REACTIONS AND REARRANGEMENTS

OF

ACETYLENES AND ALLENES

by

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Declaration and Courses Attended

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

N.M.R. Spectroscopy	R.K. Harris
Phosphorous in Organic Chemistry	J.I.G. Cadogan & I. Gosney
The Encouragement and Exploitation of Inventiveness in the Oil Industry	B.P. Ltd.
High Performance Liquid Chromatography	E.U. Wolfson Unit
From Crawford to Kemball - 260 years a-growing	W.P. Doyle
Chemistry at its Most Colourful	I.C.I. Blackley
Computer Course	C. Pounder
Strategy of Organic Synthesis	I. Gosney
Organic Departmental Seminars	

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

Acknowledgements

I would like to thank Dr. Ian Sadler for his advice, inspiration and encouragement throughout the course of study and for reading through the manuscript of this thesis.

I would also like to thank my wife, Christine, for typing this thesis.

Abstract of Thesis

This thesis describes the reactions of dimethylvinylidene and vinylvinylidene carbenes with indene and dihydronaphthalene derivatives to give cyclopropanes. Rearrangement of these by acid or base catalysis led to opening of the cyclopropane ring. The products formed depended on the site of attack of the acid or base on the molecule and an attempt was made to relate this to the structure of the cyclopropyl species.

Indene, cyclopentadiene and fluorene anions were generated with sodium in liquid ammonia or by a phase transfer technique and reacted with alkynyl bromides to give alkyne substituted derivatives. Pyrolysis of these derivatives at high temperatures in vacuo was carried out. Propargylindene derivatives were found to undergo "Cope" rearrangement giving allenylindenes. 9,9-Dipropargylfluorene rearranged to give 9-ethynylphenanthrene which in turn gave acephenanthralene.

3-(Pent-4'-ynyl)indene derivatives underwent "ene" cyclization to give methylene spirononadiene and triene derivatives which were themselves rearranged by acid catalysis to give spirononatrienes and tetraenes respectively. Ultra violet and ^{13}C n.m.r. studies on these compounds show evidence for spiro-conjugation, hitherto unreported for spirononatrienes. Pyrolysis at higher temperatures lead to fluorenes and benzofulvenes.

Propargyl, allenyl and pent-2'-en-4'-ynylcyclopentadiene and indene derivatives were found to rearrange by base catalysis to give vinylfulvene and benzovinylfulvene compounds. The ^{1}H n.m.r. spectra of these are discussed in order to determine their structures. E and Z isomerism about the fulvene-6-position was found and in many cases the individual isomers were isolated and described.

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CHAPTER 1

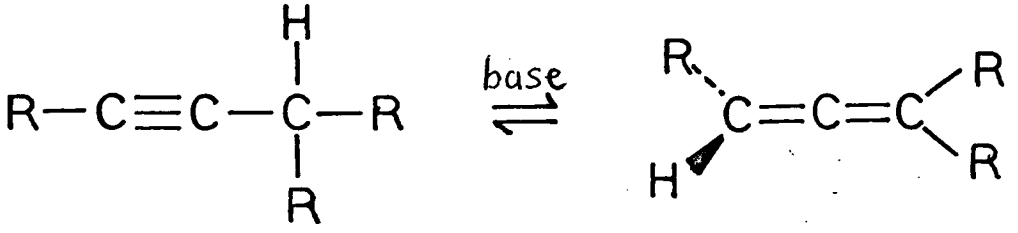
A Review of Some Reactions and Rearrangements of Acetylenes and Allenes

1.1 Introduction

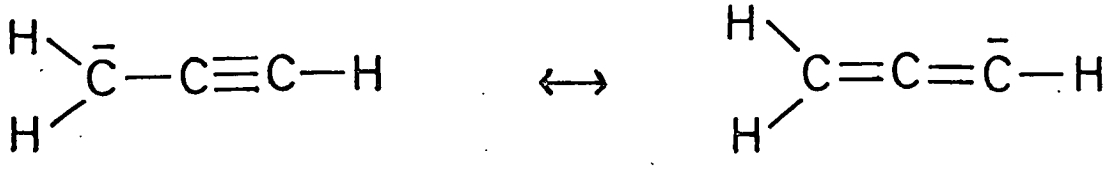
The chemistry of acetylenes and allenes has received a vast amount of attention and much of the work has been the subject of reviews and monographs.[1,2] In view of the work described later in this thesis, the present review is concerned with the well known interconversion of acetylenes and allenes and their rearrangements and cyclizations initiated either purely thermally or catalysed by acids or bases.

1.2 Propargylic Prototropic Rearrangements

The interconversions of acetylenes and allenes are often termed[3] propargylic rearrangements, by analogy with allylic rearrangements. Prototropic rearrangements are usually base catalysed. The structure of the

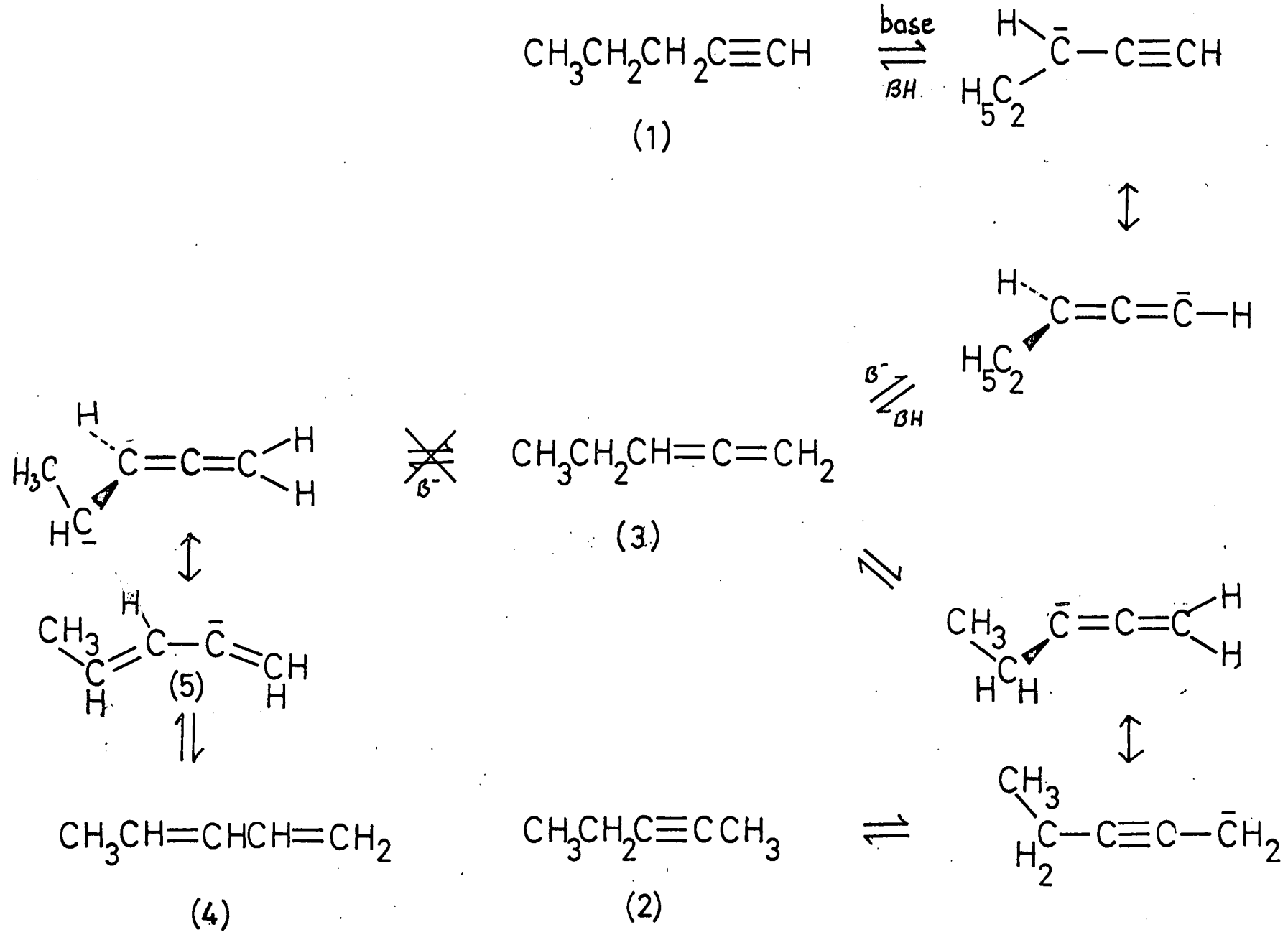


propargyl-allenyl anion intermediate is uncertain but may be similar to that of the allylic cation.[4] Such rearrangements are always possible



propargyl anion allenyl anion

when there is a hydrogen attached to a carbon atom next to the triple bond, or to one carbon atom of the allene structure. A wide range of


CH3CH2CH2C≡CH
(1)
base
βH
H
C
C≡CH
H5C2
H
C=C=C
H
H5C2
β⁻
βH
H
H3C
C=C=C
H
H
H
CH3CH2CH=C=CH2
(3)
β⁻
CH3
H
C
C=C=C
H
H
H
CH3
C
C
CH
H
H
(5)
CH3CH=CHCH=CH2
(4)
CH3CH2C≡CCH3
(2)
CH3
H2
C
C≡C
CH2

basic catalysts have been used eg. sodamide, alkali metal acetylides, potassium hydroxide and sodium carbonate. The temperature is also important and rearrangement is usually slow below zero. Temperatures range from room temperature to 200°C.

A comprehensive study of prototropic propargylic rearrangements was carried out by Jacobs et al[5] who interconverted pent-1-yne (1), pent-2-yne (2) and penta-1,2-diene (3) using alcoholic potassium hydroxide at 170°C and found a product ratio (1):(2):(3) of about 1:95:4 from any isomer. None of the conjugated diene (4) was formed and the authors suggested that the penta-1,3-dienyl ion (5) which would lead to the conjugated diene might not assume planarity and hence lack resonance stabilization. Raphael[6] has suggested that the predominant isomer pent-2-yne (2) may be stabilized by "hyperconjugation".

Analogous results were obtained for the isomerization of oct-2-yne, oct-3-yne and 1,2- and 2,3-octadiene using sodamide as base.[7] The relative heats of formation for these and related isomers, calculated according to Benson[8], and from standard enthalpy changes[9] of isomerization are given in table 1. This data shows that a terminal allene is of

Table 1. Relative Heats of Formation of C_8H_{14} isomers (kJ mole^{-1})

	$\Delta\Delta Hf^{298}$ (calc)	$\Delta\Delta Hf^{523}$ (expt)
$C_6H_{13}-C\equiv CH$	68.05	68.7
$C_5H_{11}-C=C=CH_2$	65.82	64.9
$C_4H_9-C=C=CH-CH_3$	53.51	57.4
$C_5H_{11}-C\equiv C-CH_3$	48.56	49.4
$C_3H_7-CH=CH-CH_2-CH=CH_2$	17.85	19.3
$C_4H_9-CH=CH-CH=CH_2$	0	0

lower energy than a terminal acetylene but that an internal allene is of slightly higher energy than an internal acetylene. Conjugated dienes are more stable than any of these.

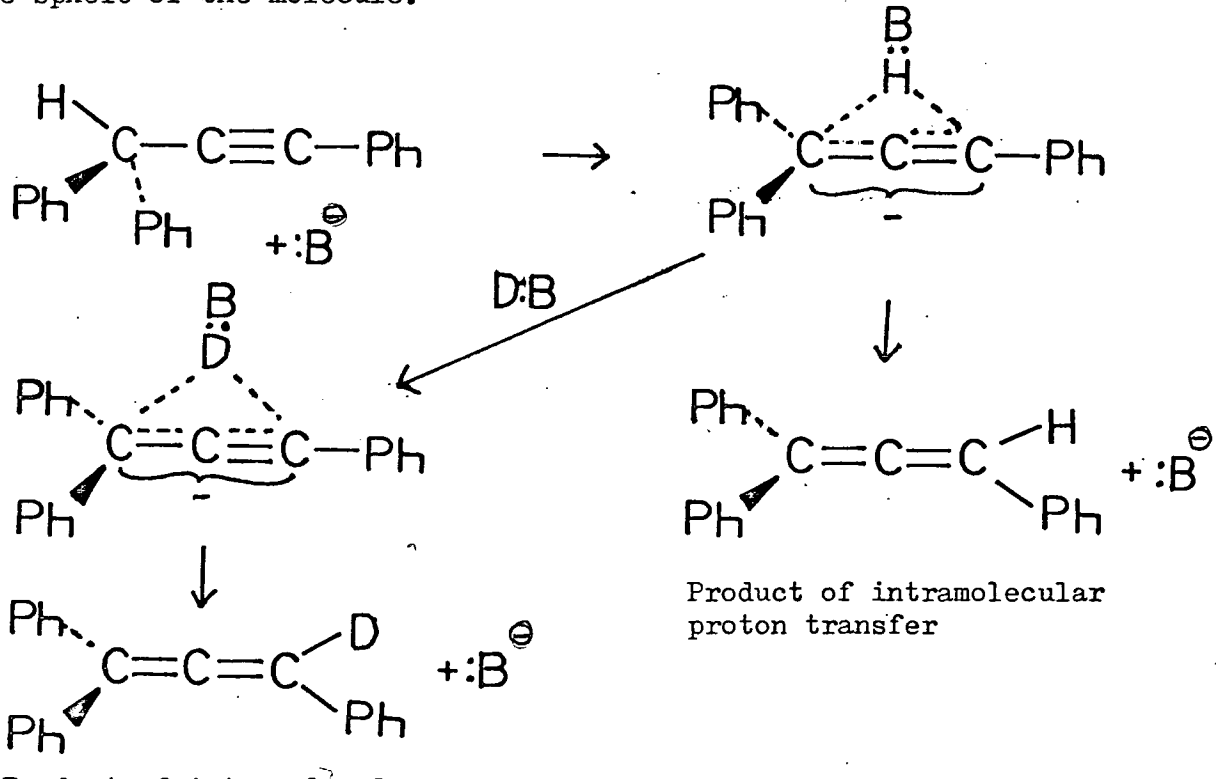
Where the free energy difference between the allene and acetylene is sufficiently different the interconversion becomes essentially irreversible.

Aryl allenes may be prepared from aryl propynes, rearrangement being effected[10,11,12] by alumina or alumina and sodium hydroxide. For example:

$$PhC{\equiv}CCHPh_2 \xrightarrow[20^\circ]{Al_2O_3} Ph.HC{=}C{=}CPh_2$$

89%

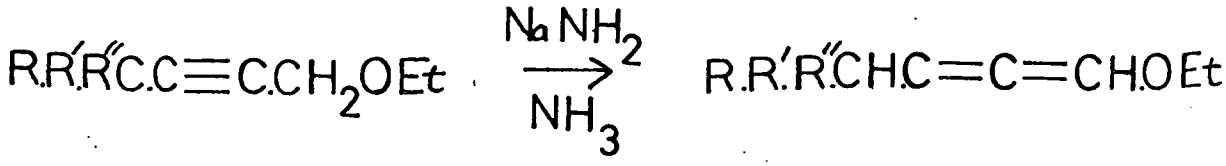
Cram[4] studied the degree of intramolecular versus intermolecular proton transfer in this reaction by allowing the rearrangement to take place in deuterated solvents, or by replacing the propargyl proton with deuterium, and found up to 88% intramolecular proton migration. He proposed a "conducted tour mechanism" in which the proton is held within the sphere of the molecule.



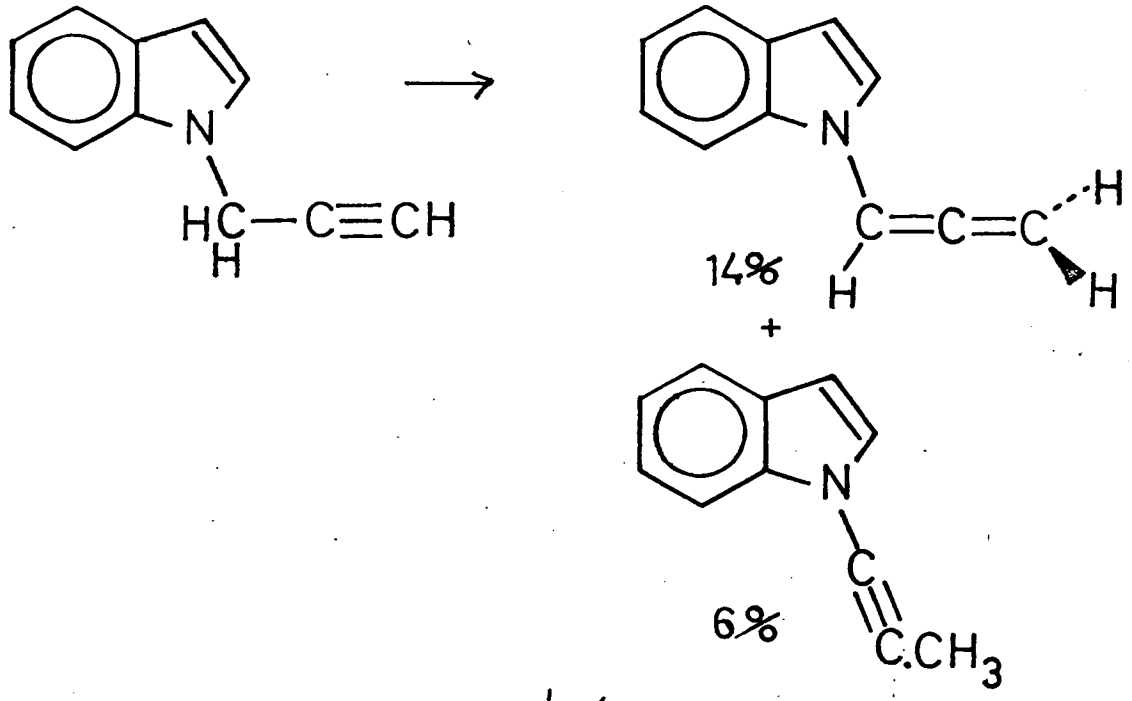
Product of intramolecular proton transfer

Product of intermolecular proton transfer

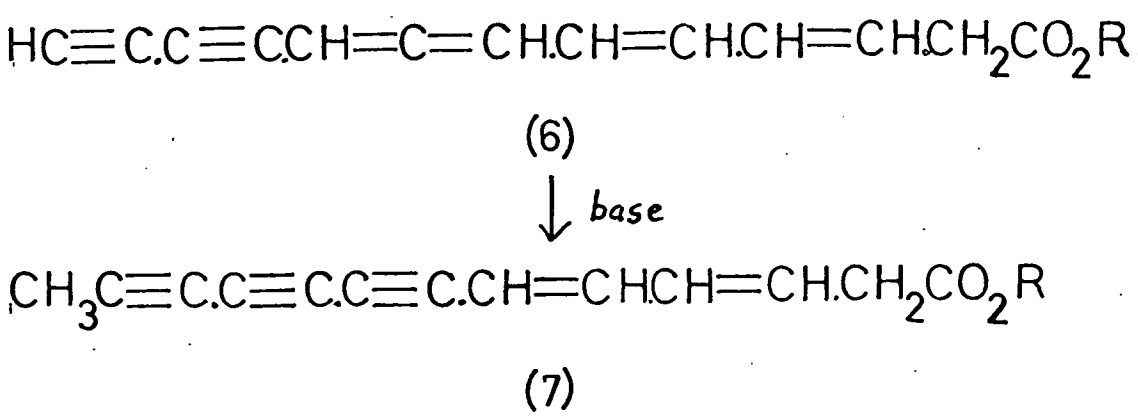
2-Alkynyl ethers may be rearranged[13] to allenic ethers in high yield.



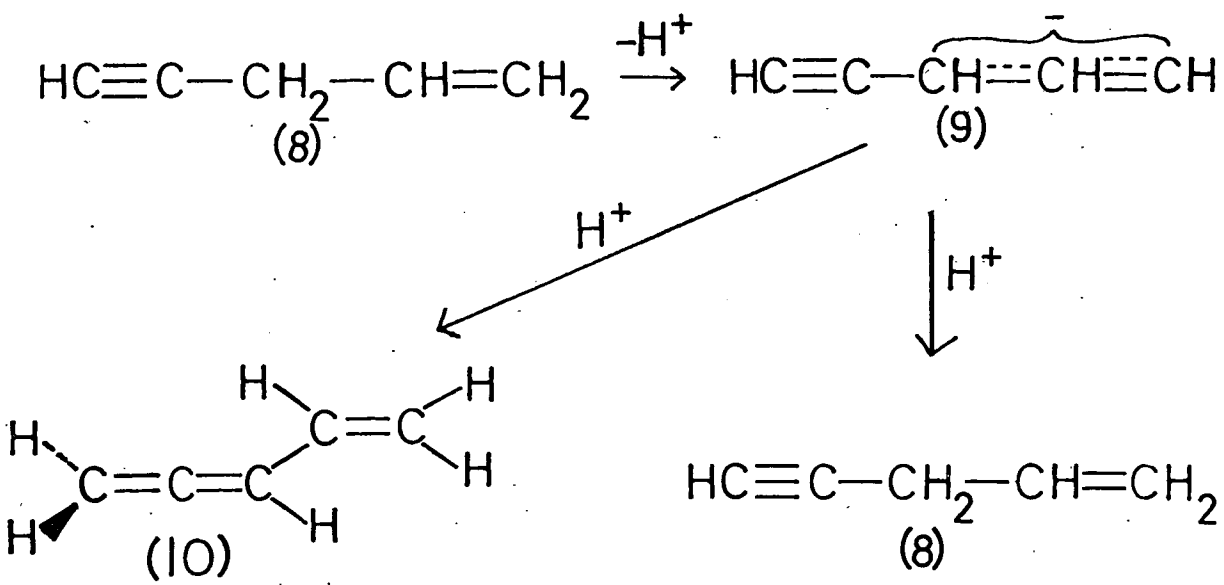
Potassium amide on alumina causes rapid isomerization of N-prop-2'-ynyl heterocycles to N-propa-1',2'-dienyl and N-prop-1'-ynyl heterocycles.[14] Attempts to repeat this rearrangement with propargylcyclopentadiene or propargylindene failed. For example:



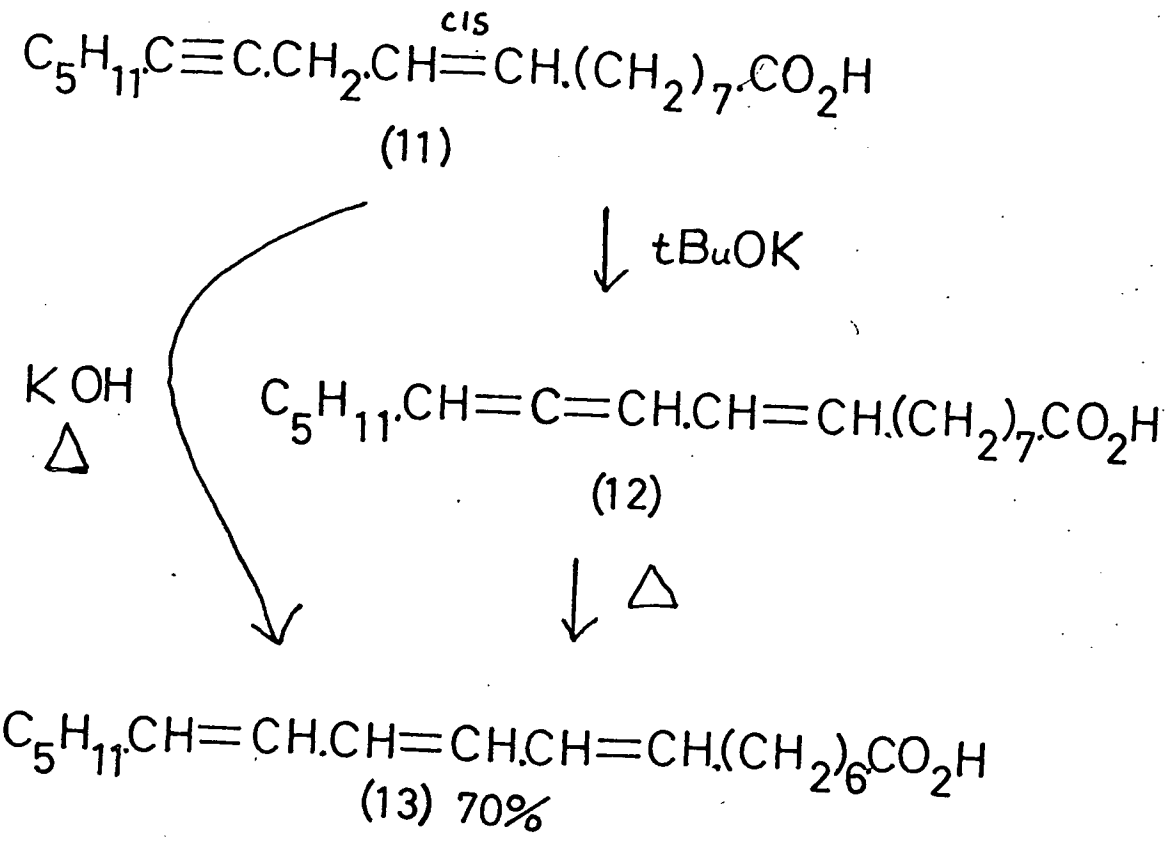
1,3-Enynes of the type $CH_3C{\equiv}C\text{-}\dot{C}{=}C'$ are converted with excess potassium amide in liquid ammonia into isomers with a terminal acetylene group, $HC{\equiv}C\text{-}\dot{C}\text{-}C{=}CH\text{-}CH\text{-}$, in good yield.[15] Incomplete equilibration yields allenes, $CH_2{=}C{=}CH\text{-}CH\text{-}\dot{C}{=}C'$, but no trienes. The rearrangement of mycomycin (6) with dilute aqueous alkali to isomycomycin (7)[16] is a complex example of enyne rearrangement.



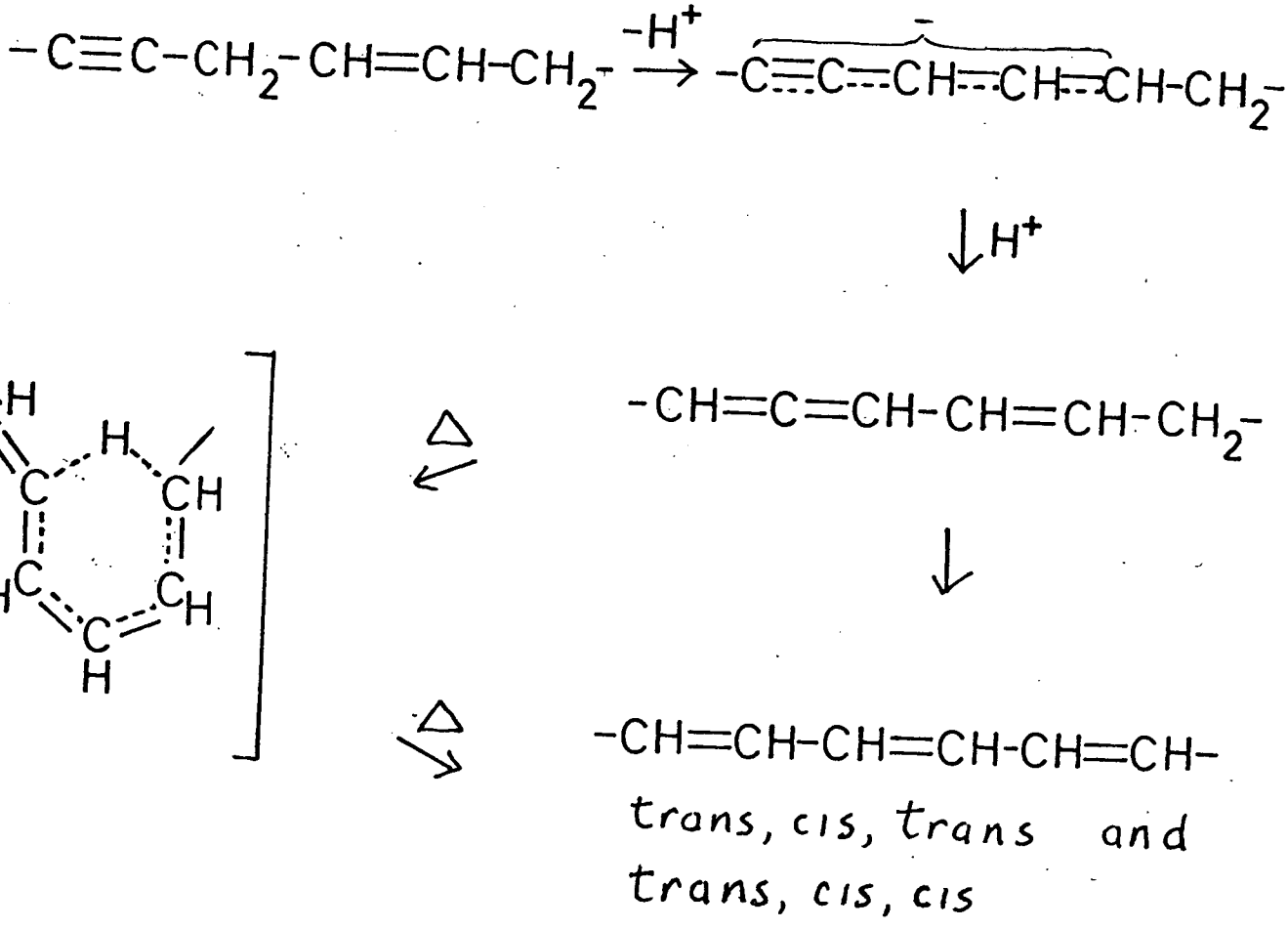
Base catalysed rearrangement of 1,4-enynes usually gives conjugated ene-allenes instead of conjugated trienes. Isomerization of allyl acetylenes in MeOH-NaOH involves a delocalised anion (9), in which the negative charge is distributed between carbons 5 and 3. If proton transfer from methanol occurs at carbon 5 the product is a vinyl allene (10). However, if transfer takes place at carbon 3, the allyl acetylene (8) is regenerated.[17]



The polyunsaturated fatty acid, cis-octadec-9-en-12-ynoic acid (11), a natural product, isomerises with KOH in ethylene glycol to give 70% yield of an octadeca-8,10,12-trienoic acid (13), and 30% yield of isomeric conjugated trienoic acids. Potassium t-butoxide rearranged (11) to the ene-allene (12), which isomerised to a conjugated trienoic acid (13) when heated:[18]

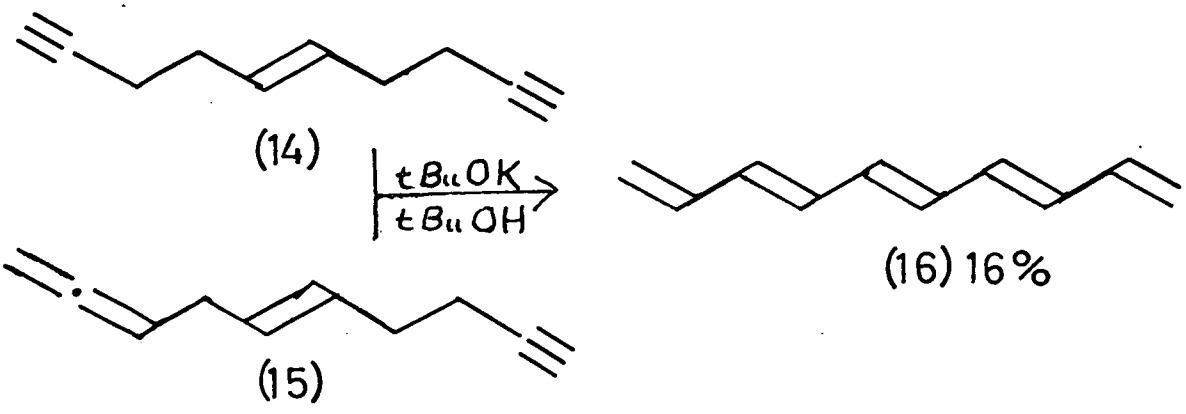


The proposed mechanism is:

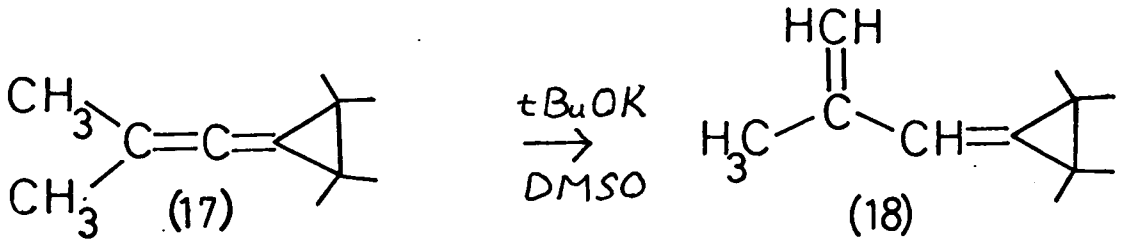


The allyl acetylene to ene-allene step is base catalysed while the ene-allene to triene step is thermal.

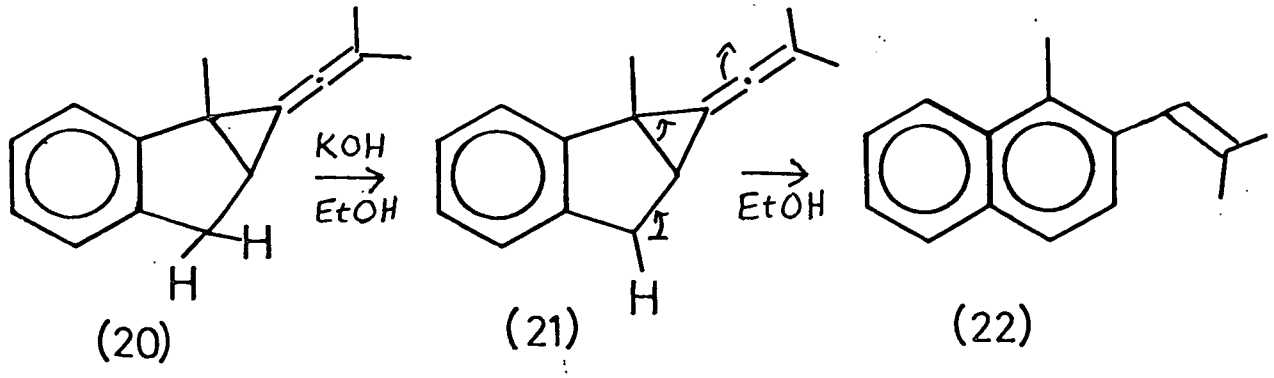
Isomerization of the 1,5 enyne, E-dec-5-en-1,9-diyne (14) or the corresponding ene-allene, E-deca-5,8,9-triene-1-yne (15) with potassium t-butoxide in t-butanol at 65°C gave the same product (16) in the same yield.[19] This provides further evidence that allene is an intermediate in acetylenic rearrangements.



Only a few examples of base catalysed rearrangements of vinylidene cyclopropanes have been reported. Crandall[20] found that hexamethylvinylidene cyclopropane (17) underwent double bond isomerism to 3-isopropenylmethylene-1,1,2,2-tetramethyl cyclopropane (18) in the presence of tBuOK.

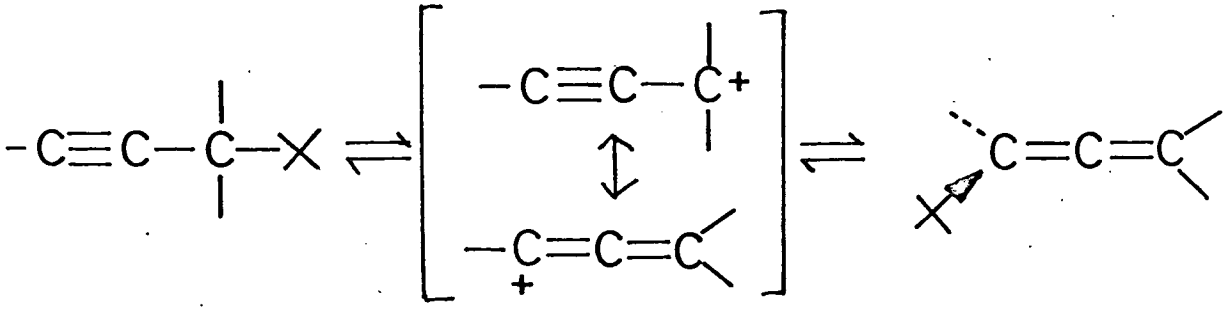


Stewart[21], however, found certain indene adducts (19) would rearrange by ring expansion to give naphthalenes (22), presumably via the indenyl anion (21). For example:

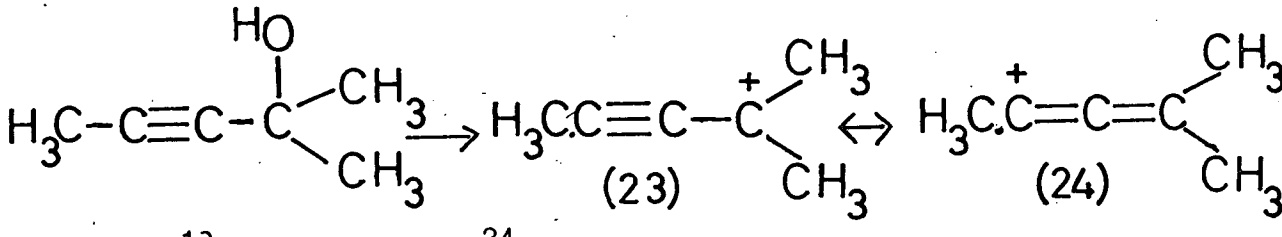


1.3 Propargylic Aniontropic Rearrangements

Rearrangements of this type are possible under a variety of conditions and with various catalysts. Frequently mixtures of products are obtained.



The intermediate propargyl/allenyl cation has been observed directly by Olah.[22] Solutions of tertiary-ethynylcarbinols in antimony pentafluoride-fluorosulphonic acid-sulphur dioxide were prepared and their proton n.m.r. spectra observed. ~~Down~~ Upfield shifts of all the methyl groups indicated strong contributions of both the propargyl (23) and the allenyl (24) cationic resonance forms to the ion structure. Richey[23] dissolved carbinols in concentrated sulphuric acid and obtained the same

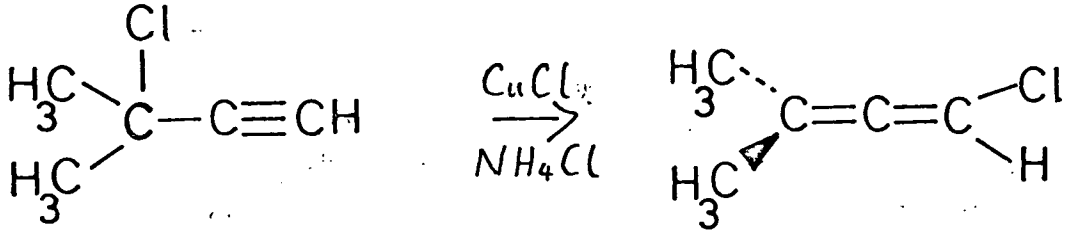


results. ^{13}C n.m.r. studies[24] also showed a large contribution of the allenyl cationic form to the ion structure.

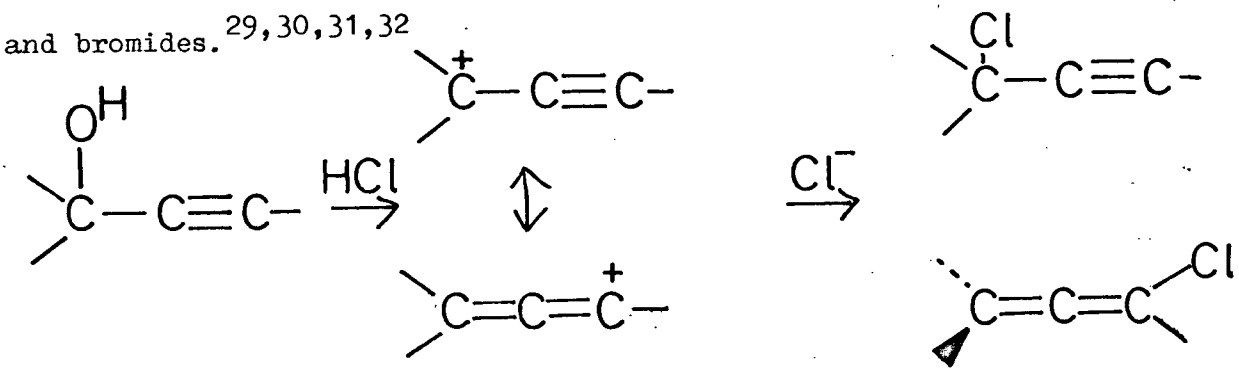
Allenyl cations have been shown[25] to be intermediate in the solvolysis of haloallenes, and the solvolytic data indicate that there is extensive delocalization involving the alkynyl cationic form.

It has been demonstrated[26] that bromo propa-1,2-diene could be prepared by rearrangement of 3-bromopropyne in the presence of cuprous salts. The reaction was reversible and the bromoallene could be obtained (60%) from the mixture by careful distillation.

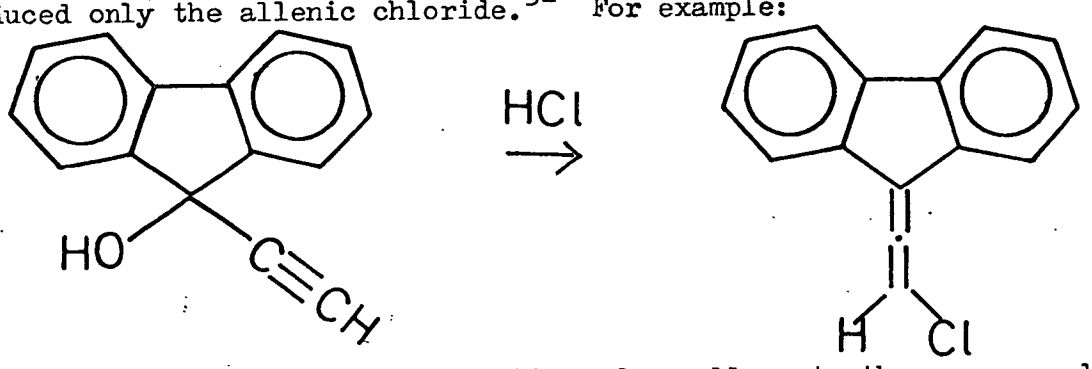
Tertiary propargylic chlorides also yielded allenes when exposed to ammonium chloride and cuprous chloride.[27] Analogous bromides have been similarly prepared.[28]



Aniontropic rearrangements are also observed during the halogenation of propargyl alcohols which yield allenic as well as propargyl chlorides and bromides.[29,30,31,32]



Tertiary propargyl alcohols tend to give allenic halides while primary propargyl alcohols give propargylic halides. Higher weight alcohols produced only the allenic chloride.[32] For example:

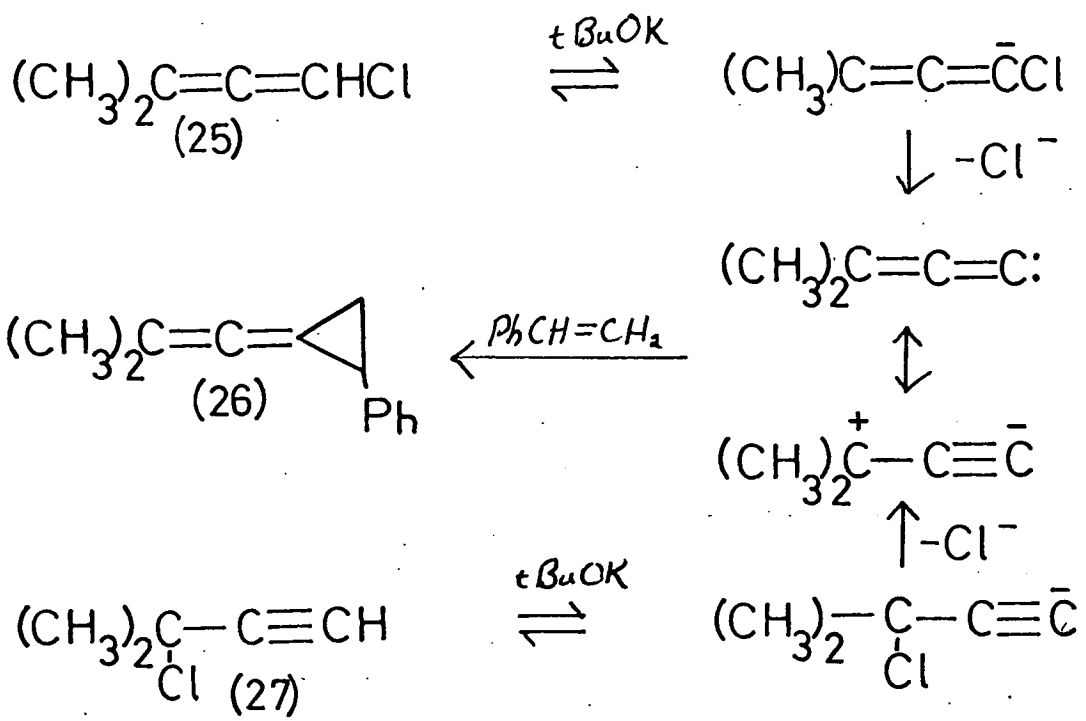


Acids also catalyse isomerization of an allene to the corresponding conjugated diene. Phosphorous pentachloride in ether at -10°C converts α-allenic secondary alcohols to α-allenic chlorides in 65-70% yield. Thionyl chloride or excess concentrated hydrochloric acid gives a 60-70% yield of a mixture of α-allenic chloride and an equal amount of 2-chloro-1,3-diene, $RCH{=}CH{-}CCl{=}CH_2$. HBr gives 85-95% yield of unrearranged

allenic bromide plus 2-bromo-1,3-diene.[33]

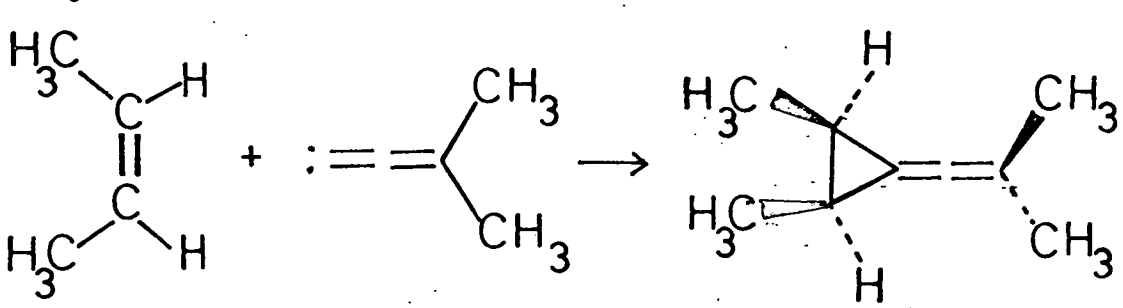
1.4 Carbene Formation

If an intermediate propargyl/allenyl ion containing a reasonably good leaving group is generated then a carbene may be formed and trapped by an olefin. Hartzler[34,35] found that the propargylic chloride (27) or the allenic chloride (25) on treatment with potassium t-butoxide produced the same cyclopropane derivative (26), at the same rate, and also observed[36] an increase in reactivity of the olefin to the carbene with increased electron density on the olefin. Hence yields increased with the number of alkyl groups on the olefin.

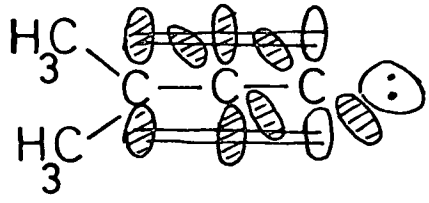


Hartzler[36] also found addition to olefins to be stereospecific. This indicates that the reaction proceeds via the carbene and not via a

e.g.

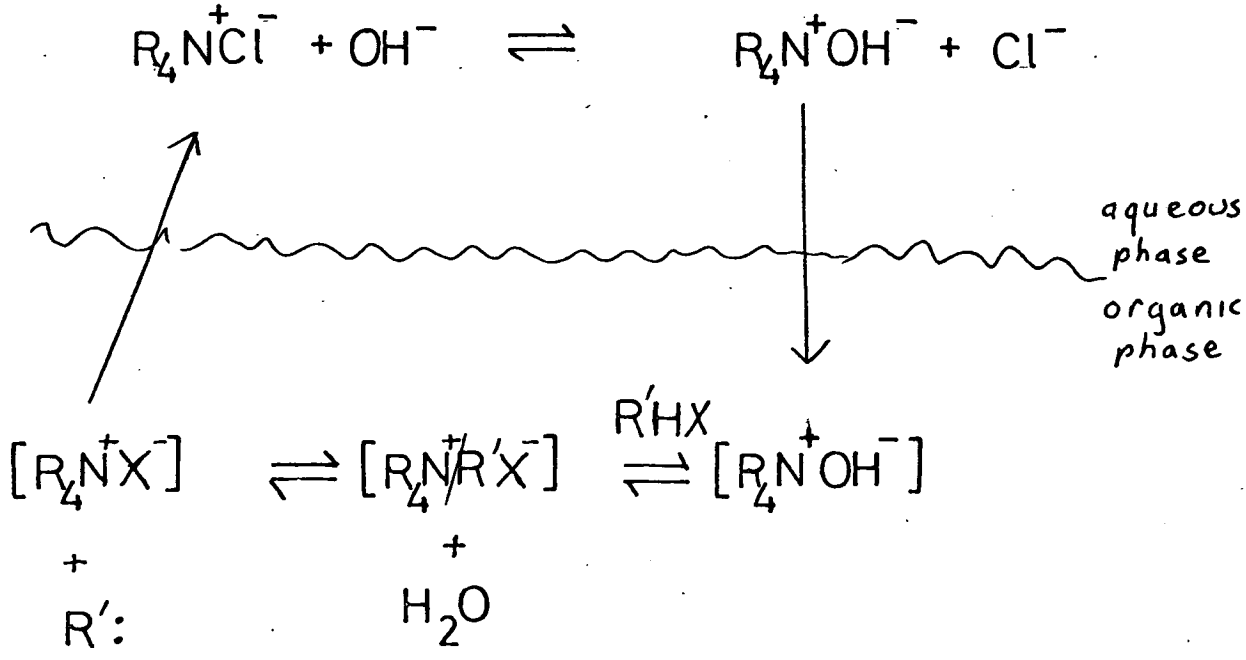


radical mechanism. The increased stability of dimethylvinylidene carbene over methylene and alkyl carbenes is attributed to overlap of the vacant p orbital with the π orbitals of the β-γ double bond:



Landor[37] showed that E and Z isomers were formed when unsymmetrical carbenes react.

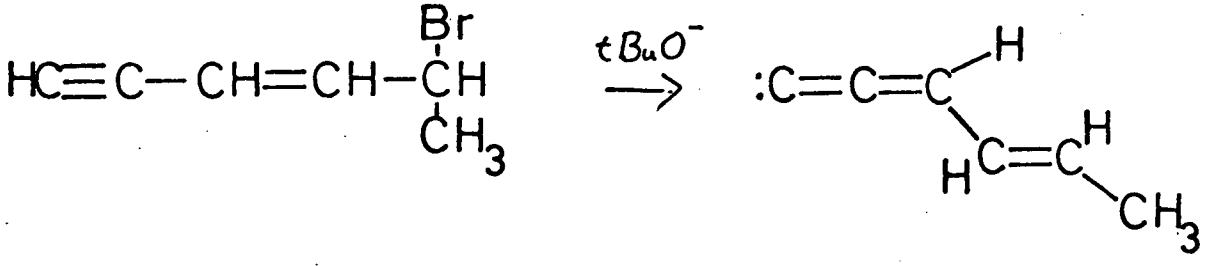
Phase transfer catalysis has been used frequently in recent years[38,39] to prepare carbenes. For example, 3-methyl-3-chlorobut-1-yne (27) was allowed[38] to react with various olefins in benzene as solvent in the presence of 50% aqueous sodium hydroxide solution containing a little benzyltriethylammonium chloride catalyst. In many cases the yield of dimethylvinylidene cyclopropane obtained was better than with potassium t-butoxide. Yields have been further improved using crown ethers as catalysts.[40] The phase transfer catalyst forms an ion pair with hydroxide ion enabling it to move into the organic layer where it reacts with the allenyl halide to form the carbene.[41]

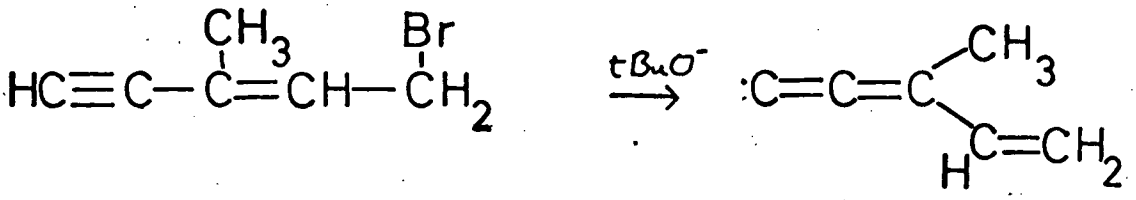


Chlorocarbene, thus generated, is particularly reactive, reacting with all available active centres. This reactivity is attributed[41] to the carbenes being formed close to the site of reaction, in high concentration. There is no evidence, however, that vinylidene carbene formed this way is particularly reactive.

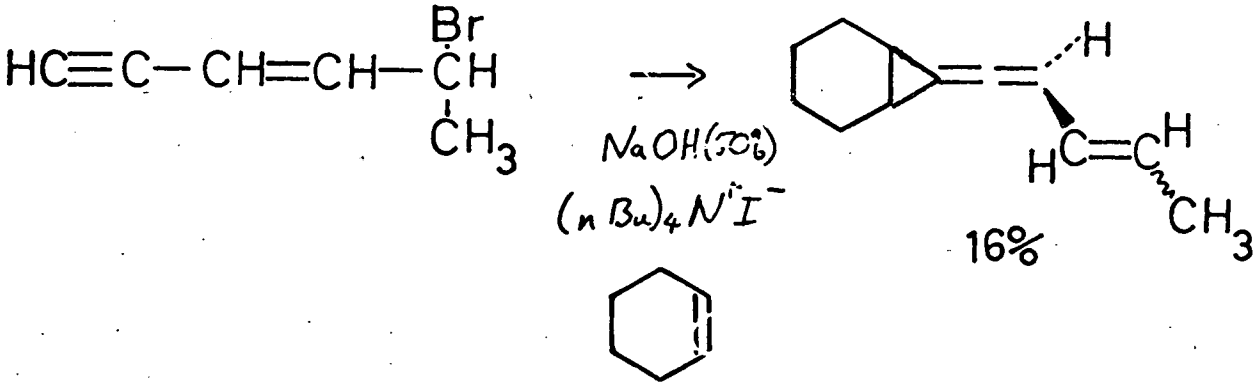
Bromoenynes have been used to obtain vinylvinylidene carbenes[43,44], which were trapped with a variety of olefins; cyclohexene, styrene, tetramethylethylene, etc, using potassium t-butoxide as base.

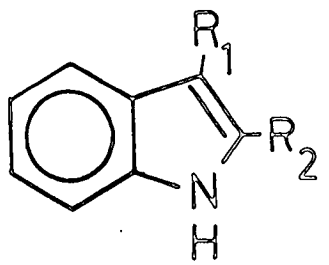
For example:





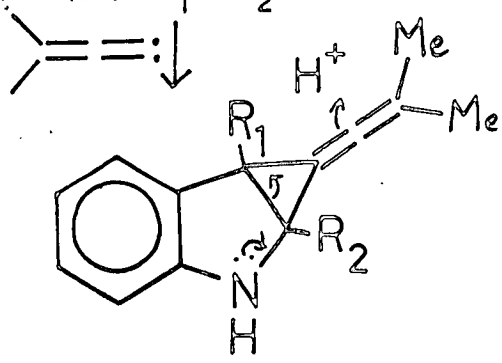
Some success was achieved using methyl lithium as base or a phase transfer process.[44] For example:

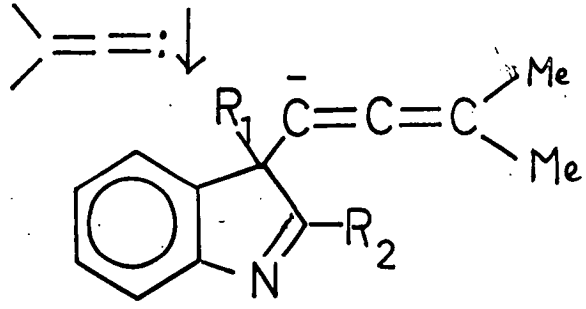


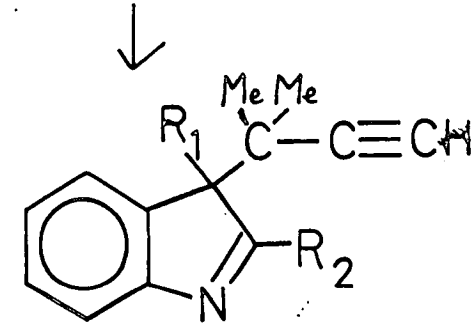


(30) R_1 = Me, R_2 = H

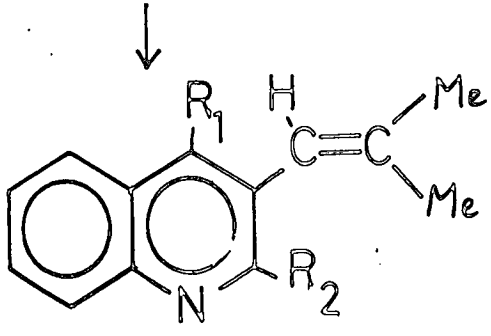
(33) R_1 = R_2 = Me





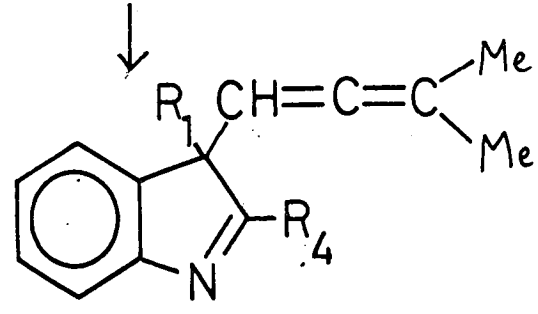


(32) R_1 = Me, R_2 = H



(31) R_1 = Me, R_2 = H

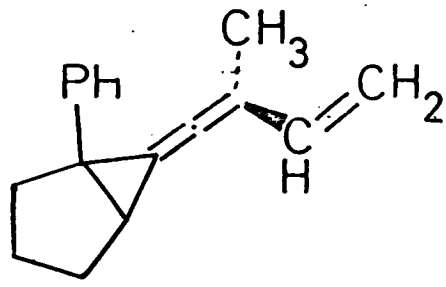
(34) R_1 = R_2 = Me



(35) R_1 = R_2 = Me

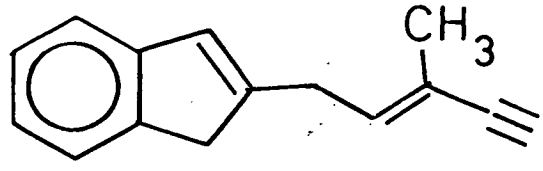
The authors reported the formation of E and Z isomers, as would be expected, on the addition of the carbenes to styrene.

Watson[45] prepared several vinylpropenylidene cyclopropanes by a tBuOK method. For example adducts with 1-phenylcyclopentene (28), diphenylethylene and α-methylstyrene have been prepared.



(28)

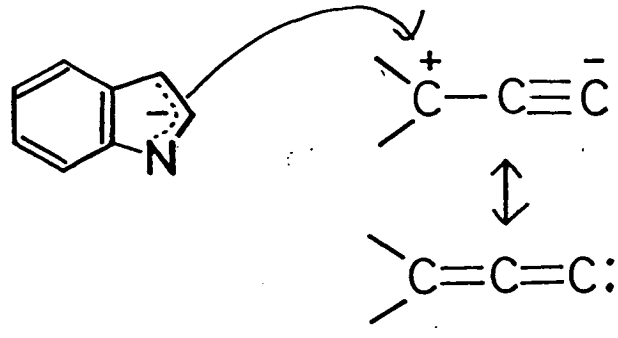
Indene however did not yield a cyclopropane.[45] Instead a compound, to which Watson assigned the structure (29), was obtained. Work



(29)

described later in this thesis shows that this assignment was incorrect. Reaction[46] of 3-methylindole (30) with 1-bromo-3-methylbuta-1,2-diene using t-BuOK as base gave a mixture of 4-methyl-3-(2'-methylprop-1'-enyl)-quinoline (31), 30%, and 3(1', 1'-dimethylprop-2'-ynyl)-3-methylindole (32), 2%. 2,3-Dimethylindole (33) gave a quinoline (34) plus 2,3-dimethyl-3-(3'-methylbuta-1',2'-dienyl)-3H-indole (35). The quinolines arise from ring expansion of the cyclopropyl adducts. The alkynyl-3H-indole (32) is attributed to attack of the carbene δ-carbon on the 3-methylindolide anion since under conditions in which no indolide anion would be formed, no alkynyl substitution was found.

i.e.

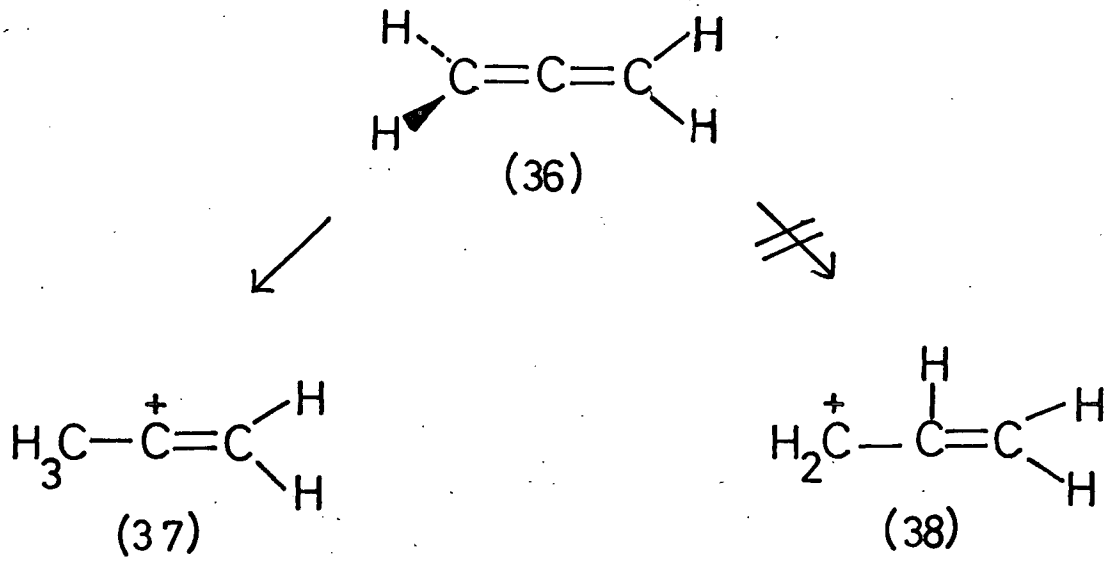


(32)

There is no evidence, however, that the carbene is the electrophile and not the bromide precursor. Formation of the allenyl compound (35) is explained by attack of the carbene α-carbon on the indolide anion although ring opening of the cyclopropane intermediate would also be possible.

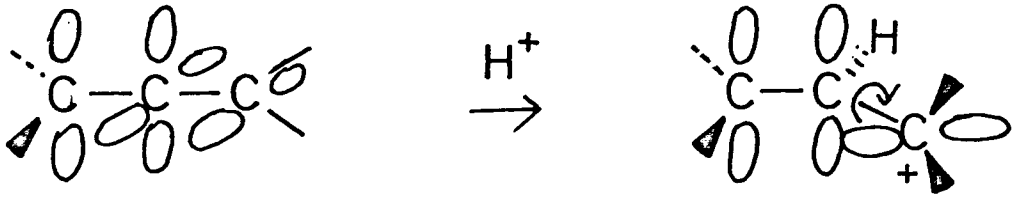
1.5 Reactions of Allenes and Vinylidene Cyclopropanes with Electrophiles

The cumulated double bonds of allenes permit electrophilic additions to follow two different pathways.[47] Additions to allene itself (36) proceed via attack at the terminal carbon to give a vinyl cation[48] (37).

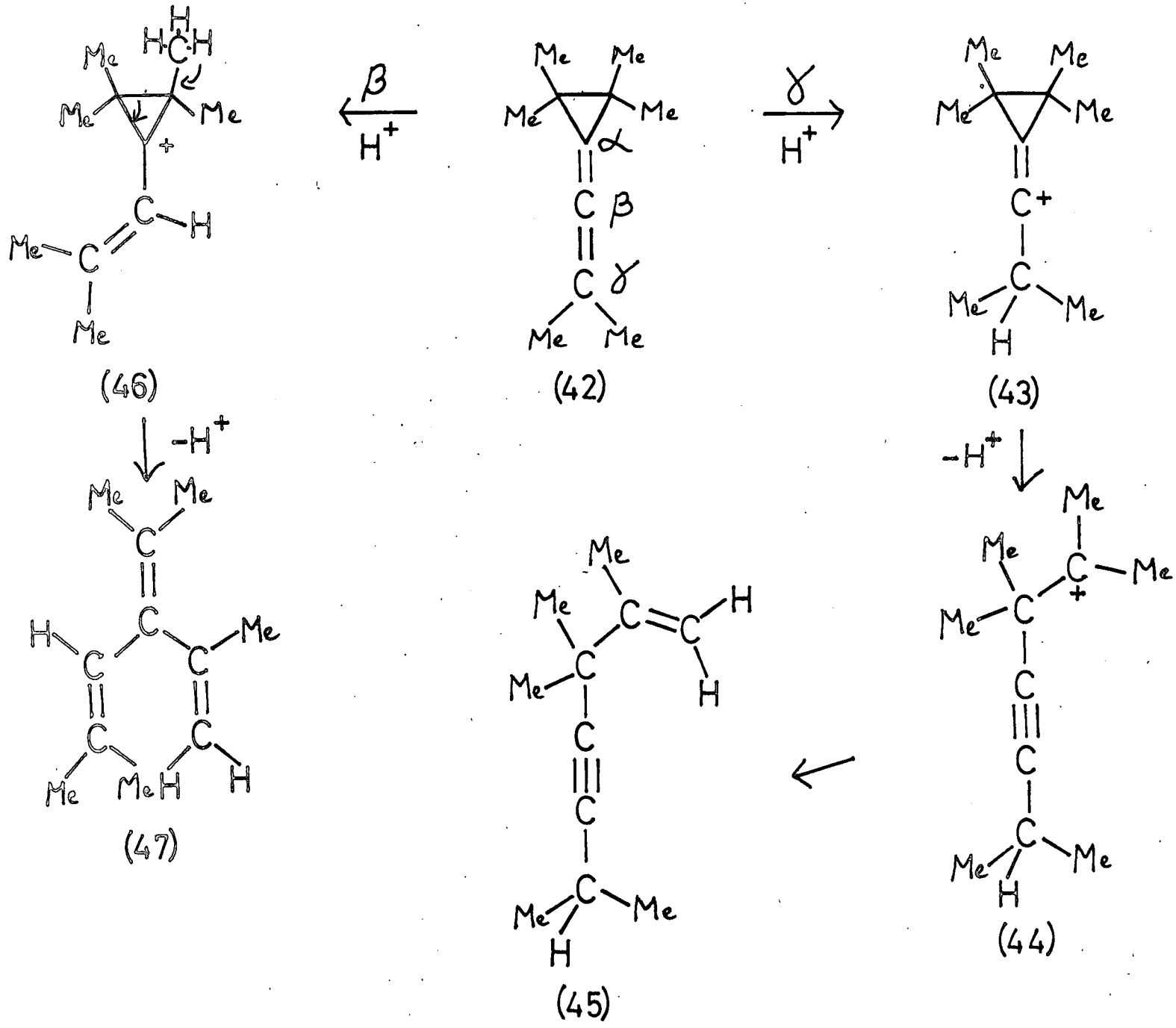


(36) (37) (38)

Attack at the central carbon atom of the allene would lead to a carbonium ion (38). This, however, is not an allyl cation as it must retain the twisted allene geometry (39) preventing overlap of the π orbitals. Resonance stabilization can only occur after a 90° rotation about the single bond.

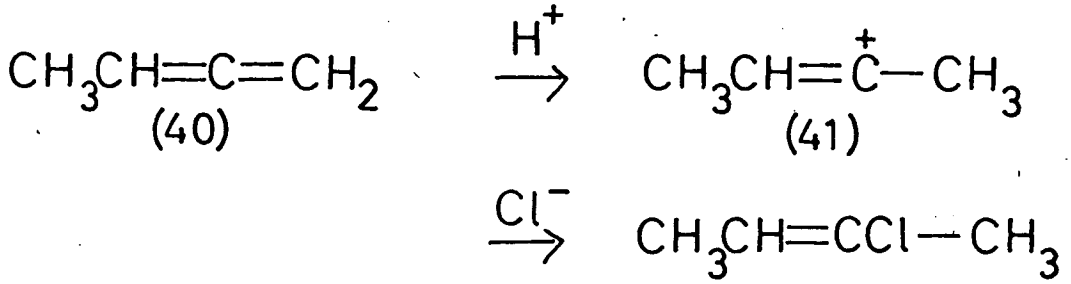


(36) (39)


(46)
(42)
(43)
(47)
(45)
(44)

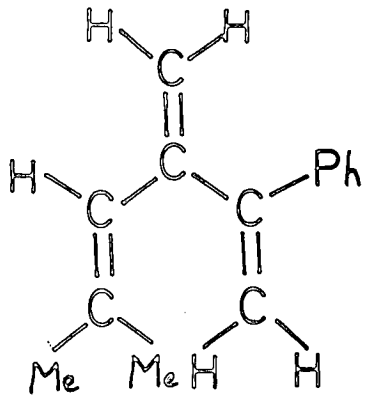
Thus acid-catalysed hydration of unsubstituted allene gives only acetone and additions of HCl and HBr give products with halogen on the central carbon.

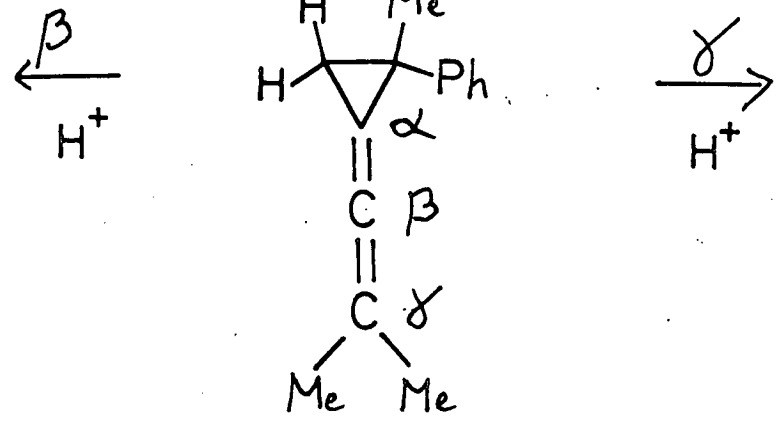
The situation becomes more complicated with substituted allenes since electron donating alkyl groups tend to stabilize transition state (39). This is illustrated by the reaction with HCl. For instance buta-1,2-diene (40) reacts at -78°C with HCl exclusively via the vinyl cation (41).[49] In contrast only partial protonation of the terminal carbon



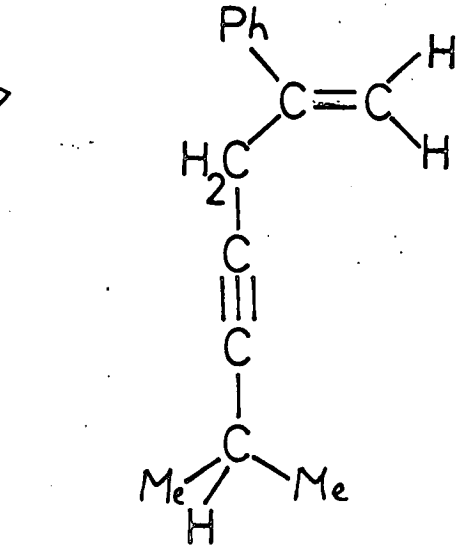
atom occurs on reaction of 1,3-dialkyl allenes with HCl, the ratio of terminal to central attack depending on reaction conditions.[49] Tetramethylallene reacts exclusively via protonation on the central carbon atom to give a tertiary carbonium ion.[49] Addition of HCl to aryl allenes in glacial acetic acid also proceeds via central attack to form the more stable benzyl cation.[50]

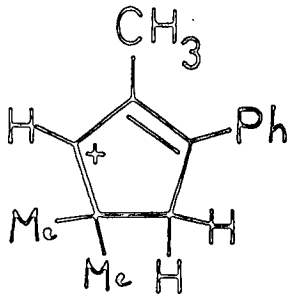
Vinylidene cyclopropanes, which are a special category of tetrasubstituted allenes undergo varied reactions. For example hexamethyl vinylidene cyclopropane (42) on reaction with acetic acid - sulphuric acid gave (45) via γ attack on the allene.[51] The vinyl cation (43) was proposed as an intermediate although (44) could be formed directly with relief of angle strain. In contrast rearrangement of (42) with p-toluenesulphonic acid in benzene solution at 25°C gave another product (47) as well as the enyne (45), (ratio (47):(45) = 1:5).[52] This arises from β attack on the allene to give the cyclopropyl cation (46). Hence although γ attack was favoured it was not exclusive. The specificity of

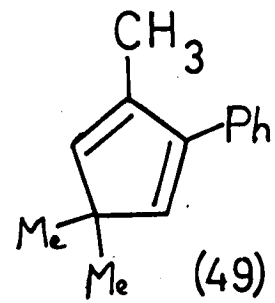




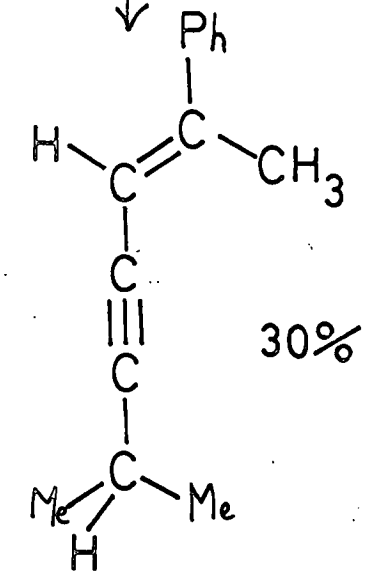
(48)





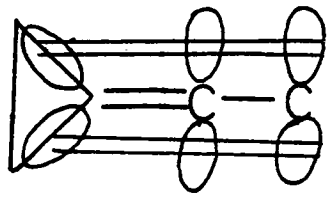


(49) 70%



30%

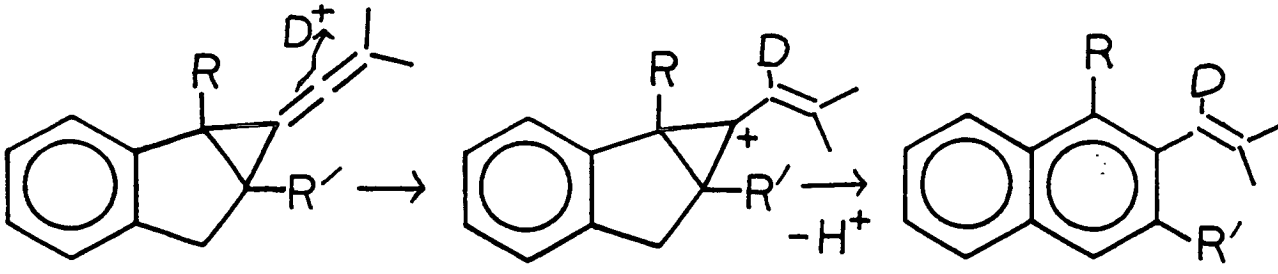
attack was explained[51] in terms of the atomic orbital overlap. The figure illustrates the overlap of the cyclopropyl π bonds with the



orbitals of the reactive olefinic unit which is rigidly enforced by the allene geometry. This allows the cyclopropyl system, with its ability to stabilize cationic centres*, to participate favourably in the transition state for electrophilic attack at this double bond without appreciable change in molecular geometry.

In contrast Harris[54] found protonation at the β position was favoured in the rearrangement of 2-dimethylvinylidene-1-methyl-1-phenylcyclopropane (48) induced either by p-toluenesulphonic acid in CCl_4 or HCl in EtOH. In these cases the cross conjugated triene underwent rearrangement to the cyclopentadiene (49).

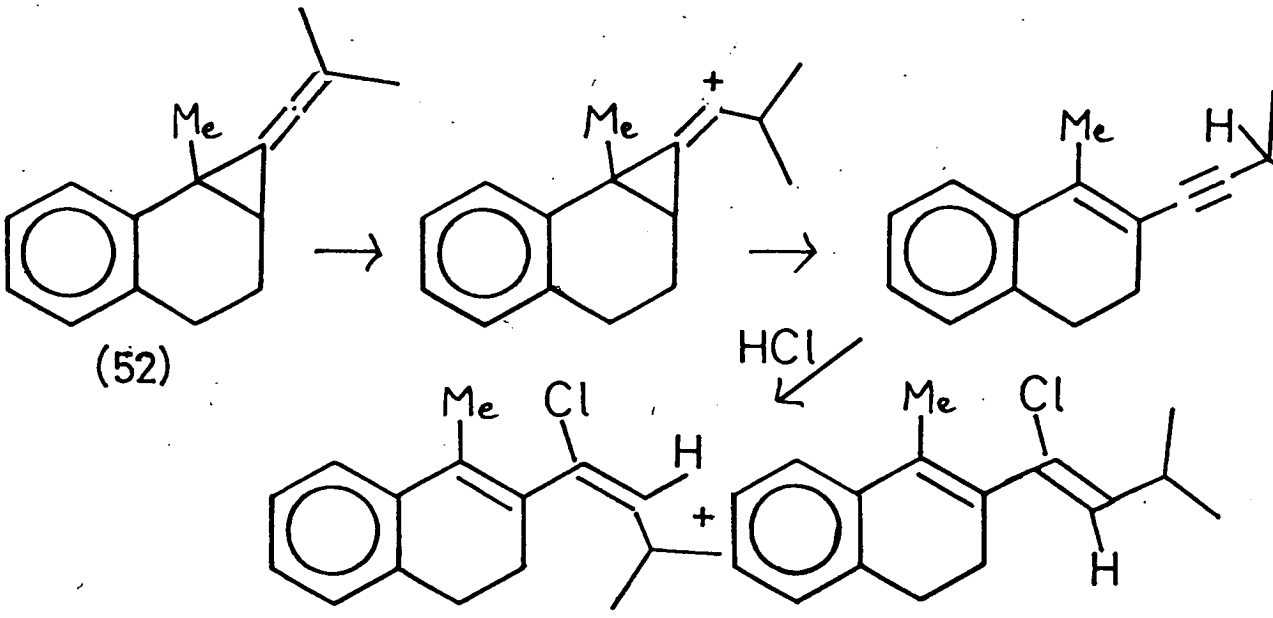
Exclusive β-protonation was obtained in the rearrangement of vinylidenecyclopropane adducts of indene and its derivatives (50).[21] Ring expansion to give a naphthalene derivative (51) occurred, the centre of attack being identified by using deuterium chloride in deuteromethanol.



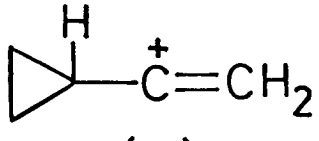
(50) (51)

* The nature of the intermediate is uncertain but the carbons have been shown to scramble.[53]

Reaction of the 4-methyl-1,2-dihydronaphthalene adduct (52) with HCl in ethanol gave exclusively γ attack, however.[21]



The cyclopropyl vinyl cation (53) would also be stabilized[55], however no



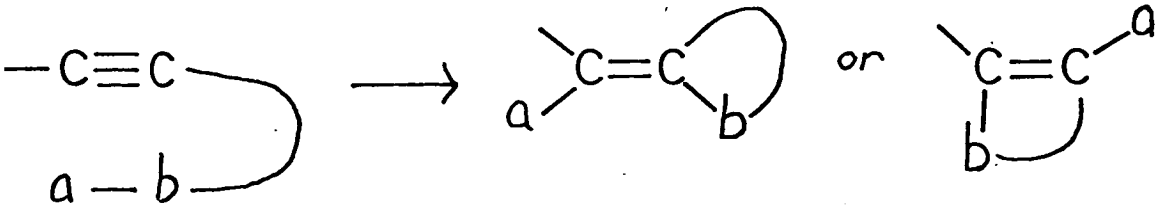
(53)

report has been made of α attack on vinylidene cyclopropanes.

Hence attack may occur on the β or γ carbons and the reason for preference are not clear and require further investigation.

