THE SYNTHESIS AND REARRANGEMENT OF VINYLIDENECYCLOPROPANES

by

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TO MY PARENTS

A B S T R A C T

A series of vinylidenecyclopropanes have been prepared by the addition of dimethylvinylidenecarbene to various styrene derivatives. These cyclopropanes underwent unimolecular rearrangement when heated in solution (80-180°) or at reduced pressure in the vapour phase when passed through a flow system (350-450°), the rearrangement conditions being dependent upon the adduct involved.

Thermal rearrangement of the adducts derived from the 1-arylalkenes and 3-methylenebenzocycloalkenes gave dimethylenecyclopropane derivatives, whereas thermolysis of the adducts formed from 1-arylcycloalkenes lead to mixtures of ring expanded and cyclopropane ring opened products, the constraints imposed on the latter systems rendering dimethylenecyclopropane formation unfavourable. Similarly, thermal rearrangement of the adducts derived from benzocycloalka-1,3-dienes lead to ring expanded or cyclopropane ring opened products depending on the ring size of the parent styrene system involved. The effect of alkyl substitution at aryl and cyclopropyl sites in these systems was also investigated.

The mechanistic nature of these rearrangements has been considered in the light of concerted and free radical pathways and, although some of the processes studied could be realised in terms of diradical intermediates, it seems likely in the majority of cases that a single transition state is probably involved.

Application of the Arrhenius equation to the first order rate constants obtained at different temperatures for the thermolysis

of the vinylidenecyclopropane derived from α-methylstyrene enabled the energy and entropy of activation for this rearrangement to be estimated, the significance of the results being discussed in terms of the two alternative mechanisms available. Attempts to identify a hypothetical diradical intermediate during the aforementioned rearrangement by chemically trapping with radical scavengers or observing the phenomenon of chemically induced dynamic nuclear polarisation were unsuccessful.

These vinylidenecyclopropanes also underwent facile acid catalysed rearrangement to form products whose formation is rationalised in terms of initial protonation at an allenic carbon atom followed by cleavage of the cyclopropane ring, support of this view being obtained from several acid catalysed rearrangements which were also carried out in deuterated solvents.

Many of the products obtained from these thermal and acid catalysed rearrangements are of synthetic and structural interest due to their ease of formation and relative inaccessibility by other routes, several were independently synthesised by other methods for direct structural proof.

During the course of this work a new reaction was observed involving the direct oxidation of certain aromatic hydrocarbons with dichlorodicyanoquinone to form α, β-unsaturated aldehydes.

A C K N O W L E D G E M E N T S

My most sincere thanks are due to Dr. I.H. Sadler for his constant guidance, encouragement and tolerance throughout the past three years which have made this period of research interesting and enjoyable.

I should also like to thank the University of Edinburgh for the provision of library and laboratory facilities and the Science Research Council for the award of a Research Studentship throughout the duration of this work.

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C O N T E N T S

1. A REVIEW OF THE REARRANGEMENTS OF CERTAIN CYCLOPROPANE DERIVATIVES.

1.1 INTRODUCTION

The rearrangements undergone by cyclopropane derivatives are extensive and diverse[1] and can be propagated by the action of heat, acid or base catalysis, and ultraviolet light. In view of the material presented later (Section 3) this review is mainly concerned with the acid catalysed and thermal unimolecular rearrangements of some cyclopropyl hydrocarbons, examples of hetero-compounds only being mentioned where they help to clarify the hydrocarbon rearrangement under discussion. These reactions can be conveniently classified under the headings:- (a) saturated cyclopropanes, where the cyclopropane ring carbon atoms are all σ-bonded and not conjugated with any non-aromatic π-electron system, (b) unsaturated cyclopropanes, where at least one of the cyclopropane carbon atoms is π-bonded and (c) vinylcyclopropanes, where at least one of the endo-cyclic cyclopropane bonds is conjugated with a non-aromatic π-electron system. In the case of molecules falling into two categories, preference in classification is given according to the nature of the reaction involved.

The thermal unimolecular rearrangements of cyclopropanes have been rationalised in terms of either a stepwise process involving a diradical intermediate or a concerted process involving a single transition state and it is often difficult or impossible

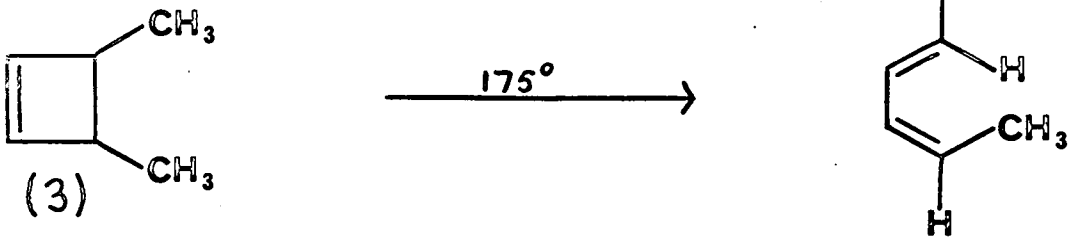
to distinguish between the two, in many cases the kinetic evidence and product identity being apparently equally compatible with each alternative. The formation of a diradical intermediate involves the distinct rupture of a cyclopropane bond which often results in a relatively large increase in the internal rotational freedom of the molecule. This process is often characterised by a relatively large positive entropy of activation and energy of activation, although this is not necessarily so in cyclic or resonance stabilised diradicals. Alternatively a process involving concerted bond breaking and bond making with no distinct open chain intermediate is characterised by a smaller, usually negative, entropy of activation and a lower activation energy.

As a result of orbital symmetry considerations[8,9] it is now possible to predict whether a postulated concerted mechanism is likely, and in some cases product identity unambiguously demonstrates the validity or otherwise of the prediction. In other favourable cases the existence of a triplet diradical has been detected by electron spin resonance, thus conclusively demonstrating the participation of a radical intermediate. However in many cases the evidence is not decisive and only tentative conclusions can be drawn by consideration of the available kinetic data and the identity of the products formed during these thermal processes. It appears that sounder distinctions will only become possible when further evidence, especially kinetic data, becomes available.

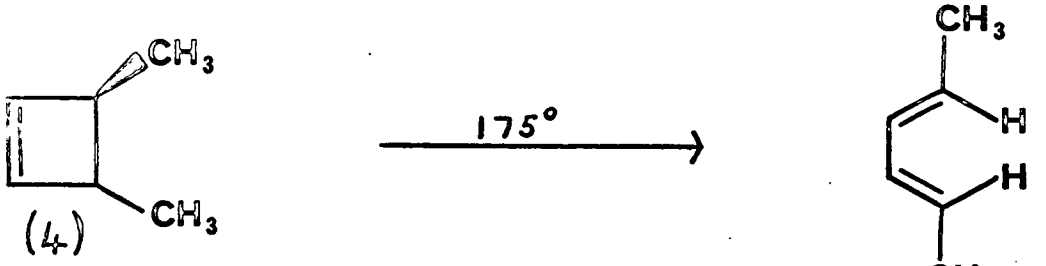
Before the rearrangements of cyclopropanes are discussed, it is useful to consider briefly the bonding characteristics of cyclopropanes and to review the Woodward-Hoffmann approach to concerted reactions.

1.2 BONDING CHARACTERISTICS IN CYCLOPROPANES

The ease of ring cleavage and thus rearrangement of cyclopropane derivatives results from the unusual and strained nature of the cyclopropane carbon-carbon bond. This high degree of strain is reflected in the heats of formation[2] of cyclopropane (12·7 Kcal.mole^{-1}) and its open chain isomer, propene (4·9 Kcal. mole^{-1}). However comparison of the ring strain[2] energy present in cyclopropane (27·6 Kcal.mole^{-1}) and cyclobutane (26·2 Kcal. mole^{-1}) shows that the former is not as highly strained as might be expected from purely angular considerations. Several attempts to rationalise this latent stability of the cyclopropane ring in terms of the hybridisation of the bonds involved have more recently[3] been re-examined by Bernett who has presented a model which unifies earlier theories. This also attempts to provide an explanation for the unusual properties and reactivity of cyclopropanes relative to other cyclic hydrocarbons, in particular the increased p-character of the carbon-carbon bonds which often undergo addition reactions rather than the substitution modes usually associated with saturated cyclic hydrocarbons. This is exemplified[4] by the vinylcyclopropane(1) which behaves in a


CH3
CH3
175°
CH3
H
CH3
H

(3)


CH3
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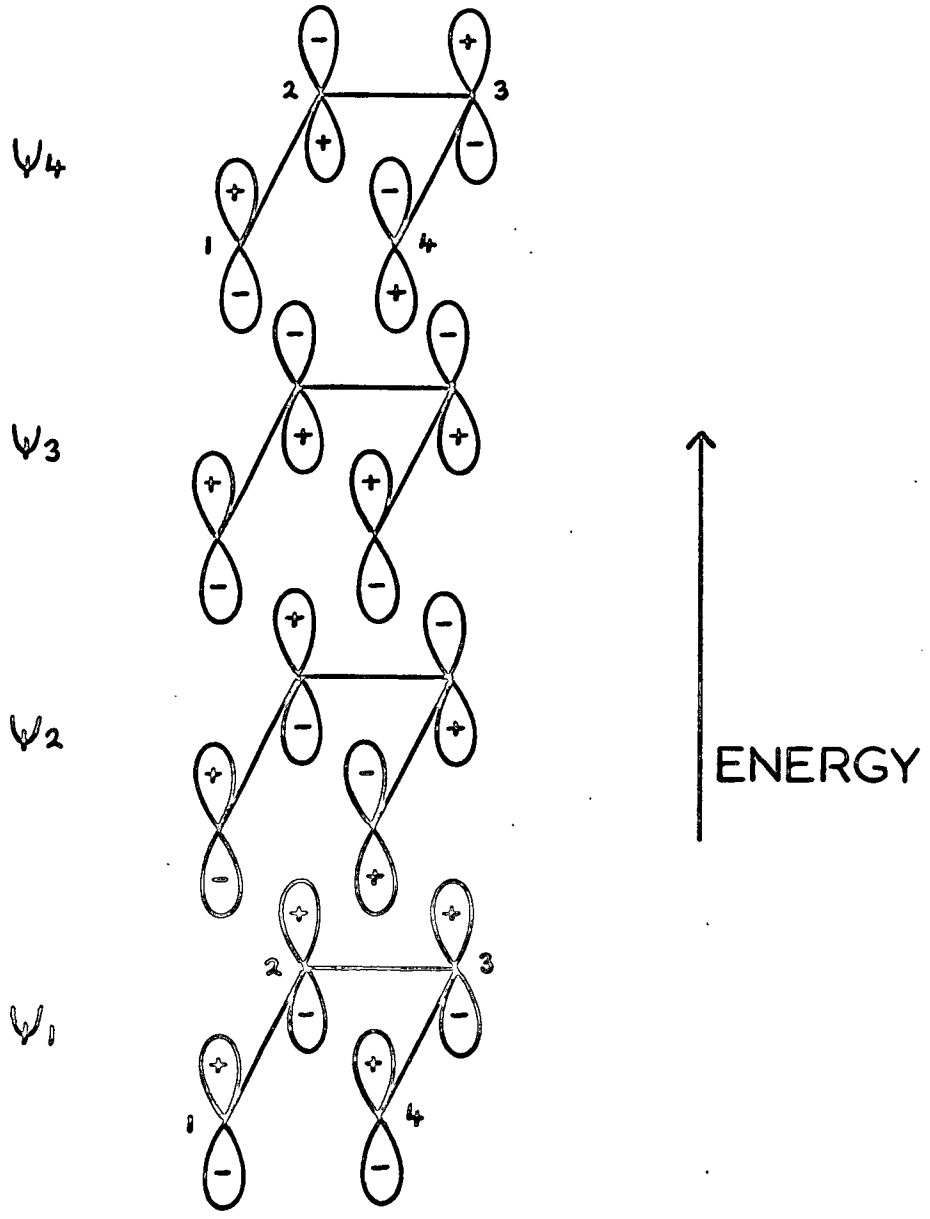
(4)

(5)


ψ4
ψ3
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1
2
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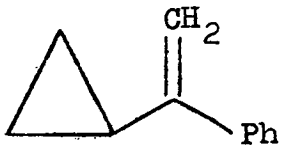
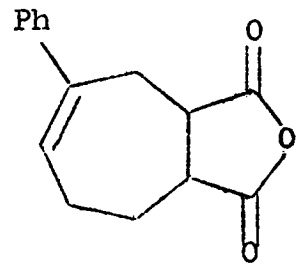
4
ENERGY

similar manner to a conjugated diene, readily forming a stable adduct(2) with maleic anhydride.



(1)

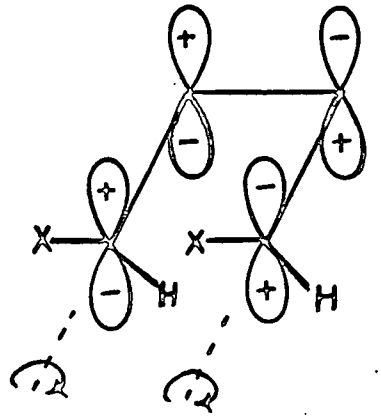
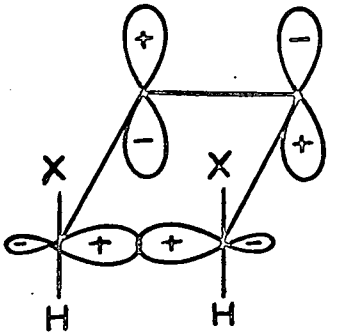


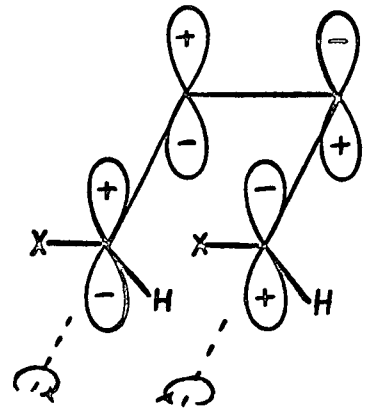
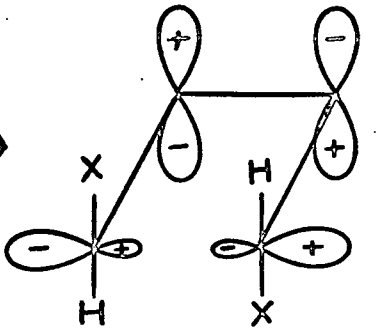
(2)

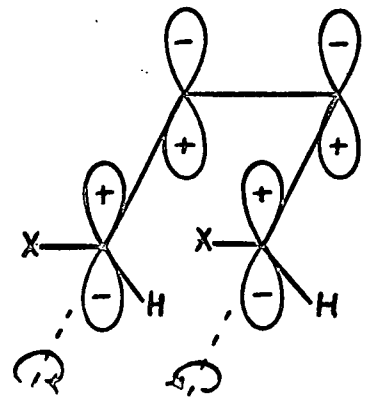
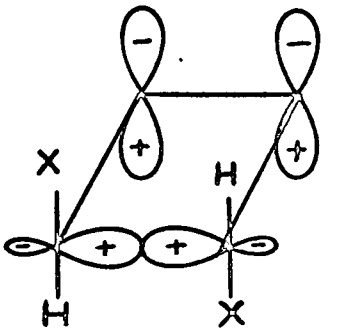
However it has been pointed out[5] that the halogenation of cyclopropanes is not of the relatively straightforward addition type as is often supposed and that in the absence of a suitable catalyst or special system, cyclopropane is unreactive towards bromine. When halogenation does occur, addition products are formed along with substitution products and are not necessarily in predominance.

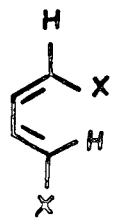
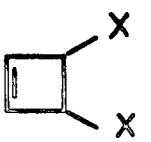
1.3 THE CONSERVATION OF ORBITAL SYMMETRY

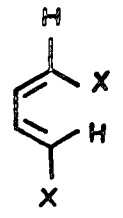
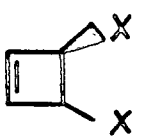
Complete stereospecificity is characteristic of a large class of ring opening and cyclisation reactions. For example, the thermal ring opening reactions of cis-dimethylcyclobutene(3) and its trans-isomer(4) have been shown[6] to give only cis, trans- and trans, trans-hexa-2,4-dienes respectively. This type of process which involved the interconversion of a conjugated polyene and a cyclic structural isomer formed by bonding between the terminal carbon atoms is termed electrocyclic.

Ψ_2  CON  (6)

Ψ_2  DIS  (7)

Ψ_3  DIS  (8)

 $\xrightarrow[\text{CON}]{\Delta}$  (9)

 $\xrightarrow[\text{DIS}]{h\upsilon}$ 

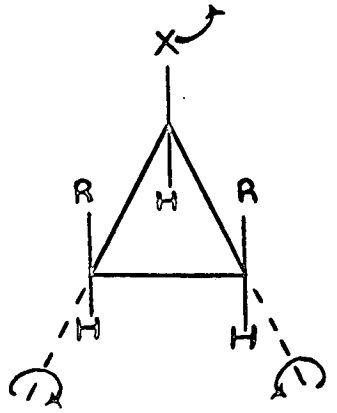
Woodward and Hoffmann in 1965 proposed[7] a theory to rationalise electrocyclic reactions. Since that time they have developed[8] their theory to include all pericyclic reactions, that is reactions in which all first order changes in bonding relationships take place in a concerted fashion. This includes electrocyclic reactions, cycloadditions and cycloreversions, sigmatropic reactions, group transfers and eliminations and others. This theory takes the form of a series of selection rules for the prediction of the feasibility and steric course of the change under consideration, and has been widely reviewed.[9,10,11]

Application of the Hückel technique to the atomic orbitals which form the π-electron system of butadiene allows the construction of four molecular orbitals Ψ_1 to Ψ_4(5). Now, the cyclisation of butadiene to cyclobutene requires rotation about both the C_1-C_2 and C_3-C_4 carbon to carbon bonds. By definition, if these rotations occur in the same direction about both bonds this is referred to as a conrotatory mode and conversely concerted rotation in opposite directions is disrotatory. Woodward and Hoffmann proposed that the highest occupied molecular orbital should determine which mode of rotation occurs. In the case of butadiene this is Ψ_2 for a thermal process and the stereochemical and orbital consequences of each mode are depicted in (6) and (7). Thus a conrotatory process leads to a bonding situation between C_1 and C_4 with a corresponding lowering of energy in the system, whereas a disrotatory process will lead to an antibonding situation and an increase in energy. In

photochemical processes however the lowest unoccupied molecular orbital is Ψ_3 and by analogy with the foregoing discussion a disrotatory process should be preferred for the photochemical cyclisation of butadiene(8). This means that the thermal and photochemical cyclisations of substituted butadienes will have different stereochemical consequences(9), and because of microscopic reversibility, the reverse of these cyclisations should occur along the same favoured paths - in other words the orbital symmetry of the system is conserved. This is in fact found to be the case.

The same basic treatment as applied to butadiene can be extended to other polyene cyclisations and the results take the form of a general rule: Thermal electrocyclic reactions of a $k\pi$ electron system will be disrotatory for $k = 4q + 2$, but conrotatory for $k = 4q$ ($q = 1,2,3...$); for photochemical processes involving the first excited state these relationships are reversed. The all important role of the highest occupied orbitals in thermal processes has been justified by the authors[8] - and the molecules themselves! These orbitals can be considered to contain the "valence electrons" of the molecule and, in the same way that atomic valence electrons exert a great influence on atomic processes it can be argued that the electrons in the highest occupied molecular orbital will determine the consequence of a ground state molecular process.

A more comprehensive treatment involving the use of correlation diagrams for the prediction of the stereochemical



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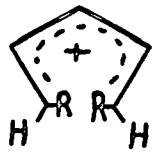
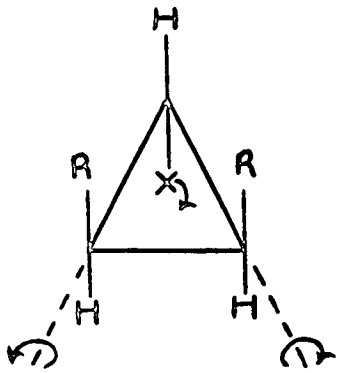


(10)



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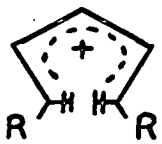

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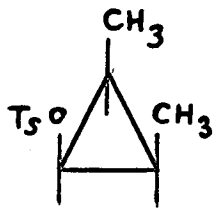
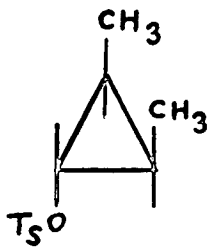




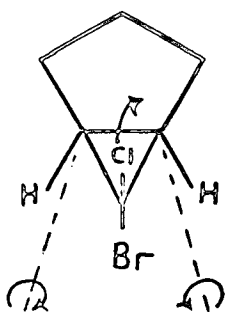
(12)

RELATIVE RATES OF ACETOLYSIS AT 150° :-

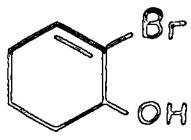
1·0

4·0

18,000



$AgNO_3/H_2O$



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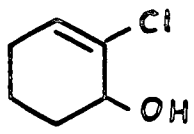
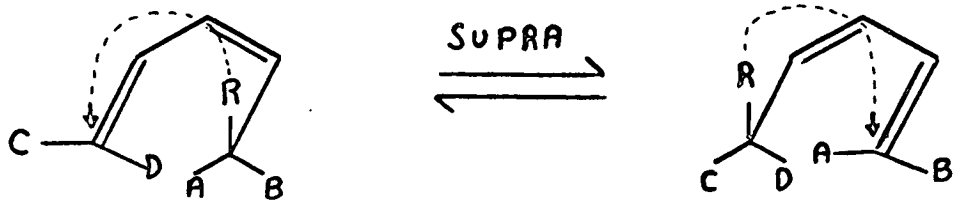


(15)

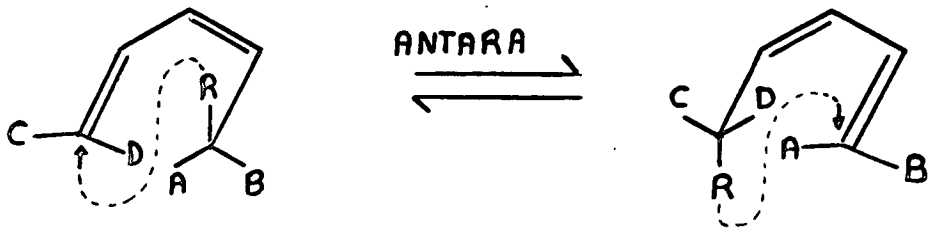
consequences of electrocyclic processes was introduced by Longuet-Higgins and Abrahamson[12] and adopted later by Woodward and Hoffmann. This approach has the advantage that all the orbitals Ψ_1- Ψ_4 of the butadiene and the orbitals that arise from them in the cyclobutene are taken into account by consideration of their symmetry with respect to the symmetry elements maintained throughout the concerted process. However many systems of interest possess no molecular symmetry and the construction of correlation diagrams becomes complicated or impossible in such cases.

Observations on the solvolysis of cyclopropyl compounds are also consistent with the above rule. The ring opening of cyclopropyl compounds should be concerted with the departure of the leaving group and directed by the principles of electrocyclic reactions, since this is in effect the conversion of a cyclopropyl cation to an allyl cation. The concerted ring opening of the cation, a $4q + 2$ π-electron system where $q = 0$, would therefore be disrotatory in the ground state. It also follows that if the leaving group is syn- to cis-substituents the ring opening should be disrotatory inwards(10), but if it is anti- the disrotatory mode should be outwards(11). The latter process would be expected to be much faster because it results in relief of steric strain. The relative rates of solvolysis[13] of cyclopropyl tosylates(12) completely fulfil this prediction.

This concept of cyclopropane ring opening also leads to the prediction that in bicyclic cyclopropanes an endo-leaving



(16)



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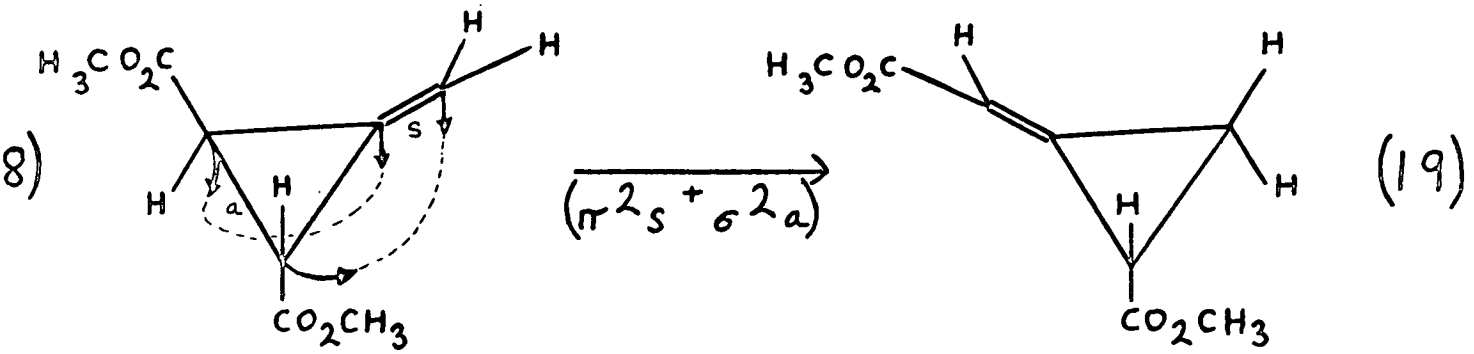

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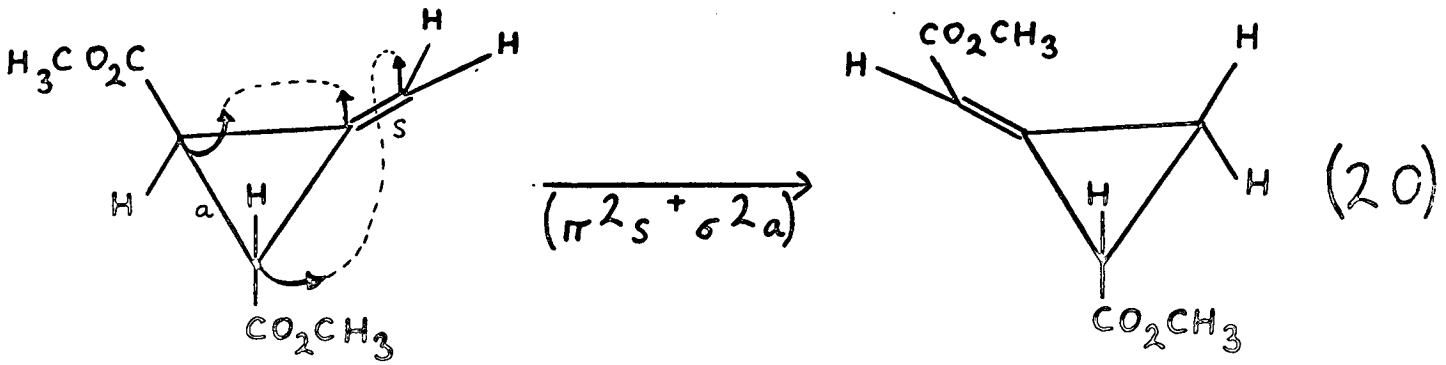

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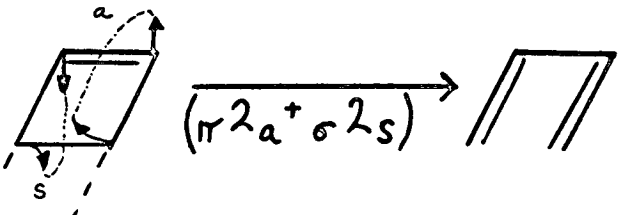


(21)

group should be preferred, the exo-leaving group requiring disrotatory outward motion which would introduce severe strain to the ring system. Thus solvolysis[14] of the gem-dihalocyclopropane(13) leads to the bromocyclohexanol(14) and not the chloro-isomer(15) as might be expected on the basis of leaving group potential.

In extending their predictions to sigmatropic rearrangements and cycloadditions, Woodward and Hoffmann defined a suprafacial process as one in which bonds made or broken lie on the same face of the system undergoing reaction. Conversely in an antarafacial process the newly formed or broken bonds lie on opposite faces of the reacting system. Thus a 1,5 shift of a group R may occur suprafacially(16) or antarafacially(17), the stereochemical consequences being different in each case. In addition, this shift may occur with retention or inversion at the migrating centre. Obviously inversion can only occur when the migrating group possesses an accessible π-orbital, and thus all hydrogen migrations are considered to occur with retention of configuration. Consideration of a transition state made up by the combination of the orbitals of the migrating group together with the highest occupied orbital of the polyenyl radical from the carbon framework between the migration termini leads to the predictions below:

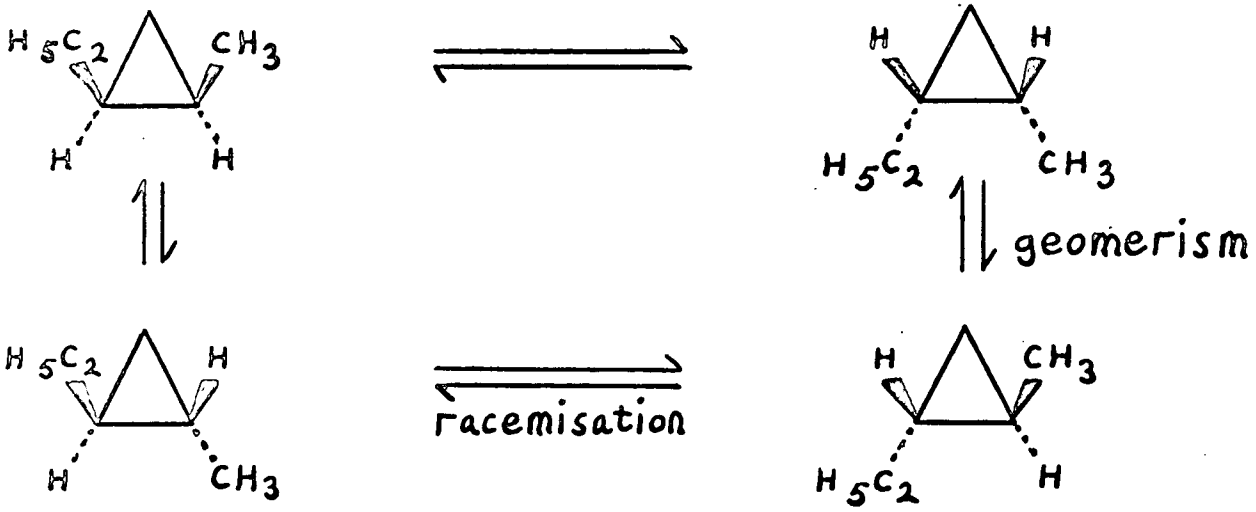
Migration	
1,3; 1,7;...	Thermally allowed antarafacial with retention.
	Thermally allowed suprafacial with inversion.

1,5; 1,9;... Thermally allowed antarafacial with inversion.
Thermally allowed suprafacial with retention.

Studies on the thermal rearrangement of optically active Feist's ester(18) have demonstrated[8] that the reaction occurs stereospecifically to give optically active products. Of the two symmetry allowed skeletal processes - 1,3 suprafacial migration with inversion at the migrating atom, and 1,3 antarafacial shift with retention - the latter is rendered inaccessible by the constraints imposed by the system. The former process can be realised in two electronically identical, but sterically different, ways to give the geometrical isomers(19),(20). The experimental results are in full agreement with this prediction.

Woodward and Hoffmann have now presented[8] a convenient generalisation for all pericyclic changes. Each bond breaking or forming component may participate suprafacially(s) or antarafacially(a) in the reaction. Suprafacial and antarafacial participation of π-systems is self evident. In the case of σ-bonds, suprafacial participation involves either inversion or retention at both centres whereas inversion at one centre and retention at the other is regarded as antarafacial participation. A ground state thermal pericyclic change is symmetry-allowed when the total number of $(4q + 2)$s and $(4r)$a components is odd. The prefixes $(4q + 2)$ and $(4r)$ represent the number of electrons in each component involved in the process, where (q) and (r) are integers and can take the values 0,1,2... Conversely when the

(26)



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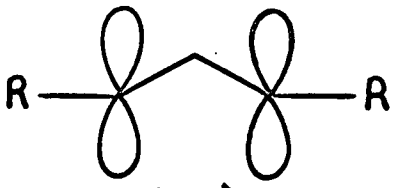
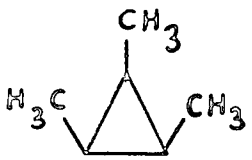
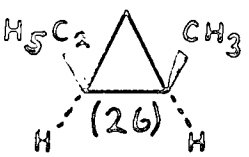


(25)

TABLE I

	E_a (Kcal.mole^{-1})		$\Delta S^{\neq}$ (e.u.)
 (22)	59·4	geomerism	8·3
 (23)	60·9	"	10·8
 (26)	57·8	racemisation and geomerism	6·7
 (27)	54·4	"	7·2

total of $(4q + 2)\underline{s}$ and $(4r)\underline{a}$ components is <u>even</u> the reaction is thermally forbidden and photochemically allowed.

Application of this approach to the ring opening of cyclobutenes implies that the allowed thermal process must have one suprafacial and one antarafacial component (i.e. $\pi^2{}_a + \sigma^2{}_s$) and this must therefore involve a ~~dis~~con rotatory process(21). Similarly the two electronically equivalent modes of rearrangement for Feist's ester(18) are thus symmetry allowed ($\pi^2{}_s + \sigma^2{}_a$) processes.

1.4 REARRANGEMENTS OF SATURATED CYCLOPROPANES

The overall thermal unimolecular rearrangements of saturated cyclopropane derivatives involve three competing processes:-

(a) geometrical isomerisation of ring substituents,

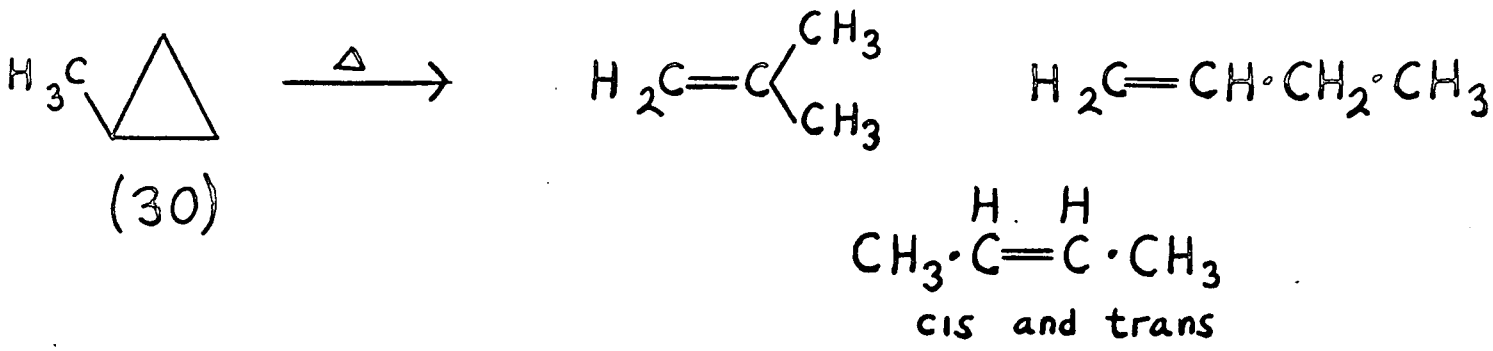
(b) racemisation of optically active ring substituents,

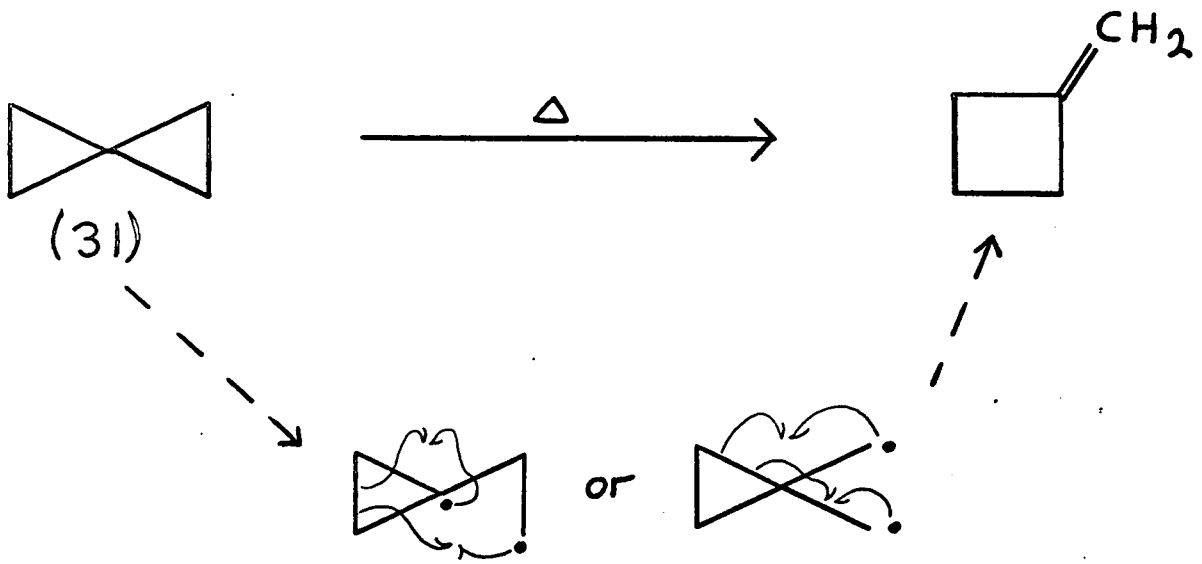
(c) structural isomerisation of the hydrocarbon system.

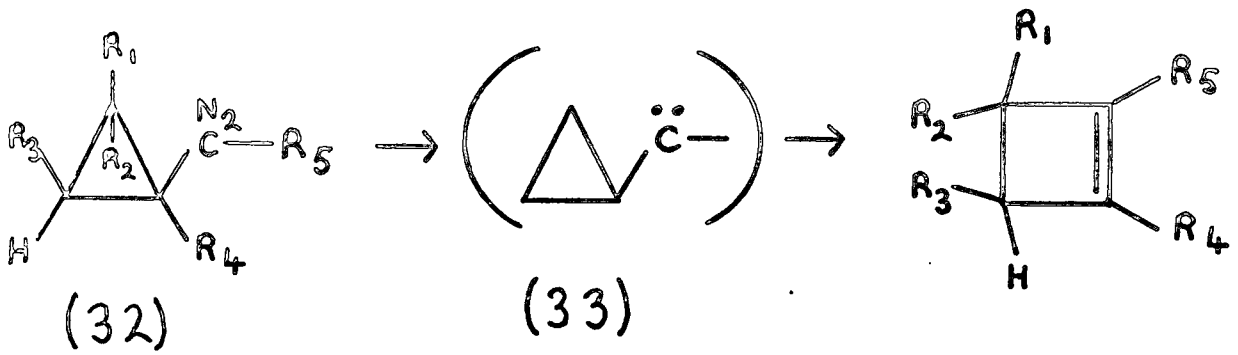
The first two of these involve thermal equilibrium of the possible products with resultant retention of the cyclopropane ring whereas the third leads to formation of open chain isomers and is irreversible.

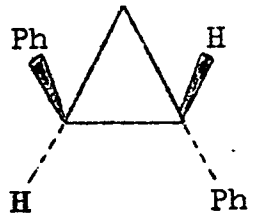
The thermal equilibrium of <u>cis</u>-1,2-dimethylcyclopropane(22) and its <u>trans</u>-isomer has been shown[15] to occur more rapidly than does ring cleavage to form pentene. A similar geometrical isomerism has been observed[16] with <u>cis</u>-1,2,3-trimethylcyclopropane(23)

at 400°. It therefore appears that the cyclopropane can undergo ring opening, bond rotation and reclosure without the occurrence of a hydrogen shift which could result in the formation of a ring opened product. The mechanism of these rearrangements can be rationalised in terms of either homolytic fission of a cyclopropane bond to form a distinct diradical intermediate(24) which can then undergo bond rotation followed by reformation or, a process involving concerted bond cleavage, rotation and bond formation by way of a transition state involving the proposed[17] π-cyclopropane(25). Attempts[18] to scavenge a diradical intermediate with alkyl iodide have been unsuccessful. However the optically active alkylcyclopropane(26) undergoes geomerism and racemisation when heated,[19] as illustrated in scheme I, and kinetic measurements have shown that both processes occur at a similar rate. If a π-transition state was involved, then concerted bond rotation and formation could readily result in racemisation of the starting material but geomerism would necessarily involve a "change-over" of rotational modes which is unfavourable, and thus the rate of racemisation would be expected to be appreciably greater than the rate of geomerism. A freely rotating diradical intermediate has no such requirement. Similar results have been obtained[20] with the optically active deuteriocyclopropane(27). Alternatively it has been estimated[21] that the rate of racemisation of optically active trans-1,2-diphenylcyclopropane(28) is 1·5 times as fast as geomerism, but in this case geometrical isomerism to form the cis-isomer(29) is unfavourable on steric consideration.

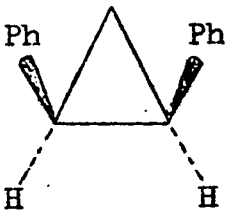

H3C
Δ
H2C=C(CH3)2
H2C=CH·CH2·CH3
(30)
H H
CH3·C=C·CH3
cis and trans


Δ
CH2
(31)
or


R1
R3
R2
N2
C
R5
H
R4
(32)
(33)
R1
R5
R2
R3
R4
H

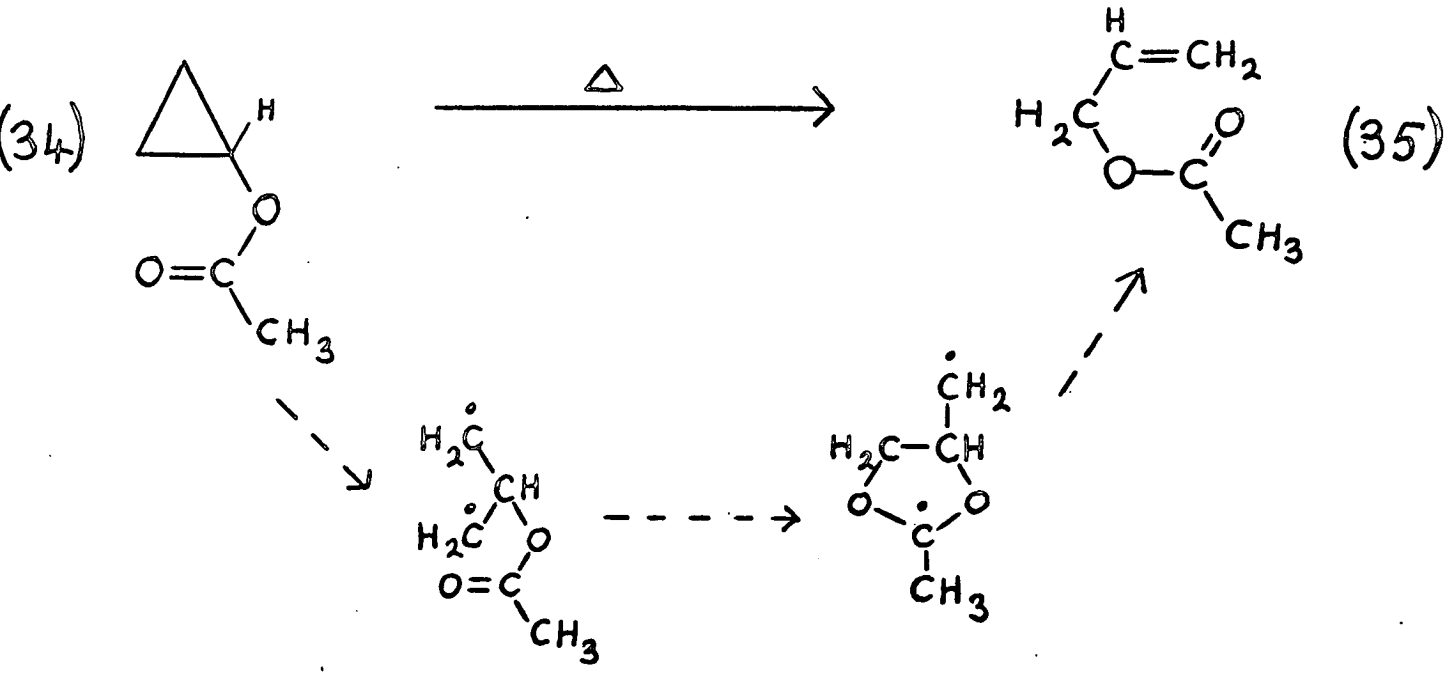


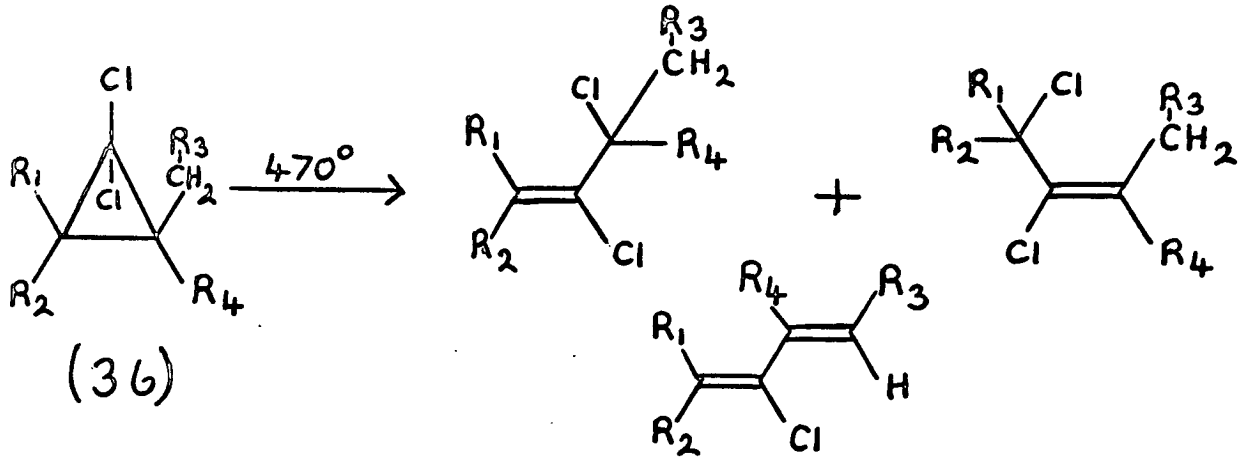
(28)



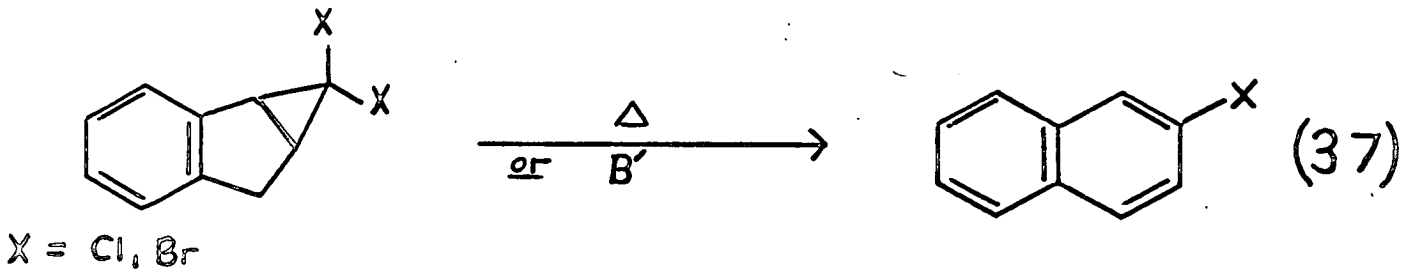
(29)

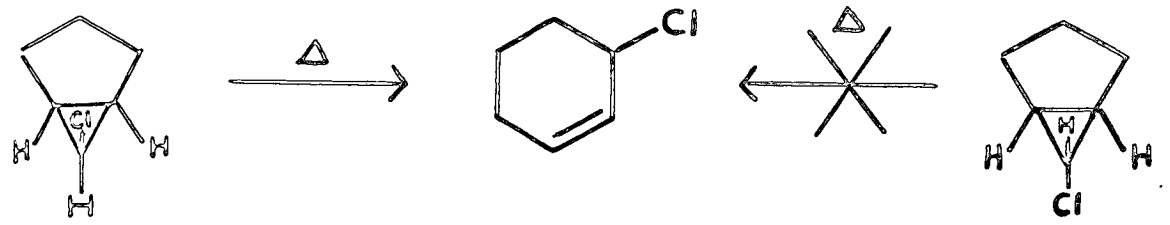
The bulk of the evidence in favour of a diradical intermediate is obtained from the kinetic parameters of these rearrangements, the relevant data being presented in table I. The relatively high values for the activation energy (E_a) and the relatively large positive entropies of activation ($\Delta S^{\ddagger}$) are characteristic[22] of carbon-carbon bond cleavage to form a discreet intermediate with a considerably higher degree of internal rotation as compared to its precursor. Further evidence in support of a diradical intermediate is obtained from the thermolytic structural isomerisation of cyclopropanes, although this cannot necessarily be directly related to the preceding cyclic isomerisation processes. The pyrolysis of cyclopropane itself[23] can lead to formation of propene. It is evident from the preceding ring isomerisation studies that a hydrogen shift is the rate determining step if this reaction follows a radical path. The pyrolysis of alkylcyclopropanes is often rather unselective, methylcyclopropane(30), for example, yielding[24] all the possible butenes. This, together with the high values of E_a (65·0 Kcal.mole^{-1}) and $\Delta S^{\ddagger}$(9·2 e.u.), supports an open





(36)





(38) (39) (40)

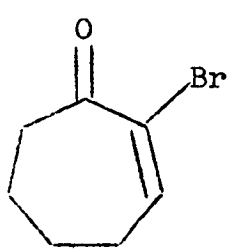
chain intermediate, the activation energy being somewhat larger than for geometrical and optical isomerisation processes (table I) due to the necessary cleavage of carbon-hydrogen bonds. Pyrolysis of bicyclopentane gives cyclopentene as the only product,[25] and spirocyclopentane(31) undergoes thermal ring expansion[26] to form methylenecyclobutane, presumably by a radical insertion process. It is significant in the latter reaction that the value of $\Delta S^{\ddagger}$ (11·1 e.u) is particularly high, and is attributable to the relatively large increase in rotational freedom which accompanies the ring opening of this rigid spirohydrocarbon.

Thermal or photochemical rearrangement of phenylcyclopropane has been shown[27] to form a mixture containing n-propylbenzene, α- and β-methylstyrene and a number of degradation products. It is concluded that there is no clear cut low energy path for ring destruction and that the reaction probably follows a radical mechanism. The thermal pyrolysis[28] of the cyclopropyldiazomethane(32) forms the cyclopropylcarbene(33) which can then undergo intramolecular insertion. This reaction provides a convenient route to cyclobutene derivatives and has been shown to be general for various alkyl substituents, R_1-R_5.

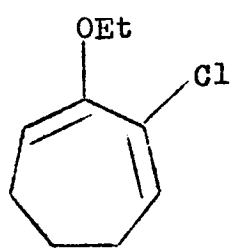
The thermal rearrangement[29] of cyclopropyl acetate(34) appears to proceed by way of a cyclic diradical intermediate which can then ring open to form the allyl acetate(35), this reaction appearing to be general for alkylcyclopropyl acetates. However 1- and 2-arylcyclopropyl acetates give rise to numerous products including methylphenylacetylene, propiophenone and indene

derivatives which can also all be formed by way of cyclopropane homolysis.

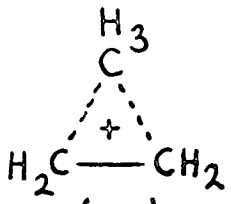
Themolysis of simple gem-dichlorocyclopropanes(36) has been shown[30] to form β-chloroallylchlorides and β-chloro-1,3-dienes. This can be rationalised by assuming the reaction to proceed by way of a quasi-ionic transition state in which the emerging cyclopropyl cation is isomerising to an allylic cation by an electrocyclic process. Further support[31] for a concerted mechanism comes from the corresponding dibromocyclopropane rearrangements which occur under relatively mild conditions (160-200°) to give similar products. Bicyclic gem-dihalocyclopropanes[32] however undergo ring expansion on heating, together with elimination of hydrogen halide. This probably occurs by rate determining ionisation of the carbon-halide bond, with concerted disrotatory ring opening to give products. The process can be conveniently accelerated by the presence of base and is of considerable synthetic important in the formation of β-halonaphthalenes(37). This reaction has more recently[33] been extended to the formation of cycloheptenones(41) and cycloheptadienes(42) by starting from the appropriate vinyl ethers. The preference of an



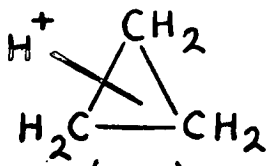
(41)



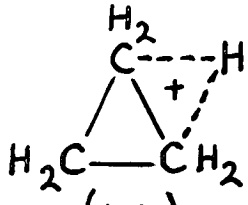
(42)



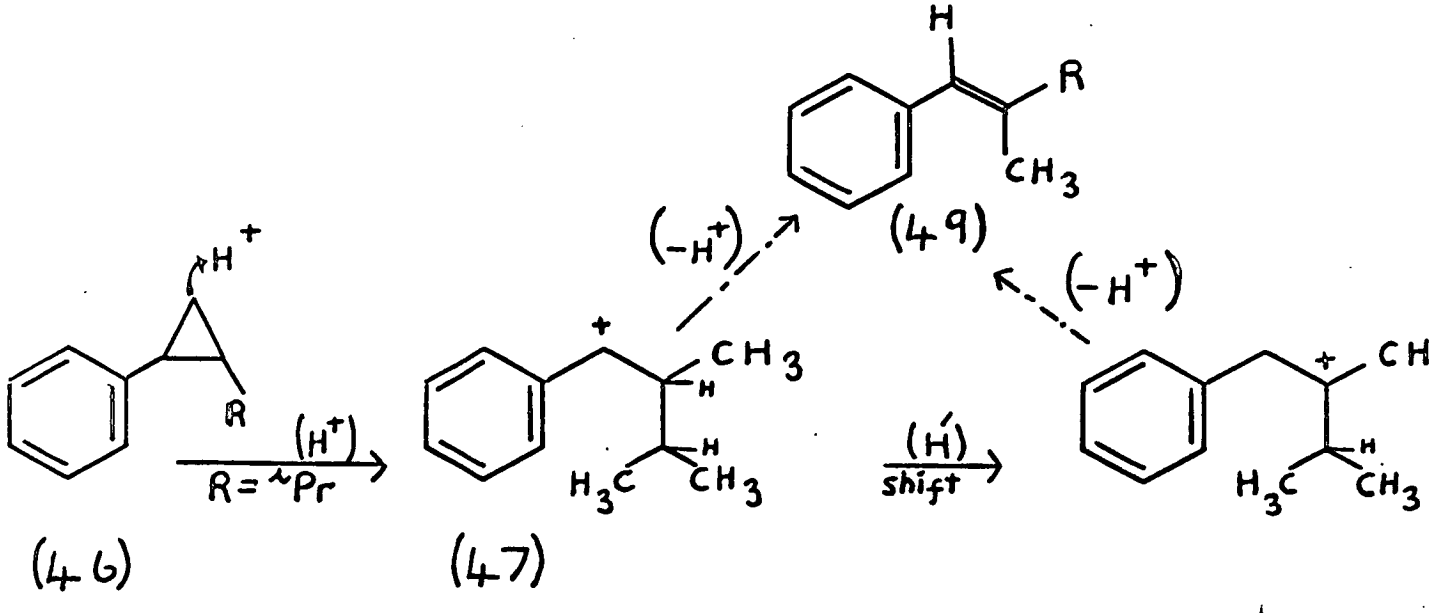
(43)



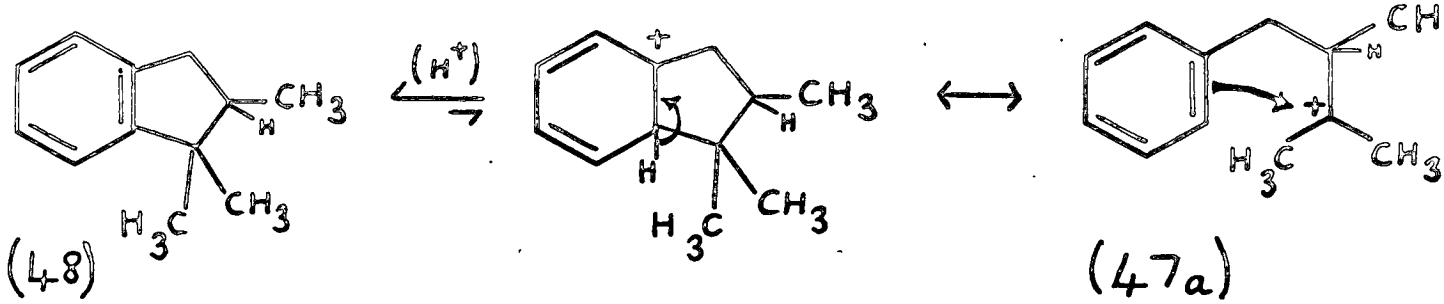
(45)



(44)



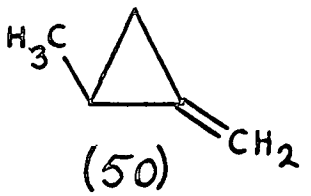
(46) (47) (49) (47a)



(48)

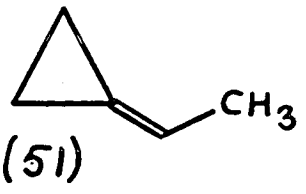
endo-leaving group during the concerted rearrangement of halocyclopropanes has previously been discussed (section 1.3). Thus[34] thermolysis of endo-chlorobicyclohexane(38) is facile at 126° to form chlorocyclohexene(39), whereas the exo-isomer(40) is inert and only undergoes elimination at 300° to form benzene.

The cyclopropane ring is readily cleaved[35] by the action of acid, but strong evidence has been presented[36] for the existence of protonated cyclopropanes as intermediates. The evidence available however cannot distinguish between the three possible forms, namely the methyl-bridged(43), the edge-protonated(44) or the face-protonated ion(45). The acid catalysed fission of substituted cyclopropanes takes place according to a modified Markownikoff rule, the proton adding to the least substituted carbon atom and cleavage occurring to give the most stable carbonium ion. Thus the arylcyclopropane (46, R = ^{i}Pr.) forms[37] a resonance stabilised carbonium ion(47) on treatment with acid, which can then undergo hydride ion transfer to form the 3°-carbonium ion(47a). The equilibrium is displaced by intramolecular electrophylic attack on the benzene ring followed by proton loss to give a thermodynamically more stable product(48). However the yield of the indane derivative is low, the majority of the product being polymeric material probably formed from intermolecular carbonium ion attack on the co-formed styrene(49, R = ^{i}Pr.). Support for a competitive elimination and cyclisation process comes from similar reactions involving the arylcyclopropanes(46, R = CH_3) and (46, R = Et). In these cases only polymeric material was isolated, the formation of a relatively stable 3°-carbonium ion

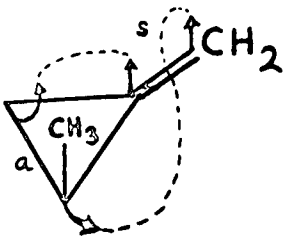


(50)

$\xrightleftharpoons{190^\circ - 230^\circ}$

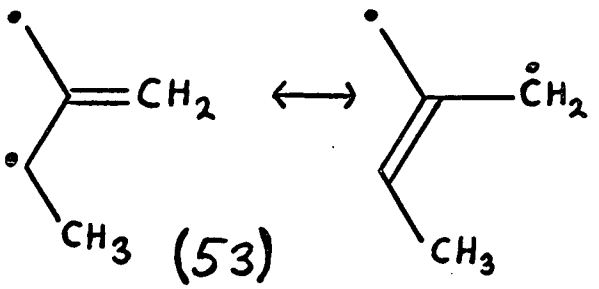


(51)

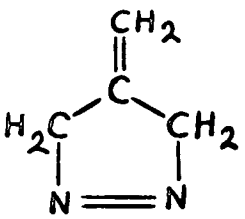


$(\pi^2 s + \sigma^2 a)$

(52)

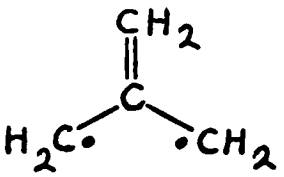


(53)



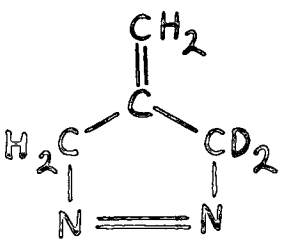
(54)

$\xrightarrow[-185^\circ]{h\upsilon}$



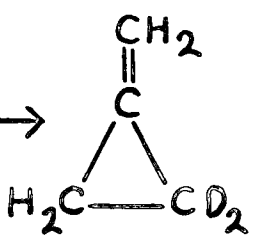
(55)

$\longleftrightarrow$ etc.



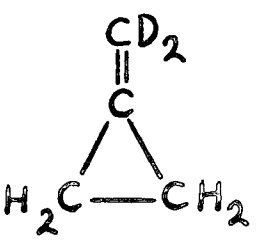
(56)

$\xrightarrow{160^\circ - 190^\circ}$



(57a)

+



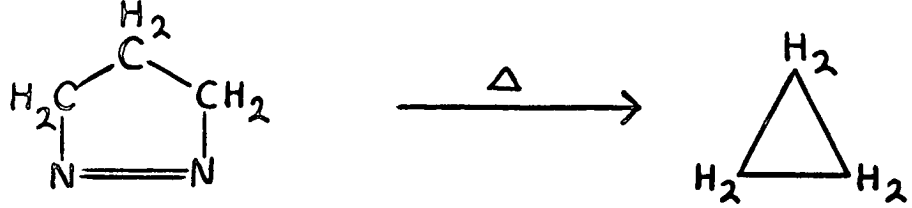
(57b)

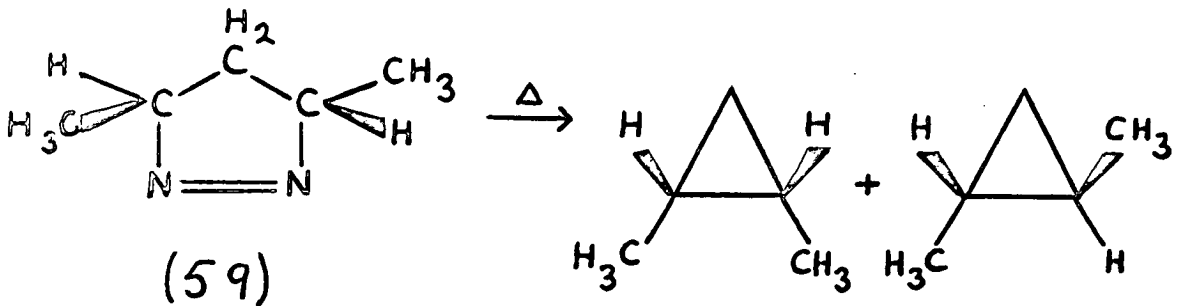
prior to cyclisation being impossible.

It is noteworthy that cyclopropanol readily rearranges under the action of acid or base to form propionaldehyde.[38]

1.5 REARRANGEMENTS OF UNSATURATED CYCLOPROPANES

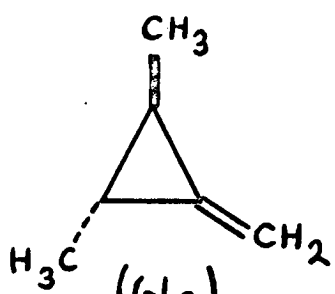
2-Methylmethylenecyclopropane(50) and ethylidenecyclopropane(51) form an equilibrium mixture when heated.[39] The energy of activation (40·4 Kcal.mole^{-1}) and entropy of activation (3·8 e.u) for this process are appreciably lower than those for the geomerism of the saturated counterpart(25, table I; E_a= 59·4 Kcal.mole^{-1}; $\Delta S^{\ddagger}$ = 8·3 e.u.), which is in support of an ordered transition state being involved in the present isomerisation. This reaction is a symmetry allowed ($_{\pi}2_s + _{\sigma}2_a$) process(52) where r = 1). However distinct bond cleavage to form the trimethylenemethane type diradical(53) would also be expected to involve a lowering of the E_a and $\Delta S^{\ddagger}$ relative to (25) due to the resonance stabilisation and resulting restricted internal rotation encountered when this intermediate is formed. The trimethylenemethane diradical has been predicted to be a ground state triplet and thus detectable by electron spin resonance,[40] photolysis of the methylenepyrazoline(54) at -185° showing a stable triplet which decays when warmed to -150°. Independent work[41] involving the deuteriolabelled methylenepyrazoline(56) has shown that thermal pyrolysis of this compound forms the methylenecyclopropanes(57a,b) in the ratio of approximately 2:1. This preference of deuterium for the ring sites would be expected if

(58) 



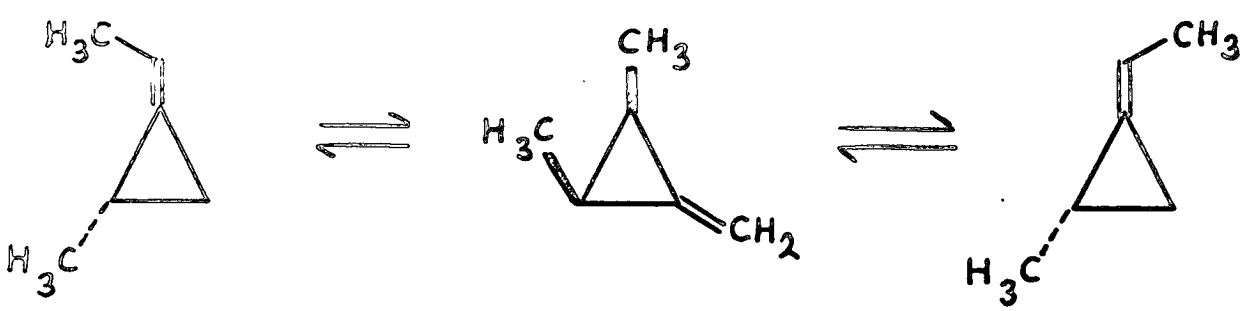
(59)

72·6% (60a) + 25·4% (60b)



(61a)

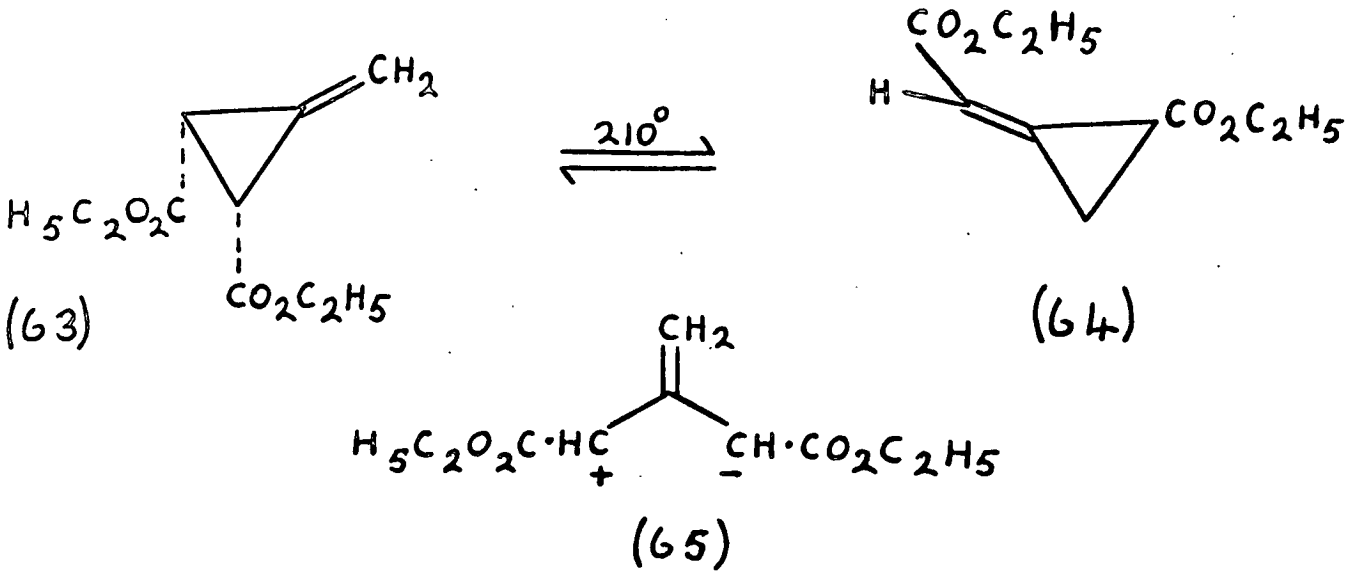
$(\pi 2_s + \sigma 2_a)$



(62a) (61b) (62b)

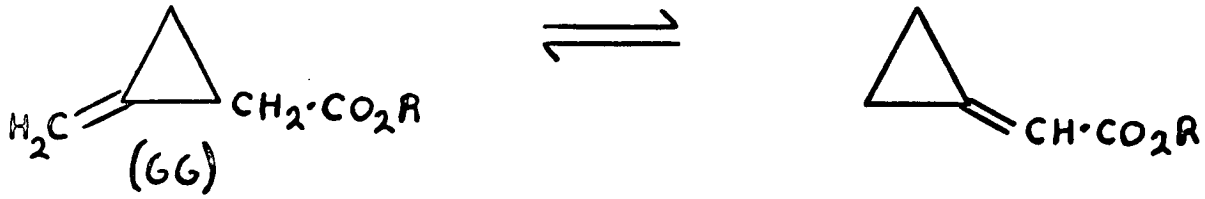
a resonance stabilised diradical was involved but the same result would arise by a concerted process. Therefore although a diradical has been conclusively identified during the photolysis of methylenepyrazoline, this does not necessarily indicate that distinct bond rupture is the only process involved, nor can this result be directly related to the thermolysis of methylenecyclopropanes. It is significant in this respect to consider the pyrolysis of pyrazolines themselves. Thus pyrolysis[52] of pyrazoline(58) forms cyclopropane, the kinetic parameters of this reaction being:- E_a = 42·2 Kcal.mole^{-1}; $\Delta S^{\ddagger}$ = 11·2 e.u. This large positive entropy of activation strongly supports a diradical process being involved. However thermolysis[43,44] of the trans-dimethylpyrazoline(59) leads to formation of the isomeric cyclopropanes(60a,b), the symmetry allowed isomer (60a) which results from one net inversion of configuration being in predominance, the proportions suggesting approximately equal contributions by both mechanisms in this instance.

The deuteriolabelled methylenecyclopropane(63a) undergoes[45] geometrical isomerisation of the ring deuterium atoms when heated, which would be expected in terms of either a concerted or diradical process. However the optically active trans-dimethylenecyclopropane(61a) has been shown[46] to undergo less than 50% racemisation after 58·5% of reaction to give the optically active ethylidenecyclopropanes (62a,b) which is conclusive evidence in support of the large contribution of a concerted mechanism, being a symmetry allowed ($_{\pi}2_s + _{\sigma}2_a$) process. Conversely, the

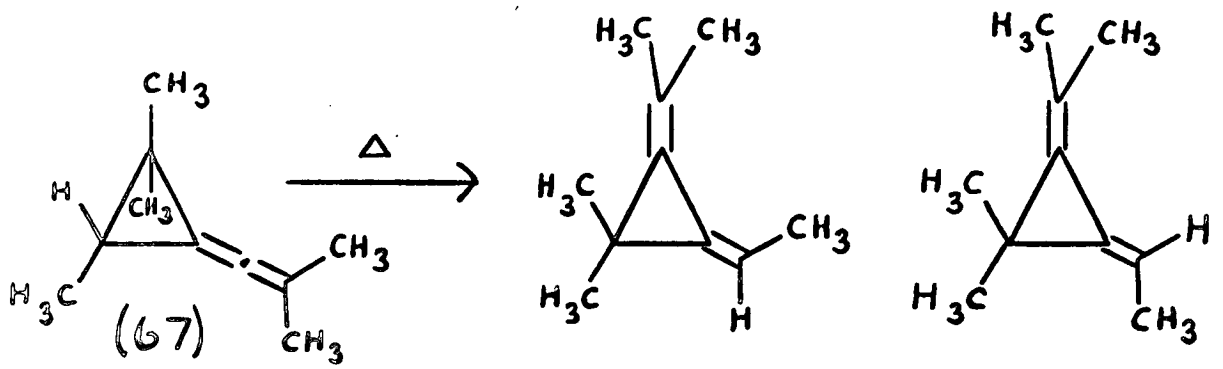


(63) (64)

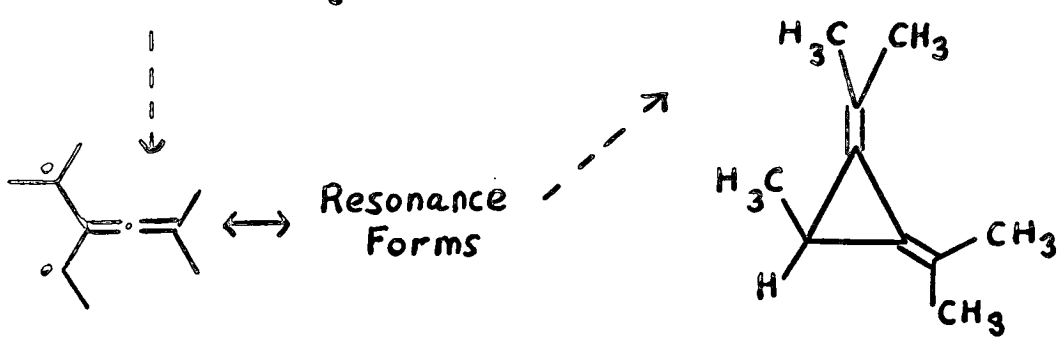
(65)



(66)



(67) (68)

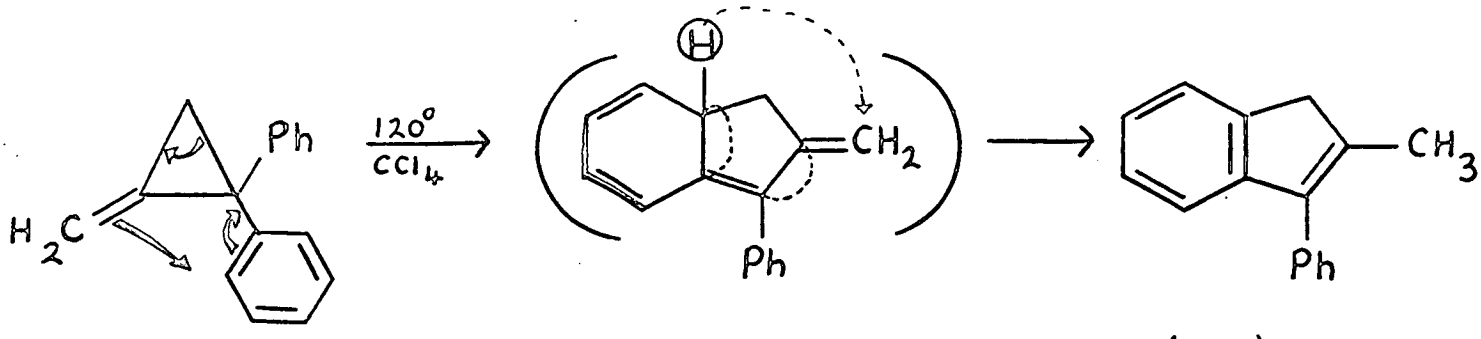


(63$_a$)

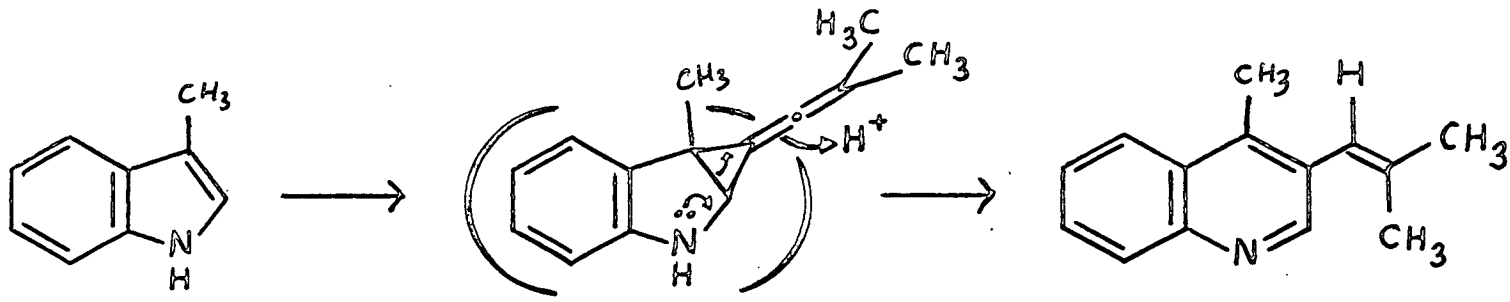
racemisation which does occur demands the co-existence of a diradical mechanism involving an open chain intermediate, although geomerism to form the cis-isomer(61b) is again symmetry allowed. A related isomerisation involving a high degree of retention of optical activity during the pyrolysis of Feist's ester(63) has already been discussed (Section 1.3). However there is again evidence[47] in this case for the partial racemisation of the products(64), which necessitates an open chain intermediate. This has been formulated as the zwitterion(65), although a diradical seems more reasonable. A similar rearrangement[48] occurs with the related methylenecyclopropane(66).

