

Synthesis and Rearrangement of Small
Ring Compounds

by

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Thesis presented for the degree of
Doctor of Philosophy

University of Edinburgh

January 1975



DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out in the Department of Chemistry, University of Edinburgh, under the supervision of Dr. I.H. Sadler, since the 1st October 1971, the date of my admission as a research student.

ACKNOWLEDGEMENTS

I would like to express my thanks to Dr. I.H. Sadler for his advice, encouragement and enthusiasm throughout the course of this study.

In addition, I would like to thank my laboratory colleagues, members of staff and technical staff for their assistance on many occasions. In particular, I would like to thank Messrs. T.E. Henderson, D.A. Thomas and J.R.A. Miller for their help and Miss M. Fleming for her patience and accuracy in typing this manuscript.

Finally my thanks are due to the Science Research Council for the award of a Research Studentship and the University of Edinburgh for providing laboratory and library facilities.

POSTGRADUATE LECTURES

I attended the following lectures and courses to obtain the minimum required number of eight units for postgraduate study:-

- | | | |
|-----|---|---------|
| (1) | Nuclear Magnetic Resonance Spectroscopy | |
| | Dr. R.M. Lynden-Bell (5 lectures) | 1 Unit |
| (2) | Electron Spin Resonance Spectroscopy and
Chemically Induced Dynamic Nuclear Polarisation | |
| | Dr. I.H. Sadler (5 lectures) | 1 Unit |
| (3) | ^{13}C and Fourier Transform Nuclear Magnetic
Resonance Spectroscopy | |
| | Dr. D. Shaw (5 lectures) | 1 Unit |
| (4) | Carbonium Ions in Syntheses | |
| | Dr. B. Capon (5 lectures) | 1 Unit |
| (5) | Recent Developments in the Theory
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| | Dr. A.J. Bellamy (5 lectures) | 1 Unit |
| (6) | Organometallic Chemistry | |
| | Professor P.L. Pauson (5 lectures) | 1 Unit |
| (7) | Computer Programming | |
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| (8) | Business Course | |
| | University of Surrey (1 week) | 2 Units |

ABSTRACT

The research programme has been concerned with the synthesis and rearrangement of unsaturated cyclopropanes obtained by the addition of dimethylvinylidenecarbene, 2,3,3-trimethylbutenylidenecarbene, 2'-(trans-prop-1-enyl)propylidenecarbene and 2'-vinylpropylidenecarbene to various olefins. The carbenes were obtained by the action of potassium t-butoxide/butanol complex on 1-bromo-3-methylbuta-1,2-diene, 1-bromo-3,4,4-trimethylpenta-1,2-diene, trans-3-bromo-3-methylhex-4-ene-1-yne and 1-bromo-3-methyl-trans-pent-2-ene-4-yne, respectively.

The cyclopropanes obtained by the addition of dimethylvinylidenecarbene and 2,3,3-trimethylbutenylidenecarbene to various olefins underwent unimolecular rearrangement at reduced pressure (0.01 m.m.) in the vapour phase when passed through a flow system (350°-450°), the rearrangement conditions and products formed being dependent on the adduct involved. The adducts obtained from the other two carbenes gave only unidentified product mixtures on attempting similar vapour phase rearrangements.

The vapour phase rearrangement (450°) of various 1-arylcyclopentene adducts of dimethylvinylidenecarbene were carried out, yielding in each case mixtures of two isomeric products having the basic structures 9-isopropenyl-1,2,3,4-tetrahydrofluorene and 9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene. The role of the substituent in influencing the proportion of each isomer formed was investigated. The effect of ring size of the cycloalkene moiety of various 1-phenylcycloalkene adducts of dimethylvinylidenecarbene, on the rearrangement products formed was also examined.

The unsymmetrical nature of the remaining three carbenes gives rise to E and Z isomers on addition to certain olefins. The

proportion of E and Z isomers formed is rationalised in terms of the mode of attack of the carbene.

Vapour phase rearrangement (350°) of the butenyliidenecarbene adducts of various substituted styrenes yield syn and anti dimethylene-cyclopropanes, again due to the unsymmetrical nature of the original carbene, whereas similar rearrangement of the adduct derived from indene yields 2-t-butyl-3-(2'-indenyl)buta-1,3-diene.

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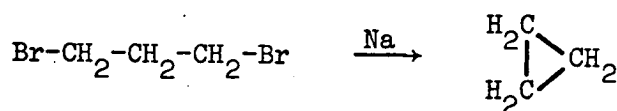
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A SURVEY OF THE PREPARATION, BONDING AND REARRANGEMENT OF
CYCLOPROPANE AND CYCLOPROPANE DERIVATIVES

1.0 Synthetic routes to cyclopropanes

In the last quarter of the nineteenth century Victor Meyer recorded¹ his doubts as to whether cyclopropanes could exist. Freund², five years later, settled matters by synthesising cyclopropane itself by the elimination of bromine from 1,3-dibromopropane using sodium.

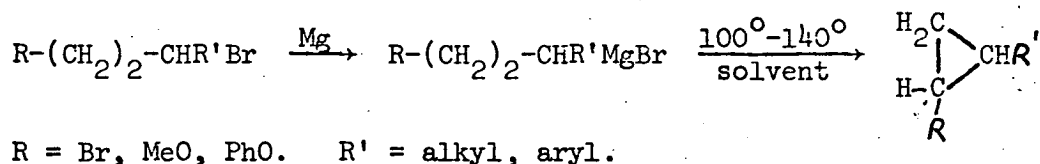


Since then numerous derivatives have been made by a great variety of routes. It is therefore possible to give only a brief survey of the general methods available. In view of the material presented later the survey will be in four sections; synthesis of saturated cyclopropanes, synthesis of vinylcyclopropanes, synthesis of methylenecyclopropanes and the synthesis of vinylidenecyclopropanes. Throughout the survey, it will be seen, that the same general methods apply to the formation of all cyclopropanes.

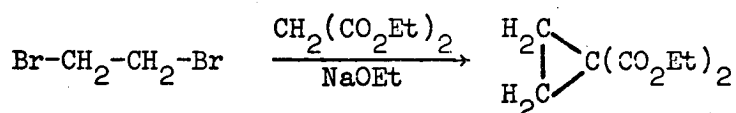
1.1 Synthesis of saturated cyclopropanes

1,1-Dimethylcyclopropane was prepared from 2,1-dichloro-2,2-dimethylpropane by Whitmore³ using Freund's method. Gustavson^{4,5}, prepared both cyclopropane and substituted cyclopropanes, eliminating bromine from 1,3-dibromoalkanes, by the use of zinc dust in refluxing aqueous ethanol. An improved yield (>90%) of substituted cyclopropanes was achieved by Boord⁶ modifying Gustavson's method by adding the alkane dropwise. Kaplan⁷, used peroxides to eliminate iodine from 1,3-diiodopropane to give cyclopropane in 90-100% yield.

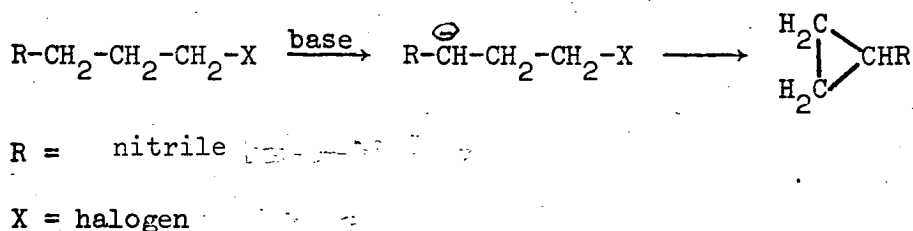
The use of magnesium with γ -bromo-ethers or α,γ -dihalo-compounds^{8,9,10} also give good yields (ca. 60-80%) of cyclopropanes.



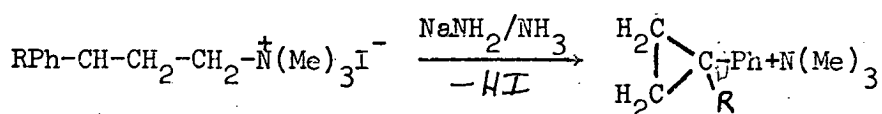
The use of a base rather than a metal to promote the elimination was used in the synthesis of 1,1-dicarbethoxycyclopropane¹¹ from malonic ester and 1,2-dibromoethane in the presence of sodium ethoxide.



A more versatile synthesis¹² involves the formation of an intermediate stabilised anion in an activated methylene compound which has a good leaving group in the γ -position.

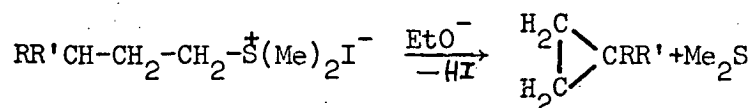


This general method of base induced intramolecular cyclisation was also employed in the synthesis of aryl substituted cyclopropanes by Bumgardner¹³ and Schmidt¹⁴. Bumgardner¹³ used 3-phenyl- and 3,3-diphenyl-propyltrimethyl ammonium iodide with sodamide in liquid ammonia to give phenylcyclopropane and 1,1-diphenylcyclopropane respectively.



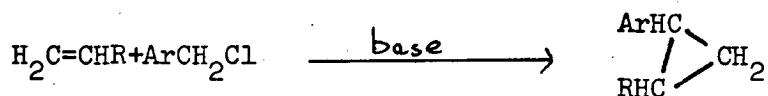
$R = H \text{ or } Ph.$

Schmidt¹⁴ used the sulphur analogue with ethoxide ion as the base to give substituted cyclopropanes.

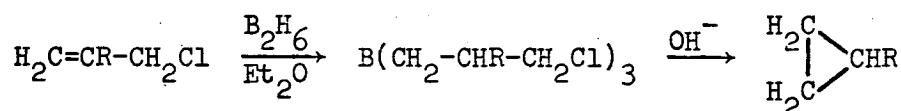


R = H, Bz, Ph or CN. R' = Bz, Ph or CN.

Certain cyclopropanes can also be formed by base induced condensation reactions. α,β -Unsaturated esters or nitriles react with α -halogeno esters and strong bases¹⁵ and substituted benzyl chlorides react with olefins in the presence of lithium-2,2,6,6-tetramethyl-piperidide¹⁶ as base. Both reactions proceed via stereospecifically cis additions thus eliminating stepwise nucleophilic attack.

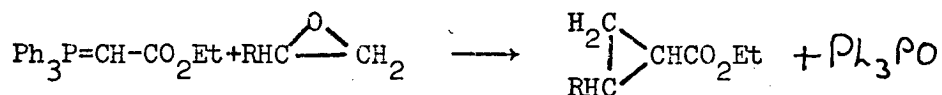


β -Alkylallyl or β -arylallyl chlorides yield substituted cyclopropanes when treated with diborane followed by base¹⁷.



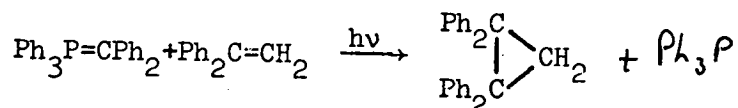
R = alkyl or aryl.

Pentavalent phosphorus compounds have also been employed in the preparation of substituted cyclopropanes. Denny¹⁸, used the action of phosphoranes on alkene oxides to form carbethoxycyclopropanes in moderate yields (20-60%),



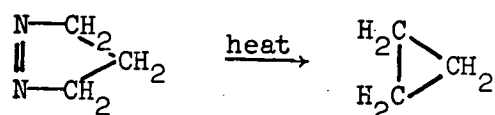
and Ritter¹⁹ irradiated phosphoranes, in the presence of excess olefin, with light of a wavelength greater than 300 m μ to give aryl substituted

cyclopropanes in good yield (ca. 70%).



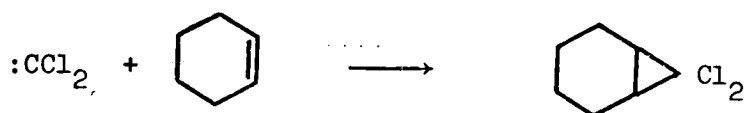
The reaction of phosphine oxides with alkene oxides has also been described²⁰ in the preparation of substituted cyclopropanes.

The action of ultraviolet light^{21,22,23} or heat²⁴ on 1- or 2-pyrazolines also leads to cyclopropanes. The mechanism of the decomposition has been the subject of a great deal of discussion. Crawford²⁵ suggested that the thermal decomposition went via a non-concerted biradical intermediate due to the large positive entropy of activation, and later substantiated this²⁶ by



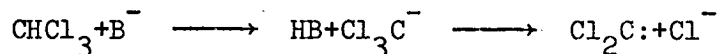
establishing from kinetic data that the transition state was nitrogen free. The biradical mechanism is accepted for both thermal and ultraviolet light methods of decomposition. The electronic state of the biradical in thermal decomposition is a ground state singlet²⁷ and in the ultraviolet light case an excited singlet²⁸. Only in the case of benzophenone sensitisation has a triplet biradical been consistently postulated²⁸.

The formation of cyclopropane rings by the addition of a carbene to an olefin was first demonstrated by Doering and Hoffmann²⁹, who obtained dichloronorcaradiene by the addition of dichlorocarbene to cyclohexene.



The dichlorocarbene was generated by the action of potassium *t*-butoxide on chloroform in an aprotic solvent. The mechanism of formation of dichlorocarbene was first postulated by Geuther³⁰ during his studies

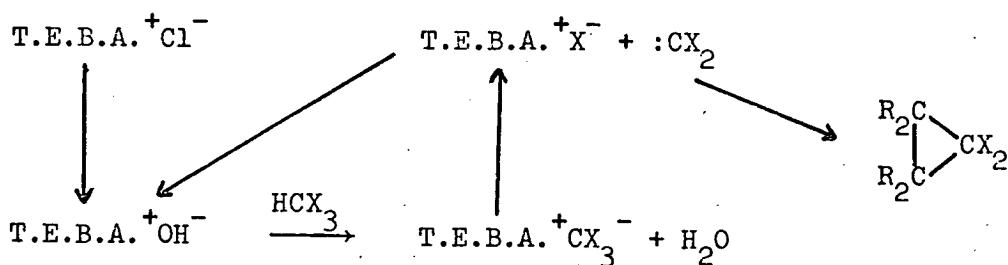
of the alkaline hydrolysis of chloroform and this



was confirmed eighty-eight years later by Hine³¹.

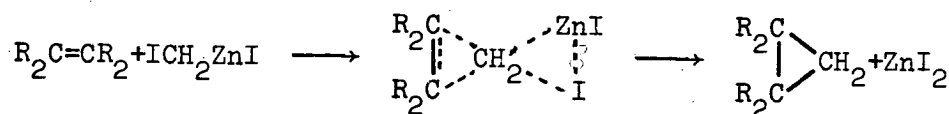
Carbenes exhibit an electrophilic rather than diradical nature^{32,33} and subsequently, yields of cyclopropanes formed by this method are higher when electron donating substituents are present on the olefinic double bond. It has been shown that carbenes generated by the action of base exist in a singlet ground state whereas other methods of carbene generation can give triplet species³⁴. Dihalocarbenes add stereospecifically to olefins^{34,35} and therefore exist as ground state singlets, whereas dicyanocarbene³⁶ does not give retention of stereochemistry, the reaction proceeding via a ground state triplet.

The use of aqueous basic conditions for the generation of dihalocarbenes has recently been described. Makosza and Wawrzyniewicz³⁷ used 50% aqueous sodium hydroxide, with a catalytic amount of triethylbenzylammonium chloride (T.E.B.A.Cl.) as catalyst, to generate dibromocarbene from bromoform which, in the presence of olefins gives good (60%-70%) yields of gem-dihalocyclopropanes. The use of other catalysts, such as cetyltrimethylammonium chloride or the detergent cetrimide, with chloroform in the presence of olefins are reported to give³⁸ even better yields of cyclopropanes (up to 98%). The mechanism of these phase transfer reactions is as follows³⁷. The catalyst e.g. T.E.B.A.Cl. reacts with the base to form the hydroxide which is insoluble in the basic medium. This solid then comes in contact with the organic phase and reacts with the haloform present to give triethylbenzylammoniumtrihalomethylide and water. This then decomposes to give dihalocarbene and T.E.B.A.halide to restart the cycle. The reaction sequence is summarised below.

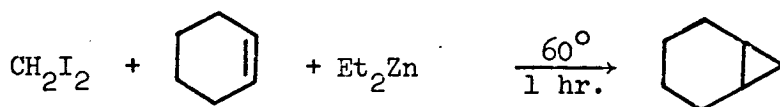


Methylene itself³⁹ can be prepared by the pyrolysis or photolysis of diazomethane or keten, however the carbene, generated in this way, is so indiscriminate, giving insertion and addition products with olefins, that it is of little preparative value. The method however has been used to form diphenylcarbene⁴⁰ by the photolysis of diphenyldiazomethane and to form substituted cyclopropanes by the action of heat on carbethoxydiazomethane in the presence of olefins⁴¹.

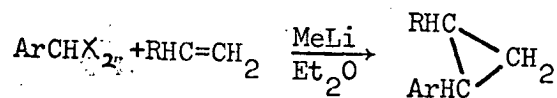
The generation of methylene from methylene halides^{42,43}, by means of a zinc copper couple in ether, affords a discriminating singlet carbene, adding stereospecifically to olefins. The intermediate⁴⁴ is not the free carbene, :CH_2 , but the complex ICH_2ZnI . This so called carbenoid intermediate reacts with the olefin present to give the cyclopropane.



Diethylzinc has also been used⁴⁵, instead of the zinc copper couple, in the reaction of methylene iodide with olefins giving moderate yields of cyclopropanes.

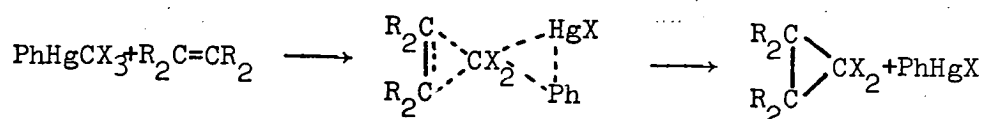


The use of various metals to produce carbenoid intermediates has been widely studied. Trichloromethyl lithium with cyclohexene yields dichloropropene⁴⁶, whilst methyl lithium with *p*-tolyl dihalomethane and an olefin⁴⁷ give arylcyclopropanes.



R = alkyl.

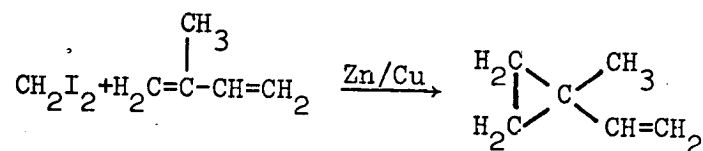
Phenyl(trihalomethyl)mercury⁴⁸ and benzylmercurioiodomethane⁴⁹ with olefins give dihalocyclopropanes and cyclopropanes respectively via a mercury carbenoid intermediate.



Similar reactions have been reported for ~~organ~~ organo-aluminium⁵⁰ and zinc⁵¹ compounds.

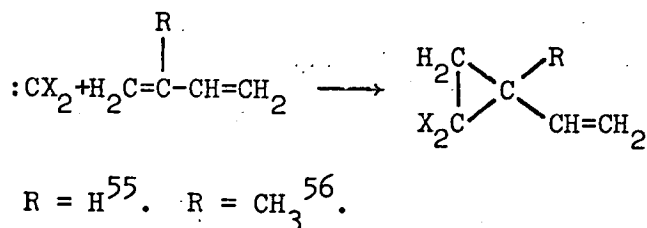
1.2 Synthesis of vinyl- and other related cyclopropanes

Vinylcyclopropane is formed during the photolysis of keten or diazomethane⁵² in the presence of buta-1,3-diene, however the indiscriminate nature of this carbene limits the preparative value of this method. Methylene, generated from methylene iodide and a zinc copper couple has been used⁵³ to prepare 1-methyl-1-vinylcyclopropane from isoprene in 65% yield.

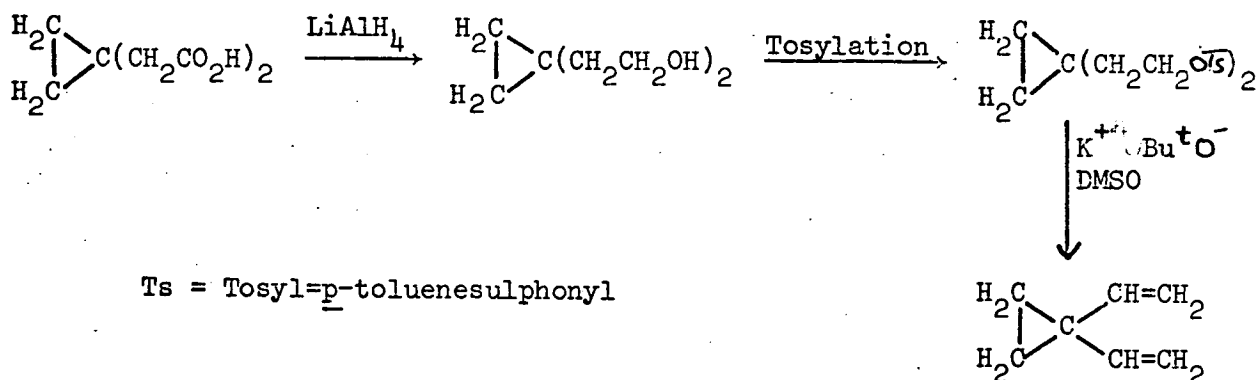


Irradiation of cyclopentene at low pressure with a mercury lamp⁵⁴ also yields vinylcyclopropane contaminated with a small amount of dimeric material.

Dihalovinylcyclopropanes have been prepared by the addition of halocarbenes, generated from haloforms and potassium t-butoxide in an aprotic medium, to buta-1,3-diene⁵⁵ and isoprene⁵⁶.



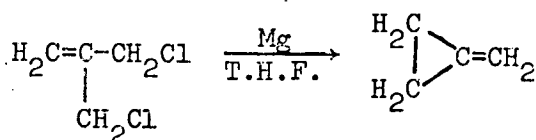
In both cases where addition of the carbene to isoprene was carried out only one product was obtained, attack of the carbene being at the methylated double bond. This is consistent with the electrophilic nature of carbenes, attack taking place at the double bond with the highest electron density^{32,33}. Dolbier⁵⁷, prepared 1,1-divinylcyclopropane from cyclopropane-1,1-diacetic acid by reduction of the acid, tosylation of the di-alcohol so formed and finally elimination using potassium t-butoxide in dimethylsulphoxide at 60°.



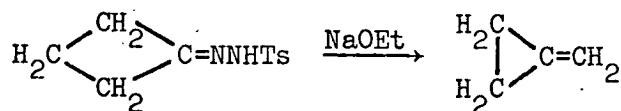
Irradiation of diazopropyne⁵⁸ with 2-methylbut-1-ene-3-yne gives 1-methyl-1,2-diethynylcyclopropane.

1.3 Synthesis of methylenecyclopropanes

Methylenecyclopropane was first prepared⁵⁹ by the elimination of chlorine from 1,3-dichloro-2-methylenepropene using magnesium in refluxing tetrahydrofuran,



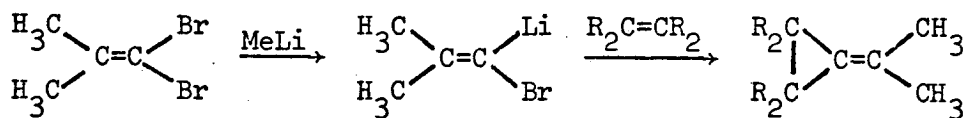
and has since been prepared in good yield by decomposition and ring contraction of cyclobutanonetosylhydrazone⁶⁰.



Ts = Tosyl.

The synthesis of substituted methylenecyclopropanes is not however possible by this method and generation of methylene carbenes from chloroalkenes⁶¹ and strong base gives low yields, even in refluxing tetrahydrofuran.

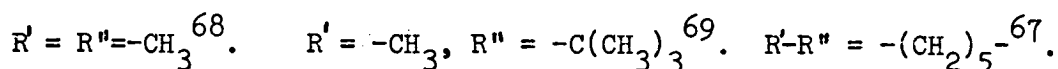
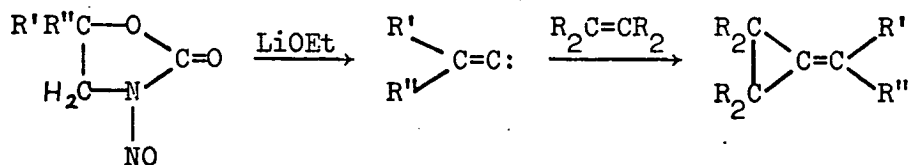
Substituted methylenecyclopropanes have been prepared in better yields (12-70%) using the method devised by Hartzler⁶². His synthesis involved the generation of isopropylidenecarbene by an α -elimination reaction from 1,1-dibromo-2-methylprop-1-ene using methyllithium in the presence of excess olefin. The reaction proceeds via the organolithium derivative and is stereospecific.



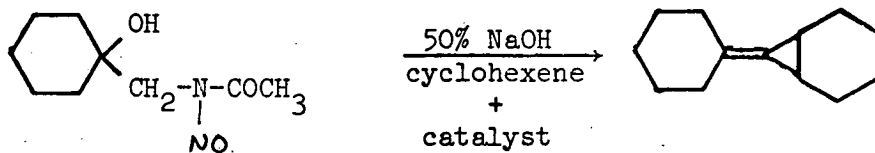
Similar results and yields⁶³ were obtained when using 1-chloro-1-iodo-bibenzylethylene or 1-chloro-2,2-bibenzyl lithium as carbene precursor.

1,2-Di-isopropylidenecyclopropanes have been formed⁶⁴ by the addition of isopropylidenecarbene, generated by Hartzler's method⁶², to tetramethylallene or 1,1-dimethylallene. Here it is noteworthy that the carbene attacks the less alkylated double bond in 1,1-dimethylallene giving only one product, this is not expected due to the electrophilic nature of carbenes. Dihalocarbene addition to allenes^{65,66} also yields substituted cyclopropanes, addition of the carbene occurring at the double bond with the greater electron density.

The base induced decomposition of N-nitroso-oxazolidones in the presence of olefins has been extensively studied⁶⁷⁻⁷¹. Newman⁶⁷⁻⁷⁰ has obtained substituted methylenecyclopropanes by the reaction of substituted N-nitroso-oxazolidones with lithium ethoxide in the presence of olefins

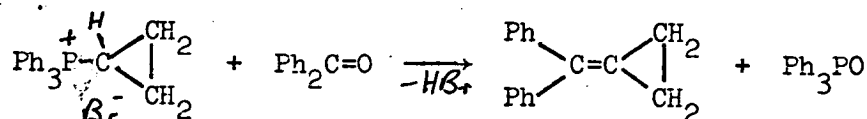


Newman⁷³ has since reported a method of preparing cyclohexylidene-cyclopropanes in good yield (60-80%) from 1-(N-nitroso-acetylaminomethyl)-cyclohexanol and olefins by the action of aqueous sodium hydroxide with methyltricaprylammonium chloride as catalyst.



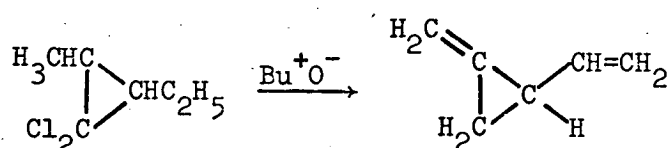
The reaction sequence here is analogous to that cited for the previous phase transfer process³⁷ (section 1.1).

Diphenylcyclopropylidenemethane has been prepared by the reaction of benzophenone with cyclopropylidenetriphenylphosphonium⁷⁴ bromide⁷⁴.



The use of base to eliminate hydrogen halides from alkyl substituted halocyclopropanes has also been used to form methylenecyclopropanes. Hanack⁷⁵ eliminated hydrogen bromide from 1-alkyl-2-

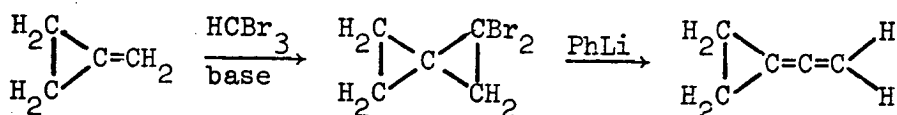
bromocyclopropane to give an alkyl substituted methylenecyclopropane and Shields⁷⁶ eliminated two moles of hydrogen chloride from 3-methyl-2-ethyl-1,1-dichlorocyclopropane to give 1-methylene-2-vinylcyclopropane in 90% yield.



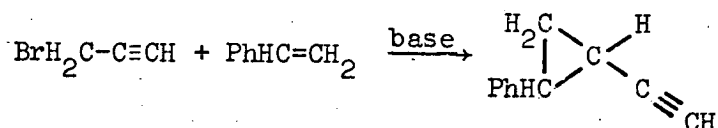
Both of these reactions proceed via a cyclopropene intermediate.

1.4 Synthesis of vinylidenecyclopropanes

Vinylidenecyclopropane has been prepared⁷⁷ by the addition of dibromocarbene to methylenecyclopropane with subsequent debromination and rearrangement of the spiro intermediate using phenyllithium.



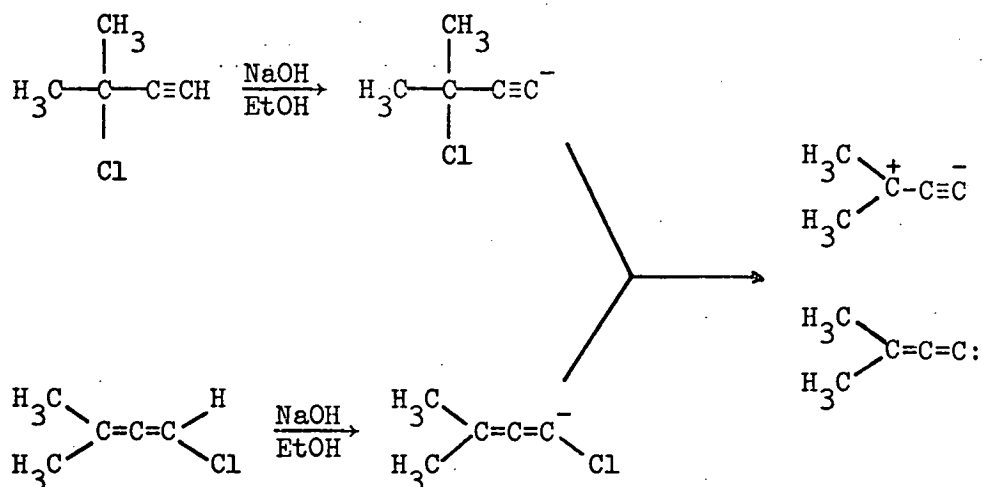
Hartzler⁷⁸ had previously attempted to synthesise 1-phenyl-2-vinylidenecyclopropane by the addition of vinylidenecarbene, formed by the action of base on 3-bromoprop-1-yne, to styrene, however he only obtained 1-phenyl-2-ethynylcyclopropane, the vinylidene-cyclopropane



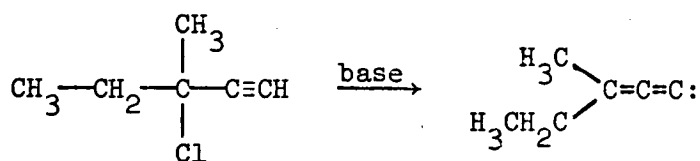
rearranging instantaneously to the less strained ethynylcyclopropane.

The most general synthesis of vinylidenecyclopropanes is by the addition of substituted vinylidenecarbenes to olefins. The existence of dimethylvinylidenecarbene as an intermediate was postulated^{79,80} in the mechanism of base catalysed hydrolysis

of 3-chloro-3-methyl-but-1-yne and 1-chloro-3-methylbuta-1,2-diene.



Hartzler^{78,81} obtained dimethylvinylidenecyclopropanes in 50% yield by reacting 3-chloro-3-methylbut-1-yne with olefins in the presence of alcohol free potassium t-butoxide. This method was later adopted⁸² for the preparation of an unsymmetrical vinylidenecarbene from 3-methyl-3-chloro-pent-1-yne.



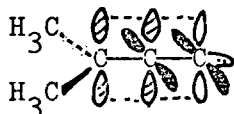
Landor⁸³ showed that E- and Z-isomers are formed when unsymmetrical carbenes react with certain olefins, Leandri⁸² however fails to report this, although he did add an unsymmetrical carbene to 2-methylbut-2-ene. Generation of vinylidenecarbenes from 1-chloroallenes⁸⁴ and 1-bromoallenes⁸³ has been reported, 1-bromoallenes with potassium t-butoxide/butanol 1:1 complex giving the better yields of vinylidenecyclopropanes in reactions with olefins. A further modification⁸⁵, namely using a solution of olefin in light petroleum instead of neat olefin leads to cleaner reactions and is less wasteful of sometimes valuable olefins.

A comparative study⁸⁶ of the addition of dimethylvinylidene-carbene and isopropylidenecarbene to para substituted styrenes showed that the ratio of isopropylidenecyclopropanes to dimethylvinylidene-cyclopropanes, from equimolar quantities of carbene precursor, was 1 to 4, demonstrating the differing reactivities of the carbenes.

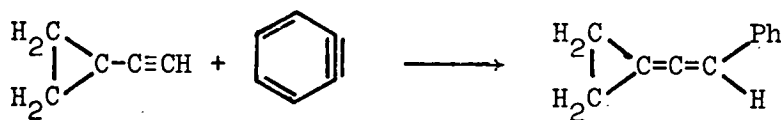
Diarylvinylidene- and di-*t*-butylvinylidenecyclopropanes have also been prepared by the action of potassium *t*-butoxide on the acetates formed from 1,1-diaryl-⁷⁸ and 1,1-di-*t*-butyl-prop-1-yne-3-ol⁸⁷ in the presence of olefins. Cyclopropane formation by this method gives yields similar to those obtained from the tertiary-acetylenic halides. Comparison of rates of addition⁸⁷ of dimethyl- and di-*t*-butylvinylidenecarbenes to various olefins shows that the steric effect of substituents on the carbenes are negligible.

Recently the use of a phase transfer system to prepare dimethylvinylidenecyclopropanes has been reported⁸⁸. 3-Methyl-3-chlorobut-1-yne was allowed to react with various olefins, in benzene as solvent, in the presence of 50% aqueous sodium hydroxide solution containing benzyltriethylammonium chloride as catalyst. The yields of dimethylvinylidenecyclopropanes obtained were better than those for corresponding olefins where 3-methyl-3-chlorobut-1-yne was treated with potassium *t*-butoxide to form the carbene.

The addition of vinylidenecarbenes to olefins proceeds stereospecifically⁸⁹, increased yields being obtained when there is an increase in electron density associated with the double bond. Vinylidenecarbenes are more stable than alkyl- or methylenecarbenes⁸⁹ due to the overlap of the vacant *p*-orbital with the π -electrons of the β,γ -double bond, this being a possible reason for the

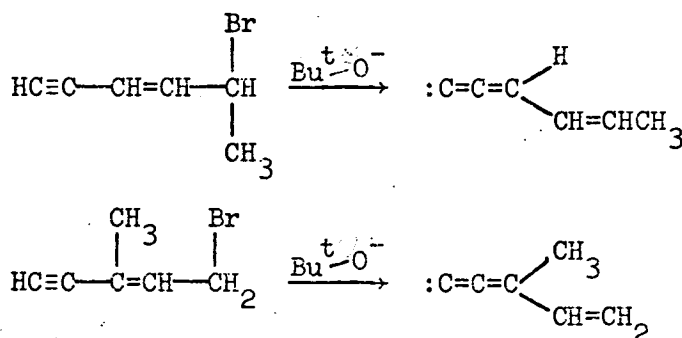


variation in reactivity between dimethylvinylidene and isopropylidene-carbenes already described⁸⁶. Other methods of formation of vinylidene-cyclopropanes are of a less general type. The addition of benzyne to 1-ethynylcyclopropane gives 1-cyclopropylidene-2-phenylethylene⁹⁰,



and the decomposition of the lithium salt of 3-methyl-3-chlorobut-1-yne⁹¹ at up to 20°C is reported to proceed via the dimethylvinylidenecarbene intermediate giving a 52% yield of 1-phenyl-2-dimethylvinylidenecyclopropane in the presence of styrene.

There are also reports of vinylidenecyclopropanes containing further unsaturated moieties. Bleiholder and Shechter⁹² have prepared 1-isopropylidene-2-dimethylvinylidenecyclopropane and 2-isopropylidene-3-dimethylvinylidene-1,1-dimethylcyclopropane by the addition of dimethylvinylidene-carbene, formed by the reaction of 3-chloro-3-methylbut-1-yne with potassium t-butoxide, to a five-fold excess of 1,1-dimethylallene and tetramethylallene respectively. Gore and Doutheau⁹³ have prepared adducts of various olefins by the action of potassium t-butoxide on 1-bromo-3-methylpent-2-ene-4-yne and 2-bromo-1-hex-3-ene-5-yne-1-yne,



the authors report the existence of E- and Z-isomers, as would be expected, on the addition of the carbenes to styrene.

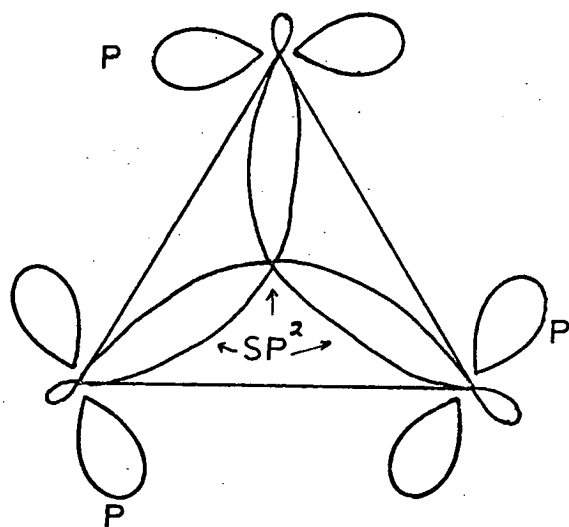


FIGURE I

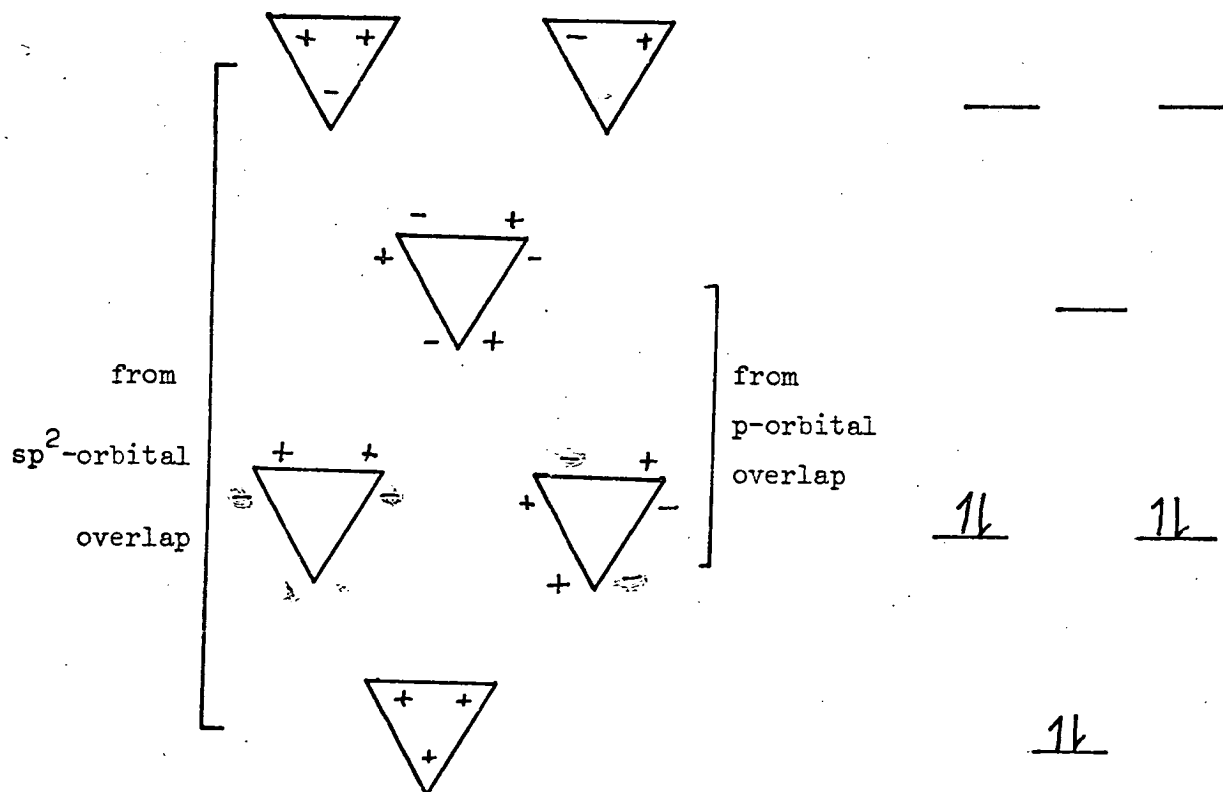
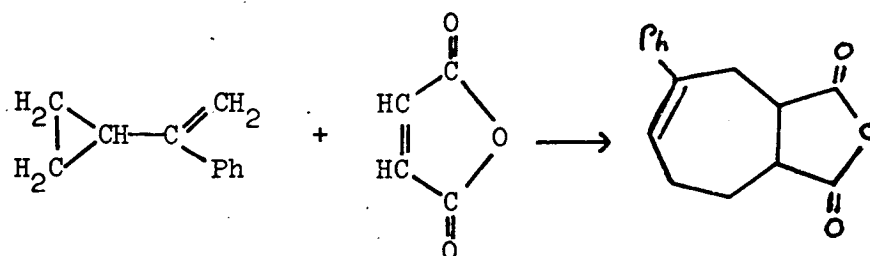


FIGURE II

2.0 Chemical behaviour and bonding characteristics of cyclopropanes

Cyclopropanes have a chemical behaviour intermediate between that of alkanes and alkenes. Addition and substitution products are formed when cyclopropane is halogenated⁹⁴ in the presence of a catalyst (e.g. light, oxygen or acid) and vinylcyclopropane acts as a conjugated diene⁹⁵, giving a stable adduct with maleic anhydride.



The carbon-carbon bonds in cyclopropanes have a strained nature allowing the ring to be easily cleaved by diborane⁹⁶, alkali metal in liquid ammonia⁹⁷ and protonated solvents⁹⁸.

This unexpected behaviour is explained in terms of the bonding in a cyclopropane ring. Two approaches have been of particular value.

Walsh⁹⁹ proposed that each carbon atom was sp^2 hybridised, giving one p-orbital and three sp^2 -orbitals per carbon atom of the cyclopropane ring. Two of the sp^2 -orbitals form C-H bonds leaving the p-orbital and one sp^2 -orbital to form the cyclopropane ring bonds. The p-orbitals of the three cyclopropane ring carbon atoms overlap round the outside of the ring, while the sp^2 -orbitals, which are directed towards the centre of the ring, overlap inside the ring (Figure I). The overlap of the p-orbitals give two bonding orbitals and one anti-bonding orbital, and the overlap of the sp^2 -orbitals give one bonding orbital and two anti-bonding orbitals (Figure II).

Coulson¹⁰⁰ later put forward the idea of bent bonds for cyclopropanes and this was extended by Randic and Maksic¹⁰¹ using the maximum overlap principle in their calculations. This approach requires two sp^2 hybridised orbitals and two sp^5 hybridised orbitals

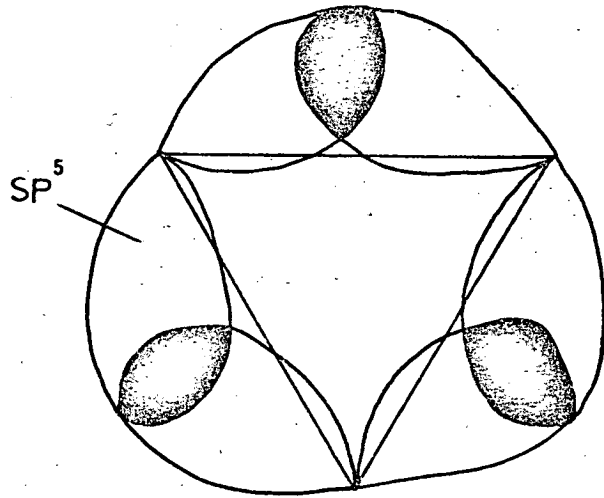


FIGURE III

at each ring carbon atom. As before the two sp^2 -orbitals form the C-H bonds, leaving the two sp^5 -orbitals of each carbon atom to overlap round the outside of the ring to form the bent bonds (Figure III).

Bernett¹⁰², in comparing the two approaches, demonstrates their equivalence. The carbon-carbon bonds in the Walsh treatment are made from one p-orbital and one sp^2 -orbital, broken down this can be written as $\frac{3}{3}p + \frac{2}{3}p + \frac{1}{3}s$, i.e. the C-C bond is made up of $\frac{1}{3}s$ and $\frac{5}{3}p$. Similarly, the Coulson treatment breaks down to be written as $2(\frac{1}{6}s + \frac{5}{6}p)$, i.e. the C-C bond is made up of $\frac{1}{3}s$ and $\frac{5}{3}p$. Both treatments show, that the carbon-carbon bond has a p-character intermediate between alkane and alkene carbon-carbon bonds and either approach is satisfactory in explaining the intermediacy of bond length and chemical behaviour which cyclopropanes exhibit, in comparison with alkanes and alkenes. X-ray diffraction data¹⁰³ supports the bent bond treatment and although it could be argued that bent bonds lose stability due to less overlap, there is a compensating effect in the decrease of angle strain¹⁰².

Studies of methylenecyclopropane¹⁰⁴ by the maximum overlap method, shows that there is less p-character in the ring bond hybrid orbitals. This, therefore, allows greater bond overlap, indicating that the presence of an exo-cyclic double bond has a stabilising effect on a cyclopropane ring. However, methylenecyclopropane is thermodynamically less stable than cyclopropane itself, therefore, the additional strain must lie in the double bond. Penn and Boggs¹⁰⁵ also report that there is a consistent shortening of the carbon-carbon bond opposite an unsaturated substituent compared with the corresponding length opposite saturated substituents. Hoffmann¹⁰⁶, in his studies of vinylcyclopropane, reports that there is a shortening of the carbon-carbon bond opposite the vinyl group due to

delocalisation of electrons, two electrons from the cyclopropane molecular orbital being able to interact with the vinyl π -system (Figure IV).

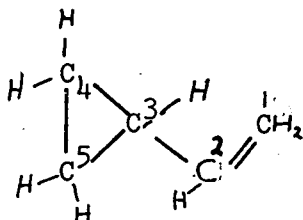
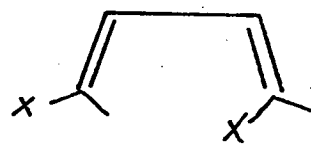
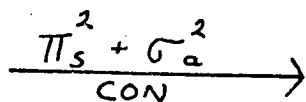
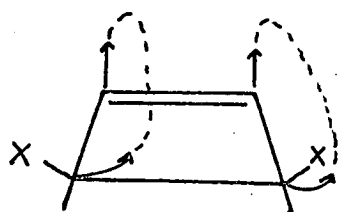


Figure IV

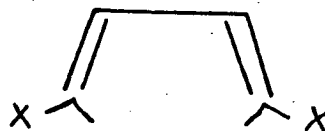
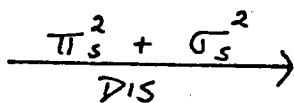
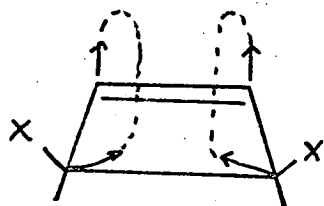
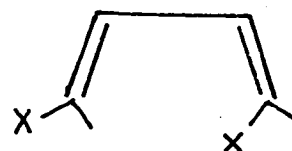
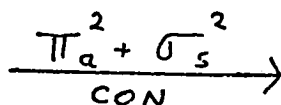
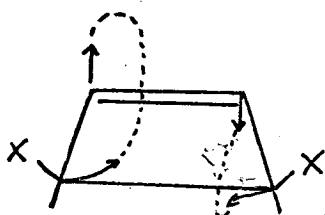
These two electrons are delocalised over the vinyl system, weakening the carbon-carbon bond between C(3)-C(4) and C(3)-C(5) and also weakening the anti-bonding between C(4)-C(5), consequently the C(4)-C(5) bond becomes stronger and therefore shorter. This is consistent with the stabilisation of cyclopropane rings which have electron acceptor groups attached to them and has been confirmed by X-ray diffraction data¹⁰³ from which bond lengths of 1.554 Å and 1.559 Å are obtained for C(3)-C(4) and C(3)-C(5) respectively while that obtained for C(4)-C(5) is only 1.501 Å, in a substituted norcaradiene.

3.0 The thermal rearrangement of cyclopropanes

The thermal unimolecular rearrangement of cyclopropane derivatives can proceed via discrete intermediates of short life, such as carbenes and diradicals, or via a concerted process involving only transition states. The precise mechanism of these rearrangements is often difficult to determine. Where diradicals are involved it is sometimes possible to confirm their presence by trapping experiments or, in the case of triplet species, by electron spin resonance spectroscopy. However, if the process is concerted no similar techniques are available. A concerted process is often associated with a negative entropy of activation and a smaller activation energy than would be expected for a stepwise process. Orbital symmetry considerations make it possible to predict whether a concerted process may take place but, even although



ALLOWED



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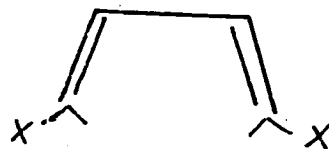
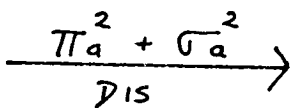
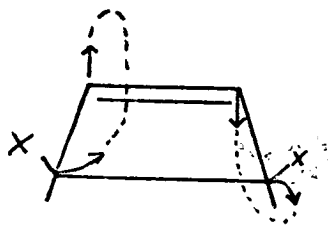


FIGURE V

a concerted process is possible, this does not exclude a diradical mechanism.

The thermal rearrangement of various types of cyclopropanes will be surveyed after a brief review of the theory of concerted processes.

3.1 The theory of thermal concerted reactions

Three general approaches to concerted reaction theory have been reported and can be used to predict if a reaction is possible and if so, the constraints which are applicable to the system. In 1965, Woodward and Hoffmann¹⁰⁷, by considering the symmetry of the highest occupied molecular orbital in reactant and product, were able to explain the stereospecific nature of certain cyclisation and ring opening reactions which had already been observed¹⁰⁸. Later, they expanded their theory¹⁰⁹ to encompass all reactions involving cyclic transition states (pericyclic reactions) and adopted the use of orbital correlation diagrams, in certain simple cases, initially introduced by Longuet-Higgins and Abrahamson¹¹⁰. From this work and further studies, they devised a generally applicable formula¹¹¹ which may be used to decide whether a concerted pathway is allowed for a given reaction, without recourse to molecular orbital theory. The formula is deduced as follows. The bond components which are involved in the pericyclic process are identified and classified according to whether they have $(4q+2)$ electrons or $(4r)$ electrons ($q, r = \text{integer}$). The bond components are then classified, according to the way in which they participate in the reaction, as suprafacial(s) or antarafacial(a). In a π -system, suprafacial participation is identified as formation of the new bonds on the same side of the π -system and antarafacial participation as

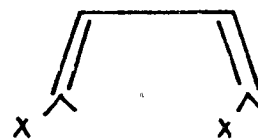
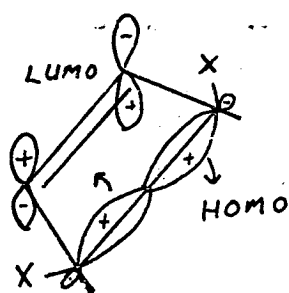
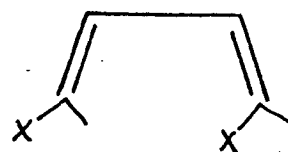
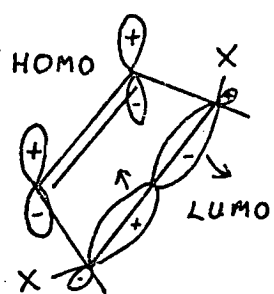
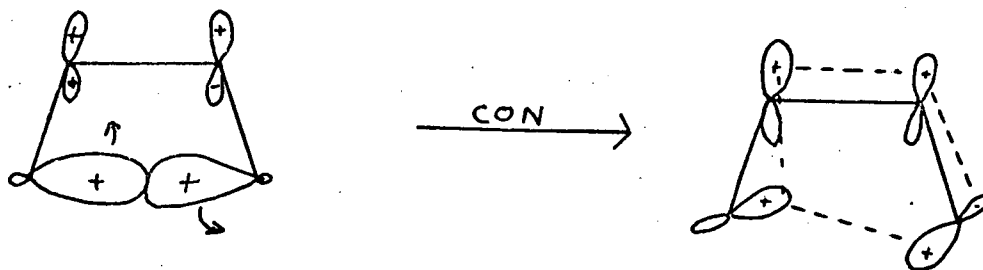


FIGURE VI

formation of the new bonds on opposite sides of the π -system. In the case of a σ -bond, suprafacial participation is defined as bond formation with retention or inversion of configuration at both centres and antarafacial participation as bond formation with retention of configuration at one centre and inversion at the other. Finally, the sum of the (total) number of $(4q+2)_s$ and $(4r)_a$ components are calculated. The reaction is thermally allowed if this sum is odd and not allowed if it is even. This can be illustrated by the thermal ring opening of cyclobutene to butadiene (Figure V) which has two $(4q+2)$ components, the π -bond and the σ -bond. There are four possible ways in which ring opening can be envisaged, however, for the reaction to be allowed one of the bonds must participate suprafacially and one antarafacially giving two allowed pathways. It is evident from the diagram that, in either of the allowed routes, the ring opening must be conrotatory to fulfil this condition, disrotatory ring opening leading to the two forbidden pathways.

The second theoretical approach¹¹² stresses the importance of the interaction between the highest occupied molecular orbital (HOMO) of one component and the lowest unoccupied molecular orbital (LUMO) of the other component, in a pericyclic reaction. The reaction takes place in the direction of maximum in phase overlap of these orbitals. This approach can also be illustrated by the thermal ring opening of cyclobutene to butadiene (Figure VI). In either case, maximum in phase overlap is obtained only if a conrotatory process takes place, disrotatory ring opening giving out of phase overlap.

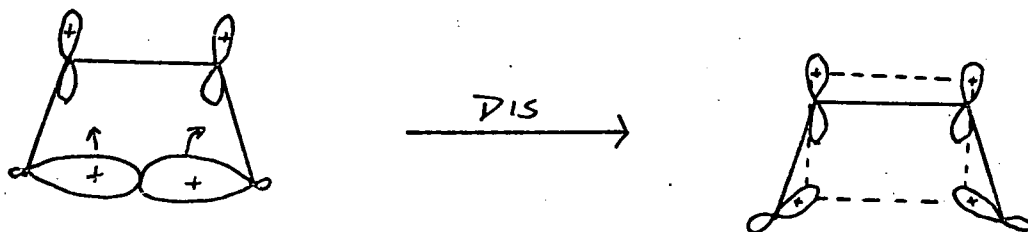
A third approach, proposed independently by Zimmerman¹¹³ and Dewar¹¹⁴, also leads to a formula applicable to reactions which have cyclic transition states. The formula is deduced as follows. The cyclic array of orbitals involved in the transition state is



Transition state has 1 node $\therefore$ is Mobius

It also involves 4 electrons

Mobius with $4N$ electrons = Allowed



Transition state has 0 nodes $\therefore$ is Hückel

It also involves $4N$ electrons

Hückel with $4N$ electrons = Forbidden

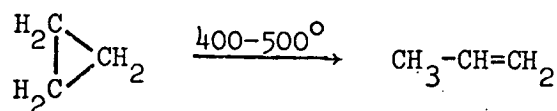
FIGURE VII

identified and arbitrarily assigned phases. The system is then defined as Mobius or Hückel in accordance with the number of sign inversions between the overlapping orbitals in the transition state. A Mobius system has an odd number of sign inversions and a Hückel system has zero or an even number of sign inversions. Finally the number of electrons involved in the components of the transition state is calculated. The reaction is thermally allowed if the transition state is Hückel and involves $(4N+2)$ electrons or if the transition state is Mobius and involves $(4N)$ electrons ($N=\text{integer}$). This approach requires no prior knowledge of the molecular orbitals of the molecule or molecules involved and is therefore particularly simple to use. The thermal ring opening of cyclobutene to butadiene again serves as a good illustration of this treatment (Figure VII). The system involves four electrons and therefore, to be allowed thermally, the transition state must be Mobius. This transition state can only be obtained by conrotation, disrotation leading to a Hückel transition state. No matter which of the three approaches is adopted the end result is always in agreement.

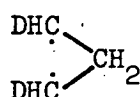
It should however be noted that these approaches take into account only simple electronic factors and no attempt has been made to modify them in the light of steric or advanced electronic factors. It has been shown^{115,116,117} that some pericyclic reactions, which are not allowed on the basis of the rules set out in the preceding pages, do take place in a concerted manner due to steric and/or electronic factors.

3.2 Thermal rearrangement of saturated cyclopropanes

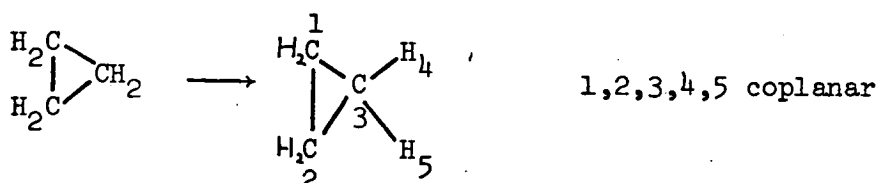
Cyclopropane, when pyrolysed at elevated temperatures, rearranges to form propylene¹¹⁸.



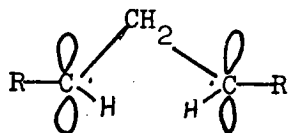
Rabinovitch¹¹⁹ studied the rearrangement of cis- and trans-1,2-di-deuteriocyclopropanes and found that equilibration of the isomers occurred sixteen times faster than the formation of the olefin. He suggested that the intermediate was the trimethylene diradical, this being consistent with his finding



that deuterium did not "exchange" during the reaction to give unsymmetrical products. Smith¹²⁰ proposed that this intermediate could be replaced by one where the hydrogen atoms, bonded to one of the carbon atoms, would be coplanar with all three carbon atoms. Collapse of this intermediate



could give retention or inversion of geometry about C(3) and migration of H(5) to C(2) with rupture of C(1)-C(2) would give the olefin. As a third possibility, Hoffmann¹²¹ has proposed a π -cyclopropane transition state allowing a concerted reaction to take place.



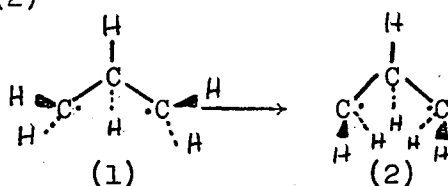
Evidence both for and against these three mechanisms has accumulated over the years. Benson provided support for the diradical mechanism by calculations based on kinetic and thermodynamic data¹²², and by kinetic isotope studies on hexadeuteriocyclopropane¹²³. This work

refuted similar isotope studies done by Blades¹²⁴, who had interpreted his own results in a way which supported the Smith¹²⁰ proposals. Geometrical isomerism occurs more rapidly than ring cleavage to the olefin during the pyrolysis of cis-1,2-dimethylcyclopropane¹²⁵ and cis-1,2,3-trimethylcyclopropane¹²⁶. These reactions have high energies and entropies of activation consistent with the rotational freedom of a diradical intermediate¹²⁷. It is also noteworthy that the pyrolysis of methylenecyclopropane¹²⁸ yields the four possible butenes, unselectively. This fact, together with the high activation energy for the reaction (65 K cal. mol⁻¹), adds further support to the diradical mechanism. Attempts to trap the diradical intermediate with alkyl iodide¹²² and to force the diradical to dimerise at high pressures (300 At.)¹²⁹ have failed, showing that the lifetime of the intermediate is less than 10⁻¹³ seconds.

