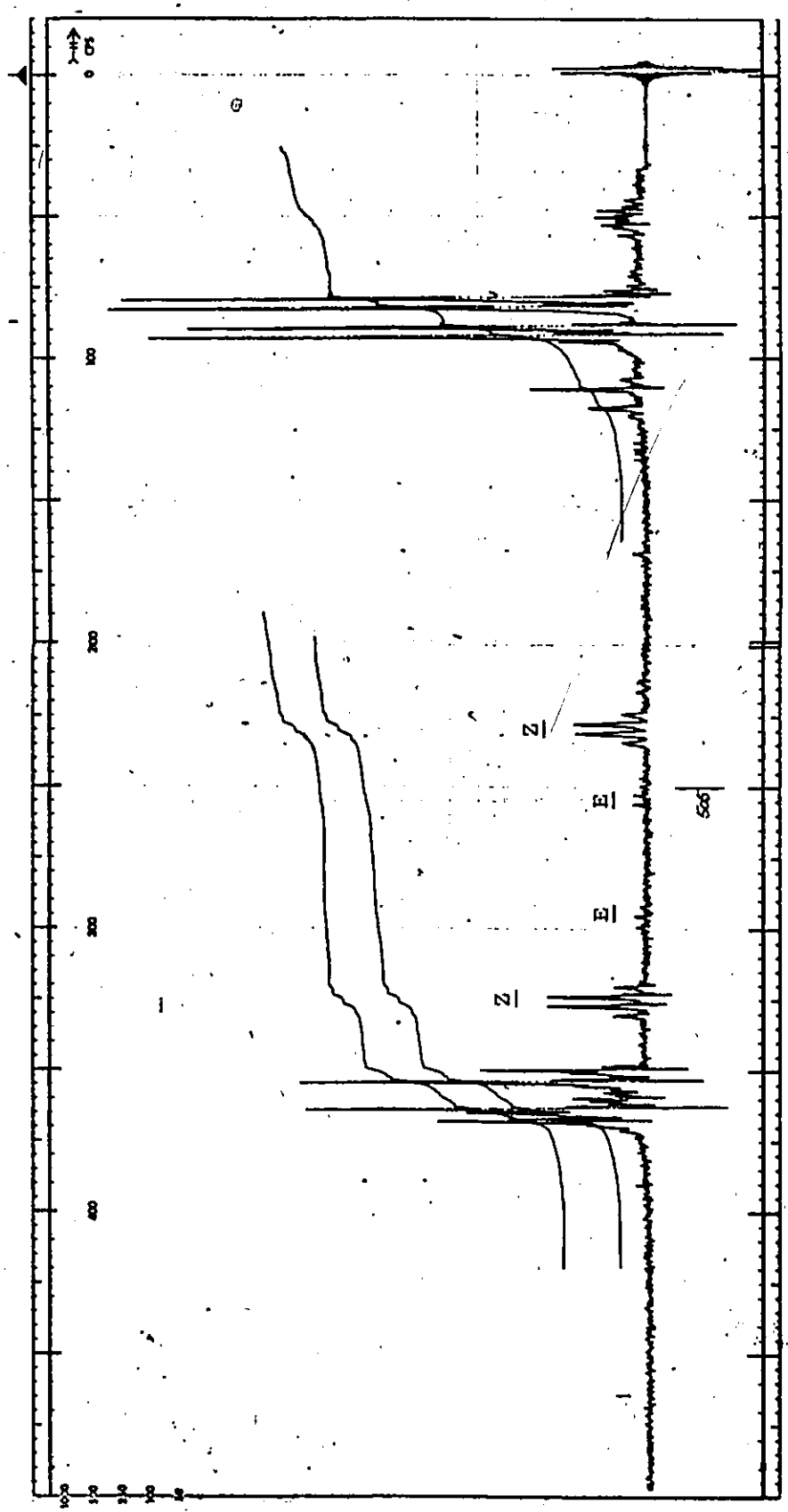
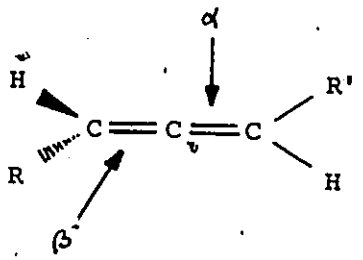


figure 6' adduct of 2-3-pentadiene with 4-bromo-benzene-sulfenyl chloride (isomerisation product)

4- KINETICALLY CONTROLLED DISTRIBUTION OF PRODUCTS :

Table (12) is the kinetically controlled productdistributions for the reactions of arenesulfenyl chlorides with 1,3-disubstituted allenes.
In this table, the ratio $\alpha : \beta$ reflects the chemoselectivity of the reaction. i.e., the proportion of attack upon one of the mutually perpendicular π-bonds relative to the other



The ratio of E:Z isomers is related to the configurational selectivity and is mainly governed by steric effects.

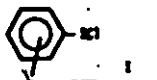
a- Symmetrical 1,3-disubstituted allenes :

As was reported in the case of 2,4-DNBSC[56], for symmetrical allenes the E : Z ratio increases as R and R' are varied from Methyl....Ethyl....Isopropyl ....TertButyl.
It is most convenient to analyse the data by comparing the sulfenyl chlorides from series A to those of series B or C

One first point of interest is the observation that in the case of sulfenyl chlorides lacking the ortho-Nitro group, the E:Z ratios are fairly constant.

TABLE 12

KINETICALLY CONTROLLED PRODUCT DISTRIBUTIONS FOR THE REACTIONS OF ARENESULFENYL CHLORIDES WITH SOME 1,3-DISUBSTITUTED ALLENES AT AMBIENT TEMPERATURE IN DICHLOROMETHANE SOLUTION.



Symmetrically Substituted Allenes R = R'	I 4-NH_2	II 4-CF_3	III 4-Cl	IV 4-H	V 4-CH_3	VI 4-CH_3O	VII 2-NO_2 4-NO_2	VIII 2-NO_2 4-Cl	IX 2-NO_2	X 2-NH_2 4-CH_3	XI 2-NO_2 4-CH_3O	XII 2-CH_3	XXXI 2-CF_3
CH_3	50:50	53:47	55:45	55:45	55:45	55:45	64:36	60:40	59:41	61:39	59:41	56:44	55:45
C_2H_5	69:31	70:30	72:28	72:28	—	—	80:20	78:22	72:28	76:24	79:21	72:28	78:22
iC_3H_7	82:18	82:18	80:20	80:20	79:21	80:20	92:8	91:9	82:18	100:0	92:8	81:19	37:63
tC_4H_9	100:0	100:0	97:3	97:3	100:0	100:0	100:0	100:0	100:0	100:0	100:0	100:0	—
Unsymmetrically Substituted Allenes													
R = CH_3 R' = C_2H_5	55:45	57:43	53:47	53:47	—	—	53:47	53:47	53:47	53:47	53:47	—	50:50
CH_3 iC_3H_7	62:38	57:43	55:45	55:45	63:37	—	52:48	51:49	48:52	50:50	53:47	66:34	—
CH_3 tC_4H_9	65:35	62:38	59:41	59:41	55:45	73:27	42:58	36:64	33:67	45:55	37:63	48:52	64:36
C_2H_5 iC_3H_7	51:49	57:43	50:50	47:53	49:51	44:56	46:54	45:55	46:54	44:56	46:54	47:53	—
C_2H_5 tC_4H_9	50:50	62:38	49:51	55:45	53:47	80:20	33:67	36:64	31:69	26:74	30:70	43:57	—
$i\text{-}C_3H_7$ tC_4H_9	50:50	50:50	50:50	56:44	60:40	53:47	38:62	38:62	31:69	41:59	40:60	34:66	40:60
CH_3 C_2H_5	53:47	58:42	56:44	56:44	—	—	68:34	58:42	60:40	60:40	64:36	—	66:34
CH_3 iC_3H_7	53:47	54:46	57:43	57:43	55:45	—	65:35	59:41	65:35	64:36	66:34	67:33	—
CH_3 tC_4H_9	54:46	52:48	58:42	68:42	55:45	52:48	69:31	69:31	73:27	71:29	76:24	69:31	80:20
C_2H_5 iC_3H_7	73:27	65:35	72:28	64:36	64:36	71:29	76:24	78:22	85:15	73:27	80:20	68:32	—
C_2H_5 tC_4H_9	70:30	61:39	73:27	67:33	64:36	58:42	76:24	69:31	84:16	85:15	83:17	63:37	—
iC_3H_7 tC_4H_9	82:18	72:28	70:30	77:23	66:34	72:28	100:0	89:11	84:16	100:0	88:12	87:13	50:50
CH_3 C_2H_5	71:29	79:21	70:30	70:30	—	—	86:14	72:28	77:23	74:26	81:19	—	58:42
CH_3 iC_3H_7	84:16	86:14	80:20	80:20	81:19	—	94:6	88:12	87:13	88:12	87:13	85:15	—
CH_3 tC_4H_9	100:0	100:0	88:12	88:12	100:0	100:0	100:0	100:0	100:0	100:0	100:0	100:0	53:47
C_2H_5 iC_3H_7	90:10	79:21	84:16	73:27	73:27	55:45	100:0	89:11	91:9	88:12	100:0	77:23	—
C_2H_5 tC_4H_9	92:8	100:0	100:0	100:0	100:0	100:0	100:0	100:0	100:0	100:0	100:0	100:0	—
iC_3H_7 tC_4H_9	100:0	100:0	88:12	88:12	100:0	100:0	100:0	100:0	100:0	100:0	100:0	100:0	75:25

* The Chemoselectivity

\+ The Configurational-Selectivity .

≠ The Configurational-Selectivity For The α And β Bonds, Respectively

E:Z Ratios For The Addition Of Arenesulfenyl Chlorides I-VI, XII and XIII To Symmetrically 1,3-Disubstituted Allenes

RCH=C=CHR

R	E:Z Ratios		
Me	50:50	to	55:45
Et	69:31	to	72:28
iPr	79:21	to	82:18
tBu	97:03	to	100:00

The effect of an ortho-Nitro group results in a 5% to 10% increase of the E:Z ratios.

Me	59:41	to	64:36
Et	72:28	to	80:20
iPr	82:18	to	92:08
tBu	100:00		

On the ground of these observations, it is not possible to say whether this effect is due to an electronic stabilization or simply a steric effect due to the bulk of the 2-Nitro substituent. One must also note that very little difference occurs within a given series.

b- Unsymmetrically 1,3-disubstituted allenes :

In addition to configurational selectivity, unsymmetrically substituted allenes allow an insight in the chemoselectivity of the reaction (i.e., α : β ratios). In the case of 2,3-hexadiene (R=Me, R'=Et), there is no selectivity with respect to which double bond is attacked by the sulfenyl chlorides (I to XIII).

The α : β ratios are roughly constant at 53-55 : 47-45

This suggest that no real difference in steric interaction exists between Me or Et groups and the sulfenyl chlorides.

However, when one goes to the next higher homologue, i.e.,

R = Me ; R' = iPr

some trends appear in the α : β ratios.

In the case of 2-Nitro substituted sulfenyl chlorides (VII to XI), the proportion of attack next to R' is found to be 5 to 10% less then with the other sulfenyl chlorides.

Allene	Sulfenyl chlorides		
$CH_3CH=C=CHiPr$	I to VI	VII to XI	XII to XIII
α : β	55:45-63:37	48:52-53:47	66:34

As one increases the steric bulk of one of the substituents, this becomes more important. In the case where R = Me and R' = tBu the difference is now of the order of 20-40%.

$CH_3CH=C=CHtBu$	55:45-73:27	33:67-45:55	48:52

Here again, little variation occurs within a given series of sulfenyl chlorides. One must note that in the case of 4-methoxybenzenesulfenyl chloride(VI) it was very difficult to obtain kinetically controlled distribution of products due to rapid isomerization of initial adducts. For this reason, one must not be suprised to find some anomalies in the table.

The E : Z ratios for the α and β bonds show trends similar to those found for symmetrically substituted allenes.

5- DISCUSSION :

In our first paper related to this work[56], we did not observe chemoselectivity with respect to which of the mutually perpendicular π bonds of the allene system was attacked :

R	R'	α : β
Me	Et	53 : 47
Me	iPr	52 : 48
Me	tBu	42 : 58

This suggested to us that the electron donating ability of the various alkyl groups was transmitted to the remote double bond. At present, more data is available and one can see that our interpretation was rather limited.

R	R'	α : β
Et	iPr	46 : 54
Et	tBu	33 : 67
iPr	tBu	38 : 62

It is now apparent that there is a slight preference for one of the double bonds attacked by the sulfur atom, the most sterically substituted double bond being favoured (in the case of 2,4-DNBSC).
As the group R' increases in bulk, the α : β ratios become smaller, especially in the case of sulfenyl chlorides bearing a substituent in the 2-position.

Of PRIME importance is the fact that this ortho- substituent need not to be a Nitro group as is exemplified by sulfenyl chlorides XII and XIII.

This observation would tend to rule out the existence of a stabilized spirosulfurane intermediate of type (17) as a Methyl or Trifluoromethyl group can behave similarly to a Nitro group in affecting the ratio of attack on one double bond relative to the other.

As a general rule, it seems that in the case of sulfenyl chlorides with no ortho- substituents, there is very little preference over which double bond is attacked, the least hindered one being favored by 5-10% in some cases. For ortho-substituted sulfenyl chlorides, there is a net preference for attack on the most sterically encumbered side (5-15% in most cases).

The effect of a Nitro group is slightly more important than for a methyl group due to the greater steric bulk of the former. The effect of a trifloromethyl group is intermediate and sometime comparable to the Nitro group.

The $\alpha : \beta$ values are therefore in accord with a steric interaction mechanism during "Steric Approach Control".

The trends observed in the E:Z ratios for the α and β bonds, for both symmetrically substituted and unsymmetrically substituted allenes, were found to be very similar. The configurational-selectivity favors the formation of the E-isomer (as governed by steric approach control) over that of the Z-isomer as the steric bulk of the substituent increases. This gives additional support to the steric involvment of an ortho-Nitro group.

To summarize, one can say that in the reaction of 1,3-disubstituted allenes with arenesulfenyl chlorides, the effect of an ortho-Nitro group is strictly one of steric nature and there does not appear to be any stabilization through novel intermediates of the spirosulfurane type (17).

PART III

THE ELECTROPHILIC ADDITION OF ARENESELENYL HALIDES TO 1,3-DISUBSTITUTED ALLENES

1- THE ADDITION OF BENZENESELENYL CHLORIDE TO 1,3-DISUBSTITUTED ALLENES :

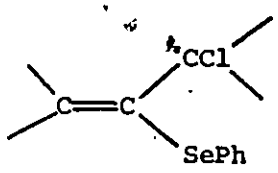
a- INTRODUCTION :

To further establish the results described in PART II, the reaction of Benzeneselenyl chloride (PhSeCl) with 1,3-disubstituted allenes was next examined. Here again attempt was made to investigate factors affecting the nature of the product distributions.

The reactions were carried out under the same experimental conditions, using the same allenes as in PART II. The products were found to be stable at low temperature but slow E⟶Z isomerization was observed at 25°C. However, the kinetically controlled product distribution was obtained by immediate ^{1}H and ^{13}C NMR analysis and was the same as for test NMR-tube reactions in CD_2Cl_2.

Analysis of products was performed by ^{1}H and ^{13}C NMR and Mass Spectrometry using the same criteria previously described.

In all cases, 1:1 adducts were formed in quantitative yield via regiospecific attack of the phenylseleno moiety on the central allenic carbon.



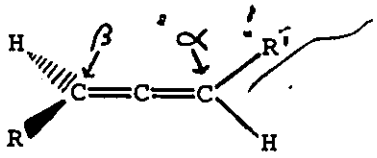
(E+Z)

Spectral Parameters for the adducts are summarized in APPENDIX IV.

The product distribution is shown in TABLE 13.

TABLE 13

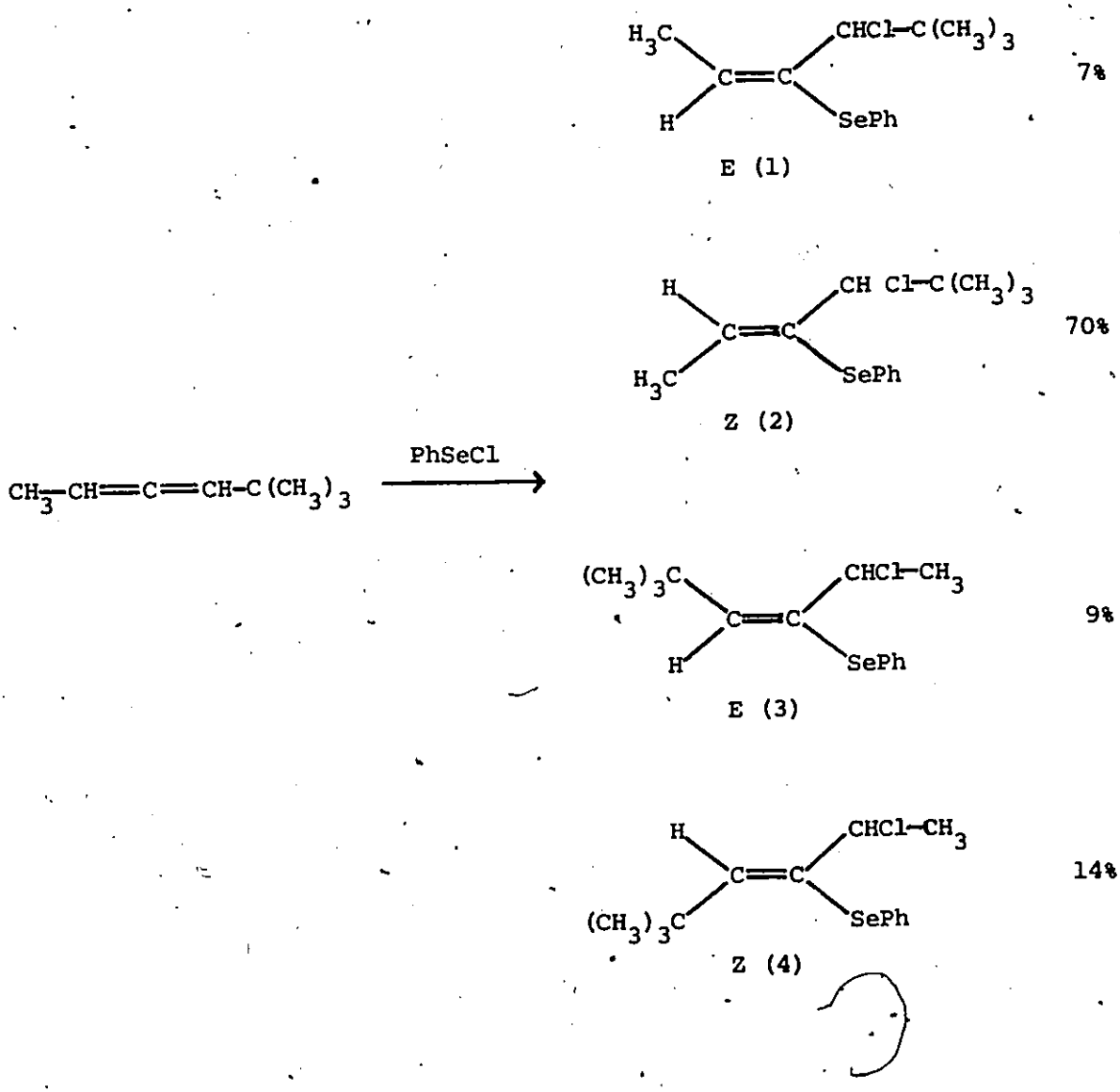
KINETICALLY CONTROLLED PRODUCT DISTRIBUTION FOR THE REACTION OF PhSeCl WITH A SERIES OF 1,3-DISUBSTITUTED ALLENES IN CH_2Cl_2 AT 25°C



SYMMETRIC ALLENES		RATIO OF ISOMERS
R = R'		E : Z
Me		26 : 74
Et		40 : 60
iPr		36 : 64
tBu		0 : 100

ASSYMMETRIC ALLENES		α/β	α	β
R	R'		E : Z	E : Z
Me	Et	33 : 67	27 : 73	30 : 70
Me	iPr	56 : 44	30 : 70	43 : 57
Me	tBu	76 : 24	09 : 91	39 : 61
Et	iPr	44 : 56	27 : 73	46 : 54
Et	tBu	80 : 20	12 : 88	27 : 73
iPr	tBu	75 : 25	11 : 89	16 : 84

To illustrate this, consider the addition of PhSeCl to 5,5-dimethyl-2,3-hexadiene.

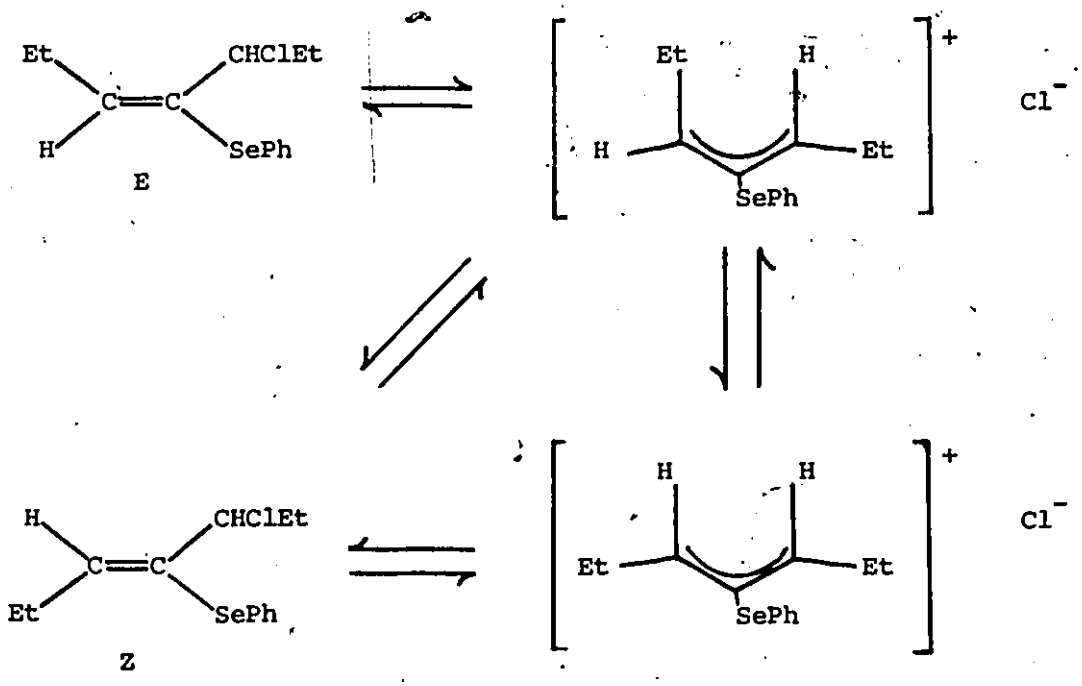


Compounds (1) and (2) both exhibit quartets in the vinyl region of their ^{1}H NMR spectra (5.88 and 6.47 ppm) and singlets for the methine protons geminal to chlorine (4.92 and 4.51 ppm). Our assignment as E and Z for (1) and (2) respectively is based on the shielding of the vinyl and methine protons and the

magnitude of the vicinal carbon-proton coupling constant $^{3}J_{\underline{C}C=C\underline{H}}$[56]. See TABLE 5 in APPENDIX IV.

Similarly, (3) and (4) were assigned the E and Z configurations respectively.[4]

The product distributions in TABLE 13 are those of kinetic control., Evidence for this is the fact that a slow isomerization of the E-alkenes to the corresponding Z-alkene was observed over a period of a few weeks. This probably proceeds by way of an allylic intermediate as shown below.



b- RESULTS :

On observation of the kinetically controlled distribution of products in TABLE 13 one can see that in the case of PhSeCl, the Z-isomer is formed preferentially.

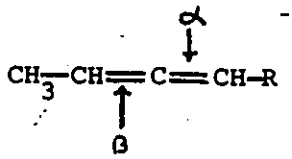
SYMMETRICAL ALLENES	RATIO OF ISOMERS
R = R'	E : Z
Me	26 : 74
Et	40 : 60
iPr	36 : 64
tBu	0 : 100

Similar trends are observed in the case of unsymmetrically substituted allenes. In addition, the double bond with the most electron donating and sterically bulky substituent is preferentially attacked as reflected by the value of the $\alpha : \beta$ ratios in TABLE 13.

Attack on a double bond with a Tert-Butyl substituent appears to favour formation of the thermodynamically more stable Z-Alkene

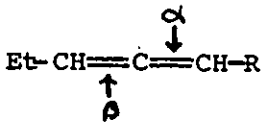
ALLENES		% ATTACK ON tBu SIDE	α
R	R'	(α)	E : Z
Me	tBu	76	09 : 91
Et	tBu	80	12 : 88
iPr	tBu	75	11 : 89
tBu	tBu	100	0 : 100

The effect of the substituent on the remote double bond with respect to the E : Z ratio appears to be negligible in the case of Methyl substituted allenes.

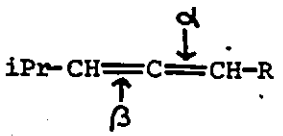


R	α : β	E : Z (α)
Me	50 : 50	26 : 74
Et	33 : 67	27 : 73
iPr	56 : 44	30 : 70
tBu	76 : 24	09 : 91

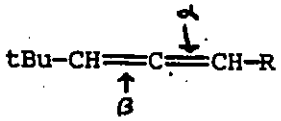
In the case of Ethyl, Isopropyl or Tert-Butyl groups, some fluctuations are apparent.



R	α : β	E : Z (α)
Me	67 : 33	30 : 70
Et	50 : 50	40 : 60
iPr	56 : 44	46 : 54
tBu	20 : 80	27 : 73



R	α : β	E : Z (α)
Me	44 : 56	43 : 57
Et	54 : 46	46 : 54
iPr	50 : 50	64 : 36
tBu	25 : 75	16 : 84



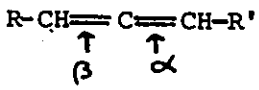
R	α : β	E : Z (α)
Me	24 : 76	39 : 61
Et	20 : 80	27 : 73
iPr	25 : 75	16 : 84
tBu	50 : 50	0 : 100

c- COMPARISON WITH THE CASE OF ADDITION OF ARENESULFENYL CHLORIDES :

In both cases (See PART II), the Thio or Seleno moiety was found to attack the central allenic carbon exclusively. However, the effect of alkyl groups on the product orientation and regiochemistry is very different as shown in TABLE 14.

TABLE 14

A comparison of the kinetically controlled product distributions for the reactions of a series of 1,3-disubstituted allenes with PhSeCl and 2,4-DNBSC at ambient temperature in CH_2Cl_2 solution.



SYMMETRIC ALLENES R = R'	RATIO OF ISOMERS; E : Z ArSeCl	Ar'SCl
Me	26 : 74	64 : 36
Et	40 : 60	80 : 20
iPr	36 : 64	92 : 08
tBu	0 : 100	100 : 00

ASSYMMETRIC ALLENES		ArSeCl	Ar'SCl
R	R'	α : β	
Me	Et	33 : 67	53 : 47
Me	iPr	56 : 44	52 : 48
Me	tBu	76 : 24	42 : 58
Et	iPr	44 : 56	54 : 46
Et	tBu	80 : 20	67 : 33
iPr	tBu	75 : 25	62 : 38
		E : Z (α)	
Me	Et	27 : 73	66 : 34
Me	iPr	30 : 70	65 : 35
Me	tBu	09 : 91	69 : 31
Et	iPr	27 : 73	00 : 100
Et	tBu	12 : 88	00 : 100
iPr	tBu	11 : 89	100 : 00
		E : Z (β)	
Me	Et	30 : 70	86 : 14
Me	iPr	43 : 57	95 : 05
Me	tBu	39 : 61	100 : 00
Et	iPr	46 : 54	24 : 76
Et	tBu	27 : 73	24 : 76
iPr	tBu	16 : 84	100 : 00

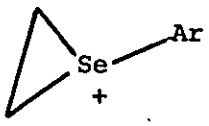
In the case of ArSCl, the E-isomer was formed preferentially. The ratio of E : Z Alkene increases as the bulk of the substituent cis to the -SAr group increases. Very little regioselectivity is observed. Also, the alkyl substituent on the double bond which is attacked does not affect the E : Z ratio to any degree. All these observations contrast with the case of PhSeCl as described above.

d- DISCUSSION :

As previously mentioned (PART II), the proposed mechanism for the addition of ArSCl to alkenes follows Ad_E2 type behavior. This is also expected in the case of PhSeCl[65].

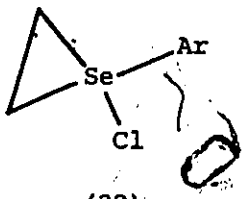
However, the two reactions must have considerably different transition state structures in both Rate and Product determining steps as reflected in TABLE 14.

It is generally accepted that in the case of olefins, bridged species of type (21) or (22) are involved in the rate determining transition state.



(21)

SELENIRANIUM ION

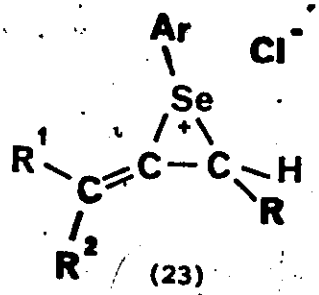


(22)

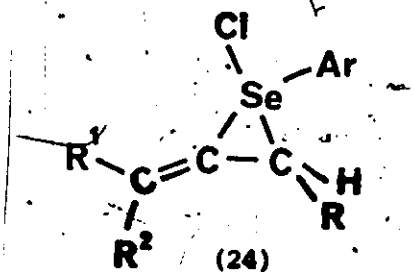
EPISELENURANE

These species subsequently undergo Anti-Nucleophilic attack by the halide ion in a fast step (See SCHEME V).

In the case of allenes the reaction is found to follow second order kinetics, first order in allene and first order in Selenyl chloride. If one assumes the stereospecificity to be similar to that of ArSCl, one can postulate the formation of intermediates such as (23) and (24).



(23)

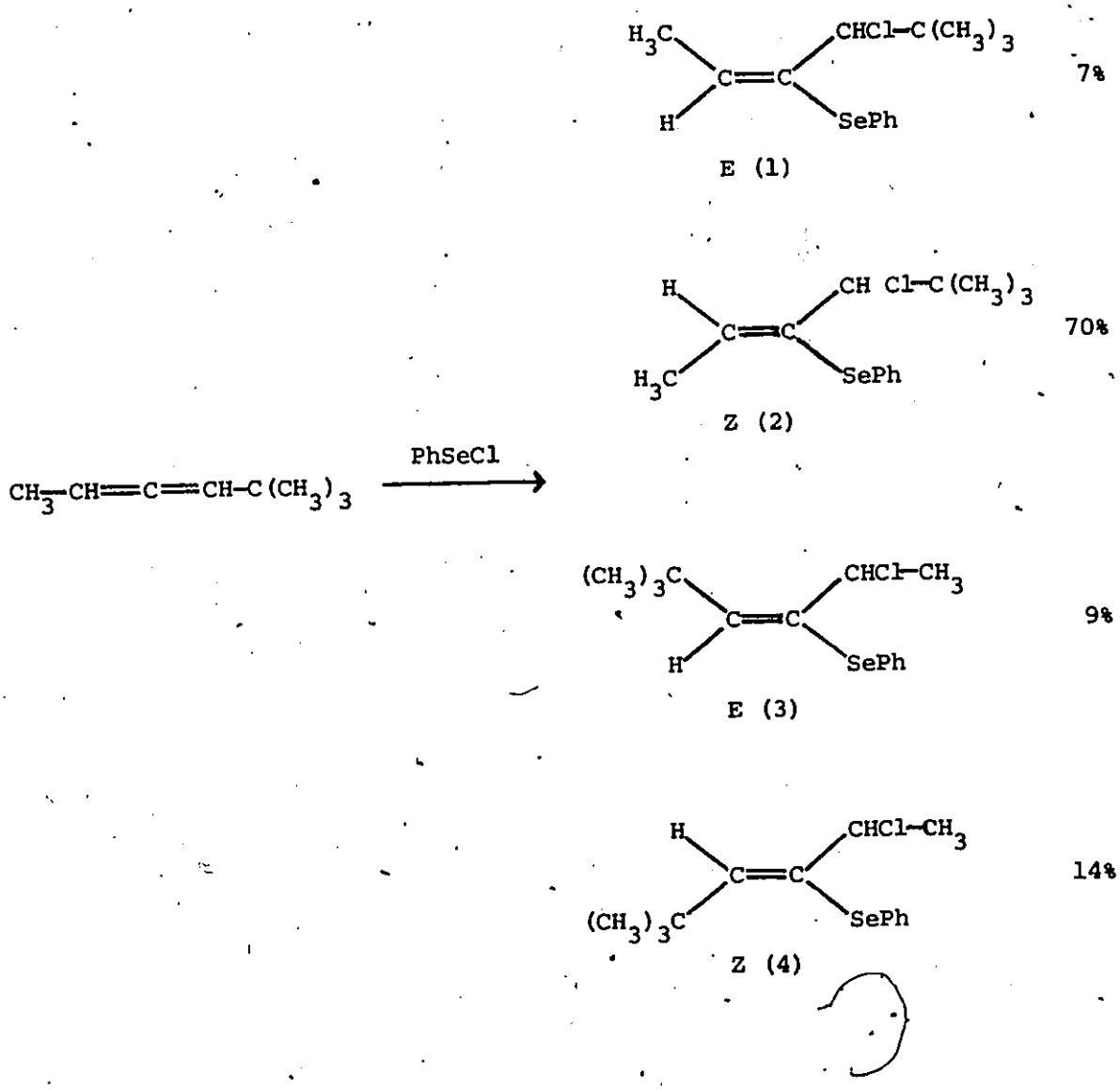


(24)

E : R^1=H; R^2=R

Z : R^1=R; R^2=H

To illustrate this, consider the addition of PhSeCl to 5,5-dimethyl-2,3-hexadiene.



Compounds (1) and (2) both exhibit quartets in the vinyl region of their ^{1}H NMR spectra (5.88 and 6.47 ppm) and singlets for the methine protons geminal to chlorine (4.92 and 4.51 ppm). Our assignment as E and Z for (1) and (2) respectively is based on the shielding of the vinyl and methine protons and the

SCHEME V

The stereospecificity of the reaction will be demonstrated latter.

On the basis of data available at present, one must still envisage the possibility of non-planar or resonance-stabilized allylic carbonium ions as possible intermediates. It will be shown later that allylic ions are not involved in the isomerization process. The predominance of the Z-Alkenes under conditions of kinetic control can be rationalized in terms of a "Preequilibrium" between 23-E and 23-Z with product determining attack by chloride ion on the sterically less hindered side of 23-Z as depicted in SCHEME VI.

2- ROLE OF STERIC VERSUS ELECTRONIC EFFECTS IN THE REACTION OF ARENESELENYL HALIDES WITH 1,3-DISUBSTITUTED ALLENES :

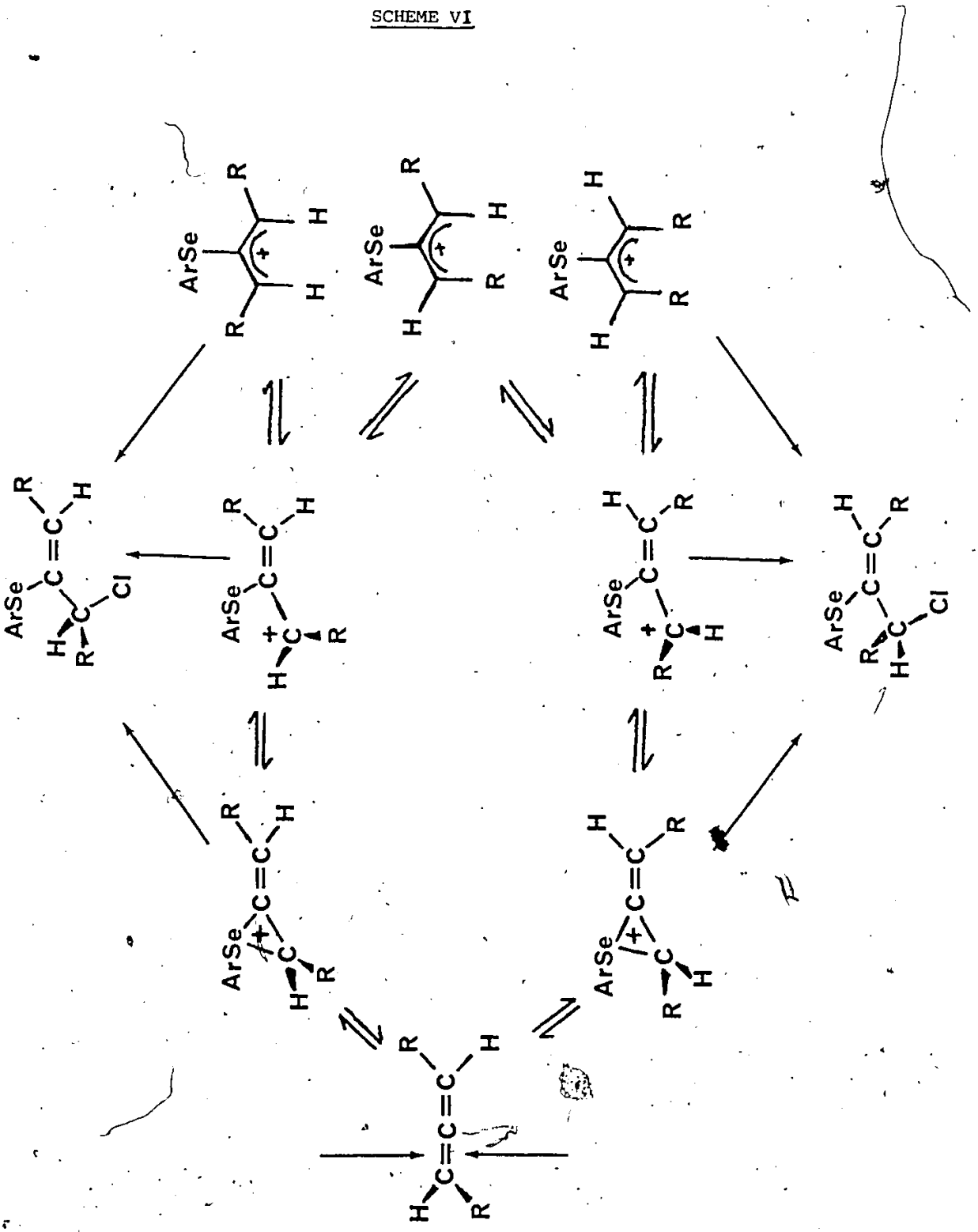
a- INTRODUCTION :

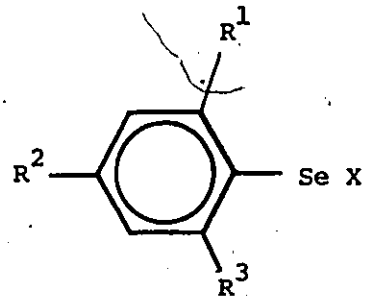
If the proposed mechanism is valid, nucleophilic attack of intermediate (23) or (24) by bromide rather than chloride should result in an increased preference for the Z-isomer.

On the other hand, if the Z-Alkylideneseleniranium ion or Z-Alkylideneepiselenurane is destabilized through steric effects from suitable Ortho-substituents on the phenyl group of the areneselenyl chloride, an increased proportion of E-isomer should be observed.

In order to verify these hypothesis the following Areneselenyl halides were synthesized and reacted with the usual 1,3-disubstituted allenes.

SCHEME VI





R^1	R^2	R^3	X
H	H	H	Cl
H	H	H	Br
CH_3	CH_3	CH_3	Br

The reactions were carried out under the same experimental conditions previously described. The Kinetically-controlled product distributions were determined by immediate ^1H NMR analysis of the reaction mixtures and are reported in TABLE 15.

The products were found to isomerize within a few days at room temperature. However immediate ^1H NMR analysis provided true kinetically controlled distributions. The product configurations were determined as usual.

TABLE 15

The kinetically controlled product distributions for the reactions of benzeneselenyl chloride, benzeneselenyl bromide, and 2,4,6-trimethylbenzeneselenyl bromide with a series of 1,3-disubstituted allenes in CH_2Cl_2 at 25°C.

$$RCH{=}\overset{\beta}{C}{=}\overset{\alpha}{C}HR'$$

Symmetrically Substituted Allenes	% Composition		
R = R'	C_6H_5SeCl	C_6H_5SeBr	$2,4,6\text{-}(CH_3)_3C_6H_2SeBr$
		E:Z	
CH_3	26:74	28:72	55:45
C_2H_5	40:60	37:63	54:46
$i\text{-}C_3H_7$	36:64	30:70	80:20
$t\text{-}C_4H_9$	0:100	0:100	100:0
$-(CH_2)_6-$	100:0	100:0	100:0
$-(CH_2)_{10}-$	36:64	32:68	100:0
Unsymmetrically Substituted Allenes			
		α : β	
R = CH_3 R' = C_2H_5	33:67	65:35	55:45
CH_3 $i\text{-}C_3H_7$	56:44	62:38	67:33
CH_3 $t\text{-}C_4H_9$	76:24	89:11	65:35
C_2H_5 $i\text{-}C_3H_7$	44:56	48:52	52:48
C_2H_5 $t\text{-}C_4H_9$	80:20	78:22	71:29
$i\text{-}C_3H_7$ $t\text{-}C_4H_9$	75:25	79:21	64:36
		α(E:Z)	
CH_3 C_2H_5	27:73	28:72	47:53
CH_3 $i\text{-}C_3H_7$	30:70	26:74	61:39
CH_3 $t\text{-}C_4H_9$	9:91	12:88	55:45
C_2H_5 $i\text{-}C_3H_7$	27:73	27:73	71:29
C_2H_5 $t\text{-}C_4H_9$	12:88	13:87	73:27
$i\text{-}C_3H_7$ $t\text{-}C_4H_9$	11:89	14:86	81:19
		β(E:Z)	
CH_3 C_2H_5	30:70	31:69	62:38
CH_3 $i\text{-}C_3H_7$	43:57	50:50	85:15
CH_3 $t\text{-}C_4H_9$	39:61	27:73	100:0
C_2H_5 $i\text{-}C_3H_7$	46:54	42:58	83:17
C_2H_5 $t\text{-}C_4H_9$	27:73	27:73	100:0
$i\text{-}C_3H_7$ $t\text{-}C_4H_9$	16:84	14:86	100:0

b- RESULTS :

On observation of TABLE 15 one notices that PhSeCl and PhSeBr behave very similarly. In both cases the product distributions reflect a preferential formation of the Z-Alkene under kinetic control.

