

SYNTHESIS AND REARRANGEMENTS OF VINYLIDENECYCLO-
PROPANES AND DIMETHYLENECYCLOPROPANES

by

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Declaration and Courses Attended

While working on this thesis I attended the following courses and seminars.

Modern Synthetic Methods in Organic Chemistry	Dr. G. Tennant
1,3-Dipoles in Organic Synthesis	Dr. J.T. Sharp and Dr. R.M. Paton
Synthesis and Mechanism of Action of the β -Lactam Antibiotics	Glaxo Group Research Ltd.
The Chemistry of Photographic Processes	Dr. L.A. Williams
N.m.r. Pulse Sequences and their Applications	Dr. G. Morris
Current Topics in Organic Chemistry	Various Lecturers
Organic Departmental Seminars	

I declare that this thesis has been composed by myself and that the work described herein is my own.

Alison McCormick

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Finally, I wish to thank my family for their continuous support and encouragement.

To my family

ABSTRACT

This thesis describes the preparation of 1-aryl-2-dimethylvinylidenecyclopropanes by the addition of the dimethylvinylidene carbene to the appropriately substituted styrenes. Acid catalysed rearrangements of these cyclopropanes proceeded by protonation at either the β and/or γ carbon atoms and resulted in ring opened products. The number and nature of the substituents on the cyclopropane ring determined the proportion of protonation at the two sites and the type of products formed. These included cyclopentadienes, iso-butenylindenes, cross-conjugated trienes and ethynyl styrenes. An attempt was made to rationalise these reactions.

Low pressure vapour phase pyrolysis of the dimethylvinylidenecyclopropanes gave isopropylidenemethylenecyclopropanes by a diradical mechanism. Reaction of these products with *p*-toluenesulphonic acid gave either 1,2-benzo-6,6-dimethylfulvenes or 2-(2'-methylprop-1'-enyl)indenes by rearrangement and 1-methyl-4-phenyl-2-(*p*-toluenesulphonyloxy)penta-1,4-dienes by addition of the acid, the nature and proportion of products being dependent on the substituents on the starting material.

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CHAPTER 1

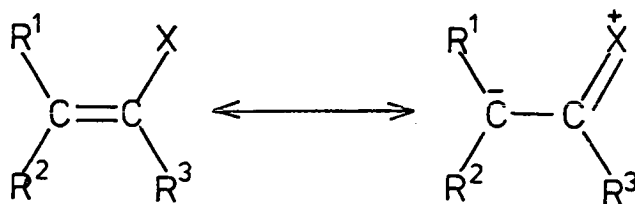
A Review of Vinyl and Cyclopropyl-allyl Cations and the Reactions of Vinylidenecyclopropanes with Acid

1.1 Introduction

In view of the work presented later in this thesis, this review is concerned mainly with vinyl and cyclopropyl-allyl cations in relation to the reactions of vinylidene-cyclopropanes with acid.

1.2 Vinyl Cations

Until fairly recently it was thought that a positive charge could not exist on the same carbon atom as a double bond. The main reason for this view was the poor reactivity of vinyl halides in solvolysis reactions.¹ However, this observation can be attributed, in part, to the increased σ -bond strength² of the carbon-halogen bond with an sp^2 hybridised carbon atom and to the partial double bond character³ of this bond in the mesomeric form.



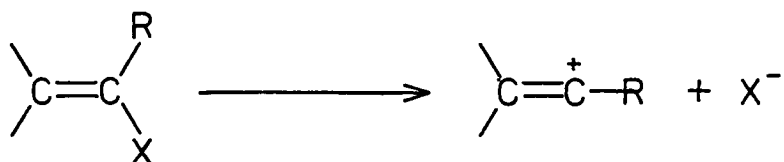
In the past twenty years studies have shown that, despite the higher energy of vinyl cations compared with their trisubstituted analogues, they can be generated by a

variety of reactions. As a result of these studies vinyl cations are no longer considered exotic intermediates and many aspects of their chemistry have recently been reviewed.⁴⁻¹⁴

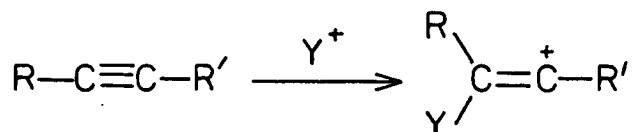
1.2.1 Formation of Vinyl Cations

There are three main routes to vinyl cations.

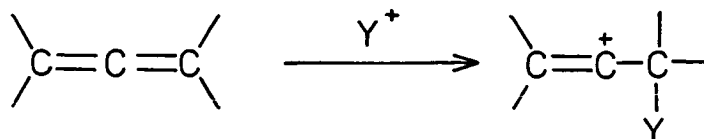
1) The heterolytic cleavage of vinyl substrates containing a suitable leaving group.



2) Electrophilic addition to triple bonds.



3) Electrophilic addition to allenes.



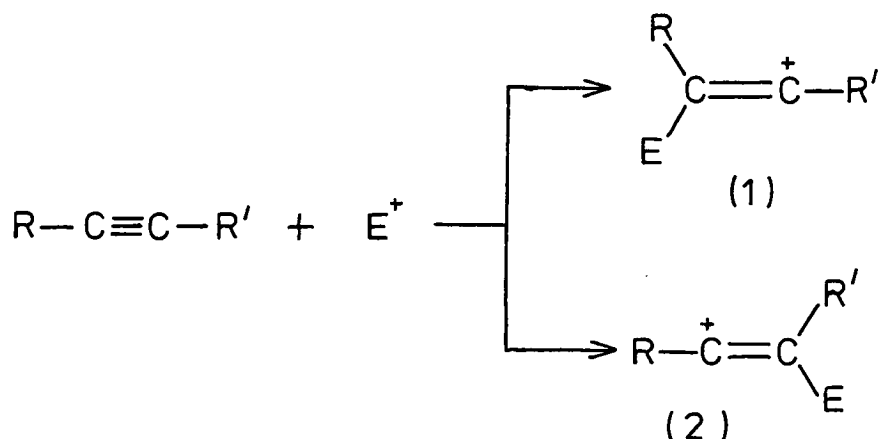
Other routes include the participation of multiple bonds in solvolysis reactions, deamination via diazonium ions, oxidative decarboxylation and fragmentation. These and other methods are covered in reviews by Z. Rappaport,¹⁴

and by M. Hanack.¹¹

The heterolysis of vinyl substrates normally requires a good leaving group and/or the stabilization of the vinyl cation by suitable substituents. Both these criteria are discussed at length in several reviews,⁸⁻¹⁴ but this review will deal mainly with the formation of vinyl cations through electrophilic additions to acetylenes and allenes.

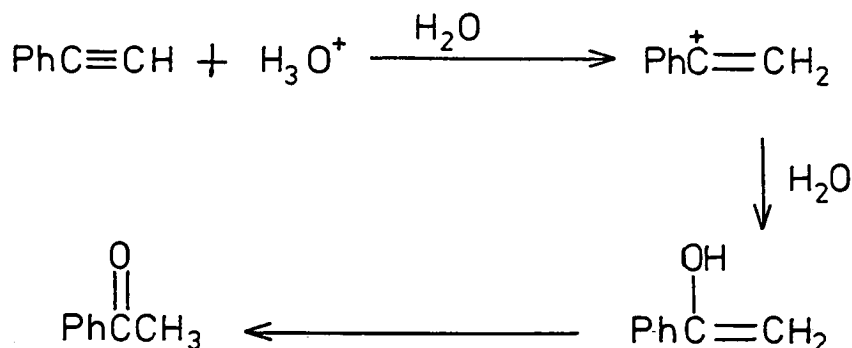
1.2.1.1 Electrophilic Addition to Acetylenes

The addition of electrophiles such as the proton, a halogen molecule or a carbenium ion to acetylenes, generates a new σ bond and a vinyl cation. Two isomeric vinyl cations can be formed (Scheme 1) and the distribution of products

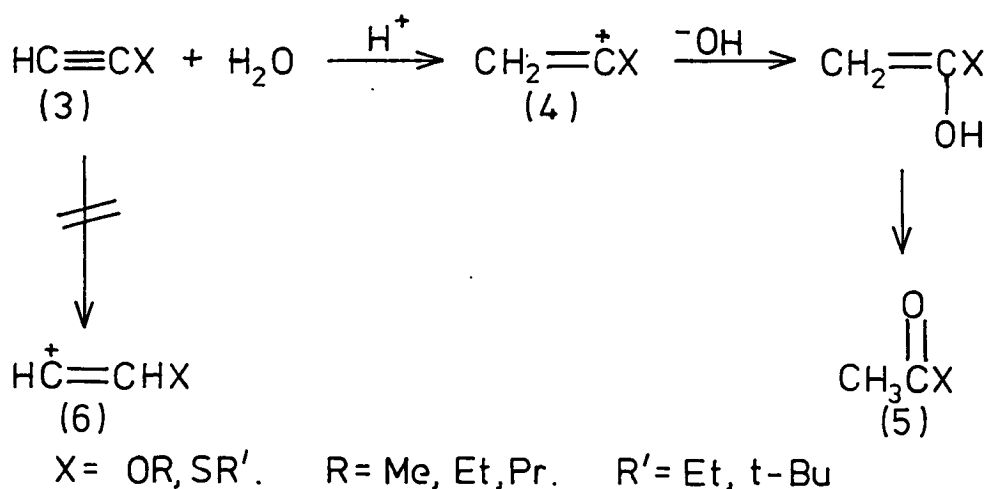


Scheme 1

serves as a direct measure of the stabilities of the two transition states leading to ions (1) and (2). In most cases R and R' are sufficiently different in their ability to stabilize a positive charge that only one vinyl cation is formed. Therefore, in monosubstituted acetylenes ($\text{R}'=\text{H}$) the products are formed via cation (2) as shown by the formation of acetophenone from acid catalysed hydration of

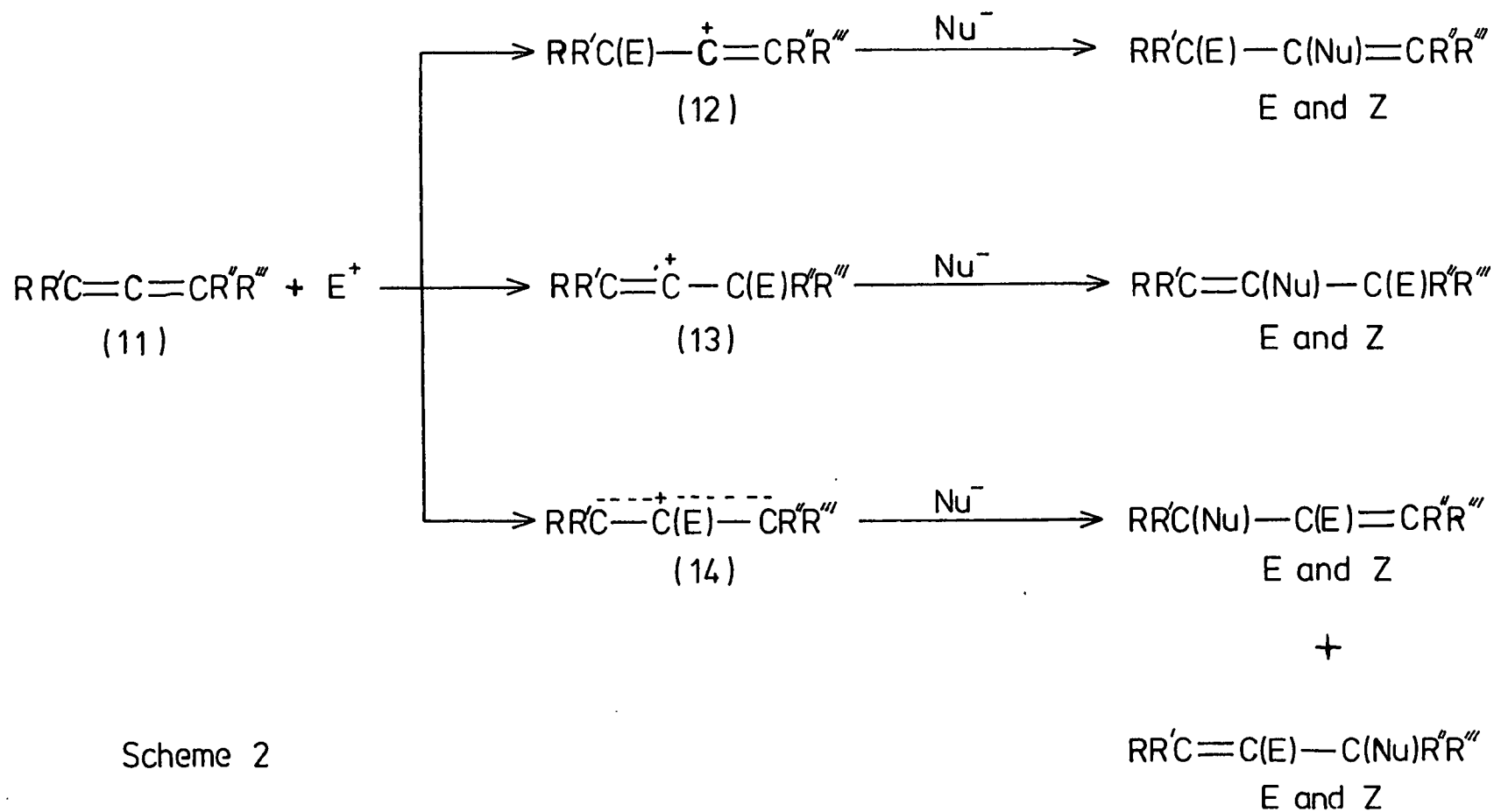


phenylacetylene.¹⁵ Similarly when $\text{R}\neq\text{R}'$ the products are always derived from the more stable vinyl cation. This is shown by the acid catalysed hydration of acetylenic ethers and thioethers (3), which gave only the corresponding esters and thioesters (5) via the vinyl cation (4), and no isomeric ketoethers and thioethers, which would result from the

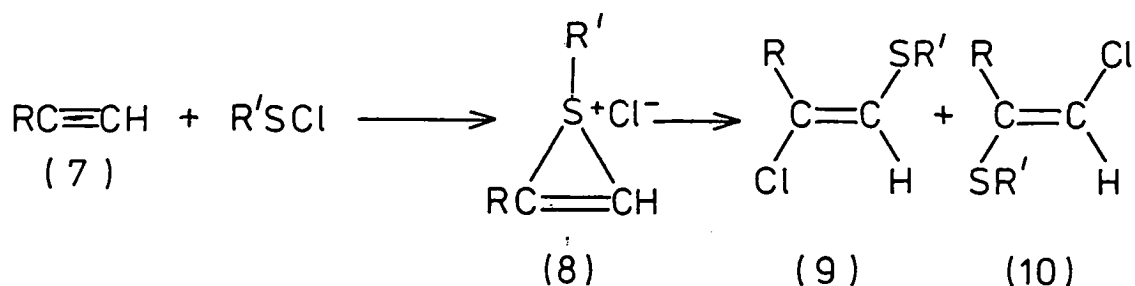


formation of cation (6).^{15,16}

Although the addition of the proton and carbenium ions proceeds via formation of a linear open vinyl cation, the addition of halogens, sulphenyl and selenenyl halides may involve formation of a bridged species. The addition of sulphenyl halides to a monosubstituted acetylene (7) produces both regio isomers (9) and (10)¹⁷ which has been taken as



Scheme 2



evidence for the intermediacy of the thiirenium ion (8), with the regiospecificity being determined by the nucleophilic ring opening of ion (8).

1.2.1.2 Electrophilic Addition to Allenes

In allenes, any of the three unsaturated carbon atoms can serve as the nucleophilic centre in electrophilic addition reactions. In unsymmetrically substituted allenes there are three possible cations (12), (13) and (14), which give rise to four possible E and Z pairs of regioisomers as shown in Scheme 2. Two vinyl cations (12) and (13) can be formed by attack at the terminal carbon atoms. Attack at the central carbon atom initially proceeds via a transition state resembling a non-resonance stabilized cation (15) in which the two

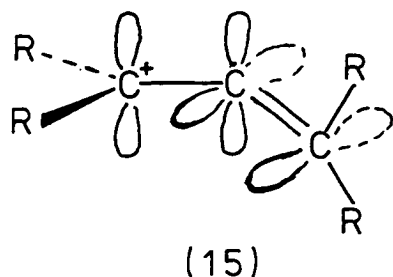
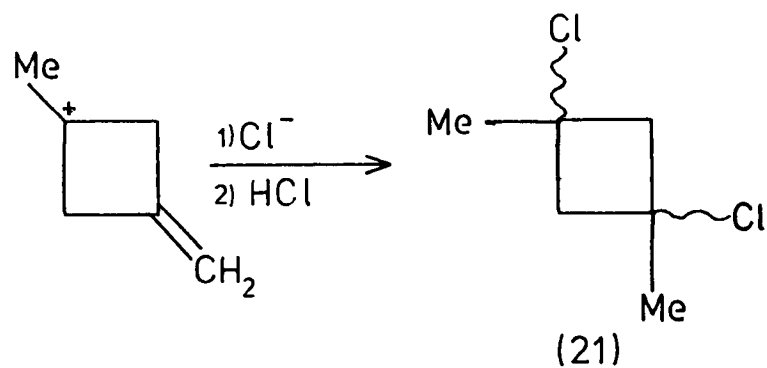
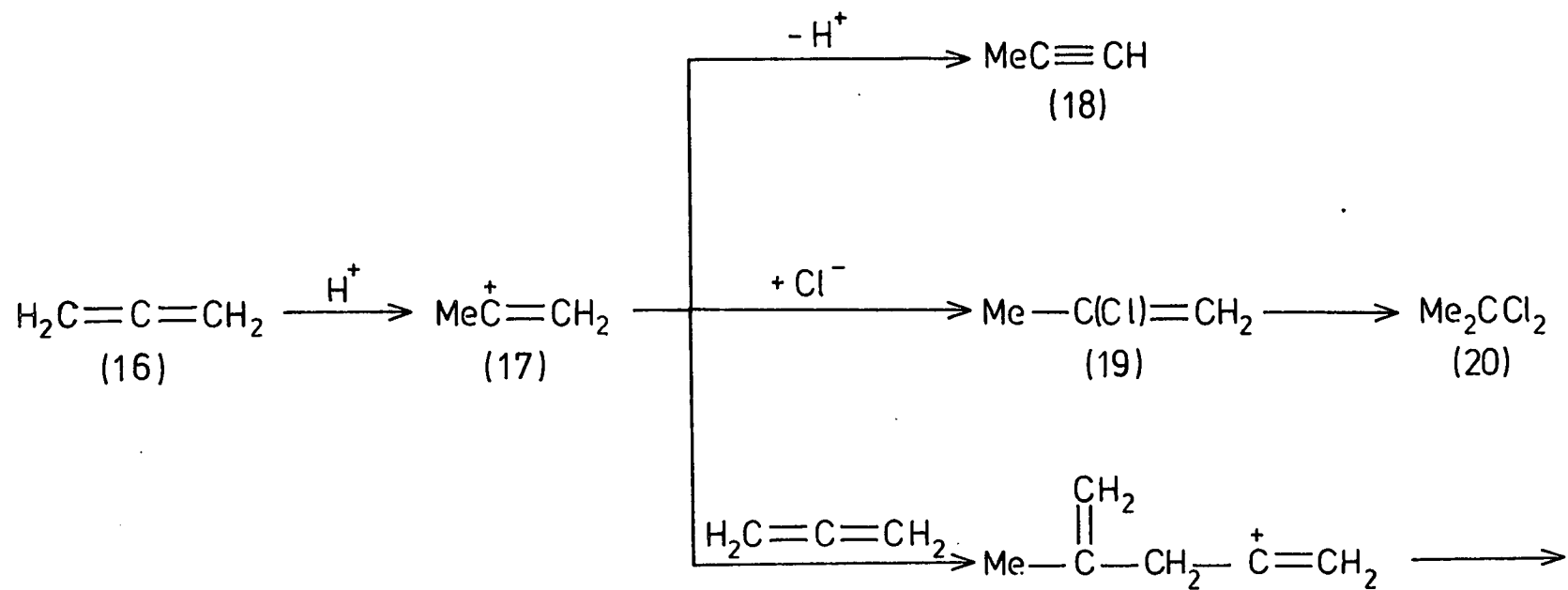


Figure 1



Scheme 3

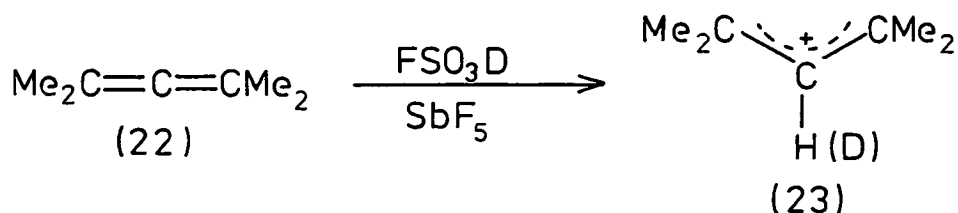
π -orbitals are orthogonal as shown in Fig.1, since the direction of attack by the electrophile, E^+ , is almost perpendicular to the double bond. Rotation by 90° about the bond linking the positively charged carbon atom to the vinyl group gives the resonance stabilized allyl cation (14).

The position of attack by E^+ , and therefore the nature of the products, depends on the relative stabilities of the transition states leading to the ions (12), (13) and (15), which are mainly determined by the nature of the substituents. When the terminal carbon atoms of allene (11) are both disubstituted, the cation (15) will be a tertiary cation and will therefore normally be formed in preference to the vinyl cations (12) and (13). For allene itself ($R, R', R'', R''' = H$) however, the ion (15) would be a primary cation and therefore attack occurs at the terminal carbon atom, resulting in formation of the more stable vinyl cation (17). In cases where (15) is a secondary cation, its stability is similar to those of ions (12) and (13) and products from attack at all positions may be observed.

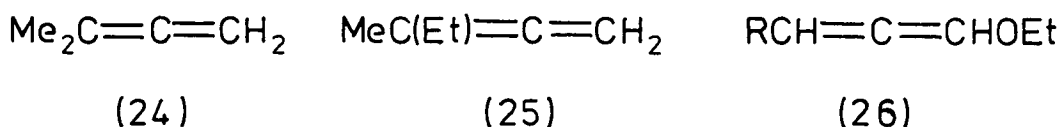
The reactions of allene (16) with hydrogen halides, either in solution¹⁸ or in the gas phase,¹⁹ gave a variety of products from the exclusive formation of the vinyl cation (17) as shown in Scheme 3. In solution,¹⁸ the Markovnikov addition products 2-chloropropene (19) and 2,2-dichloropropane (20) were formed along with both the E and Z dimers of (19), 1,3-dichloro-1,3-dimethylcyclobutane (21). In the gas phase¹⁹ (19), (20) and the rearrangement product propyne, (18), were formed with hydrogen chloride.

In contrast, protonation of tetramethylallene (22) occurs

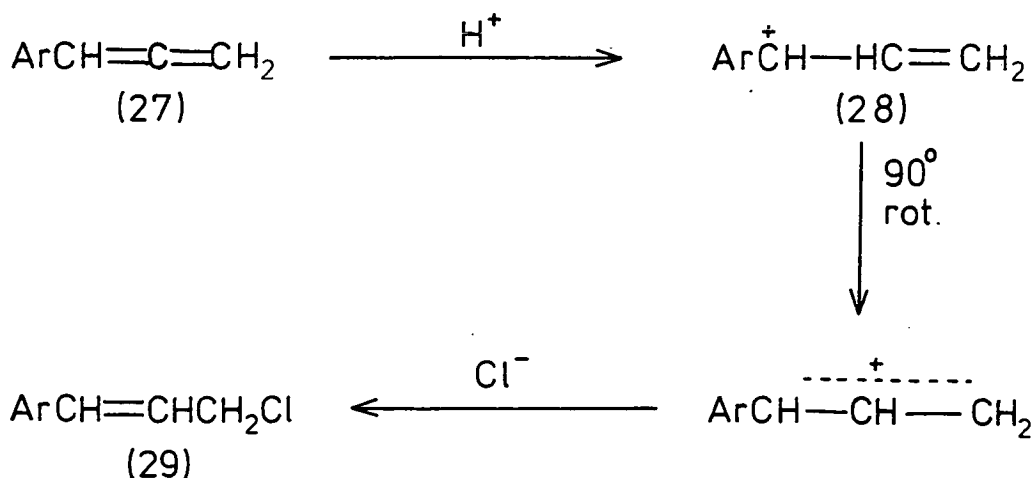
exclusively at the central carbon atom with the formation of the allyl cation²⁰ (23). The intermediate cation has also been observed at -70° by n.m.r. spectroscopy²¹ using deuterated fluorosulphonic acid and antimony pentafluoride.



Similarly, the addition of hydrogen chloride to 3-methylbuta-1,2-diene (24)²² and the addition of hydrogen bromide to 3-methylpenta-1,2-diene (25)²³ proceeded via protonation of the central carbon atom to form a tertiary ion. Acid catalysed

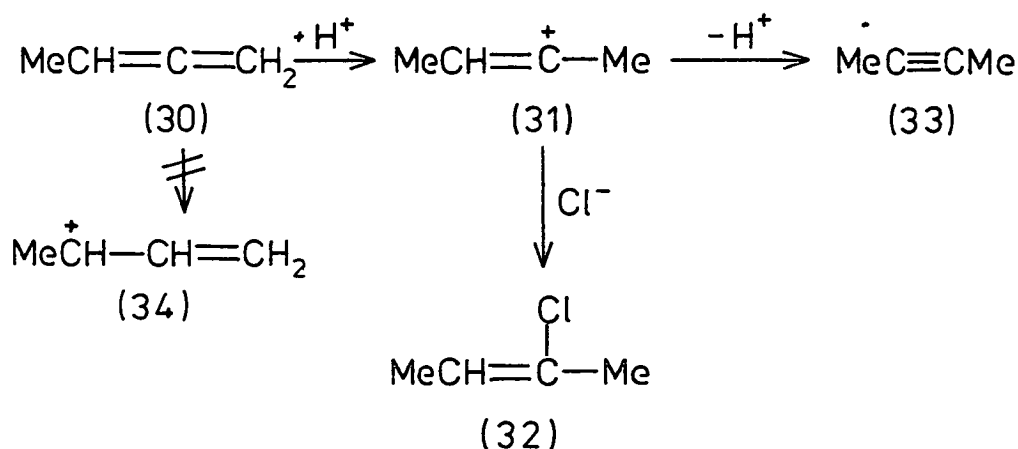


addition of water to allenyl ethers (26) also proceeded via central protonation²⁴ to give carboethoxy-allyl cations and likewise aryl-substituted allenes (27) reacted with hydrochloric acid in acetic acid to give cinnamyl chlorides²⁵ (29) through the "perpendicular allyl"-benzyl cations (28).



Protonation of penta-2,3-diene by fluorosulphonic acid²¹ occurred only at the central carbon atom, whereas addition of hydrogen bromide to other 1,3-dialkylallenes²⁶ gave mixtures of all the four possible regioisomers via central and terminal protonation.

The reaction of buta-1,2-diene (30) with hydrogen chloride gave 60% E and Z-2-chlorobut-2-ene (32) and 40% of the rearrangement product but-2-yne (33),²² all via the methyl substituted vinyl cation (31) which appeared to be more stable than the perpendicular methyl substituted allyl cation (34).



Substituents which stabilize either the perpendicular allyl or the vinyl cation strongly influence the direction of electrophilic addition to allenes.

1.2.2 Stability, Structure and Stabilization of Vinyl Cations

The structure and stability of vinyl cations determines how easily they can be formed and how they will react. When these are less stable than other intermediates or transition states, the reaction products may be obtained by alternative routes.

TABLE 1. Gas Phase Heats of Formation of Vinylic and Trigonal Cations and their Hydrocarbon Precursors

Hydrocarbon	ΔH_f° (kcal mol ⁻¹)	Cation	ΔH_f° (kcal mol ⁻¹)	Ref.
CH ₄	-17.8	CH ₃ ⁺	261	27-29
CH ₃ CH ₃	-20.1	CH ₃ CH ₂ ⁺	219	27-29
CH ₃ CH ₂ CH ₃	-25.0	CH ₃ CH ₂ CH ₂ ⁺	208	27-29
		CH ₃ ⁺ CHCH ₃	192	27-29
CH ₂ =CH ₂	12.5	CH ₂ =CH ⁺	266	28,30
CH ₃ CH=CH ₂	4.8	CH ₂ =CHCH ₂ ⁺	226	28,30
		CH ₃ C ⁺ =CH ₂	237	31
<u>Z</u> -CH ₃ CH=CHCH ₃	-1.9	CH ₃ CH=C ⁺ CH ₃	218	31,32
<u>E</u> -CH ₃ CH=CHCH ₃	-2.9			
<u>Z</u> -CH ₃ CH=CHCH ₂ CH ₃	-7.0	CH ₃ CH=C ⁺ CH ₂ CH ₃	204	31,32
<u>E</u> -CH ₃ CH=CHCH ₂ CH ₃	-7.8			
(CH ₃) ₂ C=CHCH ₃	-8.5	(CH ₃) ₂ C=C ⁺ CH ₃	202	31,32
HC≡CH	54.5			28
CH ₃ C≡CH	44.6			28
CH ₂ =C=CH ₂	45.4			28

Much effort has therefore gone into determining the stability and structure of vinyl cations and the substituents which stabilize them.

1.2.2.1 Relative Stabilities of Vinylic and Trigonal Cations

Several approaches can be used to determine the relative stabilities of vinyl and trigonal cations (R^+) relative to their hydrocarbon precursors (RH).

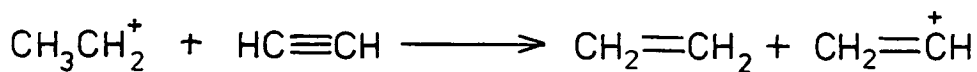
In the gas phase, mass spectroscopy and ion cyclotron resonance (I.C.R.) spectroscopy, with the appropriate thermochemical cycles, give the heats of formation (ΔH_f°) of several vinyl cations. The data for some vinylic and trigonal cations and their precursor hydrocarbons is given in Table 1 and the relative stabilities of two ions relative to their hydrocarbon precursors can be calculated by inserting the ΔH_f° values into the isodesmic hydride transfer reaction -



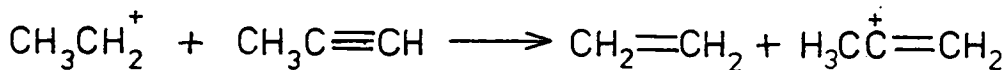
Therefore, in the gas phase, the parent vinyl cation, $CH_2=CH^+$, is $25.3 \text{ kcal mol}^{-1}$ relatively more stable than the methyl cation and $14.4 \text{ kcal mol}^{-1}$ relatively less stable than the ethyl cation. Similarly the 2-propenyl cation is comparable in stability to the 1-propyl cation but $15.2 \text{ kcal mol}^{-1}$ less stable than the 2-propyl cation. These values are for isolated molecules in the gas phase and, since energy differences of ions tend to be compressed in the liquid phase due to solvation,³³ the difference in stabilities between vinyl cations and carbenium ions in solution is likely to be even smaller.

The slow solvolysis rates of vinylic compounds was considered to indicate the low relative stability of vinyl cations. This interpretation has been disputed by H. Mayr *et al.*³⁴ who calculated that the *t*-butyl and 1-phenylvinyl cations have similar thermodynamic stabilities, although *t*-butyl bromide³⁵ solvolysed 10^{10} times faster than 1-bromostyrene.³⁶ This fact was attributed³⁴ to the transition states in vinyl solvolysis reflecting the energies of the fully developed ions to a much smaller extent than do transition states in alkyl solvolysis. Therefore vinyl cations are formed more slowly than trigonal cations of similar thermodynamic stability. Thus, kinetic data more truly reflect the relative stabilities of the transition states leading to the cations, and not necessarily the cations themselves.

The data in Table 1 indicate that proton addition to alkynes and to alkenes is energetically comparable. This is



$$\Delta H^\circ = 5.0 \text{ kcal mol}^{-1}$$

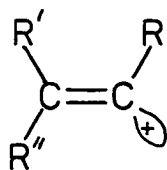


$$\Delta H^\circ = -14 \text{ kcal mol}^{-1}$$

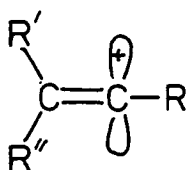
due to the higher ground state energy of alkynes compared to alkenes offsetting the higher energy of the vinyl cations and therefore making vinyl cations more accessible.

1.2.2.2 Structure of Vinyl Cations

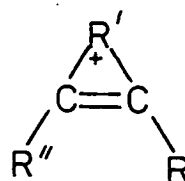
In order to determine the structure of vinyl cations, three types of structures must be considered. These are the "bent" ion (35), the linear ion (36) and the bridged species (37).



(35)

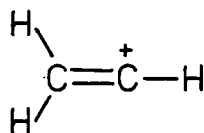


(36)

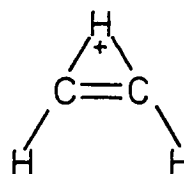


(37)

Many calculations have been performed on the parent vinyl cation with the main question being whether the ion has the linear structure (38) or the bridged structure (39), the bent ion being excluded since it was found by all calculations to be the least stable.



(38)



(39)

Early calculations gave conflicting results with some favouring the open ion (38)³⁷⁻⁴² and others favouring the bridged structure.⁴³⁻⁴⁵ However recent calculations have included configurational interaction and, when correlation energy was included, it was found that the bridged ion (39) is slightly more stable than the linear ion (38)⁴⁶⁻⁴⁹ with a very small barrier of ca. 2 kcal mol⁻¹ to interconversion

TABLE 2. Calculated Bond Lengths and Bond Angles⁴⁶ for the Open (38) and Bridged (39) Parent Vinyl Cation

Structural feature	Open	Bridged
$C_1 = C_2$	1.263Å	1.210Å
$C_1 - H_1$	1.075Å	1.276Å
$C_2 - H_2$	1.086Å	1.074Å
α	180°	179.1°
β	119.9°	61.7°

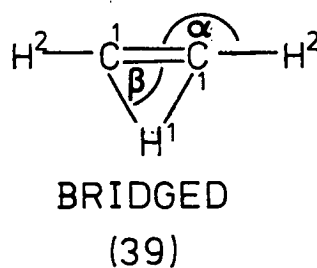
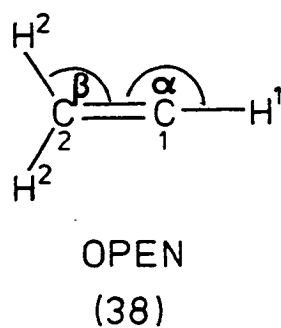


TABLE 3. Calculated Charge Distributions⁴⁶ for the Open (38) and Bridged (39) Parent Vinyl Cation

Charge/atom	Open	Bridged
C_1	0.307	0.050
C_2	-0.237	
H_1	0.308	0.271
H_2	0.311	0.314

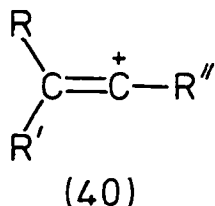
between the two.

The calculated bond lengths and angles for both the linear (38) and bridged (39) parent vinyl cations are given in Table 2 and the calculated charge distributions are given in Table 3. The geometries of both (38) and (39) were found to be planar with C_{2v} symmetry in their most stable conformation. The calculated C=C bond length for the open ion (38) is between those of ethylene ($1.330\text{\AA}$)⁵⁰ and acetylene ($1.203\text{\AA}$)⁵¹ and the C-(1), H-(1) bond length is close to that in ethylene ($1.076\text{\AA}$)⁵⁰ although the C-(2), H-(2) bonds are somewhat longer. The calculated C=C bond length for the bridged ion (39) is close to that of acetylene but the C-(1), H-(1) bonds are considerably longer than normal C-H bonds, suggesting that ion (39) resembles a π -complexed protonated acetylene.

The calculated charge distributions shown in Table 3 show that in both structures (38) and (39) the charge is largely distributed on the hydrogen atoms with a slight negative charge on C-(2) of structure (38).

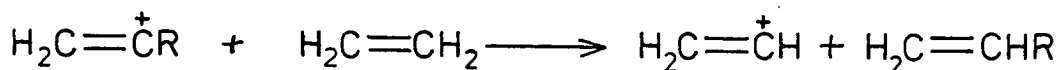
The effect of solvation on the preferred geometry is likely to be significant⁵² and therefore it is not possible to predict with confidence the preferred geometry in solution.

For substituted vinyl cations both calculations and experimental data predict the linear ion structure (40).^{34,53,54}



1.2.2.3 Stabilization of Vinyl Cations by Substituents

The effects of substituents on the stabilities of vinyl cations have been calculated at two levels of approximation (ST0-3G and 4-31G). The relative energies of some 1- and 2-substituted ions were compared by means of the isodesmic hydride transfer reactions

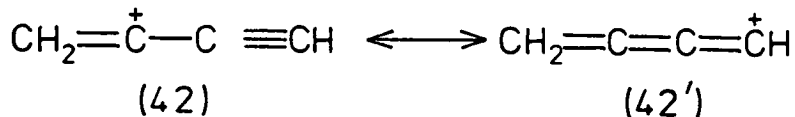
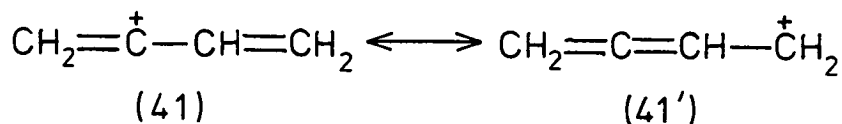


for substitution at C-(1) and



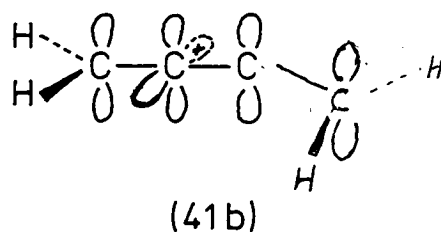
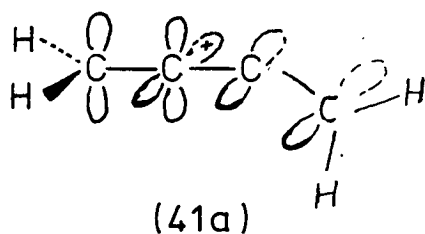
for substitution at C-(2). The results compare the relative stabilities of the substituted vinyl cations with that of the parent vinyl cation and are summarized in Table 4. A positive value indicates greater stabilisation by the substituent, relative to hydrogen, in the cation than in the corresponding alkene. From Table 4 it can be seen that all the C-(1) substituents listed stabilize the vinyl cation and in the gas phase their effectiveness follows the order $\text{Ph} \gg \text{cyclopropyl} \approx \text{CH}=\text{CH}_2 \gg \text{C}\equiv\text{CH} \approx \text{Me} \gg \text{H}$.

Both the $\text{HC}=\text{CH}_2$ and $\text{C}\equiv\text{CH}$ groups possess π electrons which can stabilize the cationic centre by allylic type conjugation as shown by $(41) \leftrightarrow (41')$ and $(42) \leftrightarrow (42')$.



However the triple bond in (42) provides much less stabilization than the double bond in (41) and this has been attributed to a destabilizing σ -withdrawal cancelling out the stabilizing π -conjugation⁵⁵ and therefore giving the ethynyl group only the same stabilizing ability as the methyl group.

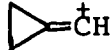
Delocalization of the positive charge into the ethenyl group in (41) is only possible when the interaction between the empty p -orbital and the HOMO of the substituent is maximised i.e. when the empty p -orbital and the p -orbitals of the substituent are coplanar as in (41a). This conformation is found

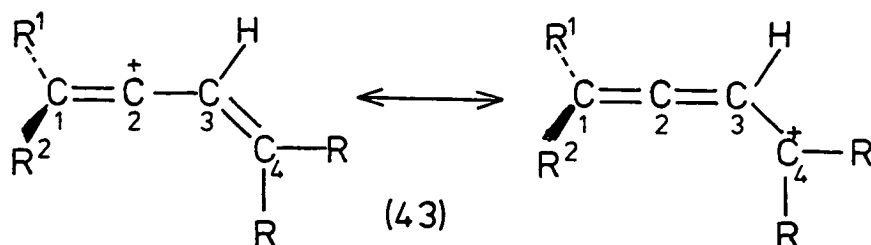


to be 22 kcal mole⁻¹ more stable than the alternative conformation (41b).⁵⁵ It has also been shown that methyl substituents on the C-(4) position of ion (43) give additional stabilization.⁵⁹ This is caused by the electron donating effect of the methyl groups on the electron deficient C-(4). In fact ions of this type (43, R=Me) are sufficiently long lived at

TABLE 4. Calculated Relative Stabilization Energies^a in kcal mol⁻¹ for 1- and 2-Substituted Vinyl Cations $\text{H}_2\text{C}=\dot{\text{C}}\text{R}$ and $\text{RHC}=\dot{\text{C}}\text{H}$

Substituent	Substitution at C-(1) ⁵⁵		Substitution at C-(2)	
	STO-3G	4-31G	STO-3G	4-31G
R				
H	0.0	0.0	0.0	0.0
Me	25.9	25.2	12.8	10.9 ⁵⁶
$\text{CH}=\text{CH}_2$	41.0	39.5		
$\text{C}\equiv\text{CH}$	27.9	25.1		
	41.7	42.5	35.0 ^b	33.7 ^{b 57}
Ph	60.1		18.0 ⁵⁸	

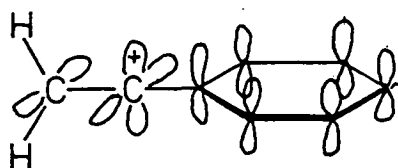
a) Using the most stable conformation of each cation. b) for 



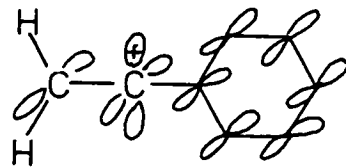
-120° to allow direct spectroscopic observation.⁶⁰

The ability of cyclopropyl and phenyl rings to stabilize a carbenium ion is well known⁶¹ although there have been disputes as to the relative stabilization provided by the two rings. I.C.R. data⁶² indicates that, in the gas phase, the phenyl group gives more stabilization than the cyclopropyl group to primary and secondary carbenium ions, whereas in solution, conflicting results are obtained.^{55,61} For vinyl cations the gas phase data in Table 4 indicates that the phenyl group provides 18.4 kcal mol⁻¹ more stabilization than the cyclopropyl group. However, in solution the reverse appears to be true, since 1-cyclopropylvinyl cations are formed 500 times faster than 1-phenylvinyl cations.⁵⁵ This discrepancy is probably due to the preferential solvation of the smaller and less polarisable 1-cyclopropylvinyl ion compared to the 1-phenylvinyl cation.⁶³

The stabilizing effect of both these groups arises from the interaction of the empty p-orbital with the HOMO of the ring. As for the ethenyl group, the phenyl and cyclopropyl groups must be orientated to allow maximum interaction. The conformation of the 1-phenylvinyl cation (44a), which allows maximum interaction of the empty p-orbital and the HOMO of the ring, is calculated to be 25 kcal mol⁻¹ more stable than conformation (44b).⁵⁵ For 1-cyclopropylvinyl cations, both

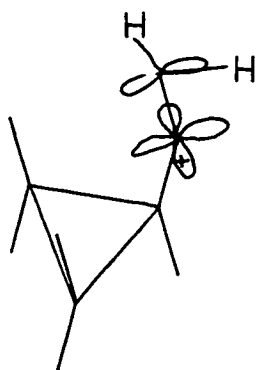


(44a)

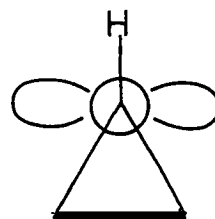


(44b)

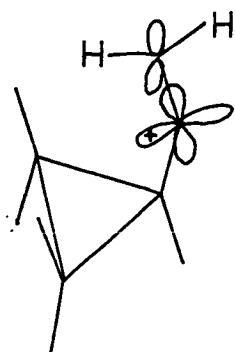
simple Huckel M.O.⁶⁴ and ab initio⁵⁵ calculations predict that the so-called bisected conformation (45a) is more stable than the perpendicular conformation (45b), as is found in the cyclopropylcarbiny system. The energy difference between (45a) and (45b) is calculated⁵⁵ to be 16 kcal mol⁻¹.



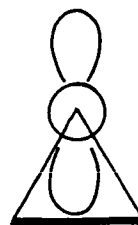
≡
(45a)



bisected



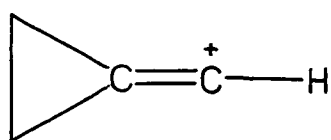
≡
(45b)



perpendicular

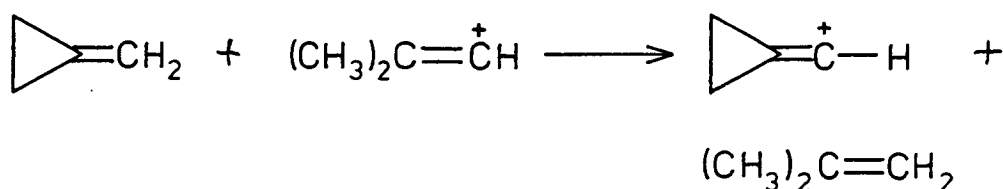
The effect of substitution on the 2-position of vinyl cations is much less marked than for substitution at the 1-position (see Table 4). However, where C-(2) of the vinyl structure is part of a cyclopropane ring a very stable

cyclopropylidenemethyl cation (46) is obtained. This was



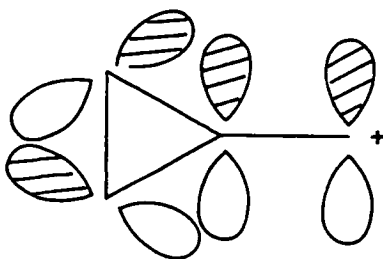
(46)

calculated to be 30-35 kcal mol⁻¹ more stable than the parent vinyl cation⁵⁷ and the increased stabilization afforded by the cyclopropane ring compared with two methyl groups is shown by the isodesmic hydride transfer reaction.⁵⁷

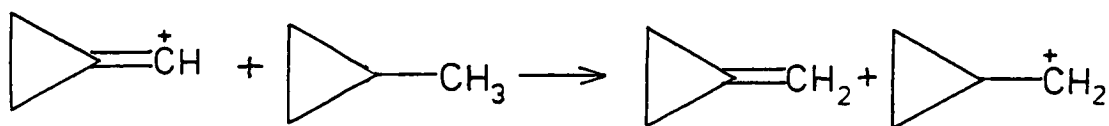


$$\Delta H^\circ = 14 \text{ kcal mol}^{-1}$$

The high stability of this primary cation arises from its special geometry which maximises the hyperconjugative interaction between the empty p-orbital and the asymmetric Walsh orbital of the β -cyclopropane ring. Vinyl cations are



generally less stable than their corresponding alkyl cations by 12-17 kcal mol⁻¹. This is not the case when comparing ion (46) with its corresponding alkyl cation (47). In fact STO-3G calculations⁵⁷ indicate that reaction (a) is almost thermoneutral, implying very similar relative stabilities.



reaction (a)

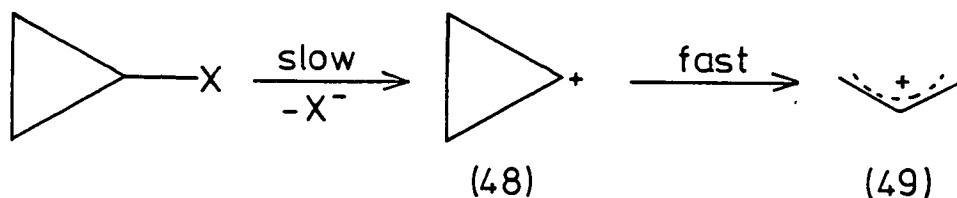
The observed reaction rates for the solvolysis of cyclopropylidenemethyl bromides⁶⁵ are in accordance with the high stability of the intermediate cations formed.

1.3 Cations from Cyclopropane Derivatives

It has been known for some time that formation of cations from cyclopropane derivatives results in the formation of ring opened products following a cyclopropyl-allyl rearrangement. Most of the information available on this cyclopropyl-allyl rearrangement has been obtained from studies on the solvolysis of cyclopropane derivatives, mainly involving the measurement of reaction rates and product distributions, and has recently been reviewed.^{66,67}

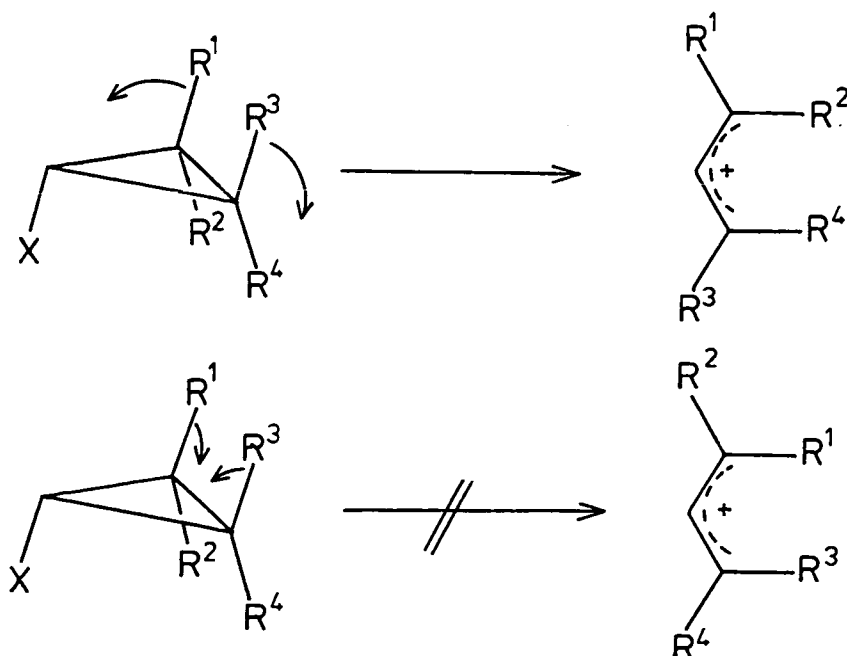
1.3.1 Mechanism of Solvolysis of Cyclopropane Derivatives

Cyclopropanes normally undergo nucleophilic substitution reactions to give allyl derivatives rather than direct substitution products. This was once believed to proceed via a two-stage mechanism,³ slow ionisation to form a cyclopropyl cation (48), followed by rapid ring opening to form the allyl cation (49). Numerous studies on the kinetics^{68,69} and quantum chemistry⁷⁰ of the solvolysis of cyclopropane derivatives have shown that it involves concerted ring opening and



anion abstraction. Woodward and Hoffmann's rules⁷¹ on the conservation of orbital symmetry predict that ring openings of cyclopropyl cations to allyl cations will occur in a disrotatory fashion. It has been shown⁷² that, in the parent ion, ring opening and rotation of the methylene groups occurs simultaneously with the central angle increasing from 60° to 120° and the molecular σ -orbitals of the terminal groups gradually becoming atomic p-orbitals. Although the most advanced ab initio calculations^{70,72} agree on the structure of the allyl C_3H_5^+ cation, they disagree on the properties of the isomeric cyclopropyl cation. The 6-31G basis⁷⁰ calculations found that the cyclopropyl cation does not represent a minimum on the energy surface, but the SCF method⁷² calculated a shallow minimum.

The two possible disrotatory ring openings of the cyclopropane are not equivalent and calculations by the extended



Hückel method^{73,74} have shown that the substituents cis to the leaving group rotate inwards and those trans to it move outwards regardless of the configuration. This result can be understood in terms of the concerted breaking of the C-(2), C-(3) bond and displacement of the leaving group X. In this disrotatory opening of the ring (Fig.2) the electron density of the C-(2), C-(3) bond, which was initially in the plane of the ring, moves above the plane and is therefore available for

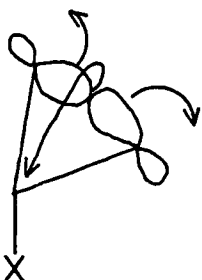


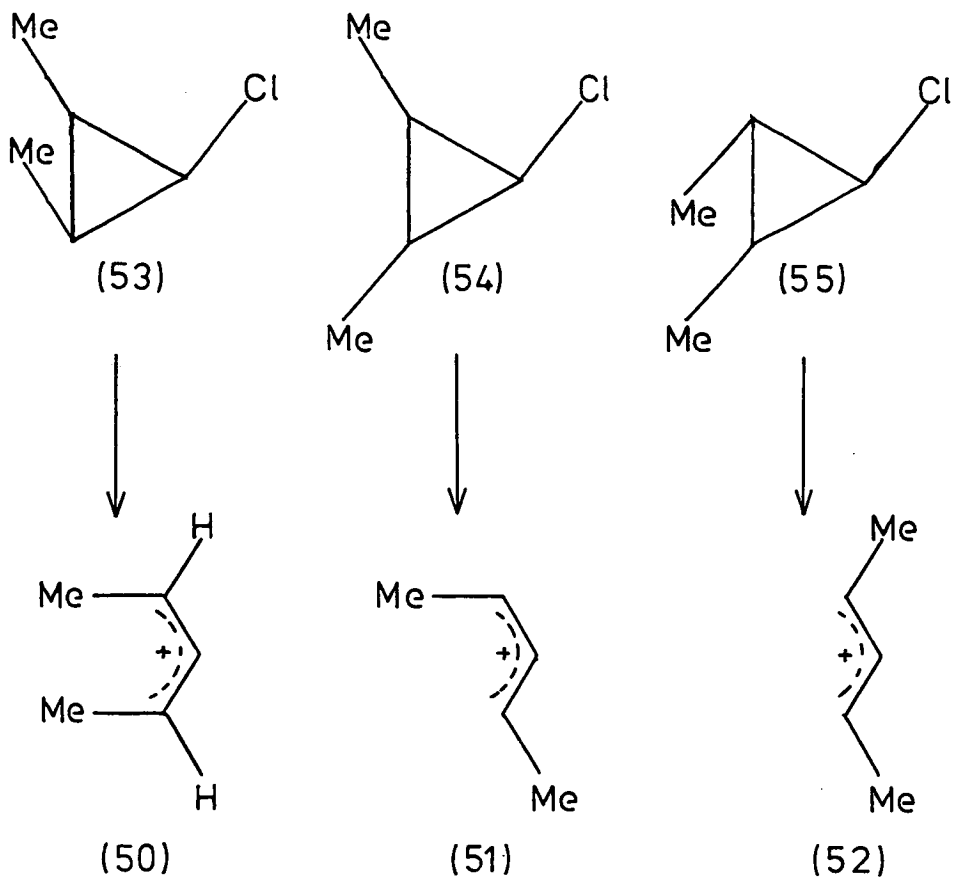
Figure 2

backside displacement of the leaving group. This makes the reaction a normal S_N2 displacement of the group X by the electrons in the C-(2), C-(3) σ -bond.

This disrotatory pathway has been confirmed by direct observation,⁷⁵ at -100° by ^1H n.m.r. spectroscopy of the three individual 1,3-dimethylalkyl cations (50), (51) and (52) from the isomeric 2,3-dimethylcyclopropyl chlorides (53), (54) and (55) respectively. This confirms the stereospecificity of the ring opening and the formation of only one allyl cation from each cyclopropyl chloride rules out the existence of the cyclopropyl cation as an intermediate since its disrotatory ring opening would give the least sterically hindered allyl cation possible. Study of the kinetics of solvolysis of cyclopropyl derivatives also confirms the synchronous nature of ionisation with ring opening.^{73,76}

TABLE 5. Relative Rates of Acetolysis at 100° for some
Monocyclic Cyclopropyl Tosylates

Substituents	Relative Rate	Reference
None	1.0	
1-Methyl	310	77
<u>cis</u> -2-Methyl	5.7	77
<u>trans</u> -2-Methyl	138	77
<u>cis</u> -2-tert-Butyl	5.0	69
<u>trans</u> -2-tert-Butyl	330	69
2,2-Dimethyl	430	77
<u>cis</u> -2- <u>trans</u> -3-Dimethyl	460	77
<u>cis</u> -2- <u>cis</u> -3-Dimethyl	2.2	77
<u>trans</u> -2- <u>trans</u> -3-Dimethyl	38000	77
2,2- <u>cis</u> -3-Trimethyl	83	77
2,2- <u>trans</u> -3-Trimethyl	44700	77
2,2,3,3-Tetramethyl	7450	77



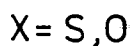
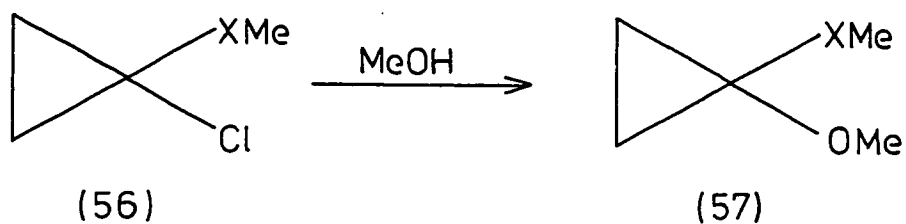
Since the preferred mode of ring opening of cyclopropyl derivatives is trans-out, cis-in disrotatory, cis and trans substituted derivatives will have different reactivities depending on the steric hinderance to formation of the allyl cation. The data in Table 5 shows that, where the 2-substituents are cis to the leaving group the reaction rates are considerably lower than where the substituents are trans. The larger the substituent, the larger the ratio $k(\text{trans})/k(\text{cis})$ and similarly the more substituents cis to the leaving group, the larger the steric hinderance to allyl cation formation.

The observation that the rates of solvolysis of cyclopropyl derivatives increases with 1-methyl,⁷⁷ 1-phenyl,⁷⁸ 2-methyl,^{69,77} 2-phenyl,^{78,79} 2-vinyl^{80,81} and 2-cyclopropyl⁸¹ substituents, implies that, in the transition state, the charge

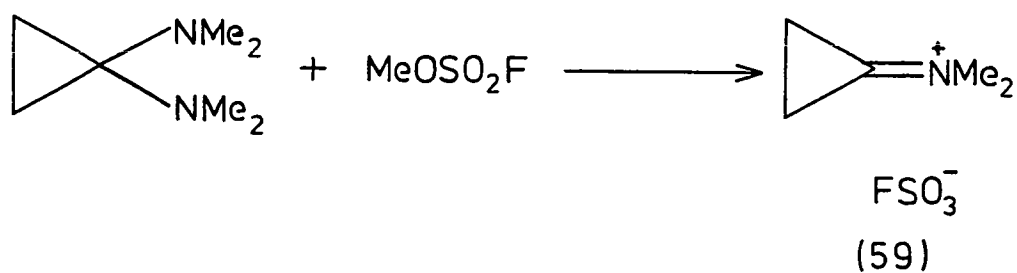
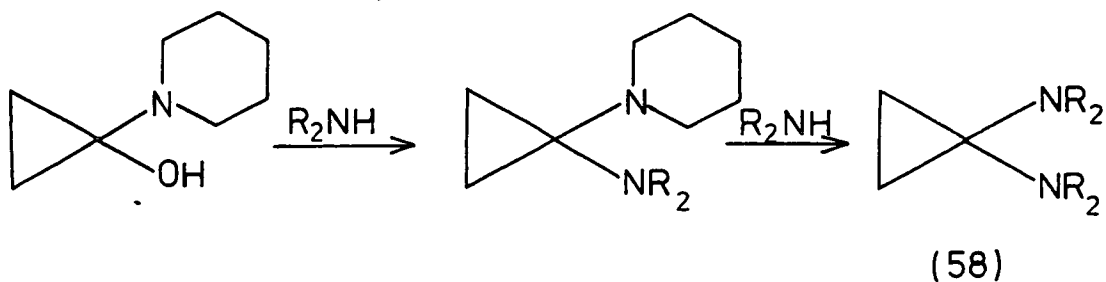
is dispersed over all three carbon atoms and therefore ionisation must be accompanied by ring opening. The 1-phenyl substituent stabilizes the developing positive charge more effectively than the 1-methyl group. However, solvolysis reactions of 1-arylcyclopropyl tosylates were highly sensitive to the introduction of substituents into the aromatic ring.⁷⁸ This led Schleyer *et al.*⁶⁹ to suggest that the transition state has a structure close to that of a cyclopropyl cation, which can be stabilized very effectively by the aryl group. This was supported by the solvolysis of 1-phenylcyclopropyl tosylate in the presence of sodium borohydride,⁸² which gave phenylcyclopropane as well as the ring opened product, 2-phenylprop-2-ene, and therefore the borohydride anion was "capturing" the 1-phenylcyclopropyl cation before it could isomerise.

Although different calculations^{74,83-85} agree that the cyclopropyl cation is considerably less stable than the parent allyl cation, MINDO/2 calculations⁸⁶ find the cyclopropyl cation to be more stable than the allyl cation. However, this is probably the result of the MINDO/2 tendency to over-estimate the stability of cyclic molecules. Calculations using the STO-3G method⁸⁷ find that substituents such as amino and hydroxyl on the central carbon atom make the cyclopropyl cation more stable than the isomeric allyl cation.

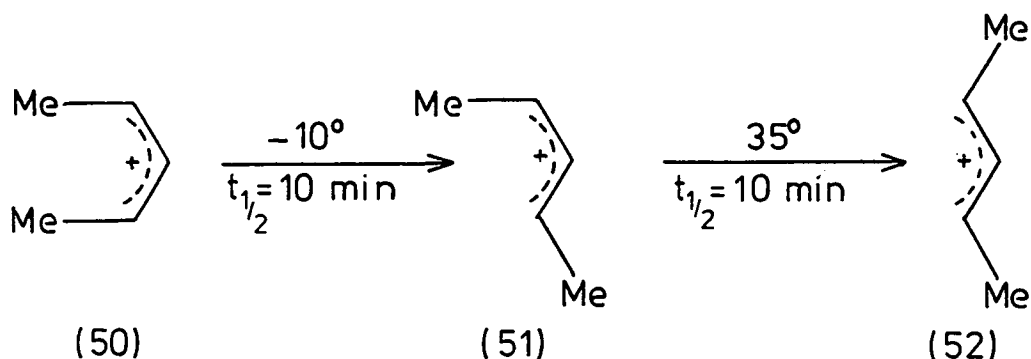
The predicted^{87,88} increased stability of the cyclopropyl cations over the allyl cations from 1-hydroxy- and 1-amino-substituted cyclopropanes is borne out by experimental evidence. The solvolyses of cyclopropyl-1-sulphides and ethers (56)⁸⁹ give the ring-retained products (57) with reaction kinetics indicating an S_N1 mechanism. Methyl substituents in the



2-position of (56) promote ring opening to the allyl cation presumably because they have a larger stabilizing effect on the allyl cation than on the cyclopropyl one.⁸⁹ Conversely, dialkylamino groups at C(1) stabilize the cyclopropyl cation very effectively and the ring-retained products (58) and (59) have been observed.^{90,91}

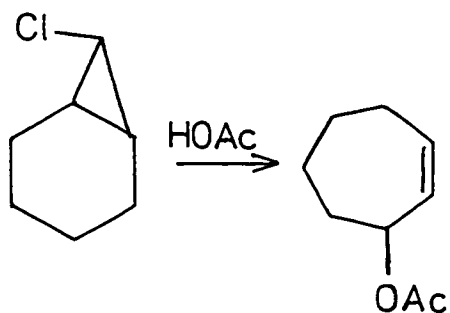


Care must be taken in using product distributions from solvolysis reactions of cyclopropane derivatives to elucidate the mechanism. Often, products can interconvert under the conditions of solvolysis. Ions also can interconvert and Scheyer *et al.*⁷⁵ found that ion (50) was converted to (51) at -10° ($E_a = 17.5 \text{ kcal mol}^{-1}$) and ion (51) was converted to (52) at 35° ($E_a = 24.0 \text{ kcal mol}^{-1}$). However the

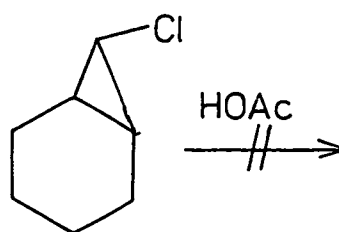


direct n.m.r. observation of the first formed ions from solvolysis of the isomeric 2,3-dimethylcyclopropyl chlorides (see p.20) shows that ring opening does occur by the cis-in, trans-out disrotatory mode described earlier.

As well as the study of the mechanism of ring opening using monocyclic cyclopropane derivatives, there has been a significant, but not as extensive study of ring openings of bicyclic compounds of the [n.1.0] type. The discovery⁷³ that 1-phenyl-exo-7-tosyloxybicyclo[4.1.0]heptane was resistant to acetolysis was part of the evidence leading to the "cis-in, trans-out" rule. The observation that endo-7-chlorobicyclo[4.1.0]heptane (60) undergoes acetolysis at 125° whereas the exo-isomer (61) shows no reaction after 2h at 210° in the presence of silver acetate,⁷⁶ is further evidence for this rule.

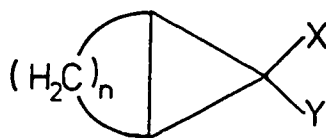


(60)

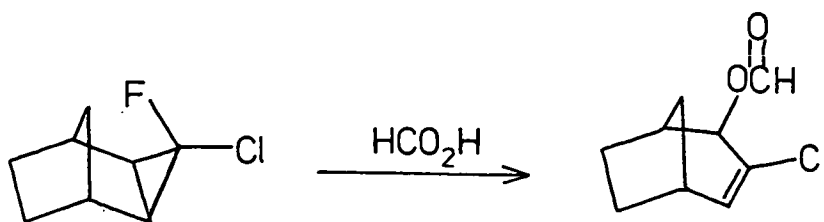


(61)

The energy difference between the solvolyses of exo and endo isomers of bicyclic compounds, where n is small, can be large enough to force solvolysis of a fluoride ion in



preference to the weaker chloride bond, as demonstrated by the solvolysis of cyclopropane (62).⁹² However, the



(62)

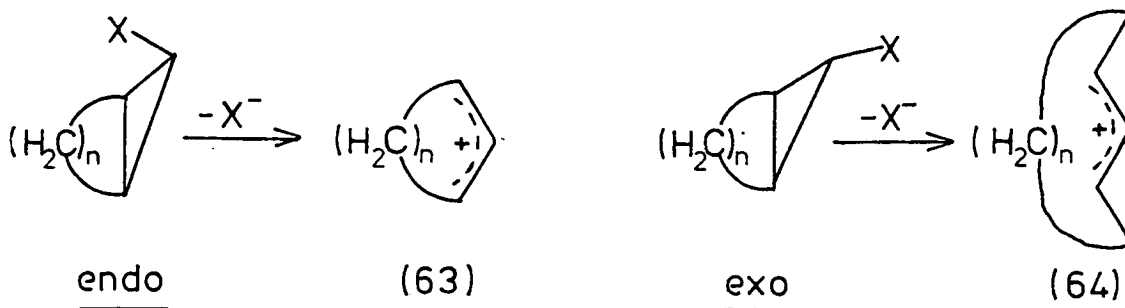
elimination of an endo leaving group is difficult in bicyclic systems with large rings, and it has been shown in several systems where $n=5,6$ that the exo-isomers are more reactive.⁹³⁻⁹⁵ Table 6 shows that the ease of opening of a three membered ring at the C-(1), C-(n+1) bond in derivatives of bicyclo[n,1,0] alkanes depends on the value of n. The reason for this is believed⁹⁴ to be that, for low values of n, the only possible mode of ring opening gives the cis-

TABLE 6.

Relative Rate Constants (k_{rel}) for the Acetolysis of endo and exo Bicyclo[n,1,0]alkyl Tosylates.⁹⁴

n	0	3	4	5	6
<u>endo</u>	1	2500	62	3.1	3.5
<u>exo</u>	1	0.01	1.7	2500	10000

allyl cation (63) since the trans cation (64) is too strained, therefore the endo isomer will react more rapidly. The strain in the trans cation (64) diminishes on increasing n and therefore the reactivity of the exo isomer is increased.



Thus, with small n values the disrotatory opening of the cyclopropane ring in a bicyclic system takes place with elimination of the endo leaving group, in contrast to the solvolysis of monocyclic cyclopropanes. With increase in n , this specific feature diminishes.

1.3.2 Reactions of Allyl Cations

Allyl cations, once formed, can undergo nucleophilic addition or deprotonation to give olefinic products or $[2+4]\pi$ -electron cycloaddition reactions. The last named reactions, where the allyl cations react with 1,3-dienes to give seven membered rings, have been reviewed by Hoffmann^{96,97}

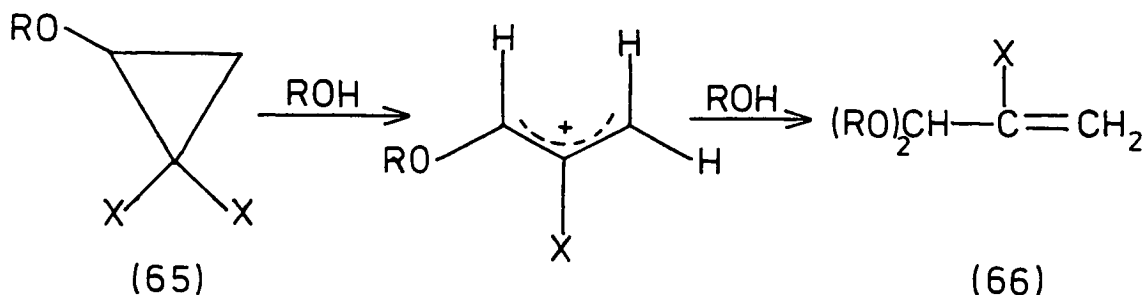


and are not covered here.