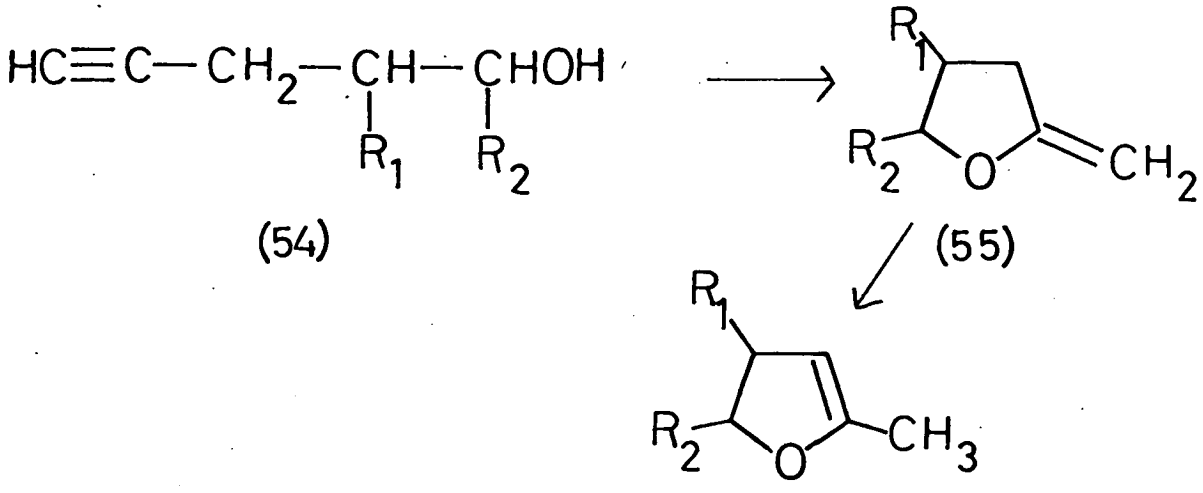
1.6 Cyclization and Pyrolysis Reactions of Acetylenes and Allenes

Ring systems can be built up when an acetylenic molecule contains a functional group which can be added to the triple bond. The ring closure is represented here:



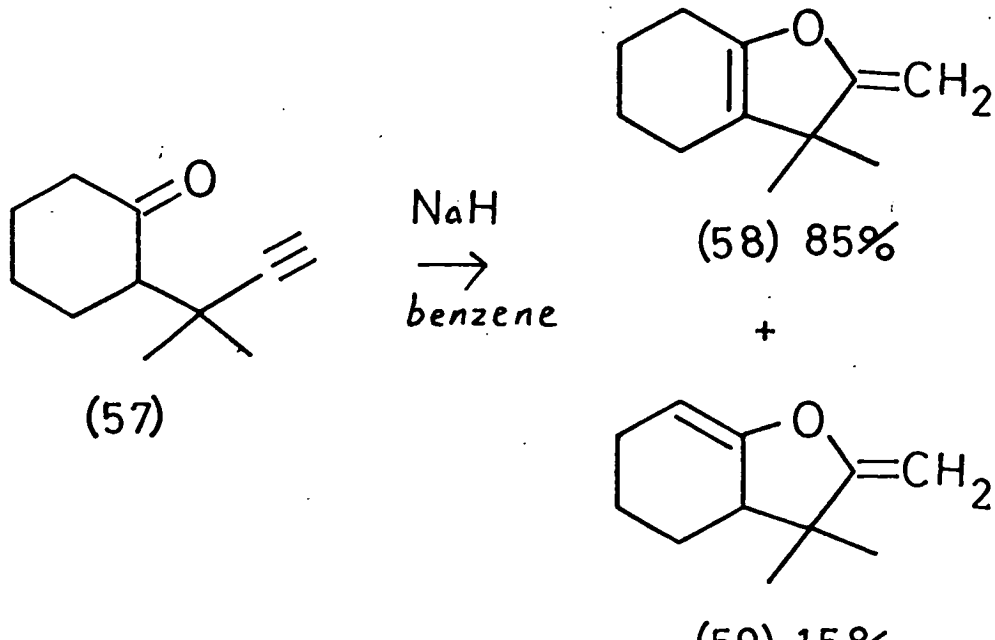
In most cases a is hydrogen. When b is nitrogen, oxygen or sulphur a variety of heterocyclic systems can be prepared. Baldwin[56] has set out rules which enable prediction of whether ring closure is possible for any given example.

γ-Acetylenic alcohols (54), when distilled over sodamide, give[57] dihydrofurans (56), via the methylene tetrahydrofuran (55) which can be isolated.



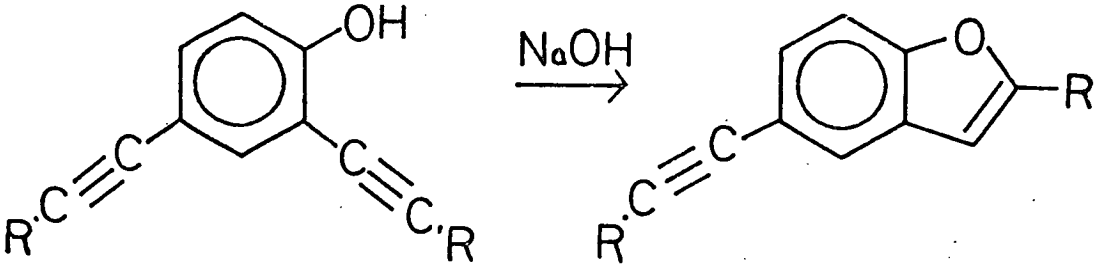
(54) (55) (56)

Many furan derivatives have been prepared in this way using a variety of reagents. For instance 2-(1',1'-dimethylpropargyl)cyclohexanone (57) cyclises with sodium hydride in benzene to give the cyclised products (58) and (59).[58]



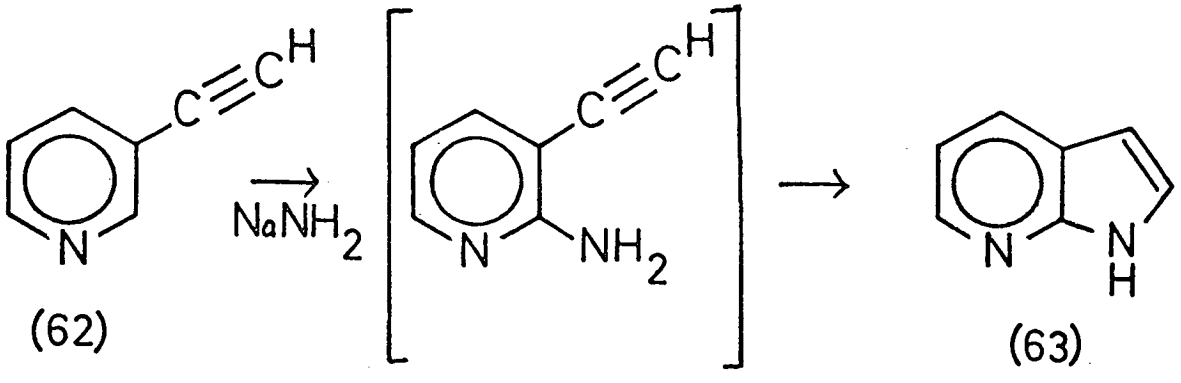
(57) (58) 85% + (59) 15%

Cyclization may also occur at the terminal acetylenic carbon. Benzofuran derivatives (61) were obtained from acetylenic phenols (60) when these are heated with aqueous NaOH.[59] Azaindole (63) was prepared



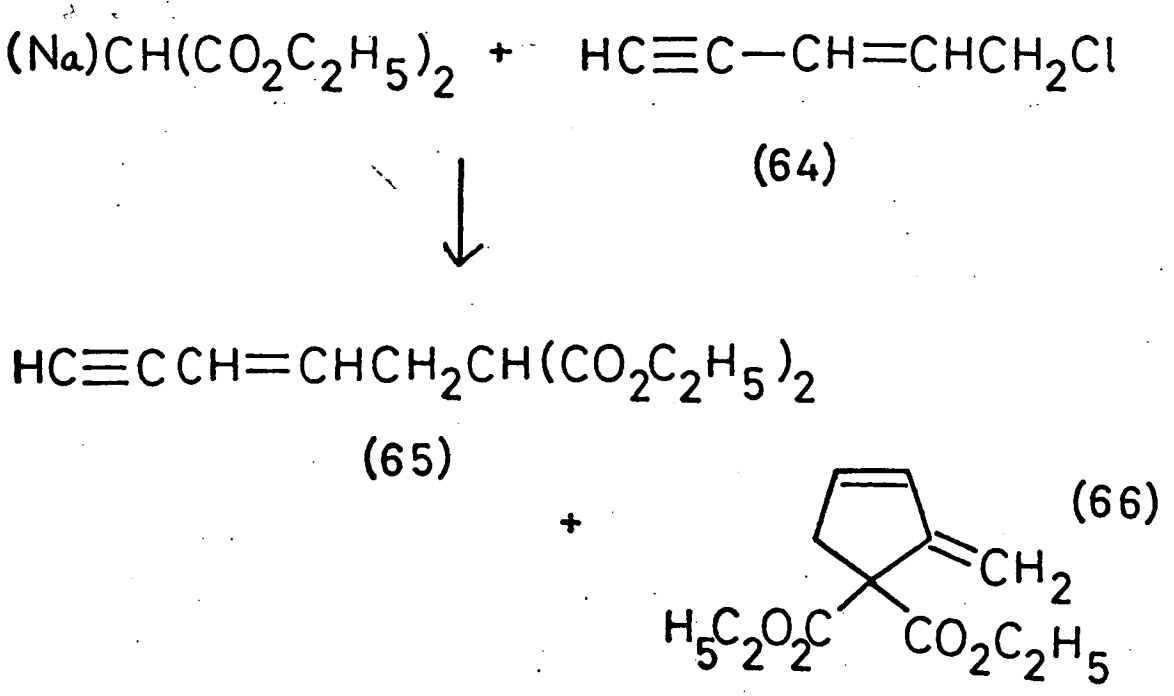
(60) (61)

by treating 3-ethynylpyridine (62) with sodamide.[60]

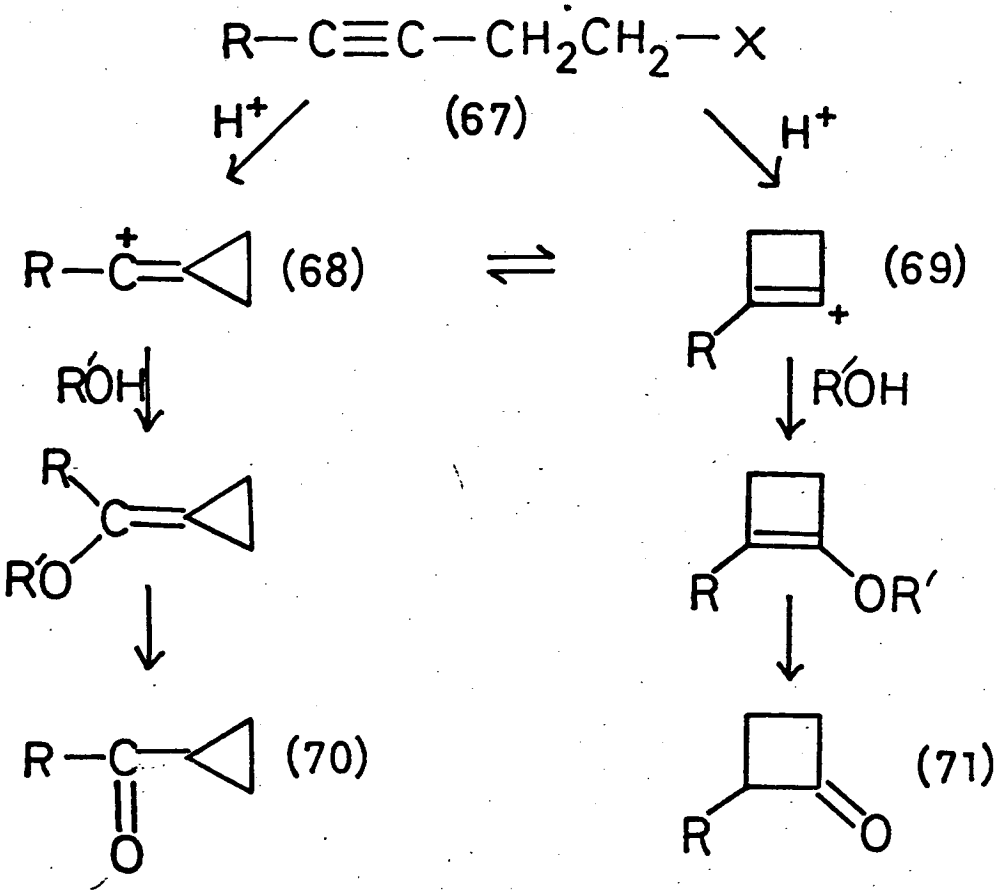


(62) (63)

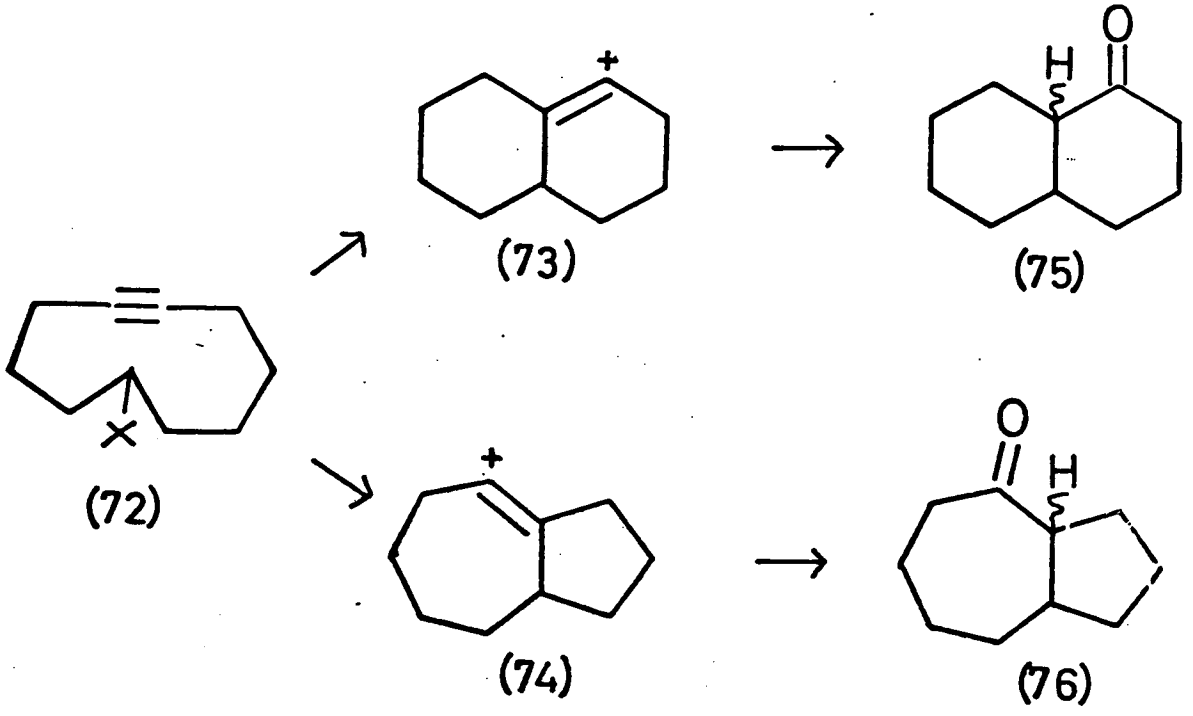
Intramolecular Michael addition to the triple bond takes place[61] in the reaction between diethyl malonate and 1-chloropent-2-en-4-yne (64). After 1 hour at room temperature in absolute ethanol, the ring closure product (66) is formed in 70% yield, together with uncyclised diethyl 2-(pent-2'-en-4'-ynyl) malonate (65).



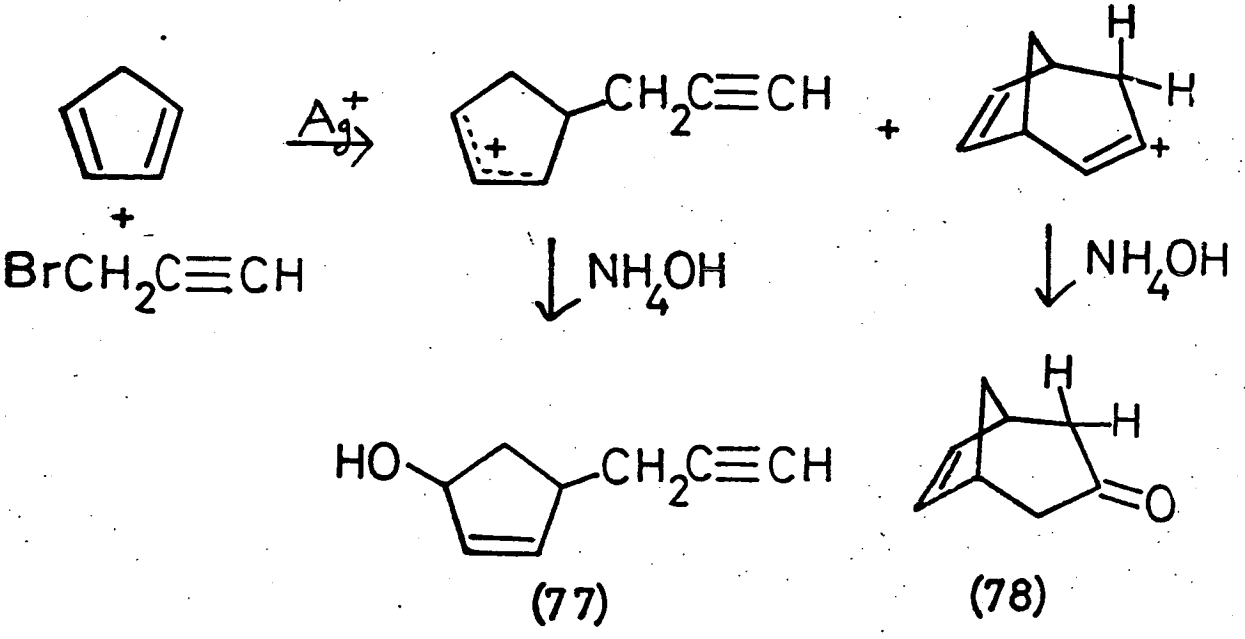
Carbonium ions readily cyclise onto acetylene or allene groups.[62] Substituted butynyl derivatives (67) have been shown[63] to cyclise via intermediate carbonium ions (68) and (69) to give the ketones (70) and (71). The products obtained depend on the substituents present.



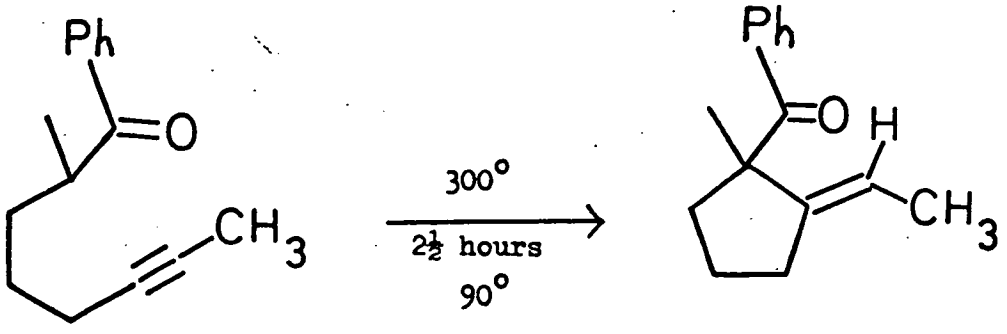
Solvolysis of 5-cyclodecynyl derivatives (72)[64] gave mainly cis and trans-1-decalone (75) while bicyclo [5.3.0] decan-2-one (76) is formed only in small amounts. The predominance of (75) is attributed to the greater stability of the vinyl cation (73) compared to (74).



Treatment of propargylbromide with cyclopentadiene and silver trifluoroacetate and hydrolysis with aqueous ammonia gave a mixture of 4-(2'-propynyl)cyclopent-2-en-1-ol (77), 85%, and bicyclo [3.2.1] oct-6-en-3-one (78), 15%.[65]

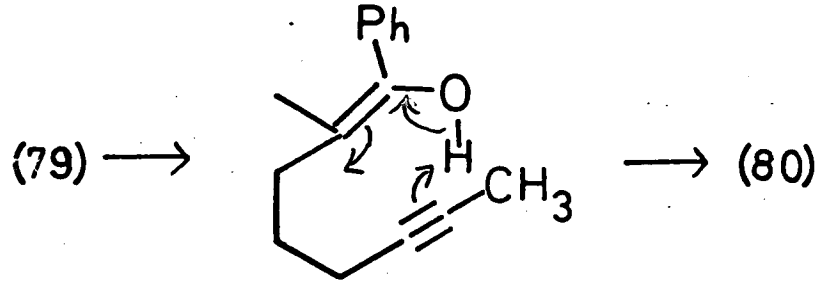


Similar cyclisations have been induced by thermal methods. The ketone (79), on heating in a sealed tube gave the benzoylcyclopentane (80).[66]



(79) (80)

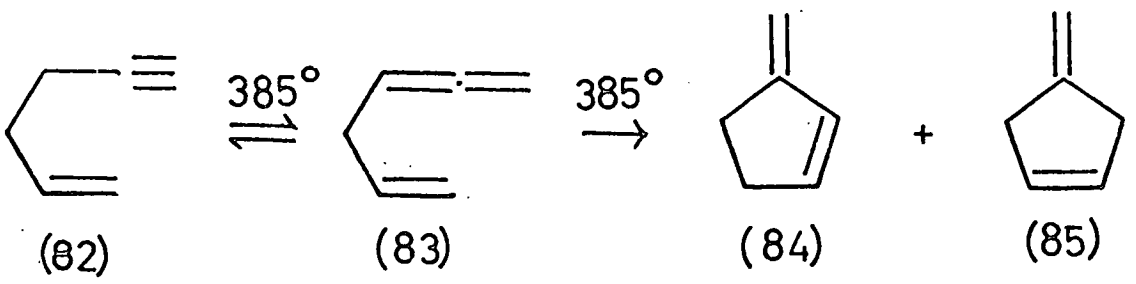
These reactions probably proceed via the enol:



However an analogous reaction which would have resulted in a spirane (81) did not occur for any obvious reason.

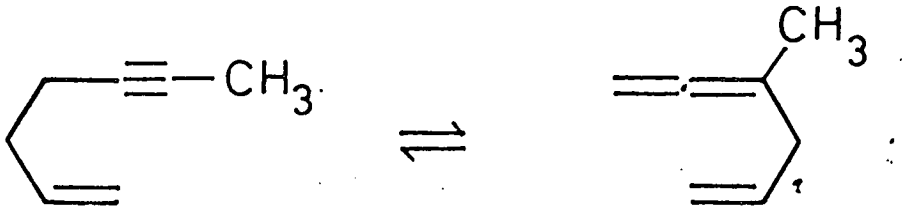
(81)

Passing hex-1-en-5-yne (82) through a hot tube at 340°C with nitrogen gives 1,2,5-hexatriene (83) which in turn cyclises to 3- and 4-methylenecyclopentenes (84) and (85).[67]

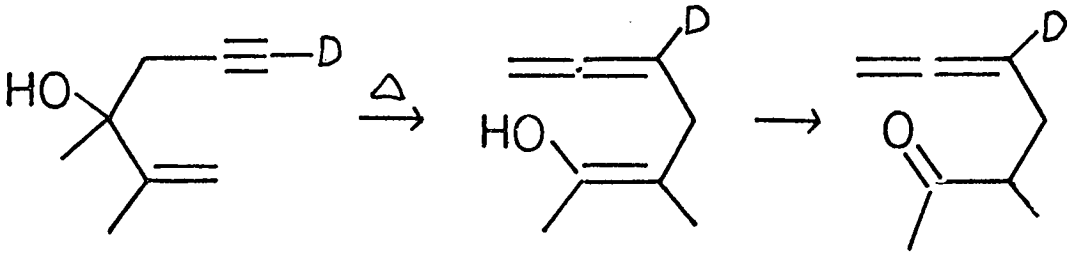


(82) (83) (84) (85)

All four compounds were isolated from the product mixture. The reversible rearrangement (82)→(83) is thought to be a "Cope" type rearrangement. For example:



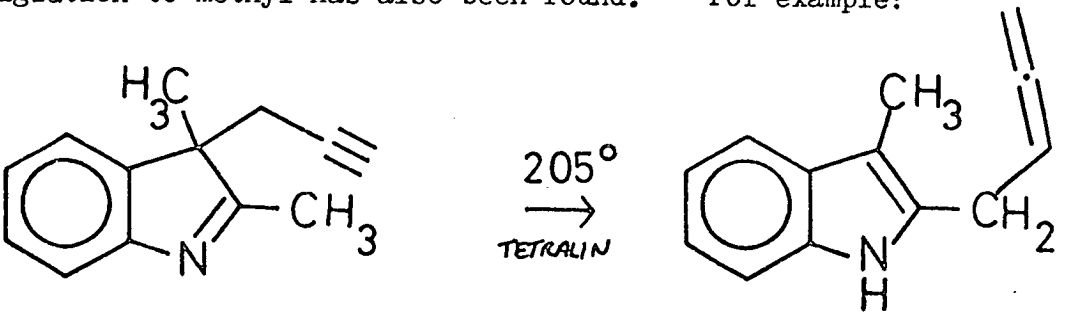
The rearrangement takes place via a 3,3 sigmatropic shift of the propargyl group. Another example[68] of 1,5 enyne rearrangement is shown:



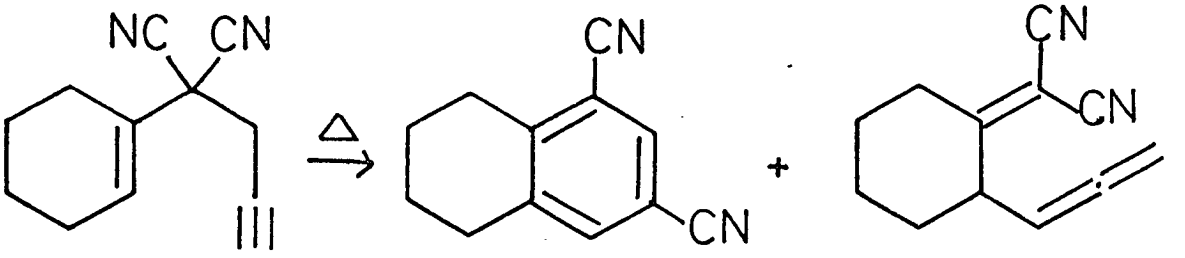
"Claisen" rearrangements* with propargyls are well known when the propargyl is attached to oxygen. For example:[69]

* So called when the rearranging group is attached to an atom other than carbon - otherwise it is called a Cope rearrangement.

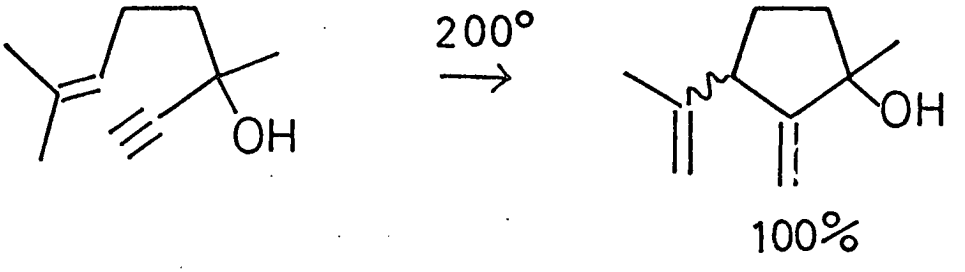
Migration to methyl has also been found.[70] For example:



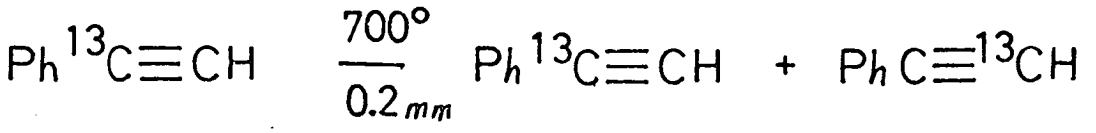
A recent example[71] also gave a cyclised product.



This is an example of an 'ene' cyclisation.[72] With 1,6 enynes, five membered rings are usually formed. For example:[73]

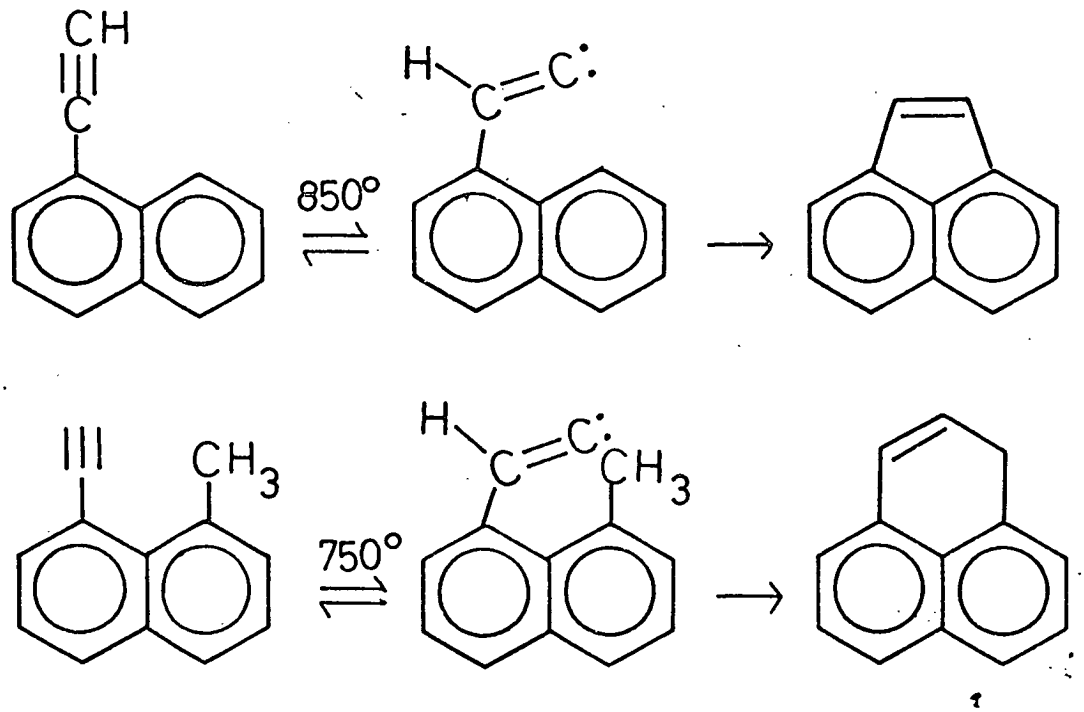


Vapour phase vacuum pyrolysis of alkyl and aryl acetylenes leads to scrambling of the acetylenic carbons above 700°C, demonstrated by carbon labelling.[74]



A carbene intermediate RCH=C: has been proposed.

Cyclisations have been described in which this carbene figures as an intermediate.[75] For example:



Object of Research

The original aim of this work was to prepare vinylidene and vinyl-vinylidene carbene adducts with a selection of indenes and dihydronaphthalenes and to study their rearrangements with acid and base in order to rationalise the routes involved. The use of phase transfer catalysis in synthesis was also attempted in order to assess the usefulness of this method. Attempted preparation of vinylvinylidene adducts has led to a variety of alkenyl derivatives which occurred as byproducts and have proved to give interesting rearrangements. This prompted a broader study of alkynyl substituted indenes, fluorenes and cyclopropanes, and their reactions; an area of chemistry which has been largely ignored.

CHAPTER 2

Synthesis of Cyclopropanes

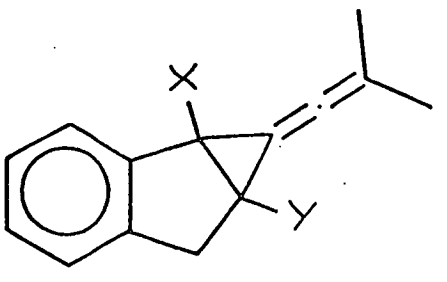
2.1 General Methods

The cyclopropanes were all prepared as adducts of a carbene and an olefin. The carbene was normally generated by the action of potassium t-butoxide on the appropriate halide, although in some cases phase transfer catalysed reactions, using potassium hydroxide as base, proved successful. Crude product mixtures were separated by alumina or silica gel chromatography, eluting with petroleum ether/ether mixtures. The adducts tended to darken and polymerise if left at room temperature and were stored at -15°C.

The formulae were confirmed by analysis and/or exact mass measurements and structures were confirmed by i.r. and n.m.r. spectroscopy. All adducts showed i.r. absorption in the region 2000-2050 cm^{-1} due to the allene group. This absorption is higher than for a normal allene (1900-2000 cm^{-1}) due to the bond strain from the cyclopropane ring.[40] The ^{13}C n.m.r. showed resonances at 188± 1p.p.m. corresponding to the central carbon of the allene system. Other pertinent features of the n.m.r. spectra are discussed in the following sections as appropriate.

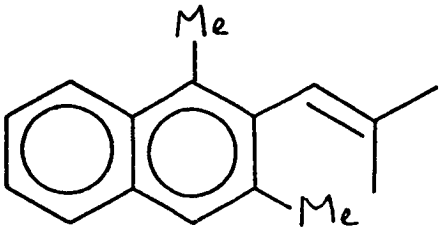
2.2 Vinylidene Cyclopropanes

Adducts (86), (87) and (88) from indene, 3-methylindene and 2-methylindene, were prepared as described by Stewart[21] and by Robertson[76] using potassium t-butoxide and 1-bromo-3-methylbuta-1,2-diene to generate the carbene.

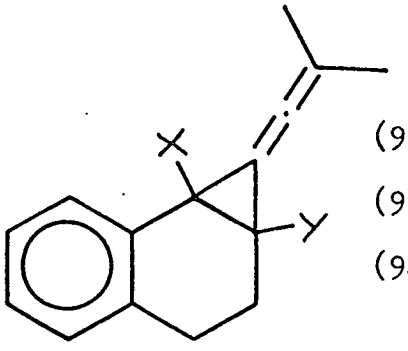


(86) X = Y = H
(87) X = CH_3; Y = H
(88) X = H; Y = CH_3
(89) X = C_2H_5; Y = H
(90) X = Y = CH_3

Adducts (89) and (90) from 3-ethylindene and 2,3-dimethylindene were similarly prepared for the first time. Attempts by Robertson[76] to prepare compound (90) yielded only 1,3-dimethyl-2(2'-methylprop-1'-enyl)naphthalene (91), presumably formed from compound (90) during the workup.



(91)



(92) X = Y = H

(93) X = H; Y = CH_3

(94) X = CH_3; Y = H

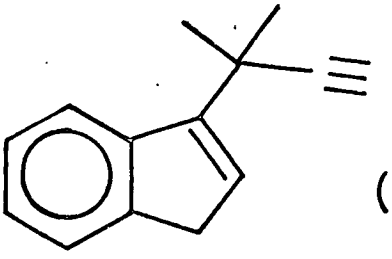
Adducts (92), (93) and (94) from 1,2-dihydronaphthalene and 3- and 4-methyl-1,2-dihydronaphthalene respectively were similarly prepared as by Stewart[21] but were obtained as white crystals for the first time.

Preparation via a phase transfer catalysed process was attempted from all of the indenes but only indene and its 3-methyl and 3-ethyl derivatives gave reasonable yield of adduct (see table 2).

Table 2

Olefin	t-BuOK Method adduct yield (%)	Phase Transfer Method adduct yield (%)
indene	26	20
3-methylindene	40 - 45%[21]	55
2-methylindene	38	0
3-ethylindene	90	20
2,3-dimethylindene	80	0

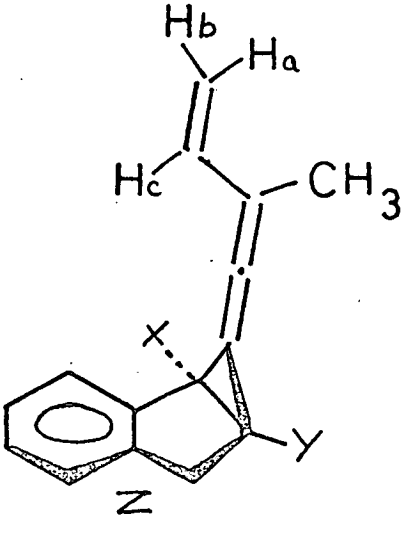
The method employed used no solvent and was found to be superior to that of Sasaki, Eguchi and Ogawa[38] which used benzene as a solvent. 3(1'-Dimethylprop-2'-ynyl)indene (95) was also isolated from the phase transfer catalysed reaction with indene and is thought to be formed via nucleophilic attack of the indenyl anion on the carbene generator.

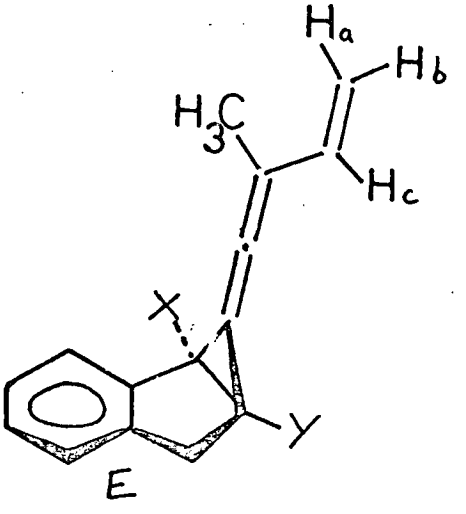


(95)

2.3 2-Vinylpropenylidene Cyclopropanes

Adducts, (96), (97) and (98) of 3-methylindene, 2-methylindene and 2,3-dimethylindene, were all prepared using potassium t-butoxide on 1-bromo-3-methylpent-2-en-4-yne to generate the carbene. The phase transfer catalysed method did not give cyclopropanes (see chapter 3.4). The cyclopropanes were isolated by alumina chromatography as mixtures containing equal amounts of the E and Z isomers.





(96) X = CH_3; Y = H Yield 45 - 60%

(97) X = H ; Y = CH_3 Yield 20%

(98) X = CH_3; Y = CH_3 Yield 33%

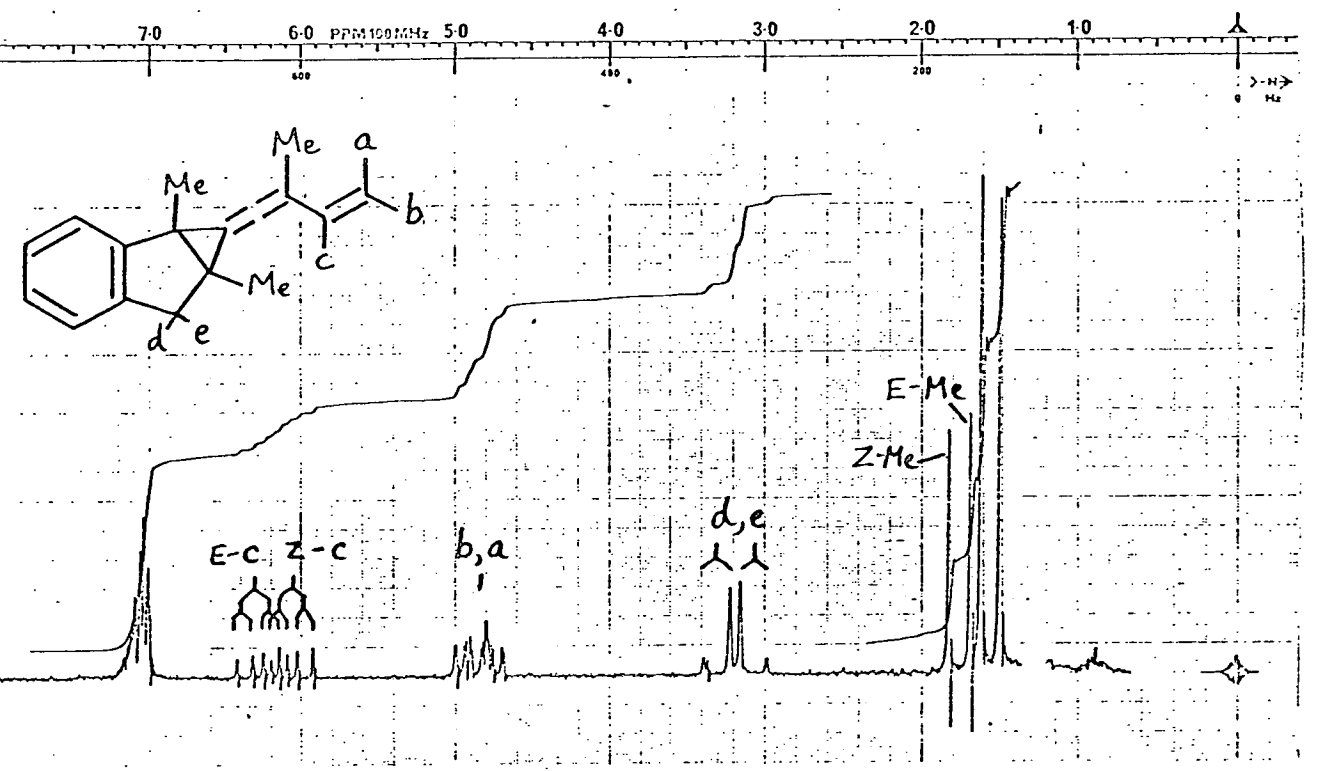


Figure 1

The proton n.m.r. spectra clearly show the two isomers. As an example the proton n.m.r. spectrum of the adduct from 2,3 dimethylindene (98) is shown in figure 1. The E-methyl protons resonate at a lower frequency (1.74δ) than the Z-methyl protons (1.82δ) due to the shielding effect of the benzene ring. The Z-vinyl proton (H_c) similarily resonates at a lower frequency (6.06δ) than the E-vinyl proton (6.28δ) for the same reason. The terminal vinyl protons (H_a and H_b) are not so greatly shifted. The non-equivalent benzylic methylene protons appear as an AB spectrum at 3.30 and 3.08δ.

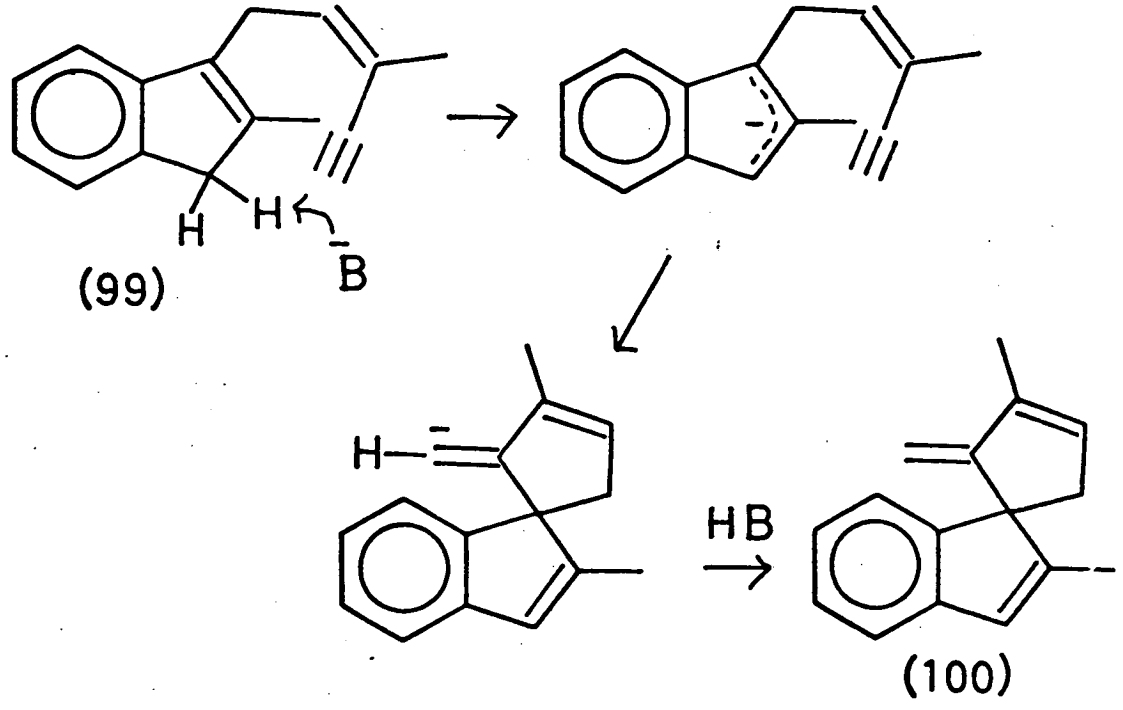
As well as the desired adducts 2-methylindene also yielded Z-3-(3'-methylpent-2'-en-4'-ynyl)-2-methylindene (99), 35%, and spiro[2-methylene-3-methylcyclopent-3-ene-1,1'-2'-methylindene] (100), 0 - 6%. 3-Methylindene also yielded Z and E-1-(3'-methylpent-2'-en-4'-ynyl)-1-methylindene (130) and (133), Z:E = 3:1, 7%, and Z-1-(3'-methylpent-2'-en-4'-ynyl)-3-methylindene (129), 14%, and spiro[2-methylene-3-methylcyclopent-3-ene-1,1'-3'-methylindene] (197), 0 - 7%. The structural identifications are discussed in chapters 3.4 and 5.2.

Reaction of indene with the bromo-enyne unfortunately gave no adduct at all (as found by Watson[45]), and yielded only Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126b). The structural identification is again discussed in chapter 3.4.

The mechanism of alkynylation is uncertain. A related reaction[46] suggests a mechanism proceeding via attack of the carbene on the indenyl anion (see chapter 1.4). However, allyl bromide, which does not form a carbene, gave 68% yield of allyl indene with tBuOK, although ethyl bromide gave no reaction. This may indicate direct attack of the indenyl anion on the allyl bromide, an activated halide; ethyl bromide not being sufficiently active for attack. The related bromoenynes will be similarly activated and may react in the same way.

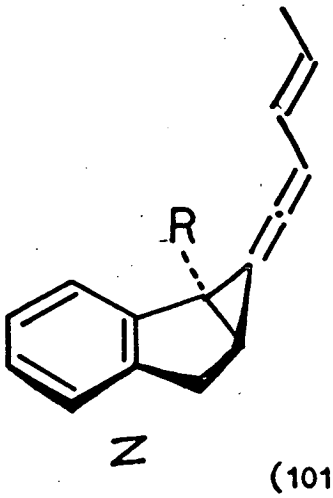
The spiro compounds are believed to arise from base catalysed

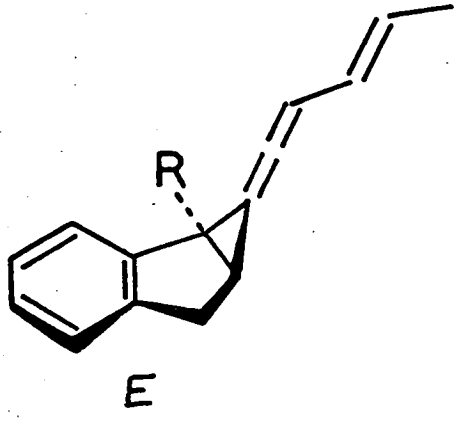
cyclisation of the acetylenic derivatives. For example the 2-methylindene derivative (99) would cyclise to give the spiro compound (100).



2.4 Pent-3-enylidene Cyclopropanes

Pent-3-enylidene cyclopropane adducts (101) and (102) were prepared from indene and 3-methylindene using potassium t-butoxide and 5-bromohex-3-en-1-yne to generate the carbene. The adducts were obtained as mixtures containing equal amounts of the E and Z isomers as was evident from the proton n.m.r. spectra.





(101) R = H Yield 10%

(102) R = CH_3 Yield 54%

The i.r. spectra showed strong absorptions at 960 cm^{-1} indicating a trans double bond, as well as the absorption due to the allene at 2000 cm^{-1}. The adduct from indene was difficult to isolate as it rearranged rapidly during chromatography on silica gel and more slowly on alumina. This rearrangement is discussed in chapter 4.3. As well as the desired adduct, indene also yielded E-3-(1'-methylpent-2'-en-4'-ynyl)indene (122a), 24%.

2.5 Conclusions

These results show that indene is much less susceptible to carbene attack than are the alkyl substituted indenes. This is because of the electron donating alkyl groups increasing the electron density of the double bond. A more accurate picture would be gained by performing competitive reactions in which two indenes are allowed to compete for a limited amount of carbene. Increasing the electron density should have the reverse effect on alkylation since the indenyl anion will be destabilized. Hence indene, as might be expected on this basis, gave alkylated product exclusively with 1-bromo-3-methylpent-2-en-4-yne.

CHAPTER 3

Preparation of Acetylenic Compounds

3.1 Introduction

The mildly acidic properties (see table 3) of cyclopentadiene, fluorene, indene and their derivatives allow the anions of these compounds

Table 3

Compound	pKa
cyclopentadiene	15
indene	18.5
phenylacetylene	18.5
fluorene	22.9
acetylene	25
toluene	35
ethylene	36.5
propane	44

to be readily generated. The anions in turn will attack alkyl halides to give substitution products. Simple alkylations are well documented but due to preparative difficulties[77] examples in which alkyne groups are substituted are little known. Two routes have been employed in the current work:

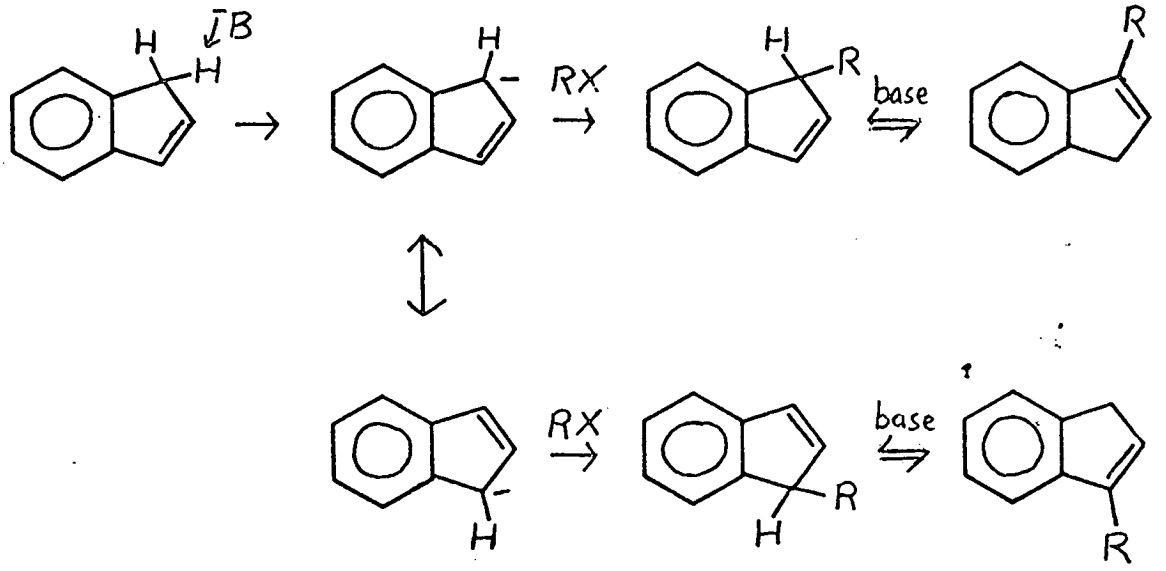
Method A. Reaction of a halide with an organo sodium derivative of the hydrocarbon in liquid ammonia.

Method B. Reaction of the halide with the hydrocarbon and aqueous potassium hydroxide in the presence of a phase transfer catalyst.

Method B has not previously been used to prepare alkynyl derivatives. Method A has been previously used to prepare propargylindene and

propargylcyclopentadiene.[77]

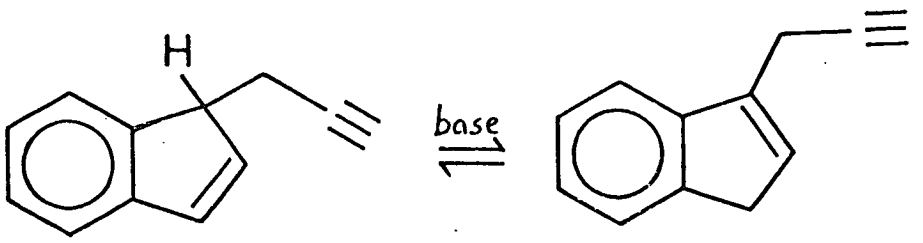
In general substituted indenes can yield several products since the generated indenyl anion is delocalized and attack may occur at either of the 1- or 3- positions. In addition, product isomerization is possible in basic media, the most highly substituted olefin normally being the most stable.



In the same way cyclopentadiene may attack to give 1-, 2- or 3- substituted products.

3.2 Reactions with Simple Bromoalkynes

The reaction of indene with propargyl bromide via method B first yields 1-propargylindene (103) but this product subsequently rearranges to 3-propargylindene (104).



(103) (104)

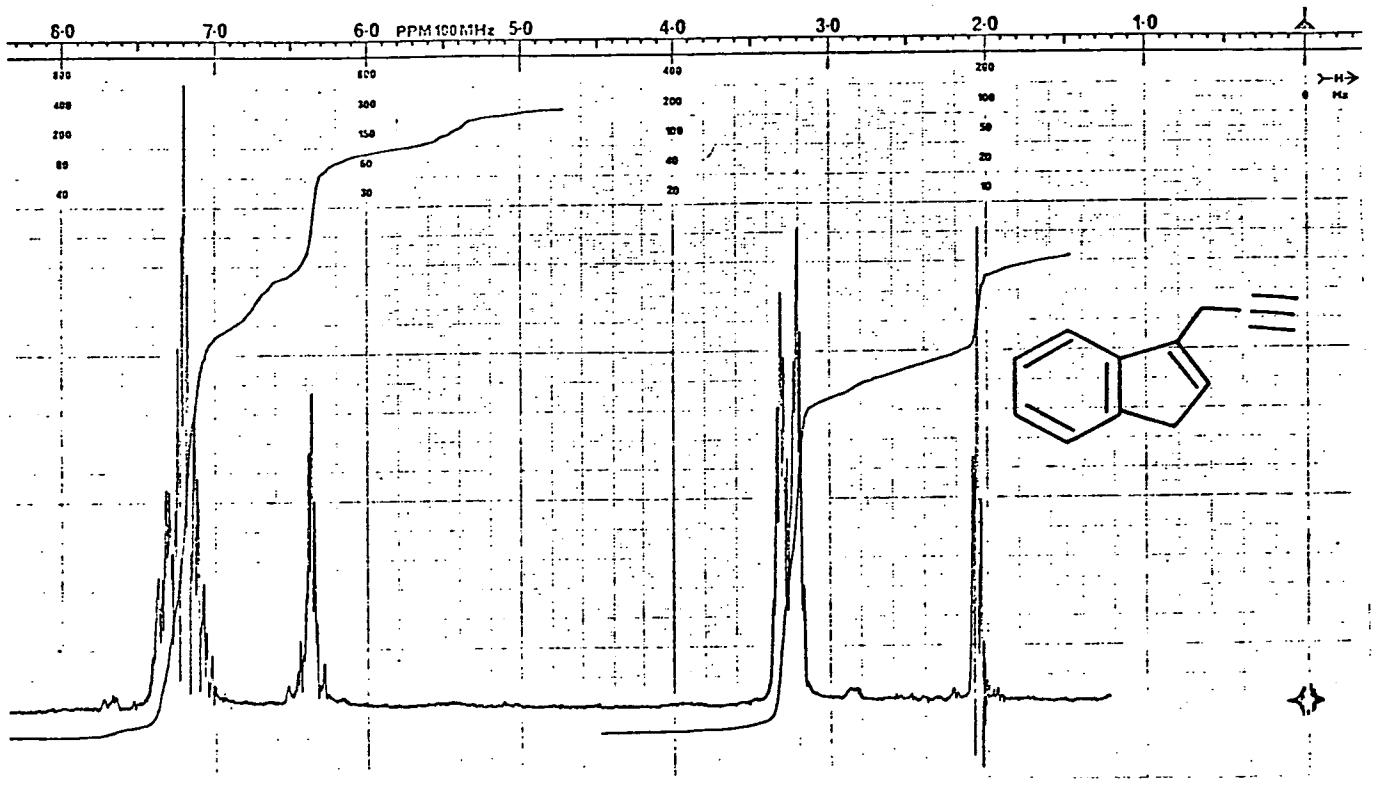


Figure 2

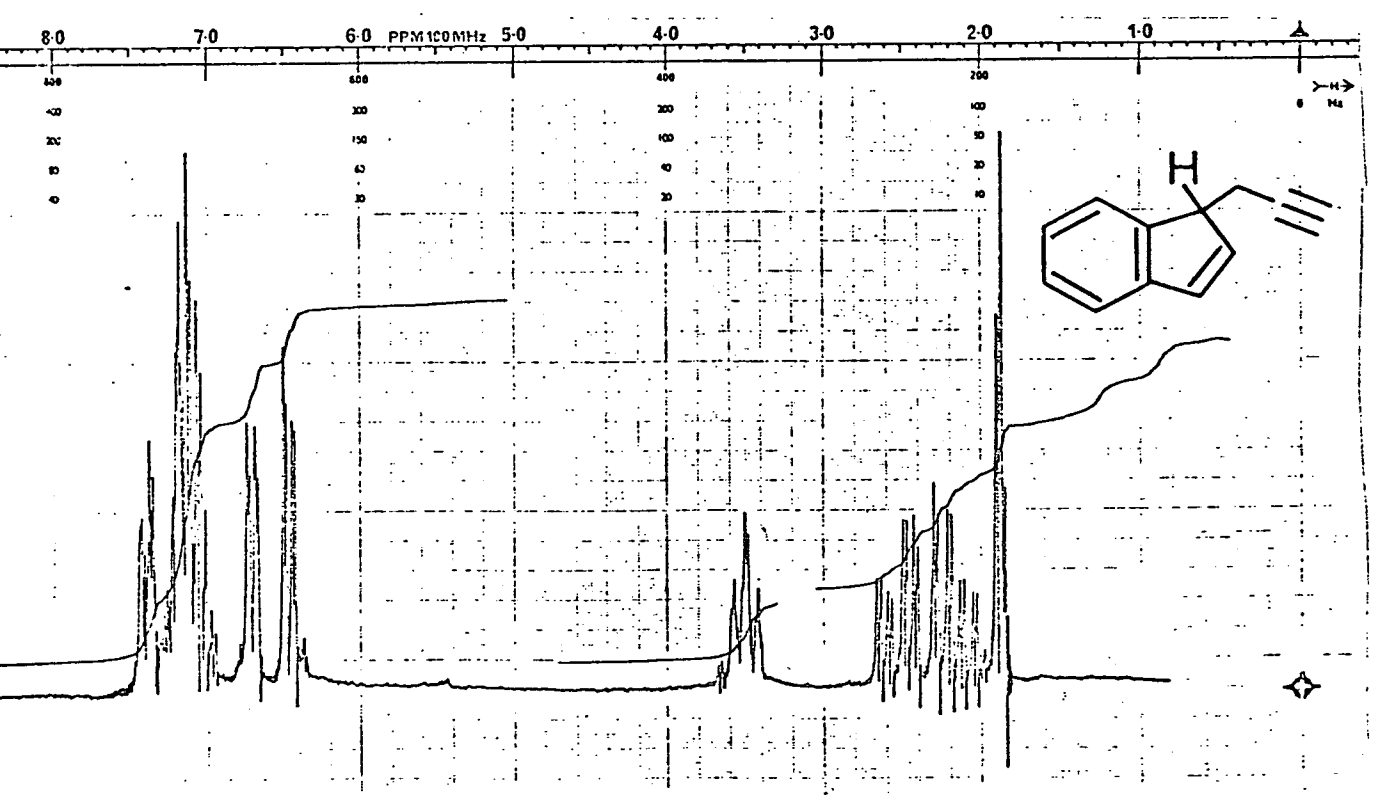
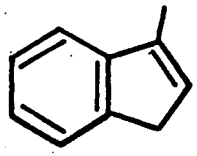
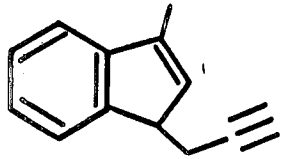
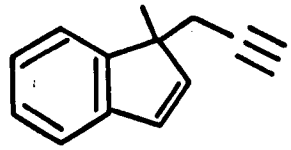
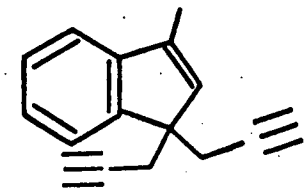
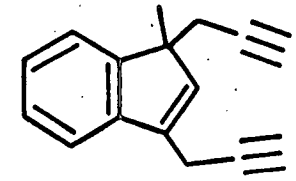
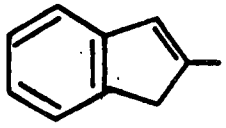
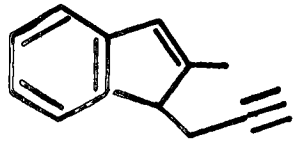
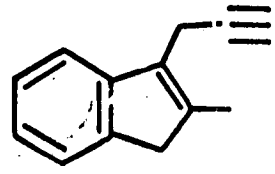
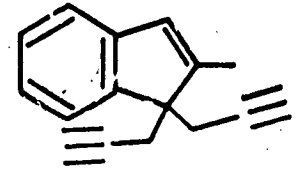
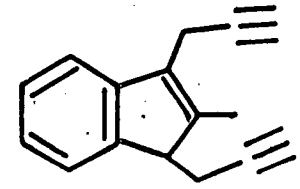
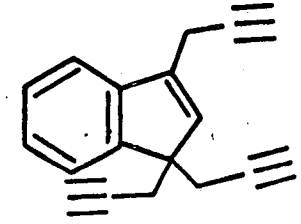
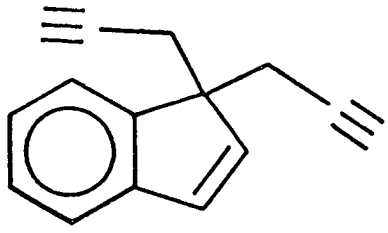


Figure 3

Table 4

Olefin	Mono-propargyl derivatives		Di-propargyl derivatives		Tri-propargyl derivatives
					
Product ratio	(106) 2	: (107) 1	(108) 1	: (108/1) 1	
					
Product ratio	(109) 1	: (110) 2	(111) 1	: (112) 2	(113)

The rearrangement is quite slow under these conditions and 1-propargylindene (103) was isolated in 20% yield by stopping the reaction before completion. 1,1-Dipropargylindene (105) could also be isolated, a higher proportion being formed if excess propargyl bromide was used.



(105)

The products all showed a strong acetylenic C-H absorption at 3300 cm^{-1} and a weak acetylenic C≡C absorption at 2100 cm^{-1} in the infra red. 1- and 3-propargylindenes (103) and (104) were readily identified from their ^1H n.m.r. spectra. 3-Propargylindene (figure 2) shows a single olefinic proton at 6.36δ and a broad 2-proton resonance at 3.32δ due to the benzylic methylene. The peak at 2.06δ is assigned to the acetylenic proton which is weakly coupling to the methylene at 3.20δ. 1-Propargylindene (figure 3) shows two olefinic protons as a pair of doublets (J = 6Hz) at 6.47δ and 6.71δ. The non-equivalent propargylmethylene gives rise to an AB spectrum (J = 17Hz) at 2.17δ and 2.53δ which is further split by the benzylic proton (J = 9Hz, lower frequency; J = 7Hz, higher frequency) at 3.50δ and by the acetylenic proton (J = 3Hz) at 1.97δ.

3-Methylindene and 2-methylindene behaved similarly with propargyl bromide. The products (see table 4) were separated by preparative vapour phase chromatography and identified by exact mass measurement and from their i.r. and ^1H n.m.r. spectra.

Cyclopentadiene and propargyl bromide gave a mixture of monopropargyl derivatives by method B, probably the 2 and 3 isomers, and also a mixture of dipropargyl derivatives. The individual compounds have not been isolated being unstable to preparative vapour phase chromatography.

Fluorene gave predominantly 9,9-dipropargylfluorene (114) with propargyl

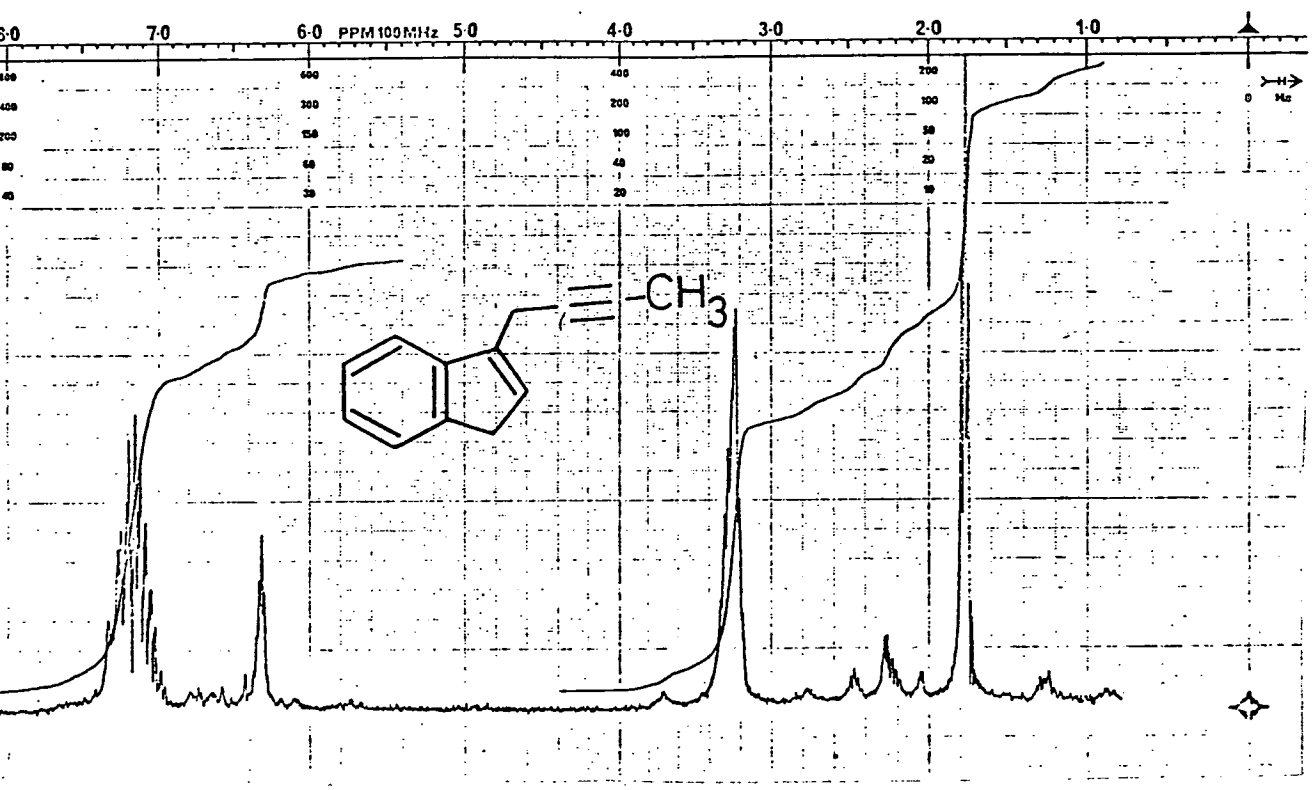
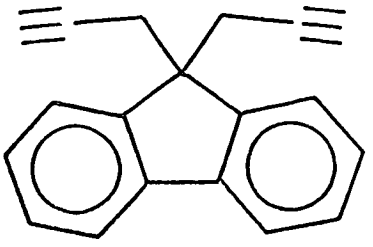
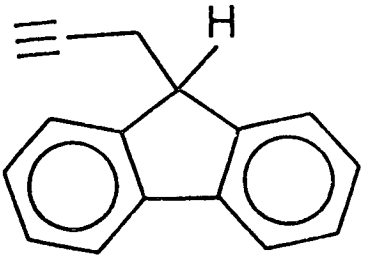


Figure 4

bromide by method B. Ready formation of disubstitution at the 9-position in fluorene has been observed elsewhere.[78] 9-Propargylfluorene (115) could only be obtained in poor yield using a large excess of fluorene.



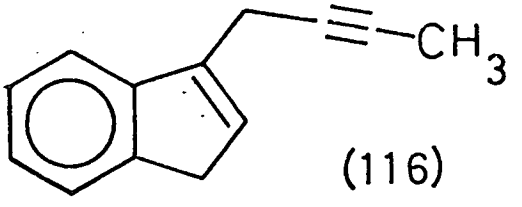
(114)



(115)

The products were isolated by alumina chromatography, the dipropargyl product (114) being obtained as white crystals. A purer disubstituted product (114) was obtained by method A.

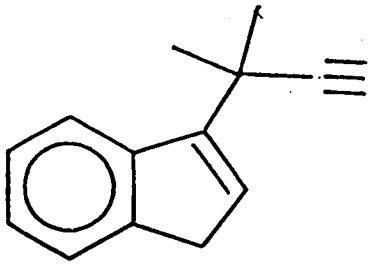
The reaction of indene and 1-bromobut-2-yne by method B gave good yields of 3(but-2'-ynyl)indene (116). This compound did not show an



(116)

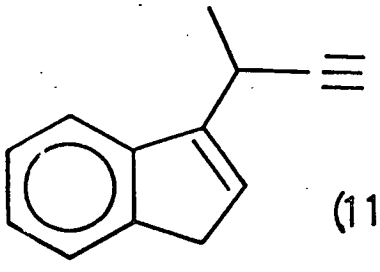
acetylenic C≡C absorption in the i.r. at 2100 cm^{-1} as might be expected. This peak is often small, however, especially with non-terminal acetylenes. The compound was characterised by exact mass measurement and from its ^1H n.m.r. (figure 4) which shows a methyl resonance at 1.76δ with long range coupling (J = 3Hz). The two methylene groups resonate in the region 3.14δ- 3.40δ and the one proton olefinic resonance at 6.32δ indicates substitution at C(3). No evidence was found for substitution at C(1) presumably due to rapid isomerism.

With 1-bromo-3-methylbuta-1,2-diene, indene gave mostly cyclopropyl adducts by method B (see chapter 2.2) and hence method A was used to obtain alkylation. The product, 3(1,1'-dimethylprop-2'-ynyl)indene (95) was identified by exact mass measurement and from its i.r. and ^{1}H n.m.r. spectra. Cyclopentadiene gave a mixture of substituted (1',1'-dimethylprop-2'-ynyl)cyclopentadienes also by method A.



(95)

Reaction of indene with 3-bromobut-1-yne by method B gave poor yields of alkynes, however a good yield of the desired product was obtained using method A. The product, 3(1'-methylprop-2'-ynyl)indene (118), was identified by exact mass measurement and from its i.r. and ^{1}H n.m.r. spectra.



(118)

Method B, however, was used to produce a mixture of monosubstituted (1'-methylprop-2'-ynyl)cyclopentadienes.

5-Bromopent-1-yne was reacted with indene and 2-methylindene by method B to give respectively 3(pent-4'-ynyl)indene (119) and 2-methyl-3(pent-4'-ynyl)indene (120) identified by exact mass measurement and from the i.r. and ^{1}H n.m.r. spectra.

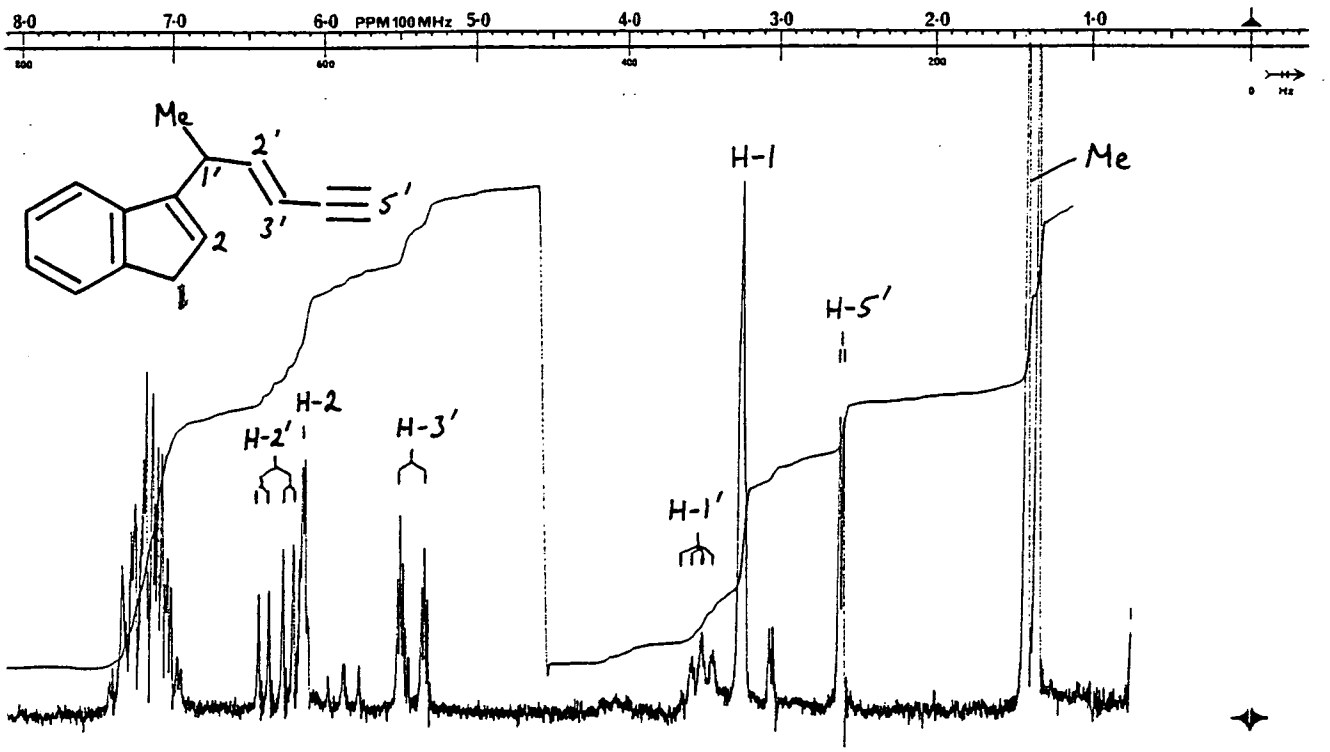


Figure 5

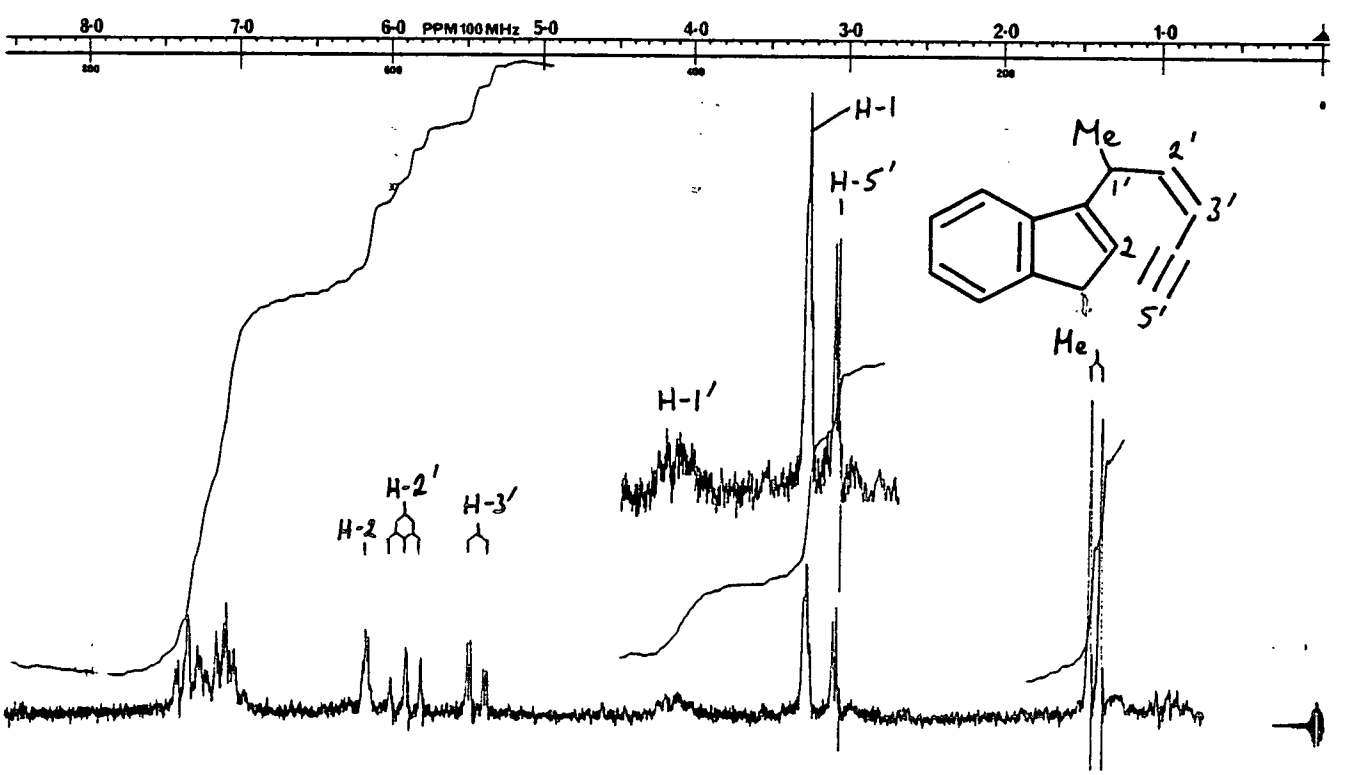
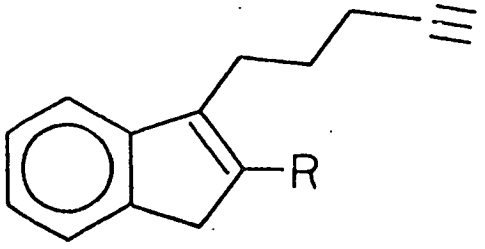


Figure 6

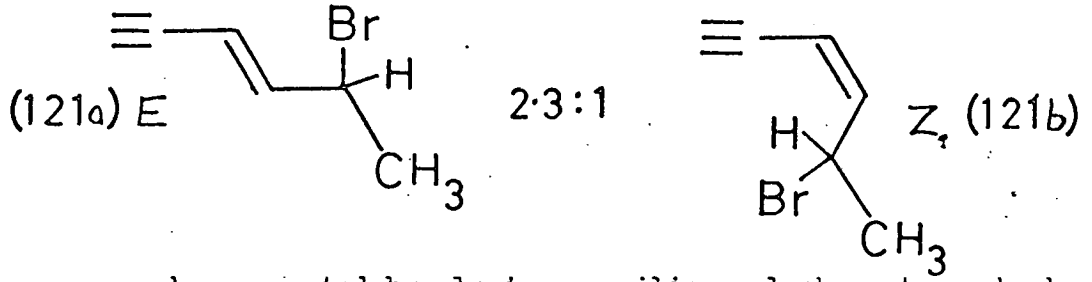


(119) R = H

(120) R = CH_3

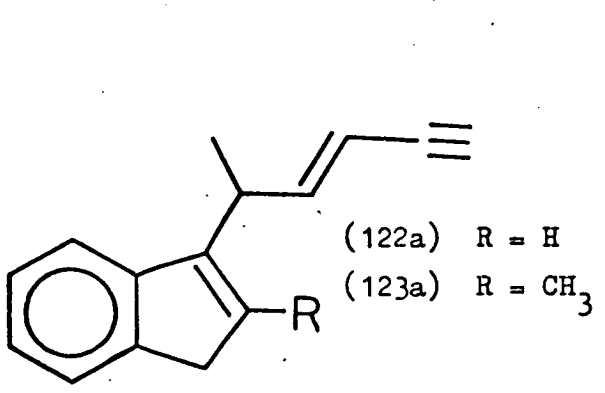
3.3 Reactions with E and Z-2-bromohex-3-en-5-yne

2-Bromohex-3-en-5-yne, as prepared, consists of a mixture of E and Z isomers (121a and b) in the ratio 2.3:1. Preparation of the chloride or the parent alcohol also gave mixtures of geometrical isomers. The



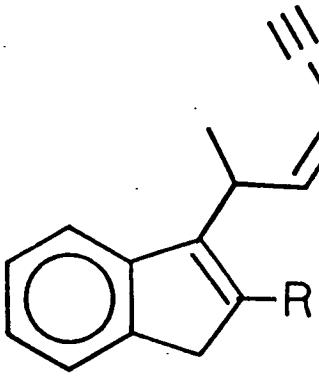
isomers may be separated by alumina or silica gel chromatography however there is a large loss of product on the column. The configurations of the two isomeric bromides were assigned from their ^1H n.m.r. and i.r. spectra. The E isomer (121a) shows olefinic proton resonance with a 15Hz coupling and an infra-red absorption at 950 cm^{-1} characteristic of a trans olefin. The Z isomer (121b) shows olefinic proton resonance with a 11Hz coupling and an infra-red absorption at 760 cm^{-1} characteristic of a cis olefin. The acetylenic proton resonances of the E and Z isomers occur at 2.81 δ and 2.23 δ respectively.