On the other hand, 2,4,6-trimethylbenzeneselenyl bromide favors E-Alkenes. For example, consider the product distributions in the case of 2,2,6,6-tetramethyl-3,4-heptadiene (1,3-ditertButyl allene).

	PhSeCl	PhSeBr	$2,4,6\text{-}Me_3C_6H_2SeBr$
E : Z RATIOS	0 : 100	0 : 100	100 : 0

Reversals of smaller magnitudes are observed throughout the series of 1,3-disubstituted allenes investigated. The fact that in the case of 2,4,6-trimethylbenzeneselenyl bromide the E-isomer is formed preferentially can be tentatively attributed to the steric bulk of the electrophile (i.e., " Steric-Approach Control ").

Kinetic data are however much more informative as will be seen in the next section.

c- KINETIC STUDIES :

Kinetic data are shown in TABLE 16. The rates of addition were determined using the stopped-flow technique as described in the Experimental section. The rate of disappearance of PhSeCl, PhSeBr and $2,4,6\text{-}Me_3C_6H_2SeBr$ were followed by measuring the decrease in their respective absorptions at 433, 468 and 497 nms. In all cases, the additions were found to exhibit Second Order Kinetics; first Order in Selenyl Halide and first Order in Allene, to at least 90% completion of the reaction.

TABLE 16

Specific and Relative rates of addition for the reactions of PhSCl, PhSeCl, PhSeBr, and 2,4,6-$(CH_3)_3C_6H_2SeBr$ with some 1,3-disubstituted allenes, RCH=C=CHR', in CH_2Cl_2 at 24.5°C.

k_2 (dm^3 mol^{-1} s^{-1})

Allene R	Allene R'	C_6H_5SCl	C_6H_5SeCl	C_6H_5SeBr	2,4,6-$(CH_3)_3C_6H_2SeBr$
CH_3	CH_3	151.	19,700	4,420	153.
C_2H_5	C_2H_5	126.	6,740	1,180	40.8
i-C_3H_7	i-C_3H_7	82.0	1,870	567.	18.2
CH_3	C_2H_5	165.	18,000	4,890	140.
CH_3	i-C_3H_7	125.	3,410	646.	35.4
CH_3	t-C_4H_9	104.	342.	79.8	3.15
C_2H_5	i-C_3H_7	99.8	2,000	316.	13.7
C_2H_5	t-C_4H_9	106.	233.	44.5	1.63
i-C_3H_7	t-C_4H_9	56.0	62.0	16.3	0.394

k_{rel}

Allene R	Allene R'	C_6H_5SCl	C_6H_5SeCl	C_6H_5SeBr	2,4,6-$(CH_3)_3C_6H_2SeBr$
CH_3	CH_3	1.00	1.00	1.00	1.00
C_2H_5	C_2H_5	0.83	0.34	0.27	0.27
i-C_3H_7	i-C_3H_7	0.54	0.095	0.13	0.12
CH_3	C_2H_5	1.09	0.91	1.11	0.92
CH_3	i-C_3H_7	0.83	0.17	0.15	0.23
CH_3	t-C_4H_9	0.69	0.017	0.018	0.021
C_2H_5	i-C_3H_7	0.66	0.10	0.071	0.090
C_2H_5	t-C_4H_9	0.70	0.012	0.010	0.011
i-C_3H_7	t-C_4H_9	0.37	0.0031	0.0037	0.0026

For purposes of comparison, the analogous rate data for PhSCl are also given in TABLE 16. There is found to be a large rate decrease upon substituting Sulfur for Selenium.

The effect of Alkyl substituents on the allene moiety on the rate of addition to PhSCl is very minor. On the other hand, PhSeCl experiences drastic fluctuations.

PhSCl[9]	:	k_2 = 56	165	($dm^3 mol^{-1} s^{-1}$)
PhSeCl	:	k_2 = 62	19,700	(" ")

In the case of PhSeCl, the rate of addition decreases as the steric bulk and electron donating ability of the Alkyl substituents on the allene increases.

The variations in rate as reflected in TABLE 16 for the addition of PhSCl to the allenes closely resembles the case of addition to similar substituted Ethylenes[66].

It appears that in the case of Arenesulfenylation, a Methyl group will stabilize the rate determining transition state as effectively as an ethylidene ($=CHCH_3$) group. Similarly, the stabilization ability of an Ethyl, Isopropyl and Tert-Butyl is comparable to that of a n-Propylidene ($=CHCH_2CH_3$), isoButylene ($=CHCH(CH_3)_2$) and neoPentylidene ($=CHC(CH_3)_3$).
This does not appear to be true in the case of PhSeCl as large fluctuations in TABLE 16 are probably of Steric origin. For example, the rate of reaction drops by a factor of 90% when substituting the Methyl groups of 2,3-pentadiene for isoPropyl groups. Similarly, substitution of only one of the Methyl groups brings about a continuous decrease in the rate of addition.

R	R'	PhSeCl k_{rel}	PhSeCl rate vs —=—=	PhSCl k_{rel}	PhSCl rate vs —=—=
Me	Me	1.00	100%	1.00	100%
Me	Et	0.91	91%	1.09	109%
Me	iPr	0.17	17%	0.83	83%
Me	tBu	0.017	1.7%	0.69	69%
tBu	iPr	0.0031	0.31%	0.37	37%

In the case of PhSeCl, the rate of addition for 1-methyl-3-tert-Butyl allene is 0.31% that of 1,3-dimethyl allene. Under the same conditions the Sulfur version gives a rate which is still 37% that of 2,3-pentadiene.
This implies different behavior of Selenium and Sulfur in the rate determining transition states[67].

On further examination of TABLE 16 the similarity between the Benzeneselenyl halides with respect to steric effects is quite significant. To clarify this idea TABLE 17 presents the ratio of the reactivity of PhSeCl over that of PhSeBr. As it can be seen, these ratios are more or less constant (Average = 4.68 ± 1.02).

Similarly, the ratio of the reactivity of PhSeBr over that of the trisubstituted Arenesulfenyl bromide is constant at 28.8 ± 4.7.

One must note that a 5-10% error is involved in the measurement of rate constants under our experimental conditions.

Contrastingly, the ratio of the reactivity of PhSCl over that of PhSeBr shows no correlation (Average = 0.203 ± 0.25). This rules out any similarity between the two Rate determining transition states.

On the other hand, it appears that all three Areneselenyl halides studied do have <u>similar</u> rate determining transition states. This together with the fact that PhSeCl and PhSeBr on the one hand and 2,4,6-trimethylbenzeneselenyl bromide on the other experience different substituent effects upon the

TABLE 17

Rate ratios as a function of changes in the nature of the Electrophilic species.

Allene RCH=C=CHR' R	R'	$k_{C_6H_5SCl}/k_{C_6H_5SeCl}$	$k_{C_6H_5SeCl}/k_{C_6H_5SeBr}$
CH_3	CH_3	0.0077	4.46
C_2H_5	C_2H_5	0.019	5.71
i-C_3H_7	i-C_3H_7	0.044	3.30
CH_3	C_2H_5	0.0092	3.68
CH_3	i-C_3H_7	0.037	5.28
CH_3	t-C_4H_9	0.30	4.29
C_2H_5	i-C_3H_7	0.050	6.33
C_2H_5	t-C_4H_9	0.46	5.24
i-C_3H_7	t-C_4H_9	0.90	3.80
			avg. 4.68

R	R'	$k_{C_6H_5SeBr}/k_{2,4,6\text{-}(CH_3)_3C_6H_2SeBr}$
CH_3	CH_3	28.9
C_2H_5	C_2H_5	28.9
i-C_3H_7	i-C_3H_7	31.2
CH_3	C_2H_5	34.9
CH_3	i-C_3H_7	18.2
CH_3	t-C_4H_9	25.3
C_2H_5	i-C_3H_7	23.1
C_2H_5	t-C_4H_9	27.3
i-C_3H_7	t-C_4H_9	41.4
	avg.	28.8

product determining transition states leads us to the further conclusion that the rate and product determining transition states are quite distinct from each other and must be separated by at least one intermediate.

The consequence of this is that the product distributions obtained for the reactions of 2,4,6-trimethylbenzeneselenyl bromide can not be rationalized in terms of " Steric approach control " despite the reversal of configurational-selectivities in favor of the E-isomer.

To further illustrate this behavior, the product distributions obtained from 2,4,6-$(CH_3)_3C_6H_2SeBr$ are compared with those obtained from PhSCl and 2,4,6-$(CH_3)_3C_6H_2SCl$ and the corresponding bromide (See TABLE 18).

The results from additions of 2,4,6-$(CH_3)_3C_6H_2SBr$ are of little utility as they may not reflect Kinetic control distribution due to rapid isomerization. However, a comparison in the behavior of the remaining electrophiles allows us to investigate Selenylation vs Sulfenylation.

In agreement with the data, the activation energy of the reaction must be large compared with the barrier to interconversion between E and Z isomers. A mechanistic Scheme compatible with the observations is given in SCHEME VII.

The main question arising from the scheme is whether an Alkylidene-seleniranium halide is formed first or is an Alkylideneepiselenurane involved as an intermediate.

(Note that the latter may collapse directly to products or dissociate first to an Alkylideneseleniranium ion).

TABLE 18

A comparison of the initial distributions of products for the reactions of $2,4,6\text{-}Me_3C_6H_2SeBr$, $2,4,6\text{-}Me_3C_6H_2SBr$, $2,4,6\text{-}Me_3C_6H_2SCl$ and PhSCl to some 1,3-disubstituted allenes in CH_2Cl_2 at 25°C

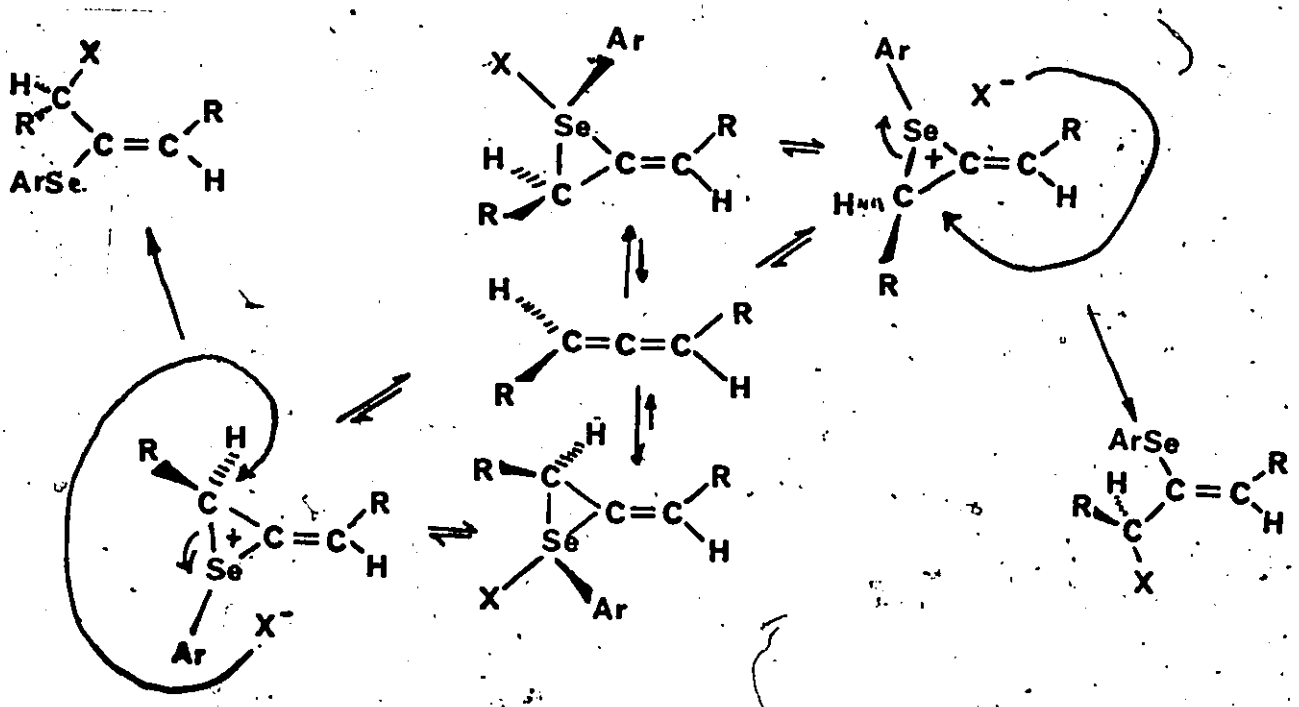
$$RCH\overset{\beta}{=}\overset{\alpha}{C}=CHR'$$

Symmetrically Substituted Allenes R = R'	% Composition ArSeBr	ArSBr*	ArSCl¶	C_6H_5SCl¶
		E:Z		
CH_3	55:45	60:40	60:40	55:45
C_2H_5	54:46	35:65	98: 2	72:28
$i\text{-}C_3H_7$	80:20	45:55	100: 0	80:20
$t\text{-}C_4H_9$	100: 0	100: 0	100: 0	97: 3
Unsymmetrically Substituted Allenes		α : β		
R = CH_3 R' = C_2H_5	55:45	45:55	60:40	53:47
CH_3 $i\text{-}C_3H_7$	67:33	40:60	70:30	55:45
CH_3 $t\text{-}C_4H_9$	65:35	60:40	82:12	59:41
C_2H_5 $i\text{-}C_3H_7$	52:48	45:55	62:38	47:53
C_2H_5 $t\text{-}C_4H_9$	71:29	56:44	83:17	55:45
$i\text{-}C_3H_7$ $t\text{-}C_4H_9$	64:36	65:35	80:20	56:44
		α(E:Z)		
CH_3 C_2H_5	47:53	18:82	60:40	56:44
CH_3 $i\text{-}C_3H_7$	61:39	35:65	80:20	57:43
CH_3 $t\text{-}C_4H_9$	55:45	57:43	100:0	58:42
C_2H_5 $i\text{-}C_3H_7$	71:29	51:49	100:0	64:36
C_2H_5 $t\text{-}C_4H_9$	73:27	29:71	100:0	67:33
$i\text{-}C_3H_7$ $t\text{-}C_4H_9$	81:19	5:95	100:0	77:23
		β(E:Z)		
CH_3 C_2H_5	62:38	38:62	100:0	70:30
CH_3 $i\text{-}C_3H_7$	85:15	33:67	100:0	80:20
CH_3 $t\text{-}C_4H_9$	100:0	78:22	100:0	88:12
C_2H_5 $i\text{-}C_3H_7$	83:17	31:69	100:0	73:27
C_2H_5 $t\text{-}C_4H_9$	100:0	89:11	100:0	100:0
$i\text{-}C_3H_7$ $t\text{-}C_4H_9$	100:0	100:0	100:0	88:12

Ar = 2,4,6-trimethylphenyl

* the adducts derived from 2,4,6-trimethylbenzenesulphenyl bromide were found to isomerize very rapidly even at -78°C. Values given in this column thus do not necessarily reflect kinetic control.

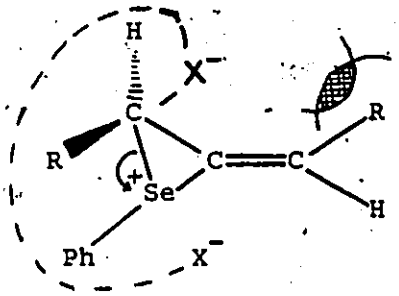
SCHEME VII



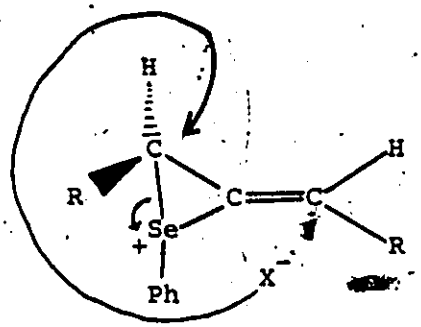
Spectral parameters for adducts of 1,3-disubstituted allenes with various Selenyl and Sulfenyl halides are tabulated in APPENDIX V.

From the available data we can postulate that the product determining transition states arise from the alkylideneseleniranium ion ion-pairs after equilibration of the various configurational isomers. Two competitive steric effects are in action as demonstrated below.

Consider the case of PhSeCl and PhSeBr (E : Z < 1).



E

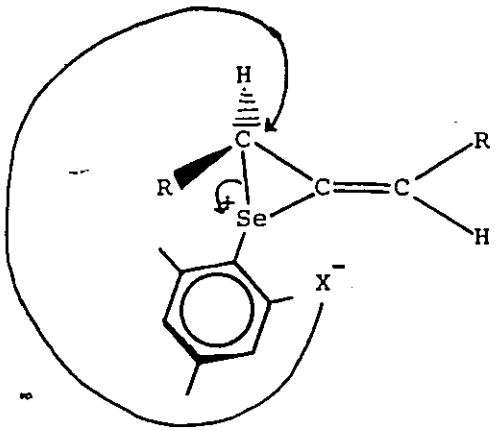


Z

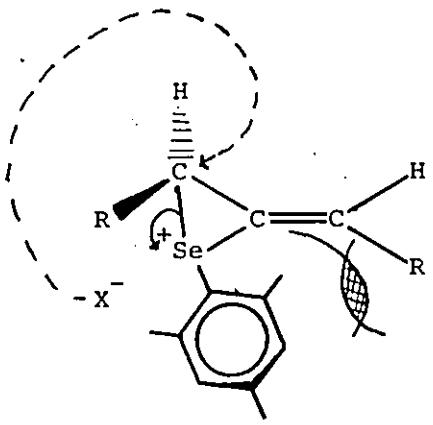
FAVORED

In the case of the E-isomer there is an interaction between the attacking nucleophile ($X^- = Cl^-$ or Br^-), and the alkyl group on the olefinic portion of the Alkylideneseleniranium ion. This interaction is minimized in the case of the Z-isomer, thus favoring the latter with respect to the E-configuration.

In the case of 2,4,6-trimethylbenzeneselenyl bromide, the situation is completely reversed as shown by a predominance of the E-isomer in the product distributions. This can be attributed to steric interaction between the same olefinic alkyl group and the ortho-Methyl groups on the Selenyl bromide as depicted below.



E



Z

FAVORED

In this case the E-configuration would be favored.

Elucidation of the structure of the Rate-determining transition state is more of a problem. The available Kinetic data confirm the presence of one molecule of Selenyl halide and one molecule of Allene in the transition state. A large steric effect is observed with respect to Alkyl substituents on the allene (especially in the case of iPr- and tBu- groups), but no change in the structure-reactivity profile is apparent upon substitution of ortho-Methyl groups for the ortho-Hydrogens on the electrophile.

Of note is the fact that there is no evidence of a steric effect in the rate-determining step as revealed by the rates of addition of PhSeCl to allene and its various Methyl-substituted derivatives[68]. (A linear correlation being found between log k_2 and $\Sigma\sigma^*$).

It thus appears that electronic effects are involved. This is also observed in the case of Ethyl-substituents. For example, compare the rates of addition to the following pairs of allenes :

R	R'	PhSeCl (k_2)	PhSeBr (k_2)
Me	Me	19,700	4,420
Me	Et	18,000	4,890
iPr	Me	3,410	646
iPr	Et	2,000	316
tBu	Me	342	79.8
tBu	Et	233	44.5

The presence of a second Ethyl group does, however lead to a significant rate retardation :

Me	Et	18,000	4,890
Et	Et	6,740	1,190

This observation implies that configurational interactions involving only one of the Alkyl groups on the allene are present in the rate-determining transition state.

If an episelenurane-like species is involved in the rate-determining transition state, the increased atomic radius of Bromine relative to Chlorine would then account for the approximately 5-fold decrease in reactivity between PhSeCl and PhSeBr. The analogous 29-fold decrease in reactivity between PhSeBr and 2,4,6-trimethylbenzeneselenyl bromide may be accounted for in a similar fashion; The increased congestion of the larger Aryl moiety leading to the rate retardation.

PART IV

1- INTRODUCTION :

It was shown in PART III that the addition of PhSeCl to 1,3-disubstituted allenes proceeds via at least one intermediate and two transition states (i.e., Rate and Product determining transition states), differing in their structures. If one recalls that the addition is stereospecific (see PART VII), the transition states are likely to have bridged structures, and resonance stabilized allylic ions are not involved.

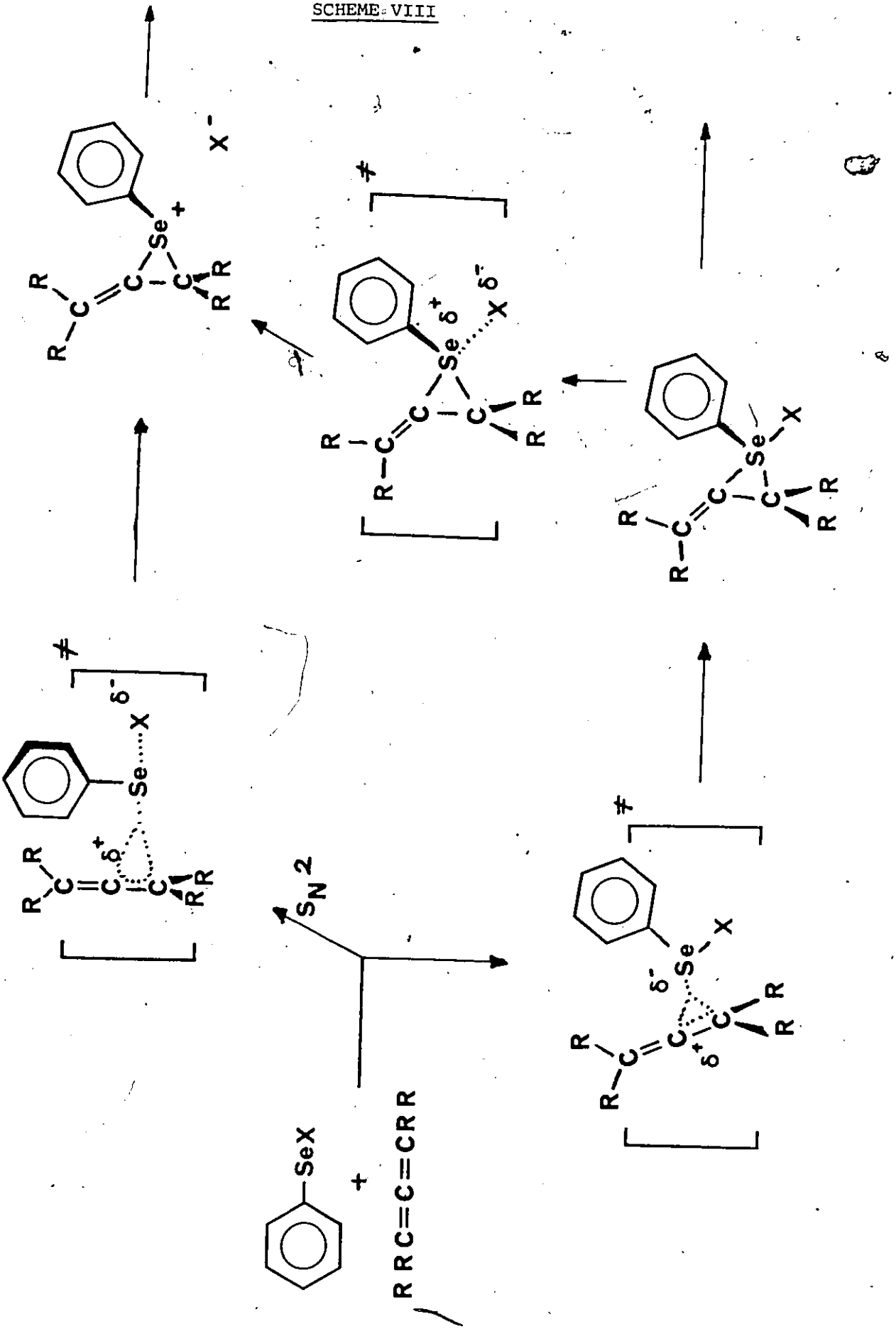
It was also mentioned that the electrophile could interact with the allenic double bond following a typical S_N2 type pathway giving rise to the formation of an Alkylideneseleniranium ion pair (23) or alternatively, a tetracovalent Alkylideneepiselenurane (24) can also be formed. The latter species can collapse to products either directly or via (23).
These ideas are summarized in SCHEME VIII.

2- KINETIC OBSERVATIONS :

a- PRELIMINARIES :

The rate of addition of PhSeCl to various allenes was measured at 24.5°C in Dichloromethane by means of the stopped-flow technique. (The rate of disappearance of PhSeCl was followed by measuring the decrease in its absorption at 433nm).

SCHEME VIII



The expression for the rate equation follows from the observation that under Pseudo-First Order conditions (large excess of allene vs PhSeCl), the rate of addition is independent of both the allene and PhSeCl concentrations as shown below.

[Allene]* (mole/l)	[PhSeCl] (mole/l)	k_2 ($dm^3 mol^{-1} s^{-1}$)
0.002351	0.001921	11,500
0.025331	0.001921	10,300
0.004310	0.001902	10,600
0.007176	0.001902	9,600

* 3-methyl-1,2butadiene

It follows that :

$$-\frac{d\,[PhSeCl]}{dt} = k_2\,[PhSeCl].[Allene]$$

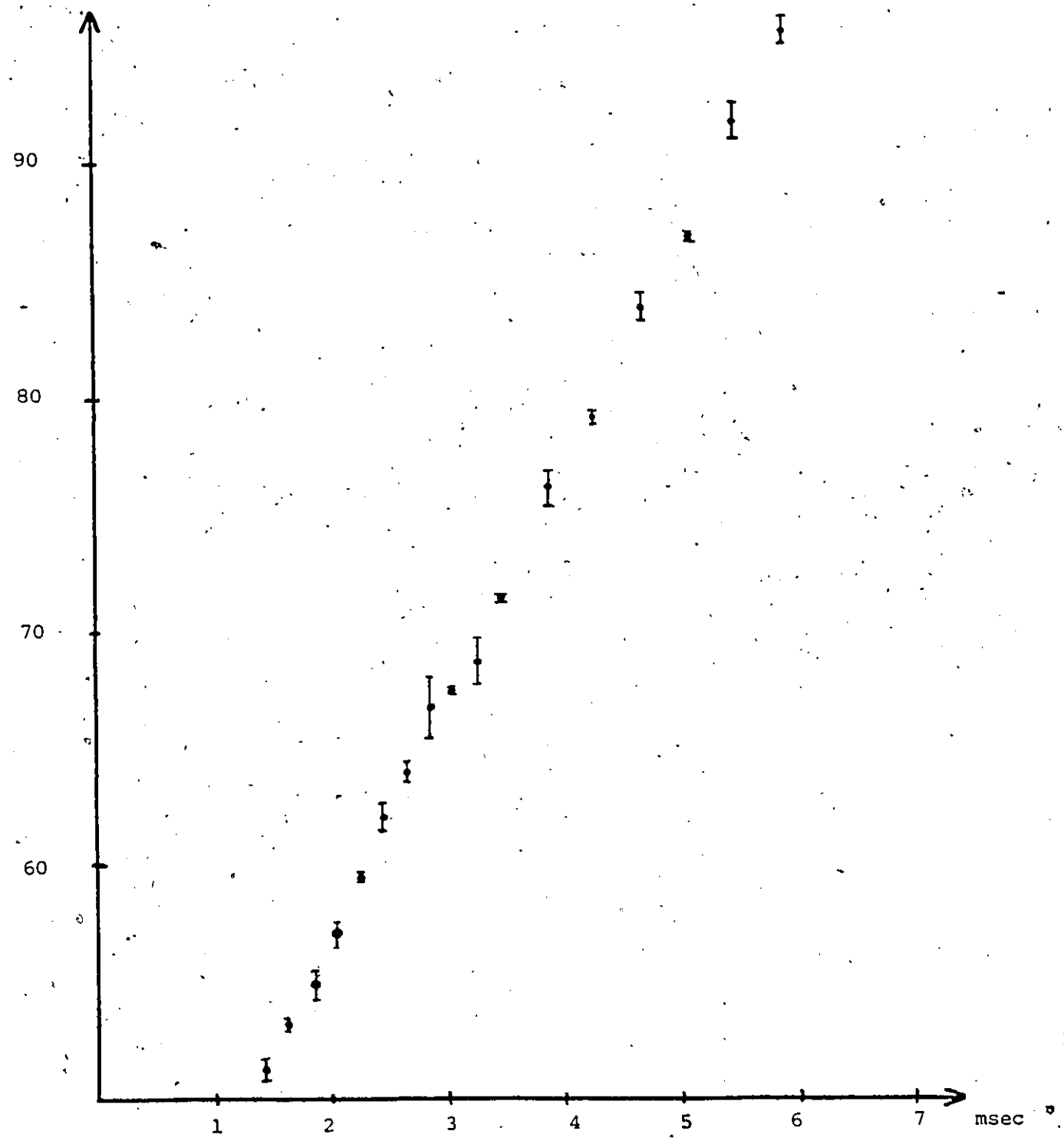
Furthermore, the best results were obtained by treating the data using a 2nd order rate program. See for example FIGURE 7.

For comparison purposes the same data were treated with a 3rd order rate program. The results are shown in FIGURE 8.

Therefore the rate determining transition state can be defined as containing one molecule of Selenyl chloride and one molecule of Allene.

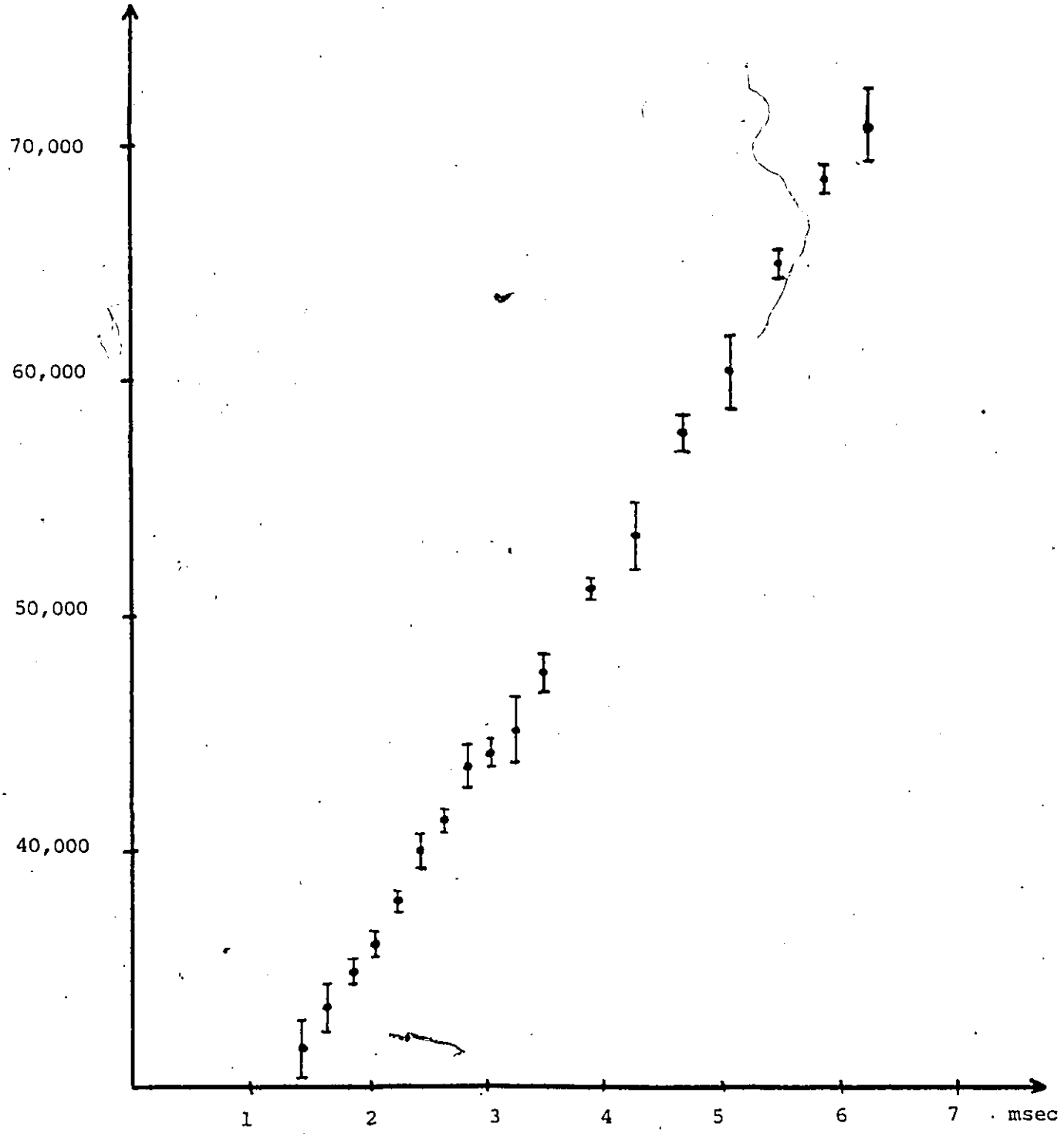
Rate data are presented in TABLE 19.

FIGURE 7



Plot of 2nd order rate equation for 3-methyl-1,2-butadiene + PhSeCl

FIGURE 8



Plot of 3rd order rate equation for 3-methyl-1,2-butadiene + PhSeCl

TABLE 19

Specific rate constants, k_2 dm^3 mol^{-1} s^{-1}, for the reaction of benzeneselenenyl chloride with some alkyl substituted allenes in methylene chloride solution at 24.5°C

$$R^1R^2C{=}C{=}CR^3R^4$$

Entry	Allene				Rate Constants	
	R^1	R^2	R^3	R^4	k_2	k_{rel}
1	H	H	H	H	8.23	1.00
2	H	H	H	CH_3	437.	53.1
3	H	H	H	C_2H_5	528.	64.2
4	H	H	H	i-C_3H_7	118.	14.3
5	H	H	H	i-$C_4H_9CH_2$	124.	15.1
6	H	H	H	t-C_4H_9	5.9	0.72
7	H	H	CH_3	CH_3	11000	1340
8	H	H	CH_3	C_2H_5	279000	33900
9	H	H	CH_3	i-C_4H_9	2880	350.
10	H	H	CH_3	t-C_4H_9	210.	25.5
11	H	H	CH_3	t-$C_4H_9CH_2$	1600	194.
12	CH_3	H	CH_3	H	19700	2390
13	C_2H_5	H	C_2H_5	H	6740	819.
14	i-C_3H_7	H	i-C_3H_7	H	1870	227.
15	CH_3	H	C_2H_5	H	18000	2190
16	CH_3	H	i-C_3H_7	H	3410	414.
17	CH_3	H	t-C_4H_9	H	342.	41.6
18	C_2H_5	H	i-C_3H_7	H	2000	243.
19	C_2H_5	H	t-C_4H_9	H	233.	28.3
20	i-C_3H_7	H	t-C_4H_9	H	62.0	7.5
21	CH_3	H	CH_3	CH_3	218000	26500
22	C_2H_5	H	CH_3	CH_3	111000	13500

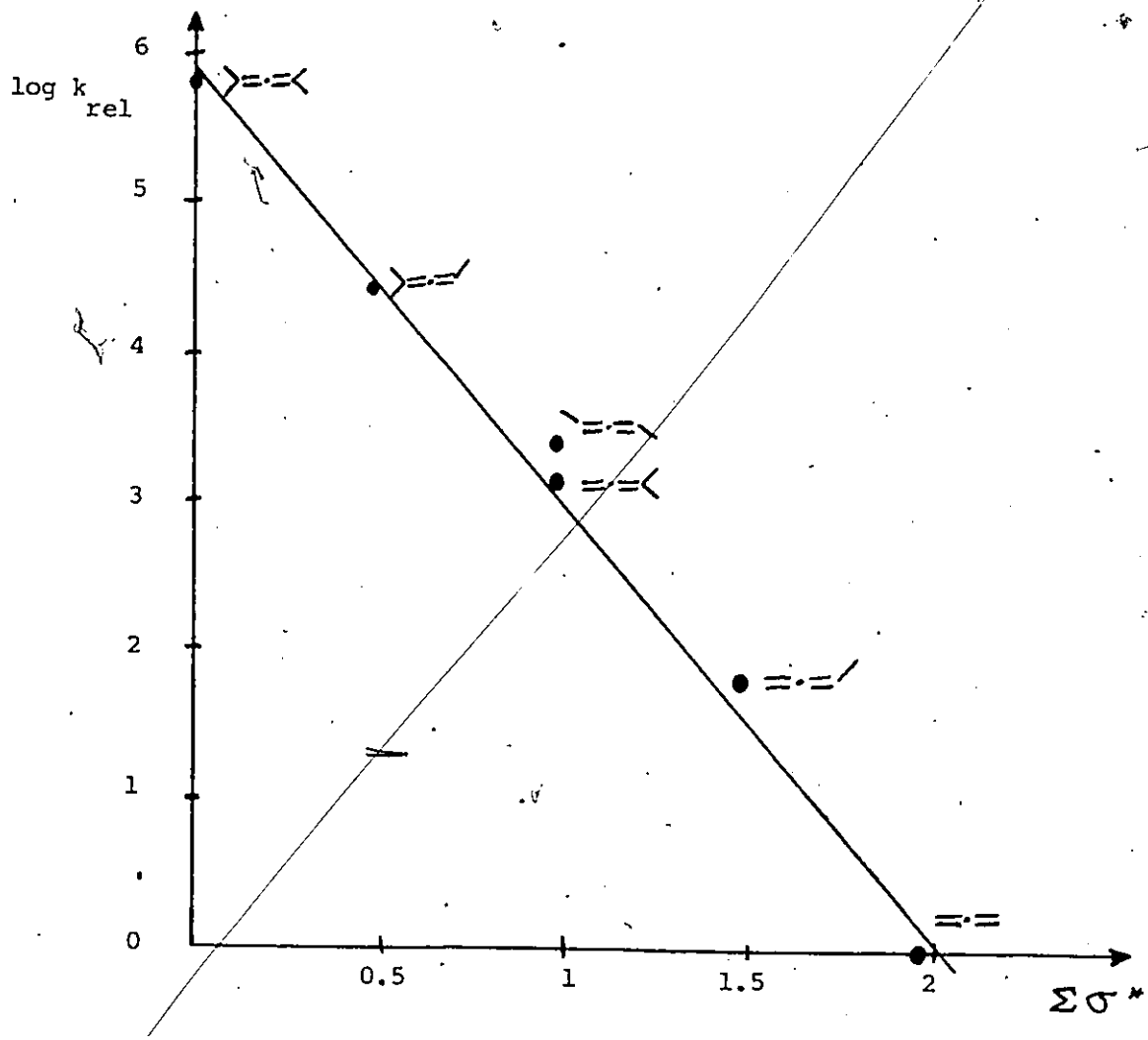
23	$i\text{-}C_3H_7$	H	CH_3	CH_3	36400	4420
24	$i\text{-}C_4H_9$	H	CH_3	CH_3	27600	3350
25	$t\text{-}C_4H_9$	H	CH_3	CH_3	1540	187.
26	C_2H_5	H	C_2H_5	C_2H_5	12400	1510
27	$i\text{-}C_3H_7$	H	C_2H_5	C_2H_5	3100	377.
28	$t\text{-}C_4H_9$	H	C_2H_5	C_2H_5	217.	26.4
29	C_2H_5	H	$-(CH_2)_5-$		132000	16040
30	$i\text{-}C_3H_7$	H	$-(CH_2)_5-$		54600	6640
31	$t\text{-}C_4H_9$	H	$-(CH_2)_5-$		6730	818.
32	CH_3	H	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	260.	31.6
33	C_2H_5	H	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	109.	13.2
34	$i\text{-}C_3H_7$	H	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	70.	8.5
35	$t\text{-}C_4H_9$	H	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	60.7	7.38
36	CH_3	H	CH_3	C_2H_5	22100	2690
37	C_2H_5	H	CH_3	C_2H_5	21700	2640
38	$i\text{-}C_3H_7$	H	CH_3	C_2H_5	14500	1760
39	$t\text{-}C_4H_9$	H	CH_3	C_2H_5	590.	71.7
40	CH_3	H	CH_3	$i\text{-}C_3H_7$	18000	2190
41	C_2H_5	H	CH_3	$i\text{-}C_3H_7$	22900	2780
42	$i\text{-}C_3H_7$	H	CH_3	$i\text{-}C_3H_7$	4690	570.
43	$t\text{-}C_4H_9$	H	CH_3	$i\text{-}C_3H_7$	2100	255.
44	$c\text{-}C_6H_{11}$	H	CH_3	$i\text{-}C_3H_7$	6180	751.
45	CH_3	H	CH_3	$t\text{-}C_4H_9$	1550	188.
46	C_2H_5	H	CH_3	$t\text{-}C_4H_9$	1390	169.
47	$i\text{-}C_3H_7$	H	CH_3	$t\text{-}C_4H_9$	324.	39.4
48	$t\text{-}C_4H_9$	H	CH_3	$t\text{-}C_4H_9$	4.55	0.553
49	$c\text{-}C_6H_{11}$	H	CH_3	$t\text{-}C_4H_9$	480.	58.3
50	$i\text{-}C_3H_7$	H	C_2H_5	$t\text{-}C_4H_9$	21.5	2.61
51	C_2H_5	H	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	33.2	4.03

52	$i\text{-}C_3H_7$	H	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	15.7	1.91
53	$t\text{-}C_4H_9$	H	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	6.2	0.75
54	CH_3	CH_3	CH_3	CH_3	5400000	656000
55	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	9.3	1.13
56	CH_3	C_2H_5	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	0.80	0.097
57	CH_3	$i\text{-}C_3H_7$	CH_3	$t\text{-}C_4H_9$	180.	21.9
58	CH_3	$i\text{-}C_3H_7$	C_2H_5	$t\text{-}C_4H_9$	155.	18.8
59	CH_3	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	8.7	1.06
60	CH_3	$t\text{-}C_4H_9$	C_2H_5	$i\text{-}C_3H_7$	22.0	2.67
61	CH_3	$t\text{-}C_4H_9$	C_2H_5	$t\text{-}C_4H_9$	2.40	0.292
62	CH_3	$t\text{-}C_4H_9$	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	0.16	0.0194

It can be seen that the rate of addition increases with increasing the electron donating ability of the substituents. This reflects the electrophilic character of the investigated reaction. However, the electron donating power of the substituent is not the only factor influencing the rate determining transition state. Steric effects are also involved to some extent.
In order to evaluate the importance of these two factors, an extended TAFT correlation[69] was attempted.