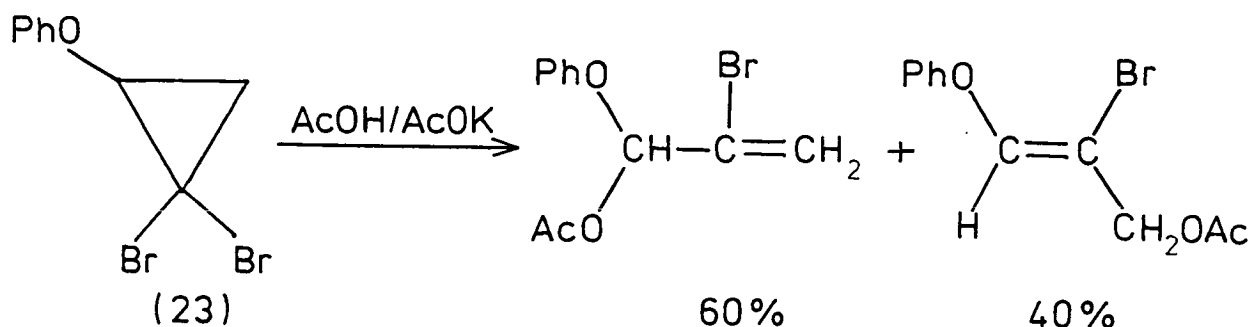
The reactions of allyl cations to give olefinic products can be controlled by either the charge distribution in the

substituted allyl cation or the stability of the olefin formed.

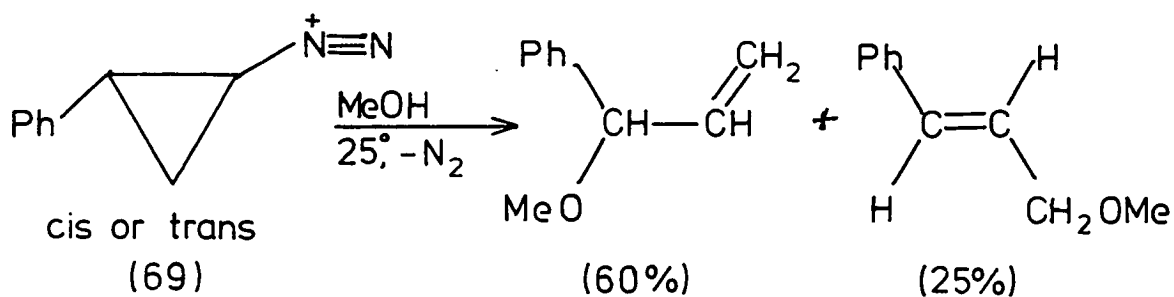
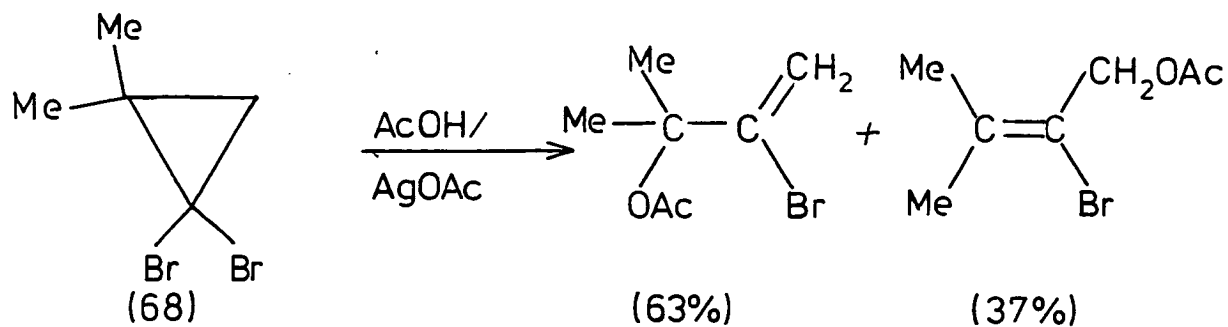
The solvolysis of 2-alkoxy-1,1-dihalogenocyclopropanes (65) results in the formation of acetals of 1-halogenoacroleins (66).^{82,98,99} Since the second alkoxy group adds at the



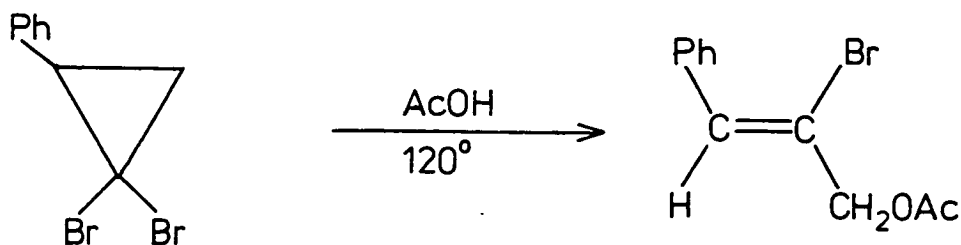
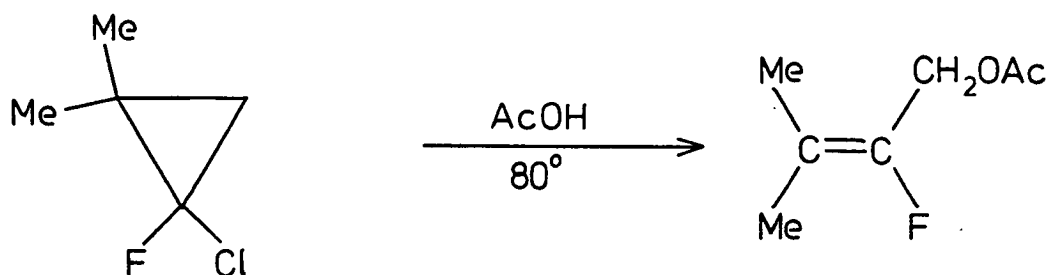
carbon atom bearing the original alkoxy group, the positive charge is principally localised at that position. The phenoxy group gives less effective stabilization of the positive charge due to the conjugation of the lone electron pair of the oxygen atom with the aromatic ring and this was seen in the solvolysis of 2-phenoxy-1,1-dibromocyclopropane¹⁰⁰ (67), which gave addition at both terminal carbon atoms of the allyl cation.



Charge distribution also appears to govern the solvolysis of the dimethylcyclopropane¹⁰¹ (68) and the phenylcyclopropane¹⁰² (69).

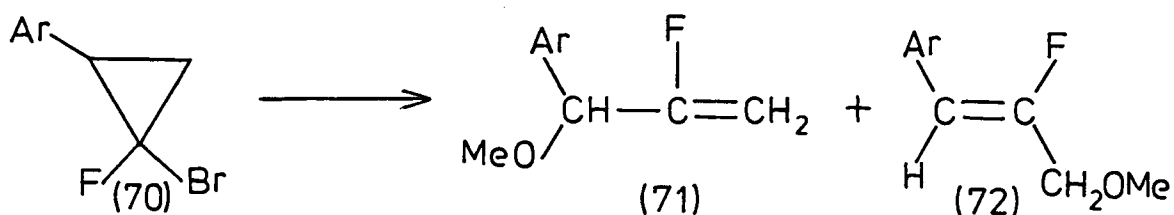


However, in many cases the structure of the products of the solvolysis of alkyl¹⁰³ and phenyl¹⁰¹ substituted dihalogenocyclopropanes is inconsistent with the charge distribution in the allyl cation. It would appear that the



factor determining the structure of the products in these cases is the stability of the olefin formed.

It has been shown¹⁰⁴ that, under kinetically controlled reaction conditions, the products of 2-aryl-1,1-dihalogenocyclopropanes (70) will be predominately olefins with a terminal methylene group. The degree of localisation of the

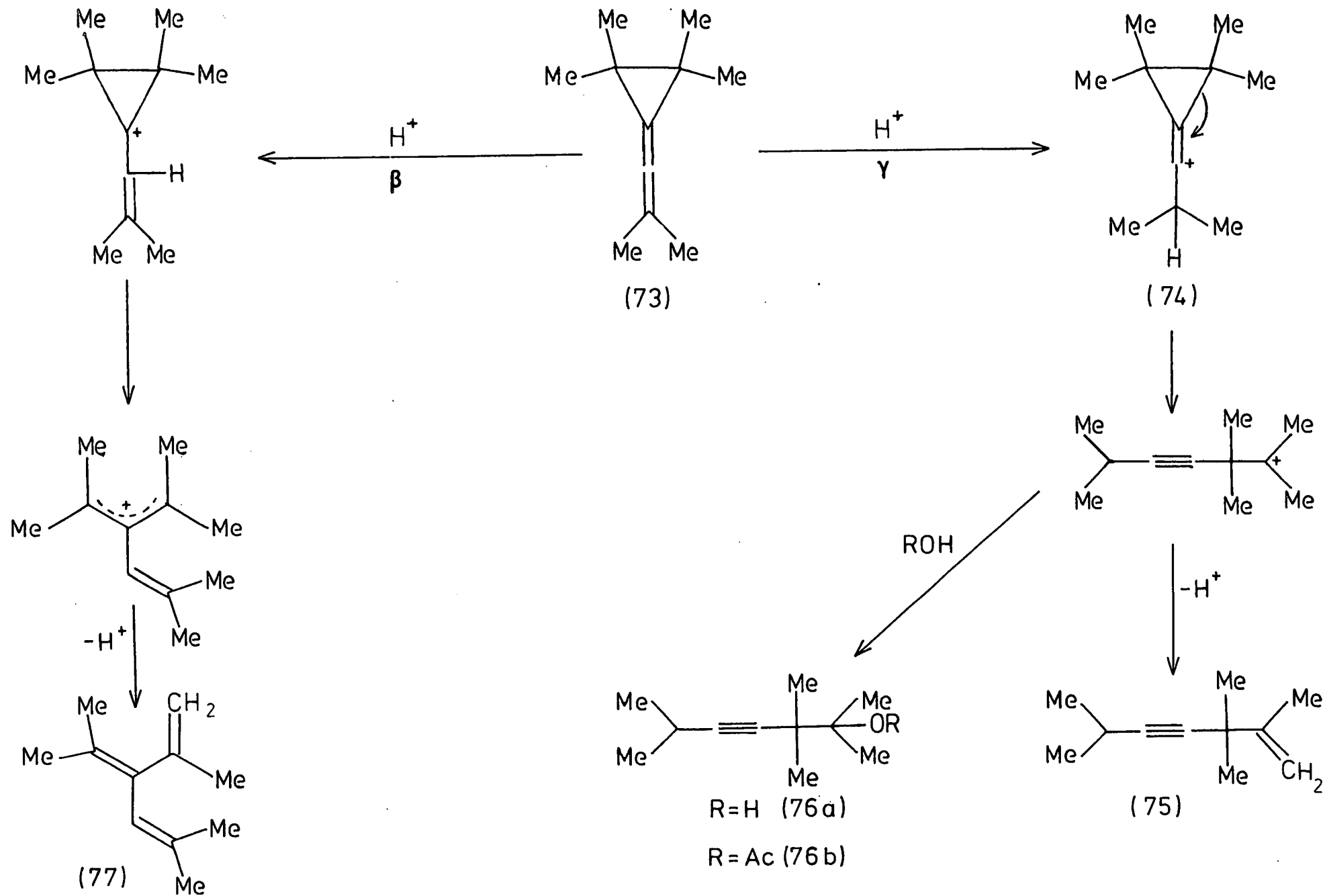


Ar	C_6H_5	$p\text{-CH}_3\text{C}_6\text{H}_4$	$m\text{-CH}_3\text{C}_6\text{H}_4$	$p\text{-BrC}_6\text{H}_4$	$m\text{-BrC}_6\text{H}_4$
(71)/(72)	2.5	4.0	3.5	2.0	1.5

charge on each of the terminal carbon atoms of the allyl cation, which was determined by the nature of the substituent, determined the product ratios. The observed predominance of (71) over (72) suggests that the charge is concentrated at the benzylic carbon atom. The increase in the ratio of (71)/(72) with the introduction of electron-donating substituents into the aromatic ring and the decrease in the ratio of (71)/(72) when electron acceptors were introduced was expected.

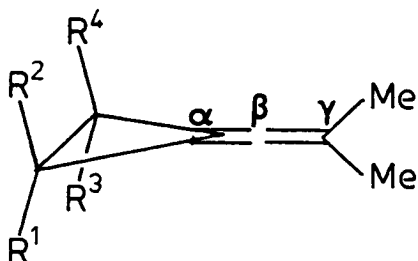
Under thermodynamically controlled reaction conditions the most stable olefin is produced. This results in the predominance of olefins where the double bond is conjugated to the aromatic group, or those with the most substituted double bond.

In most cases solvolysis of arylcyclopropanes^{73,78,101,105} has given only styrene type products, which must be attributed to the fairly severe reaction conditions ($\geq 100\text{-}120^\circ$, 20-40h) employed.



1.4 Protonation of Vinylidenecyclopropanes

Vinylidenecyclopropanes, as all allenes, can undergo electrophilic addition at one or more of the three unsaturated sites, α , β and γ . Since tetrasubstituted allenes normally

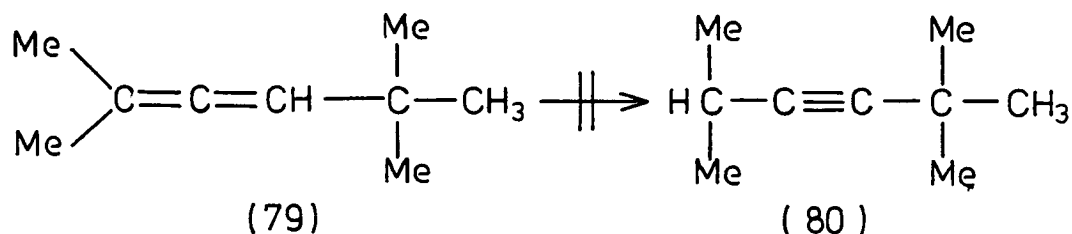


undergo electrophilic addition at the central (β) carbon atom, it might be expected that vinylidenecyclopropanes should also undergo similar additions. However, the site of electrophilic addition to these compounds has proven to be dependent on the nature of the substituents and, to a lesser extent, the nature of the electrophile.

Crandall et al.¹⁰⁶ reported that reaction of the vinylidene-cyclopropane (73) with acetic acid-sulphuric acid gave a mixture containing the enyne (75), the alcohol (76a) and the corresponding acetate (76b), all products being derived from γ -protonation. This reversal of the normal central addition to tetrasubstituted allenes was ascribed to the stability of the vinyl cation (74) (see page 17).

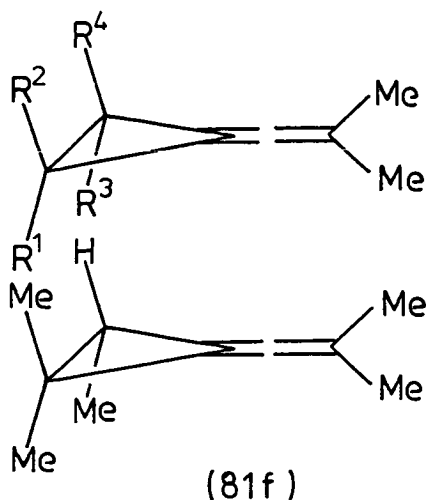
Poutsma et al.¹⁰⁷ found that on refluxing allene (73) in benzene with a catalytic amount of *p*-toluenesulphonic acid the major product (87%) was still enyne (75) but that a product from β -protonation, the triene (77), had also been formed. Rearrangement using boron trifluoride etherate in benzene also gave enyne (75) and triene (77) in the ratio 20:1.¹⁰⁷

The authors considered it unlikely that the enyne (75) had been formed by α -protonation (Scheme 4) since this would require acid catalysed isomerisation of the trisubstituted allene (78) to an acetylene rather than to a diene as is usually observed.^{18b,20b,22} They noted that treatment of allene (79), which is similar to allene (78), with boron trifluoride etherate did not give the acetylene (80).¹⁰⁸



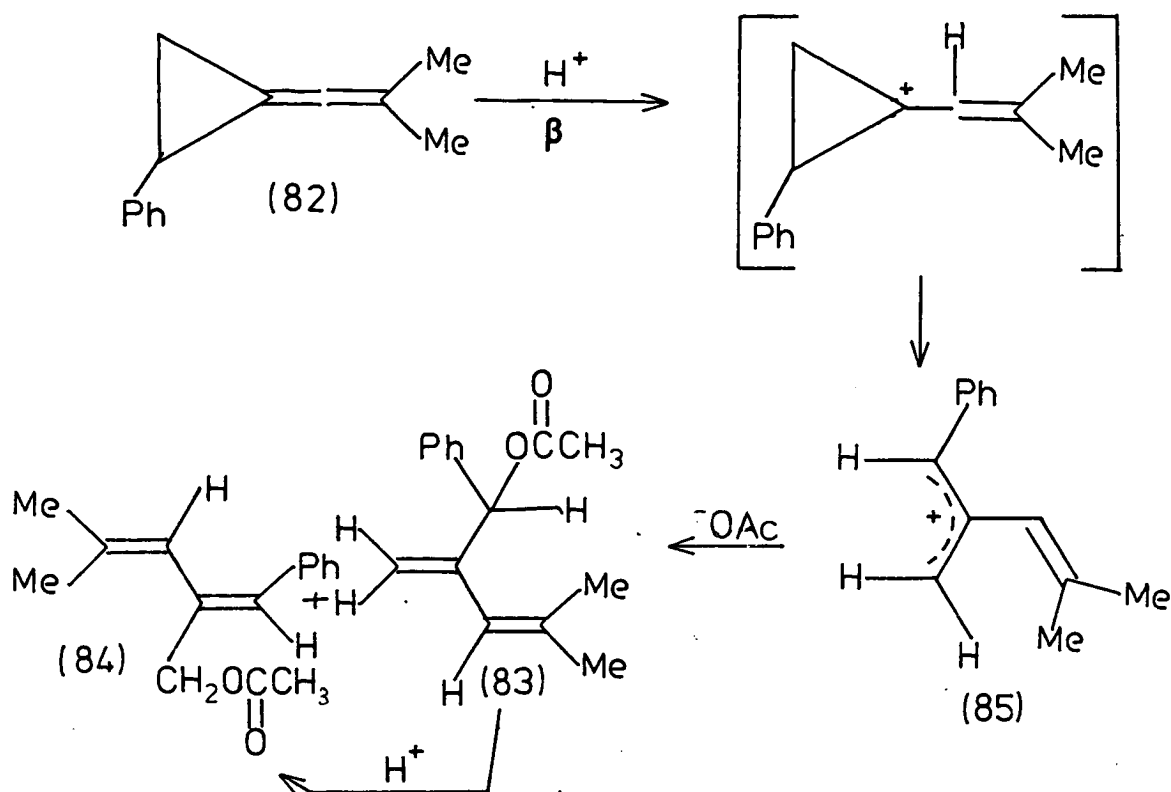
In a competitive experiment¹⁰⁷ it was shown that allene (73) is less reactive towards protonation than tetramethylallene although arguments claiming the increased stability of cation (74) would suggest the reverse.

γ -Protonation was also the mode of reaction found by Leandri *et al.*¹⁰⁹ when they reacted the vinylidenecyclopropanes (73) and (81a-f) with formic acid or *p*-toluenesulphonic acid in benzene.



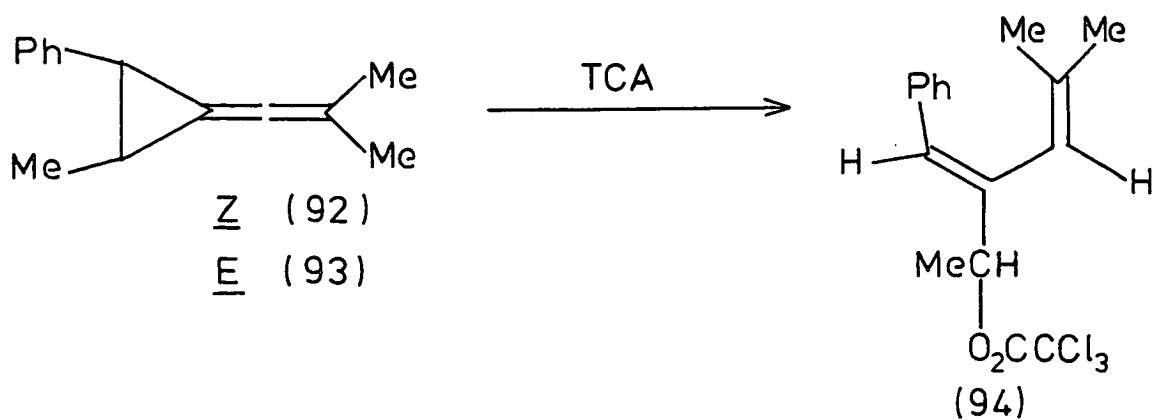
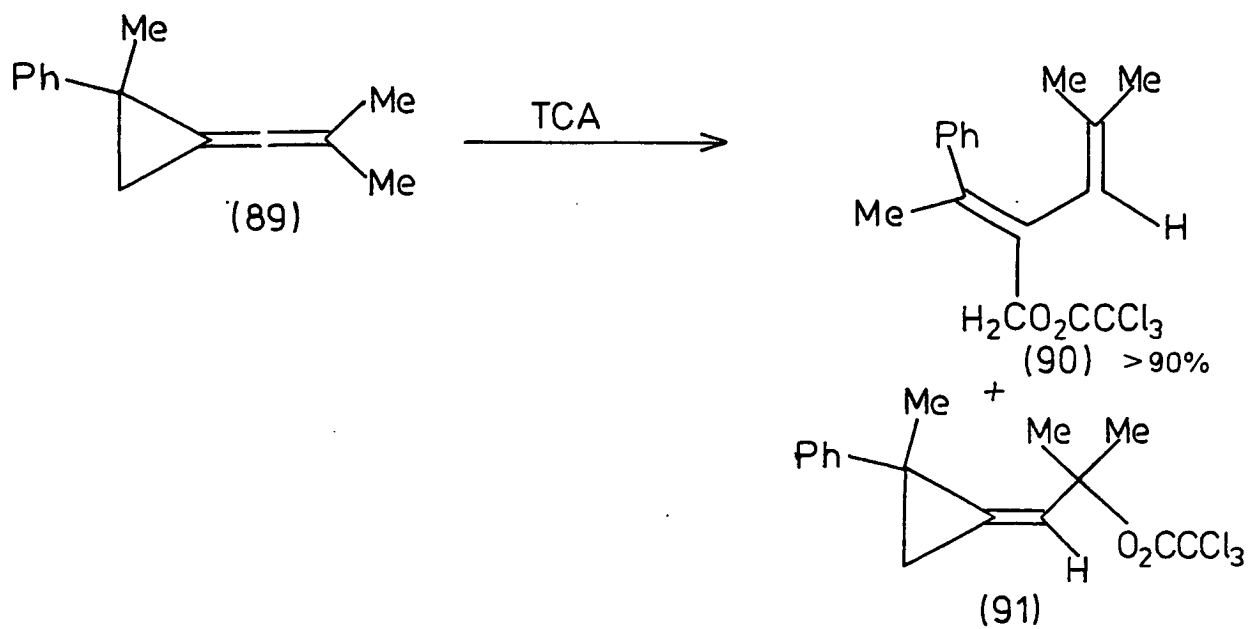
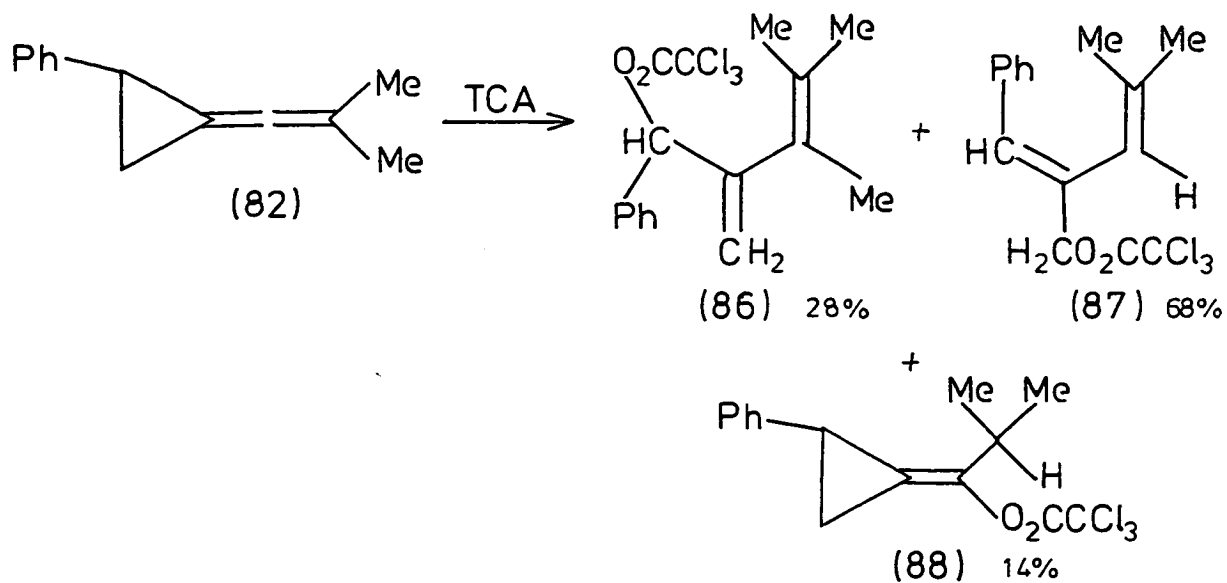
R ¹	R ²	R ³	R ⁴	
H	H	Me	Me	81a
H	Me	Me	Me	81b
H	H	Me	Et	81c
H	H	Me	CH ₂ C(CH ₃) ₃	81d
Me	CHOH -Me	Me	Me	81e

An extension of the protonation of vinylidenecyclopropanes to include phenyl substituted compounds was carried out by Pasto et al.^{110,111} Reaction of 2-dimethylvinylidene-1-phenylcyclopropane (82) with acetic acid at 115° resulted in the formation of addition products from β -protonation, the dienes (83) and (84).¹¹⁰ The stereochemistry of diene (84)



however, could not be assigned by spectroscopic methods, and the authors assumed that ring opening would proceed by the least sterically hindered route to give the allyl cation (85) which would give the adduct (84).

The reaction of allene (82) with acetic acid and a catalytic amount of *p*-toluenesulphonic acid at 70° proceeded very slowly giving only the adduct (84). Since adduct (83) isomerises at 105° in acetic acid with *p*-toluenesulphonic acid to (84), it was concluded that adduct (83) is kinetically



favoured and therefore formed initially and that (84) is thermodynamically favoured.

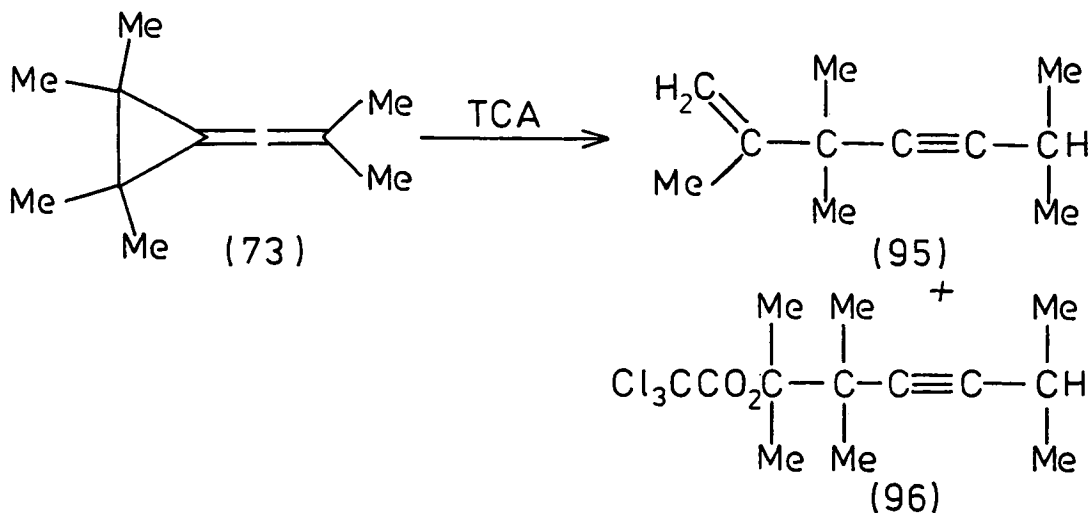
The reaction of allene (82) with trichloroacetic acid (TCA) in carbon tetrachloride¹¹¹ also proceeded via β -protonation but in addition to the dienes (86) and (87) a small amount of ring-retained product (88) was also produced.

2-Dimethylvinylidene-1-methyl-1-phenylcyclopropane (89) reacted under the same conditions to give only one ring-opened product (90) and a small amount of ring-retained adduct (91). Both cis and trans-2-dimethylvinylidene-3-methyl-1-phenylcyclopropanes (92) and (93) reacted with TCA to give a single adduct (94). In the case of adducts (87), (90) and (94) the stereochemistry has not been proven and the same argument as was used to determine the probable structure of adduct (84) gave the stereochemistry of each as indicated.¹¹¹

Adducts (88) and (91) were formed by addition of TCA across the β - γ double bond. Their formation can be attributed to a possible concerted electrophilic addition component caused by the less polar solvent used.

In contrast to the results obtained for the reactions of the phenyl-substituted vinylidenecyclopropanes, 2-dimethylvinylidene-1,1,3,3-tetramethylcyclopropane (73) reacted relatively rapidly with TCA to give the enyne (95) and the acetylinic adduct (96), both by γ -protonation.¹¹¹

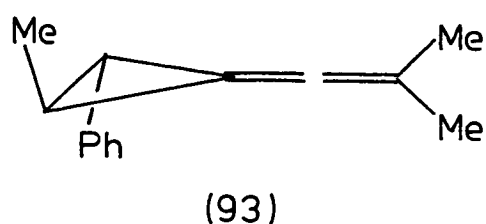
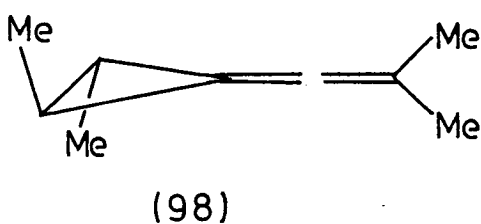
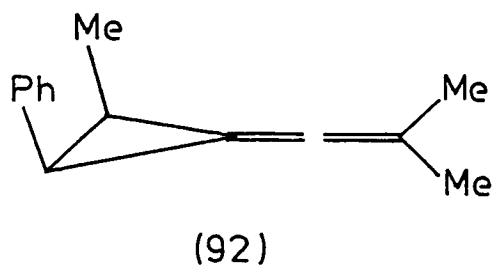
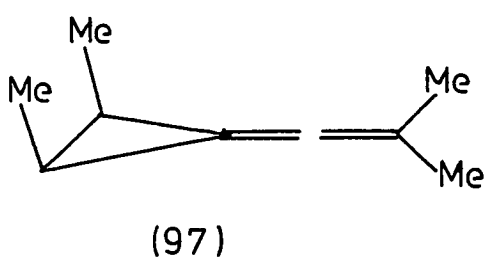
The difference in reactivity towards electrophilic attack at C- β in the phenylvinylidenecyclopropane (82) and C- γ in the tetramethyl derivative (73) has been measured at greater than 10 000.¹¹¹ This large difference has been attributed, in part, to differences in stability of the cyclopropylidene-



methyl cations which would be formed from γ -protonation of both cyclopropanes. Alkyl groups attached to a cyclopropane ring interact moderately strongly with the Walsh orbitals of the ring¹¹² because of substantial coefficients of the appropriate atomic orbitals on the saturated carbon atoms and the attached carbon atoms. Unsaturated groups, including phenyl, do not interact strongly¹¹³ due to small coefficients on the p-orbital of the atom attached to the ring. Therefore, alkyl groups on the cyclopropane ring stabilize formation of a positive charge at C- β to a greater extent than C- α , favouring γ -protonation. Unsaturated groups, it was claimed, do not stabilize charge formation at either C- α or C- β .¹¹⁰ This however was not considered to fully explain the difference in position of protonation between alkyl and aryl substituted systems. Molecular orbital calculations¹¹¹ suggest that electrophilic attack on the tetramethyl compound (73) involves the HOMO whereas electrophilic attack on the phenyl derivative (82) appears to involve the second HOMO, the positions of attack being governed by electrostatic interactions.

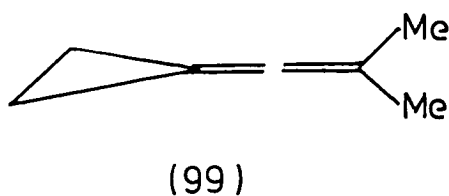
Although the arguments outlined above on the stability of the cyclopropylidenemethyl cations would appear to offer some explanation for the different addition reactions observed,

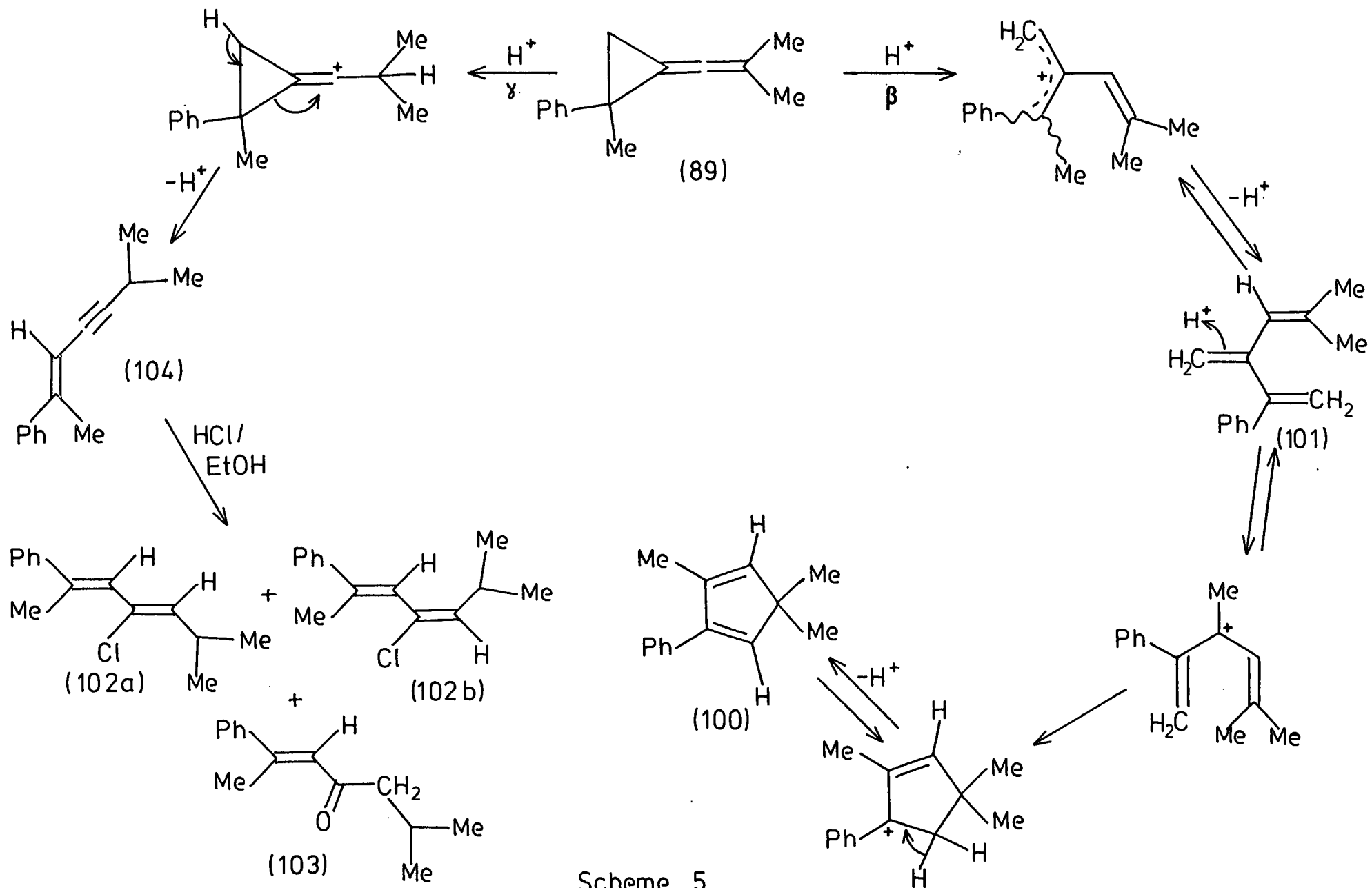
comparison of the reaction rates between the phenyl (82) and tetramethyl (73) derivatives seems unnecessary. A better comparison might be between systems where one methyl group is replaced by a phenyl group such as cyclopropanes (97) and (92) or (98) and (93) for which data is available.¹¹¹ The



difference in reactivity towards electrophilic attack in the above cases is about 100.

In the absence of results from electrophilic additions to the unsubstituted compound (99) it is not possible to



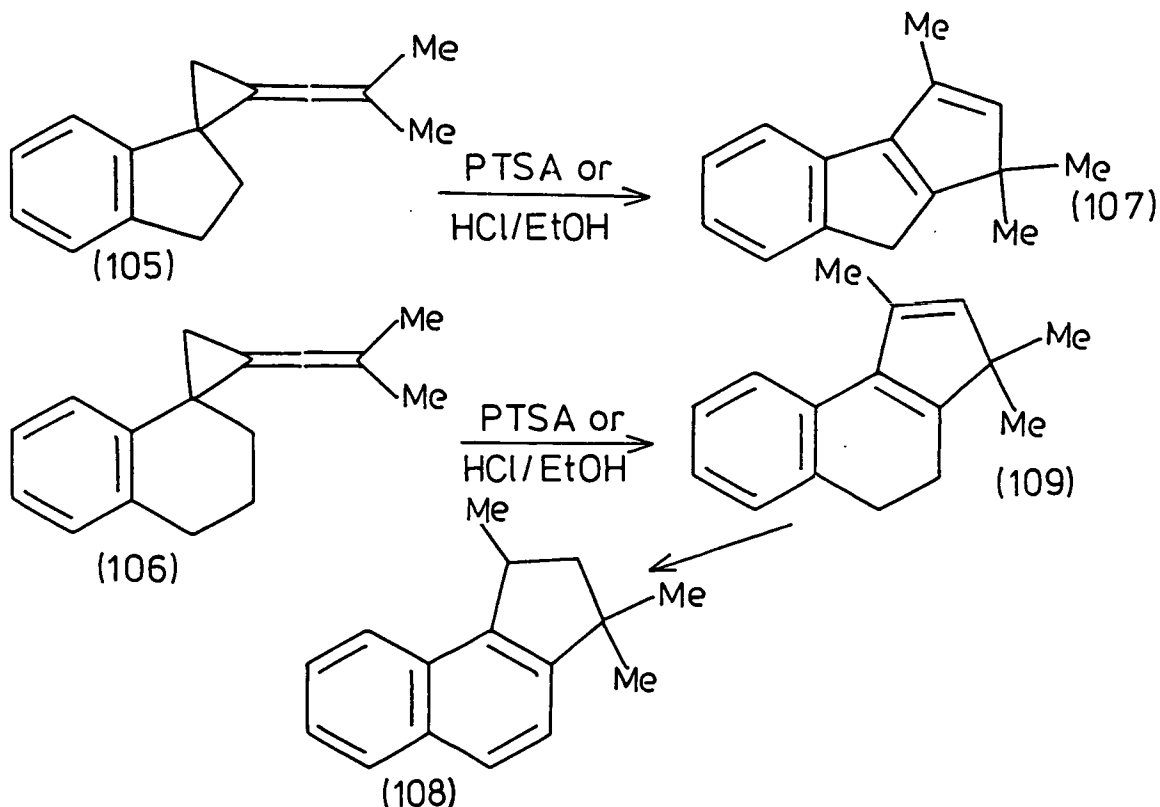


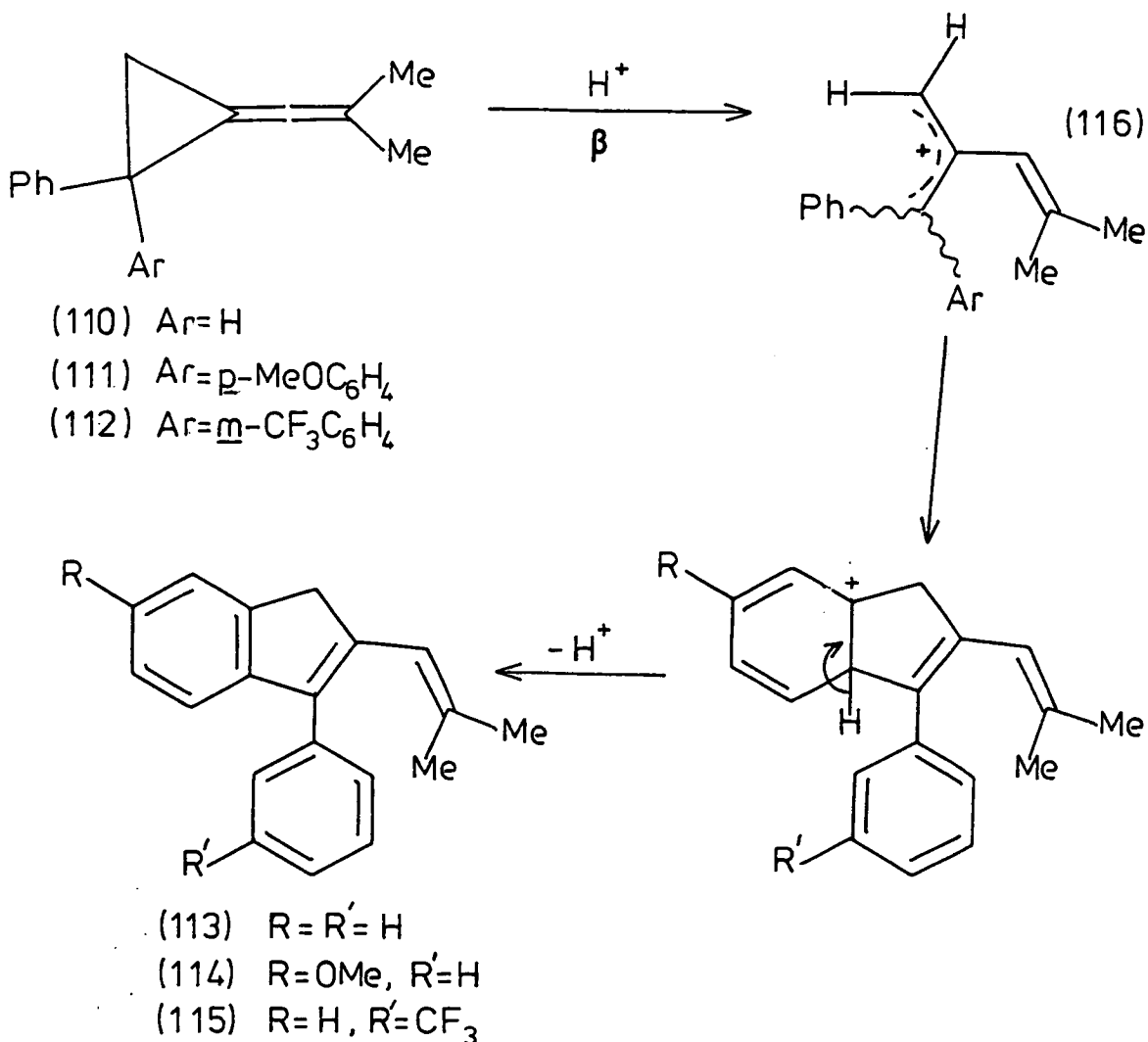
Scheme 5

determine whether γ or β -protonation is preferred in this case and it is therefore not possible to know what effect the phenyl group has on the site of electrophilic addition.

In keeping with the later observations of Pasto *et al.*¹¹¹, Harris¹¹⁴ found that protonation of 2-dimethylvinylidene-1-methyl-1-phenylcyclopropane (89) with a catalytic amount of *p*-toluenesulphonic acid (PTSA) produced products from only β -protonation, giving largely the cyclopentadiene (100) which was presumed to be derived from acid catalysed rearrangement of triene (101) as shown in Scheme 5. However, protonation using ethanolic hydrogen chloride,¹¹⁵ although still favouring β -protonation (ca.75%), also gave addition products (102a and b) and (103) which were all produced by γ -protonation followed by addition of hydrogen chloride or water to the enyne (104).

The spiro-cyclopropanes (105) and (106)^{114,115} underwent protonation exclusively at the β -position, the former giving the cyclopentadiene (107), the latter giving the naphthalene (108) from rearrangement of the cyclopentadiene (109).



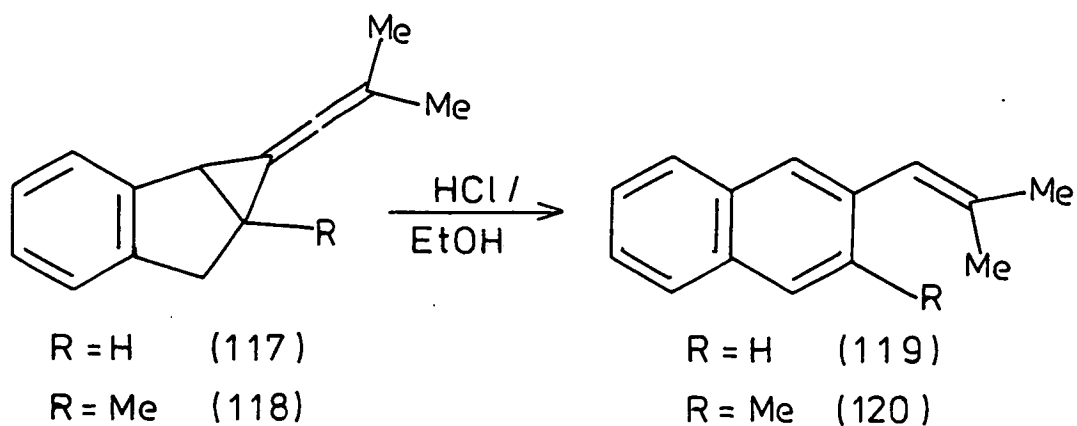


Scheme 6

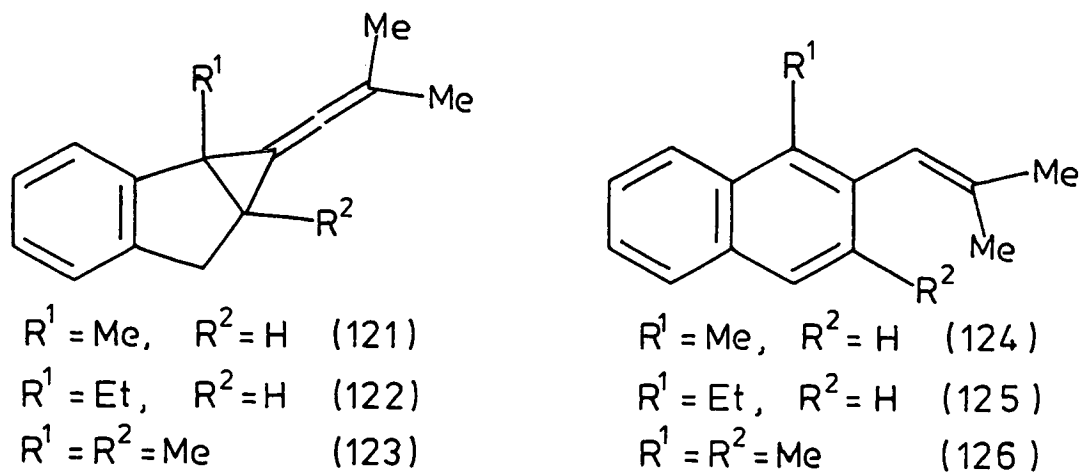
Protonation of the 1,1-diaryl systems (110), (111) and (112)¹¹⁴ also proceeded exclusively by β -protonation (Scheme 6) to give indenes (113), (114) and (115) respectively via intramolecular cyclisation of the intermediate allyl cation (116). The activating effect of the methoxy group and deactivating effect of the trifluoromethyl group were observed in the exclusive formation of the products (114) and (115). It should be noted that these 1,1-diaryl systems cannot give products analogous to triene (101) or the cyclopentadienes.

The indene derivative (117) and the 2-methylindene derivative (118) also underwent only β -protonation to give naphthalenes (119) and (120) respectively when treated with

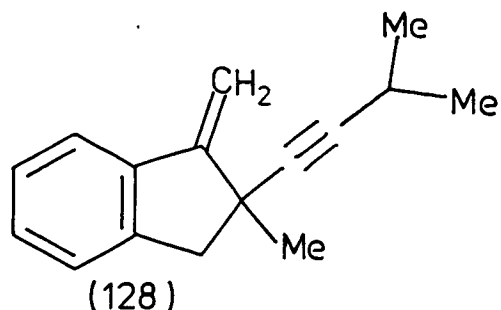
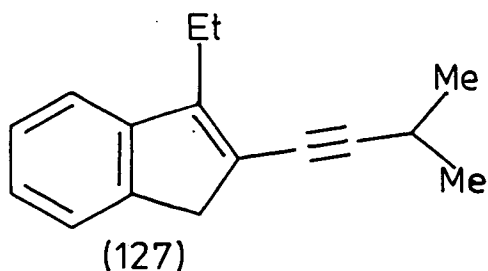
ethanolic hydrogen chloride.^{115,116}



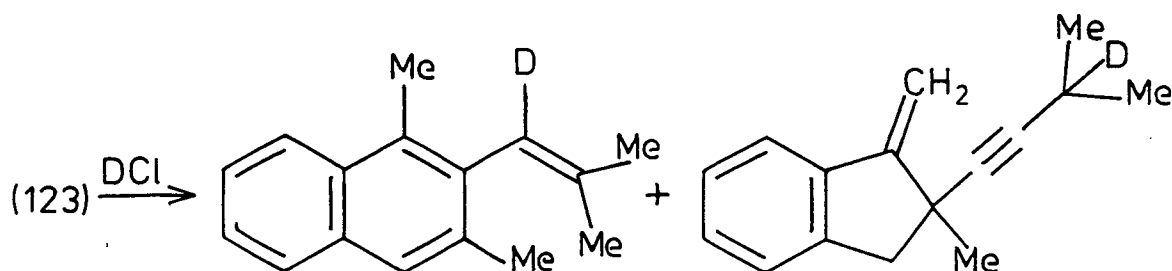
Truslove¹¹⁶ carried out the reaction of the indene derivatives (121), (122) and (123) with *p*-toluenesulphonic acid and found that the 3-methylindene derivative (121) gave only the naphthalene (124) by β -protonation, whereas



the 3-ethylindene derivative (122) gave the naphthalene (125) and the γ -protonation product, 3-ethyl-2(3'-methylbut-1'-ynyl)indene (127) in the ratio 3:1. The 2,3-dimethylindene derivative (123) gave a 1:1 mixture of the naphthalene (126) and the γ -protonation product (128). In this case, since $\text{R}^2 \neq \text{H}$, deprotonation to the conjugated enyne was not possible.



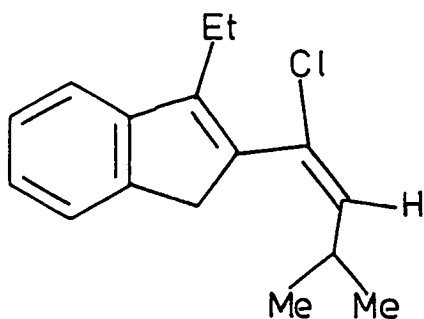
Reaction of the 2,3-dimethylindene derivative (123) with deuterium chloride in deuterated methanol¹¹⁶ gave deuterium incorporation as shown, showing that the naphthalene is formed



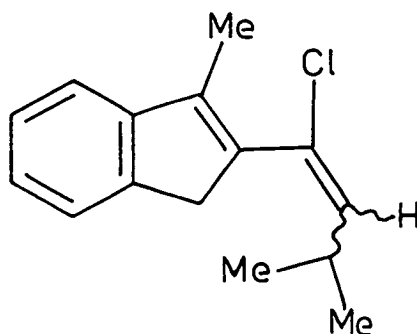
by addition to the β -carbon atom, and the enyne is formed by addition at the γ -site.

The reaction of the 3-ethylindene derivative (122) with 1.8M ethanolic hydrogen chloride¹¹⁶ gave a 1:1 mixture of the naphthalene (125) and E-2(1'-chloro-3'-methylbut-1'-enyl)-3-ethylindene (129), the latter being formed by the addition of hydrogen chloride to enyne (127).

Reactions of the 3-methylindene derivative (121) with ethanolic hydrogen chloride gave mixtures containing the naphthalene (124) and the hydrogen chloride addition products E and Z-2-(1'-chloro-3'-methylbut-1'-enyl)-3-methylindene



(129)

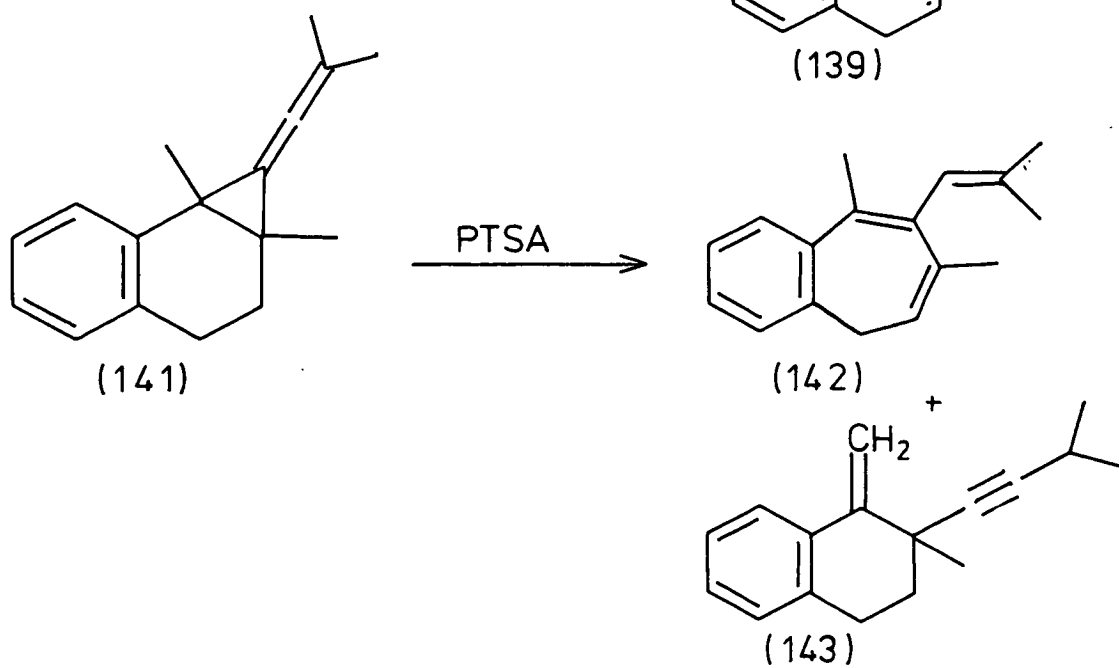
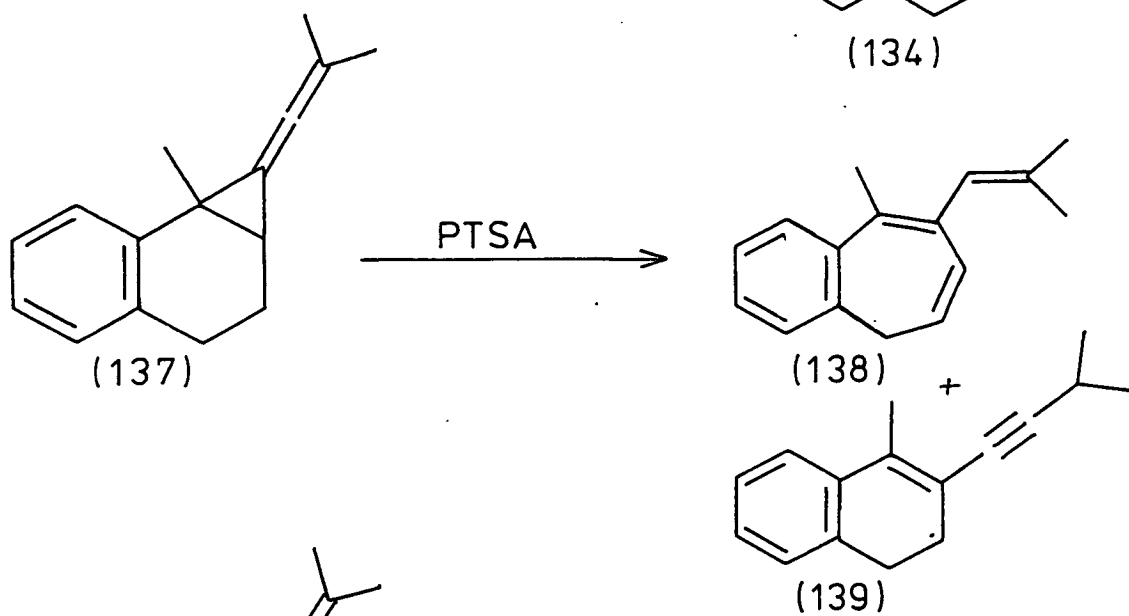
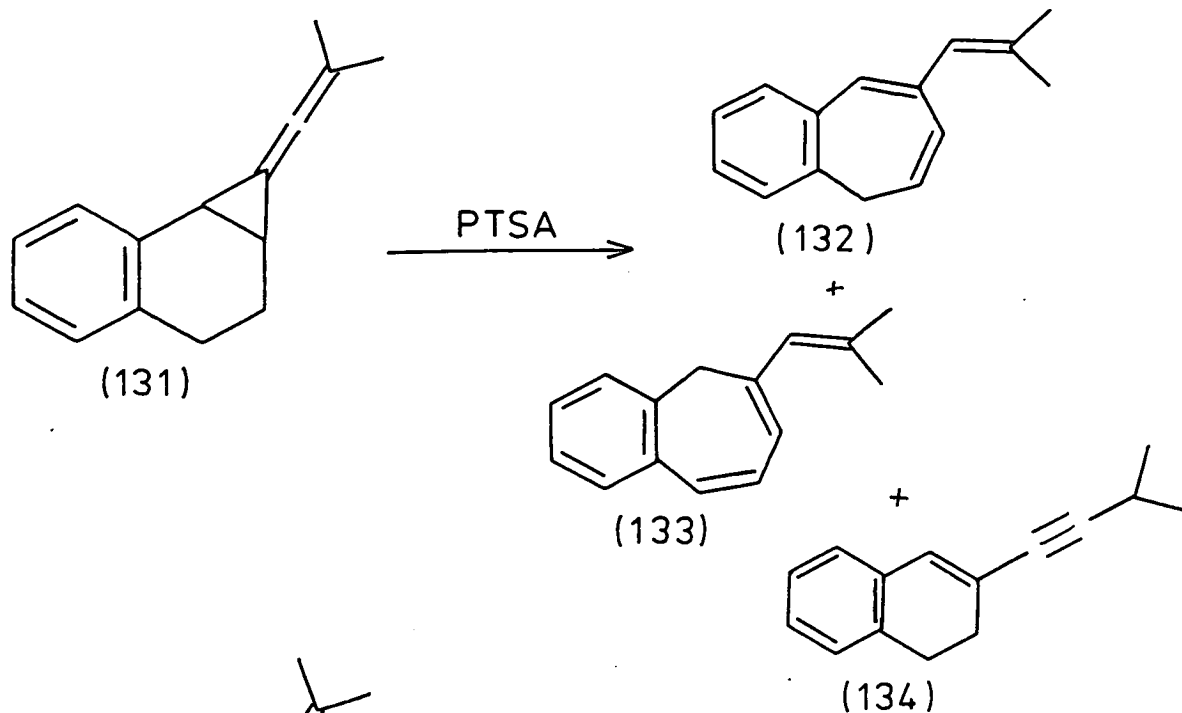
(130a) E isomer(130b) Z isomer

(130a and b) in the ratio E:Z = 9:1. The ratios of the naphthalene to the addition products varied from 62:38 (for 2.0M ethanolic hydrogen chloride) to naphthalene only (for ethanol only).¹¹⁶

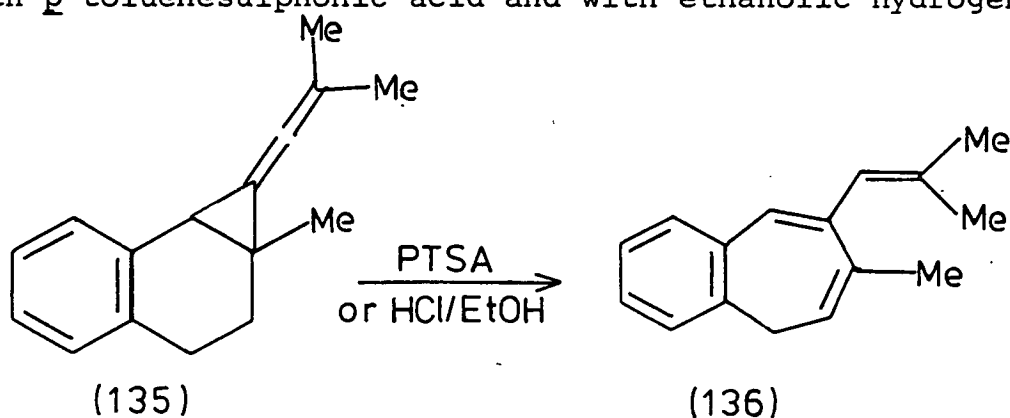
Similarly, the reactions of the 2,3-dimethylindene derivative (123) with ethanolic hydrogen chloride gave mixtures containing the naphthalene (126) and the enyne (128), the ratios varying from 55:45 (for 0.4M ethanolic hydrogen chloride) to naphthalene only (for ethanol only).¹¹⁶

This variation in product distribution with change in acid concentration has been attributed¹¹⁶ to protonation by both EtOH_2^+ and EtOH . The latter, being less reactive and more discriminating, selectively attacks the β -carbon atom, whereas the former is more reactive and less discriminating and attacks both the β - and γ -positions.

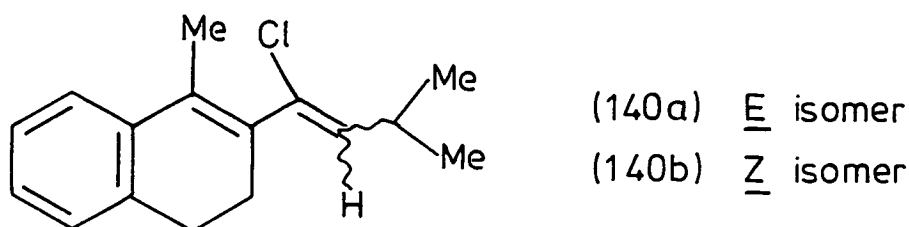
A similar series of rearrangements have been observed for vinylidenecyclopropanes obtained from 1,2-dihydronaphthalenes. In all cases product mixtures were complex and many components (up to 80%) remain unidentified, therefore the product ratios do not necessarily reflect site protonation ratios.

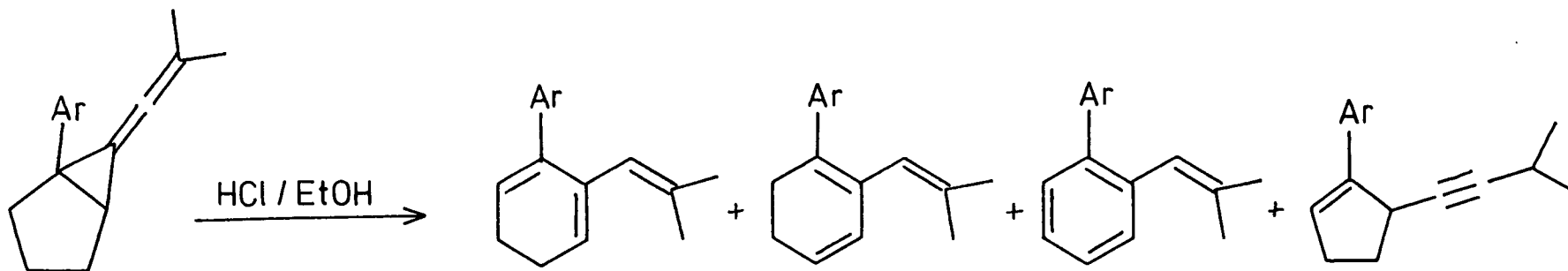


From the rearrangement of the 1,2-dihydronaphthalene derivative (131) using *p*-toluenesulphonic acid only the two benzocycloheptadienes (132) and (133), from β -protonation and the enyne (134), from γ -protonation in the ratio 1:1:3 were identified.¹¹⁶ Using ethanolic hydrogen chloride (1.8M) gave a mixture of the cycloheptadiene (132) and the enyne (134) in the ratio 6:1.¹¹⁶ Only the β -protonation product (136) was observed from the reaction of the 3-methyl derivative (135) with *p*-toluenesulphonic acid and with ethanolic hydrogen



chloride.¹¹⁶ Rearrangement of the 4-methyl derivative (137) with *p*-toluenesulphonic acid gave a mixture containing the cycloheptadiene (138) and the enyne (139) in the ratio 3:1.¹¹⁶ Using ethanolic hydrogen chloride however, gave a mixture containing only γ -protonation products (140a and b) in the ratio 2.3:1.¹¹⁶ Reaction of derivative (137) with 30% aqueous





Ar = Ph (146)

(147)

(148)

(149)

(150)

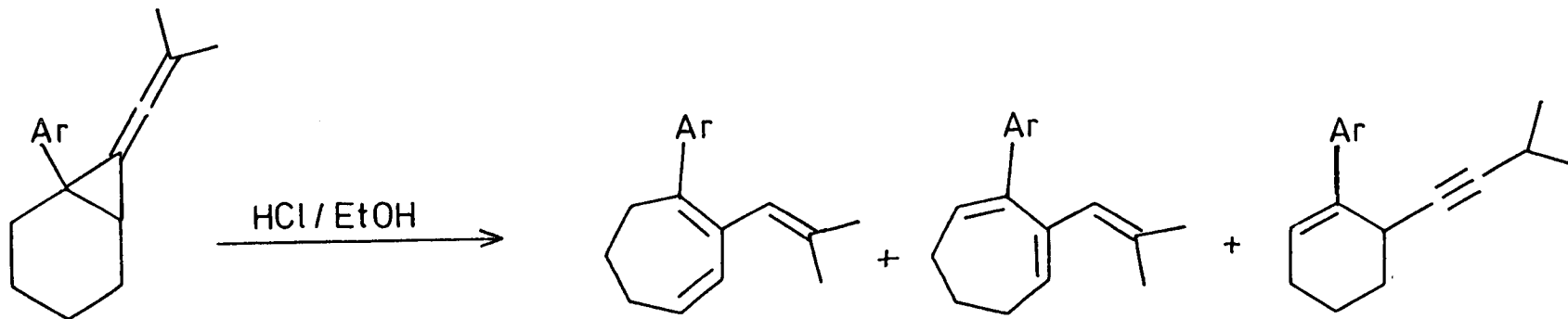
Ar = p-MeC₆H₄ (151)

(152)

(153)

(154)

(155)



Ar = Ph (156)

(157)

(158)

(159)

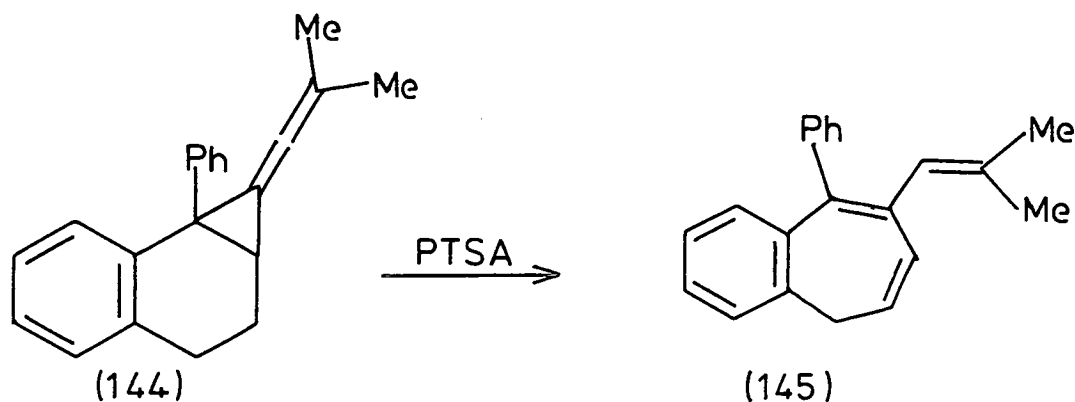
Ar = p-MeC₆H₄ (160)

(161)

(162)

(163)

hydrochloric acid dissolved in ethanol¹¹⁵ gave the same isomers in the ratio $\underline{E}:\underline{Z} = 1:1$. Rearrangement of the 3,4-dimethyl derivative (141)¹¹⁷ using *p*-toluenesulphonic acid gave a mixture containing the cycloheptadiene (142) and the enyne (143) in the ratio 1:1. Only the β -protonation product, cycloheptadiene (145), was obtained on the analogous rearrangement of the 4-phenyl derivative (144).¹¹⁷



The 1-phenylcyclopentene derivative (146) underwent rearrangement in ethanolic hydrogen chloride to give a mixture containing the β -protonation products (147), (148) and (149) and the enyne (150) in the ratio 43:43:5:5. Similarly the 1-(*p*-tolyl)cyclopentene derivative (151) reacted in ethanolic hydrogen chloride to give a mixture containing the products (152), (153), (154) and (155) in the ratio 21:21:52:3.¹¹⁵

The rearrangement of the 1-phenylcyclohexene derivative (156) in ethanolic hydrogen chloride gave a mixture containing the β -protonation products (157) and (158) and the γ -protonation product, enyne (159), in the ratio 1:1:2. Likewise, the rearrangement of the 1-(*p*-tolyl)cyclohexene derivative (160) in ethanolic hydrogen chloride gave a mixture containing (161), (162) and (163) in the ratio 1:1:2.¹¹⁵

From the results quoted here, it seems that one important

factor in determining the position of protonation is the number of alkyl substituents on the cyclopropane ring. Increasing the number of alkyl substituents generally increases the proportion of γ -protonation products, which is in keeping with Pasto's suggestion¹¹¹ on the stabilization given to the cyclopropylidenecarbonyl cations by alkyl groups.

