SYNTHETIC AND MECHANISTIC STUDIES OF CYCLOPROPENES

THESIS

submitted to the

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for the degree of

DOCTOR OF PHILOSOPHY

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M.Sc (Baghdad) 1981

To my wife Inbethak, and our children,

Tariq, Taheer, and Rucel

ACKNOWLEDGMENT

This work described in this thesis was carried out in the department of Chemistry, the University of Newcastle Upon Tyne, from September 1986 to October 1989.

I wish to extend my sincere thanks to my supervisor Dr Mark Baird for his continual encouragement and invaluable guidance throughout this research and in the preparation of the text.

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Many thanks to my friends in the Department for their helping to make my time here so enjoyable.

My thanks to Dr. W. Clegg for determining the structure of products by X-ray crystallography.

Finally, I would like to express my deepest gratitude to the Iraqi government for their financial support and to the cultural Department in the Iraqi Embassy for their help.

Juma'a Al-Dulayymi

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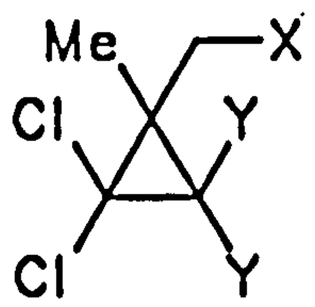
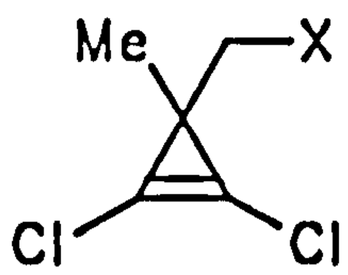
ABSTRACT

1,2-Dehalogenation of 1,1,2,2-tetrahalocyclopropanes (A, Y = Cl, X = OMe, Ar) by reaction with one equiv. of methyl-lithium at 0-20 °C leads to 1,2-dichloro-cyclopropenes (B, X = OMe, Ar); the pentachloride (A, X = Y = Cl) also react by 1,2-dechlorination to give (B, X = Cl), whereas, the bromide (A, X = Cl, Y = Br) apparently undergoes a 1,3-dehalogenation on reaction with two mol. equiv. of methyl lithium at -70 °C, leading eventually to the cyclobutene (C).



(A)



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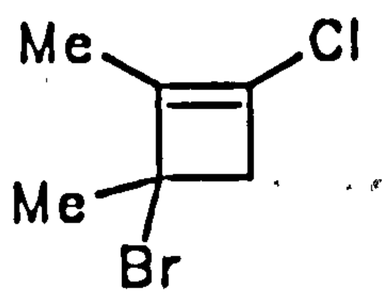
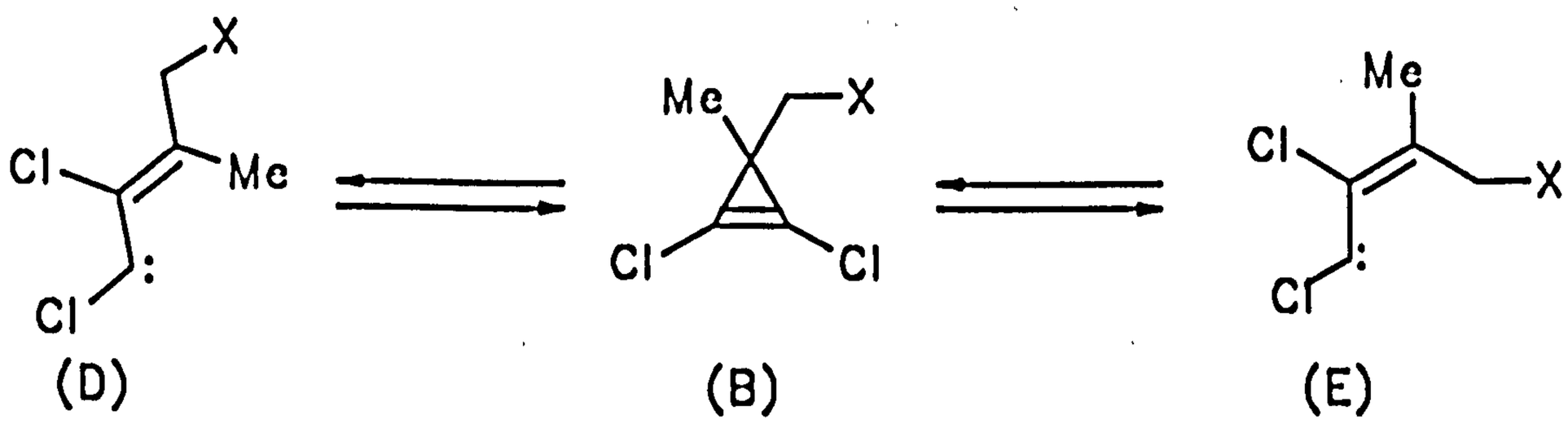


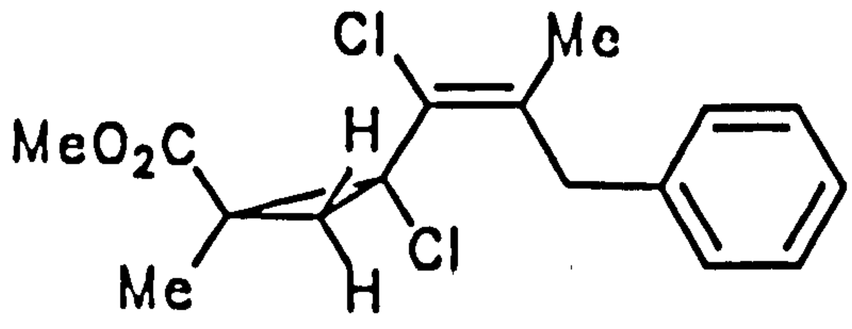
(C)

The cyclopropenes (B, X = Cl, OMe, Ar) undergo ring-opening at 0-20 °C and in principle produce two stereoisomeric carbenes (D) and (E).



(D) (B) (E)

Reaction of the cyclopropene (B, X = Ph) with methyl methacrylate leads predominantly to cyclopropane (F), the structure of which was established by an X-ray crystallographic study. This isomer is apparently derived by trapping of the carbene (E, X = Ph) rather than (D, X = Ph);

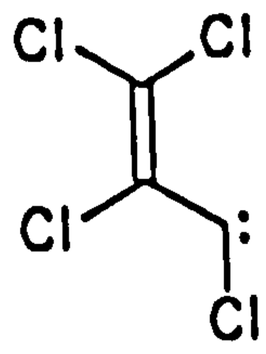


(F)

Moreover, the ester and alkene substituents are obtained with a *cis*–stereochemistry. A minor product derived by addition of (D, X = Ph) is also thought to have *cis*–stereochemistry of ester and vinyl groups. The products derived from the corresponding cyclopropenes (B, X = Cl, OMe) reflect an even more selective trapping of the carbenes (E, X = Cl, OMe).

Studies of the relative rates of cyclopropanation of a standard series of alkyl–substituted alkenes by the carbene derived from (B, X = OMe) showed that the reactivities of this carbene do not give a good linear correlation with those of ($:CCl_2$); however, they do give a linear correlation when compared to (G).

The relative rates of formation of (H) when (I, Y = H, Me, OMe, CF_3) were allowed to ring open in the presence of an excess of 2,3–dimethylbut–2–ene gave a good linear correlation with the σ_I constant for the substituent.



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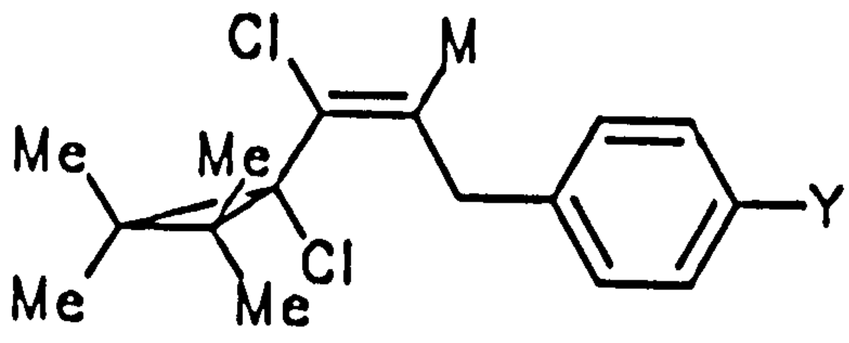

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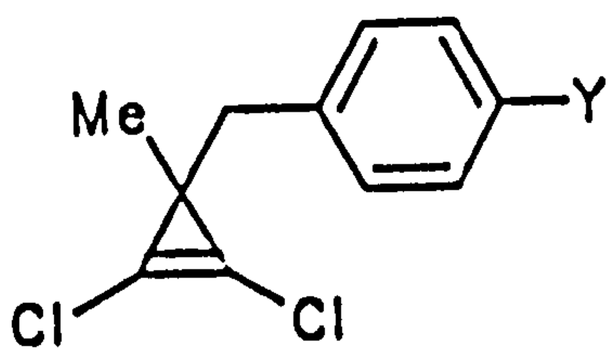
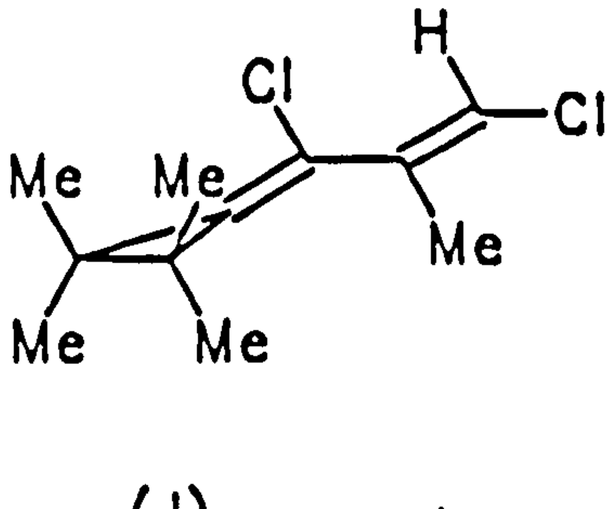
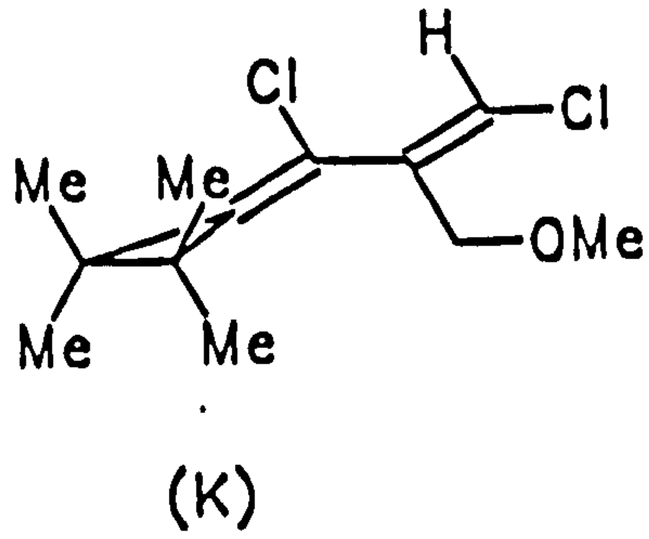


(I)

Dehydrochlorination of the derived cyclopropanes provides easy access to two series of allylidene cyclopropanes, e.g., (J) and (K).



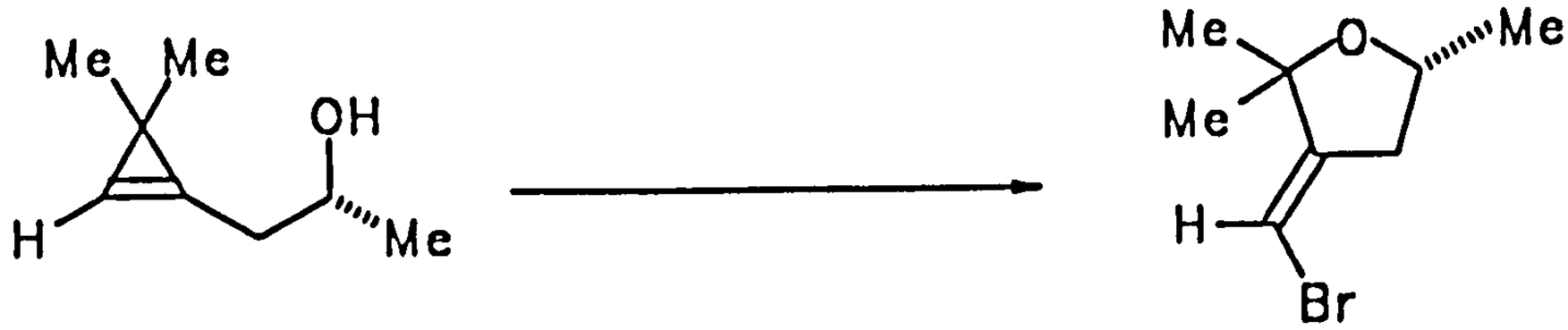
(J)



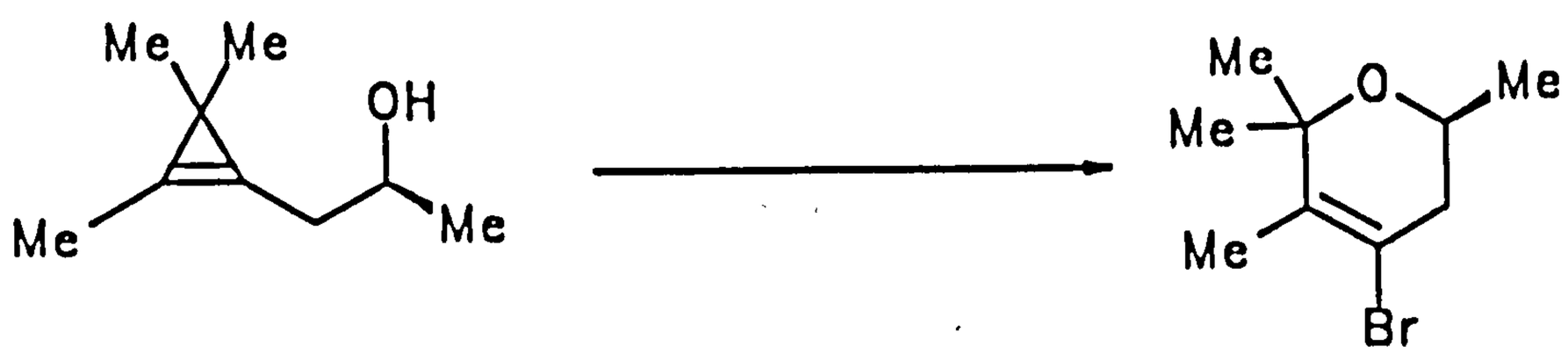
(K)

1,2–Dehalogenation of 1,1,2–trihalocyclopropanes by reaction with one mol. equiv. of methyl lithium leads to 1–halocyclopropenes. The latter reacts with second equiv. of the reagent under more vigorous conditions by a lithium halogen exchange, and the

resulting lithiocyclopropenes could be trapped by (R)-(+)- or (S)-(-)-methyloxirane to give the alcohols (L) and (M), which are converted to the optically active methylenefuran (N) and dihydropyran (O) respectively by reaction with bromine or with acid.



(L) (N)



(M) (O)

PUBLICATIONS

1- Highly functionalised carbenes and cyclopropenes from tetrahalocyclopropanes.

J.R.Al-Dulayymi and M.S.Baird, *Tetrahedron Letts.*, 6147 (1988)

2- The stereoselectivity of ring-opening of 3-substituted cyclopropenes and intermolecular trapping of derived vinylcarbenes.

J.R.Al-Dulayymi, M.S.Baird, and W.Clegg, *Tetrahedron Letts.*, 6149 (1988).

3- A novel route to optically active dihydropyrans and 3-methylenetetrahydrofurans.

J.R.Al-Dulayymi and M.S.Baird, *Tetrahedron Letts.*, 253 (1989)

4- Substituent effects in the generation and trapping of 1,2-dichloro-3,3-dialkylbut-2-en-1-ylidenes.

J.R.Al-Dulayymi, M.S.Baird, and H.H.Hussain, *Tetrahedron Letts.*, 2009 (1989).

5- A highly stereoselective generation and trapping of 1,2-dichloro-3-methyl-4-phenylbut-2-enylidenes.

J.R.Al-Dulayymi, M.S.Baird, and W.Clegg, *J.Chem.Soc.Perkin Trans. (1)*, 1799 (1989).

6- Generation and trapping of vinylcarbenes at ambient temperature: A route to functionalised vinyl- and allylidenecyclopropanes.

J.R.Al-Dulayymi and M.S.Baird, *Tetrahedron*, 7601 (1989).

7- Optically active dihydropyrans and 3-methylenetetrahydrofurans from cyclopropenyl ethanol derivatives.

J.R.Al-Dulayymi and M.S.Baird, *Tetrahedron*, 5703 (1990).

LIST OF ABBREVIATIONS

b.p	boiling point
cetrimide	cetyltrimethyl ammonium chloride
D	deuterium
DMSO	dimethylsulphoxide
equiv.	equivalent
g	gram(s)
glc	gas-liquid chromatography
h	hour(s)
ir	infra red
mCPBA	m-chloroperbenzoic acid
MHz	megahertz
mmole	millimole(s)
m.p	melting point
n.O.e	nuclear Overhauser effect
ppm	parts per million
PTC	phase transfer catalyst
TEBA	triethylbenzyl ammonium chloride
THF	tetrahydrofuran
tlc	thin layer chromatography
TMS	tetramethylsilane.

Chapter one

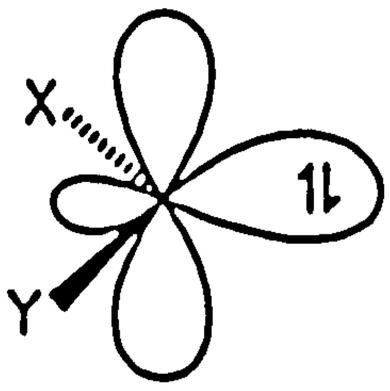
INTRODUCTION

INTRODUCTION

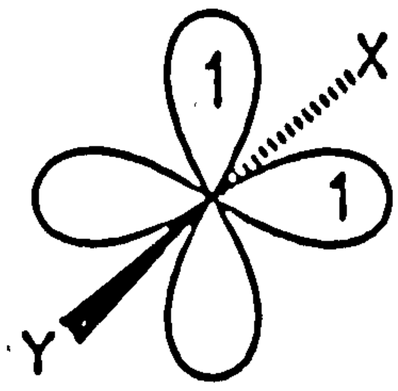
1.1 Carbenes:

These are neutral, short lived, intermediates in which a carbon has two covalent bonds to other groups and two non-bonding orbitals containing two electrons between them.[1] If the two electrons are spin paired, then the carbene is a singlet, and if the spins of the electrons are parallel, then the carbene is a triplet.

A singlet carbene is believed to have a bent sp^2 hybrid structure (1) with a vacant p orbital.



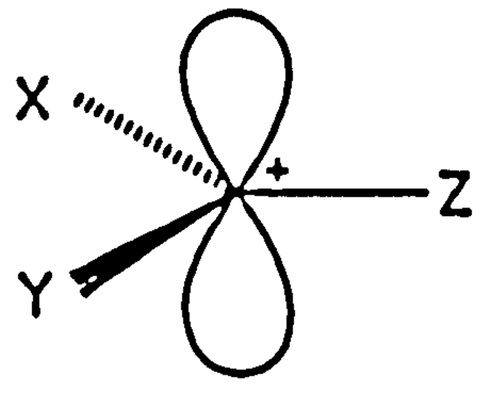
(1)



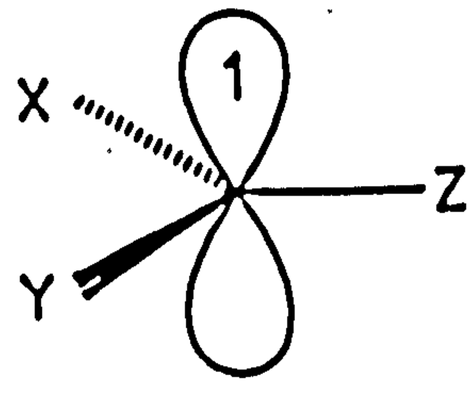
(2)

Alternatively the two electrons could have parallel spins, in which case the carbene has triplet multiplicity and will most likely conform to a linear sp hybrid structure (2), with one electron assigned to each degenerate p-orbital.

A carbene in the singlet state resembles a carbonium ion (3), whilst the triplet carbene resembles a free radical (4).



(3)



(4)

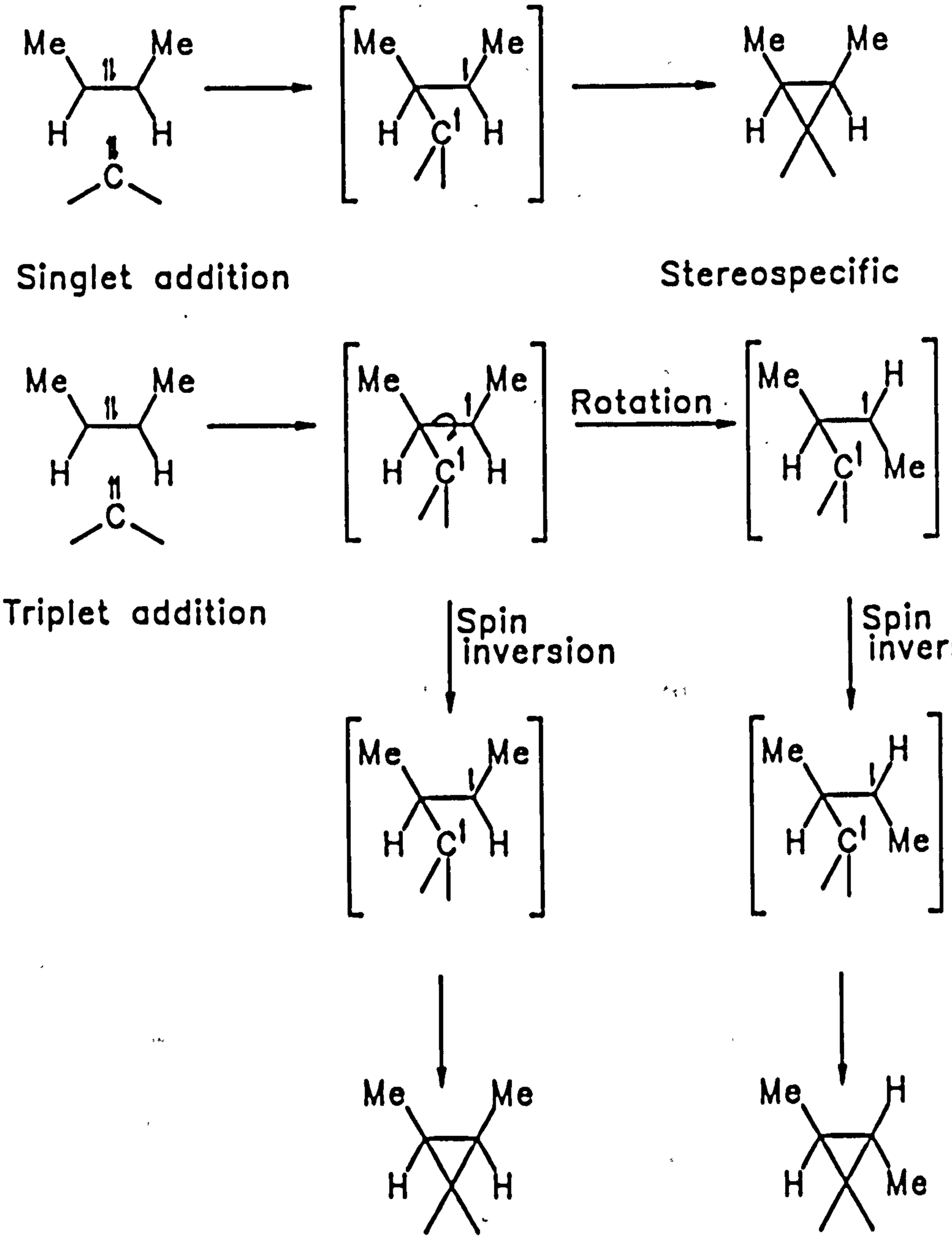
Electron spin resonance (esr) spectroscopy can be used to observe the triplet state of carbenes frozen in a solid matrix at low temperature. Usually, however, these intermediates are too reactive to permit direct observation and their existence must be inferred from their subsequent reaction products. The covalently bonded substituents (X, Y) will determine the multiplicity and energy separation between the two forms. The simplest carbene, methylene (X = Y = H), was shown to exist in a non–linear, ground state triplet configuration with a bond angle of 136^0 when generated in a low temperature matrix. The energy difference between the spin states of methylene is only 35 KJ mol^{-1} and when generated from photolysis of diazomethane the excited singlet species predominates and can react before degenerating to the ground state triplet.[1] If a carbene substituent contains a pair of electrons available for interaction with the carbenic centre, the energy difference between the spin states will be reduced and the singlet may be the lower energy form. Halogens, for example, possess a lone pair of electrons which can stabilise the singlet state by overlap into the vacant p–orbital, and consequently dihalocarbenes have singlet ground states.

In general, most carbenes with carbon, hydrogen or halogen substituents are electrophilic as the carbenic centre is electron deficient. Addition of a carbene to the π–bond of an alkene is possibly the most studied reaction of carbenes. The existence of singlet and triplets were first postulated by Skell soon after the discovery of dichlorocarbene ($:CCl_2$). He suggested that the mechanism and stereochemistry of the addition of carbenes to alkenes depends on the spin state of the carbene and proposed that the spin–paired singlet carbene would undergo a stereospecific, concerted addition to a double bond thus preserving the stereochemistry of the alkene. However, addition of a triplet carbene to a double bond would lead to a triplet diradical intermediate which must invert the spin of one electron by a collisional process before ring closure is possible (scheme 1). The intermediate may exist sufficiently long to enable rotation about the C–C bond to occur and hence the addition is non–stereospecific.[2,3,4] Skell's

hypothesis has been successful in rationalising many experimental observations; however the assumption about the relative rates of the steps may not hold in all cases.

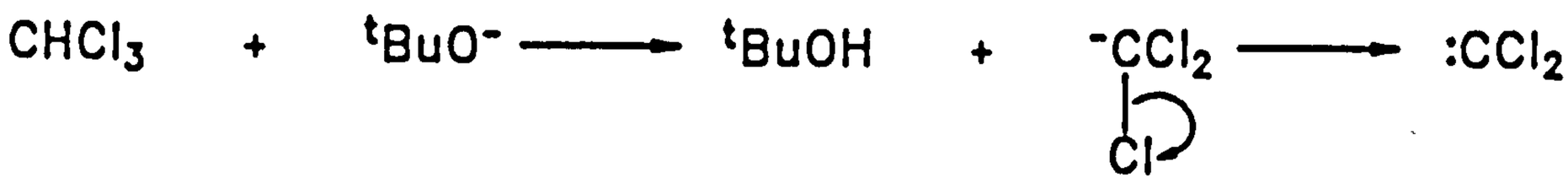
Scheme (1)

Skell's hypothesis.



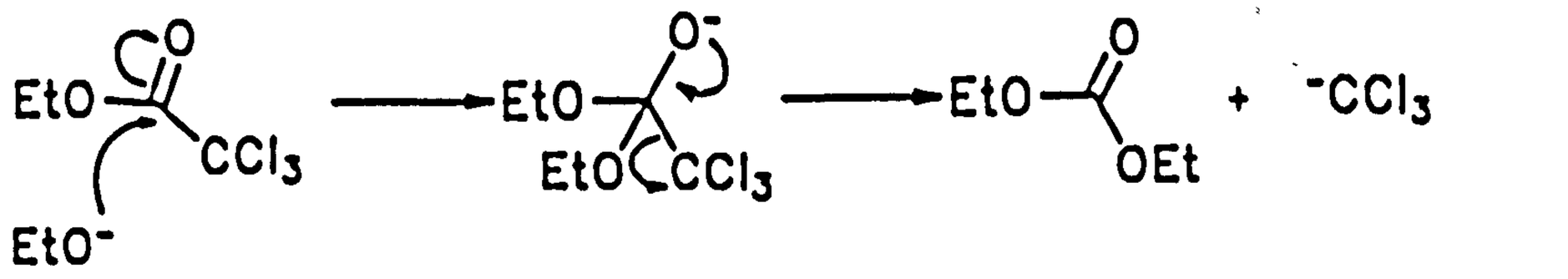
1.2: Generation of carbenes:

Doering and Hoffman, in 1954, demonstrated the first addition of dichlorocarbene to alkenes by treating chloroform with potassium t–butoxide in the presence of cyclohexene.[5,6] This reaction involves deprotonation of chloroform to give the trihalomethyl anion, followed by loss of a chloride anion to give neutral dichlorocarbene, which in turn adds to the olefin.

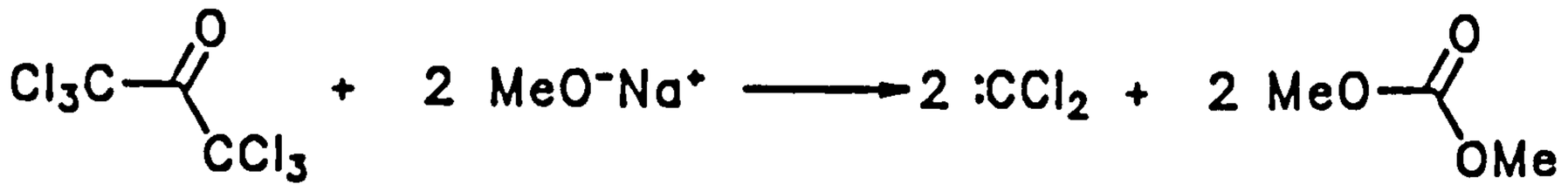


The procedure was rapidly developed into a synthetically viable route to dihalocyclopropanes, employing a variety of solvents and potassium t-butoxide as the base. A major disadvantage, however, is the formation of alcohol which can react with the carbene, and the need to use substrates which are not base sensitive.

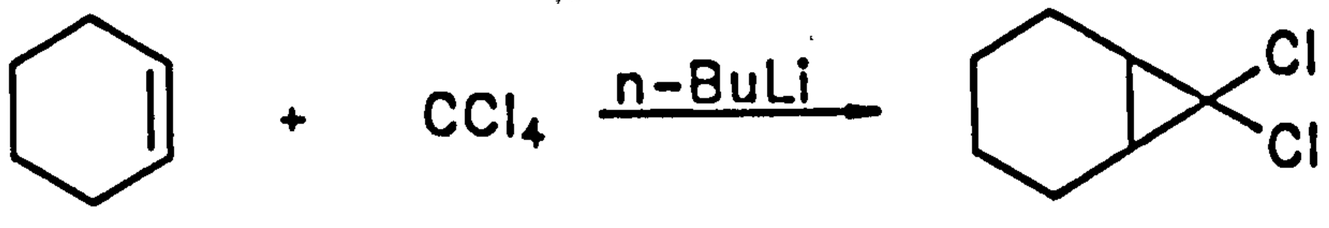
It was later found that treatment of alkyl trihaloacetates with sodium ethoxide, and thermal decomposition of sodium trihaloacetates provide general routes to dihalocarbenes which are free from the alcohol formation.[7,8]



The reaction of hexachloroacetone with sodium methoxide as above leads to two equivalents of dichlorocarbene per molecule.[9]

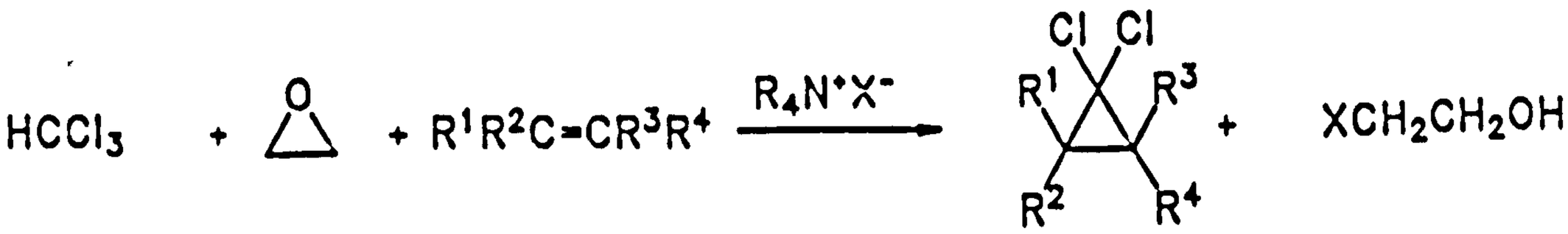


A polyhalomethane can react with an alkyl–lithium such as n–butyl–lithium at low temperature in the presence of alkene to give a dihalocyclopropane in good yield.[10]

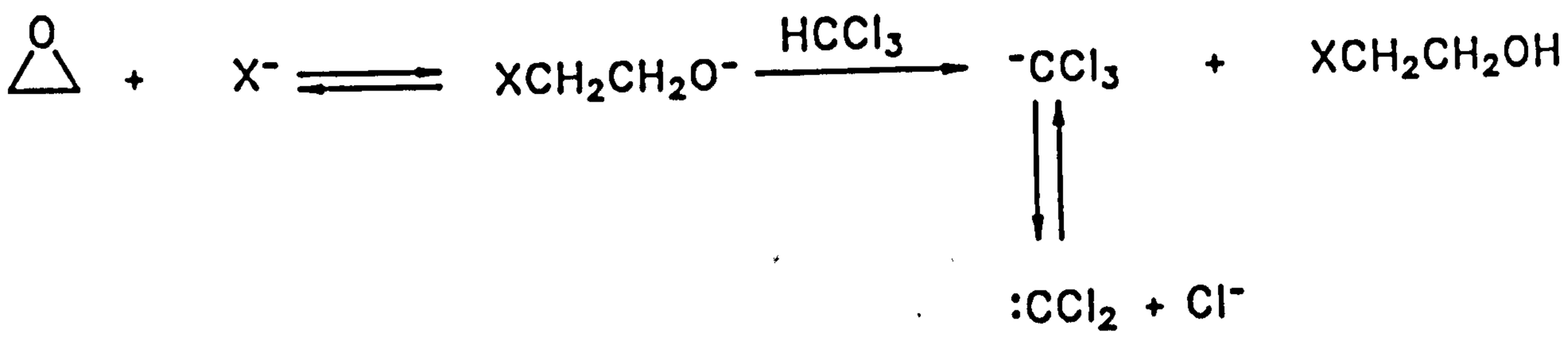


This method is useful for preparing monochlorocyclopropanes by using bromochloromethane or dichloromethane with an alkyl–lithium.

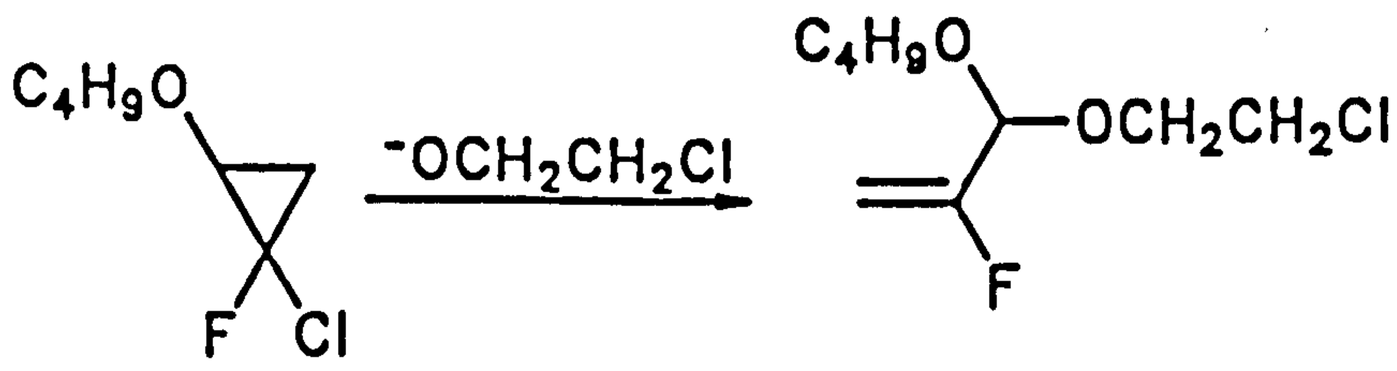
The reaction mixture of chloroform, olefin, ethylene oxide and a quaternary ammonium salt at 130–170 ^{0}C in a pressure vessel yields dichlorocyclopropanes.[11,12]



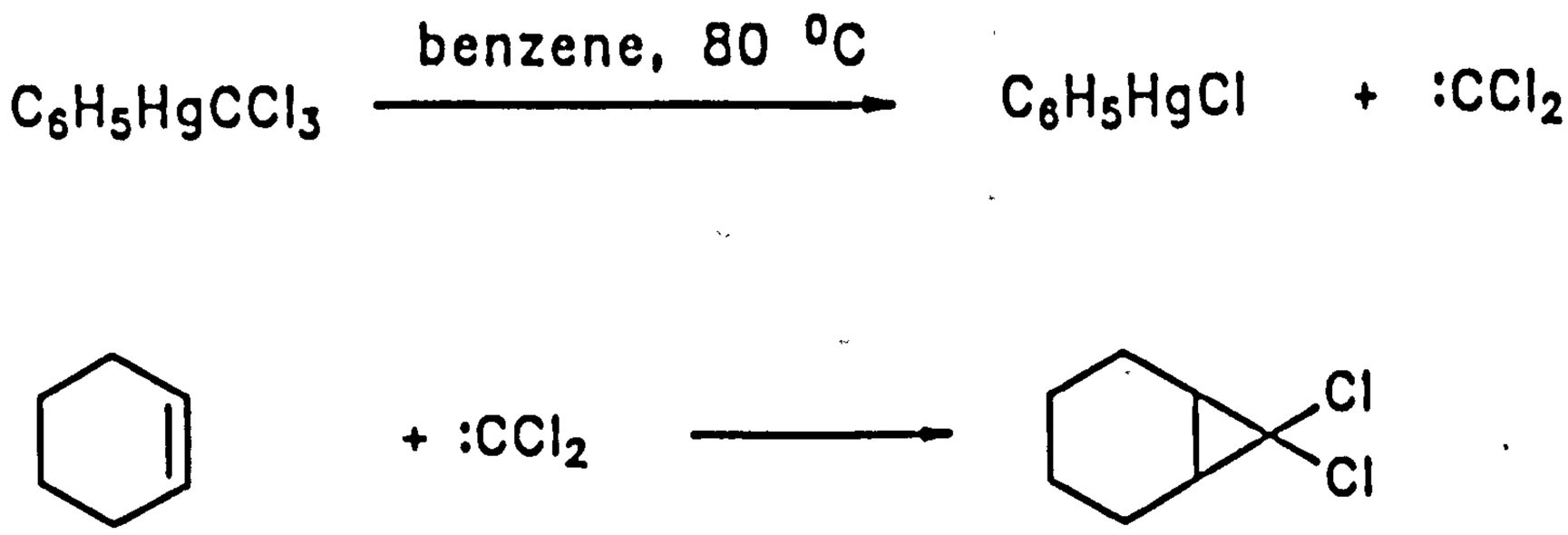
The reaction proceeds via attack of a soluble anion on ethylene oxide, forming an alkoxide anion which is capable of eliminating a proton from chloroform.



This method has been successfully used for the preparation of chlorofluoro[12,13] and difluorocyclopropanes[12] from the industrially available haloforms $HCCl_2F$ and $HCClF_2$. However, some of the cyclopropanes obtained by this method are unstable to the reaction conditions.[14]

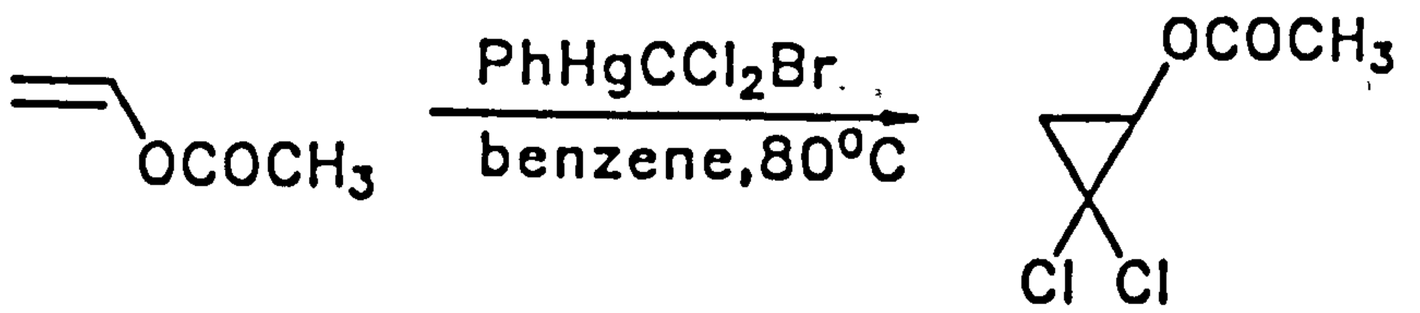


Thermolysis of trihalomethylphenylmercury compounds, introduced by Seyferth and co-workers,[15,16] is a good method for generating $:CBr_2$, $:CCl_2$, mixed carbenes (e.g., :CBrCl), monohalocarbenes (e.g., :CHBr) and methylene $:CH_2$, by suitable modification of the original mercury salt, e.g.:



This method is useful for the cyclopropanation of weakly nucleophilic olefins, e.g. trichloro- and tetrachloroethylene, leading to adducts in high yield, which had previously only been prepared in low yield.[17] It is also used to prepare cyclopropanes

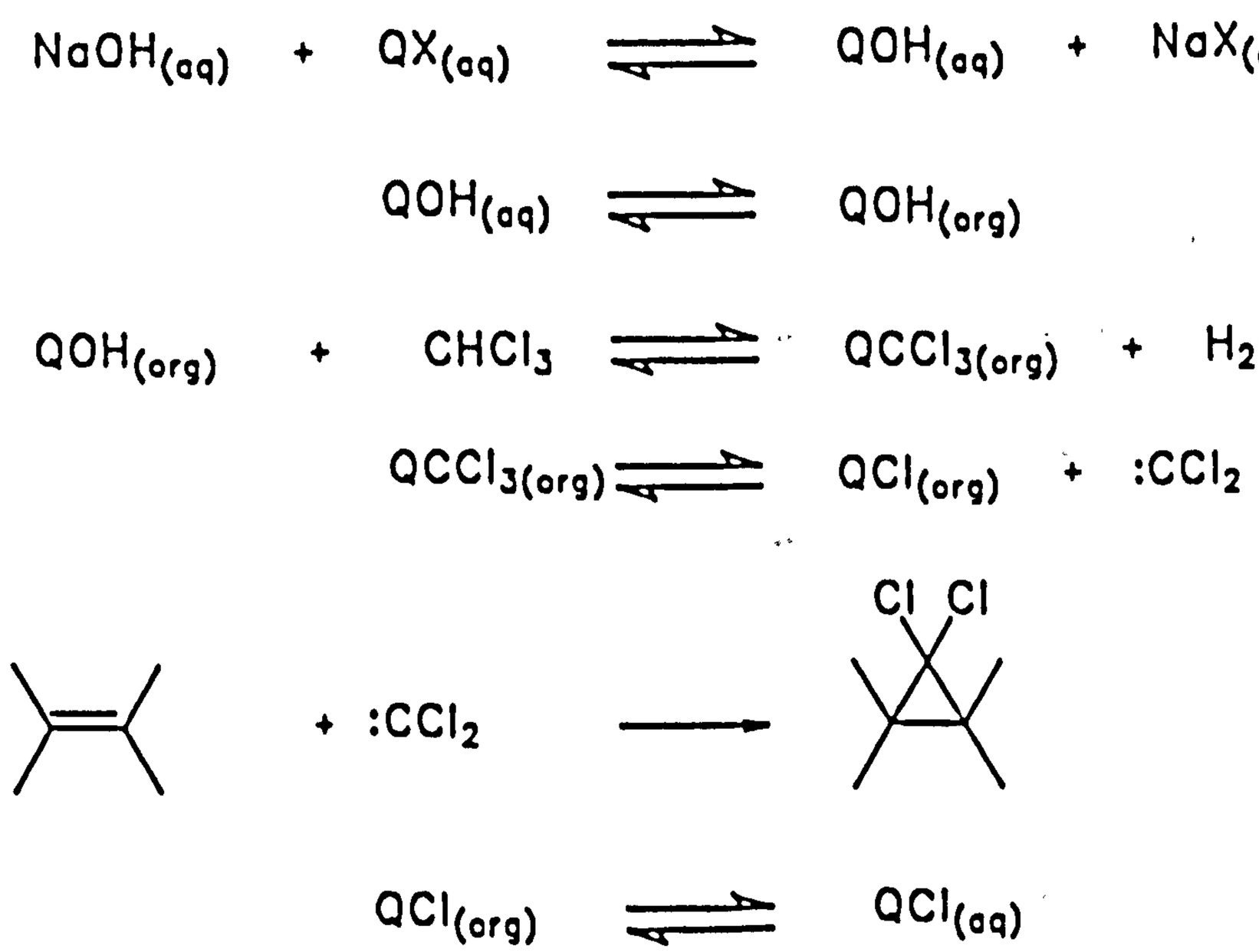
from alkenes which contain base sensitive functional groups, which react with trihalomethyl anion.[16]



Problems associated with this method, however, are the high cost and toxic nature of the reagent.

In general, all methods so far discussed require anhydrous conditions; however there is one method available, which does not, " Phase transfer catalysis " (PTC). This route was first used by Starks[18] and Makosza[19] for the generation of dichlorocarbene from chloroform and aqueous sodium hydroxide in the presence of triethylbenzyl ammonium chloride (TEBA). Using various alkenes, dichlorocyclopropanes were isolated in yields of 64–80%. In contrast, treatment of chloroform with 25% sodium hydroxide in the presence of cyclohexene but without catalyst gave 7,7–dichlorobicyclo(4.1.0)heptane in only 5% yield.[18,20]

The phase transfer process occurs as follows:

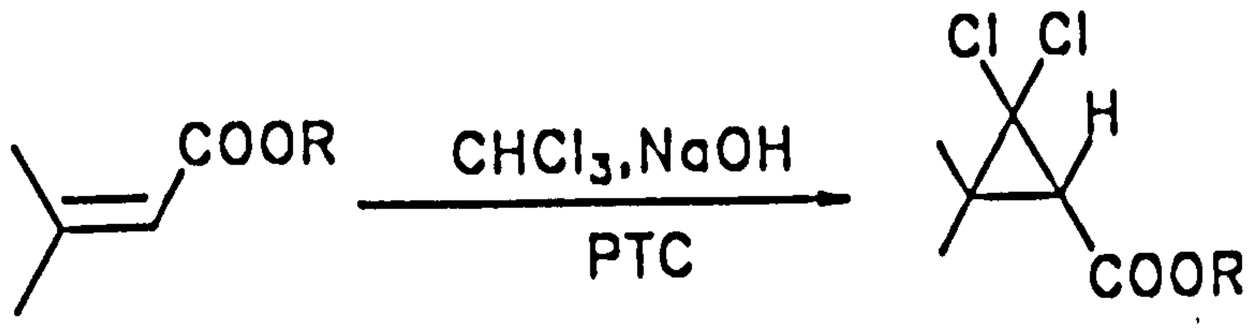


Q⁺ = quaternary ammonium ion

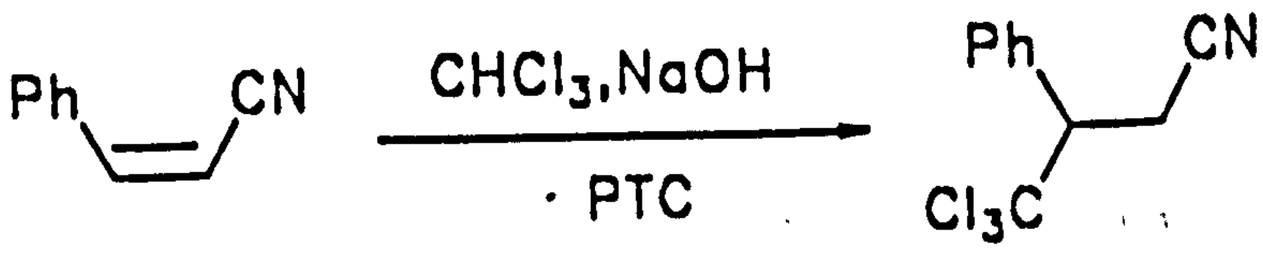
X = halogen

Sodium hydroxide is not soluble in the organic phase but reacts with the phase transfer catalyst to produce a quaternary ammonium hydroxide which is a strong base, soluble in organic solvents and the active species in the phase transfer process. The hydroxide ion is now able to deprotonate the chloroform in the organic phase or at the surface to give a trichloromethyl anion from which dichlorocarbene is generated by loss of the halide ion. The by–products of the reaction (H_2O and QCl) pass back into the aqueous phase where the catalyst is available to react with further sodium hydroxide. The dichlorocarbene generated in the organic phase reacts mainly with the alkene forming a cyclopropane, and to only a minor extent with the water.[20,21]

As stated above, the dichlorocarbene of the Makosza process is in equilibrium with the trichloromethyl anion. Depending upon whether electron rich or electron poor olefins are present, either the electrophile $:CCl_2$, or the nucleophile $^{-}CCl_3$, or in some cases both are captured.[22]



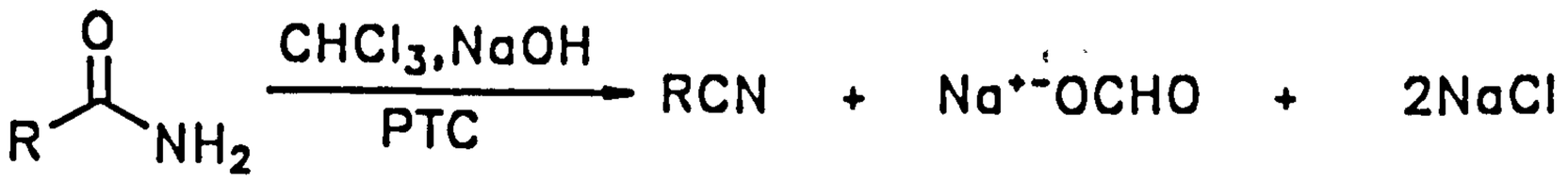
In the presence of electron deficient alkenes such as (5), the trihalomethyl anion is trapped in a Michael type addition to give the trihalomethyl–compound.[22]



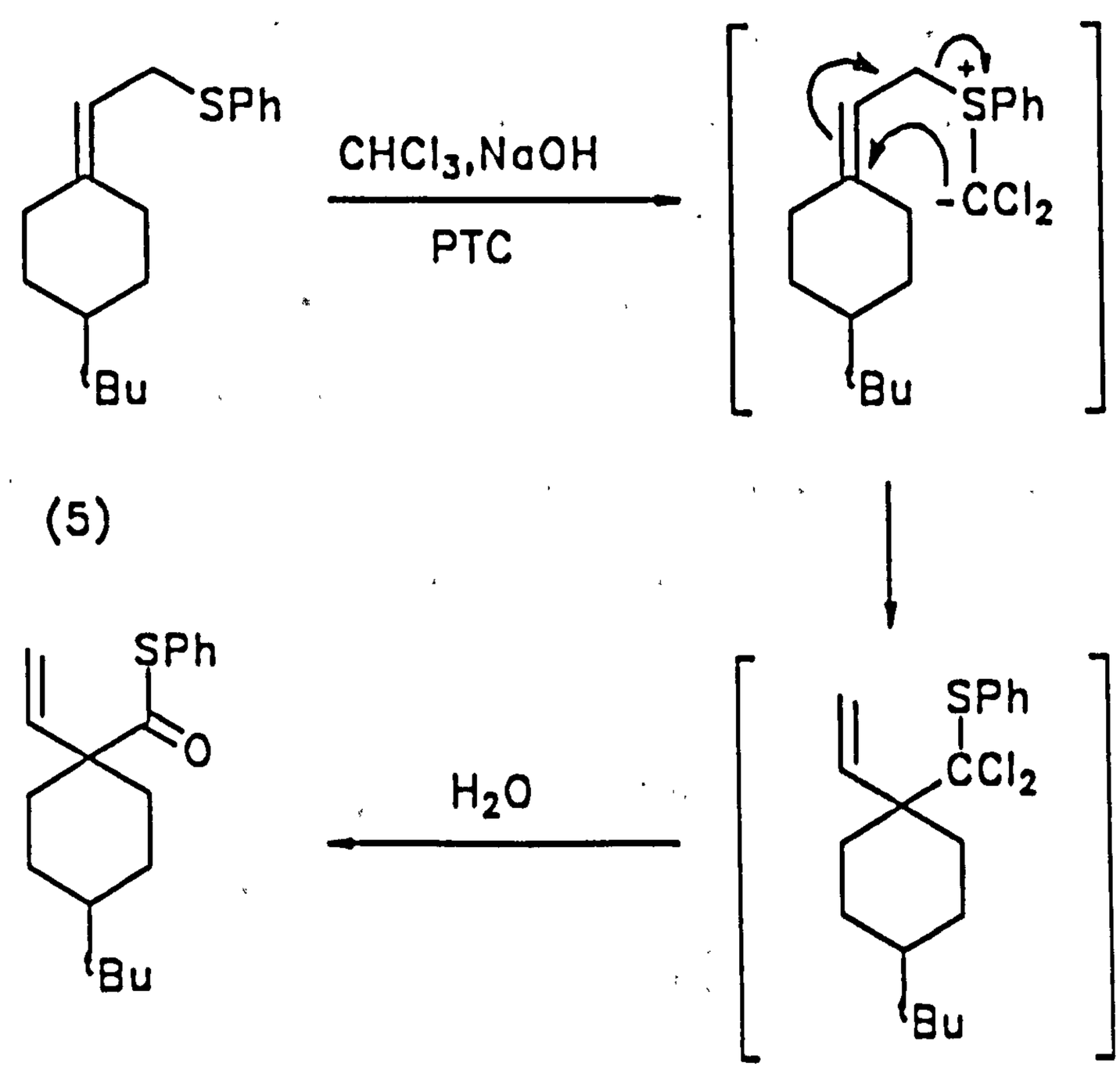
(5)

The phase transfer process utilises inexpensive reagents, a simple procedure, and thus constitutes perhaps the most useful source of dihalocarbenes.

Dihalocarbenes generated by PTC can be trapped by a number of functional groups in addition to the double bond, e.g., dichlorocarbene reacts with aliphatic and aromatic amides to give nitriles.[23]

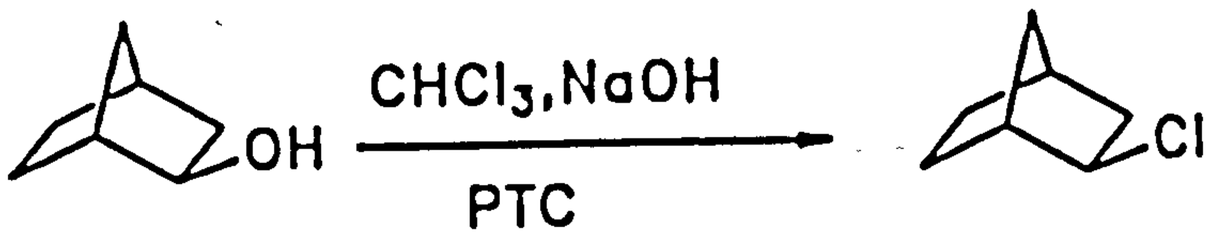


Moreover, dichlorocarbene attacks (6) at sulphur rather than at the double bond, followed by a [2,3]–sigmatropic rearrangment and hydrolysis.[23]



Dihalocarbenes generated under phase transfer catalysis also react with alcohols. Reaction of (7) with dichlorocarbene afforded (8) in excellent yield. The resulting chloride is obtained with retention of configuration and this has been explained by initial attack of dichlorocarbene on the hydroxyl group followed by an S_Ni

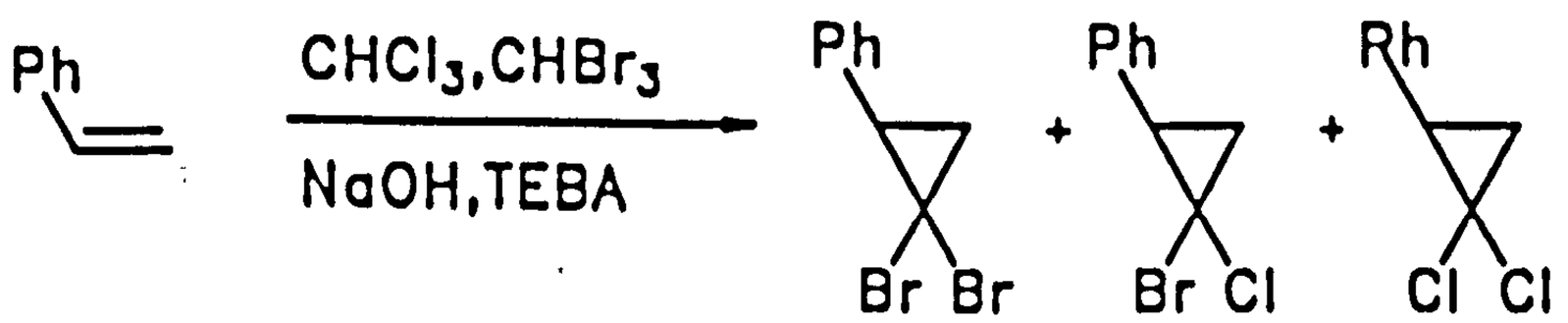
mechanism.[24]



(7) (8)

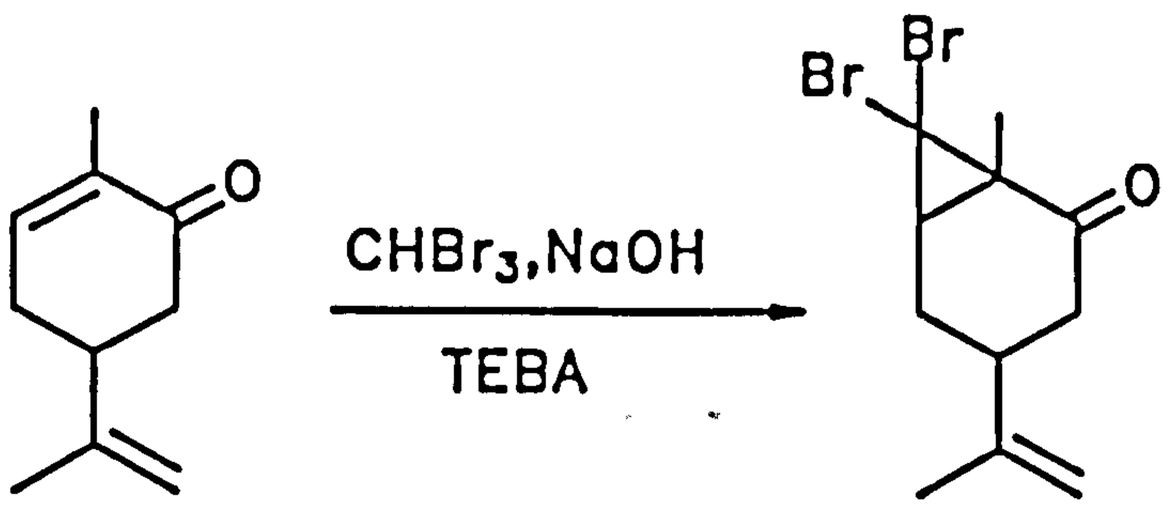
1.3: Preparation of dihalocyclopropanes.

Dihalocarbenes are electrophilic, and they react preferentially with the most nucleophilic double bond in a given molecule. The addition of dibromocarbene ($:CBr_2$) and dichlorocarbene ($:CCl_2$) to simple alkenes is characterised by good yields, convenient reaction conditions and cheap reagents (in particular when the PTC method is used). Dibromocarbene is more reactive than dichlorocarbene. It is claimed this prediction is borne out by competition experments: equal amount of chloroform and bromoform, styrene, TEBA, and concentrated sodium hydroxide give 1,1–dibromo–2–phenyl cyclopropanes as the major product.[23] However, this ignores the reversibility of carbene and carbanion formation.



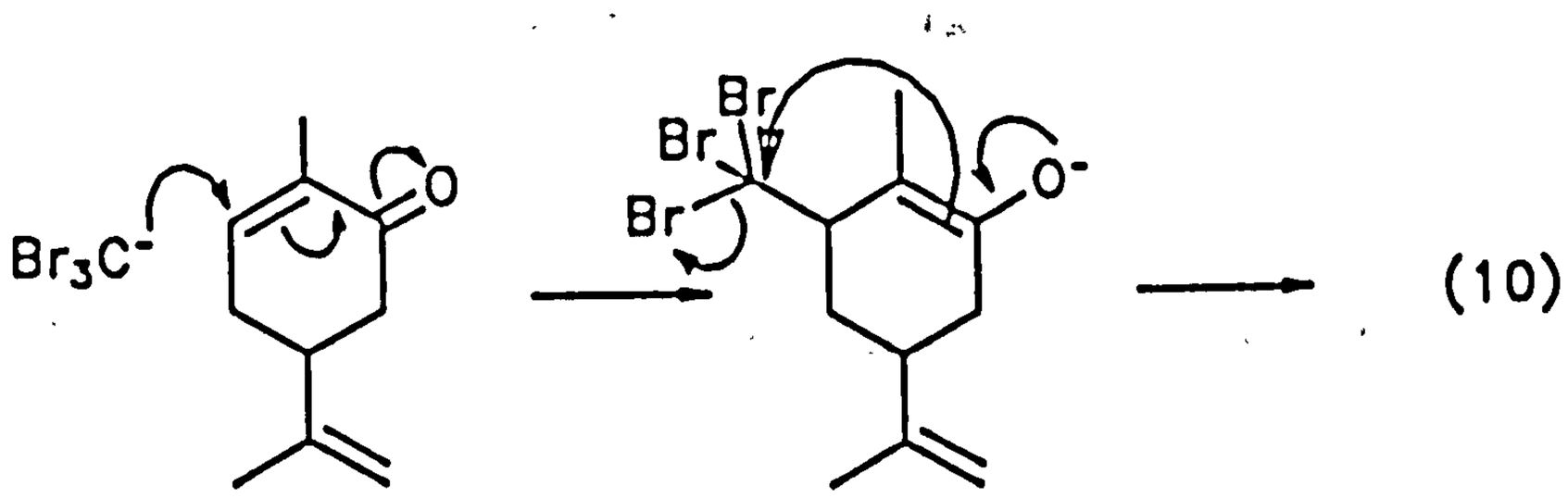
78 7.3 14.7%

As stated above, dihalocarbenes are electrophilic, but the reaction of carvone (9) with dibromocarbene generated under PTC led to the adduct (10), which is apparently produced by addition of ($:CBr_2$) to the less electron rich double bond.[25]



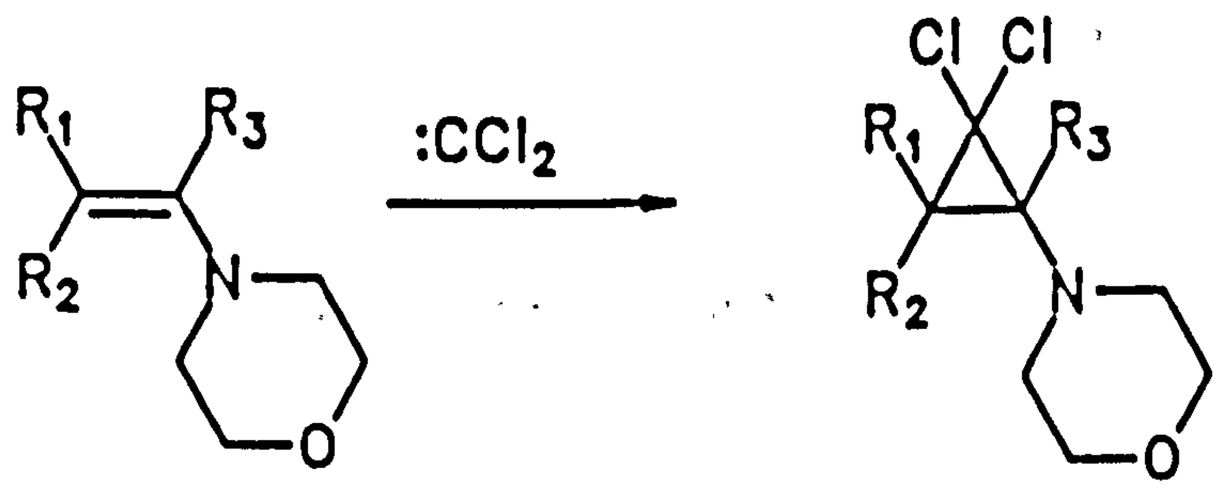
(9) (10)

This may arise from a Michael–addition of the nucleophilic tribromomethyl anion ($^{-}CBr_3$), followed by intramolecular displacement of bromide ion, rather than by a concerted carbene addition.[25]



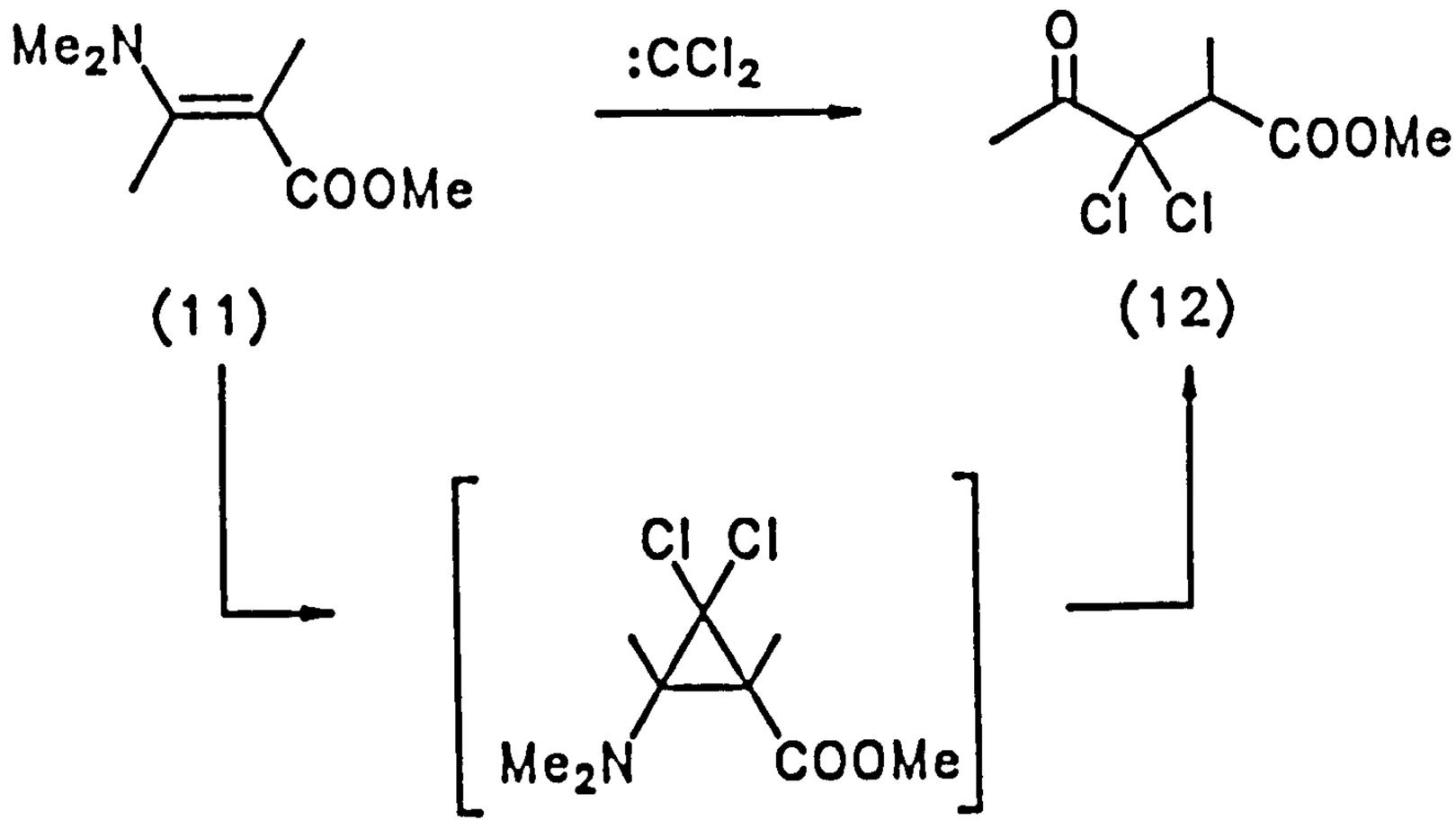
(9) (10)

Alkenes with an electron–releasing substituent adjacent to the double bond, such as an enol ether, enamine, or vinylic ester are also efficient carbene traps.[26]



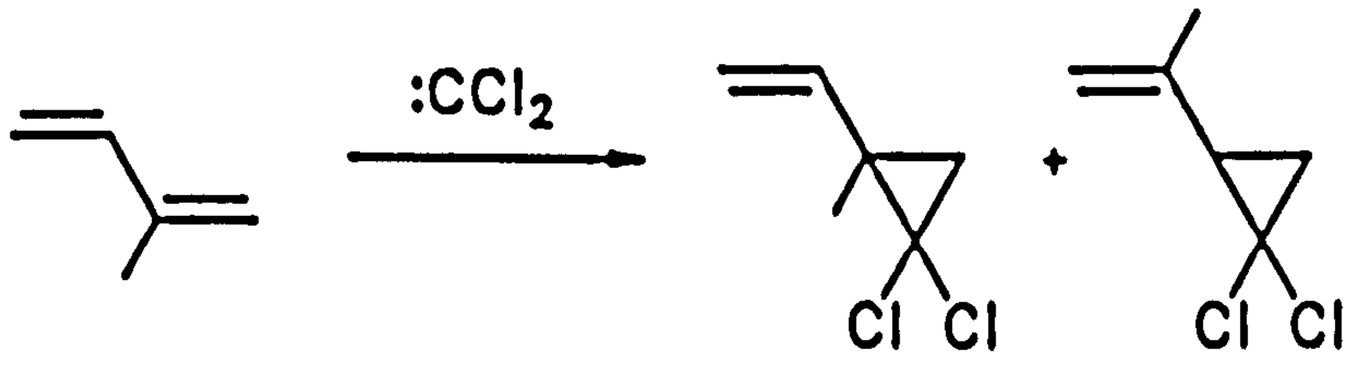
(9) (11)

However, some enamines react with dihalocarbenes to form unstable cyclopropanes which undergo ring–opening to the γ–keto ester derivative, e.g. reaction of (11) with $:CCl_2$ led to (12).[27]



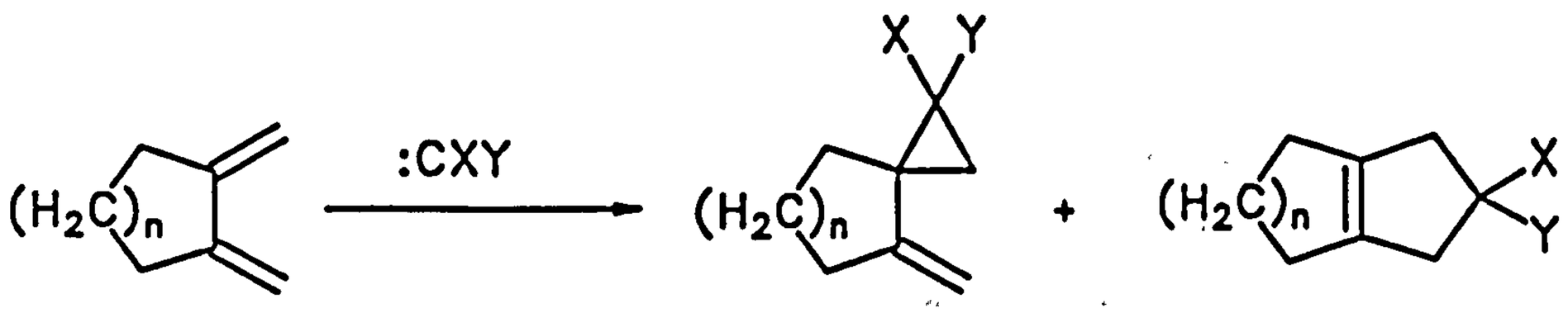
Here, the mechanism may involve the participation of the nitrogen lone pair.

Reaction of dihalocarbenes with 1,3–dienes leads to the formation of vinyl cyclopropanes, the preferred site of addition generally being the more alkylated double bond, and 1,4–addition does not normally take place.[28]



Relative rate: 49 : 1

1,4–Addition of carbenes to dienes is very rare, but it has been shown to occur in some cases.[29] When the diene (13) was allowed to react with dihalocarbene, both 1,2 and 1,4–addition were obtained, in a ratio depending on the ring size and the halogen substituent.[30]

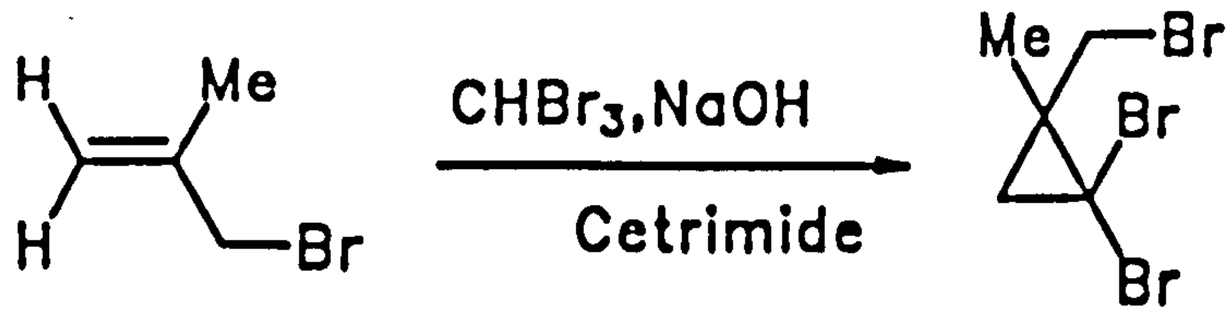


(13)

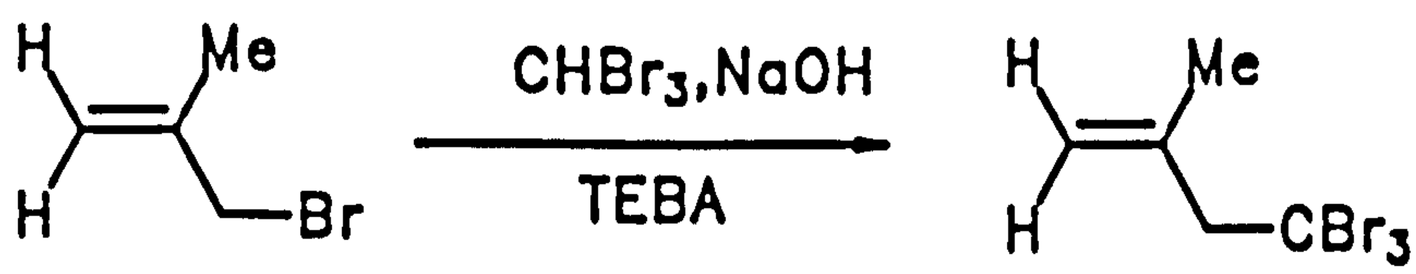
n=4,7.

X=Y=halogen.

Sometimes, the products are extremely dependent on the nature of the catalyst.[31] Treatment of (14) with a small excess of bromoform and a large excess of concentrated sodium hydroxide in the presence of cetrimide led to a single product (15). However, when the cetrimide was replaced by TEBA, the reaction followed a different course to produce (16). This is derived by nucleophilic substitution of bromide ion by tribromomethyl anion.



(14) (15)

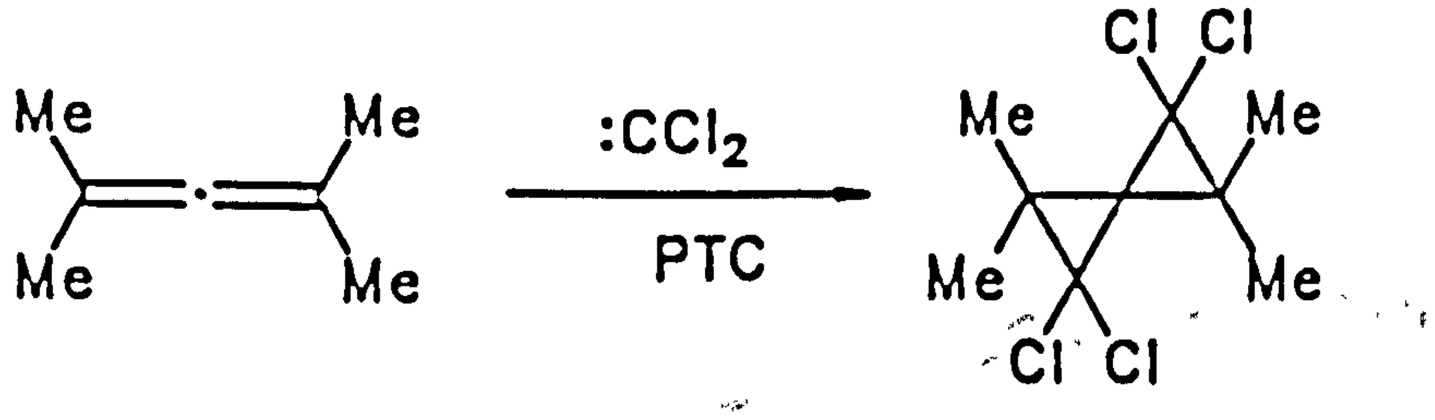


(14) (16)

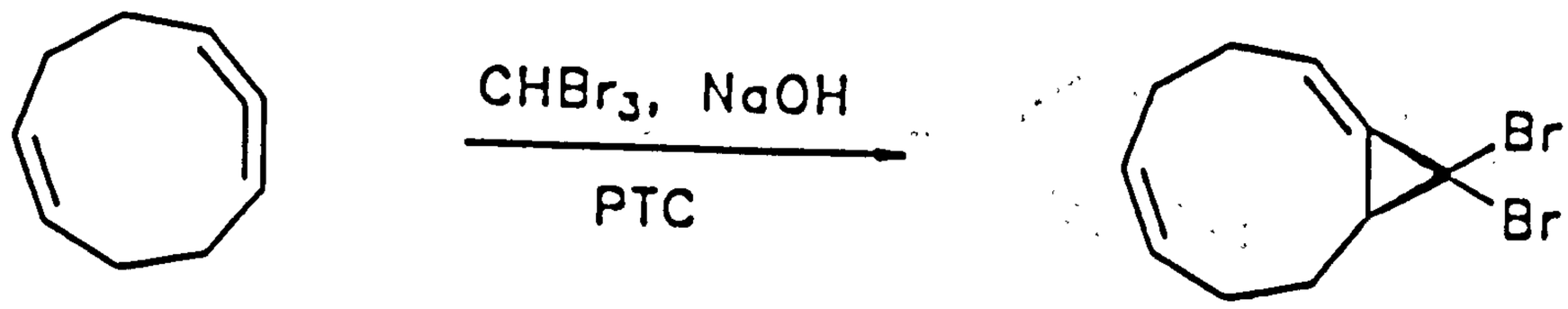
However, when an allylic chloride was used instead of the bromide, the reaction proceeded exclusively to cyclopropane. Chloride is a relatively poor leaving group, so nucleophilic displacement is slow compared to carbene addition.

The reaction between dihalocarbenes and allenes (1,2–dienes) occurs readily at the more electron rich double bond, and the product is a methylenecyclopropane.[32] However, allene itself and 1,1,3,3–tetramethylallene both give bis–adducts with

dichlorocarbene.[32]

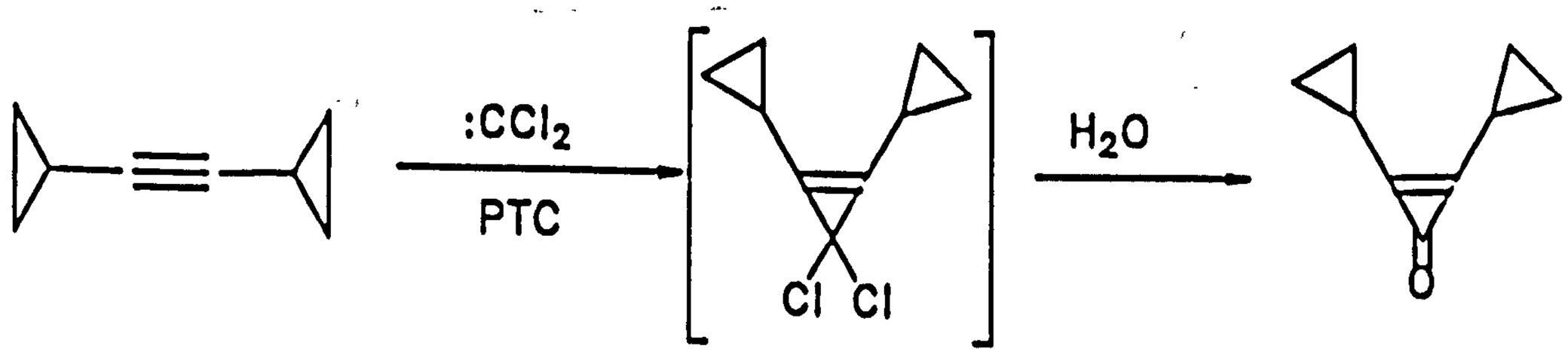


In systems containing an allenic and an olefinic linkage, addition of the carbene has been found to occur at the allenic bond. Thus, on reaction of (17) with dibromocarbene, generated under PTC, the product was (18).[33]



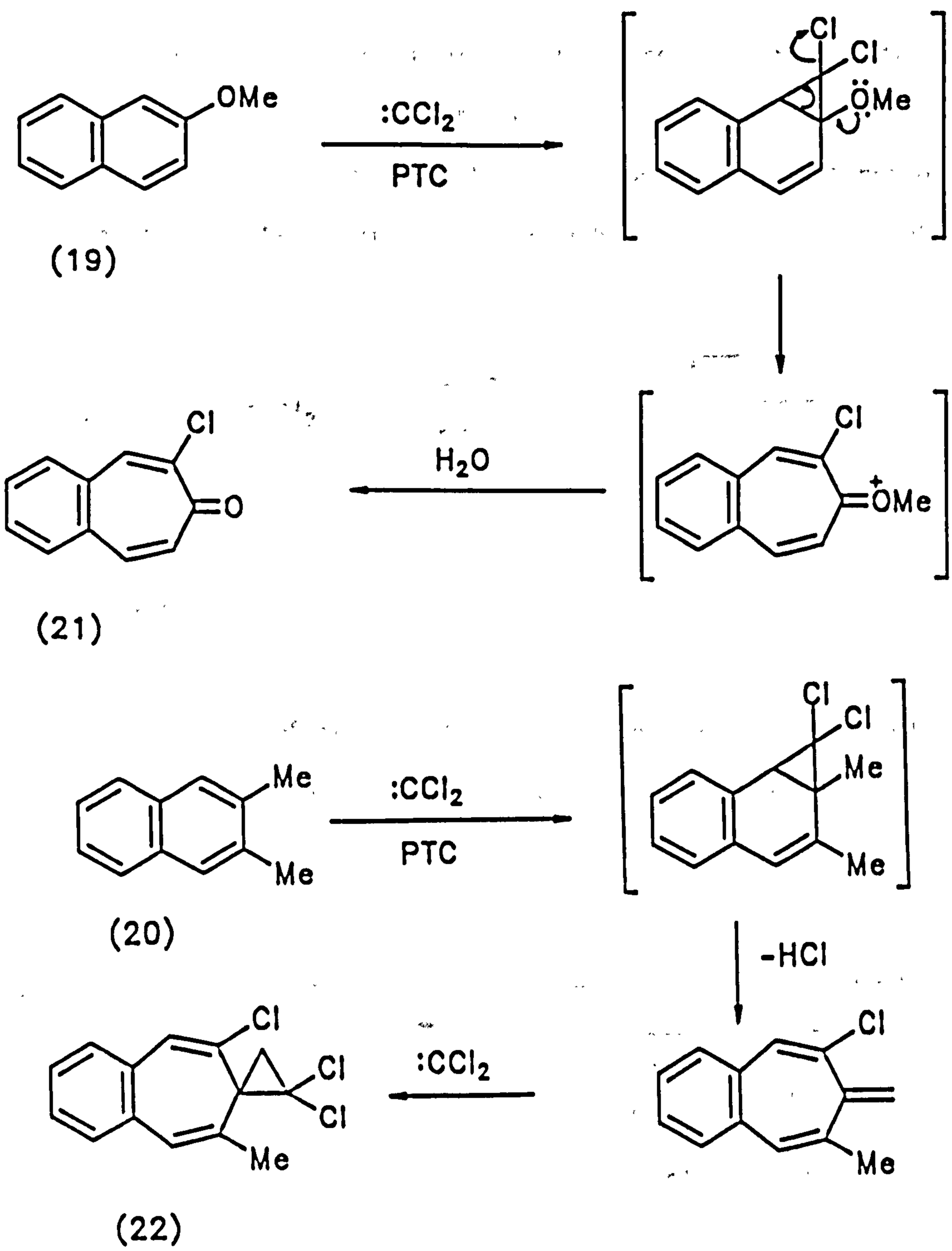
(17) (18)

The reaction of alkynes with dihalocarbenes is slow, but, when it happens, the cyclopropene is hydrolysed during the reaction. Thus the addition of dichlorocarbene generated under PTC to dicyclopropylacetylene gives the dichlorocyclopropene, which is spontaneously hydrolysed to afford the cyclopropenone.[34]



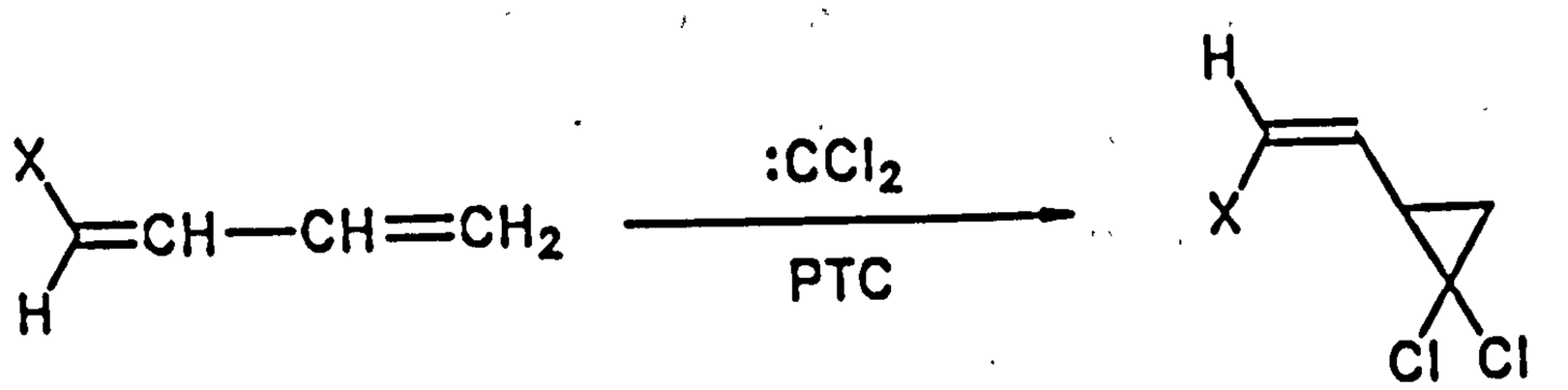
Reactions of dihalocarbenes with aromatic double bonds are mostly very slow, and in many cases are accompanied by rearrangement with ring expansion and loss of

hydrogen chloride or other small molecules.[35] Addition of dichlorocarbene to (19) and (20) gave (21) and (22) respectively in low to moderate yield.



1.4: Polyhalogenated cyclopropanes.

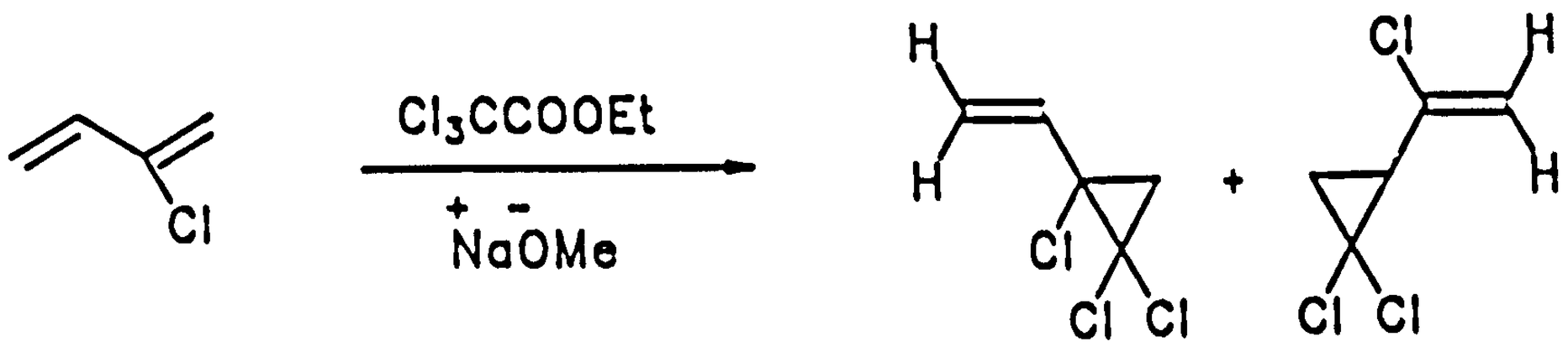
The introduction of a halogen into olefins and dienes can affect their reactivity towards dihalocarbenes.[1] From a series of competition experiments with $:CCl_2$ (generated from several routes), the reactivity of 1–chlorocyclohexene has been quoted as 0.4–0.5 compared to cyclohexene.[36] Addition of ($:CCl_2$) to dienes of type (23) proceeds selectivity at the less substituted double bond to give (24, X = halogen).[37]



(23)
X = Halogen

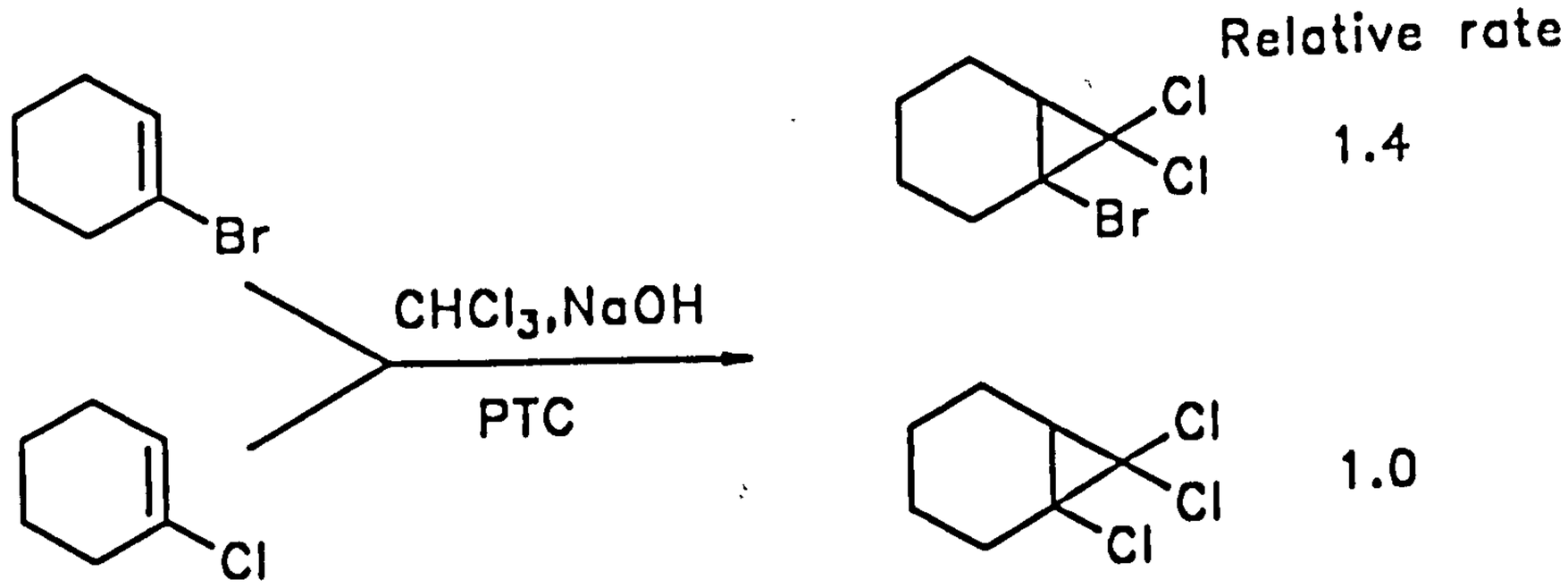
(24)

However, the addition of carbene ($:CCl_2$) to chloroprene (25) is unusual, because the reaction occurs at the substituted double bond, leading predominantly to (26) and (27) in ratio 19 :1.[38,39]



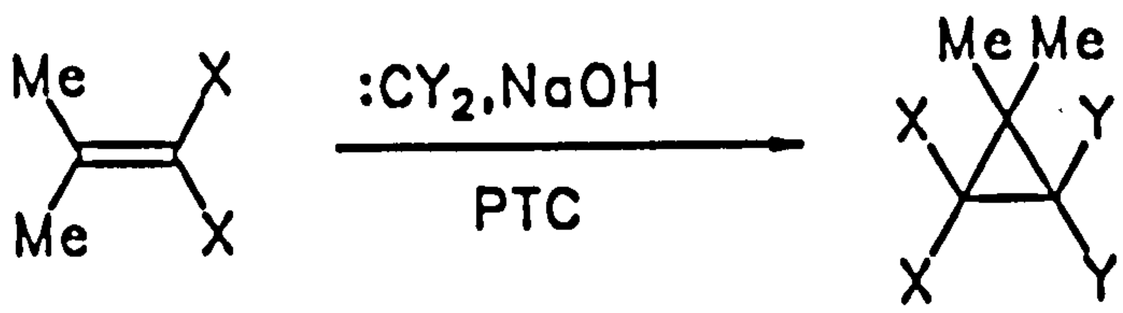
(25) (26) (27)

A series of competition experiments was carried out to examine the relative reactivity of different halogenated alkenes towards dihalocarbenes. Addition of ($:CCl_2$) generated under PTC to 1–bromocyclohexene and 1–chlorocyclohexene, shows the brominated alkene is more reactive than the chlorinated one, with a relative rate of 1.4 : 1.[36]



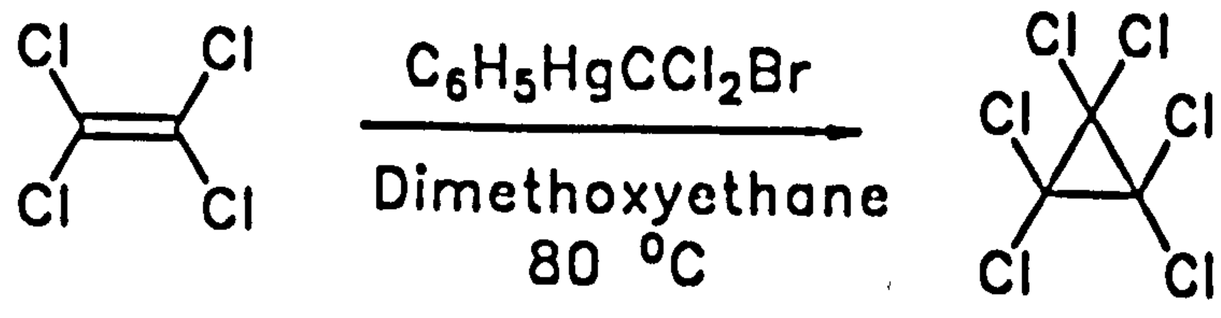
Baird and co-workers[36] have prepared tri- and tetrahalocyclopropanes in good yields, by addition of dihalocarbenes, generated under PTC to monohalo- or dihaloalkenes, e.g., addition of ($:CCl_2$) and ($:CBr_2$) to (28) and (29), gives tri- and tetrahalocyclopropanes respectively in good yield:

(28)

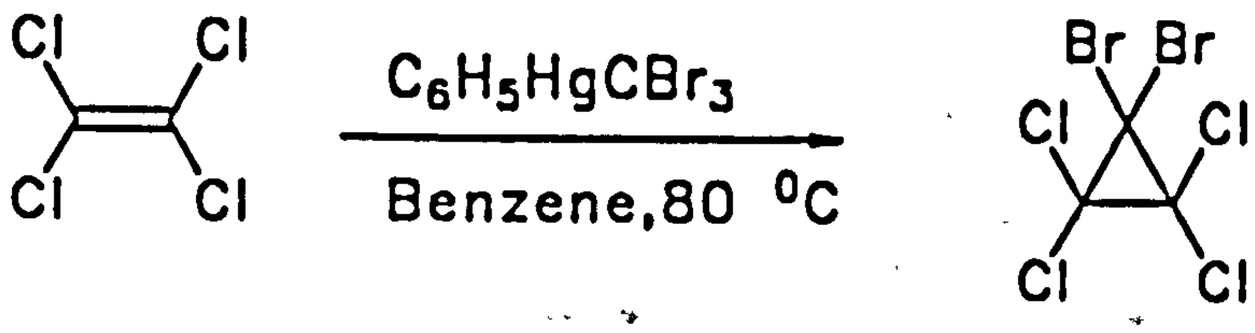


(29) X=Cl,Br
Y=Cl,Br

Hexachlorocyclopropane (31) and 1,1-dibromotetrachlorocyclopropane (32) have been prepared by heating (30) with phenyltrihalomethyl mercury.[16]



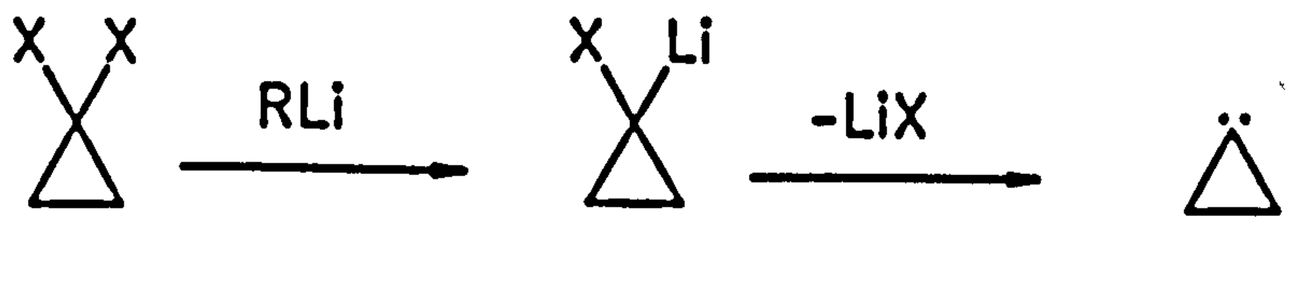
(30) (31)



(30) (32)

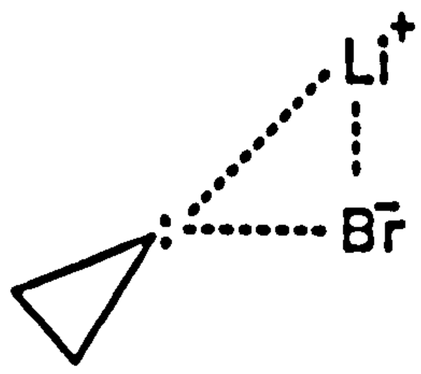
1.5: Reaction of halocyclopropanes with methyl lithium.

Reaction of gem–dibromo– or dichlorocyclopropanes with an alkyl–lithium, is a route to cyclopropylidenes (34).[40] This may arise by an initial lithium–halogen exchange to produce (33) which then loses lithium halide to produce (34).

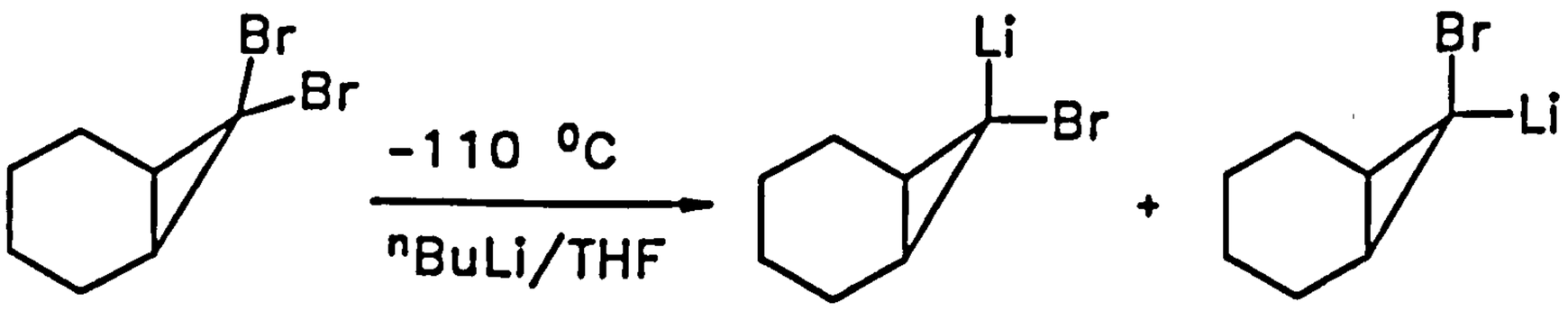


X=Cl,Br (33) (34)

The existence of the free carbene in this case is difficult to prove, and co–ordination to the lithium halide to give a carbenoid is likely.

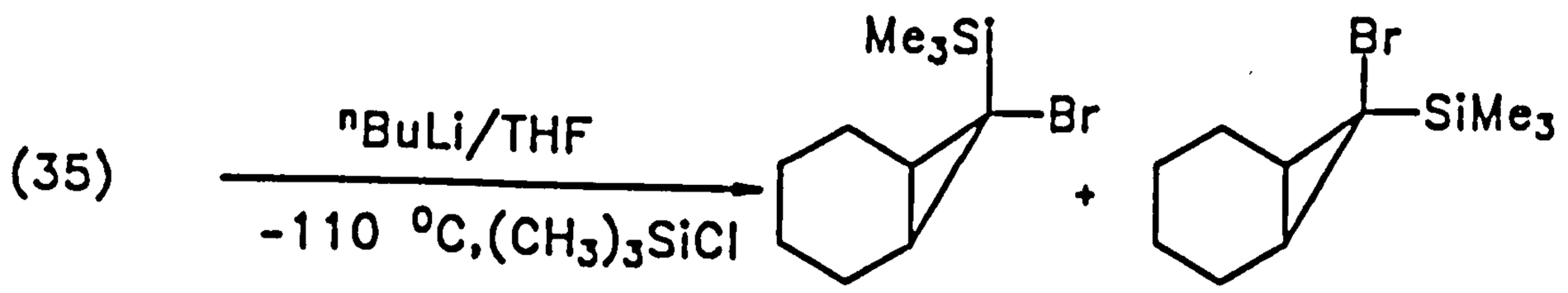


However,. the presence of the lithio–halogen intermediate (33) in the alkyl–lithium reaction was confirmed by Seyferth and Lambert[41] by reaction of (35) with n–butyl–lithium in THF at low temperature.



(35)

At –110 °C, two isomeric α–lithiobromides were stable and could be trapped by a series of electrophiles, e.g., with trimethylchlorosilane to give (36) and (37).



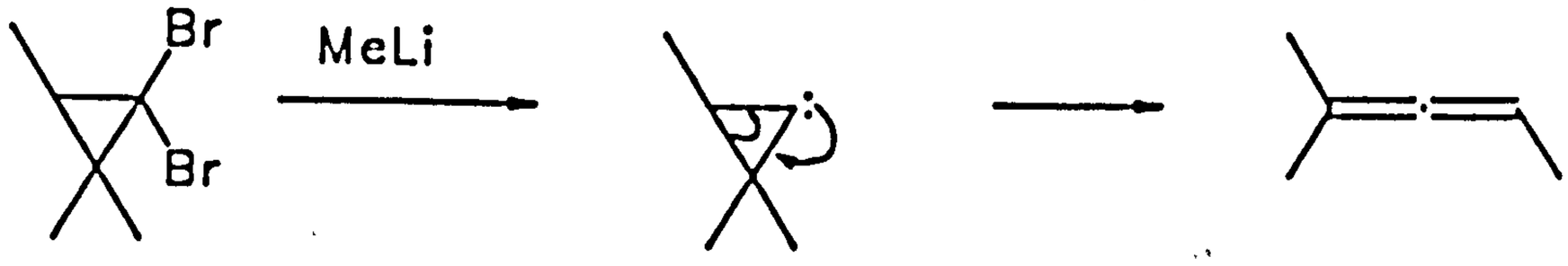
(36) (37)

The ratio of endo– to exo–products was found to be 4:1, an indication that the relatively small lithium prefers to take the crowded endo–position, and the larger bromine occupies the less crowded exo–orientation. Since the silylation proceeds with retention of configuration, the exo–bromo–endo–trimethylsilylcyclopropane predominated.

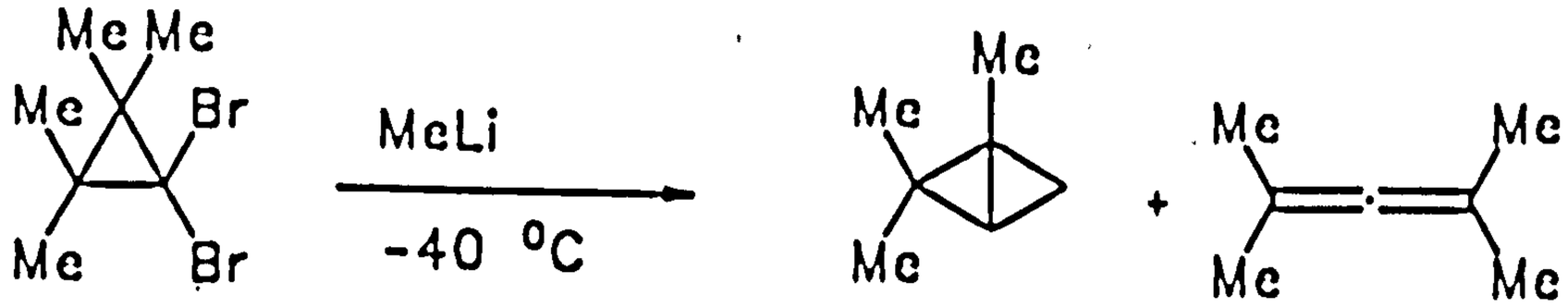
Evidence for a carbene (carbenoid) intermediate comes from trapping with alkenes. When the dibromide (38) was treated with methyl–lithium at –60 °C in the presence of cyclohexene, the spiro compound (39) was isolated.[42] This reaction proceeds by intermolecular addition of the carbene intermediate to the double bond.

(38) (39)

In the absence of trapping agent the carbenoid can undergo a variety of intramolecular processes. Rearrangment to an allene is a common pathway.[43]

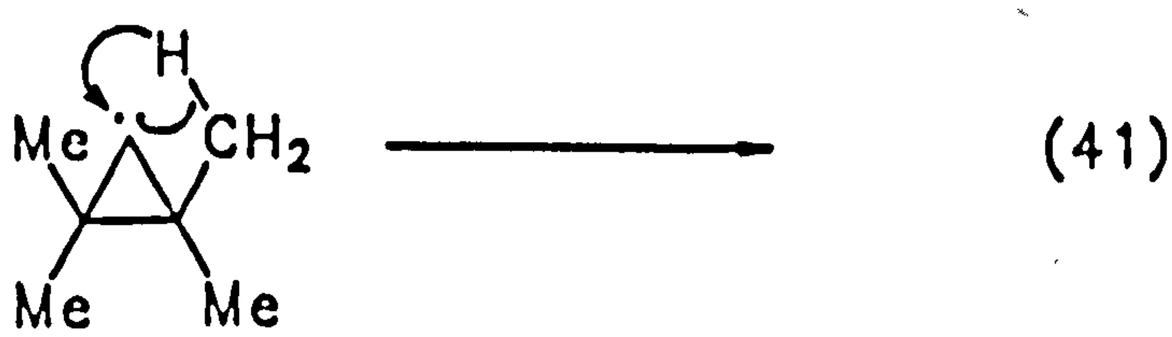


Treatment of (40) with methyl–lithium gave 1,2,2–trimethylbicyclobutane (41) in 98% yield and 2% of the allene (42).[44]



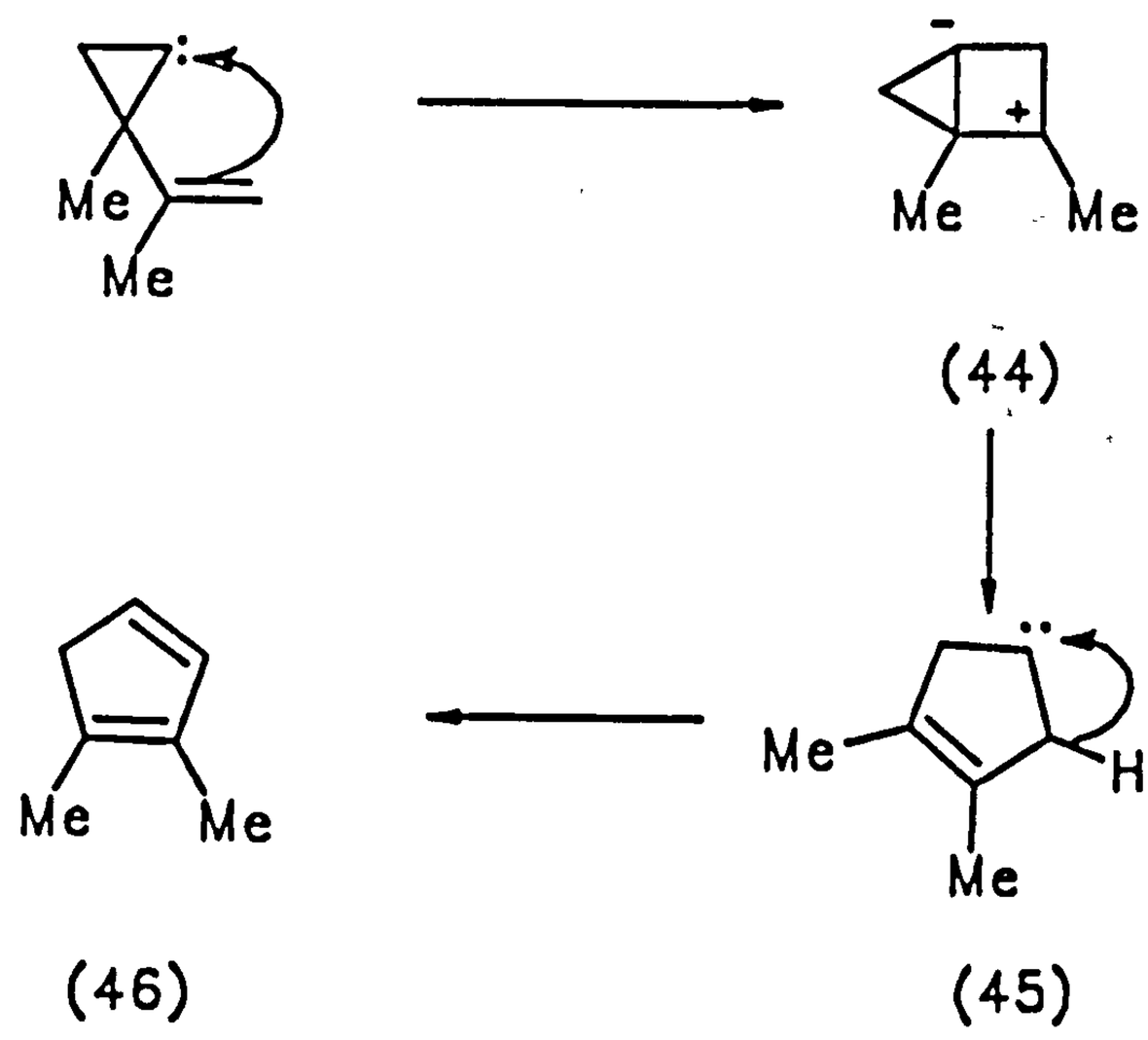
(40) (41) (42)

The bicyclobutane (41) was obtained by insertion of the intermediate carbene (43) into a C–H bond of the methyl group as shown below.



(43) (41)

If the cyclopropylidene is adjacent to a vinyl–group, rearrangment to a cyclopentadiene is possible.[43]

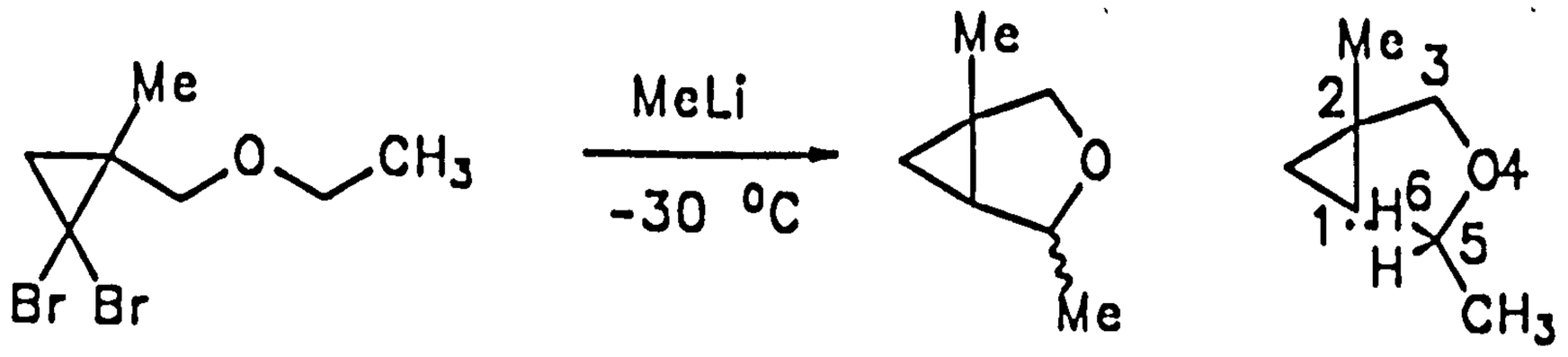


(44)

(46) (45)

This may arise through the bicyclic intermediate (44), and the rearranged carbene (45) which gives the cyclopentadiene (46) *via* a 1,2-hydrogen shift.

Intramolecular insertion of cyclopropylidenes has been observed on introduction of a side chain containing a heteroatom. Reaction of (47) with methyl-lithium at – 30 °C gave (48) as the major product.



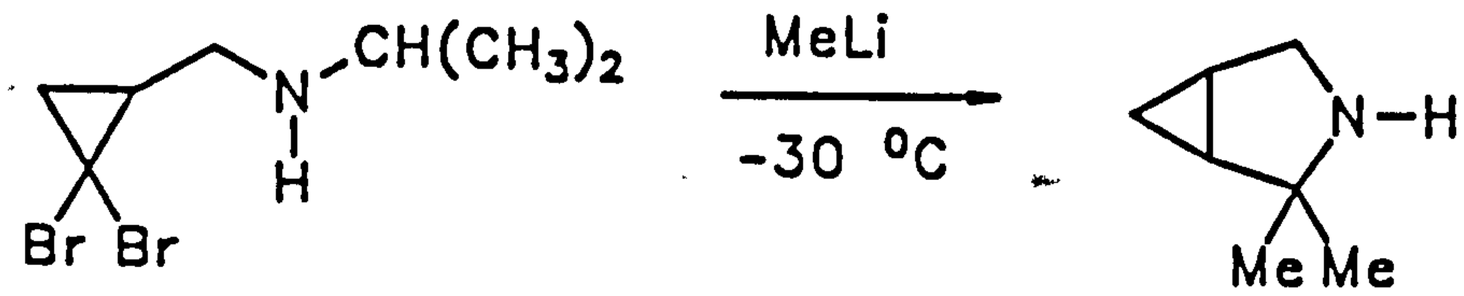
(47) (48) (49)

The product (48) arises by formal insertion of the intermediate (49) into the C–H bond 5,6–related to the carbene centre.[45] The introduction of oxygen is believed to activate the adjacent C–H bond toward insertion by the carbene.