It had been observed[70], that no steric effects are involved in the rate limiting transition state for the reaction of Allene and its Methyl-substituted derivatives with PhSeCl; a linear correlation was obtained between log k_{rel} and $\Sigma\sigma^*$ (TAFT's values[69]). This is shown in FIGURE 9.

FIGURE 9



The 62 allenes were treated similarly but unfortunately no correlation was apparent unless sterically hindered allenes were rejected from analysis. This failure in relating steric effects to the rate of addition suggest that both Polar and Steric effects are involved in the rate determining transition state.

Because of the large number of data available, the allenes were grouped into a series of subsets as indicated in TABLE 20.

TABLE 20

$R^1R^2C{=}C{=}CR^3R^4$

SUBSET I

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	H	1.0
H	H	H	Me	5.31×10
H	H	Me	Me	1.34×10^3
Me	H	Me	H	2.39×10^3
Me	H	Me	Me	2.65×10^4
Me	Me	Me	Me	6.56×10^5

SUBSET II

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	H	1.0
H	H	H	Et	6.42 X 10
Et	H	Et	H	8.19×10^2
Et	H	Et	Et	1.51×10^3

SUBSET III

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	H	1.0
H	H	H	iPr	1.43 X 10
iPr	H	iPr	H	2.27×10^2
iPr	H	iPr	iPr	8.5
iPr	iPr	iPr	iPr	1.13

SUBSET IV

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	tBu	1.0
H	H	Me	tBu	3.56 X 10
Me	H	H	tBu	5.8 X 10
Me	H	Me	tBu	2.63×10^2
Me	Me	H	tBu	2.61×10^2

SUBSET V

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	Et	1.0
H	H	Me	Et	5.28×10^2
Me	H	H	Et	3.41×10
Me	Me	H	Et	2.10×10^2
Me	H	Me	Et	4.19×10

SUBSET VI

R^1	R^2	R^3	R^4	k_{rel}
Me	Et	iPr	tBu	1.0
Me	iPr	Et	tBu	1.94×10^2
Me	tBu	Et	iPr	2.8×10

b- POLAR vs STERIC EFFECTS :

The effect of adding Methyl groups to the allene unit results in a rate enhancement. Similar trends are observed for Ethyl groups. (SUBSET II).

In the case of Ethyl groups, the effect is not as impressive due to a small participation from steric effects neutralizing electron donating ability effects.

If one goes to the next homologues (isopropyl and tertbutyl groups), steric effects take over from polar effects as depicted in SUBSET III.

The effect of one single substituent is almost one of polar nature as reflected in SUBSET IV.

However, the stereochemical location of a second substituent will lead to a significant variation in the rate of addition. This is best pictured in SUBSET V.

ALLENE	k_{rel}
$H_2C=C=CH_2$	1.00
$H_2C=C=CMeEt$	33,900
$MeCH=C=CHEt$	2190
$EtCH=C=CMe_2$	13,500
$MeCH=C=CMeEt$	2,690

This can be interpreted in terms of competition between both Steric + Polar effects inherent to the Ethyl moiety (compare the effect of a Methyl group in SUBSET I and IV where only polar factors are present).

It is apparent from SUBSET II that the electron donating ability of an Ethyl group is inferior to that of a Methyl. One can therefore imagine that the observed decrease in reactivity is due to one or both of two factors :

1- Increase in steric effects in an Ethyl group.

2- Decrease in electron donating ability.

The fact that the effect of an Ethyl group contains contributions from steric factors is revealed in TABLE 21.

TABLE 21

$R^1R^2C{=}{=}C{=}{=}CR^3R^4$

R^1	R^2	R^3	R^4	k_{rel}	k_{Me}/k_{Et}
Me	H	Me	H	2390	2.9
Et	H	Et	H	819	
Me	H	iPr	H	414	1.7
Et	H	iPr	H	243	
Me	H	tBu	H	41.6	1.5
Et	H	tBu	H	28.3	
Me	H	Me	Me	26500	2.0
Et	H	Me	Me	13500	5.1
Et	H	Me	Et	2640	1.7
Et	H	Et	Et	1510	
iPr	H	Me	Et	1760	4.7
iPr	H	Et	Et	377	
tBu	H	Me	Et	71.7	2.7
tBu	H	Et	Et	26.4	
Me	H	Me	Et	2690	1.0
Et	H	Me	Et	2640	
Me	H	Me	tBu	188	1.1
Et	H	Me	tBu	169	
iPr	H	Me	tBu	39.4	15.1
iPr	H	Et	tBu	2.61	
Me	iPr	Me	tBu	21.9	1.2
Me	iPr	Et	tBu	18.8	

The best indication of a steric effect is seen upon comparing the 1,1-diethyl allenes with the 1,1-pentamethylene allenes.

			k_{rel}
Et	H	Et Et	1510
Et	H	$-(CH_2)_5-$	16040
iPr	H	Et Et	377
iPr	H	$-(CH_2)_5-$	6640
tBu	H	Et Et	26.4
tBu	H	$-(CH_2)_5-$	818

Pentamethylene allenes react a lot faster due to conformation restrictions. In the case of an Ethyl group, the retardation is often quite small. However, if one considers the next higher homologue (i.e., iPr) where steric effects are taking over polar effects, net retardations are apparent. Compare for example 15-16, 26-27, 41-42, 58-59, and 61-62. Exceptions are allenes 39 and 43.

c- SUBSTITUTION PATTERN :

If one recalls FIGURE 9 one can see that 1,3-dimethyl allene and 1,1-dimethyl allene have a similar rate constant indicating that where polar effects dominate, there is no preferred substitution pattern. On the other hand, if substituents are present for which steric factors play a dominant role, the rate of addition is found to be very dependent on the substitution pattern. See for example SUBSET VI where the three allenes contain the same substituents arranged differently with respect to each other.

The least reactive allene appears to be that which places two bulky substituents geminal to each other.

Similar variations in the rate of addition are observed for the following allenes : 25-45, 32-42, 23-40, 22-36, 39-46 and 43-47

d- PhSeCl vs PhSCl :

TABLE 22 allows a comparison between the rates of addition of PhSeCl and PhSCl to 61 allenes. In both cases, an increase in electron donating power results in an increase in the rate of addition. The point of most importance is the fact that PhSeCl is more sensitive to steric effects than is PhSCl. (Compare k_{rel}).

We have seen that in the case of PhSeCl the case of PhSeCl the turnover from polar to steric effects is at Ethyl. For PhSCl, a similar turnover is observed somewhere between Ethyl and Isopropyl.

It has been reported that Selenium and Sulfur compounds often exhibit essentially identical bond lengths[71] which suggest that the difference is not due to a difference in size of the electrophiles. However, if the transition states are of the same size and shape, this would imply that both systems should behave the same way with respect to steric effects. TABLE 22 reveals however that this is not the case and as mentioned previously (PART III) the transition states of the rate determining steps are different for the addition of PhSeCl and PhSCl.

Similar results have been reported with respect to the analogous alkenes[72]. This however does not shine any light on what the difference is between these two transition states. Different possibilities are :

- Different geometry and/or charge distribution.
- Degree of bond-making or bond-breaking in transition states of similar structures.

TABLE 22

A comparison of the specific and relative rate constants for the reactions of benzeneselenenyl chloride and benzenesulphenyl chloride with 61 alkyl substituted allenes in methylene chloride solution at 24.5°C

$R^1R^2C{=}C{=}CR^3R^4$

Entry	Allene				C_6H_5SeCl	C_6H_5SCl	C_6H_5SeCl	C_6H_5SCl
	R^1	R^2	R^3	R^4	k_2 (dm^3 mol^{-1} s^{-1})	k_2	k_{rel}	k_{rel}
1	H	H	H	H	8.23	0.698	1.00	1.00
2	H	H	H	CH_3	437.	12.9	53.1	18.5
3	H	H	H	C_2H_5	528.	12.4	64.2	17.8
4	H	H	H	i-C_3H_7	118.	16.0	14.3	22.9
5	H	H	H	i-$C_4H_9CH_2$	124.	6.1	15.1	8.7
6	H	H	H	t-C_4H_9	5.9	4.1	0.72	5.9
7	H	H	CH_3	CH_3	11000	195.	1340	279.
8	H	H	CH_3	C_2H_5	279000	850.	33900	1220
9	H	H	CH_3	i-C_4H_9	2880	54.	350.	77.
10	H	H	CH_3	t-C_4H_9	210.	13.	25.5	19.
11	H	H	CH_3	t-$C_4H_9CH_2$	1600	32.	194.	46.
12	CH_3	H	CH_3	H	19700	151.	2390	216.
13	C_2H_5	H	C_2H_5	H	6740	126.	819.	181.
14	i-C_3H_7	H	i-C_3H_7	H	1870	82.	227.	117.
15	CH_3	H	C_2H_5	H	18000	165.	2190	236.
16	CH_3	H	i-C_3H_7	H	3410	125.	414.	179.
17	CH_3	H	t-C_4H_9	H	342.	104.	41.6	149.
18	C_2H_5	H	i-C_3H_7	H	2000	99.8	243.	143.
19	C_2H_5	H	t-C_4H_9	H	233.	106.	28.3	152.
20	i-C_3H_7	H	t-C_4H_9	H	62.0	56.0	7.5	80.2

21	CH_3	H	CH_3	CH_3	218000	1040.	26500	1490
22	C_2H_5	H	CH_3	CH_3	111000	635.	13500	910.
23	i-C_3H_7	H	CH_3	CH_3	36400	1050	4420	1504
24	i-C_4H_9	H	CH_3	CH_3	27600	565.	3350	809.
25	t-C_4H_9	H	CH_3	CH_3	1540	600.	187.	860.
26	C_2H_5	H	C_2H_5	C_2H_5	12400	250.	1540	358.
27	i-C_3H_7	H	C_2H_5	C_2H_5	3100	130.	377.	186.
28	t-C_4H_9	H	C_2H_5	C_2H_5	217.	141.	26.4	202.
29	C_2H_5	H	-$(CH_2)_5$-		132000	771.	16040	1104
30	i-C_3H_7	H	-$(CH_2)_5$-		54600	930.	6640	1330
31	t-C_4H_9	H	-$(CH_2)_5$-		6730	941.	818.	1350
32	CH_3	H	i-C_3H_7	i-C_3H_7	260.	11.0	31.6	15.8
33	C_2H_5	H	i-C_3H_7	i-C_3H_7	109.	11.4	13.2	16.3
34	i-C_3H_7	H	i-C_3H_7	i-C_3H_7	70.	36.0	8.5	51.6
35	t-C_4H_9	H	i-C_3H_7	i-C_3H_7	60.7	4.05	7.38	5.8
36	CH_3	H	CH_3	C_2H_5	22100	400.	2690	573.
37	C_2H_5	H	CH_3	C_2H_5	21700	690.	2640	989.
38	i-C_3H_7	H	CH_3	C_2H_5	14500	400.	1760	573.
39	t-C_4H_9	H	CH_3	C_2H_5	590.	250.	71.7	358.
40	CH_3	H	CH_3	i-C_3H_7	18000	280.	2190	401.
41	C_2H_5	H	CH_3	i-C_3H_7	22900	323.	2780	463.
42	i-C_3H_7	H	CH_3	i-C_3H_7	4690	204.	570.	292.
43	t-C_4H_9	H	CH_3	i-C_3H_7	2100	174.	255.	249.
44	c-C_6H_{11}	H	CH_3	i-C_3H_7	6180	233.	751.	334.
45	CH_3	H	CH_3	t-C_4H_9	1550	102.	188.	146.
46	C_2H_5	H	CH_3	t-C_4H_9	1390	124.	169.	178.
47	i-C_3H_7	H	CH_3	t-C_4H_9	324.	115.	39.4	165.

48	$t\text{-}C_4H_9$	H	CH_3	$t\text{-}C_4H_9$	4.55	39.1	0.553	56.0
49	$c\text{-}C_6H_{11}$	H	CH_3	$t\text{-}C_4H_9$	480.	233.	58.3	334.
50	$i\text{-}C_3H_7$	H	C_2H_5	$t\text{-}C_4H_9$	21.5	19.4	2.61	27.8
51	C_2H_5	H	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	33.2	7.0	4.03	10.0
52	$i\text{-}C_3H_7$	H	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	15.7	4.0	1.91	5.7
53	CH_3	CH_3	CH_3	CH_3	5400000	2360	656000	3380
54	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	9.3	53.0	1.13	75.9
55	CH_3	C_2H_5	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	0.80	0.80	0.097	1.15
56	CH_3	$i\text{-}C_3H_7$	CH_3	$t\text{-}C_4H_9$	180.	140.	21.9	200.
57	CH_3	$i\text{-}C_3H_7$	C_2H_5	$t\text{-}C_4H_9$	155.	12.5	18.8	17.2
58	CH_3	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	8.7,	3.1	1.06	4.4
59	CH_3	$t\text{-}C_4H_9$	C_2H_5	$i\text{-}C_3H_7$	22.0	120.	2.67	172.
60	CH_3	$t\text{-}C_4H_9$	C_2H_5	$t\text{-}C_4H_9$	2.40	1.85	0.292	2.65
61	CH_3	$t\text{-}C_4H_9$	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$	0.16	1.46	0.0194	2.09

The last possibility would be significant if an S_N2 type of approach of allene and electrophile is involved. This would result in more bond-making in the rate determining transition state of PhSeCl relative to that of PhSCl.

The larger steric dependence of PhSeCl can be rationalized in terms of an earlier rate determining transition state which would result in a lower Activation Energy and a faster rate of reaction relative to PhSCl. However, PhSeCl being more reactive, it should also be less selective. This is not observed as PhSeCl has a greater ability to select between the allenes then PhSCl does. As both reactions were run under identical experimental conditions, the difference would tend to be accounted for by two transition states differing in Geometry and/or charge distribution.

e- CONCLUSION :

In accord with the observations discussed above, a tentitative mechanism can be presented in which the rate determining transition state involves the formation of an Alkylideneepiselenurane species.

PART V

ELECTROPHILIC ADDITION OF BENZENESULFENYL CHLORIDE TO ALKYL SUBSTITUTED ALLENES; A KINETIC INVESTIGATION.

1- INTRODUCTION :

In order to elucidate the nature of the transition state intermediates involved in the addition of PhSCl to allenes, we have investigated the rate of addition of the sulfenyl chloride to 61 allenes. The rate of addition in anhydrous dichloromethane at 24.5°C was measured by means of the stopped-flow technique. The rate of disappearance of PhSCl was followed by measuring the decrease in its absorption at 392nm. In all cases we observed overall 2nd order kinetic behavior, first order in allene and first order in the sulfenyl chloride.
The rate of addition is given by the expression:

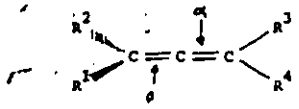
$$-\frac{d\,[PhSCl]}{dt} = k_2\,[PhSCl]\,[Allene]$$

2- RESULTS :

The rate data for the addition of PhSCl to alkyl substituted allenes is given in TABLE 27.

TABLE 27

THE KINETICALLY CONTROLLED PRODUCT DISTRIBUTIONS AND SPECIFIC RATE CONSTANTS, k_2 ($dm^3\ mol^{-1}\ s^{-1}$), FOR THE REACTIONS OF 4-CHLOROBENZENESULFENYL CHLORIDE WITH ALKYL SUBSTITUTED ALLENES IN CH_2Cl_2 SOLUTION AT 24.5°C.



	R^1	R^2	R^3	R^4	α:β	α (E:Z)	β (E:Z)	k_2	$k_{rel.}$
1	H	H	H	H	50:50			0.698	1.00
2	H	H	H	Me	73:27		71:29	12.9	18.5
3	H	H	H	Et	70:30		76:23	12.4	17.8
4	H	H	H	iPr	79:21		71:29	16.0	22.9
5	H	H	H	iBu	65:35		54:46	16.3	23.3
6	H	H	H	$iBuCH_2$	65:35		51:49	6.1	8.74
7	H	H	H	tBu	79:21		100:00	4.1	5.87
8	H	H	Me	Me	86:14			195.0	279.0
9	H	H	Me	Et				850.0	1220.0
10	H	H	Me	nPr	76:24		92:08		
11	H	H	Me	iPr	100:00				
12	H	H	Me	iBu	68:32		92:08	54.0	77.4
13	H	H	Me	sBu	85:15		100:00		
14	H	H	Me	tBu	100:00			13.0	18.6
15	H	H	Me	$tBuCH_2$	84:16		83:17	32.0	45.8
16	Me	H	Me	H	50:50	54:46	55:45	151.0	216.0
17	Et	H	Et	H	50:50	72:28	72:28	126.0	181.0
18	iPr	H	iPr	H	50:50	80:20	80:20	82.0	117.0
19	tBu	H	tBu	H	50:50	97:03	97:03		
20	Me	H	Et	H	53:47	56:44	70:30	165.0	236.0
21	Me	H	iPr	H	55:45	57:43	80:20	125.0	179.0
22	Me	H	tBu	H	59:41	58:42	88:12	104.0	149.0
23	Et	H	iPr	H	50:50	72:28	84:16	99.8	143.0
24	Et	H	tBu	H	49:51	73:27	100:00	106.0	152.0
25	iPr	H	tBu	H	50:50	70:30	90:10	56.0	80.2
26	Me	H	Me	Me	59:41	59:41		1040.0	1490.0
27	Et	H	Me	Me	58:42	40:60		635.0	910.0
28	iPr	H	Me	Me	52:48	62:38		1050.0	1504.0
29	iBu	H	Me	Me	76:24	58:42		565.0	808.0
30	tBu	H	Me	Me	100:00	57:43		600.0	860.0
31	Et	H	Et	Et	81:19	04:16		250.0	358.0
32	iPr	H	Et	Et	83:17	96:04		130.0	186.0
33	tBu	H	Et	Et	84:16	82:18		141.0	202.0
34	Et	H	$-(CH_2)_5-$		62:38	50:50		771.0	1104.0
35	iPr	H	$-(CH_2)_5-$		70:30	65:45		930.0	1330.0
36	tBu	H	$-(CH_2)_5-$		79:21	80:20		941.0	1350.0

TABLE 27 (continued)

37	Me	H	iPr	iPr	38:62	100:00			11.0	15.8
38	Et	H	iPr	iPr	34:66	88:12			11.4	16.3
39	iPr	H	iPr	iPr	47:53	89:11			36.0	51.6
40	tBu	H	iPr	iPr	88:12	44:56			4.1	5.8
41	iPr	H	tBu	tBu	100:00	100:00				
42	Me	H	Me	Et	100:00	53:47			400.0	573.0
43	Et	H	Me	Et	63:37	63:37		100:00	690.0	989.0
44	iPr	H	Me	Et	79:21	100:00		100:00	400.0	573.0
45	tBu	H	Me	Et	100:00	77:23			250.0	358.0
46	Me	H	Me	iPr	85:15	74:26		100:00	280.0	401.0
47	Et	H	Me	iPr	100:00	55:45			323.0	463.0
48	iPr	H	Me	iPr	90:10	69:31		100:00	204.0	292.0
49	tBu	H	Me	iPr	83:17	59:41		100:00	174.0	249.0
50	C_6H_{11}	H	Me	iPr	100:00	69:31			233.0	334.0
51	Me	H	Me	tBu	100:00	71:29			102.0	146.0
52	Et	H	Me	tBu	65:35	80:20		100:00	124.0	178.0
53	iPr	H	Me	tBu	63:27	86:14		100:00	115.0	165.0
54	tBu	H	Me	tBu	100:00	94:06			39.1	56.0
55	C_6H_{11}	H	Me	tBu	81:19	90:10		100:00	233.0	334.0
56	iPr	H	Et	tBu	100:00	86:14			19.4	27.8
57	Et	H	iPr	tBu	77:23	70:30		65:35	7.0	10.6
58	iPr	H	iPr	tBu	85:15	80:20		68:32	4.0	5.7
59	tBu	H	iPr	tBu	100:00	100:00				
60	Me	Me	Me	Me	50:50				2360.0	3380.0
61	iPr	iPr	iPr	iPr	50:50				53.0	75.0
62	Me	Et	iPr	tBu	100:00				0.8	1.2
63	Me	Et	tBu	tBu	100:00					
64	Me	iPr	Me	tBu	100:00	100:00			140.0	200.0
65	Me	iPr	Et	tBu	100:00	100:00			12.5	17.0
66	Me	iPr	iPr	tBu	85:15				3.1	4.4
67	Me	iPr	tBu	tBu	100:00					
68	Me	tBu	Et	iPr	30:70				120.0	171.0
69	Me	tBu	Et	tBu	00:100				1.9	2.6
70	Me	tBu	iPr	tBu	10:90				1.5	2.0

Rate constants cover a range of 2.3 X 10^3 in reactivity. The analogous reactions with PhSeCl covered a range of 3.3 X 10^7. It appears that the rate of addition of PhSCl is very much slower than for the corresponding Selenium version. However, increased substitution of the allene moiety still increases the rate of addition and therefore demonstrates the electrophilic character of the reaction (In this respect, PhSeCl and PhSCl give similar results).

Rate retardations are observed in the case of sterically hindered allenes indicating that steric effects once again play an important role in the rate limiting transition state.

In order to evaluate the relative importance of both polar and steric effects, an extended TAFT correlation[69] was attempted with all 61 allenes. As in the case of PhSeCl, no correlation was obtained demonstrating the importance of steric effects.

The presence of a single bulky group (such as tert-Butyl) does not appear to affect the electron donating ability of a methyl substituent to a great extent.

$R^1R^2C{=}C{=}CR^3R^4$

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	tBu	1.00
H	H	Me	tBu	3.2
Me	H	H	tBu	25.4
Me	H	Me	tBu	24.9
Me	Me	H	tBu	146.5

However, the location of a second alkyl substituent is of prime importance.

For example, consider the following series:

$R^1R^2C{=}C{=}CR^3R^4$

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	Et	1.0
H	H	Me	Et	68.5
Me	H	H	Et	13.3
Me	Me	H	Et	51.1
Me	H	Me	Et	32.2

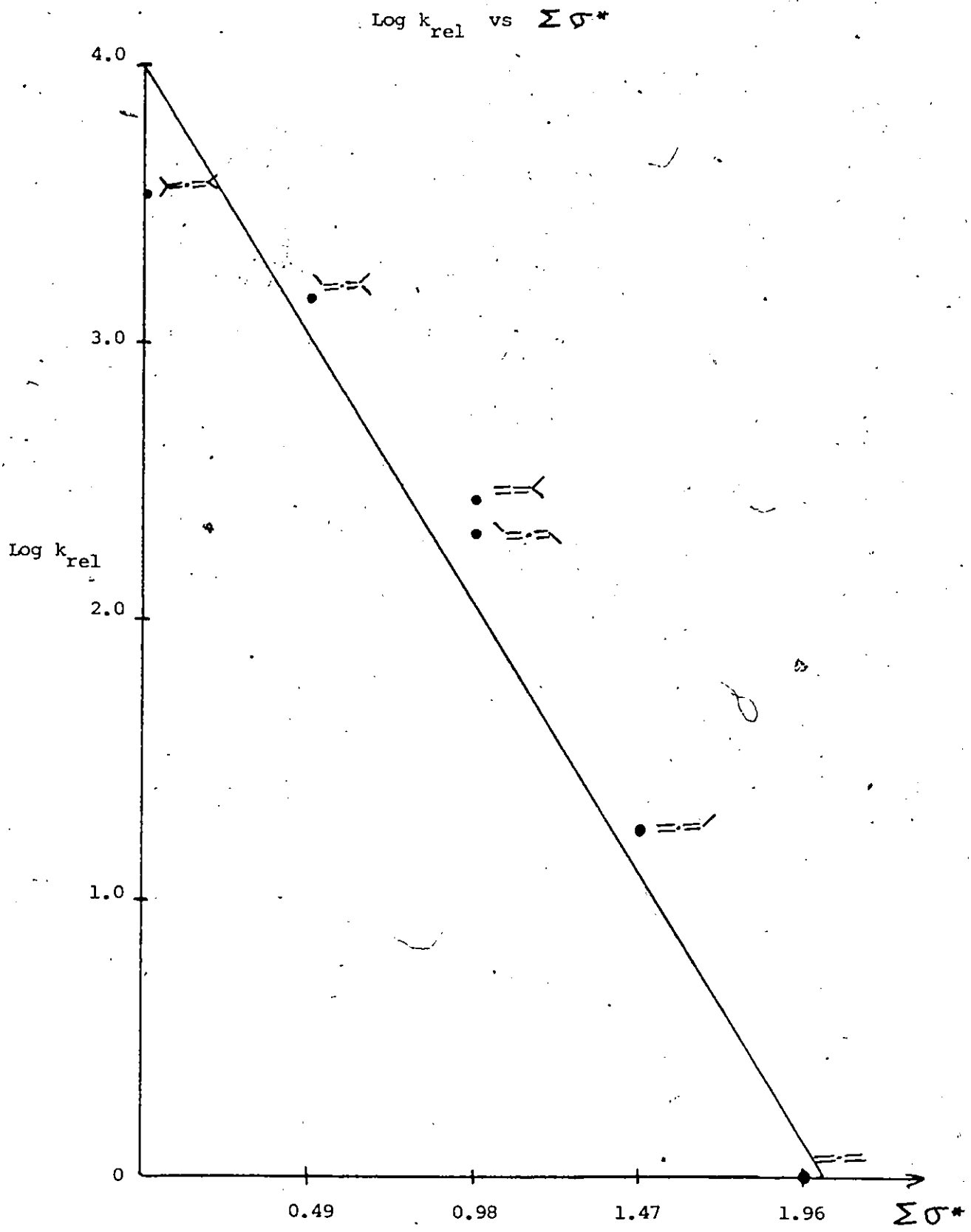
The effect is more pronounced in the case of isopropyl allenes:

$R^1R^2C{=}C{=}CR^3R^4$

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	iPr	1.0
Me	H	H	iPr	7.8
Me	H	Me	iPr	26.0
Me	Me	H	iPr	65.7

The magnitude of the rate constant depends on the stereochemical location of the substituents (similar results were obtained in the case of PhSeCl). From a graph of Log k_{rel} vs $\Sigma\sigma^*$ for Methyl-substituted allenes (FIGURE 11), it is apparent that there is very little, if any, steric effects involved.

FIGURE 11


Log k_{rel} vs $\Sigma\sigma^*$
4.0
3.0
2.0
1.0
0
Log k_{rel}
0.49
0.98
1.47
1.96
$\Sigma\sigma^*$

It would therefore appear, that the anomalous behavior of isopropyl allenes (and to a lesser extent, Ethyl allenes), as demonstrated above is due to a competition between steric and polar effects rather than a new steric effect on behalf of the methyl group. This was also observed in the case of PhSeCl where steric effects started to appear in the case of Ethyl allenes. In the sulfur version the unset lies somewhere between Ethyl and Isopropyl.

That the isopropyl group gives rise to a steric effect can be demonstrated by considering the following examples:

(Ethyl and Isopropyl groups have a smaller electron donating power then a Methyl substituent)

$$R^1R^2C{=}C{=}CR^3R^4$$

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	H	1.0
H	H	H	Me	18.5
H	H	H	Et	17.8
H	H	H	iPr	22.9
H	H	Me	Me	279.0
Me	H	H	Me	216.3
Et	H	H	Et	180.5
iPr	H	H	iPr	117.5
Me	Me	H	Me	1490.0
Et	Et	H	Et	358.0
iPr	iPr	H	iPr	51.6
Me	Me	Me	Me	3381.0
iPr	iPr	iPr	iPr	76.0

As previously noted in the case of PhSeCl, the decrease in reactivity is due to a steric effect as opposed to a reversal in the "normal electrostatic order". The substitution of both Methyl groups by Ethyls in 2,3-pentadiene leads to a 1.2 fold decrease in reactivity. If one goes to 1,3-diisopropyl allene, the factor is now 1.8

$$R^1R^2C{=}C{=}CR^3R^4$$

R^1	R^2	R^3	R^4	k_{rel}
H	H	H	H	1.0
Me	H	Me	H	216.3
Et	H	Et	H	180.5
iPr	H	iPr	H	117.5

Substitution of only one Methyl group by Ethyl or isoPropyl has only a marginal effect.

Me	H	Me	H	216.0
Me	H	Et	H	236.0
Me	H	iPr	H	179.0

Similar decreases in reactivity upon substituting Ethyl or isoPropyl for Methyl are observed in comparing the following sets of entries:

21-23-18	42-43-44
22-24-25	51-52-53
26-27-28	53-56-58
27-43-47	64-65-66

In contrast to the sometime marginal effect of substituting Ethyl for Methyl, the increased bulk of an isoPropyl group is seen to lead to large rate retardations. The rate constant is very dependent on the substitution pattern as far as steric factors are concerned. Compare for example the following allenes that contain the same substituents in a different spatial arrangement:

$$R^1R^2C{=}C{=}CR^3R^4$$

R^1	R^2	R^3	R^4	k_2
Me	Et	iPr	tBu	0.8
Me	iPr	Et	tBu	17.0
Me	tBu	Et	iPr	171.0

The least reactive allene is the one having two bulky substituents geminal to each other (This was also observed for PhSeCl).

If one compares the Sulfur and Selenium versions one comes to the conclusion that larger steric effects exist in the case of the Selenyl chloride. (See TABLE 22 in PART IV). The origin of this has been discussed in PART IV. Most importantly we have come to the conclusion that the rate determining transition states for the addition of PhSeCl and PhSCl to alkyl-substituted allenes are different. For the Selenium version we favored an attack sequence wherein the electrophile and the allene approach each other so as to form an alkylideneepiselenurane-like species during the rate determining step of the reaction.

This does not appear to be the case for the Sulfur version. In order to get more insight into the nature of the rate determining transition state for the addition of PhSCl to allenes, we have investigated the rate of addition of various sulfenyl chlorides to 1,3- and 1,1-dimethyl allenes. Results are summarized in TABLE 28.

TABLE 28

RATES OF ADDITION OF VARIOUS ARENESULFENYL CHLORIDES TO 1,3- AND 1,1-DIMETHYL ALLENES IN CH_2Cl_2 AT 24.5°C

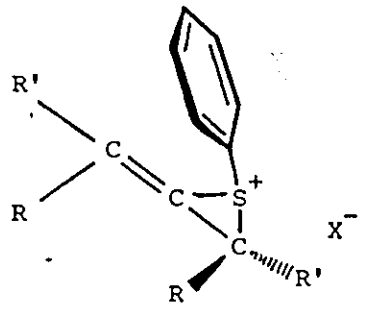
ALLENES	ARENESULFENYL CHLORIDES								
	PhSCl	2,5-Cl_2	3,4-Cl_2	4-Cl	4-Me	4-F	4-Br	4-OMe	2,4,6-Me_3
1,1-dimethyl	200	150	200	170	150	170	220	120	155
1,3-dimethyl	150	100	200	150	130	150	220	90	37

On changing the substituents on the sulfenyl chloride benzene ring, we vary the extent of charge development on the Sulfur atom. From the rate data it is clear that there is only very little effect on the value of the rate constant (a plot of Log k vs σ^* is linear with a ρ value very close to unity or slightly positive).

3- MECHANISTIC IMPLICATIONS :

We have postulated that the rate determining transition states for areneselenation and arenesulfenation differ in geometry and/or charge distribution. Data available at present strongly suggests that the rate determining step in the arenesulfenation reaction follows the S_N2 type attack.

In this case, the allenic π -orbitals are considered as nucleophiles and the halogen atom as the leaving group. Upon completion of bond breaking and bond formation, one obtains a species of the type depicted below:



This scenario is important only if the entering and leaving groups can form a colinear arangement with the Sulfur atom.

PART VI

ANALYSIS OF PRODUCT DISTRIBUTIONS FOR THE REACTIONS OF PhSeCl AND 4-Cl-C_6H_4SCl WITH ALKYL SUBSTITUTED ALLENES IN DICHLOROMETHANE SOLUTIONS AT R.T.

1- INTRODUCTION :

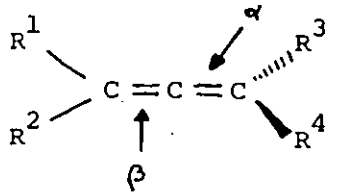
The kinetically controlled product distributions for the reactions of benzeneselenyl chloride and 4-chlorobenzenesulfenyl chloride with 70 alkyl-substituted allenes in dichloromethane solutions are given in TABLE 27 and 29. As previously mentioned, PhSeCl is more reactive then the Sulfur analogue. We would therefore expect a decrease in selectivity of the selenyl chloride. This was however not the case and a consequence of this observation is the existence of two distinct rate determining transition states for areneselenation and arene-sulfenation of allenes.

We shall now see that the product determining transition states must also differ to some extent as the product distributions are very different.

We have already seen that in the case of 1,3-disubstituted allenes, the E-isomer was formed preferentially for arenesulfenation whereas Z-alkenes were formed in the Selenium case . On observation of TABLE 27 little selectivity is found in the case of PhSCl and 1,3-disubstituted allenes with respect to which mutually perpendicular π-bond system of the allene is attacked. For the Selenium case , the analogous allenes show a net preference of attack for the double bond carrying the most electron donating and sterically bulky substituent.

TABLE 29

The kinetically controlled product distributions for the reactions of benzeneselenenyl chloride with 70 alkyl substituted allenes in methylene chloride solution at 23-25°C.



Entry	Allene				Ratio of Isomers		
	R^1	R^2	R^3	R^4	α : β	α(E:Z)	β(E:Z)
1	H	H	H	H	50:50		
2	H	H	H	CH_3	27:73		29:71
3	H	H	H	C_2H_5	30:70		24:76
4	H	H	H	i-C_3H_7	18:82		38:62
5	H	H	H	i-C_4H_9	12:88		33:67
6	H	H	H	i-$C_4H_9CH_2$	26:74		44:56
7	H	H	H	t-C_4H_9	51:49		37:63
8	H	H	CH_3	CH_3	13:87		
9	H	H	CH_3	C_2H_5	10:90		59:41
10	H	H	CH_3	n-C_3H_7	9:91		58:42
11	H	H	CH_3	i-C_3H_7	10:90		60:40
12	H	H	CH_3	i-C_4H_9	0:100		59:41
13	H	H	CH_3	s-C_4H_9	8:92		61:39
14	H	H	CH_3	t-C_4H_9	60:40		75:25
15	H	H	CH_3	t-$C_4H_9CH_2$	0:100		75:25
16	CH_3	H	CH_3	H	50:50	26:74	26:74
17	C_2H_5	H	C_2H_5	H	50:50	40:60	40:60
18	i-C_3H_7	H	i-C_3H_7	H	50:50	36:64	36:64
19	t-C_4H_9	H	t-C_4H_9	H	50:50	0:100	0:100
20	CH_3	H	C_2H_5	H	33:67	27:73	30:70
21	CH_3	H	i-C_3H_7	H	56:44	30:70	43:57
22	CH_3	H	t-C_4H_9	H	76:24	9:91	39:61
23	C_2H_5	H	i-C_3H_7	H	44:56	27:73	46:54
24	C_2H_5	H	t-C_4H_9	H	80:20	12:88	27:73
25	i-C_3H_7	H	t-C_4H_9	H	75:25	11:89	16:84

Entry	Allene				Ratio of Isomers		
	R^1	R^2	R^3	R^4	α : β	α(E:Z)	β(E:Z)
26	CH_3	H	CH_3	CH_3	11:89	23:77	
27	C_2H_5	H	CH_3	CH_3	18:82	0:100	
28	i-C_3H_7	H	CH_3	CH_3	13:87	49:51	
29	i-C_4H_9	H	CH_3	CH_3	21:79	19:81	
30	t-C_4H_9	H	CH_3	CH_3	31:69	100:0	
31	C_2H_5	H	C_2H_5	C_2H_5	29:71	48:52	
32	i-C_3H_7	H	C_2H_5	C_2H_5	40:60	68:32	
33	t-C_4H_9	H	C_2H_5	C_2H_5	100:0	85:15	
34	C_2H_5	H	-$(CH_2)_5$-		30:70	60:40	
35	i-C_3H_7	H	-$(CH_2)_5$-		51:49	71:29	
36	t-C_4H_9	H	-$(CH_2)_5$-		44:56	100:0	
37	CH_3	H	i-C_3H_7	i-C_3H_7	100:0	37:63	
38	C_2H_5	H	i-C_3H_7	i-C_3H_7	100:0	25:75	
39	i-C_3H_7	H	i-C_3H_7	i-C_3H_7	62:38	53:47	
40	t-C_4H_9	H	i-C_3H_7	i-C_3H_7	47:53	100:0	
41	i-C_3H_7	H	t-C_4H_9	t-C_4H_9	100:0	100:0	
42	CH_3	H	CH_3	C_2H_5	35:65	29:71	55:45
43	C_2H_5	H	CH_3	C_2H_5	11:89	18:82	55:45
44	i-C_3H_7	H	CH_3	C_2H_5	15:85	47:63	57:43
45	t-C_4H_9	H	CH_3	C_2H_5	50:50	78:22	47:53
46	CH_3	H	CH_3	i-C_3H_7	30:70	33:67	55:45
47	C_2H_5	H	CH_3	i-C_3H_7	30:70	23:77	66:34
48	i-C_3H_7	H	CH_3	i-C_3H_7	33:67	24:76	60:40
49	t-C_4H_9	H	CH_3	i-C_3H_7	61:39	0:100	41:59
50	c-C_6H_{11}	H	CH_3	i-C_3H_7	39:61	21:79	56:44
51	CH_3	H	CH_3	t-C_4H_9	100:0	30:70	
52	C_2H_5	H	CH_3	t-C_4H_9	100:0	53:47	
53	i-C_3H_7	H	CH_3	t-C_4H_9	100:0	54:46	
54	t-C_4H_9	H	CH_3	t-C_4H_9	100:0	46:54	
55	c-C_6H_{11}	H	CH_3	t-C_4H_9	100:0	41:59	
56	i-C_3H_7	H	C_2H_5	t-C_4H_9	100:0	65:35	

Entry	Allene				Ratio of Isomers		
	R^1	R^2	R^3	R^4	α : β	α(E:Z)	β(E:Z)
57	C_2H_5	H	i-C_3H_7	t-C_4H_9	100:0	62:38	
58	i-C_3H_7	H	i-C_3H_7	t-C_4H_9	100:0	67:33	
59	t-C_4H_9	H	i-C_3H_7	t-C_4H_9	100:0	70:30	
60	CH_3	CH_3	CH_3	CH_3	50:50		
61	i-C_3H_7	i-C_3H_7	i-C_3H_7	i-C_3H_7	50:50		
62	CH_3	C_2H_5	i-C_3H_7	t-C_4H_9	60:40	50:50	60:40
63	CH_3	C_2H_5	t-C_4H_9	t-C_4H_9	75:25	55:45	
64	CH_3	i-C_3H_7	CH_3	t-C_4H_9	100:0	50:50	
65	CH_3	i-C_3H_7	C_2H_5	t-C_4H_9	100:0	50:50	
66	CH_3	i-C_3H_7	i-C_3H_7	t-C_4H_9	80:20	50:50	50:50
67	CH_3	i-C_3H_7	t-C_4H_9	t-C_4H_9	85:15	53:47	
68	CH_3	t-C_4H_9	C_2H_5	i-C_3H_7	0:100		52:48
69	CH_3	t-C_4H_9	C_2H_5	t-C_4H_9	25:75	75:25	75:25
70	CH_3	t-C_4H_9	i-C_3H_7	t-C_4H_9	33:67	75:25	80:20

2- TERMINAL ALLENES :

a- PhSeCl : There is a net tendency for the Selenium reagent to attack the unsubstituted side of terminal allenes. As the substituents become bulkier this preference increases (compare entries 2-6). The preference is also increased on going from mono- to 1,1-disubstituted allenes (entries 2 and 8). Reversed behavior are observed in the case of allenes carrying tert-Butyl groups (7 and 14). The anomalous behavior of tert-Butyl substituted allenes has already been mentioned.