The idea¹⁰⁷ that the methyl groups in the tetramethyl derivative (73) may exert some steric hindrance to β -protonation may not necessarily be the case since, where the 1,1-dimethyl derivative (81a) undergoes γ -protonation,¹⁰⁹ the more sterically hindered 1,1-diaryl adducts (110), (111), (112) all undergo β -protonation.¹¹⁴

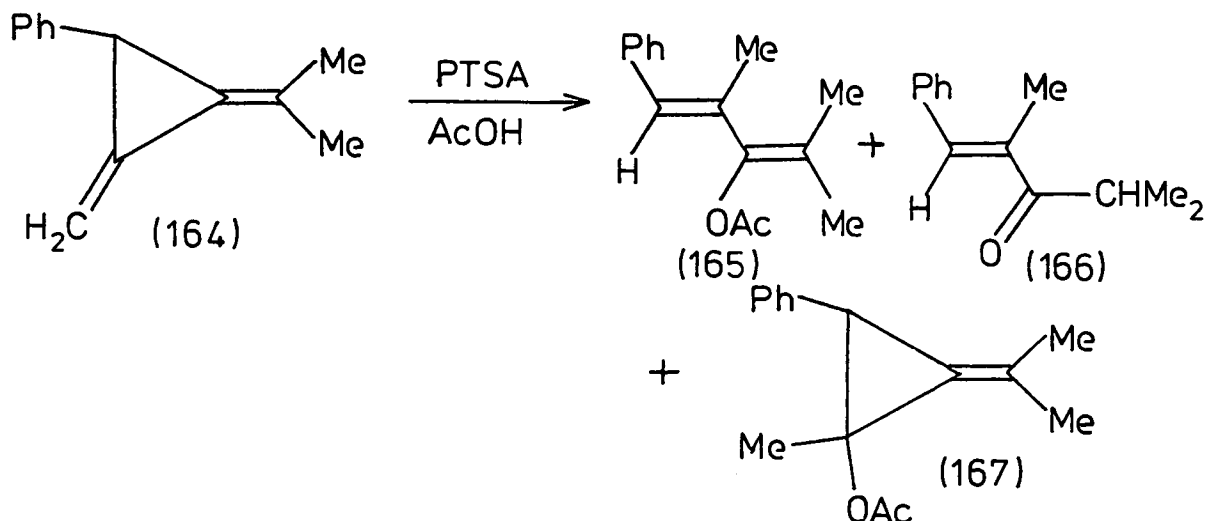
Studies on the solvolysis of cyclopropyl derivatives have shown that it involves concerted ring opening and anion abstraction. It is not therefore certain to what extent steric effects in the disrotatory ring opening of the 'cyclopropyl cation', formed by β -protonation of vinylidenecyclopropanes, will effect the site of protonation. Nor is it clear whether the stability of the allyl cation thus formed is an important factor in determining the mode of addition.

It would appear that, in many cases, ethanolic hydrogen chloride produces a less selective protonating agent than does *p*-toluenesulphonic acid, but a detailed study on protonation site ratios would be necessary to determine this.

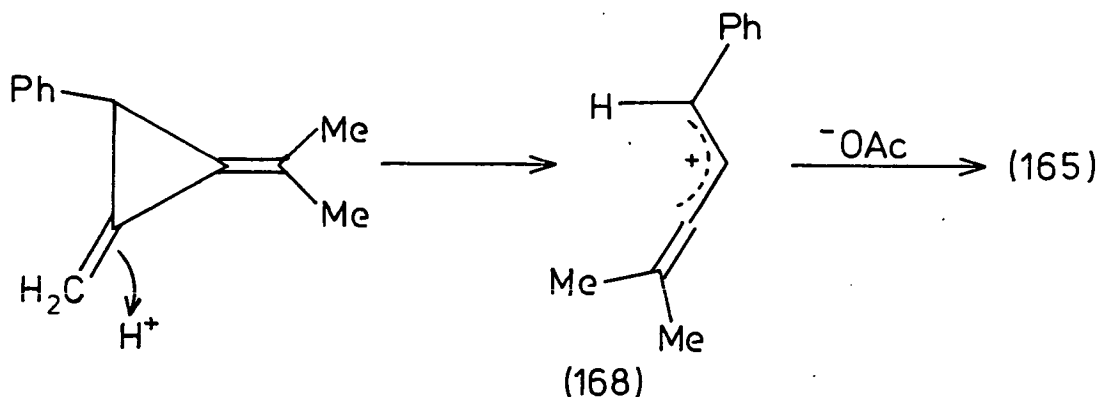
Comparisons of results from similar protonation conditions would seem to indicate that, although the number of alkyl substituents on the ring is an important factor in determining the site of protonation, there are other important factors.

There have been few reports on electrophilic additions

to dimethylenecyclopropanes. However the reaction of 2-isopropylidene-3-methylene-1-phenylcyclopropane (164) in acetic acid with a catalytic amount of *p*-toluenesulphonic acid has been reported to give the acetate (165), the ketone (166) and the ring retained product (167) in the ratio 91:6:3.¹¹⁸ The mechanism of formation of acetate (165) was



considered to be protonation of the methylene group with the less sterically hindered mode of ring opening to give allyl

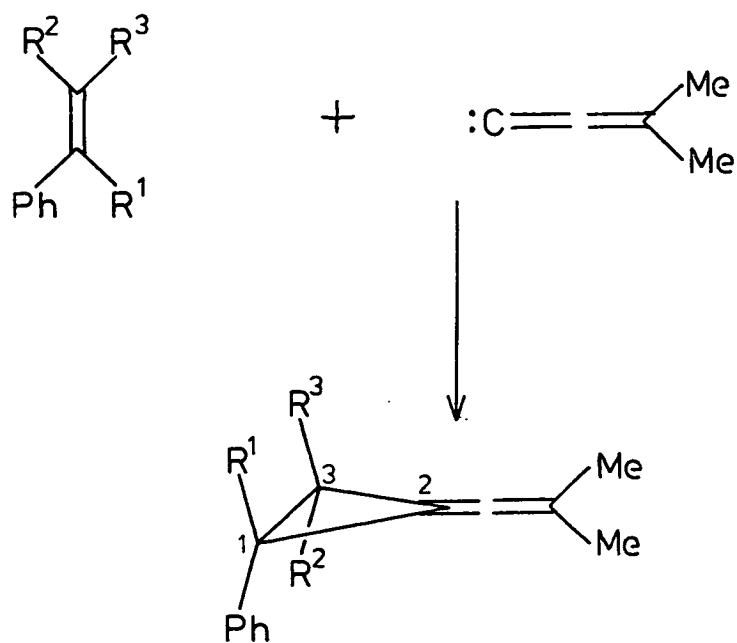


cation (168) followed by addition of the acetate anion to give product (165).

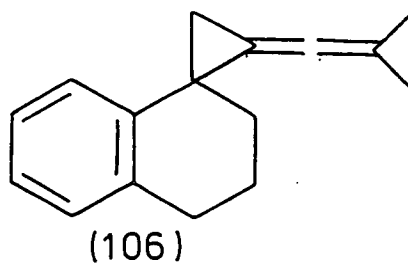
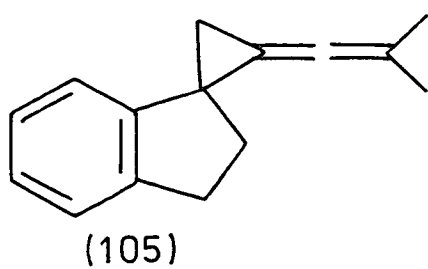
Object of Research

Although protonation of a variety of dimethylvinylidene-cyclopropanes had previously been reported, results had shown that the mode of reaction was very dependent on the acid used and the substituents on the ring. It was therefore considered worthwhile to study carefully the protonation of a series of mono-, di- and tri-alkyl substituted 1-phenyl-2-dimethylvinylidenecyclopropanes, using the same acids throughout the series. Catalytic amounts of *p*-toluenesulphonic acid were chosen since this would lead to full rearrangement, rather than addition products and ethanolic hydrogen chloride was used as a comparison since it had been shown to give both addition and rearrangement reactions.

In view of the very small amount of work on electrophilic additions to dimethylenecyclopropanes, which were readily obtained by thermolysis of the appropriate vinylidenecyclopropanes, it was decided to examine the reactions of a variety of these compounds with *p*-toluenesulphonic acid to examine the effect of substituents on the mechanism of these reactions.



R^1	R^2	R^3		R^1	R^2	R^3	
H	H	H	(82)	H	H	Me	(92)
Me	H	H	(89)	Me	Me	H	(172)
Et	H	H	(169)	Me	H	Me	(173)
iso-C ₃ H ₇	H	H	(170)	H	Me	Me	(174)
c-C ₆ H ₁₁	H	H	(171)	Me	Me	Me	(175)
H	Me	H	(93)	Ph	H	H	(110)



CHAPTER 2

Synthesis of Dimethylvinylidenecyclopropanes and Dimethylenecyclopropanes

2.1 Synthesis of Dimethylvinylidenecyclopropanes

The dimethylvinylidenecyclopropanes listed^{opposite} were prepared by the stereospecific addition of dimethylvinylidene carbene to the appropriate olefin.¹¹⁹ The carbene was generated in phase transfer catalysed reactions¹²⁰ by the action of potassium hydroxide on 1-bromo-3-methylbuta-1,2-diene in the presence of 10% benzyltri-n-butylammonium bromide. In cases where generation of the carbene was attempted using potassium t-butoxide¹¹⁹ the yields of adduct were lower and the reactions more complicated. The use of benzyltriethylammonium chloride or 3% benzyltri-n-butylammonium bromide as phase transfer catalyst also resulted in lower yields of adduct.

The dimethylvinylidenecyclopropanes tended to polymerise at room temperature and were therefore stored at 4°. Their formulae were confirmed by exact mass measurement since they readily took up oxygen, making elemental analysis very difficult. Structures were confirmed by i.r. and n.m.r. spectroscopy.

With the exception of compound (110), the 1,1-diarylvinylidenecyclopropanes during preparation underwent partial or complete rearrangement to dimethylenecyclopropanes (see below) and were not characterised separately.

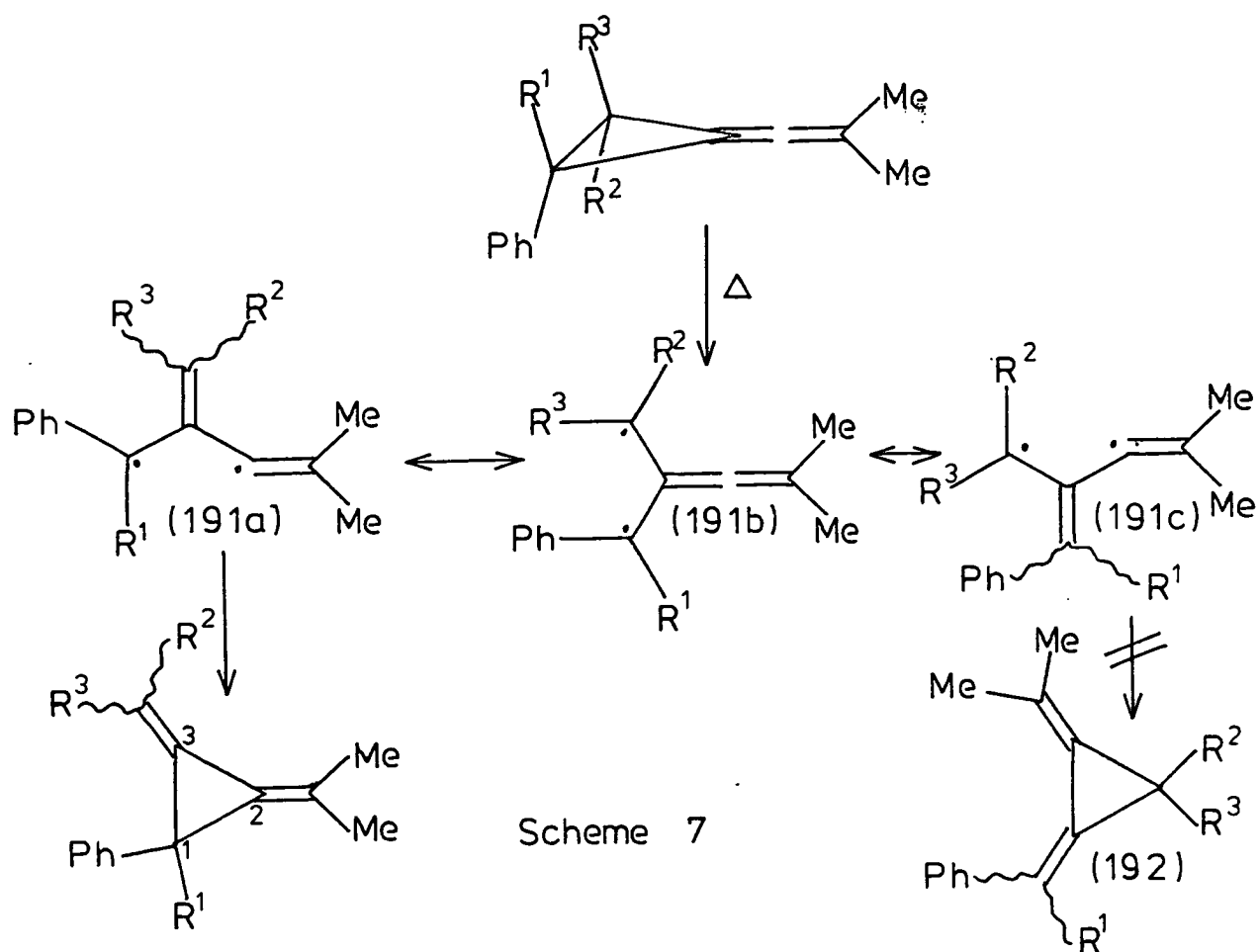
All adducts showed i.r. absorptions in the region 2000-2030 cm^{-1} due to the allene group. This value is higher than for normal allenes (1900-2000 cm^{-1}) because of the bond strain

from the cyclopropane ring.

The ^{13}C n.m.r. spectra of all adducts showed resonances at 187 ± 2 p.p.m. ($=\underline{\text{C}}=$), 98 ± 2 p.p.m. ($=\underline{\text{C}} \text{ Me}_2$) and 21.0-21.5 p.p.m. ($=\text{C}(\underline{\text{CH}}_3)_2$) which were essentially independent of cyclopropane ring substituents. As expected the chemical shifts of cyclopropane ring carbon atoms varied as substituents changed (see appendix I). It is noteworthy that the chemical shift of C-(2) increased as the number of substituents on the ring increased with values ranging from 81.8 ($\text{R}^1, \text{R}^2, \text{R}^3 = \text{H}$) to 94.1 p.p.m. ($\text{R}^1, \text{R}^2, \text{R}^3 = \text{Me}$). The value of ca.98 p.p.m. for C- γ is slightly higher than the chemical shift of the terminal carbon atom in dimethylallene.¹²¹ The value for C- β is however ca.20 p.p.m. lower than that for the central carbon atom in dimethylallene,¹²¹ presumably due to shielding by the cyclopropane ring.

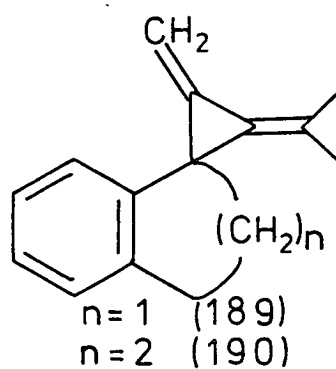
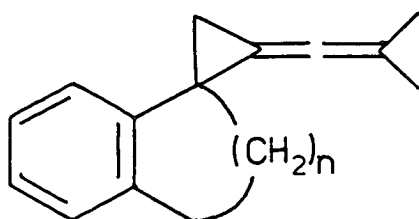
All the vinylidenecyclopropanes prepared, except compound (110), had a chiral centre at C-(1) and therefore the groups R^2 and R^3 were non-equivalent. Thus, in compounds (82), (169), (170) and (171), the hydrogen atoms bonded to C-(3) show their mutual coupling of 6.6-6.8 Hz. In compounds where $\text{R}^2 = \text{CH}_3$, the protons of this group are found at a lower chemical shift than those of the other methyl groups, confirming their location over the phenyl ring. In compounds (169)-(171) the chiral centre at C-(1) created a prochiral centre in the substituent, resulting in the non-equivalence of the methylene protons of the ethyl group in (169), the methyl groups of the isopropyl group in (170) and the methylene groups of the cyclohexyl group in (171). This was evident from the ^1H n.m.r. spectrum of (169) and the ^{13}C n.m.r. spectra of (170) and (171).

Under the conditions required to obtain mass spectra the



Scheme 7

R^1	R^2	R^3		R^1	R^2	R^3	
H	H	H	(164)	H	Me	Me	(182)
Me	H	H	(176)	Me	Me	Me	(183)
Et	H	H	(177)	Ph	H	H	(184)
iso-C ₃ H ₇	H	H	(178)	Ph	Me	H	(185a)
c-C ₆ H ₁₁	H	H	(179)	Ph	H	Me	(185b)
H	Me	H	(180a)	p-OMeC ₆ H ₄	H	H	(186)
H	H	Me	(180b)	p-ClC ₆ H ₄	H	H	(187)
Me	Me	H	(181a)	m-CF ₃ C ₆ H ₄	H	H	(188)
Me	Me	H	(181b)				



dimethylvinylidenecyclopropanes underwent thermal rearrangement to the corresponding dimethylenecyclopropanes and therefore the mass spectra of both were identical.

2.2 Synthesis of Dimethylenecyclopropanes

The dimethylenecyclopropanes (164, 176-184, 189, 190) were prepared by vapour phase thermolysis (300-350°) at low pressure (0.1-0.01 mm) of the appropriate dimethylvinylidenecyclopropanes.¹²²⁻¹²⁴ In cases where $R^2 \neq R^3$, a mixture of syn and anti isomers was obtained and no attempts were made to separate these.

The diaryldimethylenecyclopropanes (186), (187) and (188) were formed from the corresponding dimethylvinylidenecyclopropanes during distillation. The mixture of syn and anti 1,1-diphenyl-3-ethylidene-2-isopropylidenecyclopropane (185a and b) was formed during the reaction of 1,1-diphenylprop-1-ene with dimethylvinylidene carbene, presumably by thermolysis of 2-dimethylvinylidene-1,1-diphenyl-3-methylcyclopropane under the reaction conditions.

These thermolyses are considered to proceed by the diradical mechanism¹²²⁻¹²⁴ shown in Scheme 7 where homolytic cleavage of the C-(1), C-(3) bond followed by bond rotation produces the resonance stabilised diradical (191). Recombination of this diradical would lead to either the starting material, the dimethylenecyclopropane or the isomeric benzylidenemethylenecyclopropanes (192). The absence of the thermodynamically most stable isomers, the benzylidenemethylenecyclopropanes (192), is attributed to the higher stability of resonance form (191a), which is equivalent to a combination of an allyl and a benzyl

radical, over (191c), which is equivalent to a combination of a cinnamyl and a primary radical.¹²³ The formation of dimethylenecyclopropanes is thermodynamically favoured over recombination to give starting material.¹²³

The increased thermal lability of the diarylcyclopropanes can be attributed to the increased stabilization given to the diradical (191) by the introduction of a second aromatic ring.

As with their precursors, the dimethylenecyclopropanes tended to polymerise at room temperature and were stored at 4°. Their formulae were confirmed by exact mass measurement since, as with their precursors, they readily took up oxygen. Structures were confirmed by i.r. and n.m.r. spectroscopy.

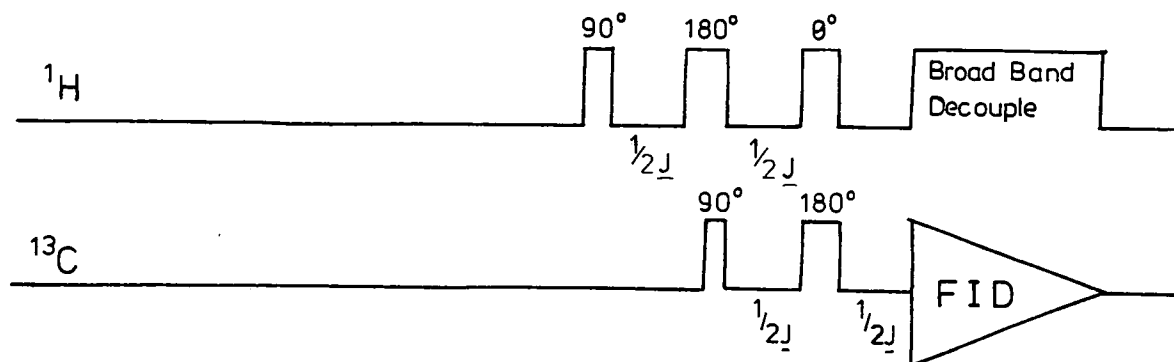
The i.r. spectra of the dimethylenecyclopropanes show absorptions about 1700-1800 cm⁻¹ which have been attributed to the strained exo-cyclic double bonds.¹²² The mass spectra of dimethylenecyclopropanes with substituents only at C-(1), show large peaks corresponding to loss of this substituent.

As with the vinylidenecyclopropanes, all the dimethylenecyclopropanes prepared except (184) and (185a and b) have a chiral centre at C-(1) and this creates a prochiral centre in the C-(1) substituents of cyclopropanes (177), (178) and (179). The effects of this can be seen in the ¹H n.m.r. spectra of cyclopropanes (177) and (178) and in the ¹³C n.m.r. spectrum of cyclopropane (179).

2.3 Assignment of Carbon-13 n.m.r. Spectra

Methyl, methylene and methyne carbon resonances were generally distinguished by spectra obtained using the DEPT pulse sequence¹²⁵ (Scheme 8). By use of the one bond coupling

(J_{CH}) between the carbon-13 nuclei and the bonded protons,

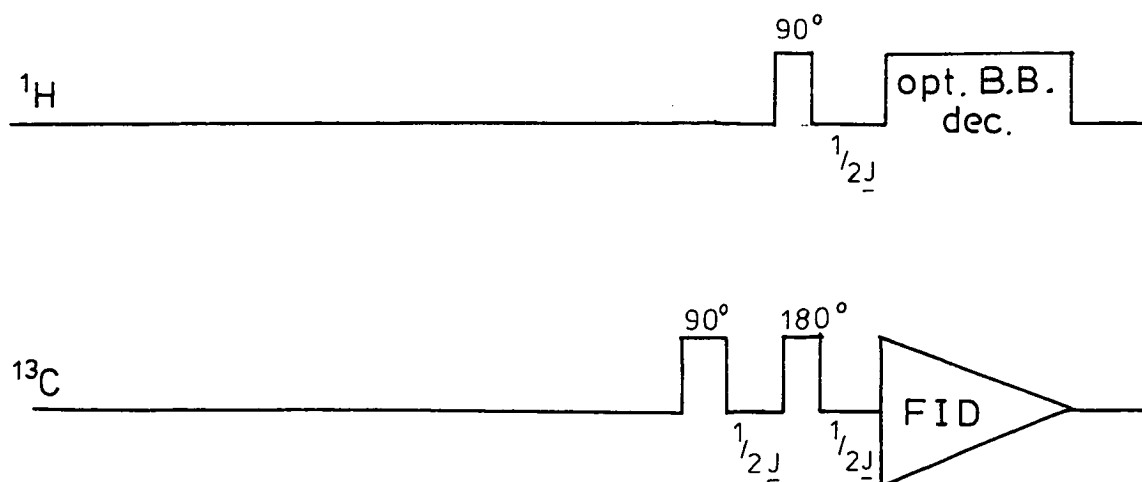


Scheme 8

this sequence gives different intensity signals for methyl, methylene and methyne carbon atoms according to the magnitude, θ , of the third proton pulse. In particular if $\theta = 90^\circ$ only signals due to methyne groups are obtained and if $\theta = 135^\circ$ signals from methyl and methyne groups are positive and signals from methylene groups are inverted. Signals are not obtained from quaternary carbon atoms using this sequence. When these could not be identified from the normal broad band proton decoupled carbon-13 n.m.r. spectrum, another pulse sequence¹²⁶ (Scheme 9) was employed to reveal signals from quaternary carbon atoms only.

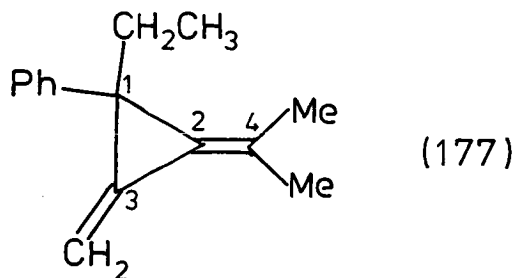
Assignment of resonances to specific carbon atoms was then made, where possible, using chemical shift arguments, however in some cases it was necessary to use fully proton coupled carbon-13 n.m.r. spectra together with the removal of long range couplings by low power irradiation of the proton region.



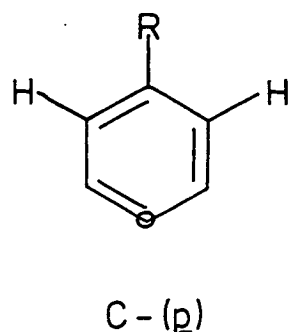
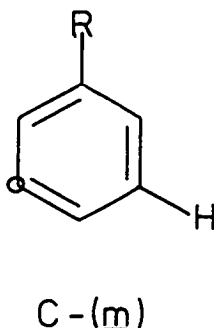
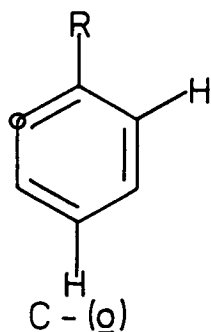


Scheme 9

Assignment of carbon-13 resonances of the dimethylene-cyclopropanes (164, 176, 178-186, 189 and 190) were made by analogy to those deduced for 1-ethyl-2-isopropylidene-3-methylene-1-phenylcyclopropane (177). The fully proton coupled ^{13}C n.m.r. spectrum (50MHz) of the region 150-110 p.p.m. of cyclopropane (177) showed proton bearing carbon atoms at 128.0 (d,d, $\underline{J}$ 159, 7Hz), 127.2 (d,t, $\underline{J}$ 158, 6.5Hz), and 125.7 (d,t, $\underline{J}$ 160, 7.5Hz) and quaternary carbon atoms at 143.0 (t,t, $\underline{J}$ 7, 3.4Hz), 135.0 (bs), 125.9 (masked), and 120.6 (bm). Since, in aromatic rings, $^1\underline{J}_{\text{CH}}$ is ca.160Hz, $^3\underline{J}_{\text{CH}}$ is



5 to 8Hz and $^2\underline{J}_{\text{CH}}$ and $^4\underline{J}_{\text{CH}}$ are normally very small (<1Hz), the aromatic $\underline{\text{C}}\text{-H}$ signals could be assigned as follows: $\underline{\text{C}}\text{-(o)}$ was assigned to the doublet of triplets centred at 127.2 p.p.m.

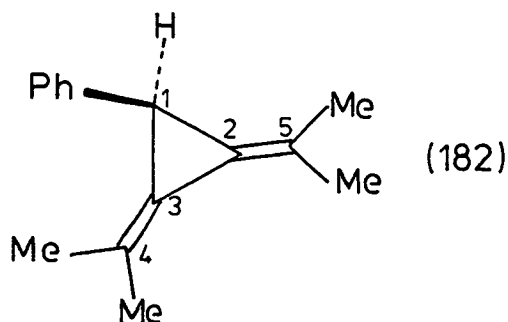


C-(m) to the doublet of doublets at 128.0 p.p.m. and C-(p) was assigned to the smaller doublet of triplets at 125.7 p.p.m. A fully coupled spectrum showing the quaternary resonances only, obtained over the same region using the pulse sequence described above, clearly showed the previously obscured resonance at 125.9 p.p.m. to be a septet ($\underline{J}$ 7Hz). On irradiation of the protons of the methylene of the ethyl group together with those of the alkene methyl groups, all of which almost coincide in the proton spectrum, and using the same pulse sequence, the signal at 143.0 p.p.m. collapsed to a triplet ($\underline{J}$ 7Hz), the signal at 135.0 p.p.m. became a broad doublet ($\underline{J}$ 2Hz), the septet at 125.9 p.p.m. collapsed to a sharp singlet and the multiplet at 120.6 p.p.m. became a doublet of doublets ($\underline{J}$ 11, 5Hz). The effect of this irradiation was to leave only couplings to the aromatic and olefinic protons. The aromatic quaternary carbon atom should therefore only show coupling to the two ortho protons and was therefore assigned the triplet at 143.0 p.p.m. No residual couplings were expected for C-(4) which was assigned the singlet at 125.9 p.p.m., the removed couplings being in agreement with those observed in similar systems.¹²⁷ The observed couplings of 11 and 5Hz are those expected for ${}^3\underline{J}_{\text{CH}}$ to E and Z olefinic protons respectively and therefore the doublet of doublets at 120.6 p.p.m. was assigned to C-(2). The remaining

quaternary, C-(3), was expected to show small couplings of 0-3Hz to the olefinic protons and the broad doublet at 135.0 p.p.m. (J 2Hz) was in agreement with this.

The ^{13}C n.m.r. data for the dimethylenecyclopropanes listed earlier in this section showed resonances at 133.8-136.3 p.p.m. corresponding to C-(3), resonances at about 126 p.p.m. for C-(4) and signals at about 120 p.p.m. for C-(2). The olefinic methyl resonances appeared at 22 to 24 p.p.m. and the methylene of the olefin resonated between 96 and 99 p.p.m. The signal for C-(1) varied considerably as the substituent R^1 changed.

The olefinic quaternary carbon atoms in the ^{13}C n.m.r. spectrum of 2,3-diisopropylidene-1-phenylcyclopropane (182) were assigned from the fully coupled spectrum of the quaternary carbon atoms only. This showed a septet at 120.5 p.p.m. (J 7Hz) and a signal with four clear peaks and additional poorly resolved peaks at 117.4 p.p.m. Since the dihedral angle



between C-(4) and the hydrogen atom on C-(1) is approximately 60° , little or no coupling would be expected between these. However a coupling constant of 5 to 7Hz would be expected from this hydrogen atom to C-(2), and C-(2) would also be expected to couple to the methyl hydrogens with a coupling constant of about 7Hz,

resulting in a complex splitting pattern, Thus C-(4) and C-(5) would be expected to give a simple septet with J ca. 7 Hz and these were therefore assigned to the signal at 120.5 p.p.m., the more complex signal at 117.4 p.p.m. being assigned to C-(2) and C-(3).

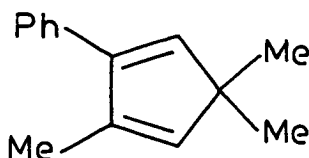
From this, the olefinic quaternary signals in the ^{13}C n.m.r. spectrum of 2,3-diisopropylidene-1-methyl-1-phenyl-cyclopropane (184) were assigned. The peak at higher chemical shift (122.8 p.p.m.) was assigned to the dimethyl carbon atom and the peak at 119.4 p.p.m. was assigned to C-(2) and C-(3).

The signals from other carbon atoms in compounds (182) and (183) were assigned by analogy with the other dimethylene-cyclopropanes described above.

The large variation in the chemical shifts of the quaternary carbon atoms in diaryldimethylenecyclopropanes (186), (187) and (188) made it impossible to assign them with any degree of certainty.

CHAPTER 3Reactions of Dimethylvinylidenecyclopropanes
with Acid3.1 Reactions of 1-Alkyl-2-dimethylvinylidene-1-phenylcyclo-
propanes

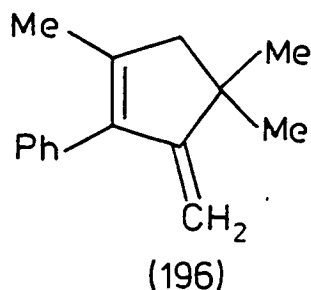
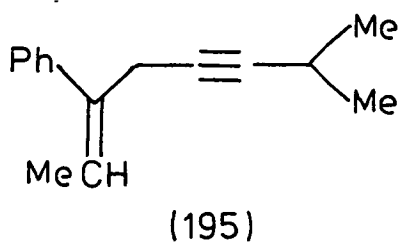
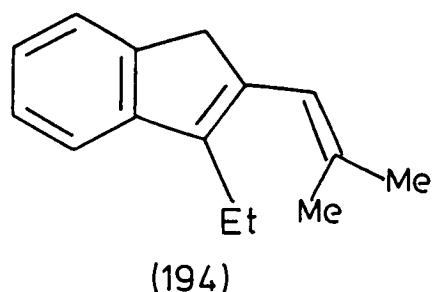
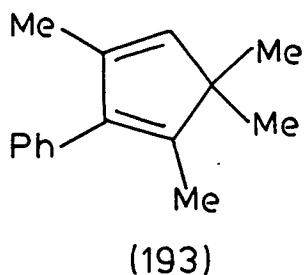
The *p*-toluenesulphonic acid catalysed rearrangement of 2-dimethylvinylidene-1-methyl-1-phenylcyclopropane (89), previously carried out by Harris,¹¹⁴ was re-examined in order to check the reaction mixture by high field ¹H n.m.r. (360MHz) spectroscopy. As previously found, the only product observed was the cyclopentadiene (100) with some polymeric material and



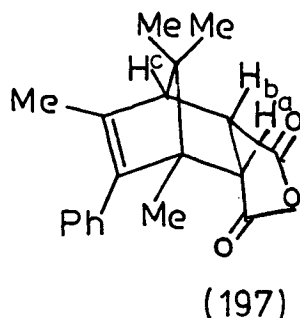
(100)

there was no evidence that γ -protonation had occurred.

The *p*-toluenesulphonic acid catalysed reaction of 2-dimethylvinylidene-1-ethyl-1-phenylcyclopropane (169) produced a mixture containing the cyclopentadiene (193), the indene (194) the enyne (195) and a compound tentatively identified as the methylenecyclopentene (196), in the ratio 5:3:1:3. The cyclopentadiene (193) was identified by comparison of its ¹H

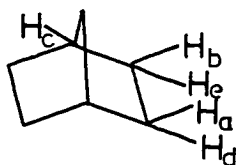


n.m.r. spectrum with that of the cyclopentadiene (100) and by conversion to its maleic anhydride adduct (197). The



cyclopentadiene (193) showed ^1H n.m.r. signals corresponding to a phenyl ring, an alkene proton, two alkene methyl groups, and two equivalent aliphatic methyl groups. The maleic anhydride adduct gave a ^1H n.m.r. spectrum analogous to that previously obtained for the adduct of the cyclopentadiene (100). In addition to phenyl and methyl resonances, it showed signals

at 3.80, 3.37 and 2.83 p.p.m., corresponding to H_a , H_b and H_c . The signal at 3.80 p.p.m. was split into a doublet of doublets from the coupling of H_b with H_a (7.9Hz) and H_c (4.8 Hz). These coupling constants, when compared with typical values in norbornane systems,¹²⁸ are consistent with the adduct (197) having the expected endo configuration as shown.

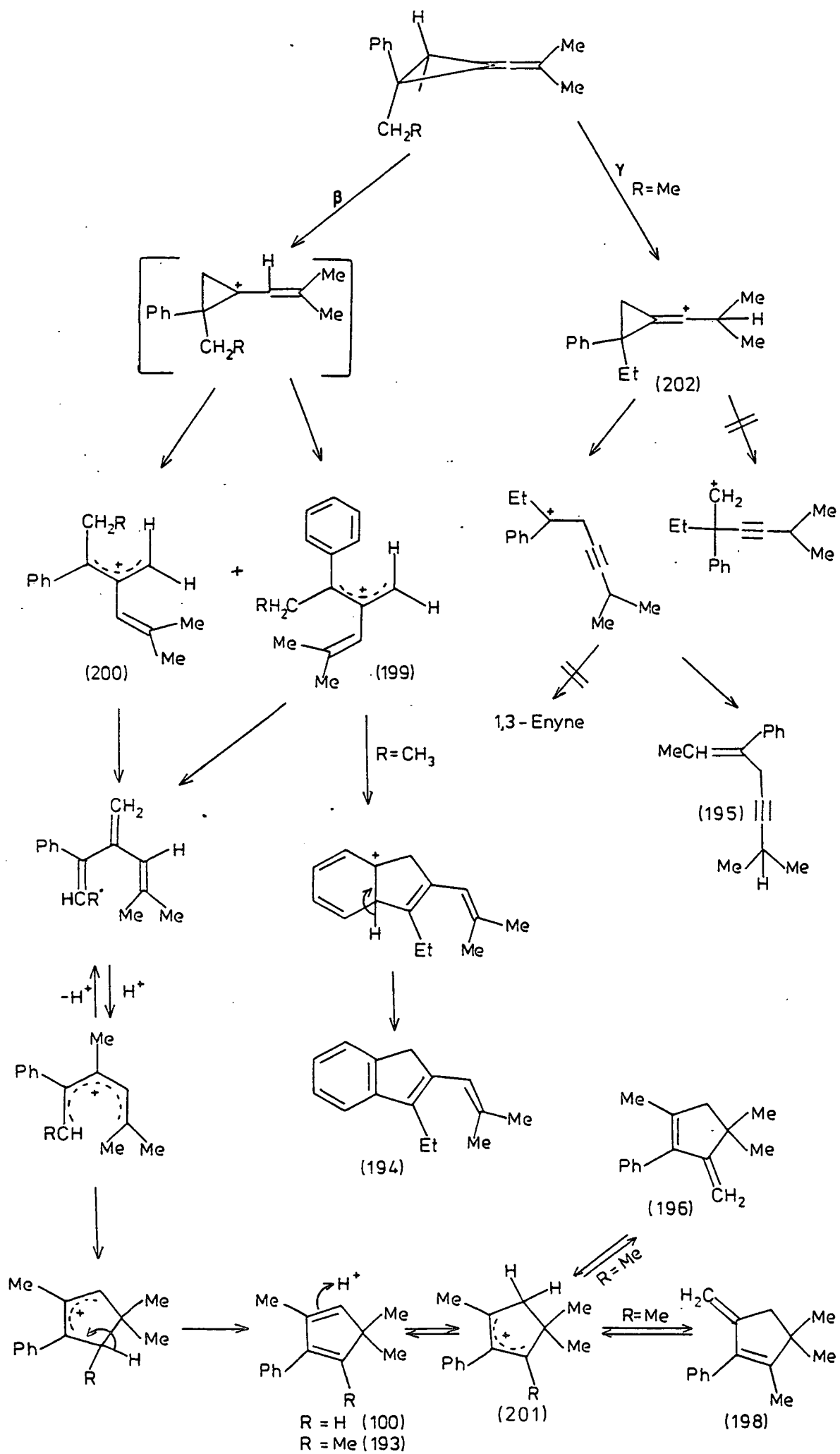


J_{ab}	9-10Hz
J_{de}	6-7Hz
J_{bc}	3-4Hz
J_{ec}	0-2Hz

The indene (194) was identified by comparison of its ^1H n.m.r. spectrum with those of 2-(2'-methylprop-1'-enyl)-3-phenylindene (113) and 3-(p-methoxyphenyl)-2-(2'-methylprop-1'-enyl)indene (114).¹¹⁴ The ^1H n.m.r. spectrum of indene (194) showed signals from the aromatic ring, the dimethyl group, the ethyl group and characteristic resonances at 2.65 and 6.32 p.p.m. from the methylene protons and the alkene proton respectively.

The ^1H n.m.r. spectrum of enyne (195) was consistent with both structures shown. In addition to the doublet from the isopropyl methyl groups, the doublet from the alkene methyl group, and the aromatic resonances, the ^1H n.m.r. spectrum showed the alkene proton as a quartet of triplets at 5.93 p.p.m. coupled to the alkene methyl and methylene protons, the methylene protons as a multiplet at 3.29 p.p.m. coupled to the alkene and isopropyl protons and a multiplet from the single isopropyl proton.

Scheme 10



The methylenecyclopentene (196) was tentatively identified from its ^1H n.m.r. spectrum and by analogy with the deuterium experiment outlined below. The ^1H n.m.r. spectrum of methylenecyclopentene (196) had signals at 1.14 p.p.m. from the alkene methyl protons shielded by the phenyl ring, 1.19 p.p.m. from the gem-dimethyl group, 1.77 p.p.m. from the methylene protons, 4.59 and 4.55 p.p.m. from the alkene protons and 7.50-7.05 p.p.m. from the aromatic protons. The isomer (196) was thought to be more likely than (198) since the low δ value of the alkene proton signals is consistent with one being shielded by a phenyl ring and the other by a gem-dimethyl group.

The reactions of both the 1-methyl and 1-ethyl derivatives (89) and (169) with ethanolic hydrogen chloride produced multi-component mixtures which were not resolved.

The mechanisms for protonation and subsequent rearrangement of the 1-methyl and 1-ethyl derivatives are given in Scheme 10. The cyclopentadienes (100) and (193), the indene (194) and the methylenecyclopentene (196) are all formed by β -protonation, whereas the enyne (195) is formed by γ -protonation.

β -Protonation followed by ring opening of both the 1-methyl and 1-ethyl derivatives can lead to formation of two allyl cations. Although the indene (194) could only have been formed directly from cation (199), both the cyclopentadienes (100) and (193), could have been formed from either allyl cation (199) or (200). ^{The formation of} analogous products by these mechanisms have previously been reported¹¹⁴⁻¹¹⁷ (see p.37-43).

The product tentatively identified as the methylenecyclopentene (196) is thought to be formed by protonation of the cyclopentadiene (193) to give allyl cation (201) which

deprotonates to give the methylenecyclopentene (196). Evidence for the analogous protonation of the cyclopentadiene (100) was obtained by reacting the 1-methyl derivative (89) with O-deuterated *p*-toluenesulphonic acid which gave deuterium incorporation at the sites shown (Fig.3). The same results were

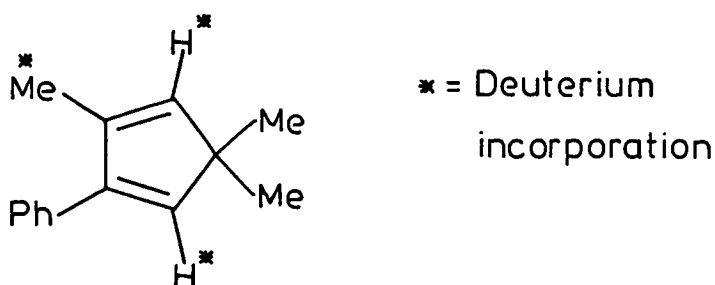


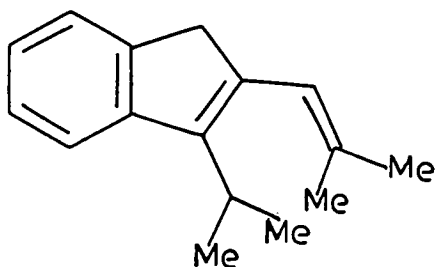
Figure 3

obtained on reacting the cyclopropane (89) with deuterium chloride in O-deuterated methanol¹¹⁵ and both results indicate that reversible protonation of the cyclopentadiene (100) takes place. Calculations of heats of formation using Benson's additivity rules³² gave the ΔH_f° value for the cyclopentadiene (193) to be 24.09 kcal mol⁻¹ and for both the methylenecyclopentenes (196) and (198) to be 27.54 kcal mol⁻¹. Similar calculations also find 2-methylcyclopentadiene to be 3.42 kcal mol⁻¹ more stable than 3-methylenecyclopentene. The small energy differences between these sets of isomers are consistent with the proposed interconversion of the cyclopentadiene (193) and the methylenecyclopentene (196).

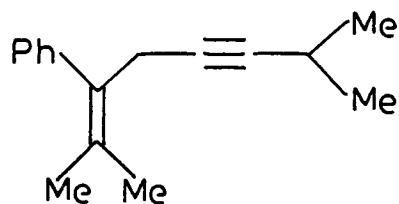
The enyne (195) is formed by γ -protonation of cyclopropane (169) to give the vinyl cation (202) followed by ring opening and deprotonation to give only one of the enyne isomers (195).

The *p*-toluenesulphonic acid catalysed reaction of the 1-isopropyl derivative (170) produced a complex mixture from which only the indene (203) could be separated and it was

identified by comparison of its ^1H n.m.r. spectrum with that of the indene (194). However, it is significant that the ^1H



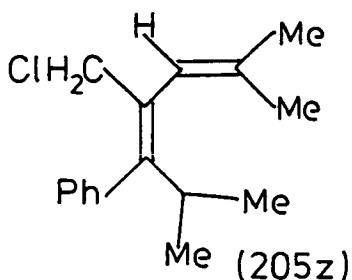
(203)



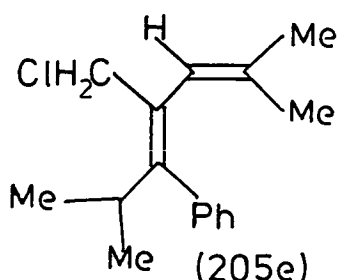
(204)

n.m.r. spectrum of the reaction mixture does not show the multiplet between 2 and 3 p.p.m. which would be expected from the methylene protons of enyne (204), therefore suggesting that γ -protonation has not taken place to a significant extent.

The reaction of cyclopropane (170) with 1 molar hydrogen chloride in ethanol produced a mixture containing both Z and E-4-chloromethyl-2,6-dimethyl-5-phenylhepta-2,4-diene (205z and e) in the ratio 4.5:1 with a significant amount (ca.20%) of several minor unidentified products.



(205z)



(205e)

The isomers (205e and z) were identified from the ^1H and ^{13}C (DEPT) n.m.r. spectra of the reaction mixture. The ^1H n.m.r. (360MHz) spectrum of the reaction mixture clearly shows resonances from all the protons in both isomers (205e) and (205z). The major isomer (205z) gives a septet at 5.78 p.p.m. from the

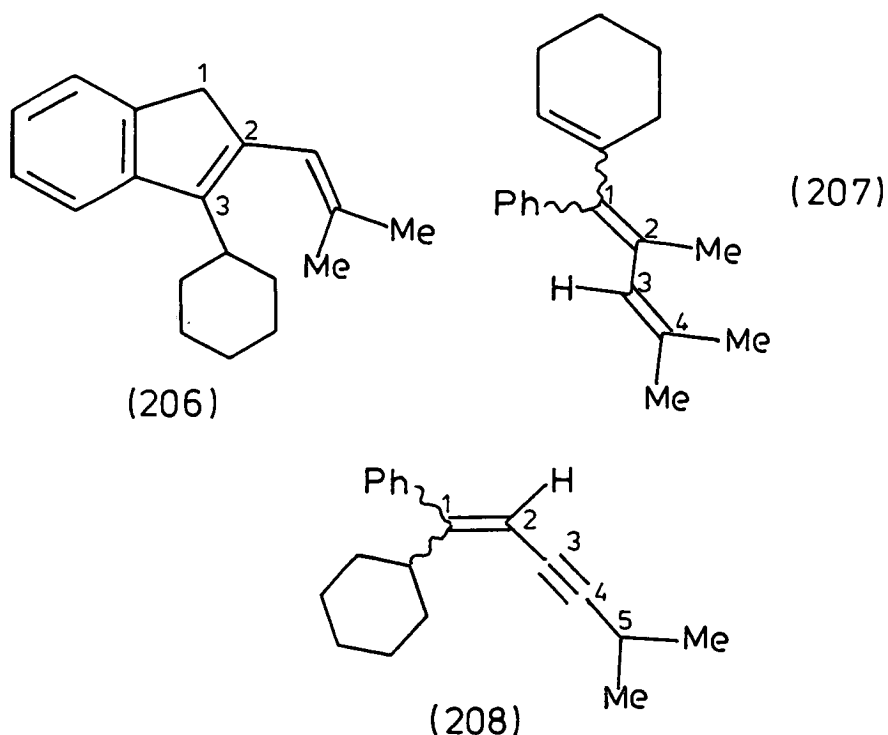
alkene proton, a singlet at 3.75 p.p.m. from the chloromethylene protons, doublets at 1.87 and 1.73 p.p.m. from the alkene methyl protons and a septet at 3.00 p.p.m. and a doublet at 0.87 p.p.m. from the protons of the isopropyl group. The minor isomer (205e) gives a septet at 5.41 p.p.m. from the alkene proton, a singlet at 4.31 p.p.m. from the chloromethylene protons, doublets at 1.82 and 1.63 p.p.m. from the alkene methyl protons and a septet at 3.55 p.p.m. and a doublet at 0.87 p.p.m. from the isopropyl group. The ^{13}C n.m.r. (DEPT) spectrum of the reaction mixture shows a methylene carbon atom signal at 47.4 p.p.m., indicating the presence of a chloromethylene group. The mass spectrum supported the presence of hydrogen chloride addition products.

The stereochemistries of (205e and z) were assigned by the position of the chloromethylene peaks in the ^1H n.m.r. spectrum of the mixture. The chemical shift of the chloromethylene group is lower in the E-isomer since the protons lie over the phenyl ring and are shielded by it.

This type of addition in the reactions of vinylidenecyclopropanes with hydrogen chloride has not previously been reported although similar additions using other acids have been observed.
110,111

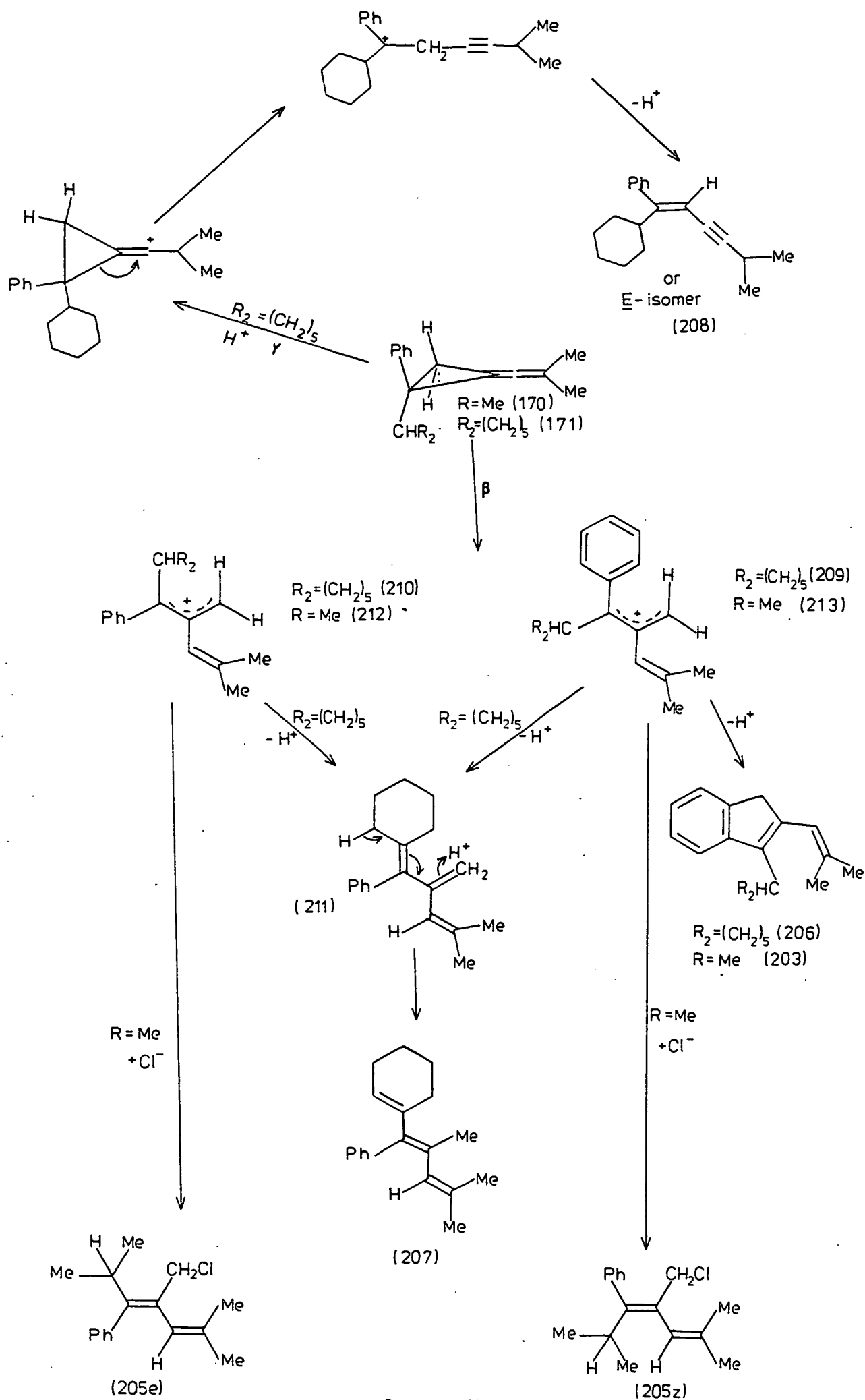
The p-toluenesulphonic acid catalysed rearrangement of the 1-cyclohexyl derivative (171) gave a mixture containing the indene (206), the triene (207), the enyne (208) and an unidentified compound in the ratio 10:1.1:0.9:1.0.

The ^1H n.m.r. spectrum of the indene (206) shows a singlet at 3.54 p.p.m. corresponding to the benzylic protons, a broad



signal at 6.27 p.p.m. for the alkene proton, signals at 1.93 and 1.89 p.p.m. for the alkene methyl protons and a triplet of triplets at 2.83 p.p.m. corresponding to the single methyne proton on the cyclohexane ring. The large coupling here (12.5Hz) is to the trans protons, the smaller coupling (3.2Hz) is to the cis protons, indicating an axial location for this proton. An envelope of peaks from 2.15 to 0.90 p.p.m. corresponds to the ten other protons in the cyclohexyl group.

The triene (207) was identified from its ^1H n.m.r. spectrum which shows only one alkene proton resonance at 5.62 p.p.m., integrating for two protons, and resonances from a phenyl group, three alkene methyl groups and eight cyclohexyl protons. Decoupling of the signal due to the alkene protons caused sharpening of all methyl proton peaks (caused by coupling from H-3) and sharpening of multiplets at 1.82 and 1.95 p.p.m.,



Scheme 11

which were due to cyclohexyl protons.

The resonance from the isopropyl proton in the ^1H n.m.r. of enyne (208) appears as a septet of doublets, as a result of coupling to the isopropyl methyl protons and a five bond coupling to H-2 ($J_5=2.0\text{Hz}$). Similarly, the signal from the alkene proton appears as a doublet. Decoupling the isopropyl proton collapsed the doublet at 1.25 p.p.m. and the doublet at 5.43 p.p.m. As with the indene (206), the single cyclohexyl methyne proton in the enyne appears as a triplet of triplets at higher chemical shift than the other cyclohexyl protons.

The reaction of the 1-cyclohexyl derivative (171) with ethanolic hydrogen chloride was not attempted.

The very high proportion of the indene (206) formed in the reaction of the 1-cyclohexyl derivative (171) with *p*-toluenesulphonic acid seems to indicate a very strong preference for β -protonation with inward rotation of the phenyl group, since the indene (206) can only be formed directly from cation (209) (Scheme 11). The formation of the triene (207) from the 1-cyclohexyl derivative (171) is rationalised by deprotonation of either allyl cation (209) or (210), to give the triene (211) which rearranges to give the more stable, fully conjugated isomer containing an endo double bond.

The reaction of the 1-isopropyl derivative (170) with ethanolic hydrogen chloride also proceeds mainly by β -protonation to give the allyl cations (212) and (213) which react with the chloride ion to give addition products (205e) and (205z) respectively. The cation (212) can only give the addition product (205e) and likewise, cation (213) can only give (205z). It might be expected that addition to the allyl cations (212)

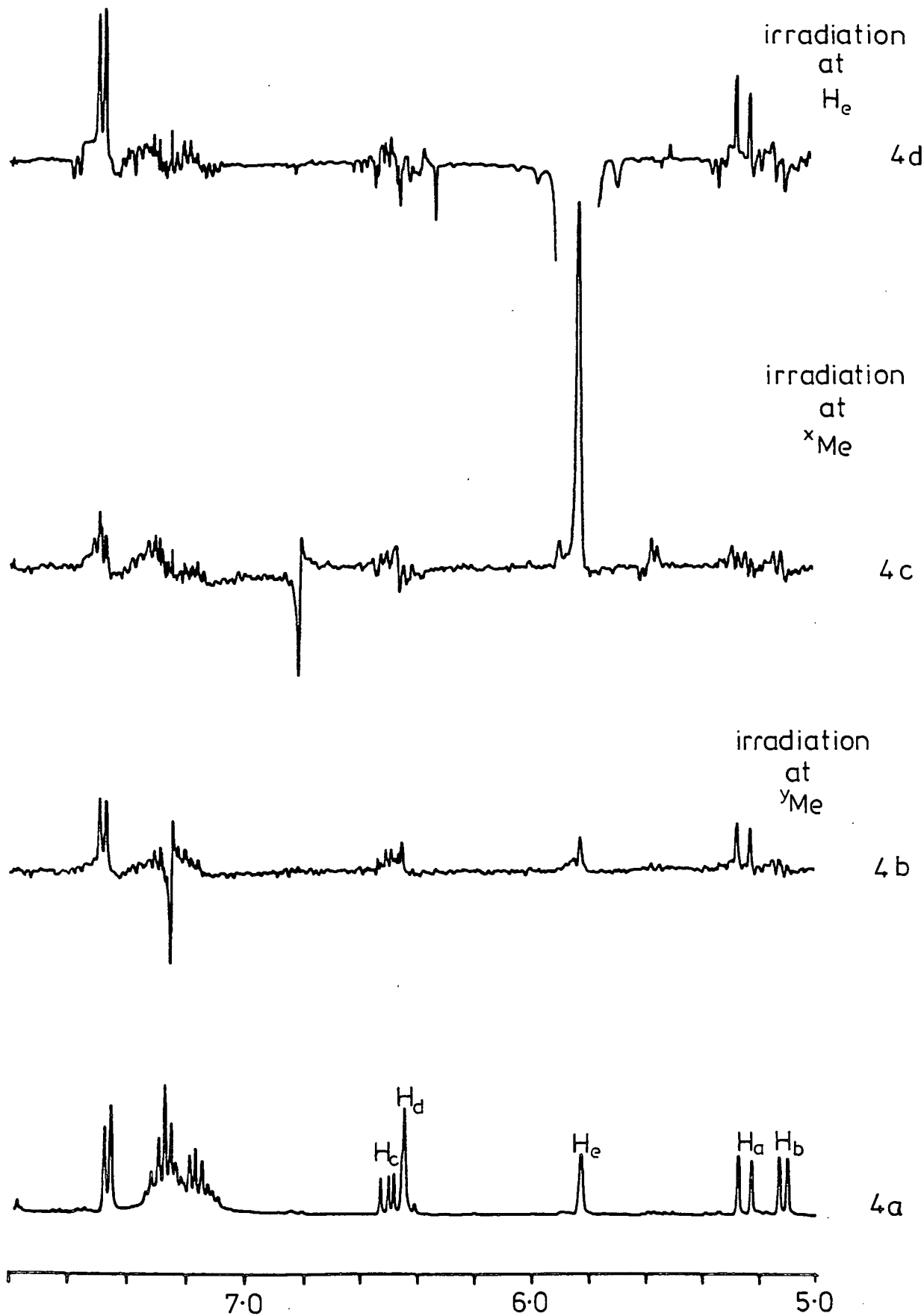
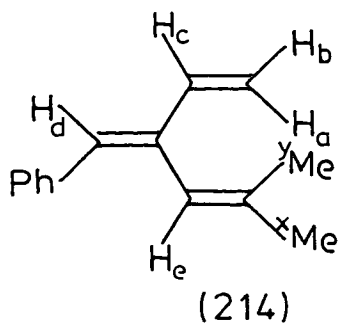
and (213) could occur at either end, but only the more stable isomers, where the double bonds are conjugated to the aromatic ring, are observed, even though the charge density is greater on the benzylic carbon atom. The addition of the chloride ion must therefore be thermodynamically controlled. If the allyl cations (212) and (213) react with the chloride ion before they are able to interconvert, then the 4.5:1 ratio of addition products (205z) to (205e) confirms that, in the disrotatory opening of the cyclopropane ring, inward rotation of the phenyl group is preferred to inward rotation of the isopropyl group.

The enyne (208) is formed by γ -protonation of the 1-cyclohexyl derivative (171) followed by ring opening to give the benzylic cation. Deprotonation occurs to give the conjugated 1,3-enyne (208) rather than the 1,4-enyne. Since all the products from this reaction decomposed, even when stored at 4°C, it was not possible to determine the stereochemistry of either the triene (207) or the enyne (208).

The above observations show that β -protonation is favoured over γ -protonation in the rearrangements of both the 1-isopropyl and 1-cyclohexyl derivatives (170) and (171), and suggest that ring opening occurs predominately by inward rotation of the phenyl group.

In these *p*-toluenesulphonic acid catalysed rearrangements of 1-alkyl-2-dimethylvinylidene-1-phenylcyclopropanes the only observed products which could have been formed from only one of the two possible allyl cations formed by β -protonation are the indenenes. Since the proportion of indene formed increased from the 1-methyl to the 1-cyclohexyl derivatives, this indicates that, as expected, the mode of ring opening is controlled by

Figure 4



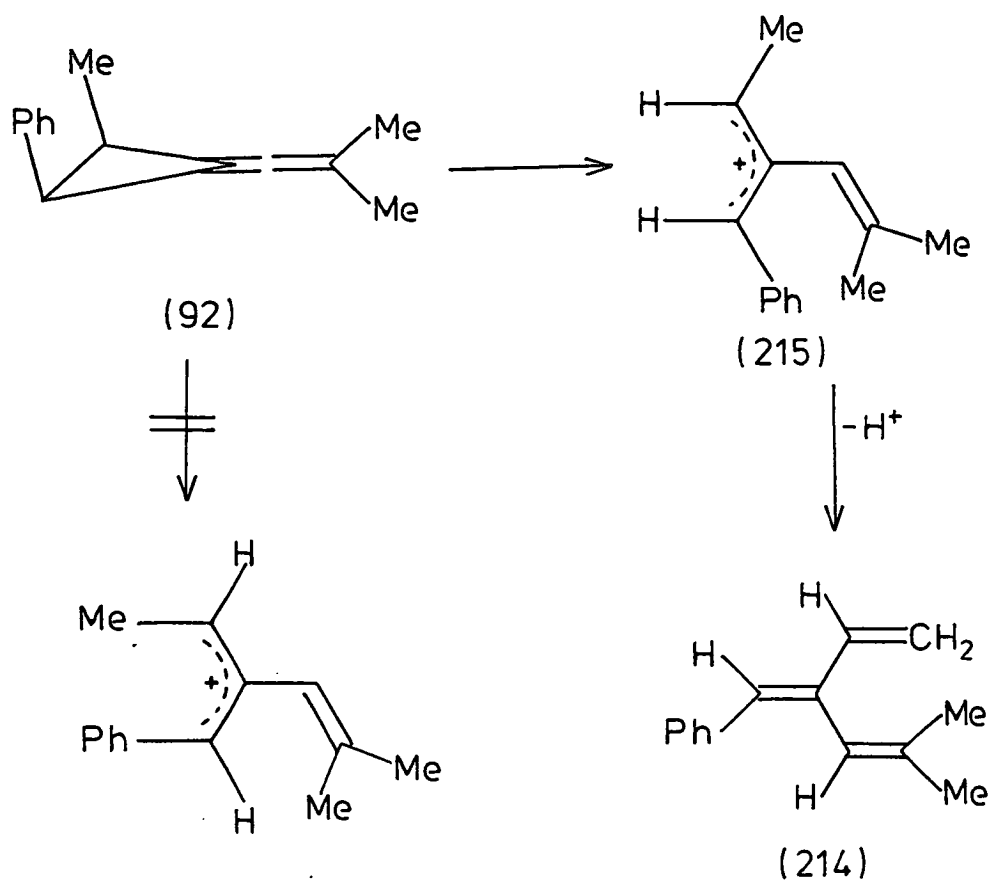
steric factors in these cases, inward rotation of the phenyl group being more favoured for larger alkyl substituents. The reaction of the 1-isopropyl derivative (170) with ethanolic hydrogen chloride gave products in keeping with the above results with inward rotation of the phenyl group in ring opening appearing to be favoured over inward rotation of the isopropyl groups.

3.2 Reactions of the E and Z-2-Dimethylvinylidene-3-methyl-1-phenylcyclopropanes (93) and (92)

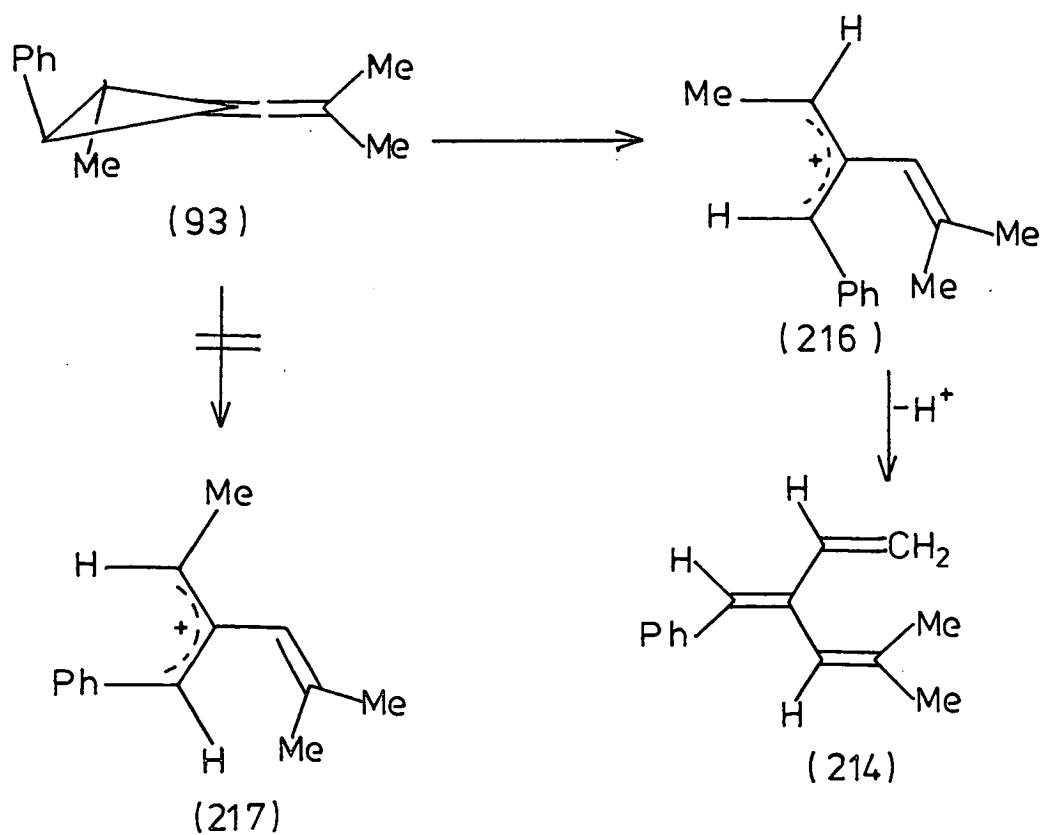
The reaction of Z-2-dimethylvinylidene-3-methyl-1-phenylcyclopropane (92) with *p*-toluenesulphonic acid gave only the triene (214) which was identified from its ^1H n.m.r. spectrum, which showed a phenyl group, a vinyl group, an isobutenyl group ($\text{Me}_2\text{C}=\text{CH}-$) and a fifth alkene proton.