A similar reaction is observed when the heteroatom is nitrogen[46] or

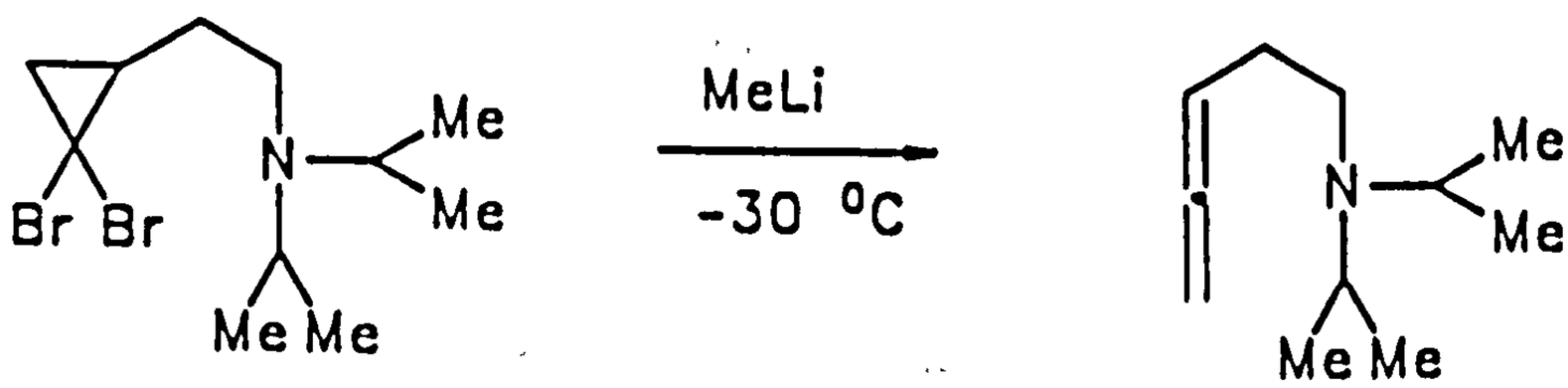
sulphur.[47,48]

Reaction of (50) with methyl–lithium leads largely to the insertion product (51).



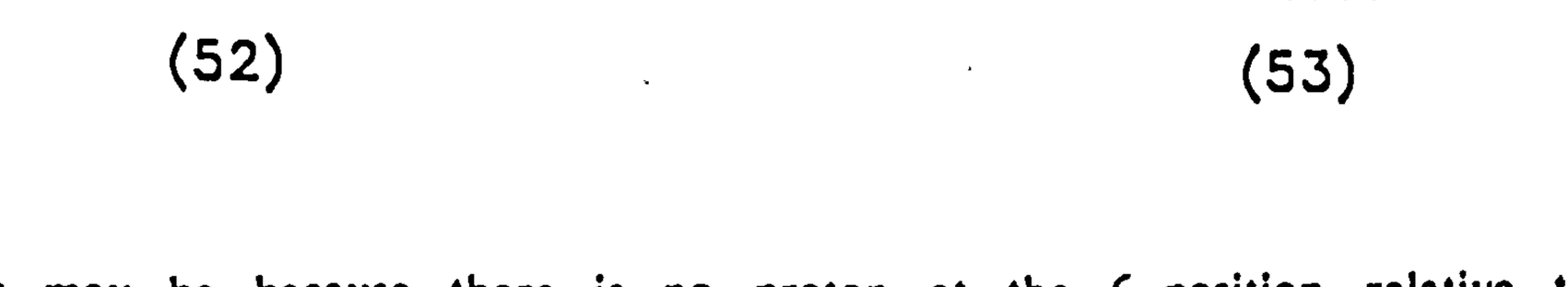
(50) (51)

In contrast, reaction of (52) with methyl–lithium, led to no insertion product and instead the allene (53) was isolated.



(52) (53)

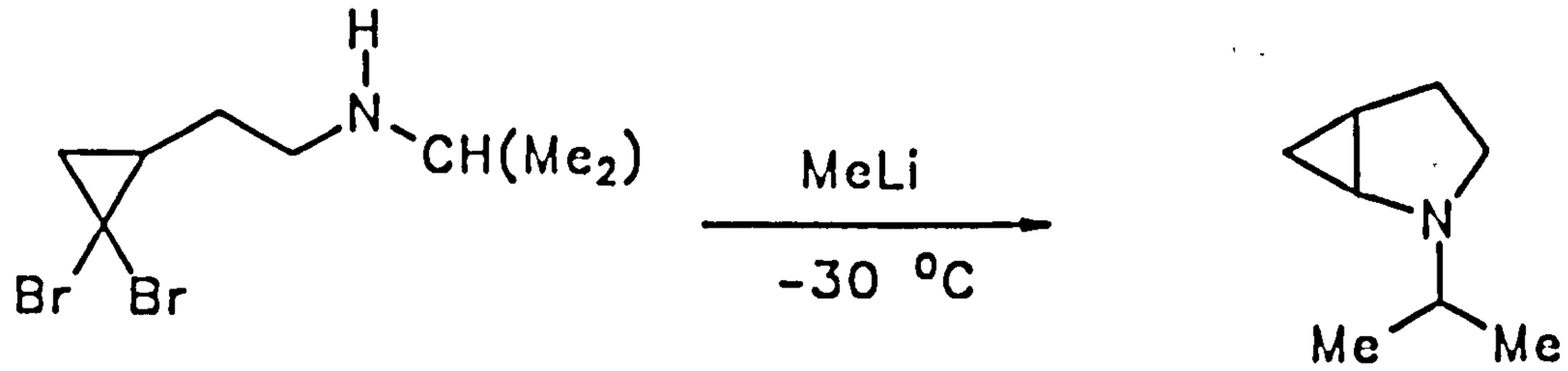
This may be because there is no proton at the 6–position relative to the carbene centre. Treatment of (54) with methyl–lithium at –30 °C leads to (55) and (56) in ratio ca. 1:1. The proportion of insertion to allene formation increases with the nature of the 5,6–C–H bond in the order $1^0 < 2^0 \approx 3^0$.[48]



(54) (55) (56)

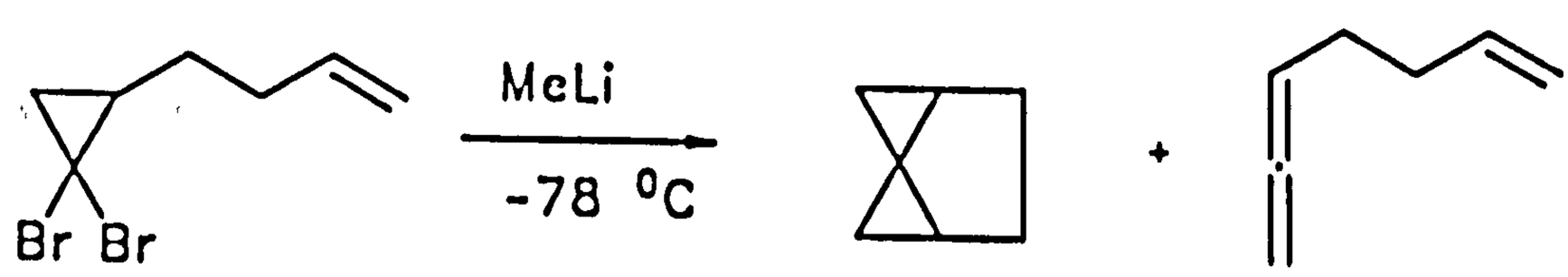
Intramolecular insertion reactions of cyclopropylidenes occur not only into C–H bonds but also into N–H[46] and O–H bonds.[47] Thus reaction of (57) with methyl–lithium

gave (58), through insertion into the N–H bond.



(57) (58)

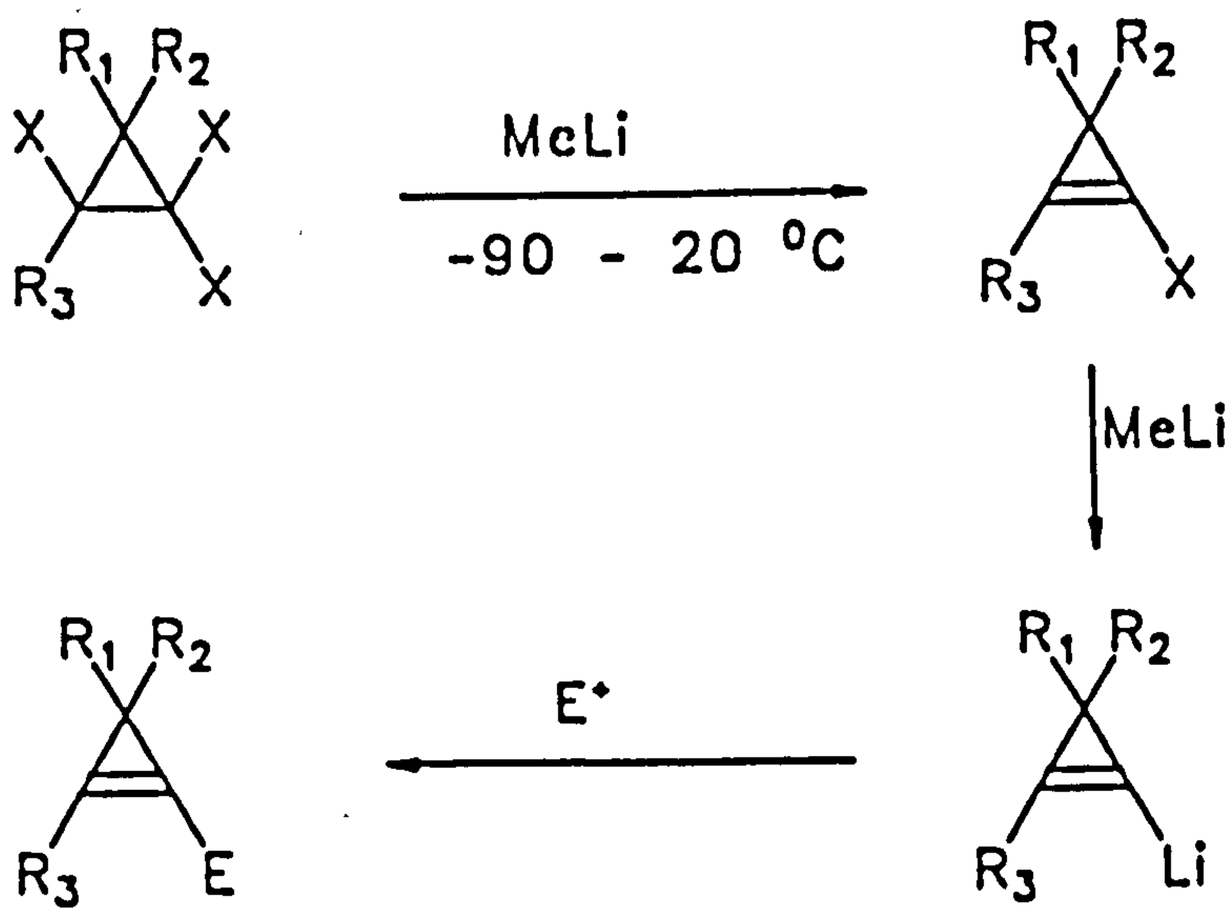
Introduction of a double bond at the 5,6–position from the carbene centre gave intramolecular addition, reaction of (59) with methyl–lithium producing a 1:1 mixture of spiro–compound (60) and allene (61).[43]



(59) (60) (61)

From these results, we can conclude that the carbene insertion into either C–H, N–H, or O–H bonds requires a 1,6–relationship between the hydrogen and the carbene centre, and, as shown above, no insertion occurs if the relationship is 1,5– or 1,7–.

Reaction of a range of 1,1,2–trihalocyclopropanes (halogen = bromine, chlorine) with methyl–lithium in ether at –90 – 20 °C leads to 1–halocyclopropenes, which react with another equivalent of methyl–lithium to generate 1–lithiocyclopropenes; these in turn are trapped by different electrophiles to give derivatives of cyclopropenes.[49]

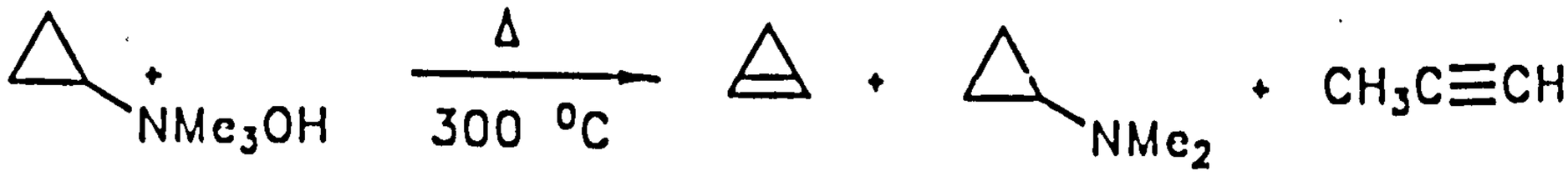


X=Cl,Br

$R_1=R_2=R_3$=alkyl or hydrogen

1.6: CYCLOPROPENES.

The first authenic preparation of cyclopropene (63) was reported in 1922 by Dem'yanov and Doyarenko who pyrolysed trimethyl cyclopropyl ammonium hydroxide (62) on platinized clay at approximately 300 °C.[50]



(62) (63)

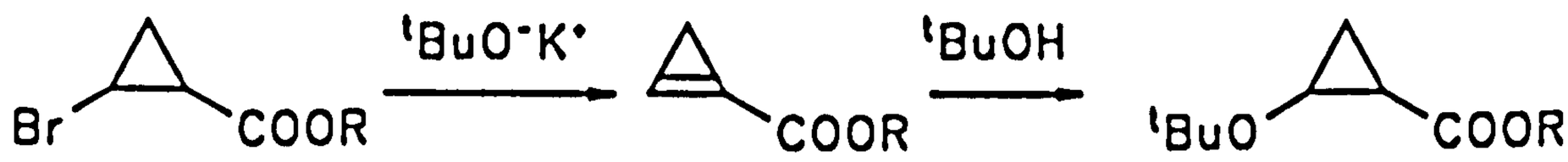
Despite these early beginnings, the chemistry of cyclopropene and its derivatives received little attention until the mid-1950's and has grown rapidly in recent years because: (1) the high strain of the ring makes it a suitable subject for theoretical treatments of bonding in organic compounds, (2) the occurrence of cyclopropenes in nature was recognized, and (3) viable routes to cyclopropenes became a reality with

the advent of carbene chemistry.[51,52]

1.6.1: SYNTHESIS OF CYCLOPROPENES.

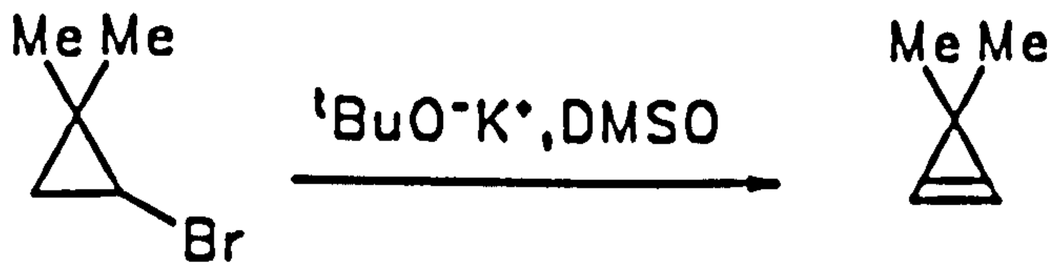
1.6.1.1: Cyclopropenes from cyclopropanes:

Cyclopropanes are used widely in the preparation of cyclopropenes. The first authenticated synthesis of a cyclopropene was by β–elimination from an activated cyclopropane.[50] Several attempts have been made to utilize β–elimination on halocyclopropanes for the synthesis of cyclopropenes. On dehydrobromination of (64) with potassium t–butoxide, the product isolated was (66); the desired cyclopropenecarboxylate (65) was apparently the initial product, but this underwent a rapid addition of t–butanol.[53]



(64) (65) (66)

However, treatment of 1–bromo–3,3–dimethylcyclopropane (67) with potassium t–butoxide in DMSO gave 3,3–dimethylcyclopropene (68) in high yield.[54]



(67) (68)

In the same way, potassium hydroxide reacts with pentachlorocyclopropane giving tetrachlorocyclopropene in excellent yield.[55]

Reaction of the dibromides (69) and (70) with one equivalent of butyl–lithium in

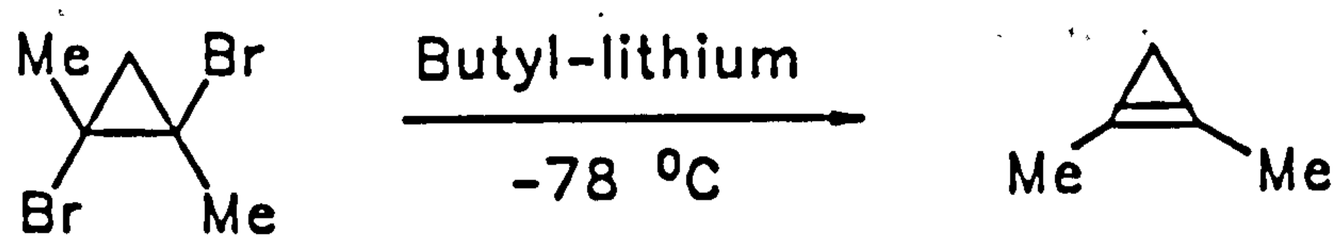
ether at –78 °C gave the cyclopropropenes (71) and (72)[56].

(Ref. 56)

(69)

n=1,2

(71)



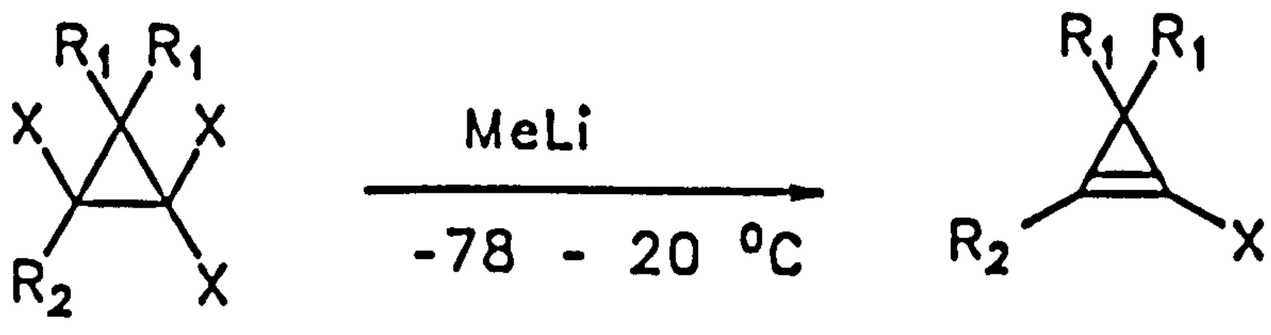
(70)

(72)

These cyclopropenes may arise by lithium–halogen exchange followed by 1,2–elimination of lithium halide.

1.2–Dihalocyclopropanes are available by carbene addition to alkenes or halogenated alkenes, and their dehydrohalogenation or 1,2–dehalogenation to 1–halocyclopropenes provides a good route to functionalised cyclopropenes.

The 1,2–dehalogenation of tri– or tetrahalocyclopropanes by an alkyl–lithium provides a method for the preparation of functionalised cyclopropenes in good to excellent yields.[57,58,59,49] Thus treatment of (73) and (74) with one equivalent of methyl–lithium in ether at –40 – 0 °C afforded the halo– and dihalocyclopropenes respectively.



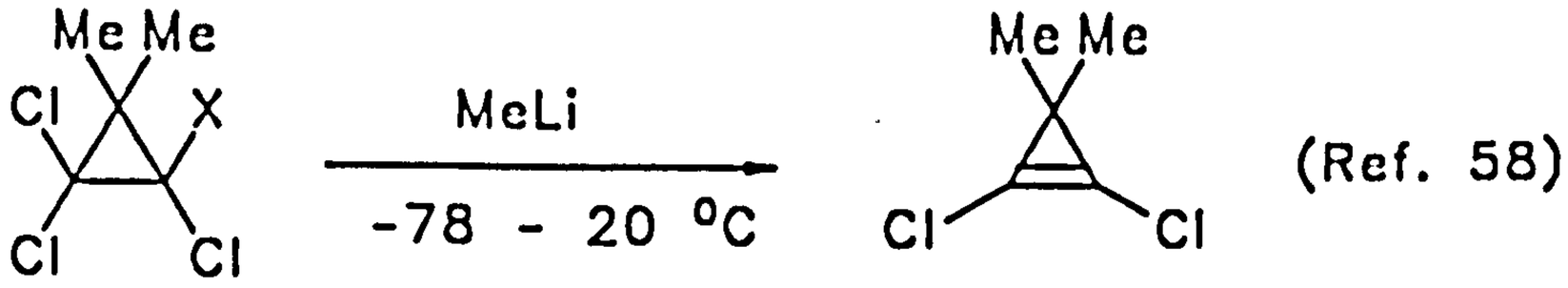
(Ref. 57,49)

(73)

X=Cl,Br

R_1=H,alkyl group

R_2=alkyl group



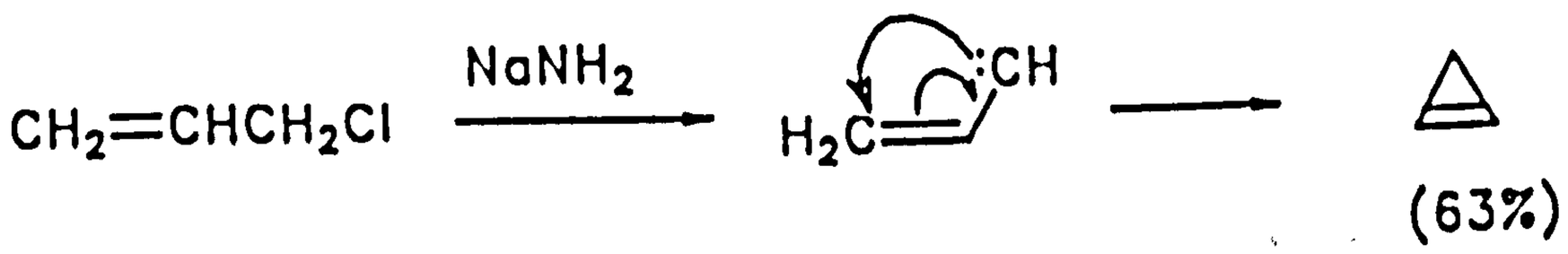
(Ref. 58)

(74)

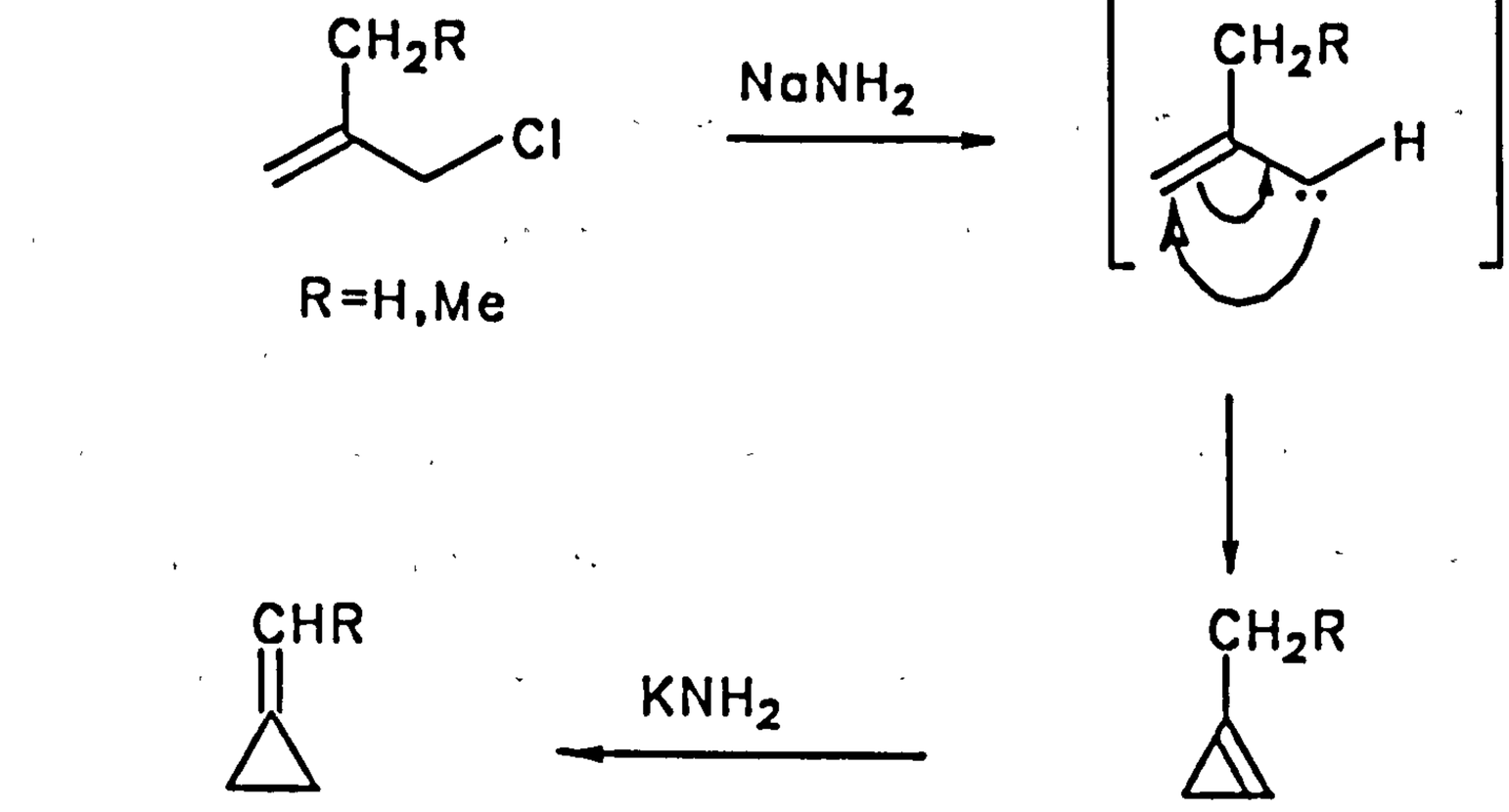
X=Cl,Br

1.6.1.2: Cyclization of α,β–unsaturated vinylcarbenes.

The rearrangment of a vinylcarbene to a cyclopropene is well known and provides a viable method for the synthesis of compounds whose substitutents range from simple to complex. Thus base induced α–elimination of HCl from allyl chlorides provides a synthesis of cyclopropenes.[59]



With substituted allylic chlorides, the strong base can react further with the cyclopropene to give a methylenecyclopropane. Thus the reaction of 3–chloro–2–methylprop–1–ene with sodium amide in THF at 65 °C can provide large quantities of 1–methylcyclopropene, but with potassium amide the product is methylene– cyclopropane.[60,61] However, lithium amide appears to be the base of choice for preparing the cyclopropene.[60,62]

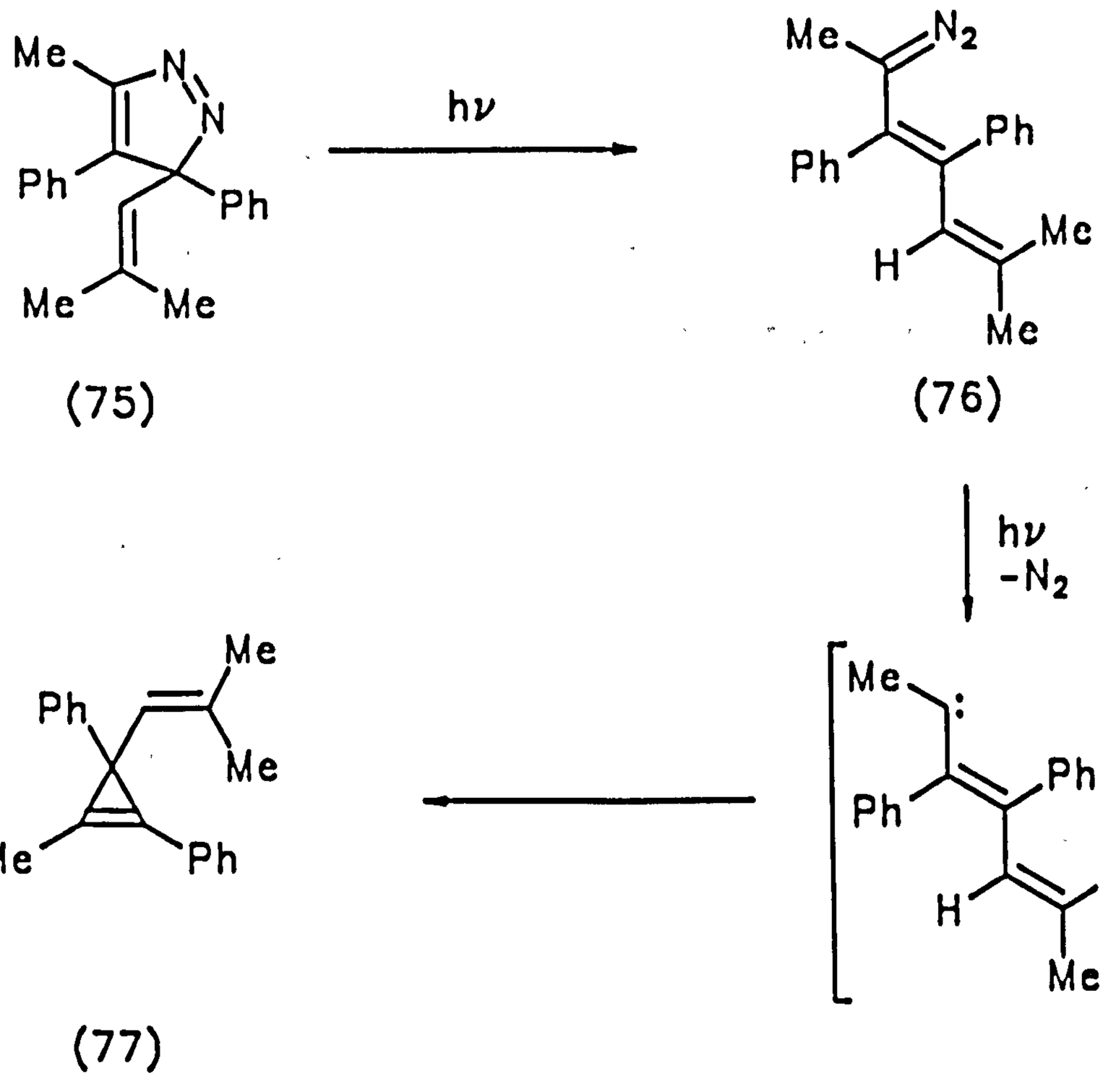


The position of the alkyl substituent in the product indicates that cyclisation occurs with rearrangment of the double bond, i.e., the reaction of an allyl chloride with base involves 1,1–elimination of hydrogen chloride.

The base–induced pyrolysis of tosylhydrazones of α,β–unsaturated aldehydes and ketones is also a convenient route to alkylcyclopropenes.[63,64] The reaction involves elimination of nitrogen to give the alkenylcarbene which cyclises to the desired cyclopropene.

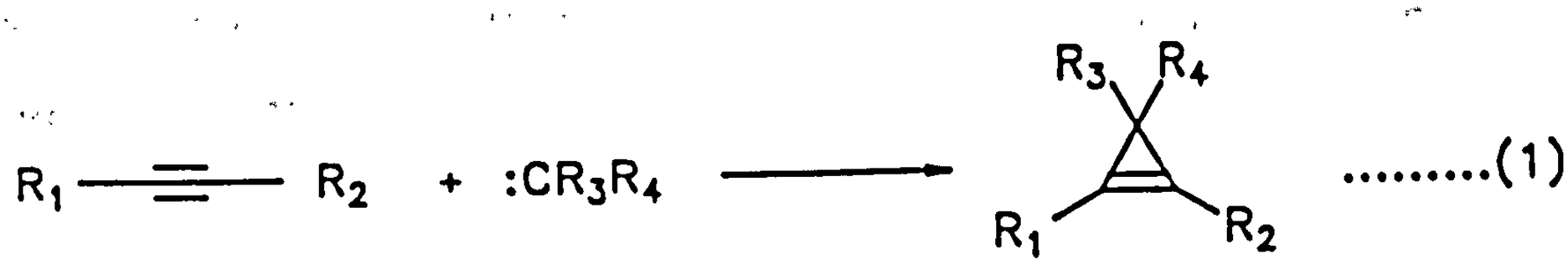
However, good yields of cyclopropenes are only obtained from unsaturated carbonyl compounds when the β–carbon atom is fully substituted with alkyl groups. In other cases pyrazole formation becomes the major reaction path.

The most common source of α,β–unsaturated carbenes for cyclopropene synthesis is the decomposition of 3H–pyrazoles. Thus photolysis of 3H–pyrazole (75) has been shown to lead the diazocompound (76) which on further photolysis is converted to cyclopropene (77).[65]



1.6.1.3: Addition of carbenes and carbenoids to Alkynes.

The addition of a carbene (or carbenoid) to an alkyne provides a convenient route to a range of cyclopropenes (eq. 1)

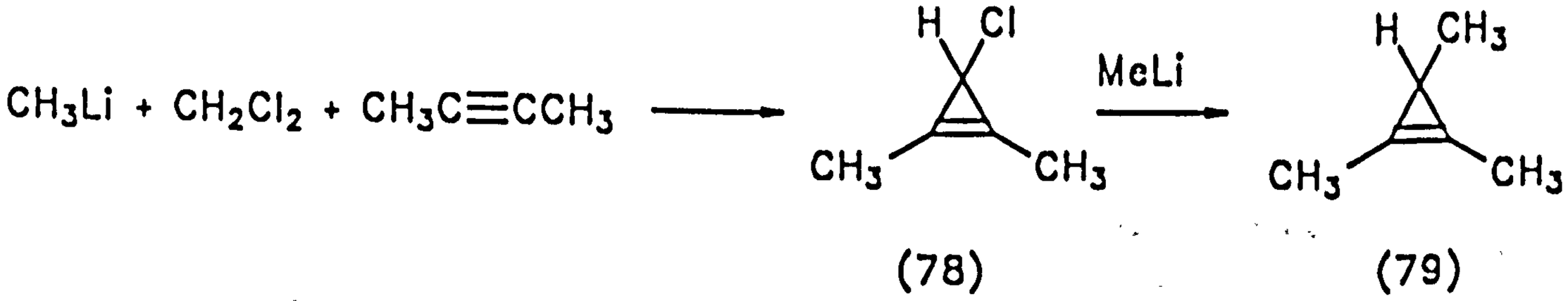


.....(1)

The cyclopropene ring is constructed in a single step by the formation of two σ bonds, but the concertedness or otherwise of the reaction is dependent upon the multiplicity of the carbene. In general this method is limited by the stability of the divalent carbon species rather than the nature of the alkyne, although terminal alkynes undergo insertion in competition with addition.

Addition of alkylcarbenes to alkynes fails to give cyclopropenes with alkyl substituents at C_3 because alkylcarbenes rearrange very rapidly to olefins and cyclopropanes.[1] Additions of dihalocarbenes and methylene to alkynes have been used to synthesise cyclopropenones and cyclopropenes.[1] Photolysis of diazomethane in the presence of 2–butyne leads to 1,2–dimethylcyclopropene in low yield.[66]

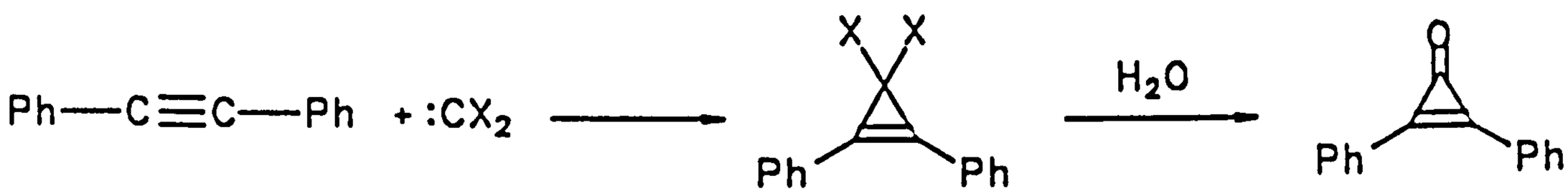
Chlorocarbene, generated from methylene chloride and methyl–lithium, adds to 2–butyne to give (78), which reacts further with methyl–lithium to produce (79).[63]



(78) (79)

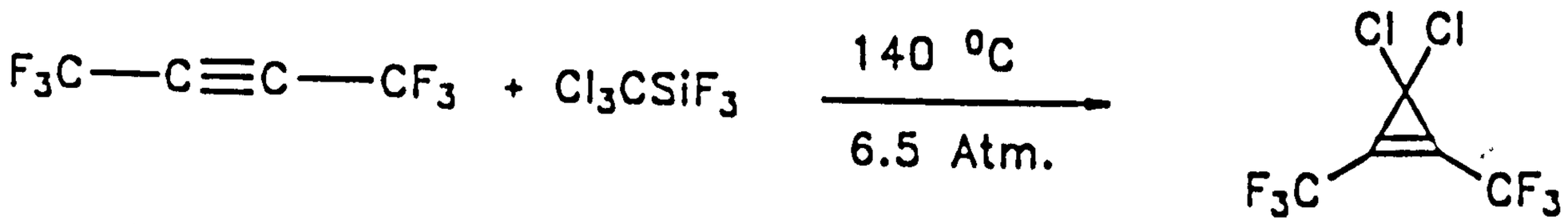
The ease and efficiency with which chloro– and bromocarbenes can be generated provides a ready route to 3–halo– and 3,3–dihalocyclopropenes.[67,35] However, these

compounds, e.g. (80), easily undergo hydrolysis during work–up to form cyclopropenones (81).



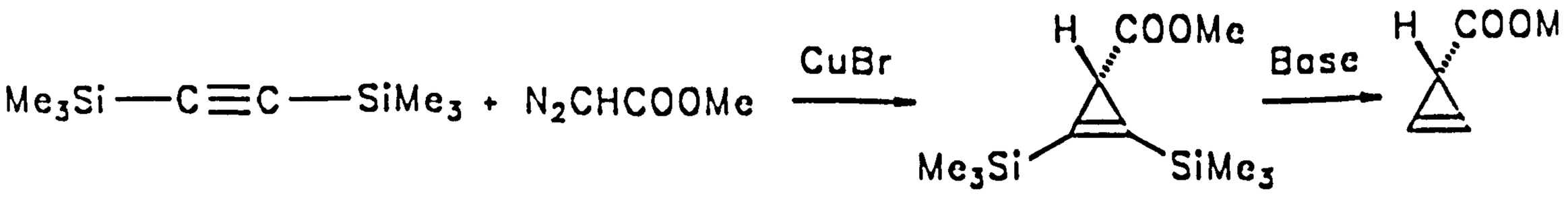
(80) (81)

A high yield of cyclopropene can be obtained by addition of carbenes generated by thermal or photochemical means, e.g. pyrolysis of (82) at 140 °C and 6.5 atm in the presence of (83) provides the cyclopropene (84) in excellent yield.[68]



(82) (83) (84)

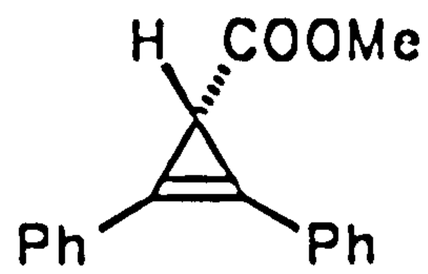
Carbalkoxycarbenes generated by thermal, photochemical or thermocatalytic decomposition of α–diazoesters provide a ready entry to 3–carbalkoxycyclopropenes upon addition to an alkyne.[69] The addition of carbalkoxycarbene, derived by catalysed decomposition of methyl diazoacetate, to several alkynes leads to low yields,[70] but reaction with 1–trimethylsilylalkynes proceeds reasonably efficiently; subsequent removal of the silyl group either by base or fluoride ion provides a route to 1–alkyl–3–cyclopropenecarboxylic acids.[71] In the same way, 1,2–bis–trimethyl–silylethylene can be converted to cyclopropene–3–carboxylic acid itself.[72]



1.7: CHEMISTRY OF CYCLOPROPENE

1.7.1: Electrophilic addition.

Cyclopropenes are more reactive than other cycloalkenes in additions to the double bond, most reactions being rapid and exothermic.[73] The addition of an electrophile to a cyclopropene double bond formally leads to a cyclopropyl cation; this may be expected to undergo ring opening to an allylic cation unless it is rapidly trapped by a nucleophile. In some cases electrophilic attack may occur at one of the σ bonds leading directly to an allylic cation.[73] Addition of halogens to cyclopropenes often occurs without ring opening to give 1,2–dihalocyclopropanes in high yields. The stereochemistry of the addition of chlorine to (85) in CCl_4 is 71% *cis*–;[74] however, the addition of bromine in $CHCl_3$ and acetic acid gave the *trans*– adduct.[75]



(85)

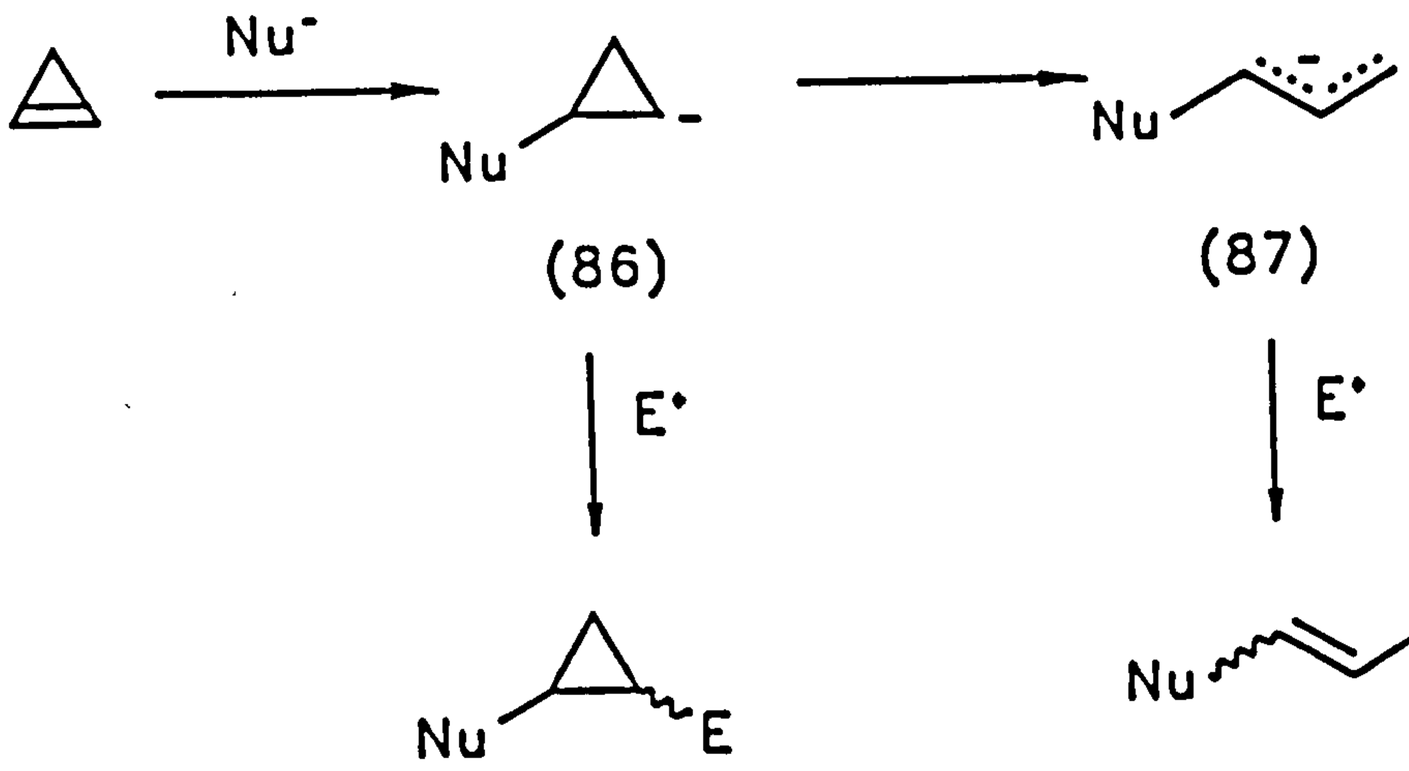
Addition of bromine to 1,2–dichloro–3,3–dimethylcyclopropene leads to a mixture of (*E*) and (*Z*) dibromodichlorides.[58]

1.7.2: Reaction with nucleophiles.

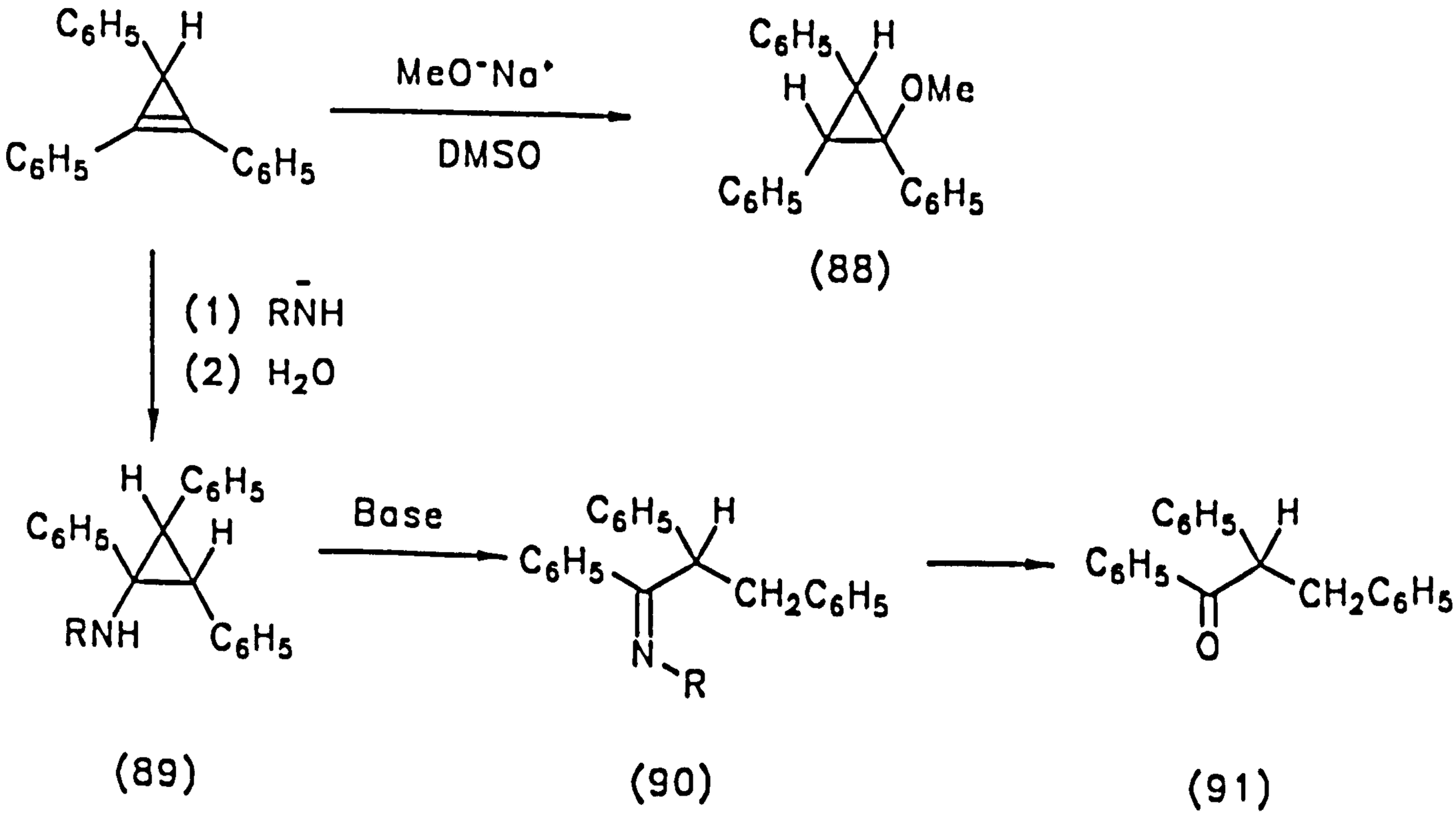
The reaction of cyclopropenes with nucleophiles (Nu^-) gives cyclopropyl anions (86), which may trapped by electrophiles (E^+) or may undergo ring opening to give an allyl anion (87) which is then trapped by an electrophile.[76] Usually some activation by

electron withdrawing groups is necessary to stabilise possible carbanion intermediates.[76]

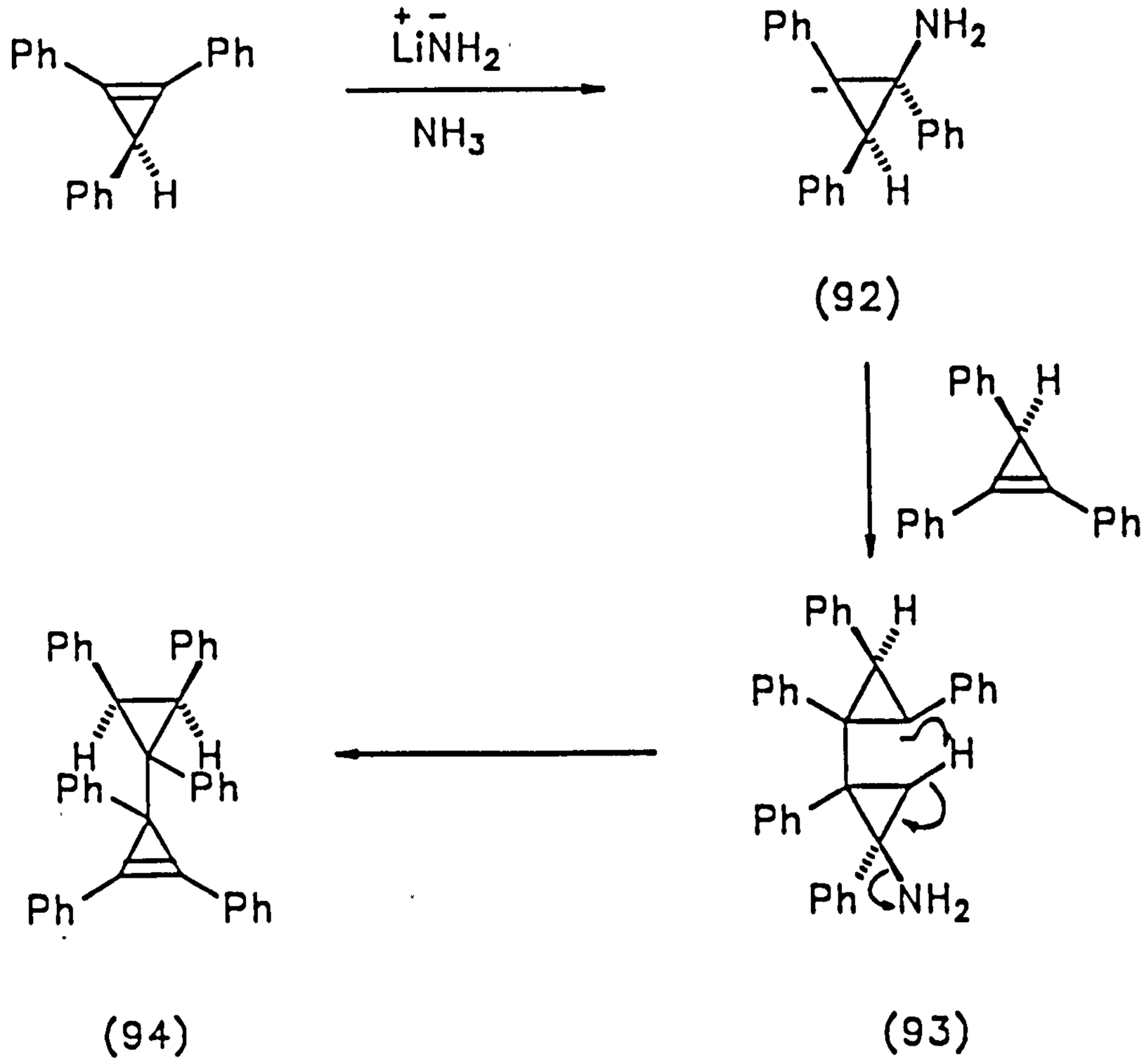
(Scheme 2)



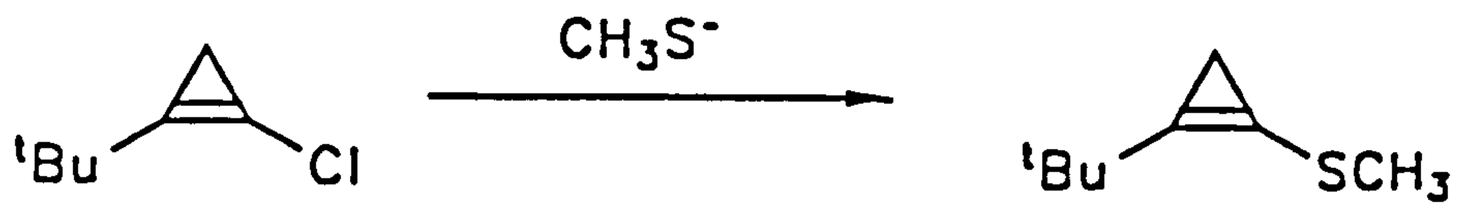
1,2,3–Triphenylcyclopropene undergoes nucleophilic addition readily,[77] and on treatment with sodium methoxide in DMSO, the corresponding methoxy–triphenylcyclopropane (88) has been isolated, but with sodium p–toluidide or with lithium propylamide in propylamine, the product isolated after hydrolysis was (91). This might be formed by addition of the nucleophile to give (89), followed by a proton shift and ring opening to give the imine (90), faciliated by delocalization of the lone pair on nitrogen. The imine (90) undergoes hydrolysis during the work–up.



The reaction of metal amides with cyclopropenes can follow a different course to that above. Attempts have been made to add lithium amide across the cyclopropene double bond; when the reaction was carried out in liquid ammonia the dimer (94) was formed in good yield. This suggests that the anion (92) is formed *via* addition of lithium amide, and is not protonated in the liquid ammonia, but instead adds to another cyclopropene molecule giving the anion dimer (93). This must abstract a proton intramolecularly, followed by elimination of amide ion. The mechanism of this reaction is confirmed by deuterium labelling studies.[77]

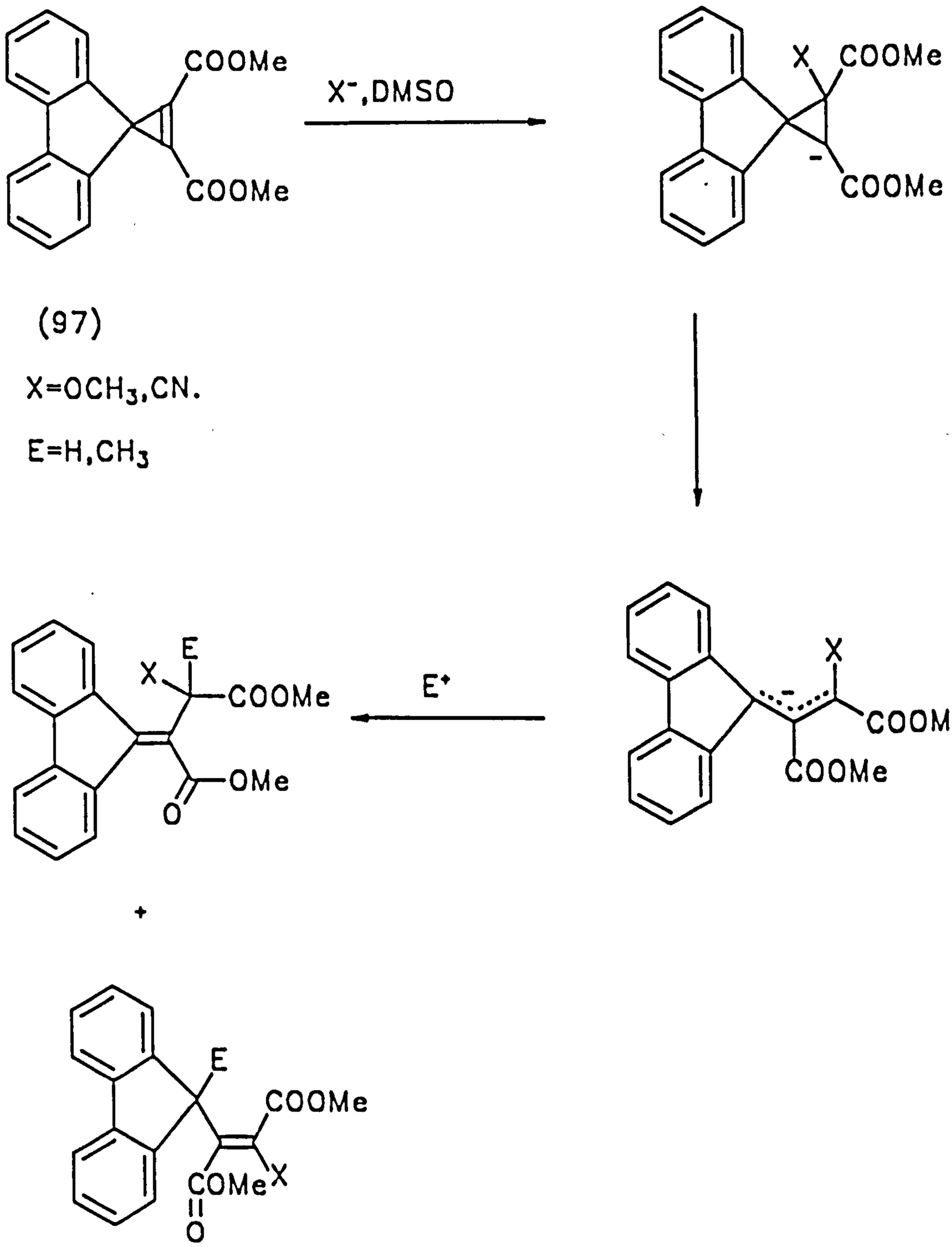


However, 1–halocyclopropenes undergo nucleophilic substitution without ring opening, e.g. methanethiolate ion attack on (95) gives the corresponding thioether (96).[78]

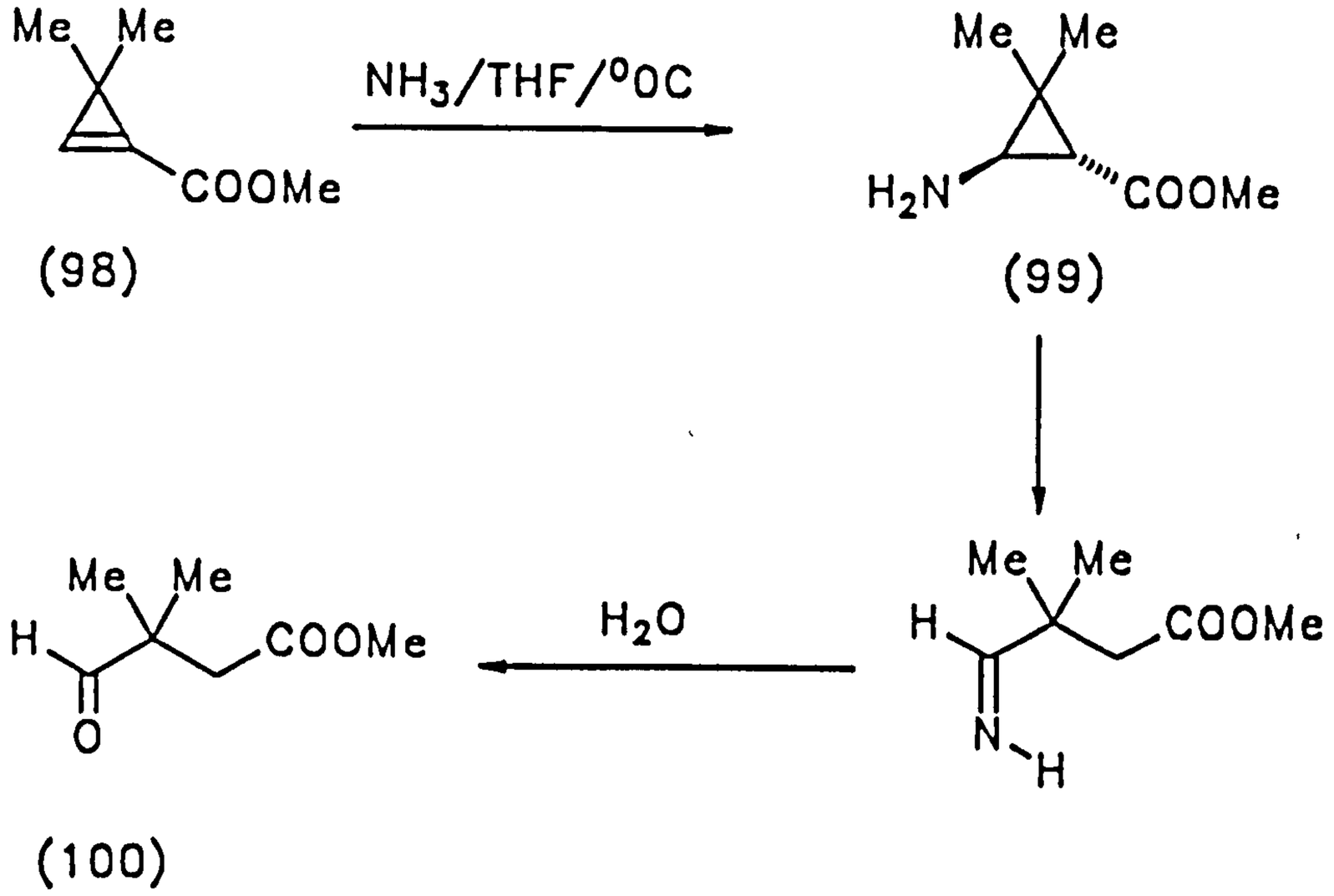


(95) (96)

Addition of nucleophiles to the cyclopropene double bond can be achieved by introducing electron withdrawing substituents, e.g. addition of methoxide or cyanide to cyclopropene (97) gives a mixture of isomeric alkenes upon methylation or protonation, *via* allyl anions.[79]



More recently, Baird and Hussain reported that reaction of (98) with ammonia in THF at 0 ^{0}C leads to (100).[80]



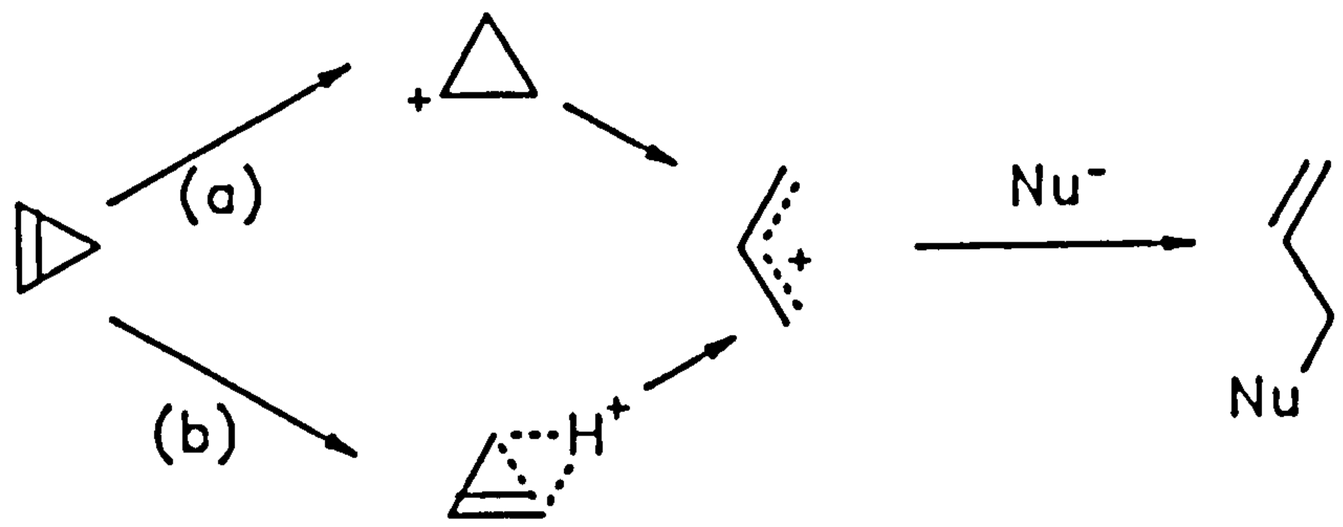
(98) (99) (100)

The aldehyde (100) arises *via* the cyclopropane (99) which undergoes a rapid rearrangment facilitated by the delocalization of the lone pair on the nitrogen atom, causing ring opening. The resulting imine is then hydrolysed during the work–up.

1.7.3: Reaction with acids.

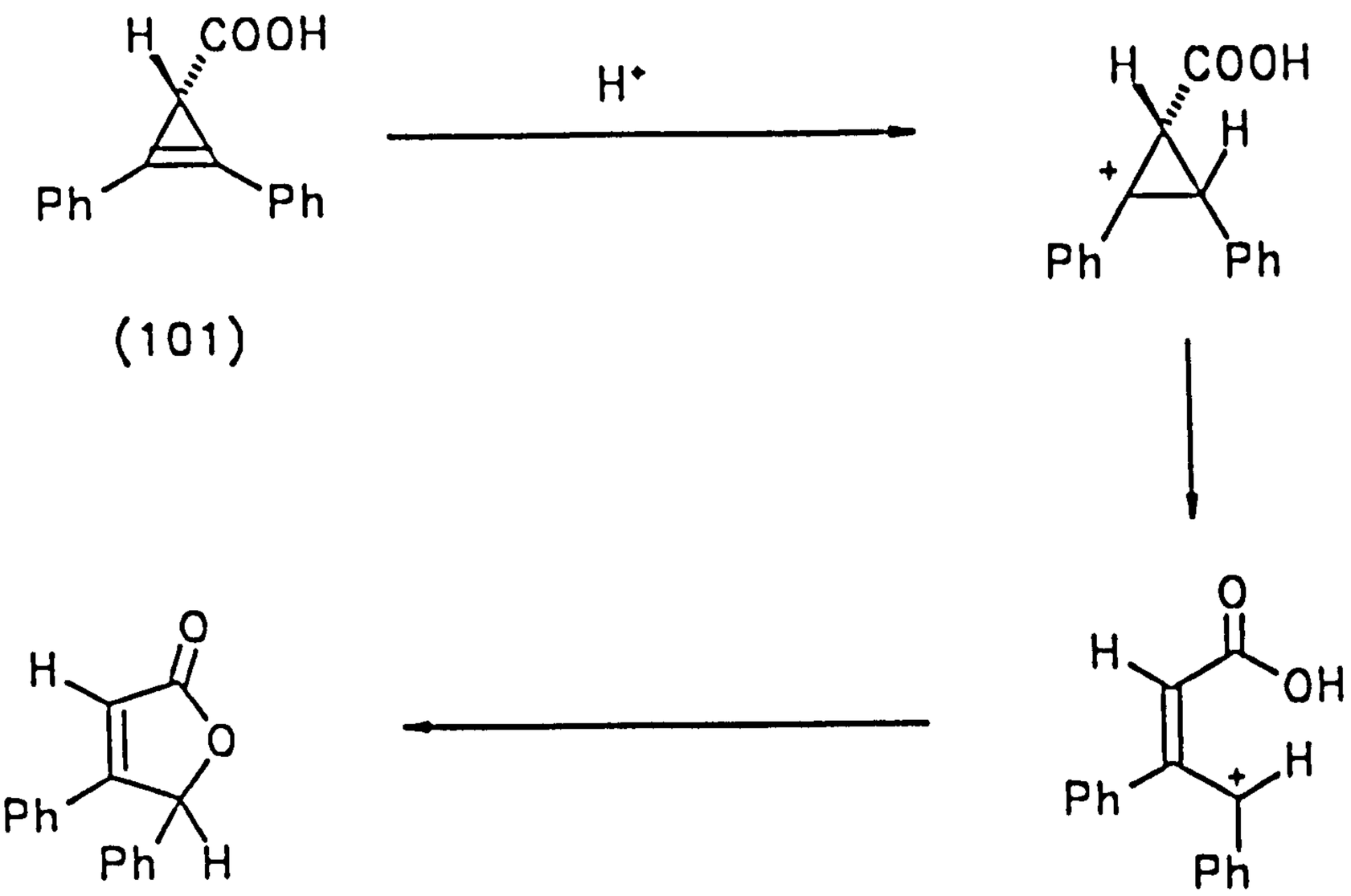
Cyclopropenes are readily cleaved by acids. The reactions are rationalized either by initial protonation of the double bond and subsequent electrocyclic ring opening of the cyclopropyl cation thus formed (Path a), or by protonation of a cyclopropene σ bond to give the allylic cation directly (Path b).[52,81] The final products of reaction are derived from nucleophilic capture of the allylcation.

(Scheme 3)



The polymerization of naturally occurring sterculic acid in the presence of a proton source, has been known for over 40 years and proceeds *via* acid catalysed opening of the cyclopropene ring.[52]

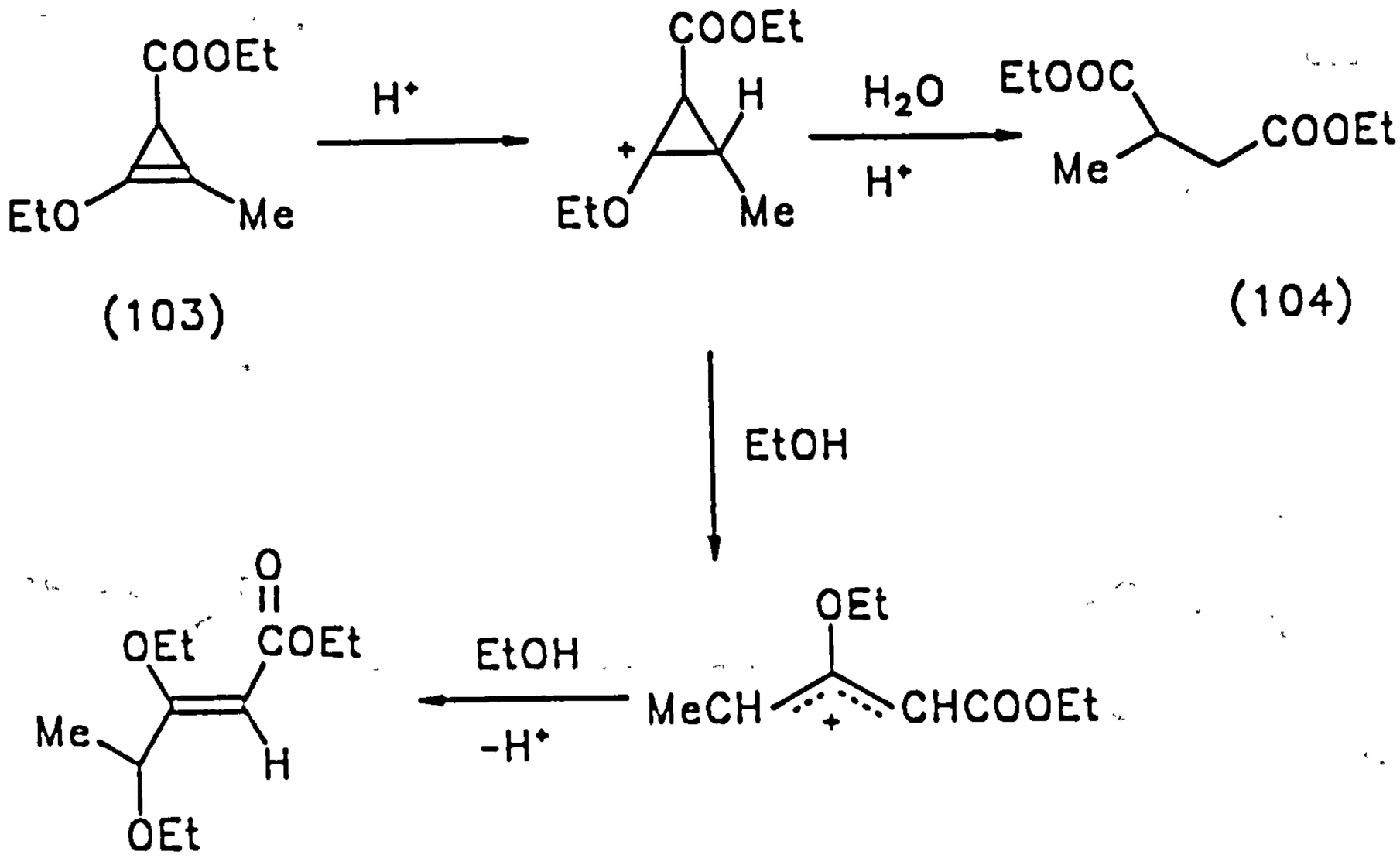
The rearrangment of cyclopropene (101) to lactone (102) is reported to proceed *via* acid catalysed protonation of the π–bond to give the cyclopropyl cation, followed by ring opening to give the allylic cation; this in turn reacts intramolecularly to give the final product.[52]



(101)

(102)

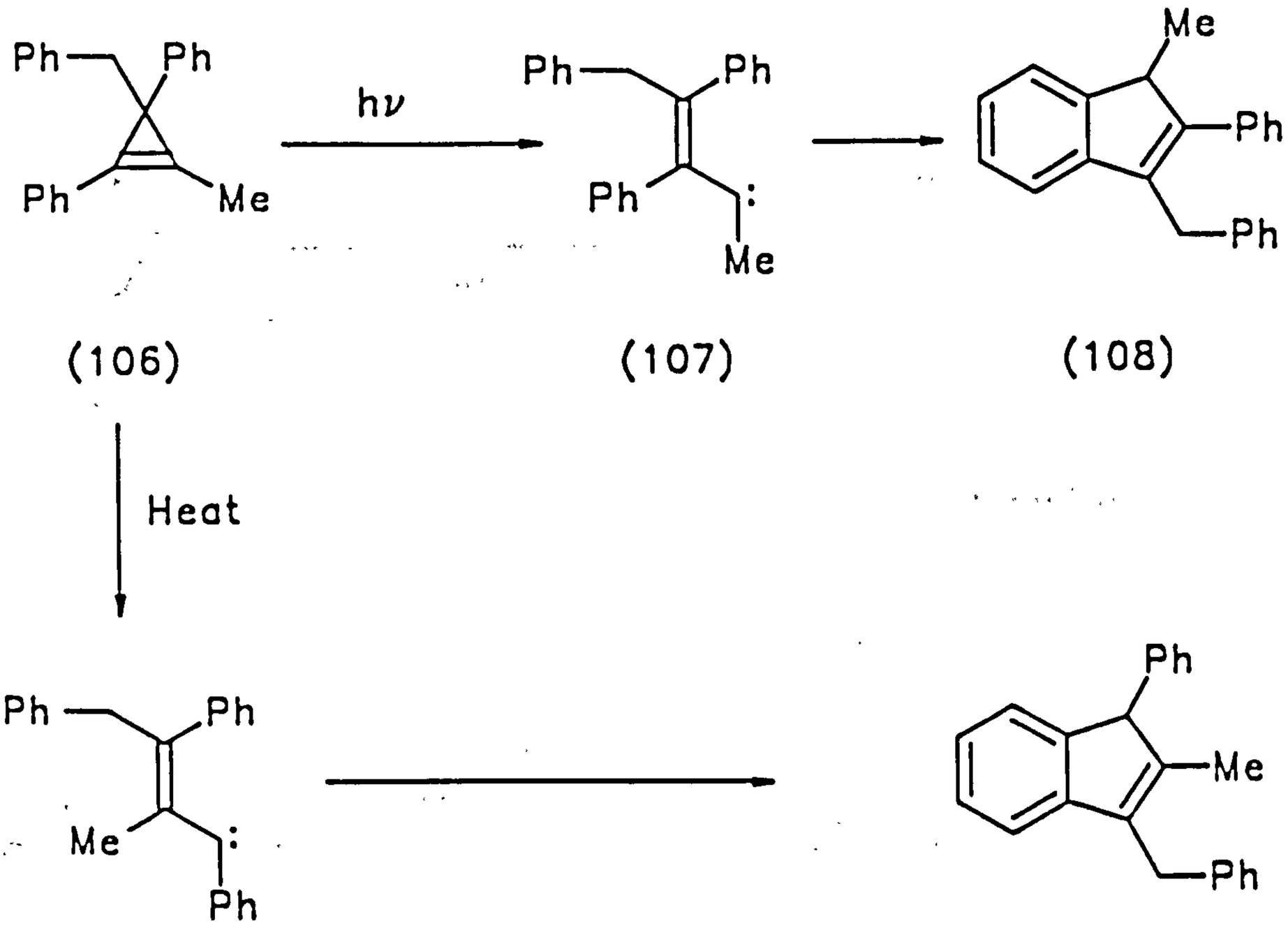
However, treatment of the cyclopropene (103) with aqueous acid gives succinate (104), but with acid in ethanol gives the α,β–unsaturated ester (105).[82]



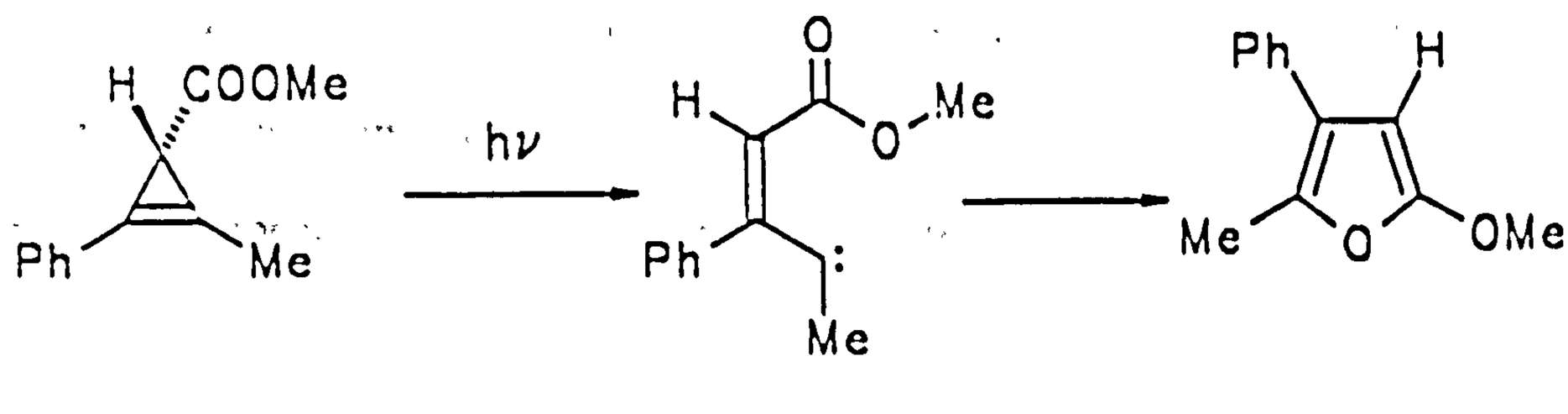
1.7.4: Polymerisation and Rearrangment.

Cyclopropene is extremely unstable in the condensed phase and can be kept for extended periods only in the solid state at liquid nitrogen temperature.[50,53] Alkylcyclopropenes are usually stable if both hydrogens at C_3 are replaced by alkyl groups. Alkyl substitution at the vinyl carbon has also some stabilizing influence, as does the presence of withdrawing groups at C_3 (e.g. CN, COOEt).[52]

Photolysis of the cyclopropene (106) has been found to give (108), apparently derived by an insertion of the carbene (107) into an adjacent C–H bond of the aromatic ring; in contrast, pyrolysis of (106) leads exclusively to (110), apparently derived from the carbene (109).[83,84,85]

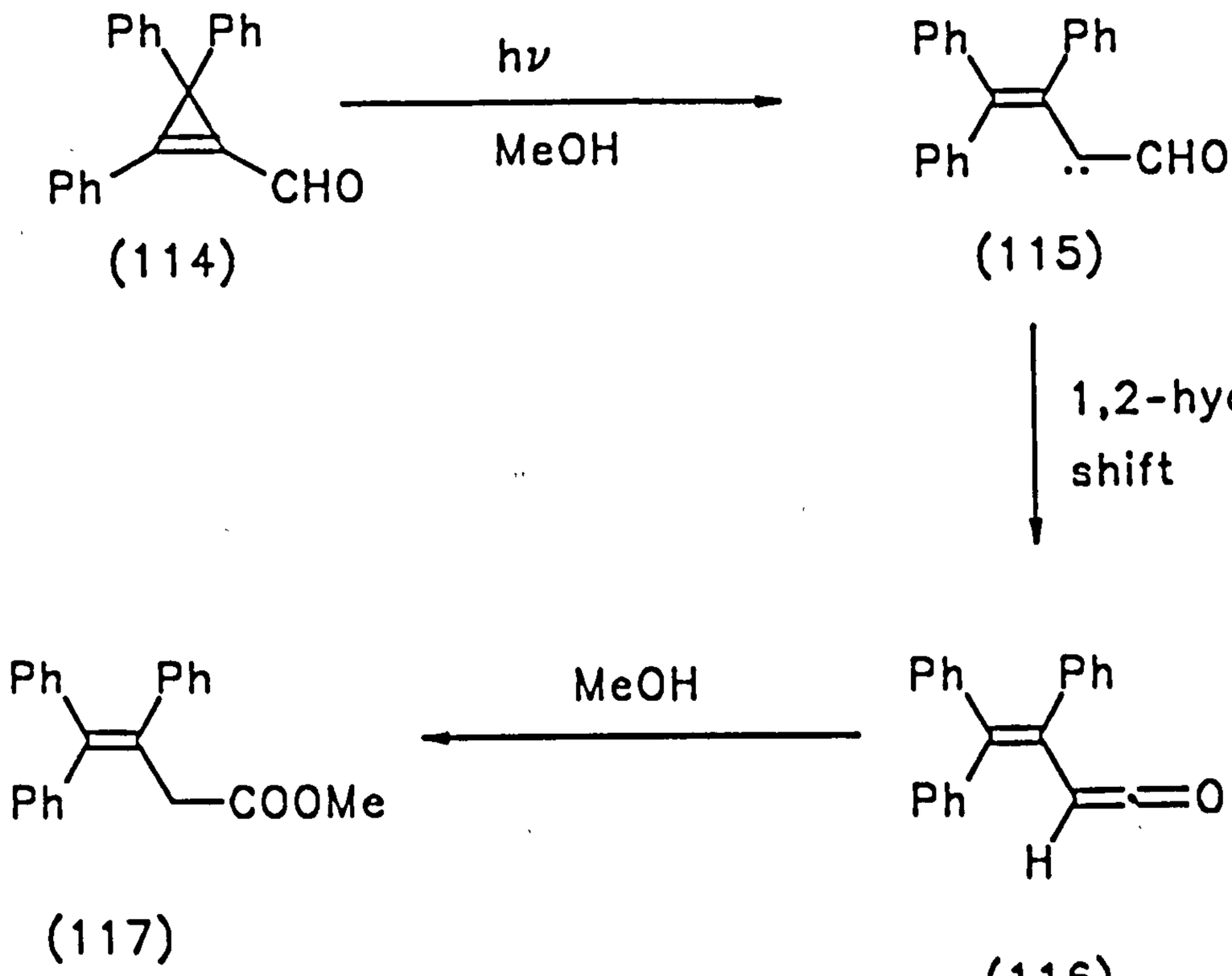


Photolysis of the cyclopropene (111) has been found to give the furan (113); this may arise by ring opening to give the carbene (112) rather than its regioisomer.[86]



The cyclopropene (114) undergoes photolysis in methanol to give (117); this may arise by ring cleavage of the C_1–C_3 bond to produce the carbene (115), which

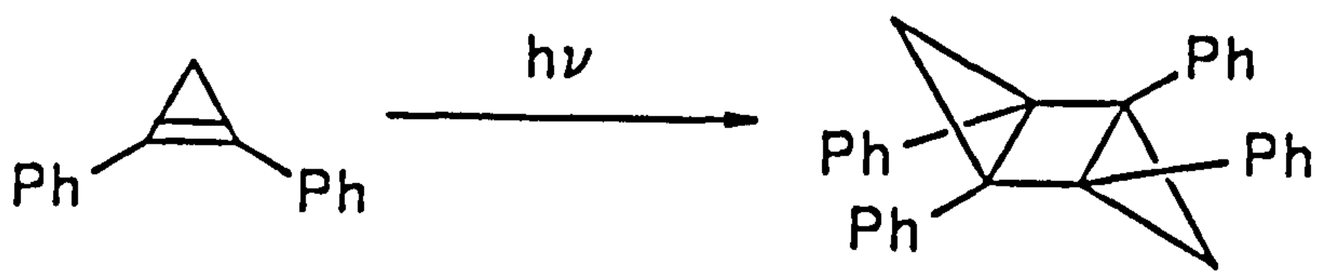
undergoes a 1,2–hydrogen shift to produce the ketene (116), which is in turn trapped by methanol.[87]



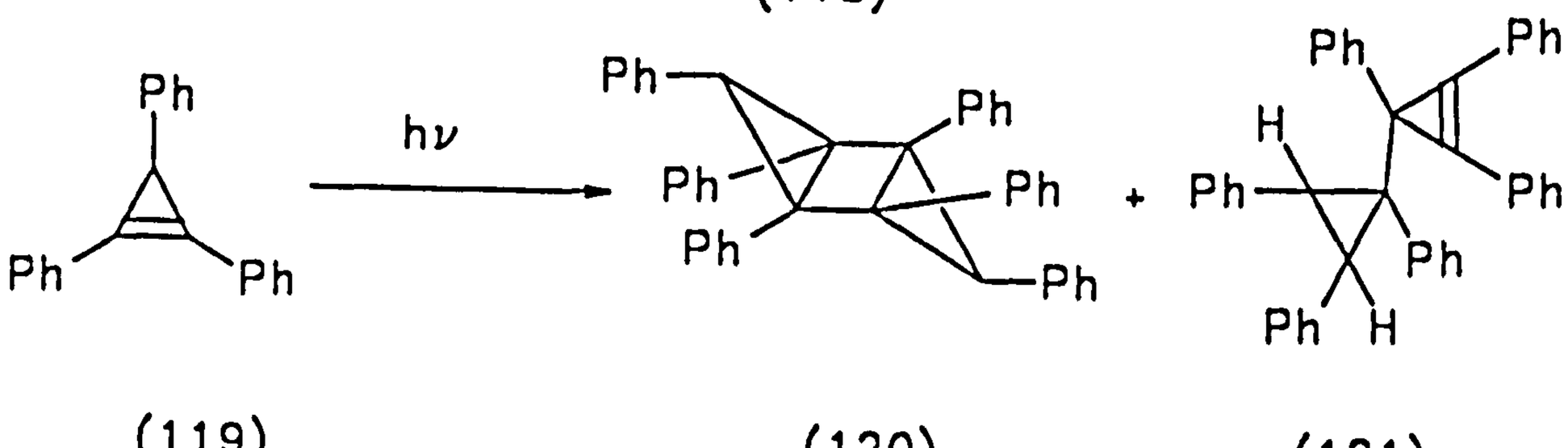
1.7.5: <u>The ene–reaction.</u>

Cyclopropenes with hydrogens at the 3–position are well known to undergo dimerization through an ene–type process, leading to cyclopropylcyclopropenes; hence, 1–methylcyclopropene dimerizes within minutes at room temperature.[88]

When there is no hydrogen substituent at C_3, the cyclopropenes can be comparatively stable, although their ring–opening on thermolysis or photolysis has been widely reported. Thus photolysis of 1,2–diphenylcyclopropene produced one product, (118), while (119) gave a mixture of two dimers, (120) and (121) in ratio 6:4 respectively. Moreover, as a consequence of steric factors, the related tetrasubstituted cyclopropenes do not dimerize:[89]



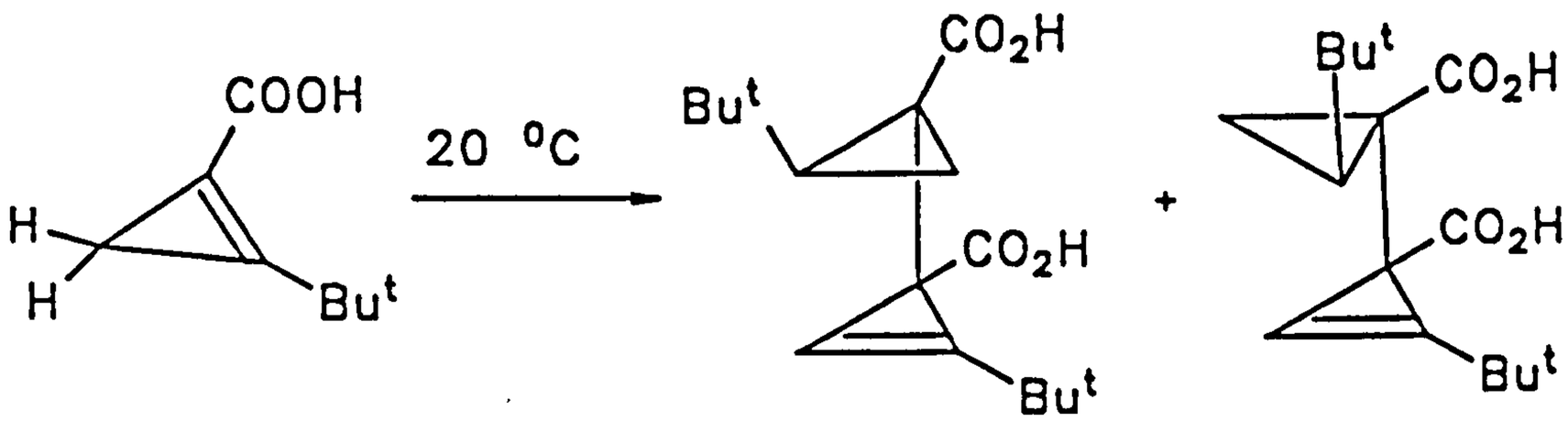
(118)



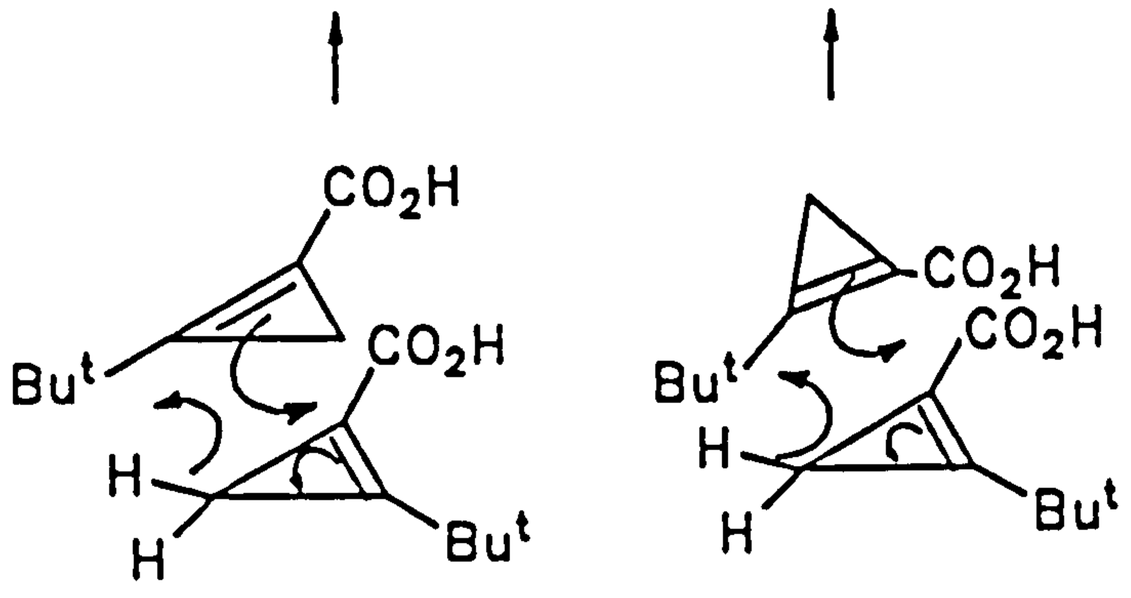
(119) (120) (121)

These photochemical reactions occur in a stepwise fashion *via* a diradical intermediate.[90] However, the dimer (121) which was also obtained by heating the cyclopropene (119) in refluxing. xylene, is believed to form through an ene–type reaction.[91]

More recently, Baird and Hussain[88] found that, when the cyclopropene (122) was allowed to stand as a neat liquid at room temperature, a mixture of two products (123) and (124) were obtained in ratio 3:2 respectively. The major product was derived *via* the ene–reaction as in (125), while the minor product goes through (126).

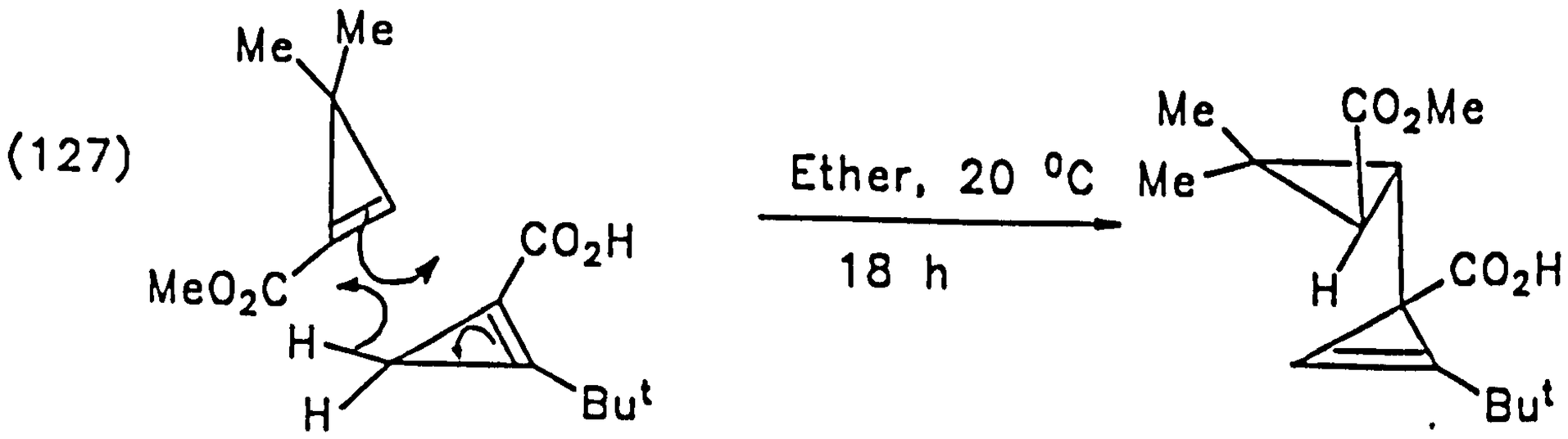


(122) (123) (124)



(125) (126)

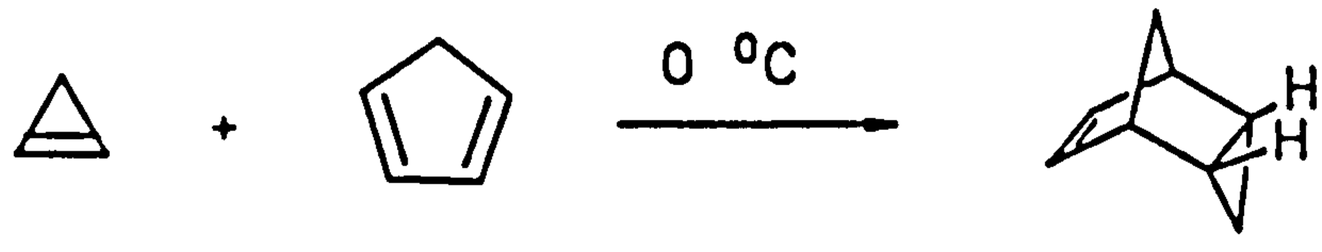
When the ester (127) was allowed to stand for 18 h in ether solution with the cyclopropene (122), a single acidic product (128) was isolated. The latter was again derived through the ene-reaction.[88]



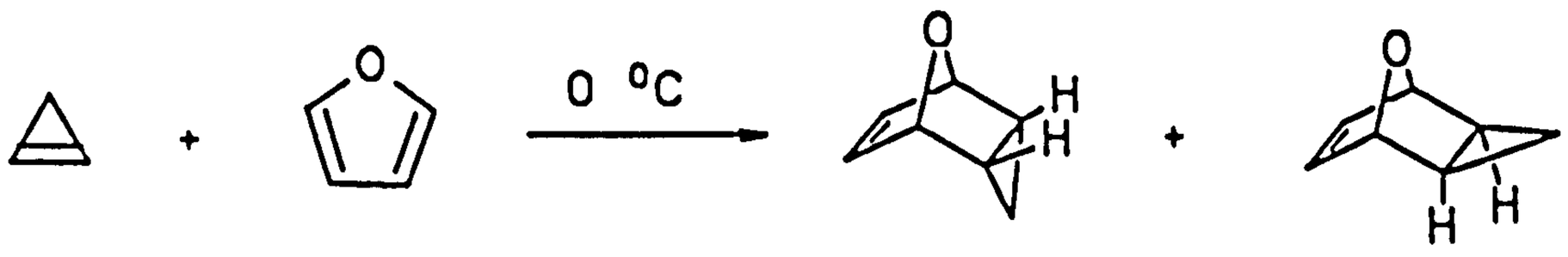
(122) (128)

1.7.6: Cycloaddition.

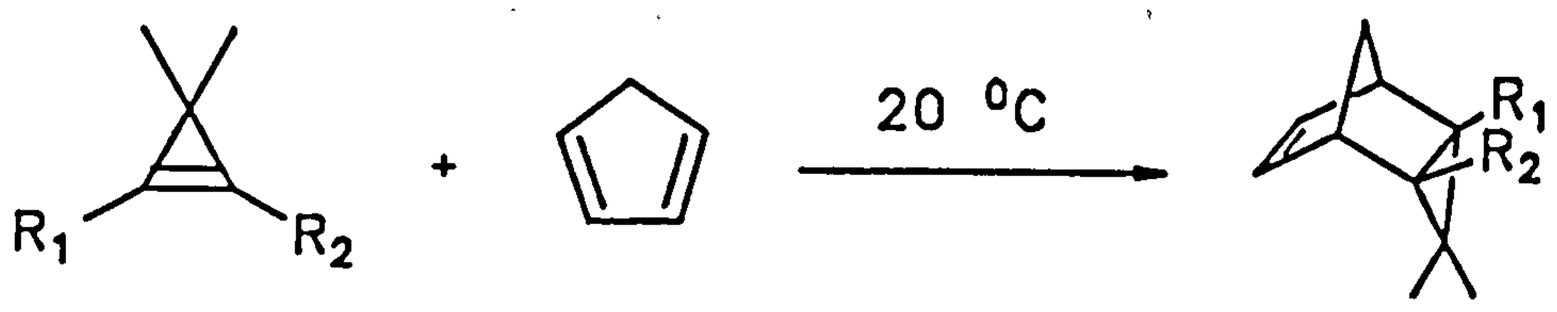
Cyclopropenes are good dienophiles and can undergo Diels – Alder reactions; however, the presence of substituents at C_3 causes steric retardation. Cyclopropene itself reacts with cyclopentadiene to form endo–adduct (129); in contrast, with furan it forms a 1:1 mixture of exo– and endo–adducts, the change in stereochemistry is probably explained by the reduction in steric repulsion on replacing the methylene group by an oxygen.[56,92]



(129)

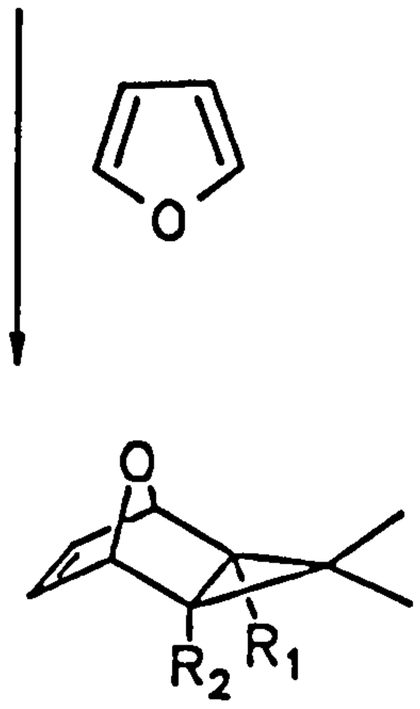


However, 3,3–dimethylcyclopropene does not add to cyclopentadiene even at 100 °C,[63] the deactivation resulting from steric hindrance due to the C_3–methyl groups. Cyclopropenes substituted with electron withdrawing groups at C_1 and C_2, e.g., esters and cyano groups, follow the same steric course of cycloaddition as non–electrophilic cyclopropenes, i.e. cyclopentadiene produces *endo*– and furan produces *exo*–adducts.[93]

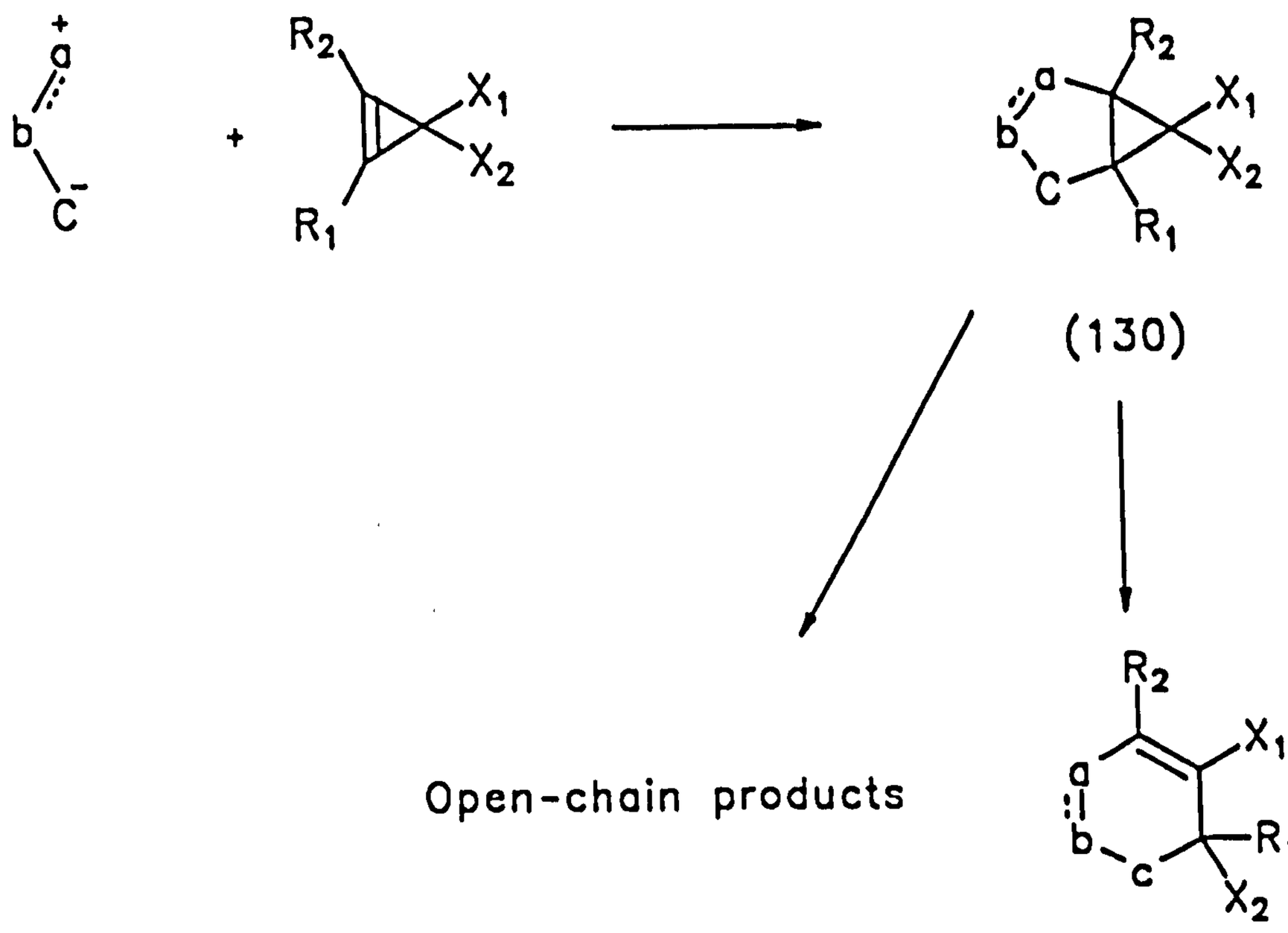


R_1=COOMe=R_2

R_1=COOMe,R_2=H

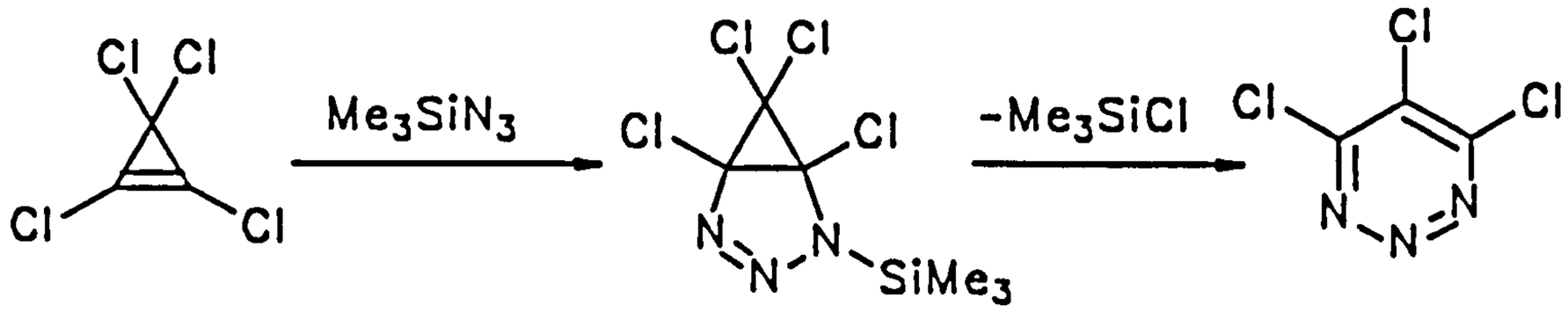


The cyclopropene π–bond acts as a dipolarophile for a wide range of a 1,3–dipoles.[94] The initial [2+3] adduct (130) (a, b and c represent substituted atoms of C, N and/or O) can expand to a six–membered heterocycle, particularly when the cyclopropene contains a good leaving group at C_3 e.g. (X_2 = Cl). Less frequently ring fission in (130) gives an open–chain product.



