REARRANGEMENTS OF ALLENES AND ACETYLENES

by

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Abstract of Thesis

This thesis describes the preparation of alkynyl derivatives of fluorene via reaction of the fluorenyl anion (generated with phenyl lithium) with alkynyl halides. Low pressure vapour phase pyrolysis of these compounds was carried out. Propargylic fluorenes gave allenyl fluorenes by an intramolecular sigmatropic shift with other, radical derived, products predominating at higher temperatures. The alkynyl fluorenes were themselves resistant to rearrangement by base but the allenyl fluorenes rearranged readily on alumina to give dibenzofulvenes.

A number of alkynyl derivatives of indene were prepared by first generating the indenyl anion with sodamide in liquid ammonia or by aqueous alkali under phase transfer catalysis conditions. The anion thus generated was then reacted with alkynyl halides. Propargylic indenes gave allenyl indenes on pyrolysis and it is shown that the allenes are produced by an intramolecular sigmatropic shift or a 'Cope' rearrangement depending on the nature of the alkynyl indene. The alkynyl indenes rearrange by base to give benzofulvenes. The benzofulvenes were produced as mixtures of geometric isomers some of which were separable. The individual isomers or mixtures of isomers were characterised largely by use of high field ^{1}H n.m.r. spectroscopy

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CHAPTER 1

A Review of Some Preparations and Rearrangements of Terminal Acetylenes

1.1 Synthesis of Terminal Acetylenes

There are a large number of syntheses of acetylenic compounds in the literature[1,2]. These may be divided into synthesis by elimination reactions or synthesis by combination with acetylene itself or other molecules with an existing triple bond.

1.1.1 Elimination Reactions

In elimination reactions the triple bond is produced by removal of atoms from the existing carbon skeleton of the molecule. The best known example of this type of reaction is the dehydrohalogenation of halo olefins which normally requires strong base. For instance phenyl acetylene (1) can be produced by reaction of β-bromostyrene with alcoholic potassium hydroxide solution[3]. Alkyl acetylenes can also be formed in

$$Ph-CH=CHBr \xrightarrow[\text{ethanol}]{KOH} Ph-C\equiv CH \quad (1)$$

this manner but under these basic conditions rearrangement of the triple bond can also occur (see p. 9). This type of reaction can also be performed without solvent by dropping the halide onto hot or molten alkali. Other bases such as

sodamide in liquid ammonia can be used as in a preparation of 3-(N-butylamino) propyne (2)[4].

$$HBrC{=}CHCH_2NHC_4H_9 \xrightarrow[NH_{3(l)}]{NaNH_2} HC{\equiv}CCH_2NHC_4H_9 \quad (2)$$

Dihaloalkanes can undergo similar elimination reactions to those of halo olefins to give acetylenes. 1,2-Dibromo-11-chloroundecane (3) gives 1-chloroundec-10-yne (4) using sodamide[5], and potassium-t-butoxide has been used in the

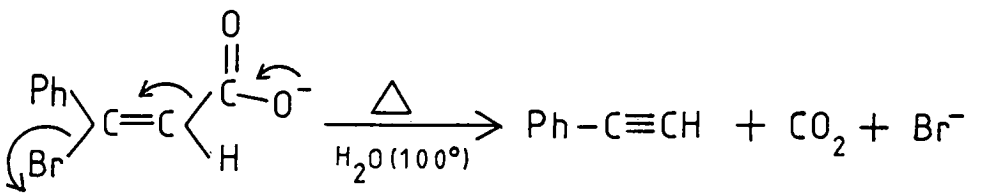
$$Cl(CH_2)_9CHBrCH_2Br \xrightarrow[-2\times HBr]{} Cl(CH_2)_9C{\equiv}CH$$
$$(3) \qquad\qquad (4)$$

presence of a crown ether catalyst[6] to generate terminal alkynes from 1,2 and 1,1 dihalides. This procedure has the

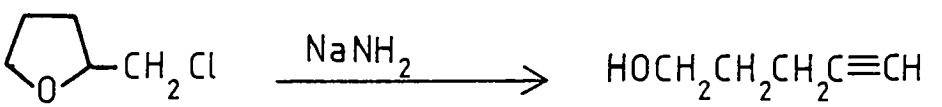
$$C_4H_9CHBrCH_2Br \xrightarrow[KOBu^t/[18]CROWN-6]{} C_4H_9C{\equiv}CH \qquad 96\%$$

advantage over classical methods because conditions are mild and the reaction mixture is easily worked up giving a high yield of products. The crown ether presumably assists the reaction by solvating the potassium anion into the non-polar solvent used.

Elimination of groups other than hydrogen halide is also possible, phenyl acetylene can also be prepared under mild conditions from β-bromocinnamic acid salts[7] by decarboxylation and loss of bromide ion.

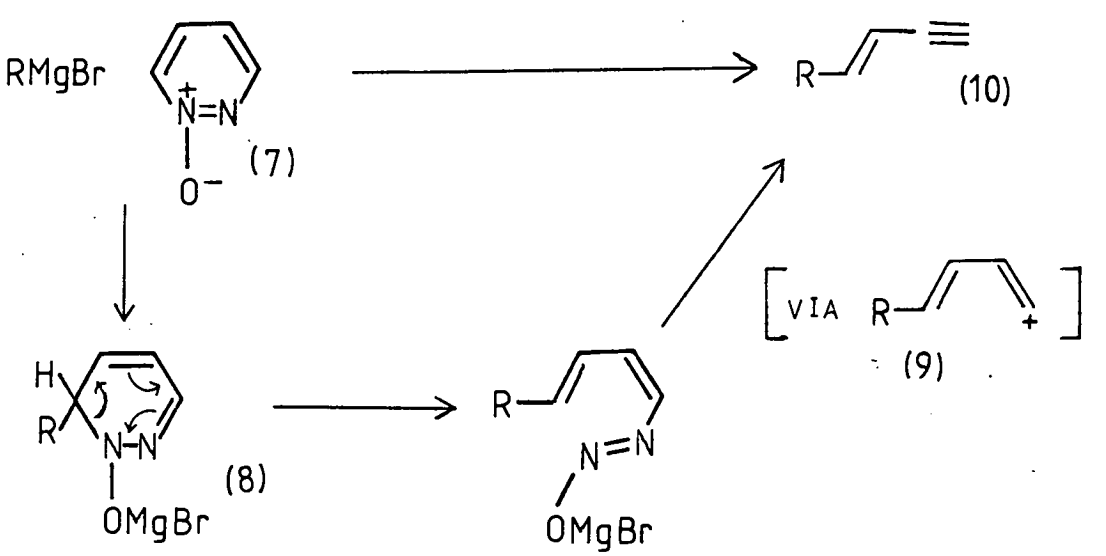


Two useful syntheses involve ring opening as well as elimination. Pent-4-yn-1-ol (5) is readily prepared from tetrahydrofurfuryl chloride (6) by sodamide in liquid ammonia[8]. Several enynes have been prepared by the reaction of Grignard

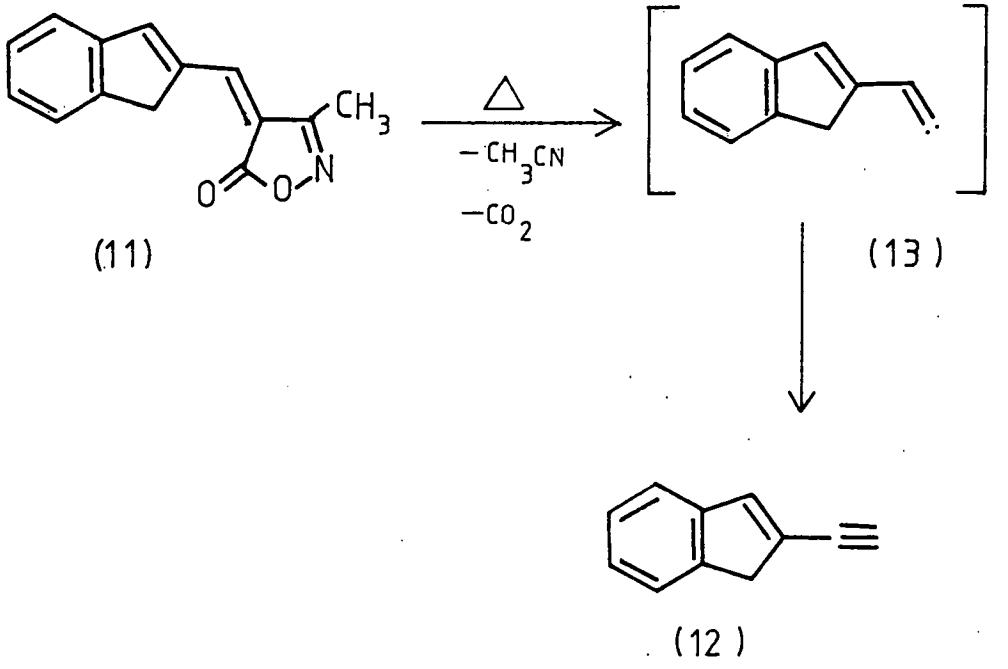


(6) (5)

reagents with pyridazine-1-oxide (7)[9]. It is believed that the reaction proceeds by ring opening of the Grignard adduct (8) followed by loss of nitrogen and $[OMgBr]^-$ to give a species such as (9) leading to the product (10).

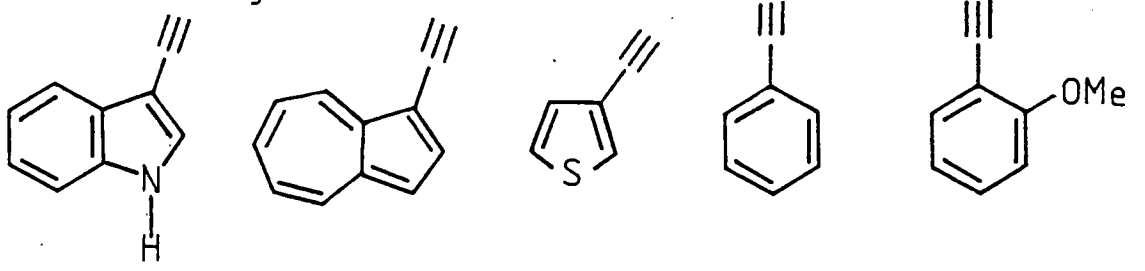


Thermal methods have also been employed. Pyrolysis of 4-(2-indenylmethylindene)-3-methylisoxazol-5(4H)-one (11) at low pressure in the vapour phase produces carbon dioxide, acetonitrile and 2-ethynylindene (12)[10]. It is thought that the reaction proceeds via loss of the acetonitrile and



(11) (13) (12)

carbon dioxide to give the methylene carbene (13) which rearranges to the product (12). This carbene has been invoked as the intermediate in some acetylene rearrangements (see p.17). The 3-methylisoxazolone derivative (11) is readily produced by stirring 3-methylisoxazolone with 2-formylindene at room temperature in chloroform, under nitrogen, for 24 h. This method provides an easy route to 2-ethynylindene (12) and several other aryl acetylenes have also been prepared by this route[11,12] e.g.



1.1.2 Synthesis from Acetylene or Molecules with an Existing Triple Bond

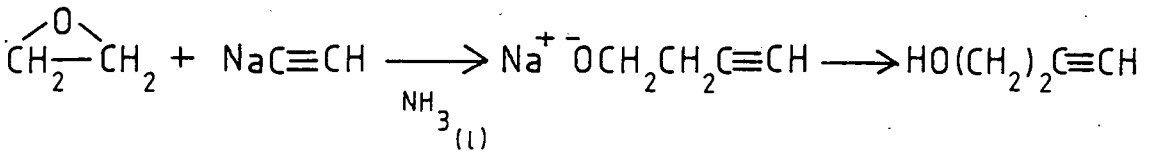
The weakly acidic acetylene proton can be removed by strong base in anhydrous solvents (e.g. $NaNH_2$ in liquid ammonia) to form the acetylide anion which readily attacks alkylating agents such as alkyl halides to form terminal acetylenes.

Reaction with alkyl halides is restricted to primary halides without branching at the β carbon[13] since elimination reactions occur with secondary and branched alkyl halides under basic conditions. As might be expected the ease of substitution is I>Br>Cl>F, e.g. reaction of sodium acetylide with 1-bromo-4-chloropropane giving 1-chlorohex-5-yne (14) and not 1-bromohex-5-yne[14].

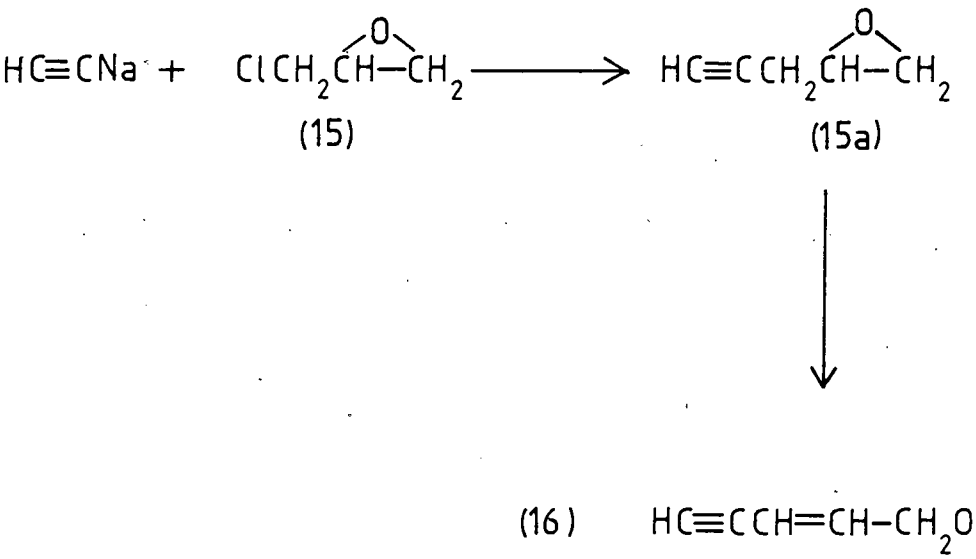
$$NaC{\equiv}CH + Br(CH_2)_4Cl \xrightarrow[NH_{3(l)}]{} HC{\equiv}C(CH_2)_4Cl + NaBr$$

Acetylenic alcohols are important intermediates in acetylene synthesis because of their ready convertion into the reactive acetylenic bromides (see p.7), and can often be prepared by addition of acetylide to aldehydes, ketones[1] or epoxides[15] as in the following examples:

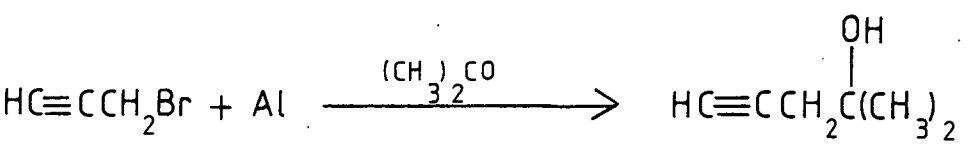
$$(CH_3)_2CO + NaC{\equiv}CH \longrightarrow (CH_3)_2C(O^-\,Na^+)-C{\equiv}CH \xrightarrow[(NH_4Cl)]{\text{HYDROLYSIS}} (CH_3)_2C(OH)-C{\equiv}CH$$



If epichlorohydrin (15) is used then pent-2-en-4-yn-1-ol (16) is produced via (15a)[16].

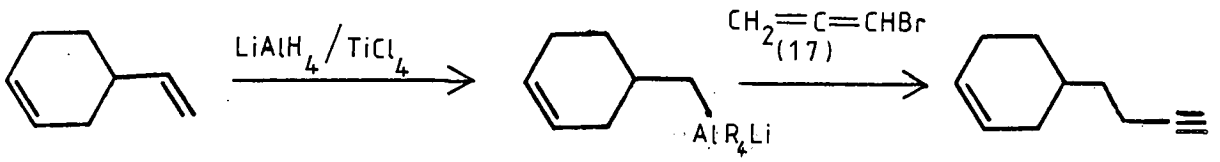


Propargyl zinc bromide[17] or propargyl aluminium bromide[18] can be used to produce alcohols with the hydroxyl function on the fourth carbon e.g.[19]



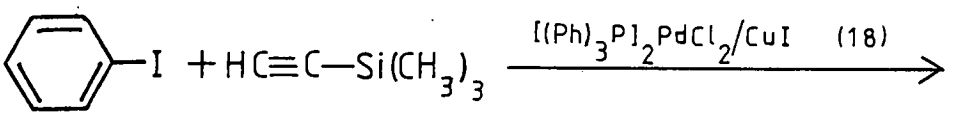
The aluminium compound is preferred since there is no allene formation in the reaction[18].

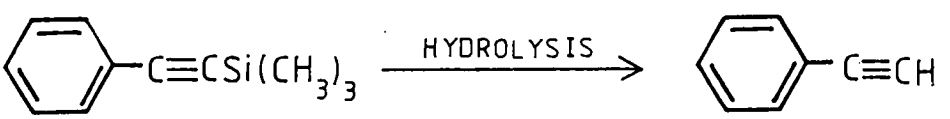
Bromoallene (17) has recently been used to introduce the propargyl group into certain alkenes[20]:-



If propargyl bromide is used in the above reaction the terminal allene is produced.

A catalytic method of producing aryl acetylenes has been reported recently[21]. For example trimethylsilylacetylene can be added to iodobenzene using the palladium and copper catalyst mixture (18) and the resulting adduct gives phenylacetylene on hydrolysis.

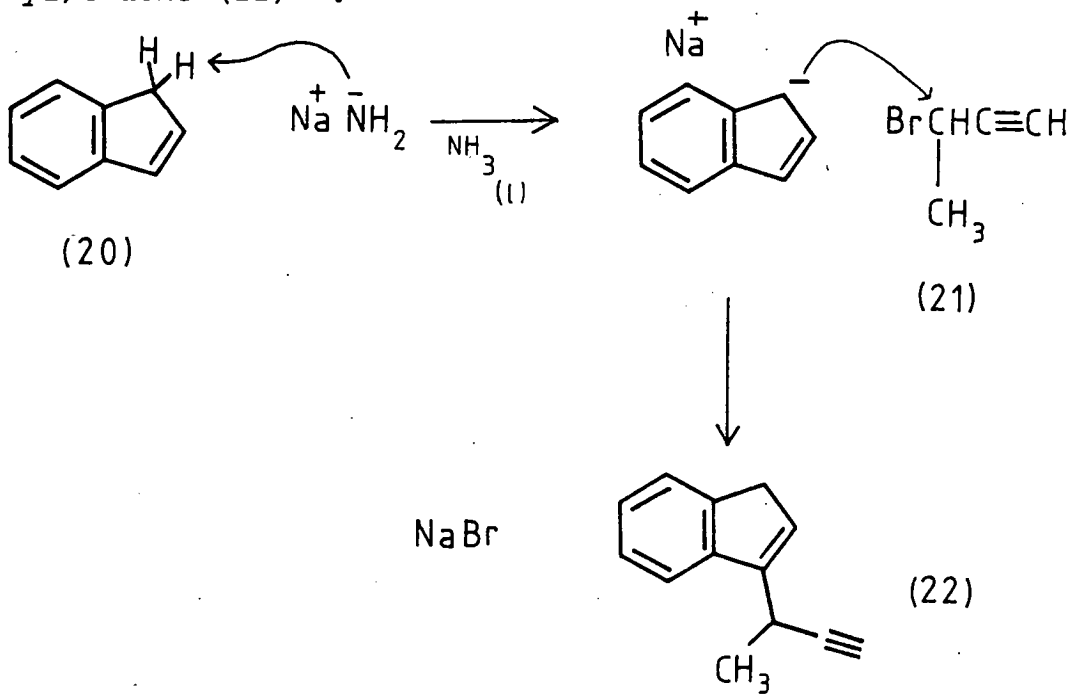




Acetylene itself gave a substantial amount of diphenylacetylene.

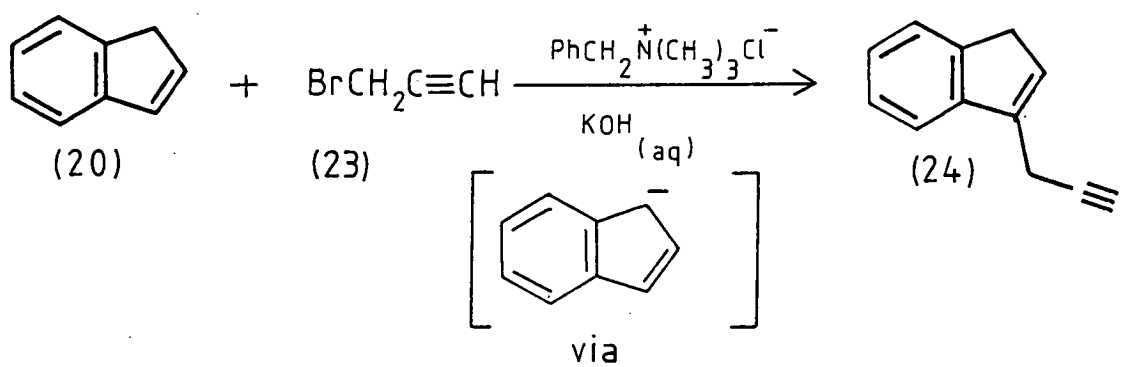
Suitable alkynyl bromides (or iodides) can be readily added to other molecules by nucleophilic substitution at the halide carbon to produce larger molecules. Two methods of carrying out this type of synthesis have been used extensively in work reported later in this thesis to produce derivatives of fluorene (19) and indene (20). The first method involves

reaction of the alkynyl halide with the sodium derivative of the hydrocarbon. For example reaction of indene (20) with sodamide followed by reaction of the indenyl sodium formed with 3-bromobut-1-yne (21) gives 3(1'-methylprop-2'-ynyl)indene (22)[22].



(20) (21) (22)

The other method involves reaction of the alkynyl halide with the hydrocarbon anion generated by using aqueous base and a phase transfer catalyst. Reaction of propargyl bromide (23) with indene (20) in the presence of aqueous potassium hydroxide and a small amount of benzyltrimethylammonium chloride gives 3-propargylindene (24)[22].



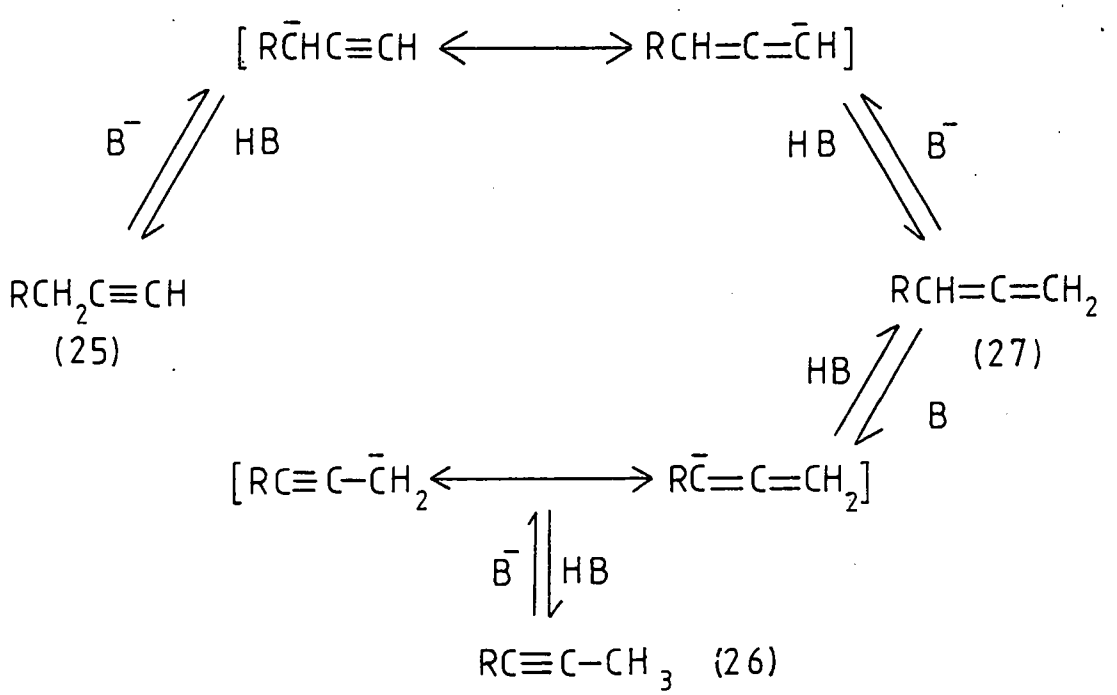
(20) (23) (24)

In both the preceeding examples the more stable 3-substituted product is obtained rather than the 1-substituted

because of the facile rearrangement of the indene double bond (see p. 31).

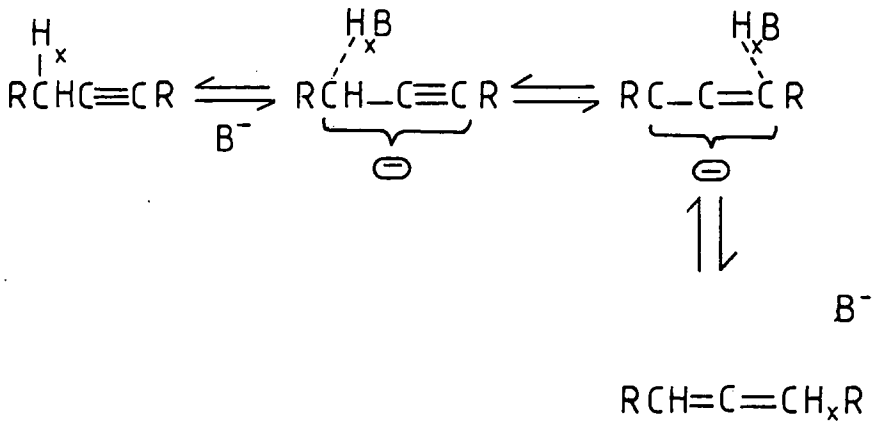
1.2 Base Induced Acetylene/Allene Interconversions

The base catalysed isomerisation of acetylenes has been known and studied extensively since Favorski[23] observed the rearrangement of alk-1-ynes (25) to alk-2-ynes (26) on heating with alcoholic potassium hydroxide solution. The isomerisations of simple acetylenes, 'ene-ynes', di- and triacetylenes have been reviewed by Bushby[23] and Wotiz[1] who show that these rearrangements can be considered as proceeding via an intermediate allene (27) and involving resonance stabilised carbanions.



This reaction has been shown by Cram[24] to proceed with a high degree of intramolecularity in suitably proton deficient

solvents. In this case he invokes a "conducted tour" mechanism as shown below, in which the "acidic" proton H_x remains associated with its parent molecule and is transported rather than abstracted by the base B.



As the steps in these types of rearrangement are reversible the product(s) are those that are more thermodynamically stable. Benson[25] et al. have used thermochemical data to show that for n-pentyne the order of stability of possible isomers is as shown in Table 1.

Table 1 Heats of Formation of C_5H_8 isomers ($kJmol^{-1}$)

	ΔH_f^{298}
$C_3H_7C{\equiv}CH$	144
$C_2H_5CH{=}C{=}CH_2$	142
$CH_3CH{=}C{=}CHCH_3$	130
$C_2H_5C{\equiv}CCH_3$	126
$CH_2{=}CHCH_2CH{=}CH_2$	106
$CH_3CH{=}CH{-}CH{=}CH_2$	76

However isomerisation of simple straight chain alkynes tends to stop at the alk-2-yne (26) stage and not to proceed to the most stable isomer (the conjugated diene), unless very strong

bases (e.g. potassium-t-butoxide) are used. This is attributed to kinetic factors. The isomerisation can be stopped at the allene if stabilising alkyl groups are present e.g.

$$HC\equiv CCH(CH_3)_2 \xrightarrow[KOH_{(alc)}]{\Delta} CH_2=C=C(CH_3)_2$$

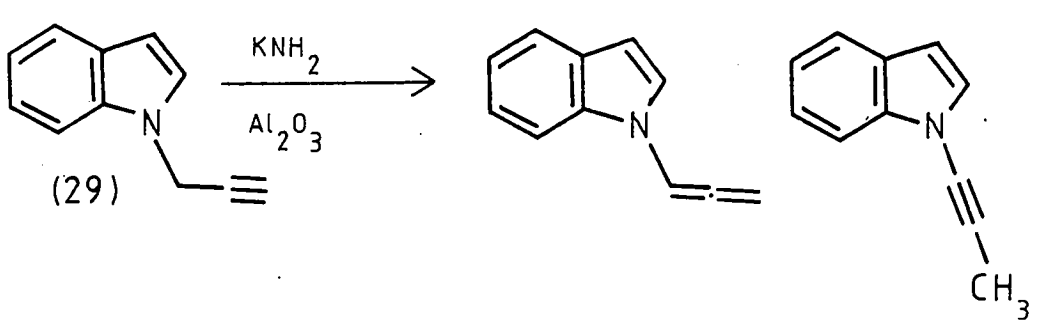
In the case of substituted monoacetylenes the stability of possible products depends on the nature of the substituent. It has been observed that acetylene bonds tend to migrate towards conjugation and away from electron withdrawing groups, due to the "electron deficient" nature of the triple bond. For example conjugated dienes (28) are readily formed from acetylenes with a β aryl group[23].

$$RC\equiv CCH_2CH_2Ar \xrightarrow{BASE} [RHC=C=CH\overset{*}{C}H_2Ar] \xrightarrow{BASE} RCH=CH-CH=CHAr$$

(28)

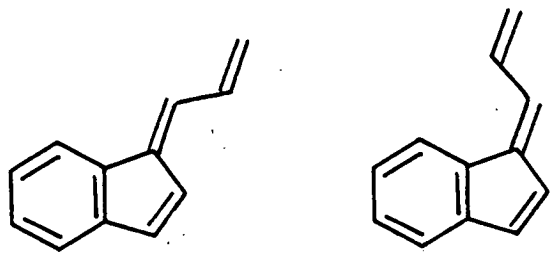
The benzylic hydrogen atoms (H^*) have increased acidity due to the presence of the aryl group and thus are readily attacked by base.

Potassium amides on alumina causes ready isomerisation of N-propargyl heterocycles such as (29)[26], but these conditions



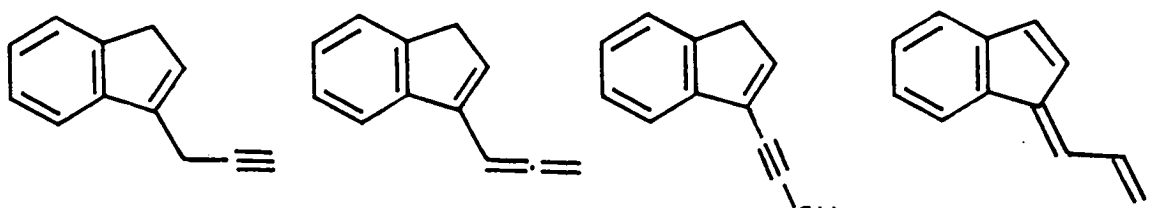
(29)

did not produce products from 3-propargyl indene (24). Truslove[22] did succeed in rearranging this compound by using sodium ethoxide in ethanol to give the vinyl benzofulvenes (30) and (31) which are the most thermodynamically stable products as can be seen from Table 2.