The vinyl signals H_a , H_b and H_c were assigned by their multiplicities and coupling constants (see Fig.4a). The doublet of doublets of doublets at 6.50 p.p.m. was assigned to H_c with coupling to H_a (17.1Hz), H_b (10.3Hz) and H_d (0.7Hz). The doublet of doublets at 5.24 ($\underline{J}$ 17.1, 1.4Hz) was assigned to H_a with its large trans coupling and small geminal coupling and the remaining doublet of doublets at 5.13 p.p.m. ($\underline{J}$ 10.3, 1.4Hz) was assigned to H_b . H_d and H_e both show broad multiplets and the alkene methyl groups both give clear doublets at 1.89 and 1.45 p.p.m.

The stereochemistry of triene (214) was determined from N.O.E. difference spectra (Fig.4b-d). Irradiation of the methyl signal at 1.45 p.p.m. resulted in a 1% increase in only



Scheme 12



Scheme 13

the signals from H_a and the ortho protons of the benzene ring, allowing the signal at 1.45 p.p.m. to be assigned to the methyl protons, H_y , and therefore the resonance at 1.89 p.p.m. was assigned to the methyl protons, H_x . Irradiation of the latter signal caused a 10% increase in the resonance at 5.84 p.p.m., allowing its assignment to H_e , since the methyl protons, H_x , cannot get close enough to H_d in either isomer to cause an N.O.E. Irradiation of the signal from H_e , at 5.84 p.p.m. caused a 2% increase in both the signals from the ortho protons and H_a but no increase in the signal from H_d . These experiments prove that the product formed is the Z-isomer, as shown, since, in the E-isomer, H_e could not get close to the phenyl group, but would be close to H_d .

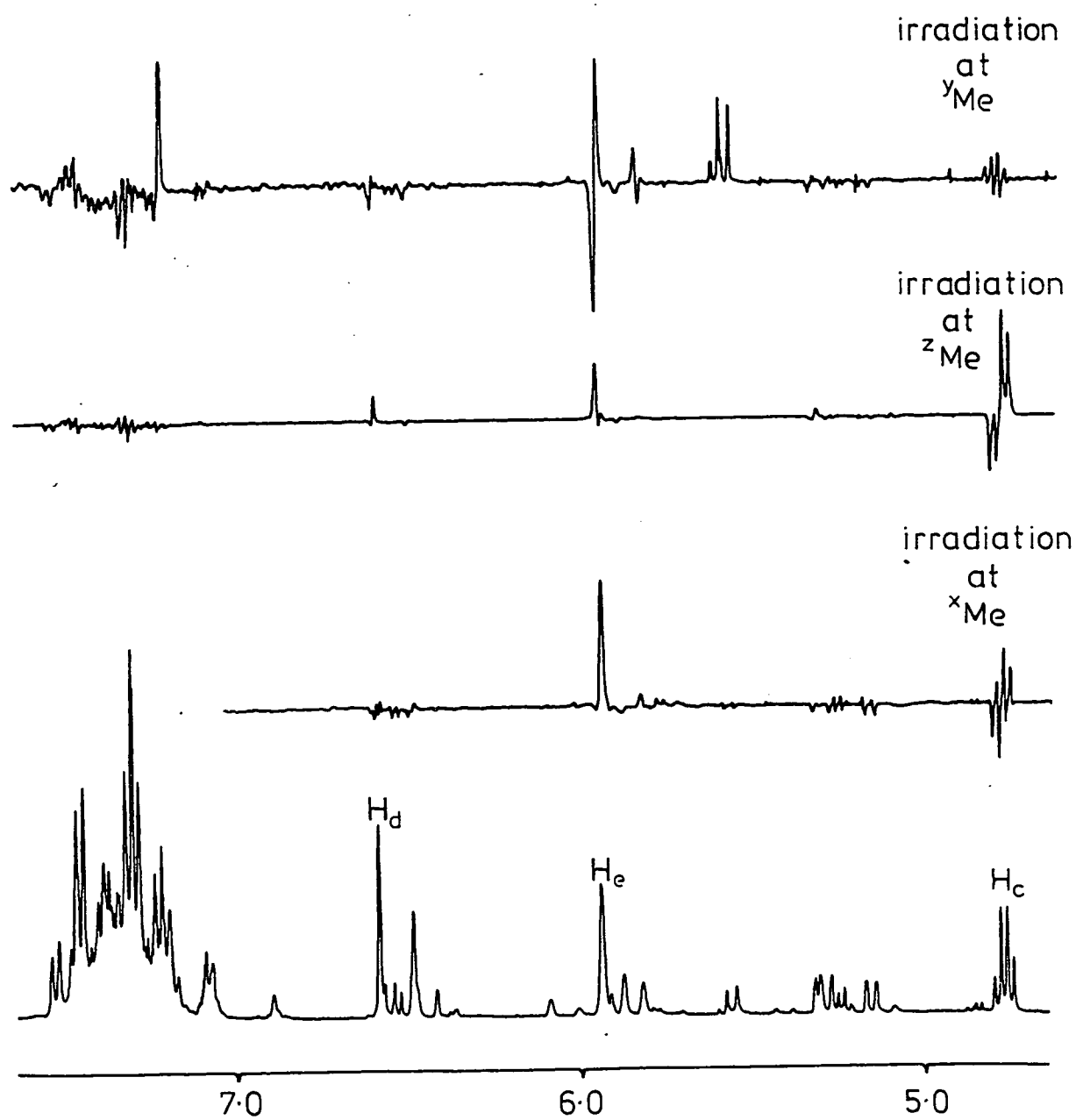
The reaction of E-2-dimethylvinylidene-3-methyl-1-phenylcyclopropane (93) with *p*-toluenesulphonic acid gave a mixture containing the triene (214), the thermolysis product, syn-3-ethylidene-2-isopropylidene-1-phenylcyclopropane (180a) and starting material in the ratio 1:1.8:0.8, with no evidence of any γ -protonation products.

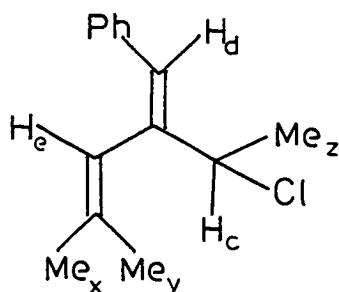
The triene (214) was formed from both the Z- and E-2-methyl derivatives (92) and (93) by β -protonation. The Z-2-methyl derivative (92) ring opens with outward rotation of both the methyl and phenyl groups to give allyl cation (215) which deprotonates to give triene (214) (Scheme 12). For protonation of the E-2-methyl derivative (93), disrotatory ring opening could give either allyl cation (216) or (217) (Scheme 13). However since only cation (216) can give the observed triene (cation (217) would give the E-isomer) and since no other protonation products were observed, it can be assumed that only

allyl cation (216), which allows the phenyl ring to be coplanar with the allyl π -system, is formed in this reaction. This ring opening of the E-2-methyl derivative (93) requires inward rotation of the methyl group and is therefore subject to steric hindrance not present in the ring opening of the Z-isomer (92). This causes a reduced rate of protonation to the allyl cation. This, together with the observation¹²³ that the E-2-methyl derivative (93) undergoes faster thermal rearrangement than the Z-isomer (92), would explain the formation of the thermolysis product (180a) from only the above reaction of the E-isomer (93). Mild conditions (130°C) for the thermolysis of the E-isomer (93) produced greater proportions of the kinetically favoured syn-isomer (180a) over the anti-isomer (180b) (98:2),¹²³ as observed in the present work.

The reaction of the Z-2-methyl derivative (92) with 1 molar hydrogen chloride in ethanol produced a mixture containing the triene (214) and E-4-benzylidene-5-chloro-2-methylhex-2-ene (218) in the ratio 1:2.3. Attempts to isolate the addition product by preparative g.l.c. at 130° resulted in its decomposition and it was therefore identified from the spectral properties of the reaction mixture. In addition to resonances from the triene (214), the ¹H n.m.r. spectrum showed major peaks consistent with the structure shown, the resonance from H_C appearing as a quartet (J 6.7Hz) at 4.74 p.p.m. and the methyl protons, H_Z, giving a doublet (J 6.7Hz) at 1.65 p.p.m. The ¹³C n.m.r. spectrum (DEPT, methyne carbon atom signals only) shows a resonance at 64.0 p.p.m., indicating the presence of a chlorinated methyne carbon atom. The mass spectrum of the mixture has peaks at m/z = 222 and 220 in the ratio 1:3 with the major

(218)





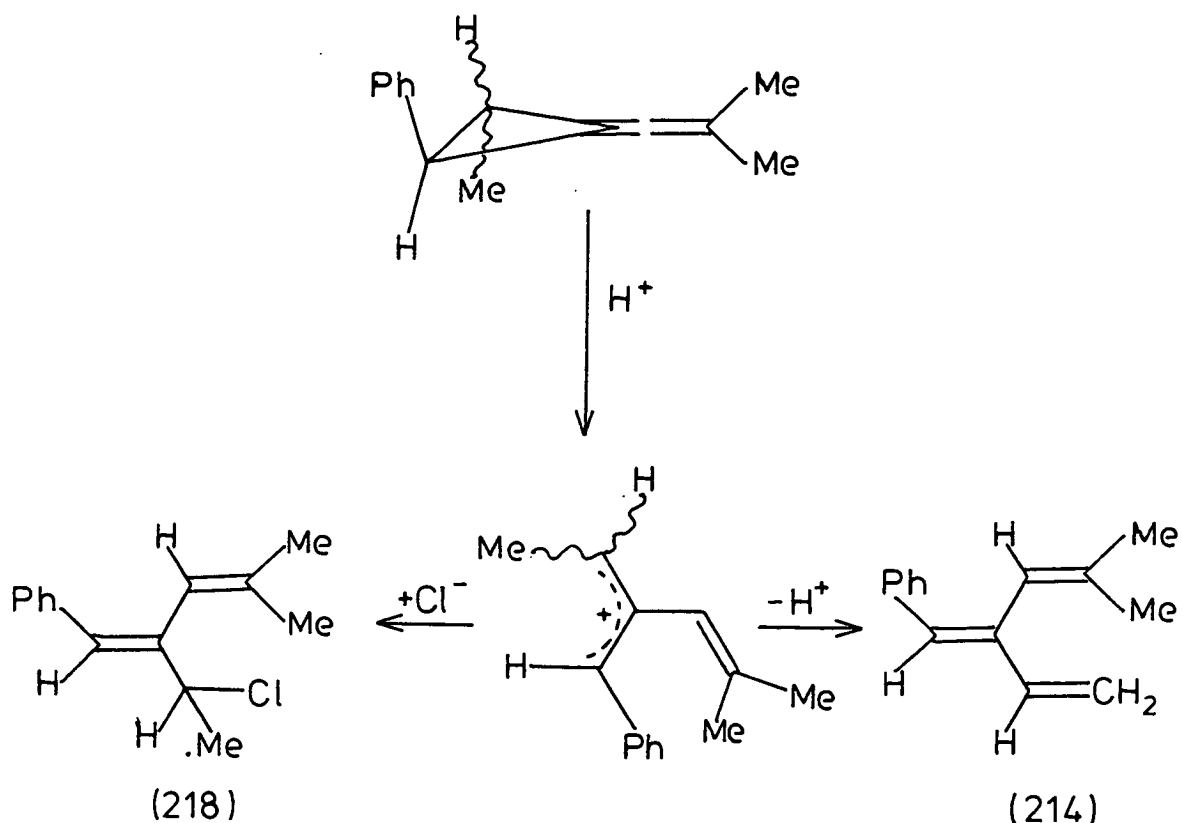
(218)

peak at $m/z = 184$, indicating loss of hydrogen chloride.

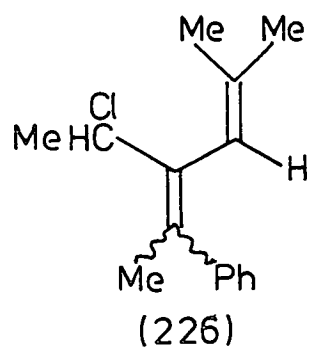
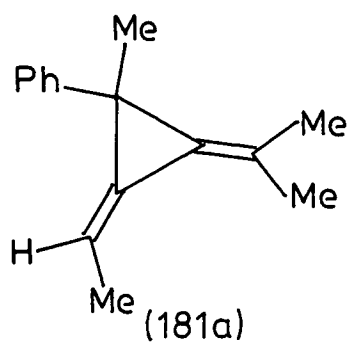
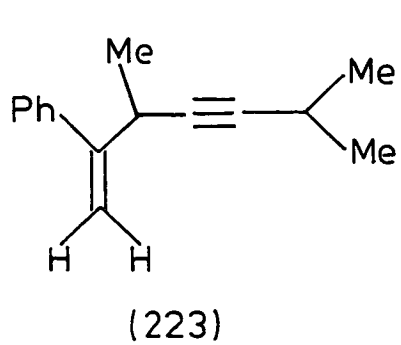
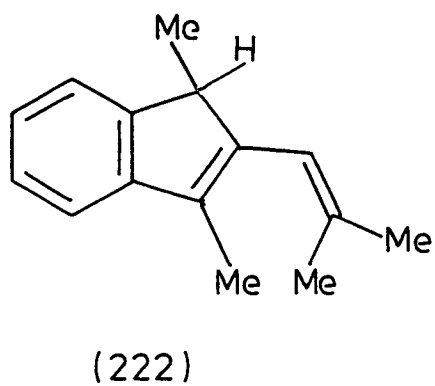
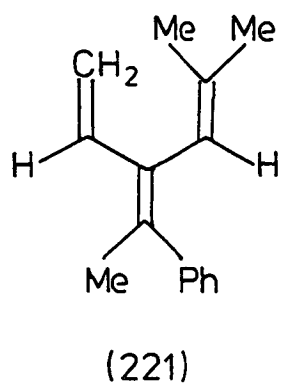
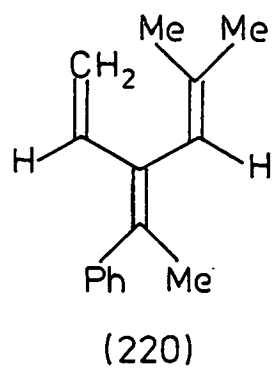
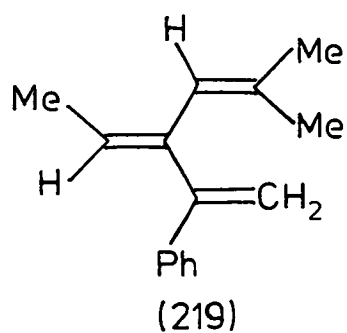
The stereochemistry of addition product (218) was determined by N.O.E. difference experiments on the reaction mixture (see Fig.5). Irradiation of the signal at 1.32 p.p.m. gave an increase in the aromatic signals but no increase in the alkene proton resonances. This proves the molecule to have the E-configuration and also allows assignment of the methyl protons, H_y , to the resonance at 1.32 p.p.m. and therefore the methyl protons, H_x , to the resonance at 1.81 p.p.m. Irradiation of the doublet at 1.65 p.p.m. from the methyl protons, H_z , produced a 2% increase in the signal at 6.55 p.p.m., a 4% increase in the signal at 5.90 p.p.m. and a 5% increase in the signal from H_c , confirming the stereochemistry of the product. Irradiation of the resonance at 1.81 p.p.m. from the methyl protons, H_x , produced a 6% increase in the resonance at 5.90 p.p.m., allowing assignment of the latter signal to H_e and therefore the signal at 6.55 p.p.m. to H_d .

The reaction of the E-2-methyl derivative (93) with hydrogen chloride in ethanol gave a mixture containing the triene (214) and the addition product (218) in the ratio 1:3.5.

The presence of the addition product, formed in both these reactions of the 2-methyl derivatives (92) and (93) with hydrogen chloride, can be explained by β -protonation with ring opening to form the same allyl cations (215) and (216) as were formed in the *p*-toluenesulphonic acid catalysed reactions, followed by reaction with the halide ion rather than deprotonation. Since the above reactions with *p*-toluenesulphonic



acid involve only a catalytic amount of acid, addition cannot occur to a significant extent. However, in the reactions with hydrogen chloride in ethanol a nine fold excess of acid was used and therefore acid addition was possible. As previously observed in the reaction of the 1-isopropyl derivative (170) with hydrogen chloride, addition at the non-benzylic carbon atom gives the thermodynamically more stable product. Similar addition reactions, using trichloroacetic acid, have



previously been reported¹¹¹ for the reactions of both the E- and Z-3-methyl derivatives (93) and (92), but no evidence for formation of the triene was obtained nor was the stereochemistry of the product proven. No evidence was found in the present study for products from γ -protonation.

3.3 Reactions of the E and Z-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropanes (172) and (173)

The reactions of both the E and Z-1,3-dimethyl-2-dimethylvinylidene-1-phenylcyclopropanes (172) and (173) with *p*-toluenesulphonic acid proved complex, with product ratios being dependent on the stereochemistry of the starting material, the concentration of the acid used and the time for which the reaction was allowed to proceed.

The reaction of the E-derivative (172) with 4% *p*-toluenesulphonic acid after 3 h gave E-3-ethylidene-5-methyl-2-phenylhexa-1,4-diene (219), both the E- and Z-isomers of 2-methyl-5-phenyl-4-vinylhexa-2,4-diene (220) and (221), 1,3-dimethyl-2-(2'-methylprop-1'-enyl)indene (222), 2,5-dimethyl-6-phenylhepta-6-ene-3-yne (223) and the thermolysis product, syn-3-ethylidene-2-isopropylidene-1-methyl-1-phenylcyclopropane (181a) in the ratio of 12:10:2:6:8:5. The evidence for the structure of these products will be given later. The reaction of the E-derivative (172) with 10% *p*-toluenesulphonic acid after 25 h gave the trienes (219) and (220), the enyne (223) and the thermolysis product (181a) in the ratio 2:1:1:3.5 with some evidence for the presence of 1,2-benzo-4-ethyl-3,6,6-trimethylfulvene (224) and E-4-ethyl-2-methyl-5-phenyl-3-(*p*-toluene-

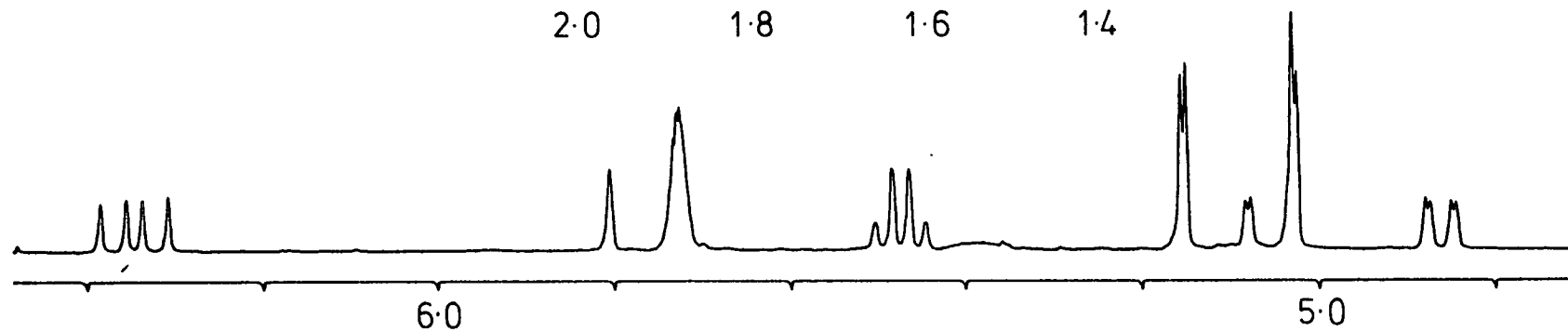
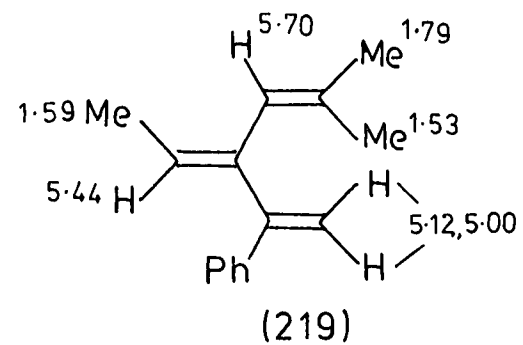
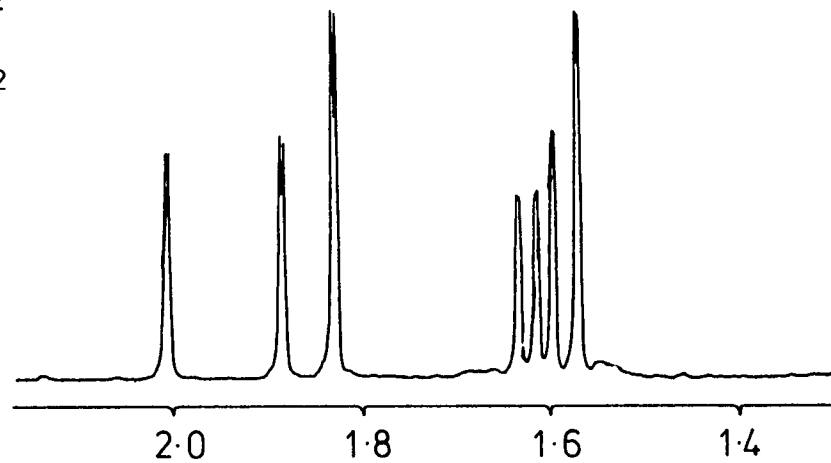
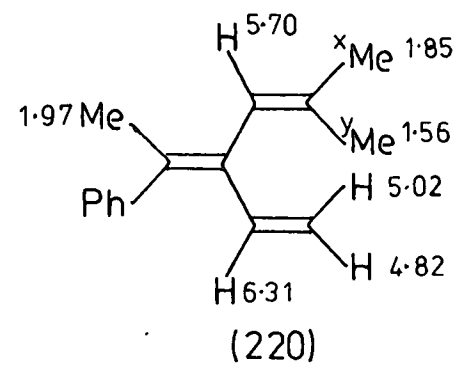
sulphonyloxy)hexa-2,4-diene (225) both from the reaction of the thermolysis product (181a) with *p*-toluenesulphonic acid (see section 4.6). No evidence was found for formation of the triene (221) or the indene (222).

The reaction of the Z-derivative (173) with 8% *p*-toluene sulphonic acid after 48 h gave the trienes (219), (220) and (221) the enyne (223) and the thermolysis product (181a) in the ratio of 25:10:5:8:30 with a small amount of a starting material and no evidence for formation of the indene (222). The reaction of the Z-derivative (173) with 10% *p*-toluenesulphonic acid after 40 h gave the trienes (219) and (220), the indene (222) and the enyne (223) in the ratio 2:2:4:7 with small amounts of the benzofulvene (224) and the ester (225). The reaction of the Z-derivative (173) with 20% *p*-toluenesulphonic acid after 15 h gave the indene (222) and the enyne (223) in the ratio 10:6 with small amounts of the benzofulvene (224) and the ester (225) and no evidence for formation of the trienes (219), (220) and (221).

The reaction of the E-derivative (172) with 1 molar hydrogen chloride in ethanol produced the trienes (219) and (220), the indene (222), the enyne (223) and the addition product 5-chloro-4-(2'-phenylethylidene)-2-methylhex-2-ene (226) in the ratio 8:9:34:15:34. The reaction of the Z-derivative under the same conditions produced the same products in the ratio 7:10:28:21:35.

The product ratios in the above reactions were deduced from careful integration of well resolved regions of the ¹H n.m.r. spectra of the reaction mixtures. Separation of these mixtures was difficult and normally resulted, at best, in two

Figure 6



component mixtures. Comparison of the high field ^1H n.m.r. spectra of the separated fractions allowed the clear selection of all the resonances of the compounds which were identified principally in this manner.

The triene (219) was identified from its ^1H n.m.r. spectrum and by a series of spin decoupling experiments and N.O.E. difference experiments. The ^1H n.m.r. spectrum (Fig.6) shows doublets at 1.79 and 1.53 p.p.m. and a multiplet at 5.70 p.p.m. indicating the presence of an isobutenyl group which was confirmed by spin decoupling. A doublet of doublets at 1.59 p.p.m. (J 7.0, 1.0Hz) coupled to a quartet of doublets at 5.44 p.p.m. (J 7.0, 0.4Hz) indicated the presence of an ethylidene group which was also confirmed by spin decoupling. Two doublets at 5.12 and 5.00 p.p.m. (J 2.0Hz) with the resonances from the aromatic protons suggested the presence of a 1'-phenylethenyl group which was supported by spin decoupling. N.O.E. difference experiments were used to assign ^1H n.m.r. signals and to determine the stereochemistry. Irradiation of the resonance at 1.79 p.p.m. produced a 12% increase in the signal at 5.70 p.p.m. allowing its assignment to the methyl protons cis to the alkene proton and the assignment of the resonance at 1.53 p.p.m. to the methyl protons trans to the same alkene proton. Irradiation of the doublet at 1.59 p.p.m. produced a 10% increase in the quartet at 5.44 p.p.m. and a 2% increase in the alkene proton resonance at 5.70 p.p.m., the latter allowing assignment of the E-stereochemistry to the product.

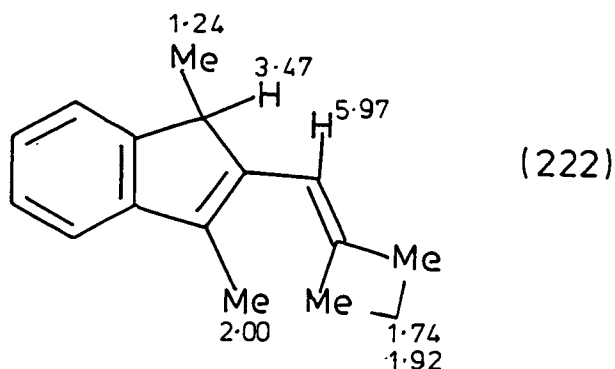
Triene (220) was similarly identified. The ^1H n.m.r. spectrum (Fig.6) shows an AMX system, due to vinyl protons at 6.31 p.p.m. (J 17.3, 10.5Hz), 5.02 p.p.m. (J 17.3, 2.1Hz) and 4.82 p.p.m. (J 10.5, 2.1Hz). This was confirmed by a spin

decoupling experiment, irradiating at 6.31 p.p.m. A multiplet at 5.70 p.p.m. together with doublets at 1.85 and 1.56 p.p.m. indicated the presence of an isobutenyl group which was also confirmed by spin decoupling. The remaining methyl proton resonance at 1.97 p.p.m. and the phenyl proton resonances were assigned to a 1'-phenylethylidene group. N.O.E. difference experiments were used to assign resonances in the ^1H n.m.r. spectrum and to determine the stereochemistry. Irradiation of the doublet of doublets at 6.31 p.p.m. produced a 5% increase in the resonance at 5.00 p.p.m. confirming the assignments of the vinyl proton resonances made on the basis of the coupling constants. Irradiation of the resonance at 1.85 p.p.m. produced a 2% increase in the resonance at 5.70 p.p.m. allowing assignment of the former to the methyl protons, H_x and the resonance at 1.56 p.p.m. to the methyl protons, H_y . Although irradiation of the resonance at 1.97 p.p.m. produced a 2% increase in the resonance at 5.70 p.p.m., it was not possible to be certain that this was not the result of some irradiation of the adjacent peak at 1.85 p.p.m. Irradiation of the aromatic resonances produced a 4% increase in the doublet of doublets at 6.31 p.p.m. and a 1% increase in the resonance at 1.97 p.p.m. The former increase allowed the assignment of the E-stereochemistry to the triene (220), the latter confirmed the presence of the 1'-phenylethylidene group.

The triene (221) was identified by comparison of its ^1H n.m.r. spectrum with that of its E-isomer, triene (220).

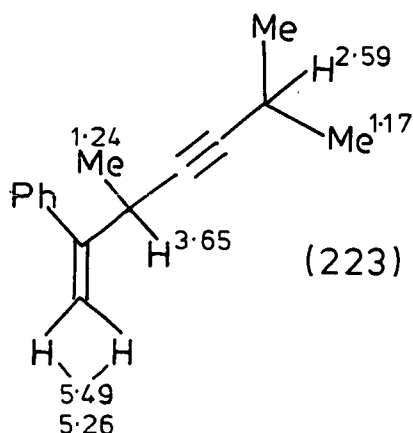
The indene (222) was identified by its ^1H n.m.r. spectrum and by comparison with other similar compounds. The ^1H n.m.r. spectrum shows a multiplet at 5.97 p.p.m. and doublets at 1.92 and 1.74 p.p.m. which indicated the presence of an isobutenyl

group. This was confirmed by spin decoupling, irradiating at 5.97 p.p.m. A quartet (J 7.1Hz) at 3.47 p.p.m. and a



doublet (J 7.1Hz) at 1.24 p.p.m. from methyl protons indicated the presence of a benzylic proton coupled to three methyl protons, which was also confirmed by spin decoupling. The broad methyl proton resonances at 2.00 p.p.m. was sharpened by irradiation at 5.97 and at 3.47 p.p.m.

The ^1H n.m.r. spectrum of the enyne (223) shows a doublet (J 6.8Hz) at 1.17 p.p.m. from the isopropyl methyl protons and a septet of doublets (J 6.8, 2.0Hz) at 2.59 p.p.m. from the isopropyl hydrogen atom. A broad quartet at 3.65 p.p.m.

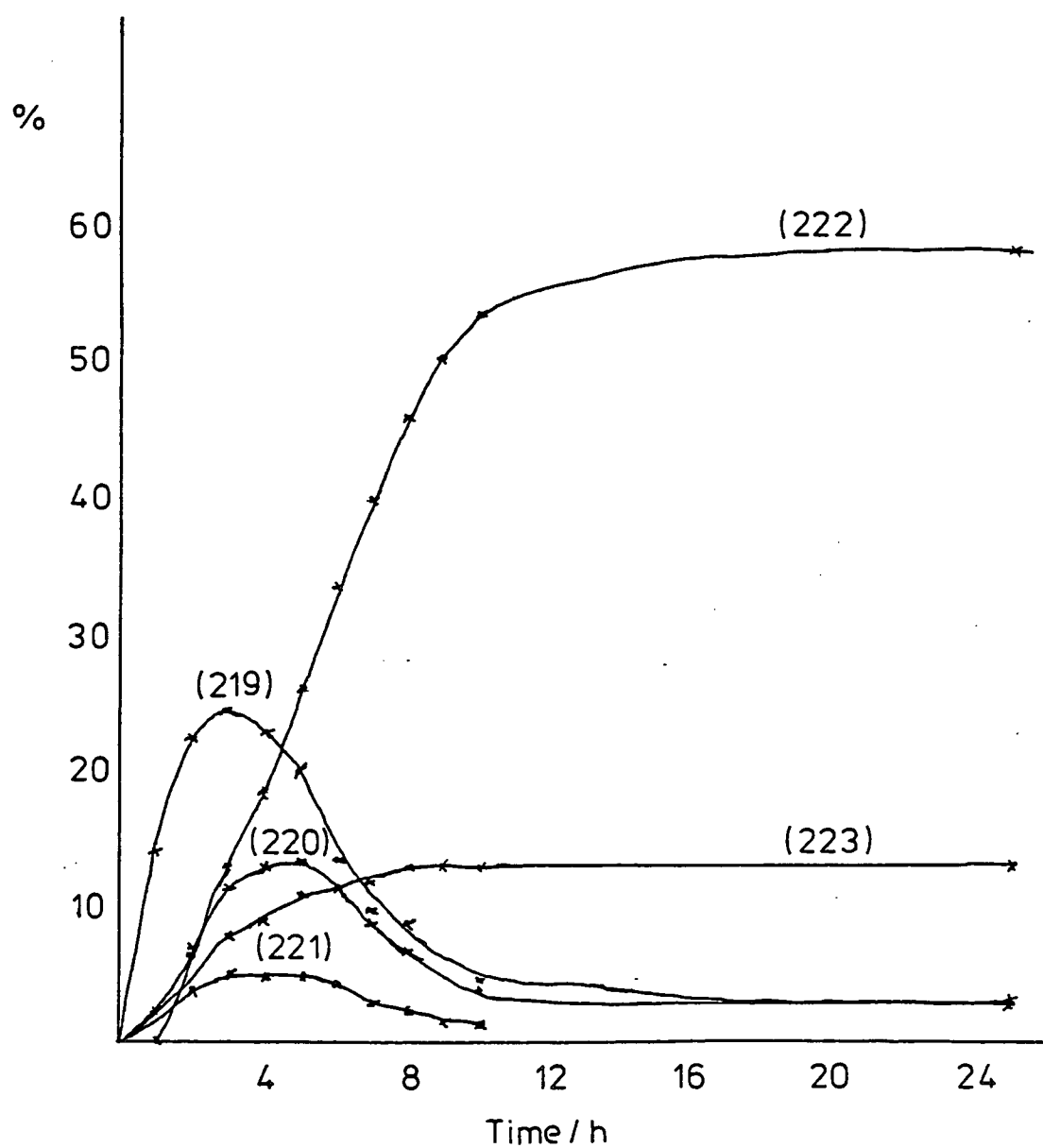


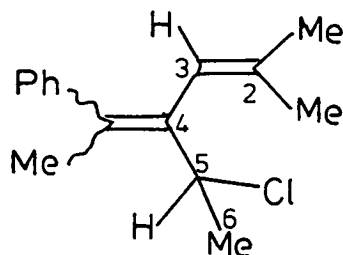
($\underline{J}$ 7.0Hz) and a doublet at 1.24 p.p.m. ($\underline{J}$ 7.0Hz) indicated the presence of a deshielded proton coupled to three methyl protons. The presence of triplets at 5.49 and 5.26 p.p.m. with small coupling constants suggested the presence of alkene protons with long range couplings. Decoupling the resonance at 1.17 p.p.m. removed the larger coupling from the signal at 2.59 p.p.m. Irradiation of this signal collapsed the doublet at 1.17 p.p.m. and sharpened the quartet at 3.65 p.p.m. Decoupling at 3.65 p.p.m. collapsed the doublet at 1.24 p.p.m., removed the smaller coupling from the isopropyl proton and produced doublets from both alkene protons, showing these to be geminal protons.

The thermolysis product (181a) was identified by comparison of its ^1H n.m.r. spectrum with that previously obtained and using the arguments of Sadler²²³ and Pasto²²⁴ to determine the stereochemistry.

The addition product (226) was identified from the spectral properties of the mixture and by comparison of its ^1H n.m.r. spectrum with that obtained from E-4-benzylidene-5-chloro-2-methylhex-2-ene (218). The ^1H n.m.r. spectrum of the addition product (226) shows a multiplet at 5.87 p.p.m. from the alkene proton and a quartet ($\underline{J}$ 6.7Hz) at 4.75 p.p.m. for the chloromethyne proton. The alkene methyl proton signals appear at 1.89 (six protons) and 1.65 p.p.m. with the protons on C-(6) appearing as a doublet ($\underline{J}$ 6.7Hz) at 1.42 p.p.m. The ^{13}C n.m.r. spectrum (DEPT, methyne carbon atom signals only) of the reaction mixture shows a resonance at 59.5 p.p.m., indicating the presence of a chlorinated methyne carbon atom. The mass

GRAPH 1 Plot of percentages of products against time in the rearrangement of derivative (173) with p-toluenesulphonic acid





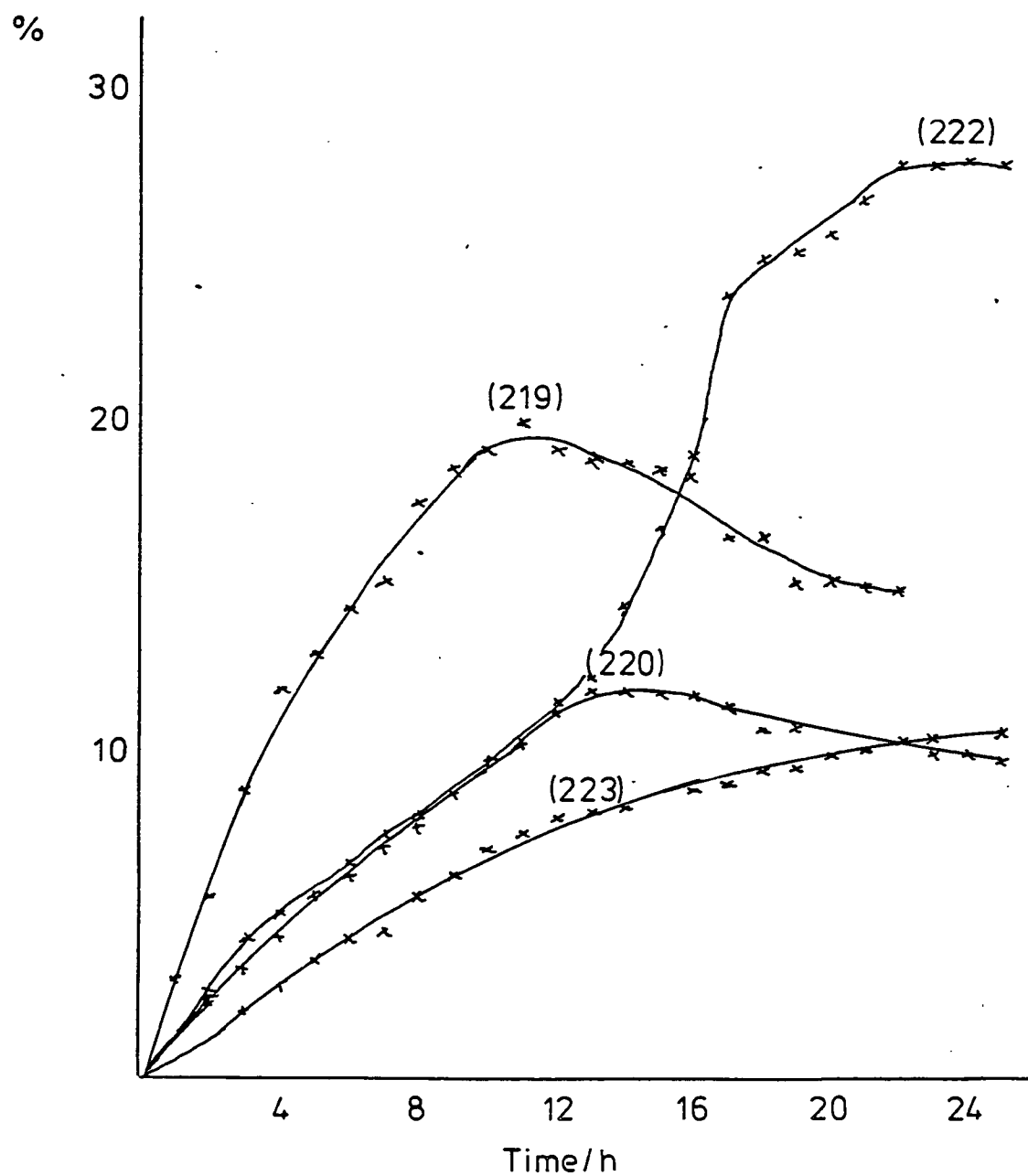
(226)

spectrum of the mixture has peaks at $m/z = 236$ and 234 in the ratio 1:3, again indicating the presence of an addition product. The stereochemistry of this product has not yet been determined.

In view of the wide variation in reaction product composition, the reactions of both the E- and Z-1,3-dimethyl-2-dimethylvinylidene-1-phenylcyclopropanes (172) and (173) with *p*-toluenesulphonic acid were followed at 75° by ^1H n.m.r. spectroscopy. Spectra (32 scans) were accumulated at intervals of 1 h over a period of ca. 25 h and transformed using an "absolute intensity" mode which enabled direct comparison of product amounts between different spectra. The results obtained for the Z-derivative (173) are recorded in Graph 1 and those for the E-derivative (172) are recorded in Graph 2, both graphs showing the change in the percentage of each protonation product as a function of time.

Graph 1 shows that, although the amounts of trienes (219), (220) and (221) present increase rapidly in the early stages of the reaction, these then decrease, whereas the amount of the indene (222) present increases steadily for the first 10 h then levels off. This suggests that the indene (222) is being formed as a secondary product from reversible protonation of

GRAPH 2 Plot of percentages of products against time in the rearrangement of derivative (172) with *p*-toluenesulphonic acid

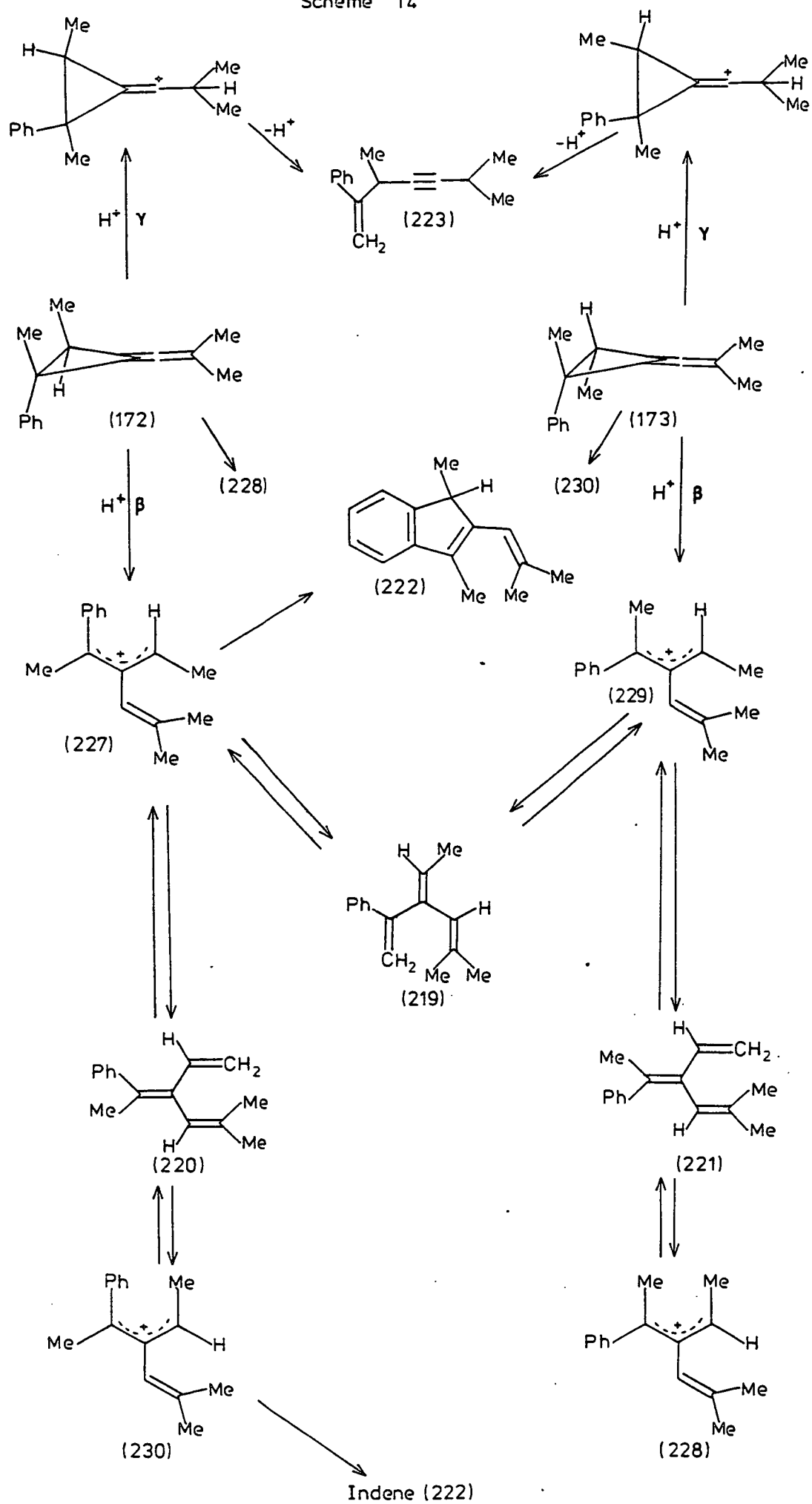


the trienes (219), (220) and (221). The ratio of products from β - and γ -protonation decreased only slightly during the course of the reaction.

A similar, but less marked effect is seen in Graph 2. The smaller depletion in the amount of trienes (219) and (220) present and the lower amount of indene (222) produced indicates that the reaction has not gone to completion. This may be attributed to the thermolysis product (181a) which was present in the starting material. The reaction of this with *p*-toluenesulphonic acid is shown later (Section 4.6) to give both a rearrangement and an addition product, the latter using up the acid present. No evidence was found in this reaction of E-1,3-dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (172) with *p*-toluenesulphonic acid for the formation of the triene (221).

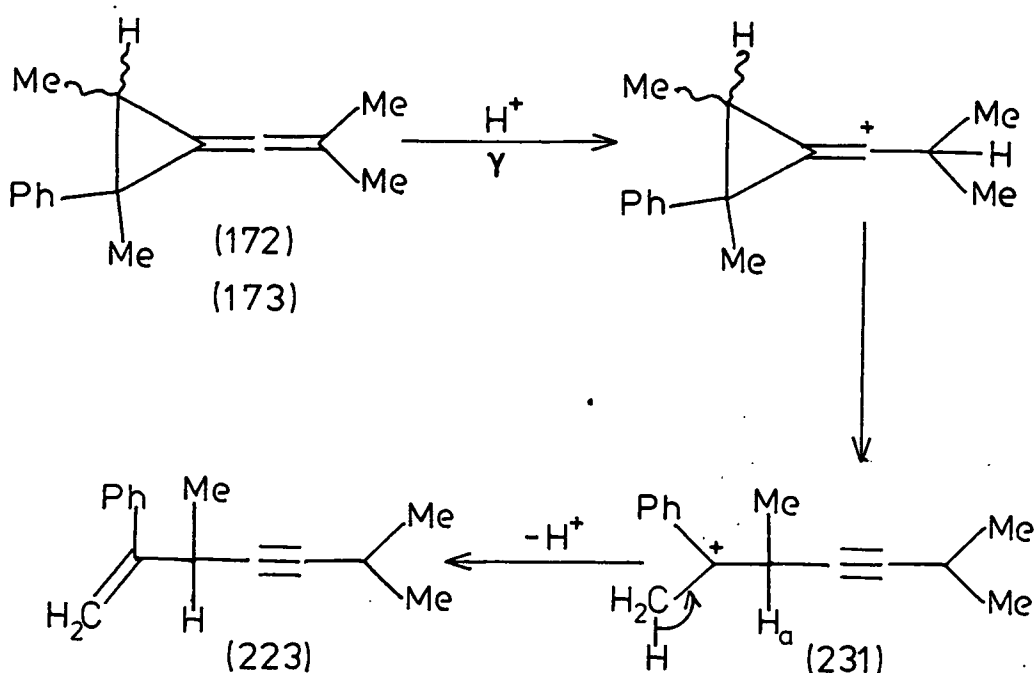
The mechanism proposed for the reactions outlined above are shown in Scheme 14. β -Protonation followed by disrotatory ring opening of the E-derivative (172) can give cations (227) and (228) whereas ring opening of the Z-derivative can give the cations (229) and (230) in each case the former being favoured on steric grounds. These allyl cations can deprotonate to give the trienes (219), (220) and (221) as shown and can inter-convert either directly or via the trienes. However formation of the thermodynamically most stable product, the indene (222), is unlikely to be reversible. This explains why the amount of the indene (222) present increases with time, whereas the amount of the trienes (219), (220) and (221) present will increase, then eventually decrease as they are converted by protonation to the indene (222). The absence of the indene

Scheme 14



(222) among the products in some cases for the rearrangements of both the E- and Z-derivatives (172) and (173) suggests that the indene (222) is formed almost entirely from the trienes (219), (220) and (221), rather than directly from the starting materials.

The enyne (223) is formed by γ -protonation followed by ring opening to give the benzyl cation (231) as shown in Scheme 15.



Scheme 15

Deprotonation results in formation of the 1,4-enyne (223), rather than the 1,3-enyne which would result from loss of H_a . This may be because H_a does not have the correct orientation for this process.

The effects of changing the percentage of *p*-toluenesulphonic acid used on the ratio of γ : β -protonation products in the rearrangement of the Z-derivative (173) are shown in Table 7. Although the percentage of *p*-toluenesulphonic acid may not be constant in reactions where substantial amounts of the thermolysis

Table 7. Ratio of γ - to β -Protonation Products against the Percentage of *p*-Toluenesulphonic Acid used for the Rearrangement of the Cyclopropane (173)

Percentage of <i>p</i> -toluenesulphonic acid	<u>Z</u> -derivative (173) γ : β -protonation
8	0.2:1
10	0.4:1
20	0.6:1

product (181a) are produced, it can be seen that increasing the amount of acid present promotes γ -protonation more than β -protonation. Similar effects have been observed by Truslove¹¹⁶ (see p.41) and may suggest that γ -protonation is reversible whereas β -protonation is not. Deprotonation would therefore be hindered by higher concentrations of acid, and this would result in higher proportions of γ -protonation products being formed.

The formation of substantial amounts of thermolysis products (181a) in some of the above reactions is consistent with measurements of the thermolysis rate for the E-derivative (172) which show its thermolysis to proceed faster than those of the E- and Z-2-dimethylvinylidene-3-methyl-1-phenylcyclopropanes (93) and (92).¹²⁹ The formation of the kinetically

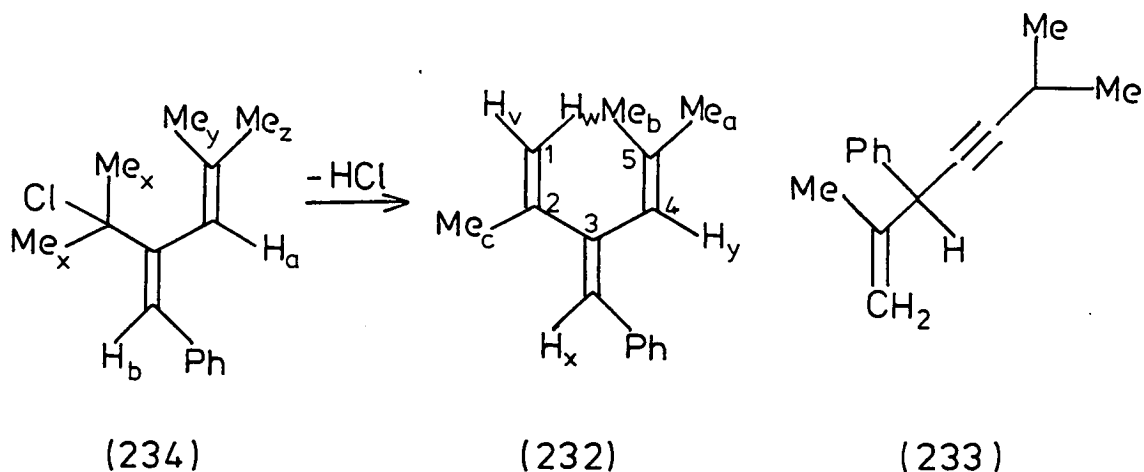
favoured syn-isomer (181a) is expected under these relatively mild conditions for thermolysis.

The addition product (226) is formed by β -protonation and ring opening followed by addition of the chloride ion to the allyl cation. As previously observed, addition occurs at the non-benzylic site to give the thermodynamically more stable regioisomer. The stereochemistry of the product (226) is not known but since both the E- and Z-cyclopropane derivatives gave the same isomer it is possible that the first formed allyl cations are isomerising to the most stable allyl cation before the addition of the chloride ion occurs.

3.4 Reactions of 3,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (174)

Rearrangement of the cyclopropane (174) with *p*-toluene-sulphonic acid gave a mixture containing E-3-benzylidene-2,5-dimethylhexa-1,4-diene (232) and 2,6-dimethyl-5-phenylhepta-6-ene-3-yne (233) in the ratio 4:1 with 10% starting material.

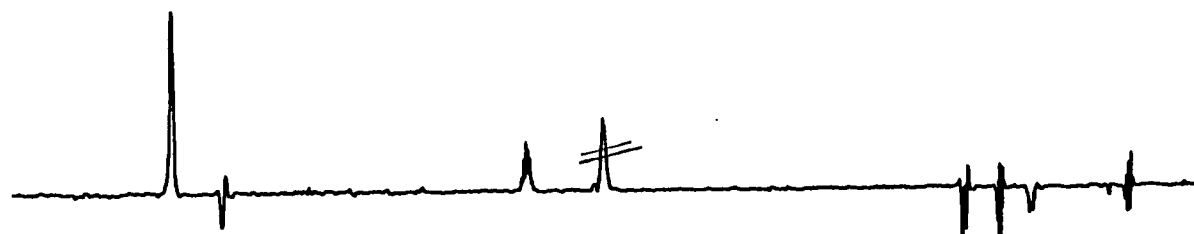
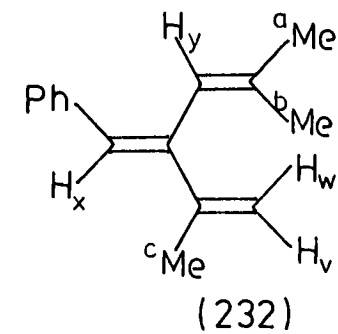
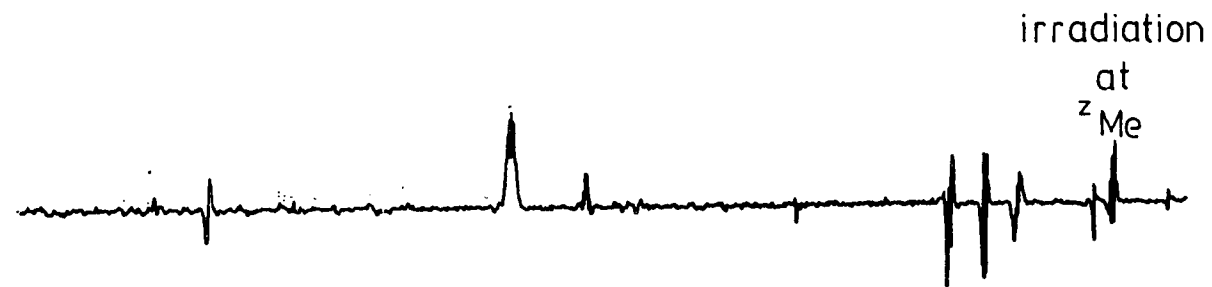
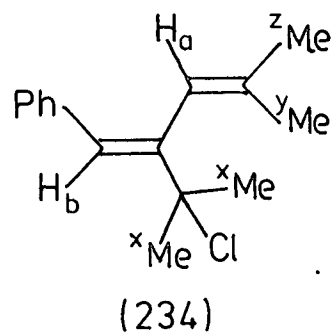
Reactions of the cyclopropane (174) in ethanolic hydrogen chloride produced a mixture containing the triene (232), the enyne (233) and the addition product E-4-benzylidene-5-chloro-2,5-dimethylhex-2-ene (234) in the ratio 4:3:3. Purification by chromatography on alumina caused dehydrochlorination of the addition product (234) to give the triene (232) and produced a mixture of the triene (232) and the enyne (233) in the ratio 2:1, from which only the enyne could be isolated.



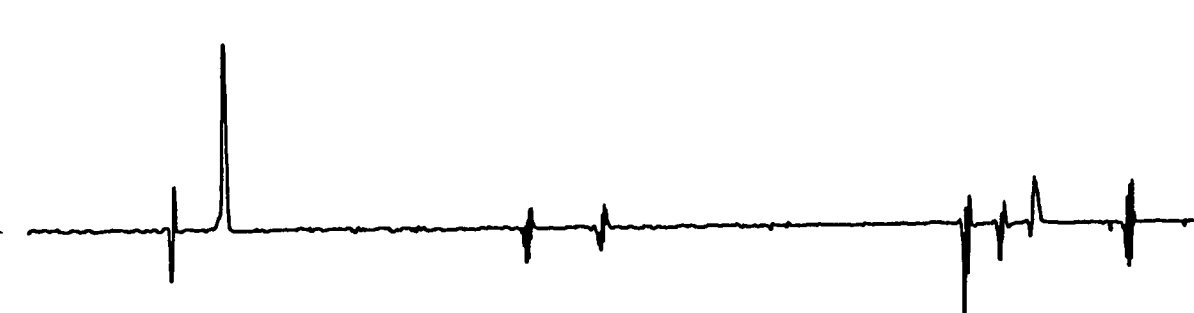
The ^1H n.m.r. spectrum of enyne (233) shows broad signals at 5.11, 4.87 and 4.32 p.p.m. from the alkene and benzylic hydrogen atoms, with a septet of doublets (J 6.8, 2.0Hz) at 2.65 p.p.m. from the isopropyl proton. The alkene methyl proton resonance appears at 1.66 p.p.m. showing coupling to the alkene protons, and the isopropyl methyl proton resonance appears as a doublet at 1.22 p.p.m. (J 6.8Hz). Decoupling at 1.66 p.p.m. produced doublets of doublets from both the alkene protons at 5.11 and 4.87 p.p.m., leaving only the geminal couplings and four bond couplings to the benzylic proton. Decoupling the isopropyl hydrogen atom sharpened the peak at 4.32 p.p.m., indicating a five bond coupling across the triple bond.

The triene (232) was identified from clear resonances in the ^1H n.m.r. spectrum of the mixture with the enyne (233). The ^1H n.m.r. spectrum of the triene (232) shows a singlet at 6.55 p.p.m. and broad signals at 5.84, 5.16 and 5.04 p.p.m., all due to alkene hydrogen atoms. All three methyl proton resonances at 2.03, 1.81 and 1.37 p.p.m. show fine splitting.

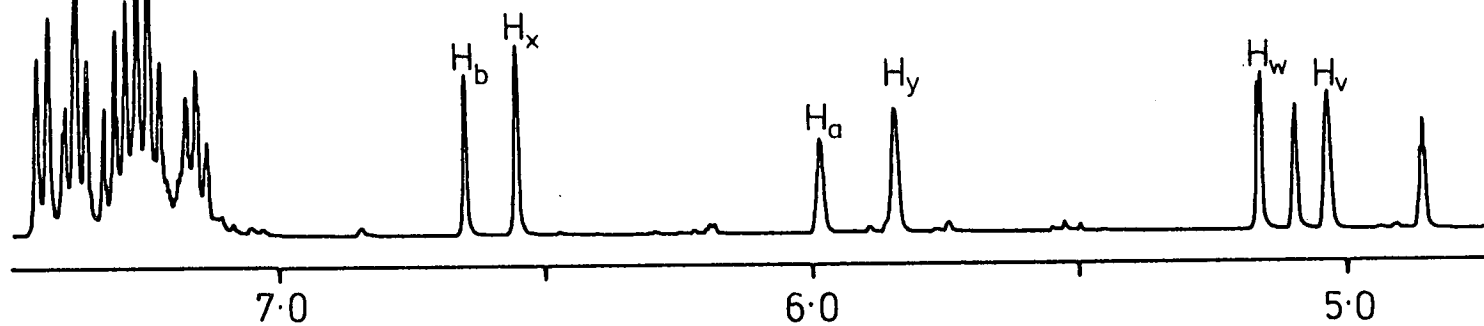
Figure 7



irradiation
at
xMe, aMe



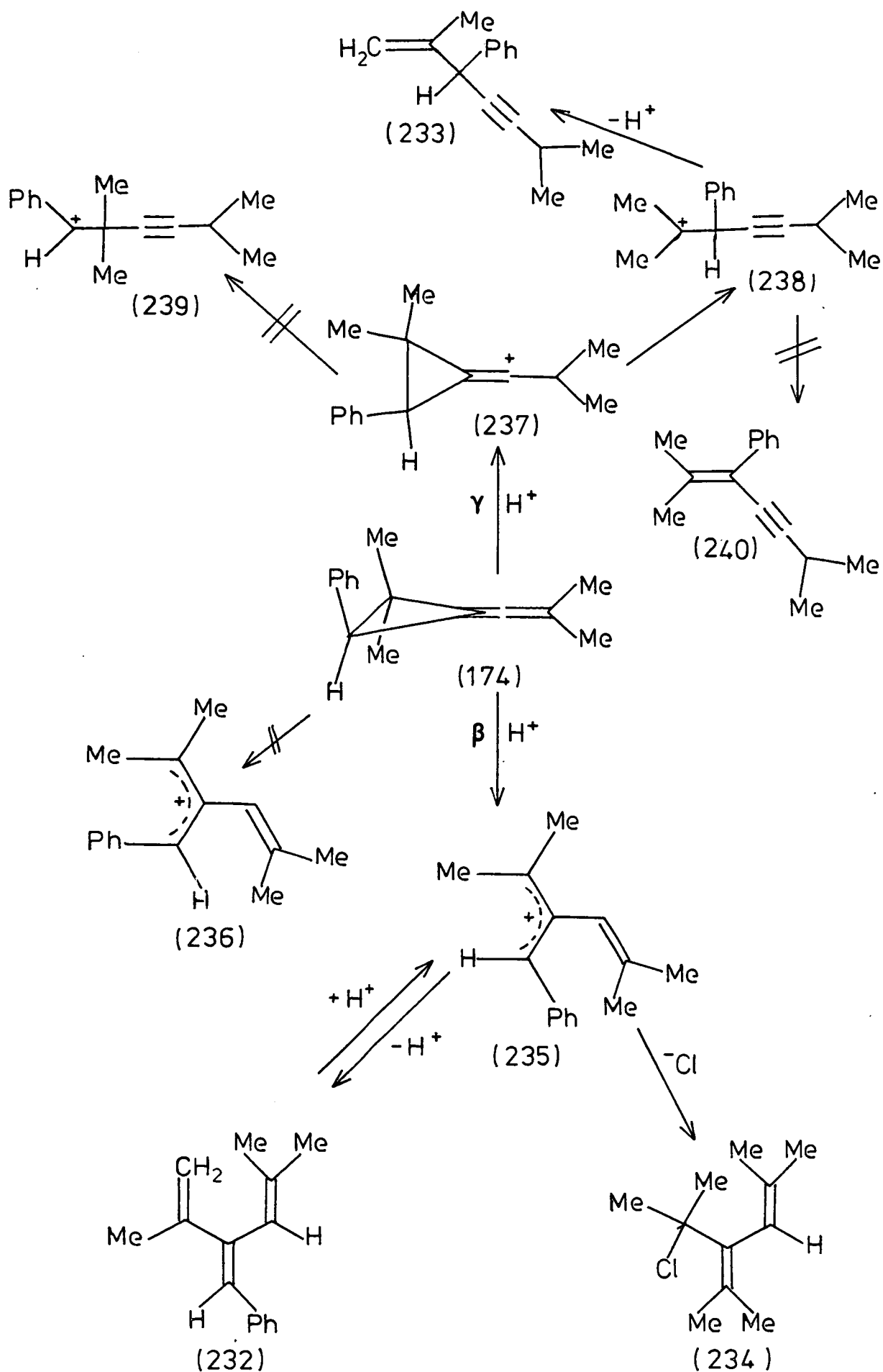
irradiation
at
cMe



Irradiation of the resonance at 2.03 p.p.m. produced doublets of doublets at 5.16 and 5.04 p.p.m., proving that these resonances all belong to the isopropenyl group. Irradiation of the signal at 1.81 p.p.m. sharpened the peak at 5.84 p.p.m., proving both resonances to be from the isobutenyl group. Irradiation at 5.84 p.p.m. sharpened the signals at 6.55, 5.16 and 5.04 p.p.m. and collapsed the doublets at 1.37 and 1.81 p.p.m., showing three, four and five bond couplings across the π -system.

The addition product (234) was identified from the ^1H n.m.r. spectrum of the initial reaction mixture which shows broad resonances at 6.65 and 6.00 p.p.m. from the two alkene protons, a singlet at 1.82 p.p.m. from the aliphatic dimethyl group and doublets at 1.74 and 1.20 p.p.m. from the alkene methyl groups. Decoupling the alkene proton signal at 6.00 p.p.m. collapsed the doublets at 1.74 and 1.20 p.p.m., and sharpened the resonance at 6.65 p.p.m. This allowed assignment of the peaks at 6.00 and 6.65 p.p.m. to H_a and H_b respectively.

The stereochemistries of the addition product (234) and the triene (232) were determined from the N.O.E. experiments shown in Fig.7. Irradiation of the aliphatic dimethyl proton resonance from the addition product at 1.82 p.p.m. caused a 15% increase in the signal at 6.65 p.p.m. from H_b and a 5% increase in the H_a resonance at 6.00 p.p.m., the former N.O.E. proving the E-configuration of the molecule. Irradiation at 1.74 p.p.m. produced a 7% increase in the signal at 6.00 p.p.m. from H_a of the addition product, allowing assignment of the former resonance to the methyl protons cis to H_a .

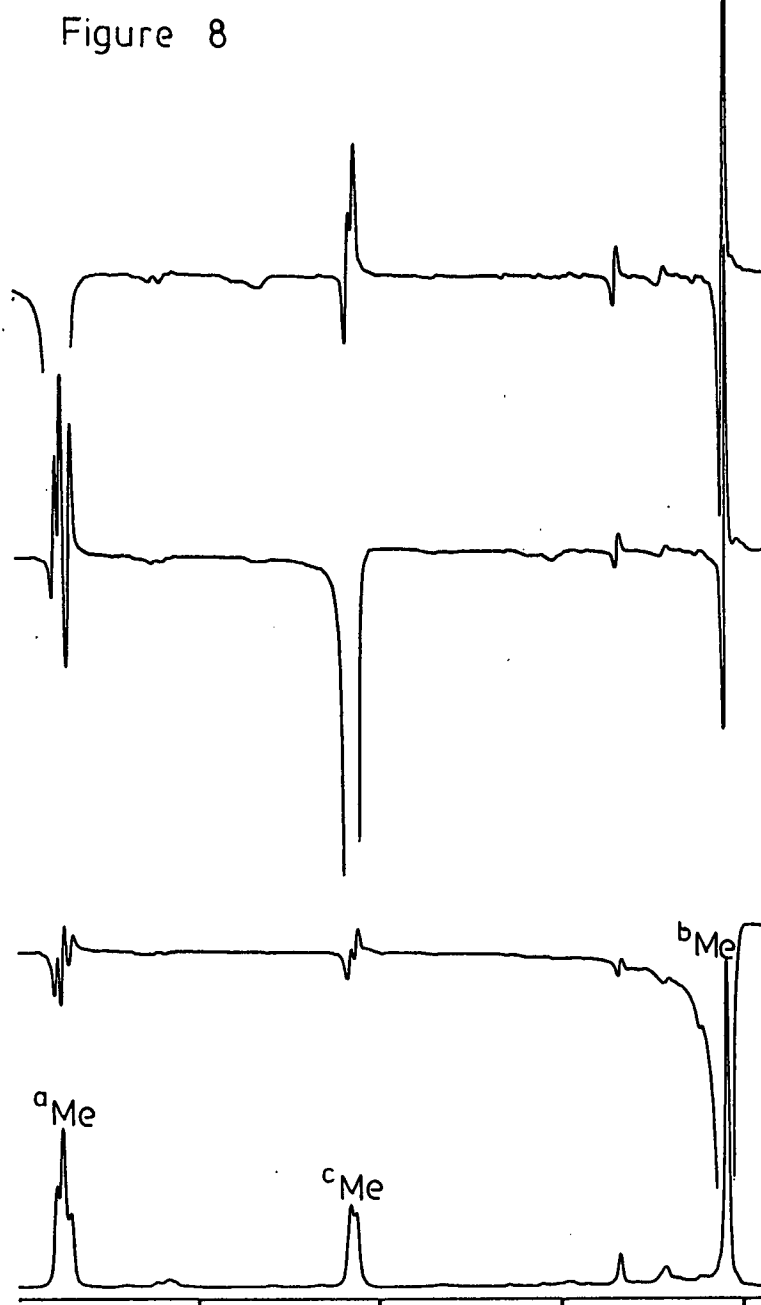
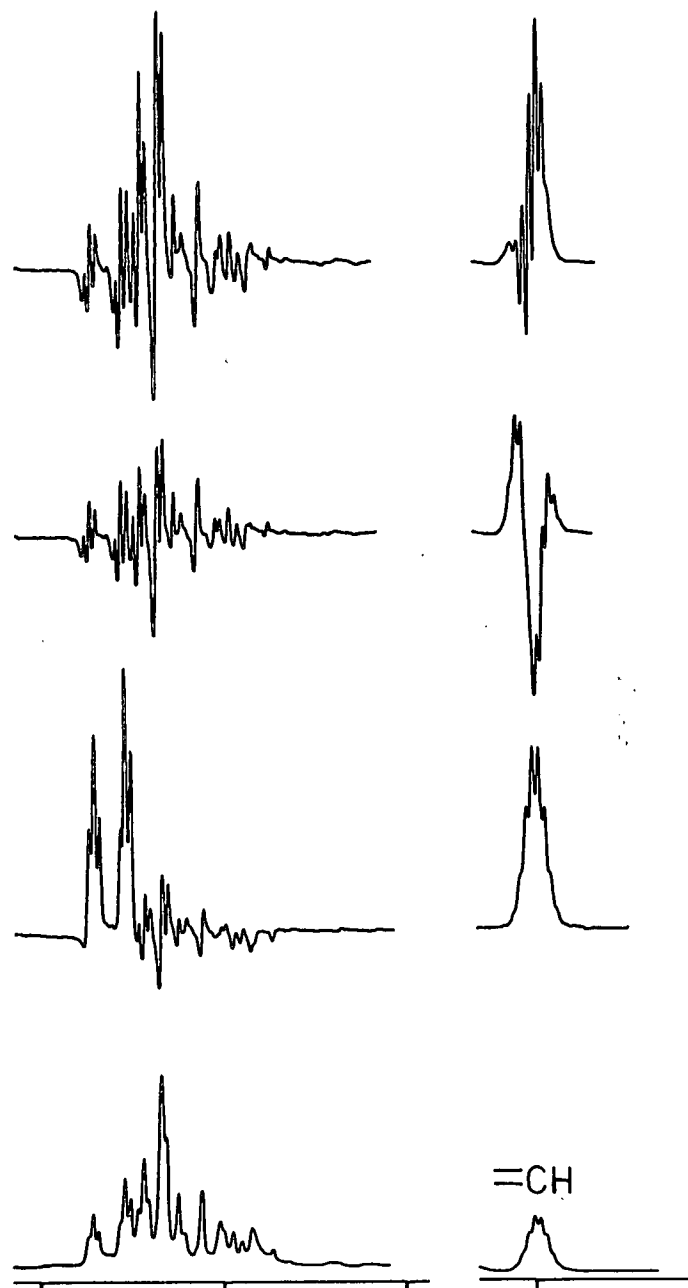


Scheme 16

Irradiation of the signal at 1.81 p.p.m. from one set of isobutenyl methyl protons in the triene (232) gave a 6% increase in the resonance at 5.84 p.p.m. and proves this methyl group to be cis to H_Y . Irradiation of the isopropenyl methyl protons at 2.03 p.p.m. produced a 12% increase in the signal at 6.55 p.p.m. from H_X , proving the E-stereochemistry shown for triene (232), and a 3% increase in the resonance at 5.04 p.p.m., allowing the assignment of the resonances at 5.04 and 5.16 to H_V and H_W respectively.