Crandall and Paulson have reported[49] that pyrolysis of the vinylidenecyclopropane(67), at low pressures through a flow system, forms the three isomeric dimethylenecyclopropanes(68). A resonance stabilised vinylidene diradical is postulated as the intermediate, but in view of the foregoing and material presented later(Section 3) it seems likely that there is at least a large contribution of a symmetry allowed ($_{\pi}2_s$ + $_{\sigma}2_a$) process.

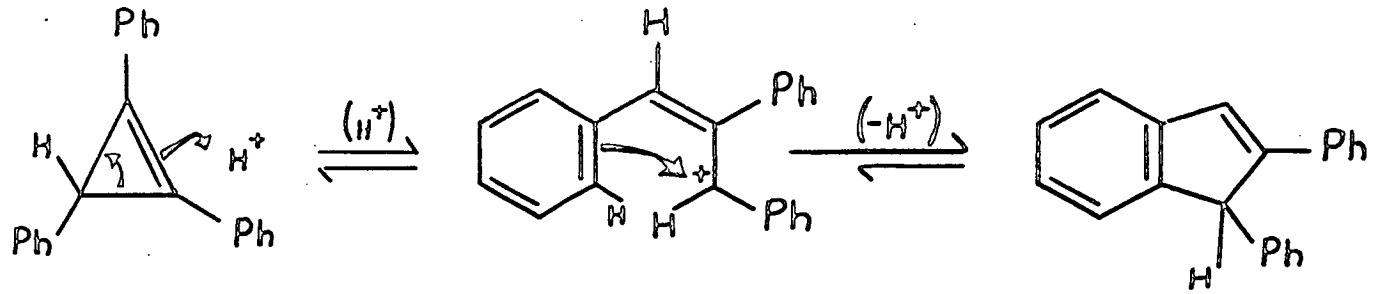
More recently[50] it has been observed that thermolysis of the optically active phenylmethylenecyclopropane(69) at 100°



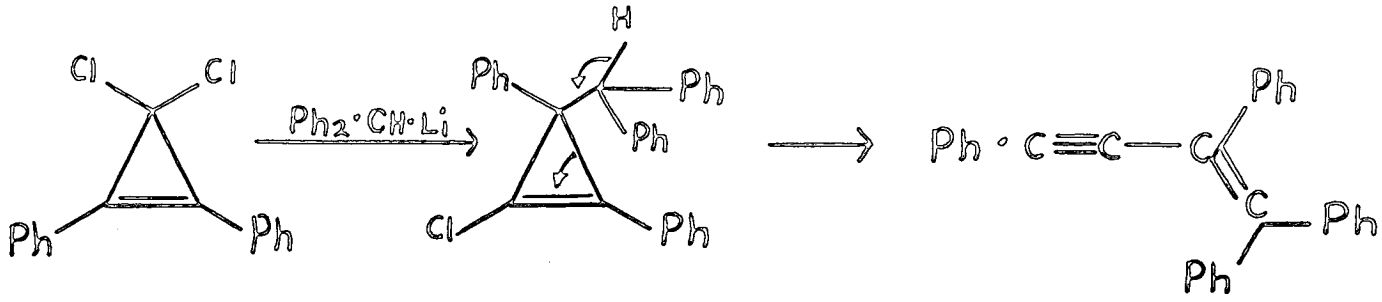
(71) (72)



(73) (74) (75)

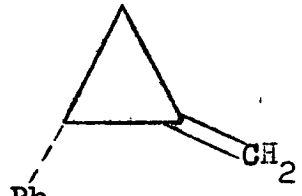


(76) (77) (78)

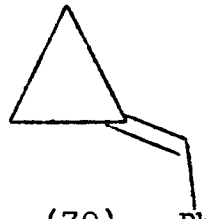


(79) (81) (80)

in chloroform leads to rapid racemisation of the starting material, which again may be realised in terms of a diradical or concerted mechanism. It is significant however that no



(69)



(70) Ph

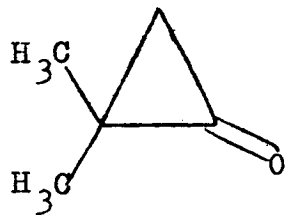
benzylidenecyclopropane(70) is detected which, although being apparently symmetry allowed, would probably not be expected to result from an open chain mechanism due to the preferred location of the intermediate radical at the aryl site. In contrast to the foregoing phenylmethylenecyclopropane thermolysis, diphenylmethylenecyclopropane(71) readily undergoes[51] ring expansion, when heated in carbon tetrachloride at 120°, to form the indene derivative(72). On consideration of the relatively mild conditions involved it seems likely that this is a concerted process, proceeding by way of an allowed 1,5 suprafacial hydrogen shift.

The attempted formation of a dimethylvinylidenecarbene adduct with skatole(73) led directly[52] to the ring expanded product(75). It is suggested that this product is formed by way of the unisolated vinylidenecyclopropane(74) which could undergo acid catalysed rearrangement with ring expansion under the mildly acid conditions of the work-up. By analogy with the indene analogue (Section 3.5) this seems very probable, although spontaneous thermal rearrangement

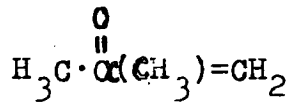
could also form the same product.

The vapour phase pyrolysis of cyclopropene[53] leads to the formation of methylacetylene, the proposed mechanism being directly analogous to its saturated counterparts (Section 1.4). Triphenylcyclopropene(76) undergoes facile ring expansion[54] on treatment with acid. The resonance stabilised carbonium ion(77) intramolecularly attacks the benzene ring to form the indene(78), thus displacing the equilibrium in favour of product formation. This process is analogous to the acid catalysed rearrangement of the phenylcyclopropane(46) already discussed, although in the present case the formation of other possible products is not recorded. An interesting rearrangement of dichlorodiphenylcyclopropene(79) provides a useful synthesis of tetraphenylbutenyne(80). Attack of diphenyllithium at the carbon-carbon double bond of (79) with expulsion of chloride ion probably forms(81). Subsequent dehydrochlorination would then lead to the enyne(80).

Cyclopropanone itself is unstable at room temperature[56] but increasing ring substitution promotes stability and pyrolysis of the dimethycyclopropanone(82) by passage through a vapour phase chromatograph induces rearrangement to methyl isopropenyl ketone(83), although pyrolysis at 250° causes degradation to isoprepene and carbon monoxide. Similarly, pyrolysis of 1,2-diphenylcyclopropanone[57] leads to diphenylacetylene and carbon monoxide. In general cyclopropanones are readily cleaved by thermolysis, acid or base.[56]

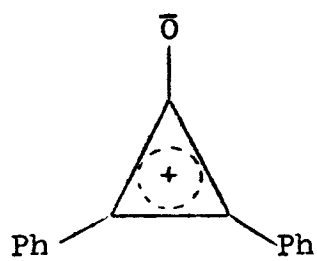


(82)

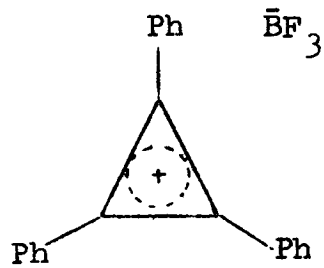


(83)

The remarkable stability of cyclopropenones is predicted from Hückel theory if,for example, 1,2-diphenylcyclopropenone exists as the cyclopropenyl catiom(84), in which case this is a stable ring system containing (4n + 2) π-electrons where n = 0.



(84)

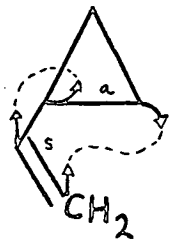


(85)

The triphenylcyclopropenyl cation(85), originally prepared by Breslow[58] as the fluoroborate, is thermally stable up to its melting point.

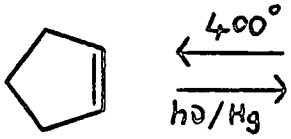
1.6 REARRANGEMENTS OF VINYL AND RELATED CYCLOPROPANES

The rearrangements of vinylcyclopropanes have received wide attention[59] and this has often resulted in conflicting opinion[22] as to the mechanistic nature of these reactions, and



$(\pi 2_s + \sigma 2_a)$

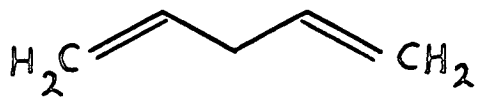
(86a)



400°

hν/Hg

hν/Hg

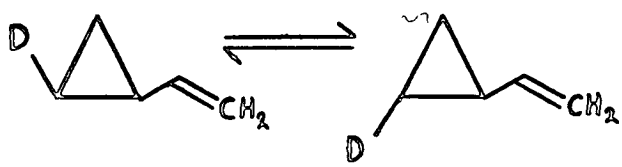


(87) (86) (89)

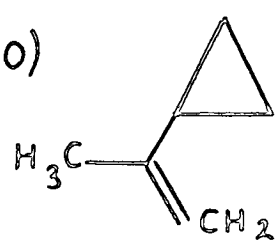
hν/Hg

nil

(88)

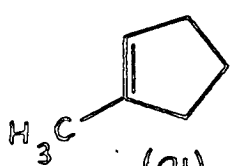


(90)

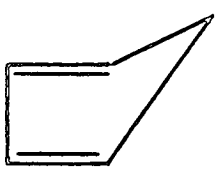


hν

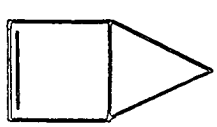
$(\pi 2_s + \sigma 2_s)$?



(91)

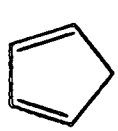


(Con)



hν

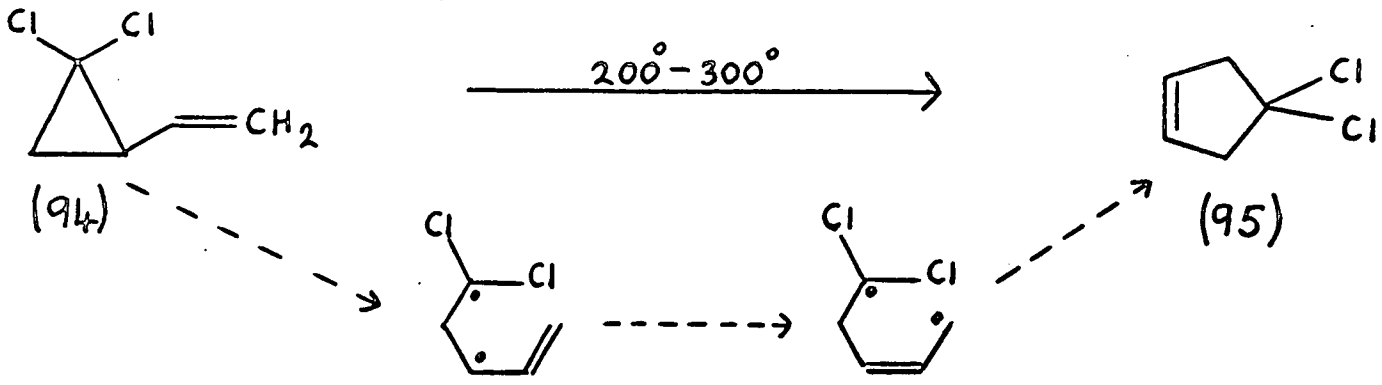
(Dis)

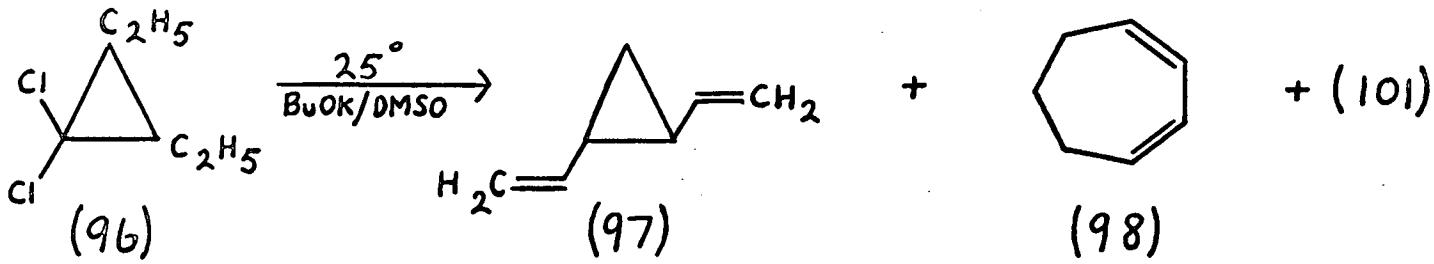


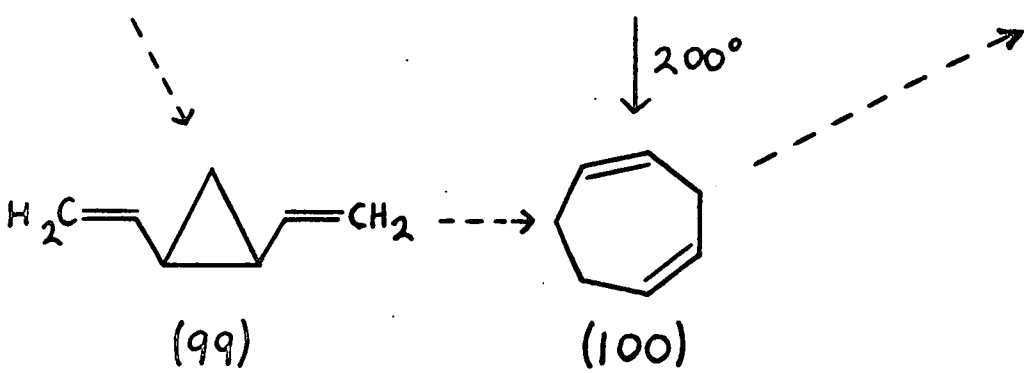
clear-cut distinctions cannot always be made between concerted and diradical pathways. The gas phase pyrolysis[60] of vinylcyclopropane(86a) itself leads to the formation of cyclopentene. The kinetic parameters (E_a = 49·7 Kcal.mole^{-1}; $\Delta S^{\ddagger}$ = 0·8 e.u.) for this isomerisation suggest both diradical and concerted ($_{\pi}2_s + _{\sigma}2_a$) mechanisms may be operating since the former process would be expected to cause increase in internal freedom as in cyclopropane pyrolysis ($\Delta S^{\ddagger} \sim 10$ e.u.) and the latter a considerable decrease in internal freedom. However the kinetic parameters (E_a = 33·5 Kcal.mole^{-1}; $\Delta S^{\ddagger}$ = -9·2 e.u.)[91] for the thermal rearrangement of 1,1-dimethyl-2-vinylcyclopropane to form cis-2-methylhexa-1,4-diene strongly support an exclusively concerted mechanism in this case and involving a 1,5 hydrogen shift, the relatively large negative entropy of activation resulting from a "tight" cyclic transition state as compared with the relatively loose precursor.

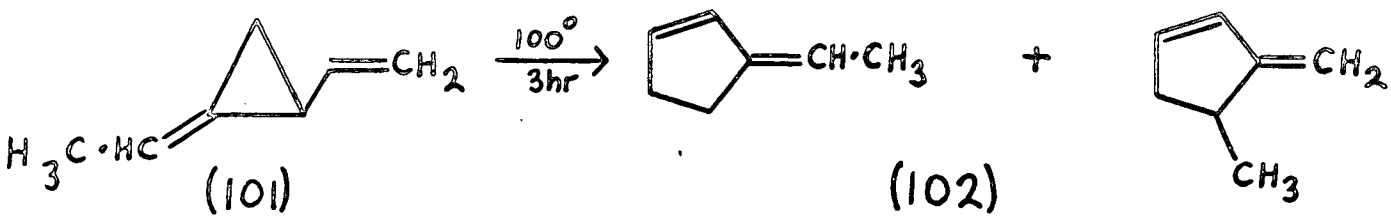
The monodeuteriovinylcyclopropanes(88) undergo rapid geometrical isomerism[61] at 360° and since cyclopentene formation is irreversible, this process requires independent rotation of the cyclopropane carbon-carbon bonds, being analogous to that previously described for saturated cyclopropanes (Section 1.4). However there is no evidence to suggest that the geomerism process and cyclopentene formation are necessarily in the same energy manifold, in which case no firm conclusion can be established.

The gas phase mercury photosensitised isomerisation[62] of the butadiene(89) yields vinylcyclopropane(86) as the major


Cl
Cl
CH2
200°-300°
Cl
Cl
(94)
(95)


C2H5
Cl
Cl
C2H5
25°
BuOK/DMSO
CH2
H2C
+
+ (101)
(96)
(97)
(98)

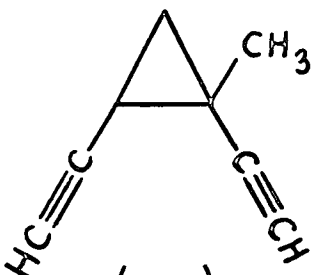

200°
H2C
CH2
(99)
(100)


CH2
100°
3hr
CH·CH3
+
CH2
H3C·HC
CH3
(101)
(102)

monomeric product, this compound being stable to prolonged irradiation, although photolysis of cyclopentene(87) affords a low yield of vinylcyclopropane. However, because photosensitisation is involved, these transformations proceed by way of a triplet state and thus would be expected to follow a radical mechanism. Conversely, non-photosensitised irradiation[63] of the isopropenylcyclopropane(90) forms a small amount of the methylcyclopentene(91) which could involve a concerted $({}_{\pi}2_{s} + {}_{\sigma}2_{s})$ process, allowed in the first excited state.

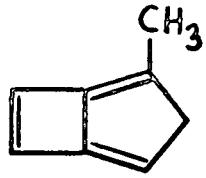
Bicyclopentene(92) is converted[64] under thermal gas phase conditions to cyclopentadiene(93). Because a thermally allowed conrotatory mode would lead to the highly strained isomer(93a), it seems certain that the thermal mechanism involves a diradical intermediate, although the formation of cyclopentadiene by a disrotatory process is photochemically allowed and observed.

It has been suggested[65] that the rearrangements of vinylcyclopropanes to form cyclopentenes may be concerted but that substitution of the ring by groups capable of stabilising radicals on the carbon atoms involved may cause this type of rearrangement to follow a free radical route, although it is not clear as to whether these groups might also be capable of stabilising a transition state. In this sense, the gem-dichlorovinylcyclopropane(94) rearranges to form the gem-dichlorocyclopentene(95) which would be expected from a radical mechanism. By analogy with the thermolysis of gem-dichlorocyclopropanes(36, Section 1.4), a concerted process might be expected to involve

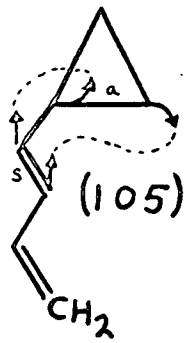


(103)

$\xrightarrow{350^\circ}$

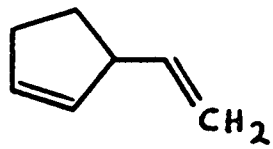


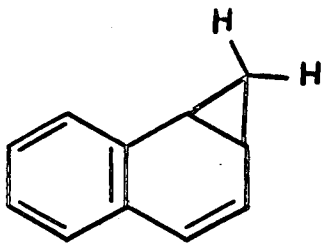
(104)



(105)

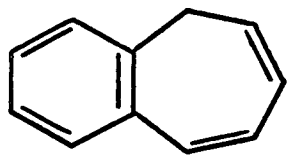
$\xrightarrow[(\pi 2_s + \sigma 2_a)]{300^\circ}$



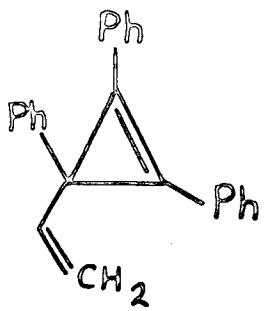


(106)

$\xrightarrow{260^\circ}$

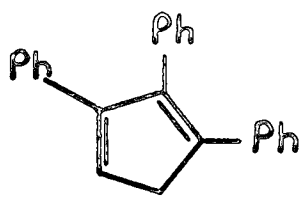


(107)



(108)

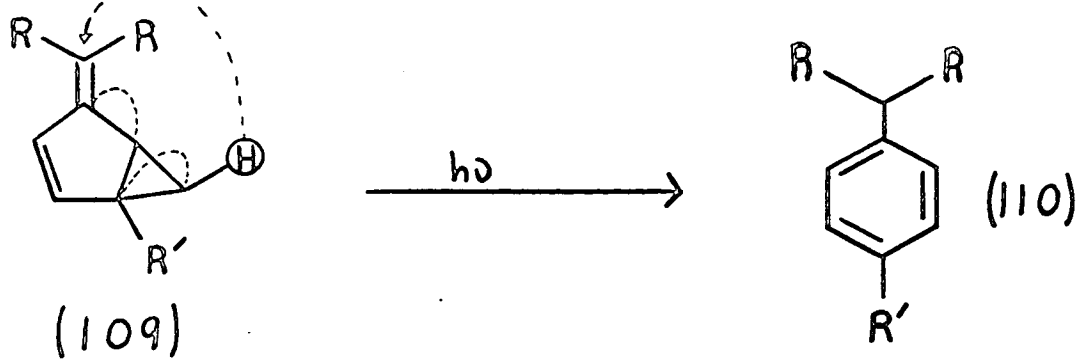
$\xrightarrow{180^\circ}$



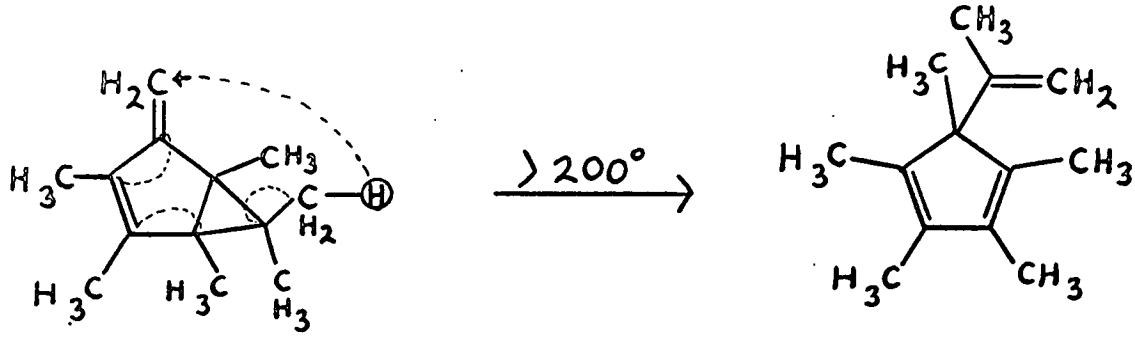
halogen migration.

A stringent stereochemical requirement is involved in the Cope rearrangement of divinylcyclopropane. Thus[66] dehydrohalogenation of the gem-dichlorocyclopropane(96) with potassium t-butoxide in dimethylsulphoxide at 25° leads to the formation of trans-divinylcyclopropane(97), cyclohepta-1,3-diene(98) and the ethylidenecyclopropane(101). The 1,3-diene is presumably formed by concerted rearrangement of cis-divinylcyclopropane(99), under the reaction conditions to form the 1,4-diene(100) followed by base catalysed isomerisation. This facile rearrangement of the cis-isomer has been independently established.[67] The trans-isomer(97) however does not fulfil the steric requirements for a cyclic transition state and only undergoes rearrangement at an elevated temperature. As might be expected the ethylidenecyclopropane(101) readily undergoes rearrangement[68] to form ring expanded products(102) and due to the mild conditions involved it seems certain that a diradical intermediate is not involved. In this context it is noteworthy that the diethynylcyclopropane(103) readily undergoes thermolysis[69] to give the bicycloheptatriene(104). This compound would appear to have interesting synthetic possibilities.

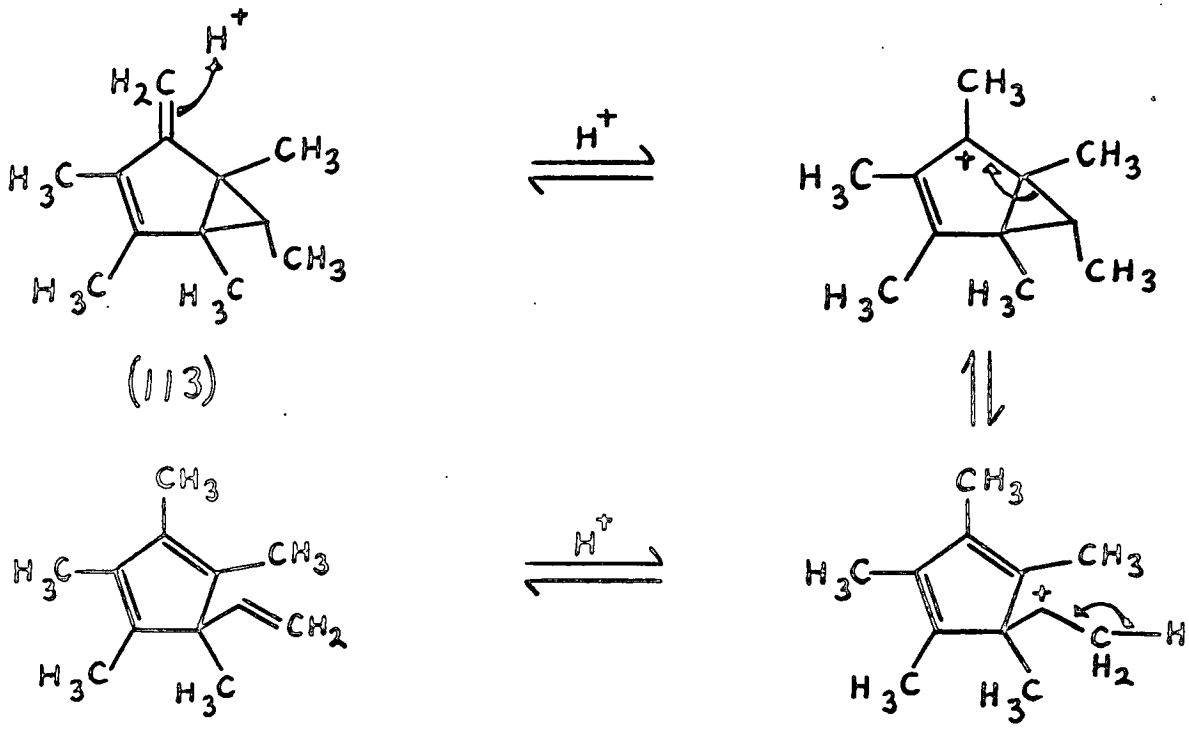
The pyrolysis[70] of the cyclopropylbutadiene(105) affords 3-vinylcyclopentene, the values of the kinetic parameters (E_a = 44·5 Kcal.mole^{-1}, $\Delta S^{\ddagger}$ = -0·3 e.u.) again suggesting competing concerted and diradical processes. Similarly, pyrolysis[71] of benzonorcaradiene(106) and its gem-deuterioanalogue forms



(109) (110)



(111) (112)

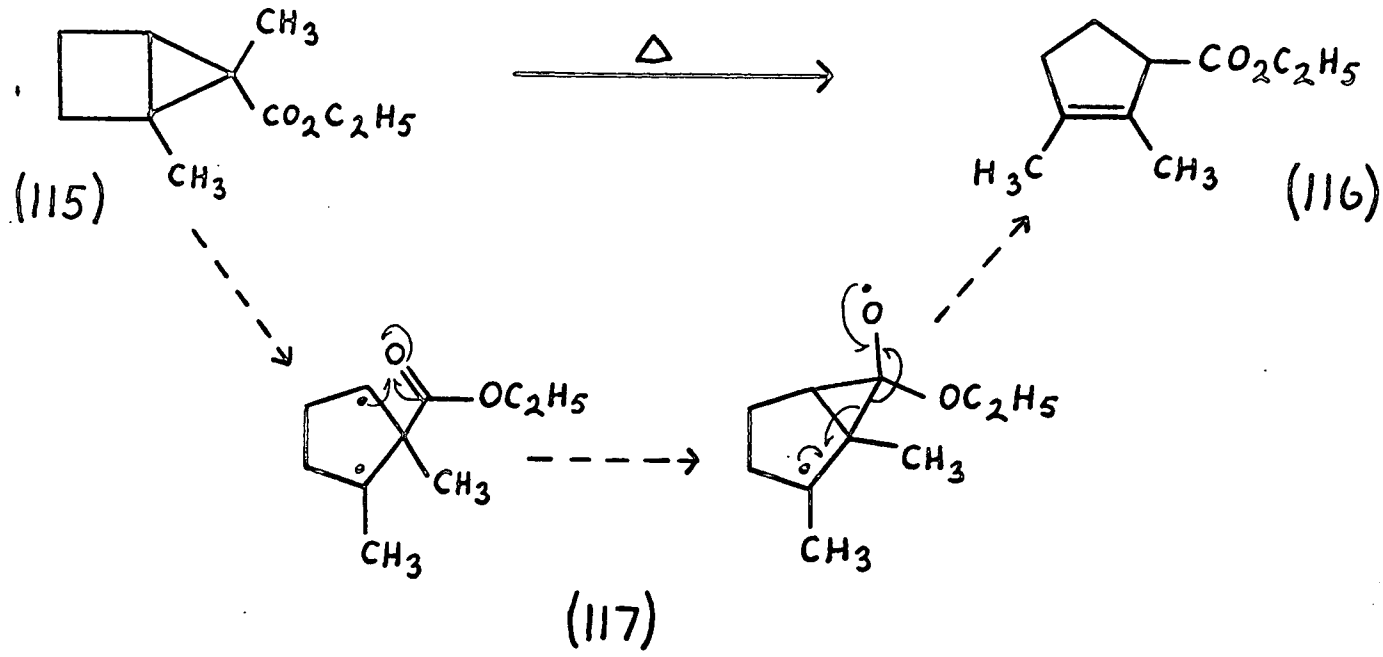


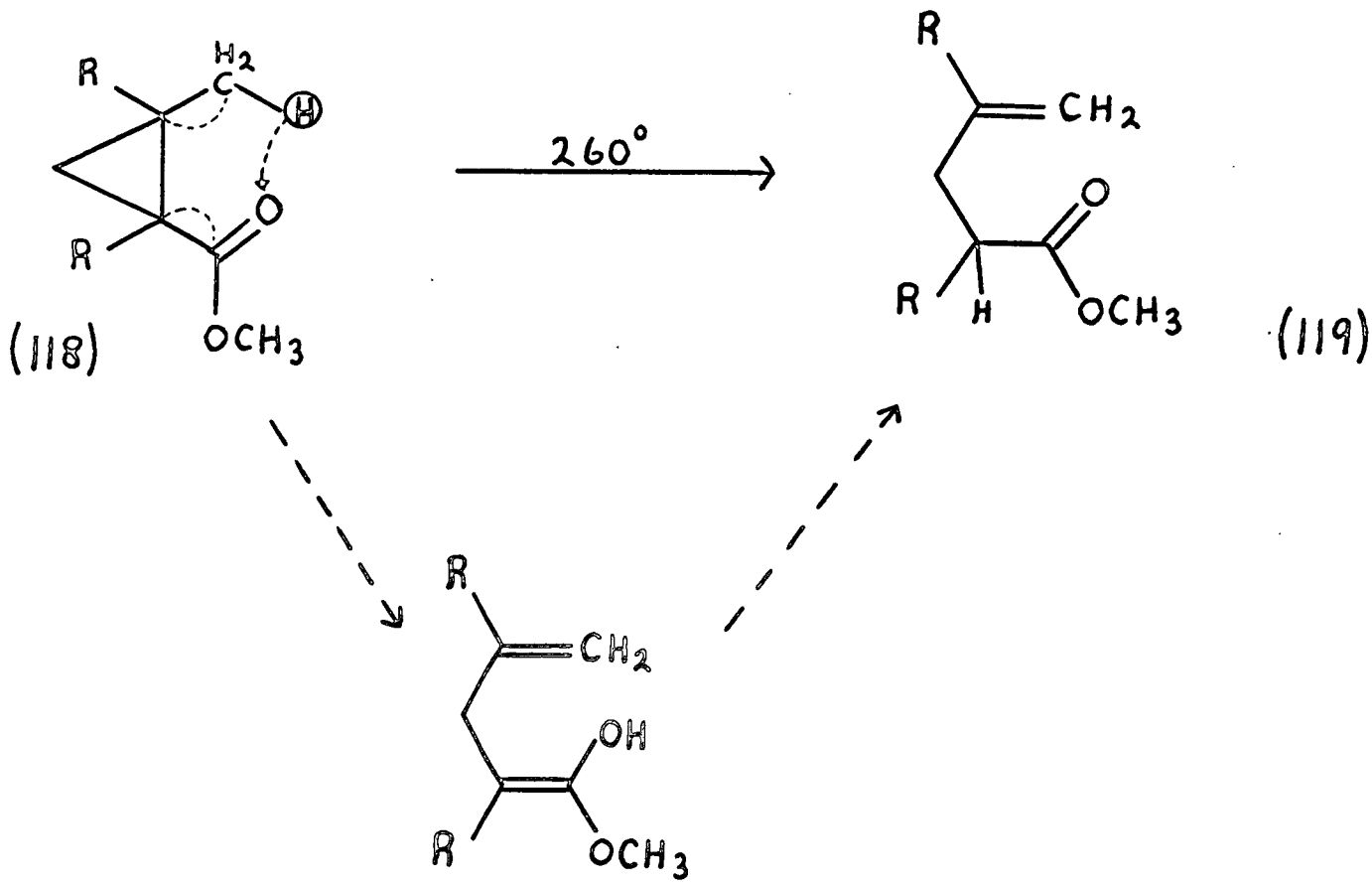
(113)

1,2-benzocycloheptatriene(107) and the evidence from the deuteriomoiety can be rationalised in terms of a concerted or radical mechanism. The thermal rearrangement of triphenylvinylcyclopropane(108) for which no kinetic data is available is particularly facile,[72] the intermediate or transition state in this transformation having a large degree of additional stabilisation available through the aromatic π-electron systems.

It has been reported[73] that the homofulvene(109) is thermally stable until polymerisation. However this compound undergoes photolysis, probably by way of an allowed 1,7 suprafacial shift, to afford the benzene derivative(110). Conversely[74] the homofulvene(111), which cannot aromatise, is thermally labile and pyrolyses to form the cyclopentadiene(112). In this latter case concerted and diradical mechanisms have been proposed but, because a suprafacial migration is involved, the former seems the less likely. Homofulvenes are also isomerised by acid. Thus[75] the homofulvene(113) readily forms the cyclopentadiene(114) upon treatment with acid. This process presumably involves protonation of the exo-cyclic methylene followed by bond migration leading to product formation.

The thermolysis of the bicyclopentane-carboxylate(115) has been rationalised in terms of an unusual 1,2-carbethoxy shift.[76] The proposed intermediate diradical(117) can be stabilised through a cyclic intermediate which can then ring open to form the product(116).


CH3
CO2C2H5
CH3
(115)
Δ
CO2C2H5
H3C
CH3
(116)
O
OC2H5
CH3
CH3
(117)
O
OC2H5
CH3
CH3


R
H2
C
H
O
R
OCH3
(118)
260°
R
CH2
O
R
H
OCH3
(119)
R
CH2
OH
R
OCH3

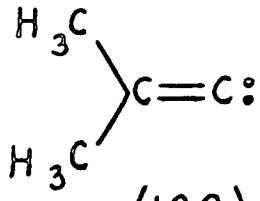
McGreer and Chiu have demonstrated[77] that methyl cyclopropane-carboxylates (118; R = H or CH_3), with an alkyl group cis- to the ester function, readily undergo isomerisation by way of a 1,5 hydrogen shift to give the γ, δ-unsaturated ester(119). It is reasonable to assume that this is a concerted process since it is accompanied by a large negative entropy of activation lying in the region -8 to -37 e.u. for various alkyl substituents, R.

1.7 CONCLUSION

The mechanisms involved in the rearrangements of cyclopropanes - especially unsaturated and vinylcyclopropanes - are the subject of much speculation. Application of the Woodward-Hoffmann approach to the thermolysis and photolysis of these compounds can indicate whether a considered change is allowed or forbidden but, although many of the processes are symmetry allowed, there is often strong evidence in support of a competing stepwise non-concerted pathway. In the case of saturated cyclopropanes, the bulk of the evidence concerning their thermolysis seems to support the intermediacy of a diradical species, but in the case of vinyl and unsaturated cyclopropanes no such apparently clear-cut distinction can be made. Concerning the latter case, although there is conclusive evidence for a concerted mechanism during the pyrolysis of optically active compounds, an open chain intermediate is required to account for the racemisation which does occur and,

indeed, the existence of the trimethylenemethane diradical has been demonstrated during the photolysis of 4-methylenepyrazoline.

It would therefore seem reasonable, in some cases at least, that rearrangements occur simultaneously by both mechanisms. In many instances more kinetic data is required before further conclusions can be drawn. In particular more data is required concerning the thermal rearrangements of unsaturated cyclopropanes, since these do not appear to have been so well treated in this respect.



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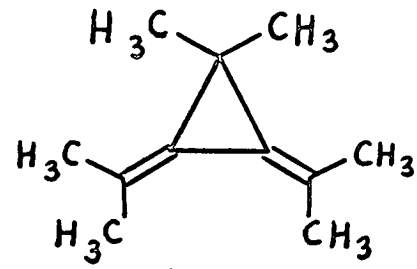

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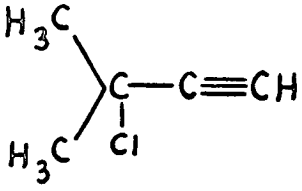

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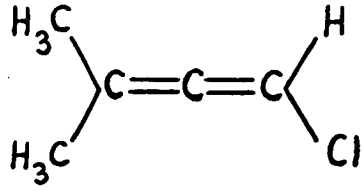

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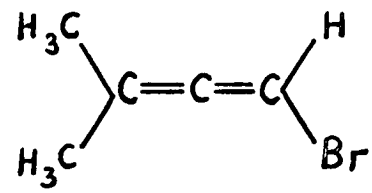

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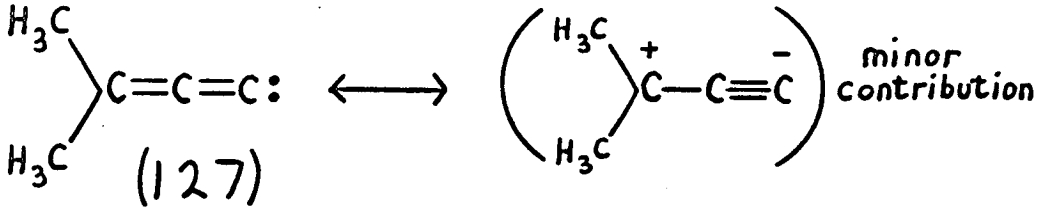

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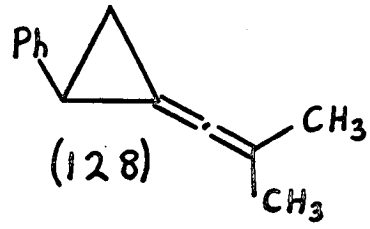

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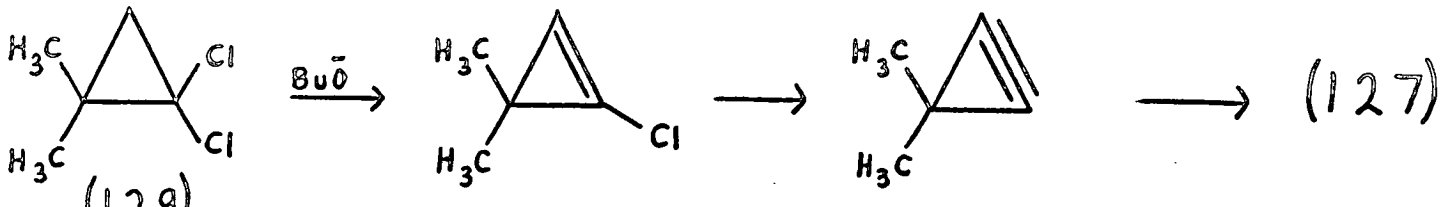
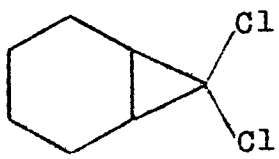


(129)

1.8 SYNTHETIC ROUTES AVAILABLE TO UNSATURATED CYCLOPROPANES.

The addition of dihalocarbenes to olefins, resulting in dihalocyclopropane formation, was originally realised by Doering and Hoffmann.[78] Thus dichlorocarbene, generated by the base solvolysis of chloroform in an aprotic medium, is trapped by cyclohexene to form dichloronorcarane(120). Similarly, methylenecyclopropanes have conveniently been prepared[79] by the addition of dichloro- or dibromocarbene to allenes, the electrophylic species ($:CX_2$) adding to the least highly alkyl



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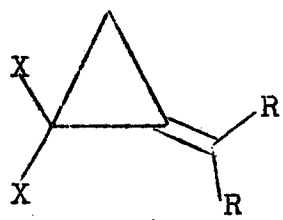
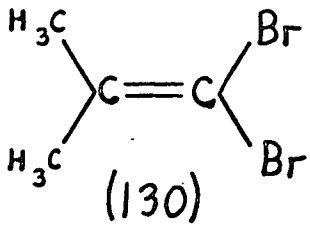


(121)

substituted site(121). Dihalocarbenes exist[80] as ground state singlets and thus add in a stereospecific manner to unsymmetrical olefins. Addition of isopropylidenecarbene(122) to tetramethylallene forms the dimethylenecyclopropane(123).

The resonance stabilised dimethylvinylidenecarbene(127) has been prepared[81] by the action of potassium t-butoxide on the propargylic halide(124). When styrene is used as solvent the vinylidenecyclopropane(128) can be isolated in moderate yield as a viscous liquid, highly susceptable to air oxidation. Dimethylvinylidenecarbene appears to exist as a ground state singlet since it adds to olefins in a stereospecific manner.



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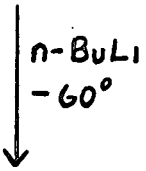
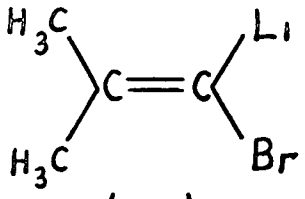
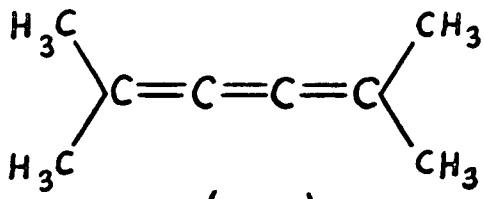
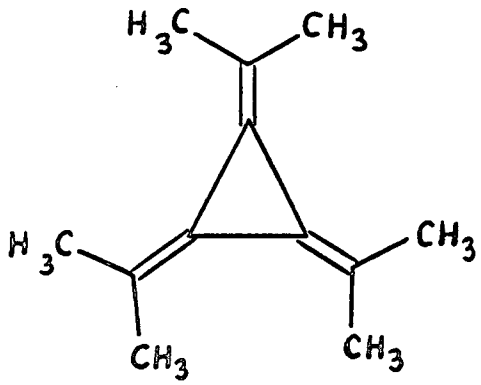




(131)

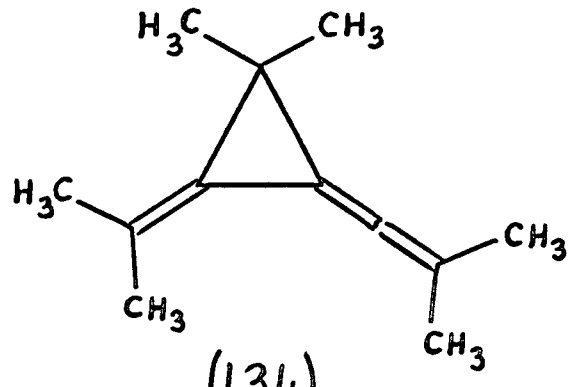


(132)



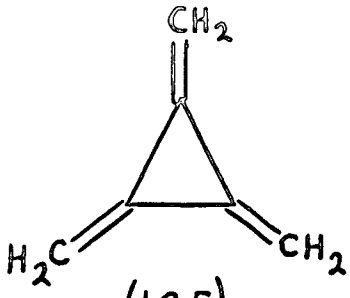
(133)

+



(134)

(133)?



(135)

This carbene has also been prepared from the allenic chloride(125)[82] and the allenic bromide(126)[83], the latter being reported as the most efficient for adduct formation. The intermediacy of dimethylvinylidenecarbene has also been reported[84] during the solvolysis of dichlorodimethylcyclopropane(129) in hexamethylphosphoramide, although the conversion is very low. The carbene is presumably formed through the intermediacy of the chlorocyclopropene and cyclopropyne.

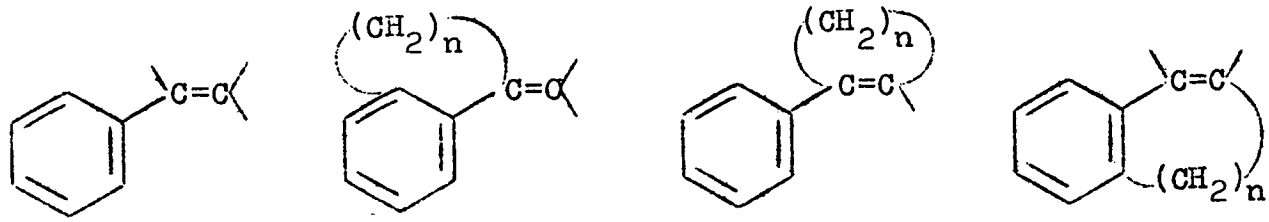
Triisopropylidenecyclopropane(133) has been prepared[85] by the action of n-butyl lithium on the dibromide(130) at -60°. This reaction probably involves dimerisation of the carbenoid(131) to form the allene(132), which can then react with a further mole of the carbenoid to form triisopropylidenecyclopropane(133) together with the allenic cyclopropane(134). The latter system has also been independently[86] prepared by the addition of dimethylvinylidenecarbene to tetramethylallene and is reported to undergo rearrangement when heated (90-150°). Although no structure is formulated for this hydrocarbon it is probably the trimethylenecyclopropane(133). The parent hydrocarbon(135), although stable at -78°, rapidly polymerises at room temperature.[87]

2. THE OBJECT OF THE RESEARCH.

During a kinetic study of the competitive addition of dimethylvinylidenecarbene to various substituted styrenes it was observed[88] that the vinylidenecyclopropanes formed were relatively thermally labile and probably underwent rearrangement to isomeric compounds.

In view of the almost complete absence of information on rearrangements of this type of cyclopropane it was decided to explore the synthetic possibilities and to attempt to elucidate the mechanisms involved. On consideration of the interesting behaviour in the presence of acid of cyclopropanes in general, the acid catalysed reactions of these compounds were also examined.

The dimethylvinylidenecyclopropanes selected for study were derived from four parent styrene skeletons:



(A) (B) (C) (D)

(A) 1-Arylalkenes; The use of dimethylvinylidenecyclopropanes obtained from these olefins permitted the primary rearrangement processes to be established and also the examination of the effect on the rearrangement of substituents in the aromatic ring and at

the α- and β-positions in the parent olefinic double bond. This approach could then be extended to systems, detailed below, where the primary rearrangement processes occurring here might be rendered inaccessible due to constraints imposed on the system.

(B) 3-Methylenebenzocycloalkenes (n = 2 or 3); The cyclopropanes derived from these olefins should allow the effect, if any, of a spiro-cyclopropyl carbon atom to be evaluated.

(C) 1-Arylcycloalkenes (n = 2,3 or 4); The vinylidenecyclopropanes derived from these cycloalkenes provided fused bicyclic systems in which ring expansion and transannular effects might become involved. The effect of alkyl substitution in these systems could also be investigated.

(D) Benzocycloalka-1,3-dienes (n = 1 or 2); The examination of the vinylidenecyclopropanes derived from these olefins should allow the effect of a fused tricyclic system to be evaluated.

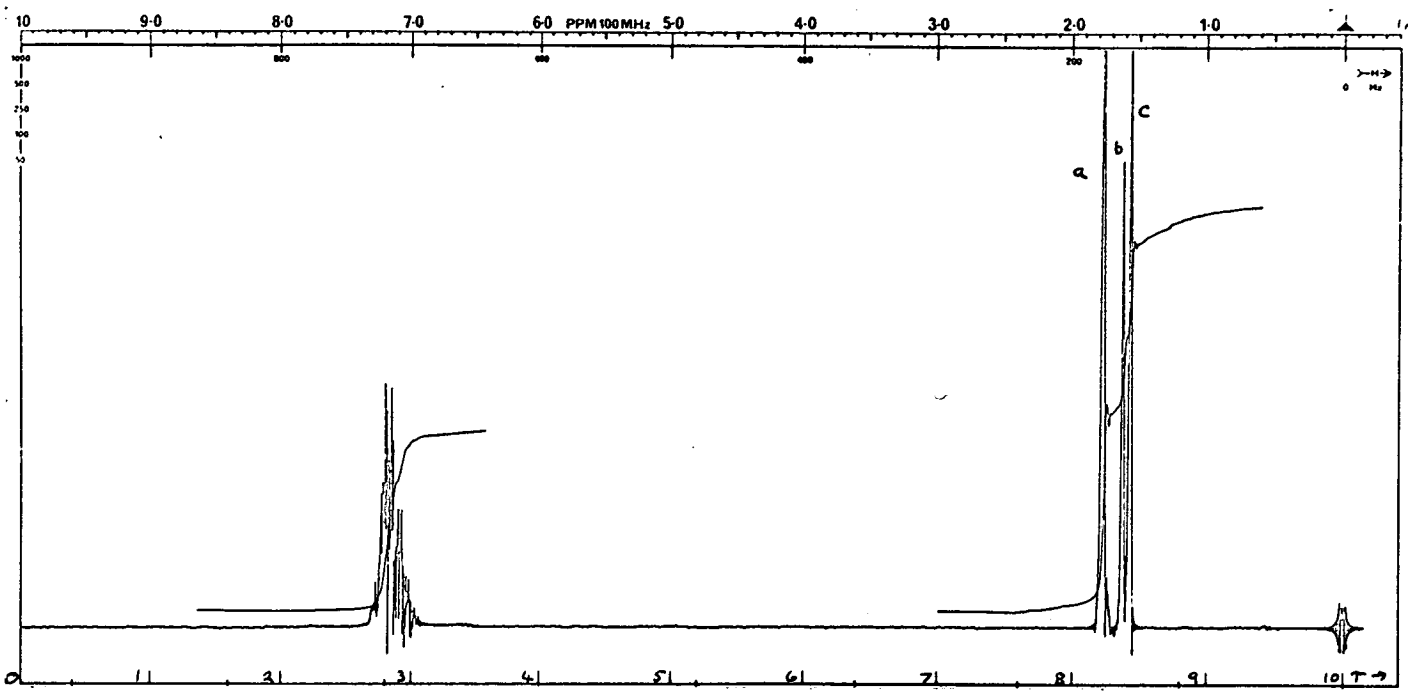
During the course of this work a new reaction of 2,3-dichloro-5,6-dicyanobenzoquinone was discovered[89] and investigated.

3. A DISCUSSION OF THE SYNTHESIS AND REARRANGEMENT OF THE VINYLIDENECYCLOPROPANES.

3.1 THE SYNTHESIS OF THE VINYLIDENECYCLOPROPANES.

The vinylidenecyclopropanes were prepared as 1:1 adducts of dimethylvinylidenecarbene and the parent olefins. Optimum yields were obtained using a twofold excess of 1-bromo-3-methylbuta-1, 2-diene(126) and potassium t-butoxide to generate the carbene and light petroleum as solvent. This bromodiene was found to be superior, as has been reported elsewhere,[83] to the chlorodiene(125) or 3-chloro-3-methylbut-1-yne(124) for adduct formation, and unlike the propargylic chloride is readily obtained in excellent yield from dimethylethyncarbinol. The use of an inert solvent rather than excess olefin allowed adducts to be prepared from relatively small amounts of often valuable olefins.

The adducts were often isolated by vacuum distillation as viscous liquids which were markedly susceptible to air oxidation and underwent polymerisation unless stored at low temperatures. The adducts prepared from indene and 3-methylindene however were obtained as colourless solids which were relatively stable at room temperature. Attempts to prepare adducts with cis-stilbene and 1-phenylpropyne were unsuccessful, starting material only being recovered. Cis- and trans-stilbene are known[92] to be unreactive towards dichlorocarbene, the low reactivity of the trans-isomer being attributed to the additional activation energy


10
9·0
8·0
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4·0
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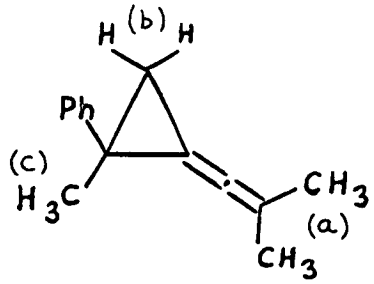
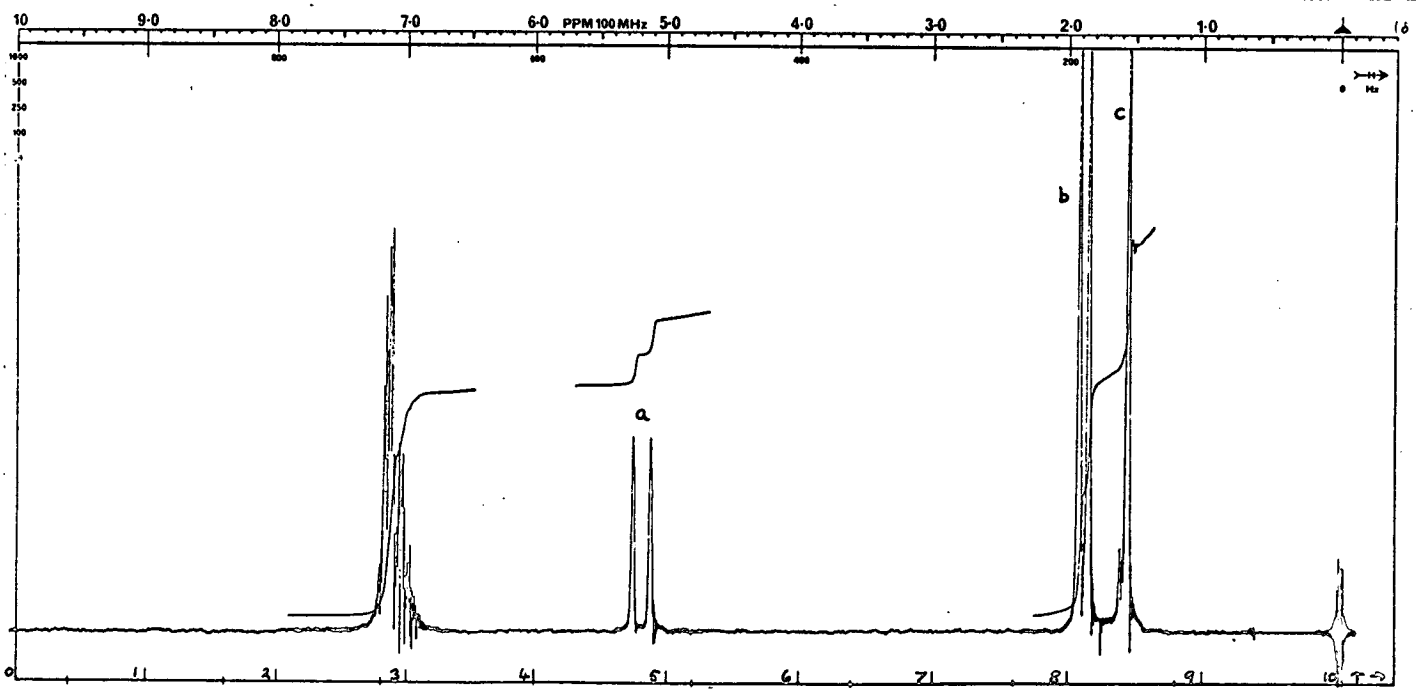
2·0
1·0
a
b
c


H
(b)
H
Ph
(c)
H3C
CH3
(a)
CH3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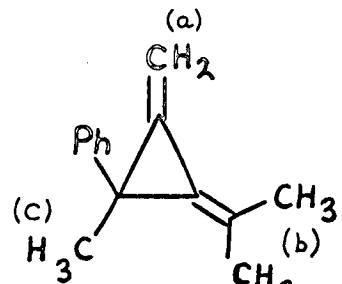
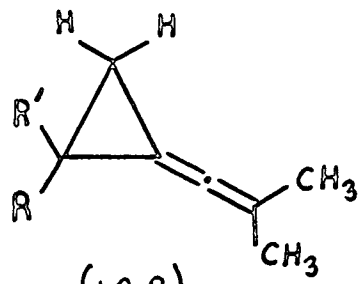

(a)
CH2
Ph
(c)
H3C
CH3
(b)
CH3

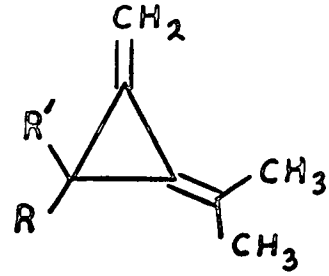
necessary to break the doubly conjugated system. However in the case of the cis-isomer the aromatic rings are not coplanar and the reason for this low reactivity is not clear. The low reactivity of the acetylene can possibly be attributed to the potential unfavourable formation of a highly strained vinylidenecyclopropene system. Similar attempts to prepare a dimethylvinylidenecarbene adduct with 9-isopropylidenefluorene were also unsuccessful, probably attributable to the additional stabilisation present in this highly conjugated system, although it is interesting that diphenylethylene readily formed the corresponding vinylidenecyclopropane in good yield.

The infrared spectra of these adducts show characteristic allenic absorptions in the region 2010-2020 $cm.^{-1}$, which is slightly higher than that normally attributed to allenes (1960-1980 $cm.^{-1}$) and is probably a result of the additional bond strain involved in this exo-cyclic allenic system.[81] The ultraviolet spectra exhibit no maximum above 220mμ., the strong end absorption tailing off into a weak shoulder in the region 220-250mμ. The structures are confirmed by the n.m.r. spectra (Section 6.4.3.) which all show absorptions due to the aromatic protons (2·7 - 3·1τ) and singlet absorptions in the region 8·1 - 8·3τ corresponding to the terminal methyl groups of the allene system. In some systems these methyl absorptions coincide. The absorption due to the cyclopropyl hydrogen atoms normally occurs in the region 7·5 - 7·9τ. A typical spectrum, that of the adduct with α-methylstyrene, is shown in Figure I.



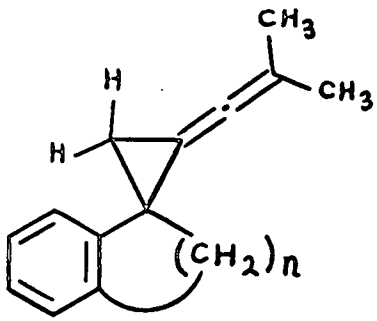
(128)

$\xrightarrow{\Delta}$



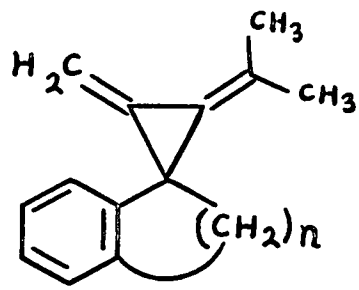
(136)

(128)	$R' = Ph$;	$R = H$	(136)
(137)	"	$R = CH_3$	(138)
(139)	"	$R = OCH_3$	(140)
(141)	"	$R = Br$	no pure product isolated.
(142)	"	$R = Ph$	(143)
(144)	$R' =$ p-Tolyl ;	$R = CH_3$	(145)



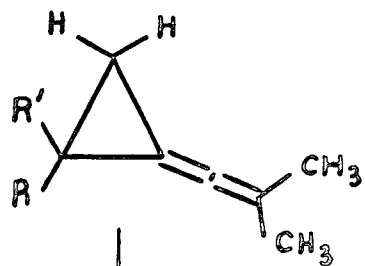
(146)

$\xrightarrow{\Delta}$

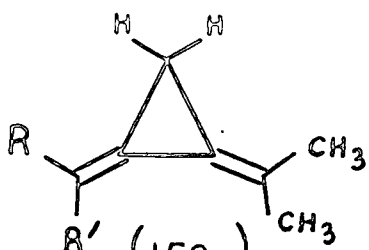


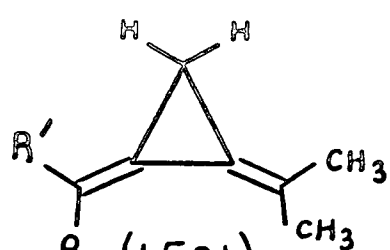
(147)

(146)	$n = 2$	(147)
(148)	$n = 3$	(149)



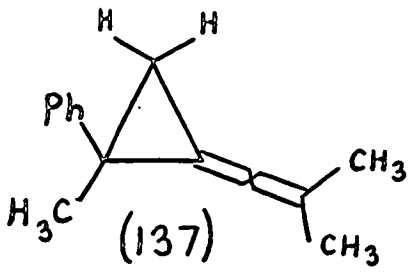
or



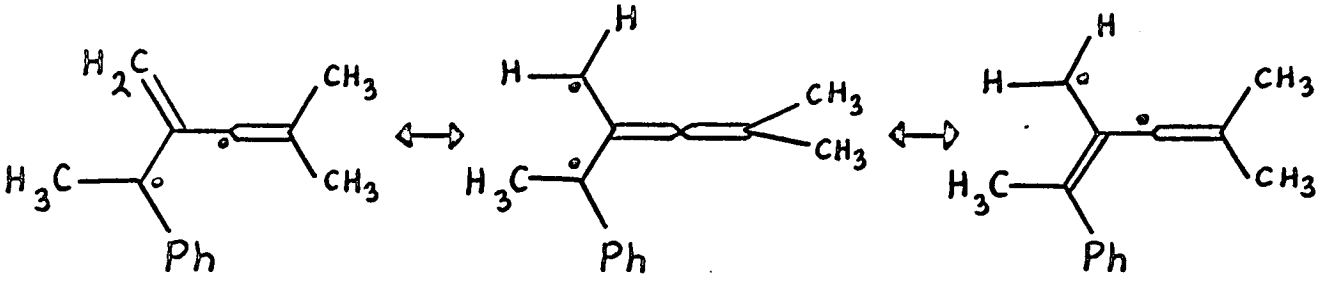


3.2 THERMAL REARRANGEMENT OF THE ADDUCTS DERIVED FROM 1-ARYLALKENES AND 3-METHYLENEBENZOCYCLOALKENES.

2-Dimethylvinylidene-1-methyl-1-phenylcyclopropane(137) underwent complete and exclusive rearrangement to 2-isopropylidene-1-methyl-1-phenyl-3-methylenecyclopropane(138) in good yield when heated in xylene at 140° for 3 hr. Prolonged heating resulted in some loss of product due to polymerisation. However excellent yields of rearrangement product were obtained by a low pressure vapour phase pyrolysis technique in which the adduct was carried in a stream of nitrogen through a flow system at 350°. The rearrangement of the (p-tolyl)vinylidenecyclopropane(144) under similar conditions to give an analogous product(145) demonstrated that the course of the rearrangement was unaltered by alkyl substitution in the p-position of the aromatic ring. Similarly the spiro-vinylidenecyclopropanes(146,148) smoothly underwent rearrangement to form 2'-isopropylidene-3'-methylenecyclopropane-1'-spiro-1-indane(147) and the tetralin homalogue(149) respectively. The methoxycyclopropane(139) also readily formed the dimethylenecyclopropane(140) which was particularly susceptible to polymerisation. The diphenylcyclopropane(142) was especially thermally labile and underwent 80% rearrangement on high vacuum distillation to form the diphenyldimethylenecyclopropane(143). The bromocyclopropane(141) rearranged under similar conditions but in this case no pure product could be isolated. In no case was there any evidence for the formation of the benzylidenemethylenecyclopropanes(150a,b).



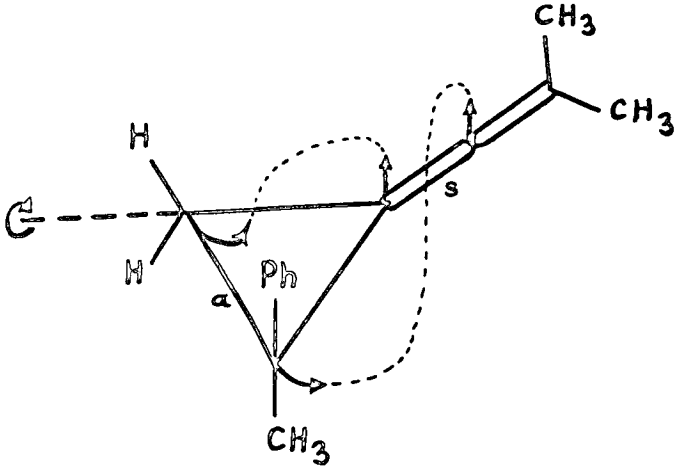
(137)



(151a) (151b) (151c)

(138) (150a)

SCHEME III



(137)

(138)

$(\pi 2_s + \sigma 2_a)$

These dimethylenecyclopropanes show characteristic bands in their i.r. spectra in the region 880-910 $cm.^{-1}$ and near 1800 $cm.^{-1}$. The former corresponds to the terminal olefinic methylene group, and the latter have been attributed[49] to the strained exo-cyclic double bonds. The u.v. spectra are consistent with the presence of a conjugated diene system in the molecules, showing a maximum in the region 245-255 mμ. The structures are confirmed by the n.m.r. spectra (Section 6.5.2); a typical spectrum, that of the dimethylenecyclopropane(138) is illustrated in Figure I.

An attempt to form the maleic anhydride adduct of the diene(138) was unsuccessful but this was not altogether unexpected since normal cycloaddition would presumably lead to the formation of a strained cyclopropene derivative.

The rearrangement of the vinylidenecyclopropanes derived from α-substituted styrenes and 3-methylenebenzocycloalkenes can be rationalised in terms of either or both of the mechanisms illustrated in schemes II and III for the α-methylstyrene adduct. The first of these (scheme II) involves homolytic fission of the cyclopropane ring to form a diradical which by bond rotation may become resonance stabilised through trimethylenemethane type intermediates. Recombination would then lead to either starting material or the observed dimethylenecyclopropane(138) or the isomeric benzylidenemethylenecyclopropanes(150a,b). The heats of formation (ΔH^{o}_{f298}) of the adduct(137), the dimethylenecyclopropane(138) and the isomeric benzylidenemethylenecyclopropanes(150a,b),

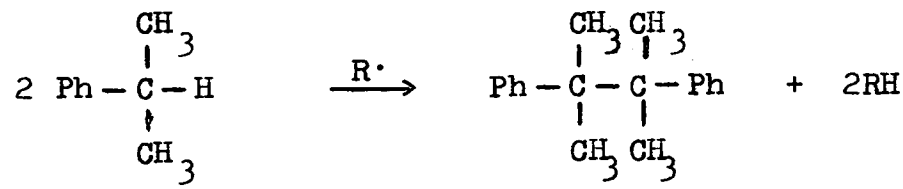
calculated using standard additivity data,[2] are 86·8, 85·5 and 79·6, 78·6 Kcal.mole^{-1} respectively. As no evidence was found for the formation of the thermodynamically most favoured products(150a,b), this suggests that the resonance form(151c) does not contribute significantly to the structure of the diradical. This may be attributed to the preferred location of one of the unpaired electrons of the intermediate diradical(151a,b) at the aryl site. This is consistent with elementary Hückel molecular orbital calculations[90] which show the unpaired electrons occupy degenerate energy levels whose electron distributions resemble those of an allyl radical and a benzyl radical. The formation of the observed dimethylenecyclopropane(138) is thus thermodynamically favourable with respect to the starting adduct(137).

In the alternative mechanism (scheme III) the reaction proceeds through a single transition state, and involves concerted ring opening and bond formation by way of a symmetry allowed ($\pi^2_s + \sigma^2_a$) process. In this system the electronically equivalent alternative mode of methylene rotation is indistinguishable with respect to product formation. Although the formation of the thermodynamically more stable products(150a,b) could apparently proceed by way of an analogous process involving inward or outward rotation of the aromatic ring, it seems likely that the electron distribution in the transition state of the rearrangement would probably resemble that of the diradical(151a) in which case formation of the isomeric benzylidenemethylenecyclopropanes by a concerted mechanism would similarly be expected to be unfavourable.

The enhanced rate of rearrangement of the diphenylcyclopropane(142) is also compatible with each mechanistic alternative, the two phenyl groups offering a higher degree of stabilisation to the intermediate diradical or rendering the transition state more accessible.

It is noteworthy that whereas the phenyl-(136) and diphenylvinylidenecyclopropanes(142) undergo an identical mode of rearrangement, the phenyl-(69) and diphenylmethylenecyclopropanes(71) do not, the former again not forming the benzylidenecyclopropane system.

With a view to distinguishing between the two mechanisms, several attempts were made to trap the hypothetical diradical. Rearrangement of the vinylidenecyclopropane(137) was carried out at 140° in hexachlorobutadiene, 1,2-dichloroethylene or tetramethylethylene as solvent but in no case was any evidence found for adduct formation, the dimethylenecyclopropane(138) being the only product isolated. Similar attempts with methyl acetylenedicarboxylate and ethane-1,2-dithiol also proved to be negative, the latter undergoing reaction with the hydrocarbon to form a mixture of products. Although no pure product was isolated it appeared that the dithiol formed a 1:1 adduct with the unsaturated system, the mass spectrum of the product showing a mass peak at m/e:278, equivalent to the combined molecular weights of the two compounds. The tertiary proton in cumene can be readily abstracted by a radical species which results in the formation of bicumyl(152), however a thermolysis carried out in cumene as

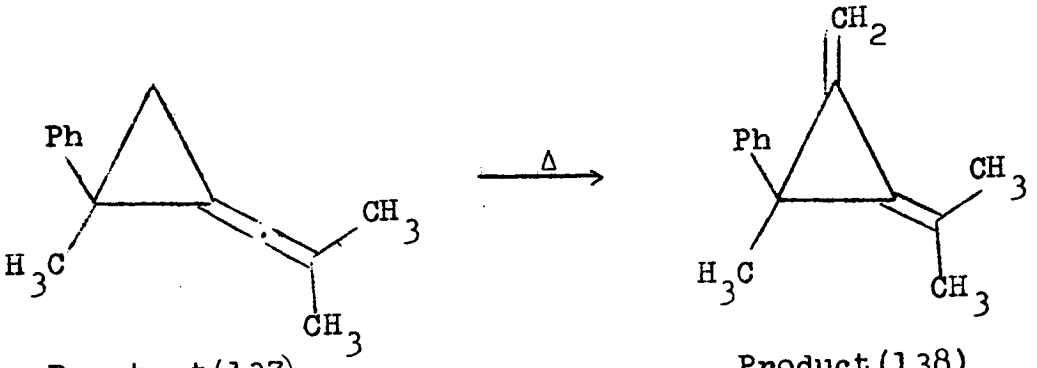


(152)

solvent again proved to be negative, no bicumyl being detected.

The phenomenon of chemically induced dynamic nuclear polarisation (C.I.D.N.P.) for the detection of radical reactions has been described by Fischer and Bargon.[93] Briefly, if a radical reaction is carried out in an n.m.r. probe and the absorption due to a proton involved a radical centre is repetitively scanned, then this may initially appear as an emission or an enhanced absorption signal due to the non-Boltzmann distribution in the spin states of the newly formed product. This abnormal signal decreases to zero and finally grows into a normal absorption signal as the reaction proceeds. The rearrangement of the adduct(137) was examined at various temperatures in a high temperature probe in an n.m.r. spectrometer. However repetitive scanning of the olefinic region showed only a normal increasing signal due to the methylene protons of the product(138), whereas a similar procedure applied to the radical decomposition[93] of dibenzoyl peroxide in cyclohexanone clearly exhibited C.I.D.N.P.

The kinetics of the transformation (137)⟶(138) were studied in order to make an estimate of the activation energy and entropy of activation for this reaction. It was found convenient



Reactant (137) Product (138)

to carry out this work using a dilute solution (10^{-4} molar) of the reactant in decalin, the progress of the reaction being followed by the change in optical density. This high dilution technique had several advantages:- (a) the entire determination could be carried out using less than 0·1g. of reactant, (b) the optical density measurements could be carried out relatively rapidly as compared with an alternative technique involving vapour phase chromatography and, (c) the conditions of high dilution favour first-order kinetics. Measurements were made at four temperatures in the range 120-155°. First-order plots showed a slight deviation from linearity after one or two half lives suggesting that the product was eventually consumed by a non first-order process. This was verified by carrying out experiments involving prolonged heating of the product, which indicated the kinetics of this reaction were complex. However this secondary effect was relatively slow as compared to the primary effect being investigated. Rate constants were determined in triplicate and correlated well ($r = 0·9997$) with the Arrhenius rate equation which gave an estimate for the activation energy of $30·4 \pm 0·3$ Kcal.mole^{-1} and the entropy of activation of $-2·5 \pm 0·7$ e.u.