Reaction between indene and the bromide mixture by method B gave E and Z-3(1'-methylpent-2'-en-4'-ynyl)indene (122 a and b) separable by preparative vapour phase chromatography in the ratio Z:E = 2:1. When pure Z-bromide was used then only the Z isomer was obtained. The E and Z isomers are readily differentiated by their ^1H n.m.r. (figures 5 and 6) and i.r. spectra in a similar way to the bromides. The acetylenic



(122a) R = H
(123a) R = CH_3

E- isomer



(122b) R = H
(123b) R = C

Z- isomer

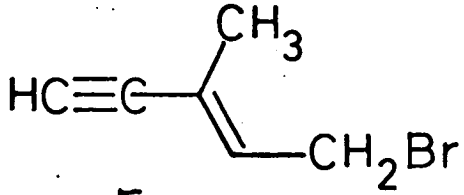
protons resonate at Z, 3.06δ and E, 2.60δ. The ^{13}C n.m.r. spectra are similar apart from the resonance of the acetylenic carbon atoms. In the Z isomer the terminal carbon resonates at a lower frequency (76.7 p.p.m.) than the non-terminal carbon (82.3 p.p.m.). In the E isomer the relative positions are reversed (terminal - 82.3 p.p.m.; non-terminal - 80.3 p.p.m.).

A mixture of E and Z-3(1'-methylpent-2'-en-4'-ynyl)-2-methylindene (123a and b) was prepared in the same way from 2-methylindene in the ratio E:Z = 2.2:1. These were separated by preparative vapour phase chromatography.

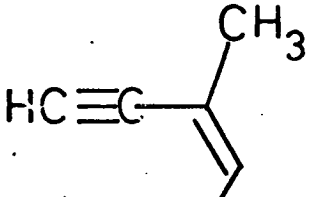
3-Methylindene gave a complex mixture by method B which has not yet been rationalized. None of these compounds could be made by method A due to polymerization of the bromoenyne.

3.4 Reactions with 1-Bromo-3-methylpent-2-en-4-yne

1-Bromo-3-methylpent-2-en-4-yne was obtained as a mixture of E and Z isomers (124a and b) in the ratio 1:6 by analytical vapour phase chromatography. The major isomer was assigned the Z configuration on the



E
(124a)



Z
(124b)

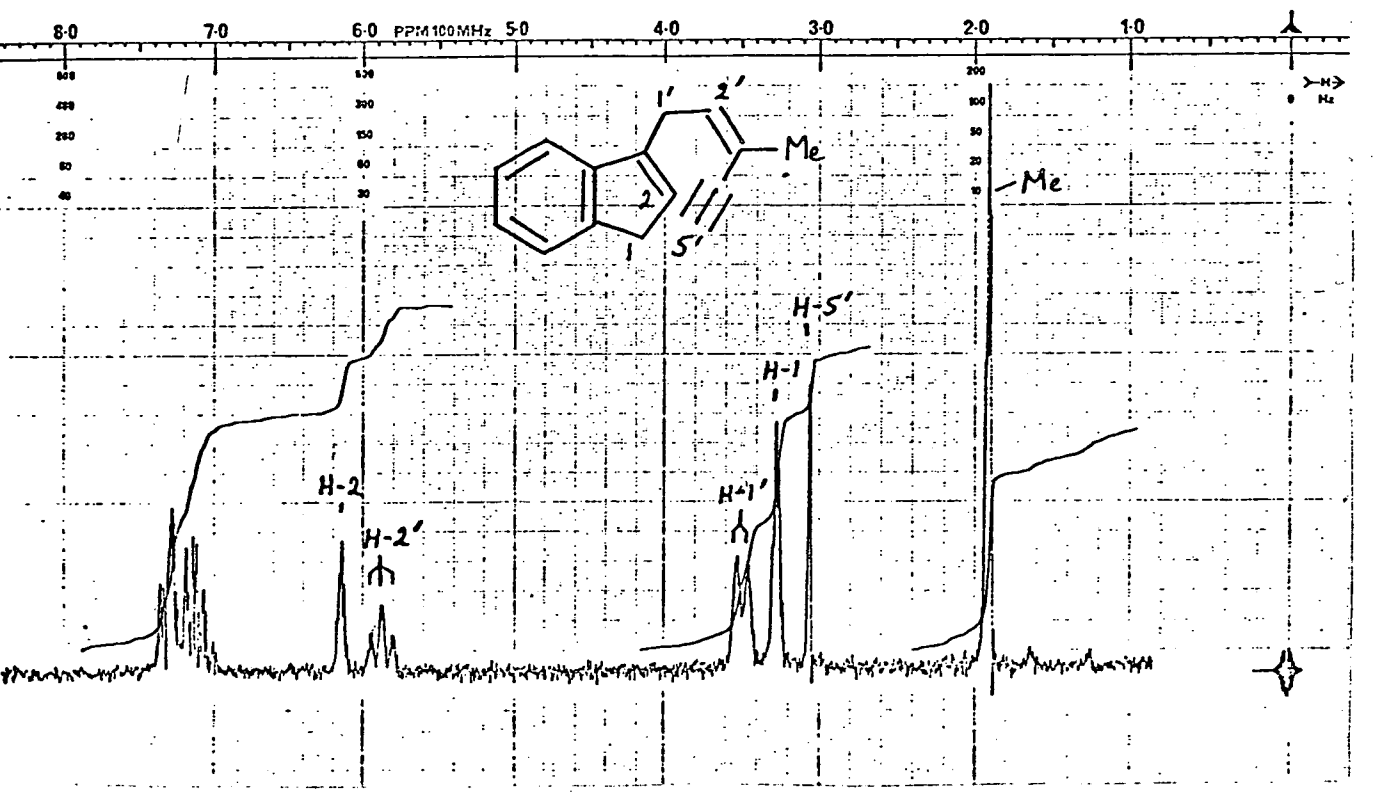
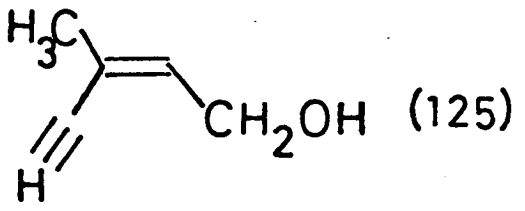


Figure 7

basis of the following observations: (a) Comparison of the ^1H n.m.r. spectrum with the published spectra of E and Z-3-methylpent-2-en-4-yn-1-ol[79], showed agreement between the acetylenic proton resonances for the

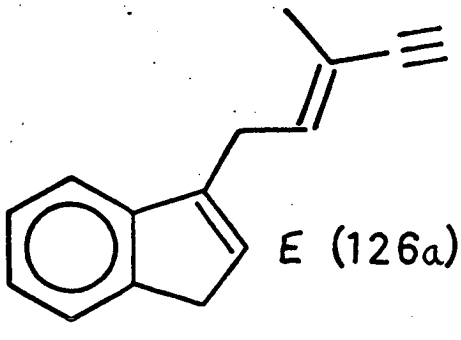


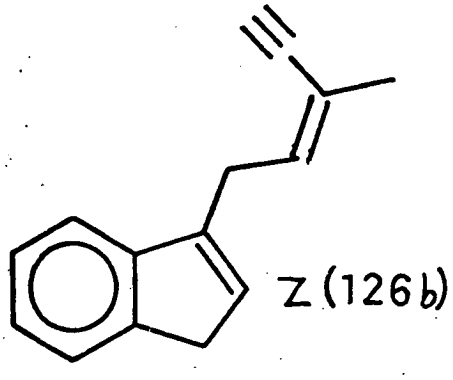
(125)

Z isomer. This alcohol is known to be formed predominantly in the Z-configuration.[80] (b) Partial hydrogenation with Lindlar's catalyst gave the diene which failed to form a Diels-Alder adduct with acetylene-dicarboxylic acid dimethylester.[81]

The preponderance of the Z isomer may be due to the bromomethylene group having a smaller interaction with the acetylene group than with the more bulky methyl group.

The reaction of indene with the bromide mixture via method B gave E and Z-3(3'-methylpent-2'-en-4'-ynyl)indene (126a and b) in the ratio 1:6, by analytical vapour phase chromatography, in 60 - 75% yield. The Z isomer (126b) was obtained free from the E isomer after recrystallization from ethanol. The structure of (126b) was deduced by analysis and from

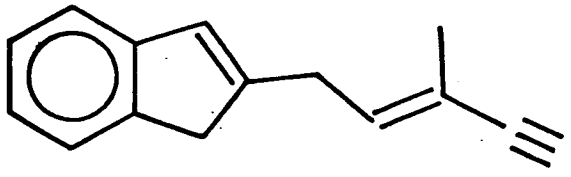

E (126a)


Z (126b)

the i.r. and ^1H n.m.r. spectra. The i.r. shows acetylenic absorptions at 3300 cm^{-1} and 2100 cm^{-1}. The ^1H n.m.r. (figure 7) shows a benzylic methylene resonance at 3.28δ and an olefinic singlet at 6.14δ indicating 3-substitution. The methylene doublet at 3.49δ is coupled to the olefinic triplet at 5.98δ. The Z-acetylene proton resonates at 3.06δ while the

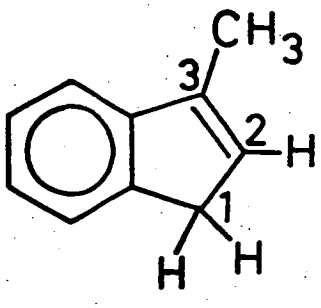
E-acetylene resonates at 2.65δ.

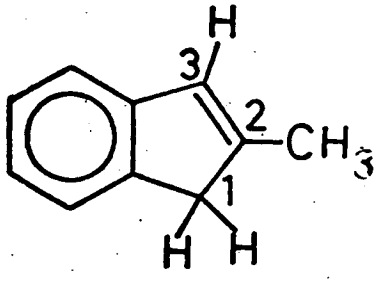
This compound is the same as that isolated in attempts to prepare the vinylpropenylidene adduct with indene (chapter 2.3). This compound was originally assigned the structure E-2-(3'-methylprop-2'-en-4'-ynyl)indene (29) by Watson[45], however no mechanism for its formation was proposed.



(29)

The 2-substitution assignment was previously made on the basis of the ^1H n.m.r. spectrum which showed a coupling of only 2Hz between the benzylic methylene protons and the indene olefinic proton. However a coupling of this magnitude is more consistent with a 3-substituted indene since in this case the dihedral angle between the protons on C-1 and C-2 is about 54°. Examination of the spectra of 2- and 3-methylindene shows a coupling constant for 3-methylindene of 2Hz between H_1 and H_2 and of

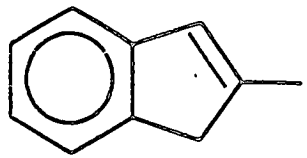
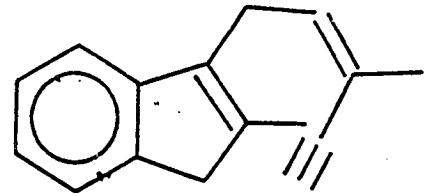
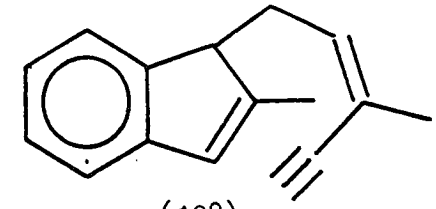
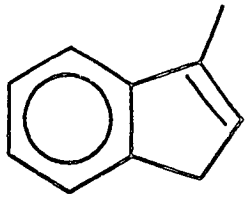
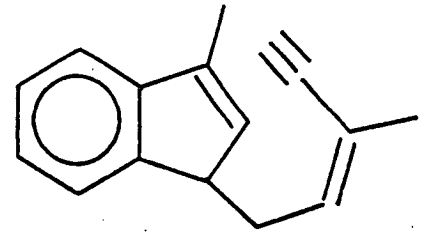
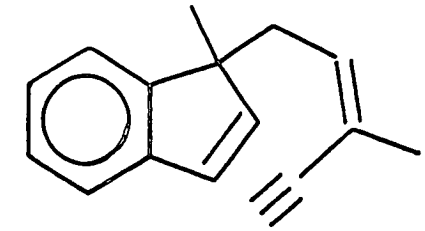
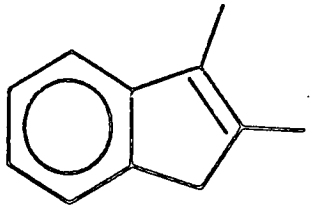
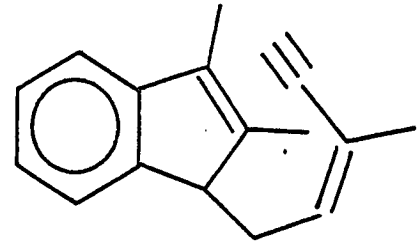
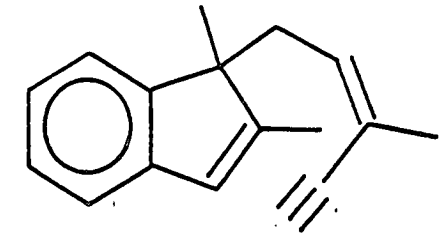




0.5Hz between H_1 and H_3 for 2-methylindene.

Thus, in the potassium t-butoxide case, under conditions normally employed for generating a carbene, the equilibrium between the base generated anions is such that substitution is preferred to carbene addition. It is uncertain whether the indene anion attacks the bromoenyne directly or reacts with the carbene followed by protonation on the ethynyl group. The phase transfer preparation is most likely to proceed by direct attack on the bromoenyne; nucleophilic displacement occurring readily under

Table 5

Olefin			
	 (127)	:	 (128)
Product ratio	1	:	2
	 (129)	:	 (130)
Product ratio	2	:	1
	 (131)	:	 (132)
Product ratio	4	:	1

these conditions even with non-activated bromides like ethyl bromide or methyl bromide.

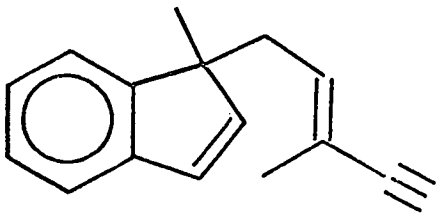
The Z-configuration of the indene was assigned for the following reasons: (a) 1-Bromo-3-methylpent-2-en-4-yne is believed to have the Z configuration and it follows that the product should also have a Z-configuration since pure Z-2-bromohex-3-en-5-yne reacts with indene to give exclusively Z-3(1'-methylpent-2'-en-4'-ynyl)indene (122b) (chapter 3.3). (b) Comparison of the acetylenic proton ^{1}H n.m.r. resonances with their 1'-methylpent-2'-en-4'-ynyl counterparts (chapter 3.3) shows agreement between the shifts of the E and Z isomers:

3(1'-methylpent-2'-en-4'-ynyl)indene: Z, 3.06 ; E, 2.60

3(3'-methylpent-2'-en-4'-ynyl)indene: Z, 3.06 ; E, 2.65

(c) Thermal cyclisation of (3'-methylpent-2'-en-4'-ynyl)indene occurs readily (chapter 5.2). With E-3(1'-methylpent-2'en-4'-ynyl)indene (122a) the yield of cyclisation product is very poor, whereas Z-3(1'-methylpent-2'-en-4'-ynyl)indene (122b) gives a good yield of cyclisation product (chapter 5.2).

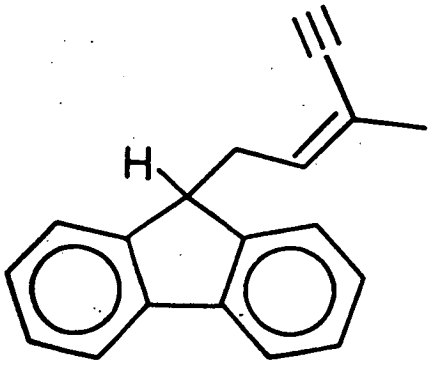
Analogous derivatives were obtained with 3-methylindene, 2-methylindene and 2,3-dimethylindene as mixtures of isomers by method B. Method A gave no isolable products, apparently due to polymerization of the bromoenyne. The products (see table 5) were isolated by preparative vapour phase chromatography and identified by exact mass measurement and from their ^{1}H n.m.r. and i.r. spectra. Only one example of an E isomer has been isolated pure. This compound is E-1(3'-methylpent-2'-en-4'-ynyl)-1-methylindene (133) and was isolated as a biproduct during preparation



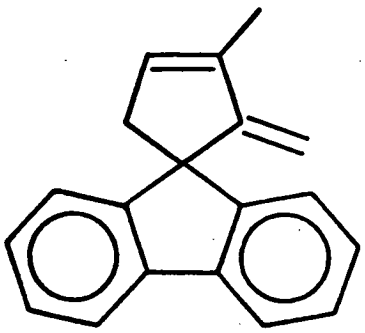
(133)

of the vinylpropenylidene adduct of 3-methylindene (chapter 2.3). The acetylenic proton in the E isomer resonates at 2.53δ whereas in the Z isomer the resonance occurs at 2.94δ.

Fluorene reacted with 1-bromo-3-methylpent-2-en-4-yne to give Z-9(3'-methylpent-2'-en-4'-ynyl)fluorene (134) in 37% yield, and also spiro [2-methylene-3-methylcyclopent-3-ene-1,9'-fluorene] (135) in 0 - 15% yield which were separated by silica gel chromatography. These compounds



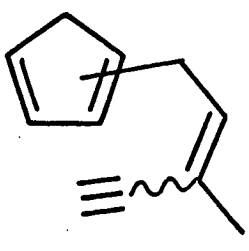
(134)



(135)

were identified by exact mass measurement and from their i.r. and ^{1}H n.m.r. spectra. The spiro-compound (135) is thought to be formed from the fluorene (134) by a base catalysed mechanism analogous to that outlined in chapter 2.3 for Z-3(3'-methylpent-2'-en-4'-yne)-2-methylindene (99). Attempts to cyclise the fluorene (134) directly to the spirane by various methods including extended phase transfer catalysed conditions, have all failed.

Cyclopentadiene reacted with the bromide to give E and Z(3'-methylpent-2'-en-4'-ynyl)cyclopentadiene (136), isolated as a mixture of isomers and identified by exact mass measurement and from the i.r. and ^{1}H n.m.r. spectra.



(136)

3.5 Conclusions

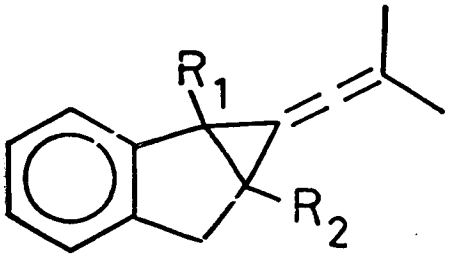
No cyclopropane adducts were obtained with the bromoenynes and hence it appears that the phase transfer catalysed method is not as successful in preparing carbenes of this form as is the t-butoxide preparation (chapter 2.2). The preference for nucleophilic attack may be attributed to the bromoenynes being activated halides in comparison with 1-bromo-3-methylbuta-1,2-diene which gave moderate yields of cyclopropane. In addition the dimethyl group in 1-bromo-3-methylbuta-1,2-diene will hinder nucleophilic attack.

CHAPTER 4

Rearrangement of Cyclopropanes

4.1 Acid Catalysed Rearrangement of Vinylidene Cyclopropanes

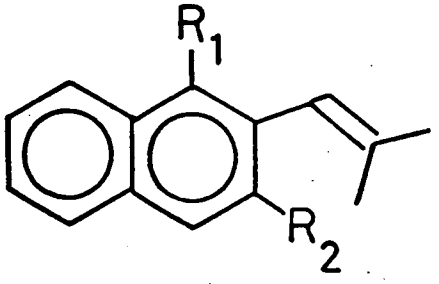
Stewart[21] and Robertson[76] found that acid catalysed rearrangement of the dimethylvinylidene cyclopropanes (86), (87) and (88), prepared from indene, 3-methylindene and 2-methylindene, exclusively underwent ring expansion to the naphthalenes (137), (138) and (139). In view of the observations described later for the 2,3-dimethylindene adduct



(86) $R_1 = R_2 = H$

(87) $R_1 = Me$, $R_2 = H$

(88) $R_1 = H$, $R_2 = Me$



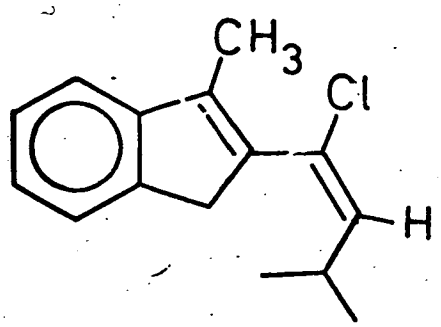
(137) $R_1 = R_2 = H$

(138) $R_1 = Me$, $R_2 = H$

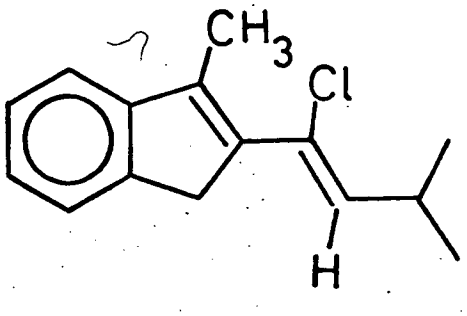
(139) $R_1 = H$, $R_2 = Me$

rearrangement, this work has been repeated.

While compounds (86) and (88) do give mainly naphthalenes (137)→(139), compound (87) when refluxed in ethanolic hydrogen chloride gave a mixture of the naphthalene (138) plus up to 38% of E and Z-2-(1'-chloro-3'-methylbut-1'-enyl)-3-methylindene (140a and 140b) in the ratio E:Z = 9:1. These isomeric chloro-compounds have been partially separated by silica gel chromatography and their structures assigned from their mass and ^1H n.m.r. spectra.



E - (140a)



Z - (140b)

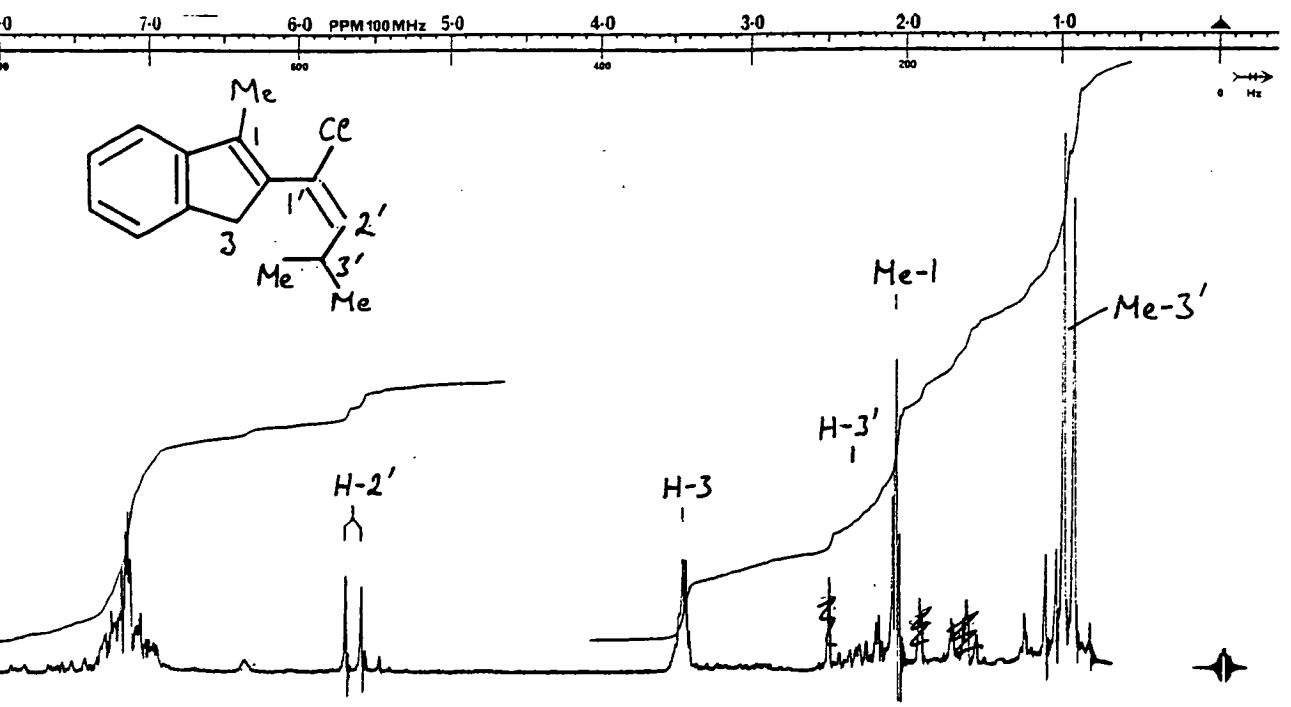


Figure 8

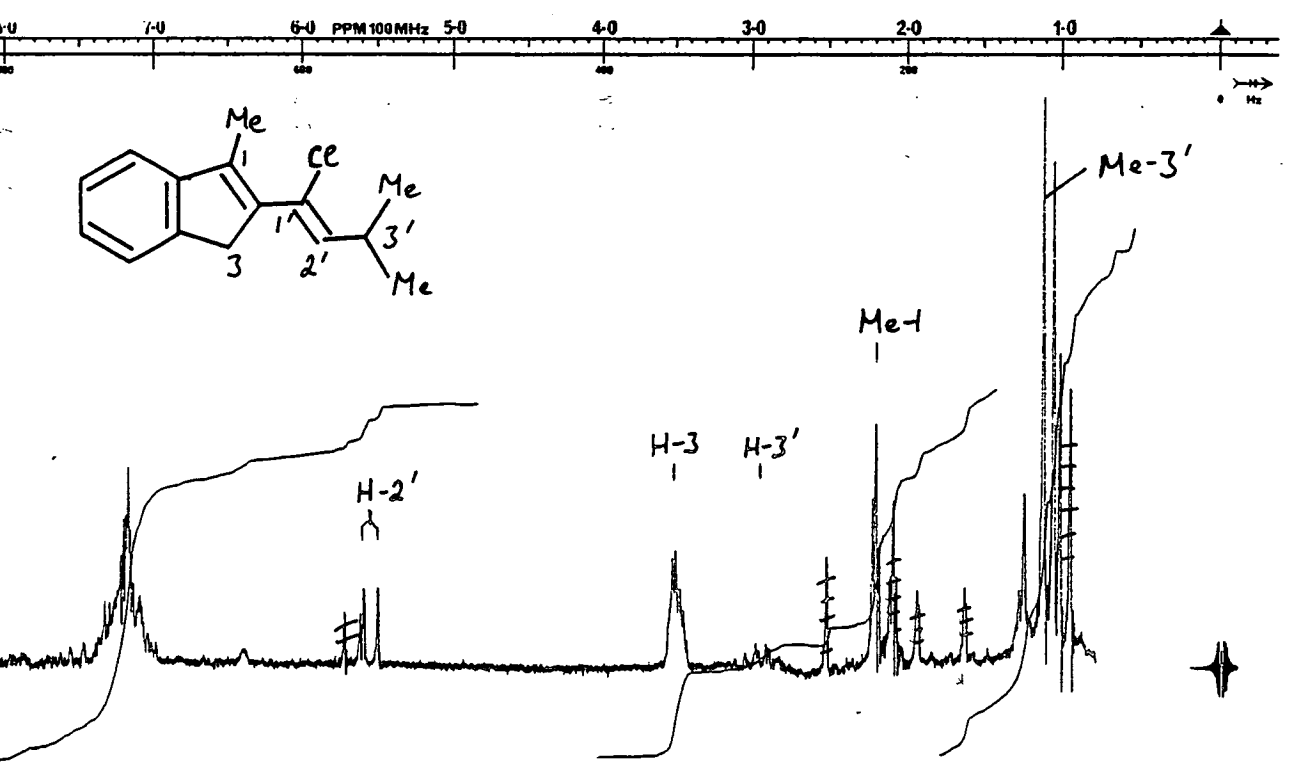
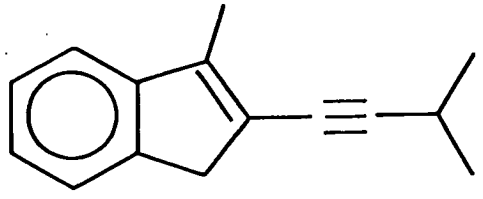


Figure 9

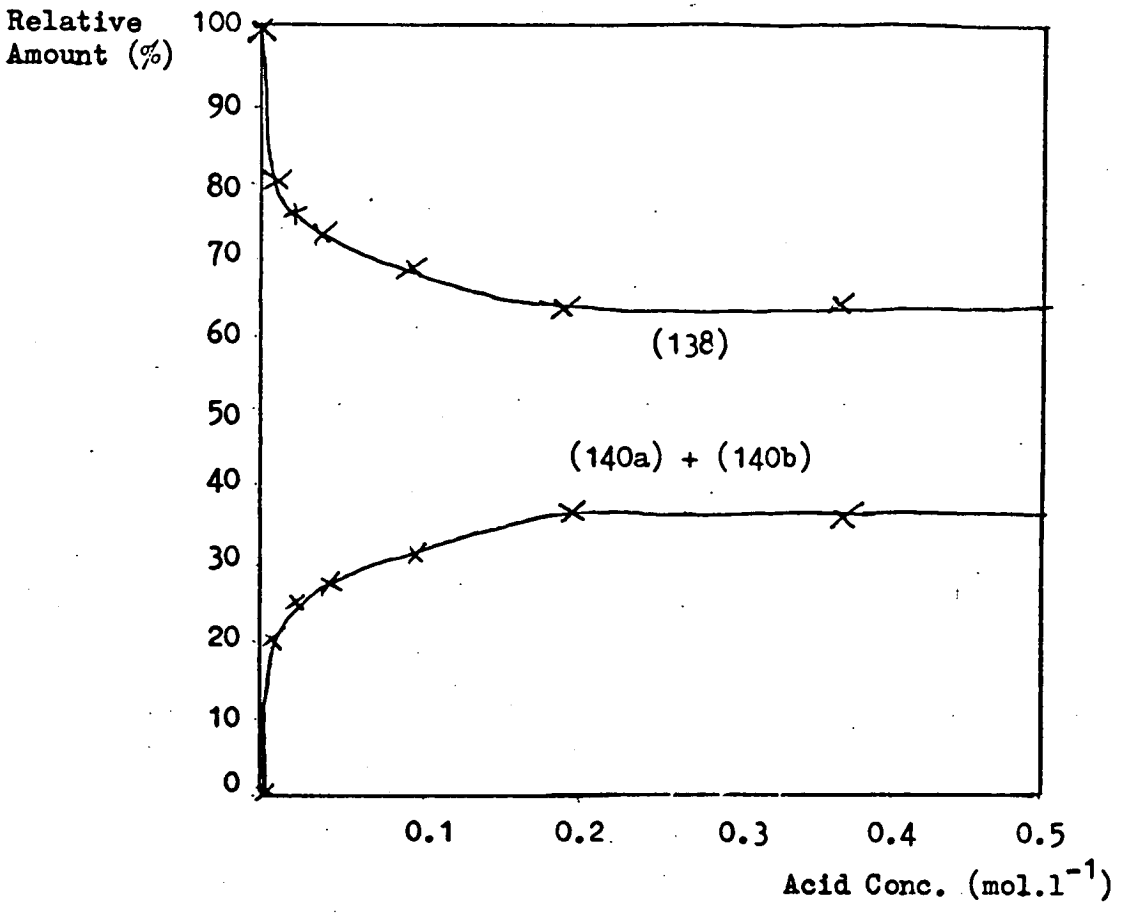
The ^{1}H n.m.r. spectra (figures 8 and 9) clearly show the isopropyl methyl groups as doublets (J = 6Hz) at 1.08 δ for the minor isomer and 0.98 δ for the major isomer. The olefinic protons occur as sharp doublets (J = 10Hz) being at higher frequency in the major isomer, 5.66δ, than the minor isomer, 5.54δ. By analogy with the spectra of related vinylic halides[82], which show olefinic protons cis to the halogen resonate at a higher frequency than when trans to the halogen, the major isomer was assigned the E-configuration.

The mixture of hydrochlorides (140a and 140b) was readily dehydrochlorinated by passage through basic alumina to give 2(3'-methylbut-1'-ynyl)-3-methylindene (141). This product was identified from its i.r. spectrum which showed a C≡C absorption at 2200 cm^{-1} and from its ^{1}H n.m.r. spectrum which showed an isopropyl doublet at 1.26δ, coupled (J = 7Hz) to a septet at 2.78δ, as well as a benzylic methylene resonance at 3.34δ, consistent with the proposed structure.



(141)

The proportion of hydrohalogenated product with respect to the naphthalene (138) varied with the concentration of acid used, as shown in the graph. The proportion of hydrochloride produced reached a maximum of 37% when 0.2 molar acid was used. At higher concentration the proportion remained constant. Below this concentration the proportion of hydrochloride fell off rapidly with respect to the naphthalene and at low concentration of acid (0.004M) other unidentified components were observed.



Graph of the Variation in Products formed from 2,3-Benzo-6-dimethylvinylidenebicyclo [3,1,0] hex-2-ene (87) with Acid Concentration.
-1-methyl

Rearrangement of the 3-methylindene adduct (87) with p-toluenesulphonic acid in carbon tetrachloride gave a complex mixture from which only the naphthalene (138) was isolated.

The 3-ethylindene adduct, 2,3-benzo-6-dimethylvinylidene-1-ethylbicyclo [3,1,0] hex-2-ene (89), behaved similarly on treatment with ethanolic hydrogen chloride to give 1-ethyl-2-(2'-methylprop-1'-enyl) naphthalene (142), 33%, plus E-2(1'-chloro-3'-methylbut-1'-enyl)-3-ethylindene (143), 33%. The hydrochloride product (143) was assigned the E configuration on the basis of the position of the olefinic resonance. No Z-isomer was found.

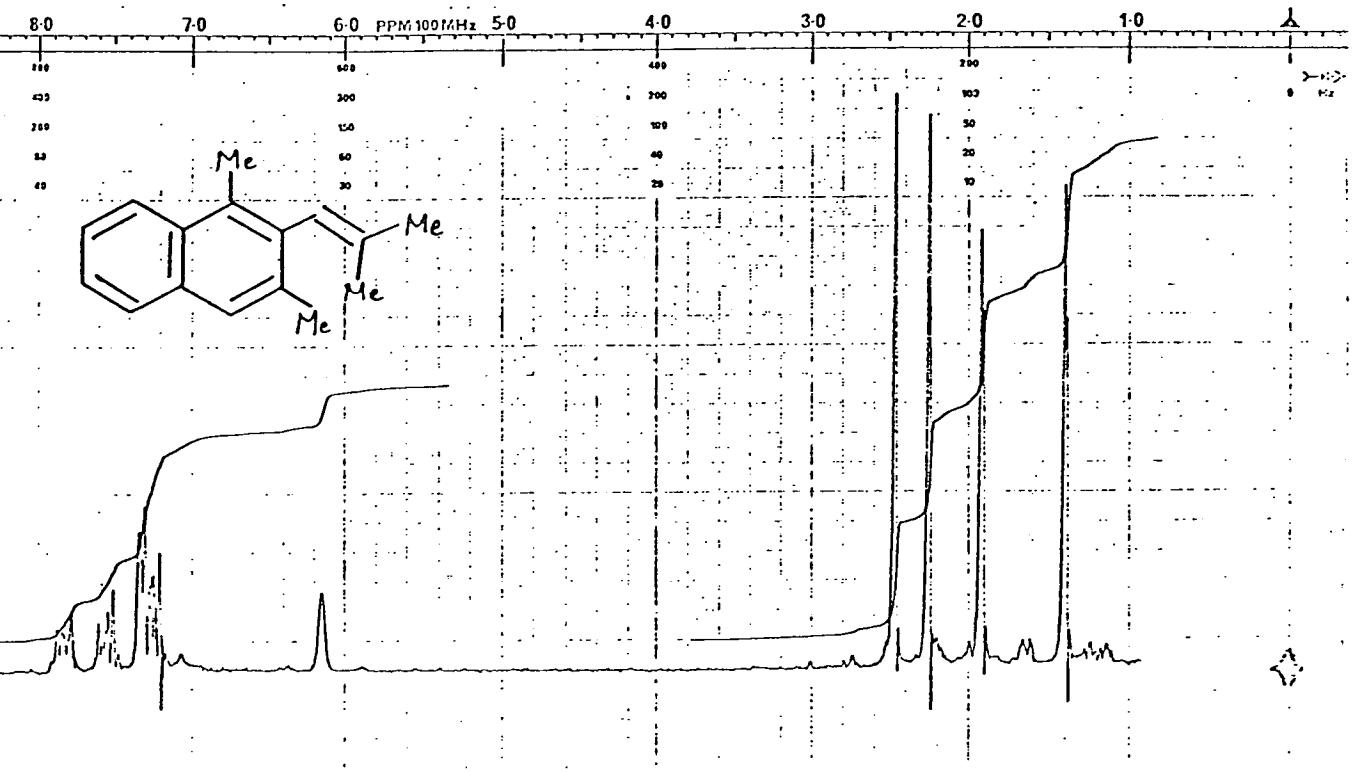


Figure 10

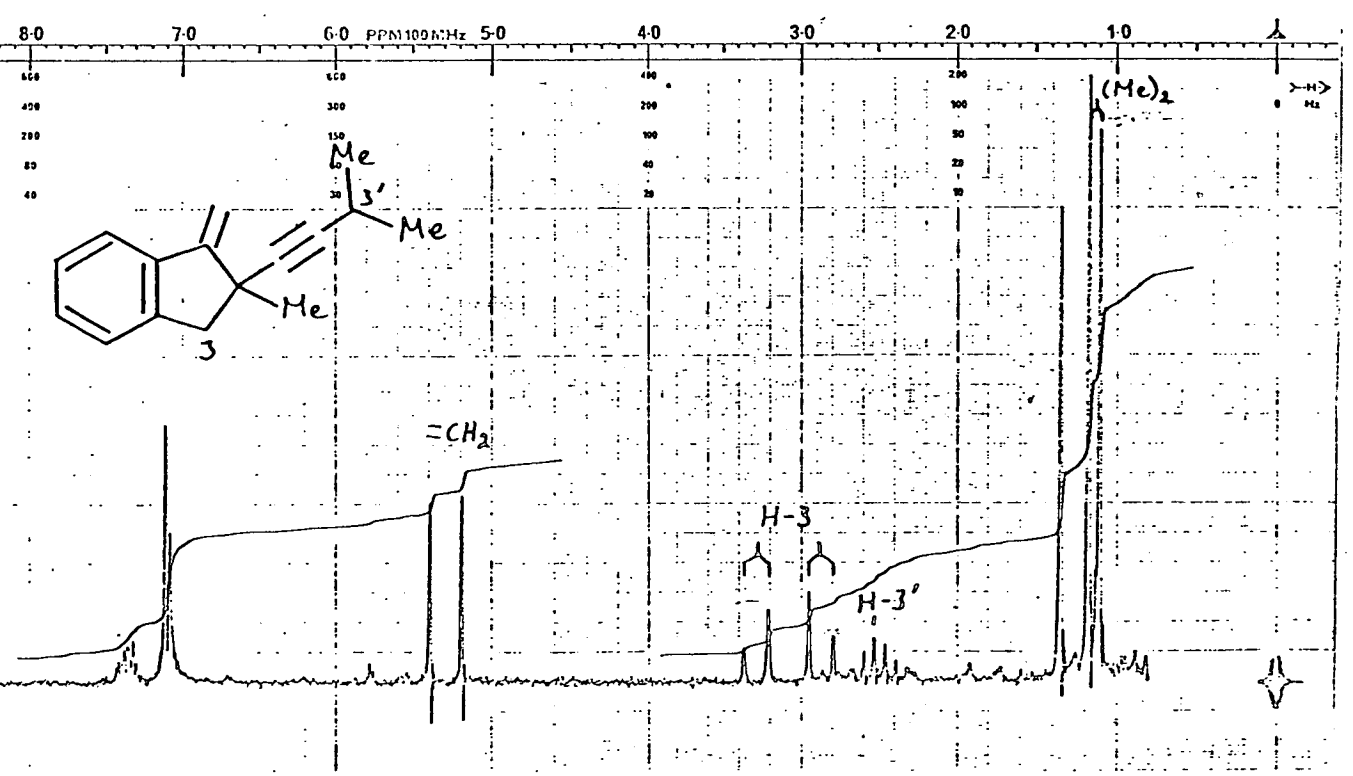
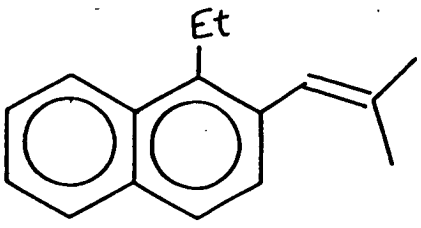
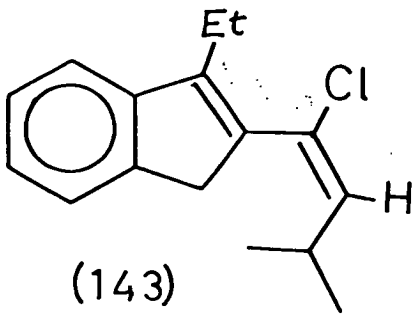


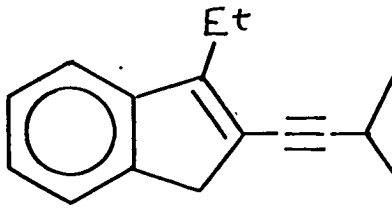
Figure 11



(142)



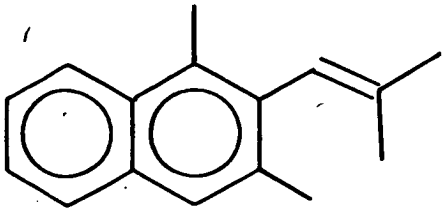
(143)



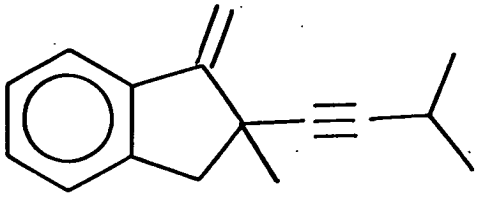
(144)

Rearrangement of the 3-ethylindene adduct (89) with p-toluenesulphonic acid in carbon tetrachloride gave a 60% yield of the naphthalene (142) and 3-ethyl-2-(3'-methylbut-1'-ynyl)indene (144) in the ratio 3:1, separated by preparative vapour phase chromatography. The products were identified from their ^{1}H n.m.r. and mass spectra and by analogy with the products from rearrangement of the 3-methylindene adduct (87).

The 2,3-dimethylindene adduct, 2,3-benzo-6-dimethylvinylidene-1,5-dimethylbicyclo [3,1,0] hex-2-ene (90), rearranged with ethanolic hydrogen chloride to give 1,3-dimethyl-2-(2'-methylprop-1'enyl)naphthalene (91) and 2-(3'-methylbut-1'-ynyl)-1-methylene-2-methylindane (145). The naphthalene (91) was identified by analogy with the products of



(91)



(145)

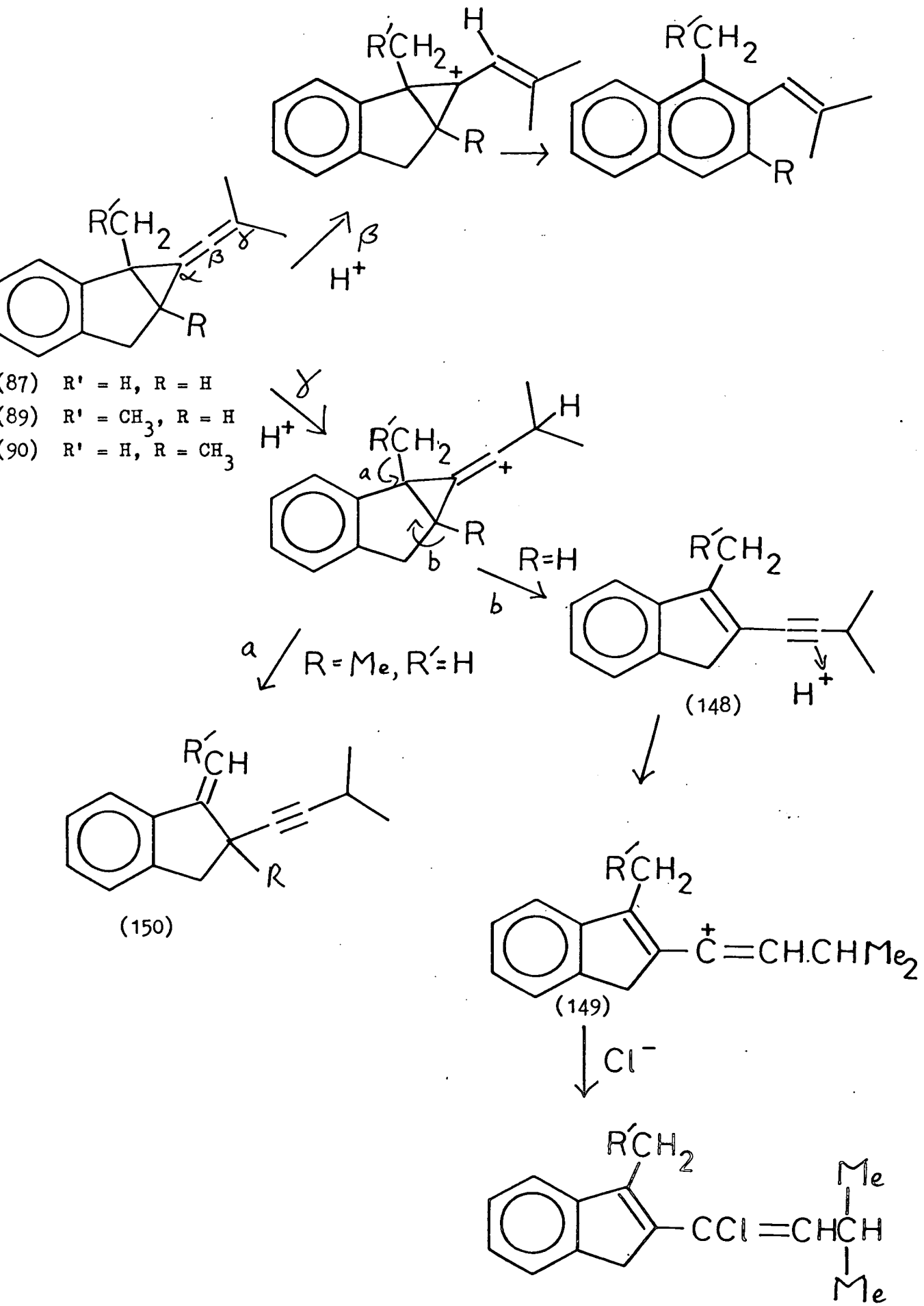
rearrangement discussed previously and from its ^{1}H n.m.r. spectrum (figure 10) which shows four methyl resonances. The two at lower frequency (1.40δ and 1.92δ) were shown by decoupling to be weakly coupled ($J \simeq 1$Hz) to the olefinic proton at 6.15δ, supporting the presence of an isobutenyl group. The methylene indane (145) was identified from its

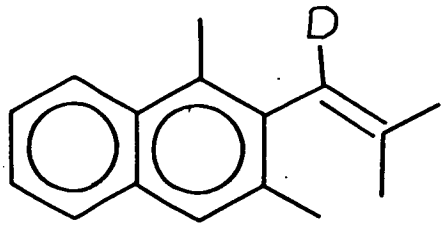
mass spectrum and its ^{1}H n.m.r. spectrum (figure 11) which shows an isopropyl group having a dimethyl doublet at 1.13 δ coupling (J = 7Hz) to a proton septet at 2.53δ. The singlet methyl resonance at 1.34 δ is probably also aliphatic. The AB spectrum (2.88δ, 3.29δ, J = 16Hz) is assigned to an indene methylene group with non-equivalent protons, caused by having two different groups α to the methylene. The two sharp singlets (5.19δ and 5.39δ) with no visible coupling are consistent with an exocyclic olefinic methylene group.

As in the reaction of the 3-methylindene adduct (87) with ethanolic hydrogen chloride the proportion of products was dependent on the acid concentration. The proportion of the methylene indane (145) was found to reach a maximum at about 0.4 molar ethanolic hydrogen chloride (ratio (91) : (145) = 1.2:1) but decreased relative to the naphthalene (91) as the acid concentration was lowered. In pure alcohol, in the absence of HCl gas, only the naphthalene (91) was obtained (90% yield), although a longer time was required for the rearrangement to proceed to completion. These results may be attributed to protonation by both $EtOH_2^+$ and EtOH. The latter, being less reactive and more discriminating, selectively attacks the β site, while the former is more reactive and less discriminating and attacks the β and γ sites. As the acid concentration decreases so does the amount of $EtOH_2^+$ and so the amount of γ attack goes down.

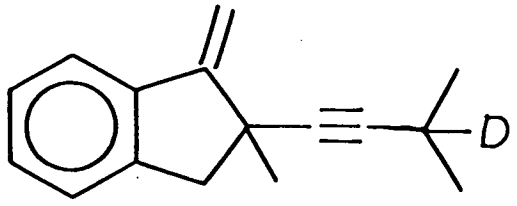
Rearrangement of the 2,3-dimethylindene adduct (90) with p-toluenesulphonic acid in CCl_4 gave the same products as with ethanolic hydrogen chloride, in equal amounts.

To attempt to elucidate the mechanism, the reaction was carried out using a solution of DCl in methanol-D. This gave the deuterated products (146) and (147). The point of deuteration was evident from the ^{1}H n.m.r. spectra. In that of the naphthalene (146), the olefinic proton resonance


R'CH2
H
R
H+
α
β
γ
(87) R' = H, R = H
(89) R' = CH3, R = H
(90) R' = H, R = CH3
a
b
R=H
R=Me, R'=H
(148)
(150)
(149)
Cl⁻
C=CH.CHMe2
CCl=CHCH
Me



(146)



(147)

(6.15δ) is virtually absent while the olefinic methyl resonances (1.40δ and 1.92δ) appear as sharp singlets. In the indane (147) the isopropyl proton resonance (2.53δ) is absent and the isopropyl methyl resonances appear as a singlet. Thus in the reactions described in this section the formation of the naphthalene may be rationalised by protonation of the allene system at the β-carbon followed by ring expansion and elimination of a benzylic proton. The formation of the acetylenic compound arises from protonation at the γ-carbon of the allene system. Proton loss and ring opening leads to the formation of a 1,3-enyne (148) except in the case of the 2,3-dimethylindene adduct (90) which gives a 1,4-enyne (150). Where the 1,3-enyne has been produced by ethanolic hydrogen chloride a further reaction, addition of HCl, can occur to give chloro compounds. Hydrochlorination only occurs in 1,3-enyne case probably because only here is the cationic intermediate (149) stabilized by the conjugated double bond.

Studies by Stewart[21] of the acid catalysed rearrangement of vinylidene-dihydronaphthalene adducts were, with one exception, largely unsuccessful. These rearrangements have now been re-examined with some success.

The 1,2-dihydronaphthalene adduct, 2,3-benzo-7-dimethylvinylidene-bicyclo [4,1,0] hept-2-ene (92), rearranged with ethanolic hydrogen chloride to give a complex mixture of products inseparable by preparative

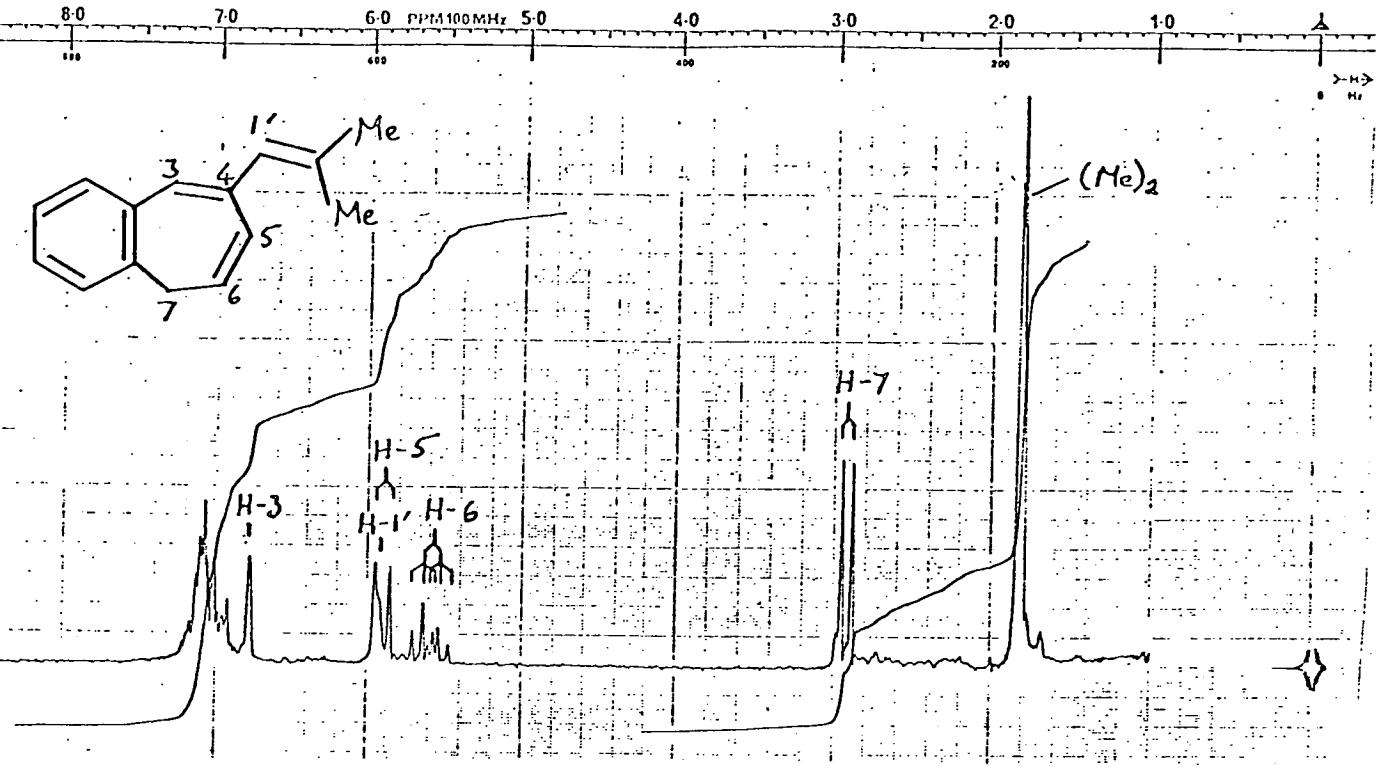


Figure 12

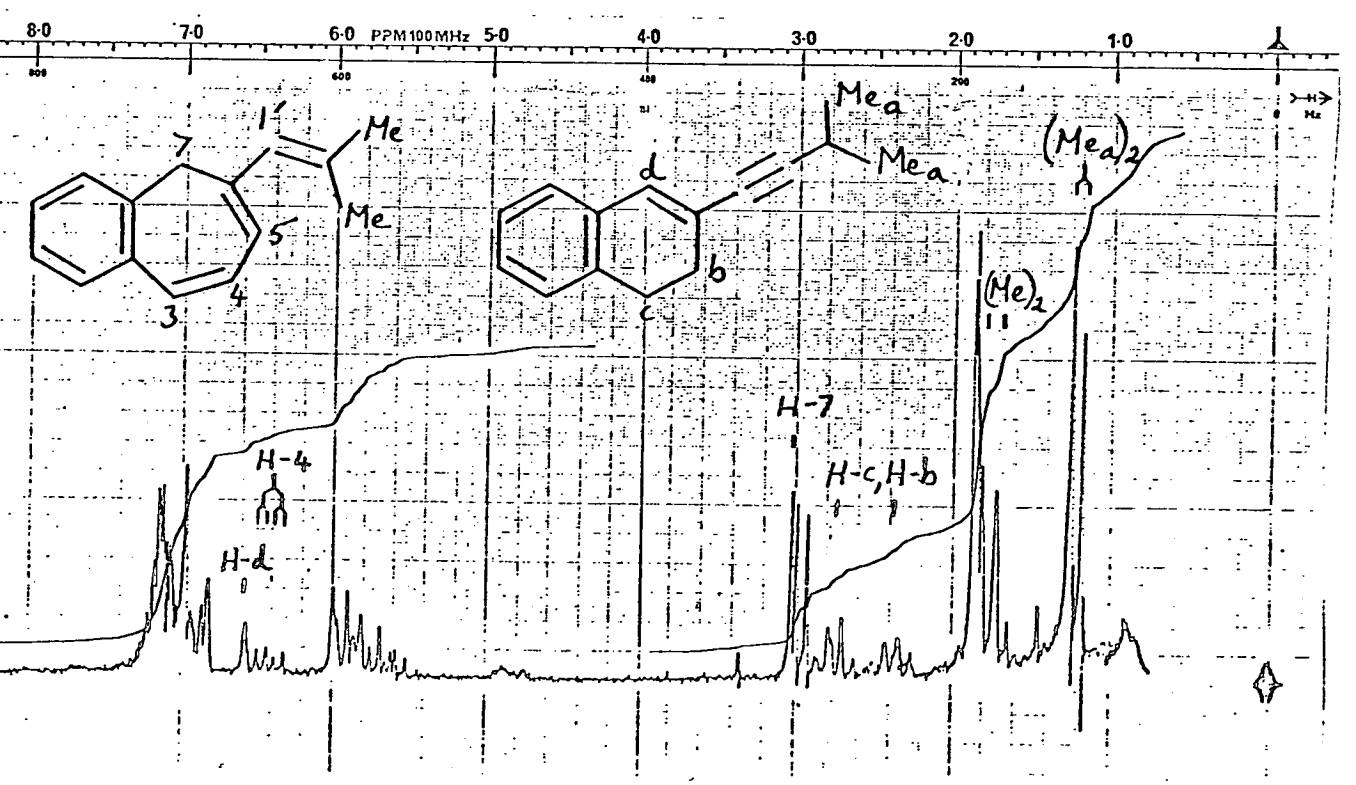
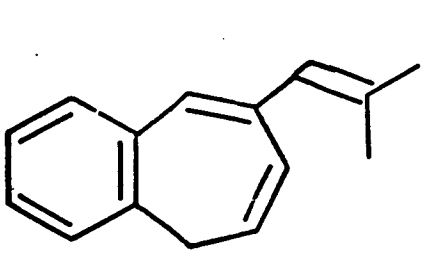


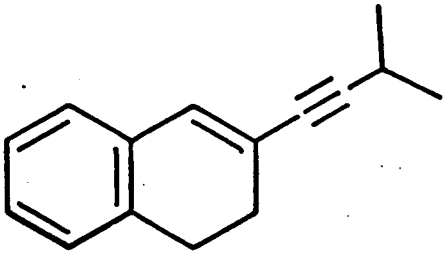
Figure 13

vapour phase chromatography. Silica gel chromatography, however, gave 1,2-benzo-4-(2'-methylprop-1'-enyl)cyclohepta-1,3,5-triene (151), 30%, plus 5% of another component, tentatively identified as 3-(3'-methylbut-1'-ynyl)-1,2-dihydronaphthalene (152), plus 40% of unidentified products.

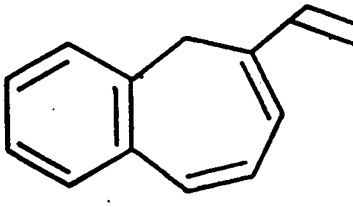
Rearrangement of the adduct (92) with p-toluenesulphonic acid in carbon tetrachloride also gave a complex mixture of products which, by preparative vapour phase chromatography, gave a fraction containing the cycloheptatriene (151), dihydronaphthalene (152), and also another compound, probably 1,2-benzo-6(2'-methylprop-1'-enyl)cycloheptatriene (153) in the ratio (151) : (152) : (153) = 1:3:1.



(151)



(152)



(153)

These products were identified from their ^{1}H n.m.r. spectra and by analogy with the methylindene adduct rearrangements described previously. The ^{1}H n.m.r. of the cycloheptatriene (151) (figure 12), shows a two-proton doublet at 2.91δ, characteristic of a benzylic methylene group, coupled (J = 6Hz) to an olefinic doublet of triplets at 5.56 δ which is also coupled (J = 10Hz) to an olefinic doublet at 5.90δ. This implies a grouping $ArCH_2CH{=}CH{-}C$. Also present are two olefinic singlets at 5.94 δ and 6.77δ, and a large six proton resonance at 1.81 δ corresponding to two methyl groups.

Compounds (152) and (153) have not been isolated pure and evidence for their presence is deduced from the spectrum of the mixture. The ^{1}H n.m.r. spectrum of the three component mixture (figure 13) isolated from the rearrangement induced by p-toluenesulphonic acid may be partially

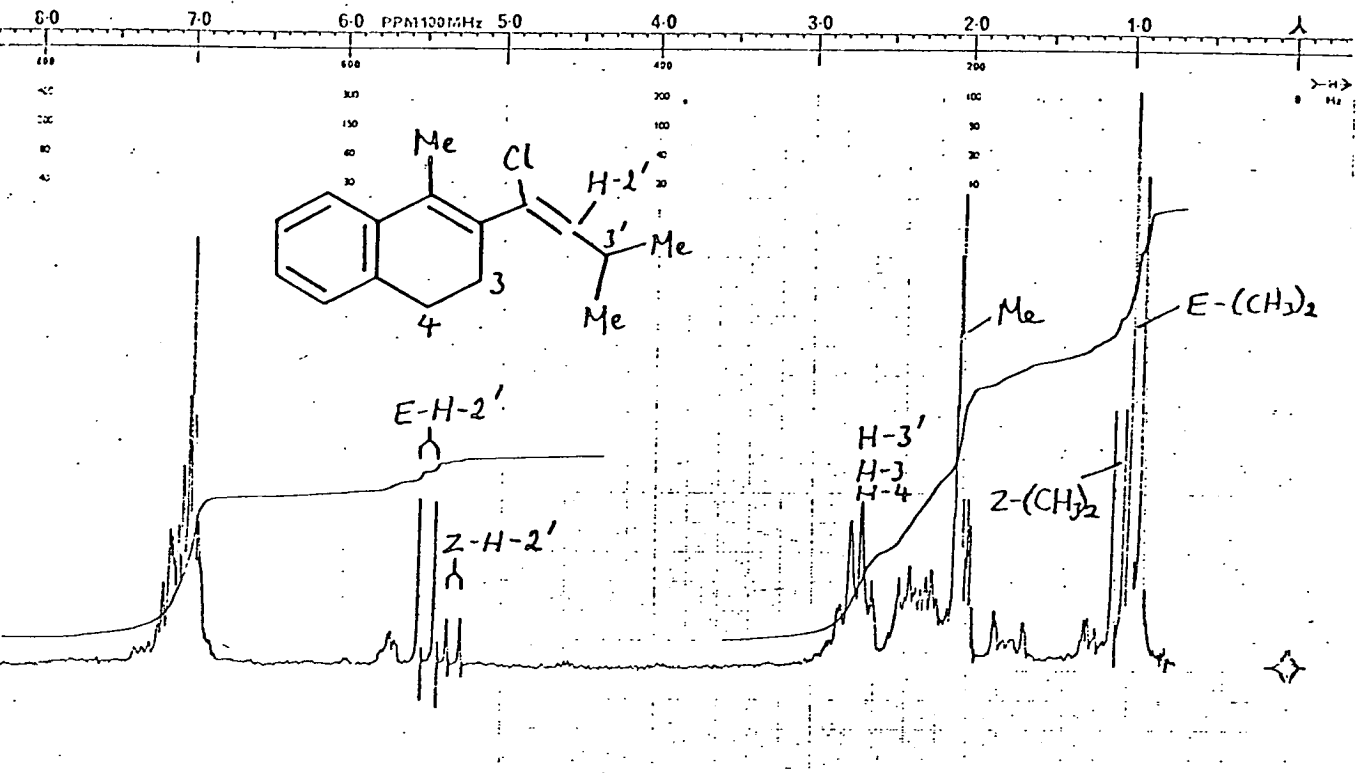


Figure 14

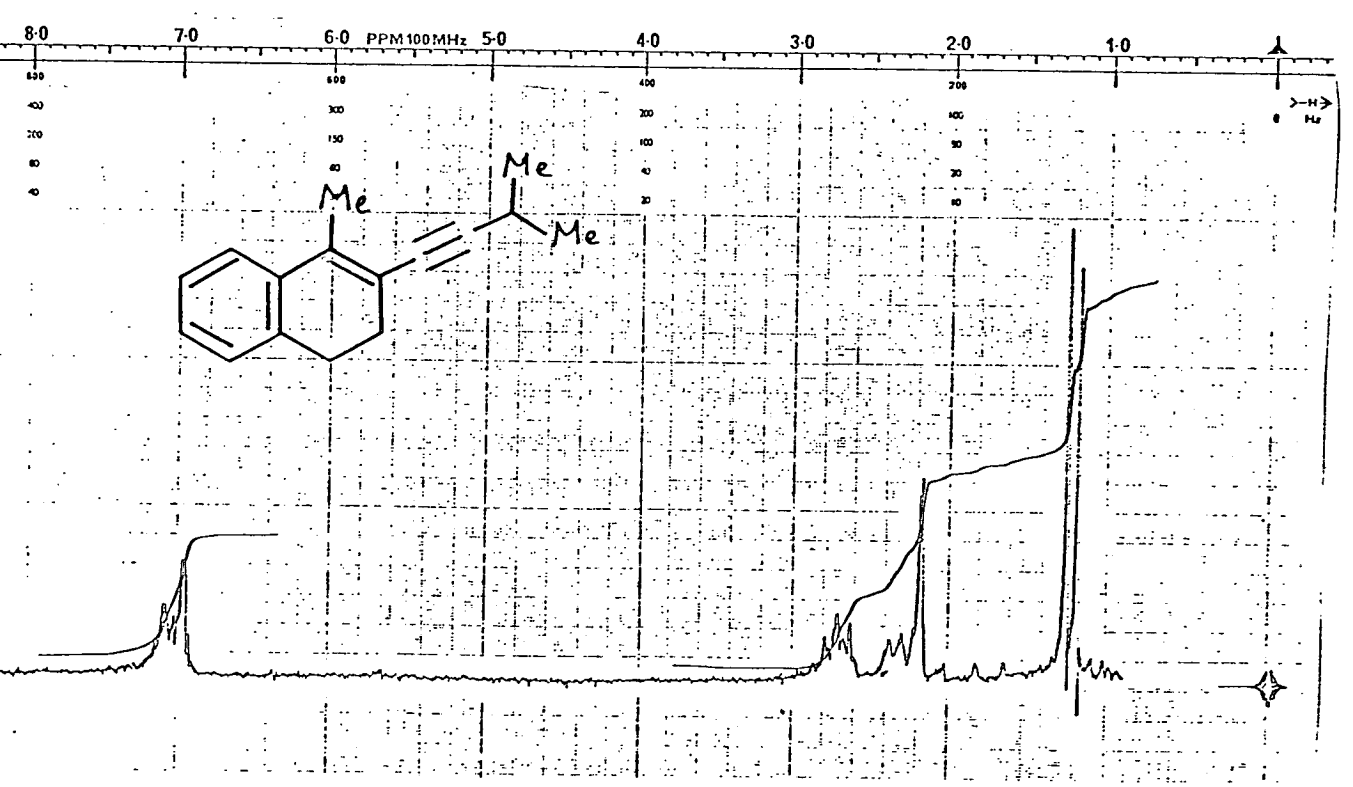
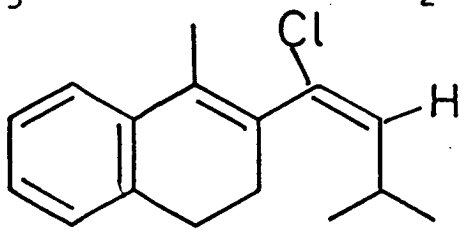


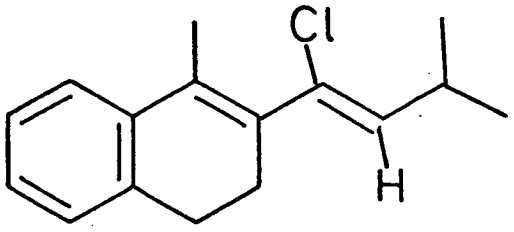
Figure 15

resolved. Resonances from the cycloheptatriene (151) are readily located. The doublet at 1.21 δ and multiplets at 2.38 δ and 2.85 δ correspond to the isopropyl methyl groups and $-CH_2CH_2-$ fragment in acetylene (152), strongly resembling those of the 4-methyl analogue identified elsewhere. The resonance at 6.57 δ corresponds to the olefinic proton. The cycloheptatriene (153) is recognizable from the methyl proton resonances at 1.81 δ and 1,71δ, the sharp singlet at 3.02 δ corresponding to an isolated benzylic methylene group and an olefinic doublet of doublets (J = 7Hz, 11Hz) at 6.40 δ arising from CH=CH-CH. The other peaks are obscured.

Rearrangement of the 4-methyl-1,2-dihydronaphthalene adduct, 2,3-benzo-7-dimethylvinylidene-1-methyl-bicyclo [4,1,0] hept-2-ene (93), with ethanolic hydrogen chloride gave mostly E and Z-2(1'-chloro-3'-methylbut-1'-enyl)-4-methyldihydronaphthalene (154a and 154b), 80%, in the ratio E:Z = 2.3:1 but no cycloheptatriene. Stewart[21] obtained the same products in the ratio 1:1, however he used 30% aqueous hydrochloric acid dissolved in ethanol which probably gives a less selective protonation, i.e. H_3O^+ in preference to $EtOH_2^+$.



E-(154a)

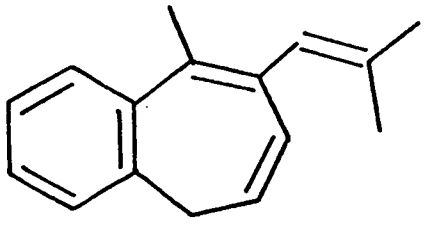


Z-(154b)

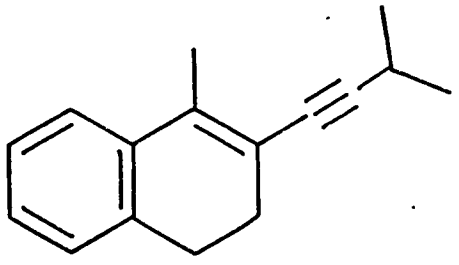
The products were not separated. In the ^1H n.m.r. (figure 14), the higher frequency olefinic doublet was assigned to the E isomer, as for the 3-methylindene analogues (139a and b). Hence the major isomer is the E isomer.

Rearrangement of the 4-methyl-1,2-dihydronaphthalene adduct (93) with p-toluenesulphonic acid in carbon tetrachloride gave an 80% yield of

a mixture which was separated by preparative vapour phase chromatography to give 1,2-benzo-4(2'-methylprop-1'-enyl)-3-methylcyclohepta-1,3,5-triene (155) and 3-(3'-methylbut-1'-ynyl)-4-methyl-1,2-dihydronaphthalene (156) in the ratio 3:1.



(155)

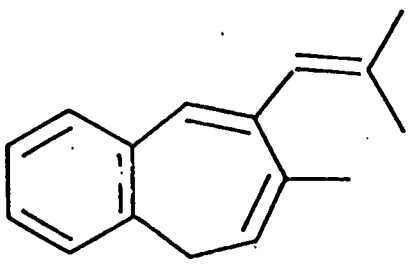


(156)

Compounds (155) and (156) were identified from their ^{1}H n.m.r. spectra and by analogy with rearrangements described previously. The ^{1}H n.m.r. of (156) is shown in figure 15, for comparison with that of (152), figure 13.

Rearrangement of the 3-methyl-1,2-dihydronaphthalene adduct, 2,3-benzo-7-dimethylvinylidene-6-methylbicyclo [4,1,0] hept-2-ene (94), with ethanolic hydrogen chloride gave a complex mixture which was separated by silica gel chromatography to give 35% of 1,2-benzo-4-(2'-methylprop-1'-enyl)-5-methylcycloheptа-1,3,5-triene (157), plus about 40% of other unidentified products.

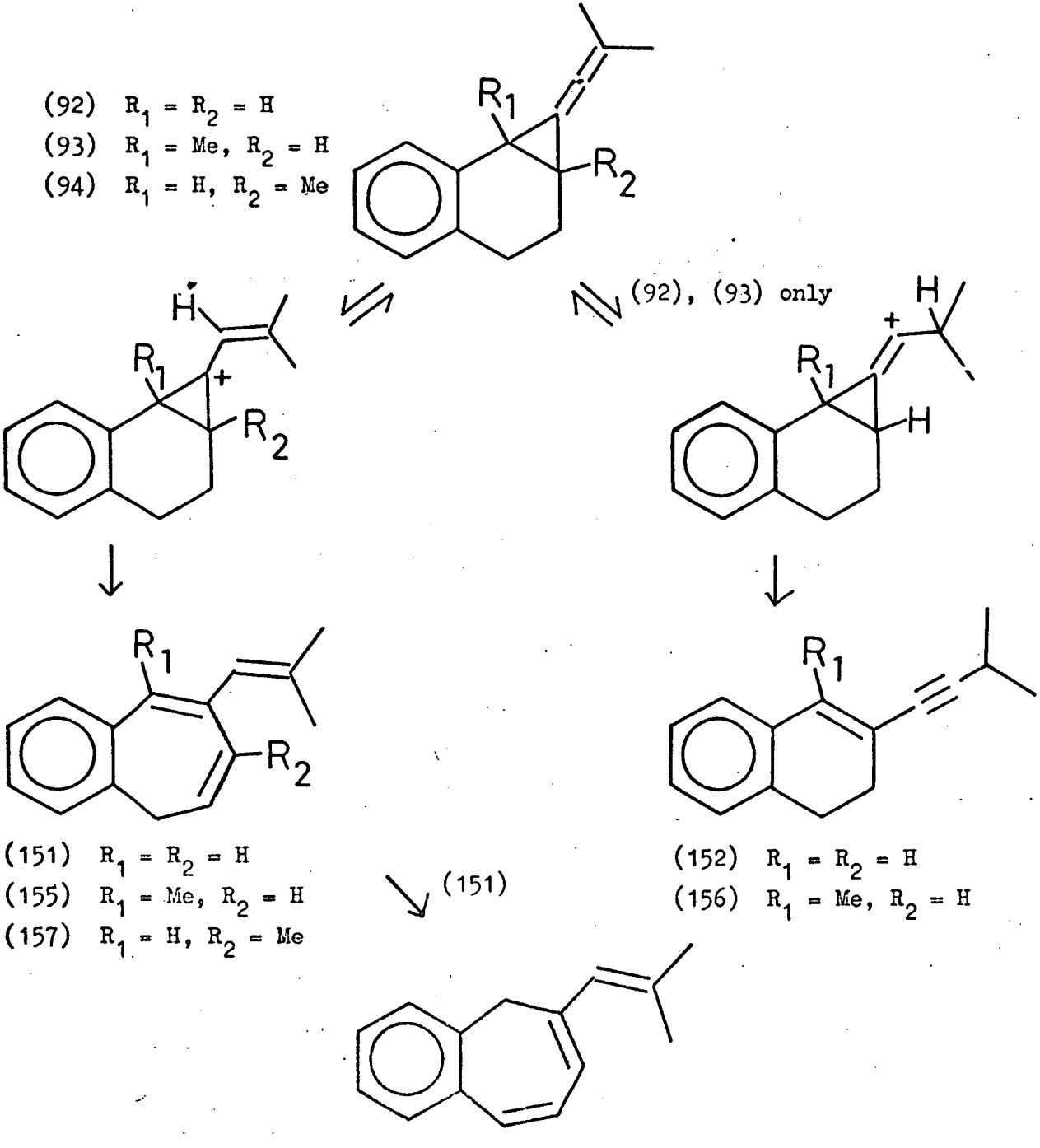
Rearrangement of the adduct (94) with p-toluenesulphonic acid in carbon tetrachloride gave a mixture containing about 20% of the cycloheptatriene (157) together with other identified products.



(157)

The cycloheptatriene (157) was identified from its ^1H n.m.r. spectrum and by analogy with rearrangement products found previously.

The products - (151), (152), (154), (155), (156) and (157) - identified or suggested above may be accounted for by routes analogous to those proposed for the acid catalysed rearrangement of the adducts of indene and its alkyl derivatives. Acid catalysed rearrangement of the cycloheptatriene (151) would yield the cycloheptatriene (153) however a thermal 1,5 shift would appear more likely since H^+ would be required to protonate in the middle of a conjugated system.



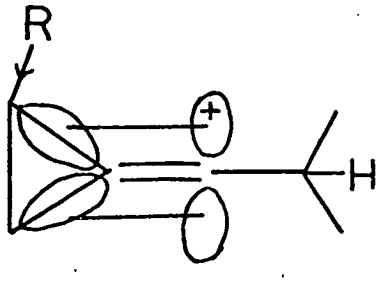
In view of the complexity of the rearrangements of the dimethylvinylidene adducts it is not possible to draw any firm conclusions about the variation in products isolated with the extent and position of methylation. However it is noticeable that the proportion of γ-attack increases with alkylation about the cyclopropane ring, particularly in the 1-position (see table 6). This may be attributed to electron donation by the alkyl

Table 6

Relative Amounts of Attack at β and γ Positions

Vinylidene adducts	HCl		p-Toluenesulphonic acid	
	β	γ	β	γ
Indene	100	0	-	-
2-methylindene	100	0	-	-
3-methylindene	63	37	100	0
3-ethylindene	50	50	75	25
2,3-dimethylindene	54	46	50	50
1,2-dihydronaphthalene	88	12	40	60
3-methyl-1,2-dihydronaphthalene	100	0	100	0
4-methyl-1,2-dihydronaphthalene	0	100	75	25

group onto the cyclopropane ring which in turn stabilizes the vinyl cation (158) (see chapter 1.5).



(158)

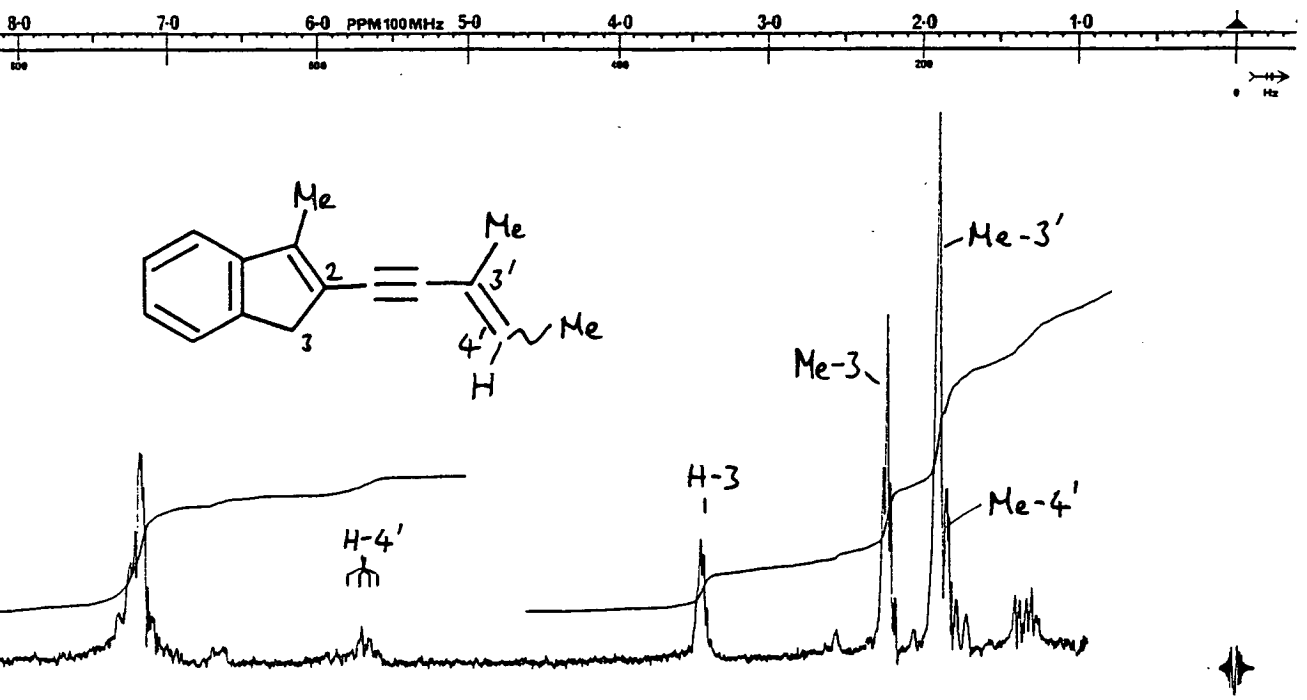
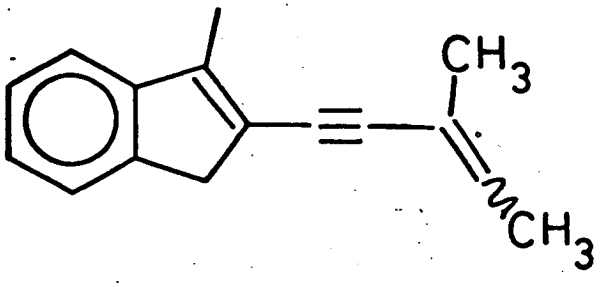


Figure 16

Formation of the acetylene type product is not possible from the 2-methylindene or 2-methyldihydronaphthalene adducts (90) or (94) since the intermediate ion has no proton available for removal.