If one considers the E : Z ratios for attack on the unsubstituted side (β) one notices interesting reversals:

In the case of monosubstituted allenes, the Z-isomer is formed preferentially as previously observed in the case of 1,3-disubstituted allenes. However, the E-alkenes are favored over the Z in the case of 1,1-disubstituted allenes.

In both cases, the steric bulk of the substituents increases the proportion of the E-isomer.

b- PhSCl : In all cases (2-15) attack of the electrophile occurs preferentially on the most substituted double bond. The only factor affecting the value of the α : β ratio is the nature of the geminal substituents. As one goes from mono- to 1,1-disubstituted allenes there is an increase in selectivity.

Substitution of a Methyl group for a Hydrogen brings about a 20% increase in the selectivity (compare the following pairs of allenes: 2-8, 4-11, 7-14).

With respect to the E : Z ratios, PhSCl follows trends previously described for 1,3-disubstituted allenes. In all cases, the E-isomer is favored over the Z. In the case of 1,1-disubstituted allenes, there is a very large preference for the former (larger than 83%).

c- PhSeCl vs PhSCl : The selectivity of the Selenium reagent is greater than that of the sulfenyl chloride. In most cases PhSeCl has a preference larger than 75% for the unsubstituted double bond whereas Sulfur is less descriminating. The selectivity of PhSeCl increases with substitution on the double bond remote from the sight of attack. In the case of monosubstituted allenes the selectivity is of the order of 70-88%. For 1,1-disubstituted allenes it increases to 87-100%. Selectivity also increases with electron donating ability of substituents.

$CH_2=C=CMeR$

R	% attack on terminal double bond
Me	87
Et	90
iPr	90
iBu	100
tBu	40

A similar trend is observed in the monosubstituted allene series. In the case of PhSCl, there is no apparent correlation between the sight of attack and the allene structure.

3- 1,3-DISUBSTITUTED ALLENES :

These cases have already been discussed in PART III and IV and in our first paper[56] for the PhSeCl and PhSCl versions respectively.

4- TRISUBSTITUTED ALLENES :

Note that in the case of 1,1-, tri- and tetra-substituted allenes, elimination of HCl from the adducts (to give dienes), was observed and often obscured the analysis.

a- PhSeCl : When the two geminal groups are not bulky, there is a net preference for attack on the monosubstituted double bond. This is observed in the following cases:

$$R^1CH=C=CR^2R^3$$

R^1	R^2	R^3	Entries
Me-tBu	Me	Me	26-30
Et, iPr	Et	Et	31-32
Me-tBu	Me	Et	42-45
Me-tBu	Me	iPr	46-50

On the other hand, bulky groups will favor attack on the disubstituted double bond.

$$R^1CH=C=CR^2R^3$$

R^1	R^2	R^3	Entries
Me-tBu	iPr	iPr	37-41
Me-tBu	Me	tBu	51-55
iPr	Et	tBu	56
Et-tBu	iPr	tBu	57-59

The reason for this is not clear.

Reversals are also observed when the steric bulk of the lonely substituent is comparable to the total bulk of the two geminal substituents on the other double bond. Compare for example entries 40, 45 and49.

When the attack does occur on the least substituted double bond, there is almost no preference for the E- or Z-alkenes. Compare the value of β (E:Z) for allenes 42 to 50. In most other cases, the E-alkenes are favored. There is no apparent correlation between the value of α (E : Z) and the allene structure. However, when the lonely substituent is tert-Butyl, the E-isomer is always formed exclusively. The only exception is entry 49.

When other substituents are present (Me, Et, iPr), the correlation is not apparent:

$R^1CH=C=CR^2R^3$

R^1	R^2	R^3	(E : Z)
Me	Me	Me	23 : 77
Et	Me	Me	00 : 100
iPr	Me	Me	49 : 51
iBu	Me	Me	19 : 81
tBu	Me	Me	100 : 00

The direction of attack seems to be very dependent on the substitution pattern on the remote double bond. One of the factors that determines the value of the E : Z ratios is the fact that the Z-alkenes are kinetically favored when little interaction takes place (as in the case of 1,3-disubstituted allenes).

b- PhSCl : As in the case of terminal allenes there is a net preference for attack on the double bond which is the most substituted as demonstrated by entries 26-59. Exceptions are allenes 37, 38, and 39. When the two geminal substituents are Methyl groups, there is only a very little preference for the disubstituted double bond. The percentage of attack on the most substituted double bond depends on the nature of the substituents on the remote double bond.

EtCH=C=CRR'

R	R'	α : β
Me	Me	58 : 42
Me	Et	63 : 37
Et	Et	81 : 19
Me	iPr	100 : 00
Me	tBu	65 : 35
iPr	iPr	34 : 66

The proportion of α-attack increases as one increases the steric bulk of the two geminal substituents until steric effects overcome polar effects at which point the ratios increase in favor of the β-attack.

In all cases the E-isomers are favored over the Z (for both α and β π-systems). The fraction of E-isomer increases as one proceeds through the series Methyl..... Ethyl.....isoPropyl.....tertButyl. (e.g., entries 51-54). There are however a few exceptions.

c- PhSeCl vs PhSCl : Once again, the Selenium and Sulfur versions have opposite preferences with respect to which double bond they will attack. When PhSeCl attacks the monosubstituted π-system, PhSCl reacts with the disubstituted double bond and viceversa.

If carbonium ion like species are involved in the product determining transition state, the direction of attack leading to the tertiary chlorides should be prefered (as in the case of PhSCl). The fact that benzeneselenyl chloride leads to preferential attack on the least substituted double bond implies that the intermediates are different. However, in some cases, Selenium does attack the most substituted side of the allene. This suggest that the product determining transition state consits of two possible structures, one of which could be common to both the Selenium and Sulfur versions. Normally, the two additions proceed via their own transition states (structurally different), but occasionally, Selenium may proceed via a Sulfur-like intermediate.

Once again, the selectivity of PhSeCl appears to be superior to that of PhSCl, especially for entries 26 to 30.

5- TETRASUBSTITUTED ALLENES :

Products of addition to tetrasubstituted allenes were difficult to analyse due to the lack of olefinic protons. It was found that the adducts readily eliminated HCl to give dienes. Analysis of the dienes led to structure identification of the original adducts.

a- PhSeCl : The selectivity of the Selenium reagent is reflected in the product distribution of allenes 62, 65 and 68. All three substrates carry the same substituents but their spatial arrangement around the allene moiety is different.

$R^1R^2C=C=CR^3R^4$

R^1	R^2	R^3	R^4	α : β
Me	Et	iPr	tBu	60 : 40
Me	iPr	Et	tBu	100 : 00
Me	tBu	Et	iPr	00 : 100

Preferential attack occurs on the double bond carrying the tert-Butyl group (i.e., most bulky substituent). The same thing is observed for the other members of the allene series. There is no preference for either the E or Z isomers with respect to attack on either side of the allenic moiety.

The only exceptions are for allenes 69 and 70. They are the only ones having two tert-Butyl substituents. In these two cases, attack on the less hindered side is favored as governed by steric approach control requirements. Also, the E isomers are favored due to the steric bulk of the tert-Butyl substituents.

b- PhSCl : If one compares allenes 62, 65 and 68, it can be seen that for tetrasubstituted allenes, the selectivity of PhSCl is greater than that of PhSeCl (> 85% in every cases vs 60% for the Selenyl chloride).

$$R^1R^2C{=}C{=}CR^3R^4$$

R^1	R^2	R^3	R^4	:
Me	Et	iPr	tBu	100 : 00
Me	iPr	Et	tBu	100 : 00
Me	tBu	Et	iPr	30 : 70

Again, attack occurs on the double bond carrying the tert-Butyl group. Similar trends are observed for the remainder of the allenes.

Not much can be said about the E : Z ratios due to lack of data but it appears (entries 64 & 65) that the tert-Butyl groups have a very large influence on the direction of approach of the electrophile, the E-alkenes being formed exclusively in both cases.

Comparing allenes 69 and 70, it seems that PhSCl also prefers to attack on the least hindered double bond of the allene.

c- PhSeCl vs PhSCl : It seems that PhSeCl and PhSCl behave very similarly with respect to tetrasubstituted allenes:

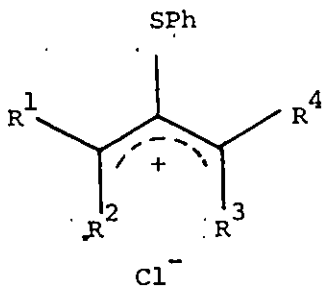
- Unusually high selectivity of PhSCl
- Preferential formation of E-alkenes in both cases
- Preference for attack on the double bond carrying the tert-Butyl group(s).

It would therefore appear that in the case of tetrasubstituted allenes, the addition of benzeneselenyl chloride and benzenesulfenyl chloride proceed via product-determining transition states that may be similar in structure.

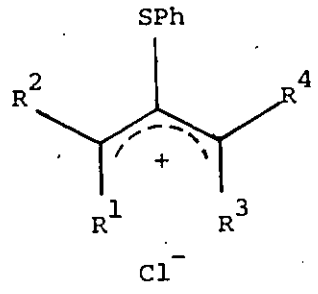
6- CONCLUSION :

From analysis of product distributions for the addition of benzeneselenyl chloride and benzenesulfenyl chloride to alkyl-substituted allenes it appears that both electrophiles can react through at least two different product determining transition states differing in structure and/or geometry. Depending on the structure of the allene the addition will proceed via one or the other of these transition states. In some cases (tetrasubstituted allenes), the intermediates for the Sulfur and Selenium versions may be very similar in structure.

The fact that tertiary chlorides (from attack on the most substituted double bond), are formed preferentially in the case of arenesulfenation suggest the presence of allylic carbonium ions (35) as possible intermediates in the product determining transition state.



and



(35)

PART VII

PRODUCT DISTRIBUTION AS A FUNCTION OF RING SIZE FOR THE ADDITION OF VARIUS ELECTROPHILES TO A SERIES OF CYCLIC ALLENES IN CH_2Cl_2 AT 25°C.

1-INTRODUCTION :

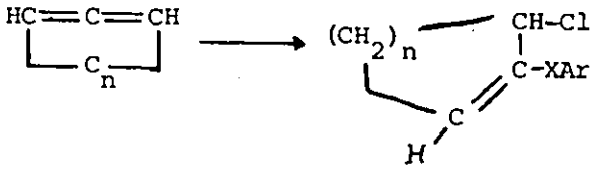
The reaction of cyclic allenes with PhSeCl, PhSCl and 2,4-DNBSC in dichloromethane was next investigated. Preliminary results have already been reported in our first paper[56].

2- RESULTS :

Studies using Dreiding models indicate that for the allene to give the Z-isomer would involve approach on the most hindered face of each double bond (i.e., From the inside of the ring). This steric hindrance to approach at one face of each double bond is reflected in the distribution of products in TABLE 26. Spectral parameters for the adducts are given in TABLE 27.

TABLE 26

THE PRODUCT DISTRIBUTIONS FOR THE REACTION OF CYCLIC ALLENES WITH PhSeCl, PhSCl AND 2,4-DNBSC IN DICHLOROMETHANE AT 25°C.



RING SIZE n	2,4-DNBSC E : Z	PhSeCl E : Z	PhSCl E : Z
6	100 : 00	100 : 00	100 : 00
7	———	———	———
8	82 : 18	54 : 46	51 : 49
9	71 : 29	41 : 59	57 : 43
10	86 : 14	36 : 64	81 : 19

1,2-cyclononadiene reacts with all three electrophiles giving the E-isomer exclusively. As the ring size is increased, the kinetically more stable isomer is formed in varying amounts depending on the flexibility of the ring.

SCHEME X illustrates the various modes of approach of the electrophile.

SCHEME X

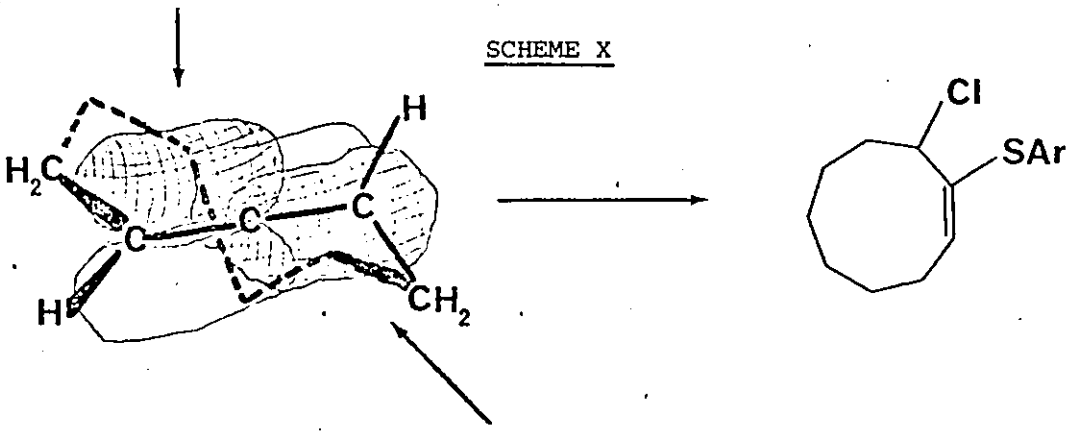
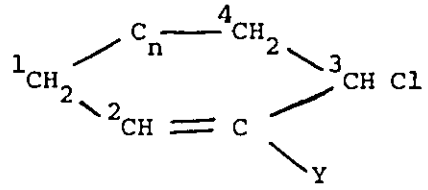


TABLE 27

^{1}H NMR SPECTRAL PARAMETERS FOR THE ADDUCTS OF CYCLIC ALLENES WITH PhSeCl, PhSCl AND 2,4-DNBSC IN DICHLOROMETHANE AT 25°C.



ring size n	Electrophile Y		Chemical shifts and coupling constants H_2	$^3J_{1,2}$	H_3	$^3J_{3,4}$	$^4J_{2,3}$
4	PhSe	E	5.90t	8.8	5.25dd	10.6;5.2	0.2
	PhSe	Z					
6	PhSe	E	5.82dd	11.5;5.2	5.17dd	11.0;4.5	
	PhSe	Z	6.51t	7.5	4.57dd	8.0;4.7	1.2
7	PhSe	E	5.82dd	11.5;5.5	5.12t	7.0	
	PhSe	Z	6.42t	7.0	4.68dd	11.0;6.5	
8	PhSe	E	5.83dd	9.5;5.5	4.92dd	9.2;5.8	0.2
	PhSe	Z	6.31t	7.0	4.53dd	8.0;5.5	
6	PhS	E	5.69dd	11.0;6.0	5.2m		
	PhS	Z	6.62t	7.5	4.53dd	7.5;6.0	1.0
7	PhS	E	5.66dd	11.7;5.5	5.16t	7.0	
	PhS	Z	6.25dd	9.0;5.5	4.78dd	10.2;5.2	
8	PhS	E	5.93dd	9.8;6.2	5.13dd	10.0;6.2	
	PhS	Z	6.50dd	7.4;7.5	4.67dd	8.9;6.4	
4	2,4-DNBSC	E	6.68t	8.5	5.33dd	10.5;3.0	
	2,4-DNBSC	Z					
6	2,4-DNBSC	E	6.47dd	10.6;6.0	5.37dd	11.0;4.5	
	2,4-DNBSC	Z			4.64t	7.0	1.5
7	2,4-DNBSC	E	6.27m		5.29t	7.0	
	2,4-DNBSC	Z	6.36t		4.81dd	10.3;5.5	
8	2,4-DNBSC	E	6.39dd	8.5;6.5	5.05dd	9.2;3.0	
	2,4-DNBSC	Z	6.72dd	7.0;6.0	4.75dd	10.5;2.5	

We have observed that in the case of Benzenesulfenyl chloride, the E-Alkenes were formed preferentially under conditions of kinetic control.

1,3-diethyl allene gave a 50:50 ratio of E- and Z-isomers.

When the ring size allows some flexibility (1,2-cycloundecadiene and 1,2-cyclododecadiene), the E- and Z-Alkenes are formed in comparable quantities (51 : 49 and 57 : 43 respectivily), indicating that there is no real steric constraints imposed on the adducts by their cyclic structures (compared to the acyclic 1,3-diethyl allene).

If one increases still the size of the ring, the allene can adopt a conformation that can once again hinder approach of the electrophile from inside of the ring to form Z-Alkenes. This is reflected in the E : Z ratio that goes back to 81 : 19 in favor of the E-isomer.

In the case of 2,4-DNBSC, a similar trend is observed but the E-isomer is always favored over the Z because of the greater steric bulk inherent to the electrophile. As a result, 2,4-DNBSC will prefer outside attack independently of the size of the ring. (compare E : Z = 80 : 20 in the case of 1,3-diethyl allene).

For the Selenium version we have seen that in the case of 1,3-diethyl allene the ratio of E to Z isomer was 40:60 in favor of the Z-Alkene. If the ring size allows approach from the inside, comparable ratios will be obtained in the case of cyclic allenes. This does not occur until one reaches the 12-membered ring (E:Z = 41:59) and the 13-membered cycle (E:Z = 36:64).

In the case of 1,2-cyclononadiene, the only allowed product is the E-Alkene. As one moves along to 1,2cycloundecadiene, the portion of Z-Alkene (kinetically favored) reaches a proportion of 46% still inferior to the acyclic case.

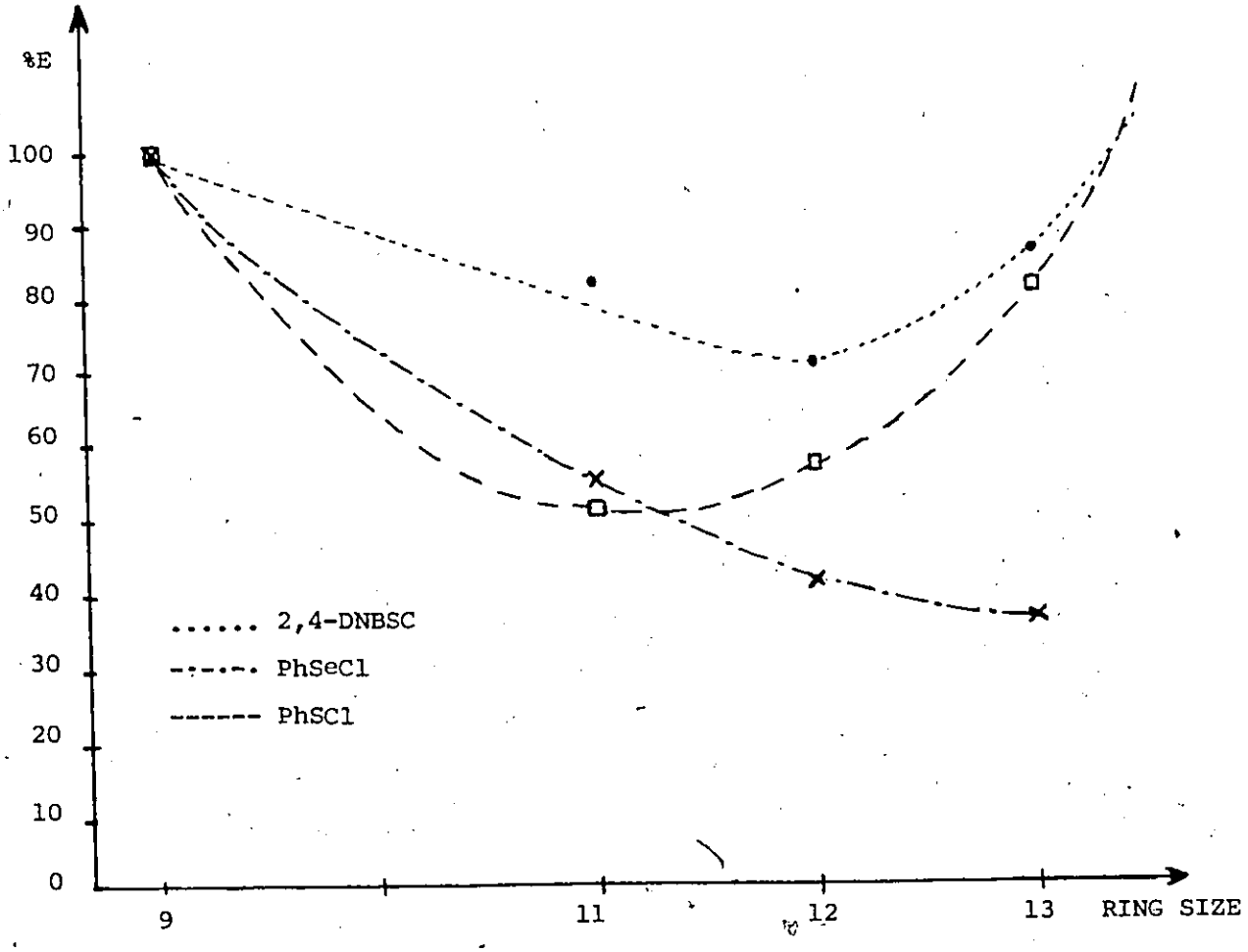
Comparing attack by PhSeCl and PhSCl it is interesting to note that in the case of 1,2-cyclotridecadiene and PhSeCl, no fold-back of the allene is observed.

The E:Z ratio increases continuously in favor of the Z-Alkene. It would be interesting to investigate the addition to the 14-membered ring to see whether the fold-back occurs at this point.

The results described in this section are summarized in FIGURE 10.

FIGURE 10

GRAPH OF % E-ISOMER vs RING SIZE



PART VIII

THE SYNTHESIS OF 2,5-DIHYDROFURAN DERIVATIVES

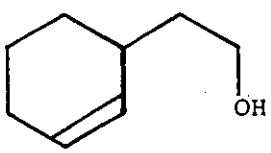
1- INTRODUCTION :

Because of the facile nature of the electrophilic addition to allenes and the quantitative yields obtained in every cases, we sought for some useful synthetic applications of this process.

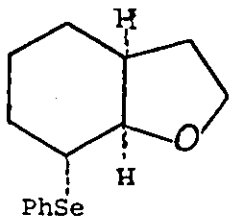
An obvious application is the synthesis of vinyl selenides. However, in most cases, complex mixtures of isomers are obtained and there are other more convenient routes to this synthon[73].

As suggested by the number of papers published every year , the synthesis of heterocycles has recently received a great deal of attention and in particular, some groups have been concerned with the synthesis of heterocycles via the electrophilically-induced cyclization of unsaturated species.

Clive and coworkers have demonstrated the utility of PhSeCl in inducing the cyclization of γ , δ -unsaturated alcohols to ring fused tetrahydrofurans[74]. For example :

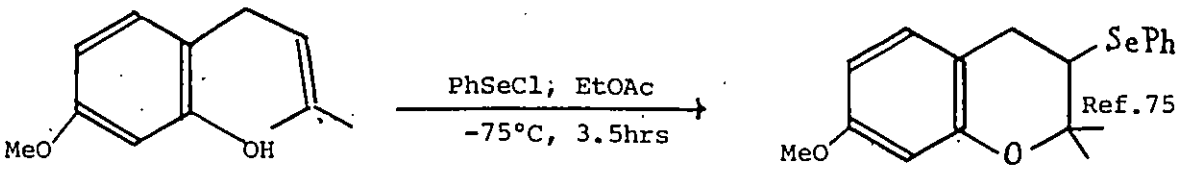


PhSeCl, EtOAc, 18 hrs
-65°C then RT



Ref.74

77%



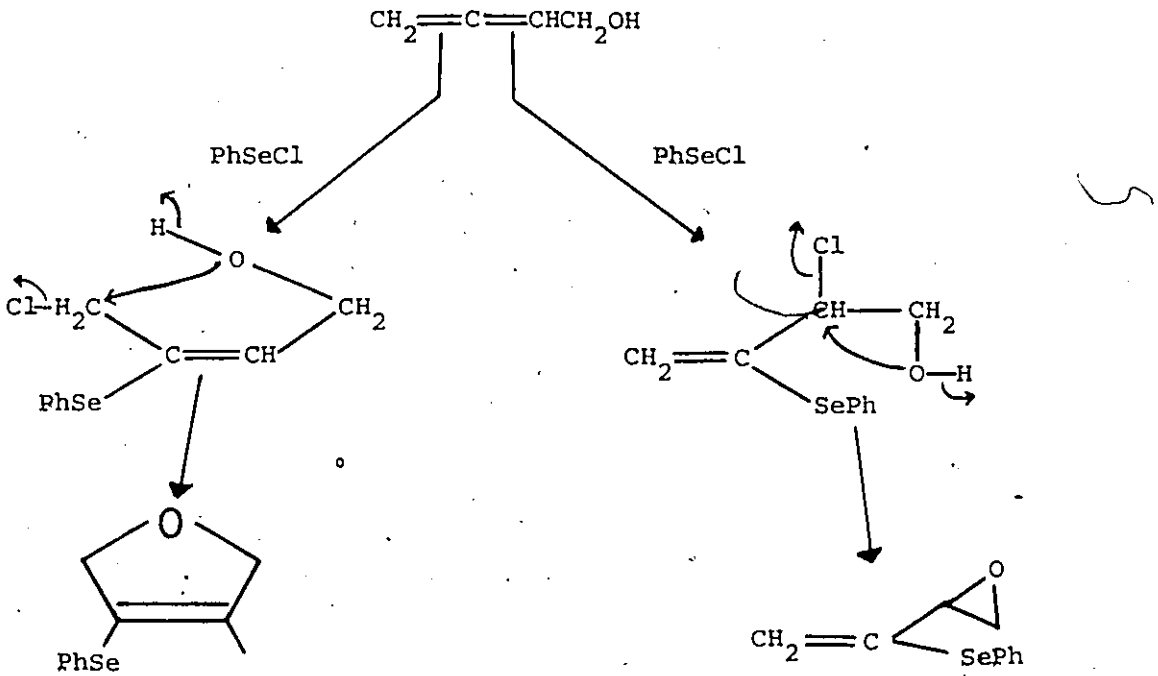
79%

This type of process is very attractive as the reaction conditions are very smooth and many functionalities may be tolerated. Moreover, the presence of the phenylseleno moiety allows further elaboration of the structure. This leaded us to investigate the reaction of α-allenic alcohols with various electrophiles.

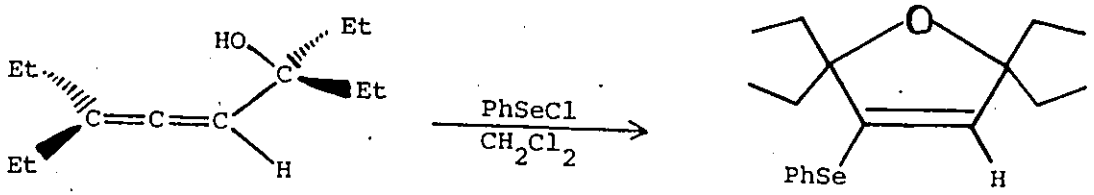
2- ADDITION OF PhSeCl TO α-ALLENIC ALCOHOLS :

a- INTRODUCTION :

Conceptually, PhSeCl should add to α-allenic alcohols giving adducts that should cyclize spontaneously as described below :



In order to establish the preferred pathway, we subjected 3,6-diethyl-4,5-octadien-3-ol (25) to one equivalent of PhSeCl in dichloromethane at room temperature. Immediate workup gave a single compound in quantitative yield, identified as (26) on the basis of its ^{1}H and ^{13}C NMR and its mass spectral fragmentation pattern.



(25) (26)

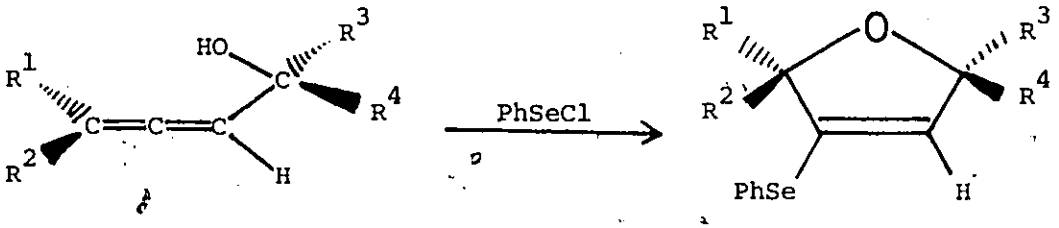
The mass spectral analysis shows the production of fragments corresponding to $(M)^{+\cdot}$, $(M-Et)^{+\cdot}$, $(M-Et-SePh)^{+\cdot}$, and $(PhSe)^{+\cdot}$. Furthermore, the infrared spectrum showed no hydroxyl or allenic absorptions.

b- RESULTS :

This ring closure reaction was found to be general as demonstrated in TABLE 23. Spectral parameters for the 2,2,5,5-tetraalkyl-3-phenylseleno-2,5-dihydrofurans are reported in TABLE 1 of APPENDIX VI.

All reactions proceeded spontaneously at room temperature as revealed by test ^{1}H NMR tube reactions. Cyclizations involving terminal allenes were found to proceed in better yields in the presence of one equivalent of triethylamine to react with the HCl which is given off.

TABLE 23

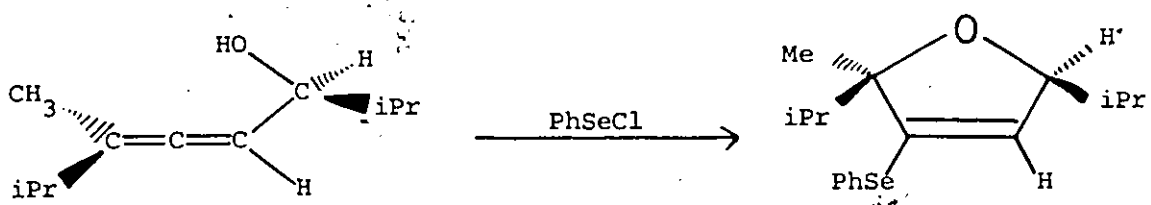


R^1	R^2	R^3	R^4	%YIELD
H	H	Et	Et	85
H	H	iPr	iPr	70
H	H	Me	tBu*	100
H	iPr	H	iPr	100
H	iPr	iPr	H	100
H	iPr	Et	Et	100
H	iPr	iPr	iPr	100
Me	Me	Me	Et	85
Me	Me	Me	iPr	100
Me	Me	Me	tBu	92
Me	Me	iPr	iPr	85
Me	Et	H	iPr	85
Me	Et	iPr	H	85
Me	Et	Me	iPr	100
Me	Et	Me	tBu	60
Me	iPr	H	iPr	100
Me	iPr	iPr	H	100
Me	iPr	Me	iPr	100
Me	iPr	iPr	Me	100
Et	Et	Et	Et	100

* In the presence of one equivalent of Et_3N

3- STEREOCHEMISTRY OF THE ADDITION OF PhSeCl TO α -ALLENIC ALCOHOLS :

The stereochemistry of the ring closure was demonstrated by the reaction of diastereomeric α-allenic alcohols :

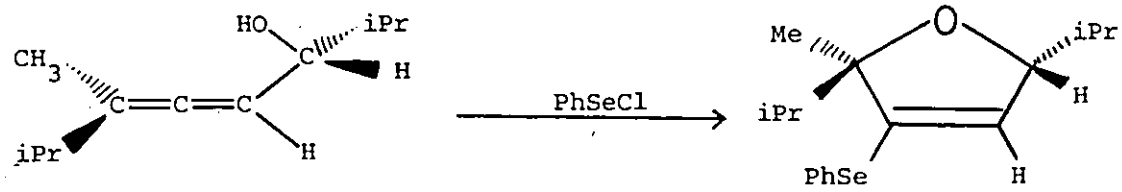


(27)

(3-RS, 5-RS) allenic alcohol

100% (28)

Z-2,5-dihydrofuran



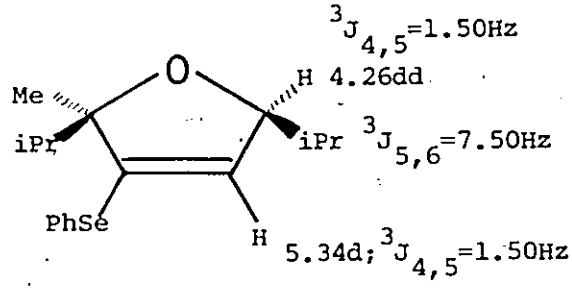
(29)

(3-RS, 5-SR) allenic alcohol

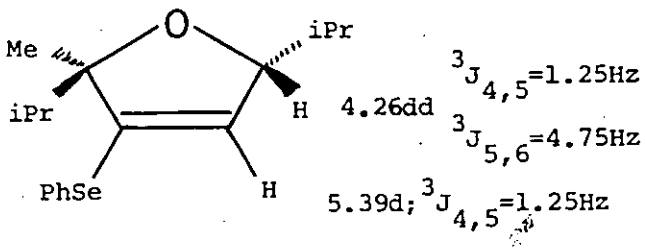
100% (30)

E-2,5-dihydrofuran

Assignment of (28) and (30) as the Z- and E-isomers respectively follows from the respective ^{1}H NMR analysis of the ring protons of the furan system :



Z (28)



E (30)

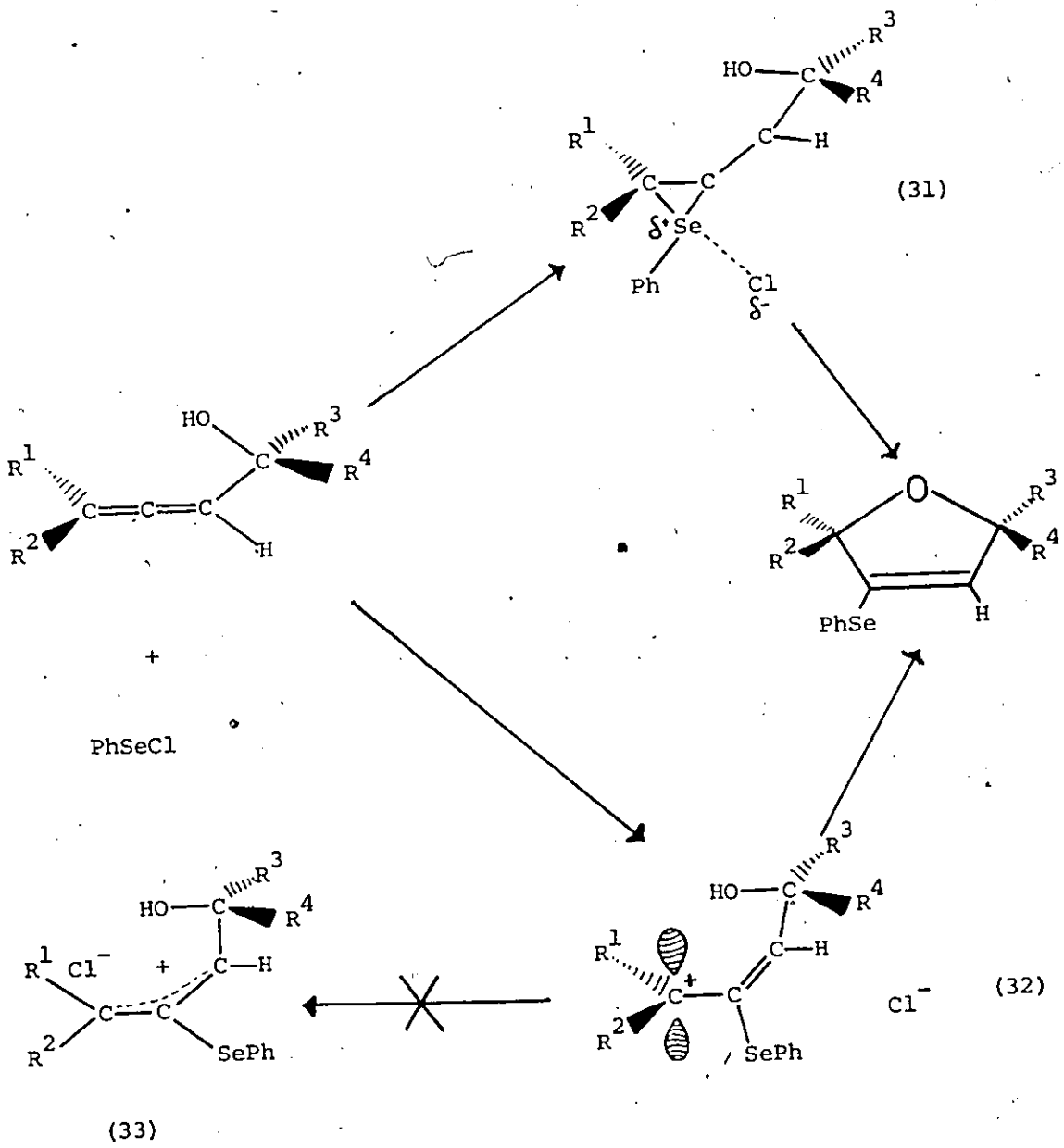
As one can see, the magnitude of $^3J_{5,6}$ is very different for the two isomers (H_6 is the methine proton of the isopropyl group directly bonded to C_5). In the Z-isomer, there is a large steric interaction between the two isopropyl groups as revealed by molecular models. In this case, protons H_5 and H_6 will tend to adopt an Anti-conformation with respect to each other . This of course gives rise to a larger coupling constant between protons H_5 and H_6. This latter conformation is more important in the Z-isomer than in the E- and it is thus natural to assign the Z-configuration to the species that exhibits the larger $^3J_{5,6}$. Similar results were obtained for the other series of diastereoisomeric allenes studied.

4- MECHANISTIC CONSIDERATIONS :

When the α-allenic alcohols were subjected to kinetic studies with PhSeCl (or PhSCl), overall 2nd order kinetics were observed; first order in both allene and electrophile. This suggest the presence of one molecule of allene and one molecule of electrophile in the rate determining transition state. This is drawn in SCHEME IX.

The intermediate (31) or the non-resonance stabilized carbonium ion (32) is involved which collapses to product before bond-rotation to the resonance-stabilized form (33) can occur. On the basis of our observations on the electrophilic addition of PhSeCl and PhSCl to allenes, the reaction hypersurface probably contains cyclic intermediates (31).

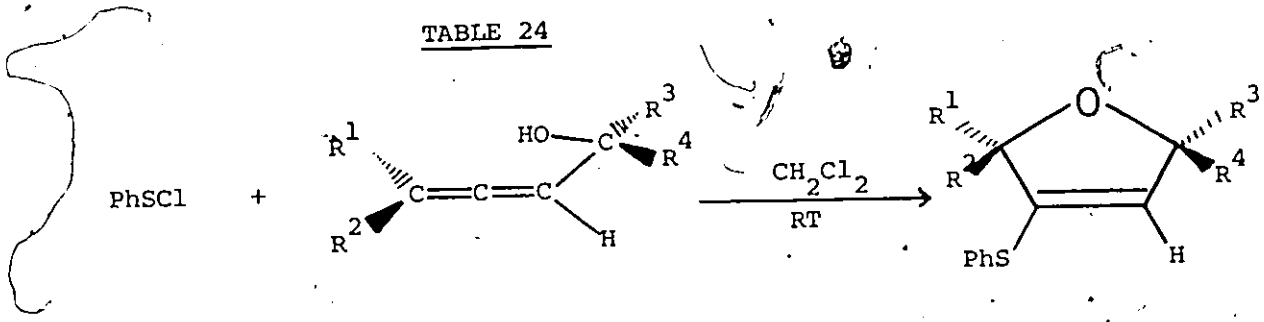
SCHEME IX



5- 3-PHENYLTHIO-2,5-DIHYDROFURANS :

PhSCl gave cyclization products similar to those described in the Selenium version. Here again, reactions were spontaneous and products were obtained in quantitative yields as shown in TABLE 24. Spectral parameters are given in TABLE 2 of APPENDIX VI.

TABLE 24



R^1	R^2	R^3	R^4	%YIELD
H	Et	Me	iPr	95
Me	Me	Me	iPr	75
Me	Me	Me	tBu	89
Me	Me	iPr	iPr	95
Me	Et	Me	Et	80
Me	Et	Me	iPr	90
Me	iPr	H	iPr	95
Me	iPr	Me	tBu	90
Me	iPr	iPr	iPr	70
Et	Et	Et	Et	100

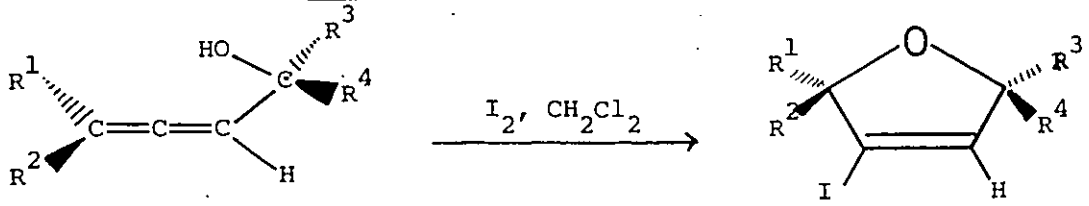
Identification of products was performed as described for the Selenium version. Additions were Stereospecific.

6- 3-IODO-2,5-DIHYDROFURANS :

Halogens add to allenes giving unsaturated dihalides. However, the addition is often complicated by elimination of HX from the products or by double addition of haldgen to both allenic double bonds.

When α-allenic alcohols were treated with one equivalent of iodine, spontaneous cyclization to the corresponding 3-iodo-2,5-dihydrofurans was observed. The reaction was not stereospecific and the products were isolated as dark labile oils. Their instability contrasted with that of the Phenylseleno and Phenylthio-derivatives which were indefinitely stable at 0°C. These adducts still gave very clean spectra and could be identified using the criteria used previously. Yields are presented in TABLE 25. See TABLE 3 in APPENDIX VI.for spectral parameters.