If the activation energy required to cleave[22] a carbon-carbon bond is 88 Kcal.mole^{-1}, the ring strain[2] present in methylenecyclopropane is 40·9 Kcal.mole^{-1} and the resonance energy attributable[94] to a benzyl radical is 13·8 Kcal.mole^{-1} then the calculated activation energy of the reaction (137)⟶(138) should be about 33 Kcal.mole^{-1}. The observed value for the energy of activation (30·4 Kcal.mole^{-1}) alone therefore does not distinguish between the concerted or diradical mechanisms. Assuming inward rotation of the aromatic ring during diradical formation to be highly unfavourable due to the severe steric interaction with the neighbouring methylene group, then outward rotation away from the remnant cyclopropane ring will give rise to the diradical intermediates illustrated in scheme II. However examination of stereomodels shows that coplanarity of the aromatic ring and the allylic system is unlikely due to interaction between an ortho-hydrogen atom on the ring and the remnant vinylidene π-electron system. This means that the benzylic radical cannot be additionally delocalised into the allylic system and therefore restricted rotation may occur about the bond joining the allyl and benzyl systems causing this hypothetical diradical intermediate to be slightly looser than the starting vinylidenecyclopropane, which might be expected to result in a slightly positive entropy of activation. Alternatively the observed slightly negative entropy of activation would probably be better suited to a concerted mechanism where increased bonding interactions would be expected to render the transition state slightly tighter than the starting

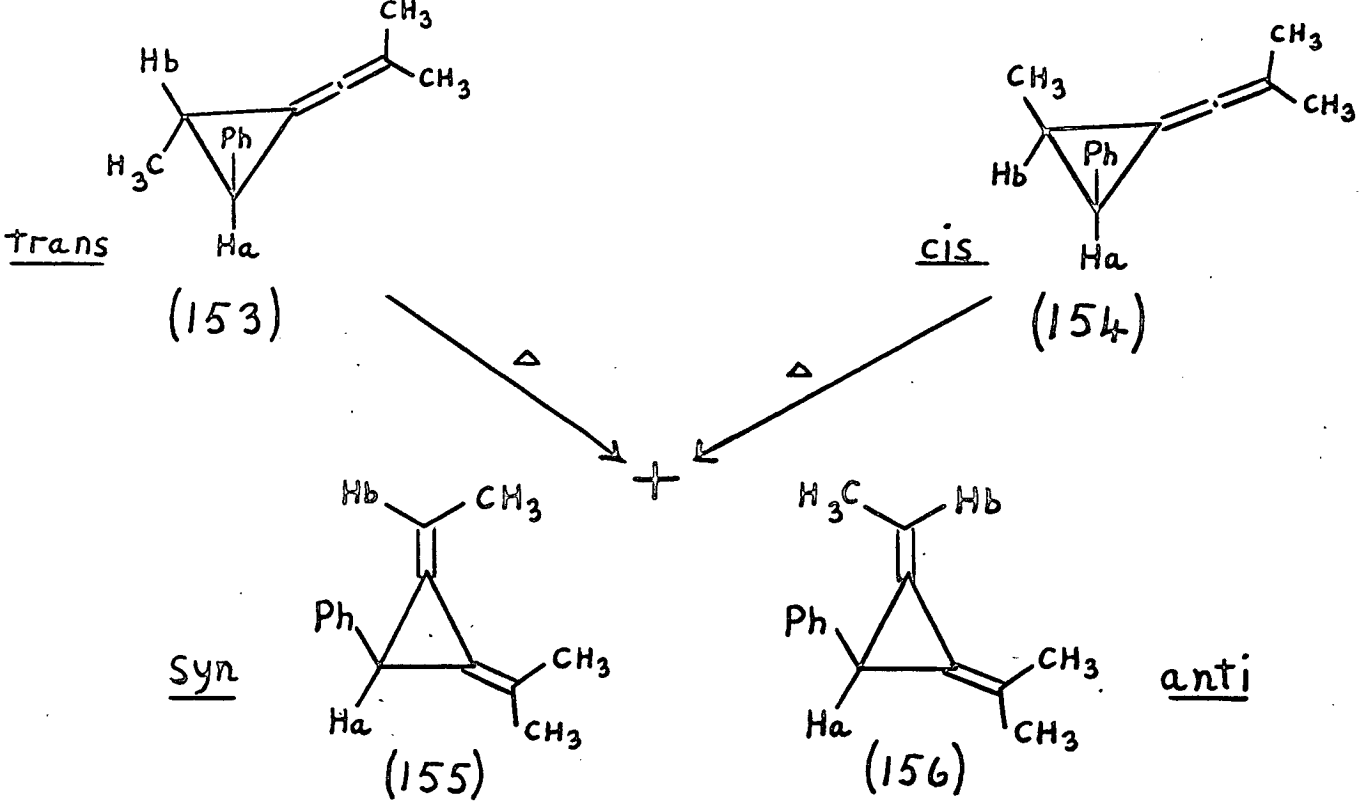


TABLE II

Isomer	Conditions	Syn (%)	Anti (%)
trans	130°, 2 hr.	98	2
"	130°, 3·5 hr.	95	5
"	180°, 1·25 hr.	31	69
"	350°, (flow system)	31	69
cis	130°, 3·5 hr.	87	13
"	180°, 1·25 hr.	30	70
"	350°, (flow system)	33	67
		30	70 (180°, 1·25 hr.)
syn	130°, 7 hr.	50	50
anti	130°, 7 hr.	10	90
"	180°, 1·25 hr.	30	70

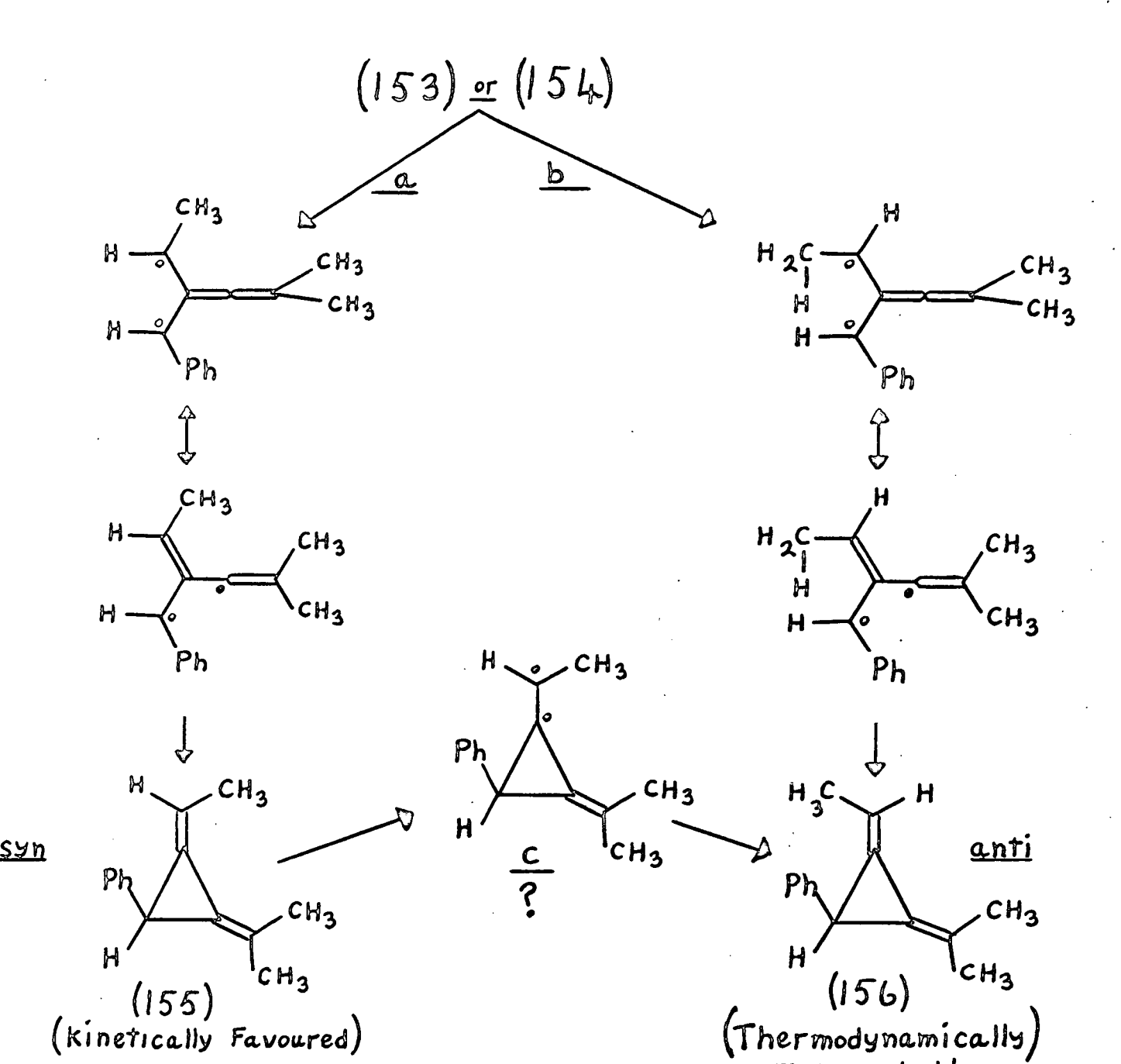
cyclopropane. However the difference is very slight and it would be imprudent to accept the concerted mechanism on this basis alone.

Addition of dimethylvinylidenecarbene to trans- and cis-β-methylstyrene occurs in a stereospecific manner to form trans-1-dimethylvinylidene-2-methyl-3-phenylcyclopropane(153; J_{trans} H_aH_b = 4·2 Hz.) and the cis-isomer(154; J_{cis} H_aH_b = 8·7 Hz.) respectively. The trans- and cis-adducts both undergo rearrangement to form mixtures of syn-1-ethylidene-2-isopropylidene-3-phenylcyclopropane(155) and the corresponding anti-isomer(156). It is to be expected[49] that the olefinic proton (H_b) of the anti-isomer(156) will resonate downfield in the n.m.r. spectrum relative to the olefinic proton (H_b) of the syn-isomer(155), since the former resides in the deshielding region of the neighbouring isopropylidene double bond. On this basis the anti-structure(156) was allocated to that isomer with an olefinic quartet centred at 4·20τ, the syn-isomer(155) having the olefinic proton(H_b) centred at 4·50τ.

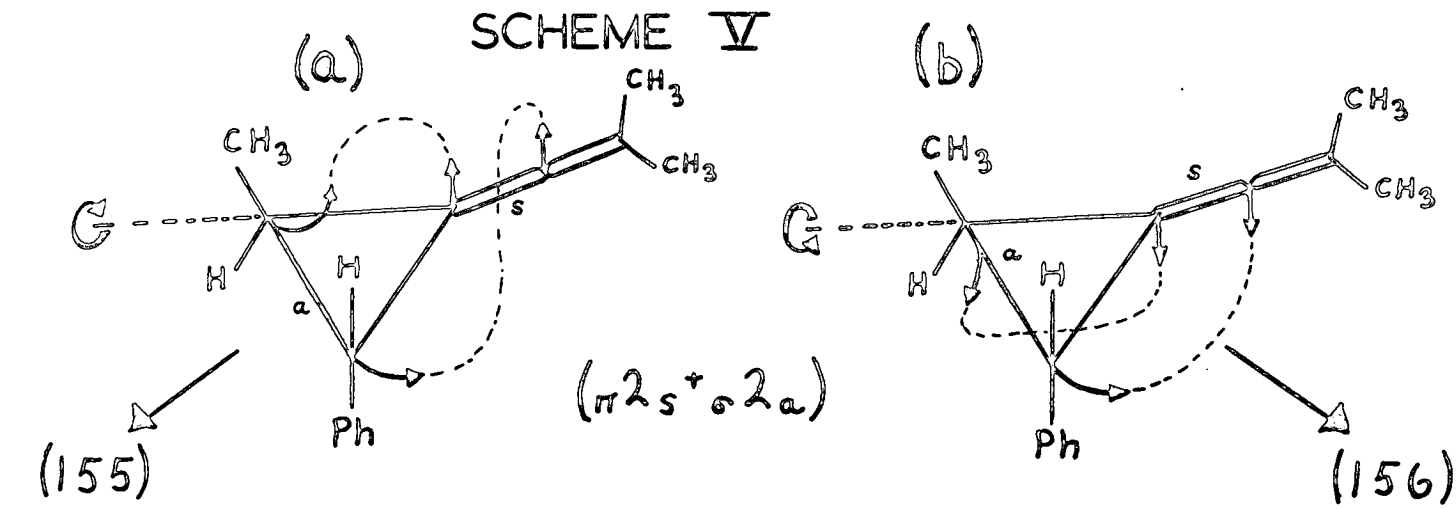
The ratios of the two thermolysis products were dependent upon the conditions employed and are summarised in table II. Thus rearrangement of the trans-adduct(153) or the cis-adduct(154) in xylene solution at 130° gave rise to mixtures containing mainly the syn-isomer(155). However passage of the adducts or the product mixtures or the pure products separately through a preparative v.p.c. column at 180° resulted in the formation of mixtures containing approximately 70% of the anti-isomer(156) and

30% of the syn-isomer(155) in each case. The composition of these mixtures remained unchanged on re-cycling through the column. These results suggest that at the lower temperature the rearrangement is kinetically controlled resulting in the predominance of the thermodynamically less stable isomer. At the higher temperature thermodynamic equilibration of the isomers competes effectively with the rearrangement process.

The equilibrium constant (2·33) for the interconversion process leads to a free energy difference for the products of 0·76 Kcal.mole^{-1}. Prolonged heating of each of the pure isomeric dimethylenecyclopropanes(155 or 156) at 130° by slow passage through the preparative v.p.c. column results in mixture compositions (table II) which demonstrate that at this temperature equilibration is slow compared with the adduct rearrangement reaction. These compositions correspond to an equilibrium constant at 130° of 5·00 which suggests a free energy difference of 1·29 Kcal.mole^{-1}. The agreement between the two estimates is poor, probably mainly due to the inaccuracy of the estimate at 130°, these isomer mixtures being collected over a half hour period. The energy difference presumably arises from the interaction of two methyl groups which is present only in the syn-isomer. Examination of stereomodels shows that this interaction is similar to that between the two methyl groups in cis-butene, where[2] $\Delta(\Delta H_f)$ is 1·00 Kcal.mole^{-1}. In this instance it is reasonable to assume that $\Delta(\Delta H_f) \doteqdot \Delta G^{\circ}$ in which case this value is of the same order of magnitude as that obtained for the two isomeric thermolysis products.


(153) or (154)
a
b
syn
anti
c
?
(155)
(Kinetically Favoured)
(156)
(Thermodynamically more stable

SCHEME V


(a)
(b)
(π2s + σ2a)
(155)
(156)

Passage of the adducts(153 or 154) through the flow system at 350° similarly formed approximately 70:30% mixtures of the anti-isomer(156) and the syn-isomer(155) respectively. However since this pyrolysis technique is relatively fast it seems likely that equilibration would not have been achieved.

Examination of the n.m.r. spectrum of partially rearranged cis-adduct(154) showed only signals attributable to this and the rearrangement products(155 and 156). Thus the equilibration of the products does not proceed by a reverse of the vinylidenecyclopropane rearrangement since this would result in some of the sterically less hindered trans-adduct(153) being formed.

The predominant formation of the syn-isomer(155) from both the trans-adduct(153) and the cis-adduct(154) is consistent with mechanisms analogous to those proposed in schemes II and III for the α-methylstyrene adduct. The corresponding diradical mechanism is illustrated in scheme IV. Rupture of the 2,3-cyclopropyl bond is followed by the sterically more favourable outward rotation of the methyl group and the aromatic nucleus(pathway a), the alternative inward rotation of the methyl group (pathway b) resulting in enhanced steric interaction between the methyl and methine groups. As has already been discussed previously (p. 40), coplanarity of the aromatic ring with the remainder of the π-electron system is sterically unfavourable. However this diradical mechanism does not account for the apparently enhanced rate of rearrangement of the trans-adduct as compared with the cis-adduct(table II). Although this is only a qualitative estimate based on the disappearance of

the allene absorption in the i.r. spectrum and v.p.c. examination, it is in contrast to what would be expected from a mechanism involving an open chain intermediate, where the bond cleavage of the cis-adduct(154) would be expected to be faster than that of the trans-adduct(153) due to the resultant greater relief in steric strain, the product ratio from a process involving identical diradical intermediates being expected to be identical in each case.

The alternative concerted mechanism is illustrated in scheme V for the trans-adduct(153), the cis-compound being expected to be analogous. In this case the two equivalent ($_{\pi}2_{s} + {}_{\sigma}2_{a}$) processes have different stereochemical consequences and lead to either the syn-isomer(155) or the anti-isomer(156) depending upon the mode of rotation involved. Mode (a) involves sterically favourable outward rotation of the ring methyl group which results in the kinetically favourable formation of the syn-isomer(155), whereas inward rotation by mode (b) with the accompanying increase in steric interaction can result in formation of the thermodynamically more stable anti-isomer(156).

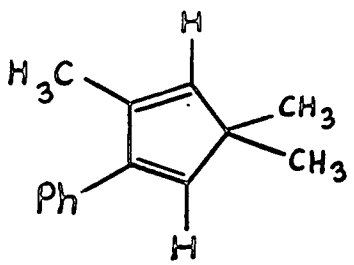
In this concerted mechanism, formation of the syn-product(155) from the trans-adduct(153) necessitates movement of the rotating orbital, which is associated with the outward rotating methyl group, away from the aromatic π-electron system. Conversely formation of the same product from the cis-adduct(154) requires movement of this orbital towards the aromatic system and if this latter process is unfavcurable, possibly due to orbital repulsion,

then this could account for the apparently slower rate of rearrangement associated with the cis-adduct. Similarly this apparently less favoured formation of the syn-product from the cis-adduct could account for the higher syn:anti product ratio obtained (table II) from the cis-adduct (87:13%) with respect to the trans-adduct(98:2%) when the rearrangement was carried to completion at 130°. This higher ratio cannot be solely attributed to the secondary isomerisation of the syn-isomer since the syn:anti ratio obtained from heating the trans-adduct at 130° for 3·5 hr. is 95:5%. A more detailed study of the kinetics of the two adduct rearrangements involved, as verification of the foregoing observations, could provide very strong evidence in support of a concerted mechanism.

Since the interconversion of the syn-isomer(155) and the thermodynamically more favourable anti-isomer(156) appears to proceed by way of a different path from the initial rearrangement, this suggests a process involving homolytic cleavage of the ethylidene double bond followed by bond rotation in the intermediate diradical and recombination as illustrated in scheme IV(pathway c).

Trans-1-dimethylvinylidene-2-isopropyl-3-phenylcyclopropane (157; J_{trans} H_aH_b = 4·0 Hz.) underwent thermolysis when passed through the flow system at 350° to form a 1:2 mixture of syn-1-isopropylidene-2-(2-methylprop-1-enylidene)-3-phenylcyclopropane(158; H_b, 4·65τ) and the corresponding anti-isomer(159; H_b, 4·29τ) respectively. This result is directly analogous with the vapour phase pyrolysis of the foregoing trans- and cis-β-methylstyrene

(161)



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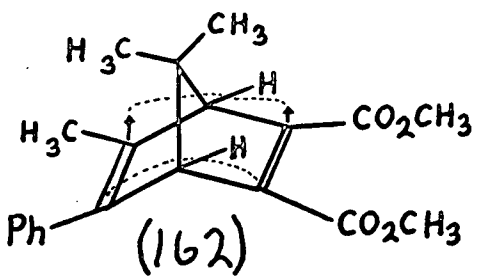

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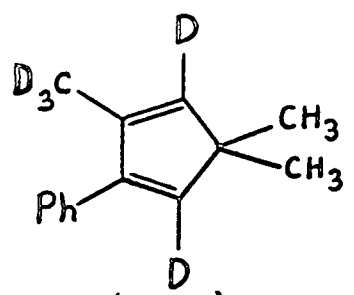
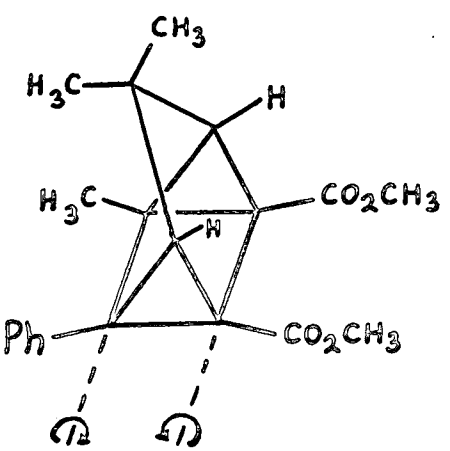


(164)

hν
$(\pi 2_s + \pi 2_s)$



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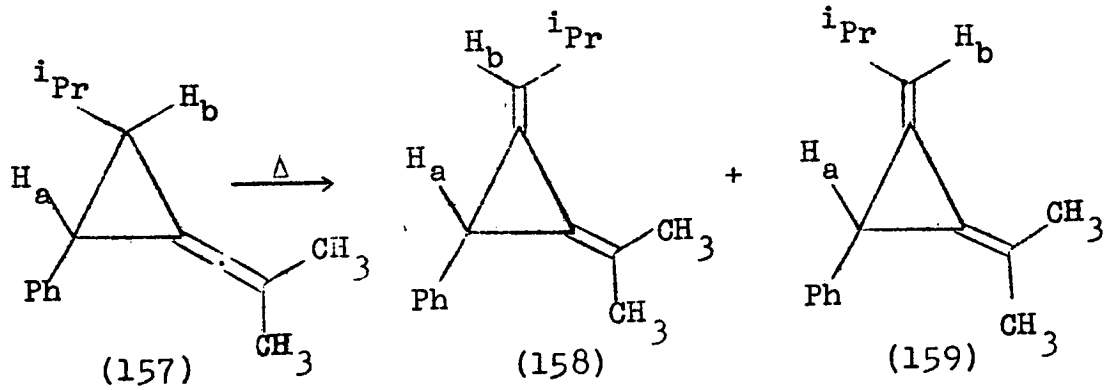
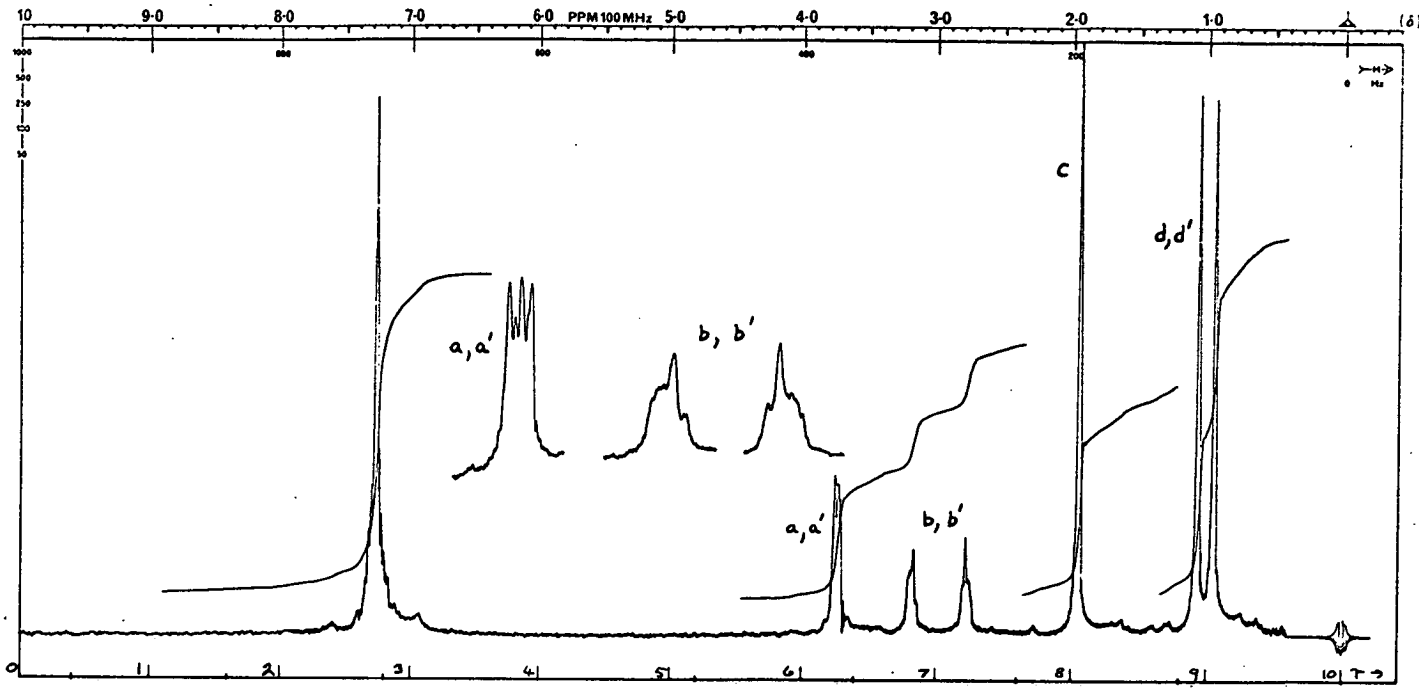
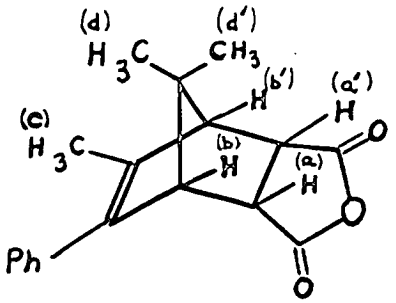


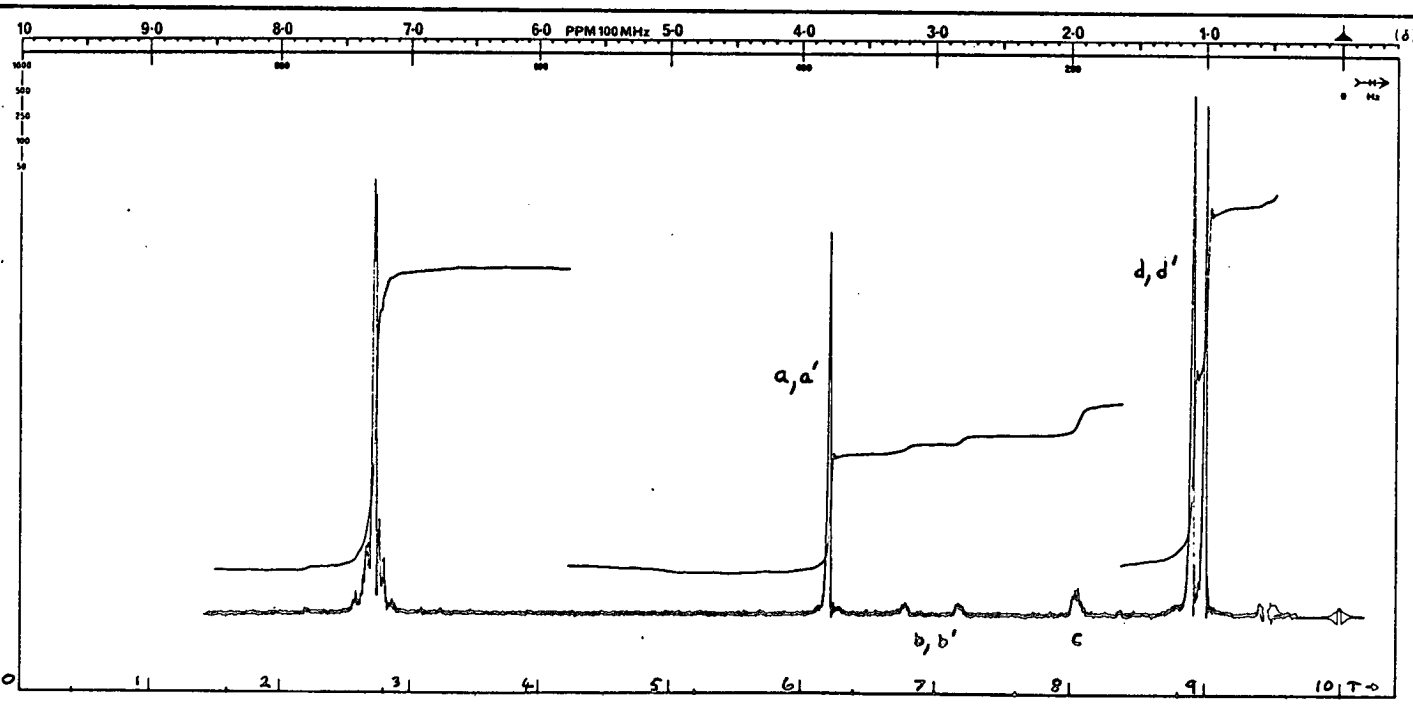
adducts(153 and 154), probably attributable to the similar steric requirements of the isopropyl group and the methyl group with respect to the neighbouring isopropylidene function, provided the isopropyl methyl groups are directed away from the sites of steric interaction. In this respect it might prove illuminating to carry out rearrangements at various temperatures with adducts derived from t-butyl substituted olefins, where additional steric interactions could not be alleviated by straightforward bond rotation.

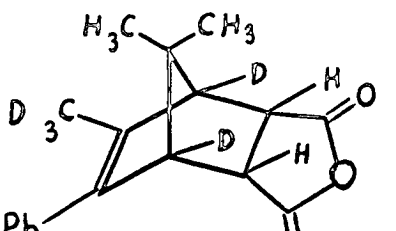
3.3 ACID CATALYSED REARRANGEMENT OF THE ADDUCTS DERIVED FROM 1-ARYLALKENES AND 3-METHYLENEBENZOCYCLOALKENES.

Treatment of the α-methylstyrene adduct(137) with 10% hydrochloric acid in ethanol at 80° formed a mixture containing 60% of a compound isomeric with the starting material together with a total of 40% of several minor components. On the basis of the evidence presented below the major compound was assigned the structure(160). The n.m.r. spectrum (p. 121) indicated the presence of a phenyl group, two equivalent methyl groups (8·82τ) probably attached to a quaternary carbon atom, a third methyl



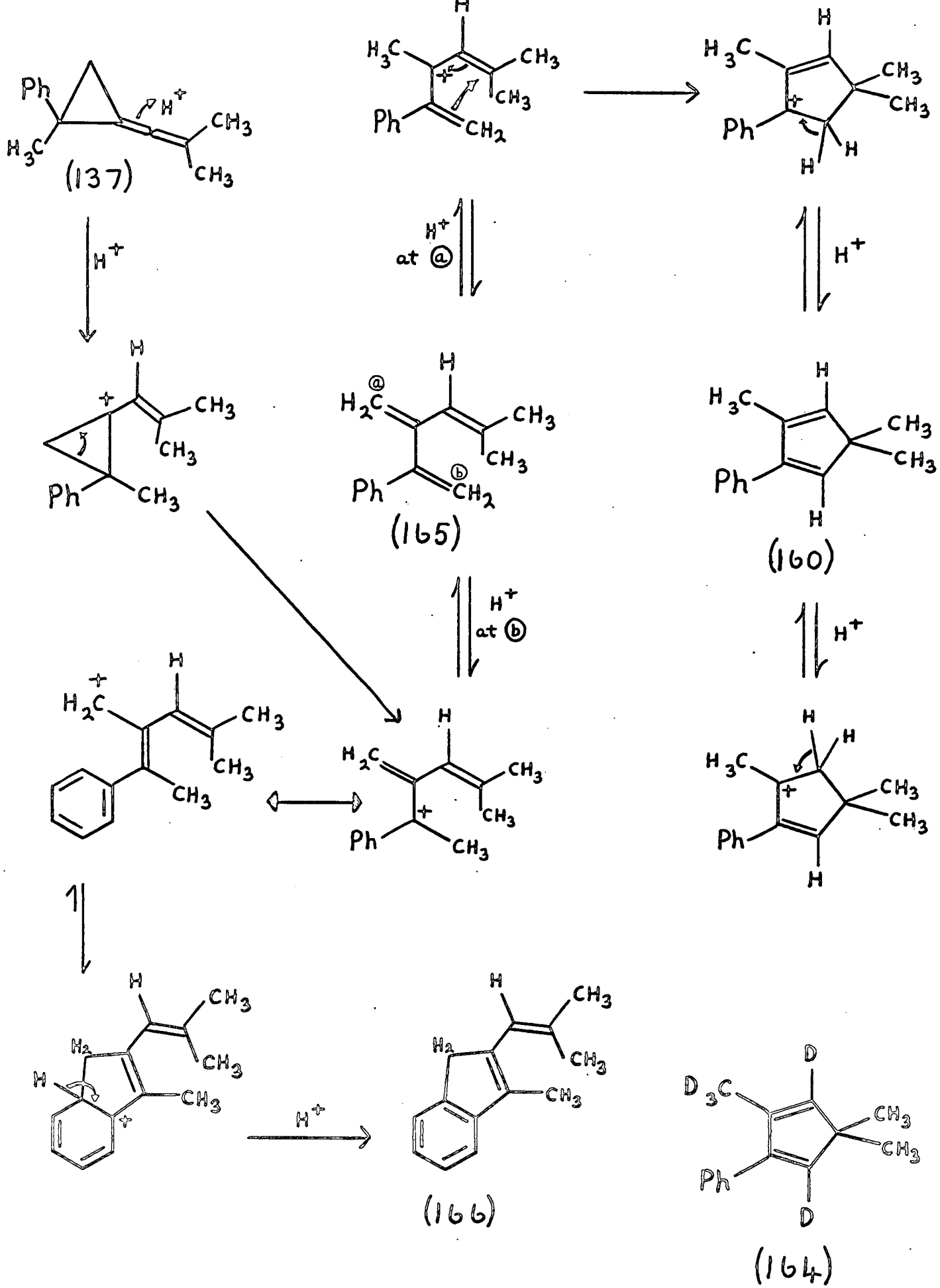






(> 85% deuterium)
exchange

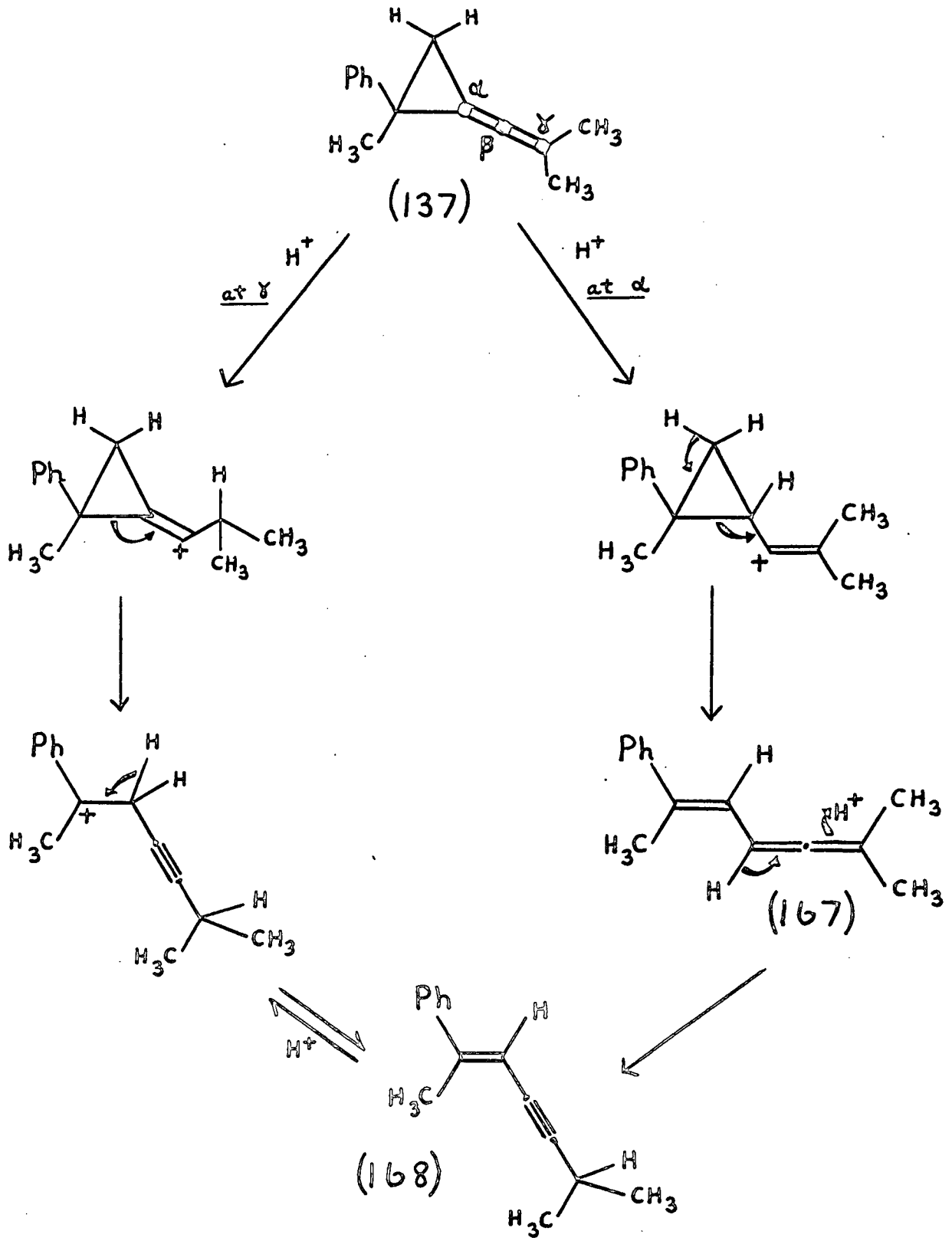
group (8·05τ) probably allylic, and two non-equivalent olefinic hydrogen atoms (3·85, 4·08τ). No major splitting indicated that none of the different types of proton present, with the exception of those in the aromatic ring, occupied sites on adjacent carbon atoms. The i.r. spectrum suggested the presence of a trisubstituted double bond and indicated the absence of allene and terminal olefinic methylene groups. The u.v. spectrum showed the presence of a conjugated system, possibly a diene, the aromatic ring in structure(160) would probably be non-coplanar with the cyclopentadiene ring due to steric interaction with the allylic methyl group. The compound readily reacted with maleic anhydride to form a 1:1 adduct whose n.m.r. spectrum is shown in figure II. The u.v. spectrum was typical of a styrene derivative($\lambda_{max.}$ = 258 mμ, ε = 8,400) while the i.r. spectrum showed strong carbonyl absorption ($\nu_{max.}$ = 1770cm.$^{-1}$). This data was consistent with the formulation of the 1:1 adduct as endo-3-phenyl-2,7,7-trimethylbicyclo[2,2,1]hept-2-en-5,6-dicarboxylic anhydride(161), the endo-configuration being assumed. The compound also readily reacted with methyl acetylenedicarboxylate to form a 1:1 adduct. The n.m.r. spectrum (p. 152) and the u.v. and i.r. spectra resemble those of the bicycloheptene(161). This was formulated as (162) and as expected photoisomerised in dilute ether solution to give a 90% conversion to methyl 6-phenyl-5,7,7-trimethyl-quadricyclo[2,2,1,$0^{2,6}$,$0^{3,5}$]heptane-2,3-dicarboxylate(163). The photoisomerisation of bicycloheptadienes to form quadricyclanes is well known[95] and can occur by way of a photochemically allowed ($_{\pi}2_{s}$ + $_{\pi}2_{s}$) process. An estimate[96] of the ring strain energy


(137)
(165)
(160)
(166)
(164)
at @
at ⓑ

involved in the parent quadricyclane system is 95 Kcal.mole^{-1} and these highly strained systems probably owe their stability to the fact that reversion to the bicycloheptadiene requires a disrotatory mode, which is thermally forbidden in this 4-electron system.

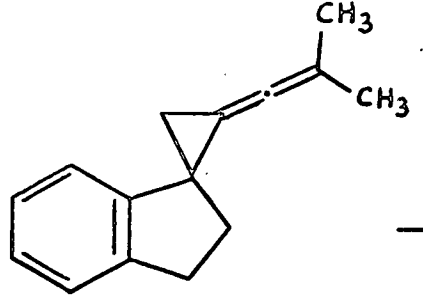
The acid catalysed rearrangement of the adduct(137) was also carried out with deuterium chloride in methanol-d and the deuterated product isolated as its 1:1 adduct with maleic anhydride. The same product was obtained on similarly treating the original cyclopentadiene(160). The n.m.r. spectrum of this deuterated adduct is also illustrated in figure II. The bridgehead protons (H_b and H_b') of the adduct(161) resonate as multiplets centred at 6·84 and 7·22τ while the allylic methyl protons (H_c) occur as a singlet at 8·06τ, the n.m.r. spectrum of the deuterated adduct showing >85% replacement by deuterium of the two olefinic protons and the three allylic methyl protons in the original diene. This is substantiated by the parent peak in the mass spectrum being five mass units above that of its non-deuterated counterpart. Deuterium exchange during the acid catalysed rearrangement of the vinylidenecyclopropane(137) therefore leads to the formation of the pentadeuterated cyclopentadiene(164). The synthesis of the cyclopentadiene(160) by another route was not attempted.

A mechanism which is consistent with the above observations is illustrated in scheme VI. Protonation of tetrasubstituted allenes normally occurs at the centre carbon atom.[97] Protonation in this manner followed by ring opening and proton elimination can lead to the triene(165). Reprotonation of this system followed by


H
H
Ph
α
γ
CH3
H3C
β
CH3
(137)
H+
at γ
H+
at α
Ph
H
+
CH3
CH3
Ph
H
+
CH3
CH3
Ph
H
H
+
H3C
H
CH3
H3C
Ph
H
H+
CH3
H3C
H
CH3
(167)
H+
Ph
H
H3C
H
CH3
(168)

ring closure and proton loss leads to the cyclopentadiene(160). The formation of the d_5-cyclopentadiene(164) by deuterium exchange during vinylidenecyclopropane rearrangement and also directly from the product itself is consistent with the protonation steps being reversible, although it seems likely that the initial cyclopropyl ring opening step is irreversible. The driving force behind the preferred formation of the cyclopentadiene would appear to result from the thermodynamic stability of the intermediates involved, the calculated heat of formation of the triene(165) being 47·3 Kcal.mole^{-1} whereas that of the cyclopentadiene(160) is 34·0 Kcal.mole^{-1}. An alternative mode of protonation at the triene(165) followed by intramolecular attack at the benzene ring and subsequent proton elimination could lead to the indene derivative(166), which is thermodynamically more stable than the cyclopentadiene(160), having a calculated heat of formation of 30·0 Kcal.mole^{-1}. As this product was never observed it seems likely that a higher activation energy is required for intramolecular electrophylic attack at the ortho-position of the benzene ring than for the process leading to formation of the cyclopentadiene(160).

The three possible sites(α, β and γ) for allenic protonation are illustrated in scheme VII. Protonation at the β-position has already been discussed and leads to formation of the cyclopentadiene(160). However protonation at the γ-site followed by an alternative mode of ring opening and bond migration, as shown in pathway (a), could lead to the enyne system(168). This could also result from protonation at the α-site by pathway (b). However



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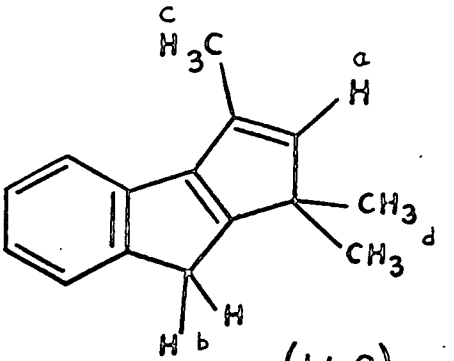

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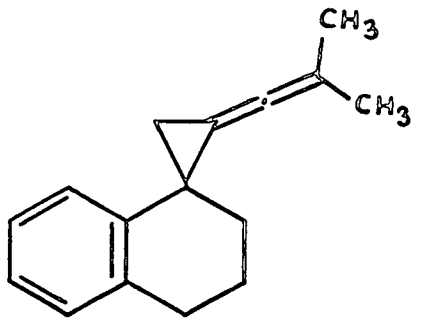
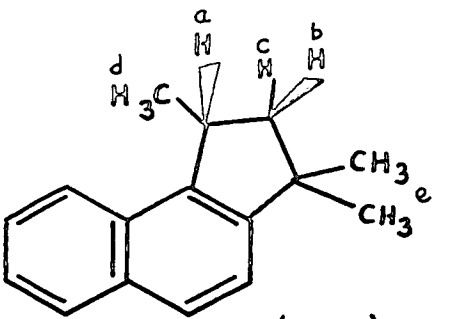
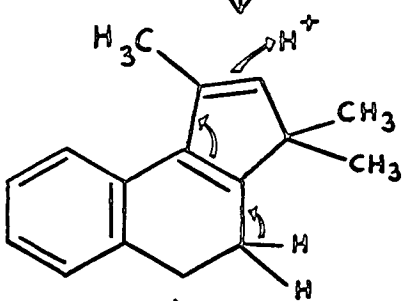


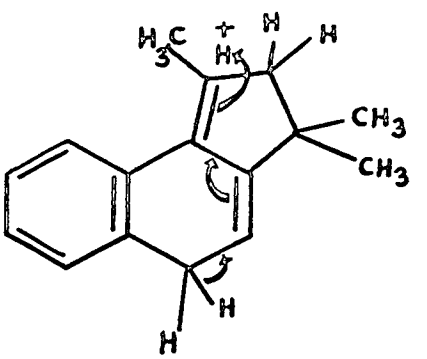
(148)



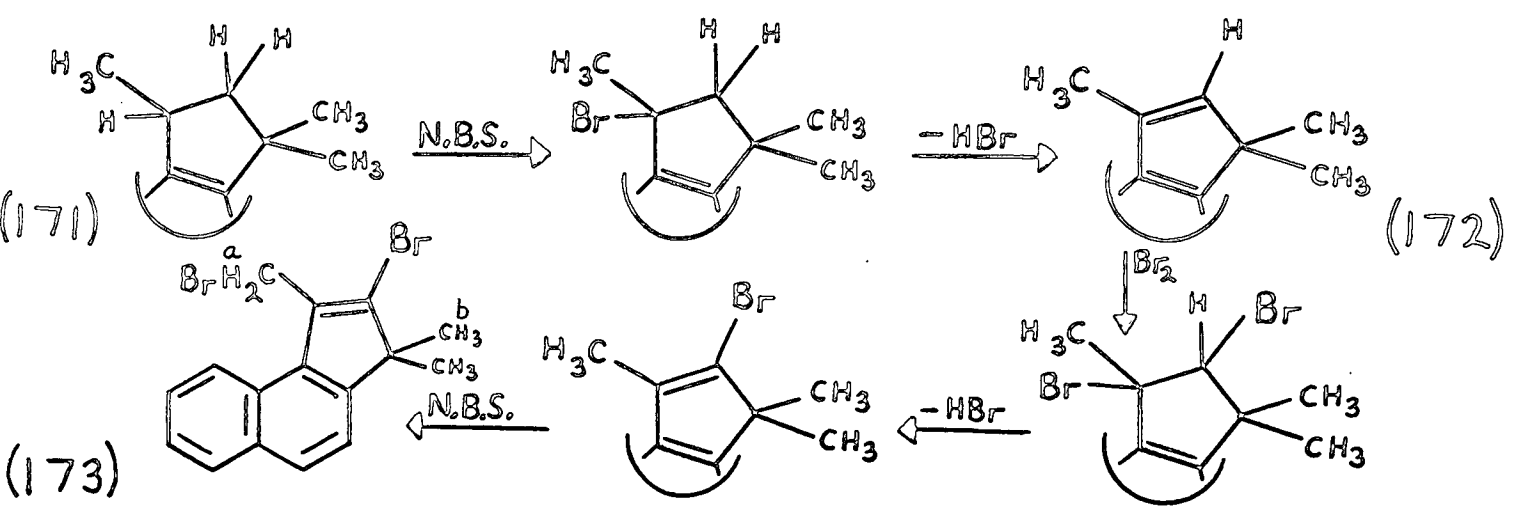
(171)



(170)



SCHEME VIII



(171)

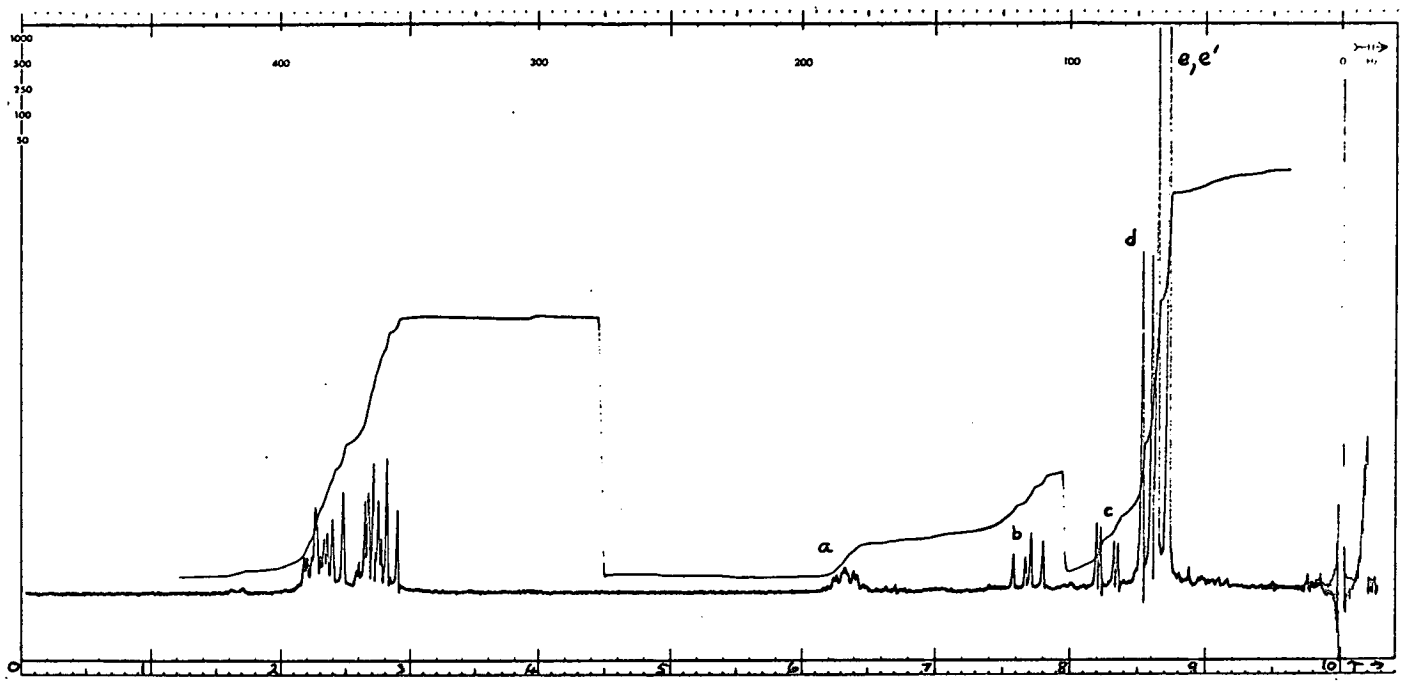
(172)

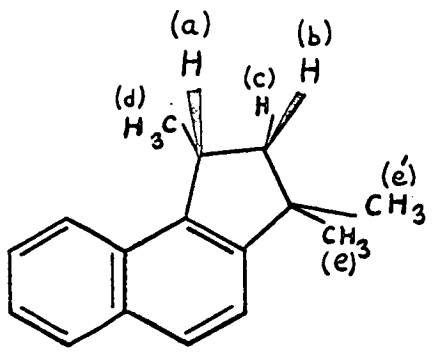
(173)

because this latter process involves intermediate deprotonation followed by reprotonation of the proposed allene intermediate(167), it is considered less likely than pathway (a). The possibility of protonation at the saturated ring sites is deferred until later (section 3.4). Although the enyne system(168) was not in fact isolated it seems likely that it would be formed, by analogy with related systems discussed later (sections 3.4 and 3.6), and in addition the n.m.r. spectrum of the crude acid catalysed product prepared from the adduct(137) showed a weak doublet (J = 7 Hz.) centred at 9·02τ which could be attributed to the isopropyl methyl protons (H_a) of the enyne(168). Further products might arise by the addition of hydrogen chloride to the enyne system as described later (section 3.6) for a related system(215) and, by analogy, this could account for several ion peaks occurring above that due to the present hydrocarbon(160) in the mass spectrum of the crude acid catalysed rearrangement product. Consequently the foregoing could then account for the complex mixture of components (40% of total) formed together with the cyclopentadiene derivative in this rearrangement.

Acid catalysed rearrangement of the spiro-indane(146) formed a mixture containing predominantly (80%) one product, the remaining 20% being a mixture of several unidentified components probably arising from the alternative modes of allenic protonation which have been discussed above. In view of the observations above and the mechanism proposed, the major product was expected to be

FIGURE III



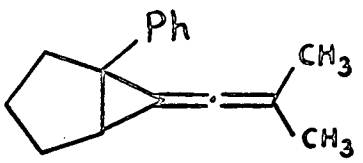


3',3',5'-trimethyl-1,2-cyclopentadienoindene(169) and the spectral properties were in accordance with this structure. The compound has a relatively simple n.m.r. spectrum due to the coplanarity and resulting symmetry of the ring systems. Thus the olefinic proton (H_a, 3·99τ), the methylene group (H_b, 7·21τ), the allylic methyl group (H_c, 7·79τ) and the gem-dimethyl protons (H_d, 8·73τ) all appear as sharp singlets. The u.v. spectrum is in accord with a cross conjugated system, having maxima at 259·5 mμ (ϵ = 26,800) and 267·5 mμ (ϵ = 26,000). This compound was relatively unstable and readily polymerised when heated. The attempted formation of a maleic anhydride adduct was unsuccessful, no doubt due to the additional strain that would result from linking the bridgehead position to the aromatic ring by way of a methylene group.

The acid catalysed rearrangement of the spiro-tetralin(148) however yielded not the expected cyclopentadienodi-hydronaphthalene(170) but a compound which was assigned the structure(171) on the basis of the following evidence. The n.m.r. spectrum of the compound is illustrated in figure III and the aliphatic region is typical of a rigid cyclopentenyl ring system. The two non-equivalent methylene protons (H_b, 7·68τ; H_c, 8·27τ) appear as quartets, being equally coupled to each other (J_{bc} = 13 Hz.) and unequally coupled to the adjacent benzylic proton (J_{ba} = 9 Hz.; J_{ca} = 3Hz.). The Karplus equation[98] for adjacently coupled protons with dihedral angles of 0° and 120° yields values of 8 and 3 Hz. respectively. The benzylic proton(H_a, 6·36τ) appears as a multiplet and the benzylic methyl group

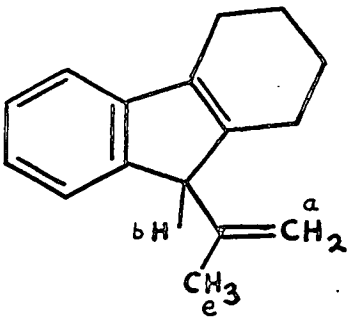
(H_d, 8·56τ) appears as a doublet (J_{da} = 7 Hz.) whereas the two non-equivalent methyl groups (H_e, 8·64, 8·73τ) appear as singlets. The i.r. spectrum confirms 1,2,3,4-tetra- and 1,2-di-aromatic substitution and the u.v. spectrum is typical of a naphthalene derivative.

Attempted dehydrogenation of the cyclopentenonaphthalene(171) with o-chloranil or 2,3-dichloro-5,6-dicyanoquinone(D.D.Q.) was unsuccessful. Further to attempts to dehydrogenate this compound, radical bromination of the cyclopentenonaphthalene(171) with N-bromosuccinimide(N.B.S.) lead directly to the formation of 4'-bromo-5'-bromomethyl-3',3'-dimethyl-1,2-cyclopenta-1',4'-dienonaphthalene(173), three molar equivalents of N.B.S. being consumed. The n.m.r. spectrum of this dibromocompound shows the methylene protons (H_a, 5·24τ) and the two equivalent methyl groups (H_b, 8·72τ) as singlets and the mass spectrum clearly shows the presence of two bromine atoms, the isotopic parent peaks for $^{79}Br_2$, ^{79}Br ^{81}Br and $^{81}Br_2$ being at m/e:364, 366 and 368 respectively. A mechanism consistent with the formation of the dibromide is illustrated in scheme VIII and involves benzylic bromination of the naphthalene derivative(171) followed by elimination of hydrogen bromide to form the cyclopentadiene(172). Further molecular bromination at the newly formed double bond followed by elimination of hydrogen bromide and final allylic bromination can form the dibromide(173). A related radical bromination of 1,1-diphenylethane has been shown[90] to lead directly to 2-bromo-1,1-diphenylethylene, no doubt by a similar route.

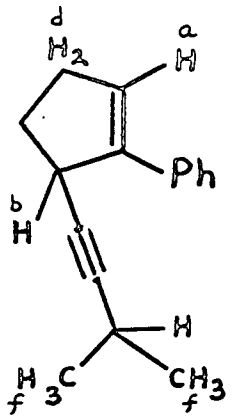


(174)

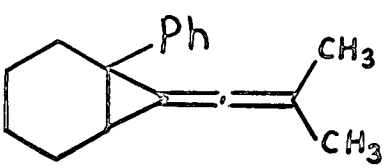
450°



(175)

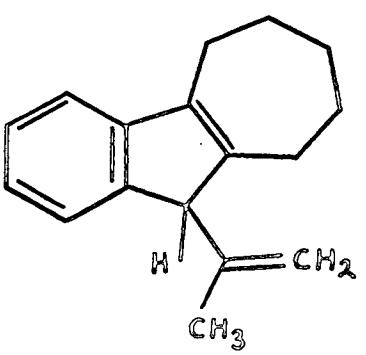


(176)

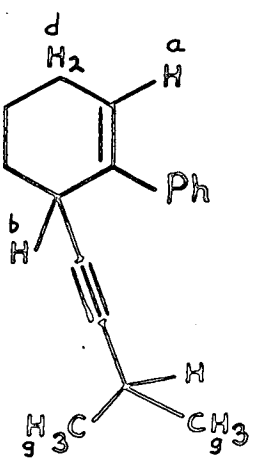


(177)

450°



(178)



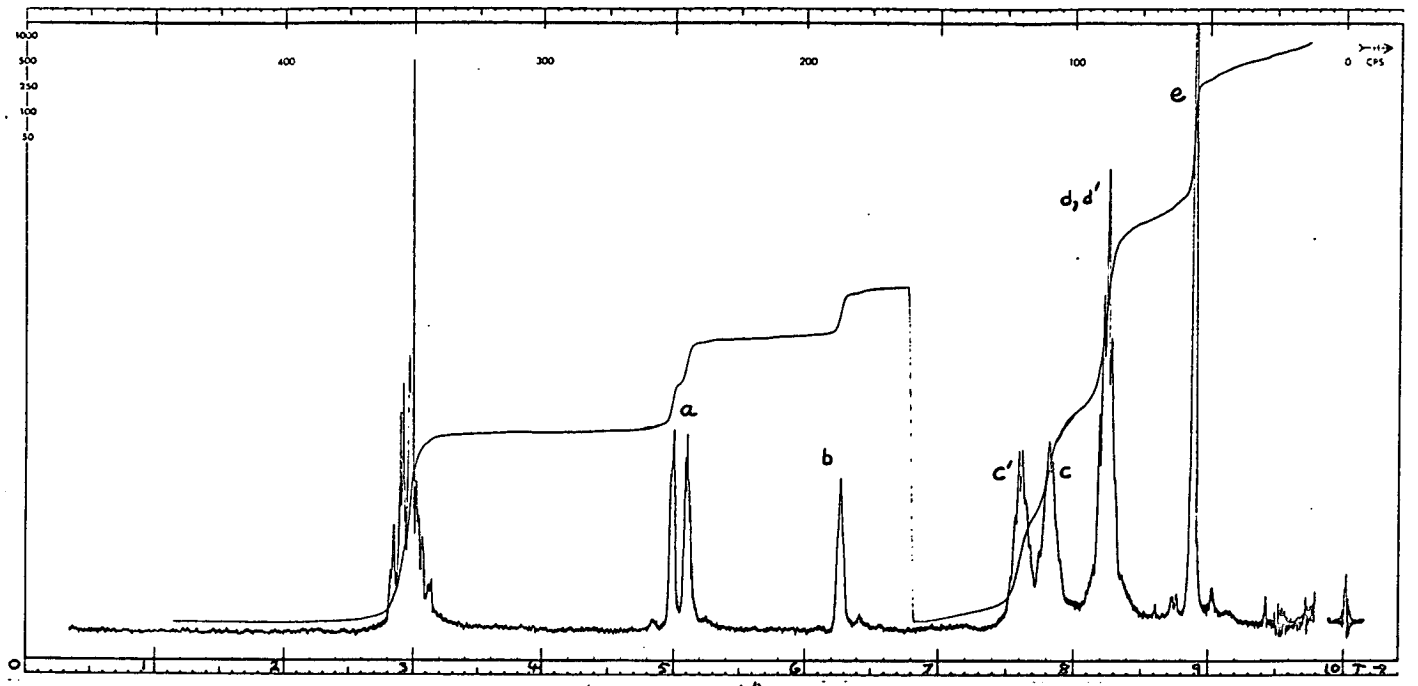
(179)

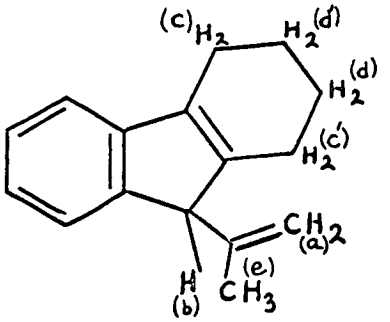
The attempted synthesis of the cyclopentenonaphthalene(171) has as yet been unsuccessful. A modified Grignard reaction[99] of β-naphthyl magnesium bromide with mesityl oxide gave the expected Michael addition product, however attempts to convert this adduct to 3,3-dimethyl-3-(β-naphthyl)propionic acid have so far failed.

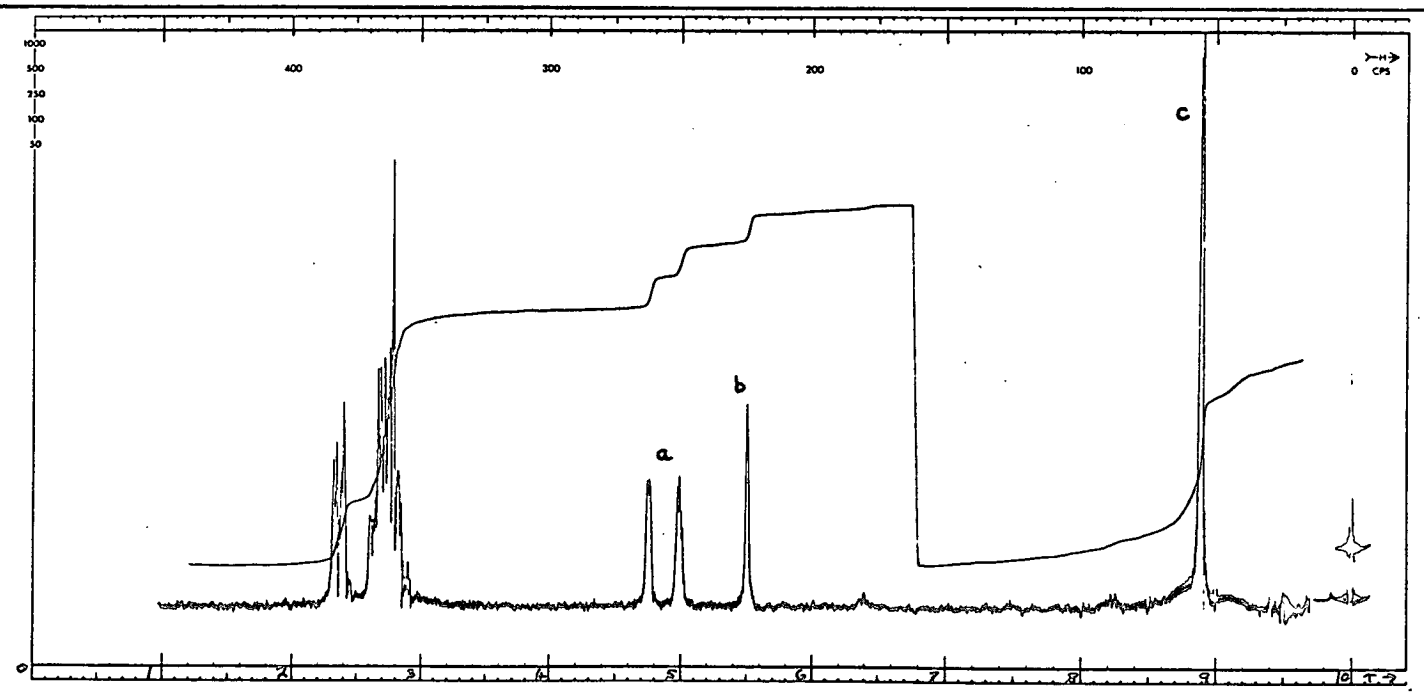
The acid catalysed formation of the cyclopentadienoindene(169) and the intermediacy of its homologue(170) in the tetralin series can be rationalised by a mechanism exactly analogous to that already described (scheme VI). However in the latter case further protonation and bond migration leads to the naphthalene derivative(171), the driving force behind this sequence being the thermodynamic stability of the components involved. Thus the calculated heat of formation of the intermediate cyclopentadienodihydronaphthalene(170) is 33·2 Kcal.mole^{-1} whereas that of the naphthalene derivative(171) is 13·4 Kcal.mole^{-1}.

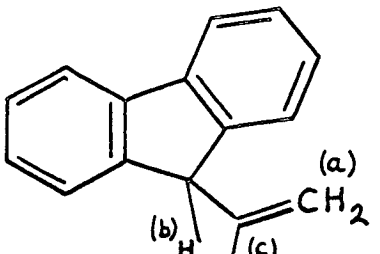
3.4 THERMAL AND ACID CATALYSED REARRANGEMENT OF THE ADDUCTS DERIVED FROM 1-ARYLCYCLOALKENES.

The thermal rearrangement of 6-dimethylvinylidene-1-phenylbicyclo[3,1,0]hexane(174), effected by heating the adduct in xylene solution at 150° for 7 hr., yielded only polymeric material and a small amount of unchanged starting material. However this adduct readily underwent rearrangement when passed through the flow system at 450° and formed a mixture containing 90% of 9-isopropenyl-1,2,3,4-tetrahydrofluorene(175), 5% of 1-(3-methylbut-1-ynyl)-2-phenylcyclopent-2-ene(176) and 5% of unidentified minor


a
b
c'
c
d, d'
e

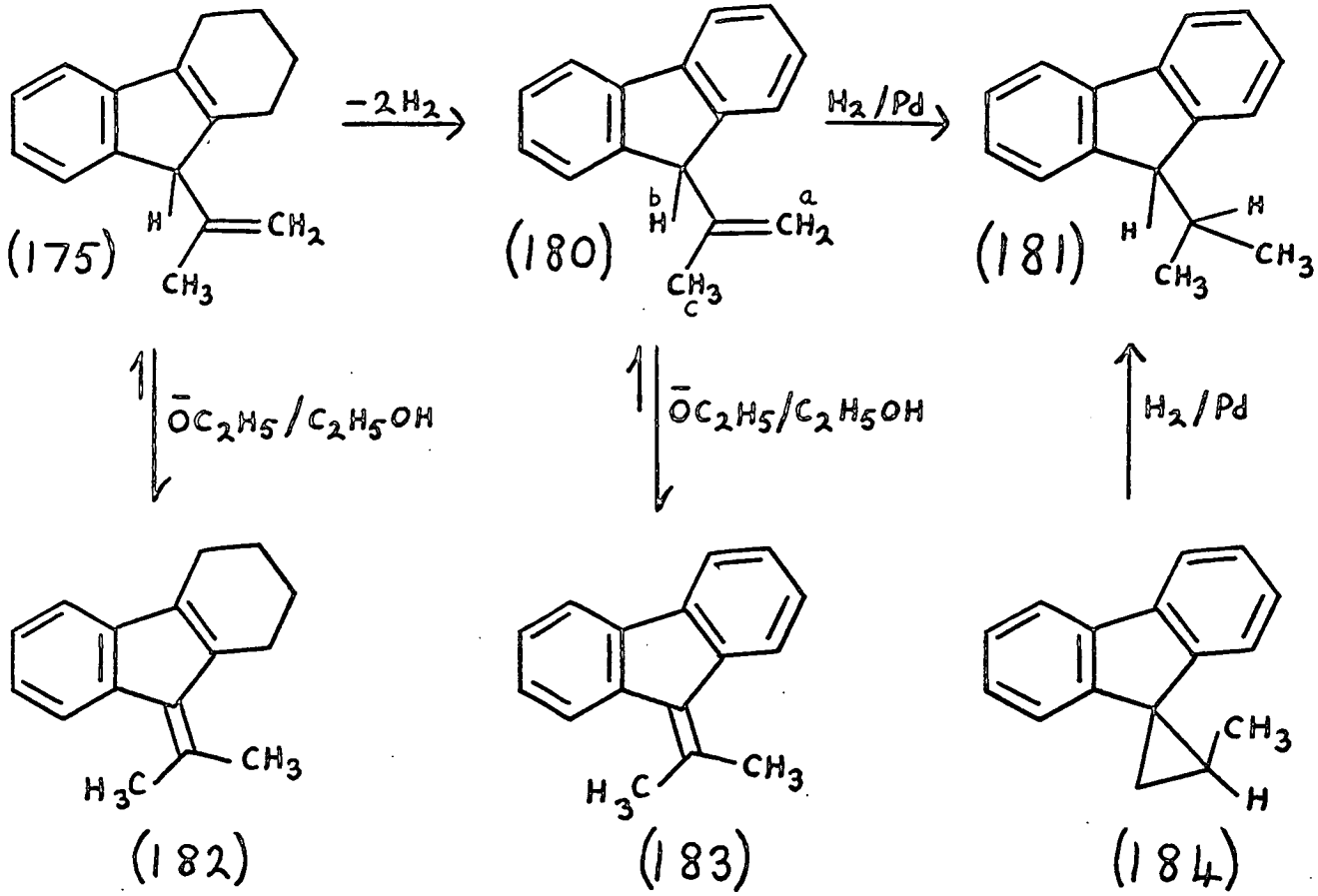

(c) H2
H2 (d)
H2 (d)
H2 (c')
CH2 (a)
H (b)
CH3 (e)

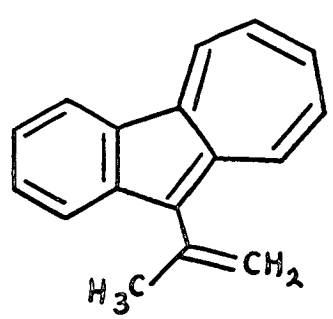

a
b
c


(a)
CH2
(b) H
(c)

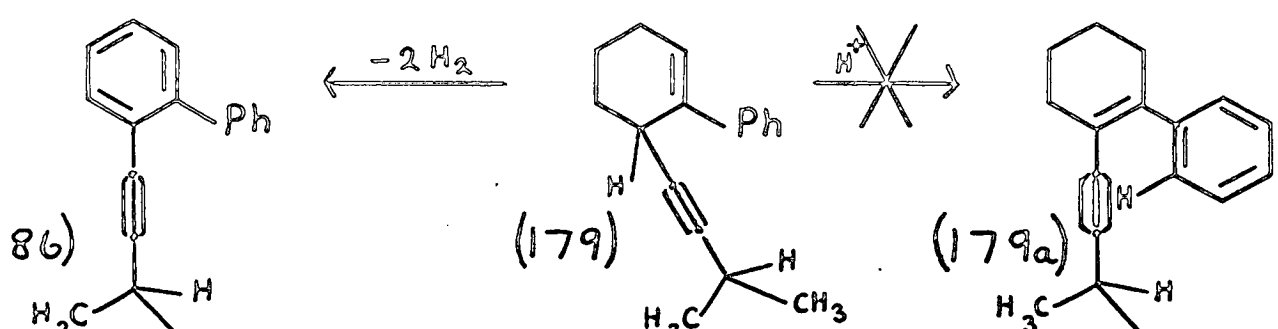
components. In a similar fashion 7-dimethylvinylidene-1-phenylbicyclo[4,1,0]heptane(177) afforded a mixture containing 75% of the hexahydro-1,2-benzazulene(178), 20% of the ethynylcyclohexene(179) and 5% of minor components. This adduct did however give a low yield of the ethynylcyclohexene(179) when heated in xylene solution at 180° for 8 hr.

The structure of the tetrahydrofluorene(175) was established from its spectral characteristics and two stage conversion to 9-isopropylfluorene, and that of the hexahydrobenzazulene(178) by its spectral similarities to the above. The n.m.r. spectrum of the tetrahydrofluorene(175) is illustrated in figure IV and shows the olefinic methylene protons (H_a, 5·00, 5·10τ) as two finely split multiplets, the benzylic proton (H_b, 6·26τ) as a broad singlet and the allylic methyl protons (H_e, 8·88τ) as a fine doublet (J = 1 Hz.). The proton allocations were confirmed by spin-spin decoupling. Examination of stereomodels shows that the methyl protons in this system lie above the plane of the aromatic ring causing them to be somewhat shielded, and therefore resonating at a higher field than is usual (8·0 - 8·3τ) for an allylic methyl group. The i.r. spectrum confirms the terminal methylene grouping and 1,2-disubstitution of the aromatic ring while the u.v. spectrum, which has a maximum at 263·0 mμ (ε = 12,300), is very similar to that of tetrahydrofluorene itself[100] ($\lambda_{max.}$ = 259·0 mμ, ε = 13,200). The spectral properties (p. 136) of the hexahydrobenzazulene derivative(178) are analogous to the foregoing.


(175)
$-2H_2$
(180)
H_2/Pd
(181)
$\bar{O}C_2H_5/C_2H_5OH$
$\bar{O}C_2H_5/C_2H_5OH$
H_2/Pd
(182)
(183)
(184)

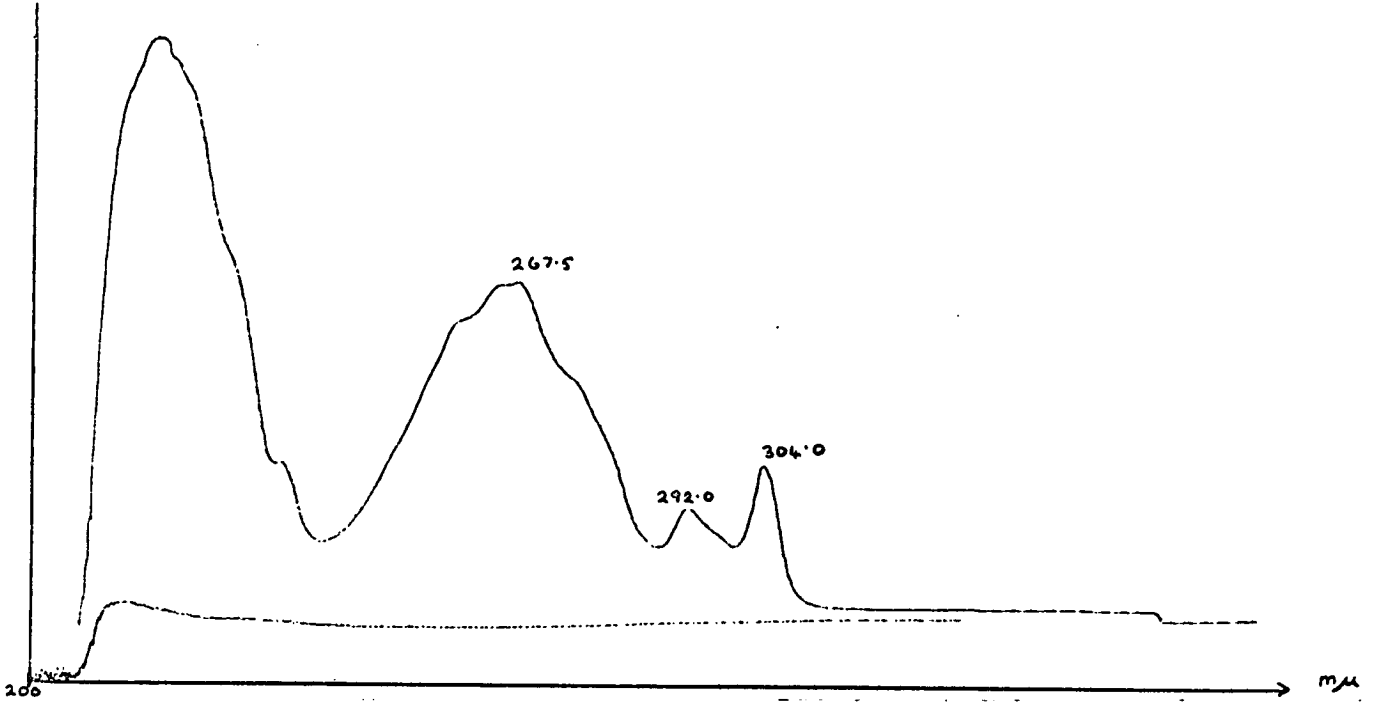


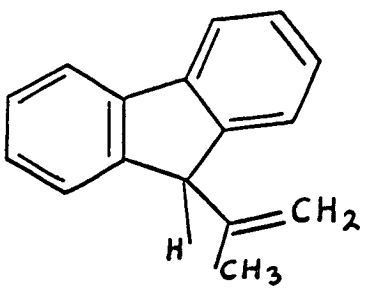
(185)

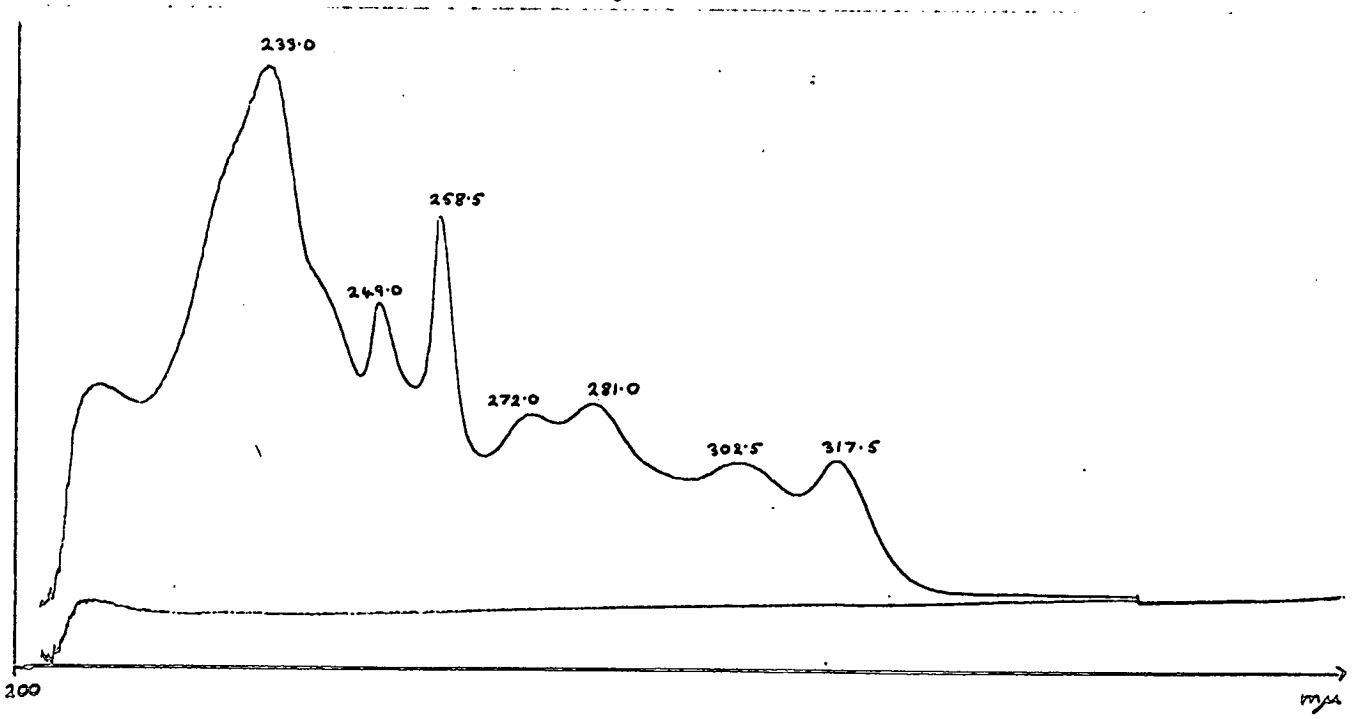

$-2H_2$
(179)
(179a)

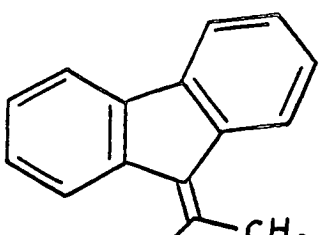
Dehydrogenation of the tetrahydrofluorene(175) with o-chloranil forms 9-isopropenylfluorene(180), the n.m.r. spectrum of this compound being illustrated in figure IV. As in the case of the tetrahydroprecursor, the allylic methyl protons (H_c, 8·90τ) of this fluorene derivative are shielded by the aromatic π-electron system, and are coupled (J_{ac} = 1 Hz.) with the olefinic methylene protons (H_a). Strong irradiation of the methyl protons caused collapse of the olefinic multiplets into two sharp doublets (J = 2Hz.), and thus the allylic coupling between the fluorenyl proton (H_b) and the olefinic protons is negligible in this system. The u.v. spectrum of this compound(180) is illustrated in figure V and is typical of 9-substituted fluorene derivatives, direct comparison being made with several compounds available in the department. It is also noteworthy that this compound was different from two other possible 9-isomers, namely 9-isopropylidenefluorene(183) and 2'-methylcyclopropane-1'-spiro-9-fluorene(184) which were prepared by known methods.[101,102] Catalytic hydrogenation of 9-isopropenylfluorene(180) formed 9-isopropylfluorene(181), identical to an authentic sample prepared by hydrogenation of the spiro-9-fluorene(184).[102]

Treatment of 9-isopropenylfluorene(180) with sodium ethoxide in ethanol causes slow isomerisation to 9-isopropylidene-fluorene(183). The ultraviolet absorptions due to the fluorenyl and fluorenylidene chromophores are readily distinguishable (figure V) and this allows the reaction to be monitored by way of its u.v. spectrum. The u.v. spectrum of the reaction mixture


267·5
304·0
292·0
200
mμ


CH2
H
CH3

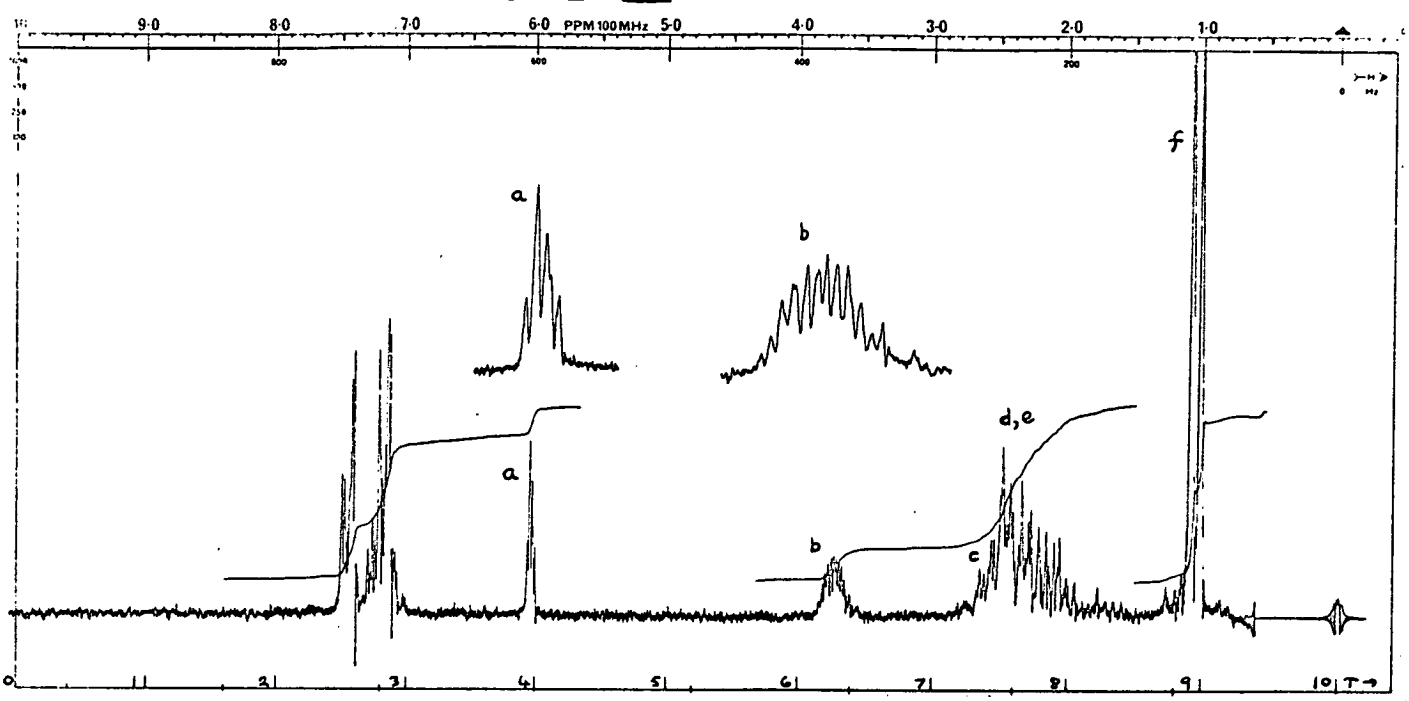

233·0
258·5
249·0
272·0
281·0
302·5
317·5
200
mμ


CH2

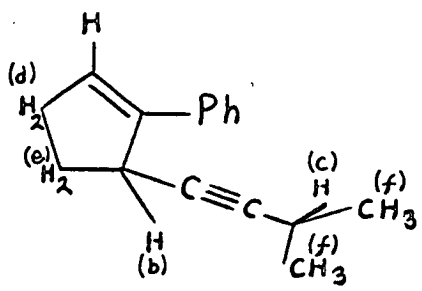
ceased to change after 20 hr., by which time it was virtually identical to that obtained from authentic 9-isopropylidene-fluorene, the extinction coefficients agreeing to within 5%. As this is an equilibrium reaction,[103] the position of equilibrium must be almost completely displaced in favour of the fluorenylidene derivative, which is in complete agreement with the results obtained by Delahunt for related systems.[103] In a similar experiment carried out with the tetrahydrofluorene(175), equilibrium was only reached after 50 hr. by which time the original styrene chromophore, which has a maximum at 263·0mμ (ε = 12,300), had increased to a maximum at 266·0mμ (ε = 26,700). This is in agreement with the proposed dimethylbenzofulvene structure(182), dimethylbenzofulvene itself[104] having a maximum at 260·0mμ (ε = 29,000). However attempted isolation of these isomerisation products was unsuccessful in both cases, neutralisation of the solutions causing destruction of the chromophore involved.