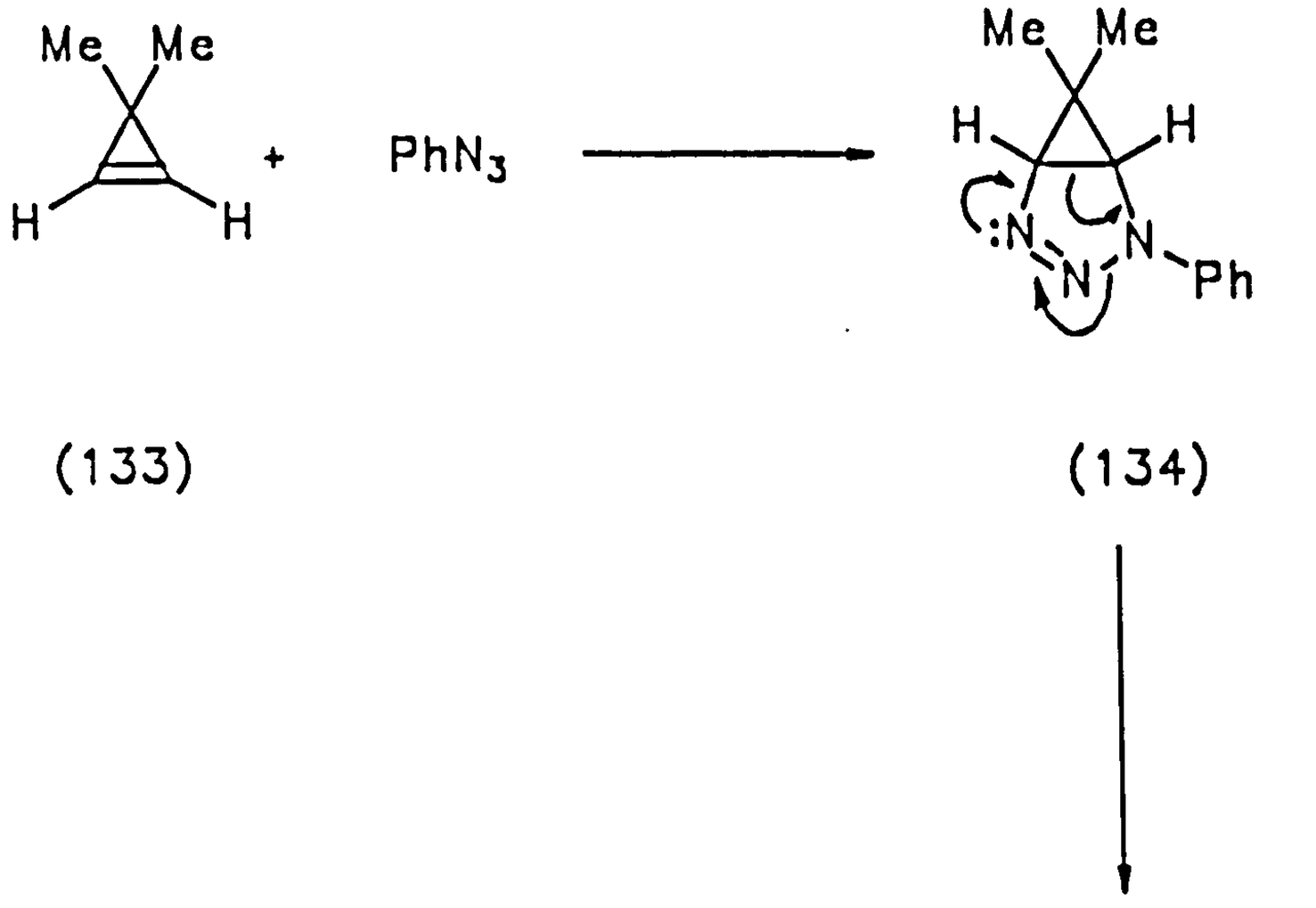
When the cyclopropene (131) was allowed to react with trimethylsilyl azide, the

final product was (132); this may arise by addition and subsequent loss of trimethylsilylchloride.[95]



(131) (132)

The reaction of 3,3–dimethylcyclpropene (133) with phenylazide gives a 2:1 adduct (135), apparently derived from initial [2+3] cycloaddition to give (134), rearrangement to the diazo–derivative, and a 1,3–dipolar addition to a second molecule of cyclopropene to give (135).[96]

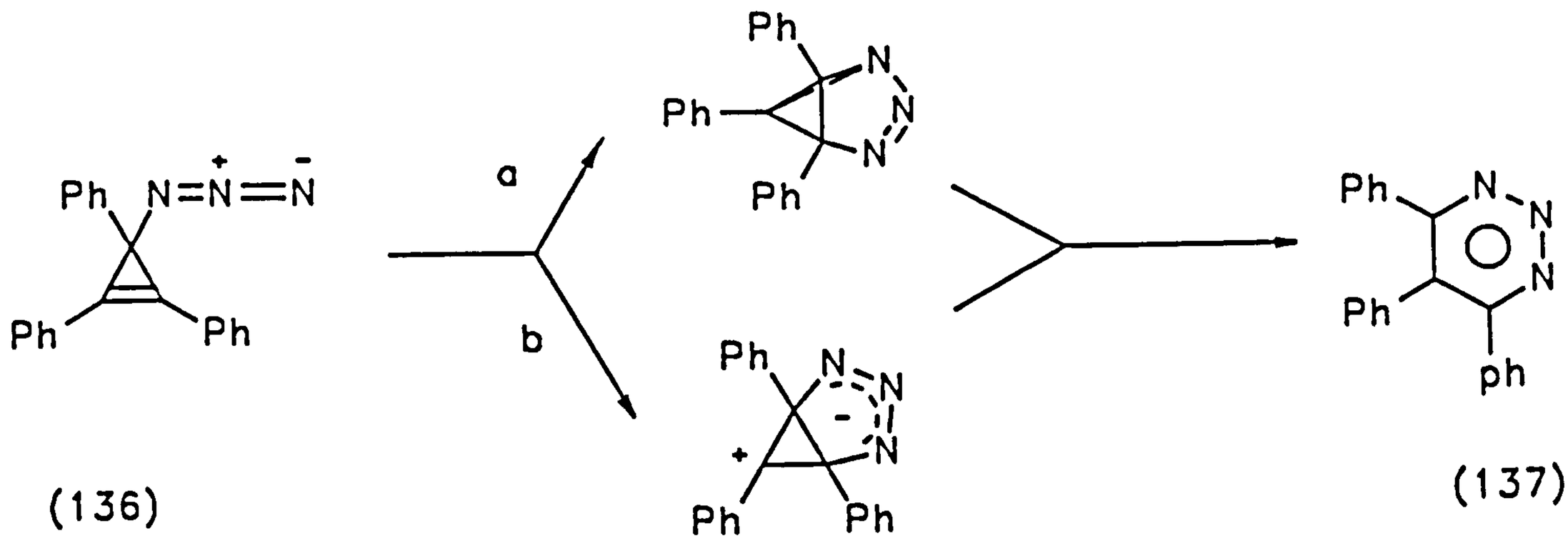


(133) (134)

(135)

The intramolecular addition of the azidocyclopropene (136) to form the triazene

(137) could involve either 1,3–dipolar addition (path a) or electrophilic attack on the cyclopropene double bond by the azide group (path b).[97]



Chapter Two

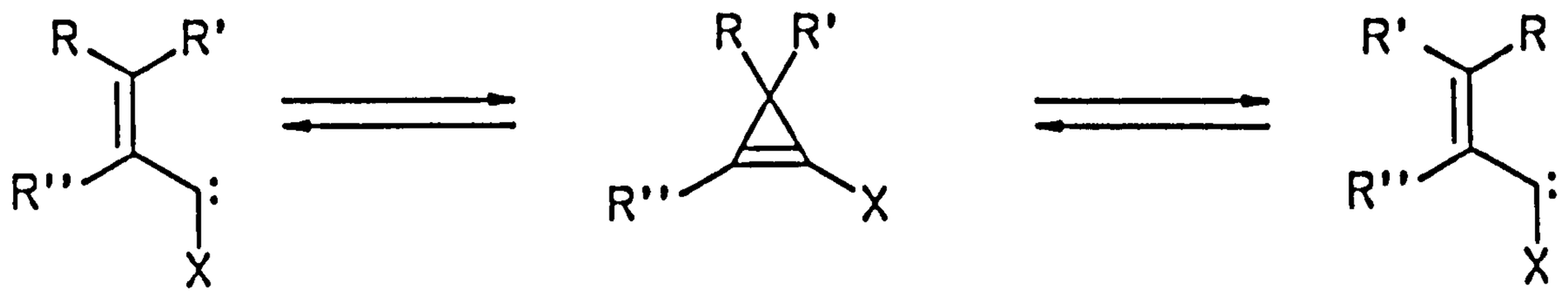
Ring opening of cyclopropenes

2.1: INTRODUCTION:

During the past few years, the chemistry of cyclopropene derivatives has attracted considerable interest, presumably as a result of the high strain energy (53 kcal/mol), associated with unsaturated three membered rings.[83]

Vinyl carbenes have frequently been proposed as intermediates in the thermal and photochemical reaction of cyclopropenes, because of the relief of ring strain, combined with possible resonance stabilization of the corresponding ring–opened species.[83]

The reaction, which in several cases is reported to be reversible, involves a formal monorotation at C_3, leading to *E*– or *Z*–isomers (139) and (140) about the double bond, which may be trapped by inter– and intra–molecular processes.[73,76]

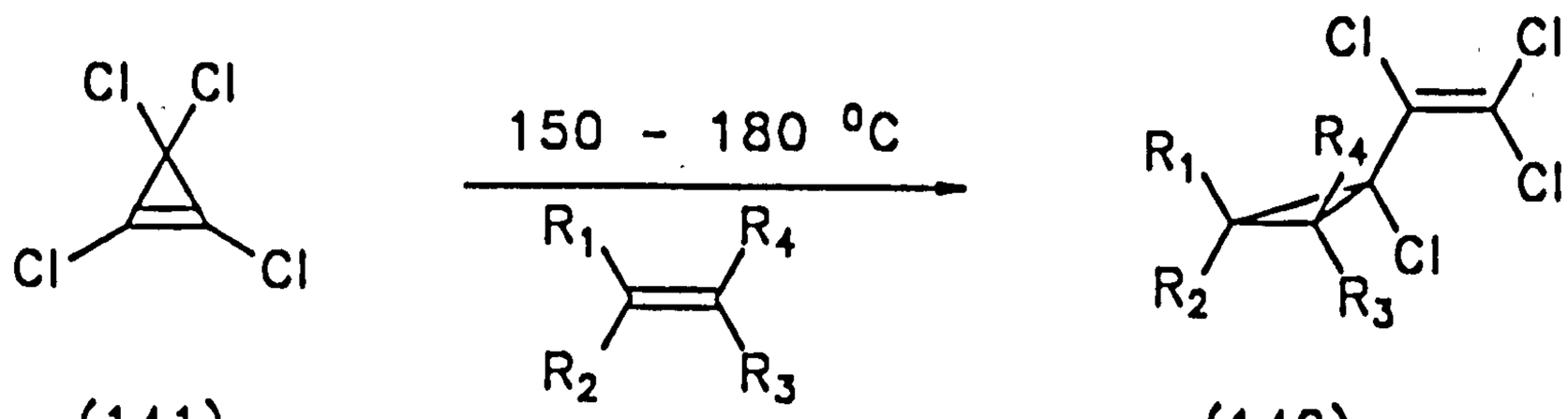


(139) (138) (140)

There are several examples of intramolecular trapping of the carbene by a 3–substituent which require these to be *Z*–related; this may arise by stereocontrolled ring–opening or could be the result of a reversible process and selective trapping of one isomer. In some cases, steric effects apparently play a controlling role; thus, while photolysis of (138, X = R'' = R = Ph, R' = CH_2OH) leads to the furan derived by trapping of the *E*–isomer (139) by the hydroxyl group, compound (138, X = R'' = R = Ph, R' = CH(Me)OH) leads to an indene by trapping of the Z–isomer of the

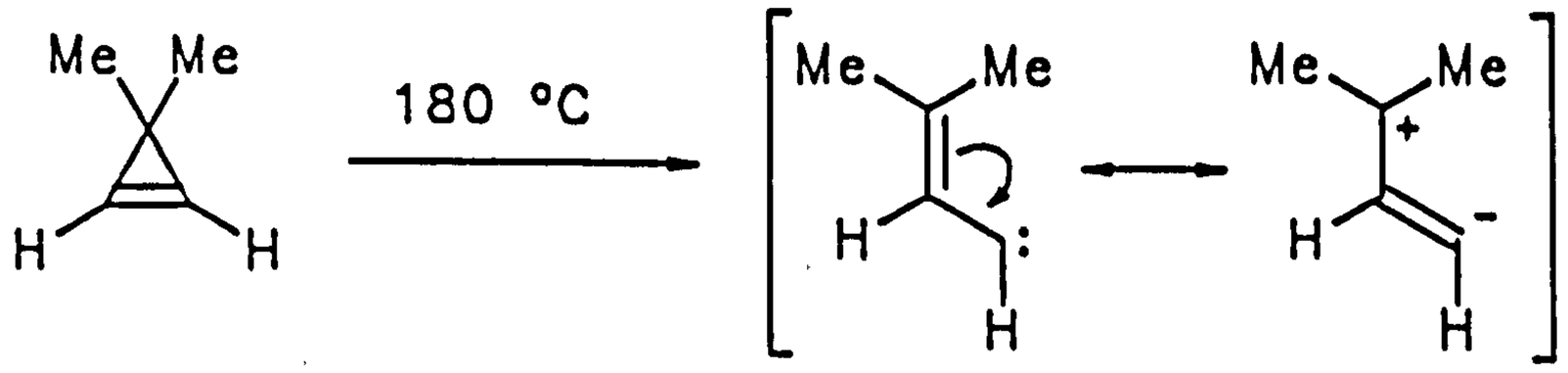
corresponding carbene (140) by the phenyl group.[98] Most reported intermolecular trappings of vinylcarbenes derived from cyclopropenes do not distinguish between the 3–substituents of the latter, though thermolysis of 3–methyl–3–phenylcyclopropene at 180 ^{0}C does lead to selective intermolecular trapping of the carbene (139, X = R'' = H, R = Ph, R' = Me) by alkenes, but in low yield.[99] Moreover, the metal induced ring–opening of (138, X = R'' = H, R = Ph, R' = Me) leads to trapping of both *E*–and *Z*–carbene isomers.[100]

The thermal reaction usually requires relatively high temperature, e.g., the tetrachlorocyclopropene (141) undergoes ring opening to the corresponding carbene at 150 – 180 ^{0}C, and in the presence of alkenes this leads to the cyclopropane adduct (142).[101]



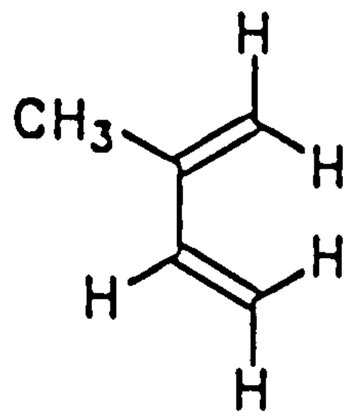
(141) (142)

Moreover, the cyclopropene (143) undergoes ring opening at 180 ^{0}C to the carbene (144) which reacts intramolecularly to give the diene (145), apparently through a 1,4–hydrogen shift.[99]



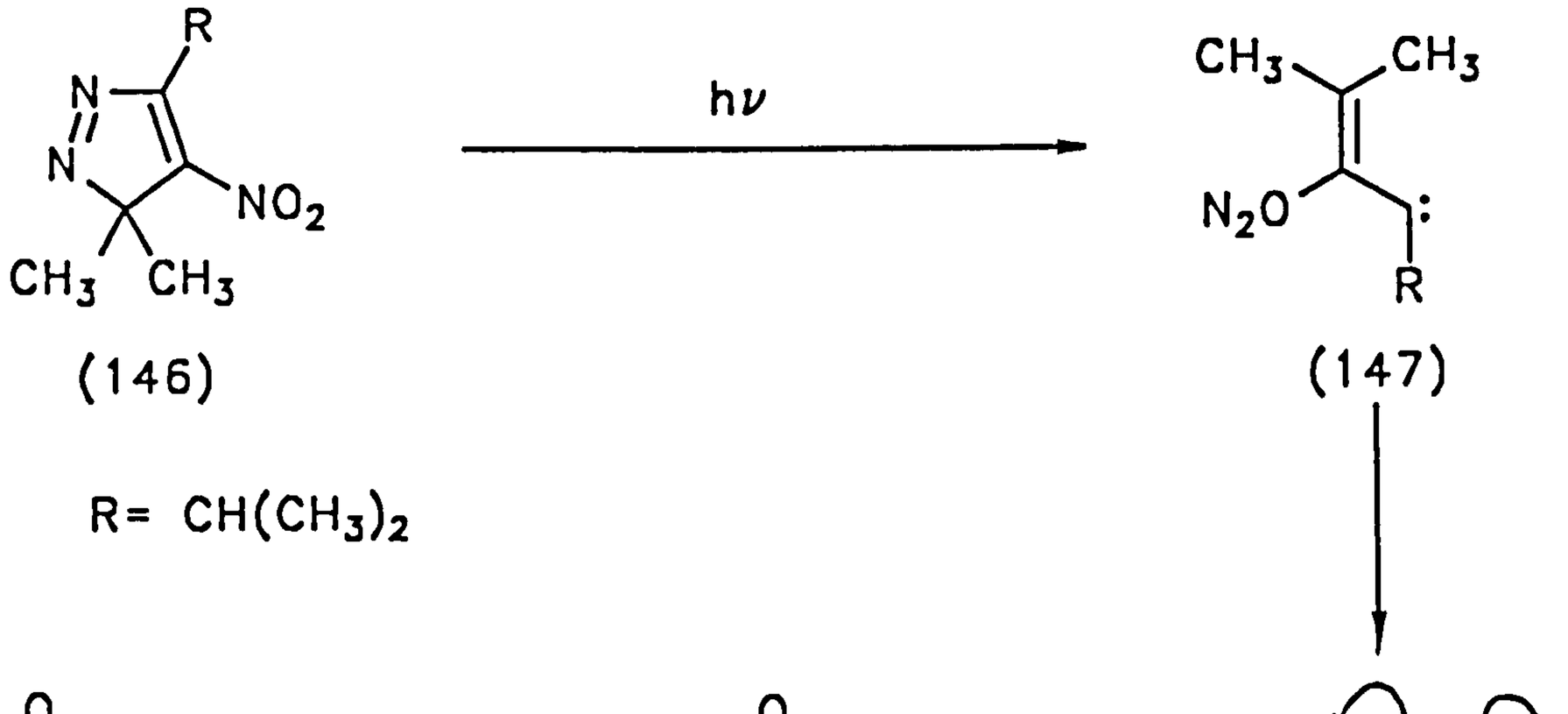
(143) (144)

1,4-hydrogen shift



(145)

Photolysis of (146) is reported to lead to the carbene (147) which reacts intramolecularly to give (148) in quantitative yield.[102]



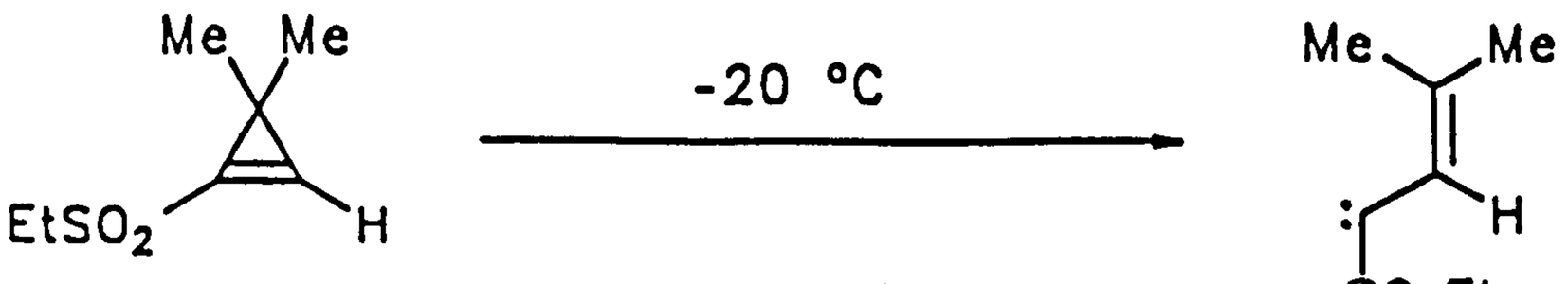
(146)

(147)

R= $CH(CH_3)_2$

(148)

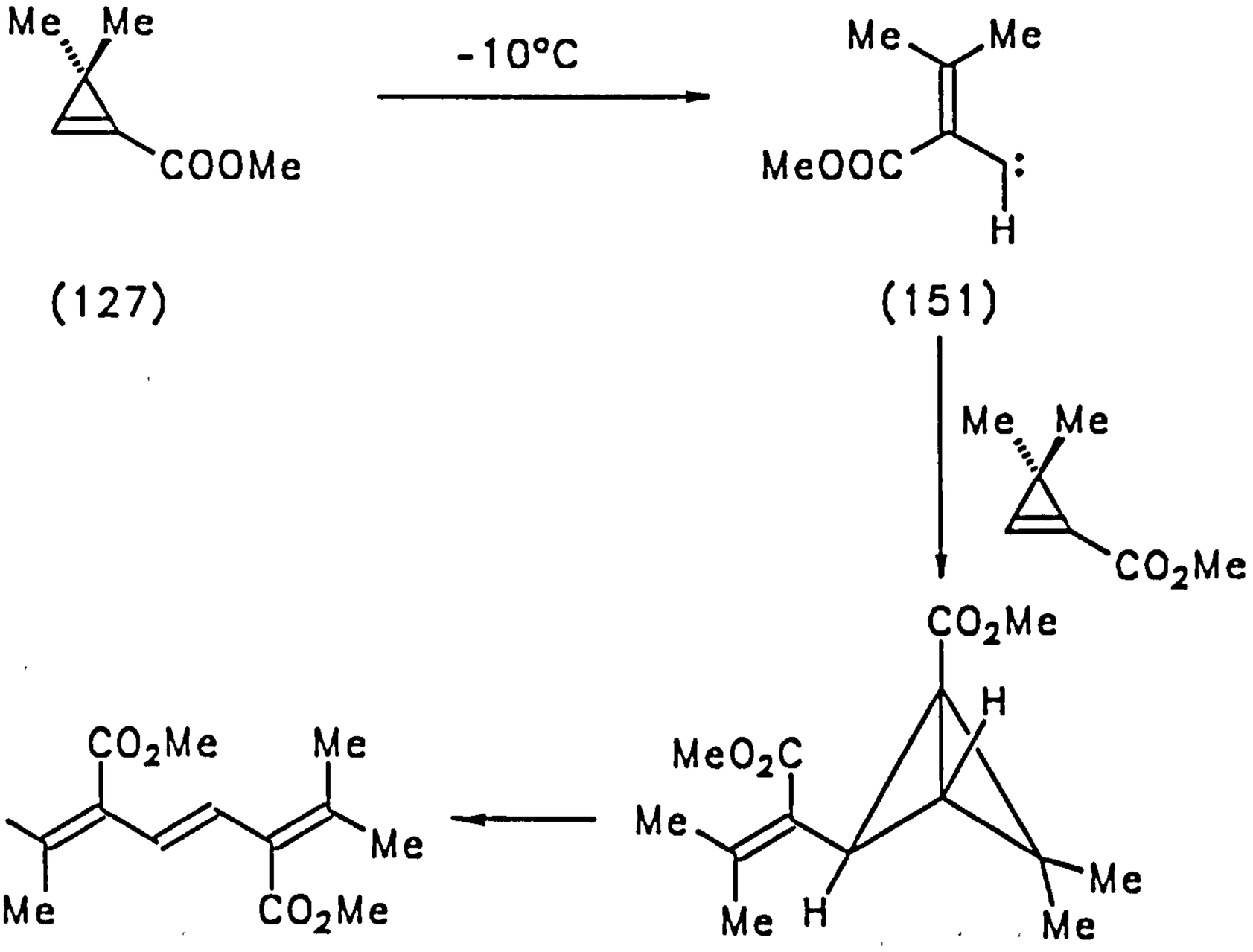
In some cases, however, the cyclopropene–carbene rearrangment can occur even at or below ambient temperature; thus, the cyclopropene (149) is reported to undergo ring opening at –20 ^0C, and the resulting carbene (150) is readily trapped by alkenes.[103]



(149) (150)

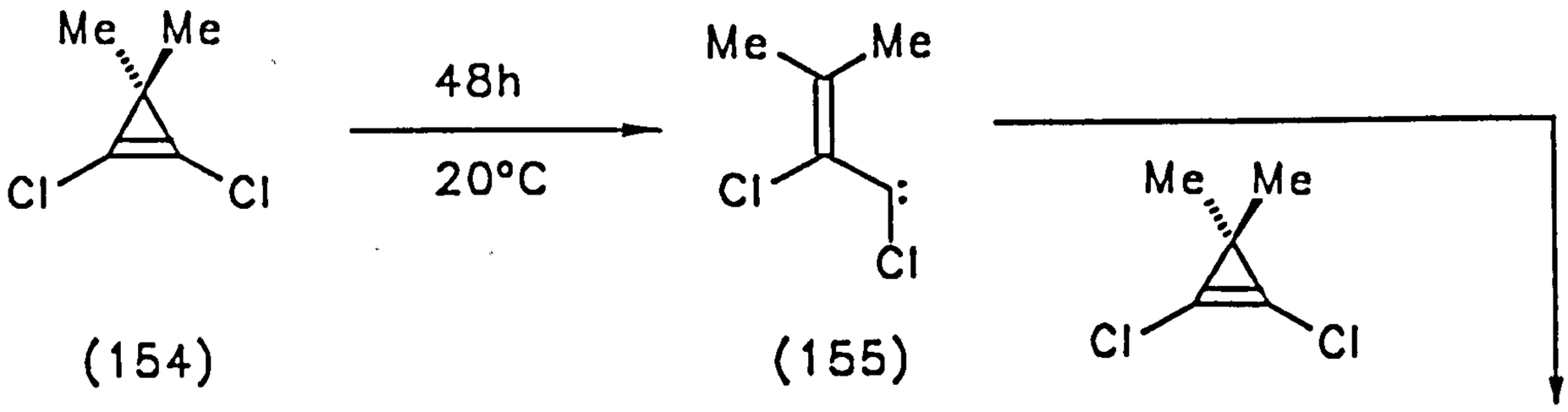
The precise factors affecting the rate of cyclopropene ring opening have not been fully established, although the presence of an electron withdrawing substituent at C_1

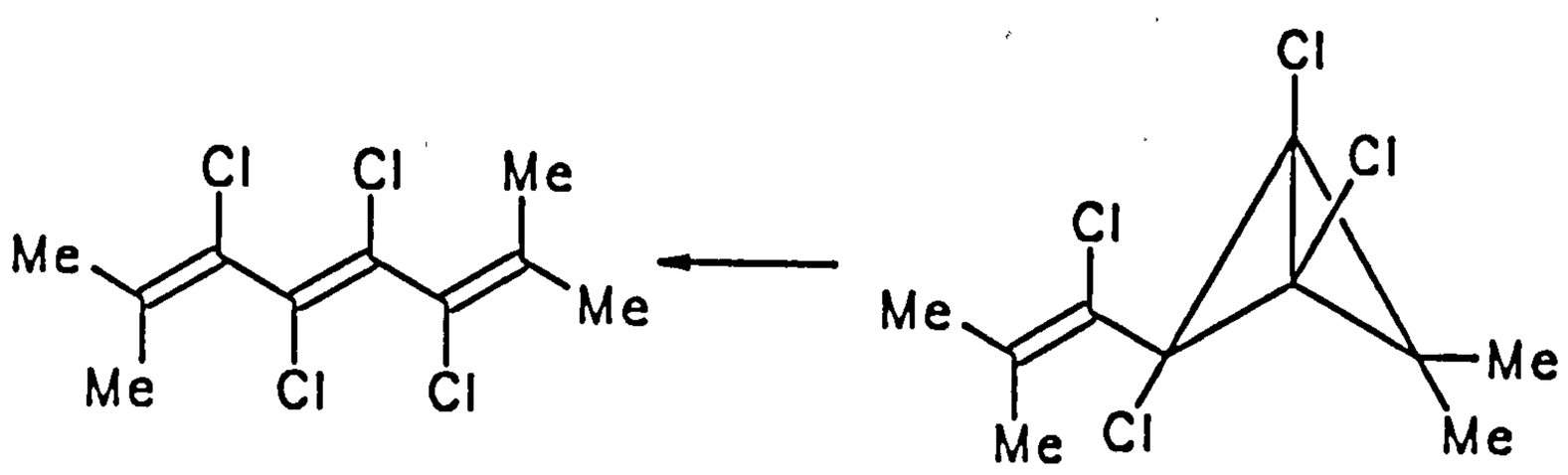
and/or C_2 and of a pair of alkyl substituents at C_3 does appear to lead to carbene formation at ambient temperature or below.[104] For example, the ring opening of cyclopropene (127) has recently been demonstrated to lead to (153), when the neat sample of (127) was allowed to stand for several days at –10 °C.[105]



(127) (151) (153) (152)

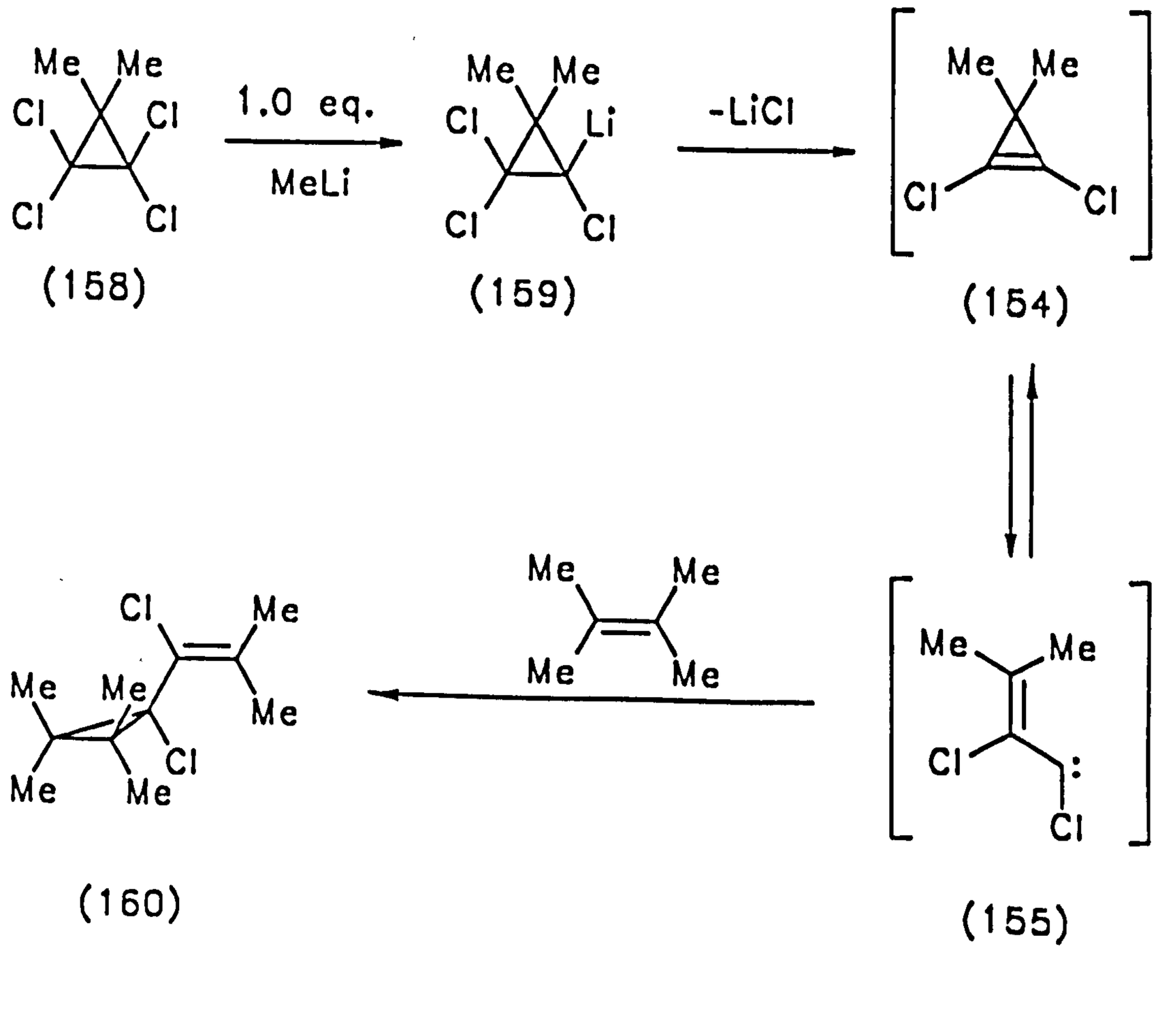
The formation of (153) probably arises by an initial ring–opening of the cyclopropene (127) to the carbene (151) which reacts with unreacted starting material to give the bicyclobutane (152) which undergoes rearrangment to give (153). However, the carbene could not be trapped by added alkylalkenes. When the cyclopropene (154) was allowed to stand for 48 h at room temperature, the dimer (157) was obtained in 86% yield. This may again arise by ring–opening of the cyclopropene to the carbene (155) which reacts with the cyclopropene (154) to give the bicyclobutane (156), followed by rearrangment to give the dimer (157) in 86% yield.[104] In this case the carbene could be trapped by added alkenes, though (156) was not detected.





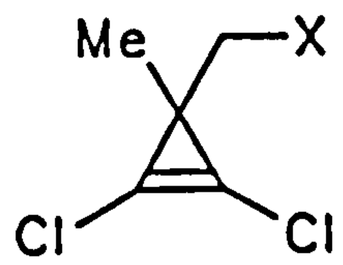
2.2: AIMS OF THE PROJECT.

Previous work at Newcastle has shown that the tetrachlorocyclopropane (158), on treatment with one equiv. of methyl-lithium at 0 ^{0}C in the presence of an alkene, e.g., 2,3-dimethylbut-2-ene, leads to (160).[104]

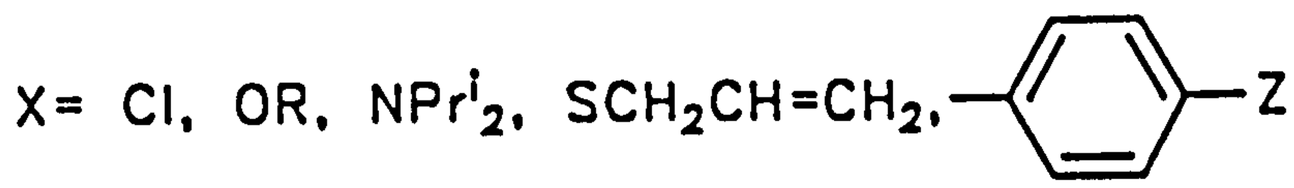


This adduct may arise by lithium–chlorine exchange to give (159), followed by or concerted with 1,2–elimination to give (154) which undergoes ring opening at 0–20 °C to give the carbene (155), which is in turn trapped by alkene to give the adduct (160).

The aim of the present work was to use this procedure to generate a range of cyclopropenes of type (161), in which the substituent (X) is varied in order to determine the factors which affect the rate of cyclopropene ring opening and stereochemistry of the resulting vinylcarbenes.



(161)

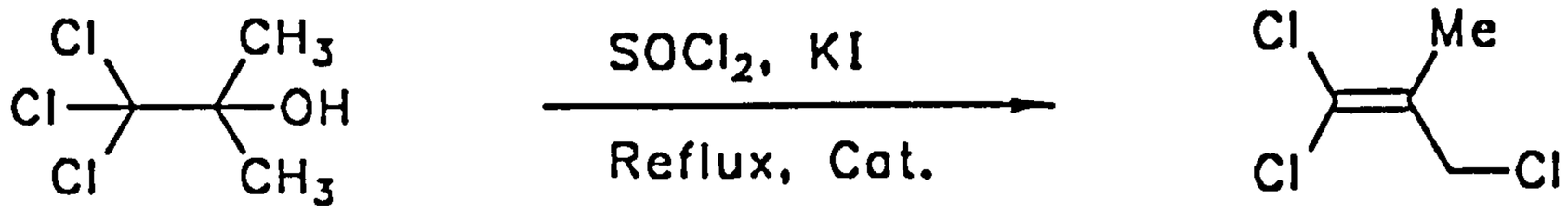


In addition, the intermolecular trapping of these vinylcarbenes with electron poor alkenes such as methyl methacrylate might provide a synthetically useful route to analogues of the pyrethroid insecticides.[101,106]

2.3: DISCUSSION.

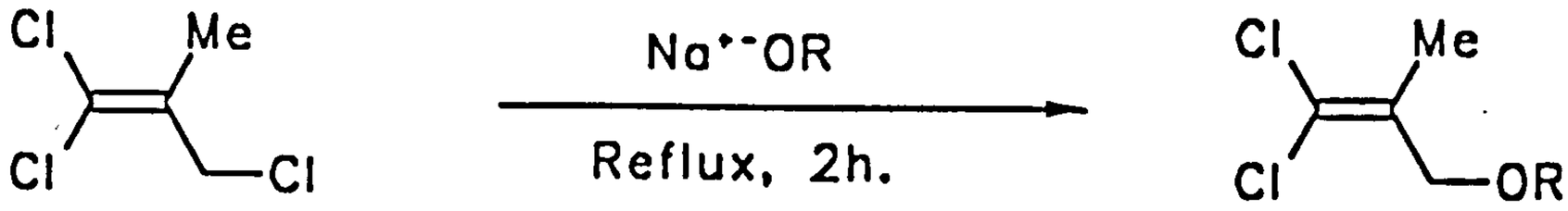
2.3.1: Preparation of tetrahalocyclopropanes.

Reaction of chloretone (162) with thionyl chloride in the presence of potassium iodide provides a convenient large scale route to the allylic trichloride (163); this is a slight modification of the literature procedure.[107]



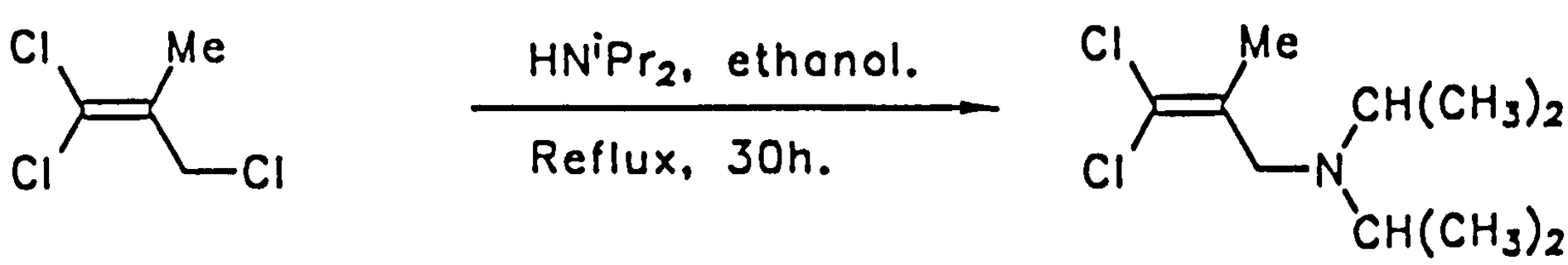
(162) (163)

The allylic trichloride (163) was readily converted to the corresponding ether (164) by refluxing with sodium alkoxide in alcohol.[108]



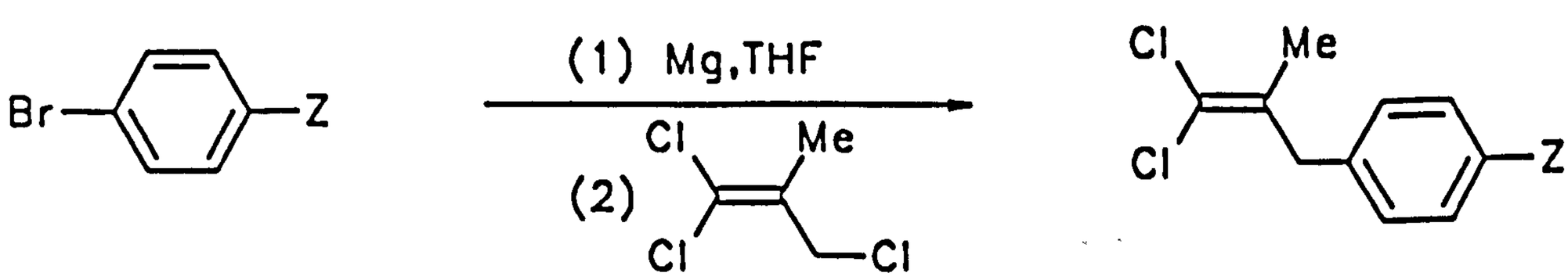
(163) (164, R= Me, Pr^i)

In the same way, the allylic trichloride (163) could be converted to the amine (165) in 62% yield by refluxing with di-isopropylamine in ethanol for 30 h.



(163) (165)

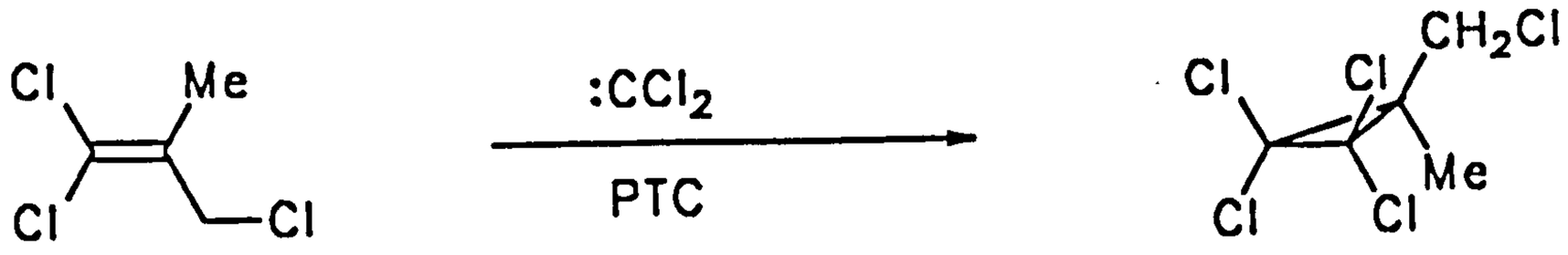
Addition of the allylic trichloride (163) to a solution of *p*–aryl magnesium bromide (166) in THF at –10 °C and stirring the resulting mixture for 18 h at 20 °C gave the dichloroalkenes (167, Z= H, CH_3, OCH_3, CF_3).



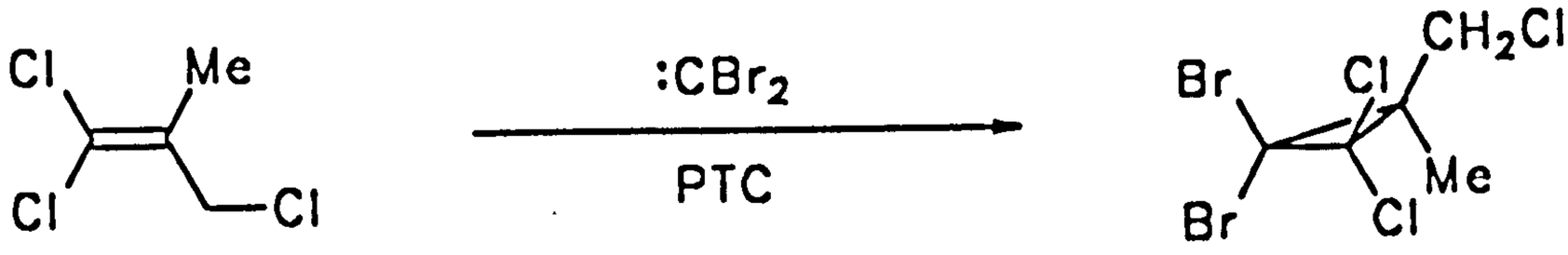
(166) (167)

Z= H, CH_3, OCH_3, CF_3.

The tetrachlorocyclopropane (168) was obtained in a good yield by reaction of (163) with dichlorocarbene ($:CCl_2$), generated under PTC from an excess of chloroform and 50% sodium hydroxide with a catalytic amount of cetrimide.[19] Monitoring the reaction by g.l.c. indicated complete consumption of starting material after 24 h at 20 °C. The product (168) showed the correct measured mass for $C_5H_5Cl_5$ and the ^1H n.m.r. spectrum contained two singlets at δ 3.78 (2H) and 1.65 (3H).



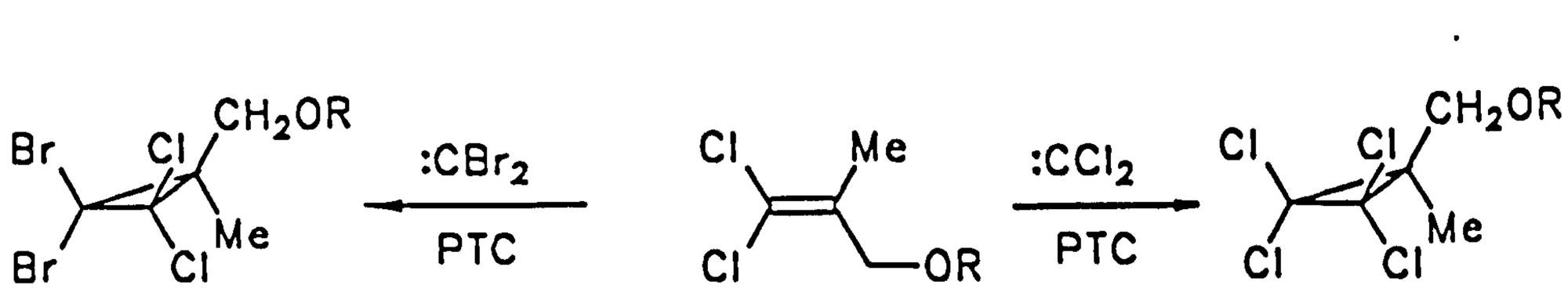
(163) (168)



(163) (169)

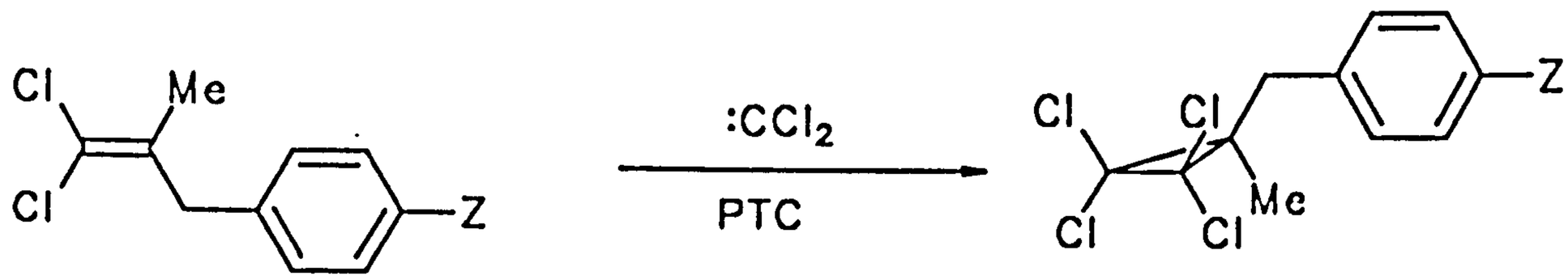
Similarly, addition of ($:CBr_2$) generated under PTC from excess of bromoform, 50% sodium hydroxide, and cetrimide to (163) gave the cyclopropane (169) in 34% yield, after two days at room temperature. The ^1H n.m.r. spectrum was very similar to (168) showing the expected two singlets for the methylene and methyl groups.

In the same way, addition of ($:CCl_2$) and ($:CBr_2$) to (164) under PTC gave the corresponding cyclopropanes (170) and (171).



(171, R= Me, Pr^i) (164) (170, R= Me, Pr^i)

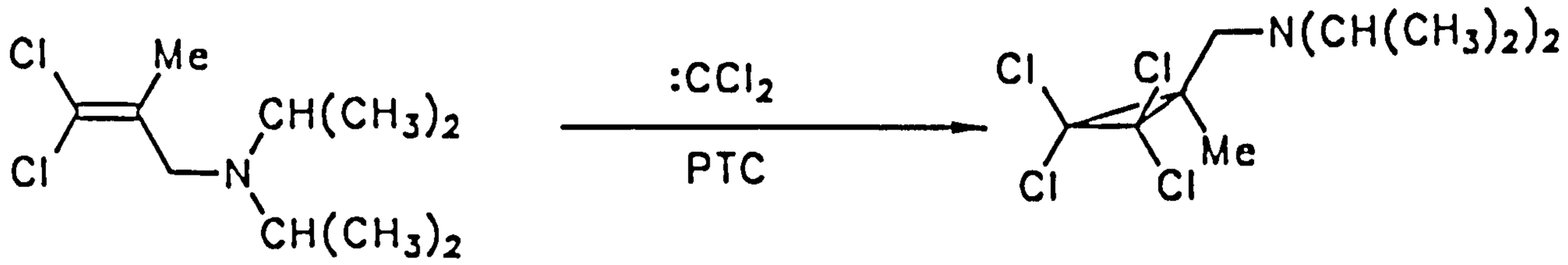
Reaction of (167, Z= H, CH_3, OCH_3, CF_3) with ($:CCl_2$) generated as described above yielded the corresponding cyclopropanes (172, Z= H, CH_3, OCH_3, CF_3).



(167) (172)

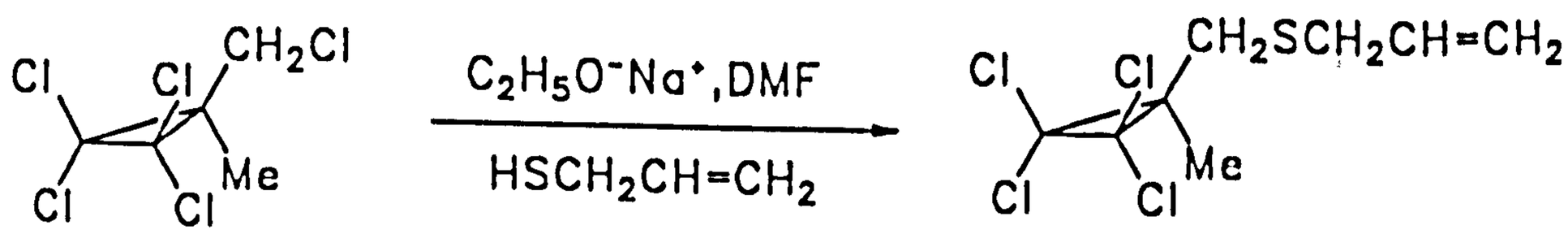
(Z= H, CH_3, OCH_3, CF_3)

Addition of ($:CCl_2$) to (165) gave the cyclopropane (173) in low yield:



(165) (173)

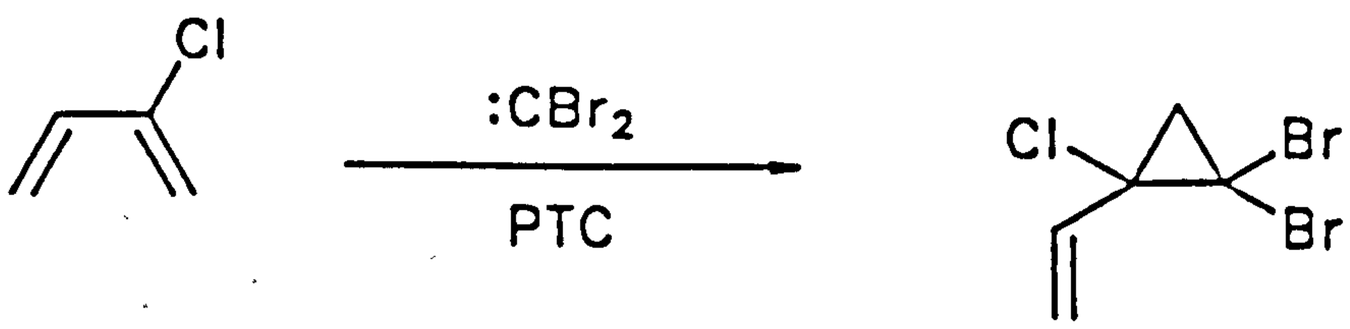
The cyclopropane (174) was prepared by a different method. The sodium salt of allylthiol was prepared *in situ* by addition of sodium ethoxide in DMF to freshly distilled allylthiol. Dropwise addition of (168) to this mixture gave (174) in 70% yield.



(168) (174)

Treatment of chloroprene (2-chloro-1,3-butadiene) with ($:CBr_2$) generated under PTC, leads to addition predominantly at the halogen substituted bond to give 1,1-dibromo-2-chloro-2-vinylcyclopropane (175) in low yield. This is contrary to the result predicted on the basis that halogen substituted bonds are less reactive to ($:CX_2$)

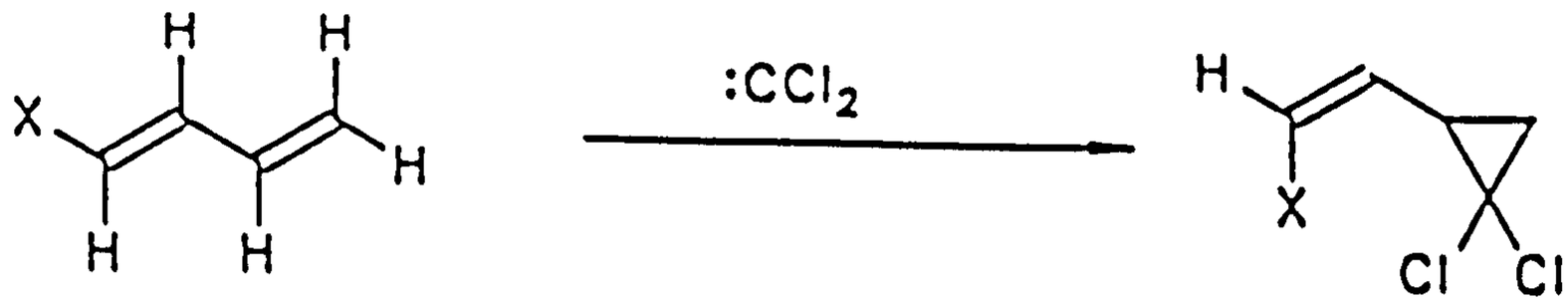
than non-halogenated ones, but is the same result as that observed for the addition of ($:CCl_2$).[38,39]



(175)

The pure cyclopropane was obtained by preparative g.l.c. The ^{13}C n.m.r. spectrum showed five signals including two in the olefinic region. The gated decoupled spectrum showed one doublet and one triplet in the olefinic region at δ 135.8 and 119.6 respectively and two singlets at δ 51.0 and 33.0, the latter characteristic for the CBr_2 carbon,[109] together with a triplet at δ 37.0.

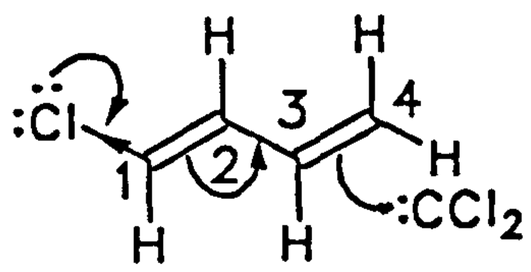
In contrast, the addition of $:CCl_2$ to dienes of type (23) is known to proceed selectivity at the less substituted double bond to give (24).[37]



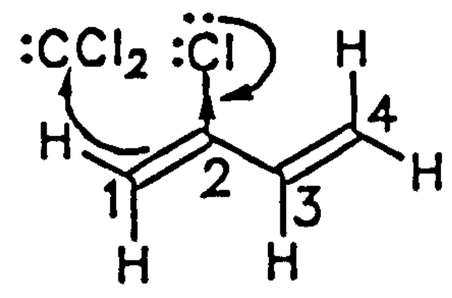
(23, X = halogen) (24)

The terminal chlorine on the diene (23) exerts a mesomeric electron releasing effect experienced by both double bonds. The inductive effect acts in the opposite direction, and falls off rapidly through the carbon skeleton; hence this effect is experienced more by the C_1–C_2 bond. The overall result is that the C_3–C_4 bond is the more nucleophilic of the two olefinic bonds and it is here that $:CCl_2$ addition is observed. In the case of chloroprene (25), the mesomeric effect of the halogen is only transmitted to the 1,2-bond. The smaller inductive effect, at the 3,4-bond, added to a significient steric effect of the halogen at C_2, is not great enough to offset this

positive mesomeric effect, and dibromocarbene therefore adds at the 1,2-bond to give the adduct (175).



(23)

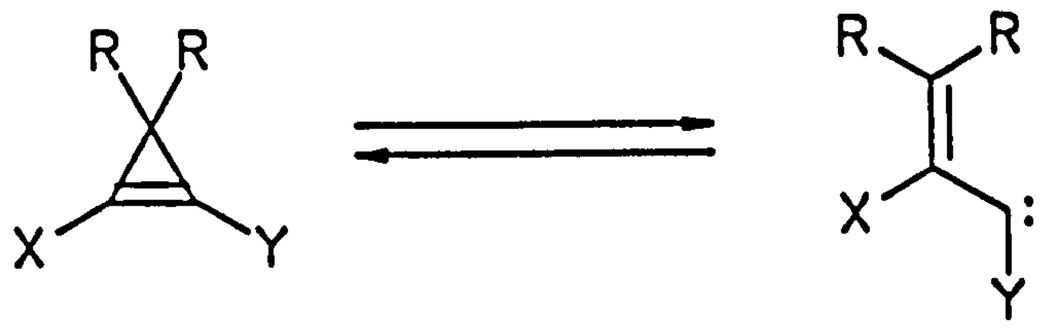


(25)

2.3.2: THE STEREOSELECTIVITY OF RING-OPENING OF 1,1-DICHLORO-3-METHYL-3-BENZYLCYCLOPROPENES AND TRAPPING OF THE DERIVED VINYL CARBENES.

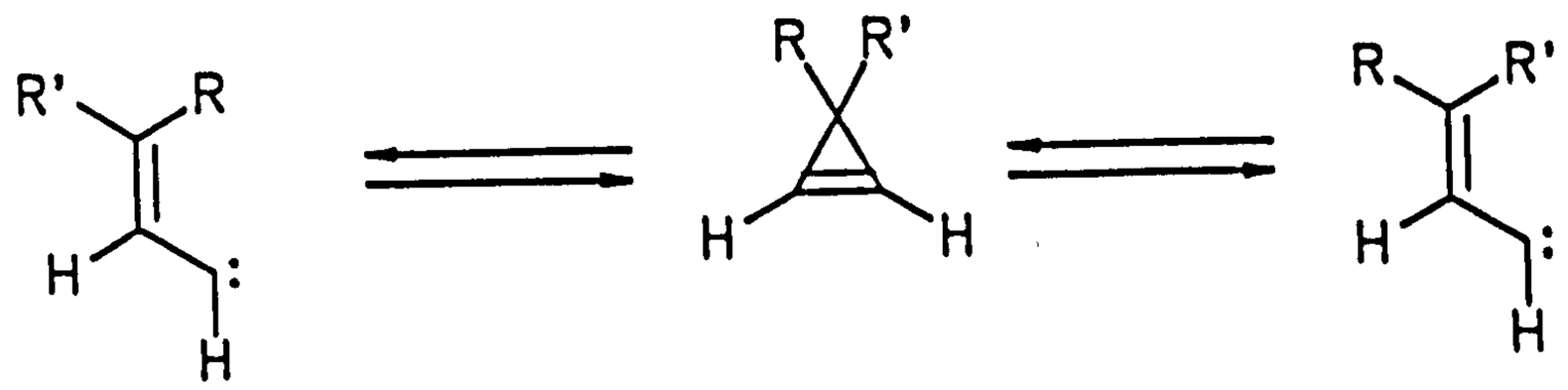
As stated above, cyclopropenes have been reported to rearrange on heating, in some cases reversibly, to give products derived from a vinyl carbene (scheme 4), and the effect of different groups X, Y, on the selectivity of the reaction has been examined.

(Scheme 4)

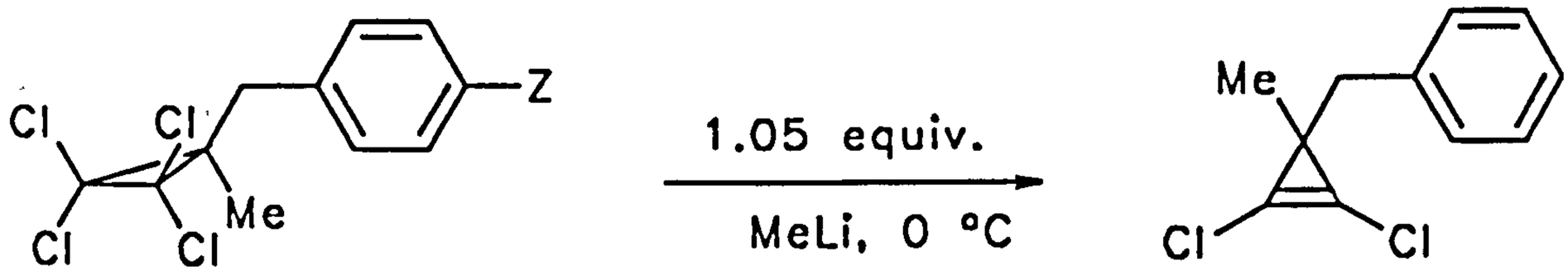


Introduction of two different groups at C_3 gives an additional possibility of two stereoisomeric carbenes (scheme 5).

(Scheme 5)

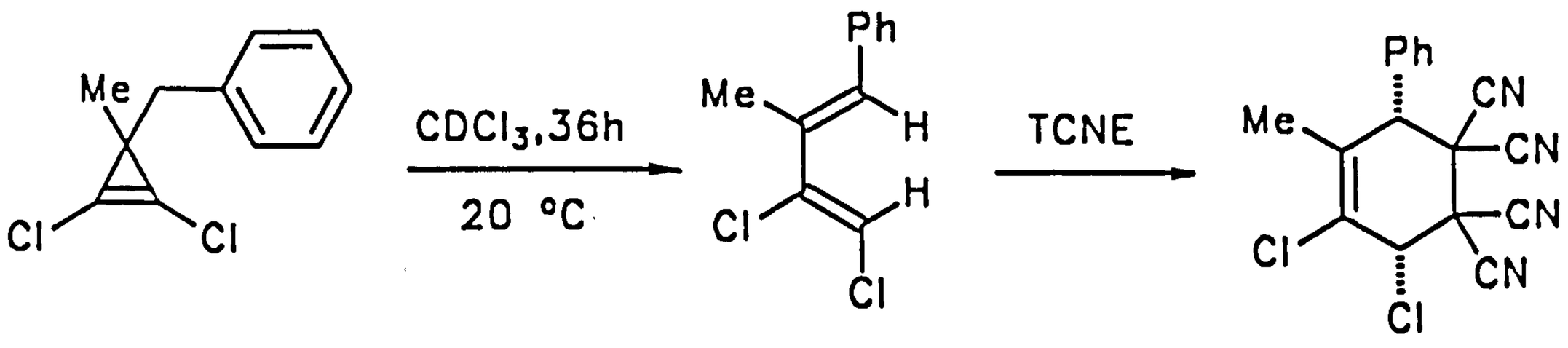


Treatment of (172, Z= H) with 1.05 eq. of methyl lithium for 20 min. at 0 ^{0}C followed by quenching with water at -40 ^{0}C and evaporation of the solvent at 0 ^{0}C gave (176) as a clear oil in 77% yield.[110]



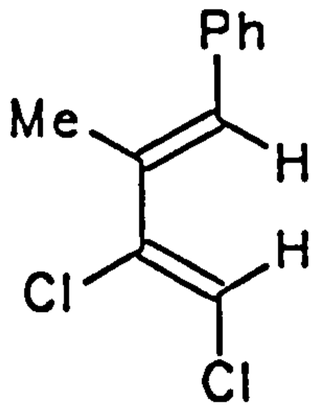
(172, Z= H) (176)

This compound showed the correct measured mass for $C_{11}H_{10}Cl_2$, and the ^1H n.m.r. spectrum contained two singlets at δ 1.23 (3H), 2.89 (2H), together with a broad singlet at δ 7.1 (aromatic protons). When the cyclopropene (176) was allowed to stand for 36 h in $CDCl_3$ at 20 °C, the diene (177) was obtained in moderate yield (35%). This compound showed the expected two vinyl hydrogen signals in its ^1H n.m.r. spectrum at δ 7.11 and 6.58, one of which showed allylic coupling to the methyl group, while the ^{13}C spectrum showed nine signals, including eight in the olefinic region and one in the high field region at δ 15.8, assigned to the methyl group.

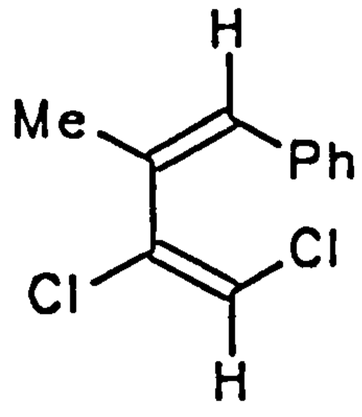


(176) (177) (178)

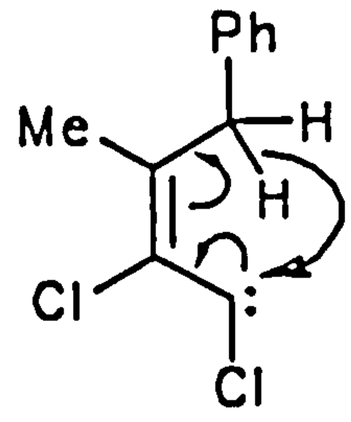
The diene (177) reacts with tetracyanoethene to give an adduct (178), the structure of which was established by X-ray crystallography (figure 1). On the basis of a concerted $4\pi_s+2\pi_s$ cycloaddition, the diene must therefore be either (177) or (179), but the latter would appear very unlikely on steric grounds and would be difficult to explain mechanistically, therefore the compound is characterised as (177). This is formally derived by a 1,4–hydrogen shift in the carbene (180).



(177)

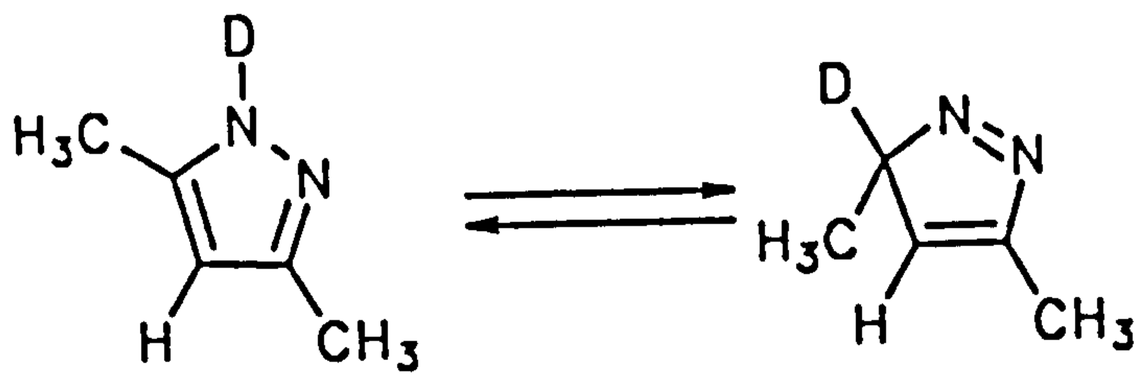


(179)

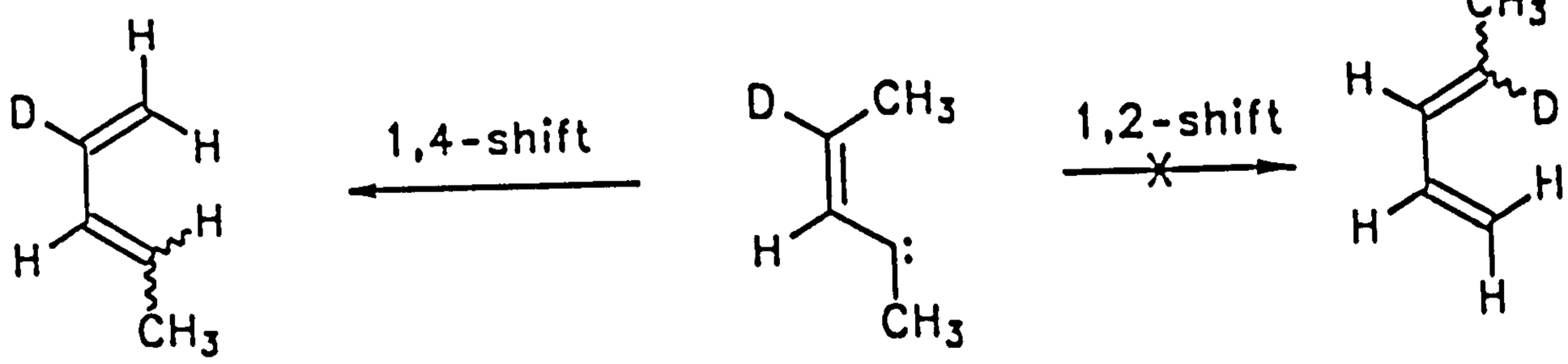


(180)

Evidence has been provided for 1,4–hydrogen shifts in other vinylcarbenes; e.g., thermolysis of the deuterium labelled hetrocycle (181) may be accounted for by a 1,4–hydrogen shift.[111]

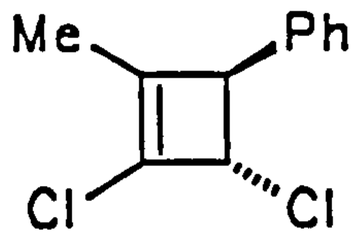


(181)

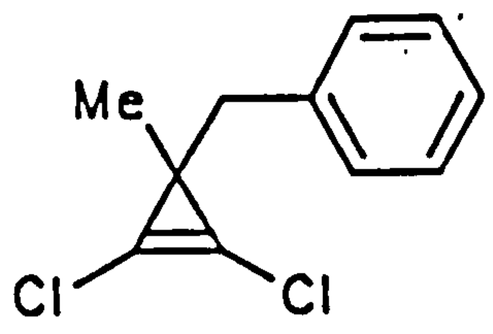


Such a rearrangment in (180) would necessarily produce a *Z*–1,2–dichloroalkene as in (177). An alternative mechanism would involve insertion of the carbene into the benzylic C–H to give a trans–cyclobutene (182) which could undergo conrotatory ring opening, again leading to the observed diene; the fact that the rearrangment of (176) to (177) occurs at ambient temperature, would suggest the highly strained cyclobutene may not be an intermediate because such ring–openings only occur at much higher temperatures.[112]

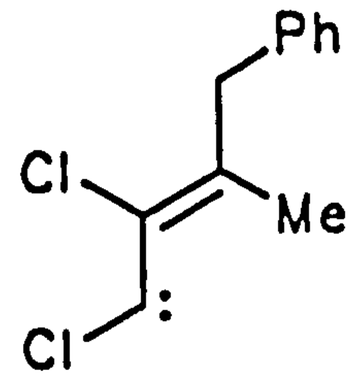
The formation of the diene (177) may therefore be interpreted in terms of selective ring opening of (176) to (180) rather than to the isomeric carbene (183); however, the benzylic C–H bond *cis* to the carbene centre in (180) would be expected to be more reactive than the C–H bonds of the methyl group which are *cis* to the carbene centre in (183), and selective trapping of one carbene in a rapid equilibrium between (176), (180) and (183) is an alternative explanation.



(182)

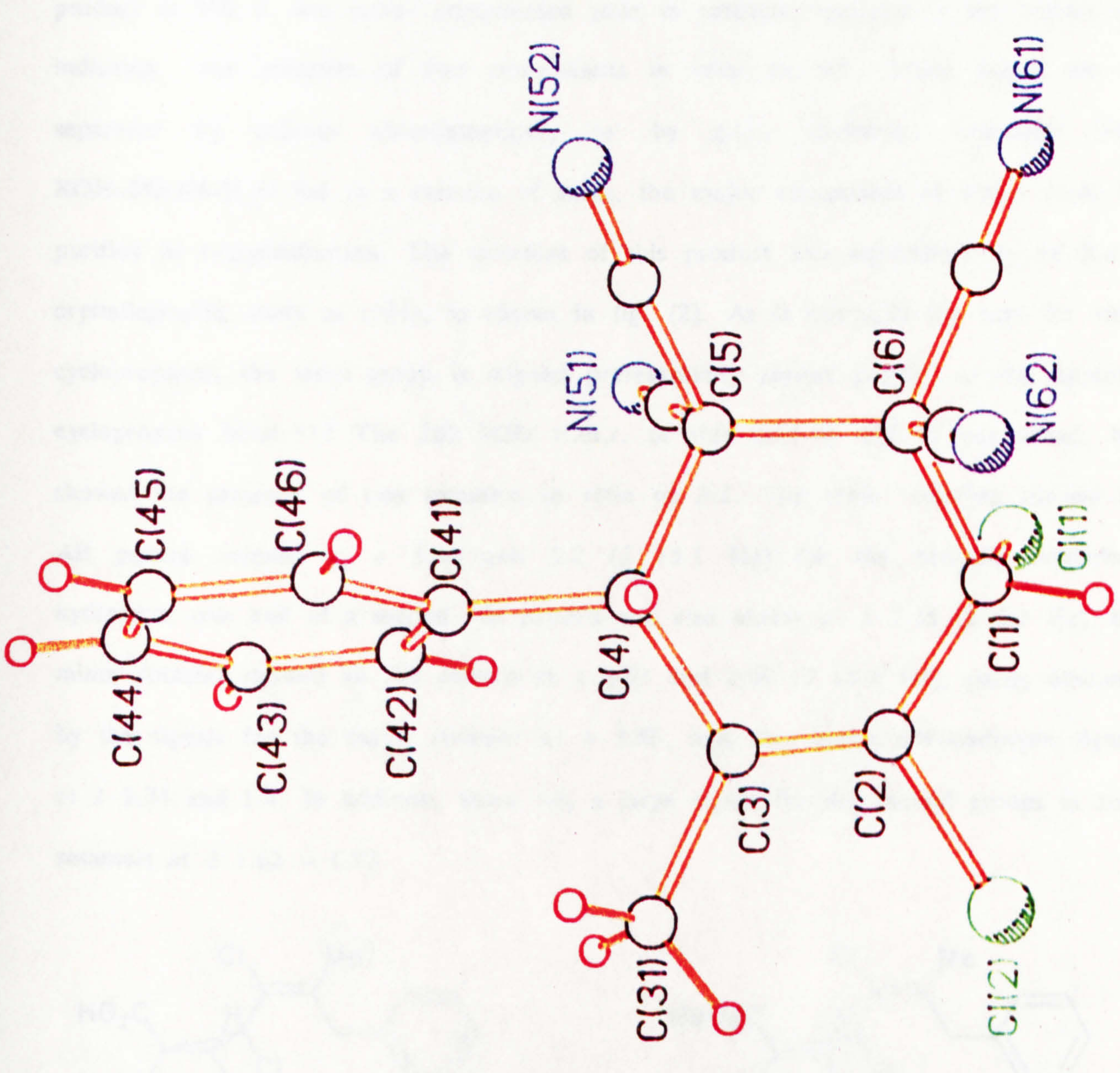


(176)

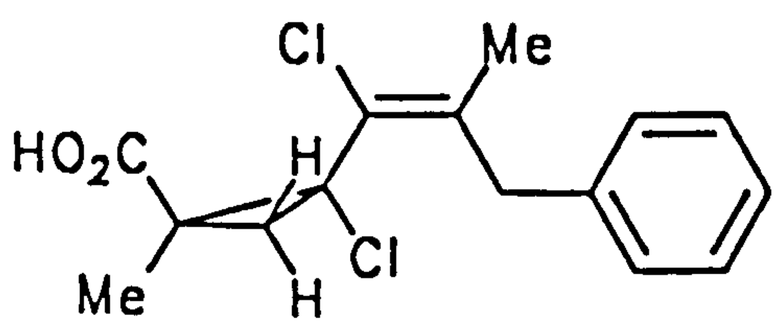


(183)

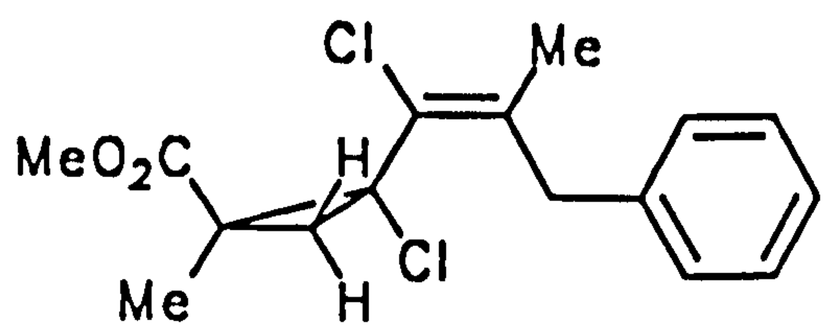
Fig.(1): Molecular structure of compound (178).



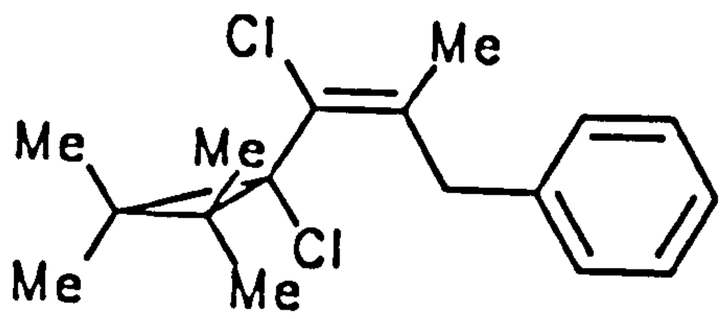
When the cyclopropene (176) was allowed to stand in ether at 20 ^{0}C in the presence of excess methyl methacrylate, complete reaction occured over a period of *ca.* 2 h. The product, which showed one peak by g.l.c., and one spot by TLC, gave the correct measured mass for $C_{16}H_{18}Cl_2O_2$, while the i.r. contained a sharp band at 1730 cm^{-1} assigned to a carbonyl group. The ^{1}H n.m.r. spectrum of the crude product at 300 K was rather complicated (due to restricted rotation – see below) but indicated the presence of two components in ratio ca 5:1. These could not be separated by column chromatography or by g.l.c. However, hydrolysis with KOH–MeOH–H_2O led to a mixture of acids, the major component of which could be purified by recrystallisation. The structure of this product was established by an X–ray crystallographic study as (184), as shown in fig. (2). As is normally the case for vinyl cyclopropanes, the vinyl group is aligned preferentially almost parallel to the opposite cyclopropane bond.[113] The 200 MHz n.m.r. of this acid at 295 K was broad, but showed the presence of two rotamers in ratio ca 3:2. The major rotamer showed an AB pattern centred at δ 3.86 and 3.7 (J 15.1 Hz) for the benzylic methylene hydrogens; one half of a second AB pattern was also visible at δ 2.45 (J 6.2 Hz); the minor rotamer showed an AB pattern at δ 3.93 and 3.09 (J 13.8 Hz), partly obscured by the signals for the major rotamer at δ 3.86, and two broad one–hydrogen signals at δ 2.34 and 1.4. In addition, there was a large signal for the methyl groups in both rotamers at δ 1.62 – 1.72.



(184)



(185)



(187)

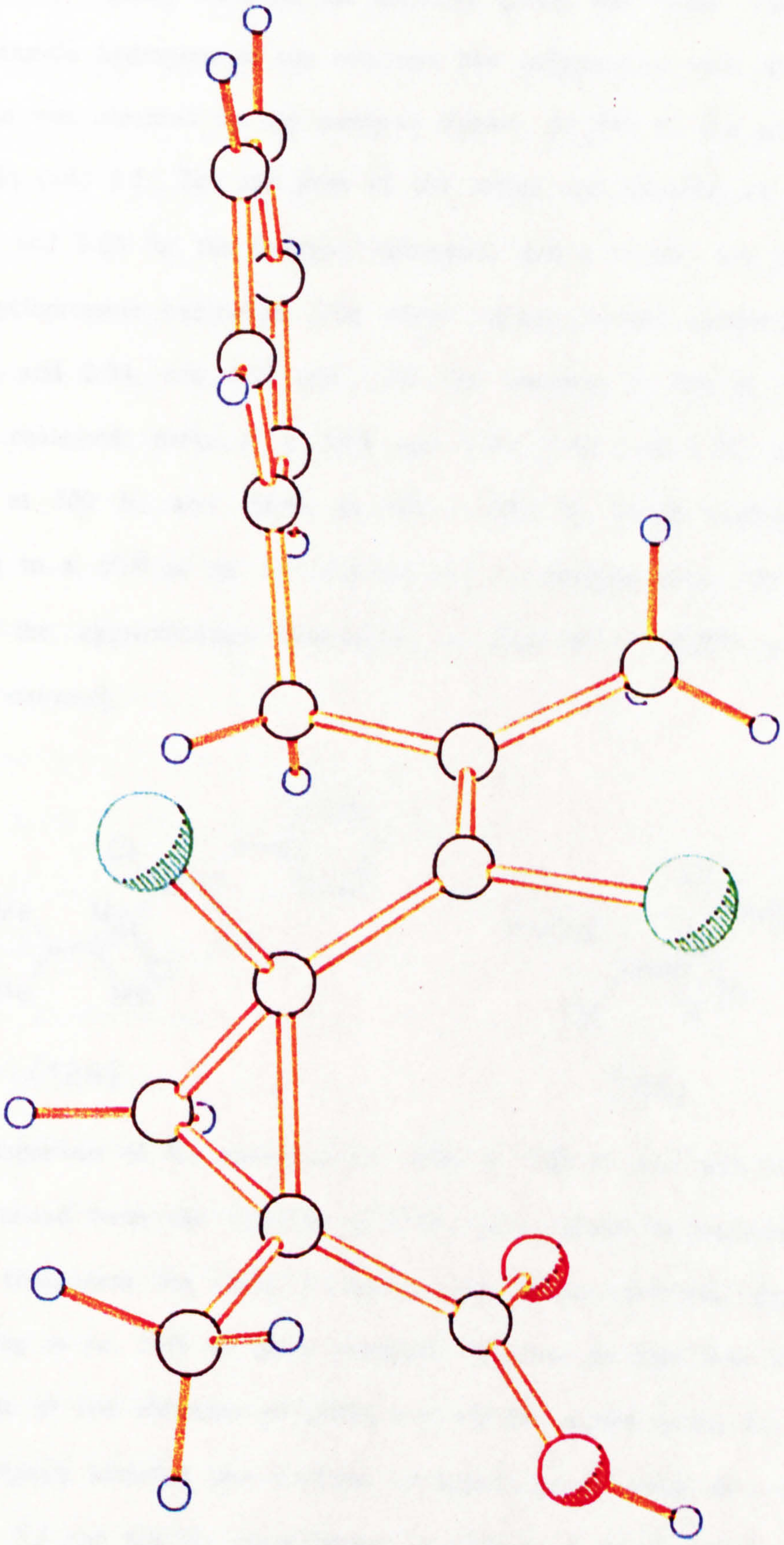
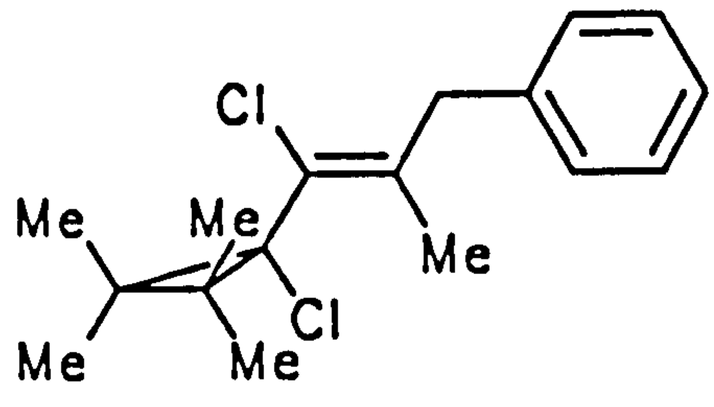
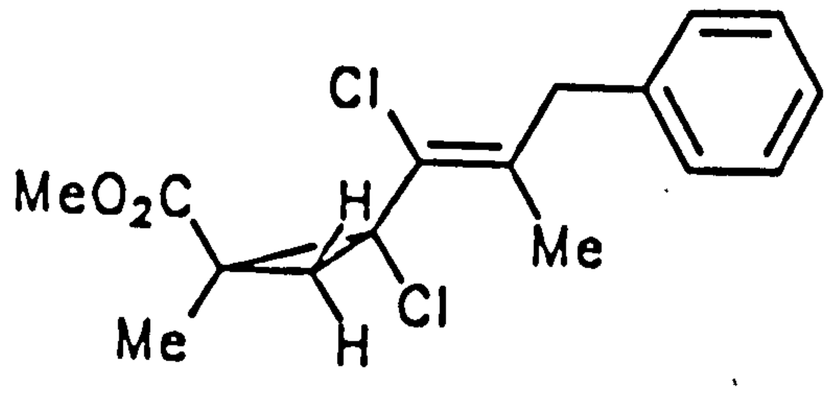


Fig.(2): Molecture structure of compound (184).

Re–esterification of (184) using diazomethane gave (185); the ^1H n.m.r. spectrum of this at 300 K was rather broad. At 330 K the spectrum simplified considerably, though some of the peaks were still broad. The C–methyls now appeared as two relatively sharp signals, although the methoxy group was broad. The two AB patterns for the benzylic hydrogens of the rotamers had collapsed to one, although one half of the pattern was obscured by the methoxy signals. At 240 K, the spectrum showed two rotamers in ratio 3:1. The spectrum of the major one included an AB double doublet at δ 3.98 and 3.63 for the benzylic hydrogens, and a second one at δ 2.42 and 1.55 for the cyclopropane hydrogens. The minor isomer showed corresponding AB patterns at δ 3.93 and 2.94, and 2.32 and 1.38. On warming to 280 K, the signals at 3.98 and 3.93 coalesced; those at δ 3.63 and 2.94, 2.42 and 2.32, and 1.55 and 1.38 coalesced at 300 K, and others at 300 – 330 K. These coalescence temperatures correspond to a $\Delta G^{\ddagger}$ of ca. 15 kcal/mol for the rotation about the exocyclic bond(s), by using the approximation developed by Gunther[114] [$\Delta G^{\ddagger} = 4.57\ T_c(9.97 + \log(T_c/\delta_\nu)$ cal/mol].



(188)

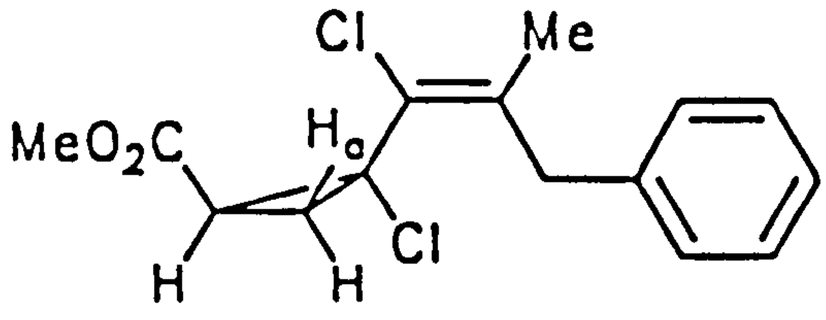


(186)

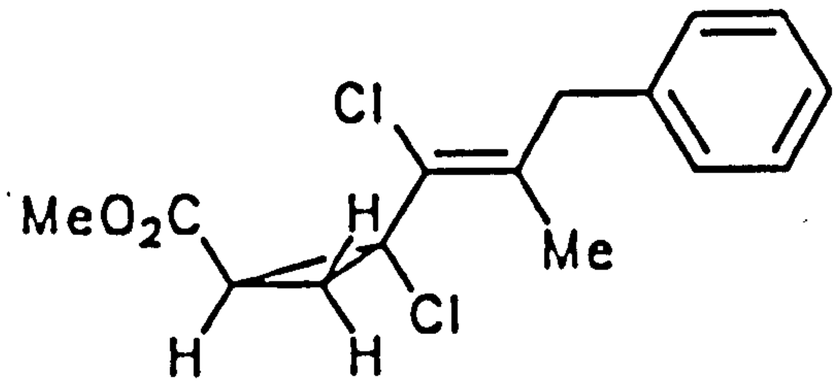
A comparison of the spectrum of (185) at 240 K with that for the mixture of isomers obtained from the reaction of (176) with methyl methacrylate confirmed that the major component was (185). However, some minor additional signals were present, corresponding to *ca.* 17% of other products. Because the spectrum was complicated by the presence of two rotamers of (185), not all the signals could be clearly seen. The additional signals included two doublets of approximately equal area centred at δ 2.35 and 2.3 (J 6.3 and 6.8 Hz respectively); in addition a doublet (J 6.8 Hz) appeared at

δ 1.33, while there were four singlets at δ 1.91, 1.68, 3.34, and 3.70, each integrating to three times the area of each of the doublets. A fourth doublet (J 16 Hz), integrating for one hydrogen, was also present at δ 3.3. When the temperature was increased to 300 K and then further to 330 K the two doublets coalesced to a single doublet; other signals also changed, but became hidden in the signals for the major isomer. Nonetheless, these result are best explained in terms of the presence of two rotamers of the minor isomer, with a similar rotation barrier to that for the major isomer. This could be isomeric with (185), either in the geometry of the cyclopropane or of the vinyl–group, or indeed of both; it is, however, characterised as (186) on the following basis. Treatment of (176) with 2,3–dimethylbut–2–ene also led to one major and one minor isomer, again in ratio *ca.* 5:1. Each of these gave ^{1}H n.m.r. spectra consistent with restricted rotation about the exocyclic bond and a preferred geometry with the vinyl–group not bisecting the cyclopropane. The major isomer, characterised as (187) by comparison with (185), showed five distinct methyl–groups, a phenyl–group, and a widely separated pair of doublets for the methylene group at δ 3.89 and 3.18 (J 14.3 Hz). The minor isomer showed a similar spectrum, though in this case, the doublets were much closer in chemical shift, at δ 3.67 and 3.54 (J 14.4 Hz); this isomer was characterised as (188). The stereochemistry was established by n.O.e. experiments; irradiation at δ 1.18 showed an n.O.e enhancement in the benzylic hydrogens of the major isomer, and a smaller increase in the signal for the olefinic methyl group at δ 1.67. In contrast, irradiation of a methyl signal at δ 1.08 arising from the minor isomer caused an enhancement in the olefinic methyl at δ 1.74, but caused no effect on the benzylic hydrogen signals of this isomer. Thus both carbene isomers, (180) and (183), are trapped by reaction of (176) with alkene in ratio 5:1; because of this, the minor isomer from the reaction of (176) with methyl methacrylate is characterised as (186). Treatment of (176) with methyl acrylate for 12 h at 20 ^{0}C led to a major single product (189). The ^{1}H n.m.r. at 300 MHz and 230 K was consistent with the presence of two rotamers in ratio ca.

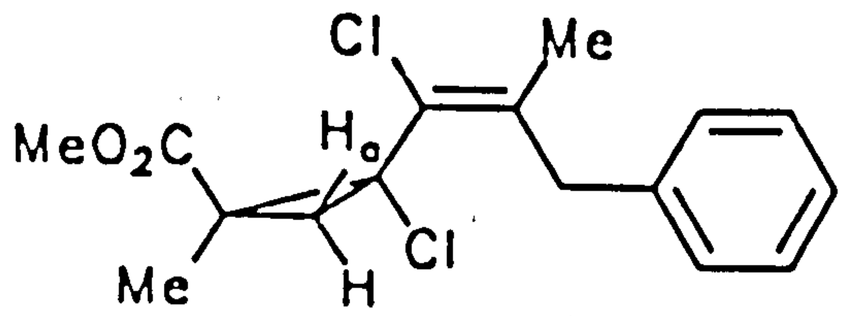
5:1. There were a number of other minor peaks at δ 3.68 (s), 3.6 (s), 3.5 (s), 3.43 (d, J ca. 15.0 Hz) and 1.7 (s); these could be interpreted in terms of a stereoisomeric minor product (190). The coupling constants for a signal at δ 2.46 in the major rotamer are typical of geminal and *trans*–coupling in cyclopropanes. This signal is therefore assigned to H_a. The chemical shift is then close to those of the doublets at δ 2.42 and 2.32 in the spectrum (185), which presumably result from the corresponding hydrogen; hydrogens *cis*– to ester groups in cyclopropanes are shifted down field.[100]



(189)

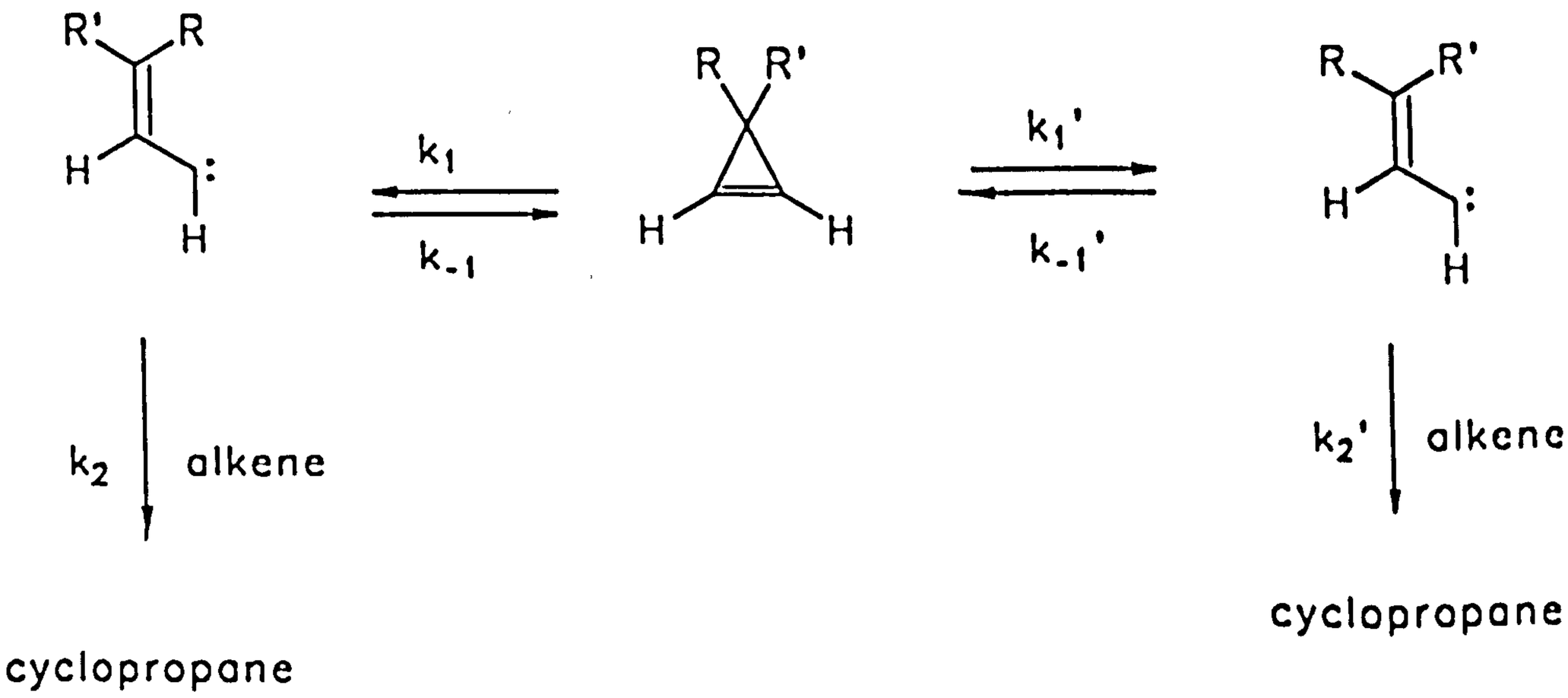


(190)



(185)

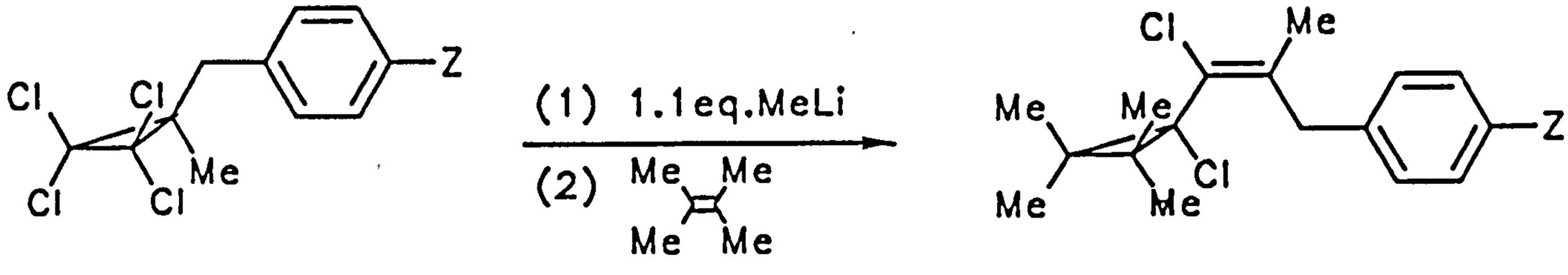
The increase in the rate of reaction of (176) in the presence of an alkene compared to its decomposition to (177) in the absence of the alkene supports the reversibility of the ring opening.



The selective trapping of one of the two carbenes may reflect differences in any one of the pairs of rates K_1/K_1', K_{-1}/K_{-1}', or K_2/K_2', or indeed in more than one of the rates. It is not clear why there should be a marked increase in K_2 relative to K_2'; the proximity of the phenyl group to the carbene centre in (180) may lead to a stabilizing interaction reducing K_{-1} relative to K_{-1}', but this same effect might be expected to reduce K_2 relative to K_2'.

The addition of vinyl carbenes to α,β–unsaturated esters has been shown in certain cases to lead to products with alkene and ester groups *cis*–related,[101] although the reaction appears to be highly dependent on substituents and in other cases leads predominantly to *trans*–products.[115] Nonetheless, the reaction leading to (185) does represent a highly stereocontrolled trapping of a carbene.

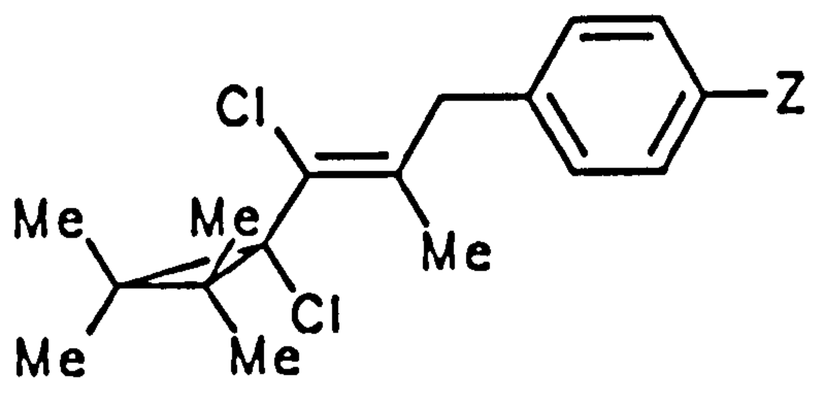
In the same way, when the cyclopropanes (172, Z=CH_3, OCH_3, CF_3) are allowed to react with 1.1 equiv. of methyl–lithium in the presence of 2,3–dimethylbut–2–ene for 2 h, the crude product was a mixture of cyclopropenes in ratio 5:1 in each case. Chromatography afforded the product as a colourless oil with no change in the isomer ratio. The major isomer in each case was characterised as (191) by comparison with (187), and the minor one as (192). The ^1H n.m.r. spectrum for the major isomer of the cyclopropane (191, Z = OCH_3) showed two doublets corresponding to the geminally coupled methylene protons at δ 3.82 and 3.11 with a coupling constant of 14.5 Hz and a singlet for the methoxy group at δ 3.7, together with a narrow doublet for the olefinic methyl at δ 1.64 with a coupling constant of 0.7 Hz, and four singlets assigned to the cyclopropropyl methyl substituents at δ 1.26, 1.22, 1.2, 1.16. The minor isomer showed two doublets for the methylene protons at δ 3.54 and 3.45 with a coupling constant of 14 Hz, together with the two singlets at δ 1.72 and 1.06, the remaining signals being obscured by those of the major isomer.



(172, Z= CH_3, OCH_3, CF_3)

(191)

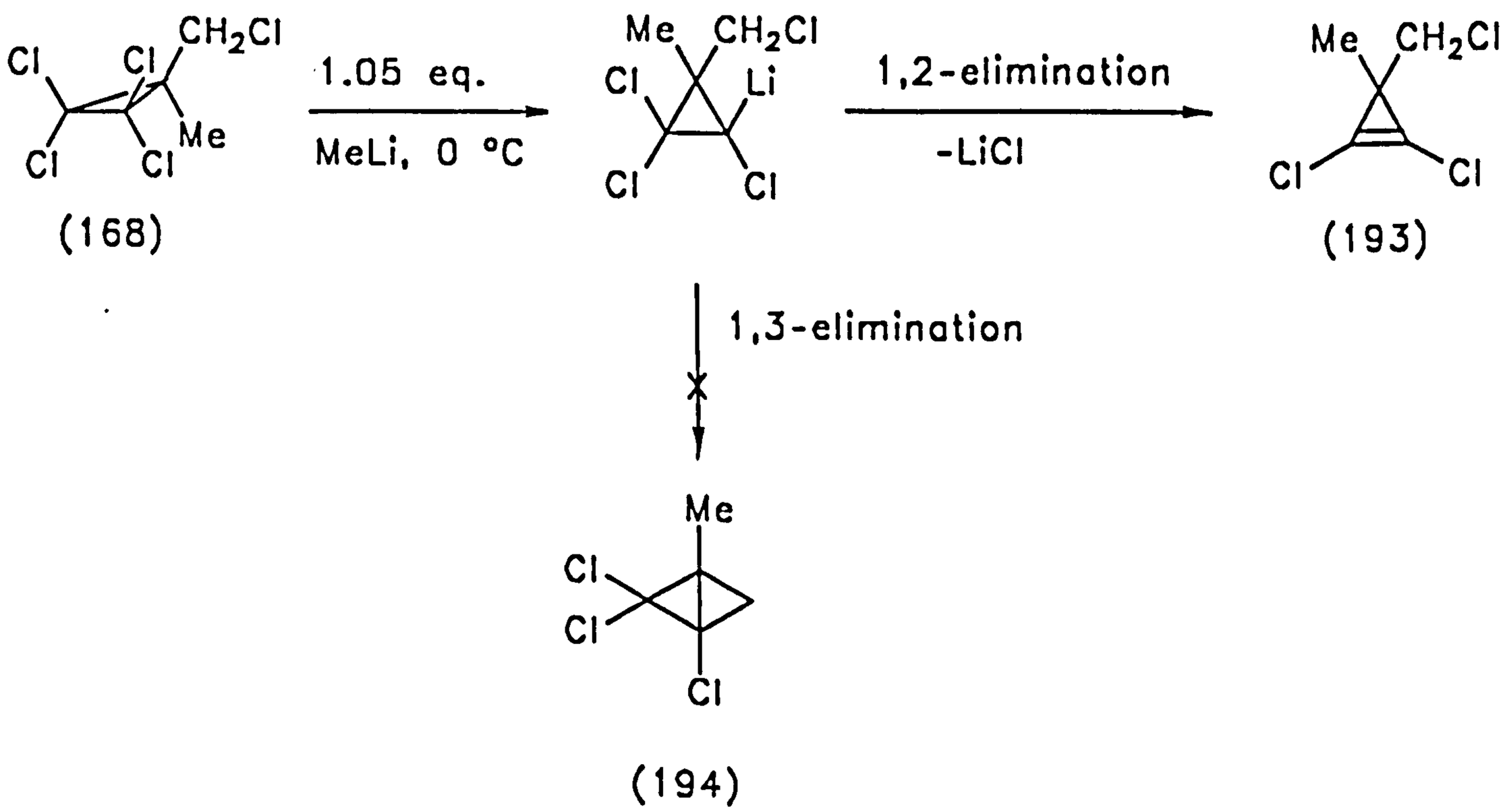
+



(192)

2.3.3: REACTION OF 3-METHYL-3-SUBSTITUTED TETRACHLOROCYCLO-PROPANES WITH METHYL LITHIUM.

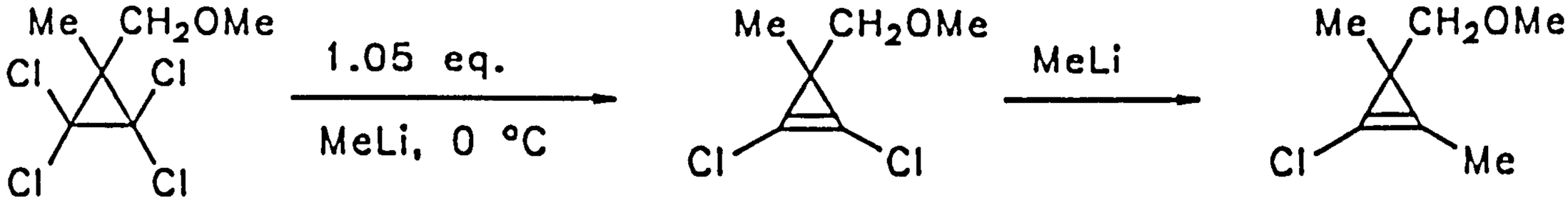
Treatment of the pentachloride (168) with a slight excess of methyl-lithium for 30 min at 0 °C gave the cyclopropene (193) in high yield (82%);[116] this exhibited two singlets in the proton n.m.r, at δ 3.6 (2H), and 1.4 (3H) in the ratio 2:3, while the ^{13}C n.m.r., showed a quaternary alkene carbon at δ 113.8 in addition to a methylene carbon at δ 51.6, a methyl carbon at δ 19.4 and a second quaternary carbon at δ 41.9. This product arises by lithium–chlorine exchange at one of the gem–dichlorides, followed by or concerted with a 1,2–elimination of lithium chloride. This process is apparently preferred over the alternative 1,3–elimination,[117] which would lead to a 1–chlorobicyclo[1.1.0]butane (194).



(168) (193) (194)

The reaction of (170, R = Me) with methyl-lithium was more difficult to control because the cyclopropene (195) reacted relatively rapidly with an excess of methyl-lithium to produce (196), apparently by addition of methyl-lithium facilated by

co–coordination of the lithium to the ether oxygen, followed by elimination of chloride ion. Careful addition of just over one equivalent of methyl–lithium to (170, R = Mc) provided the purest sample of (195), through this still contained a small amount of (196).



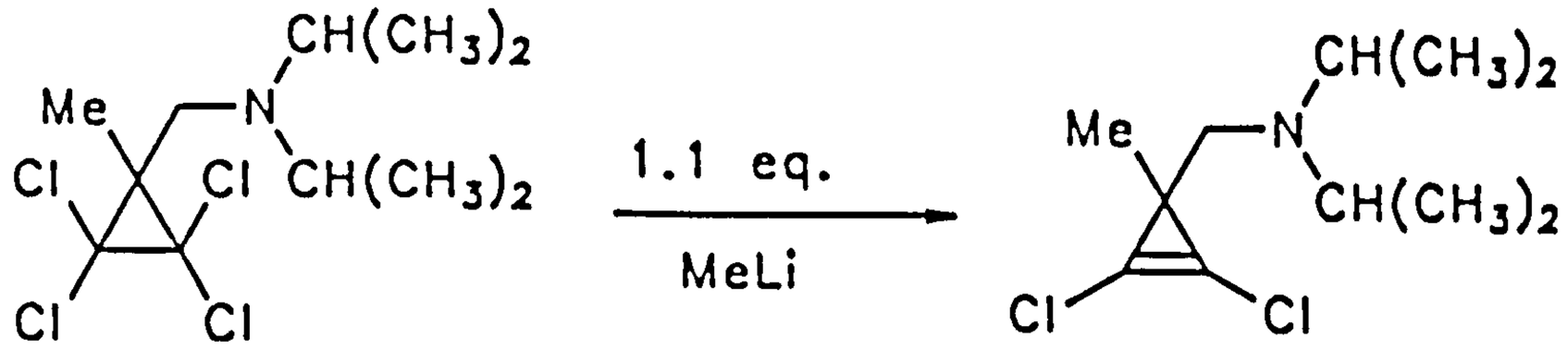
(170)
R=Me

(195)

(196)

Addition of two equivalents of methyl–lithium to (170, R = Me) afforded (196) in 40% yield, which exhibited four singlets in the ^1H n.m.r. spectrum at δ 3.39 (2H), 3.31 (3H, $-OCH_3$), 2.02 (3H), and 1.17 (3H), while the ^{13}C spectrum showed seven signals, including three primary carbons at δ 58.5, 19.4 and 8.3 assigned to the three methyl groups, and quaternary carbons at δ 117.6, 115.9 and 33.3, in addition to a triplet at δ 79.4 for the methylene carbon.

Treatment of the cyclopropane (173) with 1.1 equivalent of methyl–lithium at 0 ^0C for 30 min followed by quenching with water at –40 ^0C and evaporation of the ether at below 0 ^0C, led to the crude cyclopropene (197) in 82% yield. The ^1H n.m.r. measured at –40 ^0C was in accordance with the proposed structure.

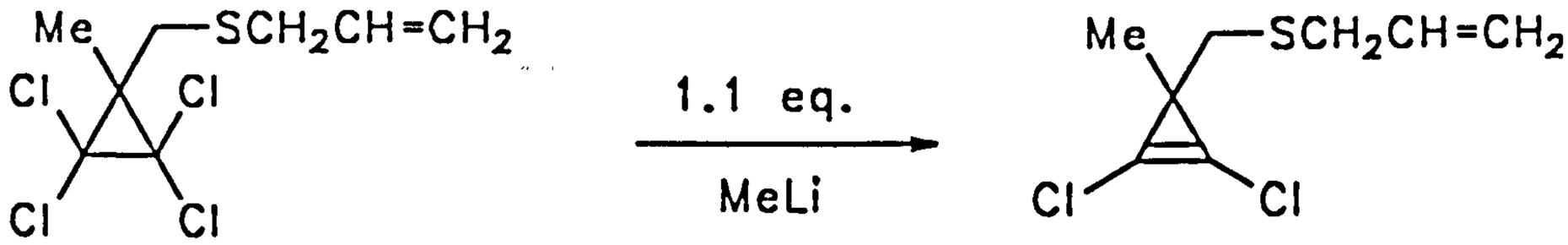


(173)

(197)

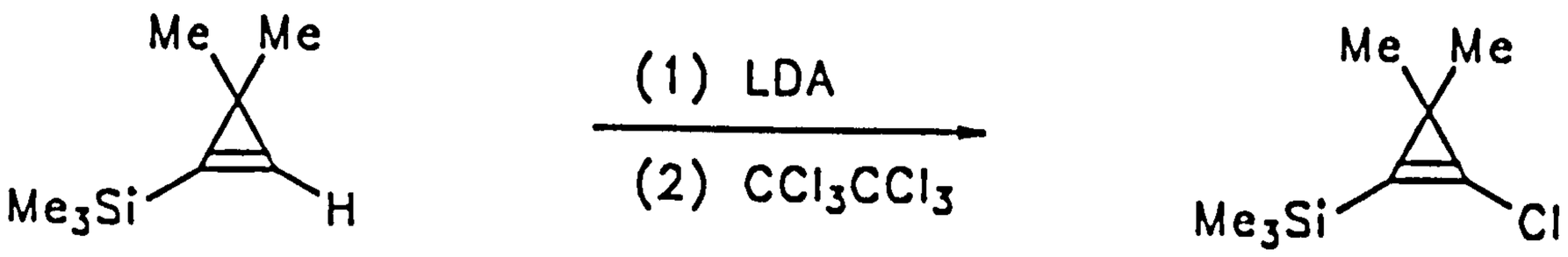
Treatment of (174) with 1.1 equivalent of methyl–lithium for 30 min at 0 ^0C, followed by quenching with water at –40 ^0C and removal of the solvent at low temperature led to the crude cyclopropene (198), which was pure by 300 MHz n.m.r

at –40 °C.



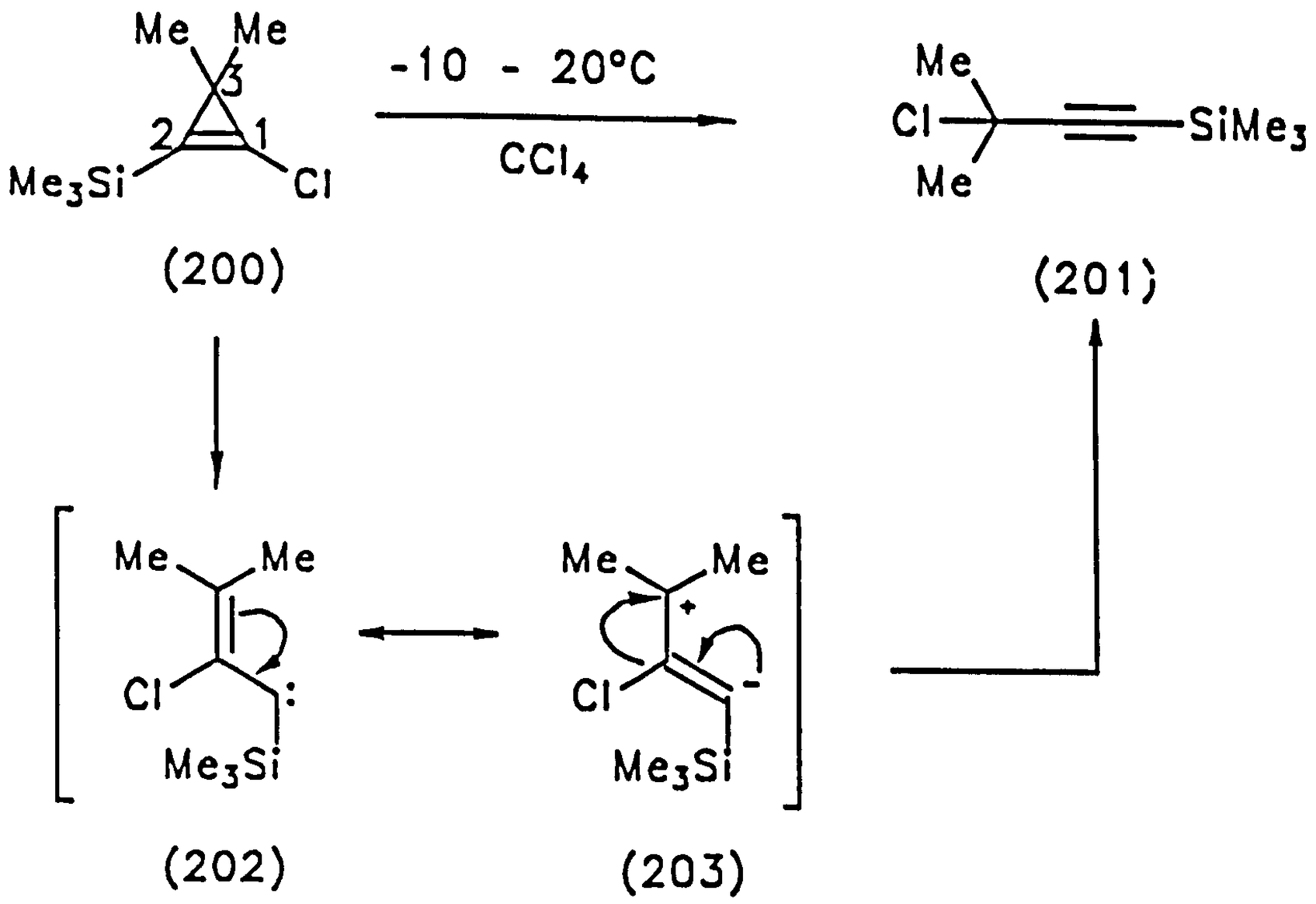
(174) (198)

The cyclopropene (200) was prepared by a different method. Reaction of 3,3–dimethyl–1–trimethylsilylcyclopropene (199) with lithium di–isopropylamide followed by quenching with hexachloroethane gave (200) in 50% yield. The ^{1}H n.m.r. spectrum contained two singlets at δ 1.2 (6H) and 0.14 (9H), while the ^{13}C spectrum showed five signals including two in the olefinic region and two at δ 31.3 and 26.8, together with the trimethylsilyl signal at δ –1.034.

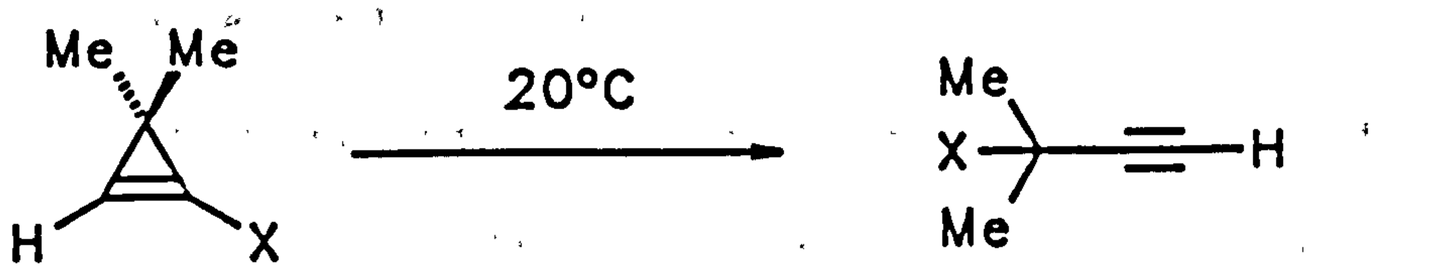


(199) (200)

The cyclopropene (200) was found to be unstable even at –10 °C, and it rearranged readily as the neat liquid or in solution, giving the alkyne (201);[49] this compound apparently arose by cleavage of the C_2–C_3 cyclopropene single bond giving the vinyl carbene (202) followed by migration of the chloride anion from the canonical structure (203).

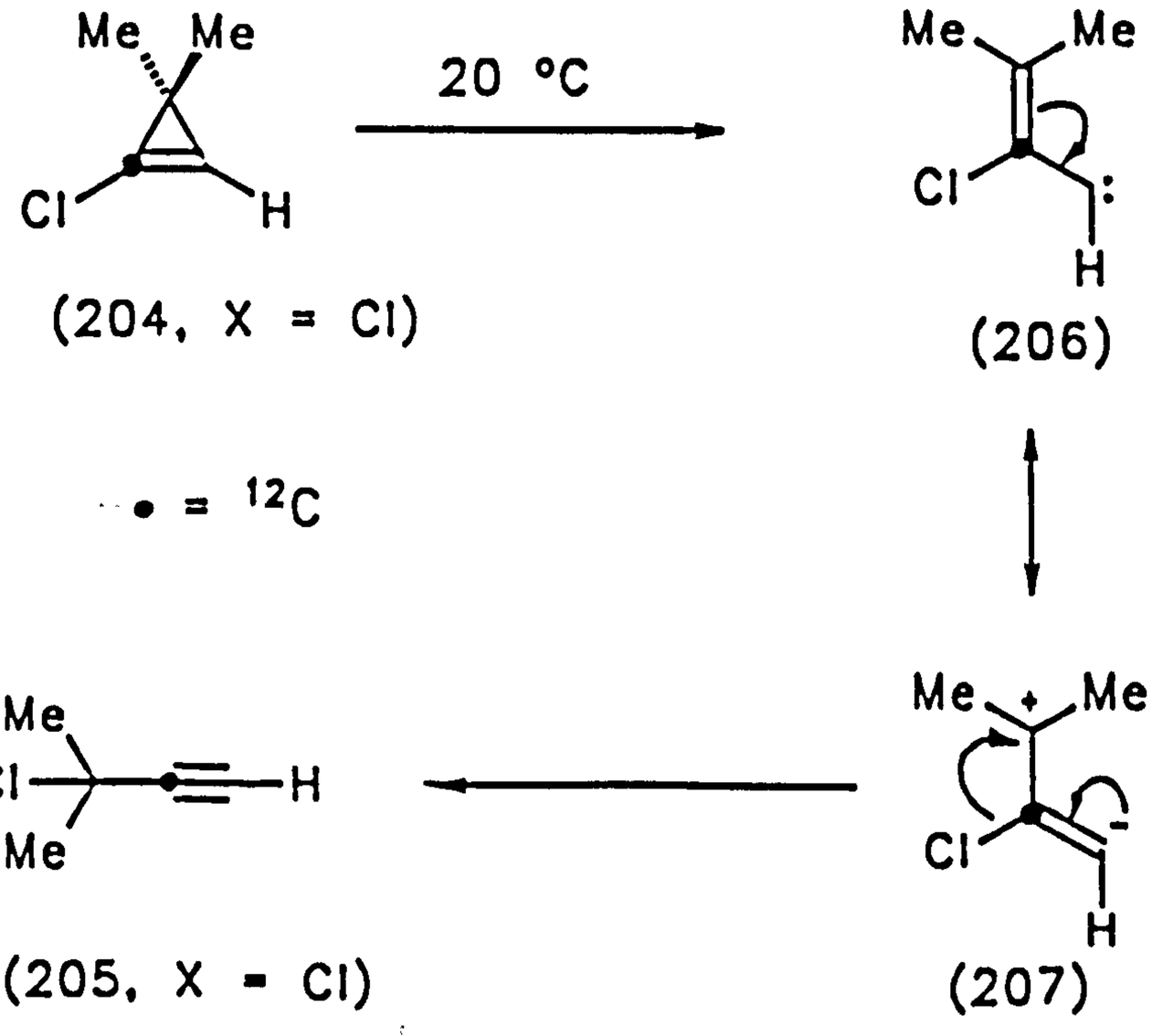


However, the cyclopropene (200) was more stable in CCl_4, and changed slowly to alkyne after one week at room temperature. The cyclopropenes (204, X = Cl, Br) have also been found to be unstable at ambient temperature, rearranging readily as neat liquids or in solution, giving the halogenated alkynes (205, X = Cl, Br).[49]



(204, X = Cl, Br) (205, X = Cl, Br)

The products also apparently arose through cleavage bond of the C_2–C_3 cyclopropene single bond giving the vinyl carbene (206), followed by migration of the chloride anion from the canonical structure (207) resulting in the formation of (205); a labelled cyclopropene was used in order to probe the mechanism of these conversions:



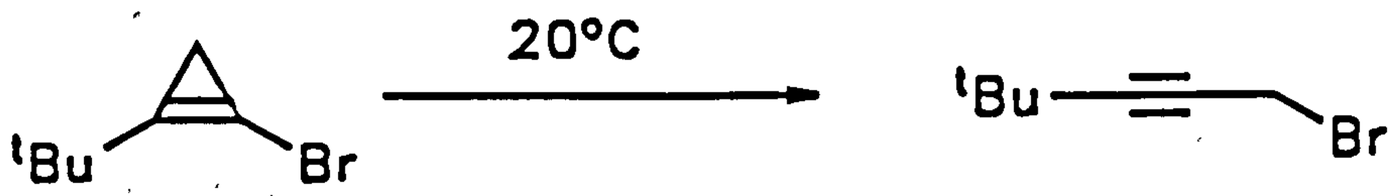
(204, X = Cl) (206)

• = ^{12}C

(205, X = Cl) (207)

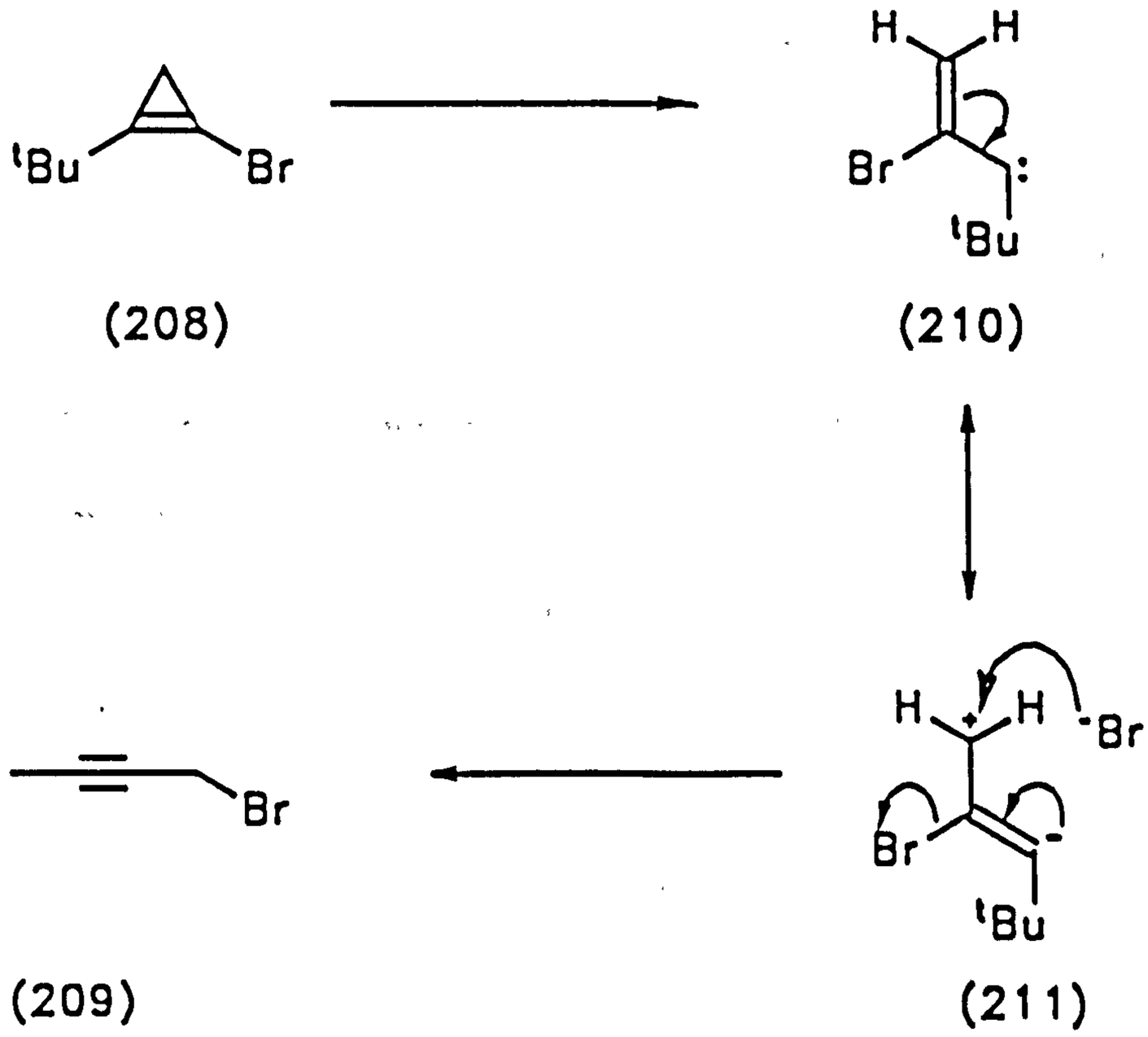
When crude cyclopropene (208) was allowed to stand as a neat liquid or in CCl_4, the alkyne (209) was obtained in quantitative yield. The i.r. spectrum of (209)

contained a sharp band at 2233 cm^{-1} assigned to the alkyne, while the ^1H n.m.r. spectrum showed the expected two singlets at δ 3.78 (2H), 1.18 (9H).



(208) (209)

However, a pure distilled sample remained unchanged for a long period; this may mean that the crude products may contain small traces of halide ion from the dehalogenation process. The alkyne (209) may be derived by ring-opening of the cyclopropene to the carbene (210) followed by attack of the bromide ion in an intermolecular manner rather than the intramolecular migration of the bromide in the canonical structure (211).