The formation of the products from these reactions (see Scheme 16) follows the general pattern seen previously with a predominance of β -protonation. The triene (232) and the addition product (234) were both formed by β -protonation and ring opening with outward rotation of the phenyl group to give allyl cation (235) rather than the more hindered route via allyl cation (236). The allyl cation (235) is not able to cyclise to give the indene, but deprotonates to give triene (232) or, where appropriate, adds a chloride ion to give the addition product (234). The enyne (233) was formed by γ -protonation via cation (237) which ring opens to give the tertiary cation (238) rather than the benzylic cation (239) which would have no simple route of deprotonation. Deprotonation of cation (238) gives only the 1,4-enyne (233) rather than the conjugated 1,3-enyne (240). The observed mode of deprotonation would be preferred on purely statistical grounds and possibly the orientation of the benzylic hydrogen atom is not correct for proton loss.

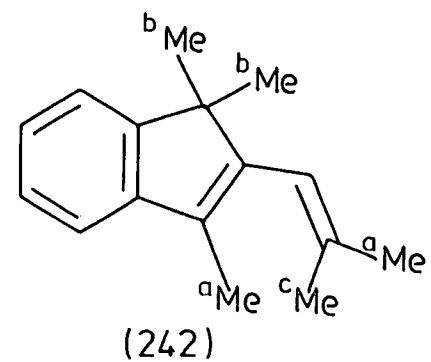
Figure 8



irradiation
at
 aMe

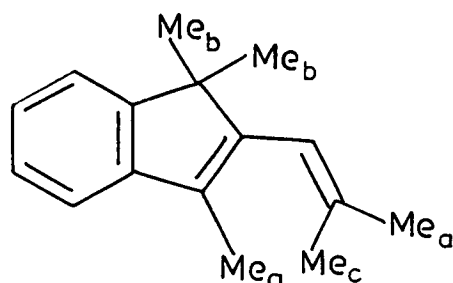
irradiation
at
 cMe

irradiation
at
 bMe

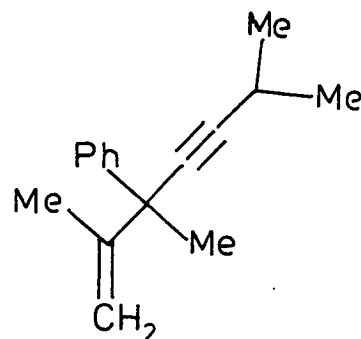


3.5 Reactions of 2-Dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane (175)

Rearrangement of the cyclopropane (175) with *p*-toluenesulphonic acid gave a mixture containing only the enyne (241) and the indene (242) in the ratio 1:1, both of which were isolated. The reaction of the cyclopropane (175) with hydrogen chloride in ethanol also gave only the enyne (241) and the indene (242) in the ratio 2:1, with two unidentified products (ca.25%).



(242)



(241)

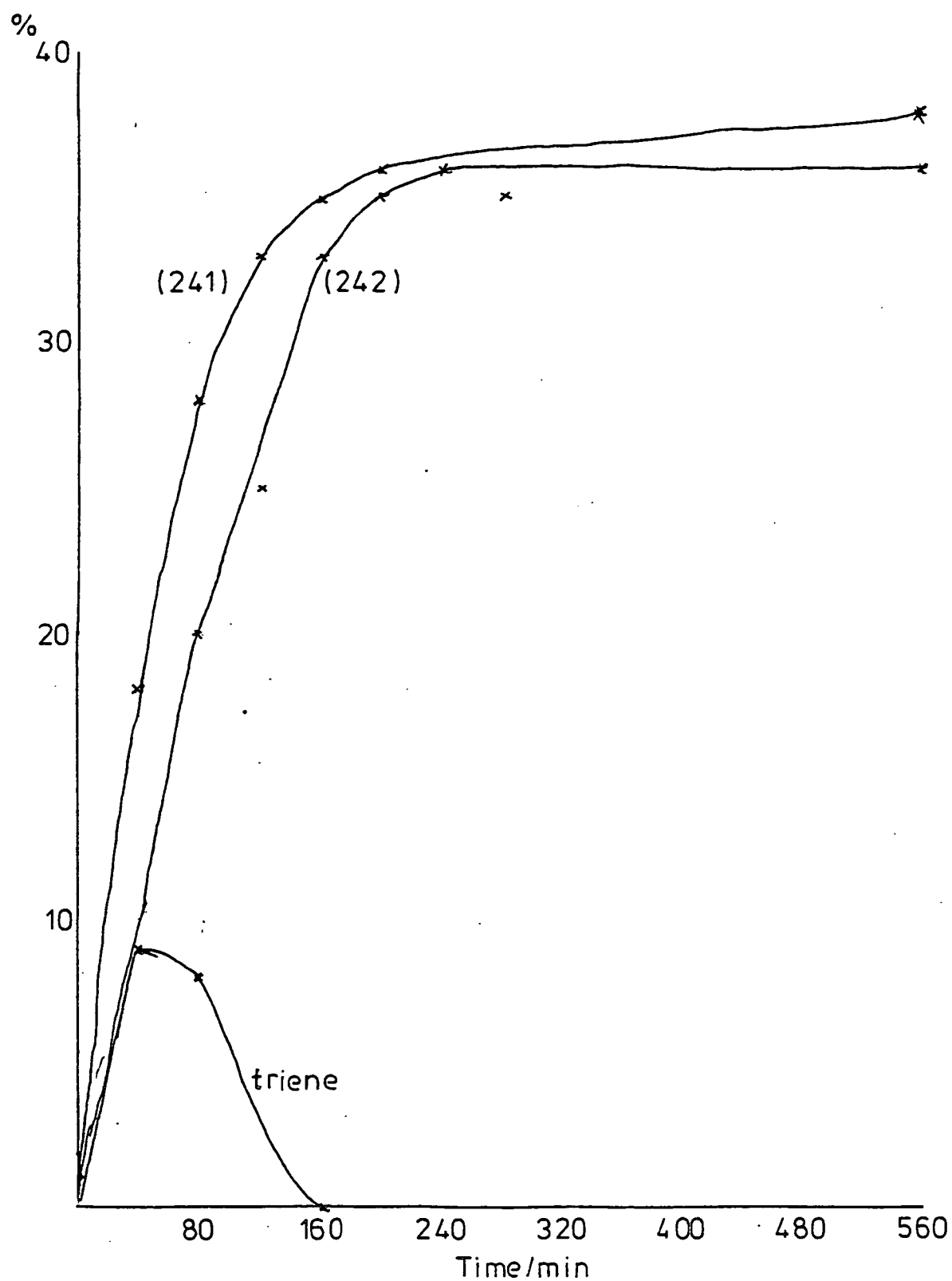
The structure of the indene (242) was deduced from its ^1H and ^{13}C n.m.r. spectra. The ^1H n.m.r. spectrum of indene (242) has an alkene proton *multiplet* at 5.76 p.p.m., doublets at 1.92, 1.91 and 1.60 p.p.m. corresponding to alkene methyl protons and a singlet at 1.18 p.p.m. from the aliphatic dimethyl protons. A series of N.O.E. difference experiments (Fig.8) was used to confirm the structure. Irradiation of the resonance at 1.18 p.p.m. produced an 11% increase in the alkene proton signal and a 9% increase in one aromatic proton resonance, confirming that the gem-dimethyl group was situated on C-(1) and that the 2-methylprop-1-enyl group was situated

on the adjacent carbon atom, C-(2). Irradiation of the methyl protons at 1.60 p.p.m. gave an 8% increase in the signals at 1.91 and 1.92 p.p.m. with no other increased resonances, therefore allowing its assignment to the methyl protons, H_c , trans to the alkene proton. Irradiation of both methyl proton H_a signals produced a 5% increase in one of the aromatic proton resonances (from irradiation of the (3)-methyl protons), a 7% increase in the alkene proton signal (from both sets of protons) and an increase in the resonance from the methyl protons, H_c .

The ^{13}C n.m.r. spectrum of the indene (242) shows signals from five quaternary aromatic and alkene carbon atoms, five protonated aromatic and alkene carbon atoms, a quaternary aliphatic carbon atom, C-(1), three alkene methyl carbon atoms and the gem-dimethyl carbon atoms.

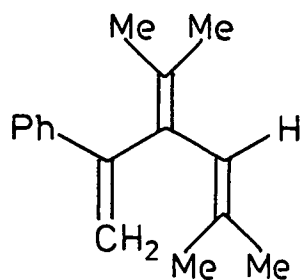
The structure of the enyne (241) was also deduced from its ^1H and ^{13}C n.m.r. spectra. The ^{13}C n.m.r. spectrum shows resonances from both an aromatic and an alkene quaternary carbon atom, the ortho, meta and para aromatic carbon atoms, the alkene methylene carbon atom, two alkyne carbon atoms, one aliphatic quaternary carbon atom, one alkene and one aliphatic methyl carbon atom and an isopropyl group. The ^1H n.m.r. spectrum shows resonances from five aromatic protons and two alkene protons at 5.13 and 4.93 p.p.m. One alkene proton appears as a sextet (J 0.7Hz) the other as a quintet (J 1.4Hz). The former has a coupling of 1.4Hz to the geminal alkene proton and a coupling of half that size, 0.7Hz, to the alkene methyl protons, giving rise to a sextet. The other alkene proton couples to the geminal proton and the alkene methyl protons, all with

GRAPH 3 Plot of percentages of products against time in the rearrangement of derivative (175) with p-toluenesulphonic acid

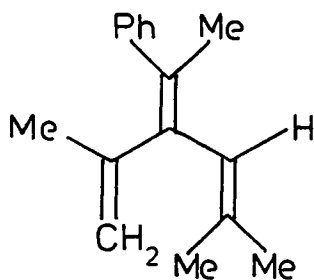


coupling constants of 1.4Hz. The alkene methyl protons are partly masked by the singlet from the aliphatic methyl protons and only one doublet (J 0.7Hz) is visible. The isopropyl proton gives rise to a septet but its methyl protons give rise to two doublets separated by 0.01 p.p.m. from restricted rotation of the isopropyl group.

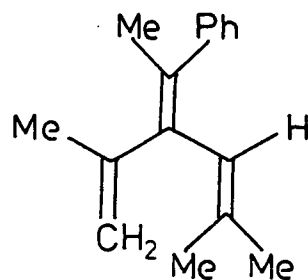
The reaction of 2-dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane (175) with *p*-toluenesulphonic acid was followed by ^1H n.m.r. as outlined in section 3.3 for the 1,3-dimethyl derivatives (172) and (173). Spectra were recorded every 40 min and the results obtained are illustrated in Graph 3. The appearance of resonances at 5.68, 5.48 and 4.97 p.p.m. did not correspond to either the indene (242) or the enyne (241) and were assumed to be from formation of one of the trienes (243), (244) or (245).



(243)

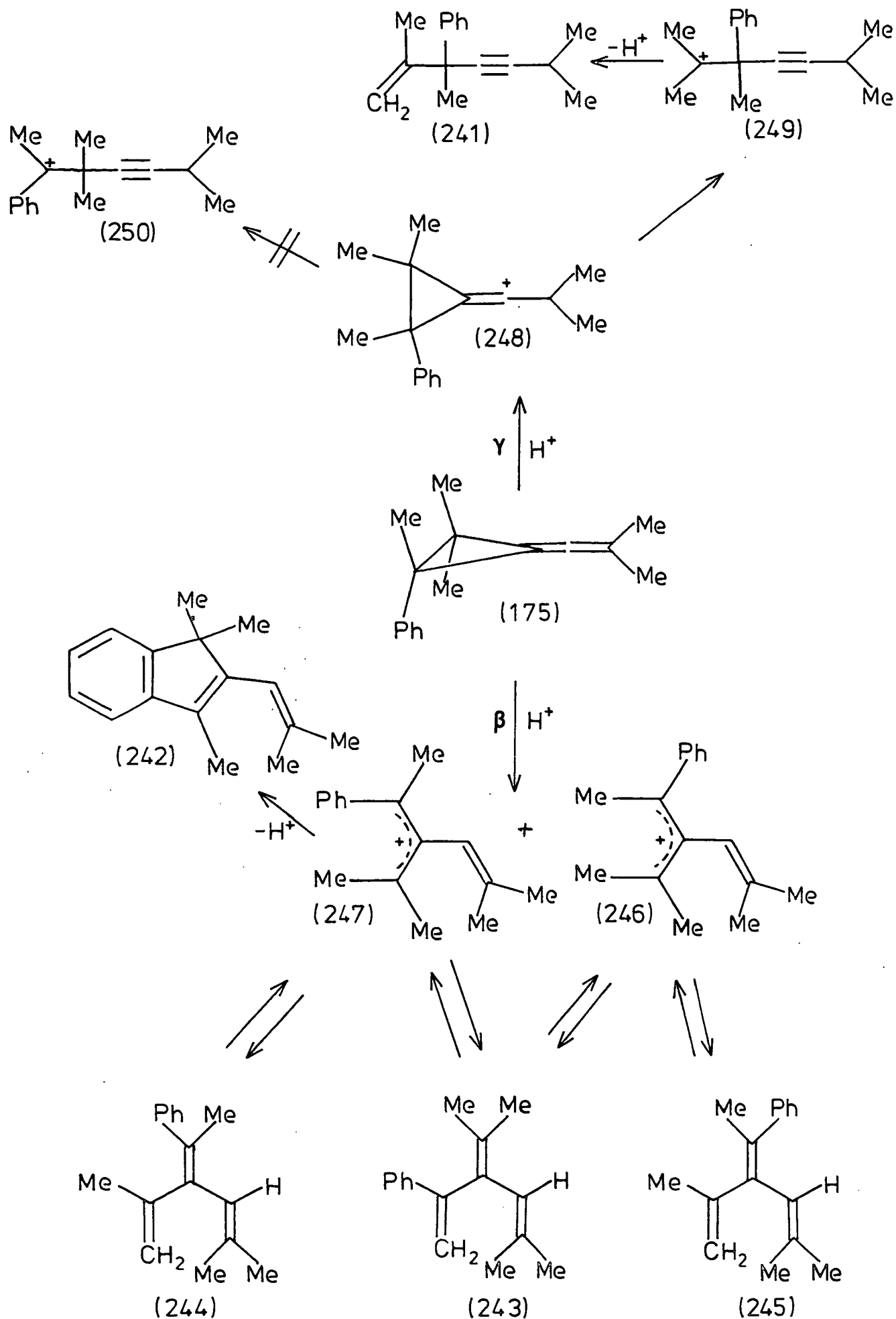


(244)



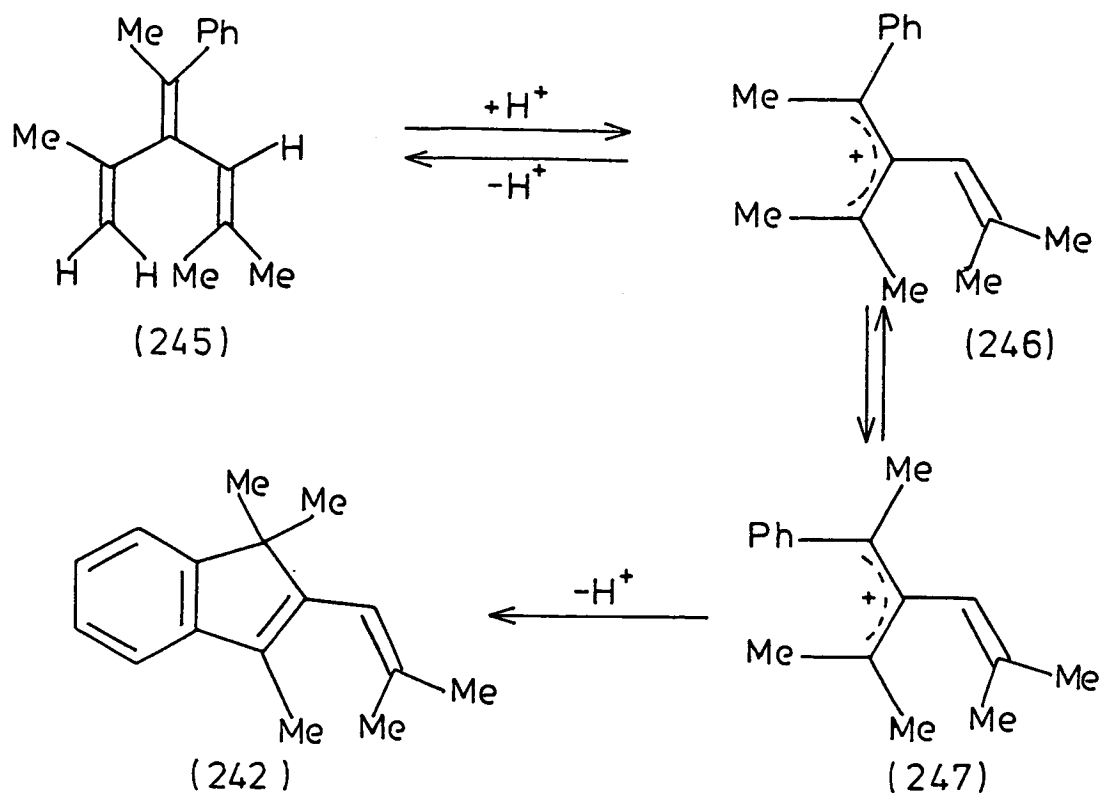
(245)

The percentage of triene present increased initially then dropped to zero as presumably it was converted to the indene (242). It should be noted that triene (245) cannot protonate to give directly an allyl cation with the required geometry



Scheme 17

to give the indene (242) and the rearrangement of the triene (245) to the indene (242) would require isomerisation of the intermediate allyl cation (246).



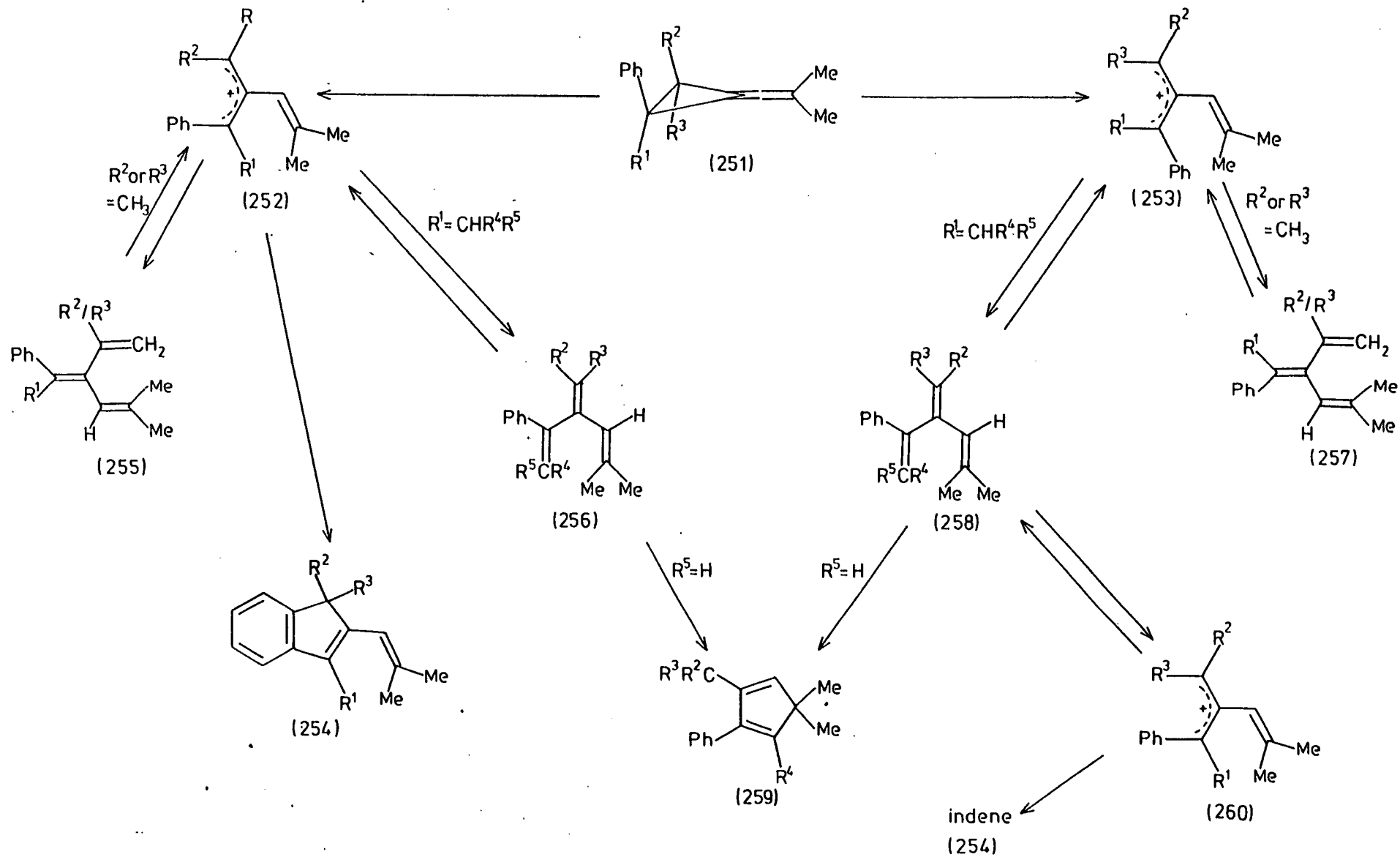
β -Protonation of the cyclopropane (175) can give two allyl cations (246) and (247) as shown in Scheme 17. Only cation (247) can give the indene (242) directly but it seems unlikely that this cation is formed exclusively. It seems more probable that the allyl cations (246) and (247) interconvert, either directly or via the triene (243) and that only the indene (242) is observed from β -protonation at the end of the reaction since its formation is not reversible, unlike formation of the trienes.

The enyne (241) was formed by γ -protonation via cation (248) which ring opens to give cation (249) rather than the benzylic cation (250). Deprotonation of cation (249) gives enyne (241).

3.6 Conclusion

From the results outlined in this chapter and in section 1.4, some general patterns can be seen in the protonation of dimethylvinylidenecyclopropanes. The ratio of γ - to β -protonation products increases with an increase in the number of alkyl substituents on the cyclopropane ring, and with an increase in the acid to cyclopropane ratio. The former observation has been explained¹¹¹ by the additional stabilization given to the intermediate cation by the presence of alkyl substituents on the cyclopropane ring (see p.35). However, the claim made¹¹¹ that the phenyl substituent has no stabilizing effect on the transition states to γ - or to β -protonation is invalidated when the results outlined here for the protonation of the 1-phenyl-3,3-dimethyl and the 1-phenyl-1,3,3-trimethyl derivatives (174) and (175) are compared with those published¹⁰⁹ for the 3,3-dimethyl and the 1,3,3-trimethyl derivatives (81a) and (81b) which proceed exclusively by γ -protonation. This means that the phenyl group stabilises the transition state for β -protonation more than for γ -protonation and may be evidence for a considerable amount of ring opening in the transition state for β -protonation.

The dependence of the proportion of γ -protonation products obtained on the proportion of acid present relative to the amount of cyclopropane, suggests that the initial protonation to give the vinyl cation may be reversible. Increasing the relative amount of acid present would make deprotonation to give starting material less favourable and would therefore promote the ring opening step. It is considered extremely



Scheme 18

unlikely that β -protonation is reversible.

The nature of products from β -protonation varies considerably with the nature, position and number of substituents on the cyclopropane ring. Ring opening of the cyclopropane (251) proceeds by the disrotatory mode and can give two possible allyl cations (Scheme 18). Inward rotation of the phenyl and R^2 groups gives allyl cation (252) whereas inward rotation of the R^1 and R^3 groups gives cation (253). Ring opening gives the more stable of the two allyl cations. The allyl cation (252) can give the indene (254) directly or can deprotonate to give trienes (255) and/or (256) depending on the nature of the R groups. The allyl cation (253) can give trienes (257) and (258). The cyclopentadiene products (259) can only be formed in cases where $R^1 = CH_2R$ and are formed from trienes (256) and (258) only when both R^2 and R^3 are hydrogen atoms, presumably because other substituents cause steric hindrance to the required protonation of the trienes (see Scheme 10). The indene (254) can also be formed by protonation of trienes (255) and (256) via allyl cation (252) and from triene (258) via allyl cation (260). The extent to which this interconversion of products occurs increases as the relative amount of acid used increases, as reaction time increases and as the stabilities of the intermediate allyl cations increase. Protonation of triene (257) gives allyl cation (253) which cannot form the indene (254) directly.

In each of the reactions carried out here, only one product has been found from γ -protonation, although it has not been possible to rationalise these reactions.

CHAPTER 4

Reactions of Dimethylenecyclopropaneswith p-Toluenesulphonic Acid4.1 Reaction of 2-Isopropylidene-3-methylene-1-phenylcyclopropane (164)

Reaction of cyclopropane (164) with excess p-toluenesulphonic acid in carbon tetrachloride gave exclusively E-2,4-dimethyl-1-phenyl-3-(p-toluenesulphonyloxy)penta-1,3-diene (261). In all these reactions, isolations were not quantitative, but the ^1H n.m.r. (200 or 360MHz) spectra of the reaction mixtures were used to determine product ratios. This ester was identified from its ^{13}C and ^1H n.m.r. spectra and by analogy with the related reaction with acetic acid¹¹⁸ (p. 45).

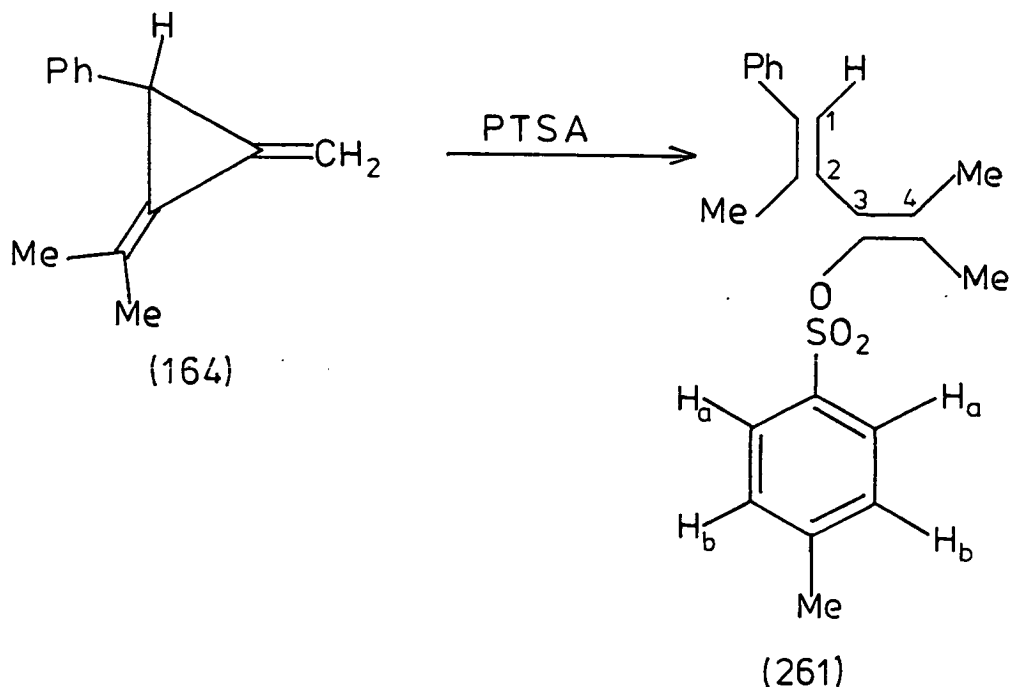
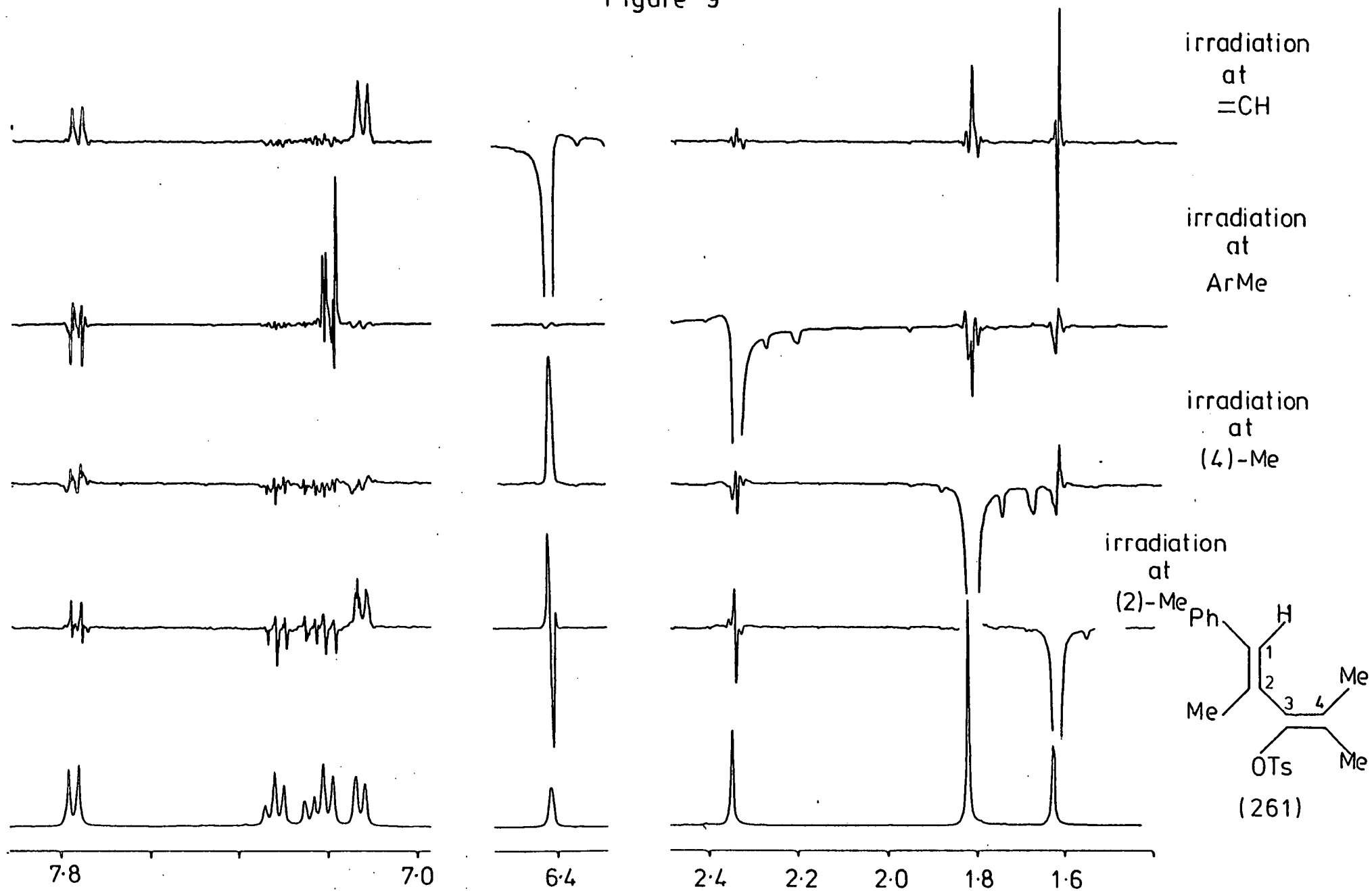


Figure 9

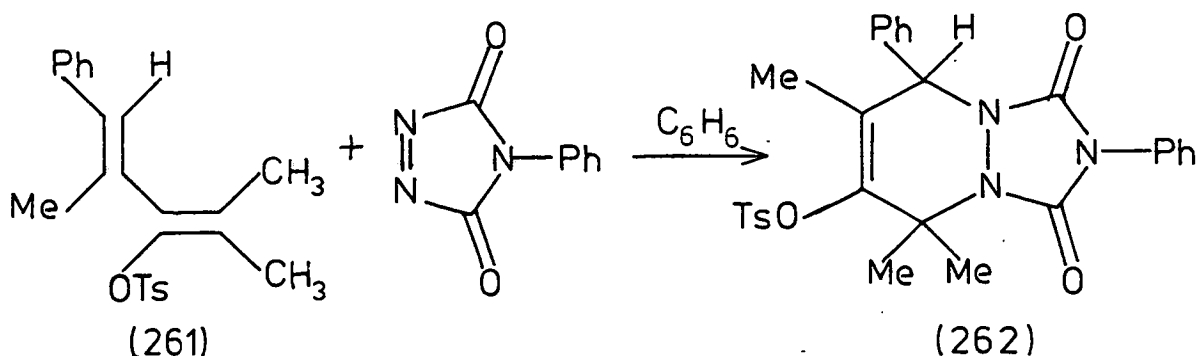


The ^1H n.m.r. spectrum clearly shows resonances for four methyl groups, an alkene proton and nine aromatic protons. Decoupling the alkene proton (6.41 δ) removed the fine coupling on the signal at 1.63 p.p.m. thus allowing assignment of the latter signal to the methyl on C-(2). Decoupling the aromatic doublet at 7.77 p.p.m. collapsed the doublet at 7.20 p.p.m. to a singlet, showing that these signals were due to the tosyl ring protons, H_a and H_b , the signal at higher chemical shift being assigned to the more deshielded H_a protons. The signal at 2.35 p.p.m. is characteristic of tosyl methyl groups and thus the terminal methyl groups coincide.

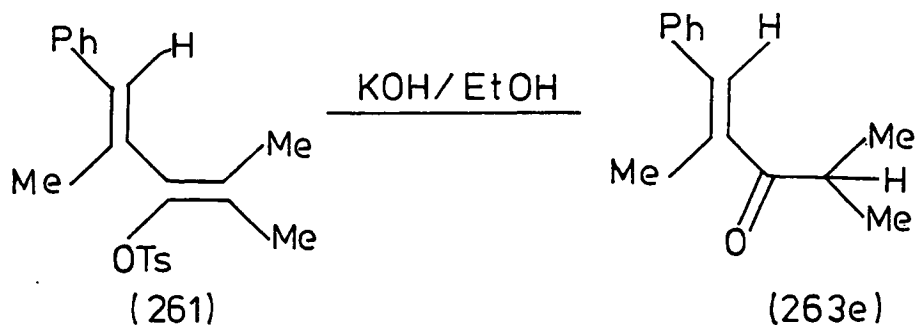
The configuration about the C-(1), C-(2) double bond was assigned by N.O.E. difference spectroscopy (fig. 9). Irradiation of the 2-methyl proton resonance (1.63 δ) produced a 1% intensity increase in the phenyl ortho protons' resonance and no increase in the alkene proton resonance. Irradiation of the resonance at 1.82 p.p.m., from the terminal methyl groups, produced a 5% increase in the signal from the alkene proton. These results show the molecule to be the E-isomer. Irradiation of the tosyl methyl resonance (2.35 δ) gave a 2% increase in the H_b signal, confirming the assignments made above and irradiation of the alkene proton resonance gave a small increase (1-2%) in the resonances from H_a , the phenyl ortho protons and terminal methyl protons, again confirming the E-configuration.

Further confirmation of the structure was obtained by reaction of the ester (261) with 4-phenyl-3H-1,2,4-triazoline-3,5-dione in refluxing benzene to give the Diels Alder adduct (262) which was characterised from its n.m.r. spectra (p.178).

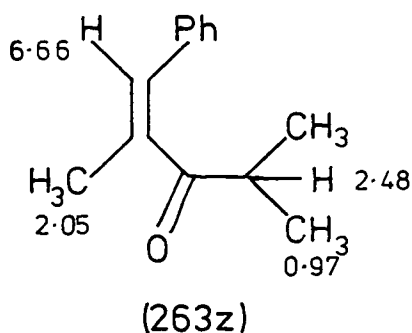
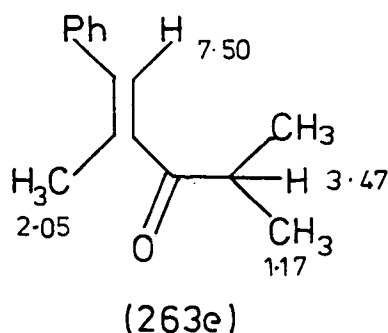
No reaction was obtained using dimethylacetylenedicarboxylate, presumably due to steric hinderance.



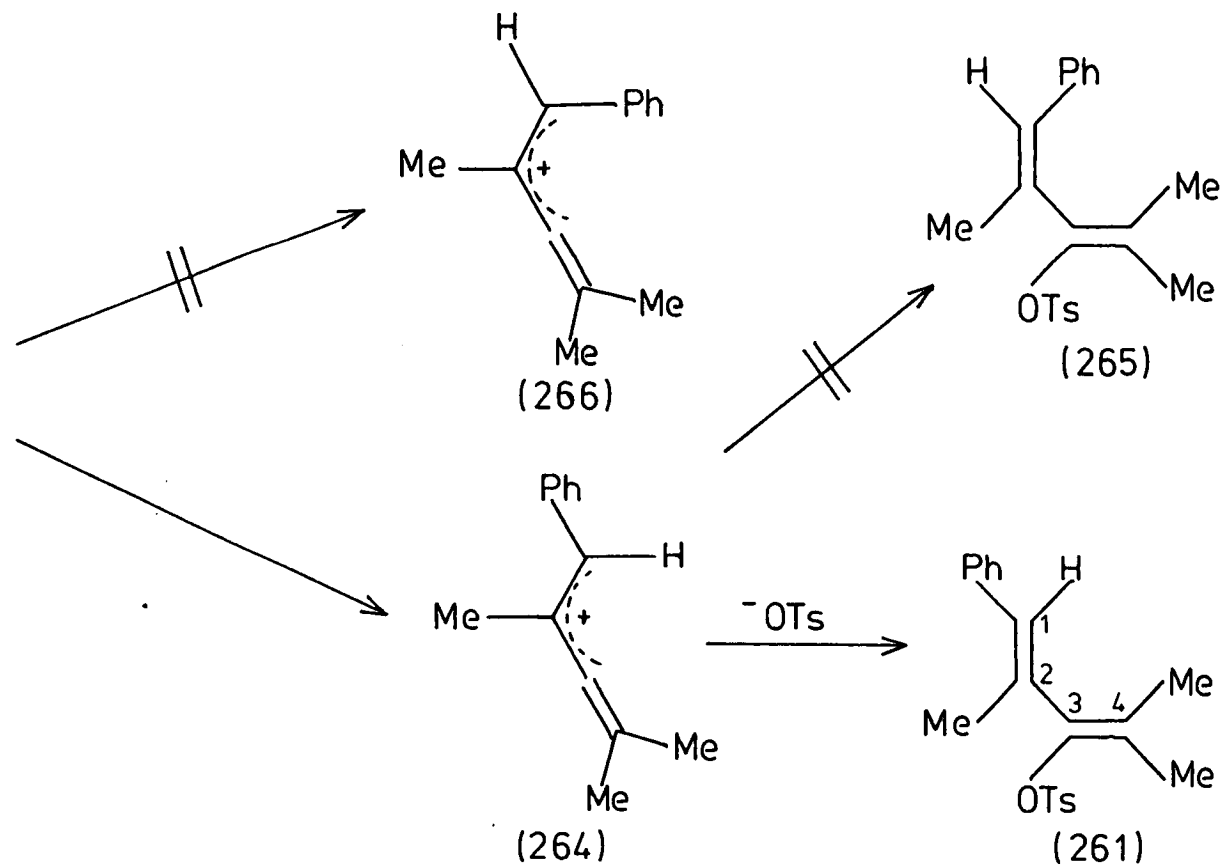
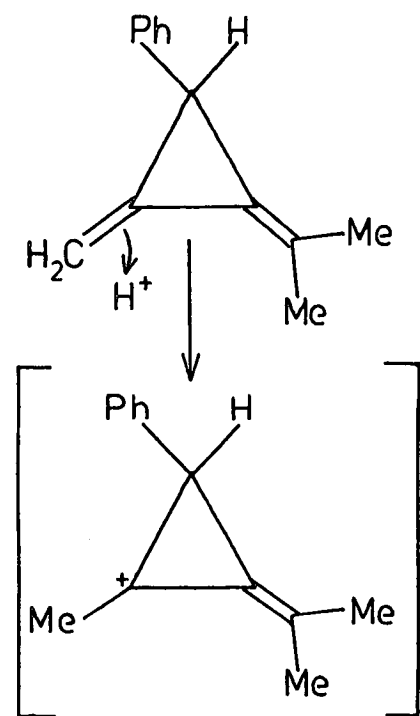
Hydrolysis of ester (261) was achieved by refluxing it in ethanolic potassium hydroxide and proceeded with retention of stereochemistry to give E-1-phenyl-2,4-dimethylpent-1-ene-3-one (263e). However, when left to stand in chloroform at room temperature for a prolonged period a mixture of the E- and Z-



isomers in the ratio 1:2 was produced. Decoupling the resonance from the 2-methyl group in ketone (263e) sharpened the resonance from the alkene proton at 7.50 p.p.m., clearly locating this proton in the aromatic region. The stereochemistries of both ketones (263 e and z) were determined by a series of N.O.E. experiments performed on the mixture.



Irradiation of the 2-methyl protons from both ketones (2.05 δ) produced a 2% intensity increase in the aromatic ortho proton resonance from ketone (263e) at 7.40 p.p.m. and a 7% increase in the alkene proton signal from ketone (263z), proving the Z-stereochemistry of the latter. Irradiation of the isopropyl methyl protons in ketone (263e) (1.17 δ) produced a small increase (<1%) in the alkene proton resonance at 7.50 p.p.m. and an 8% increase in the isopropyl proton at 3.47 p.p.m. Irradiation of the isopropyl methyl signal in ketone (263z) (0.97 δ) produced a 13% increase in the isopropyl proton signal (2.48 δ) and a 3% increase in the 2-methyl resonance at 2.05 p.p.m. Irradiation of the alkene proton signal from ketone (263z) (6.66 δ) caused 2% increases in the signal from the ortho phenyl protons and from the 2-methyl protons, confirming the stereochemistry. Irradiation of the alkene proton from ketone (263e) (7.50 δ) produced a 15% increase in the isopropyl proton resonance at 3.47 p.p.m., thus confirming the E-stereochemistry of ketone (263e). Pasto et al.¹¹⁸ claimed to have formed both these ketones, however the alkene proton and methyl resonances of one have been misquoted, as has the alkene proton resonance of the other, and the stereochemistries have



Scheme 19

been wrongly assigned.

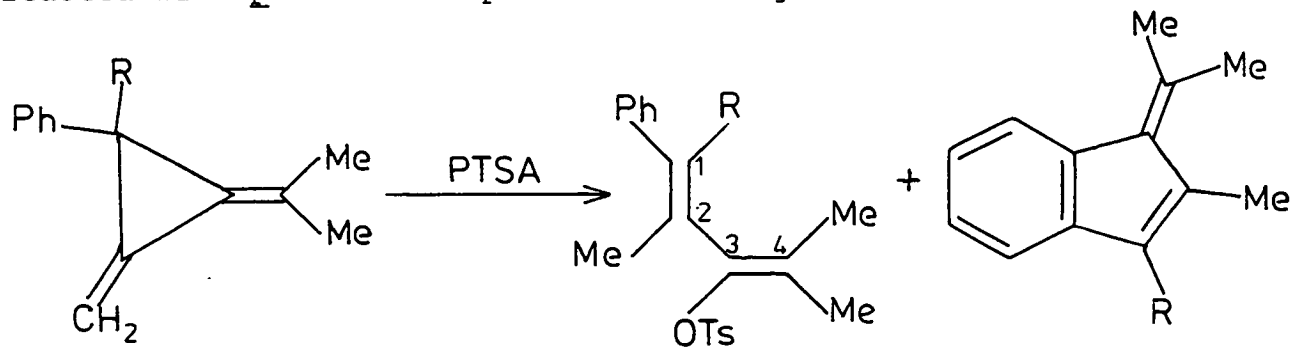
The formation of the ester (261) is consistent with protonation of the methylene group together with ring opening and outward rotation of the phenyl group to give the allyl-vinyl cation (264) as shown in Scheme 19. Reaction of this cation at C-(3) with the *p*-toluenesulphonate ion yields the ester (261). The absence of the ester (265) of opposite configuration, which would arise from cation (266), confirms that inward rotation of the phenyl group is stereochemically less favourable, as expected.

Confirmation of the site of protonation was obtained by reaction of cyclopropane (164) with O-deuterated *p*-toluenesulphonic acid which gave a product in which one deuterium atom had been incorporated in the 2-methyl group. The ^2D n.m.r. spectrum of the product shows a 1:2:1 triplet ($J_{\text{DH}} 2.2\text{Hz}$) at 1.64 p.p.m. due to coupling of the deuterium atom with the two hydrogen atoms on the same carbon atom. The ^1H n.m.r. spectrum shows a doublet ($J_{\text{HH}} 1.4\text{Hz}$) at 1.614 p.p.m. from the non-deuterated compound and a 1:1:1 triplet of doublets ($J_{\text{HD}} 2.3\text{Hz}$, $J_{\text{HH}} 1.4\text{Hz}$) at 1.597 p.p.m. from the deuterium incorporated product. The isotope shift was calculated to be 17 p.p.b., which is of the size expected¹³⁰ for protons geminal to one deuterium atom. The mass spectrum confirmed incorporation of one deuterium atom.

4.2 Reactions of the 1-alkyl-2-isopropylidene-3-methylene-1-phenylcyclopropanes

Each of the cyclopropanes (176), (177), (178) and (179)

reacted with *p*-toluenesulphonic acid to give a mixture



(176)	R = Me	(267 a)	(269 a)
(177)	R = Et	(267 b)	(269 b)
(178)	R = iso-C ₃ H ₇	(267 c)	(269 c)
(179)	R = n-C ₆ H ₁₁	(267 d)	(269 d)

containing the appropriate *p*-toluenesulphonate ester and a hydrocarbon (268) whose structure was assigned on the basis of evidence presented later. The product ratios (Table 8) were determined from the ¹H n.m.r. spectra (200 or 360MHz) of the reaction mixtures and were dependent on the nature of the alkyl group.

Products were isolated by column chromatography or preparative t.l.c. on silica or alumina using petrol with a small proportion of ether as elutant.

TABLE 8 Product Ratios for the Reaction of some
1-Alkyl-2-isopropylidene-3-methylene-1-phenyl-
cyclopropanes with p-Toluenesulphonic Acid

Alkyl group R	Ester	: Benzofulvene
Methyl	1.8	1
Ethyl	2.0	1
Isopropyl	2.7	1
Cyclohexyl	3.0	1

The ^1H n.m.r. spectra of esters (267 a-d) show characteristic two proton doublets (J 8.2-8.4Hz) at ca.7.8 p.p.m. due to the ortho protons of the p-tosyl group, and a resonance at 2.40 ± 0.06 due to the aromatic methyl protons. The protons of the methyl groups on C-(4) lie between 1.86 and 1.70 p.p.m. The protons of the 2-methyl group appear at 1.39 ± 0.02 p.p.m., which is about 0.2 p.p.m. lower than in compound (261). This is probably caused by steric interactions from alkyl groups pushing the phenyl group further out of the plane of the conjugated double bond and therefore allowing it to shield the protons of the 2-methyl group. Additionally, the resonances of the alkyl group, R, are clearly visible.

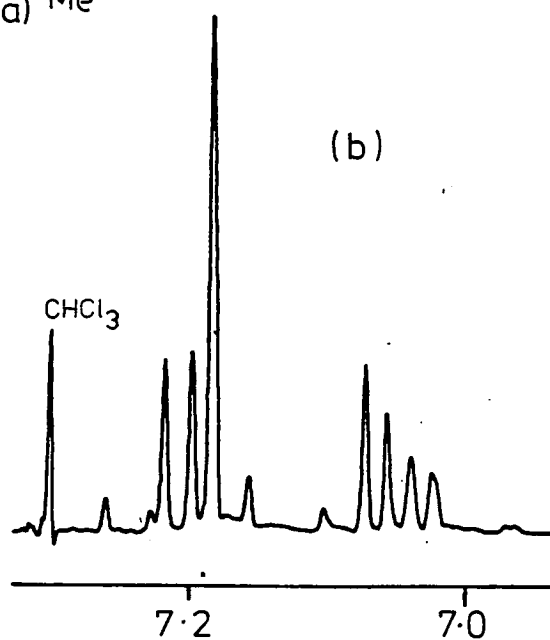
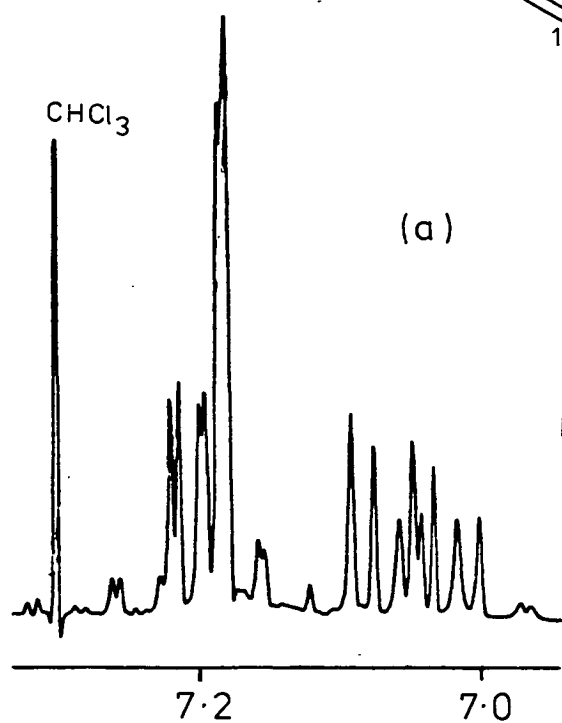
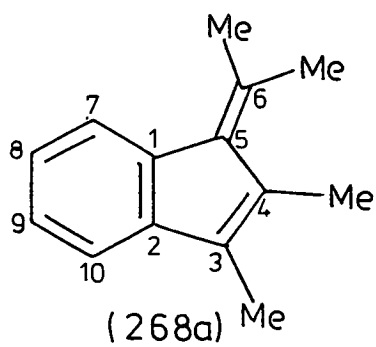
The methylene proton resonances of ester (267b) give a complex pattern resulting from their non-equivalence. This non-equivalence results from the steric interaction of the ethyl group with the large group cis to it which causes the C-(3), C-(4) double bond to move out of coplanarity with the

C-(1), C-(2) double bond. Similarly, the ^1H n.m.r. spectrum of ester (267c) gives two doublets separated by 0.01 p.p.m. for the two sets of methyl protons in the isopropyl substituent and the ^{13}C n.m.r. spectrum also gives two resonances from these methyl groups, again showing asymmetry caused by the non-coplanarity of the diene system. This same feature causes non-equivalence of the methylene carbon atoms in the cyclohexyl group of ester (267d) as shown by the presence of five methylene carbon atom signals in its ^{13}C n.m.r. spectrum.

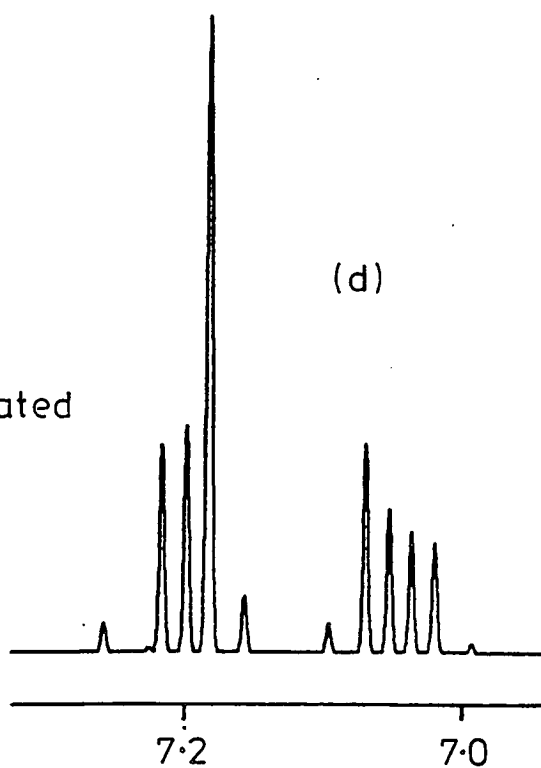
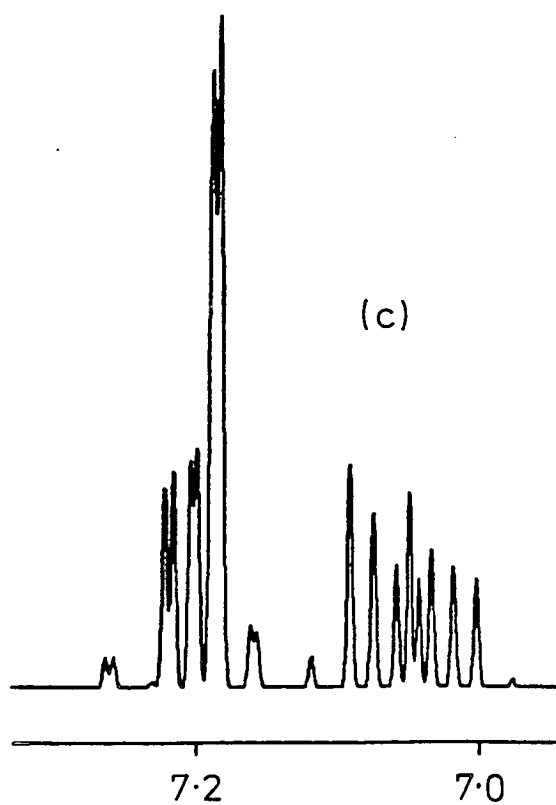
The stereochemistry of the cyclohexyl ester (267d) was determined by proton N.O.E. difference and spin decoupling experiments. Decoupling of the two tosyl ortho protons at 7.85 p.p.m. collapsed the doublet at 7.34 p.p.m., allowing assignment of the latter signal to the tosyl meta protons. The cyclohexyl methyne proton at 2.65 p.p.m. appears as a triplet of triplets (J 12.0, 2.5 Hz), consistent with an axial location. Decoupling of this signal sharpened the multiplet at 1.1 to 0.8 p.p.m. showing it to be from the adjacent protons. Irradiation of the proton resonance from the 2-methyl group produced a 4% increase in the tosyl ortho proton signals and a 3% increase in the phenyl ortho proton signals at 6.84 p.p.m., but no increase in any of the cyclohexyl proton resonances. Irradiation of the dimethyl signals at 1.75 and 1.73 p.p.m. produced increases in the tosyl ortho proton resonance and the cyclohexyl proton signals at 2.66 and 0.9 p.p.m. These results confirmed the E-stereochemistry expected by analogy with the reaction of cyclopropane (164).

Comparison of the ^1H n.m.r. spectra of the methyl, ethyl and isopropyl derivatives, (267 a-c) with those of (261)

Figure 10



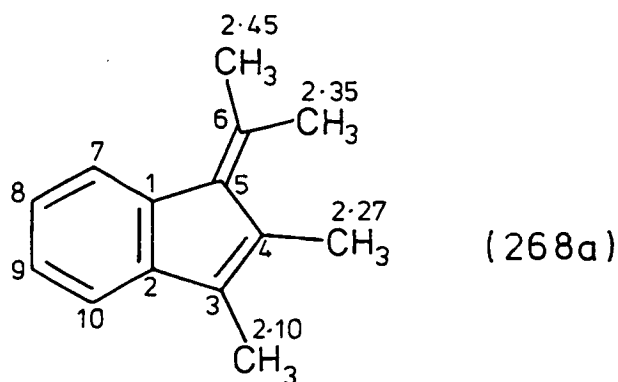
decoupling at $\text{H}-(7)$



simulated

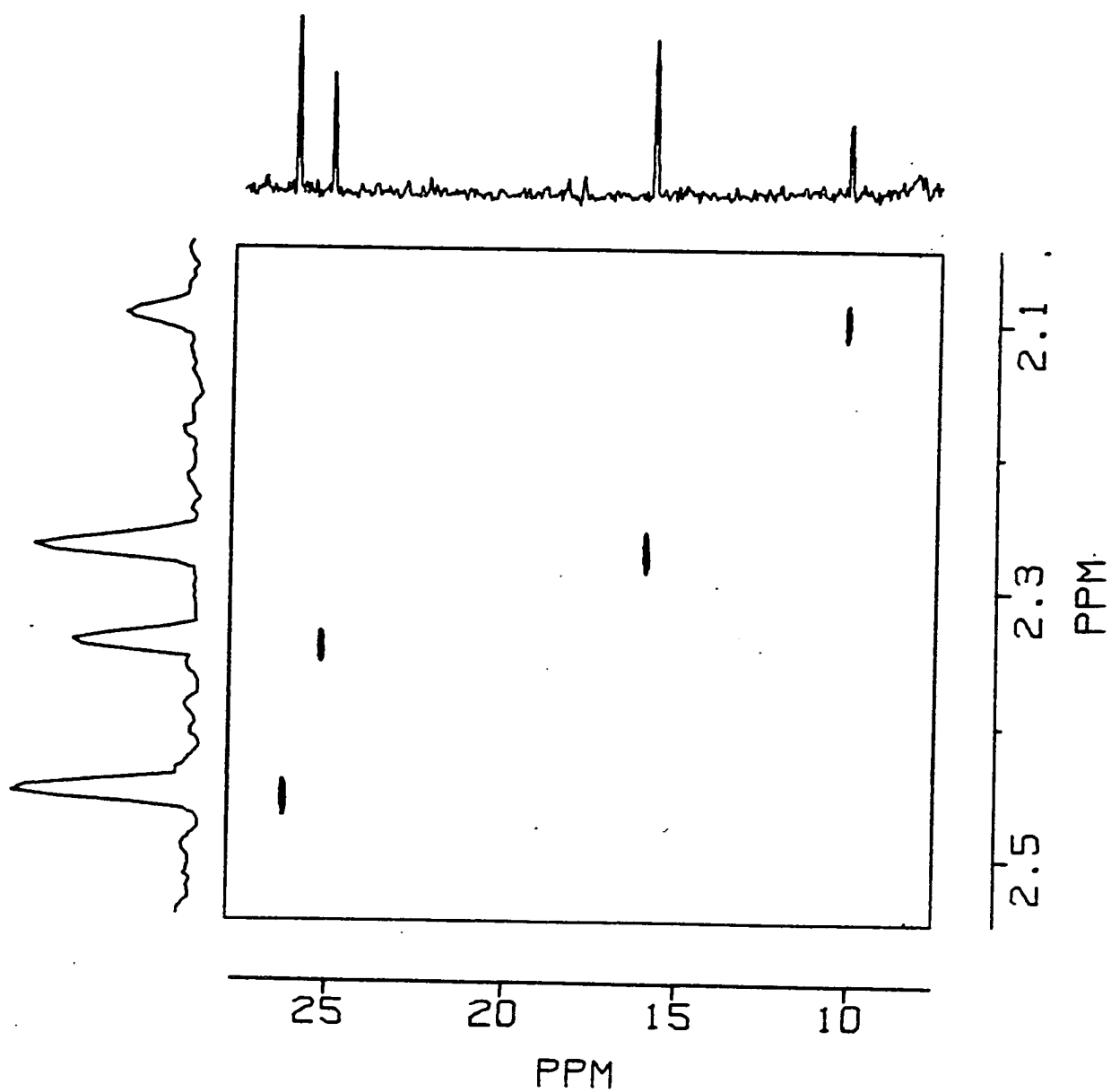
and (267d) allowed assignment of the E-stereochemistries shown.

The benzofulvene (268a) was identified from its spectral data. The mass spectrum shows it to be isomeric with the starting material. The ^{13}C n.m.r. spectrum shows separate resonances from each of four methyl groups, each of four proton bearing aromatic carbon atoms and six quaternary sp^2 hybridised carbon atoms. The ^1H n.m.r. spectrum shows four separate methyl proton resonances and the protons of an ortho disubstituted benzene ring. The ir spectrum shows a strong absorption at 750 cm^{-1} corresponding to an ortho disubstituted benzene ring. This data is only consistent with the structure (268a).

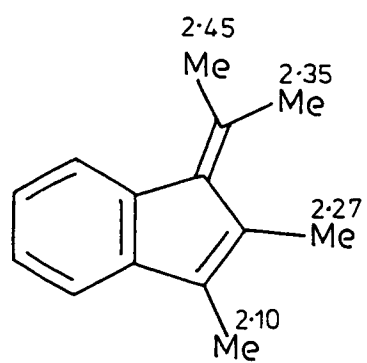


The proton n.m.r. spectrum of benzofulvene (268a) was assigned by spin decoupling and N.O.E. difference experiments. The methyl resonances appear as singlets at 2.45 and 2.34 p.p.m., a quartet (J 0.9Hz) at 2.27 p.p.m. and a broad singlet at 2.10 p.p.m. The aromatic region shows a doublet (J 7.6Hz) at 7.67 p.p.m., which by its position and multiplicity was assigned to H-7, and a complex pattern (fig. 10a) for the other three aromatic protons covering the region 7.21-7.10 p.p.m. This pattern was successfully simulated on a Bruker Aspect 2000

Figure 11



^{13}C - ^1H Correlation spectrum



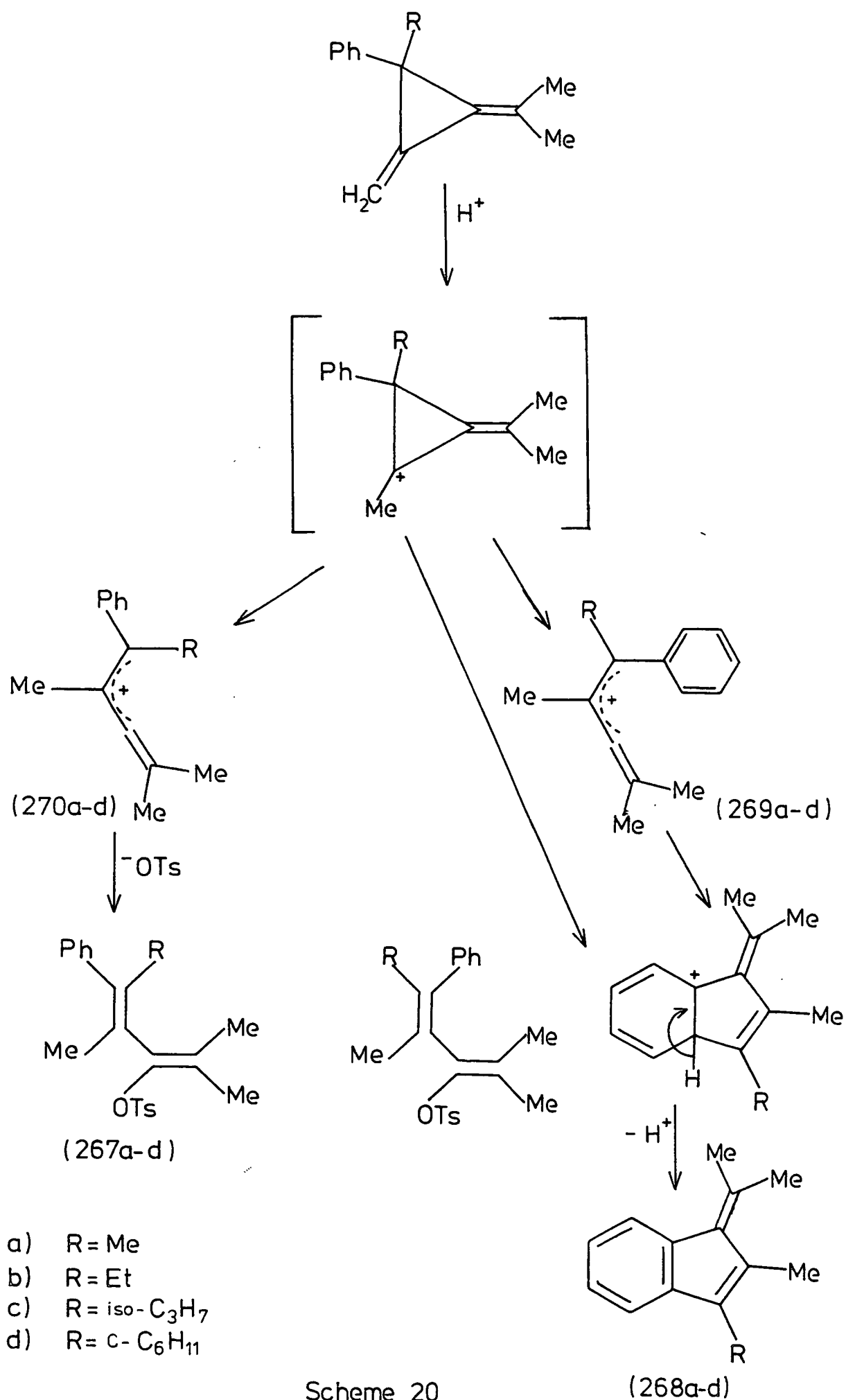
(268a)

computer using the PANIC program (fig. 10 b). This required two additional ortho couplings of 7.5Hz ($J_{8,9}$; $J_{9,10}$), meta couplings of 1.2Hz ($J_{8,10}$) and 1.0Hz ($J_{7,9}$) and a para coupling of 0.7Hz ($J_{7,10}$) and gave the chemical shifts of H-(8), H-(9) and H-(10) as 7.13, 7.20 and 7.19 p.p.m. respectively. Decoupling the signal due to H-(7) simplified the signal at 7.13 p.p.m. to a doublet of doublets and sharpened some of the peaks between 7.22 and 7.18 p.p.m. (fig. 10 c), therefore confirming the assignments made above. This pattern was also successfully simulated by equating to zero all the couplings to H-(7) (fig. 10 d).

Decoupling the methyl doublet at 2.27 p.p.m. sharpened the resonance at 2.10 p.p.m. and vice-versa suggesting that these methyls were on adjacent carbon atoms. Irradiation of the resonance at 2.45 p.p.m. produced a 17% increase in the signal from H-(7), allowing assignment of the former to the syn-6-methyl protons. Irradiation of the resonance at 2.10 p.p.m. gave a 9% increase in the signal from H-(10) allowing assignment of the signal at 2.10 p.p.m. to the 4-methyl protons, and therefore the signal at 2.27 p.p.m. to the 3-methyl protons and the signal at 2.34 p.p.m. to the anti-6-methyl protons.

The methyl resonances in the ^{13}C n.m.r. spectrum were assigned using a two dimensional ^{13}C - ^1H correlation spectrum (fig. 11). This allowed assignment of the ^{13}C n.m.r. resonances at 25.7, 24.7, 15.5 and 9.9 p.p.m. to the 6-syn, 6-anti, 4- and 3-methyl groups respectively. An attempt to correlate the aromatic region of the ^1H and ^{13}C n.m.r. spectra was unsuccessful.

The benzofulvenes (268b-d) were identified by comparison of their ^1H and ^{13}C n.m.r. spectra with those of the benzo-



Scheme 20

fulvene (268a). In all cases proton resonances from the C-(6) methyl groups lie at 2.45 ± 0.01 and 2.35 ± 0.01 p.p.m. and from the C-(4) methyl groups at 2.28 ± 0.04 p.p.m. The ^{13}C n.m.r. spectra show resonances at 24.2 to 26.5 p.p.m. from the C-(6) methyl groups and 16.1 ± 0.8 p.p.m. from the C-(4) methyl groups. Resonances from the substituents at C-(3) are clearly visible in the ^1H and ^{13}C n.m.r. spectra.

The esters (267a-d) are considered to be formed by the same mechanism as ester (261), as described above and shown in Scheme 20. The formation of the benzofulvenes (268a-d) is consistent with protonation of the methylene group with ring opening and inward rotation of the phenyl group to give allyl cations (269a-d) which could undergo intramolecular electrophilic substitution and deprotonation as shown in Scheme 20. However, concerted cyclisation and cyclopropyl ring opening cannot be excluded. It should be noted that although the cations (269a-d) might be expected to react with the tosylate anion to give the configurational isomers of esters (267a-d), no evidence of this has been found in the above reactions. The allyl cations (270a-d) cannot undergo cyclization and deprotonation to give benzofulvenes since the phenyl group is on the opposite side of the double bond to the electrophilic centre.