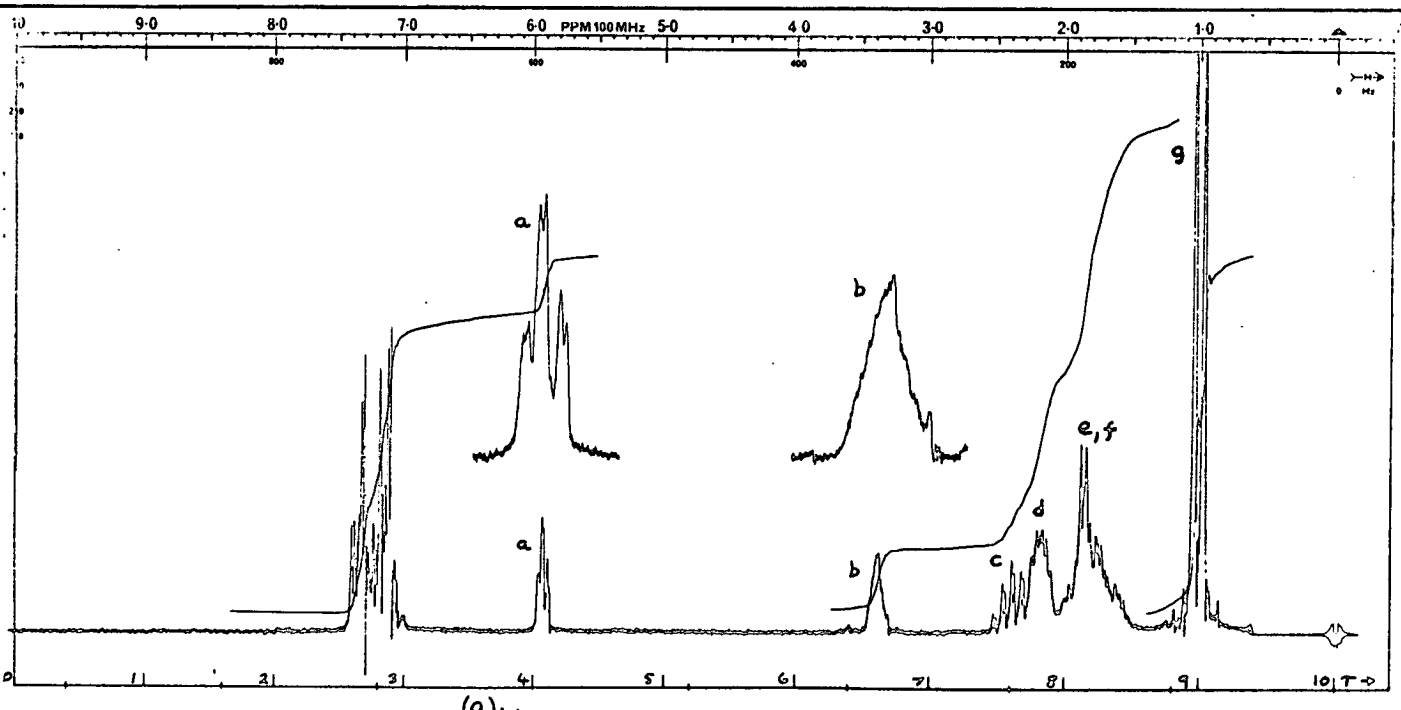
Attempted formation of 3-isopropenyl-1,2-benzazulene(185) by dehydrogenation of the hexahydrobenzazulene(178) was unsuccessful. Several attempts which were carried out with o-chloranil or palladium on charcoal did give rise to some intensely blue material, this colour being typical of benzazulenes,[105] but these were found to be multi-component mixtures and no evidence was found for the presence of the desired product.

The structure of the ethynylcyclohexene(179) and of (176) by analogy was established from its spectral characteristics and

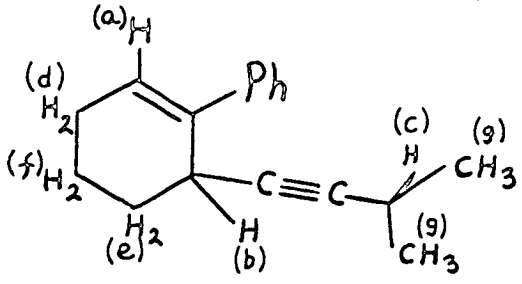

9·0
8·0
7·0
6·0 PPM 100 MHz
5·0
4·0
3·0
2·0
1·0
a
b
f
d,e
c

(a)


H
(d)
H2
Ph
(e)
H2
C≡C
(c)
H
(f)
CH3
H
(b)
(f)
CH3

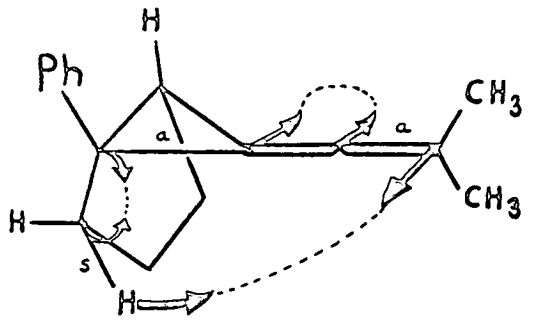

9·0
8·0
7·0
6·0 PPM 100 MHz
5·0
4·0
3·0
2·0
1·0
a
b
g
e,f
d
c

(a)


H
(d)
H2
Ph
(f)
H2
C≡C
(c)
H
(g)
CH3
H2
(e)
H
(b)
(g)
CH3

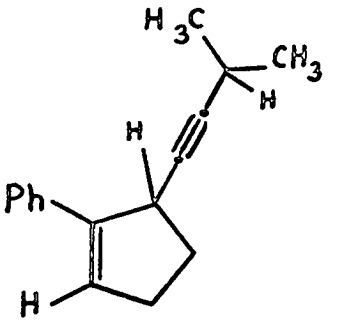
dehydrogenation with o-chloranil to give the ethynylbiphenyl(186). This compound was independently prepared by an alternative route (section 4). The n.m.r. spectra of the two ethynylcycloalkenes are illustrated in figure VI. It is significant that the olefinic proton (H_a, 3·96τ) in the cyclopentene(176) appears as a quartet, being coupled to the two non-equivalent methylene protons (H_d) in the practically rigid alicyclic ring whereas the olefinic proton (H_a, 4·08τ) in the cyclohexene(179) is a triplet, the flexibility of the cyclohexene ring allowing rapid interconversion of the two neighbouring methylene protons (H_d). The propargylic protons (H_b) of the cyclopentene and the cyclohexene occur as multiplets centred at 6·27 and 6·61τ respectively. The i.r. spectra of these compounds shows a weak absorption at 2,250 $cm.^{-1}$ due to the triple bond stretching mode, and a strong band at 1320 $cm.^{-1}$ which can be attributed to the (C-H)deformation mode of the isopropyl hydrogen atom.[106] The u.v. spectra are typical of styrene derivatives.

The acetylenic cyclohexene(179) was recovered unchanged upon treatment with acid, the apparently fully conjugated isomer(179a) not being detected. Examination of the stereochemistry of this molecule indicates that in view of the severe steric interaction that would occur between an ortho-aromatic hydrogen atom and the acetylenic bond, the aromatic ring is unlikely to be coplanar with the enyne π-electron system. It seems therefore that a choice exists between conjugation of the double bond with the aromatic ring(i.e. 179) or with the acetylenic system (i.e. 179a), in which case the former is preferred.



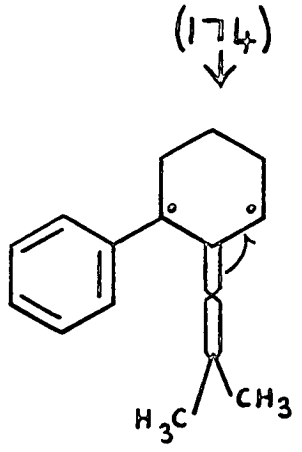
(174)

$(\pi 2a^{+} \sigma 2a^{+} \sigma 2s)$

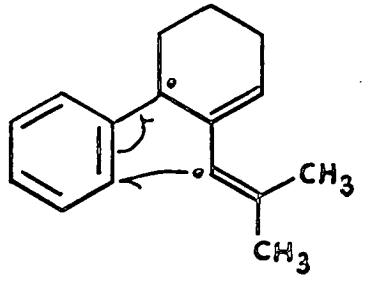


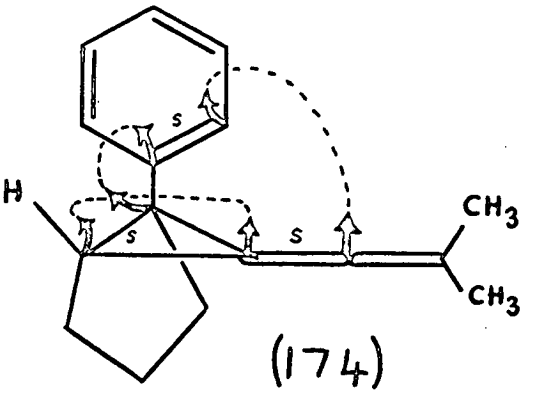
(176)

SCHEME X



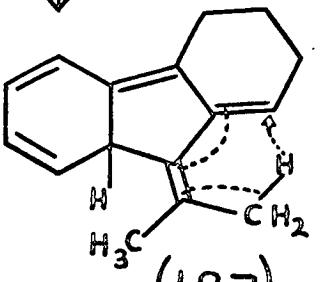
(a)



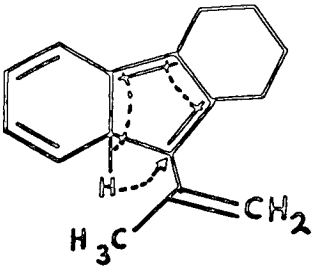


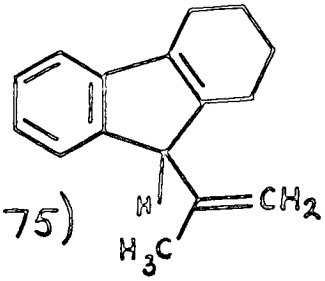
(174)

(b) $(\pi 2s^{+} \pi 2s^{+} \sigma 2s)$



(187)

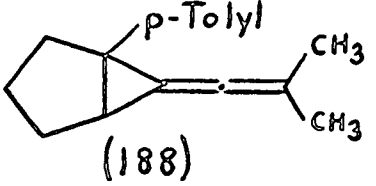




(175)

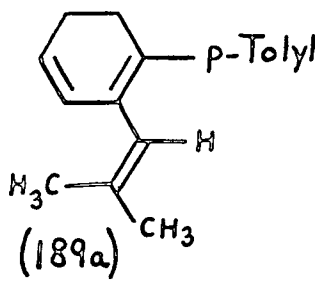
The thermal rearrangement of the adducts derived from these 1-arylcycloalkenes follows a different path to that followed by those derived from the 1-arylalkenes previously described, probably due to the formation of analogous dimethylenecyclopropane derivatives being highly unfavourable in the present case because of the resulting bridgehead double bond. A concerted mechanism which can account for the formation of the acetylenic products is shown in scheme IX in terms of the ethynylcyclopentene system(176), formation of the ethynylcyclohexene(179) being expected to follow an analogous path. This involves a disrotatory opening of the cyclopropane ring and concerted bond formation with a 1,5 suprafacial hydrogen shift, and is a thermally allowed ($_{\pi}2_a + _{\sigma}2_a + _{\sigma}2_s$) process. A stepwise diradical mechanism is considered to be highly unlikely in this instance since a hydrogen abstraction process to form the isopropyl group is sterically impossible.

The formation of the tetrahydrofluorene(175) can be rationalised in terms of a diradical mechanism or a concerted process as illustrated in scheme X, the formation of the hexahydrobenzazulene(178) being expected to be analogous. The concerted mechanism (pathway b) involves disrotatory cyclopropyl ring opening and concerted bond formation with the aromatic ring and is a thermally allowed ($_{\pi}2_s + _{\sigma}2_s + _{\sigma}2_s$) process which leads to the intermediacy of (187). This intermediate system could also be formed by the radical pathway (a), and could then undergo two 1,5 suprafacial hydrogen shifts with accompanied bond migration



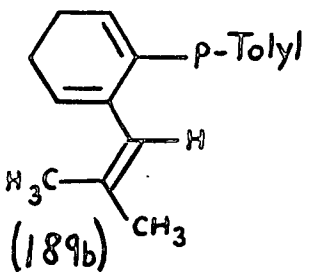
(188)

Δ

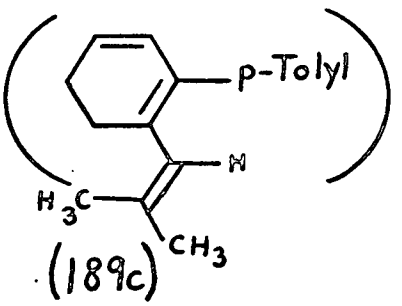


(189a)

+

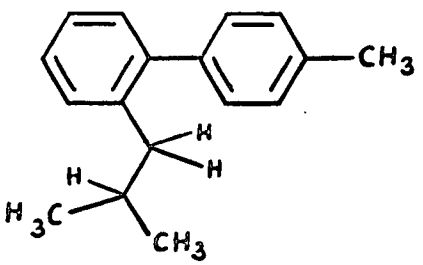


(189b)



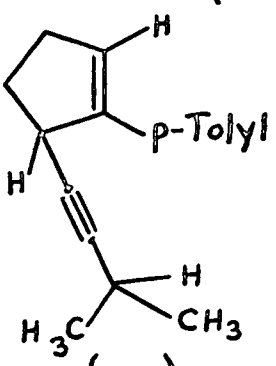
(189c)

+

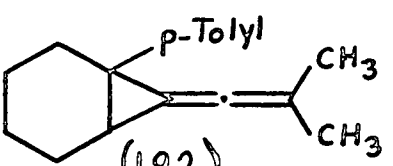


(191)

+

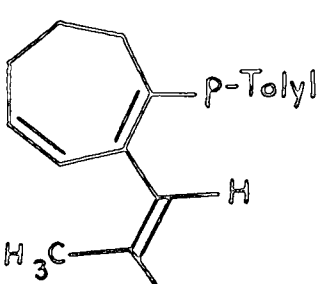


(190)



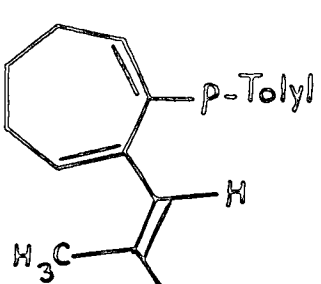
(192)

Δ



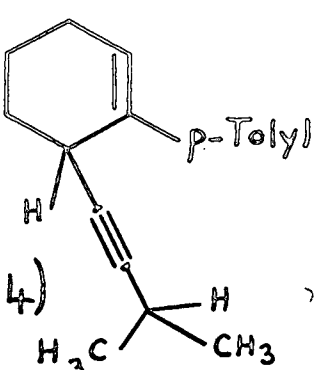
(193a)

+



(193b)

+



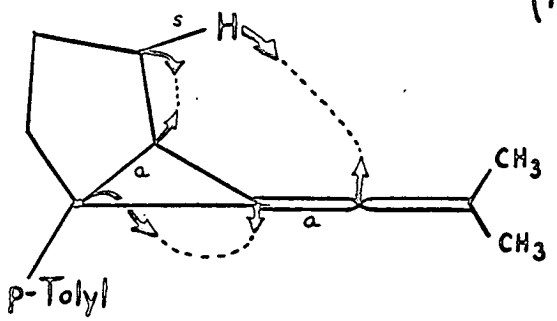
(194)

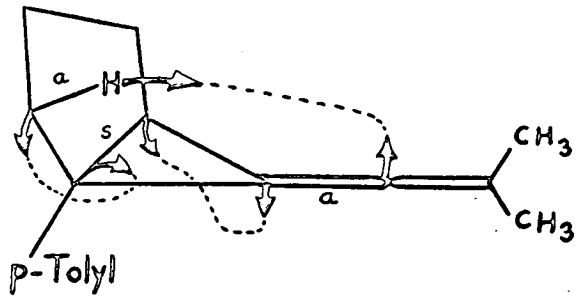
to give the product(175). A tentative choice has been made between these two alternative mechanisms and is discussed later (p. 61).

In contrast to its non-substituted homologue(174), 6-dimethylvinylidene-1-(p-tolyl)bicyclo[3,1,0]hexane(188) undergoes 25-50% rearrangement on distillation (pot temperature, 140°), depending on the conditions involved, to form a mixture of two cyclohexadienes which on the basis of evidence presented later in connection with the acid catalysed rearrangement(p. 63) were assigned the two structures (189a,b). Separation of these isomers by preparative v.p.c. was not possible. Complete rearrangement occurred when the crude adduct was heated in xylene solution at 140° for 1 hr., forming a mixture composed of 80% of the cyclohexadienes(189a,b), 10% of the ethynylcyclopentene(190), 5% of 2-isobutyl-4'-methylbiphenyl(191) and 5% of minor unidentified components. Passage of the crude adduct through the flow system at 350° formed 76% of the cyclohexadienes(189a,b), 3% of the ethynylcyclopentene(190), 19% of the biphenyl(191) and 2% of other material.

Similarly distillation of 7-dimethylvinylidene-1-(p-tolyl)bicyclo[4,1,0]heptane(192) results in up to 40% rearrangement of the adduct, the rearrangement product consisting of a 50:50 mixture of compounds considered to be the cycloheptadienes(193a,b) and unidentified material. Heating a solution of the adduct in xylene at 140° for 1 hr. caused complete rearrangement to form 25% of the cycloheptadienes(193a,b), 25%

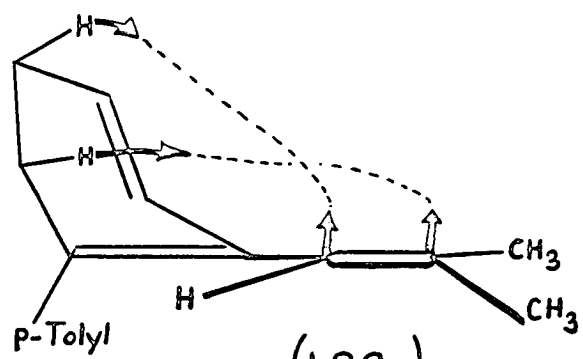
(188)



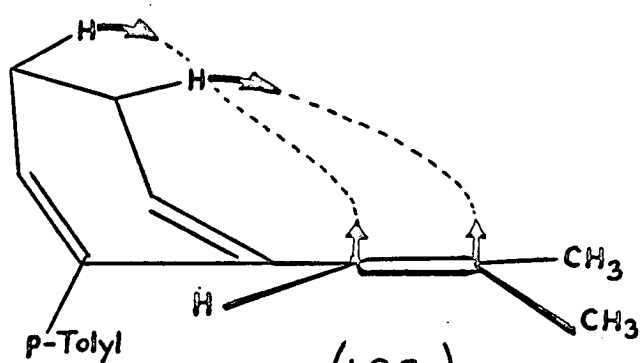


$(\pi 2a^{+} \sigma 2a^{+} \sigma 2s)$

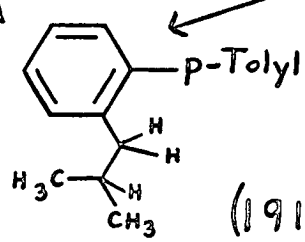
$(\pi 2a^{+} \sigma 2a^{+} \sigma 2s)$



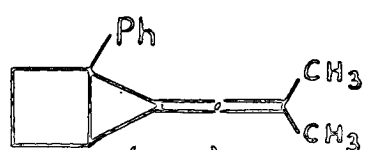
(189a)



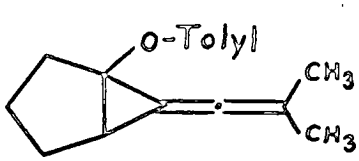
(189b)



(191)

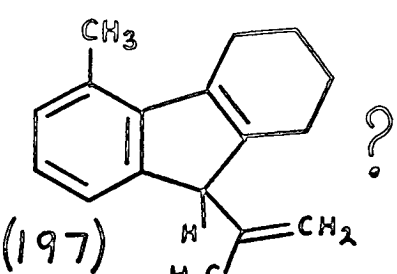


(195)



(196)

$\xrightarrow{\Delta}$



(197)

of the ethynylcyclohexene(194) and 50% of unidentified products. When the crude adduct was distilled through the flow system at 350° the only product to be identified (10% of total) was the ethynylcyclohexene(194), however subsequent examination of the cycloheptadienes(193a,b) showed them to be particularly labile at elevated temperatures giving rise to multi-component mixtures.

The acetylenic cyclopentene(190) and cyclohexene(194) were identified by spectral comparison with their non alkyl substituted homologues(176) and (179), the n.m.r. spectra showing additional sharp singlets at 7·70 and 7·73τ respectively attributed to the aryl methyl group. The structure of the substituted biphenyl(191) was verified by independent synthesis (section 4).

These particularly facile rearrangements probably involve concerted mechanisms since diradical intermediates would lead to sterically impossible hydrogen abstraction processes. Formation of the cyclohexadienes(189a,b) would result from a thermally allowed ($_{\pi}2_a + \sigma^2_a + \sigma^2_s$) process involving a 1,5 suprafacial hydrogen migration as illustrated in scheme XI, the formation of one or other isomer depending on the migrating hydrogen atom involved (pathway a or b). Formation of the isomer(189c) is impossible by either a single concerted or a diradical process. These cyclohexadienes(189a,b) could then undergo two further 1,5 hydrogen shifts to form the thermodynamically more stable biphenyl(191). The calculated heats of formation of the cyclohexadienes and the biphenyl derivative are 46·8 and 18·2 Kcal.mole^{-1} respectively, the cyclohexadienes probably owing their apparent

stability with respect to subsequent biphenyl formation to a relatively high activation energy for the conversion which would involve a considerably strained transition state (scheme XI). This is supported by the formation of the cyclohexadiene isomers(189a, b) alone at lower temperatures (i.e. distillation), but together with increasing amounts of the biphenyl(191) as the thermolysis temperature is raised or the reaction time extended. A similar concerted process would then result in the formation of the cycloheptadienes(193a,b) in which case these isomers could also undergo further hydrogen shifts or other unspecified processes to form the relatively large amounts of unidentified material formed during the thermal rearrangement of the adduct(192).

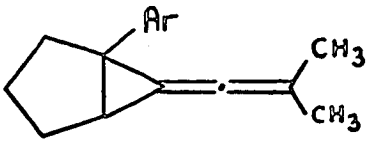
Formation of the acetylenic derivatives(190 and 194) probably occurs by way of the concerted mechanism already described(scheme IX).

A p-methyl substituent in the aromatic ring of the adducts derived from phenylcyclopentene and phenylcyclohexene has a dramatic effect on the ease of thermal rearrangement and the nature of the products which are formed. The nature of this activating influence is not clear, especially as p-methyl substitution in the acyclic series(section 3.2) has no apparent effect on either the ease or direction of thermal rearrangement. However, it could be postulated that whereas thermolysis of the unsubstituted adducts derived from phenylcyclopentene and phenylcyclohexene follows a radical pathway to form the tetrahydrofluorene(175) and the hexahydrobenzazulene(178),

concerted attack at the aromatic ring possibly being unlikely, p-alkyl substitution of the aromatic ring causes the mechanism to become concerted with resultant formation of the cyclohexadiene(189a,b) and cycloheptadiene(193a,b) systems.

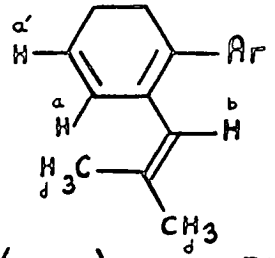
5-Dimethylvinylidene-1-phenylbicyclo[2,1,0]pentane(195) was unstable to vacuum distillation and the i.r. spectrum of the viscous distillate showed no allenic absorption near 2020 $cm.^{-1}$ The crude adduct also underwent reaction with acid to form a mixture of products, none of which was identified. The mass spectra of these mixtures show many ion peaks above that attributed to the parent compound which suggests that the predominant thermal and acid catalysed processes are not unimolecular rearrangements in the case of this adduct.

6-Dimethylvinylidene-1-(o-tolyl)bicyclo[3,1,0]hexane(196) was stable to distillation and this adduct underwent rearrangement on passing through the flow system at 450° to give two main products. These compounds were not separated, being unstable to the preparative v.p.c. conditions available. The major component (60% of total) appeared to be 9-isopropenyl-5-methyl-1,2,3,4-tetrahydrofluorene(197) from a comparison of the n.m.r. spectrum of the mixture with that of 9-isopropenyl-1,2,3,4-tetrahydrofluorene(175) itself. The characteristic protons are the olefinic methylenes (H_a, 4·99, 5·08τ) as two finely split multiplets, the benzylic proton (H_b, 6·33τ) as a broad singlet, and the allylic methyl protons (H_c, 8·88τ) as a fine doublet (J = 1 Hz.).



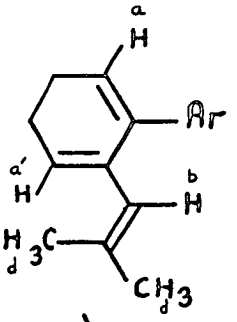
(174), Ar = Ph
(188), Ar = p-Tolyl

H^+

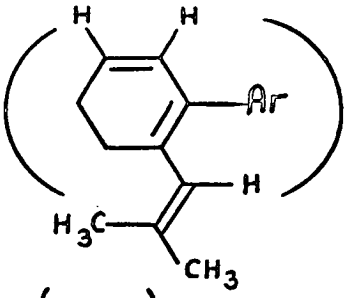


(198a), Ar = Ph
(189a), Ar = p-Tolyl

+

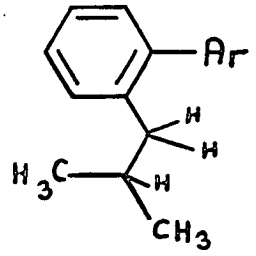


(198b), Ar = Ph
(189b), Ar = p-Tolyl

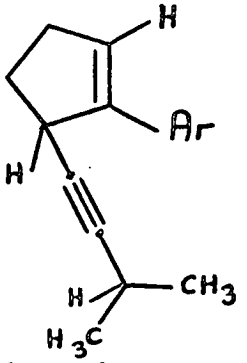


(198c), Ar = Ph
(189c), Ar = p-Tolyl

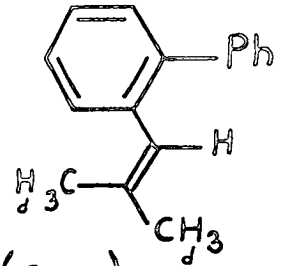
+



(199), Ar = Ph
(191), Ar = p-Tolyl



(176), Ar = Ph
(190), Ar = p-Tolyl

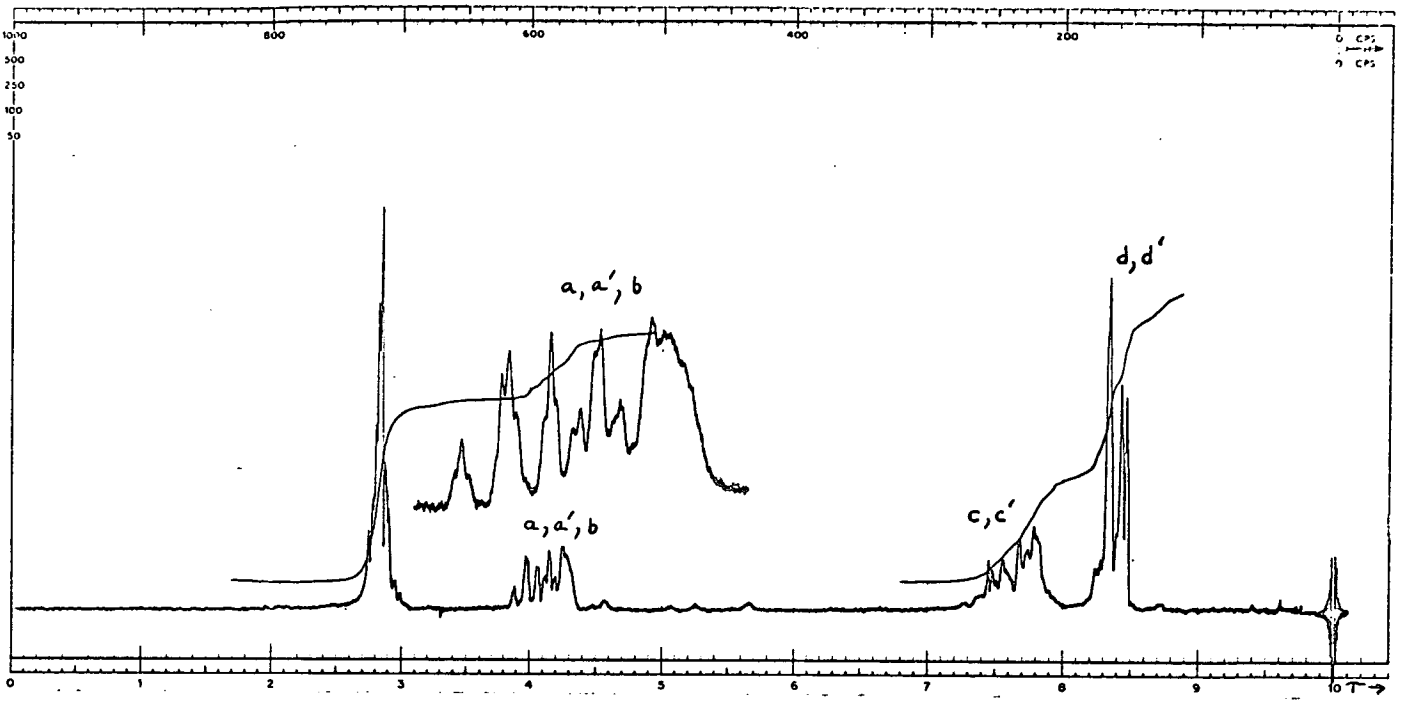


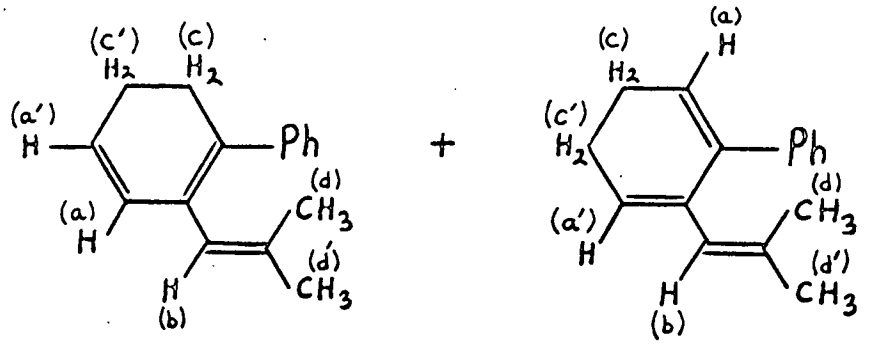
(200)

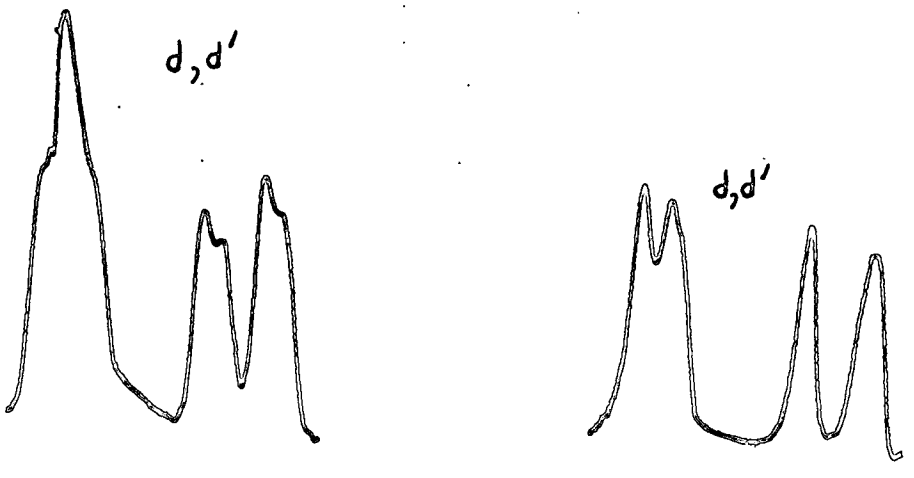
The other component was not identified and was not the corresponding acetylenic derivative or cyclohexadiene mixture. This suggests that another unknown rearrangement process is occurring in this system.

Acid catalysed rearrangement of the (p-tolyl)cyclopentene adduct(188) forms the same products as those obtained from the thermal rearrangement, the proportions being 42% of the cyclohexadienes(189a,b), 3% of the ethynylcyclopentene(190), 52% of the biphenyl derivative(191) and 3% of unidentified components. In contrast to the thermal process the acid catalysed rearrangement of the phenylcyclopentene adduct(174) follows an analogous path to the p-substituted adduct and formed 85% of the cyclohexadienes(198a,b), 5% of the ethynylcyclopentene(176), 5% of the biphenyl(199) and 5% of minor components. The structure of the isobutylbiphenyl(199) was established by independent synthesis (section 4).

The nature of the cyclohexadienes was established by the following evidence. Dehydrogenation of the phenylcyclohexadienes(198a,b) with dichlorodicyanoquinone gave 2-(2-methylprop-1-enyl)biphenyl(200), the structure of this compound being confirmed by an independent synthesis (section 4). The phenylcyclohexadiene mixture(198a,b) also reacted with maleic anhydride but the product consisted of a mixture of compounds which could not be separated or identified. The u.v. spectrum of the phenylcyclohexadienes(198a,b) shows a maximum at 310·0mμ (ϵ = 7,800) and that of the (p-tolyl)-cyclohexadienes(189a,b) shows a maximum at 305·0mμ (ϵ = 7,600),

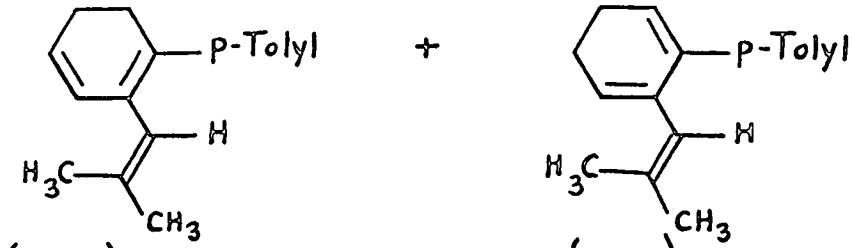






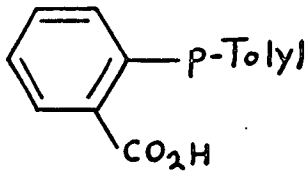
irradiation at (H) b.

consistent with conjugated aryltrienes. The n.m.r. spectrum of the phenylcyclohexadienes(198a,b) is illustrated in figure VII and shows the three olefinic protons(H_a, $H_{a'}$, H_b) as a complex multiplet (3·9 - 4·4τ). This is only consistent with the three possible structures(198a,b,c). The allylic methyl protons (H_d) appear as a three proton multiplet at 8·42 and 8·46τ (1·5 protons each). This is consistent with a 50:50 mixture of two similar isomers, the multiplet being one pair of allylic methyl groups and the two doublets being one allylic methyl group each. This was confirmed by spin-spin decoupling the olefinic proton (H_b) whereupon the downfield multiplet collapsed to two sharp singlets and the two doublets also collapsed to sharp singlets, the four peaks being in the ratio 1:1:1:1. Further decoupling of the spectrum did not give any further conclusive evidence. The n.m.r. spectra of the mixture of (p-tolyl)cyclohexadienes(189a,b) obtained from the thermal and the acid catalysed rearrangements are identical and are virtually superimposable on that of the phenylcyclohexadienes(198 a,b), the only significant difference being the presence of aryl methyl protons (7·73τ, singlet) in the former. It appears therefore that these mixtures all contain the same two cyclo-hexadiene isomers. If the thermolysis of the (p-tolyl)-adduct(188) proceeds by way of a concerted mechanism then only the (p-tolyl)-cyclohexadienes(189a,b) can be formed, thus excluding the alternative isomer(189c), in which case these(189a,b) and the corresponding 50:50 mixture of isomers(198a,b) are also formed in the acid catalysed reactions.

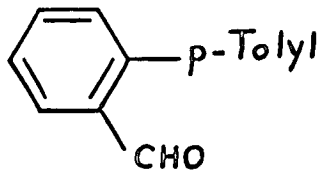


(189a) (189b)

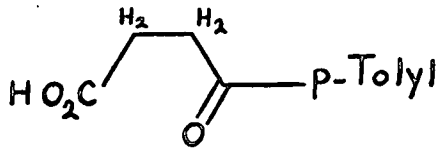
[O]



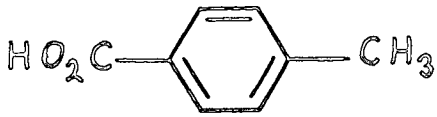
(201)



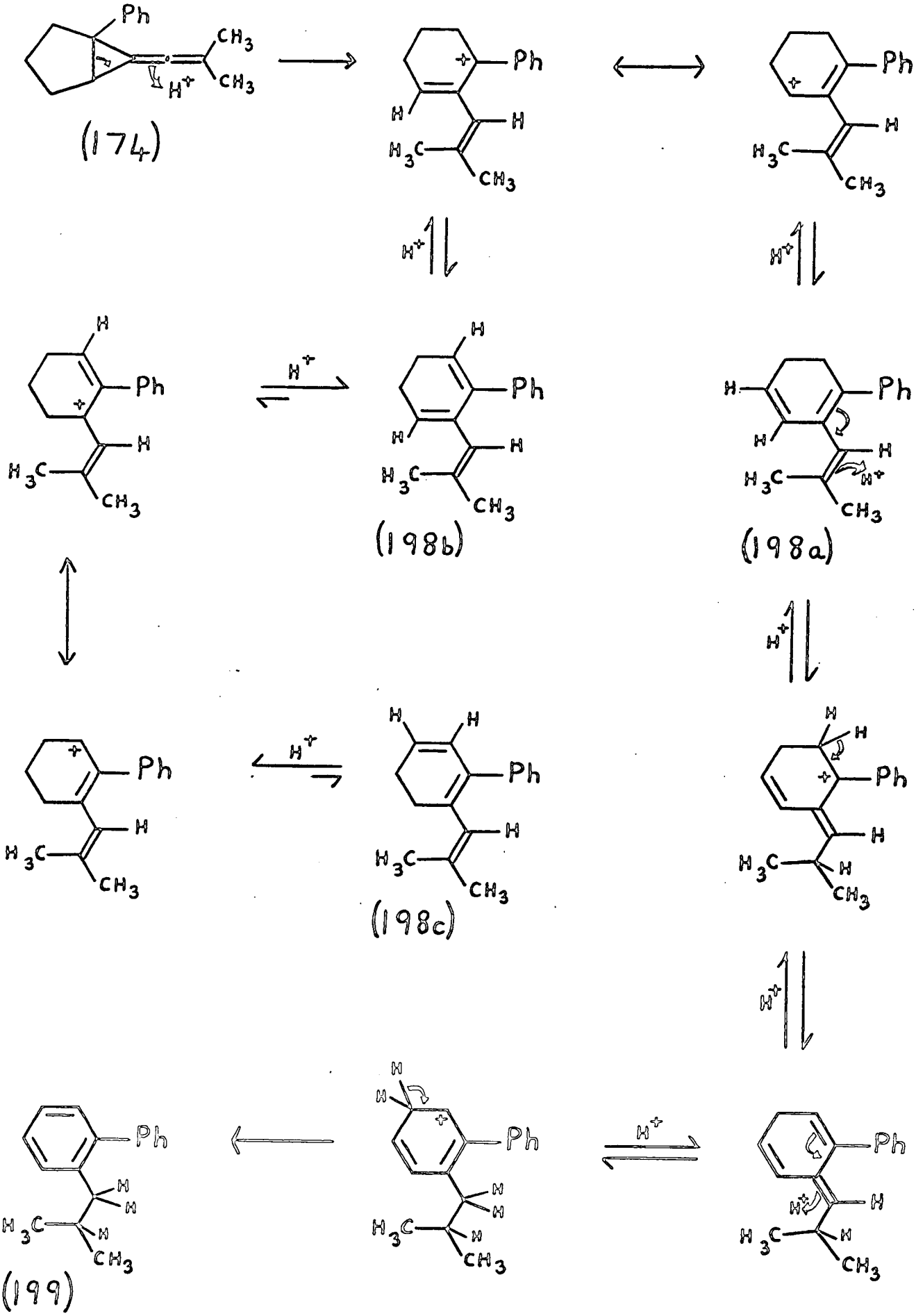
(202)



(203)

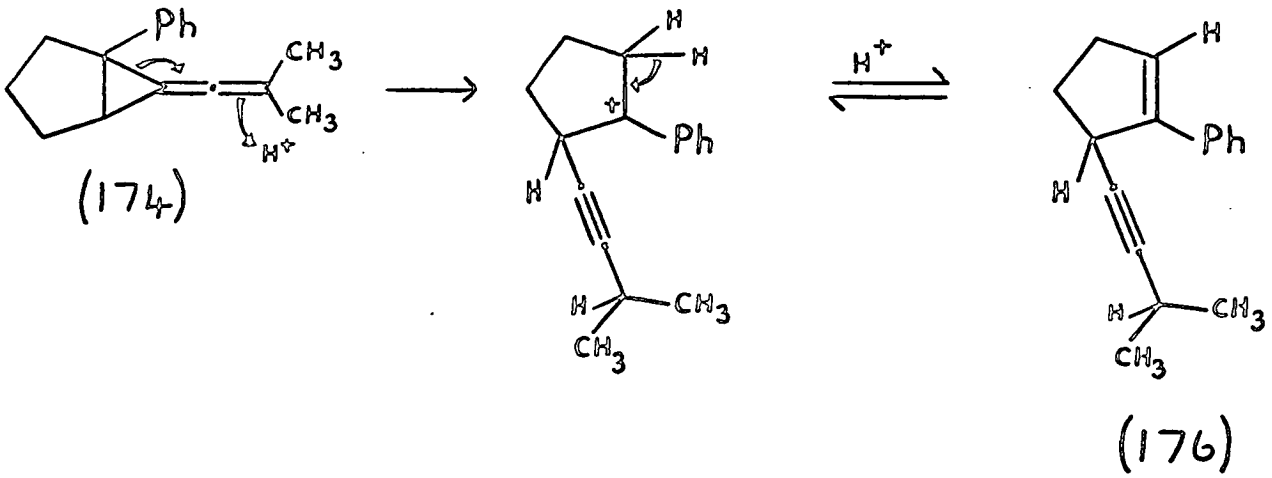


(204)


Ph
CH3
CH3
H+
(174)
Ph
H
H
H3C
CH3
Ph
H
H
H3C
CH3
H+
H+
H
Ph
H+
H
Ph
H
H
H3C
CH3
(198b)
H
Ph
H
H
H3C
H+
CH3
(198a)
H+
H+
Ph
H
H3C
CH3
H+
H
H
Ph
H
H3C
CH3
(198c)
H
H
Ph
H
H3C
H
CH3
H+
H+
Ph
H
H3C
H
CH3
H
H
Ph
H
H3C
H
CH3
H+
Ph
H
H
H3C
H
CH3
(199)

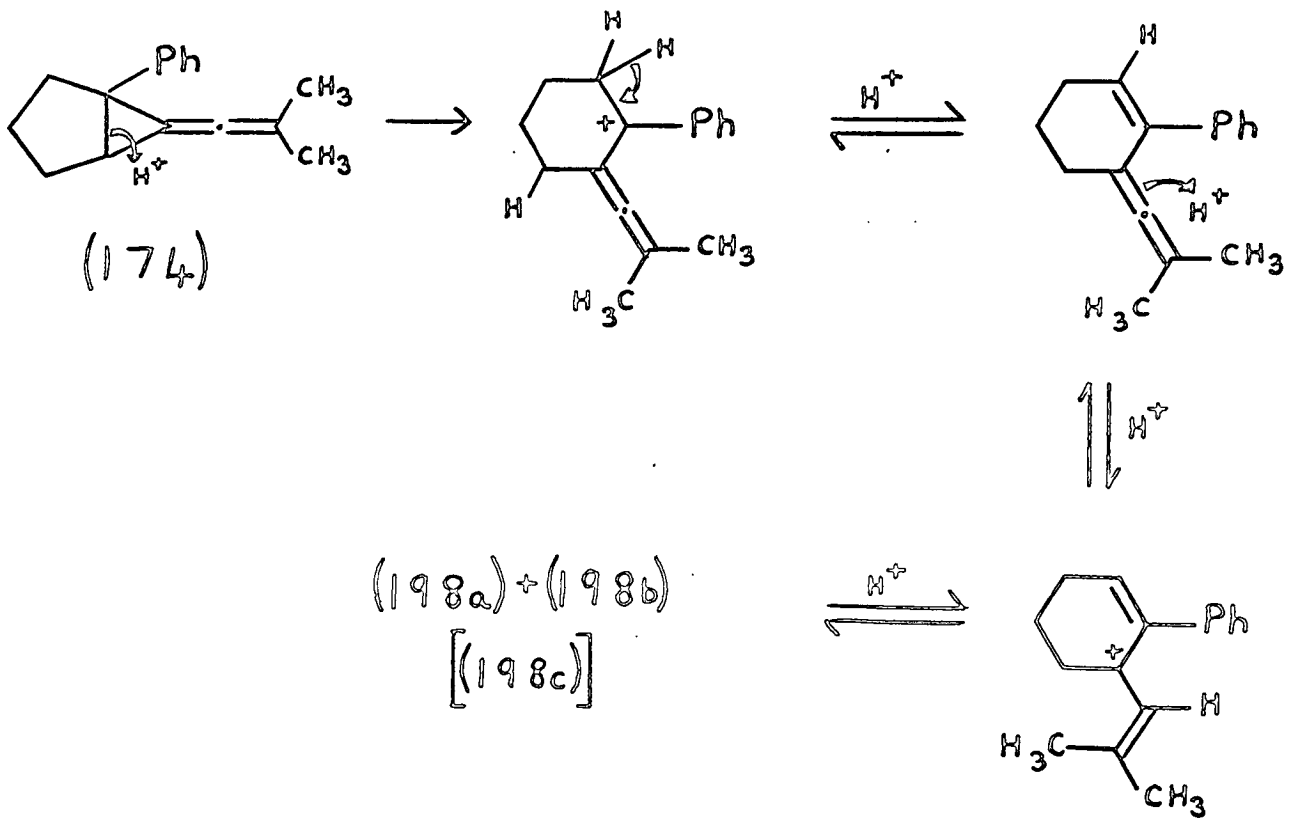
Lemieux oxidation of the (p-tolyl)cyclohexadienes(189a,b) formed a mixture of products whose mass spectrum includes strong parent peaks at m/e:212, 196, 192 and 136. These are attributed to 2-(p-tolyl)benzoic acid(201), 2-(p-tolyl)benzaldehyde(202), β-(p-methylbenzoyl)propionic acid(203) and p-toluic acid(204) respectively. The propionic acid(203) can only be formed by oxidative cleavage of (189a) whereas the remaining products could arise from degradation of either isomer(189a or b).

A mechanism rationalising the acid catalysed formation of the phenylcyclohexadienes(198a,b) and the isobutylbiphenyl(199) is illustrated in scheme XII, the formation of the (p-tolyl)-homologues being expected to be analogous. Protonation of the adduct(174) at the β-site of the allene followed by ring opening and proton elimination forms the cyclohexadienes(198a or b). Further protonation and bond migration would result in formation of the isobutylbiphenyl(199). Since these biphenyl derivatives are the thermodynamically most stable products to be isolated, the (p-tolyl)biphenyl(191) having a calculated heat of formation of 18·2 Kcal.mole^{-1} [compare the (p-tolyl)cyclohexadienes(189a,b; 46·8 Kcal.mole^{-1}) and the ethynylcyclopentene(190; 60·4 Kcal.mole^{-1})], it appears that their formation requires a relatively high activation energy and that the relative amounts which are formed are dependent on the conditions and the system involved. Thus, whereas acid catalysed rearrangement of the phenylcyclopentene adduct(174) formed a mixture containing only 5% of the biphenyl(199), under similar conditions the apparently more labile (p-tolyl)cyclopentene adduct(188) formed 52% of its isomeric biphenyl(191).



(174) (176)

SCHEME XIV

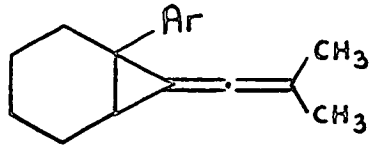


(174) (198a) + (198b) [(198c)]

As might be expected on this basis, prolonged treatment of the latter adduct with acid resulted in complete conversion to the biphenyl(191), the small amount of the ethynylcyclopentene(190) which is initially formed being destroyed under these conditions. The unobserved isomeric cyclohexadiene(198c) can also apparently be formed by protonation of the isomer(198b), however since this process unlike the others does not proceed by way of a benzyl carbonium ion this may be the reason for its absence.

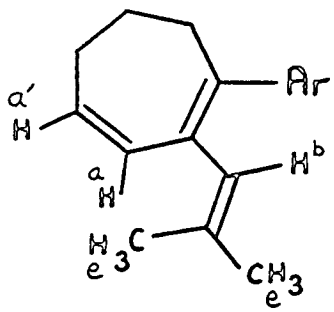
The acid catalysed formation of the acetylenic cyclopentenes(176) and (190) can be rationalised in terms of protonation at the γ-site of the allene as illustrated in scheme XIII in terms of the phenylcyclopentene adduct(174). Proton elimination from the intermediate carbonium ion could then form the observed product(176). The alternative elimination of the propargylic proton leading to the fully conjugated enyne system(179a) is unfavourable for steric reasons as previously described.

The two theoretically possible modes of protonation at the saturated cyclopropane ring sites have not been considered. Of these, protonation at the aryl-site is probably unlikely because it cannot readily lead to the formation of an intermediate benzyl carbonium ion. Protonation at the alternative saturated site, as illustrated in scheme XIV, could however form a benzyl carbonium ion which could then undergo deprotonation and further acid catalysed rearrangement of the resultant allene to form the isomeric cyclohexadienes(198a,b or c). However this mechanism is considered to be less likely than that involving protonation at the

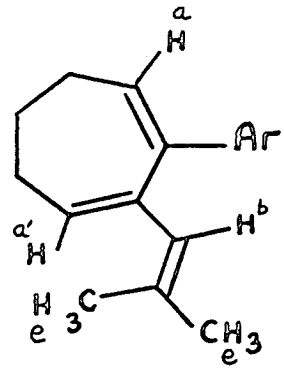


(177), Ar = Ph
(192), Ar = p-Tolyl

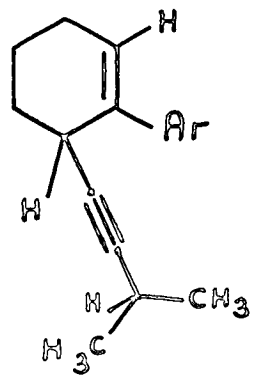
H^+



(205a), Ar = Ph
(193a), Ar = p-Tolyl



(205b), Ar = Ph
(193b), Ar = p-Tolyl



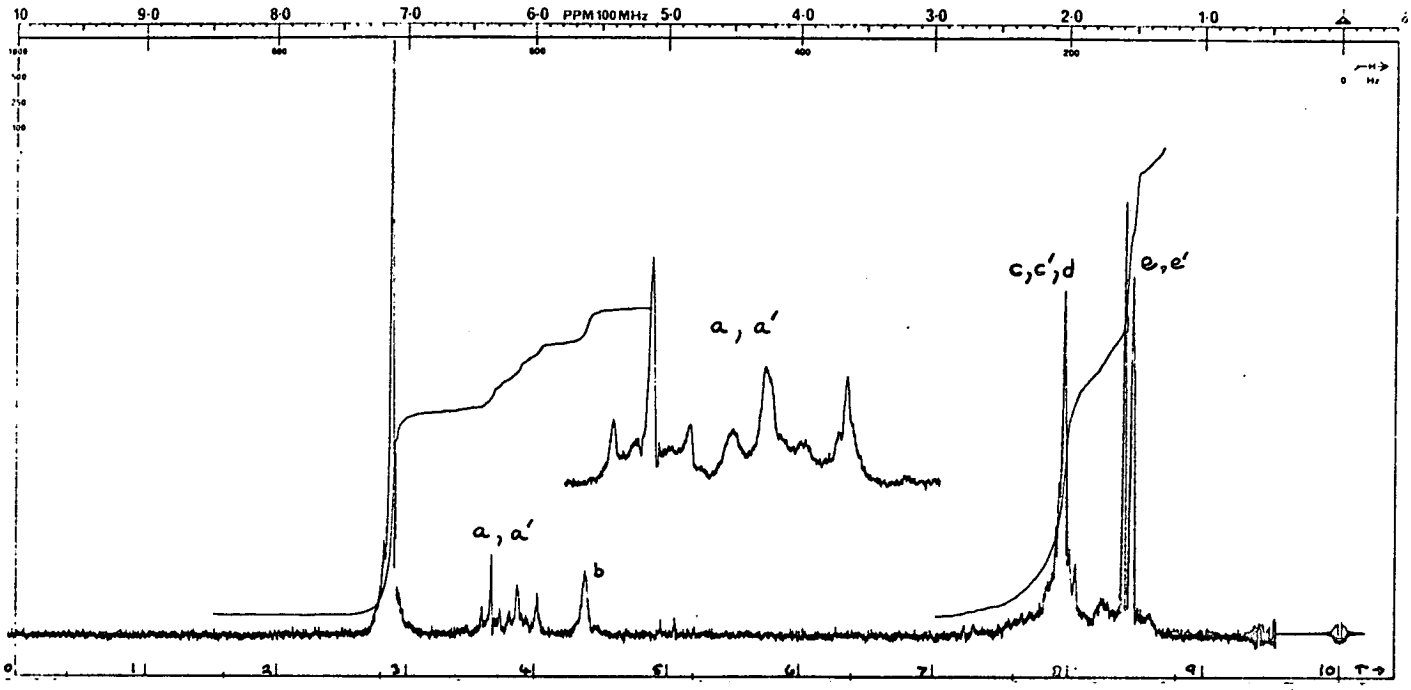
(179), Ar = Ph
(194), Ar = p-Tolyl

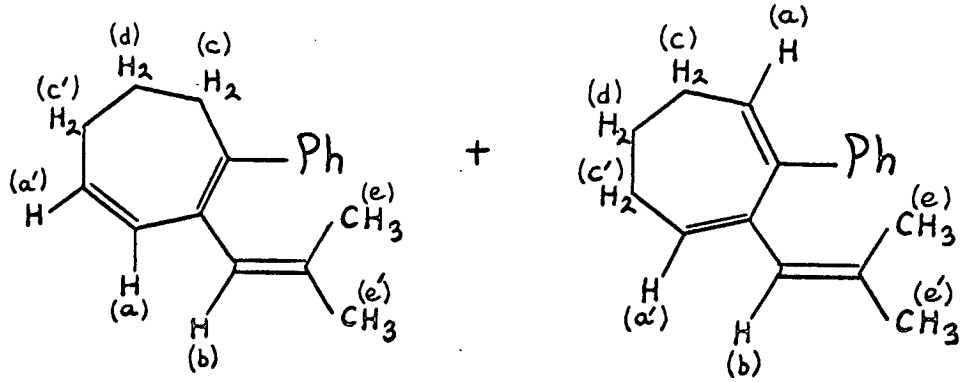
γ-site due to the formation of an allenic intermediate.

As in the preceding arylcyclopentene series the acid catalysed rearrangement of the two arylcyclohexene adducts studied gave rise to analogous products. Thus the phenylcyclohexene adduct(177) formed a 1:1 mixture of the ethynylcyclohexene(179) and the mixture of 2-(2-methylprop-1-enyl)-1-phenylcyclo-heptadienes(205a,b). Similarly the (p-tolyl)cyclohexene adduct(192) gave rise to a 1:1 mixture of the ethynylcyclohexene(194) and the cycloheptadienes(193a,b).

The structures of the cycloheptadiene isomers were assigned by comparison with their cyclohexadiene counterparts already described. The n.m.r. spectrum of the mixture of phenylcyclo-heptadienes(205a,b) is illustrated in figure VIII. This shows the endo-cyclic olefinic protons (H_a and $H_{a'}$, 3·6 - 4·1τ) as a multiplet and the exo-cyclic proton (H_b, 4·36τ) also as a multiplet, the complexity of the olefinic region supporting the presence of more than one isomer. In contrast to the cyclohexadiene isomers (compare figure VII), the pairs of similar allylic methyl protons(H_e) in the present system are virtually superimposed and form two fine doublets (J = 1 Hz.) centred at 8·41 and 8·47τ which are partially resolved into further doublets. The spectrum of the (p-tolyl)-cycloheptadienes(193a,b) is very similar to that illustrated, the only significant difference being the aryl methyl protons (7·74τ) appearing as a sharp singlet. The n.m.r. spectra of the (p-tolyl)-cycloheptadienes(193a,b) derived from the thermal and acid catalysed

FIGURE VIII


10
9·0
8·0
7·0
6·0 PPM 100 MHz
5·0
4·0
3·0
2·0
1·0
a , a'
a , a'
b
c,c',d
e,e'

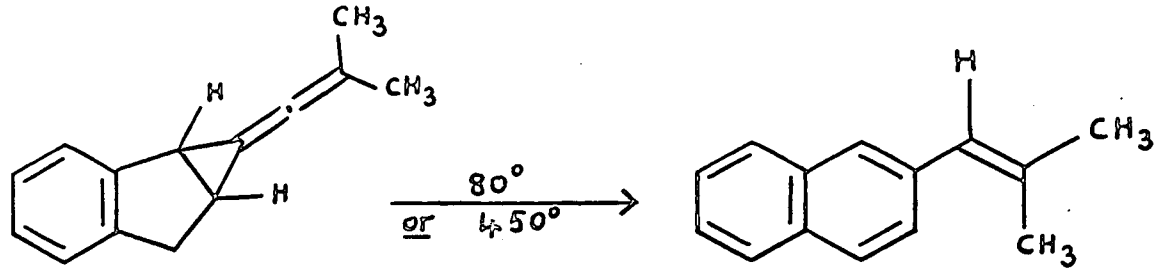

(d)
H2
(c)
H2
(c')
H2
Ph
(a')
H
(e)
CH3
H
(a)
(e')
CH3
H
(b)
+
(a)
H
(c)
H2
(d)
H2
(c')
H2
Ph
(e)
CH3
H
(a')
(e')
CH3
H
(b)

rearrangements were superimposable which, in view of the proposed thermal mechanism (scheme XI) and in analogy with the argument already presented, supports the allocated structures. No direct evidence was found to indicate the relative amounts of the two isomers.

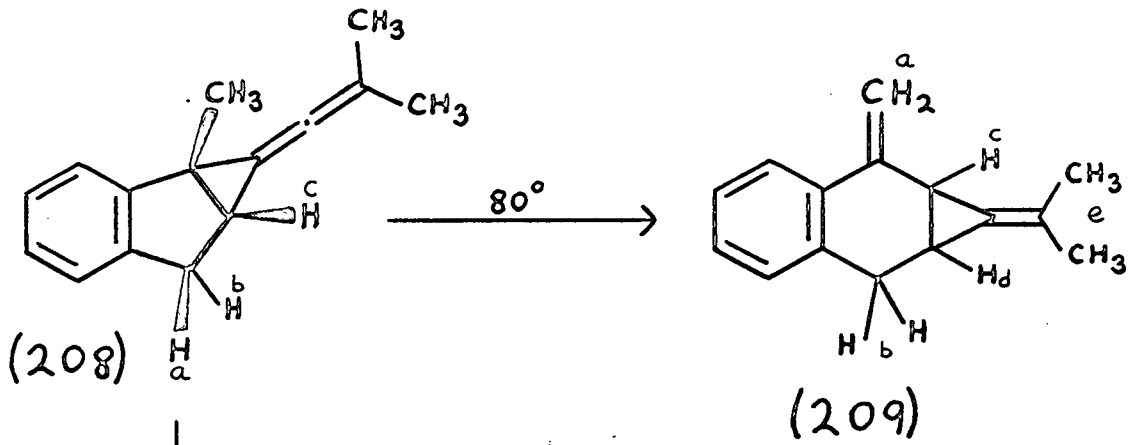
The stereochemistry of these cycloheptadiene systems allows very little overlap between adjacent π-electron systems, the rings existing in a puckered conformation. This is substantiated by the u.v. spectra of these compounds, the phenyl-isomers(205a, b) having a maximum at 242·0mμ (ϵ = 17,400) and the (p-tolyl)-isomers at 250·0mμ (ϵ = 12,700).

The mechanisms proposed above for the acid catalysed formation of the cyclohexadienes and acetylenic compounds from the arylcyclopentene adducts(174 and 188) are equally applicable to the arylcyclohexene adducts(177 and 192). Aromatisation to form a thermodynamically more stable system is not possible in these products.

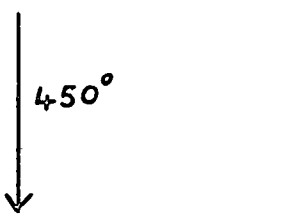
Since the acetylenic derivatives(179 and 194) contain a cyclohexene ring it might be expected that their formation would be more favourable with respect to the correspondingly more strained cyclopentene derivatives(176 and 190), possibly accounting for the higher proportions of the former in the acid catalysed products, this trend also being reflected to a lesser degree in the corresponding thermal rearrangement products. However a corollary exists in all these cases in that when the acetylenic compound is a cyclopentene derivative the accompanying products contain six

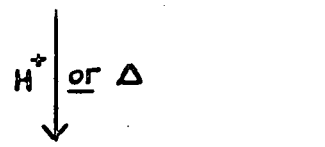


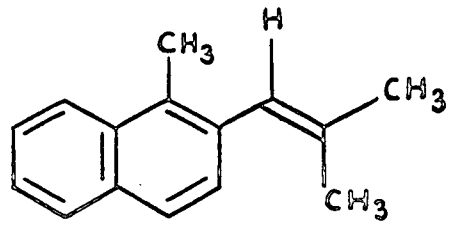
(206) (207)



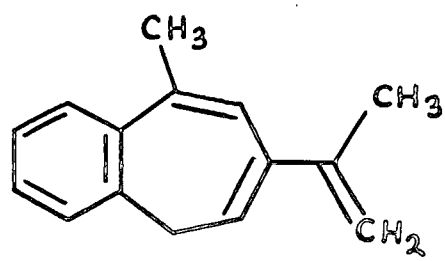
(208) (209)







(210)



(211)

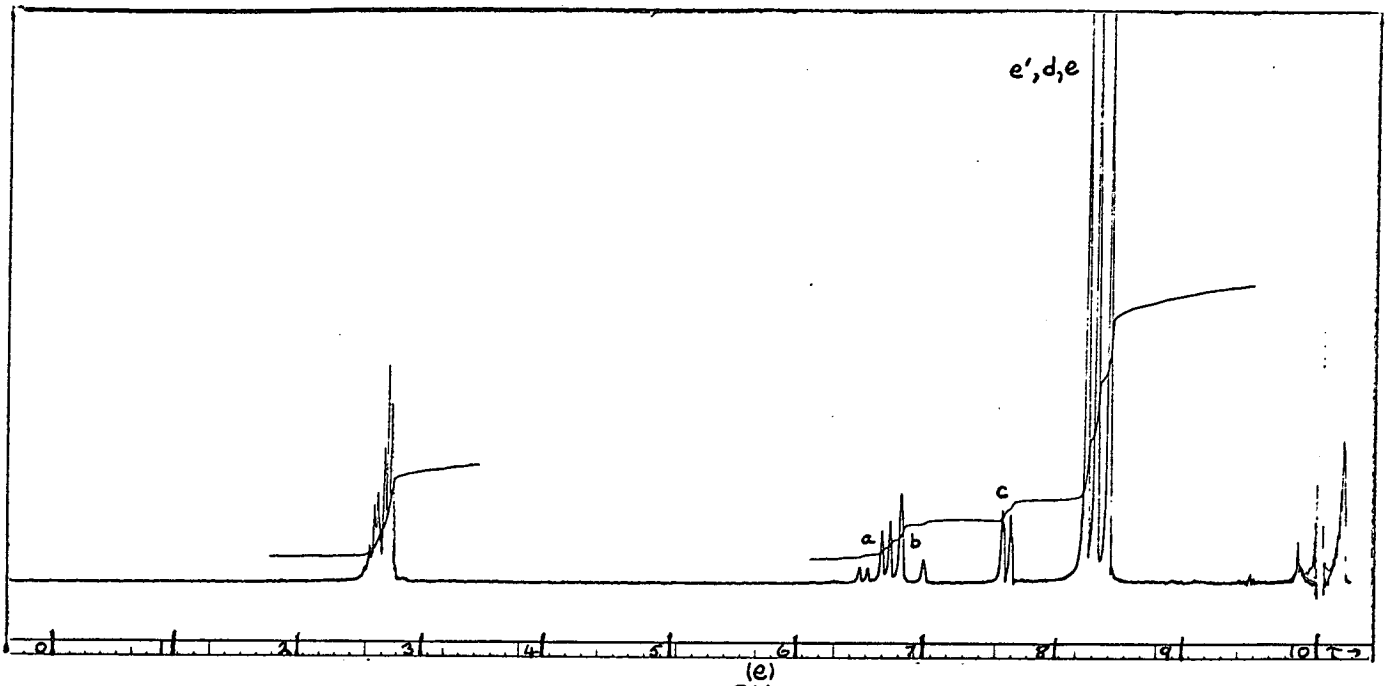
(209) + (211)

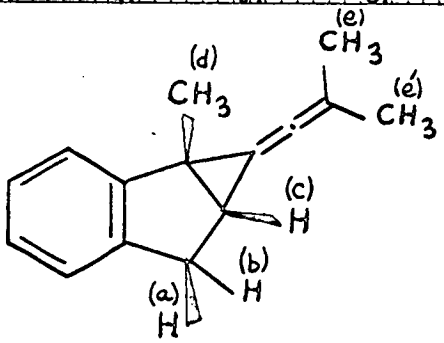
membered carbon skeletons whereas when the acetylenic compound is a cyclohexene derivative the accompanying products contain seven membered skeletons, the latter being expected to be less favourable. This is a direct result of the two distinct forms of cyclopropyl ring opening which can occur during the acid and thermal rearrangements of these adducts derived from 1-arylcycloalkenes. This involves cleavage of one or other of the cyclopropane bonds adjacent to the aromatic substituent, which seems reasonable due to the stabilising influence offered by the aromatic ring in these cases.

3.5 THERMAL AND ACID CATALYSED REARRANGEMENT OF THE ADDUCTS DERIVED FROM INDENE AND 3-METHYLINDENE.

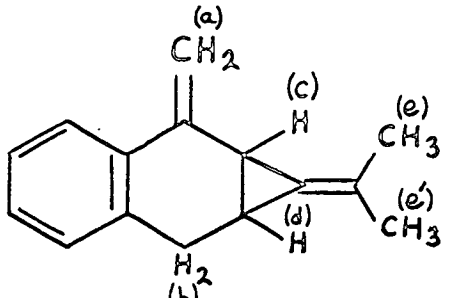
Thermal rearrangement of 2,3-benzo-6-dimethylvinylidene-bicyclo[3,1,0]hex-2-ene(206), effected by refluxing the adduct in benzene for 24 hr. or in the vapour phase by passage through the flow system at 450°, formed 2-methyl-1-(β-naphthyl)prop-1-ene(207), the yield from the solution thermolysis being poor. However, the 1-methyl derivative(208) readily rearranges when refluxed in benzene for 12 hr. to form an isomeric compound formulated as 3,4-benzo-7-isopropylidene-2-methylenebicyclo[4,1,0]hept-3-ene(209) in good yield. Pyrolysis of this adduct(208) by passage through the flow system at 450° formed a mixture containing 32% of the naphthalene(210), 52% of the bicycloheptene(209) and 16% of an isomeric compound formulated as 1,2-benzo-5-isopropenyl-3-methyl-cyclohepta-1,3,5-triene(211). Passage of the bicycloheptene(209)

FIGURE IX


e',d,e
c
a
b
0
2
3
4
5
6
7
8
9
10 τ→


(e)
CH3
(d)
CH3
(é)
CH3
(c)
H
(b)
H
(a)
H


1000
500
250
100
50
400
300
200
100
e',e
b
a
c
d
0
2
3
4
5
6
7
8
9
10 τ→

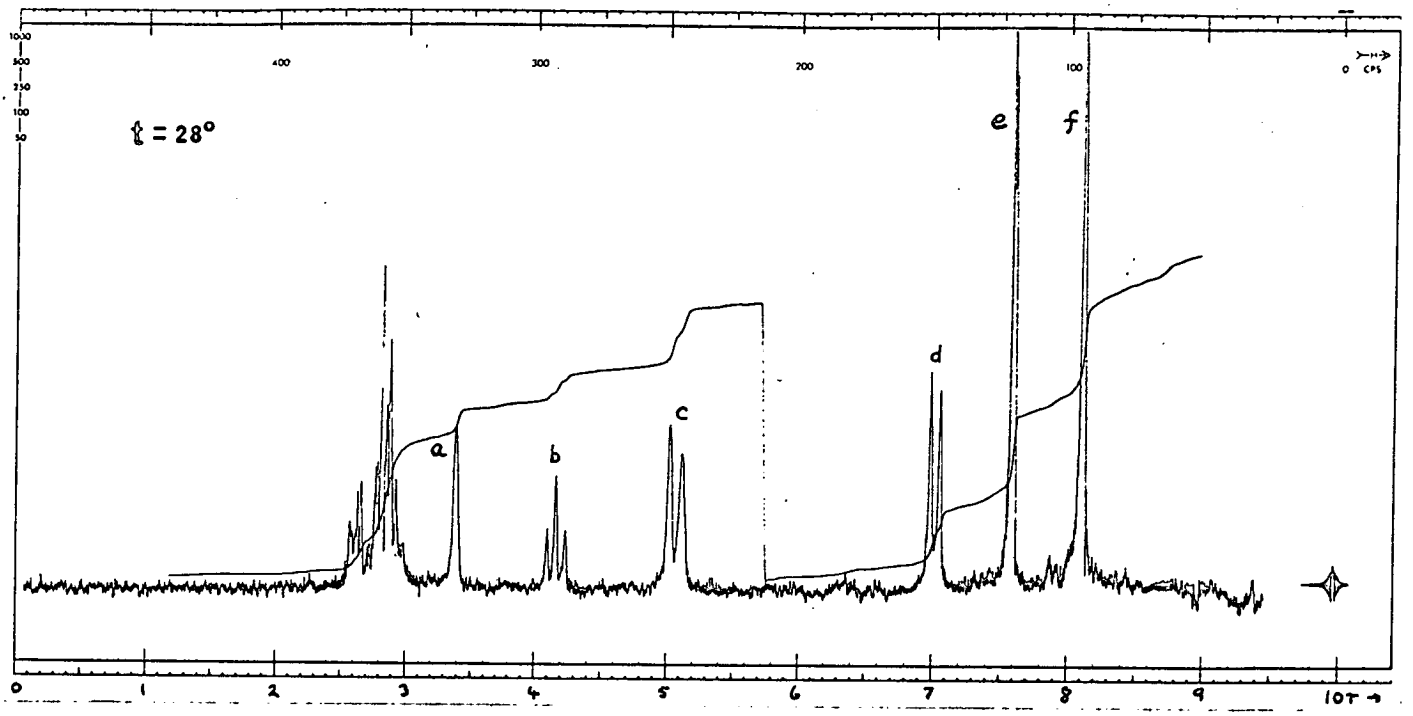

(a)
CH2
(c)
H
(e)
CH3
(e')
CH3
(d)
H
H2
(b)

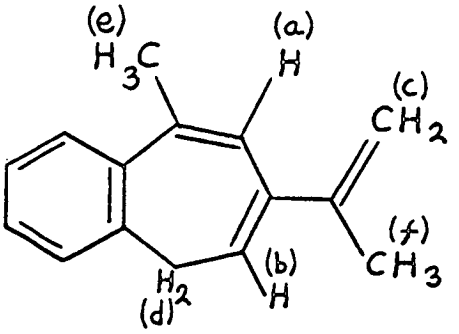
through the flow system at 350° resulted in a 5% conversion to the cycloheptatriene(211) whereas treatment of the bicycloheptene(209) with 20% hydrochloric acid causes complete isomerisation to the cycloheptatriene(211).