The thermal rearrangement of optically active cyclopropanes introduces the possibility of racemisation as well as geometrical isomerism. Crawford¹³⁰ studied the racemisation and isomerisation of trans-1,2-diphenylcyclopropane, there being no likelihood of olefin formation. They found that racemisation was faster than the conversion to the cis-isomer, due to the steric hinderance to cis-isomer formation, however their results were consistent with a diradical intermediate. Further support for a diradical intermediate was proposed by Bergman¹³¹. In his studies of optically active 1-ethyl-2-methylcyclopropane he found that the rates of racemisation and cis-trans isomerisation were similar, implying that the Hoffmann¹²¹ concerted process would be energetically less favourable than the diradical mechanism. If a concerted pathway were possible the rate of racemisation would be expected to be greater than that of cis-trans isomerisation. The Smith¹²⁰ model does not fully account for these results.

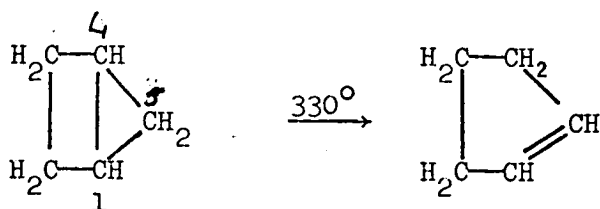
Neither Crawford¹³⁰ nor Bergman¹³¹ state that the diradical mechanism is the mechanism of the reaction, only that their results are consistent with that possibility. Berson¹³² shows, from rate constant measurements, that none of the three mechanisms can be solely responsible for the observed results. Studies of the thermal rearrangement of 1-phenylcyclopropane¹³³ show that a mixture of n-propylbenzene, α -methylstyrene, β -methylstyrene and other degradation products are formed. This was rationalised in terms of a diradical mechanism due to the indiscriminate nature of the reaction.

Recent theoretical investigations into this mechanistic problem have failed to clarify the situation. Salem¹³⁴ reports that the diradical (1) expected from cyclopropane can collapse to a "crab-like" structure (2)

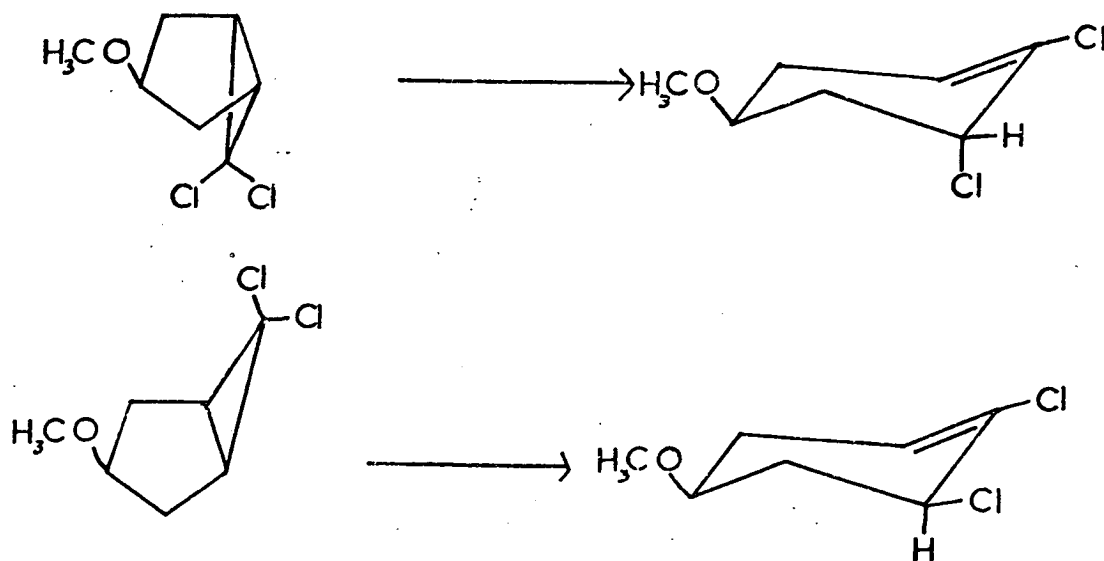


There is a gain in stabilisation energy of 6.2 K cal. mol⁻¹ in going from structure (1) to structure (2) and there is no barrier to structure (2) reclosing to form cyclopropane. Salem therefore infers that the diradical mechanism is more probable than a concerted process. However, in later communications Goddard¹³⁵ and Salem¹³⁶ both state that their molecular orbital calculations are in agreement with experimental results^{131,132} and the diradical mechanism.

Ring cleavage of bicyclic systems containing a cyclopropane ring have also been studied. Bicyclopentane rearranges at 330°C to give cyclopentene¹³⁷, the mechanism of this reaction involving cleavage of the C(1)-C(4)



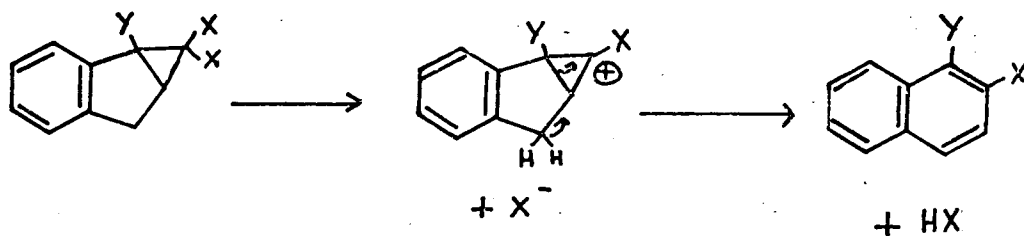
bond and migration of a hydrogen atom from C(S)¹³⁸. The thermal rearrangement of gem-dihalobicyclic systems have been extensively studied. The thermal rearrangement of 6,6-dichlorobicyclohexane¹³⁹ gives quantitative yields of 2,3-dihalocyclohex-1-ene and a similar reaction is observed for the thermal rearrangement of 9,9-dihalobicyclo-[6,1,0]nonane¹⁴⁰ which yields 2,3-dihalocyclonon-1-ene. Bergman¹³⁹, however reports that 8,8-dichlorobicyclo[5,1,0]octane is thermally stable at 225°. Fleming and Thomas^{141,142} proposed a mechanism for these bicyclic reactions. They found that the thermal rearrangement of anti-6,6-dichloro-3-methoxybicyclo[3,1,0]hexane at 160°C exclusively forms trans-1,6-dichloro-4-methoxycyclohex-1-ene while the syn-isomer exclusively forms the cis-cyclohexene.



These reactions proceed stereospecifically independent of solvent polarity and concentration. The results can be interpreted in terms of a concerted process ($\sigma_s^2 + \sigma_a^2$) or an ion pair mechanism. Any ion

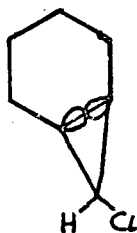
pair, however, must be intimate as rearrangement always precedes solvolysis. This was demonstrated by the fact that, if nucleophilic attack could take place before rearrangement, the cis-chloro-nucleophile isomer would be obtained from the syn-bicyclohexane, whereas, if the reverse were true, the trans-isomer would be obtained from the syn-bicyclohexane. The latter was found to be true in all cases, even when the powerful nucleophile phenylthioxide ion was used.

2,3-Benzo-6,6-dihalobicyclo[3,1,0]hexene and 1-methyl-2,3-benzo-6,6-dihalobicyclo[3,1,0]hexene rearrange¹⁴³ at 100°C to give β-halo- and α-methyl-β-halonaphthalenes respectively, kinetic data indicating that ionisation of a carbon-halogen bond is the rate determining step and is followed by, the thermally allowed, disrotatory ring opening to give the products.

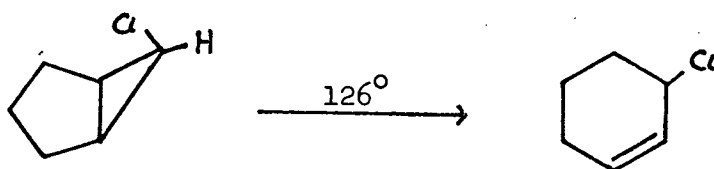


2,3-Benzonorcaradiene and its 7-gem-dideutero analogue rearrange¹⁴⁴ at 260° to give 1,1,2-benzocycloheptatriene, however, the evidence from the dideutero studies can be rationalised in terms of either a diradical or concerted process.

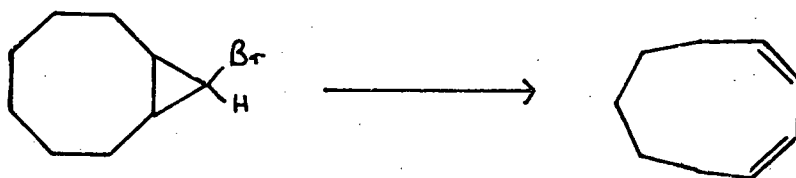
Concerted reaction theory predicts that, in monohalobicyclo systems, ring opening of the endo-isomer should be more facile than ring opening of the exo-isomer, the allowed mode of thermal ring opening being disrotatory. It can be seen that disrotation in the case of the exo-isomer would have to be inwards and would therefore be impossible.



This was confirmed by Baird and Reese^{145,146}, endo-6-chlorobicyclo[3,1,0]hexane giving the expected 3-chlorocyclohex-1-ene at 126°C and the exo-isomer being stable at 300°C.

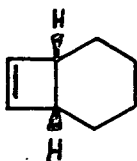


Japanese workers¹⁴⁷ showed similar results for the endo- and exo-isomers of 7-chlorobicyclo[4,1,0]heptane. Baird and Reese extended their work to larger bicyclic systems¹⁴⁰ in order to observe the effect of ring size on the reactions. The endo-isomer of 9-bromobicyclo[6,1,0]nonane is stable at 202°C while the exo-isomer rearranges at 185°C to yield cis-3-bromocyclononene, this suggesting that a non-concerted process was operating. Neither the exo- or endo-isomers of 8-bromobicyclo[5,1,0]octane rearrange at 230-250°C to the expected cycloalkene. Thermolysis of the exo- and endo-isomers of 8-bromobicyclo[5,1,0]octane in solution at 195°C both gave rise to cis-cis-cycloocta-1,3-diene as the sole product. Similarly the thermolysis of the corresponding bicyclononanes at 195°C gave only the cis-cis-cyclonona-1,3-diene.

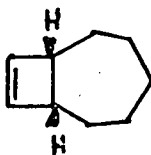


The endo-isomer would be expected to give the cis-cis-product in both cases but the exo-isomer should give the trans-cis-product, if the process were concerted. The interconversion of the cis-cis

and trans-cis-isomers is possible¹⁴⁸ via an intermediate bicyclo[4,2,0]-oct-7-ene (3) or bicyclo[5,2,0]non-8-ene (4), both of which ring



(3)

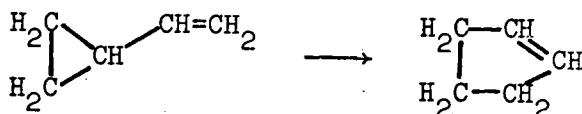


(4)

open irreversibly to give the cis-cis-isomer, however, the temperature required, for the formation of the intermediate to be favourable (300°C), is far in excess of the temperature used and therefore a non-concerted process seems more likely. The authors conclude that the thermal rearrangement of larger bicyclic compounds are not subject to the same stereochemical controls as the smaller bicyclic systems.

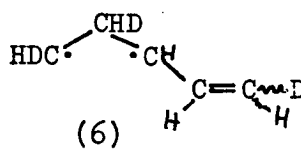
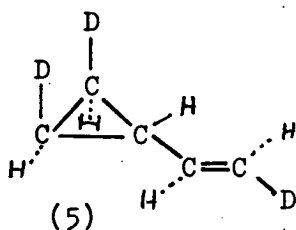
3.3 Thermal rearrangement of vinyl- and other related cyclopropanes

The thermal rearrangement of vinylcyclopropane to cyclopentene has been extensively reviewed¹⁴⁹.



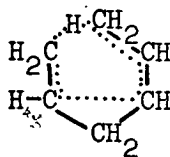
Flowers and Frey¹⁵⁰ suggest that a concerted mechanism is involved in this rearrangement, basing their postulate on the first order kinetic data which they obtained ($E_A = 49.6 \text{ K cal. mol}^{-1}$, $\Delta S = 0.3 \text{ eu}$). This proposal was later supported by Wellington¹⁵¹ who, working on the same system, proposed a concerted mechanism via a transition state in which the vinyl π -orbital interacts with the cyclopropane ring electrons. The ability of a cyclopropane ring sp^5 -orbital to conjugate with a vinyl substituent had already been demonstrated⁹⁵ and this added further credibility to Wellington's proposed mechanism. Further evidence for a concerted mechanism was put forward by Frey¹⁵², who showed that trans-1-cyclopropylbut-1-ene

rearranged to give 3-ethylcyclopentene as the product exclusively. However, the results of Willcott and Cargle^{153,154}, who studied the thermal rearrangement of selectively deuterated vinylcyclopropanes, are not interpreted in terms of a concerted process. They found that the loss of stereospecificity of the deuterium at the cyclopropane ring site was five times faster than the conversion to the cyclopentene¹⁵³ and that there was complete loss of stereochemistry in the thermal rearrangement¹⁵⁴ of 1-(trans-2-deuterovinyl)-trans-trans-2,3-dideuterocyclopropane (5)



Both of these observations are interpreted in terms of a diradical mechanism via the intermediate diradical (6) which is comparable to the trimethylenemethane diradical in the rearrangement of saturated cyclopropanes¹¹⁹.

Frey¹⁵⁵ also reports that cis-1-methyl-2-vinylcyclopropane readily rearranges at 160°C to give cis-hexa-1,4-diene via a seven membered cyclic transition state (7)



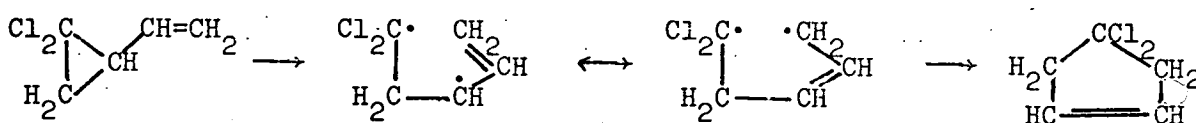
This transition state is not attainable in the trans-isomer and it was found¹⁵⁶ that a temperature of 300°C was required before the trans-isomer would rearrange to the cis-hexadiene. At this

temperature the reaction has an activation energy similar to that required for cis-trans-isomerisation and Frey suggests that, the formation of the cis-hexadiene results from the trans-1-methyl-2-vinylcyclopropane isomerising to the cis-isomer and that the cis-isomer then rearranges to the cis-hexadiene. A concerted mechanism was also proposed¹⁵⁷ for the exclusive formation of cis-2-methyl-hexa-1,4-diene from 1,1-dimethyl-2-vinylcyclopropane, a seven membered transition state analogous to that proposed for the cis-monomethyl case¹⁵⁵ (7) being possible. Similar results were observed for the thermal rearrangement of cis- and trans-1,2-divinylcyclopropane; the cis-isomer readily forms the expected cyclohepta-1,4-diene¹⁵⁸ (8) whereas the trans-isomer requires elevated temperatures¹⁵⁹ (200°C).



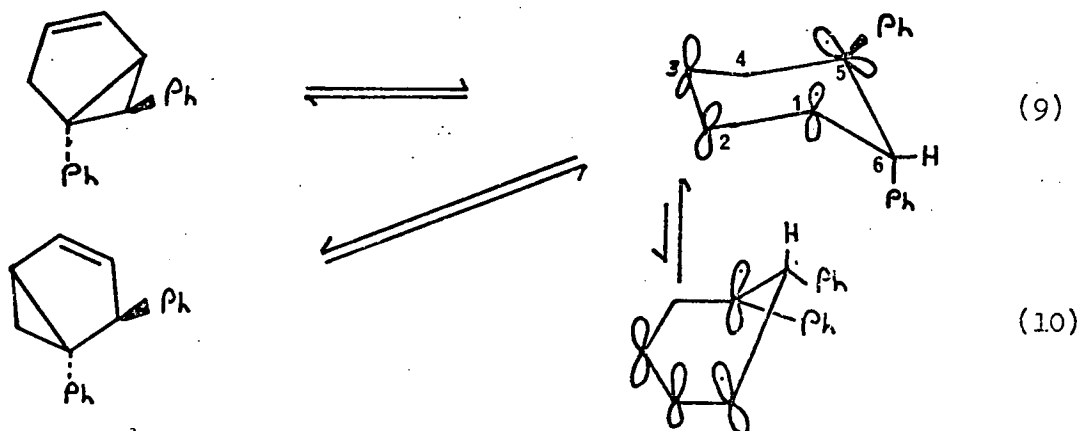
(8)

Ketley¹⁶⁰ suggests that the thermal rearrangement of vinylcyclopropane may proceed via a concerted process, however in substituted vinylcyclopropanes a diradical intermediate may be preferred, especially if the substituents are capable of stabilising the diradical. Consistent with this idea, the thermal rearrangement of 1,1-dichloro-2-vinylcyclopropane yields 1,1-dichlorocyclopent-3-ene, whereas a concerted reaction would be expected to result in a chlorine shift.



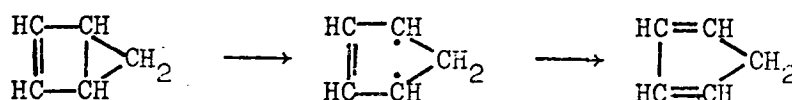
The thermal rearrangement of 1,1-divinylcyclopropane leads to the expected 1-vinylcyclopent-1-ene but it is not possible, from the kinetic data obtained ($E_A = 39.6 \text{ K cal. mol}^{-1}$, $\Delta S = -2.8 \text{ e.u.}$), to distinguish between a diradical or concerted mechanism.¹⁶¹

Vinylcyclopropane type rearrangements also take place in bicyclic systems. Trans-5,6-diphenylbicyclo[3,1,0]hex-2-ene equilibrates¹⁶² at 170° to give a mixture of 60% trans-5,6-diphenylbicyclo[3,1,0]hex-2-ene and 40% trans-4,5-diphenylbicyclo[3,1,0]hex-2-ene. This can be interpreted in terms of a concerted process or a stepwise mechanism in which ring closure of the diradical (9) is faster than rotation about C(5)-C(6). Rotation about C(5)-C(6) would lead



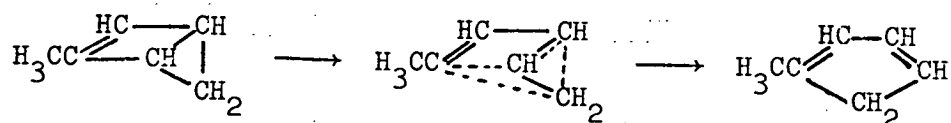
to the diradical (10) in which the steric interaction between the two phenyl groups is greatly increased, making the diradical (10) energetically less favourable.

The rearrangement of bicyclo[2,1,0]pent-2-ene to cyclopentadiene¹⁶³

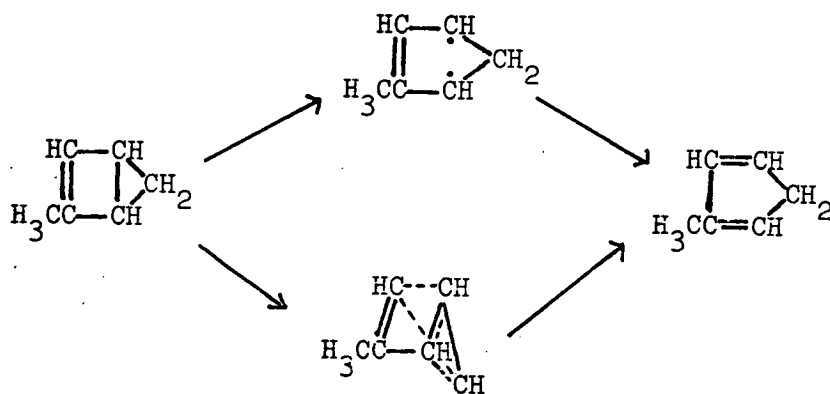


was originally considered to be a diradical process, however the

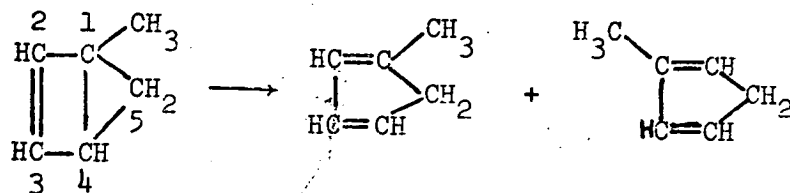
reported rearrangement¹⁶⁴ of 2-methylbicyclo[2,1,0]pent-2-ene, in solution, to give 1-methylcyclopenta-1,3-diene as the exclusive product,



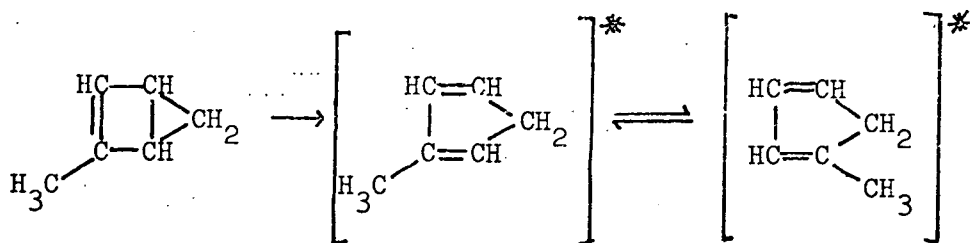
via a concerted ($\sigma_s^2 + \sigma_a^2$) process cast some doubt on the original postulate. Since the publication of this paper much controversy has raged. McLean¹⁶⁵, on repeating Baldwin's work¹⁶⁴ reports the exclusive formation of the 2-methylcyclopenta-1,3-diene



which can be formed by either a diradical or concerted ($\sigma_s^2 + \sigma_a^2$) process. Baldwin¹⁶⁶ then reported the gas phase thermolysis of 1-methylbicyclo[2,1,0]pent-2-ene and 2-methylbicyclo[2,1,0]pent-2-ene both of which give a mixture of the 1-methylcyclopentadiene and 2-methylcyclopentadiene which can be formed by a competitive ($\sigma_s^2 + \sigma_a^2$) concerted process involving bonds C(1)-C(2) and C(4)-C(5) or C(3)-C(4) and C(1)-C(5)

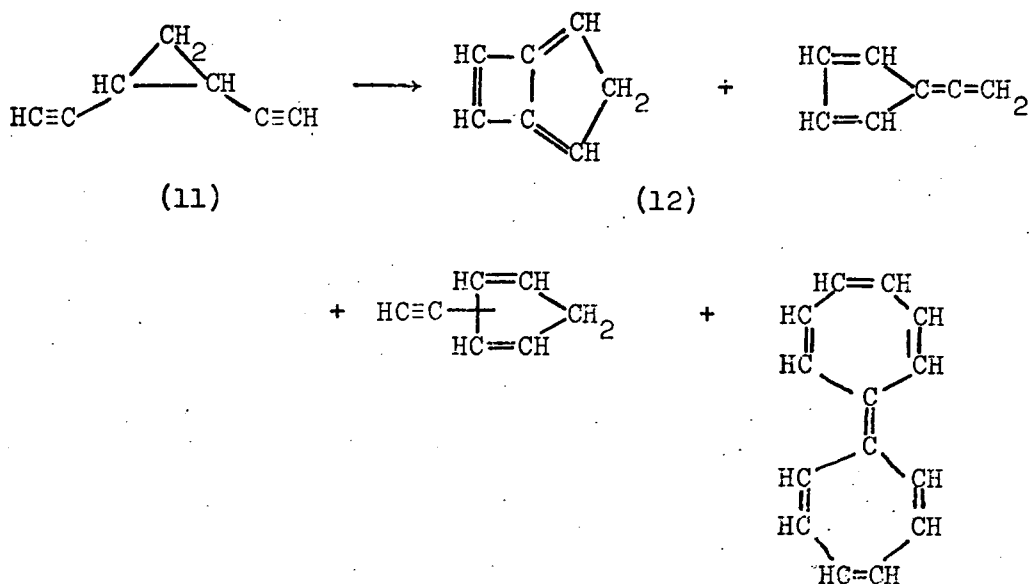


Flowers and Frey¹⁶⁷ propose the intermediacy of an activated cyclopentadiene, which can undergo a 1,5-hydrogen shift



faster than collisional deactivation. This proposal, based on RRKM calculations, was supported by experimental evidence reported by Brauman¹⁶⁸ for the gas phase rearrangement of 2-methylbicyclo[2,1,0]-pentene in the presence of various collisional deactivating species. Similar rearrangement, in solution,^{168,169} gives a high yield of the 2-methylcyclopentadiene compared to the 1-methylcyclopentadiene (ratio ca. 10:1) and these results can be interpreted in terms of a rarely proposed activated species in solution or a competitive concerted $\sigma_s^2 + \sigma_a^2$ approach similar to that suggested earlier¹⁶⁶.

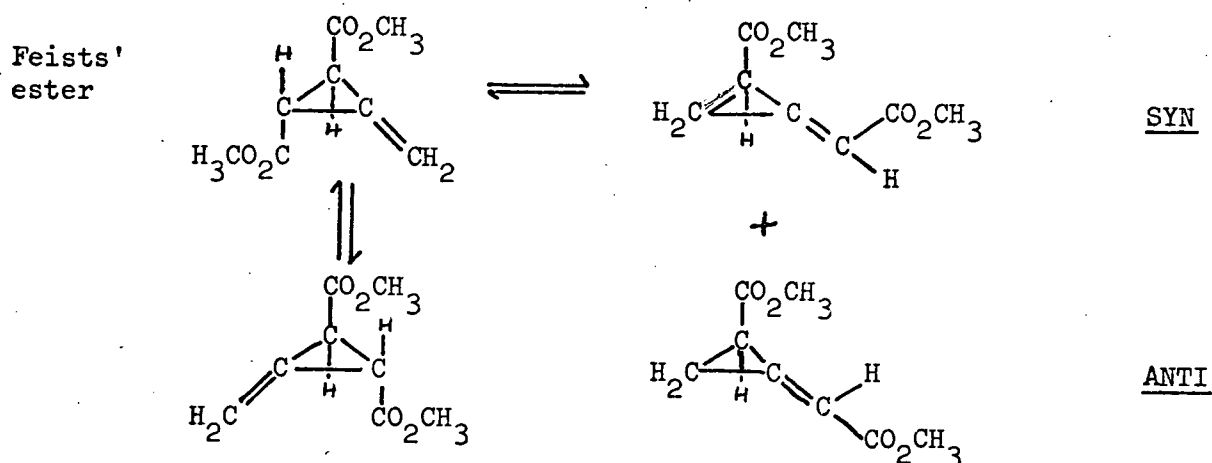
The mechanism of the thermal rearrangement of ethynylcyclopropanes is not clear. 1-Methyl-1,2-diethynylcyclopropane rearranges at 350° in the gas phase to give 2-methylbicyclo[3,2,0]hepta-1,4,6-triene¹⁷⁰, while the rearrangement of the un-methylated trans-isomer¹⁷¹ (11) gives a mixture of products at low pressure (0.02-0.1 m.m.) and the cycloheptatriene (12) alone at high pressures (100 m.m.)



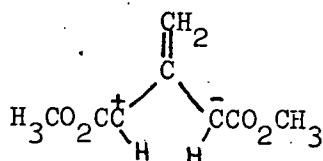
The gas phase pyrolysis¹⁷² of cis- and trans-1-methyl-2-ethynylcyclopropane at temperatures between 350°C and 530°C also gives a complex mixture of products, the trans-isomer isomerising to the cis-isomer initially before rearranging. The isomerisation is similar to that found for the analogous vinyl compound¹⁵⁶.

3.4 Thermal rearrangement of methylenecyclopropanes

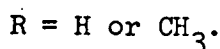
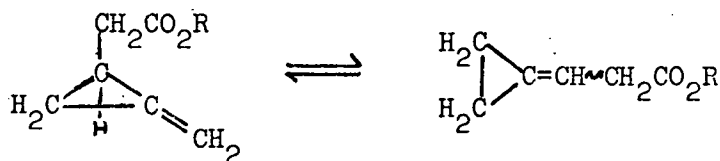
Ettlinger¹⁷³, in 1952, recognised the thermal isomerisation of Feists' ester as the first example of a degenerate rearrangement of a methylenecyclopropane. Ullman¹⁷⁴, later studied the same rearrangement and reported that Feists' ester rearranges thermally, to give two optically active isomeric products, along with racemised starting material but no cis-isomer.



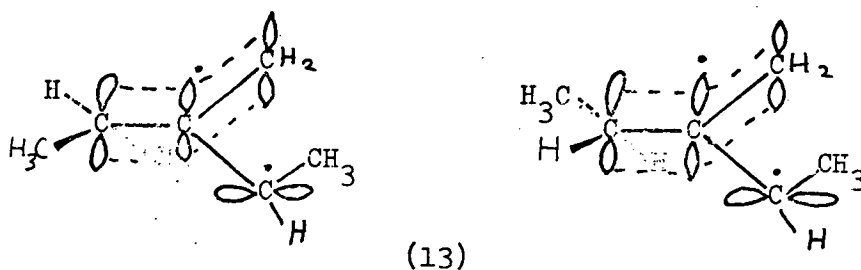
As such a high degree of optical activity was involved in the products, Ullman precluded the exclusive participation of a planar symmetrical transition state and suggested a zwitterionic intermediate.



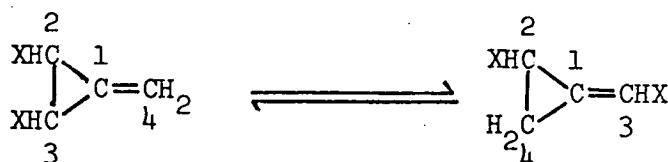
A similar reaction¹⁷⁵ showed that the isomerisation did not require a carbonyl group attached to the cyclopropane ring to stabilise the intermediate.



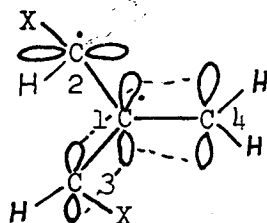
The isomerisation of 2-methyl-1-methylenecyclopropane to ethylidene-cyclopropane¹⁷⁶ was rationalised in terms of a diradical or concerted ($\sigma_a^2 + \pi_s^2$) process from kinetic data. The data gave the calculated value for the energy of activation as 40.4 K cal. mol⁻¹ and that for the entropy of activation as 3.8 e.u., which, when compared to the values found for the saturated analogue ($E_A = 59.4$ K cal. mol⁻¹, $\Delta S = 8.3$ e.u.¹²⁷) can be rationalised in terms of either a concerted process or a diradical process where the diradical is resonance stabilised with restricted internal rotation. These calculations were later repeated¹⁷⁷ to include ring strain factors and it was concluded that the diradical process was more favourable. The pyrolysis^{178,179} of either cis- or trans-2,3-dimethyl-1-methylenecyclopropane results in a mixture of syn- and anti-1-ethylidene-2-methylcyclopropane along with racemic starting material and its geometrical isomer. In this case orthogonal diradicals (13) were proposed as the intermediates in the reaction but again, as some racemisation had taken place, a planar diradical was invoked as a competitive intermediate.



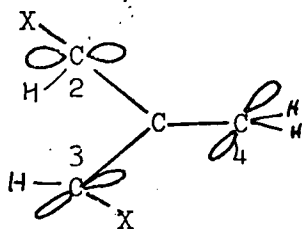
Doering and Roth¹⁷⁷ expanded Gajewski's^{178,179} original postulate using results of experiments on Feists' ester. They suggested, that during the rearrangement of Feists' ester, the asymmetric carbon atom C(2) common to both the starting material and the



product would retain its position relative to the plane of the two systems of methylenecyclopropane. If this is the case there must be an inversion of configuration at C(2) and the substituents on that carbon atom must remain perpendicular to the four carbon atoms of the methylenecyclopropane skeleton. The mechanism of this rearrangement can be rationalised in terms of a concerted or non-concerted process. In the non-concerted mechanism the intermediate is an orthogonal diradical which is formed by fission of C(2)-C(3) and rotation through 90° about C(3). The diradical is made up of a free radical in a non-bonding situation lying perpendicular to an allyl radical.



In the concerted mechanism the allyl radical is never fully developed and is at 45° to the orbital on C(2). To attain this transition state two rotations of 45° , one about C(4) and the other about C(3), are required.



The rotations required to achieve either of the two postulated intermediates can be in either of the two possible directions, thus leading to both syn and anti isomers in the product. Since the publication of this paper, Doering and Birladeanu¹⁸⁰, have established, from their work on the four diastereoisomers of 2-cyano-3-methyl-1-ethylidenecyclopropane (Figure VIII), that the 45° pivot mechanism is improbable.

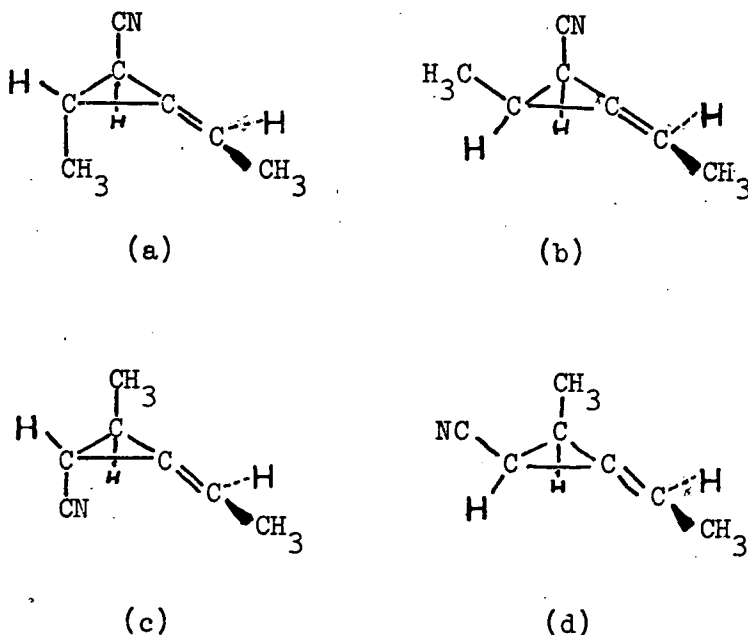
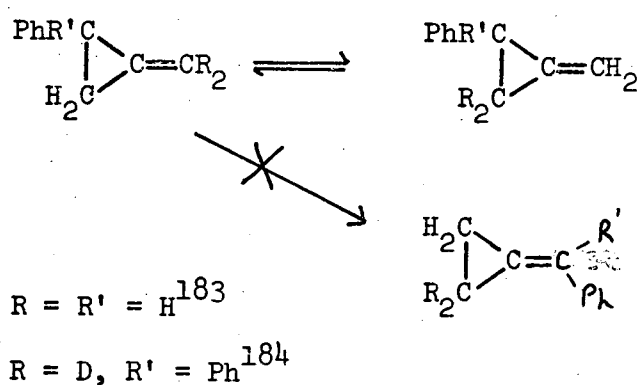


Figure VIII

If the mechanism was concerted (45°), conrotation would lead to a mixture of racemic a and racemic d only from racemic a while disrotation¹⁸¹ would give a mixture of racemic a, racemic b and racemic c from racemic a. However, all four racemic forms would be formed, from racemic a, if the mechanism involved the orthogonal diradical (90°). Their results showed that all four isomers were formed which was consistent only with the diradical mechanism.

They add that a mechanism involving a mixture of the concerted conrotatory and disrotatory processes would explain the spread of products found but this is highly unlikely. Dewar¹⁸², has calculated that the lowest energy form of the trimethylenemethane diradical is the form in which the two π -systems are at right angles to each other, thus providing further support for the orthogonal diradical mechanism.

Examination of results obtained by other workers lead Doering and Roth¹⁷⁷ to conclude that, in substituted methylene cyclopropanes, the atom which has the substituent(s) capable of stabilising a free radical, assumes the role of the atom common to the cyclopropane ring in both the starting material and the product. This hypothesis is readily demonstrated by the results from the isomerisation of 1-phenyl-2-methylenecyclopropane¹⁸³ and the analogous cyclopropane with the methylene group deuterated¹⁸⁴ where no benzylidenecyclopropane was isolated.



At higher temperatures (135°C) 1,1-diphenyl-2-methylenecyclopropane rearranges¹⁸⁵ to form 2-methyl-3-phenylindene via the intermediate (14) formed by diradical ring closure. The mechanism thereafter involves a series of 1,5-hydrogen shifts (thermally allowed) to reach the product (Figure IX).

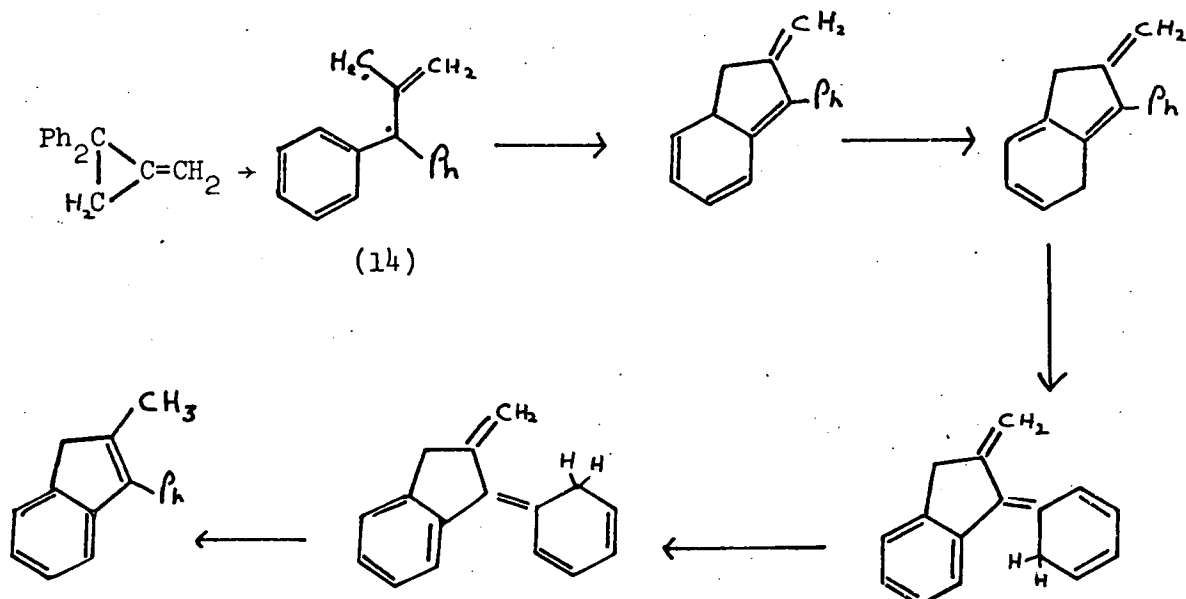
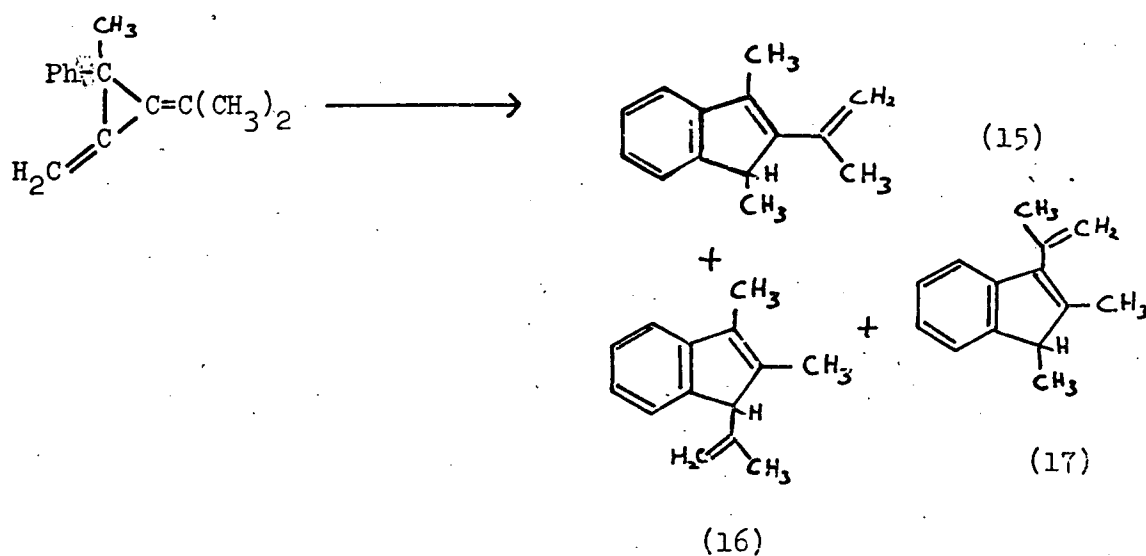


Figure IX

The proposed mechanism involves ring closure onto one of the phenyl groups and participation of the other phenyl group in three 1,5-hydrogen shift processes. If only one phenyl group is present and no other group which can participate in a 1,5-hydrogen shift, the rearrangement should not take place, if the proposed mechanism is correct. This was demonstrated⁷¹ by the vapour phase rearrangement of 1-phenyl-2-isopropylidenecyclopropane where no indene was isolated. The vapour phase rearrangement¹⁸⁶ of 1-isopropylidene-3-phenyl-3-methyl-2-methylene-cyclopropane at 530° yields a mixture of three isomeric indenenes (15), (16) and (17), and the similar rearrangement of



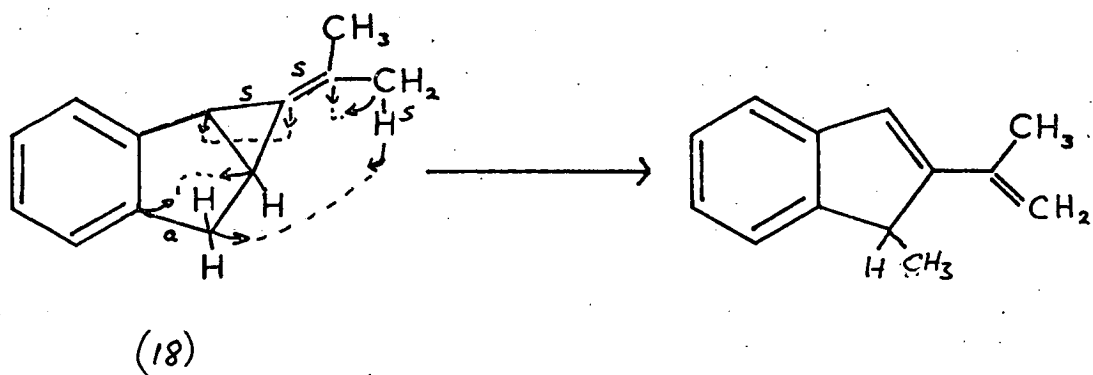


FIGURE X

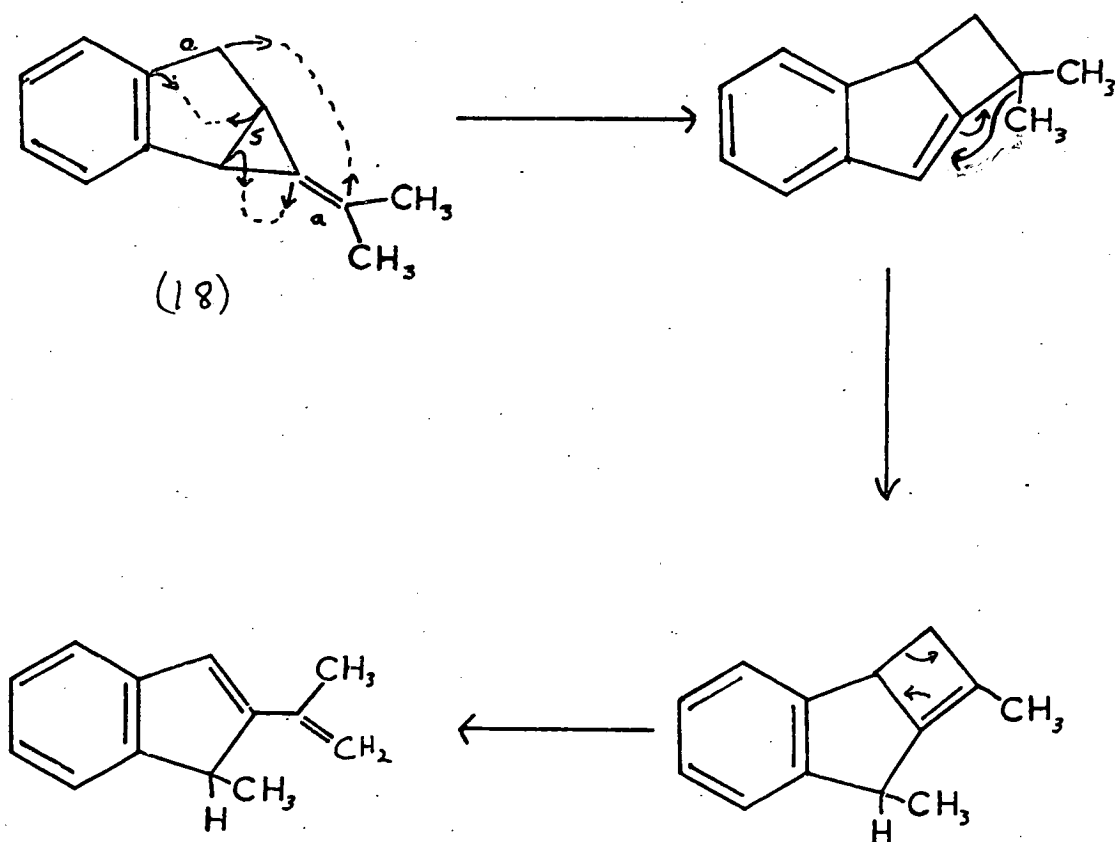
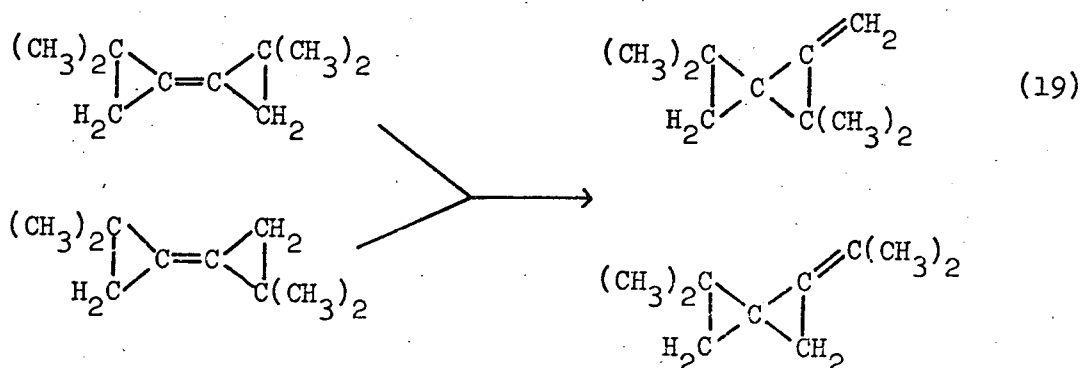


FIGURE XI

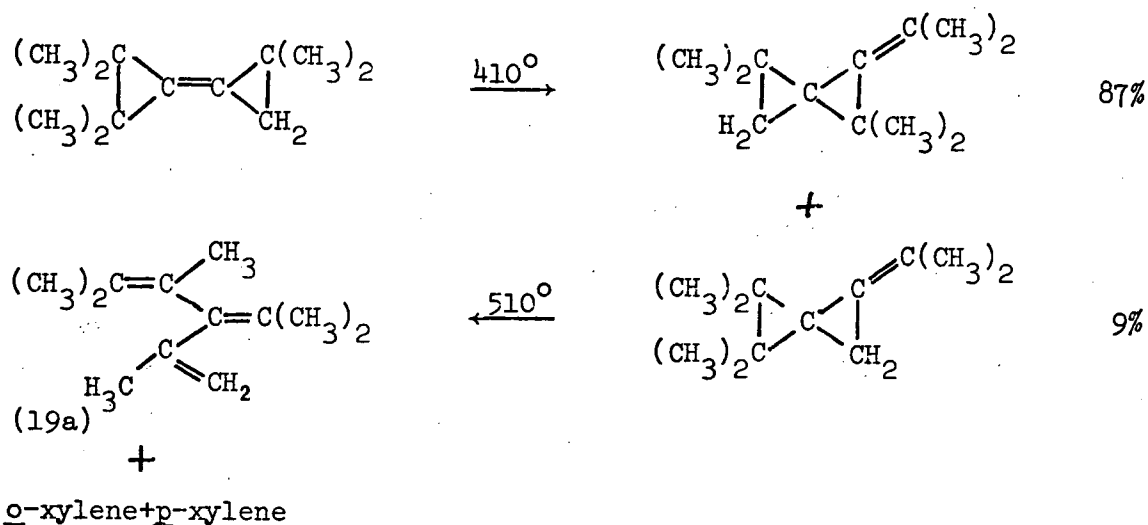
1-isopropylidene-2,2-diphenyl-3-methylenecyclopropane yields the four possible indene derivatives. The mechanism of both of these rearrangements is analogous to that described by Gilbert¹⁸⁵ (Figure IX), involving bond fission to form the diradical, followed by ring closure and a series of 1,5-hydrogen shift processes to give the products. A similar high temperature rearrangement¹⁸⁷ of 1,1-dimethyl-2,3-diisopropylidenecyclopropane yields the ring expanded 2,3,3,6-tetramethylhept-1-ene-4-yne, no phenyl group being present for indene formation.

The unsubstituted 2-isopropenylindene was formed by the vapour phase rearrangement⁷¹ of 2,3-benzo-6-isopropylidenebicyclo-[3,1,0] hex-2-ene (18) at 400°C. Two possible mechanisms were postulated for this rearrangement. The first involves a concerted ($\pi_s^2 + \sigma_s^2 + \sigma_s^2 + \sigma_a^2$) process (Figure X) and the second involves a concerted ($\sigma_a^2 + \sigma_s^2 + \pi_a^2$) process, followed by a 1,3-methyl shift and disrotatory ring opening (Figure XI). The former scheme was shown to be ~~the~~ correct¹⁸⁸ (Figure X), by the rearrangement of the adduct analogous to (18) with a deuterium substituted in the 5-position. Rearrangement via the mechanism in (Figure X) only, would give the isolated 1-deutero-2-isopropenylindene, rearrangement via the other mechanism (Figure XI) would lead to the 3-deutero-isomer.

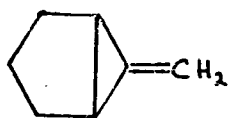
Dolbier^{189,190}, studied the thermal rearrangement of cis- and trans-2,2,2',2'-tetramethylbicyclopropylidene which gave an equilibrium mixture of two methylene spiropentanes.



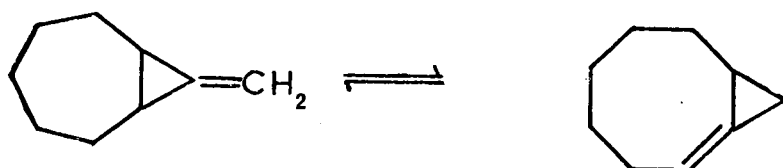
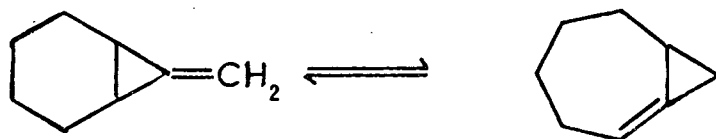
It was concluded that, as the less stable spiroopentane (19) was preferred in the equilibrium mixture, the mechanism could not involve a planar diradical, however, an orthogonal diradical intermediate would explain the observed product distribution. A similar rearrangement, carried out on 2,2,3,3,2',2'-hexamethylbicyclopropylidene^{187,191}, gave a mixture of 87% trans-2,2,2',2'-tetramethylisopropylidenespiropentane and only 9% of the 2,2,3,3-tetramethylisopropylidenespiropentane, at 400°. At 510°C, the bicyclopropylidene or the products of its rearrangement at 410°C, gave a mixture of the triene (19a) and ortho- and para-xylene



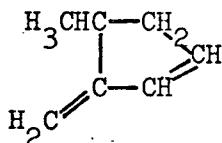
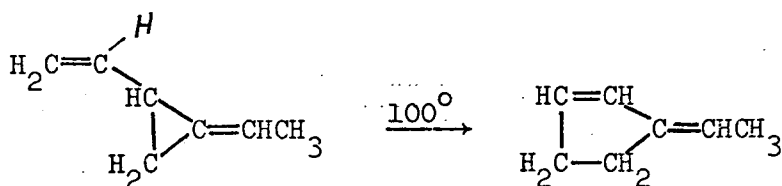
Kende and Riecke¹⁹² have reported that 6-methylenebicyclo[3,1,0]hexane is stable to isomerisation or dimerisation at up to 231°C, whereas, 7-methylenebicyclo[4,1,0]heptane and 8-methylenebicyclo[5,1,0]octane, isomerise at 180-230°C to give bicyclo[5,1,0]oct-1-ene and bicyclo[6,1,0]non-1-ene respectively.



stable up to 231°C



Thermal rearrangement of cyclopropanes containing both vinyl- and methylene-substituents have also been reported. When the methylene- and vinyl-substituents are on different sites in the cyclopropane ring^{76,193,194}, the product mixtures are consistent with methylenecyclopropane isomerisations^{176,178} and vinylcyclopropane-cyclopentene rearrangements¹⁴⁹. For example, 1-vinyl-2-ethylidenecyclopropane gives 3-ethylidene-cyclopent-1-ene and 3-methylene-4-methylcyclopent-1-ene. The first product arises from vinylcyclopropane-cyclopentene rearrangement of the starting material and the second product arises from methylenecyclopropane isomerisation of the starting material, followed by vinylcyclopropane-cyclopentene rearrangement.



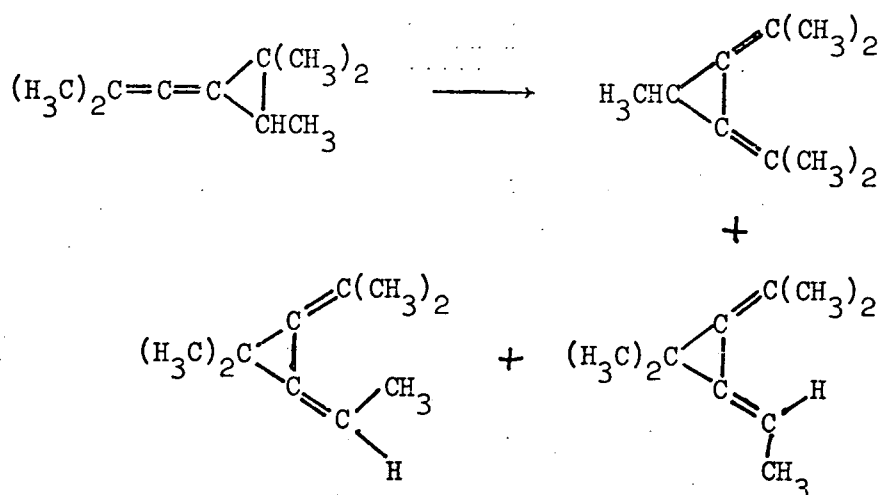
If, however, the two moieties are incorporated on the same ring carbon atom¹⁹⁵, as in 1,1-dimethyl-2-allylidene-cyclopropane, an addition reaction takes place which corresponds to the addition of a cyclopropane σ -bond to a diene to yield 1-isopropylidene-cyclopent-2-ene.



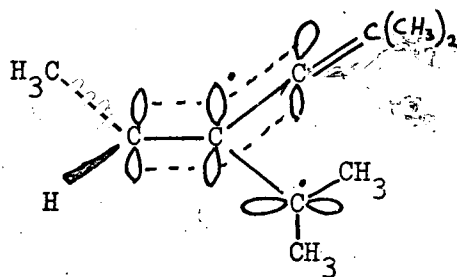
This reaction also demonstrates the high p-character of a cyclopropane ring bond which has already been shown (section 2.0).

3.5 Thermal rearrangement of vinylidenecyclopropanes

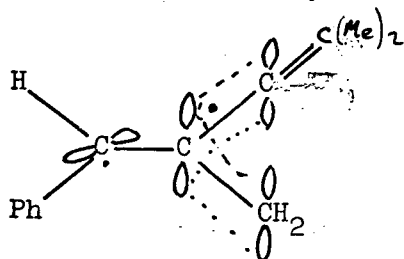
The gas phase pyrolysis (320°C) of the parent vinylidenecyclopropane¹⁹⁶ gives a high yield of 1,2-dimethylenecyclopropane, similar results being obtained¹⁹⁷ for the hexamethyl derivative. Rearrangement of the pentamethyl derivative¹⁸⁷ gives the three possible isomeric dimethylenecyclopropanes.



These rearrangements are rationalised in terms of intermediate orthogonal diradicals similar to those postulated for methylene-cyclopropane rearrangements^{178,179}.

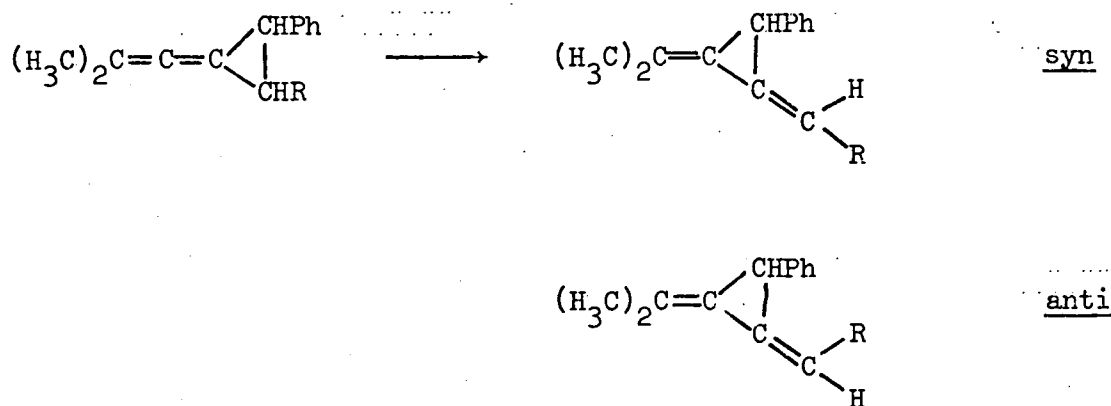


The pyrolysis^{71,85,86,186,198,199} of various aryl dimethylvinylidenecyclopropanes between temperatures of 80°C and 400°C give only the corresponding 1-isopropylidene-2-methylenecyclopropanes and no benzylidenecyclopropanes. These results are in agreement with those found for arylmethylenecyclopropanes^{183,184}, the intermediate diradical being resonance stabilised by the aryl group.



In the cases where the 1-aryl-2-dimethylvinylidenecyclopropanes possess, in addition, a single substituent at C(3), thermal

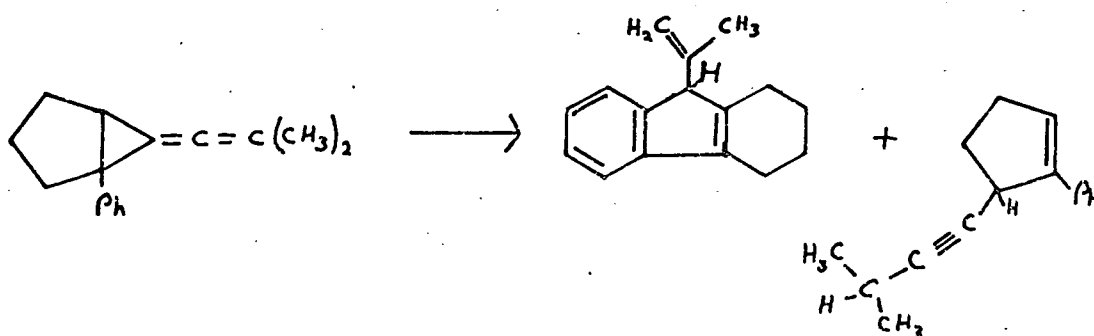
rearrangement^{71,85} leads to syn- and anti-dimethylenecyclopropanes.