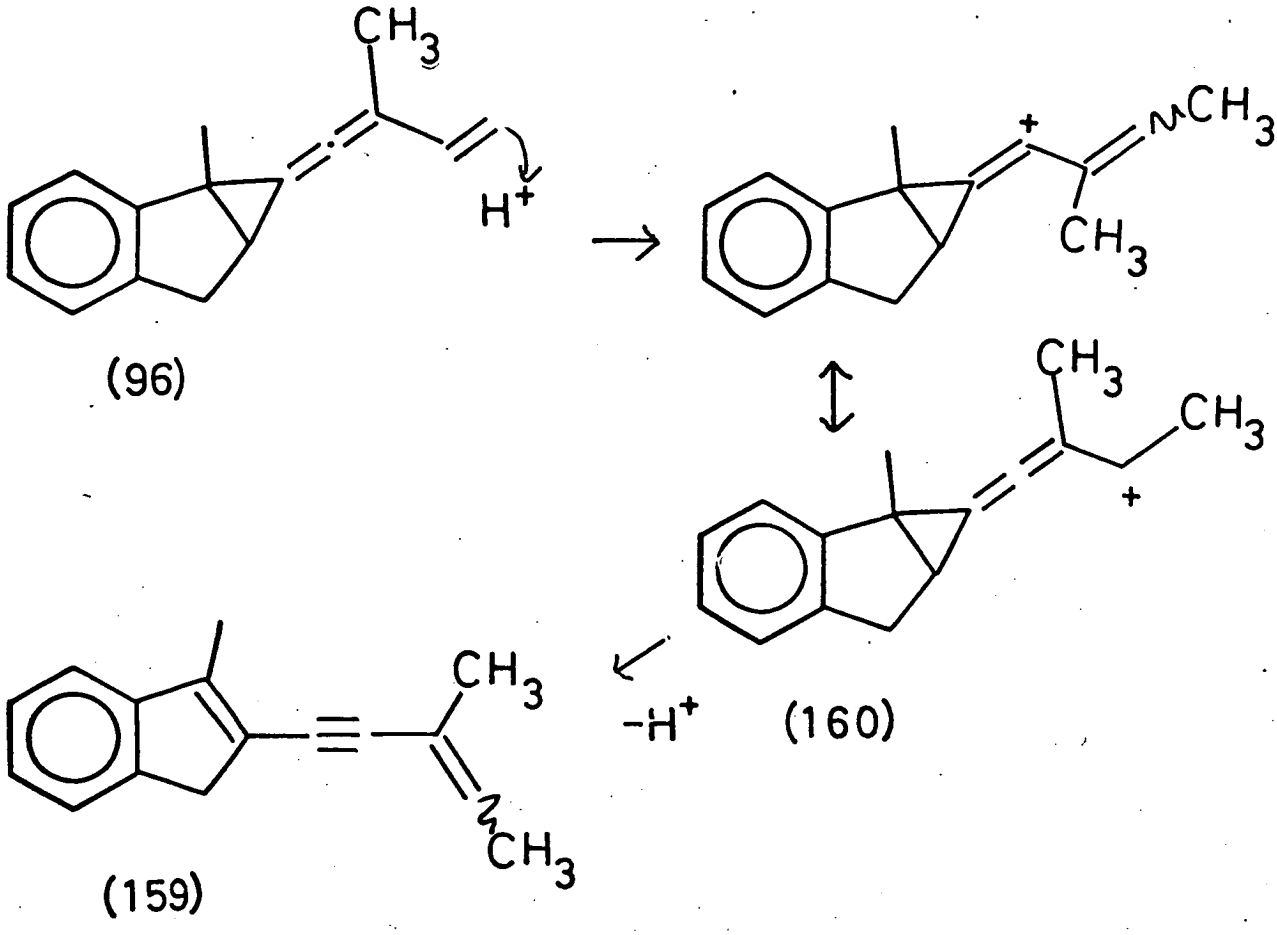
4.2 Acid Catalysed Rearrangements of 2-vinylpropenylidene Cyclopropanes

Rearrangement of the 3-methylindene adduct, E and Z-2,3-benzo-1-methyl-6-(2'-vinylpropenylidene)bicyclo [3,1,0] hex-2-ene (96), with ethanolic hydrogen chloride gave a complex mixture which has not yet been rationalized. Rearrangement of the adduct (96) with p-toluenesulphonic acid in carbon tetrachloride also gave a complex mixture of products. The major compound, 30 - 40%, isolated by preparative vapour phase chromatography has an ^{1}H n.m.r. spectrum consistent with that expected for 2(3'-methylpent-3'-en-1'-ynyl)-3-methylindene (159). The other products have not been identified.



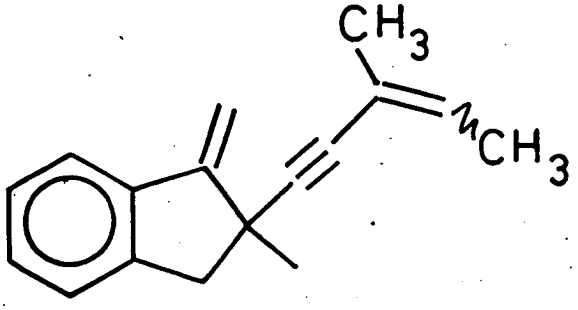
(159)

The ^{1}H n.m.r. spectrum of the product (160), figure 16, shows a methyl resonance at 1.97δ as a doublet coupled (J = 5Hz) to an olefinic quartet at 5.67δ, indicating an ethylidene group $CH_3CH=$. Another methyl resonance at 2.23δ is weakly coupled (J = 2Hz) to a benzylic methylene resonance at 3.43δ, as in 3-methylindene. A third methyl occurs as a singlet at 1.99δ. The stereochemistry about the double bond is not known. This compound would result from protonation of the vinyl group followed by bond reorganization and cyclopropane ring opening as in δ- protonation of dimethylvinylidene cyclopropanes. The intermediate (160) would be stabilized by the cyclopropane ring and by delocalisation into the



conjugated double bond.

Acid catalysed rearrangements of the 2-methylindene adduct, E and Z-2,3-benzo-5-methyl-6(2'-vinylpropenylidene)bicyclo [3,1,0] hex-2-ene (97) gave products which could not be separated or identified. Rearrangement of the 2,3-dimethylindene adduct, E and Z-2,3-benzo-1,5-dimethyl-6-(2'-vinylpropenylidene)bicyclo [3,1,0] hex-2-ene (98), with ethanolic hydrogen chloride gave a mixture of products which gave one main component by preparative vapour phase chromatography whose ^{1}H n.m.r. spectrum was consistent with that expected for 2-(3'methylpent-3'-en-1'-ynyl)-2-methyl-1-methyleneindane (161). The spectrum (figure 17) shows a methyl



(161)

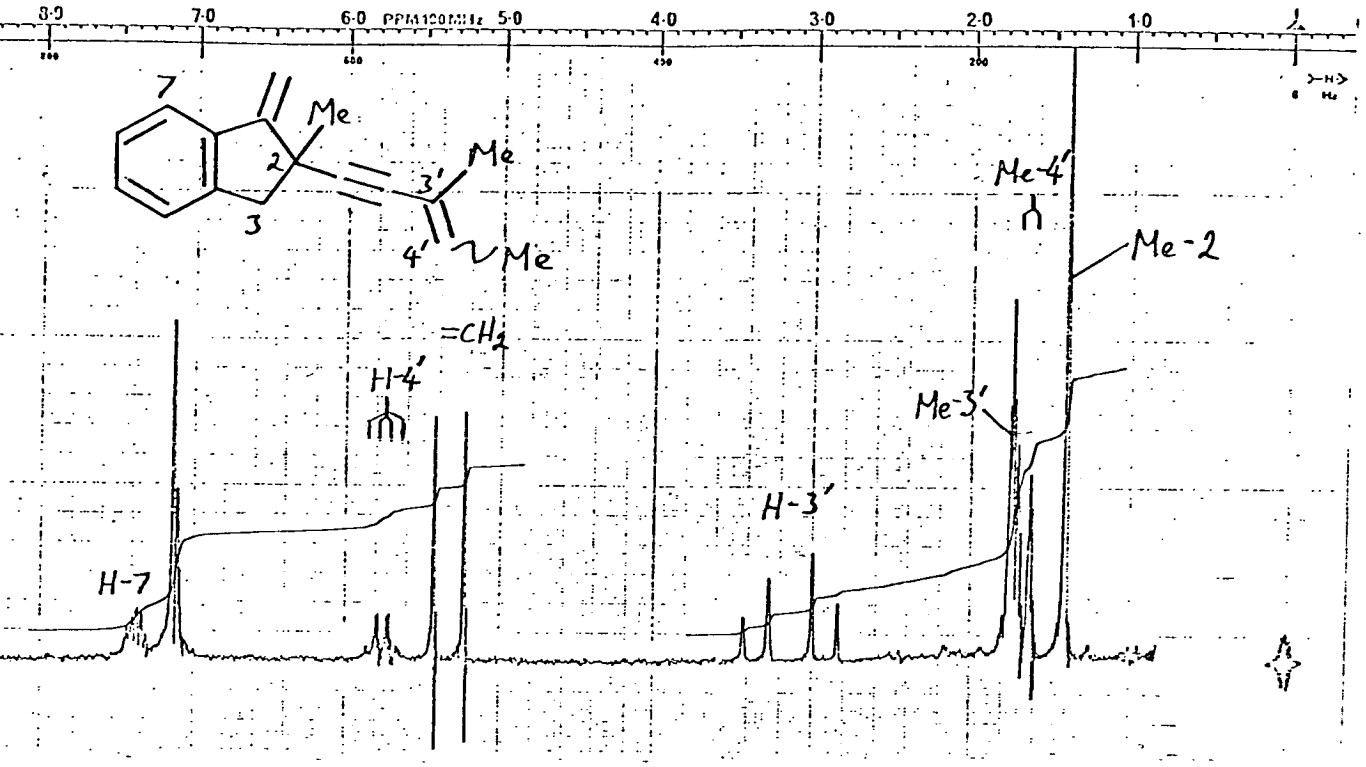


Figure 17

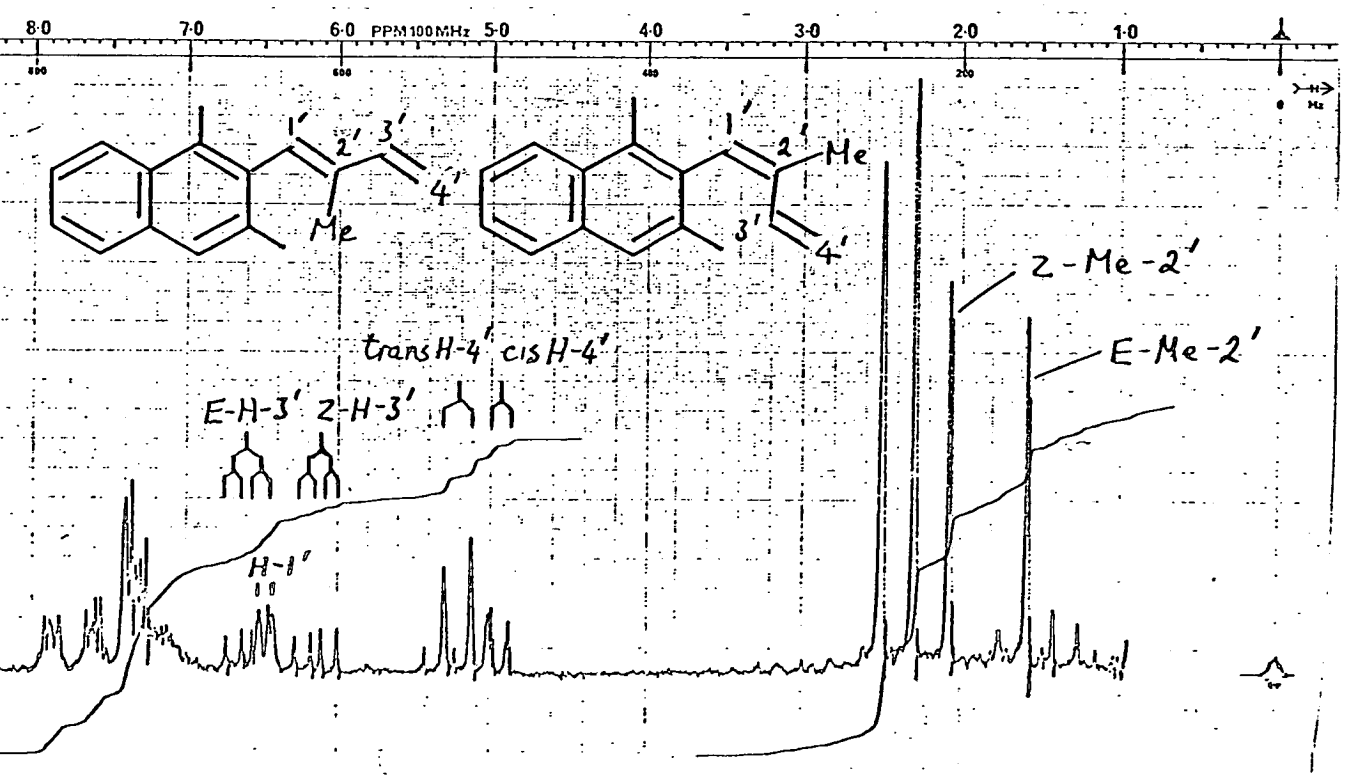
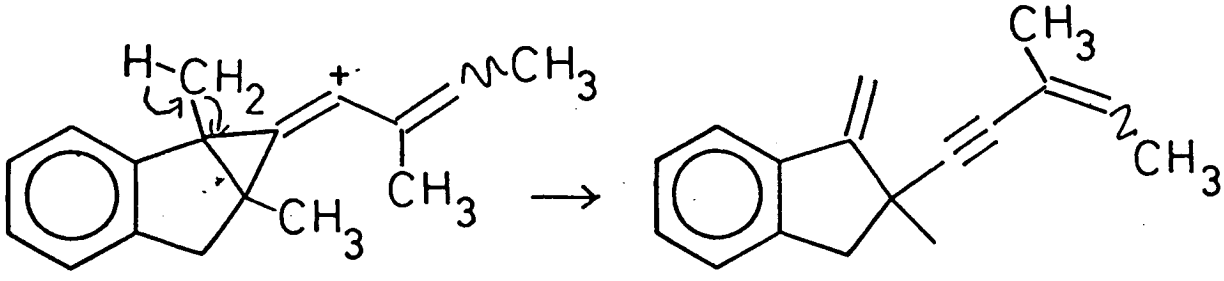


Figure 18

resonance at 1.67 δ as a doublet coupled (J = 7Hz) to an olefinic quartet at 5.75 δ which is further weakly coupled to another methyl resonance at 1.74δ. Irradiation of the quartet collapses the methyl resonances at 1.67 δ and 1.74 δ to singlets, demonstrating the presence of a $CH_3CH=C.CH_3$- group. The non-equivalent methylene protons at 2.92 δ and 3.35δ form an AB spectrum and the exocyclic olefinic methylene protons appear as singlets (5.22δ and 5.42δ) as in the analogous isopropyl derivative (145).

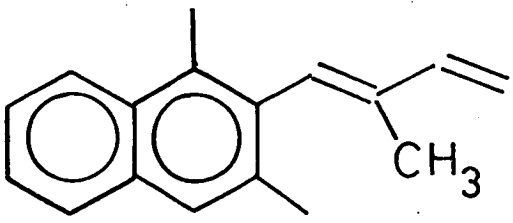
The mechanism of formation is similar to that for the 3-methylindene adduct (96), however as there is no proton available at the 2-position on the indene ring system, a proton is lost from the methyl group on position 3.

i.e.

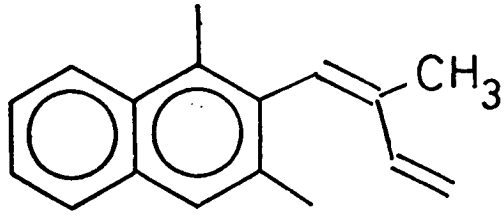


(161)

Rearrangement of the 2,3-dimethylindene adduct (98) with p-toluenesulphonic acid in carbon tetrachloride gave a mixture of products which were separated by preparative vapour phase chromatography to give the methylene indane (161) and another fraction in the ratio 1:2. The second fraction is believed to be a mixture of E and Z-2-(2'-methylbuta-1', 3'-dienyl)-1,3-dimethylnaphthalene (162a and 162b) in the ratio E:Z = 1:1.3.



E-(162a)

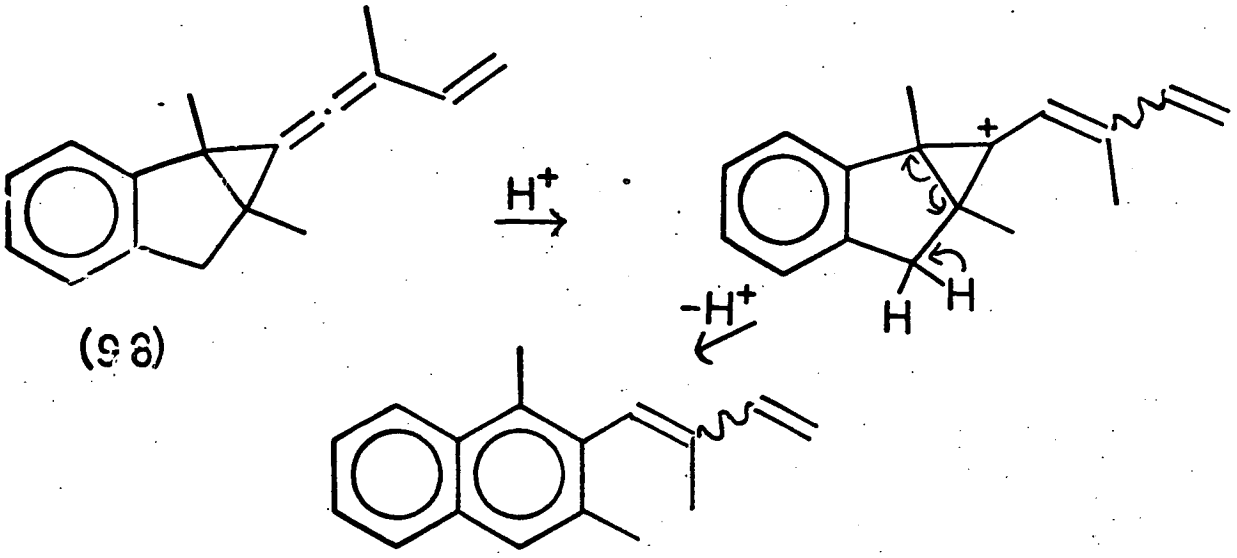


Z-(162b)

The two methyl groups attached to the naphthalene nucleus force the diene system out of the plane of the former and thus the two isomers were distinguished by the ring current induced shift to lower frequency of the protons lying over the aromatic ring. Hence in the E isomer the protons of the 2'-methyl group resonate at a lower frequency and the 3'- proton resonates at a higher frequency than the Z-isomer (see figure 18).

Refluxing the 2,3-dimethylindene adduct (98) in carbon tetrachloride only, gave exclusively the naphthalenes (162a and 162b). While a radical mechanism could be proposed it is more likely that the reaction is still acid catalysed with trace acid present.

The naphthalenes (162a and 162b) arise from protonation of the carbon followed by ring expansion and proton loss as with the vinylidene derivatives.



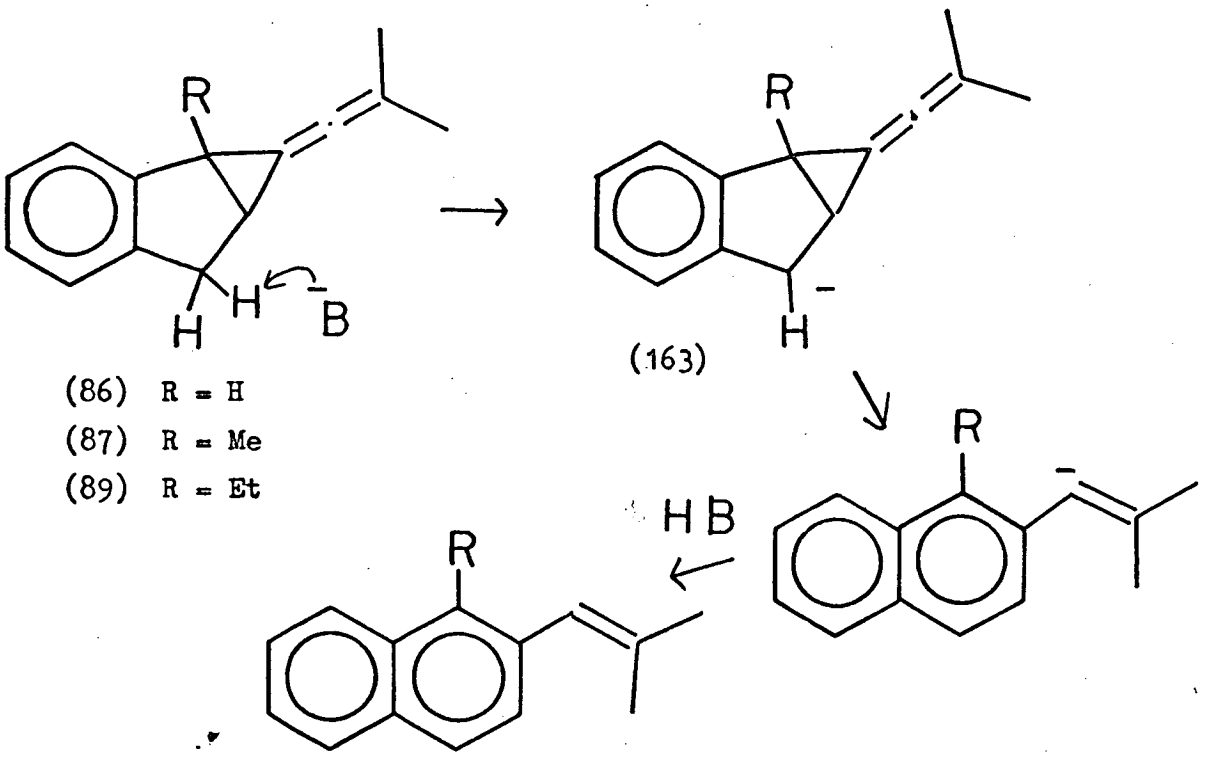
(98) (162a+b)

4.3 Base Catalysed Rearrangements of Cyclopropanes

These rearrangements were all carried out using a solution of potassium t-butoxide in dimethyl sulphoxide at 100°C.

Rearrangement of the vinylidene cyclopropane adducts (86), (87) and (89) of indene, 3-methylindene and 3-ethylindene all gave ring expansion to give the (2'-methylpropenyl)naphthalenes (137), (138) and (142). The

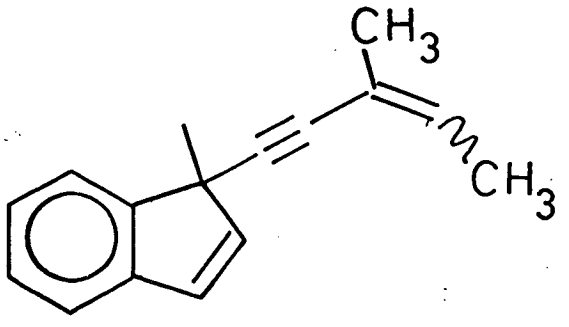
mechanism is thought to proceed by removal of the benzylic proton by the base to give the anion (163) which ring expands and abstracts a proton to give the naphthalene derivative.



(86) R = H
(87) R = Me
(89) R = Et

(137) R = H; 40%
(138) R = Me; 50%
(142) R = Et; 50%

Rearrangement of the 2-vinylpropenylidene adduct (96) of 3-methylindene gave a complex mixture of products which were separated by preparative vapour phase chromatography to give one major product, ~ 30%, whose ^{1}H n.m.r. spectrum was consistent with that expected for 1-(3'-methylpent-3'-en-1'-ynyl)-1-methylindene (164). The spectrum (figure 19)



(164)

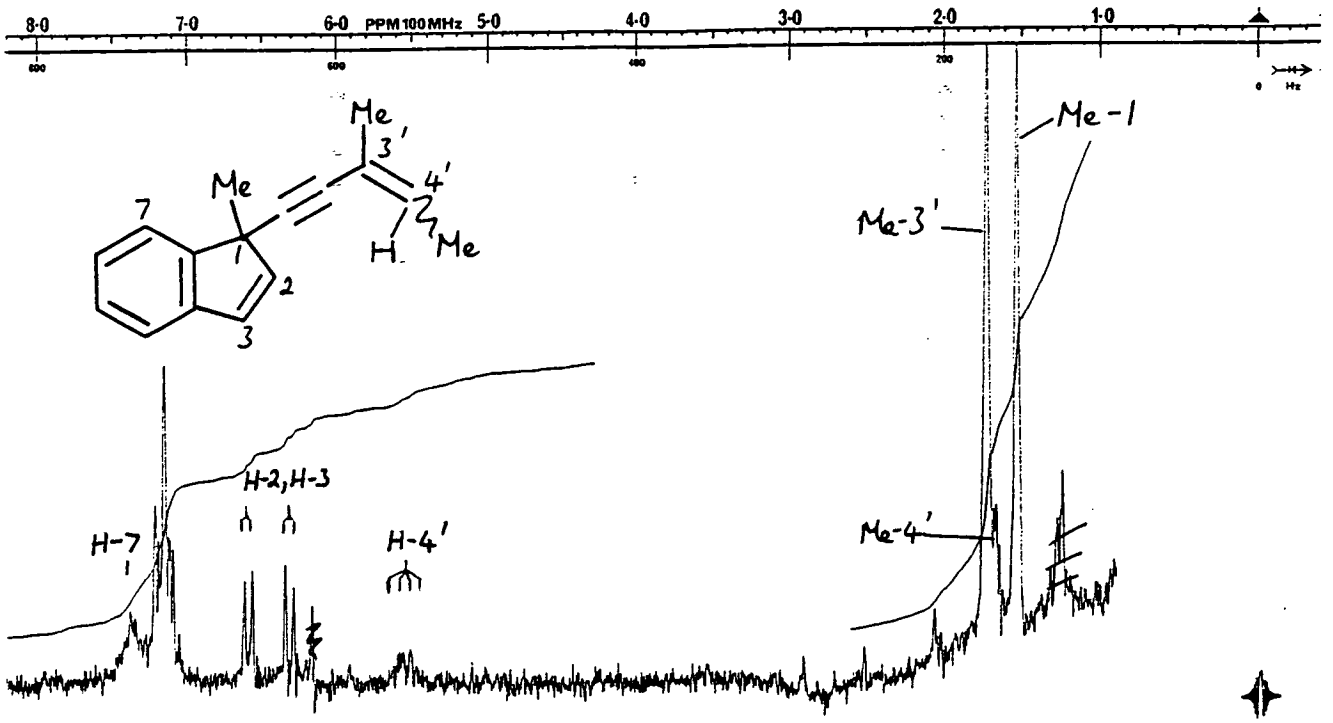


Figure 19

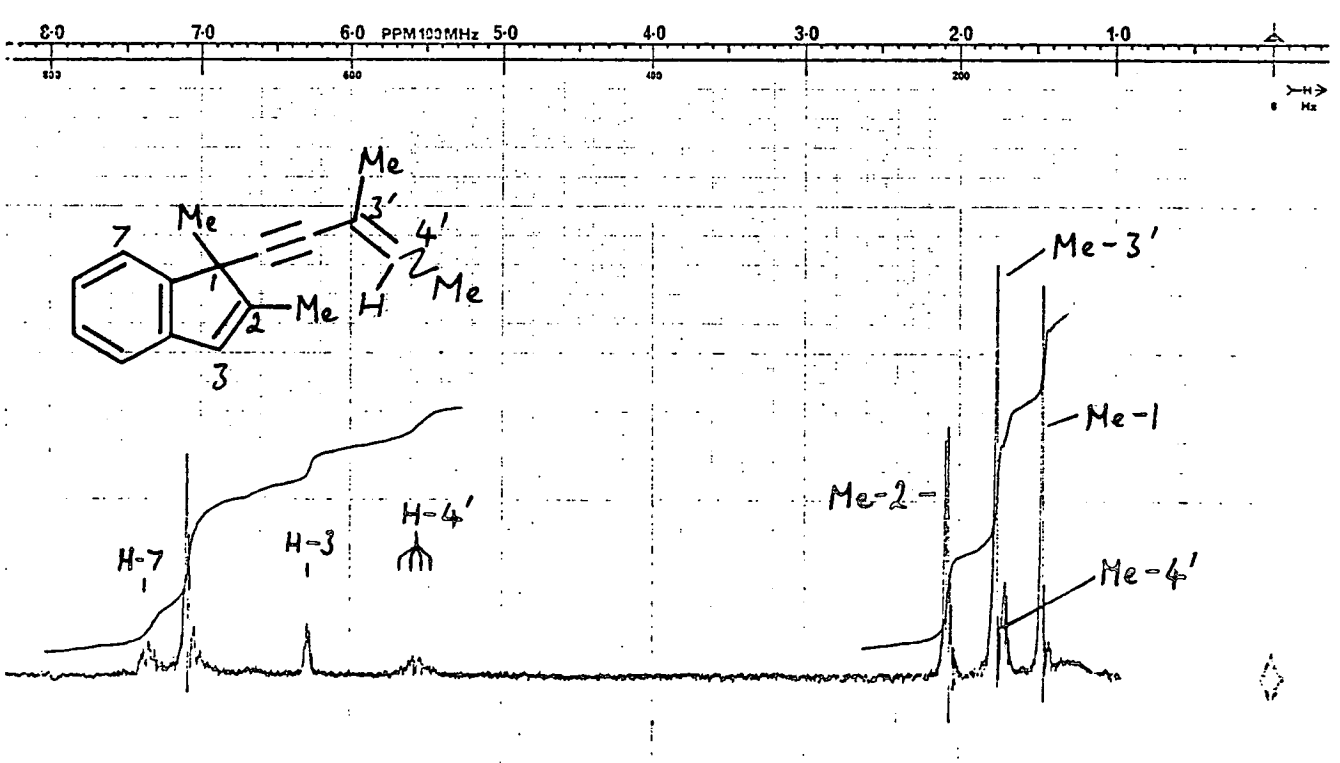
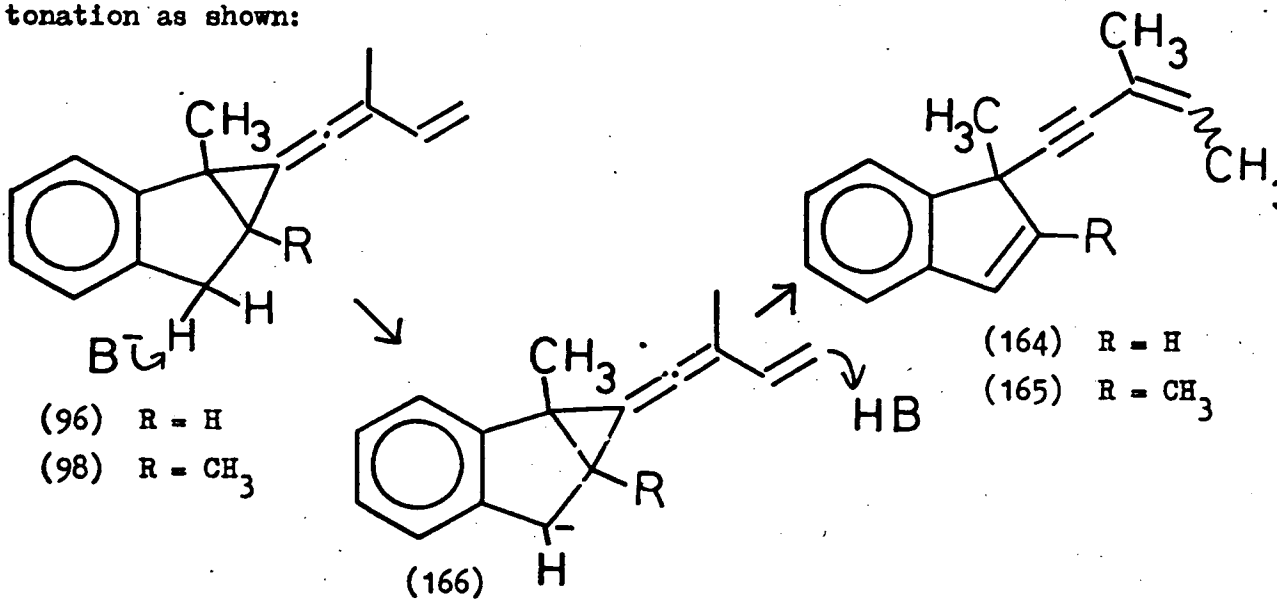


Figure 20

strongly resembles that of the 3-methylindene acid catalysed product (159) but shows a two proton AB system at 6.32δ and 6.60δ (J = 5Hz) and no benzylic methylene resonance indicating the presence of a 1,1-disubstituted indene.

Similarly the 2-vinylpropenylidene adduct (98) with 2,3-dimethylindene gave one main product identified as 1,2-dimethyl-1-(3'-methylpent-3'-en-1'-ynyl)indene (165) from its ^{1}H n.m.r. spectrum (figure 20) which is very similar to that of the 3-methylindene analogue (164), the single olefinic resonance occurring at 6.28δ.

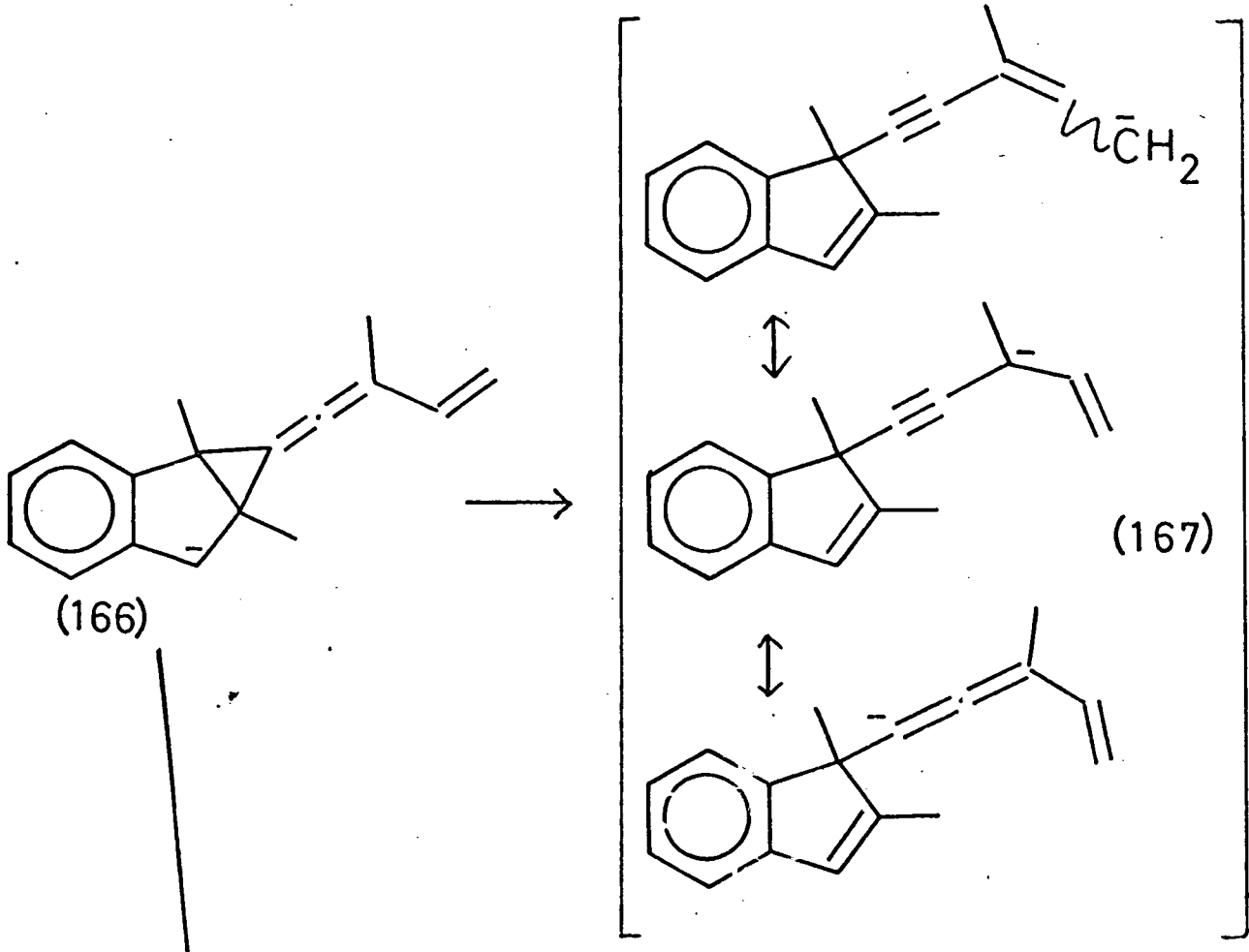
The products (164) and (165) arise from removal of a benzylic proton on the adducts (96) and (98) by base, followed by ring opening and protonation as shown:



Removal of the benzylic methylene proton to give the anion (166) means that only the formation of the 1,1-isomer enables the double bond to form.

With vinylidene adduct rearrangement only naphthalenes were formed and the difference in the reaction is presumably due to the extra vinyl group on the 2-vinylpropenylidene cyclopropanes. It is surprising that the lower energy naphthalenes are not formed more readily with 2-vinylpropenylidene adducts. However if ring opening of the indenyl anion (166) occurs before proton abstraction from the solvent then the indene anion (167) is highly stabilised by delocalisation while the naphthalene anion

(168) has a localised negative charge. Here the presence of the additional vinyl group would be expected to favour the route to the acetylenic indenes (164) and (165).



(166)

(167)

(168)

(Localised Ion)

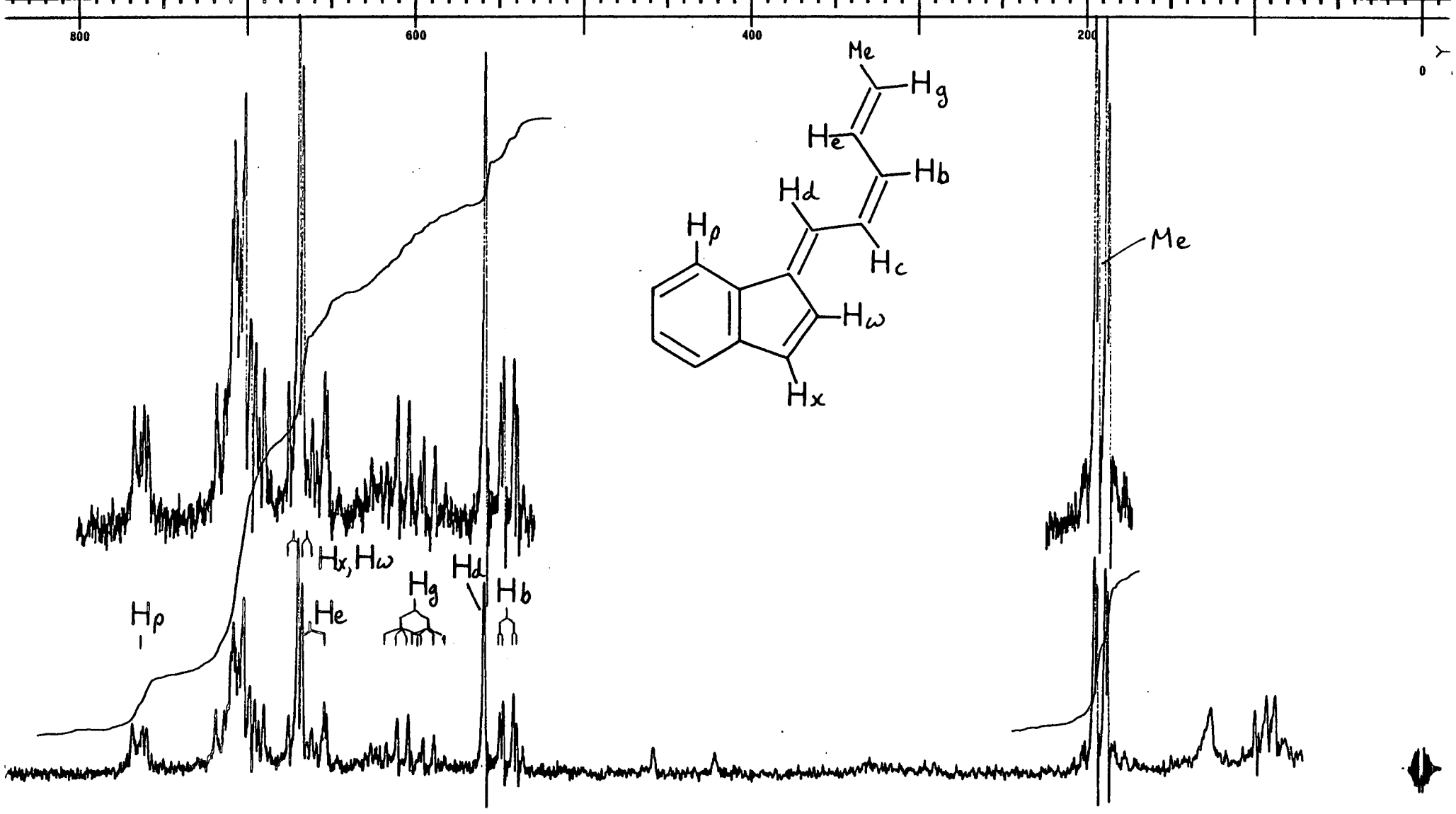
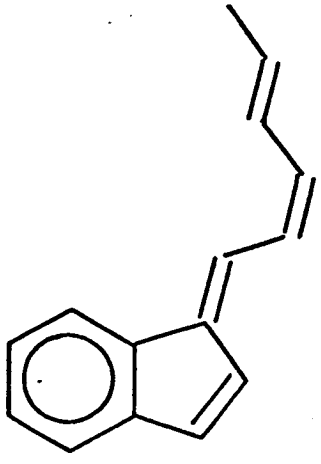


Figure 21

Rearrangement of the indene adduct, E and Z-2,3-benzo-6(pent-3'-enylidene)bicyclo [3,1,0] hex-2-ene (101), by passage through alumina gave a bright yellow oil. Comparison of the ultra violet spectrum and ^{1}H n.m.r. spectrum with those of the benzofulvene type products obtained in chapter 6, strongly suggest that this compound is a benzofulvene and it has been tentatively assigned the structure E-1,2-benzo-6-(Z,E-hexa-1',3'-dienyl)fulvene (169).

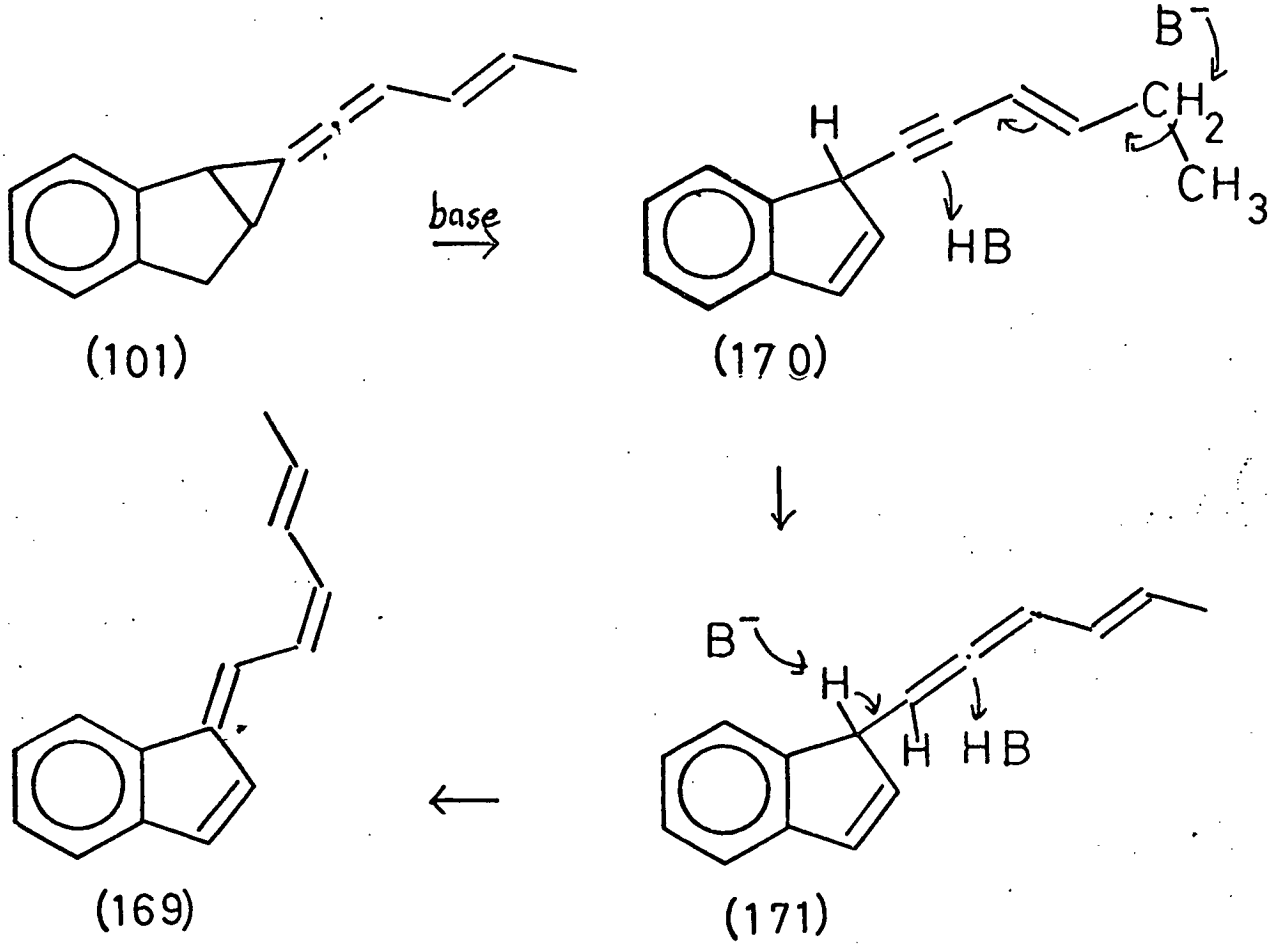


(169)

The ^{1}H n.m.r. spectrum (figure 21) shows a methyl group resonance at 1.90δ as a doublet of doublets coupled to an olefinic proton at 5.99δ (J = 6Hz) and an olefinic proton at 6.61δ (J = 1Hz). These two olefinic protons are coupled together by 15Hz indicating a trans double bond. The olefinic doublet of doublets at 5.45δ (J = 9Hz, 1Hz) is thought to indicate a cis double bond with the other proton obscured by the aromatic proton resonance. The singlet at 5.58δ is thought to be the proton H_z which does often appear as a singlet in other benzofulvenes. The AB spectrum (6.64δ, 6.73δ, J = 5Hz) is attributed to the protons H_w and H_x. Comparison of the spectrum with those of E and Z-6-vinylfulvene (229), (230), (table 12) with the observation that H_c does not appear above 7.2δ (Z conformers generally have H_c at higher frequency that 7.2δ due to the aromatic ring current) indicates an E configuration.

The mechanism may proceed as for base catalytic rearrangement of the 2-vinylpropenylidene cyclopropanes (96) and (98), giving the acetylenic

indene (170) as the first step. This enyne may then rearrange via the allene (171) to give the conjugated benzofulvene (169).



Rearrangement products (164) and (165) from the 2-vinylpropenylidene adducts (96) and (98) are prevented from going to the fulvene because of the methyl in the 1-position. It is unfortunate that the 2-vinylpropenylidene-indene adduct could not be made as it would have been expected to rearrange to a fulvene.

CHAPTER 5

Vapour Phase Vacuum Pyrolysis of Acetylenes

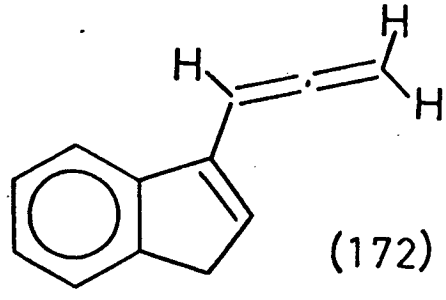
In many cases the acetylenic products obtained in chapter 3 underwent interesting rearrangements by vaporization through a hot tube (300°C - 900°C) under high vacuum. The products obtained and some of their reactions are discussed here.

5.1 Vapour Phase Vacuum Pyrolysis of Propargylic Compounds

Pyrolysis of either 1-propargylindene or 3-propargylindene at 500°C gave a mixture containing 1-propargylindene (103), 20%

3-propargylindene (104), 60%

3-allenylindene (172), 20%



(172)

from which 3-allenylindene (172) was isolated by silica gel chromatography. Pyrolysis at 400°C gave 1- and 3-propargylindene but no allene. Pyrolysis at 600°C or 700°C gave a complex mixture including acenaphthalene, but no allene. No 1-allenylindene was observed at these temperatures.

3-Allenylindene (172) was identified from its i.r. and ^{1}H n.m.r. spectra. The i.r. shows a strong allene absorption at 1930 cm^{-1}. The ^{1}H n.m.r. (figure 22) shows the indene methylene protons retained at a characteristic high frequency shift of 3.35δ. The finely split doublet at 5.14 δ is coupled (J = 7Hz) to the triplet at 6.27δ. These are assigned to the allene group - the 'a' protons are equivalent, being in a plane perpendicular to the 'b' protons, and resonate at lower frequency from

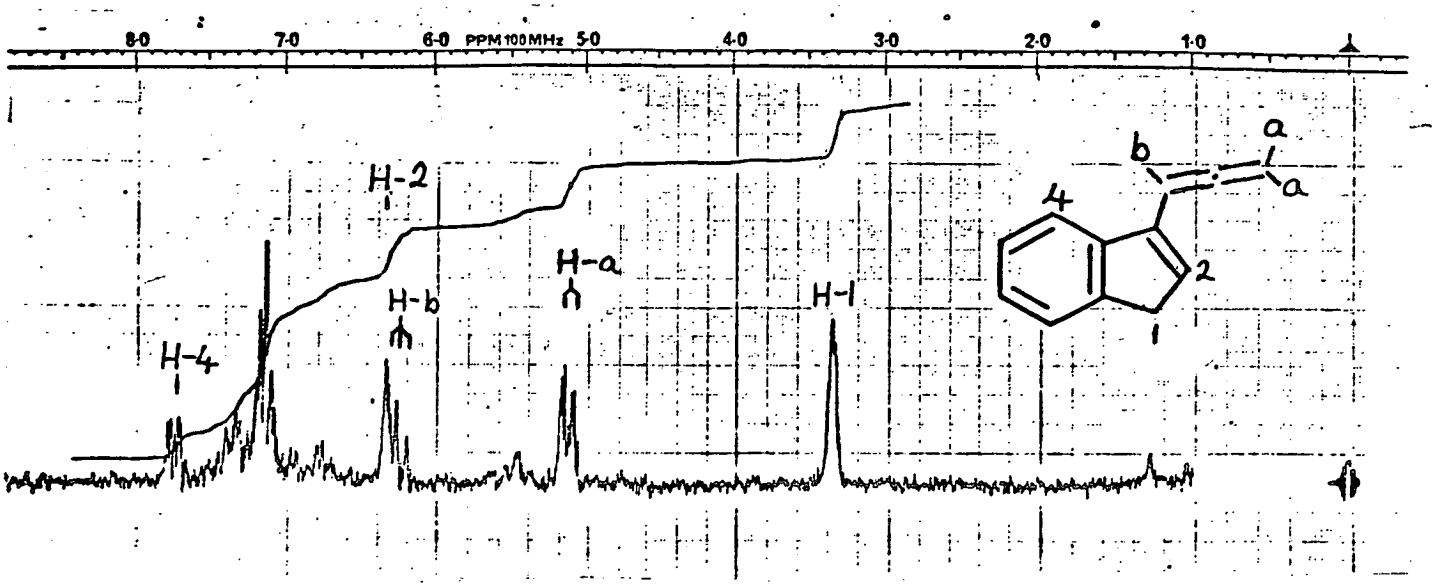


Figure 22

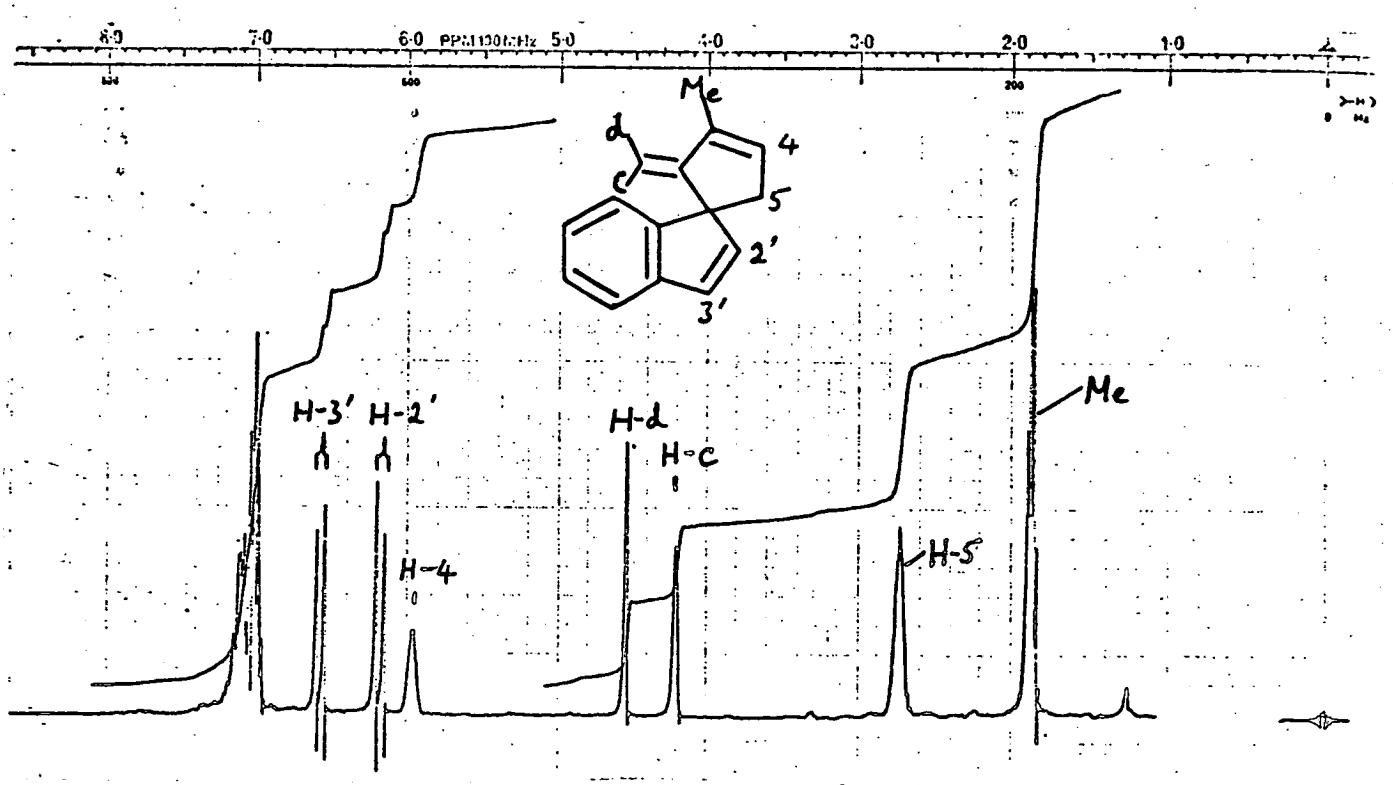
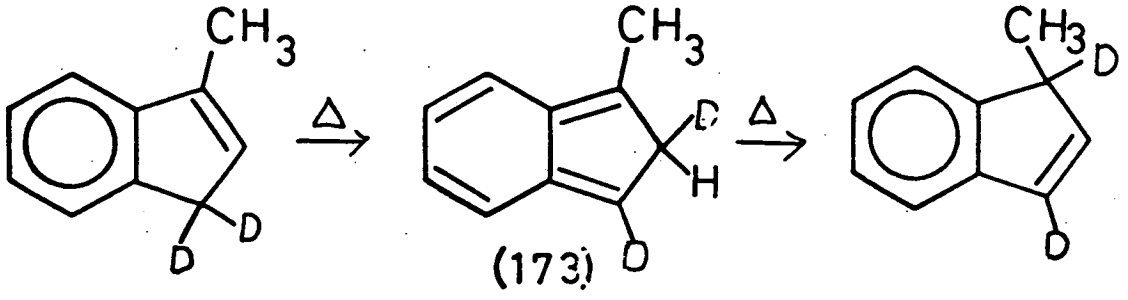


Figure 23

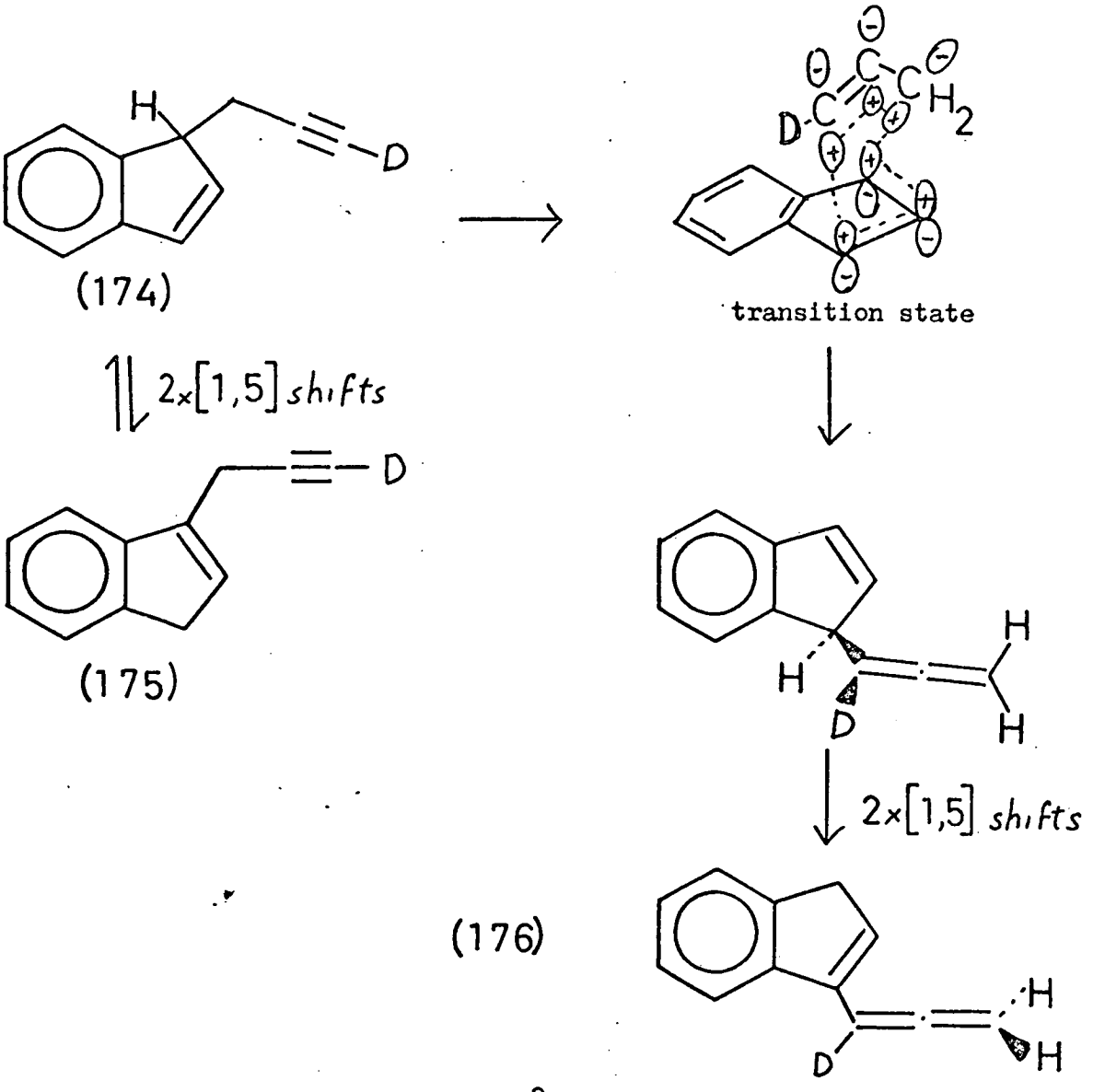
the 'b' protons. The aromatic proton H_4 lies at the high frequency value of 7.75δ, shifted by the field of the adjacent allene group.

The interconversion of 1- and 3-propargylindene appears to go readily above 300°C. Thermal hydrogen migrations across the conjugated indene system is reported to proceed via two [1,5] sigmatropic shifts through the reactive intermediate isoindene[83] (173). Isoindene has been

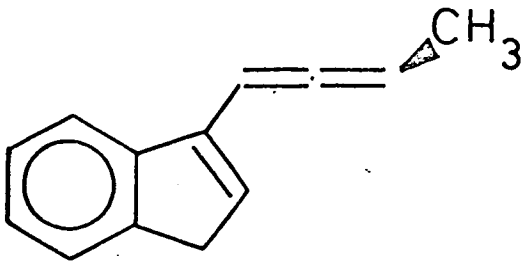


isolated from the pyrolysis of indene by trapping with maleic anhydride[84].

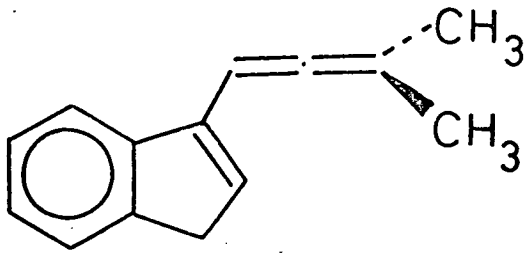
A likely route for the formation of the 3-allenylindene (172) seemed to be from 1-propargylindene (103) via a [3,3] sigmatropic shift to give 1-allenylindene followed by two [1,5] hydrogen shifts. The transition state for the [3,3] shift forms a Hückel system and since it contains six electrons the rearrangement is allowed. This path was verified by the pyrolysis of 1-(3'-deutero propargyl) indene (174) which gave, apart from unchanged starting material and 3-(3'-deutero propargyl)-indene (175), only 3-(1'-deutero allenyl)indene (176), identified by absence of the olefinic resonance H_b in the ^1H n.m.r. spectrum. This type of 'Cope' rearrangement has not previously been observed across the indene system. (see page 23)



Similar rearrangements at 500°C were observed for 3(1'-methylprop-2'-ynyl)indene (118) which gave a mixture, in 60% yield, of unchanged starting material and 3(buta-1',2'-dienyl)indene (177) in the ratio 1:1, and for 3(1',1'-dimethylprop-2'-ynyl)indene (117) which gave exclusively 3(3'-methylbuta-1',2'-dienyl)indene (178) in 80% yield. The products were identified from their ^{1}H n.m.r. and i.r. spectra and by analogy with the rearrangement of 3-propargylindene. Further confirmation of the presence of an allene group in compound (178) was provided by the ^{13}C n.m.r. spectrum which showed the absorption of the central allene carbon atom at 204.3 p.p.m. In neither case were any 1-substituted indenes obtained.



(177)



(178)

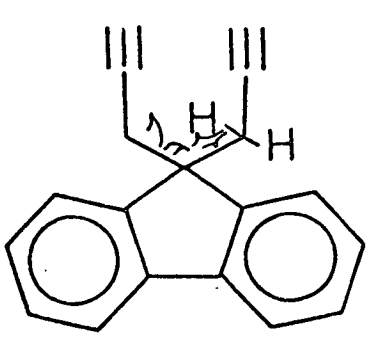
The increasing extent of conversion to the allene with the number of methyl groups parallels the increase in the difference between the calculated heats of formation[8] for the allenic and propargylic compounds, see table 7.

Table 7

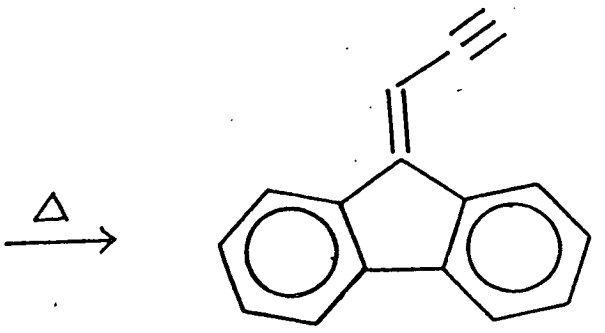
Heats of Formation (in kJ mol.$^{-1}$)

		$R_1 = R_2 = H$	$R_1 = H_1$, $R_2 = CH_3$	$R_1 = R_2 = CH_3$
$-\overset{R_1}{\underset{R_2}{C}}-C\equiv CH$	ΔH°	366	336	306
$-HC=C=C\overset{R_1}{\underset{R_2}{}}$	ΔH°	348	315	280
	$\Delta\Delta H^\circ$	18	21	26

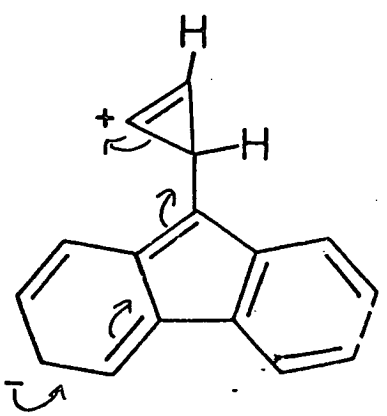
Pyrolysis of 9,9-dipropargylfluorene (114) at 700°C gave 51% of 9-ethynylphenanthrene (180), 38% of fluorene (186) and 11% of a mixture of acephenanthralene (182) and fluoranthene (184). The products (180), (186) and (182), all known compounds, were identified from their i.r., m.s. and n.m.r. spectra and from their melting points. In addition hydrogenation of 9-ethynylphenanthrene (180) gave 9-ethylphenanthrene which was identified by its ^1H n.m.r. spectrum and its melting point.

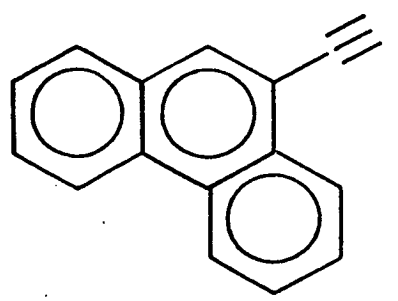


(114)

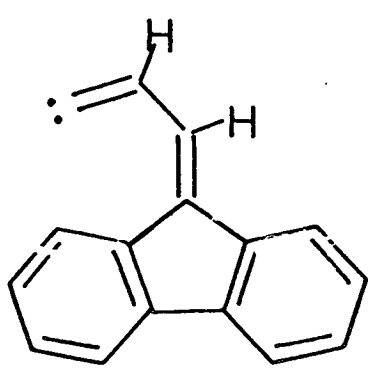


(179)

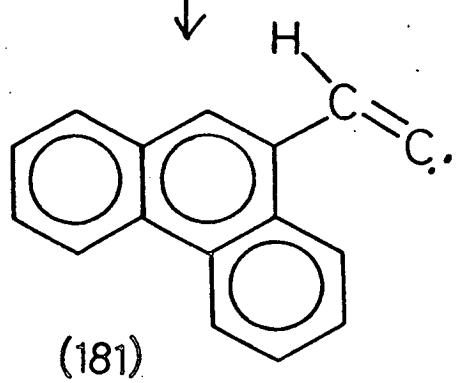




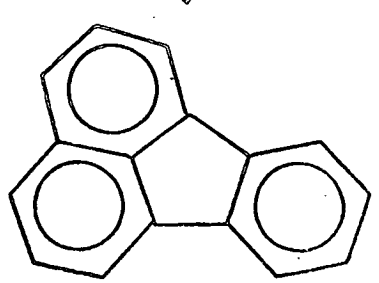
(180)



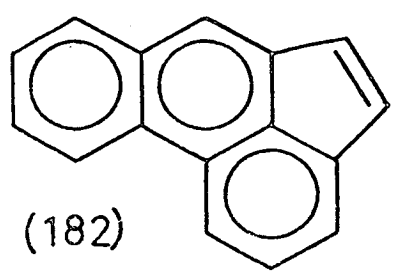
(183)



(181)



(184)



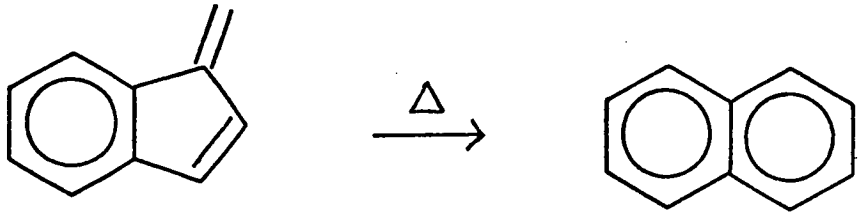
(182)

Fluoranthene (184) was not isolated pure but was identified by comparison of its ^1H n.m.r. with that of an authentic sample.

No reaction was observed below 600°C and at higher temperature the proportion of acephenanthralene (182) increased and that of 9-ethynylphenanthrene (180) decreased. Pyrolysis of pure 9-ethynylphenanthrene (180) at 850°C gave pure acephenanthralene.

Since these pyrolyses result in the loss of one or two propargyl units it seemed likely that 9-propargylfluorene might be an intermediate. However this was excluded since pyrolysis of 9-propargylfluorene (115) produced entirely different products none of which have yet been identified. Pyrolysis of 9,9-bis(3'-deuteriopropargyl)fluorene gave 9-(2'-deuterioethynyl)phenanthrene in which the deuterium was retained entirely on the ethynyl group.

Rearrangement is thought to proceed via elimination of prop-1-yne to leave the dibenzofulvene (179). Ring expansion would then give 9-ethynylphenanthrene (180). The analogous rearrangement of 1,2-benzofulvene (185) to give naphthalene has been reported.[85,86]



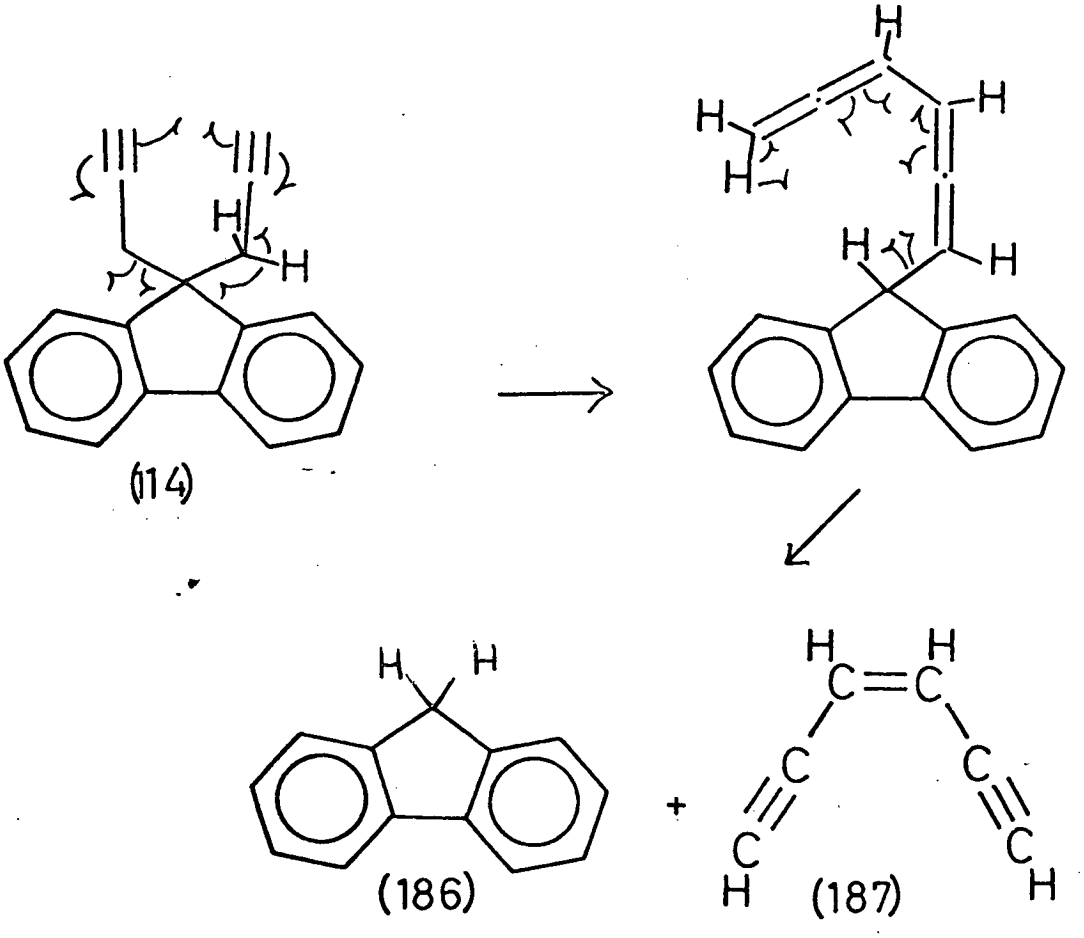
(185)

The rearrangement of 9-ethynylphenanthrene (180) to acephenanthralene (182) is believed to proceed via the carbene (181), and is analogous to that reported[75] for 1-ethynylnaphthalene rearranging to acenaphthalene which is reported to proceed via rearrangement of the acetylene group to give a carbene. (see page 25)

The rearrangement of the benzofulvene (179) to fluoranthene (184) may also proceed via rearrangement of the acetylene group to give the

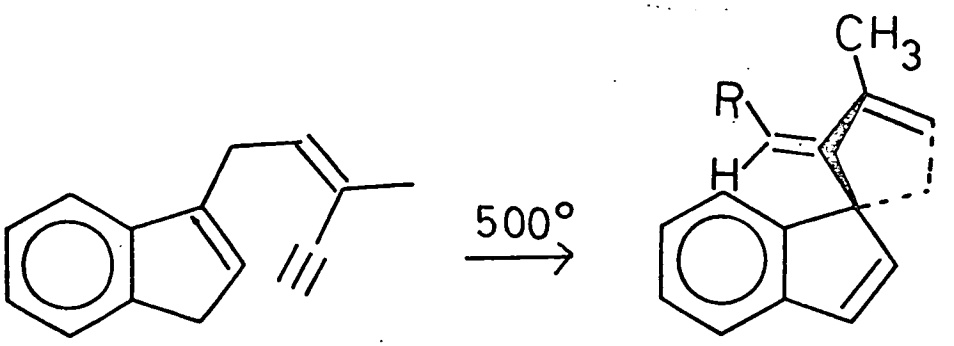
carbene (183) which would cyclise by direct insertion into the C-H bond.

Formation of fluorene is not readily explained without recourse to intermolecular abstraction of radicals. However it is possible to construct a mechanism in which 9,9-dipropargylfluorene (114) eliminates hex-3-en-1,5-diyne (187) to give fluorene (186) as shown:



5.2 Vapour Phase Vacuum Pyrolysis of Pent-2-en-4-ynyl Derivatives

Pyrolysis of Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126b) at 500°C gave spiro [2-methylene-3-methylcyclopent-3-ene-1,1'-indene] (188) in 80% yield. Evidence for this structure is provided by ^{1}H and ^{13}C n.m.r. and exact mass measurement.



(126b) R = H

(189) R = D

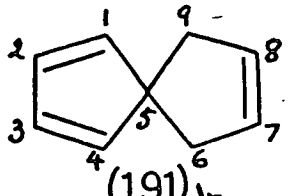
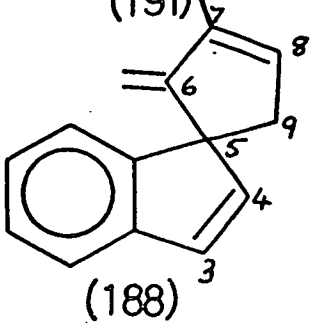
(188) R = H

(190) R = D

The ^{1}H n.m.r. spectrum (figure 23) shows four aromatic protons, an AB spectrum (6.57δ, 6.18δ, J = 5Hz) similar to that found in 1,1-disubstituted indenes (e.g. dipropargylindene (105)) and singlets due to an olefinic proton (5.96δ), an aliphatic methylene group (2.73δ), and a methyl group (1.86δ) attached to a double bond. Also present are two olefinic resonances at relatively low frequency values (4.20δ, 4.55δ) suggesting orientation over the aromatic ring where they would experience a weaker field. The resonance at lower frequency is thought to point towards the benzene ring.

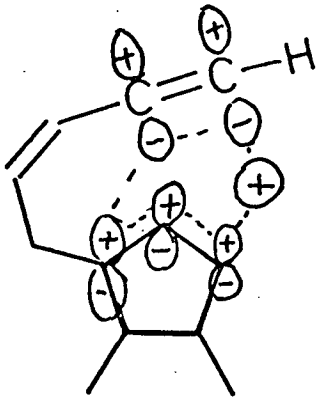
The ^{13}C chemical shifts were found to be consistent with those published for spiro [4.4] nona-1,3,7-triene (191)[87] (see table 8).

Table 8 ^{13}C Data

Carbon Number	3	4	5	6	7	8	9
 (191)	127.9	144.8	62.0	36.6	130.4	130.4	36.6 (p.p.m.)
 (188)	129.1	144.5	62.7	143.2	140.7	133.1	39.5 (p.p.m.)

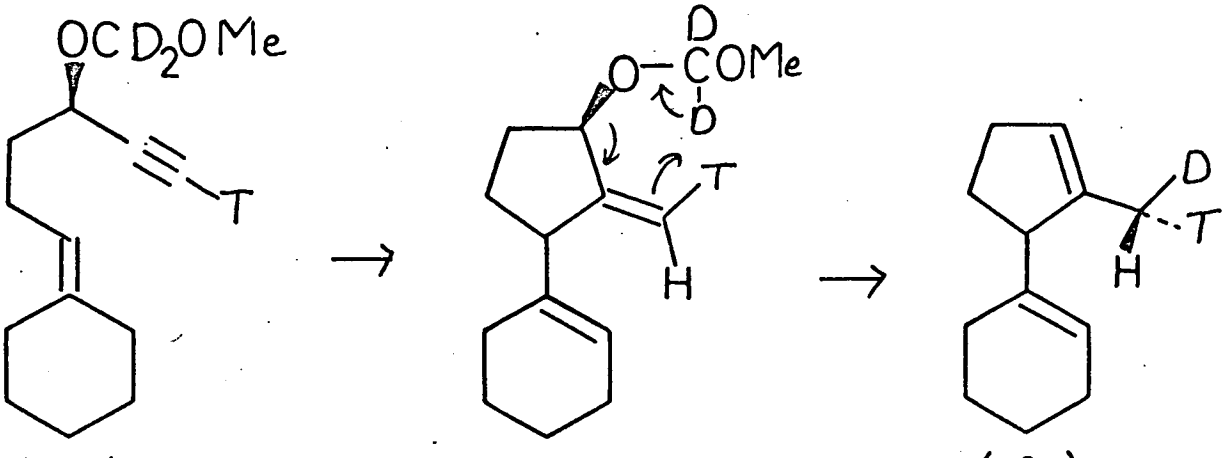
In the spiro-indene (188) the olefinic carbon-6 is very similar to carbon-4 while carbon-7 is shifted to higher frequency by the methyl group.

Pyrolysis of Z-3-(5'-deuterio-3'-methylpent-2'-en-4'-ynyl)indene (189) at 500°C led to the product having a 60% reduction in the intensity of the proton absorption at 4.20δ. Hence the product is assigned the structure (190), having the deuterium pointing away from the benzene ring. The acetylenic terminal carbon is stereospecifically picking up a proton on one side only. This points to a concerted process. The structure can orientate itself for concerted cyclisation and in the transition state (192) the atomic orbitals involved constitute a Hückel system. Since there are six electrons a concerted process is allowed.



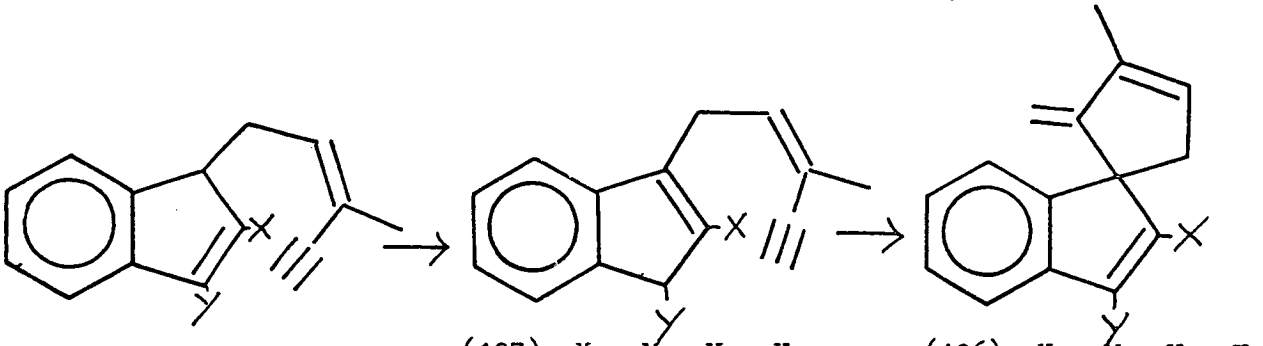
(192)

It has been reported[88] that pyrolysis of the doubly labelled chiral ether (193) leads to the formation of the product (194) containing a chiral methyl group of predictable configuration. This again indicates a stereospecific process.



Cyclisation onto the terminal acetylenic carbon is not observed since the acetylenic group cannot be aligned for concerted cyclisation on the terminal carbon with simultaneous migration of hydrogen to the internal acetylenic carbon atom. Hence terminal cyclisation would be a much higher energy process.