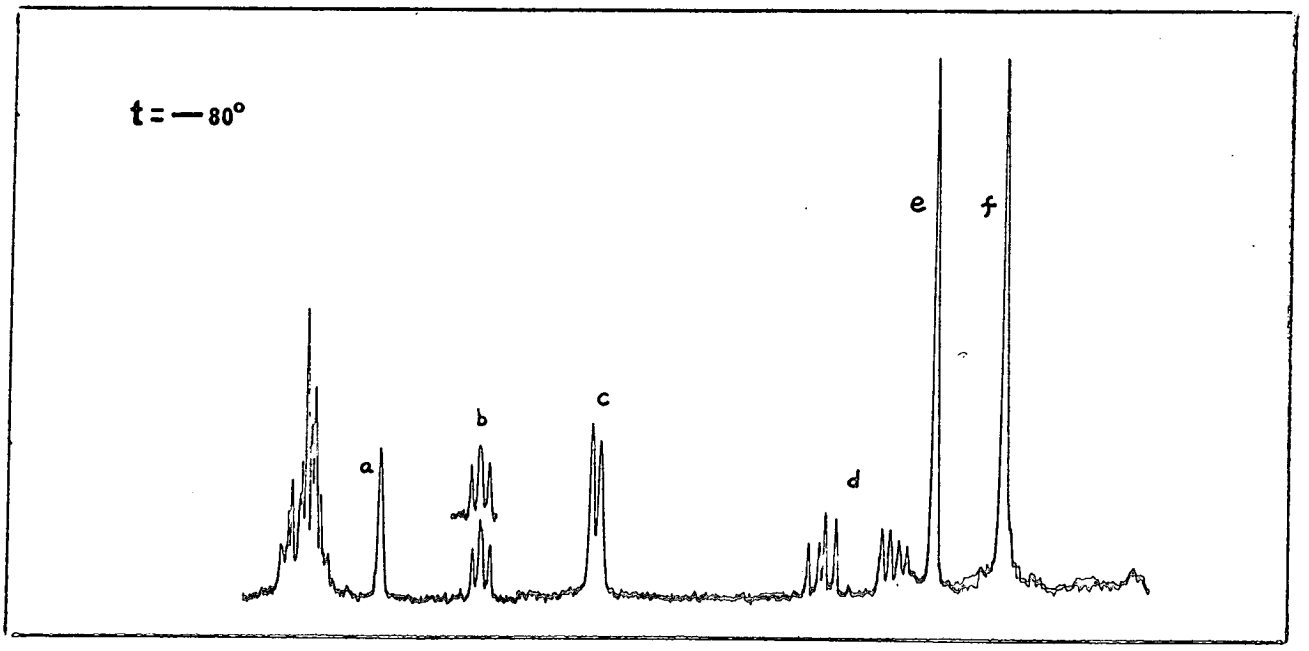
The identities of the naphthalene derivatives(207) and (210) were confirmed by independent syntheses from β-naphthaldehyde and β-bromo-α-methylnaphthalene respectively. The identities of the bicycloheptene(209) and the cycloheptatriene(211) were deduced from their spectral characteristics by comparison with model compounds.

The n.m.r. spectrum of the bicycloheptene(209) is illustrated in figure IX. The six membered alicyclic ring in this molecule is relatively flexible and allows the benzylic methylene protons (H_b, 7·00τ) to adopt equivalent positions with respect to the aromatic ring but not with respect to the isopropylidene system, these methylene protons appearing as a doublet (separation = 3 Hz.). The olefinic methylene protons (H_a, 4·85, 5·01τ) appear as a fine doublet (J = 1·5 Hz.) while the cyclopropyl protons (H_c, 7·54; H_d, 7·84τ) appear as multiplets, the isopropylidene methyl protons (H_e, 8·45τ) being split into a fine triplet. This splitting of isopropylidene methyl protons exo-cyclic to a cyclopropyl ring has been attributed[107] to long range coupling with the neighbouring cyclopropyl protons. Strong irradiation of the cyclopropyl proton (H_d) causes the methylene doublet (H_b) to collapse to a singlet whereas irradiation of the methylene protons (H_e) removes the small splittings on the cyclopropyl proton (H_c) causing this to collapse to a broad doublet

FIGURE II


t = 28°
a
b
c
d
e
f
0
1
2
3
4
5
6
7
8
9
10τ


(e)
H3C
(a)
H
(c)
CH2
(f)
CH3
(b)
H
H2
(d)

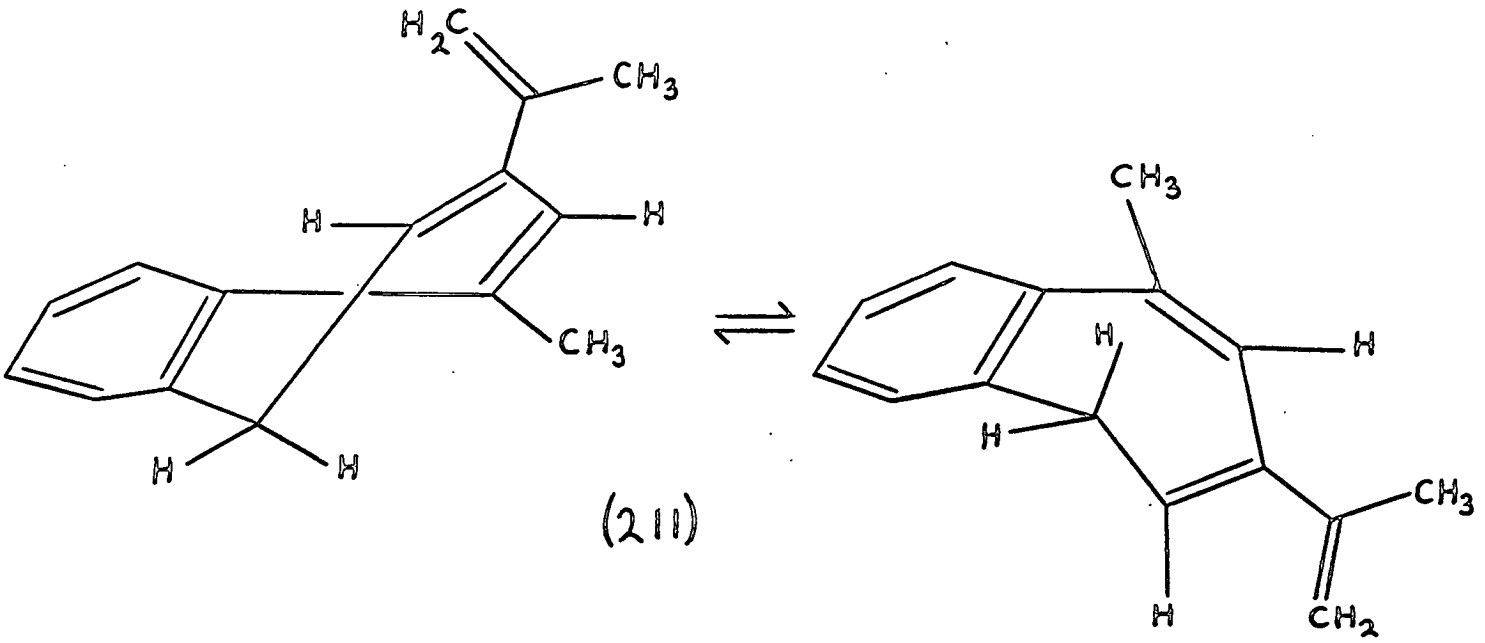

t = —80°
a
b
c
d
e
f

(J = 8 Hz.). The u.v. spectrum of the bicycloheptene(209) shows a maximum at 250·0mμ (ε = 10,600) which is typical of a styrene derivative, whereas the i.r. spectrum confirms the presence of the strained cyclopropyl double bond and the exo-cyclic methylene grouping (ν_{max} = 1,770 and 880 cm.$^{-1}$ respectively).

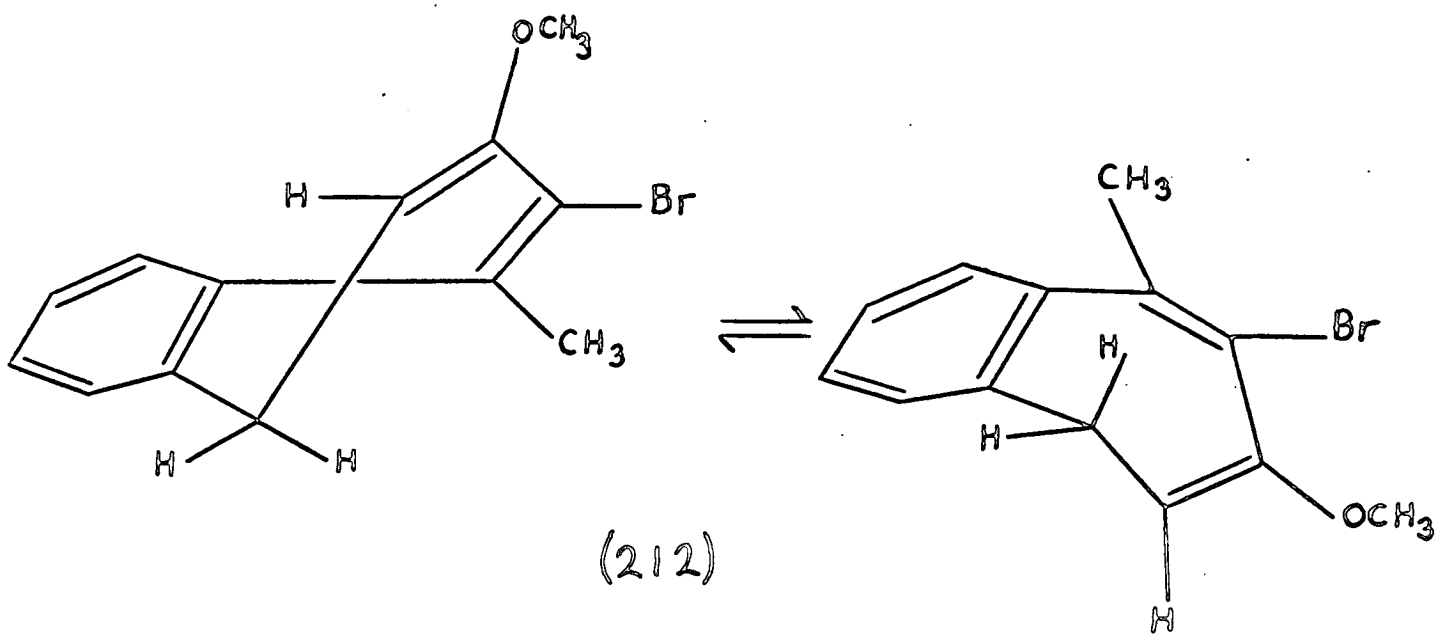
In contrast to the relatively flexible bicycloheptene system(209), the five membered ring of the bicyclohexene(208) is practically rigid and the n.m.r. spectrum of this adduct is illustrated in figure IX for comparison. The two non-equivalent benzylic protons (H_a and H_b) are centred at 6·72 and 6·99τ respectively and are split by each other into doublets (J_{ab} = 16 Hz.) which are then unequally split into further doublets (J_{ac} = 6 Hz., J_{bc} = 1 Hz.) by coupling with the neighbouring cyclopropyl proton (H_c, 7·69τ) which is split into a quartet (J_{ca} = 6 Hz., J_{cb} = 1 Hz.).

The n.m.r. spectrum of the benzocycloheptatriene(211) is illustrated in figure X. Due to the puckered and flexible nature of the cycloheptatriene ring the benzocycloheptatriene(211) can undergo ring flipping to adopt either of two favourable conformations, illustrated in scheme XV, which are mirror images. However the n.m.r. spectrum of cycloheptatriene itself[108] shows the methylene protons to be equivalent at room temperature due to rapid ring flipping. Similarly the benzylic protons (H_d, 7·05τ) of the benzocycloheptatriene(211) are equivalent at 28° and appear as a sharp doublet (J_{db} = 7 Hz.) while the olefinic proton (H_b, 4·20τ) appears as a triplet (J_{bd} = 7·0 Hz.). The olefinic proton (H_a, 3·42τ) appears as a singlet while the olefinic methylene

SCHEME XV



(211)



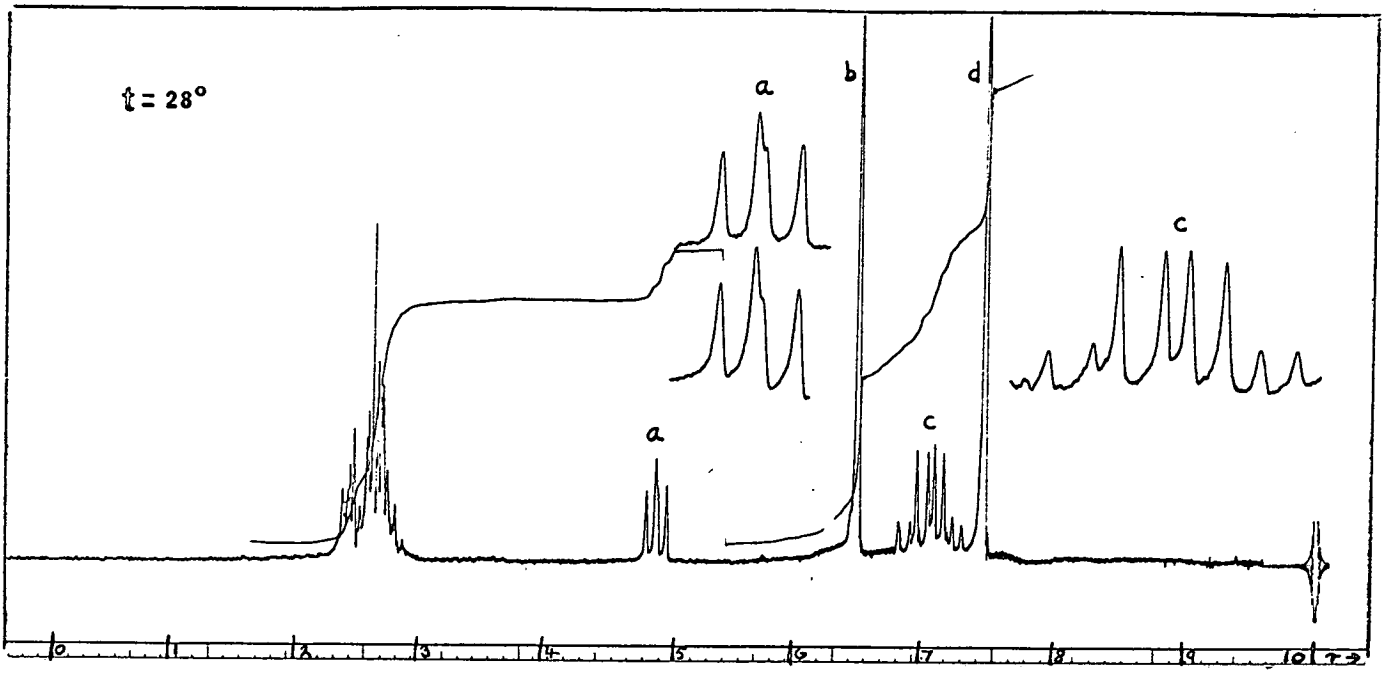
(212)

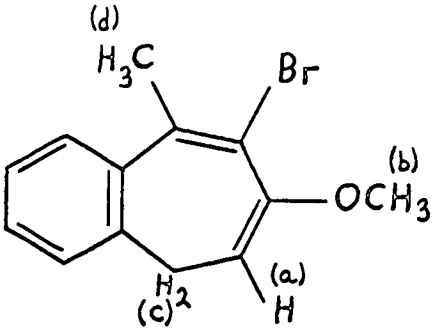
protons (H_c, 5·05, 5·15τ) are fine multiplets. The methyl protons (H_e and H_f) are fine doublets centred at 7·63τ (J = 1 Hz.) and 8·14τ (J = 0·5 Hz.) respectively. The proton allocations were confirmed by spin-spin decoupling. The i.r. spectrum confirms the presence of the exo-cyclic methylene grouping and the trisubstituted double bonds (ν_{max} = 890 and 820 cm^{-1} respectively). The puckered conformation of the benzocycloheptatriene derivative(211) is evident from its u.v. spectrum which only shows a maximum at 236·0mμ (ϵ = 26,400) and a weak shoulder at 275·0mμ due to the small degree of overlap allowed between the adjacent π-electron systems.

The low temperature n.m.r. spectrum of cycloheptatriene itself[108] shows the methylene protons to be non-equivalent at -140° due to the rate of interconversion of the two favourable conformations being appreciably less than the frequency separation of the two types of proton involved. The n.m.r. spectrum of the benzocycloheptatriene(211) at -80° is illustrated in figure X and shows the benzylic protons (H_d) to be non-equivalent, appearing as two distinct quartets centred at 6·84 and 7·37τ being equally coupled to each other (J_{dd} = 12·6 Hz.) and unequally coupled to the adjacent olefinic proton (J_{db} = 7·8, 6·6 Hz.), the olefinic proton (H_b, 4·20τ) being a quartet (J_{bd} = 7·8, 7·7 Hz.). The remainder of the spectrum was unchanged.

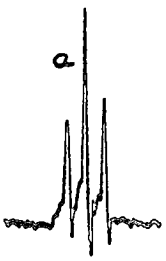
The bromocycloheptatriene(212) was prepared by an unambiguous synthesis (section 4) for spectral comparison with the above. The n.m.r. spectrum of the bromo-compound is illustrated

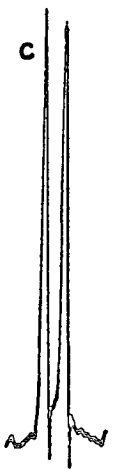
FIGURE XI





t = 120°

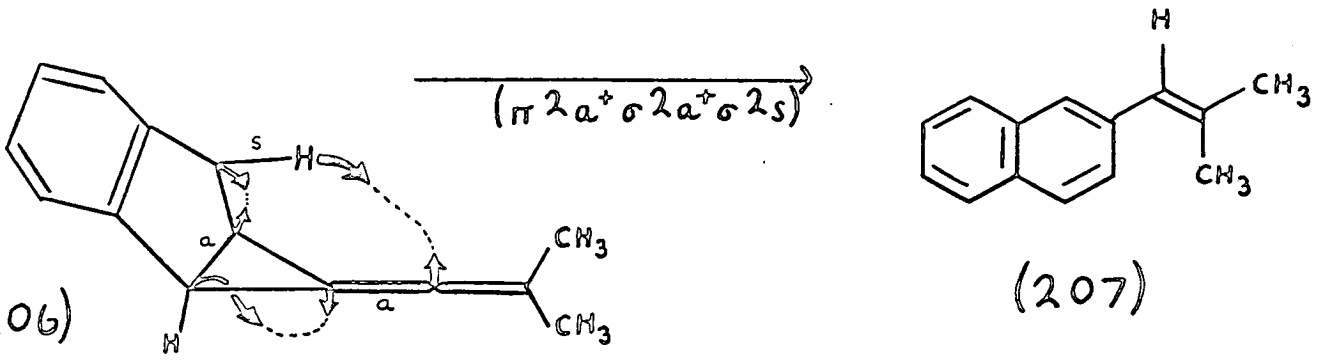




in figure XI and shows the benzylic protons (H_c) to be non-equivalent at 28°, appearing as two distinct quartets (J_{cc} = 13·5 Hz., J_{ca} = 8·0, 7·0 Hz.) centred at 7·01 and 7·27τ, the olefinic proton (H_a, 5·07τ) being a quartet (J_{ac} = 8·0, 7·5 Hz.). However the benzylic protons (H_c, 7·14τ) are equivalent to 120° and occur as a sharp doublet (J_{ca} = 7·0 Hz.) while the olefinic proton (H_a, 5·07τ) collapsed to a triplet (J_{ac} = 7·0 Hz.), which is consistent with rapid interconversion of the two favourable conformations, illustrated in scheme XV, at an elevated temperature.

The temperature of coalescence of the benzylic protons in the benzocycloheptatriene(211) and the bromo-compound(212) were found to be -16° and 72° respectively in their 100 MHz. spectra, which gives estimates for the energy barrier between the pairs of favourable conformations (scheme XV) as 12·2 and 17·0 Kcal.mole^{-1} respectively. For comparison, the coalescence temperature for the chair-boat-chair interconversion of cyclohexene is -66·7° which gives an estimate[109] of the energy barrier between the two chair conformations as 10·1 Kcal.mole^{-1}. The relatively high energy barrier associated with the bromo-compound(212) with respect to the benzocycloheptatriene(211) is attributed to a large steric interaction existing between the bromine atom and methoxyl group of the former during ring flipping.

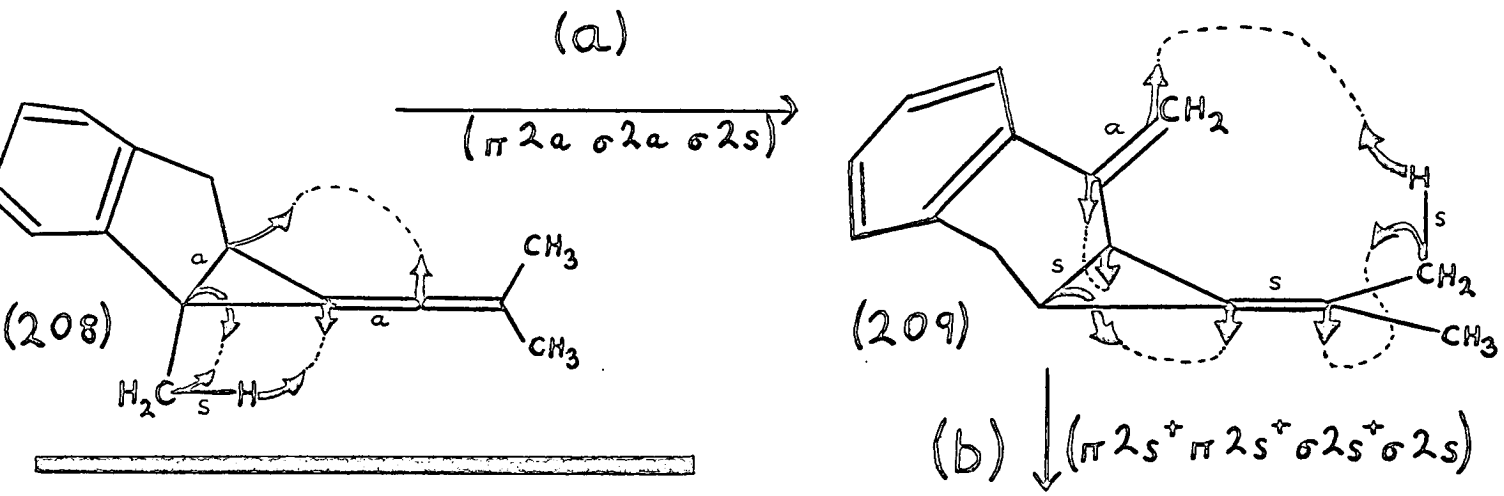
Since thermal rearrangement of the 3-methylindene adduct(208) at 80° forms exclusively the bicycloheptene(209) and pyrolysis of the bicycloheptene(209) by passage through the flow system(350°) results in partial conversion to the cycloheptatriene(211)

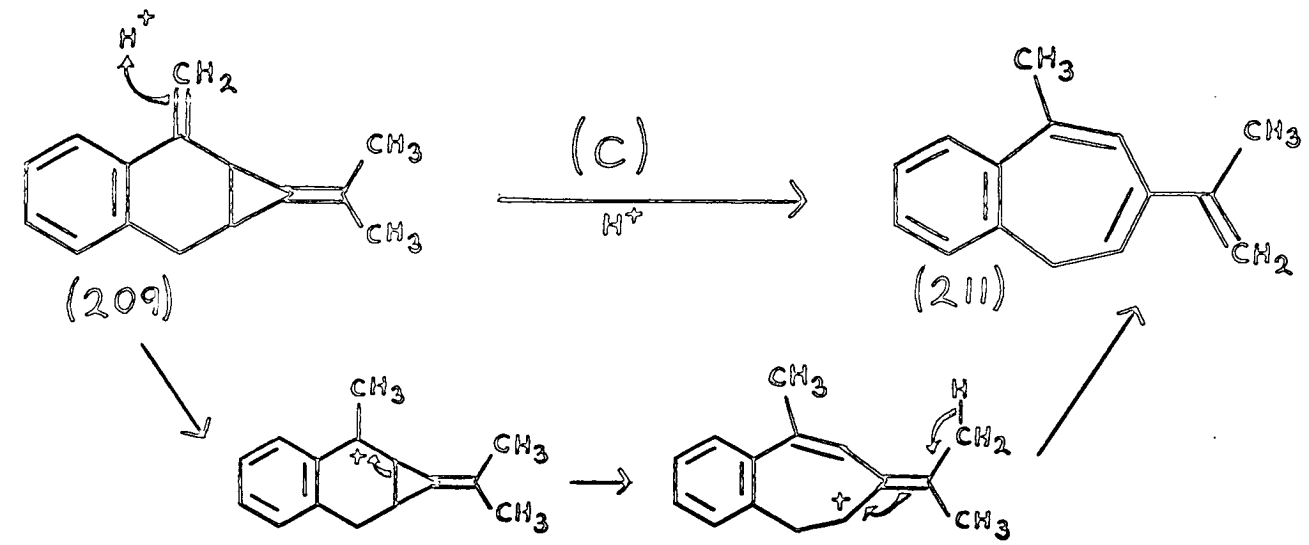


06)

(207)

SCHEME XVII



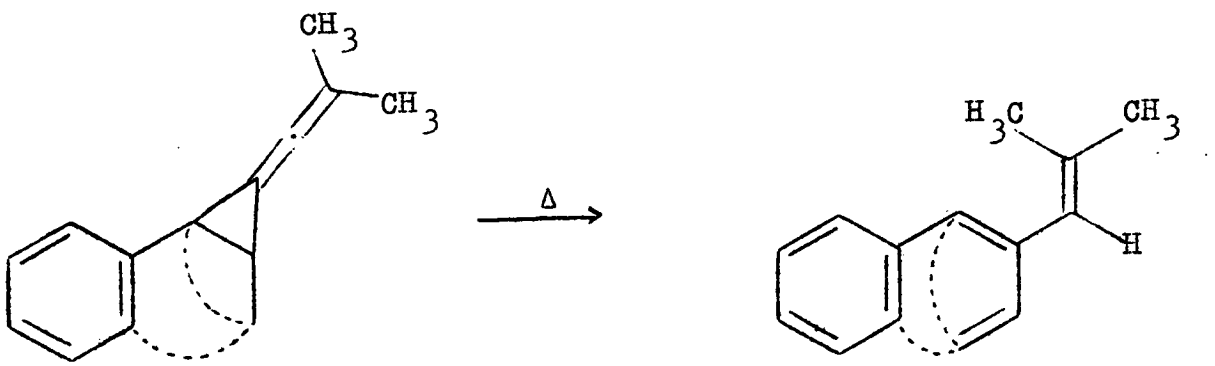


solely, the formation of the naphthalene derivative(210) must occur by way of a separate route. Thus three processes are operative:-

(a) adduct(208)⟶bicycloheptene(209)⟶cycloheptatriene(211).

(b) adduct(208)⟶naphthalene(210).

A symmetry allowed mechanism which can account for the formation of the naphthalene derivatives(207) and (210) is illustrated in scheme XVI in terms of the indene adduct(206), that of the 1-methyl derivative(208) being expected to be analogous. This mechanism involves concerted disrotatory ring opening and bond formation with a suprafacial 1,5 hydrogen migration and is a thermally allowed ($_{\pi}2_a + {}_{\sigma}2_a + {}_{\sigma}2_s$) process. This mechanism is analogous to that illustrated in scheme XI for the concerted rearrangement of the (p-tolyl)cycloalkenes(188 or 192) to form the cycloalkadiene(189a or 193a) respectively.



(206) or (208)
(188) or (192)

(207) or (210) respectively.
(189a)or(193a) "

If a suitably positioned methyl group is present, as in the 3-methylindene adduct(208), then an alternative process can occur as illustrated in scheme XVII (pathway a). This again involves concerted disrotatory ring opening and bond formation but in this

case is accompanied by a 1,3 hydrogen shift from the now available methyl group to form the bicycloheptene(209), this being a thermally allowed ($_{\pi}2_a + _{\sigma}2_a + _{\sigma}2_s$) process. It is possible that the relative ease of this process as compared to formation of the naphthalene derivative(210) results from the orientation of the migrating hydrogen atoms involved. Thus the methyl group in the adduct(208) can rotate which might allow the migrating hydrogen atom to adopt a more favourable orientation, prior to bicycloheptene(209) formation, rendering the transition state more accessible with respect to the fixed conformation of the migrating hydrogen atom involved in formation of the naphthalene derivative(210).

A concerted mechanism which is consistent with the thermal conversion of the bicycloheptene(209) to the cycloheptatriene(211) is illustrated in scheme XVII (pathway b) and is a thermally allowed ($_{\pi}2_a + _{\pi}2_s + _{\sigma}2_s + _{\sigma}2_s$) process involving a suprafacial 1,7 hydrogen migration.

The calculated heat of formation of the 3-methylindene adduct(208) is 93·3 Kcal.mole^{-1} while those of the bicycloheptene(209) and the naphthalene(210) are 73·4 and 27·8 Kcal.mole^{-1} respectively. This supports the view that the preferred formation of the bicycloheptene(209) at lower temperatures is the result of a relatively large activation energy existing between the adduct(208) and the thermodynamically favoured naphthalene system(210), in which case the latter system would be expected to become accessible at elevated temperatures as is observed. The calculated heat of formation of the cycloheptatriene(211) is 51·2 Kcal.mole^{-1} which,

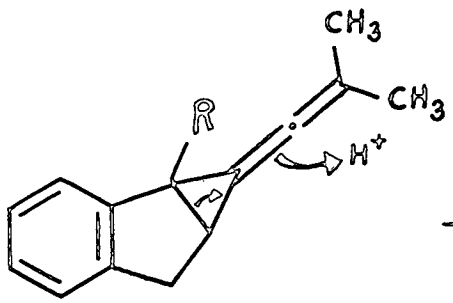
being favourably lower than its precursor(209; 73·4 Kcal.mole^{-1}) again supports the existence of a relatively high energy barrier against its formation, this view being supported by the low conversion factor involved. However in the case of the indene adduct(206), where no alternatives appear to exist, thermolysis at lower temperatures can only form the naphthalene(207) by an apparently kinetically unfavourable process which probably accounts for the relatively slower rate of rearrangement and the low yield involved.

It seems probable that formation of the bicycloheptene(209) most likely follows a concerted pathway due to the mild conditions involved. The formation of the naphthalene derivatives(207) and (210) by a diradical mechanism involving hydrogen abstraction is sterically impossible, however the formation of the cycloheptatriene(211) could conceivably involve a radical mechanism, the restricted formation of this system to high temperature vapour phase pyrolysis being comparable to formation of the tetrahydrofluorene(175) already discussed which may involve diradical intermediates.

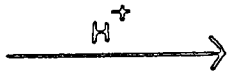
A mechanism which can account for the acid catalysed conversion of the bicycloheptene(209) to the cycloheptatriene(211) is shown in scheme XVII (pathway c) and involves protonation of the exo-cyclic methylene followed by bond migration and proton elimination from one of the exo-cyclic methyl groups.

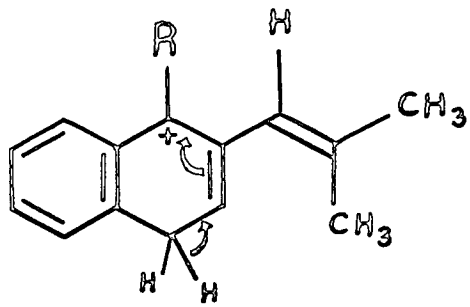
The acid catalysed rearrangement of the indene adduct(206) and the 3-methylindene adduct(208) both follow similar paths to form the naphthalene derivatives(207) and (210) respectively. A

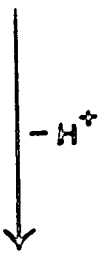
SCHEME XVIII

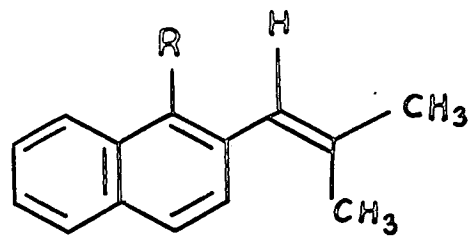


(206), R = H
(208), R = CH_3

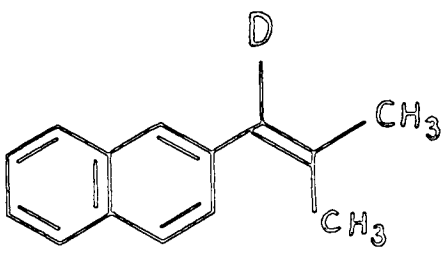








(207), R = H
(210), R = CH_3

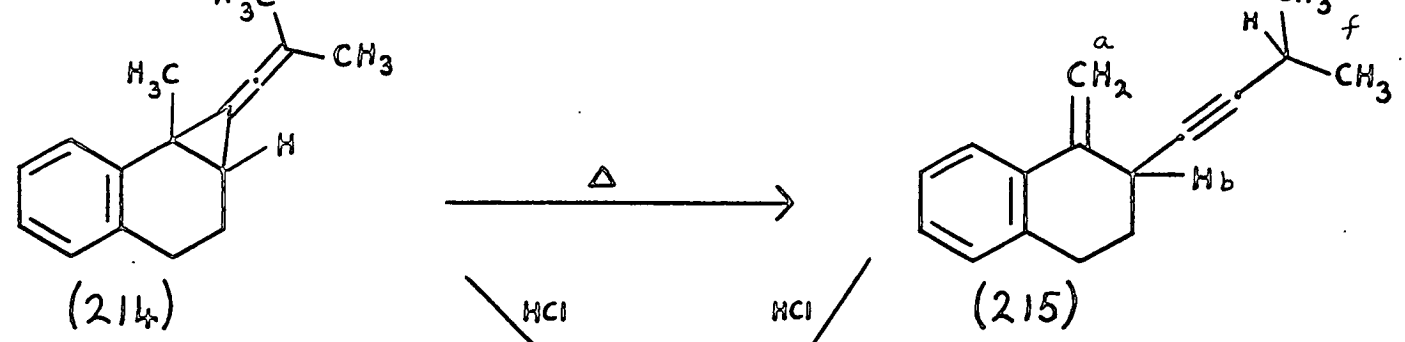


(213)

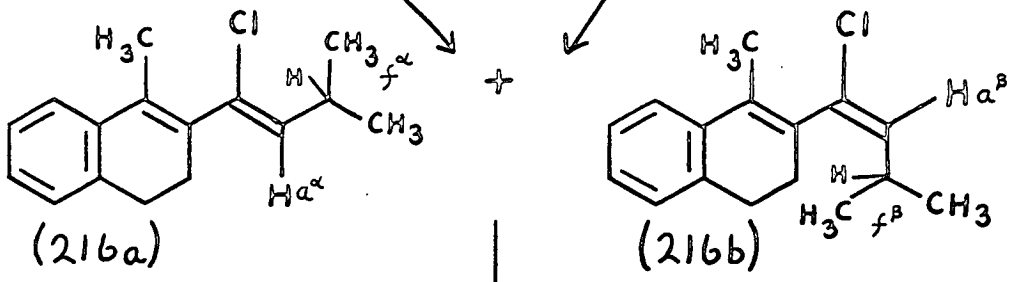
mechanism which is consistent with these observations is illustrated in scheme XVIII and involves protonation at the β-site of the allene followed by ring expansion and subsequent proton elimination to form the aromatic product. When the acid catalysed rearrangement of the indene adduct(206) was carried out with deuterium chloride and methanol-d the n.m.r. spectrum of the product(213) indicated >75% replacement of the olefinic proton (H_a) with deuterium, whereas a similar reaction with the naphthalene(207) itself showed no detectable deuterium exchange to have occurred with any proton. These observations fully confirm the proposed mechanism for these rearrangements (scheme XVIII) with regard to the protonation site and subsequent irreversible proton elimination.

A related rearrangement[52] involving the dimethylvinylindene-carbene adduct with skatole(74) has already been discussed (section 1.5). The present acid catalysed rearrangements are virtually specific towards formation of the respective naphthalene derivative, the proportion of unidentified volatile material being only 3-4% in each case. This indicates that a process involving γ-protonation of the allene (section 3.4) which would result in cleavage of the alternative aryl-substituted cyclopropyl bond with resultant retention of the indane skeleton does not occur to any appreciable extent, the favoured process being β-protonation which results in ring expansion to form a fully aromatic ring system.

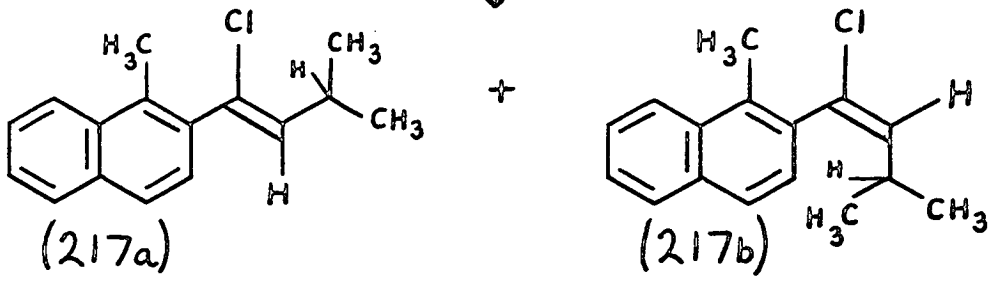
The rearrangement of the 3-methylindene adduct(208) is also effected by refluxing with a 20% solution of potassium hydroxide in aqueous ethanol for 4·5hr., forming a mixture of the bicycloheptene(209) and the naphthalene(210) in the ratio 1:5.



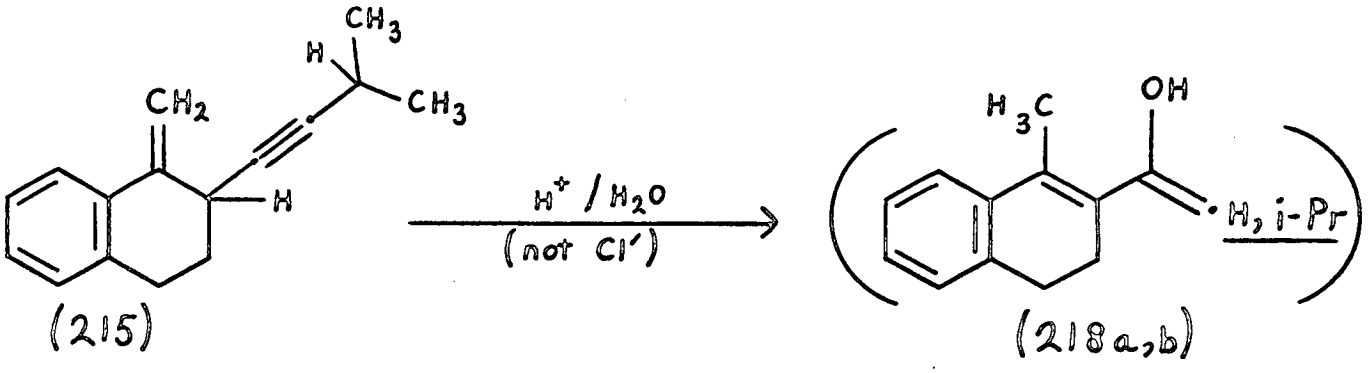
(214) (215)



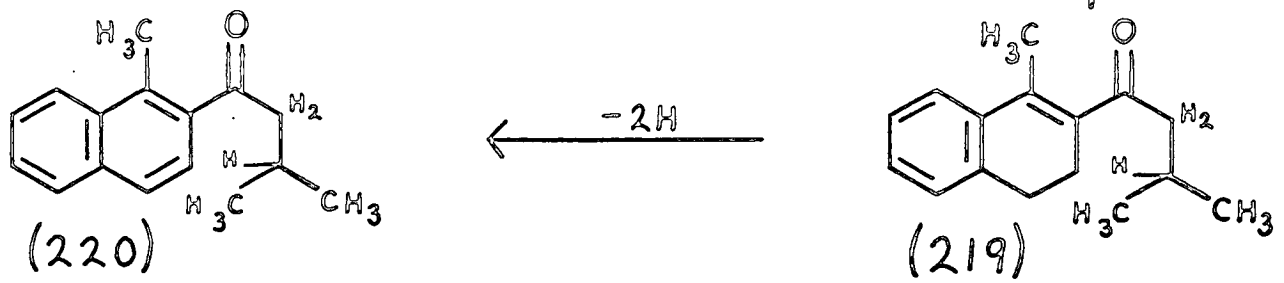
(216a) (216b)



(217a) (217b)



(215) (218a,b)



(220) (219)

This rearrangement probably involves base catalysed rearrangement of the adduct(208) by way of an indanyl anion to form the naphthalene derivative(210), this process being appreciably slower than the corresponding acid catalysed rearrangement allowing thermal rearrangement of the adduct to form the bicycloheptene(209) to compete successfully in this instance.

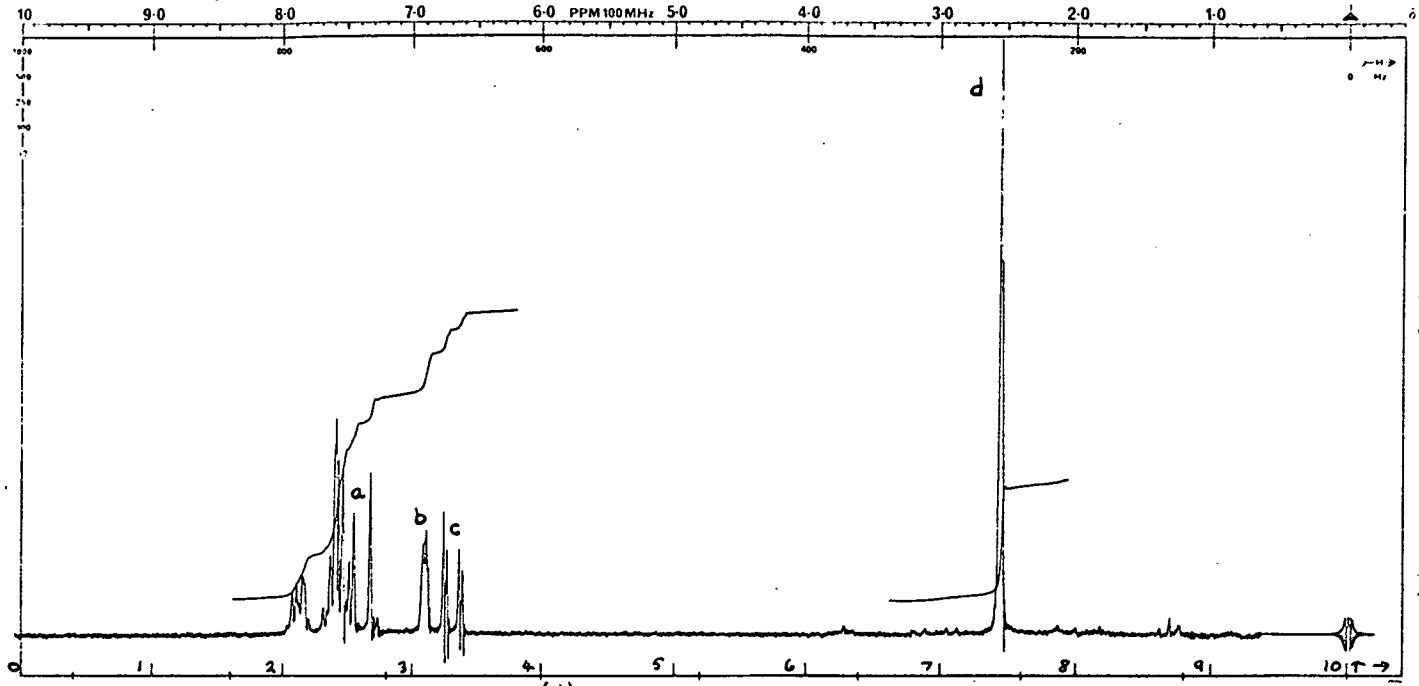
3.6 THERMAL AND ACID CATALYSED REARRANGEMENT OF THE ADDUCT DERIVED FROM 4-METHYL-1,2-DIHYDRONAPHTHALENE.

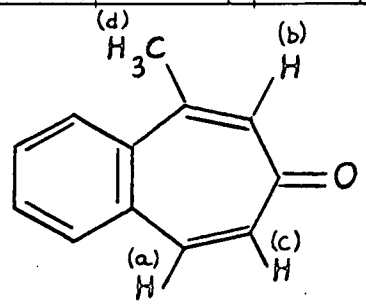
2,3-Benzo-7-dimethylvinylidene-1-methylbicyclo[4,1,0]hept-2-ene(214) undergoes complete rearrangement when heated in solution at 180° to form 1-methylene-2(3-methylbut-1-ynyl)tetralin(215) in low yield, the acetylenic product being unstable to prolonged heating. However vapour phase pyrolysis of the adduct(214) by passage through the flow system at 450° formed the ethynyltetralin(215) in good yield as the only volatile product.

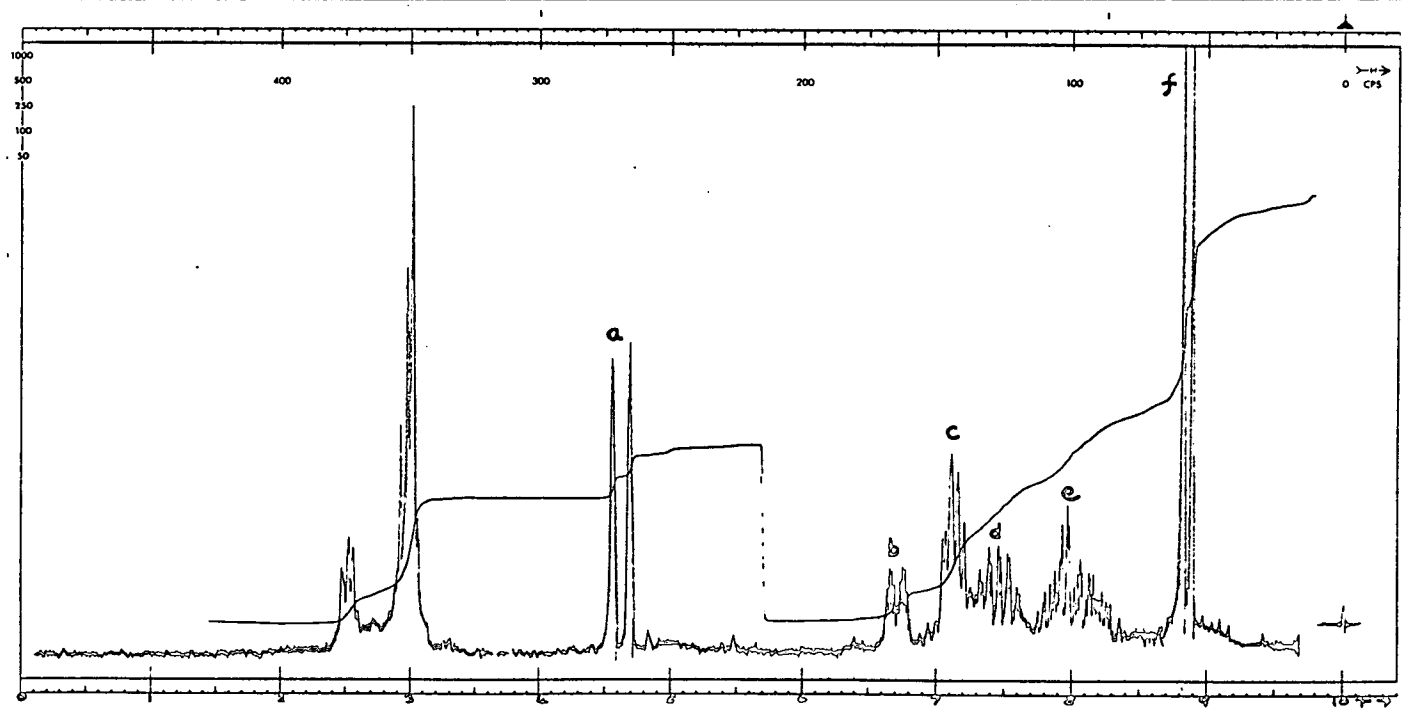
The structure of the ethynyltetralin(215) was deduced from its spectral characteristics and two stage conversion to the mixture of halonaphthalenes(216a,b) and to 1-methyl-2-(3-methylbutyryl)naphthalene(220). The structure of this ketone was confirmed by its independent synthesis from β-bromo-α-methylnaphthalene and isobutraldehyde followed by chromic acid oxidation of the resultant carbinol.

The n.m.r. spectrum of the ethynyltetralin(215) is illustrated in figure XII and shows the exo-cyclic methylene protons (H_a, 4·55, 4·68τ) as two triplets (J = 0·5 Hz.), the

FIGURE XII


10
9·0
8·0
7·0
6·0 PPM 100 MHz 5·0
4·0
3·0
2·0
1·0
d
a
b
c
0
1
2
3
4
5
6
7
8
9
10


(d)
H3C
(b)
H
O
(a)
H
(c)
H


400
300
200
100
f
a
b
c
d
e

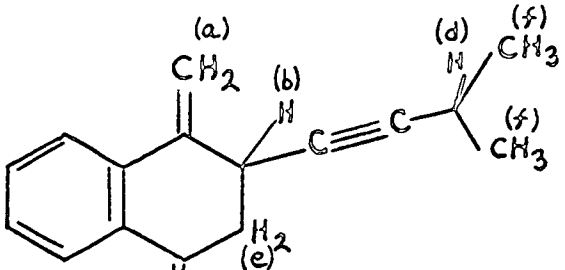
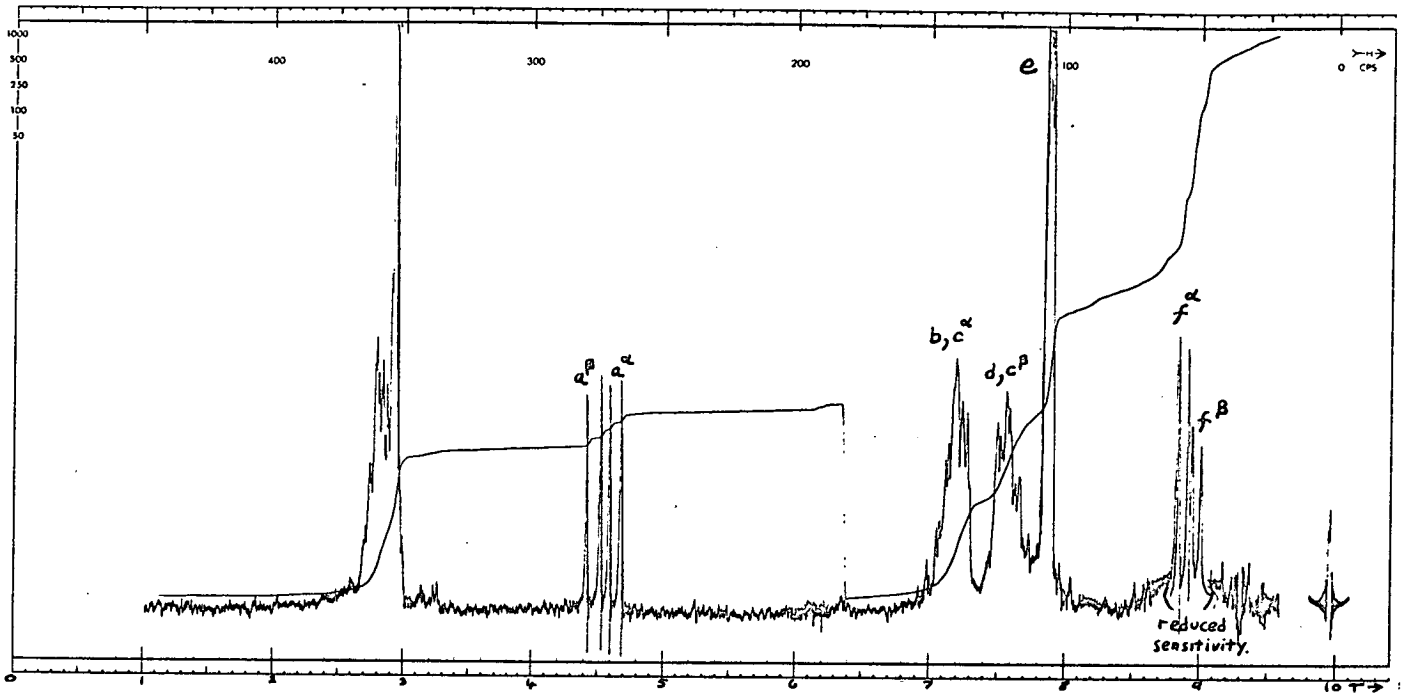
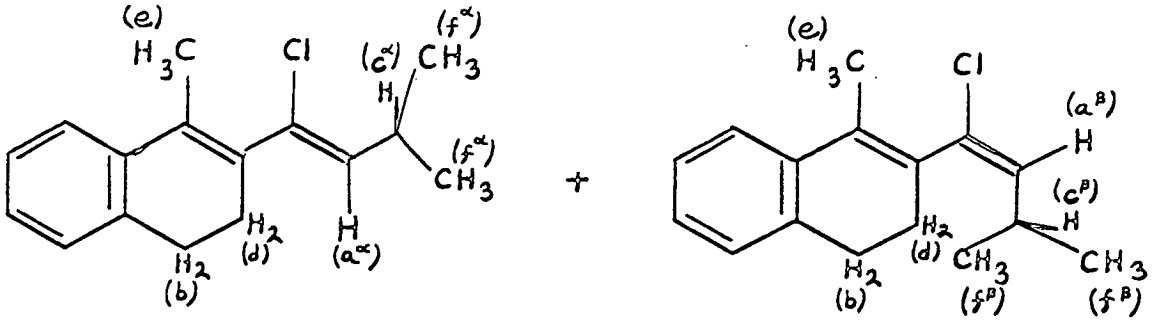

(a)
CH2
(b)
H
C≡C
(d)
N
(f)
CH3
(f)
CH3
H2
(e)2

FIGURE XIII


400
300
200
e
100
0 CPS
a^β
a^α
b, c^α
d, c^β
f^α
f^β
reduced sensitivity.
0 1 2 3 4 5 6 7 8 9 10 T


(e)
H_3C
Cl
(c^α) H
(f^α) CH_3
(f^α) CH_3
H_2 (d)
H (a^α)
H_2 (b)
+
(e)
H_3C
Cl
(a^β) H
(c^β) H
H_2 (d)
CH_3 (f^β)
CH_3 (f^β)
H_2 (b)

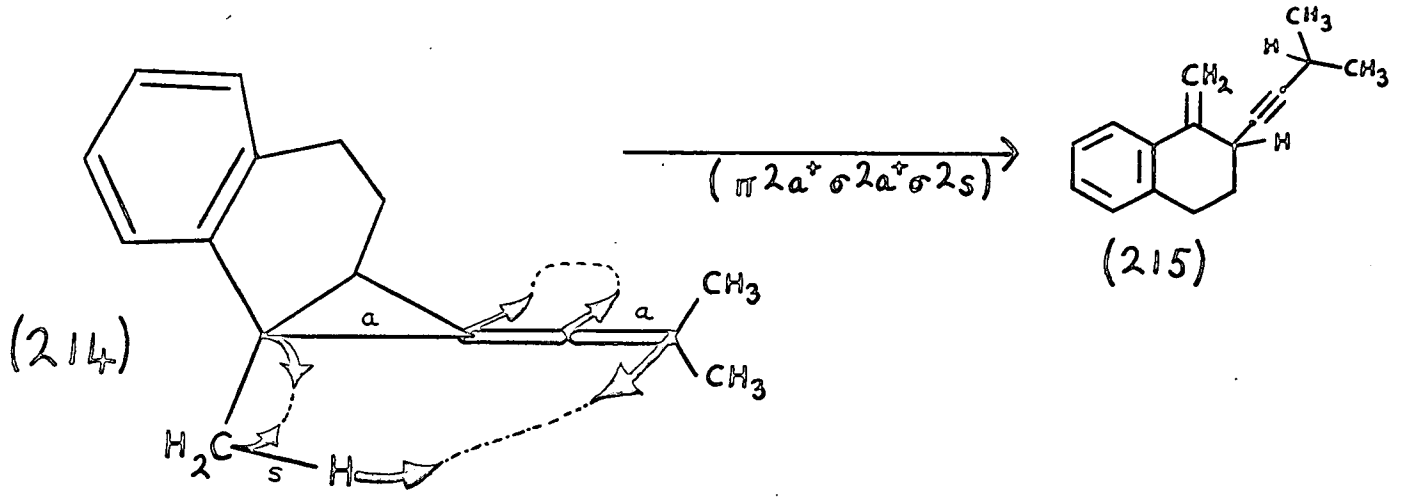
propargylic proton (H_b, 6·70τ) as a multiplet and the isopropyl methyl protons (H_f, 8·85τ) as a doublet (J = 7 Hz.). The proton allocations were confirmed by spin-spin decoupling. The i.r. spectrum shows bands attributed to the triple bond and olefinic methylene groupings (ν_{max} = 2,250 and 900 $cm.^{-1}$ respectively) while the u.v. spectrum contains a maximum at 250·0mμ (ε = 11,500) which is typical of a styrene derivative.

It was originally considered that the exo-cyclic double bond in the methylenetetralin(215) would migrate on treatment with acid to form the fully conjugated isomer(221). However treatment of the tetralin(215) with strong hydrochloric acid leads to the direct formation of a 1:1 mixture of 2-(1-chloro-3-methyl-trans-but-1-enyl)-1-methyl-3,4-dihydronaphthalene(216a) and the cis-isomer(216b). The 100 MHz. n.m.r. spectrum of this isomer mixture, which is illustrated in figure XIII, includes two doublets in the ratio 1:1 centred at 4·51 and 4·68τ which are allocated to the olefinic protons ($H_{a\alpha}$, $H_{a\beta}$). It is reasonable to assume that the downfield doublet (J = 10 Hz.) corresponds to the olefinic proton($H_{a\beta}$) which is cis- to the chlorine atom(216b) by analogy with related vinylic halides,[110] in which case the upfield doublet (J = 9 Hz.) corresponds to the olefinic proton ($H_{a\alpha}$) trans- to the chlorine atom(216a). The 60 MHz. spectrum of this isomer mixture shows the olefinic protons (H_a, 4·59τ) as a 1:2:1 triplet due to the superposition of the signals which results from the change in frequency separation between the two isomeric types, the τ-values and coupling constants of the components remaining unchanged.

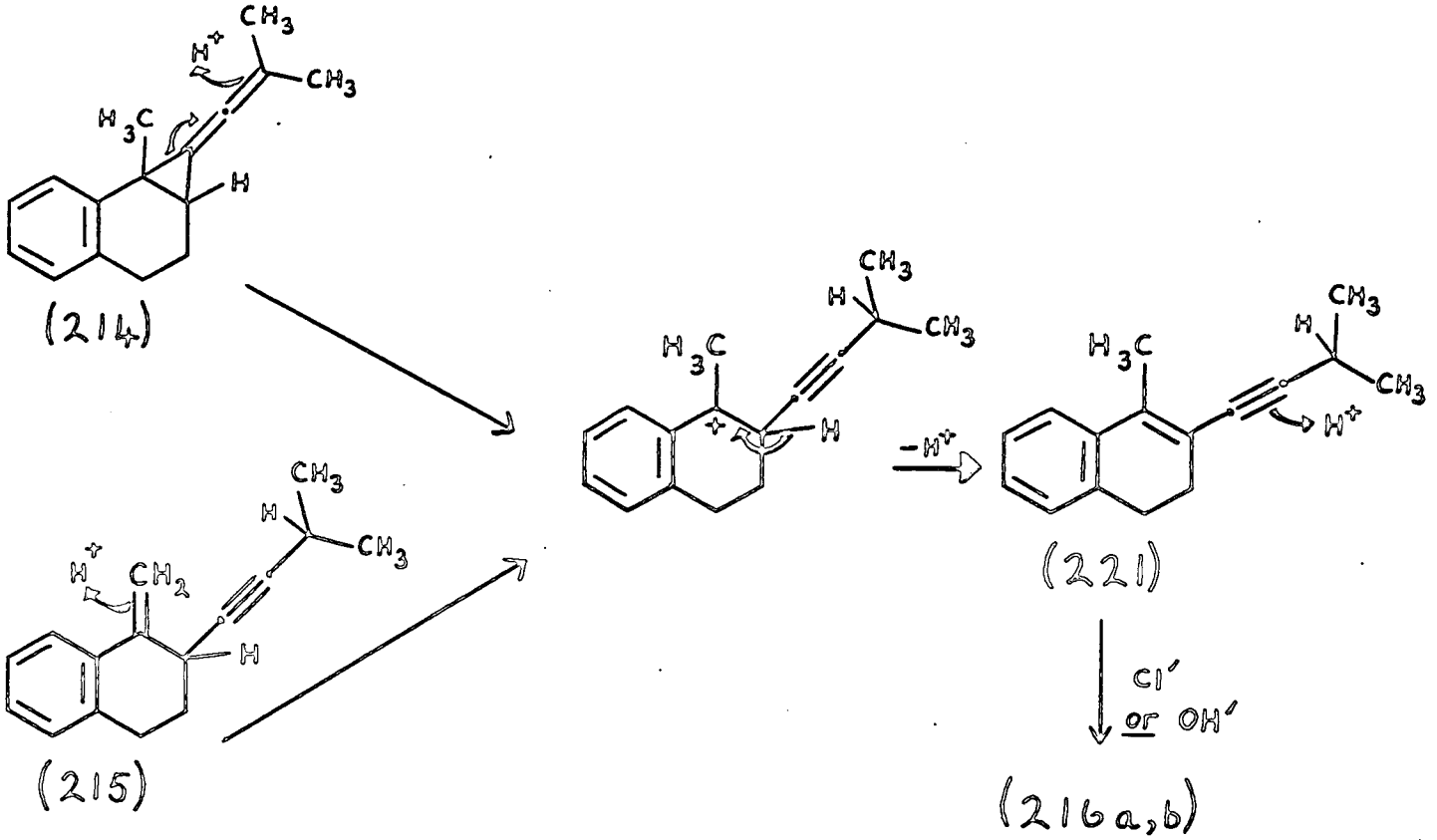
Had the original pair of doublets been caused by the splitting of intercoupled protons of a single molecule this pattern would have been unaltered at 60 MHz. A similar effect is observed with the isopropyl methyl protons (H_f) which occur as doublets (J = 7 Hz.) centred at 8·92τ(216a) and 9·02τ(216b) in the 100 MHz. spectrum but have the appearance of a 1:2:1 triplet in the 60 MHz. spectrum, centred at 8·97τ. The proton allocations were confirmed by spin-spin decoupling. The u.v. spectrum of the isomer mixture (216a,b) has a maximum at 276·0mμ (ε = 13,400) which is consistent with the proposed structure while the i.r. spectrum confirms the absence of an olefinic methylene grouping.

The addition of hydrogen chloride to the triple bonds of acyclic enyne systems has previously[111] been observed, although not under the relatively mild conditions involved in the present cyclic system. Dehydrogenation of the isomer mixture(216a,b) with o-chloranil forms the two isomeric naphthalene derivatives(217a,b) in the expected 1:1 ratio, the n.m.r. spectral properties of these isomers being analogous to their dihydro-precursors, the olefinic protons occurring as doublets (J = 10, 8 Hz.) centred at 4·20τ(217b) and 4·54τ(217a) respectively.

Further attempts to isomerise the ethynyltetralin(215) without the addition of substrate were unsuccessful, strong phosphoric acid or 50% aqueous sulphuric acid converting this to 2-(3-methylbutyryl)-1-methyl-3,4-dihydronaphthalene(219). Dehydrogenation of this compound with o-chloranil forms the ketone(220) which, assuming no skeletal rearrangements to have

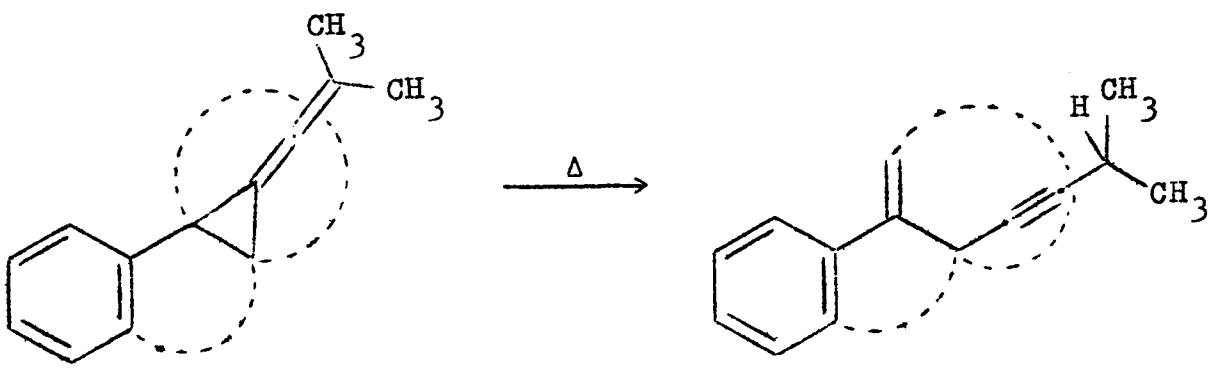

(214)
a
a
CH3
CH3
H2C
S
H
(π2a+σ2a+σ2s)
CH3
H
CH3
CH2
H
(215)

SCHEME XX


CH3
H+
CH3
H3C
H
(214)
CH3
H
CH3
H3C
H
-H+
CH3
H
CH3
H3C
H+
(221)
CH3
H
CH3
H+
CH2
H
(215)
Cl'
or OH'
(216a,b)
or (218a,b)

occurred, confirms the structure of the parent thermal rearrangement product(215).

The thermolysis of the adduct(214) to form the ethynyltetralin(215) can be rationalised in terms of the concerted mechanism presented in scheme XIX which is a thermally allowed ($_{\pi}2_a + _{\sigma}2_a + _{\sigma}2_s$) process, a stepwise diradical mechanism involving hydrogen abstraction being sterically impossible. This mechanism is directly analogous to that illustrated in scheme IX for the concerted rearrangement of the 1-arylcycloalkenes(174, 177, 188 or 192) to form the ethynylcycloalkenes(176,179, 190 or 194) respectively.



(214)
(174),(177),(188) or (192)

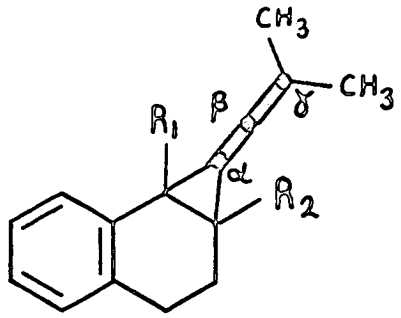
(215)
(176),(179),(190) or (194) respectively

It is noteworthy that prolonged heating of the phenylcyclohexene adduct(177) in solution also gives a low yield of the ethynylcyclohexene(179), being analogous to the solution pyrolysis of the present adduct(214). It is also significant that the direction of cyclopropane ring cleavage involved in the thermolysis of the 4-methyl-dihydronaphthalene adduct(214) results in retention of

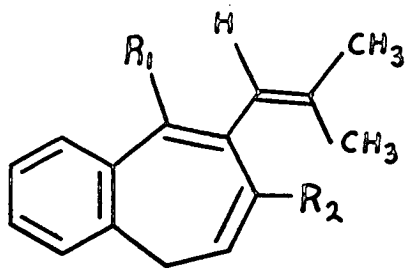
the tetralin skeleton whereas the preferred mode of rearrangement of the bicyclic adducts derived from indene and 3-methylindene (section 3.5) involves cleavage of the alternative aryl-substituted cyclopropane bond with resultant ring expansion, again forming the favoured six membered skeleton. Alternatively, the rearrangements of the bicyclic adducts derived from the 1-arylcycloalkenes (section 3.4) all involve both alternative modes of aryl-stabilised cyclopropane bond cleavage.

Hydrochloric acid catalysed rearrangement of the adduct(214) also forms the 1:1 isomer mixture(216a,b) together with several unidentified products (40% of total). A mechanism which is consistent with these observations is illustrated in scheme XX. Thus protonation at the γ-site of the allene(214) or alternatively at the exo-cyclic methylene of the ethynyltetralin(215) can both lead, by way of a common benzyl carbonium ion and subsequent proton elimination, to the enyne derivative(221). Further protonation of this system at the triple bond followed by equally favourable addition of chloride ion to either face of the resultant carbonium ion forms the 1:1 isomer mixture (216a,b). A similar process involving addition of the elements of water to the enyne derivative(221) would lead to the isomeric enol-naphthalenes(218a,b) which can then tautomerise to form the observed ketone(219).

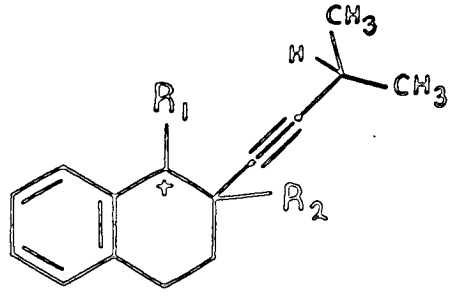
The attempted isomerisation of the ethynyltetralin(215) by distillation from p-toluenesulphonic acid was also unsuccessful, only starting material being recovered.



(214) , $R_1 = CH_3$, $R_2 = H$
(222) , $R_1 = R_2 = H$
(223) , $R_1 = H$, $R_2 = CH_3$



(224)



(225)

3.7 THERMAL AND ACID CATALYSED REARRANGEMENT OF THE ADDUCTS DERIVED FROM DIHYDRONAPHTHALENE AND 3-METHYL-1,2-DIHYDRONAPHTHALENE.

The thermal rearrangement of 2,3-benzo-7-dimethylvinylidene-bicyclo[4,1,0]hept-2-ene(222) and the 6-methyl derivative(223) in the vapour phase at 450° formed complex mixtures of products none of which were identified. In contrast to the product obtained by the vapour phase pyrolysis of the adduct(214), the i.r. spectra of these products showed weak maxima at 2020 $cm.^{-1}$ attributed to unrearranged vinylidenecyclopropane. It therefore appears that whereas the adduct(214) has a suitably placed methyl substituent which allows relatively facile thermolysis to form the ethynyltetralin(215), the non-alkyl substituted adduct(222) and the alternatively substituted adduct(223) cannot fulfil the necessary steric requirements for a cyclic transition state and thus no single low energy path is available for rearrangement, thus giving rise to the complex mixtures of products.

The hydrochloric acid catalysed rearrangement of the adducts(222) and (223) also formed complex mixtures of products which did not contain any major component. By analogy with the acid catalysed rearrangement of the adduct(214) illustrated in scheme XX, protonation at the γ-site of the allene in these adducts could conceivably lead to their corresponding benzyl carbonium ions(225). In the case of the non alkyl substituted adduct(222) this carbonium ion (225, $R_1 = R_2 = H$) could then follow a route analogous to that illustrated in scheme XX which

involves elimination of the adjacent propargylic proton prior to further protonation and final product formation. However in the case of the adduct(222) this route is apparently unfavourable and no 1:1 isomer mixture was detected in the product. It follows that the carbonium ion (225; R_1 = H, R_2 = CH_3) cannot undergo this mode of proton elimination.

On consideration of the two independent processes of β- or γ-allenic protonation which can apparently occur during the acid catalysed rearrangements of adducts derived from 1-arylcycloalkenes (section 3.4), an alternative mode of β-protonation might be expected to be available to the present series of adducts. This could follow a path analogous to that favoured by the adducts derived from indenes (compare scheme XVIII) and would result in ring expansion to form a benzocycloheptatriene derivative(224). However no evidence was found in support of this view, it being assumed that such compounds could readily be recognised by a characteristic benzylic methylene proton resonance in the region of 7τ. Alternatively these proposed benzocycloheptatrienes may be labile under the conditions involved and give rise to the large amounts of unidentified material formed during the acid catalysed rearrangement of the adduct(214) and especially the adducts(222) and (223).

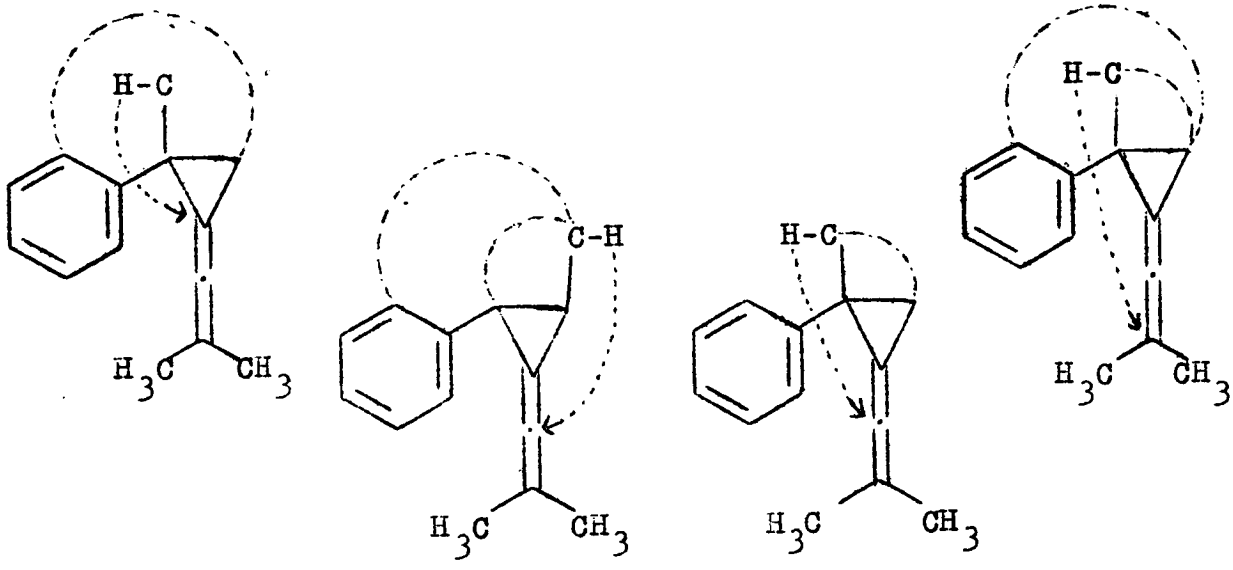
3.8 SUMMARY

Many different types of product are formed in the thermal unimolecular rearrangements of arylvinylidenecyclopropanes. Thermolysis of the adducts derived from 1-arylalkenes and 3-methylene-benzocycloalkenes forms exclusively dimethylenecyclopopane derivatives. However thermolysis of the adducts derived from 1-arylcycloalkenes and benzocycloalka-1,3-dienes can involve hydrogen migration, the constraints imposed upon these systems rendering dimethylenecyclopropane formation unfavourable. Several of the hydrogen migration pathways are listed below in the order of decreasing ease. These involve transfer of a hydrogen atom sited on a carbon atom α- to the cyclopropyl ring to:-

(a) the α-carbon atom of the allene.