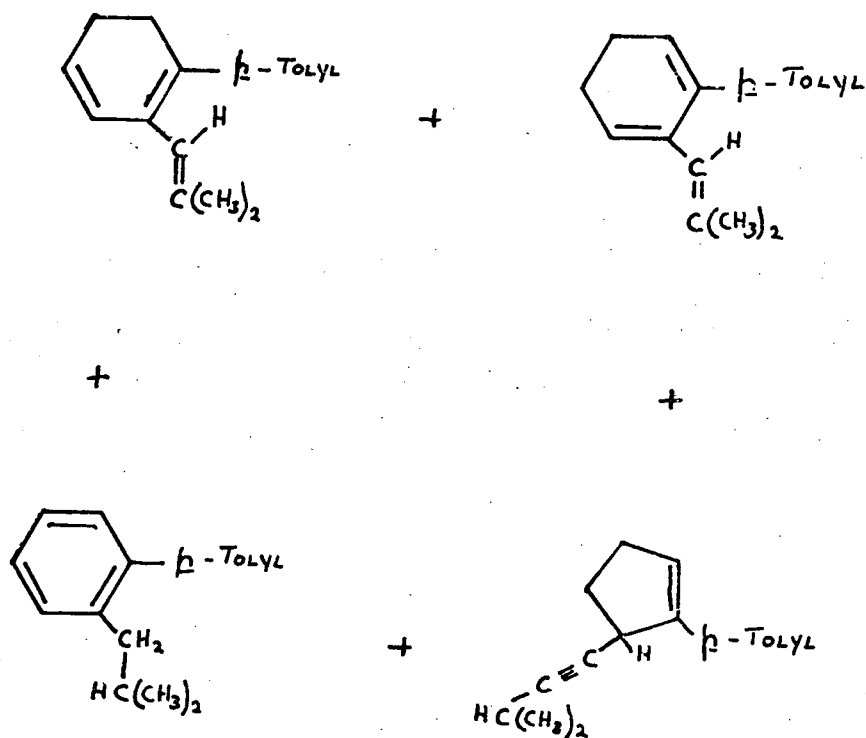
The syn-isomer predominates, under conditions where kinetic control applies (130°C , up to 3.5 hrs), however the more thermodynamically stable anti-isomer is formed when the temperature exceeds 130°C .

At higher temperatures (530°C) 1-phenyl- and 1,1-diphenyl-2-dimethylvinylidenecyclopropanes rearrange to give isomeric substituted indenenes via the 1-isopropylidene-2-methylenecyclopropanes, the rearrangements of which have already been described, (section 3.4). Similarly¹⁸⁷, the hexamethyl derivative rearranges at 520° via the diisopropylidene-cyclopropane to give a heptene-yne as previously described (section 3.4).

Where the structure of the dimethylvinylidenecyclopropane is such, that rearrangement would introduce a large amount of strain into the molecule, an alternative mode of rearrangement is observed. The vapour phase rearrangement of 6-dimethylvinylidene-1-phenylbicyclo[3,1,0]hexane at 450° is reported⁸⁵ to give a mixture of 9-isopropenyl-1,2,3,4-tetrahydrofluorene and 3-(3'-methylbut-1'-ynyl)-2-phenylcyclopent-1-ene.



However, the rearrangement of 6-dimethylvinylidene-1-(p-tolyl)bicyclo-[3,1,0]hexane, under the same conditions⁸⁵, gave a mixture of four products. These products were identified as 2-(2'-methylprop-1'-enyl)-1-(p-tolyl)cyclohexa-1,3-diene, 2-(2'-methylprop-1'-enyl)-3-(p-tolyl)-cyclohexa-1,3-diene, 2-isobutyl-4'-methylbiphenyl and 3-(3'-methylbut-1'-ynyl)-2-(p-tolyl)cyclopent-1-ene.



The thermal rearrangement of certain dimethylvinylidene-bicyclo[3,1,0]-and-bicyclo[4,1,0]alkanes also proceed by an alternative method. A concerted mechanism, involving a hydrogen atom migration from the carbon atom α to the cyclopropane ring to the central carbon of the allene skeleton was proposed for the observed²⁰⁰ rearrangement

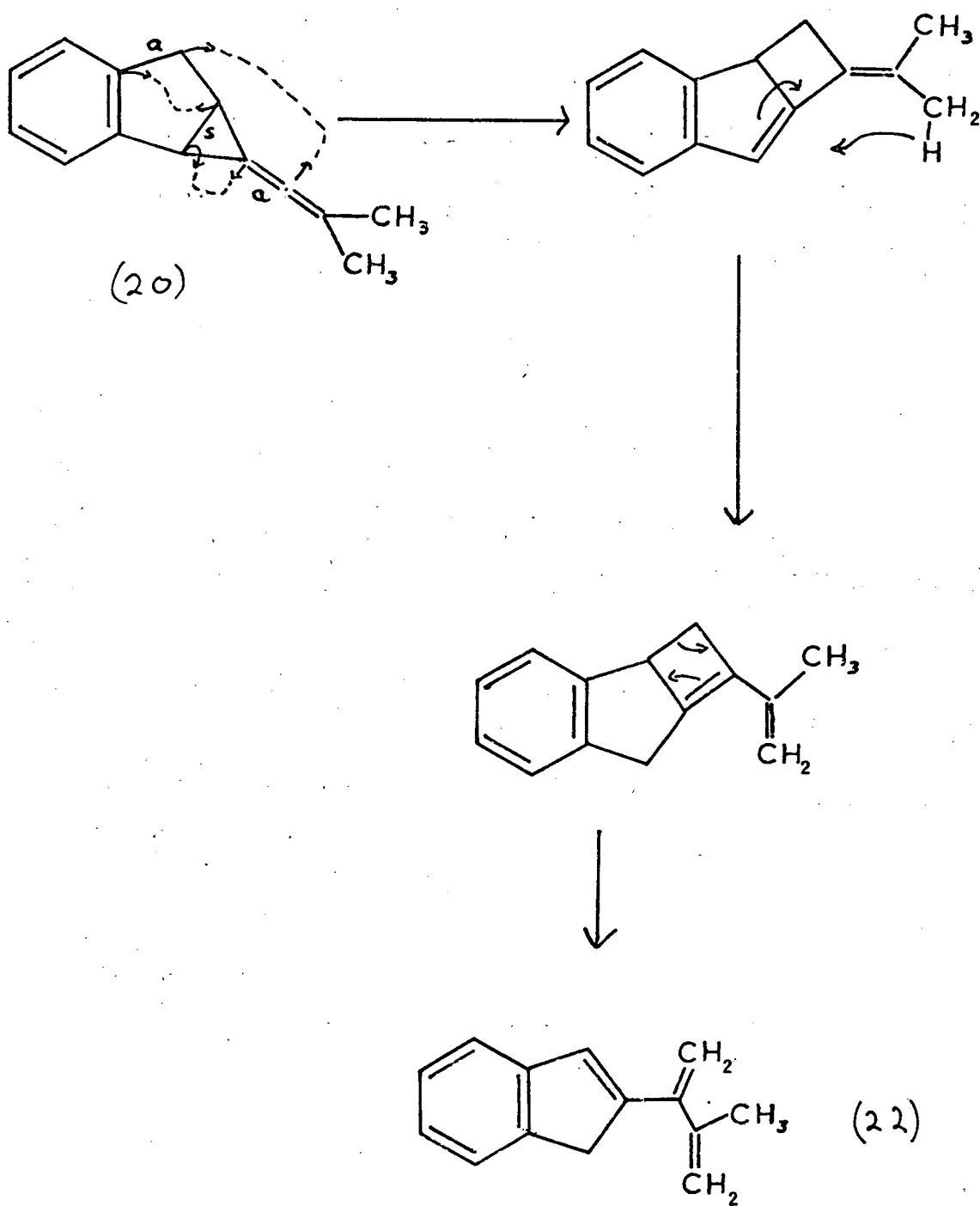
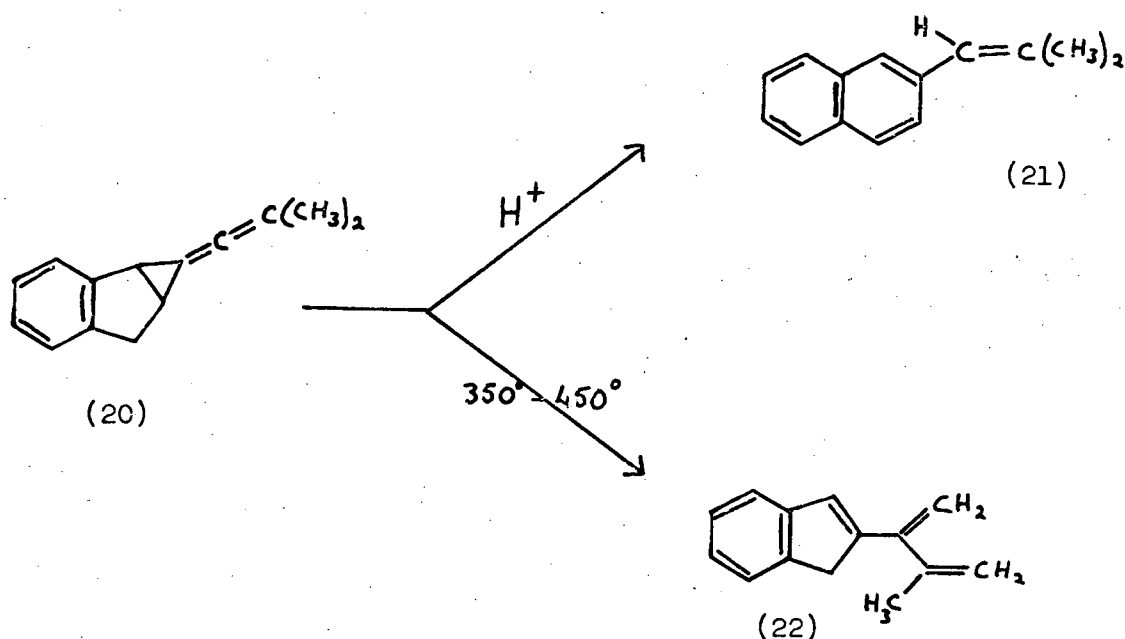


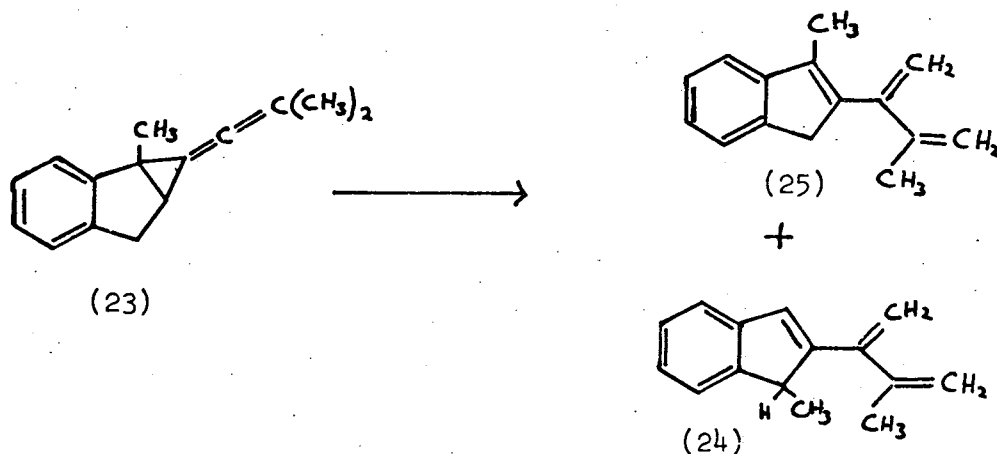
FIGURE XII

of 2,3-benzo-6-dimethylvinylidenebicyclo[3,1,0]hexene (20) to 2-methyl-1-(β -naphthyl)prop-1-ene (21). This rearrangement was observed at 80°C in solution or in the vapour phase at 450°C. However, the rearrangement has been re-examined by Robertson⁷¹, and partly as a result of work described later in this thesis, (p.88) it is now clear that this product is formed by an acid catalysed route brought about by traces of acid either in the solvent or on the glass wool. In the absence of acid the thermal rearrangement process yields 2-(2'-methyl-1-methyleneprop-2-enyl)-indene (22).

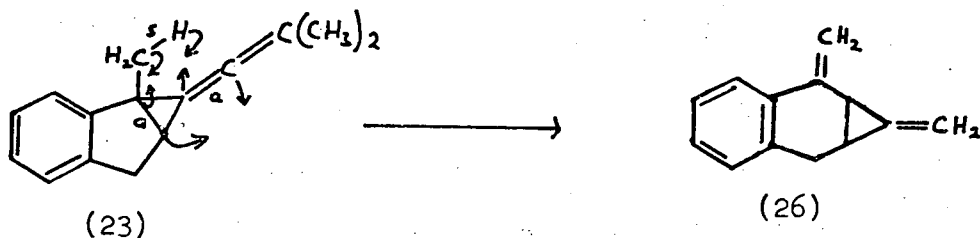


The mechanism of the thermal reaction appears to involve three consecutive concerted processes (Figure XII); a) breaking and formation of three bonds ($\sigma_a^2 + \sigma_s^2 + \pi_a^2$), b) a 1,5-hydrogen shift, and c) conrotatory ring opening of the strained cyclobutane ring. This mechanism was confirmed²⁰¹ by carrying out the thermal rearrangement of (20) selectively deuterated at C(5) which gave location of the deuterium at C(3) in the product (22). The vapour phase rearrangement²⁰⁰ of 1-methyl-2,3-benzo-6-dimethylvinylidenebicyclo[3,1,0]hex-2-ene (23) proceeds similarly to give a mixture

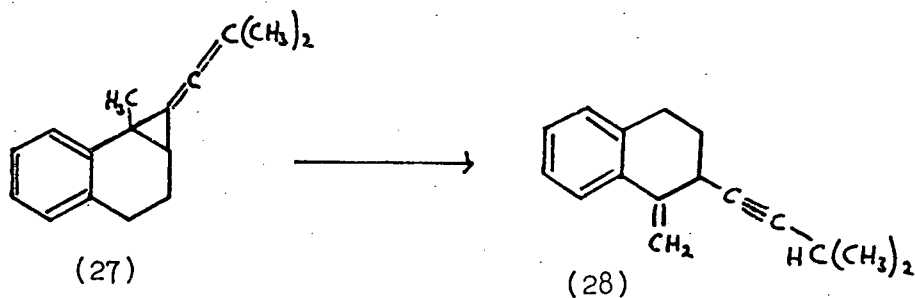
of the two possible indenenes, 3-methyl-2-(2'-methyl-1'-methyleneprop-2'-enyl)indene (25) and 1-methyl-2-(2'-methyl-1'-methyleneprop-2'-enyl)indene (24). The mechanism in this case was confirmed⁷¹ by selective deuteration of the methyl group on C(1) of (23) which, on rearrangement, gave complete retention of the deuterium in the methyl group on C(1) and C(3) of the products (24) and (25) respectively



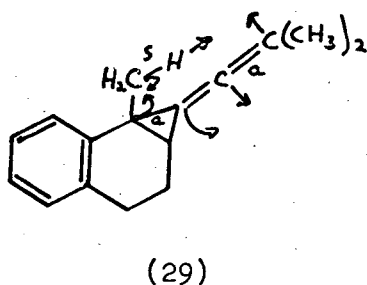
In refluxing benzene however²⁰⁰, 1-methyl-2,3-benzo-6-dimethylvinylidene-bicyclo[3,1,0]hex-2-ene (23) rearranges to 3,4-benzo-7-isopropylidene-2-methylenebicyclo[4,1,0]hept-3-ene (26), the mechanism being envisaged as a concerted ($\sigma_s^2 + \sigma_a^2 + \pi_a^2$) process.



The thermal rearrangement²⁰⁰ of 1-methyl-2,3-benzo-7-dimethylvinylidene-bicyclo[4,1,0]hept-2-ene (27) in solution at 180°C or in the vapour phase at 450°C gives 1-methylene-2-(3'-methylbut-1'-ynyl)tetralin (28)



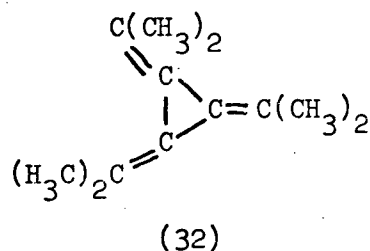
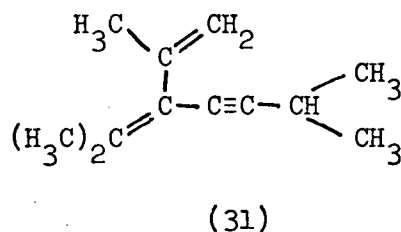
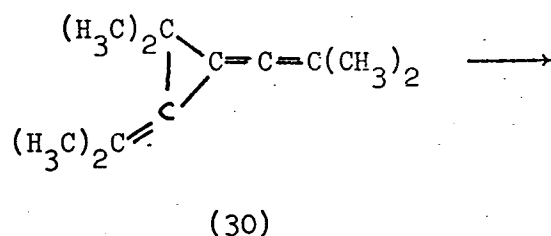
The mechanism in this case was envisaged as a thermally allowed $(\sigma_s^2 + \sigma_a^2 + \pi_a^2)$ process, involving a hydrogen atom migration to the γ -carbon of the allene group via the transition state (29)



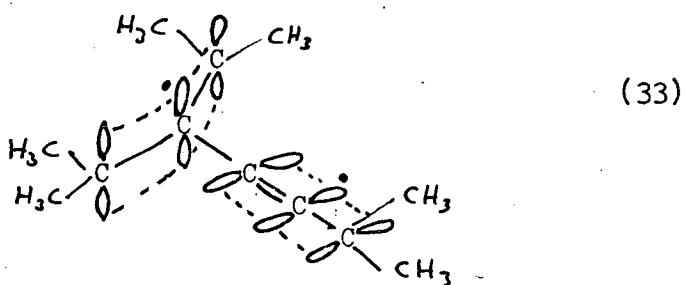
Confirmation of the proposed mechanism²⁰¹ was achieved by studying the derivative of (27) selectively deuterated at the methyl group on C(1). Rearrangement gave the product analogous to (28) with deuterium located at the olefinic methylene group and the isopropyl group only, as is to be expected from the mechanism. The rearrangement²⁰⁰ of 2,3-benzo-7-dimethylvinylidenecyclo[4,1,0]-hept-2-ene and the 6-methyl derivative, however, gave complex mixtures of products which were not identified.

Kobrich and Rosner²⁰² report the rearrangement of 1,1-dimethyl-2-isopropylidene-3-dimethylvinylidenecyclopropane (30), at 80°, to give 2-methyl-3-isopropylidene-6-methyl-hept-1-ene-4-yne (31)

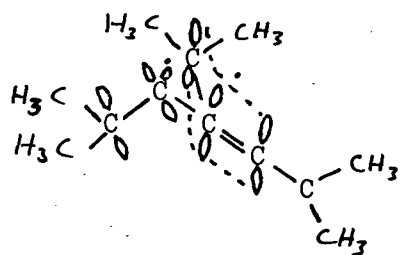
and not the triisopropylidenecyclopropane (32) as may have been expected from the rearrangement of other dimethylvinylidenecyclopropanes^{187,197}.



This product is similar to that obtained during the high temperature rearrangement of 1,1-dimethyl-2,3-diisopropylidenecyclopropane¹⁸⁷, however, no intermediacy of triisopropylidenecyclopropane is predicted in this case. The intermediate proposed is the orthogonal diradical (33) arising from fission of the C(1)-C(3) bond in (30).



This diradical is completely conjugated, the orbitals of the broken bond developing at right angles to each other and consequently parallel to the allyl and the allenyl systems. The other possible diradical (34), formed by fission of the C(1)-C(2) bond in (30), from which the triisopropylidenecyclopropane would arise, is only partially delocalised over part of the allenyl system and is therefore energetically much less favourable as an intermediate.



(34)

4.0 Object of Research

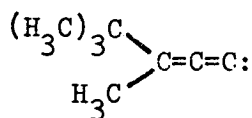
The remainder of this thesis describes the synthesis and rearrangement of cyclopropanes derived from four unsaturated carbenes.

The work falls into four sections.

Firstly, in view of the variation in products obtained by Stewart⁸⁵ for the vapour phase (450°) rearrangement of the dimethylvinylidenecarbene adducts of 1-phenylcyclopentene and 1-p-tolylcyclopentene, these were re-examined along with adducts derived from various other substituted 1-phenylcyclopentenenes, to determine the role of the substituent in influencing the mechanism of the rearrangement.

Secondly, in view of the variation in products obtained by Stewart⁸⁵ for the vapour phase (450°) rearrangement of the dimethylvinylidenecarbene adducts of 1-phenylcyclopentene and 1-phenylcyclohexene, these too were re-examined along with the adducts derived from 1-phenylcycloheptene and 1-phenylcyclooctene to determine if the size of the cycloalkene ring moiety has an effect on the rearrangement products.

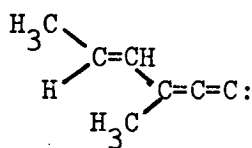
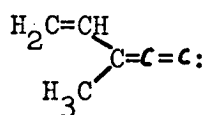
Thirdly, in view of the scarcity of information on the addition of unsymmetrical carbenes to olefins and their subsequent rearrangement, various adducts of 2,3,3-trimethylbutenylidenecarbene were prepared and the adducts and thermal rearrangement products studied.



Finally, an investigation was undertaken to discover



the effect on the rearrangement process of an unsaturated moiety attached to the γ -carbon atom of the allene moiety. Adducts were formed from carbenes in which one of the methyl groups in dimethylvinylidenecarbene had been replaced by a vinyl group and a trans-prop-1-enyl group respectively and the adducts and thermal rearrangement products studied.



DISCUSSION OF THE SYNTHESIS AND REARRANGEMENT OF VINYLIDENECYCLOPROPANES

5.1 Synthesis of dimethylvinylidenecyclopropanes

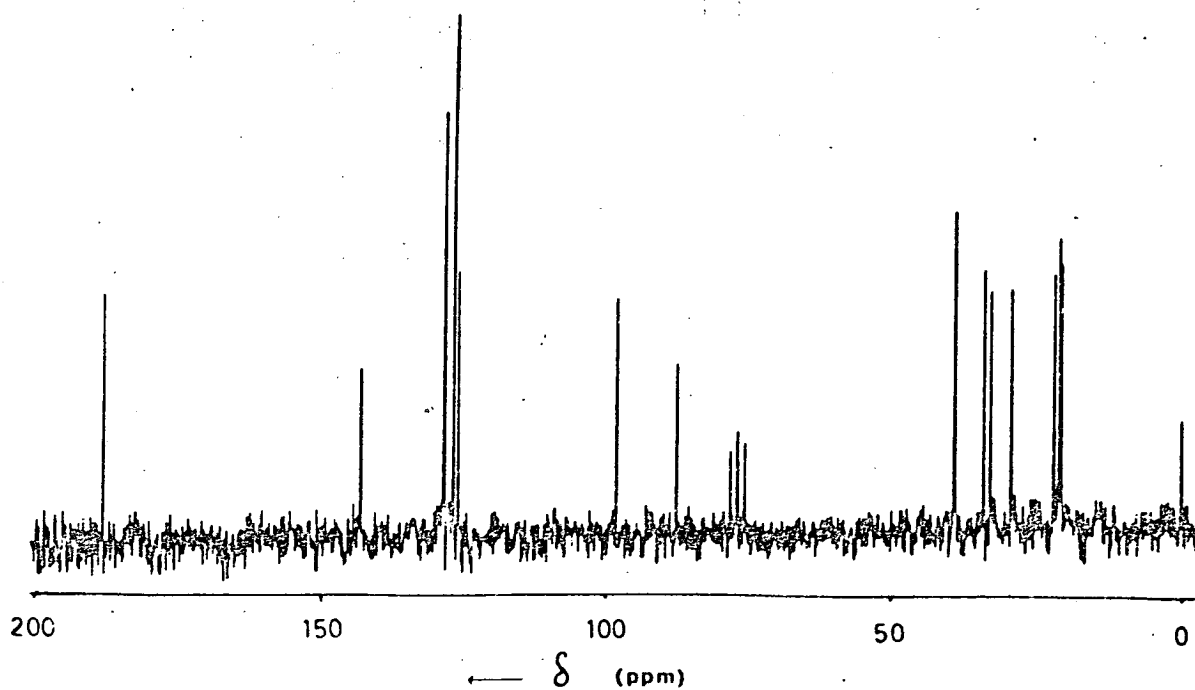
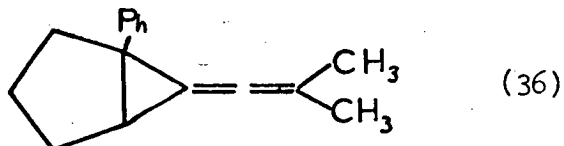
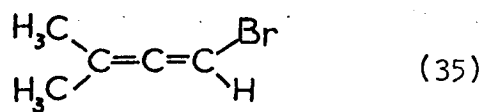
The dimethylvinylidenecyclopropanes were all prepared as 1:1 adducts of dimethylvinylidenecarbene and the appropriate olefin. The carbene was generated by the dropwise addition of a two-fold excess of 1-bromo-3-methylbuta-1,2-diene (35) to a slurry of a three-fold excess of potassium-*t*-butoxide in light petroleum. The bromodiene has been reported⁸³ to be more efficient than the corresponding chlorodiene or 3-chloro-3-methylbut-1-yne as a carbene precursor.

Purification of the crude adducts was accomplished using alumina chromatography eluting with light petroleum. In the case of para-methoxyphenylcyclopentene and para-tolylcyclopentene the adducts rearranged in contact with alumina and it was necessary to use "Florisil" as the stationary phase. Elution with light petroleum again gave the pure adducts. All the adducts showed a tendency to darken and polymerise if left at room temperature on the bench, however, they were all stable when stored at -15°C .

Molecular formulae were determined by exact mass measurement of the parent peak (P) of the mass spectrum. In addition to the parent peak the mass spectrum of each adduct showed other prominent peaks at P-CH_3 , $\text{P-C}_3\text{H}_7$ and/or $\text{P-C}_4\text{H}_9$.

The adducts all show adsorptions, in the infra-red, in the region $2000\text{--}2050\text{ cm}^{-1}$ due to the exocyclic allene group. This adsorption is higher than that normally assigned²⁰³ to an allene group ($1900\text{--}2000\text{ cm}^{-1}$) due to the additional bond strain involved in the exocyclic allene group⁷⁸.

The structures of the adducts were confirmed by n.m.r. spectroscopy. The proton off-resonance and noise decoupled ^{13}C -n.m.r. spectra of the parent phenylcyclopentene adduct (36) shows the presence of two methyl groups, three methylene groups, an aliphatic-CH group, an



^{13}C { ^1H -noise decoupled} spectrum of 6-dimethylvinylidene-1-phenylbicyclo[3,1,0]hexane

aliphatic quaternary carbon atom, two olefinic quaternary carbon atoms, three different types of aromatic-CH groups, an aromatic quaternary carbon atom and an allenic quaternary carbon atom. This is consistent with the structure assigned to the adduct (36). ^1H -n.m.r. (60 MHz and 100 MHz) spectra of all adducts show absorptions due to aromatic protons in the region 2.5-3.3 τ and absorptions due to the two terminal methyl groups of the allene system in the region 8.2-8.6 τ as singlets, either coincidentally or separately. The absorption due to the cyclopropyl hydrogen (normally in the region 7.5-8.0 τ ⁸⁵) was always masked by the absorptions due to the cyclopentane ring protons (7.7-8.2 τ). A typical spectrum, the adduct from 1-phenylcyclopentene, is illustrated (Figure XIV).

Attempts to prepare the adducts of acenaphthalene, 2-methyl-1,1-diphenylprop-1-ene and 3-phenylindene were unsuccessful, olefin only being recovered. The failure of acenaphthalene to form an adduct can be attributed to the additional activation energy required to break the completely conjugated system. This type of system also exists in trans-stilbene which is known to have a low reactivity towards dichlorocarbene²⁰⁴. In the case of 2-methyl-1,1-diphenylprop-1-ene the dimethyl- and diphenyl-groups at either end of the double bond must sterically hinder the approaching carbene adopting the required orientation for cyclopropane formation. This can be further understood from the relative yields recorded⁷¹ for the addition of dimethylvinylidenecarbene to 1,1-diphenylethylene and β,β -dimethylstyrene. 1,1-Diphenylethylene, unsubstituted on the β -carbon atom, forms an adduct in 84% yield whereas β,β -dimethylstyrene, under the same conditions, gives only a 25% yield of adduct. The carbene is relatively unhindered in the diphenylethylene case and is able to adopt the required orientation for cyclopropane formation, however, there must be substantial steric hinderance in the case of β,β -dimethylstyrene causing the large

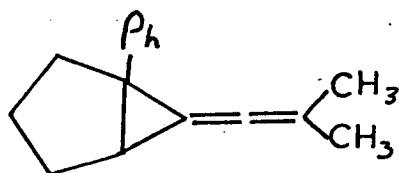
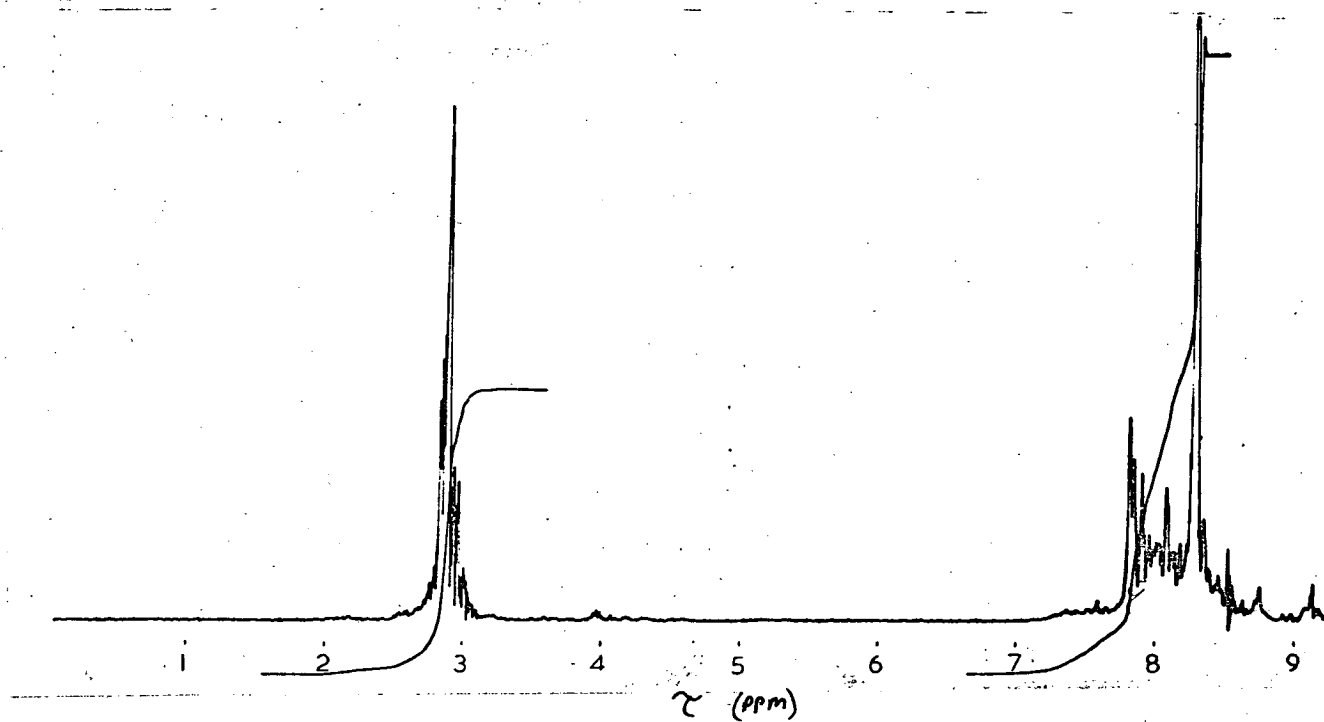
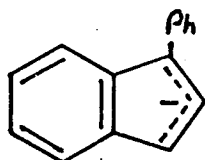


FIGURE XIV

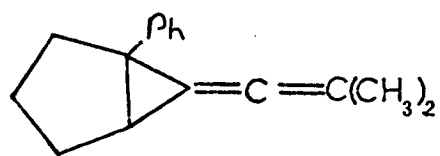
reduction in the yield of cyclopropane. The difference between β,β -dimethylstyrene and 2-methyl-1,1-diphenylprop-1-ene is the substitution of the final C-H bond with a phenyl group and this makes adduct formation completely sterically hindered. The lack of adduct formation in the case of 3-phenylindene is possibly due to the formation of the resonance stabilised anion by removal



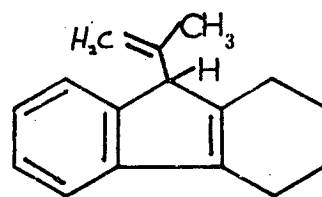
of a proton from C(1). This anion would not be susceptible to attack by a carbene. The anion forms on addition of the 3-phenylindene to the base, darkening of the butoxide slurry being almost instantaneous. On acidification, during work up, a mixture of 3-phenylindene and 1-phenylindene, identifiable by their ^1H -n.m.r. spectra, is formed.

Similar attempts to form the adducts of acrolein diethylacetal and cinnamyl alcohol also met with no success, olefin only being recovered. The reason for these failures is not clear, unless the electron withdrawing effect of the oxygen is so great to deactivate the olefinic bond. Santelli²⁰⁵ has however reported the formation of an adduct of an olefinic alcohol using 3-chloro-3-methylbut-1-yne as carbene precursor.

Attempts to form an adduct of 3-methylindole gave only the ring expanded product, 4-methyl-3-(2'-methylprop-2-enyl)-quinoline, as previously reported by Bycroft²⁰⁶. It was suggested that this product was formed via the unisolated vinylidenecyclopropane which underwent acid catalysed rearrangement under the conditions of work up. This, however, is not the case since the same product is formed when conditions are kept strongly basic during work up. The mechanism of the rearrangement involves migration of hydrogen from the nitrogen in the indole and, in an attempt to eliminate this hydrogen migration, the addition of dimethylvinylidenecarbene to 1,2-dimethylindole was

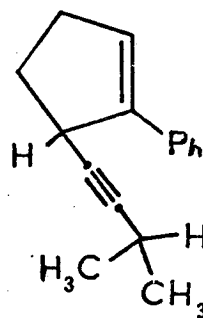


(36)

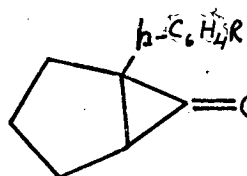


(37a)

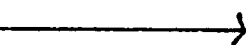
+



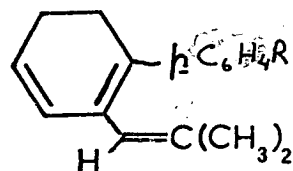
(37c)



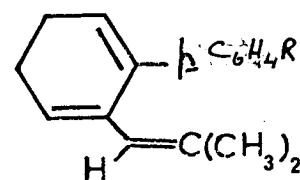
(38, R=CH₃)



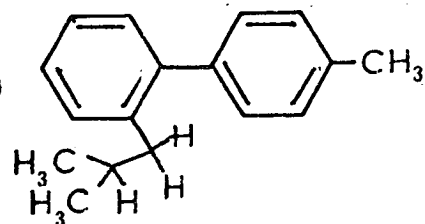
(39a, R=CH₃)



(39b, R=CH₃)



(39c, R=CH₃)



(39d, R=CH₃)

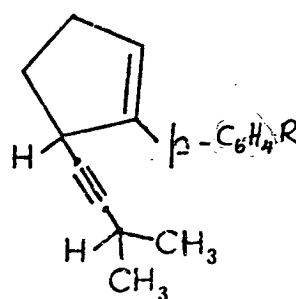


FIGURE XV

attempted, however, starting material only was recovered. These results suggest that the mechanism of quinoline formation may not necessarily be via the dimethylvinylidenecyclopropane intermediate.

Aziridine preparation by the addition of dihalocarbenes to imines has been extensively studied²⁰⁷⁻²¹⁰, the method of generation of the carbene being varied. The use of potassium-t-butoxide and a haloform to give dihalocarbene, which adds²⁰⁸ to benzylideneaniline in 68% yield, prompted the attempted preparation of a similar aziridine using 1-bromo-3-methylbuta-1,2-diene as carbene precursor. An attempt was made to prepare the adduct of N-methylbenzylimine however starting material only was recovered. This could be due to the unfavourable electronic nature in the area of the carbon-nitrogen double bond. Previous reports of unsaturated aziridine formation²¹¹⁻²¹³ have been via cyclisation rather than addition reactions. One attempt was also made to form a diazirane, by addition of dimethylvinylidenecarbene²¹⁴ to azobenzene, but once again starting material was recovered. This could be due to the high activation energy required to break the conjugated nitrogen-nitrogen double bond being similar to the trans-stilbene case.

5.2 Thermal rearrangement of the dimethylvinylidene carbene adducts of 1-arylcyclopentenes

The vapour phase rearrangement (450°) of the dimethylvinylidene carbene adduct of 1-phenylcyclopentene was reported⁸⁵ to give a mixture containing 90% of 9-isopropenyl-1,2,3,4-tetrahydrofluorene (37a) and 5% of 1-(3'-methylbut-1'-ynyl)-2-phenylcyclopent-2-ene (37c) whereas similar rearrangement of the para-methyl derivative (38, $R=CH_3$) gave a mixture of 2-(2'-methylprop-1'-enyl)-1-(p-tolyl)cyclohexa-1,3-diene (39a, $R=CH_3$) and 2(2'-methylprop-1'-enyl)-3-(p-tolyl)cyclohexa-1,3-diene (39b, $R=CH_3$) in 80% yield along with 5% of 2-isobutyl-4'-methylbiphenyl (39c, $R=CH_3$) and 5% of 3-(3'-methylbut-1'-ynyl)-2-(p-tolyl)cyclopent-1-ene (39d, $R=CH_3$) (Figure XV). In view of these unexpected results, the thermal

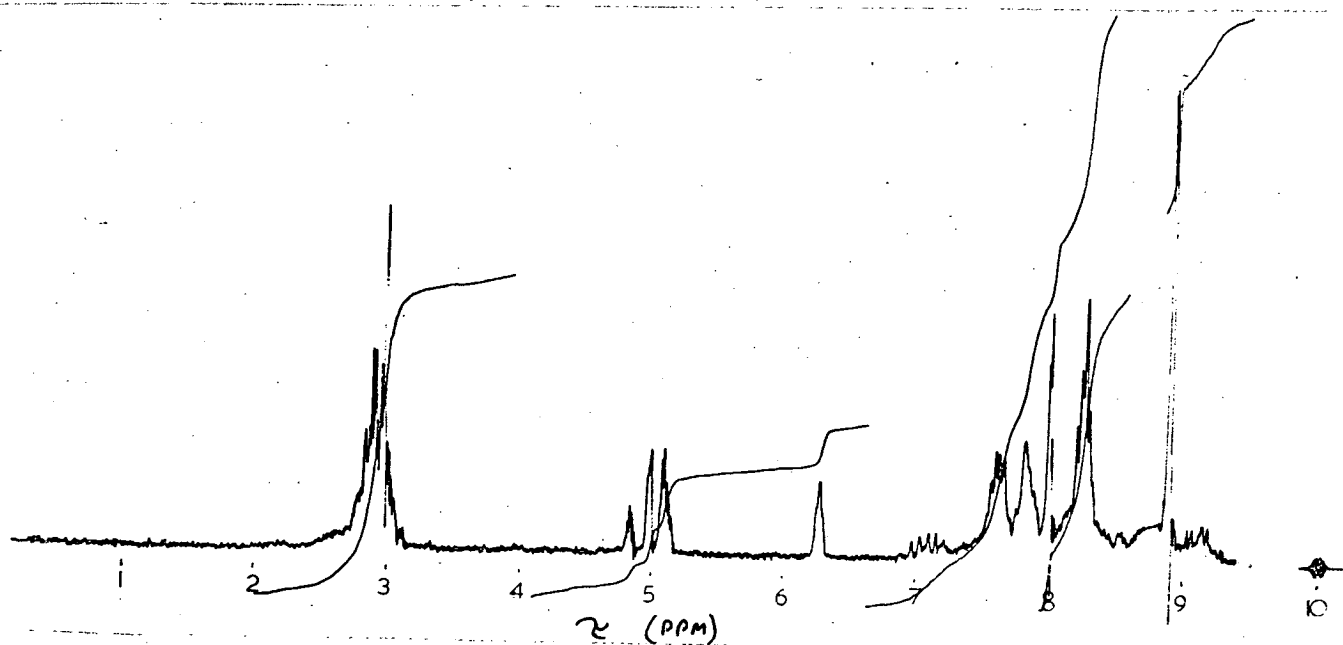
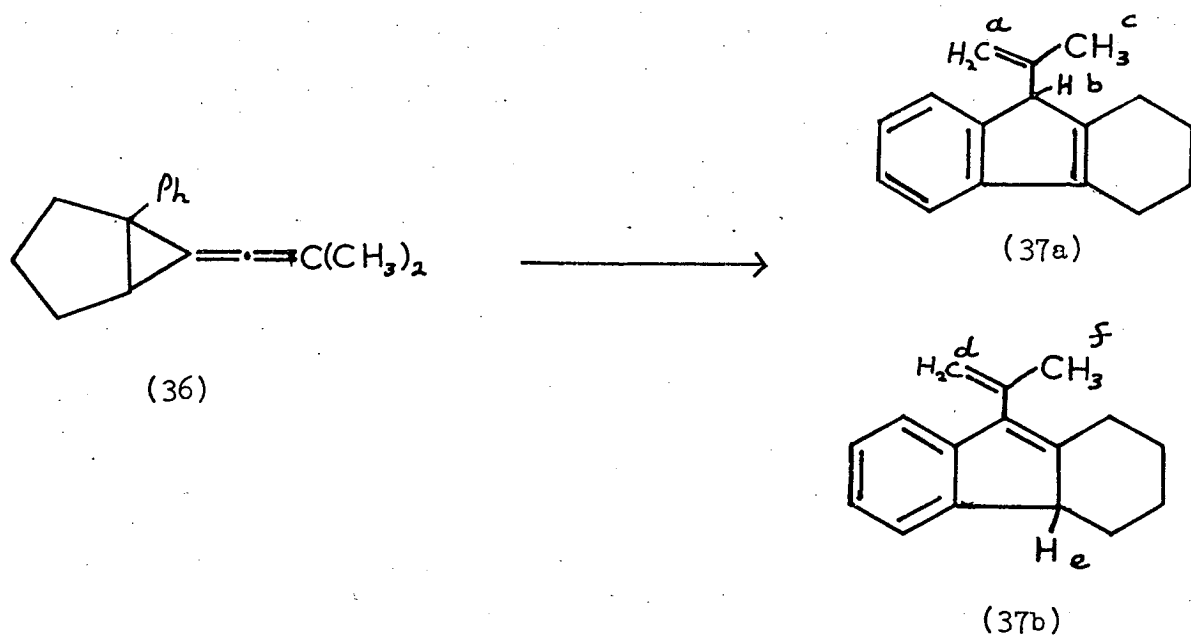


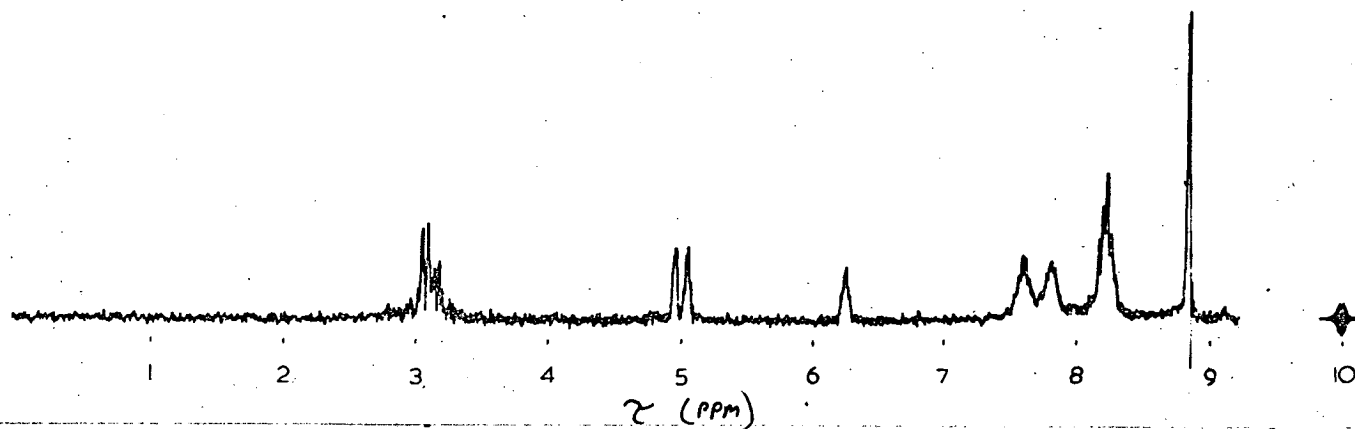
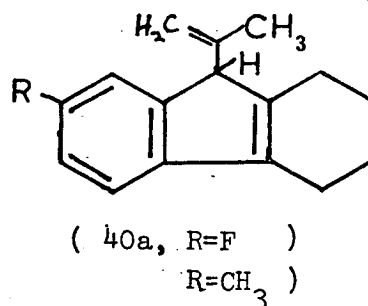
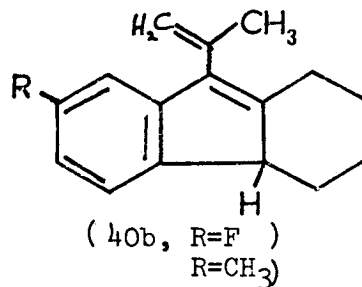
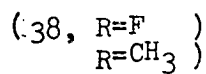
FIGURE XVI

rearrangement of the dimethylvinylidene carbene adducts of 1-phenylcyclopentene and various substituted 1-phenylcyclopentenenes was undertaken in an attempt to discover the role of the substituent groups in the rearrangement mechanism.

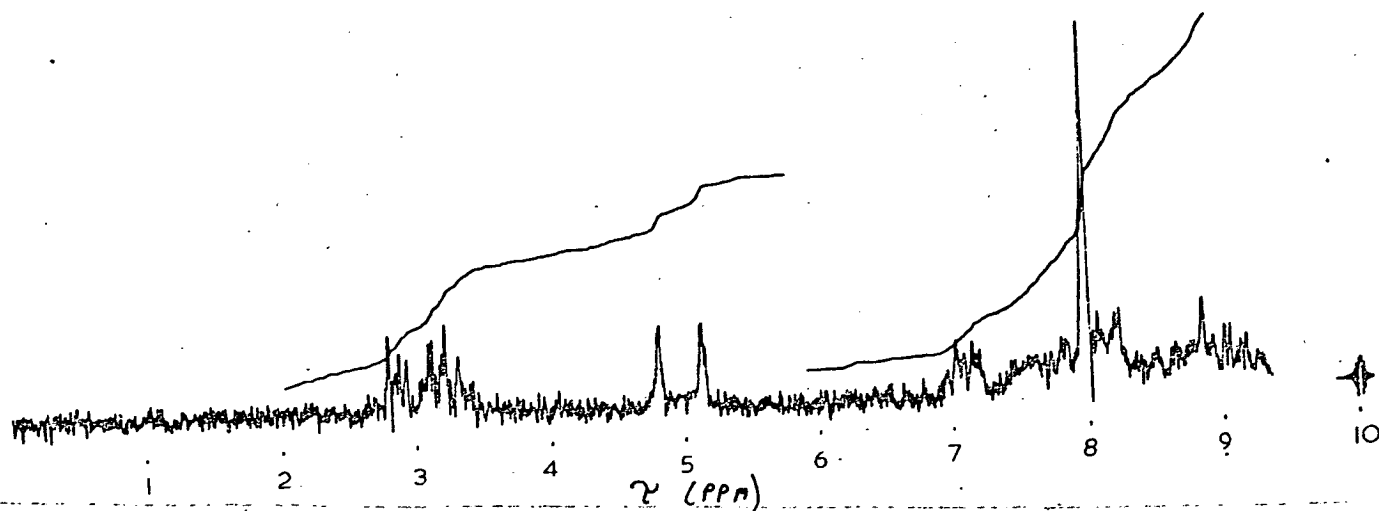
The vapour phase rearrangement of 6-dimethylvinylidene-1-phenylbicyclo[3,1,0]hexane (36) at 450° gives a mixture of two products. These two products were identified as two isomeric compounds, 9-isopropenyl-1,2,3,4-tetrahydrofluorene (37a) and 9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (37b), on the basis of the evidence presented below.

The ¹H-n.m.r. spectrum of the mixture (Figure XVI) shows resonances at 4.95 τ and 5.05 τ (Ha) which correspond to olefinic methylene protons, at 6.14 τ (Hb) corresponding to a benzylic proton and at 8.86 τ (J=1 Hz) (Hc) corresponding to a high field allylic methyl group. These resonances are all consistent with the structure, 9-isopropenyl-1,2,3,4-tetrahydrofluorene (37a), which Stewart⁸⁵ reported and unambiguously identified. The protons of the allylic methyl group lie above the plane of the aromatic ring due to the tetrahedral configuration about C(9) and are therefore in the "shielding" region of the aromatic ring which causes the resonance to occur at a higher field than is usual (8.0-8.3 τ)²¹⁴ for an allylic methyl group.

The remainder of the spectrum shows the following resonances; at 4.8 τ and 5.08 τ (Hd) corresponding to olefinic methylene protons, at 7.03 τ (He) a doublet of doublets (J=12 Hz, J=6 Hz) and at 7.96 τ (Hf) corresponding to an allylic methyl group. These resonances were attributed to the compound 9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (37b), the doublet of doublets being due to the resonance of the proton on C(4a) being split by the two protons on C(4). The resonance due to the allylic methyl group occurs at a value which is equal to that normally found for such groups, this resulting from the planar orientation of the isopropenyl group on C(9), thus differing from the value obtained for the corresponding group in the tetrahydrofluorene (37a)



(40a, R=F)



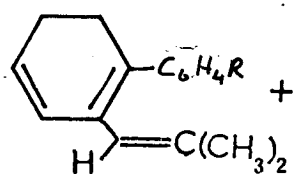
(40b, R=F)

FIGURE XVII

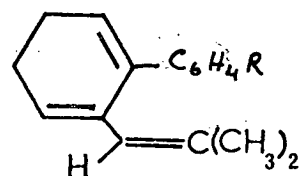
Although it was not possible to separate the two isomers in this case, 7-fluoro-9-isopropenyl-1,2,3,4-tetrahydrofluorene (40a, R=F) and 7-fluoro-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (40b, R=F), obtained similarly from 6-dimethylvinylidene-1-(p-fluorophenyl)bicyclo[3,1,0]hexane (38, R=F), were separable by preparative g.l.c. The ^1H -n.m.r. spectra of the two isomers (Figure XVII) show that the original assignments, made for the parent compound, were correct. Confirmation of the molecular formula was obtained from exact mass measurement of the parent peak in the mass spectrum of each isomer, both isomers giving masses corresponding to $\text{C}_{16}\text{H}_{17}\text{F}$.

The vapour phase rearrangement of 6-dimethylvinylidene-1-(p-tolyl)bicyclo[3,1,0]hexane (38, R=CH₃) at 450° gave a mixture of 7-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (40a, R=CH₃) and 7-methyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (40b, R=CH₃), the products being identified by ^1H -n.m.r. spectroscopy and by analogy with the foregoing results. None of the previously reported⁸⁵ products were present. Stewart⁸⁵ showed that the same products were obtained from the acid catalysed rearrangement of the p-tolylcyclopentene adduct as were found for the thermal rearrangement of the adduct. It would seem, therefore, that the products which he obtained from the thermal rearrangement, probably arose from traces of acid present in either the adduct or the thermolysis vessel. Further evidence for this was gained from the rearrangement of the 1-phenylcyclopentene adduct (36) by passing an acetone solution of the adduct, through a preparative g.l.c. column at 200°C. The resultant product was a six component mixture, four of which, accounting for 90% of the mixture, were formed by an acid catalysed mechanism and two of which were formed purely by thermolysis. The products were identified as, 2-(2'-methylprop-1'-enyl)-1-phenylcyclohexa-1,3-diene (39a, R=H), 2-(2'-methylprop-1'-enyl)-3-phenylcyclohexa-1,3-diene (39b, R=H),

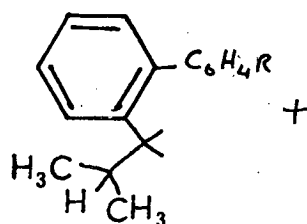
(36) $\longrightarrow$



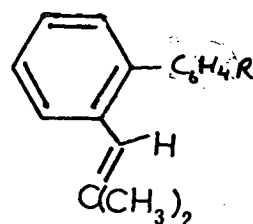
(39a, R=H)



(39b, R=H)



(39c, R=H)



(39e, R=H)

(37a)

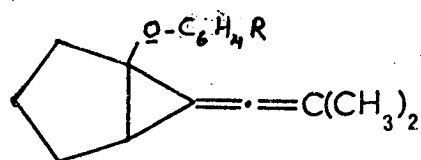
+

(37b)

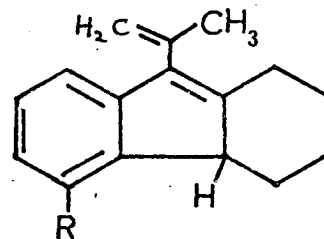
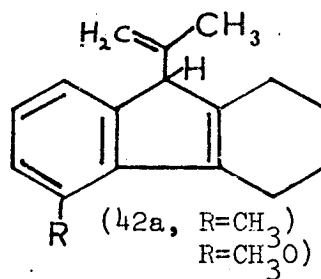
FIGURE XIX

2-(2'-methylprop-1'-enyl)biphenyl (39e, R=H) and 2-isobutylbiphenyl (39c, R=H), which were found by Stewart⁸⁵ to arise from the acid catalysed rearrangement of the adduct (Figure XIX), and the two tetrahydrofluorenes (37a) and (37b) which arise from the thermal rearrangement of the adduct. This complex series of products is due to the traces of acid present on the acid washed support in the column packing. On preparing a fresh column, the products from the acid catalysed mechanism make up 99% of the product mixture, traces of the thermal rearrangement products only being found. In this case more acid is present on the support than in the case where the column had already been used and consequently more of the acid catalysed products are formed.

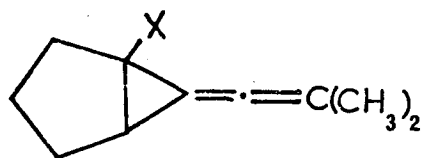
The attempted rearrangement of the 1-phenylcyclopentene adduct in refluxing benzene and refluxing toluene for 8 hr. gives only unrearranged adduct, however, the rearrangement in 1,1,2,2-tetrachloroethane (4 hr.) gave a mixture of two products. These were separated by preparative g.l.c. and identified as the two biphenyls (39c, R=H) and (39e, R=H) in equal amounts. The biphenyl (39e, R=H) appears to be formed by oxidation of the cyclohexadienes (39a, R=H) and (39b, R=H) which are formed, along with the biphenyl (39c, R=H), by an acid catalysed mechanism. This mechanism predominates over the expected thermal mechanism due to the traces of acid which are extremely difficult to remove from the solvent. Repetition of the reaction using degassed solvent decreases the amount of the biphenyl (39e, R=H), to 10% confirming that, at the reaction temperature (146°), the dissolved oxygen causes oxidation of the cyclohexadienes which otherwise at that temperature undergo further protonation and rearrangement to form the thermodynamically more stable biphenyl (39c, R=H). This again demonstrates that, even at elevated temperatures, where thermal processes can take place, traces of



(41, R=CH₃)
R=CH₃O)

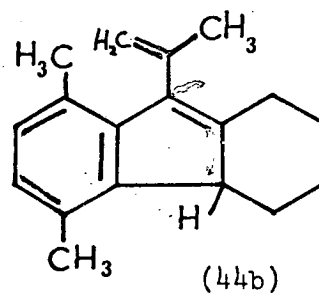
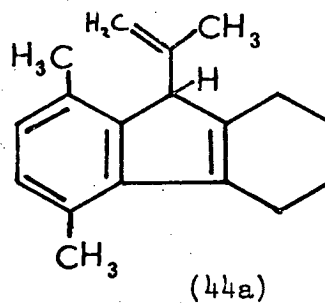


(42b, R=CH₃)
R=CH₃O)



(43)

X=2',5'-dimethylphenyl

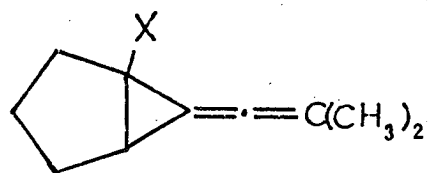


acid in the system give the products due to acid catalysis rather than purely thermolysis. Rigorous purification of the adducts eliminated the acid catalysed rearrangement of the adducts taking place in the vapour phase (450°) in all cases with the exception of 6-dimethylvinylidene-1-(p-methoxyphenyl)bicyclo[3,1,0]hexane (38, $R=CH_3O$), which, was difficult to purify and was never obtained completely "acid free".

The vapour phase rearrangement of 6-dimethylvinylidene-1-(g-tolyl)bicyclo[3,1,0]hexane (41, $R=CH_3$) at 450° gives a mixture of 5-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (42a, $R=CH_3$) and 5-methyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (42b, $R=CH_3$) and under the same conditions 6-dimethylvinylidene-1-(g-methoxyphenyl)bicyclo[3,1,0]hexane (41, $R=CH_3O$) gives a mixture of 5-methoxy-9-isopropenyl-1,2,3,4-tetrahydrofluorene (42a, $R=CH_3O$) and 5-methoxy-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (42b, $R=CH_3O$). In both cases the isomers were not separable and were identified from the ^1H -n.m.r. spectrum of the mixture.

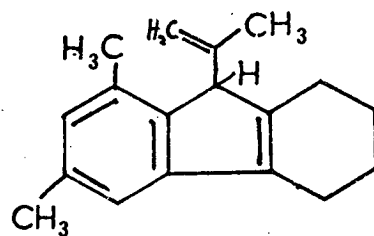
The vapour phase rearrangement (450°) of the dimethylvinylidene-carbene adducts of two disubstituted 1-phenylcyclopentenes also gave mixtures of the two tetrahydrofluorenes as products. 6-Dimethylvinylidene-1-(2',5'-dimethylphenyl)bicyclo[3,1,0]hexane (43) gives a mixture of 5,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (44a) and 5,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (44b) and 6-dimethylvinylidene-1-(3',5'-dimethylphenyl)bicyclo[3,1,0]hexane (45) gives a mixture of 6,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (46a) and 6,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (46b). Again, the products were identified from ^1H -n.m.r. spectra, a pure sample of 6,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (46a) being isolated by preparative g.l.c.