(30) (31)

Table 2 Heats of formation* for some indene derivatives

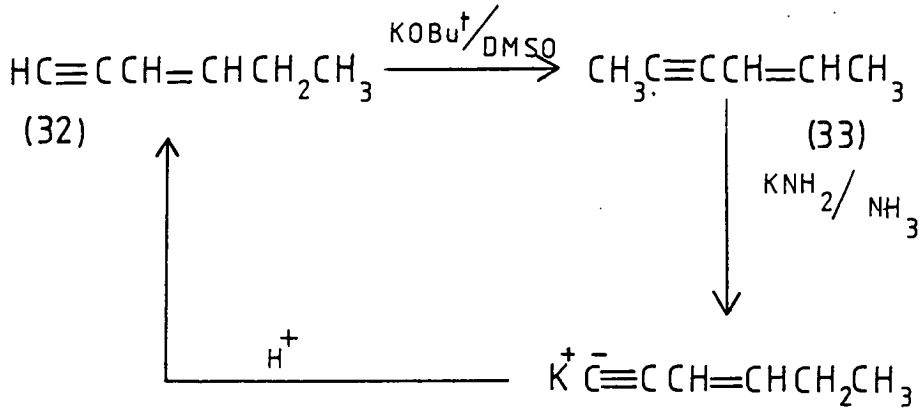


ΔH_f^{298}	387	377	374	274

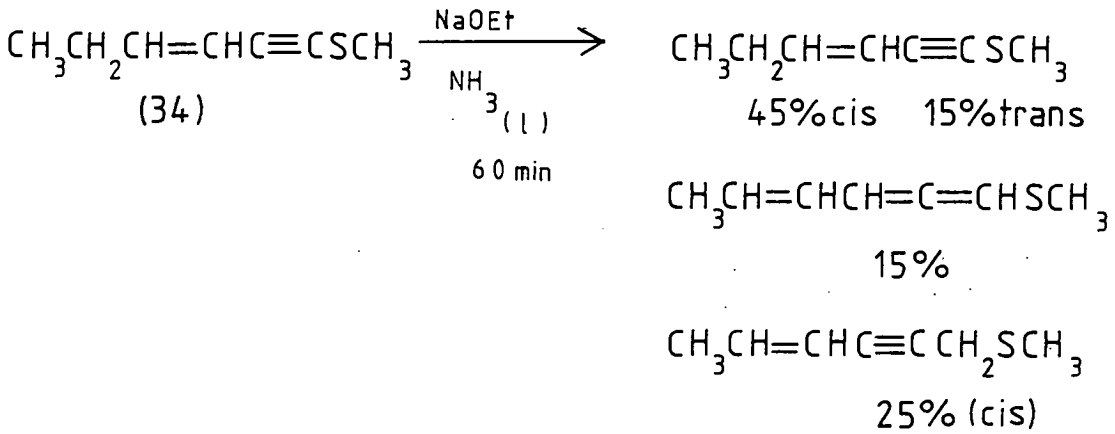
(kJmol^{-1})

*calculated by method of Benson[25]

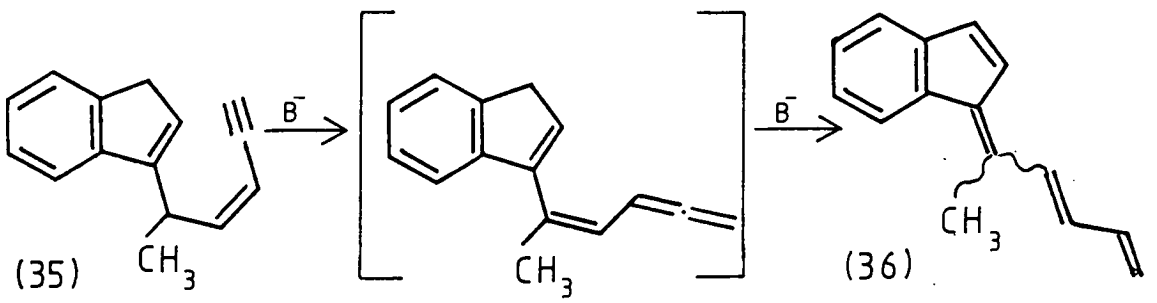
Conjugated enynes have been observed to rearrange under basic conditions in a similar manner to simple acetylenes[27,28]. For example hex-3-en-1-yne (32) gives hex-4-en-2-yne (33) on treatment with potassium-t-butoxide in dimethyl sulphoxide. Treatment of this product with potassium amide in liquid ammonia gives potassium hex-3-en-1-ynide which gives (32) again on hydrolysis.



The allene-ene (HC=C=CH-CH=CHR) has been shown to be present in the rearrangement of thioethers[29] (34), and this type of

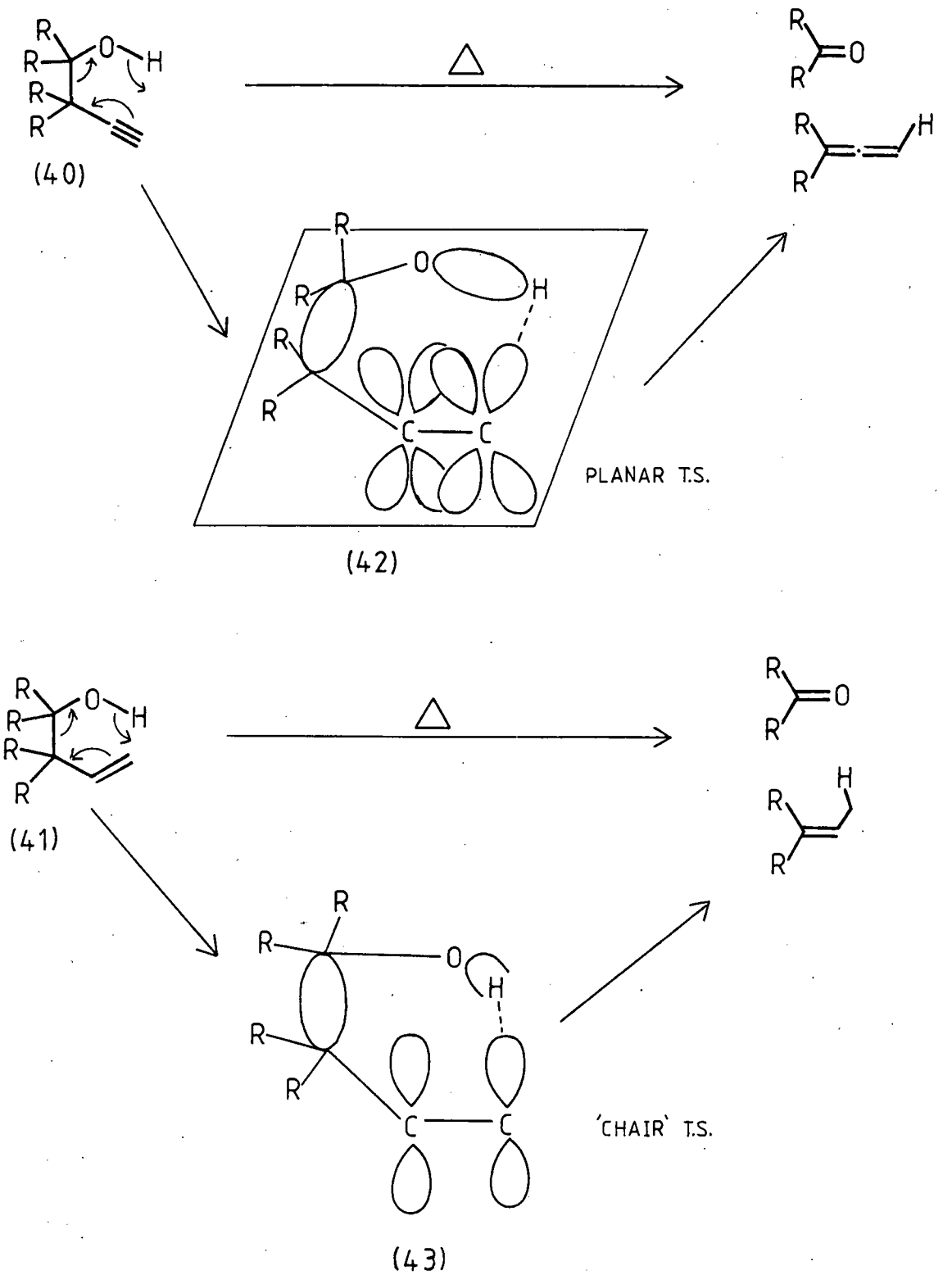


species has been suggested by Truslove[22] as the possible intermediate in the rearrangement of pentenynyl indenes (35) and cyclopentadienes to give fulvene type products (36)[22].



The stereochemistry of the products was uncertain and a re-examination of the reaction is described later in this thesis (p. 58).

FIGURE 1


R
O
H
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R
R
(40)
△
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R
H
R
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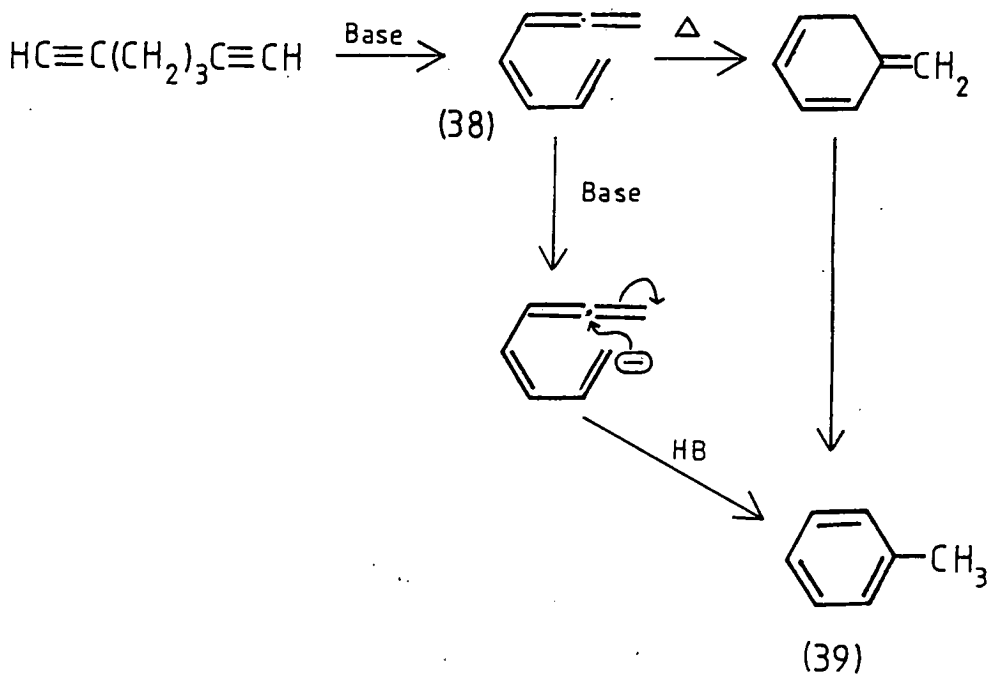
C
C
PLANAR T.S.
(42)
R
O
R
H
R
R
(41)
△
R
O
R
H
R
R
C
C
'CHAIR' T.S.
(43)

Diacetylenes of the type $HC{\equiv}C(CH_2)_nC{\equiv}CH$ (37) give alkyl benzenes on treatment with potassium-t-butoxide in diglyme (n = 3,4,5,6,10). The proposed mechanism[30] involves the production of an allene such as (38) which then cyclises either thermally or via a carbanion (39).

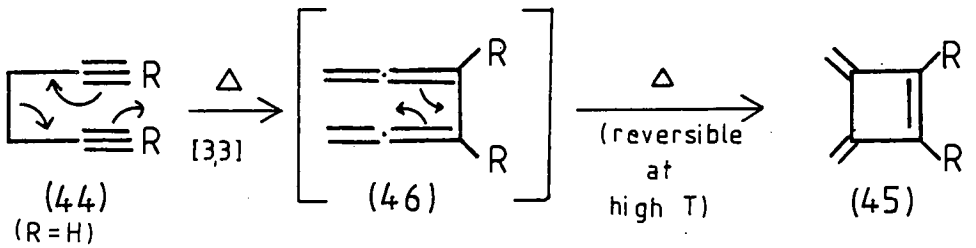


1.3 Thermal Rearrangement of Acetylenes and Allenes

Acetylenic compounds can undergo a large number of thermal rearrangements depending on the nature of the compound and the reaction conditions used. Intramolecular thermal reaction of acetylenic compounds have recently been reviewed extensively by Viola, Collins and Fillip[31]. They noted that many acetylenic compounds react at faster rates than the corresponding alkenes. For example the retro-ene cleavage of β-hydroxyacetylenes (40) shown in Fig.1 proceeds at a faster rate than that of β-hydroxyolefins (41). It is suggested that for the acetylene a planar transition state such as that

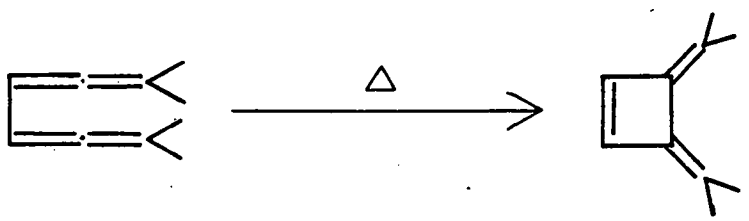
shown (42) allows maximum orbital interaction or 'aromaticity' during reaction. This geometry is not possible in the case of the olefin transition state due to the directional nature of the π orbitals of the double bond and so an orthogonal transition state such as (43) is required.

Hexa-1,5-diyne (44) and related compounds undergo a cyclisation reaction to dimethylene cyclobutenes (45)[32]. The proposed mechanism involves a [3,3] sigmatropic rearrangement to a biallene (46) and then cyclisation.

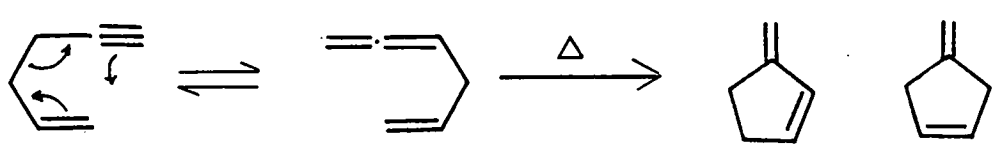


(44) (R=H) (46) (45)

The known cyclisation of biallenes[33] lends some support to the mechanism. Hex-1-en-5-yne (47) behaves similarly to

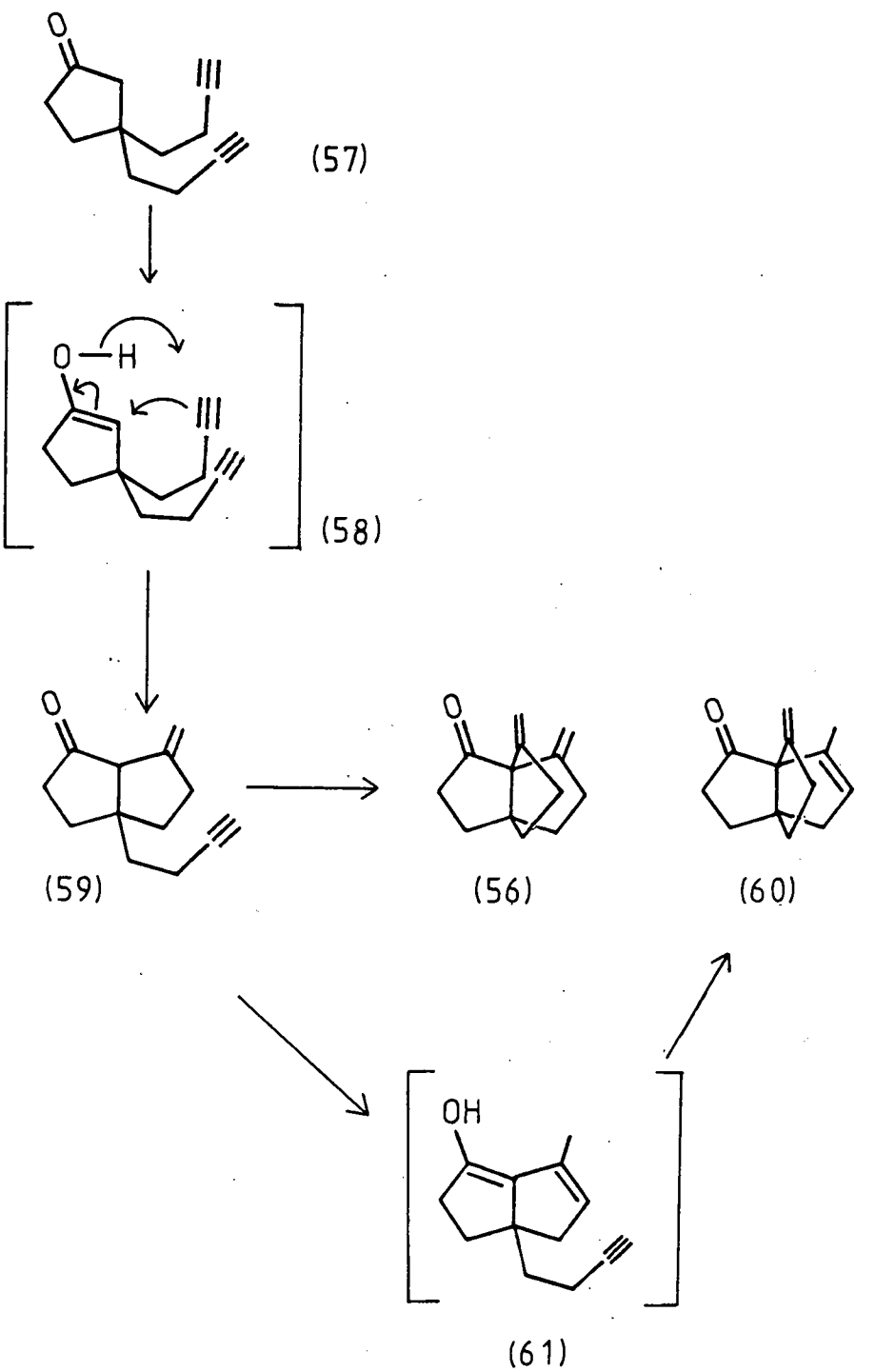


the diacetylenes by undergoing a reversible Cope type rearrangement to hexa-1,2,5-triene (48)[34]. It is believed that

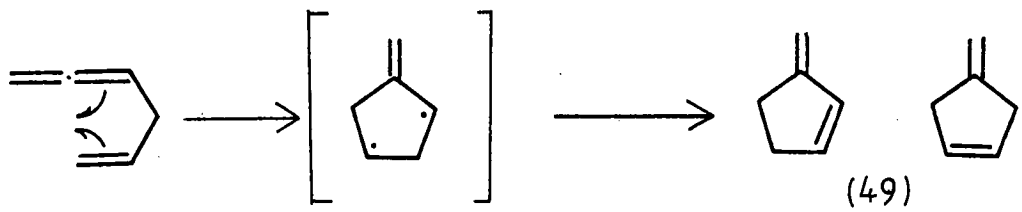


(47) (48) (49)

FIGURE 2

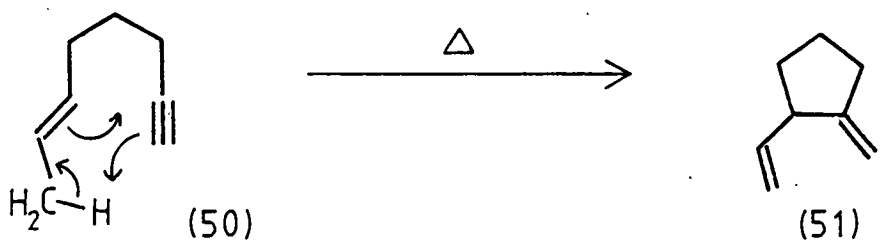


the methylene cyclopentenes (49) are formed via a diradical intermediate as shown below.



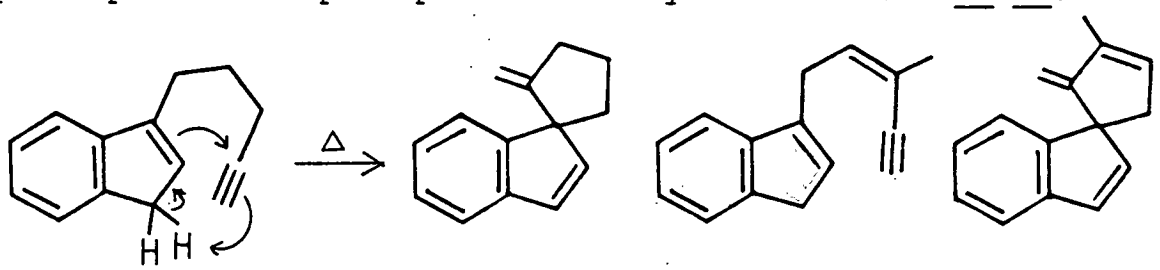
(49)

If there are a sufficient number of carbon atoms between a double and a triple bond in a molecule to permit the correct geometry for reaction then an intramolecular ene type cyclisation can occur. For example oct-2-en-7-yne (50) gives 2-vinylmethylene-cyclopentane (51) thermally[35]. This reaction



(50) (51)

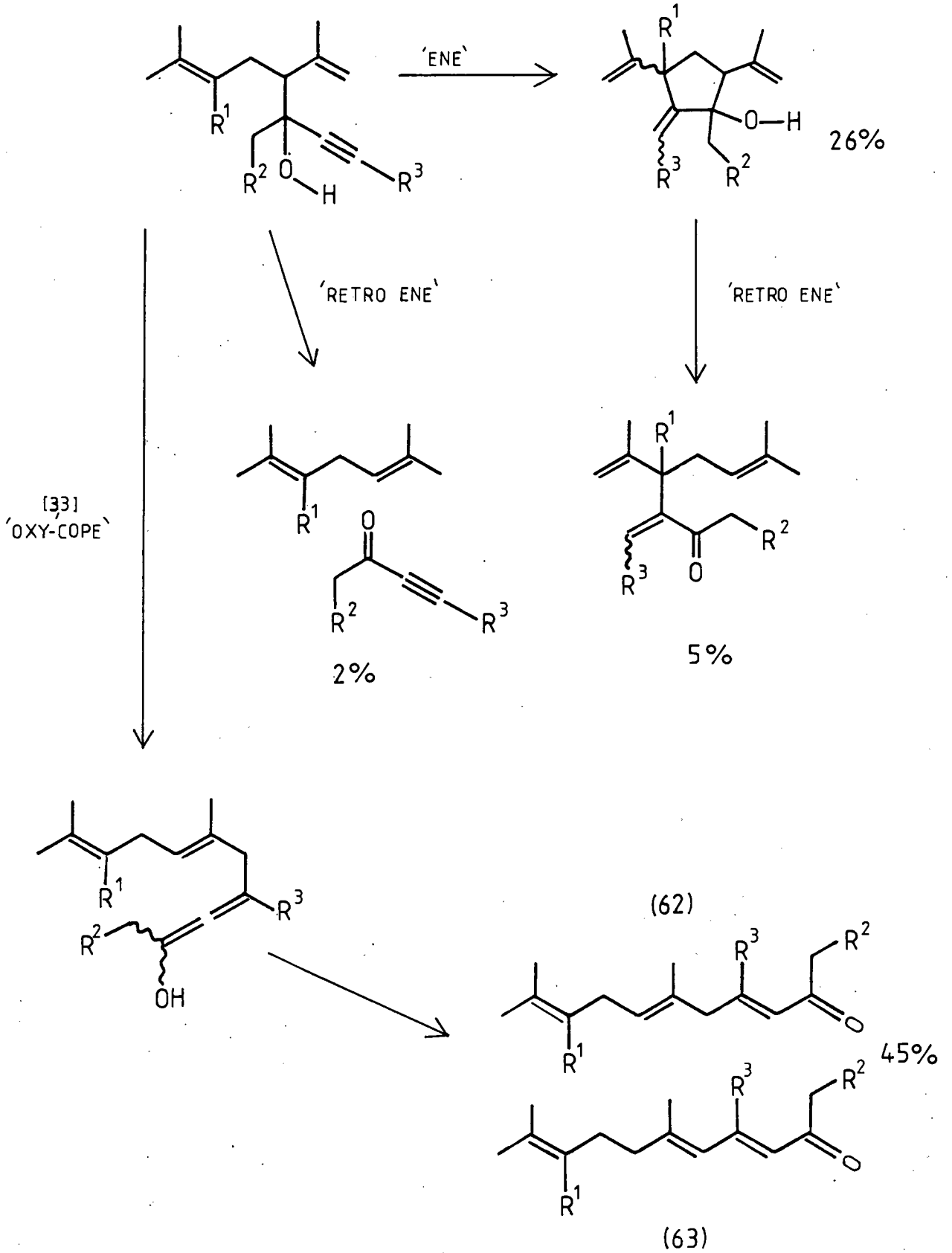
has been observed by Truslove[22] in the formation of spiro compounds (52,53) from pentynyl and pentenynyl indenes (54,55) by low pressure vapour phase thermolysis. Drouin et al.[36]



(54) (52) (55) (53)

suggest a similar mechanism for the formation of 8,9-dimethylene [3,3,3] propellan-2-one (56) from 3,3-bis(but-3'-ynyl)cyclopentanone (57, Fig.2) in decalin at 290° in sealed tubes for 100 min. The enol (58) gives product (59) which can then

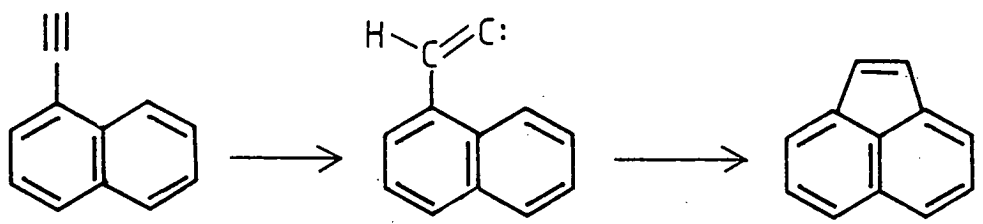
FIGURE 3



react similarly to give the major product (56) or give (60) via the isomer (61).

A recent synthesis of pseudoionones (62,63)[37] demonstrates the variety of possible reactions that can occur in a molecule with suitable reaction sites (Fig.3). The % yields quoted are those obtained on heating the undiluted alcohol (R^1, R^2, R^3=H) at 165°C for 5 h. The desired products (62,63) can be obtained in higher yield by using solvents such as N-methyl-2-pyrrolidine which seem to promote the oxy-Cope rearrangement.

In low pressure vapour phase pyrolysis of acetylenes a methylene carbene ($R_2C{=}C{:}$) intermediate has been suggested to explain the products formed. For example the formation of



(65) (64)

acenaphthalene (64) from 1-ethynylnaphthalene (65)[38]. Doubly labelled acetylene ($HC{\equiv}C^{13}D$) has been shown to 'scramble' in a manner which would be expected from the formation at the carbene intermediate and not intermolecular reaction[39]. Karpf

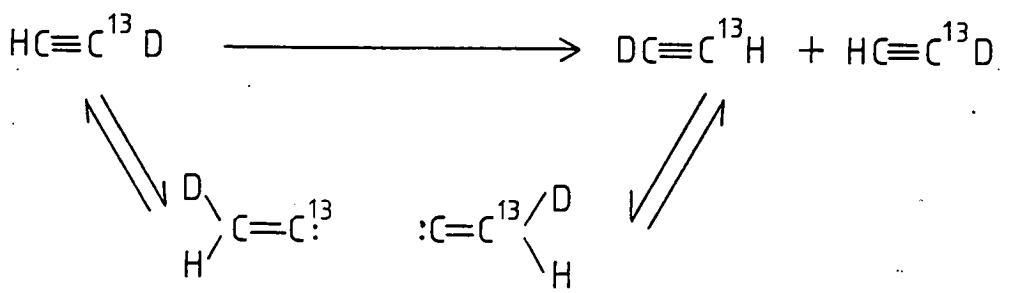
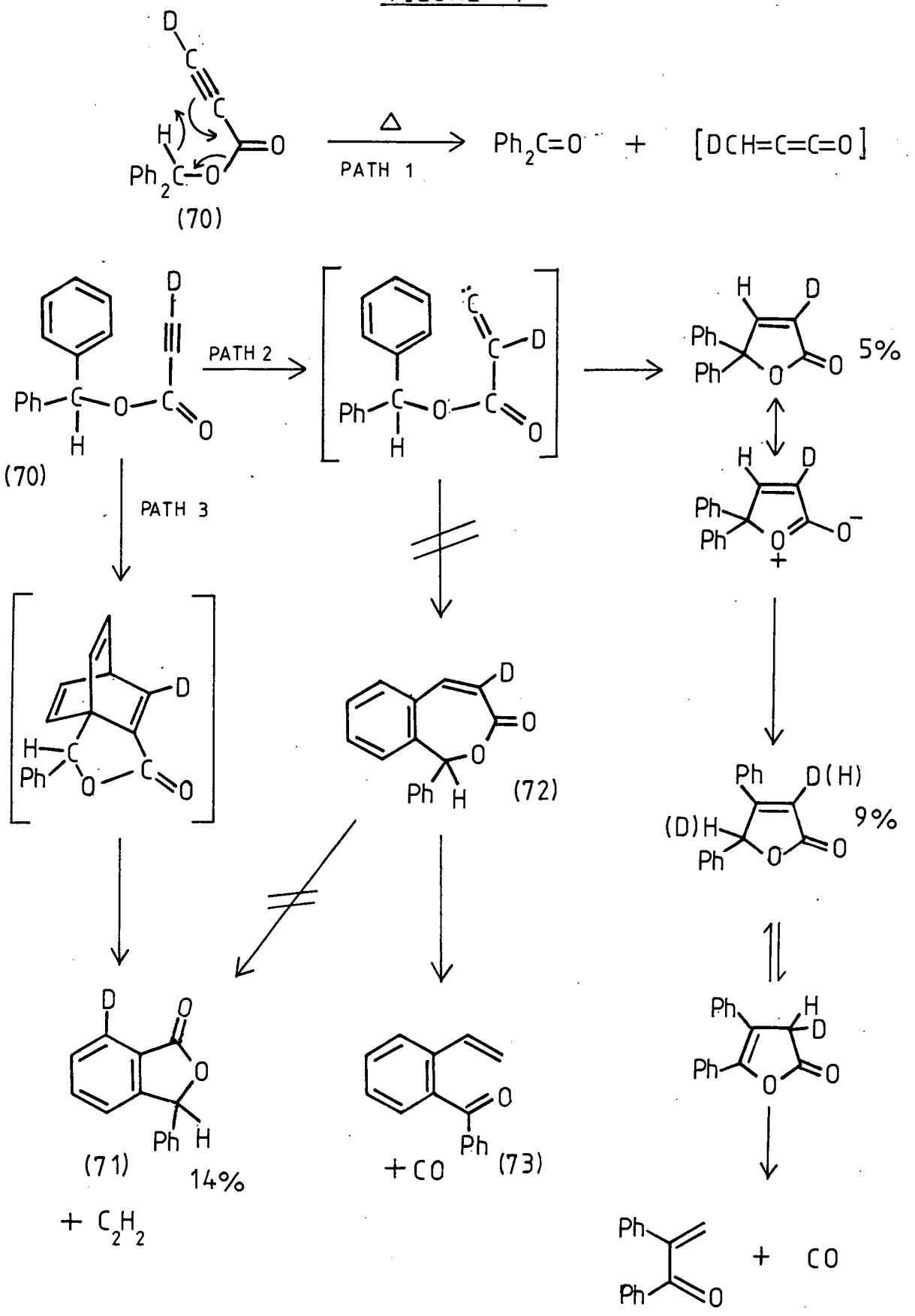
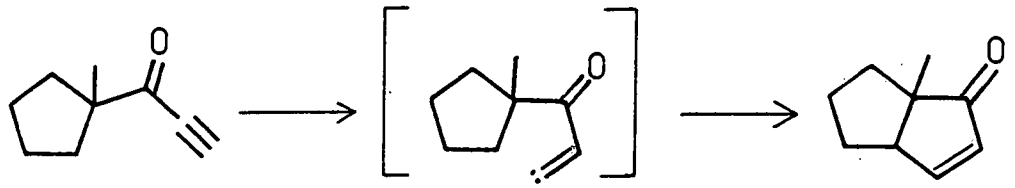


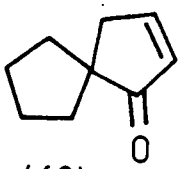
FIGURE 4



and Dreiding[40] suggest a methylene carbene intermediate (66) in the observed cyclisation at the ketone (67) to give the cyclopentenones (68,69).