(b) " β- " " " " "

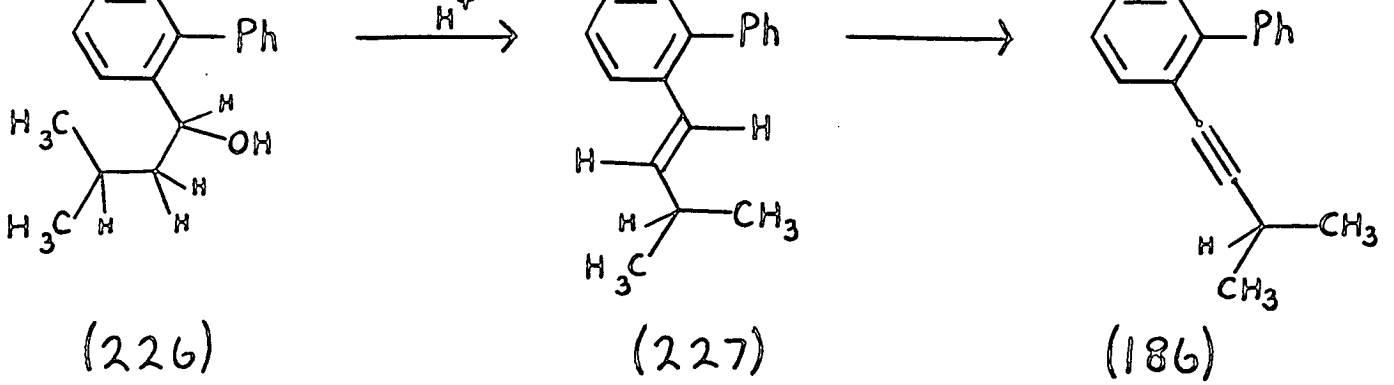
(c) " γ- " " " " "



(a) (b) (c)

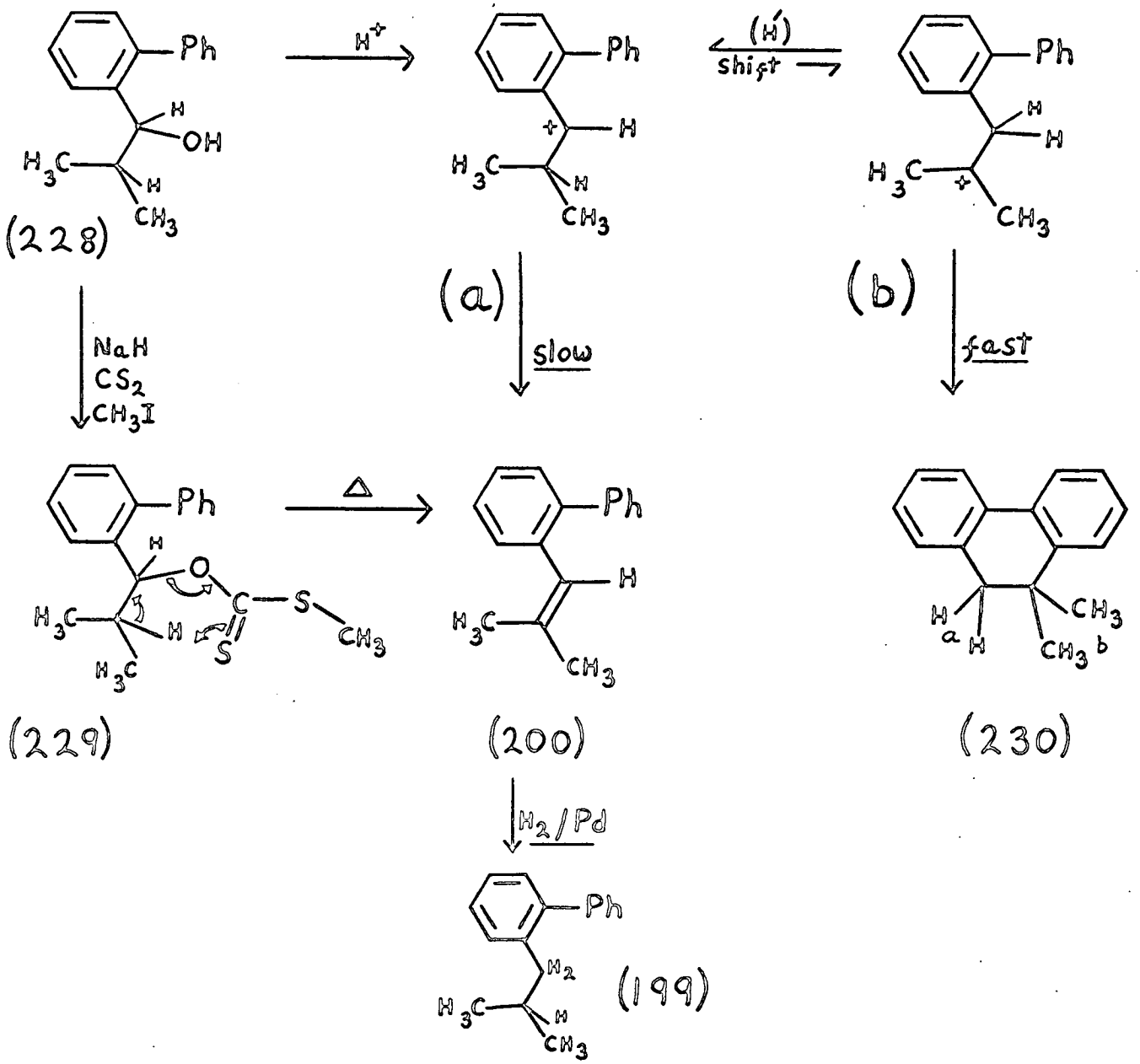
The relative ease of these processes may be dependent on the migration distance involved and the orientation which the migrating hydrogen atom can adopt, relative to the migration terminus, prior to formation of the transition state.

The major pathway in the acid catalysed rearrangement of the vinylidenecyclopropanes usually involves initial protonation at the β-carbon atom of the allene followed by formation of the thermodynamically most stable product, an alternative mode of γ-protonation of the allenic system often forming relatively minor products.



(226) (227) (186)

SCHEME XXI



(228) (a) (b) (229) (200) (230) (199)

4. INDEPENDENT SYNTHESES

2-Isobutyl-4'-methylbiphenyl(191) was synthesised by way of a Grignard reaction between 2-(p-tolyl)cyclohexanone and isobutyl magnesium bromide. Dehydration of the carbinol followed by dehydrogenation of the resulting olefin gave the desired product. The Grignard step in this synthesis gave a low yield of carbinol, much starting ketone being recovered. This can be attributed to the relative acidity of the benzylic hydrogen atom in this ketone, whereupon reaction with the Grignard reagent favours abstraction of this proton to form isobutane as compared to neucleophylic attack at the neighbouring carbonyl group. In a similar reaction involving 2-phenylcyclohexanone and isobutyl magnesium bromide no carbinol was isolated, the starting ketone only being recovered. This seems reasonable in view of the fact that the aryl methyl group in the former ketone will tend to lower the relative acidity of a para-substituent, namely the benzylic hydrogen atom.

2-(3-Methylbut-1-ynyl)biphenyl(186) was synthesised as follows. 2-(3-Methylbutanyl-1-ol)biphenyl(226) was prepared from o-phenylbenzaldehyde and isobutyl magnesium bromide. Dehydration of this carbinol with potassium bisulphate at 160° gave the desired 2-(3-methyl-trans-but-1-enyl)biphenyl(227) which underwent bromination and dehydrobromination to form the ethynylbiphenyl(186).

2-(2-Methylprop-1-enyl)biphenyl(200) and 2-isobutyl-biphenyl(199) were synthesised as follows. A Grignard reaction between o-phenylbenzaldehyde and isopropyl magnesium bromide readily

formed 2-(2-methylpropanyl-1-ol)biphenyl(228). Acid catalysed dehydration of this carbinol forms a mixture of products as detailed below. However dehydration by way of Chugaev elimination involves a cyclic transition state,[112] and thus pyrolysis of the xanthate(229) proceeded with elimination of carbon oxysulphide and methanethiol to form the olefinic biphenyl(200) as the only hydrocarbon product. Catalytic hydrogenation of this olefin over palladium-charcoal formed the biphenyl(199).

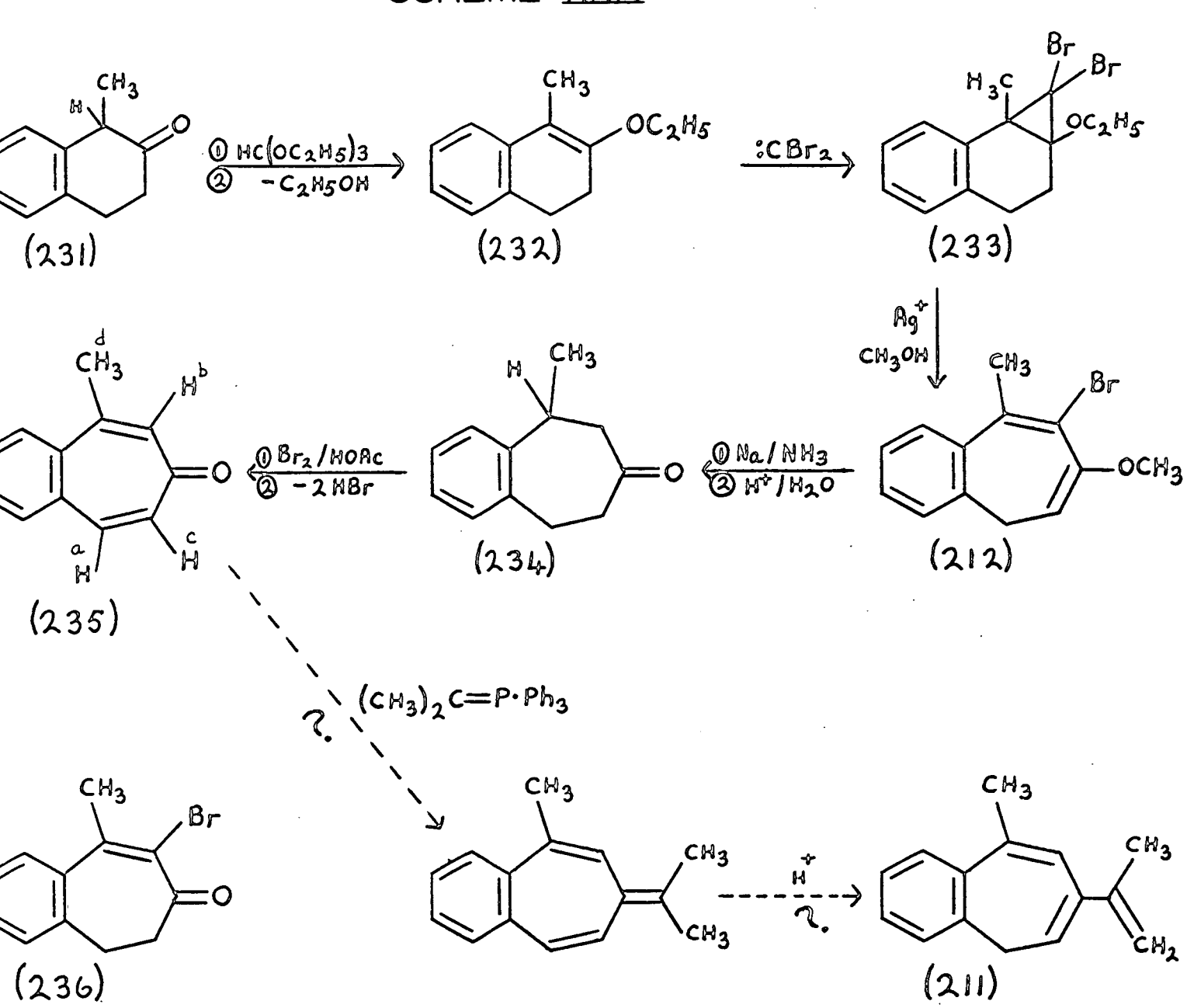
Dehydration of the carbinol(228) by heating with potassium bisulphate at 160° formed a mixture containing 48% of 9,9-dimethyl-9,10-dihydrophenanthrene(230), 48% of the biphenyl(200) and 4% of 9-isopropylfluorene(181). Alternatively vacuum distillation of the carbinol from p-toluenesulphonic acid formed 95% of the dihydrophenanthrene(230) and 5% of 9-isopropylfluorene(181). These results can be rationalised in terms of the intermediate carbonium ions involved, as illustrated in scheme XXI. Thus protonation of the carbinol(228) and elimination of water forms the benzyl carbonium ion (a) which may undergo intramolecular attack on the neighbouring aromatic ring to form the fluorene(181) or lose the α-proton to form the biphenyl(200), this latter process being reversible. However the secondary benzyl carbonium ion may also undergo a 1,2 hydride shift to form the tertiary carbonium ion (b) which could similarly intramolecularly attack the adjacent aromatic ring with subsequent irreversible proton elimination to form the dihydrophenanthrene(230). The foregoing hydride ion transfer equilibrium would be expected to favour the resonance

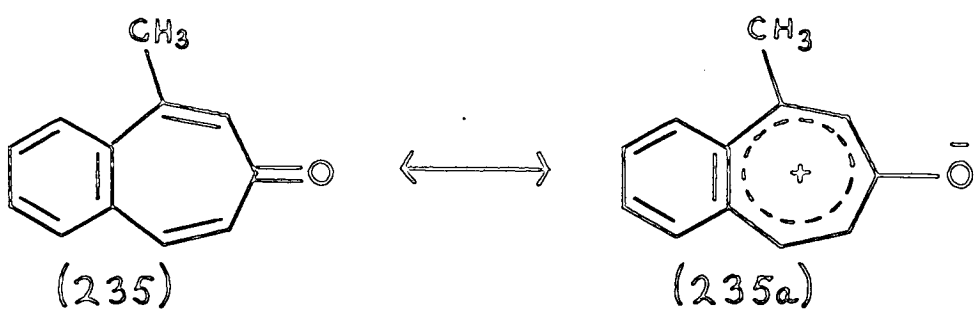
stabilised benzyl carbonium ion with a resultant predominance of products formed through pathway (a), but if pathway (b) is fast with respect to pathway (a) then final product distribution would depend on the rate of formation and stabilities of the products concerned and thus the dehydration conditions involved.

The n.m.r. spectrum of the dihydrophenanthrene(230) shows the benzylic methylene protons (H_a, 7·33τ)and the methyl protons (H_b, 8·81τ) to be equivalent, appearing as sharp singlets, and this is attributed to the rapid interconversion of the two likely conformations at room temperature. However no change is observed in the spectrum down to -80° which indicates a relatively low energy barrier existing between the two conformations (p. 73).

Dehydrations which result in the cyclisation of o-phenylbenzyl carbinols are not uncommon, dimethyl-o-xenylcarbinol cyclising to form 9,9-dimethylfluorene.[113] However it would appear from the foregoing that hydride ion transfer only becomes important with respect to product formation when this can form a tertiary carbonium ion, the dehydration of the carbinol(226) forming the olefin(227) as the only product. Related observations[37] concerning the acid catalysed rearrangement of phenylcyclopropanes(46) have already been described (section 1.4).

It was originally considered that synthesis of the cycloheptatrienone derivative(235) might have allowed independent access to the benzocycloheptatriene(211) and that the synthesis might provide model compounds for spectral comparison. The spectral


(231)
① HC(OC2H5)3
② -C2H5OH
(232)
:CBr2
(233)
Ag+
CH3OH
(212)
① Na / NH3
② H+ / H2O
(234)
① Br2 / HOAc
② -2 HBr
(235)
(CH3)2C=P·Ph3
(236)
H+
(211)

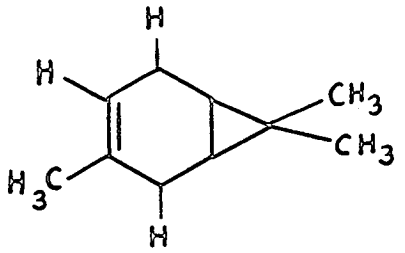

(235)
(235a)

properties of the bromocycloheptatriene(212) have already been discussed (section 3.5).

1-Methyl-β-tetralone(231) was prepared by way of a modified enamine alkylation. Formation of the diethyl ketal and elimination of ethanol afforded 2-ethoxy-1-methyl-3,4-dihydronaphthalene(232). Addition of dibromocarbene to this olefin followed by dehydrobromination of the dibromocyclopropane(233) with silver nitrate in methanol resulted in ring expansion to form 1,2-benzo-4-bromo-5-methoxy-3-methylcyclohepta-1,3,5-triene(212), which on treatment with acid gave the parent ketone namely 1,2-benzo-4-bromo-3-methylcyclohepta-1,3-dien-5-one(236). However reduction of the enol-ether(212) with sodium and liquid ammonia followed by acidification formed 1,2-benzo-3-methylcyclohepten-5-one(234) which, after bromination with a solution of bromine in acetic acid followed by dehydrobromination with lithium carbonate and lithium bromide in dimethylformamide, afforded 1,2-benzo-3-methylcycloheptatrien-5-one(235). The n.m.r. spectrum of this compound is illustrated in figure XII and shows the olefinic proton (H_a, 2·58τ) as a doublet (J_{ac} = 12 Hz.) while the olefinic protons (H_b, 3·06τ) and (H_c, 3·29τ) are a multiplet and a quartet (J_{ca} = 12 Hz., J_{cb} = 2·5 Hz.) respectively. The methyl protons (H_d, 7·44τ) appear as a fine doublet (J_{db} = 1 Hz.), these allocations being confirmed by spin-spin decoupling.

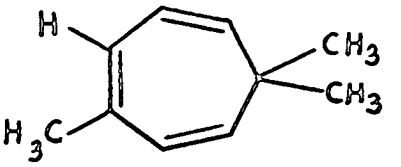
The 4-chloro derivative of this benzotropone has been prepared by another route.[114] Benzotropones do not, however, undergo the usual condensation reactions[115] common to ketones

probably attributable to a large resonance contribution of the cycloheptatrienyl cation (i.e. 235a), and due to the fact that tropones themselves[116] undergo addition of organometallic compounds to form α-alkylcycloheptadienones it is possible that the present benzotropone derivative(235) might not have undergone the desired neucleophylic addition of isopropyl magnesium bromide at the carbonyl site. Reaction of the benzotropone(235) with isopropylidenetriphenylphosphorane was not attempted on account of the small amount of ketone available and thus remains a possible route to the cycloheptatriene(211).

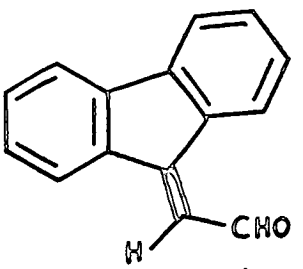


(237)

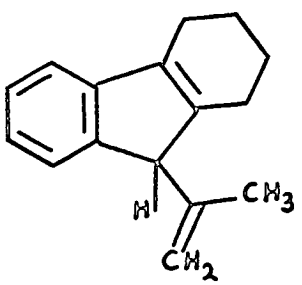
D.D.Q.



(238)

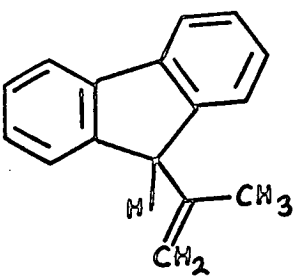


(239)



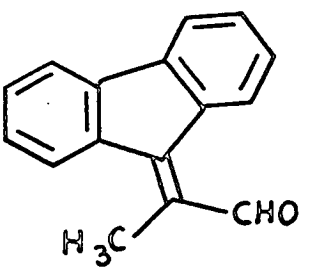
(175)

D.D.Q.
or o-chloranil



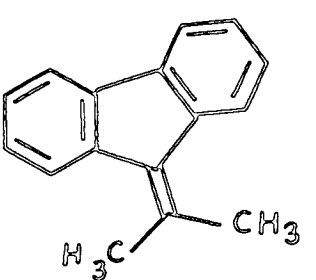
(180)

D.D.Q.



(240)

D.D.Q.



(183)

5. THE DIRECT OXIDATION OF HYDROCARBONS WITH DICHLORODICYANO-QUINONE (D.D.Q.)

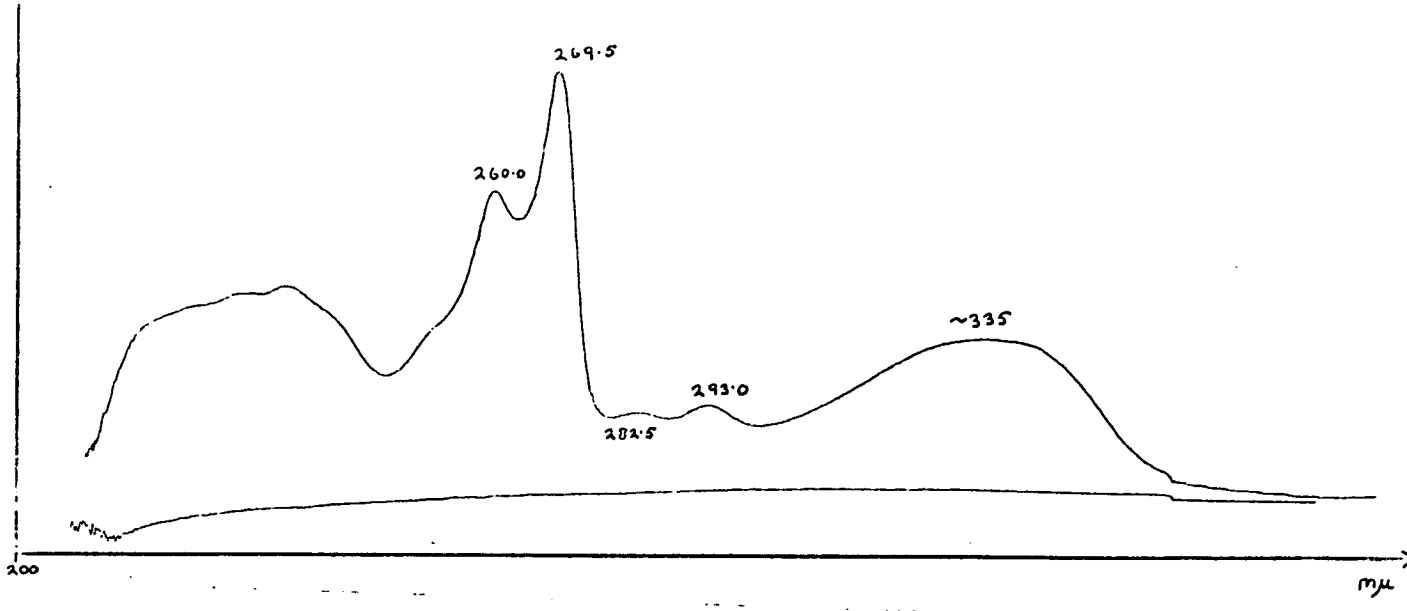
5.1 INTRODUCTION

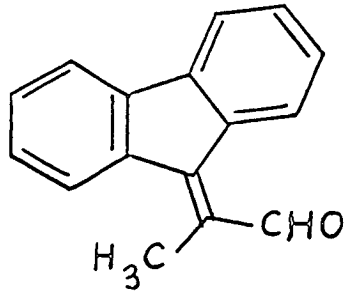
D.D.Q. has been widely used[117] for the dehydrogenation of partially saturated ring systems to form aromatic hydrocarbons and in this respect it is more reactive than o-chloranil which in turn surpasses its p-isomer. Dehydrogenations with D.D.Q. have also been extended to the formation of non-aromatic compounds, 3-carene(237) undergoing[118] dehydrogenation with accompanied ring expansion to form 3,7,7-trimethylcycloheptatriene(238). These reactions are not limited to cyclic compounds, tetramethylethylene being dehydrogenated to 2,3-butadiene which reacts with further D.D.Q. to form a Diels-Alder adduct.[119] Furthermore D.D.Q. is reported[120] to dehydrogenate primary and secondary alcohols to aldehydes and ketone respectively although the use of o-chloranil is preferable in these cases. However until the completion of this work[89] there was no report that oxidation of certain hydrocarbon systems with D.D.Q. could result in the direct formation of carbonyl compounds.

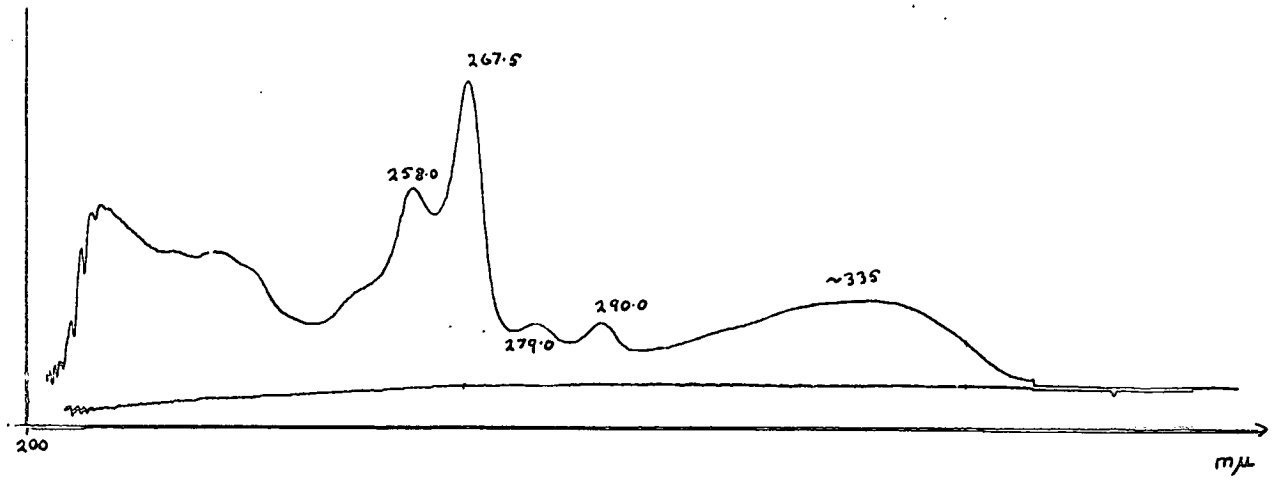
5.2 THE RESULTS AND DISCUSSION

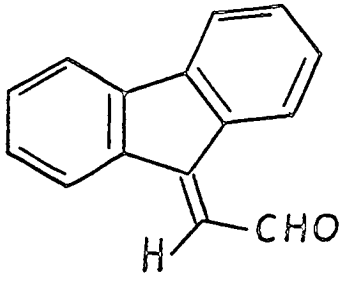
The dehydrogenation of the tetrahydrofluorene(175) with o-chloranil to form 9-isopropenylfluorene(180) has previously been discussed (section 3.4). However dehydrogenation of the

FIGURE XIV


269·5
260·0
~335
293·0
282·5
200
mμ

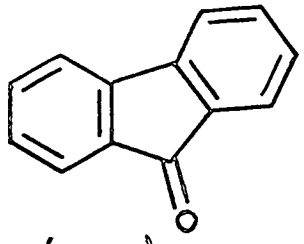

CHO
H3C


267·5
258·0
~335
290·0
279·0
200
mμ


CHO
H

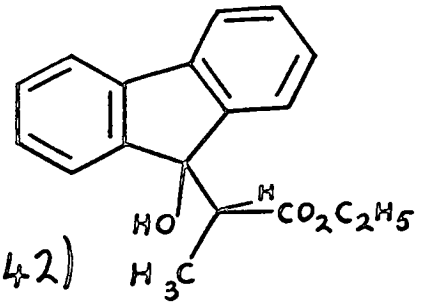
tetrahydrofluorene(175) with D.D.Q. at room temperature yields a mixture containing 30% of the fluorene(180) together with 45% of α-(9-fluorenylidene)propionaldehyde(240) which was identified from its spectral characteristics and similarity to the acetaldehyde(239) and confirmed by independent synthesis.

The u.v. spectrum of the propionaldehyde(240), illustrated in figure XIV, shows a characteristic fluorenylidene chromophore very similar to that of 9-isopropylidenefluorene(183; figure V) and 9-fluorenylideneacetaldehyde(239; figure XIV), the acetaldehyde(239) being prepared by a known[121] route for direct comparison. The n.m.r. spectrum of the propionaldehyde(240) shows the aldehydic proton (-0·74τ) and the methyl protons (7·54τ) as singlets whereas the aldehydic proton of the acetaldehyde(239) appears as a doublet centred at -0·71τ. This relatively low τ-value for these aldehydic protons is attributed to the deshielding effect of the fluorenylidene double bond and the neighbouring aromatic ring, the aldehydic proton of β-methylcinnamaldehyde(248) being relatively upfield at -0·18τ. The i.r. spectra of these 9-fluorenylidene-aldehydes shows a strong carbonyl band at 1670 $cm.^{-1}$. The identity of the propionaldehyde(240) was confirmed by its independent synthesis. Treatment of fluorenone(241) with zinc and ethyl-α-bromopropionate followed by dehydration and hydrolysis of the β-hydroxy-ester(242) afforded α-(9-fluorenylidene)-propionic acid(243). This was converted by way of the acid chloride to the aziridine which was reduced with lithium aluminium hydride to give the propionaldehyde(240).



(241)

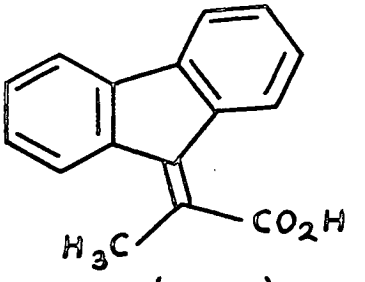
$Zn / H_3C\cdot\overset{Br}{C}H\cdot CO_2C_2H_5$



(242)

① p-TsOH, HOAc, 110°

② OH^-

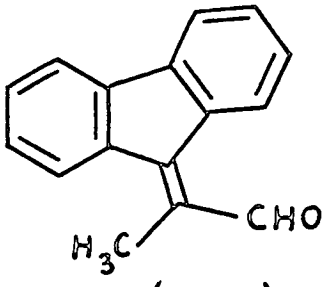


(243)

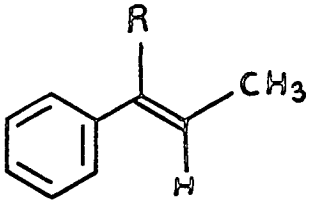
① $SOCl_2$

② $HN(CH_2)_2$ / $(C_2H_5)_3N$

③ $LiAlH_4$



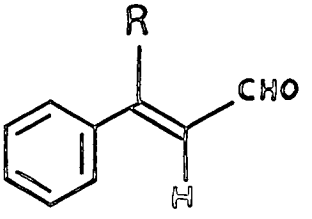
(240)



(244), R = H

(245), R = CH_3

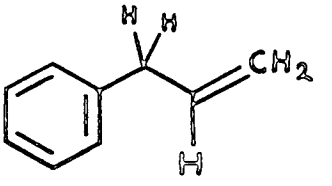
D.D.Q.



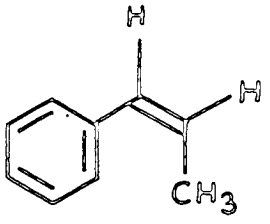
(247), R = H

(248), R = CH_3

D.D.Q.



(249)



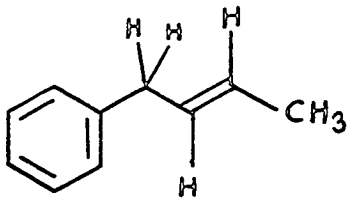
(246)

It appears that this aldehyde(240) is formed through the intermediacy of the fluorene(180) since when treated with D.D.Q. under similar conditions to the above this compound forms a similar ratio of products, heating causing complete conversion to the aldehyde(240) which was also obtained from 9-isopropylidene-fluorene(183) under somewhat milder conditions.

In view of the formation of the propionaldehyde(240) from D.D.Q. oxidation of both 9-isopropenylfluorene(180) and 9-isopropylidenefluorene(183) it seems likely that this process involves a common intermediate species. In order to test this hypothesis the oxidative sequence was applied to a series of aryl-olefins. Thus D.D.Q. oxidation of trans-(244) or cis-β-methylstyrene(246) both form trans-cinnamaldehyde(247), the identity of this compound being established by direct comparison with an authentic sample, some recovered olefin having the same geometrical configuration as the starting material in each case. The same product is obtained from the D.D.Q. oxidation of allyl-benzene(249). These observations are consistent with the intermediacy of a resonance stabilised carbonium ion;

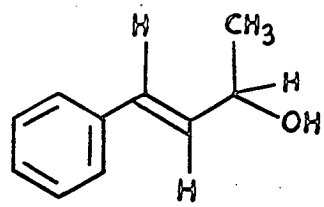
$$Ar\cdot CH=CH\cdot \overset{+}{C}H_2 \longleftrightarrow Ar\cdot \overset{+}{C}H\cdot CH=CH_2$$

which is formed by irreversible hydride ion transfer from the reacting olefin to the quinone. It was further established that whereas the trans-olefin(244) undergoes 90% oxidation in 4 hr., the cis-olefin(246) requires 30 hr. and a three fold excess of D.D.Q. over its trans-isomer to reach the same extent of reaction. This

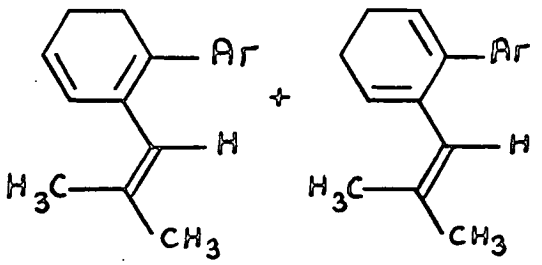


(250)

D.D.Q. →

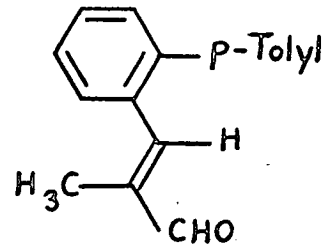


(251)



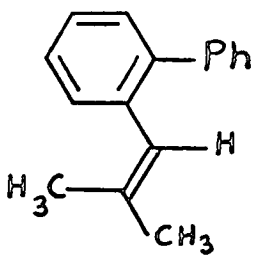
(198a,b), Ar = Ph
(189a,b), Ar = p-Tolyl

D.D.Q. (Ar = p-Tolyl) →



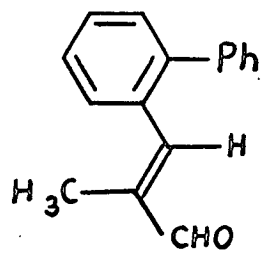
(252)

D.D.Q. (Ar = Ph) ↓

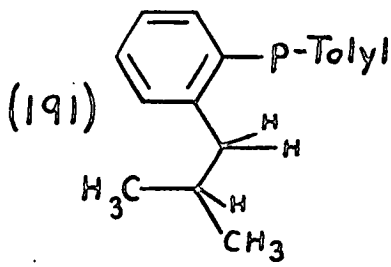


(200)

D.D.Q. (Force) →



(253)



(191)

D.D.Q. (Force) → (252)

much slower conversion rate of the cis-isomer probably results from the more hindered approach offered to the attacking quinone prior to hydride ion transfer and formation of the common carbonium ion. Further evidence in support of the proposed intermediate species was obtained from the reaction of D.D.Q. with α,β-dimethylstyrene(245) which only undergoes oxidation of the β-methyl group to form β-methyl-trans-cinnamaldehyde(248), and α-methylstyrene which failed to react, a planar resonance stabilised benzyl carbonium ion being inaccessible in this latter case. Indene also did not form an isolable carbonyl derivative although in this case and in the case of α-methylstyrene only 50% of the starting material was recovered which indicates that some destructive process does occur.

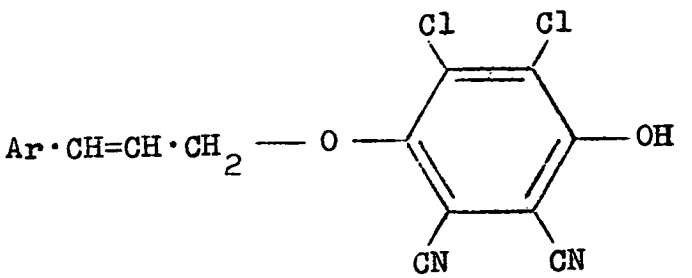
Oxidation of 4-phenyl-trans-but-2-ene(250) with D.D.Q. afforded 1-phenyl-trans-but-1-en-3-ol(251), J_{trans} = 16 Hz., some recovered olefin again having the same geometrical configuration as the starting material. Although this carbinol is reported[120] to form the corresponding ketone in the presence of D.D.Q., it seems likely in the present case that the available quinone would already have been consumed.

Further evidence in support of a carbonium ion intermediate was obtained from D.D.Q. oxidations involving substituted aryl-olefins. The dehydrogenation of the phenylcyclohexadiene isomers(198a,b) with D.D.Q. to form the biphenyl(200) has already been described (section 3.4), however D.D.Q. oxidation of the (p-tolyl)cyclohexadiene isomers(189a,b) leads directly to

α-methyl-2-(p-tolyl)cinnamaldehyde(252). Formation of this cinnamaldehyde presumably involves the intermediate (p-tolyl)-biphenyl derivative analogous to (200), however in this case the electron releasing inductive effect of the p-methyl substituent can stabilise the intermediate carbonium ion necessary for aldehyde formation and thus accelerate the oxidation. Prolonged treatment of the non alkyl substituted biphenyl derivative(200) with D.D.Q. did apparently form a small amount of the cinnamaldehyde(253), the n.m.r. spectrum of the product showing the aldehydic proton as a singlet at 0·70τ although the remainder of the spectrum was contaminated with impurity peaks. However the (p-tolyl)cinnamaldehyde(252) was readily isolated in a pure form and in good yield. The trans-configuration of this aldehyde seems likely by analogy with the preceding results and on consideration of the n.m.r. spectrum, the methyl group trans- to the olefinic proton being a doublet (J = 2 Hz.) centred at 8·03τ whereas the cis-aldehydic proton (0·64τ) is a sharp singlet. It is also noteworthy that the saturated side chain of the isobutylbiphenyl(191) undergoes slow oxidation with D.D.Q. to form the aforementioned aldehyde(252).

A quantitative attempt to measure the relative rates of this D.D.Q. oxidation, carried out by Dr. I.H. Sadler, showed that in a competitive reaction between trans-β-methylstyrene and 4-methoxy-trans-β-methylstyrene the reaction of the latter with D.D.Q. was virtually complete before any of the former was consumed and thus the 4-methoxy derivative must be at least 100 times more reactive than the parent hydrocarbon. This and the preceding

observations are consistent with the formation of an intermediate resonance stabilised carbonium ion, which could then react with the co-formed semiquinone carbanion to give a quinol ether:-



Related quinol ethers have previously[122] been isolated from reactions with D.D.Q. Hydrolytic cleavage of this system would give a carbinol or alternatively further hydride ion transfer and coupling could lead to an acetal which would decompose to give an aldehyde. No direct evidence was obtained for the existence of these quinol acetals, but it seems likely that they can undergo rapid hydrolysis during the work up, either on application to alumina or on preliminary elution over silica-gel, the hydroquinone and oxygenated compounds being the only products to be recognised.

6. EXPERIMENTAL SECTION

6.1 INTRODUCTION

Materials

Unless stated otherwise:- liquids and solutions were dried over anhydrous magnesium sulphate; melting points (m.p.) and boiling points (b.p.) are uncorrected unless stated otherwise; solvents were used without further purification; light petroleum refers to the fraction b.p. 30-40°; nitrogen used was the B.O.C. "oxygen free" grade; fractional distillation was performed using an electrically heated 50cm. helix packed column and a total reflux partial take off head.

Spectroscopy

Infrared spectra (i.r.) were recorded on a Unicam S.P.200 instrument; samples were examined as liquid films, Nujol mulls or solutions in carbon disulphide at room temperature.

Ultraviolet spectra (u.v.) were recorded on a Unicam S.P.800 instrument using 1cm. silica cells. Samples were examined at room temperature using ethanol (EtOH) as solvent. All weighings were carried out using a Cahn "Electrobalance".

Mass spectra (m.s.) were recorded on an A.E.I. M.S.902 double focusing instrument. Exact masses of parent peaks (P) were determined by the process of peak matching which is discussed elsewhere (section 6.12).

H^1 Nuclear magnetic resonance spectra (n.m.r.) were obtained using either a Perkin-Elmer R-10 spectrometer (60 MHz.) at 33° or a Varian H.A.100 spectrometer (100 MHz.) at 28°; samples were examined as solutions (5-10%) in carbon tetrachloride (CCl_4), deuterochloroform($CDCl_3$), carbon disulphide(CS_2) or trifluoroacetic acid(T.F.A.). Chemical shifts were measured relative to tetramethylsilane as internal reference, designated at 10τ. Abbreviations used are singlet(s), doublet(d), triplet(t), quartet(q) or multiplet(m).

Chromatography

Analytical vapour phase chromatography (v.p.c.) was performed on a Griffin D-6 instrument, fitted with a gas density balance detector, using a 2 metre column packed with silanised acid washed Chromosorb P (80-100 mesh) coated with 5%(w/w) Neopentyl glycol succinate. Nitrogen was used as carrier gas with an inlet pressure of 15 p.p.s.i. Peak areas were measured on a Kent "Chromolog" electronic integrator.

Preparative v.p.c. was carried out on either:

(a) A Wilkens "Autoprep" (hot wire detector) using 6' or 20' columns packed with 10% or 30% silicone oil (S.E.30) on celite respectively, with helium as carrier gas (30 p.p.s.i.).

(b) A Pye series 105 (flame ionisation detector) using a 14' column packed with 10% Apiezon L grease (A.P.L.) on Chromosorb P, with nitrogen as carrier gas (40 p.p.s.i.).

Column temperatures are quoted in the relevant section, retention times only being quoted for preparative runs.

Thin layer chromatography (t.l.c.) was carried out over Merck silicagel G.F_{254}. The fluorescent nature of this material allowed the plates to be examined directly under an ultraviolet lamp. Analytical and preparative plates had silica films 20 x 10 x 0·01 cm. and 20 x 20 x 0·1 cm. respectively. These were oven dried at 100° for 12 hr. before use. The loading for preparative plates was 50-100 mg.

Column chromatography was carried out on Hopkin and Williams silicagel or Spence type-H alumina.

Analyses were determined on a Perkin-Elmer 240 elemental analyser.

6.2 PREPARATION OF STARTING MATERIALS

6.2.1 Potassium t-butoxide

Potassium (78g., 2 mol.) was added cautiously to anhydrous t-butyl alcohol (1·2 litre), under nitrogen, and refluxed for 15 hr. The excess of t-butyl alcohol was removed under reduced pressure (15 mm.) at 100°. The residual white solid (63% potassium t-butoxide by titration) was the 1:1 complex ($Me_3 \cdot COK$-$Me_3 \cdot COH$). This material was found to be satisfactory for the present work. All subsequent mention of potassium t-butoxide refers to the 1:1 complex.

6.2.2 Dimethylethyncarbinol

This was prepared by a method based upon that of Froning and Hennion.[123] Sodium acetylide was prepared in liquid ammonia as follows. A 3-litre 3-necked flask fitted with a mechanical stirrer and a gas inlet tube and charged with liquid ammonia (1·5 litre) was saturated with acetylene (washed by passing through concentrated sulphuric acid) for 10 min. A previously prepared solution of sodium (92g., 4 mol.) dissolved in liquid ammonia (1 litre) was then cautiously added to the reaction vessel, maintaining a vigorous flow of acetylene, the rate of addition being regulated so that the reaction mixture never became completely blue (1 hr.). The pale grey suspension was then stirred for a further 15 min.

Acetone (232·5g., 4 mol.) was then added (0·5 hr.) to the stirred reaction mixture, maintaining the flow of acetylene, after which the gas flow was stopped and the ammonia allowed to evaporate overnight. The residue was taken up in ether (500 ml.) and extracted with 35% sulphuric acid (500 ml.). The organic layer was dried over anhydrous potassium carbonate and magnesium sulphate and fractionated. The material of b.p. 60-102° was refractionated to give dimethylethyncarbinol (b.p. 102-3°, lit.[123] 102·4°; 261g., 78%) as a colourless liquid.

6.2.3. 3-Chloro-3-methylbut-1-yne

This was prepared by a method essentially that of Boisselle and Hennion.[124] A 1-litre 3-necked flask equipped with mechanical stirrer, thermometer and dropping funnel was charged with cuprous

chloride (40g.) calcium chloride (56g.), copper-bronze powder (0·5g.), and concentrated hydrochloric acid (430 ml.) and cooled to 0-5°. Dimethylethyncarbinol (84g., 1 mol.) was then added during 0·5 hr. with vigorous stirring and the reaction mixture stirred at 0-5° for a further hour. The organic material was taken up in light petroleum (250 ml.) and immediately washed with cold concentrated hydrochloric acid (2 x 100 ml.), followed by water (3 x 100 ml.). The organic layer was dried over anhydrous potassium carbonate and magnesium sulphate and fractionally distilled from a small amount (0·5g.) of anhydrous potassium carbonate, to give 3-chloro-3-methylbut-1-yne (b.p. 76-77°, lit.[124] b.p. 76-7°; 27g., 26%) as a colourless liquid, pure by v.p.c., which darkened on standing.

Further distillation of the residue afforded only dark coloured fractions of variable b.p. (78-100°). These were shown (v.p.c., i.r., n.m.r.) to contain the desired product together with increasing amounts of 1-chloro-3-methylbuta-1,2-diene together with several minor components. Redistillation of these fractions gave only dark coloured material.

6.2.4 1-Bromo-3-methylbuta-1,2-diene

This was prepared by the method of Landor et al.[125] A 1-litre 3-necked flask equipped with stirrer, condenser, dropping funnel and charged with cuprous bromide (59·5g.), ammonium bromide (47·5g.), copper-bronze powder (3g.) and hydrobromic acid (46-48% w/v, 285 ml.) was allowed to equilibriate to 30° on a water bath. Dimethylethyncarbinol (100g., 1·25 mol.) was

then added over 5 minutes to the stirred mixture and stirring continued for 1·5 hr. maintaining the temperature around 30°. The mixture was filtered and the filtrate extracted with light petroleum (3 x 100 ml.). The combined extracts were washed with four or five aliquots (100 ml.) of hydrobromic acid until these showed no violet coloration. The organic layer was dried over anhydrous potassium carbonate and magnesium sulphate and the solvent carefully removed under reduced pressure (100 mm.). Fractionation of the residual liquid gave 1-bromo-3-methylbuta-1,2-diene (b.p. 70-1°/100 mm., lit.[125] 53-4°/60 mm.; 127g., 72·5%) as a colourless liquid, pure by v.p.c., which darkened on standing. The halide was stored under nitrogen at -15°.

In later preparations it was found unnecessary to fractionate the product and the yields were consistently high (90-95%) over several preparations.

6.2.5 Methylenecyclobutane and Cyclobutanone

Methylenecyclobutane was prepared essentially as described by Conia et al.[126] A mixture of pentaerythritol (136g., 1 mol.), hydrobromic acid (56-58% w/v, 400g.) and glacial acetic acid (120g.) were refluxed for 15 hr. The solvents were distilled off at atmospheric pressure (b.p. 100-125°, 600 ml.) and the residue distilled under reduced pressure to give tribromopentaerythritol (b.p. 107-17°/0·01 mm., lit.[126] 170-80°/12 mm.; 290g., 93%) as a clear viscous liquid. To the stirred tribromopentaerythritol(290g.), heated to 180° in an oil bath, was added (1·5 hr.) dropwise phosphorus tribromide (120g.). The dark reaction mixture was

then stirred at 180° for a further 12 hr., cooled and extracted with chloroform (600 ml.), the extract was treated with decolorising charcoal, washed with water (2 x 100 ml.) and dried. Evaporation of the solvent gave crude tetrabromopentaerythritol (m.p. 145°, lit.[126] 155°; 265g., 76·5%) which was used without further purification.

A 3-litre 3-necked flask was equipped with a 50 cm. helix-packed fractionating column (fitted with a take-off head), mechanical stirrer and dropping funnel. The collection vessel was cooled in a dry ice:acetone bath. The reaction vessel was charged with tetrabromopentaerythritol (260g.) and water (350 ml.), the stirrer started and powdered zinc (262g.) added. The reaction mixture was warmed to around 85° and a solution of concentrated hydrochloric acid (2 ml.) in ethanol (50 ml.) added to activate the zinc. The product started to distil and was collected over 1·5 hr. during which ethanol (200 ml.) was gradually added to the reaction vessel. Collection of the product was terminated when the stillhead temperature reached 70°. The crude product was fractionated and methylenecyclobutane (b.p. 44-5°, lit.[126] 44-5°; 10g., 21·5%) collected as a colourless liquid.

Cyclobutanone was prepared by the ozonolysis of methylenecyclobutane. A solution of methylenecyclobutane (10g., 0·15 mol.) in methylene chloride (100 ml.) and redistilled pyridine (10g.) was cooled to -80° in a dry ice bath. Ozone was then bubbled through the stirred reaction mixture for 3 hr. followed by oxygen for 1 hr. The reaction mixture was allowed to warm

to room temperature and left to stand overnight. The organic material was decanted from some dark residue and stirred vigorously with concentrated hydrochloric acid (16 ml.) for 2 hr. The organic layer was dried and fractionated to yield cyclobutanone (b.p. 98-101°, lit.[126] 97-100°; 6g., 60%) as a colourless liquid which was pure by v.p.c.

6.3 PREPARATION OF THE OLEFINS

The structures of the olefins were confirmed by their i.r. and n.m.r. spectra and were pure by v.p.c. unless stated otherwise. They were stored under nitrogen at -15°. The following olefins were redistilled:-

α-methylstyrene (b.p. 57°/13 mm., lit.[127] 55°/14 mm.), 1,1-diphenylethylene (b.p. 130°/12 mm., lit.[127] 136°/13 mm.), indene (b.p. 69°/15 mm., lit.[128] 66°/12 mm.).

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

α-methoxystyrene (b.p. 98-100°/25 mm., lit.[128] 191-3°/745 mm.), 4,α-dimethylstyrene (b.p. 69°/10 mm., lit.[129] 76-8°/19 mm.), cis-stilbene (b.p. 70°/0·01 mm., lit.[127] 97°/1 mm.), 4-methyl-1,2-dihydronaphthalene (b.p. 116-8°/20 mm., lit.[128] 111·5-112·5°/18 mm.).

Trans-β-methylstyrene was prepared by the Grignard reaction. Benzaldehyde (53g., 0·5 mol.) in sodium dried ether (100 ml.) was added over 0·5 hr. to a cooled (10°) ethereal solution

of ethyl magnesium bromide, under nitrogen. The reaction mixture was then refluxed on a water bath for 0·5 hr. and allowed to stand overnight. The reaction mixture was hydrolysed with saturated ammonium chloride solution and the crude product taken up in ether. The combined extracts were dried and the solvent removed under reduced pressure. The crude carbinol was dehydrated by distillation under reduced pressure from a small amount (ca. 0·1g.) of p-toluenesulphonic acid monohydrate, in the presence of glass wool. Redistillation of the crude olefin thus obtained gave trans-β-methylstyrene (b.p. 76°/18mm., lit.[127] 74°/15 mm.; 41g., 70%). V.p.c. at 100° showed the trans-olefin to contain 5% of the cis-isomer.

Trans-β-isopropylstyrene (b.p. 82-3°/9 mm., lit.[127] 201-3°; 68%) was similarly prepared from isobutyl magnesium bromide and benzaldehyde.

1-Phenylcyclopentene (b.p. 119-20°/20 mm., lit.[128] 124·5°-125·5°/30 mm.; 65%),
1-phenylcyclohexene (b.p. 108°/8 mm., lit.[127] 125°/14 mm.; 70%),
1-(p-tolyl)cyclopentene (b.p. 130-2°/20 mm., lit.[130] 130-3°/21 mm.; 62%),
1-(p-tolyl)cyclohexene (b.p. 129-30°/10 mm., lit.[131] 126°/9 mm.; 68%), and
1-(o-tolyl)cyclopentene (b.p. 110-12°/25 mm., lit.[132] 116-17°/30 mm.; 66%) were prepared from the corresponding aryl magnesium bromides and cyclopentanone or cyclohexanone as appropriate.

3-Methylindene (b.p. 75-6°/8 mm., lit.[128] 81°/13 mm.; 65%) and

3-methyl-1,2-dihydronaphthalene (b.p. 110-12°/20 mm., lit.[133] 115-18°/22 mm.; 72%) were similarly prepared from methyl magnesium bromide and the corresponding ketone.

1-Phenylcyclobutene was prepared by the dropwise addition over 15 min. of a solution of cyclobutanone (6g., 0·09 mol.) to a cooled (10°) ethereal solution (100 ml.) of phenyl lithium, previously prepared from lithium (1·4g., 0·2 mol.) and bromobenzene (15·7g., 0·1 mol.) under nitrogen. The reaction mixture was allowed to stand at room temperature overnight, then hydrolysed over saturated ammonium chloride solution. The product was extracted into ether (3 x 100 ml.), dried and the solvent evaporated. The crude carbinol was dehydrated by vacuum distillation from p-toluenesulphonic acid (0·05g.) in the presence of glass wool. The crude product was redistilled to give 1-phenylcyclobutene (b.p. 74-6°/4 mm., lit.[134] 74-5°/3·5 mm.; 4·0g., 36%) as a colourless liquid of 90% purity (v.p.c., 100°).

1,2-Dihydronaphthalene (b.p. 80-1°/10 mm., lit.[127] 84-5°/12 mm., 82%) was prepared by reduction of α-tetralone (0·5 mol.) with lithium aluminium hydride (0·25 mol.) in sodium dried ether (250 ml.). The carbinol thus obtained was dehydrated as described above.

1-Methyleneindane (b.p. 87°/15 mm., lit.[135] 38-9°/0·85 mm.; 70%) and
1-methylenetetralin (b.p. 105°/15 mm., lit.[136] 103°/14 mm.; 78%) were prepared by a modified Wittig reaction, as described by Sadler.[92]

cis-β-Methylstyrene was prepared by a sequence of reactions described below. 1-Phenylpropyne was first prepared essentially as described by Campbell and O'Connor.[137] Bromine (320g., 2 mol.) was added dropwise over an hour to a cooled (10°) solution of styrene (208g., 2 mol.) in carbon tetrachloride (250 ml.). The pale orange solution was stirred for a further 0·5 hr. while warming to room temperature. The solvent was then removed under reduced pressure yielding styrene dibromide as a pale yellow solid which was used without further purification.

Sodamide was prepared in liquid ammonia from sodium (92g., 4 mol.) as follows. To a stirred solution of ferric nitrate (1·2g.) in liquid ammonia (2 litre) was added sodium (1g.) and the reaction mixture stirred for 5 min. The remainder of the sodium was then rapidly added in small pieces over 1 hr. to the vigorously stirred reaction mixture. Powdered styrene dibromide (2 mol.) was then added to the sodamide as rapidly as the reaction permitted, maintaining vigorous stirring. After 2 hr., stirring was stopped and the reaction vessel allowed to stand overnight. The residue was taken up in water and ether (500 ml.) and the dark organic extract washed with 15% hydrochloric acid (2 x 200 ml.), dilute sodium carbonate solution (2 x 150 ml.) and water (100 ml.). The organic layer was dried and the solvent removed under reduced pressure (200 mm.). Fractionation of the residual material gave phenylacetylene (b.p. 75°/90 mm., lit.[137] 75°/90 mm.; 124g., 61%) as a colourless liquid.

Phenylacetylene (102g., 1 mol.) was rapidly added with vigorous stirring to sodamide in liquid ammonia (1·5 litre) prepared

from sodium (27·6g., 1·2 mol.) as detailed above. After stirring for 1·5 hr. dimethyl sulphate (189g., 1·5 mol.) was added dropwise (0·5 hr.) and the reaction mixture stirred for a final 2 hr. The reaction mixture was allowed to stand overnight and worked up as detailed above. Fractional distillation of the crude product gave 1-phenylpropyne (b.p. 75°/13 mm., lit.[137] 76°/15 mm.; 77g., 67·5%) as a pure (v.p.c.) colourless liquid.

A solution of 1-phenylpropyne (23·2g., 0·2 mol.) in cyclohexane (50 ml.) was hydrogenated over freshly prepared[138] Lindlar catalyst (1·5g.), partially poisoned with freshly distilled "synthetic" quinoline (3 ml.) as described by Foltz and Witkop.[139] The product was fractionated to give cis-β-methylstyrene (b.p. 62-62·5°/15 mm., lit.[139] 69-69·5°/28 mm.; 18·5g., 78·5%) as a colourless liquid. V.p.c. at 100° showed this to contain small quantities of the trans-isomer (3%) and n-propylbenzene (2%).

α-Bromostyrene was prepared by the dehydrobromination of styrene dibromide essentially as described by Taylor.[140] To a well stirred solution of styrene dibromide (65·5g., 0·25 mol.) in ethanol (300 ml.) was rapidly added 2N ethanolic potassium hydroxide (260 ml.). When the reaction had moderated, a temperature of around 55° was maintained for a further 0·5 hr. by external heating. During this period potassium bromide separated as a fine white solid. The reaction mixture was poured onto water (1 litre) and the product taken up in light petroleum (2 x 250 ml.). The combined extracts were washed with water (100 ml.) and dried. Most of the solvent was removed under reduced pressure and the residue fractionated.

The fraction boiling at 79-84°/7 mm. (27g.) was refractionated to give α-bromostyrene (b.p. 103-6°/24 mm., lit.[140] 81-6°/9 mm.; 25g., 57%) as a colourless liquid, 90% pure by v.p.c. Repeated fractionation did not raise the purity.

6.4 PREPARATION OF THE DIMETHYLVINYLIDENECYCLOPROPANES.

6.4.1 General Method

As a result of the preliminary experiments outlined in section 6.4.2, the following general method was used for the preparation of the dimethylvinylidenecyclopropanes. A magnetically stirred slurry of potassium t-butoxide (9·3g., 0·05 mol.), the olefin (0·02 mol.) and sodium dried light petroleum (15 ml.) was cooled to 0-1° in an ice bath under an atmosphere of nitrogen (essential). To the vigorously stirred slurry a solution of 1-bromo-3-methylbuta-1,2-diene (5·9g., 0·04 mol.) in sodium dried light petroleum (10 ml.) was added dropwise over 0·5 hr. The coloured reaction mixture was stirred for a further 1 hr., while warming to room temperature. Saturated sodium chloride solution (20 ml.) was then added and the pH. adjusted to ca. 5 with 10% aqueous hydrochloric acid. Vigorous stirring gave two clear layers. The red organic layer was separated, washed with water (20 ml.) and dried over anhydrous potassium carbonate and magnesium sulphate. Evaporation of the solvent followed by careful fractionation of the residue under reduced pressure yielded the dimethylvinylidenecyclopropane usually as a pale yellow liquid which appeared as a single

peak on v.p.c. Repeated fractionation of the distillate did not give a colourless product.

6.4.2 Results of Preliminary Experiments

Duplicate experiments were carried out with α-methylstyrene (0·02 mol.) and either 3-chloro-3-methylbut-1-yne(A) or 1-bromo-3-methylbuta-1,2-diene(B) as carbene precursor (0·04 mol.).

Experiment	Carbene Generator	Solvent	Yield
1	A	ether	40%
2	A	light petroleum	50%
3	B	light petroleum	70%

6.4.3 Characterisation of the Adducts

The molecular formulae of the adducts were confirmed by exact mass measurement (section 6.12) of the parent ion (P^+) in the mass spectrum, in many cases significant (P + 16) and (P + 32) peaks were also apparent indicating ready uptake of oxygen. In accordance with this it was usually not possible to obtain accurate elemental analyses. Structures were confirmed by i.r. and n.m.r. spectra, as expected none showed u.v. absorption maxima above 210mμ. The adducts were reasonably stable at -15°, samples stored in this manner had not deteriorated significantly during 6 months.

Details of individual adducts are summarised below. The parent olefin is given in parenthesis after each adduct.

The following adducts were stable to low pressure distillation. The yields are quoted as a range for several runs in each case:-

2-Dimethylvinylidene-1-methyl-1-phenylcyclopropane(137).

(source: α-methylstyrene).

b.p. 68-68·5°/0·4 mm. Yield: 65-70%

n.m.r. (CCl_4)τ: 2·91(m) aromatic (5H); 8·22(s) dimethyl (6H); 8·37(s) cyclopropyl (2H); 8·42(s) benzylic methyl (3H).

i.r.(film) $cm.^{-1}$: 2010(s) allene; 760(s), 700(s) monosubstitution.

(P)m/e: Found, 184·12517; calcd. for $C_{14}H_{16}$, 184·12519.

trans-1-Dimethylvinylidene-2-methyl-3-phenylcyclopropane(153).

(source: trans-β-methylstyrene).

b.p. 73-5°/0·3 mm. Yield: 50-55%

n.m.r. (CCl_4)τ: 2·91(m) aromatic (5H); 7·78 (d, 4·2 Hz.) benzylic (1H); 8·2 (m, obscure) cyclopropyl (1H); 8·22(s) dimethyl (6H); 8·63 (d, 5·1 Hz.) methyl (3H).

i.r.(film)$cm.^{-1}$: 2010(s) allene; 750(s), 700(s) monosubstitution.

(P)m/e: Found, 184·12553; calcd. for $C_{14}H_{16}$, 184·12519.

cis-1-Dimethylvinylidene-2-methyl-2-phenylcyclopropane(154).

(source: cis-β-methylstyrene).

b.p. 71-3°/0·3 mm. Yield: 45-50%

n.m.r. (CCl_4)τ: 2·89(m) aromatic (5H); 7·00 (d, 8·7 Hz.) benzylic (1H); 7·9(m, obscure) cyclopropyl (1H); 8·13(s), 8·22(s) dimethyl (3H,3H); 9·10 (d, 6·8Hz.) methyl (3H).

i.r.(film)cm.$^{-1}$: 2010(s) allene; 780(s), 740(s), 700(s) monosubstitution.

(P)m/e: Found, 184·12527; calcd. for $C_{14}H_{16}$, 184·12519.

trans-1-Dimethylvinylidene-2-isopropyl-3-phenylcyclopropane(157)

(source: trans-β-isopropylstyrene)

b.p. 67-8°/0·05 mm. Yield: 55-60%

n.m.r. (CCl_4)τ: 2·73(m) aromatic (5H); 7·50 (d, 4Hz.) benzylic (1H); 8·0-8·6(m, obscure) cyclopropyl and isopropyl (2H); 8·23(s) dimethyl (6H); 9·02 (d, 5 Hz.) isopropyl methyls (6H).

i.r. (film) cm.$^{-1}$: 2010(m) allene; 750(s), 700(s) monosubstitution.

(P) m/e: Found, 212·15682; calcd. for $C_{16}H_{20}$, 212·15649.

2-Dimethylvinylidene-1-methoxy-1-phenylcyclopropane(139).

(source: α-methoxystyrene).

b.p. 65-7°/0·05 mm. Yield: 45-50%

n.m.r. (CCl_4)τ: 2·72(m) aromatic (5H); 6·75(s) methoxy (3H); 7·88 (d, 8 Hz.), 8·34(d, 8 Hz.) cyclopropyl (1H,1H); 8·18(s) dimethyl (6H).

i.r. (film) cm.$^{-1}$: 2020(s) allene; 770(s), 730(m), 700(s) monosubstitution.

(P) m/e: Found, 200·11926; calcd. for $C_{14}H_{16}O$, 200·12011.

2-Dimethylvinylidene-1-bromo-1-phenylcyclopropane(141).

(source: α-bromostyrene).

b.p. 79-80°/0·01 mm. Yield: 30-35%

n.m.r. (CCl_4)τ: 2·70(m) aromatic 95H); 7·62(d, 8 Hz.), 7·92(d, 8 Hz.) cyclopropyl (1H,1H); 8·11(s), 8·15(s)

dimethyl (3H,3H).

i.r. (film) $cm.^{-1}$: 2020(s) allene; 760(s), 700(s) monosubstitution.

(P) m/e: Found, 248·02028, 250·02811; calcd. for $C_{13}H_{13}{}^{79}Br$, 248·02011, ^{81}Br, 250·02814.

2-Dimethylvinylidene-1-methyl-1-(p-tolyl)cyclopropane(144).

(source: 4,α-dimethylstyrene).

b.p. 71-2°/0·05 mm. Yield: 65-70%

n.m.r. (CCl_4)τ: 2·96(m) aromatic (4H); 7·75(s) aryl methyl (3H); 8·24(s) dimethyl (6H); 8·4-8·5(m, obscure) methyl and cyclopropyl (5H).

i.r. (film) $cm.^{-1}$: 2020(s) allene; 830(s) 1,4-disubstitution.

(P) m/e: Found, 198·13986; calcd. for $C_{15}H_{18}$, 198·14084.

2'-Dimethylvinylidenecyclopropane 1'-spiro-1-indane(146).

(source: methyleneindane).

b.p. 74-5°/0·01 mm. Yield 40-45%

n.m.r.(CCl_4)τ: 3·00(m), 3·22(m) aromatic (3H,1H); 7·00(t, 7Hz.) benzylic methylene (2H); 7·69(m) methylene (2H); 8·30(s) dimethyl (6H); 8·3 (obscure) cyclopropyl (2H).

i.r.(film)$cm.^{-1}$: 2020(m) allene; 760(s) 1,2-disubstitution.

(P)m/e: Found, 196·12447; calcd. for $C_{15}H_{16}$, 196·12519.

2'-Dimethylvinylidenecyclopropane-1'-spiro-1-tetralin(148).

(source: methylenetetralin).

b.p. 78-9°/0·01 mm. Yield: 45-50%

n.m.r.(CCl_4)τ: 3·11(m) aromatic (4H); 7·19(t, 4·5 Hz.) benzylic methylene (2H); 8·1(m, obscure) methylenes (4H); 8·24(s) dimethyl (6H); 8·39(s) cyclopropyl (2H).

i.r.(film)cm.$^{-1}$: 2020(s) allene; 760(s), 730(s) 1,2-disubstitution.

(P)m/e: Found, 210·14071; calcd. for $C_{16}H_{18}$, 210·14084.

6-Dimethylvinylidene-1-phenylbicyclo[3,1,0]hexane(174).

(source: phenylcyclopentene).

b.p. 72-3°/0·01 mm. Yield: 35-40%

n.m.r.(CCl_4)τ: 2·88(m) aromatic (5H); 7·8-8·2(m) methylenes (6H); 8·30(s) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 2020(m) allene; 760(s), 700(s) monosubstitution.

(P)m/e: Found, 210·14029; calcd. for $C_{16}H_{18}$, 210·14084.

7-Dimethylvinylidene-1-phenylbicyclo[4,1,0]heptane(177).

(source: phenylcyclohexene).

b.p. 76-8°/0·01 mm. Yield 40-45%

n.m.r.(CCl_4)τ: 2·82(m) aromatic (5H); 7·8-8·7(m) methylenes (8H); 8·21(s) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 2010(m) allene; 750(s), 700(s) monosubstitution.

(P)m/e: Found, 224·15715; calcd. for $C_{17}H_{20}$, 224·15649.

6-Dimethylvinylidene-1-(o-tolyl)bicylo[3,1,0]hexane(196).

(source: o-tolylcyclopentene)

b.p. 85-6°/0·01 mm. Yield 35-40%

n.m.r.(CCl_4)τ: 2·85(m), 3·04(m) aromatic (1H,3H); 7·69(s) aryl methyl (3H); 7·7-8·2(m) methylenes (6H); 8·24(s), 8·31(s) dimethyl (3H,3H).

i.r.(film)cm.$^{-1}$: 2010(s) allene; 760(s), 730(s) 1,2-disubstitution.

(P)m/e: Found, 224·15631; calcd. for $C_{17}H_{20}$, 224·15649.

2,3-Benzo-6-dimethylvinylidenebicyclo[3,1,0]hex-2-ene(206).

(source: indene).

b.p. 75-6°/0·01 mm. Yield: 35-40%

m.p. 74·5-75° (light petroleum) Yield 30%

n.m.r.(CCl_4)τ: 2·80(m), 2·95(m) aromatic (1H,3H); 6·5-7·0(m) benzylic (3H); 7·3-7·5(m) cyclopropyl (1H); 8·28(s), 8·42(s) dimethyl (3H,3H).

i.r.(nujol)cm.$^{-1}$: 2010(s) allene; 760(s), 720(s) 1,2-disubstitution.

(P) m/e: Found, 182·10946; calcd. for $C_{14}H_{14}$, 182·10954.

Analysis: Found, C, 91·99; H, 7·40; calcd., C, 92·26; H, 7·74%.

2,3-Benzo-7-dimethylvinylidenebicyclo[4,1,0]hept-2-ene(222).

(source: 1,2-dihydronaphthalene).

b.p. 88-90°/0·01 mm. Yield: 40-45%

n.m.r.(CCl_4)τ: 3·00(m) aromatic (4H); 7·1-8·1(m) benzylic, methylenes and cyclopropyl (6H); 8·29(s), 8·38(s) dimethyl (3H,3H).

i.r.(film)cm.$^{-1}$: 2010(s) allene; 750(s) 1,2-disubstitution.

(P)m/e: Found, 196·12500; calcd. for $C_{15}H_{16}$, 196·12519.

2,3-Benzo-6-dimethylvinylidene-1-methylbicyclo[3,1,0]hex-2-ene(208).

(source: 3-methylindene)

b.p. 76-7°/0·01 mm. Yield: 40-45%

m.p. 70-70·5° (light petroleum) Yield: 35%

n.m.r.(CCl_4)τ: 2·90(m), 3·00(m) aromatic (1H,3H); 6·6-7·1(m)

benzylic (2H); 7·69(m) cyclopropyl (1H);
8·30(s), 8·37(s), 8·46(s) methyls (3H,3H,3H).

i.r.(nujol)cm.$^{-1}$: 2010(s) allene; 760(s), 720(s) 1,2-disubstitution.

(P)m/e: Found, 196·12454; calcd. for $C_{15}H_{16}$, 196·12519.

Analysis: Found, C, 91·46; H, 8·03; calcd., C, 91·78; H, 8·22%.

2,3-Benzo-7-dimethylvinylidene-1-methylbicyclo[4,1,0]hept-2-ene(214).

(source: 4-methyl-1,2-dihydronaphthalene).

b.p. 74-5°/0·01 mm. Yield: 40-45%

n.m.r.(CCl_4)τ: 2·80(m), 3·04(m) aromatic (1H,3H); 7·41(m) benzylic (2H); 7·91(m) methylene (2H); 8·2(m, obscure) cyclopropyl (1H); 8·29(s), 8·36(s), 8·40(s) methyls (3H,3H,3H).

i.r.(film)cm.$^{-1}$: 2020(s) allene; 750(s) 1,2-disubstitution.

(P)m/e: Found, 210·14147; calcd. for $C_{16}H_{18}$, 210·14084.

2,3-Benzo-7-dimethylvinylidene-6-methylbicyclo[4,1,0]hept-2-ene(223).

(source: 3-methyl-1,2-dihydronaphthalene).

b.p. 80-1°/0·01 mm. Yield: 40-45%

n.m.r.(CCl_4)τ: 3·02(m) aromatic (4H); 7·50(m) benzylic (2H); 8·0-8·5(m) methylene and cyclopropyl (3H); 8·30(s), 8·40(s), 8·58(s) methyls (3H,3H,3H).

i.r.(film)cm.$^{-1}$: 2010(s) allene; 750(s) 1,2-disubstitution.

(P)m/e: Found, 210·14060; calcd. for $C_{16}H_{18}$, 210·14084.

The following adducts underwent partial rearrangement on distillation. Details are given elsewhere (section 6.5). The i.r spectra of the partial rearrangement products showed $\nu_{max.}$ (m-w) at 2010-2020 cm.$^{-1}$ (allene) due to unrearranged adduct. The τ-values of the characteristic allenic dimethyl protons are quoted below:-

2-Dimethylvinylidene-1,1-diphenylcyclopropane(142).

(source: 1,1-diphenylethylene).

n.m.r.(CCl_4)τ: 8·23(s) dimethyl.

6-Dimethylvinylidene-1-(p-tolyl)bicyclo[3,1,0]hexane(188).

(source: p-tolylcyclopentene).

n.m.r.(CCl_4)τ: 8·31(s) dimethyl.

7-Dimethylvinylidene-1-(p-tolyl)bicyclo[4,1,0]heptane(192).

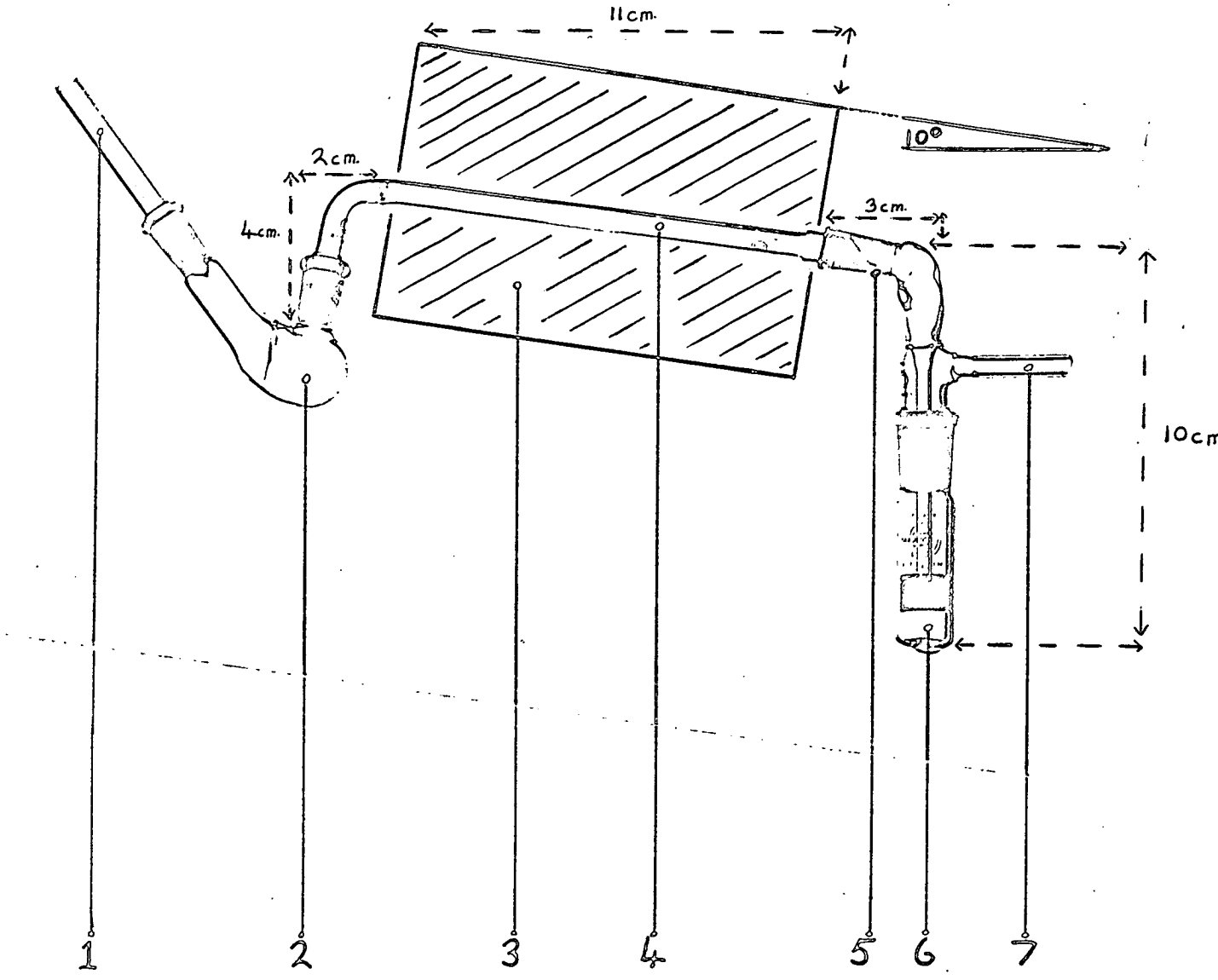
(source: p-tolylcyclohexene).

n.m.r.(CCl_4)τ: 8·22(s) dimethyl.

Distillation of the crude reaction product from the adduct preparation with 1-phenylcyclobutene gave a small amount of dark viscous material which did not contain the desired 5-dimethylvinylidene-1-phenylbicyclo[2,1,0]pentane(195). This is discussed elsewhere (section 6.5.11).

Attempted adduct formation with cis-stilbene, 9-isopropylidenefluorene and 1-phenylpropyne was unsuccessful. Chromatography of the reaction mixture on alumina led to a quantitative recovery of starting material (i.r., n.m.r.).

FIGURE XV



FLOW SYSTEM

6.5 REARRANGEMENT OF THE DIMETHYLVINYLIDECYCLOPROPANES.

6.5.1 General Procedures for Rearrangements

Thermal rearrangement in solution: Unless stated otherwise, the adduct was sealed in a pyrex tube under nitrogen with a tenfold dilution of suitable solvent and heated under the specified conditions in a constant temperature bath. Removal of the solvent under reduced pressure gave the crude product. Prolonged heating of neat adduct invariably gave low yields of product due to polymerisation.

Thermal rearrangement in the gas phase: The flow system which was employed is illustrated in figure XV. The compound to be pyrolysed was introduced onto glass wool in the 5 ml. distilling flask(2). Reduced pressure was applied at (7) by means of a rotary oil pump and nitrogen allowed to leak into the system at (1). The furnace (3), pre-calibrated and controlled by a variable autotransformer, was allowed to equilibriate at the desired temperature. The sample was then slowly distilled, from an oil bath, through the pyrolysis tube(4) which was packed loosely with glass wool. The crude product condensed on the cool area(5) and was collected in the vessel(6).

Acid catalysed rearrangement: A solution of 10% ethanolic hydrochloric acid was prepared by twofold dilution of concentrated hydrochloric acid with ethanol. The adduct and 10% ethanolic hydrochloric acid (50 ml. per 1 g. of adduct) were refluxed for 5 min.

whereupon the reaction mixture became dark in colour. The hot mixture was poured onto water (x 2 dilution) and extracted with light petroleum. The combined clear red extracts were washed with water and dried over anhydrous potassium carbonate and magnesium sulphate. Removal of the solvent under reduced pressure gave the crude product.

Isolation of products: Crude rearrangement products were examined by i.r., u.v., n.m.r., and by v.p.c. and/or t.l.c. as appropriate before being separated into their various components. The molecular formulae of the rearrangement products were confirmed by measurement of the exact mass of the parent peak in the mass spectrum. Elemental analyses were determined only where the compound was sufficiently stable and oxygen insensitive. Unstable products were stored at -15°.

6.5.2 Rearrangements of the α-methylstyrene adduct(137).

Thermal rearrangement.