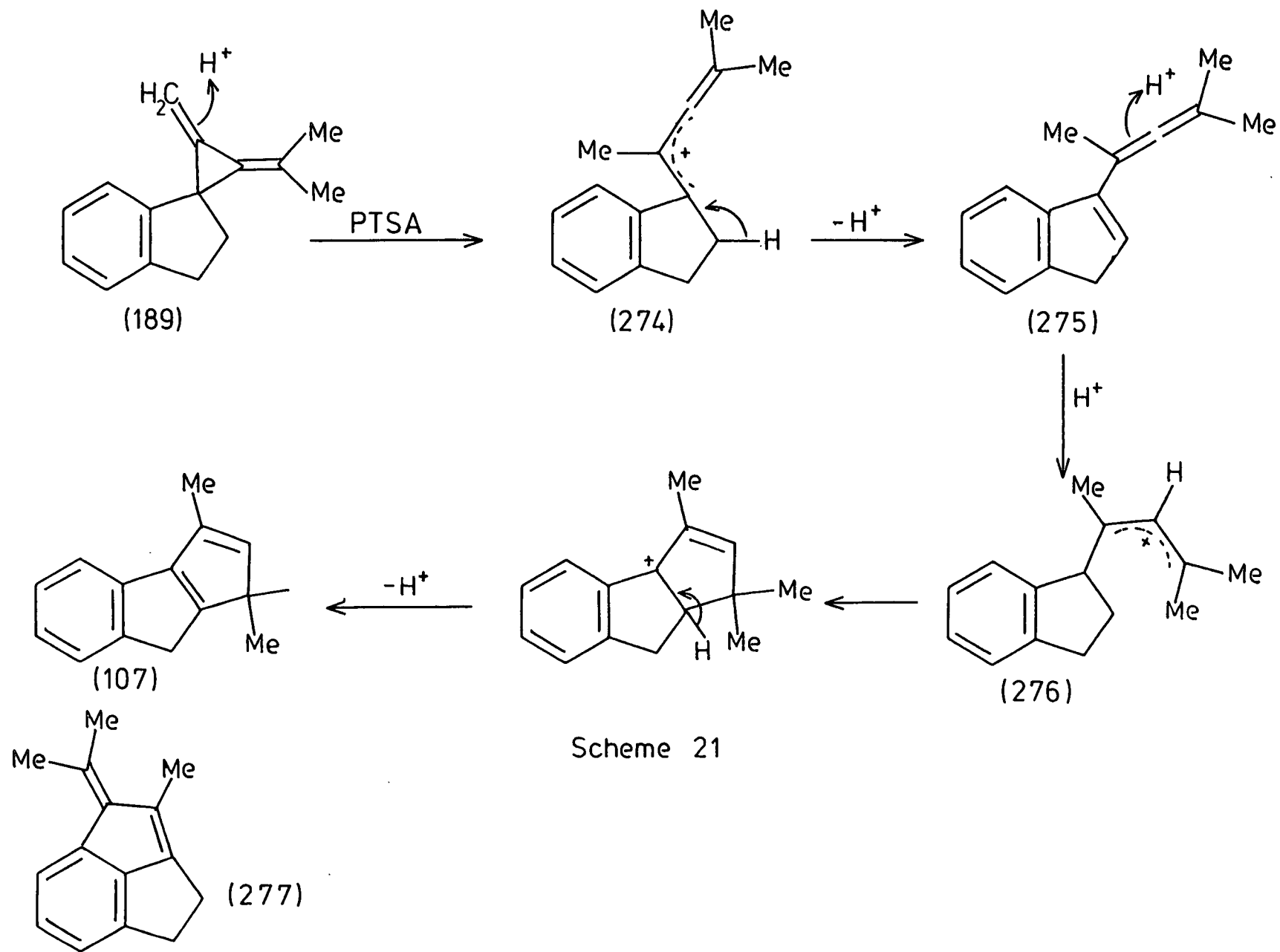
For cyclopropanes (176), (177), (178) and (179) which have 1-alkyl substituents, ring opening following protonation of the methylene group occurs by both inward and outward rotation of the phenyl groups. This was not apparent in the protonation of cyclopropane (164) because of the large difference in the size of the two C-(1) substituents, phenyl and

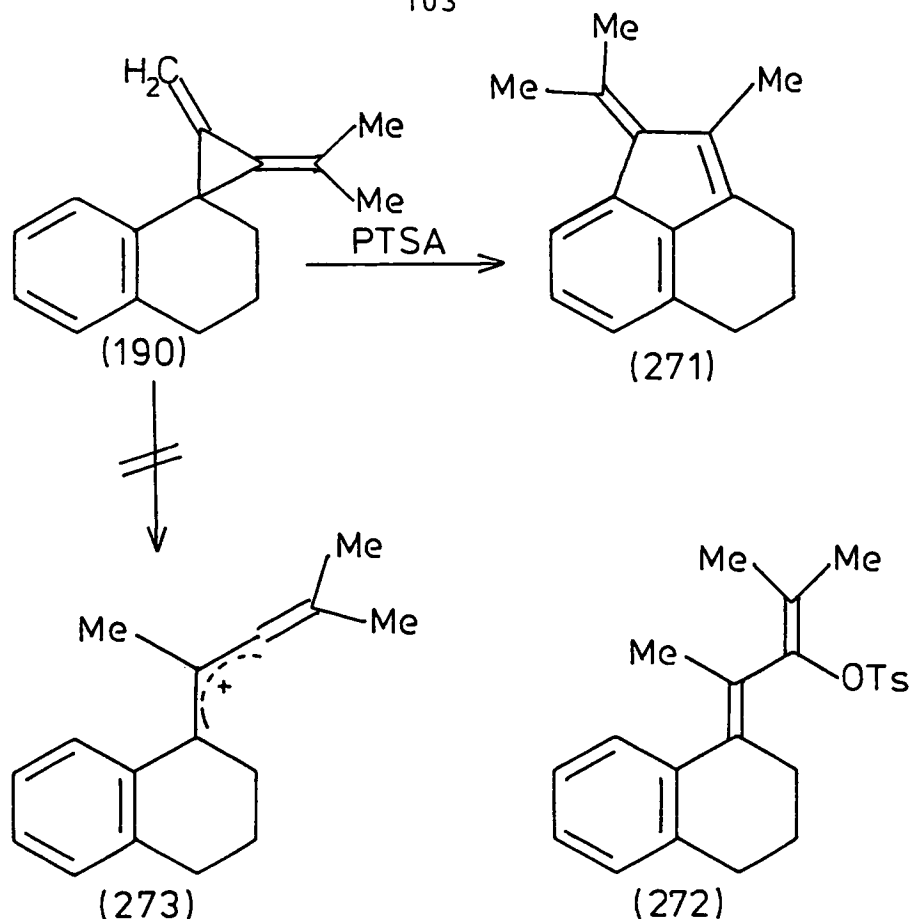
hydrogen, inward rotation of the phenyl group being much less favourable than inward rotation of the hydrogen atom.

If these reactions involve only the allyl cations (269) and (270), simple steric arguments might predict that the ratio of ester to benzofulvene should decrease as the size of the substituent R increases from methyl to cyclohexyl, since steric hindrance to inward rotation of the R group increases as its size increases. Table 8 shows that the opposite effect is observed. It is possible that increasing the size of the R substituent may prevent the phenyl group from adopting the required orientation for the intramolecular electrophilic substitution reaction and therefore, if the cations can inter-convert,⁷⁵ a greater proportion of ester from cation (270) might be expected if the activation energy for cyclisation is greater than for ester formation. However, this does not explain the absence of esters from cation (269). Alternatively, if ring opening and cyclisation are concerted and cation (270) reacts rapidly with the tosylate ion, the ester from (269) would not be expected. The activation energy for cyclisation, and therefore the proportion of benzofulvene formed, would be markedly dependent on how easily the phenyl ring could adopt the required stereochemistry, which in turn would depend on the nature of the R substituent.

4.3 Reactions of the Spirocyclopropanes (189) and (190)

The reaction of 2'-isopropylidene-3'-methylenecyclopropane-1'-spiro-1-tetralin (190) with *p*-toluenesulphonic acid gave only the benzofulvene (271) which was identified





by comparison of its ^1H and ^{13}C n.m.r. spectra with those obtained for other benzofulvenes. The absence of ester (272) was unexpected in view of the results discussed in section 4.2 and suggests that cation (273) was not formed and that the orientation in which the aromatic ring is fixed is extremely favourable for concerted cyclopropane ring opening and electrophilic substitution, making this a lower energy route than formation of either allyl-vinyl cation.

In contrast to this result, the reaction of 2'-isopropylidene-3'-methylenecyclopropane-1'-spiro-1-indane (189) with *p*-toluenesulphonic acid gave only the cyclopentadienoindene (107) which had a ^1H n.m.r. spectrum identical to that of an authentic sample.¹¹⁵ The formation of this was unexpected and can be rationalised as set out in Scheme 21. After initial protonation and formation of allyl cation (274),

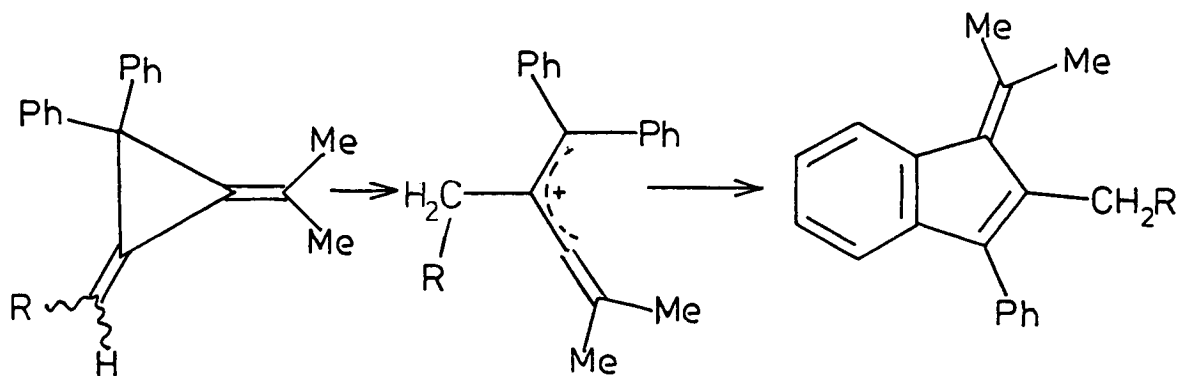
proton loss would give the allene (275). Protonation of the central carbon atom would yield the allyl cation (276) which would cyclise as described earlier (section 1.4). The absence of the benzofulvene (277) is no doubt due to the very strained transition state which would be required for its formation. The absence of a tosylate ester is not readily explained unless proton loss is particularly favourable or is concerted with cyclopropane ring opening.

4.4 Reactions of the 1,1-Diphenylmethylenecyclopropanes (184) and (185a and b)

The reaction of 1,1-diphenyl-2-isopropylidene-3-methylene-cyclopropane (184) with *p*-toluenesulphonic acid gave exclusively the benzofulvene (278) which was identified by comparison of its ^1H and ^{13}C n.m.r. spectra with those of other benzofulvenes formed. Similarly, the reaction of a mixture of the syn- and anti-1,1-diphenyl-3-ethylidene-2-isopropylidenecyclopropanes (185a and b) with *p*-toluenesulphonic acid produced only the 1,2-benzo-6,6-dimethyl-4-ethyl-3-phenylfulvene (279) which was identified from its ^1H and ^{13}C n.m.r. spectra.

Both these benzofulvenes are formed by a route analogous to that described in section 4.2, the symmetry of the molecules making ring opening in both directions identical (Scheme 22).

The initial site of protonation for benzofulvene formation was confirmed by reaction of the cyclopropane mixture (185a and b) with O-deuterated *p*-toluenesulphonic acid. This gave incorporation of a deuterium atom in the methylene group and incorporation of up to three deuterium atoms in each of



R = H (184)

(278)

R = Me (185 a and b)

(279)

Scheme 22

the methyl groups on C-(6) as shown in Fig. 12 .

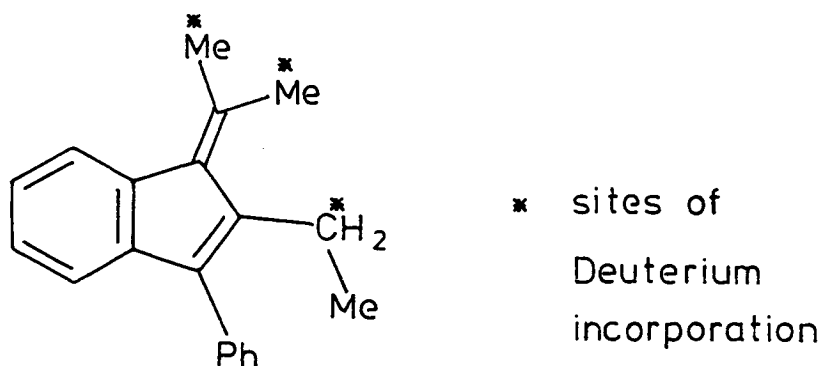


Figure 12

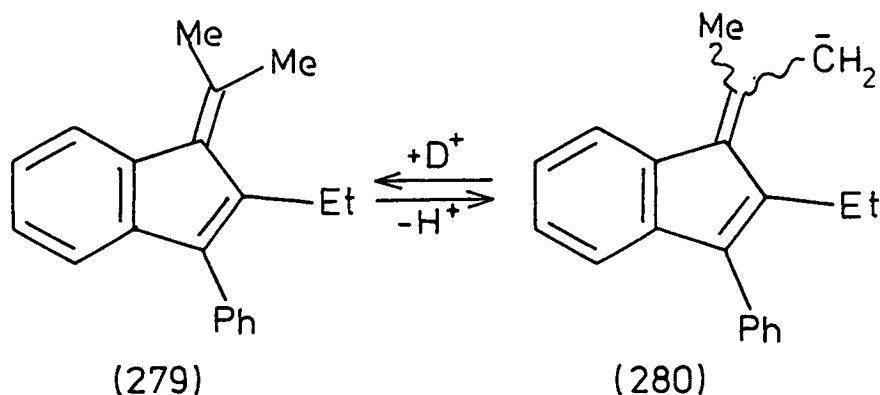
The ^2D n.m.r. spectrum, with proton decoupling, of the reaction mixture shows a broad signal at 2.69 p.p.m. from the deuterated methylene group with a group of resonances at 2.55, 2.53 and 2.51 p.p.m. and another group of resonances at 2.44, 2.42 and 2.40 p.p.m. from incorporation of one, two and three deuterium atoms in both the methyl groups on C-(6). Deuterium isotope shifts were calculated from the ^1H n.m.r. spectra, with ^2D and ^1H decoupling where necessary to indicate the

position of a masked resonance. Isotope shifts by α -deuterium atoms were measured at ca.20 p.p.b. for the methylene group and 17.3 and 21.6 p.p.b. for the methyl signals at 2.54 and 2.43 respectively. The β -deuterium shift in the methyl signal at 1.15 p.p.m. was measured at 7.9 p.p.b. These figures were in accordance with expected values.¹³⁰

Deuterium incorporations were calculated from the ^1H n.m.r. spectrum and showed 40% incorporation of one deuterium atom in the methylene group and 25% incorporation of one deuterium atom in the two methyl groups. The ^2D n.m.r. and mass spectra confirmed that a small number of molecules had incorporation of two or three deuterium atoms in the methyl groups.

In order to determine whether the deuterium atoms were incorporated during or after formation of the product, benzo-fulvene (279) was treated with O-deuterated p-toluenesulphonic acid. The ^2D n.m.r. spectrum of the product had resonances at 2.57, 2.55, 2.47 and 2.44 p.p.m. showing incorporation of one or two deuterium atoms in each of the methyl groups on C-(6). The absence of a resonance at 2.69 p.p.m. proved that incorporation of a deuterium atom into the methylene group did not occur after the formation of the benzofulvene (279), confirming that protonation is initiated at the ethylidene carbon atom as shown in Scheme 22.

The mechanism proposed for deuterium incorporation in the methyl groups on C-(6) proceeds via abstraction of a proton from one of these methyl groups by the tosylate anion to give the highly delocalised anion (280), where the negative charge is delocalised over all the fulvene and aromatic carbon atoms. Addition of a deuterium ion would give a mono-deuterated



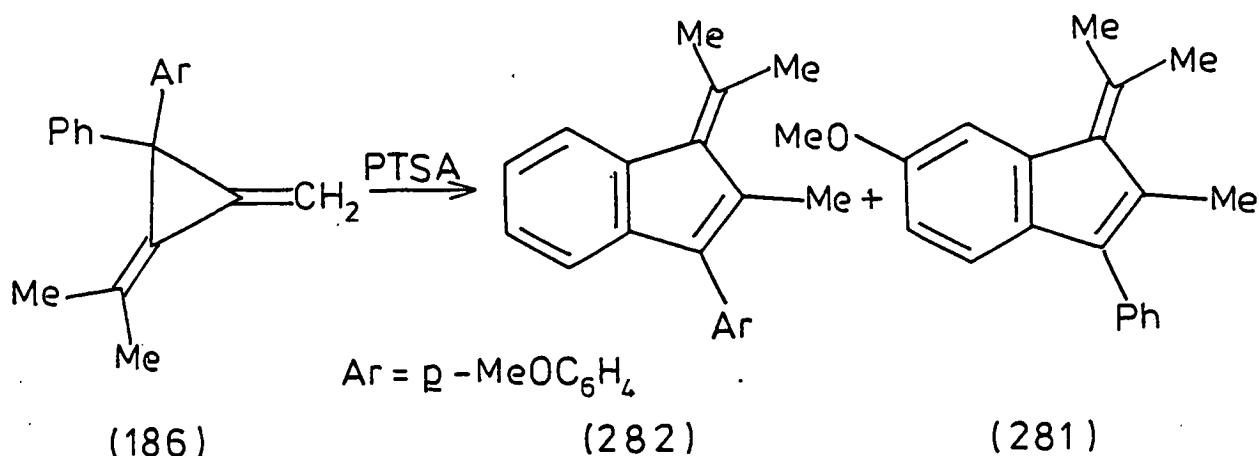
product and repetition of the process allows the incorporation of several deuterium atoms into the 6-methyl groups of the product.

4.5 Reactions of the 1,1-Diaryl-2-isopropylidene-3-methylene-cyclopropanes (186), (187) and (188)

The reaction of 1-aryl-1-phenylcyclopropanes (186), (187) and (188) were observed in order to determine whether the effect of substituents on one of the aromatic rings would reflect the proposal that benzofulvene formation involves internal electrophilic substitution.

The reaction of the *p*-methoxy derivative (186) with *p*-toluenesulphonic acid gave a mixture containing only the 1,2-benzo-8-methoxy - 3-phenyl-4,6,6-trimethylfulvene (281) and the 1,2-benzo-3-(*p*-methoxyphenyl)-4,6,6-trimethylfulvene (282) in the ratio 2.7:1.

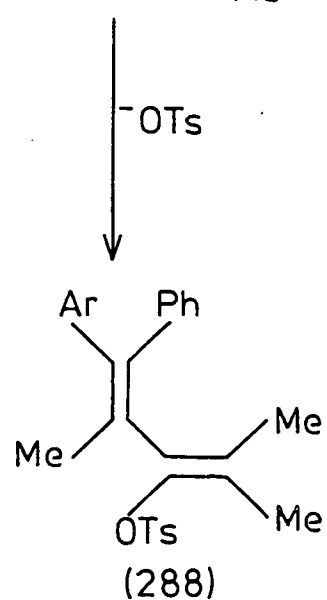
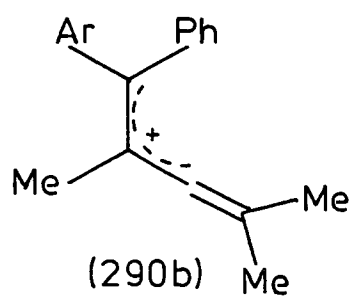
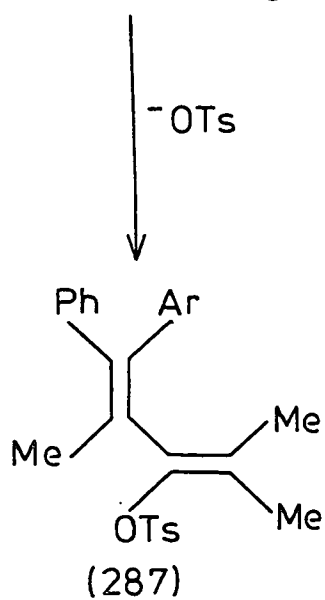
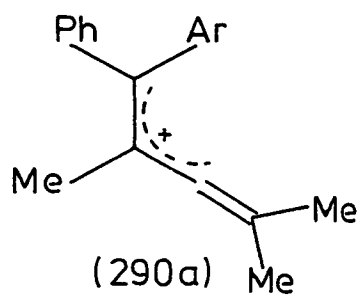
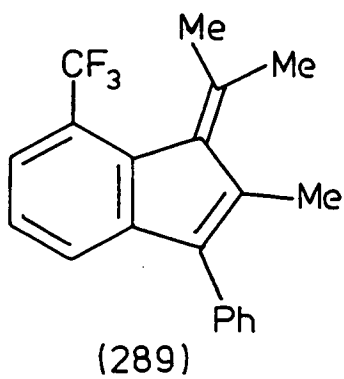
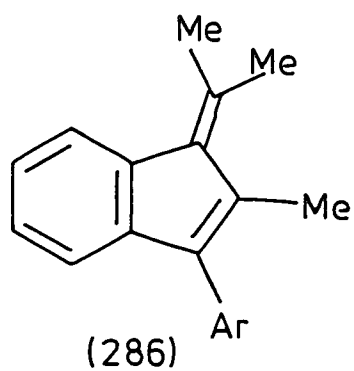
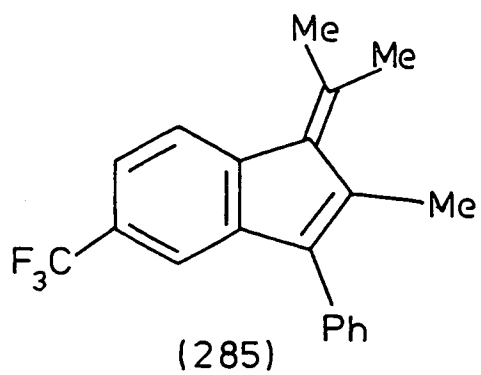
The products could not be separated but were identified by comparison of the ^1H and ^{13}C n.m.r. spectra of the mixture of isomers with those of other benzofulvenes formed and were



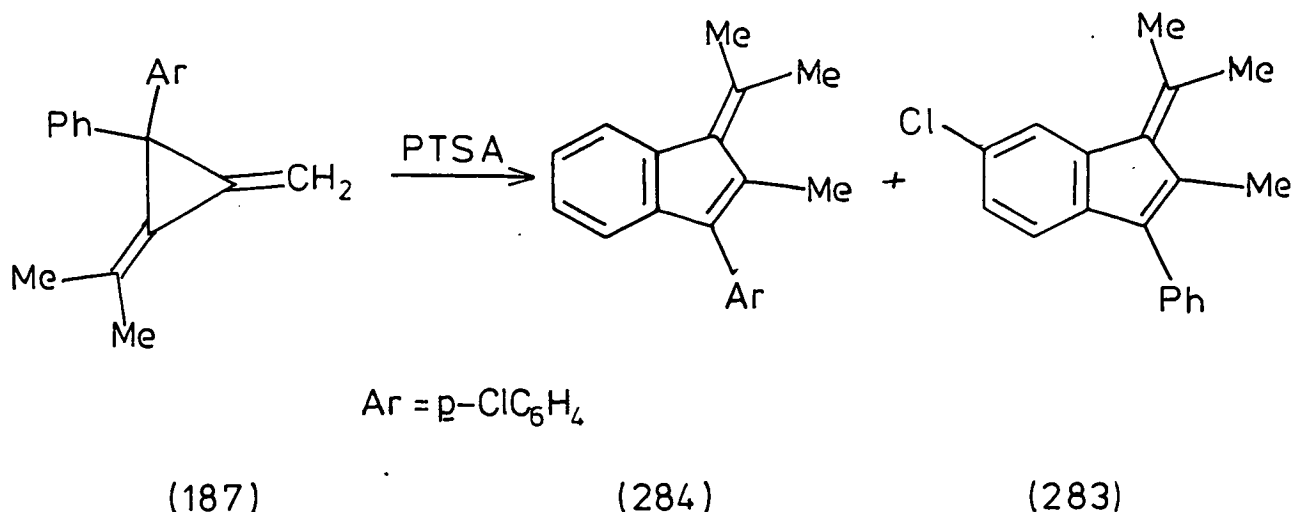
differentiated from the ^{13}C n.m.r. spectrum of the mixture of isomers. Resonances from the protonated carbon atoms, C-(7), C-(8) and C-(9) normally appear between 126 and 124 p.p.m. (see appendix IV). The effect of a methoxy group¹²¹ ortho to a carbon atom is to reduce the chemical shift of that carbon signal by ca 14.4 p.p.m. and therefore in benzo-fulvene (281) two protonated carbon signals from C-(7) and C-(9) were expected at 109.5 to 112 p.p.m.. The major isomer gives two such resonances at 109.6 and 112.1 p.p.m. and was therefore assigned structure (281) above. The minor isomer (282) gives a single resonance at 113.5 p.p.m., consistent with the expected shift of ca -14.4 p.p.m. in the signal from the two protonated aromatic carbon atoms ortho to the methoxy group from the value of 128-130 p.p.m. normally found from the 3-phenyl substituent.

The predominance of ring closure into the p-methoxy substituted ring is consistent with the activating effect of this group in electrophilic aromatic substitution reactions.

The reaction of the p-chloro derivative (187) with p-toluenesulphonic acid gave a mixture containing only the



Ar = *m*-CF₃C₆H₄



1,2-benzo-8-chloro-3-phenyl-4,6,6-trimethylfulvene (283) and the 1,2-benzo-3-(*p*-chlorophenyl)-4,6,6-trimethylfulvene (284) in the ratio 1.2:1. The products were identified by comparison of the ^1H n.m.r. spectrum of the isomer mixture with those of other benzofulvenes formed but it was not possible to differentiate between the two isomers since, unlike the methoxy group, the chlorine substituent in aromatic rings does not produce a large change in the ^{13}C n.m.r. chemical shifts of any of the ring carbon atoms.

The effect of the para chlorine substituent was, as expected, very small since only benzofulvenes were formed and the ratio of isomers was close to 1:1.

The reaction of the m-trifluoromethyl derivative (188) with p-toluenesulphonic acid gave a mixture containing two benzofulvenes (285) and (286) and also both esters (287) and (288) in the ratio 12:10:5:1.2. The benzofulvenes were separated from the esters but pure products could not be obtained. The presence of two benzofulvenes was confirmed by comparison of the ¹H n.m.r. spectrum of the benzofulvene mixture with those of other benzofulvenes formed and similarly,

comparison of the ^1H n.m.r. and mass spectra of the ester mixture with those of other esters formed allowed their identification.

Since the above reaction of cyclopropane (188) gave rise to the possibility of three isomeric benzofulvenes being formed, the two which had been formed were identified by the use of a DEPT pulse sequence experiment showing methyne carbon signals only. The effect of a trifluoromethyl group¹²¹ on the ^{13}C n.m.r. chemical shifts has been determined as -3.3 p.p.m. for an ortho carbon resonance, -0.3 p.p.m. for a meta carbon resonance and +3.2 p.p.m. for a para carbon resonance. Using these figures isomer (285) should produce a resonance at ca 116 p.p.m. from C-(10), shifted from the usual value of 119 p.p.m. Isomer (286) was predicted to give a resonance at ca 132 p.p.m. from the carbon atom para to the trifluoromethyl group, shifted from the normal value of about 129 p.p.m. and a resonance at ca 119 p.p.m. - the normal C-(10) value in these systems. All signals from benzofulvene (289) were predicted to lie between 121 and 130 p.p.m. The observed spectrum shows signals at 115.4, 118.7 and 133.1 p.p.m. as predicted for the benzofulvenes (285) and (286), the number and position of all ^1H and protonated ^{13}C signals being consistent with the presence of only these isomers. However, it was not possible to determine from the ^{13}C or ^1H n.m.r. spectra which was the major product.

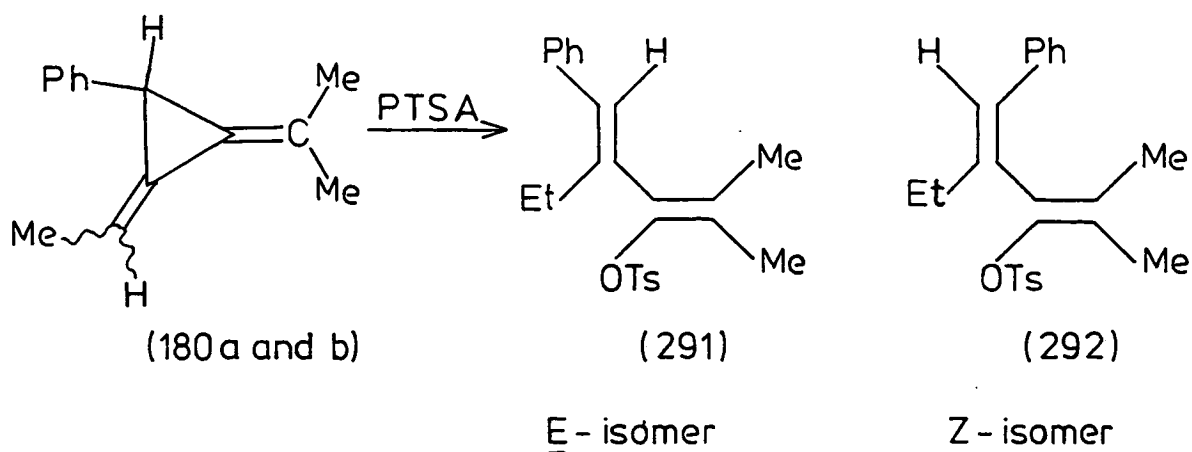
The ^1H n.m.r. spectrum of the mixture of esters (287) and (288) shows the major isomer to have methyl proton resonances at 2.44, 1.88 and 1.55 (2 peaks, 6 protons) p.p.m., attributed to the aromatic methyl protons, the methyl protons

cis to the ester group, and the protons of the remaining two methyl groups respectively. Both sets of methyl protons giving resonances at 1.55 p.p.m. are shielded by aromatic rings. The minor isomer gives resonances at 2.44 p.p.m. from the aromatic methyl protons, at 1.76 p.p.m. from the methyl protons cis to the ester group and at 1.61 and 1.52 p.p.m. from the two sets of methyl protons shielded by the aromatic rings. It is however not possible from this data to assign the isomers unambiguously.

The deactivating effect of the trifluoromethyl group does not appear to have been very significant in directing the ring closure since both benzofulvenes were formed in approximately equal amounts. The meta trifluoromethyl group does however appear to have given substantial steric hindrance to electrophilic addition at the position ortho to it, since none of the benzofulvene (289) was formed. However, the formation of esters (287) and (288) in small yields suggests that, in this case, cations of the type (290) are formed to some extent, possibly because the electron density in the aryl ring is not sufficient to ensure only concerted cyclisation.

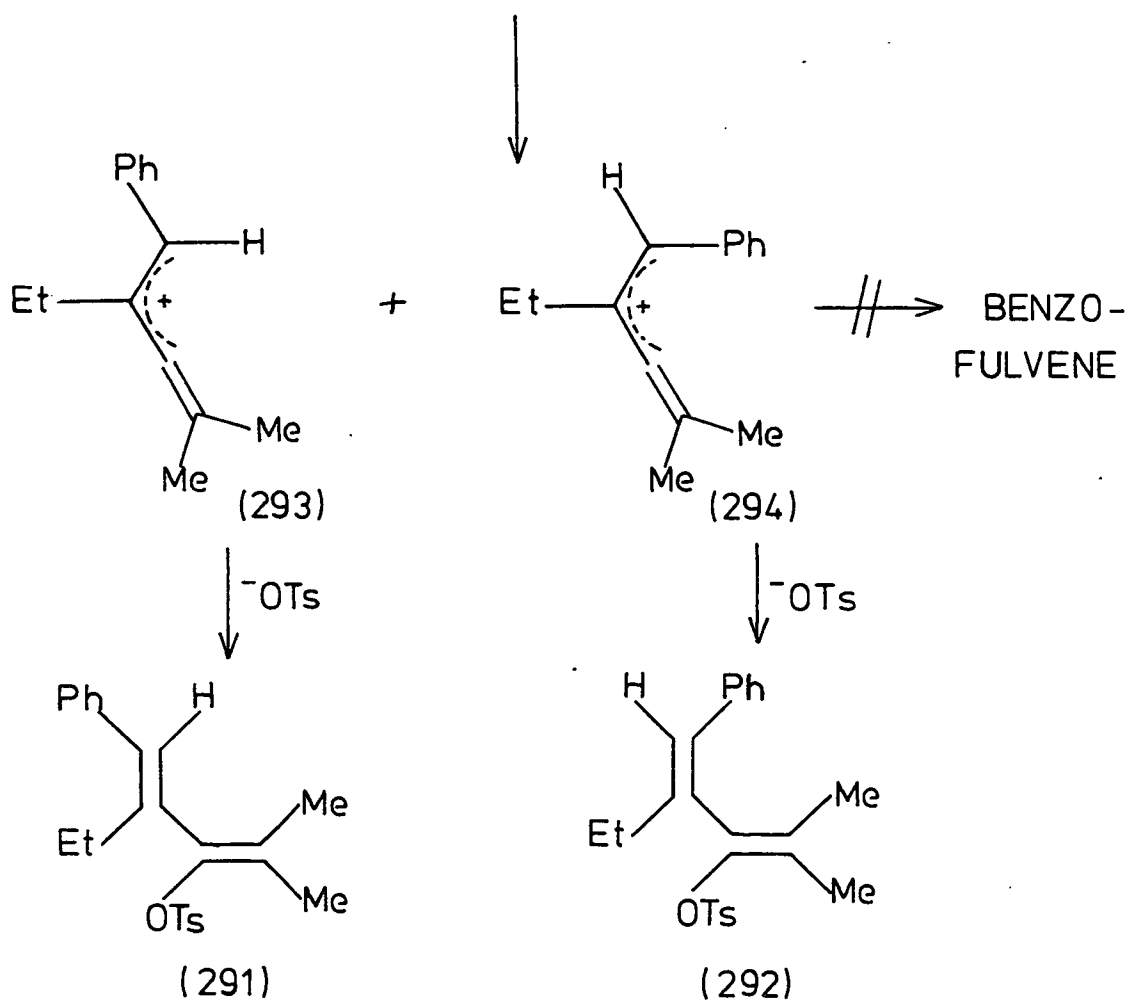
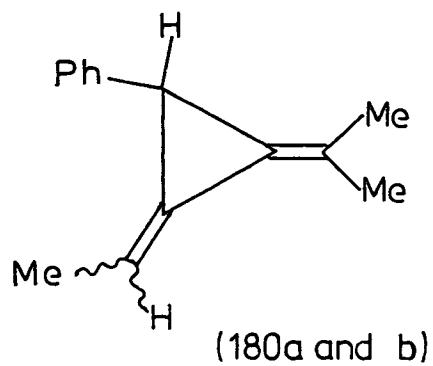
4.6 Reactions of syn and anti-3-Ethylidene-2-isopropylidene-1-phenylcyclopropanes (180a and b) and (181a and b)

Reaction of the mixture of syn and anti-3-ethylidene-2-isopropylidene-1-phenylcyclopropane (180a and b) with p-toluenesulphonic acid gave a mixture containing both E and Z-4-benzylidene-2-methyl-3-(p-toluenesulphonyloxy)hex-2-ene (291) and (292) in the ratio 3.7:1, with no benzofulvene products.



The products were differentiated by their ^1H n.m.r. spectra. The alkene methyl resonances of the E-isomer have similar chemical shifts (1.86 and 1.82 p.p.m.) as is found for all the esters where these groups could not lie over the phenyl ring. In contrast, the ^1H n.m.r. spectrum of the Z-isomer shows one alkene methyl resonance to be shifted substantially to lower frequency, 1.35 p.p.m., since it has become located over the phenyl ring and is therefore highly shielded. The methyl protons of the ethyl group also resonate at a lower frequency, 0.87 p.p.m., than in the E-isomer as a result of shielding by the tolyl ring. The strong steric interaction between the large vinyl and phenyl groups, forces the two double bonds out of coplanarity, causing the methylene protons of the ethyl group to be non-equivalent. The resulting AB pattern is further split by the methyl protons of the ethyl group and the olefinic proton and therefore appears as two complex multiplets at 1.92 and 2.04 p.p.m.. These collapsed to four broad peaks in an AB pattern (J 7.5Hz) on decoupling of the methyl proton triplet at 0.87 p.p.m..

The ^{13}C n.m.r. spectrum of ester (292) is similar to that of the E-isomer (291) with the exception of the resonance

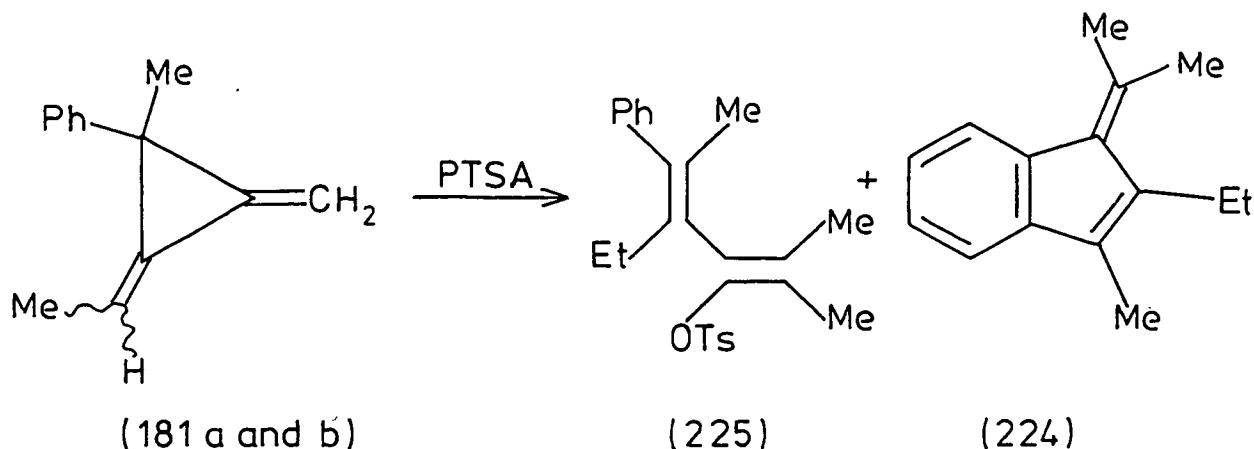


from the methylene carbon atom, which appears at 29.4 p.p.m. compared with 21.6 p.p.m. for the E-isomer, and the olefinic methyne carbon atom which gives a signal at 130.6 p.p.m. compared with 133.5 p.p.m. for the E-isomer.

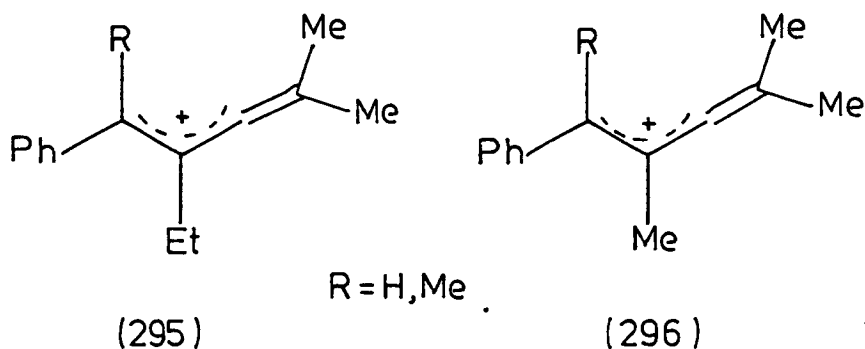
It would appear that in this reaction, although the sterically favoured mode of ring opening predominates to give the E-isomer via cation (293), the more sterically hindered mode of ring opening is not excluded and in this instance gives cation (294) and thence the Z-isomer. The absence of a benzofulvene, suggests that, in the ring opening reaction with inward rotation of the phenyl group, the phenyl ring does not have the correct orientation to allow concerted cyclisation. It is possible that, in the absence of another group containing a carbon atom on C-(1), the phenyl ring, in the formation of the Z-isomer, can adopt an orientation which allows greater overlap of its p-orbitals with those developing to the allyl cation than found when the other C-(1) substituent is larger. This might make formation of the allyl-vinyl cation (294) a lower energy route than concerted cyclisation to the benzofulvene.

The reaction of the mixture of syn- and anti-3-ethylidene-2-isopropylidene-1-methyl-1-phenylcyclopropane (181a and b) with p-toluenesulphonic acid gave a mixture containing the ester (225) and the benzofulvene (224) in the ratio 1:1.1, with no evidence for formation of the Z-isomer of ester (225).

It should be noted that both these reactions of the 3-ethylidenecyclopropanes (180a and b) and (181a and b) have produced higher proportions of products resulting from inward

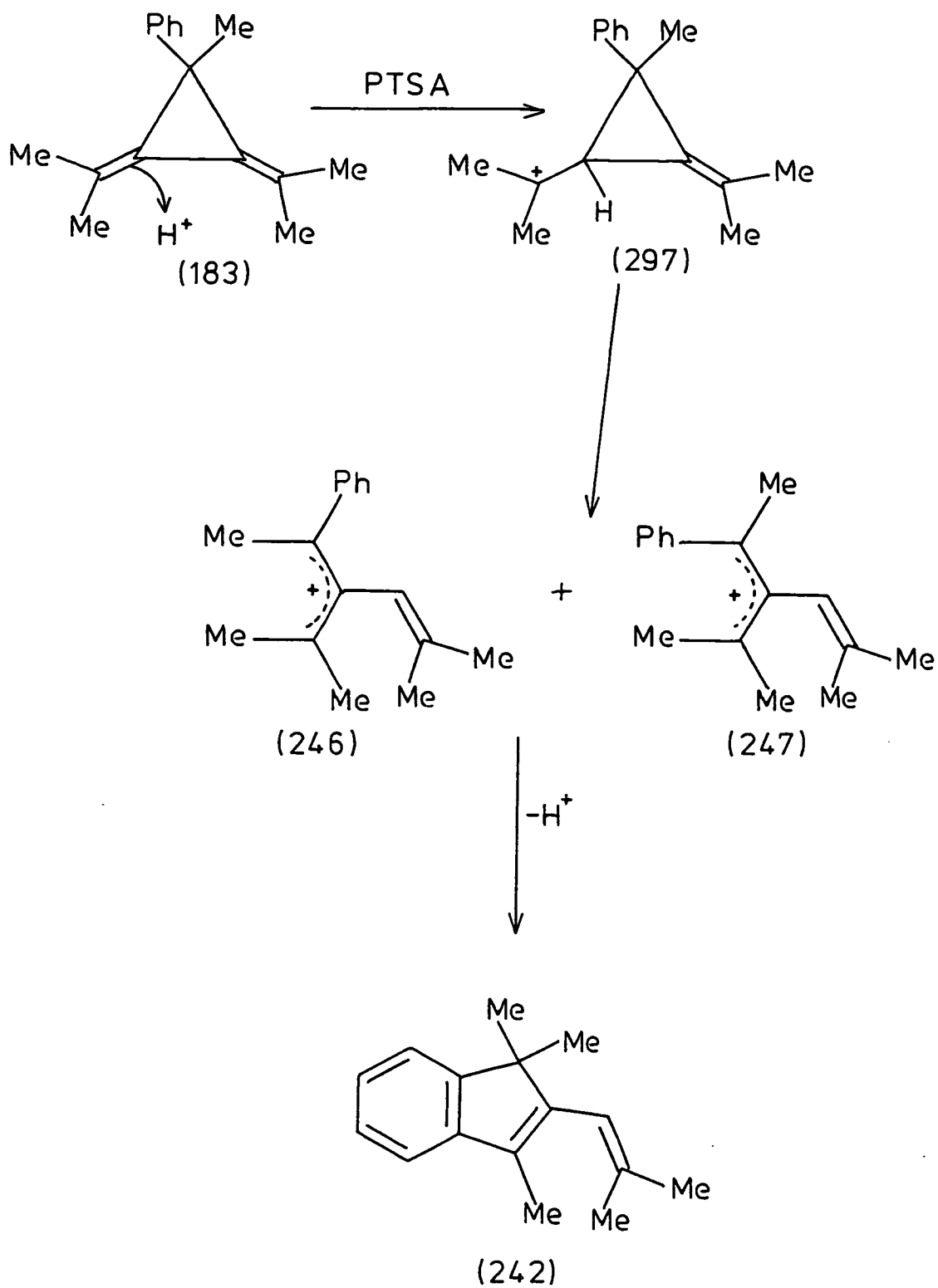


rotation of the phenyl group in the ring opening step than did the corresponding 3-methylenecyclopropanes (164) and (176). This may be caused by a greater steric interaction between the phenyl and the ethyl groups in the transition states to the cations (295) than between the phenyl and methyl groups in the transition states to the cations (296).



4.7 Reaction of 2,3-Diisopropylidene-1-methyl-1-phenylcyclopropane (183)

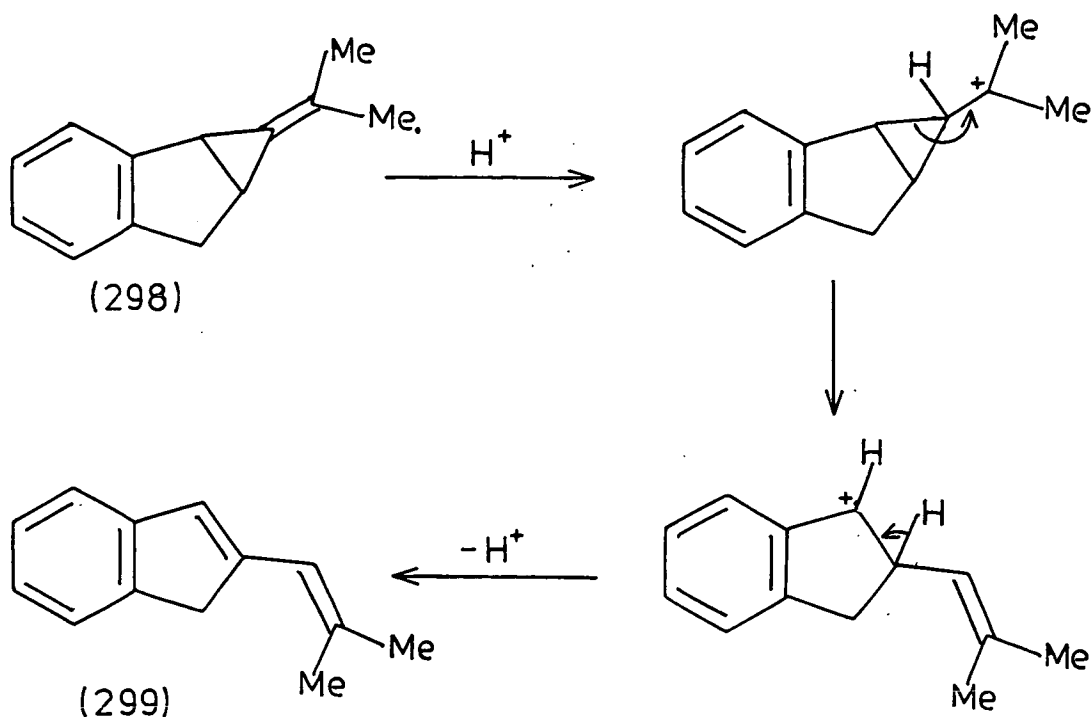
The reaction of 2,3-diisopropylidene-1-methyl-1-phenylcyclopropane (183) with *p*-toluenesulphonic acid gave exclusively 2-(2'-methylprop-1'-enyl)-1,3,3-trimethylindene (242) which was identified by comparison of its ^1H n.m.r. spectrum with that of the same compound previously obtained (p.85).



Scheme 23

This rearrangement can be rationalised by protonation of the double bond at the cyclopropane carbon atom to give the cyclopropyl carbiny l cation (297) followed by ring opening to give allyl cations (246) and/or (247) (Scheme 23) which have already been shown to eventually give the indene (242) (see section 3.5).

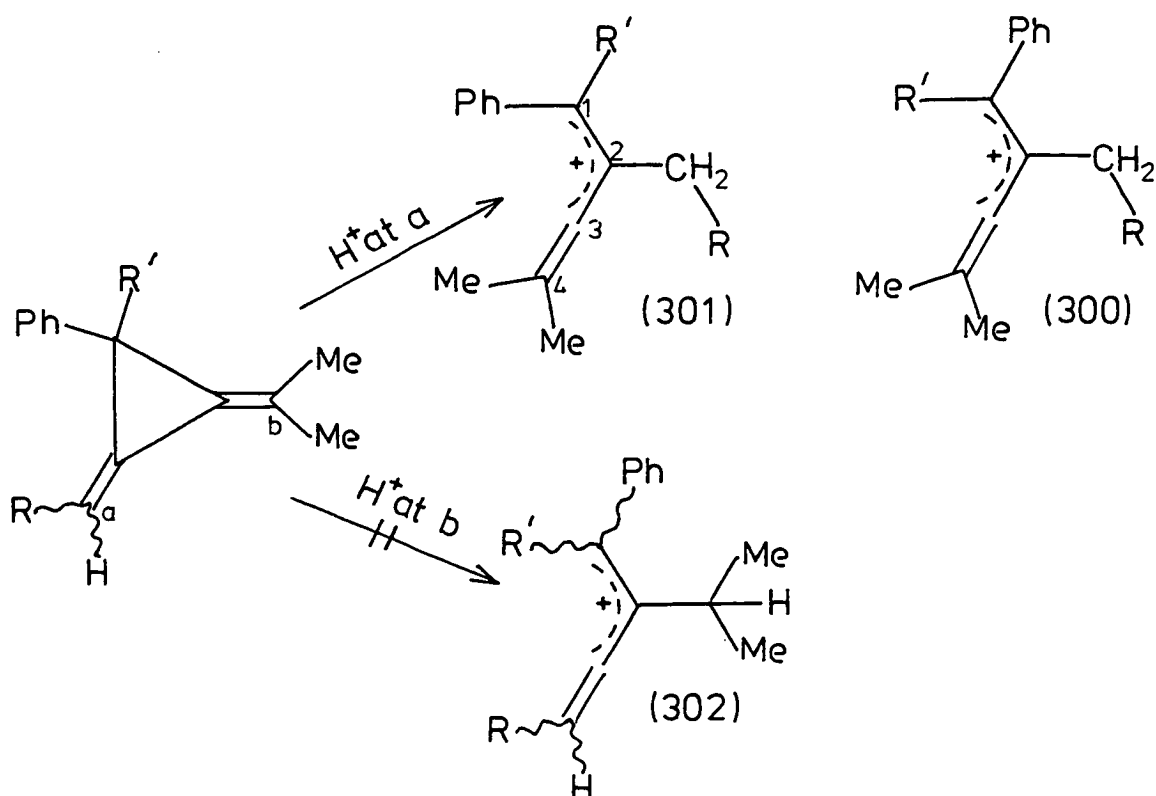
A similar protonation of an isopropylidene double bond at the cyclopropane carbon atom has been proposed by Robertson¹²⁹ for the acid catalysed rearrangement of 2,3-benzo-6-isopropylidenebicyclo[3.1.0]hex-2-ene (298) which gave the indene (299).



4.8 Conclusion

From the results described in this chapter it may be concluded that protonation of these dimethylenecyclopropanes takes place at C-(a) of the methylene or the ethylidene

groups, where present, in preference to the isopropylidene carbon atoms. The former mode of protonation may be favoured over protonation at C-(b) for two reasons.



(1) Additional stabilisation is given to the vinyl-allyl cations (300) and (301) or the transition states by the two methyl groups on C-(4) which are absent in cation (302).

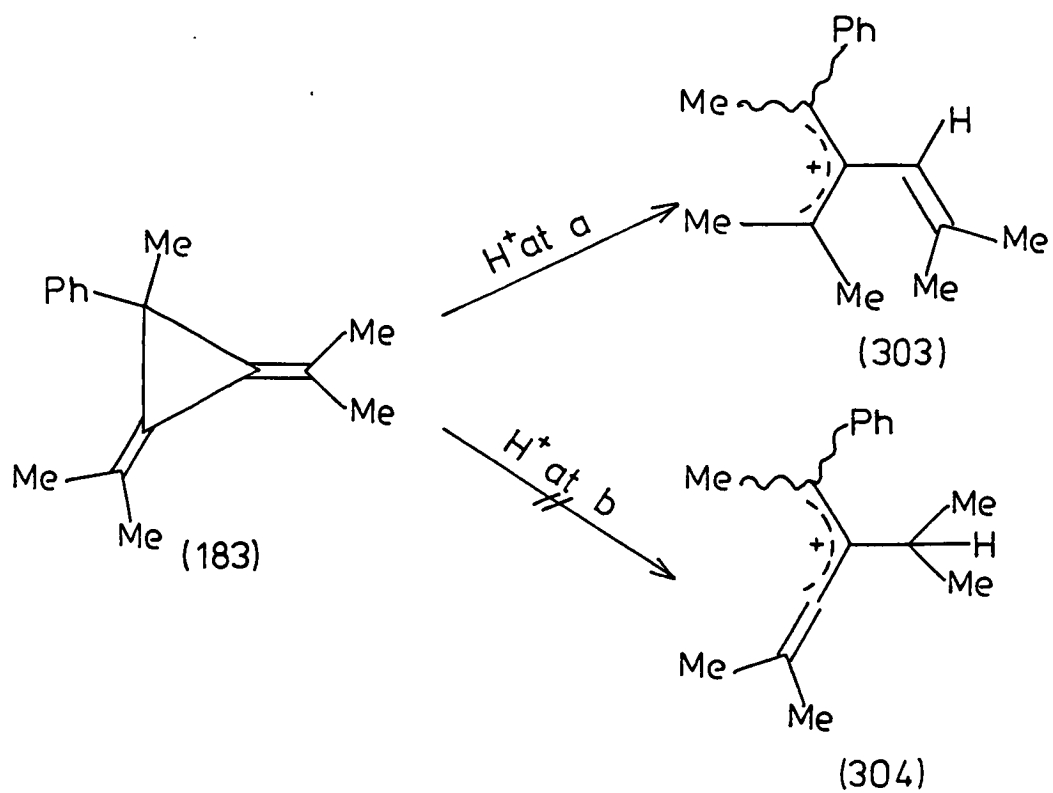
(2) Steric hindrance to protonation of the isopropylidene group caused by its two methyl substituents.

The course of the reaction after the initial protonation varies markedly with the substituents R and R'. The intermediacy of the cations (300) is demonstrated by the isolation of the corresponding tosylate esters. Examination of both intermediate cations (301) and (301) suggests that there is no strong stereochemical reason why cations (301) should not also form tosylate esters and that this might indeed be easier than

cyclisation to form the benzofulvenes. These esters are only found to a significant extent in one case ($R'=H$, $R=CH_3$), and are absent when benzofulvenes are formed ($R'\neq H$) except for a small proportion when one aromatic ring is deactivated ($R'=\text{mC}_6\text{H}_4\cdot\text{CF}_3$ $R=H$). These observations suggest that the benzofulvenes may be formed by a route not involving a discrete cation (301). Benzofulvenes are only formed where a substituent ($R'\neq H$) is present on the same carbon atom as the aryl group. This substantially restricts or prevents rotation of the aryl group and it is possible that it lies in a favourable position for cyclisation concerted with cyclopropyl ring opening. Thus the direction of ring opening would not be governed solely by relative sizes of the aryl group and the substituent, but by the orientation of the aryl group.

The behaviour of the 1-alkyl-2-isopropylidene-3-methylene-1-phenylcyclopropanes (176), (177), (178) and (179) (section 4.2) is at present not fully understood. Further information may be gained by studying the relative rates of reaction of these dimethylenecyclopropanes. Additionally, evidence for the reversibility or otherwise of the initial protonation might be obtained from the use of the O-deuterated *p*-toluenesulphonic acid in a limited reaction where starting material is recovered.

The reaction of 2,3-diisopropylidene-1-methyl-1-phenylcyclopropane (183) proceeded exclusively by protonation of the unsaturated cyclopropane carbon atom, to give allyl cation (303) rather than protonation at C-(b) to give the vinyl-allyl



cation (304). This is presumably caused by the greater stability of cation (303) than (304).

CHAPTER 5

Experimental

5.1 Introduction

Gas-liquid Chromatography

A Pye 204 chromatograph was used for analytical work and a Pye 105 automatic preparative chromatograph or a Carlo Erba Strumentazione Fractovap 2450 instrument was used for preparative work. All the above were fitted with flame ionisation detectors and nitrogen was used as the carrier gas.

Thin Layer Chromatography

Analytical thin layer chromatography was carried out on silica or alumina coated glass plates using a 0.3 mm layer of Merck Type 60G silica or Type 60G (E) alumina. Preparative thin layer chromatography was carried out on silica or alumina coated glass plates using a 1 mm layer of Merck Type 60G silica or Type 60G (E) alumina.

Column and Medium-pressure Chromatography

Column chromatography was carried out using Spence Type H basic alumina.

Medium-pressure chromatography¹³¹ was carried out using Merck silica gel 60 (40-60µm) or 10% w/w silver nitrate adsorbed onto Merck alumina (90 active, neutral) tap-fill packed glass columns.

Silver nitrate was adsorbed onto alumina by gently swirling the alumina in an aqueous solution of silver nitrate. The water was removed under vacuum and the alumina was dried in a vacuum oven (70°/0.1 mm) for 24h. The column was then packed in the normal manner but only light petroleum or light petroleum/ether mixtures were used as elutant and the column was back-flushed with ether.

Samples were either preadsorbed onto silica or applied as neat liquids. Pressures of about 20 p.s.i. were used, normally giving flow rates of 5-20 ml min⁻¹. Fractions were collected using an automatic fraction collector and samples were examined using t.l.c. for samples from the silica column and g.l.c. for samples from the 10% silver nitrate on alumina column.

Infra-red Spectroscopy

Spectra were recorded on a Perkin Elmer 157G or 781 spectrometer. Samples were examined as liquid films or nujol mulls.

Mass Spectroscopy

Mass spectra were obtained using an AE1 MS-902 double focussing instrument. Exact masses were obtained by peak matching, giving results normally within 5 p.p.m. of calculated values.

Ultra-violet Spectroscopy

Spectra were recorded on a Unicam SP 800A spectrophotometer. Samples were dissolved in either ethanol or ether.

Elemental Analyses

Microanalyses were obtained on a Perkin-Elmer 204 elemental analyser.

Nuclear Magnetic Resonance Spectroscopy

Proton n.m.r. spectra were recorded on a Bruker WP80, WP200 or WH360 spectrometer. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane using chloroform ($\delta_{\text{H}} = 7.25$) as internal standard.

Carbon-13 n.m.r. spectra were recorded on a Varian CFT-20 (20MHz) or a Bruker WP 200 (50MHz) or WH 360 (90MHz) spectrometer using deuteriochloroform ($\delta_{\text{CDCl}_3} = 76.9$ p.p.m.) as internal standard. Chemical shifts are given in parts per million relative to tetramethylsilane.

Where necessary, pulse sequence experiments were used to differentiate between methyl, methylene, methyne and quaternary carbon atoms (see p.51 and 52).

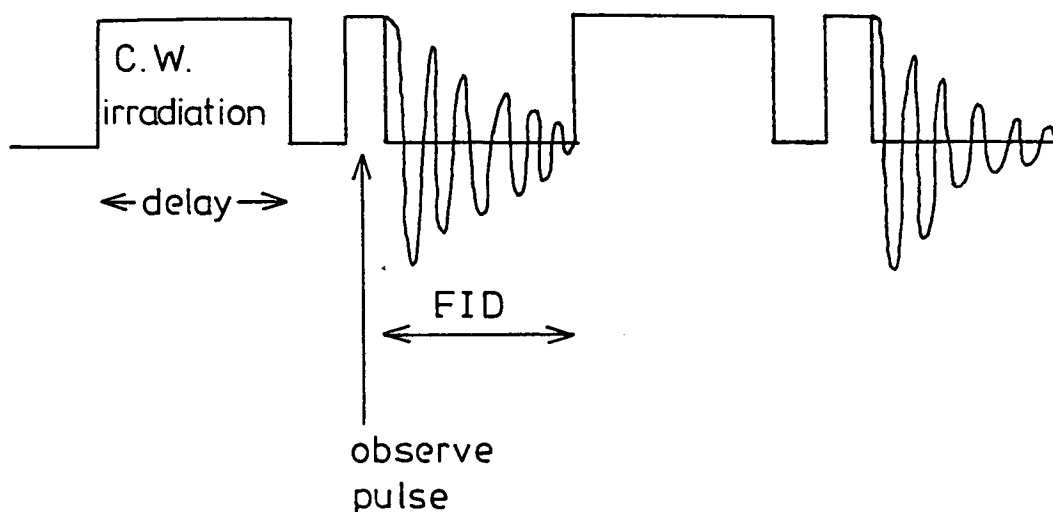
Deuterium n.m.r. spectra were recorded on a Bruker WP200 (30MHz) or WH360 (55MHz) spectrometer using deuteriochloroform ($\delta_{\text{D}} = 7.25$) as internal standard.

Fluorine n.m.r. spectra were recorded on a Bruker WP80 (75.4MHz) spectrometer and referenced to fluorotrichloromethane.

Proton, carbon-13 and fluorine n.m.r. spectra were obtained using deuteriochloroform as solvent unless otherwise stated. Deuterium n.m.r. spectra were obtained using chloroform as solvent.

N.O.E. Difference Spectroscopy

Proton N.O.E. difference spectroscopy was carried out on either the Bruker WH-360 or WP-200 n.m.r. instrument. Successive free induction decays (acquisition time ca. 2s) were separated by a delay (3s) during which, selective irradiation was applied continuously at a fixed power level (33 to 42 dB below 0.2 watt).



The same number of scans (200-1000) was acquired for irradiation at each resonance position. After scaled Fourier transformation of the decay signals, difference spectra were obtained by subtracting the off resonance spectrum from each of the others in turn. Enhancements were measured by direct integration of the difference spectra, based on the off resonance spectrum integrals as 100%.

Materials

Unless otherwise stated, liquids and solvents were dried over magnesium sulphate and reagents were used without further purification. Purity of reagents was checked by ^1H n.m.r. spectroscopy.

Dry ether refers to ether dried by, and stored over sodium wire.

Dry tetrahydrofuran was obtained by heating tetrahydrofuran under reflux, with calcium hydride, under nitrogen for 1h and then distilling into bottles containing activated molecular sieve.

Dry ethanol was obtained by a literature method.¹³²

Carbon tetrachloride was purified by passing it through a short column of alumina immediately before use, to remove traces of alcohol.

Ethanolic hydrogen chloride was obtained by dissolving dry hydrogen chloride gas in dry ethanol and was stored at 4°.

Light petroleum refers to the fraction of b.p. 40-60° unless otherwise stated.

Indan-1-one, 1,1-diphenylethene, E-2-phenylbut-2-ene and p-methoxy-1,1-diphenylethene were kindly supplied by Dr. I.H. Sadler.

5.2 Preparation of Starting Materials

5.2.1 1-Bromo-3-methylbuta-1,2-diene was prepared as described by Landor, Patel and Whiter.¹³³ 2-Methylbut-3-yn-2-ol (50 g, 0.6 mol), hydrobromic acid (48% w/w, 125 ml), cuprous bromide (25 g, 0.17 mol) and diglyme (6.0 g) were placed in a stoppered

conical flask and allowed to stand overnight. The upper organic layer was removed and the aqueous layer was washed with light petroleum (30-40°) (3x25 ml). The combined organic extracts were then washed with hydrobromic acid (3x25 ml), dried over potassium carbonate and the solvent was carefully removed. Distillation gave 1-bromo-3-methylbuta-1,2-diene (80%, b.p. 26-28°/6 mm, lit. b.p. 53-54°/60 mm¹³³).

5.2.2 Methyltriphenylphosphonium Iodide was prepared by the dropwise addition of methyl iodide (142 g, 1.0 mol) in benzene (300 ml) to a stirred solution of triphenylphosphine (262 g, 1.0 mol) in benzene (2000 ml) with heating to initiate the reaction. The mixture was then heated under reflux for 4h, cooled and the product filtered off, giving methyltriphenylphosphonium iodide (97%, m.p. 184-186°, lit. m.p. 187°¹³⁴).

5.2.3 Cyclohexyl Phenyl Ketone was prepared by a Friedel-Crafts acylation reaction. Cyclohexanoic acid (100 g, 0.78 mol) and excess thionyl chloride (200 ml) were heated under reflux for 2h. Unreacted thionyl chloride was then removed under reduced pressure (6 mm) giving the crude acid chloride. This was then added dropwise over 45 min to a stirred mixture of aluminium trichloride (133.4 g, 1.0 mol) in dry benzene (300 ml). The mixture was then heated under reflux for 1h, cooled and poured onto ice. The organic layer was removed and the aqueous layer extracted with ether (3x100 ml). The combined extracts were washed with sodium bicarbonate solution (200 ml), dried and the solvent removed. The product was recrystallised from light petroleum (b.p. 40-60°) giving cyclohexyl phenyl

ketone (36%, m.p. 55-58°, lit. m.p. 54°¹³⁵).

5.2.4 1-Phenylprop-1-yne was prepared by the methylation of phenylacetylene. Sodium (8.28 g, 0.36 mol) was dissolved in liquid ammonia (500 ml) with a little ferric nitrate present to catalyse the formation of sodamide. Phenylacetylene was then added dropwise with vigorous stirring and the mixture was stirred for a further 1.5h. Methyl iodide (63.9 g, 0.45 mol) in ether (100 ml) was then added dropwise with stirring and the ammonia allowed to evaporate overnight. Water (500 ml) was added to the residue, the organic layer removed, the aqueous layer extracted with ether (2x200 ml) and the combined extracts were washed with 15% hydrochloric acid solution (2x200 ml), dilute sodium bicarbonate solution (2x200 ml) and water (200 ml) before drying and removal of the solvent. Distillation of the residue gave 1-phenylprop-1-yne (78%, b.p. 78-80°/12 mm, lit. b.p. 76°/15 mm¹³⁶).

5.3 Preparation of Phenyl Alkenes

5.3.1 E-1-Phenylprop-1-ene was prepared by a Grignard reaction. Ethyl bromide (109 g, 1.0 mol) in dry ether (75 ml) was added dropwise with stirring to magnesium turnings in ether. The solution was then heated under reflux for 0.5h and cooled. Benzaldehyde (82.3 g, 0.76 mol) in ether (75 ml) was added dropwise to the stirred solution which was then heated under reflux for 2h before being poured onto ice. Dilute hydrochloric acid (700 ml) was added to decompose the complex, the organic layer was removed and the aqueous layer extracted with

ether (3x200 ml). The combined extracts were then washed with sodium bicarbonate solution (500 ml), water (2x250 ml) and dried before the solvent was removed. The resulting crude alcohol was dehydrated by heating under reflux with phosphorous pentoxide (40.0 g, 0.28 mol) in carbon tetrachloride (300 ml) for 3h. Water was then added carefully, the organic layer removed and the aqueous layer extracted with carbon tetrachloride (200 ml). The combined extracts were dried, the solvent removed and the product purified by distillation and medium-pressure chromatography (silica, light petroleum) to give E-1-phenylprop-1-ene (43%, b.p. 63-65°/7 mm, lit. b.p. 176-177°/760 mm¹³⁷).

5.3.2 1,1-Diphenylprop-1-ene was similarly prepared using ethyl bromide (109 g, 1.0 mol), magnesium turnings (24.0 g, 1.0 mol) and benzophenone (182 g, 1.0 mol) with phosphorous pentoxide (20 g, 0.14 mol) being used to dehydrate the alcohol. The product was purified by chromatography (alumina, light petroleum) giving 1,1-diphenylprop-1-ene (49%, m.p. 45-48°, lit. m.p. 52°¹³⁸).

5.3.3 (m-Trifluoromethyl)-1,1-diphenylethene was similarly prepared using (m-trifluoromethyl)-1-bromobenzene (22.5 g, 0.10 mol), magnesium turnings (2.4 g, 0.10 mol) and acetophenone (10.8 g, 0.09 mol) with phosphorous pentoxide (20.0 g, 0.14 mol) being used to dehydrate the alcohol. The product was purified by medium-pressure chromatography (silica, light petroleum) giving (m-trifluoromethyl)-1,1-diphenylethane (82%, b.p. 135°/16 mm, lit. b.p. 82°/1 mm¹³⁹).