The vapour phase rearrangement (450°) of dimethylvinylidene-carbene adducts of meta-substituted 1-phenylcyclopentenes gives a



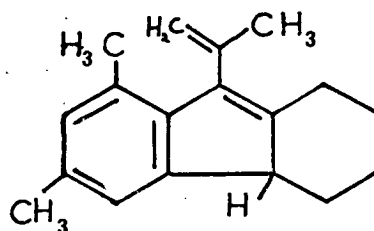
(45)

X = 3',5'-dimethylphenyl

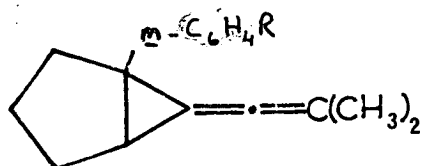


(46a)

+



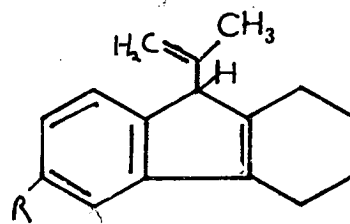
(46b)



(47, R=Bu^t)

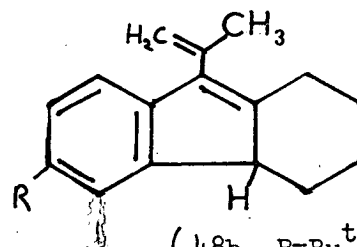
R=CF₃)

R=CH₃)



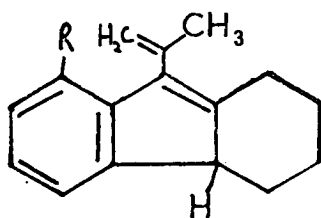
(48a, R=Bu^t)
R=CF₃)
R=CH₃)

+



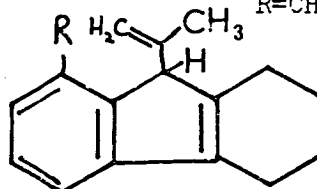
(48b R=Bu^t)
R=CF₃)
R=CH₃)

+



(49b R=Bu^t)
R=CF₃)
R=CH₃)

+

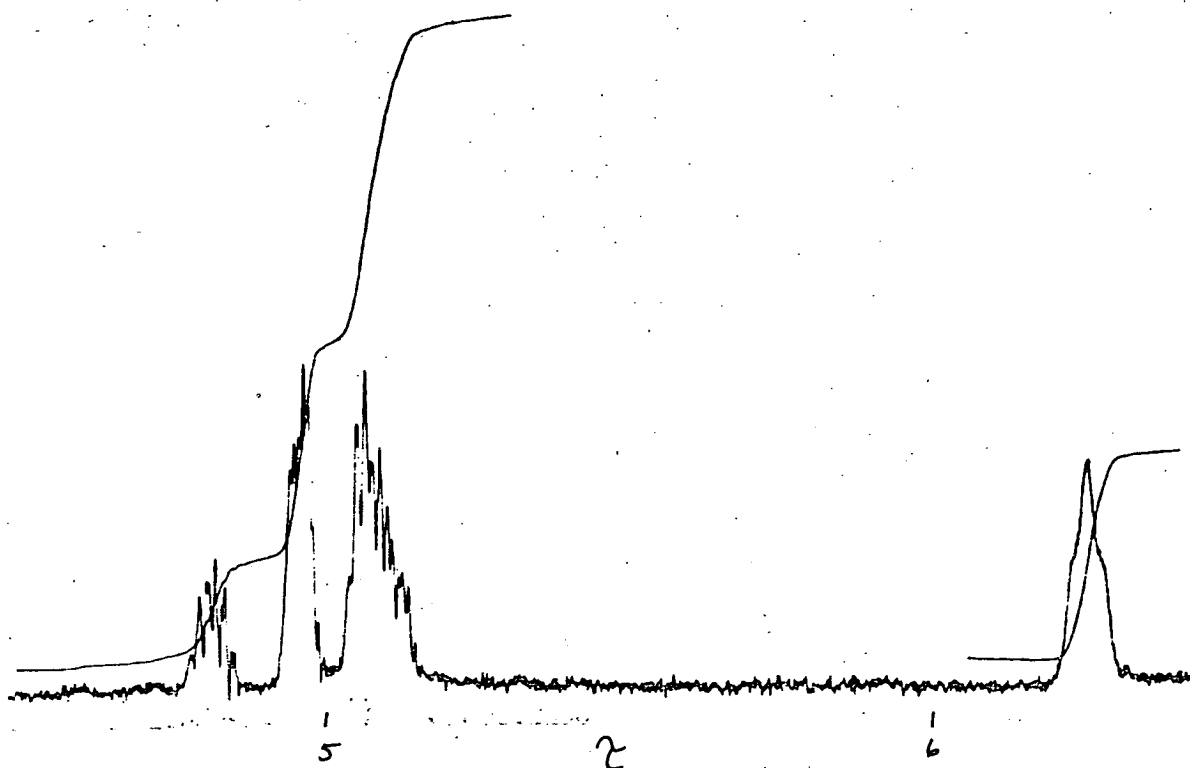


(49a R=Bu^t)
R=CF₃)
R=CH₃)

mixture of three isomeric products which were identified from ^1H -n.m.r. spectra, after partial separation by preparative g.l.c. 6-Dimethylvinylidene-1-(m-t-butylphenyl)bicyclo[3,1,0] hexane (47, $\text{R}=\text{Bu}^t$) gives a mixture of 6-t-butyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (48a, $\text{R}=\text{Bu}^t$) 8-t-butyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (49a, $\text{R}=\text{Bu}^t$) and 6-t-butyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (48b, $\text{R}=\text{Bu}^t$). Similarly 6-dimethylvinylidene-1-(m-trifluoromethylphenyl)bicyclo[3,1,0] hexane (47, $\text{R}=\text{CF}_3$) gives a mixture of 6-trifluoromethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (48a, $\text{R}=\text{CF}_3$), 8-trifluoromethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (49a, $\text{R}=\text{CF}_3$) and 6-trifluoromethyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (48b, $\text{R}=\text{CF}_3$) and 6-dimethylvinylidene-1-(m-tolyl)bicyclo[3,1,0] hexane (47, $\text{R}=\text{CH}_3$) gives a mixture of 6-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (48a, $\text{R}=\text{CH}_3$), 8-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (49a, $\text{R}=\text{CH}_3$) and 6-methyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (48b, $\text{R}=\text{CH}_3$). In each case the 8-substituted-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (49b) is absent or in such a low concentration as to be undetectable by ^1H -n.m.r., (see later). The ^1H -n.m.r. spectra of the mixtures show the resonance due to the proton on C(9) in the tetrahydrofluorene with a substituent on C(8) resonates at a different value from that due to the proton on C(9) when a substituent is on the C(6) position thus allowing the isomers to be identified.

All the rearrangement products of the substituted 1-arylcyclopentene adducts show the same characteristics in the ^1H -n.m.r. spectrum as those cited for the parent adduct (Figure XVI) varying slightly due to the effects of the substituents and showing in addition resonances due to the presence of protons in the substituents. The infra-red spectrum in each case was consistent with the presence of a terminal methylene group and a substituted aromatic ring.

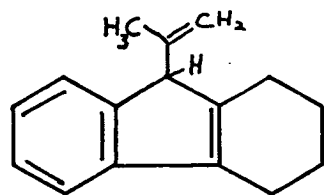
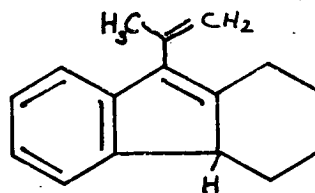
The proportion of each isomer present on the rearrangement of each adduct was calculated as follows. The ^1H -n.m.r. integral step-heights of the resonances due to the olefinic methylene groups in each isomer and the integral step-height of the resonance due to the benzylic proton were measured and the ratio calculated from them. Confirmation of this ratio was sought by rearrangement of another sample of the adduct at the same temperature and measuring the same integral step-heights in that case also. Further confirmation was often possible by measuring the integral step-heights of the resonances due to the allylic methyl groups of each isomer where these were not masked by other resonances or similarly using the resonances of proton bearing substituents if the resonances were different in each isomer. The spectral area involved is shown below and the proportions of each isomer formed is shown in Table I.



6-dimethylvinylidene-1-phenylbicyclo 3,1,0 hexane (36), ^1H -n.m.r. spectrum -- expansion of the area from - 4.5 - 6.5 τ -

Table I

Thermal rearrangement of 1-arylcyclopentene adducts at 450° in flow system A.

XY

Substituent in the phenyl ring	Proportion of <u>X</u> *	Proportion of <u>Y</u> *
none	2.3	1.0
D ₅	2.3	1.0
<u>ortho</u> -methyl	5-substituted 0.6	1.0
<u>ortho</u> -methoxy	5-substituted 1.0	1.0
<u>para</u> -methyl	7-substituted 2.0	1.0
<u>para</u> -fluoro	7-substituted 1.9	1.0
<u>meta</u> -t-butyl	6-substituted 2.6	1.0
	8-substituted 0.67	0.0
<u>meta</u> -trifluoromethyl	6-substituted 1.6	1.0
	8-substituted 1.75	0.0
<u>meta</u> -methyl	6-substituted 3.7	1.0
	8-substituted 1.4	0.0
2,5-dimethyl	2.9	1.0
3,5-dimethyl	7.0	1.0

*

The ratio of X:Y are consistent to within ±0.1.

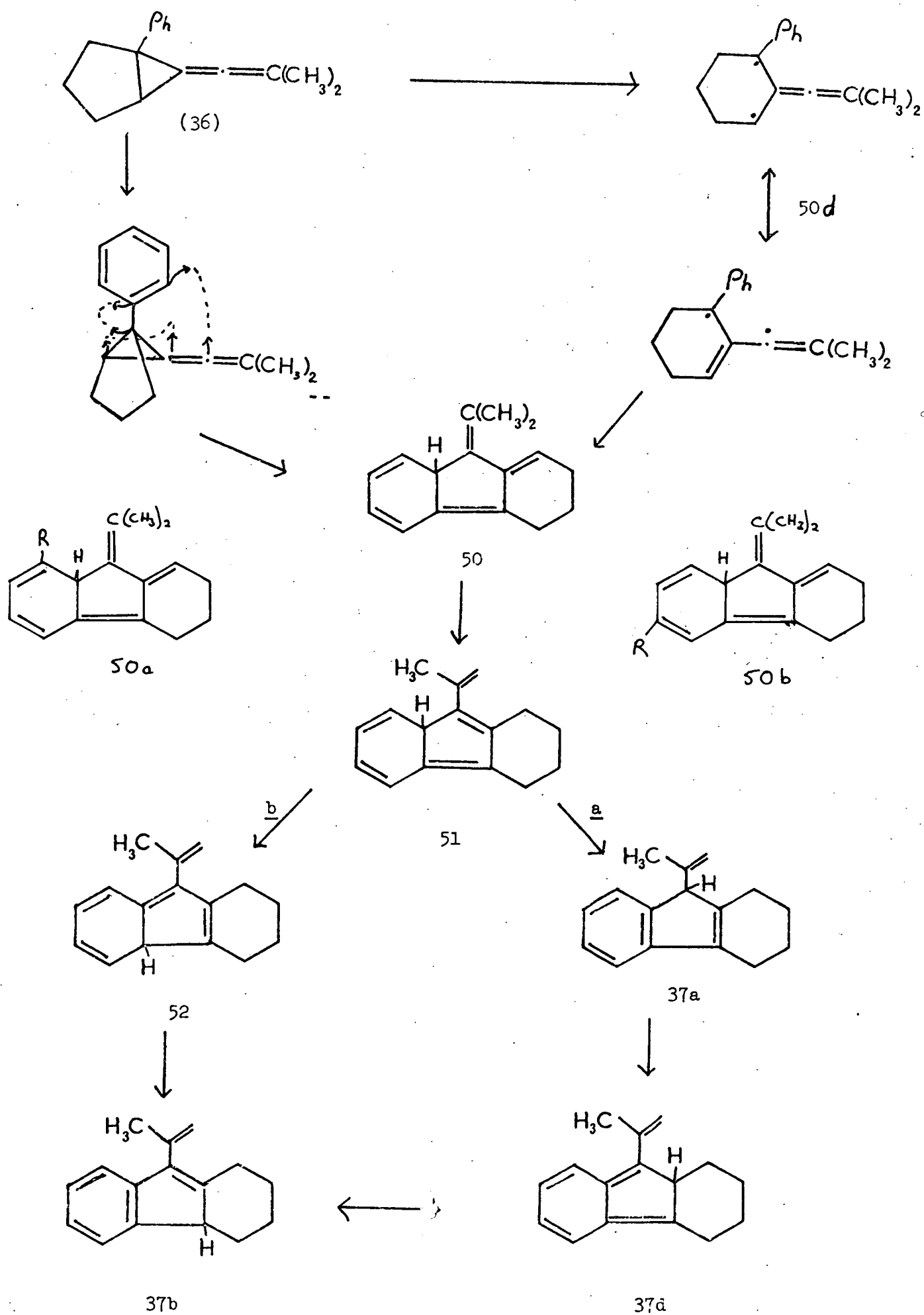


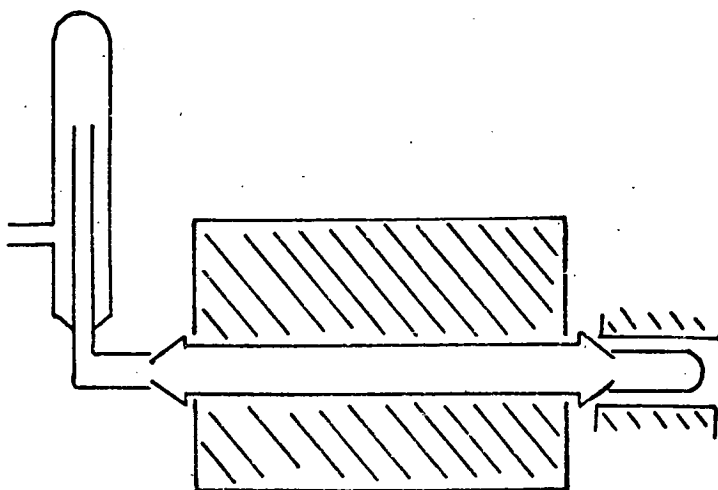
FIGURE XX

The mechanism of formation of these products can be rationalised (Figure XX) in terms of an initial, irreversible ring closure to give the intermediate (50) possibly via a diradical (50d). The concerted process also shown, is possible, but is considered less likely. Ring closure to form this intermediate takes place by attack at either of the ortho-positions in the benzene ring if it is unsubstituted, this fact being exemplified by the formation of both the 6-substituted and 8-substituted isomers in the rearrangement of the meta-substituted phenylcyclopentene adducts. The intermediate (50) may then undergo a 1,5 hydrogen migration to form intermediate (51) from which both tetrahydrofluorenes can be formed. Another 1,5-(1,9)-hydrogen migration via route a leads to a 9H-tetrahydrofluorene.

A 1,5-hydrogen migration via route b followed by a further 1,5-(1,9)-hydrogen migration yields a tetrahydro-4aH-fluorene. Alternatively, the formation of the tetrahydro-4aH-fluorene could arise from the isomerisation of the 9H-tetrahydrofluorene via the 9aH-intermediate (37d). The overall mechanism, proposed in Figure XX, was substantiated by the vapour phase rearrangement (450°C) of 6-dimethylvinylidene-1-(pentadeuterophenyl)bicyclo[3,1,0]hexane (53). The products from this rearrangement was identified as a mixture of 5,6,7,8,9-pentadeutero-9-isopropenyl-1,2,3,4-tetrahydrofluorene (54a) and 4a,5,6,7,8-pentadeutero-9-isopropenyl-1,2,3,4-tetrahydrofluorene (54b). The ¹H-n.m.r. spectrum of this mixture is virtually identical to that found for the rearrangement of the parent adduct (37a+b) Figure XIV except that the resonances due to the C(9) proton and C(4a) proton are missing due to complete deuteration at these sites. The presence of deuterium at these two sites and at no other is consistent with the proposed formation of the intermediate (50), subsequent hydrogen migrations to form (51) and thence as proposed to the products.

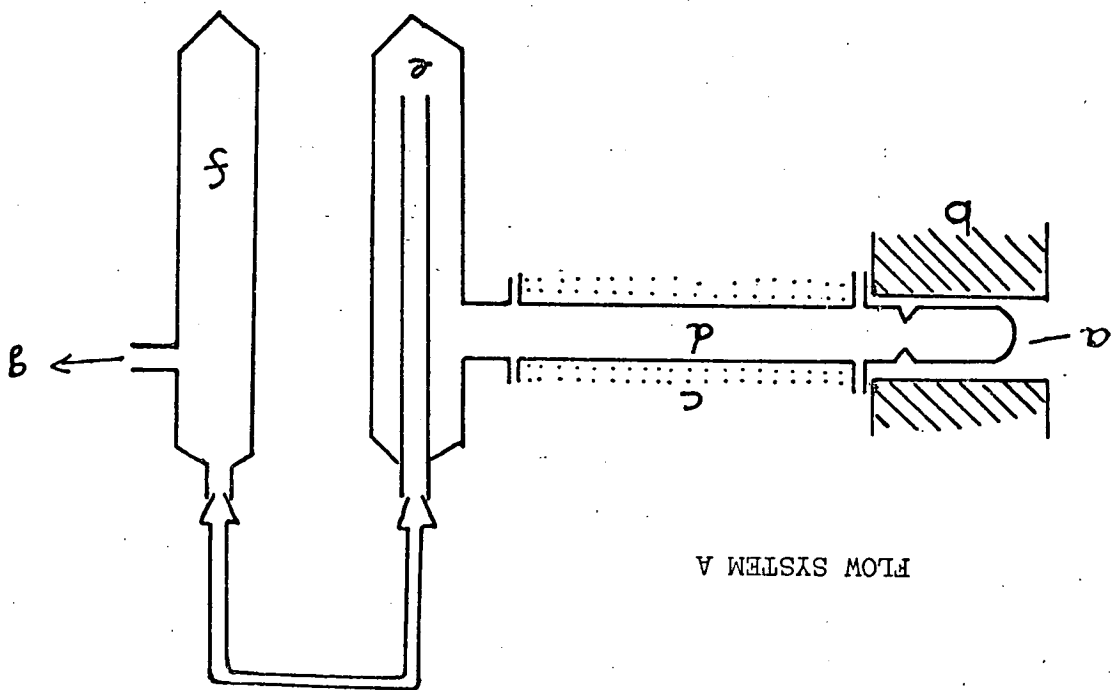
When a meta-substituent is present in the adduct (47, R=Bu^t, CF₃ or CH₃) the initial cyclisation to form the intermediate (50a) or

FIGURE XXII



FLOW SYSTEM B

FIGURE XXI



FLOW SYSTEM A

(50b) is affected by the size of the substituent. When the t-butyl substituent is present there is a large steric interaction to cyclisation to give an 8-substituted intermediate ($50a, R=Bu^t$) and the 6-substituted intermediate ($50b, R=Bu^t$) is formed in a much larger proportion (5.5:1.0). This interaction is not so large when the substituent is methyl and the ratio of 6-substituted intermediate to 8-substituted intermediate is reduced to 3.5:1.0. The presence of the trifluoromethyl group which is intermediate in size between the t-butyl and methyl groups does not give an intermediate value for the ratio, the ratio being 1.5:1.0; the reason for this deviation is, however, not clear.

All isomer ratios were found to be unaltered by recycling the rearrangement products through the flow system at the same temperature, or by distilling the rearrangement products or by passing the rearrangement products through a preparative g.l.c. column at elevated temperatures (175° - 200° C). The fact that the ratio of 9H-tetrahydrofluorene to 4aH-tetrahydrofluorene, on recycling the products, does not vary, can be interpreted either in terms of a thermodynamic equilibrium between these products having been reached or that the interconversion route has too high an activation energy.

In an attempt to elucidate which of these two possibilities was functioning various experiments were set up using the phenylcyclopentene adduct, changing the pyrolysis tube dimensions, the temperature and the amount of glass wool packed in the pyrolysis tube. The results obtained are summarised in Table II. As will be seen (Table II) in every case the two tetrahydrofluorenes (37a) and (37b) were obtained, the amounts of these two products varying with the conditions. Using flow system A (Figure XXI) an increase in packing density (i.e. the number of collisions molecules can make with the hot walls) or an increase in temperature reduced the isomer ratio to a constant ratio of 2.3:1.0. Also, recycling a mixture with a ratio greater than 2.3:1.0 through the

TABLE II

Flow system <u>A</u> or <u>B</u>	Temperature	Packing L, N or T	Isomer ratio (37a) : (37b)
<u>A</u>	500°	N	2.3:1.0
<u>A</u>	600°	N	2.1:1.0
<u>A</u>	450°	T	2.3:1.0
<u>A</u>	350°	T	2.3:1.0
<u>A</u>	450°	L	2.3:1.0
<u>A</u>	350°	L	3.1:1.0
<u>B</u>	450°	N	3.0-3.2:1.0
<u>A</u>	350°	N	2.6:1.0
<u>A</u>	450°	N	2.3:1.0

L = LOOSE N = NORMAL T = TIGHT.

TABLE III

Original Flow system <u>A</u> or <u>B</u>	Original Isomer ratio (37a):(37b)	Recycled through Flow System <u>A</u> or <u>B</u>	Final isomer ratio (37a):(37b)
<u>A</u>	2.3:1.0	<u>A</u>	2.3:1.0
<u>B</u>	3.0-3.2:1.0	<u>B</u>	2.9:1.0
<u>A</u>	2.3:1.0	<u>B</u>	2.3:1.0
<u>B</u>	3.0-3.2:1.0	<u>A</u>	2.3:1.0

flow system (Table III) allows the figure 2.3:1.0 to be approached or attained. The effect of using flow system B (Figure XXII) is to give an isomer ratio above 2.3:1.0 which is consistent with the trends found for flow system A. All these trends, along with the fact that the recycling of the rearrangement products from all adducts at 450°C did not alter the isomer ratio, indicate that an equilibrium has been established and not that the activation energy for the conversion of the 9H-tetrahydrofluorene to the 4aH-tetrahydrofluorene is too high. Further experimental evidence comes from the work of Stewart⁸⁵ who detected only the 9H-tetrahydrofluorene (37a) in a pyrolysis at 450°C using flow system B. This suggests that the pyrolysis tube was only loosely packed with glass wool, which would tend to give a high proportion of the compound most readily formed, namely, the 9H-tetrahydrofluorene (37a) hence rendering the 4aH-tetrahydrofluorene (37b) almost undetectable. This suggests that the 4aH-tetrahydrofluorene (37b) is formed from the 9H-tetrahydrofluorene (37a) by equilibration via intermediate (37d) rather than by the route via intermediate (52).

Theoretical evidence that equilibration of the two isomers had taken place was also sought. Figure XXIV shows the energy profile for the starting material, intermediates and products for the mechanism previously outlined (Figure XX), all values being calculated according to the procedure of Benson²¹⁵ (see Appendix I). The initial activation energy must be at least 30 K cal mol⁻¹ since the rearrangement of the dimethylvinylidenecarbene adduct of α -methylstyrene has an activation energy of this magnitude⁸⁵ and the rearrangement proceeds more readily. Equilibration of the isomers (37a) and (37b) is via the intermediate (37d) by 1,5-hydrogen migrations. This process involves a change in heat of formation, and the energy required for a 1,5-hydrogen migration is in the range 30-40 K cal mol⁻¹ therefore some¹²⁷ molecules will have sufficient energy to equilibrate via this route.

However the free energy difference between the 9H-isomer (37a) and the 4aH-isomer (37b) is -0.65 K cal mol⁻¹, corresponding to an equilibrium

ΔH_f° values calculated for the starting materials,
intermediates and products of the mechanism outlined
in Figure XX.

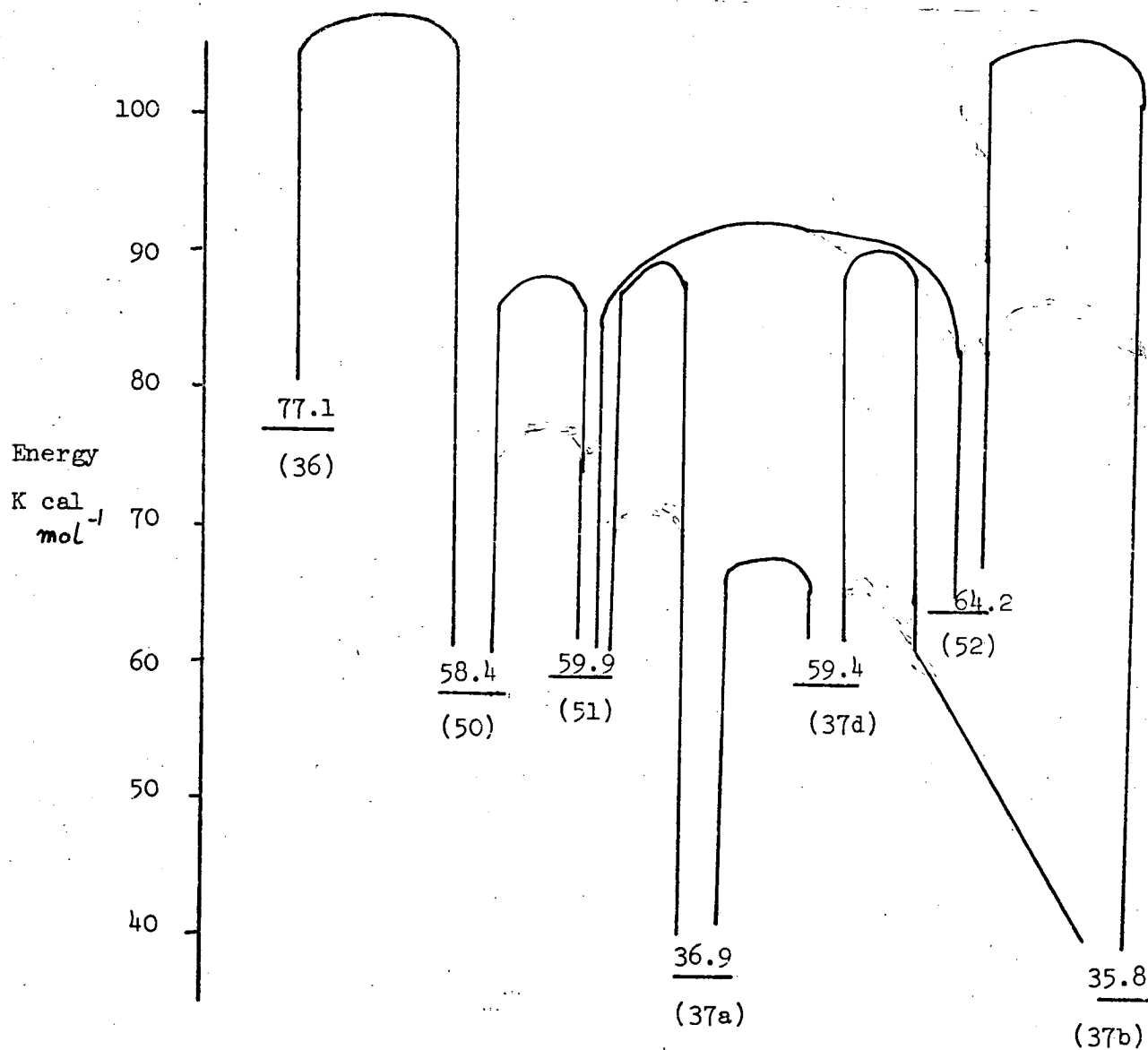


FIGURE XXIV

constant of 1.6 at 450° in favour of the 9H-isomer. This compares well with the experimental isomer ratio of 2.3:1, thus supporting the equilibration proposal. (See Appendix I)

As was stated previously (page 66) the 9H-tetrahydrofluorene (37a) is formed more readily than the 4aH-tetrahydrofluorene (37b), this being rationalised by stereochemical considerations. Examination of stereomodels shows that the rearrangement of the intermediate (51) to the 9H-tetrahydrofluorene (37a) is favoured as there is a relief of strain between the isopropenyl group on C(9) and the hydrogen attached to C(8) and the system is aromatised by the migration of the C(8a) hydrogen atom by either a 1,5 or 1,9 route to the end of a polyene system. The migration of hydrogen atoms to the end of a polyene system is more favourable than migration to the centre of a polyene system as there is a greater π -electron density associated with the terminal carbon atoms than the non-terminal carbon atoms²¹⁶. The direct formation of the 4aH-tetrahydrofluorene (37b) requires the rearrangement of intermediate (51) to intermediate (52) and subsequent rearrangement of this intermediate to give (37b). Therefore, the formation of (37b) is a two step process and the study of stereomodels shows that the rearrangement of intermediate (51) to intermediate (52) involves an increase in strain between the isopropenyl group on C(9) and the hydrogen on C(8) and involves the less favourable migration of a hydrogen to the centre of a polyene system with no aromatic stability being obtained. This makes this rearrangement less favourable than the rearrangement of intermediate (51) to 9H-tetrahydrofluorene (37a). The rearrangement of intermediate (52) to the 4aH-tetrahydrofluorene (37b) gains only the stability due to aromatisation there being no relief in the steric strain between the C(8) hydrogen and the C(9) isopropenyl group. Consequently the 9H-tetrahydrofluorene (37a) is expected to be formed more easily than the 4aH-tetrahydrofluorene (37b).

When substituents are present in the adducts these have an

effect on the course of the rearrangement and alter the proportions of each isomer in the rearrangement products. Substituents in positions C(5) and C(8) have a large steric influence on the proportions of the reaction products formed. When a substituent is present on C(5) it introduces a strain between the C(5) substituent and the C(4) hydrogen atom in the 9H-tetrahydrofluorene (37a) which does not exist if there is no C(5) substituent. In the 4aH-isomer (37b) the interaction between the C(5) substituent and the C(4) hydrogen is much less due to the shape of the molecule and this makes the formation of this isomer more favourable when a substituent is present on C(5). The size of the interaction obviously depends on the bulk of the group on C(5) and this is reflected in the isomer ratios found. With a methyl group in the C(5) position the 4aH-tetrahydrofluorene (42b, R=CH₃) is formed in preference to the 9H-isomer (42a, R=CH₃) because of the bulk steric effect whereas when the substituent is a methoxy group, the bulk steric effect is not as large, because the group can bend back out of the way of the C(4) hydrogens and consequently the two isomers (42a, 42b, R=CH₃O) are formed in equal amounts. In either case the equilibrium moves in favour of the 4aH-tetrahydrofluorene (42b).

A substituent in the C(8) position introduces a large amount of steric strain this strain being set up between the substituent on C(8) and the isopropenyl group on C(9). This strain is smaller in the 9H-tetrahydrofluorene (49a), where the isopropenyl group is not co-planar with the C(8) substituent, than it is in the 4aH-isomer (49b) where the substituent and the isopropenyl group are co-planar. Regardless of the bulk of the substituents used (R=Bu^t, CF₃, CH₃) the equilibrium is swung almost completely to the formation of the 9H-isomer (49a) and in no case was the 4aH-isomer (49b) formed in a large enough quantity to be detected.

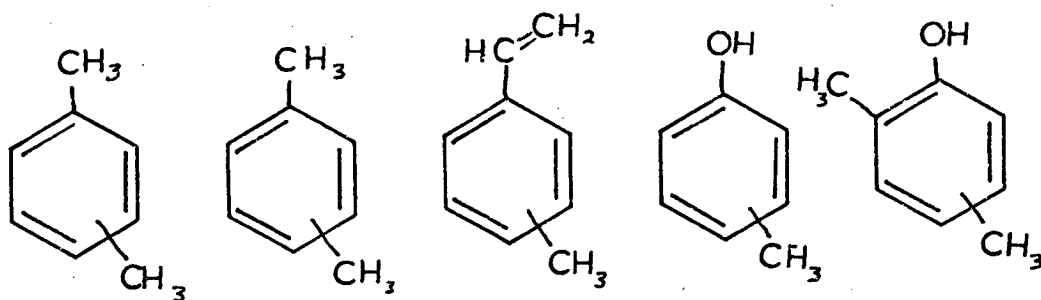
The presence of two substituents in the originally aromatic part of the adduct allows the opposing effects of substitution in the

C(5) and C(8) positions to be studied. The rearrangement of the 2,5-dimethylphenylcyclopentene adduct (43) gives the two isomeric tetrahydrofluorenes (9H:4aH) in the ratio 2.9:1.0. The products have both a C(5) and C(8) substituent present and the equilibrium set up favours the formation of the 9H-tetrahydrofluorene (44a). The C(8) substituent causes the equilibrium to greatly favour this isomer but the C(5) substituent has an opposing effect favouring the 4aH-isomer (44b). The combined effect shows, as would be expected from the study of stereomodels, that the interaction caused by the presence of a C(8) substituent is greater than that caused by a similar C(5) substituent and therefore the equilibrium favours the stronger effect and the 9H-isomer (44a) is formed in the greater proportion.

The influence of substituents in the C(6) and C(7) positions would appear to be electronic in nature. The only possible steric effect, that of buttressing, can be excluded since the methyl substituent on C(6) causes a greater deviation in the isomer ratio than does the t-butyl substituent on C(6). The following points emerge in support of an electronic effect being present. A methyl substituent on C(6) has an opposite effect than a methyl substituent on C(7), electron acceptor groups on C(6) have the same effect as electron donor groups on C(7) and an opposite effect to electron acceptor groups on C(7) and finally a methyl substituent on C(6) has a greater effect than a t-butyl group on the same position. From a comparison of the ratios of (48a, R=CH₃) to (48b, R=CH₃) and (40a, R=CH₃) to (40b, R=CH₃) which are the products from the rearrangement of the m-methylphenylcyclopentene adduct (47, R=CH₃) and the p-methylphenylcyclopentene adduct (38, R=CH₃) respectively, it can be seen that the presence of a methyl group in the C(6) position moves the equilibrium position to favour the formation of the 9H-tetrahydrofluorene whereas the presence of the methyl group in the C(7) position tends to move the equilibrium in favour of the 4aH-isomer.

Table IV

Calculated $\Delta(\Delta H_f^\circ)$ values using values of Benson²¹⁵



<u>meta</u>	4.12	-0.46	27.6	-31.6	-38.7
<u>para</u>	4.29	-0.78	27.4	-30.0	-39.0
Δ	0.17	-0.32	0.2	1.6	-0.3
more stable	<u>meta</u>	<u>para</u>	<u>para</u>	<u>meta</u>	<u>para</u>

Table V

Free energy calculated for the series of isomeric tetrahydrofluorenes

<u>Substituent</u>	<u>ΔG°</u>
None	1.19
D ₅	1.19
5-methyl	-0.73
5-methoxy	0
7-methyl	0.99
7-fluoro	0.92
6-t-butyl	1.37
6-trifluoromethyl	0.67
6-methyl	1.87
5,8-dimethyl	1.52
6,8-dimethyl	2.78

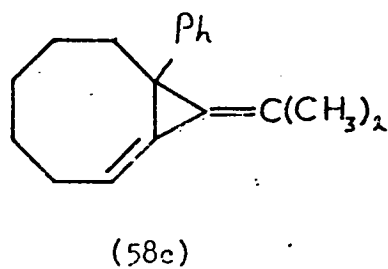
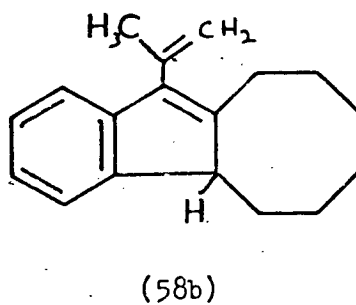
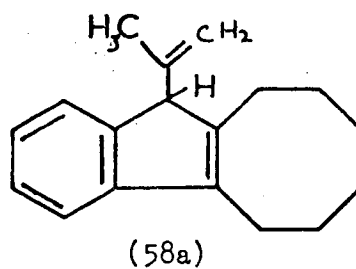
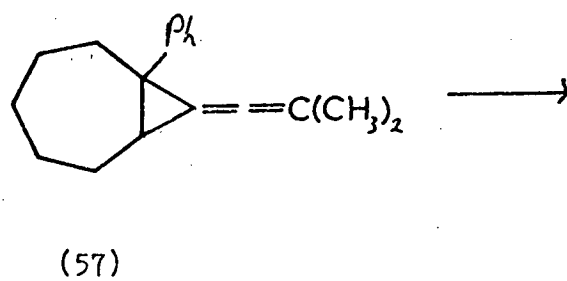
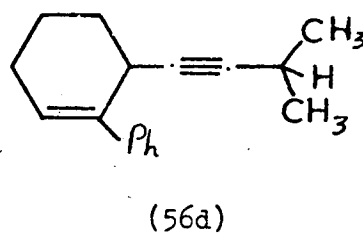
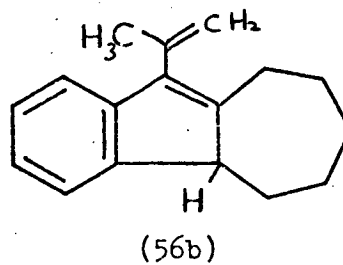
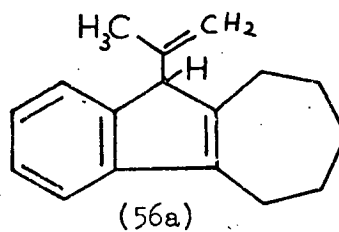
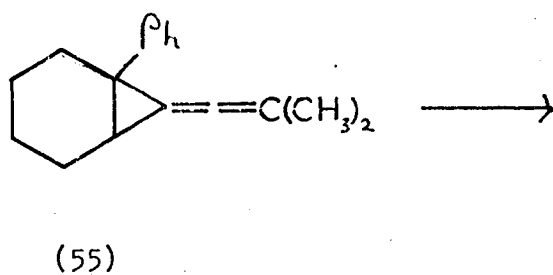
The reason for this effect is not readily explained. Calculating heats of formation differences for various meta and para substituted toluenes the stability varies between the two positions, sometimes the meta isomer is more stable and sometimes the para isomer is more stable. (Table IV) This, unfortunately, does not allow any conclusions to be drawn, however, the differences in heats of formations of the meta and para isomers are small and are similar to the differences in free energy calculated for the series of isomeric tetrahydrofluorenes studied (Table V). This gives a picture which is consistent but not readily explained.

A further adduct was prepared and its rearrangement examined to study the effects of two substituents being present. The dimethylvinylidene carbene adduct of 3,5-dimethylphenylcyclopentene (45) on rearrangement gave the two tetrahydrofluorenes (9H:4aH) in the ratio 7.0:1.0. This large proportion of the 9H-tetrahydrofluorene (46a) is due to the additive effect of the substituents. One of the methyl groups is on the C(8) position which pushes the equilibrium towards the 9H-isomer (46a) and the other methyl group is on the C(6) position which also pushes the equilibrium towards the 9H-isomer (46a). Thus, the cumulative effect makes the 9H-tetrahydrofluorene (46a) appear in a larger proportion, giving the greatest difference between the two possible isomers in the series studied.

5.3 Comparison of the rearrangement products of dimethylvinylidene-benzobicyclo[n,1,0]alkenes

With a view to elucidating the effect of ring size on the nature and proportions of the products formed, the vapour phase rearrangements of the dimethylvinylidene carbene adducts of 1-phenylcyclohexene, 1-phenylcycloheptene and 1-phenylcyclooctene were also studied.

The vapour phase rearrangement of 7-dimethylvinylidene-1-phenylbicyclo[4,1,0]heptane (55) at 350°C or 450°C gave a mixture of

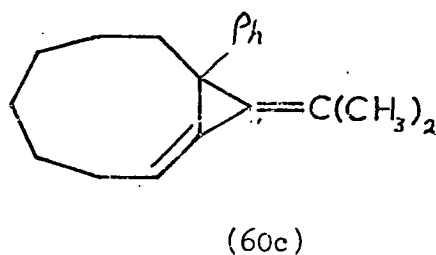
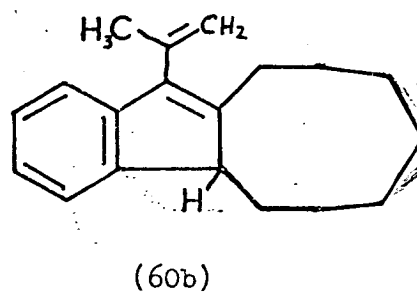
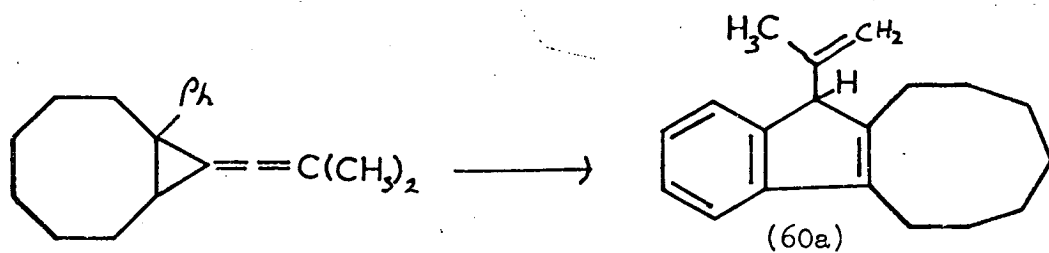


three isomeric compounds consisting of 3-(3'-methylbut-1'-ynyl)-2-phenylcyclohex-1-ene (56d), 1-isopropenyl-1,4,5,6,7,8-hexahydro-2,3-benzazulene (56a) and 1-isopropenyl-3a,4,5,6,7,8-hexahydro-2,3-benzazulene (56b). The ethynylcyclohexene (56d) was separated from the two hexahydrobenzazulenes by preparative g.l.c., however, the two benzazulenes were themselves unseparable. The structure of the ethynylcyclohexene was confirmed by comparison of the spectral details obtained with those reported by Stewart⁸⁵ for the same rearrangement. The structure of the hexahydrobenzazulene (56a) was also confirmed by comparison of the spectral data obtained with those reported by Stewart⁸⁵ and the structure of the hexahydrobenzazulene (56b) was deduced from the ¹H-n.m.r. spectrum by analogy with the ¹H-n.m.r. spectrum of the tetrahydro-4aH-fluorene (37b) found in the rearrangement of the 1-phenylcyclopentene adduct. The ¹H-n.m.r. spectrum shows the resonances due to the olefinic protons as two broad singlets at 4.80 τ and 5.12 τ , a resonance due to an allylic methyl group at 8.0 τ and one due to the bridgehead proton on C(3) at 6.74 τ . Isomer ratios were deduced from the ¹H-n.m.r. spectrum of the mixture as previously described (section 5.2) and are shown in Table VI.

The vapour phase rearrangement of 8-dimethylvinylidene-1-phenylbicyclo[5,1,0]octane (57) at 350° or at 450° also gave a mixture of three isomeric products, consisting of two cyclooctaindenes and a bicyclo[6,1,0]non-7-ene. The three isomers were not separable by preparative techniques and their structures were assigned from the i.r. spectrum and ¹H-n.m.r. spectrum of the mixture and by analogy with the spectra obtained for the rearrangement of the 1-phenylcyclopentene adduct and those reported⁸⁵ for the rearrangement of the corresponding α -methylstyrene adduct. The ¹H-n.m.r. spectrum shows resonances at 4.92 τ and 5.03 τ attributed to olefinic protons, a broad resonance at 6.2 τ attributed to a benzylic proton and a high field (8.86 τ)

Table VI

Adduct with	Product Ratios							
	350°C				450°C			
	A	B	C	D	A	B	C	D
1-Phenylcyclopentene	2.6	1.0	-	-	2.3	1.0	-	-
1-Phenylcyclohexene	2.33	1.0	1.1	1.1	2.5	1.3	1.0	1.0
1-Phenylcycloheptene	3.2	1.0	7.8	1.1	3.3	1.0	0.23	1.0
1-Phenylcyclooctene	1.0	1.0	4.0	1.1	3.5	1.0	-	-



allylic methyl resonance which are characteristic resonances of 1-isopropenyl-2,3-cyclooctenoindene (58a). It also shows resonances at 4.68 τ and 5.09 τ attributed to olefinic protons, a multiplet at 6.65-6.8 τ attributed to the bridgehead C(3a) proton and an allylic methyl resonance at 8.11 τ which are characteristic resonances of 3-isopropenyl-4,2-cyclooctenoindene (58b). The presence of 8-phenyl-9-isopropylidenebicyclo[6,1,0]non-1-ene (58c) was deduced from the following resonances in the ^1H -n.m.r. spectrum; a resonance at 3.94 τ attributed to an olefinic hydrogen and two singlets at 8.16 τ and 8.3 τ attributed to the isopropylidene methyl groups, these resonances being similar to those reported by Stewart⁸⁵ for the rearrangement of dimethylvinylidene carbene adducts of various substituted styrenes which give 1-isopropylidene-2-methylenecyclopropanes. The possibility of this isomer being the ethynylcycloheptene by analogy with the products obtained from the rearrangement of the 1-phenylcyclohexene adduct was excluded by the absence of an absorption in the i.r. spectrum in the region 2100 cm^{-1} ($-\text{C}\equiv\text{C}-$ stretch) and the absence of resonances in the ^1H -n.m.r. spectrum at 6.6 τ attributed to a propargylic hydrogen and at 8.99 τ attributed to the isopropylmethyl group. As before the isomer ratios were calculated from the ^1H -n.m.r. spectra and are shown in Table VI.

The vapour phase rearrangement of 9-dimethylvinylidene-1-phenylbicyclo[6,1,0]nonane (59) at 350° gave a mixture of three isomeric products consisting of two cyclononaindenes and a bicyclo[7,1,0]decene. The three isomers were not separable by preparative techniques and their structures were assigned from the i.r. spectrum and ^1H -n.m.r. spectrum of the mixture and by analogy with the rearrangement products of the 1-phenylcycloheptene adduct. The ^1H -n.m.r. spectrum shows resonances at 4.92 τ and 5.02 τ attributed to olefinic protons, at 6.16 τ attributed to a benzylic proton and

a high field (8.86 τ) allylic methyl resonance which are all characteristic resonances of 1-isopropenyl-2,3-cyclononenoindene (60a). It also shows resonances at 4.8 τ and 5.06 τ attributed to olefinic protons, a multiplet at 6.8 τ attributed to the bridgehead C(3a) proton and an allylic methyl resonance at 7.97 τ which are characteristic resonances of 3-isopropenyl-4,2-cyclononanoindene (60b). The presence of 9-phenyl-10-isopropylidene-bicyclo[7,1,0]dec-1-ene(60c) was deduced from the following resonances in the ^1H -n.m.r. spectrum and by analogy to the previous rearrangement products; a resonance at 6.06 τ attributed to an olefinic proton and two singlets at 8.18 τ and 8.3 τ attributed to the isopropylidene methyl groups. The possibility of the ethynylcyclooctene being present was again excluded on similar grounds as for the rearrangement products from the 1-phenylcycloheptene adduct. The vapour phase rearrangement of the adduct (59) at 450°C gave only the two cyclonona-indenes (60a) and (60b) none of the bicyclodecene being detected. As before the isomer ratios were calculated from the ^1H -n.m.r. spectra and are shown in Table VI.

Examination of Table VI reveals the following. The products of type a and b are always formed with the type a products being in greater quantity and the ratio of a:b being relatively temperature invariant. The product of type d is only formed in significant amount in the rearrangement of the phenylcyclohexene adduct. The products of type c are only formed for the larger ring sized molecules and the proportion of c to a and b falls as the temperature is increased.

The mechanisms involved in the formation of these products depend on bond fission of either bond X or bond Y in Figure XXV. Fission of bond Y leads to the products of type a and b via the mechanism which has already been discussed for the rearrangement of the 1-phenylcyclopentene adduct (36). Fission of bond Y also

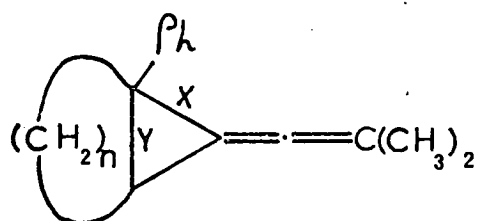


FIGURE XXV

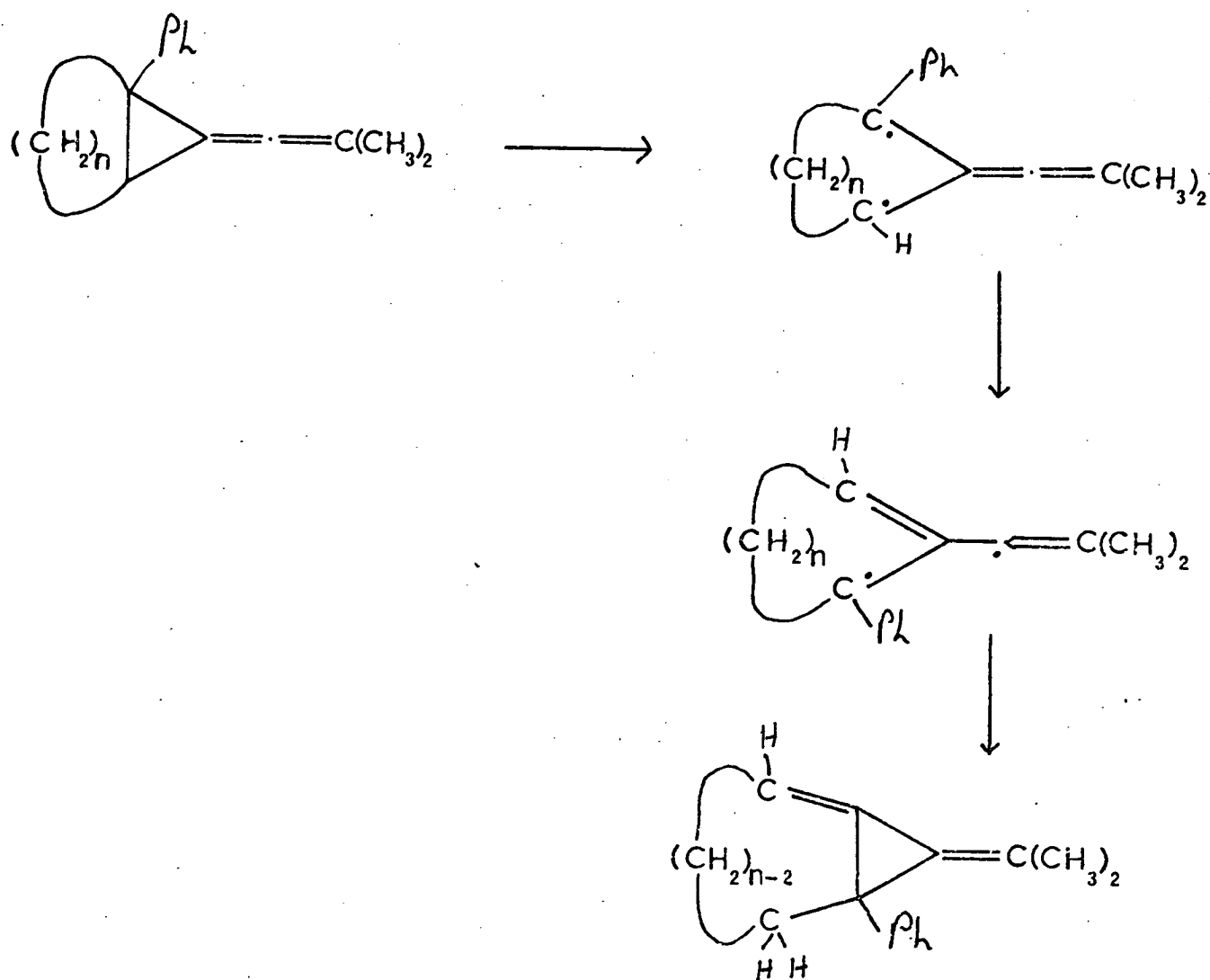


FIGURE XXVI

leads to the isopropylidenecyclopropanes (type c) by the mechanism¹⁸⁶ (Figure XXVI) proposed for the rearrangement of the dimethylvinylidene-carbene adducts of 1-arylalkenes. Fission of bond X leads to the ethynylcyclohexene (56d) via a concerted process. It was proposed⁸⁵ that the route to the ethynylcyclohexene was a disrotatory ring opening of bond X accompanied by a 1,5-suprafacial hydrogen migration (thermally allowed) as shown in Figure XXVII. A diradical mechanism was excluded since intramolecular hydrogen abstraction to form the isopropyl group is sterically extremely unlikely. These three mechanisms are possible in the rearrangement of the four 1-phenyl-cycloalkene adducts discussed, the absence of one or more of the products arising from these mechanisms being due to energy considerations in the intermediates and products.

The rearrangement of all four adducts (Table VI) lead to products of type a and b. The activation energy required for formation of these products must be easily attained at the temperatures used. By analogy with the 1-phenylcyclopentene adduct rearrangement, where heats of formation values were calculated for the starting material, intermediates and products, the products of type a and b will be more stable than the starting material. The formation of the products of type c is governed both by the stability of the product and the activation energy. The activation energy required to form the isopropylidenecyclopropanes from (57) and (59) must be less than that required to form type a or products as the proportion of c to a and b is greater at 350°C than 450°C. It is also possible to say that the isopropylidenecyclopropanes are less stable than the products of type a or b as at the higher temperature the proportion of c is very small. At this higher temperature the type c products rearrange when formed to give products of type a and b. This was shown to be the case by recycling the products obtained from the thermal rearrangement of the 1-phenylcycloheptene adduct (57) at 350°C through

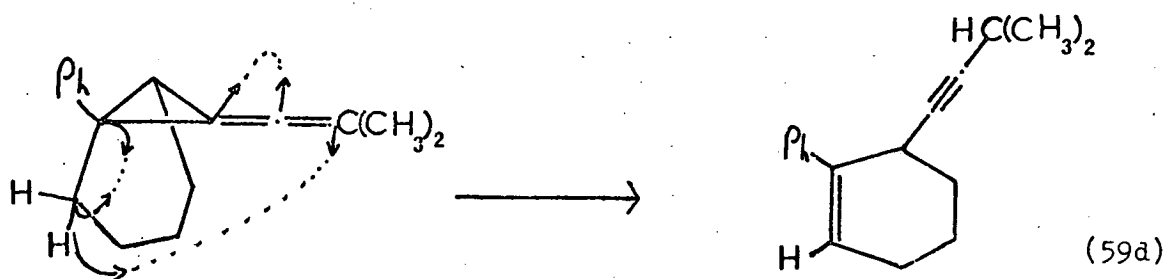
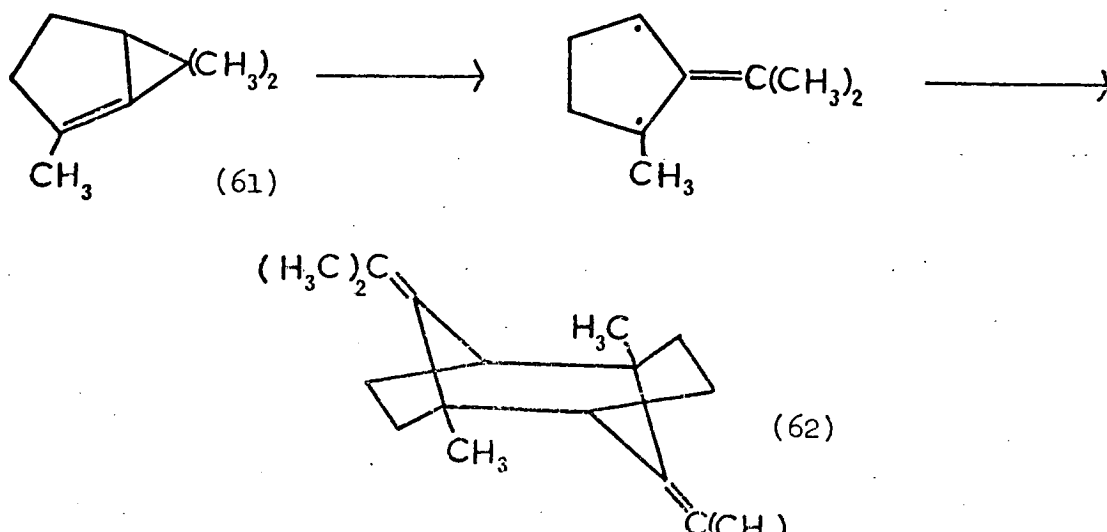
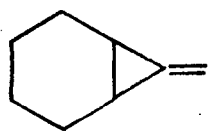


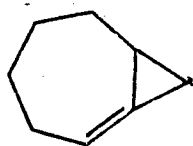
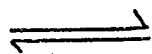
FIGURE XXVII

flow system A at 450°C . The resultant mixture contained only the two cyclooctatindenes (58a and 58b) and none of the isopropylidene-cyclopropane (58c), which had originally accounted for 65% of the mixture. In the rearrangement of the adducts derived from 1-phenylcyclopentene and 1-phenylcyclohexene the isopropylidenecyclopropanes are not detected because formation of these products would introduce the strain of a bridgehead double bond and the ring size is not large enough to allow this strain to be alleviated by puckering of the ring structure as is possible with the isopropylidenecyclopropanes derived from the 1-phenylcycloheptene and 1-phenylcyclooctene adducts. This is in agreement with Fawcetts²¹⁸ statement of the Bredt rule²¹⁹ in which he states that, in polycyclic systems with atomic bridges, the existence of a double bond at a bridgehead position is not possible except when the rings are large, because of the angle strain which would be introduced in the formation of such compounds, by distortion of bond angles or distances. Reactions which could lead to such compounds will therefore be hindered and could possibly give products with other structures. Further evidence for this statement is provided by Kobrich²²⁰ who attempted to form abicyclo[3,1,0]-hex-1-ene but failed to isolate the required product. He did however isolate the 9,10-diisopropylidenetricyclo[4,2,1,1]²²¹decane (62) and postulates the bicyclo[3,1,0]hex-1-ene (61) as being an intermediate which dimerises to the observed product (62).

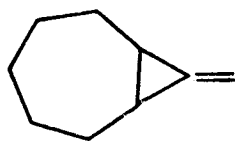




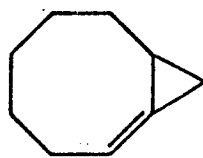
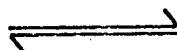
(63)



(64)



(65)



(66)

Although the existence of a bicyclo[3,1,0]hex-1-ene (61) has been proposed only as an intermediate there is evidence that in larger ring systems a bridgehead double bond can be accommodated and products isolated. Kende and Riecke¹⁹² report the equilibration of 7-methylenebicyclo[4,1,0]heptane (63) and 8-methylenebicyclo[5,1,0]octane (65) with the isomeric compounds bicyclo[5,1,0]oct-1-ene (64) and bicyclo[6,1,0]non-1-ene (66) respectively. The equilibrium constant measured for the equilibrium between 7-methylenebicyclo[4,1,0]heptane (63) and bicyclo[5,1,0]oct-1-ene (64) were 0.075 at 180°C and 0.066 at 197°C and those measured for the equilibrium between 8-methylenebicyclo[5,1,0]octane (65) and bicyclo[6,1,0]non-1-ene (66) were 1.56 at 231°C and 1.52 at 246°C. The equilibrium constants for both equilibria show that the bicycloalkene is less stable at the higher temperature, rearranging to the more stable bicycloalkane. This supports the postulate that the type c product (Table VI), obtained from the rearrangement of the 1-phenylcycloheptene adduct (57) and the 1-phenylcyclooctene adduct (59) at 350°C, rearrange at 450°C to give more stable products viz types a and b (Table VI).

The mechanism, of the formation of the ethynylcyclohexene (56d), which would lead to the d type products requires a concerted process. The activation energy required to achieve the transition state in this mechanism is the governing factor since the end product is a stable strain free molecule. It is evident that the energy required to reach the transition is only attainable in the rearrangement of the 1-phenylcyclohexene adduct (55). Stereomodels show that this adduct is not so rigid as the 1-phenylcyclopentene adduct (36) and more rigid than the larger 1-phenylcycloheptene adduct (57) and 1-phenylcyclooctene adduct (59). This intermediacy in rigidity shown by the 1-phenylcyclohexene adduct (55) allows it to attain the required transition state at a lower activation energy

than in the other three cases making the formation of the ethynylcyclohexene (56d) possible. In the other three cases the rigidity or flexibility of the adduct concerned makes the activation energy, to achieve the required transition state, unobtainable under the experimental conditions used.

In conclusion it can be said that the activation energy for formation of c type products is less than that for formation of a and b type products which in turn is less than that for formation of d type products. The presence or absence of the products is governed by the activation energy and the stability of the products. It is therefore possible to summarise the possible pathways (Figure XXVIII) and construct energy diagrams for the products formed in each reaction (Figures XXIX a, b, c, d).