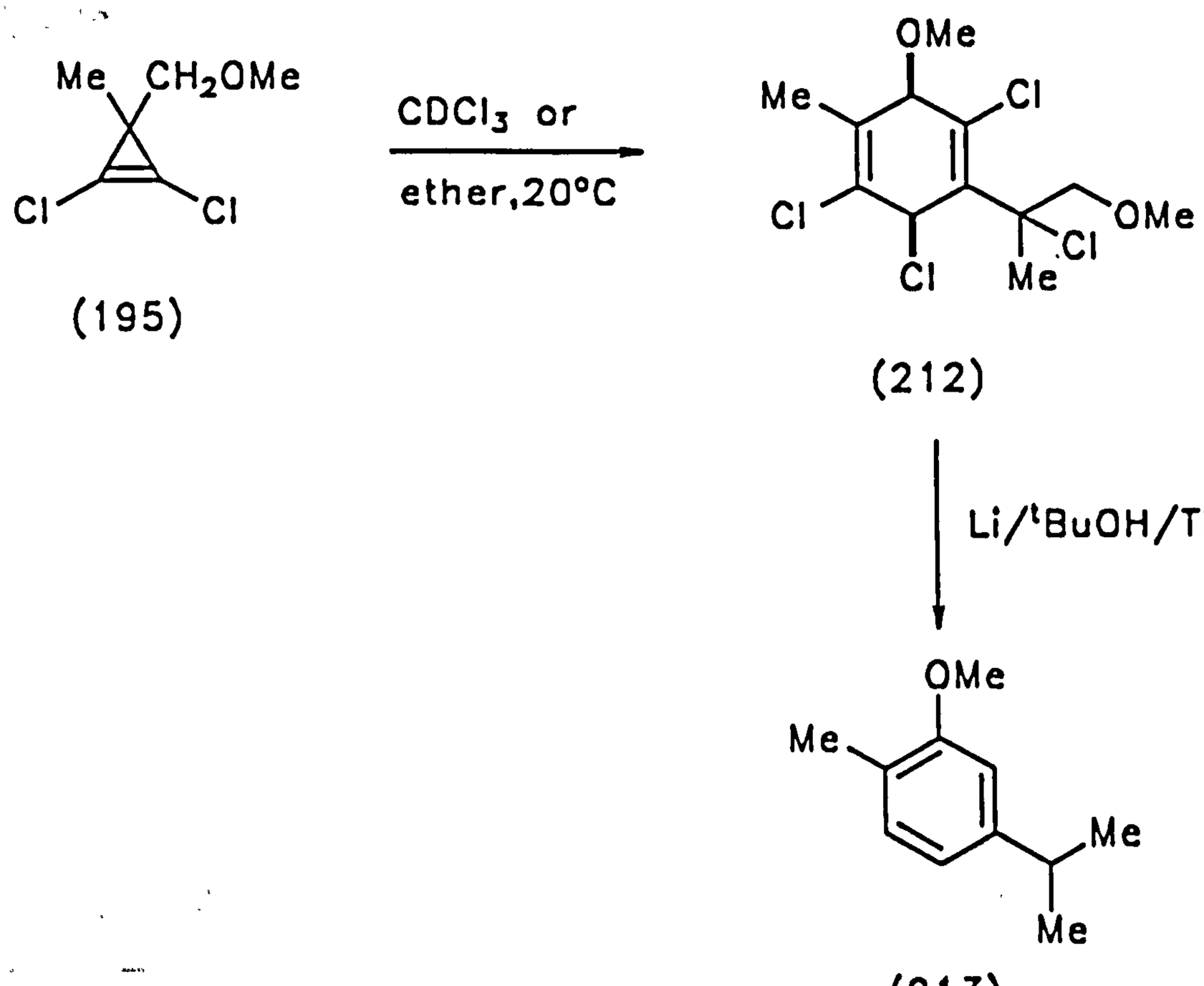


(208) (210) (209) (211)

Moreover, the alkyne (209) was also obtained when the pure cyclopropene was treated with a catalytic amount of LiBr in CH_2Cl_2 for four days at room temperature.

The cyclopropene (193) was relatively stable in ether or deuterochloroform solution at 20 °C, surviving unchanged for ca. 12 h. However, when the cyclopropene (195)

was allowed to stand for 48 h at 20 °C in deuterochloroform a dimer (212) was obtained in 61% yield. This was also obtained when (195) allowed to stand for 10 h in ether at 20 °C.



(195)

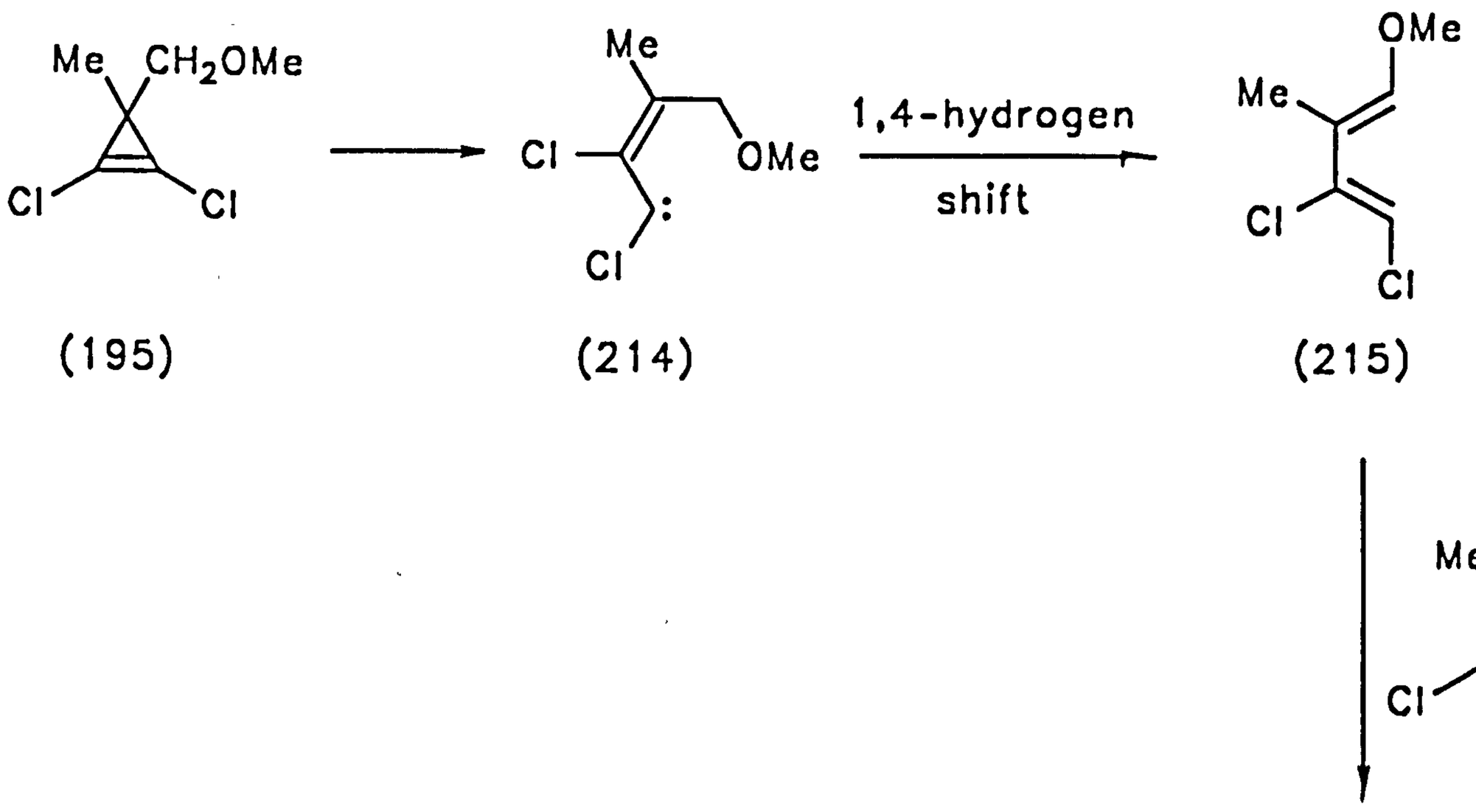
(212)

(213)

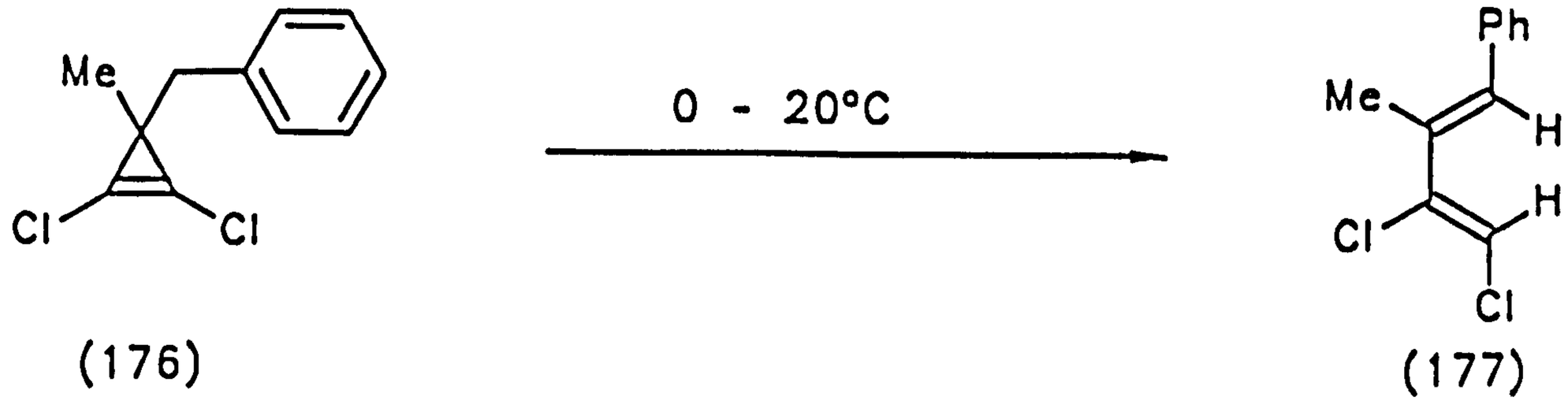
Compound (212) gave an accurate mass measurement for $C_{12}H_{16}Cl_4O_2$, while the ^1H n.m.r. spectrum showed two single–hydrogen singlets at δ 5.44 and 4.82, a two hydrogen singlet at δ 3.52, two methoxy groups at δ 3.4 and 3.3 together with two methyl group singlets at δ 2.02 and 1.17. The ^{13}C spectrum showed twelve signals, including four singlets in the olefinic region, four methyl groups (including two in the methoxy region), a CH_2–group adjacent to oxygen and two tertiary carbons at δ 80.1 and 63.7. The overall structure was confirmed by reaction of (212) with lithium–^{t}butanol–THF to give the anisole derivative (213). The spectroscopic data for (213) was identical to those reported for this compound, carvacrol methylether.[118]

The formation of (212) may be explained in terms of an initial ring–opening of the cyclopropene (195) to the carbene (214) followed by a formal 1,4–hydrogen shift[111] to give the butadiene (215); Diels–Alder addition to unreacted starting material

(195), could then lead to (216), which could then undergo loss of chloride ion to produce (217) followed by addition of chloride to give the observed product (212).

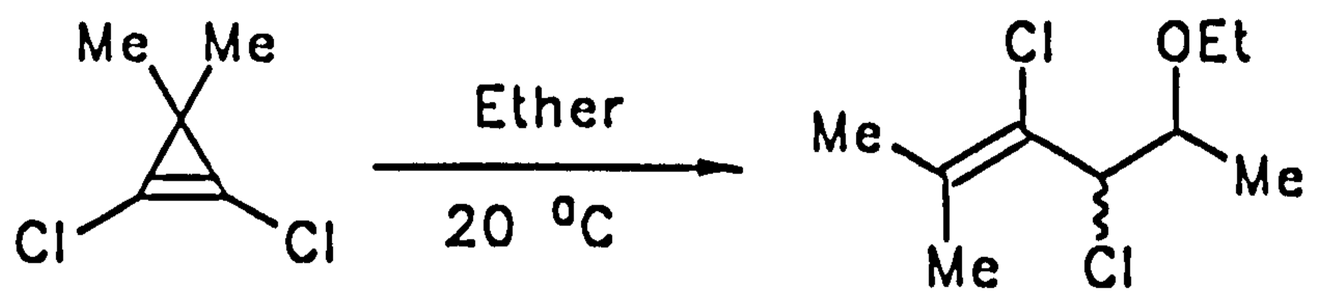


The stereochemistry, of (212) is uncertain both in respect to the methoxy and chlorine substitutents in the six–membered ring and the relative configuration of the side chain; however, the cyclopropene (176) has been shown previously (2.3.2) to rearrange to E, Z–1,2–dichloro–3–methyl–4–phenylbuta–1,3–diene (177) when allowed to stand at ambient temperature.[110]

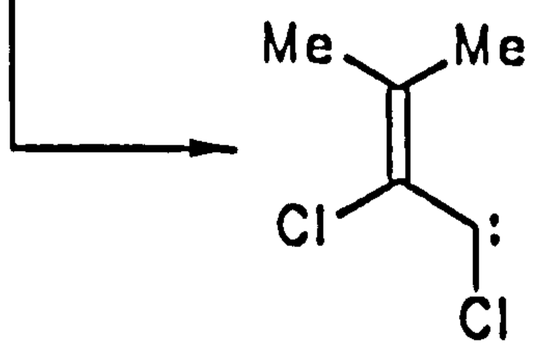


It seems likely therefore that (215) has similar stereochemistry, and that Diels–Alder addition leads to the cyclohexadiene with the methoxy and chlorine substituents *cis*–related. The selective loss of only one of the cyclopropyl chlorines in the final step presumably reflects detailed steric interactions in the transition state for cyclopropyl–allyl rearrangment. The intermediate butadiene (215) could not be trapped by addition of either tetracyanoethene or dimethyl acetylenedicarboxylate, but instead underwent rapid reaction with cyclopropene to give (212).

In contrast, when the cyclopropene (154) was allowed to stand in diethyl ether for 18 h at 20 °C it gave a 1:1 mixture of diastereoisomers of (218).[104] This compound is derived from the insertion of the carbene (155) into the C–H bond of ether α– to oxygen.



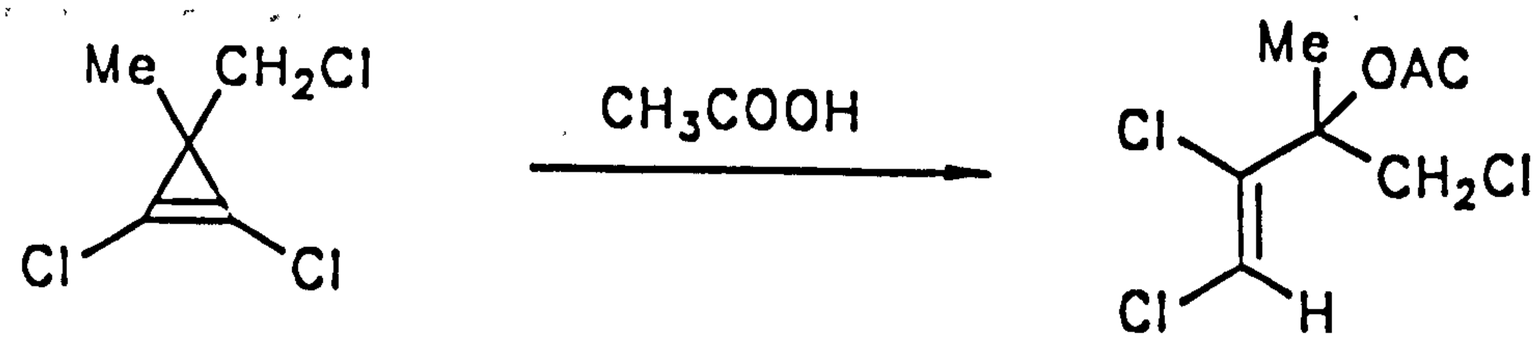
(154) (218)



(155)

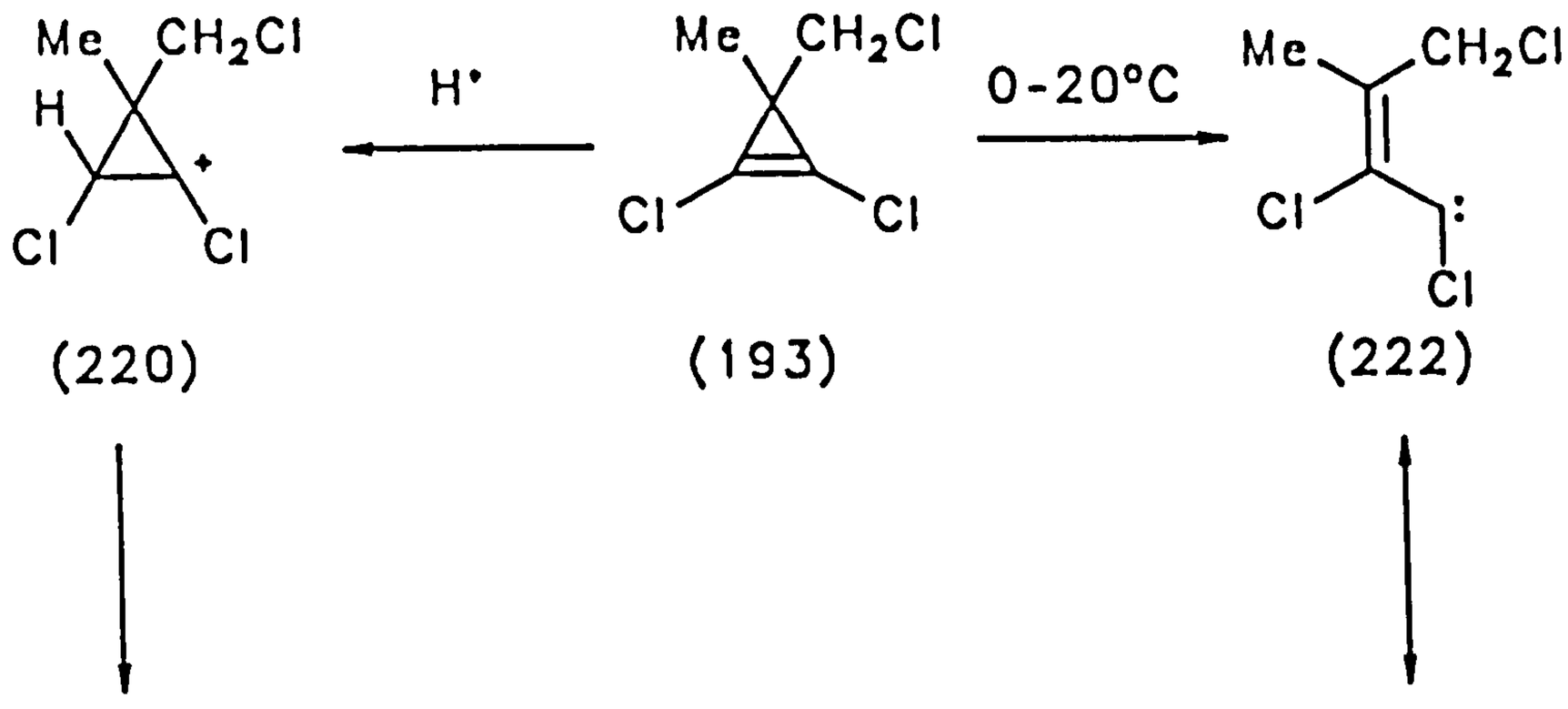
From these results we could conclude that the methoxymethyl group in (214) is more reactive towards an intramolecular reaction than the methyl group in (155).

Treatment of (193) with acetic acid gave the acetoxy compound (219) in 67% yield.



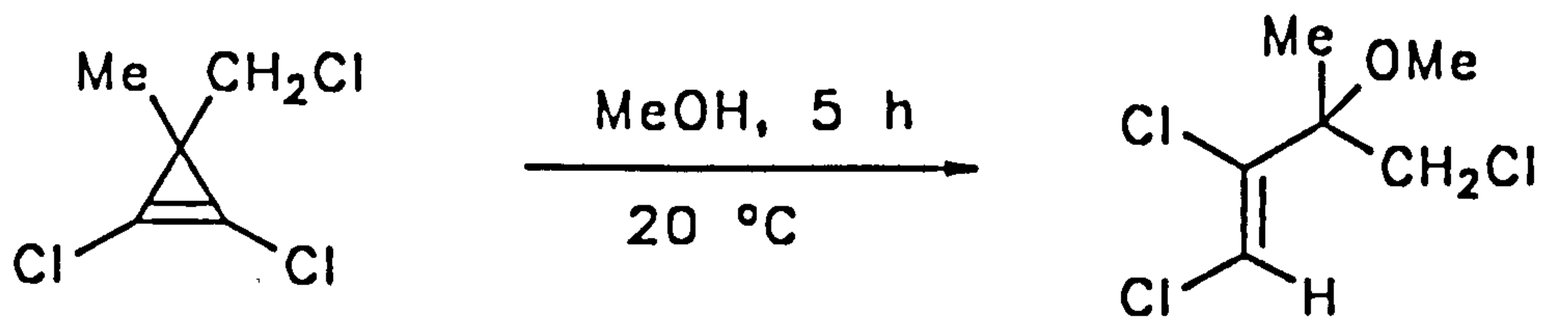
(193) (219)

This may arise either by protonation of the cyclopropene to give the cyclopropyl cation (220) followed by ring opening to give the allylic cation (221) or the reaction could involve trapping of the dipolar form (223) of the carbene (222), i.e. by proton abstraction from the solvent to give the allylic cation (221), which is then trapped by CH_3COO^- to give (219).



No reaction occurred when (2,3,3-trimethylcyclopropen-1-yl)ethanol was stirred with acetic acid at 20 °C for two days, i.e., in the case of (193) the carbene route may be more likely.

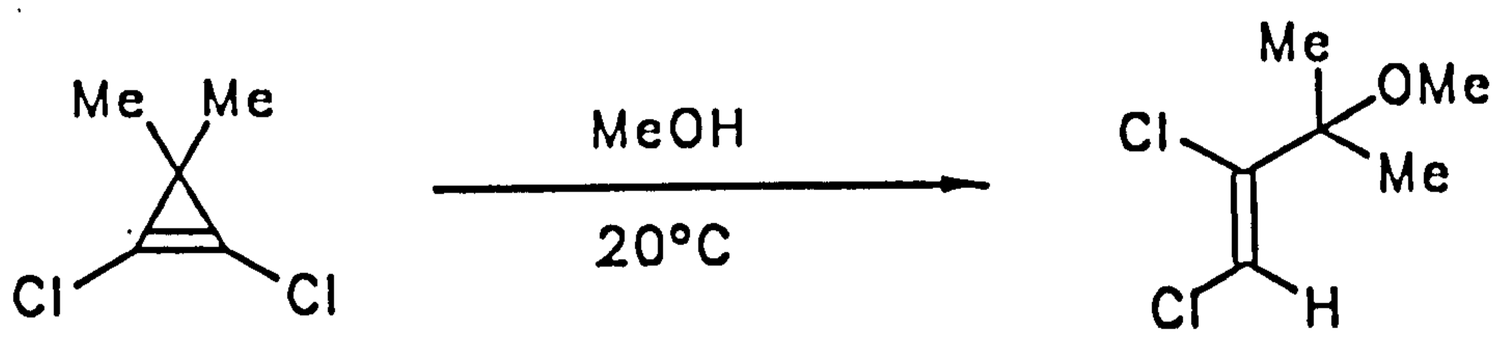
Moreover, the cyclopropene (193) also decomposed when allowed to stand in methanol for 5 h and a major product, the ether (224) was obtained.



(193) (224)

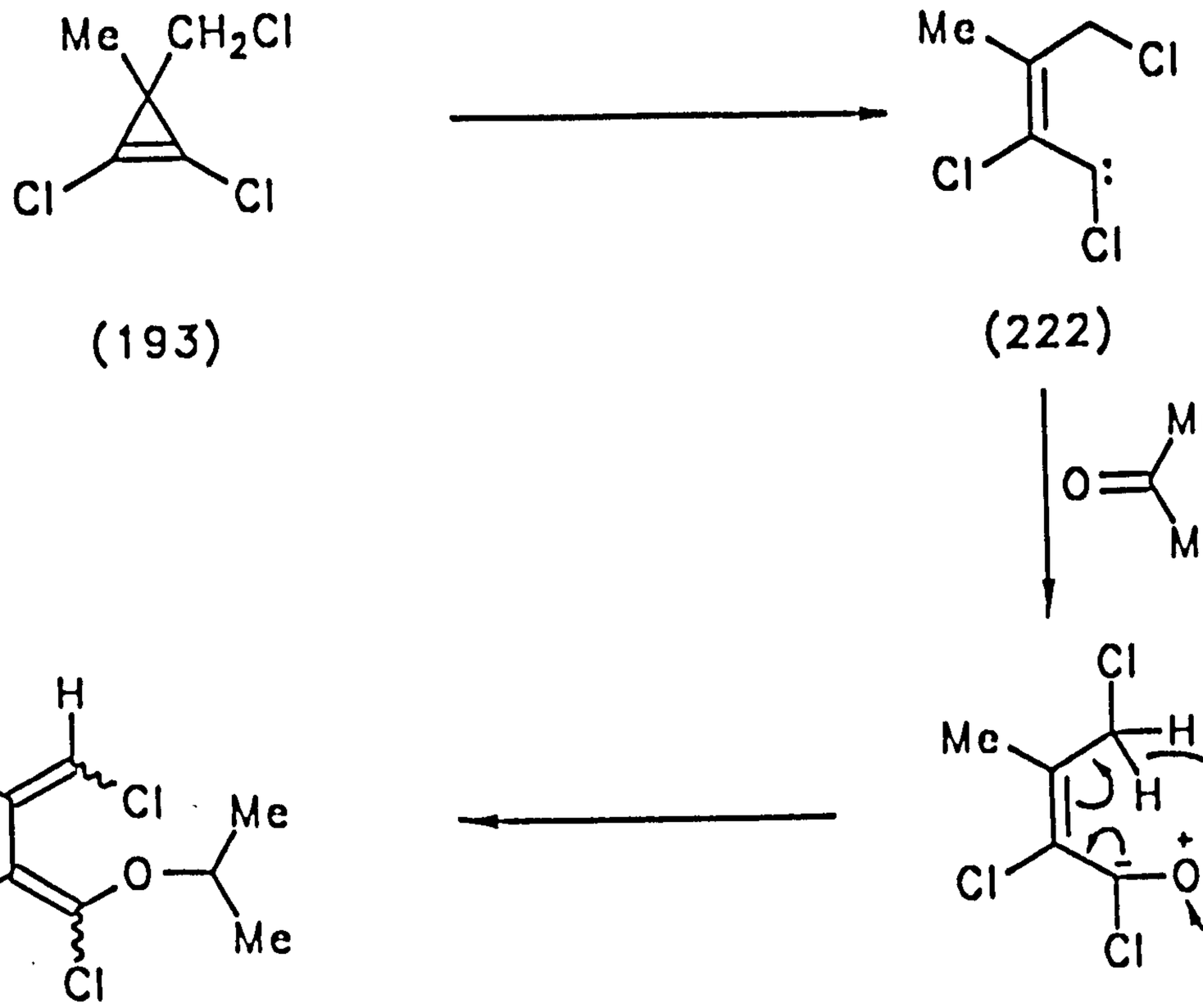
The initial reaction once again could involve trapping of the dipolar form of the carbene i.e. (223), by proton abstraction from the solvent to give an allylic cation followed by methanolysis.

Whatever the mechanism, the stereochemistry of (219) and (224) was assigned as Z– by analogy with the corresponding reaction of (154) with methanol to give (225).[104]



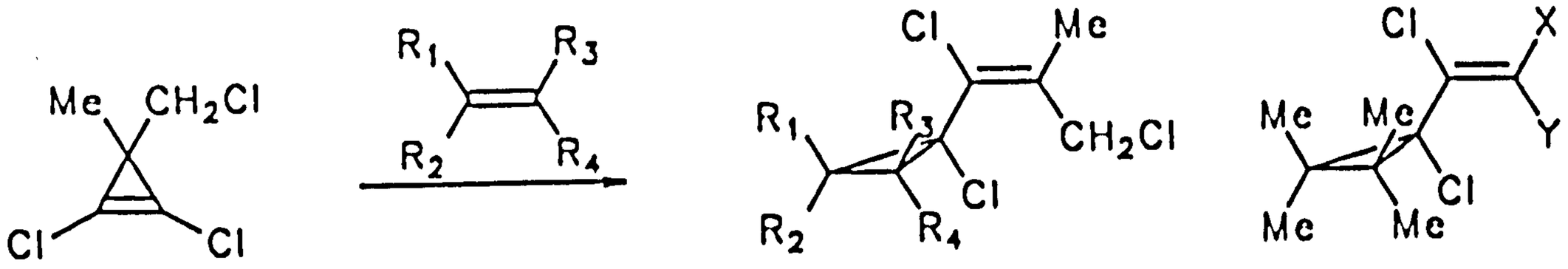
(154) (225)

When the cyclopropene (193) was allowed to stand in acetone an alternative process occurred, leading to the diene (226) of unknown stereochemistry in moderate yield. The diene may arise by ring–opening of the cyclopropene (193) to the carbene (222), which is trapped by the oxygen of the acetone, followed by an intramolecular shift to give the final product.



The diene (226) showed the expected seven signals in the ^{13}C spectrum, including four signals in the olefinic region at δ 141.7, 133.9, 118.24, 113.6.

As stated above, a solution of (193) in ether or deuterochloroform remained largely unchanged on standing for 10h at 20 °C. However, addition of 2,3–dimethylbut–2–ene led to complete reaction in ca. 2 h to give (227_a) (see table 1), suggesting either that the alkene promotes the ring opening of the cyclopropene, or that a reversible ring opening to a carbene was occurring and this was trapped rapidly in the presence of added alkene. The ^1H n.m.r. spectrum of the product showed five methyl singlets, and an AB pattern for the methylene group (J 11.6 Hz); this is in agreement with a preferred twisted conformation, and rotation about the exocyclic carbon–carbon bond which is slow on the n.m.r time scale. Moreover, there was no material change in the 300 MHz ^1H n.m.r. on heating to 400 K in $C_6D_5NO_2$.

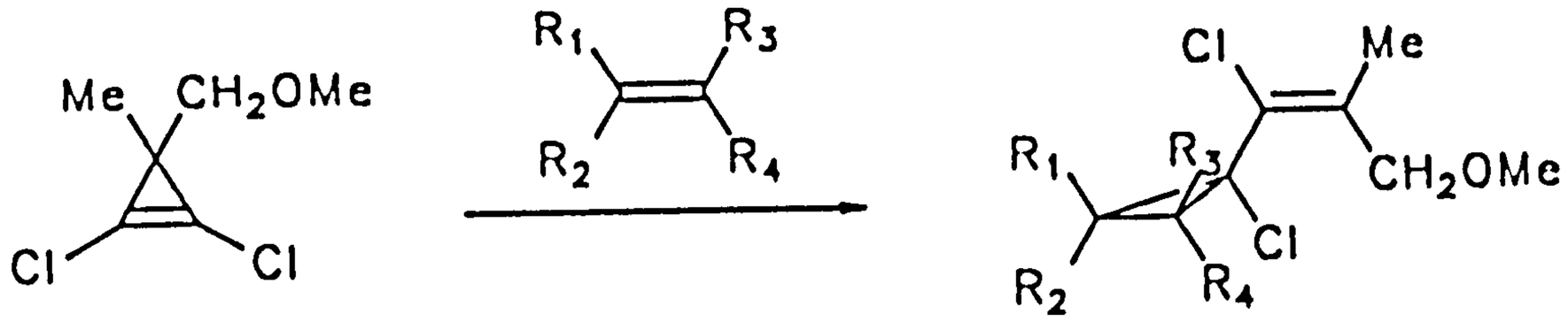


(193) (227) (228)

Similar results have been reported for (228, X = Y = Me),[104] and as previously discussed (228, X = Me, Y = CH_2Ph),[110] while extensive studies of rotation barriers in tetrachlorides such as (228, X = Y = Cl) have also been performed.[101]

In the same way, when the cyclopropene (195) was allowed to react with 2,3–dimethylbut–2–ene it gave (229_a) (table 1) after ca. 2 h. The ^1H n.m.r spectrum of the product contained six methyl singlets (including the methoxy group) and an AB pattern for the methylene group (J 11.0 Hz). There was no evidence in either case for the presence of a second stereoisomer. The stereochemistry of (229_a) about the alkene was assigned as E– because an n.O.e examination showed an enhancement in

the methylene rather than the olefinic methyl signal, when the signal for a methyl group at δ 1.07 was irradiated. This stereochemistry is the same as that observed previously (2.3.2) for the major stereoisomer of the product in the reaction of (176) with 2,3–dimethylbut–2–ene,[110] although the selectivity in the present cases is much higher.

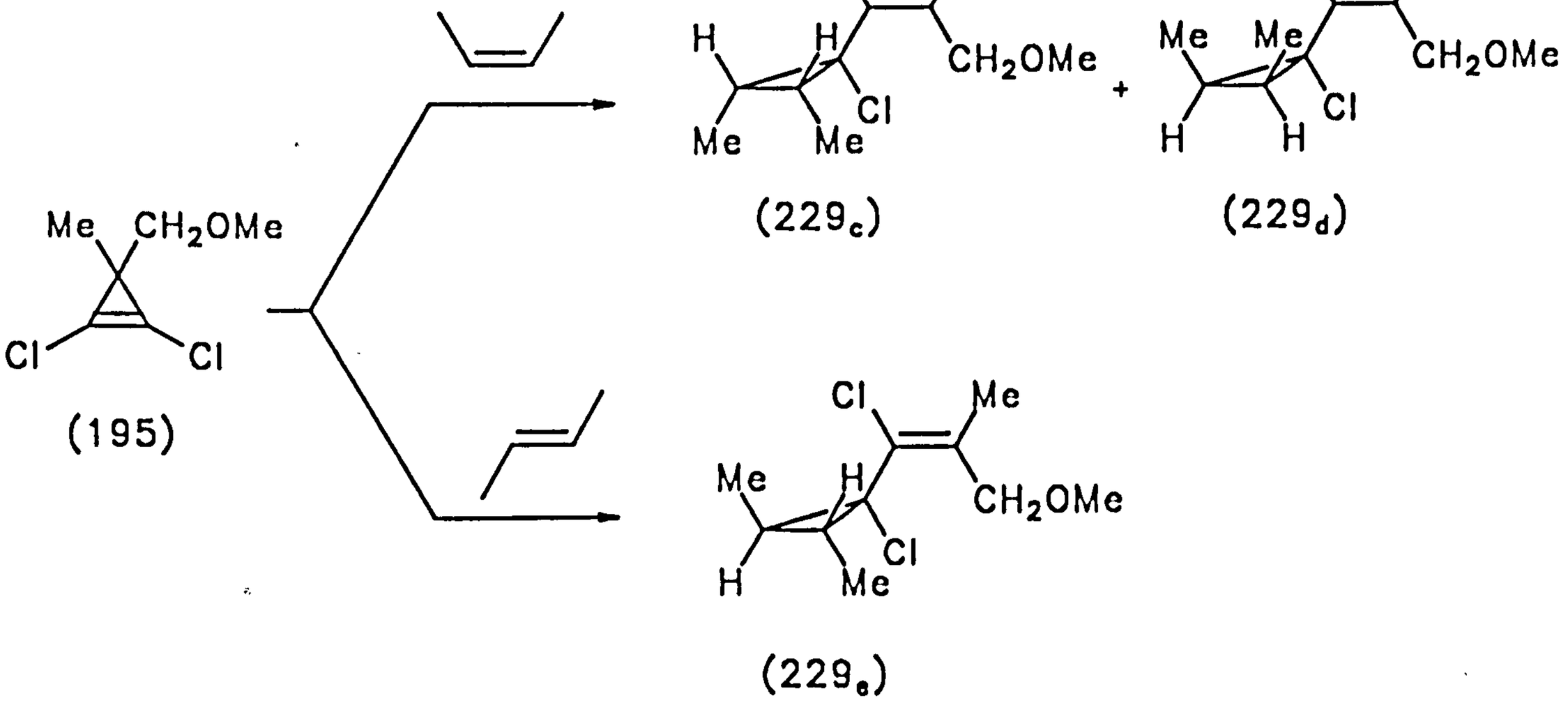


(195) (229)

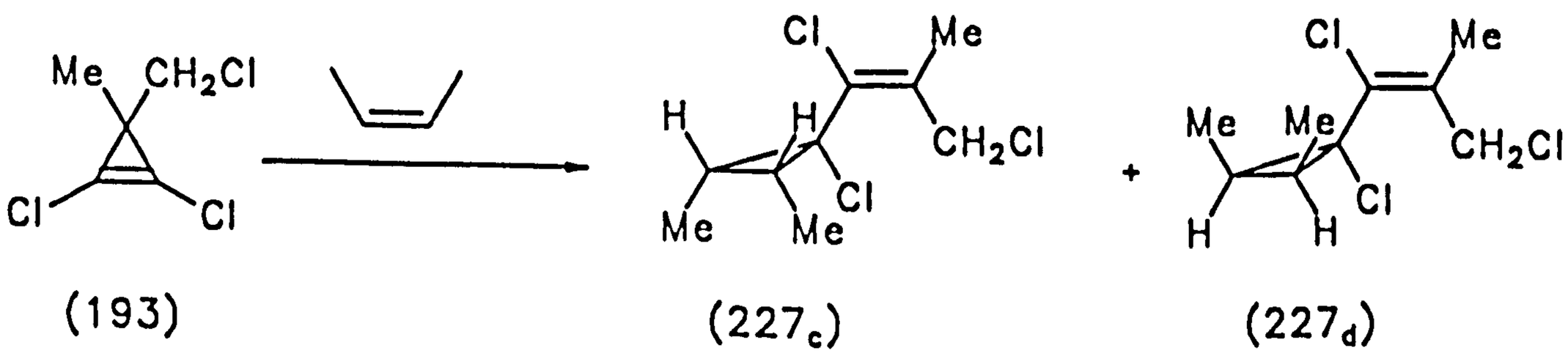
Treatment of (193) and (195) with other alkyl–substituted alkenes also led to cyclopropanes (see table 1). Reaction with 2–methyl–propene led to a single compound from each cyclopropene, (227_b) and (229b), though in each case the ^1H n.m.r spectrum was complicated by the presence of two rotamers;[104] for example the methylene group of (227_b) was evident as two pairs of AB doublets at (δ 4.69 and 3.96 and at δ 4.29 and 4.22) corresponding to two rotamers, with a geminal coupling constant of 11.2 and 11.6 Hz respectively.

(227_b) (229_b)

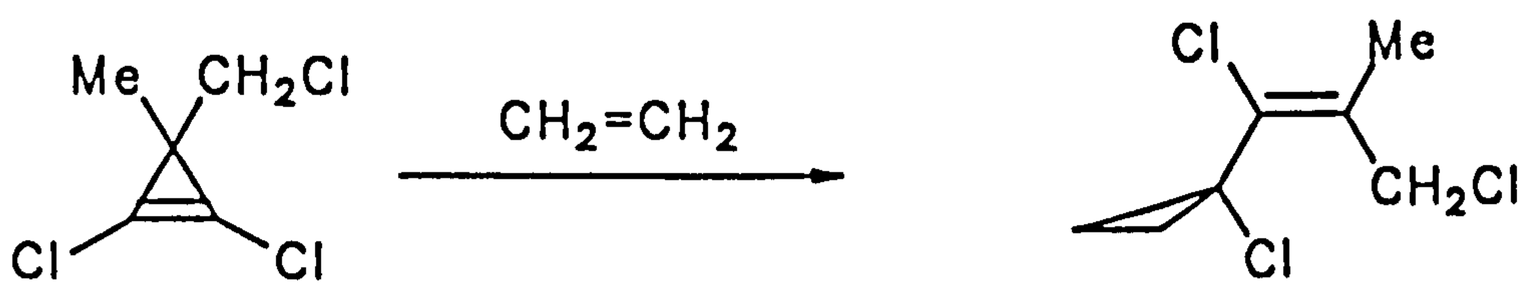
Addition of (195) to E–but–2–ene and Z–but–2–ene was found to be stereospecific. With E–but–2–ene, a single product (229_c) was obtained, but the ^1H n.m.r. at ambient temperature and 200 MHz included a number of broad signals; on cooling to –40 °C this was resolved into the spectra of two rotamers in ratio 2.5:1.



In the case of addition to Z-but-2-ene, the ^1H n.m.r. spectrum and g.l.c. analysis indicated the presence of two adducts (229_c) and (229_d), in ratio *ca.* 6:1; the major isomer showed only one doublet for the ring methyls and a multiplet for the ring hydrogens even at −40 ^0C, indicating a low barrier to rotation about the exocyclic bond, and was therefore assigned as (229_c); this may also be expected to be the major product on steric grounds. The signals for the minor isomer were not clearly resolved, but, since the allylic substituent (Cl, OMe) appears in the *E*-configuration in the above adducts (i.e., $227_a/227_b$, $229_a/229_b$), it was characterised as (229_d). G.l.c analysis showed that no (229_e) was produced in this experiment; in the same way no (229_c) was obtained from the reaction of (195) with *E*-but-2-ene. This is consistent with the addition of a singlet carbene to the alkenes. Moreover, addition of (193) to Z-but-2-ene also gave two isomers (227_c) and (227_d) in a 5:1 ratio respectively.



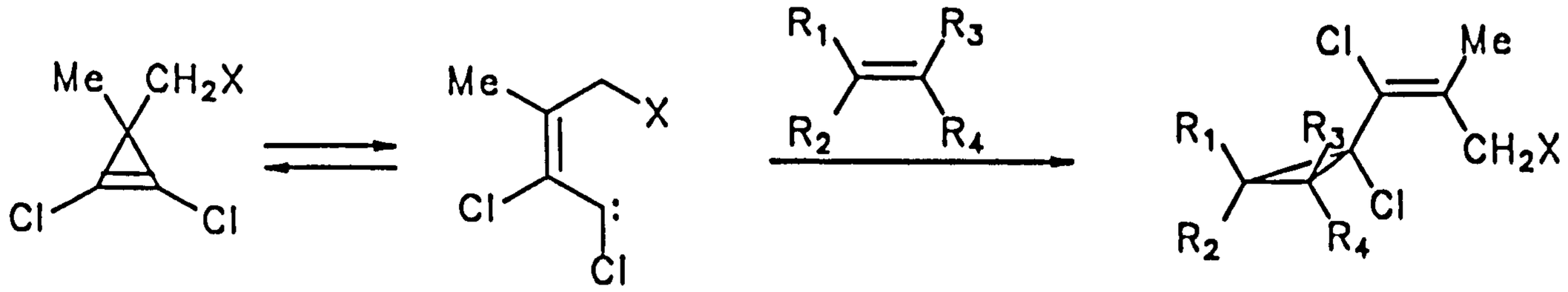
When the cyclopropene (193) was allowed to undergo ring-opening in the presence of ethene in an autoclave at room temperature, a complex mixture of other products was formed in addition to a low yield of cyclopropane (227_e).



(193) (227_e)

TABLE 1.

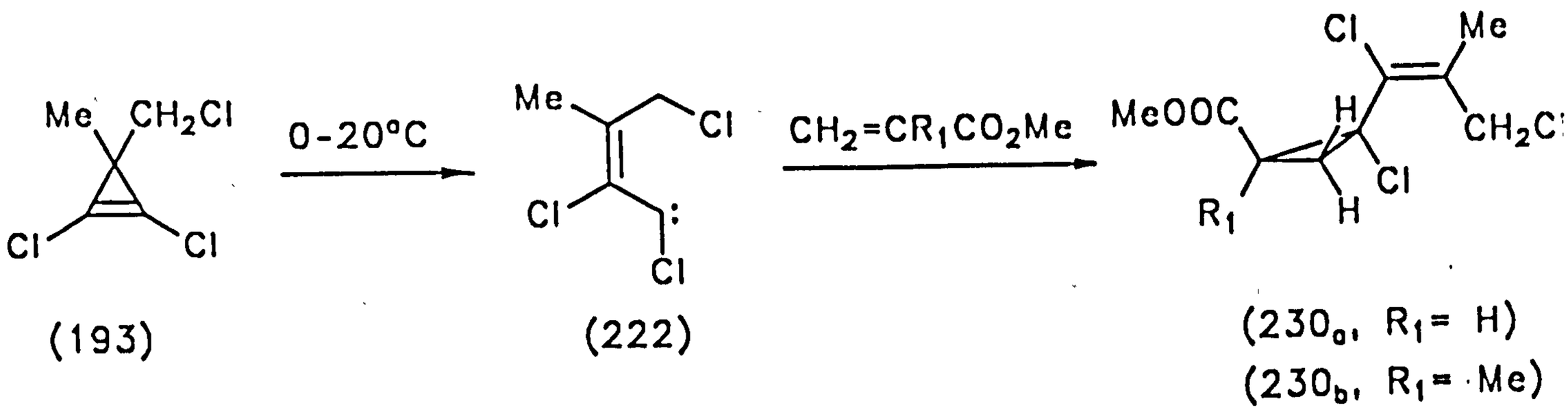
Cyclopropanes obtained from reaction of cyclopropenes (193 and 195) with alkenes.



(193, X= Cl) (222, X= Cl) (227, X= Cl)
(195, X= OMe) (214, X= OMe) (229, X= OMe)

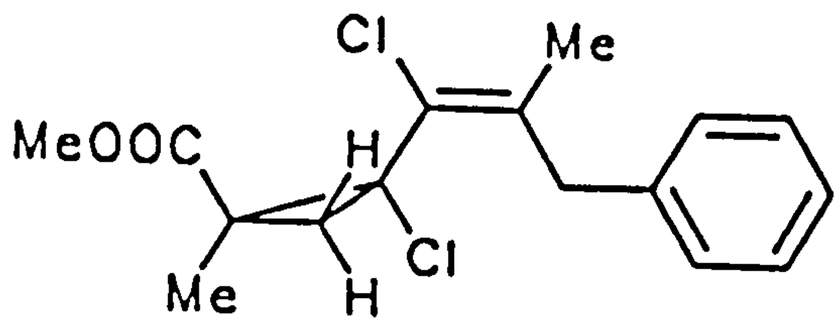
Alkene	Cyclopropane										
	R_1	R_2	R_3	R_4	X	No	%	X	No	%
$Me_2C{=}CMe_2$	Me	Me	Me	Me	Cl	227_a	77	OMe	229_a	69
$Me_2C{=}CH_2$	Me	Me	H	H	Cl	227_b	70	OMe	229_b	68
Z-MeCH=CHMe	H	Me	H	Me)	Cl	227_c	76	OMe	229_c	56
	Me	H	Me	H)	Cl	227_d		OMe	229_d	
E-MeCH=CHMe	Me	H	H	Me				OMe	229_e	54
$Me_2C{=}CHMe$	Me	Me	Me	H)				OMe	229_f	68
	Me	Me	H	Me)				OMe	229_g	
$H_2C{=}CH_2$	H	H	H	H	Cl	227_e	15			
$H_2C{=}CHCO_2Me$	H	-	-	-	Cl	230_a	75	OMe	234_a	75
$H_2C{=}CMeCO_2Me$	Me	-	-	-	Cl	230_b	82	OMe	234_b	84

As shown above, the carbenes (214) and (222) were readily trapped by electron rich alkenes. Addition to electron deficient alkenes was also examined. When the cyclopropene (193) was allowed to stand in ether solution for 12 h at 20 °C with methyl acrylate or methyl methacrylate, (230_a) and (230_b) respectively, were obtained in high yield.

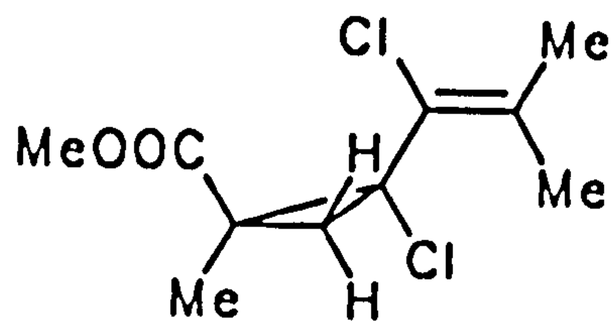


(193) (222) (230_a, R_1 = H) (230_b, R_1 = Me)

The single diastereoisomers formed in each case showed temperature-variable ^1H n.m.r. spectra. Thus, the 300 MHz spectrum of (230_b) appeared broad at 303 K, but two sets of signals were observed at 230 K, corresponding to two rotamers in ratio 2:1. The ^1H spectra at 300 MHz and 230 K of the major rotamer showed two doublets at δ 4.63 and 4.09 for the methylene protons and three singlets for the methyl groups at δ 3.71, 1.96, 1.58 together with a doublet at δ 2.67 for one of the cyclopropyl protons. The latter was downfield from the corresponding signal in the second rotamer which appeared at δ 1.62, due to the deshielding by the ester group. The ^{13}C spectrum at 230 K showed two sets of signals for the two rotamers, e.g., in the carbonyl region there were two signals at δ 171.2 and 170.9 together with four signals in the olefinic region at δ 135.1, 134.4, 132.6, 131.9. Although there were some additional signals, these only amounted to *ca.* 5% of the product and could not be interpreted in terms of a stereoisomeric minor product. The position and coupling constants of the ring hydrogens for (230_b) are close to those in (185)[110] and (231)[104] suggesting that the ester group is *cis*- to to the alkene.

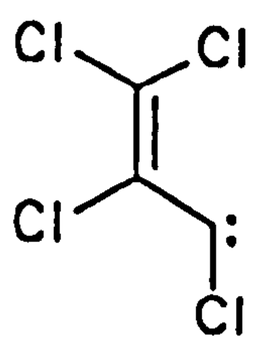


(185)

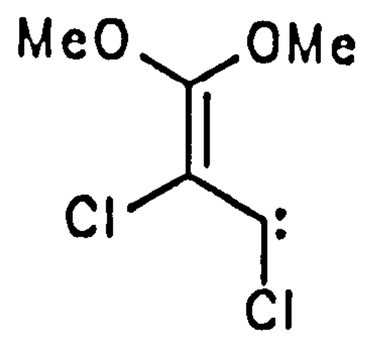


(231)

It is known that the carbene (232) can also add to acrylates to place the vinyl group *syn* to the ester;[101] it is interesting to note, however, that dimethoxycarbene (233), which leads to a *syn* product with methyl acrylate, gives a 1:1 mixture of stereoisomers on reaction with methyl methacrylate.[115]



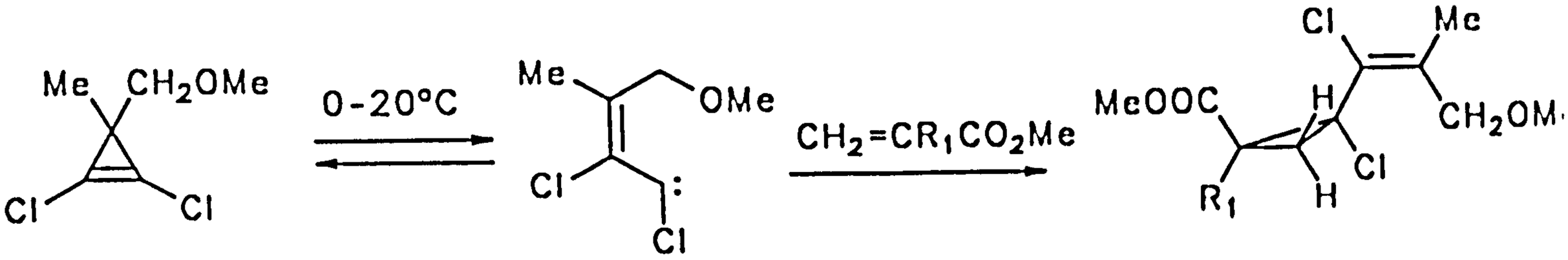
(232)



(233)

Treatment of (195) with methyl methacrylate for 12 h at 20 °C also led to a single product (234_b) in good yield. The ^{13}C n.m.r. at 20 °C showed a single carbonyl carbon at δ 171.03, two alkene signals and five other sharp peak at δ 71.9, 58.2, 52.4, 17.54 and 17.5 respectively; in addition there was an extremely broad signal at δ 29–33. The spectrum at 230 K showed two sets of signals; e.g., in the carbonyl region there were two signals at δ 171.47, 171.12 and four signals in the olefinic region at δ 137.34, 136.7, 130.87 and 129.97. The ^1H n.m.r. spectrum at 303 K was very broad and showed just one methoxy group and a broad singlet for the allylic methylene protons and very broad signal for the ring hydrogens. However, in the ^1H spectrum at 300 MHz and 230 K the methoxy signal was split into two peaks, and two pairs of doublets were seen for the allylic protons and two pairs of doublets for the ring protons ratio (6:5). This is in agreement with slow rotation on the n.m.r. time scale at this temperature, and the formation of two preferred rotamers in ratio

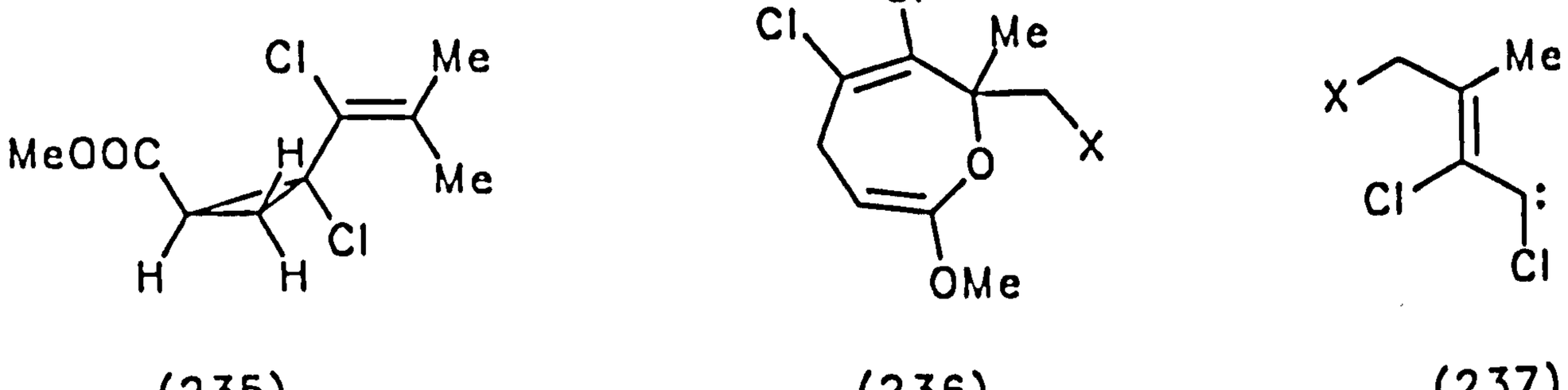
ca. 6:5. The chemical shift of the cyclopropyl protons of (234_b) are close to those in (185) and (231); this is again consistent with a *cis*-arrangment of ester and vinyl group. According to the Gunther approximation[114] the ^1H and ^{13}C spectra at different temperatures showed a barrier between the two rotamers of *ca.* 14.8 kcal/mol.



(195) (214) (234_a, R_1= H) (234_b, R_1= Me)

Reaction of (195) with methyl acrylate for 12 h at room temperature also led to a single product (234_a). The ^1H n.m.r. was again complex at 303 K, but at 330 K and 300 MHz was consistent with the presence of two rotamers in ratio *ca.* 7:3. The chemical shift and the coupling constant of the ring hydrogens for (230_a) and (234_a) are similar to those in (235)[104] suggesting that the ester group and the alkenyl group are *cis* to each other.

The stereochemistry of these cyclopropanes may arise by control in a concerted cyclopropanation or by dipolar attraction in a Michael type addition of the delocalised carbene; indeed formation of a methoxy dihydro-oxepine, e.g. (236), followed by a Claisen rearrangment would offer a possible explanation in the present case.

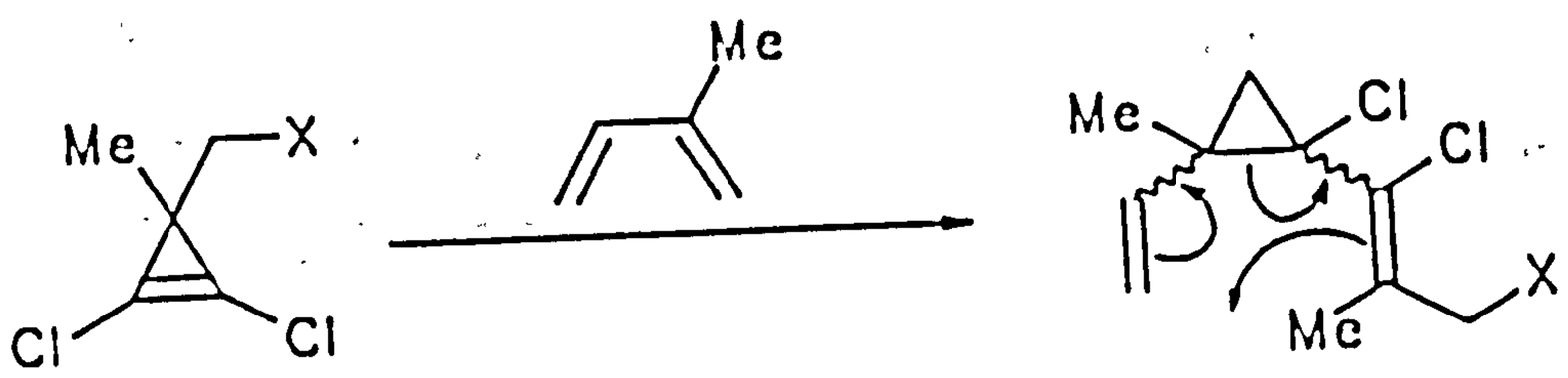


(235) (236) (237)

The above additions gave *E*-alkenes derived by trapping of carbenes (214) and (222). It is not clear why the alternative, but possibly less hindered, carbene (237, X = Cl,

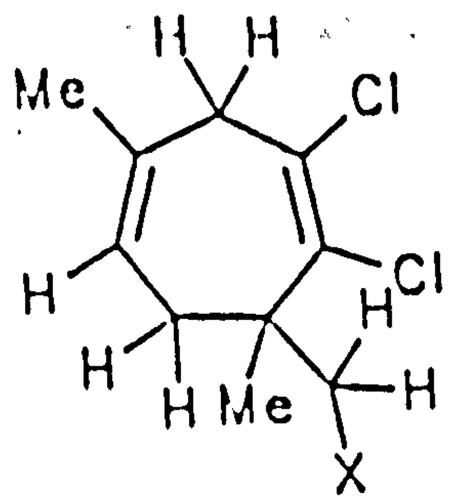
OMe), if formed, should be trapped less efficiently by the alkene. It would appear, therefore, either that the carbenes (214) and (222) were formed selectively from (195) and (193), or that the representation of these species in two geometrical forms is not correct and that more subtle factors control the geometry of addition.

The carbenes could also be trapped by dienes; when the cyclopropenes (193) and (195) were allowed to undergo ring-opening in the presence of isoprene, (239, X = Cl, OMe) were obtained after refluxing in benzene for 12 h.



(193, X = Cl)
(195, X = OMe)

(238, X = Cl, OMe)

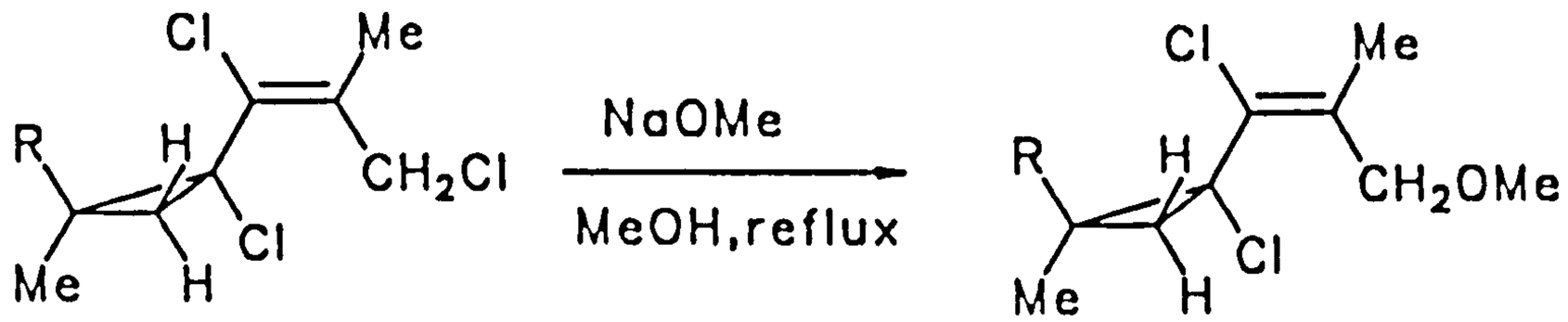


(239)

The products may arise due to trapping of the carbenes by more alkylated double bond to give the intermediate (238, X = Cl, OMe) followed by Cope rearrangements to give the final products.[119] The reaction product before refluxing gave one peak on g.l.c. perhaps due to the presence of *cis*- and *trans*- divinylcyclopropanes (238). The spectrum at this stage showed no signals for (239). The Cope rearrangement of the *trans*- isomer presumably occurs by a non- concerted mechanism. The product (239, X = Cl) showed a triplet of triplets for the olefinic proton at δ 5.89 and an AB pattern for the chloromethyl group with a coupling constant 10.8 Hz, together with a

pair of double doublets and two singlets for the methyl groups.

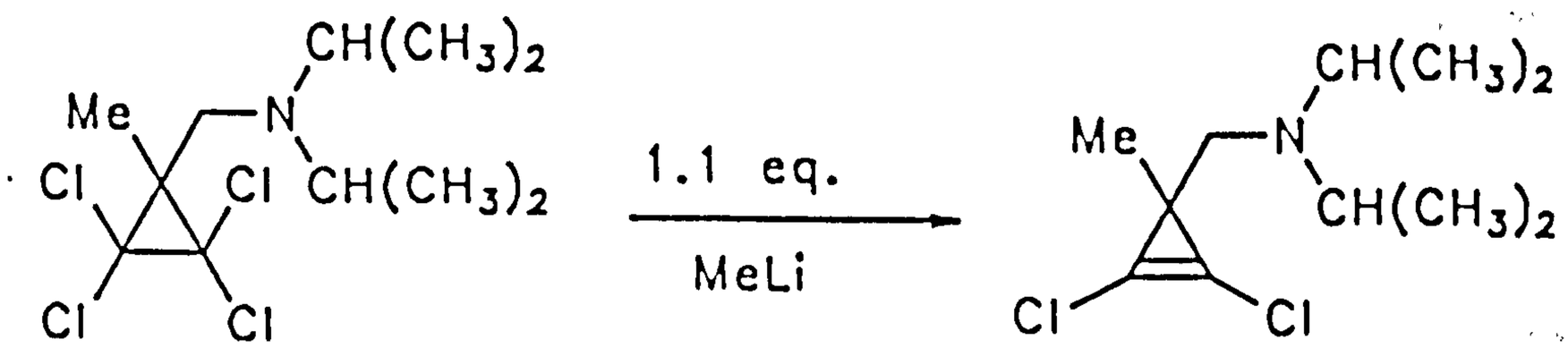
Reaction of the trichlorocyclopropanes, e.g., (227_b and 230_b) with nucleophiles did offer a possible route to introduce other substituents into the allylic position of the side chain. Thus, treatment of (227_b) or (230_b) with methoxide in methanol gave (229_b) or (234_b) respectively.



(227_a, R=Me)
(230_b, R=COOMe)

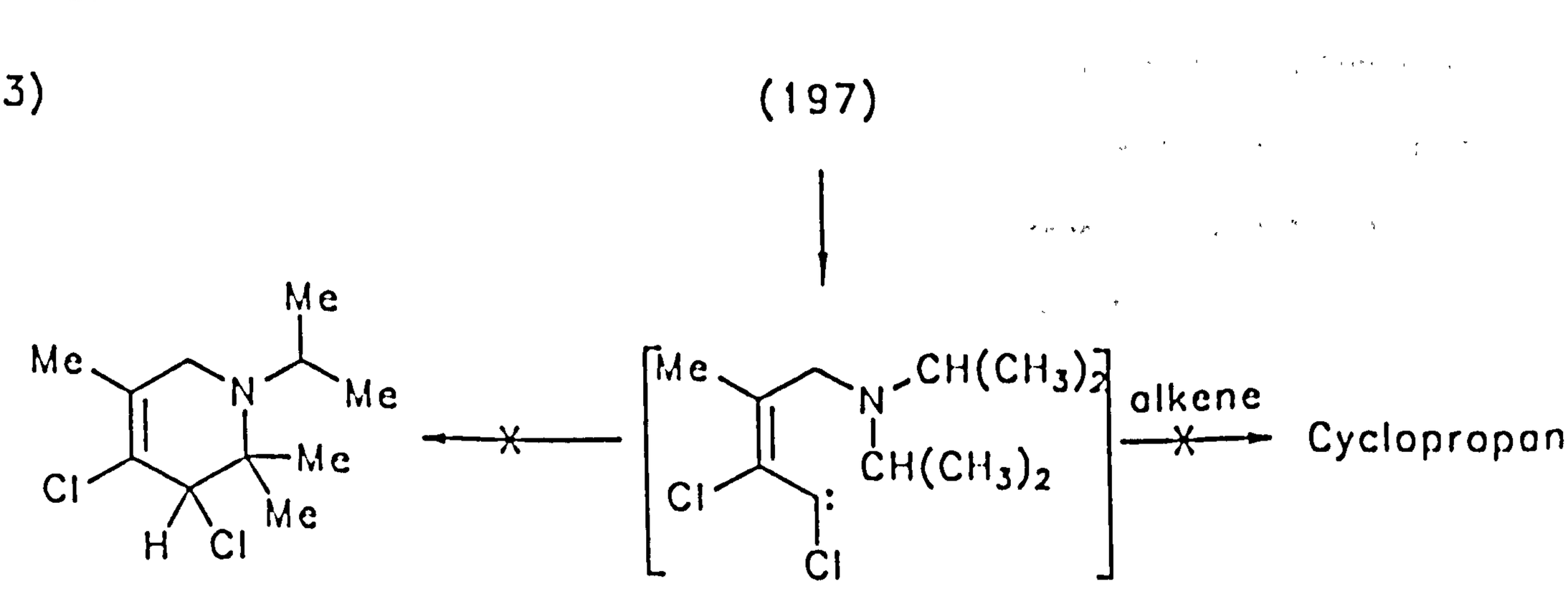
(229_b, R=Me)
(234_b, R=COOMe)

As shown above, the cyclopropenes (176), (193) and (195), were found to undergo ring-opening at 0-20 °C to the vinyl carbenes (180), (222) and (214) respectively, which could be trapped by both electron rich or electron poor alkenes. In contrast, the cyclopropene (197) did not give clean products on reaction with either electron rich or electron poor alkenes, but instead decomposed rapidly when allowed to reach room temperature, to give a complex mixture. No intramolecular insertion of an intermediate carbene into the 1,7-disposed C-H bond was observed; insertion into a 1,6- disposed C-H bond would be the preferred mode of reaction.[46,48]

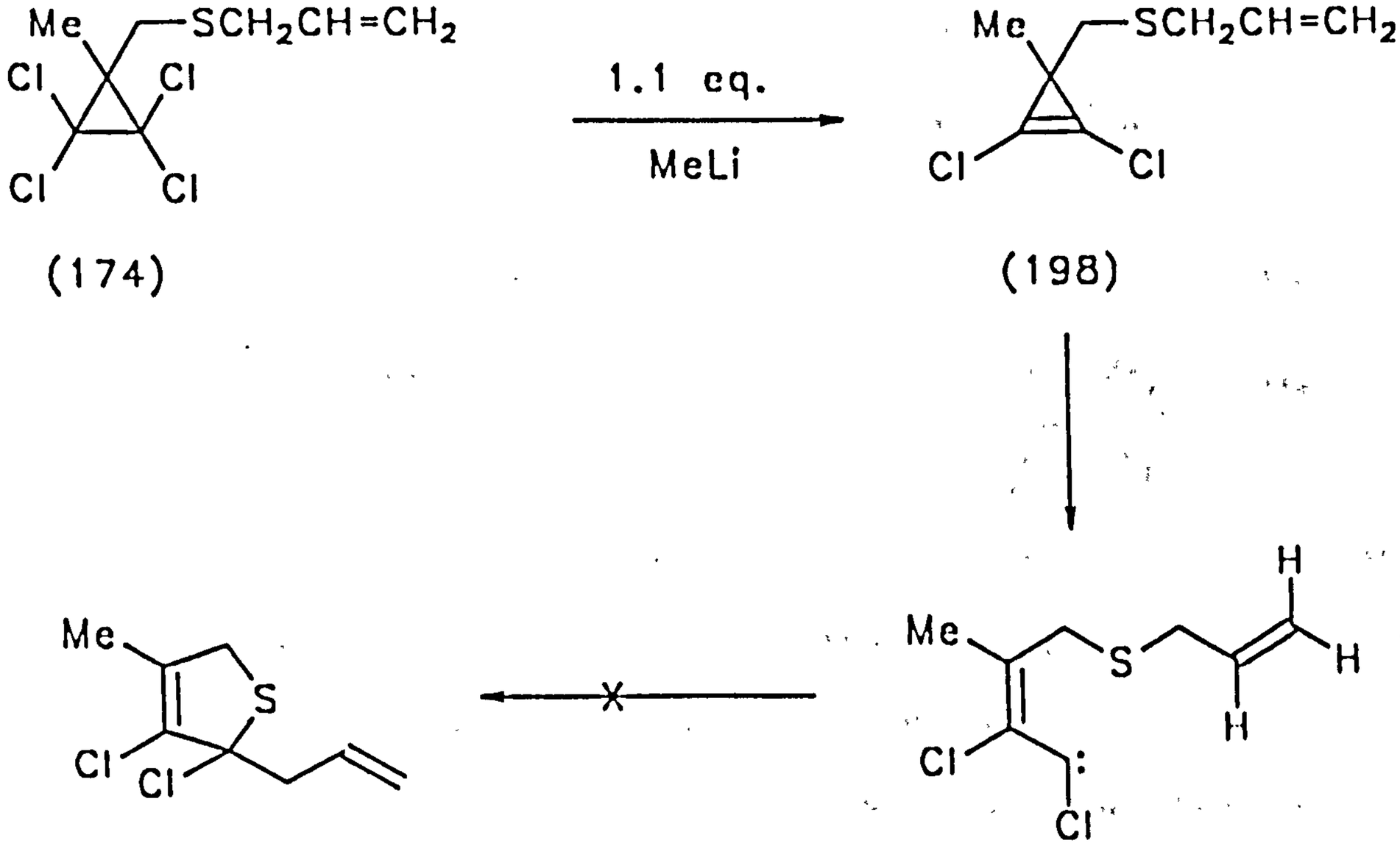


(173)

(197)



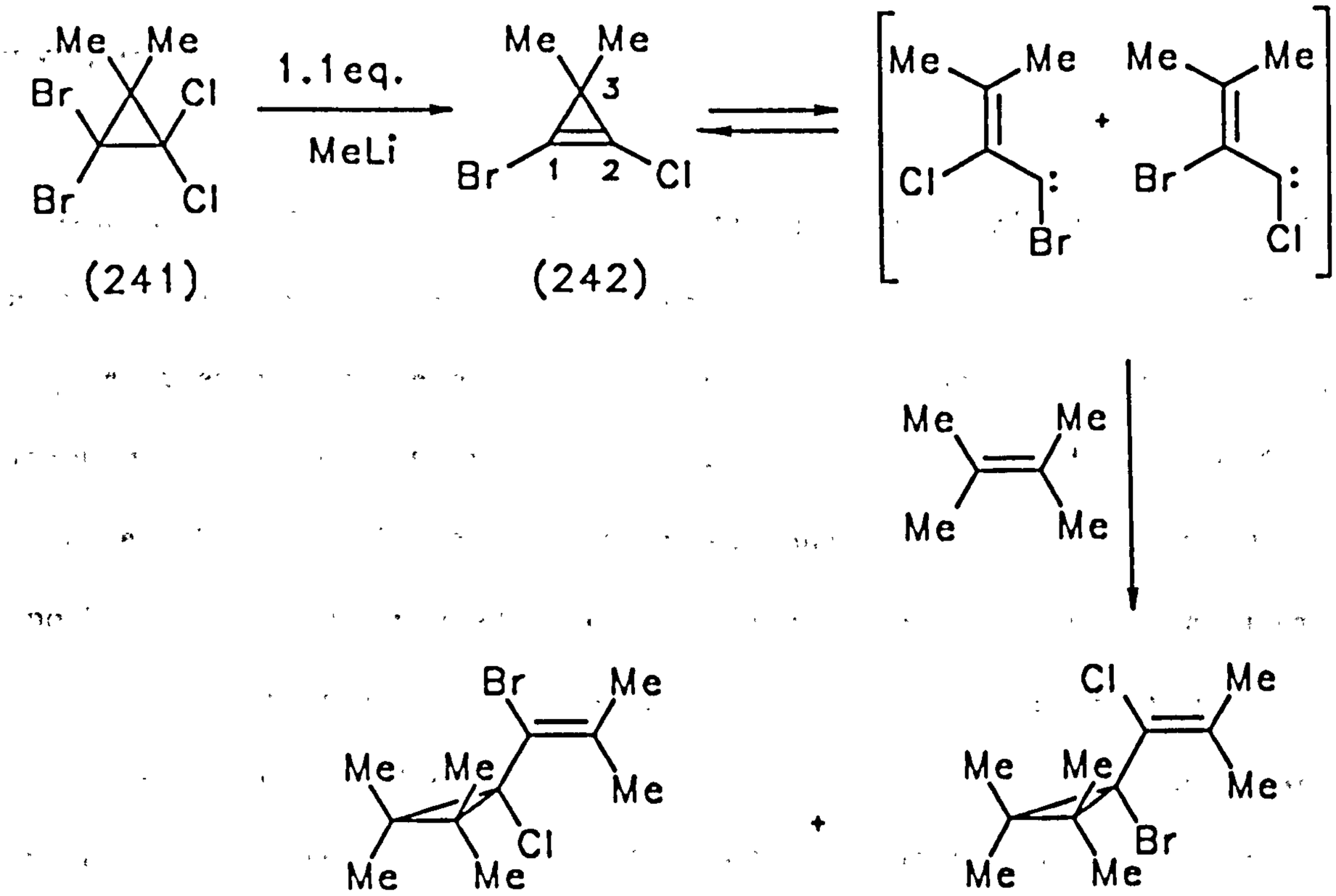
Moreover, it was anticipated that the cyclopropene (198) would undergo ylide formation followed by a [2,3] sigmatropic rearrangment to lead to (240).[46,48,120] However, the intermediate carbene could not be trapped by either electron rich or electron poor alkenes, and instead (198) decomposed rapidly even at below 0 ^{0}C.



(174) (198) (240)

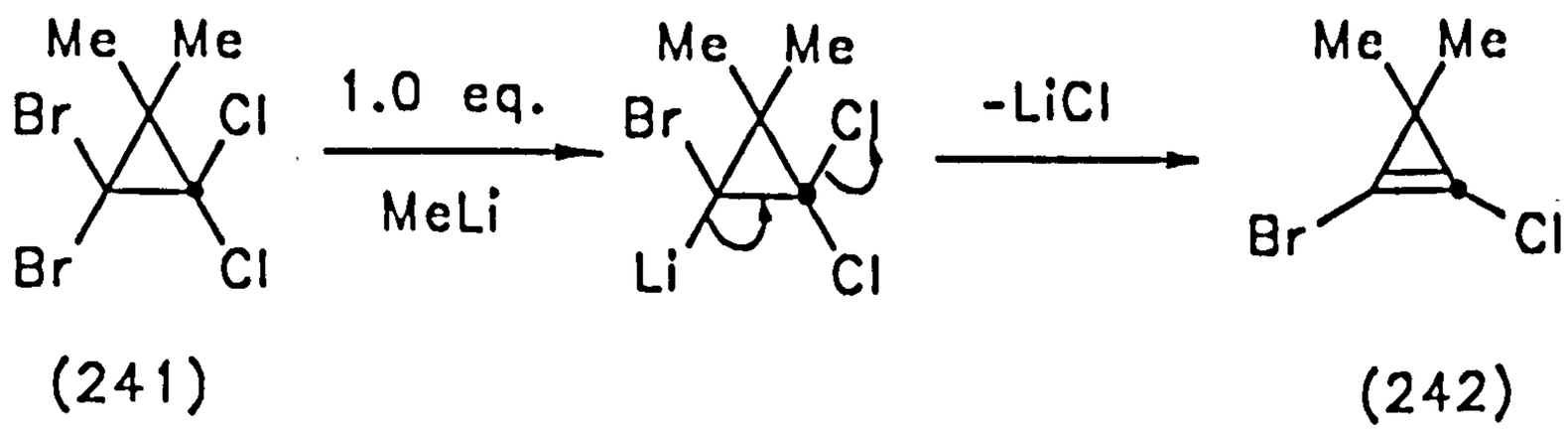
2.3.4: REACTION OF DI–BROMO–DICHLOROCYCLOPROPANES WITH METHYL LITHIUM.

It is known that the reaction of 1,1–dibromo–2,2–dichlorocyclopropanes such as (241) with one equivalent of methyl–lithium leads to a 1–bromo–2–chlorocyclopropene (242) which undergoes ring opening by cleavage of both 1,3– or 2,3– bonds to give the isomeric vinylcarbenes which are trapped in the presence of alkenes such as 2,3–dimethylbut– 2–ene, leading to a mixture of cyclopropanes.[121]



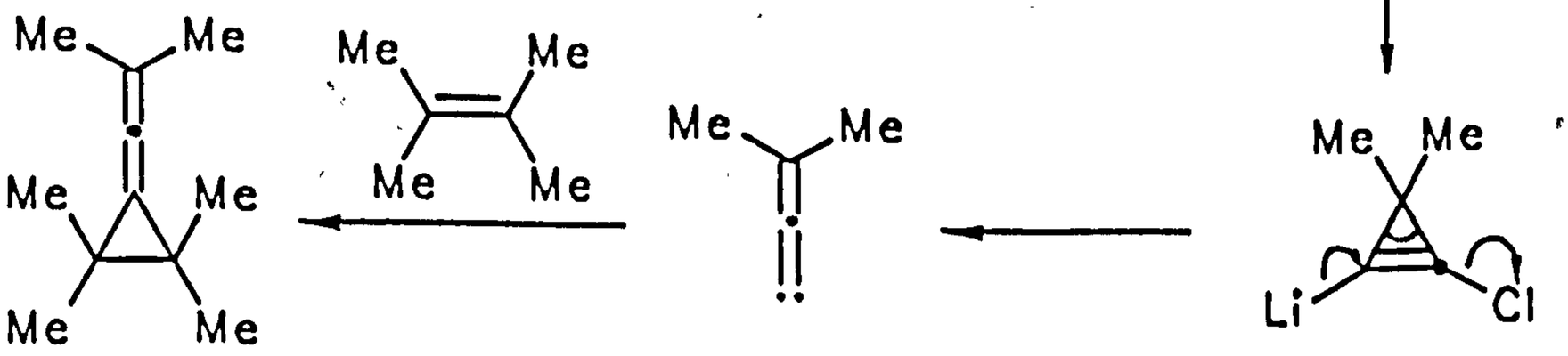
(241) (242)

However, reaction of (241) with two equivalents of methyl-lithium follows a different course leading to the allene (245). This may be explained by initial lithium–bromine exchange and 1,2–elimination of lithium chloride to give the bromochlorocyclopropene (242), which then reacts with excess of methyl-lithium to give lithiocyclopropene (243), which rearranges to an allenic isoprenoid carbene (244). This adds to alkenes, to give the allenic cyclopropane. The proposed mechanism is supported by ^{12}C labelling studies.[121]



(241) (242)

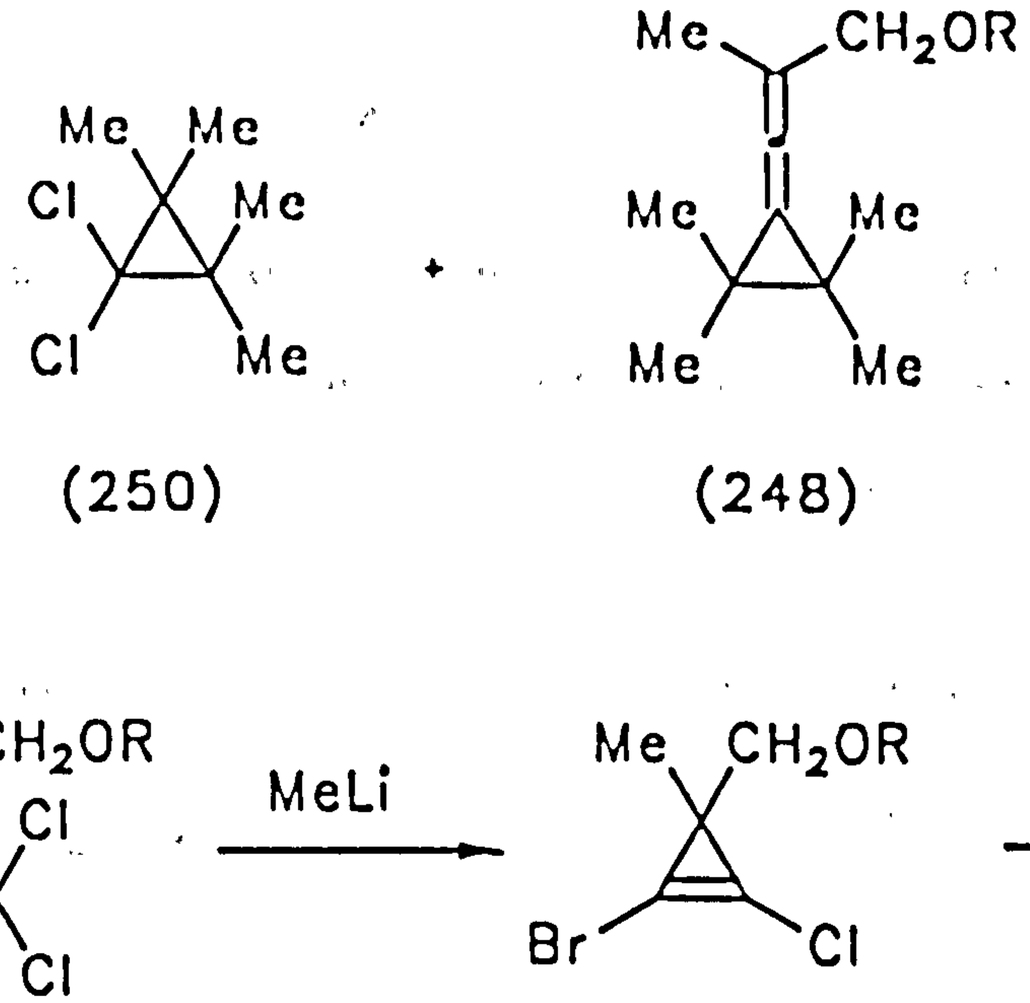
• = ^{12}C



(245) (244) (243)

DISCUSSION:

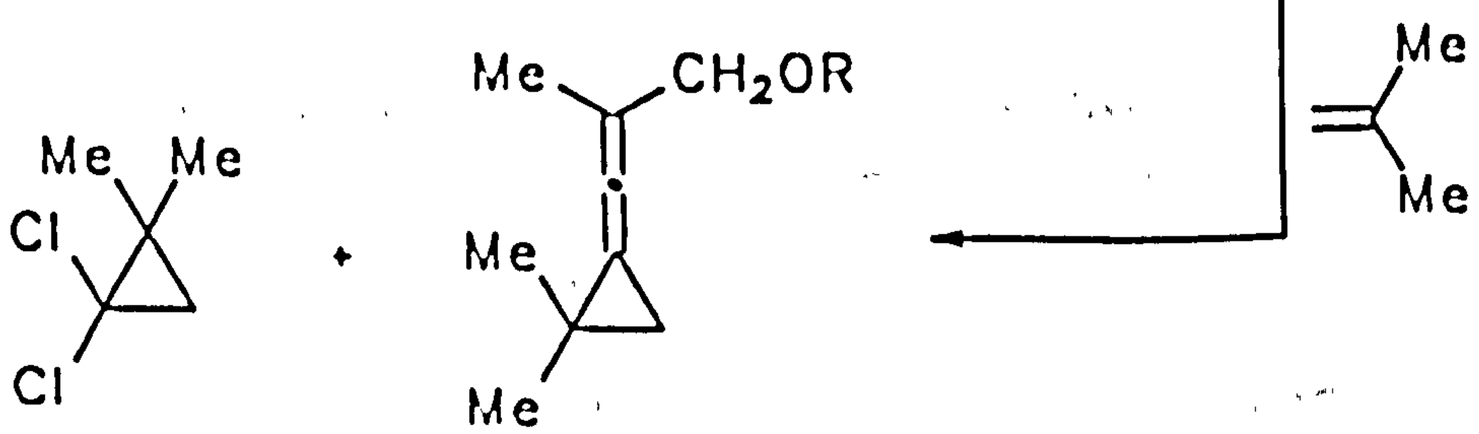
Treatment of (171, R = Me, Pr^i) with two equivalents of methyl-lithium at -78 ^{0}C in the presence of 2,3-dimethylbut-2-ene or isobutene, followed by quenching with water, gave in each case the allene (248) and (249) respectively;[116] this proceeds by lithium-bromine exchange followed by loss of lithium chloride to produce the cyclopropene (246), which react with excess methyl-lithium to give the allenic isoprenoid carbene (247) which adds to the alkenes. A minor product in each case was (250) or (251). The cyclopropane (248, X = OMe) showed the characteristic C=C=C stretching absorption at 2004 cm^{-1} in the i.r and the ^{1}H n.m.r. spectrum showed four singlets at δ 3.84 (2H), 3.23 (3H), 1.72 (3H), 1.17 (12H), while the ^{13}C showed eight signals, including two in the olefinic region and a characteristic allenic carbon singlet at δ 184.7.



(250) (248)

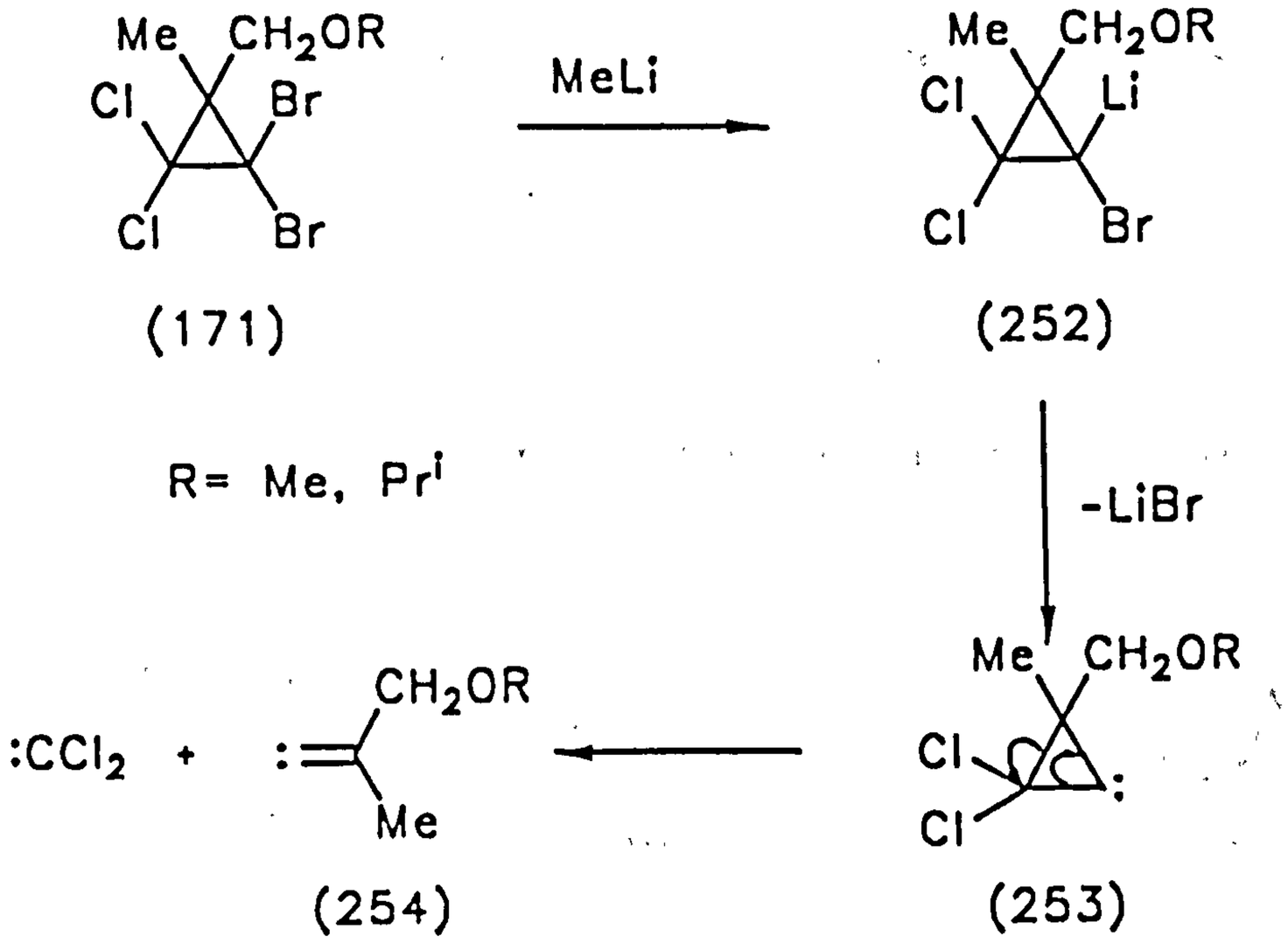
(171) (246) (247)

(R= Me, Pr^i)



(251) (249)

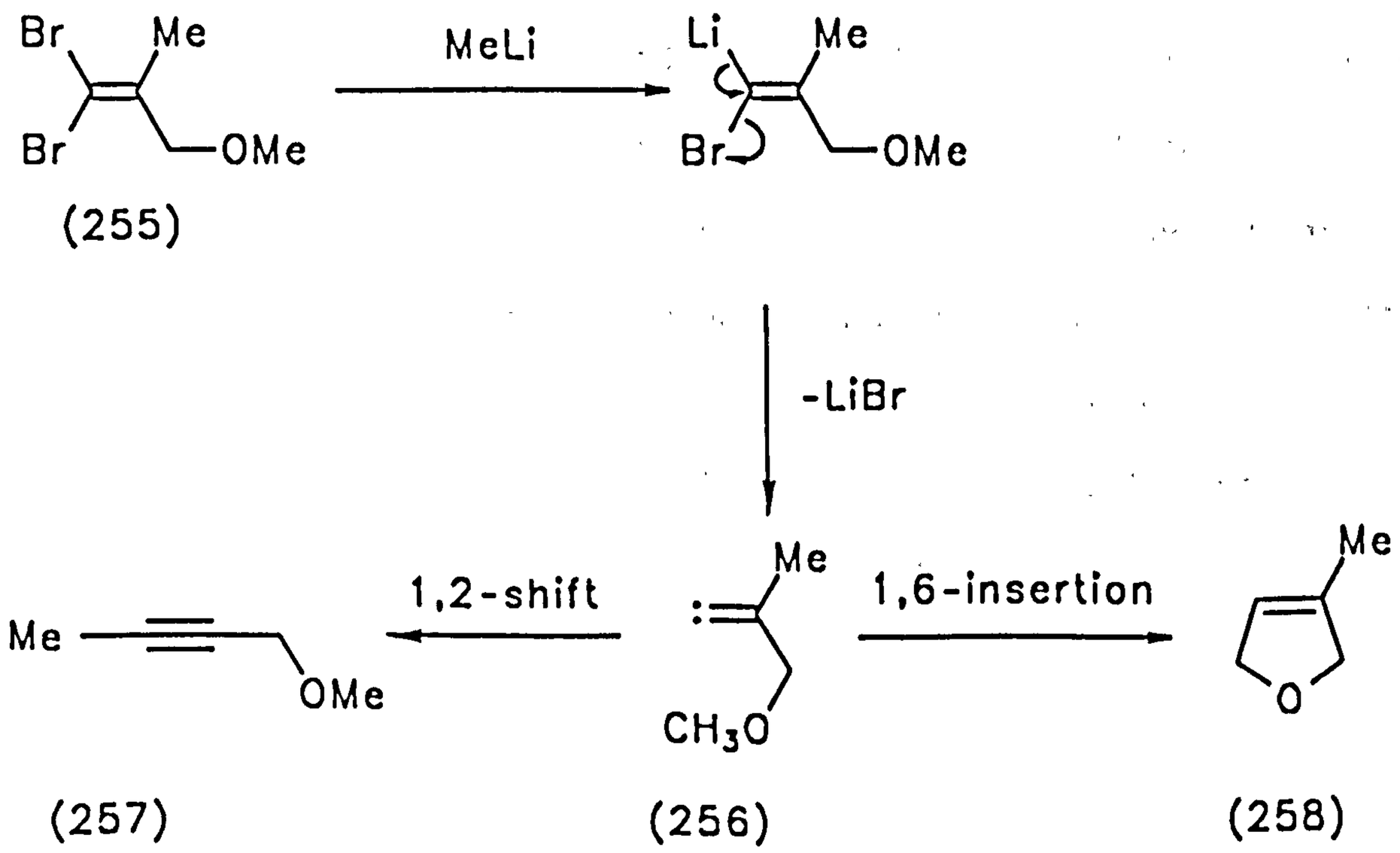
The minor products (250) and (251) are apparently derived by addition of dichlorocarbene to the alkenes. The source of this carbene is not yet clear. One novel formal route to $:CCl_2$ would be cheletropic elimination from an intermediate lithiobromide (252), or from the cyclic carbenoid (253).



(171) (252) (254) (253)

R= Me, Pr^i

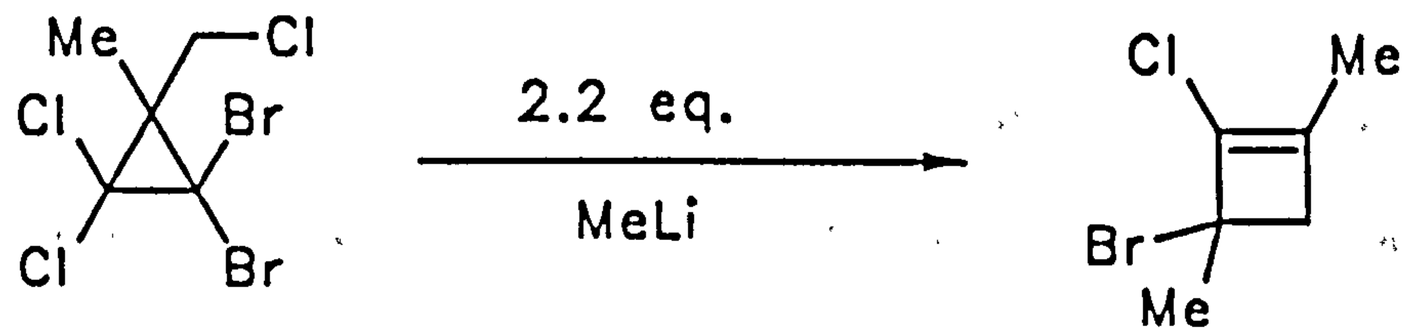
Baird and co-workers[122] found that treatment of (255) with methyl-lithium gave the carbene (256); such carbenes undergo rapid rearrangment to the acetylene (257) or insertion into a 5,6-disposed C-H bond to give the ring closed product (258).



(255) (257) (256) (258)

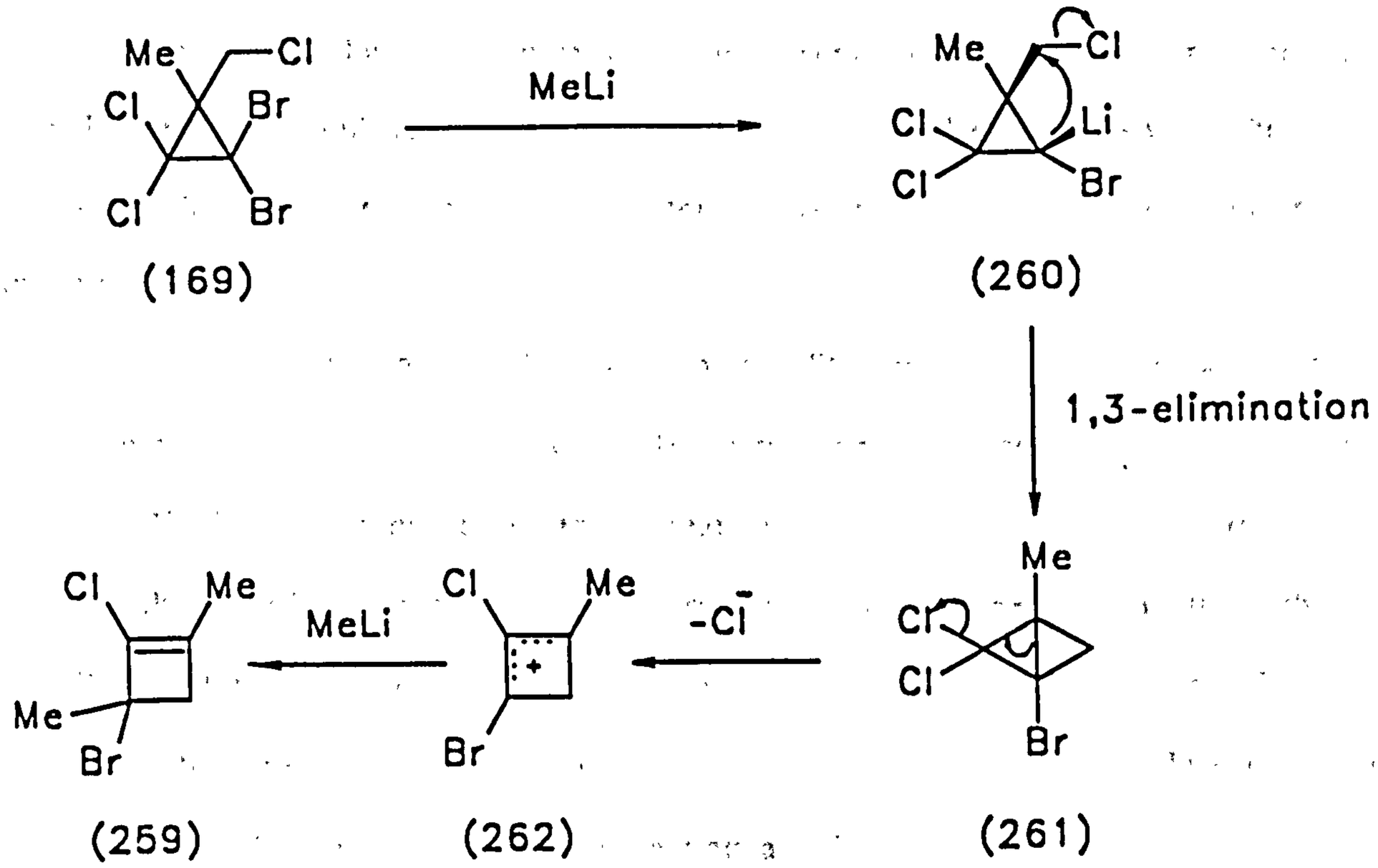
In this present work, no evidence was obtained for the presence of these compounds, and the mechanism of dichlorocarbene formation is still unclear.

As mentioned previously (2.3.3), the reaction of pentachlorocyclopropane (168) with one equivalent of methyl-lithium at 0 °C leads to 1,2-dichlorocyclopropene (193) through 1,2-elimination. The dibromodichlorocyclopropane (169) reacts with methyl lithium in a different manner. Reaction of (169) with 2.2 mol. equiv. of methyl-lithium at -78 °C in the presence of 2,3-dimethylbut-2-ene led to no products incorporating the alkene, but instead the cyclobutene (259) was obtained in 59% yield.[116]



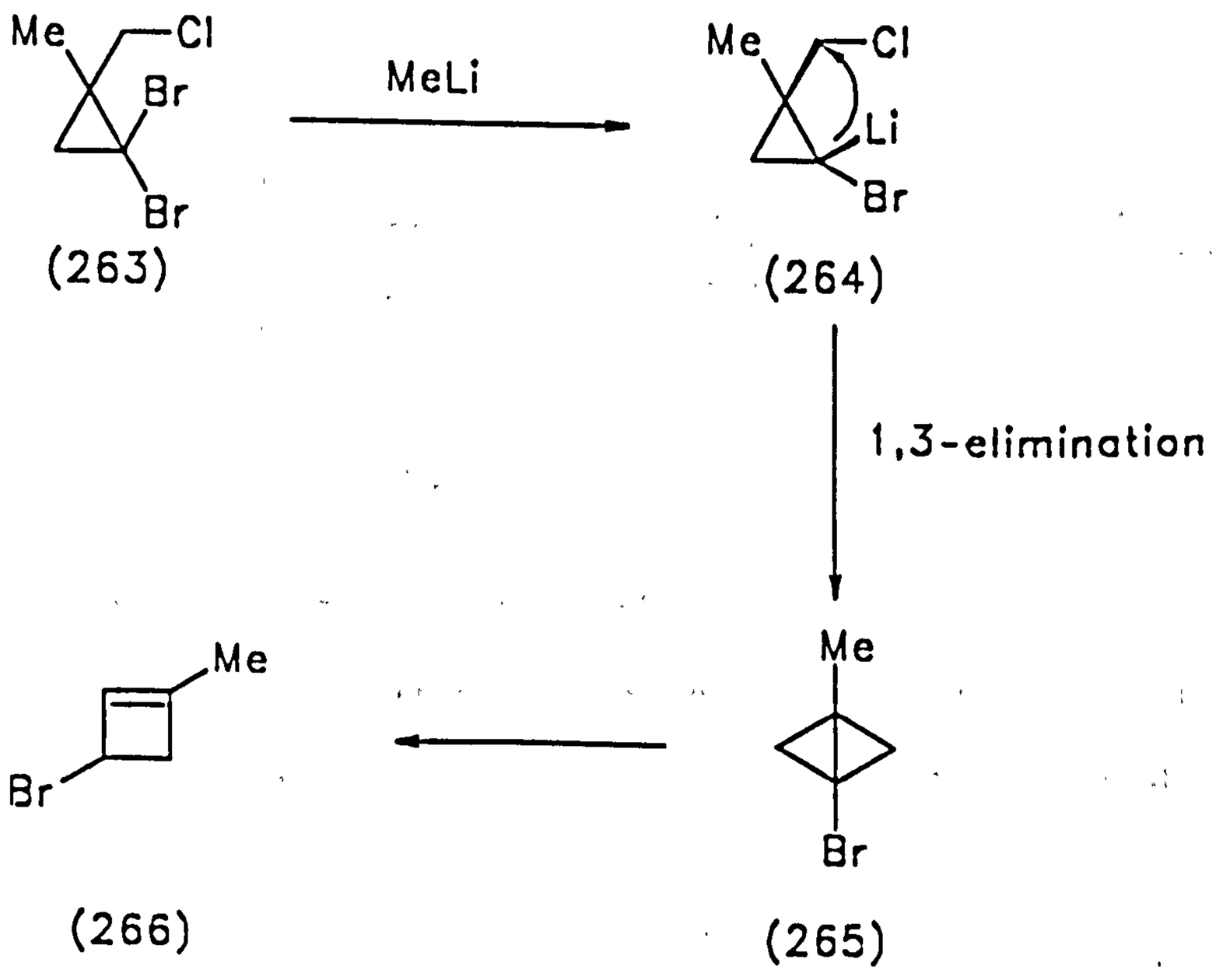
(169) (259)

The ^{1}H n.m.r. spectrum of this compound showed two methyl singlets at δ 1.87 and 1.76 together with an AB pattern for the methylene group, with a coupling constant 10.6 Hz at δ 3.02 and 2.71. The ^{13}C spectrum showed two singlets in the alkene region and two methyl carbons together with a triplet at δ 50.0 and a singlet at δ 62.0. The formation of the cyclobutene (259) is again most reasonably explained in terms of an initial lithium-bromine exchange to give the intermediate (260), followed by intramolecular displacement of chloride through 1,3-elimination to give the bicyclobutane (261); ready loss of chloride ion to produce (262), and regioselective trapping by excess methyl-lithium could then lead to the cyclobutene (259).



(169) (260) (261) (262) (259)

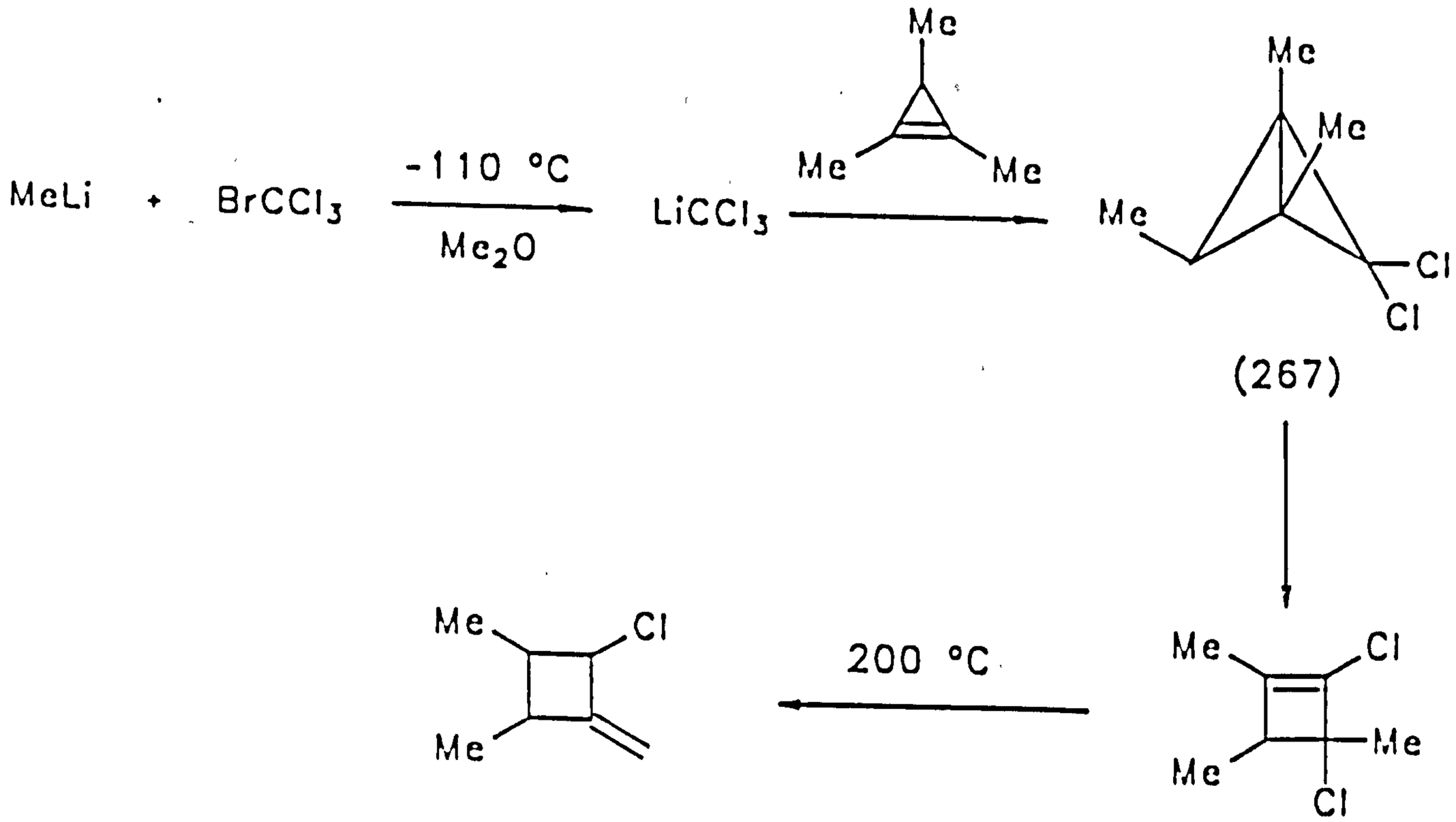
It is known that the reaction of (263) with methyl-lithium in ether leads to one major product (265). The bicyclobutane is obtained by lithium–bromine exchange to give (264) followed by intramolecular displacement of chlorine through 1,3–elimination; [117,123] after several days rearrangment to (266) occurs.



(263) (264) (265) (266)

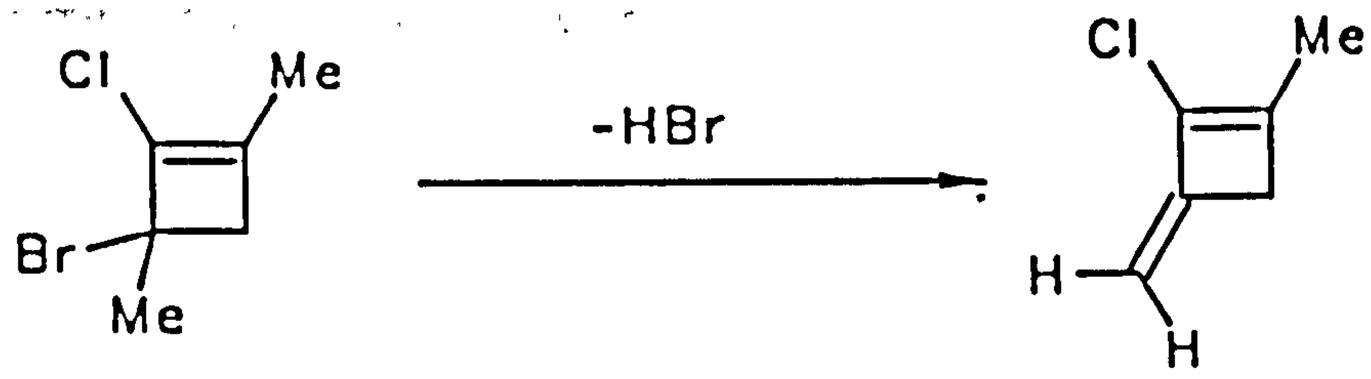
There appears to be a dramatic difference in the reaction of (168) and (169) with methyl–lithium. Since the 1,3–elimination would seem to require a *syn*–relationship of carbon–lithium bond and leaving group, the reaction may be controlled by the relative rates of lithium–halogen exchange, interconversion of geometrical isomers and elimination.

Repeating the reaction of (169) with methyl–lithium and quenching with methanol after 2 min at –78 °C, also gave (259), suggesting that the cyclobutene is formed even at –78 °C. In support of this, treatment of 1,2,3–trimethylcyclopropene with lithium trichloromethide (generated from bromotrichloromethane with methyl–lithium at –110 °C) in dimethyl ether at –95 °C is reported to give the cyclobutene (268); even at –73 °C the presumed intermediate (267) could not be detected. The cyclobutene (268) undergoes dehydrochlorination on heating at 200 °C to give (269).[124]



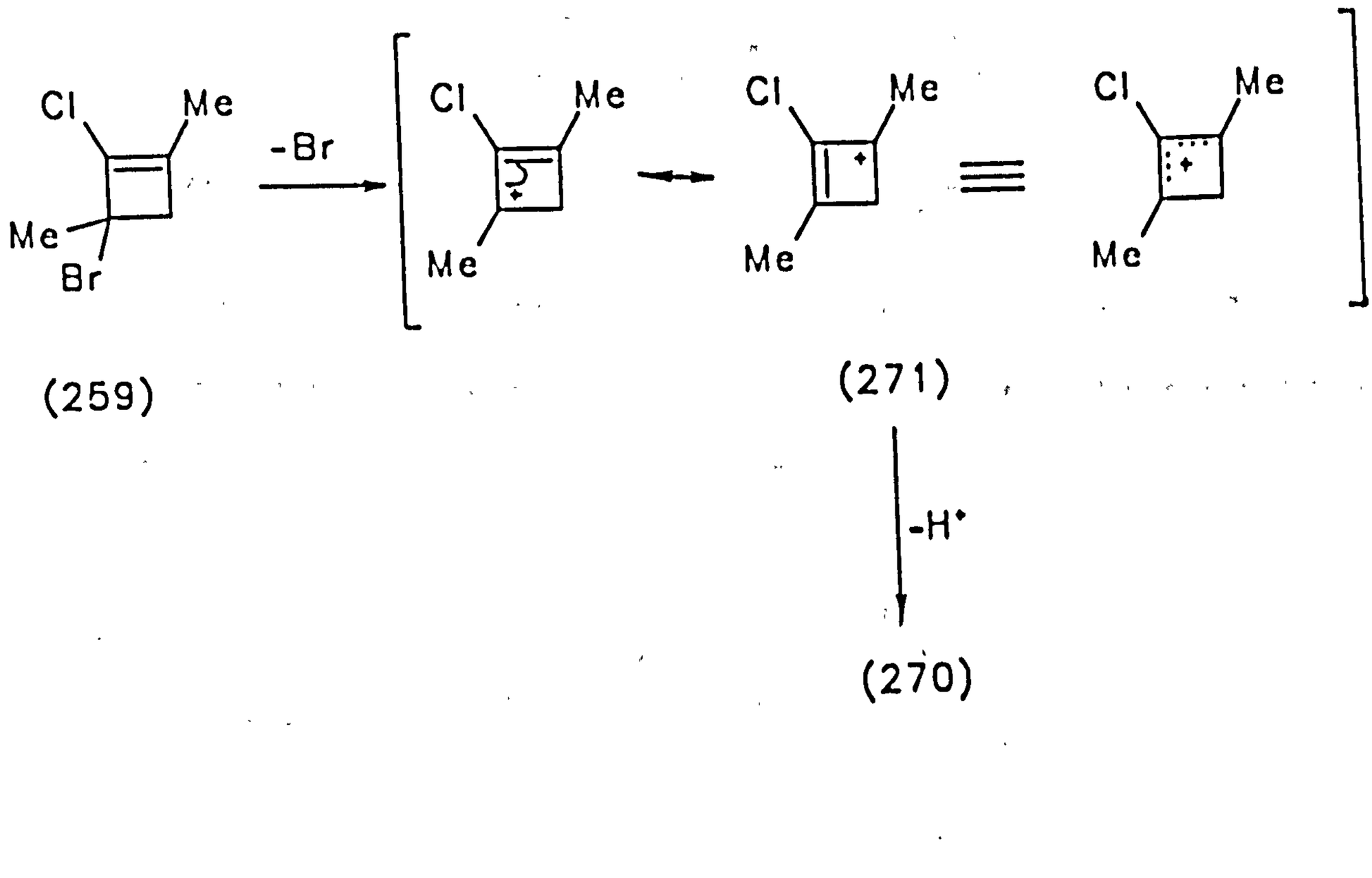
(269) (268)

Attempted preparative g.l.c of the cyclobutene (259) through a copper 6m SE30 column at 40 °C with the inlet temperature port at 150 °C, also resulted in the elimination of hydrogen bromide to give 2–chloro–1–methyl–3–methylene–1–cyclobutene (270):



(259) (270)

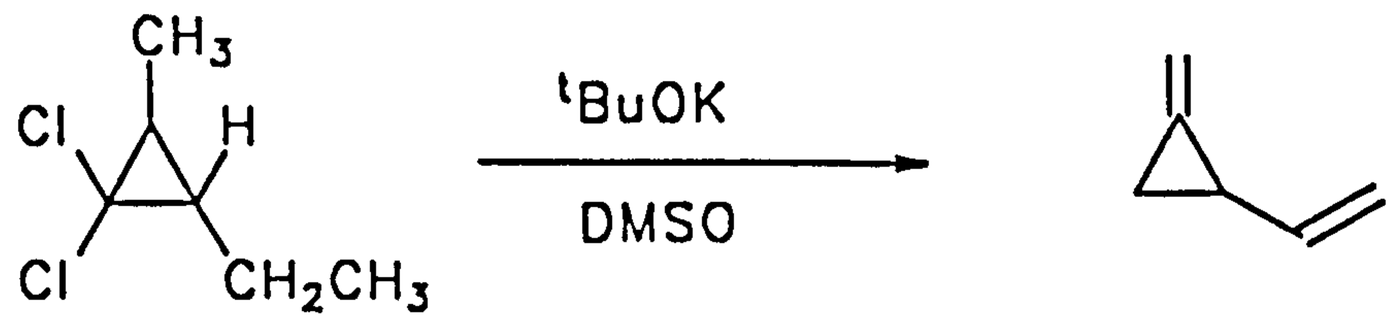
This showed two broad singlets at δ 4.68 and 4.45, and a broad singlet at δ 2.78 for the ring methylene, together with a singlet at δ 1.92 for the methyl group. This reaction presumably proceeds by initial elimination of bromide ion to give the allylic cation (271), which in turn loses a proton from the adjacent methyl to give (270). This compound decomposed rapidly even when stored at –20 °C.



2.3.5: ALKENYLIDENE CYCLOPROPANES.