(67) (66) (68)



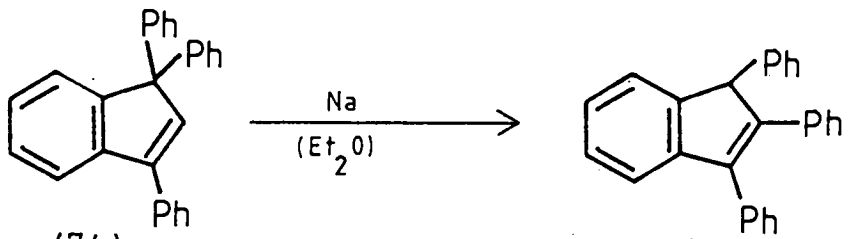
(69)

The recently reported[41] pyrolysis of diphenylmethylpropiolate (70) (Fig.4) which yields largely benzophenone (Path 1) shows an interesting side reaction giving 3-phenylphthalide (71) as a minor product. This appears to be formed via an intramolecular Diels Alder addition of the ethynyl group on the benzene ring (Path 3). The deuterium labelling experiment shown in the figure supports this hypothesis. The intermediacy of a carbene and hence 1-phenyl-2-benzoxepin-3(1H)-one (72) is excluded since pyrolysis of the latter is found to give 2-vinylbenzophenone (73). The carbene however is apparently an intermediate in the formation of small amounts of other products.

1.4 Isomerisation of Indene Derivatives

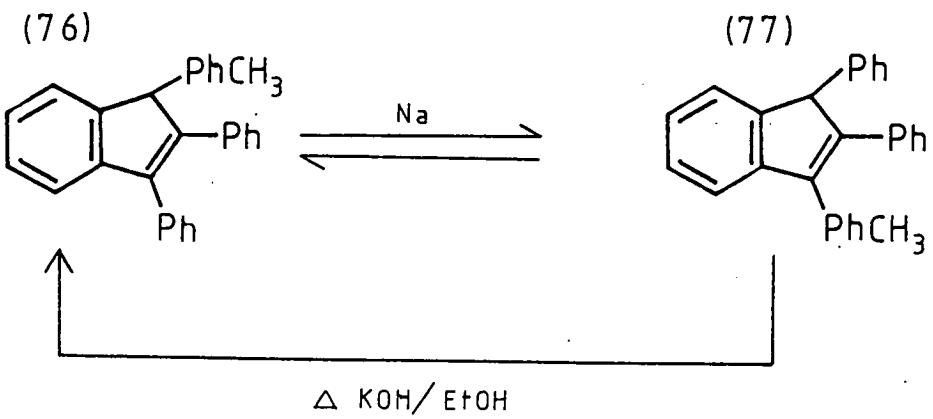
The isomerisation reactions of indene derivatives have been studied since the early years of this century[42,43] but early workers had difficulty in distinguishing between isomers.

The isomerisation of indene molecules may be carried out readily by base (generating the indenyl anion) or thermally. Koelsch[44] following Ziegler and Crossmans[45] observation that 1,1,3-triphenylindene (74) could be converted to 1,2,3-triphenylindene (75) by sodium metal, investigated



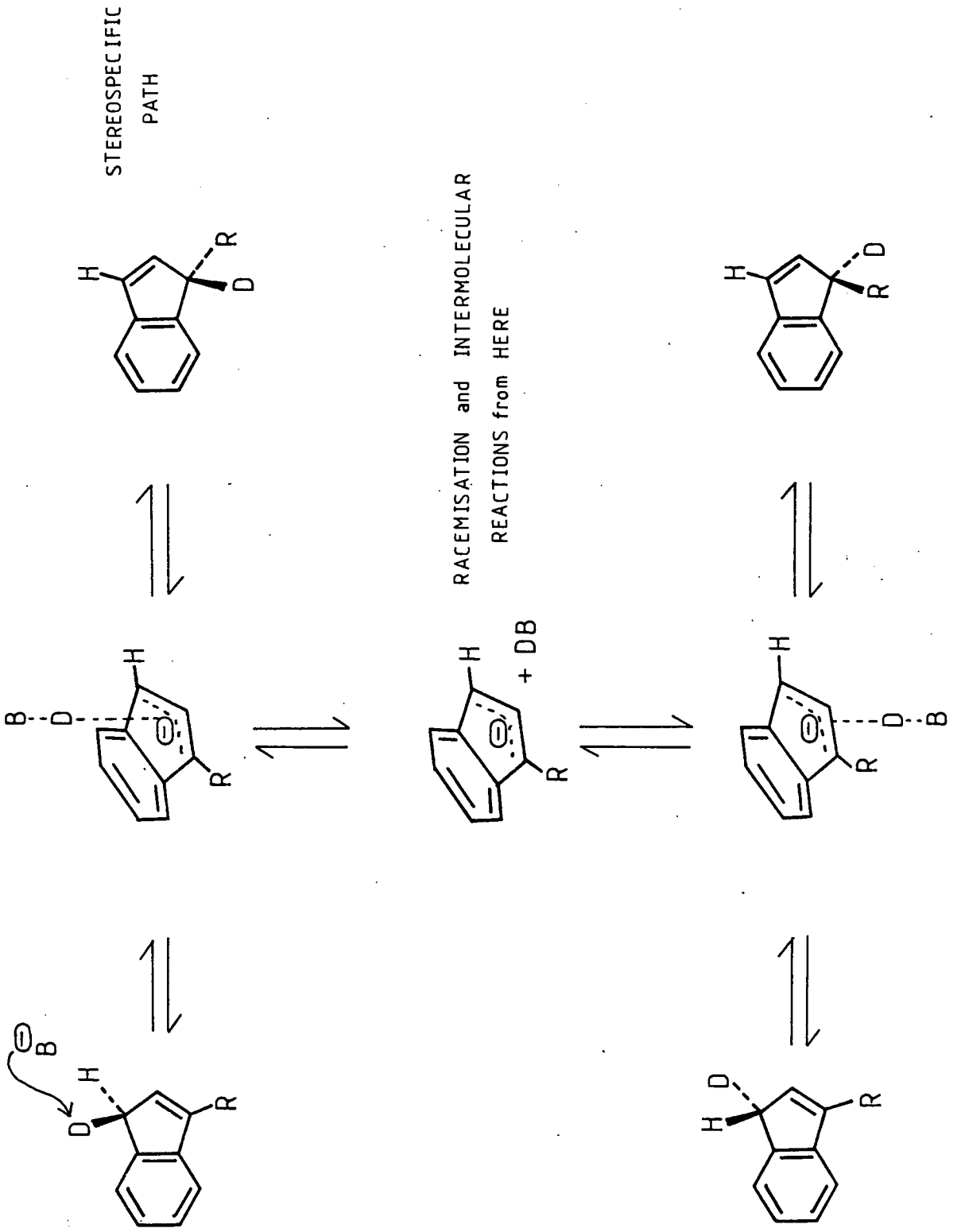
(74) (75)

the interconversion of 2,3-diphenyl-1-p-tolylindene (76) and 1,2-diphenyl-3-p-tolylindene (77). He found that the reaction with sodium was reversible, an equilibrium mixture being formed. However, if the indene (77) was boiled in alcoholic potassium hydroxide solution the former indene (76) was produced in high yield. This displacement of the equilibrium was attributed to the insolubility of the indene (76 in this medium.

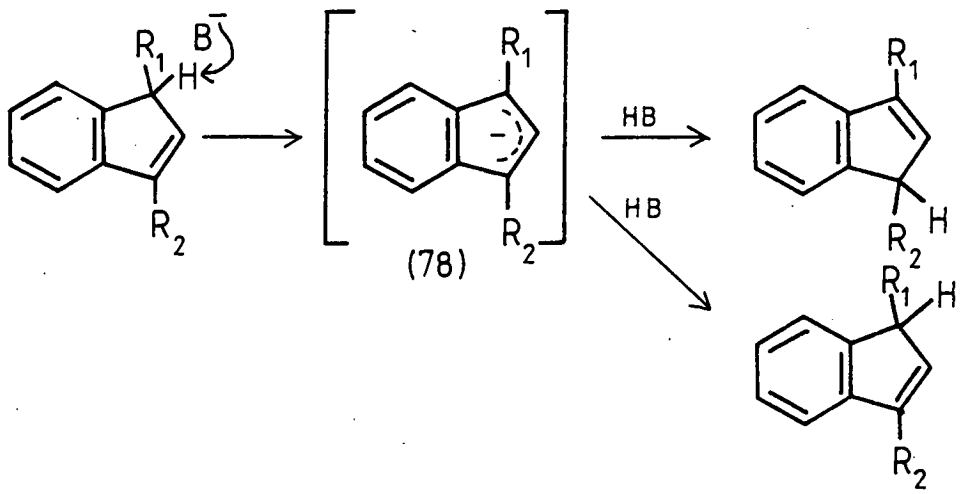


Much milder conditions can, however, be used to isomerise indenes. Bergson et al.[46] and Cram et al.[47] have studied

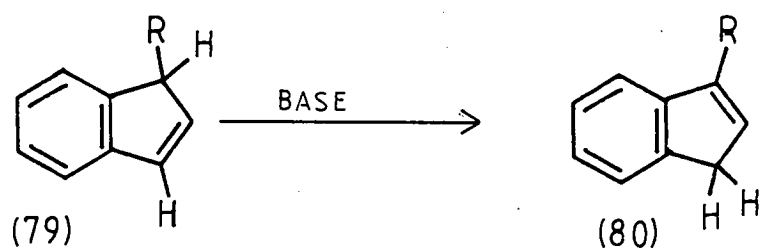
FIGURE 5


STEREOSPECIFIC
PATH
RACEMISATION and INTERMOLECULAR
REACTIONS from HERE
+ DB

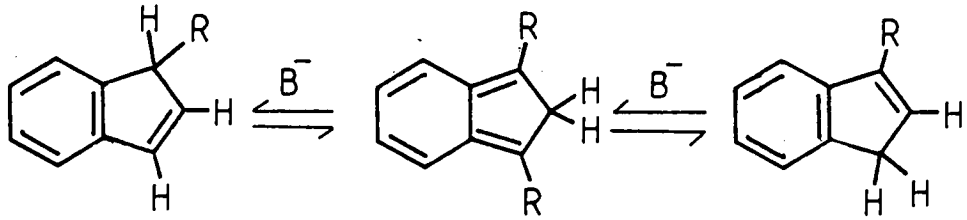
extensively the base catalysed [1,3] rearrangement of optically active indenes using amines or other bases like KOPh at moderate temperatures. The mechanism involves removal of an acidic proton from C-(1) to form the indenyl anion (78) which can then be reprotonated at either benzyl carbon atom.



With amines the isomerisation often shows a high degree of stereospecificity and intramolecularity, the proposed mechanism in this case[46j] is a conducted tour in which the migrating atom remains in close proximity to the indenyl atom when attacked by the base. The stereospecific reaction occurs when the migrating atom is transported across the face of the anion by the base (see Fig.5). The rearrangement of 1-alkylindenes (79) by base gives the more thermodynamically stable 3-derivative (80) by H transfer[46a]. At no time during

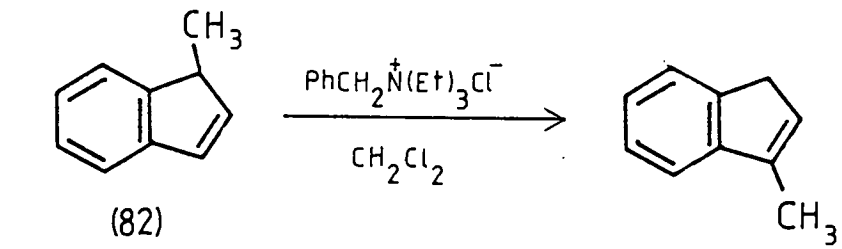


his studies of these rearrangements did Bergson[46f] observe any evidence for an isoindene (81) type of intermediate which could be present if the reaction had proceeded as shown.

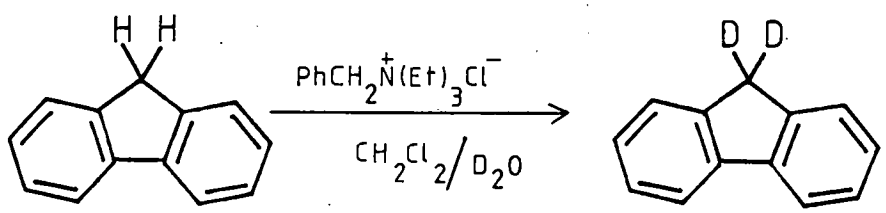


(81)

Willner et al.[48] have shown that 1-methylindene (82) is readily converted to the 3-isomer by use of quaternary ammonium salts and that indene (20) & fluorene (83) are readily deuterated by such catalysts implying that they are efficient at generating the indenyl or fluorenyl anion (see p.31).

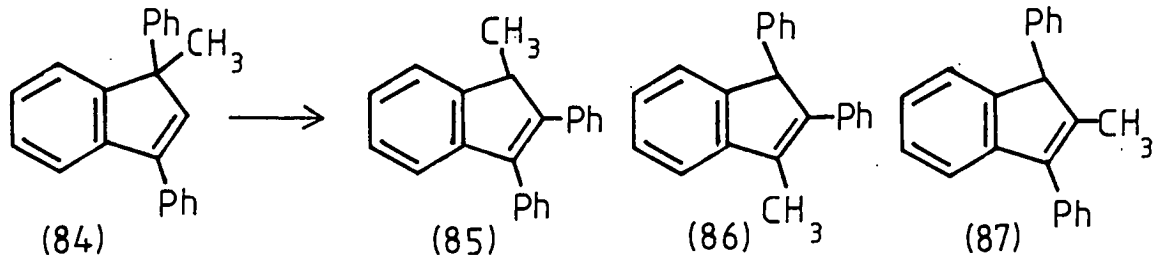


(82)

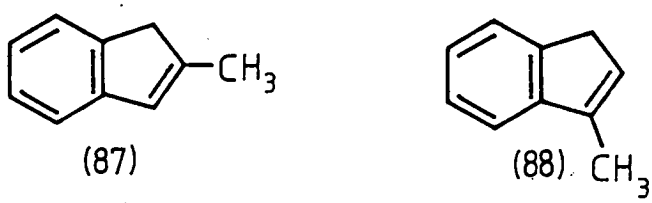


(83)

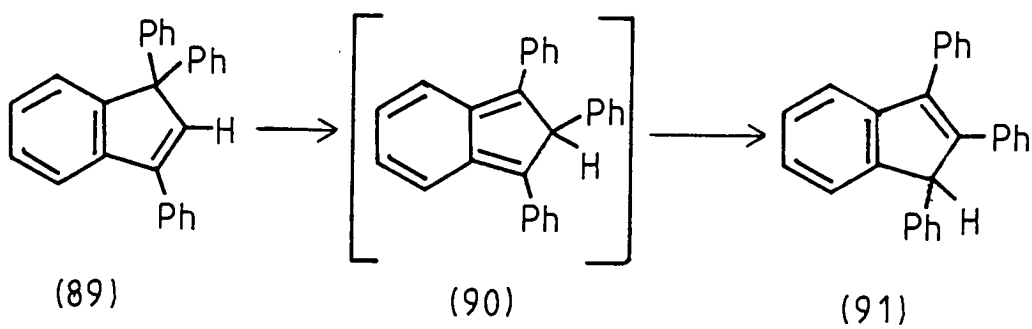
Thermal rearrangements of indene derivatives have also been studied extensively. Koelsch and Johnson[49] showed that 1,3-diphenyl-1-methylindene (84) gave 2,3-diphenyl-1-methylindene (85), 1,2-diphenyl-3-methylindene (86) and probably a little 1,3-diphenyl-2-methylindene (87) on pyrolysis. They



attempted to confirm that a methyl group could migrate in the indene system by pyrolising 2-methyl and 3-methylindene

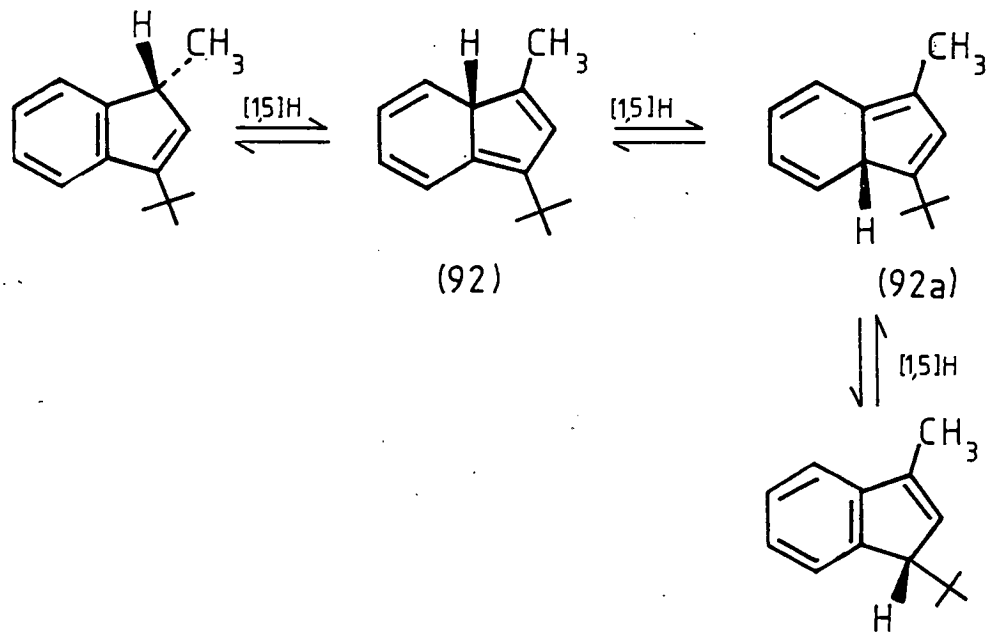


(87,88) but they found no isomerisation and so concluded that the presence of phenyl groups was required for methyl migration to occur. Miller et al.[50] studied the rearrangement of several indene derivatives in diphenyl ether and measured the rate constants for migration from the 1 to the 2 position. They concluded that migratory aptitude followed a sequence H>Ph>Me. For example the isomerisation of 1,1,3-triphenylindene (89) to 1,2,3-triphenylindene (91) occurs first by a [1,5] sigmatropic

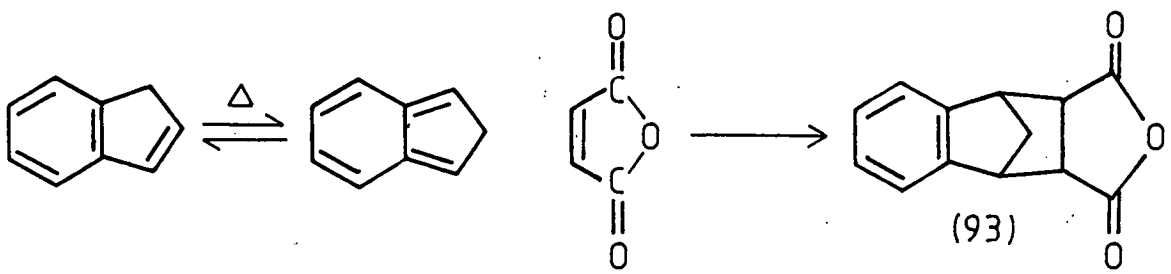


shift of phenyl to the 2 position to form an isoindene intermediate (90). A [1,5] shift of H, which is preferred to that

of phenyl, then gives the product (91). These results explain why Koelsch and Johnson[49] obtained no rearrangement of 2-methyl or 3-methylindene (87,88) the preferred migrations of H to methyl can only give the starting materials as products. Almy and Cram[51] have studied this type of migration using optically active molecules and concluded that the isoindene intermediate was the major contributor to the reaction pathway but that other species such as (92) and (92a) shown below might be responsible for a minor (∿1%) high energy route for the

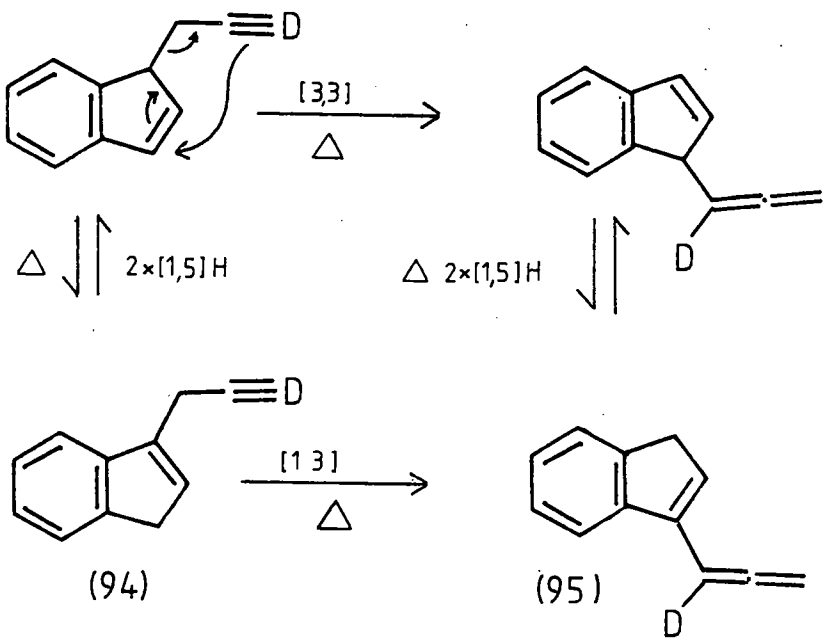


isomerisation. Further evidence for the isoindene mechanism is the trapping[52] of isoindene as a maleic anhydride adduct (93).



Field et al.[53] have studied the migratory aptitude for [1,5] sigmatropic shifts of various groups in the indene system and found the order of ease of migration HCO > Benzoyl Acetyl > H > vinyl > CONHMe > CO_2Ph > CO_2Me > CN ≈ C≡CH > alkyl. The particular ease of migration of the formyl, benzoyl and acetyl groups is suggested to be due to an interaction of the carbonyl π^* orbital with the indene π system during migration.

Truslove[22] found that propargyl indenes rearrange to allenes thermally and suggested that a Cope type rearrangement not previously observed in the indene system was responsible for the observed migration of deuterium in 3(3'-deuterio)-propargyl indene (94).



A [1,3] sigmatropic shift of indene along the propargyl group which is allowed if there is inversion at the carbon would give the same product (95). Work described later in this thesis investigates the mechanism of this reaction further.

Object of Research

The objective of this work was to prepare a number of alkynyl substituted fluorenes and indenes by reaction of fluorenyl and indenyl anions with alkynyl halides with a view to studying their intramolecular rearrangements. The rearrangements of these molecules, either thermally via low pressure vapour phase pyrolysis or by base catalysis was carried out to determine the stereochemistry and the mechanism of formation of the products. This led to a study of the base catalysed rearrangements of the thermal rearrangement products with similar aims.

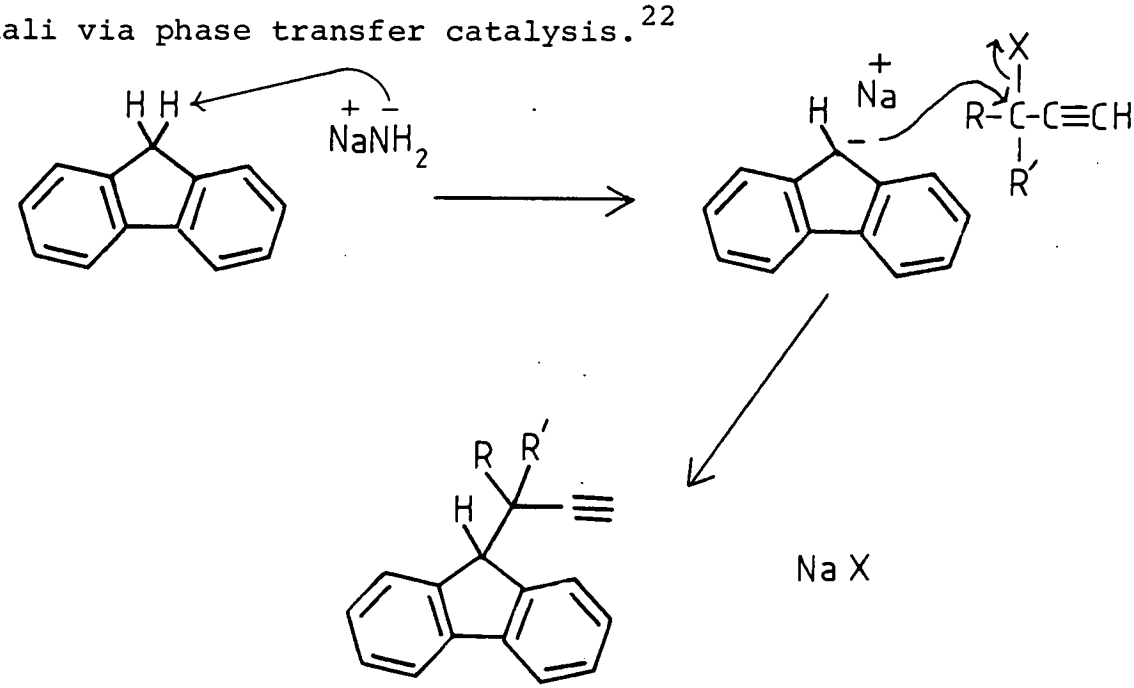
D I S C U S S I O N

CHAPTER 2

Synthesis of Acetylenes

2.1 General Strategy

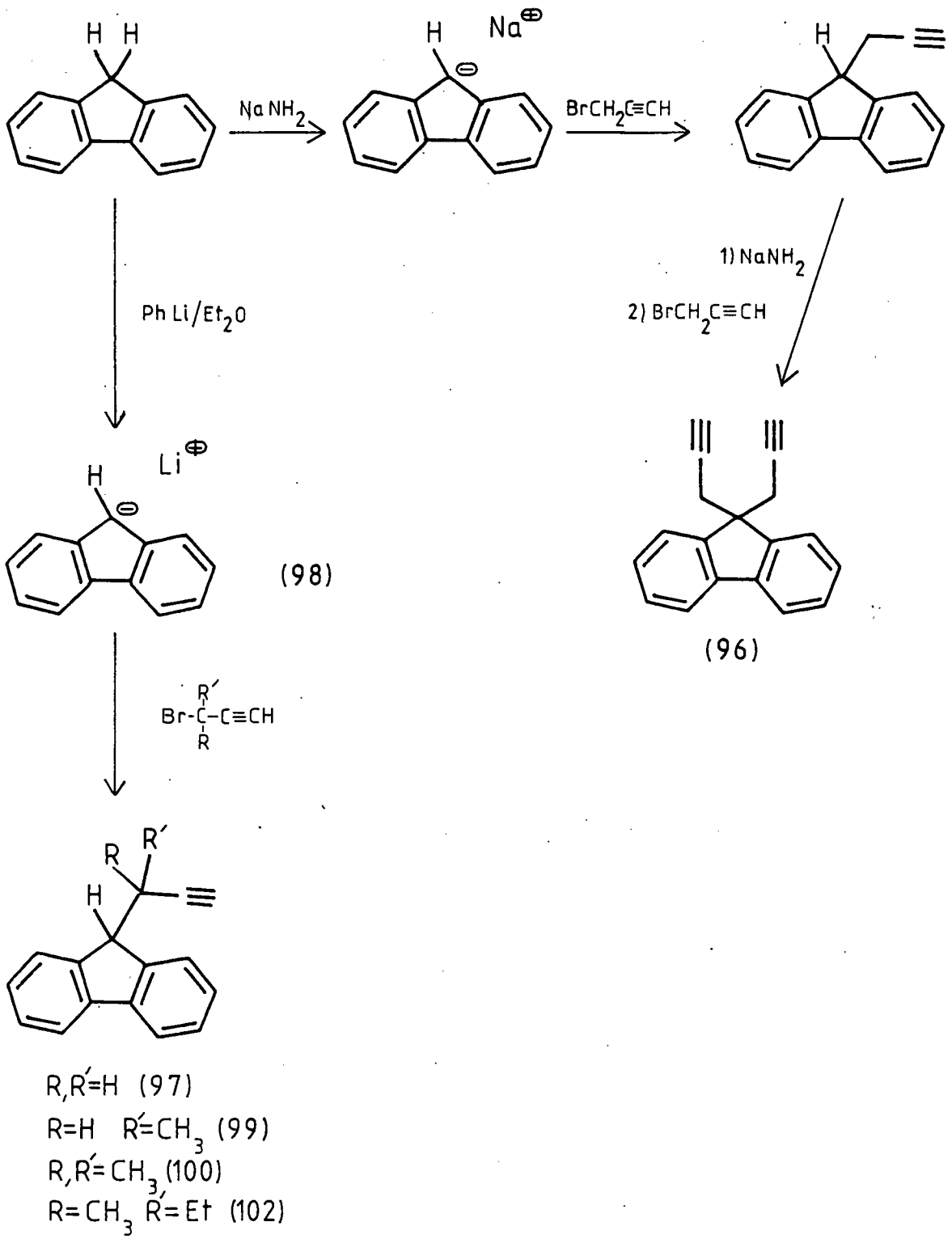
The acetylenic derivatives of indene and fluorene in this work have been prepared by the nucleophilic substitution reaction of indenyl or fluorenyl anions with an alkynyl or allenyl halide. Indene and fluorene lend themselves readily to this strategy because of the acidity (pKas 18.5 and 22.9 respectively) of their benzylic methylene protons. This permits generation of their anions by bases such as sodamide in liquid ammonia or phenyl lithium in ether[54] or by aqueous alkali via phase transfer catalysis.[22]



The halides were prepared by standard routes from the corresponding alcohols which, if not commercially available, were themselves prepared from sodium acetylide.

In all cases the identities of the indene and fluorene

FIGURE 6



R,R´=H (97)

R=H R´=CH_3 (99)

R,R´=CH_3 (100)

R=CH_3 R´=Et (102)

derivatives were confirmed by proton and carbon-13 n.m.r. spectra, infra red spectra and also by exact mass measurement or elemental analysis.

2.2 Fluorene Derivatives

Reaction of propargyl bromide with fluorenyl sodium in liquid ammonia gives predominantly 9,9-dipropargyl fluorene (96), the monosubstituted product being more reactive under these conditions than fluorene itself (fig.6). Attempts to react the related halides, 1-bromo-3-methylbuta-1,2-diene and 2-bromobut-3-yne with fluorene by the same method however gave unchanged fluorene. This was attributed to elimination reactions of the halides under the strongly basic conditions employed. Replacement of the liquid ammonia by dry dimethoxyethane[55] in an attempt to overcome this problem gave products only with propargyl bromide, which gave a mixture of 9-propargyl fluorene (97) and 9,9-dipropargyl fluorene (96) in low yield.

9-Lithiofluorene (98) in dry ether was found to give monosubstituted products when reacted with alkynyl halides, as has been reported[54] elsewhere and so this method was used to successfully prepare a number of fluorene derivatives.