Z-3-(3'-Methylpent-2'-en-4'-ynyl)-2-methylindene (127) and Z-1-(3'-methylpent-2'-en-4'-ynyl)3-methylindene (129) also underwent cyclisation at 500°C to the spirotrienes (196) and (197), the latter presumably first undergoing two [1,5]hydrogen shifts to form Z-3-(3'-methylpent-2'-en-4'-ynyl)-1-methylindene (195).



(129) X = H, Y = Me (127) X = Me, Y = H (195) X = H, Y = Me (196) X = Me, Y = H (197) X = H, Y = Me

Pyrolysis of E and Z-3-(1!methylpent-2'-en-4'-ynyl)indene (122a and 122b) at 500°C gave 30% of a cyclised spirotriene plus 30% of recovered E-starting material (122a). When the pyrolysis was repeated with pure Z-isomer (122b) the product was practically all spirane but if pure E-isomer (122a) was pyrolysed only a little spirotriene was obtained and mostly starting material was recovered. This suggests, as the mechanism requires, that only the Z isomer cyclises, and a small amount of cis-trans isomerization occurs. This also supports the assignment of Z configuration to Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126b, chapter 3.4).

In this case the spiro product was isolated as a mixture of two

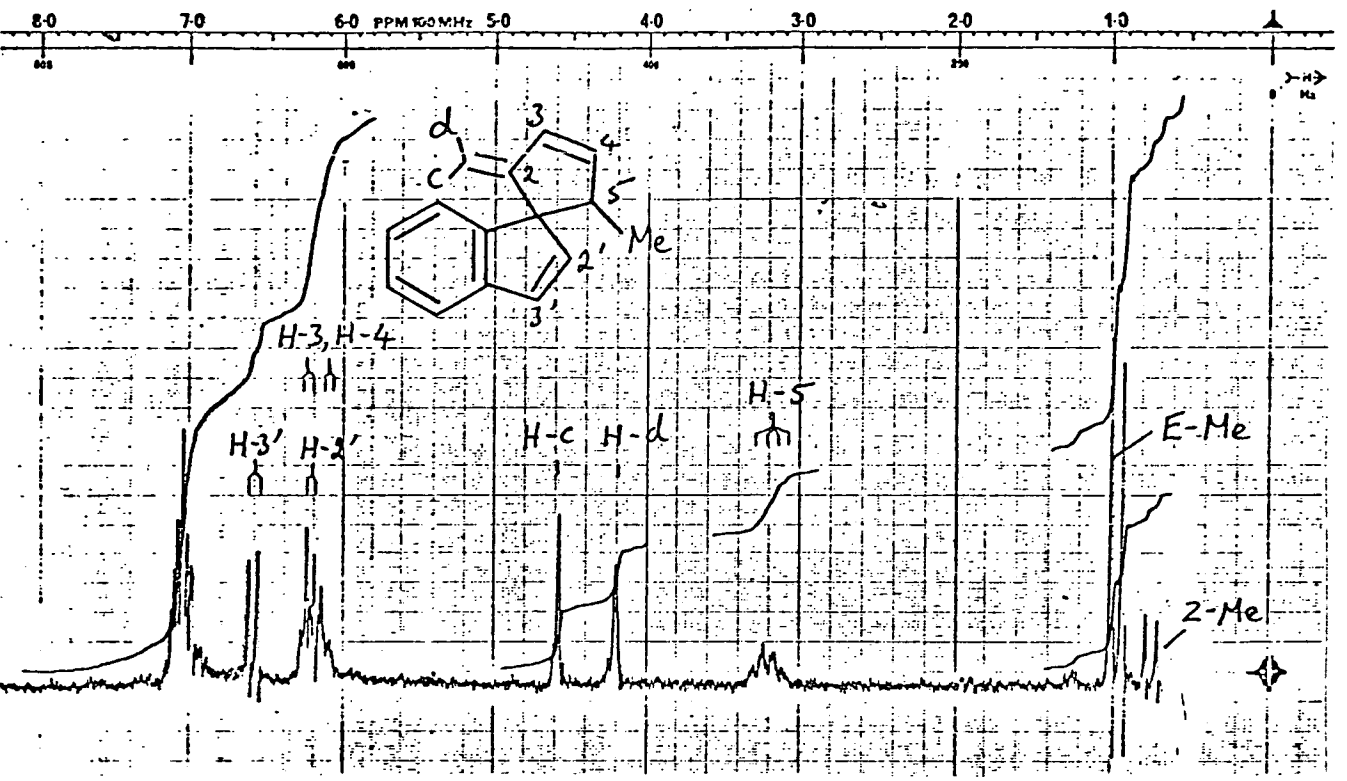


Figure 24

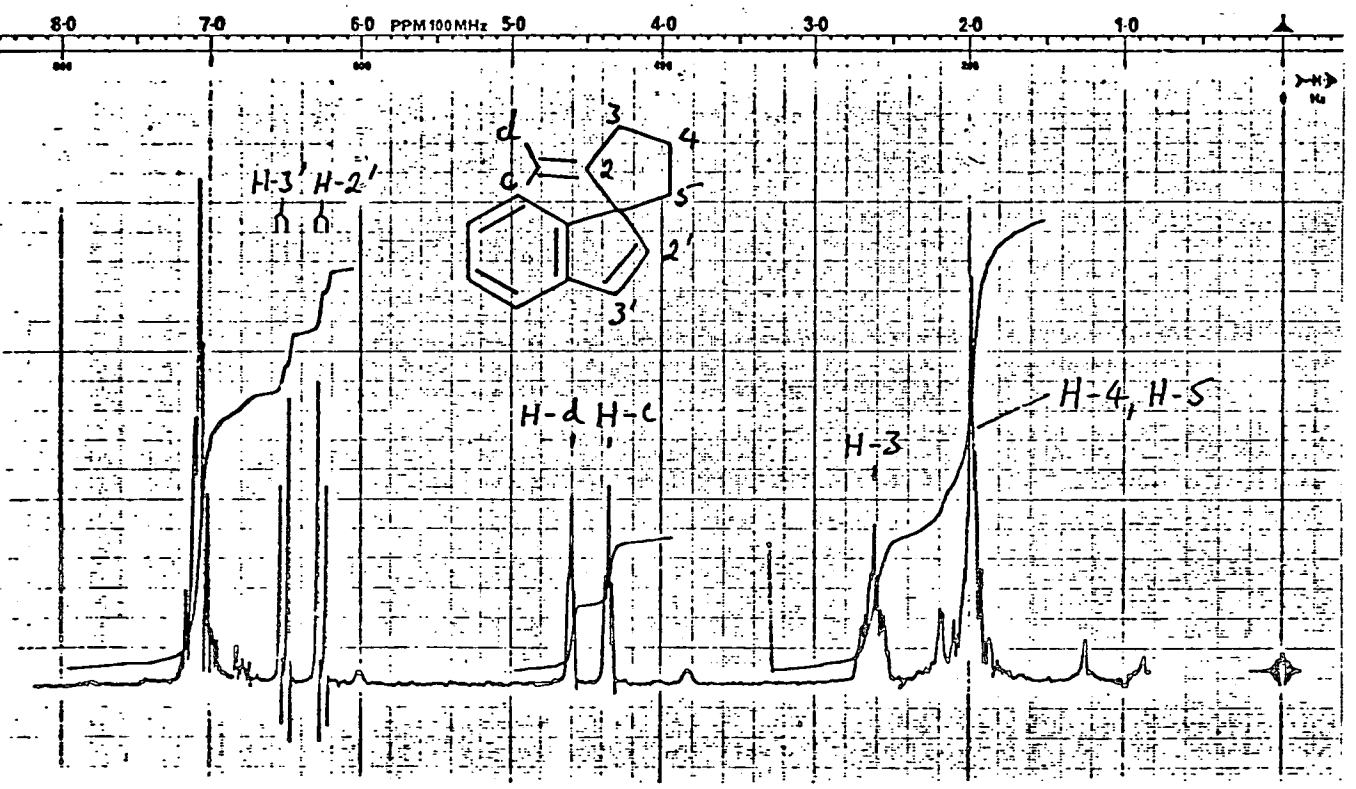
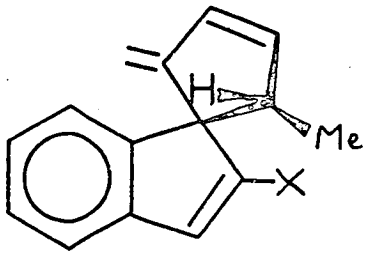
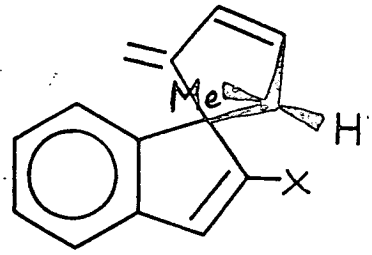


Figure 25

isomers in the ratio 5:1. These have been assigned the structures E and Z-spiro [2-methylene-5-methylpent-3-ene-1,1'-indene] (198) and



(198) X = H
(199) X = Me

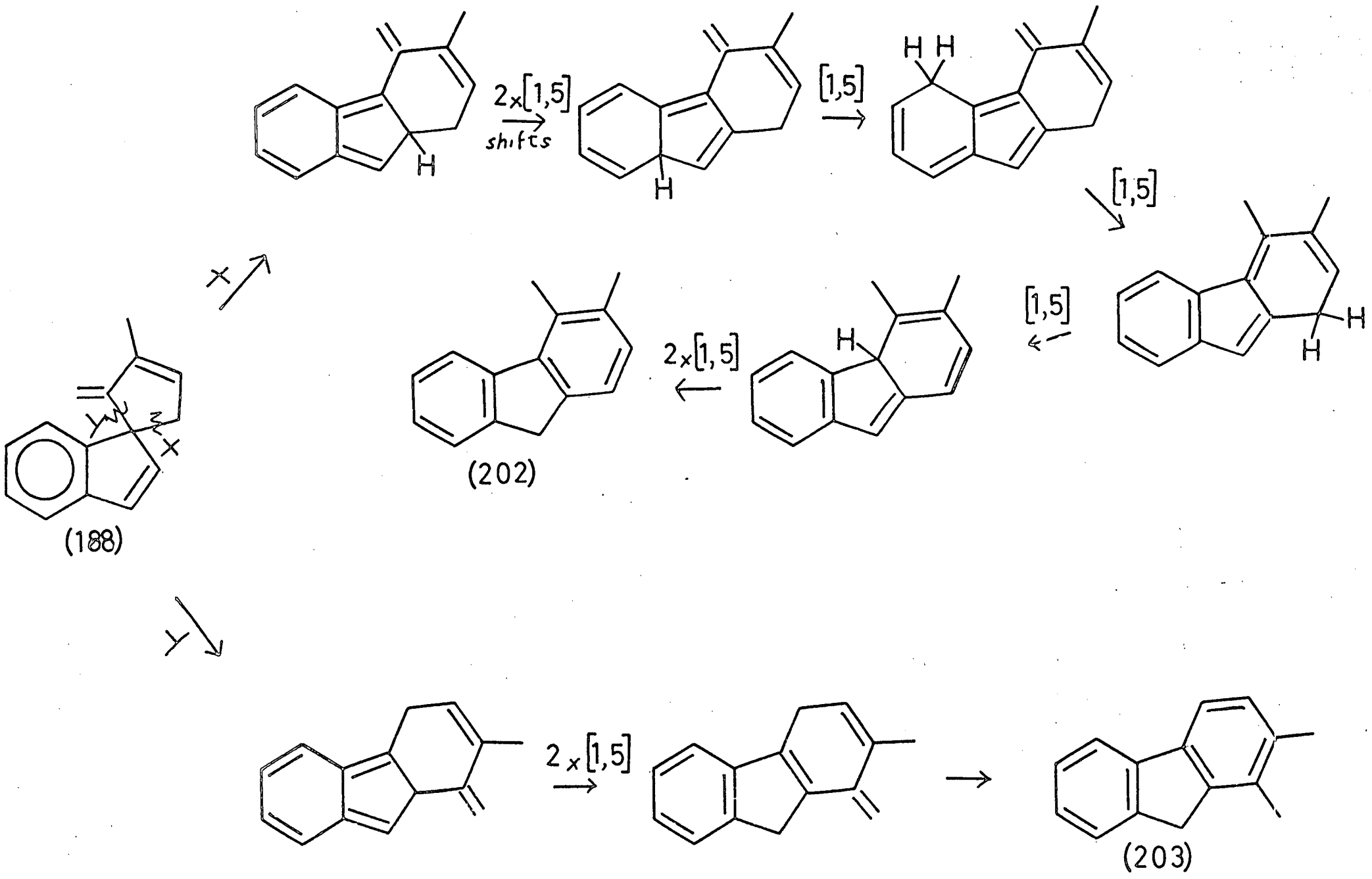


(200) X = H
(201) X = Me

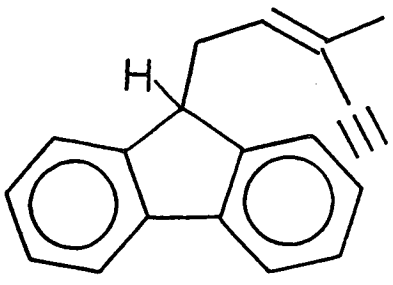
(200) and have not been separated but have been differentiated from their proton n.m.r. spectrum (figure 24). Of the two resonances occurring at 0.74 δ and 0.96 δ that at the lower frequency was assigned to the Z isomer (200) having the methyl oriented over the benzene ring. This is the minor isomer as might be expected since there will be some steric interaction between the methyl protons and the benzene ring in the transition state to isomer (200). The remainder of the spectrum shows four aromatic protons, exocyclic methylene singlets at 4.20 δ and 4.58 δ, an AB spectrum (6.12, 6.25 δ) due to the cyclopentene olefinic protons, and a second AB system (6.22, 6.60 δ) due to the indene double bond, assigned by comparison with the 2-methylindene analogue.

Pyrolysis of E and Z(1'-methylpent-2'-en-4'-ynyl)-2-methylindene (123a and b) was not very successful due to difficulty in vaporization accompanied by poor yields. Some spiro products (199) and (201) were obtained ($\simeq 3\frac{1}{2}\%$), again as two isomers.

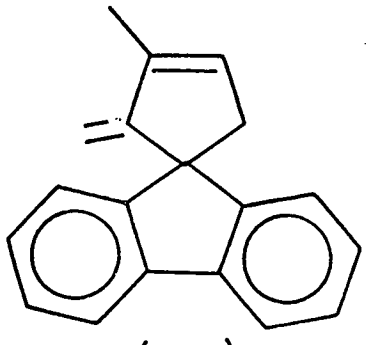
Pyrolysis of Z-9-(3'-methylpent-2'-en-4'-ynyl)fluorene (134) was unsuccessful largely because of difficulty in vaporizing the compound. Of the little product obtained no spiro-compound was recognized. This could be because there is no proton δ to the pentenynyl group which could be removed, and hence the mechanism outlined for the indene analogue is


2x[1,5]
shifts
[1,5]
[1,5]
[1,5]
2x[1,5]
X
Y
2x[1,5]
(188)
(202)
(203)

not possible. The desired spirotriene (135) has been isolated from the phase transfer preparation of Z-9-(3'-methylpent-2'-en-4'-ynyl)fluorene (134, chapter 3.4). This is probably generated by base catalysis. However all attempts to rearrange the fluorene (134) to the spirotriene (135) have so far failed.



(134)



(135)

These are examples of 'ene' reactions[72], although cyclisation to give spiro products has not been reported previously for acetylenes, (see p. 24)

Pyrolysis of Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126b) at 600°C gave a mixture containing equal amounts of 1,2-dimethylfluorene (203) and what is believed to be 3,4-dimethylfluorene (202), separated by alumina chromatography. 1,2-Dimethylfluorene was identified by its melting point[89] and its ^{1}H n.m.r. and u.v. spectrum which compares well with that of fluorene. 3,4-Dimethylfluorene has not been isolated pure enough to obtain a satisfactory melting point, however the u.v. and n.m.r. spectra are consistent with this structure and this compound would be expected from an alternative route to the formation of the 1,2-isomer.

Initially the spirane (188) is formed and further rearrangement of this could occur via a [1,5] sigmatropic carbon shift, breaking bonds X or Y followed by a sequence of [1,5] sigmatropic hydrogen shifts. Pyrolysis of the 2-methylindene analogue (127) at 600°C gives only the spiro compound (196).- formation of fluorenes would require migration adjacent to the methyl followed by migration of the methyl and does not

occur at this temperature.

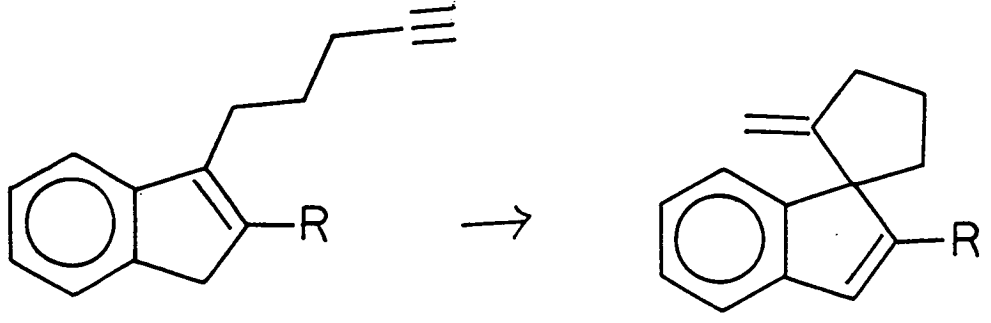
Pyrolysis of Z-1-(3'-methylpent-2'-en-4'-ynyl)-3-methylindene (129) at 600°C gave a product mixture which has not been separated but appears to contain two trimethylfluorenes - possibly 1,2,9- and 3,4,9- substituted by analogy with the indene derivative. 9-substitution is apparent because of the quartet in the ^{1}H n.m.r. spectrum at 3.80δ indicating a benzylic proton on the same carbon as a methyl group.

Pyrolysis of E- and Z-3-(1'-methylpent-2'-en-4'-ynyl)indene (122a and 122b) at 600°C gave a mixture of products as yet unidentified.

5.3 Vapour Phase Vacuum Pyrolysis of Pent-4'-ynyl Indenes

Pyrolysis of 3-(pent-4'-ynyl)indene (119) at 500°C gave about 28% spiro [2-methylenecyclopentane-1,1'-indene] (204) along with 40% of recovered starting material.

The ^{1}H n.m.r. spectrum (figure 25) shows the exocyclic olefinic methylene protons at 4.35δ and 4.60δ, the indene olefinic protons as an AB spectrum at 6.26δ and 6.52δ, and the methylene protons at 1.8 - 2.3δ and 2.62δ. Pyrolysis of 2-methyl-3-(pent-4'-ynyl)-indene (120) at 500°C again gave a spiro product (205) in 33% yield plus starting material in 33% yield.



(119) R = H
(120) R = Me

(204) R = H
(205) R = Me

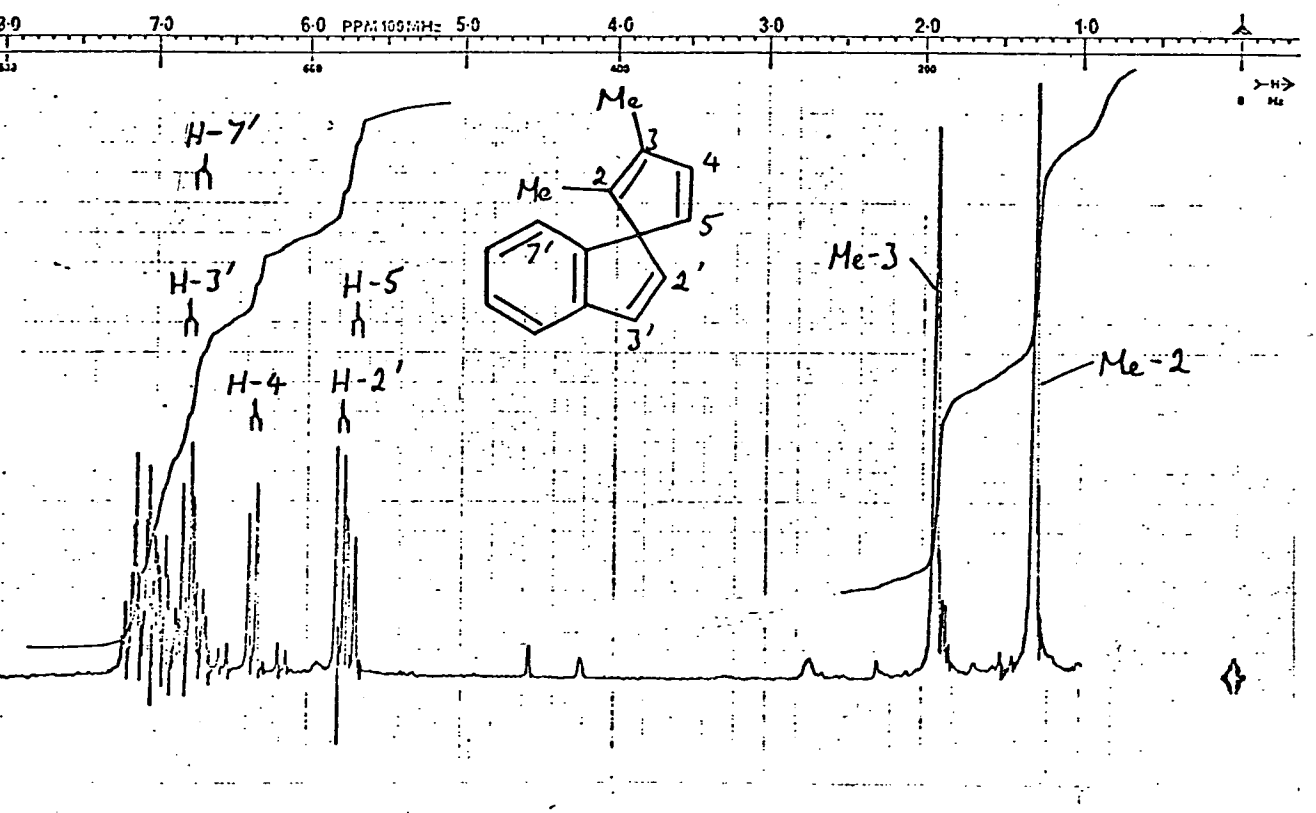

8·0
7·0
6·0
PPM (100 MHz)
5·0
4·0
3·0
2·0
1·0
H-7'
H-3'
H-5
H-4
H-2'
Me
Me
3
4
2
5
7'
2'
3'
Me-3
Me-2

Figure 26

Pyrolysis of the indene derivative (119) at 600°C gave a mixture containing no spirodiene which has not been fully rationalised.

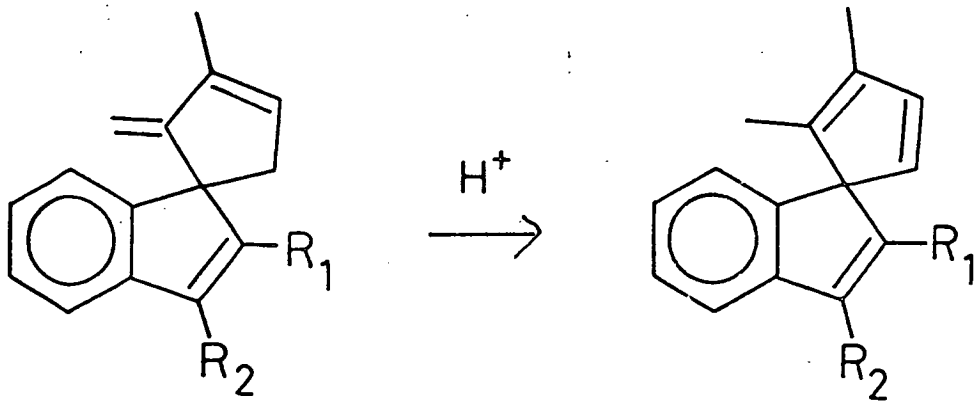
5.4 Acid Catalysed Rearrangement of the Benzospirotrienes and Thermolysis of the Products Formed

The well known acid catalysed conversion of methylene cycloalkanes to 1-methyl cycloalkenes suggested that it should be relatively simple to isomerise the methylene group of the spiro compounds obtained in chapter 5.2 and 5.3 to the endocyclic double bond. These compounds are particularly interesting from a theoretical viewpoint and their properties are discussed further in chapter 5.5.

Treatment of spiro [2-methylene-3-methyl-cyclopent-3-ene-1,1'-indene] (188) with a solution of p-toluenesulphonic acid in carbon tetrachloride gave spiro [2,3-dimethylcyclopenta-2,4-diene-1,1'-indene] (206) in 60% yield.

The ^{1}H n.m.r. (figure 26) shows two AB spectra in the olefinic region consistent with the two double bonds in the structure. Methyl proton resonances occur at 1.28δ and 1.90δ, the former being assigned to methyl-2, which will be shifted to lower frequency by lying over the benzene ring. The broad doublet at 6.70δ is attributed to the aromatic proton H-7' which lies over the cyclopentadiene ring and hence is shifted to lower frequency. The ^{13}C n.m.r. spectrum agrees with the proposed structure.

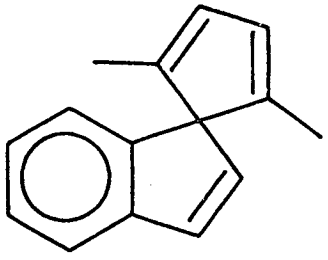
Similarly the 2-methyl and 3-methyl analogues (196) and (197) underwent acid catalysed rearrangement to the spiro compounds (207) and (208).



(188) $R_1 = R_2 = H$
(196) $R_1 = Me$, $R_2 = H$
(197) $R_1 = H$, $R_2 = Me$

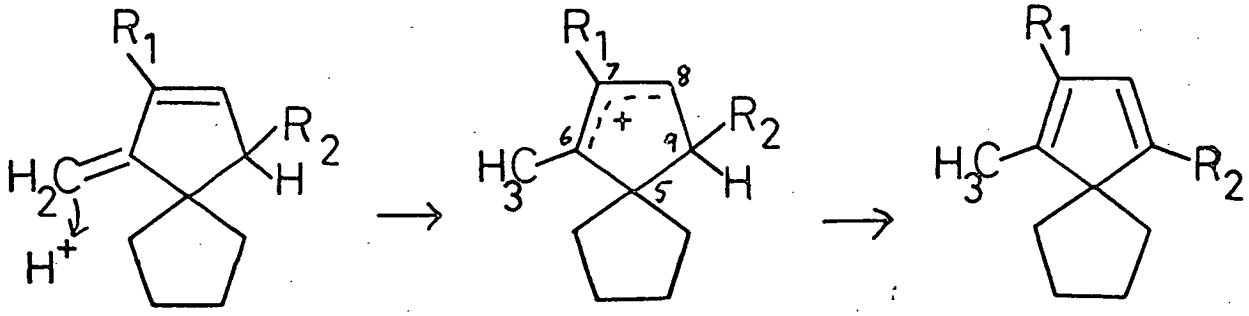
(206) $R_1 = R_2 = H$
(207) $R_1 = Me$, $R_2 = H$
(208) $R_1 = H$, $R_2 = Me$

The mixture of spirotrienes, E and Z-spiro [2-methylene-5-methylpent-3-ene-1,1'-indene] (198) and (200) gave a single product, spiro [2,5-dimethylcyclopenta-2,4-diene-1,1'-indene] (209).

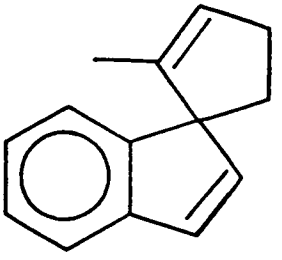


(209)

These rearrangements all appear to proceed via protonation of the exocyclic double bond, bond reorganisation and proton loss from the 9-carbon atom as shown:

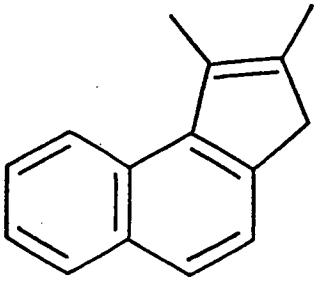


Similarly spiro [2-methylenecyclopentane-1,1'-indene] (204) rearranged with p-toluenesulphonic acid in carbon tetrachloride to give spiro [2-methylcyclopent-2-ene-1,1'-indene] (210).

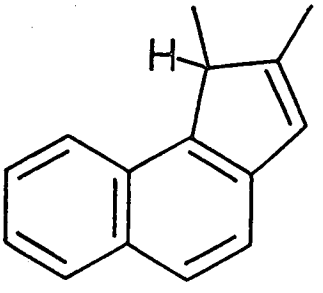


(210)

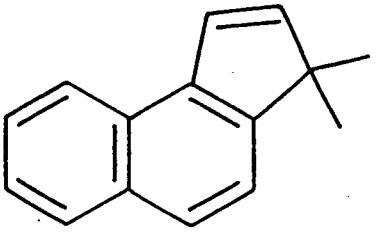
Pyrolysis of spiro [2,3-dimethylcyclopenta-2,4-diene-1,1'-indene] (206) at 500°C gave a mixture of three products isolated by preparative vapour phase chromatography and believed to be 4,5-benzo-2,3-dimethylindene (211), 6,7-benzo-1,2-dimethylindene (212) and 4,5-benzo-1,1-dimethylindene (213) in the ratio (211) : (212) : (213) = 3:1:3.



(211)

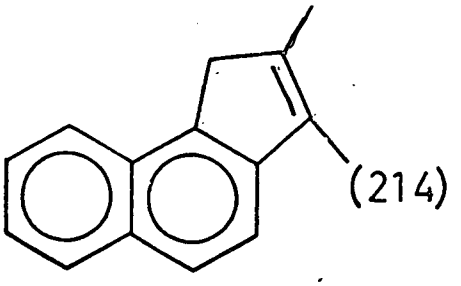


(212)



(213)

The ^{1}H n.m.r. of compound (211) shows two methyl resonances at 1.97δ and 2.37δ, a benzylic methylene resonance at 3.08δ and a complex aromatic pattern integrating for six protons. The u.v. spectrum is unlike that of fluorene and neither the u.v. nor ^{1}H n.m.r. are like those of 6,7-benzo-2,3-dimethylindene (214),[90] a possible structure. The u.v. spectrum is, however, similar to that of the benzoindene (213). (see table 9)



(214)

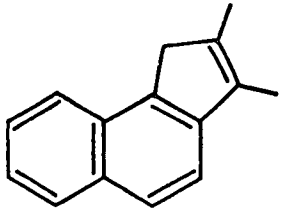
The ^{1}H n.m.r. spectrum of compound (212) shows a six proton aromatic pattern, and a methyl proton resonance as a doublet at 1.43δ coupled (J = 7Hz) to a benzylic proton quartet at 3.52δ indicating the structure $ArCH.CH_3$-. In addition there is an olefinic methyl resonance at 2.13δ and an olefinic singlet at 6.20δ. The u.v. spectrum of compound (212) is very similar to that of the benzoindene (214) supporting the proposed structure (see table 9).

The ^{1}H n.m.r. of the benzoindene (213) shows a six proton singlet resonance at 1.34δ corresponding to the dimethyl group and an olefinic AB spectrum at 6.42δ and 7.11δ.

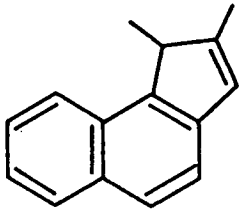
The benzoindene structures were proposed by analogy with the rearrangement of the spirotriene (188) which gave the fluorenes (202) and (203). With the conjugated spirotetraene (206) there is no obvious preference for bond breakage and the C_1' - C_2' bond breaks with [1,5] carbon migration to C_2 or C_5 to give the benzoindenes as shown below. Compound (212) is thought to be a rearrangement isomer of (211). This may be driven by high steric interference between the 3-methyl and the benzo proton in (211).

Table 9

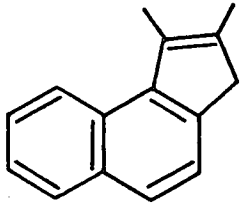
Ultra-violet Spectral Data for Benzoindenes



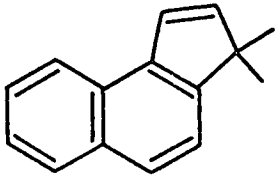
249	252	262		291	303	316	337	352	mμ
(29000)	(44000)	(53600)		(4300)	(6100)	(5600)	(1400)	(900)	ε



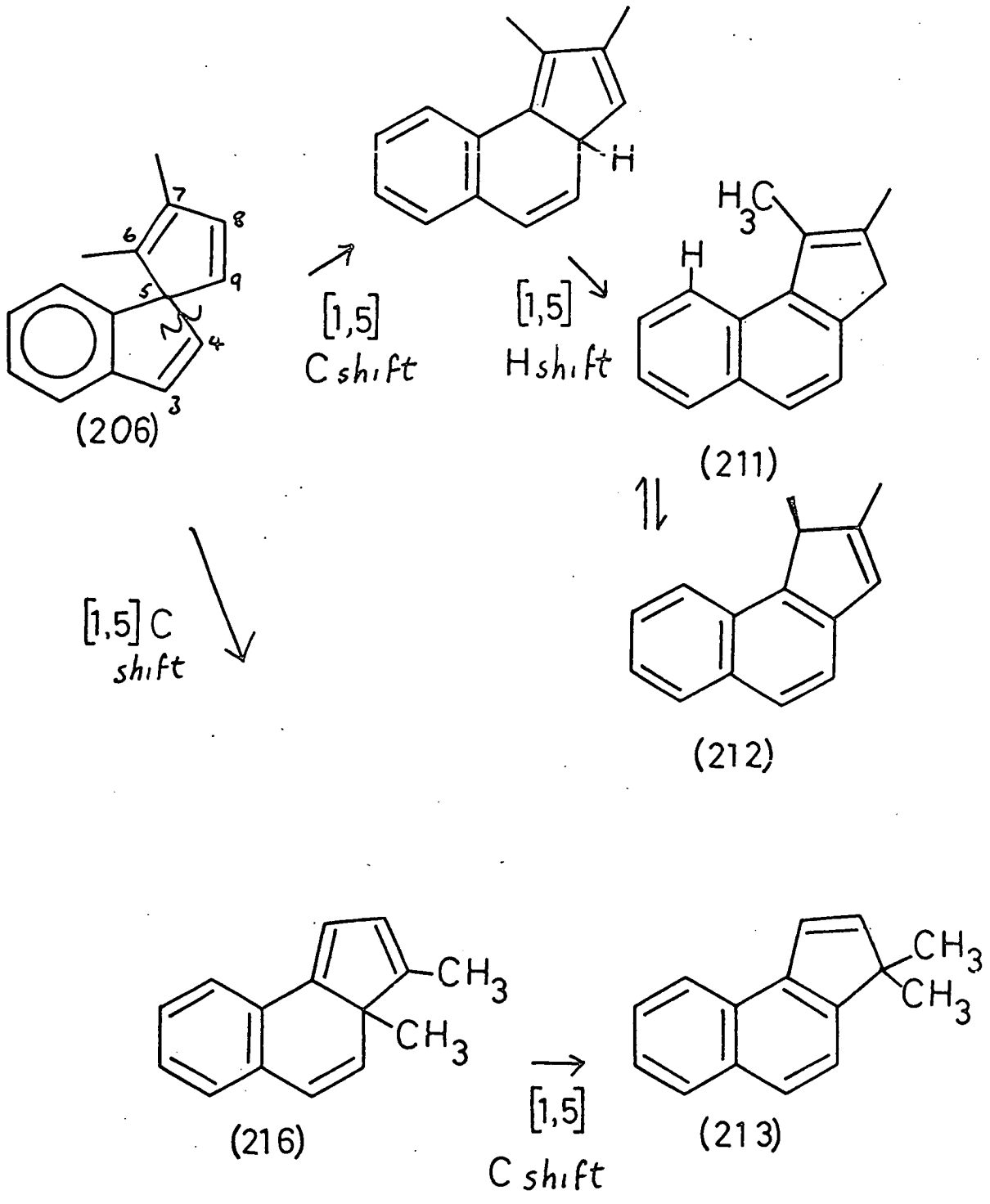
232	252	261	280	292			333	349	mμ
(17900)	(10000)	(9400)	(3200)	(2800)			(700)	(400)	ε



238	253	295			326	333	mμ
(23500)	(14500)	(5000)			(2400)	(2100)	ε



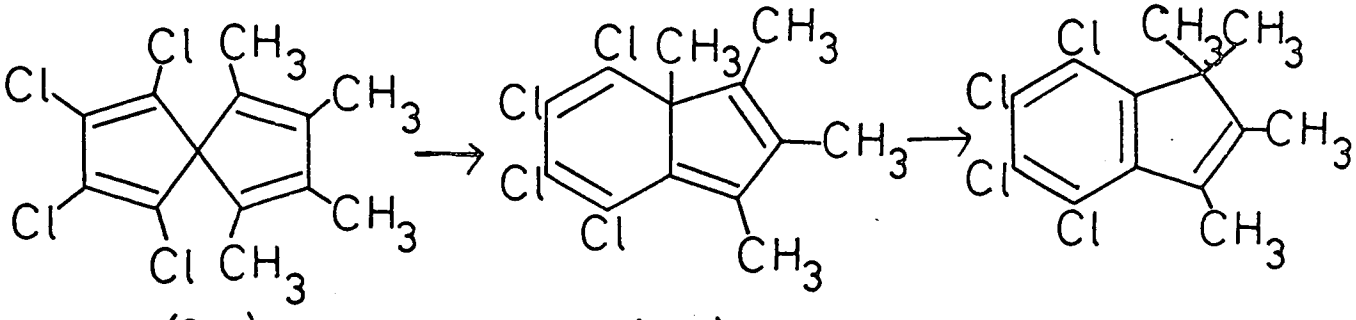
237		297	307	318	325	332	mμ
(31300)		(4700)	(5500)	(4100)	(4100)	(3000)	ε



The 1,1-dimethyl product (213) is formed from the isoindene (216) via a [1,5] methyl shift.

Liquid phase pyrolysis of the spirotetraene (206) in decalin (b.p. 208°C) for 2 hours gave a 2:1 mixture of the benzoindenes (211) and (213) but no (212). No rearrangement of (211) to (212) occurs at this temperature.

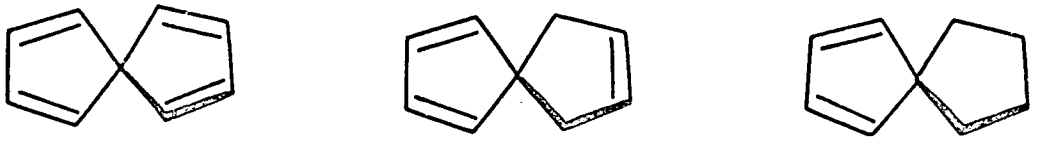
It has been reported[87] that spiro [4.4] nonatetraene (220) readily undergoes ring expansion to give indene. The analogous spirocycle (217) rearranges at 205 - 210°C in the vapour phase to give the isoindene (218) followed by a [1,5]-methyl shift to give the indene (219).[91]



(217) (218) (219)

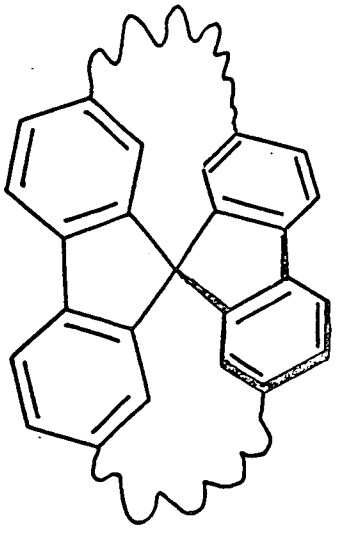
5.5 Discussion of Spiro-products

Spiro [4.4] nonatetraene (220) has appeared in the literature frequently as a result of attempts at synthesis[92,93], in discussions of the theories of spiroconjugation[94,95] and as a potential example of stabilized planar tetraco-ordinate carbon[96] (planar methane). Preparation of the parent compound (220) has been reported by Semmelhack et al[87] along with spiro [4.4] nona-1,3,7-triene (191) and spiro [4.4] nona-1,3-diene (221). The spirotetraene (220) showed a distinct bathochromic shift in the ultra violet region compared with (191) or (221) consistent with conjugation across the spiro carbon.

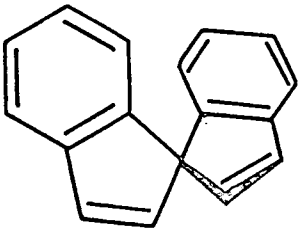


(220) (191) (221)

Derivatives of (220) with fixed aromatic rings, for example the vespiranes (222)[97], have been prepared and studied primarily for their unique optical activity due to a screw axis of symmetry. The related spirobi-indenes[98,99] (e.g. (223)) have been studied and the ultra-violet spectra show bathochromic shifts in comparison with indene.[98]

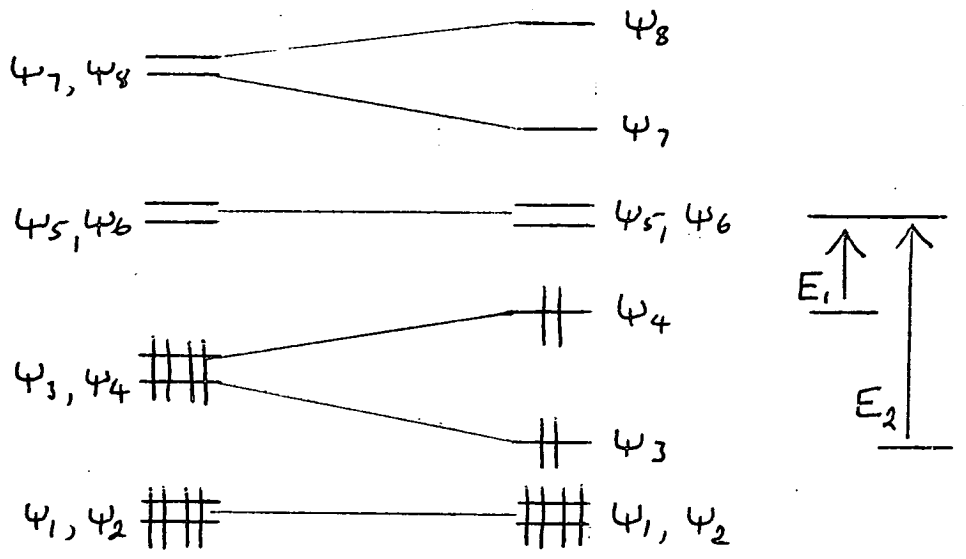


(222)



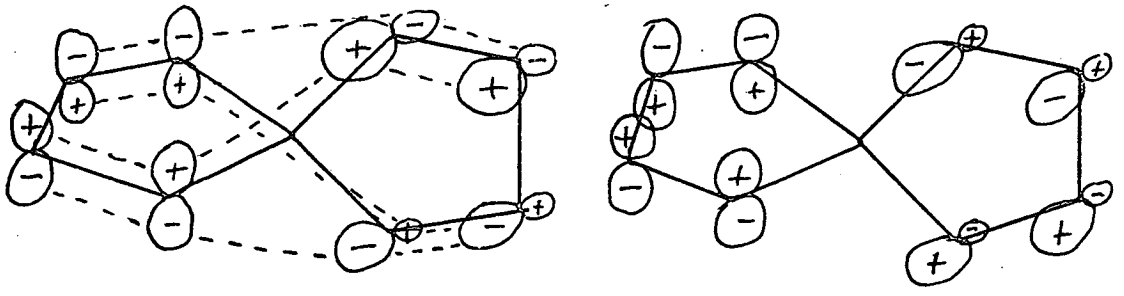
(223)

Simple symmetry considerations[94,95] have led to the prediction that molecules in the spirogeometry with p-orbitals in the radial carbon atoms might show homoconjugation across the spiro carbon (spiroconjugation). In the case of spiro [4.4] nonatetraene (220) the theory predicts splitting of the highest filled (and highest unfilled) diene π (or π^*) orbitals due to the spirointeraction. Assuming no interaction between the rings the Hückel molecular orbital picture is represented in figure 27. The four orbitals ψ_3 and ψ_4, ψ_7 and ψ_8 are of like symmetry (antisymmetric to both planes) and hence can interact to give a new orbital scheme (figure 28). This breaks the degeneracy of the orbitals to give different energy levels.



a. No spiroconjugation b. Spiroconjugation

Figure 27. π orbitals in spiro [4.4] nonatetraene.[94]



bonding anti-bonding

Figure 28. Orbital scheme of Ψ_3 and Ψ_4.[94]

The net result is no significant change in the bonding energy but a narrowing of the gap $\Psi_4 - \Psi_5$. Thus it was predicted that the ultraviolet absorption would appear at unusually long wavelength.[94,95] In addition the delocalization of the bond would affect the oscillator strength so as to lower the intensity of the absorption.[94]

The experimental results of Semmelhack[87] are shown in table 10.

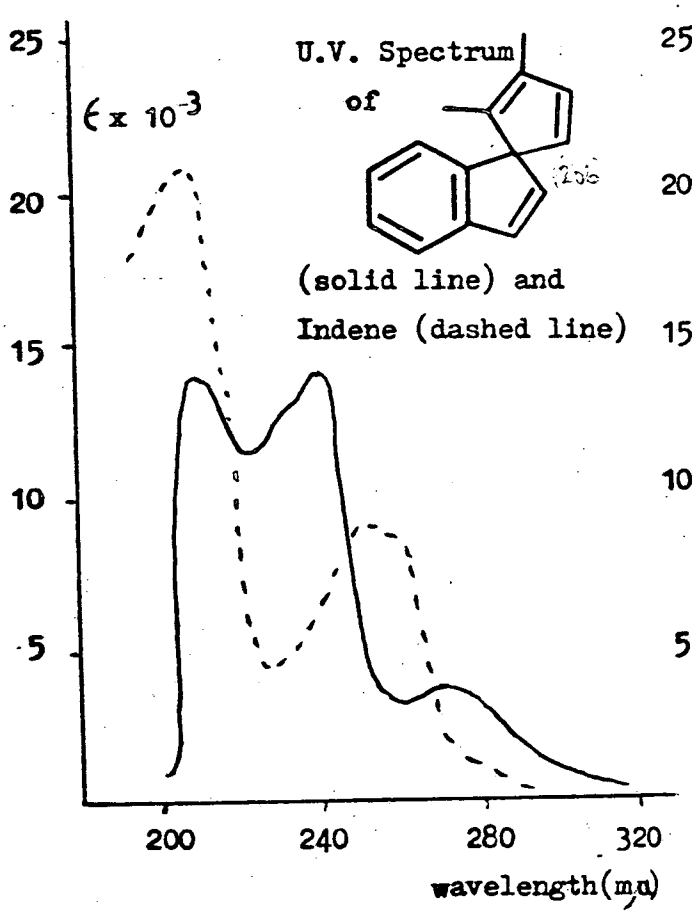


Figure 29

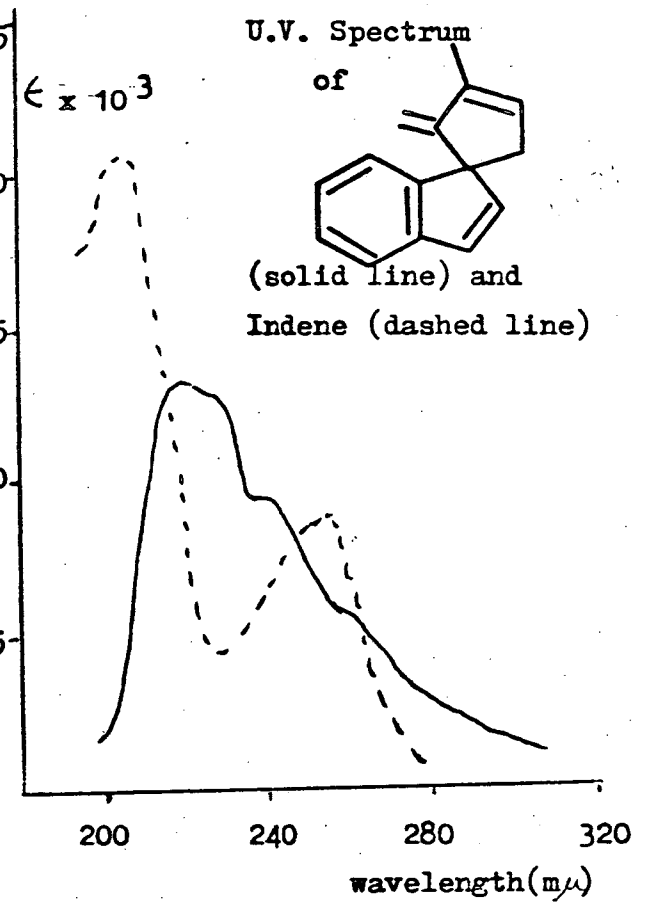


Figure 30

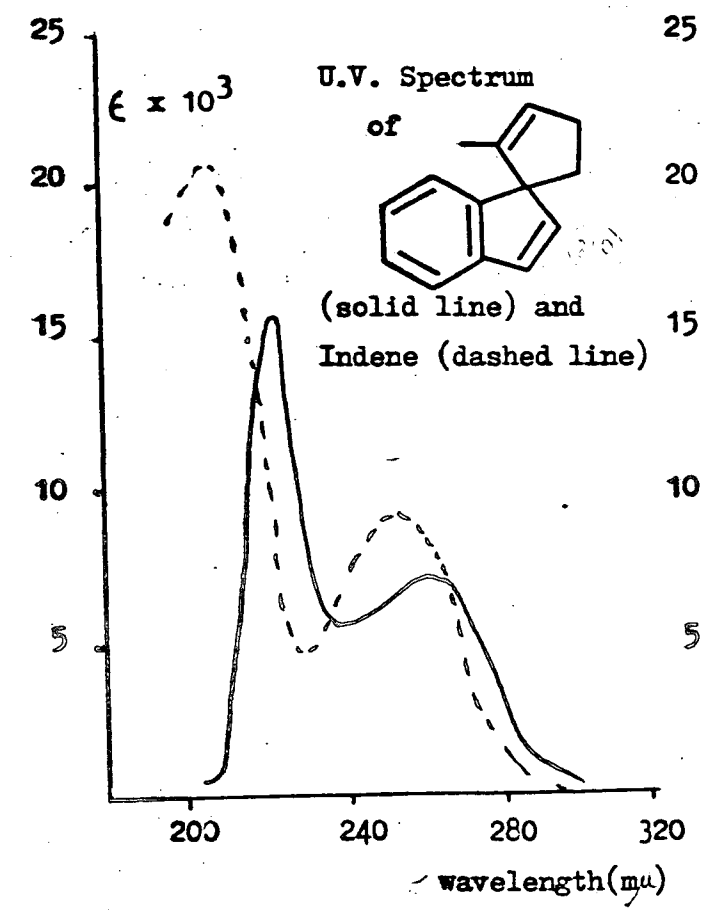


Figure 31

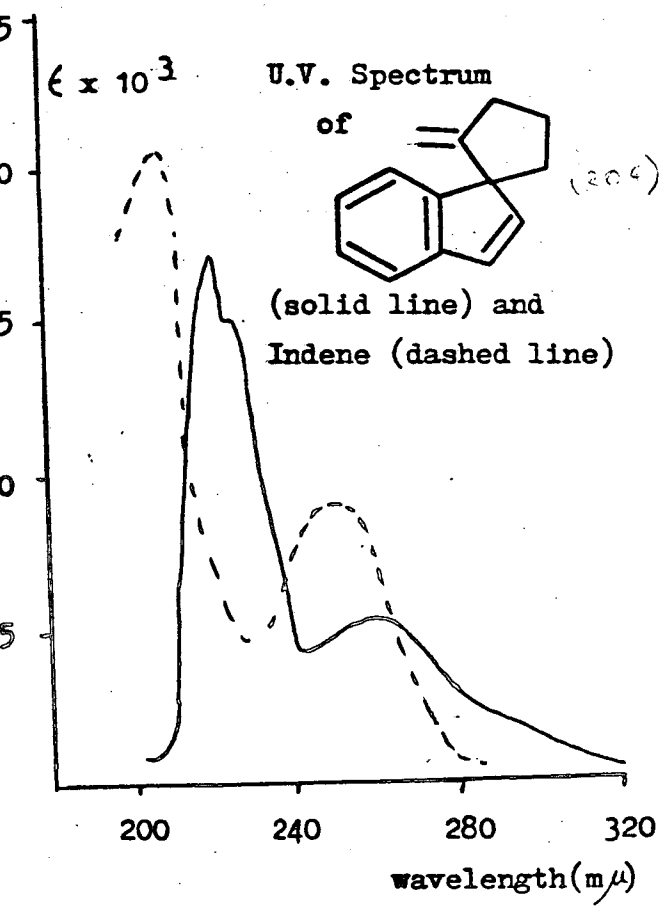


Figure 32

Table 10

UV Spectral Data (EtOH)[87]

276 mμ (ε 1120)
218 mμ (ε 5350)

254 mμ (ε 2750)

254 mμ (ε 2250)

The UV spectra of compounds (191) and (221) were found to be virtually identical while for compound (220) the $\psi_4 \rightarrow \psi_5$ gap was lowered to give an absorption maximum at 276 mμ. The intensity was also halved as predicted. The new absorption at 218 mμ was assigned to the E_2 excitation ($\psi_3 \rightarrow \psi_5$).

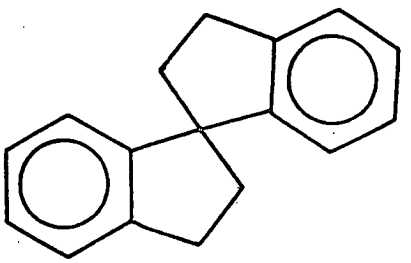
Examination of the 1,2-dimethylcyclopenta-1,3-diene-1,1'-indene (206) ultra violet spectrum (figure 29) shows agreement with these results. The two indene bands are shifted 210→240 mμ and 250→273 mμ. In addition there is an extra band at 217 mμ. The extinction coefficients are about half those of indene. This compares well with Semmelhack's data and is clear evidence for spiroconjugation.

An unexpected result was obtained with spiro[2-methylenecyclopentane-1,1'-indene] (204) and spiro[2-methylcyclopent-2-ene-1,1'-indene] (210) which both show bathochromic shifts in their ultra-violet spectra (figures 31 and 32). Compound (204) shows shifts 210→224 mμ and 250→262 mμ and compound (210) shows shifts 210→226 mμ and 250→260 mμ. There is also a decrease in the extinction coefficients although not as dramatic as for compound (206). These results evidently show spiroconjugation in

compounds (204) and (210), a phenomenon not previously predicted or observed.

The ultra-violet spectrum of spiro [2-methylene-3-methylcyclopent-3-ene-1,1'-indene] (188), figure 30, is unclear. Some bathochromic shifting may be observed however. Similar results were obtained for the methyl derivatives.

It is apparent that only three radial π orbitals are required for spiroconjugation. The ultra-violet spectrum of 1,1'-spirobiindane (124) closely matches that of indane[98] indicating that no spiroconjugation occurs with only two radial π orbitals.



(124)

Ignoring the benzene orbitals for simplicity, the highest occupied molecular orbital of the cyclopentadiene fragment can overlap with the highest occupied molecular orbital of the ethylene fragment in either compounds (204) or (210) (figure 33).

Figure 33. π Orbital Representations of Compounds (204) and (210)

The similarity of the UV spectra (figures 31 and 32) shows that there is no twisting of the double bond in compound (204) which might have occurred due to steric interaction between the methylene protons and the benzene ring.

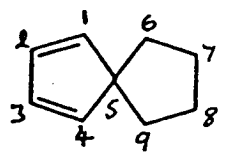
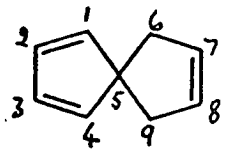
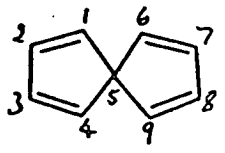
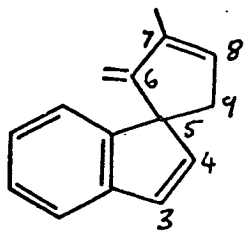
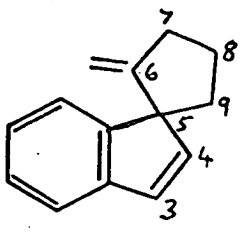
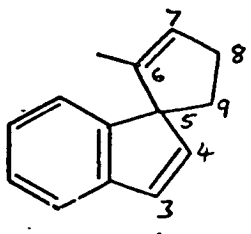
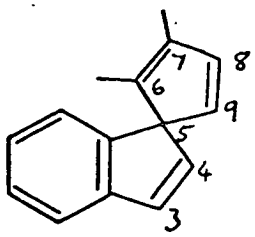
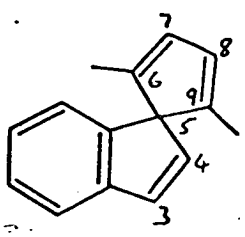
Simmons and Fukunaga[94] suggested that spiroconjugation in compound (220) would lead to unequal charge densities among the carbon atoms in the π system. They calculated a charge density q = 0.987 for the radial carbons and q = 1.013 for the peripheral carbons. The lower π electron density on the radial carbons should give rise to deshielding in the ^{13}C n.m.r.

Semmelhack's experimental results are shown in Table 11. These results show that the spirotetraene (220) charge distribution is very different from that of the spirotriene (191) or the spirodiene (221). All the absorptions are shifted to higher frequency and the effect is greatest for the peripheral carbons. Hence the effect is opposite to that predicted. The deshielding is consistent with lower π electron density at the peripheral carbon atoms than at the radial atoms. No explanation was put forward for these results except to say that other effects may be involved.

The ^{13}C chemical shifts of the benzospirotetraene derivatives (206), (207) and (209) do not show this large deshielding effect (see table 11). These derivatives show shifts in agreement with the predicted results[94] in that the radial atoms are at higher frequency than the peripheral carbons indicating a lower charge density on the radial carbons. The effect on the radial carbons is quite pronounced shifting from 144 p.p.m. in the spirotrienes to 138 p.p.m. for the spirotetraenes. These results show that the results for spiro [4.4] nonatetraene (220) are not general and must be caused by some effect other than spiroconjugation.

Table 11

^{13}C n.m.r. Chemical Shifts

		Carbon						
		3	4	5	6	7	8	9
221		127.9	143.9	64.1	32.4	26.0	26.0	32.4
191		127.9	144.8	62.0	36.6	130.4	130.4	36.6
220		151.0	150.5	77.0	150.5	151.0	151.0	150.5
188		129.1	144.5	62.7	143.2	140.7	133.1	39.6
204		128.2	144.2	64.3	143.6	33.5	24.3	36.6
210		129.6	143.3	68.2	142.5	127.6	31.4	33.6
205		132.6	137.6	75.4	136.0	135.9	132.1	137.8
07		133.7	138.4	76.5	?	128.5	128.5	?

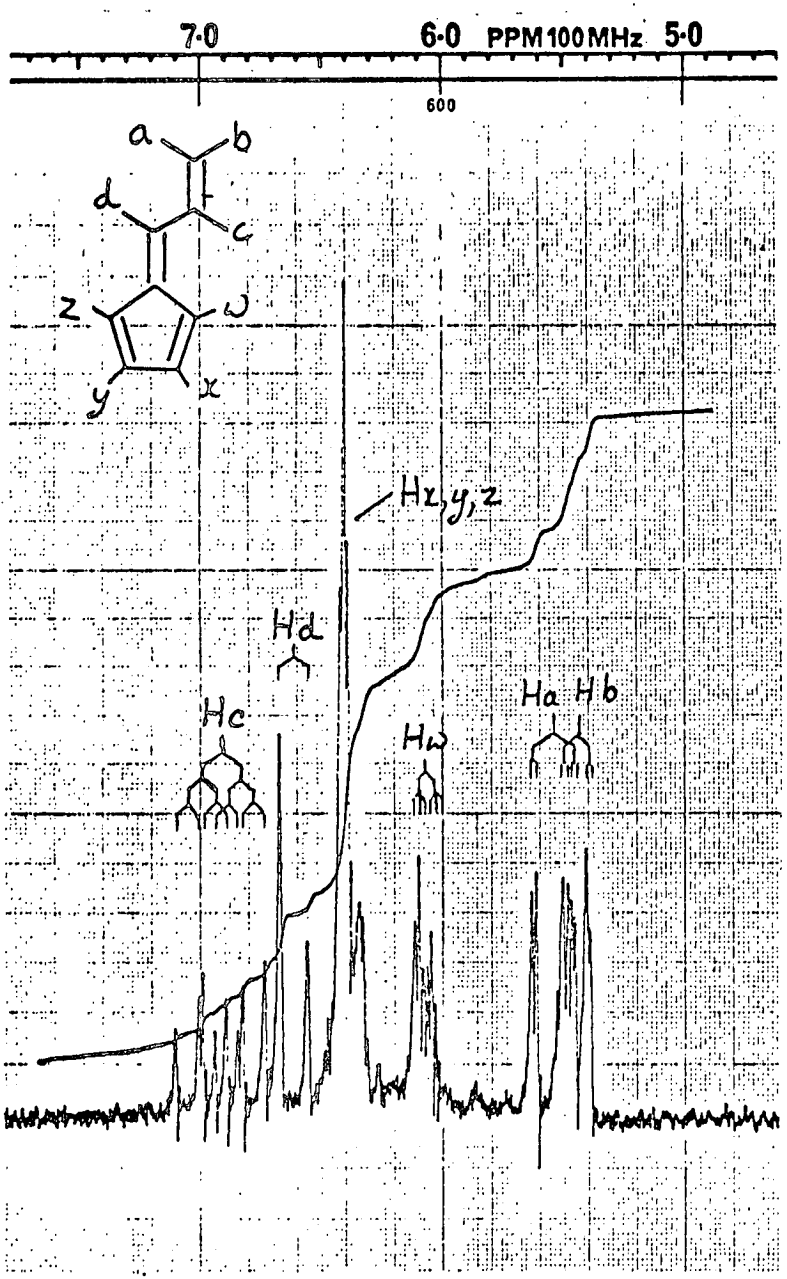


Figure 34

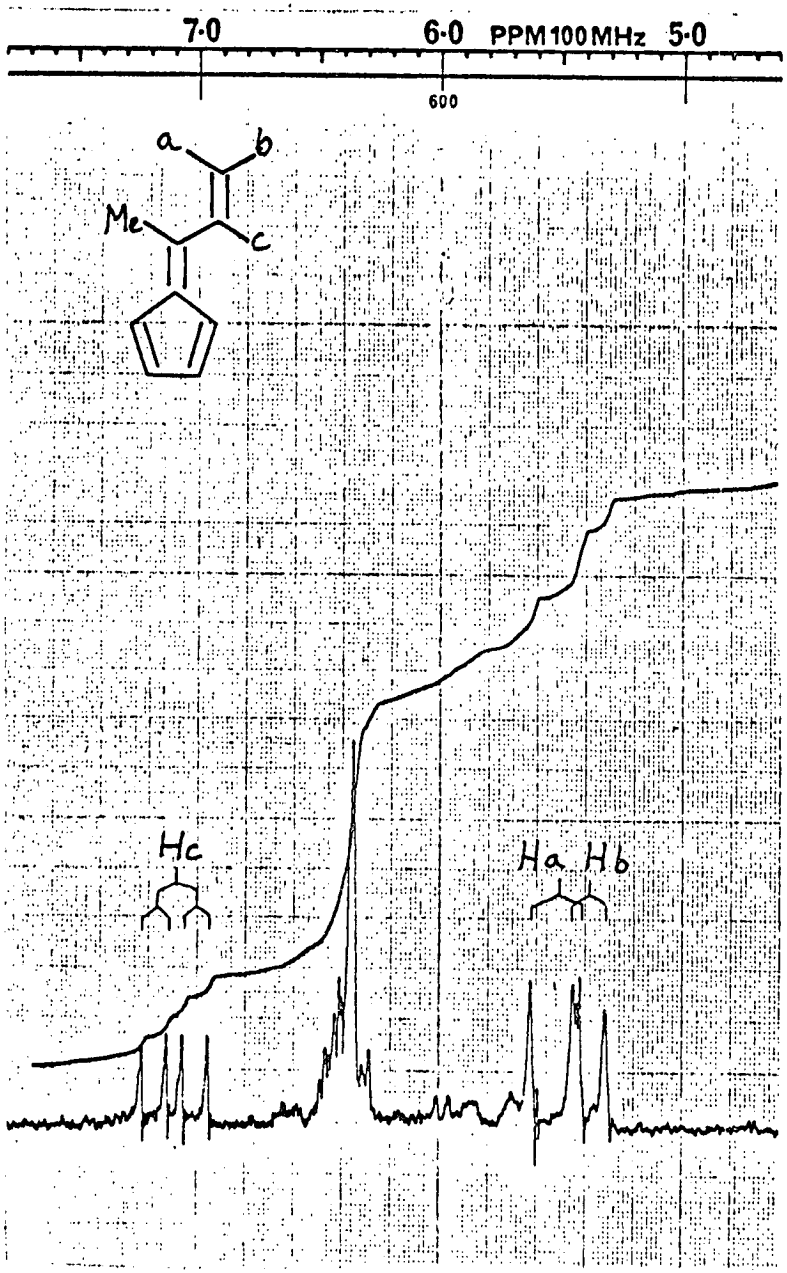


Figure 35

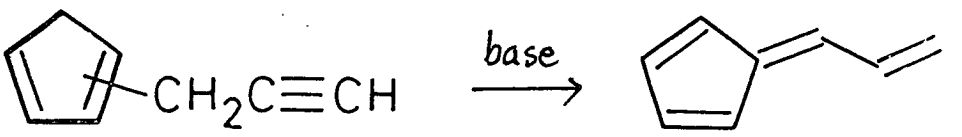
CHAPTER 6

Base Catalysed Rearrangements of Acetylenes and Allenes

In view of the well known base induced interconversion of allenes and acetylenes, the effect of base on the compounds discussed in chapters 4 and 5.1 has been examined. Rearrangement was effected by refluxing with either sodium methoxide in methanol or sodium ethoxide in ethanol. The reaction was stopped when polymerised product started to precipitate out. In many cases rearrangement was also achieved by eluting the compound through commercial basic alumina with light petroleum.

6.1 Rearrangement of Propargyl and Allenyl Compounds

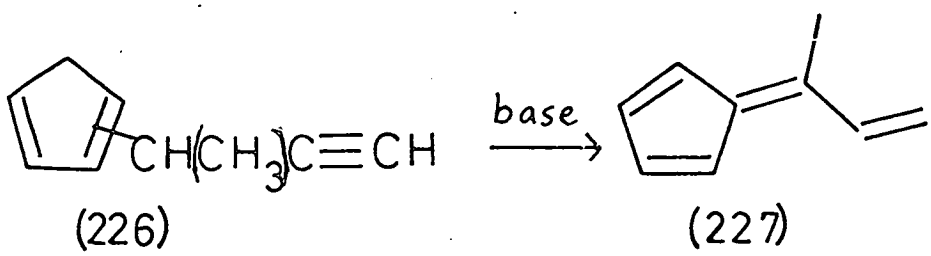
Treatment of the mixture of propargylcyclopentadiene (224) with sodium methoxide in methanol or alumina gave 6-vinylfulvene (225) in 20 - 25% yield. This compound was identified by its ^{1}H n.m.r. spectrum (figure 34) which is identical with that reported by Neuenschwander et al[100] who obtained the compound[101] in a similar yield by condensation of



(224) (225)

sodium cyclopentadienide with 3-acetoxy-3-chloroprop-1-ene, followed by elimination of acetic acid with triethylamine. The n.m.r. assignments are those of Neuenschwander.

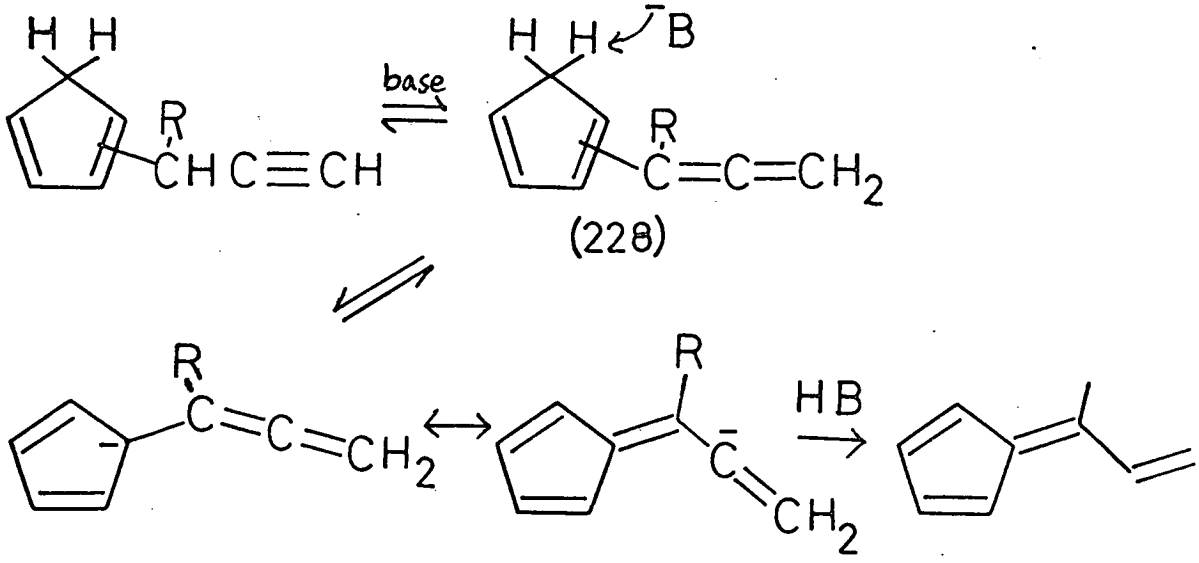
Similarly the mixture of (1'-methylprop-2'-ynyl)cyclopentadienes (226) rearranged to give 6-methyl-6-vinylfulvene (227) in 20 - 25% yield. This was also identified by its ^{1}H n.m.r. spectrum (figure 35), identical with that reported by Neuenschwander[100] who prepared the compound in 0.5% yield by base catalysed condensation of cyclopentadiene with acrolein.



(226) (227)

The most likely route for formation seems isomerisation of the propargyl unit to give allenyl cyclopentadiene (228) which would form cyclopentadienyl ions capable of abstracting a proton onto the central carbon atom of the allene, the vinylfulvene being thermodynamically more stable that either the propargyl or the allenyl cyclopentadiene.

i.e.



(228)

Where a benzene ring is fused to the cyclopentadiene ring the possibility of Z and E isomerised products arises. Refluxing 3-propargylindene (104) with sodium methoxide in methanol gave a 60% yield of E-1,2-benzo-6-vinylfulvene (229) as brilliant yellow crystals. Eluting 3-propargylindene (104) through basic alumina, however, gave a 60% yield of Z-1,2-benzo-6-vinylfulvene (230) as a bright yellow oil. The ultraviolet spectra of these compounds show absorption maxima at virtually

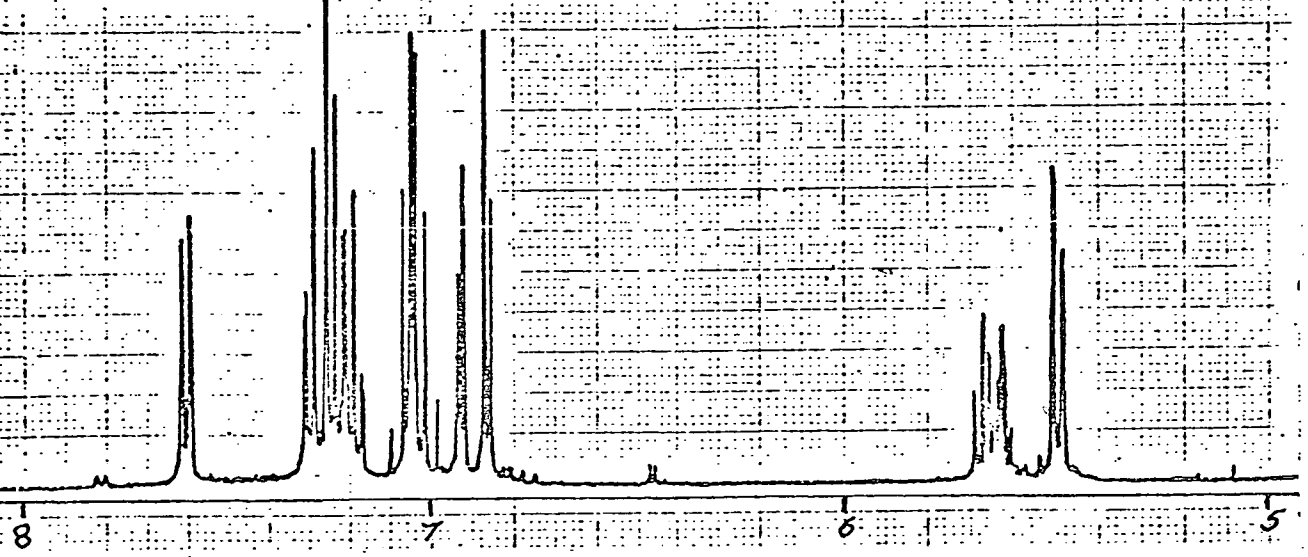


Figure 36. 360MHz Spectrum of E-1,2-benzo-6-vinylfulvene

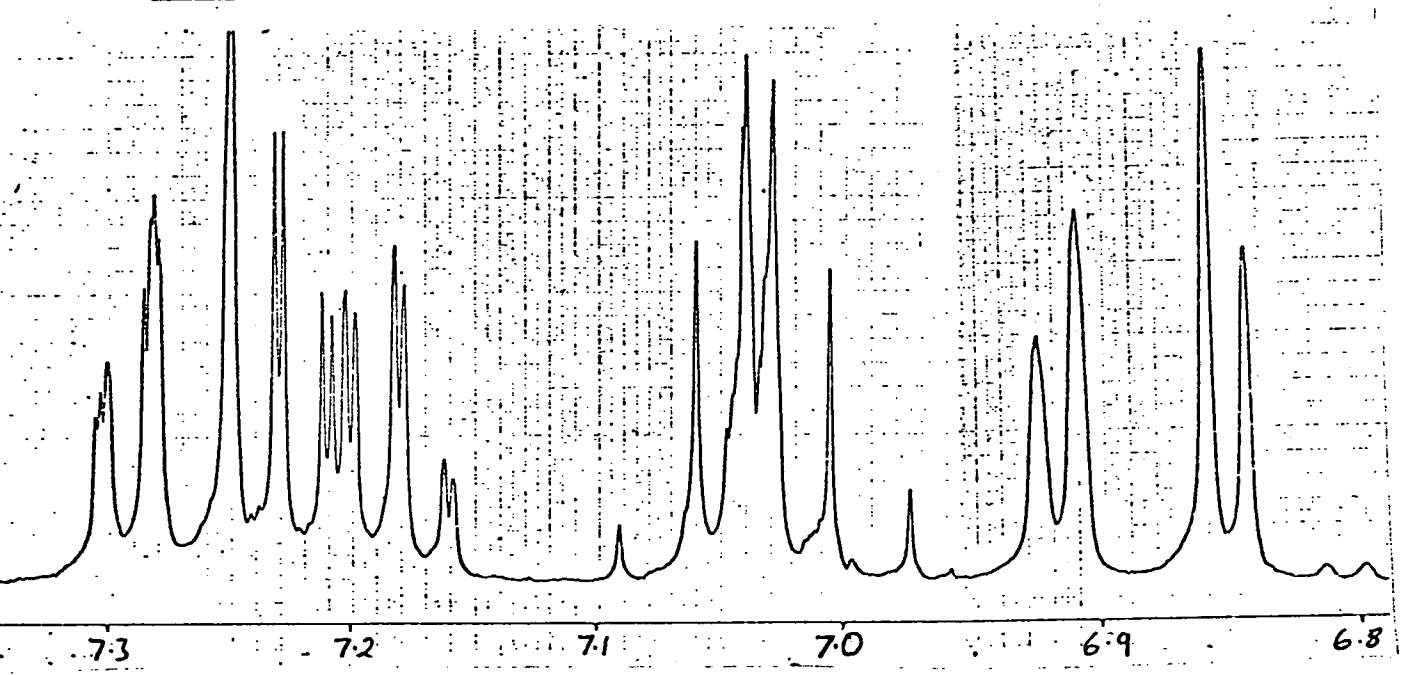


Figure 37. Expansion of the Region 6.8 - 7.3δ

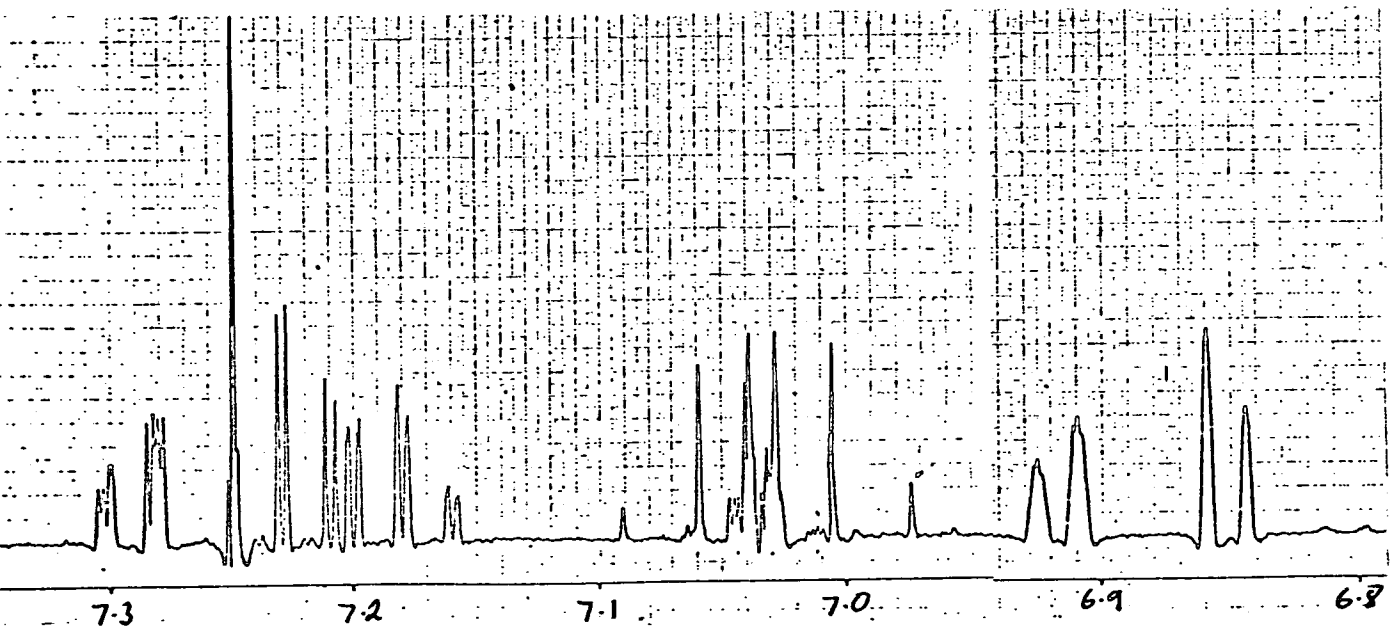


Figure 38. Expanded Spectrum after Convolution Difference

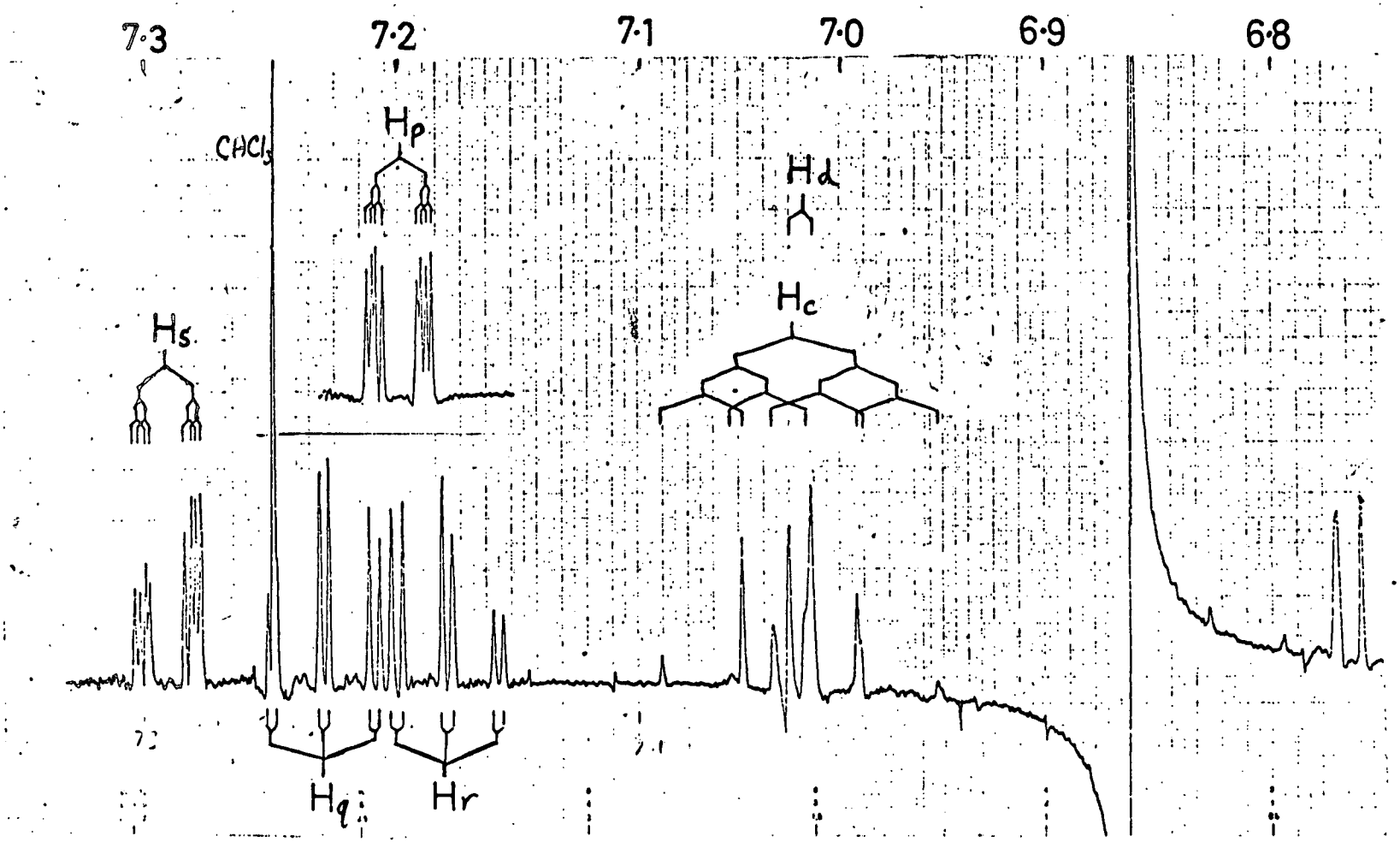
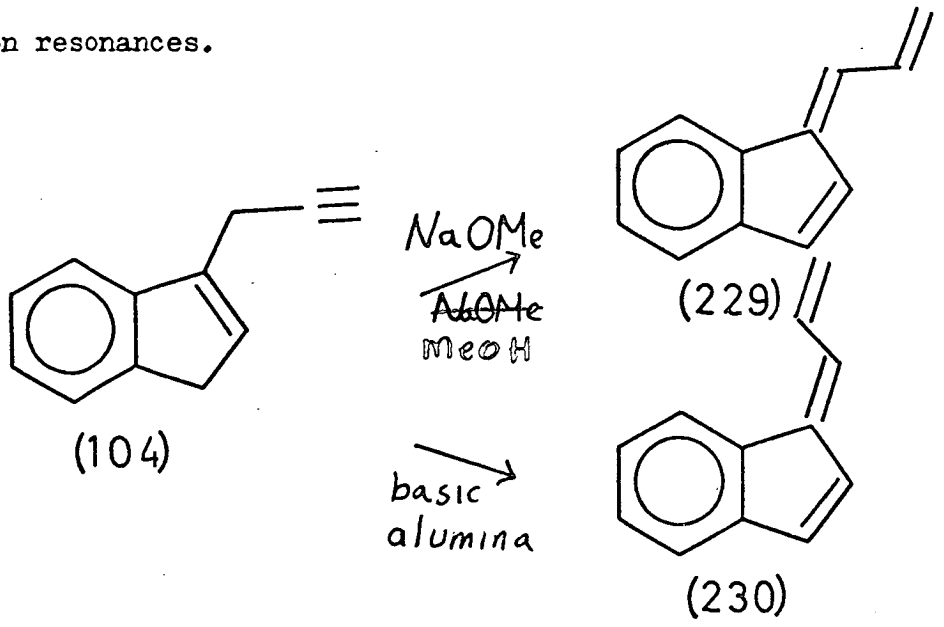


Figure 39. Expanded Spectrum of E-1,2-benzo-6-vinylfulvene after Convolution Difference and Irradiation at 6.92$

identical wavelengths; both compounds absorbing far into the blue region as would be expected for a hydrocarbon showing a high degree of conjugation. The compounds were identified and their configurations assigned from their ^1H n.m.r. spectra, which show only aromatic and unsaturated proton resonances.