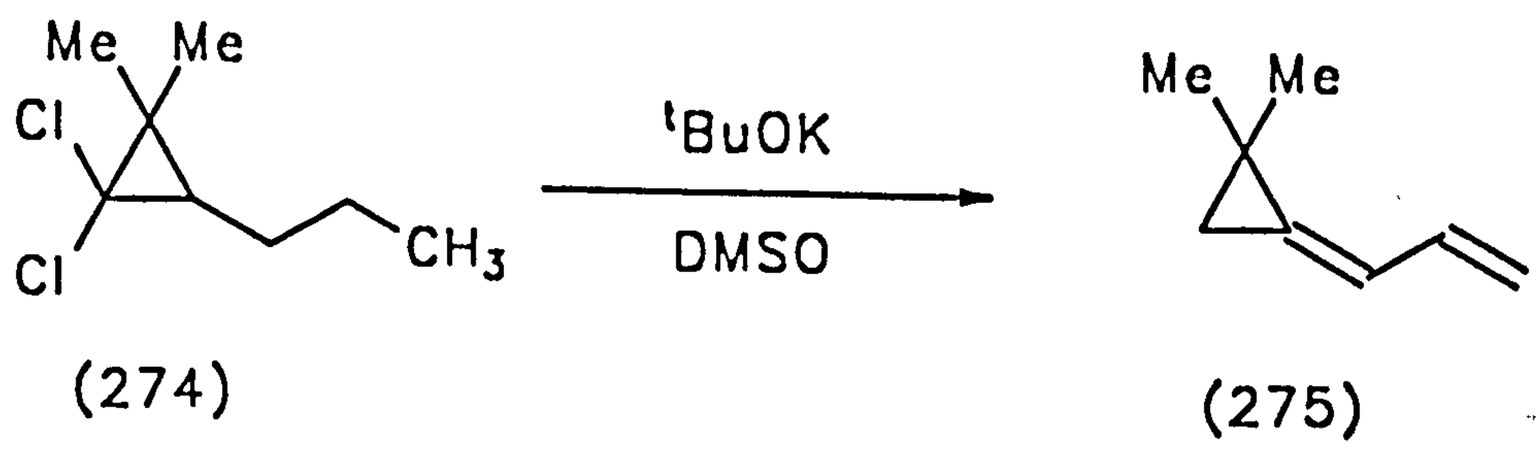
Introduction:

Base induced dehydrohalogenation of halo– and dihalocyclopropanes offers a simple route to cyclopropenes, though more typically products of isomerisation or nucleophilic addition are observed, particularly if the reagent is a strong nucleophile or the cyclopropene is highly strained. In some cases, isomerisation leads to vinylalkylidene cyclopropanes, e.g., reaction of 1,1–dichloro–2–ethyl–3–methylcyclopropane (272) with potassium t–butoxide in dimethylsulphoxide gave (273) in good yield.[125]



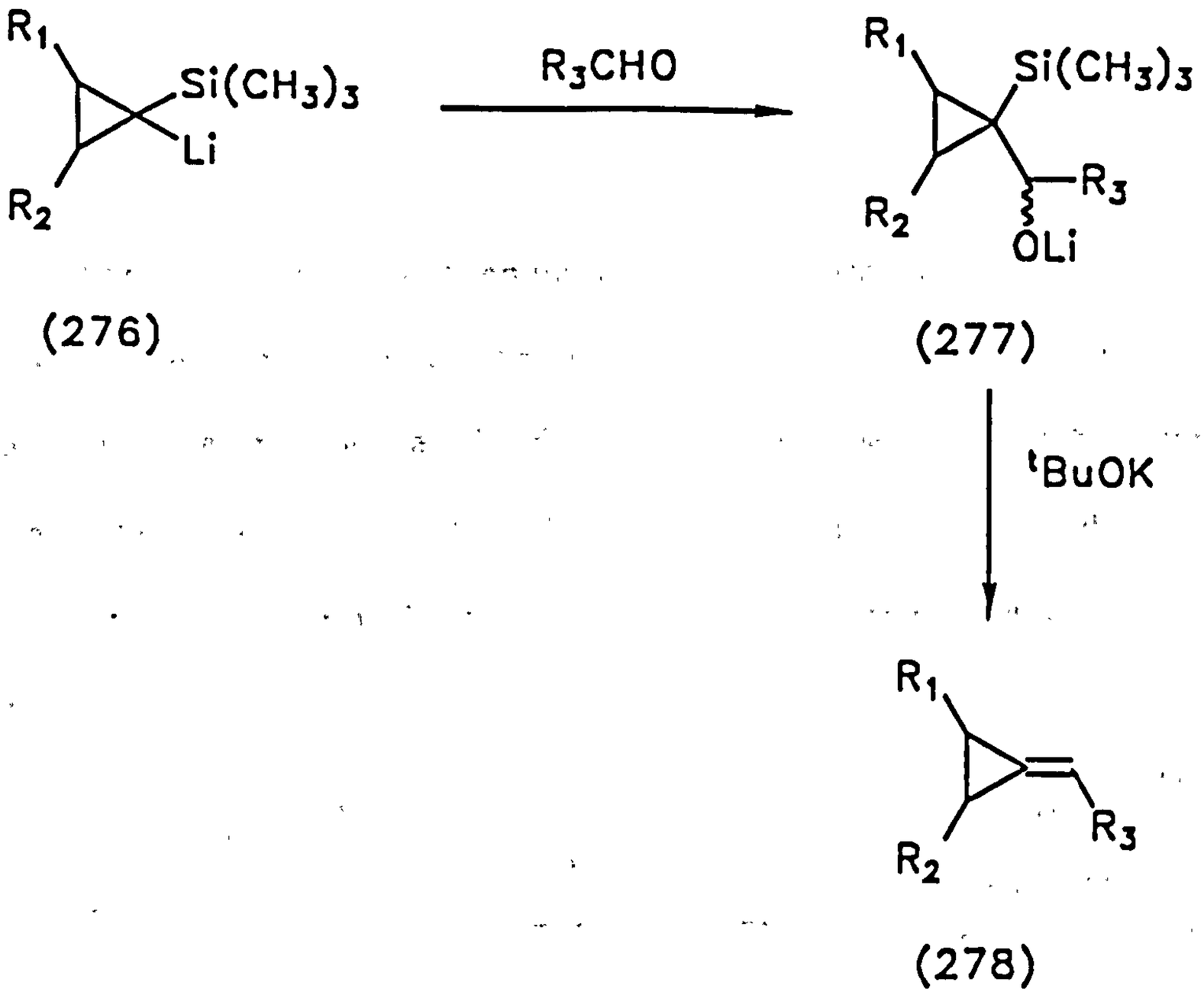
(272) (273)

Moreover, reaction of 1,1–dichloro–2,2–dimethyl–3–propylcyclopropane (274) with potassium t–butoxide in dimethyl sulphoxide, causes two hydrogen chloride eliminations to take place in the same direction to give the diene (275).[125]



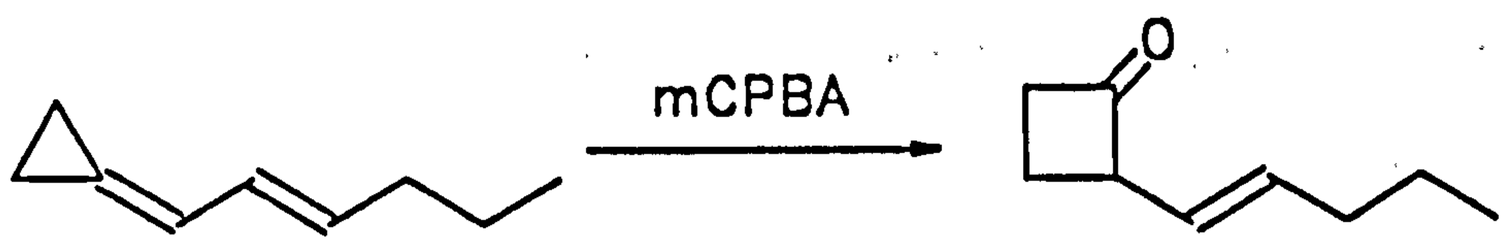
(274) (275)

However, there are generally more convenient routes to alkylidene and allylidene cyclopropanes, e.g., reaction of (276) with aldehydes gives (277), which in turn reacts further with 3.0 equiv. of potassium t–butoxide to give (278).



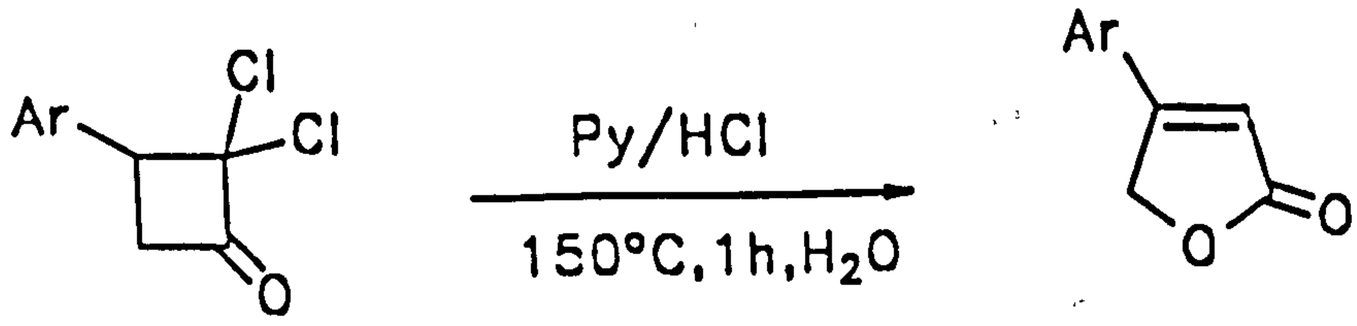
(276) (277) (278)

Allylidene cyclopropanes have been shown to be valuable intermediates in organic synthesis, e.g., oxidizing (279) with mCPBA gave, after rearrangment, the cyclobutanone (280) in good yield.[126]



(279) (280)

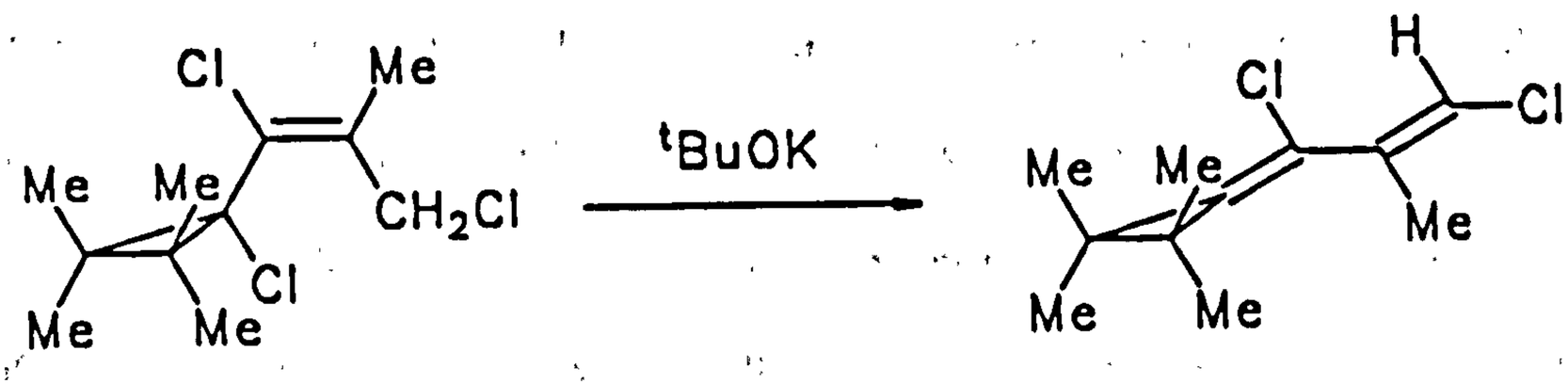
Cyclobutanones are useful intermediates in organic synthesis, and have been shown to be precursors of a variety of five, six and eight membered rings, as well as of functionalized acyclic fragments; e.g., reaction of (281) with Py/HCl in acetonitrile. gave (282) after rearrangement.[127]



(281) (282)

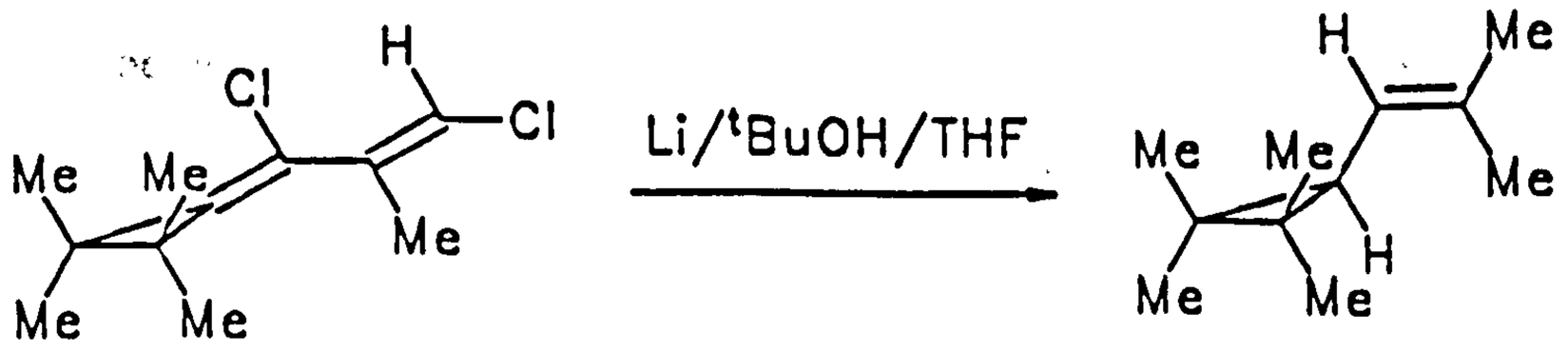
Discussion.

As mentioned before, ring–opening of the cyclopropenes (193) and (195), in the presence of alkene leads to cyclopropanes , e.g. (227). Reaction of (227_a) with potassium t–butoxide in ether at 0 °C, followed by quenching with water, removal of the solvent, then flash distillation of the residue at 35 °C and 0.3 mmHg gave 1–(1,3–dichloro–2–methylprop–2–en–1–ylidene)–2,2,3,3–tetramethylcyclopropane (283) in 89% yield.



(227_a) (283)

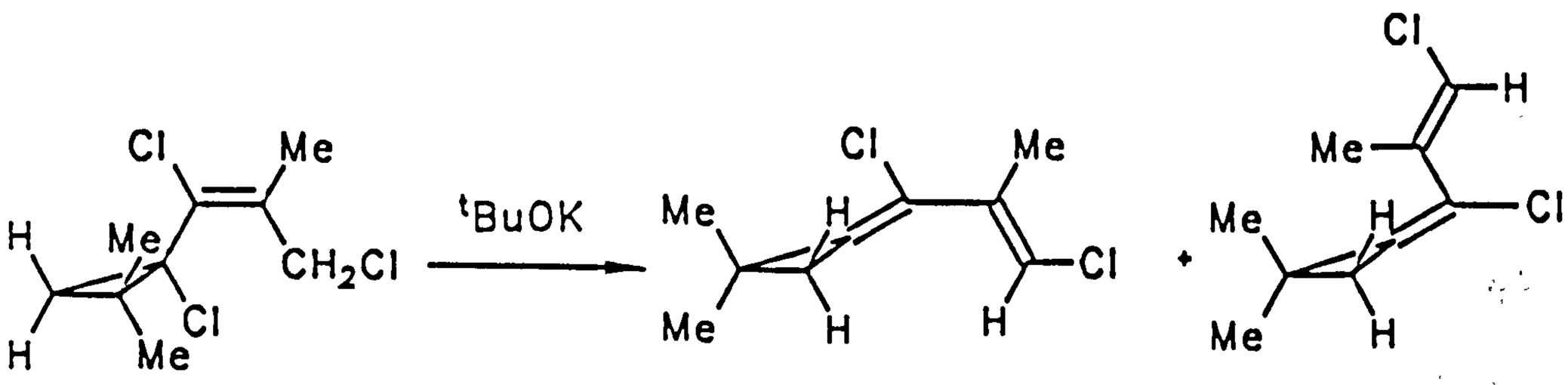
The ^1H n.m.r. spectrum of this included a narrow quartet in the olefinic region at δ 6.6 (1H) with long range coupling (1.2 Hz) with the methyl group, and a doublet at δ 1.97 (3H) (J 1.2 Hz) together with two singlets assigned to the four cyclopropyl methyl substituents at δ 1.23 (6H), 1.22 (6H). This compound is apparently derived by abstraction of the allylic proton from the chloromethyl group followed by 1,4–elimination. The stereochemistry at the terminal alkene is assigned as *E*– on steric grounds. Reduction of (283) with Li–^{t}BuOH–THF gave (284) in moderate yield.



(283) (284)

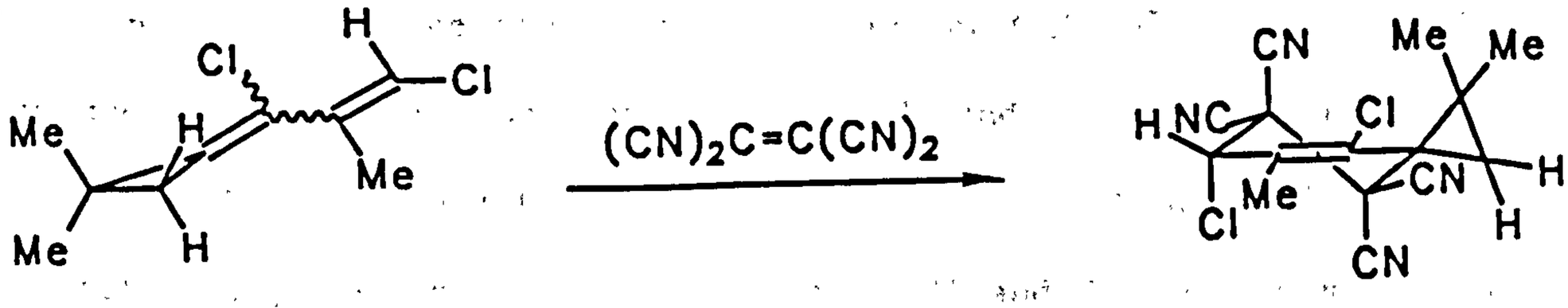
This compound gave a molecular ion with an accurate measured mass for $C_{11}H_{20}$, while the ^1H n.m.r. spectrum exhibited a broad doublet at δ 4.93 with coupling constant 7.4 Hz, further split by 1.38 Hz, together with singlets at δ 1.73 and 1.66 for the olefinic methyls and at δ 1.11 (6H) and at δ 0.93 (6H) for the cyclopropyl methyl groups; the final signal was a broad doublet at δ 0.88 with coupling constant 7.4 Hz for the cyclopropyl proton.

Reaction of (227_b) with potassium t-butoxide in ether at 0 °C for 30 min. gave a crude product which was a mixture of diastereoisomeric allylidene cyclopropanes (285) in ratio 1:1. G.l.c. showed two peaks very close together, and it was difficult to separate them by preparative g.l.c. Column chromatography of the crude product afforded the mixture as a colourless oil in 74% yield with no change in the isomer ratio. Assignment of the isomers was made by noting that the cyclopropylmethylene protons of (285_a) were shielded by the alkenyl group and resonated 0.26 ppm upfield compared with the other isomer (285_b).



(227_b) (285_a) + (285_b)

When the mixture of the diastereoisomers (285) was allowed to react with 1.1 equiv. of tetracyanoethene for 72 h at room temperature a mixture of spirocompounds (286) was obtained in ratio 1:1; this was recrystallised to afford the mixture in 35% yield with no change in the isomer ratio.



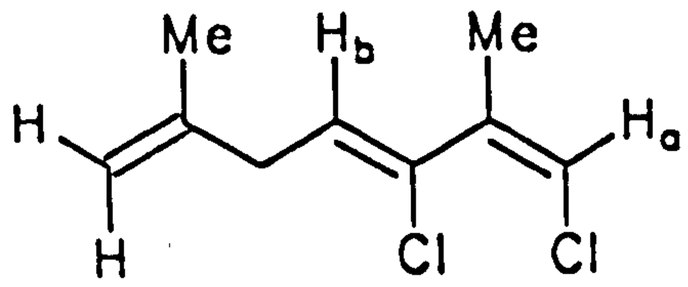
(285)

(286$_a$)

(286$_b$)

On the basis of ^1H n.m.r. spectroscopy, the first isomer was assigned as (286$_a$) because the cyclopropyl methyl protons resonated 0.43 ppm downfield from the corresponding protons of (286$_b$) due to deshielding by the cyano-group. The two isomers show a pair of doublets for the geminal protons of the cyclopropane with coupling constants 7.0 and 7.25 Hz, and a fine quartet for the allylic protons with small coupling constants of 0.93 and 1.0 Hz, due to a long rang coupling with the methyl group.

However, when the mixture of (285$_a$) and (285$_b$) was allowed to stand in $CDCl_3$ for one week, one of the isomers was largely changed to the triene (287).[128] It was difficult to separate the latter from the unchanged isomer by column chromatography or by preparative g.l.c; however, when the mixture was allowed to react with tetracyanoethene in CH_2Cl_2 for two days, the triene was left unreacted and could be separated by column chromatography.

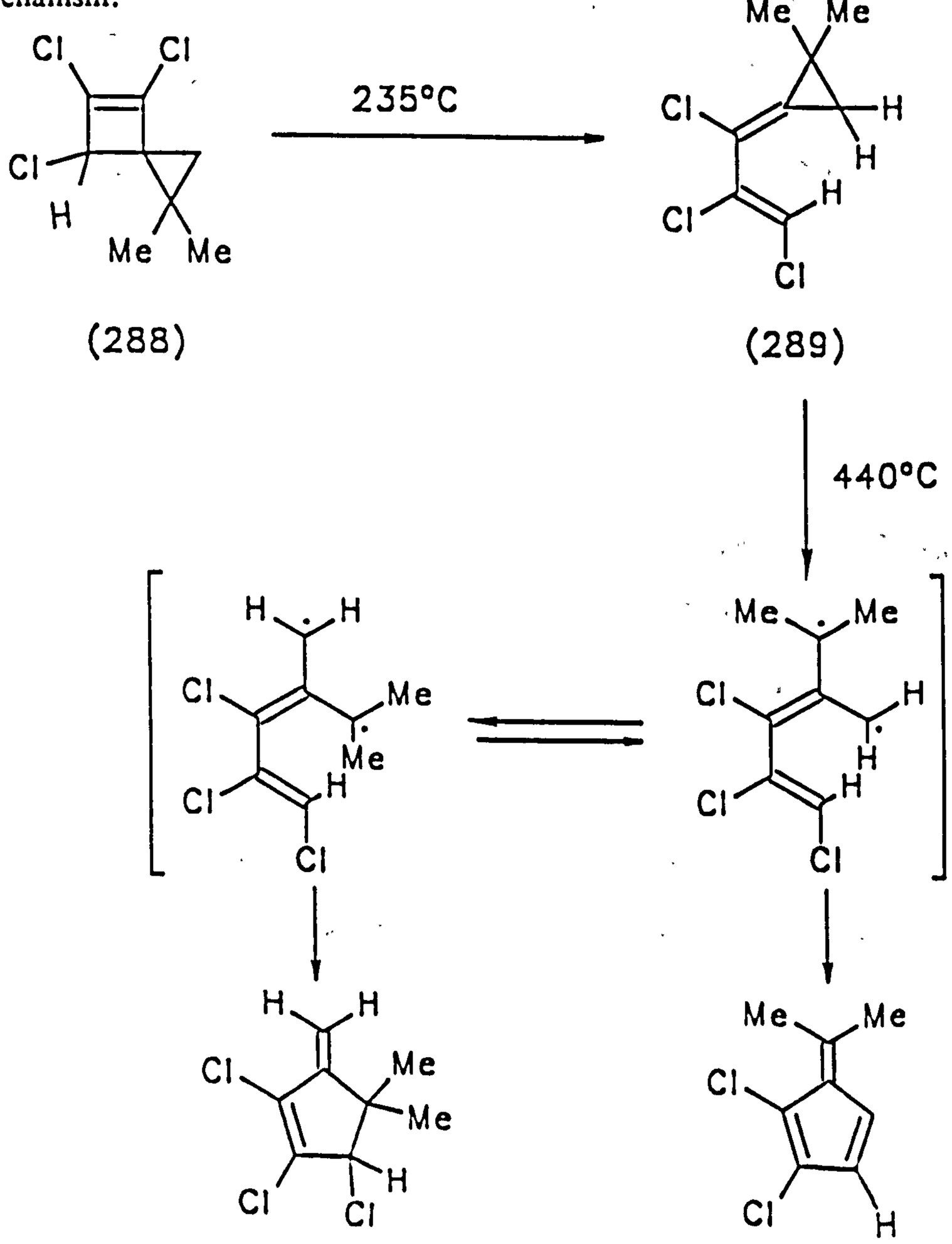


(287)

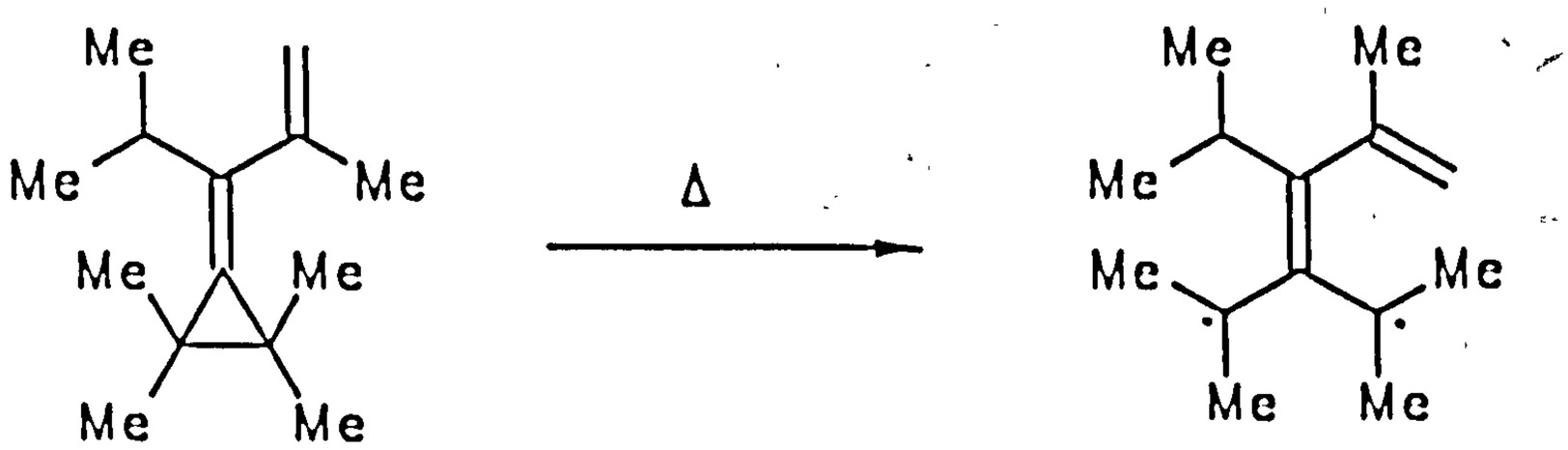
The triene (287) gave the correct measured mass for $C_9H_{12}Cl_2$ while the ^1H n.m.r. spectrum showed a broad singlet at δ 6.64 for H_a and a triplet for H_b with coupling constant 7.1 Hz, together with two broad doublets at δ 4.75 and 3.02 for the vinylic and methylene protons with coupling constants 8.94 and 7.2 Hz respectively and the olefinic methyls at δ 2.03 and 1.7.

Unfortunately, the adduct of the second isomer with tetracyanoethene could not be isolated. If the orginal ^1H n.m.r. spectrum of the mixture was compared with the triene spectrum, it was found that the triene had resulted from the rearrangement of (285_b) because the signals at δ 1.27 and 1.2 disappeared.

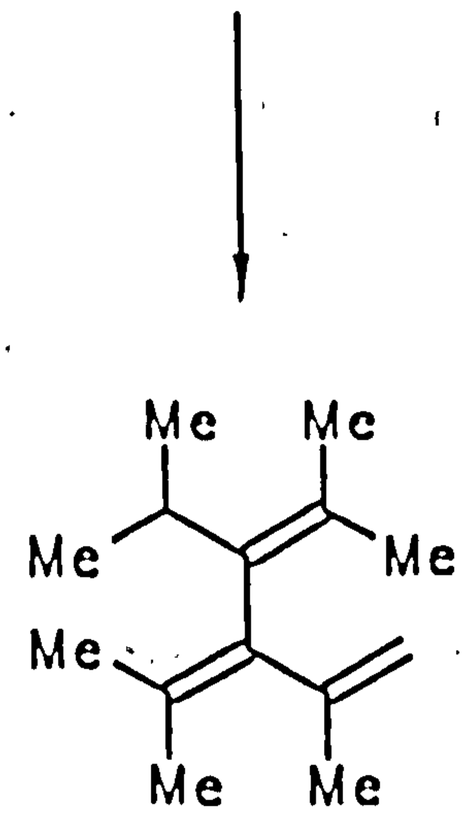
It is as yet unclear why one isomer changed and the other did not. In the literature, when the spirocompound (288) was subjected to pyrolysis at 235 ^0C it gave (289) which in turn rearranged at 440 ^0C to give (290) and (291) through a free radical mechanism.[129]



Moreover, when the allylidenecyclopropane (292) is pyrolysed the triene (294) is obtained by homolysis of the 2,3-bond of the cyclopropane to give the biradical (293); there appear to be three possible routes from this biradical to the triene, but, by deuterium labelling, it was found that a 1,6-hydrogen shift occurs.[128]

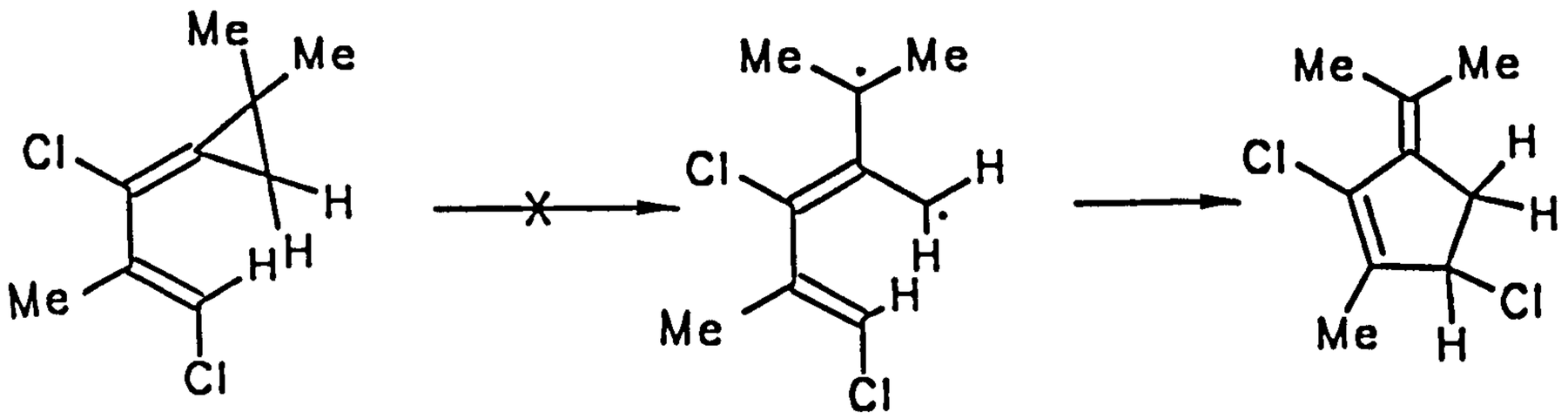


(292) (293)

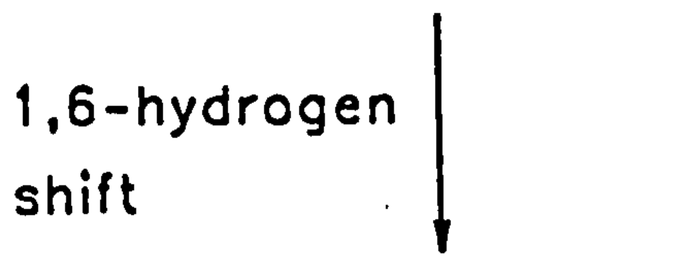


(294)

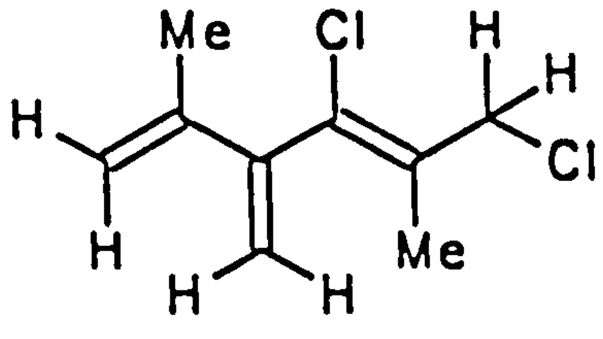
According to this, and supposing our compound gives the biradical (295), this could rearrange to afford (296) or give (297) through a 1,6-hydrogen shift.



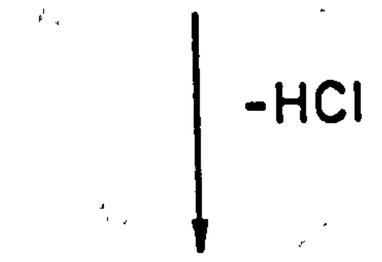
(295)



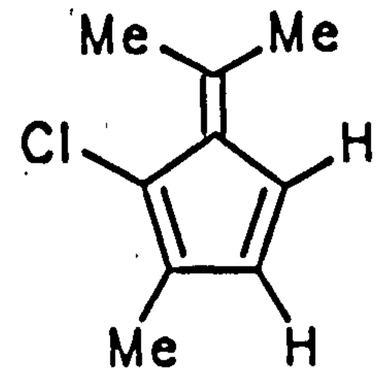
1,6-hydrogen shift



(297)



-HCl

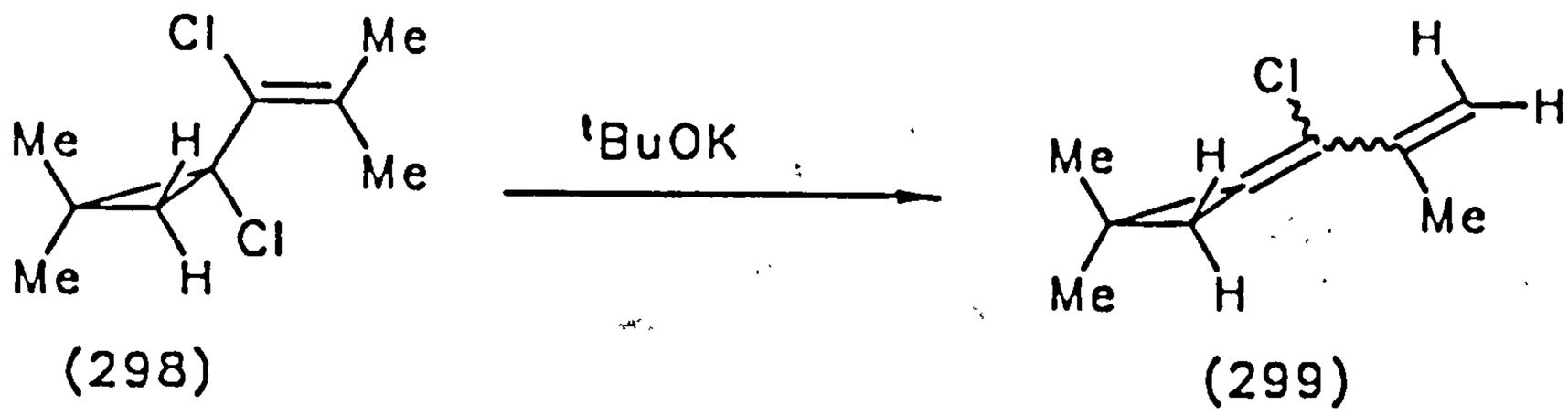


(296)

However, the ^1H n.m.r. spectrum of the product does not fit these compounds, i.e., the allylidenecyclopropane is not reacting through this free radical. It may react through an intermolecular reaction by protonation of the σ-bond of the cyclopropane or by intramolecular rearrangment.

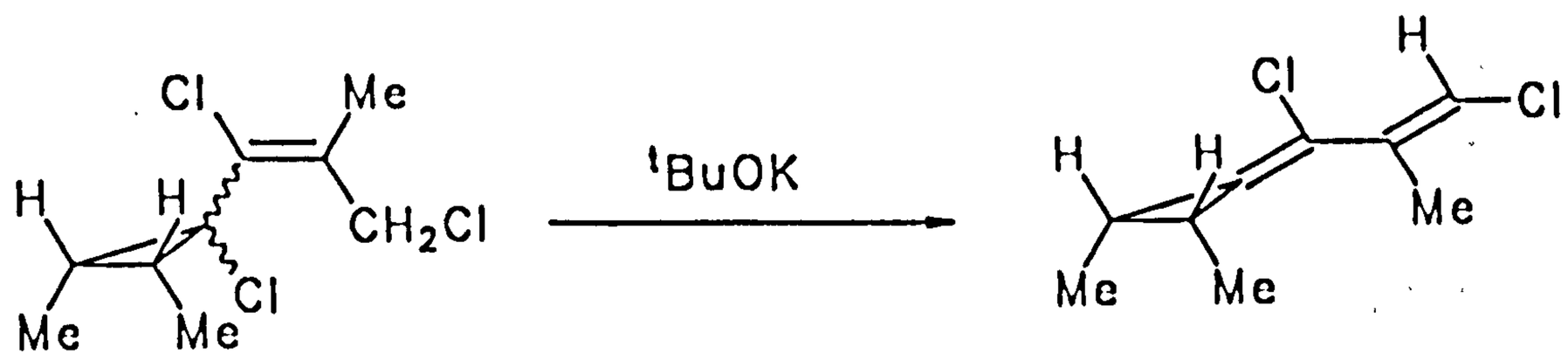
(287)

Reaction of (298) with potassium t-butoxide in ether at 0 ^0C led to a mixture of isomers of (299). These isomers were stable in $CDCl_3$ for several days.



(298) (299)

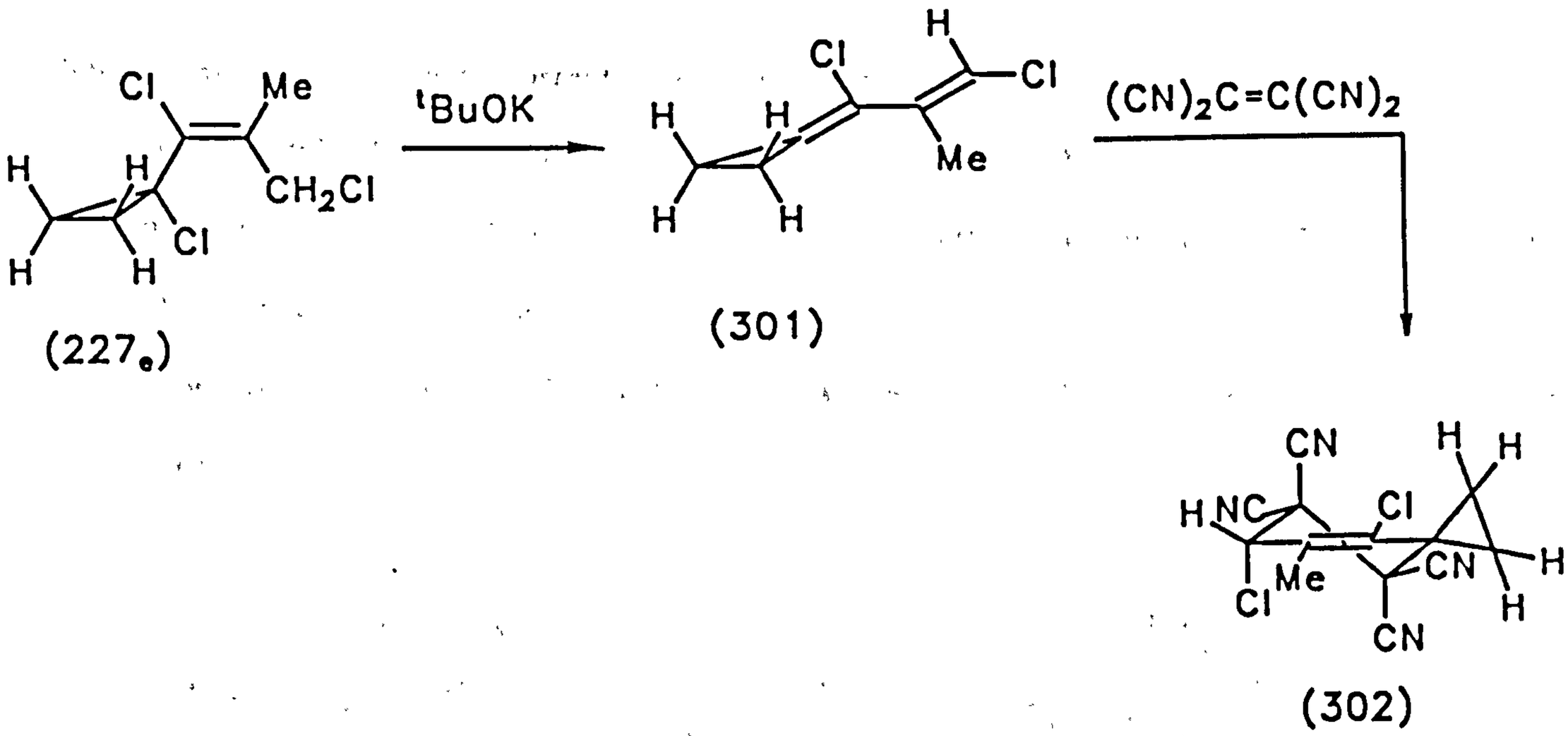
Treatment of (227_c and 227_d) with potassium t-butoxide in ether at 0 °C followed by quenching with water at 0 °C after 0.5h, gave (300) as a clear oil in 81% yield.



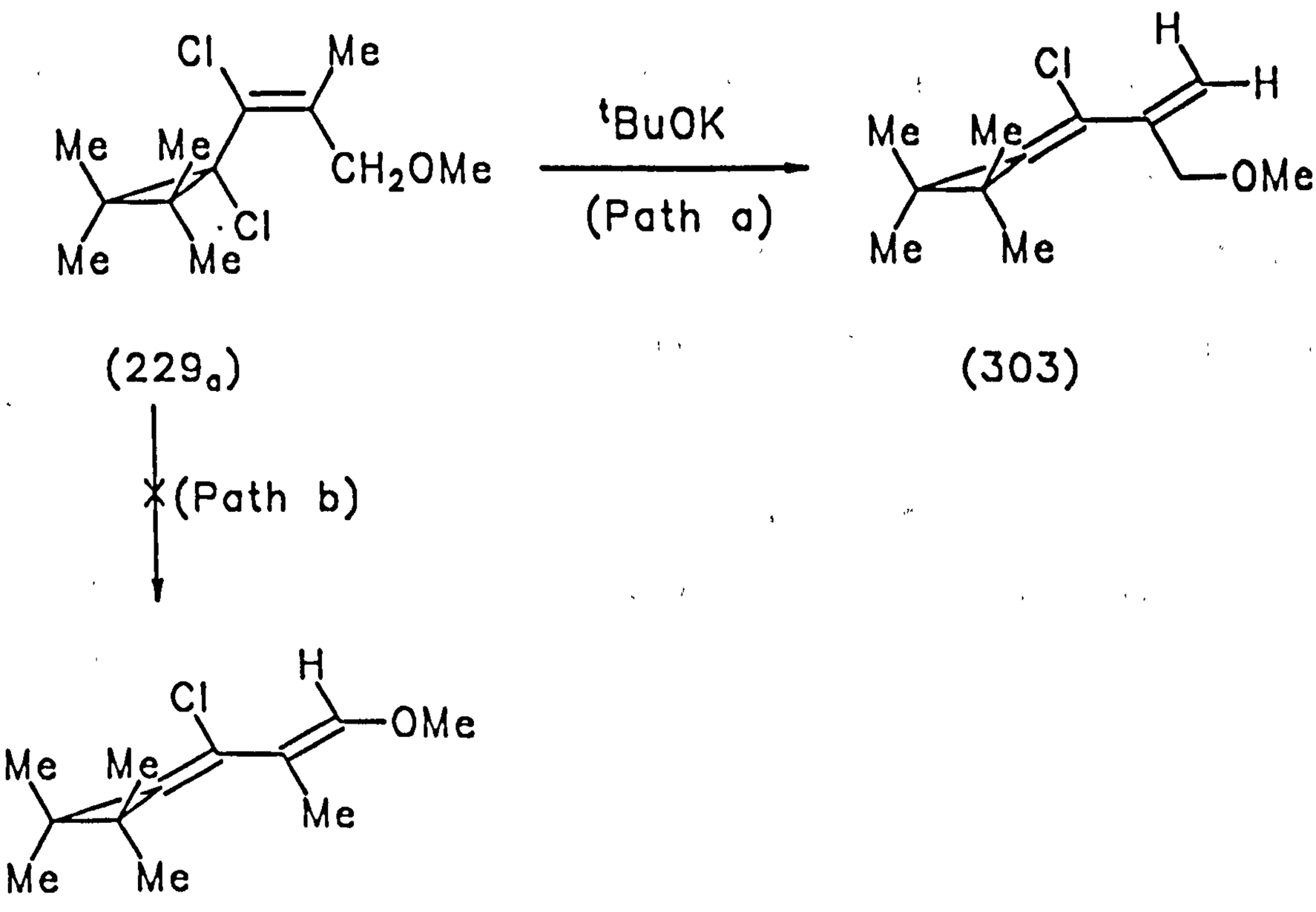
$(227_c) + (227_d)$ (300)

The ^{1}H n.m.r. spectrum of this contained a broad singlet at δ 6.68 (1H), a narrow doublet at δ 2.04 (3H), and multiplets at δ 1.98 (1H) and δ 1.74 (1H), together with a pair of doublets at δ 1.17 (3H) and at δ 1.13 (3H) with coupling constants 7.26 and 7.21 Hz. If the spectrum was taken immediately after removing the ether, the allylidenecyclopropane appeared relatively pure. However, within about one hour of attaining room temperature, the product became a complex mixture by TLC and n.m.r., which could not be separated by chromatography on silica.

Treatment of (227_e) with potassium t-butoxide at 0 °C, followed by work up as before afforded one isomer (301) in 70% yield as a clear yellow oil. The ^{1}H n.m.r spectrum showed a broad singlet at δ 6.45 (1H), a broad singlet at δ 2.2 (3H) together with a multiplet at δ 1.5 (4H). When the crude product was allowed to react with tetracyanoethene in dichloromethane, the spirocompound (302) was obtained in low yield (21%).

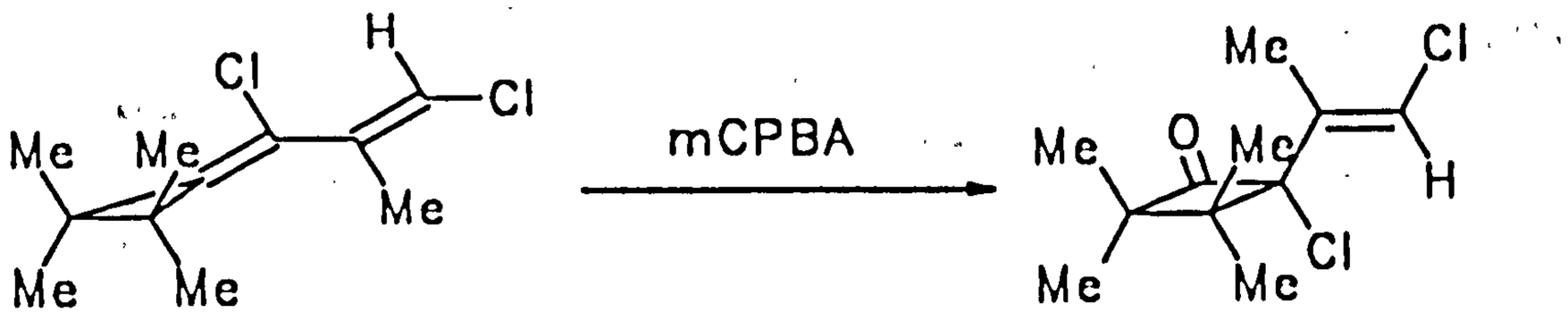


However, reaction of (229_a) with potassium t-butoxide in ether at 0 ^{0}C, followed by quenching with water, removal of the solvent, and flash distillation of the residue at 35 ^{0}C and 0.3 mmHg gave 1-(1-chloro-2-methoxymethylprop-2-en-1-ylidene)-2,2,3,3- tetramethyl cyclopropane (303) in 86% yield.[116] The product is derived by proton abstraction from the methyl group (path a) rather than from the methylene (path b), followed by 1,4-elimination.



The compound showed correct measured mass for $C_{12}H_{19}OCl$, while the proton spectrum contained two broad singlets at δ 5.58 and 5.28 for the vinylic protons, a two hydrogen singlet at δ 3.8, a singlet for the methoxy group at δ 3.3, and a singlet at δ 1.2 for cyclopropyl methyl substitutents.

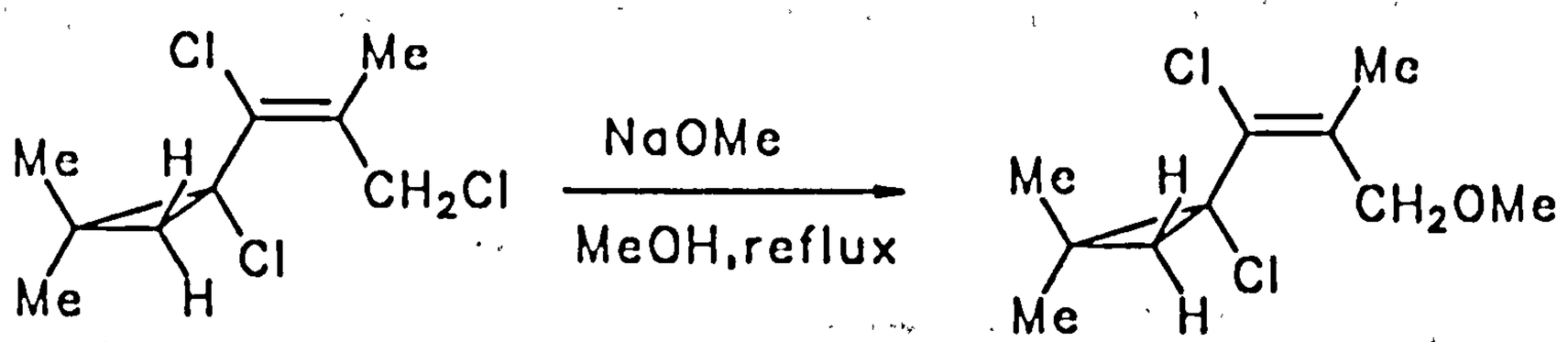
The oxidation of (283) with mCPBA gave the 2-vinylcyclobutanone (304) in moderate yield.



(283) (304)

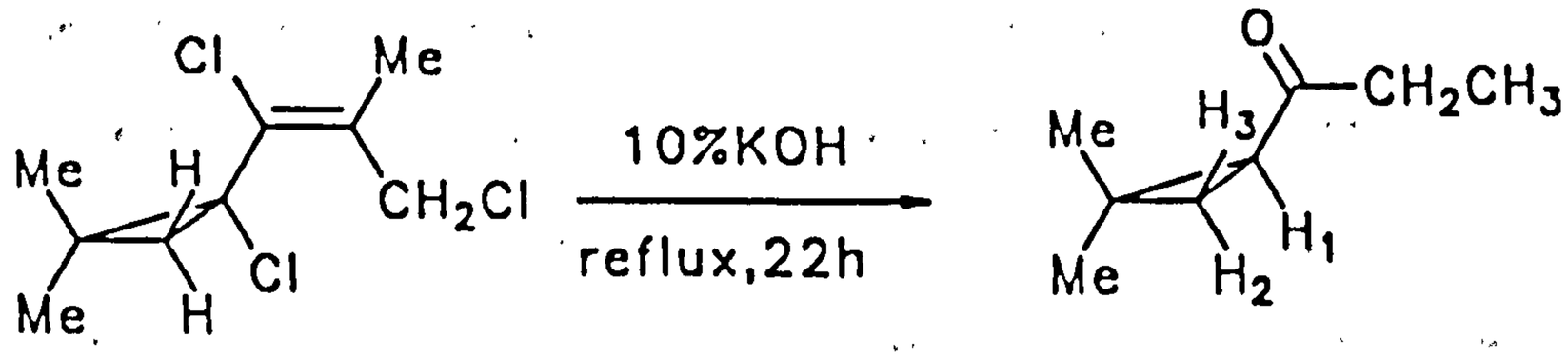
The i.r. spectrum contained a sharp band at 1782 cm^{-1} for a four ring ketone,[130] while the mass spectrum showed no molecular ion, but fragments were observed at m/e 219 ($M^+ - CH_3$), 199 ($M^+ - Cl$). The ^1H n.m.r. spectrum showed a narrow quartet at δ 6.3 (1H) with coupling constant 1.4 Hz and a narrow doublet at δ 1.85 (3H) together with three singlets at δ 1.36 (6H), 1.16 (3H) and 1.09 (3H). The first singlet appeared downfield due to the deshielding by the carbonyl group. The ^{13}C showed the expected eleven signals, including one in the saturated ketone region and two in the olefinic region, together with eight signals at δ 84.9, 61.2, 44.5, 23.1, 22.3, 21.78, 19.4 and 14.5. The product may arise by epoxidation of the double bond exocyclic to the cyclopropane rather than the terminal double bond due to its more nucleophilic character, which after rearrangment gives the final product.[126]

As stated previously (2.3.3), refluxing (227_a) with sodium methoxide in methanol leads to (229_b).



(227_b) (229_b)

However, refluxing (227_b) with 10% potassium hydroxide for 22 h, gave 2,2-dimethyl-1-cyclopropyl ethyl ketone (305) in 61% yield.

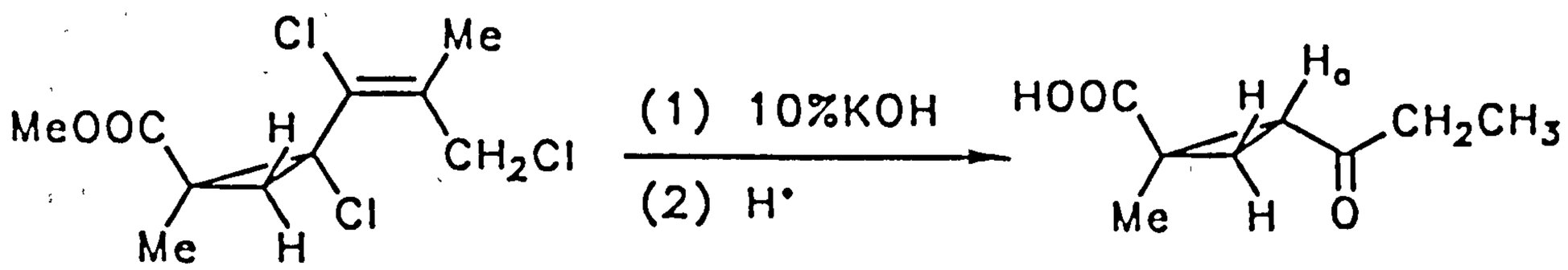


(227_b) (305)

The i.r. spectrum this compound contained a sharp band at 1697 cm^{-1} assigned to the saturated carbonyl group. The ^1H n.m.r. spectrum showed a quartet at δ 2.5 with coupling constant 7.3 Hz (2H adjacent to the carbonyl group), and three double doublets for the cyclopropyl protons; H_1 shows a double doublet at δ 1.83 with coupling constants 5.6 and 7.53 Hz, H_3 a double doublet at δ 1.23 with coupling constants 3.9 and 5.6 Hz, and H_2 a double doublet at δ 0.8 with coupling constants 3.9 and 7.6 Hz. From these values H_1 is *cis* to H_2 and trans to H_3 because it is known that the observed coupling constant for *cis* related cyclopropane protons is of the order of 6-12 Hz, whereas for *trans*-systems the values are typically in the range 4-8 Hz.[131] There were also two singlets for the cyclopropane methyl groups (one at δ 1.19 shows downfield chemical shift compared to the other methyl at δ 1.06 due to deshielding by the carbonyl group), and a triplet for the methyl protons of the ethyl group at δ 1.07 with coupling 7.3 Hz.

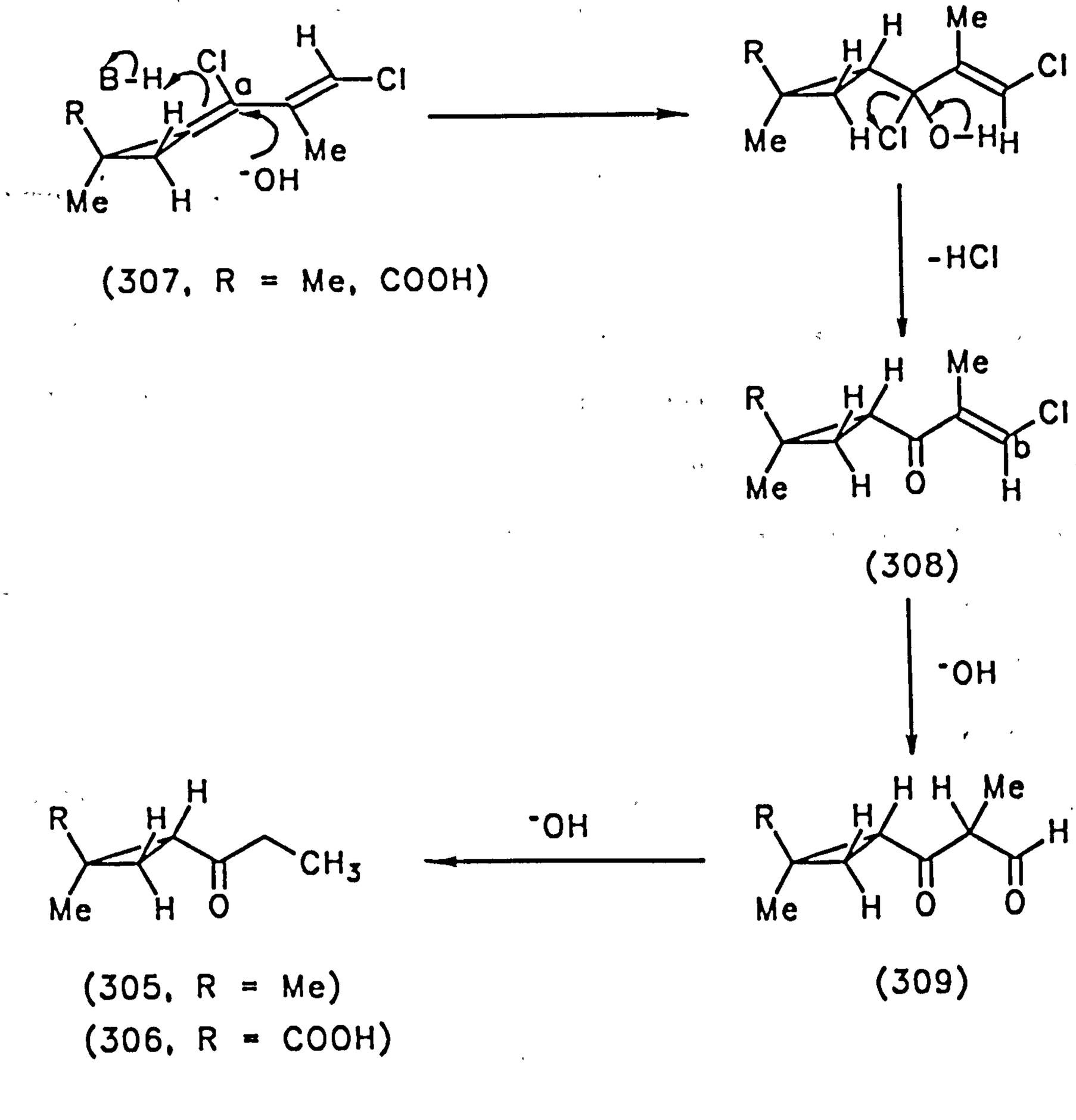
Moreover, refluxing (230_b) with 10% KOH for three hours, followed by

acidification gave 2-(propan-1-oyl)-1-methylcyclopropane carboxylic acid (306) in 90% yield:

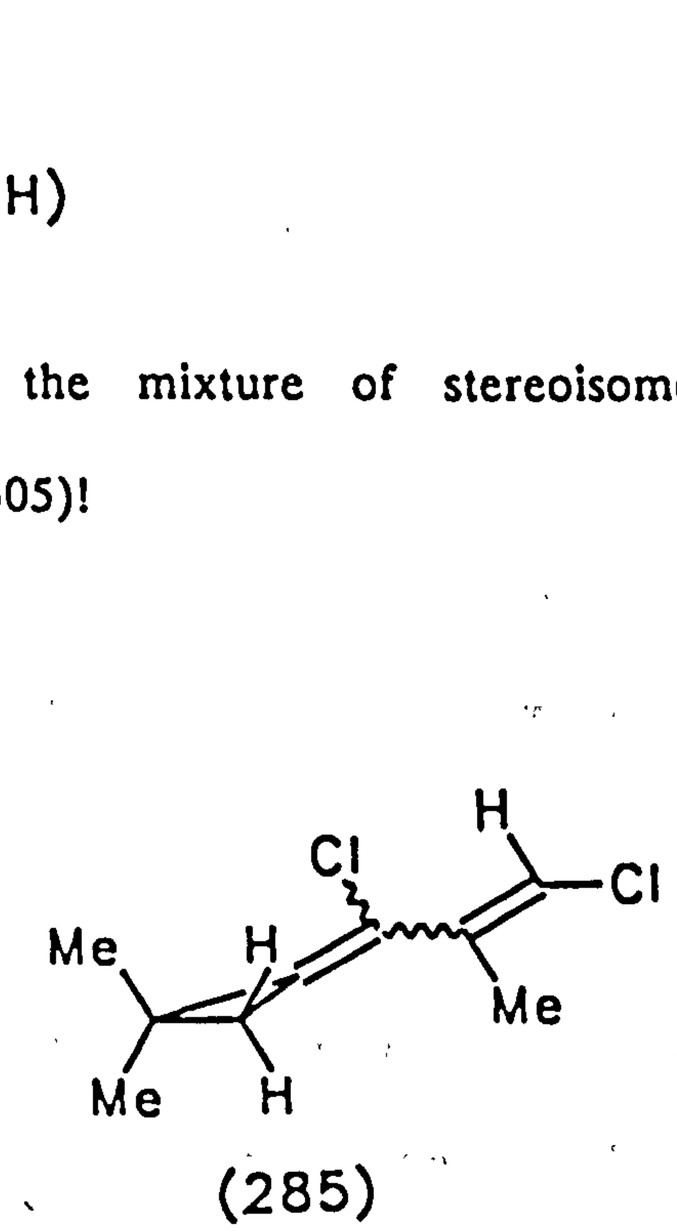


(230b) (306)

The compound showed one peak by g.l.c. and an accurate measured mass for $C_8H_{12}O_3$, while the i.r. spectrum contained a very broad band at 3086 cm^{-1} assigned to the O-H stretching of the carboxyl group and a sharp band at 1695 cm^{-1} assigned to a saturated carbonyl compound. The ^{13}C spectrum showed the expected eight signals, including two signals in the carbonyl region, one at δ 206.57, assigned to the saturated carbonyl group and the other at δ 180.35 characteristic of the carbonyl of the acid group, together with six signals in the saturated region at δ 38.34, 34.5, 29.0, 21.46, 12.28 and 8.0. The ^1H n.m.r. spectrum contained a double doublet at δ 2.68 (H_a) with coupling constant 8.35 and 6.7 Hz, a quartet at δ 2.6 for the methylene protons of the ethyl group, which appears to be split by 1.7 Hz and a pair of double doublets at δ 1.56, together with a singlet at δ 1.27 and a triplet for the methyl at δ 1.09. The stereochemistry of the acid (306) was assigned as *E*- because the signals for the two hydrogens on C_3 of the cyclopropane appeared at very similar chemical shifts, whereas in the *Z*- compound a large shift difference would have been expected.[132] A reasonable explanation of the formation of (305) and (306) may involve attack of the hydroxide ion at C_a of the diene (307, R = Me, COOH) followed by loss of chloride ion to give (308), which reacts further with hydroxide ion at C_b leading to the formation of a 1,3-dicarbonyl compound (309) and fragmentation by attack of hydroxide ion at the aldehyde carbon with concomitant loss of formic acid to give the final product.



However, treatment of the mixture of stereoisomers of (285) under the reaction condition did not give (305)!



(285)

2.3.6: The selectivity of carbene addition to alkenes.

INTRODUCTION:

Early studies on addition of halocarbenes to alkenes indicated that ($:CCl_2$) and ($:CBr_2$) are electrophilic, exhibiting higher reactivity towards alkenes with larger numbers of alkyl substitutents. Skell and Garner,[133] investigated the addition of ($:CBr_2$) to a set of alkenes. The carbene in each case was generated in the presence of known quantities of two olefins, which were chosen for the ease of separation by distillation of their respective adducts, assuming these products were stable. The relative rates of addition were calculated from equation (2), where K is the rate constant for reaction of the carbene with alkenes, X and Y; x_o and y_o are the initial alkene concentration, X and Y being the final concentration.

$$K_Y/K_X = \log (Y/y_o) / \log (X/x_o) \quad \text{.....(2)}$$

In 1958, Doering and Henderson,[134] extended this idea to ($:CCl_2$) at -10 to -20 ^{0}C, the relative quantities of the two products in the reaction mixture being determined by vapour phase chromatography. The ratio of the reaction rates was calculated from equation (3), where P is the mole fraction of product cyclopropane and O is the initial mole fraction. The error involved in the calculation is small if the alkenes (a and b) are present in more than 6 – 7 fold excess.

$$K_a / K_b = P_a / P_b \times O_b / O_a \quad \text{.....(3)}$$

Doering suggested that the selectivity, or relative rate response, of a carbene :CXY to changes in alkene structure could be defined by plotting the logarithms of the relative reactivities for :CXY (adjusted to standard alkene), against those of standard a carbene $:CCl_2$. The slope would give a measure of the carbene's ability to discriminate between alkenes.

The selectivity of a carbene may be interpreted in terms of its electrophilicity. More electrophilic carbenes react more rapidly where as less electrophilic carbenes show greater selectivity between electron rich and electron poor double bonds.

Moss[135] developed a general empirical correlation of carbene selectivity which adopted the following conventions; a standard set of alkene substrates ($Me_2C=CMe_2$, $Me_2C=CHMe$, $Me_2C=CH_2$, *cis*–MeCH=CHMe, and *trans*–MeCH=CHMe), with $Me_2C=CH_2$ as the reference alkene (K_O=1.0); a standard carbene, $:CCl_2$. Relative reactivities (K_i/K_o) are measured at 25 ^oC for :CXY and for $:CCl_2$. The carbene selectivity index, (m_{CXY}) for that carbene is then defined by equation (4).

$$\log (K_i/K_o)_{CXY} = m_{CXY} \log (K_i/K_o)_{:CCl_2} + 1.0 \quad .....(4)$$

Hence, a least squares slope of $\log (K_i/K_o)_{CXY}$ *vs* $\log (K_i/K_o)_{:CCl_2}$ would give (m_{CXY}).

Data accummulated in this way are presented in table (2).[135] For simplicity only singlet carbenes (those adding stereospecifically to alkenes) are considered.

TABLE (2)

OBSERVED AND CALCULATED CARBENE SELECTIVITY INDICES (m_{CXY})

Carbene	m_{CXY}^{obs}	m_{CXY}^{cal}
$:CF_2$	1.48	1.47
:CFCl	1.28	1.22
$:CCl_2$	1.0	0.97
$MeS\ddot{C}Cl$	0.91	
$Ph\ddot{C}F$	0.89	0.94
$Ph\ddot{C}Cl$	0.83	0.71
$Ph\ddot{C}Br$	0.70	0.64
$:CBr_2$	0.65	0.82
$Me\ddot{C}Cl$	0.50	0.58
$BrC\ddot{C}O_2Et$	0.29	0.26

Correlating the observed values of m_{CXY} with the Hammett σ_R^+ and σ_I constant leads to the dual substitution parameter correlation, eq. (5), in which $\sum_{XY}$ represents the sum of appropriate σ constants for the substituents of C_{XY}.[135]

$$m_{CXY} = -1.10 \sum_{X,Y} \sigma_R^+ + +0.53 \sum_{X,Y} \sigma_I - 0.31 \quad .....(5)$$

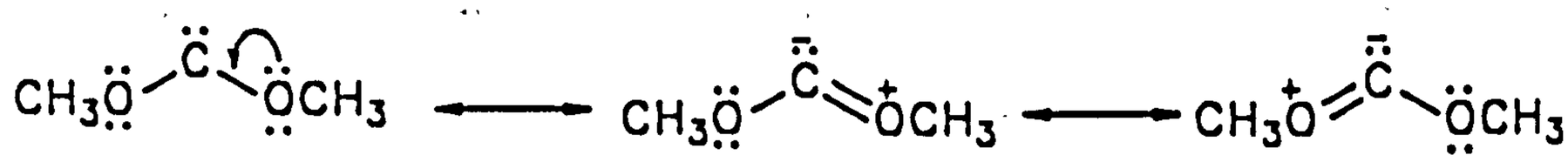
The calculated values of m_{CXY} (table 2) demonstrate the consistency of this correlation.

The m- value is a function of the carbene's stability and philicity, increasing as the selectivity increases, and the stability depends on the ability of substituents to donate electrons to the empty p-orbital, coupled with the ability to stabilise the resulting dipolar resonance form by inductive electron withdrawal; the stability of

dihalocarbenes decreases in the order.

$$:CF_2 > :CCl_2 > :CBr_2$$

With highly electron donating substituents, the dipolar resonance form e.g. (A) may become so strongly stabilized that the carbene does not add to the standard nucleophilic alkenes but instead adds to electrophilic alkenes, and in this case the m-value can not be determined experimentally but can be calculated by equation (5).[135]

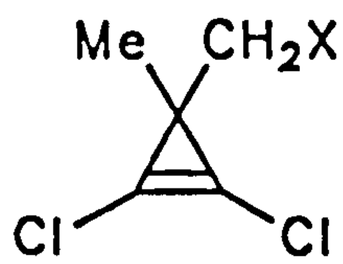


(A)

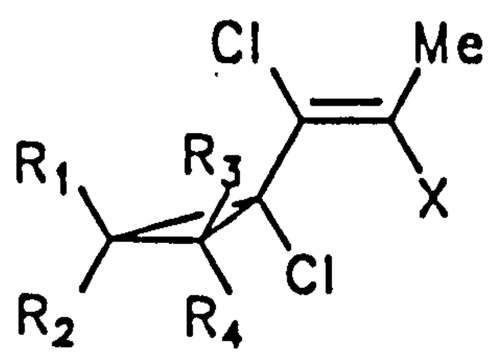
For example, the m-values of nucleophilic carbenes are 2.22 for dimethoxycarbene and 2.91 for dimethylaminocarbene. Intermediate m-values between 1.48 for $:CF_2$ and 2.22 for $:C(OCH_3)_2$ are predicted to correspond to ambiphilic carbenes. These carbenes could add to both electron poor and electron rich alkenes, with the rate of addition increased by either increasing electron density or increasing electron deficiency.

DISCUSSION.

As mentioned previously, ring–opening of cyclopropenes to unsaturated carbenes has been widely reported under both photochemical and thermal conditions.[73,76] The reverse process is also widely applied as a route to cyclopropenes.[73,76] Substituents can have a marked effect on the rate of the thermal ring–opening. In particular there are a number of reports of 3,3–dimethylcyclopropenes having an electron withdrawing substituent at C_1 which ring–open at ambient temperature or below.[103,104] Thus, while 3,3–dimethylcyclopropene[99] and 1,2,3,3–tetrachlorocyclopropene[101] undergo ring–opening at a reasonable rate only at 180 ^{0}C, the dichlorides (310, X = Cl, OMe, Ar)[110,116] which have been discussed previously and (310, X = H)[104], react with alkenes ($R_1R_2C{=}CR_3R_4$) at 20 ^{0}C or below to produce cyclopropanes (311) apparently derived by addition of the corresponding carbene (312). Although there are a number of possible singlet and triplet structures for vinylcarbenes,[136] one possible explanation for the difference in ease of ring–opening would invoke a monorotation about the C_2–C_3 bond to produce a carbene which, if drawn in its dipolar singlet resonance form (313) could be stabilized by electron releasing substituents at C_3 and electron withdrawing ones at C_1.



(310)



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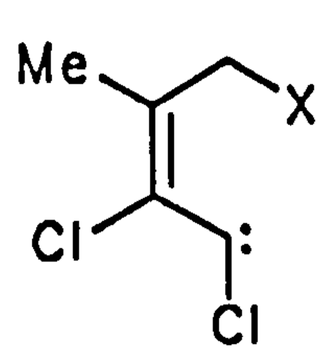
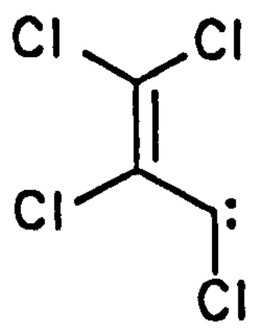
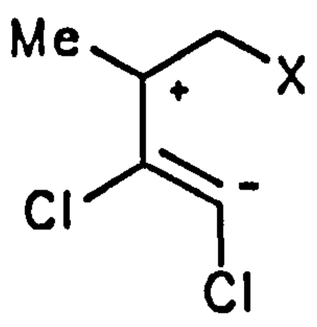


(312)



(232)



(313)

In order to probe these effects, the effect of changing the substitution pattern at C_3 on the rate of ring–opening of (310, X = Ar) and the selectivity of trapping the derived carbene (312, X = OMe) were examined.

(a) The selectivity of carbene (312, X = OMe).

Measurement of the ratio of products arising from reaction of a carbene with a competing pair of alkenes may be performed conveniently and with reasonable accuracy by capillary gas chromatography of the reaction mixture. The ratio of the areas of the peaks corresponding to the adducts will be the ratio of the product concentrations provided that the G.C. detector responses are calibrated for each adduct.

The competition reactions were carried out as follows. A binary mixture of alkenes (each *ca.* 10 fold excess) were added or condensed in a pre–weighed thick–walled glass tube, cooled in acetone/dry ice and a solution of the cyclopropene in ether was introduced. After sealing with a screw–top, the solution was stirred at room temperature for 12 h. The tubes were again cooled before opening, and the ratio of derived cyclopropanes (311, X = OMe) was determined by g.l.c., standardizing the responses with known mixtures of cyclopropanes. Each mixture of adducts was injected at least three times and the mean ratio of peak areas was calculated. Table (3) shows the relative rates of reaction for the pairs of alkenes tested, and the relative rates of addition to each alkene (K/K_0) are summarised in table (4) along with those of the related tetrachlorocarbene (232).[137]

Table (3)

Result of competition reactions.

Alkene	Relative rate
$(CH_3)_2C{=}C(CH_3)_2/(CH_3)_2C{=}CHCH_3$	1:1.09; 1:1.053; 1:1.079
$(CH_3)_2C{=}C(CH_3)_2/(CH_3)_2C{=}CH_2$	1:0.709; 1:0.698; 1:0.70
$(CH_3)_2C{=}C(CH_3)_2/cis\text{-}CH_3HC{=}CHCH_3$	1:0.32; 1:0.32; 1:0.33
$(CH_3)_2C{=}C(CH_3)_2/trans\text{-}CH_3HC{=}CHCH_3$	1:0.083; 1:0.077; 1:0.08
$(CH_3)_2C{=}C(CH_3)_2/H_2C{=}CHCO_2CH_3$	1:0.053; 1:0.063; 1:0.06
$(CH_3)_2C{=}C(CH_3)_2/CH_3HC{=}CHCO_2CH_3$	1:0.729; 1:0.78; 1:0.78

Table (4)

Relative rate of addition of carbenes (312, X = OMe) and (232)[137] to alkenes at room temperature.

Alkene	K/K_0 (312, X = OMe)	K/K_0 (232)
$(CH_3)_2C{=}C(CH_3)_2/(CH_3)_2C{=}C(CH_3)_2$	1.0	1.0
$(CH_3)_2C{=}C(CH_3)_2/(CH_3)_2C{=}CHCH_3$	1.1	1.44
$(CH_3)_2C{=}C(CH_3)_2/(CH_3)_2C{=}CH_2$	0.75	0.63
$(CH_3)_2C{=}C(CH_3)_2/cis\text{-}CH_3HC{=}CHCH_3$	0.35	0.64
$(CH_3)_2C{=}C(CH_3)_2/trans\text{-}CH_3HC{=}CHCH_3$	0.08	0.2

Table (5)

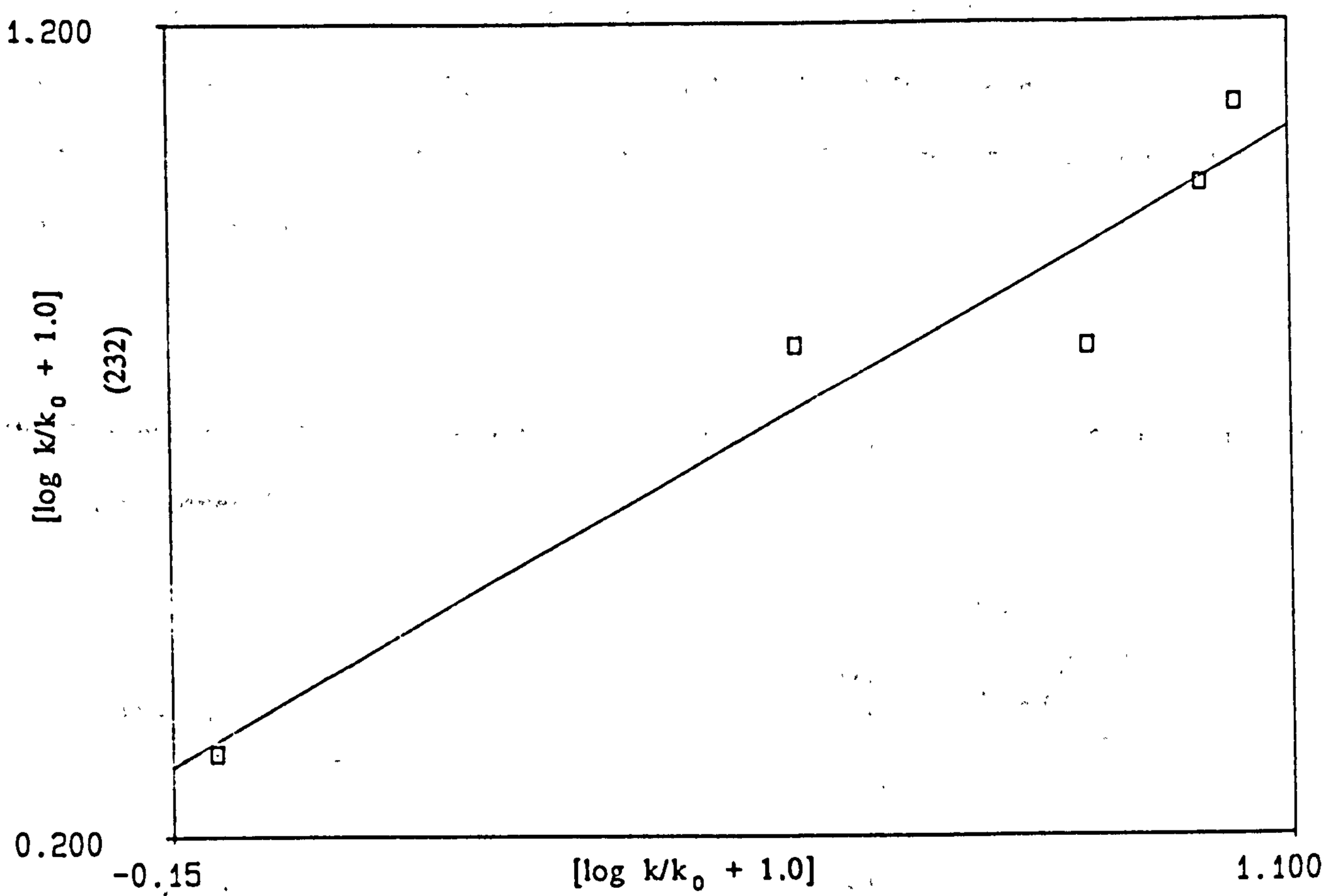
Determination of selectivity index (m) of the carbene (312, X = OMe)

Alkene	[log K/K_0 + 1.0] (312, X = OMe)	[logK/K_0 + 1.0] (232)
$(CH_3)_2C{=}C(CH_3)_2/(CH_3)_2C{=}C(CH_3)_2$	1.0	1.0
$(CH_3)_2C{=}C(CH_3)_2/(CH_3)_2C{=}CHCH_3$	1.04	1.1
$(CH_3)_2C{=}C(CH_3)_2/(CH_3)_2C{=}CH_2$	0.87	0.8
$(CH_3)_2C{=}C(CH_3)_2/cis\text{-}CH_3HC{=}CHCH_3$	0.544	0.8
$(CH_3)_2C{=}C(CH_3)_2/trans\text{-}CH_3HC{=}CHCH_3$	-0.10	0.3

A linear regression plot of the logarithms of these relative values (table 5) against the corresponding values for the tetrachlorocarbene (232) is illustrated in fig (3); the correlation is good, especially when the difference in the temperatures of the reaction (20 and 180 ^0C respectively) and slight difference in the alkenes used are taken in account.

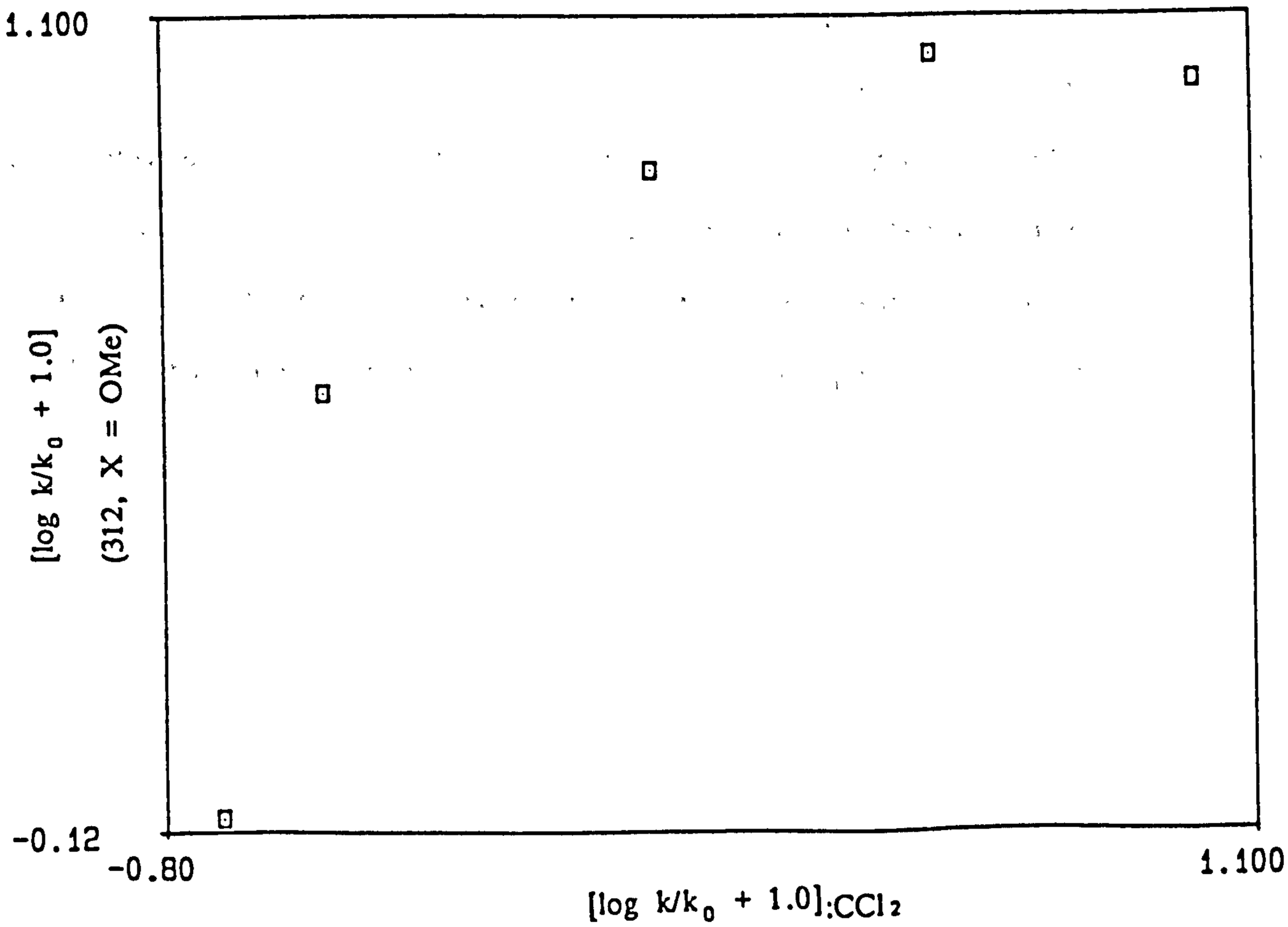
However, a plot of [log K/K_0 + 1.0] for the carbene (312, X = OMe) against the corresponding figures for dichlorocarbene[138] does not, unlike many such plots, lead to a good linear correlation (fig 4).

Fig.(3): Relative reactivities of carbenes (232) and (312, X = OMe) towards alkylalkenes compared to 2,3-dimethylbut-2-ene.



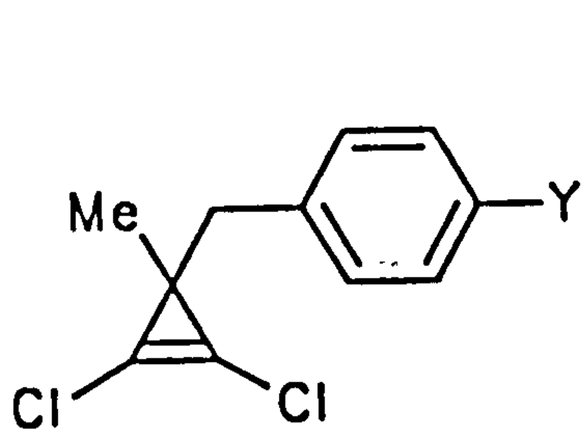
(312, X = OMe)

Fig.(4): Relative reactivities of carbenes ($:CCl_2$) and (312, X = OMe) towards alkylalkenes compared to 2,3-dimethylbut-2-ene.

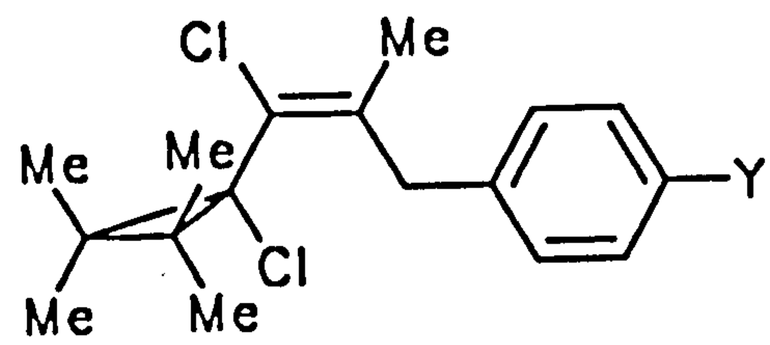


Moreover, the reactivity of the two carbenes (312, X = H, OMe) with alkylalkenes are very similar; indeed a plot of log (K/K_0) for one carbene against that for the other gives a straight line with a slope of 1.08, corresponding to carbenes of almost equal selectivity.[139]

(b) The effect of changing the substitution pattern at C_3 on the rate of ring-opening of cyclopropenes (314).



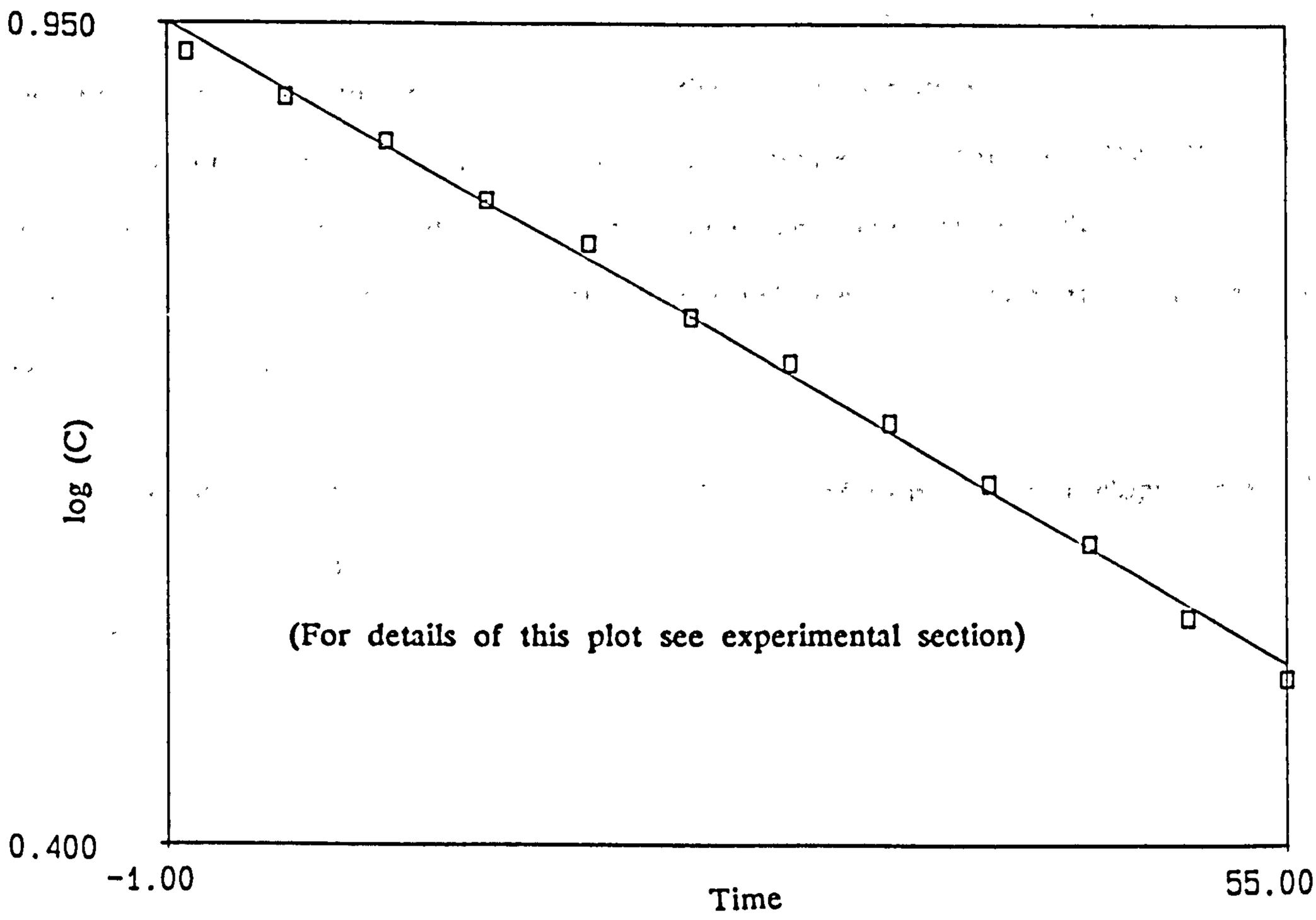
(314)



(315)

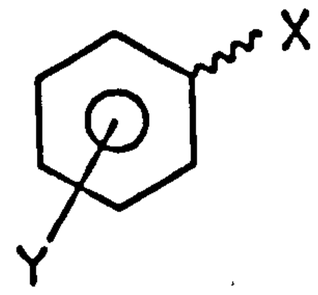
The rate of reaction of cyclopropenes (314) with 2,3-dimethylbut-2-ene to give cyclopropanes (315) can be correlated with the electronic character of the p-substituent. Equimolar quantities of pair of cyclopropenes (314, Y = H) and (314, Y = OMe, or CF_3, or Me) were allowed to react with an excess of 2,3-dimethylbut-2-ene in deuterochloroform at room temperature and the reactions were followed by 300 MHz n.m.r. using the signal for the benzylic methylene groups. In each case a plot of log(C) versus time gave a good linear correlation, such as (fig. 5). The relative rates were in the order Me> H> OCH_3> CF_3> (ca. 19:16:12:7).

Fig.(5): Typical plot of change in concentration of cyclopropene (314) with time.



(For details of this plot see experimental section)

The Hammett equation (6) applies to a series of chemical equilibria involving a family of aromatic compound (316) with different substituents, Y:[140a]



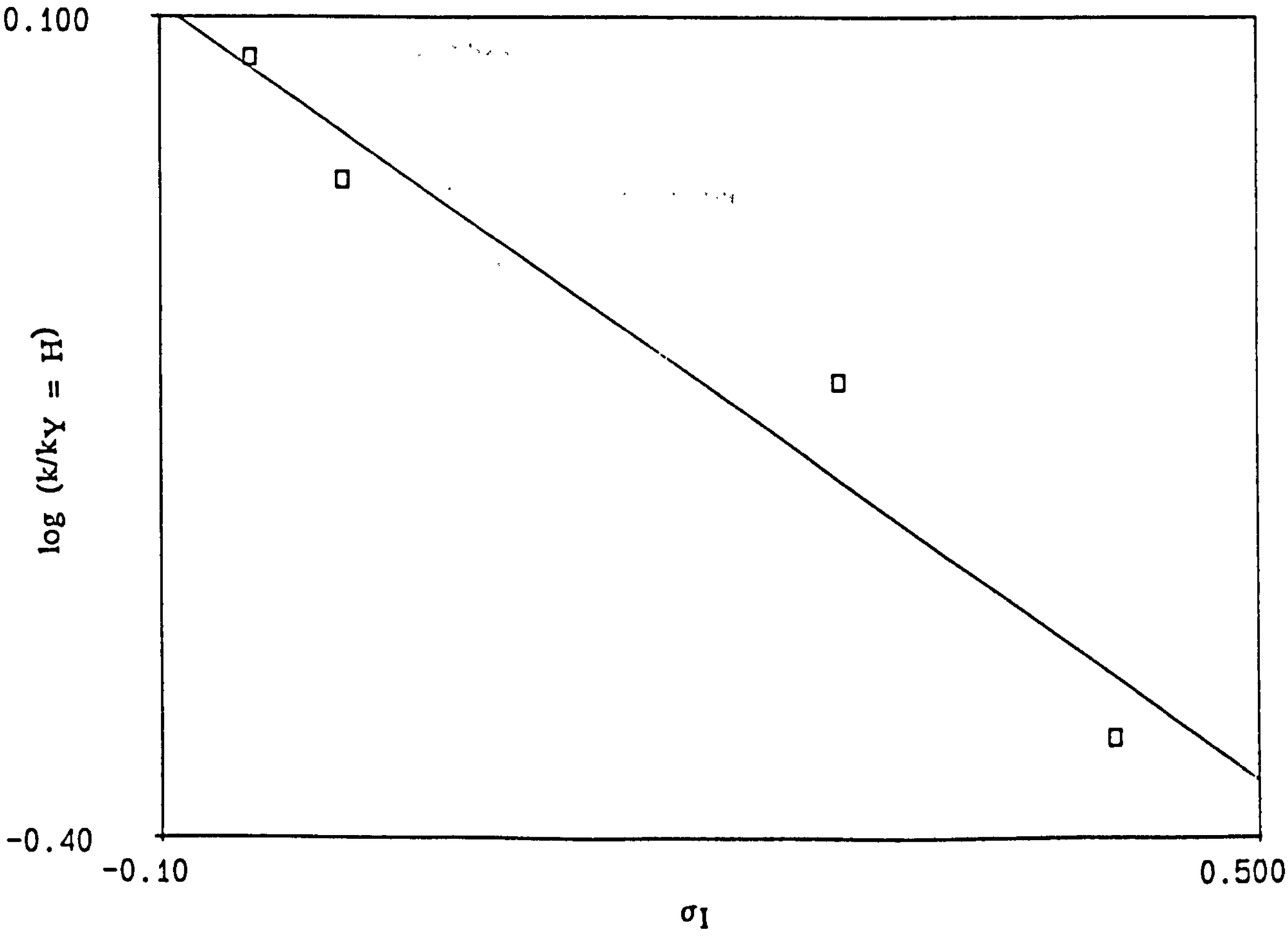
(316)

$$\log(K/K_0) = \rho.\sigma \quad \text{.....(6)}$$

where K_0 is the rate constant or equilibrium constant for Y = H, K is the constant for the group Y, ρ is a constant for a given reaction under a given set of conditions, and σ is a constant characteristic of the group Y. A strong negative ρ value indicates a large electron demand at the reaction centre. Conversely, a positive ρ value is associated with developing negative charge in the transition state.[140a]

A plot of $\log(K_Y/K_{(Y=H)})$ for the rates compared to that for (314, Y = H) against σ_I for the substituent,[140b] gives a reasonable correlation with a ρ-value of −0.8 (fig. 6), corresponding to a reaction in which electron release at C_3 causes an increase in the rate.

Fig.(6): The effect of substituents on the rate of formation of cyclopropanes (315) as a function of σ_I of Y.



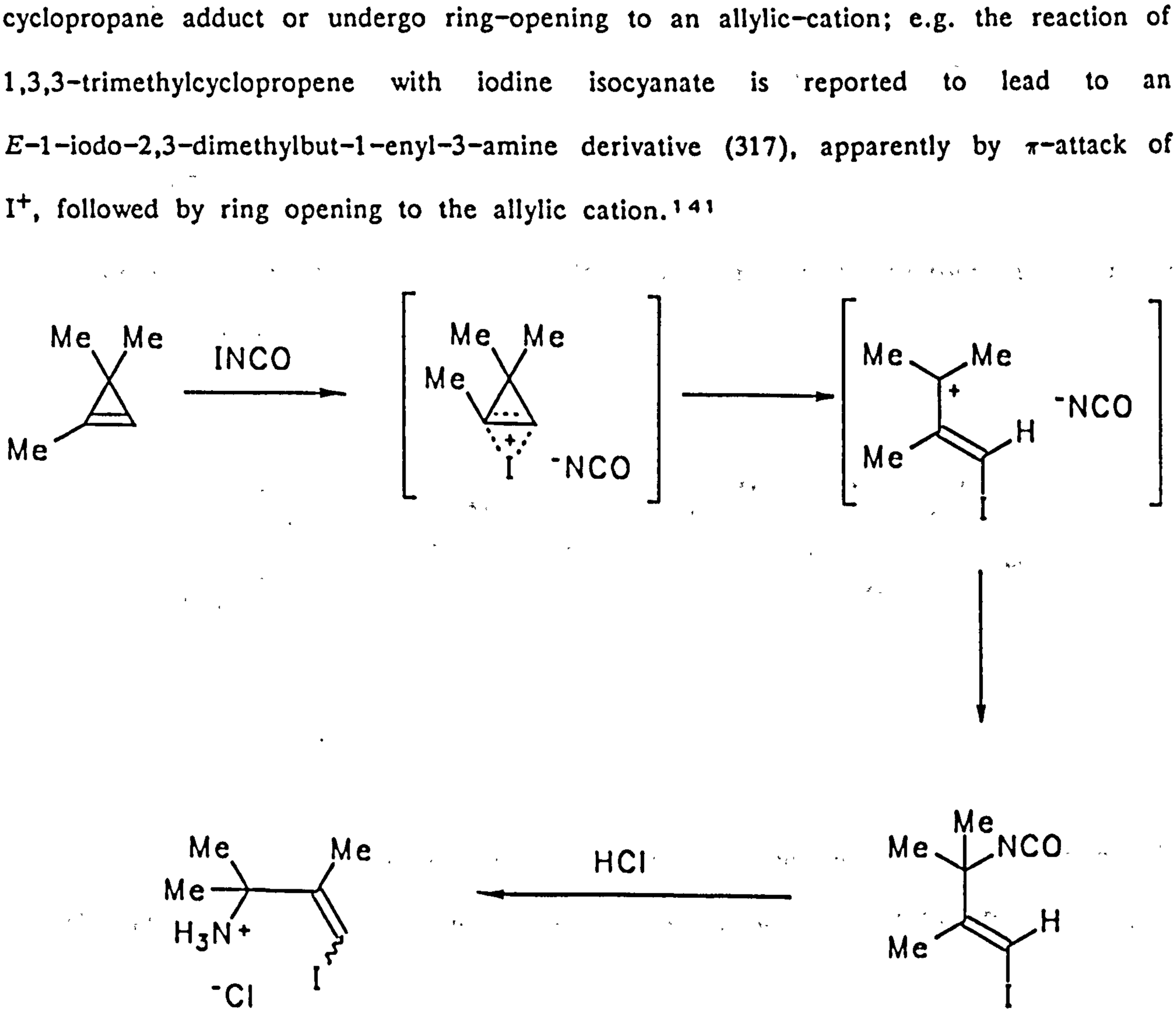
Chapter Three

Reaction of 2-(cycloprop-1-enyl)ethanol derivatives with electrophiles.

3.1 INTRODUCTION.

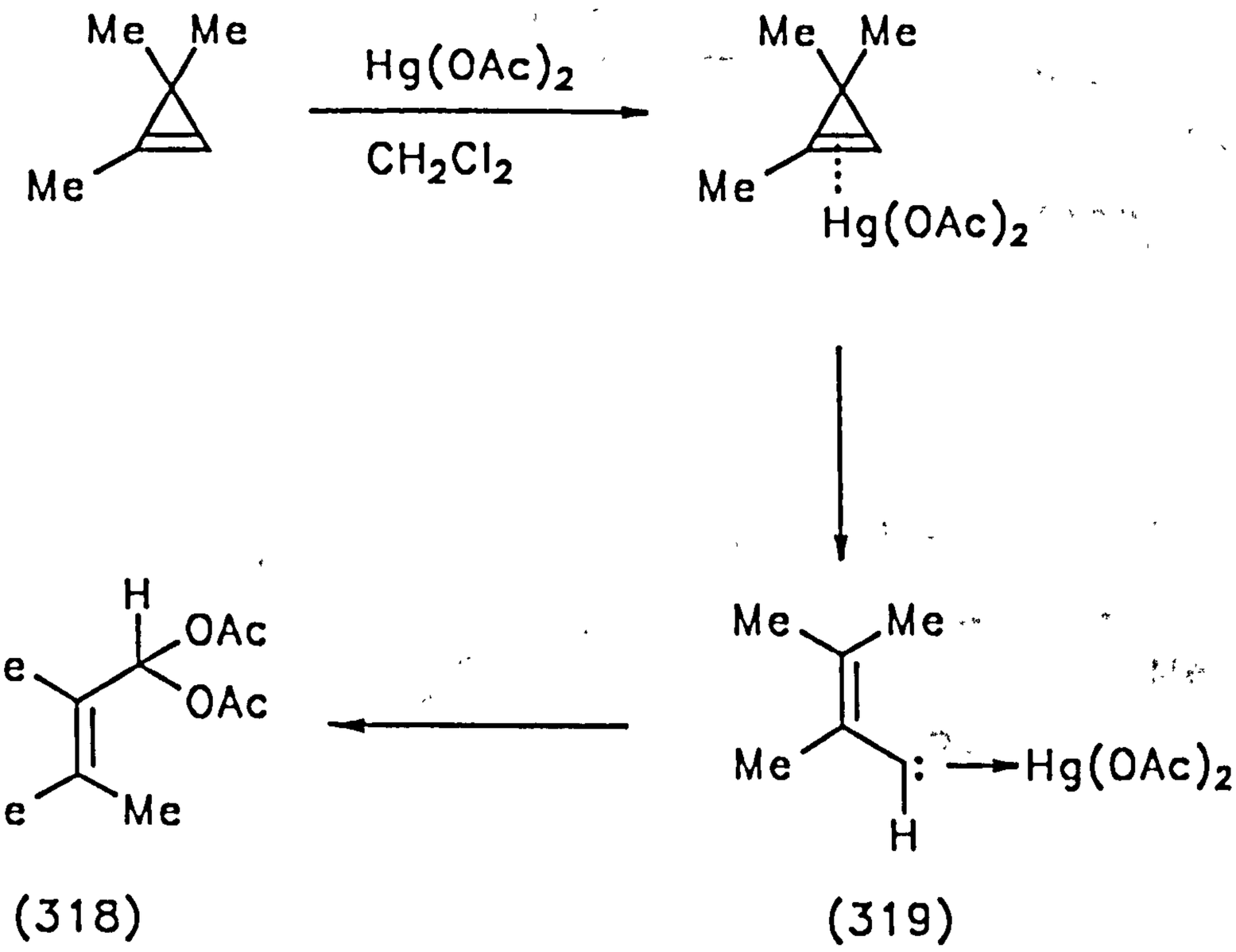
Due to the unusual bonding, compounds containing a cyclopropene ring rank among the most reactive cycloalkenes. The short bond length of the cyclopropene double bond infers it must have a very strong π–component. Nevertheless, addition reactions at the double bond are known to occur very readily and are usually highly exothermic,[52] since cyclopropenes lose strain energy of about 27 kcal/mol through saturation of the π–bond to give less strained cyclopropanes. As mentioned before, these reactions include catalytic hydrogenations, Diels–Alder reactions, cycloaddition, 1,3–dipolar addition, dimerization, and electrophilic addition.

Addition of an electrophile E^+ to the cyclopropene double bond leads to a cyclopropylcation, which can either be attacked by a counter ion to give a cyclopropane adduct or undergo ring–opening to an allylic–cation; e.g. the reaction of 1,3,3–trimethylcyclopropene with iodine isocyanate is reported to lead to an *E*–1–iodo–2,3–dimethylbut–1–enyl–3–amine derivative (317), apparently by π–attack of I^+, followed by ring opening to the allylic cation.[141]



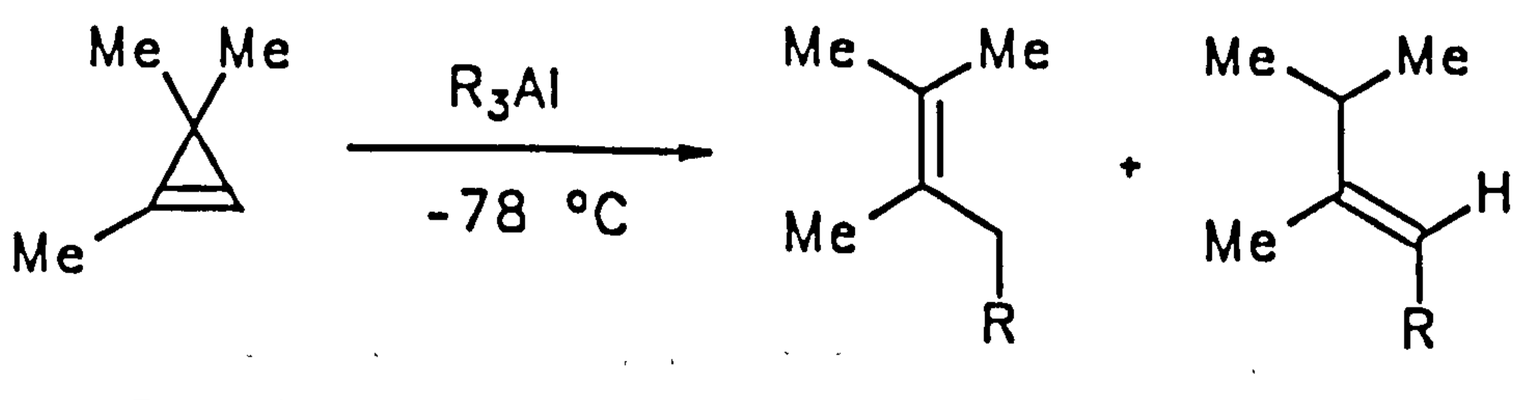
(317)

Addition of bromine to the same cyclopropene leads to 1,3-dibromo-2,3-dimethylbut-1-ene of unspecified stereochemistry.[142] In contrast, acetoxymercuration of 3,3-disubstituted-cyclopropenes leads to Z-vinylmercury species,[143] although trimethylcyclopropene reacts with mercuric acetate to give (318) in a reaction formulated to involve the carbene complex (319).[144]



(318) (319)

Moreover, reaction of 1,3,3-trimethylcyclopropene with tri-isopropyl aluminium in hexane also leads to ring-opened products.[145]

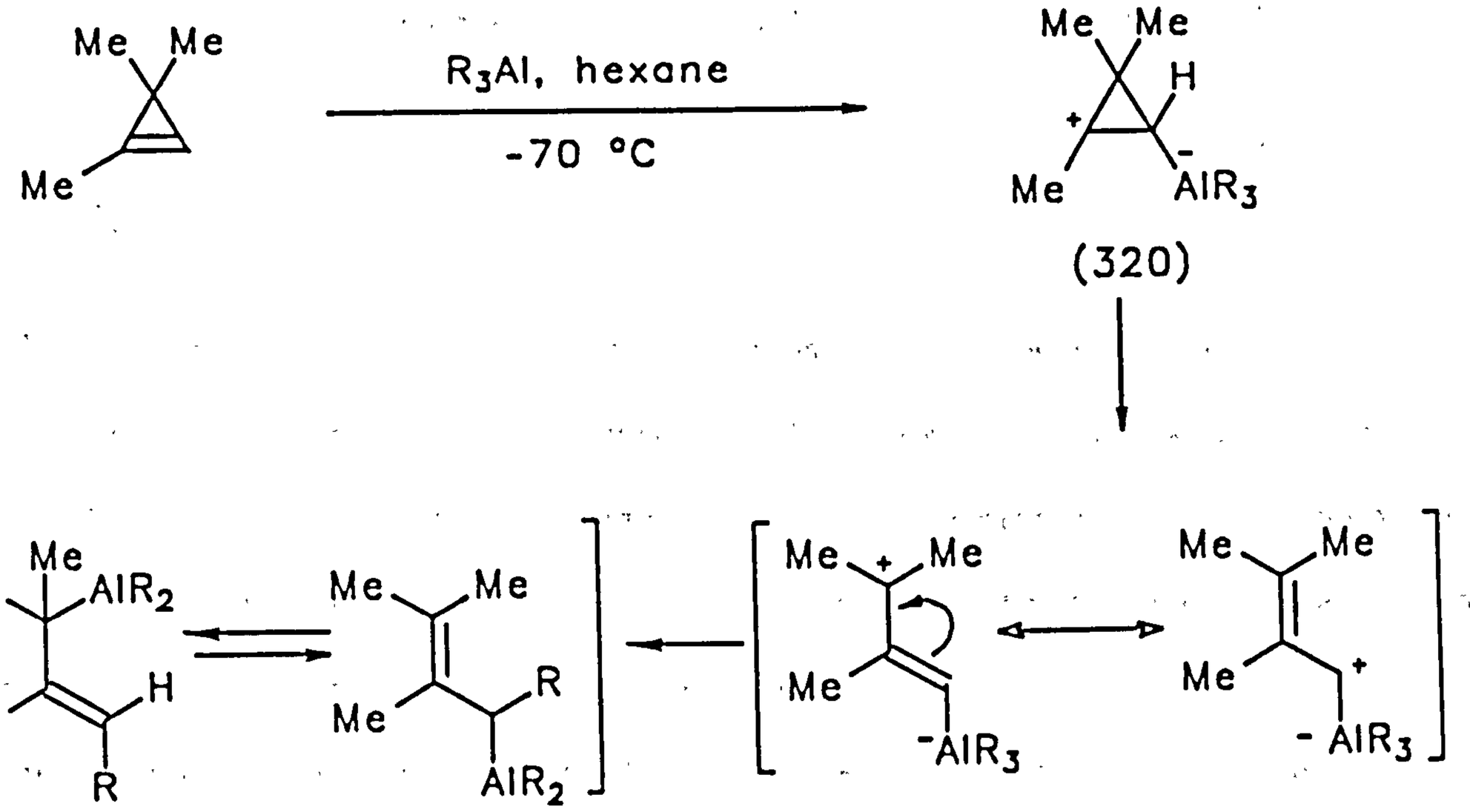


R = i-Pr.