9-Propargyl fluorene (97) was obtained in good yield from 9-lithiofluorene and propargyl bromide. The compound shows acetylenic absorptions at 3300 and 2120 cm^{-1} in the infra-red spectrum and is readily identified from its ^1H n.m.r. spectrum (fig.7) which shows the propargylic protons at 2.60δ coupled to both the fluorene 9-proton at 3.96δ (J=7 Hz) and the acetylenic proton at 1.94δ (J=2 Hz).

FIGURE 7

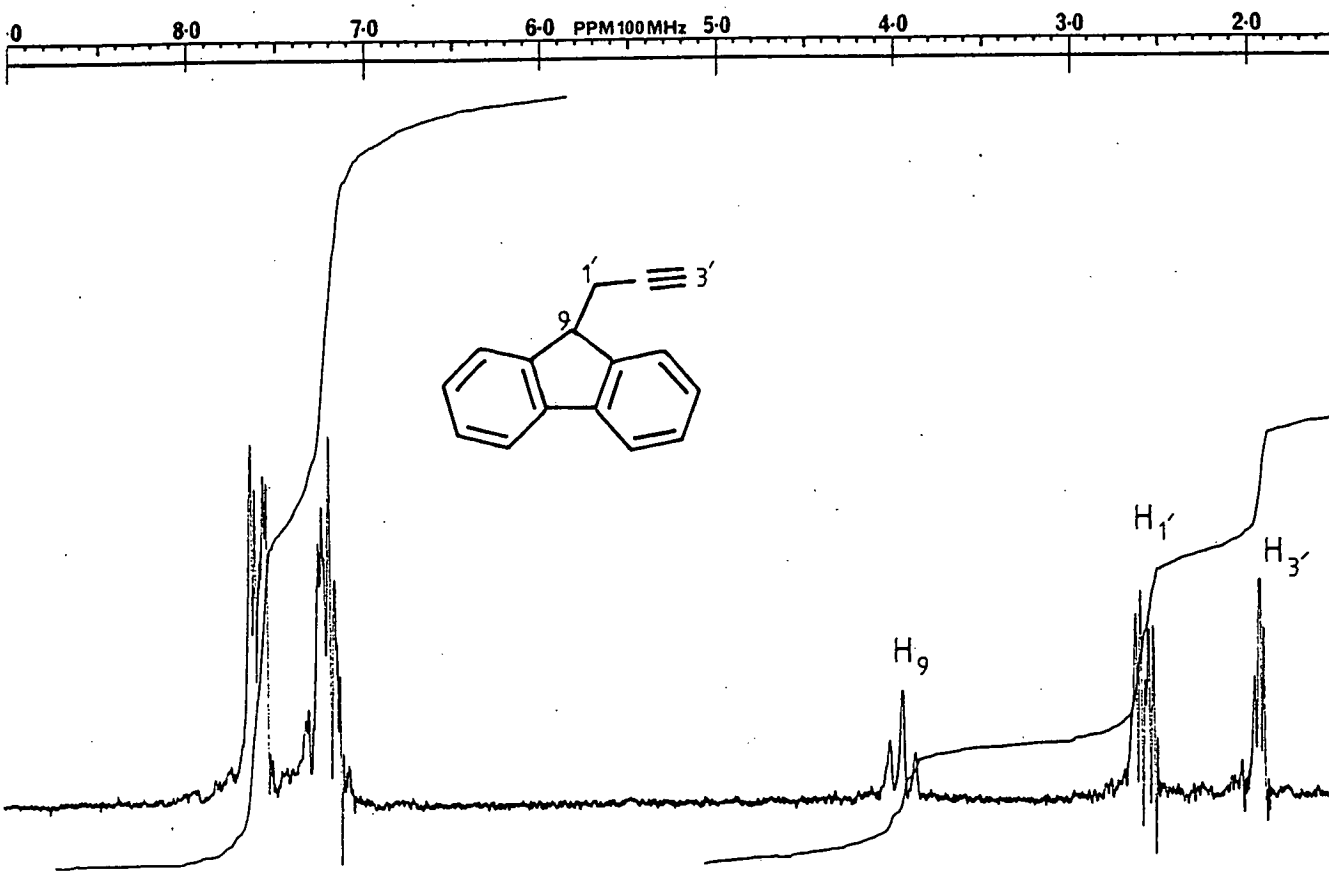
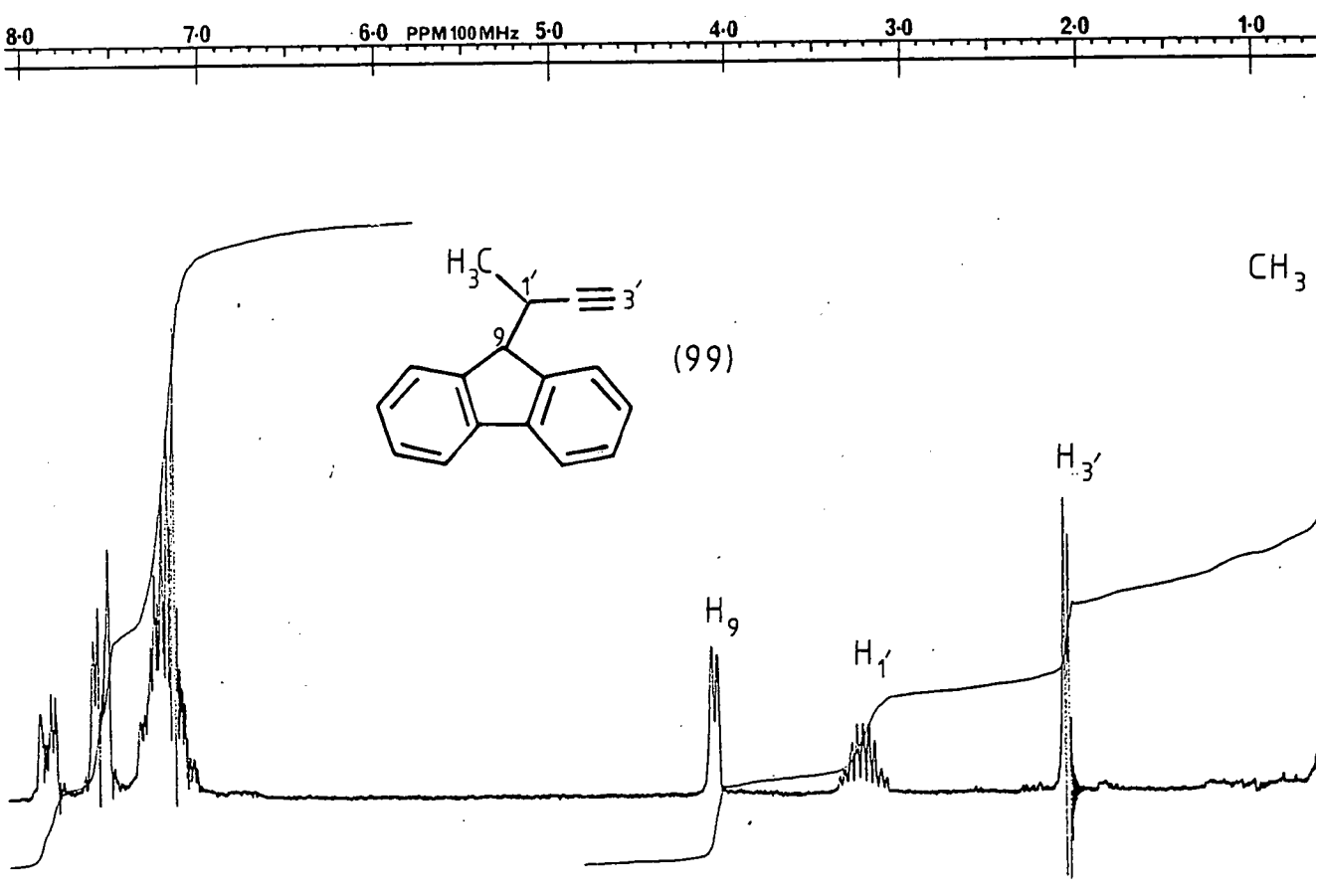
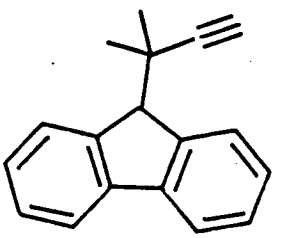


FIGURE 8



9-(1'-Methylprop-2'-ynyl)fluorene (99) was prepared similarly from 2-bromobut-3-yne. Its ^1H n.m.r. spectrum (fig.8) shows the propargylic proton at 3.24δ coupled to the acetylenic proton at 2.09δ, the C-9 proton at 4.09δ and the methyl protons at 0.59δ.

Reaction of 9-lithiofluorene with 1-bromo-3-methylbuta-1,2-diene gave the desired 9-(1',1'-dimethylprop-2'-ynyl)-fluorene (100) and also the allene 9-(3'-methylbuta-1',2'-dienyl)fluorene (101) in the ratio 2:1 as shown by the ^1H



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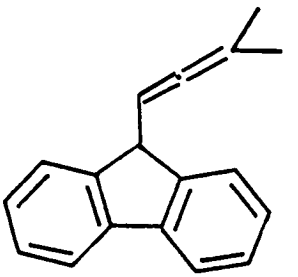
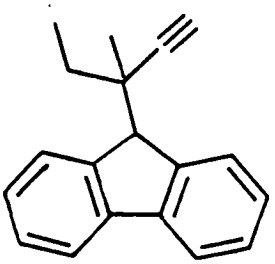


(101)

n.m.r. spectrum of the reaction mixture. Chromatography on alumina gave the purified acetylene (100) in low yield. The formation of the allene is discussed later (p. 29).

Similarly reaction of 9-lithiofluorene with 1-bromo-3-methyl-penta-1,2-diene gave a mixture of 9-(1'-methyl-1'-ethylprop-2'-ynyl)fluorene (102) and 9-(3'-methylpenta-1',2'-dienyl)-fluorene (103) (see p. 57) in the ratio 1.2:1. Chromatography



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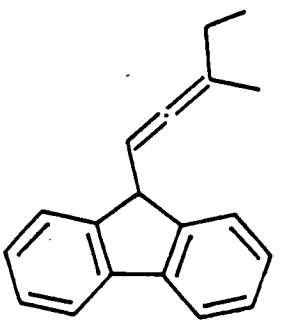


(103)

FIGURE 9

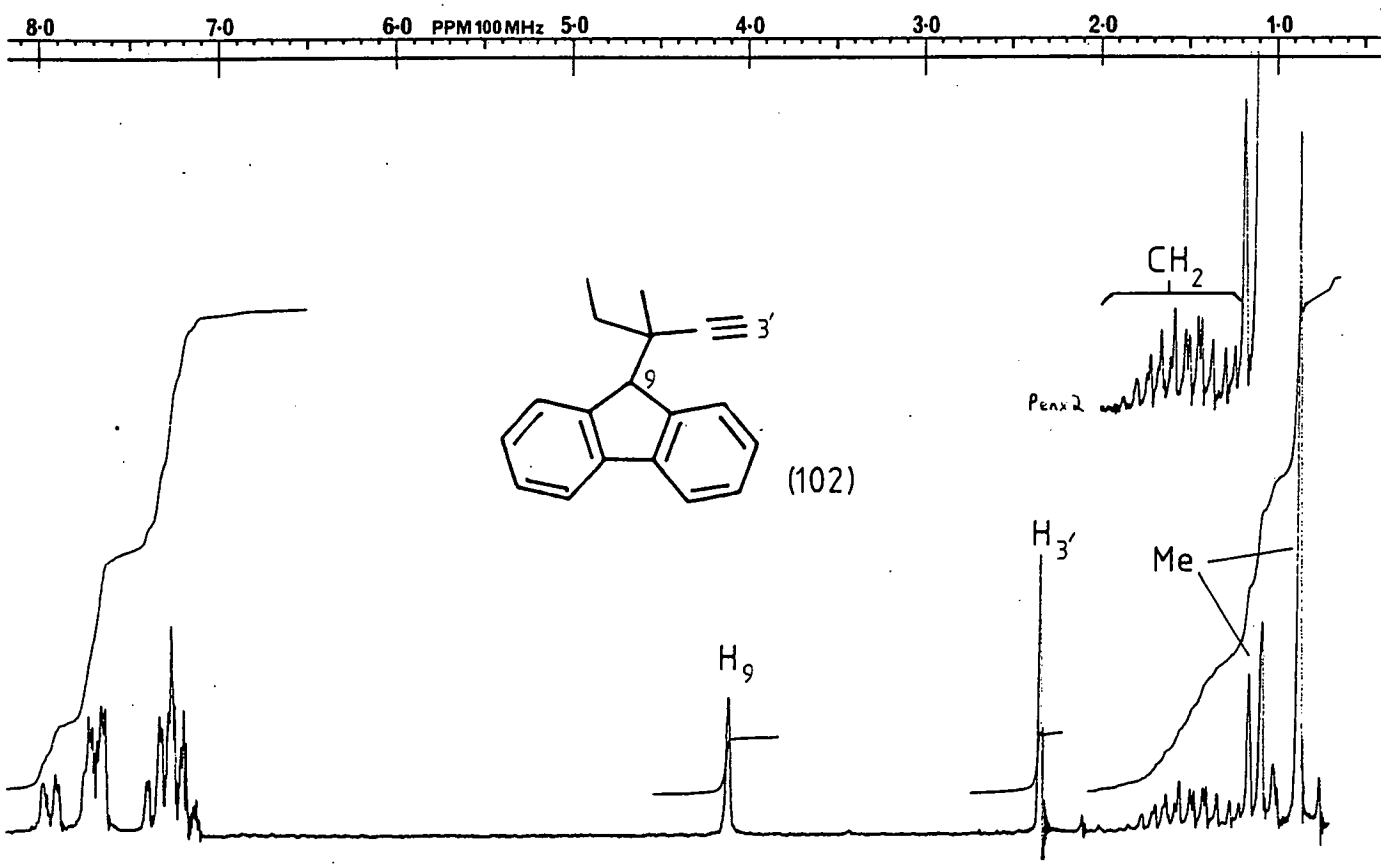
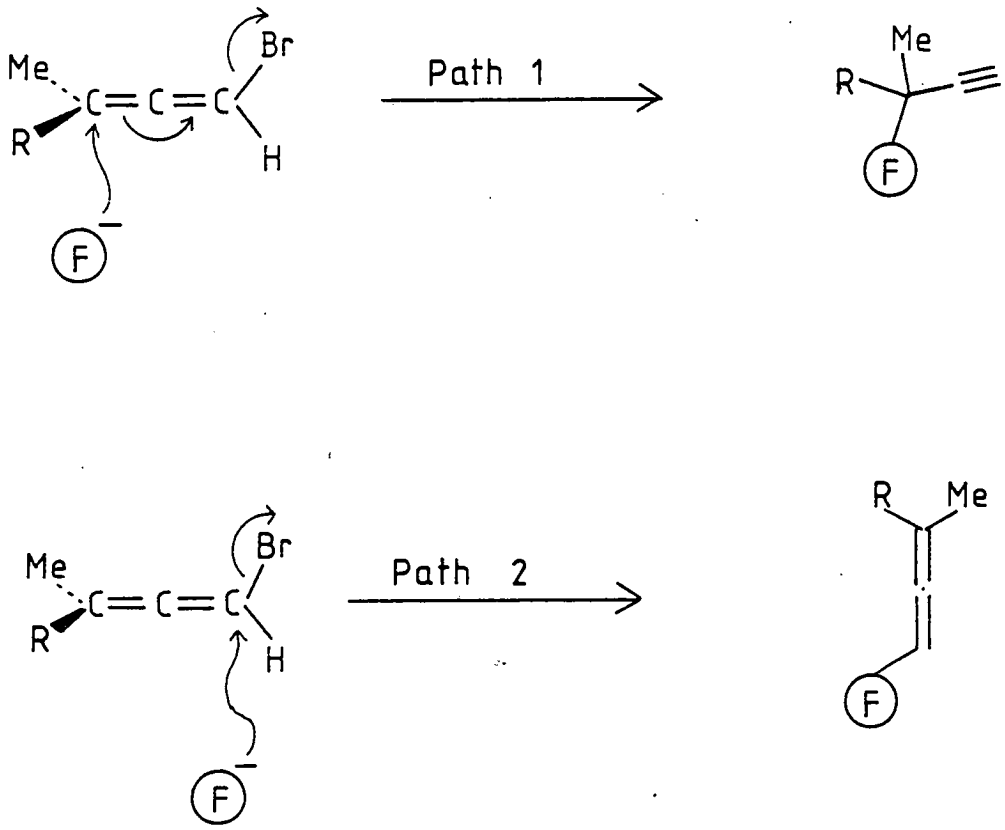


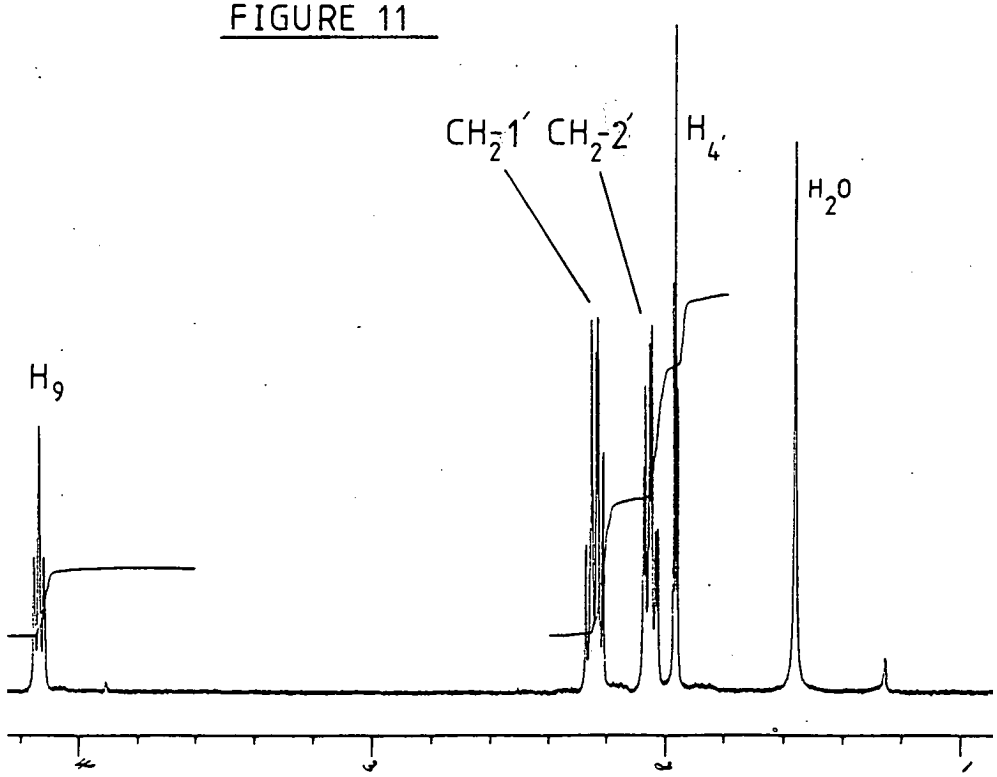
FIGURE 10

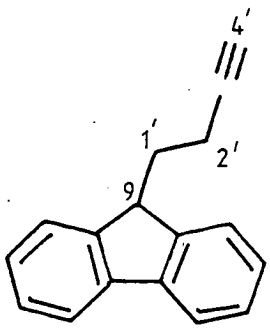


F = Fluorenyl anion

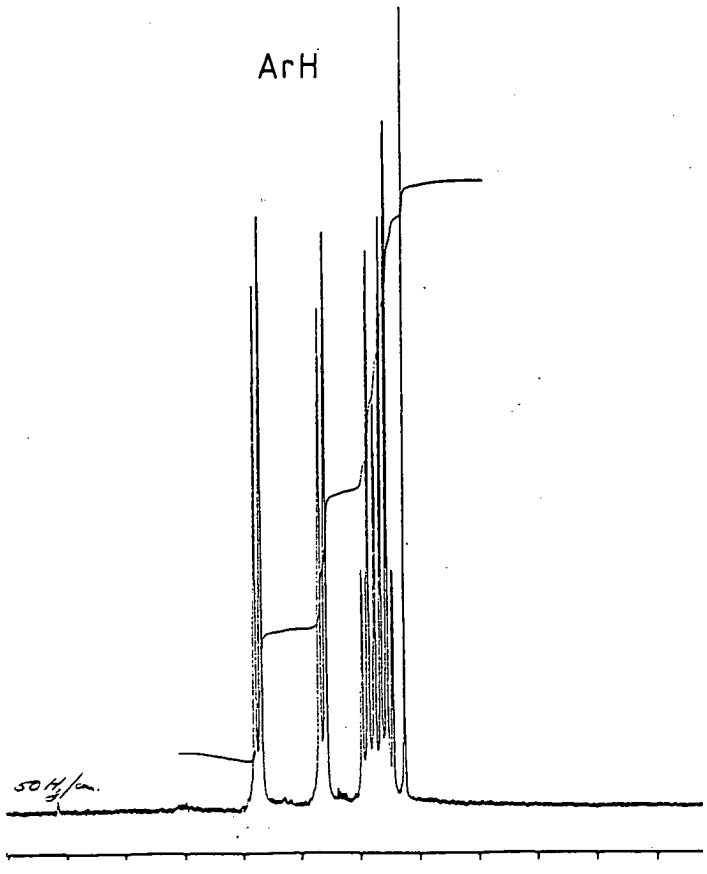
PATH 2 MORE PREFERRED cf PATH 1 IF R = Et RATHER THAN Me

FIGURE 11



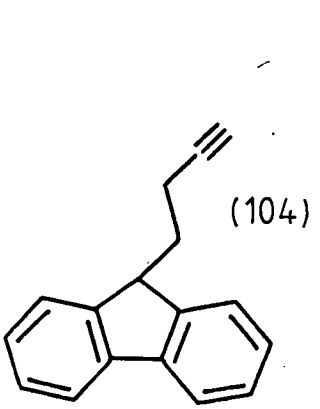


(104)



on alumina gave the acetylene (102) whose ^{1}H n.m.r. spectrum (fig.9) shows the non equivalent methylene protons of the ethyl group as a multiplet from 1.1 to 1.86δ due to coupling between the protons and with the adjacent CH_3 protons. The acetylene proton resonates at 2.34δ and the methyl groups at 0.86 and 1.11δ. The higher proportion of allene formation in this case in comparison with the previously mentioned reaction is presumably due to increased steric hindrance to attack at C-3 of this bromoallene caused by the presence of the ethyl group (see fig.10).

Reaction of 9-lithiofluorene with 1-bromobut-3-yne gave 9-but-3'-ynylfluorene (104). The 360 MHz proton n.m.r.



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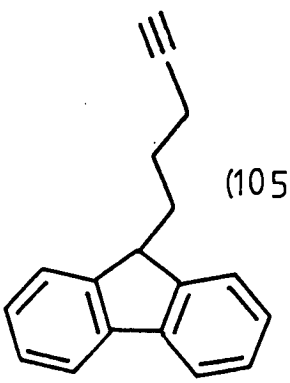
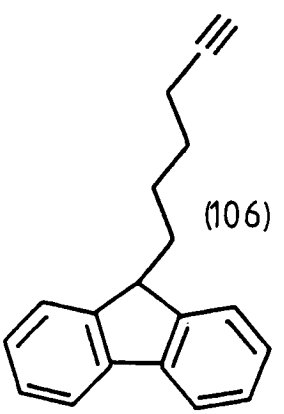


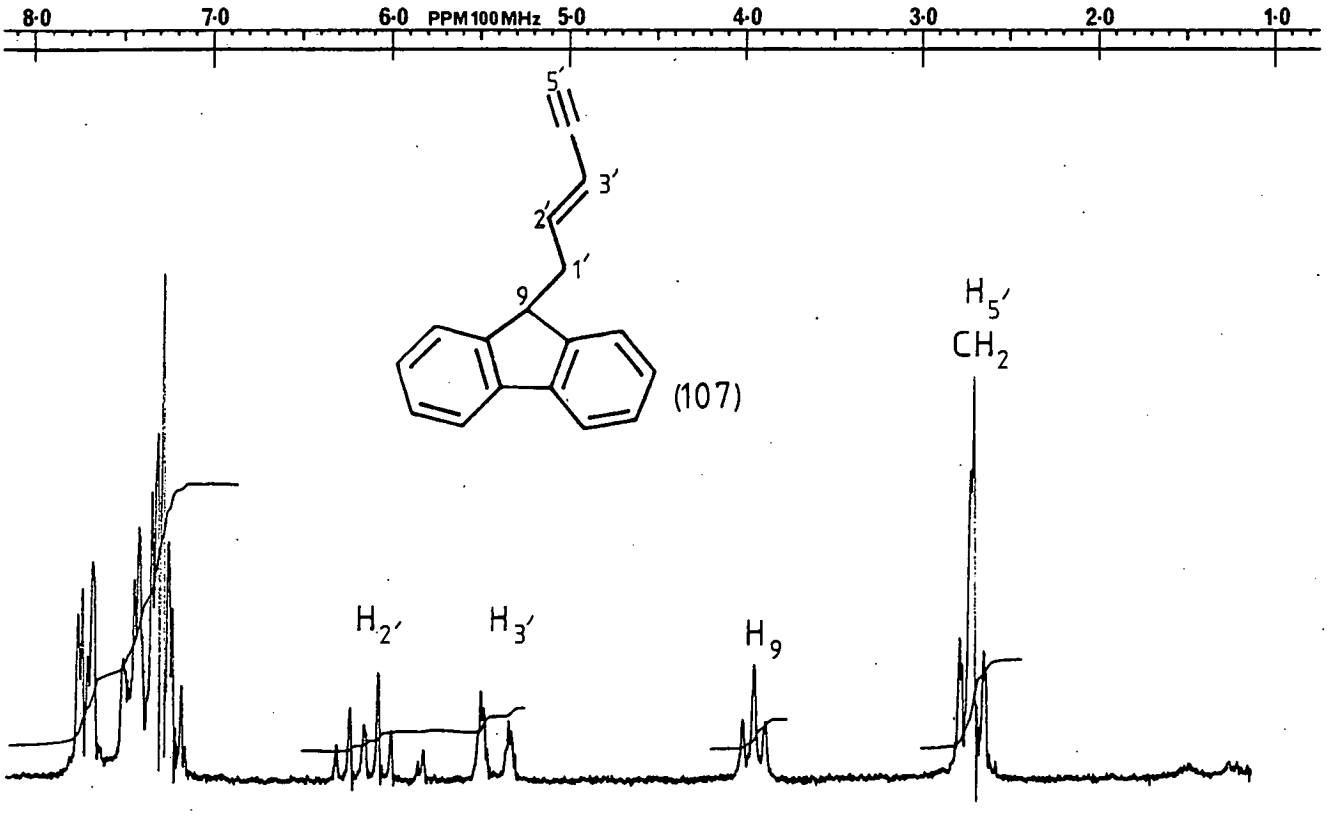
(105)



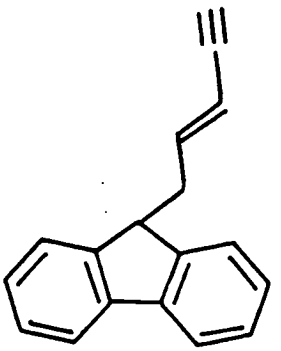
(106)

spectrum (fig.11) shows the two sets of methylene protons at 2.04δ and 2.24δ and the fluorene C-9 proton at 4.13δ with the expected couplings. 9-(Pent-4'-ynyl)fluorene (105) and 9-(hex-5'-ynyl)fluorene (106) were similarly prepared from 1-bromopent-4-yne and 1-iodohex-5-yne respectively. These compounds have been reported previously[54] and their structures confirmed by proton and ^{13}C n.m.r. spectra, infra-red spectra and elemental analyses.

FIGURE 12

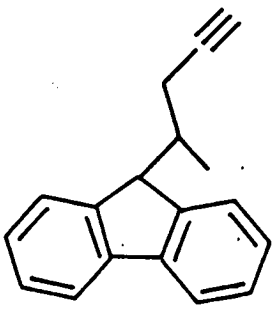


E-9-(Pent-2'-en-4'-ynyl)fluorene (107) was prepared in low (13%) yield, after purification by silica chromatography, from 9-lithiofluorene and E-1-bromopent-2-en-4-yne.

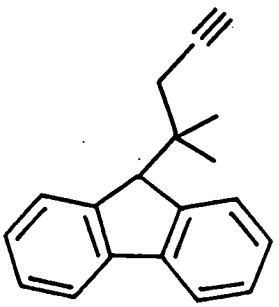


(107)

In the ^1H n.m.r. spectrum (fig.12) the acetylenic proton resonance is obscured by the CH_2 resonance at 2.70δ. The C-9 proton resonance is a triplet at 3.95δ and the olefinic protons appear as a broad doublet at 5.40δ and a doublet of triplets at 6.15δ. The 17 Hz coupling between the olefinic protons



(108)

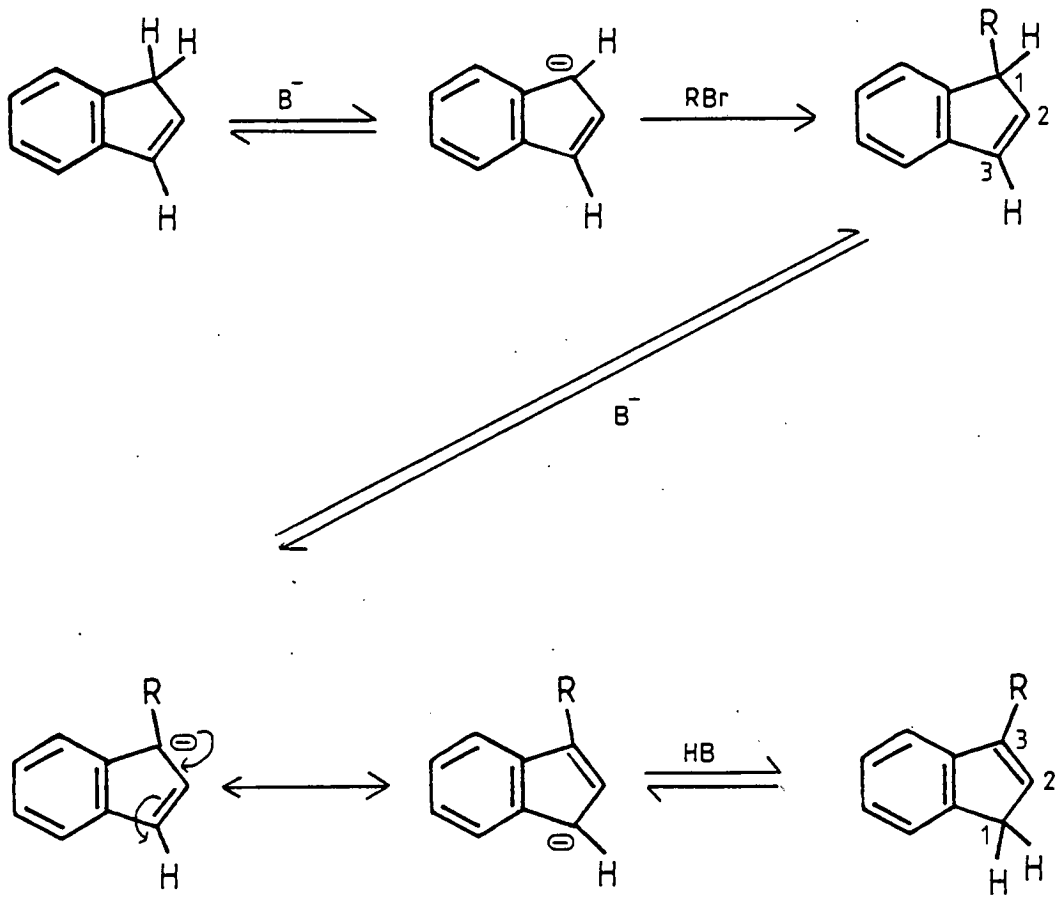


(109)

confirms the E configuration.