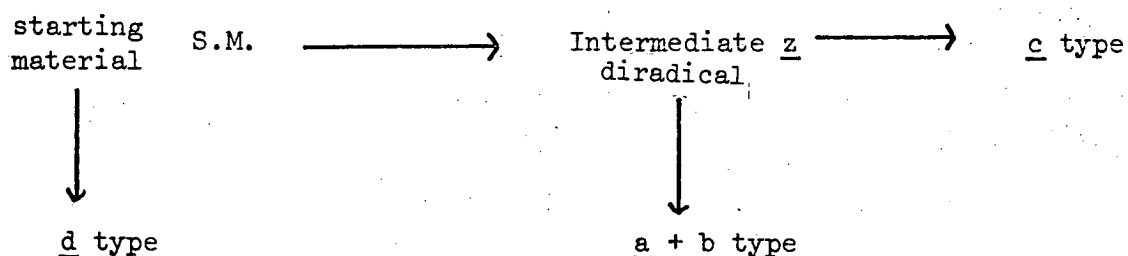


FIGURE XXVIII

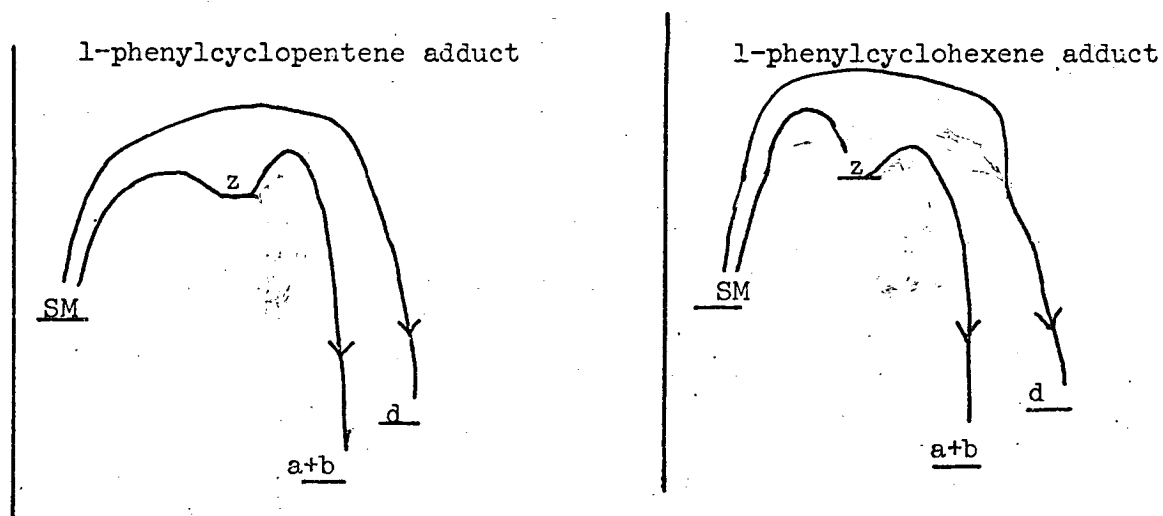


FIGURE XXIXa

FIGURE XXIXb

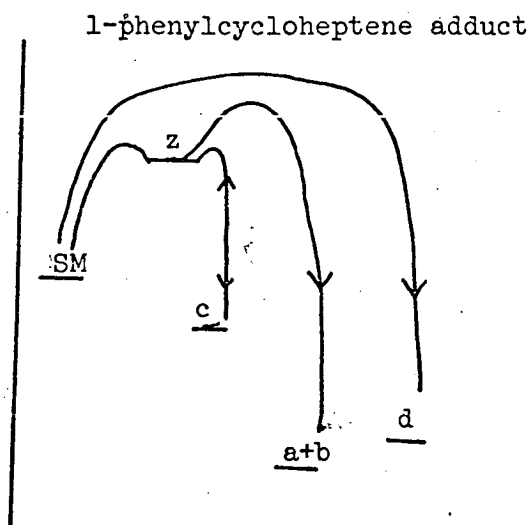


FIGURE XXIXc

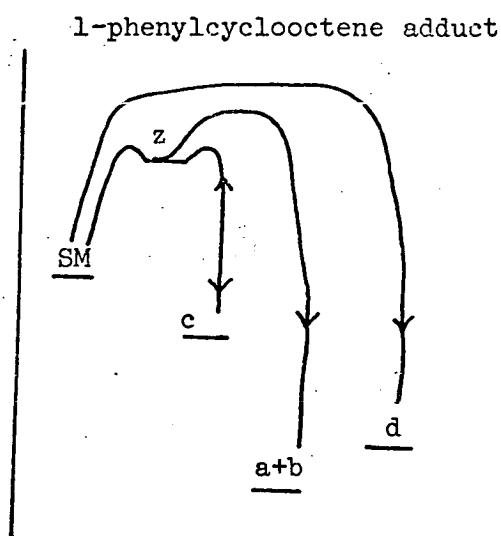
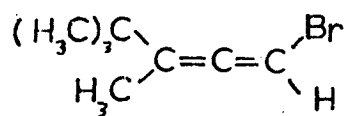
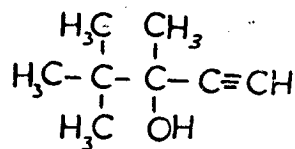


FIGURE XXIXd

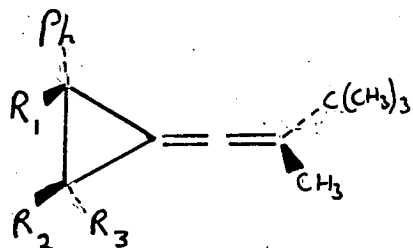
In Figure XXIXa the absence of the type c product is explained by the high strain energy involved in the bridgehead double bond of the five-membered ring and the absence of the type d product is explained by the energy of activation being too high to be attainable. In Figure XXIXb the type c product is absent for the same reasons as above but the activation energy to the type d product is attainable and the product is formed. Figures XXIXc and XXIXd show that the c type products are detected under conditions of kinetic control (350°C) but these can rearrange to a and b type products under conditions of thermodynamic control (450°C), in both cases the activation energy required to produce d type products is too great and is not attainable. The rearrangement of the adducts of 1-phenylcycloheptene and 1-phenylcyclooctene at the two temperatures are good examples of reactions being thermodynamically controlled under one set of conditions (450°C) and largely kinetically controlled under another set of conditions (350°C).



(67)



(68)



(71a) $\text{R}_1 = \text{CH}_3, \text{R}_2 = \text{R}_3 = \text{H}$

(71b)

(72a) $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{H}$

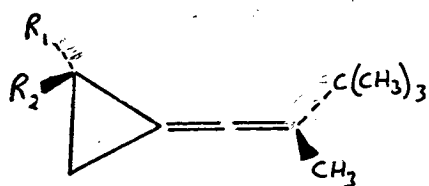
(72b)

(73a) $\text{R}_1 = \text{R}_3 = \text{H}, \text{R}_2 = \text{CH}_3$

(73b)

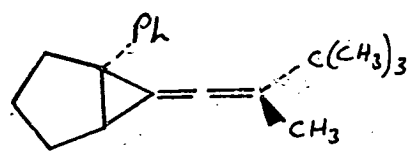
(75a) $\text{R}_1 = \text{H}, \text{R}_2 = \text{R}_3 = \text{CH}_3$

(75b)

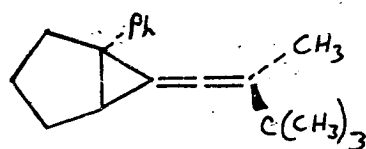


$\text{R}_1 = \text{R}_2 = \text{Ph}$ (76)

$\text{R}_1 = \text{R}_2 = \text{CH}_3$ (77)



(74a)



(74b)

6.1 The synthesis of 2,3,3-trimethylbutenyldenecyclopropanes

These cyclopropanes were all prepared, by a method similar to that used for the dimethylvinylidenecyclopropanes, using 1-bromo-3,4,4-trimethylpenta-1,2-diene (67) as carbene precursor. Some difficulty was experienced in obtaining the tertiary acetylenic alcohol, necessary for the preparation of the carbene precursor, in high yield and purity. The simplest route to the required 3,4,4-trimethylpent-1-yne-3-ol (68) is by ethynylation of pinacolone and three methods were attempted. The use, of sodium acetylide in liquid ammonia²²¹ or of lithium naphthalide and acetylene in tetrahydrofuran²²² both gave low conversion of pinacolone to the acetylenic alcohol and the resultant mixtures were difficult to separate. The method of Skattebol²²³, using ethynylmagnesium bromide in a Grignard reaction with pinacolone, gave complete reaction and pure 3,4,4-trimethylpent-1-yne-3-ol (68) was obtained.

Yields of adducts, usually in excess of 40%, were obtained using light petroleum as solvent, however, for indene and β,β -dimethylstyrene it was only possible to obtain reasonable yields of adduct by using excess olefin. Purification of the adducts was accomplished using alumina chromatography, eluting with light petroleum.

The molecular formulae of the adducts were confirmed by exact mass measurement of the parent peak (P) in the mass spectrum. Peaks at $P-CH_3$ and $P-C_4H_9$ were common in the mass spectra of the adducts. The adducts also show absorptions in the infra-red in the region $2050-2120\text{ cm}^{-1}$ due to the exo-cyclic allenic group. Their structures were confirmed by their ^1H -n.m.r. spectra which are similar to those of the corresponding dimethylvinylidenecyclopropanes^{71,85}. Absorptions due to cyclopropyl hydrogens occur between 7.25τ and 8.4τ , those due to allenic methyl groups between 8.2τ and 9.0τ and those due to the allenic t-butyl groups between 8.85τ and 9.2τ .

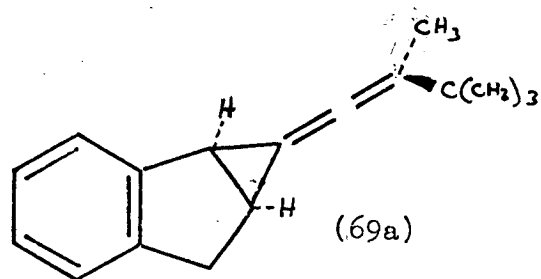
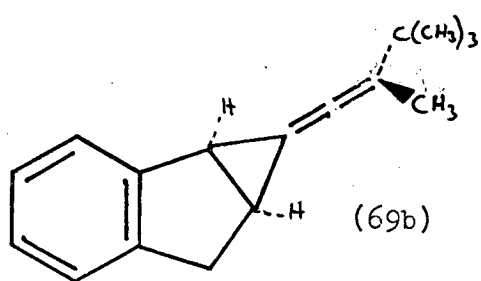
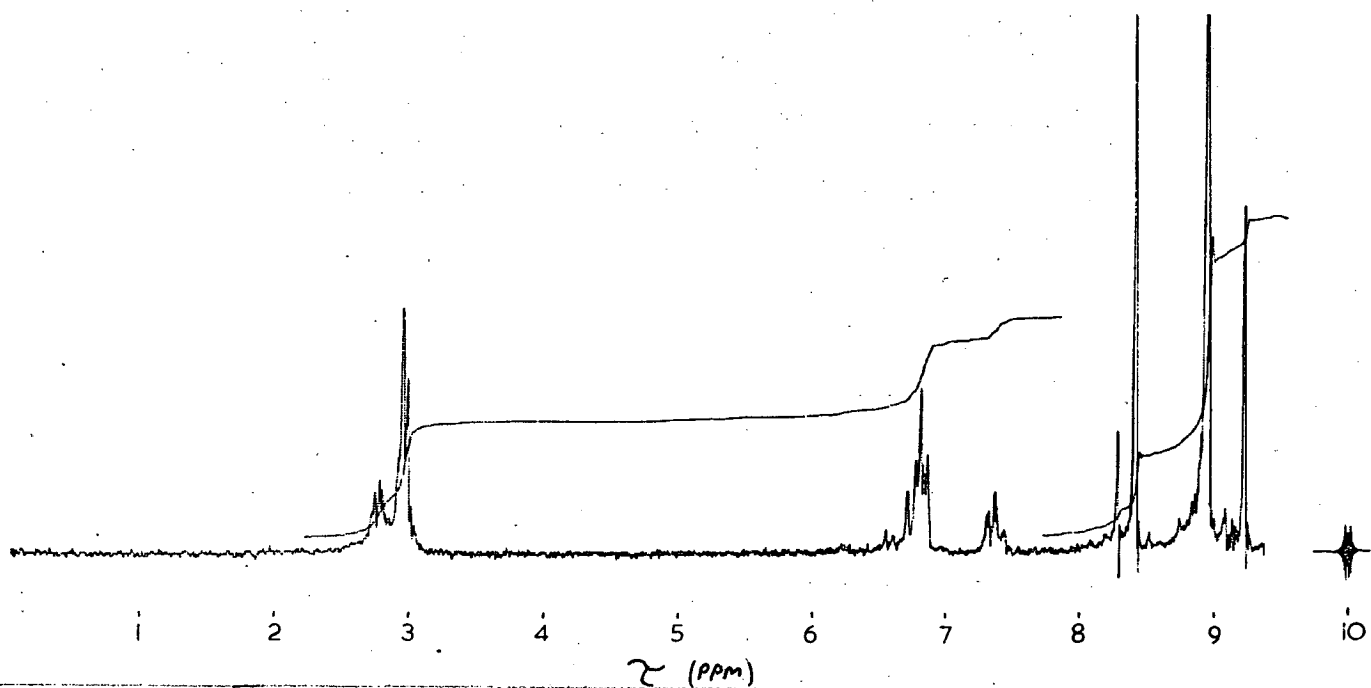


FIGURE XXX

Table VII

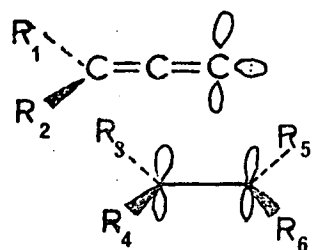
<u>Olefin</u>	<u>E</u>	<u>Z</u>
Indene	3.0	1.0
1-Phenylcyclopentene	1.5	1.0
α -Methylstyrene	1.2	1.0
β,β -Dimethylstyrene	1.0	1.0
<u>trans</u> - β -Methylstyrene	2.0	1.0
Styrene	2.0	1.0

The olefins, isobutene and 1,1-diphenylethylene, each yield a single adduct, whereas, in the case of the olefins, indene, α -methylstyrene, β,β -dimethylstyrene, trans- β -methylstyrene and styrene two isomers arise from each. This shows the stereospecific addition of the carbene to the olefins, giving E- and Z-isomers in the cases where the olefin is unsymmetrical. Where E- and Z-isomers are present their ratio may be found from the ^1H -n.m.r. spectrum of the mixture.

From a study of the molecular models of the two possible isomers of the indene adduct, it can be seen that in the Z-isomer (69a), the t-butyl group is located over the aromatic ring. Due to the magnetic anisotropy of the benzene ring this t-butyl-group will resonate at higher field than the t-butyl-group in the E-isomer (69b). Similarly, the methyl group in the E-isomer (69b) will resonate at higher field than the Z-isomer (69a). Therefore, it is possible to assign the high field t-butyl-group resonance and the low field methyl resonance to the isomer (69a) and the low field t-butyl-group resonance and the high field methyl resonance to isomer (69b). Similar arguments hold for the adduct mixtures obtained from α -methylstyrene, styrene, trans- β -methylstyrene, β,β -dimethylstyrene and 1-phenylcyclopentene. At all times the Z-isomer was assigned the structure in which the t-butyl-group resonance was at high field. The ^1H -n.m.r. spectrum of the indene adduct mixture is shown in Figure XXX.

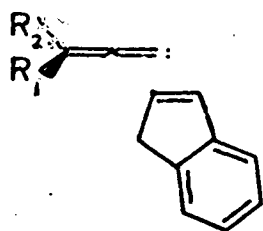
The ^1H -n.m.r. spectra also allow the measurement of the ratio of the two isomers formed. In each case, integration and peak height measurement of the t-butyl-group and methyl group resonances serves as a direct method of calculating the ratio of the two isomers present. The isomer ratios calculated for the six olefins from which two isomers were obtained are shown in Table VII.

The variation in isomer ratios can be explained by the mode of attack of the carbene. It has been shown²⁰⁴ that a singlet carbene

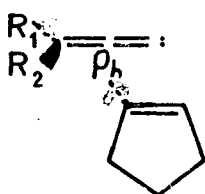


$R_1 = \text{CH}_3 \text{ or } \text{C}(\text{CH}_3)_3$
 $R_2 = \text{C}(\text{CH}_3) \text{ or } \text{CH}_3$
 $R_3 = R_4 = \text{bulky groups}$
 $R_5 = R_6 = \text{small groups}$

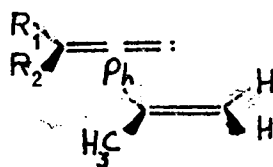
FIGURE XXXI



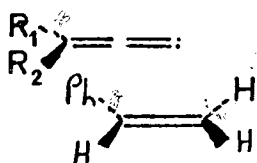
(70a)



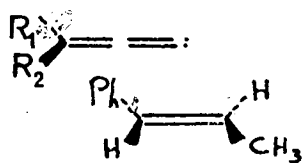
(70b)



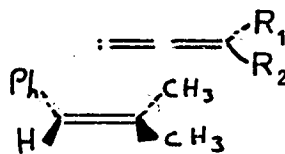
(70c)



(70d)



(70e)



(70f)

$R_1 = \text{CH}_3 \text{ or } \text{C}(\text{CH}_3)_3$

$R_2 = \text{C}(\text{CH}_3)_3 \text{ or } \text{CH}_3$

FIGURE XXXII

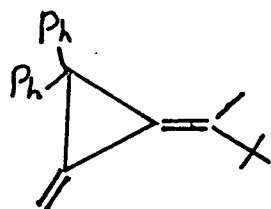
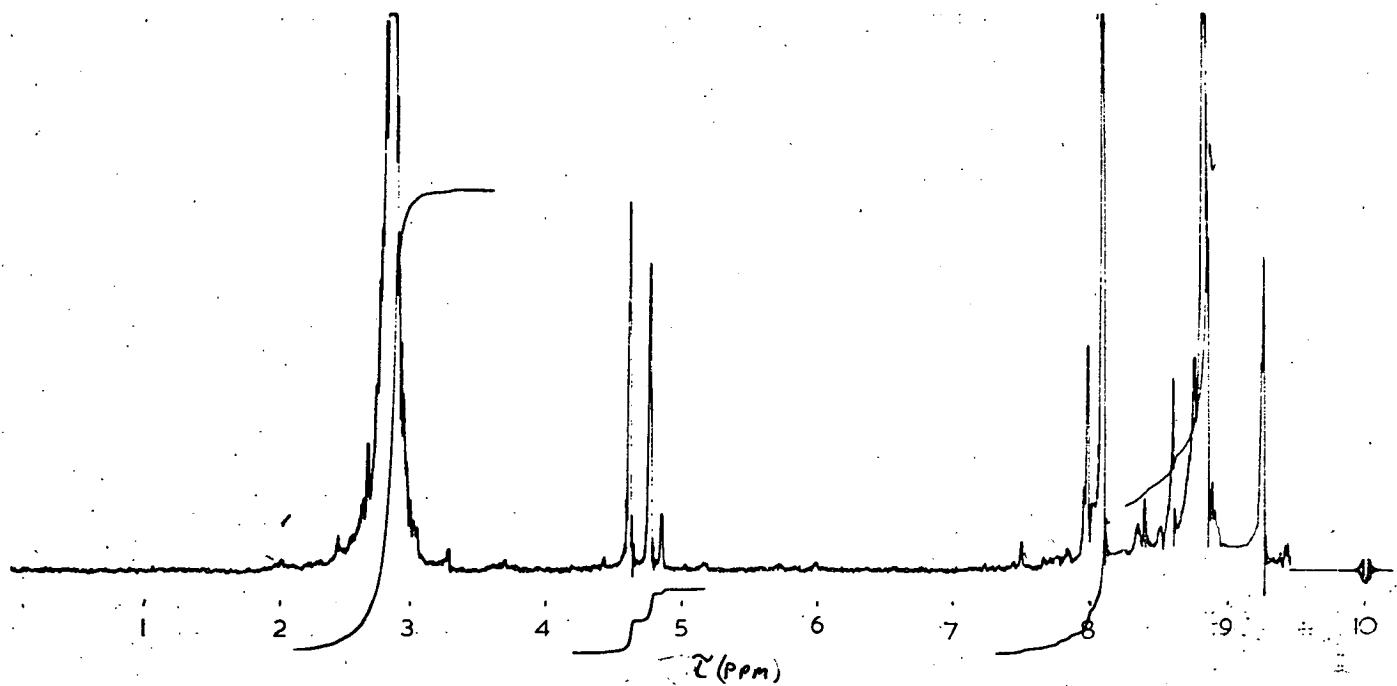
approaches an olefin above and slightly displaced towards the least sterically hindered end of that olefin and with its vacant p-orbital perpendicular to the plane of symmetry of the olefin. Partial delocalisation of the olefinic π -electrons into the carbenes vacant p-orbital is then followed by rotation of the plane of the carbene as it continues to approach the olefin and a redistribution of the electrons to form the cyclopropane. This is shown diagrammatically in Figure XXXI. In a theoretical study of the addition of methylene to ethylene Hoffmann¹²¹ has shown that this off-centre π -approach of the carbene is energetically more favourable than the more symmetrical σ -approach in which the lone pair of the carbene would impinge directly on the olefinic π -system. This process is also forbidden on orbital symmetry grounds^{111,113}. Extension of these principles to the attack of the 2,3,3-trimethylbutenylidene-carbene on the six olefins in which two isomeric adducts are possible enables the varying isomer ratios obtained to be satisfactorily explained. Assuming the orientation of this carbene is such that the lone pair is directed away from the most hindered carbon atom and that, for an effective transition state, the orbital containing the lone pair and the vacant p-orbital of the carbene must be co-planar with the olefinic p-orbitals, the six transition states can be represented as shown in Figure XXXII. In all cases, except the β,β -dimethylstyrene adduct, it is clear that the least hindered end of the olefinic double bond is as shown (Figure XXXI) and the ratio of the Z to E-isomers depends on the steric interactions between the groups attached to the carbene and the more sterically hindered end of the olefinic double bond. The t-butyl group, being much larger than the methyl group, will prefer to adopt a position, when approaching the olefinic double bond, in which it interacts with the smallest substituent on the most hindered end of the olefinic double bond. Thus the intermediates (Figure XXXII) will have the group R_2 as t-butyl and R_1 as methyl. The reasons

for the variation in isomer ratios can now be clearly seen. In each case there is, at the most sterically hindered end of the olefinic double bond, one group which is bulkier than the other and the *t*-butyl group on the carbene prefers to orientate itself so that it interacts with the least bulky group and therefore the *E*-isomers are preferred, (Table VII). The equivalence of isomer ratio between the styrene and *trans*- β -methylstyrene adducts shows the attack in these cases must be from the same end of the olefinic double bond. In the formation of the β,β -dimethylstyrene adduct the *E*- and *Z*-adducts are formed in equal amounts. This indicates that the least hindered end of the olefinic double bond is the α -carbon atom and the intermediate to adduct formation is as shown (70f) Figure XXXII. If this were not the case the isomer ratio should be the same as that found for the styrene and *trans*- β -methylstyrene adducts.

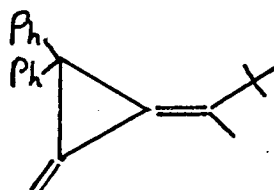
These results are consistent with the original postulate²⁰⁴ of carbene attack being off-centre with the lone pair directed towards the least sterically hindered end of the olefinic double bond. It may also be pertinent to suggest that these results show that steric interactions are a major factor in carbene additions to olefins clarifying the fact that the attempted addition of dimethylvinylidene-carbene to 2-methyl-1,1-diphenylprop-1-ene fails (see section 5.1).

6.2 Rearrangement of 1,3,3-trimethylbutenylidene-carbene adducts of 1-arylalkenes and 1-alkylalkenes

The rearrangement of aryl dimethylvinylidene cyclopropanes (e.g. 78) at temperatures between 100°C and 350°C show complete conversion to isopropylidenemethylenecyclopropanes (e.g. 79) without any formation of the thermodynamically more stable benzylidenemethylene-cyclopropane (e.g. 80)



ANTI
(82a)



SYN
(82b)

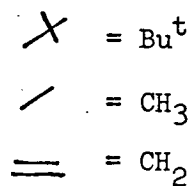
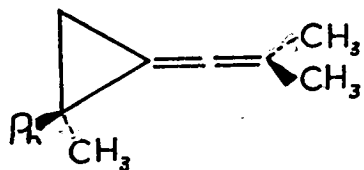
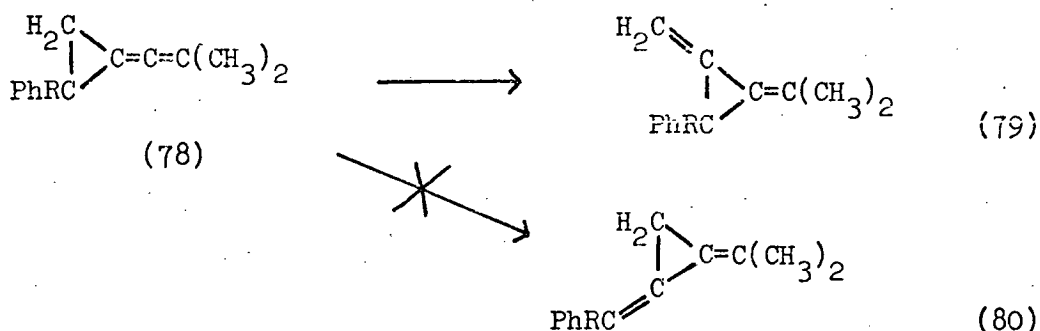


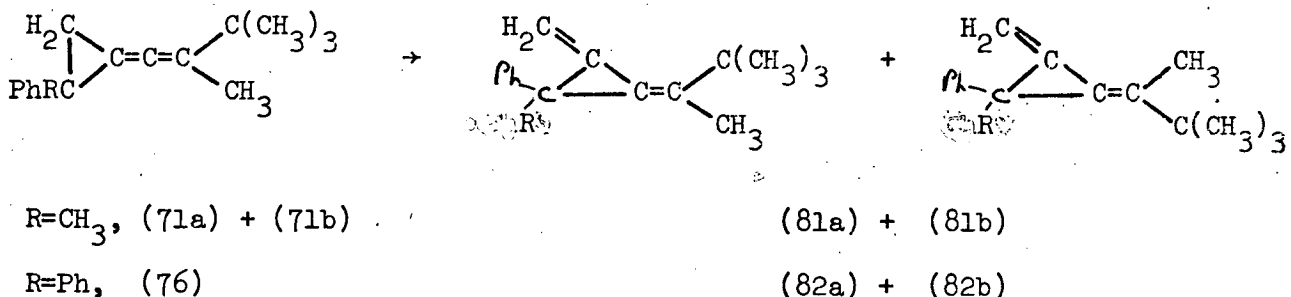
FIGURE XXXIII



(83)

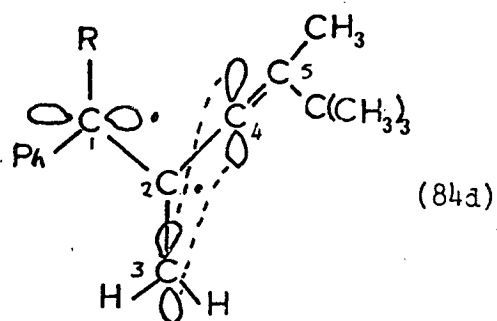
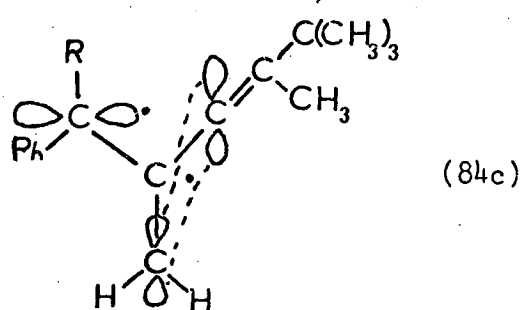
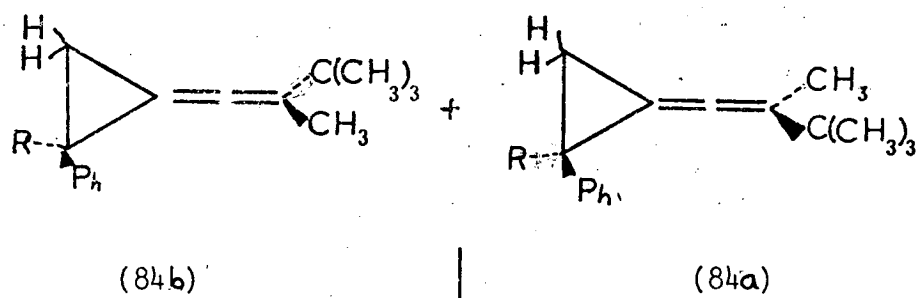


The gas phase pyrolysis (350°, 0.01 mm) of the mixture of E- and Z-2(2',3',3'-trimethylbutenylydene)-1-methyl-1-phenylcyclopropane (71a and 71b) gave a mixture of two isomeric products. These were identified as the two possible 2-((1'-t-butylethylidene)-3-methylene-1-methyl-1-phenylcyclopropanes (81a) and (81b), no benzyldenecyclopropane isomers being detected.



The two isomers are expected due to the unsymmetrical nature of the allene moiety of the adduct. Similar rearrangement of the adduct from 1,1-diphenylethylene gives the two isomeric products (82a) and (82b).

The rearrangement product mixtures were not separable by preparative t.l.c. or g.l.c., however, the mixtures showed characteristic infra-red absorptions at 1780 cm⁻¹ which were assigned to the strained exo-cyclic double bonds²⁰³, and 780 cm⁻¹ assigned to a methylene group. Structures were again confirmed by ¹H-n.m.r. spectroscopy. As in the case of the adducts, the two isomers present exhibit different resonances due to the relative position of the groups with respect to the aromatic ring. In isomers (81b) and (82b) the t-butyl group



$R = \text{CH}_3 \text{ or } \text{Ph}$

FIGURE XXXIV

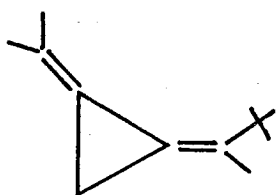
lies over the phenyl group and so resonates at a higher field than the t-butyl groups in isomers (81a) and (82a). Similarly, the methyl groups in isomers (81b) and (82b) resonate at a lower field than those in isomers (81a) and (82a), thus allowing each resonance to be assigned to a particular isomer.

The two isomeric structures were defined as syn and anti, the syn-isomer being assigned the structure with the t-butyl group above the plane of the phenyl ring. A typical spectrum of the products from the rearrangement of the 1,1-diphenylethylene adduct is shown (Figure XXXIII). Isomer ratios are again calculated from the ^1H -n.m.r. spectrum of the isomer mixture. The ratios are summarised in Table VIII.

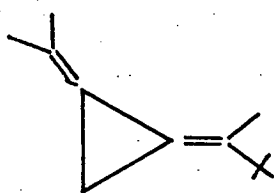
Table VIII

	<u>Syn</u> isomer		<u>Anti</u> isomer
R=CH ₃	(81b)	1 : 2.25	(81a)
R=Ph	(82b)	1 : 7.8	(82a)

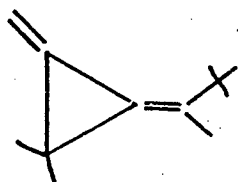
Although these results can be rationalised in terms of either a concerted or diradical approach, a kinetic study¹⁸⁶ of the rearrangement of 2-dimethylvinylidene-1-methyl-1-phenylcyclopropane (83) gave activity parameters ($E_a = 30.4 \text{ K cal mol}^{-1}$, $\Delta S = -2.5 \text{ e.u.}$) consistent with an orthogonal diradical. The kinetic parameters⁷¹ obtained for the corresponding 1,1-diphenyl derivative ($E_a = 25.8 \text{ K cal mol}^{-1}$, $\Delta S = -8.7 \text{ e.u.}$) are also consistent with a diradical intermediate. An orthogonal diradical in the present case would be formed (Figure XXXIV) by fission of the C(1)-C(3) bond and rotation at either C(1) or C(3). Rotation at C(3) leads to the diradicals (84c) and (84d) which are equivalent to a combination of an allyl radical and a benzyl radical. Rotation at C(1) leads to the diradicals (84a) and (84b) which are equivalent to a combination of a benzyl radical and an allyl radical. Rotation may be in either direction, however the diradicals (84d) and (84c) arise respectively from the two isomeric adducts (84a) and (84b). Rotation



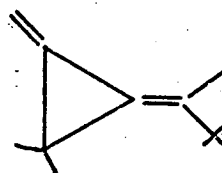
(85d)



(85c)



(85b)



(85a)

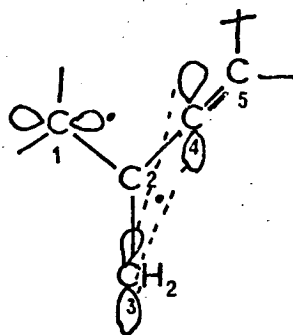
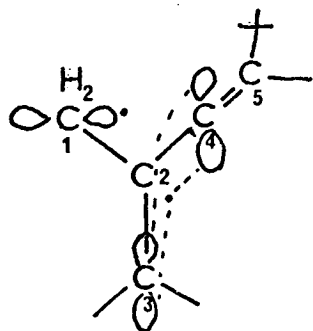
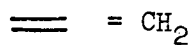
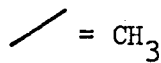
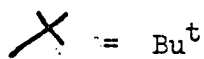


FIGURE XXXV

at C(1) leads to the diradicals which are equivalent to the combination of a cinnamyl radical and a primary radical and these are consequently energetically much less favourable which explains the absence of the thermodynamically more stable benzylidenecyclopropanes. Recombination of either diradical, (84c) or (84d), requires rotation of 90° about C(4). This involves the methyl and t-butyl groups moving to a horizontal position from their original vertical one. To achieve this position one of the groups must pass through a point which is sterically hindered by the perpendicular orientation of the groups on C(1). There is obviously less steric interaction when the methyl group passes this point rather than the t-butyl group and therefore the anti-isomer always predominates. The difference in the ratios when $R=CH_3$ and $R=Ph$ (Table VIII) can be explained by the fact that the phenyl group, being larger than the methyl group, makes the rotation of the t-butyl group past C(1) more difficult and therefore the anti-isomer is favoured to a larger extent.

The vapour phase rearrangement of the adducts from β,β -dimethylstyrene, trans- β -methylstyrene and styrene all failed to give identifiable products, multicomponent mixtures being observed. In the β,β -dimethylstyrene adduct (75a) and (75b) and trans- β -methylstyrene adducts (73a) and (73b) the formation of such mixtures may be due to the increased steric interactions due to the presence of substituents on the β -carbon atom. Assuming that the rearrangement proceeds via a diradical intermediate, ring closure by rotation of 90° about C(4) sets up a steric interaction between the groups on C(1) and C(5). In the cases where the β -carbon is unsubstituted this interaction is much less than when the β -carbon is substituted. This makes the formation of the rearrangement products less energetically favourable when β - substituents are present and therefore, there is probably no low energy pathway, similar to the one available when the

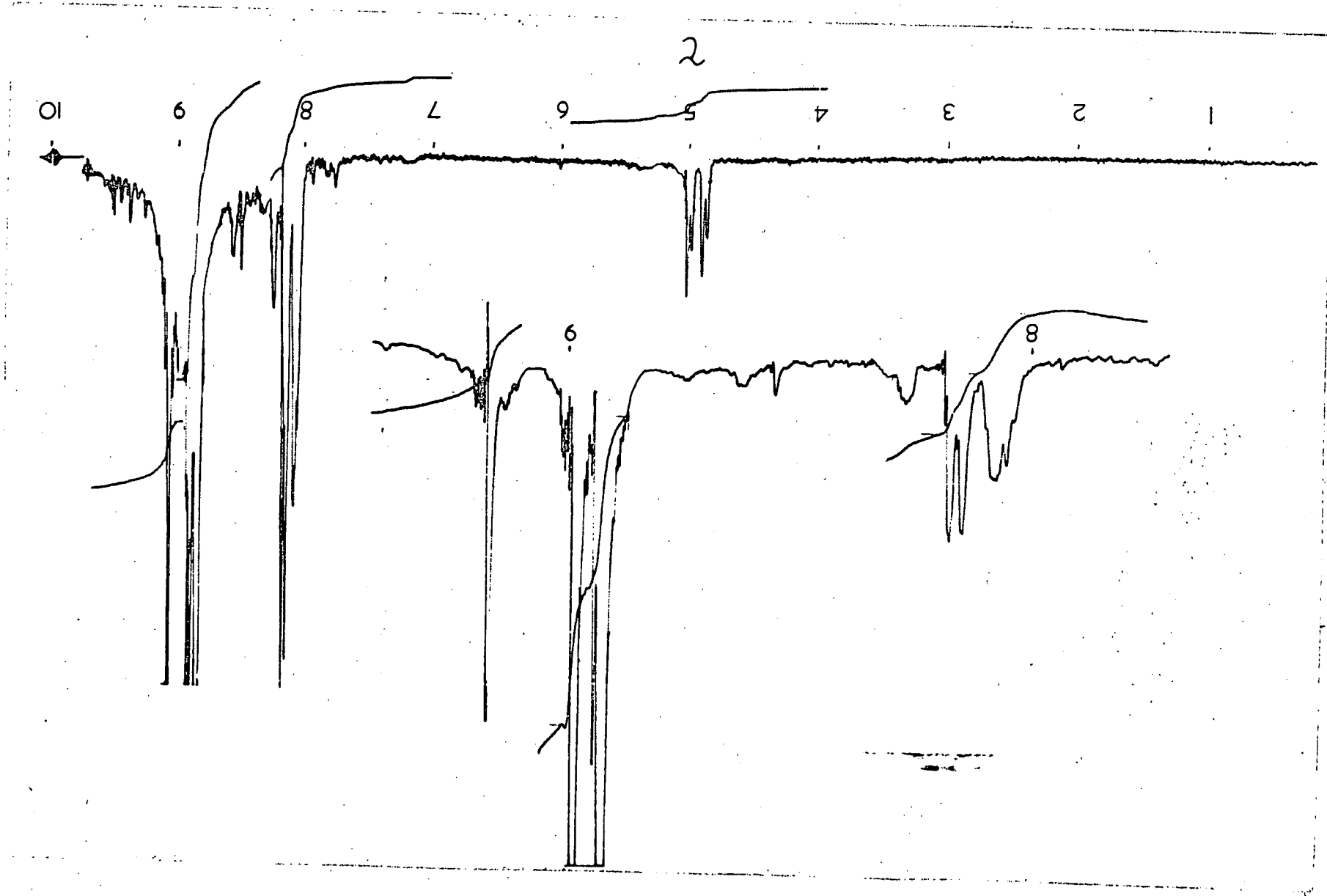


FIGURE XXXVI

β -carbon atom is unsubstituted, available and consequently a number of products result. The reasons for the diverse product formation in the rearrangement of the styrene adduct are less obvious, however, it is possible that the lack of any substituent on either the α - or β -carbon atom may make the adduct more thermally labile and at the temperatures used (350° , 450°) further rearrangement of the expected products could take place.

Four isomeric dimethylenecyclopropanes (85a-85d) are expected to result from the vapour phase rearrangement of the adduct derived from isobutene (77). The mechanism of formation of these four isomers can again be rationalised in terms of orthogonal diradical intermediates (Figure XXXV).

From the partial assignment of resonances in the ^1H -n.m.r. spectrum of the rearrangement product mixture (Figure XXXVI) it is possible to say that 75% of the product comprises of equal amounts of syn and anti-2-((1'-t-butylethylidene)-1,1-dimethyl-3-methylene-2-cyclopropane (85a) and (85b) due to the fact that the proton resonances on the methylene group which are in the deshielding region of the butenyl double bond resonate at different values and the olefinic methyl group in isomer (85a) which is in the deshielding region of the methylene double bond resonate at a different value from the olefinic methyl group in isomer (85b) which does not lie in this region. The remaining 25% of the product mixture is made up of the other two isomers syn and anti-2-((1'-t-butylethylidene)-1-isopropylidene-cyclopropane (85c) and (85d). From the ^1H -n.m.r. spectrum it is not possible to say if both of these isomers are present as only one set of resonances can be seen. It is possible that both isomers will have identical ^1H -n.m.r. spectra or that one isomer only is formed. Analogy with the β,β -dimethylstyrene adduct rearrangement products leads to the conclusion that it is possible that the anti-isomer (85d) will not be present, in a large

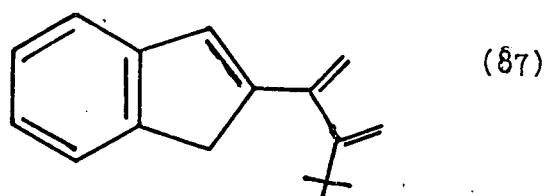
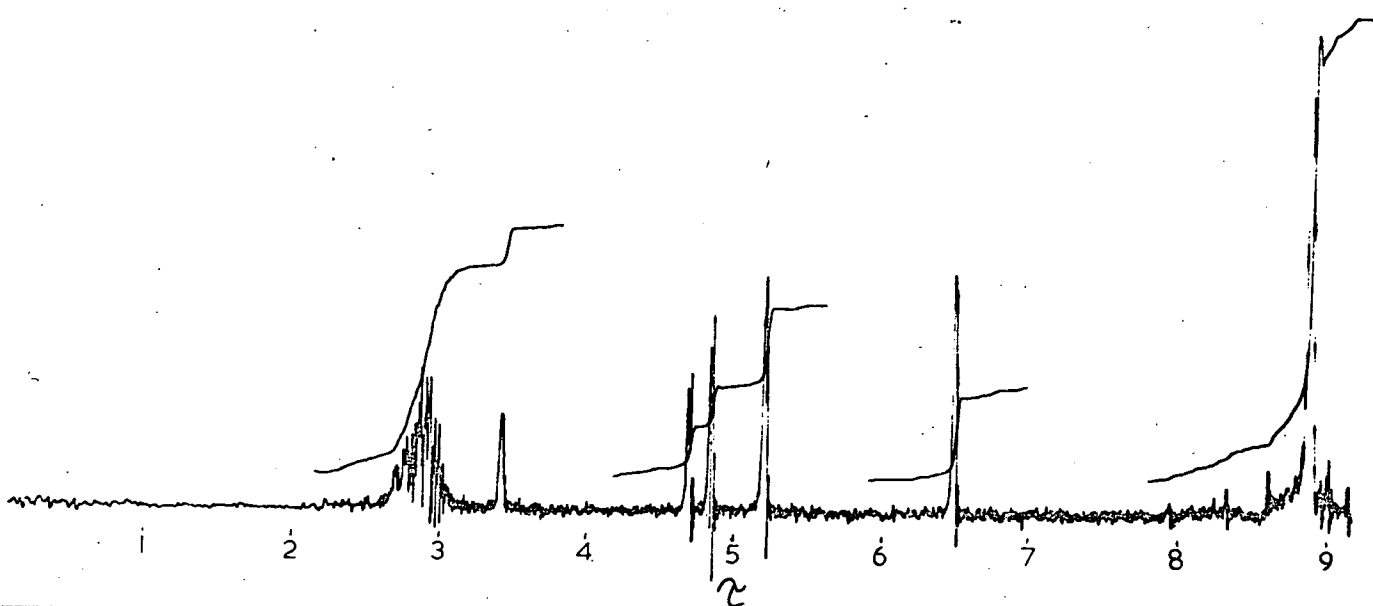
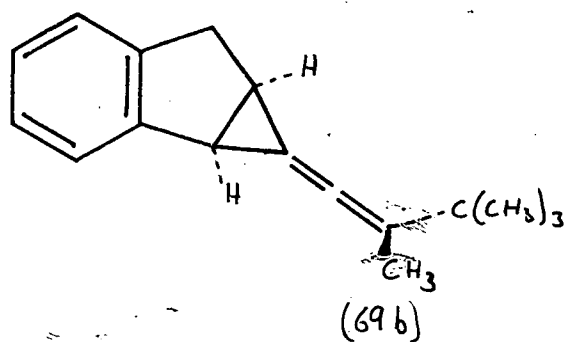
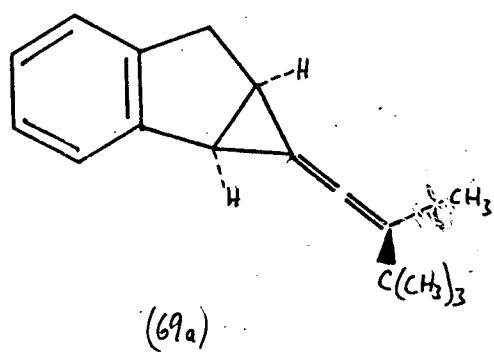


FIGURE XXXVII

enough concentration to be detected, due to steric factors. Rotation about C(4) (Figure XXXV) required for ring closure to form the anti-isomer involves a large steric interaction between the C(5) t-butyl-group and the C(3) methyl-group making this isomer unfavourable with respect to the syn-isomer (85c) which involves interaction between two methyl groups. It is, however, not possible to say with certainty whether or not both isomers are present or not.

6.3 Thermal and acid catalysed rearrangement of the 2,3,3-trimethyl-butenylidene-carbene adduct of indene

Thermolysis of the dimethylvinylidene carbene adduct of indene was initially reported⁸⁵ to give 2-methyl-1-(β -naphthyl)prop-1-ene (86) as the product. As a result of work described below, it has been shown that this was an acid catalysed rearrangement and the thermal rearrangement proceeds via a different route.

The vapour phase rearrangement (350°C) of the indene adduct mixture, E- and Z-2,3-benzo-6-(2',3',3'-trimethylbutenylidene)bicyclo-[3,1,0]hex-2-ene (69b) and (69a) gives one major product (75%), isomeric with the starting material, and a number of unidentified minor products (25%), none of which was the naphthalene corresponding to that previously reported. The major product, obtained pure by preparative g.l.c., was assigned the structure 2-t-butyl-3-(2'-indenyl)buta-1,3-diene (87) on the basis of the evidence presented below.

The ¹H-n.m.r. spectrum (Figure XXXVII) shows resonances due to four aromatic hydrogen atoms (2.6-3.1 τ) an olefinic resonance (3.44 τ) and a methylene resonance (6.51 τ) consistent with a 2-substituted indene derivative. The remainder of the spectrum shows four olefinic methylene protons, two as doublets ($J=2\text{Hz.}$, 4.51 τ , 4.86 τ) and two coincidentally as singlets (5.23 τ) and a t-butyl group (8.89 τ). The infrared spectrum shows absorptions due to a 1,2-disubstituted aromatic ring (730 cm^{-1}) and olefinic methylene groups (760 cm^{-1}). The ultraviolet

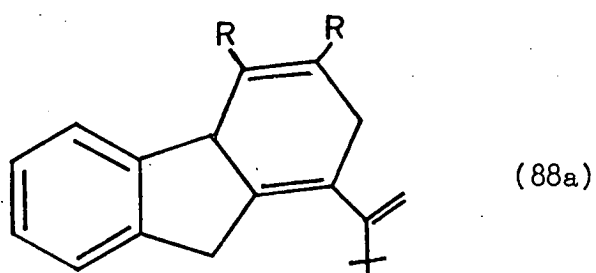
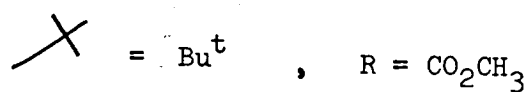
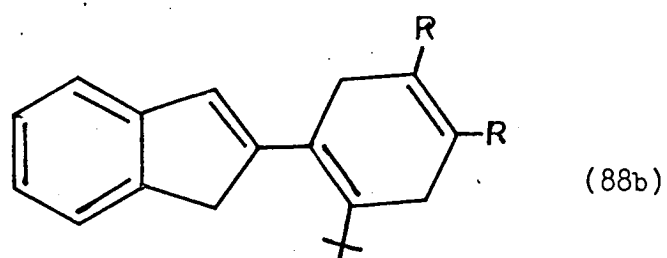


FIGURE XXXVIII

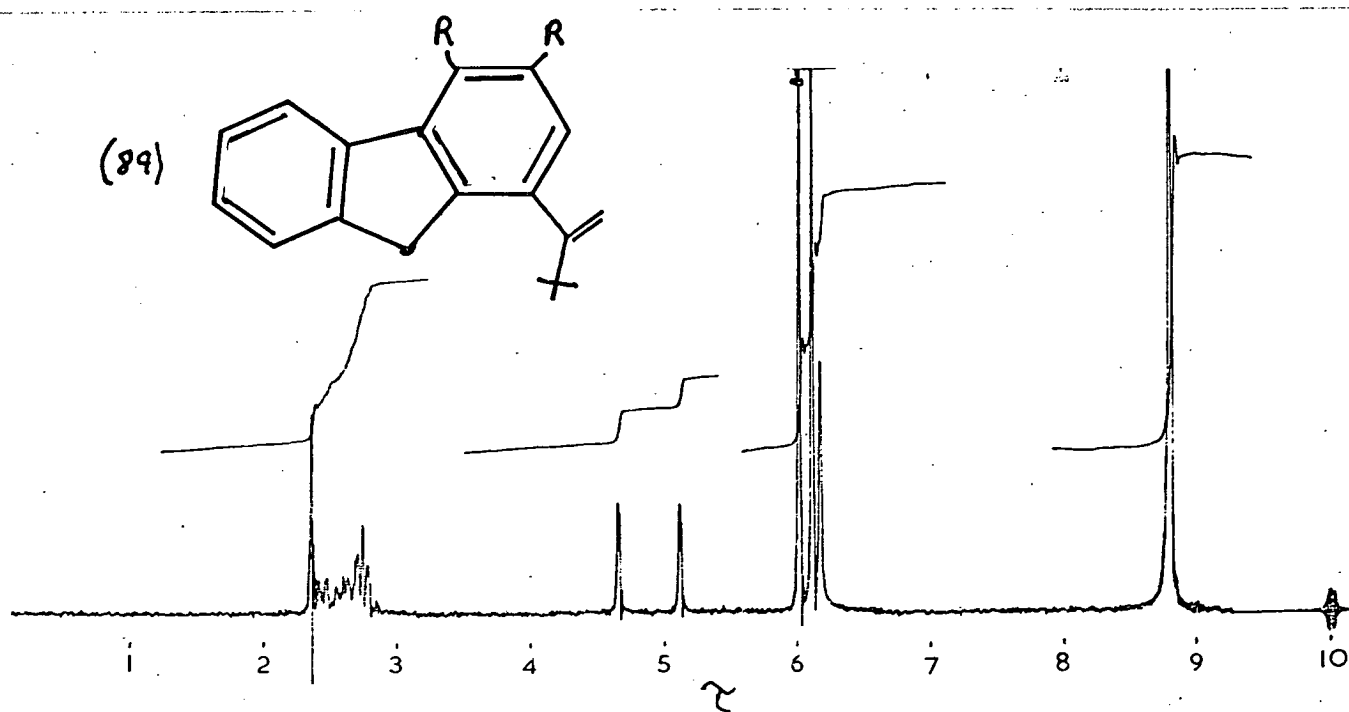
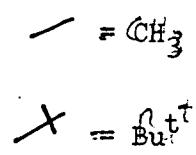
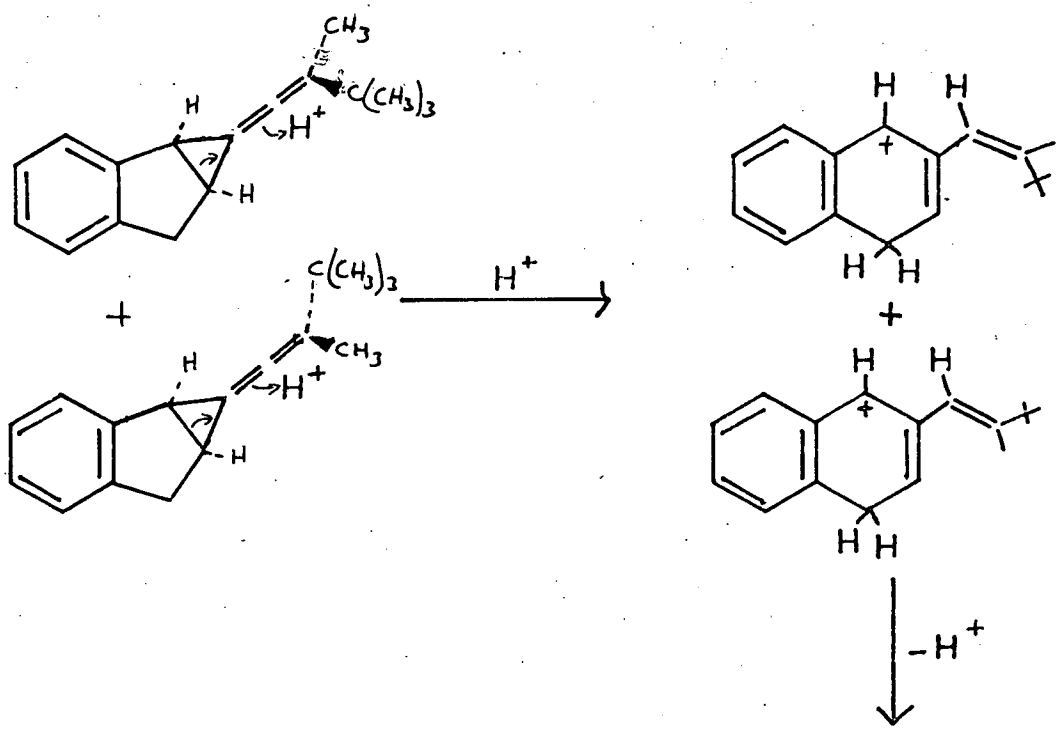
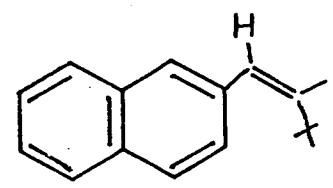


FIGURE XXXIX

spectrum is characteristic of a conjugated system (304.5 mμ, ε=11,200; 326.4 mμ, ε=5,900). Confirmation of the assigned structure was sought by attempting the formation of a Diels-Alder adduct with dimethyl-acetylenedicarboxylate. Two possible Diels-Alder adducts can be envisaged (Figure XXXVIII). The compound isolated was characterised as dimethyl 1-(2',2'-dimethyl-3-methylenepropyl)fluorene-3,4-dicarboxylate (89) from its spectroscopic data. The ¹H-n.m.r. spectrum (Figure XXXIX) is consistent with a 1,3,4-trisubstituted fluorene. The C(2) proton resonates at a lower field than the other aromatic protons due to the environment caused by the carbomethoxy groups. The ultraviolet spectrum shows maxima at 219 mμ, ε=2.38x10⁴; 243 mμ, ε=2.58x10⁴; 266.5 mμ, ε=1.46x10⁴ and 304 mμ, ε=2.88x10³ similar maxima also appearing in the combined spectra of fluorene-3-carboxylic acid and fluorene-4-carboxylic acid²¹⁷. Dimethyl 1-(2',2'-dimethyl-3-methylenepropyl)-fluorene-3,4-dicarboxylate, results from the 1,4-dehydrogenation, a thermally allowed process¹⁰⁷, of the adduct (88a). The other possible Diels-Alder adduct (88b) is not formed as the two double bonds in the butadiene moiety are not conjugated due to the bulk of the t-butyl group and the indene group. This is consistent with results found for 2,3-di-t-butylbuta-1,3-diene (90) where the double bonds were shown to be orthogonal not planar²²⁵. It is, however, possible for the double bond in the indene moiety to attain a planar cis arrangement with respect to the C(3)-C(4) double bond in the diene and thus allow the dienophile to add to form the adduct (88a). The mechanism of the thermal rearrangement of the indene adduct to give 2-t-butyl-3-(2'-indenyl)buta-1,3-diene (89) is envisaged as being the same as that outlined by Robertson⁷¹. This mechanism involving three consecutive concerted mechanisms is outlined in Figure XII of the introduction (section 3.5, page 46).



(91a)



(91b)

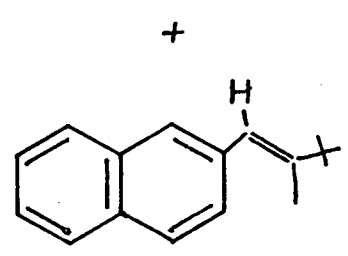
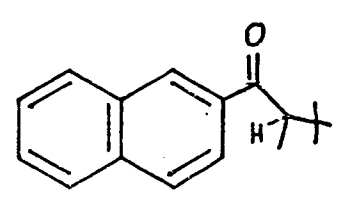
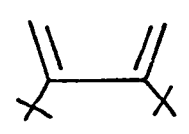


FIGURE XXXX

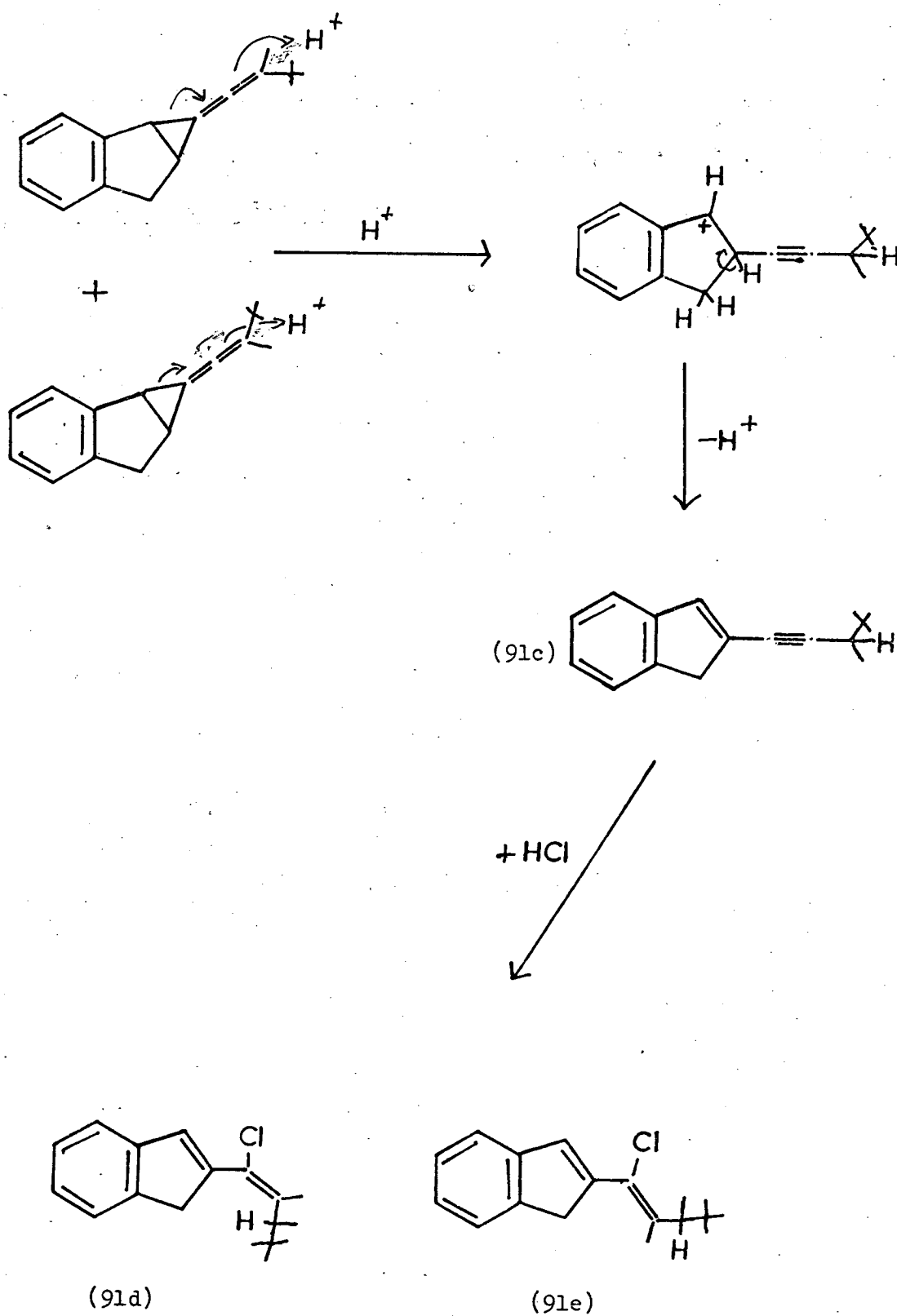
(90)



(91f)

The acid catalysed rearrangement of the indene adduct gave a mixture of five products which were separated by preparative g.l.c. and preparative t.l.c. The products, identified from ^1H -n.m.r. spectra by analogy to the products obtained by Stewart⁸⁵ for the rearrangement of the dimethylvinylidene carbene adducts of indene and 4-methyl-1,2-dihydronaphthalene, were as follows; Z- and E-2,3,3-trimethyl-1-(β -naphthyl)-but-1-ene (91a) and (91b), 2-(3',4',4'-trimethylpent-1'-ynyl)indene (91c) and E- and Z-2-(3',4',4'-trimethyl-1'-chloropent-1'-enyl)indene (91d) and (91e). The two butene isomers (91a) and (91b) are formed by attack of a proton in the β -position of the allene moiety followed by ring expansion (Figure XXXX) whereas the acetylenic indene (91c) is formed by the γ -attack of a proton on the allenic moiety followed by cyclopropyl ring opening (Figure XXXXI). The final products, olefinic indenenes (91d) and (91e) are formed by addition of hydrochloric acid to the acetylenic double bond of the indene (91c) (Figure XXXXI). These mechanisms were reported and substantiated by Stewart⁸⁵.