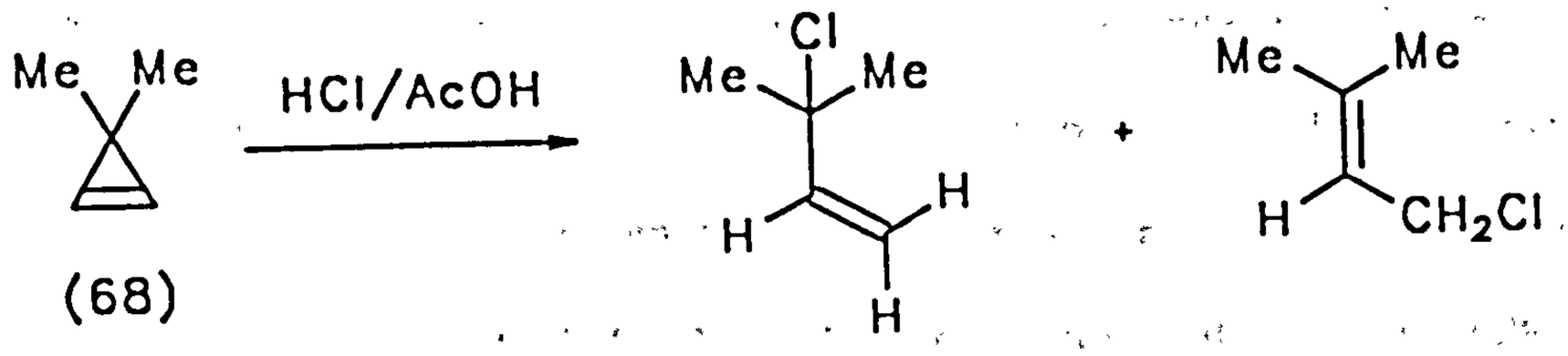
The process is believed to occur by addition to form the more stable cation (320) which undergoes a cyclopropyl-allyl rearrangement followed by a 1,2-shift of an alkyl

group to produce an allyl substituted dialkylaluminium. This is trapped by adding water, or undergoes an allylic rearrangement before being trapped (scheme 6).[145]

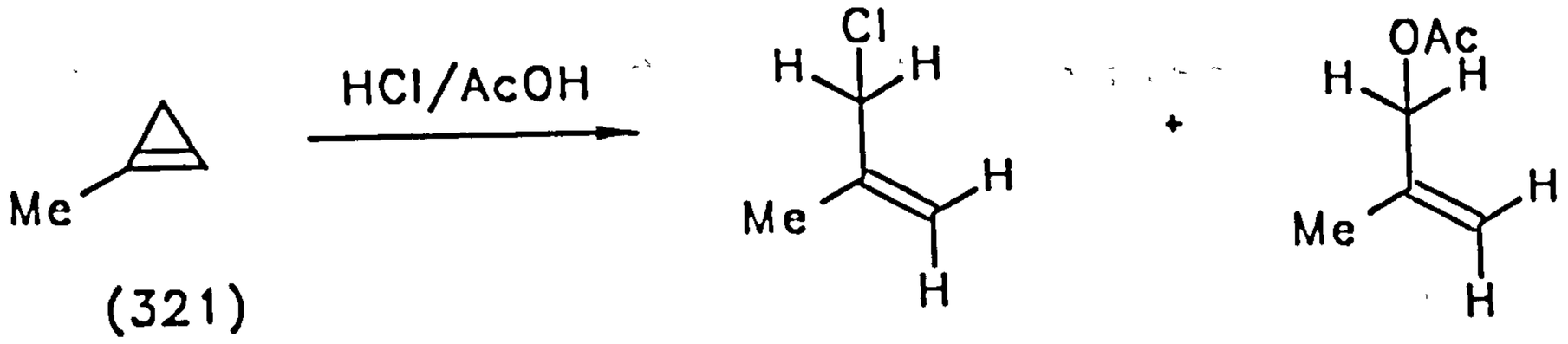
(Scheme 6)



Reaction of the cyclopropenes (68) and (321) with HCl in acetic acid also gave ring-opened products.[146]



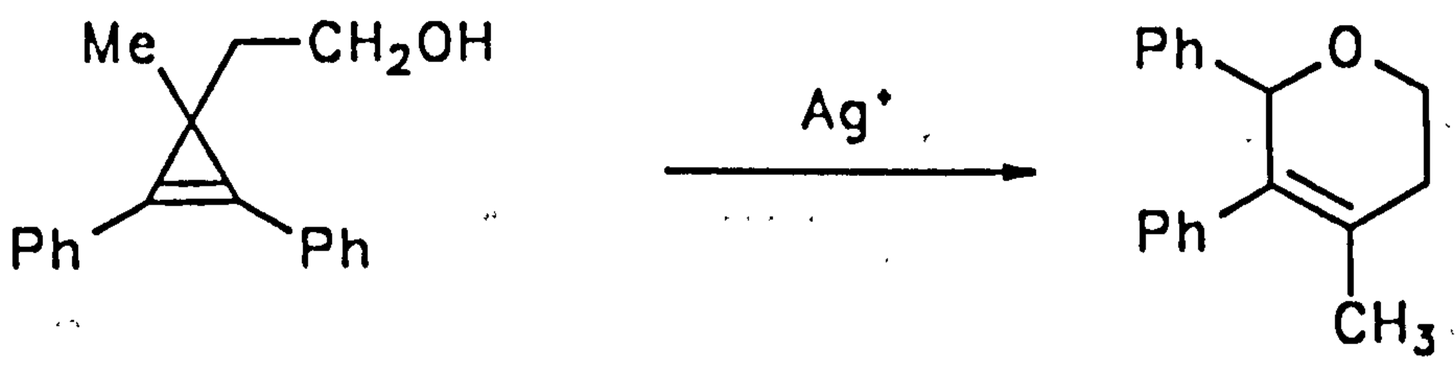
(68)



(321)

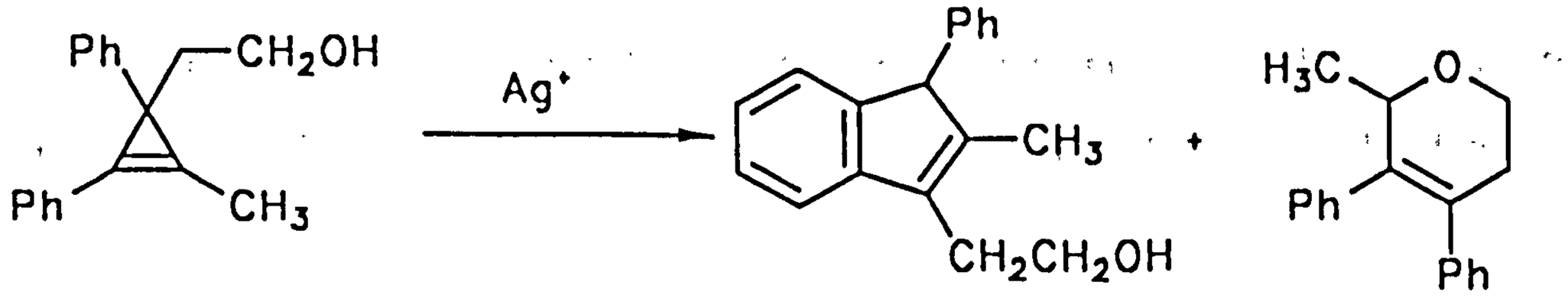
The reaction of electrophilic reagents such as silver ion with strained σ bonds has been studied. Since electrophilic reagents are also known to react with π-systems of olefins, the interesting question is raised of σ vs. π-reactivity.[147] Cyclopropenes represent an unusual class of molecules where a strained σ bond is incorporated into a substrate that already possesses a reactive π system.[147]

It is known that treatment of (322) with an excess of silver perchlorate gives 5,6-dihydro-4-methyl-2,3-diphenyl-2H-pyran (323).[147]



(322) (323)

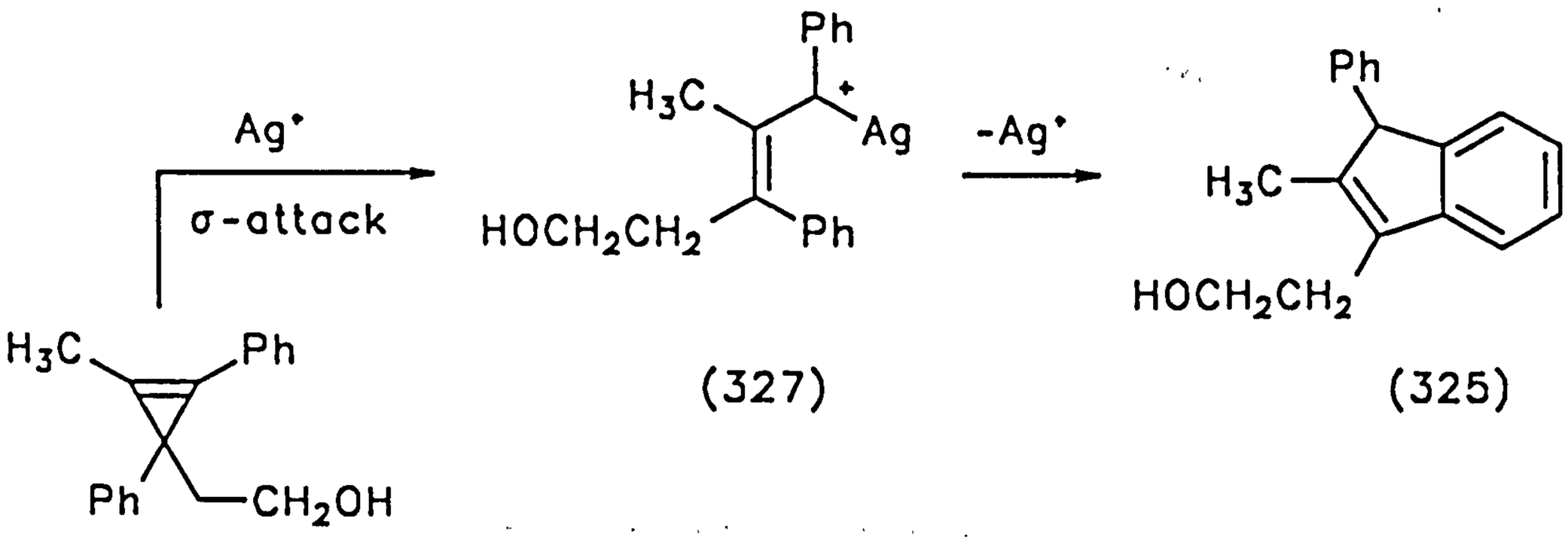
However, when the cyclopropene (324) was allowed to react with silver perchlorate in benzene, it gave a mixture of two compounds in a 2:1 ratio:[147]



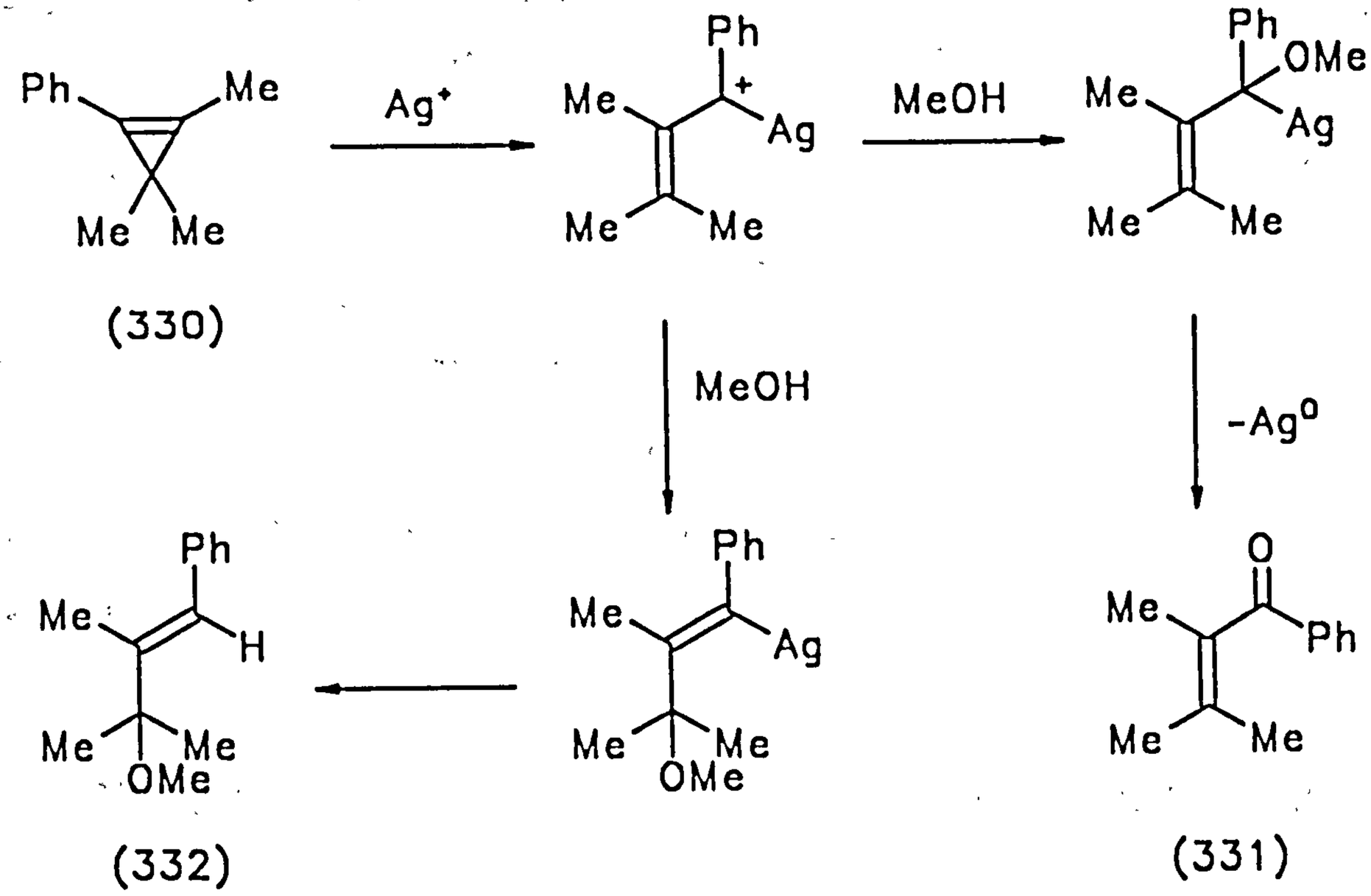
(324) (325) (326)

The major product was identified as 3-(2-hydroxyethyl)-2-methyl-1-phenylindene

(325), and the minor product was the pyran (326).[147] The indene is formally derived by attack of Ag^+ at the σ bond to give the allylic cation (327) which is trapped by an intramolecular reaction with the benzene ring. The minor product apparently arises by attack of Ag^+ on the π-bond to give the cyclopropyl cation (328) followed by ring-opening to the allylic cation (329) which reacts intramolecularly with the neighbouring hydroxyl group to give the dihydro-2H-pyran system.

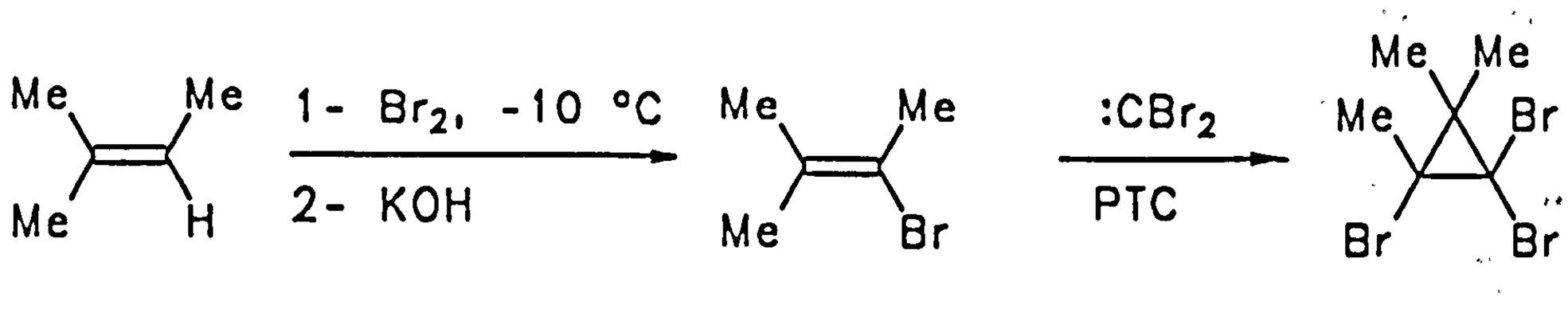


Reaction of the cyclopropene (330) with silver perchlorate in methanol gave rise to a mixture of (331) and (332), resulting from addition of Ag^+ to the π-bond of the cyclopropene.[147]

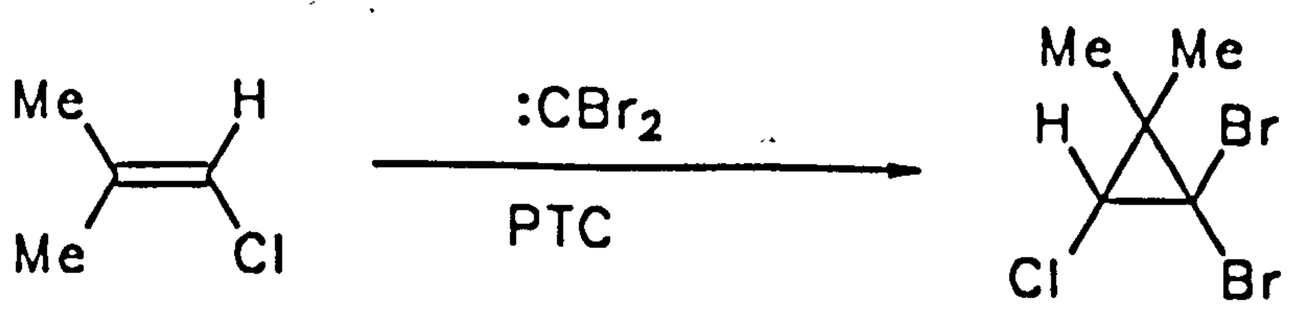


3.2 PREPARATION OF TRIHALOCYCLOPROPANES.

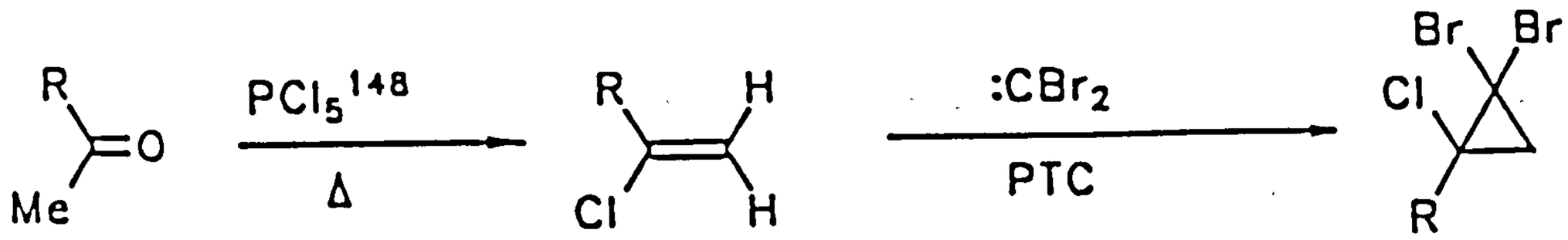
A range of trihalocyclopropanes was prepared for this work, following known procedures. The cyclopropanes (333), (334), (335, R = i-Pr, t-Butyl) and (336), were prepared in good yield by treating the corresponding haloalkenes with dibromocarbene:



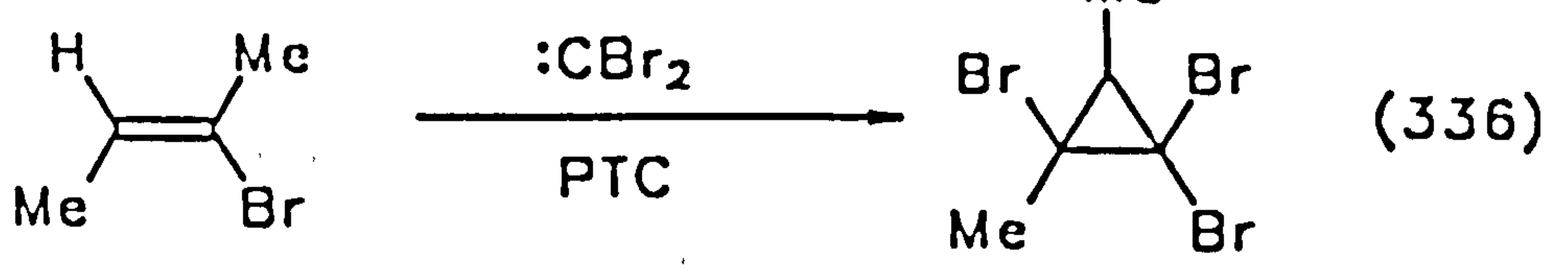
(333)



(334)



R= i-Pr, t-Butyl (335)



(336)

In each case, the ^1H n.m.r. and i.r. spectra were similar to those for an authentic sample.[36,49]

3.3 PREPARATION OF 2-(CYCLOPROP-1-EN-1-YL)ETHANOL DERIVATIVES.

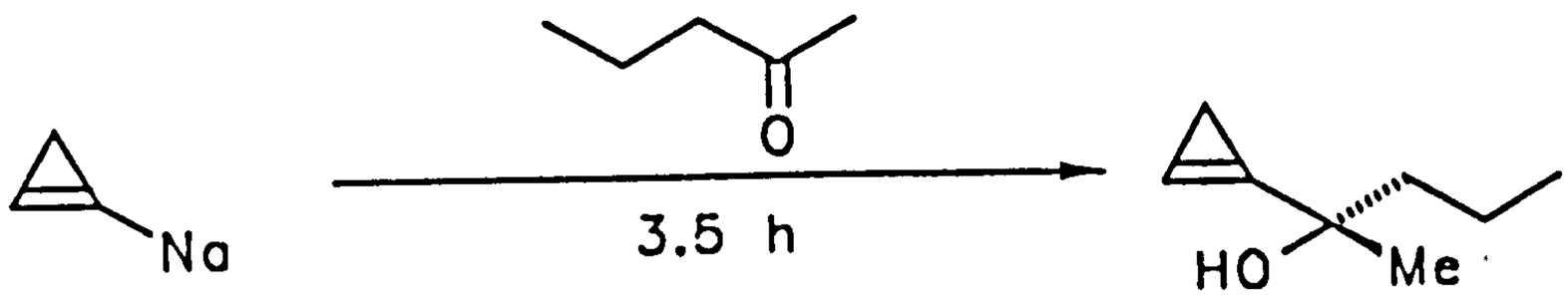
The reaction of 1,1,2-trihalocyclopropanes with two equiv. of methyl lithium is known to give 1-lithiocyclopropenes which are in turn trapped by electrophiles, e.g. when 1,1,3-tribromo-2,2,3-trimethylcyclopropane (333) was allowed to react with 2.0 mol. equiv. of methyl lithium, followed by addition of acetone, (337) was obtained in good yield.[49]

(333) (337) (338) (339)

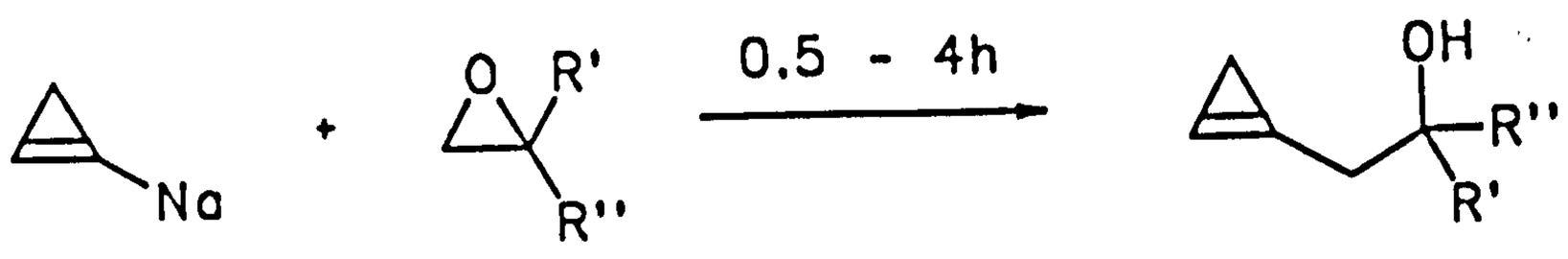
The formation of (337) presumably occurs *via* lithium-halogen exchange with one

of the bromines in (333), followed by 1,2-elimination of lithium bromide to give (338), which reacts further with another mol. equiv. of methyl lithium through lithium-halogen exchange leading to the lithiocyclopropene (339). The latter, in turn reacts with acetone to afford (337).[49]

A series of cyclopropene-1-carbinols have been prepared previously by the reaction of 1-sodiocyclopropenes with ketones.[149] The low yield obtained in some cases was related to side reactions between the ketones and the metallo-cyclopropene *via* metal-hydrogen exchange, the hydrogen adjacent to the carbonyl moiety being more acidic than the vinylic hydrogen in cyclopropene. It was also attributed to ease of polymerization of the product even at -20 °C in solution.



Moreover, (cycloprop-1-enyl)methylcarbinol (342) has been prepared previously by reaction of 1-sodiocyclopropene (340) with epoxides (341).[149]

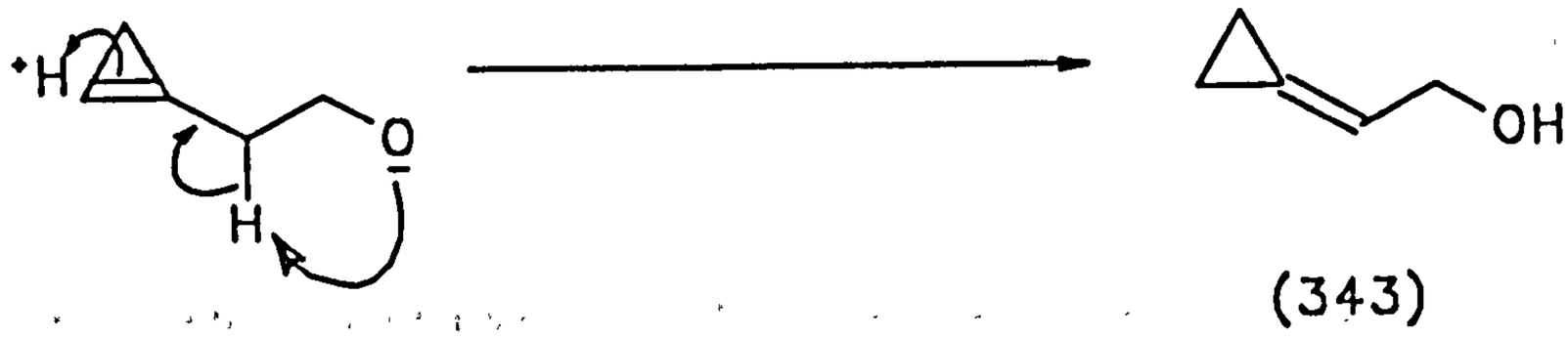


(340) (341a, R'=H, R''=CH_3) (342)

(341b, R'=R''=CH_3) 68 - 79%

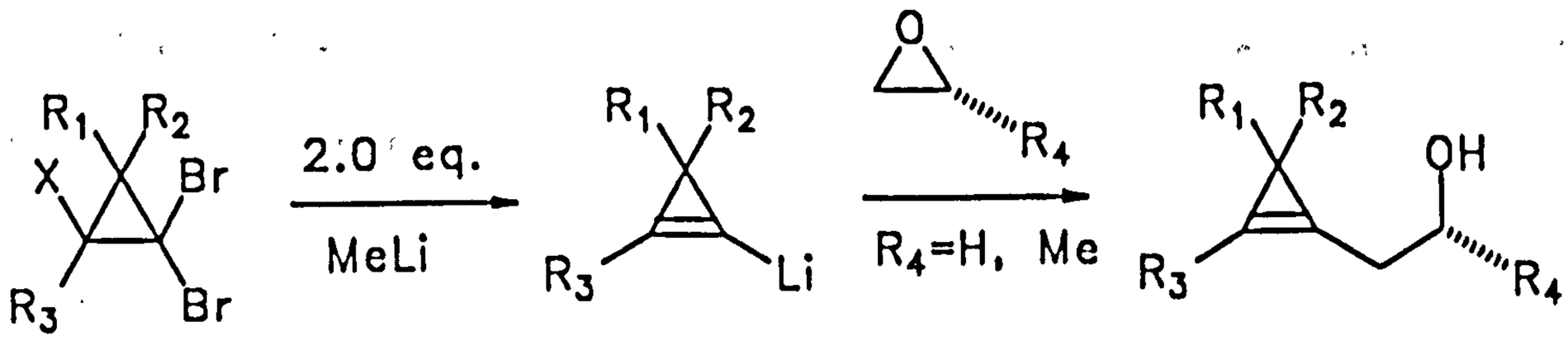
The (cycloprop-1-enyl)methyl carbinols were reported to polymerize at room temperature, even when they are dissolved in CCl_4. However, the solution could be safely stored at -20 °C for prolonged periods. In addition to the desired product, the

exocyclic isomer (343) was apparently formed directly from the product anion through the following concerted reaction.[149]



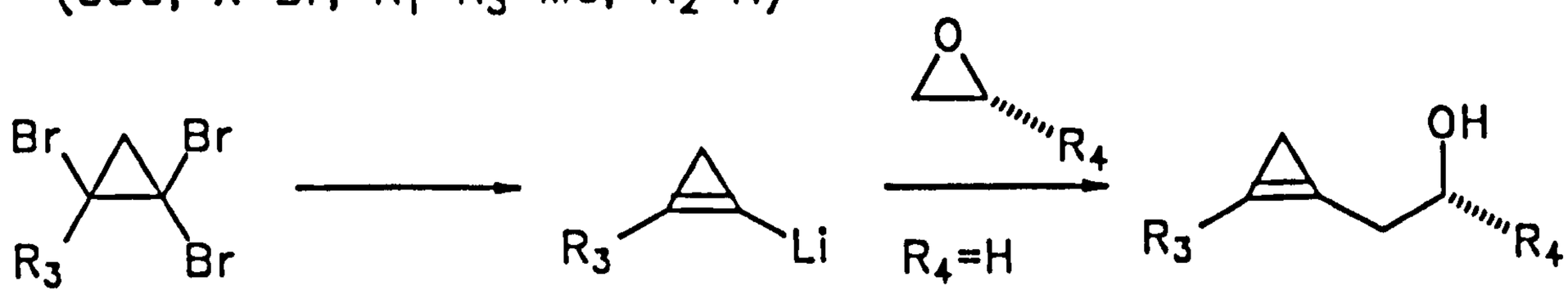
(343)

Reaction of trihalocyclopropanes (333, 334, 335 and 336) with two equiv. of methyl lithium at −78 °C or −50 °C to 20 °C followed by quenching with a range of epoxides afforded the 2−(cycloprop−1−enyl)ethanol derivatives (table 6). The reaction, as mentioned above, involves lithium−bromine exchange followed by or concerted with 1,2−elimination, to produce the halocyclopropene, which reacts further with methyl lithium to give a lithiocyclopropene. The latter reacts smoothly with ethylene oxide and with propylene oxide at the less substituted end, giving the desired product after 3 − 12 h at 20 °C.



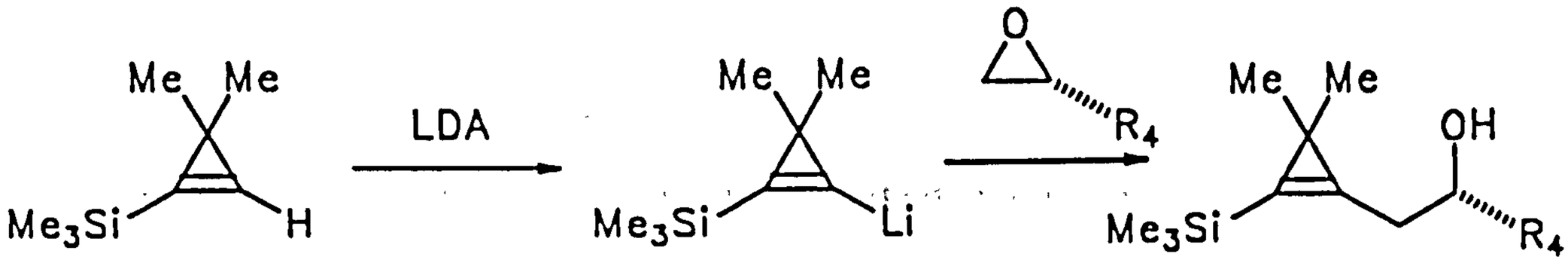
(333, X=Br, R_1=R_2=R_3=Me)
(334, X=Cl, R_1=R_2=Me, R_3=H)
(336, X=Br, R_1=R_3=Me, R_2=H)

(344)



(335, R_3=Pr^i, ^tBu)

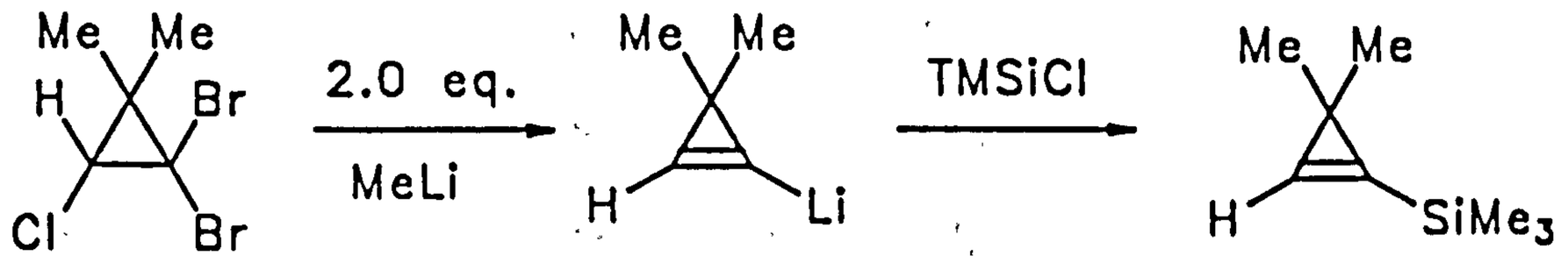
(345)



(199)
(R_4=H, Me)

(346)

The trimethylsilyl-derivatives (346) were prepared by reaction of the cyclopropene (199) with methyl lithium and di-isopropylamine followed by quenching with epoxides. The cyclopropene (199) was prepared by treatment of the cyclopropane (334) with two equiv. of methyl lithium in ether, followed by quenching with trimethylsilylchloride.[49]



(334) (199)

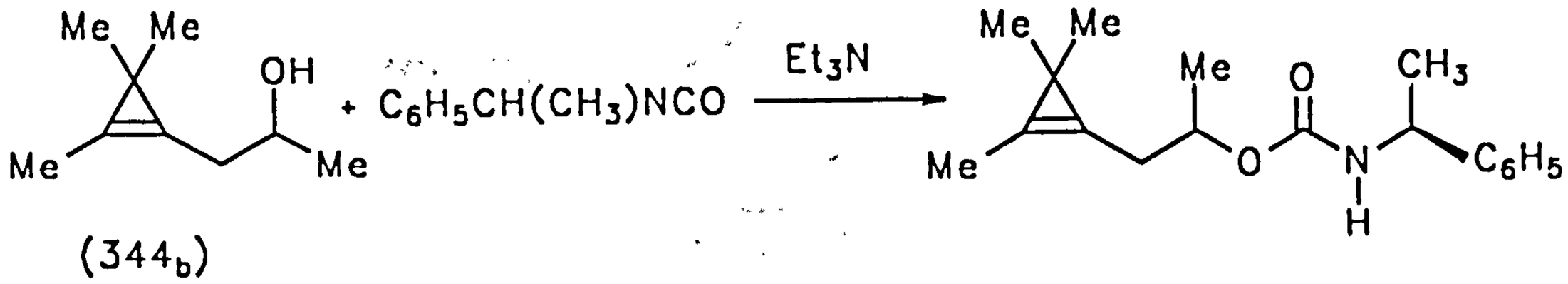
The yields in the opening of the epoxides were, however, variable (table 6) and the original, if less convenient method, involving sodiation of the cyclopropene, may in some cases be preferred.

Table (6)

Preparation of cyclopropene substituted alcohols.

Precursor				Epoxide	Product	Yield
	R_1	R_2	R_3	R_4		
(333)	Me	Me	Me	H	(344_a)	80
(333)	Me	Me	Me	Me	(344_b)	50
(333)	Me	Me	Me	(-)-(Me)	(+)-(344_b)	48
(334)	Me	Me	H	H	(344_c)	41
(334)	Me	Me	H	Me	(344_d)	33
(334)	Me	Me	H	(+)-(Me)	(-)-(344_d)	29
(336)	Me	H	Me	H	(344_e)	58
(336)	Me	H	Me	Me	(344_f)	41
(335)	-	-	^tBu	H	(345_a)	78
(335)	-	-	^iPr	H	(345_b)	77
(199)	-	-	-	H	(346_a)	42
(199)	-	-	-	(+)-(Me)	(347_b)	34

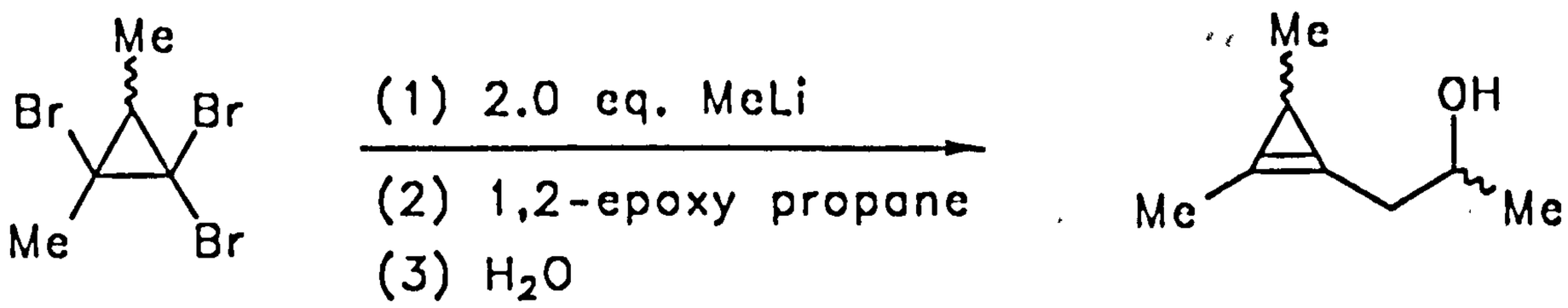
The racemic alcohol (344_b) was converted to a mixture of diastereoisomeric urethanes in ratio 1:1, by refluxing with (S)-(-)-1-phenylethylisocyanate in the presence of triethylamine in $CHCl_3$ for 6 h.



(344b)

The ^{1}H. n.m.r. spectrum of the mixture contained two sets of signals in ratio 1:1. The corresponding reaction of the optically active cyclopropene alcohol (344b) gave a single urethane, the ^{1}H n.m.r. spectrum of which showed one set of signals corresponding to the second isomer obtained from the racemic alcohol.

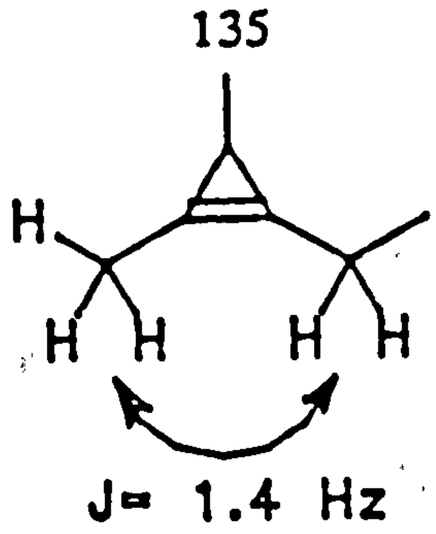
Reaction of (336) with 2.0 equiv. of methyl lithium followed by quenching with 1,2-epoxypropane gave a mixture of diastereoisomers (344f) in ratio 1:1, which could not be separated by column chromatography; apparently there is no diastereocontrol in the ring opening of the two enantiomers of epoxypropane by the racemic dimethyl lithiocyclopropene.



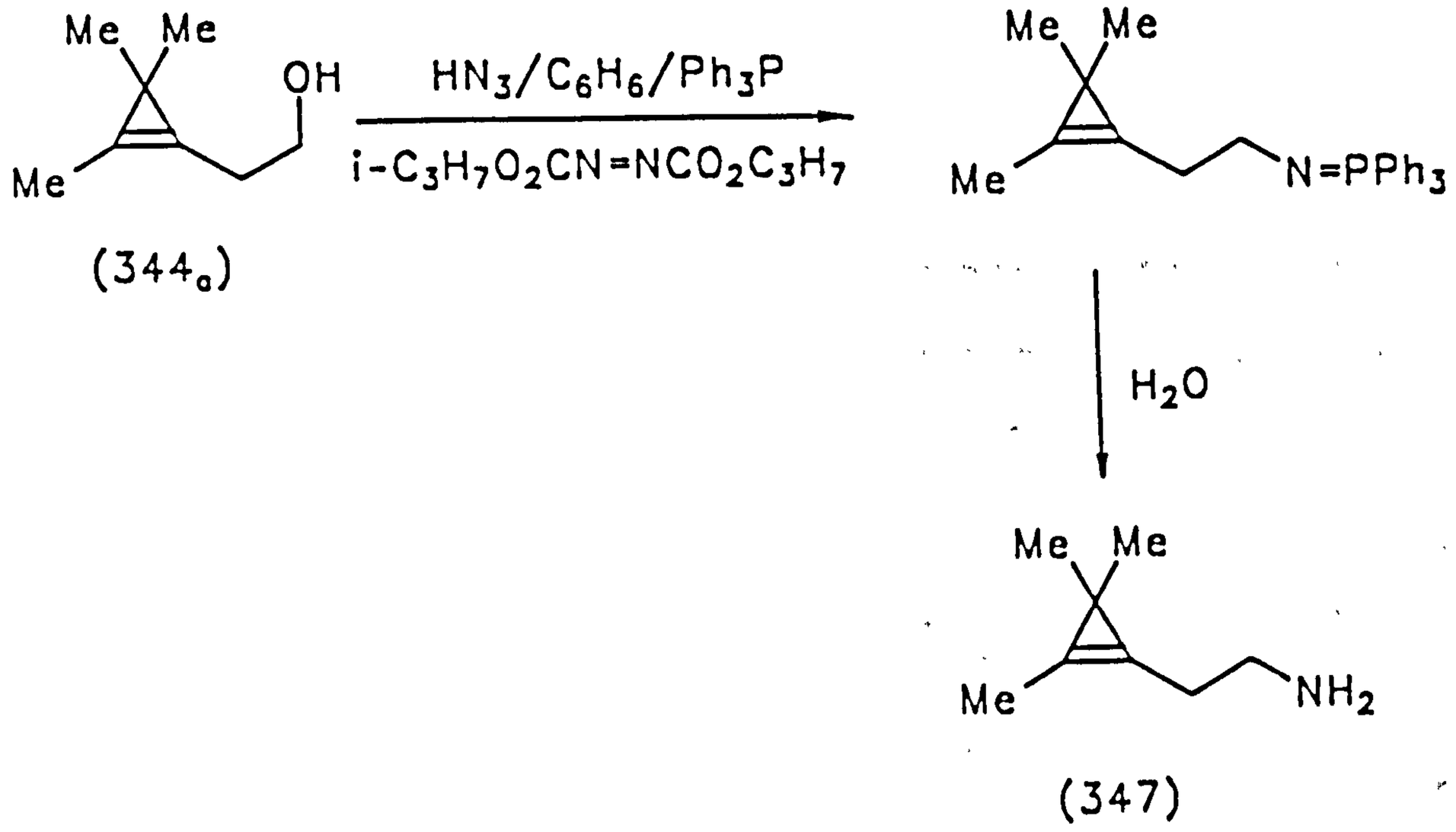
(336) (344f)

The ^{1}H n.m.r. spectrum of (344f) contained two set of signals. The first isomer, showed a sextet at δ 4.01 (1H) with coupling 6.1 Hz and a multiplet for the methylene α- to the cyclopropene. The spectrum also showed a triplet at δ 1.98 with a small coupling constant (1.4 Hz) for the methyl attached to the cyclopropene; the fine splitting was due to long range coupling across the cyclopropene homo-allylic system (fig. 7).[150] There was also a quartet at δ 1.3 (1H), and a pair of doublets at δ 1.22 and 0.95 for the other methyl groups.

(fig. 7)



The cyclopropene alcohol (344_a) was converted to the corresponding amine (347)[151] by treatment with hydrazoic acid, di-isopropyl azodicarboxylate and an excess of triphenylphosphine in THF, followed by addition of water, in 52% yield.



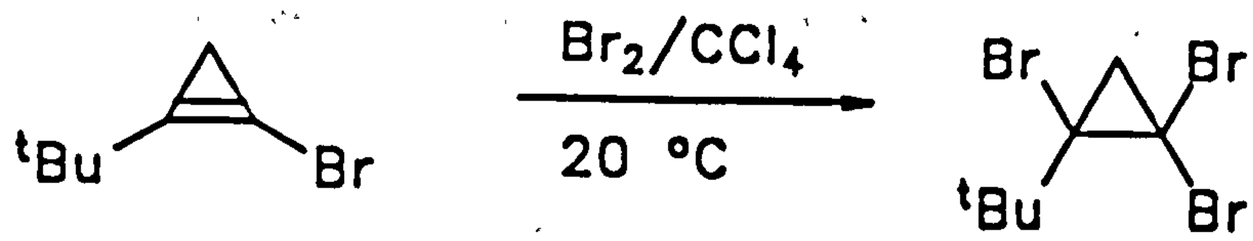
(344_a)

(347)

The i.r. spectrum of (347) contained a band at 1592 cm^{-1} assigned to the amino-group, while the ^1H n.m.r. spectrum showed two multiplets at δ 2.8 (2H) and 2.5 (2H), together with a broad singlet at δ 1.95 (3H), a singlet at δ 1.55 assigned to the amino group, and a singlet for the geminal methyl groups.

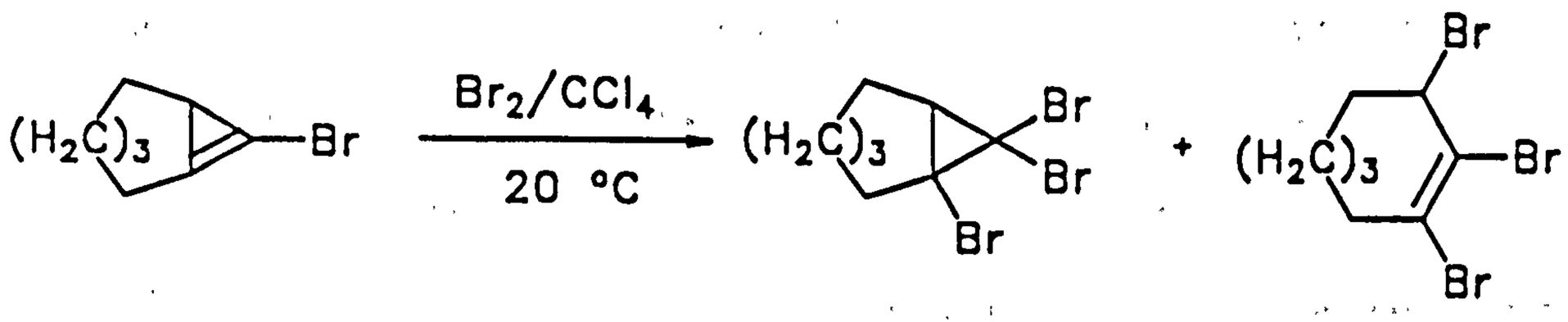
3.4: Reaction with bromine.

There are a number of reports of addition of bromine to cyclopropenes, although few have examined the mechanism in detail. In some cases addition occurs without rearrangement, leading to 1,2-dihalocyclopropenes, e.g. on addition of bromine to 1-bromo-2-t-butyl-1-cyclopropene (208) in CCl_4, a rapid exothermic reaction occurred giving the tribromide (348) in 94% yield.[152]



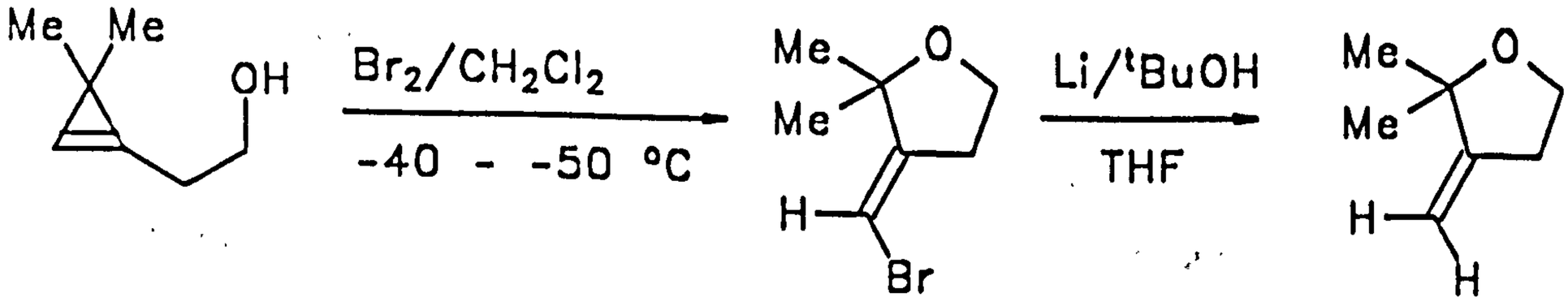
(208) (348)

In other case, addition of halogen leads to ring-opened products, e.g. addition of bromine to (349) gave (351) which was derived by the ring-opening of the cyclopropene, in addition to the bicyclic product (350).[152]



(349) (350) (351)

Reaction of (344_c) with bromine in dichloromethane for 30 m at -40 °C gave (352) in 83% yield.[153] Reduction of this with lithium-t-butanol-THF led to (353).



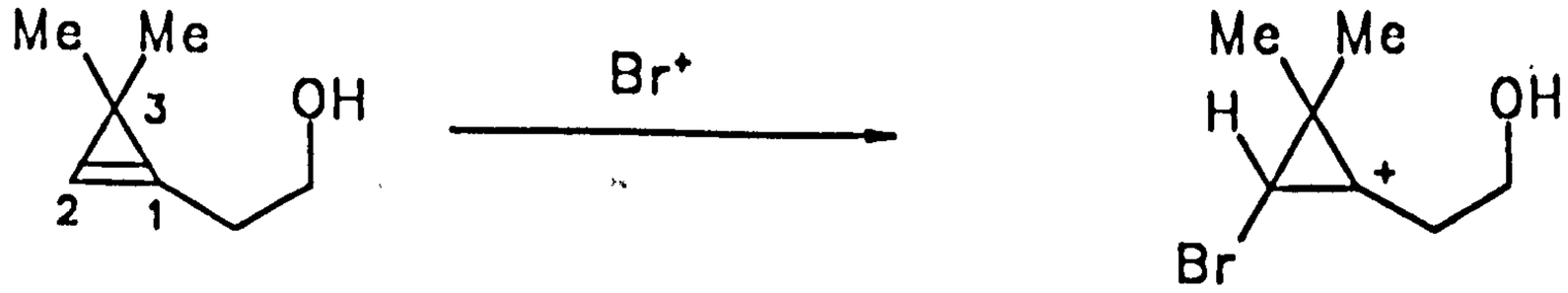
(344_c) (352) (353)

The ^{13}C spectrum of (353) included secondary and quaternary alkene carbons, in

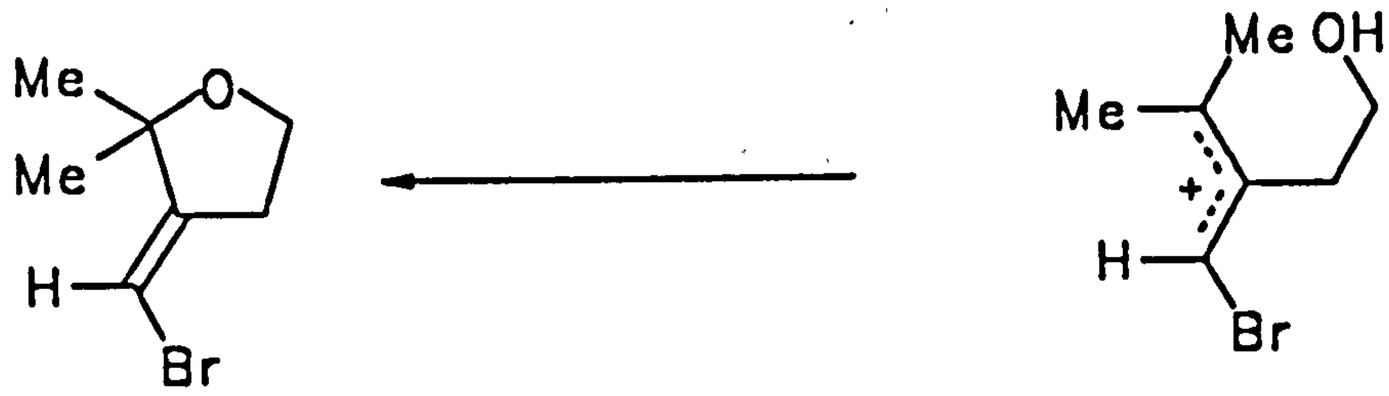
agreement with the presence of a exocyclic methylene group, together with four signals at δ 81.3s, 64.4t, 33.3t, and 27.7q respectively. The ^{1}H n.m.r. spectrum included two single hydrogen triplets at δ 4.91 and 4.79 with coupling constants 2.15 and 2.35 Hz respectively, as well as a two hydrogen triplet of triplets at δ 2.6 one of the coupling constants of which was 2.1 Hz. It could be distinguished from an alternative product, 2,2-dimethyl-5,6-dihydro-2H-pyran on the basis of its ^{13}C n.m.r., and the position of olefinic and allylic hydrogens, which are reported to occur at δ 5.68 and 2.04 respectively in the latter.[154]

The ^{1}H n.m.r. spectrum of (352) also included an alkene signal with a small triplet coupling (2.7 Hz) and a double triplet for the allylic hydrogens at δ 2.69 with coupling constants 2.7 and 7.0 Hz, together with a triplet at δ 3.95 (2H) and a singlet for the geminal methyl groups; the ^{13}C spectrum showed six signals including two in the olefinic region. The E-stereochemistry about the double bond was established by an n.O.e experiment. Irradiation of the signals for the methyl groups at δ 1.31 caused an *ca.* 12% enhancement in the alkene signal at δ 5.96. In a similar experiment with (353) only one of the alkene signals (that at δ 4.79) showed an *ca.* 10% enhancement when the corresponding methyl signals at δ 1.29 were irradiated.

Formally the formation of (352) may involve attack of Br^{+} at the less substituted end of the π-bond of (344_c) to give the cyclopropyl cation (354) which may be expected to undergo ring-opening to an allylic cation (355) followed by intramolecular reaction with the hydroxyl group at the more substituted terminus.

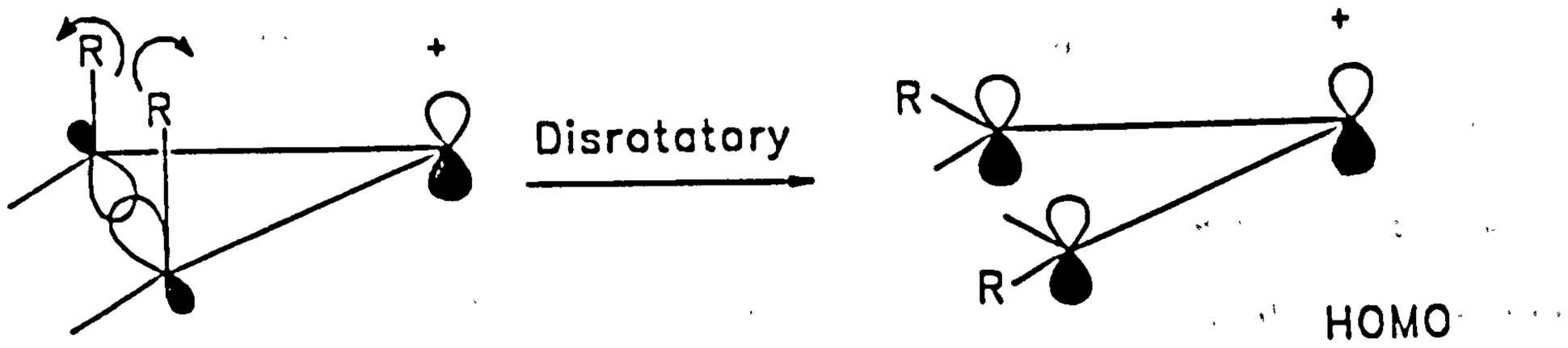


(344_c) (354)



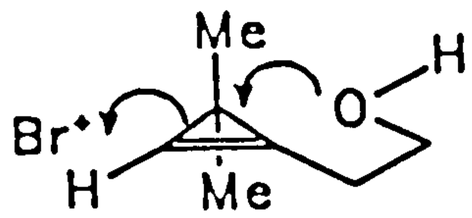
(352) (355)

In 1965 Woodward and Hofmann[155] put forward a prediction based on orbital symmetry considerations, that the conversion of a cyclopropyl cation (356) to an allylic cation (357) should proceed in a stereospecific disrotatory manner, whereby the substitutents rotate either both inwards or both outwards. This would enable the resulting allyl cation to possess the symmetry of the HOMO.



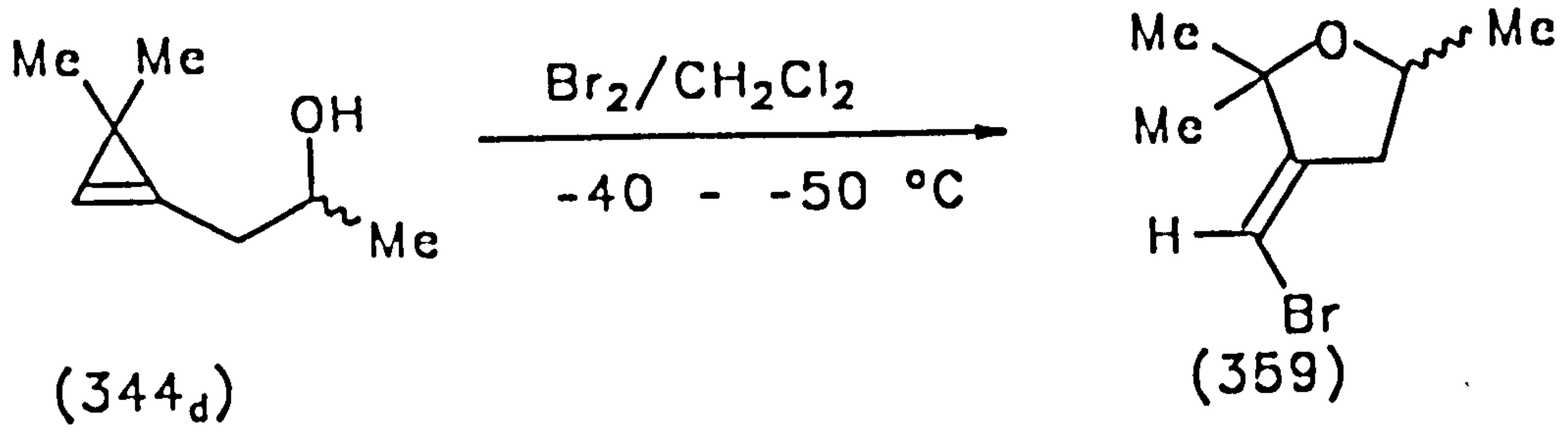
(356) (357)

The E-stereochemistry of (352) may be controlled by a preferred outward rotation of the bromine substitutent. This result involves at least two rotations, one bringing the three p-orbitals of the allyl system parallel, the second twisting the CMe_2-group approximately orthogonal to the final alkene, so that cyclisation can occur. An alternative mechanism would involve attack on the back of the 2,3-cyclopropene σ- bond of (344_c) at C_2, leading to tertiary character at C_3, concerted with attack at this position by the alcohol as in (358); this requires minimal rotational changes.



(358)

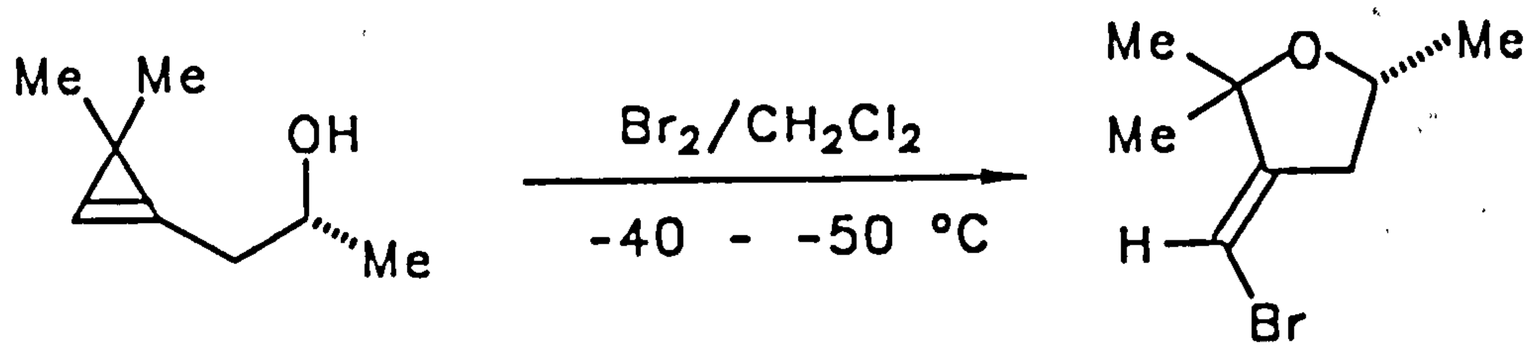
The racemic alcohol (344_d) underwent similar cyclisations, leading to (359) in a 67% yield on treatment with bromine for 30 m at −50 °C.



(344_d) (359)

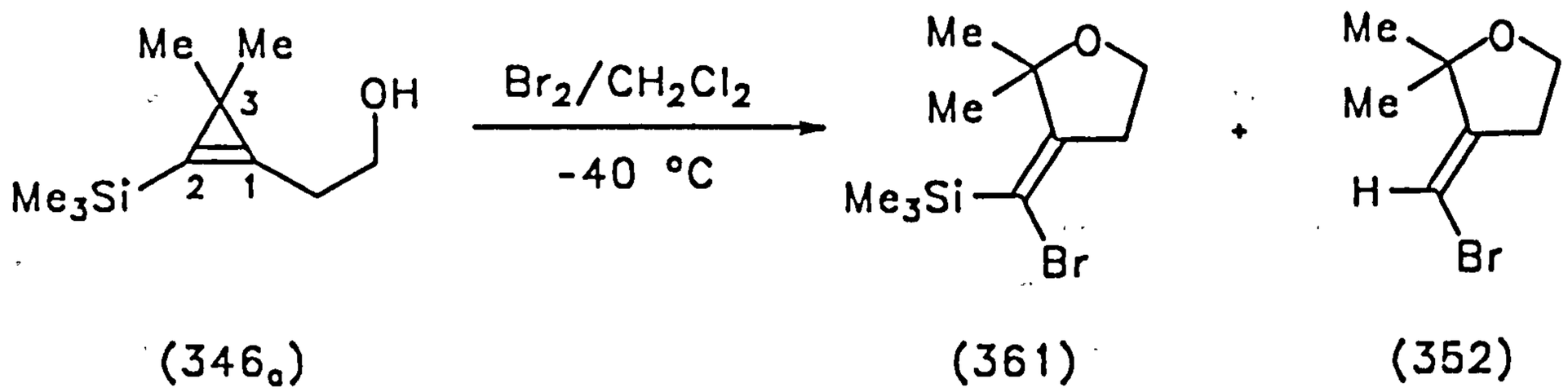
The ^1H n.m.r. spectrum of (359) showed a double doublet for the vinylic proton with allylic coupling (2.1 and 3.1 Hz) and a double pentuplet at δ 4.16 (1H) together with two pairs of double double doublets for the allylic protons at δ 2.82 and 2.22. The spectrum also showed singlets at δ 1.36 and 1.28 for the geminal methyl groups and a doublet at 1.31 (3H); the ^{13}C spectrum showed eight signals and the gated decoupled spectrum showed three quartets at δ 21.1, 27.4, and 28.9 assigned to the methyl groups, two singlets at δ 82.7 and 154.6, and a triplet for the allylic secondary carbon together with doublets at δ 71.4 and 97.2; the latter was assigned to the olefinic carbon attached to the bromine, the heavy atom effect of which made it appear at higher field than a normal alkene carbon.

In the same way, optically active alcohol (344_d) derived from (R)-(+)-methyloxirane,[156] led to the optically active furan (360) in 52% yield. The ^1H n.m.r. and the ^{13}C spectra were the same as those of the racemic compound.



(344_d) (360)

Treatment of (346_a) with bromine, as before, gave (361) in 52% yield, in addition to a minor product (352).

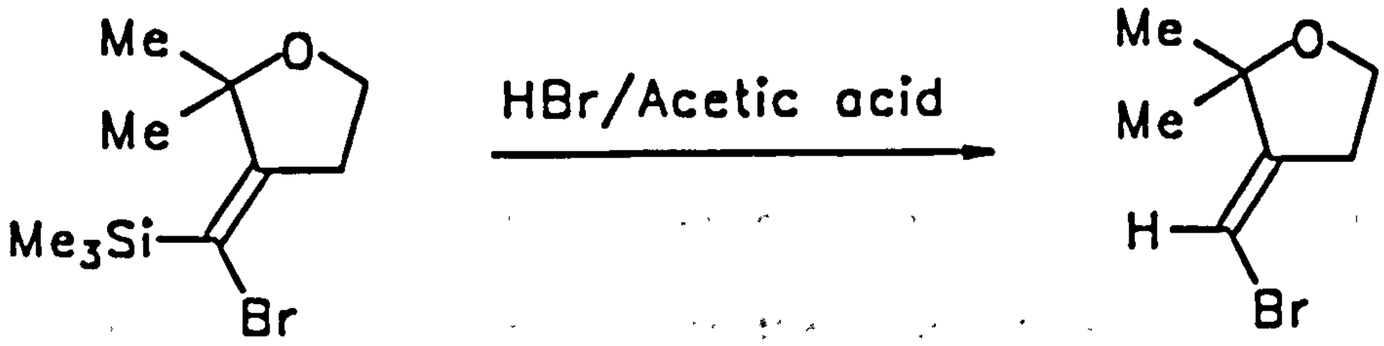


(346_a) (361) (352)

The ^1H n.m.r. spectrum of the major product showed four signals; two singlets at δ 0.34 and 1.4 for the trimethylsilyl group and the geminal methyl groups respectively, and two triplets at δ 3.9 (2H) and 2.95 (2H). The stereochemistry of the product was proved to be *E*- by an n.O.e experiment; irradiation of the signal at δ 1.4 showed an enhancement in the signal for the trimethylsilyl group at δ 0.34.

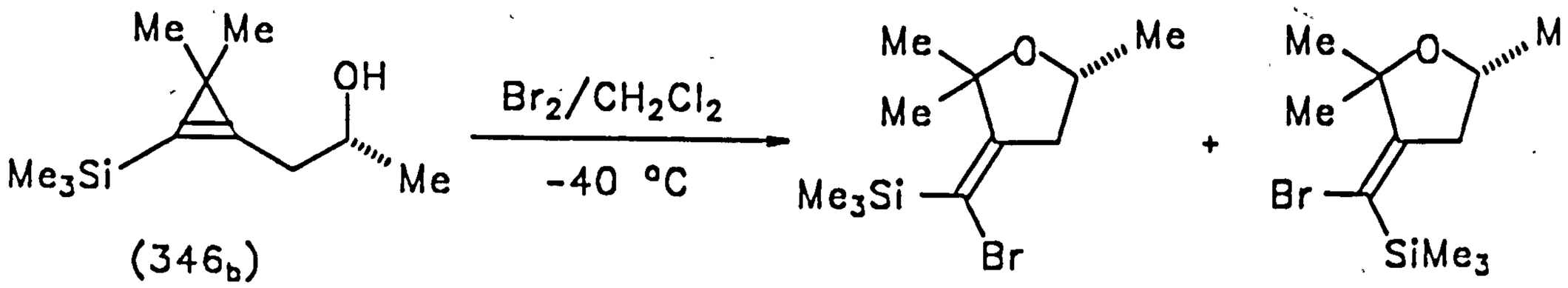
The regiochemistry may be explained by electrophilic attack of bromine at C_2 of (346_a) leading to the development of positive charge β- to the silicon,[157] rather than α, followed by ring-opening and trapping as before. The formation of the *E*- rather than the *Z*-isomer, would require the rotation of the more bulky trimethylsilyl group inwards rather than outwards, suggesting that the mechanism is more complicated than suggested above.

The minor product (352) is probably produced by reaction of the product (361) with acid (HBr) generated during the bromination. Indeed, the minor product was also obtained when (361) was treated with hydrogen bromide in acetic acid.

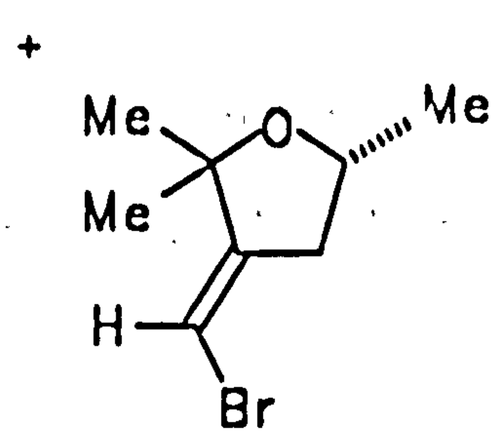


(361) (352)

Treatment of the optically active alcohol (346_b) with bromine as above, gave a 5:1 mixture of *E*- and *Z*-3-(2-bromo-2-trimethylsilylmethylene)-2,2,5-trimethyl-tetrahydrofurans (362); a minor product (360) was also obtained.



(346_b) (362_a) (362_b)



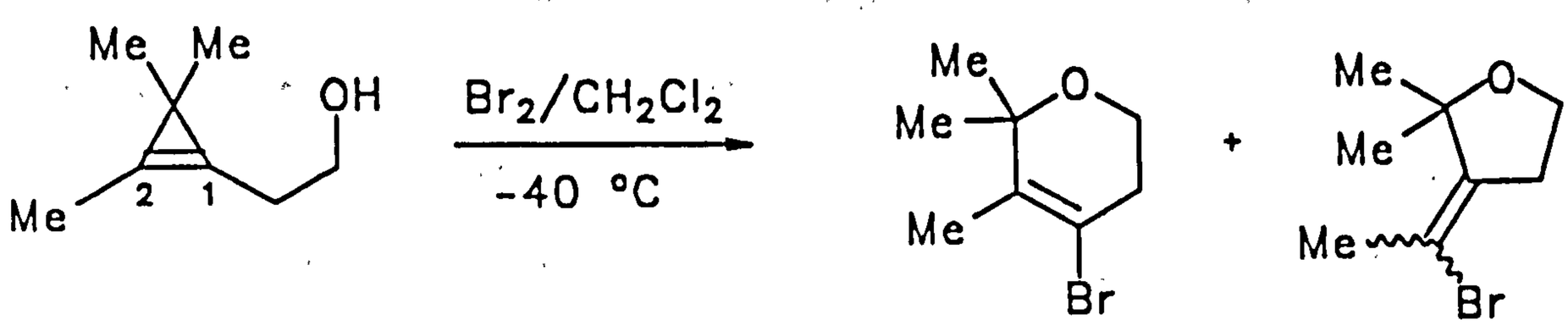
(360)

The mixture of (362_a) and (362_b) could not be separated by column chromatography. The ^1H n.m.r. spectrum of the major isomer showed a pair of double doublets for the allylic protons at δ 3.04 and 2.43; the first proton resonated downfield by 0.61 ppm from the other due to the deshielding effect of the halogen atom. In contrast, the allylic protons in the minor isomer appear at δ 2.71 and 2.17, while the geminal dimethyl groups were deshielded and resonated 0.11 ppm downfield from those of the major isomer. The major isomer was characterised as *E*- on the basis of a n.O.e. experiment; irradiation of the signal at δ 0.33 for the TMS-group in this isomer caused an *ca.* 2.44 and 1.99% enhancement in those at δ 1.47 and 1.38 respectively. Irradiation of the signals at δ 1.47 and 1.38 caused *ca.* 1.43 and 1.18%

enhancements in that at δ 0.33.

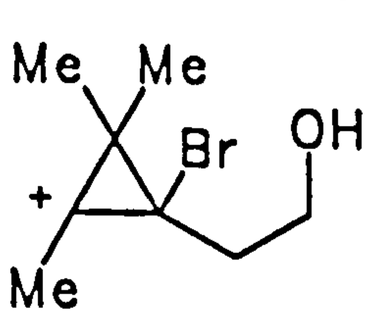
The minor product (360) was once again probably derived by the reaction of (362_a) and (362_b) with the HBr, generated during the bromination.

The introduction of a methyl group at C_2 of the cyclopropene caused an alternative cyclisation. Treatment of (344_a) with bromine in dichloromethane as before, led predominantly to the pyran (363).

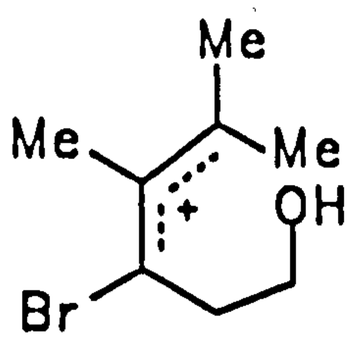


(344_a) (363) (364)

A minor product was (364) of unknown stereochemistry. Once again, the pyran (363) was apparently obtained by addition of Br^+ to the cyclopropene to generate the allylic cation (366) either directly or through the cyclopropyl cation (365), followed by cyclisation at the dialkyl substituted terminus.

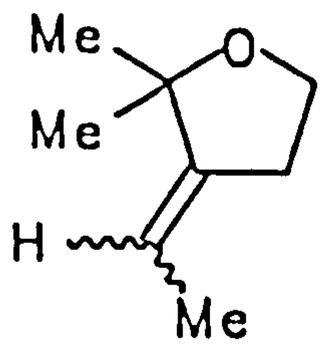


(365)

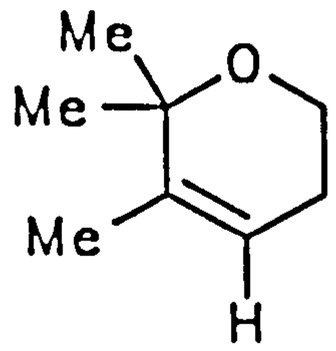


(366)

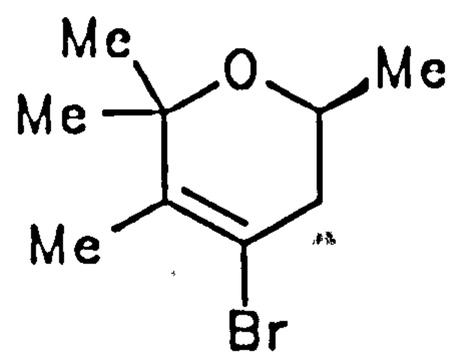
Reduction of the the mixture with lithium–t–butanol–THF led to (367) and (368); the ^1H n.m.r spectrum showed the alkene hydrogen signal for (367) as a very broad multiplet ($W_{1/2}$ *ca.* 7.0 Hz), whereas that for (368) was a quartet of triplets, with a quartet coupling of 7.0 Hz. Moreover, the allylic methylene group of the major isomer appeared at δ 2.04 whereas that in the minor one appeared at δ 2.57, in agreement with the assigned pyran and methylenetetrahydrofuran structures.[154]



(368)



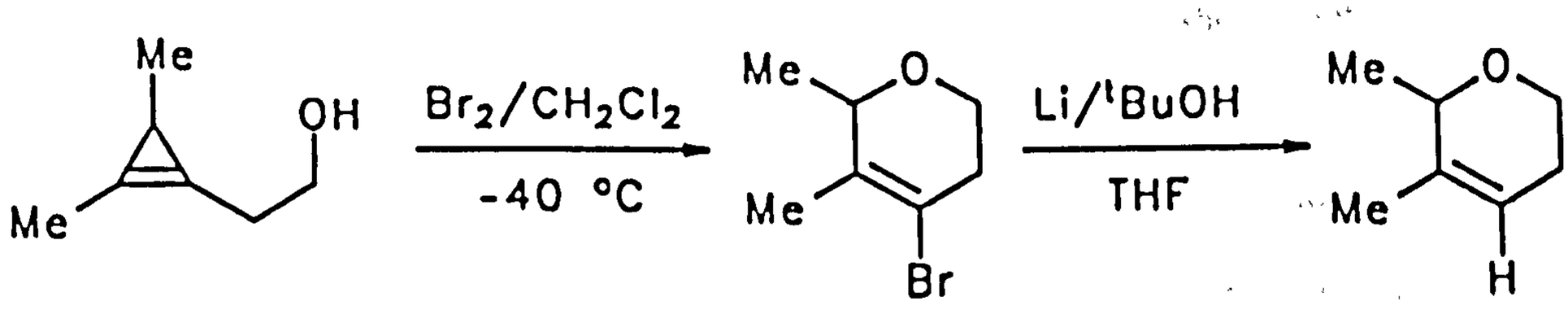
(367)



(369)

In the same way, treatment of the optically active alcohol (344_b), with the bromine as before led to an optically active pyran (369), although in low yield (32%). The ^{13}C spectrum of (369) contained nine signals, including two singlets in the olefinic region and a singlet at δ 77.0, together with a doublet at δ 65.3, a triplet at 44.2, and four quartets at δ 28.3, 24.5, 21.3, and 18.9.

The cyclopropene (344_e) also reacted with bromine as before to give only the pyran (370). The gated decoupled ^{13}C spectrum of (370) showed the expected seven carbons, two quartets at δ 18.8 and 19.36, two triplets at δ 36.5 and 63.4, together with a doublet at 74.8 and two singlets in the olefinic region.

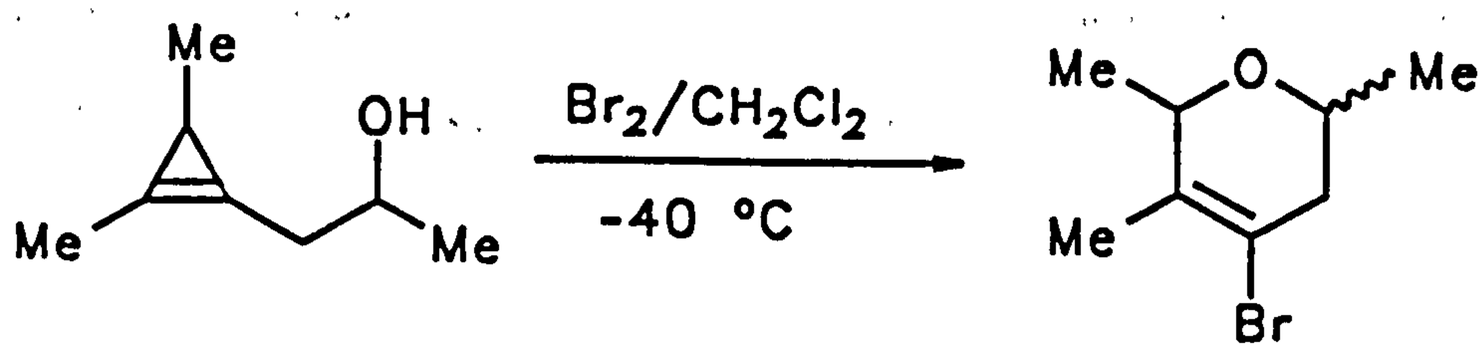


(344_e) (370) (371)

Reduction with lithium–t–butanol–THF led to (371), the ^1H n.m.r. spectrum of which showed an allylic methylene group at δ 2.2 and 1.97, and the alkene hydrogen signal as a very broad multiplet with $W_{1/2}$ *ca.* 7.0 Hz, in agreement with the pyran structure.

In the case of the 1:1 mixture of diastereoisomers of the cyclopropene alcohol (344_f), a 2:1 mixture of diastereoisomers of the pyran (372) was obtained on reaction with bromine. The two isomers showed peaks very close together by capillary g.l.c.,

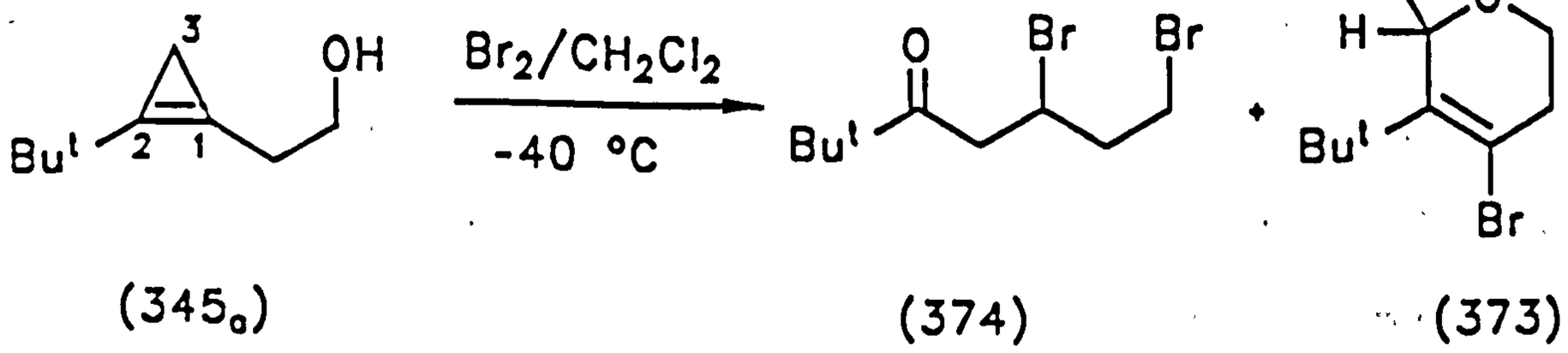
and it was difficult to separate them by preparative g.l.c., or by column chromatography.



(344$_f$) (372)

The signals for H_2 in the ^1H n.m.r. spectrum of both isomers appeared as a broad quartet at δ 4.2, suggesting that both have the C_2 methyl group equatorial. The major isomer showed a sextet (J *ca.* 6.0 Hz) for H_6, while the corresponding signal in the minor one was a double double quartet (J 3.9, 6.2, 10.5 Hz) at slightly higher field; the latter is assigned as the *cis*-isomer, both substituents occupying equatorial positions, and the former as the *trans*-isomer, the 6-substituent being axial.[158] The reason that the bromine adds only or largely to C-1 of the π-bond in (344$_a$), (344$_b$), (344$_e$) and (344$_f$) is not clear; however, related cyclopropene ring openings show subtle substitutent effects.[159]

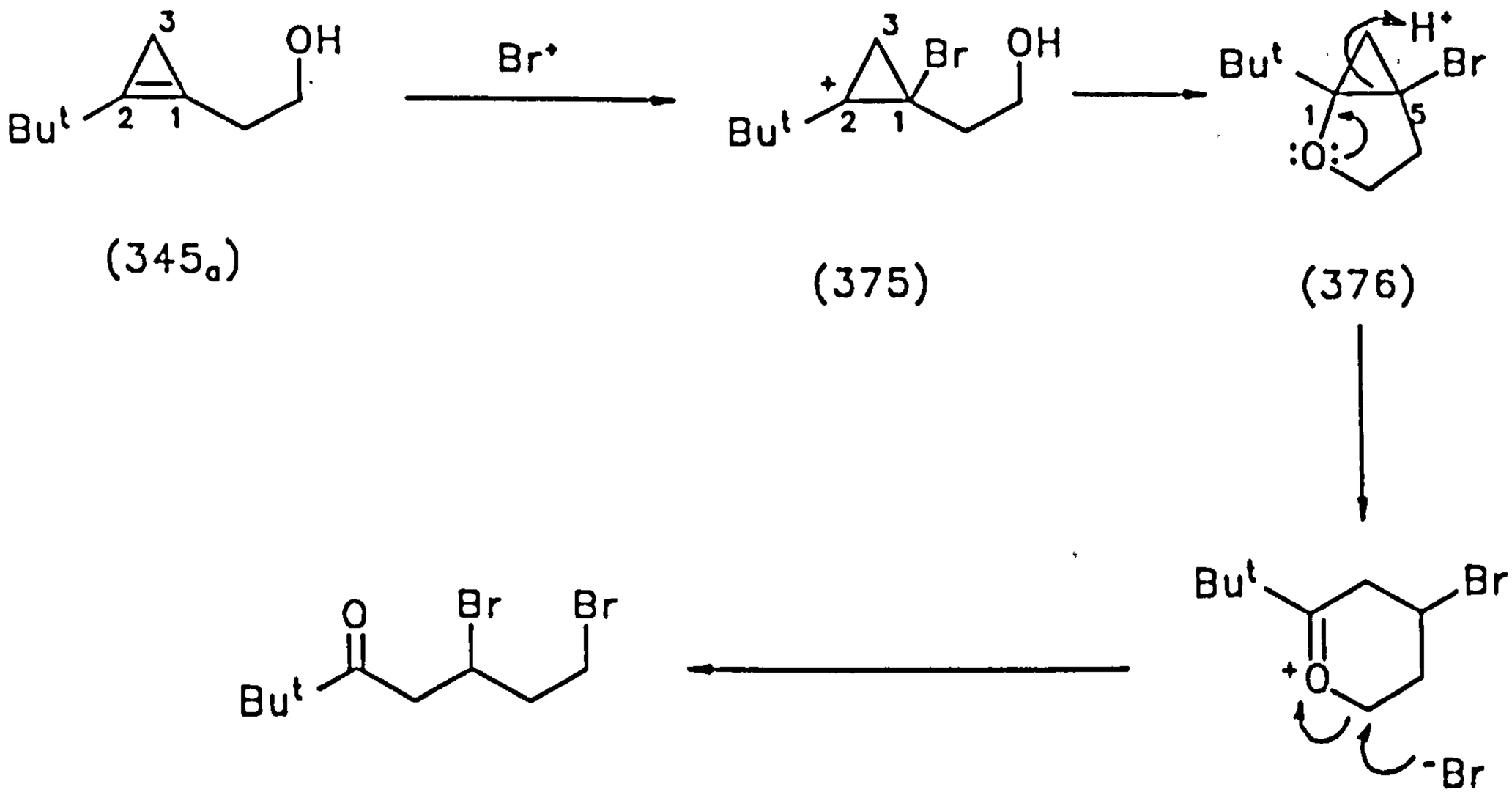
It is interesting to note that the reaction of (345$_a$) with bromine followed a different course. The minor product was the pyran (373) and the major product was the ketone (374).



(345$_a$) (374) (373)

The origin of (374) is not certain; however, the reaction may involve the initial attack by the electrophilic bromonium ion Br^+ at the less hindered end of the π-bond to

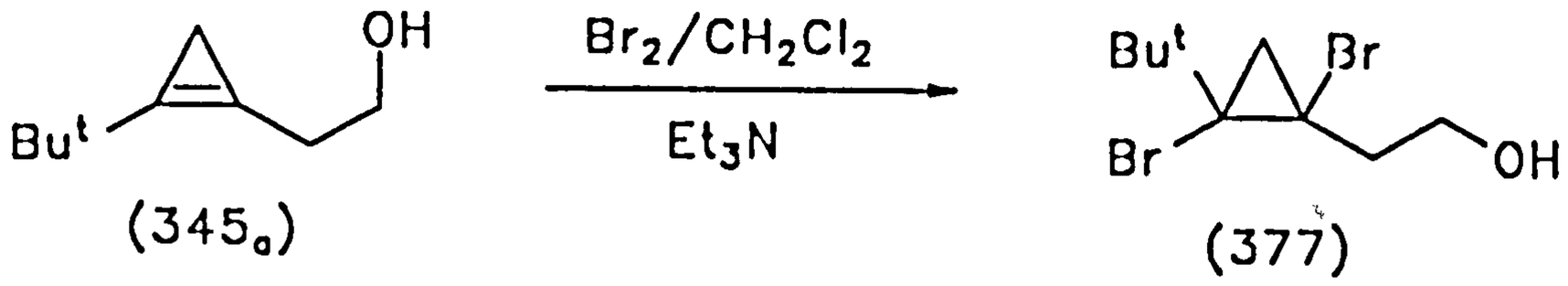
give the cyclopropyl cation (375) which is stabilized by the t-butyl group, reducing the rate of cyclopropane ring opening. Intramolecular trapping by the alcohol could lead to (376). Protonation of the 1,5-bond at C_5 by the acid generated, and cleavage of the highly sterically hindered α-oxycation by bromide at C_3 could in turn lead to (374).



(345a) (375) (376)

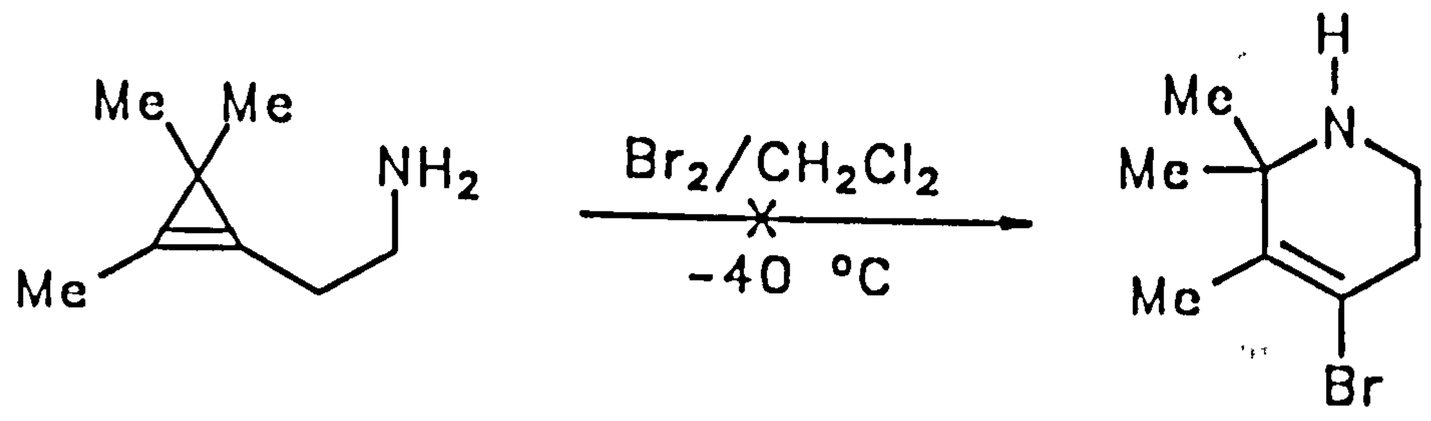
(374)

The ketone (374) gave a correct mass measurement for $C_9H_{16}Br_2O$, and the i.r. spectrum displayed a single carbonyl band at 1703 cm^{-1} for the saturated ketone, while the ^{13}C spectrum showed the expected seven signals including one signal at δ 214.7 assigned to the carbonyl carbon. To support the mechanism above, bromine was added to the same cyclopropene (345_a) in the presence of triethylamine; addition occurred at the double bond and a 1,2-dibromocyclopropane (377) was isolated. The ^1H n.m.r. spectrum showed two triplets and three singlets including the hydroxyl group. One of the singlets is assigned to the two cyclopropane hydrogens. The stereochemistry of the bromine addition was therefore assigned as *E*- because the two hydrogens in the *Z*- isomer would be expected to have a considerably different chemical shift.



(345_a) (377)

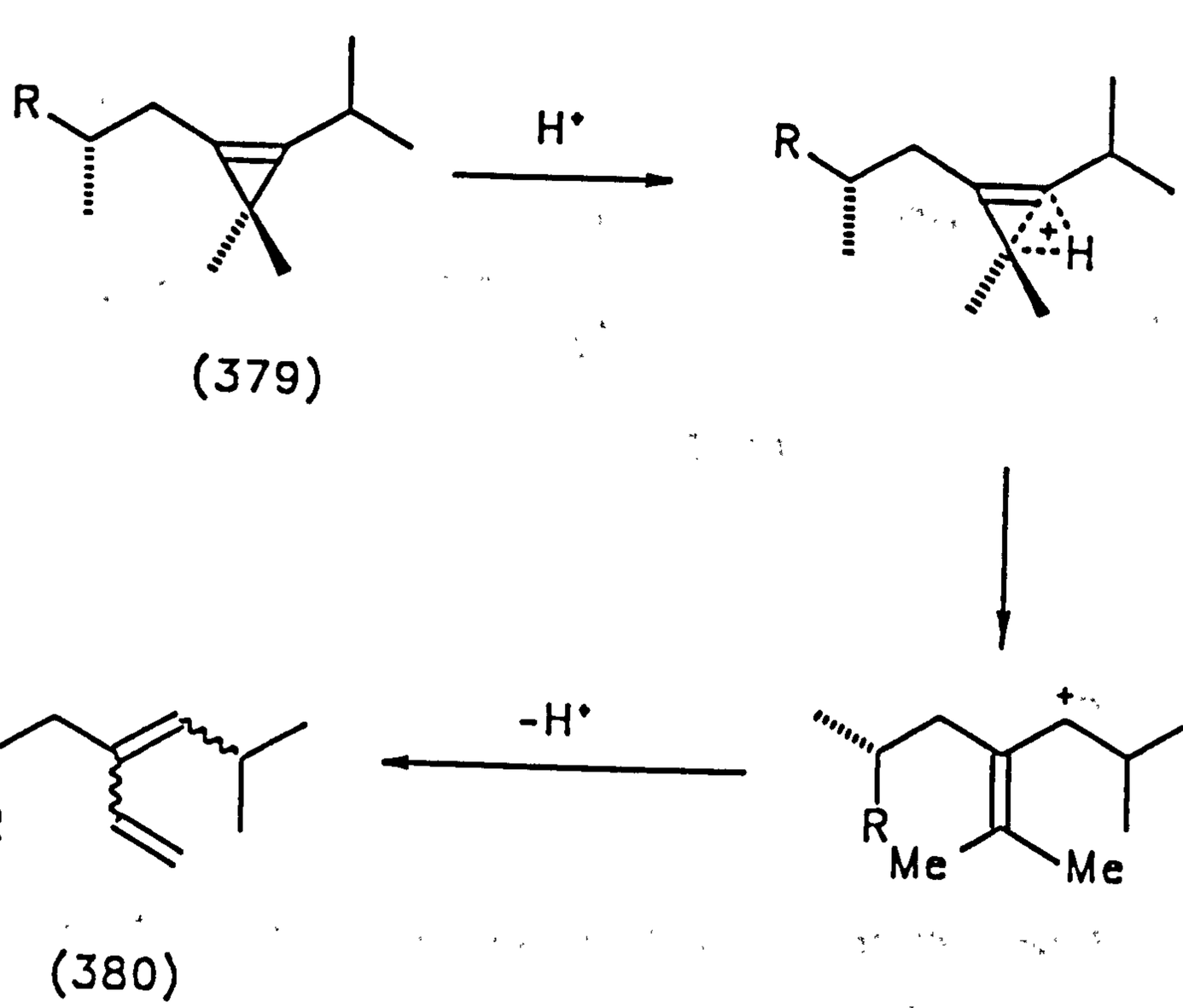
It was hoped that the cyclisation to give furans and pyrans described above could be extended to the preparation of nitrogen hetrocycles. However, treatment of the aminocyclopropene (347) with bromine as before did not give the desired a tetrahydropyridine (378), but instead, a complicated mixture was obtained.



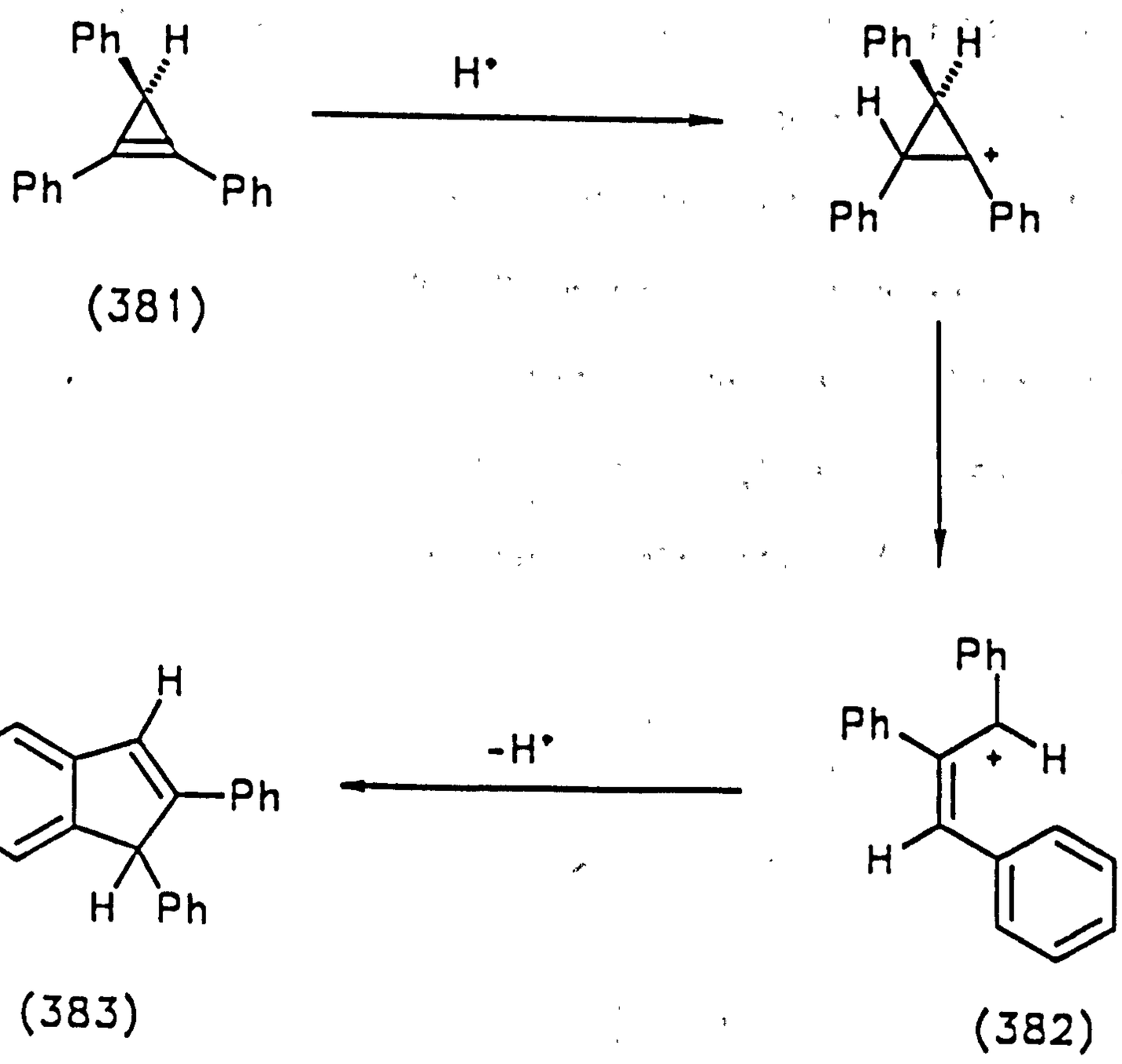
(347) (378)

3.5: Reaction with acid.

With the exception of cyclopropenones and cyclopropenyl cations, derivatives of cyclopropenes are usually sensitive to strong acid and readily undergo acid-promoted ring opening. Such acid-catalysed reactions have been rationalized by invoking a rearrangment of the cyclopropene ring to an allylic carbonium ion, either by protonation of the double bond or by protonation of the cyclopropene single bond, e.g. exposure of calysterol (379) to 0.15% p-toluene sulphonic acid in benzene at room temperature affored (380) as the major product.[159]

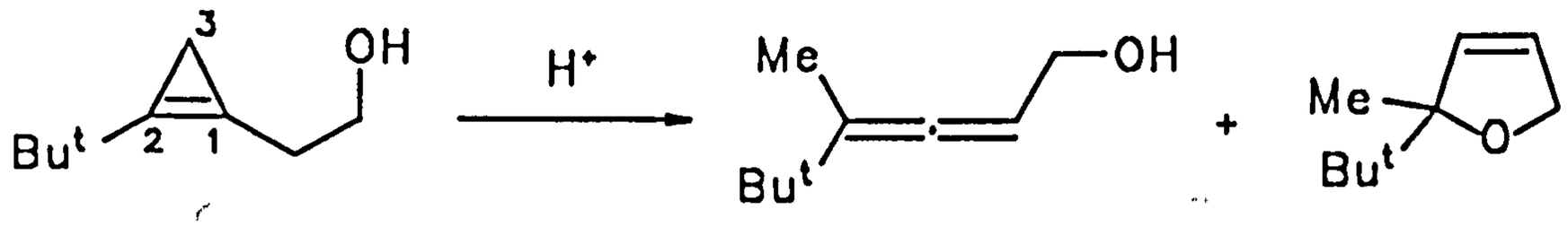


Cyclizations of the intermediate allylic carbonium ions have been observed. Thus triphenylcyclopropene (381) upon treatment with acid gives diphenylindene (383), *via* intramolecular reaction of the allylic cation (382).[52]

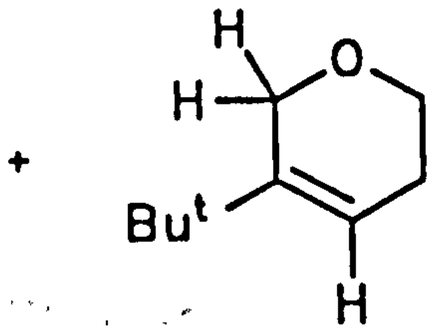


Reaction of the alcohol (345_a) with p-toluene sulphonic acid in benzene led to

three products:[153]

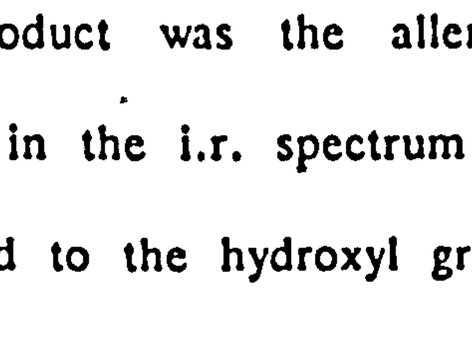


(345$_a$) (384) (385)



(386)

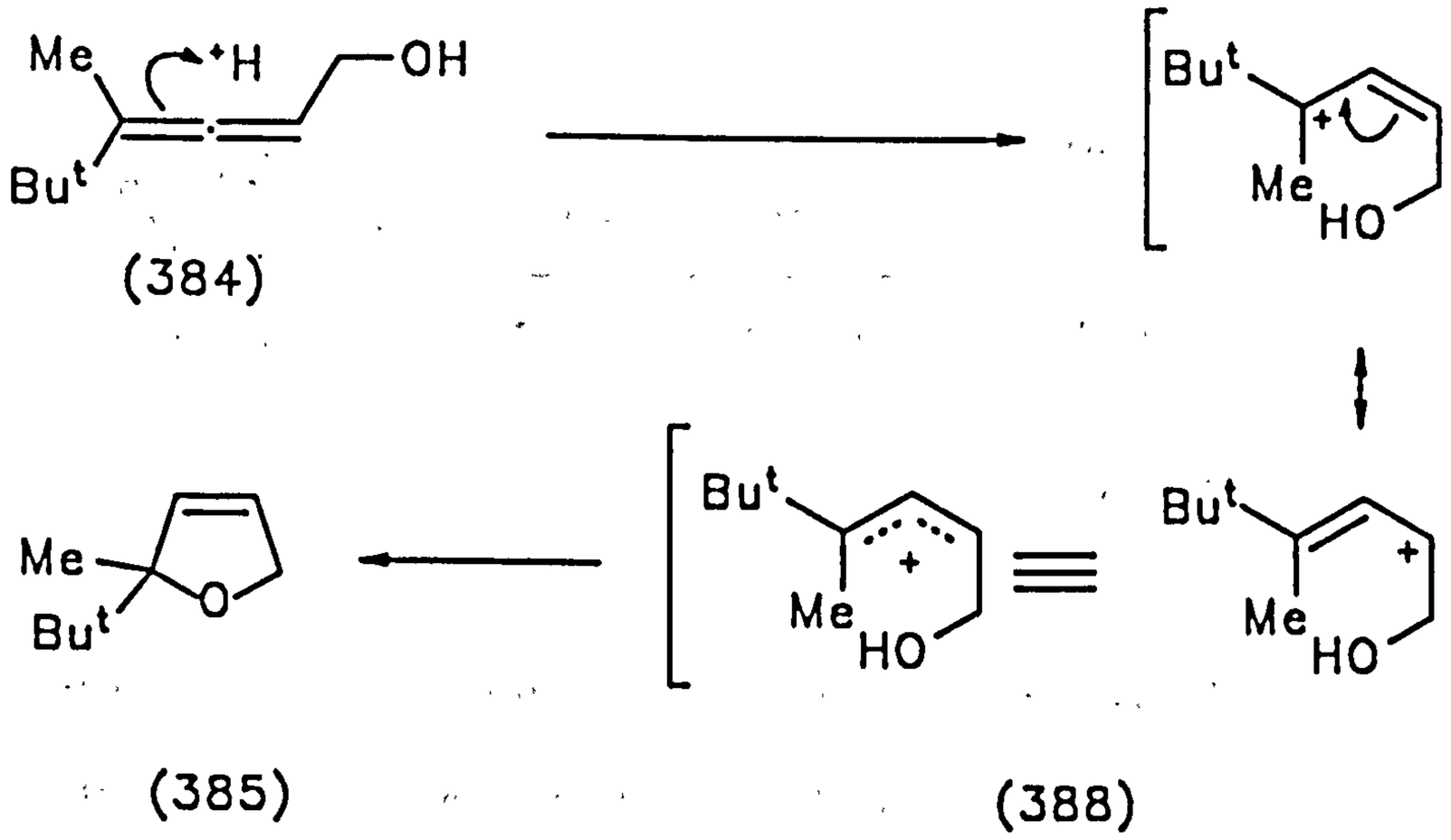
The pyran (386) was formed by attack of H^+ at the less hindered end of the π–bond of (345$_a$), and cyclopropyl–allyl ring opening followed by cyclisation as before. It could be distinguished from the corresponding methylenefuran on the basis of the very broad alkene signal which included a 5.0 Hz coupling; moreover, the protons of the C_5 methylene group appeared at δ 2.1, rather than at *ca.* δ 2.6 as in the methylenefurans.[154] The major product was the allene (384), which exhibited a characteristic allenic stretching band in the i.r. spectrum at 1950 cm^{-1}, together with a broad band at 3347 cm^{-1} assigned to the hydroxyl group. The ^1H n.m.r. spectrum included a broad multiplet for the alkene hydrogen, which was decoupled to a triplet (J 6.0 Hz) on irradiation of the doublet corresponding to the vinylic methyl group. The allene may arise by protonation of (345$_a$) at the methylene end of the 1,3–σ–bond with subsequent or concurrent elimination of a proton from the allylic methylene group such as in (387).



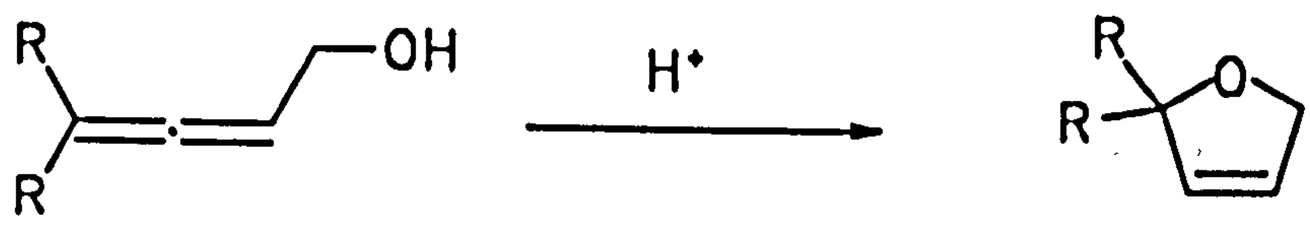
(387)

The dihydrofuran (385) may arise by acid induced reaction of (384) to give the

more stable cation (388), followed by intramolecular reaction with the hydroxyl group.

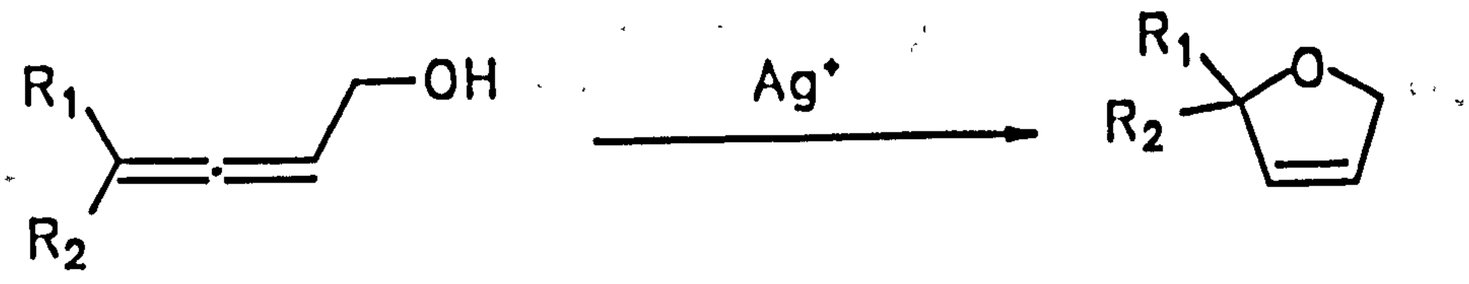


Allenic alcohols have already been shown to undergo acid- or base- catalysed cyclisation to furan derivatives.[154]



R=alkyl, aryl, alkoxy groups.

Moreover, treatment of the δ-monoalkyl or δ,δ-dialkylsubstituted α-allenic alcohol (389) with a catalytic amount of silver tetrafluoroborate led to complete cyclisation, affording 2,5-dihydrofurans.[154]



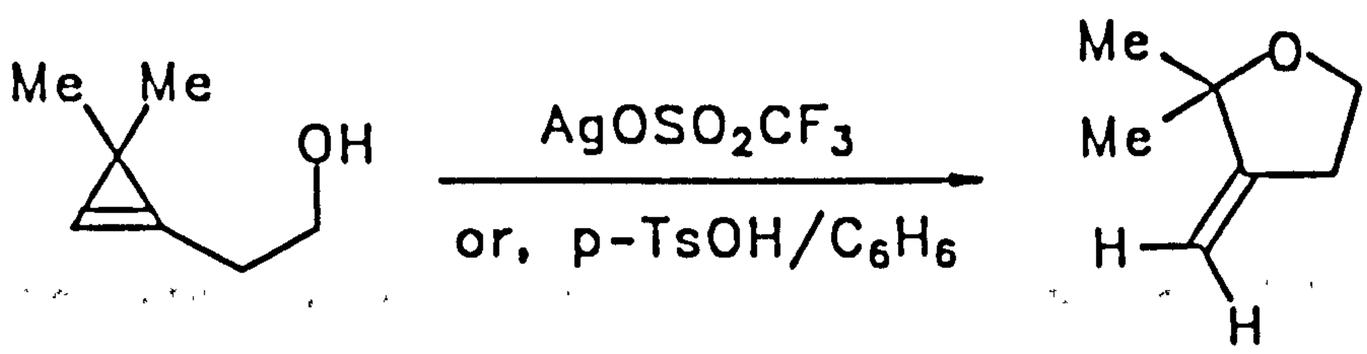
(389)

R_1=H, alkyl.

R_2=alkyl.

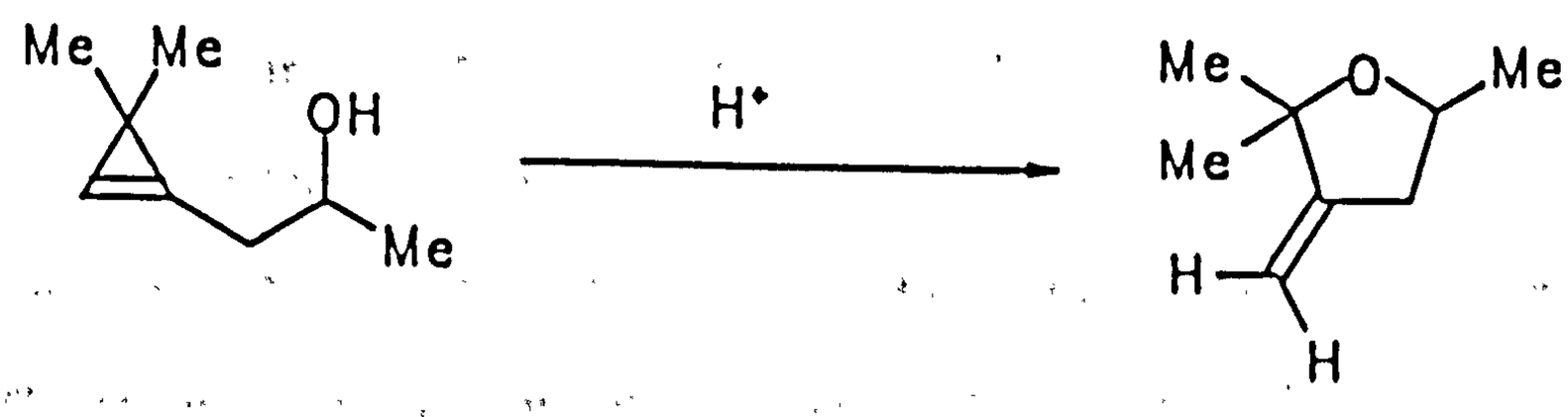
Reaction of the cyclopropene alcohol (344_c) with p-toluene sulphonic acid or

silver trifluoromethane sulphonate in benzene for 12 h at room temperature, in each case led to (353) (61%, and 47% respectively), identical to a sample obtained earlier (p. 136).



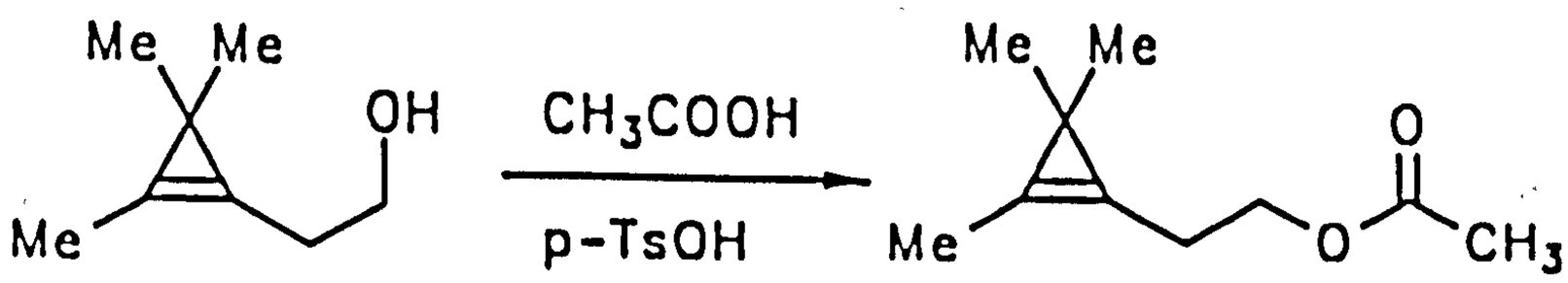
(344_c) (353)

In the same way, treatment of the racemic alcohol (344_d) with p-toluene suphonic acid as above gave the furan (390) in 51% yield.



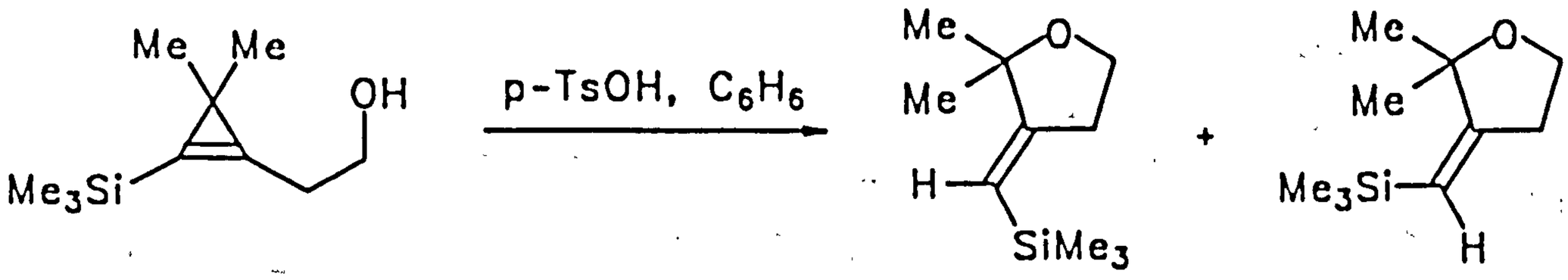
(344_d) (390)

In contrast, when the cyclopropene (344_a) was allowed to react with p-toluene sulphonic acid in acetic acid solution, only the corresponding acetate of the alcohol was produced.



(344_a)

Moreover, reaction of the cyclopropene (346_a) with p-toluene suphonic acid for 3.5 h gave a mixture of isomers in ratio *ca.* 2:1, which were separated by preparative g.l.c.:

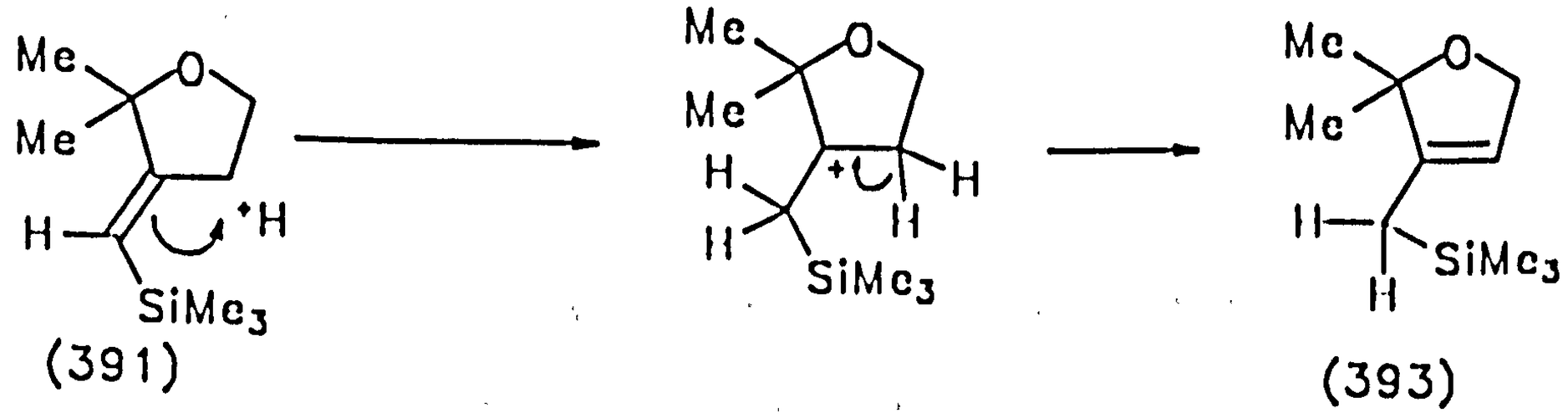


(346$_a$) (391) (392)

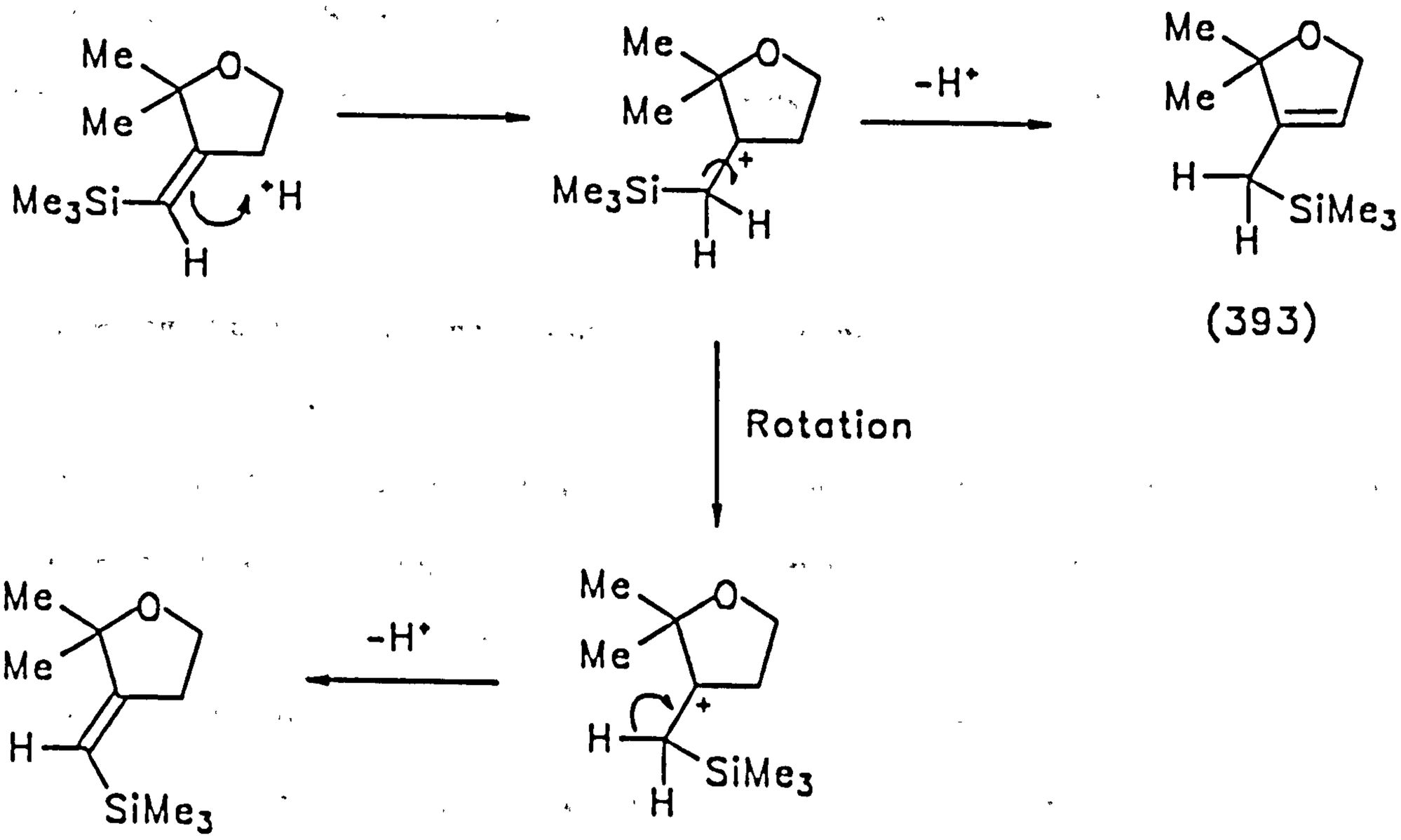
The *E*–stereochemistry of the major isomer (391) was established on the basis of an n.O.e. experiment. Irradiation of the signal at δ 1.2 showed quite a large enhancement (*ca.* 13%) for the vinylic proton at δ 5.12, and none in the signal at δ 0.1; moreover, irradition of the signal at δ 1.34 for the minor isomer caused a 4% enhancement in that at δ 0.14, but none in that at 5.4. The geminal methyl groups in the minor isomer (392) were shifted downfield relative to those of the major isomer (δ 1.34 compared to δ 1.2) possibly due to deshielding by the trimethylsilyl group.