Neither 2-bromopent-4-yne nor 2-bromo-2-methylpent-4-yne could be made to react with 9-lithiofluorene to give the derivatives 9-(1'-methylbut-3'-ynyl)fluorene (108) or 9-(1',1'-dimethylbut-3'-ynyl)fluorene (109). The halides failed to react at room temperatures or under reflux, presumably due to

FIGURE 13



the lower reactivity and steric hindrance of secondary and tertiary halides in comparison with primary halides such as 1-bromobut-3-yne which reacts readily. Reaction of these halides with 9-sodiofluorene in liquid ammonia failed due to elimination reactions of the halides under these conditions.

2.3 Indene Derivatives

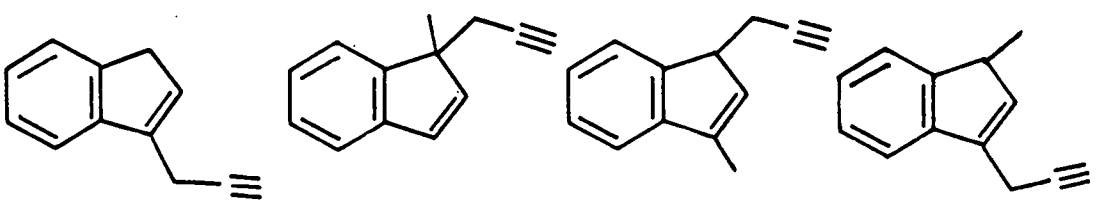
Two methods were used to produce indenyl acetylenes.

A. The alkynyl halide was reacted with the indene in the presence of aqueous potassium hydroxide and a phase transfer catalyst (benzyltrimethylammonium chloride).

B. The alkynyl halide was reacted with indenyl sodium in liquid ammonia.

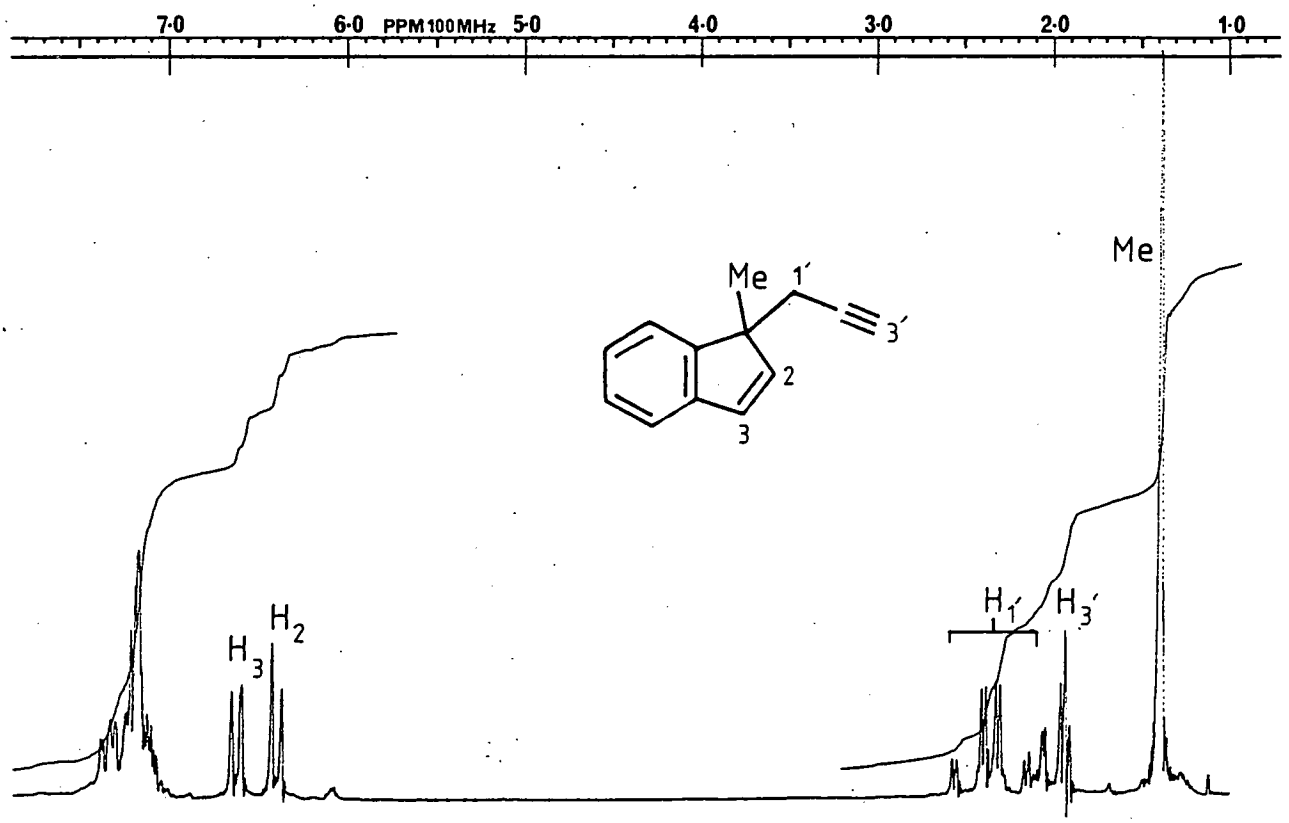
The products of the above reactions can be 1 or 3-substituted indenes due to the ready isomerisation of the indene molecule under basic conditions (fig.13). The thermodynamically more stable 3-substituted product is preferred and is therefore usually the sole product isolated from the reaction mixture.

Reaction of propargyl bromide with indene by method A at room temperature gave (after silica chromatography) 3-propargyl indene (24) which was identical to that obtained previously.[22]



(24) (110) (111) (112)

FIGURE 14

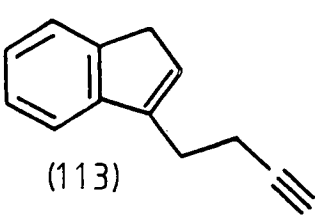


Reaction of propargyl bromide with 3-methylindene gave a mixture of products, the proportion of each depending on the method of preparation. Method A (70-75°C) gave 1-methyl-1-propargyl indene (110) and 3-methyl-1-propargyl indene (111) in the ratio 4:1 together with a small amount of 1-methyl-3-propargyl indene (112) as shown by the proton n.m.r. of the mixture of products after removal of unconverted 3-methyl-indene. Silica chromatography gave 1-methyl-1-propargyl indene (110) as a pure product. The proton n.m.r. spectrum (fig.14) is identical with that obtained by Truslove.[22]

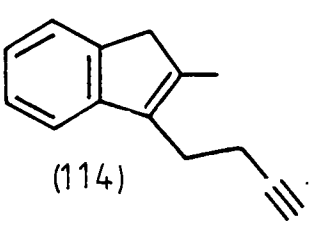
Method B gave the products (110) and (111) in the ratio 1:3. The 3-methyl-1-propargyl indene was best isolated from the mixture by preparative g.l.c. Its proton n.m.r. shows the acetylenic proton at 2.02δ coupled (J=3Hz) to the non-equivalent methylene protons which appear as two multiplets at 2.25δ and 2.59δ. The methyl protons appear at 2.11δ coupled (H=2Hz) to the olefinic proton at 6.22δ and the C-1 proton, a complex multiplet at 3.52δ.

The phenyl lithium method (p.27) was also tried to achieve this reaction, it gave a mixture of (110) and (111) in the ratio 4.5:1.

3-(But-3'-ynyl)indene (113) and 3-(but-3'-ynyl)-2-methylindene (114) were prepared by reaction of 1-bromobut-3-yne with indene and 2-methylindene by method B.

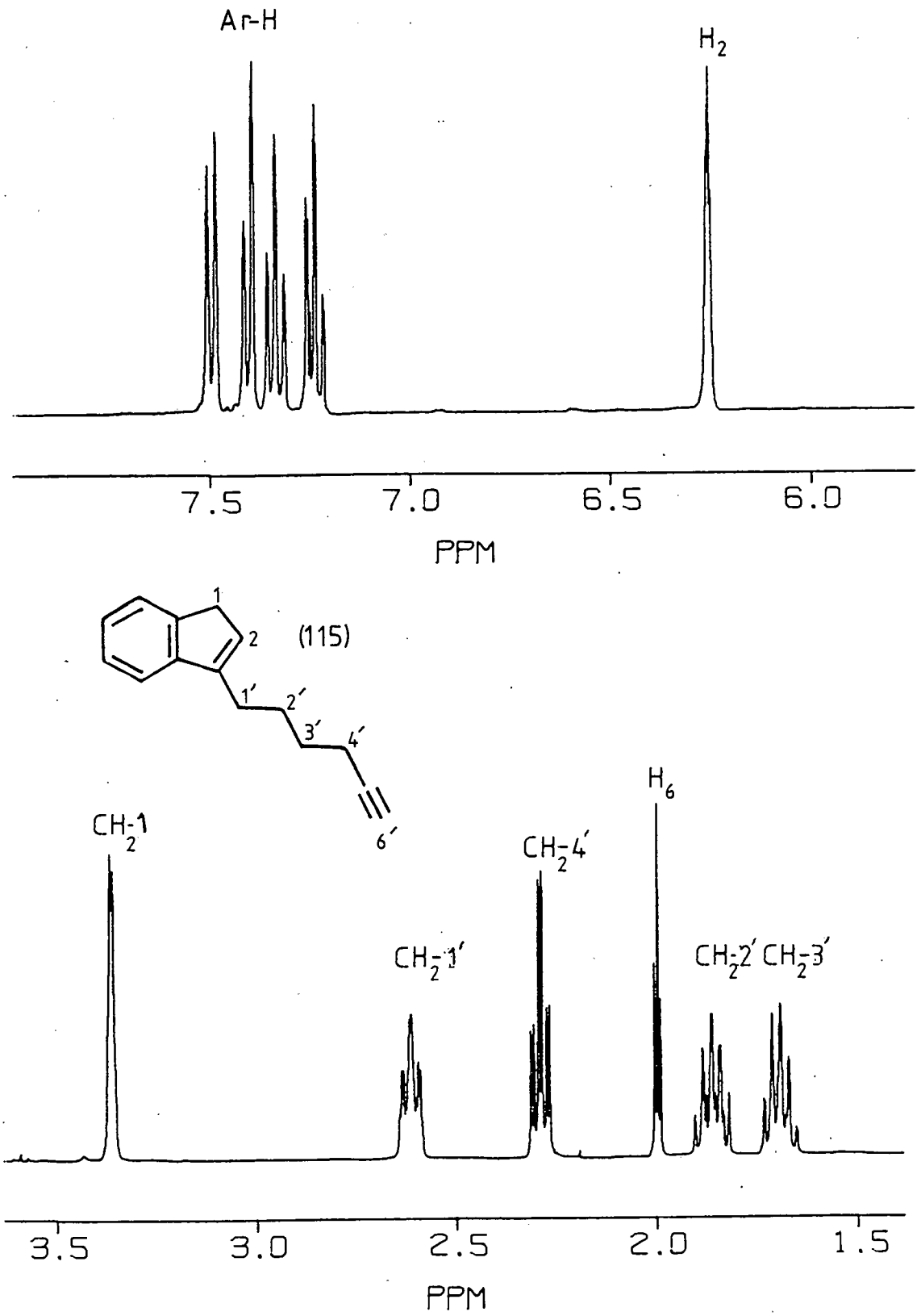


(113)

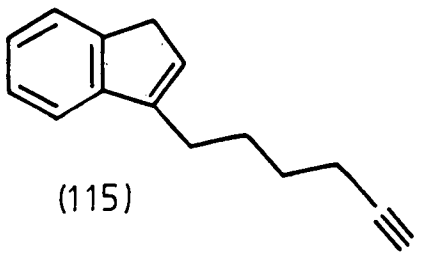


(114)

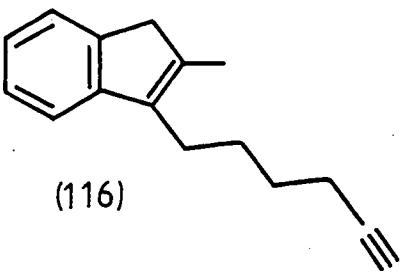
FIGURE 15


Ar-H
H2
7.5
7.0
6.5
6.0
PPM
1
2
(115)
1'
2'
3'
4'
6'
CH2-1
CH2-1'
CH2-4'
H6
CH2-2' CH2-3'
3.5
3.0
2.5
2.0
1.5
PPM

1-Iodohex-5-yne reacted by method A with indene (3 h at 60°) and 2-methylindene (7 h at 65°) to give 3-(hex-5'-ynyl) indene (115) and 3-(hex-5'-ynyl)-2-methylindene (116) respectively. Complete assignment of the hexynyl side chain proton



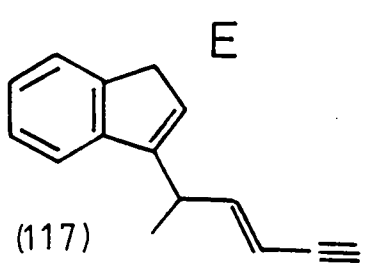
(115)



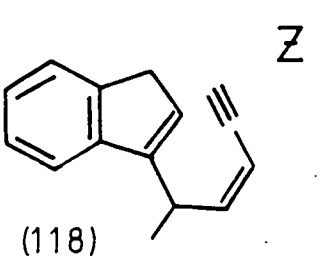
(116)

resonances in the 360MHz n.m.r. spectrum of (115) was achieved by proton decoupling experiments (fig.15). Irradiation at 2.61δ removes the coupling to the olefinic proton and simplifies the multiplet at 1.86δ. Irradiation of the multiplet at 2.30δ removes the coupling to the alkyne proton at 1.99δ and simplifies the resonance at 1.69δ. Thus in order of increasing δ the resonances correspond to the methylene protons attached to C-3', C-2', C-4' and C-1'.

E and Z-3-(1'-methylpent-2'-en-4'-ynyl)indene (117 and 118) were prepared from E and Z-2-bromohex-3-en-5-yne by method A (room temperature). The compounds were obtained as a mixture in the ratio 2.2:1 (117:118) whose proton n.m.r. spectrum agrees with that reported previously[22].

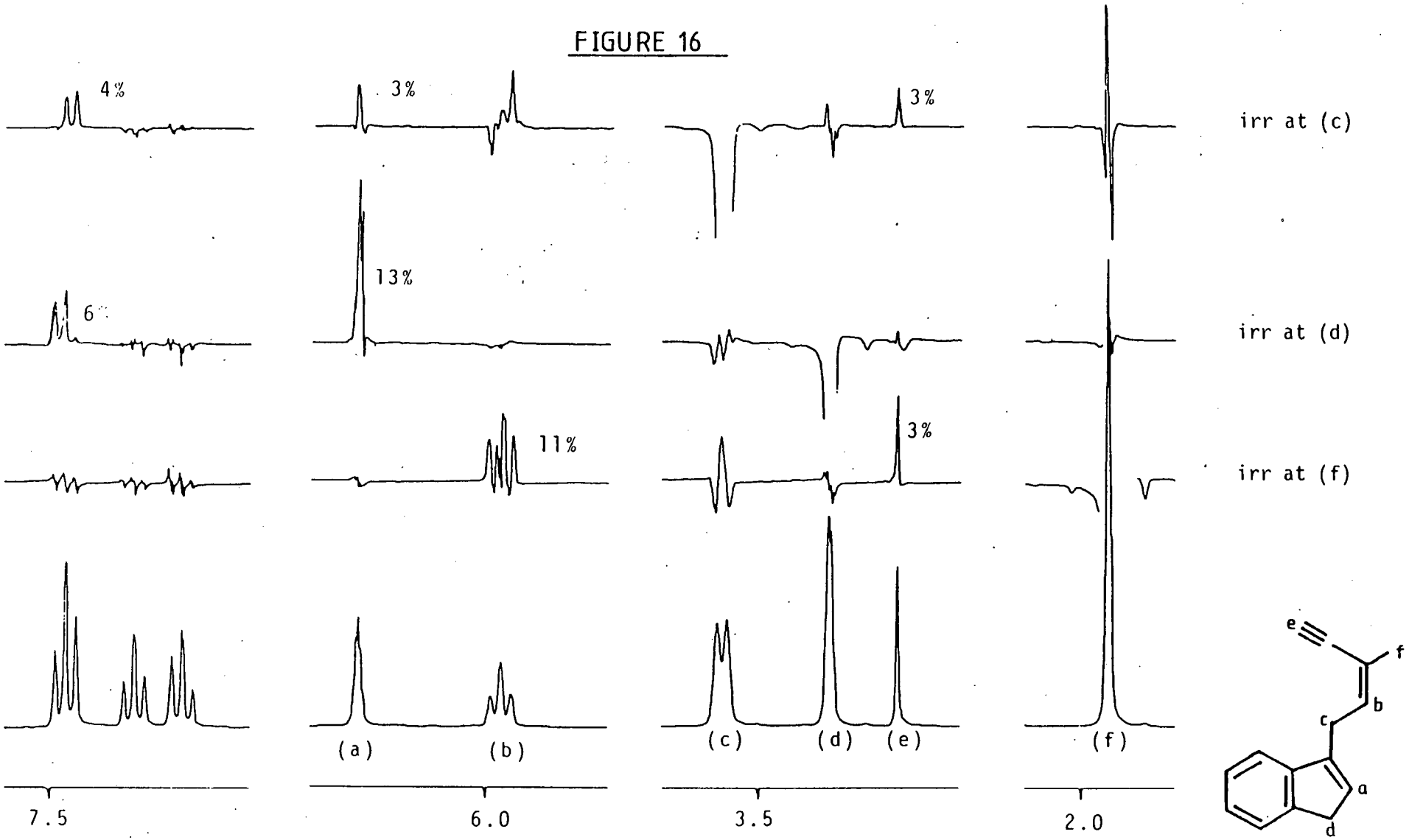


(117)



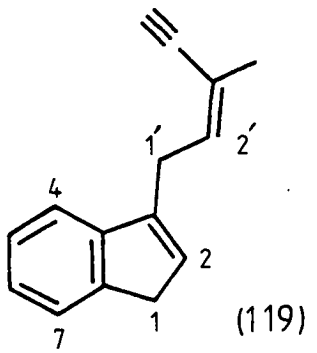
(118)

FIGURE 16



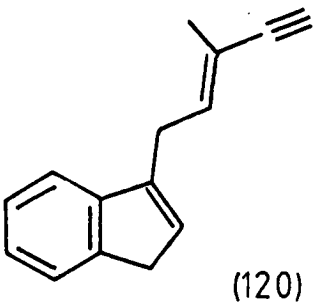
Z-3-(3'-methylpent-2'-ene-4'-ynyl)indene (119) was prepared from indene and 1-bromo-3-methylpent-2-en-4-yne by method A (room temperature). The trace of E isomer present in the mixture was removed by crystallisation from methanol. This compound has been prepared previously[22] and was assigned

Z



(119)

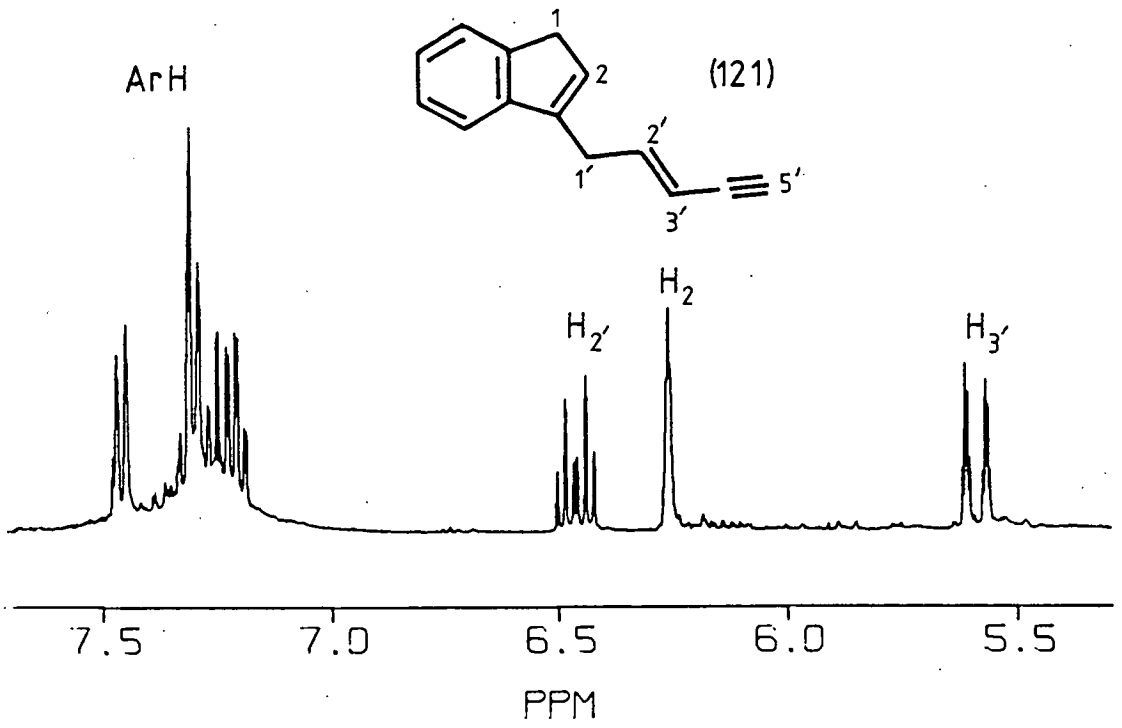
E

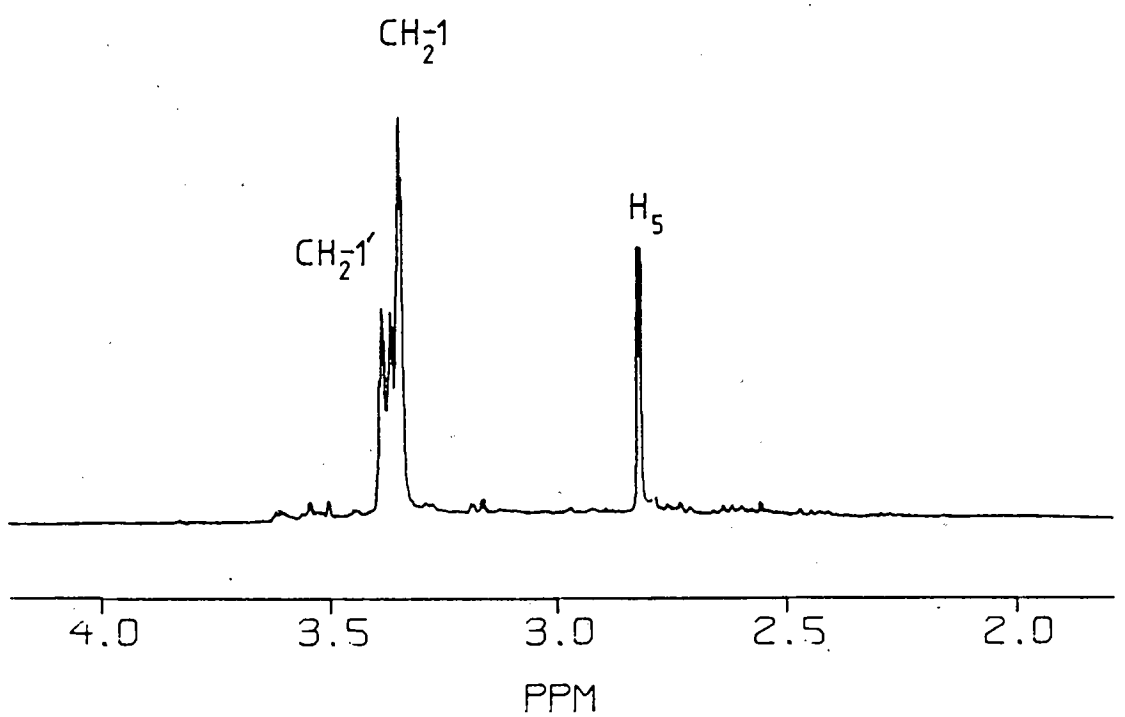


(120)

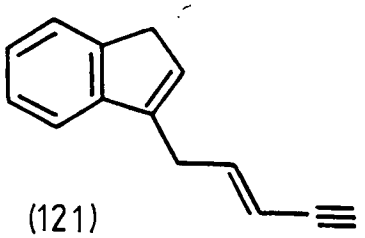
the Z configuration rather than the E (120) because the 1-bromo-2-methylpent-2-en-4-yne was shown to consist largely of the Z isomer and would thus be expected to produce mostly Z product. The assignment of Z configuration for the major product was confirmed by obtaining NOE difference spectra (fig.16) of the proton n.m.r. spectrum of this molecule. Irradiation of the methyl protons (f) gave an 11% increase in the C<u>H</u>-2' signal and a 3% increase in the acetylenic proton signal and gave no net intensity increase on any other protons. Similarly irradiating the C<u>H</u>$_2$-1' signal (c) gave small (ca.3%) increases in the C<u>H</u>-4, C<u>H</u>-2 and acetylenic proton signals with no net effect on the other protons. This clearly shows that the methyl group is in close proximity to C<u>H</u>-2' and not C<u>H</u>$_2$-1', thus proving the Z configuration. Irradiating at C<u>H</u>-2 gave a 3% increase in the C<u>H</u>$_2$-1 signal as expected but also

FIGURE 17


ArH
1
2
(121)
2′
1′
5′
3′
H2
H2′
H3′
7.5
7.0
6.5
6.0
5.5
PPM

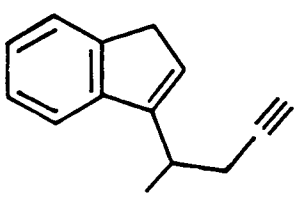

CH2-1
CH2-1′
H5
4.0
3.5
3.0
2.5
2.0
PPM

gave a 4% increase in the CH-2' signal indicating that in solution the conformation is close to that drawn with CH-2 and CH-2' in proximity.

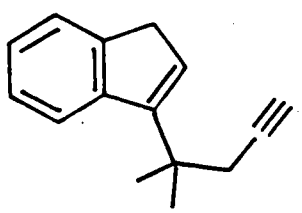


(121)

The parent compound of the enyne series, E-3-(pent-2'-en-4'-ynyl) indene (121) was prepared from E-1-bromopent-2-en-4-yne by method A at room temperature. The 360MHz spectrum (fig.17) shows that the E conformation has been retained in the product, with a coupling between the side chain olefinic protons of 15.9 Hz.



(122)



(123)

3-(1'-Methylbut-3'-ynyl)indene (122) and 3-(1',1'-dimethylbut-3'-ynyl)indene (123) could not be made from the appropriate bromides. Method A gave only unchanged indene and 2-methylpent-4-yn-2-ol formed by hydrolysis of the halide. Method B failed due to reaction between the halides and ammonia.