(a) 2-Dimethylvinylidene-1-methyl-1-phenylcyclopropane(0·40g.) in xylene solution was heated in a refluxing xylene bath at 140° for 3 hr. 2-Isopropylidene-1-methyl-1-phenyl-3-methylenecyclopropane(138) was isolated as a pale yellow liquid by distillation (b.p. 58-9°/ 0·4 mm.; 0·27g., 67·5%):

n.m.r.(CCl_4)τ: 2·86(m) aromatic (5H); 4·72(s), 4·85(s) olefinic (1H,1H); 8·08(s), 8·14(s) dimethyl (3H,3H); 8·44(s) methyl (3H).

i.r.(film)cm.$^{-1}$: 1780(m), 1600(m) C=C; 870(s) $=CH_2$; 740(s), 700(s) monosubstitution.

u.v.(EtOH)mμ: 246·0 (ε = 18,600).

(P)m/e: Found, 184·12527; calcd. for $C_{14}H_{16}$, 184·12519.

(b) The adduct (0·25g.) was passed through the flow system at 350°/0·25 mm. The crude product was redistilled to give the dimethylenecyclopropane(138), (b.p. 58-9°/0·4 mm.; 0·22g., 90%) which was pure by v.p.c. (100°).

Acid catalysed rearrangement.

The crude acid catalysed rearrangement product from the adduct(2·5g.) was distilled to give a pale yellow liquid (b.p. 50-5°/0·01 mm.; 2·0g., 80%). Examination by v.p.c. (110°) showed this to contain 50% of 1,1,3-trimethyl-4-phenylcyclopenta-2,4-diene(160) together with several unresolved components (50% of total). Attempts to resolve the components on several columns (5%, 10% N.P.G.S., 15% P.P.E.) were unsuccessful. A sample (0·06g.) was applied to a preparative t.l.c. plate and eluted with light petroleum. Careful band selection gave the cyclopentadiene(160) of 80% purity by v.p.c. (110°):

n.m.r.(CCl_4)τ: 2·77(m) aromatic (5H); 3·85(m), 4·08(m) olefinic (1H,1H); 8·05(m) methyl (3H); 8·82(s) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 1680(m), 1630(m), 1600(m) C=C; 850(s), 790(s), 760(s), 730(m), 700(s).

u.v.(EtOH)mμ: 229·0 (ε = 12,700); 254·0 (ε = 6,300).

6.5.3 Thermal rearrangement of the trans- and cis-β-methylstyrene adducts(153) and (154).

(a) trans-1-Dimethylvinylidene-2-methyl-3-phenylcyclopropane (1·0g.) in xylene solution was heated in an oil bath at 130° for 2 hr. Distillation gave a pale yellow liquid (b.p. 64-5°/0·4 mm.) containing 98% of syn-1-ethylidene-2-isopropylidene-3-phenylcyclopropane(155) and 2% of the anti-isomer(156), (overall yield of 0·75g., 75%). The proportions were determined by v.p.c. at 100°. A similar experiment carried out with cis-1-dimethylvinylidene-2-methyl-3-phenylcyclopropane (1·0g.) at 130° for 3·5 hr. afforded 87% of the syn-isomer(155) and 13% of the anti-isomer(156), (overall yield of 0·50g., 50%). The above times of heating were the minimum required to cause disappearance of the allene band (ν_{max} = 2010 $cm.^{-1}$) in the i.r. spectrum in each case.

Pure syn-isomer was obtained from this material by preparative v.p.c. (10% S.E.30; 6', 100°). The product(155) was collected as a pale yellow liquid at approximately 45 min:

n.m.r.(CCl_4)τ: 2·98(m) aromatic (5H); 4·50(q, 6·5 Hz.) olefinic (1H); 7·22(s, broad) benzylic (1H); 7·9-8·2(m) methyls (9H).

i.r.(film)$cm.^{-1}$: 1790(m), 1650(m), 1600(m) C=C; 770(s), 700(s) monosubstitution.

u.v.(EtOH)mμ: 249·0 (ε = 17,600).

(P)m/e: Found, 184·12499; calcd. for $C_{14}H_{16}$, 184·12519.

(b) The trans-adduct (1·0g.) was passed through the flow system at 350°/0·25 mm. Distillation gave the two isomers(155) and (156), (0·9g., 90%) in the ratio 31:69. A similar experiment with the cis-adduct (1·0g.) afforded the same two isomers in the ratio syn:anti as 33:67.

Pure syn-isomer was obtained from this material by preparative v.p.c. (10% S.E. 30; 6', 100°). The product(156) was obtained as a pale yellow liquid at approximately 36 min:

n.m.r.(CCl_4)τ: 2·97(m) aromatic (5H); 4·20(q, 6·0 Hz.) olefinic (1H); 7·14(s,broad) benzylic (1H); 8·0-8·3(m) methyls (9H).

i.r.(film)$cm.^{-1}$: 1790(m), 1650(m), 1600(m) C=C; 760(s), 700(s) monosubstitution.

u.v.(EtOH)mμ: 248·0 (ε = 18,700).

(P)m/e: Found, 184·12499; calcd. for $C_{14}H_{16}$, 184·12519.

(c) A 10% solution of the cis-adduct was prepared in Analar carbon tetrachloride (0·5g./5 ml.). Aliquots (1 ml.) were sealed in glass tubes under nitrogen and heated in an oil bath at 130°. The n.m.r. spectra were recorded of aliquots which were removed from the bath at 15 minute intervals ($t_{\frac{1}{2}}$ approximately 20 min.). Examination of the benzylic region (7-8τ) indicated the cis-adduct benzylic proton (7·00τ) and known product peaks only. No doublet was observed at 7·58τ due to the trans-adduct benzylic proton, this particular region being free of peaks.

(d) The trans-adduct (0·5g.) was passed through the preparative chromatograph (30% S.E. 30; 20', 180°) and the pale yellow product (0·3g., 60%) collected after approximately 1·25 hr. This contained 31% of the syn-isomer(155) and 69% of the anti-isomer (156). A similar experiment with the cis-adduct (0·5g.) gave the pale yellow liquid (0·25g., 50%) which contained the same two isomer in the ratio syn:anti as 30:70.

(e) Samples of the rearrangement products (130°) from the trans-adduct (i.e. a syn:anti ratio of 98:2) and the cis-adduct (i.e. a syn:anti ratio of 87:13) were passed separately through the preparative chromatograph (30% S.E. 30; 20', 180°) and the products collected after approximately 1·25 hr. These contained 30% of the syn-isomer and 70% of the anti-isomer in both cases. Recycling of these products caused no change in the isomer distribution.

(f) A 5% solution of the anti-isomer in xylene (0·025 g./ 0·50 ml.) was heated in an oil bath at 130° for 1 hr. Examination by v.p.c. (100°) showed no change in composition.

(g) A sample of the anti-isomer was passed through the preparative chromatograph (30% S.E. 30; 20', 130°) and the product collected after approximately 7 hr. This contained the syn- and anti-isomers in the ratio 10:90 respectively. A similar experiment with the syn-isomer gave rise to a syn:anti ratio of 50:50.

(h) A sample of the anti-isomer was passed through the preparative chromatograph (30% S.E. 30; 20°, 180°) and the eluant collected after approximately 1·25 hr. This contained the syn- and anti-isomers in the ratio 30:70 respectively.

Estimation of the Free Energy difference (ΔG°) between the syn- and anti-isomers.

Assuming the mode:- $\underset{(\text{syn})}{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(\text{anti})}{B}$

where A_0 and B_0 are the concentrations of the syn- and anti-isomer respectively at t = 0, then:

$$-dA/dt = K_1A - k_2(A_0 - A)$$

Integration gives:

$$t = (k_1 + k_2)\ln[(k_1 + k_2)A - k_2A_0]_0^t \quad \ldots\ldots\ldots(1)$$

Similarly:

$$t = (k_1 + k_2)\ln[(k_1 + k_2)B - k_1B_0]_0^t \quad \ldots\ldots\ldots(2)$$

Combining (1) and (2) gives:

$$\frac{(k_1 + k_2)A - k_2A_0}{k_1A_0} = \frac{(k_1 + k_2)B - k_1B_0}{k_2B_0}$$

Substituting the appropriate values of the syn:anti ratios at 130° (t = 7 hr.) gives:

$$\frac{k_1 + k_2 - 2k_2}{2k_1} = \frac{9k_1 + 9k_2 - 10k_1}{10k_2}$$

Since the equilibrium constant $K_1 = k_1/k_2$, solving for K_1 gives:

$$K_1 = 5 \text{ (or } -1).$$

Now $\Delta G^\circ = -RT \cdot \ln K_1$ and thus:-

$\underline{\Delta G^\circ = 1 \cdot 29 \text{Kcal.mole}^{-1}}$ (at 130°).

Also, since the syn:anti equilibrium ratio at 180° is 3:7, the equilibrium constant (K_2) is 2·33 and thus:-

$\underline{\Delta G^\circ = 0 \cdot 76 \text{Kcal.mole}^{-1}}$ (at 180°).

6.5.4 Thermal rearrangement of the trans-β-isopropylstyrene adduct(157).

trans-1-Dimethylvinylidene-2-isopropyl-3-phenylcyclopropane(0·50g.) was passed through the flow system at 350°/0·05 mm. The crude material was distilled to give the pale yellow product (b.p. 65-7°/0·01 mm.; 0·42g., 85%) which was not fully resolved by analytical v.p.c. (110°). Examination by n.m.r. showed this to contain syn-1-isopropylidene-2-(2-methylprop-1-enylidene)-3-phenylcyclopropane(158) and its anti-isomer(159) in the ratio 1:2 respectively. The proton allocations were confirmed by spin-spin decoupling:

n.m.r.(CCl_4)τ: 2·96(m) aromatic (5H); 4·29(d,7Hz.) anti-isomer olefinic (2/3 H); 4·65(d,8Hz.) syn-isomer olefinic (1/3H); 7·16(s,broad), 7·25(s,broad) anti- and syn-isomer benzylic resp. (2/3H, 1/3H); 7·3-7·8 isopropyl (1H); 8·0-8·3(m) dimethyl (6H); 8·92(d, 6Hz.), 9·05(d,6Hz.) syn- and anti-isomer isopropyl resp. (2H, 4H).

i.r.(film)cm.$^{-1}$: 1780(m), 1650(m), 1600(m) C=C; 770(m), 700(s) monosubstitution.

u.v.(EtOH)mμ: 251·5 (ε = 16,400).

(P)m/e: Found, 212·15654; calcd. for $C_{16}H_{20}$, 212·15649.

6.5.5 Thermal rearrangement of the α-methoxystyrene adduct(139).

2-Dimethylvinylidene-1-methoxy-1-phenylcyclopropane (0·50g.) in petroleum (100-120°) was heated at 112° in a refluxing toluene bath for 2 hr. Distillation gave 2-isopropylidene-1-methoxy-1-phenyl-3-methylenecyclopropane(140) as a pale yellow unstable liquid (b.p. 64-5°/0·1 mm.; 0·30g., 60%) which was pure by v.p.c. (100°):

n.m.r.(CCl_4)τ: 2.79(m) aromatic (5H); 4·61(s), 4·70(s) olefinic (1H,1H); 6·75(s) methoxy (3H); 8·00(s), 8·10(s) dimethyl (3H,3H).

i.r.(film)cm.$^{-1}$: 1730(m), 1640(w), 1600(m) C=C; 1080(s) C-O; 870(s) $=CH_2$; 740(s), 700(s) monosubstitution.

u.v.(EtOH)mμ: 254·5 (ε = 16,800).

(P)m/e: Found, 200·11926; calcd. for $C_{14}H_{16}O$, 200·12011.

6.5.6 Thermal rearrangement of the α-bromostyrene adduct(141).

(a) The adduct (0·40g.) in petroleum (100-120°) was heated at 112° on a refluxing toluene bath for 4 hr. The reaction mixture was distilled to give a small amount of dark coloured material (b.p. 85-90°/0·05 mm.; 0·05g., 12·5%). The i.r. spectrum showed no band at 2020-2010 cm.$^{-1}$(allene). The n.m.r. spectrum was complex and t.l.c. examination (light petroleum) showed a complex

mixture of products.

(b) The adduct (0·3g.) was passed through the flow system at 350°/0·05 mm. Examination of the very dark distillate (0·20g., 66%) as above indicated a complex mixture to be present and no rearrangement product was isolated.

6.5.7 Thermal rearrangement of the 4,α-dimethylstyrene adduct(144).

2-Dimethylvinylidene-1-methyl-1-(p-tolyl)cyclopropane (1·0g.) was passed through the flow system at 350°/0·1 mm. Distillation afforded 2-isopropylidene-1-methyl-1-(p-tolyl)-3-methylenecyclopropane(145) as a pale yellow liquid (b.p. 60-2°/0·05 mm.; 0·80g., 80%) which was pure by v.p.c. (110°):

n.m.r.(CCl_4)τ: 3·01(m) aromatic (4H); 4·74(s), 4·87(s) olefinic (1H,1H); 7·75(s) aryl methyl (3H); 8·06(s), 8·14(s) dimethyl (3H,3H); 8·46(s) methyl (3H).

i.r.(film)$cm.^{-1}$: 1780(m), 1730(m), 1630(w), 1600(w) C=C; 880(s) $=CH_2$; 830(s) 1,4-disubstitution.

u.v.(EtOH)mμ: 245·0 (ε = 17,500).

(P)m/e: Found, 198·13993; calcd. for $C_{15}H_{18}$, 198·14094.

6.5.8 Thermal rearrangement of the 1,1-diphenylethylene adduct(142).

Crude 2-dimethylvinylidene-1,1-diphenylcyclopropane was distilled and the yellow distillate fractionated to give the partial rearrangement product (b.p. 111-112°/0·01 mm.; 2·96g., 60% based on original olefin). The n.m.r. spectrum showed this to contain the original adduct(142) and 1,1-diphenyl-2-isopropylidene-3-methylene-cyclopropane(143) in the ratio 1:4:

n.m.r.(CCl_4)τ: 2·86(m) aromatic (10H); 4·63(s), 4·74(s) product olefinic (0·8H, 0·8H); 7·94(s) adduct cyclopropyl (0·4H); 8·03(s) product dimethyl (4·8H); 8·23(s) adduct dimethyl (1·2H).

i.r.(film)$cm.^{-1}$: 1780(s), 1730(m), 1600(s) C=C; 880(s) $=CH_2$; 760(s), 700(s) monosubstitution.

(P)m/e: Found, 246·14116; calcd. for $C_{19}H_{18}$, 246·14084.

6.5.9 Rearrangements of the 1-methyleneindane adduct(146).

Thermal rearrangement

2'-Dimethylvinylidenecyclopropane-1'-spiro-1-indane (0·45g.) in xylene was heated at 140° for 2 hr. in a refluxing xylene bath. Distillation gave 2'-isopropylidene-3'-methylenecyclopropane-1'-spiro-1-indane(147) as a pale yellow liquid (b.p. 56-7°/0·01 mm.; 0·25g., 55·5%):

n.m.r.(CCl_4)τ: 2·98(m), 3·31(m) aromatic (3H,1H); 4·75(s), 4·96(s) olefinic (1H,1H); 6·98(t, 7Hz.) benzylic (2H); 7·80(t, 7Hz.) methylene (2H); 8·04(s), 8·24(s) dimethyl (3H,3H).

i.r.(film)$cm.^{-1}$: 1780(s), 1720(m), 1600(m) C=C; 880(s) $=CH_2$; 770(s), 740(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 245·5 (ε = 19,200).

(P)m/e: Found, 196·12459; calcd. for $C_{15}H_{16}$, 196·12519.

Acid catalysed rearrangement.

Distillation of the crude acid catalysed rearrangement product obtained from the adduct (0·50g.) gave a pale yellow liquid

(b.p. 56-60°/0·01 mm.; 0·45g., 90%). Analysis by v.p.c. (120°) showed this to contain 80% of 3',3',5'-trimethyl-1,2-cyclopenta-1'-4'-dienoindene(169) and 20% of several minor components. A sample was purified by preparative v.p.c. (10% S.E. 30; 6', 200°) and the product(169) was collected as a pale yellow liquid at approximately 24 min.:

n.m.r.(CCl_4)τ: 2·56(m), 2·97(m) aromatic (1H,3H); 3·99(s) olefinic (1H); 7·21(s) benzylic (2H); 7·79(s) methyl (3H); 8·73(s) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 1660(s), 1600(m) C=C; 830(m) =CH; 780(s), 760(s), 720(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 259·5 (ε = 26,800); 267·5 (ε = 26,000).

(P)m/e: Found, 196·12466; calcd. for $C_{15}H_{16}$, 196·12519.

6.5.10 Rearrangements of the 1-methylenetetralin adduct(148).

Thermal rearrangement.

2'-Dimethylvinylidenecyclopropane-1'-spiro-1-tetralin (0·50g.) in xylene was heated at 140° in a refluxing xylene bath for 2 hr. Distillation gave 2'-isopropylidene-3'-methylenecyclopropane-1'-spiro-1-tetralin(149) as a pale yellow liquid (b.p. 6506°/0·01 mm.; 0·37g., 74%):

n.m.r.(CCl_4)τ: 3·09(m), 3·28(m) aromatic (3H,1H); 4·79(s), 4·97(s) olefinic (1H,1H); 7·15(m) benzylic (2H); 7·8-8·4(m,obscure) methylenes (4H); 8·03(s), 8·21(s) dimethyl (3H,3H).

i.r.(film)cm.$^{-1}$: 1780(m), 1730(w), 1600(w) C=C; 880(s) $=CH_2$; 770(s), 740(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 243·0 (ε = 18,800).

(P)m/e: Found, 210·14092; calcd. for $C_{16}H_{18}$, 210·14084.

Acid catalysed rearrangement.

The crude acid catalysed rearrangement product prepared from the adduct (1·0g.) was distilled to give a pale yellow liquid (b.p. 83-5°/0·01 mm.; 0·8g., 80%). Analysis of this material by v.p.c. (120°) showed it to contain 95% of 3',3',5'-trimethyl-1,2-cyclopentenonaphthalene(171) along with 5% of several minor components. A sample was purified by preparative t.l.c. (light petroleum) and careful band selection gave the product(171) as a colourless liquid, pure by v.p.c.:

n.m.r.(CCl_4)τ: 2·2-2·9(m) aromatic (6H); 6·36(m) benzylic (1H); 7·68(q, 13, 9Hz.), 8·27(q, 13, 3Hz.) methylene (1H,1H); 8·56(d, 7Hz.) methyl (3H); 8·64(s), 8·73(s) dimethyl (3H,3H).

i.r.(film)cm.$^{-1}$: 820(s), 750(s) 1,2,3,4-tetra and 1,2-disubstitution.

u.v.(EtOH)mμ: 229·0 (ε = 60,600).

(P)m/e: Found, 210·14092; calcd. for $C_{16}H_{18}$, 210·14084.

Analysis: Found, C, 91·6; H, 8·91; calcd., C, 91·37; H, 8·63%.

6.5.11 Rearrangements of the 1-phenylcyclobutene adduct(195).

Thermal rearrangement.

Crude 5-dimethylvinylidene-1-phenylbicyclo[2,1,0]pentane was distilled to give some dark viscous material (b.p. 80-100°/0·01 mm.;

0·73g., 18·5% based on original olefin). The i.r. spectrum showed no band in the region 2020-2010 cm.$^{-1}$ (allene) and analytical v.p.c. (120°) showed many unresolved peaks. The n.m.r. spectrum was complex and analytical t.l.c. (light petroleum) showed a tailing band.

Acid catalysed rearrangement.

The acid catalysed rearrangement was carried out on crude adduct and the product distilled to give a low recovery of dark viscous material (b.p. 100-140°/0·01 mm.; 12% based on original olefin). Analytical t.l.c. (light petroleum) showed a tailing unresolved band while the n.m.r. spectrum was complex. The mass spectrum showed a minor peak only corresponding to the molecular weight (m/e = 196) of the expected adduct and many peaks in the region m/e:350-196, but no peak at m/e:392 (2 x 196).

6.5.12 Rearrangements of the 1-phenylcyclopentene adduct(174).

Thermal rearrangement.

(a) 6-Dimethylvinylidene-1-phenylbicyclo[3,1,0]hexane (0·50g.) in xylene was heated at 150° in an oil bath for 7 hr. Removal of the solvent gave a viscous residue which showed a weak band at 2010 cm.$^{-1}$(allene) in the i.r. spectrum. Analysis by v.p.c. (135°) did not show a recognisable product.

(b) The adduct (1·0g.) was passed through the flow system at 450°/0·01 mm. The crude product was distilled to give a pale yellow liquid (b.p. 88-90°/0·01 mm.; 0·82g., 82%) which

contained 90% of 9-isopropenyl-1,2,3,4-tetrahydrofluorene(175), 5% of 1-(3-methylbut-1-ynyl)-2-phenylcyclopent-2-ene(176) and 5% of several unidentified minor components. Passage of the adduct through the flow system at 350°/0·01 mm. resulted in only partial rearrangement. A sample of the rearrangement product was purified by preparative t.l.c.(light petroleum). The leading band gave the tetrahydrofluorene(175) as a pale yellow liquid, pure by v.p.c. (135°):

n.m.r.(CCl_4)τ: 2·98(m) aromatic (4H); 5·00(m,fine), 5·10(m,fine) olefinic (1H,1H); 6·26(s,broad) benzylic (1H); 7·60(m), 7·82(m) allylic methylenes (2H,2H); 8·25(m) methylenes (4H); 8·88(d, 1Hz.) methyl (3H).

i.r.(film)$cm.^{-1}$: 1640(s), 1600(m) C=C; 900(s) $=CH_2$; 760(s), 740(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 263·0 (ε = 12,300).

(P)m/e: Found, 210·14117; calcd. for $C_{16}H_{18}$, 210·14084.

The second band gave a small amount of the ethynylcyclopentene(176), identified by i.r. and v.p.c.

Acid catalysed rearrangement.

The crude acid catalysed rearrangement product prepared from the adduct (1·0g.) was distilled to give a pale yellow liquid (b.p. 86-8°/0·01 mm.; 0·82g., 82%) which contained 85% of the 2-(2-methylprop-1-enyl)-1-phenylcyclohexadienes(198a,b), 5% of the ethynylcyclopentene(176), 5% of 2-isobutylbiphenyl(199) and 5% of several minor components. The product was purified by preparative

v.p.c. (10% A.P.L.; 175°), the ethynylcyclopentene(176) being unstable under these conditions. The biphenyl(199) was obtained as a colourless liquid, identical to a sample prepared by an independent route (section 6.7.5f). The cyclohexadienes(198a,b) were obtained as an unstable yellow liquid and were not resolved by v.p.c.:

n.m.r.(CCl_4)τ: 2·86(m) aromatic (5H); 3·9-4·4(m) olefinic (3H); 7·4-7·9(m) methylenes (4H); 8·36(m), 8·42(d, 1Hz.), 8·46(d, 1Hz.) dimethyl (3H, 1·5H, 1·5H).

i.r.(film)cm.$^{-1}$: 1650(w), 1600(m) C=C; 750(s), 720(m), 690(s) monosubstitution.

u.v.(EtOH)mμ: 230·0 (ε = 14,100); 310·0 (ε = 7,800).

(P)m/e: Found, 210·14053; calcd. for $C_{16}H_{18}$, 210·14084.

A pure sample of the ethynylcyclopentene(176) was obtained as follows. The distilled product (0·45g.) was applied to a t.l.c. plate (2 mm. layer) and eluted with light petroleum. The second band was removed and further purified on a t.l.c. plate (1 mm. layer). The ethynylcyclopentene(176) eluted with light petroleum and was collected as a pale yellow liquid (0·02g.), pure by v.p.c. (135°):

n.m.r.(CCl_4)τ: 2·54(m), 2·82(m) aromatic (2H,3H); 3·96(q,4·5,2·5Hz.) olefinic (1H); 6·27(m) propargylic (1H); 7·3-8·1(m) methylenes and isopropyl (5H); 8·95(d, 7Hz.) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 2250(w) C≡C; 1600(w) C=C; 1320(s) isopropyl; 750(s), 680(s) monosubstitution.

u.v.(EtOH)mμ: 254·0 (ε = 14,200).

(P)m/e: Found, 210·14127; calcd. for $C_{16}H_{18}$, 210·14084.

6.5.13 Rearrangements of the 1-phenylcyclohexene adduct(177).

Thermal rearrangement.

(a) 7-Dimethylvinylidene-1-phenylbicyclo[4,1,0]heptane (0·50g.) was heated in xylene in an oil bath at 180° for 8 hr. This material was distilled to give a yellow liquid (b.p. 75-6°/0·01 mm.; 0·05g., 10%) which contained 1-(3-methylbut-1-ynyl)-2-phenylcyclohex-2-ene(179). This material was further purified by preparative t.l.c. (light petroleum) and the ethynylcyclohexene(179) collected as a pale yellow liquid, pure by v.p.c.(135°):

n.m.r.(CCl_4)τ: 2·80(m) aromatic (5H); 4·08(t, 4Hz.) olefinic (1H); 6·61(s,broad) propargylic (1H); 7·63(m) isopropyl (1H); 7·80(m) allylic methylene (2H); 8·15(m) methylenes (4H); 8·99(d, 7Hz.) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 2250(w) C≡C; 1600(w) C=C; 1320(s) isopropyl; 750(s), 680(s) monosubstitution.

u.v.(EtOH)mμ: 245·0 (ε = 9,500).

(P)m/e: Found, 224·15671; calcd. for $C_{17}H_{20}$, 224·15649.

(b) The adduct (1·0g.) was passed through the flow system at 450°/0·01 mm. The crude product was distilled to give a pale yellow liquid (b.p. 90-2°/0·01 mm.; 0·8g., 80%) which contained 75% of 3-isopropenyl-3,4,5,6,7,8-hexahydro-1,2-benzazulene(178), 20% of the ethynylbiphenyl(179) and 5% of several minor components. A sample was purified by preparative t.l.c. (light

petroleum). The leading band gave the hexahydrobenzazulene(178) as a pale yellow liquid, pure by v.p.c.:

n.m.r.(CCl_4)τ: 2·95(m) aromatic (4H); 4·96(m,fine), 5·05(m,fine) olefinic (1H,1H); 6·28(s,broad) benzylic (1H); 7·46(m), 7·66(m) allylic methylenes (2H,2H); 8·26(m) methylenes (6H); 8·88(d,1Hz.) methyl (3H).

i.r.(film)cm.$^{-1}$: 1640(s), 1600(m) C=C; 900(s) $=CH_2$; 760(s), 740(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 266·0 (ε = 11,000).

(P)m/e: Found, 224·15587; calcd. for $C_{17}H_{20}$, 224·15649.

The second band gave the ethynylcyclohexene(179), identified by i.r., n.m.r. and v.p.c.(135°).

Acid catalysed rearrangement.

The crude acid catalysed rearrangement product prepared from the adduct (1·0g.) was distilled to give a yellow liquid (b.p. 88-90°/0·01 mm.; 0·78g., 78%). A sample was applied to a preparative t.l.c. plate and eluted with light petroleum. The first band gave the 2-(2-methylprop-1-enyl)-1-phenylcycloheptadienes(205a,b) as a yellow liquid which was unstable to v.p.c. (135°):

n.m.r.(CCl_4)τ: 3·00(m) aromatic (5H); 3·6-4·1(m) endo-cyclic olefinic (2H); 4·36(m) exo-cyclic olefinic (1H); 7·99(m) methylenes (6H); 8·41(d, 1Hz.), 8·47(d, 1Hz.) dimethyl (3H,3H).

i.r.(film)cm.$^{-1}$: 1650(w), 1600(m) C=C; 750(s), 680(s) monosubstitution.

u.v.(EtOH)mμ: 242·0 (ε = 17,400).

(P)m/e: Found, 224·15587; calcd. for $C_{17}H_{20}$, 224·15649. The second band gave the ethynylcyclohexene(179), identified by i.r., n.m.r. and v.p.c.(135°). The preparative t.l.c. recovery of the cycloheptadienes(205a,b) and the ethynylcyclohexene(179) was in the ratio 1:1.

6.5.14 Rearrangements of the 1-(p-tolyl)cyclopentene adduct(188).

Thermal rearrangement.

(a) Crude 6-dimethylvinylidene-1-(p-tolyl)bicyclo[3,1,0]hexane (section 6.4.3) was fractionally distilled to give a pale yellow product (b.p. 88-9°/0·01 mm.; 1·79g., 40% based on original olefin). Examination of the n.m.r. spectrum showed this to contain unrearranged adduct and the 2-(2-methylprop-1-enyl)-1-(p-tolyl)-cyclohexadienes(189a,b) in the ratio 7:3. The extent of rearrangement varied within the range 25-50% (189a,b) over several runs, depending on the bath temperature and the rate of distillation.

(b) The crude adduct in xylene (1:100 dilution) was refluxed (ca. 140°) under nitrogen for 1 hr. The solvent was removed under reduced pressure and the residue fractionated to give a pale yellow product (b.p. 90-1°/0·01 mm.; 1·34g., 30% based on original olefin) which contained 80% of the cyclohexadienes(189a,b), 5% of 2-isobutyl-4'-methylbiphenyl(191), 10% of 1-(3-methylbut-1-ynyl)-2-(p-tolyl)cyclopent-2-ene(190) and 5% of several minor components (v.p.c., 135°). The ethynylcyclopentene(190) was isolated from this material as follows. A sample (0·25g.) was applied to a t.l.c.

plate (2 mm. layer) and eluted with light petroleum. The second band was collected and further purified over a t.l.c. plate (1 mm. layer). Elution with light petroleum gave the product(190) as a pale yellow liquid (0·02g.) which was pure by v.p.c. (135°):

n.m.r.(CCl_4)τ: 2·6-3·1(m) aromatic (4H); 4·02(q, 4·5,2·5Hz.) olefinic (1H); 6·30(m) propargylic (1H); 7·3-8·1(m) methylenes and isopropyl (5H); 7·70(s) aryl methyl (3H); 8·96(d, 7Hz.) dimethyl (6H).

i.r.(film)$cm.^{-1}$: 2250(w) C≡C; 1620(w) C=C; 1320(s) isopropyl; 820(s) 1,4-disubstitution.

u.v.(EtOH)mμ: 258·0 (ε = 16,100).

(P)m/e: Found, 224·15607; calcd. for $C_{17}H_{20}$, 224·15649.

(c) A sample of the crude adduct was passed through the flow system at 350°/0·01 mm. and the yellow distillate (38% based on original olefin) examined by v.p.c. (135°). This contained 76% of the cyclohexadienes(189a,b), 19% of the biphenyl(191), 3% of the ethynylcyclopentene(190) and 2% of several minor components. Recycling of this material through the flow system or passage at 450°/0·01 mm. did not significantly alter the product ratio.

Acid catalysed rearrangement.

(a) The acid catalysed rearrangement was carried out on crude undistilled adduct. The product was distilled to give a pale yellow liquid (b.p. 92-3°/0·01 mm.; 30% based on original olefin) which contained 42% of the cyclohexadienes(189a,b), 52% of the biphenyl(191), 3% of the ethynylcyclopentene(190) and 3% of several

minor components (v.p.c., 135°). The product was purified by preparative v.p.c. (10% A.P.L.; 180°), the ethynylcyclopentene(190) being unstable under these conditions. The biphenyl(191) was obtained as a colourless liquid, identical (v.p.c., i.r., n.m.r.) to a sample obtained by another method (section 6.6.5a). The cyclohexadienes(189a,b) were collected as an unstable yellow liquid and were not resolved by v.p.c.:

n.m.r.(CCl_4)τ: 2·98(m) aromatic (4H); 3·8-4·3(m) olefinic (3H);
7·4-7·9(m) methylenes (4H); 7·73(s) aryl methyl (3H);
8·34(m), 8·43(d, 1Hz.), 8·47(d, 1Hz.) dimethyl (3H,1·5H,1·5H).

i.r.(film)cm.$^{-1}$: 1640(w) C=C; 820(s) 1,4-disubstitution.

u.v.(EtOH)mμ: 235·0 (ε = 13,700); 305·0 (ε = 7,600).

(P)m/e: Found, 224·15631; calcd. for $C_{17}H_{20}$, 224·15649.

(b) A sample (0·25g.) of the distilled acid catalysed rearrangement product, obtained in (a) above, was refluxed with 10% ethanolic hydrochloric acid for 6 hr. The usual work up (section 6.5.1) and distillation gave the product as a colourless liquid (b.p. 80-1°/0·01 mm.; 0·21g., 84%). Examination by v.p.c. (135°) and n.m.r. showed this to contain the biphenyl(191) only.

6.5.15 Rearrangements of the 1-(p-tolyl)cyclohexene adduct(192).

Thermal rearrangement.

(a) Crude 7-dimethylvinylidene-1-(p-tolyl)bicyclo[4,1,0]-heptane (section 6.4.3) was fractionally distilled to give a pale yellow liquid (b.p. 90-1°/0·01 mm.; 2·14g., 45% based on original olefin). This material was unstable to analytical

v.p.c. (135°). Examination by n.m.r. showed it to contain unrearranged adduct, the 2-(2-methylprop-1-enyl)-1-(p-tolyl)cycloheptadienes(193a,b) and unidentified material in the ratio 6:2:2.

(b) A solution of the crude adduct in xylene (1:100 dilution) was refluxed (ca. 140°) under nitrogen for 1 hr. The solvent was removed under reduced pressure and the residue fractionated to give a pale yellow liquid (b.p. 92-3°/0·01 mm.; 4% based on original olefin). The i.r. spectrum had no band in the region 2020-2010 cm.$^{-1}$(allene). The n.m.r. spectrum showed the product to contain the cycloheptadienes(193a,b), 1-(3-methylbut-1-ynyl)-2-(p-tolyl)cyclohex-2-ene(194) and unidentified material in the ratio 1:1:2.

(c) A sample of the crude adduct was passed through the flow system at 350°/0·01 mm. The yellow distillate was unstable to v.p.c. (135°). The n.m.r. spectrum was complex, the ethynylcyclohexene(194) being the only recognised component (ca. 10% of total). The i.r. spectrum had no band in the region 2020-2010 cm.$^{-1}$ (allene).

Acid catalysed rearrangement.

The acid catalysed rearrangement was carried out on crude undistilled adduct. The product was distilled to give a yellow liquid (b.p. 89-90°/0·01 mm.; 40% based on original olefin). A sample of this material was applied to a preparative t.l.c. plate and eluted with light petroleum. The first band gave the

cycloheptadienes(193a,b) as a yellow liquid, unstable to v.p.c. (135°):

n.m.r.(CCl_4)τ: 3·03(m) aromatic (4H); 3·6-4·1(m) endo-cyclic olefinic (2H); 4·38(m) exo-cyclic olefinic (1H); 7·74(s) aryl methyl (3H); 7·99(m) methylenes (6H); 8·42(d, 1Hz.), 8·48(d, 1Hz.) dimethyl (3H,3H).

i.r.(film)cm.$^{-1}$: 1640(w) C=C; 810(s) 1,4-disubstitution.

u.v.(EtOH)mμ: 250·0 (ε = 12,700).

(P)m/e: Found, 238·17164; calcd. for $C_{18}H_{22}$, 238·17214.

The second band gave the ethynylcyclohexene(194) as a yellow liquid, pure by v.p.c. (135°):

n.m.r.(CCl_4)τ: 2·7-3·1(m) aromatic (4H); 4·10(t, 4Hz.) olefinic (1H); 6·64(s,broad) propargylic (1H); 7·61(m) isopropyl(1H); 7·73(s) aryl methyl (3H); 7·83(m) allylic methylene (2H); 8·15(m) methylenes (4H); 8·98(d, 7Hz.) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 2250(w) C≡C; 1640(w) C=C; 1320(s) isopropyl; 800(s) 1,4-disubstitution.

u.v.(EtOH)mμ: 250·0 (ε = 12,700).

(P)m/e: Found, 238·17211; calcd. for $C_{18}H_{22}$, 238·17214.

The preparative t.l.c. recovery of the cycloheptadienes(193a,b) and the ethynylcyclohexene(194) was in the ratio 1:1.

6.5.16 Thermal rearrangement of the 1-(o-tolyl)cyclopentene adduct(196).

6-Dimethylvinylidene-1-(o-tolyl)bicyclo[3,1,0]hexane (1·0g.) was passed through the flow system at 450°/0·01 mm. and the crude

product distilled to give a pale yellow liquid (b.p. 85-6°/0·01 mm.; 0·85g., 85%). Analytical v.p.c. (135°) showed this to contain mainly (90% of total) two components in the ratio 2:1. This material was unstable under preparative v.p.c. conditions (30% S.E. 30; 20', 190°) or (10% A.P.L.; 180°). The components were not resolved by t.l.c. (light petroleum). The major component was tentatively identified as probably 9-isopropenyl-5-methyl-1,2,3,4-tetrahydrofluorene(197) from the n.m.r. spectrum, the other components being unidentified. The characteristic tetrahydrofluorene peaks are given below:

n.m.r. (CCl_4) τ: 4·99(m,fine), 5·08(m,fine) olefinic methylene; 6·33(m,broad) benzylic; 7·54(s) aryl methyl; 8·88(d, 1Hz.) methyl.

6.5.17 Rearrangements of the indene adduct(206).

Thermal rearrangement.

(a) 2,3-Benzo-6-dimethylvinylidenebicyclo[3,1,0]hex-2-ene (0·20g.) in sodium dried benzene (25 ml.) was refluxed under nitrogen for a total of 24 hr. Evaporation of the solvent and distillation of the dark residue gave a colourless liquid (b.p. 84-5°/0·01 mm.; 0·04g., 20%). Analysis by v.p.c. (135°) showed this to contain 95% of 2-methyl-1-(β-naphthyl)prop-1-ene(207) together with 5% of several minor components. The product(207) was obtained as a colourless liquid after purification by preparative t.l.c. (light petroleum) and was identical to a sample prepared by an alternative route (section 6.7.8).

n.m.r.(CCl_4)τ: 2·3-2·8(m) aromatic (7H); 3·69(s) olefinic (1H); 8·11(s), 8·12(s) dimethyl (3H,3H).

i.r.(film)cm.$^{-1}$: 1630(m), 1600(m)C=C; 900(s), 870(s), 820(s), 760(s) 1,2-di and 1,3,4-trisubstitution.

u.v.(EtOH)mμ: 245·0 (ε = 45,000); 288·0 (ε = 11,800).

(b) The adduct (1·5g.) was passed through the flow system at 450°/0·01 mm. and the crude product distilled to give a pale yellow liquid (b.p. 83-5°/0·01 mm.; 1·0g., 66%). Analysis of this material by v.p.c. (135°) showed this to contain 95% of the naphthalene(207) together with 5% of several minor components. A sample was purified by preparative t.l.c. (light petroleum).

Acid catalysed rearrangement.

Distillation of the crude acid catalysed rearrangement product prepared from the adduct (0·20g.) gave a very pale yellow liquid (b.p. 84-5°/0·01 mm.; 0·18g., 90%) which contained 97% of the naphthalene(207) together with 3% of minor components (v.p.c., 135°). A sample was purified by preparative t.l.c. (light petroleum).

6.5.18 Rearrangements of the 1,2-dihydronaphthalene adduct(222).

Thermal rearrangement.

2,3-Benzo-7-dimethylvinylidenebicyclo[4,1,0]hept-2-ene (0·50g.) was passed through the flow system at 450°/0·01 mm. and the crude product distilled to give a yellow liquid (b.p. 78-80°/0·01 mm.; 0·30g., 60%). Analytical v.p.c. (135°) showed this to contain at

least ten partially resolved peaks. The i.r. spectrum showed a weak band at 2010 cm.$^{-1}$(allene), while the n.m.r. spectrum was complex.

Acid catalysed rearrangement.

The crude acid catalysed rearrangement product prepared from the adduct (0·20g.) was examined by v.p.c. (135°) which indicated at least eight partially resolved peaks. There was no evidence for any major component.

6.5.19 Rearrangements of the 3-methylindene adduct(208).

Thermal rearrangement.

(a) 2,3-Benzo-6-dimethylvinylidene-1-methylbicyclo[3,1,0] hex-2-ene (1·0g.) in sodium dried benzene (250 ml.) was refluxed for 12 hr. under nitrogen. The solvent was removed under reduced pressure and the residue distilled to give a pale yellow liquid (b.p. 70-1°/0·01 mm.; 0·7g., 70%) which solidified on cooling. Analytical v.p.c. (135°) showed this to be a single compound. The product was crystallised from light petroleum to give 3,4-benzo-7-isopropylidene-2-methylenebicyclo[4,1,0]hept-3-ene(209) as a colourless solid (m.p. 54·5°; 0·55g., 55%):

n.m.r.(CCl_4)τ: 2·74(m), 3·02(m) aromatic (1H,3H); 4·85(d, 1·5Hz.), 5·01(d, 1·5Hz.) olefinic (1H,1H); 7·00(d,splitting: 3Hz.) benzylic (2H); 7·54(m), 7·84(m) cyclopropyl (1H,1H); 8·45 (t, 1·5Hz.) dimethyl (6H).

i.r.(nujol)cm.$^{-1}$: 1770(m), 1620(s) C=C; 880(s) $=CH_2$; 780(s), 770(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 250·0 (ε = 10,600).

(P)m/e: Found, 196·12454; calcd. for $C_{15}H_{16}$, 196·12519.

Analysis: Found, C, 91·4; H, 8·3; calcd., C, 91·78; H, 8·22%.

A solution of the bicycloheptene(209), (0·50g.) in ether (50 ml.) was vigorously shaken with 20% aqueous hydrochloric acid (75 ml.) for 2 hr. The mixture was poured onto water (150 ml.) and the organic material extracted with light petroleum (3 x 25 ml.). The combined extracts were washed with water (20 ml.) and dried over anhydrous potassium carbonate and magnesium sulphate. The solvent was evaporated and the residue distilled to give a yellow liquid (b.p. 99-100°/0·05 mm.; 0·35g., 70%) shown by v.p.c. to be a single compound. The product solidified on standing and was crystallised from light petroleum to give 1,2-benzo-5-isopropenyl-3-methylcyclohepta-1,3,5-triene(211) as a colourless solid (m.p. 44-44·5°; 0·30g., 60%):

n.m.r.(CS_2)τ: 2·65(m), 2·89(m) aromatic (1H,3H); 3·42(s) olefinic (1H); 4·20(t,7·0Hz.) olefinic (1H); 5·05(m,fine), 5·15(m,fine) olefinic methylene (1H,1H); 7·05(d, 7·0Hz.) benzylic (2H); 7·63(d, 1·0Hz.) methyl (3H); 8·14(d, 0·5Hz.) isopropenyl methyl (3H).

n.m.r.(CS_2)τ: -80°: 4·20(q, 7·7, 7·8Hz.) olefinic (1H); 6·84(q, 12·6, 7·8Hz.), 7·37(q, 12·6,6·6Hz.) benzylic (1H,1H).

The remainder of the spectrum showed no structural change at -80°. The coalescence temperature was ca. -16° (100 MHz. spectrum). An estimation of the energy barrier between the two favourable conformations is discussed elsewhere (p.148).

i.r.(nujol)cm.$^{-1}$: 1630(m), 1610(m) C=C; 890(s) =CH_2; 820(m) =CH; 780(s), 760(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 236·0 (ε = 26,400); shoulder at 275·0.

(P)m/e: Found, 196·12466; calcd. for $C_{15}H_{16}$, 196·12519.

Analysis: Found, C, 91·3; H, 8·6; calcd., C, 91·78; H, 8·22%.

(b) The adduct (1·0g.) was passed through the flow system at 450°/0·01 mm. The crude product was distilled to give a pale yellow liquid (b.p. 74-8°/0·01 mm.; 0·70g., 70%). Examination of the n.m.r. spectrum showed this to contain the bicycloheptene(209), the cycloheptatriene(211) and 2-(2-methylprop-1-enyl)-1-methylnaphthalene(210) in the ratio 3:1:2. The products were not resolved by t.l.c. (light petroleum).

A sample of the product (0·10g.) dissolved in ether (10 ml.) was shaken with 20% hydrochloric acid (15 ml.) for 2 hr. An analogous work up to that described in (a) above, followed by distillation of the residue gave a pale yellow liquid (b.p. 84-7°/0·01 mm.; 0·06g., 60%). This material was applied to a preparative t.l.c. plate and eluted with light petroleum. The first band afforded the naphthalene(210) as a colourless liquid, pure by v.p.c. (135°), which was identical to a sample prepared by an alternative route (section 6.7.9).

n.m.r.(CCl_4)τ: 2·0-2·9(m) aromatic (6H); 3·63(s) olefinic (1H); 7·72(s) aryl methyl (3H); 8·10(d, 1Hz.), 8·40(d, 0·5Hz.) dimethyl (3H,3H).

i.r.(film)cm.$^{-1}$: 1630(w), 1600(m) C=C; 820(s), 770(s), 750(s) 1,2-di and 1,2,3,4-tetrasubstitution.

u.v.(EtOH)mμ: 230·0 (ε = 36,400); 283·0 (ε = 6,800).
(P)m/e: Found, 196·12491; calcd. for $C_{15}H_{16}$, 196·12519.
Analysis: Found, C, 91·78; H, 8·4; calcd., C, 91·78; H, 8·22%.

The second band gave the cycloheptatriene(211), identified by its i.r. and n.m.r. spectra.

(c) The bicycloheptene(209), (0·2g.) was passed through the flow system at 350°/0·01 mm. Examination of the distillate by n.m.r. showed it to contain the bicycloheptene(209) and the cycloheptatriene(211) in the ratio 20:1.

Acid catalysed rearrangement.

The crude acid catalysed rearrangement product prepared from the adduct (0·20g.) was distilled to give a pale yellow liquid (b.p. 81-2°/0·01 mm.; 0·18g., 90%) which contained 96% of the naphthalene(210) and 4% of several minor components (v.p.c., 135°). A sample was purified by preparative t.l.c. (light petroleum). Neither the bicycloheptene(209) nor the cycloheptatriene(211) were detected.

Base induced rearrangement.

The adduct (0·10g.) and a 20% solution of potassium hydroxide in 50% aqueous ethanol (15 ml.) were refluxed for 4·5 hr. The mixture was poured onto water (30 ml.) and extracted with light petroleum (3 x 15 ml.), the combined extracts washed with water (20 ml.) and dried. The solvent was removed and the residue distilled to give a pale yellow liquid (b.p. 76-8°/0·01 mm.;

0·05g., 50%). Examination of the n.m.r. spectrum showed this to contain the bicycloheptene(209) and the naphthalene(210) in the ratio 1:5. Some unidentified material was also present (ca. 10% of total), however the cycloheptatriene(211) was not detected.

Estimation of the Energy Barrier ($\Delta G^{\ddagger}$) between the two favourable conformations of the cycloheptatriene(211) from the n.m.r. data.

The rate constant (K) for the interconversion of two types of proton is given[141] by the expression:

$$K = 2^{-\frac{1}{2}}\pi(\nu_a - \nu_e)$$

Where $(\nu_a - \nu_e)$ is the frequency separation of the two types of proton involved. In the case of the cycloheptatriene(211) this is 53·8 Hz. (measured at -80° in the 100 MHz. spectrum) and thus:-

$$K = 119{\cdot}6 \text{ sec.}^{-1}$$

Also, $K = [(K'K_BT)/h]\exp.(-\Delta G^{\ddagger}/RT)$.

Where: K' is the Transmission coefficient (0·5)

K_B is the Boltzmann constant ($1{\cdot}38 \times 10^{-16}$)

h is the Planck constant ($6{\cdot}625 \times 10^{-27}$)

R is the Gas constant (1·987)

T is the coalescence temperature (257°K).

Thus:-

$$\Delta G^{\ddagger} = 12{\cdot}2 \text{ Kcal.mole}^{-1}$$

6.5.20 Rearrangements of the 4-methyl-1,2-dihydronaphthalene adduct(214).

Thermal rearrangement.

(a) 2,3-Benzo-7-dimethylvinylidene-1-methylbicyclo[4,1,o]-hept-2-ene (1·0g.) in xylene was heated in an oil bath at 180° for 8 hr. The solvent was removed under reduced pressure and the residue distilled to give a yellow liquid (b.p. 72-4°/0·01 mm.; 0·2g., 20%). This showed no band at 2020 cm.$^{-1}$(allene) in the i.r. spectrum. Examination of the n.m.r. spectrum showed the product to contain 94% of 1-methylene-2(3-methylbut-1-ynyl)tetralin(215) together with 6% of minor unidentified components (v.p.c., 135°).

(b) The adduct (0·05g.) was passed through the flow system at 450°/0·01 mm. and the crude product distilled to give a yellow liquid (b.p. 72-3°/0·01 mm.; 0·40g., 80%) which contained the tetralin(215) together with 3% of minor components (v.p.c., 135°). A sample was purified by preparative t.l.c. (light petroleum) to afford the product(215) as a pale yellow liquid:

n.m.r.(CCl_4)τ: 2·52(m), 3·00(m) aromatic (1H,3H); 4·55 (t, 0·5Hz.), 4·68(t, 0·5Hz.) olefinic (1H,1H); 6·70(m) propargylic (1H); 7·11(m) benzylic (2H); 7·46(m) isopropyl(1H); 7·98(m) methylene (2H); 8·85(d, 7Hz.) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 2250(w) C≡C; 1630(m) C=C; 900(s) $=CH_2$; 780(s), 740(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 250·0 (ε = 11,500).

(P)m/e: Found, 210·14148; calcd. for $C_{16}H_{18}$, 210·14084.

Acid catalysed rearrangement.

Details of the acid catalysed rearrangement are given elsewhere (section 6.6.6b).

6.5.21 Rearrangements of the 3-methyl-1,2-dihydronaphthalene adduct(223).

Thermal rearrangement.

The adduct (0·50g.) was passed through the flow system at 450°/0·01 mm. and the crude product distilled to give a yellow liquid (b.p. 70-80°/0·01 mm.; 0·26g., 52%). The i.r. spectrum showed a weak band at 2020 $cm.^{-1}$ (allene).
Analysis by v.p.c. (135°) showed this material to contain many partially resolved components. The n.m.r. spectrum was complex.

Acid catalysed rearrangement.

Examination of the crude acid catalysed rearrangement product by v.p.c. indicated a complex mixture.

6.6 REACTIONS OF REARRANGEMENT PRODUCTS.

6.6.1 Concerning the products obtained by acid catalysed rearrangement of the α-methylstyrene adduct.

(a) Reaction of maleic anhydride with 1,3,3-trimethyl-4-phenylcyclopenta-2,4-diene(160).

The crude acid catalysed rearrangement product (0·92g.), containing the cyclopentadiene(160), (2·5 mmol.), and maleic anhydride (0·25g., 2·5mmol.) in sodium dried benzene (15 ml.) were refluxed on a water bath under nitrogen for 4 hr. The solvent was removed and the product solidified. This was crystallised from 5% benzene in light petroleum to give endo-3-phenyl-2,7,7-trimethylbicyclo[2,2,1]hept-2-en-5,6-dicarboxylic anhydride(161) as a colourless solid (m.p. 124-6°; 0·70g., 50% based on total hydrocarbon). This material was pure by t.l.c. (30% ether in light petroleum):

n.m.r.(CCl_4)τ: 2·74(m) aromatic (5H); 6·26(m) protons α- to carbonyl groups (2H); 6·84(m), 7·22(m) bridgehead protons (1H,1H); 8·06(s) allylic methyl (3H); 8·95(s), 9·06(s) dimethyl (3H,3H).

i.r.(nujol)cm.$^{-1}$: 1770(s) C=O; 780(s), 710(s) monosubstitution.

u.v.(EtOH)mμ: 258·0 (ε = 8,400).

(P)m/e: Found, 282·12610; calcd. for $C_{18}H_{18}O_3$, 282·12557.

Analysis: Found, C, 76·32; H, 6·13; calcd. C, 76·57; H, 6·43%.

(b) Reaction of methyl acetylenedicarboxylate with the cyclopentadiene(160).

The crude acid catalysed rearrangement product (0·92g.), containing the cyclopentadiene(160), (2·5 mmol.), and methyl acetylenedicarboxylate (0·30g., 2·5 mmol.) in sodium dried benzene (15 ml.) were refluxed on a water bath under nitrogen for 12 hr. The solvent was removed and the residue applied to an alumina column. The product was eluted by 50% ether in light petroleum and was crystallised from 5% benzene in light petroleum to give dimethyl 6-phenyl-5,7,7-trimethylbicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylate(162) as a colourless solid (m.p. 88-9°; 0·70g., 46% based on total hydrocarbon). This was pure by t.l.c. (20% ether in light petroleum):

n.m.r.(CCl_4)τ: 2·68(m) aromatic (5H); 6·22(s), 6·23(s) ester methyls (3H); 6·30(d, 3Hz.), 6·69(d, 3Hz.) bridgehead protons (1H,1H); 7·94(s) allylic methyl (3H); 8·79(s), 8·80(s) dimethyl (3H,3H).

i.r.(nujol)$cm.^{-1}$: 1700(s) C=O; 770(s), 700(s) monosubstitution.

u.v.(EtOH)mμ: 250·5 (ε = 17,600).

(P)m/e: Found, 326·15178; calcd. for $C_{20}H_{22}O_4$, 326·15180.

Analysis: Found, C, 73·69; H, 6·46; calcd., C, 73·60; H, 6·79%.

(c) Photoisomerisation of the Diels-Alder adduct(162).

The diester(162), (0·10g., 0·3mmol.) dissolved in ether (250 ml.) was irradiated in a medium pressure photochemical reactor, under nitrogen, for 16 hr. The solvent was evaporated and the

residue applied to a preparative t.l.c. plate. Elution with light petroleum gave a single band which was collected as a pale yellow liquid (0·06g., 60%). The n.m.r. spectrum showed this to be a mixture of dimethyl 6-phenyl-5,7,7-trimethylquadricyclo[2,2,1,$0^{2,6}$,$0^{3,5}$]heptane-2,3-dicarboxylate(163) and the original diester(162) in the ratio 9:1:

n.m.r.(CCl_4)τ: 2·70(m) aromatic (5H); 6·28(s), 6·49(s) ester methyls (3H,3H); 7·62(d, 2Hz.), 8·05(d, 2Hz.) bridgehead protons (1H,1H); 8·64(s) dimethyl (6H); 8·70(s) methyl (3H).

i.r.(film)cm.$^{-1}$: 1700(s) C=O; 770(s), 700(s) monosubstitution.

u.v.(EtOH)mμ: weak shoulder at 250·0 due to the original diester.

(P)m/e: Found, 326·15148; calcd. for $C_{20}H_{22}O_4$, 326·15180.

6.6.2 Concerning the products obtained by acid catalysed rearrangement of the 1-methyleneindane and 1-methylenetetralin adducts(148) and (148).

(a) Attempted reaction of maleic anhydride with 3',3',5'-trimethyl-1,2-cyclopenta-1',4'-dienoindene(169).

The dienoindene(169(,(0·20g., 1 mmol.) and maleic anhydride (0·10g., 1 mmol.) in sodium dried benzene (5 ml.) were refluxed under nitrogen on a water bath for 12 hr. Examination of the mixture by v.p.c. (100°) showed no maleic anhydride to have been consumed. The original hydrocarbon was destroyed under these conditions of prolonged heating. Examination by t.l.c. (30% ether in light petroleum) did not show any adduct to be present.

(b) Attempted dehydrogenation of 3',3',5'-trimethyl-1,2-cyclopentenonaphthalene(171).

The naphthalene(171), (0·05g., 0·24 mmol.) and o-chloranil (4 mol. equivalent) in sodium dried benzene (15 ml.) were refluxed under nitrogen for 20 hr. Examination by v.p.c. (135°) showed starting material only to be present. Similar experiments with (a) D.D.Q. (4 mol. equivalent) in refluxing benzene, (b) o-chloranil (4 mol. equivalent) in refluxing xylene, gave the same result. Passage of the naphthalene through the flow system at 450°/0·01 mm., packed with a mixture of 5% palladium-charcoal and fibrous asbestos, also gave only starting material (v.p.c., n.m.r.).

(c) Reaction of the cyclopentenonaphthalene(171) with N-bromosuccinimide.

Preliminary experiments indicated that 3-equivalents of N-bromosuccinimide (N.B.S.) were necessary for complete reaction of the starting material.

A mixture of the naphthalene(171), (0·63g., 3 mmol.), N.B.S. (1·62g., 9 mmol.) and several crystals of dibenzoyl peroxide in carbon tetrachloride (25 ml.) was refluxed for 15 min. The initially vigorous reaction moderated with the production of an orange-red colouration. Hydrogen bromide was liberated. The reaction mixture was cooled, succinimide filtered off and the filtrate evaporated. The residue was distilled to give a clear viscous liquid (b.p. 160-1°/0·01 mm.; 0·73g., 66%). Analytical t.l.c. (light petroleum) indicated one main spot and a sample was

further purified by preparative t.l.c. (light petroleum). The main band afforded 4'-bromo-5'-bromomethyl-3',3'-dimethyl-1,2-cyclopenta-1',4'-dienonaphthalene(173) as a colourless viscous oil:

n.m.r.(CCl_4)τ: 2·2-2·8(m) aromatic (6H); 5·24(s) methylene (2H); 8·72(s) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 820(s), 750(s) 1,2-di and 1,2,3,4-trisubstitution.

u.v.(EtOH)mμ: 238·5 (ε = 45,700); 320·5 (ε = 8,700); 335·0 (ε = 7,900).

(P)m/e: Found, 363·94621; 365·94399; 367·94246; calcd. for $C_{16}H_{14}{}^{79}Br_2$, 363·94632; $^{79}Br^{81}Br$, 365·94435; $^{81}Br_2$, 367·94238.

6.6.3 Concerning the products obtained by rearrangement of the 1-phenylcyclopentene adduct(174).

(a) Dehydrogenation of 9-isopropenyl-1,2,3,4-tetrahydrofluorene(175) with o-chloranil.

The tetrahydrofluorene(175), (0·050g., 0·24 mmol.) and o-chloranil (3 mol. equivalent) in benzene (15 ml.) were gently refluxed on a water bath for 12 hr. The cooled reaction mixture was eluted through an alumina pad with 50% ether in light petroleum (to remove the hydroquinone and unreacted quinone) and the eluant evaporated. The residue was purified by preparative t.l.c. (light petroleum) and the single band collected. Crystallisation of the crude product from light petroleum gave 9-isopropenylfluorene(180) as a colourless solid (m.p. 54-6°; 0·032g., 64%):

n.m.r.(CCl_4)τ: 2·37(m), 2·78(m) aromatic (2H,6H); 4·76(m,fine), 4·98(m,fine) olefinic (1H,1H); 5·50(s) benzylic (1H); 8·90(d, 1Hz↓) methyl (3H).

i.r.(CS_2)cm.$^{-1}$: 1640(m) C=C; 900(s) $=CH_2$; 750(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 267·5 (ε = 16,600); 292·0 (ε = 5,500); 304·0 (ε = 7,400).

(P)m/e: Found, 206·10948; calcd. for $C_{16}H_{14}$, 206·10954.

Analysis: Found, C, 93·18; H, 7·09; calcd., C, 93·16; H, 6·84%.

(b) Oxidation of the tetrahydrofluorene(175) with D.D.Q.

The tetrahydrofluorene(175), (0·100g., 0·48 mmol.) and D.D.Q. (3 mol. equivalent) were stirred at room temperature in benzene (15 ml.) for 6 hr. The reaction mixture was eluted through an alumina pad with 50% ether in light petroleum and the eluant evaporated. The residue was applied to a preparative t.l.c. plate and eluted with 12% ether in light petroleum. The leading band afforded 9-isopropenylfluorene (0·028g., 30%), identified by its i.r. and n.m.r. spectra. The second band gave a yellow viscous oil which was crystallised from 5% benzene in light petroleum to give α-(9-fluorenylidene)propionaldehyde(240) as a yellow solid (m.p. 130-3°; 0·051g., 45%):

n.m.r.(CCl_4)τ: -0·74(s) aldehydic (1H); 2·2-2·9(m) aromatic (8H); 7·54(s) methyl (3H).

i.r.(CS_2)cm.$^{-1}$: 1670(s) C=O; 790(s), 740(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 229·0 (ε = 11,800); 260·0 (ε = 16,000);

269·5 (ε = 22,300); 282·5 (ε = 4,200); 293·0 (ε = 4,400); 335·0 (ε = 8,000).

(P)m/e: Found, 220·08839; calcd. for $C_{16}H_{12}O$, 220·08881.

Analysis: Found, C, 87·5; H, 5·2; calcd. C, 87·24; H, 5·49%.

(c) Base catalysed isomerisation of 9-isopropenylfluorene(180).

The method was similar to that of Delahunt[103] for a related system.

A solution of sodium (0·5g.) in spectroscopic ethanol (ca. 250 ml.) was prepared under anhydrous conditions. An accurately weighed sample of 9-isopropenylfluorene (ca. 1 mg.) was diluted with this solution to 100 ml. in a standard flask and the u.v. spectrum recorded as required. Equilibrium was reached after 20 hr. (i.e. the spectrum ceased to change). The spectrum was identical (extinction coefficients agreed to within 5%) to that of authentic 9-isopropylidenefluorene(183):

u.v.(EtOH)mμ; 249·0 (ε = 26,200); 258·5 (ε = 31,700);
(t = 20 hr.) 272·0 (ε = 16,800); 281·0 (ε = 17,400);
302·5 (ε = 12,300); 317·5 (ε = 12,300).

The solution was carefully neutralised by dropwise addition of dilute hydrochloric acid and most of the solvent evaporated. The residue was diluted with water (20 ml.) and extracted with light petroleum (3 x 15 ml.). The combined extracts were washed with water, dried and the solvent evaporated. Re-examination of the u.v. spectrum indicated loss of the characteristic fluorenylidene chromophore.

(d) Base catalysed isomerisation of the tetrahydrofluorene(175).

An identical procedure to that detailed in (c) above was carried out with the tetrahydrofluorene(175). Equilibrium was reached after 50 hr:

u.v.(EtOH)mμ: 266·0 (ε = 26,700)
(t = 50 hr.)

Neutralisation of the solution with dilute hydrochloric acid resulted in the formation of many maxima in the u.v. spectrum.

(e) Catalytic hydrogenation of 9-isopropenylfluorene(180).

9-Isopropenylfluorene (0·015g., 0·073 mmol.), dissolved in ethanol (15 ml.), was hydrogenated at atmospheric pressure over 10% palladium-charcoal (5 mg.). The mixture was filtered, the solvent evaporated and the product purified by preparative t.l.c. (light petroleum). 9-Isopropylfluorene(181) was obtained as a colourless solid (m.p. 51-3°, lit.[142] 53-5°., 0·012g., 81%), identical to an authentic sample:

n.m.r.(CCl_4)τ: 2·3-3·0(m) aromatic (8H); 6·17(d, 3Hz.) benzylic (1H); 7·48(m) isopropyl (1H); 9·17(d, 7Hz.) dimethyl (6H).

i.r.(nujol)$cm.^{-1}$: 750(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 268·0 (ε = 17,400); 292·5 (ε = 5,700); 304·0 (ε = 8,500).

(f) Attempted reaction of maleic anhydride with the 2-(2-methylprop-1-enyl)-1-phenylcyclohexadienes(198a,b).

The cyclohexadienes(198a,b), (0·021g., 0·1 mmol.) and maleic anhydride (0·010g., 0·1 mmol.) in sodium dried benzene (15 ml.) were gently refluxed under nitrogen for 12 hr. Examination by v.p.c. (135°) showed the original hydrocarbon and maleic anhydride to have been consumed. The solvent was evaporated and the residue applied to a preparative t.l.c. plate. Elution with 25% ether in light petroleum gave a series of unresolved bands which could not be crystallised (0·025g.). The n.m.r. spectrum of this material was complex.

(g) Oxidation of the cyclohexadienes(198a,b) with D.D.Q.

The cyclohexadienes(198a,b), (0·050g., 0·24 mmol.) and D.D.Q. (3 mol. equivalent) in sodium dried benzene (10 ml.) were stirred at room temperature for 4 hr. The reaction mixture was eluted through an alumina pad with 50% ether in light petroleum and the eluant evaporated. Analytical t.l.c. (light petroleum) indicated one non-polar component. The crude product was purified by preparative t.l.c. (light petroleum) and 2-(2-methylprop-1-enyl)-biphenyl(200) obtained as a colourless liquid (0·035 g., 71%) which was pure by v.p.c. (135°):

n.m.r.(CCl_4)τ: 2·81(m) aromatic (9H); 4·00(m) olefinic (1H); 8·26(d, 1Hz.), 8·31(d, 1Hz.) dimethyl (3H,3H).

i.r.(film)$cm.^{-1}$: 1660(m), 1600(m) C=C; 740(s), 690(s) monosubstitution and 1,2-disubstitution.

u.v.(EtOH)mμ: 234·0 (ε = 19,500); shoulder at 257·0.

(P)m/e: Found, 208·12521; calcd. for $C_{16}H_{16}$, 208·12519.

Analysis: Found, C, 92·1; H, 7·83; calcd. C, 92·26; H, 7·74%.

A duplicate experiment in which the reaction mixture was refluxed under nitrogen on a water bath for 6 hr. was carried out. The crude product was applied to a preparative t.l.c. plate and eluted with 12% ether in light petroleum. The leading band was identified (v.p.c., 135°) as the biphenyl (200), (5 mg., 11%). The second band afforded a small amount of viscous oil (ca. 1 mg.). Examination by n.m.r. (C.A.T.) indicated a singlet at 0·70τ attributed to the aldehydic proton of α-methyl-o-phenylcinnamaldehyde(253), the remainder of the spectrum being obscured by impurity peaks.

6.6.4 Concerning the products obtained by rearrangement of the 1-phenylcyclohexene adduct(177).

(a) Attempted acid catalysed isomerisation of 1-(3-methylbut-1-ynyl)-2-phenylcyclohex-2-ene(179).

The cyclohexene(179), (0·015g., 0·067 mmol.) dissolved in ether (10 ml.) was shaken vigorously with 38% hydrochloric acid (15 ml.) for 3 hr. The reaction mixture was poured onto water (20 ml.) and extracted with light petroleum (3 x 15 ml.). The combined extracts were washed with water, dried and evaporated. The n.m.r. spectrum of the residue indicated starting material only.

(b) Dehydrogenation of the ethynylcyclohexene(179) with o-chloranil.

The ethynylcyclohexene(179), (0·020g., 0·089 mmol.) and o-chloranil (3 mol. equivalent) in benzene (15 ml.) were refluxed on a water bath for 12 hr. The cooled reaction mixture was eluted through an alumina pad with 50% ether in light petroleum and the eluant evaporated. The residue was purified by preparative t.l.c. (light petroleum) and the main band afforded 2-(3-methylbut-1-ynyl)biphenyl(186) as a colourless liquid (0·012g., 62%):

n.m.r.(CCl_4)τ: 2·4-3·0(m) aromatic (9H); 7·44(m) isopropyl (1H); 8·94(d, 7Hz.) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 2250(m) C≡C; 1320(s) isopropyl; 760(s), 740(s), 700(s) monosubstitution and 1,2-disubstitution.

u.v.(EtOH)mμ: 234·0 (ε = 20,300); shoulder at 256·0.

(P)m/e: Found, 220·12496; calcd. for $C_{17}H_{16}$, 220·12519.

Analysis: Found, C, 92·9; H, 7·35; calcd. C, 92·68; H, 7·32%.

(c) Attempted dehydrogenation of 3-isopropenyl-3,4,5,6,7,8-hexahydro-1,2-benzazulene(178) with o-chloranil.

The hexahydrobenzazulene(178), (0·035g., 0·16 mmol.) and o-chloranil (10 mol. equivalent) in sodium dried benzene (15 ml.) were warmed at 40-50° for 0·5 hr. under nitrogen. The cooled mixture was eluted through an alumina pad with ether and the eluant evaporated. The dark residue was applied to a preparative t.l.c. plate and eluted with 5% ether in light petroleum. A blue coloured band co-eluted with multiple colourless and yellow bands, the partially

resolved blue band being collected as a dark viscous oil (8 mg.). Analytical t.l.c. (3% ether in light petroleum) indicated the blue material to be heavily contaminated with impurities. The n.m.r. spectrum of this material showed no evidence for the expected 3-isopropenyl-1,2-benzazulene(185) and the mass spectrum showed no parent peak at m/e:218.

(d) Attempted dehydrogenation of the hexahydrobenzazulene(178) with palladium-charcoal.

The thermal rearrangement product (section 6.5.13) containing the hexahydrobenzazulene (0·60g., 75%) was passed through the flow system, packed with a mixture of 10% palladium-charcoal and fibrous asbestos, at 450°/0·01 mm. The initial distillate was colourless but was followed by a blue-green viscous liquid. The total distillate (0·52g.) was taken up in light petroleum (25 ml.) and extracted (3 x 15 ml.) with syrupy phosphoric acid. The combined acid extracts were washed with light petroleum (3 x 10 ml.) then poured onto water (100 ml.). The organic material was taken up in light petroleum (3 x 15 ml.), washed with water (15 ml.), dried and the solvent evaporated to give a blue-green residue (0·33g.). A sample of this material was processed by preparative t.l.c. as described in (c) above but no benzazulene was detected (n.m.r., m.s.).

6.6.5 Concerning the products obtained by rearrangement of the 1-(p-tolyl)cyclopentene adduct(188).

(a) Oxidation of the 2-(2-methylprop-1-enyl)-1-(p-tolyl)cyclohexadienes(189a,b) with D.D.Q.

The distilled acid catalysed rearrangement product (section 6.5.14) containing the cyclohexadienes(189a,b), (42%), the biphenyl(191), (52%) and the ethynylcyclopentene(190), (3%) was oxidised directly as follows. The hydrocarbon mixture (0·220g., 1 mmol.) and D.D.Q. (1·5 mol. equivalent) in benzene (20 ml.) were gently refluxed on a water bath for 3 hr. The cooled mixture was eluted through an alumina pad (50% ether in light petroleum) and the eluant evaporated. Examination by v.p.c. (135°) indicated the biphenyl(191) to be the only volatile component present. The residue was applied to a preparative t.l.c. plate (2 mm. layer) and eluted with 12% ether in light petroleum. The first band gave 2-isobutyl-4'-methylbiphenyl(191) as a colourless liquid (0·101g., (45·5%):

n.m.r.(CCl_4)τ: 2·92(m) aromatic (8H); 7·56(d, 7Hz.) methylene (2H); 7·62(s) aryl methyl (3H); 8·35(m) isopropyl (1H); 9·26(d, 7Hz.) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 830(s), 760(s), 740(s) 1,2- and 1,4-disubstitution.

u.v.(EtOH)mμ: 237·5 (ε = 9,900)

(P)m/e: Found, 224·15671; calcd. for $C_{17}H_{20}$, 224·15649.

Analysis: Found, C, 91·3; H, 9·23; calcd., C, 91·01; H, 8·99%.

The second band gave a pale yellow viscous oil which was crystallised from 5% benzene in light petroleum to give α-methyl-2-(p-tolyl)-cinnamaldehyde(252) as a colourless solid (m.p. 55-6°; 0·078g., 31%):

n.m.r.(CCl_4)τ: 0·64(s)aldehydic (1H); 2·6-2·9(m) aromatic (8H); 2·92(m) olefinic (1H); 7·61(s) aryl methyl (3H); 8·03(d, 2Hz.) methyl (3H).

i.r.(CS_2)$cm.^{-1}$: 1680(s) C=O; 820(s), 750(s) 1,2- and 1,4-disubstitution.

u.v.(EtOH)mμ: 250·0 (ε = 10,300).

(P)m/e: Found, 236·11978; calcd. for $C_{17}H_{16}O$, 236·12011.

(b) Oxidation of 2-isobutyl-4'-methylbiphenyl(191) with D.D.Q.

The biphenyl(191), (0·205g., 0·91 mmol.) and D.D.Q. (3 mol. equivalent) in sodium dried benzene (20ml.) were refluxed on a water bath for a total of 60 hr. under nitrogen. The reaction mixture was then treated as in (a) above. The leading band from preparative t.l.c. gave the original biphenyl(191), (0·098g., 48%) identified by v.p.c.(135°) and its n.m.r. spectrum. The second band afforded α-methyl-2-(p-tolyl)cinnamaldehyde(252), (0·033g., 15·5%), identical to the sample obtained in the previous experiment (i.r., n.m.r.).

(c) Lemieux oxidation of the cyclohexadienes(189a,b).

The following solutions were available:

Solution A: sodium metaperiodate (0·02 molar).

Solution B: potassium permanganate (0·005 molar).

Solution C: potassium carbonate (0·05%).

A reaction mixture of the cyclohexadienes(189a,b), (0·10g., 0·45 mmol.), solution A(180 ml.), solution B(18 ml.), solution C(30 ml.) and Analar acetone (50 ml.) was gently refluxed for 10 hr. The

reaction mixture was cooled and the precipitated manganese dioxide filtered off, the basic filtrate extracted with methylene chloride (2 x 20 ml.), and the extract dried and evaporated. The resulting red viscous oil (0·071g.) was purified by preparative t.l.c. (20% ether in light petroleum). The leading band gave hydrocarbon material (0·048g.). The second band gave a yellow viscous oil (0·010g.), the mass spectrum of which had the parent ion at m/e:196 corresponding to 2-(p-tolyl)benzaldehyde (M.W.,196).

The aqueous solution was acidified with dilute hydrochloric acid and extracted with methylene chloride (2 x 20 ml.), the combined extracts dried and the solvent evaporated to give a buff solid (0·021g.). The mass spectrum of this material indicated parent ions at m/e: 212, 192 and 136 corresponding to 2-(p-tolyl)benzoic acid (M.W., 212), β-(p-methylbenzoyl)propionic acid (M.W., 192) and p-toluic acid (M.W., 136).

6.6.6. Concerning the products obtained by rearrangement of the 4-methyl-1,2-dihydronaphthalene adduct(214).

(a) Reaction of 1-methylene-2(3-methylbut-1-ynyl)tetralin(215) with hydrochloric acid.

The ethynyltetralin(215), (0·055g., 0·26 mmol.), dissolved in ether (10 ml.), was vigorously shaken with 38% hydrochloric acid (15 ml.) for 3 hr. The yellow mixture was poured onto water (40 ml.) and extracted with light petroleum (3 x 15 ml.). The combined extracts were dried, the solvent evaporated and the residue purified by preparative t.l.c. (light petroleum). The main band

gave the product as a colourless liquid (0·051g., 79%) which was unstable to v.p.c. (135°). Analysis of the n.m.r. spectrum showed this material to be a mixture of two configurational isomers namely, 2-(1-chloro-3-methyl-trans-but-1-enyl)-1-methyl-3,4-dihydronaphthalene(216a) and 2-(1-chloro-3-methyl-cis-but-1-enyl)--1-methyl-3,4-dihydronaphthalene(216b) in the ratio 1:1. No attempt was made to separate these isomers but proton allocations in the n.m.r. spectrum were confirmed by complete spin-spin decoupling, assuming the olefinic proton of the cis-isomer to be downfield relative to that of the trans-isomer:

n.m.r.(CCl_4)τ: 2·7-3·0(m) aromatic (4H); 4·51(d, 10Hz.), 4·68(d, 9Hz.) cis- and trans-olefinic resp. (0·5H,0·5H); 7·24(m) benzylic and trans-isopropyl (2·5H); 7·60(m) methylene and cis-isopropyl (2·5H); 7·92(m) allylic methyl (3H); 8·92(d, 7Hz.), 9·02 (d, 7Hz.) trans- and cis-dimethyl resp. (3H,3H).

i.r.(film)cm.$^{-1}$: 1650(w), 1620(m) C=C; 800(m) C=CH; 760(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 221·0 (ε = 16,900); 276·0 (ε = 13,400).

(P)m/e: Found, 246·11710, 248·11469; calcd. for $C_{16}H_{19}{}^{35}Cl$, 246·11752, ^{37}Cl, 248·11457.

(b) Acid catalysed rearrangement of the 4-methyl-1,2-dihydronaphthalene adduct(214).

The acid catalysed rearrangement was carried out exactly as described (section 6.5.1) with 2,3-benzo-7-dimethylvinylidene-1-methylbicyclo[4,1,0]hept-2-ene(214), (0·50g.). The crude product was distilled to give a yellow liquid (b.p. 90-6°/0·01 mm.; 0·42g.). This material was not resolved by t.l.c. (light petroleum). The n.m.r. spectrum showed this to contain (ca. 60% of total) the trans-isomer(216a) and the cis-isomer(216b) in the ratio 1:1 as obtained in (a) above, together with some unidentified components. This material was unstable to v.p.c. (135°).

(c) Dehydrogenation of the trans(216a) and cis(216b) isomer mixture with o-chloranil.

The mixture of isomers(216a,b), (0·040g., 0·16 mmol.) obtained in (a) above and o-chloranil (2 mol. equivalent) in benzene (15 ml.) were gently refluxed for 12 hr. The cooled mixture was eluted through an alumina pad (50% ether in light petroleum), the eluant evaporated and the residue purified by preparative t.l.c. (petrol). The main band gave the product as a colourless liquid (0·029g., 73%). Analysis of the n.m.r. spectrum showed this to be a 1:1 mixture of the expected isomers namely, 2-(1-chloro-3-methyl-trans-but-1-enyl)-1-methylnaphthalene (217a) and 2-(1-chloro-3-methyl-cis-but-1-enyl)-1-methylnaphthalene(217b). The proton allocations in the n.m.r. spectrum were

confirmed by spin-spin decoupling:

n.m.r.(CCl_4)τ: 2·0-2·8(m) aromatic (6H); 4·20(d, 10Hz.), 4·54(d, 8Hz.) cis- and trans-olefinic resp. (0·5H, 0·5H); 7·04(m) trans-isopropyl (0·5H); 7·34(s) aromatic methyl (3H); 7·95(m) cis-isopropyl (0·5H); 9·88(d, 7Hz.), 9·09(d, 7Hz.) trans- and cis-dimethyl resp. (3H,3H).

i.r.(film)cm.$^{-1}$: 820(s), 800(s),780(s), 750(s) 1,2-di and 1,2,3,4-tetrasubstitution.

u.v.(EtOH)mμ: 230·0 (ε = 57,600); 283·0 (ε = 6,000).