(104) (229) (230)

The 100MHz proton spectrum of the E isomer (229) is very complex, however considerable simplification was obtained at 360MHz (figure 36). Further improvement in resolution was obtained using a convolution difference technique.[102] This is illustrated in figures 37 and 38 which show an expansion of the region 6.8δ- 7.3δ, before and after convolution difference. Figure 39 shows the expanded spectrum after convolution difference and decoupling of the resonance at 6.92δ.

Careful examination of these spectra allows the following assignments: The four single proton resonances centred at 7.61δ, 7.29δ, 7.23δ and 7.18δ are assigned to the aromatic ring protons. The first two resonances show an ortho coupling, a meta coupling, and a para coupling and are assigned to H_p and H_s respectively. The third and fourth show two ortho couplings and a meta coupling, and are assigned to H_q and H_r. These resonances are considerably sharpened on spin decoupling (figure 39) of the single proton resonance centred at 6.92δ which is coupled strongly (J = 4.5Hz) to the single proton resonance at 6.85δ. These last two

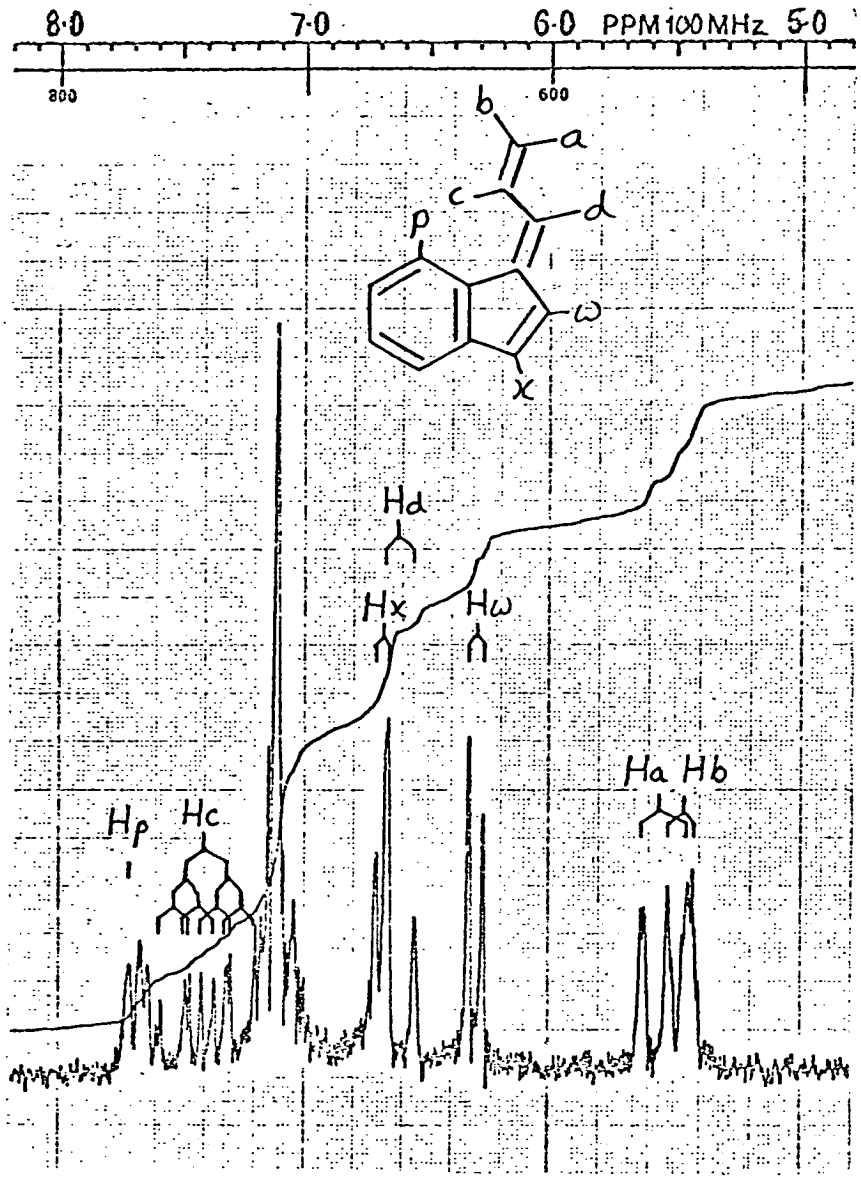


Figure 40

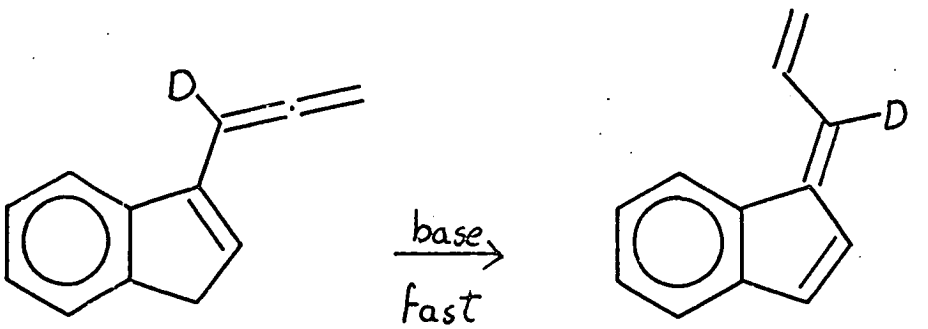
resonances constitute an AB spectrum and are assigned to the protons H_x and H_w. The two single olefinic resonances at 5.64δ and 5.49δ are assigned to H_a and H_b. H_a shows a trans coupling (J = 19Hz) to H_c at 7.03δ while H_b shows a cis coupling (J = 10.5Hz) to H_c. The geminal coupling J_{ab} is 1.5Hz. The proton H_d, resonates at 7.04δ, and is coupled (J = 10.5Hz) to H_c and (J = 6.5Hz) to H_a, and is shown by decoupling to be weakly coupled (J ≏ 1Hz) to H_x.

The ^1H n.m.r. spectrum of the Z-isomer (230) at 100MHz was sufficiently well resolved to allow assignments (figure 40). The absorption at 7.70δ is assigned to H_p. H_c resonates at 7.36δ and is coupled to H_a (J = 17Hz) at 5.54δ, to H_b (J = 9Hz) at 5.48δ and to H_d (J = 11Hz) at 6.60δ. The protons H_w and H_x appear as an AB spectrum at 6.30δ and 6.71δ (J = 5Hz).

The configurations of the two isomers were assigned from the shifts of the vinyl protons (H_c). In the Z-isomer, H_c lies in the deshielding region of the benzene ring and resonates at higher frequency (7.36δ) than for the E-isomer (7.03δ). Similarly H_d in the E-isomer resonates at higher frequency (7.03δ) than in the Z-isomer (6.60δ). The coupling constant J_{cd} in the Z-isomer is 11Hz and in the E-isomer is 11.5Hz indicating a transoid geometry for both isomers and this stereochemistry would account for the shift of H_w in the E-isomer to higher frequency with respect to the Z-isomer, due to H_w lying in the deshielding region of the vinyl group.

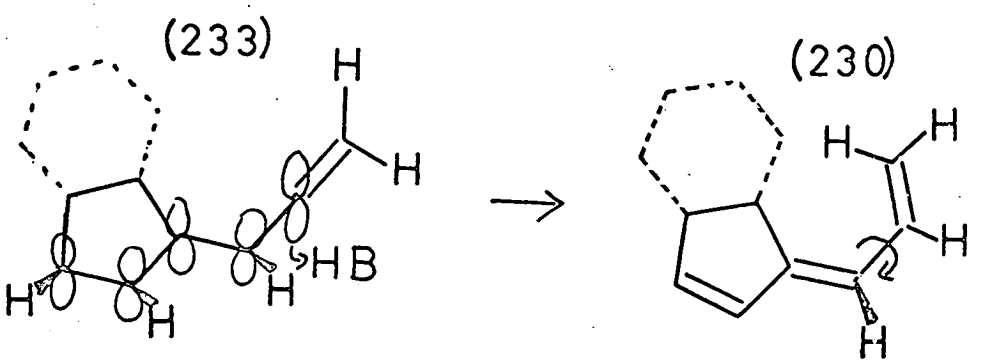
3-Allenylindene (172) rearranged very quickly on contact with alumina or with cold sodium methoxide to give the Z-benzofulvene (230). When 3-(1'-deuteroallenyl)indene (231) was used the benzofulvene (232) produced had deuterium in place of H_d shown by the disappearance of the corresponding doublet in the ^1H n.m.r. spectrum. This provides evidence for the earlier suggestion that these rearrangements proceed with the

intermediacy of allenyl derivatives. The ease of reaction of the allene to give the fulvene suggests that the acetylene-allene conversion is the slow step.

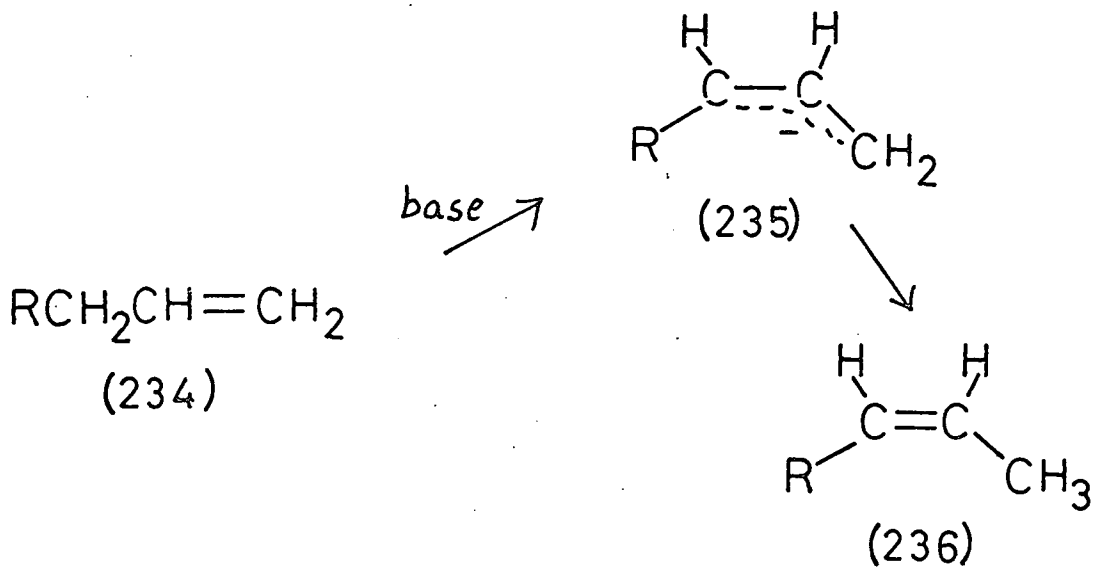


(231) (232)

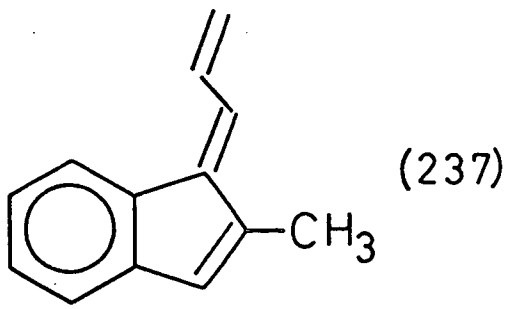
When the Z-benzofulvene was refluxed in NaOMe/HOMe it rearranged to give the E-isomer (229). The formation of Z is therefore kinetically controlled. The E-isomer is the thermodynamically more stable product as might be expected.



The formation of the Z-isomer (230) is perhaps surprising. It cannot be attributed to some property of the alumina since stirring 3-allenylindene (172) with cold sodium methoxide in methanol also gave the Z-isomer. Formation of compound (230) suggests that the intermediate ion (233) prefers to adopt a W-conformation.



The related rearrangement of terminal olefins (234) via the allylic anion (235) to internal olefins has been found in kinetically controlled processes to favour the Z product (236),[103] presumably because the Z-configuration in the allylic anion is favoured.

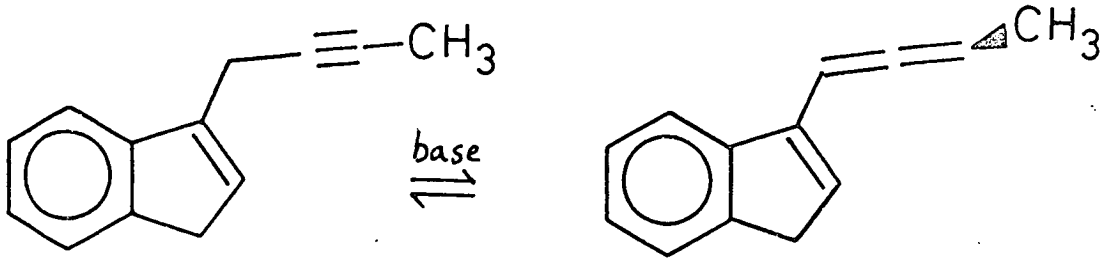


A mixture of 1-propargyl and 3-propargyl-2-methylindene (109) and (110) was rearranged with sodium methoxide in methanol (20% yield) or alumina (50% yield) to give a single product. By comparison of its ^{1}H n.m.r. spectrum with those of E and Z-6-vinylbenzofulvene (229) and (230), it has been assigned to Z-1,2-benzo-4-methyl-6-vinylfulvene (237). The chemical shifts of protons H_a, H_b, H_c, H_d, H_w and H_p are virtually identical to those of the Z-isomer (230) (see Table 12).

Again J_{cd} is large (11Hz) indicating a transoid geometry. Presumably no E-isomer is formed because of the steric effect of the methyl group.

3-Methyl-1-propargylindene (106) unfortunately declined to react under any conditions.

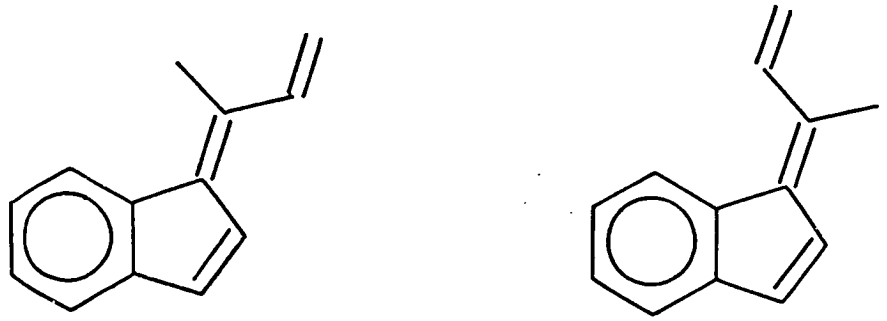
3-(But-2'-ynyl)indene (116) did not rearrange even after extended refluxing however this can be attributed to the greater stability of the starting acetylene compared with the corresponding allene (see page 2), so that the rearrangement of the acetylene (116) to the allene (177) is unfavourable. This result lends support to the proposal that the



(116) (177)

acetylene-allene interconversion is the first step in the rearrangement to the fulvenes.

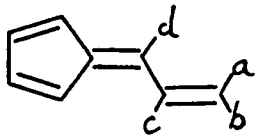
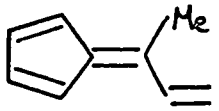
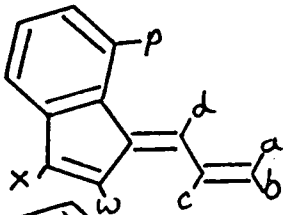
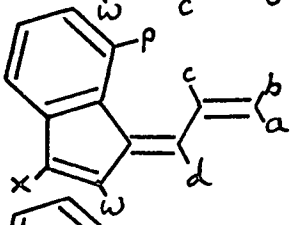
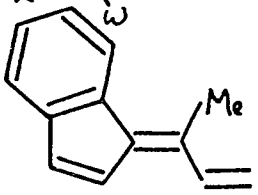
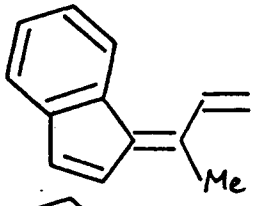
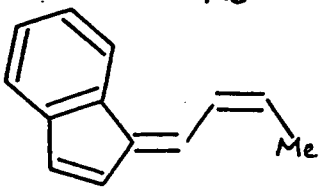
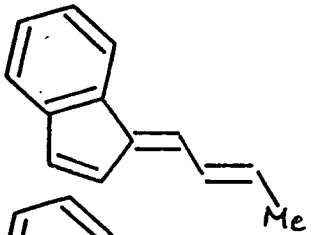
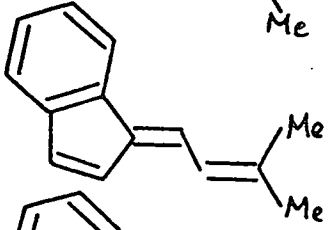
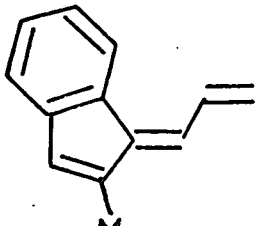
3-(1'-Methylprop-2'-ynyl)indene (118) on refluxing with sodium methoxide in methanol gave equal quantities of two fulvene products in 40% yield, which were separated on alumina to give E and Z-1,2-benzo-6-methyl--6-vinylfulvene (238) and (239). Rearrangement on alumina was slow but a small amount of the Z-isomer only was obtained. Further refluxing of the E/Z mixture gave no further change in composition indicating an equilibrium mixture.



(238) (239)

Table 12

^{1}H n.m.r. Chemical Shifts (δ) of Fulvene Compounds

	a	b	c	d	w	x	p
	5.56	5.27	6.90	6.62			
	5.53	5.38	7.09	2.20 (Me)			
	5.64	5.49	7.03	7.04	6.85	6.92	7.61
	5.53	5.48	7.36	6.60	6.30	6.71	7.70
	5.53	5.33	7.19	2.42 (Me)	6.66	6.82	7.6
	5.58	5.45	7.60	2.28 (Me)	6.70	6.70	7.6
	1.89 (Me)	5.86	ca7.2	6.76	6.33	6.60	7.65
	6.01	1.88 (Me)	6.80	6.56	6.74	6.74	7.45
	1.98 (Me)	1.92 (Me)	6.80	6.80	6.31	6.60	6.7
	5.30	5.22	7.34	6.50	2.06 (Me)	6.34	7.5

(Note: The Shifts of w and x may be Reversed)

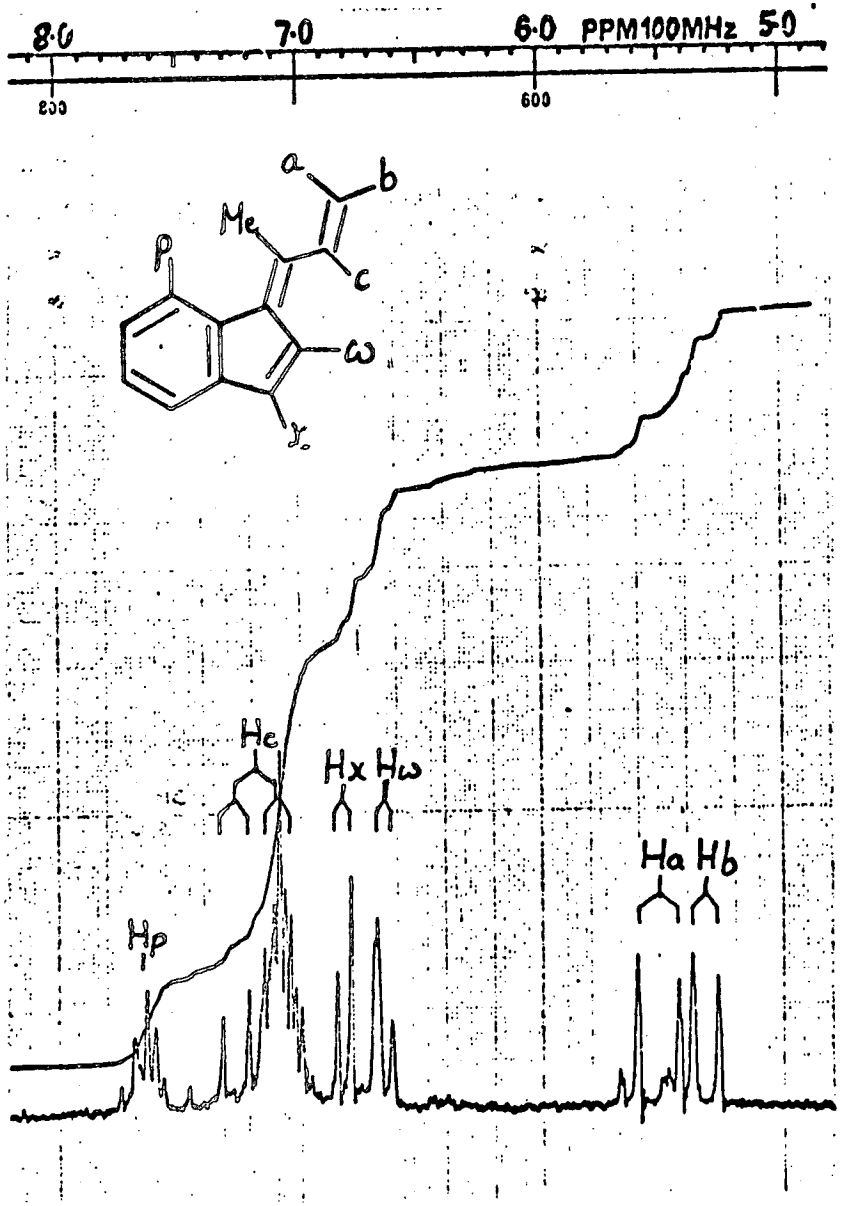


Figure 41

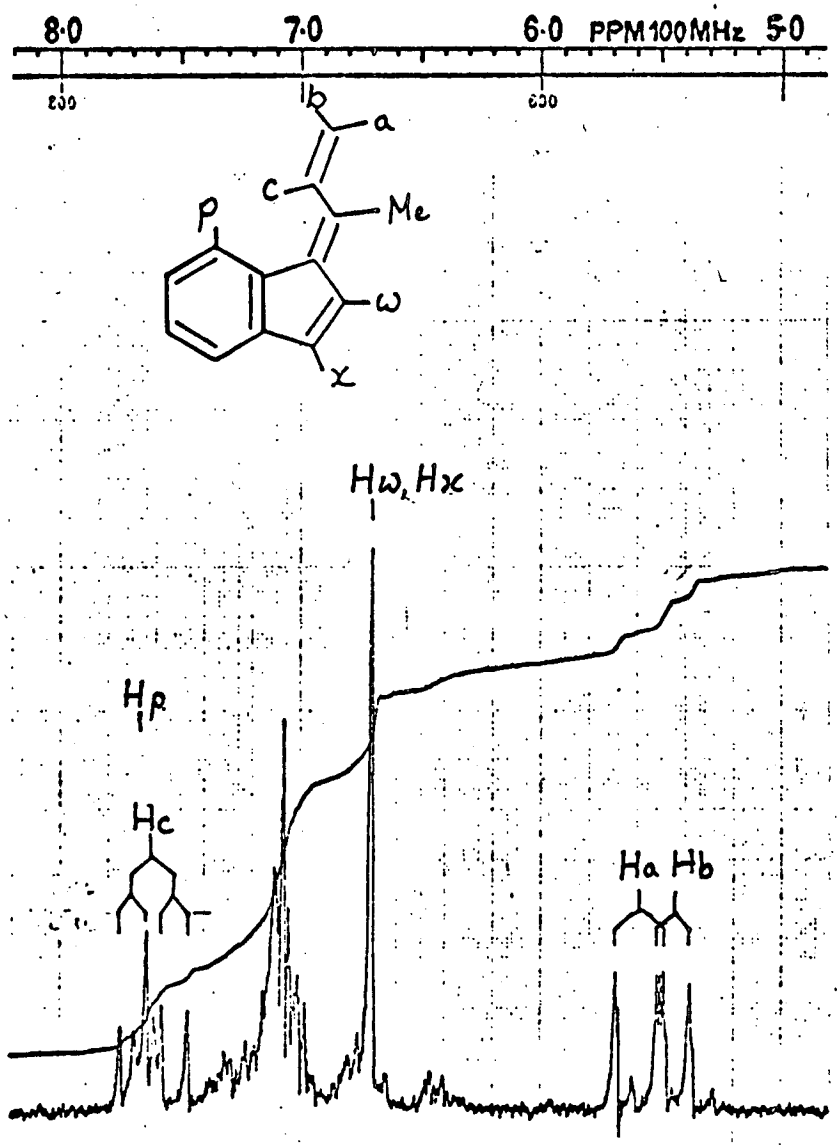
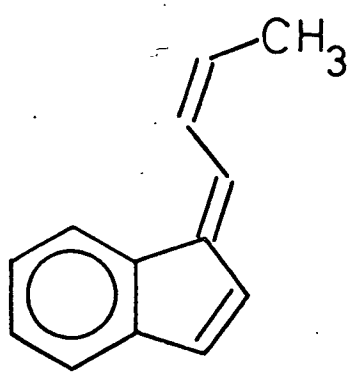


Figure 42

The isomers are readily differentiated by their ^{1}H n.m.r. spectra (figures 41 and 42) which were assigned as indicated, by reasoning similar to that for E and Z-1,2-benzo-6-vinylfulvene (229) and (230). The vinyl proton, H_c, resonates at a lower frequency in the E-isomer (7.19δ) than in the Z-isomer (7.60δ) since in the Z-isomer it lies in the deshielding region of the benzene ring. Similarly the methyl protons in the E-isomer resonate at higher frequency (2.42δ) than in the Z-isomer (2.28δ). The protons w and x appear as a singlet in the Z-isomer and as an AB spectrum in the E-isomer.

Rearrangement of 3-(buta-1',2'-dienyl)indene (177) with sodium methoxide in methanol (70% yield) or alumina (80% yield) gave the same benzofulvene product. Of the four possible structures, the product has been assigned the structure Z-1,2-benzo-6-(Z-prop-1'-enyl)fulvene (240) from its i.r. and ^{1}H n.m.r. spectra. The i.r. has an absorption at



(240)

750 cm^{-1} and no absorption at 960 cm^{-1} indicating a <u>cis</u> double bond. The ^{1}H n.m.r. (figure 43) shows the proton H_a at 5.86δ coupling (J = 8Hz) to the methyl proton resonance at 1.89δ and (J = 9Hz) to the proton H_c ($\sim$7.2δ) indicating a cis double bond. The proton H_d resonates at 6.76δ and is coupled (J = 6Hz) to H_c which is obscured by the aromatic region. The configuration about the 6-position is uncertain but has been assigned Z because of the similarity of the ^{1}H n.m.r. spectrum to that of Z-1,2-benzo-6-vinylfulvene (130) (see Table 12).

An isomer of this compound has been prepared by Quére and Maréchal[104]

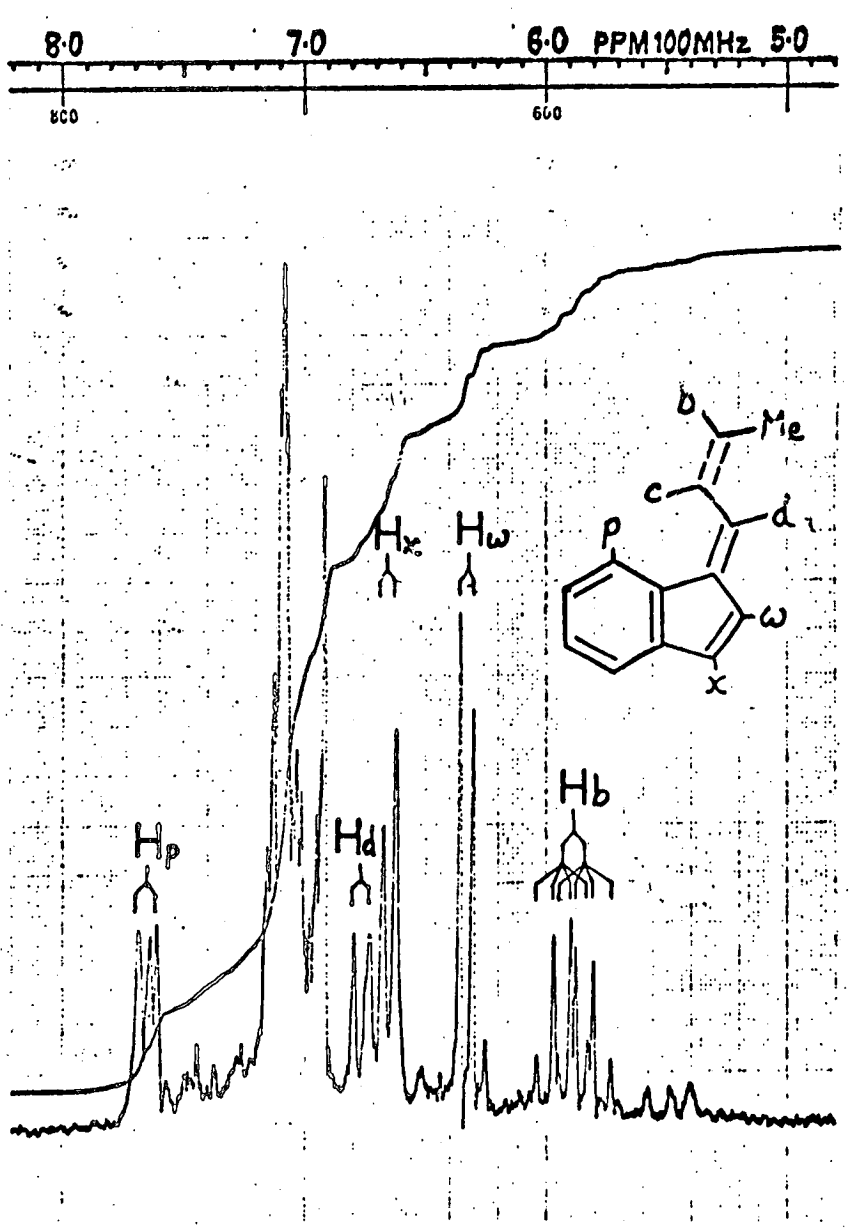


Figure 43

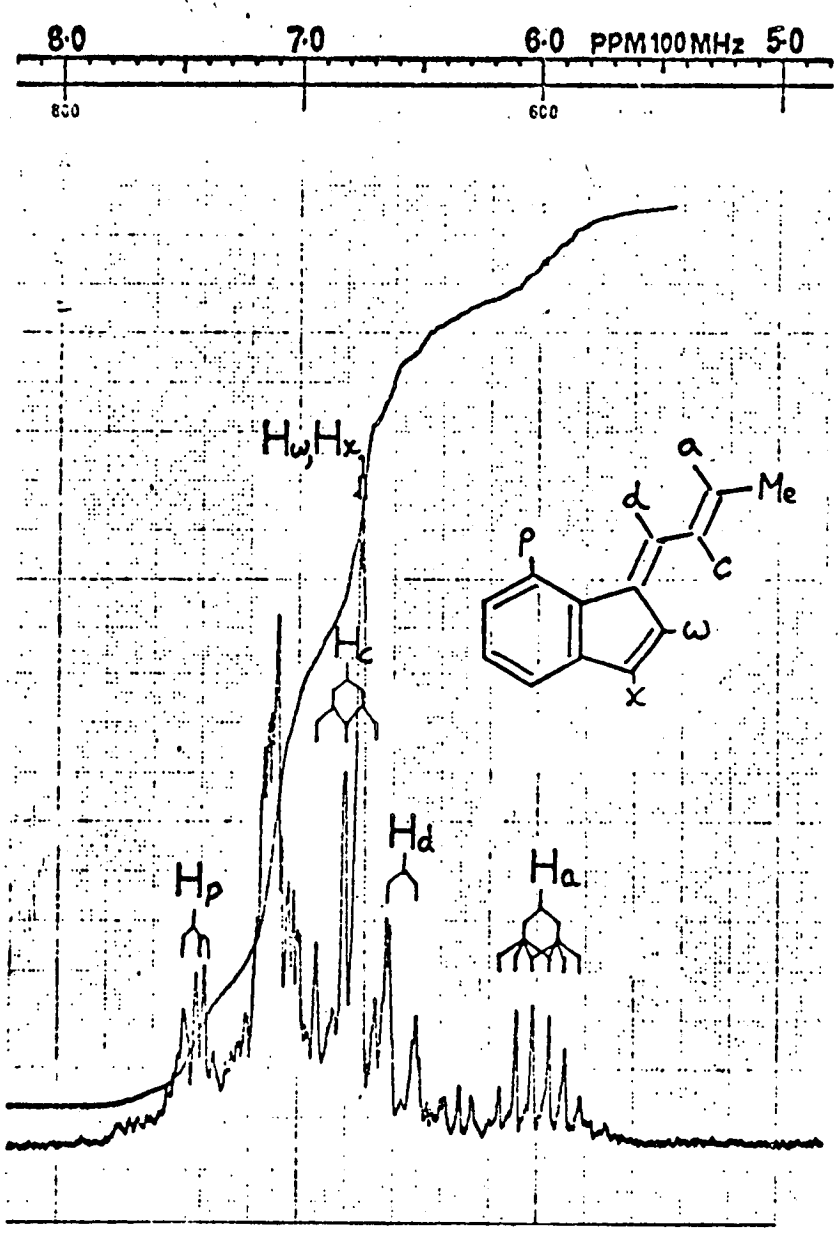
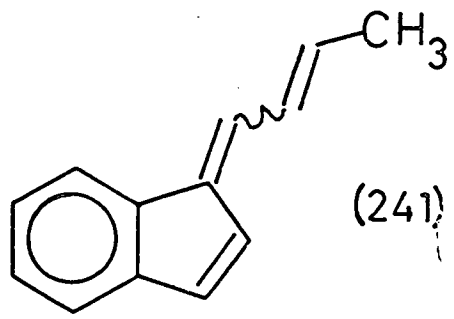


Figure 44

who, by condensing indene with crotonaldehyde, isolated a fulvene product in 1% yield, to which they assigned the structure 1,2-benzo-6-(Z-prop-1'-enyl)fulvene (241) on the basis of the i.r. spectrum. The very poor



(241)

yield is attributable to the harsh experimental conditions; i.e., refluxing with potassium methoxide in methanol. Repeating the experiment by stirring indene and crotonaldehyde with 2 molar sodium ethoxide in ethanol for 5 minutes gave, after distillation of the product, 35 - 40% yield of the fulvene, a yellow oil.

The product is in agreement with structure (241). The configuration was assigned from the i.r. and ^{1}H n.m.r. spectrum. The i.r. absorption at 960 cm^{-1} indicates a trans olefinic group. The ^{1}H n.m.r. spectrum (figure 44) is assigned as shown on the figure, and the coupling J_{ac} is 12Hz indicating a <u>trans</u> isomer. Because of the similarity of the chemical shifts to E-1,2-benzo-6-vinylfulvene (129) (see Table 12) and the position of the proton H_c at high frequency, the structure has been tentatively assigned the E configuration about the 6-position.

3-(3'-Methylbuta-1',2'-dienyl)indene (178) rearranged with sodium methoxide in methanol (30% yield) or alumina (70% yield) to give the same benzofulvene product; 1,2-benzo-6-(2'-methylprop-1'-enyl)fulvene (242). Examination of the ^{1}H n.m.r. spectrum (figure 45) shows mainly one isomer with possibly a little of the other. The protons H_d and H_c appear in the major isomer as a singlet at 6.80δ. The AB spectrum at 6.13δ and 6.60δ is assigned to the protons H_w and H_x. The small peak at 6.72δ varies in intensity between different fractions off the alumina column and is

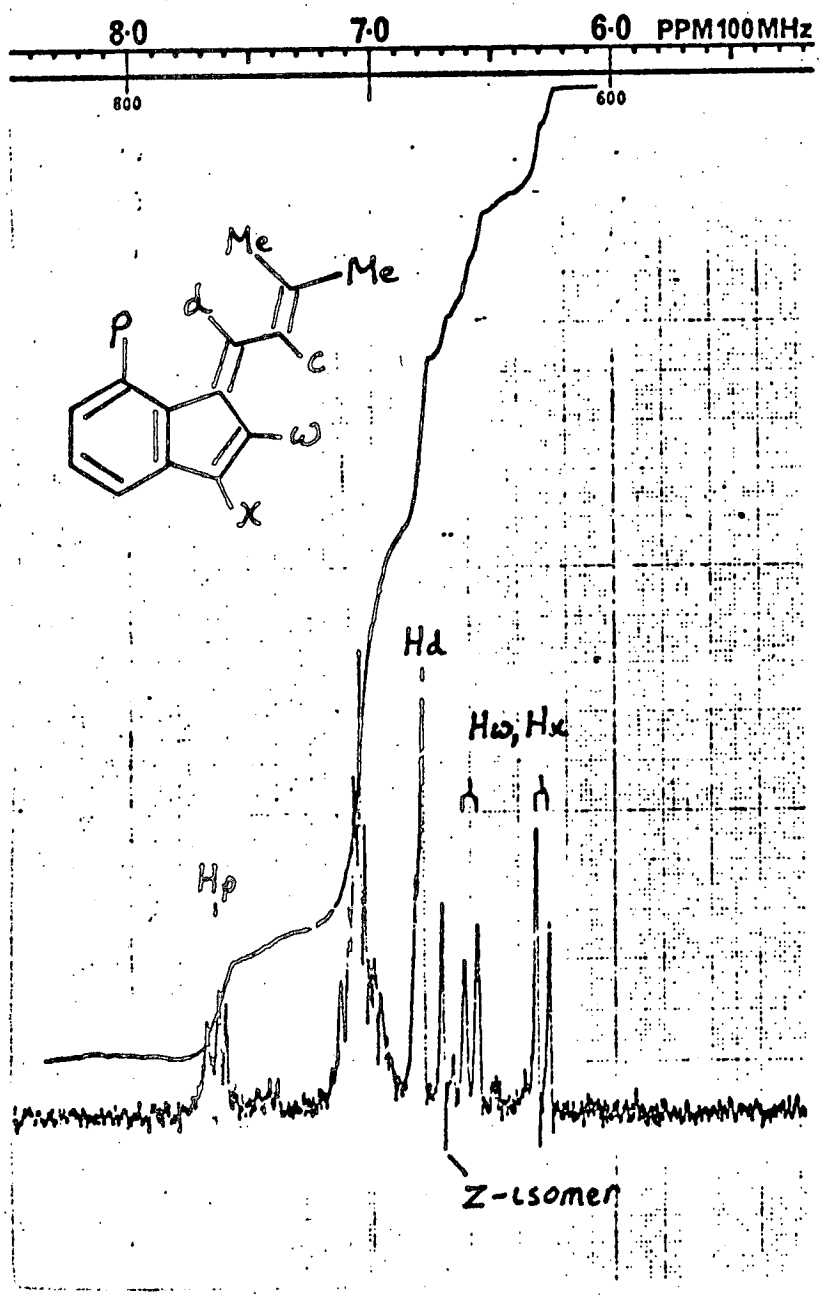


Figure 45

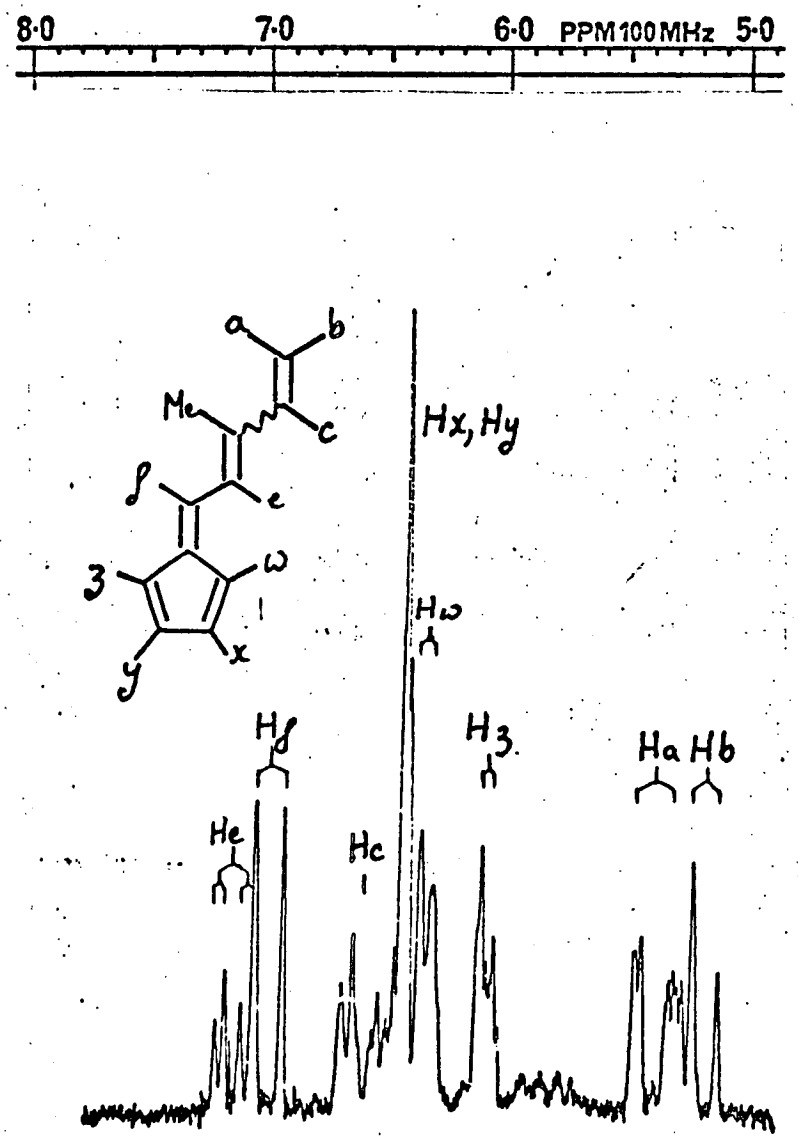
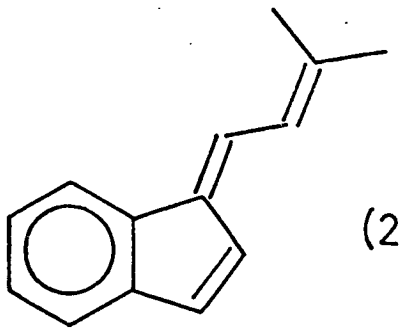


Figure 46

attributed to the other isomer. The methyl protons resonate at 2.00δ and 1.94δ. Because of the similarity of the chemical shifts of the protons H_c and H_d with those of E-1,2-benzo-6-vinylfulvene (130) (see Table 12), the main isomer has been assigned the E configuration (242).

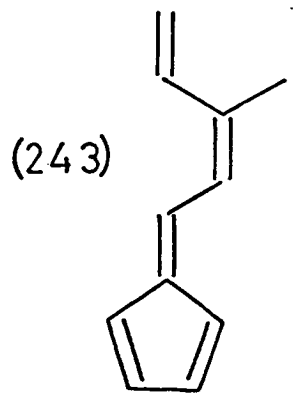


(242)

6.2 Rearrangement of Pentenynyl Indenes and Cyclopentadienes

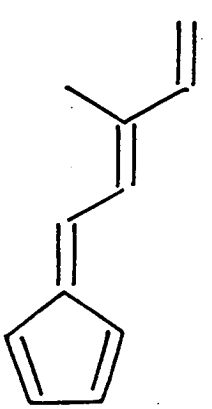
These compounds rearranged on refluxing with sodium methoxide in methanol or sodium ethoxide in ethanol to give fulvene type products. The rearrangement was slower than that of the propargyl derivatives and no rearrangement occurred on alumina. In view of the greater number of isomers and closely positioned proton resonances, assignment of the product was considerably more difficult than in the simpler vinylfulvene derivatives.

Z-3-(3'-methylpent-2'-en-4'-ynyl)cyclopentadiene (136) rearranged with sodium methoxide in methanol to give a red fulvene in 20% yield believed to be 6-(2'-methylbuta-1',3'-dienyl)fulvene (243) or (244). The ^{1}H n.m.r. spectrum (figure 46) was analysed by comparison with the spectrum of 6-vinylfulvene (figure 34).



(243)

or



(244)

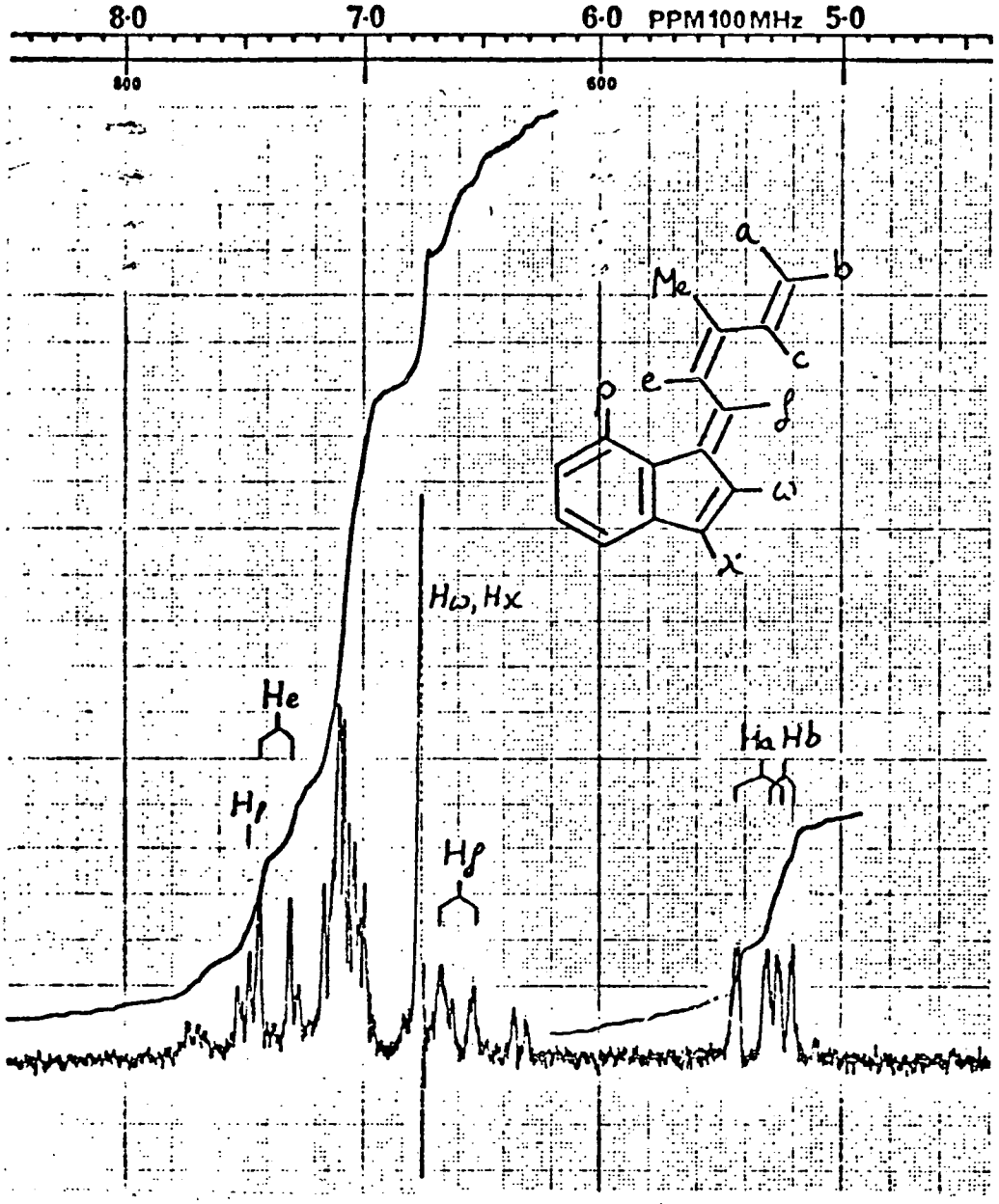
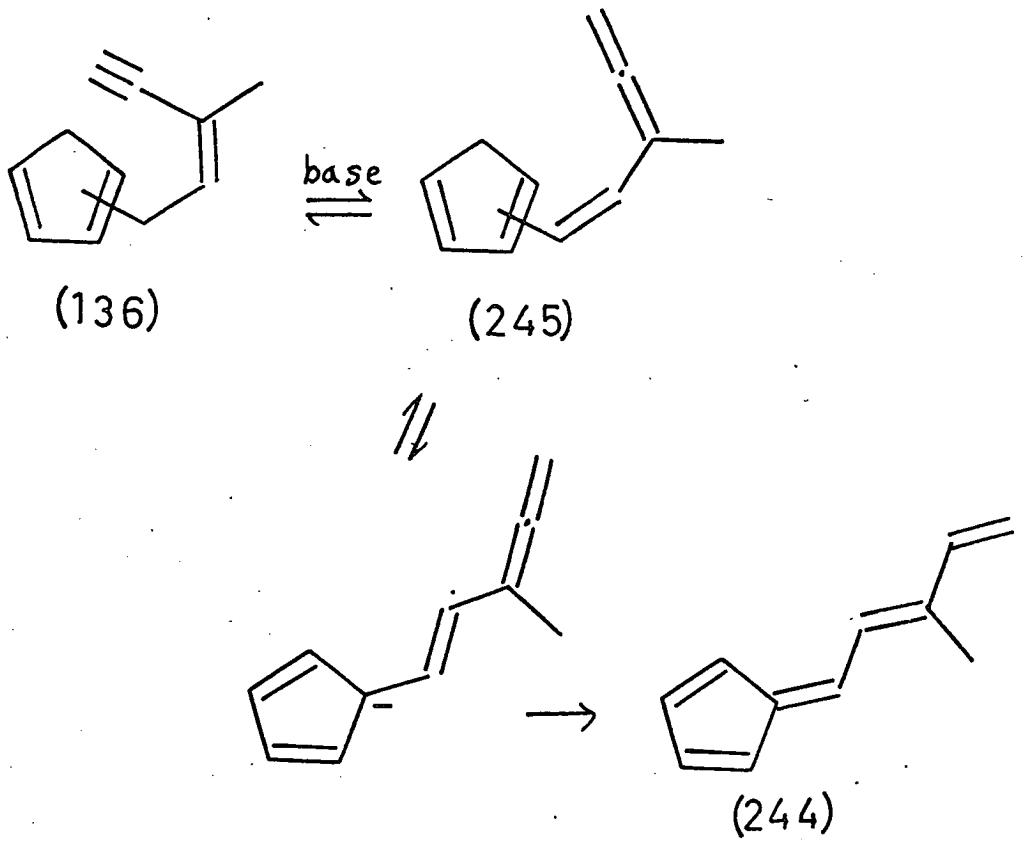


Figure 47

The methyl protons resonate at 2.02δ. The doublet at 6.98δ is assigned to proton H_p and is coupled (J = 12Hz) to proton H_e at 7.12δ which is again coupled (J = 2Hz) possibly to H_c or H_a. Proton H_a at 5.37δ shows a <u>trans</u> coupling (J = 15Hz) to H_c while H_b at 5.17δ shows a <u>cis</u> coupling (J = 11Hz) to H_c. H_c itself is obscured by the cyclopentadiene protons. The stereochemistry about the 3'-carbon is not known.

The mechanism for this rearrangement probably proceeds via the allene (245) in a similar way to the propargyl derivatives as shown below.



Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126b) rearranged with sodium ethoxide in ethanol to give a yellow crystaline product in 55% yield, which appears by ^{13}C n.m.r. to be a mixture of two fulvene isomers. Only one of the isomers, apparently the major isomer, has been separated reasonably pure by alumina chromatography. The ^{1}H n.m.r. spectrum (figure 47) shows the protons H_a and H_b at 5.36δ and 5.26δ respectively. The doublet at 7.37δ is assigned to the proton H_e coupling (J = 13Hz) to the

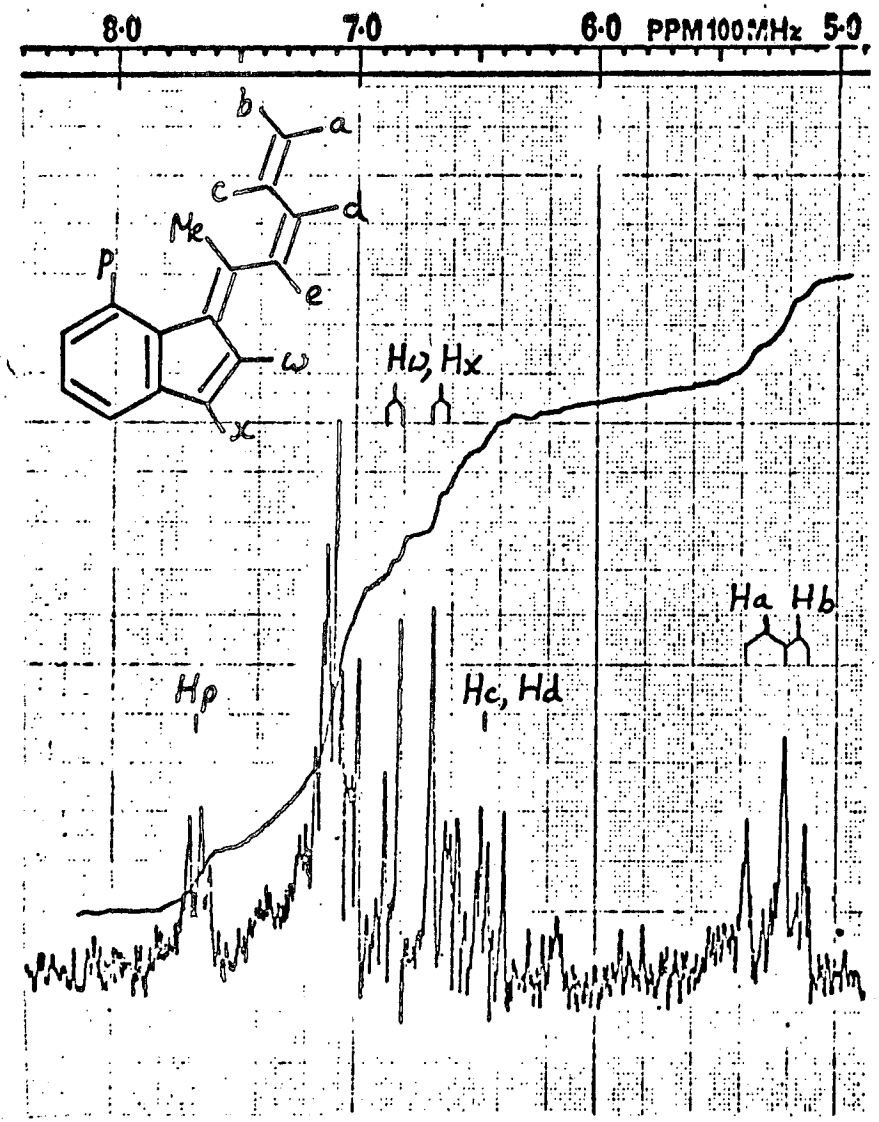


Figure 48

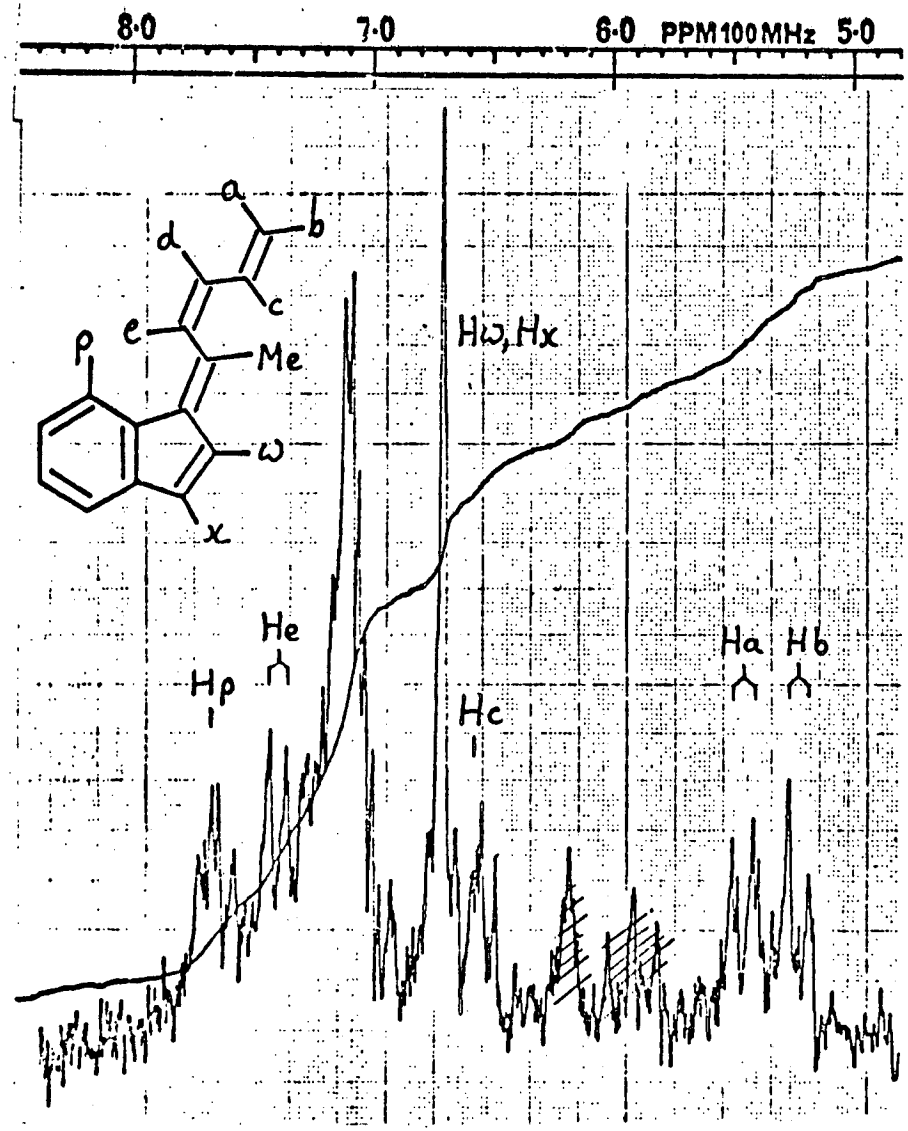
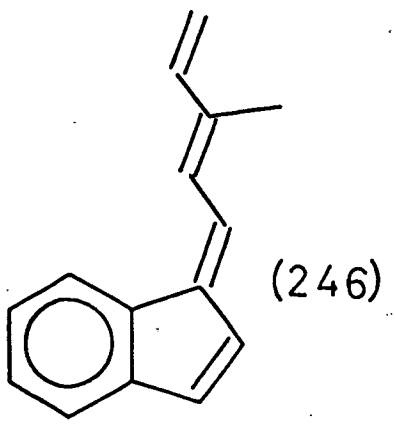


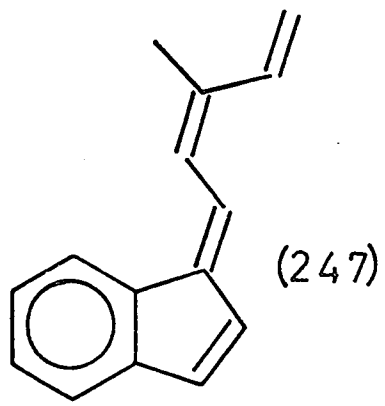
Figure 49

proton H_f at 6.60δ. The protons H_w and H_x appear as a singlet at 6.76δ. The chemical shifts of protons H_c and H_d are in close agreement with those for Z-1,2-benzo-6-vinylfulvene (130) and the compound has been tentatively assigned the structure Z-1,2-benzo-6-(2'-methylbuta-1',3'-dienyl)fulvene. Two isomeric forms about the 2' position are possible:- structures (246) and (247).

Attempts to obtain a Diels-Alder adduct with dimethylacetylenedicarboxylate have failed. Such a reaction might have been expected for the isomer (246) and so the structure has been assigned a Z configuration in the buta-1',3'-dienyl chain structure (247).



(246)

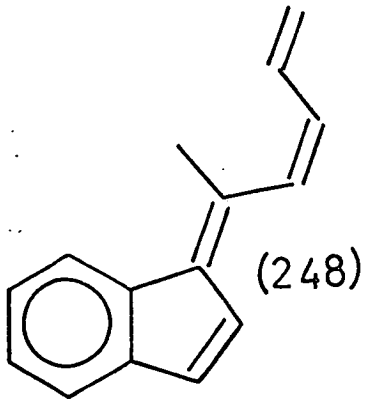


(247)

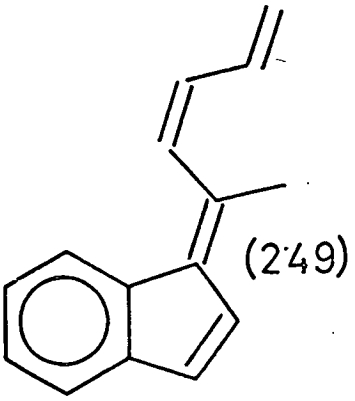
E- and Z-3-(1'-methylpent-2'-en-4'-ynyl)indene (122a and b) rearranged with sodium ethoxide in ethanol to give a mixture of two fulvenes, A and B, in 27% yield in the ratio 1.3:1 by ^1H n.m.r. These have been partially separated by alumina chromatography. Comparison of the ^1H n.m.r. spectra (figures 48 and 49) with those of E and Z-1,2-benzo-6-methyl-6-vinylfulvene (figures 41 and 42) shows a marked similarity between the E-isomer and A, and the Z-isomer and B.

The ^1H n.m.r. of compound A (figure 48) shows the methyl protons resonating at higher frequency (2.46δ) than compound B (2.26δ) and the proton H_e resonates below 7.3δ in compound A possibly indicating the E configuration about the 6-position. The protons H_w and H_x appear as an AB spectrum at 6.65δ and 6.85δ and the protons H_a and H_b resonate at 5.30δ

and 5.15δ. Both the protons H_c and H_d appear as a multiplet at about 6.5δ. The i.r. spectrum shows a strong absorption at 750 cm^{-1} and no peak about 960 cm^{-1} suggesting a cis olefin. Hence compound A is assigned structure (248).



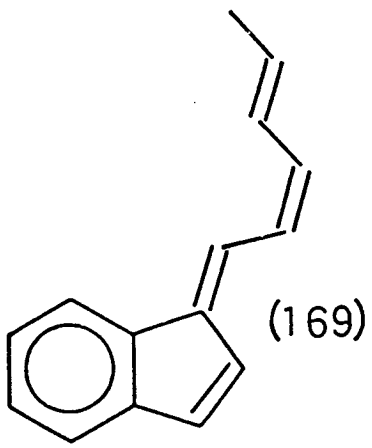
(248)



(249)

The ^1H n.m.r. of compound B (figure 49) shows the methyl proton resonance at lower frequency (2.26δ) than compound A and the proton H_e resonates at 7.4δ with a <u>cis</u> coupling (J = 6Hz) to proton H_d. In addition protons H_w and H_x appear as a singlet at 6.67δ, and the protons H_a and H_b at 5.22δ and 5.45δ. The spectrum as a whole is very similar to that of Z-1,2-benzo-6-methyl-6-vinylfulvene (figure 42), and on this basis is assigned the Z configuration about the 6-position. The i.r. has a very strong peak at 750 cm^{-1} which along with the cis coupling constant J_{de} indicates a cis olefin. Hence B has been assigned the structure (249).

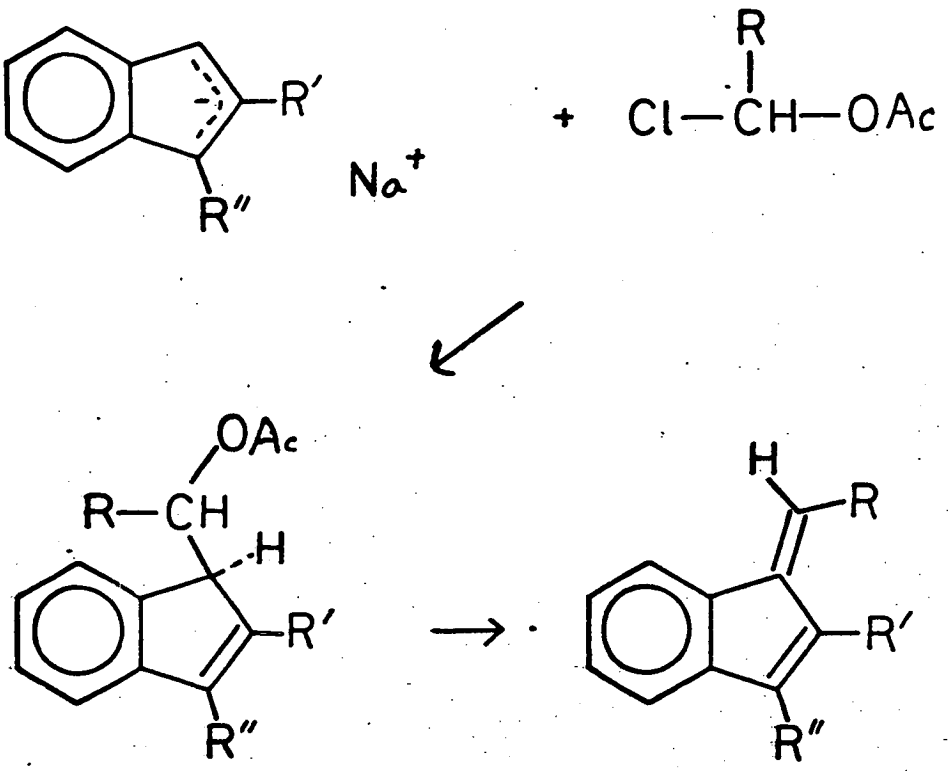
The related fulvene (169) (chapter 4.3) also showed a cis olefinic structure consistent with these results.



(169)

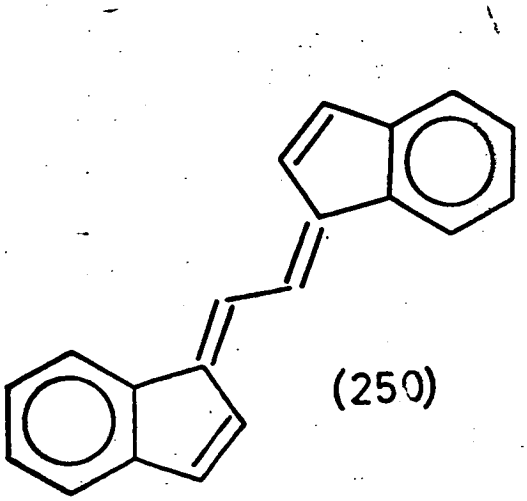
6.3 Discussion of Some Methods for Synthesis of Fulvenes

Benzofulvenes are difficult to prepare[105] by classical methods such as condensation with aldehydes or dehydration of carbinols. Neuenschwander[106] has successfully prepared some simple benzofulvenes using 1-chloroalkyl acetates as shown:

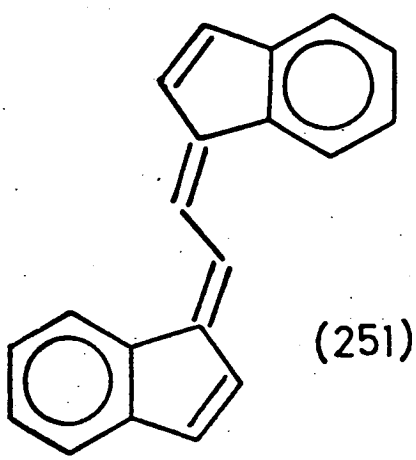


These are obtained as yellow crystals.

Preparation of 6,6'-bis(1,2-benzofulvenyl) in the same way[106] gave a mixture of the E,E and Z,Z isomers (250) and (251).



(250)



(251)

Examples of E and Z isomerism about the 6-position are uncommon and this has been attributed[107] to the exocyclic bond being highly polar - approaching a single bond. This would arise since the dipolar ion would be pseudo-aromatic having six π electrons about the ring. The ^{13}C n.m.r. spectra run showed no evidence for any localisation of electrons indicating that the vinyl fulvene electron system is more like that of a conjugated olefin.

1,2-Benzo-6-vinylfulvenes and 6-vinylfulvenes are even more difficult to prepare, presumably due to polymerisation of the vinyl group during synthesis. Neuenschwander[100,101] has prepared several vinylfulvenes although the yields were often poor e.g. 6-isopropenylfulvene - 2.2%, 6-methyl-6-vinylfulvene - 0.5% yield. The only known example of a 1,2-benzo-6-vinylfulvene (241), discussed in chapter 6.2, was reported in 1% yield.[104]

The vinylfulvenes prepared as described in this section were all simply prepared in moderate yield. They include the first isolated examples with the Z configuration. This reaction appears to be a useful, simple method of preparing vinylfulvenes.

CHAPTER 7

Experimental

7.1 Introduction

7.1.1 Gas-liquid Chromatography For preparative work a Pye 105 automatic preparative chromatograph with a flame ionization detector was used. The column was packed with either 10% polymetaphenylether (PMPE) or 10% neopentylglycolsuccinate (NPGS) on Phase Prep A 60 - 80 mesh as support.

For analytical work a Griffin & George D6 chromatograph, employing a gas density balance, was used. The column was packed with 5% NPGS on Chromosorb P 80 - 100 mesh. Nitrogen was used as the carrier gas.

7.1.2 Infra-red Spectroscopy Spectra were recorded on a Perkin Elmer 157G instrument as liquid films unless otherwise indicated.

7.1.3 Ultra-violet Spectroscopy A Unicam SP800 spectometer was used. Samples were examined in a 1cm cell at room temperature using ethanol or n-hexane as solvent. Solutions were made by direct weighing using a Cahn Electrobalance.

7.1.4 Mass Spectroscopy Mass spectra were obtained using an AEI MS-902 double focussing instrument. Exact masses of parent peaks (P) were determined by peak matching which gave results within 10 p.p.m. of the calculated value.

7.1.5 Proton Magnetic Resonance Unless otherwise stated the spectra were run on a Varian HA-100 Spectrometer. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane used as an internal standard. Carbon tetrachloride was normally used as the solvent. The usual symbols are used e.g. d = doublet, t = triplet, etc.

7.1.6 Carbon-thirteen Magnetic Resonance Spectra were recorded on a Varian CFT-20 (20MHz, 18,682 gauss) at 35 - 38°C in $CDCl_3$ as solvent

and internal standard. Chemical shifts are given in parts per million relative to tetramethylsilane. Shift values are followed by parenthesis giving the assignment deduced in conjunction with the off resonance proton decoupled spectrum.

7.1.7 Materials Unless otherwise stated liquids and solvents were dried over magnesium sulphate and the reagents were used without further purification. Light petroleum refers to the fraction of b.p. 30 - 40°C and was redistilled before use.

7.2 Purification of Starting Materials

7.2.1 Methyl vinyl ketone, supplied containing 10% water, was treated with anhydrous potassium carbonate (0.2ml per ml of ketone) and allowed to stand until two layers separated. The organic layer was removed, filtered and distilled under reduced pressure. It was stored at -10°C over molecular sieve.

7.2.2 But-1-yne-3-ol, supplied as a 50% solution in water, was dried as for methyl vinyl ketone but repeating the potassium carbonate drying. It was stored at -10°C.

7.3 Preparation of Starting Materials

7.3.1 Acetyl Bromide[108] Phosphorous tribromide (111g, 39ml, 0.41 mol.) was added slowly with stirring to an excess of acetic anhydride (160ml) boiling under reflux. The boiling point dropped as acetyl bromide was formed and when the addition was complete acetyl bromide was distilled from the reaction mixture (80%, b.p. 81°, lit.[108] b.p. 81°).

7.3.2 Triphenylphosphite dibromide[109] was prepared by adding bromine (0.8 mol.) slowly to triphenylphosphite (1 mol) with ice cooling, stirring, and rigorous exclusion of moisture. The product was prepared immediately before use.

7.3.3 Cyclopentadiene was prepared by thermal decomposition of dicyclopentadiene. The dimer was carefully heated in a flask fitted with a vigreux column and cyclopentadiene (b.p. 42°, lit.[110] b.p. 41 - 42°) was slowly distilled off and used immediately.

7.3.4 Potassium t-butoxide was prepared by adding potassium (80g, 2.1 mol.) in small pieces to t-butanol (1.7l) under nitrogen. When all the potassium had dissolved the solution was refluxed overnight. Excess of solvent was removed under reduced pressure. The resultant white solid was the 1:1 complex $(CH_3)_3CO^-K^+$-$(CH_3)_3COH$ and was used without further purification.

7.3.5 Indan-2-one was prepared essentially as described by Robertson.[76] Indene (116g, 1.0 mol.) was added dropwise to a mixture of formic acid (700ml) and hydrogen peroxide (140ml, 100 Vols., 30%) with stirring and keeping the temperature at 35 - 40°C using an ice bath. The reaction was then stirred for a further hour at room temperature. The formic acid was removed under reduced pressure leaving yellow crystals of 1-formyl-2-hydroxyindan.

The crude ester was boiled under reflux (2hr) with sulphuric acid (21, 7%) and the reaction mixture steam distilled. The distillate was extracted with ether (3 x 200ml), the ether layers washed with saturated sodium chloride solution, and dried. Removal of the solvent gave the crude product which was distilled under reduced pressure (0.01mm Hg) to give indan-2-one (50%, m.p. 53°, lit.[110] m.p. 58°).

7.3.6 2-Methylindene was prepared by a Grignard reaction. Indan-2-one (40g, 0.36 mol.) in sodium dried ether (150ml) was added dropwise over 0.5hr to an ethereal solution of methyl magnesium bromide (0.4 mol.) and the reaction stirred for a further hour. The mixture was then poured onto ice and water and acidified with dilute hydrochloric acid until both layers were clear. The aqueous layer was extracted (2 x 50ml) and the

combined ether layers were washed with saturated sodium chloride solution and dried. Removal of the ether gave 2-methylindan-2-ol. The carbinol was refluxed with phosphorous pentoxide (25g) in sodium dried benzene (400ml) for one hour. The benzene solution was decanted and the benzene removed. Distillation of the residue under reduced pressure gave 2-methylindene (70%, b.p. 62 - 65°, 20mm, lit.[110] b.p. 62-5/20mm).

7.3.7 3-Methylindene Sodium (11.5g, 0.5 mol.) was added in small pieces to liquid ammonia (500ml) containing ferric nitrate (0.2g) catalyst, and stirred until the blue colour disappeared. Indene (58g, 0.5 mol.) was added and the mixture stirred for one hour. Methyl bromide (2 x 38.5g phials, 0.8m) was added dropwise and the mixture stirred overnight to evaporate the ammonia. The mixture was extracted with ether (3 x 100ml), the extracts dried and the solvent removed under reduced pressure. Distillation of the residue gave 3-methylindene (73%, b.p. 85°/10mm, lit.[110] b.p. 198.5°).

7.3.8 3-Ethylindene was prepared via a phase transfer reaction similar to the method described by Makosza.[111] Indene (10g, 0.086 mol.) and ethyl bromide (12g, 1.1 mol.) were added to aqueous potassium hydroxide (50ml, 50%) and benzyltriethylammonium chloride and the mixture was stirred vigorously for 10 hours after which water (50ml) was added. The organic layer was extracted into light petroleum (3 x 20ml), dried and the solvent removed under reduced pressure. The residue was distilled to give 3-ethylindene (88%, b.p. 86°/5mm, lit.[112] b.p. 116°/18mm).

7.3.9 2,3-Dimethylindene was prepared as by Robertson.[76] Diethyl malonate (160g, 1 mol.) was added dropwise to sodium ethoxide (1 mol.) in dry ethanol (1l) while maintaining the temperature at 50°C. Methyl iodide (142g, 1 mol.) was then added and the whole gently refluxed with stirring overnight before cooling to 40°C. Sodium (23g, 1 mol.) was

added and, when the reaction was complete, benzyl chloride (126.5g, 1 mol.) was added. After refluxing for 4 hours the solution was neutralised, water (250ml) added and the ethanol removed under reduced pressure. The organic material was extracted into ether (3 x 200ml) which was dried and the solvent removed to give diethyl benzylmethylmalonate. The crude ester was hydrolysed with potassium hydroxide (112g) in aqueous ethanol (500ml, 20%) to give the benzylmethylmalonic acid. This acid was decarboxylated by heating at 160°C until carbon dioxide evolution ceased. The crude product was distilled under reduced pressure to give white crystals of α-methyl-β-phenylpropionic acid (35%, m.p. 22 - 23°, lit.[76] not obtained crystaline).

α-Methyl-β-phenylpropionic acid (53g, 0.32 mol.) was boiled under reflux with excess thionyl chloride (70g, 0.6 mol.) in sodium dried benzene (150ml) for 20 hours. The solvent and thionyl chloride were removed under reduced pressure and the residue distilled. The acid chloride thus obtained was dissolved in dry carbon disulphide (250ml) and powdered $AlCl_3$ (45g, 0.34 mol.) was added slowly. After refluxing for one hour the cooled mixture was cautiously added to ice/water and the organic layer separated. The aqueous layer was extracted with chloroform and the combined organic layers dried over magnesium sulphate. The solvents were removed and the product distilled to give 2-methylindan-1-one (70%, b.p. 120°/15mm, lit.[110] b.p. 125°/18mm).

This ketone was converted to 2,3-dimethylindene (64%, b.p. 109°, lit.[112] b.p. 111.5 - 112.5°) by reaction with methyl magnesium bromide followed by dehydration of the carbinol with phosphorous pentoxide, as described for 2-methylindene.