FIGURE 18

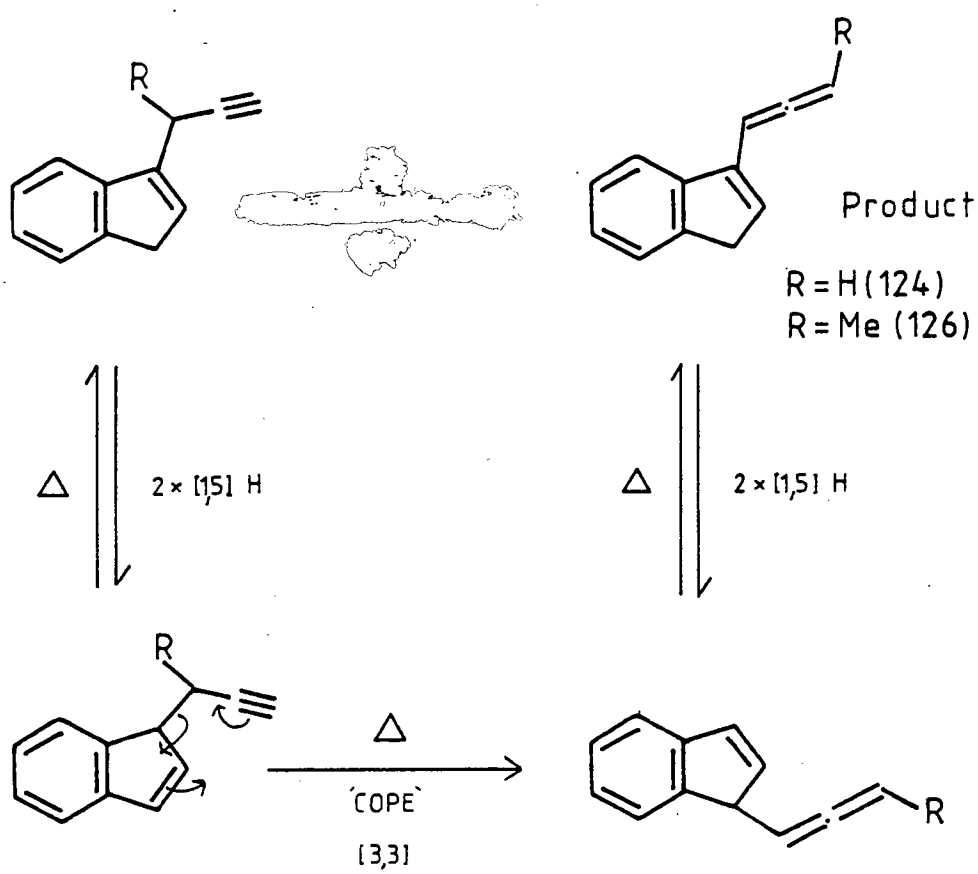


Table 3

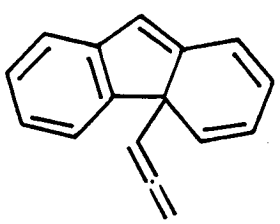
Compound	T (°C)	% Products			
		Starting Material	Fluorene	Allene	9,9'-Bifluorenyl
9-Propargylfluorene	400	100	-	-	-
	500	70	5	22	3
	550	37	10	34	11
	600	-	40	50	9
	650	-	73	9	13
	700	-	84	-	13
9-(1'-Methylprop-2'-ynyl)fluorene	500	27	10	40	-
	550	-	35	63	-
	600	-	43	22	11
9-(1',1'-Dimethylprop-2'-ynyl)fluorene	500	-	6	75	6
	550	-	40	48	11
	600	-	85	-	8

CHAPTER 3

Thermal Rearrangement of Acetylenes

3.1 Vapour Phase Pyrolysis of Fluorene Derivatives

The low pressure vapour phase thermolysis of 3-propargyl indene (24) at 500°C has been shown by Truslove [22] to give 3-allenyl indene (124) (fig.18). When 3-(1'-methylprop-2' ynyl)indene (125) was pyrolysed under the same conditions the product was 3-(buta-1',2'-dienyl)indene (126). The suggested mechanism for this reaction was a 'Cope' type [3,3] sigmatropic rearrangement across the indene system as shown in figure 18. However it seemed unlikely that propargylic derivatives of fluorene would react by this mechanism, since it requires the disruption of the benzene ring π system to give intermediates such as (127). The pyrolysis of 9-propargyl

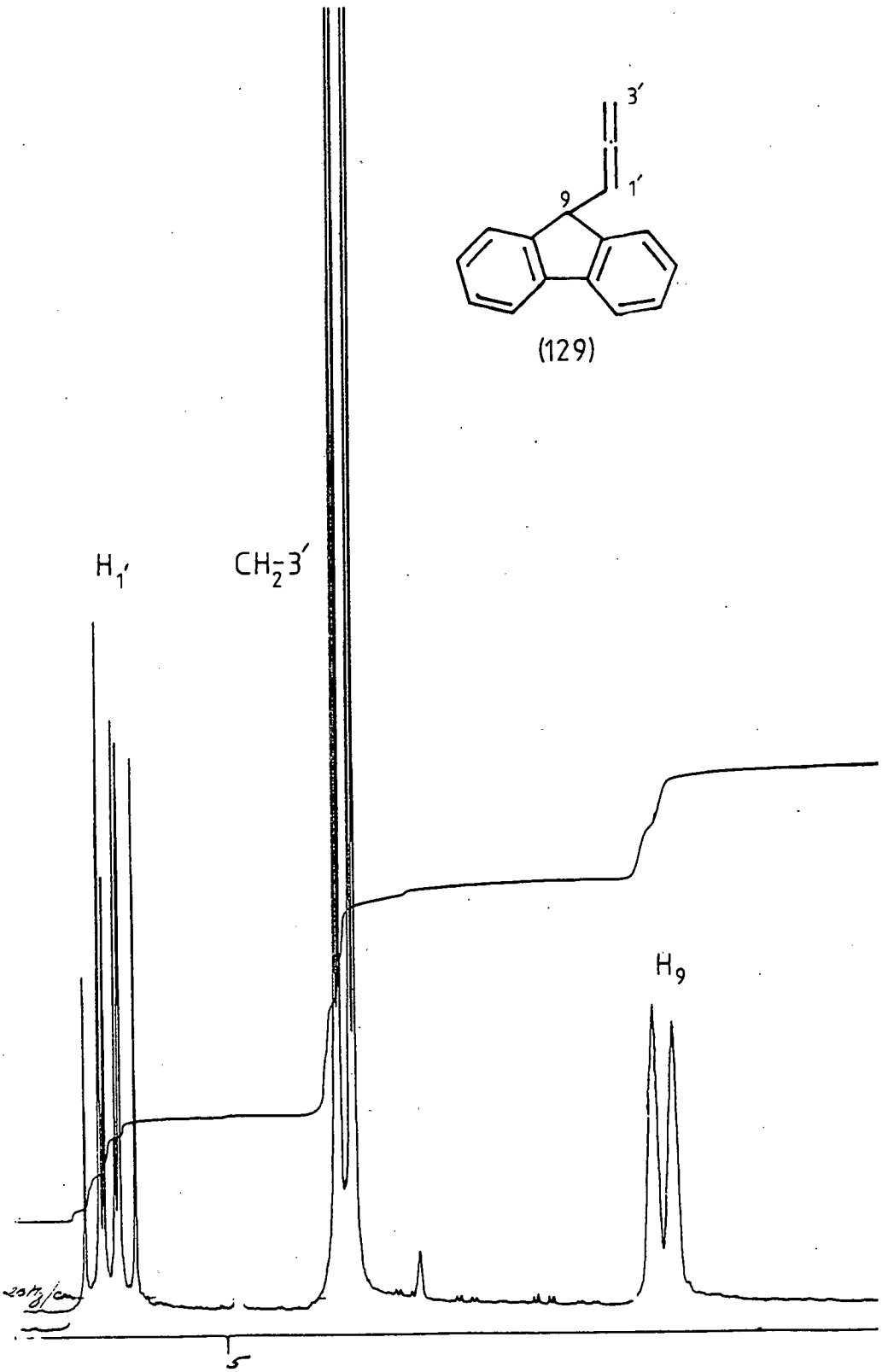


(127)

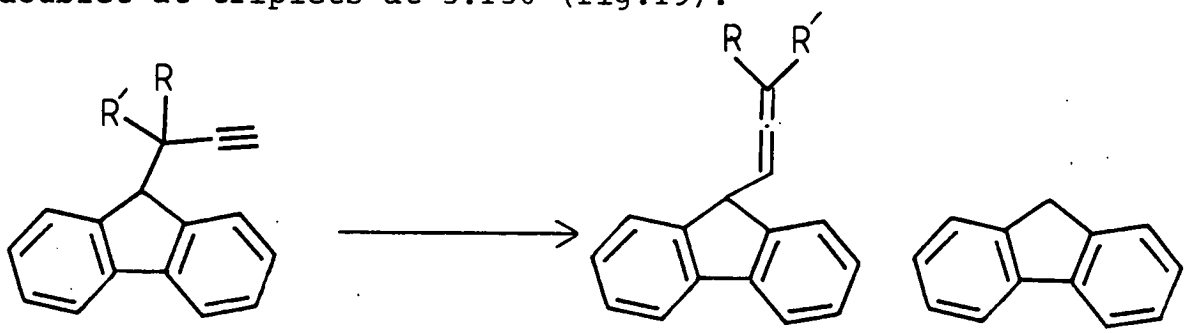
fluorene and other fluorene derivatives whose preparation is described earlier (p.27) have therefore been studied.

Pyrolysis of 9-propargylfluorene (97) at temperatures ranging from 500° to 600° gave mixtures of products identified as fluorene (19), 9,9'-bifluorenyl (128) 9-allenylfluorene (129) in varying proportions (Table 3). The identification

FIGURE 19



of the fluorene and 9,9'-bifluorenyl was achieved by comparison with authentic samples of these materials. The allene could not be isolated due to rearrangement on alumina (see p.55) but its presence was clearly shown by the 360MHz proton n.m.r. spectrum of the product mixture. The C-9 proton is a broad doublet at 4.49δ, the allene CH_2 protons a doublet of doublets at 4.87δ and the allene CH proton a doublet at triplets at 5.15δ (fig.19).

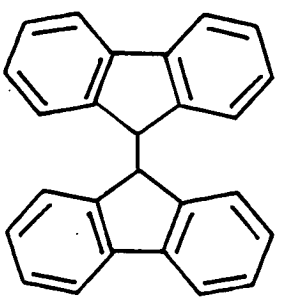


R,R´=H (97)

R=H, R´=CH_3 (99)

R,R´=CH_3 (100)

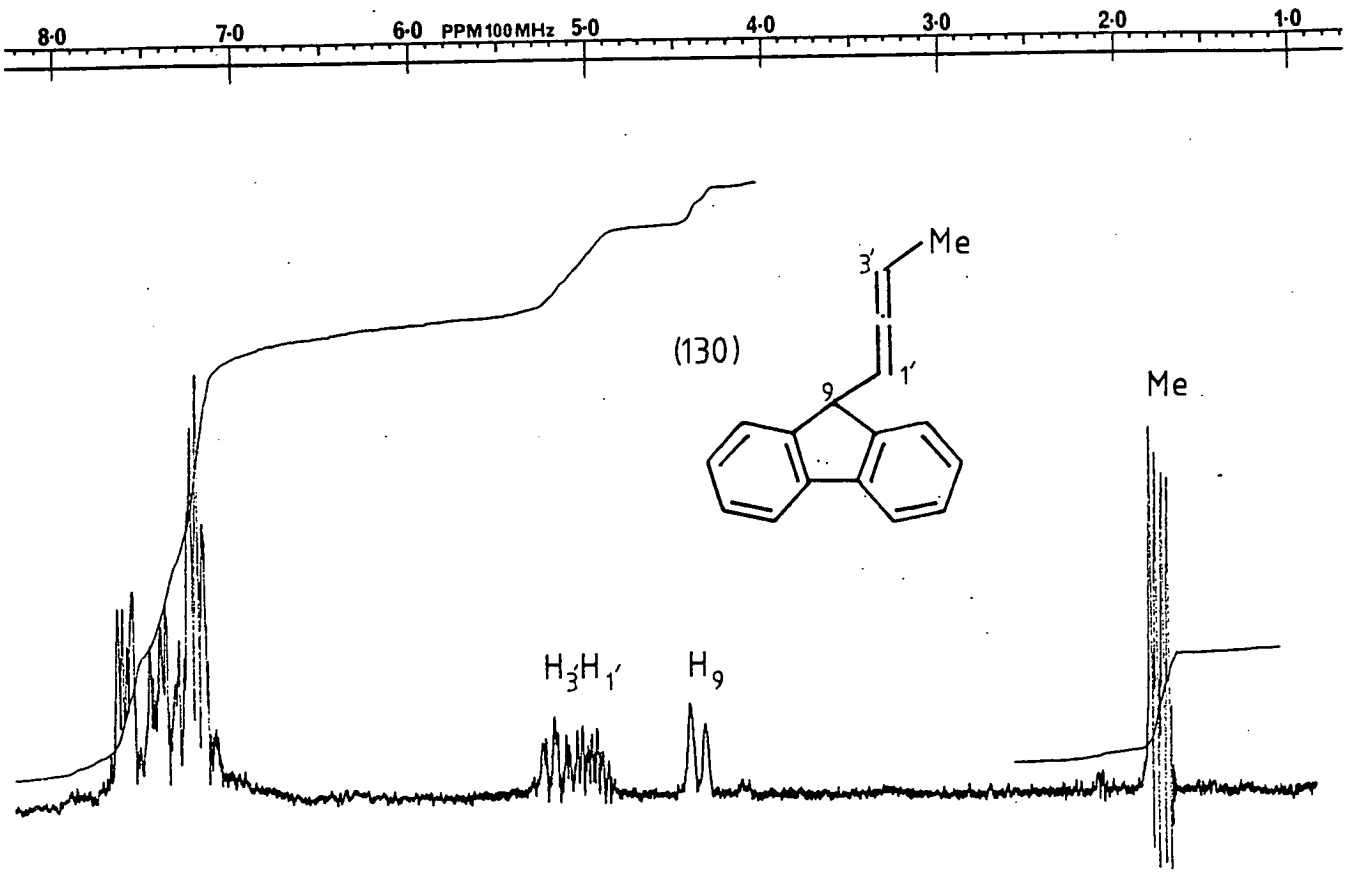
(19)



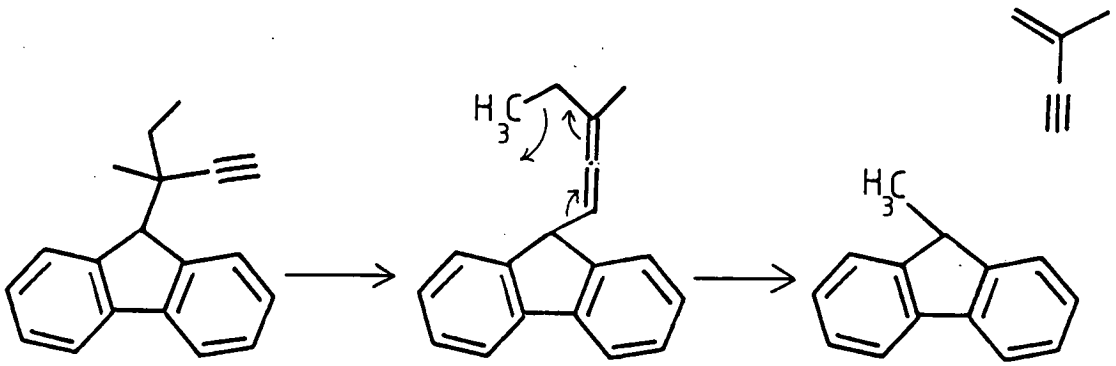
(128)

The pyrolysis of 9-(1'-methylprop-2'-ynyl)fluorene (99) and 9-(1',1'-dimethylprop-2'-ynyl)fluorene (100) yielded analogous products (Table 3). As for 9-allenylfluorene (129) the allenes 9-(3'-methylbuta-1',2'-dienyl)fluorene (101) and 9-(buta-1',2'-dienyl)fluorene (130) rearranged on alumina chromatography but (130) was isolated by preparative g.l.c.

FIGURE 20



Its proton n.m.r. spectrum (fig.20) shows the methyl group as a doublet of doublets at 2.74δ coupling to the C-3' and C-1' protons at 4.86-5.34δ. The C-9 proton appears as a broad doublet at 4.39δ.

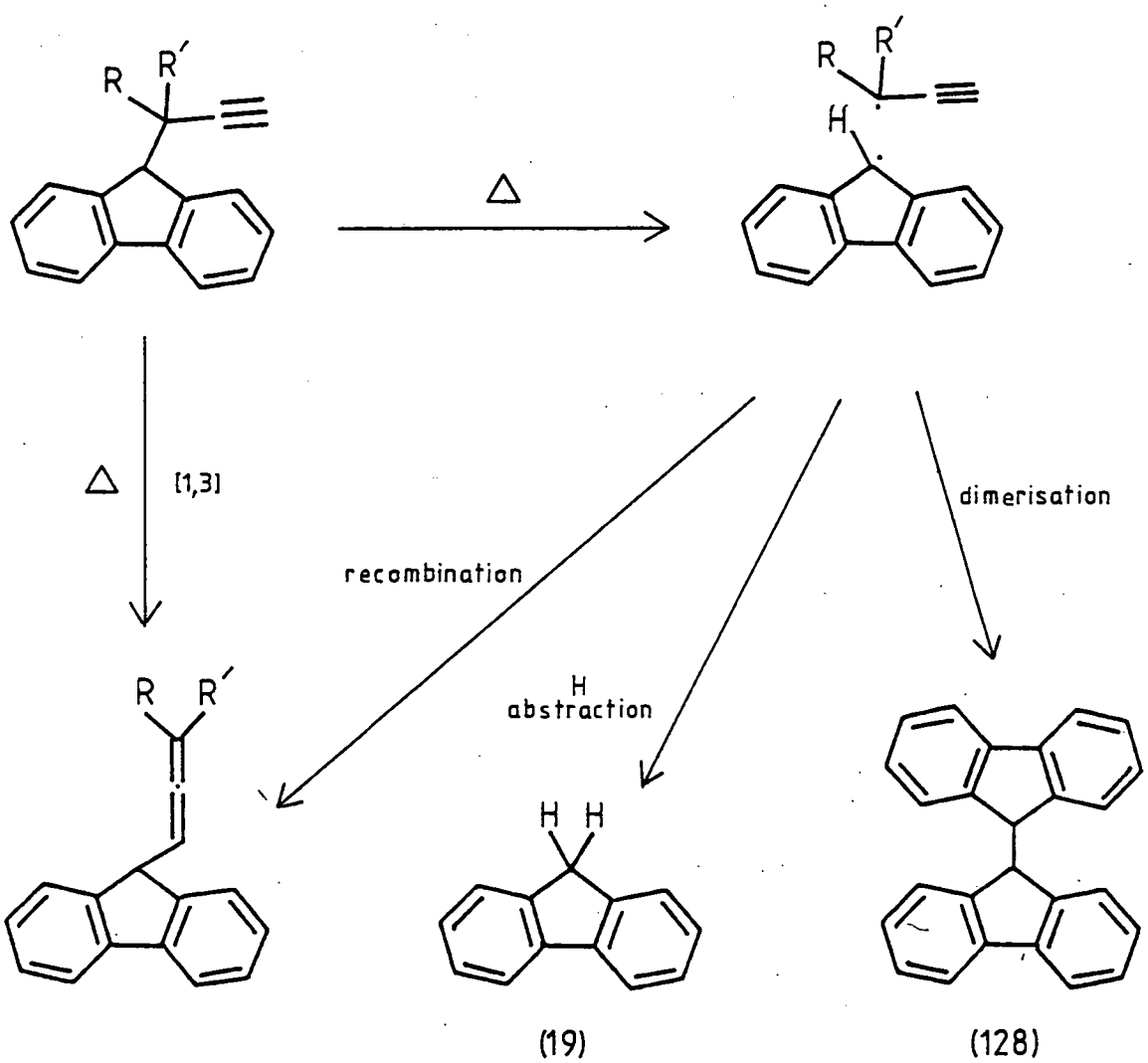


(102) (103) (131)

Pyrolysis of 9-(1'-ethyl-1'-methylprop-2'-ynyl)fluorene (102) behaved similarly but gave some additional products not found in the other reactions. At 500° unreacted acetylene (35%), 9-(3'-methylpenta-1',2'-dienyl)fluorene (35%) (103), fluorene (19) (4%), 9-methylfluorene (131) (8%) and 9,9'-bifluorenyl (128) (20%) were obtained. However at 600° only a mixture of fluorene and 9-methylfluorene (131), identified by proton and ^{13}C n.m.r., formed in the ratio 1:2 were obtained. This mixture could not be separated by silica or alumina chromatography. The formation of 9-methylfluorene (131) in this case and not in preceding examples can be explained by the operation of a concerted rearrangement of the allene (103) as shown in the preceding diagram, this is only possible for this particular allene and not for those formed from the other acetylenes.

The mechanism of the preceding pyrolyses of propargylic fluorenes is clearly not that suggested for 3-propargyl indene

FIGURE 21



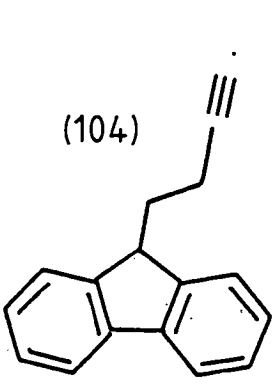
(19)

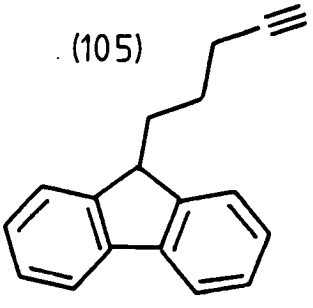
(128)

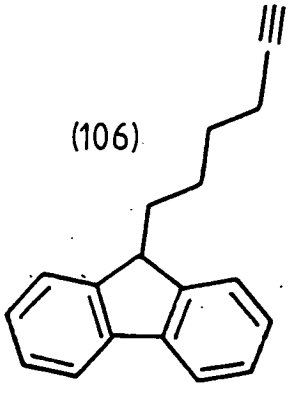
(24) since the products are not derived from a [3,3] sigmatropic shift of propargyl across the fluorene system. The presence of 9,9'-bifluorenyl (128) suggests a radical process occurs in which the bond between fluorene and the propargylic side chain is broken to give a 9-fluorenyl radical and a propargylic radical. Dimerisation of two of the 9-fluorenyl radicals would then give 9,9'-bifluorenyl. Such a radical dimerisation is not a process normally observed in gas phase pyrolysis at low pressure. Products from the propargylic radical were not observed but they would be too volatile to be caught in the product trap of the flow system used (p.100). Rapid reaction of the two radicals initially formed could produce fluorene by hydrogen transfer or the allene derivative by recombination (see fig.21). The allenyl fluorenes could also be produced by a [1,3] sigmatropic shift, with inversion at carbon, of fluorenyl along the propargyl carbon chain. This process should be reasonably easy, the developing allene system of the transition state would be quite flexible (C=C=C has a low 354 cm^{-1}, vibrational bending frequency[23]), assisting the migration of fluorenyl.

It is not clear from the results whether a radical or concerted process is responsible for the allene formation. As the temperature of pyrolysis increases (Table 3) the proportion of allene in the products decreases while the proportion of the main fragmentation products increases steadily. This might indicate that the [1,3] sigmatropic shift operates at moderate temperatures and is 'swamped' by radical fragmentation at higher temperatures however the allenyl fluorenes

may themselves be fragmenting to give fluorene at higher temperatures.


(104)


(105)

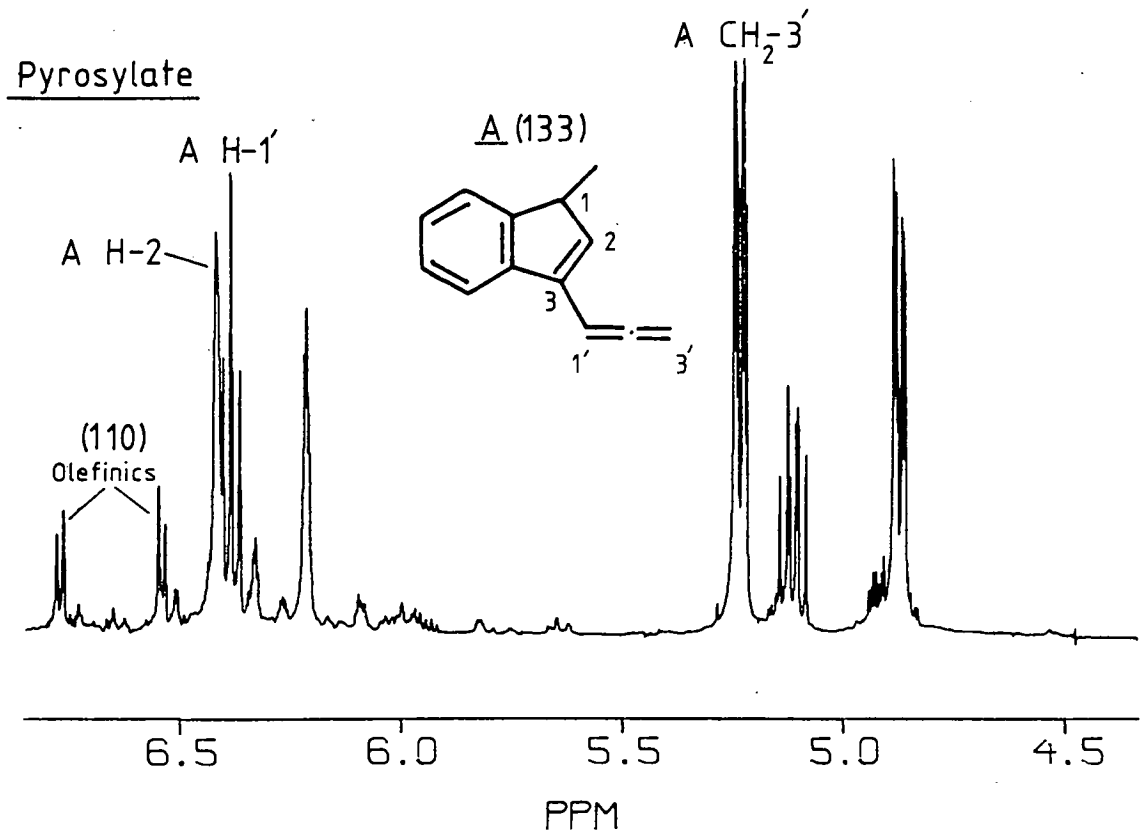

(106)

Pyrolysis of 9-(but-3'-ynyl)fluorene (104) gave unchanged acetylene at 500°, acetylene with a little fluorene at 550° and a little fluorene with other unidentified products predominating at 600°. Similarly pyrolysis of 9-(pent-4'-ynyl)fluorene (105) and 9-(hex-5'-ynyl)fluorene (106) at temperatures from 600°-700° gave mixtures containing some fluorene and bifluorenyl with unidentified aromatic products predominating at higher temperatures.

3.2 Vapour Phase Pyrolysis of Indene Derivatives

The [1,3] sigmatropic shift proposed as a possible mechanism for the production of allenes from pyrolysis of propargylic fluorenes would, if it occurs in propargylic indenes, lead to the observed products (fig.18). A radical mechanism is unlikely since no products derived from fragmentation reactions were observed. The mechanism of propargylic indene rearrangements has therefore been investigated further in an attempt to distinguish between a [1,3] shift or a [3,3]

FIGURE 22


Pyrosylate
A H-1′
A H-2
(110)
Olefinics
A (133)
1
2
3
1′
3′
A CH2-3′
6.5
6.0
5.5
5.0
4.5
PPM

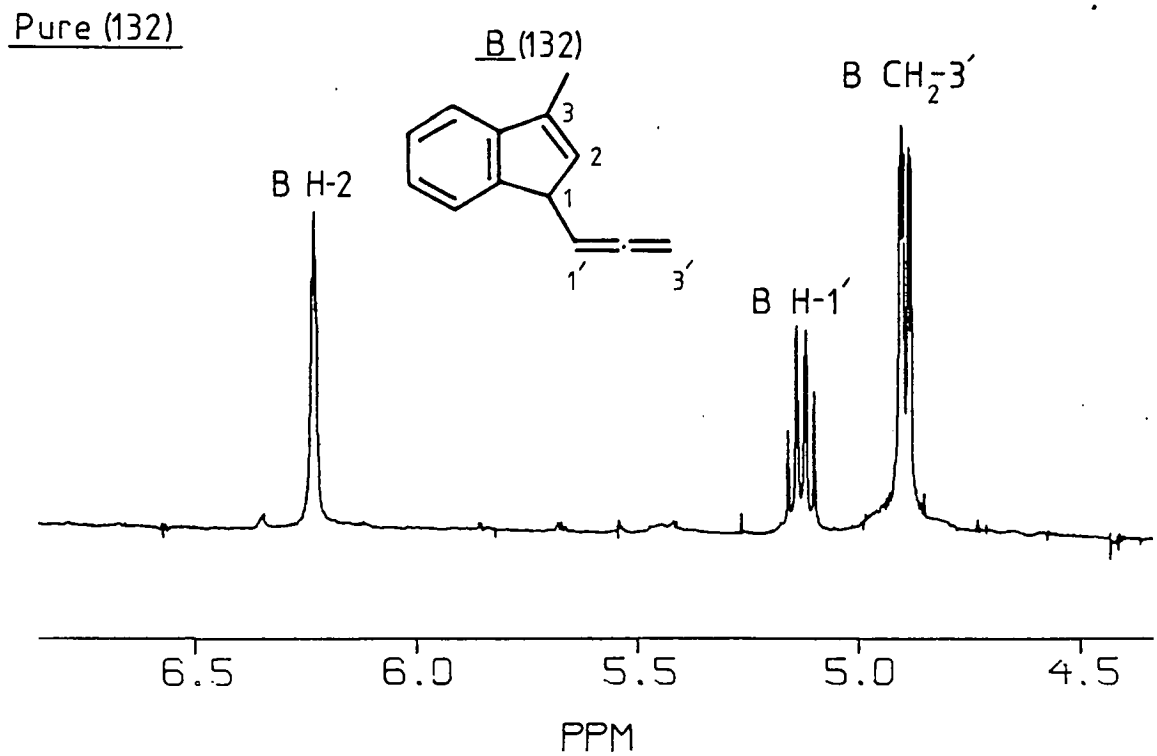
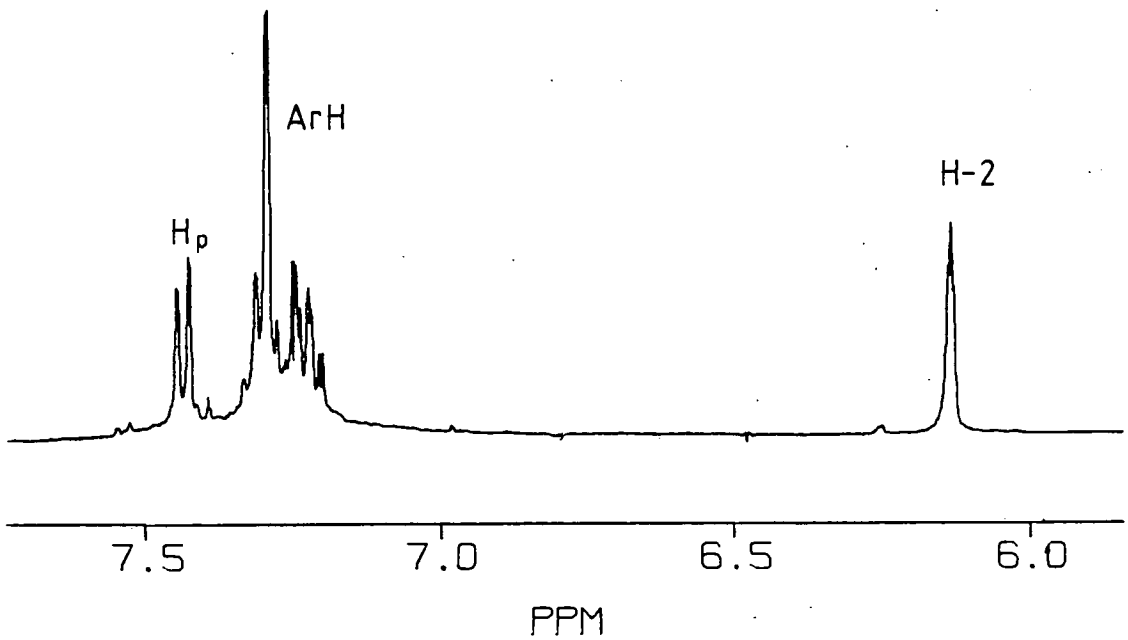
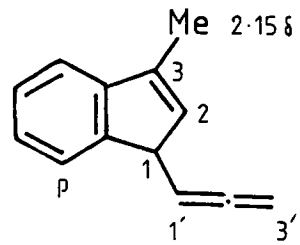
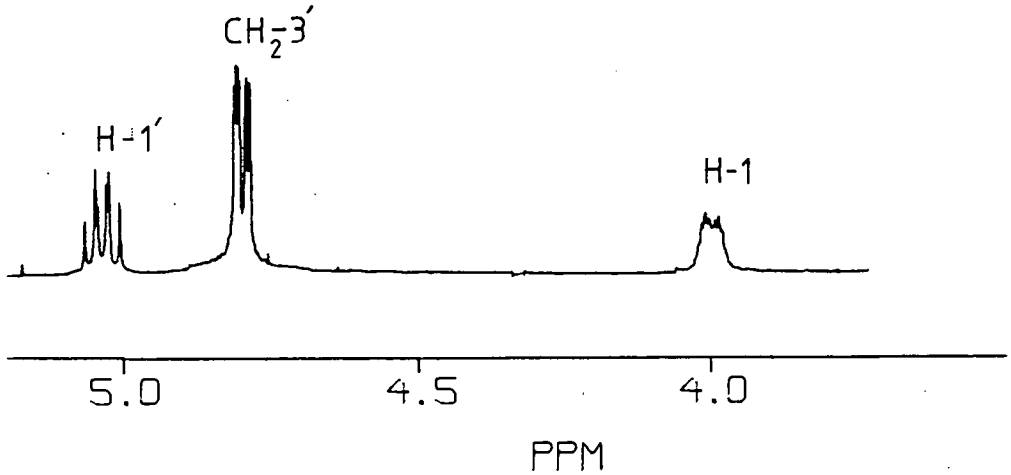

Pure (132)
B (132)
3
2
1
1′
3′
B H-2
B H-1′
B CH2-3′
6.5
6.0
5.5
5.0
4.5
PPM

FIGURE 23



(132)





Cope type rearrangement (fig.18).