(P)m/e: Found, 244·10178, 246·09881; calcd. for $C_{16}H_{17}{}^{35}Cl$, 244·10187, ^{37}Cl, 246·09892.

(d) Reaction of the ethynyltetralin(215) with aqueous sulphuric acid, aqueous phosphoric acid and glacial acetic acid.

The ethynyltetralin(215), (0·040g., 0·19 mmol.), dissolved in ether (10 ml.), was vigorously shaken with 50% aqueous sulphuric acid (15 ml.) for 0·5 hr. The red mixture was poured onto water (40 ml.) and extracted with light petroleum (3 x 15 ml.). The combined extracts were washed with water (20 ml.), dried and the solvent evaporated. The residue was purified by preparative t.l.c. (5% ether in light petroleum) to give 2-(3-methylbutyryl)-1-methyl-3,4-dihydronaphthalene(219), a colourless liquid (0·022g., 50%), as the only product which was pure by v.p.c. (135°):

n.m.r.(CCl_4)τ: 2·6-3·0(m) aromatic (4H); 7·32(m) benzylic (2H); 7·5-7·9(m) methylenes and isopropyl (5H); 7·86(m)

allyl methyl (3H); 9·08(d, 7Hz.) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 1780(s) C=O; 1600(m) C=C; 760(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 227·0 (ε = 10,900); 290·0 (ε = 10,900).

(P)m/e: Found, 228·15083; calcd. for $C_{16}H_{20}O$, 228·15141.

A similar experiment with 89% phosphoric acid gave the ketone(219), (55%).

A similar experiment with glacial acetic acid, but shaking the reaction mixture for 3 hr., gave starting material only (v.p.c., n.m.r.).

Distillation of the ethynyltetralin(215) from a small amount of p-toluenesulphonic acid similarly afforded only unchanged starting material.

(e) Dehydrogenation of the ketone(219) with o-chloranil.

The ketone(219), (0·041g., 0·18 mmol.) and o-chloranil (2 mol. equivalent) in benzene (15 ml.) were gently refluxed for 12 hr., cooled, eluted through an alumina pad (50% ether in light petroleum) and the eluant evaporated. The residue was purified by preparative t.l.c. (5% ether in light petroleum) whereupon the main band afforded a viscous oil which was crystallised from light petroleum (40-60°). 1-Methyl-2-(3-methylbutyryl)naphthalene(220) was obtained as a colourless solid (m.p. 48-50°; 0·028g., 69%):

n.m.r.(CCl_4)τ: 2·00(m), 2·2-2·7(m) aromatic (1H,5H); 7·33(d, 6Hz.) methylene (2H); 7·37(s) aryl methyl (3H); 7·74(m)

isopropyl (1H); 9·06(d, 7Hz.) dimethyl (6H).

i.r.(nujol)cm.$^{-1}$: 1780(s) C=O; 830(s), 770(s), 760(s) 1.2-di and 1,2,3,4-tetrasubstitution.

u.v.(EtOH)mμ: 225·0 (ε = 51,400); 245·0 (ε = 51,600); 286·0 (ε = 11,700).

(P)m/e: Found, 226·13592; calcd. for $C_{16}H_{18}O$, 226·13576.

Analysis: Found, C, 84·96; H, 7·81; calcd., C, 84·91; H, 8·02%.

6.7 INDEPENDENT SYNTHESES OF REACTION PRODUCTS AND SYNTHESIS OF MODEL COMPOUNDS.

6.7.1 Preparation of 9-fluorenylidene-acetaldehyde(239).

The acetaldehyde(239) was prepared from fluorenone as described by Hennion and Fleck.[121] 9-Ethynyl-9-fluorenol was first obtained as pale yellow needles (m.p. 107-8°, lit.[121] 1-7-8°; 79·5%) from carbon tetrachloride. This was converted to 9-fluorenylidene-acetaldehyde which was collected as orange-yellow needles (m.p. 115·5-117·5°, lit.[121] 116·5-117·5°; 62·5%) from aqueous ethanol:

n.m.r.(CCl_4)τ: -0·71(d, 7·5Hz.) aldehydic (1H); 2·0-2·8(m) aromatic (8H); 3·30(d, 7·4Hz.) olefinic (1H).

i.r.(CS_2)cm.$^{-1}$: 1660(s) C=O; 780(s), 730(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 225·0 (ε = 26,000); 258·0 (ε = 36,100); 267·5 (ε = 55,000); 279·0 (ε = 11,200); 290·0 (ε = 10,600); 335·0 (ε = 15,400).

6.7.2 Synthesis of α-(9-fluorenylidene)propionaldehyde(240).

(a) Reformatsky reaction.

This preparation was carried out under nitrogen. The zinc wool employed in this reaction was activated by washing briefly with 10% hydrochloric acid followed by ethanol and finally ether. Activated zinc wool (6·6g., 0·11 mol.) was placed in a 250 ml. 3-necked flask equipped with stirrer, dropping funnel and condenser. A solution of fluorenone (18·0g., 0·10 mol.) and ethyl α-bromopropionate (21·6g., 0·12 mol.) in sodium dried benzene (100 ml.) was placed in the dropping funnel and ca. 25 ml. run into the reaction flask. A crystal of iodine was added and the mixture gently refluxed until the reaction started (10 min.). The remainder of the solution was then slowly added (1·5 hr.) with vigorous stirring, maintaining reflux by external heating as required. When the zinc had dissolved the mixture was allowed to cool to room temperature and sufficient 15% hydrochloric acid added to dissolve the zinc salts. The organic material was extracted into ether (3 x 60 ml.) and the combined extracts washed with 10% sulphuric acid (50 ml.), saturated sodium bicarbonate solution (50 ml.) and water (50 ml.). The organic layer was dried and the solvent evaporated to give the crude carbinol as a yellow oil.

The carbinol was dehydrated directly by refluxing with glacial acetic acid (250 ml.) and p-toluenesulphonic acid (2g.) for 20 hr., most of the solvent was removed under reduced pressure, the residue poured onto water (100 ml.), the organic material extracted into ether (3 x 60 ml.), the combined extracts washed with saturated

sodium bicarbonate solution (3 x 60 ml.) followed by water (100 ml.), and dried. Evaporation of the solvent gave crude ethyl α-(9-fluorenylidene)propionate as a red oil which was hydrolysed directly by refluxing with aqueous 2N sodium hydroxide (250 ml.) and ethanol (50 ml.) for 1·5 hr. The cooled reaction mixture was extracted with chloroform (3 x 80 ml.), the combined extracts dried and evaporated to give unchanged fluorenone (12g., 66·6%). The aqueous solution was acidified with concentrated hydrochloric acid, the crude product collected, washed thoroughly with water and dried. Crystallisation from aqueous acetic acid gave α-(9-fluorenylidene)-propionic acid(243) as a pale yellow solid (m.p. 177-9°; 6·0g., 78·5% based on unrecovered fluorenone):
n.m.r.(T.F.A.)τ: 2·3-2·9(m) aromatic (8H); 7·50(s) methyl (3H):
i.r.(nujol)cm.$^{-1}$: 1680(s) C=O; 790(s), 740(s) 1,2-disubstitution.
(P)m/e: Found, 236·08370; calcd. for $C_{16}H_{12}O_2$, 236·08372.
Analysis: Found, C, 81·20; H, 5·01; calcd., C, 81·34; H, 5·12%.

(b) Reduction via. the Acyl Aziridine.

The method is an adaptation of that used by Irving.[143] α-(9-Fluorenylidene)propionic acid(243), (2·36g., 0·01 mol.) and an excess of thionyl chloride (15 ml.) were heated on a water bath for 0·5 hr. The excess of thionyl chloride was then removed under reduced pressure. A solution of the resultant crude acid chloride in sodium dried ether (25 ml.) was added over 20 min. to a stirred mixture of triethylamine (1·01g., 0·01 mol.), ethyleneimine (0·04g., 0·01 mol.) and dry ether (30 ml.) cooled to 0-1°, and the mixture

stirred for a further 30 min. The precipitated triethylamine hydrochloride was filtered off, washed with ether (30 ml.) and the total filtrate collected. This material, containing the acyl aziridine, was cooled to 0-1° in an ice bath and a suspension of lithium aluminium hydride (0·08g., 0·002 mol.) in dry ether (15 ml.) added during 15 min. and stirring continued for a further 30 min. The reaction mixture was hydrolysed with 5% sulphuric acid and the product extracted into ether (3 x 50 ml.), the combined extracts washed with 10% sulphuric acid (50 ml.), water (50 ml.), saturated sodium bicarbonate solution (50 ml.), water (50 ml.) and dried. Evaporation of the solvent afforded a yellow viscous oil which was applied to a silicagel column and the product eluted with 15% ether in light petroleum. Crystallisation from 5% benzene in light petroleum gave α-(9-fluorenylidene)propionaldehyde(240) as a yellow solid (m.p. 131-3°; 0·23g., 10·5%), identical (i.r., u.v., n.m.r.) to the material obtained previously (section 6.6.3.).

The bulk of the material was only eluted from the column with chloroform and methanol and examination by t.l.c. indicated several partially resolved components, none of which were identified.

6.7.3 Preparation of 9-isopropylidenefluorene(183).

The isopropylidenefluorene(183) was prepared from fluorene as described by Kice.[101] The product(183) was collected as buff needles (m.p. 112-115°, lit.[101] 113-116°; 54·5%) from methanol:

n.m.r.(CCl_4)τ: 7·66(s) dimethyl.

u.v.(EtOH)mμ: 233·0 (ε = 45,500); 249·0 (ε = 25,800); 258·5 (ε = 32,600); 272·0 (ε = 16,200); 281·0 (ε = 16,800); 302·5 (ε = 11,700); 317·5 (ε = 11,700).

6.7.4 Preparation of 9-isopropylfluorene(181).

(a) 9-Cyanofluorene

This was prepared from fluorene by the method of Wislicenus and Rus.[144] 9-Formylfluorene was obtained as a yellow viscous liquid (b.p. 112-14°/0·05 mm., lit.[144] 138-40°/0·05 mm.; 62%). This was converted to the oximes, a mixture of the α- and β-isomers, which were obtained as colourless plates (m.p. 130-45°, lit.[144] 130-45°; 90·5%). These were converted to 9-cyanofluorene, pale yellow needles (m.p. 151-2°, lit.[144] 151-2°; 54·5%).

(b) 2'-Methylcyclopropane-1'-spiro-9-fluorene(184).

This was prepared from 9-cyanofluorene by the method of Greenhow and McNeil.[102] The crude product was purified by elution through an alumina column (light petroleum) followed by crystallisation from methanol. The fluorene(184) was obtained as colourless plates (m.p. 96-7°, lit.[102] 97-8°; 66%).

(c) Catalytic hydrogenation.

The spiro-fluorene(184) was hydrogenated over 10% palladium-charcoal as described.[102] 9-Isopropylfluorene(181)

was obtained as colourless plates (m.p. 52-4°, lit.[145] 53-5°; 90%) from methanol.

6.7.5 Synthesis of 9,9-dimethyl-9,10-dihydrophenanthrene(230) and 2-(2-methylprop-1-enyl)biphenyl(200) and 2-isobutylbiphenyl(199)

(a) o-Phenylbenzaldehyde.

o-Phenylbenzoic acid was prepared from fluorene by the method of Hey, Leonard and Rees.[146] (m.p. 111-12°, lit.[146] 112-13°; 90%). This was converted to the methyl ester which was obtained as a colourless liquid (b.p. 98-100°/0·01 mm., lit.[127] 308°; 92%). The aldehyde was prepared from this ester by a McFadyen-Stefen reaction as described by Cook et al.[147] The hydrazide (m.p. 134-6°, lit.[147] 136·5°; 72·5%) was converted to the benzenesulphonyl-hydrazide (m.p. 173-5°, lit.[147] 175·5°; 95%) which afforded o-phenylbenzaldehyde as a colourless liquid (b.p. 98-9°/0·05 mm., lit.[147] 162°/12 mm.; 81%; 1690 cm.$^{-1}$(s), C=O; 0·16τ(s), aldehydic proton).

(b) 2-(2-methylpropanyl-1-ol)biphenyl(228).

The Grignard reagent was prepared from isopropyl bromide (8·6g., 0·07 mol.) and magnesium turnings (1·9g., 0·08 mol.) in sodium dried ether (100 ml.), under nitrogen. A solution of o-phenylbenzaldehyde (9·1g., 0·05 mol.) in dry ether (50 ml.) was then added to the cooled (10°) Grignard reagent (20 min.). The reaction mixture was allowed to stand overnight then hydrolysed with saturated ammonium chloride solution. The product was extracted

into ether (3 x 100 ml.), the combined extracts washed with water (100 ml.), dried and the solvent evaporated to give the crude carbinol (228) which was dehydrated directly.

(c) Dehydration with p-toluenesulphonic acid.

The carbinol(228), obtained in (b) above, was distilled from p-toluenesulphonic acid (50 mg.) in the presence of glass wool (b.p. 98-100°/0·05 mm.). Examination of the crude product by n.m.r. and v.p.c. (135°) showed it to contain 95% of 9,9-dimethyl-9,10-dihydrophenanthrene(230) and 5% of 9-isopropylfluorene(181), the latter being identified by comparison with an authentic sample. The distillate was crystallised from methanol to give the phenanthrene(230) as a colourless solid (m.p. 64-5°; 6·2g., 60% based on the aldehyde):

n.m.r.(CCl_4)τ: 2·44(m), 2·88(m) aromatic (2H,6H); 7·33(s) methylene (2H); 8·81(s) dimethyl (6H).

i.r.(nujol)$cm.^{-1}$: 770(s), 740(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 266·0 (ε = 18,600); shoulder at 290·0; 300·5 (ε = 4,600).

(P)m/e: Found, 208·12531; calcd. for $C_{16}H_{16}$, 208·12519.

Analysis: Found, C, 92·54; H, 7·60; calcd., C, 92·26; H, 7·74%.

The low temperature n.m.r.(CS_2) spectrum showed no change in structure down to -80°.

(d) Dehydration with potassium bisulphate.

The carbinol(228), (1·0g.), obtained in (b) above, and potassium bisulphate (5g.) were heated on an oil bath at 160° for

0·5 hr. The cooled residue was extracted with light petroleum (100 ml.), the extract washed with water, dried and evaporated. Distillation of the residue afforded a colourless liquid (b.p. 92-4°/ 0·01 mm.; 0·7 g.). Examination of this material by n.m.r. and v.p.c. (135°) showed it to contain 48% of the phenenthrene(230), 48% of the biphenyl(200) and 4% of 9-isopropylfluorene(181) by comparison with authentic samples.

(e) Dehydration via. Chugaev elimination.

The method was based upon that of Delahunt.[103] The crude carbinol(228), (7·5g., 0·033 mol.), obtained in (b) above, sodium hydride (0·8g., 0·033 mol.) and sodium dried ether (100 ml.) were refluxed under nitrogen for 2 hr. Carbon disulphide (2·6 g., 0·033 mol.) was then added and refluxing continued for 2·5 hr., during which time a bulky white precipitate separated. Methyl iodide (4·8g., 0·033 mol.) was added and the reaction mixture refluxed for a final 2·5 hr., the bulky white precipitate being replaced by a fine white suspension. The reaction mixture was cautiously hydrolysed with water (100 ml.), the organic layer separated, washed with water (100 ml.), dried and evaporated to give the crude xanthate as a yellow oil.

This material was pyrolysed by heating in an open flask on an oil bath. Decomposition started near 140° and the reaction was complete when the temperature had reached 180°. The dark residue was applied to an alumina column and the crude product (1·9g.) eluted with light petroleum, the original carbinol(228), (3·5g., 46·5%) being eluted with 1% ether in light petroleum.

Material eluting with chloroform and methanol was a mixture, by t.l.c. examination. The crude product was further purified by application to a silicagel column and careful elution with light petroleum. The product was finally distilled to give 2-(2-methyl-prop-1-enyl)biphenyl(200) as a colourless liquid (b.p. 71-2°/0·01 mm., 1·0g., 27% based on recovered carbinol). This material was identical (v.p.c., i.r., u.v., n.m.r.) to the sample obtained previously (section 6.6.3g).

(f) Catalytic hydrogenation of the olefinic biphenyl(200).

The biphenyl(200), (0·30g., 0·14 mmol.) in ethanol (25 ml.) was hydrogenated over 10% palladium-charcoal (50 mg.) at atmospheric pressure and room temperature. The mixture was filtered, the solvent evaporated and the residue distilled to give 2-isobutyl-biphenyl(199) as a colourless liquid (b.p. 79-80°/o·ol mm.; 0·25g., 82·5%).

n.m.r.(CCl_4)τ: 2·82(m) aromatic (9H); 7·56(d, 7Hz.) methylene (2H); 8·37(m) isopropyl (1H); 9·28(d, 7Hz.) dimethyl (6H).

i.r.(film)cm.$^{-1}$: 760(s), 700(s) mono and 1,2-disubstitution.

u.v.(EtOH)mμ: 234·0 (ε = 7,600).

(P)m/e: Found, 210·14077; calcd. for $C_{16}H_{18}$, 210·14084.

Analysis: Found, C, 91·5; H, 9·02; calcd. C, 91·37; H, 8·63%.

6.7.6 Synthesis of 2-(3-methylbut-1-ynyl)biphenyl(186).

(a) 2-(3-Methyl-trans-but-1-enyl)biphenyl(227).

The Grignard reagent was prepared from isobutyl bromide (9·6g., 0·07 mol.) and magnesium turnings (1·9g., 0·08 mol.) in

sodium dried ether (100 ml.), under nitrogen. A solution of o-phenylbenzaldehyde (9·1g., 0·05 mol.) in dry ether (50 ml.) was then added to the cooled (10°) isobutyl magnesium bromide during 20 min. and the reaction mixture allowed to stand overnight. A similar work up to that previously described (section 6.7.5b) afforded crude 2-(3-methylbutanyl-1-ol)biphenyl(226) as a yellow oil. This carbinol was dehydrated by heating at 160° for 40 min. with potassium bisulphate (45g.) as already described for a related system (section 6.7.5d). Distillation of the crude dehydration product yielded the trans-biphenyl(227) as a colourless liquid (b.p. 88-90°/0·01 mm.; 7·2g., 64·5%) which was crystallised from light petroleum to give colourless plates (m.p. 41-2°, lit.[148] 41-2°; 980 cm.$^{-1}$(s), trans HC=CH; J_{trans}, 16 Hz.).

(b) Bromination and dehydrobromination.

Bromine (0·8g., 5 mmol.), dissolved in carbon tetrachloride (5 ml.), was added dropwise (15 min.) to a magnetically stirred solution of the trans-olefin(227), (1·1g., 5 mmol.) in carbon tetrachloride (10 ml.) at room temperature. The solvent was removed under reduced pressure to afford the crude dibromide as a viscous oil. This material was dehydrobrominated by refluxing for 15 min. with 5N ethanolic potassium hydroxide (10 ml.). The very dark mixture was poured onto water (30 ml.) and the product extracted into light petroleum (3 x 50 ml.), some insoluble material being discarded. The combined extracts were washed with water (50 ml.), dried, the solvent evaporated and the residue distilled to

give a pale yellow liquid (b.p. 92-4°/0·01 mm.; 0·64g.). This material was applied to a preparative t.l.c. plate (2 mm. layer) and eluted with light petroleum. The leading band (0·30g.) had a complex n.m.r. spectrum and was not identified. The second band was distilled to give the ethynylbiphenyl(186) as a colourless liquid (b.p. 91-2°/0·01 mm.; 0·28g., 25·5%) which was identical (i.r., u.v., n.m.r.) to the sample obtained previously (section 6.6.4b).

6.7.7 Synthesis of 2-isobutyl-4'-methylbiphenyl(191).

(a) 2-(p-tolyl)cyclohexanone

This ketone was prepared from (p-tolyl)cyclohexene (17·2g., 0·1 mol.) by a standard hydroboration procedure.[149] The carbinol, 2-(p-tolyl)cyclohexanol, was oxidised directly by a standard method[150] and the crude product crystallised from petroleum (60-80°) to give 2-(p-tolyl)cyclohexanone as a colourless solid (m.p. 50-1°, lit.[151] 50·5-51·5°; 6·1g., 32·5%).

(b) Grignard reaction and dehydrogenation.

1-Isobutyl-2-(p-tolyl)cyclohexene was prepared from 2-(p-tolyl)cyclohexanone (1·9g., 0·01 mol.), isobutyl bromide (2·7g., 0·02 mol.) and magnesium turnings (0·5g., 0·02 mol.) by the general method previously described for trans-β-methylstyrene (section 6.3). The crude dehydration product was applied to an alumina column and the olefin (0·25g.) eluted with light petroleum. Elution with 50% ether in light petroleum gave recovered

2-(p-tolyl)cyclohexanone (1·5g., 79%). The olefin was not further purified but was dehydrogenated by the method of Benkeser, Schroeder and Thomas.[152] The crude olefin (0·23g., ca. 1 mmol.), dissolved in carbon tetrachloride (10 ml.), was brominated with a solution of bromine (0·16g., 1 mmol.) in carbon tetrachloride (5 ml.) at room temperature. The crude dibromide, obtained as a viscous liquid after evaporation of the solvent, was distilled under reduced pressure whereupon hydrogen and hydrogen bromide were eliminated. The distillate was redistilled to give 2-isobutyl-4'-methylbiphenyl(191) as a colourless liquid (b.p. 91-2°/0·01 mm.; 0·16g., 34% based on unrecovered ketone). This material was identical (v.p.c., i.r., u.v., n.m.r.) to the sample obtained previously (section 6.6.6a).

A similar experiment carried out with 2-phenylcyclohexanone and isobutyl magnesium bromide gave recovered ketone (95%) only. Addition of the ketone to the Grignard reagent resulted in liberation of a considerable amount of volatile material (presumably isobutane) in both these reactions.

6.7.8 Preparation of 2-methyl-1-(β-naphthyl)prop-1-ene(207).

The olefin(207) was prepared from β-naphthaldehyde (3·1g., 0·02 mol.), isopropyl bromide (3·7g., 0·03 mol.) and magnesium (1·0g., 0·04 mol.) by a Grignard reaction similar to that previously described for trans-β-methylstyrene (section 6.3). Distillation of the dehydration product afforded the naphthalene(207) as a colourless liquid (b.p. 85-6°/0·05 mm., lit.[153] 85-90°/0·3 mm.; 2·0g.,

55%) which was identical (v.p.c., i.r., n.m.r.) to the sample obtained previously (section 6.5.17).

6.7.9 Synthesis of 2-(2-methylprop-1-enyl)-1-methylnaphthalene(210).

(a) 2-Bromo-1-methylnaphthalene.

This was prepared from 3-methylindene, bromoform and potassium t-butoxide as described by Parham et al.[32] The crude product was distilled to give a pale yellow liquid (b.p. 83-6°/ 0·05 mm.; 95·5%) which solidified and was crystallised from light petroleum to give 2-bromo-1-methylnaphthalene as colourless plates (m.p. 55-7°, lit.[32] 55-7°; 90·5%).

(b) Grignard reaction.

The olefin(210) was prepared from 2-bromo-1-methyl-naphthalene (4·4g., 0·02 mol.), isobutraldehyde (2·2g., 0·03 mol.) and magnesium (1·0g., 0·04 mol.) by a similar technique to that described for trans-β-methylstyrene (section 6.3). Distillation of the crude dehydration product gave the olefinic naphthalene(210) as a colourless liquid (b.p. 81-2°/0·01 mm.; 2·6g., 65%), identical (v.p.c., i.r., n.m.r.) to the sample obtained previously (section 6.5.19).

6.7.10 Synthesis of 1-methyl-2-(3-methylbutyryl)naphthalene(220).

The carbinol was prepared from 2-bromo-1-methylnaphthalene (11·0g., 0·05 mol.), isovaleraldehyde (4·3g., 0·05 mol.) and magnesium (1·7g., 0·07 mol.) by a Grignard reaction similar to that previously described (section 6.7.5b). The crude carbinol was

oxidised as follows. To a stirred solution of the carbinol in benzene (50 ml.), cooled (10-12°) on an ice bath, was added a solution of sodium dichromate dihydrate (6·0g.) in water (25 ml.), concentrated sulphuric acid (8 ml.) and glacial acetic acid (2·5 ml.), during an hour, and the reaction mixture stirred for a further hour at this temperature. The mixture was poured onto water (200 ml.), the organic material extracted into light petroleum (2 x 150 ml.), the extracts washed with water (100 ml.), saturated sodium bicarbonate solution (2 x 100 ml.), water and dried. The solvent was evaporated and the residue distilled to give a pale yellow viscous liquid (b.p. 116-117°/0·01 mm.) which solidified. Crystallisation from light petroleum (40-60°) gave the naphthalene(220) as colourless plates (m.p. 49-50°; 6·5g., 60%), identical (i.r., u.v., n.m.r.) to the sample obtained previously (section 6.6.6e).

6.7.11 Synthesis of 1,2-benzo-3-methylcycloheptatriene-5-one(235).

(a) β-Tetralone.

This was prepared from β-naphthol by a Birch reduction as described by Fujimoto, Horton and Zwahlen.[154] The ketone was collected as a colourless liquid (b.p. 127-8°/8mm., lit.[154] 139°/18 mm.; 60·5%).

(b) 1-Methyl-β-tetralone.

This was prepared by a modified enamine alkylation.[155] A mixture of β-tetralone (36·5g., 0·25 mol.), cyclohexylamine

(25·0g., 0·25 mol.) and p-toluenesulphonic acid (50 mg.), dissolved in benzene (300 ml.), was refluxed under a Dean and Stark trap for 4 hr., after which the theoretical amount of water had been collected. The solvent was removed under reduced pressure and the crude imine used without further purification. Ethyl magnesium bromide (0·25 mol.) was prepared in sodium dried tetrahydrofuran, under nitrogen, and a solution of the imine in dry tetrahydrofuran (250 ml.) added (20 min.) at room temperature with stirring. The mixture was refluxed for a further hour after which gas evolution had ceased. Methyl iodide (42·6g., 0·3 mol.) was added (10 min.) to the cool reaction mixture and stirring and refluxing continued for 12 hr. The solvent was partially removed under reduced pressure and the residue (ca. 50% original volume) hydrolysed by refluxing with 10% aqueous hydrochloric acid (600 ml.) for 1·5 hr. The cold mixture was extracted with light petroleum (3 x 200 ml.), the extracts washed with water (200 ml.), dried and the solvent evaporated. The residue was fractionated to give 1-methyl-β-tetralone as a colourless liquid (b.p. 135-8°/18 mm., lit.[156] 138-142°/20 mm.; 28·5g., 70·5%), pure by v.p.c. (135°).

(c) 2-Ethoxy-1-methyl-3,4-dihydronaphthalene(232).

A mixture of 1-methyl-β-tetralone (24·1g., 0·15 mol.), triethyl orthoformate (44·4g., 0·3 mol.) and p-toluenesulphonic acid (50 mg.) was refluxed for 15 min. The crude ketal was then distilled rapidly under reduced pressure (b.p. 90-100°/0·01 mm.) whereupon ethanol was eliminated. The distillate was redistilled to give 2-ethoxy-1-methyl-3,4-dihydronaphthalene(232) as

a colourless viscous liquid (b.p. 93-4°/0·01 mm.; 23·4g., 83%), pure by t.l.c. (1% ether in light petroleum):

n.m.r.(CCl_4)τ: 3·03(m) aromatic (4H); 6·24(q, 7Hz.) ethoxyl methylene (2H); 7·22(m) benzylic (2H); 7·60(m) methylene (2H); 8·08(m) allylic methyl (3H); 8·78(t, 7Hz.) ethoxyl methyl (3H).

i.r.(film)cm.$^{-1}$: 1640(s) C=C; 760(s) 1,2-disubstitution.

u.v.(EtOH)mμ: 275·0 (ε = 7,200).

(P)m/e: Found, 188·12032; calcd. for $C_{13}H_{16}O$, 188·12011.

Analysis: Found, C, 82·73; H, 8·5; calcd., C, 82·93; H, 8·57%.

(d) 1,2-Benzo-4-bromo-5-methoxy-3-methylcyclohepta-1,3,5-triene(212).

The method was based on a general route described by Parham et al.[33]

Bromoform (10·1g., 0·04 mol.) was added (20 min.) to a stirred slurry of potassium t-butoxide (9·3g., 0·05 mol.), 2-ethoxy-1-methyl-3,4-dihydronaphthalene(232), (3·8g., 0·02 mol.) and sodium dried light petroleum (15 ml.) cooled (0-1°) under nitrogen. The dark brown reaction mixture was stirred for 0·5 hr. warming to room temperature. Water (30 ml.) and light petroleum (60 ml.) were added, the mixture filtered, the organic layer separated, washed with water (30 ml.) and dried. Evaporation of the solvent afforded the crude dibromocyclopropane(233) as a brown liquid which was used without further purification.

The dibromocyclopropane(233), silver nitrate (6·8g., 0·04 mol.) and methanol (50 ml.) were stirred (6 hr.) at room temperature during which a brown precipitate separated (silver

bromide). The reaction mixture was filtered, the filtrate poured onto water (200 ml.), the product extracted into light petroleum (2 x 100 ml.), the combined extracts washed with water (100 ml.), dried and evaporated. The yellow viscous residue was applied to an alumina column and eluted with 10% ether in light petroleum to give 1,2-benzo-4-bromo-5-methoxy-3-methylcyclohepta-1,3,5-triene(212) as a colourless viscous liquid (b.p. 119-20°/0·01 mm.; 3·2g., 60·5%).

n.m.r.(CCl_4)τ: 2·6-3·1(m) aromatic (4H); 5·07(q, 8·0, 7·5Hz.) olefinic (1H); 6·60(s) methyl (3H); 7·01(q, 13·5, 8·0Hz.), 7·27(q, 13·5, 7·0Hz.) benzylic (1H,1H); 7·54(s)allylic methyl (3H).

n.m.r.(o-dichlorobenzene)τ: 5·07(t,7·0Hz.) olefinic (1H); [120°;lock:-silicone oil] 7·14(d, 7·0Hz.) benzylic (2H).

Consideration of the frequency separation (25·5 Hz.; 100 MHz. spectrum) and the coalescence temperature (72°) of the two interconverting benzylic protons gave estimates for the rate constant (K; 56·7 $sec.^{-1}$) and the energy barrier ($\Delta G^{\ddagger}$; 17·0 Kcal. $mole^{-1}$) related to the two favourable conformations, the calculation being analogous to that previously described (section 6.5.19).

i.r.(film)$cm.^{-1}$: 1620(s) C=C; 750(s), 760(s) 1,2-disubstitution.

(P)m/e: Found, 264·01403, 266·01230; calcd. for $C_{13}H_{13}O^{79}Br$, 264·01502; ^{81}Br, 266·01305.

(e) 1,2-Benzo-4-bromo-3-methylcyclohepta-1,3-dien-5-one(236).

The bromocycloheptatriene(212),(1·3g., 5 mmol.), dissolved in ether (10 ml.), was shaken with concentrated hydrochloric acid (15 ml.) for 10 min. The mixture was poured onto water (50 ml.), the organic material extracted into light petroleum (3 x 50 ml.), the combined extracts washed with water (50 ml.), dried over anhydrous potassium carbonate and magnesium sulphate and the solvent evaporated. The residue was distilled to give 1,2-Benzo-4-bromo-3-methylcyclohepta-1,3-dien-5-one(236) as a colourless viscous liquid (b.p. 118-20°/0·01 mm.; 1·1g., 84·5%):

n.m.r.(CCl_4)τ: 2·7-2·9(m) aromatic (4H); 7·08(m) benzylic (2H); 7·25(m) methylene (2H); 7·56(s) methyl (3H).

i.r.(film)cm.$^{-1}$: 1680(s) C=O; 770(s), 760(s), 1,2-disubstitution.

(P)m/e: Found, 249·99818; 251·99677; calcd. for $C_{12}H_{11}O^{79}Br$, 249·99937; ^{81}Br, 251·99740.

(f) 1,2-Benzo-3-methylcyclohepten-5-one(234).

The bromocycloheptatriene(212), (1·00g., 4 mmol.), dissolved in cyclohexane (10 ml.), was rapidly added to a stirred solution of sodium (0·92g., 0·04 mol.) in liquid ammonia (100 ml.) and the mixture stirred for 40 min. Sufficient solid ammonium chloride was added to render the mixture colourless, followed by water (50 ml.) and the ammonia allowed to evaporate overnight. The colourless residue was acidified with 20% hydrochloric acid and the organic material extracted into ether (3 x 80 ml.), the combined extracts washed with water (50 ml.), dried and the solvent evaporated.

The yellow residue was applied to an alumina column and the product was eluted with ether. The eluant was evaporated and the residue distilled to give 1,2-Benzo-3-methylcyclohepten-5-one(234) as a colourless liquid (b.p. 76-7°/0·01 mm.; 0·41g., 58·5%):

n.m.r.(CCl_4)τ: 2·90(m) aromatic (4H); 6·8-7·8(m) methylenes and benzylic (7H); 8·65(d, 7Hz.) methyl (3H).

i.r.(film)cm.$^{-1}$: 1700(s) C=O; 770(s) 1,2-disubstitution.

(P)m/e: Found, 174·10420; calcd. for $C_{12}H_{14}O$, 174·10446.

(f) 1,2-Benzo-3-methylcycloheptatrien-5-one(235).

The cycloheptenone(234), (0·35g., 2 mmol.), dissolved in glacial acetic acid (10 ml.), was dibrominated by the slow addition (30 min.) of a solution of bromine (0·64g., 8 mmol.) in glacial acetic acid (8 ml.) at room temperature, the theoretical amount of bromine being absorbed. The pale yellow solution was poured onto water (50 ml.) and the product extracted into ether (3 x 20 ml.), the combined extracts washed with saturated sodium bicarbonate solution (2 x 20 ml.) followed by water (20 ml.), dried and the solvent evaporated. The crude dibromide, 1,2-benzo-4,5-dibromo-3-methylcyclohepten-5-one, was obtained as a clear viscous oil (0·65g.,) and was used without further purification.

The dibromide (0·65g., ca. 2 mmol.), lithium bromide (0·8g.) and lithium carbonate (0·7g.) in dimethyl formamide (25 ml.) were refluxed (30 min.) under nitrogen. The cooled mixture was poured onto water (30 ml.) and carefully neutralised with dilute hydrochloric acid. The product was extracted into ether (4 x 25 ml.),

the combined extracts dried and the solvent evaporated. The dark residue was applied to a silicagel column and progressively eluted with 0-90% ether in light petroleum to give a complex mixture of components (t.l.c.) which were not identified, these fractions containing 80% of the total crude product. The benzotropone(235) was eluted with 100% ether and was further purified by preparative t.l.c. (ether) to give a small amount (0·02g., 6%) of 1,2-benzo-3-methylcycloheptatrien-5-one(235):

n.m.r.(CCl_4)τ: 2·10(m), 2·40(m) aromatic (1H,3H); 2·58(d, 12Hz.) benzylic olefinic (1H); 3·06(m) olefinic (1H); 3·29(q,12·0,2·5Hz.) olefinic (1H); 7·44(d,1Hz.) methyl(3H).

(P)m/e: Found, 170·07314; calcd. for $C_{12}H_{10}$), 170·07316.

6.8 ATTEMPTS TO DETECT A DIRADICAL IN THE THERMAL REARRANGEMENT OF 2-DIMETHYLVINYLIDENE-1-METHYL-1-PHENYLCYCLOPROPANE(137).

6.8.1 Investigation of the thermal rearrangement of the α-methylstyrene adduct(137) in the high temperature n.m.r. probe.

(a) A 20% solution of the adduct(137) in redistilled anisole, containing 5% silicone oil as locking signal, was examined in the high temperature H.A.100 probe. This allowed the olefinic doublet (4·72, 4·85τ) of the thermal rearrangement product, 2-isopropylidene-1-methyl-1-phenyl-3-methylenecyclopropane(138), to be repeatedly scanned and recorded approximately every 4 seconds. The experiment was carried out at 120, 130, 135 and 140° and in no case was an emission (negative) signal observed.

(b) A similar experiment was carried out with neat adduct(137) at 140 and 160° and again only a normal positive signal, of increasing intensity, was observed.

(c) A control experiment was carried out with a system known to exhibit emission characteristics.[93] A solution of dibenzoyl peroxide in cyclohexanone, with silicone oil as lock, was repeatedly scanned over the aromatic region, at 100°. In this case an initially strong emission (negative) peak died to zero and finally became an absorption (positive) signal, as a function of time.

6.8.2 Investigation of the thermal rearrangement of the α-methylstyrene adduct(137) in various solvents.

(a) Hexachlorobutadiene.

A solution of the adduct(137), (0·25g.) in hexachlorobuta-1,2-diene(2·5 ml.) was sealed in a pyrex tube under nitrogen and heated at 140° for 3 hr. in a refluxing xylene bath. Analysis of the dark red reaction product by v.p.c. (100°) showed this to contain the dimethylenecyclopropane(138) and solvent only. The product (0·15g., 60%) was isolated by distillation and further identified by its n.m.r. spectrum (section 6.5.2).

(b) Tetramethylethylene and 1,2-dichloroethylene.

Similar experiments, to that described in (a) above, were carried out with 10% solutions of the adduct(137) in tetramethylethylene and 1,2-dichloroethylene. Analysis (v.p.c., n.m.r.) of

the dark red reaction products showed these similarly to contain the dimethylenecyclopropane(138) and solvent only.

(c) Cumene.

A similar experiment was carried out with a 10% solution of the adduct(137) in redistilled sodium dried cumene. Analysis (v.p.c.; 100°, 135°) of the dark red reaction product showed the dimethylenecyclopropane(138) and cumene to be present. Bicumyl was absent, by direct comparison with an authentic sample supplied by Dr. I.H. Sadler.

(d) Methyl acetylenedicarboxylate.

The adduct(137), (0·20g., 1·1 mmol.) and methyl acetylenedicarboxylate (0·20g., 1·7 mmol.) were sealed in a pyrex tube under nitrogen and heated at 140° for 3 hr. The dark red reaction mixture formed a viscous oil when cooled which was not further investigated.

(e) Ethane-1,2-dithiol.

The adduct(137), (0·25g.) and ethane-1,2-dithiol (1 ml.) were sealed in a pyrex tube under nitrogen and heated at 130° for 3 hr., the reaction mixture in this case remaining pale yellow throughout. Analysis by v.p.c. (100°) showed the adduct(137) to be absent and the mass spectrum showed no parent peaks at m/e:186 or 184. The main peaks occurred at m/e:280, 278 and 237, possibly attributable to an adduct between the dithiol (M.W.,94) and the original adduct(137),(M.W.,184), however attempts to isolate a

pure product by distillation and preparative t.l.c. were unsuccessful.

6.9 ACID CATALYSED REARRANGEMENTS IN DEUTERATED SOLVENTS.

Deuterium oxide and 38% deuterium chloride in deuterium oxide were obtained commercially.

Methanol-d was prepared exactly as described by Strong, Streitwieser and Verbit.[157] The product was distilled directly through a short Vigreux column and methanol-d was collected as a colourless liquid (b.p. 66-66·5°, lit.[157] 66-66·5°; 90%).

A stock solution of approximately 10% deuterium chloride in methanol-d was prepared by twofold dilution of 38% deuterium chloride with methanol-d.

6.9.1 Acid catalysed rearrangement of the indene adduct(206) with deuterium chloride.

The adduct(206), (0·020g., 0·11 mmol.) and 10% deuterium chloride in methanol-d(1 ml.) were refluxed (5 min.) under nitrogen. The mixture was cooled, extracted with Analar carbon tetrachloride (5 ml.), the extract dried over anhydrous potassium carbonate and magnesium sulphate and the solvent evaporated. The n.m.r. spectrum of the residue indicated > 75% replacement by deuterium of the olefinic proton in the product(207):

n.m.r.(CCl_4)τ: 2·3-2·8(m) aromatic (7H); 3·69(s) olefinic (< 0·25H); 8·12(d) dimethyl (6H).

A similar experiment, carried out with 2-methyl-1-(β-naphthyl)prop-1-ene(207), (0·020g., 0·11 mmol.), indicated no replacement of the olefinic proton with deuterium (n.m.r. spectrum).

6.9.2 Acid catalysed rearrangement of the α-methylstyrene adduct(137) with deuterium chloride.

(a) The adduct(137), (0·184g., 1 mmol.) and 10% deuterium chloride in methanol-d (20 ml.) were refluxed (5 min.) under nitrogen. The reaction mixture was cooled, extracted with Analar carbon tetrachloride (2 x 20 ml.), the combined extracts dried over anhydrous potassium carbonate and magnesium sulphate and the solvent evaporated. The product was characterised by formation of the Diels-Alder adduct as previously described (section 6.6.1a). Thus the crude product, maleic anhydride (0·049g., 0·5 mmol.) and sodium dried benzene (15 ml.) were refluxed (4 hr.) under nitrogen. The solvent was evaporated and the residue crystallised from 5% benzene in light petroleum. Examination of the n.m.r. spectrum of the maleic anhydride adduct indicated > 85% replacement by deuterium of the allylic methyl protons (3H) and the bridgehead protons (2H):

n.m.r.(CCl_4)τ: 2·74(m) aromatic (5H); 6·23(s) protons α- to carbonyl (2H); 6·84(m), 7·22(m) bridgehead protons (< 0·15H, <0·15H); 8·06(m) allylic methyl (<0·45H); 8·93(s), 9·02(s) dimethyl (3H,3H).

i.r.(nujol)$cm.^{-1}$: 2200(m) C—D; (P)m/e: 287.

(b) The susceptibility of the cyclopentadiene(160) to deuterium replacement was tested as follows. The vinylidenecyclopropane(137),

(0·184g., 1 mmol.) and 10% ethanolic hydrochloric acid (20 ml.) were refluxed (5 min.) under nitrogen, the product extracted into carbon tetrachloride, the extract dried and evaporated. The residue, containing the crude cyclopentadiene(160), was refluxed (5 min.) with 10% deuterium chloride in methanol-d, under nitrogen, and the product characterised by formation of the maleic anhydride adduct as described in (a) above. The n.m.r. spectrum was identical to that previously described (a).

6.10 DIRECT OXIDATION OF HYDROCARBONS WITH 2,3-DICHLORO-5,6-DICYANOBENZOQUINONE(D.D.Q.).

6.10.1 General method.

A solution of the hydrocarbon (0·5 mmol.), D.D.Q. (molar equivalent as stated) and sodium dried benzene (15 ml.) was stirred at room temperature or refluxed as required. Addition of D.D.Q. to the hydrocarbon in benzene immediately gave a deep green coloration which faded to a pale yellow solution. The reaction mixture was eluted through an alumina pad (to remove the hydroquinone and unreacted D.D.Q.) with 50% ether in light petroleum and the eluant concentrated. The residue was purified by preparative t.l.c. and the products were eluted with 12% ether in light petroleum to give dehydrogenated or the original hydrocarbon as the leading band and oxygenated product as the second band, where applicable. The structures of known products were confirmed by their n.m.r. and i.r. spectra and by comparison with authentic samples.

TABLE III

Hydrocarbon	D.D.Q. (equivalents)	time(hr.) ‡	Recovered original Hydrocarbon, %.	Products (%)
9-isopropenyl-1,2,3,4-tetrahydrofluorene	3	6[a]	0	9-isopropenylfluorene(30) ≠ α-(9-fluorenylidene)propionaldehyde(45)
"	10	2[b]	0	α-(9-fluorenylidene)propionaldehyde(64)
9-isopropenylfluorene	3	6[a]	30	" (40)
"	3	6[b]	0	" (50)
9-isopropylidenefluorene	2	2[a]	0	" (47)
trans-β-methylstyrene	3	4[b]	10(trans)	trans-cinnamaldehyde(53)++
cis- "	9	30[b]	12(cis)	" (27)
allylbenzene	1·5	12[a]	10	" (50)
trans-α,β-dimethylstyrene	2	30[a]	10	β-methyl-trans-cinnamaldehyde[158](20)*
4-phenyl-trans-but-2-ene	1·5	12[a]	15(trans)	1-phenyl-trans-but-1-en-3-ol[159](18)*
α-methylstyrene	3	12[b]	50	nil.
indene	2	30[b]	40	nil.

‡ [a] stirred at room temperature [b] under reflux.

≠ see section 6.6.3b.

++ by n.m.r. comparison with an authentic sample

* for n.m.r. spectrum see section 6.10.2.

6.10.2 Results.

Details of the D.D.Q. oxidation of the cyclohexadienes(198a,b), the biphenyl(191) and the cyclohexadienes(189a,b) have previously been described (sections: 6.6.3g; 6.6.5b; 6.6.5a resp.).

The other results are summarised in table III.

Spectroscopic data.

β-Methylcinnamaldehyde; n.m.r.(CCl_4)τ: -0·18(d, 8Hz.) aldehydic (1H); 2·78(m) aromatic (5H); 3·62(d, 8Hz., further split to multiplets) olefinic trans- to methyl (1H); 7·45(d, 2Hz.) methyl (3H).

1-Phenyl-trans-but-1-en-3-ol; n.m.r.(CCl_4)τ: 2·70(m) aromatic (5H); 3·25(d, 16Hz.) benzylic olefinic (1H); 3·79(q,16,6Hz.) olefinic (1H); 5·54(m) methine (1H); 8·24(s) hydroxyl(1H); 8·64(d, 6Hz.) methyl (3H).

6.11 A KINETIC STUDY OF THE THERMAL REARRANGEMENT OF 2-DIMETHYLVINYLIDENE-1-METHYL-1-PHENYLCYCLOPROPANE(137).

In the following, reactant refers to 2-dimethylvinylidene-1-methyl-1-phenylcyclopropane(137) while product refers to 2-isopropylidene-1-methyl-1-phenylcyclopropane(138).

6.11.1 Solvents and materials.

Decalin, (Koch-Light "puriss" grade) was further purified by washing with concentrated sulphuric acid (x3), water (x2),

drying (potassium carbonate and magnesium sulphate) and refluxing for 12 hr., under nitrogen, over sodium. The decalin was finally fractionated and collected as a mixture of the *cis*- and *trans*-isomers (b.p. 185-95°). It was deoxygenated prior to use by refluxing over a stream of nitrogen for several hours before being allowed to cool to room temperature in a stream of nitrogen.

The following solvents were used to provide constant temperature baths: toluene and xylene mixture (*ca.* 120°), chlorobenzene (*ca.* 130°), xylene (*ca.* 140°), cumene (*ca.* 150°).

6.11.2 Apparatus and experimental details.

(a) The apparatus consisted of a reaction thimble, under an atmosphere of nitrogen, maintained at constant temperature by complete immersion in a bath containing a suitable refluxing solvent. The temperature of the bath was measured to ± 0·25° by means of an accurately calibrated and corrected thermometer.

A standard solution of the reactant (*ca.* 1 mg.) in decalin (50 ml.) was introduced to the reaction thimble as rapidly as possible (time = 0). Aliquots (2·5 ml.) were then rapidly withdrawn by a syringe at suitable time intervals and chilled by immersion in liquid nitrogen to quench the reaction. The aliquots were allowed to equilibriate to room temperature and the optical density of each aliquot determined at 246·0 mμ on a Unicam S.P.500 spectrophotometer, in 1cm. silica cells against a solvent blank. The cells were corrected. All weighings were carried out on a Cahn "electrobalance".

(b) The extinction coefficients of the reactant and the product were determined at 246·0 mμ under the conditions described in (a) above. These values were the average of three concordant (within 5%) determinations in both cases:

Reactant:- $\text{Extinction}_{246\cdot0\ m\mu} = 4{,}100\ (\epsilon_R)$.

Product:- $\text{Extinction}_{246\cdot0\ m\mu} = 15{,}500\ (\epsilon_P)$.

The reactant extinction was caused by a shoulder and was not a maximum as in the case of the product.

6.11.3 Treatment of results.

(a) As the reaction proceeds, the reactant (R) will be consumed resulting in a decrease in the extinction coefficient due to this chromophore. This will be accompanied by an increase in the extinction due to the product(P). The overall effect will be an increase in the extinction coefficient(ϵ_t), measured at 246·0 mμ, as a function of time(t).

Assuming the mode: $R \longrightarrow P$

Let:

R_o, R_t, R_∞ = concentration of reactant at t = o, t = ∞.

P_o, P_t, P_∞ = concentration of product at "

A_o, A_t, A_∞ = optical density at t = o, t = ∞.

$\epsilon_o, \epsilon_t, \epsilon_\infty$ = extinction coefficient at t = o, t = ∞.

It follows:

$$[P_t] = [R_o] - [R_t]$$

$$[R_o] = [P_\infty]$$

$$[R_\infty] = [P_o] = 0$$

TABLE IV

Temperature(°C)	121·5		122·5		122·5	
Concentration (10^4mol.litre^{-1})	1·348		1·123		1·372	
ϵ_o	4,100		4,100		4,200	
A_∞	2·089		1·741		2·127	
t(min.)	A_t	$\ln(A_\infty-A_t)$	A_t	$\ln(A_\infty-A_t)$	A_t	$\ln(A_\infty-A_t)$
0	0·555	0·428	0·456	0·250	0·577	0·438
8	0·608	0·393	0·529	0·192	0·639	0·397
16	0·679	0·344	0·569	0·158	0·722	0·340
24	0·747	0·298	0·624	0·110	0·795	0·286
32	0·810	0·246	0·675	0·064	0·856	0·239
40	0·860	0·206	0·719	0·021	0·907	0·198
48	0·909	0·166	0·767	0·027	0·958	0·156
56	0·950	0·130	0·817	-0·079	1·014	0·107
64	0·990	0·095	0·847	-0·112	1·056	0·068
72	1·025	0·062	0·880	-0·150	1·096	0·030
80	1·063	0·026	0·917	-0·194	1·130	-0·003
88	1·105	-0·016	0·949	-0·234	1·170	-0·044
96	1·142	-0·050	0·972	-0·263	1·206	-0·083
104	1·177	-0·092	0·998	-0·297	1·235	-0·115
112	1·209	-0·127	1·028	-0·339	1·269	-0·154
120	1·228	-0·149	1·053	-0·374	1·296	-0·186

TABLE V

Temperature(°C)	132·5		132·5		132·5	
Concentration (10^4mol.litre^{-1})	1·239		1·038		1·070	
ε_o	4,100		4,100		4,200	
A_∞	1·920		1·609		1·658	
t(min.)	At	$\ln(A_\infty-A_t)$	A_t	$\ln(A_\infty-A_t)$	A_t	$\ln(A_\infty-A_t)$
0	0·504	0·348	0·425	0·169	0·459	0·182
4	0·532	0·328	0·470	0·130	0·488	0·157
8	0·615	0·266	0·531	0·075	0·567	0·087
12	0·701	0·198	0·605	0·004	0·633	0·025
16	0·781	0·130	0·668	-0·061	0·703	-0·045
20	0·845	0·073	0·723	-0·121	0·764	-0·111
24	0·912	0·008	0·780	-0·188	0·818	-0·174
28	0·966	-0·047	0·824	-0·242	0·862	-0·227
32	1·016	-0·100	0·870	-0·303	0·921	-0·304
36	1·058	-0·148	0·906	-0·352	0·962	-0·362
40	1·105	-0·204	0·943	-0·407	0·999	-0·416
44	1·148	-0·258	0·968	-0·445	1·021	-0·450
48	1·183	-0·305	0·998	-0·493		
52	1·212	-0·345	1·016	-0·523		
56	1·237	-0·381	1·043	-0·569		
60	1·264	-0·421	1·078	-0·633		
64	1·289	-0·460	1·092	-0·660		
68	1·312	-0·497	1·114	-0·703		

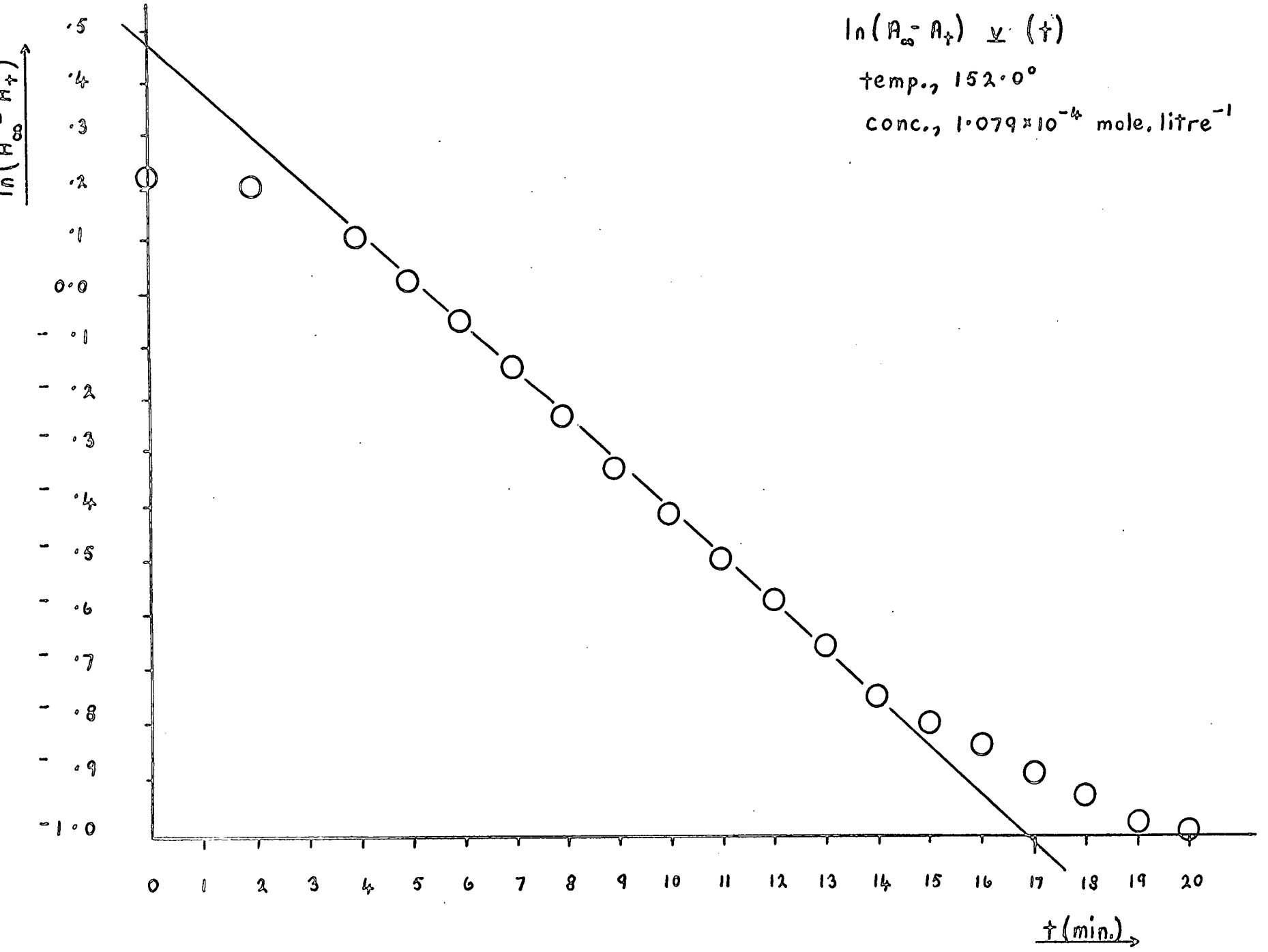
TABLE VI

Temperature(°C)	142·5		142·5		142·5	
Concentration (10^4mol.litre^{-1})	1·217		1·120		1·206	
ϵ_o	4,100		4,100		4,100	
A_∞	1·886		1·736		1·869	
t(min.)	At	$\ln(A_\infty-A_t)$	A_t	$\ln(A_\infty-A_t)$	A_t	$\ln(A_\infty-A_t)$
0	0·502	0·325	0·461	0·243	0·500	0·314
4	0·575	0·271	0·529	0·188	0·574	0·259
6	0·667	0·198	0·617	0·112	0·655	0·194
8	0·776	0·105	0·711	0·025	0·746	0·116
10	0·874	0·012	0·787	-0·052	0·829	0·039
12	0·946	-0·061	0·869	-0·143	0·909	-0·040
14	1·009	-0·131	0·949	-0·239	0·984	-0·122
16	1·076	-0·210	0·999	-0·305	1·045	-0·193
18	1·128	-0·277	1·043	-0·367	1·090	-0·249
20	1·177	-0·343	1·095	-0·445	1·145	-0·322
22	1·222	-0·409	1·135	-0·509	1·195	-0·394
24	1·256	-0·461	1·169	-0·567	1·248	-0·476
26	1·288	-0·514	1·202	-0·627	1·277	-0·524
28	1·325	-0·577	1·232	-0·685	1·314	-0·588
30	1·354	-0·630	1·253	-0·728	1·343	-0·642
32	1·374	-0·669	1·275	-0·774	1·364	-0·683
34	1·398	-0·717	1·299	-0·828	1·386	-0·727
36	1·416	-0·754	1·315	-0·865	1·413	-0·785

TABLE VII

Temperature (°C)	152·0		152·0		152·5	
Concentration (10^4mol.litre^{-1})	1·079		1·100		1·081	
ε	4,100		4,100		4,100	
A_∞^o	1·672		1·705		1·675	
t(min.)	A_t	$\ln(A_\infty-A_t)$	A_t	$\ln(A_\infty-A_t)$	A_t	$\ln(A_\infty-A_t)$
0	0·440	0·209	0·445	0·231	0·442	0·210
2	0·466	0·188	0·462	0·217	0·457	0·198
4	0·547	0·118	0·552	0·142	0·585	0·087
5	0·627	0·044	0·657	0·047	0·687	0·011
6	0·707	-0·035	0·741	-0·037	0·766	-0·095
7	0·788	-0·123	0·829	-0·132	0·852	-0·194
8	0·868	-0·218	0·905	-0·223	0·934	-0·299
9	0·945	-0·318	0·976	-0·316	0·997	-0·388
10	1·002	-0·400	1·035	-0·400	1·052	-0·472
11	1·049	-0·472	1·097	-0·498	1·099	-0·551
12	1·098	-0·554	1·141	-0·573	1·139	-0·623
13	1·143	-0·636	1·185	-0·654	1·180	-0·702
14	1·186	-0·721	1·220	-0·724	1·218	-0·782
15	1·217	-0·786	1·252	-0·792	1·245	-0·843
16	1·238	-0·834	1·281	-0·858	1·268	-0·898
17	1·260	-0·886	1·301	-0·906	1·290	-0·953
18	1·279	-0·933	1·318	-0·949	1·310	-1·006
19	1·299	-0·985	1·337	-1·000	1·322	-1·040

FIGURE XVI


$\ln(A_\infty - A_t)$ v (t)
temp., 152·0°
conc., $1·079 \times 10^{-4}$ mole. litre^{-1}
$\ln(A_\infty - A_t)$
·5
·4
·3
·2
·1
0·0
- ·1
- ·2
- ·3
- ·4
- ·5
- ·6
- ·7
- ·8
- ·9
-1·0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
t (min.)

In terms of optical densities:

$$A_o = \epsilon_R[R_o]$$
$$A_\infty = \epsilon_P[P_\infty] = \epsilon_P[R_o]$$

Now:

$$A_t = \epsilon_R[R_t] + \epsilon_P[P_t] = \epsilon_R[R_t] + \epsilon_P[R_o] - \epsilon_P[R_t]$$

Thus:

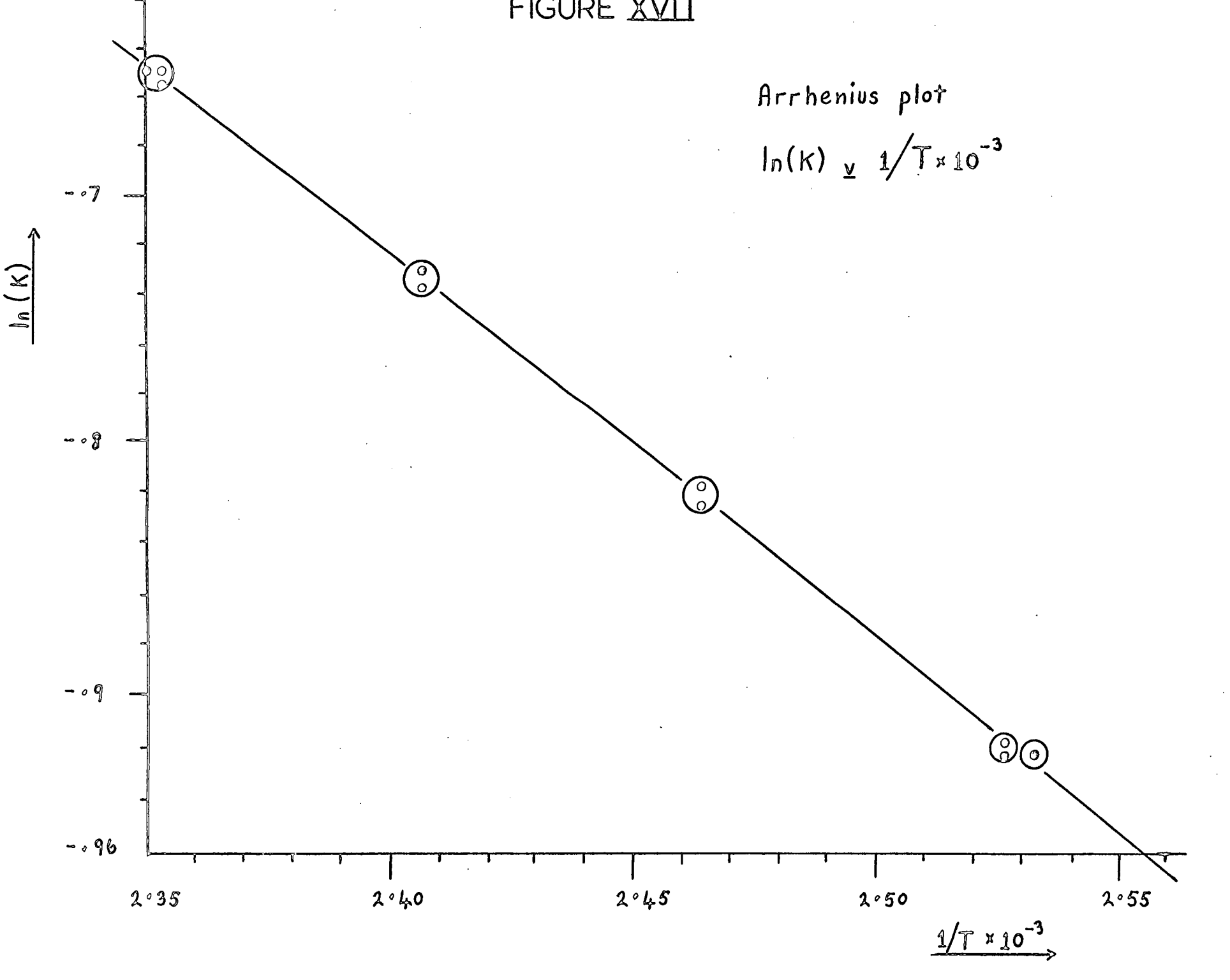
$$[R_t] = \frac{A_t - A_\infty}{\epsilon_R - \epsilon_P}$$

For a first order process a plot of $\ln(A_\infty - A_t)$ $\underline{v}$ (t) will be linear with slope: -K, where K is the first order rate constant.

(b) Assuming the reaction to be 100% efficient in the formation of P (only one product has been detected), A_∞ was calculated from the known value of ϵ_∞ and the molar concentration of reactant. The molar concentration involved in each determination was checked by calculation of ϵ_o and comparison with the known reactant extinction coefficient (ϵ_R).

In practice plots of $\ln(A_\infty - A_t)$ $\underline{v}$ (t) gave good straight lines after the sample had reached thermal equilibrium (2 - 4 min.). The product was unstable to prolonged heating (section 6.11.5) and this resulted in a tailing off of the last few points. Visual estimation of the slope allowed this to be accommodated. The rate constants were determined in triplicate (within 5%) at four temperatures in the range 120-150°, the results being recorded in tables IV-VII. A sample plot is illustrated in figure XVI and the rate constants are given in section 6.11.4.

FIGURE XVII


Arrhenius plot
ln(K) v 1/T × 10^-3
ln(K)
-·7
-·8
-·9
-·96
2·35
2·40
2·45
2·50
2·55
1/T × 10^-3

6.11.4 Estimation of the energy of activation (E_a) and the entropy of activation ($\Delta S^{\ddagger}$).

The rate constant, $K = A \cdot \exp(-E_a/RT)$, where A is the Arrhenius parameter, R is the gas constant (1·987 cal.$^{o}K^{-1}$mole^{-1}) and T is the absolute temperature. Thus a plot of ln(K) v (T^{-1}) should be linear with slope $-E_a/R$ and intercept ln(A). The relevant values are given in the table:

Temp. (^{o}C)	$10^3/T$	K(sec.$^{-1}$)	-ln(K)
152·0	2·353	1·482 x 10^{-3}	6·514
152·0	"	1·522 x "	6·488
152·5	2·350	1·549 x "	6·470
142·5	2·407	6·335 x 10^{-4}	7·364
142·5	"	6·561 x "	7·329
142·5	"	6·354 x "	7·361
132·5	2·466	2·649 x 10^{-4}	8·236
132·5	"	2·639 x "	8·240
132·5	"	2·727 x "	8·207
122·5	2·528	9·969 x 10^{-5}	9·213
122·5	"	9·587 x "	9·252
121·5	2·535	9·653 x "	9·246

The Arrhenius plot is illustrated in figure XVII. The slope, intercept and correlation coefficient were calculated on a Wang electronic calculator using a least squares program. Each value

of K was treated as a separate point. The error in the slope and intercept was determined from a least squares program run on an I.B.M. 360/50 computer:

slope, $1{\cdot}531\ (\pm\ 0{\cdot}013) \times 10^{4}$

intercept, $2{\cdot}952\ (\pm\ 0{\cdot}032) \times 10$.

correlation coefficient r, 0·9997.

Thus the energy of activation,

$$\underline{E_a = 30{\cdot}4\ (\pm\ 0{\cdot}3)\ \text{Kcal.mole}^{-1}}$$

The Arrhenium parameter,

$$\underline{A = 6{\cdot}57\ (\pm\ 0{\cdot}07) \times 10^{12}\ \text{sec.}^{-1}}$$

(whence $\log(A) = 12{\cdot}82$)

A correct thermodynamic formulation of absolute rate theory[22] for unimolecular reactions leads to the relationship:

$A = \frac{e \cdot K_B \cdot T_m}{h} \cdot \exp(\Delta S^{\ddagger}/R)$ where T_m is the mean absolute temperature(410), K_B is the Boltzmann constant ($1{\cdot}380 \times 10^{-16}$) and h is the Planck constant ($6{\cdot}625 \times 10^{-27}$). Thus the mean entropy of activation,

$$\underline{\Delta S^{\ddagger} = -2{\cdot}5 \pm 0{\cdot}7\ \text{e.u.}}$$

6.11.5 Product decomposition.

An identical kinetic run to those previously described was carried out with the product, at 152·0°. The results are given in the table:

Temperature (°C) 152·0 Concentration (10^4 mol.litre^{-1}) 1·198			
t(min.)	A_t	t(min.)	A_t
0	1·830	90	1·310
12	1·785	100	1·303
20	1·688	110	1·292
30	1·592	120	1·283
40	1·500	130	1·282
50	1·430	140	"
60	1·390	150	"
70	1·350	330	1·600
80	1·324	1,440	>2·0

It is evident that the product is consumed by a process involving complex kinetics. Product instability was evident in the plots of $\ln(A_\infty - A_t)$ v (t) as the last points deviated from linearity. However, this effect was negligible up to one to two half lives, over which region the plot was linear. Thus visual estimation allowed the slope to be estimated, the validity of this method being borne out by the correlation of the results.

6.12 EXACT MOLECULAR WEIGHT DETERMINATION.

The A.E.I. M.S.902 is equipped to enable exact masses to be determined by the process of peak matching. Two ion peaks of relatively higher to lower mass to charge ratio can be matched (maxima superimposed) on the oscilloscope by the adjustment of a series of decade dials, which give variance down to 1 p.p.m. These dials are coupled to a variable resistance (ΔR) which, when in circuit, causes ions to be subjected to a diminished accelerating voltage. Thus for an optimised machine setting, where a given lower mass peak is focused on the collector, switching in this resistance results in a given higher mass peak being focused, with no change to the electrostatic or electromagnetic field amplitudes. With automatic switching the two peaks can be alternatively and repeatedly displayed on the oscilloscope whereupon they can be accurately matched.

Low resolution scans were carried out by introducing the sample directly into the source by means of a probe. Manual inspection and counting of the recorded trace allowed the integer value of the mass to charge ratio (m/e) of the parent ion(P) to be determined. Normal ionisation scans were carried out near 70 e.V., whereas low ionisation scans were run near 20 e.V.

High resolution peak matching was carried out using heptacosafluorotributylamine as reference compound. This was introduced into a reservoir from which, through a leak, it diffused into the source for as long as required. The cracking pattern of this compound contains distinct ions of accurately

known mass and abundance lying at intervals of approximately ten mass units. Thus a suitable lower mass reference peak was chosen at a value below m/e for the parent ion being measured. This was matched against a suitable higher mass reference peak lying above m/e for the parent and the machine correction factor (p.p.m. per mass unit) determined over this region. The reference peaks were chosen to be as close together as possible. The sample to be measured could then be introduced by way of the probe and its parent peak, now the higher mass peak(B), matched against the lower mass peak(A). Since m/e is proportional to $1/V_{accelerating}$[160] and since the accelerating voltage is switched between full voltage (position A) and a value (position B) equal to $10^6/10^6 + \Delta R$ of the full voltage:

$$\frac{\text{Higher mass (B)}}{\text{Lower mass (A)}} = \frac{10^6 + \Delta R}{10^6} = \frac{1 \cdot XXXXXX}{1}$$

where $\cdot XXXXXX$ is the decade dial reading for matched peaks.

Since the mass of the reference peak was accurately known, that of the unknown ion could be calculated taking into account the machine correction factor. The molecular formula of the parent ion could then be determined from mass abundance tables.[161] The found and calculated values usually agreed to within 3 p.p.m. and always to within 5 p.p.m.

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APPENDIX

Direct Oxidation of Hydrocarbons to Unsaturated Aldehydes using 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ)

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Summary Treatment of β-methylstyrene, allylbenzene, and related hydrocarbons with an excess of DDQ in benzene yields unsaturated aldehydes.

The reactions of DDQ with hydroaromatic compounds are well documented[1] and recently the dehydrogenation of a simple alkene has been reported.[2] However there is no previous report that certain hydrocarbon dehydrogenation reactions may result in the formation of carbonyl compounds in addition to, or instead of, the desired product.

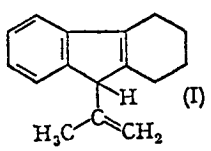
In attempting the dehydrogenation of 9-isopropenyl-1,2,3,4-tetrahydrofluorene (I) with DDQ (3 molar equiv.) in benzene at room temperature we obtained the aldehyde (II) (45%) together with the expected product 9-isopropenylfluorene (IV) (30%). In refluxing benzene, (II) only was formed (64%). The structure of (II), m.p. 131°, was established by elemental composition and spectroscopic data [u.v. λ_{max} (EtOH) 270, 260 nm. (ϵ 22,350, 16,050); i.r. ν_{max} (CCl_4) 1670, 2710 cm.$^{-1}$; n.m.r. τ −0·74 (s, 1H, C*H*O), 2·1—3·0 (m, 8H, Ar–*H*), 7·55 (s, 3H, CH_3)]. We believe that (II) is formed from (IV) since the same ratio of products is obtained when (IV) is similarly treated with DDQ. 9-Isopropylidinefluorene (III) also reacts with DDQ to give (II) (50%).

The applicability of the reaction is indicated in the Table. Addition of an excess of DDQ to a solution of the hydrocarbon in benzene immediately gave a deep green colouration which faded to a pale yellow solution. The solution was washed with dilute mineral acid, the solvent removed, and the residue chromatographed on alumina.

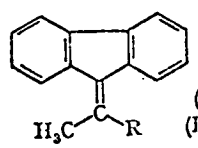
TABLE

Hydrocarbon	DDQ (molar equiv.)	Time† (hr.)	Product‡ (% yield)
Ph·CH_2·CH:CH_2	1·5	12[a]	Ph·CH=CH·CHO (50)
Ph·CH=CH·Me	9	30[b]	,, (27)
Ph·CH=CH·Me	3	4[b]	,, (55)
4-MeO·C_6H_4·CH=CH·Me ..	1·5	2[a]	4-MeO·C_6H_4·CH=CH·CHO (50)
Ph·CMe=CHMe	2	30[b]	Ph·CMe=CH·CHO (20)

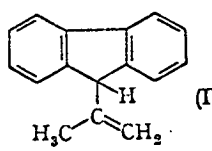
† [a] Stirred at room temperature. [b] Under reflux.
‡ Identified by n.m.r. spectra and comparison with authentic samples.



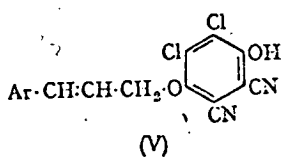
(I)



(II) R=CHO
(III) R=CH3



(IV)



(V)

No attempt was made to adjust the reaction conditions to give optimum yields. Indene and α-methylstyrene failed to react, starting material only being recovered.

A competitive reaction between *trans*-β-methylstyrene and 4-methoxy-*trans*-β-methylstyrene showed that the reaction of the latter with DDQ was virtually complete before any of the former was consumed. Thus the 4-methoxy-derivative must be at least 100 times more reactive than the parent hydrocarbon. This observation, together with the observation that allylbenzene, and *cis*- and *trans*-β-methylstyrene all yield *trans*-cinnamaldehyde indicates that the reaction involves hydride-ion transfer from the olefin to the quinone to form a resonance stabilised carbonium ion, *viz.*: Ar·CH:$\overset{+}{C}$H·CH_2 ⟷ Ar·$\overset{+}{C}$H·CH:CH_2, which probably reacts with the semiquinone ion also formed to give the quinol ether (V). Quinol ethers have previously been isolated[3] in reactions of DDQ. Further hydride-ion abstraction and coupling would lead to an acetal which would readily decompose to give an aldehyde. The mechanistic details are at present being studied.

o- and *p*-Chloranil do not react in the above manner and therefore their use is preferred when dehydrogenation only is required.

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ABSTRACT OF THESIS

Name of Candidate JAMES ALEXANDER GEORGE STEWART

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Degree Ph.D. *Date* August 1970

Title of Thesis THE SYNTHESIS AND REARRANGEMENT OF VINYLIDENECYCLOPROPANES

A series of vinylidenecyclopropanes have been prepared by the addition of dimethylvinylidenecarbene to various styrene derivatives. These cyclopropanes underwent unimolecular rearrangement when heated in solution (80-180°) or at reduced pressure in the vapour phase when passed through a flow system (350-450°), the rearrangement conditions being dependent upon the adduct involved.

Thermal rearrangement of the adducts derived from the 1-arylalkenes and 3-methylenebenzocycloalkenes gave dimethylenecyclopropane derivatives, whereas thermolysis of the adducts formed from 1-arylcycloalkenes lead to mixtures of ring expanded and cyclopropane ring opened products, the constraints imposed on the latter systems rendering dimethylenecyclopropan formation unfavourable. Similarly, thermal rearrangement of the adducts derived from benzocycloalka-1,3-dienes lead to ring expanded or cyclopropa ring opened products depending on the ring size of the parent styrene system involved. The effect of alkyl substitution at aryl and cyclopropyl sites in these systems was also investigated.

The mechanistic nature of these rearrangements has been considered in the light of concerted and free radical pathways and, although some of the processes studied could be realised in terms of diradical intermediates, i seems likely in the majority of cases that a single transition state is probably involved.

Application of the Arrhenius equation to the first order rate constants obtained at different temperatures for the thermolysis of the vinylidenecyclopropane derived from α-methylstyrene enabled the energy and entropy of activation for this rearrangement to be estimated, the significance of the results being discussed in terms of the two alternativ mechanisms available. Attempts to identify a hypothetical diradical intermediate during the aforementioned rearrangement by chemically trappin with radical scavengers or observing the phenomenon of chemically induced dynamic nuclear polarisation were unsuccessful.

These vinylidenecyclopropanes also underwent facile acid catalysed rearrangement to form products whose formation is rationalised in terms of initial protonation at an allenic carbon atom followed by cleavage of the cyclopropane ring, support of this view being obtained from several acid catalysed rearrangements which were also carried out in deuterated solvents.

Many/

Use other side if necessary.

Many of the products obtained from these thermal and acid catalysed rearrangements are of synthetic and structural interest due to their ease of formation and relative inaccessibility by other routes, several were independently synthesised by other methods for direct structural proof.

During the course of this work a new reaction was observed involving the direct oxidation of certain aromatic hydrocarbons with dichlorodicyanoquinone to form α,β-unsaturated aldehydes.