7.3.10 1,2-Dihydronaphthalene was prepared by the reduction of α-tetralone. Sodium borohydride (3.4g, 0.09 mol.) in sodium hydroxide solution (6ml, 2N) plus water (54ml) was added to α-tetralone (41.5g,

o.25 mol) in methanol (300ml), keeping the temperature between 18 and 25°C. The reaction was stirred for a further hour and most of the methanol removed by distillation. The crude carbinol thus obtained was dehydrated by refluxing with phosphorous pentoxide (35.5g, 0.25 mol.) in sodium dried benzene (200ml) for 1 hour. The benzene solution was decanted, the solvent removed and the residue distilled to give 1,2-dihydronaphthalene (62%, b.p. 87°/15mm, lit.[110] b.p. 84-5°/12mm).

7.3.11 3-Methyl-1,2-dihydronaphthalene (66%, b.p. 104-6°/14mm, lit.[113] b.p. 115-8°/22mm) was prepared from β-tetralone and methyl magnesium bromide followed by dehydration of the carbinol with phosphorous pentoxide, as described for 2-methylindene.

7.3.12 4-Methyl-1,2-dihydronaphthalene (64%, b.p. 107°/15mm, lit.[112] b.p. 111.5°/18mm) was similarly prepared from α-tetralone.

7.3.13 3-Methylpent-1-en-4-yn-3-ol was prepared as follows. It was essential that no water was allowed to enter the reaction. Lithium acetylide was prepared by bubbling acetylene gas, dried by passage through concentrated H_2SO_4, into liquid ammonia (250ml) with stirring. Lithium (5.25g, 0.75 mol.) was added in small pieces, allowing the blue colour which develops to disappear, to give a grey mixture. Methyl vinyl ketone (30g, 0.4ml) in sodium dried ether (100ml) was added dropwise and the reaction stirred for a further hour. Ammonium chloride (53.5g, 1 mol.) was added, followed by ether (200ml) and the ammonia allowed to evaporate off. The reaction was then filtered and the ether removed by fractional distillation through a vigreux column at atmospheric pressure. The product was distilled under reduced pressure to give 3-methylpent-1-en-4-yn-3-ol (60 - 70%, b.p. 54°/15mm, lit.[45] b.p. 56°/17mm) as a colourless liquid.

7.3.14 Hex-4-en-1-yn-3-ol was prepared as described in Organic Synthesis.[114] A solution of ethyl magnesium bromide (0.64 mol.) in sodium dried tetrahydrofuran (350ml) under nitrogen was added from a dropping funnel in small portions over 3 hours to tetrahydrofuran (200 ml), through which a continuous stream of dry acetylene was passing. The reaction vessel was cooled in ice/water, and crotonaldehyde (35g, 41ml, 0.5 mol.) in tetrahydrofuran (50ml) added over 45 minutes. The reaction was stirred overnight and then added to saturated ammonium chloride solution (1.5l). The aqueous phase was extracted with ether (3 x 250ml) and the combined organic fractions dried. The solvents were removed and the residue distilled to give hex-4-en-1-yn-3-ol (65%, b.p. 42°/0.1mm, lit.[110] b.p. 157-9°).

7.3.15 Propargyl bromide was prepared as described by Birch and McAllan.[115] Propargyl alcohol (96g, 1.0 mol.) was mixed with pyridine (36ml) in a 250ml flask fitted with a dropping funnel, thermometer and calcium chloride guard tube. Phosphorous tribromide (52ml) was added dropwise during 1 - 1.5 hours, with stirring, at -15°C. The product was distilled directly from the flask under reduced pressure, washed with iced water, then chilled sodium hydrogen carbonate solution, and dried over calcium chloride to give propargyl bromide (68%, b.p. 30°/100mm, lit.[110] b.p. 35°/130mm).

7.3.16 2-Bromo-but-3-yne was prepared by the method of Black, Landor, Patel & White .[116] A solution of but-3-yn -2-ol (28g, 0.4 mol.) in pyridine (32g) was added dropwise to triphenylphosphite dibromide (235g, 0.5 mol.) with ice cooling and stirring. Stirring was continued at room temperature for 3 hours and the product removed by distillation under reduced pressure. The distillate was washed with dilute hydrochloric acid and then water and dried (49%, b.p. 35 - 40°/100mm, lit.[110] b.p. 43 - 45°/100mm).

The product was found to contain two isomers and no attempt has been made to separate them. They are believed to be 2-bromo-but-3-yne and 1-bromobuta-1,2-diene in the ratio 2:1 by n.m.r.

^{1}H n.m.r.(60MHz, δ) 2-bromobut-3-yne: 1.8 (d, J = 7Hz, 3H, $C\underline{H}_3$), 2.5 (d, J = 2Hz, 1H, $\equiv C\underline{H}$), 4.4 (d of q, J = 2Hz, 7Hz, 1H, $C\underline{H}Br$); 1-bromobuta-1,2-diene: 1.8 (d of d, J = 2Hz, 7Hz, 3H, $C\underline{H}_3$), 5.25 (d of q, J = 6Hz, 7Hz, 1H, $CH_3C\underline{H}$), 5.8 (m, 1H, $C\underline{H}Br$)

i.r.(cm^{-1}): 3300(s) $\equiv$CH, 2100(w) C$\equiv$C, 1960(w) C=C=C

7.3.17 1-Bromobut-2-yne was prepared as described by Couffignal, Gaudemar & Perriot.[117] A solution of sodium hydroxide (110g) in water (110g) was added dropwise at 10 - 15°C to propargyl alcohol (112g, 2 mol.), dimethyl sulphate (130g, 1.03 mol.) and water (70ml), and the mixture stirred for 30 minutes at room temperature. The reaction mixture was distilled to give 1-methoxyprop-2-yne (26%, b.p. 61°).

This product (36g) was added dropwise to sodium (12g, 0.52 mol.) in liquid ammonia (500ml) containing ferric nitrate (1g), and the mixture stirred for 2 hours. Methyl iodide (71g, 0.5 mol.) was added dropwise over 1.5 hours and the mixture left for 50 hours to allow the ammonia to evaporate. Extraction of the product with ether, filtering and removal of solvent gave 1-methoxybut-2-yne (12g, 27%).

A mixture of 1,2-dibromoethane (2g), zinc (0.7g) and THF (5ml) was refluxed until the metal dissolved, the solvent removed and the residue maintained at 120°C and 0.5mm for 2 hours. This mixture was then cooled and combined with acetyl bromide (19g, 0.15 mol.) heated to 60°C and 1-methoxybut-2-yne (12g, 0.14 mol.) added dropwise and stirred for 0.5 hours. The mixture was poured out onto ice and extracted into ether. Drying the ether fractions, removal of the solvent and distillation of the product under reduced pressure gave 1-bromobut-2-yne (71%, b.p. 52°, lit.[117] b.p. 52.5°).

7.3.18 1-Bromo-3-methylbuta-1,2-diene was prepared as described by Watson.[45] 3-Methylbut-1-yne-3-ol (50g, 0.6 mol.), hydrobromic acid (48%w/w, 125ml), cuprous bromide (25g, 0.17 mol.) and diglyme (6.0g) were placed in a stoppered conical flask and left for 6 hours at room temperature. After this time the original solution had separated into two phases. The top organic layer was separated and washed with hydrobromic acid (3 x 25ml) and dried. Distillation gave 1-bromo-3-methylbuta-1,2-diene, (60 - 70%, b.p. 69 - 70°/95mm, lit.[112] b.p. 53.4°/60mm), as a colourless liquid which was stored at -15°C under nitrogen.

7.3.19 1-Bromopent-4-yne Pent-4-yne-1-ol (12.5g, 0.149 mol.) in pyridine (10g) was added slowly to triphenylphosphite dibromide (130g) and stirred for 2 hours. The reaction mixture was carefully distilled under reduced pressure to give 1-bromopent-4-yne (46%, b.p. 38 - 44°/30mm).

7.3.20 E and Z-5-Bromohex-3-en-1-yne (121a) and (121b) were prepared by the method of Dulcère, Gore and Roumestant.[118] Hex-4-en-1-yn-3-ol (28g, 0.29 mol.) was added quickly to hydrobromic acid (100ml, 48%), stirring for one minute, and extracting into light petroleum. Drying of the extracts and removal of the solvent gave 5-bromohex-3-en-1-yne (73%, b.p. 72 - 80°/46mm, lit.[118] b.p. 44 - 48°/12mm). The product was shown by ^{1}H n.m.r. to consist of the E and Z isomers in the ratio 2.3 :1. These could be separated by alumina or silica gel chromatography (eluting in the order Z and then E with light petroleum) but resulted in a large loss of product.

E-5-bromohex-3-en-1-yne (121a)

^{1}H n.m.r.(δ): 1.73 (d, J = 7Hz, 3H, CH_3), 2.81 (d, J = 2Hz, 1H, $\equiv CH$), 4.56 (d of q of d, J = 8Hz, 7Hz, 1Hz, 1H, BrCH), 5.54 (d of d of d, J = 15Hz, 2Hz, 1Hz, 1H, $\equiv C.CH=$), 6.26 (d of d, J = 15Hz, 8Hz, 1H, $=CH.CBr$)

i.r.(cm^{-1}): 3290(s) ≡CH, 2100(w) C≡C, 950(s) trans olefin

Z-5-bromohex-3-en-1-yne (121b)

^{1}H n.m.r.(δ): 0.81 (d, J = 7Hz, 3H, CH_3), 2.23 (d, J = 2Hz, 1H, ≡CH), 4.20 (d of q, J = 11Hz, 7Hz, 1H, BrCH-), 4.41 (d of d, J = 11Hz, 2Hz, 1H, ≡CCH-), 5.16 (d of d, J = 11Hz, 11Hz, 1H, =CH.CHBr)

i.r.(cm^{-1}): 3290(s) ≡CH, 2100(w) C≡C, 760(s) cis olefin

7.3.21 E and Z-1-Bromo-3-methylpent-2-en-4-yne (124a) and (124b) was prepared as described by Watson.[45] Hydrobromic acid (48%w/w, 25ml), copper I bromide (5g, 0.03 mol.) and diglyme (1.2g) were placed in a 50ml separating funnel and 3-methylpent-1-ene-4-yne-3-ol (10g, 0.1 mol.) in petroleum ether (10ml) added. The reaction occurs very rapidly and after 1 minute the organic layer was removed. The acid layer was extracted with light petroleum (3 x 20ml) and the combined petroleum fractions washed with hydrobromic acid (3 x 10ml) and dried. The solvent was removed and the residue distilled to give 1-bromo-3-methylpent-2-en-4-yne (60 - 65%, b.p. 74°/27mm, lit.[45,118] b.p. 54°/15mm, 47°/12mm).

The product shows two peaks by gas chromatography in the ratio 1 : 6. The major isomer is believed to be the Z-isomer.

Z-1-bromo-3-methylpent-2-en-4-yne (124b)

^{1}H n.m.r.(60MHz, δ): 1.9 (bs, 3H, CH_3), 3.3 (s, 1H, ≡CH), 4.1 (d, J = 8Hz, 2H, CH_2Br), 6.0 (bt, J = 8Hz, 1H, =CH)

i.r.(cm^{-1}): 3280(s) ≡CH, 2090(w) C≡C, 1620(s) alkene conjugated to C≡C, 1430(s), 1200(s), 850(s)

7.4 Preparation of Dimethylvinylidene Cyclopropanes

Dimethylvinylidene cyclopropanes were prepared by either method A or method B detailed below. The products were characterised by i.r. and n.m.r. spectroscopy and were stored at -15°C.

Method A: 1-Bromo-3-methylbuta-1,2-diene (12g, 0.08ml) in light petroleum (10ml) was added, under nitrogen, over 0.5 hours, to a magnetically stirred slurry of potassium t-butoxide (18.6g, 0.1 mol.) in a solution of olefin (0.04 mol.) in light petroleum (10ml) at -10°C. The coloured reaction mixture was stirred for a further 1 hour and then allowed to attain room temperature. Water (20ml) was added and the pH adjusted to about 5 with dilute hydrochloric acid while vigorously stirring (there is an accompanying colour change). The red organic layer was separated and the aqueous layer extracted with light petroleum (3 x 20ml). The combined organic layers were washed with water, saturated sodium chloride solution, and then dried. The solvent was removed and the excess olefin distilled off under high vacuum (0.1mm) to leave the crude adduct which was purified by alumina chromatography.

Method B: The olefin (0.03mol.), 1-bromo-3-methylbuta-1,2-diene (7g, 0.05 mol.) plus aqueous potassium hydroxide (50g, 50%) and benzyltriethylammonium chloride (0.2g) were stirred vigorously using a magnetic stirrer for several hours with external heating in some cases. The mixture was diluted with water (50ml), extracted with light petroleum (3 x 20ml) and dried. Excess starting materials were removed under high vacuum (0.1mm) and the products purified by alumina chromatography.

Pertinent details for each cyclopropane prepared are given below.

7.4.1 2,3-Benzo-6-dimethylvinylidenebicyclo [3,1,0] hex-2-ene (86)[21]

olefin : indene

Method A: yield 26%

Method B: The reaction mixture was stirred for 4 hours with no external heating; yield 20%. A small amount (7%) of 3-(1'-dimethylprop-2'-ynyl)indene (95) was also obtained (for spectra see section 7.7.9).

The cyclopropane product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.[21]

7.4.2 2,3-Benzo-6-dimethylvinylidene-1-methylbicyclo [3,1,0] hex-2-ene (87)[21]

olefin : 3-methylindene

Method A was used by Stewart,[21] yield 40 - 45%, and has not been repeated.

Method B: The reaction mixture was stirred for 3 hours at 80°C; yield 55%.

m.p.(ethanol): 65°, lit.[21] 70 - 70.5°

The cyclopropane product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.[21]

7.4.3 2,3-Benzo-6-dimethylvinylidene-1-ethylbicyclo [3,1,0] hex-2-ene (89)

olefin : 3-ethylindene

Method A: yield 90%

Method B: The reaction mixture was stirred for 6 hours at 80°C; yield 20%.

m.p.(ethanol): 28 - 29°

^1H n.m.r.(δ): 0.98 (t, J = 7Hz, 3H, $CH_2\underline{CH}_3$), 1.58 (s, 3H, $C\underline{H}_3$), 1.73 (s, 3H, $C\underline{H}_3$), 2.04, 2.15 (2 x q, J = 7Hz, 2H, non-equivalent $C\underline{H}_2CH_3$), 2.37 (d of d, J = 6Hz, 1Hz, 1H, cyclopropyl $\underline{H}$), 3.04 (bd, J = 17Hz, Ar$C\underline{H}$ syn to cyclopropyl H), 3.30 (d of d, J = 17Hz, 6Hz, 1H, Ar$C\underline{H}$ anti to cyclopropyl $\underline{H}$), 7.0 - 7.2 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 2010(w) allene, 1440(s), 760(s) o-disubstitution

m.s.(m/e): 210.141594 (M^+, base peak; $C_{16}H_{18}$ requires 210.140844), 195, 181, 167

analysis: found C, 91.2 ; H, 8.7, $C_{16}H_{18}$ requires C, 91.4 ; H, 8.6

7.4.4. 2,3-Benzo-6-dimethylvinylidene-5-methylbicyclo [3,1,0] hex-2-ene (88)[76]

olefin : 2-methylindene

Method A: yield 38%

Method B: no product was isolated

The product was identified by comparison of its ^1H n.m.r. and i.r. spectra with those published.[76]

7.4.5 2,3-Benzo-6-dimethylvinylidene-1,5-dimethylbicyclo [3,1,0] hex-2-ene (90)

olefin : 2,3-dimethylindene

Method A: yield 80%

Method B: yield negligible after 10 hours

m.p.(ethanol): 46 - 47°

^1H n.m.r.(δ): 1.40, 1.51, 1.56, 1.70 (4 x s, 12H, 4 x CH_3), 3.01, 3.21 (AB spectrum, J = 14Hz, 2H, $ArCH_2$), 6.9 - 7.2 (m, 4H, ArH)

^{13}C n.m.r.(p.p.m.): 13.5, 17.2 (2 x cyclopropyl CH_3); 21.2, 21.8 (2 x olefinic CH_3), 34.7, 40.7 (C-1 and C-5), 42.5 (C-4), 91.1 (CMe_2), 94.8 (C-6), 122.1, 124.6, 125.5, 126.1 (Aromatic CH), 141.5, 148.3 (C-2 and C-3), 183.0 (allenic C)

i.r.(cm^{-1}): 2000(s) allene, 1430(s), 1060(m), 1030(s), 760(s), 720(s)

analysis: found C, 91.2 ; H, 8.7, $C_{16}H_{18}$ requires C, 91.4 ; H, 8.6

7.4.6 2,3-Benzo-7-dimethylvinylidenebicyclo [4,1,0] hept-2-ene (92)

olefin : 1,2-dihydronaphthalene

Method A: yield 30%

Method B: no reaction after 6 hours at 80°

m.p.(ethanol): 50 - 52°

^{1}H n.m.r.(δ): 1.63, 1.72 (2 x s, 6H, 2 x C$\underline{H}_3$), 2.0 - 2.7 (m, 5H, aliphatic C$\underline{H}$), 2.81 (d, J = 8Hz, H-5 coupled to the inequivalent proton on the same carbon), 6.8 - 7.3 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 2010(s) allene, 740(s)

analysis: found C, 91.8 ; H, 8.4, $C_{15}H_{16}$ requires C, 91.8 ; H, 8.2

7.4.7 2,3-Benzo-7-dimethylvinylidene-1-methylbicyclo [4,1,0] hept-2-ene (94)

olefin : 4-methyl-1,2-dihydronaphthalene

Method A: yield 90%

m.p.(ethanol): 34 - 35°

^{1}H n.m.r.(δ): 1.62, 1.65, 1.72 (3 x s, 9H, 3 x C$\underline{H}_3$), 2.00 - 2.30 (m, 3H, C$\underline{H}_2$ + C$\underline{H}$), 2.46 - 2.70 (m, 2H, C$\underline{H}_2$), 6.86 - 7.40 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 2010(m) allene, 1440(s), 740(s)

analysis: found C, 91.2 ; H, 8.7, $C_{16}H_{18}$ requires C, 91.4 ; H, 8.6

7.4.8 2,3-Benzo-7-dimethylvinylidene-6-methylbicyclo [4.1.0] hept-2-ene (93)

olefin : 3-methyl-1,2-dihydronaphthalene

Method A: yield 34%

m.p.(ethanol): 51 - 53°

^{1}H n.m.r.(δ): 1.44, 1.63, 1.72 (3 x s, 9H, 3 x C$\underline{H}_3$), 2.03 (d of t, J = 13Hz, 4Hz, 1H, cyclopropyl-$\underline{H}$), 2.45 - 2.70 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$), 6.8 - 7.2 (m, 4H, Ar$\underline{H}$)

i.r.(mull, cm^{-1}): 2010(s) allene, 1460(s), 1375(s), 750(s)

analysis: found C, 91.2 ; H, 8.7, $C_{16}H_{18}$ requires C, 91.4 ; H, 8.6

7.5 Preparation of 2-Vinylpropenylidene Cyclopropanes

These were prepared using potassium t-butoxide, as in section 7.4 method A, and a twofold excess of 1-bromo-3-methylpent-2-en-4-yne over the olefin. The product mixtures were separated by alumina chromatography to give the cyclopropanes as pale yellow oils or white crystals which were stored at -15°C. The products consisted of equal amounts of the E and Z isomers (by ^{1}H n.m.r.). These were not separated.

Several side reactions occur, the most important being nucleophillic attack on the bromide by the indenyl anion to give (3'-methylpent-2'-en-4'-ynyl)indenes. These are better prepared pure by a phase transfer catalysed reaction and are described in section 7.7. No cyclopropanes were obtained using the phase transfer method.

The order of elution from an alumina column using light petroleum and light petroleum-ether mixtures was recovered olefin - spiro compound - cyclopropane - acetylenes.

7.5.1 E and Z-2,3-Benzo-6(2'-vinylpropenylidene)bicyclo [3,1,0] hexene

olefin : indene

These have not been isolated and their presence was only observed by an allene absorption (2000 cm^{-1}) in the infra-red spectrum of the crude product mixture. The main product was E and Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126a) and (126b) (20 - 25%, E:Z = 1 : 5.7 by ^{1}H n.m.r.)

7.5.2 E and Z-2,3-Benzo-1-methyl-6-(2'-vinylpropenylidene)bicyclo [3,1,0] hex-2-ene (96)

olefin : 3-methylindene

yield: 45 - 60%, semicrystaline

^{1}H n.m.r.(δ): 1.68 (s, 3/2H, CH_3 over ring), 1.71 (s, 3H, indene-

$C\underline{H}_3$), 1.83 (s, 3/2H, $C\underline{H}_3$ away from ring), 2.50 (bd, J = 15Hz, 1H, cyclopropyl $\underline{H}$), 3.09, 3.36 (AB spectrum, J = 17Hz, 3.36 is d of d, J = 5Hz, 2H, $ArC\underline{H}_2$), 6.05 (d of d, $C\underline{H}=CH_2$ isomer over ring), 6.32 (d of d, $C\underline{H}=CH_2$, isomer away from ring), 7.0 - 7.3 (m, 4H. $Ar\underline{H}$)

^{13}C n.m.r.(p.p.m.): 15.3, 15.7 (allyl CH_3 - 2 isomers), 17.1 (CH_3), 32.3 (C-5), 36.1 (C-4), 40.0 (C-1), 90.7 (C-6), 103.8, 103.9 (C-2', 2 isomers), 110.8 (C-4'), 122.2, 125.1, 126.0, 126.4 (aromatic C-H), 137.0 (C-3'), 141.3, 146.7 (aromatic C), 188.7 (allene C-1')

i.r.(cm^{-1}): 2000(s) allene, 1440(s), 900(s) vinyl, 765(s), 725(s)

m.s.(m/e): 208.125194 (M^+, base peak, $C_{16}H_{18}$ requires 208.127189), 193, 178

Also isolated were E and Z-1-(3'-methylpent-2'-en-4'-ynyl)-1-methylindene (133) and (130), Z-1-(3'-methylpent-2'-en-4'-ynyl)-3-methylindene (129), (20% in total, ratio (133) : (130) : (129) = 1 : 3 : 6) separated by preparative g.l.c.; and spiro [2-methylene-3-methylcyclopent-3-ene-1,1'-3'-methylindene] (197), 0 - 8%, (see section 7.9.8).

7.5.3 <u>E and Z-2,3-Benzo-5-methyl-6(2'-vinylpropenylidene)bicyclo [3,1,0] hex-2-ene</u> (97)

olefin : 2-methylindene

yield: 20%, semicrystaline

^1H n.m.r.(δ): 1.54 (s, 3H, indene $C\underline{H}_3$), 1.67 (s, 3/2H, $C\underline{H}_3$ over ring), 1.81 (s, 3/2H, $C\underline{H}_3$ away from ring), 3.00 (s, 1H, cyclopropyl $\underline{H}$), 3.08, 3.27 (AB spectrum, J = 16Hz, 2H, $ArC\underline{H}_2$), 4.6 - 5.0 (m, 2H, $=CH_2$), 5.9 - 6.5 (2 x d of d, 1H, -CH= 2 isomers), 6.8 - 7.4 (m, 4H, $Ar\underline{H}$)

i.r.(cm^{-1}): 1950(s) allene, 1620(m), 900(s) vinyl, 750(s), 730(m)

m.s.(m/e): 208.127732 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 193, 178

Also isolated were Z-3(3'-methylpent-2'-en-4'-ynyl)-2-methylindene (99), 35%, and spiro [2-methylene-3-methylcyclopent-3-en-1,1'-2-methyl-

indene] (196), 0 - 6% (see section 7.9.7).

7.5.4 E and Z-2,3-Benzo-1,5-dimethyl-6-(2'-vinylpropenylidene)-bicyclo [3,1,0] hex-2-ene (98)

olefin : 2,3-dimethylindene

yield: 31 - 33%

m.p.(ethanol): 63°

^{1}H n.m.r.(δ): 1.48, 1.60 (2 x s, 6H, indene $C\underline{H}_3$'s), 1.74 (s, 3/2H, E-$C\underline{H}_3$), 1.82 (s, 3/2H, Z-$C\underline{H}_3$), 3.08, 3.30 (AB spectrum, J = 15Hz, 2H, Ar$C\underline{H}_2$), 4.60 - 5.0 (m, 2H, $=C\underline{H}_2$, 2 isomers), 6.06 (d of d, J = 10Hz, 17Hz, -C$\underline{H}$=, Z-isomer), 6.28 (d of d, J = 10Hz, 17Hz, 1H, -C$\underline{H}$=, E-isomer), 7.0 - 7.2 (m, 4H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 13.5 ($\underline{C}H_3$-C-5), 15.3, 15.7 (allenic CH_3, 2 isomers), 17.2 ($\underline{C}H_3$-C-1), 29.7 (C-5), 36.9 (C-1), 42.7 (C-4), 94.5 (C-6), 103.6, 103.9 (C-2', 2 isomers), 110.5, 110.6 (C-4', 2 isomers), 122.2, 124.7, 125.8, 126.3 (aromatic C-H), 137.0, 137.3 (C-3', 2 isomers), 141.3, 147.7 (aromatic C), 187.6, 187.7 (allenic C-1', 2 isomers)

i.r.(cm^{-1}): 1980(s) allene, 1610(m), 1460(s), 890(s) vinyl, 770(m), 730(m)

analysis: found C, 91.7 ; H, 8.3, $C_{17}H_{18}$ requires C, 91.8 ; H, 8.2

There was also a small fraction (~10%) containing acetylenic compounds but these were not isolated. No spiro compounds were observed.

7.6 Preparation of Pent-3 -enylidene Cyclopropanes

These were prepared as described in section 7.5 using a two-fold excess of E and Z-5-bromohex-3-en-1-yne over the olefin. The products were separated by alumina or silica gel chromatography. E and Z-isomers were found as in section 7.5. (1'-Methylpent-2'-en-4'-ynyl)indenes were formed as biproducts and these are described, with their spectra, in section 7.7. The products were eluted with light petroleum and light

petroleum-ether mixtures. The order of elution was recovered olefin - cyclopropane - acetylene.

7.6.1 E and Z-2,3-Benzo-6(E-pent-3'-enylidene)bicyclo[3,1,0]hex-2-ene (101)

olefin : indene

yield: 10%, yellow oil

^{1}H n.m.r.(δ): 1.61 (d, J = 5Hz, 3/2H, C$\underline{H}_3$), 1.72 (d, J = 6Hz, 3/2H, C$\underline{H}_3$), 2.60 - 2.80 (m, 1H, $\underline{H}$-5), 3.10 - 3.46 (m, 3H, $\underline{H}$-4 plus $\underline{H}$-1), 5.20 - 6.30 (m, 3H, olefinic protons), 6.90 - 7.40 (m, 4H, Ar$\underline{H}$)

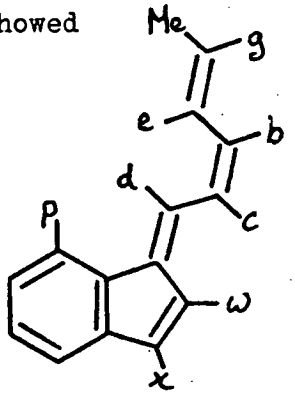
i.r.(cm^{-1}): 2000(s) allene, 960(s) trans olefin, 755(s), 720(m)

m.s.(m/e): 194.109294 (M^+, base peak, $C_{15}H_{14}$ requires 194.109545), 179, 178

Also isolated was E-3-(1'-methylpent-2'-en-4'-ynyl)indene (122a), 24% (see section 7.7). The cyclopropane adduct was difficult to isolate since it rearranged readily on silica gel and more slowly on alumina to give E-1,2-benzo-6-(Z,E-penta-1',3'-dienyl)fulvene (169), a bright yellow oil.

E-1,2-benzo-6-(Z,E-penta-1',3'-dienyl)fulvene (169)

^{1}H n.m.r.(δ): 1.90 (d of d, J = 6Hz, J = 1Hz, 3H, C$\underline{H}_3$), 5.45 (d of d, J = 9Hz, J = 2Hz, 1H, $\underline{H}_b$), 5.58 (s, 1H, $\underline{H}_d$), 5.99 (d of q, J = 15Hz, J = 6Hz, 1H, $\underline{H}_g$ trans to H_e), 6.61 (d of d, J = 15Hz, J = 1Hz, 1H, $\underline{H}_e$), 6.64 (d, J = 5Hz, 1H, $\underline{H}_w$), 6.73 (d, J = 5Hz, 1H, $\underline{H}_x$), 6.88 - 7.20 (m, 4H, Ar$\underline{H}$ + $\underline{H}_c$), 7.54 - 7.72 (m, 1H, $\underline{H}_p$), decoupling showed the methyl is coupled to H_e and H_g



i.r.(cm^{-1}): 1440(s), 1370(m), 960(m) trans olefin, 750(s) o-disubstitution, 720(m) cis olefin

u.v.(n-hexane, mμ): 208 (ε 20600), 238 (12300), 286 (11800), 342 (14500)

m.s.(m/e): 194.107978 (M^+, base peak, $C_{15}H_{14}$ requires 194.109545),

179, 178, 115

7.6.2 E and Z-2,3-Benzo-1-methyl-6(E-pent-3'-enylidene)bicyclo [3,1,0] hex-2-ene (102)

olefin : 3-methylindene

yield: 54%; pale yellow oil

^{1}H n.m.r.(δ): 1.57 - 1.74 (m, 6H, indene-C$\underline{H}_3$ plus =CH-C$\underline{H}_3$ - 2 isomers), 2.40 - 2.58 (m, 1H, cyclopropyl $\underline{H}$), 3.32, 3.06 (AB spectrum, J = 16Hz, 3.32 is d of d, J = 5Hz, 2H, ArC$\underline{H}_2$), 5.2 - 6.0 (m, 3H, H-3', H-4', H-5'), 6.9 - 7.2 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 2000(s) allene, 1480(m), 1450(s), 960(s) trans olefin, 760(s), 720(m)

m.s.(m/e): 208.125337 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 193, 178

No other products were isolated.

7.7 Preparation of Allenes and Acetylenes

Preparation of these compounds was initially attempted by a phase transfer catalytic method, Method A, and, if this was unsuccessful, a method involving sodium in liquid ammonia, Method B, was used.

Method A: The hydrocarbon (0.1 mol.) and the alkynyl bromide (0.12 mol.) were added to aqueous potassium hydroxide (50g, 50%) and benzyltriethylammonium chloride (0.2g). The mixture was stirred at high speed and the reaction followed using ^{1}H n.m.r. If no reaction occurred after a few hours then the mixture was heated in a water bath until reaction occurred. The reaction was diluted with water (50ml), extracted into light petroleum (2 x 20ml), and dried. After removal of the solvent the products were purified by silica gel or alumina chromatography or by preparative g.l.c. Unless otherwise stated the products were obtained as pale yellow oils.

Method B: Sodium (2.3g, 0.1 mol.) was added in small pieces to liquid ammonia (100ml) containing ferric nitrate catalyst (few crystals), and stirred until the blue colour disappeared. Indene, cyclopentadiene or fluorene (0.1 mol.) was added and the mixture stirred for 1 hour. The alkynyl bromide (0.1 mol.) was added dropwise and the mixture stirred overnight to evaporate the ammonia. The mixture was extracted with ether (3 x 20ml), the extracts dried, and the solvent removed under reduced pressure. The products were purified by silica gel or alumina chromatography.

This method was found to give only tars when used for the bromo-enynes.

7.7.1 The Reaction of Indene with Propargyl Bromide

Method A: Stirring for 4 hours gave 3-propargylindene (104), 60%, and 1,1-dipropargylindene (105), 30%. Stirring for 2 hours at 80°C yielded indene, 50%, 1-propargylindene (103), 20%, and 3-propargylindene, 10%. The products were separated by silica gel chromatography eluting with light petroleum and light petroleum-ether mixtures. The products eluted in the order printed above. When excess bromide was used the percentage of dipropargyl product increased.

3-propargylindene (104)

b.p.: 118°/10mm, 58°/0.2mm, lit.[14,119] 74°/0.5mm, 65°/0.5mm

^{1}H n.m.r.(δ): 2.06 (t, J = 3Hz, 1H, ≡C-H), 3.20 (bs, 2H, CH_2-C≡), 3.32 (bs, 2H, ArCH_2), 6.36 (t, J = 2Hz, =CH-), 7.0 - 7.5 (m, 4H, ArH), decoupling triplet at 2.06δ affects the peak at 3.20δ.

^{13}C n.m.r.(p.p.m.): 17.9 (CH_2), 37.5 (ArCH_2), 70.2 (≡C-H), 80.8 (-C≡), 118.7, 123.7, 124.9, 126.0, 129.7 (aromatic and olefinic CH), 138.6, (olefinic C), 143.9, 144.3 (aromatic C)

i.r.(cm^{-1}): 3300(s) ≡CH, 2120(w) C≡C, 1460(s), 1420(m), 910(s), 770(s), 720(s), 625(s)

m.s.(m/e): 154.077499 (M^+, base peak, $C_{12}H_{10}$ requires 154.078247)

1-propargylindene (103)

b.p.: 54°/0.2mm

^1H n.m.r.(δ): 1.97 (t, J = 3Hz, 1H, ≡C<u>H</u>), 2.17, 2.53 (AB spectrum, J = 17Hz, lower frequency doublet split d of d, J = 9Hz, 3Hz, higher frequency doublet split d of d, J = 7Hz, 3Hz, 2H, C<u>H</u>$_2$C≡), 3.50 (bt, J = 8Hz, ArC<u>H</u>), 6.47, 6.71 (AB spectrum, J = 6Hz, split d, J = 2Hz, 2H, C<u>H</u>=C<u>H</u>), 6.94 - 7.32 (m, 3H, Ar<u>H</u>), 7.33 - 7.50 (m, 1H, Ar<u>H</u>)

^{13}C n.m.r.(p.p.m.): 21.0 (CH_2), 48.7 (CH), 69.2 (≡CH), 82.6 (-C≡), 121.1, 123.0, 125.0, 127.0, 131.7, 138.1 (olefinic and aromatic CH), 144.1, 146.0 (aromatic C)

i.r.(cm^{-1}): 3300(s) ≡CH, 2110(w) C≡C, 1460(s), 800 - 650 (4 strong bands) cyclic CH=CH

m.s.(m/e): 154.077049 (M^+, base peak, $C_{12}H_{10}$ requires 154.078247)

1,1-dipropargylindene (105)

m.p.(methanol): 53 - 54°, white crystals

^1H n.m.r.: 1.91 (t, J = 2Hz, 2H, 2 x ≡C<u>H</u>), 2.58 (m, 4H, 2 x C<u>H</u>$_2$), 6.44, 6.69 (AB spectrum, J = 6Hz, 2H, C<u>H</u>=C<u>H</u>), 7.0 - 7.3 (m, 3H, Ar<u>H</u>), 7.47 - 7.62 (bd, J = 6Hz, 1H, Ar<u>H</u>)

i.r.(cm^{-1}): 3300(s) ≡CH, 2110(w) C≡C, 1720(m), 1460(m), 1420(m), 1360(m), 785(s), 760(s)

analysis: found C, 93.5 ; H, 6.3, $C_{15}H_{12}$ requires C, 93.7 ; H, 6.3

7.7.2 <u>Reaction of 3-Methylindene with Propargyl Bromide</u>

Method A: Stirring the reaction mixture for 3 hours at 80° gave complete reaction. The products were separated on silica gel to give 3-methyl-1-propargylindene (106) and 1-methyl-1-propargylindene (107) as

a mixture, 59%, in the ratio 2:1 and 1,1-dipropargyl-3-methylindene (108) and 1,3-dipropargyl-1-methylindene (108/1) as a mixture, 35%. in the ratio 1:1. The isomers were separated pure using preparative g.l.c. (10% PMPE, 150°).

m.s. of mixture (m/e): 206 (dipropargylmethylindene), 168.092913 (monopropargylmethylindene; $C_{13}H_{12}$ requires 168.093896), 167, 129

3-methyl-1-propargylindene (106)

^{1}H n.m.r.(δ): 1.86 (m, 1H, ≡C<u>H</u>), 2.08 (d, J = 2Hz, 3H, C<u>H</u>$_3$), 2.13, 2.52 (AB spectrum, J = 16Hz, lower frequency doublet split d of d, J = 8Hz, 3Hz, higher frequency doublet split d of d, J = 7Hz, 3Hz, 2H, C<u>H</u>$_2$), 3.44 (bt, J ≏ 7Hz, 1H, ArC<u>H</u>), 6.14 (bs, 1H, =C<u>H</u>), 6.95 - 7.26 (m, 3H, Ar<u>H</u>), 7.28 - 7.48 (bd, J = 6Hz, 1H, Ar<u>H</u>)

1-methyl-1-propargylindene (107)

^{1}H n.m.r.(δ): 1.40 (s, 3H, C<u>H</u>$_3$), 1.89 (t, J = 3Hz, 1H, ≡C<u>H</u>), 2.20, 2.48 (AB spectrum, J = 16Hz, split d, J = 3Hz, 2H, C<u>H</u>$_2$), 6.38, 6.60 (AB spectrum, J = 5Hz, 2H, C<u>H</u>=C<u>H</u>), 7.00 - 7.36 (m, 4H, Ar<u>H</u>)

i.r.(cm^{-1}): 3270(s) ≡CH, 2100(w) C≡C, 1500(s), 770(s), 755(s) cyclic olefin

1,1-dipropargyl-3-methylindene (108)

^{1}H n.m.r.(δ): 1.87 (t, J = 2Hz, 2H, 2 x ≡C<u>H</u>), 2.08 (bs, 3H, C<u>H</u>$_3$), 2.52 (bs, 4H, 2 x C<u>H</u>$_2$), 6.09 (bs, 1H, =C<u>H</u>-), 6.95 - 7.20 (m, 3H, Ar<u>H</u>), 7.40 - 7.56 (bd, J = 6Hz, 1H, Ar<u>H</u>)

i.r.(cm^{-1}): 3270(s) ≡CH, 2110(w) C≡C, 760(s), 750(s)

m.s.(m/e): 206.107415 (M^+, base peak, $C_{16}H_{14}$ requires 206.109545), 191, 167, 152

1,3-dipropargyl-1-methylindene (108/1)

^{1}H n.m.r.(δ): 1.40 (s, 3H, C<u>H</u>$_3$), 1.99 (t, J = 3Hz, 1H, ≡C<u>H</u>), 2.30,

2.37 (AB spectrum, J = 3Hz, 2H, $CH_3.C.C\underline{H}_2$), 3.32 (m, 2H, $=C.C\underline{H}_2$), 6.52 (m, 1H, $=C\underline{H}-$), 7.0 - 7.4 (m, 4H, Ar$\underline{H}$)

7.7.3 Reaction of 2-Methylindene with Propargyl Bromide

Stirring the reaction mixture two hours gave a complex mixture partially separated on silica gel and the individual fractions were fully separated using preparative g.l.c. (10% NPGS, 160°) to give 2-methyl-1-propargylindene (109) and 2-methyl-3-propargylindene (110), 58%, ratio 1:2; 1,1 and 1,3-dipropargyl-2-methylindene (111) and (112), 16%, ratio 1:2; 2-methyl-1,1,3-tripropargyl-2-methylindene (113), < 5%, and unchanged 2-methylindene, 23%.

m.s. of mixture (m/e): 244 - tripropargyl product, 206 - dipropargyl product, 168.093503 - monopropargyl product ($C_{13}H_{12}$ requires 168.093896).

2-methyl-1-propargylindene (109)

^{1}H n.m.r.(δ): 1.79 (t, J = 3Hz, 1H, $\equiv C\underline{H}$), 2.08 (bs, 3H, $C\underline{H}_3$), 2.32, 2.62 (AB spectrum, J = 17Hz, lower frequency doublet split d of d, J = 8Hz, 3Hz, higher frequency doublet split d of d, J = 6Hz, 3Hz, 2H, $C\underline{H}_2$), 3.24 (bt, 7Hz, 1H, C$\underline{H}$), 6.34 (bs, 1H, $=C\underline{H}$), 6.86 - 7.14 (m, 3H, Ar$\underline{H}$), 7.43 (bd, J = 6Hz, 1H, Ar$\underline{H}$)

i.r.(cm^{-1}): 3280(s) ≡CH, 2120(w) C≡C, 1460(s), 1430(s), 750(s)

2-methyl-3-propargylindene (110)

^{1}H n.m.r.(δ): 1.79 (t, J = 2Hz, 1H, $\equiv C\underline{H}$), 2.09 (s, 3H, $C\underline{H}_3$), 3.22, 3.32 (2 x bs, 4H, 2 x $C\underline{H}_2$), 6.94 - 7.34 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 3290(s) ≡CH, 2120(w) C≡C, 1720(s), 1460(s), 760(s)

1,1-dipropargyl-2-methylindene (111)

^{1}H n.m.r.(δ): 1.75 (t, J = 3Hz, 2H, 2 x $\equiv C\underline{H}$), 2.01 (d, J = 2Hz, 3H, $C\underline{H}_3$), 2.41, 2.69 (AB spectrum, J = 16Hz, split d, J = 3Hz, 4H,

2 x $C\underline{H}_2$), 6.33 (bs, 1H, =$C\underline{H}$-), 6.96 - 7.16 (m, 3H, Ar$\underline{H}$), 7.38 - 7.48 (m, 1H, Ar$\underline{H}$)

1,3-dipropargyl-2-methylindene (112)

m.p.(ethanol): 77 - 78°, white crystals

^{1}H n.m.r.(δ): 1.78 (t, J = 3Hz, 1H, 2 x ≡$C\underline{H}$), 2.40 (s, 3H, $C\underline{H}_3$), 2.29, 2.61 (AB spectrum, J = 16Hz, lower frequency doublet split d of d, J = 8Hz, 3Hz, higher frequency doublet split d of d, J = 6Hz, 3Hz, 2H, $CHC\underline{H}_2$), 3.24 (bt, 1H, $C\underline{H}$), 3.28 (d, J = 3Hz, 2H, =C.$C\underline{H}_2$), 6.92 - 7.30 (m, 3H, Ar$\underline{H}$), 7.44 (bd, J = 5Hz, 1H, Ar$\underline{H}$)

2-methyl-1,1,3-tripropargylindene (113)

^{1}H n.m.r.(δ): 1.70 - 1.82 (m, 3H, 3 x ≡$C\underline{H}$), 2.00 (s, 3H, $C\underline{H}_3$) 2.41, 2.68 (AB spectrum, J = 17Hz, split d, J = 3Hz, 4H, $C\underline{H}_2$-C-$C\underline{H}_2$), 3.30 (d, J = 2Hz, 2H, =C.$C\underline{H}_2$), 7.00 - 7.54 (m, 4H, Ar$\underline{H}$)

7.7.4 The Reaction of Fluorene with Propargyl Bromide

By method A, stirring at 80°C for 5 hours gave mainly 9,9-dipropargylfluorene (114), 50%, plus recovered fluorene (40%). A little 9-propargylfluorene (115), 23%, was prepared using excess fluorene. The mixture was separated on alumina eluting with light petroleum and light petroleum-ether. The compounds elute in the order fluorene - monopropargyl - dipropargyl.

9,9-Dipropargylfluorene (114) was better prepared by method B using 2 moles of propargyl bromide to 1 mole of fluorene. Chromatography through alumina followed by recrystalization from ethanol gave 9,9-dipropargylfluorene (114), (80%, white crystals: m.p. 112 - 114°).

9-propargylfluorene (115)

^{1}H n.m.r.(δ): 1.95 (t, J = 2Hz, 1H, ≡$C\underline{H}$), 2.60 (d of d, J = 7Hz, 2Hz, 2H, $C\underline{H}_2$), 3.96 (t, J = 7Hz, 1H, $C\underline{H}$), 7.06 - 7.40 (m, 4H, Ar$\underline{H}$),

7.54 - 7.74 (m, 4H, ArH)

i.r.(cm^{-1}): 3300(s) ≡CH, 2120(w) C≡C, 1450(s), 740(s)

m.s.(m/e): 204.091561 (M^+, base peak, $C_{16}H_{12}$ requires 204.093896), 165

9,9-dipropargylfluorene (114)

^1H n.m.r.(δ): 1.89 (t, J = 3Hz, 2H, 2 x ≡CH), 2.74 (d, J = 3Hz, 4H, 2 x CH_3), 7.10 - 7.40 (m, 4H, ArH), 7.54 - 7.76 (m, 4H, ArH)

^{13}C n.m.r.(p.p.m.): 27.5 (CH_2), 49.9 (C), 70.7 (≡CH), 80.9 (C≡), 119.9, 123.7, 127.2, 128.0 (aromatic CH), 139.9, 148.4 (aromatic C)

i.r.(cm^{-1}, mull): 3260(s) ≡CH, 2120(w) C≡C, 1450(s), 1200(m), 760(s), 735(s), 665(s), 640(s)

m.s.(m/e): 242.109195 (M^+, base peak, $C_{19}H_{14}$ requires 242.109545), 203

analysis: found C, 94.1 ; H, 5.7, $C_{19}H_{14}$ requires C, 94.2 ; H 5.8

7.7.5 The Reaction of Cyclopentadiene with Propargyl Bromide

The monopropargyl product was prepared by method A keeping the reaction temperature below 30°C for 2 hours to prevent polymerisation; yield, 35 - 42%. Dipropargyl products were also formed, ~30%, and were separated by silica gel chromatography, eluting with light petroleum. The products were not stable enough for separation by preparative g.l.c. and were obtained as mixtures of isomers.

1- and 2-propargylcyclopentadiene (224)

b.p.: 40°/0.2mm, lit.[14] 80°/15mm

^1H n.m.r.(δ): 1.92 (t, J = 3Hz, 1H, ≡CH), 2.84 - 3.00 (m, 2H, CH_2C≡), 3.14 - 3.36 (m, 2H, cyclopentadiene CH_2), 6.10 - 6.50 (m, 3H, cyclopentadiene protons)

i.r.(cm^{-1}): 3300(s) ≡CH, 2120(w) C≡C, 1420(s), 740(s) cis olefin

m.s.(m/e): 142 - dipropargyl, 104.062050 (M^+, base peak, C_8H_8 requires 104.062597)

7.7.6 The Reaction of Indene with 1-Bromobut-2-yne

Method A: Heating the reaction mixture for 1 hour at 40° gave 3(but-2'-ynyl)indene (116), 90%, purified by chromatography on alumina eluting with light petroleum.

3(but-2'-ynyl)indene (116)

^{1}H n.m.r.(δ): 1.76 (t, J = 3Hz, 3H, $C\underline{H}_3$), 3.14 - 3.40 (m, 4H, 2 x $C\underline{H}_2$), 6.32 (t, J = 2Hz, 1H, =C$\underline{H}$), 7.00 - 7.40 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 1430(s), 760(s)

m.s.(m/e): 168.094402 (M^+, base peak, $C_{13}H_{12}$ requires 168.093896), 153, 115

7.7.7 The Reaction of Indene with 2-Bromobut-3-yne (and 1-bromobuta-1,2-diene)

Method A was unsuccessful giving only ~20% of a mixture of products plus recovered indene (~80%).

Method B gave 3-(1'-methylprop-2'-ynyl)indene (118), 35%, and indene, 37%, separated by alumina chromatography eluting with light petroleum and light petroleum-ether mixtures.

3-(1'-methylprop-2'-ynyl)indene (118)

b.p.: 60°/0.2mm

^{1}H n.m.r.(δ): 1.50 (d, J = 7Hz, 3H, $C\underline{H}_3$), 2.02 (d, J = 3Hz, 1H, ≡C$\underline{H}$), 3.22 (bs, 2H, Ar$C\underline{H}_2$), 3.66 (bq, 7Hz, 1H, $C\underline{H}_3CH_3$), 6.31 (bs, 1H, =C$\underline{H}$), 7.02 - 7.46 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 3300(s) ≡CH, 2110(w) C≡C, 1455(s), 780(m), 765(s)

m.s.(m/e): 168.093327 (M^+, base peak, $C_{13}H_{12}$ requires 168.093896), 153,115

7.7.8 The Reaction of Cyclopentadiene with 2-Bromobut-3-yne

Using method A, the reaction mixture was stirred for 2 hours at 30°C. Purification by silica gel chromatography eluting with light petroleum gave a mixture of (1'-methylprop-2'-ynyl)cyclopentadienes (226) in 50% total yield.

(1'-methylprop-2'-ynyl)cyclopentadiene (226)

^{1}H n.m.r.(60MHz, δ): 1.4 (d, J = 6Hz, 3H, $C\underline{H}_3$), 1.8 (d of d, J = 6Hz, 2Hz, 1H, $C\underline{H}CH_3$), 2.0 (d, J = 2Hz, $\equiv C\underline{H}$), 2.9 (bs, 2H, $C\underline{H}_2$), 5.0 - 6.6 (m, 3H, cyclopentadiene $\underline{H}$)

i.r.(cm^{-1}): 3300(s) $\equiv C\underline{H}$, 2100(w) C≡C, 1710(m), 1450(m), 1360(s), 900(m), 780(m), 750(m)

m.s.(m/e): 118.077533 (M^+, base peak, C_9H_{10} requires 118.078247), 103, 91

7.7.9 The Reaction of Indene with 1-Bromo-3-methylbuta-1,2-diene

As the vinylidene cyclopropane was obtained by method A (section 7.4.1), method B was used. Purification by chromatography on alumina gave 3(1',1'-dimethylprop-2'-ynyl)indene (117), 44%.

3(1',1'-dimethylprop-2'-ynyl)indene (117)

b.p.: 64°/0.2mm

^{1}H n.m.r.(δ): 1.60 (s, 6H, 2 x $C\underline{H}_3$), 2.05 (s, 1H, $\equiv C\underline{H}$), 3.20 (d, J = 2Hz, 2H, $ArC\underline{H}_2$), 6.22 (t, J = 2Hz, 1H, $=C\underline{H}-$), 6.96 - 7.40 (m, 3H, Ar$\underline{H}$), 7.62 - 7.78 (d, J = 6Hz, 1H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 29.1 ($(CH_3)_2$), 31.9 (C), 37.2 (CH_2), 68.9 (≡CH), 90.1 (C≡), 121.9, 123.9, 124.5, 124.7, 125.7 (aromatic and olefinic CH), 142.9, 145.2, 148.4 (aromatic and olefinic C)

i.r.(cm^{-1}): 3300(s) ≡CH, 2100(w) C≡C, 1460(s), 770(s)

m.s.(m/e): 182.108605 (M^+, base peak, $C_{14}H_{14}$ requires 182.109545)

7.7.10 The Reaction of Cyclopentadiene with 1-Bromo-3-methylbuta-1,2-diene

Method B gave the monosubstituted cyclopentadiene as a mixture of isomers, yield 22%.

(1',1'-dimethylprop-2'-ynyl)cyclopentadiene

^{1}H n.m.r.(δ, 60MHz): 1.4 (bs, 6H, $(C\underline{H}_3)_2$), 2.0 (s, 1H, $\equiv C\underline{H}$), 2.9 (bs, 2H, $C\underline{H}_2$), 6.0 - 6.7 (m, 4H, cyclopropyl $\underline{H}$)

7.7.11 The Reaction of Indene with 1-Bromopent-4-yne

Method A was used. Stirring the reaction mixture for 3 hours gave 3(pent-4'-ynyl)indene (119), 50%.

3(pent-4'-ynyl)indene (119)

^{1}H n.m.r.(δ): 1.83 (t, J = 2Hz, 1H, $\equiv C\underline{H}$), 1.70 - 2.04 (m, 2H, $CH_2C\underline{H}_2CH_2$), 2.19 (t of d, J = 6Hz, 2Hz, 2H, $C\underline{H}_2C$), 2.60 (bt, J = 7Hz, 2H, indene-$C\underline{H}_2$), 3.20 (bs, 2H, $ArC\underline{H}_2$), 6.09 (bs, 1H, $=C\underline{H}-$), 7.00 - 7.50 (m, 4H, $Ar\underline{H}$)

i.r.(cm^{-1}): 3300(s) $\equiv$CH, 2110(w) C$\equiv$C, 1460(s), 1400(s), 960(m), 770(s), 720(s)

m.s.(m/e): 182.107504 (M^+, base peak, $C_{14}H_{14}$ requires 182.109545), 167, 130, 115

7.7.12 The Reaction of 2-Methylindene with 1-Bromopent-4-yne

Method A: Heating the reaction mixture at 80°C for 1 hour gave a 43% yield of 2-methyl-3(pent-4'-ynyl)indene (120)

2-methyl-3(pent-4'-ynyl)indene (120)

^{1}H n.m.r.(δ): 1.80 (t, J = 2Hz, 1H, $\equiv C\underline{H}$), 1.65 - 1.92 (m, 2H, $CH_2C\underline{H}_2CH_2$), 2.03 (s, 3H, $C\underline{H}_3$), 1.96 - 2.34 (m, 2H, $C\underline{H}_2C\equiv$), 2.60 (t, J = 7Hz, 2H, indene-$C\underline{H}_2$), 3.16 (s, 2H, $ArC\underline{H}_2$), 6.85 - 7.30 (m, 4H, $Ar\underline{H}$)

i.r.(cm^{-1}): 3300(s) ≡CH, 2110(w) C≡C, 1460(s) $CH_2C{\equiv}C$, 760(s), 720(s)

m.s.(m/e): peak at 196 is small, large peak at 195 ($C_{15}H_{15}$), 182, 167, 165, 155

7.7.13 The Reaction of Indene with E and Z-2-Bromohex-3-en-5-yne

Method A: Stirring the reaction mixture with the E and Z bromoenyne for 3 hours gave E and Z-3-(1'-methylpent-2'-en-4'-ynyl)indene (122a) and (122b), 80 - 87%, ratio E:Z = 2:1, plus a trace of E-1,2-benzo-6-(Z,E-penta-1',3'-dienyl)fulvene (169), (see section 7.6.1). The E and Z isomers were separated using chromatography on silica gel eluting in the order Z then E with light petroleum or by preparative g.l.c. (20% N.P.G.S., 160°C).

When pure Z-bromoenyne was used only the Z-product was formed.

m.s. of mixture (m/e): 194.108730 (M^+, base peak, $C_{15}H_{14}$ requires 194.109545), 179

E-3-(1'-methylpent-2'-en-4'-ynyl)indene (122a)

^{1}H n.m.r.(δ): 1.34 (d, J = 7Hz, 3H, CH_3), 2.60 (d, J = 2Hz, 1H, ≡C<u>H</u>), 3.22 (s, 2H, $C\underline{H}_2$), 3.50 (bt, J = 7Hz, 1H, H-1'), 5.41 (d of q, J = 16Hz, 1Hz, H-3'), 6.13 (bs, 1H, H-2), 6.30 (d of d, J = 16Hz, 7Hz, 1H, H-2'), 6.9 - 7.5 (m, 4H, Ar<u>H</u>)

^{13}C n.m.r.(p.p.m.): 18.8 (CH_3), 35.9 (CH), 37.7 (CH_2), 76.8 (≡CH), 82.3 (C≡), 108.2, 119.6 (CH=CH), 123.8, 124.7, 126.0, 128.0 (ArCH), 144.2, 144.5, 145.4, 148.9

i.r.(cm^{-1}): 3290(s) ≡CH, 2100(w) C≡C, 1455(s), 920(s), 770(s), 720(m)

Z-3-(1'-methylpent-2'-en-4'-ynyl)indene (122b)

^{1}H n.m.r.(δ): 1.40 (d, J = 7Hz, 3H, C$\underline{H}_3$), 3.06 (d, J = 2Hz, 1H, ≡C$\underline{H}$), 3.25 (bs, 2H, ArC$\underline{H}_2$), 3.96 - 4.25 (m, 1H, =C$\underline{H}$CH$_3$), 5.41 (d of d, J = 11Hz, 2Hz, 1H, =C$\underline{H}$-C≡), 5.89 (d of d, J = 10Hz, 11Hz, 1H, cis C$\underline{H}$=CH), 6.14 (bs, 1H, =C$\underline{H}$), 7.00 - 7.45 (m, 4H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 19.0 (CH_3), 34.0 (CH), 37.7 (CH_2), 80.3 (≡C), 82.3 (≡CH), 107.6, 119.8 (CH=CH), 123.7, 124.7, 126.0, 126.9 (aromatic CH), 144.5, 144.7 147.3 (aromatic and olefinic C), 149.2 (indene =CH-)

i.r.(cm^{-1}): 3290(s) ≡CH, 2090(w) C≡C, 1455(s), 770(s), 750(m), 720(m)

7.7.14 <u>The Reaction of 3-Methylindene with E and Z-2-Bromohex-3-en-5-yne</u>

Method A, stirring for 4 hours, gave a complex mixture not yet rationalised.

7.7.15 <u>The Reaction of 2-Methylindene with E and Z-2-Bromohex-3-en-5-yne</u>

Method A was used. Stirring for 4 hours gave a 65% yield of a mixture of E and Z-3(1'-methylpent-2'-en-4'-ynyl)-2-methylindene (123a) and (123b) in the ratio 1:2.2, separated by preparative g.l.c. (20% N.P.G.S., 170°C).

m.s. of mixture (m/e): 208.124773 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 193, 130

E-3-(1'-methylpent-2'-en-4'-ynyl)-2-methylindene (123a)

^{1}H n.m.r.(δ): 1.37 (d, J = 7Hz, 3H, C$\underline{H}_3$CH), 2.03 (s, 3H, C$\underline{H}_3$), 2.59 (d, J = 1Hz, 1H, ≡C$\underline{H}$), 3.18 (s, 2H, C$\underline{H}_2$), 3.67 (m, 1H, C$\underline{H}$), 5.38 (bd, J = 16Hz, 1H, trans =C$\underline{H}$-C≡), 6.40 (d of d, J = 16Hz, 5Hz, 1H, CH-C$\underline{H}$=), 6.80 - 7.30 (m, 4H, Ar$\underline{H}$)

Z-3-(1'-methylpent-2'-en-4'-ynyl)-2-methylindene (123b)

^{1}H n.m.r.(δ): 1.40 (d, J = 7Hz, 3H, $C\underline{H}_3CH$), 2.09 (s, 3H, $C\underline{H}_3$), 2.92 (d, J = 1Hz, 1H, $\equiv C\underline{H}$), 3.16 (bs, 2H, $C\underline{H}_2$), 4.2 (m, 1H, $C\underline{H}$), 5.31 (bd, J = 10Hz, 1H, cis $=C\underline{H}-C\equiv$), 6.36 (d of d, J = 10Hz, 10Hz, 1H, $CH-C\underline{H}=$), 6.9 - 7.4 (m, 4H, Ar$\underline{H}$)

7.7.16 The Reaction of Indene with E and Z-1-Bromo-3-methylpent-2-en-4-yne

Method A was used. Stirring the reaction mixture for 4 hours gave a product which was purified on alumina to give E and Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126a) and (126b) in 60 - 75% yield. Recrystalisation from methanol gave white crystals of pure Z-isomer m.p. 42 - 43°C. The E:Z ratio in the crude product was 1:6 by analytical g.l.c. (5% N.P.G.S., 75°C).

Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126b)

^{1}H n.m.r.(δ): 1.91 (bs, 3H, $C\underline{H}_3$), 3.06 (s, 1H, $\equiv C\underline{H}$), 3.28 (bs, 2H, $ArC\underline{H}_2$), 3.49 (bd, J = 7Hz, $C\underline{H}_2.CH=$), 5.98 (bt, J = 7Hz, 1H, $CH_2C\underline{H}=$), 6.14 (bs, 1H, $=C\underline{H}-$), 7.00 - 7.40 (m, 4H, Ar$\underline{H}$), the E isomer acetylenic proton resonates at 2.65δ in the mixture

i.r.(cm^{-1}): 3300(s) $\equiv$CH, 2100(w) C$\equiv$C, 1460(s), 770(s)

analysis: found C, 92.5 ; H, 7.3, $C_{15}H_{14}$ requires C, 92.7 ; H, 7.3

7.7.17 The Reaction of 3-Methylindene with E and Z-1-Bromo-3-methylpent-2-en-4-yne

Method A was used. Stirring the reaction mixture at 80°C for 2 hours gave a mixture of products, purified on alumina, in 80% yield. These were separated by preparative g.l.c. (10% P.M.P.E., 155°C). Z-1-(3'-methylpent-2'-en-4'-ynyl)-1-methylindene (130) and Z-1-(3'-methylpent-2'-en-4'-ynyl)-3-methylindene (129) were isolated in the ratio

1:2. (The E-isomer of (130), compound (133), was isolated from the preparation of the cyclopropane (96) (see section 7.5.2) and its ^{1}H n.m.r. spectrum is given below for comparison.)

Z-1-(3'-methylpent-2'-en-4'-ynyl)-1-methylindene (130)

^{1}H n.m.r.(δ): 1.39 (s, 3H, indene $C\underline{H}_3$), 1.72 (bs, 3H, $C\underline{H}_3$), 2.42 - 2.90 (m, 1H, $C\underline{H}_2$), 2.94 (s, 1H, $\equiv C\underline{H}$), 5.26 (bt, J = 8Hz, 1H, $=C\underline{H}.CH_2$), 6.26, 6.58 (AB spectrum, J = 5Hz, 2H, $C\underline{H}=C\underline{H}$), 7.00 - 7.30 (m, 4H, Ar$\underline{H}$)

E-1-(3'-methylpent-2'-en-4'-ynyl)-1-methylindene (133)

^{1}H n.m.r.(δ): 1.29 (s, 3H, $C\underline{H}_3$), 1.69 (s, 3H, indene $C\underline{H}_3$), 2.28 - 2.54 (m, 2H, $C\underline{H}_2$), 2.54 (s, 1H, $\equiv C\underline{H}$), 5.68 (bt, J = 8Hz, 1H, $CH_2-C\underline{H}=$), 6.26, 6.61 (AB spectrum, J = 5Hz, $C\underline{H}=C\underline{H}$), 7.00 - 7.36 (m, 4H, Ar$\underline{H}$)

Z-1-(3'-methylpent-2'-en-4'-ynyl)-3-methylindene (129)

^{1}H n.m.r.(δ): 1.78 (bs, 3H, CH_3), 2.08 (t, J = 2Hz, 3H, indene $C\underline{H}_3$), 2.20 - 2.90 (m, 2H, CH_2), 2.93 (s, 1H, $\equiv C\underline{H}$), 3.38 (bt, J = 7Hz, 2H, $C\underline{H}$), 5.57 (bt, J = 7Hz, 1H, $CH_2C\underline{H}=$), 6.02 (bs, 1H, $=C\underline{H}-$), 6.96 - 7.38 (m, 4H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 12.9 (CH_3), 22.8 (indene CH_3), 32.5 (CH_2), 48.5 (benzylic CH_2), 81.1 ($\equiv CH$), 83.0 ($C\equiv C$), 118.9, 122.8, 124.7, 126.5 (aromatic CH), 133.6 (C-2), 137.0 (C-2'), 121.4, 139.1, 145.7, 147.7 (aromatic and olefinic C)

m.s.(m/e): 208.126277 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 193, 129

7.7.18 The Reaction of 2-Methylindene with E and Z-1-Bromo-3-methylpent-2-en-4-yne

Stirring the reaction mixture for 4 hours gave a mixture, in 35% yield, from which were isolated by preparative g.l.c. (10% P.M.P.E. 155°)

Z-1- and 3-(3'-methylpent-2'-en-4'-ynyl)-2-methylindene (128) and (127) in the ratio 2:1, plus some other unidentified products. Passing the mixture through alumina caused rearrangement of the 1- to the 3- isomer.

Z-1-(3'-methylpent-2'-en-4'-ynyl)-2-methylindene (128)

^{1}H n.m.r.(δ): 1.70 (bs, 3H, C$\underline{H}_3$), 2.04 (bs, 3H, indene C$\underline{H}_3$), 2.82 (bt, J = 6Hz, 2H, C$\underline{H}_2$), 2.97 (s, 1H, ≡C$\underline{H}$), 3.27 (bt, J = 5Hz, 1H, C$\underline{H}$.CH$_2$), 5.18 (bt, J = 7Hz, 1H, CH$_2$C$\underline{H}$=), 6.34 (bs, 1H, =C$\underline{H}$), 6.88 - 7.38 (m, 4H, Ar$\underline{H}$)

Z-3-(3'-methylpent-2'-en-4'-ynyl)-2-methylindene (127)

^{1}H n.m.r.(δ): 1.80 (bs, 3H, C$\underline{H}_3$), 2.04 (s, 3H, indene C$\underline{H}_3$), 3.08 (s, 1H, ≡C$\underline{H}$), 3.16 (bs, 2H, ArC$\underline{H}_2$), 3.40 (bd, J = 7Hz, 2H, C$\underline{H}_2$CH=), 5.66 (bt, 7Hz, 1H, =C$\underline{H}$-), 6.84 - 7.26 (m, 4H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 14.0 (indene CH$_3$), 22.8 (CH$_3$), 27.2 (CH$_2$), 42.7 (benzylic CH$_2$), 81.4 (≡CH), 83.3 (-C≡), 118.5, 123.1, 123.7, 126.1 (aromatic CH), 136.7 (=CH-), 117.7, 134.9, 139.2, 142.5, 146.4 (aromatic and olefinic C)

i.r.(cm^{-1}): 3300(s) ≡CH, 2090(w) C≡C, 1460(s), 1430(s), 750(s)

m.s.(m/e): 208.124585 (M$^+$, base peak, $C_{16}H_{16}$ requires 208.125194), 193, 129, 128

7.7.19 <u>The Reaction of 2,3-Dimethylindene with E and Z-1-Bromo-3-methylpent-2-en-4-yne</u>

Stirring the reaction mixture for 2 hours gave a 45% yield of a mixture which was separated by preparative g.l.c. (10% P.M.P.E., 180°C) to give Z-2,3-dimethyl-1-(3'-methylpent-2'-en-4'-ynyl)indene (131) and Z-1,2-dimethyl-1-(3'-methylpent-2'-en-4'-ynyl)indene (132) in the ratio 4:1.

m.s. of mixture (m/e): 222.139682 (M$^+$, base peak, $C_{17}H_{18}$ requires

222.140844), 207, 143

Z-2,3-dimethyl-1-(3'-methylpent-2'-en-4'-ynyl)indene (131)

^{1}H n.m.r.(δ): 1.69 (bs, 3H, C$\underline{H}_3$), 1.95, 1.98 (2 x bs, 6H, 2 x indene C$\underline{H}_3$), 2.78 (bt, J = 6Hz, 2H, C$\underline{H}_2$), 2.95 (s, 1H, ≡C$\underline{H}$), 3.12 - 3.34 (m, 1H, ArC$\underline{H}$), 5.18 (bt, J = 7Hz, 1H, =C$\underline{H}$-), 6.88 - 7.40 (m, 4H, Ar$\underline{H}$), irradiation of the broad singlet at 1.69 sharpened the triplet at 5.18 and vice versa

i.r.(cm^{-1}): 3290(s) ≡CH, 2090(w) C≡C, 1450(s), 760(s)

Z-1,2-dimethyl-1-(3'-methylpent-2'-en-4'-ynyl)indene (132)

^{1}H n.m.r.(δ): 1.20 (s, 3H, C$\underline{H}_3$-1), 1.62 (bs, 3H, C$\underline{H}_3$), 1.90 (d, J = 2Hz, 3H, C$\underline{H}_3$-2), 2.69 (bd, J = 7Hz, 2H, C$\underline{H}_2$), 2.95 (s, 1H, ≡C$\underline{H}$), 4.83 (bt, J = 7Hz, 1H, CH$_2$C$\underline{H}$=), 6.28 (bs, 1H, =C$\underline{H}$), 6.92 - 7.26 (m, 4H, Ar$\underline{H}$), irradiation of the broad singlet at 6.28 sharpened the methyl peak at 1.90, irradiation of the broad triplet at 4.83 decoupled the doublet at 2.69 and sharpened the methyl peak at 1.62

i.r.(cm^{-1}): 3290(s) ≡CH, 1450(s), 750(s)

7.7.20 <u>The Reaction of Fluorene with E and Z-1-Bromo-3-methylpent-2-en-4-yne</u>

Stirring the reaction mixture at 80°C for 2 hours gave a mixture which was separated by silica gel chromatography to give Z-9-(3'-methylpent-2'-en-4'-ynyl)fluorene (134) in 40 - 90% yield, and spiro-[2-methylene-3-methylcyclopent-3-en-1,9'-fluorene], (135), in inconsistent yield - up to 15%.

Z-9-(3'-methylpent-2'-en-4'-ynyl)fluorene (134)

^{1}H n.m.r.(δ): 1.48 (bs, 3H, C$\underline{H}_3$), 2.86 - 3.20 (m, 3H, C$\underline{H}_2$-C$\underline{H}$), 4.98 (bt, J = 7Hz, 1H, C$\underline{H}_2$), 7.00 - 7.90 (m, 8H, Ar$\underline{H}$)

i.r.(cm^{-1}): 3290(s) ≡C<u>H</u>, 2090(w) C≡C, 1450(s), 730(s)

m.s.(m/e): 322 - dialkylation, 244.122927 (M^+, base peak , $C_{19}H_{16}$ requires 244.125194), 228

spiro[2-methylene-3-methylcyclopent-3-en-1,9'-fluorene] (135)

m.p.(ethanol): 60 - 62°, white crystals

^1H n.m.r.(δ): 1.91 (bs, 3H, C<u>H</u>$_3$), 2.91 (bs, 2H, C<u>H</u>$_2$), 4.00, 4.58 (2 x bs, 2H, =C<u>H</u>$_2$), 6.04 (bs, 1H, =C<u>H</u>), 7.04 - 7.40 (m, 6H, Ar<u>H</u>), 7.47 - 7.70 (m, 2H, Ar<u>H</u>)

m.s.(m/e): 244.125930 (M^+, base peak , $C_{19}H_{16}$ requires 244.125194), 229, 165

analysis: found C, 93.2 ; H, 6.4, $C_{19}H_{16}$ requires C, 93.4 ; H, 6.6

7.7.21 <u>The Reaction of Cyclopentadiene with E and Z-1-Bromo-3-methylpent-2-en-4-yne</u>

The reaction mixture was stirred for one hour to give the product which was purified on silica gel to give E and Z-(3'-methylpent-2'-en-4'-ynyl)cyclopentadiene (136), 31%, as a mixture of isomers.

E and Z-(3'-methylpent-2'-en-4'-ynyl)cyclopentadiene (136)

^1H n.m.r.(δ): 1.86 (bs, 3H, C<u>H</u>$_3$), 2.76 - 2.84 (m, 2H, cyclopentadiene C<u>H</u>$_2$), 2.96 (s, 1H, ≡C<u>H</u> Z-isomer), 3.30 (bt, J = 6Hz, 2H, C<u>H</u>$_2$-CH=), 5.66 - 6.46 (m, 4H, cyclopentadiene =C<u>H</u> and CH_2C<u>H</u>=), a small peak at 2.59 is probably due to E isomer acetylenic proton

i.r.(cm^{-1}): 3300(s) ≡CH, 2100(w) C≡C, 1430(m), 1330(s), 890(s)

m.s.(m/e): 144.092390 (M^+, base peak , $C_{11}H_{12}$ requires 144.093896), 129

7.8 Rearrangement of Cyclopropanes

The cyclopropanes prepared in sections 7.4, 7.5 and 7.6 were rearranged either by acid catalysis - methods I and II, or in some cases by base catalysis - method III.

Method I: A solution of ethanolic hydrogen chloride was prepared by bubbling dry HCl gas through ethanol. The molarity was estimated by titration with sodium hydroxide. Unless otherwise stated 1.8M acid was employed.

The cyclopropane (1g) was refluxed in ethanolic hydrogen chloride (25ml) for 5 minutes. Water (25ml) was added, the product extracted into light petroleum (3 x 20ml), dried, and the solvent removed under reduced pressure.

Method II: The cyclopropane (1g) was refluxed with paratoluene-sulphonic acid (0.02g) in carbon tetrachloride (25ml) for several hours until reaction was complete. The reaction was followed by sampling and observing the disappearance of the allène absorption ($2000cm^{-1}$) in the infra-red spectrum. The solution was washed with water, dried and the solvent removed under reduced pressure.

Method III: The cyclopropane (1g) was heated with potassium t-butoxide (1g) in dimethylsulphoxide (25ml) at $100^{\circ}C$ for 0.5 hours. Water (50ml) was added and the product extracted into ether (3 x 20ml). The extracts were dried and the solvent removed under reduced pressure.

In all rearrangements the crude products were examined by ^{1}H n.m.r. before attempting separation and/or purification procedures.

7.8.1 Rearrangement of 2,3-Benzo-6-dimethylvinylidene-bicyclo-[3,1,0] hex-2-ene (86)

Method I gave exclusively 2-(2'-methylprop-1'-enyl)naphthalene (137),

90%, as reported by Stewart[21].

Method III also gave naphthalene (137), 40%, plus intractable material. The product was purified by alumina chromatography eluting with light petroleum.

7.8.2 Rearrangement of 2,3-Benzo-6-dimethylvinylidene-5-methylbicyclo[3,1,0]hex-2-ene (88)

Method I gave mostly 2-(2'-methylprop-1'-enyl)-3-methylnaphthalene (139), 60%, as reported by Robertson[78] which was isolated by preparative g.l.c. (10% P.M.P.E., 180°C). There was also about 20% of other unidentified products.

7.8.3 Rearrangement of 2,3-Benzo-6-dimethylvinylidene-1-methylbicyclo[3,1,0]hex-2-ene (87)

Method I employing various molarities of acid gave product mixtures with up to 38% of components other than the 2-(2'-methylprop-1'-enyl)-1-methylnaphthalene (138) found exclusively by Stewart.[21] (See table 13)

Table 13

Molarity of HCl	(138), %	(140a) + (140b), %
1.87	61	39
0.93	64	36
0.37	64	36
0.19	63	37
0.09	69	31
0.04	73	27
0.02	75	25
0.004	80	20

Exact repetition of Stewart's conditions also gave a mixture of products. The mixture was separated by silica gel chromatography giving as additional components E and Z-2-(1'-chloro-3'-methylbut-1'-enyl)-3-methylindene (140a) and (140b) in the ratio E:Z = 9:1 (by ^{1}H n.m.r.). The products eluted in the order (138), (140b) and then (140a) with light petroleum.

Method II after 12 hours still gave incomplete reaction with some decomposition. There appeared to be several unidentified products but only 2-(2'-methylprop-1'-enyl)-1-methylnaphthalene (138) was isolated by preparative g.l.c., yield 40%.

Method III gave only the naphthalene (138), 50%, after extraction with light petroleum from intractable product.

E and Z-2(1'-chloro-3'-methylbut-1'-enyl)-3-methylindene (140a and b)

m.s. of mixture (m/e): 234.099500 (M^+, base peak, $C_{15}H_{17}{}^{37}Cl$ requires 234.098922), 232.102423 ($C_{15}H_{17}{}^{35}Cl$ requires 232.101872), 196, 181

E-isomer (140a)

^{1}H n.m.r.(δ): 0.98 (d, J = 6Hz, 6H, $C(C\underline{H}_3)_3$), 2.09 (t, J = 2Hz, 3H, indene-$C\underline{H}_3$), 2.20 - 2.48 (m, 1H, $C\underline{H}(CH_3)_2$), 3.48 (q, J = 2Hz, 2H, $ArC\underline{H}_2$), 5.66 (d, J = 10Hz, 1H, =C<u>H</u>-), 6.9 - 7.4 (m, 4H, Ar<u>H</u>)

Z-isomer (140b)

^{1}H n.m.r.(δ): 1.08 (d, J = 6Hz, 6H, $C(C\underline{H}_3)_2$), 2.20 (t, J = 2Hz, indene-$C\underline{H}_3$), 2.68 - 3.20 (m, 1H, $C\underline{H}(CH_3)_2$), 3.52 (q, J = 2Hz, 2H, $ArC\underline{H}_2$), 5.54 (d, J = 9Hz, 1H, =C<u>H</u>-), 7.0 - 7.4 (m, 4H, Ar<u>H</u>)

7.8.4 Rearrangement of 2,3-Benzo-6-dimethylvinylidene-1-ethyl-bicyclo[3,1,0]hex-2-ene (89)

Method I gave a 66% yield of a mixture of equal amounts of 1-ethyl-2-(2'-methylprop-1'-enyl)naphthalene (142) and 2-(1'-chloro-3'-methyl-but-1'-enyl)-3-ethylindene (143). The hydrochloride has not been isolated pure yet but 22% of the pure naphthalene (142) was isolated.

Method II after 8 hours gave a 60% yield of a 3:1 mixture of the naphthalene (142) and 3-ethyl-2-(3'-methylbut-1'-ynyl)indene (144). These were separated by preparative g. l.c. (10% P.M.P.E., 150°C).

Method III gave a 50% yield of the naphthalene plus intractable material.

2-(2'-methylprop-1'-enyl)-1-ethylnaphthalene (142)

b.p.: 86 - 88°/0.3mm

^{1}H n.m.r.(δ): 1.20 (t, J = 8Hz, 3H, $CH_2\underline{CH}_3$), 1.67 (d, J = 1Hz, 3H, $C\underline{H}_3$), 1.95 (d, J = 1Hz, 3H, $C\underline{H}_3$), 3.04 (q, J = 8Hz, 2H, $C\underline{H}_2CH_3$), 6.41 (bs, 1H, -C$\underline{H}$=), 7.04 - 8.00 (m, 6H, Ar$\underline{H}$)

i.r.(cm^{-1}): 1450(s), 1380(m), 800(m), 760(m), 740(m)

m.s.(m/e): 210.139123 (M^+, base peak, $C_{16}H_{18}$ requires 210.140844), 195, 165

2-(1'-chloro-3'-methylbut-1'-enyl)-3-ethylindene (143)

m.s. of mixture (m/e): 248.11630 (M^+, base peak, $C_{16}H_{19}{}^{37}Cl$ requires 248.114571), 246.117658 ($C_{16}H_{19}{}^{35}Cl$ requires 246.117521), 231, 210, 195

^{1}H n.m.r.(60MHz, δ) part spectrum: 1.0 (d, J = 6Hz, $(CH_3)_2$), 1.2 (d of t, J = 1Hz, 6Hz, $C\underline{H}_3CH_2$), 2.3 - 2.8 (m, $CH_3C\underline{H}_2$ + $C\underline{H}(CH_3)_2$), 3.5 (s, $C\underline{H}_2$), 5.7 (d, J = 10Hz, =C$\underline{H}$)

3-ethyl-2-(3'-methylbut-1'-ynyl)indene (144)

^{1}H n.m.r.(δ): 1.20 (t, J = 8Hz, 3H, $CH_2\underline{CH}_3$), 1.24 (d, J = 7Hz, 6H, $C(\underline{CH}_3)_2$, 3.04 (bq, J = 8Hz, $\underline{CH}_2CH_3$), 2.7 - 3.2 (m, 1H, $\underline{CH}(CH_3)_2$), 3.34 (bs, 2H, $ArCH_2$), 7.0 - 7.6 (m, 4H, Ar$\underline{H}$)

m.s.(m/e): 210.139422 (M^+, base peak, $C_{16}H_{18}$ requires 210.140844), 195, 165, 156

7.8.5 Rearrangement of 2,3-Benzo-6-dimethylvinylidene-1,5-dimethylbicyclo[3,1,0]hex-2-ene (90)

Method I gave a 90% yield of two products separated by preparative g.l.c. (10% P.M.P.E., 170°C). The products are 1,3-dimethyl-2-(2'-methylprop-1'-enyl)naphthalene (91) and 2-(3'-methylbut-1'-ynyl)-1-methylene-2-methylindane (145). With 2 molar acid the mixture contained 55% of (91) and 45% of (145) and decreasing the molarity of the acid, the proportion of (145) decreased until in pure alcohol only naphthalene (91) was obtained after refluxing for 30 minutes, 90%.

Method II after 1 hour gave a 90% yield of equal amounts of the indane (145) and the naphthalene (91) by ^{1}H n.m.r.

1,3-dimethyl-2-(2'-methylprop-1'-enyl)naphthalene (91)

^{1}H n.m.r.(δ): 1.40 (d, J = 1Hz, 3H, $=CC\underline{H}_3$), 1.91 (d, J = 1Hz, 3H, $=CC\underline{H}_3$), 2.25 (s, 3H, CH_3-3), 2.46 (s, 3H, $C\underline{H}_3$-1), 6.15 (bs, 1H, =CH-), 7.14 - 7.40 (m, 3H, Ar$\underline{H}$), 7.45 - 7.64 (m, 1H, Ar$\underline{H}$), 7.72 - 7.93 (m, 1H, Ar$\underline{H}$), irradiation of the peak at 6.15δ collapsed the peaks at 1.40δ and 1.91δ to singlets

^{13}C n.m.r.(p.p.m.): 15.7, 21.2 (2 x olefinic CH_3), 19.0 (CH_3-2), 25.0 (CH_3-1), 124.1, 124.2, 124.8, 124.9, 125.5, 127.6 (olefinic and aromatic C-H), 131.4, 131.5, 132.7, 135.2, 135.5, 136.1 (olefinic and aromatic C)

i.r.(cm^{-1}): 1430(s), 1360(s), 870(m), 790(s), 750(s)

m.s.(m/e): 210.141686 (M^+, base peak, $C_{15}H_{16}$ requires 210.140844)

2-(1'-methylbut-1'-ynyl)-1-methylene-2-methylindane (145)

^1H n.m.r.(δ): 1.13 (d, J = 7Hz, 6H, $CH(C\underline{H}_3)_2$), 1.35 (s, 3H, $C\underline{H}_3$), 2.53 (septet, J = 7Hz, 1H, $C\underline{H}(CH_3)_2$), 2.88, 3.29 (AB spectrum, J = 16Hz, 2H, $ArC\underline{H}_2$), 5.19, 5.39 (2 x s, 2H, $=C\underline{H}_2$), 7.00 - 7.18 (m, 3H, Ar$\underline{H}$), 7.25 - 7.46 (m, 1H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 20.6 (CH_3-2), 23.5 ($(CH_3)_2$), 31.0 ($\underline{C}H(CH_3)_2$), 41.3 (C-2), 47.5 (CH_2-3), 85.1, 86.8 (C≡C), 103.5 (olefinic CH_2), 121.4, 125.3, 126.8, 128.7 (aromatic CH), 138.9, 142.5, 157.3 (aromatic and olefinic C)

The cyclopropane (90) was refluxed in DCl/MeOH (2%, 15ml) (prepared by dissolving deuterium chloride (6ml, 30% in H_2O) in deuteromethanol (94ml)) for 5 minutes to give products containing deuterium. These were separated by preparative g.l.c. as before. The ^1H n.m.r. spectrum of (91)-D showed loss of the olefinic absorption at 6.15δ while the olefinic methyl peaks at 1.40δ and 1.91δ appeared as sharp singlets. This indicates deuteration on C-1'. With (145)-D the isopropyl septet at 2.53δ was absent while the isopropyl methyl doublet at 1.13δ was collapsed to a singlet. This indicates deuteration on C-3'.