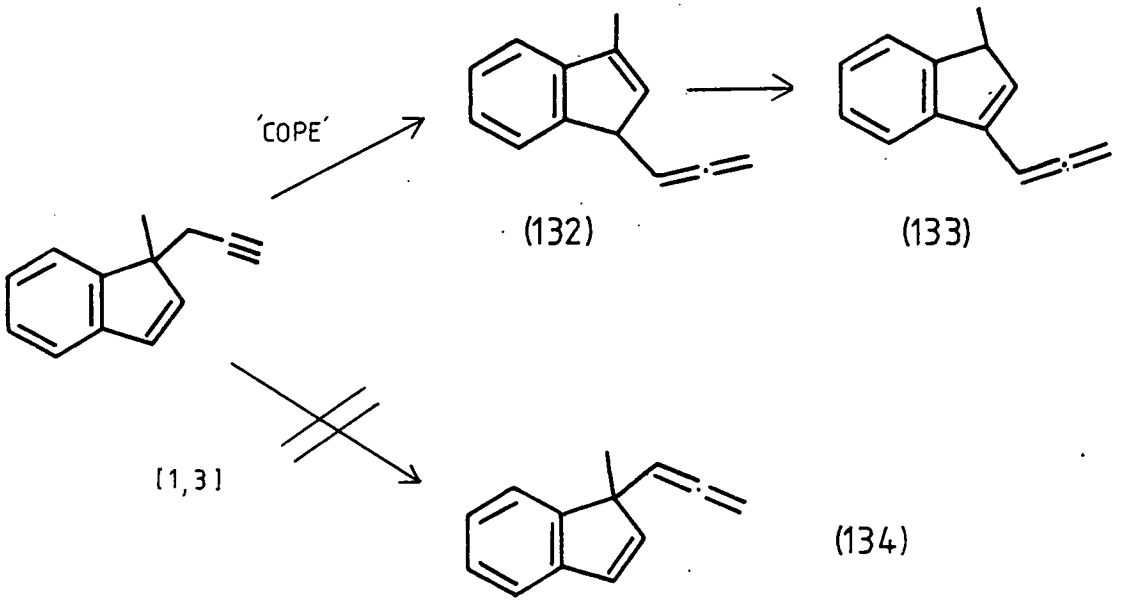
Pyrolysis of 1-methyl-1-propargylindene (110) at 550° gave a mixture of unchanged 1-methyl-1-propargylindene (110), 1-allenyl-3-methylindene (132) and 3-allenyl-1-methylindene (133) in the ratio 1:4.2:5 as shown by the 360 MHz proton n.m.r. spectrum of the mixture. Figure 22 shows the alkene/allene region of the spectrum.

The $C\underline{H}_2$-3' resonance for the 3-allenyl-1-methylindene appears as a multiplet at 5.24δ coupled to C<u>H</u>-1', C<u>H</u>-2 and either C<u>H</u>-1 or C<u>H</u>-4. The C<u>H</u>-1' resonance is deshielded by proximity to the indenes double bond (the allene π system is conjugated to the indene π system) and so appears at 6.38δ as a triplet of doublets, coupled to the $C\underline{H}_2$ -3' protons and to C<u>H</u>-2 (J=7.0 and 0.7Hz). The indene CH-2 proton appears as a broad singlet at 6.41δ. Other resonances identified for this molecule were at 1.38δ ($C\underline{H}_3$, J=7.6Hz to C<u>H</u>-1), 3.55δ (m, C<u>H</u>-1), 7.2-7.4 (m, $C\underline{H}_5$, $C\underline{H}_6$), 7.52δ (d, J=7.3Hz, $\underline{H}_7$) and 7.92δ (d, J=7.4Hz, H_4).

The 1-allenyl-3-methylindene (132) was isolated by preparative g.l.c. Its 360 MHz spectrum (fig.23) shows the methyl group at 2.15δ as a triplet coupled to C<u>H</u>-2 and to C<u>H</u>-1 at 6.13δ and 4.0δ respectively. The allene C<u>H</u> proton is a doublet of triplets at 5.03δ coupling to the allene $C\underline{H}_2$ (J=6.6Hz) and C<u>H</u>-1 (J=8.1Hz). The two (non equivalent) allene protons appear as a multiplet at 4.8δ.

The ^{13}C n.m.r. spectrum of this molecule shows a characteristic allene carbon (=C=) resonance at 209.3δ, the other allenic carbon resonances being at 75.7δ (CH_2) and 89.0δ (CH).

These products show that in this case the Cope type rearrangement is operating exclusively since only 1-allenyl-3-methylindene (132) and its isomer (133), formed via two [1,5] sigmatropic H shifts, are produced. No 1-allenyl-1-methylindene (134), the expected product from a [1,3] shift, was detected.



The observed products could not be produced by two [1,5] methyl shifts since the preferential migration of hydrogen in the isoindene (135) intermediate formed by the first [1,5] methyl shift would give the 2-methylindene derivative (136) which is not present.

Pyrolysis of 3-methyl-1-propargylindene (111) at 550^{o} is more complex yielding:- 3-methyl-1-propargylindene (46%), 1-methyl-3-propargylindene (112) (22%), 1-allenyl-1-methylindene (134) (12%), 1-allenyl-3-methylindene (132) (10%) and 3-allenyl-1-methylindene (133) (10%). These compounds were identified as follows from the 360 MHz proton spectrum of the

FIGURE 24a

Pyrosylate

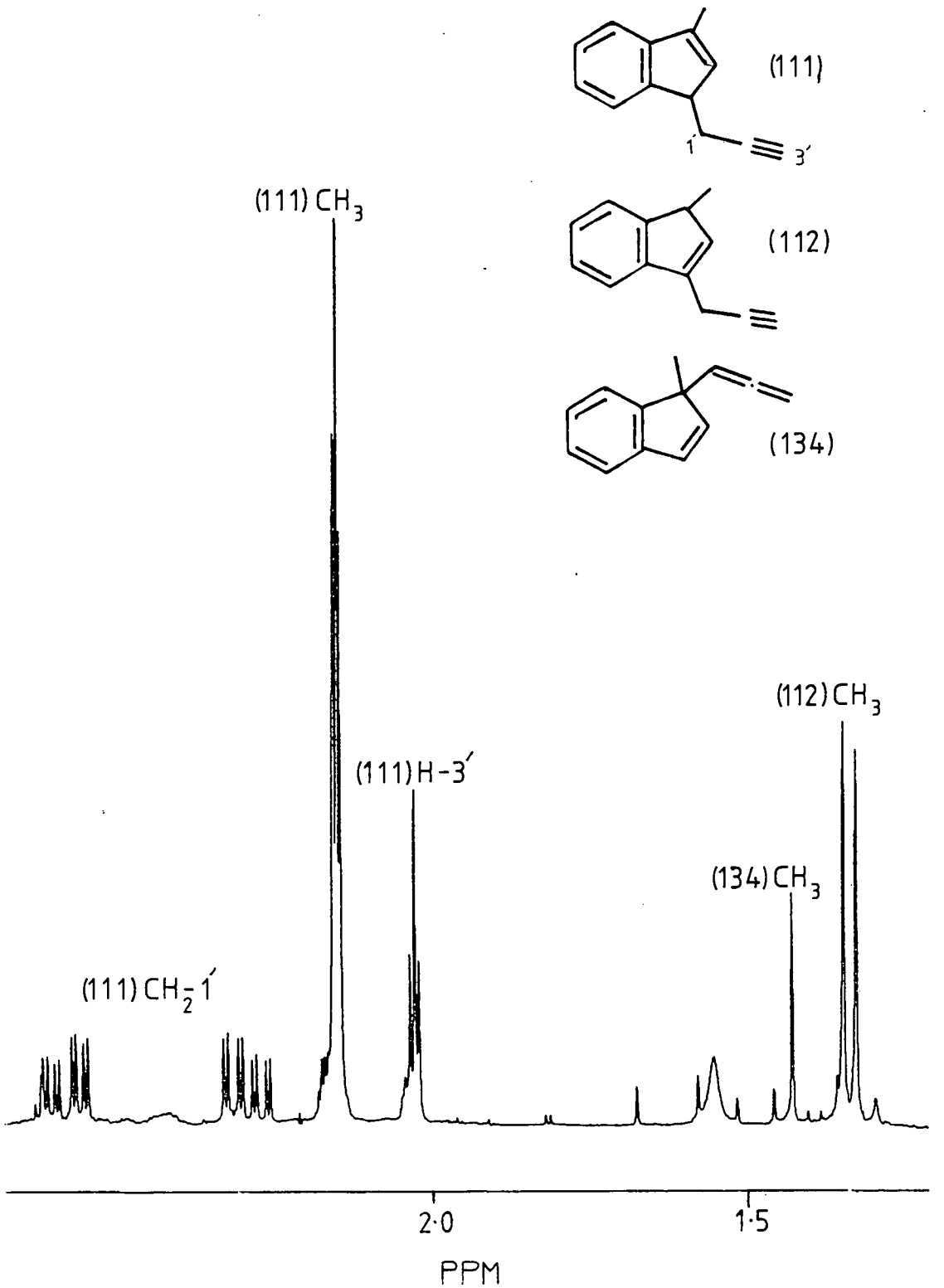
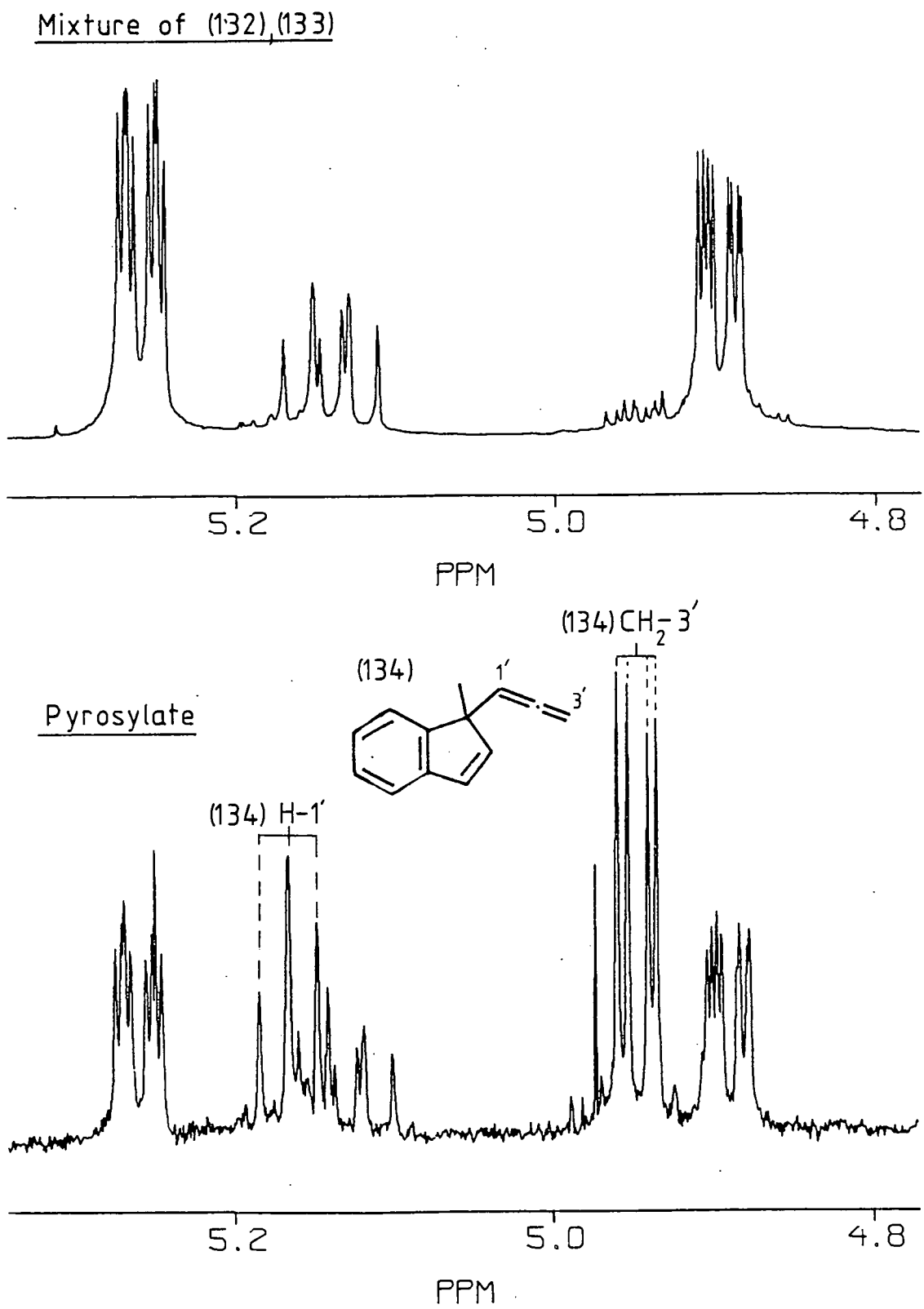
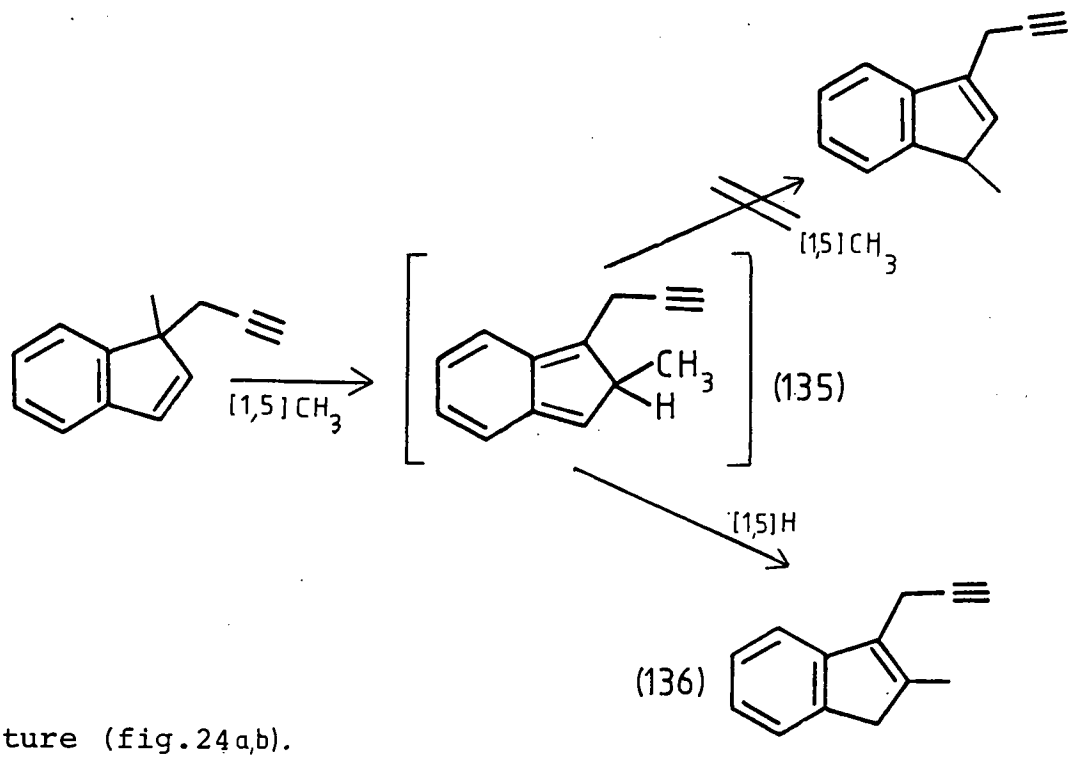


FIGURE 24b

ALLENE REGION



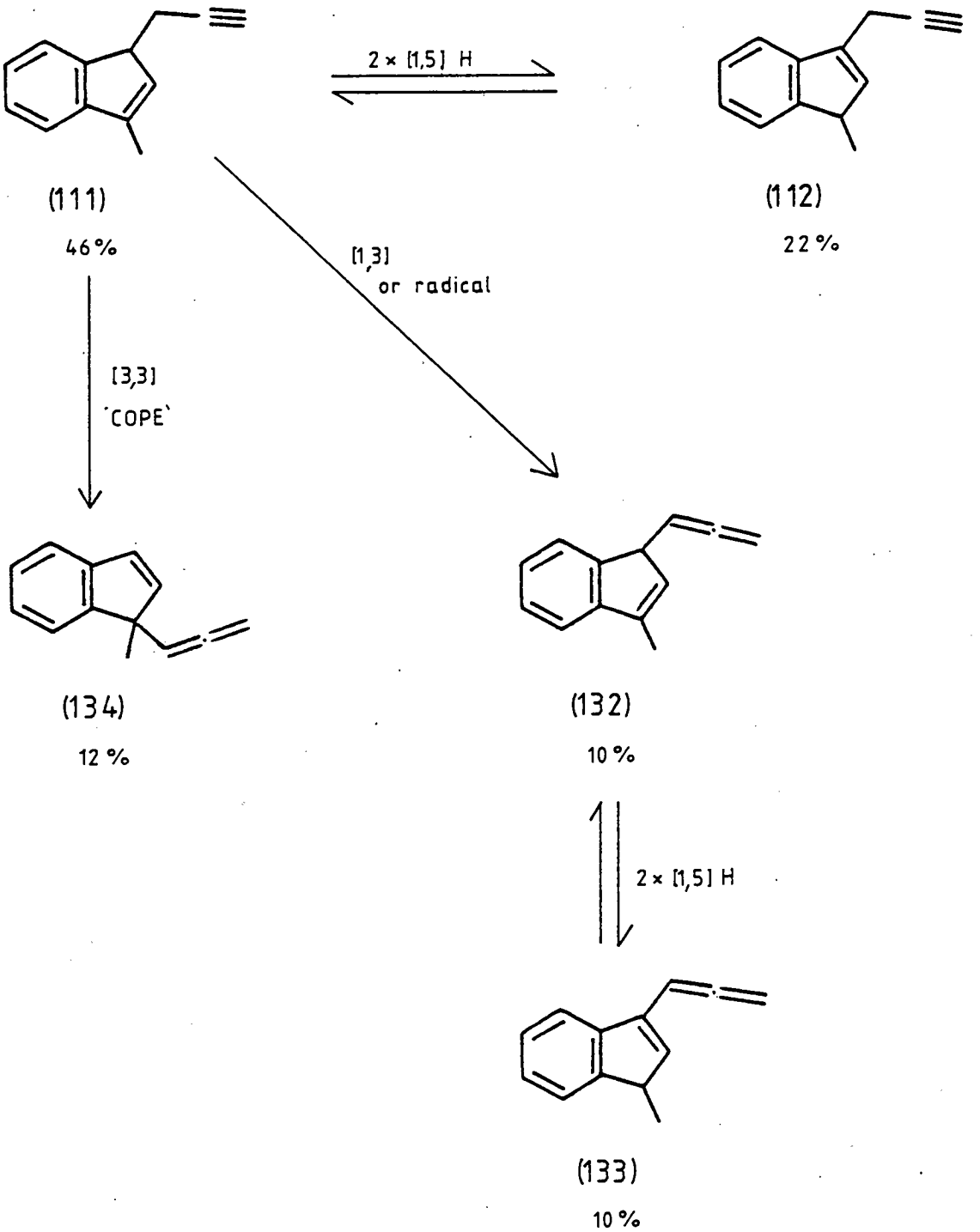


mixture (fig.24a,b).

The unchanged starting material (111) shows the same resonances in the mixture as originally, 1-methyl-3-propargyl-indene (112) shows its methyl protons as a doublet at 1.33δ (J=7.6Hz) coupled to C<u>H</u>-1, a multiplet at 3.56δ. The acetylenic proton is obscured by the resonance from the starting material at 2.04δ. The propargylic protons appear as a multiplet at 3.46δ and the indene olefinic proton as a multiplet at 6.45δ. Of the three allenic products only one has not been identified in the preceding rearrangement, 1-allenyl-1-methylindene. This molecule has a methyl resonance at 1.42δ and shows allene resonances at 4.87δ (d of d, J=6.6Hz, 1.9Hz) for the C<u>H</u>$_2$-3' protons coupled to the C<u>H</u>-1' proton at 5.09δ (t, J=6.6Hz). The indene olefinic protons appear as two doublets (J=5.4Hz) at 6.37δ (C<u>H</u>-2) and 6.70δ (C<u>H</u>-3).

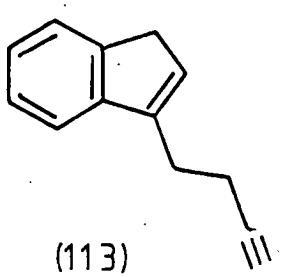
In contrast to the rearrangement of 1-methyl-1-propargyl-indene (110), the rearrangement of 3-methyl-1-propargylindene (111) is more difficult, a high proportion of the 3-methyl-1-

FIGURE 25

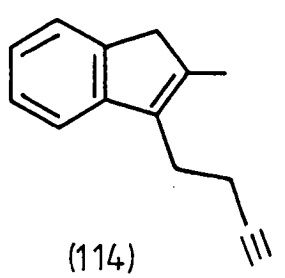

2 × [1,5] H
(111)
46 %
(112)
22 %
[1,3]
or radical
[3,3]
'COPE'
(134)
12 %
(132)
10 %
2 × [1,5] H
(133)
10 %

propargylindene (111) remains unreacted at 550° or is simply isomerised to 1-methyl-3-propargylindene (112) by facile [1,5] H shifts. Only 32% of the material was rearranged to allenes and only one third of these would appear to have been produced by the [3,3] Cope mechanism. The remainder appears to have rearranged in similar manner to the propargyl fluorenes, either by [1,3] sigmatropic shift of indene along the propargyl system or a radical mechanism. The pathways to the reaction products are shown in Figure 25.

The difference in rearrangement pathways between the two indenes (110) and (111) is probably largely steric in origin. The [3,3] Cope rearrangement of 1-methyl-1-propargyl-indene (110) will relieve steric strain between methyl and propargyl groups to produce a 1,3-substituted indene (132). The [3,3] Cope rearrangement of the 3-methyl-1-propargylindene is, by comparison, disfavoured sterically because it involves bonding the propargyl system to a carbon with a methyl group already attached. Competition by other rearrangement mechanisms is therefore more likely in the latter rearrangement, hence the production of (132) and (133) with a relatively small proportion of (134).



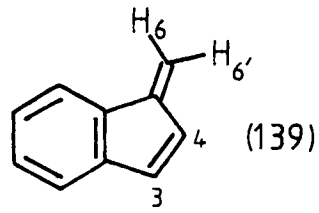
(113)



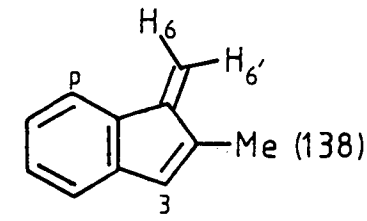
(114)

Pyrolysis of 3-(but-3'-ynyl)indene (113) at 500° gave

Table 4



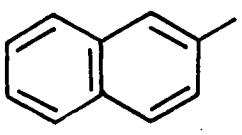
(139)



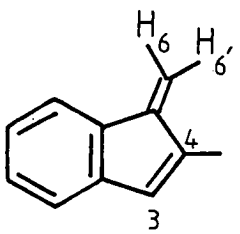
(138)

Benzofulvene ^{1}H (δ)	4-Methylbenzofulvene ^{1}H (δ
-	2.14 (d, J=1.5Hz, CH_3)
5.72 (H-6')	5.67 (bs, H-6')
6.06 (H-6, J_{63}=1.6Hz)	6.00 (d, J-1.7Hz, H-6)
6.52 (H-4)	-
6.88 (H-3)	6.55 (m, H-3)
7.74 (3xArH)	7.72 (m, 3xArH)
7.45-7.75 (ArH)	7.49 (d of d, J=7.3, 1.1H:

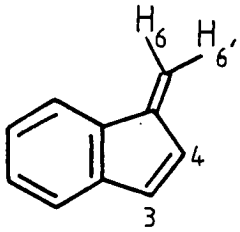
unchanged starting material. At 600° and 700° complex mixtures which could not be identified were obtained. At 700° 3-(but-3'-ynyl)-2-methylindene (114) gave a mixture of 2-methylnaphthalene (137) and 1,2-benzo-4-methylfulvene (138) together with polymeric material. The two compounds (137) and (138) were isolated as a mixture by preparative g.l.c. The 2-methylnaphthalene was identified from its 360 MHz proton n.m.r. spectrum by comparison with the spectrum of an authentic sample and the 1,2-benzo-4-methylfulvene by comparison of its 360 MHz proton n.m.r. spectrum in the mixture with that of benzofulvene (139) (see Table 4).[74]



(137)



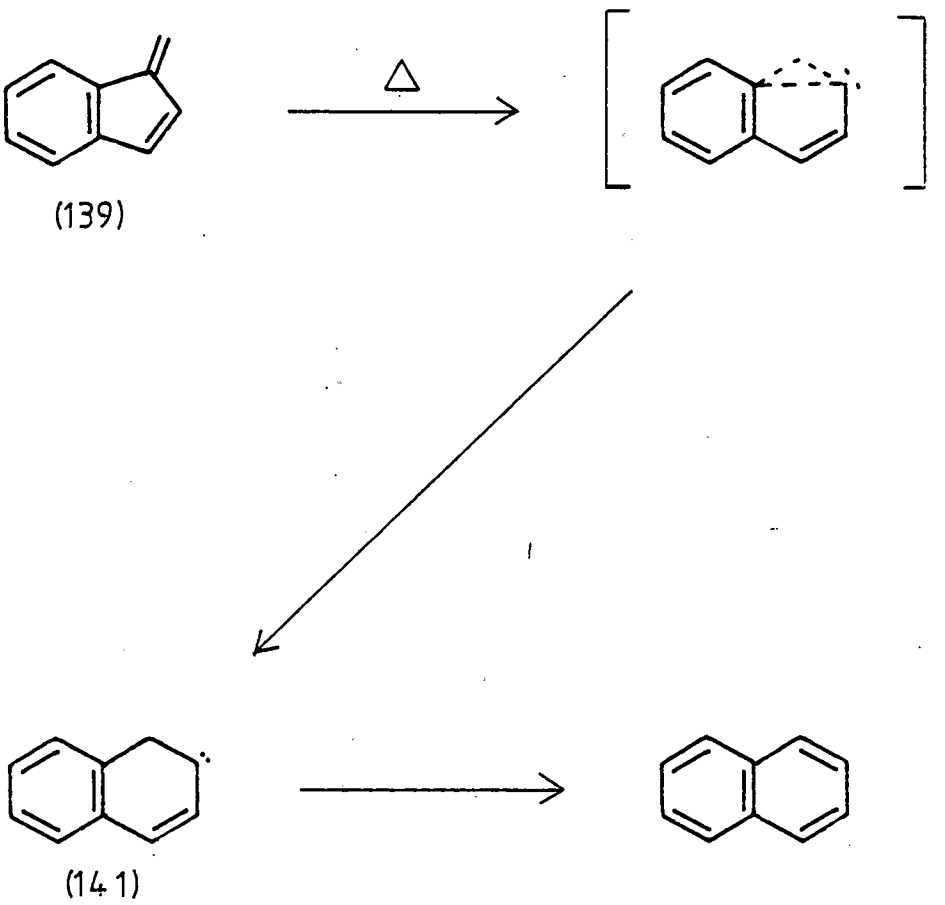
(138)



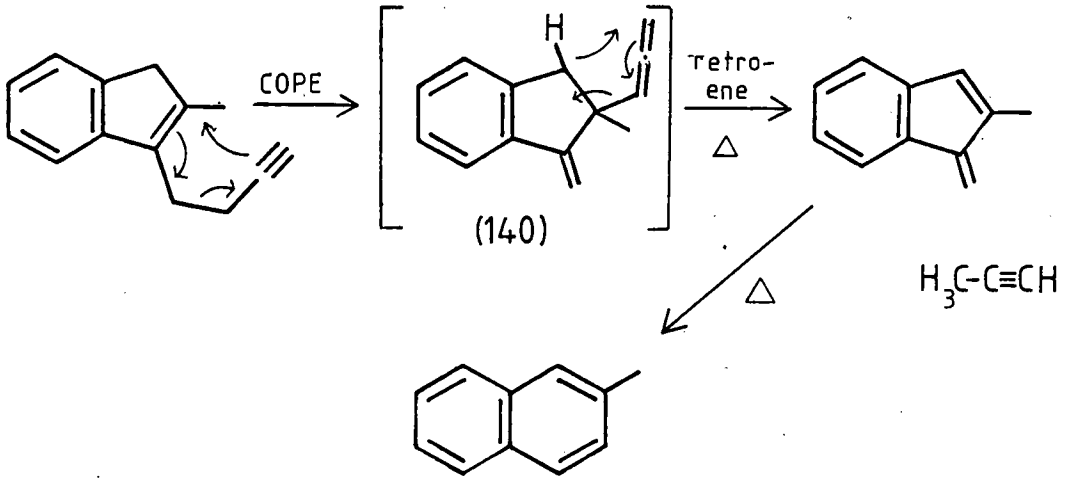
(139)

The 4-methylbenzofulvene spectrum shows the following similarities to that of benzofulvene. H-6' for both molecules appears as a broad singlet (5.72 and 5.67δ respectively) and H-6 as a fine doublet coupled to H-3 (at 6.06 and 6.00). H-3 for (138) appears at 6.55δ as opposed to 6.88δ for (139) presumably due to shielding from the methyl group. For both fulvenes $\underline{H}_p$ is deshielded slightly with respect to the other benzene ring protons appearing at 7.55 for benzofulvene and 7.49 for 4-methylbenzofulvene.

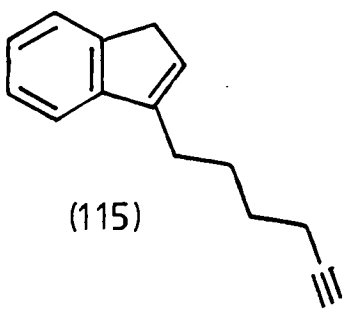
FIGURE 26

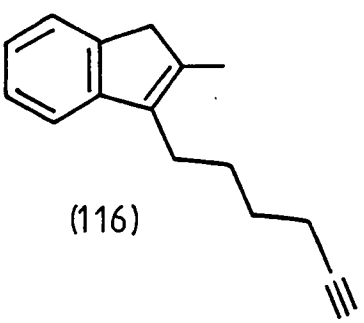


The reaction is considered to proceed by a Cope rearrangement to the species (140) which by a further 'retro-ene' cleavage gives the benzofulvene. The rearrangement of



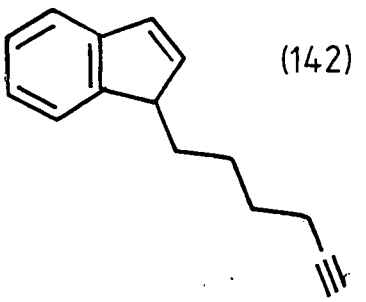
benzofulvene to naphthalene is well known [76], in this case the 1,2-benzo-4-methylfulvene rearranged to 2-methyl-naphthalene simply on standing in solution at room temperature for a long period. The rearrangement in the gas phase may proceed as shown in fig. 26 via the cyclic carbene (141).


(115)


(116)

At 600° 3-(hex-5'-ynyl)indene (115) gave a mixture consisting largely of unchanged starting material with a small quantity of another compound, possibly 1-(hex-5'-ynyl)-indene (142), as shown by the presence of two doublets J=6Hz, J=1Hz, in the indene double bond region at 6.5δ and 6.85δ. This could be formed by rearrangement of the indene double

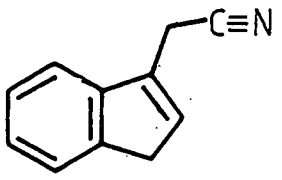
bond by [1,5] H shifts.