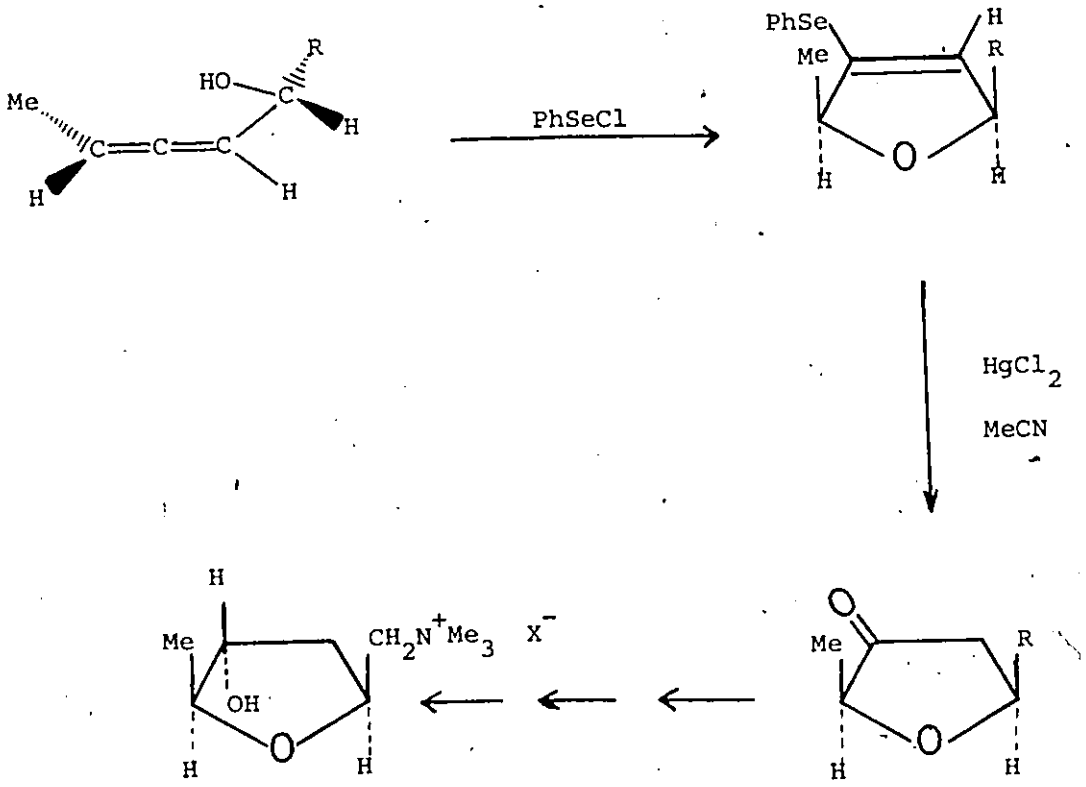
TABLE 25



R^1	R^2	R^3	R^4	%YIELD
H	iPr	Et	Et	90
H	iPr	iPr	iPr	85
Me	Me	Me	Et	90
Me	Me	Me	iPr	85
Me	Me	Me	tBu	85
Me	Me	iPr	iPr	90
Me	iPr	H	iPr	90
Et	Et	Et	Et	100

7- CONCLUSION :

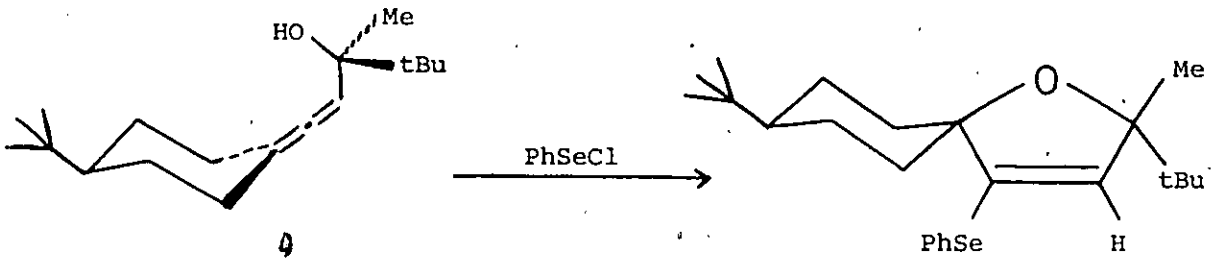
The electrophilic addition of PhSeCl, PhSCl and I_2 to α-allenic alcohols has been successfully applied to the synthesis of 3-functionalized-2,5-dihydrofurans. Stereospecific introduction of the vinylic Phenylseleno moiety can be elaborated to give a Furanone[76] which could eventually lead to the alkaloid Muscarine (34)



MUSCARINE (34)

(2S,3R,5R)

The method was also applied to the synthesis of spiro-2,5-dihydrofurans :



The only other route to the synthesis of such species is that described by D.Gange and P.Magnus[77]. Their procedure involves the cyclization of α-allenic alcohols using Potassium hydride in THF at reflux in the presence of dicyclohexyl-18-crown-6. (12 hrs to 4 days). Yields are of the order of 75%.
No mention is made about the stereochemistry of the reaction.

It would probably prove very fruitful to apply this method to the stereospecific synthesis of 2,5-dihydrothiophenes, 2,5-dihydropyrroles and derivatives.

CONCLUSION

Areneselenyl halides and arenesulfenyl halides add to alkyl-substituted allenes with exclusive attack of the Arylseleno or Arylthio moiety on the central allenic carbon atom.

Arenesulfenyl chlorides lacking ortho- substituents show no selectivity with respect to which double bond is attacked. For ortho-substituted sulfenyl chlorides there is a net preference for attack on the most sterically encumbered side. The configurational selectivity favors the formation of the E-isomer as the steric bulk of the substituent increases. In the reaction of 1,3-disubstituted allenes with arenesulfenyl chlorides, the effect of an ortho-Nitro group is stictly one of steric nature and there is no stabilization through novel intermediates of the spirosulfurane type.

Benzeneselenyl chloride adds to allenes in a fashion similar to that of sulfenyl chlorides. The reaction follows 2nd order kinetics and is stereospecific (as in the case of PhSCl). PhSeCl attacks the double bond with the most electron donating and sterically bulky substituent. The phenylseleno moiety always attacks the central allenic carbon. In every case , the Z-isomer is formed preferentially. PhSeCl and PhSeBr were found to behave very similarly towards electrophilic attack. On the basis of kinetic studies we have come to the conclusion that the areneselenyl halides studied all have a similar rate-determining transition state. Furthermore, the rate and product determining transition states are different and separated by at least one intermediate. We have postulated that the product determining transition states arise from alkylideneseleniranium ions and there is evidence for an alkylideneepiselenurane-like species in the rate-determining transition state. The rate determining transition states for PhSeCl and PhSCl are different. For the sulfur version there is strong evidence that the rate determining step follows the S_N2 type attack (through a thiiranium ion intermediate).

There is strong evidence for several intermediates in the product-determining transition states for both areneselenation and arenesulfenation of allenes. In the case of sulfur, allylic carbonium ion type intermediates may be involved. The allene structure determines the nature of the intermediate. The reactions of PhSeCl, PhSCl and 2,4-DNBSC with cyclic allenes show a net dependence of the E : Z ratio on the ring size.

Finally, the addition of PhSeCl, PhSCl or Iodine to α-allenic alcohols appears to be a very efficient route to the stereospecific synthesis of 2,5-dihydrofuran derivatives. This method can be extended to the formation of dihydropyrans from β-allenic alcohols. However, spectral proof for this process is not available at present.

EXPERIMENTAL

I- Technical information:

a- Instrumental:

Nuclear magnetic resonance spectra (nmr) were obtained using Varian T-60, HA-100 and FT-80-16K instruments; the latter was used for the ^{13}C nmr spectra. Chemical shifts are reported in parts per million down field from internal TMS (δ). Chloroform-D (Silanor C) was used as an internal lock and reference for carbon spectra. Probe temperature was approximately 30°C for carbon spectra and ^{1}H nmr spectra were run at room temperature.

The following abbreviations will be used in tables:

s = singlet	q = quartet
d = doublet	q'= quintet
t = triplet	m = multiplet

Infrared (IR) spectra were measured on a Unicam SP1100 spectrometer and are not calibrated. Sodium chloride optics and carbon tetrachloride or chloroform-D solutions were used.

Melting points (Mp) were obtained on a Fisher-Johns melting point apparatus All boiling and melting points are uncorrected.

b- Reagents and solvents:

Reagents and solvents were commercial grades and used without further purification unless specified. Tetrahydrofuran was distilled from lithium aluminum hydride and stored over 4Å molecular sieves.

c- Kinetic measurements:

A Durrum model D-150 stopped flow spectrometer was used. It was operated in the transmittance mode. Decay of transmittance was stored and photographed from an oscilloscope using a BIOMATION model 805 waveform recorder. Temperature was maintained at 24.5 $\pm$ .1°C using a HAAKE model KT33 constant temperature bath circulator.

All measurements were done in reagent grade dichloromethane.

The following wavelength and extinction coefficients were used throughout the experiments.

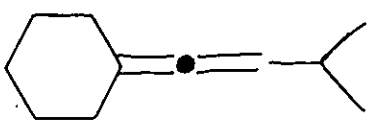
	λ max (nm)	ϵ ($l.mole^{-1}cm^{-1}$)
Benzeneselenyl chloride	433	267.04
All arylsulfenyl chlorides	392	399.5
Benzeneselenyl bromide	468	238
2,4,6-trimethylbenzeneselenyl bromide	497	183

Results were computer analysed and only runs having a correlation coefficient better then 0.996 were considered. Experiments were repeated until three different runs agreed within 5%.

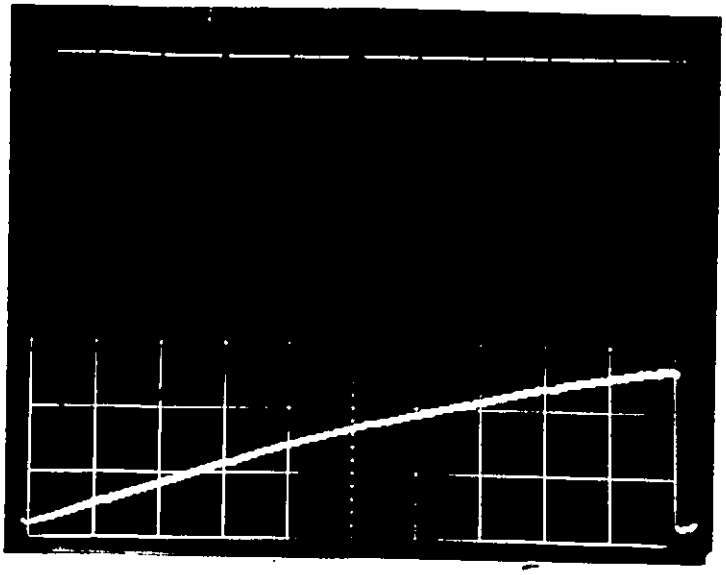
To ensure pseudo-first order kinetic behavior, allene solutions were made approximately ten times more concentrated then the electrophile solutions

Computer program for data analysis:

The detailed computer printout is shown below for the reaction of 3-methyl-butenylidenecyclohexane (17) with benzeneselenyl chloride.



(17)



Oscilloscope trace of transmittance (y axis) vs time (X axis) for the reaction of (17) with benzeneselenyl chloride.

(The baseline represents 100% transmittance)

```
      $JOB  ACCT-NUM,'P.L.BEAULIEU',PAGES=20,TIME=20
    1       DIMENSION  A(500),T(500),D(500), DY(500),  RK(500)
    2    12 READ,  NP,  A0,  B0,  IRUN
    3       READ, (T(I),I=1,NP)
    4       READ, (A(I), I=1,NP)
    5       DO 51 I=1,NP
    6       TP=(86.5-A(I))/86.5
    7       A(I)=-ALOG(TP)
    8       A(I)=A(I)/534.0876
    9       D(I)=(ALOG(B0*A(I)/(A0*(B0-A0+A(I)))))/(A0-B0)
   10    51 CONTINUE
   11       CALL  LTSQ(T,D,NP,W,B,RMSUM,CC,DY)
   12       RK(1)=0.0
   13       DO 70 I=2,NP
   14       RK(I)=D(I)/T(I)
   15    70 CONTINUE
   16       WRITE(6,71) IRUN
   17    71 FORMAT(1H1,20H RESULTS FOR RUN NO.,I4,7H FOLLOW)
   18       WRITE(6,72)
   19    72 FORMAT(1H0,8X,5H (A0),10X,5H (B0),10X,3H K ,10X,25H CORRELATION CO
     1EFFICIENT ,5X,15H MEAN DEVIATION//<
   20       WRITE(6,73) A0,B0,W,CC,RMSUM
   21    73 FORMAT(6X,F10.8,5X,F10.8,5X,E18.7,5X,F10.6,13X,E18.6//)
   22       WRITE(6,74) B
   23    74 FORMAT(2H0 ,22H INTERCEPT OF LINE IS ,E18.6//)
   24       WRITE(6,76)
   25    76 FORMAT(1H0,10X,4HTIME,10X,7HCONC. A,8X,13HRATE CONSTANT,6X,5HPOINT,
     110X,9HDEVIATION//)
**WARNING**  EXPECTING COMMA BETWEEN FORMAT ITEMS NEAR INTIO
   26    75 FORMAT(1H0,I6,F10.6,F15.8,F18.7,2F15.6)
   27       WRITE(6,75)(I,T(I),A(I),RK(I),D(I),DY(I),I=1,NP)
   28       GO TO 12
   29       STOP
**WARNING**  UNNUMBERED EXECUTABLE STATEMENT FOLLOWS A TRANSFER
   30       END

   31       SUBROUTINE LTSQ(X,Y,N,A,B,RMSUM,CC,DY)
   32       DIMENSION X(N),Y(N),DY(N)
   33       SUMX=0.0
   34       SUMY=0.0
   35       SUMXX=0.0
   36       SUMYY=0.0
   37       SUMXY=0.0
   38       SUMP=0.0
   39       DO 50  I=1,N
   40       SUMX=SUMX+X(I)
   41       SUMY=SUMY+Y(I)
   42       SUMXX=SUMXX+X(I)*X(I)
   43       SUMYY=SUMYY+Y(I)*Y(I)
   44       SUMXY=SUMXY+X(I)*Y(I)
   45    50 CONTINUE
   46       Z=N
   47       R=Z*SUMXY-SUMX*SUMX
   48       A=(Z*SUMXY-SUMX*SUMY)/R
   49       B=(SUMXX*SUMY-SUMX*SUMXY)/R
   50       S=Z*SUMYY-SUMY*SUMY
   51       CC=(Z*SUMXY-SUMX*SUMY)/SQRT(R*S)
   52       DO 60 I=1,N
   53       CY=A*X(I)+B
   54       DY(I)=Y(I)-CY

   55       P=DY(I)*DY(I)
   56       SUMP=SUMP+P
   57    60 CONTINUE
   58       RMSUM=SQRT(SUMP/P)
   59       RETURN
   60       END

      $ENTRY
```

RESULTS FOR RUN NO.	A (A0)	B FOLLOW (B0)	K	CORRELATION COEFFICIENT	MEAN DEVIATION
	0.00192108	0.00268660	0.5378461E 05	0.999378	0.364548E 03

INTERCEPT OF LINE IS -0.773405E 02

	TIME	CONC. A	RATE CONSTANT	POINT	DEVIATION
1	0.003277	0.00140242	0.0000000E 00	130.877700	31.976760
2	0.004096	0.00130867	0.3991950E 05	163.510300	20.548910
3	0.004915	0.00119465	0.4246702E 05	208.733900	21.712310
4	0.005734	0.00111053	0.4304148E 05	246.817000	15.735150
5	0.006554	0.00103754	0.4330191E 05	283.783400	8.641113
6	0.007373	0.00094207	0.4595475E 05	338.815100	19.612790
7	0.008192	0.00089261	0.4527209E 05	370.868800	7.606201
8	0.009011	0.00083764	0.4548345E 05	409.860500	2.537354
9	0.009830	0.00079083	0.4539703E 05	446.270900	-5.112549
10	0.010650	0.00075161	0.4501295E 05	479.369800	-16.073970
11	0.011469	0.00070372	0.4564310E 05	523.471600	-16.032710
12	0.012288	0.00066319	0.4593298E 05	564.424500	-19.140130
13	0.013107	0.00062653	0.4613826E 05	604.743400	-22.881590
14	0.013926	0.00059653	0.4598368E 05	640.387200	-31.298330
15	0.015565	0.00052355	0.4747345E 05	738.914700	-20.891110
16	0.017203	0.00046993	0.4793059E 05	824.559500	-23.367180
17	0.018842	0.00042051	0.4863611E 05	916.382000	-19.565280
18	0.020480	0.00037500	0.4955499E 05	1014.886000	-9.281982
19	0.022119	0.00033834	0.5003067E 05	1106.598000	-5.690430
20	0.023757	0.00030749	0.5028059E 05	1194.505000	-5.903564
21	0.025395	0.00027461	0.5125206E 05	1301.556000	13.026120
22	0.027034	0.00025456	0.5085394E 05	1374.765000	-1.885986
23	0.028672	0.00023407	0.5073285E 05	1451.000000	

Explanation of symbols:

- NP : number of points used in analysis

- AO : initial concentration of electrophile after mixing with substrate. (=1/2 original concentration) in moles/liter.

- BO : initial concentration of substrate after mixing with electrophile in moles/liter.

- IRUN: 4 character identification number for each runs.

- T(I): time data points (sec.).

- A(I): transmittance data from analysis of photographs. (In mm)

- Line 6: is to convert mm in actual transmittance.

- Line 7: conversion of transmittance into absorbance.

- Line 8: conversion of absorbance into concentration using

$A = \varepsilon l c$ A = absorbance

E = extinction coefficient

l = light pathway (= 2 cm)

- Line 9: rate equation

For 2nd order: `D(I) = (ALOG(BO*A(I)/(AO*(BO-AO+A(I)))))/(AO-BO)`

For 3rd order:
```
D(I) = ((-1/(AO-BO))*((1/A(I))-(1/AO)))+
       1((ALOG(BO*A(I)/(AO*(BO-AO+A(I)))))/(AO-BO)**2)
```

2- 1,1-DIBROMOCYCLOPROPANES:

a- General procedure: Gem-dibromides were prepared according to standard literature methods[35,36,37,38]. A slurry was made by mixing freshly prepared alcohol-free potassium t-butoxide with a pentane solution of an olefin at room temperature. A pentane solution of bromoform was then slowly added. The mixtures were stirred at room temperature for approximately twenty hours. After aqueous work up, extraction with ether, drying over anhydrous magnesium sulfate and evaporation of the solvent, the products were purified by high vacuum distillation (1mm). Gemdibromocyclopropanes were characterized by their ^1H nmr spectra. (no olefinic signals).

b- 1,1-dibromo-Z-2,3-diethyl cyclopropane: A slurry was made by mixing fresh potassium t-butoxide (0.040 mole) with a solution of Z-3-hexene (0.025 mole) in 20 mls of pentane. Bromoform (0.020 mole) in 10 mls of pentane was added over a period of one hour and the mixture was further stirred for 20 hours at room temperature. Aqueous work up and vacuum distillation yielded pure 1,1-dibromo-Z-2,3-diethyl cyclopropane (Bp. 54°/1mm) in 55% yield based on bromoform.

Yields and boiling points of various gem-dibromo cyclopropanes are reported in table(I). Low yields are due to mechanical loss during distillation.

3- ALLENES FROM 1,1-DIBROMOCYCLOPROPANES:

a- general procedure: All gem-dibromocyclopropanes were dehalogenated using methyllithium according to the method of L. Skatebøl[35]. The 1,1-dibromocyclopropane derivative was diluted with 50 mls of anhydrous ether under an inert nitrogen atmosphere. The mixture was cooled in dry ice/acetone at -60°C.

TABLE (I)

Starting alkene	% Yield[b]	Boiling points[a] °C/mmHg
E-2-pentene	70	63-67 /11
4-methyl-2-pentene	-	-
Z-4,4-dimethyl-2-pentene	36	52 /1
Z-3-hexene	58	54-56 /1
Z-2,5-dimethyl-3-hexene	20	75 /.5
2-methyl-2-pentene	59	43 /1
2,4-dimethyl-2-pentene	50	-
2,4,4-trimethyl-2-pentene	32	78 /1
2,5-dimethyl-2-hexene	42	69 /1
3-methyl-2-pentene	64	50 /2
E-3,4-dimethyl-2-pentene	60	57 /1
3,4,4-trimethyl-2-pentene	21	83 /.5
3-ethyl-3-hexene	48	76 /.5
3-methyl-1-butene	38	60-63 /14
4-methyl-1-pentene	34	62 /.5
5-methyl-1-hexene	25	70 /.3
2-methyl-1-pentene	52	50 /1
2,3-dimethyl-1-butene	23	49.5 /1
2,4-dimethyl-1-pentene	40	64 /1
2,3-dimethyl-1-pentene	24	64 /1

2,3,3-trimethyl-1-butene	25	68 /.125
2,4,4-trimethyl-1-pentene	28	74 /1
Cyclooctene	63	148-154 /14
E+Z-cyclododecene	55	160-162 /1

a- Boiling points are uncorrected.

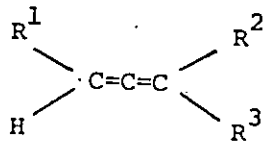
b- Yields are based on starting bromoform.

An etheral solution of methyllithium (20-50% excess of a 1.3 M solution) was added dropwise over a period of one hour. The reaction mixture was further stirred for 2 hours allowing the temperature to raise gradually to room temperature. This was followed by an aqueous work up, extraction with ether, drying over anhydrous magnesium sulfate and evaporation of the solvent. The allene was purified by ordinary distillation. Allenes were identified by IR and ^{1}H nmr spectroscopy.

b- 3,4-heptadiene: 1,1-dibromo-Z-2,3-diethyl cyclopropane (0.017 mole) was diluted in 50 mls of anhydrous ether under dry nitrogen and the solution was cooled to -60°C. A 50% excess of methyllithium was added dropwise over a period of one hour. The reaction mixture was further stirred for two hours allowing the temperature to raise gradually. After normal work up, the allene was purified by distillation. 3,4-heptadiene (Bp. 101°C) was obtained in 46% yield. Results are summarized in table (II).

TABLE (II)

ALLENES FROM GEM-DIBROMO CYCLOPROPANES



R^1	R^2	R^3	Yield %	Boiling points °C	Pressure mmHg
H	H	iPr	40	70	760
H	H	iBu	25		
H	H	3-methyl-propyl	53		
H	Me	nPr	50		
H	Me	iPr	40		
H	Me	iBu	55		
H	Me	secBu	35		
H	Me	tBu	50		
H	Me	3,3-dimethyl-propyl	56		
Me	Et	H	45	75	760
Me	iPr	H	44	74-75	760
Me	tBu	H	26	94-96	760
Et	Et	H	65	101	760
iPr	iPr	H	10	128-130	760
Et	Me	Me	40		
iPr	Me	Me	50		
iBu	Me	Me	50		
tBu	Me	Me	57		
Me	Me	Et	52		
Me	Me	iPr	65		
Me	Me	tBu	38		
Et	Et	Et	61		
$-(CH_2)_6-$		H	80	72-74	17
$-(CH_2)_8-$		H			
$-(CH_2)_9-$		H			
$-(CH_2)_{10}-$		H	49	85	1
$-(CH_2)_6-$		Me	50		

4- TERMINAL PROPARGYL ALCOHOLS; $HC{\equiv}C\text{-}CR^1R^2OH$:

a- General procedure: Terminal propargyl alcohols were isolated from the reaction of ethynylmagnesium bromide with various ketones and aldehydes in tetrahydrofuran solutions.

Simple aldehydes and ketones were commercially available from Aldrich, Chem. Sample Co . and Eastman Kodak.

3-methyl-2-pentanone was prepared according to known methods[39].

2,2-dimethyl-3-propanal was obtained by alkylation of isobutyraldehyde using solid-liquid phase transfer catalysis according to the method of V.G. Purohit and R. Subramanian[40].

Ethynylmagnesium bromide was prepared by the slow addition of ethylmagnesium bromide to a saturated solution of purified acetylene in THF under a vigorous stream of acetylene. The ketone or aldehyde was subsequently added and the mixture refluxed over-night. Hydrolysis with dilute hydrochloric acid, extraction with ether, drying over anhydrous magnesium sulfate and distillation yielded the alcohols in 40-50% yields.

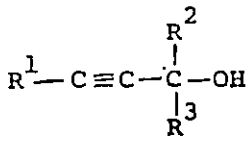
b- 3-isopropyl-2-methyl-4-pentyne-3-ol: Acetylene was purified by passing through a trap at -50°C, concentrated sulfuric acid, sodium hydroxide pellets and anhydrous calcium sulfate. It was then bubbled for ten minutes in 200 mls of dried THF before the addition of 0.5 moles of ethylmagnesium bromide in 250 mls of THF was started. The Grignard was added very slowly while a vigorous stream of acetylene was going through the reaction mixture. The solution turned dark brown while ethane was evolved. Subsequently, 2,4-dimethyl-3-pentanone (0.3 moles) was added and the mixture refluxed overnight. Normal acidic work up and distillation under normal pressure yielded the desired alcohol in 62% yield (Bp. 168-169 °C). The alcohols were characterized by their IR absorptions and their ^1H nmr spectrum.

5- DISUBSTITUTED PROPARGYL ALCOHOLS; $R^1CCCR^2R^3OH$:

a- General procedure: Monosubstituted acetylenes (from Chem. Sample co .) were treated with a 10% excess of n-butyllithium in tetrahydrofuran at 0°C under inert atmosphere. The resulting mixture was stirred for two hours and subsequently, a 10% excess of an aldehyde or ketone was added in THF and the mixture refluxed for another two hours. Saturated aqueous ammonium chloride hydrolysis, extraction with ether, evaporation of solvent and distillation yielded the pure alcohols in good yields.

b- 5-cyclohexyl-2-methyl-4-pentyne-3-ol: Cyclohexyl-ethyne (0.1 mole) was dissolved in 25 mls of dried THF under a nitrogen atmosphere. A 10% excess of 1.6 M n-BuLi in hexane was added at 0°C. The mixture was stirred for two hours and subsequently, 0.11 moles of isobutyraldehyde was added at room temperature. Reflux for two hours, normal work up and distillation under reduced pressure yielded the pure alcohol in 81% yield. (Bp. 120-122°C/14 mm). Yields, physical and spectroscopic properties of propargyl alcohols are reported in table(III).

TABLE III



R^1	R^2	R^3	Bp °C	Pres. mmHg	Yield %	IR absorptions cm^{-1} HC≡C	C≡C	OH	OH Free
H	H	H	113	760		3375s	2140w	3500sb	3700s
H	H	Me	108-110	760	32	3370s	2150w	3300-3700sb	3700s
H	H	Et	124-126	760	33	3380s	2150w	3400-3600sb	3700m
H	H	iPr	102-104	760	50	3380s	2140w	3510sb	3700m
H	H	tBu	139-145	760	30	3370s		3500sb	
H	H	Ph	117-120	10	61	3375s	2150w	3500sb	3700m
H	H	1-naphtyl	180-186	.35	35	3375s		3400-3600sb	3700m
H	Me	Me	110-112	760	47	3370s		3500mb	3680m
H	Me	Et	120	760	52	3375s		3500sb	3690m
H	Me	iPr	130-131	760	43	3370s		3500mb	3690m
H	Me	tBu	145-148	760	62	3365s		3550mb	3690m
H	Me	Ph	108-111	7	41	3370s	2140w	3500sb	
H	Et	Et	50-55	10	44	3380s		3500sb	3690m
H	iPr	iPr	168-169	760	62	3370s	2140w	3550sb	3700m
H	tBu	tBu	70-80	11	17	3370s	2140w		3700s
H	iBu	iBu	84-89	2	54	3370s		3550mb	3700m
H	Ph	Ph	150-160	.25	75	3370s	2145w	3600mb	
H	R^2= R^3= cyclohexyl		81-83	10	61	3375s	2140w	3400sb	3680m
H	R^2= R^3= 3-Mecyclohexyl		90-98	18	59	3365s		3400-3600mb	3680m
H	R^2= R^3= 4-tBucyclohexyl		Mp; 98-99		56	3370s		3500wb	3670m
H	R^2= R^3= d-camphor		Mp: 207.5-209		47	3375s		3500wb	3690m
H	R^2= R^3= d-fenchone		83-85	.25	46	3375s	2140w	3550mb	3695m
H	R^2= R^3= l-fenchone		107-110	10	40	3375s		3450-3660sb	3700m
cyclohexyl	H	iPr	120-121	12	81			3300-3600sb	3700m
Et	Et	Et	172-176	760	45		2265w	3400-3600sb	3700m
Et	Me	tBu	78-80	13	62		2270w	3450-3650sb	3710m
iPr	H	tBu	77-79	10	39			3400-3600sb	3695s
iPr	iPr	iPr	89-90.5	12	42		2265w	3550wb	3700m
tBu	H	Me						3300-3600wb	3710w
tBu	H	Et			60			3300-3600mb	3710w
tBu	H	iPr	176-178	760	60		2265w	3400-3600sb	3700m
tBu	H	tBu			40		2265w	3400-3600mb	3705w
tBu	Me	Et			45			3400-3600mb	3700w
tBu	Me	iPr	72-77	10	75		2280w	3400-3600sb	3705m
tBu	Me	tBu	80-84	10	68		2280w	3500-3600sb	3710s
iBu	iBu	iBu	138-139	4	58			3400-3600sb	3700m
2-methyl -butyl	H	iPr			60			3400-3600mb	3720w

6- ALLENES FROM PROPARGYL ALCOHOLS:

a- General procedure: Propargyl alcohols were converted to allenes according to known literature methods[41].

In a first stage the alcohols were converted into sulfinate esters. This was achieved by treating a dichloromethane solution of the alcohol at -50°C with an excess of triethylamine and methane sulfinyl chloride[42]. Meanwhile an organocuprate was prepared from an alkylmagnesium bromide or chloride, freshly prepared cuprous bromide[43] and anhydrous lithium bromide in THF at -50°C under inert atmosphere. Finally, the sulfinate ester in THF was carefully added to the vigorously stirred suspension of the organocuprate at -50°C. The mixture was subsequently stirred for one hour at room temperature and hydrolyzed in saturated aqueous ammonium chloride in the presence of a small quantity of sodium cyanide. Extraction with pentane, washing with water, drying over anhydrous magnesium sulfate and distillation yielded the allenes in 40-60% yield.

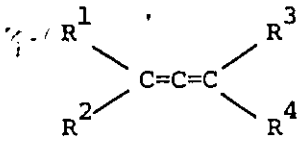
b- Sulfinate ester: 2,3-dimethyl-4-pentyne-3-ol (2.16g; .02 moles) was dissolved in 50 mls of dry CH_2Cl_2 and cooled to -60°C. Addition of 5 mls of triethylamine and .025 moles of CH_3SOCl gave at once a white precipitate indicating the formation of the amine hydrochloride. The mixture was further stirred one hour at room temperature. At this point, a yellow to orange slurry was obtained. This was worked up in 100 mls of water. Extraction with 50 mls of CH_2Cl_2 followed by drying and evaporation of the solvent yielded the crude ester in quantitative amount. It was characterized by its IR spectrum (disappearance of hydroxyl strech, HC≡C at 3375 cm^{-1}, C≡C at 2140 cm^{-1}) and its ^1H nmr spectrum (2.50-2.60 s, CH_3 , disappearance of hydroxyl signal). The ester was used without further purification in the next step of the synthesis.

c- Cyclohexyl-$CuMgBr_2$.LiBr: The Grignard was prepared in 50 mls of dry THF by reacting .035 moles of magnesium turnings with a small excess of bromocyclohexane. After cooling to room temperature it was added dropwise to a solution of 5.02 g of cuprous bromide and 3.045 g of lithium bromide in 50 mls of THF at -60°C under inert atmosphere. The mixture was allowed to stir for 15 mins before dropwise addition of the sulfinate ester in 25 mls of THF. The solution was brought to room temperature and stirred for one hour. Subsequently, it was hydrolyzed in 200 mls of saturated aqueous NH_4Cl in the presence of 1 g of NaCN. 50 mls of pentane were added and the mixture stirred vigorously for 30 mins. This was repeated and the combined extracts were washed with water, dried over magnesium sulfate and distilled under reduced pressure. The allene was obtained in 64% yield at 93-96°C/12mm.

NOTE: Allenes with aromatic substituents were found to be very sensitive to heat, oxygen and silica gel. Therefore they could not be purified. Polyaromatic allenes (e.g. with naphtyl groups) on the other hand were found to be stable and could be safely chromatographed.

Yields and physical properties of allenes obtained via the organocuprate route are reported in table (IV).

TABLE (IV)



$R^3C{\equiv}CR^1R^2OH$			$R^4CuMgBr_2.LiBr$	Yield	Bp.	Pressure
R^1	R^2	R^3	R^4	%	°C	mmHg
H	H	H	tBu	24	77-79	760
H	Me	H	iPr	26	74-75	760
H	Me	H	tBu	28	94-96	760
H	Et	H	iPr	28	100-104	760
H	Et	H	tBu	27	118-121	760
H	iPr	H	iPr	40	128-130	760
H	iPr	H	tBu	36	127-130	760
H	tBu	H	tBu	33		
H	1-naphtyl	H	1-naphtyl		mp: 239-242	
H	1-naphtyl	H	2-naphtyl	33	mp: 109-113	
H	1-naphtyl	H	9-phenanthryl			
Me	Me	H	Ph	34	86-90	9
Me	Me	H	p-tolyl	22		
Me	Me	H	p-chlorobenzene	35		
Me	Me	H	p-methoxybenzene	25		
Me	Et	H	Et	20	115-118	760
Me	Et	H	iPr	23	90-93	760
Me	Et	H	tBu			
Me	iPr	H	Et	42	125-128	760
Me	iPr	H	iPr	33	125-130	760
Me	iPr	H	tBu	45	135-136	760
Me	iPr	H	cyclohexyl	64	93-96	12
Me	tBu	H	Et	49	135-138	760
Me	tBu	H	iPr	45	125-135	760
Me	tBu	H	tBu	50	54-56	12
Me	tBu	H	cyclohexyl	60	103	12
Et	Et	H	Me			
Et	Et	H	iPr	16	41-45	12
Et	Et	H	tBu	34	45-46	12
Et	tBu	H	iPr	33	57-60	9
iPr	iPr	H	Me	20	92-95	760

iPr	iPr	H	Et	45	140-148	760
iPr	iPr	H	iPr	40	48-50	12
iPr	iPr	H	tBu	46	65-66	12
iPr	tBu	H	Et	20	50-55	7
iPr	tBu	H	iPr	29	60-70	9
iPr	tBu	H	tBu	18	74-75	9
tBu	tBu	H	iPr		120	7
tBu	2-methylpropyl	H	iPr	22	80-86	12
cyclohexyl		H	Et	27	72	16
cyclohexyl		H	iPr	53	65-69	12
cyclohexyl		H	tBu	38	73-75	12
4-tBucyclohexyl		H	tBu	27	111-115	12
Me	Et	tBu	iPr	27	62-64	9
Me	Et	tBu	tBu	29	64-68	9
Me	iPr	tBu	Me		54-60	14
Me	iPr	tBu	Et	21	66-67	9
Me	iPr	tBu	iPr	35	72-73	11
Me	iPr	tBu	tBu	20	75-80	12
Me	tBu	Et	iPr	25	64-74	10
Me	tBu	tBu	Et	31	71-73	7
Me	tBu	tBu	iPr	32	76-80	7
iPr	iPr	iPr	iPr	38	82-84	14

Spectral parameters of allenes are reported in APPENDIX I

7- α-ALLENIC ALCOHOLS FROM PROPARGYL ALCOHOLS

a- General procedure: Propargyl alcohols were treated with a 20% excess of 2,3-dihydropyran under mild acidic conditions. The corresponding tetrahydropyranates were purified by distillation under reduced pressure[44]. Boiling points and yields are reported in table (V).

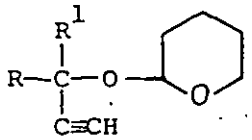
The protected alcohols were then coupled to aldehydes or ketones via a Grignard reaction using THF as solvent. This first involves exchange of the acetylenic hydrogen with ethylmagnesium bromide followed by the addition of the carbonyl substrate. Reaction times were typically of the order of 10 hours at room temperature. After acidic work up, the monoprotected diols were isolated via high vacuum distillation. In some cases they were used directly without purification.

Yields and boiling points are reported in table (VI).

Rearrangement of the acetylenic derivatives to allenic alcohols was achieved with lithium aluminum hydride in THF, according to the method of Landor and al.[45] Allenes were isolated by distillation under reduced pressure.

Yields and boiling points are reported in table(VII).

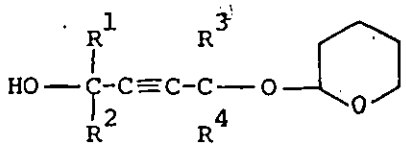
TABLE (V)



R	R^1	%yield	Bp°C	Pressure mmHg	IR;cm^{-1} (HC≡C)
H	H	92	178-181	760	3370s
H	Et	69	95-103	22	3370s
H	iPr	85	88-97	14	3370s
Me	Me	68	64.5-65.5	8	3370s
Me	Et	63	103-107	16	3380s
Me	iPr	42	118-125	21	3380s

$R=R^1$= 4-tBucyclohexyl				3380s
$R=R^1$= d,l-3-methylcyclohexyl	86	114-118	.3	3370s

TABLE (VI)

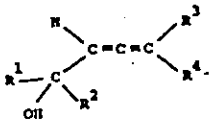


R^1	R^2	R^3	R^4	Yield %	Bp °C	Pressure mmHg
Me	Me	H	H	66	120-133	.6
Me	Et	H	H	61	125-128	.65
Me	iPr	H	H	69	137-138	.5
Me	tBu	H	H	60	137-139	.45
Me	Ph	H	H	87		
Et	Et	H	H	63	125-131	.4
iPr	iPr	H	H	55	153-156	.75
Me	H	H	Et	58	125-130	.3
iPr	H	H	Et	48	125-130	.25
Me	Me	H	Et	49	115-120	.25
Me	Et	H	Et	59	130-135	.25
Me	iPr	H	Et	41	130-135	.35
Me	tBu	H	Et	46	130-135	.3
Et	Et	H	Et	47	145-150	.27
iPr	iPr	H	Et	54	140-145	.25
Me	H	iPr	H	64	125-130	.85
Et	H	iPr	H	51	145-150	.24
iPr	H	iPr	H	61	140-144	.5
Me	Me	iPr	H	52	140-143	1.5
Me	Et	iPr	H	88	145-150	.5
Me	iPr	iPr	H	69	147-153	.4
Me	tBu	iPr	H	46	156-160	.75
Et	Et	iPr	H	54	148-152	1.6

iPr	iPr	iPr	H	77	165-170	.4
iPr	H	Me	Me	60	135-138	.4
Me	Et	Me	Me	75	113-116	.4
Me	iPr	Me	Me	60	120-129	.4
Me	tBu	Me	Me	64	125-128	.3
H	Et	Et	Me	84		
H	iPr	Et	Me	87		
Me	Et	Et	Me	85		
Me	iPr	Et	Me	67		
Me	tBu	Et	Me	72		
iPr	iPr	Et	Me	75		
H	iPr	iPr	Me	80		
Me	iPr	iPr	Me	80		
Me	tBu	iPr	Me	77		

Boiling points are not indicated when the material was not purified prior to reduction.