7.8.6 Rearrangement of 2,3-Benzo-7-dimethylvinylidenebicyclo-[4,1,0]hept-2-ene (92)

Method I gave a complex mixture which was inseparable by preparative g.l.c. The mixture was partially separated by silica gel chromatography to give 1,2-benzo-4-(2'-methylprop-1'-enyl)cyclohepta-1,3,5-triene (151), 30%, pure, plus a little of what is probably 3-(3'-methylbut-1'-ynyl)-1,2-dihydronaphthalene (152), 5%, plus other unidentified components.

Method II gave an 80% yield of a complex mixture. Preparative g.l.c. (10%, P.M.P.E.) gave one peak. The ^{1}H n.m.r. spectrum shows the presence of the compounds (151), (152) and another compound, possibly 1,2-benzo-6-(2'-methylprop-1'-enyl)cyclohepta-1,3,5-triene (153) in the ratio 1:3:1.

1,2-benzo-4-(2'-methylprop-1'-enyl)cyclohepta-1,3,5-triene (151)

^{1}H n.m.r.(δ): 1.81 (bs, 6H, CH_3), 2.91 (d, J = 7Hz, 2H, H-7), 5.59 (d of t, J = 10Hz, 7Hz, 1H, H-6), 5.90 (d, J = 10Hz, 1H, H-5), 5.94 (bs, 1H, H-1'), 6.77 (s, 1H, H-3), 6.84 - 7.30 (m, 4H, ArH)

^{13}C n.m.r.(p.p.m.): 19.9, 27.0 (2 x olefinic CH_3), 34.5 (CH_2-7), 124.5, 125.5, 127.2, 127.6, 128.2, 128.3, 128.5, 132.0 (aromatic and olefinic CH), 135.9, 136.1, 138.4 (aromatic and olefinic C)

m.s.(m/e): 196.126725 (M^+, base peak, $C_{15}H_{16}$ requires 196.125194), 181, 165, 153, 141, 128, 115

3-(3'-methylbut-1'-ynyl)-1,2-dihydronaphthalene (152)

^{1}H n.m.r.(δ) part spectrum: 1.21 (d, J = 7Hz, $CH(CH_3)_2$), 2.2 - 2.5, 2.6 - 2.9 (m, CH_2CH_2), 6.57 (bs, =CH-)

1,2-benzo-6-(2'-methylprop-1'-enyl)cyclohepta-1,3,5-triene (153)

^{1}H n.m.r.(δ) part spectrum: 1.71, 1.81 (2 x olefinic CH_3), 3.02 (s, H-7), 6.40 (d of d, J = 7Hz, 11Hz, H-4)

7.8.7 Rearrangement of 2,3-Benzo-7-dimethylvinylidene-1-methylbicyclo[4,1,0]hept-2-ene (93)

Method I gave mostly E and Z-2-(1'-chloro-3'-methylbut-1'enyl)-4-methyl-1,2-dihydronaphthalene, (154a) and (154b), 80%, the isomer ratio being E:Z = 2.3:1. These isomers were not separated. No cycloheptatriene was obtained. The compounds were identified by comparison of the spectra with those published by Stewart.[21]

Method II gave a complex mixture, 80%, separated by preparative g.l.c. (10% P.M.P.E., 150°C), to give 1,2-benzo-3-methyl-4-(2'-methylprop-1'-enyl)cyclohepta-1,3,5-triene (155) and 3-(3'-methylbut-1'-ynyl)-4-methyl-1,2-dihydronaphthalene (156) in the ratio 3:1.

E and Z-2-(1'-chloro-3'-methylbut-1'-enyl)-4-methyl-1,2-dihydronaphthalene (154a) and (154b)

^{1}H n.m.r.(δ): 1.94 (d, J = 6Hz, E-$(C\underline{H}_3)_2$), 1.05 (d, J = 6Hz, Z-$(C\underline{H}_3)_2$), 2.03 (bs, 3H, $C\underline{H}_3$), 2.10 - 2.54 (m, 3H, $C\underline{H}_2$ + $C\underline{H}$), 2.55 - 2.96 (bq, J = 7Hz, 2H, Ar$C\underline{H}_2$), 5.30 (d, J = 8Hz, Z-H-2'), 5.47 (d, J = 10Hz, E-H-2'), 6.84 - 7.40 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 1450(s), 1380(m), 1300(m), 1170(m), 940(m), 890(s), 790(s), 750(s), 740(m)

1,2-benzo-3-methyl-4-(2'-methylprop-1'-enyl)cyclohepta-1,3,5-triene (155)

^{1}H n.m.r.(δ): 1.63, 1.81 (2 x s, 6H, $(C\underline{H}_3)_2$), 2.22 (s, 3H, $C\underline{H}_3$), 2.84 (bd, J = 6Hz, 2H, H-7), 5.60 - 5.80 (m, 2H, H-5, H-6), 5.96 (bs, 1H, H-1'), 6.80 - 7.40 (m, Ar$\underline{H}$)

i.r.(cm^{-1}): 1450(s), 1370(m), 780(m), 750(s)

3-(3'-methylbut-1'-ynyl)-4-methyl-1,2-dihydronaphthalene (156)

^{1}H n.m.r.(δ): 1.20 (d, J = 7Hz, 6H, $CH(C\underline{H}_3)_2$), 2.18 (bs, 3H, $C\underline{H}_3$), 1.24 - 1.44 (m, 2H, H-2), 2.58 - 2.90 (m, 3H, H-1, H-3'), 6.88 - 7.20 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 2200(w) C≡C, 1450(s), 1320(m), 760(s), 740(m)

m.s.(m/e): 210.142695 (M^+, base peak, $C_{16}H_{18}$ requires 210.140844)

7.8.8 Rearrangement of 2,3-Benzo-7-dimethylvinylidene-6-methylbicyclo[4,1,0]hept-2-ene (94)

Method I gave a complex mixture separated by silica gel chromatography to give 1,2-benzo-4-(2'-methylprop-1'-enyl)-5-methylcyclohepta-

1,3,5-triene (157), 33%, pure, plus about 40% of other components inseparable by preparative g.l.c.

Method II gave a mixture separated by preparative g.l.c. (10% P.M.P.E., 160°C) to give the cycloheptatriene (157) as the minor product, 20%, plus a mixture of unidentified products.

1,2-benzo-4-(2'-methylprop-1'-enyl)-5-methylcyclohepta-1,3,5-triene (157)

^{1}H n.m.r.(δ): 1.74, 1.78, 1.84 (3s, 9H, 3 x CH_3), 2.86 (d, J = 7Hz, 2H, H-7), 5.56 (t, J = 7Hz, 1H, H-6), 6.01 (bs, 1H, H-1'), 6.72 (s, 1H, H-3), 6.9 - 7.3 (m, 4H, ArH)

^{13}C n.m.r.(p.p.m.): 19.3, 26.1 ($C(CH_3)_2$), 21.0 (CH_3), 34.0 (C-7), 122.7, 125.4, 126.2, 126.6, 127.9, 128.3, 131.0 (aromatic and olefinic CH), 134.1, 135.6, 136.0, 138.1, 140.9 (aromatic and olefinic C)

i.r.(cm^{-1}): 1450(s), 1380(m), 790(s), 750(s)

m.s.(m/e): 210.139123 (M^+, base peak, $C_{16}H_{18}$ requires 210.140844), 165, 152

7.8.9 Rearrangement of E and Z-2,3-Benzo-1-methyl-6-(2'-vinylpropenylidene)bicyclo[3,1,0]hex-2-ene (196)

Method I gave a complex mixture which has not been rationalised as yet.

Method II gave a complex mixture. Attempts at separation by alumina chromatography or using preparative g.l.c. (10% P.M.P.E., 190°C) gave one major product, 30 - 40%, believed to be 2-(3'-methylpent-3'-en-1'-ynyl)-3-methylindene (159). No other products were identified.

Method III gave a 50% yield of a complex mixture. This was separated by preparative g.l.c. (10% P.M.P.E., 150°C) to give several fractions, the major fraction being 1-(3'-methylpent-3'-en-1'-ynyl)-1-methylindene (164). No other compounds have been identified.

2-(3'-methylpent-3'-en-1'-ynyl)-3-methylindene (159)

^{1}H n.m.r.(δ): 1.97 (d, J = 5Hz, CH_3-4'), 1.99 (s, 3H, CH_3-3'), 2.23 (t, J = 2Hz, 3H, CH_3-3), 3.43 (q, J = 2Hz, 2H, H-1), 5.67 (q, J = 5Hz, 1H, H-4'), 7.0 - 7.5 (m, 4H, ArH)

i.r.(cm^{-1}): 2130(w) C≡C, 1450(s), 1370(m), 720(m)

m.s.(m/e): 208.123645 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 193, 178, 165

1-(3'-methylpent-3'-en-1'-ynyl)-1-methylindene (164)

^{1}H n.m.r.(δ): 1.53 (s, 3H, CH_3-1), 1.70 (m, 3H, CH_3-4'), 1.72 (s, 3H, CH_3-3'), 5.55 (q, J = 5Hz, 1H, H-4), 6.32, 6.60 (AB spectrum, J = 5Hz, 2H, H-2, H-3), 7.0 - 7.5 (m, 4H, ArH)

m.s.(m/e): 208.126103 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 181, 147

7.8.10 Rearrangement of E and Z-2,3-Benzo-5-methyl-6-(2'-vinylpropenylidene)bicyclo[3,1,0]hex-2-ene (97)

No products have been identified from rearrangement by methods I and II.

7.8.11 Rearrangement of E and Z-2,3-Benzo-1,5-dimethyl-6-(2'-vinylpropenylidene)bicyclo[3,1,0]hex-2-ene (98)

Method I gave a mixture separated by preparative g.l.c. (10% P.M.P.E., 170°C) to give only 2-(3'-methylpent-3'-en-1'-ynyl)-2-methyl-1-methyleneindane (161), 30%.

Method II gave a 70% yield of a product mixture which was separated by preparative g.l.c. (10% P.M.P.E., 190°C) to give the indane (161) and a mixture of E and Z-1,3-dimethyl-2-(2'-methylbuta-1',3'-dienyl)naphthalene (162a) and (162b) in the ratio 1.2:1:1.3 by ^{1}H n.m.r. The E and Z isomers were not separated.

Method III gave a complex mixture separated by preparative g.l.c. (10% P.M.P.E., 170°C) to give 1,2-dimethyl-1-(3'-methylpent-3'-en-1'-ynyl)indene (165), 40%, and several unidentified products.

2-(3'-methylpent-3'-en-1'-ynyl)-2-methyl-1-methyleneindane (161)

^{1}H n.m.r.(δ): 1.40 (s, 3H, CH_3-2), 1.67 (bd, J = 7Hz, CH_3-4'), 1.74 (bs, 3H, CH_3-3'), 2.92, 3.35 (AB spectrum, J = 16Hz, 2H, H-3), 5.22, 5.42 (2s, 1H, 1H, $=CH_2$), 5.75 (bq, J = 7Hz, 1H, H-4'), 7.00 - 7.22 (m, 3H, ArH), 7.28 - 7.48 (m, 1H, H-7), irradiation of the quartet at 5.74δ collapses the peaks at 1.67δ and 1.74δ to sharp singlets

i.r.(cm^{-1}): 2220(w) C≡C, 885(m), 790(s), 780(s)

m.s.(m/e): 222.140327 (M^+, base peak, $C_{17}H_{18}$ requires 222.140844), 210, 207

E and Z-1,3-dimethyl-2-(2'-methylbuta-1',3'-dienyl)naphthalene (162a) and (162b)

^{1}H n.m.r.(δ): 1.57 (d, J = 2Hz, 3/2H, Z-CH_3-2'), 2.06 (d, J = 2Hz, 3/2H, E-CH_3-2'), 2.28, 2.49 (2s, 3H, 3H, CH_3-1, CH_3-3), 4.94 (bd, J = 11Hz, cis H-4'), 5.21 (bd, J = 17Hz, 1H, trans H-4'), 6.14 (d of d, J = 11Hz, 17Hz, ½H, Z-H-3'), 6.43, 6.51 (2 x bs, 1H, Z & E-H-1'), 6.60 (d of d, J = 10Hz, 17Hz, E-H-3'), 7.0 - 7.5 (m, 3H, ArH), 7.5 - 7.7 (m, 1H, ArH), 7.8 - 8.0 (m, 1H, ArH)

m.s.(m/e): 222.141882 (M^+, base peak, $C_{17}H_{18}$ requires 222.140844), 207, 192

1,2-dimethyl-1-(3'-methylpent-3'-en-1'-ynyl)indene (165)

^{1}H n.m.r.(δ): 1.47 (s, 3H, CH_3-1), 1.73 (bd, J = 6Hz, 3H, CH_3-4'), 1.75 (s, 3H, CH_3-3'), 2.08 (m, J = 2Hz, 3H, CH_3-2) 5.56 (bq, J = 6Hz, 1H, H-4'), 6.28 (q, J = 2Hz, 1H, H-3), 7.0 - 7.2 (m, 3H, ArH), 7.28 - 7.42 (m, 1H, H-7), irradiation of the peak at 6.28δ collapsed the

quartet at 6.28δ; irradiation at 5.56δ collapsed the doublet at 1.73δ

m.s.(m/e): 222.140324 (M^+, base peak, $C_{17}H_{18}$ requires 222.140844), 156, 155

7.9 Vapour Phase Pyrolysis of Acetylenes

The samples (0.2 - 2g) were passed through an electrically heated quartz tube (see figure 50) filled with glass wool (300 - 600°C) or quartz wool (600 - 900°C), under high vacuum (0.005mm) and collected in a cold trap. In some cases further reactions of the products were carried out. Unless otherwise indicated the products were obtained as pale yellow oils.

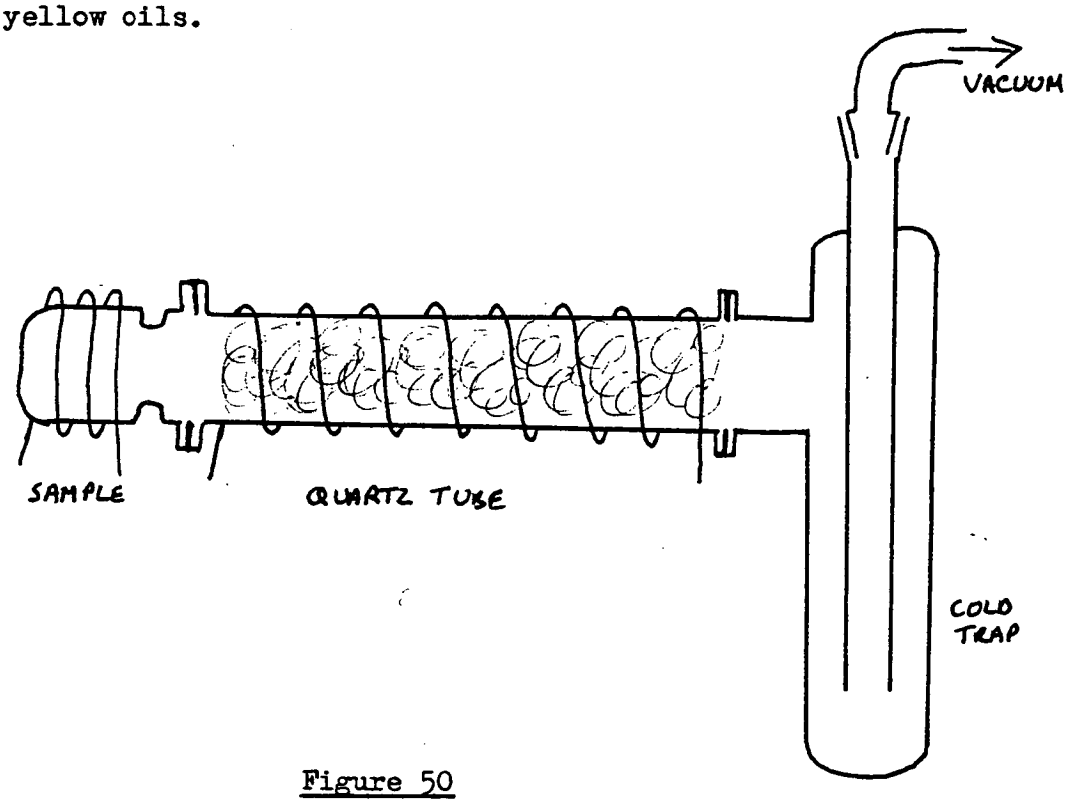


Figure 50

7.9.1 Rearrangement of 1- and 3-Propargylindene (103) and (104)

Pyrolysis of either 1- or 3-propargylindene at 500°C gave a mixture

containing 1-propargylindene (103), 20%, 3-propargylindene (104), 60%, and 3-allenylindene (172), 20%. The allene was separated from the acetylenes by silica gel chromatography, eluting before the acetylenes with light petroleum. It was found to be unstable at room temperature and stored at -15°C.

Pyrolysis of 1- or 3-propargylindene separately at 400°C gave a mixture of indenes (103) and (104) in the ratio 1:3, but no allene. Pyrolysis at 600°C or 700°C gave a complex mixture containing acenaphthalene (15%) identified by comparison of its ^{1}H n.m.r. spectrum with that of an authentic sample. The other components have not been identified.

3-allenylindene (172)

^{1}H n.m.r.(δ): 3.37 (bs, 2H, H-1), 5.14 (fsd, J = 7Hz, 2Hz, 2H, allenyl C$\underline{H}_2$), 6.27 (t, J = 7Hz, 1H, allenyl C$\underline{H}$), 6.35 (bs, 1H, H-2), 7.0 - 7.4 (m, 3H, Ar$\underline{H}$), 7.7 - 7.8 (m, 1H, H-4), decoupling experiments showed coupling between the allenic CH_2 and CH of 7Hz, and between the allenic CH_2 and H-1 of 2Hz

i.r.(cm^{-1}): 1930(s) allene, 1450(s), 850(s), 760(s), 720(m)

Pyrolysis of 1-(3'-deuteropropargyl)indene (175) gave 3-(1'-deuteroallenyl)indene (176) as well as recovered propargyl products. The ^{1}H n.m.r. showed a broad singlet at 5.14δ and no resonance at 6.27δ.

7.9.2 Rearrangement of 3-(1'-Methylprop-2'-ynyl)indene (118)

Pyrolysis of the indene (118) at 500°C gave a 60% yield of a mixture containing equal amounts of 3-(buta-1',2'-dienyl)indene (177) and recovered 3-(1'-methylprop-2'-ynyl)indene (118). These were separated by silica gel chromatography. The allene was unstable at room temperature and was stored at -15°C.

3-(buta-1',2'-dienyl)indene (177)

^{1}H n.m.r.(δ): 1.82 (d of d, J = 7Hz, 3Hz, 3H, $C\underline{H}_3$), 3.30 (bs, 2H, H-1), 5.42 (m, 1H, H-3'), 6.15 (m, 1H, H-1'), 6.25 (bs, 1H, H-2), 6.9 - 7.5 (m, 3H, Ar$\underline{H}$), 7.5 - 7.7 (m, 1H, H-4)

i.r.(cm^{-1}): 1950(s) allene

7.9.3 Rearrangement of 3-(1', 1'-dimethylprop-2'-ynyl)indene (117)

Pyrolysis of the indene (117) at 500°C gave exclusively 3-(3'-methylbuta-1',2'-dienyl)indene (178), 80%, which was purified by silica gel chromatography. The product was quite stable at room temperature for a few days but was stored at -15°C.

3-(3'-methylbuta-1',2'-dienyl)indene (178)

^{1}H n.m.r.(δ): 1.83 (d, J = 3Hz, 6H, $(CH_3)_2$), 3.29 (d, J = 2Hz, 2H, H-1), 6.08 (septet, J = 3Hz, 1H, allenyl C$\underline{H}$), 6.22 (t, J = 2Hz, 1H, H-2), 6.9 - 7.4 (m, 3H, Ar$\underline{H}$), 7.56 (d of d, J = 6Hz, 2Hz, 1H, H-4)

^{13}C n.m.r.(p.p.m.): 20.6 ($(CH_3)_2$), 37.6 (CH_2), 86.7 (allenyl CH), 97.0 (C-3'), 120.4, 123.6, 124.8, 126.1, 130.4 (aromatic and olefinic CH), 138.0, 143,5, 144.7 (aromatic and olefinic C), 204.3 (C-2')

i.r.(cm^{-1}): 1955(m) allene, 1450(s), 1390(m), 1360(m), 970(m), 830(m), 760(s), 720(s)

m.s.(m/e): 182.109112 (M^+, base peak, $C_{14}H_{14}$ requires 182.109545), 167, 165, 115

7.9.4 Rearrangement of 9,9-Dipropargylfluorene (114)

Pyrolysis of 9,9-dimethylfluorene at 500°C gave unchanged starting material, and at 600°C gave largely unchanged starting material. However at 700°C a product mixture was obtained, which was separated by alumina chromatography to give 25% of fluorene, 11% of a mixture of fluoranthene (184) and acephenanthalene (182), and 51% of 9-ethynyl-

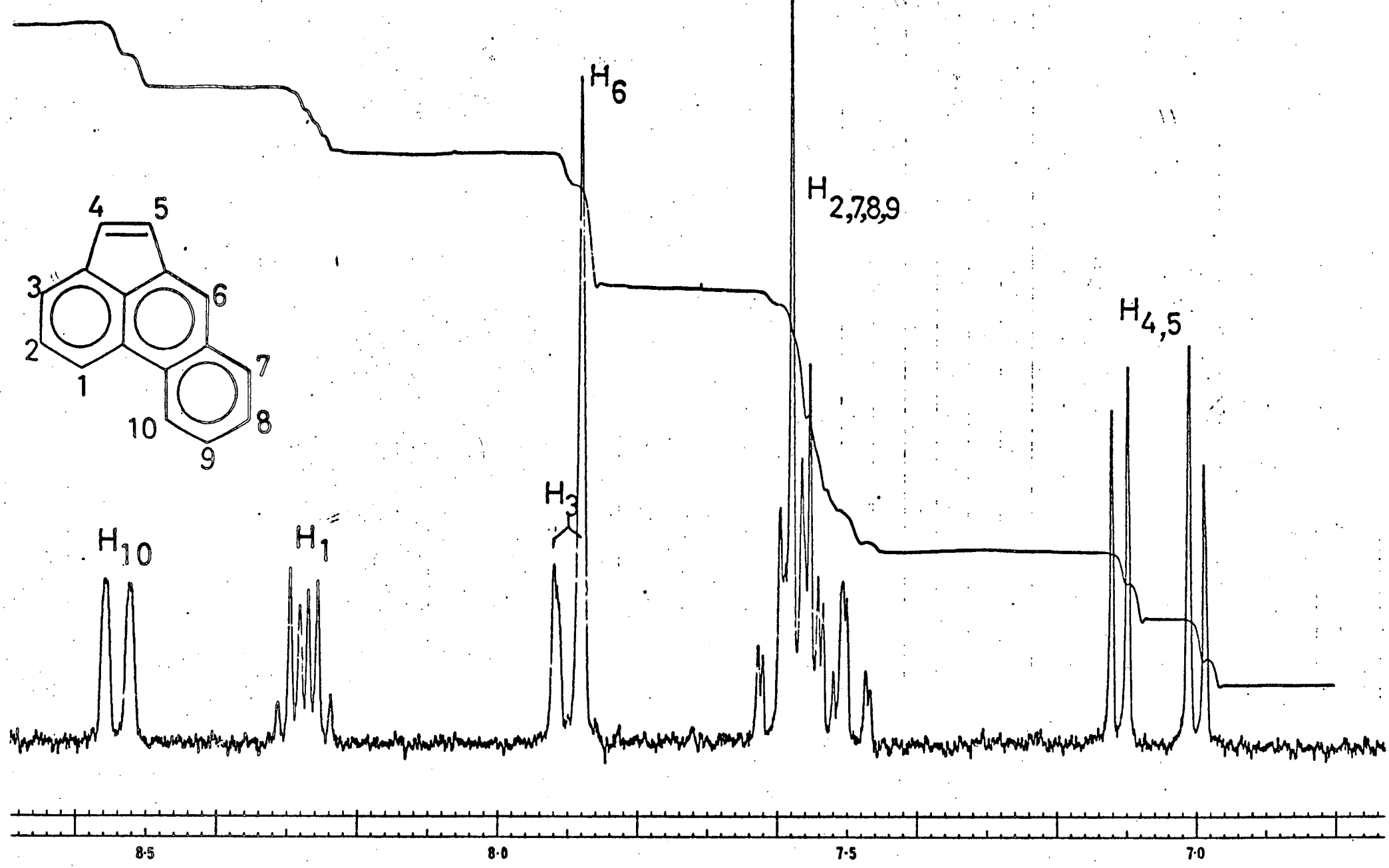


Figure 51

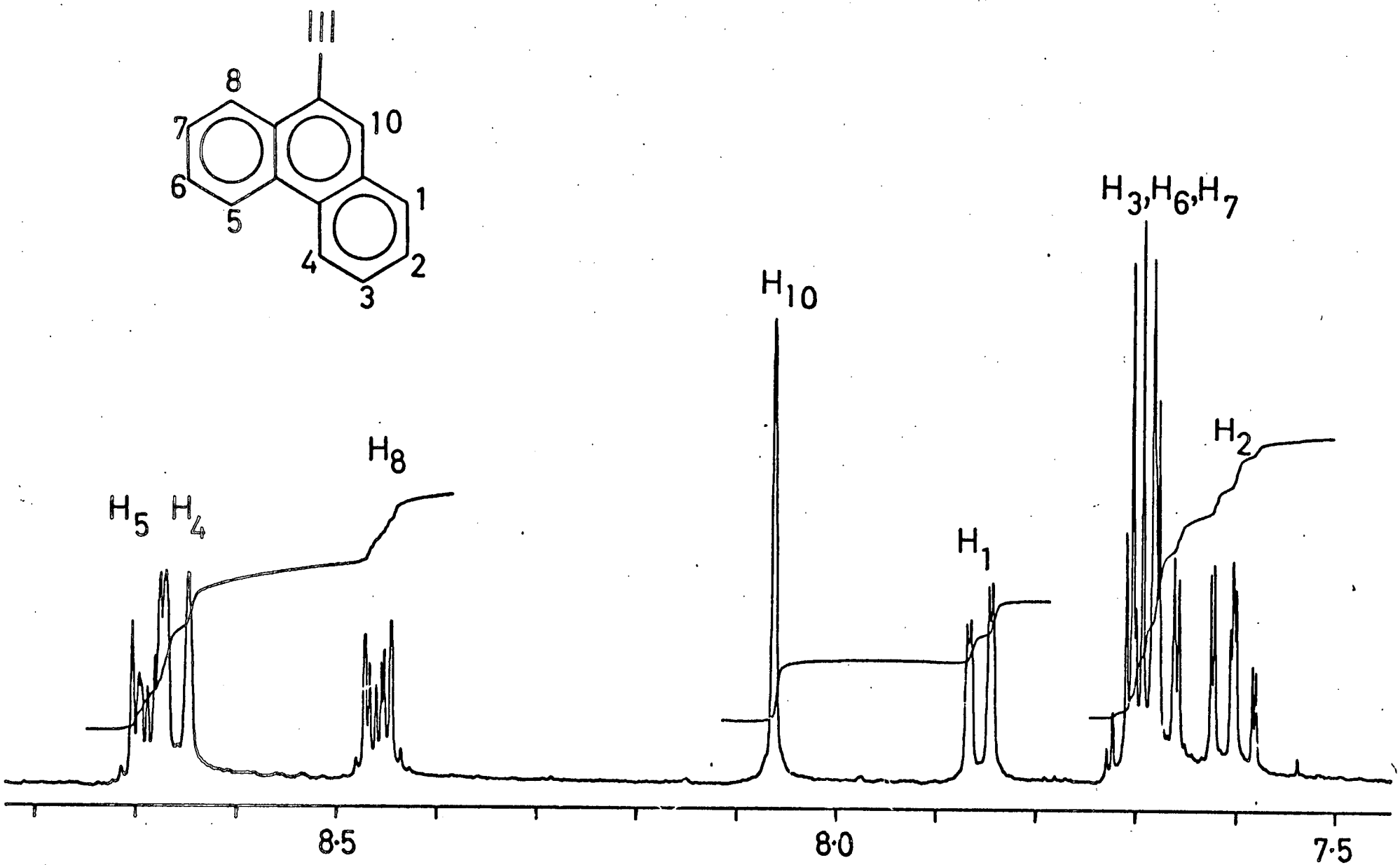


Figure 52

phenanthrene (180), eluting with light petroleum, light petroleum-ether mixtures, in that order.

Pyrolysis of the 9,9-dipropargylfluorene (114) at higher temperatures gave more acephenanthralene and less 9-ethynylphenanthrene. Pyrolysis of 9-ethynylphenanthrene (180) pure gave exclusively acephenanthralene (182), 80%.

acephenanthralene (182)

m.p.(ethanol): 130 - 135°, lit.[120] 143 - 144°, yellow crystals

^{1}H n.m.r.(220MHz, $CDCl_3$, figure 51, δ): 7.00, 7.12 (AB spectrum, J = 5Hz, 2H, H-4 and H-5), 7.46 - 7.64 (m, 4H, H-2,7,8,9), 7.88 (s, 1H, H-6), 7.90 (d, J = 9Hz, 1H, H-3), 8.28 (d of t, J = 6Hz, 2Hz, 1H, H-1), 8.54 (d, J = 9Hz, 1H, H-10)

m.s.(m/e): 202.079090 (M^+, base peak, $C_{16}H_{10}$ requires 202.078247)

9-ethynylphenanthrene (180)

m.p.(ethanol): 56 - 57°, lit.[121] 61 - 62°, white crystals

^{1}H n.m.r.(360MHz, $CDCl_3$, figure 52, δ): 3.50 (s, 1H, CH), 7.60 (m, 1H, H-2), ca 7.7 (m, 3H, H-3, H-6, H-2), 7.86 (bd, J = 8Hz, 1H, H-1), 8.06 (s, 1H, H-10), 8.46 (m, 1H, H-8), 8.66 (d, J = 8Hz, 1H, H-4), 8.69 (m, 1H, H-5)

^{13}C n.m.r.(p.p.m.): 80.5 (≡CH), 81.9 (C≡C), 122.5, 122.7, 126.8, 126.8, 127.0, 127.6, 128.5, 132.9 (aromatic CH), 127.4, 130.0, 130.4, 130.9, 131.0 (aromatic C)

i.r.(cm^{-1}): 3290(s) ≡CH, 2100(w) C≡C

u.v.(ethanol, mμ): 214 (ϵ 35800), 234 (34600), 257 (50800), 260 (49100), 273 (21600), 288 (11500), 299 (19000), 312 (22800)

Fluorene and fluoranthene (184) were identified by comparison of their ^{1}H n.m.r. with authentic samples.

Hydrogenation of 9-ethynylphenanthrene (180) (0.5g) in ethanol (25ml) over 10% palladium charcoal (0.05g) at atmospheric pressure,

followed by purification by alumina chromatography eluting with light petroleum gave 9-ethylphenanthrene.

9-ethylphenanthrene

m.p.(methanol): 58 - 59°, lit.[122] 62 - 63°, white crystals

^{1}H n.m.r.(δ): 1.40 (t, J = 8Hz, 3H, C$\underline{H}_3$), 3.08 (q, J = 8Hz, 2H, C$\underline{H}_2$), 7.06 - 7.26 (m, 1H, Ar$\underline{H}$), 7.34 - 7.75 (m, 6H, Ar$\underline{H}$), 7.88 - 8.06 (m, 1H, Ar$\underline{H}$), 8.40 - 8.66 (m, 1H, Ar$\underline{H}$)

Pyrolysis of 9,9-(3'-deuteropropargyl)fluorene at 700°C gave a mixture containing 9-(2'-deuteroethynyl)phenanthrene, with loss of the acetylenic proton resonance in the ^{1}H n.m.r.

7.9.5 Rearrangement of 9-Propargylfluorene (115)

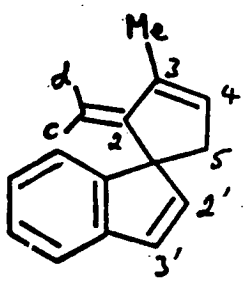
Pyrolysis of 9-propargylfluorene (115) at 700°C lead to a mixture of products as yet unseparated. The ^{1}H n.m.r. spectrum of this mixture suggests that these products are not the same as those obtained from the pyrolysis of 9,9-dipropargylfluorene (114).

7.9.6 Rearrangement of Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126b)

Pyrolysis of the indene derivative (126b) at 500°C gave spiro [2-methylene-3-methylcyclopent-3-ene-1,1'-indene] (188), 80%. At lower temperatures the rearrangement was incomplete.

spiro[2-methylene-3-methylcyclopent-3-ene-1,1'-indene] (188)

^{1}H n.m.r.(δ): 1.86 (fss, 3H, C$\underline{H}_3$), 2.73 (bs, 2H, H-5), 4.20 (bs, 1H, H_c), 4.55 (s, 1H, H_d), 5.96 (bs, 1H, H-4), 6.57, 6.18 (AB spectrum, J = 5Hz, 2H, H-2', H-3'), 6.9 - 7.2 (m, 4H, Ar$\underline{H}$)



^{13}C n.m.r.(p.p.m.): 13.0 (CH_3), 39.5 (C-5), 62.7 (C-1), 100.6 ($=CH_2$), 120.8, 121.2, 125.6, 126.5 (aromatic CH), 129.1 (C-3'), 133.1 (C-4), 140.7 (C-3), 143.2 (C-2), 144.5 (C-2'), 153.3, 155.8 (aromatic C)

i.r.(cm^{-1}): 1620(s), 1450(s), 865(s)

u.v.(ethanol, mμ): 217 (ε 13300) , 240 (8100)

m.s.(m/e): 194.107790 (M^+, base peak, $C_{15}H_{14}$ requires 194.109545), 179

Pyrolysis of Z-3-(5'-deutero-3'-methylpent-2'-en-4'-ynyl)indene (189) at 500°C gave a spiro product having a 60% reduction in the intensity of the resonance at 4.55δ in the ^1H n.m.r., i.e. H_d.

Pyrolysis of Z-3-(3'-methylpent-2'-en-4'-ynyl)indene (126b) at 600°C gave a mixture containing equal amounts of two fluorenes separated by alumina chromatography and recrystallization from ethanol. The products are 1,2-dimethylfluorene (203) and 3,4-dimethylfluorene (202), the latter not being obtained entirely free from the former isomer.

1,2-dimethylfluorene (203)

m.p.(ethanol): 118 - 119°, lit.[89] 119 - 121°

^1H n.m.r.(δ): 2.22 (s, 3H, $C\underline{H}_3$), 2.28 (s, 3H, $C\underline{H}_3$), 3.62 (s, 2H, $ArC\underline{H}_2$), 6.95 - 7.65 (m, 6H, $Ar\underline{H}$)

3,4-dimethylfluorene (202)

m.p.(ethanol): 80°, lit.[123] 100°

^1H n.m.r.(δ): 2.28 (s, 3H, $C\underline{H}_3$), 2.49 (s, 3H, $C\underline{H}_3$), 3.64 (s, 2H, $ArC\underline{H}_2$), 6.83 - 7.85 (m, 6H, $Ar\underline{H}$)

u.v.(hexane, mμ mixture): 228 (ε 9200), 260 (16000), 269 (19000), 292 (5300), 304 (5400)

Refluxing spiro[2-methylene-3-methylcyclopent-3-ene-1,1'-indene] (188) (0.5g) in carbon tetrachloride (25ml) with p-toluenesulphonic acid (0.02g) for 0.5 hours, followed by washing with water (2 x 20ml), drying of the organic layer and removal of the solvent under reduced pressure gave spiro[2,3-dimethylcyclopenta-2,4-diene-1,1'-indene] (206), purified by alumina chromatography; yield 60%.

spiro[2,3-dimethylcyclopenta-2,4-diene-1,1'-indene] (206)

^{1}H n.m.r.(δ): 1.28 (bs, 3H, C$\underline{H}_3$-2), 1.90 (s, 3H, C$\underline{H}_3$-3), 5.71 (d, J = 6Hz, 1H, H-5), 5.78 (d, 6Hz, 1H, H-2'), 6.35 (d, J = 6Hz, 1H, H-4), 6.70 (bd, J = 7Hz, 1H, H-7'), 6.80 (d, J = 6Hz, 1H, H-3'), 6.9 - 7.3 (m, 3H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 9.1 ($\underline{C}H_3$-C-3), 12.4 ($\underline{C}H_3$-C-2), 75.4 (C-1), 121.0, 121.7, 125.2, 126.8 (aromatic CH), 132.1 (C-4), 132.6 (C-3'), 137.6 (C-2'), 137.8 (C-5), 143.4, 145.4 (aromatic C)

i.r.(cm^{-1}): 1460(s), 780(s), 750(s), 720(m)

u.v.(n-hexane, mμ): 217 (ε 13800), 240 (14200), 272 (3500)

m.s.(m/e): 194.108542 (M^+, base peak, $C_{15}H_{14}$ requires 194.109545), 179

Pyrolysis of spiro [2,3-dimethylcyclopenta-2,4-diene-1,1'-indene] (206) at 500°C gave 4,5-benzo-2,3-dimethylindene (211), 6,7-benzo-1,2-dimethylindene (212) and 4,5-benzo-1,1-dimethylindene (213) in the ratio (211) : (212) : (213) = 3:1:3 which were separated by preparative g.l.c. (10% N.P.G.S., 170°C).

Refluxing the spirane (206) in decalin (b.p. 208°C) for 2 hours gave 80% of a 2:1 mixture of benzoindenes (211) and (213) but no (212).

4,5-benzo-2,3-dimethylindene (211)

^{1}H n.m.r.(δ): 1.97 (s, 3H, C$\underline{H}_3$), 2.37 (bs, 3H, C$\underline{H}_3$), 3.08 (bs, 2H,

$C\underline{H}_2$), 7.0 - 7.8 (m, 6H, Ar$\underline{H}$)

u.v.(n-hexane, mμ): 238 (ε 23500), 253 (14500), 295 (5000), 326 (2400), 333 (2100)

6,7-benzo-1,2-dimethylindene (212)

^{1}H n.m.r.(δ): 1.43 (d, J = 7Hz, 3H, $C\underline{H}_3$-1), 2.13 (bs, 3H, $C\underline{H}_3$-2), 3.52 (q, 1H, H-1), 6.20 (bs, 1H, H-3), 7.1 - 7.9 (m, 6H, Ar$\underline{H}$)

u.v.(n-hexane, mμ): 232 (ε 17900), 252 (10000), 261 (9400), 280 (3200), 292 (2800), 333 (700), 349 (400)

4,5-benzo-1,1-dimethylindene (213)

^{1}H n.m.r.(δ): 1.34 (s, 6H, 2 x $C\underline{H}_3$), 6.42, 7.11 (AB spectrum, J = 5Hz, H-2, H-3), 7.24 - 8.00 (m, 6H, Ar$\underline{H}$)

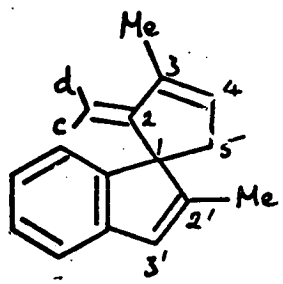
u.v.(n-hexane, mμ): 237 (ε 31300), 297 (4700), 307 (5500), 318 (4100), 325 (4100), 332 (3000)

7.9.7 Rearrangement of Z-3-(3'-methylpent-2'-en-4'-ynyl)-2-methylindene (127)

Pyrolysis of the 2-methylindene derivative (127) at 500°C gave spiro[2-methylene-3-methylcyclopent-3-ene-1,1'-(2'-methylindene)](196), 80%.

spiro[2-methylene-3-methylcyclopent-3-ene-1,1'-(2'-methylindene)](196)

^{1}H n.m.r.(δ): 1.73 (fss, 3H, $C\underline{H}_3$-2'), 1.90 (fss, 3H, $C\underline{H}_3$-3), 2.62 (bs, 2H, H-5), 4.10 (bs, 1H, $\underline{H}_c$), 4.62 (s, 1H, $\underline{H}_d$), 5.95 (bs, 1H, H-4), 6.25 (fss, 1H, H-3'), 6.9 - 7.2 (m, 4H, Ar$\underline{H}$)



^{13}C n.m.r.(p.p.m.): 12.5 ($\underline{C}H_3$-C-2'), 12.8 ($\underline{C}H_3$-C-3), 39.5 (C-5), 63.5 (C-1), 100.6 (=CH_2), 119.5, 121.1, 124.3, 125.3 (aromatic CH),

126.3 (C-4), 141.0 (C-3), 143.5 (C-2), 152.7, 154.1 (aromatic C), 156.4 (C-2')

i.r.(cm^{-1}): 1620(m), 1450(s), 1020(m), 860(m), 840(m), 750(s)

u.v.(ethanol, mμ): 222 (ε 15700), 258 (14400)

m.s.(m/e): 208.124021 (M^+, base peak, $C_{16}H_{16}$ requires 208,124021), 193, 178

Pyrolysis of the 2-methylindene derivative (127) at 600°C gave only the spiro compound (196).

Refluxing spiro[2-methylene-3-methylcyclopent-3-ene-1,1'-(2'-methylindene)] (196) with p-toluenesulphonic acid in carbon tetrachloride, as in section 7.9.6, gave spiro[2,3-dimethylcyclopenta-2,4-diene-1,1'-(2'-methylindene)], (207), 60%.

spiro [2,3-dimethylcyclopenta-2,4-diene-1,1'-(2'-methylindene)] (207)

^{1}H n.m.r.(δ): 1.21 (bs, 3H, $C\underline{H}_3$-2), 1.54 (d, J = 2Hz, 3H, $C\underline{H}_3$-2'), 1.93 (bs, 3H, $C\underline{H}_3$-3), 5.69 (d, J = 5Hz, 1H, H-5), 6.40 (d, J = 5Hz, 1H, H-4), 6.50 (bs, 1H, H-3'), 6.66 (bd, J = 7Hz, 1H, H-7'), 6.8 - 7.2 (m, 3H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 9.1 (CH_3-C-3), 12.4 (CH_3-C-2'), 12.9 (CH_3-C-2), 77.1 (C-1), 119.7, 121.7, 124.1, 126.7 (aromatic CH), 128.4 (C-4), 133.7 (C-3'), 136.4, 136.8 (C-2, C-3), 138.0 (C-5), 143.2, 145.7 (aromatic C), 147.6 (C-2')

i.r.(cm^{-1}): 1455(s), 1440(s), 840(m), 750(s), 725(s)

u.v.(ethanol, mμ): 215 (ε 17200), 244 (14200), 274 (4800)

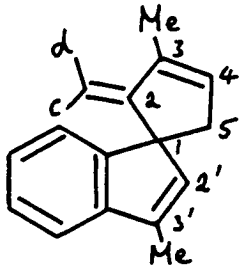
m.s.(m/e): 208.123269 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 193, 178, 165

7.9.8 Rearrangement of Z-1-(3'-Methylpent-2'-en-4'-ynyl)-3-methylindene (129) and Z-1-(3'-Methylpent-2'-en-4'-ynyl)-1-methylindene (195)

These were used as the 2:1 mixture, obtained by phase transfer

catalytic methods (section 7.7.17) since separation was difficult. Pyrolysis at 500°C gave a mixture of spiro [2-methylene-3-methylcyclopent-3-ene-1,1'-(3'-methylindene)] (197), ~50%, together with unchanged starting material ~10%, separated by alumina chromatography, eluting with light petroleum, in the order spirane then acetylene.

spiro[2-methylene-3-methylcyclopent-3-ene-1,1'-(3'-methylindene)] (197)



^{1}H n.m.r.(δ): 1.83 (bs, 3H, C$\underline{H}_3$-3), 2.09 (d, J = 1Hz, 3H, CH_3-3'), 2.70 (bs, 2H, H-5), 4.16 (s, 1H, $\underline{H}_c$), 4.51 (s, 1H, $\underline{H}_d$), 5.85 (bs, 1H, H-2'), 5.93 (bs, 1H, H-4), 6.9 - 7.3 (m, 4H, Ar$\underline{H}$), decoupling experiments showed H-2' coupled to CH_3-3', and H-4 coupled to CH_3-3

m.s.(m/e): 208.122705 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 193

Pyrolysis of the 3-methylindene derivatives (129) and (195) at 600°C gave a mixture which has not been separated yet but appears to contain 1,2,9- and 3,4,9-trimethylfluorene.

Rearrangement of spiro[2-methylene-3-methylcyclopent-3-ene-1,1'-(3'-methylindene)] (197) with p-toluenesulphonic acid in carbon tetrachloride as in section 7.9.6 gave spiro[2,3-dimethylcyclopenta-2,4-diene-1,1'-(3'-methylindene)] (208), 60%.

spiro[2,3-dimethylcyclopenta-2,4-diene-1,1'-(3'-methylindene)](208)

^{1}H n.m.r.(δ): 1.26 (bs, 3H, C$\underline{H}_3$-2), 1.90 (s, 3H, C$\underline{H}_3$-3), 2.13 (d, J = 11Hz, 3H, C$\underline{H}_3$-3'), 5.45 (bs, 1H, H-2'), 5.71 (d, J = 5Hz, 1H, H-5), 6.31 (d, J = 5Hz, 1H, H-4), 6.68 (bd, J = 6Hz, 1H, H-7'), 6.8 - 7.2 (m, 3H, Ar$\underline{H}$)

m.s.(m/e): 208.123832 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 193, 178

7.9.9 Rearrangement of Z-9-(3'-methylpent-2'-ene-4'-ynyl)-fluorene (134)

This compound would not vaporize satisfactorily and poor results were obtained. The little product mixture obtained does not appear to contain the spirotriene (135).

7.9.10 Rearrangement of Z-(3-methylpent-2'-en-4'-ynyl)cyclopentadiene (136)

Pyrolysis of this compound gave complex mixtures which have not yet been rationalised.

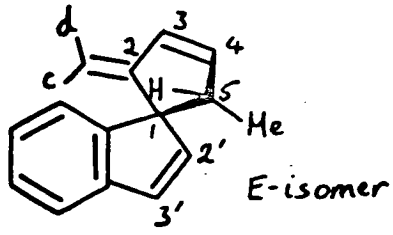
7.9.11 Rearrangement of E and Z-3-(1'-methylpent-2'-en-4'-ynyl)-indene (122a) and (122b)

Pyrolysis of the E/Z mixture (122a) and (122b), ratio 2:1, at 500°C gave E and Z spiro[2-methylene-5-methylcyclopent-3-ene-1,1'-indene] (198) and (200), 30%. The ^{1}H n.m.r. spectrum of the product showed that two isomers were obtained in the ratio 5:1; the major isomer being the E-isomer (198). These have not been separated. 30% of E-3-(1'-methylpent-2'-en-4'-ynyl)indene (122a) was recovered, and was separated from the spiro compounds by alumina chromatography. Eluting with light petroleum followed by light petroleum/ether mixtures gave the spiranes first.

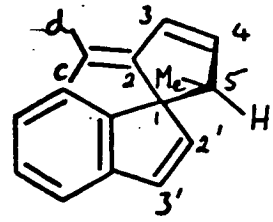
Pyrolysis of pure Z-3-(1'-methylpent-2'-en-4'-ynyl)indene (122b) gave mainly the spiro products while pyrolysis of the E-isomer (122a) gave little spirane with most of the starting material being recovered unchanged.

E and Z-spiro[2-methylene-5-methylcyclopent-3-en-1,1'-indene] (198) and (200)

^{1}H n.m.r.(δ): 0.74 (d, J = 7Hz, Z-C$\underline{H}_3$-5), 0.96 (d, J = 7Hz,



E-isomer



Z-isomer

E-C$\underline{H}_3$-5), 3.21 (bq, J = 7Hz, 2H, H-5), 4.20 (s, 1H, $\underline{H}_c$), 4.58 (s, 1H, $\underline{H}_d$), 6.12, 6.25 (AB spectrum, J = 6Hz, 2H, H-3, H-4), 6.22, 6.60 (AB spectrum, J = 6Hz, 2H, H-2', H-3'), 6.9 - 7.2 (m, 4H, Ar$\underline{H}$)

i.r.(cm^{-1}): 1630(m), 1460(s), 870(m), 795(m), 780(s), 750(s)

m.s.(m/e): 194.109670 (M^+, base peak, $C_{15}H_{14}$ requires 194.109545), 179

Pyrolysis of E and Z-3-(1'-methylpent-2'-en-4'-ynyl)indene (122a) and (122b) at 600°C gave a product mixture which has not yet been rationalized.

Rearrangement of the spirotrienes (198) and (200) with p-toluenesulphonic acid in carbon tetrachloride as in section 7.9.6 gave spiro-[2,5-dimethylcyclopenta-2,4-diene-1,1'-indene] (209), purified by alumina chromatography, 85%.

spiro[2,5-dimethylcyclopenta-2,4-diene-1,1'-indene] (209)

^{1}H n.m.r.(δ): 1.40 (s, 6H, C$\underline{H}_3$-2, C$\underline{H}_3$-5), 5.83 (d, J = 5Hz, 1H, H-2'), 6.17 (s, 2H, H-3, H-4), 6.76 (d, J = 6Hz, 1H, H-7'), 6.96 (bd, J = 5Hz, 1H, H-3'), 7.0 - 7.4 (m, 3H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 12.6 ($\underline{C}H_3$-C-2, $\underline{C}H_3$-C-5), 76.5 (C-1), 121.0, 121.5, 125.5, 126.9 (aromatic CH), 128.5 (C-3, C-4), 133.7 (C-3'), 138.4 (C-2'), 143.2, 145.9 (aromatic C)

u.v.(hexane, mμ): 221 (ε 12560), 228 (11170), 244 (9400)

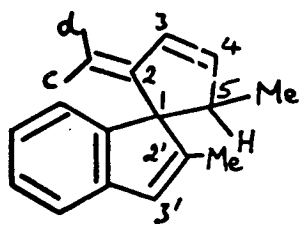
m.s.(m/e): 194.108730 (M^+, base peak, $C_{15}H_{14}$ requires 194.109545), 179

7.9.12 Rearrangement of E and Z-3-(1'-methylpent-2'-en-4'-ynyl)-2-methylindene (123a) and (123b)

Pyrolysis of the E/Z mixture at 450°C gave only 14% collected product, of which only 25% was spirane, the remainder being recovered starting material. The poor yield is due in part to the difficulty in vaporizing the acetylenes. The product obtained after alumina chromatography, eluting with light petroleum, light petroleum ether mixtures, was E and Z spiro[2-methylene-5-methylcyclopent-3-en-1,1'-(2-methylindene)] (199) and (201), 3½%, followed by recovered E-3-(1'-methylpent-2'-en-4'-ynyl)-2-methylindene (123a), 10%. The two spirane isomers were obtained in the ratio E:Z = 2:1.

E and Z-spiro[2-methylene-5-methylcyclopent-3-en-1,1'-(2'-methylindene)] (199)

^{1}H n.m.r.(δ): 0.72 (d, J = 7Hz, Z-C$\underline{H}_3$-5), 0.84 (d, J = 7Hz, E-C$\underline{H}_3$-5), 1.80 (d, J = 1Hz, 3H, C$\underline{H}_3$-2'), 2.9 - 3.5 (m, 1H, H-5), 4.10 (bs, 1H, $\underline{H}_c$), 4.67 (s, 1H, $\underline{H}_d$), 6.0 - 6.5 (m, 3H, H-3', H-3, H-4), 6.8 - 7.5 (m, 4H, Ar$\underline{H}$)



m.s.(m/e): 208.123457 (M^+, base peak, $C_{16}H_{16}$ requires 208.125194), 193, 178, 165

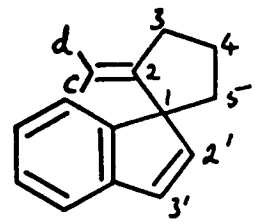
7.9.13 Rearrangement of 3-(pent-4'-ynyl)indene (119)

Pyrolysis of 3-(pent-4'-ynyl)indene at 500°C gave a mixture separated by alumina chromatography with light petroleum, light petroleum ether mixtures, to give spiro[2-methylenecyclopentane-1,1'-indene] (204), 28%, followed by unchanged starting material, 40%.

spiro[2-methylenecyclopentane-1,1'-indene] (204)

^{1}H n.m.r.(δ): 1.8 - 2.3 (m, 4H, H-4, H-5), 2.62 (bt, J = 6Hz, 2H,

H-3), 4.35 (t, J = 2Hz, 1H, $\underline{H}_c$), 4.60 (bs, 1H, H_d), 6.26, 6.52 (AB spectrum, J = 5Hz, H-2', H-3'), 6.9 - 7.2 (m, 4H, Ar$\underline{H}$)



^{13}C n.m.r.(p.p.m.): 24.3 (C-5), 35.5 (C-4), 36.6 (C-3), 64.3 (C-1), 105.6 (=CH_2), 120.8, 122.1, 125.2, 126.4 (aromatic CH), 128.2 (H-3'), 143.6 (H-2), 144.2 (H-2'), 152.1, 153.4 (aromatic C)

i.r.(cm^{-1}): 1460(s), 855(s), =CH_2, 780(s), 750(s), 730(s)

u.v.(n-hexane, mμ): 224 (ε 17200), 262 (5300)

m.s.(m/e): 182.109957 (M^+, base peak, $C_{14}H_{14}$ requires 182.109545), 167

Pyrolysis of 3-(pent-4'-ynyl)indene (119) at 600°C gave a mixture containing no spiro compound or starting material. The components have not been identified.

Rearrangement of the spiro compound (204) by refluxing with p-toluenesulphonic acid in carbon tetrachloride as in section 7.9.6, gave spiro[2-methylcyclopent-2-en-1,1'-indene] (210), 80%.

spiro[2-methylcyclopent-2-en-1,1'-indene] (210)

^{1}H n.m.r.(δ): 1.16 (fss, 3H, C$\underline{H}_3$-2), 2.10 - 2.32 (m, 2H, H-5), 2.24 - 2.68 (m, 2H, H-4), 5.60 (bs, 1H, H-3), 6.17, 6.60 (AB spectrum, J = 6Hz, H-2', H-3'), 6.9 - 7.2 (m, 4H, Ar$\underline{H}$)

^{13}C n.m.r.(p.p.m.): 12.1 ($\underline{C}H_3$-C-2), 31.4 (C-4), 33.6 (C-5), 68.2 (C-1), 120.7, 121.9, 125.1, 126.5 (aromatic CH), 127.6 (C-3), 129.6 (C-3'), 142.5 (C-2), 143.3 (C-2'), 143.6, 151.0 (aromatic C)

i.r.(cm^{-1}): 1460(m), 800(m), 780(m), 750(s)

u.v.(n-hexane, mμ): 226 (ε 15400), 260 (7000)

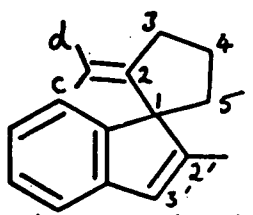
m.s.(m/e): 194.108730 (M^+, base peak, $C_{15}H_{14}$ requires 194.109545), 179

7.9.14 Rearrangement of 2-Methyl-3-(pent-4'-ynyl)indene (120)

Pyrolysis of 2-methyl-3-(pent-4'-ynyl)indene at 500°C gave a mixture separated by alumina chromatography, eluting with light petroleum, light petroleum-ether mixtures, to give spiro[2-methylenecyclopentane-1,1'-(2'-methylindene)] (205), 33%, followed by unchanged starting material, 33%.

spiro[2-methylenecyclopentane-1,1'-(2'-methylindene)] (205)

^{1}H n.m.r.(δ): 1.84 (d, J = 2Hz, 3H, CH_3-2'), 1.88 - 2.12 (m, 2H, H-4, H-5), 2.48 - 2.74 (m, 2H, H-3), 4.24 (bs, 1H, H_c), 4.70 (bs, 1H, H_d), 6.24 (bs, 1H, H-3'), 6.80 - 7.18 (m, 4H, ArH)



^{13}C n.m.r.(p.p.m.): 13.17 (CH_3-C-2'), 24.9 (C-5), 34.6 (C-4), 35.9 (C-3'), 64.8 (C-1), 105.5 (=CH_2), 119.6, 121.4, 124.1, 125.6 (aromatic CH), 126.0 (H-3'), 143.2 (C-2), 153.3, 154.0 (aromatic C), 155.2 (C-2')

i.r.(cm^{-1}): 1460(s), 1440(s), 880(s), 835(s), 745(s)

7.10 Base Catalysed Rearrangements of Acetylenes and Allenes

Two methods have been used to effect rearrangement.

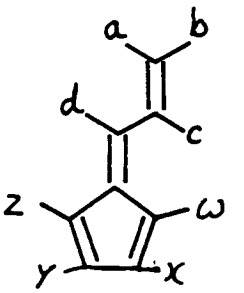
Method 1: The sample (1g) was refluxed with sodium methoxide in methanol (25ml, 2M) or sodium ethoxide in ethanol (25ml, 2M) for a few minutes until precipitation of polymer was observed. The reaction was diluted with water (25ml) and extracted into light petroleum (3 x 20ml), dried and the solvent removed. The products were separated by alumina chromatography.

Method 2: In some cases rearrangement could be effected by passage through a column (2 x 30cm) of commercial basic alumina eluting with light petroleum. The products elute before the starting materials.

7.10.1 Rearrangement of Propargylcyclopentadiene (224)

Refluxing in NaOMe/HOMe (0.5M) for 0.5 hours gave 6-vinylfulvene (225) in 20% yield. Rearrangement on alumina gave the same product, in 25% yield. This is a red liquid and the ^{1}H n.m.r. and i.r. agree with those published.[100]

6-vinylfulvene (225)



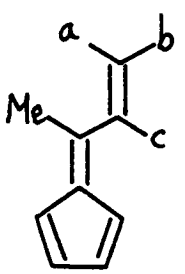
^{1}H n.m.r.(δ): 5.27 (bd, J = 10Hz, $\underline{H}_b$), 5.56 (d of d, J = 16Hz, 2Hz, 1H, $\underline{H}_a$), 6.08 (bd, J = 5Hz, 1H, H_w), 6.30 - 6.50 (m, 3H, $\underline{H}_{xyz}$), 6.62 (d, J = 12Hz, 1H, $\underline{H}_d$), 6.90 (d of d of d, J = 16Hz, 12Hz, 10Hz, 1H, $\underline{H}_c$)

i.r.(cm^{-1}): 1610(s), 1590(s), 1470(s), 1410(s), 1360(s), 1070(s), 910(s), 880(s)

7.10.2 Rearrangement of (1'-methylprop-2'-ynyl)cyclopentadiene (226)

(1'-Methylprop-2'-ynyl)cyclopentadiene (226) rearranged by refluxing in NaOMe/HOMe (0.5M) for 0.5 hours to give 6-methyl-6-vinylfulvene (227), isolated from polymeric material by alumina chromatography, eluting with light petroleum; yield 20%. Passage through alumina also gave 6-methyl-6-vinylfulvene, 25%. The ^{1}H n.m.r. spectrum is in agreement with that published.[100]

6-methyl-6-vinylfulvene (227)



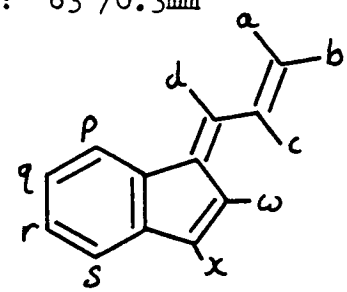
^{1}H n.m.r.(δ): 2.20 (s, 3H, $C\underline{H}_3$), 5.38 (d, J = 10Hz, 1H, $\underline{H}_b$), 5.53 (d, J = 17Hz, 1H, H_a), 6.26 - 6.53 (m, 4H, cyclopentadiene $\underline{H}$), 7.09 (d of d, J = 10Hz, 17Hz, 1H, H_c)

7.10.3 Rearrangement of 3-Propargylindene (104)

Refluxing 3-propargylindene with 2M sodium methoxide in methanol for 10 minutes gave a product which was purified by silica gel

chromatography eluting with light petroleum to give E-1,2-benzo-6-vinylfulvene (229), 60%, brilliant yellow crystals.

E-1,2-benzo-6-vinylfulvene (229)



m.p.(ethanol): ~40° with decomposition; b.p.: 63°/0.3mm

^{1}H n.m.r.(360MHz, $CDCl_3$, δ): 5.49 (d of d, J = 10.5Hz, 1.5Hz, 1H, $\underline{H}_b$), 5.64 (bd, J = 19Hz, 1H, $\underline{H}_a$), 6.85, 6.92 (AB spectrum, J = 4.5Hz, 2H, $\underline{H}_w$, H_x), 7.03 (d of d of d, J = 19Hz, 10.5Hz, 10.5Hz, 1H, H_c), 7.04 (broad d of d, J = 10.5Hz, 6.5Hz, 1H, $\underline{H}_d$), 7.18 (t of d, J = 7Hz, 1.5Hz, 1H, $\underline{H}_r$), 7.23 (t of d, J = 7Hz, 1.5Hz, 1H, $\underline{H}_q$), 7.29 (d of d of d, J = 7Hz, 2Hz, 1Hz, 1H, $\underline{H}_s$), 7.61 (d of d of d, J = 7Hz, 2Hz, 1Hz, 1H, $\underline{H}_p$)

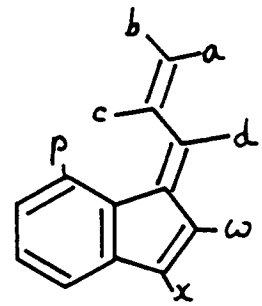
u.v.(mμ, ethanol): 204 (ε 27800), 274 (41000), 283 (37700), 333 (21600)

m.s.(m/e): 154.077499, (M^+, base peak, $C_{12}H_{10}$ requires 154.078247)

analysis: found C, 93.5 ; H, 6.5, $C_{12}H_{10}$ requires C, 93.5 ; H, 6.5

Passing 3-propargylindene (104) through alumina gave Z-1,2-benzo-6-vinylfulvene (230), 60%, a yellow oil. This product rearranged to the E isomer (229) on refluxing in NaOMe/HOMe (2M) for 5 minutes.

Z-1,2-benzo-6-vinylfulvene (230)



b.p.: 50°/0.1mm

^{1}H n.m.r.(δ): 5.48 (bd, J = 9Hz, 1H, $\underline{H}_b$), 5.53 (bd, J = 17Hz, 1H, $\underline{H}_a$), 6.30, 6.71 (AB spectrum, J = 5Hz, $\underline{H}_w$, $\underline{H}_x$), 6.60 (d, J = 11Hz, 1H, $\underline{H}_d$), 7.0 - 7.2 (m, 3H, Ar$\underline{H}$), 7.36 (d of d of d, J = 19Hz, 11Hz, 9Hz, 1H, $\underline{H}_c$), 7.70 (m, 1H, H_p)

i.r.(cm^{-1}): 1450(m), 1410(m), 1370(m), 970(m), 920(s), 750(s)

u.v.(mμ, n-hexane): 223 (ε 7700), 266 (15500), 273 (16500), 283 (13300), 318 (7900), 329 (8300), 344 (4700)

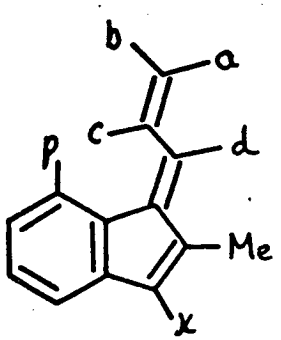
7.10.4 Rearrangement of 3-Allenylindene (172)

This allene rearranged by passage through alumina by standing in cold sodium methoxide for 10 minutes, to give Z-1,2-benzo-6-vinylfulvene (230), ~60%. 3(1'-Deuteroallenyl)indene (231) rearranged on alumina to give Z-1,2-benzo-6-deutero-6-vinylfulvene (232) with loss of the ^{1}H n.m.r. proton resonance at 6.60δ and sharpening of the vinyl resonances at 5.48δ and 5.53δ.

7.10.5 Rearrangement of 2-Methyl-1- and 3-propargylindene (109) and (110)

These compounds rearranged by refluxing in NaOMe/HOMe (2M) for 15 minutes to give a fulvene in 20% yield isolated from polymeric material by passage through basic alumina with light petroleum. Rearrangement on basic alumina gave the same product, in 50% yield, Z-1,2-benzo-4-methyl-6-vinylfulvene (237).

Z-1,2-benzo-4-methyl-6-vinylfulvene (237)



^{1}H n.m.r.(δ): 2.06 (d, J = 1Hz, 3H, CH_3), 5.22 (d, J = 10Hz, 1H, H_b), 5.30 (d, J = 16Hz, 1H, H_a), 6.34 (bs, 1H, H_x), 6.50 (d, J = 11Hz, 1H, H_d), 6.80 - 7.10 (m, 3H, ArH), 7.34 (d of d of d, J = 16Hz, 11Hz, 10Hz, 1H, H_c), 7.26 - 7.60 (m, 1H, H_p)

i.r.(cm^{-1}): 1450(s), 980(m) vinyl, 910(s) vinyl, 830(s), 740(s)

7.10.6 Rearrangement of 3-Methyl-1-propargylindene (106)

This compound did not undergo base catalysed rearrangement even after refluxing for 1 hour in NaOEt/HOEt (4M).

7.10.7 Rearrangement of 3-(But-2'-ynyl)indene (116)

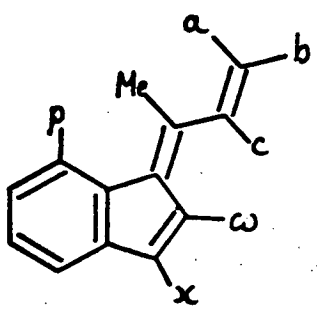
This compound did not undergo base catalysed rearrangement even after refluxing with sodium ethoxide in ethanol for 2 hours.

7.10.8 Rearrangement of 3-(1'-Methylprop-2'-ynyl)indene (118)

Refluxing in NaOMe/HOMe (2M) for 1 hour gave a mixture, 40%, containing equal amounts of two isomers, which were separated on alumina to give E and Z-1,2-benzo-6-methyl-6-vinylfulvene (238) and (239) as yellow oils. Rearrangement on alumina was incomplete but gave ~5% of the Z isomer only, plus unreacted starting material.

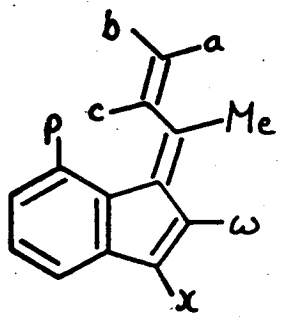
E-1,2-benzo-6-methyl-6-vinylfulvene (238)

^{1}H n.m.r.(δ): 2.42 (s, 3H, CH_3), 5.33 (d, J = 11Hz, 1H, H_b), 5.53 (d, J = 17Hz, 1H, H_a), 6.66 (d, J = 6Hz, 1H, H_x), 6.82 (d, J = 6Hz, 1H, H_w), 7.0 - 7.2 (m, 3H, ArH), 7.19 (d of d, J = 11Hz, 17Hz, 1H, H_c), 7.57 - 7.76 (m, 1H, H_p)



Z-1,2-benzo-6-methyl-6-vinylfulvene (239)

^{1}H n.m.r.(δ): 2.28 (s, 3H, CH_3), 5.45 (d, J = 12Hz, 1H, H_b), 5.58 (d, J = 18Hz, 1H, H_a), 6.70 (s, 2H, H_w, H_x), 6.9 - 7.4 (m, 3H, ArH), 7.60 (d of d, J = 12Hz, 18Hz, 1H, H_c), 7.55 - 7.70 (m, 1H, H_p)

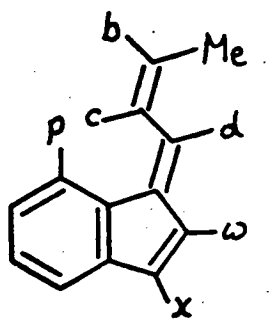


7.10.9 Rearrangement of 3-(Buta-1',2'-dienyl)indene (177)

Refluxing for two minutes in NaOMe/HOMe (2M) or passing through alumina gave the same product in 70% and 80% yield respectively, believed to be Z-1,2-benzo-6-(Z-prop-1'-enyl)fulvene (240).

Z-1,2-benzo-6-(Z-prop-1'-enyl)fulvene (240)

^{1}H n.m.r.(δ): 1.89 (d of d, J = 8Hz, 2Hz, 3H, CH_3), 5.86 (d of q, J = 9Hz, 8Hz, 1H, H_b), 6.33, 6.60 (AB spectrum, J = 6Hz, 2H, H_w, H_x), 6.76 (d, J = 6Hz, 1H, H_a), 6.90 - 7.30



(m, 4H, ArH + H_c), 7.60 - 7.70 (m, 1H, H_p)

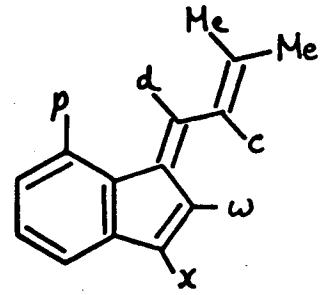
i.r.(cm^{-1}): 1580(m), 1445(s), 1370(s), 905(s), 790(m), 750(s), 725(m)

u.v.(mμ, n-hexane): 230 (ε 9700), 282 (19300), 323 (15000), 333 (18700), 348 (10300)

7.10.10 Rearrangement of 3-(3'-Methylbuta-1',2'-dienyl)indene (178)

Stirring in cold NaOMe/HOMe (2M) for 10 minutes followed by alumina chromatography eluting with light petroleum to remove the polymeric material, or passing through alumina gave 1,2-benzo-6-(2'-methylprop-1'-enyl)fulvene (247) in 30% and 70% respectively, as mainly the E isomer.

E-1,2-benzo-6-(2'-methylprop-1'-enyl)fulvene (247)

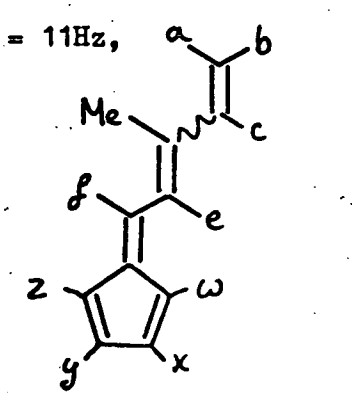


^{1}H n.m.r.(δ): 1.92 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 6.31, 6.60 (AB spectrum, J = 5Hz, 2H, H_w, H_x), 6.80 (s, 2H, H_c, H_d), 6.90 - 7.20 (m, 3H, ArH), 7.60 - 7.76 (m, 1H, H_p)

7.10.11 Rearrangement of Z-3-(3'-Methylpent-2'-en-4'-ynyl)-cyclopentadiene (136)

Refluxing with NaOMe/HOMe (2M) for 20 minutes gave 6-(2'-methylbuta-1',3'-dienyl)fulvene isolated from residual starting material and polymeric material, in 20% yield, by alumina chromatography, eluting with light petroleum.

6-(2'-methylbuta-1',3'-dienyl)fulvene



^{1}H n.m.r.(δ): 2.02 (bs, 3H, CH_3), 5.17 (d, J = 11Hz, 1H, H_b), 5.37 (bd, J = 15Hz, 1H, H_a), 6.07 (bd, J = 5Hz, 1H, H_z), 6.32 (bd, J = 4Hz, 1H, H_w), 6.38 - 6.50 (m, 2H, H_y, H_x), ~6.6 (m, 1H, H), 6.98 (d, J = 12Hz, 1H, H_f), 7.12

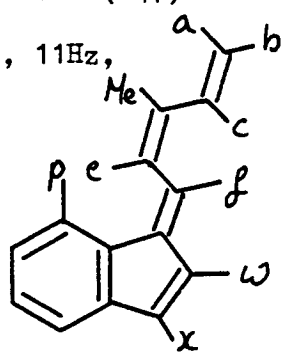
(d of d, J = 12Hz, J = 2Hz, $\underline{H}_e$)

u.v.(mμ, n-hexane): 230 (ε 6100), 330 (29400), 343 (29100)

7.10.12 Rearrangement of Z-3-(3'-methylpent-2'-en-4'-ynyl)-indene (126b)

Refluxing with NaOEt/HOEt (2M) for 0.5 hours gave, after removal of polymeric material eluting with light petroleum, a yellow crystaline product in 55% yield, apparently containing two isomeric fulvenes. The major product has been isolated reasonably pure by alumina chromatography and assigned the structure Z-1,2-benzo-6-(Z-2'-methylbuta-1',3'-dienyl)fulvene (247). m.p.: 89 - 92°

Z-1,2-benzo-6-(Z-2'-methylbuta-1',3'-dienyl)fulvene (247)



^{1}H n.m.r.(δ): 2.02 (s, 3H, $C\underline{H}_3$), 5.26 (d, 11Hz, 1H, $\underline{H}_b$), 5.36 (bd, J = 17Hz, 1H, $\underline{H}_a$), 6.60 (bd, J = 13Hz, 1H, $\underline{H}_f$), 6.76 (s, 2H, $\underline{H}_w$, $\underline{H}_x$), 6.94 - 7.20 (m, 4H, Ar$\underline{H}$ + $\underline{H}_c$), 7.37 (d, J = 13Hz, 1H, $\underline{H}_e$), 7.4 - 7.6 (m, 1H, $\underline{H}_p$)

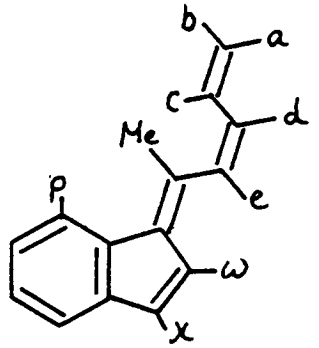
u.v.(mμ, n-hexane): 239 (ε 9100), 292 (15000), 302 (13000), 348 (29400), 357 (34400)

m.s.(m/e): 194.109062 (M^+, base peak, $C_{15}H_{14}$ requires 194.109545), 179

7.10.13 Rearrangement of E and Z-3-(1'-methylpent-2'-en-4'-ynyl)-indene (122a) and (122b)

Refluxing in NaOEt/HOEt (2M) for 0.5 hours gave a mixture of two fulvenes A and B in the ratio 1.3:1 in 27% yield. These have been partially separated, as yellow powders, by alumina chromatography.

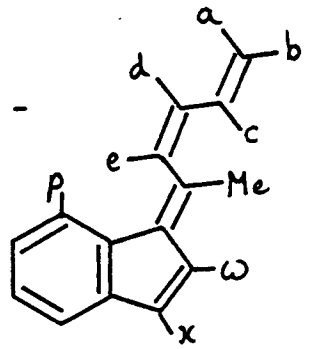
A: E-1,2-benzo-6-methyl-6-(Z-buta-1',3'-dienyl)fulvene (246)



^{1}H n.m.r.(δ): 2.46 (s, 3H, C$\underline{H}_3$), 5.15 (bd, J = 9Hz, 1H, $\underline{H}_b$), 5.30 (d, J = 15Hz, 1H, $\underline{H}_a$), 6.35 - 6.60 (m, 2H, $\underline{H}_c$ and $\underline{H}_d$), 6.65, 6.85 (AB spectrum, J = 6Hz, 2H, $\underline{H}_w$, $\underline{H}_x$), 6.97 - 7.4 (m, 4H, Ar$\underline{H}$ + $\underline{H}_e$), 7.57 - 7.75 (m, 1H, $\underline{H}_p$)

i.r.(cm^{-1}): 1445(s), 1370(m), 1000(m), 750(s) cis olefin, 720(m)

B: Z-1,2-benzo-6-methyl-6-(Z-buta-1',3'-dienyl)fulvene (247)



^{1}H n.m.r.(δ): 2.26 (s, 3H, C$\underline{H}_3$), 5.22 (bd, J = 8Hz, 1H, $\underline{H}_b$), 5.45 (bd, J = 9Hz, 1H, $\underline{H}_a$), 6.5 - 6.8 (m, 1H, $\underline{H}_c$), 6.69 (s, 2H, $\underline{H}_w$, $\underline{H}_x$), 7.0 - 7.4 (m, 4H, Ar$\underline{H}$ + $\underline{H}_d$), 7.38 (bd, J = 6Hz, 1H, $\underline{H}_e$), 7.53 - 7.73 (m, 1H, $\underline{H}_p$)

i.r.(cm^{-1}): 1445(s), 1370(m), 1000(m), 750(s) cis olefin, 720(m)

7.11 Miscellaneous Reactions

7.11.1 Preparation of 1-(3'-Deuteropropargyl)indene (175)

Ethyl magnesium bromide Grignard was prepared from magnesium (0.63g, 0.026 mol.) in 50ml ether and ethyl bromide (2.83g, 0.026 mol.). 1-Propargylindene (3.8g, 0.025 mol.) was added and the mixture refluxed until evolution of ethane ceased. The mixture was cooled and deuterium oxide (4g, 0.2 mol.) was added slowly. The mixture was filtered and the solvent removed under reduced pressure. The product was cleaned on silica gel; yield 84%. The product showed loss of the acetylenic proton resonance in the ^{1}H n.m.r.

7.11.2 Preparation of (5'-Deutero-3'-methylpent-2'-en-4'-ynyl)-indene (189)

This was prepared as in 7.11.1. The acetylenic proton resonance

intensity in the ^1H n.m.r. was reduced to 25% of the original level.

7.11.3 9,9-Bis(3'-deuteropropargyl)fluorene was similarly prepared with complete loss of the acetylenic proton resonance.

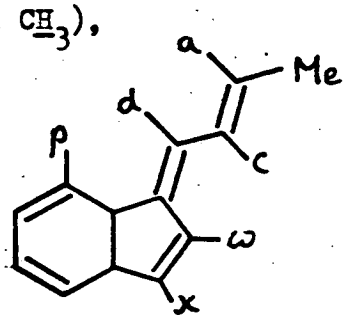
7.11.4 Preparation of E-1,2-Benzo-6-(E-prop-1'-enyl)fulvene (241)

Crotonaldehyde (4.5g, 0.06 mol.) and indene (5.8g, 0.05 mol.) was added to warm sodium ethoxide in ethanol (50ml, 2M) with evolution of heat. After one minute water (50ml) was added and the product extracted into petrol, dried and the solvent removed. The product was distilled under reduced pressure (some polymerisation) to give E-1,2-benzo-6-(E-prop-1'-enyl)fulvene (241) (3.3g, 35%).

E-1,2-benzo-6-(E-prop-1'-enyl)fulvene (241)

b.p.: 95 - 100°/0.2mm, lit.[105] m.p. 298 - 299°

^1H n.m.r.(δ): 1.88 (d of d, J = 7Hz, 1Hz, 3H, CH_3), 6.01 (d of q, J = 14Hz, 7Hz, 1H, H_a), 6.56 (bd, J = 12Hz, H_d), 6.80 (d of d, J = 12Hz, 12Hz, 1H, H_c), 6.74 (bs, 2H, H_w and H_x), 6.9 - 7.3 (m, 3H, ArH), 7.30 - 7.60 (m, 1H, H_p)



i.r.(cm^{-1}): 1630(s), 1445(s), 960(s), 780(s), 750(s), 720(m)

u.v.(mμ, n-hexane): 220 (ε 7725), 252 (13905), 257 (15800), 278 (20700), 287 (19500), 325 (15800), 335 (18200), 348 (12600)

m.s.(m/e): 168.093983 (M^+, base peak, $C_{13}H_{12}$ requires 168.093896), 153, 152

7.11.5 Reaction of Allyl Bromide with Indene

This was done using the conditions described in section 7.4 replacing 1-bromo-3-methylbuta-1,2-diene with allyl bromide.

Method A gave a 68% yield of 3-allenylindene characterised by

comparison of the ^{1}H n.m.r. with the published spectrum.[124]

Method B - a preparation of 3-allenylindene by a method similar to method B has been reported by Makosza[125], yield 73%.

7.11.6 Reaction of Ethyl Bromide with Indene

This was done using the conditions described in section 7.4, replacing 1-bromo-3-methylbuta-1,2-diene with ethyl bromide.

Method A gave no reaction.

Method B gave 80% of 3-ethylindene (see section 7.3.8).

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