On standing in deuteriochloroform at 20 °C the *E*–isomer (391) rearranged to 2,2–dimethyl–3–(trimethylsilylmethyl)–2,5–dihydrofuran (393), the reaction being *ca.* 50% complete after four days. Under the same conditions, the *Z*–isomer (392) rearranged to a 1:2:1 mixture of itself, the E–isomer and the dihydrofuran. Presumably both processes occur by protonation of the exocyclic alkene by traces of acid in the solvent, to generate a tertiary cation β– to silicon,[157] followed by alternative deprotonations (scheme 7 and 8).

(Scheme 7)

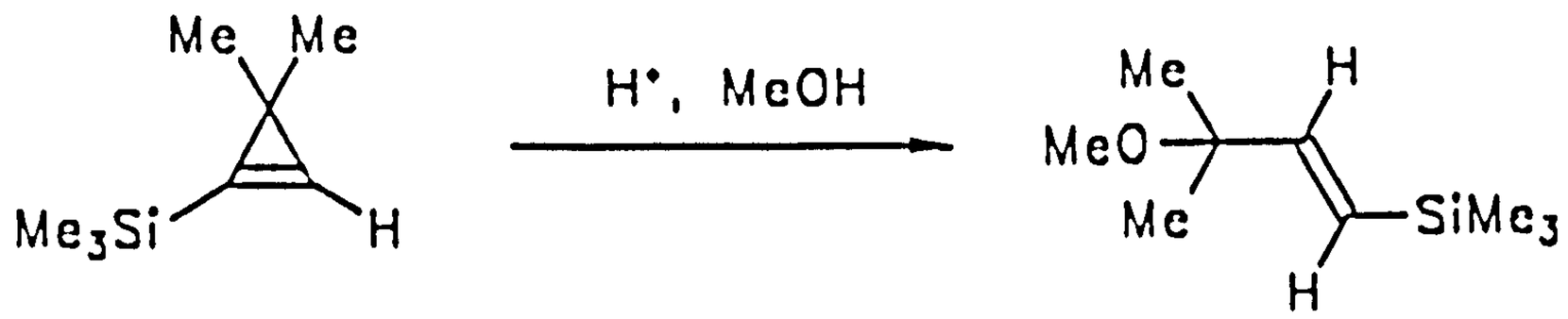


(Scheme 8)



Such a process could clearly occur in the reaction of (346_a) with acid, altering the *E*/*Z*-ratio in favour of the *E*-form. However, since less than 5% of the dihydrofuran was observed in this process and the ratio was 2:1, this isomerisation is apparently not occurring to a major extent under the reaction conditions.

The corresponding reaction of 3,3-dimethyl-1-trimethylsilylcyclopropene (199) with p-toluene sulphonic acid in methanol led exclusively to *E*-3-methoxy-3-methyl-1-trimethylsilylbut-1-ene (394). The *E*-stereochemistry was established on the basis of the coupling constant between the two vinylic protons (J 19.6 Hz).[130]



(199) (394)

Its appears from the above that the reaction of cyclopropene alcohols with acid is much slower than bromination, which was discussed above (3.4), because the reaction with the acid required 3 – 12 h at room temperature, while that with the bromine

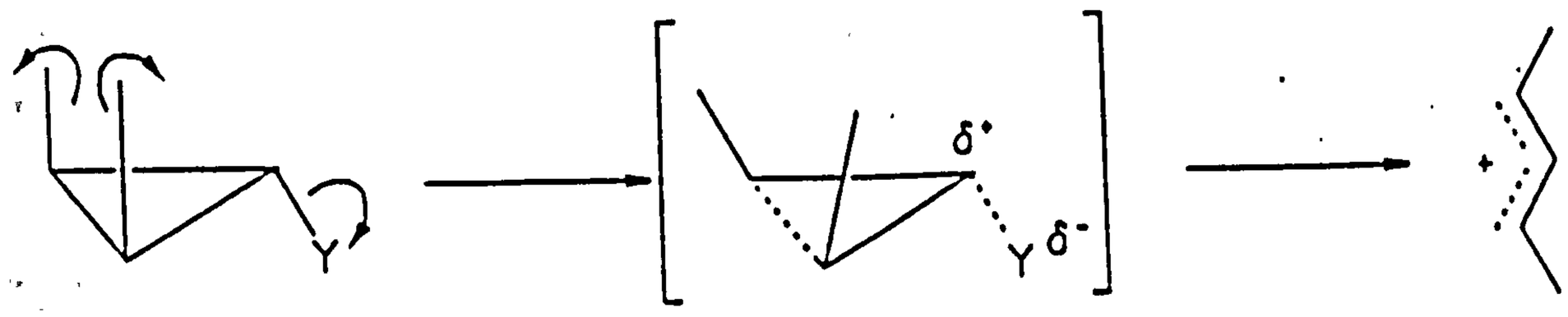
required 0.5 h at −50 °C. In agreement with this, a mole of HBr is apparently generated during the bromination but no products of protonation were observed; this agrees with the known greater reactivity of the π−bonds to Br^+ than to H^+.[160]

3.6: Labelling studies on the mechanism of ring−opening.

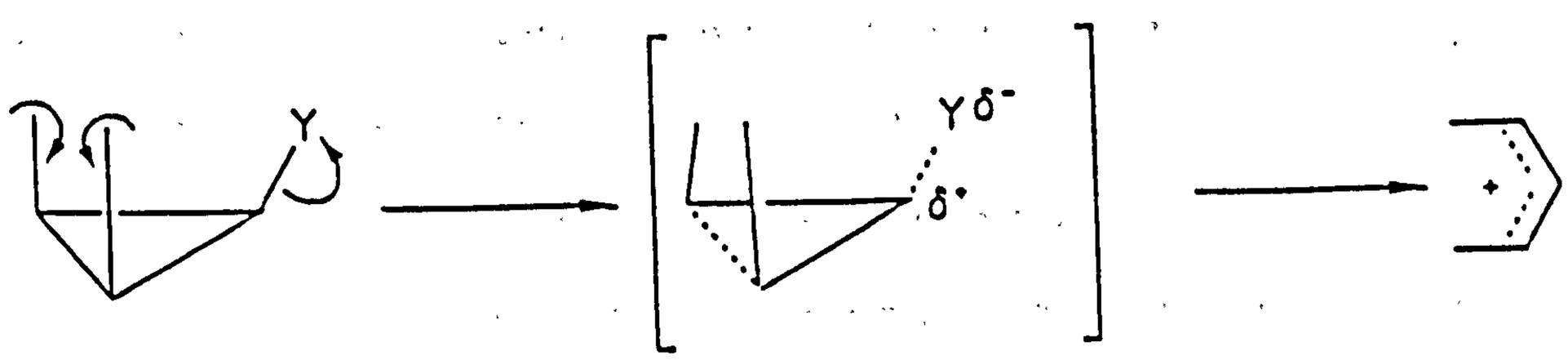
In general, it is assumed that addition of an electrophile to cyclopropenes occurs at the π−bond and the resulting cyclopropyl cation ring−opens to an allyl cation, although the possibility of σ− attack was recognised at an early stage.[52,76]

Cyclopropyl cations have previously been implicated in the solvolysis or thermolysis of cyclopropyl tosylates and halides which are known to proceed by concerted breaking of the bond to the leaving group and cyclopropyl−allyl ring opening. The groups which are *trans* to the leaving group will rotate outwards (path A) with the release of strain, while groups which are *cis*− related must rotate inwards (path B) leading to an increase in strain as they move closer together. The rates of the two processes may therefore be different.[161]

(A)

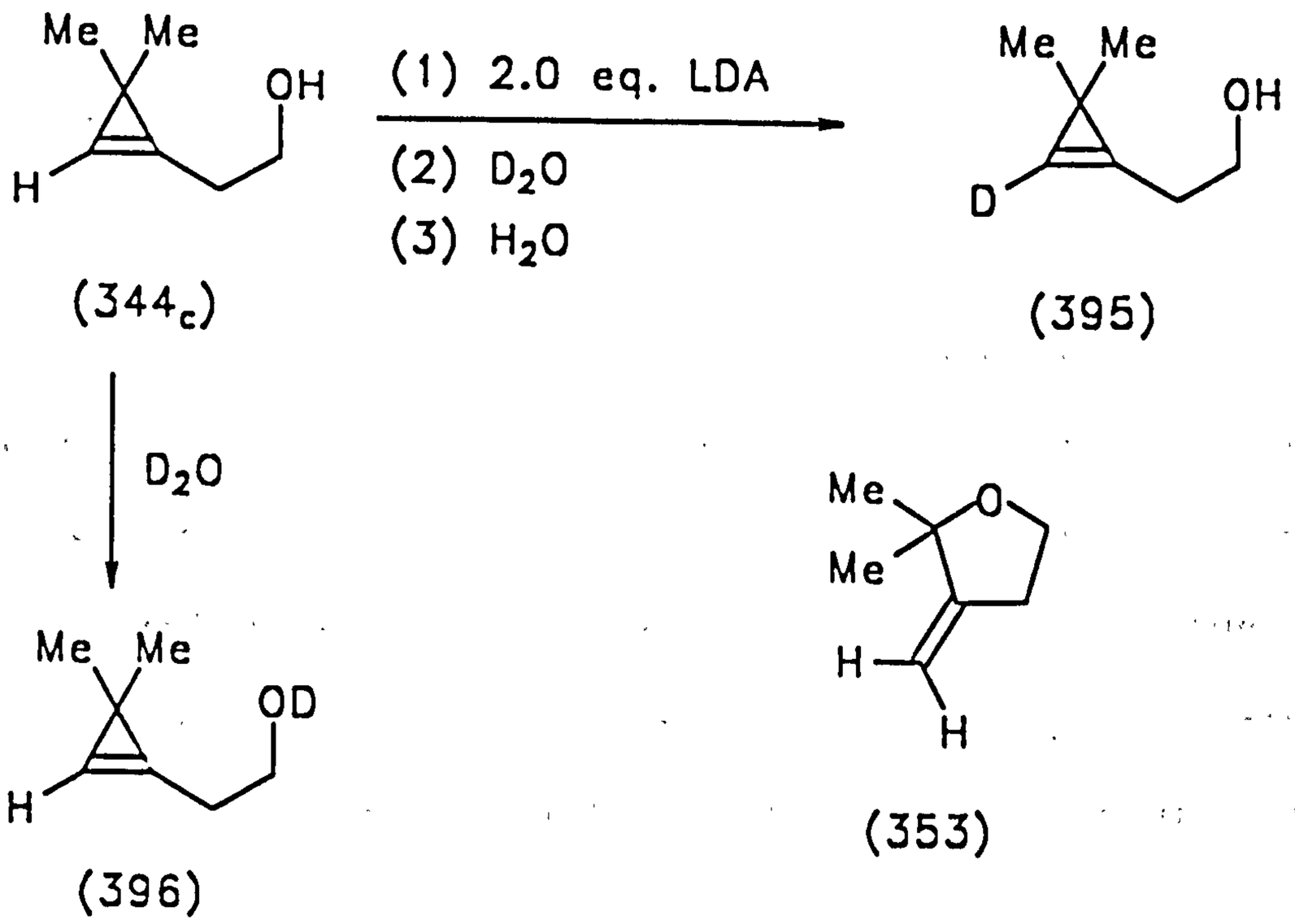


(B)



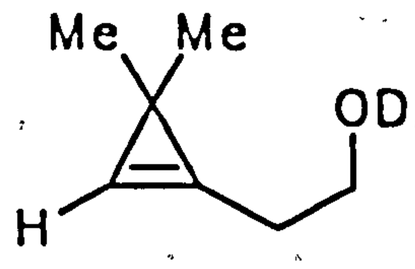
The addition of an electrophile to the π−bond of a cyclopropene in principle

provides a route to the cyclopropyl cation from a different point on the energy surface and the disrotation in the cyclopropyl–allyl ring opening might be controlled by steric and electronic effects of substituents on the C_2 and C_3 positions of the cation. Alternatively the cyclopropyl–allyl rearrangement may be concerted with addition and the disrotation process may be controlled by the incoming electrophile. In order to probe the mechanism of H^+ attack, the two deuterium–labelled cyclopropenes (395) and (396) were examined. The ring–deuterated cyclopropene was prepared by reaction of the cyclopropene alcohol (344_c) with two equivalents of lithium di–isopropylamide followed by quenching the dianion with D_2O and then replacing the exchangeable deuterium with water.

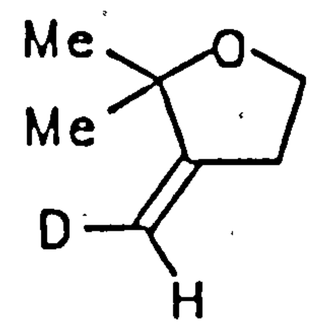


Treatment of (396) with p–toluene sulphonic acid in which the acidic hydrogen had been exchanged for deuterium by shaking with D_2O, and treatment of (395) with p–toluene sulphonic acid in benzene led to monodeuterated methylene furans. The ratio of deuteration at the two alkene positions was determined in each case by deuterium n.m.r.. The signals for the two hydrogens (deuteriums) occurred at δ 4.94, and 4.82; the one at lower field was assigned to the *E*–hydrogen because irradiation of the

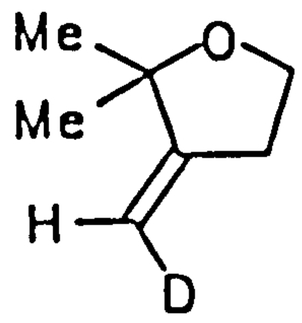
geminal methyl signal in (353) caused an n.O.e. enhancement in the proton signal at δ 4.79. The results are summarised below:



(396)



2.7



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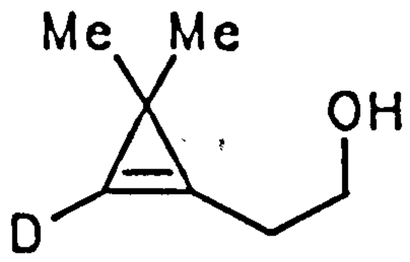
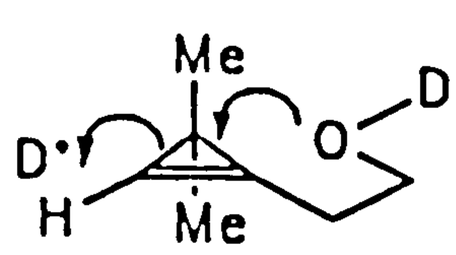


(395)

1

2.7

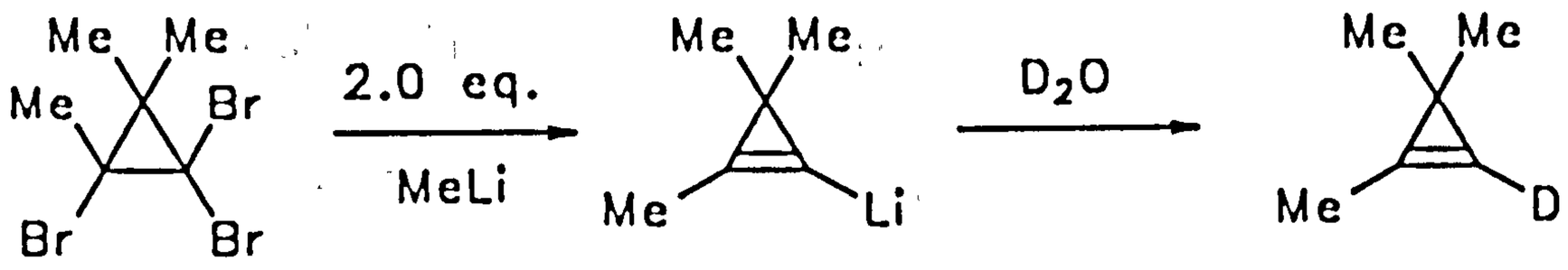
The isomer ratio can not be explained in terms an intermediate free planar cyclopropyl cation, because in this case, identical ratios of *E*- and *Z*-products, probably close to 1:1, would be expected. It is not yet clear whether the results are best explained by π-attack concerted with ring-opening, by σ-attack predominantly from the side of C_2-C_3 bond, or by a mixed mechanism. It is interesting to note, however, that the molecule is well arranged for σ-attack concerted with cyclisation as in (397).



(397)

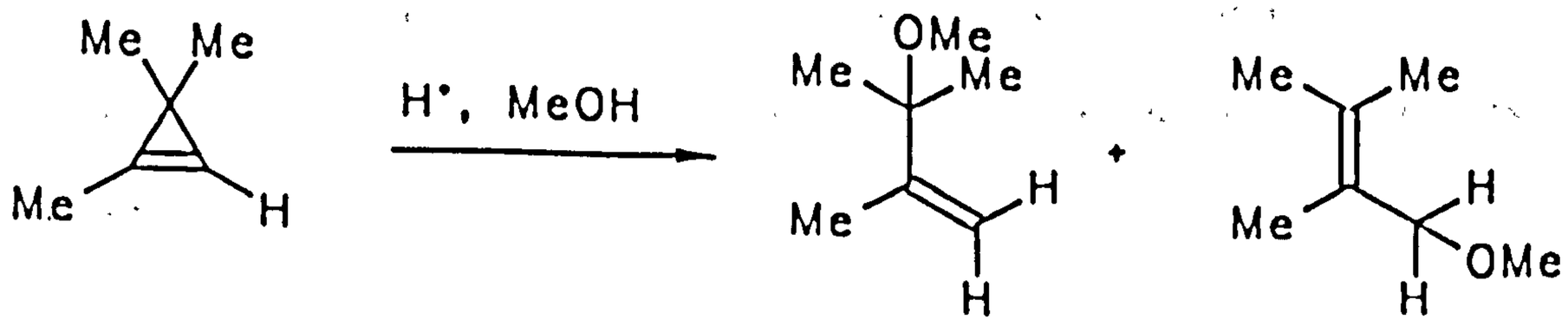
In order to probe this mechanism further, the ring opening of 1,3,3-

trimethylcyclopropene with acid in the presence of methanol was examined. The deuterium labelled cyclopropene (398) was prepared by reaction of the trihalocyclocyclopropane (333) with two equiv. of methyl lithium and removal of the solvent at high vacuum to give the solid lithiocyclopropene, which was quenched with deuterium oxide; the cyclopropene was distilled directly into a cooled receiver. The cyclopropene (399) was prepared in the same way.



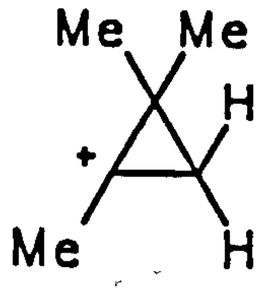
(333) (398) (399)

Treatment of the cyclopropene (399) with p-toluene sulphonic acid in the presence of methanol for 66 h at room temperature gave a mixture of (400) and (401) in ratio *ca.* 1.6:1. The olefinic hydrogen signal at lower field in the ^1H n.m.r. spectrum of (400) was assigned as being *Z*- to the methyl group, because it showed a slightly larger allylic coupling constant.[162]

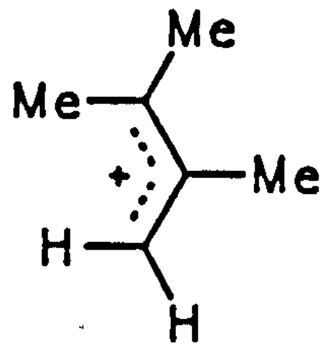


(399) (400) (401)

The products (400) and (401) may arise once again by addition of H^+ to the π– bond of the cyclopropene to generate the more stable cyclopropyl cation (402) followed by ring–opening to the allylic cation (403) which in turn is intercepted by methanol. The two products could not be separated but were distinguishable by ^1H n.m.r. spectroscopy.

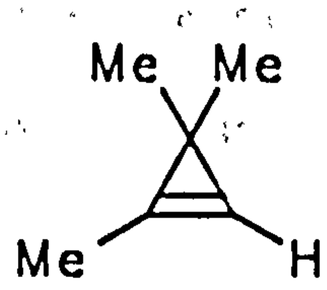


(402)

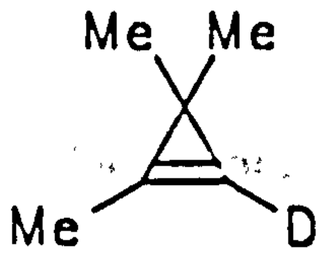


(403)

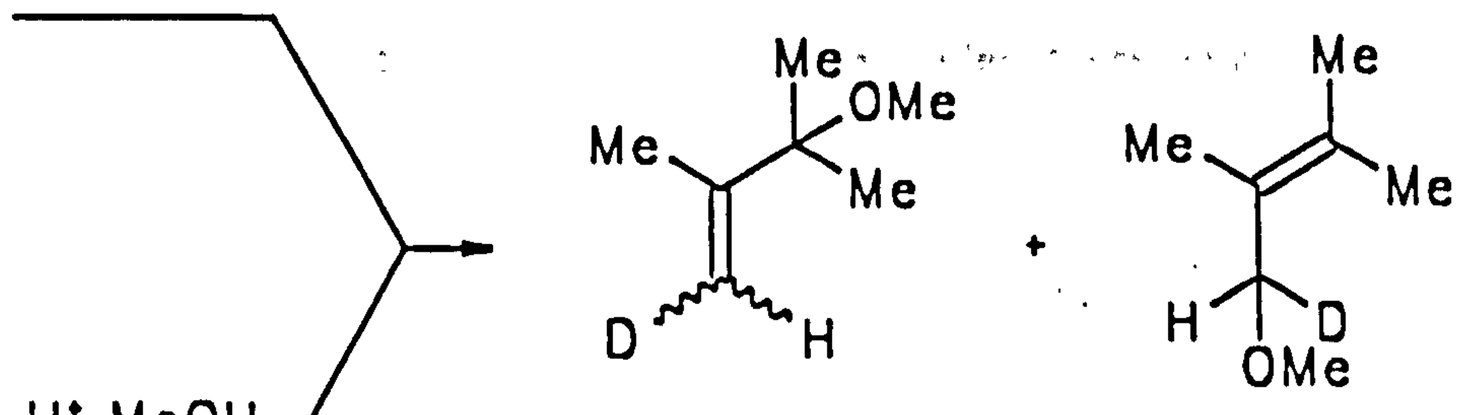
Treatment of (399) with p–toluene sulphonic acid in which the acidic hydrogen had been exchanged for deuterium in the presence of CH_3OD and treatment of (398) with p–toluene sulphonic acid in the presence of methanol led to the same products as above but containing one deuterium.



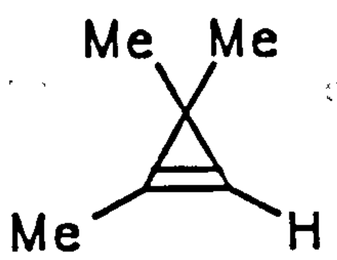
(399)



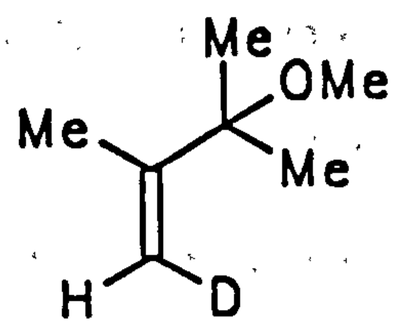
(398)



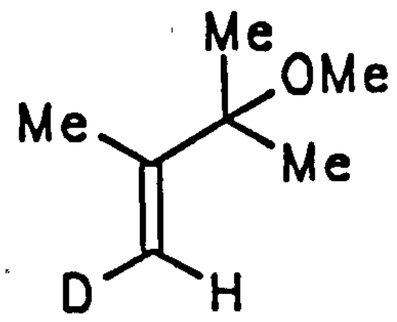
The ratio of deuteration at the two alkene position was determined by deuterium n.m.r., the signals appearing at δ 4.95 and 4.92; as in (400). The results are summarised below:



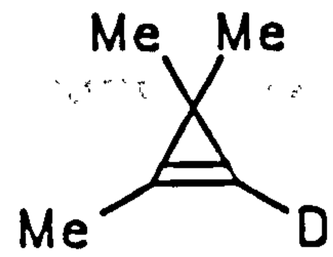
D⁺,MeOD



3.5



1



H⁺,MeOH

1

3.2

The ratio above is again difficult to explain if a free cyclopropyl cation is involved because in this case equal ratios of *Z*- and *E*- of hydrogens would be expected in the alkene position. Therefore, the mechanism appears to be similar whether the cation is trapped in an inter- or intra-molecular procees. Moreover, the ratio of isomers remained unchanged between 0.5 h and 55 h as the reaction proceeded, and therefore the products are not equilibrating under these conditions.

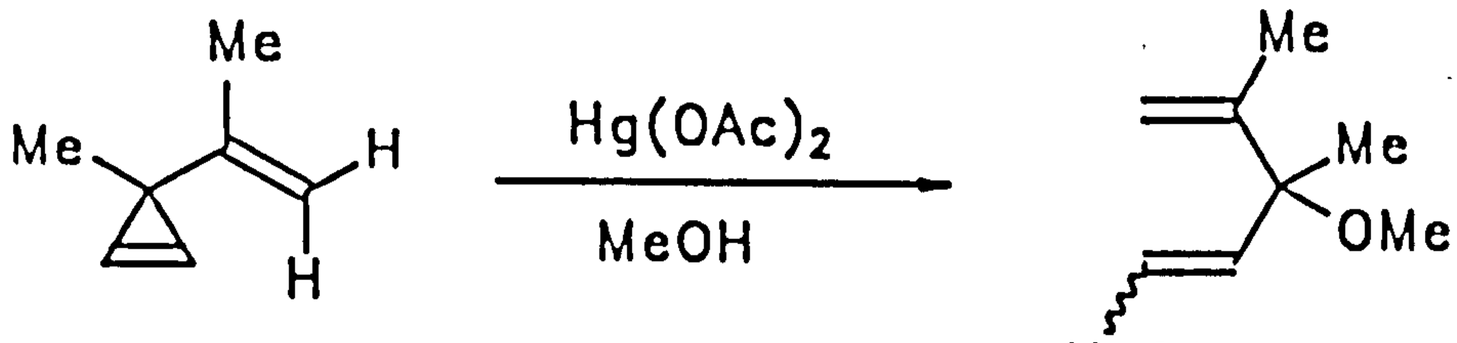
3.7: Conclusion.

The cyclopropene alcohols (344_c), (344_d), (346_a) and (346_b) react with bromine at −50 °C, and with acid or silver trifluoromethane sulphonate at room temperature to give dihydrofurans, while (344_a), (344_b), and (344_e) react with bromine at −50 °C to give the pyrans. However, the reactions of the cyclopropene alcohol (345_a) with H^+ or Br^+, follow a different course and can be explained in one case by σ-attack and in other case by π-attack. This is in agreement with the known greater rate of reaction

of bromine than a proton with the π-bond, but greater rate of reaction of protons with the σ-bonds of cyclopropanes.[163] Moreover, labelling studies shows that the ring opening of the cyclopropene does not occur *via* a free cyclopropyl cation and the mechanism is more complicated.

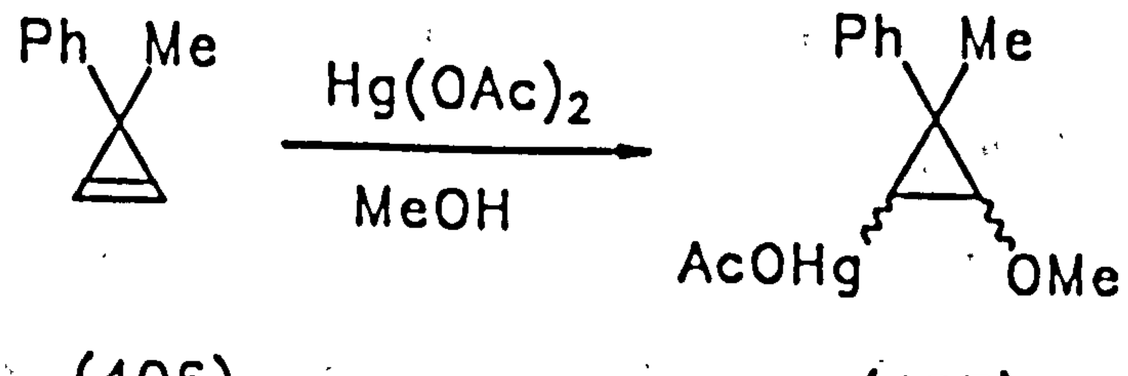
3.8: OXYMERCURATION.

As mentioned before (p. 124), oxymercuration of 1,3,3-trimethylcyclopropene leads to a ring opened product.[144] Moreover, the cyclopropene (404) is converted to (405) with mercuric acetate in methanol, presumably by solvolysis of an intermediate ring opened allyl cation.[73]



(404) (405)

However, oxymercuration of cyclopropenes can also occur without ring opening. Thus reaction of cyclopropene (406) with mercuric acetate in methanol gave (407) in addition to (408) and (409).



(406) (407)

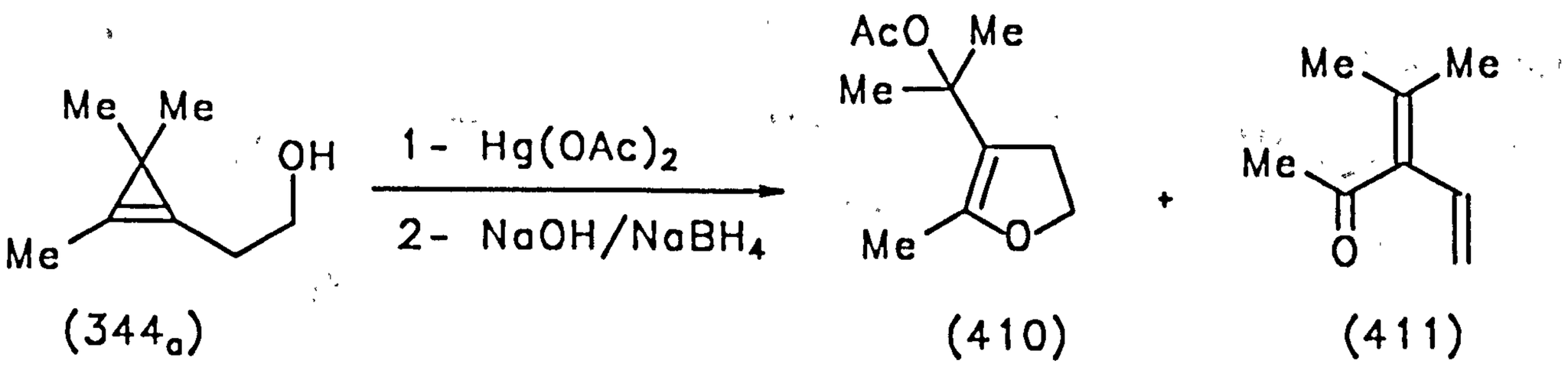
+ Z-MeOCMePhCH=CHHgOAc

(408)

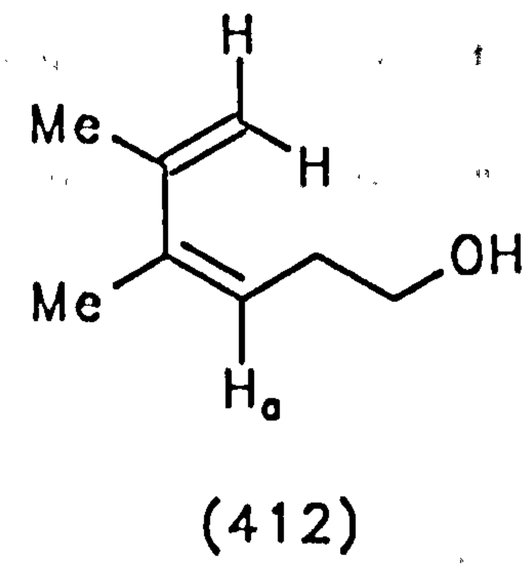
+ $(Z\text{-MeOCMePhCH=CH})_2Hg$

(409)

Once again, intramolecular trapping of an intermediate allyl cation can lead to cyclisation products. Treatment of the cyclopropene alcohol (344_a) with mercuric acetate in THF followed by reduction with $NaOH-NaBH_4$ gave the dihydrofuran (410) as the major product; two minor compounds (411) and (412) were also formed. The three components were separated by preparative g.l.c.

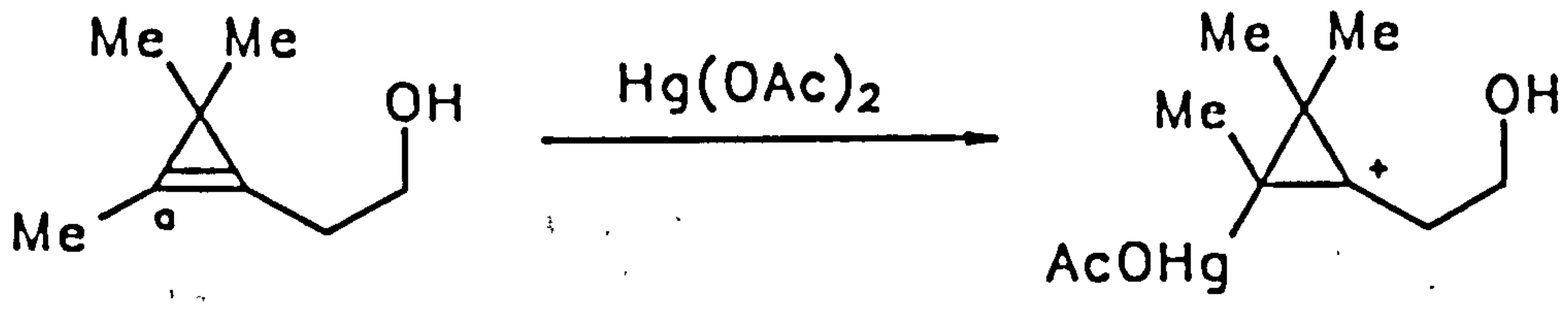


(344_a) (410) (411)

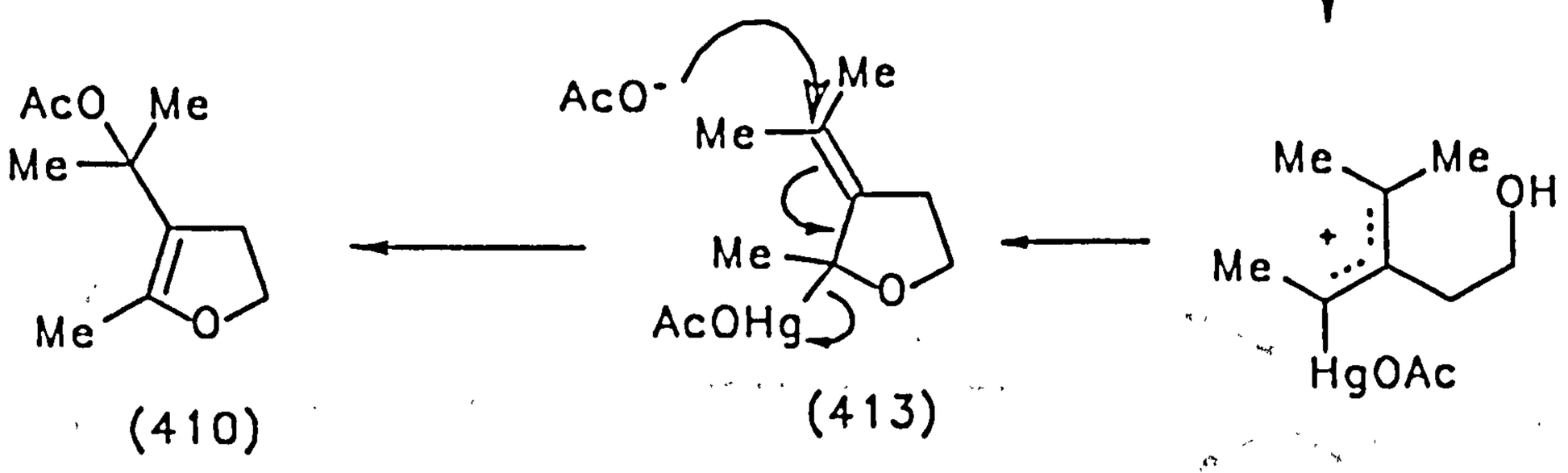


(412)

The furan (410) showed a single carbonyl band at 1741 cm^{-1} in the i.r. spectrum, assigned to the acetyl group, while the ^1H n.m.r. spectrum showed two triplets with a coupling constant of 6.3 Hz together with three singlets at δ 2.02 (3H), 1.83 (6H) and 1.77 (3H). The origin of this product is not certain; however, the reaction may involve initial attack of $^+Hg(OAc)$ at C_a of the cyclopropene followed by ring opening to an allylic cation and cyclisation to give (413), which in turn undergoes intermolecular reaction with CH_3COO^- to give the furan.

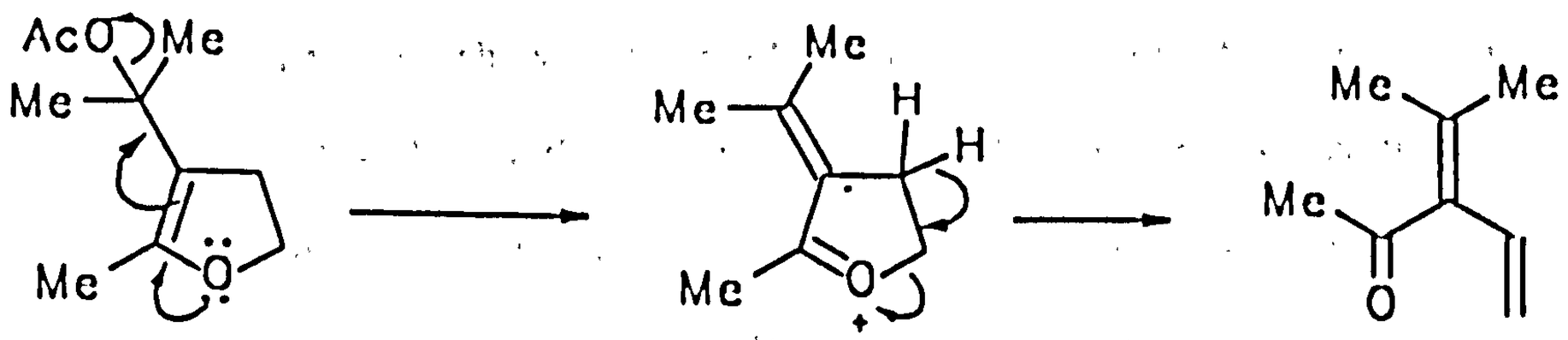


(344$_a$)



(410) (413)

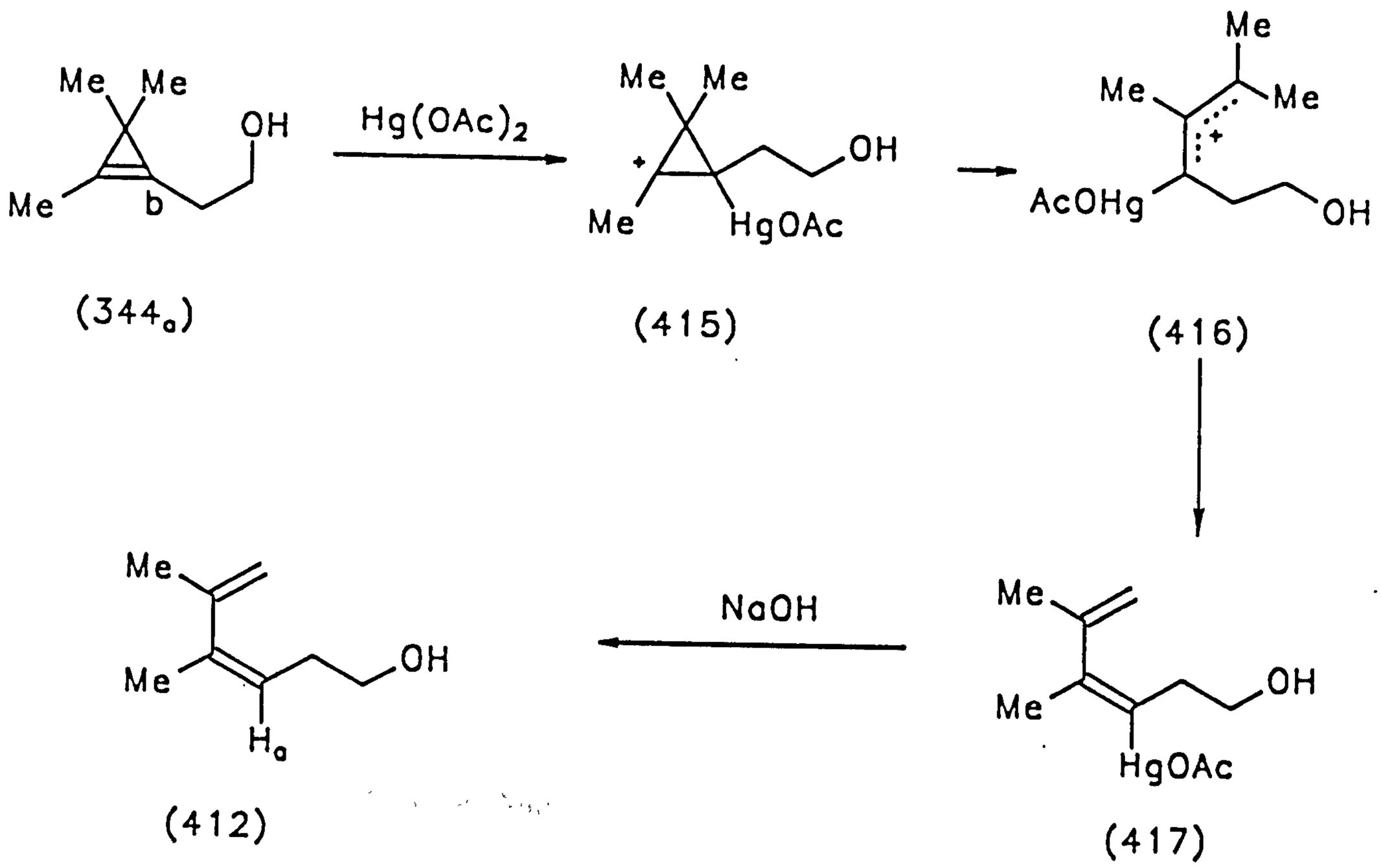
The ketone (411) may arise by loss of the acetate group from (410) by delocalization of the electrons on the oxygen to give (414) and cleavage of the highly sterically hindered α-oxycation by deprotonation at C_4.



(410) (414) (411)

The i.r. spectrum of (411) showed a strong band at 1658 cm^{-1}, assigned to the α,β-unsaturated carbonyl group.

The alcohol (412) may arise by attack of $^{+}Hg(OAc)$ at C_b of the cyclopropene to give the cation (415) followed by ring-opening to the allylic cation (416) which loses a proton from one of the geminal dimethyl group to give the diene (417), which in turn reacts with NaOH to give the diene.



(344a) (415) (416)

(412) (417)

The i.r. spectrum showed a broad band at 3342 cm^{-1} assigned to the hydroxyl group, while the ^1H n.m.r. spectrum showed a broad triplet for H_a and two broad singlets for the vinylic protons, together with a triplet at δ 3.72 (2H) and a quartet at 2.4 with coupling constant 6.8 Hz. The spectrum also showed a narrow doublet for the methyl group with an allylic coupling of 0.88 Hz, and a singlet at δ 1.84 (3H).

Chapter Four

Experimental

4.1: GENERAL EXPERIMENTAL DETAILS:

Solvents were purified and dried by established methods.[164] Petroleum ether and dichloromethane were generally distilled and used without further purification. Diethyl ether was dried using calcium hydride followed by distillation from lithium aluminium hydride or by standing over sodium wire; tetrahydrofuran was distilled over lithium aluminium hydride or calcium hydride immediately prior to use. Ethanol and methanol were dried by distillation from magnesium turnings and stored over 3A molecular sieves. Reagents obtained commercially were used without further purification unless otherwise stated. Methyl lithium was obtained from the Aldrich Chemical Company as a ca. 1.5 M solution in diethyl ether saturated with lithium bromide. The accurate molarity of this solution was determined by titration with diphenylacetic acid.[165] Melting points were carried out on a Kofler hot stage apparatus and are uncorrected. Infra-red spectra were obtained as a potassium bromide disc (solids), or as a thin film (liquids), on Perkin-Elmer 257 or Nicolet F.T. instruments.

Electron impact mass spectra were obtained on an AEI MS9 or Kratos MS 80RF Spectrometer. Peak and mass measurements refer to the isotopes ^{79}Br and ^{35}Cl where applicable. Gas liquid chromatography was performed using a Packard 427 gas chromatograph using a wall coated open tubular column coated with SE 52, or a Varian Aerograph 2700 preparative gas chromatograph containing 6 or 12 foot copper columns packed with 10% SE 30 on celite.

^{1}H n.m.r. spectra were recorded at 60 MHz using a Hitachi Perkin Elmer R-24B spectrometer, at 200 MHz on a Bruker WM 200, or at 300 MHz using a Bruker WP 300-WB instrument. The abbreviation $W_{1/2}$ refers to the width at half height of a broad signal and unless otherwise stated, spectra were recorded at 60 MHz. Chemical shifts are quoted as parts per million (ppm) downfield of tetramethylsilane (TMS). ^{13}C

N.m.r. spectra were recorded at the corresponding frequency on the same instruments; generally the carbon spectra were broad-band or gated decoupled.

Purity of compounds was assessed by elemental analysis, g.l.c. or t.l.c.. Organic solutions were dried using anhydrous magnesium sulphate and solvents generally removed on a rotary evaporator at ca. 14 mmHg. T.l.c was performed on Schleicher and Sheull plastic sheets coated with silica gel (F 1500 LS 254), which were visualised under an ultra violet light source and then developed in iodine vapour.

All reactions involving an alkyl lithium were conducted under a nitrogen atmosphere.

4.2: EXPERIMENTS:

EXPERIMENT (1).

1,1,3-Trichloro-2-methyl-1-propene (163).

Thionyl chloride (360 ml) was added slowly to a cooled mixture of 1,1,1-trichloro-2-methyl-2-propanol (186 g) and tetrabutylammonium bromide (1.9 g). The reaction was stirred at 0 °C for 0.5 h then potassium iodide (5 g) was added and the mixture was refluxed for 72 hr. When t.l.c. showed no starting material was left, the excess of thionyl chloride was removed by distillation and the residue was distilled at 158-160 °C to give *1,1,3-trichloro-2-methyl-1-propene* (120 g, 72%)[107] (Found M^+: 157.9477. Required for $C_4H_5Cl_3$: 157.9489) which showed δ_H (CCl_4): 4.04 (2H, s), 1.95 (3H, s); ν_{max} 1622, 898 cm^{-1}; m/z 158 (M^+), 123 (M^+-Cl).

EXPERIMENT (2).

3,3-Dichloro-2-methylprop-2-enyl methyl ether (164, R= Me).

1,1,3-Trichloro-2-methylprop-1-ene (4.3 g) was added over 5 min. to a stirred solution of sodium methoxide prepared from sodium (1.5 g) and methanol (50 ml). After refluxing for 2 hr, the products were treated with water (50 ml) and extracted with dichloromethane (2 x 50 ml), the organic layer was dried and solvent was removed at 14 mm Hg; flash distillation of the residue gave *3,3-dichloro-2-methyl-prop-2-enyl methyl ether*,[108] b.p 20-22 °C at 0.3 mm Hg (3.1 g, 74 %) (Found M^+: 153.9949. Required for $C_5H_8OCl_2$: 153.9952) which showed δ_H 4.0 (2H, s), 3.22 (3H, s), 1.85 (3H, s); ν_{max} 1610, 894 cm^{-1}; m/z 154 (M^+), 139 (M^+-CH_3), 119 (M^+-Cl).

EXPERIMENT (3).

3,3-Dichloro-2-methylprop-2-enyl isopropyl ether (164, R= Pr^i).

1,1,3-Trichloro-2-methylprop-1-ene (4.3 g) was added over 5 m to a solution of sodium isopropoxide prepared from sodium (1.5 g) and isopropanol (50 ml). After refluxing for 2 h, the products were treated with water (50 ml) and extracted with dichloromethane (2 x 100 ml). The organic layer was dried and the solvent was removed at 24 mm Hg; distillation of the residue gave *3,3-dichloro-2-methylprop-2-enyl isopropyl ether*, b.p. 28-30 °C at 0.4 mm Hg (2.6 g, 53%) (Found: M^+, 182.0257. Calculated for $C_7H_{12}OCl_2$: 182.0258) which showed δ_H 4.0 (2H, s), 3.6 (1H, septet, J 6 Hz), 1.9 (3H, s), 1.25 (6H, d, J 6 Hz); ν_{max} 895 s cm^{-1}; m/z 182 (M^+), 147 (M^+-Cl).

EXPERIMENT (4).

3,3-Dichloro-2-methylprop-2-enyl di-isopropyl amine (165).

1,1,3-Trichloro-2-methylprop-1-ene (5 g) was refluxed with di-isopropylamine (30 ml) in ethanol (50 ml). After 30 h the solvent and excess amine were removed at 14 mm Hg and the residue was dissolved in ether (50 ml) and extracted with 4M hydrochloric acid. The aqueous layer was brought to pH 10 by addition of 4M sodium hydroxide and extracted with ether (2 x 50 ml). Drying and removal of the solvent at 14 mm Hg gave an oil which was purified by flash distillation and characterised as *3,3-dichloro-2-methylprop-2-enyl di-isopropyl amine*, b.p 54-56°C at 0.4 mmHg (4.6 g, 65 %) (Found M^+: 223.0901. Required for $C_{10}H_{19}NCl_2$: 223.0895) which showed δ_H 3.1 (2H, s), 2.85 (1H, septet, J ca. 6 Hz), 1.8 (3H, s), 0.92 (6H, d, J 6 Hz); ν_{max} 2966, 2931, 1674, 1621, 1462, 1379, 1180, 895 cm^{-1}; m/z 223 (M^+), 208 (M^+-Me), 188 (M^+-Cl).

EXPERIMENT (5).

1,1-Dichloro-2-methyl-3-phenylprop-1-ene (167, Z= H).

1,1,3-Trichloro-2-methylprop-1-ene (15.0 g) was added carefully to phenyl magnesium bromide prepared from bromobenzene (17.7 g) and magnesium (3.0 g) in dry tetrahydrofuran (15 ml). The products were refluxed for 2 h and then stirred for 18 h at 20 °C. The products were quenched with water; 15% hydrochloric acid was added to dissolve the precipitate, and the aqueous layer was saturated with sodium chloride. The organic layer was separated and the aqueous layer was extracted with ether (2 x 40 ml). The combined organic layers were washed with saturated aq. sodium bicarbonate (30 ml) and brine (30 ml), and dried; the solvent was removed at 14 mmHg to give an oil which was distilled to give *1,1-dichloro-2-methyl-3-phenyl-prop-1-ene* (13.2 g, 70 %), b.p. 66 °C at 0.4 mmHg (Found M^+: 200.0140. Required for $C_{10}H_{10}Cl_2$: 200.0159) which showed δ_H 7.02 (5H, s), 3.55 (2H, s), 1.8 (3H, s); ν_{max} 3062, 3030, 2918, 1624, 1599, 1481, 737, 698 cm^{-1}; m/z 200 (M^+), 185 (M^+-CH_3), 165 (M^+-Cl).

EXPERIMENT (6).

1,1-Dichloro-2-methyl-3-(p-methoxyphenyl)prop-1-ene (167, Z= OMe).

1,1,3-Trichloro-2-methylprop-1-ene (15.0 g) was added carefully to p-methoxy-phenyl magnesium bromide prepared from p-bromoanisole (21.0 g) and magnesium (3.017 g) in dry tetrahydrofuran (15 ml). The products were refluxed for 2h and then stirred for 18h at 20 °C, and worked up as before, and the solvent was removed at 14 mmHg. The residue was purified by column chromatography over silica eluting with petrol and ether (10:2) to give *1,1-dichloro-2-methyl-3-(p-methoxyphenyl)prop-1-ene* (12.5 g, 57.5%) (Found M^+: 230.0275. Required for $C_{11}H_{12}OCl_2$: 230.0265) which

showed δ_H 7.0–6.6 (4H, m), 3.7 (3H, s), 3.5 (2H, s), 1.8 (3H, s); ν_{max} 1610, 1511, 1248, 1037, 891 cm^{-1}; m/z 230 (M^+), 195 (M^+–Cl).

EXPERIMENT (7).

1,1–Dichloro–2–methyl–3–(p–methylphenyl)prop–1–ene (167, Z= CH_3).

1,1,3–Trichloro–2–methylprop–1–ene (7.0 g) was added carefully to p–methylphenyl magnesium bromide prepared from p–bromotoluene (9.0 g) and magnesium (1.17 g) in dry tetrahydrofuran (10 ml). The products were refluxed for 2h, then stirred at room temperature for 18h. After work up as before, the solvent was removed at 14 mm Hg, and the residue was purified by column chromatography over silica eluting with petrol to give *1,1–dichloro–2–methyl–3–(p–methylphenyl)prop–1–ene* (3.75 g, 40%) (Found M^+: 214.0312. Required for $C_{11}H_{12}Cl_2$: 214.0316) which showed δ_H 7.0–6.6 (4H, m), 3.48 (2H, s), 2.2 (3H, s), 1.75 (3H, s); ν_{max} 2920, 2856, 1623, 1513, 1441, 1377, 1041, 890 cm^{-1}; m/z 214 (M^+), 179 (M^+–Cl).

EXPERIMENT (8).

1,1–Dichloro–2–methyl–3–(p–trifluoromethylphenyl)–1–propene (167, Z= CF_3).

1,1,3–Trichloro–2–methylprop–1–ene (7.5 g) was added carefully to p–trifluoro–methylphenyl magnesium bromide prepared from p–trifluoromethylbromobenzene (12.7 g) and magnesium (1.5 g) in dry tetrahydrofuran (10 ml). The products were refluxed for 2h and then stirred at room temperature for 18h. After work up as before, the solvent was removed at 14 mmHg, and the residue was purified by column chromatography on silica eluting with petrol to give *1,1–dichloro–2–methyl–3–(p–trifluoromethylphenyl)–1–propene* (2.51 g, 20 %) (Found M^+: 268.0037. Required for $C_{11}H_9Cl_2F_3$: 268.0033) which showed δ_H (CCl_4): 7.4 (2H, d, J 6 Hz), 7.1 (2H, d, J 6 Hz), 3.55 (2H, s), 1.75 (3H, s); ν_{max} 2923, 1620, 1325, 1166, 1127, 1068,

894, 829 cm^{-1}; m/z 268 (M^+), 233 (M^+–Cl).

EXPERIMENT (9).

3–Chloromethyl–3–methyl–1,1,2,2–tetrachlorocyclopropane (168).

Sodium hydroxide (45.0 g) in water (45 ml) was added to a rapidly stirred solution of 1,1,3–trichloro–1–propene (30.0 g) and cetrimide (3 g) in chloroform (150 ml). After 48 h at 20 °C, nmr showed no signals corresponding to the starting material. Work up as before and distillation of the residue gave *3–chloromethyl–3–methyl–1,1,2,2–tetrachlorocyclopropane,* bp 48 °C at 0.4–0.5 mmHg (28 g, 61.5%) (Found M^+: 239.8853. Calculated for C_5H_5Cl: 239.8833) which showed δ_H 3.78 (2H, s), 1.65 (3H, s); ν_{max} 861, 762, 737, cm^{-1}; m/z 240 (M^+), 205 (M^+–Cl), 191 (M^+–CH_2Cl).

EXPERIMENT (10).

3–Chloromethyl–1,1–dibromo–2,2–dichloro–3–methylcyclopropane (169).

Sodium hydroxide (45.0 g) in water (45 ml) was added to a rapidly stirred solution of 1,1,3–trichloroprop–1–ene (30.0 g) and cetrimide (3 g) in dichloromethane (50 ml) and bromofrom (100 g). After 48 h at 20 °C, n.m.r. showed no signals corresponding to the starting alkene. The products were poured into water (200 ml), and extracted with dichloromethane (6 x 100 ml). Removal of the solvent from the dried ($MgSO_4$) organic layer at 14 mmHg followed by distillation of unreacted bromoform at 30 °C and 0.4–0.5 mm Hg gave a brown oil which was purified by distillation to give *3–chloromethyl–1,1–dibromo–2,2–dichloro–3–methylcyclopropane,* b.p. 84 °C at 0.4–0.5 mmHg (21 g, 34%) (Found: C, 17.82; H, 1.34. Calculated for $C_5H_5Br_2Cl_3$: C, 18.12; H, 1.52) which showed δ_H 3.78 (2H, s), 1.78 (3H, s); ν_{max} 800 s, 756 m cm^{-1}; m/z 293 (M^+–Cl), 279 (M^+–CH_2Cl).

EXPERIMENT (11).

1,1,2,2–Tetrachloro–3–methoxymethyl–3–methylcyclopropane (170, R= Me).

Sodium hydroxide (15.0 g) in water (15 ml) was added to a rapidly stirred solution of 3,3–dichloro–2–methyl–prop–2–en–1–yl methyl ether (5.0 g) and cetrimide (0.4 g) in chloroform (50 ml). After 48 h, n.m.r. showed no signals corresponding to the starting alkene. Work up as before gave *1,1,2,2–tetrachloro–3–methoxymethyl–3–methyl–cyclopropane,* bp 50–52 °C at 0.5 mmHg (5.04 g, 70%) (Found: C, 30.54, H, 3.26. Calculated for $C_6H_8Cl_4O$: C, 30.28; H, 3.38) which showed δ_H 3.55 (2H, s), 3.36 (3H, s), 1.52 (3H, s); ν_{max} 1117 s, 858 cm^{-1}; m/z 205 (M^+–OMe).

EXPERIMENT (12).

1,1–Dibromo–2,2–dichloro–3–methoxymethyl–3–methylcyclopropane (171, R= Me).

Sodium hydroxide (15.0 g) in water (15 ml) was added to a rapidly stirred solution of 3,3–dichloro–2–methylprop–2–enyl–1–yl methyl ether (5 g) and cetrimide (0.5 g) in dichloromethane (25 ml) and bromoform (25 g). After 48 h at 20 °C, n.m.r. showed no signals due to the starting alkene. Work up as before gave *1,1–dibromo–2,2–dichloro–3–methoxymethyl–3–methylcyclopropane,* bp 78 °C at 0.5 mmHg (5.5 g, 52%) which consisted of a single component by glc (Found: C, 21.92; H, 2.20. Calculated for $C_6H_8Br_2Cl_2O$: C, 22.04; H, 2.46) which showed δ_H 3.65 (2H, s), 3.45 (3H, s), 1.6 (3H, s); ν_{max} 1114 s, 799 m cm^{-1}; m/z 289 (M^+–Cl), 245 (M^+–Br).

EXPERIMENT (13).

1,1–Dibromo–2,2–dichloro–3–isopropoxymethyl–3–methylcyclopropane (171, R= Pr^i).

Sodium hydroxide (15.0 g) in water (15 ml) was added in two portions to a rapidly stirred solution of 3,3-dichloro-2-methylprop-2-enyl isopropyl ether (5.0 g) and cetrimide (0.5 g) in dichloromethane (25 ml) and bromoform (25 ml). After stirring for 48 h at 20 °C, nmr showed complete reaction of the starting material. Work up as before gave *1,1-dibromo-2,2-dichloro-3-isopropoxymethyl-3-methylcyclopropane*, b.p. 82 °C at 0.3-0.4 mm Hg (4.9 g, 51%) (m/z 317 (M^+-Cl), 293 (M^+-C_3H_7O)) which showed δ_H 3.58 (2H, s), 3.56 (1H, septet, J 6.5 Hz), 1.50 (3H, s), 1.15 (6H, d, J 6.5 Hz); ν_{max} 795.7s, 670s cm^{-1}.

EXPERIMENT (14).

3-Benzyl-3-methyl-1,1,2,2-tetrachlorocyclopropane (172, Z= H).

Sodium hydroxide (20.0 g) in water (20 ml) was stirred vigorously with 1,1-dichloro-2-methyl-3-phenylprop-1-ene (10.0 g) and cetrimide (1.0 g) in chloroform (75 ml). After 48 h at 20 °C the products were extracted with water (3 x 50 ml); the aqueous layer was washed with dichloromethane (3 x 100 ml). The combined organic layers were washed with brine (100 ml), dried and the solvent was removed at 14 mmHg. The residue was purified by column chromatography over silica, eluting with petrol, and characterised as *3-benzyl-3-methyl-1,1,2,2-tetrachloro-cyclopropane*, m.p. 45 - 47 °C (7.6 g, 54 %) (Found M^+: 281.9525; C 46.46, H 3.40. Calculated for $C_{11}H_{10}Cl_4$: M, 281.9537; C, 46.51, H, 3.54) which showed δ_H 7.15 (5H, br.s), 2.9 (2H, s), 1.18 (3H, s); ν_{max} 1453, 1200, 863, 725, 698 cm^{-1}; m/z 282 (M^+), 247 (M^+-Cl), 212 (M^+-Cl_2).

EXPERIMENT (15).

3-p-Methylbenzyl-3-methyl-1,1,2,2-tetrachlorocyclopropane (172, Z= Me).

Sodium hydroxide (10.0 g) in water (10 ml) was stirred vigorously with

1,1-dichloro-2-methyl-3-(p-methylphenyl)prop-1-ene (2.5 g) and cetrimide (0.5 g) in chloroform (30 ml). After 48h at 20 °C, n.m.r showed no signals corresponding to the starting material. After work up as before, the solvent was removed at 14 mmHg and the residue was purified by column chromatography over silica eluting with petrol to give *3-p-methylbenzyl-3-methyl-1,1,2,2-tetrachlorocyclopropane*, m.p. 84-85 °C (2.2 g, 64%) (Found M^+: 295.9720. Required for $C_{12}H_{12}Cl_4$: 295.9693) which showed δ_H (CCl_4): 6.8 (5H, br.s), 2.85 (2H, br.s), 2.16 (3H, s), 1.14 (3H, s); ν_{max} 3044, 3001, 2978, 2923, 1511, 1448, 859, 838, 596, 520, 481 cm^{-1}; m/z 296 (M^+), 261 (M^+-Cl), 225 (M^+-Cl_2).

EXPERIMENT (16).

<u>3-p-Methoxybenzyl-3-methyl-1,1,2,2-tetrachlorocyclopropane (172, Z= OMe).</u>

Sodium hydroxide (20.0 g) in water (20 ml) was stirred vigorously with 1,1-dichloro-2-methyl-3-p-methoxyphenylprop-1-ene (10 g) and cetrimide (1 g) in chloroform (75 ml). After 48h at 20 °C, nmr showed no signals corresponding to the starting alkene. Work up as before, and removal of the solvent at 14 mmHg gave a solid which was recrystallised from petrol to give *3-p-methoxybenzyl-3-methyl-1,1,2,2-tetrachlorocyclopropane*, m.p. 81-83 °C (5.3 g, 39%) (Found M^+: 311.9646. Required for $C_{12}H_{12}OCl_4$: 311.9642) which showed δ_H 7.0 (4H, m), 3.7 (3H, s), 3.0 (2H, s), 1.25 (3H, s); ν_{max} 2933, 1612, 1512, 1246, 1178, 1032, 842, 815, 512 cm^{-1}; m/z 312 (M^+), 277 (M^+-Cl), 241 (M^+-Cl_2).

EXPERIMENT (17).

<u>3-p-Trifluoromethylbenzyl-3-methyl-1,1,2,2-tetrachlorocyclopropane (172, Z= CF_3).</u>

Sodium hydroxide (10.0 g) in water (10 ml) was stirred vigorously with 1,1-dichloro-2-methyl-3-p-trifluoromethylphenylprop-1-ene (2.5 g) and cetrimide (0.5

g) in chloroform (30 ml). After 48h at 20 °C, nmr showed no signals due to starting alkene. Work up as before, and removal of the solvent at 14 mmHg gave an oil which was purified by column chromatography over silica eluting with petrol to give *3-p-trifluoromethylbenzyl-3-methyl-1,1,2,2,-tetrachlorocyclopropane* (1.14 g, 35%) (m/z 331 (M^+-F), 281 (M^+-CF_3)) which showed δ_H (CCl_4): 7.55 (2H, d, J 7Hz), 7.25 (2H, d, J 7 Hz), 3.12 (2H, S), 1.3 (3H, s); ν_{max} 2936, 1618, 1324, 1128, 1069, 860 cm^{-1}.

EXPERIMENT (18).

<u>2,2-Dibromo-1-chloro-1-vinylcyclopropane (175).</u>

Sodium hydroxide (15.0 g) in water (15 ml) was added in two portions to a rapidly stirred solution of 2-chloro-1,3-butadiene (7.0 g) dissolved in xylene, and cetrimide (1.0 g) in dichloromethane (10 ml) and bromoform (23.7 g). After stirring for 48 h at 20 °C, the products were extracted with dichloromethane (3 x 100 ml) and the combined organic layers were dried and the solvent was removed at 14 mmHg, then the excess of bromoform and xylene was removed at 20 °C and 0.4-0.5 mmHg. Flash distillation of the residue at 35 °C and 0.3 mmHg yielded 2,2-dibromo-1-chloro-1-vinylcyclopropane (6.5 g, 32%) which was further purified by column chromatography over silica eluting with petrol; the compound was still not pure by n.m.r., but an analytical sample, obtained by preparative g.l.c. showed δ_H 5.3 - 6.3 (3H, m), 2.2 (2H, s); δ_C 135.8d, 119.6t, 51s, 37t, 33s; m/z 223 (M^+-Cl), 179 (M^+-79).

EXPERIMENT (19).

<u>1,1,2,2-Tetrachloro-3-methyl-3-(di-isopropylaminomethyl)cyclopropane (173).</u>

Sodium hydroxide (10.0 g) in water (10 ml) was stirred vigorously with

3,3-dichloro-2-methylprop-2-en-1-yl di-isopropylamine (5.0 g) and cetrimide (0.8 g) in chloroform (40 ml). After 48 h at 20 °C the products were extracted with dichloromethane (3 x 30 ml) and the combined organic layers were dried and the solvent removed at 14 mmHg. The residue was purified by column chromatography over silica eluting with petrol to give *1,1,2,2-tetrachloro-3-methyl-3-(di-isopropylamino-methyl)cyclopropane* (2.5 g, 36 %), m.p. 57 - 59 °C (Found M^+: 305.0265. Calculated for $C_{11}H_{19}Cl_4N$: 305.0272) which showed δ_H 2.95 (2H, septet, J 6 Hz), 2.75 (2H, s), 1.4 (3H, s), 1.0 (12H, d, J 6 Hz); ν_{max} 2966, 2932, 1458, 1384, 1189, 852 cm^{-1}; m/z 305 (M^+), 290 (M^+-CH_3), 191 ($M^+-C_7H_{16}N$).

EXPERIMENT (20).

<u>1,1,2,2-Tetetrachloro-3-methyl-3-(allylthio)methylcyclopropane (174).</u>

Allylmercaptan (1.83 g, 0.024 mole) was added slowly to a stirred solution of sodium ethoxide (1.68 g, 0.024 mole) in DMF. The reaction was stirred at room temperature for 0.5h and 1,1,2,2-tetrachloro-3-chloromethylcyclopropane (5 g, 0.0206 mole) was added slowly, when a yellow precipitate formed; the reaction was heated to 50 °C for 2 h, stirred at room temperature for 12h, and then diluted with with water (100 ml) and extracted with ether (2 x 100ml). The combined organic layers were washed with aq. 5% sulphuric acid (100 ml), followed by water (2 x 50 ml) and dried. The solvent was removed by distillation at 760 mmHg. The residue was purified by chromatography over silica eluting with petrol to give *1,1,2,2-tetrachloro-3-methyl-3-(allylthio)methylcyclopropane* (4.2 g, 73 %) (Found M^+: 277.9235. Required for $C_8H_{10}SCl_4$: 277.9257) which showed δ_H 5.7 (1H, m), 5.05 (2H, m), 3.18 (2H, d, J ca. 6 Hz), 2.8 (2H, s), 1.53 (3H, s); ν_{max} 1635, 1451, 1381, 1227, 921, 859 cm^{-1}; m/z 278 (M^+), 243 (M^+-Cl), 167 ($M^+-C_3H_6S$).

EXPERIMENT (21).

1,2-Dichloro-3-benzyl-3-methylcyclopropene (176).

Methyl lithium (1.3 ml, 1.5 M) was added over 1 min. to a stirred solution of 1,1,2,2-tetrachloro-3-benzyl-3-methylcyclopropane (0.5 g, 1.76 mmole) in ether (5 ml) under nitrogen at 0 °C. After 0.5 h the products were quenched with water (1 ml) at -40 °C; the organic layer was washed with water (1 ml) at that temperature, and the solvent was removed carefully at 14 mmHg to give *1,2-dichloro-3-benzyl-3-methyl-cyclopropene* (0.29 g, 77 %) (Found M^+: 212.0139. Calculated for $C_{11}H_{10}Cl_2$: 212.0160) which showed δ_H 7.1 (5H, br.s), 2.89 (2H, s), 1.23 (3H, s); ν_{max} 2917, 2856, 1494, 1451, 1375, 918, 737, 699 cm^{-1}; m/z 212 (M^+), 177 (M^+–Cl).

EXPERIMENT (22).

Z,E-1,2-Dichloro-3-methyl-4-phenylbuta-1,3-diene (177).

1,2-Dichloro-3-methyl-3-benzylcyclopropene (1.0 g) was allowed to stand for 36 h at 20 °C in deuterochloroform (5 ml). No starting material remained. The solvent was removed at 14 mmHg to leave an oil which was purified by column chromatography over silica, eluting with petrol b.p. 40 - 60 °C, to give a colourless oil characterised as *Z,E-1,2-dichloro-3-methyl-4-phenylbuta-1,3-diene* (35 %) (Found M^+: 212.0170. Required for $C_{11}H_{10}Cl_2$: 212.0159) which showed δ_H 7.29 (5H, s), 7.11 (1H, s), 6.58 (1H, s), 2.07 (3H, s); δ_C 138.8, 136.9, 131.8, 130.9, 129.5, 128.4, 127.5, 116.4, 15.8; ν_{max} 1694, 1494, 1026, 868, 749, 699 cm^{-1}; m/z 212 (M^+), 177 (M^+–Cl). A second fraction (ca. 0.2 g) showed a very complex n.m.r. spectrum.

EXPERIMENT (23).

1,6-Dichloro-2-methyl-3-phenyl-4,4,5,5-tetracyanocyclohexene (178).

1,2-Dichloro-3-methyl-4-phenylbuta-1,3-diene (0.18 g) in dichloromethane (5 ml)

was allowed to stand for 48h at 20 °C with tetracyanoethene (0.12 g). Removal of the solvent at 14 mmHg gave a solid which was recrystallised from ether and petrol to give *1,6-dichloro-2-methyl-3-phenyl-4,4,5,5-tetracyanocyclohexene*, m.p. 159 - 161 °C (0.12 g, 39 %) (Found M^+: 340.0250. Required for $C_{17}H_{10}N_4Cl_2$: 340.0282) which showed δ_H 7.4 (5H, br.s), 5.1 (1H, br.s), 4.3 (1H, br.s), 1.8 (3H, s); ν_{max} 2257, 1649, 1457, 1253, 1088, 789, 736, 719, 700 cm^{-1}; m/z 340 (M^+), 305 (M^+–Cl).

The structure of this compound was established by X-ray crystallography (see below).

Table (7): The bond lengths (A^0) and angles (^{0}) for the compound (178).

Bond lengths (^{0})

C(1)-C(2)	1.491(3)	C(1)-C(6)	1.543(3)
C(1)-Cl(1)	1.805(3)	C(2)-C(3)	1.333(3)
C(2)-Cl(2)	1.736(2)	C(3)-C(4)	1.511(3)
C(3)-C(31)	1.494(3)	C(4)-C(5)	1.556(3)
C(4)-C(41)	1.515(3)	C(5)-C(6)	1.580(3)
C(5)-C(51)	1.483(3)	C(5)-C(52)	1.473(3)
C(6)-C(61)	1.473(4)	C(6)-C(62)	1.475(4)
C(41)-C(42)	1.393(4)	C(41)-C(46)	1.386(4)
C(42)-C(43)	1.361(4)	C(43)-C(44)	1.335(5)
C(44)-C(45)	1.379(6)	C(45)-C(46)	1.409(4)
C(51)-N(51)	1.142(4)	C(52)-N(52)	1.154(4)
C(61)-N(61)	1.150(4)	C(62)-N(62)	1.135(4)

Bond angles (A^0)

C(2)-C(1)-C(6)	112.2(2)	C(2)-C(1)-Cl(1)	110.3(2)
C(6)-C(1)-Cl(1)	111.7(2)	C(1)-C(2)-C(3)	126.9(2)
C(1)-C(2)-Cl(2)	112.1(2)	C(3)-C(2)-Cl(2)	120.9(2)
C(2)-C(3)-C(4)	121.5(2)	C(2)-C(3)-C(31)	121.9(2)
C(4)-C(3)-C(31)	116.3(2)	C(3)-C(4)-C(5)	113.1(2)
C(3)-C(4)-C(41)	113.3(2)	C(5)-C(4)-C(41)	112.0(2)
C(4)-C(5)-C(6)	110.1(2)	C(4)-C(5)-C(51)	112.2(2)
C(6)-C(5)-C(51)	109.7(2)	C(4)-C(5)-C(52)	109.0(2)
C(6)-C(5)-C(52)	108.4(2)	C(51)-C(5)-C(52)	107.3(2)
C(1)-C(6)-C(5)	111.7(2)	C(1)-C(6)-C(61)	111.6(2)
C(5)-C(6)-C(61)	110.6(2)	C(1)-C(6)-C(62)	108.0(2)
C(5)-C(6)-C(62)	106.9(2)	C(61)-C(6)-C(62)	107.9(2)
C(4)-C(41)-C(42)	121.5(2)	C(4)-C(41)-C(46)	119.9(2)
C(42)-C(41)-C(46)	118.6(2)	C(41)-C(42)-C(43)	121.4(3)
C(42)-C(43)-C(44)	120.5(3)	C(43)-C(44)-C(45)	120.8(3)
C(44)-C(45)-C(46)	119.9(3)	C(41)-C(46)-C(45)	118.8(3)
C(5)-C(51)-N(51)	178.0(3)	C(5)-C(52)-N(52)	173.5(3)
C(6)-C(61)-N(61)	178.2(3)	C(6)-C(62)-N(62)	178.1(3)

EXPERIMENT (24).

3-Chloro-3-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1,1,2,2-tetramethyl-cyclopropane (187).

Methyl lithium (1.09 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2-tetrachloro-3-benzyl-3-methylcyclopropane (0.41 g) in ether (5 ml) at 0 °C. After 30 m the products were quenched with water (1 ml) at -40 °C and decanted from the ice which remained. 2,3-Dimethylbut-2-ene (2.0 g) was added and the mixture was allowed to stand for 12 h at 20 °C. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by column chromatography over silica eluting with petrol to give *3-chloro-3-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane* (0.36g, 84 %) (Found M^+: 296.1098. Calculated for $C_{17}H_{22}Cl_2$: 296.1098) which showed δ_H (60 MHz) 7.18 (5H, br.s), 3.85 (1H, d, J 12 Hz), 3.12 (1H, d, J 12 Hz), 1.65 (3H, s), 1.2 (12H, s); (200 MHz) 7.15 - 7.4 (5H, m), 3.92 (1H, d, J 14.4 Hz), 3.20 (1H, dd, J 0.7, 14.4 Hz), 1.67 (3H, d, J 0.7 Hz), 1.29 (3H, s), 1.25 (3H, s), 1.23 (3H, s), 1.18 (3H, s); in addition there were signals for a minor isomer at δ 3.68 (1H, d, J 14.3 Hz), 3.54 (1H, d, J 14.3 Hz), 1.76 (3H, s), 1.09 (3H, s), the remaining signals being obscured by those for the major isomer (ratio 1:5); ν_{max} 2922, 1602, 1452, 1378, 1191, 751, 731, 700 cm^{-1}; m/z 296 (M^+), 219 ($M^+-C_6H_5$).

EXPERIMENT (25).

3-Chloro-3-(1-chloro-2-methyl-3-p-methoxyphenylprop-1-enyl)-1,1,2,2-tetramethyl-cyclopropane (191, Z= OMe).

Methyl lithium (1.16 ml, 1.5 M) was added over 1 min. to a stirred solution of 1,1,2,2-tetrachloro-3-p-methoxybenzyl-3-methylcyclopropane (0.5 g) in ether (5 ml) at

0 °C. After 30 min. the products were quenched with water (1 ml) at −40 °C and decanted from the ice which remained. 2,3−Dimethyl−2−butene (2 g) was added and the mixture was allowed to stand 12h at 20 °C; removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by column chromatography over silica eluting with petrol and ether (10:2) to give *3−chloro−3−(1−chloro−2−methyl−3−p−methoxyphenylprop−1−enyl)−1,1,2,2−tetramethylcyclopropane* (0.39 g, 75%) (Found M^+: 326.1211. Required for $C_{18}H_{24}OCl_2$: 326.1204) which showed δ_H (200 MHz): 7.18 (2H, d, J 8.5 Hz), 6.82 (2H, d, J 8.5 Hz), 3.82 (1H, d, J 14.5 Hz), 3.7 (3H, s), 3.11 (1H, d, J 14.5 Hz), 1.64 (3H, d, J 0.7 Hz), 1.26 (3H, s), 1.22 (3H, s), 1.2 (3H, s), 1.16 (3H, s); in addition there were signals for a minor isomer at 7.09 (2H, d, J 8.8 Hz), 3.54 (1H, d, J 14 Hz), 3.45 (1H, d, J 14 Hz), 1.72 (3H, s), 1.06 (3H, s), the remaining signals being obscured by those for the major isomer (ratio 1:5); ν_{max} 3002, 2954, 2875, 1610, 1511, 1248, 1178, 1036, 708 cm^{-1}.

EXPERIMENT (26).

3−Chloro−3−(1−chloro−2−methyl−3−p−trifluoromethylphenylprop−1−enyl)−1,1,2,2−tetramethylcyclopropane (191, Z= CF_3).

Methyl lithium (1.04 ml, 1.5 M) was added over 1 min. to a stirred solution of 1,1,2,2−tetrachloro−3−p−trifluoromethylbenzyl−3−methylcyclopropane (0.5 g) in ether (5 ml) at 0 °C. After 30 min. the products were quenched with water (1 ml) at −40 °C and decanted from the ice which remained. 2,3−Dimethyl−2−butene (2 g) was added and the mixture was allowed to stand for 12h at 20 °C. Removal of the solvent at 14 mmHg gave an oil which was purified by column chromatography over silica eluting with petrol to give *3−chloro−3−(1−chloro−2−methyl−3−p−trifluoromethyl−phenylprop−1−enyl)−1,1,2,2−tetramethylcyclopropane* (0.34 g, 65.5%) (Found M^+: 364.0996. Required for $C_{18}H_{21}Cl_2F_3$: 364.0972) which showed δ_H (200 MHz): 7.55 (2H, br.d,

J 8.1 Hz), 7.39 (2H, br.d, J 8.1 Hz), 3.93 (1H, d, J 14.6 Hz), 3.24 (1H, d, J 14.6 Hz), 1.65 (3H, d, J 0.7 Hz), 1.27 (3H, s), 1.23 (3H, s), 1.21 (3H, s), 1.17 (3H, s); in addition there were signals for a minor isomer at 7.29 (2H, br.d, J 7.88 Hz), 3.65 (2H, br.s), 1.74 (3H, s), 1.26 (3H, s), 1.24 (3H, s), 1.09 (3H, s), the remaining signals being obscured by those for the major isomer (ratio 1:6); ν_{max} 3005, 2956, 1617, 1324, 1165, 1127, 1068, 1019 cm^{-1}.

EXPERIMENT (27).

3-Chloro-3-(1-chloro-2-methyl-3-p-methylphenylprop-1-enyl)-1,1,2,2-tetramethyl-cyclopropane (191, Z= CH_3).

Methyl lithium (1.23 ml, 1.5 M) was added over 1 min. to a stirred solution of 1,1,2,2-tetrachloro-3-p-methylbenzyl-3-methylcyclopropane (0.5 g) in ether (5 ml) at 0 °C. After 30 min. the products were quenched with water (1 ml) at -40 °C and decanted from the ice which remained. 2,3-Dimethylbut-2-ene (2.0 g) was added and the mixture was allowed to stand for 12h at 20 °C. Removal of the solvent at 14 mmHg gave an oil which was purified by column chromatography over silica eluting with petrol to give *3-chloro-3-(1-chloro-2-methyl-3-p-methylphenylprop-1-enyl)-1,1,2,2-tetramethyl-cyclopropane* (0.37, 70%) (m/z 179 (M^+-$C_7H_{12}Cl$)) which showed δ_H (200 MHz): 7.14 (2H, br.s), 7.09 (2H, d, J 8 Hz), 3.83 (1H, d, J 14.3 Hz), 3.14 (1H, d, J 14.3 Hz), 2.32 (3H, s), 1.65 (3H, d, J 0.7 Hz), 1.25 (3H, s), 1.22 (3H, s), 1.21 (3H, s), 1.16 (3H, s); in addition there were signals for a minor isomer at 3.63 (1H, d, J 14.3 Hz), 3.47 (1H, d, J 14.3 Hz), 2.31 (3H, s), 1.72 (3H, s), 1.23 (3H, s), 1.07 (3H, s), the remaining signals being obscured by those for the major isomer (ratio 4.7:1); ν_{max} 3005, 2957, 2926, 1618, 1325, 875, 846 cm^{-1}.

EXPERIMENT (28).

Methyl 2-chloro-2-(1-chloro-2-methyl-3-phenylprop-1-en-1-yl)-1-cyclopropane

carboxylate (189).

Methyl lithium (0.94 ml, 1.5 M) was added over 1 min. to stirred solution of 1,1,2,2-tetrachloro-3-benzyl-3-methylcyclopropane (0.35 g) in ether (5 ml) at 0 °C. After 30 min. the products were quenched with water (1 ml) at -40 °C and decanted from the ice which remained. Methyl acrylate (5 ml) was added and the mixture was allowed to stand for 12h at 20 °C. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by column chromatography over silica eluting with petrol and ether (10 : 2) to give *methyl 2-chloro-2-(1-chloro-2-methyl-3-phenylprop-1-en-1-yl)cyclopropane carboxylate* (0.25 g, 68%) (Found M^+: 298.0507. calculated for $C_{15}H_{16}Cl_2O_2$: 298.0527) which showed δ_H (300 MHz, 230 K) (rotamer 1) 7.4-7.2 (5H, complex), 4.01 (1H, d, J 15.5 Hz), 3.63 (1H, d, J 15.5 Hz), 2.46 (1H, dd, J 6.9, 9.1 Hz), 2.18 (1H, t, J 6.7 Hz), 2.02 (1H, dd, J 6.3, 9.1 Hz), 1.76 (3H, s); (rotamer 2) 7.4 - 7.2 (5H, complex), 4.15 (1H, d, J ca. 15.0 Hz), 3.38 (3H, s), 3.15 (1H, d, J ca. 15.0 Hz), 2.1 (1H, dd, J 9.0, 7.0 Hz), 1.92 (3H, s), 2.24 (1H, t, J 7.0 Hz); the remaining signals being obscured by those for the major rotamer (ratio of rotamers 5:1); m/z 298 (M^+), 263 (M^+-Cl), 262 (M^+-HCl).

EXPERIMENT (29).

Methyl 2-chloro-2-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1-methylcyclopropane carboxylate (185).

(a) Methyl lithium (0.94 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2-tetrachloro-3-benzyl-3-methylcyclopropane (0.35 g) in ether (5 ml) at 0 °C. After 30 m the products were quenched with water (1 ml) at -40 °C and decanted from the ice which remained. Methyl methacrylate (5 ml) was added and the mixture was allowed to stand for 12 h at 20 °C. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by column chromatography

over silica eluting with petrol and ether (10 : 2) to give *methyl 2-chloro-2-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1-methylcyclopropane carboxylate* (0.31 g, 80 %) (Found M^+: 312.0700. Calculated for $C_{16}H_{18}Cl_2O_2$: 312.0684) which ν_{max} 2949, 1730, 1454, 1300, 1199, 1164 cm^{-1}; m/z 312 (M^+), 277 (M^+–Cl), 221 (M^+–C_7H_7). The ^1H n.m.r. spectrum of this (300 MHz, 230 K) included all the signals present in the spectrum of the pure ester described in (b), together with some additional minor signals corresponding to the presence of ca. 17 % of two rotamers (ratio ca. 1:1) of a second component: δ_H 2.35 (d, J 6.3 Hz) 2.30 (d, J 6.8 Hz), 1.33 (d, J 6.8 Hz), 1.91 (s), 1.68 (s), 3.34 (s), 3.70 (s), 3.30 (d, J 16 Hz) in ratio 1:1:1:3:3:3:3:1. Other signals were presumably hidden by those of the major isomer. Increasing the temperature to 300 – 330 K caused the doublets at δ 2.35 and 2.30 to coalesce to a single doublet.

(b) The free acid (described below) was converted to the methyl ester by reaction with a slight excess of diazomethane in ether, followed by removal of the solvent at 14 mmHg. The ester showed δ_H (300 MHz, 330 K) 7.2 – 7.4 (5H, complex), 3.9 (1H, d, J 16 Hz), 3.7 (4H, v.br.), 2.4 (1H, v.br.), 1.7 (3H, s), 1.6 (3H, s), 1.5 (2H, br.m.); (240 K)(rotamer 1) 7.1 – 7.4 (5H, complex), 3.98 (1H, d, J 15.7 Hz), 3.79 (3H, s), 3.63 (1H, d, J 15.7 Hz), 2.42 (1H, d, J 6.3 Hz), 1.73 (3H, s), 1.60 (3H, s), 1.55 (1H, d, J 6.3 Hz);(rotamer 2) 7.1 – 7.4 (5H, complex), 3.93 (1H, d, J 14.9 Hz), 3.68 (3H, s), 2.94 (1H, d, J 14.9 Hz), 2.32 (1H, d, J 6.7 Hz), 1.64 (6H, s), 1.38 (1H, d , J 6.7 Hz) (the ratio of the rotamers was 3.3:1). The signals at 3.98 and 3.93 coalesced at 280 K; those at 3.63 and 2.94, 2.42 and 2.32 and 1.55 and 1.48 at 300 K, and others at 300 – 330 K.

EXPERIMENT (30).

2-Chloro-2-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1-methylcyclopropane

carboxylic acid (184).

The above ester (Expt. 29_a) (1.0 g) was refluxed for 15m with sodium methoxide (prepared from sodium (1 g)) in methanol (10 ml) and water (0.5 ml). The products were neutralised with dil. hydrochloric acid and extracted with ether (3 x 30 ml). The organic layer was dried and the solvent was removed at 14 mmHg; the residue was recrystallised from ether and petrol to give *2-chloro-2-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1-methylcyclopropane carboxylic acid* (0.54 g, 54 %), m.p. 59 - 61 °C (Found M^+: 298.0525. Required for $C_{15}H_{16}O_2Cl_2$: 298.0527) which showed δ_H (200 MHz, 293 K) 7.21 - 7.37 (5H, complex), 2.34 (1H, broad), 1.71 - 1.58 (complex), 1.40 (1H, v.broad) and (rotamer 1) 3.93 (1H, partly hidden), 3.09 (1H, br.d, J 13.8 Hz); (rotamer 2) 3.86 (1H, br.d, J 15.1 Hz), 3.70 (1H, br.d, J 15.1 Hz), 2.45 (1H, d, J 6.2 Hz) (ratio of rotamers 1:2); ν_{max} 3000 - 2500 vbr, 1698s cm^{-1}; m/z 298 (M^+), 263 (M^+-Cl), 262 (M^+-HCl). The structure of this product was determined by X-ray crystallography (see below).

Table (8): The bond lengths (A°) and angles (°) for the compound (184)..

Bond lengths (A°).

C(1)-C(2)	1.497(2)	C(1)-O(1)	1.280(3)
C(1)-O(2)	1.245(2)	C(2)-C(3)	1.508(3)
C(2)-C(4)	1.515(3)	C(2)-C(5)	1.534(3)
C(4)-C(5)	1.487(3)	C(5)-C(6)	1.482(3)
C(5)-Cl(1)	1.782(2)	C(6)-C(7)	1.318(3)
C(6)-Cl(2)	1.755(2)	C(7)-C(8)	1.505(3)
C(7)-C(9)	1.517(4)	C(9)-C(10)	1.515(3)
C(10)-C(11)	1.375(4)	C(10)-C(15)	1.382(3)
C(11)-C(12)	1.388(5)	C(12)-C(13)	1.358(5)
C(13)-C(14)	1.358(6)	C(14)-C(15)	1.395(4)
O(1)-H(1)	0.895(27)		

Bond angles (°).

C(2)-C(1)-O(1)	115.9(2)	C(2)-C(1)-O(2)	120.(2)
O(1)-C(1)-O(2)	124.1(2)	C(1)-C(2)-C(3)	115.7(2)
C(1)-C(2)-C(4)	115.2(2)	C(3)-C(2)-C(4)	120.7(2)
C(1)-C(2)-C(5)	115.1(2)	C(3)-C(2)-C(5)	119.6(2)
C(4)-C(2)-C(5)	58.4(1)	C(2)-C(4)-C(5)	61.5(1)
C(2)-C(5)-C(4)	60.2(1)	C(2)-C(5)-C(6)	121.6(1)
C(4)-C(5)-C(6)	123.3(2)	C(2)-C(5)-Cl(1)	115.3(1)
C(4)-C(5)-Cl(1)	116.5(1)	C(6)-C(5)-Cl(1)	111.3(1)
C(5)-C(6)-C(7)	126.9(2)	C(5)-C(6)-Cl(2)	112.3(1)
C(7)-C(6)-Cl(2)	120.8(2)	C(6)-C(7)-C(8)	122.8(2)
C(6)-C(7)-C(9)	121.3(2)	C(8)-C(7)-C(9)	115.9(2)
C(7)-C(9)-C(10)	111.5(2)	C(9)-C(10)-C(11)	120.9(2)
C(9)-C(10)-C(15)	120.9(2)	C(11)-C(10)-C(15)	118.1(2)
C(10)-C(11)-C(12)	120.6(3)	C(11)-C(12)-C(13)	120.7(3)
C(12)-C(13)-C(14)	119.5(3)	C(13)-C(14)-C(15)	120.7(3)
C(10)-C(15)-C(14)	120.3(3)	C(1)-O(1)-H(1)	112.9(20)

X-Ray Crystallography

Crystal Data for (178): $C_{17}H_{10}Cl_2N_4$, M_r = 341.2. Monoclinic, $P2_1/c$, a = 11.757(2), b = 11.470(2), c = 12.233(2), β = 96.05(2)°, V = 1640.5 Å^3, Z = 4, D_{calc} = 1.381 gcm^{-3}, $F(000)$ = 696, μ = 3.65 mm^{-1} for Cu-K_α radiation (λ = 1.54184 Å).

Crystal Data for (184): $C_{15}H_{16}Cl_2O_2$, M_r = 299.2. Monoclinic, $P2_1/c$, a = 11.113(2), b = 12.169(3), c = 11.247(2), β = 112.04(1)°, V = 1502.5 Å^3, Z = 4, D_{calc} = 1.322 gcm^{-3}, $F(000)$ = 624, μ = 3.92 mm^{-1} for Cu-K_α radiation.

Data Collection and Processing All X-ray data were measured at 293 K with a Stoe-Siemens diffractometer. For compound (9) [for (4) in square brackets where different]: crystal size 0.3x0.5x0.5 [0.4x0.5x0.5] mm, cell parameters from 2θ values for 32 reflections measured at $\mp\omega$, with 2θ 30 - 40 ° [20 - 30 °]. Intensity measurements in ω/θ scan mode with variable measuring time and width on-line profile fitting,[166] $2\theta_{max}$ = 130 °, index ranges h -13 → 13, k 0 → 13, l 0 → 14 [h -13 → 13, k 0 → 15, l 0 → 13, together with Friedel opposites, h 8 → 13 only]; no significant variation in the standard reflection intensities, no absorption correction. 2764 [2847] reflections measured, 2629 [2507] unique reflections R_{int} = 0.01 [0.04], 2167 [2357] with $F > 4\sigma_c(F)$ for structure determination and refinement; $\sigma_c(F)$ based on counting statistics only.

Structure Determination and Refinement[167] Direct methods, blocked-cascade least-squares refinement to minimise $\sum w\Delta^2$, $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 34 - 169G + 269G^2 - 91S + 57S^2 + 238GS$ [$\sigma^2(F_c) + 2 - 8G + 21G^2 - 3S + S^2 - 10GS$]. ($G = F_o/F_{max}$, $S = \sin\theta/\sin\theta_{max}$).[168] Anisotropic thermal parameters for all non-hydrogen atoms, hydrogen atoms included with constraints: C-H = 0.96 Å, H-C-H = 109.5 °, aromatic H on ring angle external bisectors, O-H freely refined, $U(H) = 1.2U_{eq}(C)$ or $1.2U_{eq}(O)$. Parameters refined 212 [182], extinction x = 9(4)x10^{-6} [1.5(1)x10^{-5}] to give $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{0.25}$, R = 0.075 [0.039], wR = 0.081 [0.048], slope of normal probability plot = 1.34 [0.93], max.shift/e.s.d. = 0.12

[0.04], mean = 0.02 [0.01], no significant features in a final difference synthesis, scattering factors from reference 169.

EXPERIMENT (31).

1,2-Dichloro-3-chloromethyl-3-methylcyclopropene (193).

Methyl lithium (3.2 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2-tetrachloro-3-chloromethyl-3-methylcyclopropane (1.0 g, 4.12 mmole) in ether (10 ml) under nitrogen at 0 °C. After 0.5 h the products were quenched with water (1 ml) at -40 °C; the organic layer was washed with water (1 ml) at that temperature, the solvent was removed carefully at 14 mmHg and the residue was flash distilled at 20 °C and 14 mmHg to give *1,2-dichloro-3-chloromethyl-3-methyl-cyclopropene* (0.57g, 82 %) (Found M^+: 169.9472. Calculated for $C_5H_5Cl_3$; 169.9457) which showed δ_H (60 MHz); 3.6 (2H, s), 1.4 (3H, s); δ_C 113.8s, 51.6t, 41.9s, 19.4q; ν_{max} 2978, 2953, 2941, 1444, 1377, 1265, 933, 733 cm^{-1}; m/z 170 (M^+), 135 (M^+-Cl), 121 (M^+-CH_2Cl).

EXPERIMENT (32).

1,2-dichloro-3-methyl-3-methoxymethyl-1-cyclopropene (195).

Methyl-lithium (3.2 ml, 1.5 M) was added over 2 min to 1,1,2,2-tetrachloro-3-methyl-3-methoxymethylcyclopropane (1.0 g) in dry ether (15 ml) under N_2 at 0 °C. The reaction was stirred at this temperature for 30 min, before quenching with water (2 ml) at -40 °C and shaking the products at that temperature until a clear solution was obtained; the ether layer was decanted into a cool flask and further ether (2 ml) was added at -40 °C to -50 °C, and the procedure repeated. The solvent was removed from the combined ether layers at -40 °C at 0.5-0.3 mmHg to give *1,2-*

dichloro-3-methyl-3-methoxymethyl-1-cyclopropene (0.5 g, 77.9%) which showed δ_H (60 MHz): 3.28 (2H, s), 3.17 (3H, s), 1.25 (3H, s). The compound could not be separated from ca. 5% of *2-chloro-1,3-dimethyl-3-methoxymethylcyclopropane*.

EXPERIMENT (33).

2-Chloro-1,3-dimethyl-3-methoxymethylcyclopropene (196).

(a) Methyl lithium (2.6 ml, 1.6 M) was added over 2 m to a stirred solution of 1,1,2,2-tetrachloro-3-methoxymethyl-3-methylcyclopropane (0.5 g) in ether (15 ml) in the presence of isobutene (2 ml) at 0 °C. After 30 m, the products were allowed to reach 20 °C for 30 m and were then quenched with water (5 ml) and worked up as before. Removal of the solvent at 14 mmHg and distillation of the residue at 20 °C and 0.5 mm Hg gave *2-chloro-1,3-dimethyl-3-methoxymethylcyclopropene* (0.12 g, 40%) (Found M^+: 146.0514. Calculated for $C_7H_{11}ClO$: 146.0498) which showed δ_H 3.39 (2H, s), 3.31 (3H, s), 2.02 (3H, s), 1.17 (3H, s); δ_H 117.6s, 115.9s, 79.4t, 58.5q, 33.3s, 19.4q, 8.3q; ν_{max} 1449 m, 1108 vs, 734 m cm^{-1}; m/z 146 (M^+), 131 (M^+-CH_3), 101 ($M^+-C_2H_5O$).

(b) The above reaction was repeated in the absence of isobutene, but using 1.5 mol equiv. of methyl lithium; the same product was obtained (44%).

EXPERIMENT (34).

1,2-Dichloro-3-methyl-3-(di-isopropylaminomethyl)cyclopropene (197).

Methyl lithium (1.26 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2-tetrachloro-3-methyl-3-(di-isopropylaminomethyl)cyclopropane (0.52 g) in ether (10 ml) at 0 °C. After 30 m the products were quenched with water at -40 °C, decanted from the ice and evaporated at that temperature and 1 mmHg to give *1,2-dichloro-3-methyl-3-(di-isopropylaminomethyl)cyclopropene* (0.33 g, 83%) which

was very unstable at 20 °C, giving a very thick brown oil in a period of minutes. However, the n.m.r. at 230 K showed δ_H 2.87 (2H, septet, J 6.7), 2.57 (2H, s), 1.24 (3H, s), 0.94 (12H, d, J 6.7 Hz); δ_C 114s, 50.4t, 46.9d, 43.8s, 22.5q, 20.6q.

EXPERIMENT (35).

1,2-Dichloro-3-methyl-3-(allylthio)methylcyclopropene (198).

Methyl lithium (1.5 ml, 1.2 eq.) was added to a rapidly stirred solution of 1,1,2,2-tetrachloro-3-methyl-3-(allylthio)methylcyclopropane (0.51 g, 1.8 mmol) in ether (8 ml) at 0 °C. After 2 min. a yellow precipitate formed; the reaction was stirred at 0 °C for 0.5 h before quenching with water at -40 °C. The solvent was removed at -30 °C and 0.4 mmHg to give *1,2-dichloro-3-methyl-3-(allylthiol)methyl-cyclopropene* (0.25 g, 65 %) which showed δ_H (300 MHz at -40 °C) 5.72 (1H, m), 5.1 (2H, m), 3.19 (2H, d, J 7.3 Hz), 2.72 (2H, s), 1.4 (3H, s).

The crude product was pure by n.m.r.; however, within minutes of attaining 0 °C, a solution of the cyclopropene in $CDCl_3$ darkened and the ^1H n.m.r. spectrum became very complicated.

EXPERIMENT (36).

1-Chloro-3,3-dimethyl-2-trimethylsilyl-1-cyclopropene (200).

(a) Methyl lithium (3.1 ml) was added to a stirred solution of 3,3-dimethyl-1-trimethylsilylcycloprop-1-ene (0.5 g) and di-isopropylamine (0.43 g) in ether (10 ml) at -70 °C. The mixture was allowed to reach room temperature and after one hour was cooled again to -50 °C. Hexachloroethane (1.26 g) in ether (10 ml) was added slowly and the mixture was stirred for one hour at -10 °C before quenching with water (2 ml) at -40 °C, shaking the products at that temperature until a clear solution was obtained. The ether layer was decanted into a cooled flask and more ether (2 ml)

was added at −40 to −30 °C and the procedure was repeated. The organic layer was washed with hydrochloric acid (0.5 M) at −10 °C, dried, and the solvent removed at −30 °C and 0.3 mmHg. The residue was immediately distilled at 0.2 mmHg and 0 − 20 °C to give *1−chloro−3,3−dimethyl−2−trimethylsilyl−1−cyclopropene* (0.31g, 50%) which showed δ_H (300 MHz at 230K): 1.2 (6H, s), 0.14 (9H, s); δ_C 124.4, 120.2, 31.3, 26.8, −1.036; ν_{max} 2961, 2167, 1251, 1119, 863, 843 cm^{-1}; m/z 174 (M^+), 139 (M^+−Cl).

(b) Methyl lithium (5.6 ml, 1.5 M) was added to a stirred solution of 3,3−dimethyl−1−trimethylsilylcycloprop−1−ene (0.91 g) in ether (10 ml) and di−isopropylamine (1.1 ml) at −78 °C. The mixture was allowed to reach room temperature and after one hour was cooled to −50 °C. Hexachloroethane (3.02 g) in ether (10 ml) was added slowly to the stirred mixture. After 15 m at −50 °C the reaction mixture was allowed to warm to room temperature and then stirred for another 2 h. Water (5 ml) was added at −10 °C and the organic layer was separated. The aqueous layer was washed with ether (3 x 10 ml) and the combined organic layers were washed with hydrochloric acid (2 x 10 ml, 0.5 M), dried, and the solvent was removed at 14 mmHg. The residue was flash distilled at 0.3 mmHg and 25 °C to give a mixture of *1−chloro−3,3−dimethyl−2−trimethylsilylcycloprop−1−ene* and *3−chloro−3−methyl−1−trimethylsilyl−1−butyne* (201) (0.88 g, 78%) in ratio (2:1).

After 12 h at −10 °C, the cyclopropene rearranged to *3−chloro−3−methyl−1−trimethyl−1−butyne* and a large amount of impurities. A portion of the crude product was columned over silica eluting with petrol. The first fraction (0.13 g) showed a complicated n.m.r spectrum; the second fraction was identified as *3−chloro−3−methyl−1−trimethylsilyl−1−butyne* (50 mg) (Found M^+: 174.0639. Required for $C_8H_{15}SiCl$: 174.0632) which showed δ_H: 1.82 (6H, s), 0.2 (9H, s); ν_{max} 2961, 2167, 1252, 1119, 863, 843 cm^{-1}.

(c) When the crude undistilled cyclopropene was allowed to stand in CCl_4 for one week at room temperature, the n.m.r. spectrum showed that only the alkyne was

present.

EXPERIMENT (37).

1-Bromo-4,4-dimethyl-2-pentyne (209).

(a) Methyl lithium (2.5 ml) was added to stirred solution of 1-chloro-2,2-dibromo-1-t-butylcyclopropane (1.0 g, 3.4 mmol) in ether (5 ml) at -78 °C. After 10 min. at room temperature, the products were quenched with water (2 ml) and the aqueous layer was extracted with ether (2 x 5 ml), dried, and the solvent was removed carefully at 14 mmHg to give crude *1-bromo-2-t-butylcycloprop-1-ene* (0.42 g, 70%) which was identical to the authenic sample by n.m.r.[49] When the crude cyclopropene was allowed to stand in $CDCl_3$ or as a neat sample for 6-7 days at room temperature, it reacted completely; flash distillation of the crude product at 20 °C and 0.3 mmHg gave *1-bromo-4,4-dimethyl-1-pentyne* (0.37 g, 62%) (Found M^+: 174.0020. Required for $C_7H_{11}Br$: 174.0018) which showed δ_H (60 MHz): 3.78 (2H, br.s), 1.18 (9H, s); ν_{max} 2980, 2880, 2242, 1365, 1270, 1210, 835 cm^{-1}; m/z 174 (M^+), 95 (M^+-Br).

(b) 1-Bromo-2-t-butylcycloprop-1-ene (0.2 g) in ether (5 ml) was stirred with lithium bromide (50 mg) for 4 days; the n.m.r then showed that no starting material was left. The products were diluted with ether (5 ml) and filtered; removal of the solvent carefully at 14 mmHg gave *1-bromo-4,4-dimethyl-2-pentyne* (0.15 g, 75%) which was pure by n.m.r. and identical to the above product.

EXPERIMENT (38).

Dimerisation of 1,2-dichloro-3-methyl-3-methoxymethylcycloprop-1-ene (195).

(a) Methyl lithium (3.1 ml, 1.5 M) was added to a stirred solution of 1,1,2,2-tetrachloro-3-methyl-3-methoxymethylcyclopropane (1.0 g) in ether (10 ml) at

0 °C. After 30m the products were quenched with water and worked up as before; the solvent was removed at −20 °C and 14 mmHg and the residual brown oil was dissolved in chloroform (3 ml) and allowed to stand for 2 days at 20 °C. The solvent was removed at 14 mmHg and a minor volatile component *1−chloro−2,3−dimethyl−3−methoxymethylcyclopropene* was removed by flash distillation at 1 mmHg. The residue was purified by column chromatography over silica eluting with petrol and ether (10 : 1) to give *1,3,4−trichloro−2−(2−chloro−3−methoxy−prop−2−yl)−6−methoxy−5−methyl−cyclohexa−1,4−diene* (212) (0.85 g, 61 %) (Found M^+: 331.9937. Calculated for $C_{12}H_{16}O_2$: 331.9904) which showed δ_H 5.44 (1H, s), 4.82 (1H, s), 3.52 (2H, s), 3.4 (3H, s), 3.3 (3H, s), 2.02 (3H, s), 1.17 (3H, s); δ_C 137.6s, 135.1s, 134.5s, 127.5s, 80.1d, 76.2q, 63.6, 59.35, 58.3, 53.1, 21.2, 18.2; ν_{max} 2989, 2927, 2825, 1453, 1110 cm^{-1}; m/z 332 (M^+), 287 ($M^+-C_2H_5O$), 225 ($M^+-C_4H_8OCl$).

(b) <u>Reduction with lithium−t−butanol</u>: Lithium (200 mg) was added to the above diene (0.35 g) in t−butanol (2.0 g) and tetrahydrofuran (10 ml). After 3 min. an exothermic reaction occurred which was controlled at a steady reflux for 1 h by periodic cooling. After stirring for 2 h at 20 °C, the products were poured into ice−water (20 ml) and extracted with ether (5 x 20 ml). The organic layer was washed with water (3 x 20 ml) and then with sat. brine (20 ml). The solvent was removed at 14 mmHg to give an oil which was purified by column chromatography over silica eluting with petrol and ether (10:1) to give 5−isopropyl−2−methylanisole (213) (0.12 g, 69 %)[118] which showed δ_H 7.04 (1H, d, 7.5 Hz), 6.0 (1H, d, J 7.5 Hz), 6.7 (1H, s), 3.83 (3H, s), 2.83 (1H, septet, J 6.9 Hz), 2.18 (3H, s), 1.24 (6H, d, J 6.9 Hz); ν_{max} 2959, 1612, 1584, 1253, 1132, 1042, 851, 814 cm^{-1}; m/z 164 (M^+), 149 (M^+-CH_3).

EXPERIMENT (39).

<u>3−Acetoxy−1,2,4−trichloro−3−methylbut−1−ene (219).</u>

A solution of 1,2-dichloro-3-chloromethyl-3-methylcyclopropene (0.5g) in acetic acid (5 ml) was stirred for 4 h at 20 °C. The products were treated with sat. aq. sodium bicarbonate (50 ml) and extracted with ether (5 x 10 ml). Removal of the ether at 14 mmHg gave an oil which was one major spot by t.l.c.; this was purified by column chromatography over silica, eluting with petrol and ether (10 : 0.5) to give *3-acetoxy-1,2,4-trichloro-3-methylbut-1-ene* (0.45 g, 67 %) (Found M^+: 229.9660. Calculated for $C_7H_9Cl_3O_2$: 229.9668) which showed δ_H 7.3 (1H, s), 4.2 (2H, s), 2.18 (3H, s), 2.1 (3H, s); ν_{max} 1769, 1372, 1203, 1031, 708 cm^{-1}; m/z 230 (M^+), 195 (M^+-Cl).

EXPERIMENT (40).

<u>3-Methoxy-1,2,4-trichloro-3-methylbut-1-ene (224).</u>

1,2-Dichloro-3-chloromethyl-3-methylcyclopropene (0.4 g) was stirred in methanol (5 ml) for 5 h at 20 °C. Removal of the solvent at 14 mmHg gave an oil (0.27 g) which was chromatographed over silica eluting with petrol and ether (10:1) to give a mixture of products; preparative g.l.c. of the major component gave *1-methoxy-1,2,4-trichloro-3-methylbut-2-ene* (Found M^+: 201.9716. $C_6H_9OCl_3$ requires 201.9719) which showed δ_H 6.48 (1H, br.d), 3.65 (2H, d, J 3 Hz), 3.2 (3H, s), 1.5 (3H, s); ν_{max} 3096, 2991, 2832, 1605, 1459, 1126, 1099, 1052, 801, 759; m/z 202 (M^+), 187 (M^+-CH_3), 171 (M^+-OCH_3), 153 (M^+-CH_2Cl).

EXPERIMENT (41).

<u>1-Isopropoxy-3-methyl-1,2,4-trichlorobuta-1,3-diene (226).</u>

A solution of 1,2-dichloro-3-chloromethyl-3-methylcyclopropene (0.5 g) in acetone (5 ml) was stirred for 3 days at 20 °C. The solvent was removed at 14 mmHg to give an oil (0.41 g) which was one major spot on t.l.c.. Column chromatography over

silica, eluting with petrol (b.p. 40 – 60 °C) gave *1-isopropoxy-3-methyl-1,2,3-trichlorobuta-1,3-diene* (0.35 g, 52 %) (Found M^+: 227.9855. Calculated for $C_8H_{11}Cl_3O$: 227.9875) which showed δ_H 5.85 (1H, br.q), 4.4 (1H, septet, J ca. 6.0 Hz), 1.85 (3H, br.t), 1.2 (6H, d, J ca. 6.0 Hz); δ_C 141.7, 133.9, 118.24, 113.6, 75.8, 21.93, 19.87; ν_{max} 2981, 1633, 1377, 1198, 1097, 984, 618 cm^{-1}; m/z 228 (M^+).

EXPERIMENT (42).

3-Chloro-3-(1,3-dichloro-2-methylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane (227_a).

Methyl lithium (15.1 ml, 1.5 M) was added over 2 min. to a stirred solution of 1,1,2,2-tetrachloro-3-chloromethylcyclopropane (5 g) in ether (15 ml) at 0 °C. After 30 min. the products were quenched with water (2 x 5 ml) at -40 °C and decanted from the ice which remained. 2,3-Dimethyl-2-butene (3.4 g) was added and the mixture was allowed to stand for 12 h at 20 °C. Removal of the solvent at 14 mmHg gave an oil which was one peak by glc. Kugelrohr distillation at 0.3 mmHg (oven temperature 70 °C) gave *3-chloro-3-(1,3-dichloro-2-methylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane* (4.03 g, 77 %) (Found M^+: 254.0342. Required for $C_{11}H_{17}C_3$: 254.0396) which showed δ_H 4.19 (1H, d, J 11.6 Hz), 4.1 (1H, d, J 11.6 Hz), 1.97 (3H, s), 1.28 (3H, s), 1.2 (3H, s), 1.17 (3H, s), 1.15 (3H, s); δ_H ($C_6D_5NO_2$) 4.4 (2H, s), 2.05 (3H, s), 1.35 (3H, s), 1.25 (3H, s), 1.2 (3H, s), 1.15 (3H, s) (unchanged on heating to 400 K); ν_{max} 3005, 2924, 1452, 1379, 1264, 1132, 780, 710 cm^{-1}; m/z 254 (M^+), 239 (M^+-CH_3), 205 (M^+-CH_2Cl).

EXPERIMENT (43).

3-chloro-3-(1,3-dichloro-2-methylprop-1-enyl)-1,1-dimethylcyclopropane (227_b).

Methyl lithium (15.1 ml, 1.5 M) was added over 2 min. to a stirred solution of

1,1,2,2–tetrachloro–3–methyl–3–chloromethylcyclopropane (5.0 g) in ether (10 ml) at 0 °C. After 30 m the products were quenched with water (2 ml) at –40 °C and decanted from the ice which remained into a cold thick–walled glass tube (20 ml volume) containing isobutene (6.0 g). The tube was sealed with a screw–top and stirred at 20 °C for 12h. The tube was cooled before opening, and the solvent was removed at 14 mmHg, to give an oil which was one a single peak by g.l.c. Kugelrohr distillation (oven temperature 50 °C) at 0.2 mmHg gave *3–chloro–3–(1,3–dichloro–2–methylprop–1–enyl)–1,1–dimethylcyclopropane* (3.26 g, 70 %) (Found M^+: 226.0059. Required for $C_9H_{13}Cl_3$: 226.0082) which showed δ_H (200 MHz)(rotamer 1): 4.96 (1H, d, J 11.1 Hz), 3.96 (1H, d, J 11.1 Hz), 1.95 (3H, s), 1.56 (1H, d , J 6 Hz), 1.36 (3H, s), 1.26 (1H, d, J 6 Hz), 1.18 (3H, s), (rotamer 2) 4.29 (1H, d, J 11.6 Hz), 4.22 (1H, d, J 11.6 Hz), 1.98 (3H, s), 1.43 (3H, s), 1.24 (1H, d, J 6.5 Hz), 1.11 (3H, s), 1.09 (1H, d, J 6.5 Hz) (ratio of rotamers *ca* 8:7); ν_{max} 1637, 723 cm^{-1}; m/z 226 (M^+), 177 ($M^+–CH_2Cl$).

EXPERIMENT (44).

<u>3–Chloro–3–(1,3–dichloro–2–methylprop–1–enyl)–Z–1,2–dimethylcyclopropane (227$_c$).</u>

Methyl lithium (9 ml, 1.5 M) was added over 2 m to 3–chloromethyl–3–methyl–1,1,2,2–tetrachlorocyclopropane (3.0 g, 2.3 mmol) in ether (15 ml) and *cis*–butene (6 ml) at 0 °C. The products were allowed to stand at 20 °C for 12 h in a sealed tube before quenching with water (5 ml). Work up as above and bulb–to–bulb distillation at 80 °C and 0.3 mmHg gave an oil (2.16 g, 76%) which showed two peaks close together by g.l.c. (ratio *ca* 5:1); the major isomer was characterised as *3–chloro–3–(1,3–dichloro–2–methylprop–1–enyl)–Z–1,2–dimethylcyclopropane* (Found M^+: 226.0027. $C_9H_{13}Cl_3$ requires: 226.0083), which showed δ_H (200 MHz): 4.2 (2H, s), 1.93 (3H, s), 1.51 (2H, m), 1.14 (3H, d, J 4.07 Hz), 1.13 (3H, d, J 4.01 Hz); in addition small signals were seen at δ 2.0 (s), 1.09 (br.d), presumably caused by the

minor isomer; ν_{max} 2961, 2932, 1637, 1446, 1265, 738, 706 cm^{-1}; m/z 226 (M^+), 191 (M^+–Cl), 177 (M^+–CH_2Cl).

EXPERIMENT (45).

1–Chloro–1–(1,3–dichloro–2–methylprop–1–enyl)cyclopropane (227_e).