TABLE (VII)



R^1	R^2	R^3	R^4	Yield %	Bp °C	Pressure mmHg	IR, cm^{-1} (C=C=C)	IR, cm^{-1} (OH)	^1H nmr spectral parameters ppm downfield from TMS
H	H	H	H	25	125-128	760	1975s	3300-3600 sb	5.30q' (1H); 4.80m(1H); 4.30s(OH); 4.13m(2H)
Me	Me	H	H	35	85-88	760		3530 sb	
Me	Et	H	H	74	98-101	760	1980w	3400-3600 wb	5.20m (1H); 4.07m(2H); 2.63bs(OH); 2.17q(2H); 1.25s(3H); 1.12t(3H
Me	iPr	H	H	22	95-97	760	1970w	3450-3600 wb	4.97m (1H); 4.83s(2H); 1.03s(3H); 1.03d(6H)
Me	tBu	H	H	30			1970m	3500-3560 wb	4.87s (2H); 4.77s(1H); 1.25s(3H); 0.93s(9H)
Me	Ph	H	H	34	120-124	13		3400-3600 sb	
Et	Et	H	H	42			1980m	3520-3580 wb	5.00bs(1H); 4.87bs(2H); 1.02t(6H)
iPr	iPr	H	H	30	105-113	760	1985w	3400-3500 wb	4.83m (3H); 0.87dd(12H)
Me	H	Et	H	32	72-79	18	1980m	3400-3600 sb	
iPr	H	Et	H	79	125-128	45	1972m	3400-3550 wb	
Me	Me	Et	H	30	67-70	16		3400-3550 wb	
Me	Et	Et	H	54	75-80	17		3450-3600 wb	5.9-5.3m(2H); 2.10m(4H); 1.73s(3H); 1.00t(6H)
Me	iPr	Et	H	56	75-80	17		3480-3560 wb	5.9-5.2m(2H); 2.17m(3H); 1.72s(3H); 1.00d(6H); 1.00t(6H)
Me	tBu	Et	H	49	85-88	16		3480-3600 wb	6.0-5.6m(2H); 2.13m(2H); 1.73s(3H); 1.07s(9H); 1.07t(3H)
Et	Et	Et	H	63	85-90	14		3480-3600 wb	6.0-5.3m(2H); 2.33-1.83m(6H); 1.00dt(9H)
iPr	iPr	Et	H	50	95-100	15	1970w	3400-3700 wb	5.8-5.2m(2H); 2.97q' (2H); 2.1m(2H); 1.03d(12H); 1.00t(3H)
Me	H	iPr	H	36	110-115	760		3400-3600 wb	5.65-5.2m(2H); 3.63q' (1H); 1.73d(3H); 1.00d(6H)
Et	H	iPr	H	13	110-115	15	1973w	3400-3600 wb	5.23m(2H); 4.00q(1H); 1.63m(3H); 1.03d(6H); 1.00t(3H)
iPr	H	iPr	H	30	90-95	15		3400-3600 wb	5.65-5.20m(2H); 1.02d(6H); 1.00d(6H)
Me	Me	iPr	H	22	75-80	14		3400-3600 wb	5.47m(2H); 1.13m(6H); 1.00d(6H)
Me	Et	iPr	H	33	80-85	14	1975w	3400-3550 wb	5.65-5.0m(2H); 2.10m(2H); 1.72m(3H); 1.00d(6H); 1.00t(3H)
Me	iPr	iPr	H	32	90-98	13	1980w	3400-3600 wb	5.65-5.0m(2H); 1.70s(3H); 1.00d(12H)
Me	tBu	iPr	H	47	105-110	14	1975w	3400-3600 wb	5.65-5.0m(2H); 1.73s(3H); 1.07s(9H)
Et	Et	iPr	H	48	100-110	17	1975m	3400-3700 wb	5.5-5.0m(2H); 1.50m(4H); 1.05d(6H); 0.98t(6H)
iPr	iPr	iPr	H	45	115-120	16	1975m	3500-3700 wb	5.65-5.0m(2H); 2.2-1.35m(3H); 1.03d(12H); 0.90d(6H)
iPr	H	Me	Me	60	85-93	760	1985m	3400-3600 wb	5.27d(1H); 1.76s(3H); 1.07dd(6H); 1.73s(3H)
Me	Et	Me	Me	59	124-127	760	1972m	3460-3560 sb	5.00m(1H); 1.75s(3H); 1.70s(3H); 1.18s(3H); 0.97t(3H)
Me	iPr	Me	Me	76	127-133	760	1980w	3460-3560 sb	5.00m(1H); 1.78s(3H); 1.73s(3H); 1.27s(3H); 1.00d(6H)
Me	tBu	Me	Me	74	150-165	760	1985w	3440-3600 wb	5.13m(1H); 1.73s(3H); 1.70s(3H); 1.26s(3H); 0.92s(9H);
iPr	iPr	Me	Me	20	85-94	10	1985m	3460-3600 sb	4.93m(1H); 1.78s(3H); 1.73s(3H); 0.97dd(12H)
H	Et	Et	Me	10	95-100	5	1985w	3400-3650 sb	
H	iPr	Et	Me	24	85-90	3	1985w	3400-3600 sb	5.9-5.4m(1H); 2.10m(3H); 1.72s(3H); 1.00d(6H); 1.00t(3H)
Me	Et	Et	Me	44	100-105	3		3480-3650 wb	
Me	iPr	Et	Me	56	90-94	20		3480-3600 sb	
Me	tBu	Et	Me	54	97-100	19		3400-3600 wb	6.0m(1H); 2.1m(2H); 1.73d(3H); 1.05d (12H)
iPr	iPr	Et	Me	45	116-120	14	1980w	3400-3600 wb	
H	iPr	iPr	Me	28	100-105	14	1972m	3400-3700 wb	5.17m(1H); 3.78t(1H); 1.73d(3H); 1.03d(6H); 0.93d(6H);
Me	iPr	iPr	Me	45	105-108	14		3480-3600 wb	
Me	tBu	iPr	Me	37	108-113	21		3400-3700 wb	6.1-5.7m(1H); 1.70s(3H); 1.20s(3H); 1.05s(9H); 1.05d(6H)
Et	Et	Et	Et	43			1975m	3400-3600 wb	
Me	tBu	4-tBucyclohexyl						3400-3600 wb	5.60-5.1m(1H); 2.3-1.0m(10H); 1.07s(3H); 1.03s&1.02s(9H)
R^1= R^2= R^3= R^4= 4-tBucyclohexyl								3400-3600 wb	5.07m(1H); 2.33-1.00m(19H); 0.88s(18H)

b- Preparation of 4-isopropyl-5-methyl-1,2-hexadiene-4-ol:

A 100 mls round bottomed flask was charged with 0.3 moles of propargyl alcohol (Aldrich chemical Co.) and 0.36 moles of 2,3-dihydropyran (Aldrich). The flask was equipped with a reflux condenser protected by a $CaCl_2$ drying tube. Upon addition of a crystal of p-toluenesulfonic acid an exothermic reaction started at once. The mixture was stirred for 30 mins. Anhydrous potassium carbonate (.5 g) was added and the slurry stirred overnight at room temperature. The product was decanted and distilled under normal pressure.

(Bp: 178-181°C; yield: 92%)

NOTE: In the case of more sterically hindered alcohols it was found necessary to heat the mixture to 50-60°C to affect the formation of the tetrahydropyranate.

Ethylmagnesium bromide was prepared in THF from 0.018 moles of magnesium turnings and 0.02 moles of ethyl bromide. 0.015 moles of the tetrahydropyranate was added to the Grignard and the mixture stirred 30 mins at room temperature. This was followed by the addition of 1.71g of diisopropyl ketone and reflux overnight. The reaction mixture was worked up in saturated aqueous ammonium chloride and extracted with ether. After washing and drying over $MgSO_4$, the solvent was evaporated and the product distilled under high vacuum (Bp: 153-156°C/.75 mmHg; yield: 55%). IR shows disappearance of HC≡C stretch and strong hydroxyl band.

The acetylenic derivative was added to 0.00825 moles (0.313lg) of lithiumaluminum hydride in 30 mls of dried THF. The mixture was refluxed overnight and worked up in 25% aqueous HCl followed by extraction with ether, washing and drying over $MgSO_4$. The product was recovered by distillation under normal pressure: Bp 105-113°C; 30% yield.

IR shows weak absorption in the 1975 cm^{-1} region and a strong hydroxyl band.

c- 1,2-butadiene-4-ol:

4-chloro-2-butyne-1-ol was prepared according to the method of Bailey and Fujiwara[46] and converted to the allenic alcohol following a procedure by Bailey and Pfeifer[47].

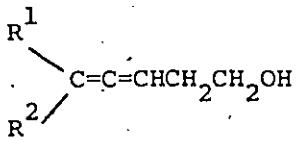
Found, Bp: 125-128°C; yield: 23%

d- β-allenic alcohols:

They were prepared according to the same procedure as for the α-allenic alcohols except that ethylene oxide was condensed to the tetrahydropyranates instead of aldehydes or ketones.

Yields, boiling points and spectral properties are reported in table (VIII).

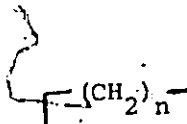
TABLE (VIII)



R^1	R^2	Yield %	Bp °C	Pressure mmHg	IR, cm^{-1} C=C=C	IR, cm^{-1} OH
H	H	32	100-110	760	1974m	3300-3600sb
H	Et	36	150-155	760		
H	iPr	23				
Me	Et	26	110-115	760	1978w	3300-3700sb
Me	tBu	27	105-110	11	1978w	3300-3700sb
Et	Et	27	107-112	8	1974w	3300-3700sb

TABLE (VIII) continued

R^1	R^2	^1H nmr spectral parameters ppm downfield from TMS
H	Et	5.10m(2H);4.17-3.17m(2H);2.00-1.33m;1.00t(3H)
H	iPr	5.13m(2H);4.00-3.33m;2.00-1.33m;1.00d(6H)
Et	Et	5.27m(1H);3.58m(2H);2.00-1.33m;1.00t(6H)

8- CYCLIC ALLENES:  n = 8,9

Cyclodecanone (1g) and cycloundecanone (1g) were reduced to the alcohol stage with sodium borohydride (.3g) by stirring overnight at room temperature in 10 mls of absolute ethanol. The reaction mixtures were treated with 20 mls of 10% NaOH and extracted with CH_2Cl_2. After drying and evaporation of the solvent, the alcohols were obtained in quantitative yields. IR shows strong OH absorption and no carbonyl band.

The alcohols were dehydrated in benzene (30 mls) with 5 mls of 85% orthophosphoric acid by refluxing for 4 hours. The benzene solutions were washed with water and saturated sodium bicarbonate, dried and the solvent evaporated yielding the corresponding olefins in quantitative amounts.
IR shows no OH band; ^1H nmr contains olefinic signals in 5.0-6.0 ppm region.

The alkenes were treated with a 4 fold excess of potassium t-butoxide and a 2 fold excess of bromoform in 20 mls of pentane according to the usual procedure. The corresponding gem-dibromocyclopropanes were obtained in good yields. They were converted to the allenes with methyllithium as described previously.

1,2-cycloundecadiene: 50% overall yield Bp: 175-180°C/18mmHg

1,2-cyclododecadiene: 60% " "

9- CHLOROALLENES, $ClCH=C=CR^1R^2$:

Chloroallenes were prepared from:

* 3-isopropyl-4-methyl-1-pentyne-3-ol
* 3,4,4-trimethyl-1-pentyne-3-ol
* 3,3-diphenyl-1-propyne-3-ol

The propargyl alcohol was dissolved in 25 mls of dioxane in a round bottomed flask equipped with a reflux condenser protected from moisture by a calcium chloride drying tube. A 30% excess of thionyl chloride was added dropwise and the mixture refluxed for two hours. The intensely coloured reation mixture was worked up with saturated aqueous sodium bicarbonate and ether. After drying the products were recovered by distillation under reduced pressure. The allenes were contaminated with alkenyne products but could be purified by distillation or column chromatography on silica with CH_2Cl_2 as eluant.

1-chloro-3-isopropyl-4-methyl-1,2-pentadiene: 50% yield; Bp: 65-66°C/20mm

1-chloro-3,3-diphenyl-1,2-propadiene: Mp 190-194°C

1-chloro-3,4,4-trimethyl-1,2-pentadiene: Bp 117-120°C

NOTE: In the case of 3,4,4-trimethyl-1-pentyne-3-ol and 3,3-diphenyl-1-propyne-3-ol, one equivalent of pyridine was used to absorb the HCl produced in the reaction.

10- BIS(2,4-DINITROPHENYL)SULFIDE:

This was prepared according to a revised procedure for bis(o-nitrophenyl) disulfide[48]. Sodium disulfide (0.1 moles) was prepared as follows: Sodium monosulfide nonahydrate (0.1 moles) was dissolved in 200 mls of hot 95% ethanol. An equimolar amount of sulfur (0.1 moles) was added and the mixture was stirred until a clear red-brownish solution resulted (15 mins). Meanwhile a 30% excess of 2,4-dinitrochlorobenzene was dissolved in 30 mls of hot ethanol. The sodium disulfide solution was slowly added and the mixture refluxed for two hours. The precipitated mixture of organic disulfide and sodium chloride was washed with water and a few mls of cold ethanol. The product was dried overnight under vacuum.

Pure bis(2,4-dinitrophenyl)disulfide (Mp: 245-290°C dec.) was obtained in 63% yield. (Ref. Mp is 240-280°C dec.)

11- 2,4-DINITROBENZENESULFENYL CHLORIDE; (2,4-DNBSC):

This material was prepared following the procedure described by D.Lawson and N.Kharasch[49]. Bis(2,4-dinitrophenyl)disulfide (3.0g) was suspended in 100 mls of CCl_4. A catalytic amount of pyridine (0.5 mls) and a large excess of redistilled sulfuryl chloride (10 mls) were added and the mixture refluxed for two hours. The resulting clear yellow solution was treated with decolorizing charcoal, filtered and concentrated by evaporation of the solvent. Cooling and recrystallization from hot CCl_4 gave pure 2,4-DNBSC as yellow needles (Mp: 96-96.5°C) in 45% yield. Product of lower purity could be recovered from the mother liquor. (Mp: 97-98°C).

12- 2-NITRO-4-CHLOROBENZENESULFENYL CHLORIDE[50]:

p-dichlorobenzene (20g) was nitrated using 10 mls of concentrated nitric acid and 12 mls of conc. sulfuric acid by stirring overnight at 135°C. The mixture was poured over ice, washed with Na_2CO_3 and water and recrystalized from 95% ethanol. 2,5-dichloronitrobenzene was obtained in 76% yield (Mp: 53°C). This material was converted to the sulfenyl chloride using the same procedure as for 2,4-dinitrobenzenesulfenyl chloride.

Disulfide:	68% yield	Mp: 214-218°C	Ref. Mp: 212-218°C
Sulfenyl chloride:	61% yield	Mp: 98-98.5°C	Ref. Mp: 98°C

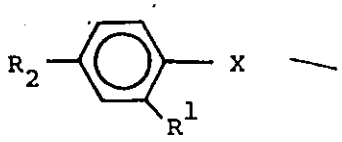
13- 2-METHYL-4-NITRO, 4-METHYL-2-NITRO AND 4-METHOXY-2-NITRO-BENZENESULFENYL CHLORIDE FROM ANILINES:

Anilines were first converted to the aryl bromides via a Sandmeyer reaction. These then yielded the sulfenyl chlorides by the usual route.

The aniline (0.1 moles) was heated in 25 mls of 1:1 aqueous sulfuric acid. Cuprous bromide was prepared by refluxing a mixture of cupric sulfate (0.04 moles), copper metal turnings (0.032 moles) and sodium bromide (0.15 moles) in 100 mls of water containing 2 mls of conc. sulfuric acid. The aniline solution was cooled to 0°C and sodium nitrite (0.11 moles) was slowly added. The resulting clear solution was poured into the slurry of cuprous bromide previously cooled to 0°C. Diazotization was accomplished by heating the mixture at 60°C for 2 hours. Extraction with CH_2Cl_2, drying over $MgSO_4$, evaporation of the solvent and distillation under high vacuum or recrystallization from ethanol yielded the pure bromides.

These were converted to the disulfides and chlorinated in the usual manner to give the corresponding sulfenyl chlorides. (See table IX).

TABLE(IX)



R^1	R^2	X	Yield %	Bp °C/mm	Mp °C
NO_2	CH_3O	Br	55	128-130/.15	
NO_2	CH_3O	disulfide	74		140-148
NO_2	CH_3O	SCl	72		106-107 dec.
NO_2	CH_3	Br	55	115/.8	
NO_2	CH_3	disulfide	51		194-194.5
NO_2	CH_3	SCl	69		85-90
CH_3	NO_2	Br	45		75-77
CH_3	NO_2	disulfide	95		157-163
CH_3	NO_2	SCl			40-41

14- 2-NITROBENZENESULFENYL CHLORIDE:

Available from Aldrich Chemical Co.

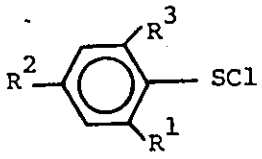
Recrystallization from CCl_4 Mp: 76°C (Lit. 74.5-75°C)

15- p-METHYL, o-METHYL, p-ETHYL, o-&p-METHOXY, p-CHLORO, 2,4-DIMETHYL, 2,6-DIMETHYL, 2,4,6-TRIMETHYL AND o- & p-TRIFLUOROMETHANE-BENZENESULFENYL CHLORIDE:

The corresponding bromides were converted to the thiols by a Grignard reaction with elemental sulfur and subsequently chlorinated to the sulfenyl chloride using chlorine gas at low temperature.

The Grignard was prepared in THF from 0.030 moles of Mg turnings and 0.030 moles of an aromatic bromide. Sulfur (0.030 moles) was added and the mixture stirred overnight at room temperature. Hydrolysis with cold dilute HCl, extraction with ether, drying and evaporation of the solvent yielded the corresponding thiol. The thiol was dissolved in 50 mls of dry carbon tetrachloride and cooled to 0°C before chlorine gas was bubbled through the solution for 15 mins.
The solvent was evaporated from the red solution and the residue distilled under reduced pressure. Yields and boiling points are reported in table (X).

TABLE (X)



R^1	R^2	R^3	Yield %	Bp °C	Pressure mmHg
H	CH_3	H	60	85	1
H	Cl	H	80	71-72	.12
H	Et	H	25	78-82	.25
H	OCH_3	H	38	125-140	.1
CH_3	H	H	53	85-100	.5
H	H	H	95		

2,4-dimethyl, 2,4,6-trimethyl, para- and ortho-trifluoromethane- benzenesulfenyl chloride were used without purification due to unstability of material. p-chloro and p-methyl thiophenol were commercially available from Aldrich Chemical Co.

16- p-NITROBENZENESULFENYL CHLORIDE:

Commercial p-nitrothiophenol (Aldrich) was chlorinated in dry dichloromethane at 0°C. No attempt was made to purify the unstable sulfenyl chloride which was used immediately after preparation.

17- 2,4,6-TRIISOPROPYLBENZENESULFENYL CHLORIDE:

The commercially available (Aldrich Chem. Co.) sulfonyl chloride was reduced to the corresponding thiol following a standard procedure[51]. Distillation under high vacuum afforded the thiol along with some triisopropylbenzene. The thiol was chlorinated at 0°C in CCl_4 and the orange sulfenyl chloride purified by high vacuum distillation. (Bp: 130-136°C/.45mm).

18- 1-NAPHTYL AND 9-PHENANTHRYL SULFENYL CHLORIDES:

The bromides (Aldrich Chem. Co.) were converted to the corresponding thiols via a Grignard reaction as described before.

1-naphtyl thiol: 84% yield (brownish oil)

9-phenanthrylthiol: Mp 170-176°C (light yellow crystals)

A dichloromethane solution of the thiol was stirred 30 mins at room temperature with one equivalent of N-chlorosuccinimide. The solution progressively took an orange coloration.

The solvent was evaporated and the sulfenyl chloride was separated from the succinimide by three sucessive washings with anhydrous ether. Evaporation of the solvent yielded dark red oils that could not be purified.

The sulfenyl chlorides were found to be very sensitive to atmospheric moisture.

19- BENZENESELENYL AND 2,4,6-TRIMETHYLBENZENESELENYL BROMIDES:

The diselenides were first prepared from the corresponding aryl bromides via a Grignard reaction.

To Mg turnings (0.05 moles) in 25 mls of dried THF was added 0.05 moles of the aryl bromide. The reaction was initiated with a crystal of iodine and gentle warming. Powdered selenium (0.05 moles) was then carefully introduced and the mixture refluxed for two hours. This was followed by a dilute aqueous HCl work up, extraction with ether, washing and drying over $MgSO_4$.

The remaining selenols were oxidized to the diselenide stage by passing air through the etheral extracts.

The products were crystalized from ethanol as light orange needles.

Bis(2,4,6-trimethylbenzene)diselenide: 58% yield; Mp 113.5-115°C

The diselenides were subsequently brominated at 0°C in CCl_4 using elemental bromine. The deep purple solutions were stirred at room temperature for 2 hours and the solvent evaporated.

Benzeneselenyl bromide: 80% yield

2,4,6-trimethylbenzeneselenyl bromide: 91% yield Mp 66-67°C

20- 2,4,6-TRIMETHYLBENZENESULFENYL BROMIDE:

This material was prepared following the procedure for the selenium derivative.

Aryl bromide: 0.05 moles

Magnesium: 0.05 moles

Sulfur: 0.05 moles

The thiol was brominated at room temperature in CH_2Cl_2 using elemental bromine. The product was obtained as a dark fuming red oil and could not be purified.

21- ^{77}SELENIUM ENRICHED BENZENESELENYL BROMIDE:

94.38 atom% ^{77}Se was obtained from M.S.D. Isotopes. 50 mg of ^{77}Se was diluted to 200 mg with natural selenium and added to 2.2 mls of 1.76 M phenyllithium in benzene under inert atmosphere. 20 mls of dried THF were used as cosolvent. The selenium dissolved within 30 mins at room temperature giving a deep orange solution. This was worked up in saturated NH_4Cl and the product was extracted with ether. To ensure complete oxidation to the diselenide, air was passed through the solution for one hour. Evaporation of the solvent gave the diselenide as yellow needles. (yield: 84%).

The diselenide was brominated at room temperature with bromine in dry CH_2Cl_2. Yield after evaporation of solvent was 66%.

22- ADDITION OF 2,4-DNBSC TO ALLENES:

a- General procedure: Equimolar amounts of the allenes and 2,4-DNBSC were dissolved in CH_2Cl_2. The clear yellow solution was stirred at room temperature for a period of 5-6 days. A slight darkening of the solution usually occured. The solvent was evaporated and the resulting orange oil was dried overnight under high vacuum. This usually yielded a mixture of oil and crystals which was analyzed by ^1H and ^{13}C nmr spectroscopy.

b- E and Z-5-chloro-3-hepten-4-yl-2',4'-dinitrophenyl sulfide: 3,4-heptadiene (1.41 mmoles) and 2,4-DNBSC (1.40 mmoles) were dissolved in 10 mls of CH_2Cl_2. After stirring for 6 days at room temperature, the solvent was evaporated. The pure adduct was obtained in quantitative yield and was shown by nmr to consist of a mixture of E and Z isomers in a 80:20 ratio.

23- ADDITION OF BENZENESELENYL CHLORIDE TO ALLENES:

Benzeneselenyl chloride was commercially available from Aldrich Chem. Co.

a- General procedure: The allene was dissolved in 20 mls of dry CH_2Cl_2. An equivalent of PhSeCl was added in 2 mls of the same solvent. The addition was carried out such that the allene was always retained in excess. Instantaneous decolorization of the selenyl chloride occured giving an essentially colorless solution. The solvent was immediatly evaporated at a temperature of 45°C. Traces of dichloromethane were azeotroped off using $CHCl_3$-D. After drying under high vacuum for 2 hours, the yellowish oil was analyzed within 24 hours. (Samples were stored at low temperature to prevent product isomerization). Control experiments run in CD_2Cl_2/TMS and subjected to immediate nmr analysis showed the same product distribution.

b- E- and Z-5-chloro-3-hepten-4-yl-phenyl selenide:

3,4-heptadiene (6.00 mmoles) in 20 mls of CH_2Cl_2 was reacted with an equivalent amount of PhSeCl. After normal work up, the residual oil which corresponded to a quantitative yield, was analyzed by ^1H and ^{13}C nmr and consisted of a mixture of the E and Z isomers in a 40:60 ratio.

24- ADDITION OF ARYLBENZENESULFENYL HALIDES TO ALLENES:

The following arylsulfenyl halides gave addition products with allenes which were found to isomerize rapidly at room temperature under the experimental conditions. In order to obtain kinetic product distribution, these reactions were carried out in nmr tubes at o°C and the ^1H nmr spectra were recorded immediately

- 4-methoxybenzenesulfenyl chloride
- 4-methyl- " "
- 4-chloro- " "
- 2,4-dimethyl- " "
- 2,4,6-trimethylbenzenesulfenyl chloride
- 2,4,6-triisopropyl " "
- 4-trifluoromethyl- " "
- 2-trifluoromethyl- " "
- 9-phenanthrylbenzenesulfenyl chloride
- 1-naphtyl " "
- 2-methyl- " "
- benzenesulfenyl chloride
- " " bromide
- 2,4,6-trimethylbenzenesulfenyl bromide

The following arylsulfenyl chlorides were run as previously described under "addition of 2,4-DNBSC to allenes".

- 4-nitrobenzenesulfenyl chloride
- 2-nitro " " "
- 4-chloro-2-nitrobenzenesulfenyl chloride
- 4-methyl-2- " " "
- 4-methoxy-2- " " "

25- ADDITION OF ARYLSELENYL BROMIDES TO ALLENES:

Benzeneselenyl and 2,4,6-trimethylbenzeneselenyl bromides were reacted with allenes under the same conditions as described under "addition of PhSeCl to allenes".

26- FORMATION OF 2,5-DIHYDROFURANS:

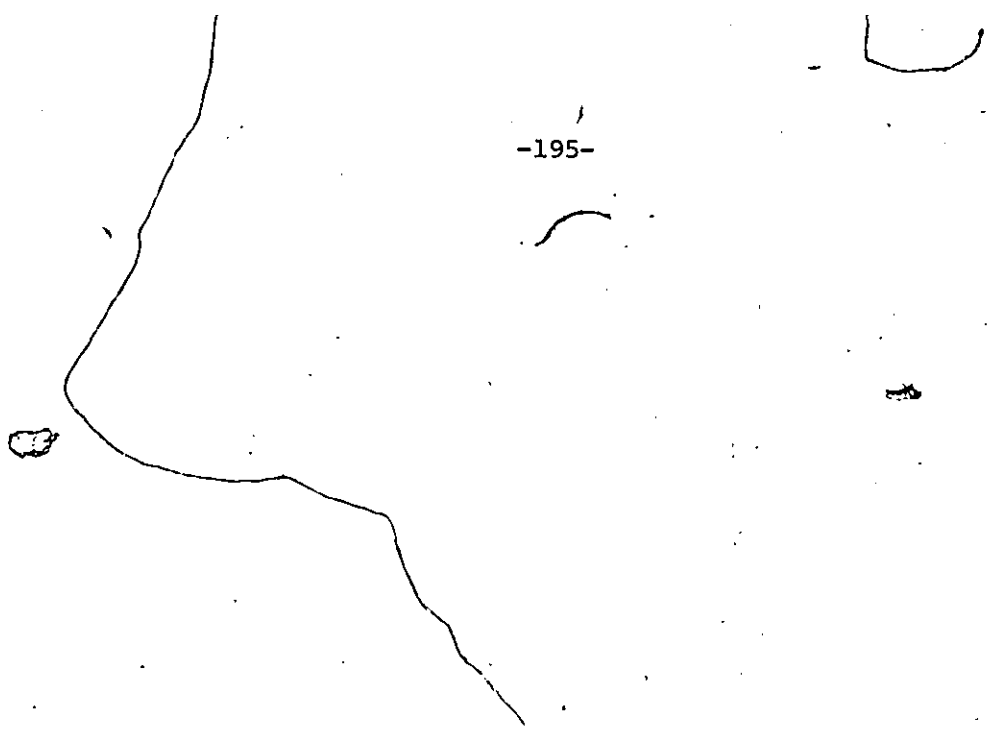
ADDITION OF PhSCl, PhSeCl AND IODINE TO α-ALLENIC ALCOHOLS:

All reactions were spontaneous in dichloromethane at room temperature. Except for iodine adducts, all products were stable. Reactions were performed by adding one equivalent of the electrophile to one equivalent of the allene in 20 mls of CH_2Cl_2. The mixtures were decolorized instantaneously except for iodine which gave deep purple products. The solvent was evaporated after stirring at room temperature for 5 mins. IR spectra showed disappearance of OH absorption and structures were revealed by ^{1}H, ^{13}C nmr and Mass spectroscopy.

In the case of terminal allenic alcohols, it was found necessary to add one equivalent of triethylamine to the reaction mixture in order to promote cyclisation.

In most cases, yields were quantitative.

2,5- dihydrofuran derivatives could be purified by column chromatography on silica gel if necessary.



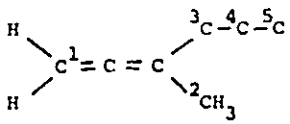
APPENDIX

APPENDIX I

IR AND ^1H NMR SPECTRAL PARAMETERS FOR ALLENES

TABLE 1

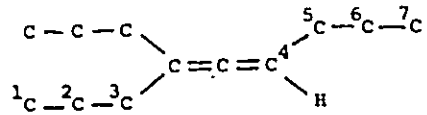
IR AND ^{1}H NMR PARAMETERS FOR TERMINAL ALLENES



$H_2C=C=CRCH_3$ R	H_1	$^2J_{1,1}$	H_2	$^5J_{1,2}$	H_3	$^5J_{1,3}$	H_4	$^3J_{3,4}$	H_5	$^3J_{4,5}$	IR cm^{-1} C=C=C
nPr	4,53h	3.4	1.67t	3.0					0.92t	6.2	1973
iPr	4.55q'	3.4	1.65t	3.4			2.1m		1.02d	6.8	1972
3-methyl-butyl	4.53m	2	1.63t	3.6			0.9d	6.0	1.03t	5.2	1971
iBu	4.50m	3.8	1.63t	3.8	1.8m		2.1m		0.92d	6.4	1975
tBu	4.28q	4.4	1.42t	3.8					0.93s		1968
neopentyl	4.57m	2	1.77t	3.2					0.97s		1971

TABLE 2

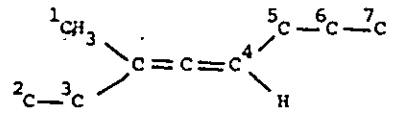
IR AND ^{1}H NMR SPECTRAL PARAMETERS FOR TRISUBSTITUTED ALLENES



RRC=C=CHR^1 R	R^1	H_2	$^3J_{2,3}$	H_3	$^5J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6	$^3J_{6,7}$	H_7	IR cm^{-1} C=C=C
Me	Et			1.67d	2.8	4.96m	7.7	1.97q'	7.6	0.98t			1981
Me	iPr			1.67d	3.0	4.93m		2.2m	7.0	0.97d			1981
Me	iBu			1.67d	2.8	4.83m					6.2	0.92d	1980
Me	tBu			1.67d	3.2	4.87m				1.00s			1979
Et	Et	1.00t	8.0	1.97dq	1.3	5.25m		1.97m	8.0	1.00t			1975
Et	iPr	1.00t	7.0	1.93dq		5.2m			6.8	1.00d			1975
Et	tBu	1.00t	7.0	1.97dq	2.6	5.17m				1.02s			
iPr	Me	1.00d	6.0		2.0	5.12tq	7.6	1.62d					1975
iPr	Et	1.00d	6.0		2.0	5.20tt	6.0	2.0m					1970
iPr	iPr	1.01d	6.7		2.0	5.22td	5.0			1.01d			1970
iPr	tBu	1.00d	6.9	2.0m	2.2	5.20t				1.02s			1971
C_6H_{11}	Et					4.9m			6.8	0.97t			1984
C_6H_{11}	iPr					4.9m			6.5	0.97d			1979
C_6H_{11}	tBu					4.9m				1.00s			1980

TABLE 3

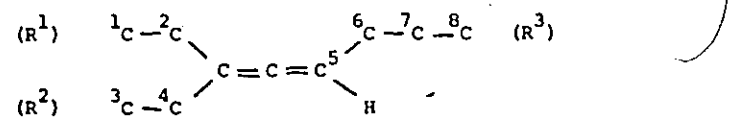
IR AND ^{1}H NMR SPECTRAL PARAMETERS FOR TRISUBSTITUTED ALLENES



$CH_3R^1C{=}C{=}CHR^3$ R^1	R^2	H_1	$^5J_{1,4}$	H_2	$^3J_{2,3}$	H_3	$^5J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6	IR cm^{-1} C=C=C
Et	Me	1.67d	2.0	0.97t	8.0	1.93dq	3.0	4.9m	7.2	1.60d			1985
Et	iPr	1.67d	3.0	0.97t	7.0		2.9	5.00m			7.0	0.97d	1979
Et	tBu	1.65d	3.0	0.98t	6.8	1.97dq	3.0	4.95m				1.00s	1980
iPr	Me	1.67d	3.7	1.00d	7.0	2.17m		5.07m	7.6	1.63d			1980
iPr	Et	1.67d	3.4	1.00d	6.2			5.05m					1980
iPr	iPr	1.67d	3.7	0.98d	7.0	2.1m		5.01m		2.1m	7.0	0.98d	1978
iPr	tBu	1.67d	3.5			1.8m	3.2	5.00q'				1.02s	1977
iPr	C_6H_{11}	1.67d	3.7	1.02d	7.2			5.03m					1975
tBu	Et	1.65d	3.3	1.03s				4.97m		1.85m			1975
tBu	iPr	1.67d	3.0	1.03s				5.03m			7.5	1.00d	1976
tBu	tBu	1.65d	2.9	1.03s				5.00q				1.00s	1977
tBu	C_6H_{11}	1.67d	3.3	1.03s				5.00m					1975
Et	Et	1.67d	3.0	0.97t	8.0			5.00m			8.0	0.97t	1980

TABLE 4

IR AND ^{1}H NMR SPECTRAL PARAMETERS FOR TRISUBSTITUTED ALLENES



R^1	$R^1R^2C{=}C{=}CHR^3$ R^2	R^3	H_1	H_3	$^5J_{4,5}$	H_5	$^3J_{5,6}$	H_6	$^3J_{6,7}$	H_7	IR cm^{-1} C=C=C
tBu	Et	iPr	1.03s		2.0	5.13dt	5.4		7.0	0.97d	1974
tBu	iPr	Et	1.06s			5.25t	6.0	2.07m			1970
tBu	iPr	iPr	1.07s	1.13d		5.22d	5.9		7.0	1.00d	1970
tBu	iPr	tBu	1.03s			5.14s				1.03s	1970
tBu	tBu	iPr	1.22s	1.22s		4.01d	5.8		7.0	0.93d	1973
secBu	tBu	iPr		1.05s		5.13d	5.9				1968
R^1= R^2= 4-$tBuC_6H_{10}$		tBu	ring tBu: 0.87s (cis + trans)			4.87m				1.00s	1982

TABLE 5

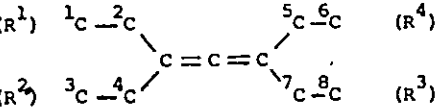
^{1}H NMR SPECTRAL PARAMETERS FOR 1,3-DISUBSTITUTED ALLENES

$$^1C-^2C-^3CH=C=CH^4-^5C-^6C$$

$R^1CH=C=CHR^2$														
R^1	R^2	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	$^5J_{2,4}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^5J_{3,5}$	H_6	$^3J_{5,6}$
Me	Me			1.63dd	5.6	5.2	5.03q'	5.6	5.03q'	5.6	1.63dd			
Et	Et	0.97t	5.8	1.97m	5.0		5.05q'	5.0	5.05q'	5.0	1.97m		0.97t	5.8
iPr	iPr	1.00d	6.8	2.2m	4.1		5.12t	4.1	5.12t	4.1	2.2m		1.00d	6.8
tBu	tBu	1.03s					5.17s		5.17s				1.03s	
Me	Et			1.95dd	6.0	4.0	5.00m		5.00m	5.2	2.0m		1.00t	7.0
Me	iPr			1.63dd	5.0	4.1	5.03q'		5.03q'	5.0	2.17m			
Me	tBu			1.65dd	6.0	4.0	5.13dq	2.0	5.05s				1.02s	
iPr	Et	0.98d	6.6	1.9m			5.02m		5.02m		1.9m		1.00t	7.0
iPr	tBu	0.90d	5.0			4.0	5.22d		5.22d	4.0			1.03s	
tBu	Et	1.00s					5.10m		5.10m		1.8m		1.00t	6.2

TABLE 6

^{1}H NMR SPECTRAL PARAMETERS FOR TETRASUBSTITUTED ALLENES



$R^1R^2C{=}C{=}CR^3R^4$

R^1	R^2	R^3	R^4	H_1	$^3J_{1,2}$	H_2	$^3J_{3,4}$	H_3	H_4	$^3J_{5,6}$	H_5	$^3J_{7,8}$	H_6	H_8
Me	Et	iPr	tBu			1.63s	7.0	1.17t	1.90q				1.00s	
Me	Et	tBu	tBu			1.66s		1.37t					1.17s	1.22s
Me	iPr	Me	tBu			1.73s					1.78s			1.26s
Me	iPr	Et	tBu			1.66s	6.4	0.99d		6.4			1.20t	1.03s
Me	iPr	tBu	iPr			1.70s	6.4	1.00d				6.4	1.03s	1.00d
Me	iPr	tBu	tBu			1.66s	6.4	0.93d					1.20s	1.20s
Et	iPr	Me	tBu	1.00t			7.0	1.00d			1.66s			1.08s
iPr	iPr	iPr	iPr	1.00d	6.7		6.7	1.00d		6.7		6.7	1.00d	1.00d
tBu	Et	Me	tBu	1.03s			7.4		1.93q		1.66s			1.03s
tBu	iPr	Me	tBu	1.03s					2.17m		1.66s			1.02s

APPENDIX II

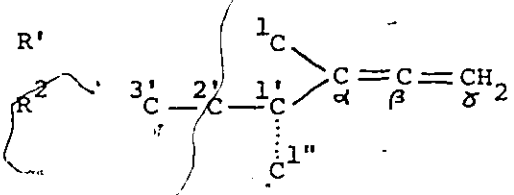
CARBON-13 NMR SPECTRAL PARAMETERS FOR ALLENES

TABLE 1 : 1,1-disubstituted allenes

TABLE 2 : Trisubstituted allenes

TABLE 1

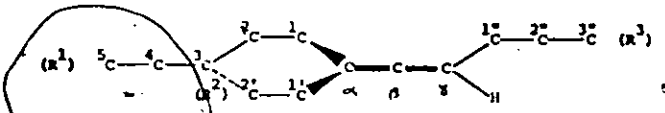
OBSERVED ^{13}C NMR CHEMICAL SHIFTS FOR A SERIES OF 1,1-DISUBSTITUTED ALLENES



R^1	R^2	C_α	C_β	C_γ	C_1	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{1''}$
Me	Me	93.8	206.9	72.5	20.0	20.0			
Me	nPr	98.3	206.4	73.7		35.8		13.8	
Me	sBu	102.7	206.0	74.0	18.8	38.7	27.8	11.6	16.5
Me	tBu	107.2	205.4	74.2	14.8	32.6	29.0		
Me	$tBuCH_2$	95.9	208.8	72.7	21.4	47.8	34.5	29.8	

TABLE 2

CARBON-13 CHEMICAL SHIFTS OF SOME TRISUBSTITUTED ALLENES



R^1	R^2	R^3	C_α	C_β	C_γ	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{1''}$	$C_{2''}$	$C_{1'''}$	$C_{2'''}$	$C_{3'''}$	$C_{4'''}$	$C_{5'''}$
Me	Me	Me	94.0	202.8	83.3	14.7			20.5		20.5				
Me	Me	Et	95.3	201.4	90.6	22.4	13.5		20.7		20.7				
Me	Me	iPr	95.8	200.3	96.6	28.4	22.6		20.8		20.8				
Me	Me	tBu	96.4	199.2	101.1	32.1	30.4		20.9		20.9				
Me	Me	iBu	93.9	202.6	87.4	38.9	28.5	22.2	20.6		20.6				
Me	Et	Me	100.8	202.3	85.6	15.2			27.5	12.5	19.3				
Me	Et	Et	101.7	200.5	92.6	22.5	13.5		27.1	12.3	19.3				
Me	Et	iPr	102.2	199.2	98.4	28.4	{22.63 22.53		27.0	12.2	19.3				
Me	Et	tBu	102.8	198.0	103.0	32.0	30.3		27.1	12.3	19.5				
Me	iPr	Me	104.8	201.3	85.4	14.9			32.2	{21.60 21.44	17.3				
Me	iPr	Et	106.2	199.9	92.8	22.5	13.5		32.1	{21.70 21.55	17.6				
Me	iPr	iPr	106.7	198.6	98.7	28.4	{22.75 22.57		32.0	{21.69 21.54	17.7				
Me	iPr	tBu	107.2	197.3	103.2	32.1	30.4		32.1	{21.70 21.55	17.8				
Me	tBu	Me	105.8	201.2	84.7	15.0			33.4	29.1	15.0				
Me	tBu	Et	108.8	200.0	92.0	22.3	13.2		33.1	29.1	15.1				
Me	tBu	iPr	109.4	198.8	98.0	28.4	{22.65 22.47		33.2	29.2	15.3				
Me	tBu	tBu	109.8	197.5	102.4	32.0	30.3		33.3	29.2	15.4				
Et	Et	Et	108.5	199.8	94.7	22.6	13.5		25.7	12.3	25.7	12.3			
Et	Et	iPr	109.1	198.5	100.7	28.5	22.7		25.8	12.4	25.8	12.4			
Et	Et	tBu	109.7	197.1	105.3	32.0	30.4		25.9	12.4	25.9	12.4			
Et	Et	$HOC(C_2H_5)_2$	113.4	196.9	101.1	74.0	33.3	8.2	26.0	12.5	26.0	12.5			
Et	tBu	iPr	116.6	197.8	101.0	28.4	22.59		33.4	29.5	20.0	12.9			
$-(CH_2)_5-$		Et	102.9	197.9	90.4	22.3	13.3		31.8	27.5	31.8	27.5	26.2		
"		iPr	103.5	196.8	96.3	28.2	22.5		32.0	27.6	32.1	27.8	26.3		
"		tBu	104.1	195.6	101.0	31.9	30.4		32.1	27.8	32.1	27.8	26.4		
tBu at C_3		tBu E	104.2	195.3	101.0	32.0	30.4		32.2	28.8	32.2	28.8	48.0		27.6
		tBu Z	103.9	195.3	101.1		30.4		32.2	28.8	32.2	28.8	48.0		27.6
iPr	iPr	Me	117.3	199.9	88.6	15.0			29.6	{22.50 22.21	29.6	{22.50 22.21			
iPr	iPr	Et	118.6	198.5	96.1	22.5	13.4		29.7	{22.57 22.31	29.7	{22.57 22.31			
iPr	iPr	iPr	119.1	197.2	102.2	28.5	22.7		29.8	{22.73 22.39	29.8	{22.73 22.39			
iPr	iPr	tBu	119.4	195.7	106.6	31.9	30.4		29.8	{22.73 22.35	29.8	{22.73 22.35			
iPr	tBu	Me	120.3	200.0	88.6	15.0			34.0	29.3	26.9	{24.85 24.31			
iPr	tBu	Et	121.4	198.8	96.1	22.5	13.4		34.0	29.4	26.8	{24.94 24.39			
iPr	tBu	iPr	121.5	197.2	101.8	26.5	{22.51 22.51		34.6	29.3	28.3	{24.87 24.21			
tBu	tBu	iPr	123.1	201.7	107.7	28.4	21.7		35.3	30.0	35.3	30.0			