5.3.4 2-Methyl-1-phenylprop-1-ene was similarly prepared using 2-bromopropane (123 g, 1.0 mol), magnesium turnings (24.0 g, 1.0 mol) and benzaldehyde (106 g, 1.0 mol) with phosphorous pentoxide (20.0 g, 0.14 mol) being used to dehydrate the alcohol. The product was purified by distillation giving 2-methyl-1-phenylprop-1-ene (b.p. 70°/10 mm, lit. b.p. 180-182°/760 mm¹⁴⁰) and some of the isomeric 2-benzylprop-1-ene in the ratio 4:1. The latter was removed by medium-pressure chromatography (10% AgNO₃ on alumina, light petroleum) to give the required product (64%). ¹H n.m.r. δ_H 7.35-7.05 (5H, m, ArH), 6.24 (1H, m, =CH), 1.85 (3H, d, $\underline{J}$ 1.0Hz, =CCH₃), 1.82 (3H, d, $\underline{J}$ 0.6Hz, =CCH₃).

5.3.5 2-Methyl-3-phenylbut-2-ene and 3-methyl-2-phenylbut-1-ene were prepared by the dehydration of 3-methyl-2-phenylbutan-2-ol,¹⁴¹ which was prepared by a Grignard reaction using 2-bromopropane (61.5 g, 0.50 mol), magnesium turnings (12.0 g, 0.50 mol) and acetophenone (56.0 g, 0.40 mol) as described above (section 5.3.1). The resulting 3-methyl-2-phenylbutan-2-ol was dehydrated by heating it with phosphoric acid (88%, 200 ml) at 40 mm and the distillate collected up to 62°. The product was extracted with light petroleum (3x100 ml), the combined extracts dried and the solvent was removed. The products were purified by distillation and separated by medium-pressure chromatography (10% AgNO₃ on alumina, light petrol-50% ether in light petroleum) giving 2-methyl-3-phenylbut-2-ene (24%, b.p. 178-180°/760 mm, lit. b.p. 187-188°/760 mm¹⁴²), ¹H n.m.r. δ_H 7.5-6.9 (5H, m, ArH), 1.95 (3H, q, $\underline{J}$ 1.0Hz, CH₃) 1.85 (3H, s, CH₃), 1.60 (3H, q, $\underline{J}$ 1.0Hz, CH₃) and 3-methyl-2-phenylbut-

1-ene (20%, b.p. 178-180°/760 mm, lit. b.p. 82°/12 mm¹⁴³),
¹H n.m.r. δ_H 7.44-7.25 (5H, m, ArH), 5.19 (1H, t, J 0.6Hz, =CH), 5.08 (1H, t, J 1.3Hz, =CH) 2.89 (1H, septet, J 6.7Hz, CH(CH₃)₂), 1.15 (6H, d, J 6.7Hz, CH(CH₃)₂).

5.3.6 2-Phenylbut-1-ene was prepared by the modified Wittig reaction described by Sadler.¹⁴⁴ Methyltriphenylphosphonium iodide (40.4 g, 0.10 mol), potassium t-butoxide (37.2 g, 0.20 mol) and propiophenone (13.4 g, 0.10 mol) in dry hexane (700 ml) were shaken violently for 6h. The mixture was then poured onto water (1000 ml), the organic layer removed, the aqueous layer extracted with hexane (3x300 ml) and the solvent was removed. The product was then purified by continuous steam extraction and chromatography (alumina, light petroleum) to give 2-phenylbut-1-ene (65% b.p. 58°/16 mm, lit. b.p. 81-82°/20 mm¹⁴⁵).

5.3.7 1-Cyclohexyl-1-phenylethene was similarly prepared using phenyl cyclohexyl ketone (18.8 g, 0.10 mol), methyltriphenylphosphonium iodide (48.5 g, 0.12 mol) and potassium t-butoxide (37.2 g, 0.20 mol) in hexane (2.0 l) and the mixture was shaken for 1 week. The product was purified by continuous steam extraction to give 1-cyclohexyl-1-phenylethene (64%, b.p. 98°/17 mm, lit. b.p. 110°/15 mm¹⁴⁶).

5.3.8 p-Chloro-1,1-diphenylethene was similarly prepared using p-chlorobenzophenone (43.3 g, 0.20 mol), methyltriphenylphosphonium iodide (97.0 g, 0.24 mol) and potassium t-butoxide (44.8 g, 0.40 mol) in ether (1.8 l) and the mixture was shaken

for 18h. The product was purified by distillation and medium-pressure chromatography (silica, light petroleum) to give *p*-chloro-1,1-diphenylethene (80%, b.p. 166°/12 mm, lit. b.p. 164°/16 mm¹⁴⁷).

5.3.9 1-Methyleneindane was similarly prepared using indan-1-one (13.2 g, 0.10 mol) methyltriphenylphosphonium iodide (48.5 g, 0.12 mol) and potassium *t*-butoxide (22.4 g, 0.20 mol) in ether (1.50 l) and the mixture was shaken for 18h. The product was purified by continuous steam extraction giving 1-methyleneindane (79% b.p. 98°/17 mm, lit. b.p. 38-39°/0.05 mm¹⁴⁸).

5.3.10 1-Methylenetetralin was similarly prepared using α -tetralone (14.6 g, 0.10 mol), methyltriphenylphosphonium iodide (40.4 g, 0.10 mol) and potassium *t*-butoxide (13.4 g, 0.12 mol) in hexane (700 ml) and the mixture was shaken for 18h. The product was purified by continuous steam extraction and medium-pressure chromatography (silica, light petroleum) to give 1-methylenetetralin (69% b.p. 116°/16 mm, lit. b.p. 103°/14 mm¹⁴⁹).

5.3.11 Z-1-Phenylprop-1-ene was prepared by hydrogenation of 1-phenylprop-1-yne over Lindlar's catalyst.¹⁵⁰ A solution of 1-phenylprop-1-yne (23.2 g, 0.20 mol) in cyclohexane (50 ml) over Lindlar's catalyst (1.5 g) poisoned with quinoline (3 ml)¹⁵¹ was hydrogenated at slightly above atmospheric pressure at 20°. When the uptake of hydrogen had ceased the catalyst was filtered off, washed with cyclohexane and the solvent was

removed from the filtrate. The product was purified by distillation to give Z-1-phenylprop-1-ene (77% b.p. 62-68°/14 mm, lit. b.p. 69-69.5°/28 mm¹⁵¹).

5.3.12 Z-2-Phenylbut-2-ene was prepared by the method described by Sato¹⁵² from 1-phenyl-1-propenylmagnesium bromide and methyl iodide. Isobutylmagnesium bromide was prepared by the dropwise addition of isobutyl bromide (32.9 g, 0.24 mol) in dry ether (50 ml) to magnesium turnings (5.76 g, 0.24 mol) in ether (150 ml) under nitrogen, using iodine to initiate the reaction. When the addition had subsided, the mixture was heated under reflux for 1.0h, cooled to room temperature and then the catalyst, bis(cyclopentadienyl)titanium dichloride (1.49 g, 6 mmol), was added. 1-Phenylprop-1-ene (23.2 g, 0.2 mol) in ether (50 ml) was added dropwise to the stirred mixture which was then stirred for a further 1h. Tetrahydrofuran (150 ml) was added and the ether was distilled off at atmospheric pressure. Methyl iodide (56.8 g, 0.40 mol) in tetrahydrofuran (50 ml) was added dropwise to the stirred mixture, producing a smooth exothermic reaction. The mixture was then heated under reflux for 4h before being poured onto water (400 ml). The organic layer was removed, the aqueous layer extracted with ether (3x200 ml), the combined extracts dried and the solvent was removed. The resulting mixture was shown by g.l.c. (10% P.E.G.A.) and ¹H n.m.r. to contain Z-2-phenylbut-2-ene (80%) and 2-methyl-1-phenylprop-1-ene (20%). Distillation, followed by medium-pressure chromatography (10% AgNO₃ on alumina, light petroleum) gave Z-2-phenylbut-2-ene (33% b.p. 79-85°/14 mm, lit. b.p. 193°/760 mm¹⁵²), δ_{H} 7.4-7.2 (5H, m, Ar-H), 5.52 (1H, q, q, J 6.9, 1.5Hz =CH), 2.02 (3H,

d,q, J 1.5, 1.5Hz, 1-CH₃), 1.59 (3H, d,q, J 6.9, 1.5Hz, 4-CH₃).

5.4 Preparation of Dimethylvinylidenecyclopropanes

General Method: All the dimethylvinylidenecyclopropanes were prepared by the addition of dimethylvinylidene carbene, generated from 1-bromo-3-methylbuta-1,2-diene, to the appropriate olefin under phase transfer catalysis conditions.¹¹⁶ The olefin (1.0 molar equivalents), 1-bromo-3-methylbuta-1,2-diene (1.67 molar equivalents) plus aqueous potassium hydroxide (50% w/w, 75 molar equivalents) and benzyltri-n-butylammonium bromide (0.1 molar equivalents) were vigorously stirred, with heating, until all the olefin had reacted. The mixture was then diluted with water, the organic layer removed and the aqueous layer extracted with light petroleum. The extracts and organic layer were combined, dried and the solvent was removed. Excess 1-bromo-3-methylbuta-1,2-diene was removed by distillation and the product was purified by bulb to bulb distillation and, where required, chromatography (alumina, light petroleum).

The products were characterised by ¹H n.m.r. and i.r. spectroscopy and were stored at 4°C. ¹³C n.m.r. data is recorded in appendix I. Other details for each dimethylvinylidenecyclopropane prepared are given below.

5.4.1 2-Dimethylvinylidene-1-phenylcyclopropane (82) (77% b.p. 100°/0.25 mm, lit. b.p. 78°/0.5 mm¹¹⁹).

Olefin: phenylethylene, Conditions: 10h at 70°.

The product was identified by comparison of its ¹H n.m.r.

and i.r. spectra with those published.¹¹⁹

5.4.2 2-Dimethylvinylidene-1-methyl-1-phenylcyclopropane

(89) (66% b.p. 70°/0.2 mm, lit. b.p. 68°/0.4 mm¹²³).

Olefin: 1-methyl-1-phenylethylene. Conditions: 2.5h at 50°.

The product was identified by comparison of its ¹H n.m.r. and i.r. spectra with those published.¹²³

5.4.3 2-Dimethylvinylidene-1-ethyl-1-phenylcyclopropane

(169) (58% b.p. 100°/0.1 mm).

Olefin: 2-phenylbut-2-ene. Conditions: 2h at 70°.

¹H n.m.r. δ_H 7.40-7.10 (5H, m, Ar-H), 2.11 (1H, dq, J 13.8 and 7.3Hz, CH-CH₃[prochiral]), 1.88 (3H, s, =C-CH₃) 1.87 (3H, s, =CCH₃), 1.76 (1H, d, J 6.6Hz, cyclopropyl H), 1.73 (1H, dq, J 13.8 and 7.3Hz, CH-CH₃[prochiral]), 1.66 (1H, d, J 6.6Hz, cyclopropyl H), 0.95 (3H, t, J 7.3Hz, CH₂-CH₃).

I.r. $\nu_{\max}$ 2025 cm⁻¹ (C=C=C).

M.s. (m/z) 198.14058 (M⁺, C₁₅H₁₈ requires 198.14084), 169 (M⁺ - C₂H₅).

5.4.4 2-Dimethylvinylidene-1-isopropyl-1-phenylcyclopropane

(170) (37% b.p. 110°/0.7 mm).

Olefin: 3-methyl-2-phenylbut-1-ene. Conditions: 4h at 70°.

¹H n.m.r. δ_H 7.50-7.06 (5H, m, ArH), 1.88 (1H, septet, J 6.8Hz, CH(CH₃)₂), 1.87, 1.82 (6H, s,s, =C(CH₃)₂), 1.75 (1H, d, J 6.6Hz, cyclopropyl H), 1.63 (1H, d, J 6.6Hz, cyclopropyl H), 0.94 (6H, d, J 6.8Hz, CH(CH₃)₂).

I.r. $\nu_{\max}$ 2025 cm⁻¹ (C=C=C).

M.s. (m/z) 212.154889 (M⁺, C₁₆H₂₀ requires 212.156493), 169 (M⁺ - C₃H₇).

5.4.5 1-Cyclohexyl-2-dimethylvinylidene-1-phenylcyclopropane (171) (31% b.p. 65-70°/0.05 mm).

Olefin: 1-cyclohexyl-1-phenylethene. Conditions: 10h at 50°.

^1H n.m.r. δ_{H} 7.40-7.20 (5H, m, ArH), 1.88, 1.83 (6H, s, s, =C(CH₃)₂), 1.75, 1.66 (2H, AB pattern, $\underline{J}$ 6.6Hz, cyclopropyl H) 2.64-1.76 (11H, m, cyclohexyl H's).

I.r. ν_{max} 2020 cm^{-1} (C=C=C).

M.s. (m/z) 252.185785 (M^+ , $\text{C}_{19}\text{H}_{24}$ requires 252.187792), 169 ($\text{M}^+ - \text{C}_6\text{H}_{11}$).

5.4.6 E-2-Dimethylvinylidene-3-methyl-1-phenylcyclopropane

(93) (43% b.p. 90°/0.03 mm, lit. b.p. 74°/0.3 mm¹²³).

Olefin: E-1-phenylprop-1-ene. Conditions: 1.25h at 70°.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

5.4.7 Z-2-Dimethylvinylidene-3-methyl-1-phenylcyclopropane

(92) (41% b.p. 85-95°/0.01 mm, lit. b.p. 72°/0.3 mm¹²³).

Olefin: Z-1-phenylprop-1-ene. Conditions: 3h at 70°.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

5.4.8 E-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane

(172) (53% b.p. 125°/0.07 mm, lit. b.p. 68-68.5°/0.01 mm¹²⁹).

Olefin: E-2-phenylbut-2-ene. Conditions: 1.5h at 75°.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²⁹

5.4.9 Z-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (173) (33% b.p. 90-110°/0.01 mm).

Olefin: Z-2-phenylbut-2-ene. Conditions: 7h at 70°.

¹H n.m.r. δ_H 7.31-7.22 (5H, m, ArH), 1.86, 1.83 (6H, s, s, =C(CH₃)₂), 1.58 (3H, s, 1-CH₃), 0.85 (3H, d, J 6.2Hz, 3-CH₃), 3-H masked by =C(CH₃)₂ signal.

I.r. $\nu_{\max}$ 2015 cm⁻¹ (C=C=C).

M.s. (m/z) 198.140251 (M⁺, C₁₅H₁₈ requires 198.140844), 183 (M⁺ - CH₃).

5.4.10 3,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (174) (30% b.p. 105°/0.7 mm, m.p. 35-40°, lit b.p. 65°/0.01 mm¹²⁹).

Olefin: 2-methyl-1-phenylprop-1-ene. Conditions: 3h at 70°.

The product was identified by comparison of its ¹H n.m.r. and i.r. spectra with those published.¹²⁹

5.4.11 2-Dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane (175) (31% b.p. 110°/0.25 mm).

Olefin: 3-methyl-2-phenylbut-2-ene. Conditions: 4h at 65°.

¹H n.m.r. δ_H 6.98-7.30 (5H, m, ArH), 1.83, 1.79 (6H, s, s, =C(CH₃)₂), 1.54 (3H, s, 1-CH₃), 1.38 (3H, s, 2-CH₃ E to Ph), 0.83 (3H, s, 2-CH₃ Z to Ph).

I.r. $\nu_{\max}$ 2005 cm⁻¹ (C=C=C).

M.s. (m/z) 212.154682 (M⁺, C₁₆H₂₀ requires 212.156493).

5.4.12 2-Dimethylvinylidene-1,1-diphenylcyclopropane (110) (53% b.p. 115-25°/0.001 mm, lit. b.p. 112°/0.01 mm¹²³).

Olefin: 1,1-diphenylethene. Conditions: 7h at 70°.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

5.4.13 2'-Dimethylvinylidenecyclopropane-1'-spiro-1-indane

(105) (80% b.p. $79^\circ/0.01$ mm, lit. b.p. $75^\circ/0.01$ mm¹²³).

Olefin: 1-methyleneindane. Conditions: 6h at 40° .

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

5.4.14 2'-Dimethylvinylidenecyclopropane-1'-spiro-1-tetralin

(106) (59% b.p. $100^\circ/0.1$ mm, lit. b.p. $79^\circ/0.01$ mm¹²³).

Olefin: 1-methylenetetralin. Conditions: 5.5h at 70° .

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

5.5 Preparation of Dimethylenecyclopropanes

General method: The following dimethylenecyclopropanes were prepared by pyrolysis of the corresponding dimethylvinylidenecyclopropanes. The starting materials (50 mg - 2.0 g) were passed through a hot (electrically heated) glass tube (lightly packed with glass wool), under high vacuum and the products were collected in a trap cooled by liquid nitrogen.

The products were characterised by ^1H n.m.r. and i.r. spectroscopy and were stored at 4° . ^{13}C n.m.r. data is recorded in appendix II. Other details for each dimethylenecyclopropane are given below.

5.5.1 2-Isopropylidene-3-methylene-1-phenylcyclopropane (164)

Starting material: 2-dimethylvinylidene-1-phenylcyclopropane (82).

Conditions: 350°, 0.004 mm. Yield: 98%.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

5.5.2 2-Isopropylidene-1-methyl-3-methylene-1-phenylcyclopropane (176).

Starting material: 2-dimethylvinylidene-1-methyl-1-phenylcyclopropane (89).

Conditions: 350°, 0.01 mm. Yield: 94%.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

5.5.3 1-Ethyl-2-isopropylidene-3-methylene-1-phenylcyclopropane (177).

Starting material: 2-dimethylvinylidene-1-ethyl-1-phenylcyclopropane (169).

Conditions: 350°, 0.001 mm. Yield: 95%.

^1H n.m.r. δ_{H} 7.50-7.00 (5H, m, Ar-H), 5.34, 5.23 (2H, s, s, 2x =CH), 1.94 (8H, s+m, =C(CH₃)₂ + CH₂CH₃ [prochiral]), 0.89 (3H, t, CH₂CH₃).

I.r. ν_{max} 1795, 1740 cm^{-1} (C=C).

M.s. (m/z) 198.13965 (M^+ , C₁₅H₁₈ requires 198.14084), 169. ($\text{M}^+ - \text{C}_2\text{H}_5$).

5.5.4 1-Isopropyl-2-isopropylidene-3-methylene-1-phenylcyclopropane (178).

Starting material: 2-dimethylvinylidene-1-isopropyl-1-phenylcyclopropane (170).

Conditions: 350°, 0.01 mm. Yield: 95%.

^1H n.m.r. δ_{H} 7.50-7.00 (5H, m, Ar-H), 5.36, 5.28 (2H, bs, bs, 2x =CH), 2.27 (1H, septet, J 6.7Hz, CH(Me)₂), 2.04 (3H, d, J 0.6Hz, =C CH₃), 1.94 (3H, d, J 0.5Hz, =CCH₃), 0.92 (3H, d, J 6.7Hz, CHCH₃), 0.89 (3H, d, J 6.7Hz, CHCH₃).

I.r. ν_{max} 1790, 1735 cm^{-1} (C=C).

M.s. (m/z) 212.15661 (M^+ , C₁₆H₂₀ requires 212.15649), 169 ($\text{M}^+ - \text{C}_3\text{H}_7$).

5.5.5 1-Cyclohexyl-2-isopropylidene-3-methylene-1-phenyl-cyclopropane (179).

Starting material: 1-cyclohexyl-2-dimethylvinylidene-1-phenylcyclopropane (171).

Conditions: 350°, 0.005 mm. Yield: 99%.

^1H n.m.r. δ_{H} 7.40-7.10 (5H, m, Ar-H), 5.38 (1H, s, =CH), 5.32 (1H, d, J 0.5Hz, =CH), 2.06 (3H, d, J 0.5Hz, =CCH₃), 1.95 (3H, d, J 0.5Hz, =CCH₃), 2.00-0.90 (11H, m, cyclohexyl H's).

I.r. ν_{max} 1790 cm^{-1} (C=C).

M.s. (m/z) 252.18846 (M^+ , C₁₉H₂₄ requires 252.18779), 169 ($\text{M}^+ - \text{C}_6\text{H}_{11}$).

5.5.6 syn and anti-3-Ethylidene-2-isopropylidene-1-phenyl-cyclopropane (180a and b)

Starting material: 2-2-dimethylvinylidene-3-methyl-1-phenylcyclopropane (92).

Conditions: 350°, 0.01 mm. Yield: 87%.

This produced a mixture of the syn and anti-isomers in

the ratio 1:1, which were identified by comparison of the ^1H n.m.r. spectrum of the mixture with the ^1H n.m.r. spectra published for each isomer.¹²³

5.5.7 syn and anti-3-Ethylidene-2-isopropylidene-1-methyl-1-phenylcyclopropane (181a and b).

Starting material: Z-1,3-dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (173).

Conditions: 300°, 0.01 mm. Yield: 75%.

This produced a mixture containing the syn and anti isomers in the ratio 1:1, which were identified by comparison of the ^1H n.m.r. spectrum of the mixture with that published.¹²⁹

5.5.8 2,3-Diisopropylidene-1-phenylcyclopropane (182).

Starting material: 3,3-dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (174).

Conditions: 350°, 0.01 mm. Yield: 97%.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²⁹

5.5.9 2,3-Diisopropylidene-1-methyl-1-phenylcyclopropane (183).

Starting material: 2-dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane (175).

Conditions: 350°, 0.01 mm. Yield: 73%.

^1H n.m.r. δ_{H} 7.60-7.05 (5H, m, ArH), 2.03 (6H, s, 2x =C(CH₃)), 1.86 (6H, s, 2x =C(CH₃)), 1.63 (3H, s, 1-CH₃).

I.r. ν_{max} 1715 cm^{-1} (C=C).

M.s. (m/z) 212.15597 (M^+ , $\text{C}_{16}\text{H}_{20}$ requires 212.15649).

5.5.10 1,1-Diphenyl-2-isopropylidene-3-methylenecyclopropane (184).

Starting material: 2-dimethylvinylidene-1,1-diphenylcyclopropane (110).

Conditions: 350°, 0.01 mm. Yield: 87%.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

5.5.11 2'-Isopropylidene-3'-methylenecyclopropane-1'-spiro-1-indane (189).

Starting material: 2'-dimethylvinylidenecyclopropane-1'-spiro-1-indane (105).

Conditions: 300°, 0.005 mm. Yield: 96%.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

5.5.12 2'-Isopropylidene-3'-methylenecyclopropane-1'-spiro-1-tetralin (190).

Starting material: 2'-dimethylvinylidenecyclopropane-1'-spiro-1-tetralin (106).

Conditions: 350°, 0.01 mm. Yield: 82%.

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.¹²³

The dimethylvinylidenecyclopropanes from 1,1-diphenylprop-1-ene, *p*-methoxy-1,1-diphenylethene, *p*-chloro-1,1-diphenylethene and *m*-(trifluoromethyl)-1,1-diphenylethene were allowed to undergo partial or complete thermal rearrangement to the corresponding dimethylenecyclopropanes either during preparation or distillation. The dimethylvinylidenecyclopropanes were

prepared by the phase transfer method described previously (p.131) and details of the synthesis of the dimethylenecyclopropanes are given below.

As before, the products were stored at 4° and the ^{13}C n.m.r. data are recorded in appendix II.

5.5.13 syn and anti-1,1-Diphenyl-3-ethylidene-2-isopropylidenecyclopropane (185a and b)

Olefin: 1,1-diphenylprop-1-ene. Conditions: 10h at 70°.

Under the reaction conditions the dimethylvinylidene-cyclopropane underwent complete thermal rearrangement to give a 0.8:1.0 mixture of syn and anti-1,1-diphenyl-3-ethylidene-2-isopropylidenecyclopropane which was purified by distillation (44% b.p. 128-135°/0.1 mm). No attempt was made to separate the mixture.

^1H n.m.r. (syn) δ_{H} 7.3-7.2
(5H, m, ArH), 5.75 (1H, q, J 6.0Hz, =CH), 2.09 (3H, s, =C(CH₃)), 2.02 (3H, d, J 6.0Hz, =CHCH₃), 2.01 (3H, s, =C(CH₃)).

^1H n.m.r. (anti) δ_{H} 7.3-7.2
(5H, m, ArH), 5.93 (1H, q, J 6.6Hz, =CHCH₃), 1.97 (3H, s, =C(CH₃)), 1.94 (3H, s, =C(CH₃)), 1.92 (3H, d, J 6.6Hz, =CHCH₃).

M.s. (mix) (m/z) 260.15424 (M^+ , $\text{C}_{20}\text{H}_{20}$ requires 260.15649).

5.5.14 p-Methoxy-1,1-diphenyl-2-isopropylidene-3-methylene-cyclopropane (186)

Olefin: p-methoxy-1,1-diphenylethene.

Conditions: 12h at 40°.

The adduct underwent complete thermal rearrangement to the dimethylenecyclopropane during distillation (44% b.p. 120-130°/0.005 mm).

^1H n.m.r. 7.31-7.20 (5H, m, ArH), 7.25, 6.84 (4H, AB pattern, J 8.9Hz, ArH) 5.48 (1H, d, J 0.5Hz, $=\text{CH}$), 5.38 (1H, d, J 0.5Hz, $=\text{CH}$), 3.79 (3H, s, OCH_3), 2.04 (6H, s, $=\text{C}(\text{CH}_3)_2$).

I.r. ν_{max} 1790 cm^{-1} (C=C).

M.s. (m/z) 276.149514 (M^+ , $\text{C}_{20}\text{H}_{20}\text{O}$ requires 276.151407), 261 ($\text{M}^+ - \text{CH}_3$), 246 ($\text{M}^+ - 2\times\text{CH}_3$), 245 ($\text{M}^+ - \text{OCH}_3$), 215.

5.5.15 p-Chloro-1,1-diphenyl-2-isopropylidene-3-methylene-cyclopropane (187)

Olefin: p-chloro-1,1-diphenylethene. Conditions 18h at 40°.

The adduct underwent complete thermal rearrangement to the dimethylenecyclopropane during distillation (51% b.p. 120-130°/0.1 mm).

^1H n.m.r. δ_{H} 7.35-7.25 (9H, m, ArH), 5.50 (1H, m, $=\text{CH}$), 5.40 (1H, m, $=\text{CH}$), 2.05, 2.04 (6H, s,s, $=\text{C}(\text{CH}_3)_2$).

I.r. ν_{max} 1790, 1740 cm^{-1} (C=C).

M.s. (m/z) 282.10038 (M^+ (^{37}Cl), $\text{C}_{19}\text{H}_{17}^{37}\text{Cl}$ requires 282.09892), 280.10080 (M^+ (^{35}Cl), $\text{C}_{19}\text{H}_{17}^{35}\text{Cl}$ requires 280.10187), 245 ($\text{M}^+ - \text{Cl}$), 215.

5.5.16 m-(Trifluoromethyl)-1,1-diphenyl-2-isopropylidene-3-methylenecyclopropane (188)

Olefin: m-(trifluoromethyl)-1,1-diphenylethene.

Conditions: 7h at 70°.

The adduct underwent partial rearrangement to the dimethylenecyclopropane during distillation (60%, b.p. 110°/0.02 mm). Total conversion to the dimethylenecyclopropane was obtained by passing a portion of the mixture through the flow system at 350° and 0.001 mm, giving the required product (55% overall yield).

^1H n.m.r. δ_{H} 7.62-7.25 (9H, m, ArH), 5.57 (1H, d, J 0.7Hz, =CH), 5.46 (1H, d, J 0.7Hz, =CH), 2.10 (3H, d, J 0.6H, =C(CH₃)), 2.09 (3H, d, J 0.6Hz, =C(CH₃)).

I.r. ν_{max} 1790, 1710 cm^{-1} (C=C).

M.s. (m/z) 314.12799 (M^+ , $\text{C}_{20}\text{H}_{17}\text{F}_3$ requires 314.12822), 299 ($\text{M}^+ - \text{CH}_3$), 215.

5.6 Reactions of Dimethylvinylidenecyclopropanes with Acid

Rearrangements with p-Toluenesulphonic Acid

The vinylidenecyclopropane (50 mg - 1.0 g) and a catalytic amount of p-toluenesulphonic acid (5-40 mg) in ethanol free carbon tetrachloride (5-100 ml) were heated under reflux until all the vinylidenecyclopropane had reacted. The mixture was then poured onto water (5-100 ml), the organic layer removed and the aqueous layer was extracted with ether (3x5-100 ml). The organic layer and extracts were combined, dried and the solvent was removed. At this stage, product recoveries were invariably greater than 90%. The reaction mixture was examined by ^1H n.m.r. (360MHz) spectroscopy before the products were

separated by chromatographic methods as described below in individual cases. Product ratios were calculated from the integrals of their alkene proton and other clear resonances in the ^1H n.m.r. spectrum of the reaction mixture before separation.

Details for individual reactions are given below.

Reactions with Ethanolic Hydrogen Chloride

A solution of the vinylidenecyclopropane (50-500 mg) in ethanolic hydrogen chloride (1M, 2.5-25 ml) was heated under reflux for 5-10 min. The solvent was removed and the reaction mixture was examined by ^1H n.m.r. (360MHz) spectroscopy before separation.

Details for individual reactions are given below.

5.6.1 Rearrangement of 2-Dimethylvinylidene-1-methyl-1-phenylcyclopropane (89)

2-Dimethylvinylidene-1-methyl-1-phenylcyclopropane (500 mg, 2.72 mmol) and *p*-toluenesulphonic acid (40 mg, 0.21 mmol) in carbon tetrachloride (100 ml) were heated under reflux for 30 h. This gave a mixture containing 2-phenyl-3,5,5-trimethylcyclopenta-1,3-diene (100) with ca.40% of unidentified minor products. The cyclopentadiene (100) was identified by comparison of its ^1H n.m.r. spectrum with that published.¹¹⁵

5.6.2 Rearrangement of 2-Dimethylvinylidene-1-ethyl-1-phenylcyclopropane (169)

2-Dimethylvinylidene-1-ethyl-1-phenylcyclopropane (489 mg,

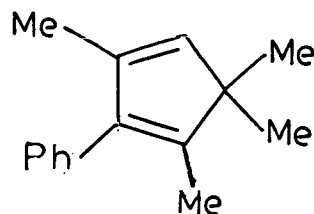
2.47 mmol) and *p*-toluenesulphonic acid (44 mg, 0.23 mmol) in carbon tetrachloride (25 ml) were heated under reflux for 21 h. This yielded a mixture containing 2-phenyl-1,3,5,5-tetramethylcyclopenta-1,3-diene (193), 3-ethyl-2-(2'-methylprop-1'-enyl)indene (194), 3-methylene-2-phenyl-1,4,4-trimethylcyclopent-1-ene (196) and 2-methyl-6-phenylocta-6-ene-3-yne (195) in the ratio 5:3:3:1 respectively, with only a small amount (ca.10%) of unidentified minor products. Separation of the reaction mixture by medium-pressure chromatography (silica, light petroleum) gave one fraction containing mainly the indene (194) and another containing mostly enyne (195) with several mixed fractions. Attempts to isolate components from each fraction by preparative g.l.c. (15% NPGS at 130-180°) were unsuccessful although ^1H n.m.r. signals from the cyclopentadiene (193) and the methylenecyclopentene (196) were observed in some preparative g.l.c. fractions.

The reaction of these products with maleic anhydride is described in section 5.9.

2-Phenyl-1,3,5,5-tetramethylcyclopenta-1,3-diene (193)

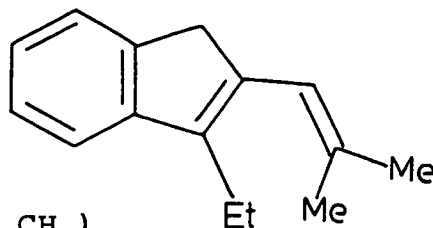
^1H n.m.r. δ_{H} 7.50-7.05

(5H, m, ArH), 5.94 (1H, q, $\underline{J}$ 1.6Hz, =CH), 1.80 (3H, d, $\underline{J}$ 1.6Hz, 3-CH $_3$), 1.74 (3H, s, 1-CH $_3$), 1.19, 1.09 (6H, s,s, C(CH $_3$) $_2$).

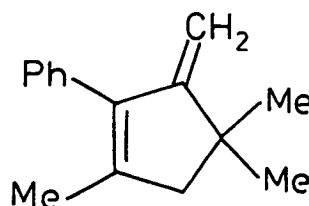


3-Ethyl-2-(2'-methylprop-1'-enyl)indene (194)

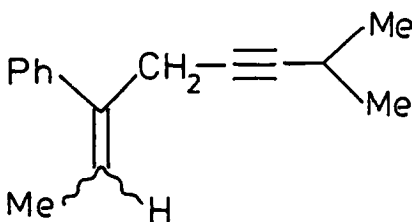
^1H n.m.r. δ_{H} 7.90-7.00
 (4H, m, ArH), 6.32 (1H, m, =CH),
 3.65 (2H, s, ArCH₂), 2.60 (2H, q,
 $\underline{J}$ 7.6Hz, CH₂CH₃), 1.93, 1.92 (6H,
 s, s, =C(CH₃)₂), 1.15 (3H, t, $\underline{J}$ 7.6Hz, CH₂CH₃).

3-Methylene-2-phenyl-1,4,4-trimethylcyclopent-1-ene (196)

^1H n.m.r. δ_{H} 7.50-7.05 (5H,
 m, ArH), 4.59, 4.55 (2H, s, s,
 =CH₂), 1.77 (2H, s, CH₂), 1.19
 (6H, s, C(CH₃)₂), 1.14 (3H, s, =CCH₃).

2-Methyl-6-phenylocta-6-ene-3-yne (195)

^1H n.m.r. δ_{H} 7.46-7.02
 (5H, m, ArH), 5.90 (1H, q,
 t, $\underline{J}$ 6.9, 0.7Hz, =CH), 3.29
 (2H, m, CH₂), 2.47 (1H, m, CH(CH₃)₂), 1.86 (3H, d, $\underline{J}$ 6.9Hz,
 =CHCH₃), 1.08 (6H, d, $\underline{J}$ 6.7Hz, CH(CH₃)₂).



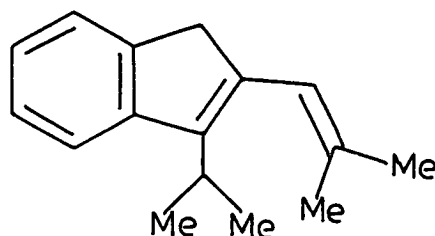
5.6.3 Reactions of 2-Dimethylvinylidene-1-isopropyl-1-phenylcyclopropane (170)

2-Dimethylvinylidene-1-isopropyl-1-phenylcyclopropane
 (494 mg, 2.33 mmol) and p-toluenesulphonic acid (43 mg, 0.23
 mmol) in carbon tetrachloride (25 ml) were heated under reflux
 for 24 h. This gave a complex mixture from which only
 starting material and 3-isopropyl-2-(2'-methylprop-1'-enyl)-

indene (203) were identified although other products were formed. Attempts to separate the mixture by medium-pressure chromatography (silica, light-petroleum) and preparative g.l.c. (15% N.P.G.S. at 150°) resulted in isolation of only the indene (203).

3-Isopropyl-2-(2'-methylprop-1'-enyl)indene (203)

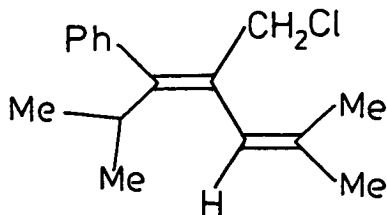
^1H n.m.r. δ_{H} 7.54-7.08 (4H, m, ArH), 6.26 (1H, m, =CH), 3.54 (2H, bs, CH₂), 3.23 (1H, septet, J 7.0Hz, CH(CH₃)₂), 1.89 (6H, bs, =C(CH₃)₂), 1.35 (6H, d, J 7.0Hz, CH(CH₃)₂).



2-Dimethylvinylidene-1-isopropyl-1-phenylcyclopropane (53 mg, 0.25 mmol) in ethanolic hydrogen chloride (2.5 ml) was heated under reflux for 7 min. This gave a mixture containing Z and E-4-chloromethyl-2,6-dimethyl-5-phenylhepta-2,4-diene (205z and e) in the ratio 4.5:1 respectively with a small amount (ca.20%) of minor products. No attempt was made to separate the mixture.

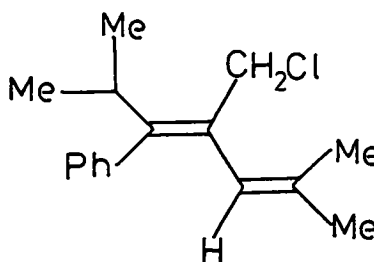
Z-4-Chloromethyl-2,6-dimethyl-5-phenylhepta-2,4-diene (205z)

^1H n.m.r. δ_{H} 7.0-7.8 (5H, m, ArH), 5.78 (1H, m, =CH), 3.75 (2H, s, CH₂Cl), 3.00 (1H, septet, J 6.9Hz, CH(CH₃)₂), 1.87 (3H, d, J 1.5Hz, =CCH₃), 1.73 (3H, d, J 1.3Hz, =CCH₃), 0.87 (6H, d, J 6.9Hz, CH(CH₃)₂).



E-4-Chloromethyl-2,6-dimethyl-5-phenylhepta-2,4-diene
(205e)

^1H n.m.r. δ_{H} 7.0-7.8 (5H, m, ArH), 5.41 (1H, m, =CH), 4.32 (2H, s, CH_2Cl), 3.55 (1H, septet, J 6.9Hz, $\text{CH}(\text{CH}_3)_2$), 1.82 (3H, d, J 1.3Hz, =CCH $_3$), 1.63 (3H, d, J 0.8Hz, =CCH $_3$), 0.87 (6H, d, J 6.9Hz, $\text{CH}(\text{CH}_3)_2$).



^{13}C n.m.r. - a DEPT pulse sequence experiment on the reaction mixture, set up to show CH_2 signals negative, gave a resonance at 47.4 p.p.m., indicating the presence of a CH_2Cl group.

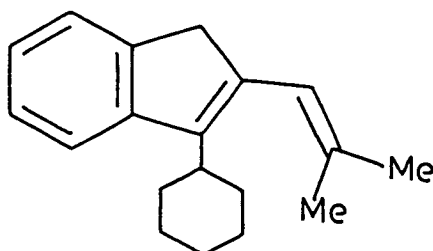
M.s. (reaction mixture) (m/z) 250, 248 (M^+), 184 ($\text{M}^+ - \text{HCl}$).

5.6.4 Rearrangement of 1-Cyclohexyl-2-dimethylvinylidene-1-phenylcyclopropane (171)

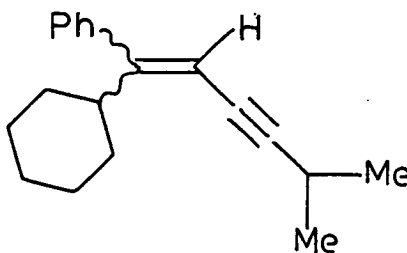
1-Cyclohexyl-2-dimethylvinylidene-1-phenylcyclopropane (180 mg, 0.72 mmol) and p-toluenesulphonic acid (23 mg, 0.12 mmol) in carbon tetrachloride (25 ml) were heated under reflux for 24 h. This gave a mixture containing 3-cyclohexyl-2-(2'-methylprop-1'-enyl)indene (206), 1-cyclohexyl-5-methyl-1-phenylhex-1-ene-3-yne (208) and 1-(cyclohex-1'-enyl)-2,4-dimethyl-1-phenylpenta-1,3-diene (207) in the ratio of 10: 0.9: 1.1 respectively, with only a small amount (ca.15%) of unidentified minor products. The compounds were separated by preparative t.l.c. (silica, light petroleum).

3-Cyclohexyl-2-(2'-methylprop-1'-enyl)indene (206)

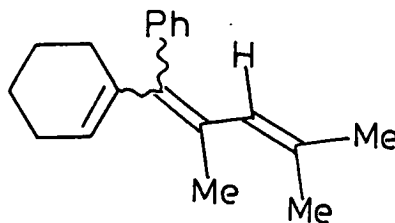
^1H n.m.r. δ_{H} 7.56-7.11 (4H, m, ArH), 6.27 (1H, m, =CH), 3.54 (2H, s, ArCH₂), 2.83 (1H, t, t, $\underline{J}$ 12.5, 3.2Hz, 1''-H), 1.93 (3H, d, $\underline{J}$ 1.0Hz, =C(CH₃)), 1.89 (3H, d, $\underline{J}$ 1.7Hz, =C(CH₃)), 2.15-0.90 (10H, m, cyclohexyl H's).

1-Cyclohexyl-5-methyl-1-phenylhex-1-ene-3-yne (208)

^1H n.m.r. δ_{H} 7.38-7.10 (5H, m, ArH), 5.43 (1H, d, $\underline{J}$ 2.0Hz, 2-H), 2.90 (1H, t, t, $\underline{J}$ 12.2, 3.3Hz, 1'-H), 2.77 (1H, septet, d, $\underline{J}$ 6.9, 2.0Hz, 5-H), 1.25 (6H, d, $\underline{J}$ 6.9Hz, CH(CH₃)₂), 2.11-0.68 (10H, m, cyclohexyl H's).

1-(Cyclohex-1'-enyl)-2,4-dimethyl-1-phenylpenta-1,3-diene (207)

^1H n.m.r. δ_{H} 7.55-6.80 (5H, m, ArH), 5.62 (2H, m, 2x=CH), 1.87 (3H, d, $\underline{J}$ 0.7Hz, 4-CH₃), 1.27 (3H, d, $\underline{J}$ 1.0, 2-CH₃), 1.26 (3H, d, $\underline{J}$ 1.2Hz, 2-CH₃), 2.25-0.50 (8H, m, cyclohexyl H's).

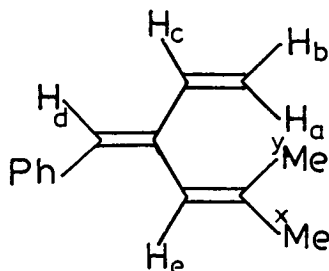
5.6.5 Reactions of E and Z-2-Dimethylvinylidene-3-methyl-1-phenylcyclopropane (93) and (92)

Z-2-Dimethylvinylidene-3-methyl-1-phenylcyclopropane (406 mg, 2.21 mmol) and p-toluenesulphonic acid (21 mg, 0.11

mmol) in carbon tetrachloride (25 ml) were heated under reflux for 6 days. This gave Z-3-benzylidene-5-methylhexa-1,4-diene (214) with only a small amount (ca.5%) of unidentified minor products. The triene was purified by medium-pressure chromatography (silica, light petroleum).

Z-3-Benzylidene-5-methylhexa-1,4-diene (214)

^1H n.m.r. δ_{H} 7.50-7.16 (5H, m, ArH), 6.50 (1H, d,d,d, $\underline{J}$ 17.1, 10.3, 0.7Hz, $\underline{H}_{\text{C}}$), 6.47 (1H, m, $\underline{H}_{\text{d}}$), 5.84 (1H, m, $\underline{H}_{\text{e}}$), 5.26 (1H, d,d, $\underline{J}$ 17.1, 1.4Hz, $\underline{H}_{\text{a}}$), 5.13 (1H, d,d, $\underline{J}$ 10.3, 1.4Hz, $\underline{H}_{\text{b}}$), 1.89 (3H, d, $\underline{J}$ 1.3Hz, x- $\underline{\text{CH}}_3$), 1.45 (3H, d, $\underline{J}$ 1.0 Hz, y- $\underline{\text{CH}}_3$).



M.s. (m/z) 184.12505 (M^+ , $\text{C}_{14}\text{H}_{16}$ requires 184.12519), 169, 105.

E-2-Dimethylvinylidene-3-methyl-1-phenylcyclopropane (495 mg, 2.69 mmol) and p-toluenesulphonic acid (50 mg, 0.26 mmol) in carbon tetrachloride (25 ml) were heated under reflux for 24 h. This gave a mixture containing the triene (214), the thermolysis product, syn-3-ethylidene-2-isopropylidene-1-phenylcyclopropane (180a) and starting material in the ratio 1:1.8:0.8, with only a small amount (ca.10%) of unidentified minor products.

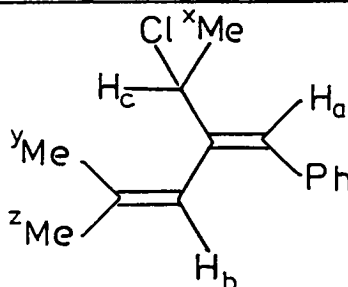
syn-3-Ethylidene-2-isopropylidene-1-phenylcyclopropane (180a) was identified by comparison of its ^1H n.m.r. spectrum with that published.¹²³

E-2-Dimethylvinylidene-3-methyl-1-phenylcyclopropane

(500 mg, 2.72 mmol) in ethanolic hydrogen chloride (25 ml) was heated under reflux for 7 min. This gave a mixture containing the triene (214) and the addition product, E-4-benzylidene-5-chloro-2-methylhex-2-ene (218) in the ratio 1:3.5, with only a small amount (ca.10%) of unidentified minor products. Attempts to separate the products by preparative g.l.c. at 130° resulted in the thermolysis of the addition product (218) to give an unidentified product.

E-4-Benzylidene-5-chloro-2-methylhex-2-ene (218)

^1H n.m.r. δ_{H} 7.52-7.00 (5H, m, ArH), 6.55 (1H, s, H_a), 5.90 (1H, m, H_b), 4.74 (1H, q, J 6.7Hz, H_c), 1.81 (3H, d, J 1.5Hz, z-CH₃), 1.65 (3H, d, J 6.7Hz, x-CH₃), 1.32 (3H, d, J 1.3Hz, y-CH₃).



^{13}C n.m.r. - A DEPT pulse sequence experiment on the reaction mixture, set up to show CH signals only, gave a resonance at 64.0 p.p.m., indicating the presence of a CHCl group.

M.s. (reaction mixture) (m/z) 222, 220 (M^+), 184 ($\text{M}^+ - \text{HCl}$).

Z-2-Dimethylvinylidene-3-methyl-1-phenylcyclopropane (510 mg, 2.77 mmol) in ethanolic hydrochloric acid (25 ml), was heated under reflux for 5 min. This gave a mixture containing the triene (214) and the addition product (218) in the ratio 1:2.3, with only a small amount (ca.10%) of unidentified minor products.

5.6.6 Reactions of E and Z-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (172) and (173)

E-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (1.00 g, 5.13 mmol) and *p*-toluenesulphonic acid (20 mg, 0.11 mmol) in carbon tetrachloride (25 ml) were heated under reflux for 3h. This gave a complex mixture containing E-3-ethylidene-5-methyl-2-phenylhexa-1,4-diene (219), E-2-methyl-5-phenyl-4-vinylhexa-2,4-diene (220), Z-2-methyl-5-phenyl-4-vinylhexa-2,4-diene (221), 2,5-dimethyl-6-phenylhepta-6-ene-3-yne (223), 1,3-dimethyl-2-(2'-methylprop-1'-enyl)indene (222) and the thermolysis product syn-3-ethylidene-2-isopropylidene-1-methyl-1-phenylcyclopropane (181a) in the ratio 6:5:1:4:3:2.5 with only a small amount (ca.10%) of unidentified minor products.

Chromatography (alumina, light-petroleum) gave three major fractions. The first fraction contained the three trienes (219), (220) and (221) and the thermolysis product (181a). The second fraction contained the enyne (223) and the indene (222) in the ratio of 1:1 and the third fraction contained the same isomers in the ratio of 3:1 respectively. The isomers in the first fraction were further separated by preparative g.l.c. (15% NPGS, 100°) to give a fraction containing the triene (221) and an unidentified minor product, a second fraction containing the trienes (219) and (220) in the ratio of 1:1 and a third fraction containing the thermolysis product (181a). The above separations allowed the products to be identified by their ¹H n.m.r. spectra (360MHz), as described in section 3.3.

E-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (49 mg, 0.25 mmol) and *p*-toluenesulphonic acid (5 mg, 0.026

mmol) in carbon tetrachloride (2.5 ml) were heated under reflux for 25 h. This gave a mixture containing the trienes (219) and (220), the enyne (223) and the thermolysis product (181a) in the ratio 4:2:2:7 with small amounts of 1,2-benzo-4-ethyl-3,6,6-trimethylfulvene (224) and E-4-ethyl-2-methyl-5-phenyl-3-(p-toluenesulphonyloxy)hexa-2,4-diene (225) (see section 5.7.7) and only a small amount (ca.15%) of unidentified minor products.

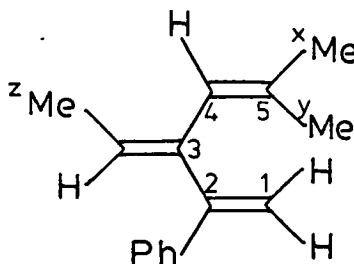
Z-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (497 mg, 2.51 mmol) and p-toluenesulphonic acid (38 mg, 0.20 mmol) in carbon tetrachloride (25 ml) were heated under reflux for 48 h. This gave a mixture containing the trienes (219), (220) and (221), enyne (223) and the thermolysis product (181a) in the ratio 2.5:1.0:0.5:0.8:3.0 with only a small amount (ca. 10%) of unidentified minor products. The signals from the indene (222) were absent from the ¹H n.m.r. spectrum of the reaction mixture.

Z-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (103 mg, 0.52 mmol) and p-toluenesulphonic acid (9 mg, 0.05 mmol) in carbon tetrachloride (5 ml) were heated under reflux for 40 h. This gave a mixture containing the trienes (219) and (220), the indene (222) and the enyne (223) in the ratio 2:2:7:4 with small amounts of the benzofulvene (224) and the ester (225) and only a small amount (ca.15%) of unidentified minor products.

Z-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (218 mg, 1.10 mmol) and p-toluenesulphonic acid (40 mg, 0.21 mmol) in carbon tetrachloride (10 ml) were heated under reflux for 15 h. This gave a mixture containing the indene (222) and the enyne (223) in the ratio 10:6 with small amounts of trienes (219) and (220) and only a small amount (ca.15%) of unidentified minor products.

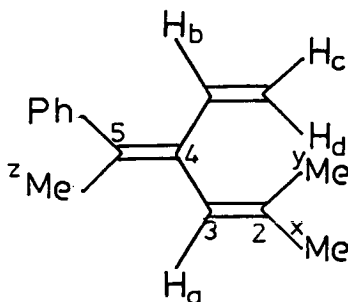
E-3-Ethylidene-5-methyl-2-phenylhexa-1,4-diene (219)

^1H n.m.r. δ_{H} 7.32-7.14 (5H, m, ArH), 5.70 (1H, m, 4-H), 5.44 (1H, q,d, $\underline{J}$ 7.0, 0.4Hz, =CH CH₃), 5.12 (1H, d, $\underline{J}$ 2.0Hz, 1-H), 5.00 (1H, d, $\underline{J}$ 2.0Hz, 1-H), 1.79 (3H, d, $\underline{J}$ 1.4Hz, x-CH₃), 1.59 (3H, d,d, $\underline{J}$ 7.0, 1.0Hz, z-CH₃), 1.53 (3H, d, $\underline{J}$ 1.1Hz, y-CH₃).



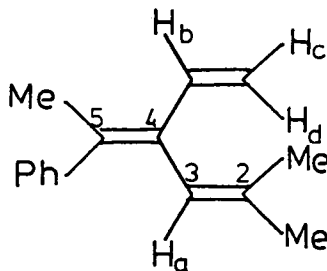
E-2-Methyl-5-phenyl-4-vinylhexa-2,4-diene (220)

^1H n.m.r. δ_{H} 7.32-7.14 (5H, m, ArH), 6.31 (1H, d,d, $\underline{J}$ 17.3, 10.5Hz, H_b), 5.70 (1H, m, H_a), 5.02 (1H, d,d, $\underline{J}$ 17.3, 2.1Hz, H_d), 4.82 (1H, d,d, $\underline{J}$ 10.5, 2.1Hz, H_c), 1.97 (3H, d, $\underline{J}$ 0.4Hz, z-CH₃), 1.85 (3H, d, $\underline{J}$ 1.4Hz, x-CH₃), 1.56 (3H, d, $\underline{J}$ 1.0Hz, y-CH₃).

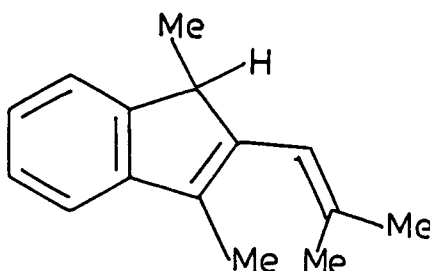


Z-2-Methyl-5-phenyl-4-vinylhexa-2,4-diene (221)

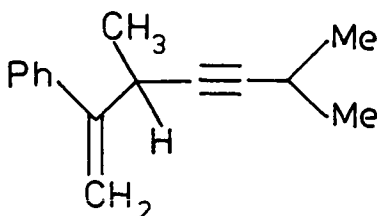
^1H n.m.r. δ_{H} 7.40-7.05 (5H, m, ArH), 6.85 (1H, d, d, $\underline{J}$ 17.5, 10.0Hz, $\underline{H}_{\text{b}}$), 5.90 (1H, m, $\underline{H}_{\text{a}}$), 5.22 (1H, d, d, $\underline{J}$ 17.5, 2.0Hz, $\underline{H}_{\text{d}}$), 5.13 (1H, d, d, $\underline{J}$ 10.0, 2.0Hz, $\underline{H}_{\text{c}}$), 2.17 (3H, d, $\underline{J}$ 1.2Hz, =CCH $\underline{\text{H}}_3$), 1.80 (3H, d, $\underline{J}$ 1.4Hz, =CCH $\underline{\text{H}}_3$), 1.73 (3H, s, 5-CH $\underline{\text{H}}_3$).

1,3-Dimethyl-2-(2'-methylprop-1'-enyl)indene (222)

^1H n.m.r. δ_{H} 7.40-7.16 (4H, m, ArH), 5.97 (1H, m, 1'-H), 3.47 (1H, q, $\underline{J}$ 7.1Hz, 1-H), 2.00 (3H, bs, 3-CH $\underline{\text{H}}_3$), 1.92 (3H, d, $\underline{J}$ 0.9Hz, 2'-CH $\underline{\text{H}}_3$), 1.74 (3H, d, $\underline{J}$ 0.9Hz, 2'-CH $\underline{\text{H}}_3$), 1.24 (3H, d, $\underline{J}$ 7.1Hz, 1-CH $\underline{\text{H}}_3$).

2,5-Dimethyl-6-phenylhepta-6-ene-3-yne (223)

^1H n.m.r. δ_{H} 7.40-7.16 (5H, m, ArH), 5.49 (1H, t, $\underline{J}$ 1.3Hz, 7-H), 5.26 (1H, t, $\underline{J}$ 0.6Hz, 7-H), 3.65 (1H, bq, $\underline{J}$ 7.1Hz, 5-H), 2.59 (1H, septet, d, $\underline{J}$ 6.8, 2.0Hz, 2-H), 1.24 (3H, d, $\underline{J}$ 7.1Hz, 5-CH $\underline{\text{H}}_3$), 1.17 (6H, d, $\underline{J}$ 6.8Hz, CH(CH $\underline{\text{H}}_3$) $_2$).



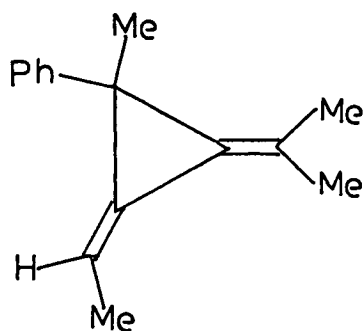
syn-3-Ethylidene-2-isopropylidene-1-methyl-1-phenyl-cyclopropane (181a) was identified by comparison of its ^1H n.m.r. spectrum with that obtained previously and using the

Table 9. Percentages of Compounds Present Against Time
in the Reaction of Z-1,3-Dimethyl-2-dimethylvinyl-
idene-1-phenylcyclopropane (173) with p-Toluene-
sulphonic Acid

Compound Time/h	Starting material	Triene (219)	Triene (220)	Triene (221)	Indene (222)	Enyne (223)
0	100	0	0	0	0	0
1	75.6	14.0	2.2	2.2	0	-
2	45.6	22.4	6.4	3.9	6.4	-
3	20.0	24.4	11.3	5.0	12.6	7.8
4	8.9	22.7	12.8	4.6	18.3	8.9
5	-	20.0	13.3	4.8	25.7	10.8
6	-	13.3	11.1	4.4	33.3	11.1
7	-	9.8	8.8	2.9	39.6	11.9
8	0	8.8	6.8	2.3	45.6	12.7
9		5.6	5.6	1.5	50.0	13.0
10		4.8	3.7	1.4	53.3	12.8
25		3.1	2.8	-	55.3	12.8

arguments of Sadler¹²³ and Pasto¹²⁴ to determine the stereochemistry.

¹H n.m.r. δ_H 7.39-7.11 (5H, m, ArH), 5.57 (1H, q, J 6.9Hz, =CH), 2.04 (3H, d, J 0.4Hz, =CCH₃), 1.96 (3H, d, J 6.9Hz, =CHCH₃), 1.89 (3H, d, J 0.5Hz, =CCH₃), 1.56 (3H, s, 1-CH₃).



The reaction of Z-1,3-dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (49 mg, 0.25 mmol) with *p*-toluenesulphonic acid (6 mg, 0.03 mmol) in carbon tetrachloride (0.25 ml) at 75° was followed by ¹H n.m.r. (360MHz) spectroscopy. Spectra (32 scans) were accumulated over a period of ca.25 h then analysed using a "constant intensity" mode which allowed direct comparison of product ratios between spectra therefore allowing percentages of products to be determined relative to the amount of Z-1,3-dimethyl-2-dimethylvinylidenecyclopropane present at time *t*=0h being set at 100%. The results obtained are shown in Table 9.

The reaction of E-1,3-dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (61 mg, 0.31 mmol) and *p*-toluenesulphonic acid (6 mg, 0.03 mmol) in carbon tetrachloride (0.25 ml) at 75° was similarly followed by ¹H n.m.r. (360MHz) spectroscopy. Spectra were recorded over a period of ca.26 h. The data was analysed as outlined above, the percentages of products being determined relative to the amount of E-1,3-dimethyl-2-

Table 10. Percentages of Compounds Present Against Time in the Reaction of E-1,3-Dimethyl-2-dimethyl-vinylidene-1-phenylcyclopropane (172) with p-Toluenesulphonic Acid

Compound Time /h	Starting material	Triene (219)	Triene (220)	Indene (222)	Enyne (223)
0	100	0	0	0	0
1	96	3.0	-	-	-
2	83	5.5	2.7	2.4	-
3	73	8.7	4.2	3.3	2.0
4	64	11.7	5.0	4.3	2.7
5	58	12.8	5.6	5.4	3.5
6	-	14.2	6.5	6.1	4.2
7	-	15.0	7.3	7.0	4.4
8	-	17.4	7.6	7.9	5.5
9	-	18.4	8.6	8.4	6.1
10	-	19.0	9.6	9.5	6.9
11	-	19.8	10.1	10.3	7.4
12	-	19.0	11.0	11.4	7.8
13	-	18.6	11.7	12.1	8.0
14	-	18.6	11.7	14.3	8.2
15	-	18.4	11.6	16.6	-
16	-	18.2	11.6	18.8	8.7
17	0	16.3	11.3	23.7	8.9
18		16.4	10.5	24.7	9.3
19		15.0	10.6	25.0	9.4
20		15.0	10.1	25.5	9.8
21		14.9	10.1	26.6	9.9
22		14.8	10.2	27.6	10.2
24		-	9.8	27.6	10.2
25		-	9.8	27.7	-
26		-	9.6	27.6	10.4

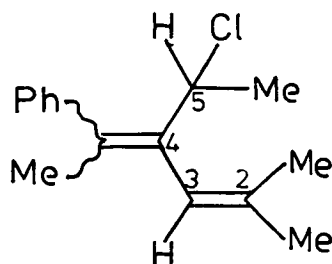
dimethylvinylidene-1-phenylcyclopropane present at time $t=0\text{h}$ being set at 100%. Analysis of the ^1H n.m.r. spectrum of the starting material showed it to contain ca.38% of syn-3-ethylidene-2-isopropylidene-1-methyl-1-phenylcyclopropane (181a). The results obtained are shown in Table 10.

E-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (49 mg, 0.25 mmol) in ethanolic hydrogen chloride (2.5 ml) was heated under reflux for 7 min. This gave a mixture containing the trienes (219) and (220), the indene (222), the enyne (223) and the addition product 5-chloro-2-methyl-4-(2'-phenylethylidene)hex-2-ene (226) in the ratio 8:9:34:15:34, with only a small amount (ca.10%) of unidentified minor products.

Z-1,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (506 mg, 2.56 mmol) in ethanolic hydrogen chloride (25 ml) was heated under reflux for 10 min. This gave a mixture containing the trienes (219) and (220), the indene (222), the enyne (223) and the addition product (226) in the ratio 9:6:42:13:31, with only a small amount (ca.10%) of unidentified minor products.

5-Chloro-4-(2'-phenylethylidene)-2-methylhex-2-ene (226)

^1H n.m.r. δ_{H} 7.40-7.13
 (5H, m, ArH), 5.87 (1H, m, 3-H)
 4.75 (1H, q, $\underline{J}$ 6.7Hz, 5-H), 1.89,
 1.88 (6H, s,s, $2x=\text{CCH}_3$), 1.65
 (3H, d, $\underline{J}$ 1.2Hz, $=\text{CCH}_3$), 1.42 (3H, d, $\underline{J}$ 6.7Hz, 5- CH_3).



^{13}C n.m.r. - A DEPT pulse sequence experiment on the reaction mixture, set up to show CH signals only, gave a resonance at 59.5 p.p.m., indicating the presence of a CHCl group.

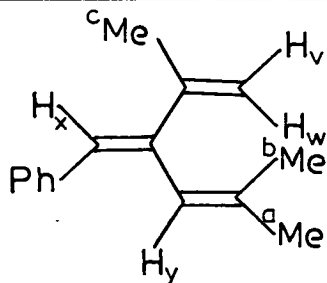
M.s. (reaction mixture) (m/z) 236, 234 (M^+), 198.

5.6.7 Reactions of 3,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (174)

3,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (103 mg, 0.52 mmol) in ethanolic hydrogen chloride (5 ml) was heated under reflux for 7 min. This gave a mixture containing E-3-benzylidene-2,5-dimethylhexa-1,4-diene (232), 2,6-dimethyl-5-phenylhepta-6-ene-3-yne (233) and the addition product E-4-benzylidene-5-chloro-2,5-dimethylhex-2-ene (234) in the ratio 4:3:3, with only a small amount (ca.5%) of unidentified minor products. Attempts to separate the compounds by chromatography (alumina, light petroleum) resulted in the dehydrochlorination of the addition product (234) to give the triene (232). Attempts to separate the triene (232) and the enyne (233) by preparative g.l.c. (30% NPGS at 150°) resulted in only the enyne being obtained pure.

E-3-Benzylidene-2,5-dimethylhexa-1,4-diene (232)

^1H n.m.r. δ_{H} 7.45-7.14 (5H, m, ArH), 6.55 (1H, s, H_{x}), 5.84 (1H, m, H_{y}), 5.16 (1H, bd, H_{w} , J 2.3Hz, H_{w}), 5.04 (1H, bs, H_{v}), 2.03 (3H, q, J 0.7Hz, c- CH_3), 1.81 (3H, d, J 1.3Hz, a- CH_3),



1.37 (3H, d, J 1.0 Hz, b-CH₃).

2,6-Dimethyl-5-phenylhepta-6-ene-3-yne (233)

¹H n.m.r. δ_H 7.42-7.23

(5H, m, ArH), 5.11 (1H, m, =CH),

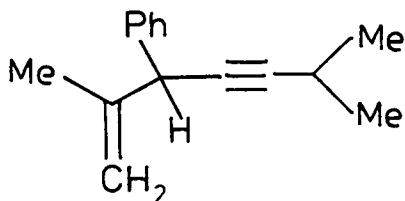
4.87 (1H, m, =CH), 4.32 (1H, m,

PhCH), 2.65 (1H, septet, d, J

6.8, 2.0 Hz, CH(CH₃)₂), 1.66 (3H, q, J 0.7 Hz, =CCH₃), 1.22

(6H, d, J 6.8 Hz, CH(CH₃)₂).

M.s. (m/z) 198.14078 (M⁺, C₁₅H₁₈ requires 198.14084), 183, 155.



E-4-Benzylidene-5-chloro-2,5-dimethylhex-2-ene (234)

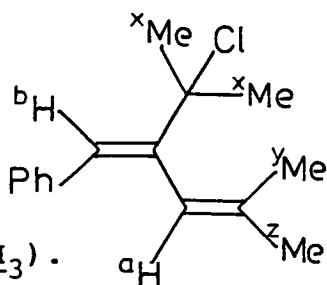
¹H n.m.r. δ_H 7.49-7.18

(5H, m, ArH), 6.65 (1H, bs, H_b),

6.00 (1H, m, H_a), 1.82 (6H, s,

x-CH₃), 1.74 (3H, d, J 1.5 Hz,

z-CH₃), 1.20 (3H, d, J 1.2 Hz, y-CH₃).



¹³C n.m.r. - a pulse sequence experiment on the reaction mixture, set up to show quaternary carbons only, had a resonance at 72.7 p.p.m. indicating the presence of an R₂CCl group.

M.s. (reaction mixture) (m/z) 236, 234 (M⁺), 198.

3,3-Dimethyl-2-dimethylvinylidene-1-phenylcyclopropane (300 mg, 1.51 mmol) and *p*-toluenesulphonic acid (20 mg, 0.11 mmol) in carbon tetrachloride (100 ml) were heated under reflux

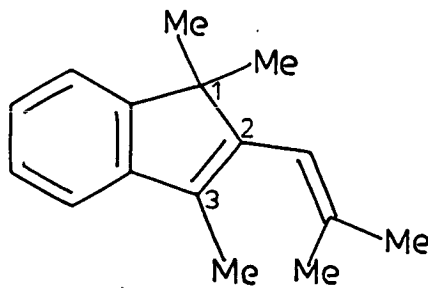
for 18.5 h. This gave a mixture containing the triene (232) and the enyne (233) in the ratio 4:1 with some starting material (10%) and only a small amount (ca.5%) of unidentified minor products.

5.6.8 Reactions of 2-Dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane (175)

2-Dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane (78 mg, 0.37 mmol) and *p*-toluenesulphonic acid (7 mg, 0.037 mmol) in carbon tetrachloride (4 ml) were heated under reflux for 14 h. This gave a mixture containing 2-(2'-methylprop-1'-enyl)-1,1,3-trimethylindene (242) and 5-phenyl-2,5,6-trimethylhept-3-yne-6-ene (241) in the ratio of 1:1, with only a small amount (10%) of unidentified minor products. The mixture was purified by preparative t.l.c. (alumina, light-petroleum) and the products were separated by preparative g.l.c. (30% PEGA at 150°).

2-(2'-Methylprop-1'-enyl)-1,1,3-trimethylindene (242)

^1H n.m.r. (360MHz) δ_{H} 7.31-7.15 (4H, m, ArH), 5.76 (1H, m, =CH), 1.92 (3H, d, $\underline{\text{J}}$ 1.4Hz, a-CH $\underline{\text{3}}$), 1.91 (3H, d, $\underline{\text{J}}$ 1.3Hz, a-CH $\underline{\text{3}}$), 1.60 (3H, d, $\underline{\text{J}}$ 1.3Hz, c-CH $\underline{\text{3}}$), 1.18 (6H, s, b-CH $\underline{\text{3}}$).



^{13}C n.m.r. (360MHz) δ_{C} 153.4, 149.6, 144.5, 137.4, 130.3

Table 11. Percentages of Compounds Present Against Time in the Reaction of 2-Dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane (175) with p-Toluenesulphonic Acid

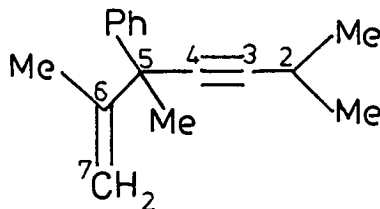
Compound Time/min	Starting material	Triene	Indene (242)	Enyne (241)
0	100	0	0	0
40	33	9	9	18
80	10	8	20	28
120	-	-	25	33
160	0	0	33	35
200			35	35
240			36	36
280			35	36
560			36	38

(aromatic and olefinic $\underline{\text{C}}$), 126.2, 124.4, 120.8, 118.6 (aromatic $\underline{\text{CH}}$), 117.8 ($=\underline{\text{CH}}$), 50.0 ($\underline{\text{C}}-1$), 25.6, 20.1, 11.7 ($=\underline{\text{CCH}}_3$), 24.12 ($1-(\underline{\text{CH}}_3)_2$).

M.s. (m/z) 212.15659 (M^+ , $\text{C}_{16}\text{H}_{20}$ requires 212.15649), 197 ($\text{M}^+ - \text{CH}_3$), 149.

5-Phenyl-2,5,6-trimethylhepta-3-yne-6-ene (241)

^1H n.m.r. (360MHz) δ_{H} 7.50-7.12 (5H, m, ArH), 5.13 (1H, q, $\underline{\text{J}}$ 0.7Hz, $=\underline{\text{CH}}$), 4.92 (1H, septet, $\underline{\text{J}}$ 1.3Hz, $=\underline{\text{CH}}$), 2.62 (1H, septet, $\underline{\text{J}}$ 6.9Hz, $\underline{\text{CH}}(\underline{\text{CH}}_3)_2$), 1.63 (3H, d, $\underline{\text{J}}$ 0.7Hz, $\underline{\text{CH}}_3$), 1.62 (3H, d, $\underline{\text{J}}$ 0.7Hz, $\underline{\text{CH}}_3$), 1.20 (6H, d, $\underline{\text{J}}$ 6.9, 1.8Hz, $\underline{\text{CH}}(\underline{\text{CH}}_3)_2$).