During the preparative g.l.c. separation of a pure sample of 2-t-butyl-3-(2'-indenyl)buta-1,3-diene (87) two other products were identified. Neither of these two products were in the original 25% unidentified products from the thermal rearrangement of the indene adduct and the formation of these products must have taken place on the g.l.c. column. The two products were Z-2,3,3-trimethyl-1-(β -naphthyl)but-1-ene (91a) in 15% yield identified by comparison to the acid catalysed product and 5% of an isomer tentatively assigned the structure 2,3,3-trimethyl-1-(β -naphthyl)butan-1-one (91f) on the basis of ^1H -n.m.r. and mass spectral evidence. Both of these products can be rationalised as being formed by an acid catalysed mechanism from the indene adduct (Figure XXXX and Figure XXXXI), however, they could also have arisen from the 25% minor products in the mixture of thermal



$\text{X} = \text{But}^t$

$\text{—} = \text{CH}_3$

FIGURE XXXXI

rearrangement products and as these were unidentified the true mechanism of formation of these products cannot be ascertained.

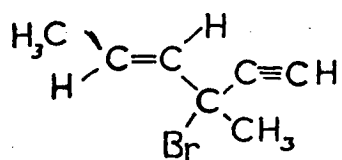
6.4 Thermal rearrangement of the adduct derived from 1-phenylcyclopentene

The vapour phase rearrangement of the adducts derived from 1-phenylcyclopentene (74a) and (74b) leads to a complex mixture of products which are not separable by physical means. There is some similarity in the ^1H -n.m.r. spectrum of the mixture to that of the two isomeric tetrahydrofluorenes obtained in the rearrangement of the comparable dimethylvinylidene adduct (37a) and (37b). If the butenylidene-carbene adduct rearranges via a similar mechanism to that of dimethylvinylidene adduct (Figure XX) it may not be possible for it to achieve the required geometry in one of the transition states due to the bulky nature of the t-butyl group. This could have the effect of increasing the activation energy of this route and thus make other, normally inaccessible routes attainable giving rise to the different products found.

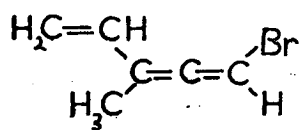
7.1 The synthesis and rearrangement of vinylidenecyclopropanes having an unsaturated group on the allene moiety

The work which has been described has involved the addition of a vinylidene-carbene, containing two saturated groups on the γ -carbon atom, to an olefin and the subsequent rearrangement of the cyclopropanes formed. An investigation was undertaken to discover the effect on the rearrangement process of an unsaturated group attached to the γ -carbon atom.

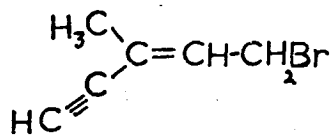
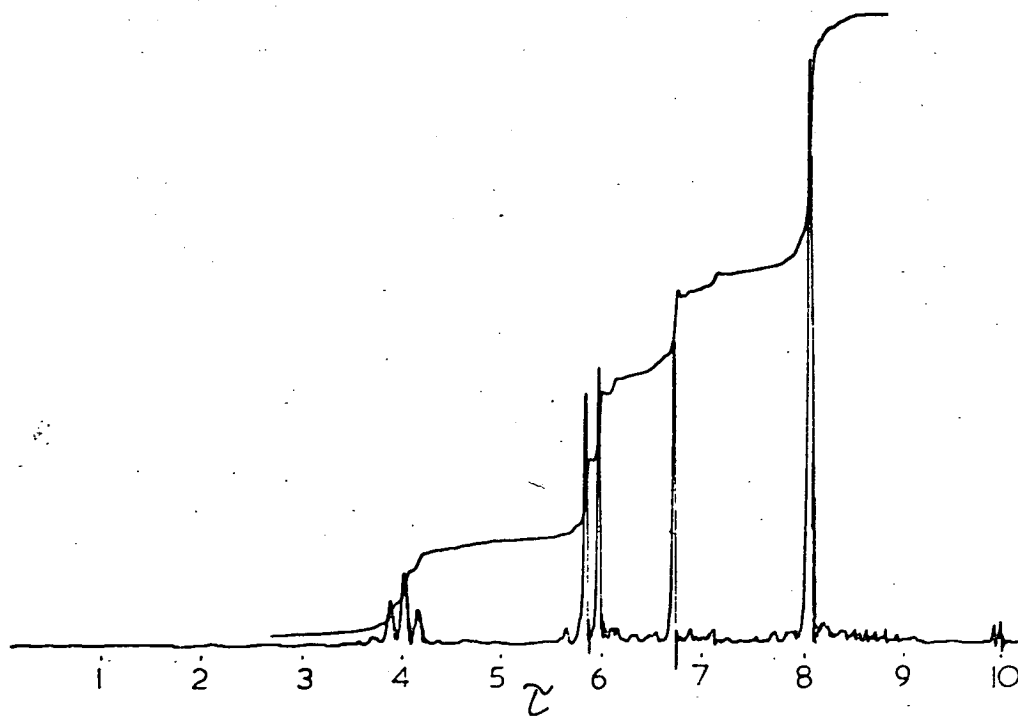
Three carbenes were chosen for study in which one of the methyl groups of dimethylvinylidene carbene was respectively replaced by an ethynyl group, a vinyl group and a trans-prop-1-enyl group. It was envisaged that the syntheses of these carbenes could be achieved by a similar route to that for the vinylidene-carbenes previously



(95)



(98)



(97)

described i.e. formation of the t-acetylenic alcohol followed by conversion to the allenic bromide and thence to the carbene by the action of strong base.

The ethynylation of methylethynylketone to form 2,2-diethynylethan-2-ol (92) was not possible using either the method of Skattebol²²³ or Heilbron²²⁶. No other suitable method was discovered for the preparation of this t-acetylenic alcohol and consequently formation of the carbene precursor and carbene was not possible.

The ethynylation of trans-pent-3-ene-2-one (93), prepared by the method of Ramirez²²⁷, was achieved by the method of Heilbron²²⁶ yielding trans-3-methylhex-4-ene-1-yne-3-ol (94). This alcohol was converted into the t-acetylenic bromide, trans-3-bromo-3-methylhex-4-ene-1-yne (95), using phosphorus tribromide in ether²²⁸. Tertiary acetylenic halides are known to give allenic carbenes on treatment with strong base^{78,81}. Attempted conversion of the alcohol to the allenic bromide by the method of Landor²²⁹ resulted only in complex tarry products.

The ethynylation of methylvinylketone was also achieved by the method of Heilbron²²⁶, 3-methylpent-1-ene-4-yne-3-ol (96) being formed in 35% yield. Attempted conversion of this alcohol to the allenic bromide by the method of Landor²²⁹ or the acetylenic bromide by the method of Henbest²²⁸ led to a product which was identified from spectroscopic data given below as 1-bromo-3-methyl-trans-pent-2-ene-4-yne (97) and not the expected 1-bromo-3-methylpenta-1,2,4-triene (98). The ¹H-n.m.r. spectrum (Figure XXXXII) shows resonances attributed to, an olefinic proton at 4.07 τ (triplet), a methylene group attached to a bromine atom at 5.93 τ (doublet), an acetylenic proton at 6.81 τ and an olefinic methyl group at 8.08 τ . The ¹³C-n.m.r. spectrum is also consistent with this formulation. The trans-relationship of the methyl group and the hydrogen atom about the double bond was proposed on the

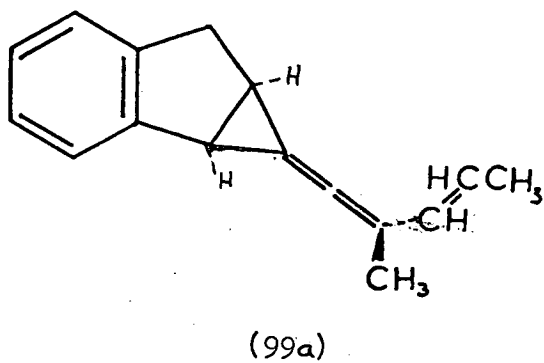
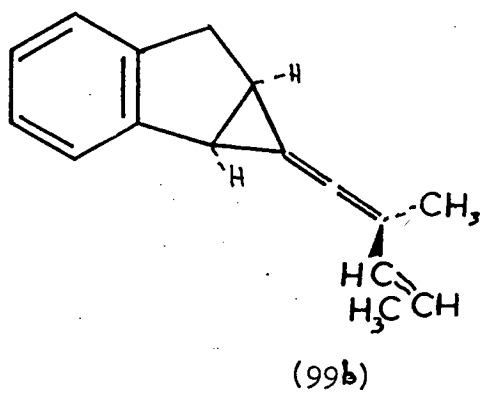
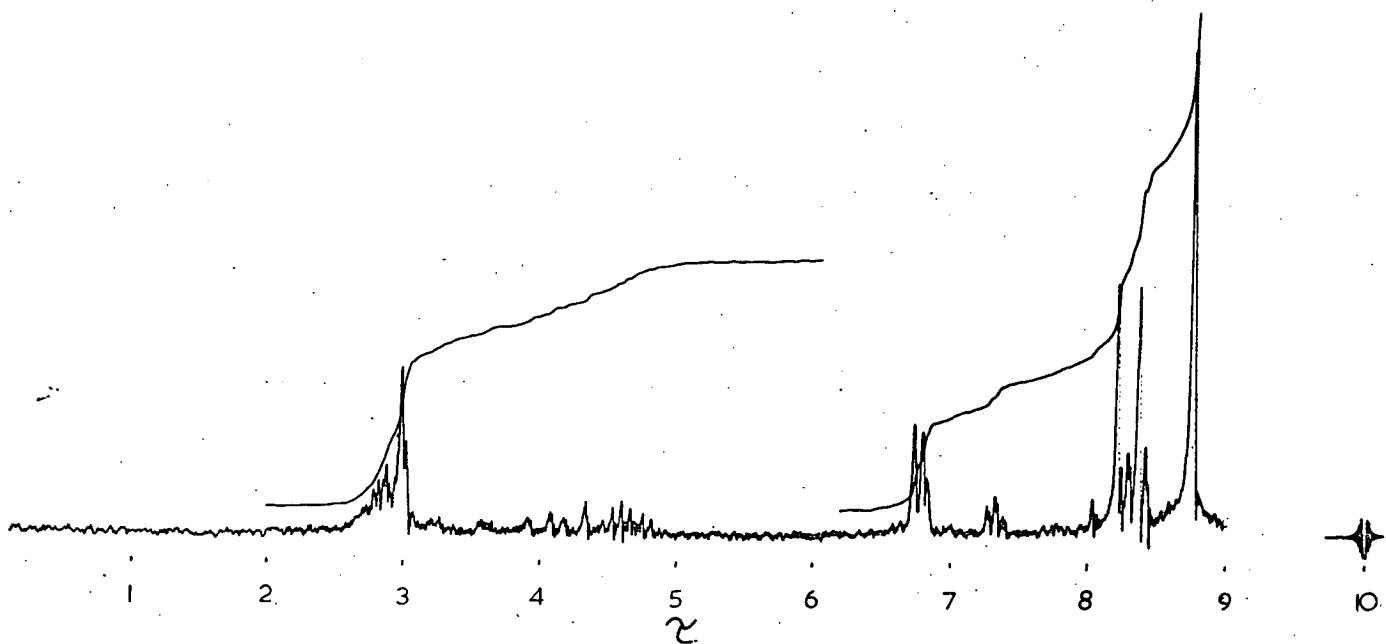
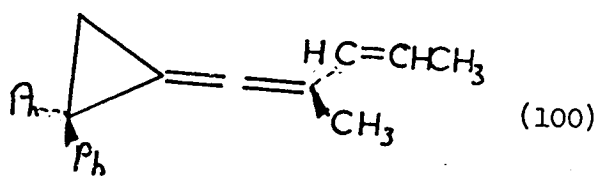


FIGURE XXXXIII



following grounds. No nuclear Overhauser enhancement²³⁰ of the olefinic proton (4.07 τ) was observed when irradiating the methyl group (8.08 τ), which might have been expected if these two moieties had a cis relationship. Also the long range coupling constant between these moieties (1.5 Hz.) is consistent with the long range coupling in a trans-orientation rather than a cis- (c.f. cis and trans- β -methylstyrene $J_{\text{trans}} = 1.8$ Hz., $J_{\text{cis}} = 0.8$ Hz.).

Both trans-3-bromo-3-methylhex-4-ene-1-yne (95) and 1-bromo-3-methyl-trans-pent-2-ene-4-yne (97) were used as carbene precursors.

7.2 The synthesis and rearrangement of 2-(trans-prop-1-enyl)propenylidene-cyclopropanes

The adducts of 1,1-diphenylethylene and indene were prepared by the action of potassium t-butoxide on the carbene precursor, trans-3-bromo-3-methylhex-4-ene-1-yne, in the presence of the olefin. Purification was achieved using alumina chromatography eluting with light petroleum.

The structures of these adducts were confirmed by ¹H-n.m.r. spectroscopy, the characteristic peaks being as follows; 2.5-3.1 τ absorptions attributed to the aromatic protons, 3.9-4.2 τ and 4.5-4.7 τ absorptions attributed to the olefinic protons of the propenyl group appearing as a broad doublet and a doublet of quartets respectively, 8.1-8.4 τ absorptions attributed to the allenic methyl group and 8.2-8.4 τ absorptions attributed to the methyl group of the propenyl moiety, appearing as a doublet. The adducts showed absorptions, in the infra-red spectrum, in the region 2020-2050 cm^{-1} due to the exo-cyclic allene group and in the regions 1680 cm^{-1} and 960-990 cm^{-1} due to the trans-double bond. Molecular formulae of the adducts were confirmed by exact mass measurement of the parent ion (P) in the mass spectrum. In the case of the indene adduct two isomers, E and Z-2,3-benzo-6-[2'-(trans-prop-1"-enyl)propenylidene]bicyclo[3,1,0]hex-2-ene (99a) and (99b) were formed whereas a single adduct 2-[2'-(trans-prop-1"-enyl)

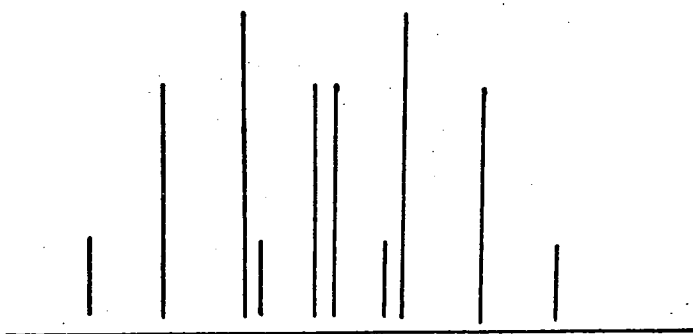
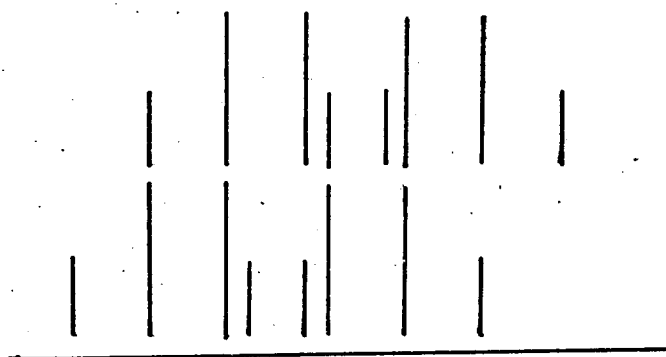


FIGURE XXXIV

propenylidene]-1,1-diphenylcyclopropane (100), only is possible from 1,1-diphenylethylene. Where two isomers exist it is possible to measure the amount of each isomer present from the ^1H -n.m.r. spectrum (Figure XXXXIII). The spectrum shows four methyl resonances of the same intensity (8.0-8.5 τ) indicating equal proportions of each isomer. The multiplet in the region 4.4-5.0 τ arises from a doublet of quartets from each isomer. The pattern does not show the sixteen lines as would be expected but only ten lines as the difference in the frequency at which the two isomers resonate is equivalent to the coupling constant $J_{\text{H-CH}_3}$. A simplification of this area of the spectrum is shown in Figure XXXXIV. As before the high field resonance due to the propenyl group and the low field resonance of the allenic methyl group were associated with the Z-isomer and the low field resonance due to the propenyl group and the high field resonance of the allenic methyl group associated with the E-isomer.

The addition of the carbene to α -methylstyrene and 1-phenylcyclopentene in each case gave mixtures of the two possible isomeric adducts along with other unidentified products which were not separable.

The thermal rearrangement of the two adducts isolated, from indene and 1,1-diphenylethylene, at 350° and 450° in flow system A gave only product mixtures containing no adduct, as indicated by the absence of the allenic absorption in the infra-red spectrum, however, it was not possible to separate or identify any products.

7.3 Synthesis and rearrangement of 2'-vinylpropenylidene-cyclopropanes

The adducts of α -methylstyrene, 1,1-diphenylethylene and 1-phenylcyclopentene were all prepared by the action of potassium *t*-butoxide on 1-bromo-3-methyl-trans-pent-2-ene-4-yne. This carbene

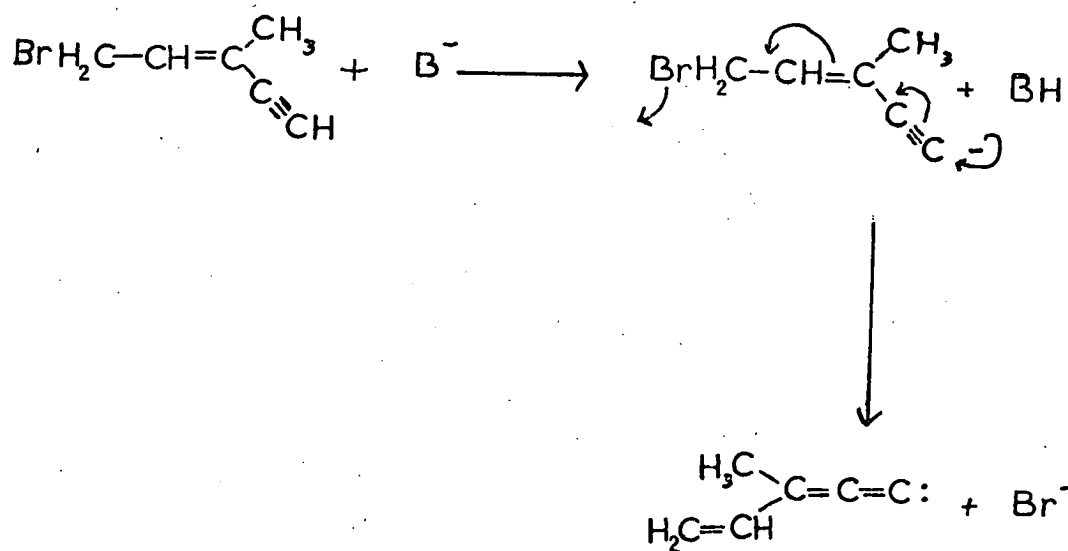


FIGURE XXXXV

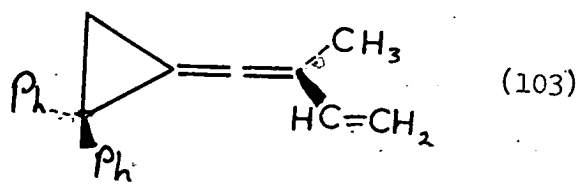
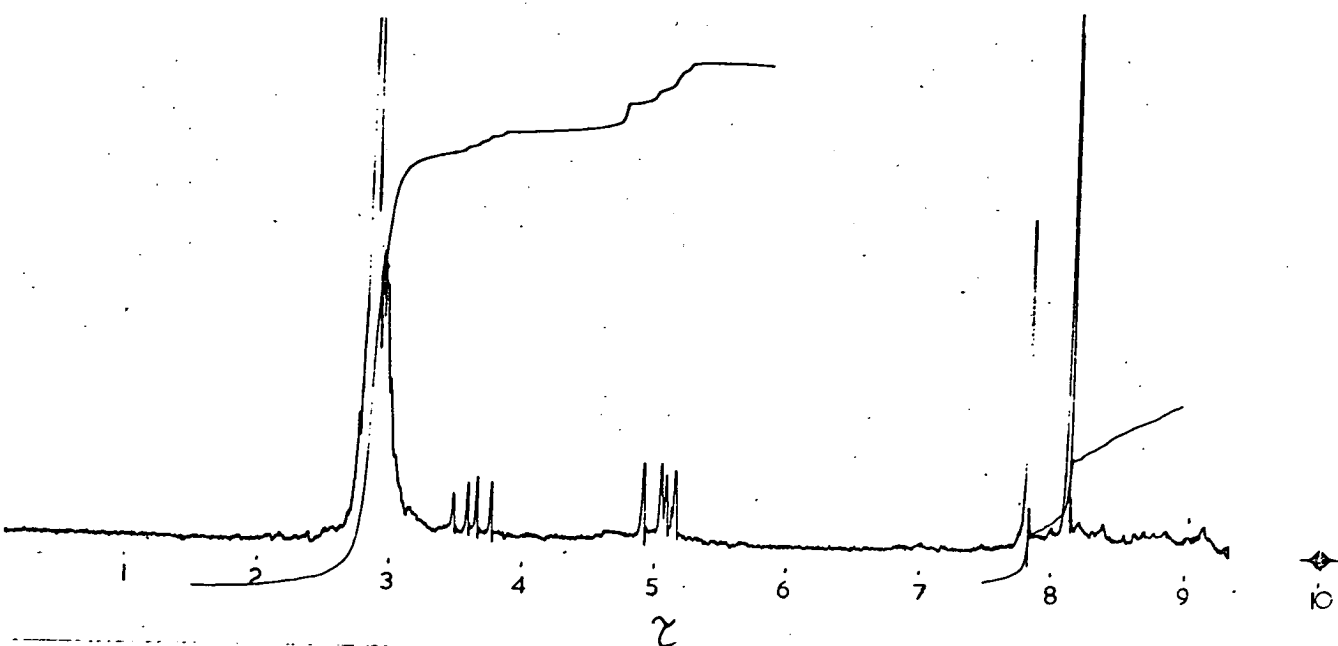
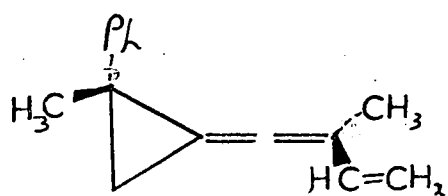


FIGURE XXXXVI

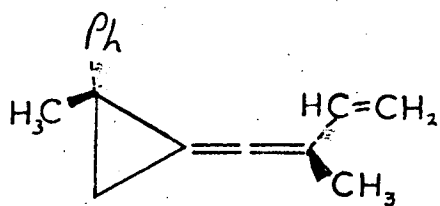
precursor, in the presence of strong base, rearranges as shown (Figure XXXXV) to give the required carbene. The structures of the adducts were confirmed from spectroscopic data. The ^1H -n.m.r. spectra show absorptions attributed to cyclopropyl hydrogens between 7.8-8.25 τ , absorptions attributed to the allenic methyl group between 8.16 and 8.42 τ and the characteristic absorptions due to the vinyl group between 3.6 τ and 5.15 τ . A typical spectrum is shown opposite (Figure XXXXVI).

As expected, two isomers were obtained from α -methylstyrene namely, E- and Z-2-(2'-vinylpropenylidene)-1-methyl-1-phenylcyclopropane (101a) and (101b), and 1-phenylcyclopentene, E and Z-6-(2'-vinylpropenylidene)-1-phenylbicyclo [3,1,0] hexane (102a) and (102b). In both these cases it is possible to measure the proportions of each isomer present using the ^1H -n.m.r. spectrum, the ratios obtained are recorded in Table IX. The high field methyl resonance and high field vinyl resonances arise from the same (Z) isomer, however, the ratios obtained are comparable to those found in the butenylidenecyclopropanes (section 6.1). Only one product was formed from 1,1-diphenylethylene namely 2-(2'-vinylpropenylidene)-1,1-diphenylcyclopropane (103) as expected.

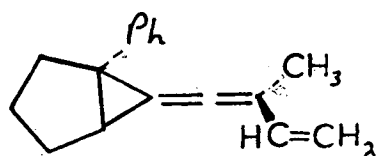
The attempted preparation of the indene adduct did not result in the expected E and Z-bicyclohexenes but yielded a single product. The ^1H -n.m.r. spectrum (Figure XXXXVII) shows resonances at 3.88 τ and 6.53 τ attributed to indene C(3) and C(1) protons respectively, a triplet at 4.14 τ attributed to an olefinic proton attached to two aliphatic protons resonating at 6.5 τ . This data, together with comparison of the ^1H -n.m.r. spectrum with that of the carbene precursor, led to the structure being assigned as a 2-(3'-methylpent-2'-ene-4'-ynyl)indene. Only one isomer was present and on similar grounds as were used to identify the carbene precursor (lack of Nuclear Overhauser enhancement and long-range coupling constants (1.45 Hz.) between the olefinic proton and methyl group) the product was assigned the E-configuration to give E-2-(3'-methyl-



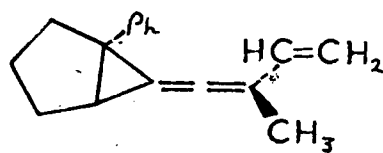
(101a)



(101b)



(102a)



(102b)

Table IX

	<u>E</u>	:		<u>Z</u>
(101a)	1.0	:	(101b)	1.3
(102a)	1.0	:	(102b)	1.5

pent-2'-ene-4-ynyl)indene (104).

In an attempt to elucidate the mechanism of this reaction, attempts were made to prepare similar adducts from 3-phenylindene and trans-stilbene, both of which do not form adducts with dimethylvinylidene carbene, however in both cases only olefin was recovered.

Normally²³¹, base catalysed alkylation of indenenes introduces a substituent on C(1) and all 2-substituted indenenes are synthesised via cyclisation reactions from benzene derivatives rather than formed by a substitution reaction from indene. The present reaction does not seem to involve the intermediate formation of the adduct (105) and its subsequent rearrangement, there being no obvious mechanism for the rearrangement of the adduct to the single isomer product, via either a base or acid catalysed route. In an attempt to elucidate the mechanism it was decided to attempt the preparation of 3-bromo-3-methylpent-1-ene-4-yne (106) from 3-methylpent-1-ene-4-yne-3-ol (96) by the method of Henbest²²⁸ as this compound, in the presence of strong base was expected, by analogy, to be a vinylidene carbene precursor. Attempted formation of the tertiary acetylenic bromide however led to a mixture containing 85% 1-bromo-3-methyl-trans-pent-2-ene-4-yne (97) and 15% of an inseparable unidentified product. The ¹H-n.m.r. of this unidentified product was not consistent with the required 3-bromo-3-methylpent-1-ene-4-yne (106). The formation of the terminal bromo compound is obviously energetically more favourable than the formation of the tertiary acetylenic bromide or the allenic bromide.

The thermal rearrangement of the adducts formed at 350° and 450° in flow system A, gave product mixtures. These mixtures again contained no adduct, the allenic absorption in the infra-red spectrum not being present, however it was not possible to separate or identify any of the products.

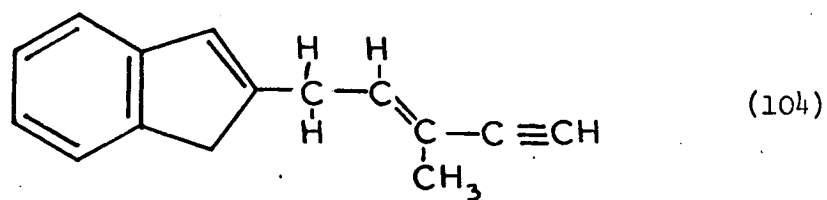
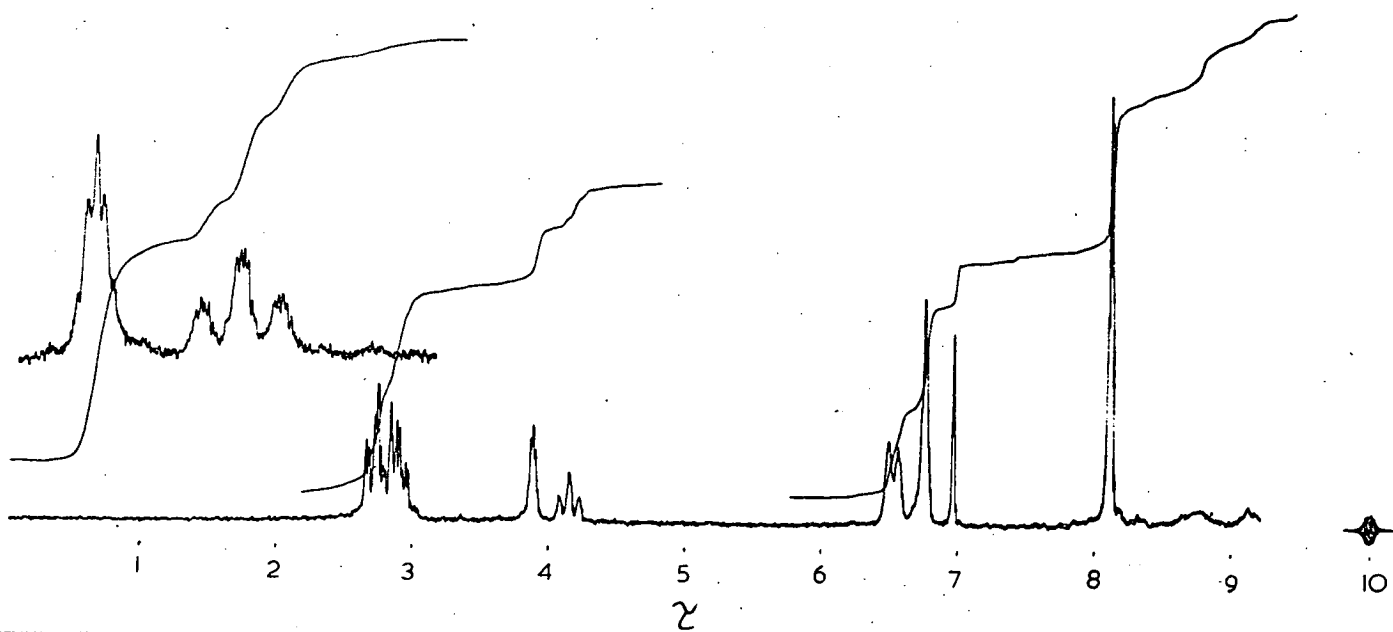
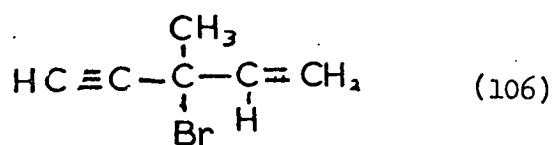
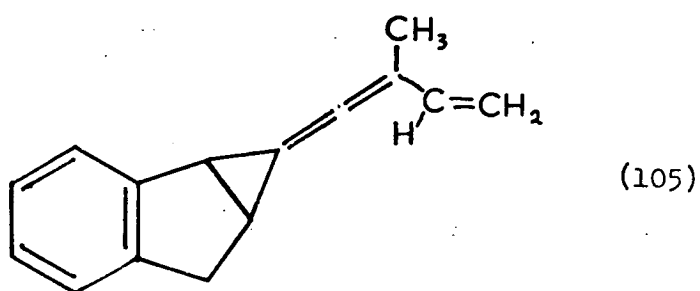


FIGURE XXXXVII



Experimental Section

8.1 Introduction

8.1.1 Spectroscopy

Infrared Spectroscopy: Routine spectra were recorded on a Unicam S.P.200 instrument, samples being examined as liquid films, Nujol mulls or solutions in carbontetrachloride, at room temperature.

Ultraviolet Spectroscopy: Spectra were recorded at room temperature on a Unicam S.P.800 instrument using a 1 cm. cell. Solutions were made up in ethanol (EtOH), all weighings being carried out using a Cahn Electrobalance.

Mass Spectroscopy: Spectra were recorded on an A.E.I. MS-902 double focussing instrument. Exact mass measurement of the parent peak (P) was determined by peak matching giving figures normally within 5 p.p.m. of the calculated values.

Proton Magnetic Resonance Spectroscopy: Spectra were recorded on one of the following machines: a Perkin-Elmer Model R-10 Spectrometer (60 MHz, 14,100 gauss), probe temperature 33.5°C; a Varian EM360 Spectrometer (60 MHz, 14,100 gauss) probe temperature 28°C; or a Varian HA-100 Spectrometer (100 MHz, 23,490 gauss) probe temperature 28°C. Samples were examined as solutions (5-15% w/v) in carbon tetrachloride, deuteriochloroform or deuterobenzene as solvents. Chemical shifts (τ) are expressed in parts per million relative to tetramethylsilane ($\tau=10$) used as internal standard. Abbreviations used are singlet(S), doublet(d), triplet(t), quartet(q), multiplet(M), fine(f), broad(b).

Carbon 13 Magnetic Resonance Spectroscopy: Spectra were recorded on a Varian XL-100 Spectrometer (25.2 MHz, 23,500G) probe temperature 28°C. Samples were examined as solutions (10-25% w/v) in deuteriochloroform as solvent. Chemical shifts (δ_c) are expressed in

parts per million relative to tetramethylsilane ($\delta_c=0$) used as internal standard.

8.1.2 Chromatography

Column Chromatography: Unless otherwise stated Spence type-H alumina (Brockmann activity I or II) was used.

Thin Layer Chromatography: (t.l.c.) Merk silicagel GF₂₅₄ was used, the fluorescent nature of this material allowing direct detection of components on examination under an ultraviolet lamp. Plates of film thickness 0.25 m.m. and 1.00 m.m. were used for analytical and preparative plates respectively.

Gas Liquid Chromatography: (g.l.c.) Analytical work was carried out using a Griffin and George D6 chromatograph fitted with a gas density balance detector and employing two meter glass columns packed with silanised, acid washed, Chromosorb P (80-100 mesh), coated with 5% (w/w) neopentylglycolsuccinate (N.P.G.S.). Nitrogen (inlet pressure 15 p.s.i.) was used as carrier gas. Preparative work was carried out on a Pye 105 automatic preparative chromatograph fitted with a flame ionisation detector. Columns used were 5 meter or 2 meter glass columns packed with Phasesep NI, coated with 25% (w/w) polymetaphenylether (P.M.P.E.), Phaseprep A coated with 10% polymetaphenylether (P.M.P.E.) or Phaseprep A coated with 10% neopentylglycolsuccinate (N.P.G.S.). Nitrogen (inlet pressure 35 p.s.i.) was used as carrier gas.

8.1.3 Materials

Unless otherwise stated, commercially available chemicals were used without further purification. Light petroleum refers to the fraction b.p. 30-40° which was redistilled before use, all other solvents being used without further purification. Nitrogen was the BOC "oxygen-free" grade. All products were dried in solution over anhydrous

magnesium sulphate and anhydrous potassium carbonate. Melting points (m.p.) and boiling points (b.p.) are uncorrected. The glass wool used was cleaned by continuous elution with boiling carbontetrachloride (8 hrs.) and dried in an oven at 100°C (8 hrs.) before use.

8.2 Preparation of Starting Materials

8.2.1 Potassium t-butoxide was prepared by the careful addition of potassium (80 grams, 2.1 mol.) to anhydrous t-butyl alcohol (1.7 l) under nitrogen and refluxing for 15 h. Excess t-butyl alcohol was removed under reduced pressure (15 m.m., 100°). The resultant white solid was the 1:1 complex $((\text{CH}_3)_3\text{CO}^-\text{K}^+-(\text{CH}_3)_3\text{COH})$. The potassium t-butoxide was used as the 1:1 complex (65% $(\text{CH}_3)_3\text{CO}^-\text{K}^+$ by titration against standard dilute hydrochloric acid) and all future mention of potassium t-butoxide refers to the complex unless otherwise stated.

8.2.2 Pinacolone was prepared in 50-55% yield from acetone via pinacol hydrate as described by Vogel²³² B.P. 105-106° Lit.²³³ 106°.

8.2.3 Trans-pent-3-ene-2-one was prepared by the method of Ramirez and Dirshovitz²²⁷. Triphenylphosphine (100 gms., 0.38 mol.) and chloroacetone (37.5 gm., 0.41 mol.) were dissolved in chloroform (300 mls) and refluxed for 45 minutes. The solution was filtered hot and poured into ether (2.5 litres). The white solid which formed, (acetonyltriphenylphosphonium chloride 100 gm., 70%), was collected, sucked dry and shaken with aqueous sodium carbonate (10% w/v, 2 litres) for 8 hrs. After this time the white solid which formed, (triphenylphosphineacetylmethylene, 70 gm., 58%), was collected, dried and dissolved in methylene chloride (450 mls). The methylene chloride solution was treated with acetaldehyde (19 gms., 0.45 mol.) and refluxed for 6 hrs. The solvent was removed through a 50 cm Vigreux column and pentane (150 mls) added. The cream precipitate of triphenylphosphine oxide which separated on the addition of the pentane was filtered off, washed with petrol, and the filtrate

and petrol solution dried. The solvent was removed and the residue distilled to give trans-pent-3-ene-2-one (117-112°, lit.²²⁷, 113-119°, 30%).

8.3 Preparation of acetylenic alcohols

8.3.1 3,4,4-Trimethylpent-1-yn-3-ol (67) Three routes to this compound were attempted.

(1) Following the method of Campbell, Campbell and Ely²²¹, pinacolone was added to a solution of sodium acetylide in liquid ammonia, to give 3,4,4-trimethylpent-1-yn-3-ol in low yield (ca. 20%). This product was only separated from the unreacted pinacolone with difficulty.

(2) The method of Suga, Watanabe and Suzuki²²² using lithium naphthalide in tetrahydrofuran to convert the pinacolone to the desired acetylenic alcohol also gave low yields (ca. 15%). Difficulty was again experienced in separation of the product from the starting materials.

(3) A satisfactory route was essentially that described by Skattebøl, Jones and Whiting²²³. A solution of ethylmagnesium bromide (1.5 mol.) in tetrahydrofuran (1 l) was carefully added dropwise, over a period of 3 h., with stirring, to tetrahydrofuran (600 ml.) through which purified acetylene²³⁴ was passed. The resultant ethynylmagnesium bromide was cooled in ice and pinacolone (100 gm., 1.0 mol.) in tetrahydrofuran (150 ml) added dropwise with rapid stirring and the solution allowed to stir overnight while warming to room temperature. The brown solution was then added to saturated ammonium chloride solution, the tetrahydrofuran layer separated and the aqueous phase extracted with ether (3x100 ml). The combined organic layers were dried and the solvents removed to give 3,4,4-trimethylpent-1-yn-3-ol (b.p. 140-142°, lit.²³⁵ 144°, 60%) as a colourless liquid which was stored at -15° under nitrogen.

8.3.2 3-Methylpent-1-ene-4-yne-3-ol (96) was prepared by the method of Heilbron²²⁶. Aqueous methylvinylketone (90% w/w) was first purified,

by shaking with potassium carbonate, (0.2 g/ml ketone) to salt out the water. The water was separated, the crude ketone dried and then distilled to yield pure dry methylvinylketone. Methylvinylketone (0.3 mol.) was added to a solution of sodium acetylide (1.5 mol.) in liquid ammonia (1 litre) over $1\frac{1}{2}$ hours. The solution was stirred for a further $1\frac{1}{2}$ hours, ammonium chloride (100g) added, the liquid ammonia allowed to evaporate overnight, and the remaining solid extracted with ether (3x200 mls). The solvent was removed from the dried extract and the product 3-methylpent-1-ene-4-yne-3-ol distilled as a colourless liquid (b.p. $56^{\circ}/17$ m.m. 35%).

n.m.r.	(CCl ₄) ₂	: 4.2 (d of d, $J_{\text{trans}}=16.5\text{Hz.}$, $J_{\text{cis}}=10\text{Hz.}$, 1H, H ₂ C:CH), 4.7, 4. (d of d, d of d, $J_{\text{trans}}=16.5\text{Hz.}$, $J_{\text{cis}}=10\text{Hz.}$, $J_{\text{gem}}=2\text{Hz.}$, 2H, H ₂ C:CH), 7.7 (s, 1H, C:CH), 7.9 (s, 1H, -OH), 8.6 (s, 3H, -CH ₃).
i.r.	(film) cm ⁻¹	: 3800 (s) O-H, 3600 (s) C≡CH, 2250 (m) C≡C, 1650 (m) C=C olefinic, 990 (m), 920 (s) C=CH.
m.s.	m/e	: P=96.056147; Calculated for C ₆ H ₈ O, 96.057511. 96 (C ₆ H ₈ O), 95 (P-H), 81 (P-CH ₃) base peak, 165 (P-CHO).

8.3.3 Trans-3-methyl-hex-4-ene-1-yne-3-ol (94) was prepared by the method of Heilbron²²⁶ as described for the preparation of the previous alcohol, from trans-pent-2-ene-4-one to give the required product (b.p. $82-84^{\circ}/15$ m.m., 40%).

n.m.r.	(CCl ₄) ₂	: 4.05 (d of q, $J=16\text{Hz.}$, $J=6.5\text{Hz.}$, 1H, :CHCH ₃), 4.44 (d, $J=16\text{Hz.}$, 1H, :CH),
--------	----------------------------------	--

			4.37 (bs, 1H, <u>OH</u>), 7.46 (s, 1H, : <u>CH</u>),
			8.31 (d of d, J=6.5Hz., J=1Hz., 3H, :CH <u>CH</u> ₃),
			8.49 (s, 3H, <u>•CCH</u> ₃).
i.r.	(film) cm ⁻¹	:	3400 (s) -OH, 3300 (s) C≡C-H,
			2100 (w) C≡C, 1675 (m) C=C, 975 (m)
			C=CH.
m.s.	m/e	:	P=110.072266; Calculated for C ₃ H ₁₀ O,
			110.073161
			110 (C ₇ H ₁₀ O), 109 (P-H), 95 (P-CH ₃) base
			peak.

8.4 Preparation of Carbene Precursors

8.4.1 1-Bromo-3-methylbuta-1,2-diene (35) was prepared by a revised method of Landor²²⁹ 3-methylbut-1-yn-3-ol (42 gms., 0.5 mol.), hydrobromic acid (48% w/w, 125 mls), cuprous bromide (25 gms., .17 mol.) and diglyme (6.0 gm.) were placed in a stoppered conical flask and left for 6 h. at room temperature. After this time the originally homogeneous solution had separated into two phases. The top organic layer was separated, washed with hydrobromic acid (48% w/w, 3x25 ml) and dried. Distillation gave 1-bromo-3-methylbuta-1,2-diene (b.p. 69-70°/95 m.m. lit.²³⁵ 53.4/60 m.m., 85%) a colourless liquid stored at -15° under nitrogen.

¹³ C	$(H_3C)_2C=C=CHBr$	No.	No. of Atoms	Type of Atom	Chemical shift (γ)
		4	2	=C(<u>CH</u> ₃) ₂	20.2
		3	1	= <u>C</u> (CH ₃) ₂	69.9
		2	1	= <u>CH</u> Br	106.4
		1	1	= <u>C</u> =	199.7

8.4.2 1-Bromo-3,4,4-trimethylpenta-1,2-diene (67) was prepared from 3,4,4-trimethylpent-1-yn-3-ol (50 gm., 0.4 mol.) by stirring with hydrobromic

acid (48% w/w, 140 mls), copper bronze (1.5 gms.), cuprous bromide (30 gms., 0.2 mol.) ammonium bromide (24 gms., 0.25 mol.) and petroleum ether (200 mls, boiling range 40-60°) at 40°C as described by Landor²³⁶. The product, 1-bromo-3,4,4-trimethylpenta-1,2-diene (b.p. 63°/13 mm, lit.²³⁷ 59-61°/8 m.m. 60%) a colourless liquid, was stored at -15° under nitrogen.

¹³C

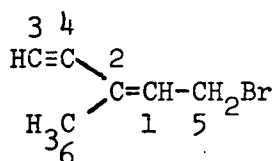
	No.	No. of Atoms	Type of Atom	Chemical shift (δ)
$ \begin{array}{c} \begin{array}{cc} 5 & 4 \\ (H_3C)_3C & \backslash \\ & C=C=CHBr \\ & / \\ H_3C & 2 \end{array} \\ \begin{array}{ccc} & 1 & 3 \end{array} \\ 6 \end{array} $	6	1	=CCH ₃	14.7
	5	3	-C(CH ₃) ₃	28.6
	4	1	-C(CH ₃) ₃	34.0
	3	1	=CHBr	71.3
	2	1	=CCCH ₃	119.1
	1	1	=C=	198.3

8.4.3 1-Bromo-3-methyl-trans-pent-2-ene-4-yne (97) was prepared by the method of Landor²²⁹ as described above from 3-methylpent-1-ene-4-yne-3-ol to give the required product (b.p. 54°/15 m.m., 70%) a colourless liquid stored at -15° under nitrogen.

n.m.r.	(CCl ₄) _τ	:	4.07 (bt, J=8Hz., 1H, C:CH), 5.93 (d, J=8Hz., 2H, ·CH ₂ Br), 6.81 (s, 1H, C≡CH), 8.08 (bs, 3H, :CCH ₃)
i.r.	(film) cm ⁻¹	:	3350 (s) C≡CH, 2150 (m) C≡C, 1680 (m), 1620 (m) C=C olefinic, 1440 (m) C-CH ₃ , 850 (m) C=CH, 700 (m) C-Br.
m.s.	m/e	:	P=157.972599 and 159.971072, Calculated for C ₆ H ₇ ⁷⁹ Br, 157.973163 and for C ₆ H ₇ ⁸¹ Br 159.971193

160 ($C_6H_7^{81}Br$), 158 ($C_6H_7^{79}Br$),
79 ($P-^{81}Br$) basepeak, 77 ($P-^{79}Br$).

^{13}C



No.	No. of Atoms	Type of Atom	Chemical shift (δ)
6	1	$=C\text{CH}_3$	22.6
5	1	$-\text{CH}_2\text{Br}$	28.9
4	1	$\text{HC}\equiv\text{C}-\text{C}$	80.6
3	1	$\text{HC}\equiv\text{C}-\text{C}$	84.4
2	1	$=\text{C}(\text{C})_2$	122.0
1	1	$=\text{CH}$	133.2

8.4.4 Trans-3-bromo-3-methyl-hex-4-ene-1-yne (95) was prepared by the method of Henbest²²⁸. Phosphorus tribromide (31 gm., 0.11 mol.) in ether (50 mls) was added dropwise to trans-3-methyl-hex-4-ene-1-yne-3-ol (35 gm., 0.32 mol.) in pyridine (5 mls) at -15° . The resultant slurry was stirred for a further hour while warming to room temperature and ether (50 mls) added. The mixture was filtered and the etherial solution washed with water (25 mls) and dried. The ether was then removed and the residue distilled to give trans-3-bromo-3-methyl-hex-4-ene-1-yne (b.p. $57^\circ/13$ m.m., 40%).

n.m.r. (CCl_4)₂ : 4.07 (bd, $J=10\text{Hz.}$, 1H, $:\text{CH}$), 4.85 (d of q, $J=10\text{Hz.}$, $J=7\text{Hz.}$, 1H, $:\text{CHCH}_3$), 6.52 (s, 1H, $:\text{CH}$), 8.14 (d, $J=2\text{Hz.}$, 3H, $\cdot\text{CCH}_3$), 8.265 (bd, $J=7\text{Hz.}$, 3H, $:\text{CHCH}_3$).

i.r. (film) cm^{-1} : 3350 (s) $\text{C}\equiv\text{CH}$, 2100 (w) $\text{C}\equiv\text{C}$, 1640 (m) $\text{C}=\text{C}$.

TABLE X

Olefin	N.M.R. (CCl ₄) _γ			Substituent	Exact mass measurement	M.P. or B.P. °C	Literature reference
	Ar <u>H</u>	:CH	-(CH ₂) _n n=3-6				
<u>Cyclo-</u> <u>pentenes</u>							
1-phenyl	2.55-3.0, M,5H	3.98, M,1H	7.25-7.68, 7.91-8.25, M,M,4H+2H	-	-	119°/20mm	124.5/30mm ²³⁵
1- <u>ortho-</u> tolyl	2.9-3.0, S,4H	4.35,M, 1H	7.2-7.7, 7.8-8.3, M,M,4H+2H	7.75, S, 3H	-	110°/24mm	116-117/30mm ⁸⁵
1- <u>ortho-</u> methoxy	2.8-3.34 M,4H	3.78,M, 1H	7.2-7.6, 8.88,m,t, J=6Hz., 4H+2H	6.23,S, 3H	174.104957 Calculated for C ₁₂ H ₁₄ O, 174.104459	42-44°/15mm	-
1- <u>para-</u> fluoro	2.5-3.2, M,4H	4.0,M, 1H	7.2-7.7, 7.7-8.3, M,M,4H+2H	-	-	M.P. 38-40°	232°/760mm ²⁴²

m.s. m/e : P=not possible to record
174 ($C_7H_9^{81}Br$), 172 ($C_7H_9^{79}Br$).

8.5 Olefins

8.5.1 The following commercially available olefins were redistilled.

Indene (b.p. $69^{\circ}/15$ m.m., lit.²³³, $182^{\circ}/760$ m.m.)

α -methylstyrene (b.p. $56^{\circ}/11$ m.m., lit.²³³, $55^{\circ}/14$ m.m.)

Acenaphthalene (M.P. 92° , lit.²³⁵, $92-93^{\circ}$)

cinnyl alcohol (M.P. 32-32.5°, lit.²³³, 33°)

3-methylindole (b.p. 112°/12 m.m., lit.²³³, 265-6°/755 m.m.)

1,2-dimethylindole (M.P. 54° , lit.²³³, 56°)

azobenzene (M.P. 67° , lit.²³³, 68°)

isobutene (lit.²³³, b.p.-66°) was used directly from the cylinder due to its volatility and styrene (lit.²³³, 145°) was used directly due to its tendency to polymerise)

The following olefins were kindly supplied by Dr. I.H. Sadler.

β,β -dimethylstyrene (b.p. $74^{\circ}/10$ m.m., lit.²³³, $76-7^{\circ}/11$ m.m.)

trans-stilbene (M.P. 123°, lit.²³³, 124°); trans- β -methylstyrene (76°/18 m.m. lit.²³³, 176-177°)

2-methyl-1,1-diphenylprop-1-ene (b.p. 121-123°/11 m.m., lit.²³⁵ 293°/760 m.m.)

All other olefins used were prepared in the laboratory, details

of individual methods follow.

8.5.2 3-Phenylindene was prepared by the reaction of phenylmagnesium

bromide (0.6 mol.) with indan-1-one (0.5 mol.) in ether. Dehydration of the intermediate alcohol was achieved by refluxing with aqueous hydrochloric acid (10%) for 1 hour. The crude olefin was extracted with ether, the extracts dried, the ether removed and the residue distilled to give the product (b.p. 150-152°/15 m.m., lit.²³³, 200-201/29 m.m., 80%). The product was stored at room temperature in the dark.

TABLE X cont/d.

Olefin	N.M.R. (CCl ₄) τ			Substituent	Exact mass measurement	M.P. or B.P. °C	Literature reference
	Ar <u>H</u>	: <u>CH</u>	-(CH ₂) _n n=3-6				
<u>Cyclo-pentenes</u>							
1- <u>para</u> -methyl	2.78,3.32 d,d,J=8Hz., 2H+2H	4.1,M, 1H	7.26-7.66, 7.88-8.22, M,M,4H+2H	6.35,S,3H	-	79-80°	81° 242
1- <u>para</u> -tolyl	2.6-3.15, M,4H	4.0,M, 1H	7.2-8.2,M, 6H	7.75,S,3H	-	135°/24mm	130-133/21mm 85
1- <u>meta</u> -tert-butyl	2.6-3.0 M,4H	3.93,M, 1H	7.1-8.4, M,6H	8.70,S,9H	200.154977 Calculated for C ₁₅ H ₂₀ 200.156493	62-63°/16mm	-
1- <u>meta</u> -trifluoro-methyl	2.25-3.05, M,4H	3.83,M, 1H	7.1-7.75, 7.75-8.3, M,M,4H+2H	-	212.081407 Calculated for C ₁₂ H ₁₁ F ₃ 212.081278	37-39°/15mm	-
1- <u>meta</u> -methyl	2.8-3.0 3.0-3.2 M,M,4H	4.0,t, J=3Hz 1H	7.2-7.8 M, 6H	7.76, S, 3H			

8.5.3 1,1-Diphenylethylene was prepared in a similar manner from methylmagnesium bromide and benzophenone. Dehydration of the intermediate carbinol gave the required olefin (b.p. $130^{\circ}/12$ m.m., lit.²³³, $136^{\circ}/13$ m.m., 64%).

8.5.4 Acrolein diethylacetal was prepared by the following method²³⁸
Acrolein (50 mls), ethanol (50 mls), ethylorthoformate (100 mls) and ammonium nitrate (3 grms.) were stirred together for 7 hours at room temperature. After careful removal of the excess ethanol and ethyl orthoformate the residue was distilled from sodium carbonate to give the diethylacetal (b.p. 118-120°, lit.²³⁸, 120-124°, 50%).

8.5.5 N-methylbenzylimine was prepared by the following method²³⁹. Equimolar quantities of benzaldehyde and aqueous methylamine were stirred together for 20 minutes. The mixture was then extracted with ether, dried, the solvent removed and the crude product distilled to give the imine (B.P. $63^{\circ}/12$ m.m., lit²³⁵ 180°).

n.m.r. $(\text{CCl}_4)_2$: 1.92 (fq, $J=2\text{Hz.}$, 1H, :CH), 2.3-2.44 (M, 2H, ArCH-ortho), 2.64-2.8 (M, 3H, ArCH), 6.59 (d, $J=2\text{Hz.}$, 3H, NCH₃).

8.5.6 Arylcycloalkanes The following olefins Table X, pure by g.l.c., characterised by their i.r. and n.m.r. spectra, were all prepared by the reaction of an aryl-magnesium bromide (0.6 mol.) with the corresponding ketone (0.5 mol.) in ether, dehydration of the intermediate alcohol being achieved by refluxing with aqueous hydrochloric acid (10%) for 1 hour. The crude olefin was extracted with ether, dried, distilled and stored at room temperature in the dark.

The aryl bromides used were commercially available with the exception of 2,5- and 3,5-dimethylbromobenzene and meta-t-butylbromobenzene; details of the preparation of these compounds are given below.

TABLE X cont/d.

Olefin	N.M.R. (CCl ₄) ₂			Substituent	Exact mass measurement	M.P. or B.P. °C	Literature reference
Ar <u>H</u>	:CH	-(CH ₂) _n n=3-6					
<u>Cyclo-</u> <u>pentenes</u>							
1-(2,5- dimethyl	2.9-3.2 M, 3H	4.3, M, 1H	7.2-8.6, M, 6H	7.8, S, 6H	172.125084 Calculated for C ₁₃ H ₁₆ 172.125194	72-74°/15mm	-
1-(3,5- dimethyl	2.92-3.3, M, 3H	4.0, M, 1H	7.1-8.46, M, 6H	7.76, S, 6H	172.125083 Calculated for C ₁₃ H ₁₆ 172.125194	76-78°/12mm	-
1-penta- deutero phenyl	-	3.95, M, 1H	7.1-7.75, 7.75-8.3, M, M, 4H+2H	-	149.125366 Calculated for C ₁₁ H ₇ D ₅ 149.125283	116-117°/15mm	-

8.5.7 2,5-Dimethylbromobenzene was prepared by the following route.

para-Xylene (106 gm., 1 mol.) containing a catalytic amount of aluminium bromide was placed in a 500 ml round bottomed flask. Bromine (180 gm., 2.25 mol.) was run in over 0.5 h and the hydrogen bromide evolved was absorbed in water. The temperature of the reaction mixture was raised to 70°C for 1 h when all traces of bromine vapour had disappeared. The resultant red product was washed successively with water (4x100 mls) and sodium hydroxide (10% w/w, 3x100 mls) until the washings were alkaline. The dried product was then distilled to give 2,5-dimethylbromobenzene (b.p. 90-92°/12 m.m., lit.²³³, 205-210°/770 m.m. 90%).

8.5.8 3,5-Dimethylbromobenzene was prepared in the following reaction sequence. N-bromosuccinimide (36 gms., 0.2 mol.) in methylene chloride (100 mls) was cooled to 0°C in an ice bath. A solution of ice cold 2,6-dimethylaniline (24 gms., 0.2 mol.) in methylene chloride (100 mls) was added to the slurry of N-bromosuccinimide, the mixture was stirred at 0° for 15 minutes, then at room temperature for 1 hour. The mixture was filtered, dried and the solvent removed, to give 4-bromo-2,6-dimethylaniline (38 gms., 95%). The amine was then deaminated by diazotisation with sodium nitrite and hydrochloric acid and treatment with hypophosphorus acid (150 mls, 50%, 6 fold excess) at 0°C for 30 hours. The solution was then extracted with ether, dried and the solvent removed to give 3,5-dimethylbromobenzene (b.p. 85-86°/11 m.m., lit.²³⁵, 204°/760 m.m., 95%).

8.5.9 Meta-t-butylbromobenzene was prepared from t-butylbenzene using the following synthesis. t-Butylbenzene (134 gm., 1 mol.) was nitrated by the normal method using concentrated nitric acid (105 mls) and concentrated sulphuric acid (120 mls) as nitrating agent. This gave para-nitro-t-butylbenzene (90%) with a trace of the ortho isomer also. This mixture was then reduced by adding concentrated hydrochloric acid (6 mls) dropwise to a stirred solution of

TABLE X cont/d.

Olefin	N.M.R. (CCl ₄) ₂			Substituent	Exact mass measurement	M.P. or B.P. °C	Literature reference
	Ar <u>H</u>	: <u>CH</u>	-(CH ₂) _n n=3-6				
<u>Cyclo- hexene</u>							
1-phenyl	2.6-3.0, M,5H	4.0,M, 1H	7.2-8.5, M,8H	-	-	110°/10mm	125/14mm ²³³
<u>Cyclo- heptene</u>							
1-phenyl	2.7-3.0, 6S,5H	4.0,t, J=6Hz. 1H	7.3-8.6,M, 10H	-	-	120-122/20mm	115-116°/15mm ²⁴⁰
<u>Cyclo- octene</u>							
1-phenyl	2.6-3.0, M,5H	4.05,t, J=8Hz. 1H	7.2-8.1, 8.15-8.75, M,M,4H+8H	-	-	96-98°/14mm	82-83°/0.2mm ²⁴¹

p-nitro-t-butylbenzene (36 gm., 0.2 mol.) in aqueous ethanol (170 mls, 50%) and iron powder (45 gms.). After the initial reaction had died down (15 minutes) the solution was refluxed overnight, filtered through celite and extracted with benzene (3x100 mls). The combined extracts were washed with water (3x50 mls), dried and the solvent removed to yield para-t-butylaniline (30 gms., 95%) with a trace of the ortho isomer. The amine mixture was then brominated using the N-bromo-succinimide method as described in section (8.5.8) to yield 2-bromo-4-t-butylaniline only. Bromination can only occur ortho to the amine group and so only one product is obtained from the two isomers. Deamination was carried out as described in section (8.5.8) to yield meta-t-butylbromobenzene (b.p. 114-116°/14 m.m., lit.²³⁵, 231-232/710 m.m., 85%).