APPENDIX III

^1H NMR SPECTRAL PARAMETERS FOR ADDUCTS OF ARENESULFENYL CHLORIDES WITH 1,3-DISUBSTITUTED ALLENES

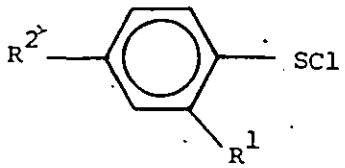


TABLE	R^1	R^2
1	H	OCH_3
2	H	CH_3
3	H	CF_3
4	H	NO_2
5	CH_3	H
6	CF_3	H
7	NO_2	H
8	NO_2	OCH_3
9	NO_2	Cl
10	NO_2	CH_3
11	NO_2	NO_2

APPENDIX III (CONTINUED)

CARBON-13 NMR SPECTRAL PARAMETERS FOR ADDUCTS OF

ARENESULFENYL CHLORIDES WITH 1,3-DISUBSTITUTED ALLENES

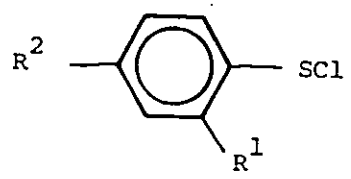
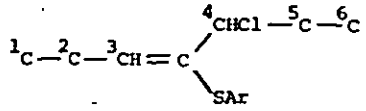
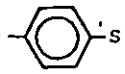


TABLE	R^1	R^2
12	NO_2	NO_2
13	NO_2	NO_2

TABLE 1

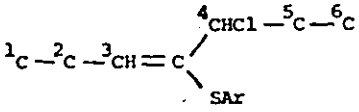


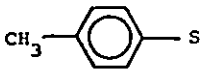
SAr = CH_3O 

$R^1CH=C<^{CHClR^2}_{SAr}$			Chemical shifts and proton-proton coupling constants								
R^1	R^2	Configuration	H_1	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	H_6
iPr	iPr	E	0.96d	2.74m		5.37d		4.55d	10.2	2.27m	0.94d
		Z			9.5	6.14d	1.5	4.18d	6.0		
tBu	tBu	E	1.19s			5.42s		5.19s			1.11s
Me	tBu	E			6.6	5.46q		4.88s			1.15s
		Z			6.9	6.43q		4.32s			1.04s
tBu	Me	E				5.70s		5.43q	7.0		
		Z									
iPr	Et	E			10.0	5.36d		4.34t	7.5		
		Z			9.3	6.10d					
Et	iPr	E			7.7	5.35t		4.55d	10.0		
		Z			7.0	6.30t	1.2	4.21d	6.0		
iPr	tBu	E	1.09d		10.0	5.21d		4.86s			1.14s
		Z	0.94d		9.5	6.18d		4.23s			
tBu	iPr	E	1.15s			5.50s		4.84d	10.4		0.95d
		Z									
tBu	Et	E	1.05s			5.64s		5.15t	7.5		
		Z									
Et	tBu	E			7.7	5.35t		4.85s			1.16s
		Z			7.2	6.34t		4.27s			1.13s

Methoxy protons : 3.78-3.79 ppm

TABLE 2

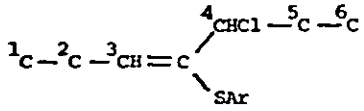


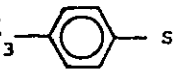
SAr = 

$R^1CH{=}C\langle^{CHClR^2}_{SAr}$			Chemical shifts and proton-proton coupling constants										
R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6
iPr	iPr	E	0.93d	6.8		10.2	5.40d		4.55d	10.2		6.8	0.95d
												6.8	1.06d
		Z	1.15d	6.5		10.0	6.23d	1.0	4.21d	5.5			0.90d
													0.98d
tBu	tBu	E	1.19s				5.62s		5.20s				1.13s
		Z											
Me	iPr	E			1.89d	7.3	5.57q		4.57d	10.0			
		Z			1.75d	6.8	6.47q	1.0	4.26d	6.8			
iPr	Me	E				10.0	5.63d		5.14q	6.9	1.65d		
		Z				10.0	6.23d	1.0	4.49q	6.0			
Me	tBu	E			1.88d	7.4	5.63q		4.87s				1.15s
		Z			1.75d	7.0	6.49q		4.34s				1.05s
tBu	Me	E	1.19s				5.89s		5.46q	6.8	1.64d		
		Z											
iPr	Et	E				10.0	5.57d		4.84t	7.5			
		Z				9.0	6.22d		4.22t	7.0			
Et	iPr	E				7.6	5.54t		4.55d	10.0			
		Z				7.5	6.40t						
iPr	tBu	E				10.1	5.44d		4.87s				1.03s
		Z					5.75d		4.24s				0.96s
tBu	iPr	E	1.14s				5.70s		4.86d	10.0			
		Z											
tBu	Et	E	1.17s				5.83s		5.16t	7.5			
		Z											
Et	tBu	E				8.0	5.56t	1.0	4.85s				1.15s
		Z				7.3	6.42t		4.30s				1.05s

Aromatic methyl groups : 2.31-2.32 ppm

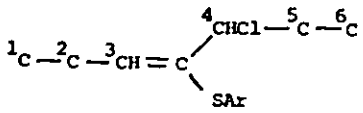
TABLE 3

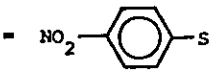


SAr = 

$R^1CH{=}C\langle^{CHClR^2}_{SAr}$			Chemical shifts and proton-proton coupling constants											
R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6
Me	Me	E			1.95d	7.1	6.20q		5.18q	6.8	1.66d		
		Z			1.85d	6.6	6.66q	1.5	4.69q	6.5	1.61d		
Et	Et	E	1.00t	7.6	2.34m	7.5	6.12t		4.87t	7.5	1.97m	7.5	0.97t
		Z				7.5	6.54t	1.8	4.41t	7.0			
iPr	iPr	E	1.15d 1.09d	8.0 6.3		10.2	5.85d		4.60d	10.0		6.5 8.0	1.06d 1.00d
		Z				9.8	6.40dd	2.0	4.24dd				
tBu	tBu	E	1.21s				5.98s		5.22s				1.15s
		Z											
Me	Et	E			1.93d	7.5	6.15q		4.79t	7.5		6.9	0.98t
		Z			1.86d	7.0	6.62q		4.44t	7.0		6.9	0.98t
Et	Me	E	1.14t	7.6		8.0	6.13t		5.17q	6.9	1.62d		
		Z	1.01t	7.5		7.5	6.55t		4.66q	7.1	1.67d		
Me	iPr	E			1.90d	7.5	6.08q		4.60d	10.0			
		Z			1.87d	7.0	6.63q	2.0	4.29d	6.8			
iPr	Me	E				10.0	5.95d		5.19q	6.8	1.63d		
		Z				9.2	6.40d						
Me	tBu	E				7.5	6.14q		4.90s				1.12s
		Z				7.0	6.64q		4.38s				1.06s
tBu	Me	E	1.26s				6.18s		5.48q	6.8			
		Z											
iPr	Et	E				10.0	5.93d		4.88t	7.5			
		Z				9.5	6.37d						
Et	iPr	E				7.5	6.01t		4.59d	10.0			
		Z				7.5	6.55t	2.1	4.27d				
iPr	tBu	E				10.3	5.84d		4.89s				1.13s
		Z				9.2	6.41d		4.27s				1.13s
tBu	iPr	E	1.23s				6.08s		4.89d	10.0		6.5 6.7	1.04d 1.02d
tBu	Et	E	1.25s				6.18s		5.19t	7.4			
Et	tBu	E				7.5	6.04t		4.87s				1.12s
		Z				7.0	6.58t		4.34s				1.01s

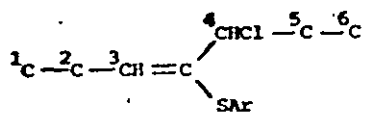
TABLE 4

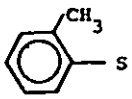


SAr = 

$R^1CH{=}C(SAr)CHClR^2$			Chemical shifts and proton-proton coupling constants										
R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6
Me	Me	E			2.03d	7.5	6.35q		5.25q	7.0	1.62d		
		Z			1.86d	6.8	6.74q		4.78q	6.8	1.69d		
Et	Et	E	1.11t	7.5	2.39m	7.7	6.25t		4.90t	7.5	1.96m		
		Z				7.0	6.59t		4.46t	7.0			
iPr	iPr	E	1.16d 1.11d	6.5 6.7	2.86m	10.0	6.00d		4.64d	10.0	2.19m	6.5	1.07d
		Z				9.9	6.44dd	1.2	4.26d	6.5			
tBu	tBu	E	1.25s				6.10s		5.23s				1.15s
Me	Et	E			2.01d	7.2	6.35q		4.93t	7.2		7.6	1.06t
		Z			1.87d	6.8	6.71q		4.49t	7.0		7.6	0.99t
Et	Me	E	1.14t	7.5	2.42q'	8.0	6.25t		5.21q	6.9	1.63d		
		Z	1.02t	7.7		7.5	6.63t	1.5	4.73q	6.9	1.69d		
Me	iPr	E			1.97d	7.3	6.31q		4.62d	10.0			
		Z				7.0	6.69dq	1.7	4.33d	7.5			
iPr	Me	E				10.2	6.06d		5.25q	6.9	1.62d		
		Z				9.8	6.46d				1.67d		
Me	tBu	E			1.97d	7.3	6.36q		4.94s				1.12s
		Z			1.87d	7.0	6.73q		4.42s				1.07s
tBu	Me	E	1.30s				6.30s		5.52q	6.7	1.63d		
iPr	Et	E				10.3	6.07d		4.92t	7.4			
		Z				10.0	6.43d	1.5	4.41t	6.8			
Et	iPr	E				7.6	6.20t		4.62d	10.0			
		Z				7.1	6.60t	1.8	4.29d	7.0			
iPr	tBu	E				10.5	5.98d		4.91s				1.11s
		Z				10.0	6.46d		4.30s				
tBu	iPr	E	1.27s				6.21s		4.89d	10.0			
tBu	Et	E	1.28s				6.29s		5.22t	7.5	1.91m	7.5	1.07t
		Z					6.70s						
Et	tBu	E			2.38m	8.0	6.21t		4.92s				1.11s
		Z				7.5	6.62t		4.38s				

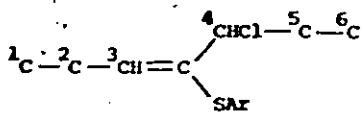
TABLE 5

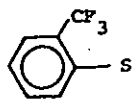


SAr = 

$R^1CH{=}C\langle^{CHClR^2}_{SAr}$			Chemical shifts and proton-proton coupling constants											
R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6
Me	Me	E			1.85dd	7.0	5.55dq		5.16dq	6.9	1.65dd		
		Z			1.81d	7.0	6.58q		4.56q	7.0	1.68d		
Et	Et	E	1.00t	7.7		7.8	5.37dd	1.6	4.84dd	7.5		7.7	0.96t
		Z	1.00t	7.7		7.0	6.45t					7.7	0.96t
iPr	iPr	E				10.0	5.09dd	1.9	4.57dd	10.0			
		Z				9.5	6.32d		4.17d	9.0			
tBu	tBu	E	1.21s				5.24d	2.0	5.12d (J=1Hz)				1.12s
		Z											
Me	iPr	E							5.06d	10.0		6.8	0.99d
		Z				7.0	6.55q	2.0	4.58dd	10.3			
iPr	Me	E				9.5	5.31d						
		Z				9.9	6.30d						
iPr	Et	E							4.85t	7.3			
		Z				11.0	6.28d						
Et	iPr	E							4.55d	10.0			
		Z				7.0	6.57t						
iPr	tBu	E					5.14dd		4.88s				
		Z				9.6	6.33d		4.36d	9.0			
tBu	iPr	E			(J= 5.8Hz)		5.36d	1.5	4.88d	10.5			
		Z					6.21s						
tBu	Et	E			(J= 3.8Hz)		5.51d	1.5	5.18t	7.5			
		Z					6.21s						
Et	tBu	E				6.0	5.28t	1.5	4.86d				
		Z				7.5	6.49t						

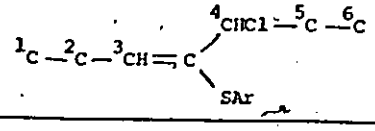
TABLE 6

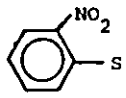


SAr = 

$R^1CH=C(CHClR^2)SAr$			Chemical shifts and proton-proton coupling constants				
R^1	R^2	Configuration	$^3J_{2,3}$	H_3	$^3J_{4,5}$	H_4	Other protons
Me	Me	E	7.0	5.08q		4.55m	
		Z	7.2	6.06q		4.55m	
Et	Et	E	7.7	5.94t	7.4	4.76t	
		Z	7.6	6.24t	6.6	4.25t	
iPr	iPr	E	10.0	4.90d	10.5	4.56d	
		Z	10.2	5.66d	10.0	4.51d	
Me	Et	E	7.5	5.19q	7.4	4.76t	
		Z	7.0	6.15q			
Et	Me	E	7.7	5.97t	7.2	5.04q	
		Z	7.0	6.56t	7.2	4.09q	
Me	tBu	E				5.03s	
		Z				4.79s	
tBu	Me	E		6.03s	6.8	5.45q	H_1 : 0.84s
		Z		6.22s			
tBu	Et	E		6.01s	7.5	5.16t	H_1 : 1.18s
		Z		6.25s	7.0	4.01t	
Et	tBu	E				4.78s	H_6 : 1.10s
		Z	8.0	5.92t		4.23s	

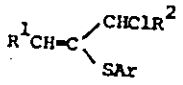
TABLE 7

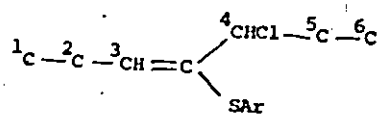


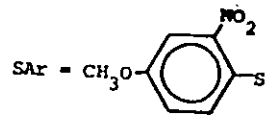
SAr = 

$R^1CH{=}C\langle^{CHClR^2}_{SAr}$			Chemical shifts and proton-proton coupling constants											
R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6
Me	Me	E			2.06d	7.3	6.43q	2.0	5.20q	6.8	1.66d		
		Z			1.87d	7.0	6.82q		4.72q	6.7	1.68d		
Et	Et	E	1.13t	7.5	2.45q'	7.8	6.32t		4.80t	7.5	1.99m	7.5	0.99t
		Z	1.13t	7.5		7.4	6.70t	1.0	4.37t	7.5		8.0	1.02t
iPr	iPr	E	1.14d	6.8		10.0	6.08d		4.55d	10.0		6.8	1.08d
			1.12d	6.8								6.8	0.96d
		Z					6.54d		4.19d				
tBu	tBu	E	1.24s				6.13s		5.25s				1.16s
Me	Et	E			2.04d	7.5	6.43q		4.82t	7.5		7.6	0.99t
		Z			1.89d	6.9	6.79q	1.5	4.41t	6.5		7.5	1.02t
Et	Me	E	1.14t	7.6	2.47q'	8.0	6.32t		5.10q	7.0	1.63d		
		Z	1.22t	7.6	2.38q'	7.5	6.71t		4.62q	6.8	1.70d		
Me	iPr	E			2.02d	7.4	6.40q		4.57q	9.6	2.31m	6.8	1.10d
		Z			1.91d	6.8	6.79dq	1.0	4.27dd	6.5		6.9	1.00d
iPr	Me	E	1.13d	6.5	3.03m	10.3	6.12d		5.12q	6.7	1.64d	6.9	0.98d
		Z				9.5	6.54d				1.69dd		
Me	tBu	E			2.03d	7.5	6.42q		4.81s				1.13s
		Z			1.94d	7.0	6.80q		4.30s				1.08s
tBu	Me	E	1.30s				6.29s		5.51q	7.0	1.65d		
iPr	Et	E		7.0	3.02m	10.5	6.12d		4.79t	7.3	2.00q'	7.5	
		Z				10.0	6.53d						
Et	iPr	E		7.5	2.43q'	7.6	6.30t		4.53d	9.8			
		Z				7.6	6.71t	1.0	4.23d	6.0			
iPr	tBu	E				10.7	6.06d		4.80s				1.13s
		Z				9.9	6.55d		4.18s				1.21s
tBu	iPr	E	1.27s				6.26s		4.93d	10.0		10.0	1.07d
												10.0	1.00d
tBu	Et	E	1.29s				6.30s		5.23t	7.5	1.90q'	7.6	1.01t
		Z											
Et	tBu	E		7.8	2.43q'	7.6	6.27t		4.80s				1.12s
		Z				7.0	6.72t		4.25s				1.09s

TABLE 8





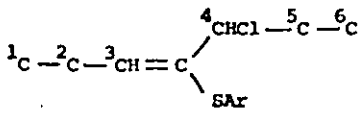


Chemical shifts and proton-proton coupling constants

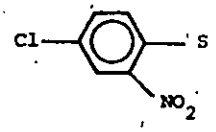
R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^3J_{4,5}$	H_4	$^3J_{5,6}$	H_5	H_6
Me	Me	E			2.03d	7.1	6.41q	6.9	5.06q		1.61d	
		Z			1.87d	7.0	6.78dq	7.1	4.63qm		1.68d	
Et	Et	E	1.12t	7.2	2.2m	7.2	6.33t	7.3	4.82t		2.2m	0.98t
		Z	1.15t	6.9	2.2m	7.2	6.71t	6.7	4.27t		2.2m	0.96t
iPr	iPr	E	1.13d	6.5	2.8m	10.1	6.08d	9.8	4.51d		2.7m	0.99d
		Z	1.17d	6.7	2.8m	9.9	6.54dd	10.1	4.18dd		2.7m	1.03d
tBu	tBu	E	1.22s									1.02d
Me	Et	E					6.03s		5.25s			0.96d
		Z			1.99d	7.4	6.32q	7.5	4.77t	7.5	1.97q'	1.16s
Et	Me	E	1.11t	7.5	1.88d	7.0	6.73q			7.5		0.97t
		Z			2.42q'	7.5	6.22t	6.8	5.05q			1.01t
Me	iPr	E				7.0	6.66t	7.2			1.61d	
		Z			1.96d	7.5	6.27q	10.0	4.53d		1.47d	
iPr	Me	E			1.90d	7.0	6.72q	6.8	4.25d			
		Z				10.0	6.02d	6.8	5.08q	7.0	1.63d	
Me	tBu	E							4.58q	7.0	1.47d	
		Z			1.97d	7.3	6.29q		4.79s			1.11s
tBu	Me	E	1.26s		1.91d	7.0	6.75q		4.27s			1.06s
iPr	Et	E					6.21s	6.6	5.49q		1.62d	
Et	iPr	E				10.0	6.02d	7.5	4.75t			
		Z				8.0	6.17t	9.5	4.50d			
iPr	tBu	E	1.15d	8.0				6.5	4.24d			
		Z				10.5	5.95d		4.78s			1.12s
tBu	iPr	E	1.24s						4.30s			
tBu	Et	E	1.25s				6.16s	10.0	4.89d	8.3		1.04d
Et	tBu	E	1.06t	7.5			6.21s	7.5	5.19t	7.5		0.97d
		Z				7.5	6.16t		4.76s			0.99t
									4.22s			1.10s

Aromatic Methoxy signal : 3.84-3.86 ppm (s)

TABLE 9

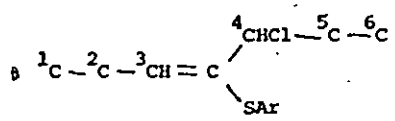


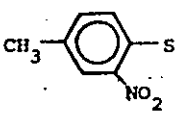
SAr =



$R^1CH{=}C(SAr)CHClR^2$			Chemical shifts and proton-proton coupling constants											
R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6
Me	Me	E			2.04d	7.2	6.38q		5.12q	6.8	1.63d		
		Z			1.87d	6.8	6.82q	1.0	4.71q	6.8	1.69d		
Et	Et	E	0.98t	7.5	2.43q'	7.6	6.32t		4.76t	7.3	1.98q'	7.0	1.12t
		Z	1.02t	7.5	2.35q'	7.5	6.67t	1.0			1.91q'		1.21t
iPr	iPr	E	1.11d 1.14d	6.8 6.5	2.99m	10.3	6.09d		4.55d	10.0	2.30m	6.8 6.8	1.07d 0.95d
		Z				8.5	6.54d	1.0	4.23d	9.6	2.27m		
tBu	tBu	E	1.25s				6.16s		5.27s				1.16s
Me	Et	E			2.05d	7.0	6.45q		4.83t	7.5	2.00q'	7.5	0.99t
		Z			1.89d	6.5	6.80q		4.42t	7.0		7.5	1.03t
Et	Me	E	1.15t	7.5	2.46q'	7.6	6.33t		5.12q	6.7	1.64d		
		Z				7.5	6.72t		4.63q	7.0	1.70d		
Me	iPr	E			2.02d	7.2	6.42q		4.58d	9.5		6.5	1.10d
		Z			1.90d	6.8	6.78q		4.25d	6.5		6.9	0.94d
iPr	Me	E	1.14d	6.5		10.3	6.12d		5.12q	6.6	1.65d		
		Z	1.01d	6.5		10.0	6.55d				1.68d		
Me	tBu	E			2.00d	7.5	6.45q		4.82s				1.10s
		Z							4.29s				1.06s
tBu	Me	E	1.29s				6.30s		5.50q	6.8	1.63d		
iPr	Et	E				10.3	6.14d		4.81t	7.1			
		Z				7.5	6.76d		4.24t				
Et	iPr	E				7.5	6.31t		4.55d	9.7			
		Z				9.5	6.48t						
iPr	tBu	E				10.6	6.06d		4.81s				1.13s
		Z							4.17s				
tBu	iPr	E	1.28s				6.26s		4.92q	10.0			
tBu	Et	E	1.28s				6.33s		5.21t	7.5			1.01t
		Z											
Et	tBu	E	1.08t			8.0	6.30t		4.79s				1.11s
		Z							4.24s				

TABLE 10



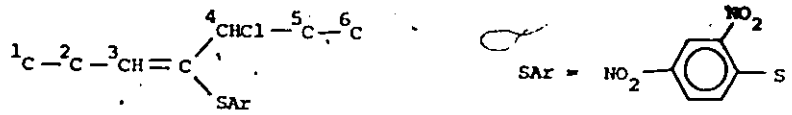
SAr = 

$R^1CH{=}C<^{CHClR^2}_{SAr}$ — Chemical shifts and proton-proton coupling constants

R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6
Me	Me	E			2.02d	7.3	6.39q		5.09q	6.8	1.60d		
		Z			1.86d	6.8	6.79dq	1.0	4.63q	7.3	1.67d		
Et	Et	E	1.12t	7.2	2.46q'	7.8	6.29t		4.75t	7.3		7.5	0.98t
		Z	1.14t		2.38q'	6.9	6.67t		4.34t	6.5		7.5	1.02t
iPr	iPr	E	1.13d	6.5	3.03m	10.5	6.03d		4.51d	10.0	2.30m	7.0	0.99d
			1.09d	6.5								6.8	0.95d
		Z											
tBu	tBu	E	1.24s				6.11s		5.26s				1.16s
Me	Et	E			2.02d	7.0	6.39q		4.80t	7.5		7.5	1.12t
		Z			1.88d	6.8	6.76q		4.40t	6.5		7.7	1.01t
Et	Me	E	0.98t	7.5		7.8	6.28t		5.08q	6.8	1.61d		
		Z	1.20t	7.5		7.5	6.70t		4.61q	6.5	1.68d		
Me	iPr	E			2.01d	7.3	6.36q		4.56d	9.5			
		Z			1.91d	7.0	6.76q	1.0	4.36d	6.4			0.99d
iPr	Me	E				10.1	6.08d		5.11q	6.8	1.68d		
		Z					6.52d				1.64d		
Me	tBu	E			1.99d	7.5	6.36q		4.79s				1.11s
		Z			1.92d	7.0	6.76q		4.28s				1.06s
tBu	Me	E	1.28s				6.25s		5.50q	6.7	1.62d		
iPr	Et	E				10.3	6.08d		4.78t	7.5	1.98q'		
		Z				9.5	6.51d						
Et	iPr	E				7.7	6.24t		4.52d	9.6			
		Z				7.5	6.68t						
iPr	tBu	E	1.15d	9.5		11.0	6.02d		4.78s				1.12s
tBu	iPr	E	1.27s				6.22s		4.91d	10.0		9.6	1.07d
		Z										10.0	0.99d
tBu	Et	E	1.27s				6.27s		5.20t	7.5		7.3	1.00t
Et	tBu	E				7.7	6.24t		4.76s				1.11s
		Z	1.08t	7.5					4.23s				

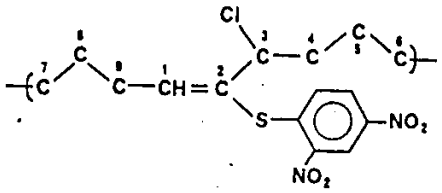
Aromatic CH_3 protons at 2.37-2.40 ppm

TABLE 11



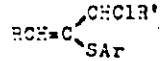
$R^1CH{=}C(SAr)CHClR^2$			Chemical shifts and proton-proton coupling constants											
R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6
Me	Me	E			2.11d	7.0	6.47q	0.2	5.21q	6.5	1.68d		
		Z			1.90d	6.5	6.89qd	0.6	4.75qd	6.5	1.74d		
Et	Et	E	1.13t	6.8	2.63q'	6.7	6.57t	0.2	5.07t	6.6	2.13q'	6.8	1.32t
		Z	1.1 t	7.0	2.6 m		6.90t	0.5	4.62t		2.2 m		1.3 t
iPr	iPr	E	1.16d	6.6	2.8 m	10.2	6.15d	0.2	4.58d	9.8	2.2 m	6.5	1.10d
		Z	1.18d	6.6		10.0	6.47dd	1.1	4.18dd	9.0	2.2 m	6.5	0.97d 1.12d
tBu	tBu	E	1.31s				6.26s		5.33s				0.99d 1.18s
Me	Et	E			2.14d	6.8	6.56q		4.96t	7.0	2.06q'		1.31t
		Z			1.95d	6.7	6.89dq	0.5	4.62ddd	7.0			1.11t
Et	Me	E	1.06t	7.5	2.54q'	7.5	6.42t		5.24q	6.5	1.72d		
		Z	1.11t	7.3			6.81td	0.5	4.78qd	6.8	1.77d		
Me	iPr	E			2.05d	7.2	6.51q		4.67d	9.6	2.3 m	6.7	1.13d
		Z			1.92d	7.1	6.85q		4.30d	7.4	2.3 m	6.7	1.02d
iPr	Me	E			2.8 m	10.4	6.19d		5.42q	6.8	1.67d		
		Z			2.8 m	7.8	6.84d		4.58q	6.6	1.73d		
Me	tBu	E			2.07d	7.2	6.63q		5.03s				1.14s
		Z			1.95d	7.2	7.00q		4.43s				1.10s
tBu	Me	E	1.34s				6.47s		5.67q	6.4	1.69d		
iPr	Et	E				10.2	6.22d		4.91t	7.0	2.02m	7.4	
Et	iPr	E		7.5	2.49m.	7.5	6.40t		4.62d 4.26d	9.8 7.5			
		Z											
iPr	tBu	E				10.7	6.16d		4.90s				1.14s
		Z											
tBu	iPr	E	1.32s				6.35s		4.98d	10.0			
tBu	Et	E	1.32s				6.39s		5.27t	7.5		7.0	1.03t
		Z											
Et	tBu	E				7.5	6.39t		4.90s				1.12s
		Z							4.31s				

Observed Carbon-13 Magnetic Resonanse Parameters for the Products of Addition of 2,4-Dinitrobenzenesulphenyl Chloride to 1,3-Disubstituted Allenes



RCH=C(CHClR')SAr R	R'	Configuration	Chemical Shift Assignments C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_S	C_{oNO_2}	Aromatics C_m	C_{pNO_2}	$C_{i'}$	C_o	Other Carbons
CH_3	CH_3	E	146.8	132.8	54.8	23.7					15.7	132.6	144.3	126.7	147.5	121.2	129.5	
		Z	142.0	131.9	61.5	24.5					15.7	132.0	143.4	126.9	144.7	121.7	128.6	
C_2H_5	C_2H_5	E	154.0	144.5	61.7	30.5	11.4			13.2	23.3		144.5	126.5	147.7	121.2	129.7	
		Z	149.5		68.1	30.9	11.2			12.9	23.7			126.8		121.7	129.0	
1-C_3H_7	1-C_3H_7	E	153.5		67.5	34.3	22.0			20.4	29.4		144.5	126.5	147.9	121.5	129.7	
		Z	155.3		72.7	33.8	21.8			20.9	30.2			126.6		121.2	129.3	
-$(CH_2)_6$-		E	152.1	144.2	60.0	36.8	27.7	23.6	25.5	26.7	30.1	130.2	144.5	126.3	147.7	121.3	130.4	
-$(CH_2)_{10}$-		E	153.9	144.6	59.3	36.8	27.8	27.0	27.2	27.4	28.5		144.6	126.6	147.5	121.3	130.0	26.2, 26.0, 24.5, 23.9
		Z	150.0		66.0	37.0	29.3	26.8	27.1	28.3	29.5			126.8		121.7	129.4	
CH_3	C_2H_5	E	147.2		61.5	30.5	11.4				15.9			126.5		121.4	129.5	
		Z	142.9		68.3	30.9	11.4				15.9			126.9		120.8	128.9	
CH_3	1-C_3H_7	E	146.7		67.0	33.7	20.3				15.9			126.7		121.3	129.1	
		Z	142.7		73.4	33.3	20.0, 20.7, 21.3				15.9			126.9		121.6	128.7	
CH_3	t-C_4H_9	E	148.0		69.8	38.4	27.5				17.1			126.6		121.2	128.7	
		Z	144.3		75.7	37.6	27.2				16.2			127.1		121.7	129.6	
C_2H_5	CH_3	E	153.5		55.1	24.2				13.2	23.3			126.6		121.8	129.3	
		Z	148.7		61.5	24.9				13.2	23.7			127.2		121.3	128.7	
1-C_3H_7	CH_3	E	158.5		55.3	24.4				22.3	34.4			126.7		121.7	129.3	
		Z	155.2		61.0	24.8				22.0, 21.7, 21.3	34.3			127.0		121.9	128.7	
t-C_4H_9	CH_3	E	161.1	148.4	55.3	24.0				30.6	35.2	131.4	144.3	126.5	148.7	121.2	129.0	

TABLE 12



Carbon-13 Proton Coupling Constants

$J_{C,H}$ = Hz

R	R'	Configuration	$J_{1,1}$	$J_{1,3}$	$J_{1,9}$	$J_{3,3}$	$J_{3,4}$	$J_{3,1}$	$J_{4,4}$	$J_{4,3}$	$J_{4,5}$	$J_{9,9}$	$J_{9,1}$	$J_{\alpha,\alpha}$	$J_{\alpha,\alpha'}$	$J_{\alpha',\alpha'}$	$J_{\alpha',\alpha}$	$J_{o,o}$
CH_3	CH_3	E	159.2	6.9	3.0	151.6	4.3	9.1	129.4	2.8		128	2	172.0	5.0	173.9	4.6	171.7
		Z	154.2	6.8	4.2	150.6	4.5	2.4	129.9	2.3		128	2	172.5	5.4	174.9	4.9	171.2
C_2H_5	C_2H_5	E	156.4			147.8	4.6	10.4	127.5			127.9		173.7	4.9	171.8	4.8	171.3
		Z	152.			152.7	4.5	3.1	127			127.						
1-C_3H_7	1-C_3H_7	E				153.6	4.3	10.4	127.6			128.3		172.6	5.3	174.8	4.7	171.5
		Z																
	$-(CH_2)_6-$	E	170.0			149.5	4.1	6.0	134.			130.8		171.9	5.5	174.3	4.6	172.0
	$-(CH_2)_{10}-$	E	157.6	6.9	3.8	149.5	4.0	6.8	133.3	2.9				171.9	5.4	174.0	4.7	171.9
		Z				147.5	4.4	2.3										
CH_3	C_2H_5	E	162.3	6.7	3.0	146.4	4.3	8.3	127.	3.4		127.6	2.8	172.1	5.5	174.5	5.3	171.6
		Z	153.	5.5	3.9	151.0	4.3	2.3	127.			127.6		172.8	5.4	173.6	4.0	170.9
CH_3	1-C_3H_7	E				151.	4.0	9.8	129.									
		Z				149	4.5	3.1										
CH_3	t-C_4H_9	E	154.6	6.4	4.0	148.	4.5	10.0	125.7*			128		172.0	5.3	174.5	4.4	171.8
		Z				151	4.0	1.8										
C_2H_5	CH_3	E	164.3			149.5	3.6	9.4	128.2	3.3		128.5	3.	172.3	5.6	174.0	4.2	171.4
		Z							128.5	3.1		128.						172.7
1-C_3H_7	CH_3	E				152.	4.2	8.4	128.			129.						
		Z																
t-C_4H_9	CH_3	E	153.9			151.7	4.0	11.1	130.1	2.6		126.8*	4.6*	172.0	5.4	174.3	4.6	171.3

Couplings marked with a * refer to the next carbon on the chain. Thus $J_{4,4}$ should read $J_{5,5}$ and $J_{9,9}$ as $J_{8,8}$ et cetera.

Due to problems of overlapping signals it was not possible to measure all coupling interactions between carbon and hydrogen.

TABLE 13

APPENDIX IV

^{1}H AND ^{13}C NMR SPECTRAL PARAMETERS FOR ADDUCTS OF PhSeCl WITH VARIOUS ALLENES IN CH_2Cl_2 AT 25°C

- TABLE 1 : ^{1}H NMR parameters for adducts of PhSeCl with mono- and 1,1-disubstituted allenes.
- TABLE 2 : ^{1}H NMR spectral parameters for adducts of PhSeCl with 1,3-disubstituted allenes.
- TABLE 3 : Carbon-13 NMR parameters for adducts of PhSeCl with mono- and 1,1-disubstituted allenes.
- TABLE 4 : Carbon-13 NMR parameters for adducts of PhSeCl with 1,3-disubstituted allenes.
- TABLE 5 : Proton-carbon coupling constants for the adducts of PhSeCl with 1,3-disubstituted allenes.

TABLE 1

^{1}H NMR SPECTRAL PARAMETERS FOR THE ADDUCTS OF PhSeCl AND A SERIES OF MONO AND 1,1-DISUBSTITUTED ALLENES

1,1-disubstituted-3-chloro-2-phenylselenopropenes

(R) $^6C—^5C—^4C$ $^3C=^2C$ $^1CH_2Cl$

(R') $^{6'}C—^{5'}C—^{4'}C$ $^3C=^2C$ SePh

R	R'	H_1	H_3	H_4	H_5	$H_{6/7}$	$H_{4'}$	$H_{5'}$	$H_{6'/7'}$	$^4J_{HC=CCH}$	$^5J_{HCC=CCH}$
H	Me	4.10q'	6.33qt								
Me	H	4.15s	6.19q	1.72d			1.88dt			1.40	1.25
H	Et	4.17dt	6.33tt							0.3	0.3
Et	H	4.21s	6.20t	2.38q'	1.08t		2.05q'	1.03t		1.00	1.04
H	iPr	4.10d	6.12dt							0.3	0.3
iPr	H	4.18s	6.02d	2.92m	1.05d		3.02m	1.03d		2.3	0.3
H	tBu	4.01d	6.43t							0.3	0.3
tBu	H	4.16s	6.25s		1.23s			1.27s		2.0	
H	iBu	4.14ddd	6.32tt							0.5	
iBu	H	4.19s	6.18t	2.12m	1.73m.	0.93d	2.28m	1.73m	0.93d	2.50	2.1
H	$iBuCH_2$	4.14dt	6.29tt							0.3	0.3
$iBuCH_2$	H	4.19s	6.18t	2.22	1.2m	1.2m/0.88d	2.37	1.2m	1.2m/0.88d	2.1	1.5
Me	Me	4.29bs		1.99s			2.05s			0.5	0.5
Me	Et	4.28s		1.99s			2.48q	1.01t			
Et	Me	4.31s		2.36q	1.12t		2.04s				
Me	nPr	4.25s		1.98s							
nPr	Me	4.30s		2.46t	1.56tq	0.95t	2.46t	1.56tq	0.95t		
Me	iPr	4.29s			1.88s		2.02s				
iPr	Me	4.34s		3.13m	1.69d		3.45m	0.99d			
Me	iBu	4.26s		1.99s			1.98s				
iBu	Me	4.32s		2.23d	1.93m	1.00d	2.40d	1.93m	0.93d		
Me	sBu	4.28s		1.85s			2.02s				
sBu	Me	4.34ABq		2.85tq	1.44dq / 1.07d	0.93t	3.24tq	1.38dq / 1.07d	0.85t		
Me	$tBuCH_2$	4.24s		2.05s			1.89s				
$tBuCH_2$	Me	4.31s		2.31s	1.00s		2.31s	1.00s			
							2.05s				

3,3-disubstituted-3-chloro-2-phenylselenopropenes

^1H, ^2H $C=C$ $^3C(^{4'}C)(CCl)—^4C—^5C—^6C—^7C$ SePh

R	R'	H_1	H_2	H_3	H_4	H_5	$H_{6/7}$	$H_{4'}$	$^2J_{1,2}$	$^4J_{HC=CCH}$ cis	$^4J_{HC=CCH}$ trans
H	Me	5.90dd	5.26dd	4.65qdd	1.67d				0.3	1.5	0.3
H	Et	5.95dd	5.32d	4.38tdd	2.04q'	1.11t			0.3	0.8	0.3
H	iPr	5.88dd	5.27d	4.27dd	2.32m.	1.20d / 1.11d			2.0	2.0	0.3
H	tBu	5.82s	5.24s	4.27s		1.12s					
H	$iBuCH_2$	5.88dd	5.25s	4.45	1.97	1.2m	1.2m/0.9d				
H	iBu	5.87dd	5.23d						0.3	1.4	0.3
Me	Me	5.87d	5.06d		1.87s			1.87s	1.8	2.0	0.3
Me	Et	5.90d	5.09d			0.97t		1.81s	1.02		
Me	nPr	5.88d	5.07d			1.57m	0.92t	1.81s			
Me	iPr	5.90d	5.04d		2.57m	1.08d		1.73s			
Me	sBu	5.87dd	5.05d		1.42dq / 0.82d		0.82t	1.66s			
Me	tBu	5.88d	5.23d		1.05s			1.88s	2.3		

TABLE 2

The observed ^1H NMR parameters for the products of addition of PhSeCl to some 1,3-disubstituted allenes in CH_2Cl_2 at 25°C.