^{13}C n.m.r. (360MHz) δ_{C} 149.2, 145.1 (aromatic and olefinic $\underline{\text{C}}$), 127.9, 126.4 (4x aromatic $\underline{\text{CH}}$), 126.2 (aromatic $\underline{\text{CH}}$), 110.3 ($=\underline{\text{CH}}_2$), 89.8, 83.5 ($\equiv \underline{\text{C}}$), 45.7 ($\underline{\text{C}}-5$), 29.2 (6- $\underline{\text{CH}}_3$), 23.3 ($\underline{\text{CH}}(\underline{\text{CH}}_3)_2$), 20.6 ($\underline{\text{C}}-2$), 20.0 (5- $\underline{\text{CH}}_3$).

M.s. (m/z) 212.15552 (M^+ , $\text{C}_{16}\text{H}_{20}$ requires 212.15649), 149, 91.

The reaction of 2-dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane (51 mg, 0.24 mmol) and *p*-toluenesulphonic acid (5 mg, 0.026 mmol) in carbon tetrachloride (0.25 ml) at 75° was followed by ^1H n.m.r. (360MHz) spectroscopy. Spectra were recorded over a period of ca. 560 min. The data were analysed as outlined earlier with percentages of products being determined relative to the amount of 2-dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane present at time $t=0$ min being set at 100%. The results obtained are shown in Table 11.

Resonances at 5.68, 5.48 and 4.97 p.p.m. were assumed to be from the alkene protons of one of the trienes, 3-isopropylidene-5-methyl-2-phenylhexa-1,4-diene (243) or E- or Z-5-methyl-3-(1'-methylethenyl)-2-phenylhexa-2,4-diene (245) and (244), although it was not possible to determine which.

2-Dimethylvinylidene-1-phenyl-1,3,3-trimethylcyclopropane (300 mg, 1.42 mmol) in ethanolic hydrogen chloride (25 ml) was heated under reflux for 10 min. This gave the indene (242) and the enyne (241) in the ratio 2:1, with two unidentified products (ca.25%), which were thought to be geometrical isomers, but could not be identified.

5.7 Reactions of Dimethylenecyclopropanes with p-Toluene-sulphonic Acid

General method: The dimethylenecyclopropane (1.0 molar equivalent) and p-toluenesulphonic acid (~1.1 molar equivalents) were dissolved in carbon tetrachloride and heated under reflux until all the starting material had reacted, the reaction being followed by t.l.c. (silica, light-petroleum). Water was added to the mixture, the organic layer removed and the aqueous layer was extracted with ether. The organic layer and combined extracts were dried and the solvent was removed. The reaction mixture was examined by ^1H n.m.r. spectroscopy (360 or 200MHz) and the products were separated by the chromatographic procedures given below for individual mixtures. Ratios of products were calculated from integrals in the ^1H n.m.r. spectra of the reaction

mixture.

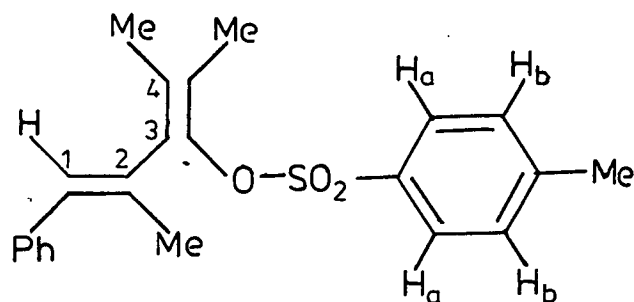
The products were characterised and stored at 4°C. ^{13}C n.m.r. data for sulphonate esters and benzofulvenes are presented in appendices III and IV respectively. ^{13}C n.m.r. data for other compounds are given below, where appropriate. Other details for each reaction are given below.

5.7.1 Reaction of 2-Isopropylidene-3-methylene-1-phenyl-cyclopropane (164)

The cyclopropane (1.20 g, 7.06 mmol) and *p*-toluenesulphonic acid (1.62 g, 8.53 mmol) in carbon tetrachloride (100 ml) were heated under reflux for 2.5 h. This gave only E-2,4-dimethyl-1-phenyl-3-(p-toluenesulphonyloxy)penta-1,3-diene (261) which was recrystallised from ethanol in 31% yield.

M.p.: 89–90°.

^1H n.m.r. (360MHz) δ_{H} 7.77 (2H, d, $\underline{J}$ 8.2Hz, $\underline{\text{H}}_{\text{a}}$), 7.20 (2H, d, d, $\underline{J}$ 8.2, 0.7Hz, $\underline{\text{H}}_{\text{b}}$), 7.34–7.11 (5H, m, $\text{Ph}\underline{\text{H}}$), 6.41 (1H, bs, $=\underline{\text{CH}}$), 2.35 (3H, s, $\text{Ar}\underline{\text{CH}}_3$), 1.82 (6H, s, $=\text{C}(\underline{\text{CH}}_3)_2$), 1.63 (3H, d, $\underline{J}$ 1.2Hz, 2- $\underline{\text{CH}}_3$),



U.v. (EtOH) 223 m μ (ϵ , 19400), 260 m μ (ϵ 13900).

M.s. (m/z) 342 (M^+), 187 ($\text{M}^+ - \text{Ts}$), 117 ($\text{M}^+ - \text{C}_{11}\text{H}_{13}\text{O}_3\text{S}$), 91.

Analysis: found C, 70.04; H, 6.22%.

$\text{C}_{20}\text{H}_{22}\text{O}_3\text{S}$ requires C, 70.18; H, 6.43%.

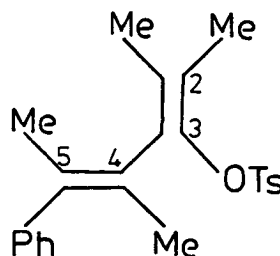
5.7.2 Reaction of 2-Isopropylidene-1-methyl-3-methylene-1-phenylcyclopropane (176)

The cyclopropane (44 mg, 0.24 mmol) and *p*-toluenesulphonic acid (57 mg, 0.30 mmol) in carbon tetrachloride (10 ml) were heated under reflux for 2.3 h. This gave a mixture containing E-2,4-dimethyl-5-phenyl-3-(*p*-toluenesulphonyloxy)hexa-2,4-diene (267a) and 1,2-benzo-3,4,6,6-tetramethylfulvene (268a) in the ratio 1.8:1. The products were separated by preparative t.l.c. (silica, 5% ether/light petroleum).

E-2,4-Dimethyl-5-phenyl-3-(*p*-toluenesulphonyloxy)hexa-2,4-diene (267a) (27%)

M.p.: 103-108°.

^1H n.m.r. δ_{H} 7.82 (2H, d, $\underline{J}$ 8.3Hz, $\underline{\text{o-TsH}}$), 7.34-7.20 (5H, m, $\underline{\text{ArH}}$), 6.88-6.76 (2H, m, $\underline{\text{ArH}}$), 2.45 (3H, s, $\underline{\text{ArCH}_3}$), 1.93 (3H, d, $\underline{J}$ 1.3Hz, 5- $\underline{\text{CH}_3}$), 1.86, 1.70 (6H, s,s, =C($\underline{\text{CH}_3}$) $_2$), 1.37 (3H, d, $\underline{J}$ 1.3Hz, 4- $\underline{\text{CH}_3}$).



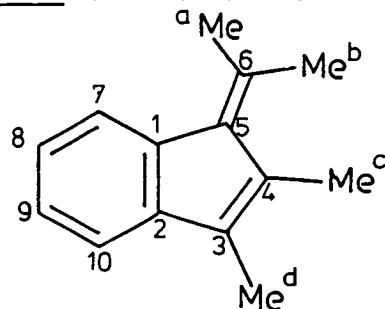
U.v. (EtOH) 226 m μ (ϵ 19600).

M.s. (m/z) 356.142925 (M^+ , $\text{C}_{21}\text{H}_{24}\text{O}_3\text{S}$ requires 356.1446067), 201 ($\text{M}^+ - \text{Ts}$), 169, 91.

1,2-Benzo-3,4,6,6-tetramethylfulvene (268a) (18%)

M.p. 49-53°.

^1H n.m.r. (360MHz) δ_{H} 7.67 (1H, d, $\underline{J}$ 7.6Hz, $\underline{\text{H-7}}$), 7.21-7.10 (3H, m, $\underline{\text{ArH}}$), 2.45 (3H, s, a- $\underline{\text{CH}_3}$),



2.34 (3H, s, b-CH₃), 2.27 (3H, d, $\underline{J}$ 0.9Hz, c-CH₃), 2.10 (3H, bd, d-CH₃).

U.v. (EtOH) 268 m μ (ϵ 13900).

M.s. (m/z) 184.12598 (M⁺, C₁₄H₁₆ requires 184.12519), 169 (M⁺ - CH₃).

5.7.3. Reaction of 1-Ethyl-2-isopropylidene-3-methylene-1-phenylcyclopropane (177)

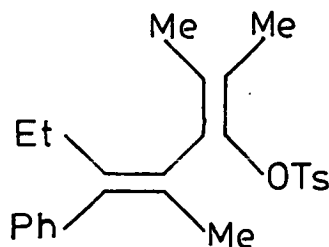
The cyclopropane (51 mg, 0.26mmol) and *p*-toluenesulphonic acid (53 mg, 0.28 mmol) in carbon tetrachloride (10 ml) were heated under reflux for 2.0 h. This gave a mixture containing E-2,4-dimethyl-5-phenyl-3-(p-toluenesulphonyloxy)hepta-2,4-diene (267b) and 1,2-benzo-3-ethyl-4,6,6-trimethylfulvene (268b) in the ratio 2.0:1. The products were separated by preparative t.l.c. (silica, 5% ether/light petroleum). The benzofulvene was isolated as an oil and the ester was recrystallised from ethanol.

E-2,4-Dimethyl-5-phenyl-3-(p-toluenesulphonyloxy)hepta-2,4-diene (267b) (31%)

M.p. 77-78°.

¹H n.m.r. (360MHz) δ_H 7.83 (2H, d, $\underline{J}$ 8.3Hz, o-TsH), 7.3-7.20 (5H, m, ArH) 6.82 (2H, d, d, $\underline{J}$ 8.2, 1.4Hz, ArH), 2.46 (3H, s, ArCH₃), 2.39 (2H, q, t, $\underline{J}$ 7.5, 0.9Hz, CH₂CH₃), 1.81, 1.71 (6H, s, s, 2-CH₃), 1.40 (3H, t, $\underline{J}$ 1.1Hz, 4-CH₃), 0.75 (3H, t, $\underline{J}$ 7.5Hz, CH₂CH₃).

U.v. (EtOH) 226 m μ (ϵ 19900).



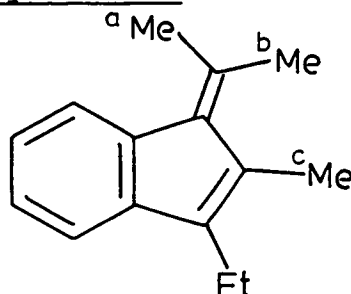
M.s. (m/z) 370 (M^+), 215 ($M^+ - Ts$), 145 ($M^+ - (C_{11}H_{13}O_3S)$), 91.

Analysis: found C, 71.42; H, 7.00%.

$C_{22}H_{26}SO_3$ requires C, 71.35; H, 7.03%.

1,2-Benzo-3-ethyl-4,6,6-trimethylfulvene (268b) (12%)

^1H n.m.r. δ_H 7.66-7.62 (1H, m, ArH), 7.25-7.10 (3H, m, ArH), 2.58 (2H, q, J 7.5Hz, CH_2CH_3), 2.45 (3H, s, a- CH_3), 2.34 (3H, s, b- CH_3), 2.26 (3H, s, c- CH_3), 1.13 (3H, t, J 7.5Hz, CH_2CH_3).



M.s. (m/z) 198.1408 (M^+ , $C_{15}H_{18}$ requires 198.1403), 183, 169.

5.7.4 Reaction of 1-Isopropyl-2-isopropylidene-3-methylene-1-phenylcyclopropane (178)

The cyclopropane (50 mg, 0.24 mmol) and *p*-toluenesulphonic acid (61 mg, 0.32 mmol) in carbon tetrachloride (10 ml) were heated under reflux for 2.0 h. The resulting mixture contained *E*-5-phenyl-3-(*p*-toluenesulphonyloxy)-2,4,6-trimethylhepta-2,4-diene (267c) and 1,2-benzo-3-isopropyl-4,6,6-trimethylfulvene (268c) in the ratio 2.7:1. The products were separated by preparative t.l.c. (silica, 5% ether, light petroleum). The benzofulvene was isolated as a semi-solid.

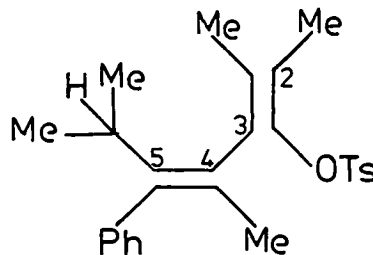
E-5-Phenyl-3-(*p*-toluenesulphonyloxy)-2,4,6-trimethylhepta-2,4-diene (267c) (35%)

M.p. 48-50°.

^1H n.m.r. δ_{H} 7.86 (2H, d, $\underline{J}$ 8.4Hz, $\underline{\text{o-TsH}}$), 7.36-7.23 (5H, m, $\underline{\text{ArH}}$), 6.84 (2H, bd, $\underline{J}$ 6.9Hz, $\underline{\text{ArH}}$), 3.06 (1H, septet, $\underline{J}$ 6.8Hz, $\underline{\text{CH(CH}_3)_2}$), 2.46 (3H, s, $\underline{\text{ArCH}_3}$), 1.76, 1.74 (6H, s,s, $=\text{C(CH}_3)_2$), 1.39 (3H, s, 4- $\underline{\text{CH}_3}$), 0.87 (3H, d, $\underline{J}$ 6.8Hz, $\underline{\text{CH(CH}_3)}$), 0.86 (3H, d, $\underline{J}$ 6.8Hz, $\underline{\text{CH(CH}_3)}$).

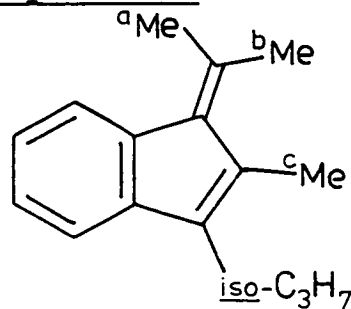
U.v. (EtOH) 225 m μ (ϵ 24900).

M.s. (m/z) 384.17632 (M^+ , $\text{C}_{23}\text{H}_{28}\text{O}_3\text{S}$ requires 384.17591), 229 ($\text{M}^+ - \text{Ts}$), 213, 197.



1,2-Benzo-3-isopropyl-4,6,6-trimethylfulvene (268c) (18%)

^1H n.m.r. δ_{H} 7.80-7.10 (4H, m, $\underline{\text{ArH}}$), 3.25 (1H, septet, $\underline{J}$ 7.1Hz, $\underline{\text{CH(CH}_3)_2}$), 2.45 (3H, s, a- $\underline{\text{CH}_3}$), 2.35 (3H, s, b- $\underline{\text{CH}_3}$), 2.28 (3H, s, c- $\underline{\text{CH}_3}$), 1.36 (6H, d, $\underline{J}$ 7.1Hz, $\underline{\text{CH(CH}_3)_2}$).



U.v. (EtOH) 267 m μ (ϵ 15000).

M.s. (m/z) 212.15638 ($\text{C}_{16}\text{H}_{20}$ requires 212.15649), 197, 184, 169.

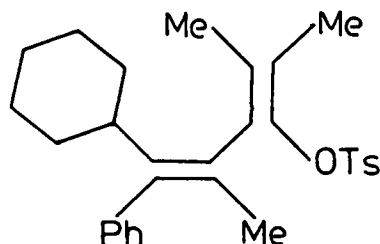
5.7.5 Reaction of 1-Cyclohexyl-2-isopropylidene-3-methylene-1-phenylcyclopropane (179)

The cyclopropane (58 mg, 0.23 mmol) and *p*-toluenesulphonic acid (69 mg, 0.36 mmol) in carbon tetrachloride (10 ml) were heated under reflux for 1.5 h. The resulting mixture contained *E*-1-cyclohexyl-2,4-dimethyl-1-phenyl-3-(*p*-toluenesulphonyloxy)-penta-1,3-diene (267d) and 1,2-benzo-3-cyclohexyl-4,6,6-

trimethylfulvene (268d) in the ratio 3.0:1. The products were separated by preparative t.l.c. (silica, 5% ether/light petroleum), the resulting ester being a colourless oil.

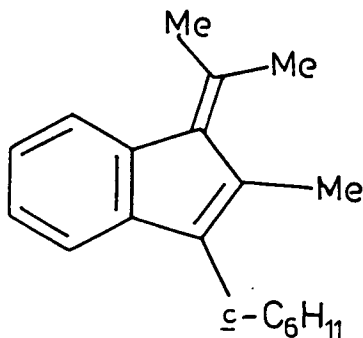
E-1-Cyclohexyl-2,4-dimethyl-1-phenyl-3-(p-toluenesulphonyloxy)penta-1,3-diene (267d) (40%)

^1H n.m.r. δ_{H} 7.85 (2H, d, $\underline{J}$ 8.3Hz, $\underline{\text{o-TsH}}$), 7.39-7.20 (5H, m, $\underline{\text{ArH}}$), 6.84 (2H, m, $\underline{\text{ArH}}$), 2.65 (1H, t,t, $\underline{J}$ 12, 2.5Hz, cyclohexyl $\underline{\text{H}}$), 2.46 (3H, s, $\underline{\text{ArCH}_3}$), 1.75, 1.73 (6H, s,s, $\underline{=\text{C}(\text{CH}_3)_2}$), 1.37 (3H, s, $\underline{2-\text{CH}_3}$), 1.73-0.50 (10H, m, cyclohexyl $\underline{\text{H}}$'s).
M.s. (m/z) 424.20699 (M^+ , $\text{C}_{26}\text{H}_{32}$ requires 424.20720), 269 ($\text{M}^+ - \text{Ts}$), 251.



1,2-Benzo-3-cyclohexyl-4,6,6-trimethylfulvene (268d) (24%)

M.p. 68-70°.
 ^1H n.m.r. δ_{H} 7.71 (1H, d,d, $\underline{J}$ 7.0, 1.5Hz, $\underline{\text{ArH}}$), 7.51 (1H, d,d, $\underline{J}$ 7.0, 1.5Hz, $\underline{\text{ArH}}$), 7.25-7.07 (2H, m, $\underline{\text{ArH}}$), 2.85 (1H, t,t, $\underline{J}$ 12.0, 3.5Hz, cyclohexyl $\underline{\text{H}}$), 2.46 (3H, s, $\underline{\text{a-CH}_3}$), 2.36 (3H, s, $\underline{\text{b-CH}_3}$), 2.31 (3H, s, $\underline{\text{c-CH}_3}$), 2.1-0.9 (10H, m, cyclohexyl $\underline{\text{H}}$'s).
U.v. (EtOH) 266 m μ (ϵ 10600).
M.s. (m/z) 252.187728 (M^+ , $\text{C}_{19}\text{H}_{24}$ requires 252.187792), 218, 169, 91.

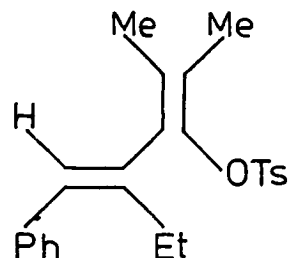


5.7.6 Reaction of syn and anti-3-Ethylidene-2-isopropylidene-1-phenylcyclopropane (180a and b)

The cyclopropanes (87mg, 0.47 mmol) and p-toluenesulphonic acid (94 mg, 0.49mmol) in carbon tetrachloride (20 ml) were heated under reflux for 1.7 h. This gave both E- and Z-4-benzylidene-2-methyl-3-(p-toluenesulphonyloxy)hex-2-ene (291) and (292) in the ratio 3.7:1. The products were separated by preparative t.l.c. (silica, 15% ether/light petroleum), both esters being isolated as colourless oils. Both esters were further purified by chromatography (silica, 15% ether/light petroleum).

E-4-Benzylidene-2-methyl-3-(p-toluenesulphonyloxy)hex-2-ene (291) (23%)

^1H n.m.r. δ_{H} 7.76 (2H, d, $\underline{\text{J}}$ 8.3Hz, $\underline{\text{o-TsH}}$), 7.20 (2H, d, d, $\underline{\text{J}}$ 8.4, 0.5Hz, $\underline{\text{m-TsH}}$), 7.31-7.08 (7H, m, $\underline{\text{ArH}}$), 6.39 (1H, bs, $\underline{=\text{CH}}$), 2.35



(3H, s, $\underline{\text{ArCH}_3}$), 1.99 (2H, q, $\underline{\text{J}}$ 7.5Hz, $\underline{\text{CH}_2\text{CH}_3}$), 1.86, 1.82 (6H, s, s, $\underline{=\text{C}(\text{CH}_3)_2}$), 0.89 (3H, t, $\underline{\text{J}}$ 7.5Hz, $\underline{\text{CH}_2\text{CH}_3}$).

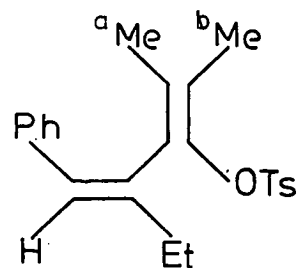
M.s. (m/z) 356.14288 (M^+ , $\text{C}_{21}\text{H}_{24}\text{O}_3\text{S}$ requires 356.14461), 201 ($\text{M}^+ - \text{Ts}$), 91.

Z-4-Benzylidene-2-methyl-3-(p-toluenesulphonyloxy)hex-2-ene (292) (3%)

^1H n.m.r. δ_{H} 7.74 (2H, d, $\underline{\text{J}}$ 8.4Hz, $\underline{\text{o-TsH}}$), 7.53 (2H, d, $\underline{\text{J}}$ 8.4Hz, $\underline{\text{m-TsH}}$), 7.31-7.18 (5H, m, $\underline{\text{ArH}}$), 6.18 (1H, bs, $\underline{=\text{CH}}$),

2.40 (3H, s, ArCH₃), 2.04, 1.92 (2H, m, CH₂CH₃), 1.81 (3H, s, =C(CH₃)_b), 1.35 (3H, s, =C(CH₃)_a), 0.87 (3H, t, $\underline{J}$ 7.5Hz, CH₂CH₃).

M.s. (m/z) 356.14522 (M⁺, C₂₁H₂₄SO₃ requires 356.14461), 201 (M⁺ - Ts), 169.



5.7.7 Reaction of syn and anti-3-Ethylidene-2-isopropylidene 1-methyl-1-phenylcyclopropane (181a and b)

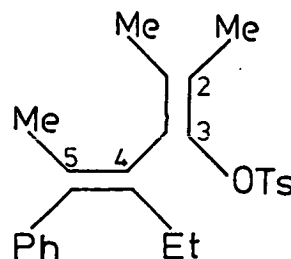
The cyclopropanes (138 mg, 0.69 mmol) and p-toluene-sulphonic acid (142 mg, 0.75 mmol) in carbon tetrachloride (30 ml) were heated under reflux for 4.0 h. The resulting mixture contained E-4-ethyl-2-methyl-5-phenyl-3-(p-toluenesulphonyloxy)hexa-2,4-diene (225) and 1,2-benzo-4-ethyl-3,6,6-trimethylfulvene (224) in the ratio 1:1.1. The products were separated by preparative t.l.c. (silica, 5% ether/light petroleum). The benzofulvene was isolated as an oil.

E-4-Ethyl-2-methyl-5-phenyl-3-(p-toluenesulphonyloxy)-hexa-2,4-diene (225) (12%)

M.p. (EtOH) 84-86°.

¹H n.m.r. δ_{H} 7.81 (2H, d, $\underline{J}$ 8.4Hz, o-TsH), 7.33-7.19 (5H, m, ArH), 6.79 (2H, m, ArH), 2.45

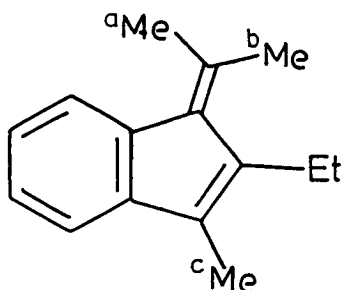
(3H, s, ArCH₃), 1.94 (3H, d, $\underline{J}$ 1.2Hz, 6-H), 1.91 (3H, s, 2-CH₃), 1.72 (3H, s, 2-CH₃), 1.67 (2H, m, CH₂CH₃), 0.70 (3H, t, $\underline{J}$ 7.5Hz, CH₂CH₃).



M.s. (m/z) 370.1610952 (M^+ , $C_{22}H_{26}O_3S$ requires 370.1602557), 215 ($M^+ - Ts$), 198, 172, 169.

1,2-Benzo-4-ethyl-3,6,6-trimethylfulvene (224) (31%)

^1H n.m.r. δ_H 7.77-7.67 (1H, m, ArH), 7.25-7.11 (3H, m, ArH), 2.78 (2H, q, J 7.4Hz, CH_2CH_3), 2.50 (3H, s, a- CH_3), 2.40 (3H, s, b- CH_3), 2.16 (3H, s, c- CH_3), 1.20 (3H, t, J 7.4Hz, CH_2CH_3).



U.v. (EtOH) 267 m μ (ϵ 15700).

M.s. (m/z) 198.14055 (M^+ , $C_{15}H_{18}$ requires 198.14084), 183.

5.7.8 Reaction of 2-Diisopropylidene-1-methyl-1-phenylcyclopropane (183)

The cyclopropane (49 mg, 0.23 mmol) and *p*-toluenesulphonic acid (47 mg, 0.25 mmol) in carbon tetrachloride (10 ml) were heated under reflux for 2.0 h. This gave only 2-(2'-methyl-prop-1'-enyl)-1,1,3-trimethylindene (242) which was purified by preparative t.l.c. (silica, light-petroleum) (44%) and was identified by comparison of its ^1H n.m.r. spectrum with that found in section 5.6.8..

5.7.9 Reaction of 1,1-Diphenyl-2-isopropylidene-3-methylene-cyclopropane (184)

The cyclopropane (47 mg, 0.17 mmol) and *p*-toluenesulphonic

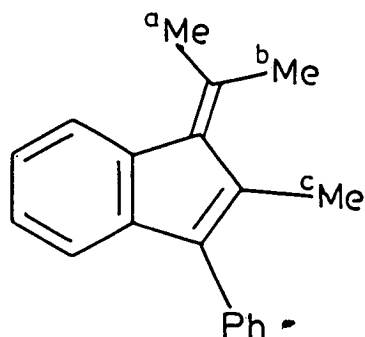
acid (49 mg, 0.26 mmol) in carbon tetrachloride (10 ml) were heated under reflux for 2.5 h. This gave only 1,2-benzo-3-phenyl-4,6,6-trimethylfulvene (278) which was purified by preparative t.l.c. (silica, light-petroleum) (91%).

M.p. 90-92°.

^1H n.m.r. δ_{H} 7.69-6.90 (9H, m, ArH), 2.47 (3H, s, a-CH₃), 2.36 (3H, s, b-CH₃), 2.24 (3H, s, c-CH₃).

U.v. (EtOH) 262 m μ (ϵ 23,100).

M.s. (m/z) 246.14088 (M^+ , $\text{C}_{19}\text{H}_{18}$ requires 246.140844).



5.7.10 Reaction of syn and anti-1,1-Diphenyl-3-ethylidene-2-isopropylidenecyclopropane (185a and b)

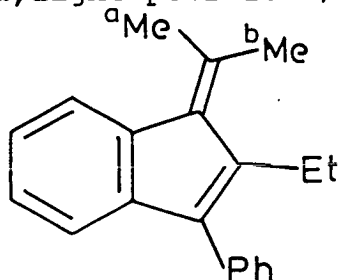
The cyclopropanes (500 mg, 1.92 mmol) and *p*-toluene-sulphonic acid (360 mg, 1.92 mmol) in carbon tetrachloride (100 ml) were heated under reflux for 3.0 h. This gave only 1,2-benzo-6,6-dimethyl-4-ethyl-3-phenylfulvene (279) which was purified by chromatography (alumina, light petroleum) (80%).

M.p. 87.5-93.5°.

^1H n.m.r. δ_{H} 7.95-7.05 (9H, m, ArH), 2.73 (2H, q, $\underline{\text{J}}$ 7.4Hz, CH₂CH₃), 2.56 (3H, s, a-CH₃), 2.45 (3H, s, b-CH₃), 1.19 (3H, t, $\underline{\text{J}}$ 7.4Hz, CH₂CH₃).

U.v. (Et₂O) 266 m μ (ϵ 18,400).

M.s. (m/z) 260.157874 (M^+ , $\text{C}_{20}\text{H}_{20}$ requires 260.156493).



5.7.11 Reaction of 2'-Isopropylidene-3'-methylenecyclopropane-1'-spiro-1-indane (189)

The cyclopropane (501 mg, 2.56 mmol) and *p*-toluene-sulphonic acid (486 mg, 2.56 mmol) in carbon tetrachloride (100 ml) were heated under reflux for 3.0 h. This gave only 3',3',5'-trimethyl-1,2-cyclopenta-1',4'-dienoindene (107) which was purified by medium pressure chromatography (silica, light-petroleum) (24%) and was identified by comparison of its ^1H n.m.r. spectrum with that published.¹¹⁵

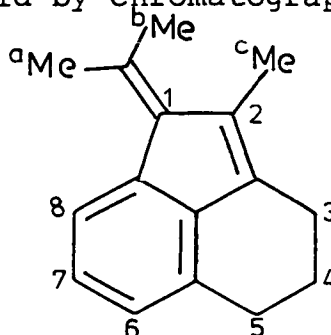
^{13}C n.m.r. δ_{C} 164.5, 150.2, 147.0, 141.8, 129.9 (aromatic and olefinic $\underline{\text{C}}$), 126.7, 122.5, 121.8, 120.2, 111.6 (aromatic and olefinic $\underline{\text{CH}}$'s), 60.8 ($\underline{\text{C}}\text{-3}$), 37.3 ($\underline{\text{C}}\text{-3'}$), 29.0 ($3'\text{-(}\underline{\text{CH}}_3)_2$), 16.4 ($5'\text{-}\underline{\text{CH}}_3$).

5.7.12 Reaction of 2'-Isopropylidene-3'-methylenecyclopropane-1'-spiro-1-tetralin (190)

The cyclopropane (500 mg, 2.38 mmol) and *p*-toluene-sulphonic acid (540 mg, 2.84 mmol) in carbon tetrachloride (100 ml) were heated under reflux for 5 h. This gave only 2-dehydro-1-isopropylidene-2-methyl-3,4,5-trihydroacenaphthene (271) which was purified in 60% yield by chromatography (alumina, light petroleum).

M.p. 90-91°.

^1H n.m.r. δ_{H} 7.48 (1H, d, $\underline{\text{J}}$ 7.5Hz, 8- $\underline{\text{H}}$), 7.10-6.98 (3H, m, Ar $\underline{\text{H}}$), 2.80 (2H, t, $\underline{\text{J}}$ 6.0Hz, 5- $\underline{\text{H}}$), 2.64 (2H, t, $\underline{\text{J}}$ 6.0Hz, 3- $\underline{\text{H}}$), 2.45 (3H, s, a- $\underline{\text{CH}}_3$), 2.36 (3H, s, b- $\underline{\text{CH}}_3$), 2.26 (3H, s, c- $\underline{\text{CH}}_3$), 1.96 (3H, m, 4- $\underline{\text{H}}$).



U.v. (EtOH) 260 m μ (ϵ 23,500).

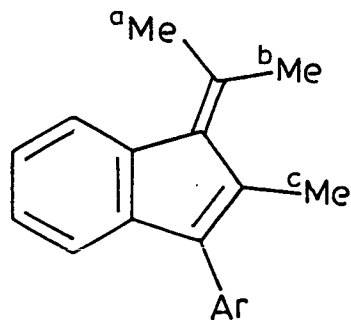
M.s. (m/z) 210.141873 (M^+ , C₁₆H₁₈ requires 210.140844), 195.

5.7.13 Reaction of p-Methoxy-1,1-diphenyl-2-isopropylidene-3-methylenecyclopropane (186)

The cyclopropane (99 mg, 3.58 mmol) and p-toluenesulphonic acid (68 mg, 3.58 mmol) in carbon tetrachloride (200 ml) were heated under reflux for 0.5 h. This gave a mixture containing only 1,2-benzo-3-(p-methoxyphenyl)-4,6,6-trimethylfulvene (282) and 1,2-benzo-8-methoxy-3-phenyl-4,6,6-trimethylfulvene (281) in the ratio 1:2.7. The mixture was purified by chromatography (alumina, 10% ether, light-petroleum) (76%) but the two isomers could not be separated by column chromatography (silica or alumina) or g.l.c..

1,2-Benzo-3-(p-methoxyphenyl)-4,6,6-trimethylfulvene
(282)

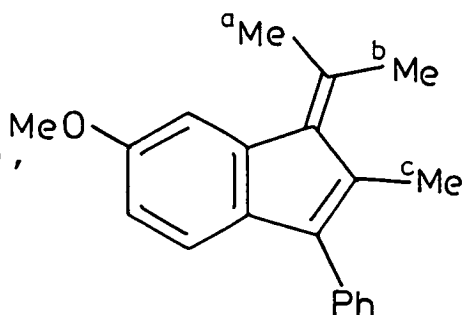
¹H n.m.r. (360MHz) δ_H 7.49-6.72 (8H, m, ArH), 3.88 (3H, s, OCH₃), 2.53 (3H, s, a-CH₃), 2.42 (3H, s, b-CH₃), 2.31 (3H, s, c-CH₃).



1,2-Benzo-8-methoxy-3-phenyl-4,6,6-trimethylfulvene
(281)

¹H n.m.r. (360MHz) δ_H 7.49-6.72 (8H, m, ArH), 3.85

(3H, s, OCH₃), 2.50 (3H, s, a-CH₃),
2.42 (3H, s, b-CH₃), 2.29 (3H, s,
c-CH₃).

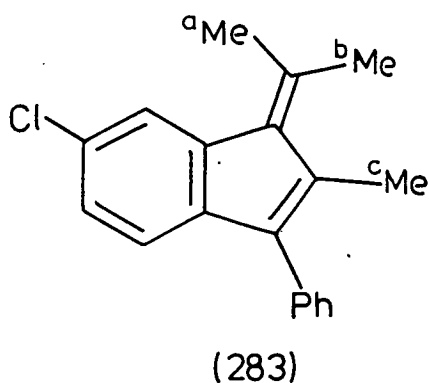
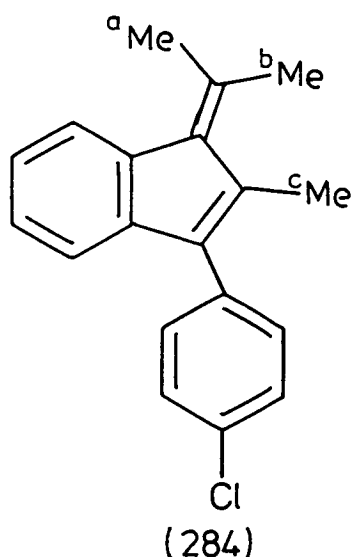


M.s. (mix) (m/z) 276.150042 (M⁺, C₂₀H₂₀O requires 276.151407), 135.

The ¹³C n.m.r. of the mixture showed the following signals with intensities shown in parentheses. δ_c 158.4 (7), 157.4 (21), 143.1 (8), 143.0 (28), 139.8 (18), 137.9 (21), 136.8 (8), 136.7 (19), 136.4 (30), 135.7 (20), 133.5 (6), 132.1 (27), 130.7 (38), 129.5 (97), 128.0 (99), 127.7 (12), 126.7 (42), 125.6 (18), 124.1 (17), 123.6 (14), 119.0 (40), 113.6 (28), 112.1 (45), 109.6 (44), 55.4 (40), 54.9 (16), 26.0 (44), 25.1 (39), 16.7 (43).

5.7.14 Reaction of p-Chloro-1,1-diphenyl-2-isopropylidene-3-methylenecyclopropane (187)

The cyclopropane (1.28 mg, 4.57 mmol) and *p*-toluene-sulphonic acid (0.87 mg, 4.57 mmol) in carbon tetrachloride (200 ml) were heated under reflux for 1.5 h. This gave only 1,2-benzo-3-(p-chlorophenyl)-4,6,6-trimethylfulvene (284) and 1,2-benzo-8-chloro-3-phenyl-4,6,6-trimethylfulvene (283) in the ratio 1.2:1. The mixture was purified by medium-pressure chromatography (silica, light-petroleum) (69%) but the two isomers could not be separated by column chromatography (silica or alumina) or g.l.c.. It was not possible to determine which isomer was which.



Major isomer

^1H n.m.r. (360MHz) δ_{H} 7.76–7.02 (9H, m, ArH), 2.53 (3H, s, a-CH₃), 2.41 (3H, s, b-CH₃), 2.27 (3H, s, c-CH₃).

Minor isomer

^1H n.m.r. (360MHz) δ_{H} 7.76–7.02 (9H, m, ArH), 2.51 (3H, s, a-CH₃), 2.42 (3H, s, b-CH₃), 2.28 (3H, s, c-CH₃).

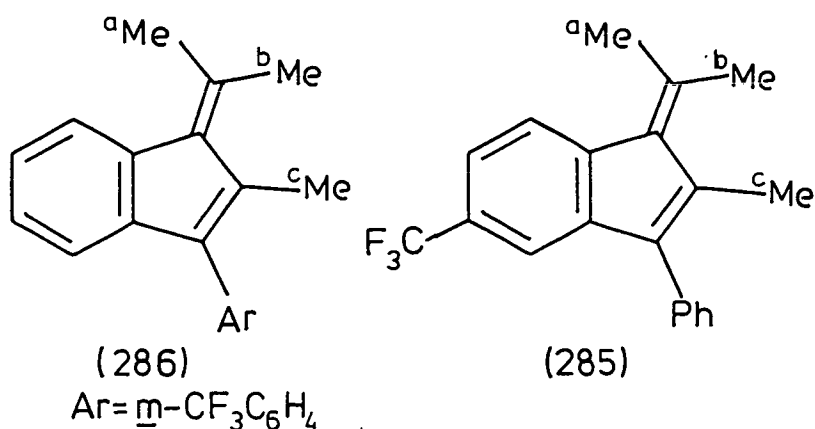
M.s. (mix) (m/z) 282.09974 (M^+ (^{37}Cl), $\text{C}_{19}\text{H}_{17}^{37}\text{Cl}$ requires 282.09892), 280.10129 (M^+ (^{35}Cl), $\text{C}_{19}\text{H}_{17}^{35}\text{Cl}$ requires 280.10187).

5.7.15 Reaction of m-(Trifluoromethyl)-1,1-diphenyl-2-isopropylidene-3-methylenecyclopropane (188)

The cyclopropane (154 mg, 0.49 mmol) and p-toluenesulphonic acid (146 mg, 0.77 mmol) in carbon tetrachloride (30 ml) were heated under reflux for 2 h. This gave a mixture containing 1,2-benzo-3-(m-trifluoromethylphenyl)-4,6,6-trimethylfulvene (286), 1,2-benzo-3-phenyl-9-trifluoromethyl-4,6,6-trimethylfulvene (285) and the E- and Z-isomers of 2,4-dimethyl-5-phenyl-3-(p-toluenesulphonyloxy)-5-(m-trifluoromethylphenyl)penta-2,4-diene

(288) and (287) in the ratio 12:10:5:1.2. The benzofulvenes were separated from the esters by preparative t.l.c. (silica, 10% ether/light-petroleum) to give a fraction containing only the two benzofulvenes (55%) and a fraction containing only the two esters (13%). It was not possible to differentiate between the esters or between the benzofulvenes.

Benzofulvenes



Minor isomer

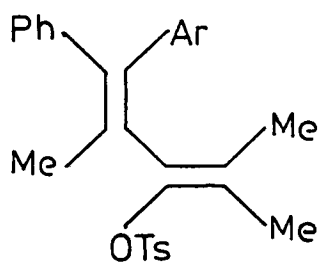
^1H n.m.r. (360MHz) δ_{H} 7.85-7.00 (8H, m, ArH), 2.57 (3H, s, a-CH₃), 2.46 (3H, s, b-CH₃), 2.33 (3H, s, c-CH₃).

Major isomer

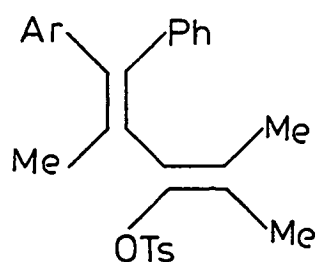
^1H n.m.r. (360MHz) δ_{H} 7.85-7.00 (8H, m, ArH), 2.56 (3H, s, a-CH₃), 2.44 (3H, s, b-CH₃), 2.31 (3H, s, c-CH₃).

M.s. (mix) (m/z) 314.12923 (M^+ , $\text{C}_{20}\text{H}_{17}\text{F}_3$ requires 314.12821), 299, 215.

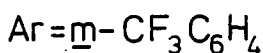
The ^{13}C n.m.r. spectrum (DEPT, CH signals only) showed peaks at 133.1 p.p.m. from the methyne carbon atom meta to the CF_3 group in isomer A, 118.7 p.p.m. from C-(10) in isomer A and 115.4 p.p.m. from C-(10) in isomer B.

Esters

(287)



(288)



Major isomer

^1H n.m.r. (360MHz) δ_{H} 7.78 (2H, d, J 8.4Hz, o-TsH), 7.50–7.15 (9H, m, ArH), 6.98 (2H, d, J 8.2Hz, ArH), 2.44 (3H, s, ArCH_3), 1.88 (3H, s, $=\text{CCH}_3$), 1.55 (6H, s,s, $2\times=\text{CCH}_3$).

Minor isomer

^1H n.m.r. (360MHz) δ_{H} 7.81 (2H, d, J 8.4Hz, o-TsH), 7.50–7.30 (11H, m, ArH), 2.44 (3H, s, ArCH_3), 1.76, 1.61, 1.52 (9H, s,s,s, $3\times=\text{CCH}_3$).

M.s. (mix) (m/z) 486.14906 (M^+ , $\text{C}_{27}\text{H}_{25}\text{F}_3\text{O}_3\text{S}$ requires 486.14764), 331 ($\text{M}^+ - \text{Ts}$), 330, 314, 304, 303, 187, 159.

5.8 Preparation of Derivatives5.8.1. Attempted Reaction of 1-Ethyl-2-isopropylidene-3-methylene-1-phenylcyclopropane (177) with 4-Phenyl-3H-1,2,4-triazoline-3,5-dione

The cyclopropane (110 mg, 0.56 mmol) and the dienophile (97 mg, 0.55 mmol) in dry benzene (2 ml) were heated under reflux for 10 h with no reaction. Changing the solvent to dry toluene (2 ml) and heating under reflux for 36 h resulted in decomposition of the starting material.

2.8.2 Attempted Reaction of E-2,4-Dimethyl-1-phenyl-3-(p-toluenesulphonate)penta-1,3-diene (261) with Dimethyl Acetylenedicarboxylate

The diene (100 mg, 0.29 mmol) and dimethyl acetylene-dicarboxylate (73 mg, 0.51 mmol) in dry benzene (2 ml) were heated under reflux for 18 h with no reaction. Changing the solvent to dry toluene and heating under reflux for 66 h resulted in decomposition of the acetylene.

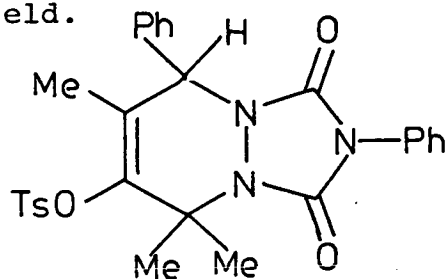
5.8.3 Reaction of E-2,4-Dimethyl-1-phenyl-3-(p-toluenesulphonyloxy)penta-1,3-diene (261) with 4-Phenyl-3H-1,2,4-triazoline-3,5-dione

The diene (103 mg, 0.30 mmol) and the dienophile (57 mg, 0.33 mmol) in dry benzene (2 ml) were heated under reflux for 18 h. After cooling, the product was filtered off and recrystallised from benzene to give 5,8-diphenyl-3-(p-toluenesulphonyloxy)-2,2,4-trimethyl-1,6,8-triazabicyclo[4.3.0]non-3-ene-7,9-dione (262) in 44% yield.

M.p. 179.5–180.5°.

^1H n.m.r. δ_{H} 7.89 (2H, d, J 8.4 Hz, ArH), 7.42–7.25 (12H, m, ArH), 5.43 (1H, s, PhCH), 2.45 (3H, s, ArCH₃), 1.89 (3H, s, =CCH₃), 1.68, 1.54 (6H, s, s, C(CH₃)₂).

^{13}C n.m.r. δ_{C} 152.52, 151.18 (C=O), 145.26, 145.15, 134.44, 134.35, 130.94, 122.56 (aromatic and olefinic C), 129.83, 128.89, 128.79, 128.67, 128.19, 125.26 (12x aromatic CH), 129.13, 127.45 (2x aromatic CH), 62.10 (C-4), 60.59



(C-1), 23.22, 21.54, 20.84, 15.96 (4x CH₃).

I.r. $\nu_{\max}$ 1710 cm^{-1} (C=O).

M.s. (m/z) 517 (M^+), 502 ($M^+ - \text{CH}_3$), 372, 153, 145, 91.

Analysis: found C, 64.78; H, 5.15; N, 7.82%.

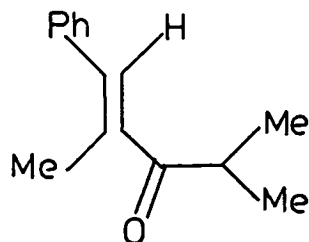
$\text{C}_{28}\text{H}_{27}\text{N}_3\text{O}_5\text{S}$ requires C, 64.99; H, 5.22;
N, 8.12%.

5.8.4 Hydrolysis of E-2,4-Dimethyl-1-phenyl-3-(p-toluene-sulphonyloxy)penta-1,3-diene (261)

The ester (54 mg, 0.16 mmol) and potassium hydroxide (11.26 mg, 0.20 mmol) in ethanol (5 ml) were heated under reflux for 5 h. The solvent was removed and the residue taken up in methylene chloride (10 ml) and water (10 ml). The organic layer was removed and the aqueous layer was washed with methylene chloride (2x10 ml). The combined organic extracts were washed with water, dried and the solvent removed. The product was purified by preparative t.l.c. (silica, 5% ether/light petroleum) to give E-2,4-dimethyl-1-phenylpent-1-ene-3-one (263e) (67%). On prolonged standing in deuteriochloroform at room temperature a mixture containing the E and Z isomers in the ratio 1:2 was obtained. Heating this mixture at 50° for 48 h did not alter the isomer ratio.

E-2,4-Dimethyl-1-phenylpent-1-ene-3-one (263e)

^1H n.m.r. δ_{H} 7.50 (1H, q, J 1.3Hz, =CH), 7.42-7.25 (5H, m, ArH), 3.47 (1H, septet, J 6.8Hz, CH(CH₃)₂), 2.05 (3H, d, J 1.4Hz, 2-CH₃), 1.17 (6H, d, J 6.8Hz, CH(CH₃)).



^{13}C n.m.r. (DEPT, $\underline{\text{CH}}_3$, $\underline{\text{CH}}_2$ and $\underline{\text{CH}}$ only) δ_{C} 137.7 ($\underline{\text{p-C}}$), 129.5, 128.2 ($\underline{\text{o-}}$ and $\underline{\text{m-C}}$), 34.0 ($\underline{\text{C-4}}$), 19.5 ($4\text{-}\underline{\text{CH}}_3$), 13.3 ($2\text{-}\underline{\text{CH}}_3$).

Z-2,4-Dimethyl-1-phenylpent-1-ene-3-one (263z)

^1H n.m.r. (360MHz) δ_{H} 7.41-7.11 (5H, m, $\text{Ar}\underline{\text{H}}$), 6.65 (1H, bs, $=\underline{\text{CH}}$), 2.49 (1H, septet, $\underline{\text{J}}$ 7.1Hz, $\underline{\text{CH}}(\underline{\text{CH}}_3)_2$), 2.04 (3H, d, $\underline{\text{J}}$ 1.7Hz, $2\text{-}\underline{\text{CH}}_3$), 0.96 (6H, d, $\underline{\text{J}}$ 7.1Hz, $\underline{\text{CH}}(\underline{\text{CH}}_3)_2$).

5.8.5 Reaction of the Products from the Acid Catalysed Rearrangement of 2-Dimethylvinylidene-1-ethyl-1-phenylcyclopropane (169) with Maleic Anhydride

The cyclopropane (489 mg, 2.47 mmol) and *p*-toluene-sulphonic acid (44 mg, 0.23 mmol) in carbon tetrachloride (25 ml) were heated under reflux for 21 h. The reaction mixture was washed with water (25 ml) and the aqueous layer was extracted with ether (3x25 ml). The combined organic extracts were dried and the solvent was removed. The resulting mixture of products and maleic anhydride (242 mg, 2.47 mmol) in dry benzene were heated under reflux under nitrogen for 2.5 h. Removal of solvent followed by medium-pressure chromatography (silica, light petroleum - 10% ether/light petroleum) gave a fraction containing mostly 3-ethyl-2-(2'-prop-1'-enyl)indene (194) (9%) and a fraction containing endo-3-phenyl-2,4,7,7-tetramethylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic anhydride (197) which was purified by medium pressure chromatography (silica, 50% ether/light petroleum) (22% from cyclopropane (169)). 3-Ethyl-2-(2'-prop-1'-enyl)-

indene (194) was identified by comparison of its ^1H n.m.r. with that previously obtained.

endo-3-Phenyl-2,4,7,7-tetramethylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic anhydride (197)

M.p. 118-120°.

^1H n.m.r. δ_{H} 7.36-7.00 (5H, m, ArH), 3.80 (1H, d, d, $\underline{\text{J}}$ 7.9, 4.8Hz, 6-H), 3.37 (1H, d, d, $\underline{\text{J}}$ 7.9, 0.4Hz, 5-H), 2.83

(1H, d, $\underline{\text{J}}$ 4.8Hz, 1-H), 1.77 (3H, s, 2-CH₃), 1.22 (3H, s, 4-CH₃), 1.01 (3H, s, b-CH₃), 0.93 (3H, s, a-CH₃).

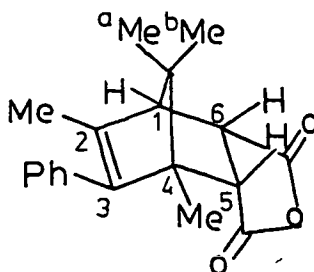
^{13}C n.m.r. δ_{C} 171.3, 171.6 (C=O), 141.7, 139.4, 134.3 (aromatic and olefinic C), 128.6, 128.0 (o- and m-CH), 127.1 (p-CH), 64.7, 62.5 (C-4, C-7), 58.6, 53.0 (C-5, C-6), 47.4 (C-1), 19.7, 18.7, 15.3, 12.2 (4xCH₃).

I.r. ν_{max} 1855, 1780 cm^{-1} (C=O).

M.s. (m/z) 296 (M^+), 198, 109, 105, 91.

Analysis: found C, 77.12; H, 6.71%

$\text{C}_{19}\text{H}_{20}\text{O}_3$ requires C, 77.03; H, 6.76%.



5.9 Deuterium Studies

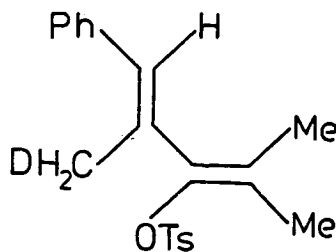
O-Deutero-p-toluenesulphonic Acid was prepared by dissolving p-toluenesulphonic acid in D_2O followed by removal of the solvent under high vacuum (10^{-4} mm).

5.9.1 Reaction of 2-Isopropylidene-3-methylene-1-phenylcyclopropane (164) with O-Deutero-p-toluenesulphonic Acid

The cyclopropane (490 mg, 2.88 mmol) and O-deutero-p-toluenesulphonic acid (700 mg, 3.68 mmol) in carbon tetrachloride (100 ml) were heated under reflux for 2.0 h. This gave only E-2-deuteromethyl-4-methyl-1-phenyl-3-(p-toluenesulphonyloxy)penta-1,3-diene, which was purified in 37% yield by medium-pressure chromatography (silica, 10% ether/light petroleum) and recrystallised from methanol.

M.p. 89-90.5°.

^1H n.m.r. δ_{H} 7.76 (2H, d, J 8.3Hz, ArH), 7.35-7.13 (7H, m, ArH), 6.41 (1H, bs, =CH), 2.35 (3H, s, ArCH₃), 1.82 (6H, s, =C(CH₃)₂), 1.61 (1.8H, d, J 1.4Hz, =C CH₃), 1.59 (0.8H, t, d, J 2.3, 1.4Hz, CH₂D).



^2D n.m.r. δ_{D} 1.64 (t, J 2.3Hz, CH₂D).

M.s. (m/z) 343.134565 (M^+ , 33.3%, C₂₀H₂₁DO₃S requires 343.135235), 342.126623 (19.3%, C₂₀H₂₂O₃S requires 342.128958), 188 (59.6%, C₁₃H₁₄DO), 187 (100%, C₁₃H₁₅O), 186 (47.4%), 118 (35.1%, C₉H₈D), 117 (63.2%, C₉H₉), 91.

Analysis: found C, 69.74; H/D, 6.43%.

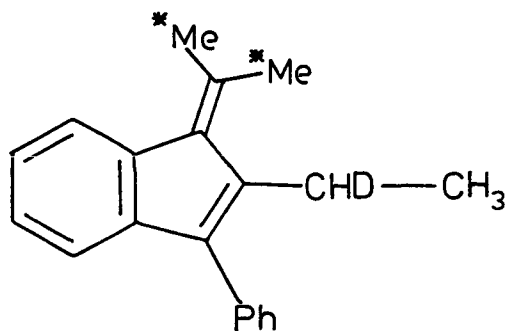
C₂₁H₂₁DO₃S requires C, 69.97; H/D, 6.70%.

5.9.2 Reaction of syn and anti-1,1-Diphenyl-3-ethylidene-2-isopropylidenecyclopropane (185a and b) with O-Deutero-p-toluenesulphonic Acid

The cyclopropanes (490 mg, 2.88 mmol) and deuterio-*p*-toluenesulphonic acid (352 mg, 1.85 mmol) in carbon tetrachloride (100 ml) were heated under reflux for 5.5 h. This gave only 1,2-benzo-6,6-dimethyl-4-ethyl-3-phenylfulvene (279) with deuterium incorporation at both 6-methyl groups and the methylene group, which was purified in 75% yield by chromatography (alumina, light petroleum).

M.p. 93.5–99.5°.

^1H n.m.r. δ_{H} 7.49–7.00 (7H, m, ArH), 2.69 (1.6H, q, $\underline{\text{J}}$ 7.4Hz, CHDCH_3), 2.54 (2.2H, s, 6- CH_3), 2.52 (0.5H, t, $\underline{\text{J}}$ 2.3Hz, 6- CH_2D), 2.43 (2.2H, s, 6- CH_3), 2.41 (0.5H, t, $\underline{\text{J}}$ 2.3Hz, 6- CH_2D), 1.16 (1.8H, t, $\underline{\text{J}}$ 7.4Hz, CH_2CH_3), 1.15 (1.2H, d, $\underline{\text{J}}$ 7.5Hz, CHDCH_3).



$^2\text{D}\{^1\text{H}\}$ δ_{D} 2.69 (broad, CHDCH_3), 2.55 (6- CH_2D), 2.53 (6- CHD_2), 2.51 (6- CD_3), 2.44 (6- CH_2D), 2.42 (6- CHD_2), 2.40 (6- CD_3).

M.s. (m/z) 260.154277 (64%, $\text{C}_{20}\text{H}_{20}$ requires 260.156493, $\text{C}_{20}\text{H}_{18}\text{D}$ requires 260.154946), 261.162186 (100%, $\text{C}_{20}\text{H}_{19}\text{D}$ requires 261.162770), 262.166755 (72%, $\text{C}_{20}\text{H}_{18}\text{D}_2$ requires 262.169047), 263.172866 (36%, $\text{C}_{20}\text{H}_{17}\text{D}_3$ requires 263.175325), 264 (17%), 265 (8%), 266 (4%).

Analysis: found C, 92.02; H/D, 8.32%.

$\text{C}_{20}\text{H}_{19}\text{D}$ requires C, 91.95; H/D, 8.05%.

5.9.3 Reaction of 1,2-Benzo-6,6-dimethyl-4-ethyl-3-phenylfulvene (279) with O-Deutero-p-toluenesulphonic Acid

The fulvene (100 mg, 3.85 mmol) and deutero-p-toluenesulphonic acid (75 mg, 3.85 mmol) in carbon tetrachloride (20 ml) were heated under reflux for 5.5 h. This gave only 1,2-benzo-6,6-dimethyl-4-ethyl-3-phenylfulvene (279) with deuterium incorporation at the 6-methyl groups.

^1H n.m.r. δ_{H} 7.51–7.01 (9H, m, ArH), 2.71 (2H, q, J 7.4Hz, CH_2CH_3), 2.56 (1.8H, s, 6- CH_3), 2.54 (0.8H, t, J 2.3Hz, 6- CH_2D), 2.45 (0.8H, t, J 2.3Hz, 6- CH_2D), 1.17 (3H, t, J 7.4Hz, CH_2CH_3),

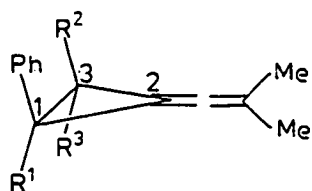
$^2\text{D}\{^1\text{H}\}$ δ_{D} 2.57 (6- CH_2D), 2.55 (6- CHD_2), 2.47 (6- CH_2D), 2.44 (6- CHD_2).

5.9.4 Reaction of 2-Dimethylvinylidene-1-methyl-1-phenylcyclopropane (89) with O-Deutero-p-toluenesulphonic Acid

The cyclopropane (462 mg, 2.51 mmol) and O-deutero-p-toluenesulphonic acid (46 mg, 0.24 mmol) in carbon tetrachloride (25 ml) were heated under reflux for 18h. This gave 2-phenyl-3,5,5-trimethylcyclopenta-1,4-diene (100) with deuterium incorporation at C-(1), C-(4) and in the methyl group on C-(3).

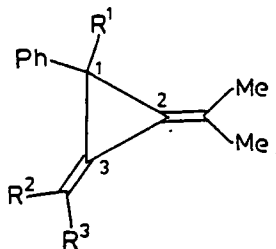
^2D n.m.r. δ_{D} 6.32 ($=\text{CD}$), 6.07 ($=\text{CD}$), 2.04 (3- CD).

APPENDIX 1

 ^{13}C n.m.r. Spectra of Dimethylvinylidenecyclopropanes

R^1	R^2	R^3	$\text{C}-(1)$	$\text{C}-(2)$	$\text{C}-(3)$	$=\text{C}=\text{C}$	$=\text{CMe}_2$	$=\text{C}(\text{CH}_3)_2$	Aromatic	R
H	H	H	23.5	81.8	17.1	187.5	99.3	21.2 21.0	141.6 (q) 128.3 (o) 126.4 (m) 126.0 (p)	-
Me	H	H	27.5	86.9	23.6	186.6	99.0	21.3 21.3	144.9 (q) 128.2 (o+) 127.6 (m) 125.9 (p)	24.4
Et	H	H	33.2	84.5	21.6	187.0	98.2	21.3 21.2	143.3 (q) 127.9 (o+m) 126.0 (p)	31.5 (CH) 11.1 (CH ₃)
iso-C ₃ H ₇	H	H	37.4	83.9	19.6	186.9	98.0	21.3 21.1	141.9 (q) 129.7 (o+) 127.4 (m) 126.2 (p)	35.5 (CH) 19.7 (CH ₃) 19.3 (CH ₃)
c-C ₆ H ₁₁	H	H	37.2	83.8	19.3	187.0	97.7	21.3 21.1	142.5 (q) 129.7 (o+) 127.4 (m) 126.2 (p)	45.4 (CH) 30.2 (CH ₂) 29.8 " " " " " " " "
H	Me	H	27.8	84.7	20.9	187.7	98.4	21.4 20.9	137.1 (q) 128.9 (o+) 127.7 (m) 125.9 (p)	12.0
H	H	Me	31.8	87.5	25.7	186.5	98.9	21.2 21.2	141.6 (q) 128.1 (o+) 126.2 (m) 125.6 (p)	18.0
Me	Me	H	32.3	90.3	27.8	186.7	97.9	21.5 21.2	141.6 (q) 128.6 (o+) 127.8 (m) 126.0 (p)	26.5 14.1
H	Me	Me	35.9	89.6	27.5	186.9	98.2	21.5 21.1	138.1 (q) 128.8 (o+) 127.8 (m) 125.9 (p)	19.0 26.3
Me	Me	Me	35.5	94.1	29.2	185.6	97.6	21.5 21.4	144.0 (q) 128.2 (o+) 127.8 (m) 125.7 (p)	22.8 22.0 21.0
Ph	H	H	35.8	85.9	24.0	186.9	100.2	21.0	143.5 (q) 128.0 (o+m) 126.1 (p)	-
(CH ₂) ₂	H	H	34.9	86.6	22.6	185.8	99.2	21.5 21.2	146.3 (q) 143.3 " " " " " " " "	34.5 30.7

APPENDIX II

¹³C n.m.r. Spectra of Dimethylenecyclopropanes

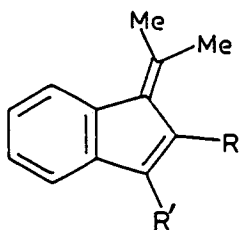
R ¹	R ² =R ³	C-(1)	C-(2)	C-(3)	=CMe ₂	=CR ¹ R ²	=C(CH ₃) ₂	Aromatic	R
H	H [*]	29.2	121.6	136.3	126.0	97.1	23.6 22.1	144.4 (q) 128.2 (m) 126.4 (o) 125.5 (p)	-
Me	H	29.2	121.5	136.3	126.2	97.1	23.5 22.0	144.4 (q) 128.0 (m) 126.2 (o) 125.4 (p)	22.0
Et	H	35.4	120.6	135.0	125.9	97.6	23.6 22.5	143.0 (q) 128.0 (m) 127.2 (o) 125.6 (p)	29.3 (CH ₂) 11.3 (CH ₃)
iso-C ₃ H ₇	H	40.4	119.8	133.8	125.7	98.1	23.8 22.8	142.8 (q) 128.4 (m) 127.8 (o) 125.7 (p)	33.6 (CH) 19.9 (2xCH ₃)
c-C ₆ H ₁₁	H	40.1	119.8	133.9	125.5	98.0	23.8 22.9	142.9 (q) 128.5 (m) 127.8 (o) 125.8 (p)	43.7 (CH) 30.4 (CH ₂) 30.2 " 26.6 " 26.5 " 26.2 "
H	Me	25.9	117.5	117.5	120.3	120.3	23.6 22.1	142.2 (q) 128.7 (m) 126.3 (o) 124.9 (p)	-
Me	Me	28.0	119.4	119.4	122.8	122.8	23.6 21.8	145.2 (q) 127.8 (o) 126.0 (m) 124.8 (p)	20.7
(CH ₂) ₂	H	37.3	119.8	134.7	125.7	96.4	23.4 22.0	146.4 (q) 143.9 (q) 126.3 CH 125.6 " 124.1 " 120.7 "	34.0 31.0

* Chemical shifts taken from ref.124.

R ¹	R ²	Aromatic and olefinic <u>C</u>	Aromatic <u>CH</u>	Ar <u>CH</u> ₃	=C(<u>CH</u> ₃) ₂	R ¹	R ²
H	Me	144.9, 144.3, 136.4, 134.5, 130.0, 124.7	129.2, 128.7, 128.1 127.9, 126.9	21.2	20.0 18.5	- <u>C</u> -a at 133.8	16.0
Me	Me	144.3, 142.9, 142.4, 139.6, 135.3, 125.1, 124.6	129.3, 127.9, 127.7 127.4, 126.5	21.4	19.3 18.2	22.8	18.0
Et	Me	145.4, 144.2, 142.2, 141.0, 135.3, 124.7, 124.1	129.4, 128.1, 127.8, 127.7, 126.4	21.4	19.6 18.5	28.3 (<u>CH</u> ₂) 11.7 (<u>CH</u> ₃)	18.1
<u>CH</u> (<u>CH</u> ₃) ₂	Me	149.7, 144.2, 141.7, 138.9, 135.2, 124.6, 124.4	129.4, 129.1, 127.7, 127.5, 126.2	21.4	19.7 19.3	31.9 (<u>CH</u>) 20.8 (<u>CH</u> ₃) 20.7 (<u>CH</u> ₃)	18.0
<u>C</u> - <u>C</u> ₆ H ₁₁	Me	149.4, 144.1, 142.0, 140.0, 135.5, 124.9, 124.2	129.4, 128.6, 127.7, 127.5, 126.1	21.4	19.7 19.2	43.1 (<u>CH</u>) 31.0, 31.0 26.9, 26.2 25.9 (5x <u>CH</u> ₂)	18.0
H	Et	144.3, 143.3, 136.4, 136.2, 134.7, 126.6	129.2, 128.5, 128.2, 128.0, 127.0	21.4	20.2 18.6	- <u>C</u> -a at 133.5	21.6 (<u>CH</u> ₂) 12.0 (<u>CH</u> ₃)
Me	Et	144.3, 143.1, 140.4, 139.1, 135.4, 130.7, 127.1	129.3, 128.0, 127.8, 127.2, 126.5	21.4	19.6 18.2	23.2	23.6 (<u>CH</u> ₂) 12.3 (<u>CH</u> ₃)

Z-4-Benzylidene-2-methyl-3-(p-toluenesulphonyloxy)hex-2-ene (292):- 144.4, 139.6, 136.8, 134.6 (× 3), (aromatic and olefinic C), 127.0, 129.2, 128.5, 128.2, 127.9 (aromatic CH), 130.6 (olefinic CH), 29.4 (CH₂), 21.5, 19.8, 18.6, 12.3 (CH₃).

APPENDIX IV

 ^{13}C n.m.r. Spectra of Benzofulvenes

R	R'	Aromatic and olefinic $\underline{\text{C}}$	Aromatic $\underline{\text{CH}}$	6- $\underline{\text{CH}}_3$	R	R'
Me	Me	143.9, 139.7, 136.7, 136.5, 134.0, 132.6	125.5, 123.8, 123.2, 117.3	25.7 24.7	15.5	9.9
Me	Et	142.9, 140.5, 140.4, 136.9, 136.8, 132.0	125.6, 123.8, 123.5, 117.4	25.9 24.9	15.4	18.0 ($\underline{\text{CH}}_2$) 13.4 ($\underline{\text{CH}}_3$)
Me	isop.	143.7, 142.0, 140.4, 137.4, 137.2, 131.6	125.3, 123.7, 123.4, 119.4	26.3 25.3	15.8	26.2 ($\underline{\text{CH}}$) 21.0 ($\text{CH}(\underline{\text{CH}}_3)_2$)
Me	Cyclo- hexyl	143.0, 142.5, 140.5, 137.5, 137.2, 132.0	125.5, 123.8, 123.5, 119.5	26.5 25.5	16.2	37.8 ($\underline{\text{CH}}$) 31.0, 27.5 ($4 \times \underline{\text{CH}}_2$) 26.5 ($\underline{\text{CH}}_2$)
Et	Me	143.9, 139.6, 139.0, 136.9, 135.8, 134.2	125.7, 124.1, 123.6, 117.5	26.2 24.5	20.9 ($\underline{\text{CH}}_2$) 14.6 ($\underline{\text{CH}}_3$)	9.8
Me	Ph	143.4, 143.2, 140.5, 137.1, 136.6, 134.0	125.8, 124.3 123.8, 119.1	26.3 25.3	16.9	129.7, 128.2 ($\text{o\&m-}\underline{\text{CH}}$) 126.9 ($\text{p-}\underline{\text{CH}}$) 135.8 ($\underline{\text{C}}$)
Et	Ph	143.4, 142.6, 140.5, 136.8, 136.0, 135.7	125.8, 124.4, 124.0, 119.2	26.5 24.7	21.4 ($\underline{\text{CH}}_2$) 15.6 ($\underline{\text{CH}}_3$)	129.4, 128.2 ($\text{o\&m-}\underline{\text{CH}}$) 126.9 ($\text{p-}\underline{\text{CH}}$) 140.2 ($\underline{\text{C}}$)
Me	($\underline{\text{CH}}_2$) ₃	140.2 (x2), 137.5, 135.8, 135.2, 130.4, 128.5	124.3, 124.0, 121.4	25.4 24.2	15.3	27.6, 23.5, 23.7 ($3 \times \underline{\text{CH}}_2$)

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