8.6 Preparation and characterisation of dimethylvinylidene - cyclopropanes

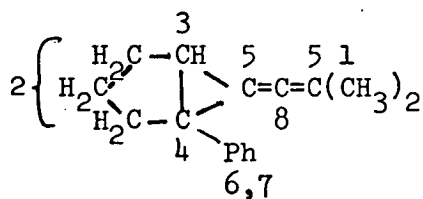
8.6.1 Dimethylvinylidene-cyclopropanes were prepared under anhydrous nitrogen by the dropwise addition of 1-bromo-3-methyl-but-1,2-diene (12 gm., 0.08 mol.) in light petroleum (10 mls) over 0.5 hours, to a magnetically stirred slurry of potassium t-butoxide (18.6 gm., 0.1 mol.) in either pure olefin (indene and isobutene) as solvent or a solution of olefin (.04 mol., all other olefins) in light petroleum (20 mls) at -10°. The coloured reaction mixture was stirred for a further 1 hour and then allowed to attain room temperature. Water (20 mls) was added and the pH adjusted to ca. 5 with aqueous hydrochloric acid (10%) while vigorously stirring. The mixture was allowed to stand, the red organic layer separated, and the aqueous layer extracted with light petroleum (2x20 ml). The combined organic layers were washed with water (3x20 ml) (to remove traces of t-butanol) and saturated sodium chloride solution (20 ml), then dried. The light petroleum was removed under reduced pressure and the excess olefin

removed under high vacuum (0.1 m.m.) to leave the crude adduct which was purified by alumina chromatography eluting with light petroleum, unless otherwise stated. The adducts were characterised by i.r. and n.m.r. spectra (no u.v. absorption occurring above 210 m μ) and their molecular formulae confirmed by exact mass measurement of the parent ion (P) in the mass spectrum. All the adducts were stable when stored at -15°C.

8.6.2 6-Dimethylvinylidene-1-phenylbicyclo[3,1,0]hexane (36)

Starting olefin	:	phenylcyclopentene
B.P.	:	71-72°/0.01 m.m.
Yield	:	50-55%
n.m.r.	(CCl ₄) ₂	: 2.7-3.05 (M, 5H, ArH), 7.7-8.2 (M, 7H, (·CH ₂) ₃ +·CH), 8.26 (s, 6H, :C(CH ₃) ₂).
i.r.	(film) cm ⁻¹	: 2010 (m) allene, 1600 (m) C=C aromatic, 760 (s), 700 (s) monosubstitution.
m.s.	m/e	: P=210.140292; Calculated for C ₁₆ H ₁₈ , 210.140842.210 (C ₁₆ H ₁₈), 195 (P-CH ₃), base peak, 167 (P-C ₃ H ₇), 144 (P-C ₅ H ₆), 143 (P-C ₅ H ₇).

No.	No. of Atoms	Type of Atom	Chemical shift (δ)
1	2	$\underline{\text{CH}}_3$	21.0, 21.3
2	3	$\underline{\text{CH}}_2$	22.3, 29.6, 33.2
3	1	$\underline{\text{CH}}$	34.3
4	1	$\underline{\text{C}}$	39.4
5	2	$=\underline{\text{C}}$	87.6, 98.0
6	5	$\text{Ar}\underline{\text{CH}}$	125.5, 126.3, 127.9
7	1	$\text{Ar}\underline{\text{C}}-$	142.6
8	1	$=\underline{\text{C}}=$	187.5



8.6.3 6-Dimethylvinylidene-1-(2-tolyl)bicyclo[3,1,0]hexane (41, R=CH₃)

Starting olefin	:	<u>ortho</u> -tolylcyclopentene
B.P.	:	95°/0.1 m.m.
Yield	:	30-35%
n.m.r.	(CCl ₄)	: 2.72-2.92 (M, 1H, $\text{Ar}\underline{\text{H}}$), 3.0 (S, 3H, $\text{Ar}\underline{\text{H}}$), 7.68 (S, 3H, $\text{Ar}\underline{\text{CH}}_3$), 7.74-8.10 (M, 7H, $(\cdot\text{CH}_2)_3 + \cdot\text{CH}$), 8.23, 8.30 (S, S, 6H, $:\text{C}(\underline{\text{CH}}_3)_2$).
i.r.	(film) cm ⁻¹	: 2020 (s) allene, 1610 (m) C=C aromatic 760 (s), 730 (s) 1,2-disubstitution.
m.s.	m/e	: P=224.156352; Calculated for C ₁₇ H ₂₀ , 224.156493. 224 (C ₁₇ H ₂₀), 209 (P-CH ₃) base peak, 181 (P-C ₃ H ₇).

8.6.4 6-Dimethylvinylidene-1-(2-methoxyphenyl)bicyclo[3,1,0]hexane
(41, R=CH₃O)

Starting olefin	:	<u>ortho</u> -methoxyphenylcyclopentene
B.P.	:	60-60.5°C, white solid, (light petroleum)
Yield	:	45%
n.m.r.	(CCl ₄) ₂	: 2.81 (d of d, $J_1=7\text{Hz.}$, $J_2=2\text{Hz.}$, 2H, ArH), 3.16-3.40 (M, 2H, ArH), 6.6 (S, 3H, O-CH ₃), 7.8-8.1 (M, 7H, ($\cdot\text{CH}_2$) ₃ + $\cdot\text{CH}$), 8.24, 8.27 (S, S, 6H, :C(CH ₃) ₂)
i.r.	(film) cm ⁻¹	: 2010 (m) allene, 1600 (m) C=C aromatic, 1260 (m) C-O, 760 (m) 1,2 disubstitution
m.s.	m/e	: P=240.151822; Calculated for C ₁₇ H ₂₀ O ⁺ 240.151407. 240 (C ₁₇ H ₂₀ O ⁺), 225 (P-CH ₃) base peak, 209 (P-CH ₃ -O), 197 (P-C ₃ H ₇), 166 (P-C ₄ H ₁₀ O).

8.6.5 6-Dimethylvinylidene-1-(4-tolyl)bicyclo[3,1,0]hexane (38, R=CH₃)

Starting olefin	:	<u>para</u> -tolylcyclopentene
B.P.	:	rearranges on distillation
Purification	:	column chromatography using "florisil" eluting with light petroleum
Yield	:	60-65%
n.m.r.	(CCl ₄) ₂	: 2.6-3.2 (M, 4H, ArH), 7.2-7.7 (M, 2H; $\cdot\text{CH}_2$), 7.8 (S, 3H, ArCH ₃), 7.82-8.2 (M, 5H, ($\cdot\text{CH}_2$) ₂ + $\cdot\text{CH}$), 8.3 (S, 6H, :C(CH ₃) ₂).
i.r.	(film) cm ⁻¹	: 2075 (s) allene, 840 (s) 1,4 disubstitution
m.s.	m/e	: P=224.156308; Calculated for C ₁₇ H ₂₀ , 224.156493. 224 (C ₁₇ H ₂₀) base peak, 209 (P-CH ₃), 181 (P-C ₃ H ₇), 165 (P-C ₄ H ₁₁).

8.6.6 6-Dimethylvinylidene-1-(4-fluorophenyl)bicyclo[3,1,0]hexane (38, R=F)

Starting olefin	:	<u>para</u> -fluorophenylcyclopentene
B.P.	:	47-48°/0.01 m.m.
Yield	:	50-55%
n.m.r.	(CCl ₄) _γ	: 2.72-2.96 (M, 2H, ArH), 3.02-3.25 (M, 2H, ArH), 7.80-8.20 (M, 7H, (•CH ₂) ₃ +•CH), 8.60 (S, 6H, :C(CH ₃) ₂)
i.r.	(film) cm ⁻¹	: 2050 (s) allene, 1650 (m) C=C aromatic, 1240 (s) C-F aromatic, 845 (s) 1,4-disubstitution
m.s.	m/e	: P=228.130418; Calculated for C ₁₆ H ₁₇ F, 228.131421.228 (C ₁₆ H ₁₇ F), 213 (P-CH ₃) base peak, 185 (P-C ₃ H ₇).

8.6.7 6-Dimethylvinylidene-1-(4-methoxyphenyl)bicyclo[3,1,0]hexane (38, R=CH₃O)

Starting olefin	:	<u>para</u> -methoxyphenylcyclopentene
B.P.	:	rearranges on distillation
Purification	:	column chromatography using "florisil" eluting with light petroleum
Yield	:	35-40%
n.m.r.	(CCl ₄) _γ	: 2.875 (d, 2H, J=15Hz., ArH), 3.295 (d, 2H, J=15Hz., ArH), 6.29 (S, 3H, O-CH ₃), 7.7-8.2 (M, 7H, (•CH ₂) ₃ +•CH), 8.28 (S, 6H, :C(CH ₃) ₂)
i.r.	(film) cm ⁻¹	: 2030 (s) allene, 1615 (s) C=C aromatic, 840 (s) 1,4-disubstitution
m.s.	m/e	: P=240.151129; Calculated for C ₁₇ H ₂₀ O, 240.151407, 240 (C ₁₇ H ₂₀ O), 225 (P-CH ₃) base peak, 209 (P-CH ₃ -O), 197 (P-C ₃ H ₇), 173 (P-C ₅ H ₇).

8.6.8 6-Dimethylvinylidene-1-(3-trifluoromethylphenyl)bicyclo[3,1,0]
hexane (47, R=CF₃)

Starting olefin	:	<u>meta</u> -trifluoromethylphenylcyclopentene
B.P.	:	54-55°C/0.01 m.m.
Yield	:	30%
n.m.r.	(CCl ₄) τ	: 2.5 (s, 1H, ArH), 2.6 (s, 3H, ArH), 7.7-8.1 (M, 7H, ($\cdot\text{CH}_2$) ₃ $\cdot\text{CH}$), 8.22 (s, 6H, :C(CH ₃) ₂)
i.r.	(film) cm ⁻¹	: 2040 (s) allene, 1620 (m) C=C aromatic, 1350 (s) C-F ₃ , 810 (s) 1,3-disubstitution, 705 (s) C-F ₃
m.s.	m/e	: P=278.127833; Calculated for C ₁₇ H ₁₇ F ₃ , 278.128226, 278 (C ₁₇ H ₁₇ F ₃), 263 (P-CH ₃) base peak, 235 (P-C ₃ H ₇), 209 (P-CF ₃).

8.6.9 6-Dimethylvinylidene-1-(3-t-butylphenyl)bicyclo[3,1,0]
hexane (47, R=Bu^t)

Starting olefin	:	<u>meta</u> -t-butylphenylcyclopentene
B.P.	:	83-84°C/0.01 m.m.
Yield	:	30-35%
n.m.r.	(CCl ₄) τ	: 2.76-3.10 (M, 4H, ArH), 7.75-8.20 (M, 7H, ($\cdot\text{CH}_2$) ₃ $\cdot\text{CH}$), 8.25 (s, 6H, :C(CH ₃) ₂), 8.72 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$).
i.r.	(film) cm ⁻¹	: 2050 (s) allene, 1630 (s) C=C aromatic, 800 (s) 1,3-disubstitution
m.s.	m/e	: P=266.203536; Calculated for C ₂₀ H ₂₆ , 266.203441, 266 (C ₂₀ H ₂₆), 251 (P-CH ₃), 210 (P-C ₄ H ₈), 209 (P-C ₄ H ₉) base peak.

8.6.10 6-Dimethylvinylidene-1-(3-methyl)bicyclo[3,1,0]hexane
(47, R=CH₃)

Starting olefin	:	<u>meta</u> -methylphenylcyclopentene
B.P.	:	69-71°/0.01 m.m.
Yield	:	40-45%
n.m.r.	(CCl ₄) ₂	: 2.8-3.12 (M, 4H, ArH), 7.70 (S, 3H, ArCH ₃), 7.72-8.40 (M, 7H, (·CH ₂) ₃ +·CH), 8.26 (S, 6H, :C(CH ₃) ₂)
i.r.	(film) cm ⁻¹	: 2020 (s) allene, 1610 (s) C=C aromatic, 780 (m) 1,3 disubstitution
m.s.	m/e	: P=224.156965; Calculated for C ₁₇ H ₂₀ 224.156493, 224 (C ₁₇ H ₂₀), 209 (P-CH ₃) base peak, 181 (P-C ₃ H ₇).

8.6.11 6-Dimethylvinylidene-1-pentadeuterophenylbicyclo[3,1,0]hexane
(53)

Starting olefin	:	pentadeuterophenylcyclopentene
B.P.	:	66-68°C/0.01 m.m.
Yield	:	85%
n.m.r.	(CCl ₄) ₂	: 7.7-8.2 (M, 7H, (·CH ₂) ₃ +·CH), 8.27 (S, 6H, :C(CH ₃) ₂)
i.r.	(film) cm ⁻¹	: 2330 (s) C-D, 2060 (s) allene, 1580 (s) C=C aromatic
m.s.	m/e	: P=215.172003; Calculated for C ₁₆ H ₁₃ D ₅ , 215.172231, 215 (C ₁₆ H ₁₃ D ₅), 200 (P-CH ₃) base peak, 185 (P-C ₂ H ₆), 172 (P-C ₃ H ₇), 133 (P-C ₆ D ₅).

8.6.12 6-Dimethylvinylidene-1-(2,5-dimethylphenyl)bicyclo[3,1,0]hexane
(43)

Starting olefin	:	2,5-dimethylphenylcyclopentene
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B.P.		: 48-49°C/0.01 m.m.
Yield		: 20%
n.m.r.	(CCl ₄) _γ	: 3.0-3.3 (M, 3H, ArH), 7.74, 7.78 (S, S, 6H, ArCH ₃), 7.8-8.2 (M, 7H, (·CH ₂) ₃ +·CH), 8.23, 8.3 (S, S, 6H, :C(CH ₃) ₂).
i.r.	(film) cm ⁻¹	: 2015 (s) allene, 1610 (m) C=C aromatic, 890 (m), 810 (m) 1,2,5-trisubstitution
m.s.	m/e	: P=238.171352; Calculated for C ₁₈ H ₂₂ , 238.172142, 238 (C ₁₈ H ₂₂), 223 (P-CH ₃) base peak, 195 (P-C ₃ H ₇).

8.6.13 6-Dimethylvinylidene-1-(3,5-dimethylphenyl)bicyclo[3,1,0] hexane
(45)

Starting olefin		: 3,5-dimethylphenylcyclopentene
m.p.		: 30-30.5°C white solid
Yield		: 54%
n.m.r.	(CCl ₄) _γ	: 3.25 (S, 2H, ArH) 3.34 (S, 1H, ArH), 7.78 (S, 6H, ArCH ₃), 7.8-8.2 (M, 7H, (·CH ₂) ₃ +·CH), 8.28 (S, 6H, :C(CH ₃) ₂)
i.r.	(film) cm ⁻¹	: 2050 (s) allene, 1610 (s) C=C aromatic, 840 (m) 1,3,5-trisubstitution
m.s.	m/e	: P=238.170714; Calculated for C ₁₈ H ₂₂ , 238.172142, 238 (C ₁₈ H ₂₂), 223 (P-CH ₃), 195 (P-C ₃ H ₇)

8.6.14 7-Dimethylvinylidene-1-phenylbicyclo[4,1,0] heptane (55)

Starting olefin		: phenylcyclohexene
B.P.		: 68-69°C/0.01 m.m.
Yield		: 25%
n.m.r.	(CCl ₄) _γ	: 2.7-3.0 (M, 5H, ArH), 7.8-8.15 (M, 6H, (·CH ₂) ₃), 8.2 (S, 6H, :C(CH ₃) ₂), 8.4-8.6

			: (M, 3H, $\cdot\text{CH}_2 + \cdot\text{CH}$)
i.r.	(film) cm^{-1}		: 2000 (s) allene, 1600 (s) C=C aromatic, 740 (s), 680 (s) monosubstitution
m.s.	m/e		: P=224.156527; Calculated for $\text{C}_{18}\text{H}_{20}$, 224.156493, 224 ($\text{C}_{18}\text{H}_{20}$) base peak, 209 (P- CH_3), 181 (P- C_3H_7), 167 (P- C_4H_9).

8.6.15 8-Dimethylvinylidene-1-phenylbicyclo[5,1,0]octane (57)

Starting olefin		: phenylcycloheptene
B.P.		: 82-83°C/0.01 m.m.
Yield		: 25%
n.m.r.	(CCl_4) τ	: 2.7-3.2 (M, 5H, ArH), 7.6-8.15 (M, 5H, $(\cdot\text{CH}_2)_2 + \cdot\text{CH}$), 8.2, 8.25 (S,S, 6H, $\text{:C}(\text{CH}_3)_2$), 8.3-8.6 (M, 6H, $(\cdot\text{CH}_2)_3$)
i.r.	(film) cm^{-1}	: 2050 (s) allene, 1600 (s) C=C aromatic, 770 (s), 710 (s) monosubstitution
m.s.	m/e	: P=238.171814; Calculated for $\text{C}_{18}\text{H}_{22}$, 238.172142, 238 ($\text{C}_{18}\text{H}_{22}$) base peak, 223 (P- CH_3), 195 (P- C_3H_7), 181 (P- C_4H_9).

8.6.16 9-Dimethylvinylidene-1-phenylbicyclo[6,1,0]nonane (59)

Starting olefin		: phenylcyclooctene
B.P.		: 79-80°C/0.01 m.m.
Yield		: 40%
n.m.r.	(CCl_4) τ	: 2.6-3.0 (M, 5H, ArH), 7.5-8.2 (M, 5H, $(\cdot\text{CH}_2)_2 + \cdot\text{CH}$), 8.26, 8.40 (S, S, 6H, $\text{:C}(\text{CH}_3)_2$), 8.42-8.8 (M, 8H, $(\cdot\text{CH}_2)_4$).
i.r.	(film) cm^{-1}	: 2000 (s) allene, 1600 (s) C=C aromatic, 750 (s), 685 (s) monosubstitution
m.s.	m/e	: P=252.186513; Calculated for $\text{C}_{19}\text{H}_{24}$,

252.187792, 252 ($C_{19}H_{24}$) base peak,
 237 ($P-CH_3$), 209 ($P-C_3H_7$), 181 ($P-C_5H_{11}$)
 167 ($P-C_6H_{13}$), 155 ($P-C_7H_{14}$).

8.6.17 2-Dimethylvinylidene-1,1-dimethylcyclopropane (107)

Starting olefin : isobutene
 B.P. : rearranges on distillation
 Yield : 50%
 n.m.r. (C_6H_6)₂ : 8.25 (s, 6H, $:C(CH_3)_2$), 8.74 (s, 2H, $\cdot CH_2$), 8.82 (s, 6H, $\cdot C(CH_3)_2$)
 i.r. (film) cm^{-1} : 2050 (s) allene
 m.s. m/e : P=122.109244; Calculated for C_9H_{14} ,
 122.109545, 122 (C_9H_{14}), 107 ($P-CH_3$),
 105 ($P-CH_5$), 91 ($P-C_2H_7$), 79 ($P-C_3H_7$)
 base peak, 78 ($P-C_3H_8$), 77 ($P-C_3H_9$).

8.6.18 Addition of dimethylvinylidenecarbene ~~to~~ to the following olefins was attempted but no adduct was formed, olefin only being recovered.

Acenaphthylene, 3-phenylindene, 2-methyl-3,3-diphenylprop-2-ene,
 Acrolein diethylacetal, cinnamyl alcohol
 Azobenzene
 N-methylbenzylimine
 1,2-dimethylindole

In the case of 3-methylindole, 20% of the ring expanded product, 4-methyl-3-(2'-methylprop-2-enyl)-quinoline, as reported by Bycroft²⁰⁶ was formed.

8.7 Preparation and characterisation of 2,3,3-trimethylbutenyldene-cyclopropanes

8.7.1 These cyclopropanes were prepared by a method analogous to that for dimethylvinylidenecyclopropanes using 1-bromo-3,4,4-trimethylpenta-

1,2-diene (16 gm, 0.08 mol.) as carbene precursor. The adducts were characterised by i.r. and n.m.r. (no u.v. absorption occurring above 210 mμ) and their molecular formulae confirmed by exact mass measurement of the parent ion (P) in the mass spectrum. All the adducts were stable when stored at -15°C.

8.7.2 Z and E 2,3-benzo-6-(2',3',3' -trimethylbutenyldiene)bicyclo[3,1,0]hex-2-ene (69a) and (69b)

Starting olefin		:Indene
m.p.		:67-69°C white crystals, mixture (light petroleum)
Yield		:35-40%
Isomer ratio		:the ratio varied depending on crystallisation. Crude product ratio <u>Z:E</u> 1:3.
<u>Z isomer (69a)</u>		
n.m.r.	(CCl ₄) _γ	:2.7-3.1 (M, 4H, ArH), 6.75-6.95 (M, 3H, ArCH), 7.35-7.5 (M, 1H, •CH), 8.3 (S, 3H, •CH ₃), 9.28 (S, 9H, •C(CH ₃) ₃).
	(C ₆ H ₆) _γ	6.81 (d, J=6Hz., 1H, ArCH), 6.92 (d, J=6Hz 2H, ArCH ₂), 7.4-7.6 (M, 1H, •CH), 8.22 (S, 3H, •CH ₃), 9.17 (S, 9H, •C(CH ₃) ₃).
<u>E isomer (69b)</u>		
n.m.r.	(CCl ₄) _γ	:2.7-3.1 (M, 4H, ArH), 6.75-6.95 (M, 3H, ArCH), 7.35-7.5 (M, 1H, •CH), 8.46 (S, 3H, •CH ₃), 9.0 (S, 9H, •C(CH ₃) ₃).
	(C ₆ H ₆) _γ	:6.81 (d, J=6Hz., 1H, ArCH), 6.92 (d, J=6Hz 2H, ArCH ₂), 7.4-7.6 (M, 1H, •CH), 8.5 (S, 3H, CH ₃), 8.93 (S, 9H, •C(CH ₃) ₃).
<u>Mixture</u>		
i.r.	(CCl ₄) cm ⁻¹	:2120 (s) allene, 1630 (m) C=C aromatic, 1120 (m), 1160 (m) 1,2-disubstitution.

m.s. m/e : P=224.156527; Calculated for $C_{17}H_{20}$,
224.156943, 224 ($C_{17}H_{20}$), 209 (P- CH_3),
167 (P- C_4H_9) base peak, 152 (P- C_5H_{12}).

8.7.3 2-(2',3',3'-trimethylbutenyldiene)-1,1-diphenylcyclopropane (76)

Starting olefin : 1,1-diphenylethylene
m.p. : 78-79°C white needles (light petroleum)
Yield : 40%
n.m.r. (CCl_4) τ : 2.65-3.0 (M, 10H, ArH), 7.755 (d, J=6.7 Hz., 1H, $\cdot CH$), 8.025 (d, J=6.7 Hz., 1H, $\cdot CH$), 8.19 (s, 3H, $\cdot CH_3$), 8.98 (s, 9H, $\cdot C(CH_3)_3$)
i.r. (CCl_4) cm^{-1} : 2120 (m) allene, 1620 (m) C=C aromatic, 1090 (m), 708 (s) monosubstitution
m.s. m/e : P=288.187193; Calculated for $C_{22}H_{24}$,
288.187792, 288 ($C_{22}H_{24}$) base peak, 273 (P- CH_3), 231 (P- C_4H_9), 216 (P- C_5H_{12}), 204 (P- C_6H_{12}).

8.7.4 2-(2',3',3'-trimethylbutenyldiene)-1,1-dimethylcyclopropane (77)

Starting olefin : isobutene
b.p. : 39-40°C/0.01 m.m.
Yield : 42%
n.m.r. (CCl_4) τ : 8.08 (s, 2H, $\underline{CH_2}$), 8.8 (s, 3H, $\cdot CCH_3$), 8.82 (s, 3H, $\cdot CCH_3$), 8.86 (s, 9H, $\cdot C(CH_3)_3$), 9.02 (s, 3H, $\cdot CCH_3$).
i.r. (film) cm^{-1} : 2120 (m) allene
m.s. m/e : P=164.156557; Calculated for $C_{12}H_{20}$,
164.156493, 164 ($C_{12}H_{20}$), 149 (P- CH_3), 121 (P- C_3H_7) base peak, 107 (P- C_4H_9).

8.7.5 Z and E 2-(2',3',3'-trimethylbutenylidene)-1-methyl-1-phenyl
cyclopropane (71a) and (71b)

Starting olefin	:	α -methylstyrene
b.p.	:	56-58°C/0.05 m.m.
Yield	:	60-65%
Isomer ratio	:	<u>Z</u> : <u>E</u> 1:1.2
<u>Z</u> isomer (71a)		
n.m.r.	(CCl ₄) γ	: 2.7-3.0 (M, 5H, ArH), 8.14 (S, 3H, :CCH ₃), 8.31-8.38 (fM, 2H, $\cdot$ CH ₂), 8.45 (S, 3H, $\cdot$ CCH ₃), 8.9 (S, 9H, $\cdot$ C(CH ₃) ₃).
<u>E</u> isomer (71b)		
n.m.r.	(CCl ₄) γ	: 2.7-3.0 (M, 5H, ArH), 8.18 (S, 3H, :CCH ₃), 8.31-8.38 (fM, 2H, $\cdot$ CH ₂), 8.45 (S, 3H, $\cdot$ CCH ₃), 8.86 (S, 9H, $\cdot$ C(CH ₃) ₃).

Mixture

i.r.	(film) cm ⁻¹	: 2050 (s) allene, 1605 (m) C=C aromatic, 900 (m), 780 (m), 700 (m) mono-substitution
m.s.	m/e	: P=226.172071; Calculated for C ₁₇ H ₂₂ , 226.172142, 226 (C ₁₇ H ₂₂) base peak, 211 (P-CH ₃), 183 (P-C ₃ H ₇), 170 (P-C ₄ H ₈), 169 (P-C ₄ H ₉), 142 (P-C ₆ H ₁₂)

8.7.6 Z and E 2-(2',3',3'-trimethylbutenylidene)-1,1-dimethyl-2-phenyl-
cyclopropane (75a) and (75b)

Starting olefin	:	β , β -dimethylstyrene
B.P.	:	56-57°C/0.01 m.m.
Yield	:	15%
Isomer ratio	:	<u>Z</u> : <u>E</u> 1:1

Z isomer (75a)

n.m.r. $(\text{CCl}_4)_\gamma$: 2.8-2.9 (fM, 5H, ArH), 7.28 (S, 1H, $\cdot\text{CH}$), 8.14 (S, 3H, $\cdot\text{CCH}_3$), 8.90 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$), 9.05-9.17 (fM, 6H, $\cdot\text{C}(\text{CH}_3)_2$)

E isomer (75b)

n.m.r. $(\text{CCl}_4)_\gamma$: 2.8-2.9 (fM, 5H, ArH), 7.28 (S, 1H, $\cdot\text{CH}$), 8.20 (S, 3H, $\cdot\text{CCH}_3$), 8.86 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$), 9.05-9.17 (fM, 6H, $\cdot\text{C}(\text{CH}_3)_2$).

Mixture

i.r. (film) cm^{-1} : 2050 (s) allene, 1605 (m) C=C aromatic, 780 (m), 720 (m) monosubstitution

m.s. m/e : P=240.186932; Calculated for $\text{C}_{18}\text{H}_{24}$, 240.187792, 240 ($\text{C}_{18}\text{H}_{24}$), 225 (P- CH_3), 183 (P- C_4H_9) base peak, 168 (P- C_5H_{12}), 156 (P- C_6H_{12}).

8.7.7 Z and E 6-(2',3',3'-trimethylbutenylidene)-1-phenylbicyclo[3,1,0]hexane (74a) and (74b)

Starting olefin : 1-phenylcyclopentene

B.P. : 89-90°C/0.01 m.m.

Yield : 65-70%

Isomer ratio : $\text{Z:E} \approx 1.0:1.5$

Z isomer (74a)

n.m.r. $(\text{CCl}_4)_\gamma$: 2.8-3.0 (M, 5H, ArH), 7.7-8.2 (M, 7H, $\cdot\text{CH}_2)_3 + \cdot\text{CH}$), 8.3 (S, 3H, $\cdot\text{CCH}_3$), 9.02 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$)

E isomer (74b)

n.m.r. $(\text{CCl}_4)_\gamma$: 2.8-3.0 (M, 5H, ArH), 7.7-8.2 (M, 7H, $(\cdot\text{CH}_2)_3 + \cdot\text{CH}$), 8.3 (S, 3H, $\cdot\text{CCH}_3$), 8.96 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$)

Mixture (film) cm^{-1} : 2050 (s) allene, 1610 (m) aromatic, 775 (s), 705 (s) monosubstitution

m.s. m/e : P=252.187242; Calculated for $\text{C}_{19}\text{H}_{24}$, 252.187792, 252 ($\text{C}_{19}\text{H}_{24}$), 237 (P- CH_3), 195 (P- C_4H_9) base peak, 168 (P- C_6H_{12}).

8.7.8 Z and E 2-(2',3',3'-trimethylbutenyldiene)-1-phenylcyclopropane
(72a) and (72b)

Starting olefin : styrene

b.p. : 49-51°C/0.01 m.m.

Yield : 65%

Isomer ratio : Z:E 1.0:2.0

Z isomer (72a)

n.m.r. (CCl_4) τ : 2.9 (s, 5H, ArH), 7.14-7.32 (m, 1H, ArCH), 8.0-8.16 (m, 1H, $\cdot\text{CH}$)
 8.26 (s, 3H, $\cdot\text{CCH}_3$), 8.4-8.64 (m, 1H, $\cdot\text{CH}$) 8.98 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$).

E isomer (72b)

n.m.r. (CCl_4) τ : 2.9 (s, 5H, ArH) 7.14-7.32 (m, 1H, ArCH)
 8.0-8.16 (m, 1H, $\cdot\text{CH}$), 8.23 (s, 3H, $\cdot\text{CCH}_3$), 8.4-8.64 (m, 1H, $\cdot\text{CH}$), 8.96 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$)

Mixture

i.r. (film) cm^{-1} : 2010 (s) allene, 1610 (s) C=C aromatic, 700 (s) monosubstitution

m.s. m/e : P=212.155717; Calculated for $\text{C}_{16}\text{H}_{20}$, 212.156493, 212 ($\text{C}_{16}\text{H}_{20}$), 197 (P- CH_3)
 169 (P- C_3H_7), 155 (P- C_4H_9) base peak

8.7.9 Z and E 2-(2',3',3'-trimethylbutenyldene)-trans-1-methyl-3-phenylcyclopropane (73a) and (73b)

Starting olefin	:	<u>trans</u> - β -methylstyrene
b.p.	:	45-46°C/0.01 m.m.
Yield	:	45%
Isomer ratio	:	<u>Z</u> : <u>E</u> 1.0:2.0
<u>Z</u> isomer (73a)		
n.m.r.	(CCl ₄) τ	: 2.8-3.0 (M, 5H, ArH), 7.6 (bd, J=6Hz., 1H, ArCH), 8.24 (s, 3H, :CCH ₃), 8.3 (bM, 1H, $\cdot$ CH), 8.63 (d, J=6Hz., 3H, $\cdot$ CH ₃), 8.95 (s, 9H, $\cdot$ C(CH ₃) ₃).
<u>E</u> isomer (73b)		
n.m.r.	(CCl ₄) τ	: 2.8-3.0 (M, 5H, ArH), 7.6 (bd, J=6Hz., 1H, ArCH), 8.21 (s, 3H, :CCH ₃), 8.3 (bM, 1H, $\cdot$ CH), 8.65 (d, J=6Hz., 3H, CH ₃) 8.94 (s, 9H, $\cdot$ C(CH ₃) ₃).

Mixture

i.r.	(film) cm ⁻¹	: 2010 (s) allene, 1605 (m) C=C aromatic, 810 (m), 700 (s) monosubstitution
m.s.	m/e	: P=226.171633; Calculated for C ₁₇ H ₂₂ , 226.172142, 226 (C ₁₇ H ₂₂), 211 (P-CH ₃) 183 (P-C ₃ H ₇), 169 (P-C ₄ H ₉) base peak

8.8 Preparation and characterisation of 2-(trans-prop-1'-enyl)-propenyldienecyclopropanes

8.8.1 The preparation of these cyclopropanes was carried out using the same method as in section (8.6.1) using trans-3-bromo-3-methyl-hex-4-ene-1-yne (15.75 gm, 0.08 mol.) as carbene precursor. The adducts were characterised by n.m.r. spectra and their molecular formulae confirmed by exact mass measurement of the parent ion (P) in the mass spectrum. All the adducts were stable when stored at -15°C.

8.8.2 Z and E 2,3-benzo-6-[2'-(trans-prop-1"-enyl)propenylidene]bicyclo
[3,1,0]hex-2-ene (99b) and (99a)

Starting olefin : indene
 b.p. : rearranges/decomposes on distillation
 Yield : 25%
 Isomer ratio : Z:E 1.0:1.0.
Z isomer (99b)
 n.m.r. (CCl₄)₂ : 2.6-3.06 (M, 4H, ArH), 4.16 (bd, J=16Hz.,
 1H, H₃CHC:CH), 4.70 (d of q, J=16Hz.,
 J=6.5Hz., 1H, H₃CHC:CH), 6.72-6.86 (M,
 3H, ArCH), 7.34 (bt, J=6Hz., 1H, ·CH),
 8.22 (s, 3H, :CCH₃), 8.27 (d of d,
 J=6.5Hz., J=1.5Hz., 3H, HC:CHCH₃).

E isomer (99a)

n.m.r. (CCl₄)₂ : 2.6-3.06 (M, 4H, ArH), 4.0 (bd, J=16Hz.,
 1H, H₃CHC:CH), 4.64 (d of q, J=16Hz.,
 J=6.5Hz., 1H, H₃CHC:CH), 6.72-6.86 (M,
 3H, ArCH), 7.34 (bt, J=6Hz., 1H, ·CH),
 8.40 (d of d, J=6.5Hz., J=1.5Hz., 3H,
 HC:CHCH₃), 8.38 (s, 3H, :CCH₃).

Mixture

i.r. (film) cm⁻¹ : 2050 (m) allene, 1690 (m) C=C olefinic,
 1610 (m) C=C aromatic, 980 (m) C=CH,
 760 (s) 1,2-disubstitution
 m.s. m/e : P=208.123457; Calculated for C₁₆H₁₆,
 208.123194, 208 (C₁₆H₁₆), 193 (P-CH₃)
 base peak, 178 (P-C₂H₆), 165 (P-C₃H₇)

8.8.3 2-[2'-(trans-prop-1"-enyl)propenylidene]-1,1-diphenylcyclopropane (100)

Starting olefin	:	diphenylethylene
b.p.	:	rearranges/decomposes on distillation
Yield	:	40%
n.m.r.	(CCl ₄) ₂	: 2.5-3.1 (M, 10H, ArH), 3.92 (bd, J=16Hz., 1H, H ₃ CHC:CH), 4.515 (d of q, J=16Hz., J=7Hz., 1H, H ₃ CHC:CH), 7.82 (s, 2H, ·CH ₂), 8.13 (s, 3H, H ₃ C·C:C), 8.215 (d of d, 3H, J=7Hz., J=1.5Hz., 3H, H ₃ CHC:CH)
i.r.	(film) cm ⁻¹	: 2050 (m) allene, 1680 (s) C=C olefinic, 1620 (s) C=C aromatic, 960 (m) C=CH, 780 (s), 700 (s) monosubstitution
m.s.	m/e	: P=272.156444; Calculated for C ₂₁ H ₂₀ , 272.156493, 272 (C ₂₁ H ₂₀) base peak, 257 (P-CH ₃), 242 (P-C ₂ H ₆), 215 (P-C ₄ H ₉).

8.9 Preparation and characterisation of 2'-vinylpropenylidene - cyclopropanes

8.9.1 The preparation of these cyclopropanes was carried out using the same method as in section(8.6.1) using 1-bromo-3-methyl-trans-pent-2-ene-4-yne as carbene precursor (13 gm, 0.08 mol.). The adducts were characterised by i.r. and n.m.r. spectra and their molecular formulae confirmed by exact mass measurement of the parent ion (P) in the mass spectrum. All the adducts were stable when stored at -15°C.

8.9.2 2-(2'-vinylpropenylidene)-1,1-diphenylcyclopropane (103)

Starting olefin	:	diphenylethylene
B.P.	:	rearranges/decomposes on distillation
Yield	:	25-40%
n.m.r.	(CCl ₄) ₂	: 2.66-3.12 (M, 10H, ArH), 3.605 (d of d,

			$J_{\text{trans}}=18\text{Hz.}, J_{\text{cis}}=11\text{Hz.}, 1\text{H}, \underline{\text{HC:CH}_2},$ 4.99, 5.095, (d, d, $J_{\text{trans}}=18\text{Hz.}, J_{\text{cis}}=$ 11Hz., 2H, HC:CH_2), 7.82 (s, 2H, $\cdot\text{CH}_2$), 8.13 (s, 3H, CH_3)
i.r.	(film) cm^{-1}	:	2030 (s) allene, 1620 (s) C=C olefinic, 1580 (m) C=C aromatic, 900 (s) :CH olefinic, 770 (s), 700 (s) mono- substitution
m.s.	m/e	:	P=258.139418; Calculated for $\text{C}_{20}\text{H}_{18}$, 258.140844, 258 ($\text{C}_{20}\text{H}_{18}$) base peak, 243 (P- CH_3), 228 (P- C_2H_6), 215 (P- C_3H_7), 199 (P- C_5H_7).

8.9.3 Z and E 2-(2'-vinylpropenylidene)-1-methyl-1-phenyl-
cyclopropane (101b) and (101a)

Starting olefin	:	α -methyl styrene
B.P.	:	rearranges/decomposes on distillation
Yield	:	46-50%
Isomer ratio	:	<u>Z:E</u> 1.3:1.0
<u>Z</u> isomer (101b)		
n.m.r.	$(\text{CCl}_4)_\tau$	: 2.7-3.06 (M, 5H, ArH), 3.635 (d of d, $J_{\text{cis}}=11\text{Hz.}, J_{\text{trans}}=18\text{Hz.}, \underline{\text{HC:CH}_2}$), 5.02, 5.11 (bd, bd, $J_{\text{cis}}=11\text{Hz.}, J_{\text{trans}}=18\text{Hz.},$ 2H, HC:CH_2), 8.14 (s, 3H, $:\text{CCH}_3$), 8.24 (s, 2H, $\cdot\text{CH}_2$), 8.41 (s, 3H, $\cdot\text{CH}_3$)
<u>E</u> isomer (101a)		
n.m.r.	$(\text{CCl}_4)_\tau$	: 2.7-3.06 (M, 5H, ArH), 3.645 (d of d, $J_{\text{cis}}=11\text{Hz.}, J_{\text{trans}}=18\text{Hz.}, \underline{\text{HC:CH}_2}$), 5.02, 5.11 (bd, bd, $J_{\text{cis}}=11\text{Hz.}, J_{\text{trans}}=18\text{Hz.},$ 2H, HC:CH_2), 8.15 (s, 3H, $:\text{CCH}_3$), 8.24

(s, 2H, $\cdot\text{CH}_2$), 8.42 (s, 3H, $\cdot\text{CH}_3$).

Mixture

i.r. (film) cm^{-1} : 2020 (m) allene, 1630 (w) C=C olefinic, 1600 (m) C=C aromatic, 900 (s) :CH olefinic, 770 (s), 700 (s) mono-substitution.

m.s. m/e : P=196.125148; Calculated for $\text{C}_{15}\text{H}_{16}$, 196.125194, 196 ($\text{C}_{15}\text{H}_{16}$), 181 (P- CH_3) base peak, 166 (P- C_2H_6), 165 (P- C_2H_7).

8.9.4 Z and E -6-(2'-vinylpropenylidene)-1-phenylbicyclo[3,1,0]hexane
(102b) and (102a)

Starting olefin : 1-phenylcyclopentene

B.P. : rearranges/decomposes on distillation

Yield : 30%

Isomer ratio : Z:E 1.5:1.0

Z isomer (102b)

n.m.r. (CCl_4)₂ : 2.7-3.0 (M, 5H, ArH), 3.695 (d of d, $J_{\text{cis}}=10\text{Hz.}$, $J_{\text{trans}}=17\text{Hz.}$, 1H, HC:CH_2) 5.065, 5.145 (bd, bd, $J=17\text{Hz.}$, $J=10\text{Hz.}$, 2H, HC:CH_2), 7.6-8.1 (M, 7H, $(\cdot\text{CH}_2)_3^+$ $\cdot\text{CH}$), 8.16 (s, 3H, $:\text{CCH}_3$).

E isomer (102a)

n.m.r. (CCl_4)₂ : 2.7-3.0 (M, 5H, ArH), 3.705 (d of d, $J_{\text{cis}}=10\text{Hz.}$, $J_{\text{trans}}=17\text{Hz.}$, 1H, HC:CH_2), 5.065, 5.145 (bd, bd, $J=17\text{Hz.}$, $J=10\text{Hz.}$, 2H, HC:CH_2), 7.6-8.1 (M, 7H, $(\cdot\text{CH}_2)_3^+$ $\cdot\text{CH}$), 8.18 (s, 3H, $:\text{CCH}_3$).

Mixture

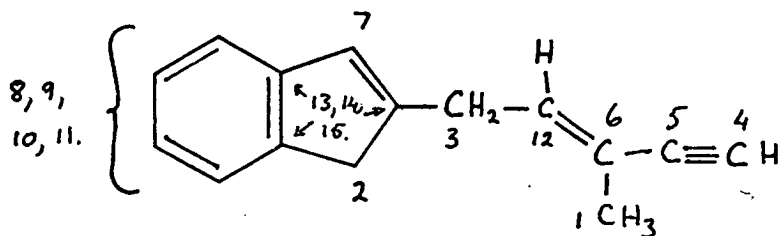
i.r. (film) cm^{-1} : 2010 (m) allene, 1600 (m) C=C aromatic,

900 (m) :CH olefinic, 760 (s), 700 (m)
monosubstitution

m.s. m/e : P=222.140984; Calculated for $C_{17}H_{18}$,
222.140844, 222 ($C_{17}H_{18}$), 207 (P- CH_3),
179 (P- C_3H_7) base peak, 178 (P- C_3H_8),
165 (P- C_4H_9), 104 (P- C_9H_{10}).

8.9.5 E-2-(-3'-methylpent-2'-ene-4'-ynyl)-indene (104)

Starting olefin : indene
M.P. : 40-40.5° (light petroleum)
Yield : 20-30%
n.m.r. (CCl_4) : 2.62-3.06 (M, 4H, ArH) 3.88 (M, 1H, ArCH), 4.14 (bt, J=7Hz., 1H, C:CH), 6.525 (bd, J=7Hz., 2H, $\cdot CH_2$), 6.76 (bs, 2H, ArCH $_2$), 6.97 (s, 1H, :CH), 8.12 (d, J=2Hz., 3H, :CCH $_3$).
i.r. (film) cm^{-1} : 3350 (s) C $\equiv$ CH, 2130 (w) C $\equiv$ C, 1630 (m) C=C olefinic, 1605 C=C aromatic, 1480 (m) -CH $_2$ -, 790 (m) :CH olefinic, 720 (m) 1,2-disubstitution
m.s. m/e : P=194.108918; Calculated for $C_{15}H_{14}$
194.109545, 194 ($C_{15}H_{14}$), 179 (P- CH_3) base peak, 105 (P- C_7H_5).



<u>No.</u>	<u>No. of Atoms</u>	<u>Type of Atom</u>	<u>Chemical Shift (δ)</u>
1	1	$\underline{\text{CH}}_3$	22.8
2	1	$\underline{\text{CH}}_2$ (indene)	29.5
3	1	$\underline{\text{CH}}_2$	37.7
4	1	$\equiv\text{CH}$	81.5
5	1	$\equiv\text{C}$	82.9
6	1	$=\text{C}$	118.5
7	1	$=\text{CH}$ (indene)	119.2
8	1	$\text{Ar}\underline{\text{CH}}$	123.7
9	1	$\text{Ar}\underline{\text{CH}}$	124.6
10	1	$\text{Ar}\underline{\text{CH}}$	126.1
11	1	$\text{Ar}\underline{\text{CH}}$	128.5
12	1	$=\underline{\text{CH}}$	136.2
13	1	$\underline{\text{C}}$	142.3
14	1	$\underline{\text{C}}$	144.4
15	1	$\underline{\text{C}}$	145.0

8.9.6 Addition of 12-vinylpropenylidenecarbene to the following olefins gave no addition products, olefin only being recovered. trans-stilbene, 3-phenylindene.

8.10 Rearrangement of Adducts

General Procedures

8.10.1 Thermal rearrangement in the vapour phase

The two types of flow system used are illustrated Figure (XXI) and Figure (XXII).

The system A was used for the pyrolysis of all adducts. The compound to be pyrolysed was introduced into the sample vessel (a) and the system evacuated by means of a rotary oil pump at (g), the trap (f) was then immersed in a Dewar of liquid nitrogen. The pyrolysis tube, (d) (230 m.m. x 25 m.m. I.D., pyrex for temperatures $\leq 500^\circ\text{C}$ and quartz for temperatures $> 500^\circ\text{C}$) which was packed with glass wool, was allowed to equilibrate (ca. $\frac{1}{2}$ hr.) at the required temperature by means of a precalibrated electrically heated jacket (c). Another Dewar of liquid nitrogen was placed round

the receiver (e) and the sample slowly distilled through the pyrolysis tube using an electric heater (b), the product condensing in the receiver (e). After pyrolysis was complete, nitrogen was allowed into the system via (g) and the product, pale yellow in colour, isolated for examination.

The system B was used in the study of the phenylcyclopentene adduct when different sizes of pyrolysis tube were desired. The operation of this system was identical to that of system A, the pyrolysis tube's dimensions being 110 m.m. x 5 m.m. I.D..

8.10.2 Thermal rearrangement in solution

A solution of the purified adduct, in a tenfold dilution of suitable solvent was boiled under reflux in an atmosphere of nitrogen. Removal of the solvent under reduced pressure gave the crude product. Prolonged heating of the neat adduct gave low yields of polymeric material.

8.10.3 Acid catalysed rearrangements

A solution of 10% methanolic hydrochloric acid was prepared by a two fold dilution of concentrated hydrochloric acid with methanol. The adduct and 10% methanolic hydrochloric acid (50 ml/1 gm) were refluxed for 5 minutes. The solution was poured onto water (100 mls/ 1 gm adduct) and extracted with light petroleum (3x50 ml). The combined extracts were washed with water, dried and the solvent removed to give the crude product.

8.10.4 Examination and isolation of products

The crude products were examined by g.l.c., i.r. and n.m.r., purified as necessary and separated where possible. Molecular formulae were confirmed from the mass spectrum and exact mass measurement. All compounds were stored at -15°C . Ratios are quoted to an accuracy of ± 0.1 .

8.11 Rearrangement of dimethylvinylidenecyclopropanes

8.11.1 Rearrangement of phenylcyclopentene adduct (36)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-phenylbicyclo[3,1,0]hexane (0.5 gm, 2.5 m mol) was pyrolysed in flow system A (450°, 0.01 m.m.). The rearrangement product (0.4 gm, 80%), purified by alumina chromatography, was identified as a mixture of 9-isopropenyl-1,2,3,4-tetrahydrofluorene (37a) and the isomeric compound 9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (37b). The ratio of (37a) to (37b) was found from n.m.r. to be 2.3:1.0, taken over two separate rearrangements. Separation of the two isomers was unsuccessful using t.l.c. Preparative g.l.c. (10% P.M.P.E., 190°, 2 metre column) gave only partial separation nevertheless this allowed confirmation of the n.m.r. data of the two isomers.

9-isopropenyl-1,2,3,4-tetrahydrofluorene (37a)

n.m.r. (CCl₄)₂ : 2.90 (M, 4H, ArH), 4.95, 5.05 (fM, fM, 2H, :CH₂), 6.14 (bs, 1H, ·CH), 7.5-7.7, 7.7-7.9 (M, M, 4H, ·C(1)H₂+·C(4)H₂), 8.1-8.3 (M, 4H, ·C(2)H₂+C(3)H₂), 8.86 (d, J=1Hz., 3H, ·CH₃).

9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (37b)

n.m.r. (CCl₄)₂ : 2.90 (M, 4H, ArH), 4.8, 5.08 (fM, fM, 2H, :CH₂), 7.03 (d of d, J=12Hz., J=6Hz., 1H, ·CH), 7.5-7.7, 7.7-7.9 (M, M, 4H, ·C(1)H₂+·C(4)H₂), 7.96 (M, 3H, ·CH₃), 8.1-8.3 (M, 4H, ·C(2)H₂+·C(3)H₂).

Mixture of isomers

i.r. (film) cm⁻¹ : 1640 (m) C=C olefinic, 1600 (m) C=C aromatic, 1460 (m) -CH₂-, 905 (m) :CH₂, 760 (s) 1,2-disubstitution

TABLE II

Flow system <u>A</u> or <u>B</u>	Temperature	Packing L, N or T	Isomer ratio (37a) : (37b)
<u>A</u>	500°	N	2.3:1.0
<u>A</u>	600°	N	2.1:1.0
<u>A</u>	450°	T	2.3:1.0
<u>A</u>	350°	T	2.3:1.0
<u>A</u>	450°	L	2.3:1.0
<u>A</u>	350°	L	3.1:1.0
<u>B</u>	450°	N	3.0-3.2:1.0
<u>A</u>	350°	N	2.6:1.0
<u>A</u>	450°	N	2.3:1.0

TABLE III

Original Flow system <u>A</u> or <u>B</u>	Original Isomer ratio (37a):(37b)	Recycled through Flow System <u>A</u> or <u>B</u>	Final isomer ratio (37a):(37b)
<u>A</u>	2.3:1.0	<u>A</u>	2.3:1.0
<u>B</u>	3.0-3.2:1.0	<u>B</u>	2.9:1.0
<u>A</u>	2.3:1.0	<u>B</u>	2.3:1.0
<u>B</u>	3.0-3.2:1.0	<u>A</u>	2.3:1.0

m.s. m/e : P=210.14117, Calculated for $C_{16}H_{18}$,
 210.14084, 210 ($C_{16}H_{18}$) base peak,
 195 (P- CH_3), 167 (P- C_3H_7).

b) The following series of rearrangements were carried out on the adduct using (0.5 gm. 2.5 m mol.) samples. Conditions of temperature, pyrolysis tube packing, and flow system were varied as stated. The products obtained in every case were the same as those found in a), the ratios only differing. The pressure at all times was 0.01 m.m. Normally (N) the pyrolysis tube was packed with glass wool (ca. 12 gm), in the case of loose packing (L) glass wool (ca. 6 gm) was used and in the case of tight packing (T) glass wool (ca. 18 gm) was used. The results are summarised in Table II.

c) The following series of experiments were carried out on the rearrangement products obtained in section b). The products of rearrangement at 450° from flow systems A and B were recycled at 450° . All rearrangements were carried out with normal packing in the pyrolysis tube. Details are given in Table III.

Rearrangement in solution

a) The adduct (0.3 gm, 1.5 m mol) was dissolved in Analar carbon tetrachloride and refluxed for 8 hrs. The solvent was removed and the product examined by n.m.r., i.r. and g.l.c. These showed that only unchanged adduct was present.

b) The adduct (0.3 gm, 1.5 m mol) was dissolved in sodium dried toluene and refluxed for 8 hrs. The solvent was removed and the product examined by n.m.r. This again showed only unchanged adduct.

c) The adduct (0.3 gm, 1.5 m mol) was dissolved in sodium dried 1,1,2,2-tetrachloroethane and refluxed for 4 hrs. The solvent was removed and the product identified by n.m.r. as a mixture of 2-isobutylbiphenyl (39c R=H) and 2-(2'-methylprop-1'-enyl)biphenyl (39e, R=H) in equal amounts.

This result was confirmed by preparative g.l.c. (25% P.M.P.E., 180°, 5 metre column), the two products being separated and identified by their characteristic n.m.r. absorptions⁸⁵.

2-isobutyl biphenyl (39c, R=H)

n.m.r. (CCl₄)_τ : 2.6-2.9 (M, 9H, ArH), 7.56 (d, J=7Hz., 2H, •CH₂), 8.2-8.6 (M, 1H, •CH), 9.3 (d, J=7Hz., 6H, •C(CH₃)₂)

2-(2'-methylprop-1'-enyl)biphenyl (39e, R=H)

n.m.r. (CCl₄)_τ : 2.7-2.9 (M, 9H, ArH), 4.2 (bs, 1H, :CH), 8.26, 8.3 (d,d, J=1.5Hz., 6H, :C(CH₃)₂).

d) The adduct (0.5 gm, 2.5 m mol) was dissolved in sodium dried 1,1,2,2-tetrachloromethane and transferred to a glass tube. The contents of the tube were degassed and the tube sealed under vacuum. The tube was placed in a bath of refluxing 1,1,2,2-tetrachloroethane for 4 hrs. The tube was then removed, opened, the solvent removed and the product examined by n.m.r. The product consisted of a mixture of 2-isobutyl biphenyl and 2-(2'-methylprop-1'-enyl)biphenyl in the ratio 9.0 to 1.0

Rearrangement on a g.l.c. column

a) The adduct (0.5 gm, 2.5 m mol) was dissolved in acetone (5 mls) and passed through the preparative g.l.c. (25% P.M.P.E., 200°, 5 metre column). The product was collected, the solvent removed and examined by n.m.r. The product was identified as a mixture of six components identifiable by their characteristic n.m.r. spectra⁸⁵ as, 2-(2'-methylprop-1'-enyl)-1-phenylcyclohexa-1,3-diene (39a, R=H), 2-(2'-methylprop-1'-enyl)-3-phenylcyclohexa-1,3-diene (39b, R=H), 2-(2'-methylprop-1'-enyl)biphenyl (39e, R=H), 2-isobutylbiphenyl (39c, R=H) and the two tetrahydrofluorenes (37a) and (37b). The ratio of the product was as follows, 4.0:4.0:3.0:1.0:1.0:traces, on a column which had been used over a period of time, and altered to 1.5:1.5:1.0:1.0:traces:traces on a column which was freshly prepared.

2-(2'-methylprop-1'-enyl)-1-phenylcyclohexa-1,3-diene (39a, R=H) and
2-(2'-methylprop-1'-enyl)-3-phenylcyclohexa-1,3-diene (39b, R=H) mixture.

n.m.r. $(\text{CCl}_4)_2$: 2.6-3.06 (M, 10H, ArH), 3.9-4.4 (M, 6H, :CH), 7.4-7.9 (M, 8H, :CH_2), 8.34-8.36, 8.45, 8.50 (s, s, s, s, 12H, $\text{:C(CH}_3)_2$).

8.11.2 Rearrangement of 2-tolylcyclopentene adduct (41, R=CH₃)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-(2-tolyl)bicyclo[3,1,0]hexane (0.5 gm, 2.2 mmol) was pyrolysed in flow system A (450°C, 0.01 m.m.). The rearrangement product (0.4 gm, 80%), purified by alumina chromatography, was identified as a mixture of 5-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (42a, R=CH₃) and the isomeric compound 5-methyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (42b, R=CH₃). The ratio of (42a, R=CH₃) to (42b, R=CH₃) was found from n.m.r. to be 1.0:1.54: taken over two separate rearrangements. Separation of the two isomers was unsuccessful using t.l.c. and preparative g.l.c. (25% P.M.P.E., 10% P.M.P.E., 20% N.P.G.S.).

5-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (42a, R=CH₃)

n.m.r. $(\text{CCl}_4)_2$: 2.9-3.3 (M, 3H, ArH), 4.97, 5.14 (fm, fm, 2H, :CH_2), 6.32 (bs, 1H, :CH), 7.2-7.35, 7.7-7.9 (M, M, 4H, $\text{:C(1)H}_2 + \text{:C(4)H}_2$), 7.57 (s, 3H, ArCH_3), 8.18-8.36 (M, 4H, $\text{:C(2)H}_2 + \text{:C(3)H}_2$), 8.87 (s, 3H, :CH_3)

5-methyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (42b, R=CH₃)

n.m.r. $(\text{CCl}_4)_2$: 2.9-3.3 (M, 3H, ArH), 4.82, 5.13 (fm, fm, 2H, :CH_2), 6.99 (d of d, J=12Hz., J=6Hz., 1H, :CH), 7.2-7.35, 7.7-7.9 (M, M, 4H,

$\cdot\text{C}(1)\underline{\text{H}}_2 + \cdot\text{C}(4)\underline{\text{H}}_2$), 7.66 (s, 3H, ArCH_3), 8.0 (s, 3H, $\cdot\text{CH}_3$), 8.18-8.36 (m, 4H, $\cdot\text{C}(2)\underline{\text{H}}_2 + \cdot\text{C}(3)\underline{\text{H}}_2$).

Mixture of isomers

i.r. (film) cm^{-1} : 1650 (m) C=C olefinic, 1600 (m) C=C aromatic, 1460 (s) $-\text{CH}_2-$, 910 (m) $:\text{CH}_2$, 765 (s) 1,2,3-trisubstitution

m.s. m/e : P=224.156308; Calculated for $\text{C}_{17}\text{H}_{20}$, 224.156493, 224 ($\text{C}_{17}\text{H}_{20}$) base peak, 209 (P- CH_3), 181 (P- C_3H_7).

8.11.3 Rearrangement of 2-methoxyphenylcyclopentene adduct (41, R=CH₃O)
Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-(2-methoxyphenyl)bicyclo [3,1,0] hexane (0.5 gm, 2.1 m mol) was pyrolysed in flow system A (450°C, 0.01 m.m.) The rearrangement product (0.45 gm, 90%), purified by alumina chromatography, was identified as a mixture of 5-methoxy-9-isopropenyl-1,2,3,4-tetrahydrofluorene (42a, R=CH₃O) and the isomeric compound 5-methoxy-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (42b, R=CH₃O). The ratio of (42a, R=CH₃O) to (42b, R=CH₃O) was found from n.m.r. to be 1.0:1.0 taken over two separate rearrangements. Separation of the two isomers was unsuccessful using t.l.c. and preparative g.l.c. (10% P.M.P.E., 180°, 2 metre column) gave poor separation. Changing the column packing and/or conditions did not assist in the separation. The n.m.r. data of each isomer was however confirmed.