RCH=C(SePh)CHClR'

R	R'	Configuration	Adduct number	H_1	$J_{1,2}$	H_2	$J_{2,3}$	H_3	$J_{3,4}$	H_4	$J_{4,5}$	H_5	$J_{5,6}$	H_6
				Chemical Shifts and Coupling Constants										
CH_3	CH_3	E	10			1.75 d	7.25	6.01 q	≤0.3	5.12 q	6.75	1.61 d		
		Z	11			1.93 d	6.75	6.46 qd	0.9	4.65 qqd	6.75	1.63 d		
C_2H_5	C_2H_5	E	24	1.02 t	7.2	2.24 dq'	7.4	5.72 t	≤0.2	4.71 t	7.3	1.96 ddq	7.2	0.96 t
		Z	25	1.03 t	7.2	2.32 dq'	6.9	6.29 td	1.6	4.31 tm	6.4	1.98 ddq	7.2	0.96 t
i-C_3H_7	i-C_3H_7	E	26			2.31 h'	10.0	5.62 dd	0.2	4.54 dd	9.8	2.9 m		
		Z	27			2.36 h'	9.2	6.16 dd	1.0	4.27 dd	5.6	2.9 m		
t-C_4H_9	t-C_4H_9	Z	28	1.27 s				6.67 d	0.62	4.30 d				1.06 t
-$(CH_2)_6$-		E	30			2.0 m	8.8	5.90 t	≤0.2	5.25 dd	10.6 5.2	2.3 m		
-$(CH_2)_{10}$-		E	31				9.5/5.5	5.83 dd	≤0.2	4.92 dd	9.2/5.8			
		Z	32				7.0	6.31 t		4.53 dd	9.0/5.5			
CH_3	C_2H_5	E	12			1.80 d	7.0	5.99 q	≤0.2	4.87 t	7.2	2.2 m	7.2	0.96 t
		Z	13			1.87 d	6.7	6.43 qd	1.0	4.43 ddd	6.8/6.7	2.2 m	7.2	0.96 t
C_2H_5	CH_3	E	14	1.02 t	7.1	2.2 m	7.5	5.97 t	≤0.2	5.14 q	6.6	1.63 d		
		Z	15	0.98 t	7.0	2.2 m	6.8	6.36 t	≈0.5	4.66 qm	7.0	1.67 d		
CH_3	i-C_3H_7	E	16			1.76 d	7.0	5.83 q		4.58 d	8.5	2.3 m		
		Z	17			1.88 dd	6.7	6.41 q		4.31 dm	6.5	2.3 m		
i-C_3H_7	CH_3	E	18			2.3 m	10.0	5.78 d		5.13 q	6.6	1.63 d		
		Z	19			2.3 m	9.0	6.16 d		4.55 qm	7.0	1.65 d		
CH_3	t-C_4H_9	E	20			1.73 d	6.8	5.68 q		4.92 s				1.23 s
		Z	21			1.78 d	7.0	6.47 q		4.51 s				1.06 s
t-C_4H_9	CH_3	E	22	1.27 s				6.07 s		5.19 q	7.0	1.58 d		
		Z	23	1.13 s				6.65 s		4.49 q	7.0	1.63 d		

all chemical shifts are reported δppm relative to internal TMS in $CDCl_3$

s = singlet; d = doublet; q = quartet; q' = quintet; h' = heptet; m = multiplet; dd = doublet of doublets; qd = quartet of doublets; td = triplet of doublets; qqd = quartet of quartets of doublets; t = triplet; dq' = doublet of quintets; qm = quartet of multiplets; dm = doublet of multiplets; tm = triplet of multiplets; ddm = doublet of doublets of multiplets; ddq = doublet of doublets of quartets.

numbering scheme:

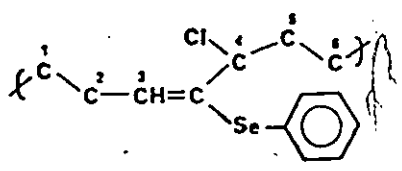
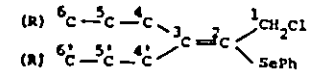


TABLE 3

^{13}C NMR SPECTRAL PARAMETERS FOR THE ADDUCTS OF PhSeCl AND A SERIES OF MONO AND 1,1-DISUBSTITUTED ALLENES

1,1-disubstituted-3-chloro-2-phenylselenopropenes

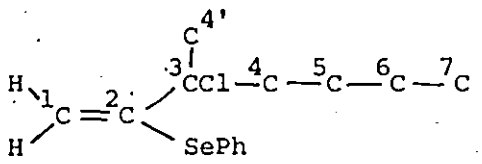


R	R'	C_1	C_2	C_3	C_4	C_5	$C_{6/7}$	$C_{4'}$	$C_{5'}$	$C_{6'/7'}$	$^3J_{CC=CH}$	$^1J_{C_1H}$	$^1J_{C_4H}$	$^1J_{C_{4'}H}$
H	Me	50.0	128.1	134.4				17.6			6.4	153.0		127.5
Me	H	43.2	127.5	135.1	15.4						9.7	147.5	127.9	
H	Et	49.8	128.6	143.1				25.4	13.4		6.7	150.3		
Et	H	43.4	129.7	141.8	23.3	13.6					9.8	151.9		
H	iPr	49.8		147.2				31.5	22.4					
iPr	H	43.7		151.1	31.3	22.6								
H	tBu	50.8						37.0	30.5					
tBu	H	44.1			37.0	30.7								
H	iBu	49.9	132.5	139.4				40.9	28.8	22.5				
iBu	H	43.7		142.9	38.9	31.0	22.5							
H	$iBuCH_2$	49.9	128.1	152.9				38.1	30.0	27.7 22.3				
$iBuCH_2$	H	42.9	130.6	150.3	37.5	29.6	27.6 22.2							
Me	Me	47.1	134.8	122.1	20.8			25.9				152.0	127.3	127.4
Me	Et	47.1			18.4			32.6	12.6					
Et	Me	46.7			28.0	13.1		23.4						
Me	nPr	47.0			18.6			41.3	21.5	13.9				
nPr	Me	46.8			36.9	21.7	14.1	23.8						
Me	iPr	47.4			17.9			31.5	20.6					
iPr	Me	46.3			31.5	21.0		18.3						
Me	iBu	48.0			19.2			43.8	27.7	22.5				
iBu	Me	46.8			43.8	27.4	22.6	24.0						
Me	sBu	47.1	135.7	153.5	17.7			46.4	28.9t 18.7q	12.2				
sBu	Me	46.4	135.7	153.9	42.9	28.0t 18.7q	12.4	19.2						
Me	$tBuCH_2$	48.2			26.8			47.0	33.0	30.7				
$tBuCH_2$	Me	48.0			47.1	33.0	30.7	29.9						

TABLE 3 (continued)

^{13}C NMR SPECTRAL PARAMETERS FOR THE ADDUCTS OF PhSeCl AND A SERIES OF 1,1 AND MONO-SUBSTITUTED ALLENES

3,3-disubstituted-3-chloro-2-phenylselenopropenes



R	R'	C_1	C_2	C_3	C_4	C_5	C_6	C_7	$C_{4'}$
H	Me	119.6	143.2	60.5	25.3				
H	Et	119.9	145.3	67.2	31.2	11.0			
H	iPr	120.1	147.2	72.8	33.5	{20.6 18.0			
H	tBu	121.5	149.0	75.4	33.8	27.5			
H	iBu	119.2	142.8	64.3	43.6	25.6	{21.7 21.6		
H	$iBuCH_2$	120.5	143.3	70.2	37.5	31.3	27.5	22.2	
Me	Me	117.2	146.2	72.0	33.0				33.0
Me	Et	118.1	151.8	78.4	37.2	9.6			30.2
Me	nPr	117.9		79.8	46.5	21.0	18.6		30.7
Me	iPr	117.2	155.0	82.5	37.9	26.6			35.9
Me	sBu	117.2		83.4	46.7	{29.2t 26.0q	12.7		
Me	tBu	119.3	153.2	86.1	38.1	29.3			36.0
Me	$tBuCH_2$	117.2		81.9	46.6	31.6	30.7		33.5

TABLE 4

The observed Carbon-13 NMR parameters for the products of addition of PhSeCl to 1,3-disubstituted allenes.

$RCH{=}C(SePh)CHClR'$

R	R'	Configuration	Adduct Number	C_1	C_3	C_4	C_5	C_6	C_7	C_8	C_9
CH_3	CH_3	E	10		56.0	24.6					15.2
		Z	11		63.0	25.2					17.7
C_2H_5	C_2H_5	E	24	142.3	62.6	31.4	11.5			13.7	23.0
		Z	25	142.7	69.5	31.1	11.1			13.3	25.5
$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	E	26	147.7	60.3	34.3	20.7 20.4			22.4	29.1
		Z	27	148.2	73.9	33.1	21.2 17.2			22.4	31.7
$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	Z	28	149.3	70.0	34.2	30.6			27.5	31.7
$-(CH_2)_6-$		E	30	136.5	61.1	37.5	26.5	25.9	24.1	27.9	29.6
$-(CH_2)_{10}-$		E	31	143.4	59.8	37.7	28.1	27.2	26.7	27.7	31.1
		Z	32	143.0	66.7	36.9	27.9	27.0	25.8	27.4	31.0
CH_3	C_2H_5	E	12		62.4	31.4	11.5				15.3
		Z	13	135.9	69.9	31.2	11.3				17.9
C_2H_5	CH_3	E	14	143.9	56.2	25.4				13.7	23.0
		Z	15	141.9	62.9	25.2				13.3	25.4
CH_3	$i\text{-}C_3H_7$	E	16	134.7	66.5	34.8	20.0 19.7				15.4
		Z	17	136.1	74.6	33.3	20.9 17.9				17.1
$i\text{-}C_3H_7$	CH_3	E	18	149.9	56.7	25.4				21.3	31.6
		Z	19	147.1	62.6	25.3				21.1	31.3
CH_3	$t\text{-}C_4H_9$	E	20	139.9	70.4	38.1	27.5				17.1
		Z	21	138.6	77.3	37.7	27.5				18.3
$t\text{-}C_4H_9$	CH_3	E	22	151.0	56.8	25.3				28.4	31.2
		Z	23	148.8	62.9	25.1				27.8	30.7

all chemical shifts are reported δ ppm, with respect to internal TMS solutions were approximately 30 % w/w in $CDCl_3$

numbering scheme:

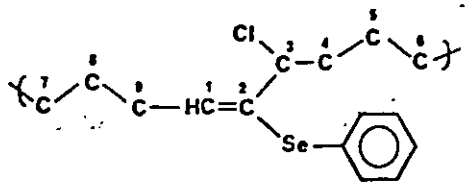


TABLE 5

Observed Proton-Carbon coupling constants for the adducts of PhSeCl to 1,3-disubstituted allenes.

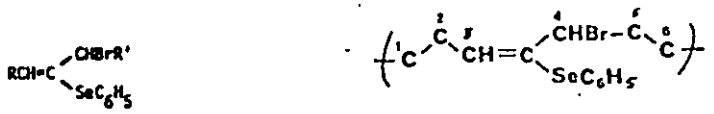
E - Isomers			Z - Isomers		
Adduct Number	$^{1}J_{3,3}$	$^{3}J_{3,1}$	Adduct Number	$^{1}J_{3,3}$	$^{3}J_{3,1}$
10	152.8	11.3	11	151.8	4.8
12	154.1	11.5	13	157.2	3.1
14	152.4	9.8	15	149.6	4.3
16	151.8	10.1	17	155.1	3.5
18	152	9.9	19	149.8	4.2
20			21	153.0	3.1
22			23	146.9	2.1
24	150.2	11.8	25	153.1	2.5
26	151.3	12.4	27	146.7	1.2
			28	153.1	5.2
30	149.4	8.7			
31	150.3	9.1	33	147.5	2.4

APPENDIX V

PROTON NMR SPECTRAL PARAMETERS FOR THE PRODUCTS OF THE ADDITION OF ARENESELENYL AND ARENESULFENYL HALIDES TO A SERIES OF 1,3-DISUBSTITUTED ALLENES.

TABLE 1

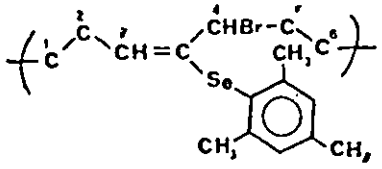
^{1}H NMR parameters for the addition of PhSeBr to 1,3-disubstituted allenes.



R	R'	Configuration	H_1	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	H_6
CH_3	CH_3	E		1.75 d	7.2	6.03 q	≤ 0.3	5.12 q	7.2	1.75 d	
		Z		2.13 d	7.2	6.53 dq	1.5	4.95 m	7.2	2.13 d	
C_2H_5	C_2H_5	E	0.96 t	2.27 m	7.1	5.87 t		5.00 t	7.4	2.0 m	0.94 t
		Z	0.96 t	2.27 m	7.1	6.33 t		4.59 t	7.1	2.04 m	0.94 t
i-C_3H_7	i-C_3H_7	E		2.88 m	10.0	5.08 d		4.77 d	10.1	2.25 m	
		Z		2.81 m	9.4	6.21 dd	1.3	4.45 dd	6.6	2.25 m	
CH_3	C_2H_5	E			7.1	5.93 q		5.02 t	7.5		0.96 t
		Z		1.84 d	6.5	6.44 dq	1.5	4.62 t	7.0		0.94 t
CH_3	i-C_3H_7	E			7.3	5.77 q		4.77 d	9.5		
		Z		1.83 d	6.6	6.46 dq	2.0	4.51 d	7.2	2.27 m	
CH_3	t-C_4H_9	E				6.03 q		5.16 s			
		Z		1.80 d	6.7	6.49 q		4.72 s			1.10 s
C_2H_5	CH_3	E	0.97 t		7.4	5.94 t		5.30 q	6.7	1.68 d	
		Z	1.01 t		6.7	6.36 dt	1.5	4.83 q	7.0	1.99 d	
C_2H_5	i-C_3H_7	E			7.5	5.71 t		4.74 d	9.2		
		Z			7.2	6.35 dt	1.0	4.49 d			
C_2H_5	t-C_4H_9	E				5.98 t		5.16 s			1.15 s
		Z	0.95 t		7.0	6.42 t		4.69 s			1.10 s
i-C_3H_7	CH_3	E	0.99 d	1.80 m	9.3	5.76 d		5.32 q	6.6	2.06 d	
		Z	1.05 d	1.80m	9.5	6.19 dd		4.76 q	7.0	2.15 d	
i-C_3H_7	C_2H_5	E		2.79 m	10.0	5.71 d		5.02 t	7.3		0.98 t
		Z		2.83 m	9.5	6.15 dd	1.0	4.53 t	6.9		0.93 t
i-C_3H_7	t-C_4H_9	E				5.81 d		5.18 s			1.14 s
		Z			9.5	6.28 d		4.64 s			1.04 s
t-C_4H_9	CH_3	E	1.24 s			6.00 s		5.58 q	6.7	1.89 d	
		Z	1.16 s			6.65 d	1.0	4.58 q	7.0	2.09 d	
t-C_4H_9	C_2H_5	E	1.07 s			5.95 s		5.29 t	7.0		0.93 t
		Z	1.21 s			6.64 d	1.6	4.38 t	6.5		0.98 t
t-C_4H_9	i-C_3H_7	E				5.81 s		5.02 d	10.3		
		Z				6.70 d	1.5	4.36 d	5.0		

TABLE 2

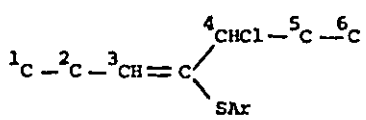
^{1}H NMR parameters for the adducts of 2,4,6-$(Me)_3C_6H_2SeBr$ with 1,3-disubstituted allenes at 25°C.

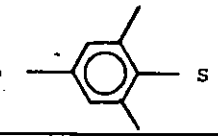


RCH=C(CHBrR')Se[2,4,6-$(CH_3)_3C_6H_2$]

R	R'	Configuration	H_1	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	H_6
CH_3	CH_3	E		1.90 d	6.6	5.27 q	≤0.4	4.88 q	6.9	1.75 d	
		Z		1.94 d	7.1	6.36 qd	1.8	4.25 dq	7.2	1.61 d	
C_2H_5	C_2H_5	E	1.03 t	2.0 m	6.5	4.88 t	≤0.4	4.72 t	6.8	2.0 m	0.87 t
		Z	1.01 t	2.0 m	6.6	6.20 tq	1.2	3.91 tm	6.8	2.0 m	0.84 t
i-C_3H_7	i-C_3H_7	E	1.20 d		10.2	4.77 d		4.53 d	10.0		0.82 d, 1.03 d
		Z	1.24 d		9.0	6.12 dd	1.6	4.01 dd	4.5		0.85 d, 1.01 d
CH_3	C_2H_5	E		1.90 d	7.0	5.31 q		4.85 t	7.5		0.85 t
		Z		1.92 d	6.8	6.32 qd	1.4	4.04 dt	7.0		0.85 t
CH_3	i-C_3H_7	E		1.91 d	7.1	5.30 q		4.67 d	10.0		0.81 d
		Z		1.92 d	6.7	6.35 dq	1.1	4.07 d	5.0		0.84 d
CH_3	t-C_4H_9	E		2.11 d	6.9	5.87 q		4.83 s			1.03 s
		Z		2.08 d	7.1	6.51 dq	1.6	4.28 d			1.05 s
C_2H_5	CH_3	E	1.02 t		7.5	5.02 t		4.89 q	5.8	1.57 d	
		Z	1.02 t		7.0	6.83 dt	2.0	4.28 dq	7.0	1.73 d	
C_2H_5	i-C_3H_7	E			7.5	5.01 t		4.63 d	10.0		
		Z			7.0	6.28 dt	1.3	4.04 dd	9.2		
C_2H_5	t-C_4H_9	E	0.96 t		7.4	5.31 t		4.78 s			1.01 s
		Z	0.98 t		7.0	6.34 t		4.20 s			1.06 s
i-C_3H_7	CH_3	E	0.89 d		10.5	4.77 d		4.79 q	7.1	1.56 d	
		Z	1.20 d		9.5	6.07 dd	1.0	4.37 q	7.0	1.71 d	
i-C_3H_7	C_2H_5	E	1.17 d	2.5 m	10.3	4.75 d		4.72 t	7.6	2.0 m	1.01 t
		Z	1.22 d	2.5 m	8.2	6.07 dd	1.0	3.99 dt	7.1	2.0 m	0.93 t
i-C_3H_7	t-C_4H_9	E			10.6	5.06 d		4.66 s			1.01 s
		Z			9.5	6.18 d		4.13 s			1.05 s
t-C_4H_9	CH_3	E	1.23 s			5.30 s		4.89 q	6.8	1.68 d	
		Z	unknown								
t-C_4H_9	C_2H_5	E	1.32 s			5.18 s		4.66 t	7.7	2.1 m	0.97 t
		Z	1.28 s			6.32 s		4.21 t	7.5	2.1 m	0.97 t
t-C_4H_9	i-C_3H_7	E	1.22 s			5.21 s		4.44 d	9.5	2.7 m	1.04 d, 1.09 d
		Z	unknown								

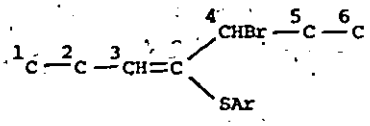
TABLE 3

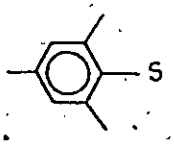


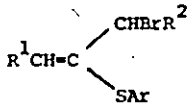
SAr = 

$R^1CH=C<^{CHClR^2}_{SAr}$			Chemical shifts and proton-proton coupling constants											
R^1	R^2	Configuration	H_1	$^3J_{1,2}$	H_2	$^3J_{2,3}$	H_3	$^4J_{3,4}$	H_4	$^3J_{4,5}$	H_5	$^3J_{5,6}$	H_6
Me	Me	E			1.94d	7.0	5.18q		4.56q	7.0	1.53d		
		Z			1.78d	7.0	6.18q	1.9	4.02q	7.0	1.62d		
Et	Et	E	1.02t	7.9		7.8	4.86t		4.52t	7.8		8.0	0.83t
		Z											
iPr	iPr	E	1.17d 1.13d	7.0 6.8		10.6	4.59d		4.29d	9.8		6.8 7.0	0.83d 0.81d
		Z											
tBu	tBu	E	1.26s				5.24s		4.38s				1.02s
		Z											
Me	tBu	E				6.7	5.51q		4.50s				1.02s
		Z											
tBu	Me	E	1.21s				4.95s						
		Z											
iPr	Et	E				10.5	4.59d		4.49t	7.6			
		Z											
Et	iPr	E	1.05t	7.5		7.7	4.88t		4.36d	9.8		6.7 6.7	0.86d 0.82d
		Z											
iPr	tBu	E					4.96s		4.23d	10.0			
		Z											
tBu	iPr	E				10.5	4.90d		4.45s				1.01s
		Z											
tBu	Et	E	1.07s				4.93s		4.50t				
		Z											
Et	tBu	E	1.20t	6.8		7.5	5.20t		4.50s				1.02s

TABLE 4



SAr = 



Chemical shifts and proton-proton coupling constants

R^1	R^2	Configuration	H_2	$^3J_{2,3}$	H_3	H_4	$^3J_{4,5}$	H_5	H_6
Me	Me	E		7.5	5.27q	6.21q	7.3		
		Z	1.93d	6.9	4.55q	4.12q	6.9	1.69d	
Et	Et	E			4.88t	4.08dd			
		Z		7.3	6.10t	3.88t	6.8		
iPr	iPr	E		11.0	4.77d	4.24d	9.7		
		Z		9.3	6.03d				
Me	Et	E		7.1	5.26q				
		Z		6.9	6.21q				
Et	Me	E		8.0	4.98t	4.59q	7.5		
		Z		7.3	6.16t				
Me	iPr	E		7.0	5.29q	4.32d	9.8		
		Z		6.8	6.24q	3.93d	6.9		
iPr	Me	E		10.7	4.76d	4.50q	7.2		
		Z		9.2	5.96d	4.07q	7.0		
Me	tBu	E				4.19s			
		Z		7.0	6.30q	4.02s			
tBu	Me	E			5.68s	4.46q	7.4		
		Z			6.10s				
iPr	Et	E		10.6	4.73d	4.44t	7.5		
		Z		9.1	5.95d	3.94t	7.0		
Et	iPr	E		7.5	5.00t	4.32d	10.0		
		Z		7.2	6.17t	3.83d	7.0		
iPr	tBu	E							
		Z		9.5	6.09d	3.97s			1.05s
tBu	iPr	E			5.18s				
		Z							
tBu	Et	E			5.14s	4.40t	7.5		
		Z			6.08s				
Et	tBu	E		7.5	5.31t	4.46s			
		Z		7.0	6.24t	4.00s			

APPENDIX VI

SPECTRAL PARAMETERS FOR 2,5-DIHYDROFURANS

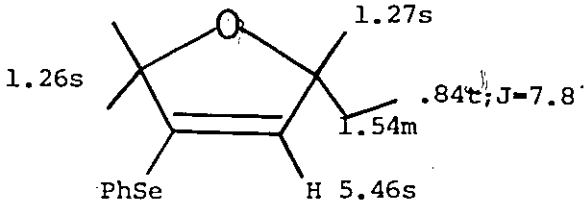
TABLE 1 : 3-Phenylseleno-2,5-dihydrofurans (^{1}H NMR)

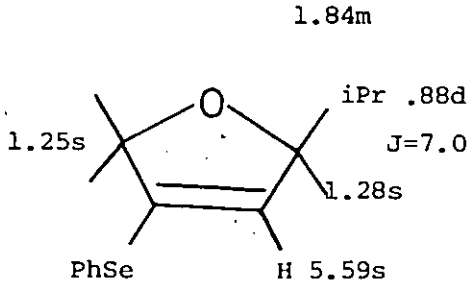
TABLE 2 : 3-Phenylthio-2,5-dihydrofurans (^{1}H NMR)

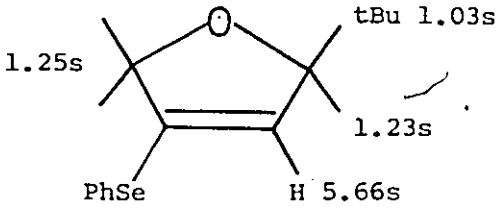
TABLE 3 : 3-Iodo-2,5-dihydrofurans (^{1}H NMR)

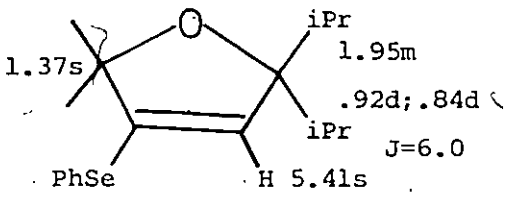
TABLE 4 : 3-Phenyl-2,5-dihydrofurans (^{13}C NMR)

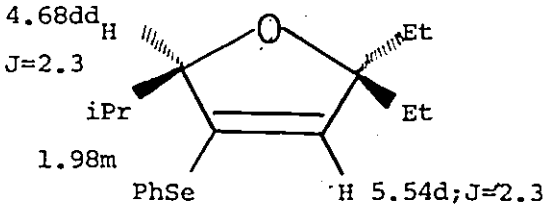
TABLE 1

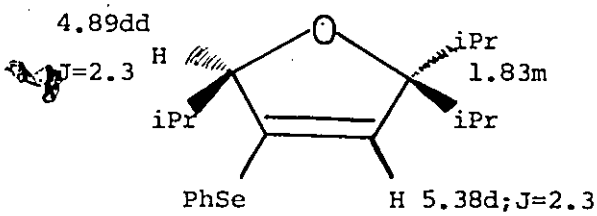

1.27s
1.26s
.84t;J=7.8
1.54m
PhSe
H 5.46s

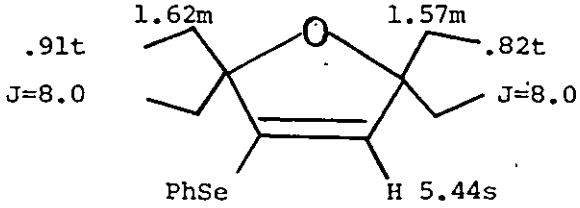

1.84m
iPr .88d
J=7.0
1.25s
1.28s
PhSe
H 5.59s


tBu 1.03s
1.25s
1.23s
PhSe
H 5.66s


iPr
1.95m
1.37s
.92d;.84d
iPr
J=6.0
PhSe
H 5.41s


4.68dd
H
J=2.3
Et
iPr
Et
1.98m
PhSe
H 5.54d;J=2.3


4.89dd
H
J=2.3
iPr
1.83m
iPr
iPr
PhSe
H 5.38d;J=2.3


1.62m
1.57m
.91t
.82t
J=8.0
J=8.0
PhSe
H 5.44s

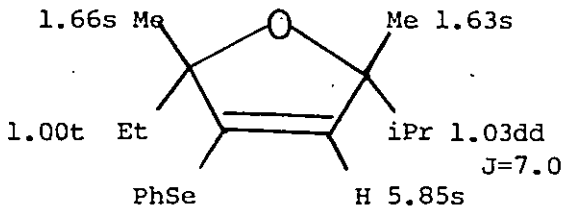
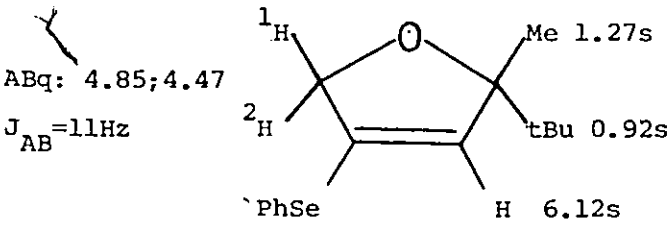
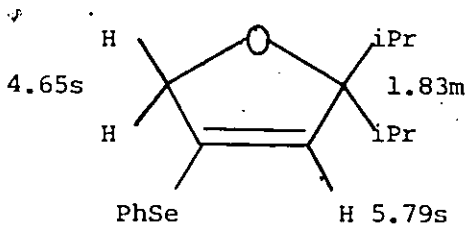
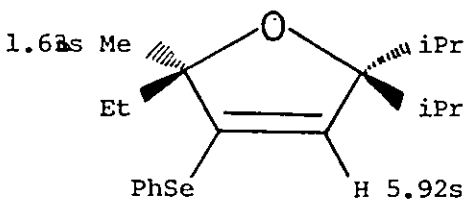
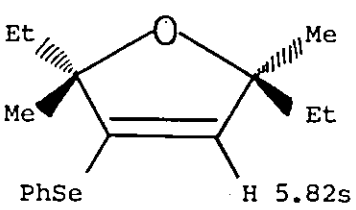

1.66s Me
Me 1.63s
1.00t Et
iPr 1.03dd
J=7.0
PhSe
H 5.85s

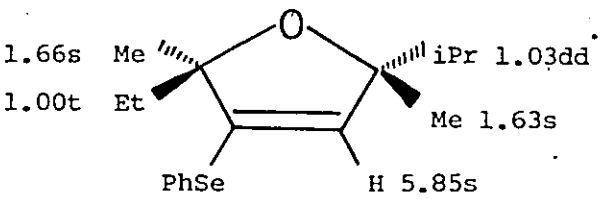
TABLE 1 (continued...)

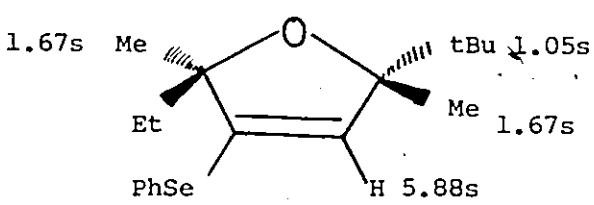


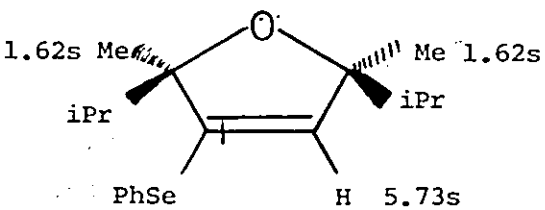












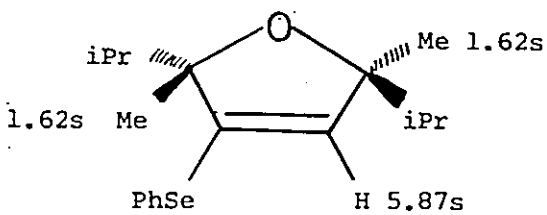
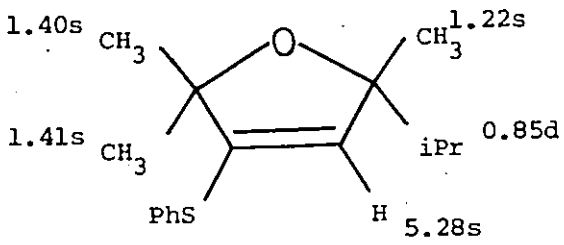
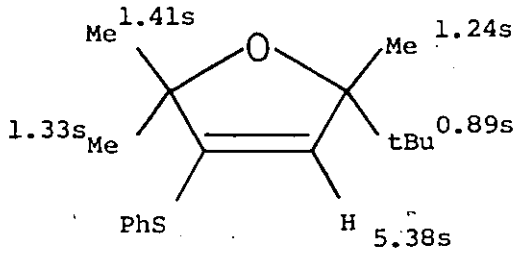
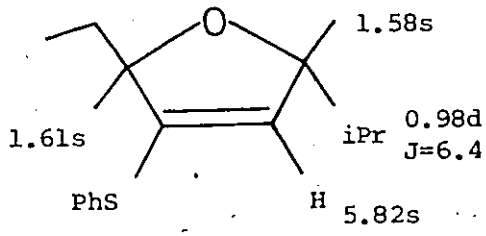
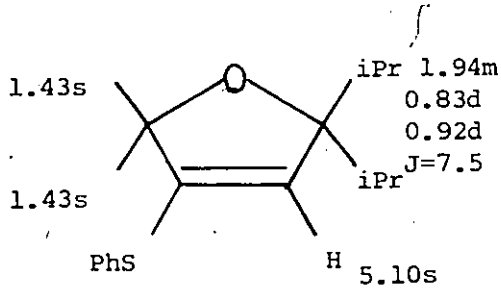


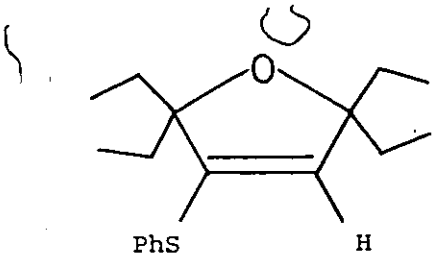
TABLE 2

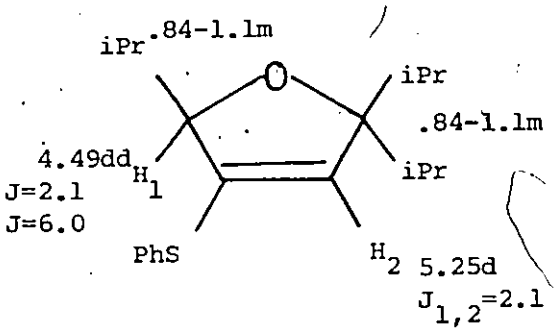




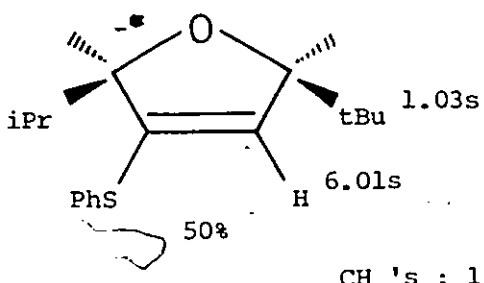


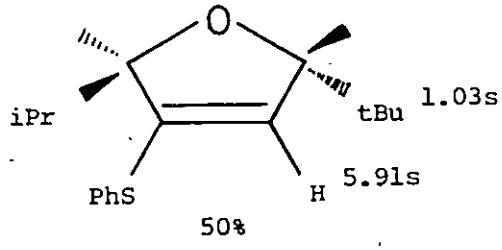






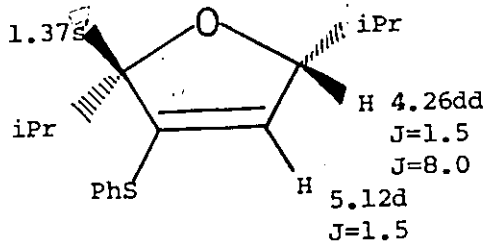
Other protons: 2.2-1.44m

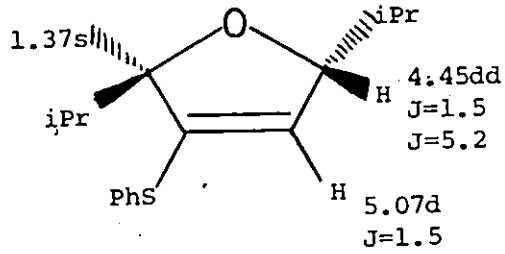


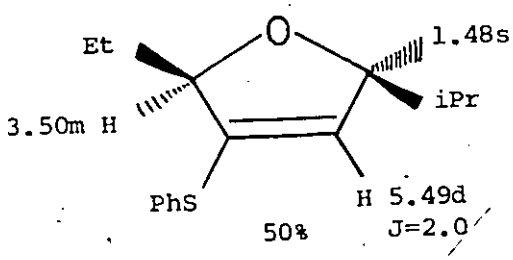


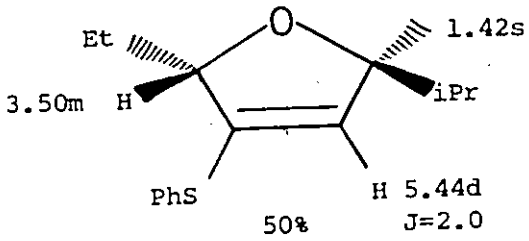
CH_3's : 1.54-1.70 m

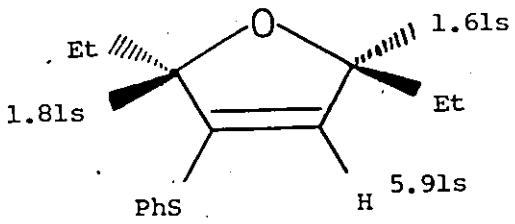
TABLE 2 (continued...)











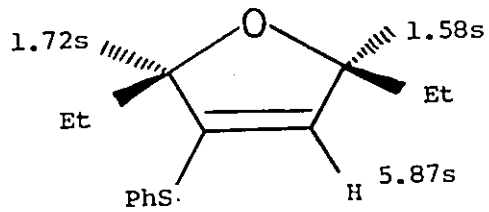
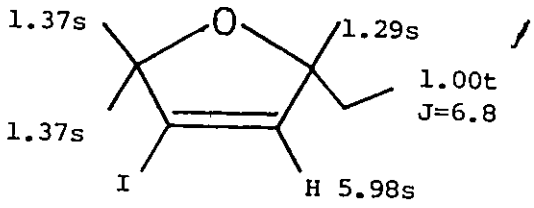
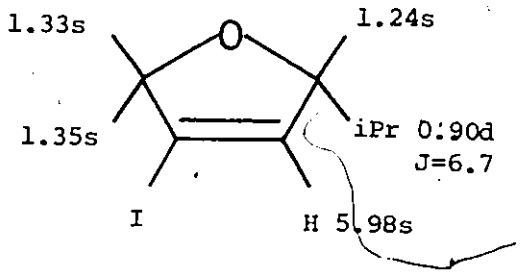
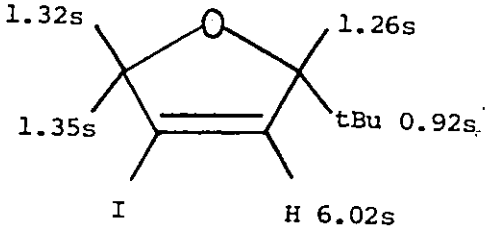
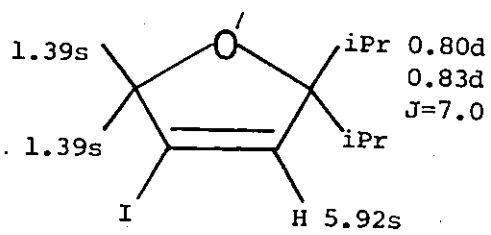


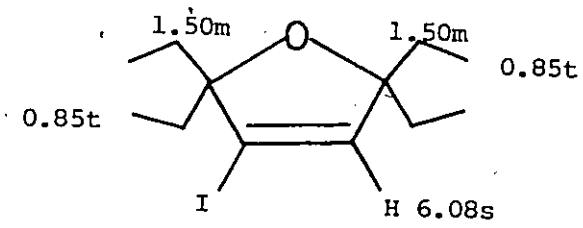
TABLE 3

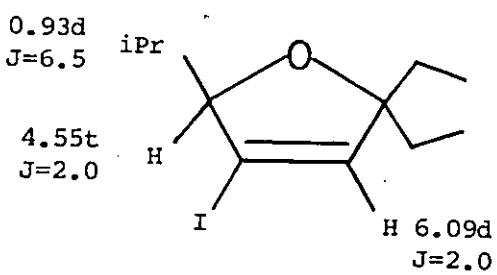

1.37s
1.29s
1.00t
J=6.8
1.37s
I
H 5.98s


1.33s
1.24s
1.35s
iPr 0.90d
J=6.7
I
H 5.98s


1.32s
1.26s
1.35s
tBu 0.92s
I
H 6.02s


1.39s
iPr 0.80d
0.83d
J=7.0
1.39s
iPr
I
H 5.92s


1.50m
1.50m
0.85t
0.85t
I
H 6.08s


0.93d
J=6.5
iPr
4.55t
J=2.0
H
I
H 6.09d
J=2.0

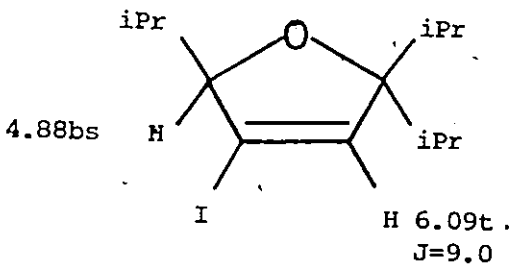
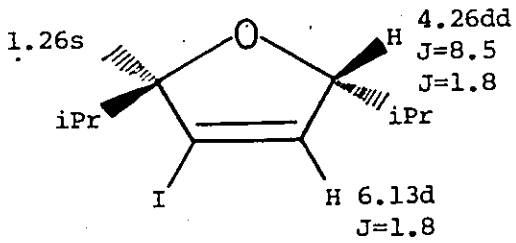
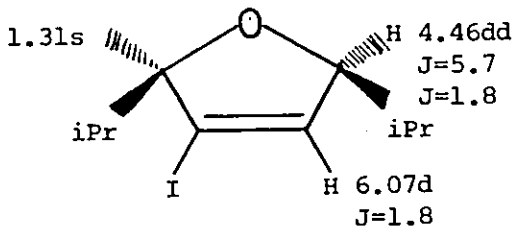

iPr
iPr
4.88bs
H
iPr
I
H 6.09t.
J=9.0

TABLE 3 (continued...)



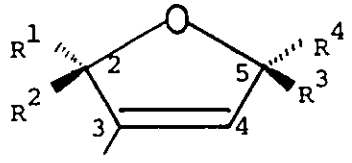


Other protons : 0.90m (24H)

Ratio of two isomers : 62 : 38

TABLE 4

Carbon-13 NMR parameters for some 3-phenylseleno-2,5dihydrofurans



R^1	R^2	R^3	R^4	C_2	C_3	C_4	C_5	R^1	R^2	R^3	R^4	AROMATIC
Et	Et	Et	Et	91.6	135.5	132.7	94.0	31.6t 8.6q	31.6t 8.6q	31.0t 8.7q	31.0t 8.7q	134.7;131.6; 128.1;129.3
Me	Me	Me	Et	89.4	135.0	131.6	89.1	26.9q	28.6q	27.8q	34.5t 9.1q	133.8;129.2 127.7;;3;.4
Me	Me	Me	iPr	89.3	133.8	131.6	91.5	29.7q	28.3q	25.1q	37.7d 18.2q 17.9q	134.8;129.2 127.7;131.3
Me	Me	Me	tBu	89.3	135.1	131.6	93.6	29.7q	27.5q	23.6q	37.3s 26.3q	133.7;129.2 127.7;129.4
Me	Me	iPr	iPr	89.3		131.6	97.3	28.6q	28.6q	33.5d 19.5q 18.4q	33.5d 19.5q 18.4q	134.3;129.2 127.9

ACKNOWLEDGEMENTS

The author is indebted to Dr D.G.Garratt for his interest in the present project, his invaluable suggestions and his unfailing assistance throughout the experimental work and the writting of this thesis. Recording and assistance in the interpretation of Carbon-13 NMR was particularly appreciated.

I also wish to express my gratitude to V.M.Morisset who synthesized the allenic alcohols and ran part of the kinetic experiments.

Special words of thanks go to Dr R.R.Fraser and Mr R.Capoor for the use of the 100 MHz ^{1}H NMR instrument, Dr K.J.Laidler for the use of his stopped-flow apparatus and Dr J.Krausa for recording the Mass spectra.

Finally I would like to acknowledge a Province of Ontario Scholarship for the period 1978-80.

CLAIMS TO ORIGINAL RESEARCH

Arenesulfenyl and areneselenyl halides add to the allenic functionality, in a 1:1 fashion with exclusive attack of the heteroatom on the central allenic carbon.

The mechanism of these reactions was investigated. It was found that the additions follow Ad_E2 type behavior.

In the case of sulfur there is evidence for an S_N2 type of attack leading to the formation of an alkylidenethiiranium ion. In the case of selenium it is suggested that an alkylideneepiselenurane-like species is formed during the rate determining step.

The electrophilic addition of PhSeCl, PhSCl and iodine to α-allenic alcohols leads to 2,5-dihydrofuran derivatives in quantitative yields. In the case of PhSeCl and PhSCl, the reactions are stereospecific.

A separate investigation was concerned with the first observation of axial dissymmetry induced magnetic nonequivalence in the Carbon-13 NMR of allenes.

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