1,2–Dichloro–3–chloromethyl–3–methylcyclopropene (5.0 g) in ether (5 ml) was mixed with an excess of ethylene (condensed in high pressure vessel at –90 °C). The reaction was left at room temperature for 3 days. The solvent was removed at 14 mmHg to leave a brown oil, which was purified by column chromatography over silica eluting with petrol to give *1–chloro–1–(1,3–dichloro–2–methylprop–1–enyl)cyclopropane* (0.87 g, 15%) (Found M^+: 197.9787. Required for $C_7H_9Cl_3$: 197.9770) which showed δ_H 4.2 (2H, s), 1.85 (3H, s), 1.38 (4H, s); ν_{max} 3097, 3012, 2958, 2921, 1641, 1447, 1263, 1179, 1154, 1041, 989, 705, 683 cm^{-1}; m/z 198 (M^+), 163 (M^+–Cl), 149 (M^+–CH_2Cl).

EXPERIMENT (46).

Methyl 2–chloro–2–(1,3–dichloro–2–methylprop–1–enyl)cyclopropane carboxylate (230_a).

Methyl lithium (1.6 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2–tetrachloro–3–chloromethyl–3–methylcyclopropane (0.5 g) in ether (10 ml) at 0 °C. After 30 m the products were quenched with water (1 ml) at –40 °C and decanted from the ice which remained. Methyl acrylate (5 ml) was added and the mixture was allowed to stand for 12 h at 20 °C. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by column chromatography over silica eluting with petrol and ether (10 : 1) to give *methyl 2–chloro–2–(1,3–dichloro–2–methylprop–1–enyl)cyclopropane carboxylate* (0.4 g, 75 %) (Found M^+: 255.9803. Calculated for $C_9H_{11}Cl_3O$: 255.9825) which showed δ_H (300

MHz, 230 K) (rotamer 1): 4.62 (1H, d, J 11.2 Hz), 4.11 (1H, d, J 11.2 Hz), 3.76 (3H, s), 2.4 (2H, m), 2.09 (1H, dd, J 5.1, 8.1 Hz), 2.0 (3H, s), (rotamer 2) 4.51 (1H, d, J 11.2 Hz), 4.2 (1H, d, J 11.2 Hz), 3.74 (3H, s), 2.76 (1H, br.t), 1.97 (3H, s), 1.85 (2H, br. t); in ratio (5:1); δ_H (60 MHz, 300 K) 4.4 (1H, d J 12 Hz), 4.05 (1H, d J 12 Hz), 3.55 (3H, s), 1.9 – 2.6 (2H, m) 1.8 (3H, s); ν_{max} 2954, 1738, 1440, 1374, 1207, 698 cm^{-1}; m/z 256 (M^+), 221 (M^+–Cl), 207 (M^+–CH_2Cl).

EXPERIMENT (47).

Methyl 2–chloro–2–(1,3–dichloro–2–methylprop–1–enyl)–1–methylcyclopropane carboxylate (230_b).

Methyl lithium (1.6 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2–tetrachloro–3–chloromethyl–3–methylcyclopropane (0.5 g) in ether (10 ml) at 0 °C. After 30 m the products were quenched with water (1 ml) at –40 °C and decanted from the ice which remained. Methyl methacrylate (5 ml) was added and the mixture was allowed to stand for 12 h at 20 °C. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by column chromatography over silica eluting with petrol and ether (10 : 2) to give *methyl 2–chloro–2–(1,3–dichloro–2–methylprop–1–enyl)–1–methylcyclopropane carboxylate* (0.46 g, 82%) (Found M^+: 269.9968. Calculated for $C_9H_{11}Cl_3O$: 269.9981) which showed δ_H (300 MHz, 230 K) (rotamer 1) 4.63 (1H, d, J 11.1 Hz), 4.09 (1H, d J 11.1 Hz), 3.71 (3H, s), 2.67 (1H, d, J 6.2 Hz), 1.96 (3H, s), 1.62 (1H, d, J 6.5 Hz), 1.58 (3H, s), (rotamer 2) 3.825 (1H, d, J 10 Hz), 3.67 (3H, s), 2.29 (1H, d, J 6.8 Hz), 2.015 (1H, d, J 8.2 Hz), 1.66 (3H, s) [the remaining signals being obscured by those for the major rotamer] (ratio of rotamers 2:1); δ_H (60 MHz, 300 K) 4.3 (1H, br.d, J 11 Hz), 4.0 (1H, d, J 11 Hz), 3.6 (3H, s), 2.5 (1H, br.d, J 6 Hz), 1.9 (3H, s), 1.46 (1H, d, J 6 Hz); δ_C (230 K) 171.2, 170.9, 135.1, 134.4, 132.6, 131.9, 53.5, 53.0, 52.4, 44.9, 44.7, 36.6, 31.5, 31.2, 29.6, 18.6, 17.4, 17.3; ν_{max} 2952, 1732,

1300, 1165, 704 cm^{-1}; m/z 270 (M^+), 235 (M^+–Cl), 221 (M^+–CH_2Cl).

EXPERIMENT (48).

<u>3–(1–chloro–2,2,3,3–tetramethylcyclopropyl)–3–chloro–2–methyl–2–propenyl methyl ether (229_a).</u>

Methyl lithium (1.56 ml, 1.5 M) was added over 1 min to 1,1,2,2–tetrachloro–3–methyl–3–methoxymethylcylopropane (0.5 gm, 2.1 x 10^{-3} mole) in ether (12 ml) under nitrogen at 0 °C. The reaction mixture was stirred at this temperature for 0.5 h before quenching with water at –40 to –50 °C. The ether layer was decanted to a cooled reaction flask, more ether (2 ml) was added at –40 – 50 °C, and the procedure was repeated. G.l.c. of the combined ether layers showed one major peak and no starting material. 2,3–Dimethylbut–2–ene (1.8 g) was added and the reaction was allowed to reach room temperature. After 3 h, the solvent was removed at 14 mmHg. The residue was flash distilled at 0.1 mmHg and 70 °C to give pure *3–(1–chloro– 2,2,3,3–tetramethylcyclopropyl)–3–chloro–2–methyl–2–propenyl methyl ether* (0.36 g, 69%) (Found M^+: 250.0867. $C_{12}H_{20}OCl_2$ requires: 250.0891) which showed δ_H (200 MHz) 4.01 (1H, d, J 11.4 Hz), 3.84 (1H, d, J 11.4 Hz), 3.35 (3H, s), 1.88 (3H, s), 1.27 (3H, s), 1.2 (3H, s), 1.16 (3H, s), 1.07 (3H, s); ν_{max} 3004, 2924, 2821, 1684, 1451, 1379, 1105, 885 782 cm^{-1}; m/z 250 (M^+). Irradiation at δ 1.07 caused a 6 % n.O.e. enhancement in the signal at 4.01, 3 % in that at 3.84 and 2 % in that at 1.88; enhancements in these signals on irradiation at δ 1.27, 1.20 or 1.16 were all below 2 %.

EXPERIMENT (49).

<u>3–(1–Chloro–2,2,3–trimethylcyclopropyl)–3–chloro–2–methyl–2–propenyl methyl ether (229_f).</u>

Methyl lithium (1.56 ml, 1.5 M) was added over 1 min to 1,1,2,2–tetrachloro–3–methyl–3–methoxymethylcyclopropane (0.5 gm, 2.1 x 10^{-3}) in ether 12 ml under

nitrogen at 0 °C. The reaction mixture was stirred at this temperature for 0.5 h before quenching with water. Water (2 ml) was added at −40 °C. After work up as above, 2-methyl-2-butene (1.8 g) was added; after 3 h at room temperature, the solvent was removed at 14 mmHg. The residue was flash distilled at 60 °C and 0.1 mmHg to give *3-(1-chloro-2,2,3-trimethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether* (0.33 g, 68%). (Found M^+: 236.0726. $C_{11}H_{18}OCl_2$ requires 236.0735) which showed ν_{max} 1455m, 1379m, 1103s, 760m cm^{-1}; m/z 236 (M^+), 191 ($M^+-C_2H_5O$). The ^1H n.m.r (200 MHz) was complex but included signals in the regions 3.7 – 4.2, 3.33 – 3.37, 1.88 – 1.89, and 1.0 – 1.5 in the ratio 2:3:3:10. There were two singlets in ratio 1:1 at 1.88 and 1.89, and four in the ratio 6:2:3:8 at δ 3.37, 3.36, 3.35, and 3.33, and at least three AB patterns in the low field region, at δ 4.18 and 3.81 (J 11.0 Hz), 4.0 and 3.96 (J 11.5 Hz), and 4.02 and 3.87 (J 11.4 Hz). The high field region included a large number of signals. The ^{13}C spectrum included eight signals in the alkene region at δ 138.3, 138.0, 137.0, 136.1, 135.1, 132.6, 131.4, as well as groups of signals at δ 72 – 73, 55 – 58, and 10 – 36.

EXPERIMENT (50).

<u>3-(1-Chloro-2,2-dimethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether (229_b)</u>.

(a) Methyl lithium (1.6 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2-tetrachloro-3-methoxymethyl-3-methylcyclopropane (0.5 g) in ether (12 ml) under N_2 at 0 °C. After 0.5 h at this temperature the products were quenched with water and worked up as before. Excess isobutene (4.0 g) was added; after 12 h, the solvent was removed at 14 mmHg, and the residue was distilled at 50 °C and 0.1–0.2 mmHg to give *3-(1-chloro-2,2-dimethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether* (0.29 g, 62%) (Found M^+: 222.0582. $C_{10}H_{16}Cl_2O$ requires: 222.0578) which showed δ_H (rotamer 1): 4.39 (1H, d, J 11.0 Hz), 3.88 (1H, d, J 11.0 Hz), 3.37 (3H, s), 1.9 (3H, s), 1.4 (3H, s), 1.2 (2H, m), 1.05 (3H, s); (rotamer 2): 4.05

(1H, d J 11.5 Hz), 3.98 (1H, d J 11.5 Hz), 3.34 (3H, s), 1.8 (3H, s), 1.3 (3H, s), 1.2 (2H, m), 1.19 (3H, s); two pairs of doublets were also seen at δ 1.34 (J 6.1 Hz), 1.25 (J 6.1 Hz), and 1.20 (J 6.3 Hz) and 1.05 (J 6.3 Hz), but these were not definitely assigned to a particular rotamer (ratio of rotamers 6:5); ν_{max} 1650, 943 cm^{-1}; m/z 222 (M^+), 187 (M^+–Cl), 177 (M^+–C_2H_5O).

(b) 3–Chloro–2–(1,3–dichloro–2–methylprop–1–en–1–yl)–1,1–dimethylcyclopropane (0.5 g) was refluxed for 2 h with sodium methoxide (0.54 g) in methanol (6 ml). The products were treated with water (10 ml) and extracted with ether (2 x 20 ml), dried, and the solvent was removed at 14 mmHg; the residue was chromatographed over silica eluting with petrol and ether (10:1) to give *3–(1–chloro–2,2–dimethyl–cyclopropyl)–3–chloro–2–methylprop–2–enyl methyl ether* (0.35 g, 71%) identical by n.m.r. and i.r. to that obtained above.

EXPERIMENT (51).

3–(1–Chloro–*trans*–2,3–dimethylcyclopropyl)–3–chloro–2–methyl–2–propenyl methyl ether (229_e).

Methyl lithium (1.6 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2–tetrachloro–3–methyl–3–methoxymethyl–cyclopropane (0.5 g, 2.1 mM) in ether (12 ml) under N_2 at 0 °C. After 0.5 h the products were quenched with water and worked up as before; *trans*–but–2–ene (1.8 g) was added and after 12 h at ambient temperature the solvent was removed at 14 mmHg. The residue was flash distilled at 50 °C and 0.1 mmHg to give *3–(1–chloro–trans–2,2–dimethylcyclopropyl)–3–chloro–2–methyl–2–propenyl methyl ether* (0.25 g, 54%) which showed a single peak by g.l.c. (Found M^+: 222.0582. Calculated for $C_{10}H_{16}Cl_2O$: 222.0578) which showed δ_H (300 MHz, 220 K) (rotamer 1) 4.18 (1H, d, J 10.6 Hz), 3.81 (1H, d, J 10.6 Hz), 3.33 (3H, s), 1.88 (3H, s), 1.35 (3H, d, J 5.9 Hz) and (rotamer 2) 4.20 (1H, d, J 10.6 Hz), 4.07 (1H, d, J 10.6 Hz), 3.38 (3H, s), 1.88 (3H, s), 1.25 (3H, d J 6.1 Hz), 1.02 (3H, d, J 6.1 Hz) in ratio 2.5:1, together with a broad multiplet at *ca* δ 1.2

integrating to five hydrogens. At 303K, the 200 MHz spectrum showed sharp singlets at 3.35 and 5.40 for the two methyl signals, together with a broad three hydrogen doublet at δ 1.33 and a very broad five hydrogen singlet at 1.11; in addition one half of the AB pattern was visible at δ 4.15, the other half apparently appearing as an extremely broad signal centred at δ 3.9; ν_{max} 1104, 752 cm^{-1}; m/z 222 (M^+), 187 (M^+–Cl).

EXPERIMENT (52).

3–(1–Chloro–*cis*–2,3–dimethylcyclopropyl)–3–chloro–2–methyl–2–propenyl methyl ether (229_c).

Methyl lithium (1.56 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2–tetrachloro–3–methyl–3–methoxycyclopropane (0.5 g, 2.1 mM) in ether (12 ml) at 0 °C. After 5 h the products were quenched with water and worked up as above. *cis*–But–2–ene (1.8 g) was added to the ethereal solution and the products were allowed to stand for 12 h at 20 °C. Removal of the solvent at 14 mmHg and distillation of the residue gave an oil which showed two peaks close together by g.l.c. (ratio *ca* 6.5:1); the major component was characterised as *3–(1–chloro–cis–2,3–dimethylcyclopropyl)–3–chloro–2–methyl–2–propenyl methyl ether*, b.p. 55 °C at 0.1 mmHg (0.26 g, 56%) (Found M^+: 222.0571. Calculated for $C_{10}H_{16}OCl_2$: 222.0578) which showed δ_H (200 MHz) 4.05 (2H, s), 3.34 (3H, s), 1.81 (3H, s), 1.36 (2H, m), 1.13 (6H complex); in addition small signals were seen at δ 3.36 (s), 1.91(s), and 1.0–1.2, presumably caused by the minor isomer; ν_{max} 1102s, 738s cm^{-1}; m/z 222 (M^+), 187 (M^+–Cl). No *trans*–isomer was seen by g.l.c.

EXPERIMENT (53).

Methyl 2–chloro–2–(1–chloro–3–methoxy–2–methylprop–1–enyl)cyclopropane carboxylate (234_a).

Methyl lithium (1.6 ml, 1.5 M) was added over 1 m to a stirred solution of

1,1,2,2-tetrachloro-3-(methoxymethyl)-3-methylcyclopropane (0.5 g, 2.1 mmole) in ether (12 ml) at 0 °C. The products were stirred for 30 m and then quenched with water and worked up as above. Methyl acrylate (5 ml) was added; after 12 h at 20 °C, g.l.c showed complete reaction had occurred. The solvent was removed 14 mmHg and the residue was distilled to give *methyl 2-chloro-2-(1-chloro-3-methoxy-2-methylprop-1-enyl)-cyclopropanecarboxylate* (0.28 g, 54%), b.p. 65 °C at 0.1 mmHg (Found: 252.0303. Calculated for $C_{10}H_{14}Cl_2O_3$: 252.0320) which showed δ_H (200 MHz, 303 K) 4.07 – 4.3 (2H, complex), 3.65 (3H, s), 3.3 (3H, s), 2.5 (1H, br.dd, J 6.9 Hz), 2.2-1.8 (5H, m), including 1.85 (3H, s); δ_H (300 MHz, 230K): (rotamer 1) 4.35 (1H, d, J 11.8 Hz), 4.15 (1H, d, J 11.8 Hz), 3.75 (3H, s), 3.37 (3H, s), 2.43 (1H, dd, J 9.2, 6.9 Hz), 2.16 (1H, t, J 6.9 Hz), 2.09 (1H, dd, J 9.2, 6.9 Hz); (rotamer 2) 4.17 (1H, d, *ca* J 11.6 Hz), 3.97 (1H, d, J 11.6 Hz), 3.71 (3H, s), 3.35 (3H, s), 2.70 (1H, dd, *ca* J 9.3, 7 Hz), 1.96 (1H, t, *ca* J 7 Hz), 1.89 (3H, s), 1.79 (1H, dd, J 6.7, 9.3 Hz) (ratio of rotamers *ca* 7:3); δ_C (230 K) 169.4, 169.2, 130.6, 130.2, 129.3, 127.6, 71.4, 71.3, 50.3, 50.1, 53.0, 48.0, 47.3, 35.5, 30.3, 27.0, 24.3, 17.7; together with minor signals; ν_{max} 1739vs, 702 cm^{-1}; m/z 252 (M^+), 217 (M^+-Cl), 207 (M^+-C_2H_5O).

EXPERIMENT (54).

<u>Methyl 2-chloro-2-(1-chloro-3-methoxy-2-methylprop-1-enyl)-1-methylcyclopropane carboxylate (234_b)</u>.

(a) Methyl lithium (1.6 ml, 1.5 M) was added over 1 m to a stirred solution of 1,1,2,2-tetrachloro-3-methyl-3-methoxymethylcyclopropane (0.5 g, 2.1 mmole) in ether (12 ml) at 0 °C. Reaction and work up as above using methyl methylacrylate led to *methyl 2-chloro-2-(1-chloro-3-methoxy-2-methylprop-1-enyl)-1-methylcyclopropane carboxylate*, b.p. 70 °C at 0.1 mmHg which was single component by g.l.c (0.29 g, 52%) (Found M^+: 266.0470. Calculated for $C_{11}H_{16}Cl_2O_3$ 266.0476) which showed δ_H

(60 MHz): 4.01 (2H, br. s), 3.25 (3H, s), 2.3 (1H, d, J 6 Hz), 1.82 (3H, s), 1.58 (3H, s), 1.4 (1H, d, J 6 Hz); (300 MHz, 230 K) (rotamer 1) 4.35 (1H, d, J 11.8 Hz), 4.13 (1H, d, J 11.8 Hz), 3.72 (3H, s), 3.37 (3H, s); (rotamer 2) 3.91 (1H, d, J 11.6 Hz), 3.89 (1H, d, J 11.6 Hz), 3.65 (3H, s), 3.34 (3H, s) in ratio *ca* 6:5, together with 2.40 (1H, d, J 6.3 Hz), 2.26 (1H, d, J 6.7 Hz), 1.34 (1H, d, J 6.7 Hz); the exact integrals of these final signals could not be determined; the fourth doublet required for the two rotamers was apparently partly obscured by the signal at 1.64, but was centred at 1.63; δ_C (50.3 MHz, 300 K) 171.0, 137.3 br, 130.7br, 71.9, 58.3, 53.8, 52.5, *ca*. 32 (very broad), 29.6 (very broad), 17.55, 17.5; δ_C (75.5 MHz, 230 K) 171.5, 171.1, 137.3, 136.7, 130.9, 130.0, 71.8, 71.3, 58.6, 58.3, 53.9, 53.1, 52.9, 52.7, 37.7, 36.6, 32.8, 31.1, 29.2, 17.5, 17.4; ν_{max} 1733 s, 718 m cm^{-1}; m/z 266 (M^+), 231 (M^+–Cl), 221 (M^+–C_2H_5O).

(b) Methyl 2–chloro–2–(1,3–dichloro–2–methylprop–1–en–1–yl)–1–methylcyclo–propane carboxylate (0.5 g) in methanol (0.5 ml) was added to a stirred solution of sodium methoxide (prepared from sodium (0.22 g) in methanol (6 ml)). After refluxing for 1.5 h, the products were treated with water (10 ml) and extracted with ether (2 x 10 ml), dried, and the solvent was removed at 14 mmHg; the residue was chromatographed over silica eluting with petrol and ether (10:2) to give methyl 2–chloro–2–(1–chloro–3–methoxy–2–methylprop–1–en–1–yl)–1–methylcyclopropane carboxylate (0.32 g, 65%) which was identical by n.m.r. and i.r. to that above.

EXPERIMENT (55).

<u>7–Chloromethyl–7–methyl–1,2–dichloro–4–methylcyclohepta–1,4–diene (239, X= Cl).</u>

1,2–Dichloro–3–chloromethyl–3–methylcyclopropene (0.5 g) in ether (5ml) was allowed to stand for 12h at 20 °C with isoprene (3ml). The solvent and excess isoprene were removed at 14 mmHg to give an oil (0.55 g) which showed a complex n.m.r. spectrum. The product was refluxed for 12 h in benzene (5 ml) when g.l.c.

showed only one major component. The solvent was removed at 14 mmHg and the residue was purified by column chromatography over silica, eluting with petrol and ether (10:1) to give *7-chloromethyl-7-methyl-1,2-dichloro-4-methylcyclohepta-1,4-diene* (0.5g, 71 %) which was further purified by preparative g.l.c. (Found M^+: 238.0097. Calculated for $C_{10}H_{13}Cl_3$: 238.0083) which showed δ_H (200 MHz) 5.59 (1H, tt, J 0.87, 8 Hz), 3.8 (1H, d, J 10.8 Hz), 3.46 (1H, d, 10.8 Hz), 3.43 (1H, d, J 18.7 Hz), 3.17 (1H, d, J 17.6 Hz), 2.75 (1H, dd, J 6.67, 14 Hz), 2.11 (1H, dd, J 7.3, 14 Hz), 1.8 (3H, s), 1.26 (3H, s); ν_{max} 2971, 2934, 1609, 1454, 1375, 975, 803, 734 cm^{-1}; m/z 238 (M^+), 203 (M^+–Cl), 189 (M^+–CH_2Cl).

EXPERIMENT (56).

<u>7-Methoxymethyl-7-methyl-1,2-dichloro-4-methylcyclohepta-1,4-diene (239, X= OMe).</u>

Methyl lithium (3.4 ml) was added over 1 m to a stirred solution of 1,1,2,2-tetrachloro-3-chloromethyl-3-methylcyclopropane (1.0 g) in ether (10 ml) at 0 °C. After 30 m the products were quenched with water at -40 °C, decanted from the ice and allowed to stand for 12h at 20 °C with isoprene (3ml). The solvent and excess isoprene were removed at 14 mmHg to give an oil (0.71 g) which showed a complex n.m.r. spectrum. The product was refluxed for 12 h in benzene (5 ml) when g.l.c. showed only one major component. The solvent was removed at 14 mmHg and the residue was purified by column chromatography over silica, eluting with petrol and ether (10:1) to give *7-methoxymethyl-7-methyl-1,2-dichloro-4-methyl-cyclohepta-1,4-diene* (0.65 g, 66 %) which was further purified by preparative g.l.c. (Found M^+: 234.0568. Calculated for $C_{11}H_{16}Cl_2O$: 234.0578) which showed δ_H (200 MHz) 5.57 (1H, tt, J 1.5, 7.4 Hz), 3.56 (1H, d, J 9 Hz), 3.5 (1H, d, 17.4 Hz), 3.34 (3H, s), 3.18 (1H, d, J 9 Hz), 3.05 (1H, d, J 17.4 Hz), 2.75 (1H, dd, J 6.6, 14 Hz), 2.05 (1H, dd, J 7.58, 14 Hz), 1.8 (3H, s), 1.13 (3H, s); ν_{max} 2975, 2929, 1610, 1450, 1110, 951, 804, 767, 677 cm^{-1}; m/z 234 (M^+), 199 (M^+–Cl), 189 (M^+–C_2H_5O).

EXPERIMENT (57).

Reaction of 1,1–dibromo–2,2–dichloro–3–methoxymethyl–3–methylcyclopropane (171, R= OMe) with methyl lithium.

(a) In the presence of 2,3–dimethylbut–2–ene: Methyl lithium (4 ml, 2.6 M) was added over 3 m to a stirred solution of the dibromodichloride (0.5 g) in ether (20 ml) in the presence of 2,3–dimethylbut–2–ene (2 g) at –78 °C. The products were allowed to reach room temperature and after 1.5 h were quenched with water (5 ml). The aqueous layer was extracted with ether (2 x 10 ml) and the combined organic layers were washed with water (5 ml), dried and the solvent was removed at 14 mmHg. Bulb–to–bulb distillation of the residue gave 1,1–dichlorotetramethylcyclo–propane (250), b.p. 20 °C at 0.15 mmHg (30 m, 11.7%), which was identical by n.m.r, i.r, and g.l.c to an authentic sample, followed by *(2–methyl–3–methoxyprop–1–enylidene)– 2,2,3,3–tetramethylcyclopropane* (248, R= Me) b.p. 50–55 °C and 0.2–0.3 mmHg (0.13 g, 48%) (Found: M^+, 180.1427. Calculated for $C_{12}H_{20}O$: 180.1514) which showed δ_H 3.84 (2H, s), 3.23 (3H, s), 1.72 (3H, s), 1.17 (12H, s); δ_C 184.7, 97.6, 96.6, 75.9, 57.1, 28.5, 21.4, 16.9; ν_{max} 2004 cm^{-1}; m/z 180 (M^+), 165 ($M^+–CH_3$).

(b) In the presence of 2–methylpropene: The above reaction was repeated using 2–methylpropene (5 ml) in place of 2,3–dimethylbut–2–ene. Work up as before followed by removal of the solvent at 760 mmHg gave a residue which was distilled at 14 mmHg. The first fraction contained *1,1–dichloro–2,2–dimethylcyclopropane* (251) (8.5%) which was identical by n.m.r and g.l.c to an authentic sample. The second fraction was *(2–methyl–3–methoxyprop–1–enylidene)–2,2–dimethylcyclopropane*, (0.1 g, 43%), b.p. 0.4–0.3 mmHg at 40 °C (Found M^+: 152.1269. Calculated for $C_{10}H_{16}O$: 152.1241) which showed δ_H 3.93 (2H, s), 3.3 (3H, s), 1.78 (3H, s), 1.38 (2H, s), 1.26 (6H, s); δ_C 187, 98, 88, 75.6, 57.3, 29.8, 24.6, 22.4, 22, 16.9; ν_{max} 2100

cm^{-1}; m/z 152 (M^+), 137 (M^+-CH_3).

EXPERIMENT (58).

Reaction of 1,1-dibromo-2,2-dichloro-3-isopropoxymethyl-3-methylcyclopropane (171, R= Pr^i) with methyl lithium.

(a) In the presence of 2,3-dimethylbut-2-ene: Methyl lithium (4 ml, 1.6 M) was added over 2 m to a rapidly stirred solution of 1,1-dibromo-2,2-dichloro-3-isopropoxymethyl-3-methylcyclopropane (0.5 g) in ether (15 ml) in the presence of 2,3-dimethylbut-2-ene (2 g) at -78 °C. The products were allowed to reach 20 °C and after 1 h were quenched with water (5 ml). Work up as before gave *(2-methyl-3-isopropoxyprop-1-enylidene)-2,2,3,3-tetramethylcyclopropane* (248, R= Pr^i) b.p. 50-55 °C at 0.3 - 0.4 mmHg (0.127 g, 43%) as the major product (Found: M^+, 208.1811. Calculated for $C_{14}H_{24}O$: 208.1827) which showed δ_H 3.95 (2H, s), 3.65 (1H, septet, J 6 Hz), 1.75 (3H, s), 1.2 (12H, s), 1.5 (6H, d, J 6 Hz); ν_{max} 2005m cm^{-1}; m/z 208 (M^+), 165 ($M^+-C_3H_7$).

(b) In the presence of 2-methylpropene: The above reaction was repeated using 2-methylpropene (5 ml) in place of 2,3-dimethylbut-2-ene. Work up as before and bulb-to-bulb distillation at 0.3-0.4 mmHg 40 °C gave *(2-methyl-3-isopropoxy-prop-1-enylidene)-2,2-dimethylcyclopropane* (249, R= Pr^i) (0.1 g, 39%) (Found: M^+, 180.1519. Calculated for $C_{12}H_{20}O$: 180.1514) which showed δ_H 3.95 (2H, s), 3.65 (1H, septet, J 6 Hz), 1.78 (3H, s), 1.35 (2H, s), 1.23 (6H, s), 1.17 (6H, d, J 6 Hz); ν_{max} 2013 cm^{-1}; 180 (M^+), 165 (M^+-CH_3), 137 ($M^+-C_3H_7$).

G.C.-M.S. of the crude product showed a number of minor components, one of which was 1,1-dichloro-2,2-dimethylcyclopropane.

EXPERIMENT (59).

3-Bromo-2-chloro-1,3-dimethylcyclobutene (259).

An excess of methyl lithium (4 ml, 1.6 M) was added over 1 m to a stirred solution of 1,1-dibromo-2,2-dichloro-3-chloromethyl-3-methylcyclopropane (0.5 g) in ether (15 ml) in the presence of 2,3-dimethylbut-2-ene (2.0 g) at -78 °C. After 3 m the products were allowed to reach 20 °C and after 30 m were quenched with water (5 ml). The aqueous layer was washed with ether (3 x 15 ml) and the combined organic layers were dried and evaporated at 14 mmHg. The residue was flash distilled to give *3-bromo-2-chloro-1,3-dimethylcyclobutene* (0.17 g, 59 %), b.p. 20 °C at 0.003 mmHg (Found: C, 36.76; H, 3.9. Calculated for C_6H_8BrCl: C, 36.86; H, 4.12) which showed δ_H 3.02 (1H, d, J 10.6 Hz), 2.71 (1H, d, J 10.6 Hz), 1.87 (3H, s), 1.76 (3H, s); δ_C 138s, 129s, 62s, 50t, 28q, 13q; ν_{max} 2967, 2919, 1669, 1057, 812, 664 cm^{-1}; m/z 115 (M^+-Br).

Preparative g.l.c. of the above product through a copper 6 m SE30 column at 40 °C with the inlet port at 150 °C caused the elimination of hydrogen bromide and gave *2-chloro-1-methyl-3-methylenecyclobutene* (270) (Found M^+: 114.0234. Calculated for C_6H_7Cl: 114.0236) which showed δ_H 4.68 (1H, br.s), 4.45 (1H, br.s), 2.78 (2H, br.s), 1.92 (3H, s); ν_{max} 2914, 1621, 1260, 862, 1074 cm^{-1}; m/z 114 (M^+), 79 (M^+-Cl). This compound decomposed rapidly even when stored at -20 °C.

EXPERIMENT (60).

Reaction of 1-chloro-1-(1,3-dichloro-2-methyl-2-prop-1-enyl)-2,2,3,3-tetramethylcyclopropane (227_a)with potassium t-butoxide.

(a) Potassium t-butoxide (2.07 g, 18.5 mmole) was added over 5 min. to a stirred solution of 1-chloro-1-(1,3-dichloro-2-methylprop-1-enyl)-2,2,3,3-tetramethylcyclopropane (1.35 g, 5.28 mmole) in dry ether (30 ml) at 0 °C. After 15 m at room temperature, the solution was diluted with water (20 ml) and petrol (30 ml). The

organic layer was washed several times with water and dried. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by flash distillation at 35 °C and 0.4 mmHg to give *1-(1,3-dichloro-2-methylprop-2-en-1-ylidene)-2,2,3,3-tetramethylcyclopropane* (283) (1.03 g, 89%) (Found M^+: 218.0609. Required for $C_{11}H_{16}Cl_2$: 218.0629) which showed δ_H (200 MHz): 6.6 (1H, q, J 1.2 Hz), 1.97 (3H, d, J 1.2), 1.23 (6H, s), 1.22 (6H, s); ν_{max} 3099, 2989, 2950, 2920, 2867, 1709, 1606, 1448, 1111, 926, 787 cm^{-1}; m/z 218 (M^+), 183 (M^+-Cl), 148 (M^+-Cl_2).

(b) Lithium (0.5 g) was stirred with 1-(1,3-dichloro-2-methylprop-2-en-1-ylidene)-2,2,3,3-tetramethylcyclopropane (1.25 g) in t-butanol (2.0 g) and tetrahydrofuran (10 ml). After 3 m, an exothermic reaction occurred which was controlled at a steady reflux for one hour. After 2 h at room temperature, the products were poured into ice-water (20 ml) and extracted with ether (5 x 20 ml) and then saturated-brine (20 ml). The solvent was removed carefully at 14 mmHg to give an oil; flash distillation at 0.3 mmHg gave *1-(2-methyl-1-propenyl)-2,2,3,3-tetramethylcyclopropane* (284) (0.35 g, 40%) (Found M^+: 152.1570. $C_{11}H_{20}$ requires 152.1575), which showed δ_H 4.93 (1H, br.d septet, J 7.4 Hz), 1.73 (3H, br.s), 1.66 (3H, br.s), 1.11 (6H, s), 0.93 (6H, s), 0.88 (1H, br.d, J 7.4 Hz); ν_{max} 2990, 2930, 1455, 1380 cm^{-1}; m/z 152 (M^+), 137 (M^+-CH_3).

EXPERIMENT (61).

<u>Reaction of 1-chloro-1-(1,3-dichloro-2-methyl-2-prop-1-enyl)-2,2-dimethylcyclopropane (227_b) with potassium t-butoxide.</u>

(a) Potassium t-butoxide (4.34 g, 38.4 mmole) was added over 5 m to a stirred solution of 1-chloro-1-(1,3-dichloro-2-methylprop-1-enyl)-2,2-dimethylcyclopropane (2.5 g, 11 mmole) in ether (30 ml) at 0 °C. After 15 m at room temperature, the solution was diluted with water (30 ml) and petrol (50 ml). The organic extract was

washed several times with water and dried. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by column chromatography over silica, eluting with petrol to give *E*- and *Z*-*1*-*(1,3*-*dichloro*-*2*-*methyl*-*2*-*propen*-*1*-*ylidene)*-*2,2*-*dimethylcyclopropane* (285) in ratio 1:1 (1.5 g, 74%) (Found M^+: 190.0316. Required for $C_9H_{12}Cl_2$: 190.0316) which showed δ_H (200 MHz): (1st isomer) 6.7 (1H, br.s), 2.06 (3H, d, J 1.2 Hz), 1.47 (2H, s), 1.27 (6H, s); (2nd isomer): 6.7 (1H, br.s), 2.01 (3H, d, J 1.2), 1.25 (6H, s), 1.21 (2H, s); ν_{max} 3098, 2962, 2928, 2866, 1786, 1730, 1606, 1450, 1373, 1122, 933, 786 cm^{-1}; m/z 190 (M^+), 155 (M^+–Cl).

(b) When the two isomers were allowed to stand in $CDCl_3$ at room temperature for one week, one of them changed to *1,3*-*dichloro*-*2,6*-*dimethyl*-*1,3,6*-*heptatriene* and the other isomer was unchanged. The mixture (0.91 g) in dichloromethane (5 ml) was stirred with tetracyanoethene (0.67 g) for three days at room temperature. The solvent was removed at 14 mmHg to give a thick oil which was diluted with petrol, filtered, and then evaporated at 14 mmHg to give a brown oil. This was further purified by column chromatography over silica eluting with petrol to give *1,3*-*dichloro*-*2,6*-*dimethyl*-*1,3,6*-*heptatriene* (287) (0.16 g, 35%) (Found M^+: 190.0298. Required for $C_9H_{12}Cl_2$: 190.0307) which showed δ_H (200 MHz): 6.64 (1H, br.s), 5.9 (1H, t, J 7.2 Hz), 4.75 (2H, br.d, J 8.94 Hz), 3.02 (2H, d, J 7.2 Hz), 2.03 (3H, narrow, d, J 1.2 Hz), 1.7 (3H, s); ν_{max} 2980, 2940, 1720, 1620, 1450, 1380, 900, 810, 730 cm^{-1}; m/z 190 (M^+), 155 (M^+–Cl).

EXPERIMENT (62).

<u>Reaction of E- and Z-1-(1,3-dichloro-2-methyl-2-propen-1-ylidene)-2,2-dimethylcyclopropane (285) with tetracyanoethene</u>

The mixture of *E*- and *Z*-1-(1,3-dichloro-2-methyl-2-propen-1-ylidene)-2,2-dimethylcyclopropane (0.16 g, 0.84 mmole) in dichloromethane (5 ml) was stirred with

tetracyanoethene (0.113g, 0.88 mmole) for 72 h at room temperature. Removal of the solvent at 14 mmHg gave a solid which was recrystallised from ether and petrol to give *E- and Z-4,6-dichloro-5-methyl-7,7,8,8-tetracyano-1,1-dimethylspiro-[2.5]-oct-2-ene* (286) in the ratio (1:1) (0.094g, 35%) (Found M^+: 318.0418. Required for $C_{15}H_{12}N_4Cl_2$: 318.0439) which showed δ_H (200 MHz): (1st isomer) 5.15 (1H, d, J 1 Hz), 2.22 (1H, d, J 7 Hz), 2.21 (3H, d, J 1 Hz), 1.83 (3H, s), 1.75 (3H, s), 1.5 (1H, d, J 7 Hz); (2nd isomer) 4.96 (1H, d, J 0.93 Hz), 2.16 (3H, d, J 0.93 Hz), 2.07 (1H, d, J 7.25 Hz), 1.66 (1H, d, J 7.25 Hz), 1.4 (3H, s), 1.3 (3H, s); ν_{max} (KBr) 3094, 3038, 2984, 2937, 2250, 1619, 1465, 1382, 1232, 1110, 971, 761 cm^{-1}; m/z 318 (M^+), 303 (M^+-CH_3), 283 (M^+-Cl).

EXPERIMENT (63).

Reaction of 1-chloro-1-(1-chloro-2-methylprop-1-enyl)-2,2-dimethylcyclopropane (298) with potassium t-butoxide.

Potassium t-butoxide (4.0 g) was added over 5 m. to a stirred solution of 1-chloro-1-(1-chloro-2-methylprop-1-enyl)-2,2-dimethylcyclopropane (2.0 g) in dry ether (30 ml) at 0 ^{0}C. After 15 m. at 20 ^{0}C, work up as above and flash distillation at room temperature and 0.3 mmHg gave *E- & Z-1-(1-chloro-2-methylprop-2-en-1-ylidene)-2,2-dimethylcyclopropane* (299) (1.3 g, 79.5%) (m/z 157 (M^+H), 156 (M^+), 141 (M^+-CH_3)) which showed δ_H (1st isomer) 5.49 (1H, m), 5.07 (1H, br.d), 2.0 (3H, dd, J 1.37, 7.3 Hz), 1.27 (6H, s), 1.19 (2H, s); (2nd isomer) 5.49 (1H, m), 5.07 (1H, br.d), 1.87 (3H, d, J 1.7 Hz), 1.25 (6H, s), 1.08 (2H, s); ν_{max} 2955, 2868, 1622, 1452, 893, 831, 731 cm^{-1}.

EXPERIMENT (64).

Reaction of 1-chloro-1-(1,3-dichloro-2-methylprop-1-enyl)-Z-2,3-dimethylcyclopropane (227_c) with potassium-t-butoxide.

Potassium t-butoxide (1.7 g) was added over 2 min. to a stirred solution of 1-chloro-1-(1,3-dichloro-2-methylprop-1-enyl)-2,3-dimethylcyclopropane (1.0 g, 4.3 mmole) in dry ether (30 ml) at 0 °C. After 10 m at room temperature the solution was diluted with water (20 ml) and the solvent was removed at 0 °C and 14 mmHg to give *1-(1,3-dichloro-2-methylprop-2-en-1-ylidene)-Z-2,3-dimethylcyclopropane* (300) (0.67 g, 81%) (Found M^+: 190.0292. Required for $C_9H_{12}Cl_2$: 190.0316) which showed δ_H ($CDCl_3$) 6.68 (1H, br.s), 2.04 (3H, narrow doublet), 1.98 (1H, m), 1.74 (1H, m), 1.17 (3H, d, J 7.21 Hz), 1.13 (3H, d, J 7.21 Hz); ν_{max} 2976, 2931, 1731, 1665, 1611, 1447, 1379, 1193, 797 cm^{-1}; m/z 190 (M^+), 155 (M^+-Cl).

EXPERIMENT (65).

Reaction of 1-chloro-1-(1,3-dichloro-2-methylprop-1-enyl)cyclopropane (227_e) with potassium t-butoxide.

(a) Potassium t-butoxide (0.41 g, 3.68 mmole) was added over 2 m to a stirred solution of 1-chloro-1-(1,3-dichloro-2-methylprop-1-enyl)cyclopropane (0.21g, 1.05 mmole) in dry ether (30 ml) at 0 °C. After 15 m at room temperature, the products were diluted with water (20 ml) and petrol (30 ml). The organic layer was washed several times with water, dried, and the solvent was removed at 14 mmHg and 0 °C, to give *1-(1,3-dichloro-2-methyl-2-propen-1-ylidene)cyclopropane* (301) (0.12g, 70%), as a clear yellow oil which was pure by n.m.r. δ_H ($CDCl_3$): 6.45 (1H, br, s), 2.2 (3H, s), 1.5 (4H, m).

(b) Crude 1-(1,3-dichloro-2-methyl-2-propen-1-ylidene)cyclopropane (0.1 g) in dichloromethane (5 ml) was stirred with tetracyanoethene (0.08 g) for 72 h at room

temperature. Removal of the solvent at 14 mmHg gave a brown oil; this was further purified by column chromatography, eluting with petrol to give *4,6-dichloro-5-methyl-7,7,8,8-tetracyanospiro[2.5]oct-2-ene* (302) (37 mg, 21%). (Found M^+: 290.0134. Required for $C_{13}H_8Cl_2N_4$: 290.0126) which showed δ_H 5.19 (1H, narrow d, J 1.05 Hz), 2.4 (3H, narrow d, J 1.04 Hz), 1.9 (1H, m), 1.76 (2H, m), 4.2 (1H, m); ν_{max} 2940, 2262, 1635, 1430, 1270, 980, 910, 730 cm^{-1}; m/z 290 (M^+), 255 (M^+–Cl).

EXPERIMENT (66).

<u>Reaction of 3-(1-chloro-2,2,3,3-tetramethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether (229_a) with potassium t-butoxide.</u>

Potassium t-butoxide (2.34 g, 20 mmole) was added over 5 m to a stirred solution of 3-(1-chloro-2,2,3,3-tetramethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether (1.5 g, 6 mmole) in dry ether (30 ml) at 0 °C. After 15 m at room temperature, the solution was diluted with water (30 ml) and petrol (30 ml). The organic layer was washed several times with water and dried. Removal of the solvent at 14 mmHg gave an oil which was one spot by t.l.c.; this was further purified by flash distillation at 30 °C and 0.5 mmHg to give *1-(1-chloro-2-methoxymethylprop-2-en-1-ylidene)-2,2,3,3-tetramethylcyclopropane* (303) (1.1 g, 85.8%) (Found M^+: 214.1130. Required for $C_{12}H_{19}OCl$: 214.1124) which showed δ_H (60 MHz): 5.58 (1H, br.s), 5.28 (1H, br.s), 3.8 (2H, s), 3.3 (3H, s), 1.2 (12H, s); ν_{max} 2988, 2922, 2870, 1714, 1451, 1373, 1111, 909, 734 cm^{-1}; m/z 214 (M^+), 199 (M^+–CH_3), 179 (M^+–Cl).

EXPERIMENT (67).

<u>Reaction of 1-(1,3-dichloro-2-methyl-2-propen-1-ylidene)-2,2,3,3-tetramethylcyclopropane (283) with m-chloroperbenzoic acid.</u>

A solution of m-chloroperbenzoic acid (1.0 g) in dichloromethane (10 ml) was

added to 1-(1,3-dichloro-2-methyl-2-propen-1-ylidene)-2,2,3,3-tetramethylcyclopropane (1.068 g) in dichloromethane (10 ml) at 0 °C. The mixture was stirred at room temperature for 18 h when t.l.c. showed no starting material was left. The products were washed with sodium sulphite then extracted with ether (3 x 10 ml), washed with sodium bicarbonate, dried, and the solvent was removed at 14 mmHg to give a yellow oil; this was further purified by column chromatography over silica, eluting with petrol and ether (10:1) to give *2-chloro-2-(2-chloro-1-methylethenyl)-3,3,4,4-tetramethylcyclobutanone* (304) (0.719 g, 67%) (m/z 219 (M^+-CH_3), 199 (M^+-Cl) which showed δ_H 6.34 (1H, narrow q, J 1.4 Hz), 1.85 (3H, narrow d, J 1.4 Hz), 1.36 (6H, s), 1.16 (3H, s), 1.12 (3H, s); δ_C: 209.7, 134.7, 119.4, 85, 61.2, 44.5, 23.1, 22.36, 21.7, 19.4, 14.5.; ν_{max} 3096, 2971, 2928, 1782, 1622, 1452, 1378, 1252, 1001, 783 cm^{-1}.

EXPERIMENT (68).

<u>Reaction of 2-chloro-2-(1,3-dichloro-2-methyl-2-prop-1-enyl)-1,1-dimethylcyclopropane (227_b) with 10% KOH.</u>

Potassium hydroxide (1.0 g) in water (10 ml) was refluxed with 2-chloro-2-(1,3-dichloro-2-methyl-2-prop-1-enyl)-1,1-dimethylcyclopropane (0.5 g) for 22 h, when t.l.c. showed no starting material remained. The products were treated with water (10 ml) and extracted with ether (3 x 5 ml). The organic layer was dried and the solvent was removed at 14 mmHg to give an oil which was one spot by t.l.c.; this was further purified by flash distillation to give *2,2-dimethyl-1-cyclopropyl ethyl ketone* (305) (0.17 g, 61.38%) (Found M^+: 126.1055. Required for $C_8H_{14}O$: 126.1045) which showed δ_H (200 MHz): 2.5 (2H, q, J 7.3 Hz), 1.83 (1H, dd, J 5.6, 7.53 Hz), 1.23 (1H, dd, J 3.9, 5.6 Hz), 1.19 (3H, s), 1.07 (3H, t, J 7.3 Hz), 1.06 (3H, s), 0.8 (1H, dd, J 3.9 7.6 Hz); ν_{max} 2973, 2947, 2876, 1697, 1395, 1131, 1026, 918, 733 cm^{-1}; m/z 126 (M^+), 111 (M^+-CH_3), 97 ($M^+-C_2H_5$).

EXPERIMENT (69).

Reaction of methyl 2-chloro-2-(1,3-dichloro-2-methyl-2-prop-1-enyl)-1-methylcyclopropane carboxylate (230_b) with 10% KOH.

Potassium hydroxide (1.0 g) in water (10 ml) was refluxed with methyl 2-chloro-2-(1,3-dichloro-2-methylprop-1-enyl)-1-methylcyclopropane carboxylate (0.5 g) for 3 h, when t.l.c. showed no starting remained. The products were treated with water (10 ml) and extracted with ether (2 x 10 ml). The organic layer was dried, and the solvent was removed at 14 mmHg and no product was obtained. The aqueous layer was treated with 2M hydrochloric acid and extracted with ether (4 x 10 ml), dried, and the solvent was removed at 14 mmHg. The remaining thick yellow oil (0.26 g, 90.3%) was one peak by g.l.c.; column chromatography over silica eluting with ether gave *2-propan-1-oyl-1-methylcyclopropanecarboxylic acid* (306) (Found M^+: 156.0775. Required for $C_8H_{12}O_3$: 156.0786) which showed δ_H (200 MHz): 2.68 (1H, dd, J 8.35, 6.7 Hz), 2.6 (2H, q, J 7.2 Hz), 1.56 (1H, dd, J 4.0, 8.35 Hz), 1.5 (1H, dd, J 4.0, 6.7 Hz), 1.27 (3H, s), 1.09 (3H, t, 7.2 Hz); δ_C 206.57, 180.35, 38.34, 34.5, 29.0, 21.47, 12.28, 8.0; ν_{max} 3086 (v.br), 2978, 2679, 1694, 1385, 1300, 1198, 1124, 887 cm^{-1}; m/z 156 (M^+), 127 ($M^+-C_2H_5$), 99 ($M^+-C_3H_5O$).

EXPERIMENT (70)

General method for relative reactivity experiments.

The competing pair of alkenes A and B (approximately 0.0105 mol of each), were added or condensed in a pre-weighed, thick-walled glass tube (10 ml) cooled in acetone/dry-ice. The tube was weighed after adding each alkene. A freshly prepared solution of 1,2-dichloro-3-methyl-3-methoxymethylcyclopropene (0.3 g) in ether (10 ml) was added to the cooled alkene mixture and the tube sealed with a screw-top.

After stirring at room temperature for 12 h, the tube was again cooled in acetone/CO_2 before opening. Removal of the excess alkenes and solvent at 14 mmHg gave the cyclopropane mixture. The product compostion was measured directly by g.l.c.

EXPERIMENT (71)

Competition experiment between two arylcyclopropenes.

Methyl lithium (1.1 eq. 1.5M) was added to a stirred solution of an equimolar mixture of 1,1,2,2-tetrachloro-3-methyl-3-benzylcyclopropane and 1,1,2,2-tetrachloro-3-methyl-3-(p-methoxy or p-methyl or p-trifluoromethylbenzyl)cyclopropane (0.25 g) in ether (5 ml) at 0 ^{0}C. The reaction mixture was stirred at this temperature for 20 m. before quenching with water (3 ml), work up as before gave a mixture of cyclopropene. 2,3-Dimethylbut-2-ene (5 eq.) in $CDCl_3$ (0.8 ml) was added to the cyclopropenes, the product composition was measured directly by 300 MHz.

EXPERIMENT (72)

2-(2,3,3-Trimethylcyclopropen-1-yl)ethan-1-ol (344_a).

Methyl lithium (31.2 ml, 1.25 M, 2.5 mol.equiv.) was added over 5 m to a stirred solution of 1,2,2-tribromo-1,3,3-trimethylcyclopropane (5.0 g, 0.015 mole) in ether (80 ml) at -40 - -50 ^{o}C. The mixture was allowed to reach ambient temperature and after 15 m was cooled again to -50 ^{o}C. Ethylene oxide (6 ml) was added and the mixture was stirred for 15 m at that temperature and then allowed to reach ambient temperature and stirred for a further 3 h. Water (10 ml) was added and the organic layer was separated; the aqueous layer was washed with ether (3 x 30 ml) and the combined organic layers were washed with water (2 x 10 ml), dried over $MgSO_4$, and the solvent was removed at 14 mmHg. The residue was flash distilled at 35 ^{o}C and 0.4 mmHg to give *2-(2,3,3-trimethylcyclopropen-1-yl)ethan-1-ol* (1.6 g, 80

%) (Found M^+: 126.1055. $C_8H_{14}O$ requires: 126.1045) which showed δ_H 3.74 (2 H, t, J 6.0 Hz), 3.42 (2H, m), 1.95 (3H, t, J 6.0 Hz), 1.05 (6H, s); ν_{max} 3342, 2928, 2853, 1047 cm $^{-1}$; m/z 126 (M^+), 111 (M^+–CH_3).

EXPERIMENT (73)

1–(2,3,3–Trimethylcyclopropen–1–yl)propan–2–ol (344_b).

(a) The above reaction was repeated using methyl lithium (26 ml) and the tribromide (5.0 g) but using 1,2–epoxypropane (1.1 ml) in place of ethylene oxide and stirring for 12 h at ambient temperature before work up. The residue obtained after removal of the solvent was subjected to column chromatography, eluting with 10:1 petrol and ether to give *1–(2,3,3–trimethylcyclopropen–1–yl)propan–2–ol* (1.14 g, 50 %) (Found M^+: 140.1189. $C_9H_{16}O$ requires: 140.1201) which showed δ_H 3.80 (1H, br.sextet, J ca. 6 Hz), 3.3 (1H, br.s), 2.4 (1H, ddq, J 14.2, 8.8, 1.5 Hz), 2.33 (1H, ddq, J 14.2, 8.8, 1.5 Hz), 1.79 (3H, t, J 1.5 Hz), 1.08 (3H, d, J 6.2 Hz), 0.91 (6H, s); ν_{max} 3361, 2957, 2928, 2854, 1440, 1364, 1175, 1121, 944 cm^{-1}; m/z 140 (M^+), 125 (M^+–CH_3).

(b) 1–(2,3,3–Trimethylcyclopropen–1–yl)propane–2–ol was refluxed for 6 h with triethylamine (50 mg) and (S)–(–)–phenylethyl isocyanate (0.11 g). After removal of the solvent at 14 mmHg, the residue was chromatographed over silica eluting with petrol and ether (10:2) to give the urethane as a mixture of diastereoisomers (Found M^+: 287.1884. $C_{18}H_{25}N_2O$ required: 287.1885) which showed δ_H (First isomer) 7.3 (5H, br.s), 4.96 (1H, q, J 6.3 Hz), 4.84 (2H, br.m), 2.57 (2H, m), 1.89 (3H, br.s), 1.47 (3H, d, J 6.7 Hz), 1.33 (3H, d, J 6.3 Hz), 1.02 (6H, s); (second isomer) 7.31 (5H, br.s), 4.97 (1H, q, J 6.3 Hz), 4.84 (2H, br.m), 2.57 (2H, m), 1.93 (3H, br.s), 1.47 (3H, d, J 6.7 Hz), 1.33 (3H, d, J 6.3 Hz), 1.05 (6H, s); m/z 287 (M^+), 272 (M^+–CH_3).

EXPERIMENT (74)

(S)-(+)-1-(2,3,3-Trimethylcyclopropen-1-yl)propan-2-ol (344_b).

The above reaction was repeated using (S)-(-)-1,2-epoxypropane (1.04 g). Work up as above gave *(S)-(+)-1-(2,3,3-trimethylcyclopropen-1-yl)propan-2-ol* (1.1 g, 48 %) (Found M^+: 140.1189), $[\alpha]_D^{22}$ + 15 °. The alcohol was converted into the urethane by reaction with (S)-(-)-1-phenylethyl isocyanate as above (Found M^+: 287.1884. $C_{18}H_{25}N_2O$ requires: 287.1885); the ^1H n.m.r. showed only the signals corresponding to the second isomer obtained from the racemic alcohol.

EXPERIMENT (75)

2-(3,3-Dimethylcyclopropen-1-yl)ethan-1-ol (344_c).

The above reaction was repeated using methyl lithium (32 ml, 1.5 M), 1-chloro-2,2-dibromo-3,3-dimethylcyclopropane (5.0 g) and ethylene oxide (6 ml), stirring for 3 h at ambient temperature before quenching. Careful removal of the solvent at 14 mmHg and column chromatography eluting with 10:1 petrol and ether gave *2-(3,3-dimethylcyclopropen-1-yl)ethan-1-ol* (0.9 g, 41 %) (Found M^+: 112.0883. $C_7H_{12}O$ requires: 112.0888) which showed δ_H 6.85 (1H, br.s), 3.72 (2H, t, J 6 Hz), 3.1 (1H, br.s), 2.68 (2H, br.dt, J 6.5 Hz), 1.12 (6H, s); ν_{max} 3343, 2931, 1760, 1451, 1049 cm^{-1}; m/z 112 (M^+), 111 (M^+-H), 97 (M^+-CH_3), 81 (M^+-CH_2OH).

EXPERIMENT (76)

1-(3,3-Dimethylcyclopropen-1-yl)propan-2-ol (344_d).

The above reaction was repeated except that 1,2-epoxypropane (6 ml) was added in place of ethylene oxide. Work up and chromatography as above led to *1-(3,3-dimethylcyclopropen-1-yl)propan-2-ol* (0.8 g, 33 %) (Found M^+: 126.1052.

$C_8H_{14}O$ requires: 126.1045) which showed δ_H 6.85 (1H, br.s), 4.03 (1H, sextet, J 6 Hz), 2.72 (2H, d, J 6 Hz), 2.35 (1H, br.s), 1.35 (3H, d, J 6 Hz), 1.21 (3H, s), 1.15 (3H, s); ν_{max} 3366, 2965, 2931, 1758, 1453, 1366, 735 cm^{-1}; m/z 126 (M^+), 111 (M^+-CH_3).

EXPERIMENT (77)

(R)-(-)-1-(3,3-Dimethylcyclopropen-1-yl)propan-2-ol (344_d).

The above reaction was repeated using (R)-(+)-1,2-epoxypropane (1.2 g), giving (R)-(-)-*1-(3,3-Dimethylcyclopropen-1-yl)propan-2-ol* (29 %) (Found M^+: 126.1052), m/z 126 (M^+), 111 (M^+-CH_3).

EXPERIMENT (78)

2-(2,3-Dimethylcyclopropen-1-yl)ethan-1-ol (344_e).

The above reaction was repeated using 1,1,3-tribromo-2,3-dimethylcyclopropane (5.0 g) and adding ethylene oxide (5 ml) as above, stirring for 4 h at ambient temperature before work up. Column chromatography, eluting with 10:2 petrol and ether gave *2-(2,3-dimethylcyclopropen-1-yl)ethan-1-ol* (1.05 g, 58 %) (Found M^+: 112.0882. $C_7H_{12}O$ requires: 112.0888) which showed δ_H 3.75 (2H, t, J 6 Hz), 2.6 (2H, br.t, J 6 Hz), 2.2 (1H, br.s), 2.0 (3H, narrow m), 1.3 (1H, m), 1.0 (3H, d, J 5.0 Hz); ν_{max} 3371, 2941, 2891, 1718, 1661, 1439, 1370, 1049 cm^{-1}; m/z 112 (M^+), 97 (M^+-CH_3).

EXPERIMENT (79)

1-(2,3-Dimethylcyclopropen-1-yl)propan-2-ol (344_f).

The above reaction was repeated but 1,2-epoxypropane (6 ml) was added in place

of ethylene oxide, and the products were stirred for 20 h at ambient temperature before work up. Column chromatography as above gave *1-(2,3-dimethyl-cyclopropen-1-yl)propane-2-ol* as a mixture of diastereoisomers in ratio 1:1 (0.84 g, 41%) which was a single spot on t.l.c. (Found M^+: 126.1050. $C_8H_{14}O$ requires 126.1045) which showed δ_H (first isomer) 4.01 (1H, sextet, J 6.1 Hz), 2.5 (2H, m), 2.06 (1H, br.s), 1.98 (3H, t, J 1.4 Hz), 1.3 (1H, q, J 4.5 Hz), 1.23 (3H, d, J 6.2 Hz), 0.96 (3H, d, J 4.5 Hz); (second isomer) 4.01 (1H, sextet, J 6.1 Hz), 2.5 (2H, m), 2.06 (1H, br.s), 1.98 (3H, t, J 1.4 Hz), 1.3 (1H, q, J 4.5 Hz), 1.22 (3H, d, J 6.2 Hz), 0.95 (3H, d, J, 4.5 Hz); ν_{max} 3410, 2969, 2933, 1713, 1375, 1116, 1076, 733 cm^{-1}; m/z 126 (M^+), 111 (M^+-CH_3).

EXPERIMENT (80)

<u>2-(3,3-Dimethyl-2-trimethylsilylcyclopropen-1-yl)ethan-1-ol (346_a).</u>

Methyl lithium (31 ml, 1.3 mol.equiv.) was added to a stirred solution of 1-trimethylsilyl-3,3-dimethylcyclopropene (5.0 g, 0.0357 mol.) and di-isopropylamine (6 ml) in ether (30 ml) at -78 °C. After 5 m, the products were allowed to reach ambient temperature and then cooled again to -50 °C. Ethylene oxide (6 ml) was added rapidly at that temperature. After 30 m, the temperature was allowed to increase to ambient and after 16 h water (20 ml) was added. The aqueous layer was washed with ether (2 x 30 ml) and the combined organic layers were washed with water (30 ml), 0.5 M hydrochloric acid (30 ml), saturated aq. sodium bicarbonate (30 ml) and brine (30 ml) and dried. Removal of the solvent at 14 mmHg gave a brown oil which was purified by column chromatography eluting with 10:2 petrol and ether to give *2-(3,3-dimethyl-2-trimethylsilylcyclopropen-1-yl)ethan-1-ol* (2.8 g, 42 %) (Found M^+: 184.1286. $C_{10}H_{20}OSi$ requires: 184.1283) which showed δ_H 0.0 (9H, s), 0.95 (6H, s), 2.55 (2H, t, J 6.5 Hz), 3.6 (2H, t, J 6.5 Hz); ν_{max} 3339, 2957, 1780, 1249, 841 cm^{-1}; m/z 184 (M^+), 169 (M^+-CH_3).

EXPERIMENT (81)

(–)–1–(3,3–Dimethyl–2–trimethylsilylcyclopropen–1–yl)propan–2–ol (346_b).

The above reaction was repeated using methyl lithium (15.5 ml), cyclopropene (2.5 g) and di–isopropylamine (3 ml) and adding (R)–(+)–epoxypropane (1.3 ml). Column chromatography eluting with 10:2 petrol and ether gave *(–)–1–(3,3–dimethyl–2–trimethylsilylcyclopropen–1–yl)propan–2–ol* (1.2 g, 34 %) (Found M^+: 198.1430. $C_{11}H_{22}OSi$ requires 198.1440) which showed δ_H 4.0 (1H, sextet, J 6.2 Hz), 2.65 (2H, d, J 6.2 Hz), 1.25 (3H, d, J 6.2 Hz), 1.1 (3H, s), 1.09 (3H, s), 0.13 (9H, s); ν_{max} 3342, 2958, 2925, 1780, 1249, 1123, 840 cm^{-1}; m/z 198 (M^+), 183 ($M^+–CH_3$); $[\alpha]_D^{22}$ –14.85 °.

EXPERIMENT (82)

2–(2–(dimethylethyl)cyclopropen–1–yl)ethan–1–ol (345_a).

Methyl lithium (28.7 ml, 1.5 M) was added as above to 2–t–butyl–2–chloro–1,1–dibromocyclopropane (5.0 g) in ether and after treatment as above, ethylene oxide (6 ml) was added. After 3 h at ambient temperature the products were worked up as before to give a residue which was purified by distillation giving *2–(2–(dimethylethyl)–cyclopropen–1–yl)ethan–1–ol* (1.9 g, 78%), b.p. 45 °C at 0.4 mmHg (Found M^+: 140.1215. $C_9H_{16}O$ requires 140.1201) which showed δ_H 3.8 (2H, t, J 6 Hz), 2.68 (2H, t, J 6 Hz), 2.02 (1H, s), 1.15 (9H, s), 0.84 (2H, s); ν_{max} 3349, 2963, 1361, 1050 cm^{-1}; m/z 140 (M^+), 125 ($M^+–CH_3$).

EXPERIMENT (83)

2–(2–(Methylethyl)cyclopropen–1–yl)ethan–1–ol (345_b).

The above reaction was repeated using methyl lithium (30.2 ml), 2-isopropyl-2-chloro-1,1-dibromocyclopropane (5.0g) and ethylene oxide (6 ml). Work up and distillation gave *2-(2-(methylethyl)cyclopropen-1-yl)ethan-1-ol* (1.75 g, 77%), b.p. 40 ^{o}C at 0.4 mmHg (Found M^{+}: 126.1042. $C_8H_{14}O$ requires 126.1045) which showed δ_H 3.78 (2H, t, J 6.7 Hz), 3.52 (1H, s), 2.69 (3H, m), 1.2 (6H, d, J 6.7 Hz), 0.85 (2H, s); ν_{max} 3344, 2963, 2867, 1464, 1050, 1010 cm $^{-1}$; m/z 126 (M^{+}), 111 ($M^{+}-CH_3$).

EXPERIMENT (84)

Reaction of 1,2,2-tribromo-1,3,3-trimethylcyclopropane (333) with methyl-lithium in the presence of 1-chloro-2,3-epoxypropane.

Methyl-lithium (26 ml, 1.5 M) was added over 5 m to a stirred solution of 1,2,2-tribromo-1,3,3-trimethylcyclopropane (5.0 g) in ether (80 ml) at -40 ^{o}C. The mixture was allowed to reach ambient temperature and after 15 m was cooled again to -50 ^{o}C, when 1-chloro-2,3-epoxypropane was added rapidly. After 12 h at 20 ^{o}C, work up as above and chromatography eluting with 10:1 petrol and ether gave two components. The first compound to be eluted was *1,3,3-trimethyl-1-cyclopropenyl-2-epoxypropane* (0.43 g, 20%) (m/z 123 ($M^{+}-CH_3$), 95 ($M^{+}-C_2H_3O$)), which showed δ_H 2.9 (1H, m), 2.5 (4H, m), 1.92 (3H, narrow t), 1.2 (6H, s); ν_{max} 2955, 2916, 2853, 1438, 1362, 1176, 846 cm^{-1}. The second compound to be eluted was *3-(1,2,2-trimethyl-1-cyclopropenyl)-1-chloro-2-hydroxypropane* (0.84 g, 31%) (Found $M^{+}-CH_3$: 159.0586. $C_8H_{12}OCl$ requires 159.0577. Found M^{+}-Cl: 139.1133. $C_9H_{15}O$ requires 139.1123), which showed δ_H (200 MHz) 4.02 (1H, m), 3.66 (1H, dd, J 11.1, 6.4 Hz), 3.56 (1H, dd, J 11.1, 3.9 Hz), 2.67 (2H, dd, J 6.4, 1.5 Hz), 1.97 (3H, t, J 1.5 Hz), 1.06 (6H, s); ν_{max} 3404, 2955, 2913, 2853, 1434, 1363, 1053, 739 cm^{-1}.

EXPERIMENT (85)

2-(2,2,3-Trimethylcyclopropen-1-yl)ethylamine (347).

Hydrozoic acid solution in benzene (16 ml, 1.1 M) was added to a stirred solution of 2-(2,3,3-trimethylcyclopropene-1-yl)ethanol (1.2 g, 10 mmol) in tetrahydrofuran (5 ml) followed by di-isopropyl azodicarboxylate (3.02 g, 15 mmol) in tetrahydrofuran (5 ml). Triphenylphosphine (7.86 g, 30 mmol) in tetrahydrofuran (30 ml) was added dropwise to the resulting mixture. The reaction was exothermic and the temperature was controlled below 30 ^{o}C. After one hour at room temperature, and 3 h at 50 ^{o}C; water (1 ml) was added and the temperature maintained at 50 ^{o}C for another 3h. Removal of the solvent at 14 mmHg gave the residue which was partitioned between dichloromethane (40 ml) and hydrochloric acid (40 ml, 1 M). The aqueous layer was extracted with dichloromethane (3 x 20 ml). The aqueous phase was adjusted to pH 12 with sodium hydroxide, extracted with ether (4 x 20 ml) and dried. The solvent was removed at 14 mmHg to give a yellow oil which was further purified by flash distillation at 28 ^{o}C and 0.4 mmHg to give *2-(2,3,3-trimethyl-cyclopropen-1-yl)ethylamine* (0.66 g, 53%) (Found M^+: 125.1195. Required for $C_8H_{15}N$: 125.1204) which showed δ_H (60 MHz): 2.8 (2H, m), 2.5 (2H, m), 1.95 (3H, br.s), 1.55 (2H, s), 1.05 (6H, s); ν_{max} 2953, 2925, 2852, 1592, 1438, 1361, 1176, 1079, 755 cm^{-1}; 125 (M^+), 110 (M^+-CH_3).

EXPERIMENT (86)

E-3-(Bromomethylene)-2,2-dimethyltetrahydrofuran (352).

Bromine (0.39 g) in dichloromethane (5 ml) was added dropwise to a stirred solution of 2-(3,3-dimethylcyclopropen-1-yl)ethanol (0.25 g) in dichloromethane (5 ml) at -40 ^{o}C. After 30 m, the mixture was allowed to reach ambient temperature and the solvent was removed at 14 mmHg. The residue was subjected to column chromatography eluting with 10:1 petrol and ether to give *E-3-(bromomethylene)-*

2,2-dimethyltetrahydrofuran (Found M^+: 190.0003. $C_7H_{11}BrO$ requires 189.9993) which showed δ_H 5.96 (1H, t, J 2.7 Hz), 3.95 (2H, t, J 7.0 Hz), 2.69 (2H, dt, J 2.7, 7.0 Hz), 1.31 (6H, s); δ_C 153.5s, 97.5d, 82.3s, 63.9t, 34.0t, 27.3q; ν_{max} 3074, 2975, 2867, 1649, 1285, 1155, 1040, 741, 712 cm^{-1}; m/z 190 (M^+), 175 (M^+-CH_3), 111 (M^+-Br). Irradiation of the signal at δ 1.31 caused an ca. 12% n.O.e. enhancement in the signal at δ 5.96.

EXPERIMENT (87)

<u>E-3-(Bromomethylene)-2,2,5-trimethyltetrahydrofuran (359).</u>

Bromine (0.41 g) in dichloromethane (5 ml) was added dropwise to a stirred solution of 1-(3,3-dimethylcyclopropen-1-yl)propan-2-ol (0.30 g) in dichloromethane (5 ml) at -50 °C. After 30 m, the reaction mixture was allowed to reach ambient temperature and then the solvent was removed at 14 mmHg. The residue was subjected to column chromatography eluting with 10:1 petrol and ether to give *E-3-(bromomethylene)-2,2,5-trimethyltetrahydrofuran* (0.32 g, 67%) (Found M^+: 204.0146. $C_8H_{13}OBr$ requires 204.0150) which showed δ_H 5.92 (1H, dd, J 2.1, 3.1 Hz), 4.16 (1H, d.pentuplet, J 9.4, 6.0 Hz), 2.82 (1H, ddd, J 2.1, 5.8, 16.8 Hz), 2.22 (1H, ddd, J 3.1, 9.4, 16.8 Hz), 1.36 (3H, s), 1.31 (3H, d, J 6 Hz), 1.28 (3H, s); ν_{max} 3074, 2974, 2929, 1649, 1457, 1382, 1282, 1166, 1108, 971 cm^{-1}; m/z 204 (M^+), 189 (M^+-CH_3), 125 (M^+-Br).

EXPERIMENT (88)

<u>(-)-E-2-(Bromomethylene)-2,2,5-trimethyltetrahydrofuran (360).</u>

Bromine (0.39 g) in dichloromethane (5 ml) was added dropwise to a stirred solution of (-)-1-(3,3-dimethylcyclopropen-1-yl)propan-2-ol (0.30 g) in dichloromethane (5 ml) at -50 °C. After 30 m, the reaction mixture was allowed to reach

ambient temperature and the solvent was removed at 14 mmHg. The residue was subjected to column chromatography eluting with 10:1 petrol and ether to give *(-)-E-2-(bromomethylene)-2,2,5-trimethyltetrahydrofuran* (0.25 g, 52 %) (Found M^+: 204.0146. $C_8H_{13}BrO$ requires 204.0150) which showed δ_H 5.92 (1H, dd, J 2.1, 3.1 Hz), 4.16 (1H, m), 2.82 (1H, ddd, J 2.1, 5.8, 16.8 Hz), 2.22 (1H, ddd, J 3.1, 9.4, 16.8 Hz), 1.36 (3H, s), 1.31 (3H, d, J 6 Hz), 1.28 (3H, s); δ_C 154.6s, 97.2d, 82.7s, 71.4d, 41.7t, 28.9q, 27.4q, 21.1q; $[\alpha]_D^{25}$ -23.63 °.

EXPERIMENT (89)

2,2-Dimethyl-E-3-(2-bromo-2-trimethylsilylmethylene)tetrahydrofuran (361).

(a) Bromine (0.48 g) in dichloromethane (5 ml) was added to a stirred solution of 2-(3,3-dimethyl-2-trimethylsilylcyclopropen-1-yl)ethanol (0.5 g) in dichloromethane (5 ml) as described above. Work up followed by column chromatography eluting with 10:1 petrol and ether gave *2,2-dimethyl-E-3-(2-bromo-2-trimethylsilylmethylene)-tetrahydrofuran* (0.38 g, 53 %) (m/z 247 (M^+-CH_3), 189 (M^+-$SiMe_3$), 183 (M^+-Br)) which showed δ_H 3.9 (2H, t, J 6 Hz), 2.95 (2H, t, J 6 Hz), 1.5 (6H, s), 0.34 (9H, s); ν_{max} 2975, 2863, 1600, 1251, 1148, 1056, 878, 843, 734 cm^{-1}. The stereochemistry was established as E- on the basis of an n.O.e. enhancement. Irradiation of the signal at δ 1.4 caused an ca. 2% n.O.e. enhancement in the signal for the trimethylsilyl group at δ 0.34. A second minor product (40 mg, 8%) was 3-(bromomethylene)-2,2-dimethyl-tetrahydrofuran, identical by n.m.r. and i.r. and g.l.c. to that obtained above.

(b) 2,2-Dimethyl-E-3-(2-bromo-2-trimethylsilylmethylene)tetrahydrofuran (50 mg) was stirred for 1h with 48% hydrogen bromide in acetic acid (2 ml) in tetrahydrofuran (2 ml), when t.l.c showed no starting material remained. The mixture was washed with saturated aq. sodium bicarbonate and extracted with ether (3 x 5 ml). Removal of the solvent from the dried organic layer at 14 mmHg gave an oil which was one peak by

g.l.c. This was collected and shown to be identical to *3-(bromomethylene)-2,2-dimethyltetrahydrofuran.*

EXPERIMENT (90)

<u>E- and Z-3-(2-bromo-2-trimethylsilylmethylene)-2,2,5-trimethyltetrahydrofuran (362).</u>

Bromine (0.41 g) in dichloromethane (5 ml) was added over 5 m to 3-(2-trimethylsilyl-3,3-dimethylcyclopropen-1-yl)propan-2-ol (0.5 g) in dichloromethane (5 ml) at -40 ^{0}C as above. After 30 m, the products were allowed to reach 20 ^{0}C, the solvent was removed at 14 mmHg and the residue was purified by column chromatography over silica eluting with petrol and ether (10:1) to give an oil (0.34 g, 49%) which was a mixture of *E-* and *Z-3-(2-bromo-2-trimethylsilyl-methylene)-2,2,5-trimethyltetrahydrofurans* in ratio (5:1) (Found M^{+}: 276.0521. $C_{11}H_{21}BrOSi$ requires 276.0545) which showed δ_H (major isomer) 4.1 (1H, m), 3.04 (1H, dd, J 4.45, 17.4 Hz), 2.43 (1H, dd, J 10.2, 17.4 Hz), 1.47 (3H, s), 1.38 (3H, s), 1.27 (3H, d, J 6.0 Hz), 0.33 (9H, s); (minor isomer) 4.1 (1H, m), 2.71 (1H, dd, J 4.8, 15.3 Hz), 2.17 (1H, dd, J 10.5, 15.4 Hz), 1.58 (3H, s), 1.5 (3H, s), 1.27 (3H, d, J 6.0 Hz), 0.25 (9H, s); ν_{max} 2973, 2932, 1600, 1382, 1249, 1162, 1116, 1056, 971, 868, 842, 763, 695 cm^{-1}; m/z 276 (M^{+}), 261 ($M^{+}-CH_3$), 203 ($M^{+}-SiMe_3$), 197 (M^{+}-Br). The major isomer was characterised as E- on the basis of n.O.e. experiment. Irradiation of the signal at δ 0.33 caused an ca. 2.44 and 1.99% enhancements in those at δ 1.47 and 1.38 respectively. Irradiation of the signals at δ 1.47 and 1.38 caused an ca. 1.43 and 1.18% enhancements in that at δ 0.33.

EXPERIMENT (91)

<u>4-Bromo-2,2,3-trimethyl-5,6-dihydro[2H]pyran (363).</u>

Bromine (0.69 g) in dichloromethane (5 ml) was added to a stirred solution of

2-(2,3,3-dimethylcyclopropen-1-yl)ethanol (0.5 g) in dichloromethane (5 ml) as described above. Work up followed by column chromatography eluting with 10:1 petrol and ether gave an oil (0.41 g, 47 %) (Found M^+: 204.0164. $C_8H_{13}BrO$ requires 204.0150) which was one peak by g.l.c., but was an ca. 5:1 mixture of *4-bromo-2,2,3-dimethyl-5,6-dihydro[2H]pyran* which showed δ_H 3.75 (2H, t, J 7 Hz), 2.55 (2H, tq, J 7, 2 Hz), 1.83 (3H, t, J 2 Hz), 1.35 (6H, s); δ_C 137.9s, 116.6s, 60.0t, 36.8t, 26.0q, 19.0q, and *3-(1-bromoethylidene)-2,2-dimethyl-tetrahydrofuran* which showed δ_H 3.85 (2H, t, J 7 Hz), 2.75 (2H, tq, J 7, 2 Hz), 2.37 (3H, t, J 2 Hz), 1.4 (6H, s); δ_C 146s, 113.1s, 81.6s, 38.9t, 26.0q (the remaining signals were presumably underneath those of the major isomer). The mixture showed ν_{max} 2976, 2930, 2869, 1656, 1276, 1115, 724 cm^{-1}; m/z 204 (M^+), 189 (M^+-CH_3), 125 (M^+-Br).

EXPERIMENT (92)

2,2,3-Trimethyl-5,6-dihydro[2H]pyran (367).

Lithium metal (150 mg) was added to a stirred solution of 4-bromo-2,2,3-trimethyl-5,6-dihydro[2H]pyran and 3-(1-bromoethylidene)-2,2-dimethyltetrahydrofuran (0.5 g) and t-butanol (1.0 g) in tetrahydrofuran (10 ml). After 5 m, an exothermic reaction ensued which was controlled by cooling so that a gentle refluxing occurred for 1 h. The products were then refluxed for a further 1 h and stirred at ambient temperature for 2 h, before being poured into ice water and extracted with ether (5 x 20 ml). The combined organic layers were washed with water (3 x 10 ml) and brine (20 ml), and dried and the solvent was removed by careful distillation at 760 mmHg. Column chromatography of the residue, eluting with 10:1 petrol and ether, gave an oil (0.19 g, 67 %) which was a mixture of two components in ratio ca. 5:1 by g.l.c. (Found M^+: 126.1039. $C_8H_{14}O$ requires 126.1045). These could not be separated but the major component was characterised as

2,2,3-trimethyl-5,6-dihydro[2H]pyran. An analytical sample was obtained by preparative g.l.c. (Found M^+: 126.1039. $C_8H_{14}O$ requires 126.1039) which showed δ_H 5.4 (1H, m), 3.75 (2H, t, J 5.5 Hz), 2.04 (2H, m), 1.64 (3H, m), 1.28 (6H, s); ν_{max} 2974, 2923, 1451, 1217, 1094, 1052 cm^{-1}; m/z 126 (M^+), 111 (M^+-CH_3). The minor component was provisionally characterised as either *E-* or *Z-3-ethylidene-2,2-dimethyltetrahydrofuran* and showed δ_H 5.37 (1H, tq, J 2, 7.3 Hz), 3.79 (2H, t, J 5.5 Hz), 2.57 (2H, m), 1.59 (3H, m), 1.38 (6H, s);

EXPERIMENT (93)

4-Bromo-2,2,3,6-tetramethyl-5,6-dihydro[2H]pyran (369).

Bromine (0.25 g) in dichloromethane (5 ml) was added to a stirred solution of 1-(2,3,3-trimethylcyclopropen-1-yl)propan-2-ol (0.2 g) in dichloromethane (5 ml) as described above. Work up followed by column chromatography eluting with 10:1 petrol and ether gave *4-bromo-2,2,3,6-tetramethyl-5,6-dihydro[2H]pyran* (0.105 g, 32 %) (Found M^+: 218.0313. $C_9H_{15}BrO$ requires 218.0306) which showed δ_H 3.94 (1H, complex m), 2.44 (1H, v.complex), 2.35 (1H, v.complex d, J 15 Hz), 1.79 (3H, dd, J 1.5, 2.4 Hz), 1.32 (3H, s), 1.30 (3H, s), 1.19 (3H, d, J 6.1 Hz); δ_C 137.5s, 116.4s, 77.0s, 65.3d, 44.2t, 28.3q, 24.5q, 21.3q, 18.9q; ν_{max} 2976, 2931, 1668, 1445, 1382, 1360, 1212, 910, 734 cm^{-1}; m/z 218 (M^+), 203 (M^+-CH_3), 139 (M^+-Br).

EXPERIMENT (94)

(+)-4-Bromo-2,2,3,6-tetramethyl-5,6-dihydro[2H]pyran (369).

Bromine (0.25 g) in dichloromethane (5 ml) was added to a stirred solution of (S)-(+)-1-(2,3,3-trimethylcyclopropen-1-yl)propan-2-ol (0.5 g) in dichloromethane (5 ml) as described above. Work up followed by column chromatography eluting with 10:1 petrol and ether gave *(+)-4-bromo-2,2,3,6-tetramethyl-5,6-dihydro[2H]pyran* (0.102 g,

33 %) (Found M^+: 218.0313. $C_9H_{15}BrO$ requires 218.0306), $[\alpha]_D^{22}$ (+)-115°.

EXPERIMENT (95)

4-Bromo-2,3-dimethyl-5,6-dihydro[2H]pyran (370).

Bromine (0.72 g) in dichloromethane (5 ml) was added to a stirred solution of 2-(2,3-dimethylcyclopropen-1-yl)ethanol (0.5 g) in dichloromethane (5 ml) as described above. Work up followed by column chromatography eluting with 10:1 petrol and ether gave *4-bromo-2,3-dimethyl-5,6-dihydro[2H]pyran* (0.41 g, 47 %) (Found M^+: 190.0010. $C_7H_{11}BrO$ requires: 189.9993) which showed δ_H 4.18 (1H, br.q, J 6.6 Hz), 3.96 (1H, dddd, J 0.4, 3.9, 5.4, 11.2 Hz), 3.68 (1H, ddd, J 11.2, 8.3, 4.3 Hz), 2.66 (1H, v.complex d, J 14.0 Hz), 2.44 (1H, v.complex d, J 14.0 Hz), 1.75 (3H, ddd, 0.95, 1.7, 2.2 Hz), 1.28 (3H, d, J 6.6 Hz); δ_C 135.15s, 116.0s, 74.8d, 63.4t, 36.5t, 19.36q, 18.84q; ν_{max} 2976, 2933, 2858 1665, 1373, 1266, 1120, 1078, 871, 785 cm^{-1}; m/z 190 (M^+), 175 (M^+-CH_3).

EXPERIMENT (96)

2,3-Dimethyl-5,6-dihydro[2H]pyran (371).

Lithium metal (100 mg) was added to a stirred solution of 4-bromo-2,3-dimethyl-5,6-dihydro[2H]pyran (0.5 g) and t-butanol (1.0 g) in tetrahydrofuran (10 ml). After 5 m, an exothermic reaction ensued which was controlled by cooling so that a gentle refluxing occurred for 1 h. The products were then refluxed for a further 1 h and stirred at ambient temperature for 2 h, before being poured into ice-water and extracted with ether (5 x 10 ml). The combined organic layers were washed with water (10 ml) and brine (20 ml), and dried. The solvent was removed by careful distillation at 760 mmHg to give *2,3-dimethyl-5,6-dihydro[2H]pyran* (0.19 g, 67 %). An analytical sample was obtained by

preparative g.l.c. (Found M^+: 112.0867. $C_7H_{12}O$ requires: 112.0888) which showed δ_H 5.5 (1H, m, $W_{1/2}$ 7 Hz), 4.08 (1H, br.q, J 6.5 Hz), 3.9 (1H, ddd, J 3.7, 5.4, 11.1 Hz, further split into t, J ca.6.5 Hz), 3.6 (1H, ddd, J 4.2, 8.7, 11.1 Hz), 2.2 (1H, complex), 1.97 (1H, complex), 1.61 (3H, narrow m), 1.25 (3H, d, J 6.5 Hz); δ_C 136.5s, 119.0d, 72.5d, 62.0t, 25.3t, 19.0q, 18.8q; ν_{max} 2970, 2940, 1710, 1442, 1372, 1115, 1080, 1046, 889, 860, cm^{-1}; m/z 112 (M^+), 111 (M^+–H), 97 (M^+–CH_3).

EXPERIMENT (97)

4–Bromo–2,3,6–trimethyl–5,6–dihydro[2H]pyran (372).

Bromine (0.66 g) in dichloromethane (5 ml) was added to a stirred solution of 1–(2,3–dimethylcyclopropen–1–yl)propan–2–ol (0.5 g) in dichloromethane (5 ml) as described above. Work up followed by column chromatography eluting with 10:1 petrol and ether gave a mixture of *cis*– and *trans–4–bromo–2,3,6–trimethyl–5,6–dihydro–[2H]pyran* (0.3 g, 37 %) (Found M^+: 204.0157. $C_8H_{13}BrO$ requires 204.0150). These appeared as two peaks on capillary g.l.c. but could not be separated by preparative g.l.c. The mixture showed δ_H (major isomer) 4.2 (1H, m), 4.01 (1H, sextet, J ca. 6.5 Hz), 2.4 (2H, m), 1.75 (3H, narrow t), 1.32 (3H, d, J 6.6 Hz), 1.2 (3H, d, J 6.2 Hz); (minor isomer) 4.2 (1H, m), 3.72 (1H, ddq, J 3.9, 6.2, 10.5 Hz), 2.4 (2H, m), 1.75 (3H, narrow t), 1.27 (3H, d, J 6.6 Hz), 1.22 (3H, d, J 6.1 Hz); ν_{max} 2976, 2931, 1668, 1445, 1382, 1360, 1212, 910, 734 cm^{-1}; m/z 204 (M^+), 189 (M^+–CH_3).

EXPERIMENT (98)

Reaction of 2–(2–(dimethylethyl)cyclopropen–1–yl)ethanol (345_a)with bromine

(a) Bromine (1.14 g) in dichloromethane (5 ml) was added as before to a stirred solution of 2–(2–(dimethylethyl)cyclopropen–1–yl)ethanol (1.0 g) in dichloromethane (5

ml). Work up as before followed by column chromatography eluting with 20:1 petrol and ether gave two products. The first was *3-(dimethylethyl)-4-bromo-5,6-dihydro-[2H]pyran* (373) (0.28 g, 18 %) (Found M^+: 218.0294. $C_9H_{15}BrO$ requires: 218.0306) which showed δ_H 4.18 (2H, t, J 2.5 Hz), 3.68 (2H, t, 5.7 Hz), 2.62 (2H, tt, J 2.5, 5.7 Hz), 1.26 (9H, s); ν_{max} 1671, 1255, 1111, 1049, 759 cm^{-1}; m/z 218 (M^+), 161 ($M^+-C(CH_3)_3$). The second was *1,3-dibromo-6,6-dimethylheptan-5-one* (374) (1.3 g, 61 %) (Found M^+: 297.9556. $C_9H_{16}Br_2O$ requires: 297.9556) which showed δ_H 3.65 (1H, br.pent, J ca. 6.3 Hz), 3.55 (1H, dd, J 7.0, 9.9 Hz), 3.42 (1H, br.dt, J 10.4, 6.8 Hz), 3.31 (2H, m), 2.23 (1H, dq, J 14.7, 7.0 Hz), 2.06 (1H, dq, J 14.7, 6.8 Hz); δ_C 214.7s, 46.3d, 44.8s, 34.8t, 31.7t, 30.1t, 26.4q; ν_{max} 2970, 2909, 1703, 1478, 1368, 1271, 654 cm^{-1}; m/z 298 (M^+), 241 ($M^+-C(CH_3)_3$).

(b) Bromine (0.24 g) in dichloromethane (3 ml) was added to a stirred solution of 2-(2-(dimethylethyl)cyclopropen-1-yl)ethanol (0.2 g) in dichloromethane (5 ml) and triethylamine (0.7 g) at 0 °C. The mixture was stirred for one hour, diluted with dichloromethane (10 ml) and water (5 ml), and the organic layer was washed with 1M HCl, dried, and the solvent was removed at 14 mmHg. The residue was chromatographed over silica, eluting with petrol and ether (5:1), to give *E-2-(1,2-dibromo-2-t-butyl-1-cyclopropyl)ethanol* (377) (0.16 g, 37%) (Found M^+: 297.9548. $C_9H_{16}OBr_2$ requires 297.9568) which showed δ_H 3.7 (2H, t, J ca. 6.0 Hz), 2.6 (2H, t, J ca. 6.0 Hz), 2.0 (1H, br.s), 1.05 (9H, s), 0.78 (2H, s); ν_{max} 3334, 2962, 2865, 1361, 1049, 1008 cm^{-1}; m/z 298 (M^+), 219 (M^+-Br).

EXPERIMENT (99)

<u>Reaction of 2-(2-(dimethylethyl)cyclopropen-1-yl)ethanol (345_a) with acid</u>

2-(2-(dimethylethyl)cyclopropen-1-yl)ethanol (1.0 g) was stirred for 12 h at 20 °C with p-toluene sulphonic acid (0.4 g) in benzene (10 ml). Work up as above gave an oil which was flash distilled at 20 °C and 14 mmHg to give *2-methyl-2-t-butyl-2,5-*

dihydrofuran (385) (0.1 g, 10 %) which showed δ_H 5.7 (2H, narrow m), 4.65 (1H, d, J 21 Hz), 4.60 (1H, ddd, J 21, 0.7, 1.5 Hz), 1.2 (3H, s), 0.9 (9H, s); δ_C 132.5d, 125.2d, 95.2s, 75.2t, 38.04s, 25.6q, 21.6t; ν_{max} 2963, 2871, 2842, 1365, 1084, 1038, 712 cm $^{-1}$; m/z 83 (M^+–$C(CH_3)_3$). The residue was separated into two components by column chromatography eluting with 10:1 petrol and ether. The first component was *3-t-butyl-5,6-dihydro[2H]pyran* (386) (0.18 g, 18 %) (Found M^+: 140.1215. $C_9H_{16}O$ requires: 140.1201) which showed δ_H 5.5 (1H, m), 4.15 (2H, m), 3.68 (2H, t, J 6.0 Hz), 2.15 (2H, m), 1.05 (9H, s); ν_{max} 2964, 2907, 1689, 1464, 1364, 1112, 911 cm^{-1}; m/z 140 (M^+), 125 (M^+–CH_3), 83 (M^+–$C(CH_3)_3$). The second component was *4,5,5-trimethylhexa-2,3-dien-1-ol* (384) (0.35 g, 35 %) (Found M^+: 140.1208) which showed δ_H 5.22 (1H, m), 4.05 (2H, d, J 6 Hz), 1.7 (3H, d, J 3 Hz), 1.42 (1H, br.s), 1.02 (9H, s); ν_{max} 3347, 2964, 2869, 1960, 1688, 1362, 1012, 735 cm^{-1}; m/z 140 (M^+), 123 (M^+–OH), 109 (M^+–CH_2OH). Irradiation of the signal at δ 1.7 reduced the signal at δ 5.22 to a triplet (J 6.0 Hz).

EXPERIMENT (100)

2,2-Dimethyl-3-methylenetetrahydrofuran (353).

(a) 2-(3,3-Dimethylcyclopropen-1-yl)ethan-1-ol (0.3 g) was stirred for 12 h at 20 °C with silver trifluoromethane sulphonate (0.3 g) in benzene (10 ml), when t.l.c. showed that no starting material remained. Work up as above, removal of the solvent at 760 mmHg and column chromatography of the residue over silica eluting with petrol and ether (10:0.5) gave *2,2-dimethyl-3-methylenetetrahydrofuran* (0.14 g, 47%) (Found M^+: 112.0867. $C_7H_{12}O$ requires. 112.0888) which showed δ_H 4.91 (1H, t, J 2.2 Hz), 4.79 (1H, t, J 2.2 Hz), 3.8 (2H, t, J 6.9 Hz), 2.6 (2H, tt, J 2.2, 6.9 Hz), 1.29 (6H, s); ν_{max} 3077, 2974, 2929, 2860, 1664, 1360, 1160, 1042, 886 cm $^{-1}$; m/z 97 ($M^+ - CH_3$); δ_C 156.5s, 103.6t, 81.3s, 64.4t, 33.3t, 27.7q. Irradiation of the signal at δ 1.29 caused an ca. 10% n.O.e. enhancement in the alkene signal at δ 4.79, with

no enhancement in that at δ 4.91.

(b) The above reaction was repeated using p-toluene sulphonic acid (0.15 g) in place of the silver salt. Work up as above gave *2,2-dimethyl-3-methylene-tetrahydrofuran* (0.18 g, 61%) identical by n.m.r. and i.r. to that obtained in (a).

(c) Lithium metal (100 mg) was added to a stirred solution of E-2-(bromo-methylene)-2,2-dimethyltetrahydrofuran (0.5 g) and t-butanol (1.0) in tetrahydrofuran (10 ml). After 5 m, an exothermic reaction began; this was controlled by cooling so that the mixture refluxed gently over a period of 1 h. After a further 2 h at ambient temperature the products were poured into ice-water and extracted with ether (5 x 10 ml). The combined organic layers were washed with water (10 ml) and brine (20 ml), and dried; the solvent was removed by careful distillation at 760 mmHg to give an oil which was characterised as 2,2-dimethyl-3-methylenetetrahydrofuran (0.21 g, 71 %) which was identical by n.m.r. and i.r. to that obtained above.

EXPERIMENT (101)

<u>3-Methylene-2,2,5-trimethyltetrahydrofuran (390).</u>

1-(3,3-Dimethylcyclopropen-1-yl)propan-2-ol (0.25 g) and p-toluene sulphonic acid (0.11 g) were stirred for 15 h at 20 ^{o}C in benzene, when no starting material was left; the products were diluted with petrol, washed with saturated aq. sodium bicarbonate and then brine, and dried. Removal of the solvent by careful distillation at 760 mmHg gave an oil which was purified by column chromatography eluting with 10:2 petrol and ether to give *3-methylene-2,2,5-trimethyltetrahydrofuran* (0.13 g, 51 %) which was one peak by g.l.c. (Found M^{+}: 126.1045. $C_{8}H_{14}O$ requires 126.1038) which showed δ_{H} 4.86 (1H, dd, J 1.63, 2.5 Hz), 4.76 (1H, dd, J 1.7, 2.8 Hz), 4.05 (1H, m), 2.66 (1H, ddt, J 1.63, 5.5, 15.4 Hz), 2.26 (1H, ddt, J 2.8, 9.59, 15.45 Hz), 1.33 (3H, s), 1.26 (3H, d, J 7 Hz), 1.26 (3H, s); ν_{max} 2972, 2931, 1449, 1366, 1176, 1037, 937, 813, 756, 669 cm^{-1}; m/z 126 (M^{+}), 125 (M^{+}-H), 111 (M^{+}-CH_{3}).

EXPERIMENT (102)

E- and Z-2,2-Dimethyl-3-(trimethylsilylmethylene)tetrahydrofurans

2-(3,3-Dimethyl-1-trimethylsilylcyclopropen-1-yl)ethanol (0.4 g) was stirred for 3.5 h at 20 °C with p-toluene sulphonic acid (0.12 g) in benzene (5 ml). Work up as before followed by column chromatography eluting with 10:1 petrol and ether gave an oil which consisted of a 2:1 mixture of isomers (0.21 g, 53 %). These were separated by preparative g.l.c. The major isomer was characterised as *2,2-dimethyl-E-3-(trimethylsilylmethylene)tetrahydrofuran* (391) (Found M^+: 184.1290. $C_{10}H_{20}OSi$ requires 184.1283) which showed δ_H 5.12 (1H, t, J 2 Hz), 3.8 (2H, t, J 7 Hz), 2.67 (2H, dt, J 2, 7 Hz), 1.2 (6H, s), 0.1 (9H, s); δ_C 164.6s, 116.1d, 82.8s, 64.3d, 32.6t, 27.4q, -0.5q; ν_{max} 2972, 1634, 1376, 1359, 1247, 1154, 1073, 869, 843 cm^{-1}. The stereochemistry was established as E- on the basis of an n.O.e experiment. Irradiation of the signal at δ 1.2 caused an ca. 13% enhancement in that at δ 5.12 and none in that at δ 0.1. The second isomer was *2,2-dimethyl-Z-3-(trimethylsilylmethylene)tetrahydrofuran* (392) (Found M^+: 184.1296) which showed δ_H 5.4 (1H, t, J 2 Hz), 3.7 (2H, t, J 7 Hz), 2.7 (2H, dt, J 2, 7 Hz), 1.34 (6H, s), 0.14 (9H, s); ν_{max} 2970, 2955, 1629, 1377, 1360, 1249, 1148, 1047, 839 cm^{-1}. Irradiation of the signal at δ 1.34 caused an ca. 4% enhancement in that at δ 0.14, but none in that at δ 5.4; irradiation at δ 0.14 caused an equal enhancement at δ 1.34; m/z 184 (M^+), 169 (M^+-CH_3), 139 ($M^+-(CH_3)_3$).

EXPERIMENT (103)

2-(2-Deuterio-3,3-dimethylcyclopropen-1-yl)ethanol (395).

Methyl lithium (6.8 ml, 1.5 M) was added over 2 min to a stirred solution of 2-(3,3-dimethylcyclopropen-1-yl)ethanol (0.5 g) and di-isopropylamine (0.92 g) in

ether (20 ml) at - 70 °C. After 5 m, the mixture was allowed to reach ambient temperature and then stirred for 1 h before cooling to - 30 °C and adding D_2O (3 ml). The products were again allowed to reach ambient temperature, treated with water (5 ml) and extracted with ether (3 x 20 ml). The combined organic layers were washed with 0.5 M hydrochloric acid and then brine, dried, and the solvent was removed at 760 mmHg. The remaining oil was flash distilled to give *2-(2-deuterio-3,3-dimethylcyclopropen-1-yl)ethanol* (0.25 g, 50 %) (m/z 111 (M^+ - D), 98 (M^+ - Me)) which showed δ_H 3.8 (2H, t, J 6.4 Hz), 2.7 (2H, t, J 6.4 Hz), 1.87 (1H, br.s), 1.12 (6H, s); ν_{max} 3352, 2959, 2930, 2857, 1714, 1450, 1364, 1049 cm^{-1}.

EXPERIMENT (104)

Reaction of 2-(2-deuterio-3,3-dimethylcyclopropen-1-yl)ethanol (395) with acid

A solution of 2-(2-deuterio-3,3-dimethylcyclopropen-1-yl)ethanol (0.2 g) in dry benzene (6 ml) was stirred for 12 h at 20 °C with p-toluene sulphonic acid (50 mg). T.l.c. then showed that all the starting material had been consumed. The mixture was washed with saturated aq. sodium bicarbonate and extracted with ether (3 x 10 ml), dried, and the solvent was carefully removed at 760 mmHg. The product was one peak by g.l.c., but consisted of a mixture of *Z*- and *E*-isomers of *3-(deuterio-methylene)-2,2-dimethyltetrahydrofuran* by n.m.r. (0.13 g, 65 %). The mixture was further purified by preparative g.l.c. (Found M^+: 113.0997. $C_7H_{11}DO$ requires 113.1001) and showed a very similar proton n.m.r. to the undeuterated material apart from in the alkene region, and δ_D 4.94 (1D, br.s), 4.82 (1D, br.s) in ratio 2.7:1; m/z 113 (M^+), 98 (M^+-CH_3).

EXPERIMENT (105)

Reaction of O-deuterio-2-(3,3-dimethylcyclopropen-1-yl)ethanol (396) with acid

O-Deuterio-2-(3,3-dimethylcyclopropen-1-yl)ethanol was prepared by shaking 2-(3,3-dimethylcyclopropen-1-yl)ethanol (0.2 g) in ether (10 ml) with D_2O (4 x 2ml), drying and evaporating the solvent. The cyclopropene was dissolved in dry benzene (6 ml) and stirred for 12 h at 20 °C with O-deuterio-p-toluenesulphonic acid (50 mg) [prepared by dissolving the acid in D_2O (2 ml) and evaporating the solvent to dryness at 14 mmHg. This was repeated four times in all] T.l.c. then showed that no starting material remained. Work up as above gave *3-(deuteriomethylene)tetrahydrofuran* (0.14 g, 70 %) which was again purifed by preparative g.l.c. and showed δ_D 4.94 (1D, br.s), 4.82 (1D, br.s) in ratio 1:2.7.

EXPERIMENT (106)

Reaction of 2-(2,3,3-trimethylcyclopropen-1-yl)ethanol (344_a) with acetic acid.

2-(2,3,3-Trimethylcyclopropen-1-yl)ethanol (0.2 g) was stirred for 24 h with acetic acid (0.1 g) in benzene (2 ml); t.l.c. showed only starting material. p-Toluene sulphonic acid (30 mg) was added; after 1 h no starting material remained. Work up and column chromatography over silica eluting with petrol and ether (10:2) gave *2-(2,3,3-trimethyl-1-cyclopropenyl)ethyl acetate* (0.15 g, 55%) (Found M^+: 168.1157. $C_{10}H_{16}O_2$ requires: 168.1150) which showed δ_H 4.15 (2H, t, J 6 Hz), 2.62 (2H, br.t), 2.05 (3H, s), 1.92 (3H, narrow t), 1.01 (6H, s); ν_{max} 1744 cm^{-1}; m/z 168 (M^+), 153 (M^+-CH_3).

EXPERIMENT (107)

3-Methoxy-3-methyl-1-trimethylsilylbut-1-ene (394).

3,3-Dimethyl-1-trimethylsilylcyclopropene (0.5 g) was stirred for 48 h at 20 °C with p-toluene sulphonic acid (0.13 g) and methanol (2 m) in dry benzene (6 ml). T.l.c. then showed complete reaction. The products were washed with saturated aq.

sodium bicarbonate and the aqueous layer was extracted with ether (3 x 15 ml), dried and the solvent removed by careful distillation at 760 mmHg. The residue was characterised as *E-3-methoxy-3-methyl-1-trimethylsilylbut-1-ene* (0.38 g, 62 %) (m/z 157 (M^+–CH_3), 141 (M^+–OMe) which showed δ_H 5.97 (1H, d, J 19.2 Hz), 5.76 (1H, d, J 19.2 Hz), 3.14 (3H, s), 1.2 (6H, s), 0.07 (9H, s); ν_{max} 2976, 2957, 2167, 1735, 1618, 1461, 1375, 1249, 1076 cm^{-1}.

EXPERIMENT (108)

2-Deuterio-1,3,3-trimethylcyclopropene (398).

Methyl lithium (9.6 ml) was added to a stirred solution of 1,1,2-tribromo-2,3,3-trimethylcyclopropene (2.0 g) in ether (10 ml) at -78 °C. After allowing the products to reach ambient temperature for 10 m, the mixture was cooled to -20 °C and the volatiles were removed at 1 mmHg; when most had been removed the temperature was allowed to reach 20 °C, maintaining the vacuum for about 2 h. The remaining white solid was cooled to -20 °C and treated with D_2O (5 ml); the products were distilled directly at 1 mm Hg, collecting in a cooled receiver to give *2-deuterio-1,3,3-trimethylcyclopropene* (0.27 g, 52 %) which showed δ_H 1.93 (3H, s), 1.02 (6H, s).

EXPERIMENT (109)

1,3,3-Trimethylcyclopropene (399).

The above reaction was repeated using methyl-lithium (9.6 ml) and the tribromide (2.0 g) but using H_2O (5 ml) in place of D_2O. Work up as above and the product was distilled directly at 1.0 mmHg to give 1,3,3-trimethylcyclopropene (0.31 g, 61%) and showed δ_H 6.5 (1H, br.s), 1.95 (3H, s), 1.05 (6H, s).

EXPERIMENT (110)

Reaction of 1,3,3-trimethylcyclopropene (399) with methanol and acid

1,3,3-Trimethylcyclopropene (0.2 g) was stirred with p-toluenesulphonic acid (50 mg) in ether (2 ml) and methanol (2 ml). After 66 h, t.l.c. showed that no starting material remained. The products were washed with saturated aq. sodium bicarbonate (2 x 5 ml) and then water (3 x 5 ml); the aqueous layer was re-extracted with ether (3 x 10 ml) and the combined organic layers were dried and the solvent was removed by distillation at 760 mmHg. The remaining oil (0.15 g, 54 %) consisted of a 1.6:1 mixture of *2,3-dimethyl-3-methoxybut-1-ene* (400) and (401) *2,3-dimethyl-4-methoxybut-2-ene* (Found M^+: 114.1048. $C_7H_{14}O$ requires 114.1045). The former showed δ_H 4.92 (1H, br.m), 4.89 (1H, br.m), 3.07 (3H, s), 1.73 (3H, br.s), 1.3 (6H, s). The latter showed δ_H 3.9 (2H, br.s), 3.28 (3H, s), 1.7 (3H, s), 1.29 (6H, s); ν_{max} 3090, 2981, 2924, 1674, 1645, 1451, 1374, 1173, 1077 cm^{-1}; m/z 114 (M^+), 112 (M^+-2H), 99 (M^+-CH_3), 83 (M^+-OCH_3).

EXPERIMENT (111)

Reaction of 2-Deuterio-1,3,3-trimethylcyclopropene (398) with methanol and acid

The above reaction was repeated using 2-deuterio-1,3,3-trimethylcyclopropene (0.2 g), leading to an oil (0.14 g, 48 %). This consisted of a 2:1 mixture of *1-deuterio-3-methoxy-2,3-dimethylbut-1-ene* and *4-deuterio-4-methoxy-2,3-dimethyl-but-2-ene*; which showed a very similar proton n.m.r. to the undeuterated material apart from in the alkene region, and δ_D 4.95 (1D, br.s), 4.92 (1D, br.s), 3.9 (2D, br.s) in the ratio (2.3:1:2.6); m/z 100 (M^+-15).

EXPERIMENT (112)

Reaction of 1,3,3-trimethylcyclopropene (399) with methanol-OD and deuterated acid

A solution of 1,3,3-trimethylcyclopropene (0.2 g) was treated as above, but using methanol-OD (2 ml) and p-toluene sulphonic acid-OD (40 mg). Work up as before gave the same mixture of compounds (0.12g, 43 %).

EXPERIMENT (113)

Reaction of 2-(1,3,3-trimethylcyclopropen-1-yl)ethanol (344_a) with mercuric acetate

Mercuric acetate (1.26 g) was stirred for 15 m in tetrahydrofuran (10 ml); the cyclopropene (0.5 g) was added and the mixture was stirred for 3 h. Sodium hydroxide (6 ml, 3 M) and sodium borohydride (6 ml, 0.5 M in 3M sodium hydroxide) were then added. After 5 m, brine was added and the organic layer was separated and dried and the solvent was carefully removed at 760 mmHg. The residue (0.7 g) contained three components in ratio 5:1:1, which were separated by preparative g.l.c.

The major component was *2-methyl-3-(2-acetoxyprop-2-yl)-4,5-dihydrofuran* (410) (Found M^+: 184.1083. $C_{10}H_{16}O_3$ requires: 184.1099) which showed δ_H 4.37 (2H, t, J 6.3 Hz), 2.84 (2H, t, J 6.3 Hz), 2.02 (3H, s), 1.83 (6H, s), 1.77 (3H, s); ν_{max} 2920, 1741, 1687, 1241, 733 cm^{-1}; m/z 184 (M^+), 125 (M^+-CH_3COO). The second was *4,5-dimethylhexa-3,5-dien-1-ol* (412) (Found M^+: 126.1054. $C_8H_{14}O$ requires: 126.1045) which showed δ_H 5.6 (1H, br. t, J 7.25 Hz), 5.03 (1H, br.s), 4.92 (1H, br.s), 3.72 (2H, t, J 6.6 Hz), 2.44 (2H, q, J 6.8 Hz), 1.92 (3H, d, J 0.88 Hz), 1.84 (3H, s); ν_{max} 3342, 3093, 2948, 1607, 1441, 1374, 1047 cm^{-1}; m/z 126 (M^+), 111 (M^+-CH_3). The third component was *4-methyl-3-vinylpent-3-en-2-one* (411) (Found M^+: 124.0893. $C_8H_{12}O$ requires: 124.0888) which showed δ_H 6.5 (1H, m), 6.1 (1H, dd, J 3, 9 Hz), 5.85 (1H, dd, J 3, 9 Hz), 1.8 (9H, s); ν_{max} 2980, 2920, 1658, 1604, 1450, 1399, 733 cm^{-1}; m/z 124 (M^+), 109 (M^+-CH_3), 97 (M^+-CH_2CH).

INDEX OF EXPERIMENTS

(23) 1,6-Dichloro-2-methyl-3-phenyl-4,4,5,5-tetracyanocy clohexene

(24) 3-Chloro-3-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane

(25) 3-Chloro-3-(1-chloro-2-methyl-3-p-methoxyphenylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane

(26) 3-Chloro-3-(1-chloro-2-methyl-3-p-trifluoromethylphenylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane

(27) 3-Chloro-3-(1-chloro-2-methyl-3-p-methylphenylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane

(28) Methyl 2-chloro-2-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1-cyclopropane carboxylate

(29) Methyl 2-chloro-2-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1-methylcyclopropane carboxylate

(30) 2-Chloro-2-(1-chloro-2-methyl-3-phenylprop-1-enyl)-1-methyl-cyclopropane carboxylic acid

(31) 1,2-Dichloro-3-chloromethyl-3-methylcyclopropene

(32) 1,2-Dichloro-3-methyl-3-methoxymethylcyclopropene

(33) 2-Chloro-1,3-dimethyl-3-methoxymethylcyclopropene

(34) 1,2-Dichloro-3-methyl-3-(di-isopropylaminomethyl)cyclopropene

(35) 1,2-Dichloro-3-methyl-3-(allylthio)methylcyclopropene

(36) 1-Chloro-3,3-dimethyl-2-trimethylsilyl-1-cyclopropene

(37) 1-Bromo-4,4-dimethyl-2-pentyne

(38) Dimerisation of 1,2-dichloro-3-methyl-3-methoxymethylcycloprop-1-ene

(39) 1-Acetoxy-1,2,4-trichloro-3-methylbut-2-ene

(40) 1-Methoxy-1,2,4-trichloro-3-methylbut-2-ene

(41) 1-Isopropoxy-3-methyl-1,2,4-trichlorobuta-1,3-diene

(42) 3-Chloro-3-(1,3-dichloro-2-methylprop-1-enyl)-1,1,2,2-tetramethylcyclopropane

(43) 3-Chloro-3-(1,3-dichloro-2-methylprop-1-enyl)-1,1-dimethyl-cyclopropane

(44) 3-Chloro-3-(1,3-dichloro-2-methylprop-1-enyl)-Z-1,2-dimethyl-cyclopropane

(45) 1-Chloro-1-(1,3-dichloro-2-methylprop-1-enyl)cyclopropane

(46) Methyl 2-chloro-2-(1,3-dichloro-2-methylprop-1-enyl)cyclo-propane carboxylate

(47) Methyl 2-chloro-2-(1,3-dichloro-2-methylprop-1-enyl)-1-methyl cyclopropane carboxylate

(48) 3-(1-Chloro-2,2,3,3-tetramethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether

(49) 3-(1-Chloro-2,2,3-trimethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether

(50) 3-(1-Chloro-2,2-dimethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether

(51) 3-(1-Chloro-*trans*-2,3-dimethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether

(52) 3-(1-Chloro-*cis*-2,3-dimethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether

(53) Methyl 2-chloro-2-(1-chloro-3-methoxy-2-methylprop-1-enyl)-cyclopropane carboxylate

(54) Methyl 2-chloro-2-(1-chloro-3-methoxy-2-methylprop-1-enyl)-1-methylcyclopropane carboxylate

(55) 7-Chloromethyl-7-methyl-1,2-dichloro-4-methylcyclohepta-1,4-diene

(56) 7-Methoxymethyl-7-methyl-1,2-dichloro-4-methylcyclohepta-1,4-

diene

(57) Reaction of 1,1-dibromo-2,2-dichloro-3-methoxymethyl-3-methyl-cyclopropane with methyl lithium in the presence of:

(a) 2,3-Dimethylbut-2-ene. (b) 2-Methylprop-1-ene.

(58) Reaction of 1,1-dibromo-2,2-dichloro-3-isopropoxymethyl-3-methylcyclopropane with methyl lithum in the presence of :

(a) 2,3-Dimethylbut-2-ene (b) 2-Methylprop-1-ene

(59) 3-Bromo-2-chloro-1,3-dimethylcyclobutene

(60) Reaction of 1-chloro-1-(1,3-dichloro-2-methyl-2-prop-1-enyl)-2,2,3,3-tetramethylcyclopropane with potassium t-butoxide

(61) Reaction of 1-chloro-1-(1,3-dichloro-2-methyl-2-prop-1-enyl)-2,2-dimethylcyclopropane with potassium t-butoxide

(62) Reaction of E- and Z-1-(1,3-dichloro-2-methyl-2-propen-1-ylidene)-2,2-dimethylcyclopropane with tetracyanoethane

(63) Reaction of 1-chloro-1-(1-chloro-2-methylprop-1-enyl)-2,2-dimethylcyclopropane with potassium t-butoxide.

(64) Reaction of 1-chloro-1-(1,3-dichloro-2-methylprop-1-enyl)-Z-2,3-dimethylcyclopropane with potassium t-butoxide

(65) Reaction of 1-chloro-1-(1,3-dichloro-2-methylprop-1-enyl)-cyclopropane with potassium t-butoxide.

(66) Reaction of 3-(1-chloro-2,2,3,3-tetramethylcyclopropyl)-3-chloro-2-methyl-2-propenyl methyl ether with potassium t-butoxide.

(67) Reaction of 1-(1,3-dichloro-2-methyl-2-propen-1-ylidene)-2,2,3,3-tetramethylcyclopropane with m-chloroperbenzoic acid.

(68) Reaction of 2-chloro-2-(1,3-dichloro-2-methyl-2-prop-1-enyl)-1,1-dimethylcyclopropane with 10% KOH.

(69) Reaction of methyl 2-chloro-2-(1,3-dichloro-2-methyl-2-prop-1-enyl)-1-methylcyclopropane carboxylate with 10% KOH.

(70) Genernal method for relative reactivity experiments.

(71) Competition experiment between two arylcyclopropenes

(72) 2-(2,3,3-Trimethylcyclopropen-1-yl)ethan-1-ol

(73) 1-(2,3,3-Trimethylcyclopropen-1-yl)propan-2-ol

(74) (S)-(+)-1-(2,3,3-Trimethylcyclopropen-1-yl)propan-2-ol

(75) 2-(3,3-Dimethylcyclopropen-1-yl)ethan-1-ol

(76) 1-(3,3-Dimethylcyclopropen-1-yl)propan-2-ol

(77) (R)-(-)-1-(3,3-Dimethylcyclopropen-1-yl)propan-2-ol

(78) 2-(2,3-Dimethylcyclopropen-1-yl)ethan-1-ol

(79) 1-(2,3-Dimethylcyclopropen-1-yl)propan-2-ol

(80) 2-(3,3-Dimethyl-2-trimethylsilylcyclopropen-1-yl)-ethan-1-ol

(81) (-)-1-(3,3-Dimethyl-2-trimethylsilylcyclopropen-1-yl)-propan-2-ol

(82) 2-(2-(Dimethylethyl)cyclopropen-1-yl)ethan-1-ol

(83) 2-(2-(methylethyl)cyclopropen-1-yl)ethan-1-ol

(84) Reaction of 1,2,2-tribromo-1,3,3-trimethylcyclopropane with methyl lithium in the presence of 1-chloro-2,3-epoxy-propane.

(85) 2-(2,2,3-Trimethylcyclopropen-1-yl)ethylamine

(86) E-3-(Bromomethylene)-2,2-dimethyltetrahydrofuran

(87) E-3-(bromomethylene)-2,2,5-trimethyltetrahydrofuran

(88) (-)-E-2-(bromomethylene)-2,2,5-trimethyltetrahydrofuran

(89) 2,2-Dimethyl-E-3-(2-bromo-2-trimethylsilylmethylene)-tetrahydrofuran

(90) E- and Z-3-(2-bromo-2-trimethylsilylmethylene)-2,2,5-trimethyltetrahydrofuran

(91) 4-Bromo-2,2,3-trimethyl-5,6-dihydro[2H]pyran

(92) 2,2,3-Trimethyl-5,6-dihydro[2H]pyran

(93) 4-Bromo-2,2,3,6-tetramethyl-5,6-dihydro[2H]pyran

(94) (+)-4-Bromo-2,2,3,6-tetramethyl-5,6-dihydro[2H]pyran

(95) 4-Bromo-2,3-dimethyl-5,6-dihydro[2H]pyran

(96) 2,3-Dimethyl-5,6-dihydro[2H]pyran

(97) 4-Bromo-2,3,6-trimethyl-5,6-dihydro[2H]pyran

(98) Reaction of 2-(2-(dimethylethyl)cyclopropen-1-yl)ethanol with bromine

(99) Reaction of 2-(2-(dimethylethyl)cyclopropen-1-yl)ethanol with acid

(100) 2,2-Dimethyl-3-methylenetetrahydrofuran

(101) 3-Methylene-2,2,5-trimethyltetrahydrofuran

(102) E- and Z-2,2-Dimethyl-3-(trimethylsilylmethylene)-tetrahydrofurans

(103) 2-(2-Deuterio-3,3-dimethylcyclopropen-1-yl)ethanol

(104) Reaction of 2-(2-deuterio-3,3-dimethylcyclopropen-1-yl)-ethanol with acid

(105) Reaction of O-deuterio-2-(3,3-dimethylcyclopropen-1-yl)-ethanol with acid

(106) Reaction of 2-(2,3,3-trimethylcyclopropen-1-yl)ethanol with acetic acid

(107) 3-Methoxy-3-methyl-1-trimethylsilylbut-1-ene.

(108) 2-Deuterio-1,3,3-trimethylcyclopropene.

(109) 1,3,3-Trimethylcyclopropene.

(110) Reaction of 1,3,3-trimethylcyclopropene with methanol and acid.

(111) Reaction of 2-deuterio-1,3,3-trimethylcyclopropene with methanol and acid.

(112) Reaction of 1,3,3-trimethylcyclopropene with methan-OD and deuterated acid.

(113) Reaction of 2-(1,3,3-trimethylcyclopropen-1-yl)ethanol with mercuric acetate.

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