5-methoxy-9-isopropenyl-1,2,3,4-tetrahydrofluorene (42a, R=CH₃O)

n.m.r. (CCl_4) τ : 2.86-3.54 (m, 3H, ArH), 5.0, 5.1 (fm, fm, 2H, $:\text{CH}_2$), 6.29 (bs, 1H, $\cdot\text{CH}$), 6.25 (s, 3H, OCH_3), 7.1-7.4, 7.7-7.92 (m, m, 4H, $\cdot\text{C}(1)\underline{\text{H}}_2 + \cdot\text{C}(4)\underline{\text{H}}_2$), 8.18-8.36 (m, 4H, $\cdot\text{C}(2)\underline{\text{H}}_2 + \cdot\text{C}(3)\underline{\text{H}}_2$), 8.86 (s, 3H, $\cdot\text{CH}_3$)

5-methoxy-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (42b, R=CH₃O)

n.m.r. (CCl₄) τ : 2.86-3.54 (M, 3H, ArH), 4.85, 5.14
(fM, fM, 2H, :CH₂), 6.22 (S, 3H, OCH₃),
6.92 (d of d, J=12Hz., J=6Hz., 1H, ·CH),
7.1-7.4, 7.7-7.92 (M, M, 4H, ·C(1)H₂+
·C(4)H₂), 8.0 (S, 3H, ·CH₃), 8.18-
8.36 (M, 4H ·C(2)H₂+·C(3)H₂)

Mixture of isomers

i.r. (film) cm⁻¹ : 1650 (s) C=C olefinic, 1610 (s) C=C
aromatic, 1480 (s) -CH₂-, 1280 (s)
C-O, 910 (s) :CH₂, 750 (s), 1,2,3-
trisubstitution

m.s. m/e : P=240.152515; Calculated for C₁₇H₂₀O⁰
240.151407, 240 (C₁₇H₂₀O) base peak,
225 (P-CH₃), 197 (P-C₃H₇)

8.11.4 Rearrangement of 4-tolylcyclopentene adduct (38, R=CH₃)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-(4-tolyl)bicyclo[3,1,0]
hexane (0.5 gm, 2.2 mmol) was pyrolysed in flow system A (450°, 0.01 m.m.).
The rearrangement product (0.4 gm, 80%), purified by alumina chromatography,
was identified as a mixture of 7-methyl-9-isopropenyl-1,2,3,4-tetrahydro-
fluorene (40a, R=CH₃) and the isomeric compound 7-methyl-9-isopropenyl-
1,2,3,4-tetrahydro-4aH-fluorene (40b, R=CH₃). The ratio of (40a, R=CH₃)
to (40b, R=CH₃) was found from n.m.r. to be 2.0:1.0 taken over two
rearrangements. Separation of the two isomers was unsuccessful by both
preparative t.l.c. and preparative g.l.c. (various columns and conditions)
7-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (40a, R=CH₃)

n.m.r. (CCl₄) τ : 2.5-3.2 (M, 3H, ArH), 5.0, 5.08 (fM,
fM, 2H, :CH₂), 6.3 (bS, 1H, ·CH), 7.5-
7.9 (M, 4H, ·C(1)H₂+·C(4)H₂), 7.69 (S,

3H, ArCH₃), 8.18-8.4 (M, 4H,
 •C(2)H₂+•C(3)H₂), 8.86 (s, 3H,
 •CH₃).

7-methyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (40b, R=CH₃)

n.m.r. (CCl₄)₂ : 2.5-3.2 (M, 3H, ArH), 4.82, 5.12 (fM,
 fM, 2H, :CH₂), 7.07 (d of d, J=12Hz.,
 J=6Hz., 1H, •CH), 7.5-7.9 (M, 4H,
 •C(1)H₂+•C(4)H₂), 7.72 (s, 3H, ArCH₃),
 7.98 (s, 3H, •CH₃), 8.18-8.4 (M, 4H,
 •C(2)H₂+•C(3)H₂)

Mixture of isomers : 1650 (m) C=C olefinic, 1610 (m) C=C
 aromatic, 1460 (s) -CH₂-, 910 (m)
 :CH₂, 770 (m) 1,2,4-trisubstitution

m.s. m/e : P=224.156527; Calculated for C₁₇H₂₀,
 224.156493, 224 (C₁₇H₂₀), 209 (P-CH₃),
 181 (P-C₃H₇).

8.11.5 Rearrangement of 4-fluorophenylcyclopentene adduct (38, R=F)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-(4-fluorophenyl)bicyclo
 [3,1,0] hexane (0.5 gm, 2.2 m mol), was pyrolysed in flow system A (450°,
 0.01 m.m.) The rearrangement product (0.45 gm, 90%), purified by alumina
 chromatography, was identified as a mixture of 7-fluoro-9-isopropenyl-1,2,
 3,4-tetrahydrofluorene (40a, R=F) and the isomeric compound 7-fluoro-9-
 isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (40b, R=F). The ratio of (40a,
 R=F) to (40b, R=F) was found from n.m.r. to be 1.9:1.0 taken over two
 rearrangements. Separation of the two isomers was achieved by preparative
 g.l.c. (10% P.M.P.E., 180°, 2 metre column).

7-fluoro-9-isopropenyl-1,2,3,4-tetrahydrofluorene (40a, R=F)

n.m.r. (CCl₄)₂ : 3.02-3.24 (M, 3H, ArH), 4.97, 5.05

i.r.	(CCl ₄) cm ⁻¹	(fm, fm, 2H, :CH ₂), 6.26 (bs, 1H, CH), 7.5-7.7, 7.7-7.94 (M, ~~M~~ , 4H, C(1)H ₂ +C(4)H ₂), 8.16-8.36 (M, 4H, C(2)H ₂ +C(3)H ₂), 8.85 (s, 3H, CH ₃) : 1650 (m) C=C olefinic, 1615 (m) C=C aromatic, 1480 (s) -CH ₂ -, 1260 (m) C-F aromatic, 940 (m) 1,2,4-trisubstitution
m.s.	m/e	: P=228.131554; Calculated for C ₁₆ H ₁₇ F, 228.131421, 228 (C ₁₆ H ₁₇ F) base peak, 213 (P-CH ₃), 199 (P-C ₂ H ₅), 187 (P-C ₃ H ₅), 185 (P-C ₃ H ₇), 183 (P-C ₃ H ₉), 159 (P-C ₅ H ₉).
7-fluoro-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (4Ob, R=F)		
n.m.r.	(CCl ₄) ₂	: 2.8-3.4 (M, 3H, ArH), 4.8, 5.12 (fm, fm, 2H, :CH ₂), 7.11 (d of d, J=12Hz., J=6Hz., 1H, CH), 7.4-7.9 (M, 4H, C(1)H ₂ +C(4)H ₂), 7.98 (s, 3H, CH ₃), 8.0-8.3 (M, 4H, C(2)H ₂ +C(3)H ₂).
i.r.	(CCl ₄) cm ⁻¹	: 1640 (m) C=C olefinic, 1610 C=C aromatic, 1480 (m) -CH ₂ -, 1260 (s) C-F aromatic, 935 (w) 1,2,4-trisubstitution
m.s.	m/e	: P=228.131554; Calculated for C ₁₆ H ₁₇ F, 228.131421, 228 (C ₁₆ H ₁₇ F), 213 (P-CH ₃), 198 (P-C ₂ H ₆), 185 (P-C ₃ H ₇), 184 (P-C ₃ H ₈), 183 (P-C ₃ H ₉), 159 (P-C ₅ H ₉).

8.11.6 Rearrangement of 3-*t*-butylphenylcyclopentene adduct (47, R=Bu^t)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-(3-*tert*-butylphenyl)-bicyclo[3,1,0]hexane (0.5 gm, 1.8 m mol) was pyrolysed in flow system A (450°, 0.01 m.m.). The rearrangement product (0.44 gms, 88%), purified by alumina chromatography, was identified as a mixture of three isomeric tetrahydrofluorenes, 6-*tert*-butyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (48a, R=Bu^t), 8-*tert*-butyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (49a, R=Bu^t) and 6-*tert*-butyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (48b, R=Bu^t). The ratio of the three isomers (48a, R=Bu^t):(49a, R=Bu^t):(49b, R=Bu^t) was found from n.m.r. to be 2.6:0.67:1.0, taken over two separate rearrangements. The three isomers were partially separated using preparative g.l.c. (10% P.M.P.E., 180°, 2-metre column), allowing identification of each isomer from its n.m.r. spectrum.

6-*tert*-butyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (48a, R=Bu^t)

n.m.r. (CCl₄)₂ : 2.7-2.9 (M, 1H, ArH), 2.96 (S, 2H, ArH), 4.98, 5.09 (fM, fM, 2H, :CH₂), 6.28 (bS, 1H, ·CH), 7.46-7.68, 7.68-7.90 (M, 4H, ·C(1)H₂+·C(4)H₂), 8.12-8.30 (M, 4H, ·C(2)H₂+·C(3)H₂), 8.68 (S, 9H, ·C(CH₃)₃), 8.84 (d, J=1Hz., 3H, ·CH₃).

8-*tert*-butyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (49a, R=Bu^t)

n.m.r. (CCl₄)₂ : 2.74 (S, 1H, ArH), 2.94 (S, 2H, ArH), 4.9-5.04 (M, 2H, :CH₂), 5.9 (bS, 1H, ·CH), 7.5-7.72, 7.72-7.9 (M, M, 4H, ·C(1)H₂+·C(4)H₂), 8.1-8.28 (M, 4H, ·C(2)H₂+·C(3)H₂), 8.62 (S, 9H, ·C(CH₃)₃), 8.97 (S, 3H, ·CH₃).

6-tert-butyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (48b, R=Bu^t)

n.m.r. (CCl₄)_γ : 2.8 (s, 1H, ArH), 2.9 (s, 2H, ArH), 4.84, 5.15 (fm, fm, 2H, :CH₂), 7.035 (d of d, J=11Hz., J=6Hz., 1H, ·CH) 7.5-7.72, 7.72-7.9 (M, M, 4H, ·C(1)H₂+ ·C(4)H₂) 7.97 (s, 3H, ·CH₃), 8.1-8.28 (M, 4H, ·C(2)H₂+·C(3)H₂), 8.67 (s, 9H, ·C(CH₃)₃).

Mixture of isomers

i.r. (film) cm⁻¹ : 1645 (s) C=C olefinic, 1615 (s) C=C aromatic, 1480 (s) -CH₂-, 885 (s) 1,2,4-trisubstitution, 780 (m) 1,2,4- and 1,2,3-trisubstitution.

m.s. m/e : P=266.203007; Calculated for C₂₀H₂₆, 266.203441, 266 (C₂₀H₂₆), 251 (P-CH₃) base peak, 209 (P-C₄H₉).

8.11.7 Rearrangement of 3-methylphenylcyclopentene adduct (47, R=CH₃)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-(3-methylphenyl)bicyclo [3,1,0] hexane (0.5 gm, 2.2 m mol) was pyrolysed in flow system A (450°, 0.01 m.m.). The rearrangement product (0.41 gms, 82%), purified by alumina chromatography, was identified as a mixture of three isomeric tetrahydrofluorenes; 6-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (48a, R=CH₃) 8-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (49a, R=CH₃) and 6-methyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (48b, R=CH₃). The ratio of the three isomers (48a, R=CH₃):(49a, R=CH₃):(48b, R=CH₃) was 3.7:1.4 :1.0 taken over two separate rearrangements. The three isomers were not separable by preparative methods which made identification of the three isomers difficult.

6-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (48a, R=CH₃)

n.m.r. (CCl₄)₂ : 2.8-3.34 (M, 3H, ArH), 4.94, 5.02, (fM, fM, 2H, :CH₂), 6.21 (bS, 1H, CH), 7.46-7.94, (M, 4H, C(1)H₂+C(4)H₂), 7.68 (S, 3H, ArCH₃), 8.04-8.40 (M, 4H, C(2)H₂+C(3)H₂), 8.91 (fM, 3H, :CCH₃)

8-methyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (49a, R=CH₃)

n.m.r. (CCl₄)₂ : 2.8-3.34 (M, 3H, ArH), 4.86, 5.10 (fM, fM, 2H, :CH₂), 6.28 (bS, 1H, CH), 7.46-7.94 (M, 4H, C(1)H₂+C(4)H₂), 7.77 (S, 3H, ArCH₃), 8.04-8.40 (M, 4H, C(2)H₂+C(3)H₂), 8.89 (fM, 3H, :CCH₃).

6-methyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (48b, R=CH₃)

n.m.r. (CCl₄)₂ : 2.8-3.34 (M, 3H, ArH), 5.04, 5.16 (fM, fM, 2H, :CH₂), 7.46-7.94 (M, 4H, C(1)H₂+C(4)H₂); 7.98 (fM, 3H, :CCH₃), 8.04-8.40 (M, 4H, C(2)H₂+C(3)H₂).

Mixture

i.r. (film) cm⁻¹ : 1640 (m) C=C olefinic, 1600 (w) C=C aromatic, 1450 (s) -CH₂-, 880 (s) 1,2,4-trisubstitution, 780 (s) 1,2,3- and 1,2,4-trisubstitution

m.s. m/e : P=224.156965; Calculated for 224.156493, 224 (C₁₇H₂₀) base peak, 209 (P-CH₃), 183 (P-C₃H₅), 181 (P-C₃H₇).

8.11.8 Rearrangement of 3-trifluoromethylphenylcyclopentene adduct (47,

R=CF₃)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-(3-trifluoromethylphenyl)

bicyclo[3,1,0]hexane (0.5 gm., 1.8 m mol) was pyrolysed in flow system A (450°, 0.01 m.m.). The rearrangement product (0.38 gm, 76%), purified by alumina chromatography, was identified as a mixture of three isomeric components in the ratio 1.6:1.75:1.0, 6-trifluoromethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (48a, R=CF₃), 8-trifluoromethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (49a, R=CF₃), 6-trifluoromethyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (48b, R=CF₃). The three isomers were partially separated by preparative g.l.c. (10% P.M.P.E. at 160°, 2 metre column), allowing identification of each isomer by its n.m.r. spectrum.

6-trifluoromethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (48a, R=CF₃)

n.m.r. (CCl₄)₂ : 2.6 (M, 1H, ArH), 2.7 (S, 2H, ArH), 4.92, 5.02 (fM, fM, 2H, :CH₂), 6.18 (bS, 1H, ·CH₂), 7.44-7.66, 7.66-7.88 (M, M, 4H, ·C(1)H₂+C(4)H₂), 8.1-8.3 (M, 4H, ·C(2)H₂+·C(3)H₂), 8.86 (d, J=1Hz., 3H, ·CH₃).

8-trifluoromethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (49a, R=CF₃)

n.m.r. (CCl₄)₂ : 2.62-2.82 (M, 3H, ArH), 4.95, 5.00 (fM, fM, 2H, :CH₂), 5.91 (bS, 1H, ·CH), 7.46-7.66, 7.66-7.86 (M, M, 4H, ·C(1)H₂+·C(4)H₂), 8.06-8.3 (M, 4H, ·C(2)H₂+·C(3)H₂), 8.9 (d, J=1Hz., 3H, ·CH₃).

6-trifluoromethyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (48b, R=CF₃)

n.m.r. (CCl₄)₂ : 2.46-2.82 (M, 3H, ArH), 4.78, 5.12 (fM, fM, 2H, :CH₂), 6.945 (d of d, J=13Hz., J=6Hz., 1H, ·CH), 7.44-7.66, 7.66-7.9 (M, M, 4H, ·C(1)H₂+·C(4)H₂), 7.99 (d, J=1Hz., 3H, ·CH₃), 8.04-8.3 (M, 4H, ·C(2)H₂+·C(3)H₂).

Mixture of isomers:

i.r. (film) cm⁻¹ : 1625 (m) C=C olefinic, 1620 (m) C=C

olefinic, 1450 (s) $\text{-CH}_2\text{-}$, 1340 (s) -CF_3 ,
1170 (s) C-F, 1140 (s) C-F, 900 (m) 1,2,4-
trisubstitution, 800 (s) 1,2,3- and
1,2,4-trisubstitution.

m.s. m/e : P=278.127833; Calculated for $\text{C}_{17}\text{H}_{17}\text{F}_3$,
278.127225, 278 ($\text{C}_{17}\text{H}_{17}\text{F}_3$), 263 (P- CH_3)
base peak, 235 (P- C_3H_7), 209 (P- CF_3).

8.11.9 Rearrangement of pentadeuterophenylcyclopentene adduct (53)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-(pentadeuterophenyl)bicyclo
[3,1,0] hexane (0.5 gm, 2.5 m mol) was pyrolysed in flow system A (450° , 0.01
m.m.). The rearrangement product (0.42 gms, 84%), purified by preparative
t.l.c. (light petroleum), was identified as a mixture of 5,6,7,8,9-penta-
deutero-9-isopropenyl-1,2,3,4-tetrahydrofluorene (54a) and 4a,5,6,7,8-penta-
deutero-9-isopropenyl-1,2,3,4-tetrahydrofluorene (54b) in the ratio 2.3:1.0.
The isomers were not separable by t.l.c. or by preparative g.l.c. (various
columns and conditions)

5,6,7,8,9-pentadeutero-9-isopropenyl-1,2,3,4-tetrahydrofluorene (54a)

n.m.r. (CCl_4)₂ : 4.97, 5.06 (fM, fM, 2H, :CH_2), 7.46-7.71,
7.71-7.92 (M, M, 4H, $\text{:C(1)H}_2 + \text{:C(4)H}_2$)
8.14-8.34 (M, 4H, $\text{:C(2)H}_2 + \text{:C(3)H}_2$), 8.86
(d, $J=1\text{Hz.}$, 3H, :CH_3).

4a,5,6,7,8-tetradutero-9-isopropenyl-1,2,3,4-tetrahydrofluorene (54b)

n.m.r. (CCl_4) : 4.82, 5.10 (fM, fM, 2H, :CH_2), 7.46-7.71,
7.71-7.92 (M, M, 4H, $\text{:C(1)H}_2 + \text{:C(4)H}_2$),
7.97 (d, $J=1\text{Hz.}$, 5H, :CH_3), 8.14-8.34
(M, 4H, $\text{:C(2)H}_2 + \text{:C(3)H}_2$).

Mixtures of isomers

i.r. (CCl_4) cm^{-1} : 2300 (s) C-D aromatic, 2100 (m) C-D
aliphatic, 1640 (s) C=C olefinic, 1615 (m)

C=C aromatic, 1460 (m) $-\text{CH}_2-$.

m.s. m/e : P=215.172830; Calculated for $\text{C}_{16}\text{H}_{13}\text{D}_5$,
215.172231, 215 ($\text{C}_{16}\text{H}_{13}\text{D}_5$) base peak,
200 ($\text{P}-\text{CH}_3$), 172 ($\text{P}-\text{C}_3\text{H}_7$).

8.11.10 Rearrangement of 2,5-dimethylphenylcyclopentene adduct (43)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-1-(2,5-dimethylphenyl) bicyclo[3,1,0]hexane, (0.5 gm, 2.0 mmol) was pyrolysed in flow system A (450° , 0.01 m.m.). The rearrangement product (0.4 gm, 80%), purified by alumina chromatography, was identified as a mixture of 5,8-dimethyl-9-isopropenyl 1,2,3,4-tetrahydrofluorene (44a) and 5,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (44b) in the ratio 2.9:1.0, taken over two separate rearrangements. Separation of the two isomers was not possible by preparative t.l.c. or preparative g.l.c. (various columns and conditions)

5,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (44a)
n.m.r. (CCl_4) : 3.0-3.45 (M, 2H, ArH), 4.95, 5.04 (fM, fM, 2H, $:\text{CH}_2$), 6.33 (bS, 1H, $\cdot\text{CH}$), 7.2-7.5, 7.66-7.75 (M, M, 4H, $\cdot\text{C}(1)\text{H}_2 + \cdot\text{C}(4)\text{H}_2$) 7.58, 7.84 (S, S, 6H, $2\text{Ar}(\text{CH}_3)$) 8.18-8.5 (M, 4H, $\cdot\text{C}(2)\text{H}_2 + \cdot\text{C}(3)\text{H}_2$), 8.92 (d, $J=1\text{Hz.}$, 3H, $\cdot\text{CH}_3$).

5,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (44b)

n.m.r. (CCl_4) : 3.0-3.45 (M, 2H, ArH), 4.86, 5.18 (fM, fM, 2H, $:\text{CH}_2$), 7.075 (d of d, $J=13\text{Hz.}$, $J=6\text{Hz.}$, 1H, $\cdot\text{CH}$), 7.2-7.5, 7.66-7.75 (M, M, 4H, $\cdot\text{C}(1)\text{H}_2 + \cdot\text{C}(4)\text{H}_2$), 7.64, 7.72 (S, S, 6H, 2ArCH_3), 8.05 (d, $J=1\text{Hz.}$, 3H, $\cdot\text{CH}_3$), 8.18-8.5 (M, 4H, $\cdot\text{C}(2)\text{H}_2 + \cdot\text{C}(3)\text{H}_2$).

Mixture of isomers.

i.r. (film) cm^{-1} : 1640(m) C=C olefinic, 1610 (m) C=C aromatic, 1495 (m) $-\text{CH}_2-$, 1440 (s) C- CH_3 , 880 (s) 1,2,3,4-tetrasubstitution.

m.s. m/e : P=238.171352; Calculated for $\text{C}_{18}\text{H}_{22}$, 238.172142, 238 ($\text{C}_{18}\text{H}_{22}$) base peak, 223 (P- CH_3), 209 (P- C_2H_4), 197 (P- C_3H_5), 165 (P- C_5H_{13}).

8.11.11 Rearrangement of 3,5-dimethylphenylcyclopentene adduct (45)

Vapour phase rearrangement

a) The adduct, 6-dimethylvinylidene-(3,5-dimethylphenyl)bicyclo [3,1,0] hexane (0.5 gm, 2.0 m mol) was pyrolysed in flow system A (450° , 0.01 m.m.). The rearrangement product (0.39 gms, 78%), purified by alumina chromatography, was identified as a mixture of 6,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (46a) and 6,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (46b) in the ratio 7.0:1.0 taken over two separate experiments. The 1,2,3,4-tetrahydrofluorene isomer was separable by preparative g.l.c. (180° , 10% P.M.P.E., 2 metre column), however it was not possible to isolate the other isomer for identification, it being identified from its characteristic n.m.r. spectrum.

6,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydrofluorene (46a)

n.m.r. (CCl_4) τ : 3.33, 3.44 (s, s, 2H, ArH), 4.98, 5.06 (fm, fm, 2H, $:\text{CH}_2$), 6.28 (bs, 1H, $\cdot\text{CH}$), 7.52-7.96 (m, 4H, $\cdot\text{C}(1)\text{H}_2 + \cdot\text{C}(4)\text{H}_2$), 7.73, 7.83 (s, s, 6H, 2Ar CH_3), 8.14-8.4 (m, 4H, $\cdot\text{C}(2)\text{H}_2 + \cdot\text{C}(3)\text{H}_2$), 8.92 (d, $J=1\text{Hz.}$, 3H, $\cdot\text{CH}_3$).

i.r. (CCl_4) cm^{-1} : 1640 (s) C=C olefinic, 1610 (s) C=C aromatic, 1460 (s) $-\text{CH}_2-$, 880 (s)

1,2,3,5-tetrasubstitution.

m.s. m/e : P=238.171607; Calculated for $C_{18}H_{22}$,
 238.172142, 238 ($C_{18}H_{22}$) base peak,
 223 (P- CH_3), 210 (P- C_2H_4), 197 (P- C_3H_5), 195 (P- C_3H_7), 179 (P- C_4H_{11}),
 169 (P- C_5H_9), 165 (P- C_5H_{13}), 89
 (P- $C_{11}H_{17}$).

6,8-dimethyl-9-isopropenyl-1,2,3,4-tetrahydro-4aH-fluorene (46b)

n.m.r. (CCl_4) : 3.9-4.5 (M, 4H, ArH), 4.9, 5.1 (fM,
 fM, 2H, $:CH_2$), 7.4-8.0 (M, 5H,
 $\cdot C(2)H_2 + \cdot C(3)H_2 + \cdot C(4a)H$), 8.04 (bs,
 3H, $\cdot CH_3$), 8.15-8.45 (M, 4H,
 $\cdot C(1)H_2 + \cdot C(4)H_2$).

8.11.12 Rearrangement of isobutene adduct (207)

Vapour phase rearrangement

a) The adduct, 2-dimethylvinylidene-1,1-dimethylcyclopropane (0.3 gm., 2.5 m mol) was pyrolysed in flow system A (450°, 0.01 m.m.). The rearrangement product (0.15 gm, 50%) was unidentifiable by n.m.r., bearing no resemblance to the expected products.

b) The adduct, (0.3 gms, 2.5 m mol) was pyrolysed in flow system A (350°, 0.01 m.m.). The product was found to be unrearranged adduct.

8.11.13 Rearrangement of phenylcyclohexene adduct (55)

Vapour phase rearrangement

a) The adduct, 7-dimethylvinylidene-1-phenylbicyclo[4,1,0]

heptane (0.3 gm, 1.3 m.mol) was pyrolysed in flow system A (450° , 0.01 m.m.). The rearrangement product (0.22 gm, 75%), purified by alumina chromatography, was identified as a mixture of 1-isopropenyl-1,4,5,6,7,8-hexahydro-2,3-benzazulene (56a), 1-isopropenyl-3,4,5,6,7,8-hexahydro-2,3-benzazulene (56b) and 3-(3'methylbut-1'-ynyl)-2-phenylcyclohex-1-ene (56d) in the ratio 2.5:1.3:1.0, taken over two separate rearrangements. These were identified by their characteristic n.m.r. spectra. The two benzazulenes were separable from the ethynylhexene by preparative g.l.c. (180° , 10% P.M.P.E., 2 metre column), however, the two benzazulenes themselves were not completely separated by preparative t.l.c. or preparative g.l.c. (180° , 10% P.M.P.E., 2 metre), a pure sample of (56d) only being separated

1-isopropenyl-1,4,5,6,7,8-hexahydro-2,3-benzazulene (56a)

n.m.r. $(\text{CCl}_4)_2$: 2.72-3.20 (M, 4H, ArH), 4.94, 5.04 (bS, bS, 2H, $:\text{CH}_2$), 4.26 (bS, 1H, $\cdot\text{CH}$), 7.31-7.52, 7.52-7.74 (M, M, 4H, $\cdot\text{C}(4)\text{H}_2 + \cdot\text{C}(8)\text{H}_2$), 8.04-8.54 (M, 6H, $\cdot\text{C}(5)\text{H}_2 + \cdot\text{C}(6)\text{H}_2 + \cdot\text{C}(7)\text{H}_2$, 8.89 (s, 3H, $\cdot\text{CH}_3$).

1-isopropenyl-3,4,5,6,7,8-hexahydro-2,3-benzazulene (56b)

n.m.r. $(\text{CCl}_4)_2$: 2.52-3.12 (M, 4H, ArH), 4.80, 5.12 (fM, fM, 2H, $:\text{CH}_2$), 6.74 (M, 1H, $\cdot\text{CH}$), 7.20-7.52, 7.52-7.74 (M, M, 4H, $\cdot\text{C}(4)\text{H}_2 + \cdot\text{C}(8)\text{H}_2$), 8.0 (s, 3H, $\cdot\text{CH}_3$), 8.04-8.50 (M, 6H, $\cdot\text{C}(5)\text{H}_2 + \cdot\text{C}(6)\text{H}_2 + \cdot\text{C}(7)\text{H}_2$).

Mixture of isomers

i.r. $(\text{CCl}_4) \text{ cm}^{-1}$: 1650 (m) C=C olefinic, 1600 (m) C=C aromatic, 1460 (s) $-\text{CH}_2-$

m.s. m/e : P=224.155870; Calculated for $C_{17}H_{20}$, 224.156493, 224 ($C_{17}H_{20}$)
base peak, 209 (P-CH₃), 181 (P-C₃H₉)

3-(3'methylbut-1'-ynyl)-2-phenylcyclohex-1-ene (56d)

n.m.r. (CCl₄)₂ : 2.54-3.16 (M, 5H, ArH), 4.08 (fM, 1H, :CH), 6.60 (fM, 1H, C(1')H), 7.50-8.60 (bM, 7H, C(4)H₂ + C(5)H₂ + C(6)H₂ + C(3')H), 8.99 (d, J=6Hz., 6H, C(CH₃)₂)

i.r. (CCl₄) cm⁻¹ : 2100 (w) C≡C, 1440 (m) -CH₂-, 700 (s) monosubstitution

m.s. m/e : P=224.156089; Calculated for $C_{17}H_{20}$, 224.156493, 224 ($C_{17}H_{20}$), 223 (P-H), 197 (P-C₂H₃) base peak.

b) The adduct, (0.3 gm, 1.3 m mol) was pyrolysed in flow system A (350°, 0.01 m.m.). The rearrangement product (0.2 gm, 66%), purified by alumina chromatography, was identified as a mixture of the two benzazulenes (56a) and (56b) together with the ethynylcyclohexene (56d) in the ratio 2.33:1.0:1.1, taken over two separate rearrangements.

8.11.14 Rearrangement of phenylcycloheptene adduct (57)

Vapour phase rearrangement

a) The adduct, 8-dimethylvinylidene-1-phenylbicyclo[5,1,0]octane (0.5 gm., 2.0 m mol) was pyrolysed in flow system A (450°, 0.01 m.m.). The rearrangement product (0.3 gm, 60%) purified by alumina chromatography was identified as a mixture of 1-isopropenyl-2,3-cyclooctenoindene (58a), 3-isopropenyl-1,2-cyclooctanoindene (58b) and 8-phenyl-9-isopropylidene-bicyclo[6,1,0]non-7-ene (58c) in the ratio 3.3 : 1.0 : 0.23, taken over two separate rearrangements. The isomers were only partially separable by preparative g.l.c. (10% P.M.P.E., 185°, 2 metre column) allowing them to be more accurately identified from their n.m.r. spectra.

1-isopropenyl-2,3-cyclooctenoindene (58a)

n.m.r. $(\text{CCl}_4)_2$: 2.65-3.04 (M, 4H, ArH), 4.92, 5.03 (fM, fM, 2H, $:\text{CH}_2$), 6.2 (bS, 1H, $\cdot\text{CH}$), 7.34, 7.59 (M, M, 4H, $\cdot\text{C}(4)\text{H}_2 + \cdot\text{C}(9)\text{H}_2$), 8.06-8.68 (M, 8H, $\cdot\text{C}(5)\text{H}_2 + \cdot\text{C}(6)\text{H}_2 + \cdot\text{C}(7)\text{H}_2 + \cdot\text{C}(8)\text{H}_2$), 8.86 (s, 3H, $\cdot\text{CH}_3$).

3-isopropenyl-1,2-cyclooctanoindene (58b)

n.m.r. (CCl_4) : 2.54-3.10 (M, 4H, ArH), 4.68, 5.09 (M, fM, 2H, $:\text{CH}_2$), 6.65-6.8 (M, 1H, $\cdot\text{CH}$), 7.16-7.88 (M, 4H, $\cdot\text{C}(4)\text{H}_2 + \cdot\text{C}(9)\text{H}_2$), 8.11 (s, 3H, $\cdot\text{CH}_3$), 8.0-8.8 (bM, 8H, $\cdot\text{C}(5)\text{H}_2 + \cdot\text{C}(6)\text{H}_2 + \cdot\text{C}(7)\text{H}_2 + \cdot\text{C}(8)\text{H}_2$).

8-phenyl-9-isopropylidenebicyclo[6,1,0]non-1-ene (58c)

n.m.r. (CCl_4) : 2.86, 2.9 (s, s, 5H, ArH), 3.94 (M, 1H, $:\text{CH}$), 7.05-8.7 (bM, 10H, $(\text{CH}_2)_5$), 8.16, 8.30 (s, s, 6H, $:\text{C}(\text{CH}_3)_2$).

Mixture of isomers

i.r. (film) cm^{-1} : 1640 (m) C=C olefinic, 1600 (m) C=C aromatic, 1460 (s) $-\text{CH}_2-$, 750 (m) 1,2-disubstitution, 750 (m), 720 (m) monosubstitution

m.s. m/e : P=238.172507; Calculated for $\text{C}_{18}\text{H}_{22}$, 238.172142, 238 ($\text{C}_{18}\text{H}_{22}$) base peak, 223 (P- CH_3), 195 (P- C_3H_7), 181 (P- C_4H_{11}), 169 (P- C_5H_9)

b) The adduct, (0.5 gm, 2.0 m mol), was pyrolysed in flow system A (350°, 0.01 m.m.). The rearrangement product (0.35 gm. 70%),

purified by alumina chromatography was identified as a mixture of the two cyclooctaindenes (58a) and (58b) and the bicyclononene (58c) in the ratio 3.2:1.0:7.8 taken over two separate rearrangements.

8.11.15 Rearrangement of phenylcyclooctene adduct (59)

Vapour phase rearrangement

a) The adduct, 9-dimethylvinylidene-1-phenylbicyclo[6,1,0]nonane (0.5 gm, 1.8 m mol) was pyrolysed in flow system A system (450°C, 0.01 m.m.). The rearrangement product, purified by alumina chromatography was identified by n.m.r. and i.r. as a mixture of 1-isopropenyl-2,3-cyclononenoindene (60a) and 3-isopropenyl-1,2-cyclononanoindene (60b) in the ratio 3.5:1.0 taken over two separate rearrangements. The isomers were only partially separable by preparative g.l.c. (185°, 10% P.M.P.E., 2 metre column) allowing identification of each isomer by ¹H-n.m.r. spectroscopy.

1-isopropenyl-2,3-cyclononenoindene (60a)

n.m.r. (CCl₄)₂ : 2.7-3.1 (M, 4H, ArH), 4.92, 5.02 (fM, fM, 2H, :CH₂), 6.16 (bS, 1H, CH), 7.2-8.04, 8.04-8.8 (M, M, 14H, (CH₂)₇), 8.86 (fd, J=1Hz., 3H, CH₃).

3-isopropenyl-1,2-cyclononanoindene (60b)

n.m.r. (CCl₄)₂ : 2.6-3.1 (M, 4H, ArH), 4.8, 5.06 (M, M, 2H, :CH₂), 6.8 (M, 1H, CH) 7.2-7.94, 8.02-8.8 (M, M, 14H, (CH₂)₇) 7.97 (fM, 3H, CH₃).

Mixture of isomers

i.r. (film) cm⁻¹ : 1640 (m) C=C olefinic, 1600 (m) C=C aromatic, 1460 (s) -CH₂-, 770 (s) 1,2-disubstitution

m.s. m/e : P=252.186999; Calculated for C₁₉H₂₄, 252.187792, 252 (C₁₉H₂₄) base peak, 121 (P-C₁₀H₁₁), 119 (P-C₁₀H₁₃), 117 (P-C₁₀H₁₅).

b) The adduct, (0.5 gm, 1.8 m mol) was pyrolysed in flow system A (350°C, 0.01 m.m.). The rearrangement product was identified from n.m.r. and i.r. as a mixture of the two cyclononaindenes (60a) and (60b) together with 9-phenyl-10-isopropylidenebicyclo[7,1,0]dec-1-ene (60c) in the ratio 1.0:1.0:4.0 plus a small proportion of unidentifiable product (5%), taken from two separate experiments. The bicyclodecene was separable from the other isomers by preparative g.l.c. (185°, 10% P.M.P.E.)

9-phenyl-10-isopropylidenebicyclo[7,1,0]dec-1-ene (60c)

n.m.r.	(CCl ₄) ₂	: 2.5-3.2 (M, 5H, ArH), 6.06 (M, 1H, :CH), 7.2-8.1, 8.35-8.9 (M, M, 14H, (CH ₂) ₇), 8.18, 8.3 (S, S, 6H, :C(CH ₃) ₂).
i.r.	(film) cm ⁻¹	: 1600 (m) C=C aromatic, 1460 (m) -CH ₂ - 700 (m) C=CH
m.s.	m/e	: P=252.186999; Calculated for C ₁₉ H ₂₄ , 252.187792, 252 (C ₁₉ H ₂₄), base peak, 209 (P-C ₃ H ₇), 195 (P-C ₄ H ₉), 155 (P-C ₇ H ₁₃).

8.12 Rearrangement of 2,3,3-trimethylbutenylidenecyclopropanes

8.12.1 Rearrangement of isobutene adduct (77)

Vapour phase rearrangement

a) The adduct, 2-(2',3',3'-trimethylbutenylidene)1,1-dimethylcyclopropane (0.5 gm, 3.5 m mol) was pyrolysed in flow system A (350°, 0.01 m.m.). The rearrangement product (0.35 gm, 70%), purified by alumina chromatography, was identified from its n.m.r. spectrum as a mixture of four isomers; syn and anti 2-(1'-t-butylethylidene)-1,1-dimethyl-3-methylenecyclopropane, in equal amounts and syn and anti 2-(1'-t-butylethylidene)-1-isopropylidenecyclopropane. The ratio of methylenecyclopropanes to

isopropylidenecyclopropanes was 3.0:1.0. None of the isomers were separable by preparative t.l.c. or preparative g.l.c.

syn-2-(1'-t-butylethylidene)-1,1-dimethyl-3-methylenecyclopropane (85a)

n.m.r. $(\text{CCl}_4)_2$: 4.86, 4.98 (s, s, 2H, $:\text{CH}_2$), 8.14 (s, 3H, $:\text{CCH}_3$), 8.84 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$), 8.89 (s, 6H, $\cdot\text{C}(\text{CH}_3)_2$).

anti-2-(1'-t-butylethylidene)-1,1-dimethyl-3-methylenecyclopropane (85b)

n.m.r. $(\text{CCl}_4)_2$: 4.90, 5.01 (s, s, 2H, $:\text{CH}_2$), 8.17 (s, 3H, $:\text{CCH}_3$), 8.84 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$), 8.89 (s, 6H, $\cdot\text{C}(\text{CH}_3)_2$).

syn-2-(1'-t-butylethylidene)-1-isopropylidenecyclopropane (85c)

n.m.r. $(\text{CCl}_4)_2$: 8.05 (s, 3H, $:\text{C}(\text{CH}_3)\text{Bu}^t$), 8.07 (s, 6H, $:\text{C}(\text{CH}_3)_2$), 8.86 (s, 2H, $\cdot\text{CH}_2$), 9.06 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$).

anti-2-(1'-t-butylethylidene)-1-isopropylidenecyclopropane (85d)

n.m.r. $(\text{CCl}_4)_2$: 8.05 (s, 3H, $:\text{C}(\text{CH}_3)\text{Bu}^t$), 8.07 (s, 6H, $:\text{C}(\text{CH}_3)_2$), 8.86 (s, 2H, $\cdot\text{CH}_2$), 9.06 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$).

Mixture

i.r. (film) cm^{-1} : 1460 (m) C-CH₃, 760 (m) olefinic CH₂.
 m.s. m/e : P=164.156404; Calculated for C₁₂H₂₀, 164.156493, 164 (C₁₂H₂₀), 139 (P-C₂H), 121 (P-C₃H₇), 108 (P-C₄H₆), 107 (P-C₄H₇), 93 (P-C₅H₁₁).

8.12.2 Rearrangement of 1,1-diphenylethylene adduct (76)

Vapour phase rearrangement

a) The adduct, 2-(2',3',3'-trimethylbutenylidene)1,1-diphenylcyclopropane (0.5 gm, 1.8 m mol) was pyrolysed in flow system A. The rearrangement product (0.45 gm, 90%) was identified from its n.m.r. spectrum as a mixture of syn and anti 2-(1'-t-butylethylidene)-1,1-diphenyl-3-methylene-

cyclopropane (82a) and (82b). The isomers, which were inseparable by preparative t.l.c. or preparative g.l.c., were in the ratio syn:anti 1.0:7.8.

syn-2-(1'-t-butylethylidene)-1,1-diphenyl-3-methylenecyclopropane (82a)

n.m.r. $(\text{CCl}_4)_\tau$: 2.6-3.0 (M, 10H, ArH), 4.62, 4.76 (S, S, 2H, $:\text{CH}_2$), 7.98 (S, 3H, $:\text{CCH}_3$), 9.26 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$).

$(\text{C}_6\text{H}_6)_\tau$: 4.37, 4.55 (S, S, 2H, $:\text{CH}_2$), 7.86 (S, 3H, $:\text{CCH}_3$), 8.96 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$).

anti-2-(1'-t-butylethylidene)-1,1-diphenyl-3-methylenecyclopropane (82b)

n.m.r. $(\text{CCl}_4)_\tau$: 2.6-3.0 (M, 10H, ArH), 4.62, 4.76 (S, S, 2H, $:\text{CH}_2$), 8.09 (S, 3H, $\cdot\text{CCH}_3$), 8.82 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$).

$(\text{C}_6\text{H}_6)_\tau$: 4.36, 4.54 (S, S, 2H, $:\text{CH}_2$), 7.93, (S, 3H, $:\text{CCH}_3$), 8.71 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$).

Mixture

i.r. (film) cm^{-1} : 1780 (m) olefinic CH_2 , 1610 (m) C=C aromatic, 1510 (s) C=C aromatic, 1460 (m) C- CH_3 , 780 (m) olefinic CH_2 , 760 (m), 710 (s) monosubstitution,

m.s. m/e : P=288.187109; Calculated for $\text{C}_{22}\text{H}_{24}$, 288.187792, 288 ($\text{C}_{22}\text{H}_{24}$) base peak, 273 (P- CH_3), 231 (P- C_4H_9), 216 (P- C_5H_{13}).

8.12.3 Rearrangement of α -methylstyrene adduct (71a) and (71b)

Vapour phase rearrangement

a) The adduct, Z and E 2-(2',3',3'-trimethylbutenylidene)-1-methyl-1-phenylcyclopropane (0.5 gm, 2.2 m mol) was pyrolysed in flow system A (350°, 0.01 m.m.). The rearrangement product (0.41 gm, 82%) was identified from its n.m.r. spectrum as a mixture of syn and anti 2-(1'-t-butylethylidene)-1-phenyl-1-methyl-3-

methylenecyclopropane (81a) and (81b). The isomers, which were not separable by preparative t.l.c. or preparative g.l.c., were in the ratio syn:anti 1:2.25.

syn-2-(4-tert-butylethylidene)-1-phenyl-1-methyl-3-methylenecyclopropane (81a)

n.m.r. $(\text{CCl}_4)_\tau$: 2.72-3.0 (M, 5H, ArH), 4.69, 4.92 (S, S, 2H, $:\text{CH}_2$), 8.02 (S, 3H, $:\text{CCH}_3$), 8.23 (S, 3H, $\cdot\text{CCH}_3$), 9.02 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$).

anti-2-(4-tert-butylethylidene)-1-phenyl-1-methyl-3-methylenecyclopropane (81b)

n.m.r. $(\text{CCl}_4)_\tau$: 2.7-3.0 (M, 5H, ArH), 4.73, 4.91 (S, S, 2H, $:\text{CH}_2$), 8.20 (S, 3H, $:\text{CCH}_3$), 8.45 (S, 3H, $\cdot\text{CCH}_3$), 8.85 (S, 9H, $\cdot\text{C}(\text{CH}_3)_3$).

Mixture

i.r. (film) cm^{-1} : 1780 (m) olefinic CH_2 , 1610 (m) C=C aromatic, 1510 (m), 1490 (m) C=C aromatic, 1480 (m), 1460 (m) C- CH_3 , 780 (m) olefinic CH_2 , 705 (s) mono-substitution

m.s. m/e : P=226.172290; Calculated for $\text{C}_{17}\text{H}_{22}$, 226.172142, 226 ($\text{C}_{17}\text{H}_{22}$), 211 (P- CH_3), 183 (P- C_3H_7), 169 (P- C_4H_9), base peak

8.12.4 Rearrangement of β,β -dimethylstyrene adduct (75a) and (75b)

Vapour phase rearrangement

a) The adduct, Z- and E-2-(2',3',3'-trimethylbutenylidene)-1,1-dimethyl-2-phenylcyclopropane (0.2 gm, 0.85 m mol) was pyrolysed in flow system A (350°C, 0.01 m.m.). The rearrangement product (0.15 gm, 75% was not identified. Analysis by g.l.c. showed that the product was at least a six component mixture but the separation was not good enough to allow preparative g.l.c. to be successful.

b) The adduct, (0.2 gm, 0.85 m mol) was pyrolysed in flow system A (450° , 0.01 m.m.). The rearrangement product (0.16 gm, 78%) was again an unidentifiable multicomponent mixture.

8.12.5 Rearrangement of phenylcyclopentene adduct (74a) and (74b)

Vapour phase rearrangement

a) The adduct, Z- and E-6-(2',3',3'-trimethylbutenylidene)-1-phenylbicyclo[3,1,0]hexane (0.5 gms, 2.0 m mol) was pyrolysed in flow system A (350° , 0.01 m.m.). The rearrangement product (0.43 gm, 86%) was identified as unrearranged adduct.

8.12.6 Rearrangement of indene adduct (69a) and (69b)

Vapour phase rearrangement

a) The adduct, Z- and E-2,3-benzo-6-(2',3',3'-trimethylbutenylidene)bicyclo[3,1,0]hex-2-ene (0.5 gm, 2.2 m mol) was pyrolysed in flow system A (350° , 0.01 m.m.). The rearrangement product, purified by preparative t.l.c. (light petroleum), was identified as a mixture of products. The major product (75%) was identified as 2-t-butyl-3-(2'-indenyl)-buta-1,3-diene (87) with 25% unidentified minor products.

2-t-butyl-3-(2'-indenyl)-buta-1,3-diene (87)

n.m.r.	(CCl ₄) ₂	: 2.8-3.08 (M, 4H, ArH), 3.44 (S, 1H, ArCH), 4.51, 4.86 (d, d, J _{gem} =2Hz., 2H, :CH ₂), 5.23 (S, 2H, :CH ₂), 6.51 (S, 2H, ArCH ₂), 8.89 (S, 9H, •C(CH ₃) ₃)
i.r.	(film) cm ⁻¹	: 1780 (m) :CH ₂ , 1640 (w) C=C olefinic, 1620 (m) C=C olefinic, 1590 (m) C=C aromatic, 1480 (m) C-CH ₃ , 760 (m) :CH ₂ , 730 (s) 1,2-disubstitution
m.s.	m/e	: P=224.156308; Calculated for C ₁₇ H ₂₀ , 224.156493, 224 (C ₁₇ H ₂₀), 209 (P-CH ₃) base peak, 181 (P-C ₃ H ₇), 168 (P-C ₄ H ₈)

167 (P-C₄H₉)U.V. μ (EtOH) : 304.5 ($\epsilon=11.2 \times 10^3$), 326.4 ($\epsilon=5.9 \times 10^3$).

b) Separation of the butadiene from the unidentifiable products was accomplished by preparative g.l.c. (20% N.P.G.S., 175°, 2 metre column). This gave the pure butadiene and two other components. One was identified as Z-2,3,3-trimethyl-1-(β -naphthyl)-but-1-ene (91a) and the other tentatively assigned the structure 2,3,3-trimethyl-1-(β -naphthyl)butan-1-one (91f).

Z-2,3,3-trimethyl-1-(β -naphthyl)but-1-ene (91a)

n.m.r. (CCl₄) τ : 2.24-3.06 (M, 7H, ArH), 3.56 (bS, 1H, :CH), 8.108 (d, J=1.5Hz., 3H, :CCH₃), 9.02 (S, 9H, $\cdot C(CH_3)_3$)

i.r. (CCl₄) cm⁻¹ : 1610 (m) C=C aromatic, 1460 (m) C-CH₃, 870 (m) 2-substituted naphthylene.

m.s. m/e : P=224.156527; Calculated for C₁₇H₂₀, 224.156493, 224 (C₁₇H₂₀), 210 (P-CH₂), 209 (P-CH₃), 203 (P-CH₉), 195 (P-C₂H₅) base peak, 179 (P-C₃H₉), 165 (P-C₄H₁₁).

2,3,3-trimethyl-1-(β -naphthyl)-butan-1-one (91f)

n.m.r. (CCl₄) τ : 2.2-3.0 (M, 7H, ArH), lack of olefinic hydrogen, lack of olefinic methyl

i.r. (CCl₄) cm⁻¹ : 1710-1730 (m) C=O.

m.s. m/e : P=240.151241; Calculated for C₁₇H₂₀O, 240.151407, 240 (C₁₇H₂₀O)

c) The rearrangement product mixture (0.15 gm, 0.67 m mol) and dimethylacetylenedicarboxylate (0.095 gm, 0.67 m mol) were refluxed, under nitrogen, in sodium dried benzene (15 mls) for 16 hr. The solvent and

excess ester were removed under reduced pressure and the residue purified by preparative t.l.c. (20% ether in light petroleum) to give dimethyl-1-(2',2'-dimethyl-3'-methylenepropyl)fluorene-3,4-dicarboxylate (89) in 40% yield.

dimethyl-1-(2',2'-dimethyl-3'-methylenepropyl)fluorene-3,4-dicarboxylate

m.p.		:	142-142.6° (MeOH)
n.m.r.	(CCl ₄) ₂	:	2.35 (s, 1H, ArH), 2.4-2.82 (m, 4H, ArH), 4.66, 5.12 (d, d, J _{gem} =2Hz., 2H, :CH ₂), 6.02, 6.12 (s, s, 6H, C ³ OCH ₃ , C ⁴ OCH ₃), 6.18 (s, 2H, ArCH ₂), 8.81 (s, 9H, •C(CH ₃) ₃)
m.s.	m/e	:	P=364.166624; Calculated for C ₂₃ H ₂₄ O ₄ , 364.167448, 364 (C ₂₃ H ₂₄ O ₄) base peak, 333 (P-CH ₃ O),
U.V.	μμ	:	219 (ε=2.38x10 ⁴), 243 (ε=2.58x10 ⁴), 266.5 (ε=1.46x10 ⁴), 304.2 (ε=2.88x10 ³)
Analysis		:	Found C, 75.79% H, 6.74% Calculated for C ₂₃ H ₂₄ O ₄ C, 75.82% H, 6.59%.

Acid catalysed rearrangement

d) The adduct, (0.3 gm, 1.4 mmol) was refluxed with methanolic hydrochloric acid for 5 minutes, extracted and dried as described in section. The product, purified by t.l.c. was identified as a mixture of five products. Preparative g.l.c. (20% N.P.G.S., 2 metre column, 177°) gave separation into four fractions, the first being a mixture of two isomers, separable by preparative t.l.c. (light petroleum). The five products were identified as Z and E-2,3,3-trimethyl-1-(β-naphthyl)but-1-ene (91a) and (91b), 2-(3',4',4'-trimethylpent-1'-ynyl) indene (91c) and E and Z-2-(

3',4',4'-trimethyl-1'-chloropent-1'-enyl)indene (91d) and (91e) in the ratio 1.0:2.5:1.0:2.2:1.5.

Fe-2,3,3-trimethyl-1-(β -naphthyl)-but-1-ene (91b)

n.m.r.	(CCl ₄) τ	: 2.24-2.84 (M, 7H, ArH), 3.57 (bs, 1H, C:CH), 8.15 (d, J=1.5Hz., 3H, $\cdot\text{CH}_3$), 8.82 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$).
i.r.	(CCl ₄) cm ⁻¹	: 1630 (m) C=C olefinic, 1605 (m) C=C aromatic, 1470 (s) C-CH ₃ , 865 (s) 2-substituted naphthylene.
m.s.	m/s	: P=224.155651; Calculated for C ₁₇ H ₂₀ , 224.156493, 224 (C ₁₇ H ₂₀), 209 (P-CH ₃) base peak, 203 (P-CH ₉), 167 (P-C ₄ H ₉)

2-(3',4',4'-trimethylpent-1'-ynyl)indene (91c)

n.m.r.	(CCl ₄) τ	: 2.7-3.02 (M, 4H, ArH), 3.16 (fM, 1H, ArCH), 6.58, 6.60 (s, s, 2H, ArCH ₂), 8.025 (q, J=7H, 1H, $\cdot\text{CH}$), 8.835 (d, 3H $\cdot\text{CH}_3$), 9.02 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$).
i.r.	(CCl ₄) cm ⁻¹	: 1480 (s) C-CH ₃
m.s.	m/e	: P=224.156089; Calculated for C ₁₇ H ₂₀ , 224.156493, 224 (C ₁₇ H ₂₀), 203 (P-CH ₃), 195 (P-C ₂ H ₅), 167 (P-C ₄ H ₉) base peak, 115 (P-C ₈ H ₁₃).

Fe-2-(3',4',4'-trimethyl-1'-chloropent-1'-enyl)indene (91d)

n.m.r.	(CCl ₄) τ	: 2.6-2.95 (M, 4H, ArH), 3.06 (bs, 1H, ArCH), 4.235 (d, J=11Hz., 1H, C:CH), 6.36, 6.40 (s, s, 2H, ArCH ₂), 7.44 (d of q, J _{HH} =11Hz., J _{H,CH₃} =7Hz., 1H, $\cdot\text{CH}$), 8.975 (d, J=7Hz., 3H, $\cdot\text{CH}_3$), 9.10 (s, 9H, $\cdot\text{C}(\text{CH}_3)_3$).
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i.r. (CCl_4) cm^{-1} : 1610 (m) aromatic, 1470 (s) C-CH₃,
870 (s) C=CH.

m.s. m/e : P=260.133204 and 262.132319;
Calculated for CH³⁵Cl, 260.133171
and for CH³⁷Cl, 262.130221, 262
(CH³⁷Cl), 260 (CH³⁵Cl), base peak
245 (P-CH₅), 224 (P-HCl), 168
(P-C₇H₁₁).

Z-2-(3',4',4'-trimethyl-1'-chloropent-1'-enyl)indene (91e)

n.m.r. $(\text{CCl}_4)_\gamma$: 2.65-3.0 (M, 4H, ArH), 3.04 (bs, 1H,
ArCH), 4.15 (d, J=10Hz., 1H, C:CH),
6.60 (s, 2H, ArCH₂), 7.325 (d of q,
J_{HH}=10Hz., J_{H·CH₃}=7Hz., 1H, ·CH),
9.025 (d, J=7Hz., 3H, ·CH₃), 9.08
(s, 9H, ·C(CH₃)₃).

i.r. (CCl_4) film : 1615 (m) C=C aromatic, 1470 (s)
C-CH₃ 860 (s) C=CH.

m.s. m/e : P=260.132175 and 262.129491;
Calculated for C₁₇H₂₁³⁵Cl, 260.133171
and C₁₇H₂₁³⁷Cl, 262.130221, 262 (C₁₇H₂₁³⁷Cl),
260 (C₁₇H₂₁³⁵Cl), 205 (P-C₄H₉), 203
(P-C₄H₉) base peak, 167 (P-C₇H₁₁).

8.13.1 Rearrangements of adducts from 2-vinylpropenylidenecarbene

Rearrangement of 0.5 gm samples of the adducts of the above carbene precursor with 1,1-diphenylethylene, α-methylstyrene and phenylcyclopentene were all attempted at 350°C and 450°C in flow system A. The products of the pyrolysis were, however, unidentifiable mixtures.

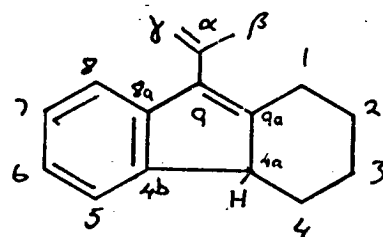
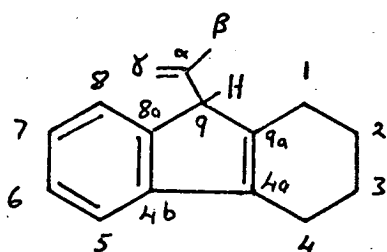
Attempted rearrangement by refluxing in benzene for 6 hours gave only starting material.

8.14.1 Rearrangement of adducts from 2-(trans-prop-1-enyl)propenylidene-
carbene

Rearrangement of 0.5 gm samples of the adducts of the above carbene precursor with 1,1-diphenylethylene, α -methylstyrene, phenylcyclopentene and indene, were all attempted at 350°C and 450°C in flow system A. The products of the pyrolyses were, however, unidentifiable mixtures.

Appendix I

Calculations of ΔH° , ΔS° and ΔG° by the method of Benson²¹⁵ were carried out as shown over. Values not available from Benson's Tables were calculated, these calculations also being shown.



ΔH°	S°	C_p°	Atom	ΔH°	S°	C_p°	
-4.76	9.8	8.32	1	-4.76	9.8	8.32	
-4.95	9.42	8.25	2	-4.95	9.42	8.25	
-4.95	9.42	8.25	3	-4.95	9.42	8.25	
-4.76	9.8	8.32	4	-4.95	9.42	8.25	
8.64	-14.6	5.93	4a	[-1.00]	[-12.0]	[7.5]	
5.68	-7.8	4.38	4b	5.51	-7.69	3.68	
			5				
13.2	46.12	21.84	6	13.2	46.12	21.84	
			7				
			8				
5.51	-7.69	3.68	8a	5.68	-7.8	4.38	
[-1.00]	[-12.0]	[7.5]	9	[7.91]	[-15.55]	[6.4]	*
10.34	-12.7	4.99	9a	10.34	-12.7	4.99	
10.34	-12.7	4.99	α	[9.61]	[-13.65]	[5.46]	*
-10.08	30.41	9.40	β	-10.08	30.41	9.40	
+ 6.26	27.61	7.51	γ	6.26	27.61	7.51	
6.0	NV	NV		6.0	NV	NV	
1.4	21.5	-1.98		-	-	-	
				0	18.8	-3.3	
TOTAL	36.87	96.59	101.38	33.82	91.61	100.93	

NV = no value available

[] = computed value

$$\therefore \Delta H^\circ = 3.05 \text{ kcal mol}^{-1}$$

$$\Delta S^\circ = 4.98 \text{ cal T}^{-1} \text{ mol}^{-1}$$

$$\Delta C_p^\circ = 0.45 \text{ cal mol}^{-1}$$

$$\Delta G^\circ = -0.65 \text{ kcal mol}^{-1}$$

* Average value see later

$$\Delta H_T^\circ = \Delta H_{T_0}^\circ + \Delta C_{pT_m}^\circ (T - T_0) \quad T_m = \frac{T + T_0}{2}$$

$$\Delta S_T^\circ = \Delta S_{T_0}^\circ + \Delta C_{pT_m}^\circ \ln T/T_0$$

14 At 450°C i.e. 723° K = T

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$$

$$\text{i.e. } \Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ + \Delta C_{p510}^\circ \{T - T_0 - T \ln T/T_0\}$$

$$\text{for (37a)} \rightleftharpoons (37b)$$

$$\Delta G_{723}^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ + \Delta C_{p510}^\circ \frac{425 - 723 \times 0.88632}{1000}$$

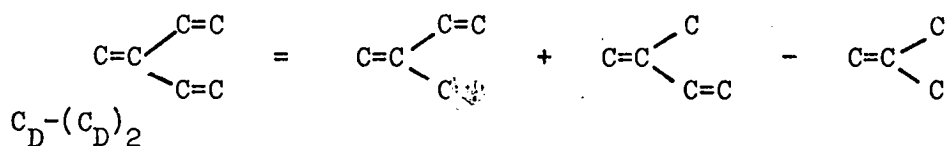
$$= \Delta H_{298}^\circ - T\Delta S_{298}^\circ - 216 \Delta C_{p510}^\circ$$

$$= 3.05 - \frac{723 \times 4.98}{1000} - \frac{216 \times 0.45}{1000} \text{ k cal}$$

$$\Delta G^\circ = \underline{\underline{-0.65}} \text{ k cal}$$

$$\Delta G^\circ = -RT \ln K \therefore K = 1.6$$

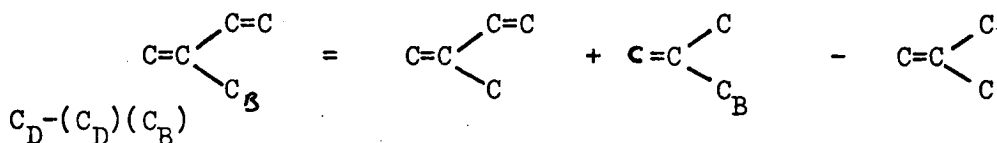
Calculation of figures for centers not in table. (effectively Hess' Law).



$$\Delta H_f = 8.88 + 8.88 - 10.34 = 7.42$$

$$\Delta S = -14.6 - 14.6 + 12.7 = -16.5$$

$$\text{C}_{p_{500}} = 5.93 + 5.93 - 4.99 = 6.87$$



$$\Delta H_f = 8.88 + 8.64 - 10.34 = 7.18$$

$$\Delta S = -14.6 - 14.6 + 12.7 = -16.5$$

$$\text{C}_{p_{500}} = 5.93 + 5.93 - 4.99 = +6.87$$

Calculated average of $\text{C}_D-(\text{C}_B)(\text{C})$ and $\text{C}_D-(\text{C}_B)(\text{C}_D)$ for $\angle (g)$

Calculated average of $\text{C}_D-(\text{C})(\text{C})$ and $\text{C}_D(\text{C})(\text{C}_D)$ for $\angle (\alpha)$

	ΔH_f°	ΔS°	$\text{C}_{p_{500}}$	
$\text{C}_D-(\text{C}_B)(\text{C}_D)$	7.18	-16.5	6.87	
$\text{C}_D-(\text{C}_B)(\text{C})$	8.64	-14.6	5.93	
Average	7.91	-15.55	6.40	for $\angle (g)$
$\text{C}_D-(\text{C})(\text{C}_D)$	8.88	-14.6	5.93	
$\text{C}_D-(\text{C})(\text{C})$	10.34	-12.7	4.99	
Average	9.61	-13.65	5.46	for $\angle (\alpha)$

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