(142)

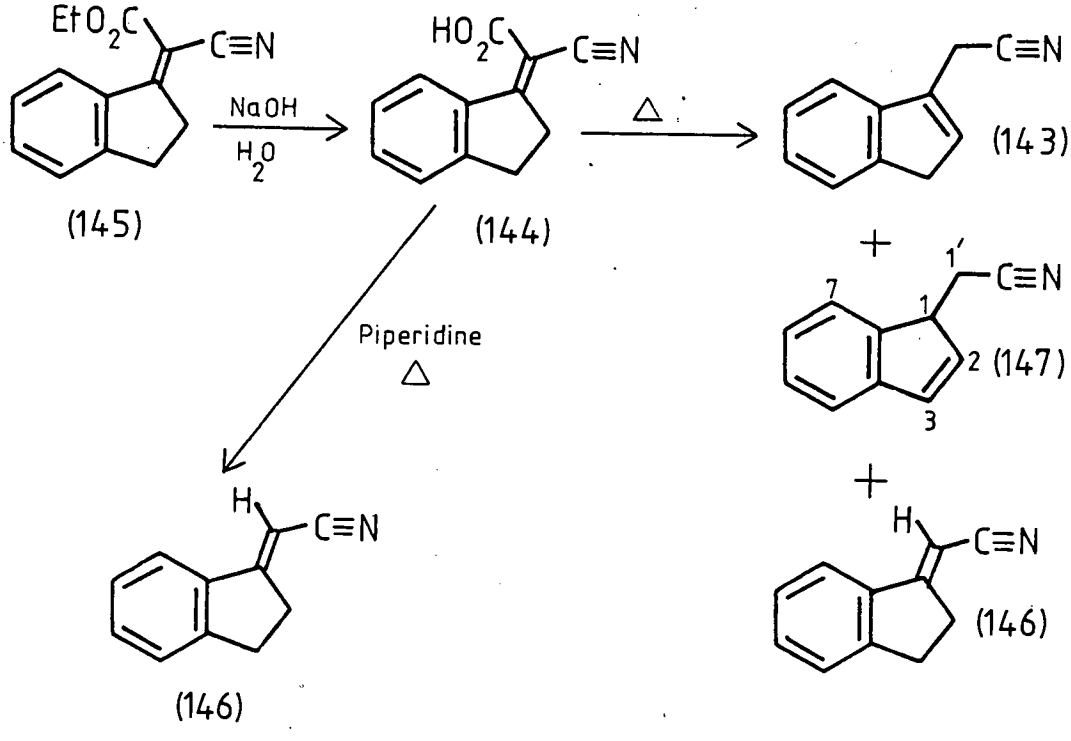
At 650° and 700° this compound gave complex mixtures which could not be separated or identified. Similarly 3-(hex-5'-ynyl)-2-methylindene (116) gave complex mixtures at 600° and 700° which could not be identified.

3.3 Preparation and Pyrolysis of 3-Cyanomethylindene (143)



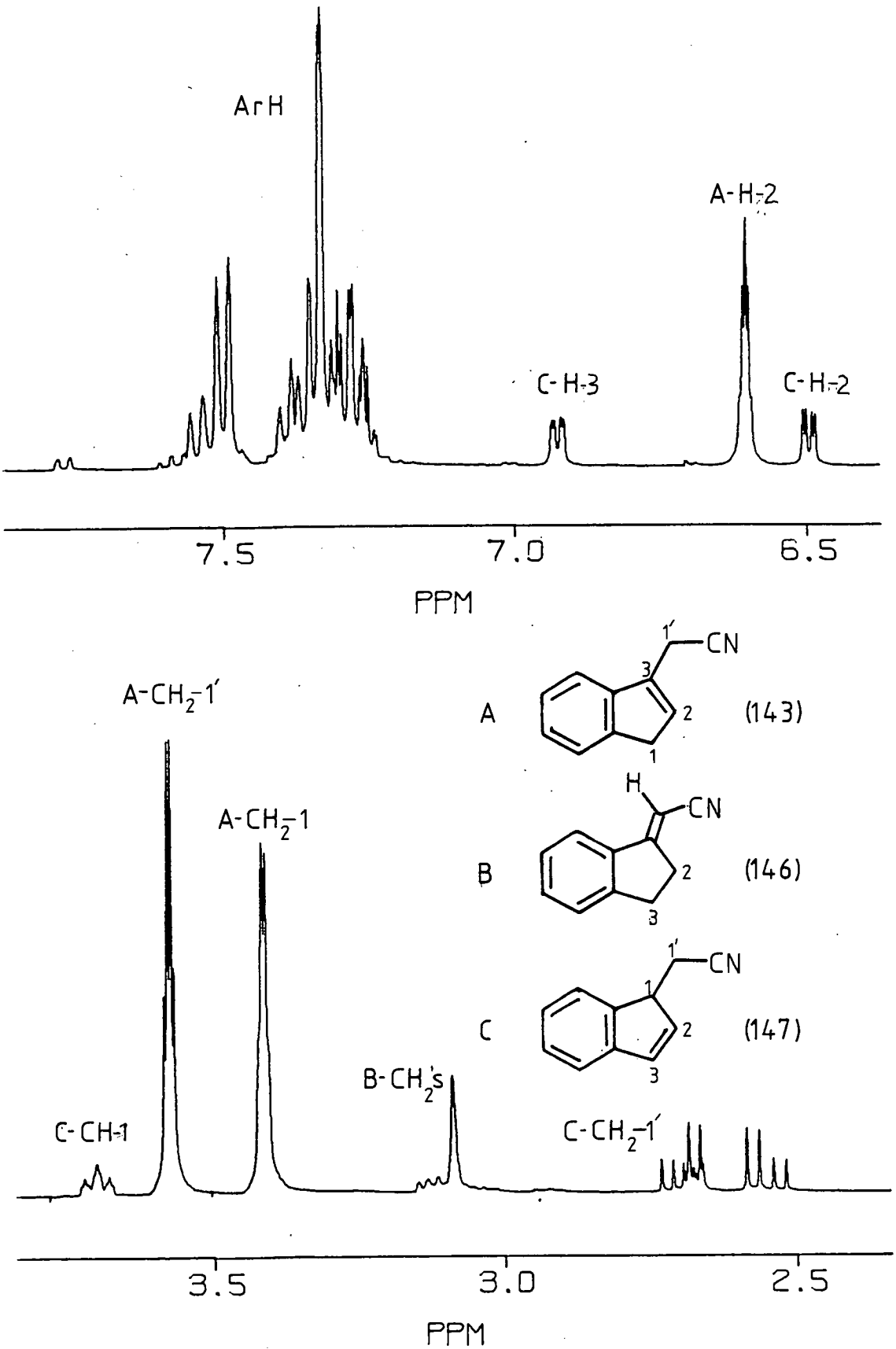
(143)

3-Cyanomethylindene (143) is isoelectronic with 3-propargylindene (24) and so it was decided to prepare this compound and investigate its vapour phase pyrolysis. The desired nitrile has been prepared by decarboxylation of indan-1-ylidenecyanoacetic acid (144) which is itself prepared from the ester condensation product (145) of indan-1-one and ethylcyanoacetate.[56] The products of the decarboxylation of



the acid (144) however depends on the method used. Heating the solid acid with a few drops of piperidine[57] gave only E-1-cyanomethyleneindane (146) in low yield, but vapour phase

FIGURE 27

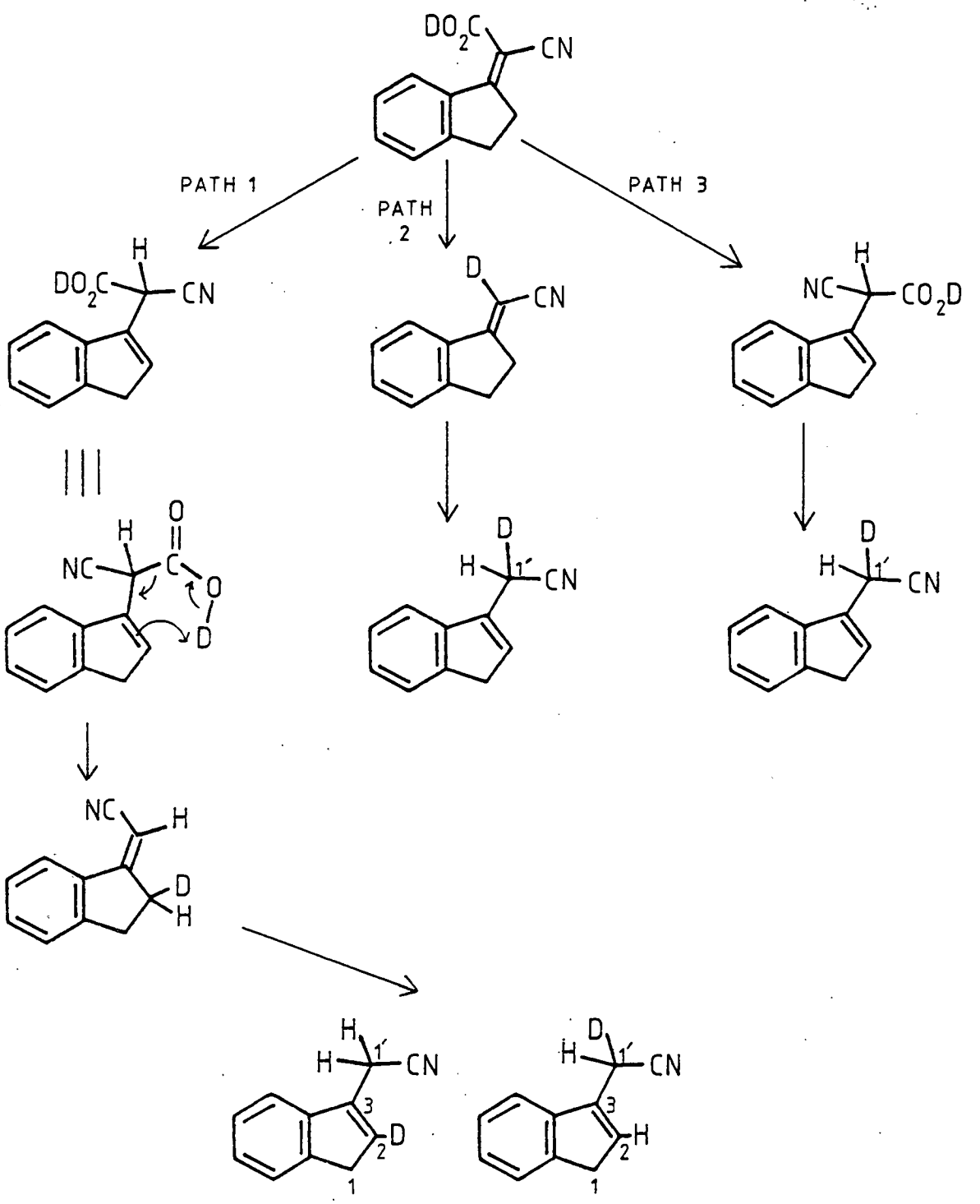

ArH
A-H-2
C-H-3
C-H-2
7.5
7.0
6.5
PPM
A-CH2-1'
A-CH2-1
C-CH-1
B-CH2's
C-CH2-1'
3.5
3.0
2.5
PPM
A
(143)
B
(146)
C
(147)
CN
H

pyrolysis of the acid at 600° gave a mixture of products 3-cyanomethylindene (143), 1-cyanomethylindene (147) and E-1-cyanomethyleneindane (146) in the ratio 10:3:1 as shown by the ^1H n.m.r. spectrum of the mixture (fig. 27). The resonance due to the E-1-cyanomethyleneindane (146) were identified by comparison with the sample prepared by warming the acid (144) with piperidine and those of the 3-cyanomethylindene from the published data [56]. The 1-cyanomethylindene (147) shows distinctive resonances in the mixture. The two (non equivalent C-1' protons appear as doublets of doublets at 2.52 and 2.66δ coupling to each other (J=16.8Hz) and to the C-1 proton (J= 7.8Hz) which appears as a broad triplet at 3.67δ. The olefinic indene protons appear at 6.46δ and 6.89δ as doublets of doublets coupling to each other (J=5.6Hz) and to the C-1 proton (J=1.8Hz C*H*-2, J=1.2Hz C*H*-3).

The C-7 proton appears at 7.51δ clear of the other aromatic proton resonances presumably deshielded by the proximity of the nitrile function. The major product of the decarboxylation, 3-cyanomethylindene (143) was obtained from the mixture by crystallisation of -78° from a mixture of ether and light petroleum (1:5).

In an attempt to elucidate the mechanism of the vapour phase decarboxylation O-deuterioindan-1-ylidenecyanoacetic acid was prepared by treating the acid (144) with D_2O. Pyrolysis of this compound was carried out as before and the major product isolated by crystallisation at -78°. The proton n.m.r. spectrum for this compound shows a reduction of 50% in the integral of one of the CH_2 resonances i.e. indicating that in the 3-cyanomethylindene formed the deuterium is on C-1' or

FIGURE 28


DO2C
CN
PATH 1
PATH 2
PATH 3
H
DO2C
CN
D
CN
H
NC
CO2D
O
H
NC
C
O
D
D
H
1'
CN
D
H
1'
CN
NC
H
D
H
H
1'
CN
3
D
2
1
D
H
1'
CN
3
H
2
1

C-1. The proton broad band decoupled carbon-13 n.m.r. spectrum shows clearly that the deuterium is located on C-1' which appears as a triplet (J=19.5Hz) at 16.6δ. The mechanism of this rearrangement is not clear. Decarboxylation of α,β unsaturated carboxylic acids has been thought to proceed in some cases [58] by a mechanism such as Path 1 in Figure 28 when the double bond shifts to the β,γ position to allow decarboxylation to proceed via the cyclic transition state shown. This type of mechanism does not appear to operate in the present case since the deuterium label appears exclusively on C-1', not on C-2. Path 2 which involves decarboxylation followed by double bond shift or Path 3 (double bond shift then decarboxylation by a different mechanism from Path 1) are both feasible from the deuterium labelling observed in the product.

Pyrolysis of 3-cyanomethylindene at 600° gave largely unreacted starting material together with 1-cyanomethylindene (147) in the ratio 8:2.4. The nitrile is therefore resistant to the type of reaction undergone by 3-propargylindene and the nitrile merely undergoes 1,5 H shifts to give 1-cyanomethylindene.

CHAPTER 4

Base Catalysed Rearrangement of Acetylenes and Allenes

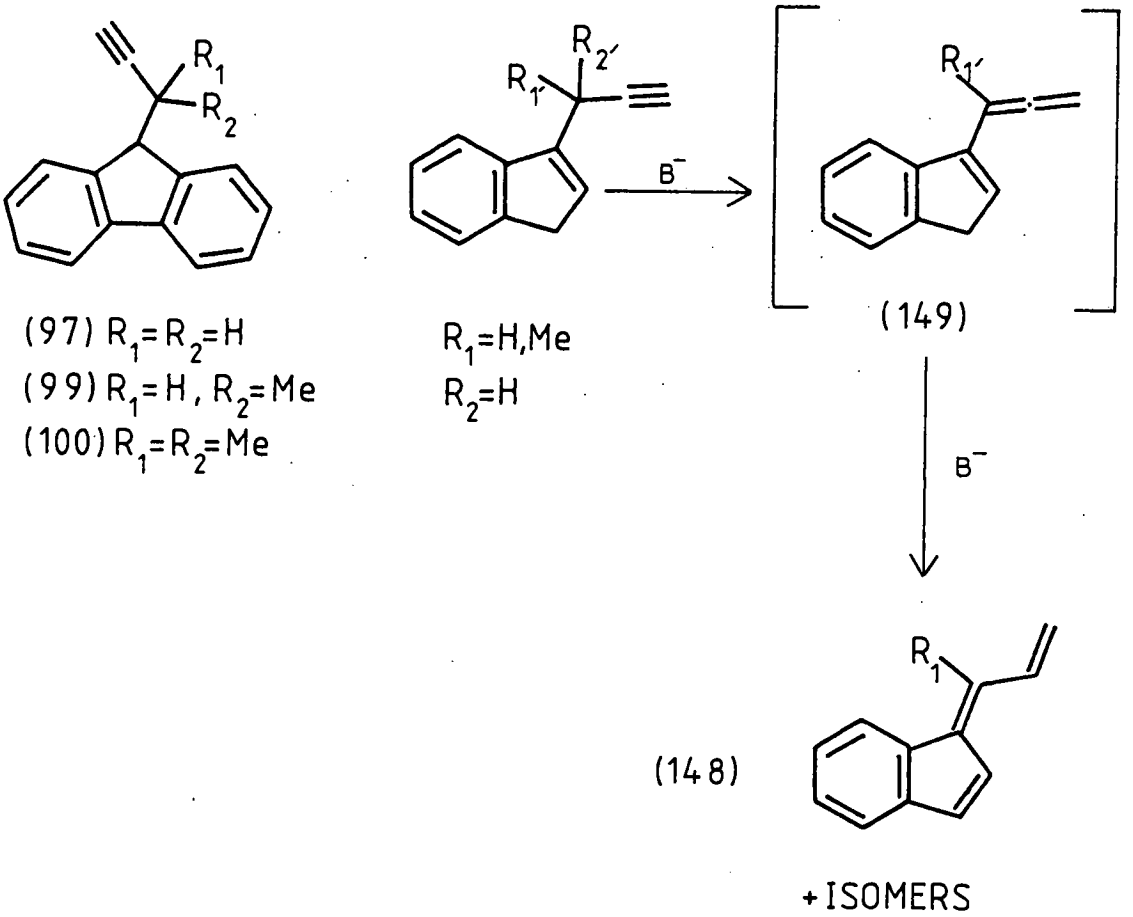
The ready base induced rearrangement of many acetylenic and allenic compounds suggested the examination of base induced intramolecular rearrangement of the acetylenic and allenic compounds described earlier in this thesis.

The rearrangement of the acetylenic compounds was attempted either by heating with sodium ethoxide in ethanol (Method I) or by using benzyltrimethylammonium hydroxide (Triton B), as the base, in pyridine solution (Method II). Method II is known to be an efficient way of generating the fluorenyl anion[59]. Allenic compounds were readily rearranged by stirring in chloroform solution with basic alumina or on attempting to purify them using alumina chromatography (Method III).

4.1 Acetylenic and Allenic Derivatives of Fluorene

9-Propargylfluorene (97), 9-(1'-methylprop-2'-ynyl)-fluorene (99) and 9-(1',1'-dimethylprop-2'-ynyl)fluorene (100) did not react by either method I or method II. In each case prolonged heating gave only insoluble polymer. This behaviour contrasts with that of the corresponding indene derivatives which readily give benzofulvenes (148) by method I.[22]

The reaction for indenes is believed to proceed via the reactive allene (149). It is later shown (p. 55) that allenyl fluorenes are rearranged to fulvenes under basic conditions and therefore the failure of the propargyl fluorenes to react

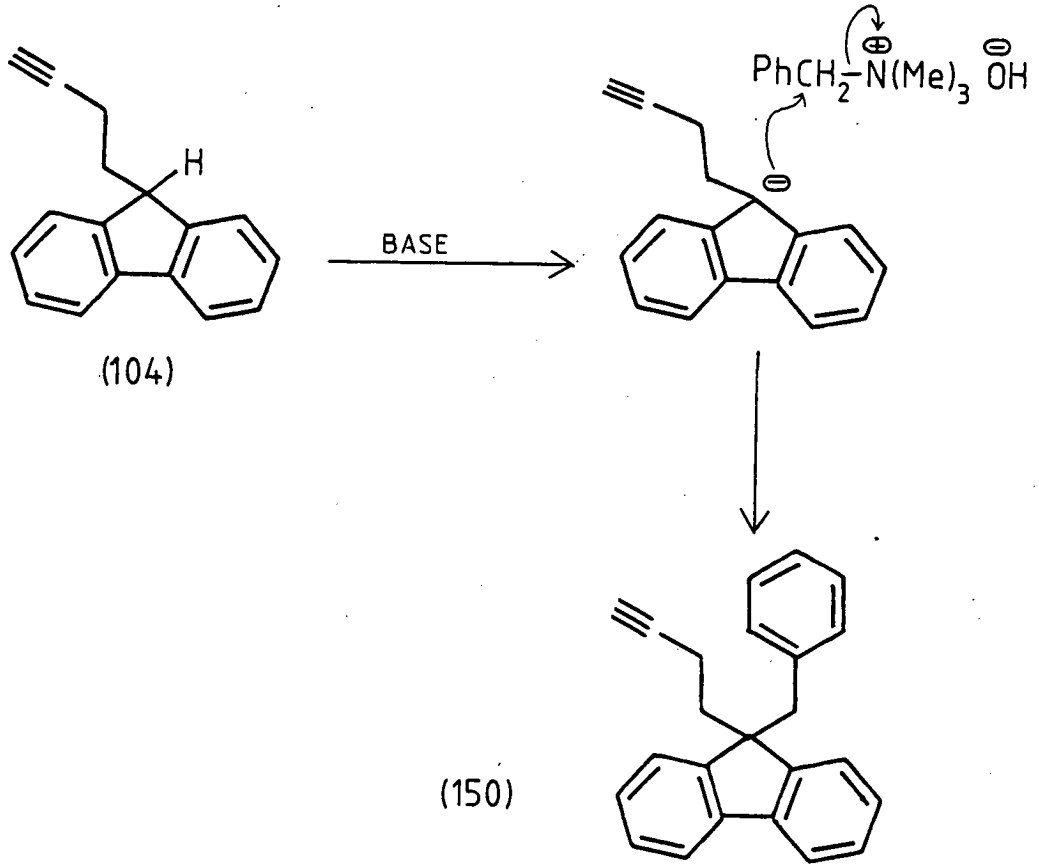


(97) $R_1=R_2=H$
(99) $R_1=H$, $R_2=Me$
(100) $R_1=R_2=Me$

$R_1=H,Me$
$R_2=H$

is due to difficulty in forming the allene from the acetylene, possibly because fluorene is less electron withdrawing than indene leaving the propargylic proton(s) insufficiently acidic for reaction.

The attempted rearrangement of 9-(but-3'-ynyl)fluorene (104) at room temperature by method II gave no reaction. Heating under reflux gave 9-benzyl-9-(but-3'-ynyl)fluorene (150) by reaction of the anion of (104) with the Triton B, showing that the fluorene 9 proton is more acidic than the propargylic protons in this system.

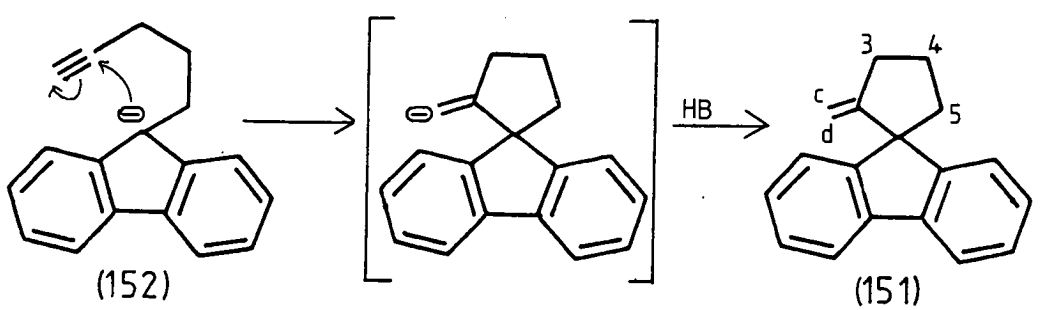


(104)

(150)

The compound (150) was identified by ^{1}H and ^{13}C n.m.r. and mass spectroscopy.

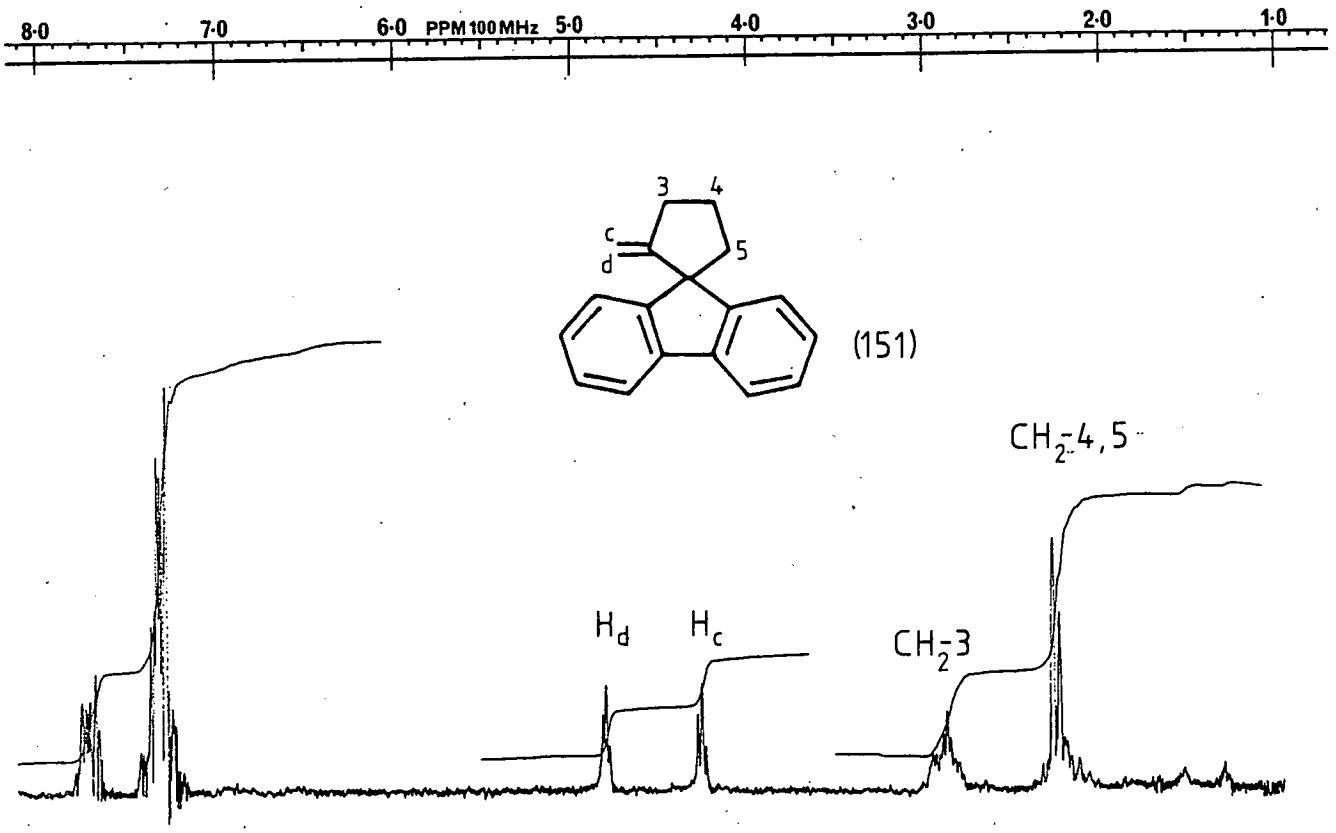
An attempt to induce rearrangement of 9-(pent-4'-ynyl)-fluorene (105) by method I also failed. Method II gave irreproducible results. In one instance, where an old sample of Triton B was used, the spiro compound, spiro [2-methylene-cyclopentane-1,9'-fluorene] (151) was formed, by presumably cyclisation of the anion (152).



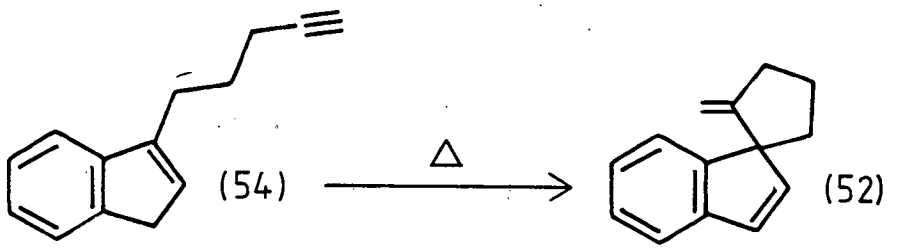
(152)

(151)

FIGURE 29

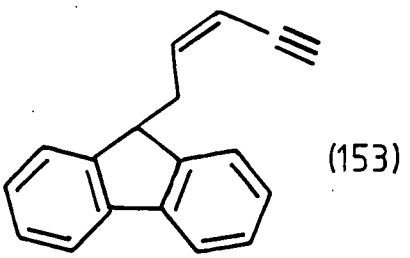


The spiro compound (151) was identified from its ^{1}H n.m.r. spectrum which is directly comparable with that of spiro[2-methylenecyclopentane-1,1'-indene] (52) prepared by Truslove



from pyrolysis of 3-(pent-4'-ynyl) indene (54)[22]. The spectrum of (151) (fig.29) shows H_c and H_d as triplets at 4.42 and 4.78δ coupled to the C-3 protons which appear as a multiplet at 2.86δ, with the C-4 and C-5 protons as a multiplet at 2.20δ. In all other attempts to carry out reaction by method II no products were formed except after prolonged heating when reaction with the Triton B as in the previous reaction occurred.

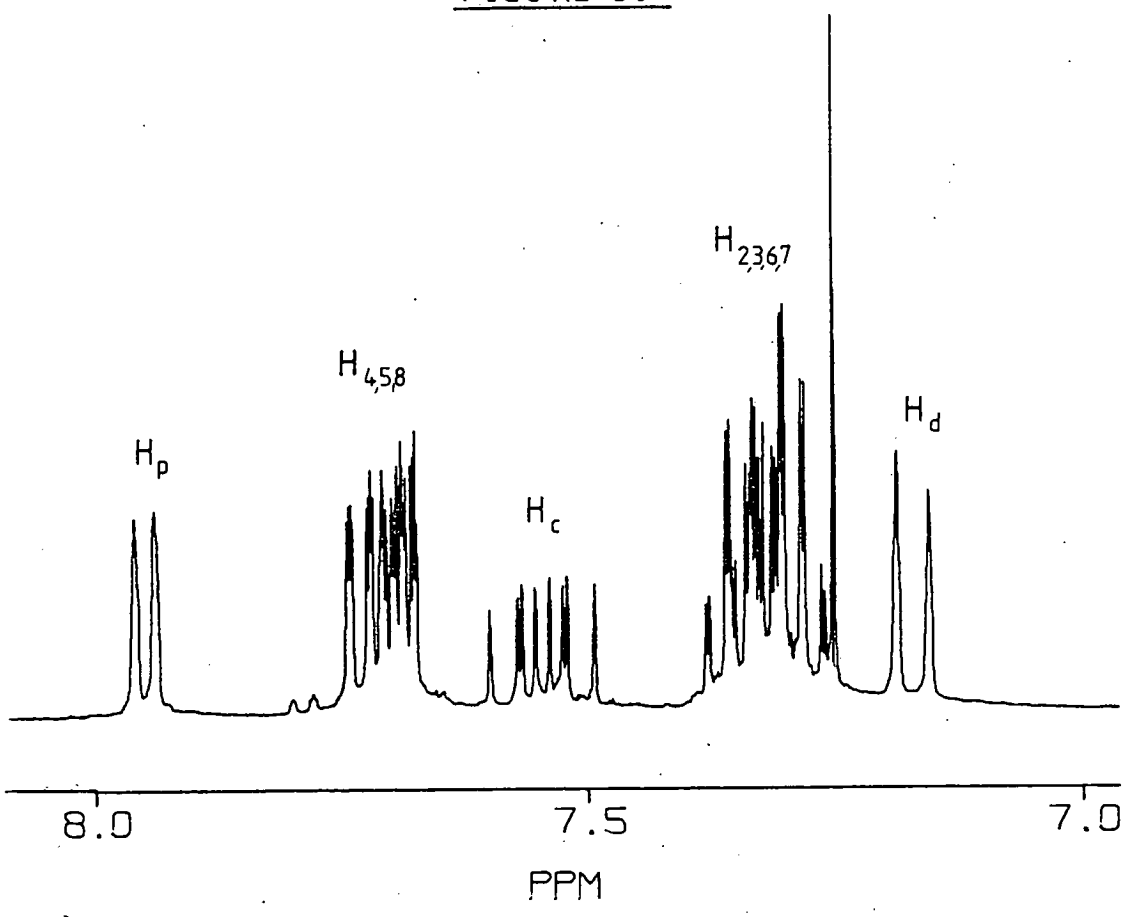
The rearrangement of E-9-(pent-2'-en-4'-ynyl)fluorene (107) by method I produced a large quantity of black tarry material from which only one product was isolated, a trace of Z-9-(pent-2'-en-4'-ynyl)fluorene (153) which may have been present in the starting material. The olefinic protons show a 13.2Hz coupling

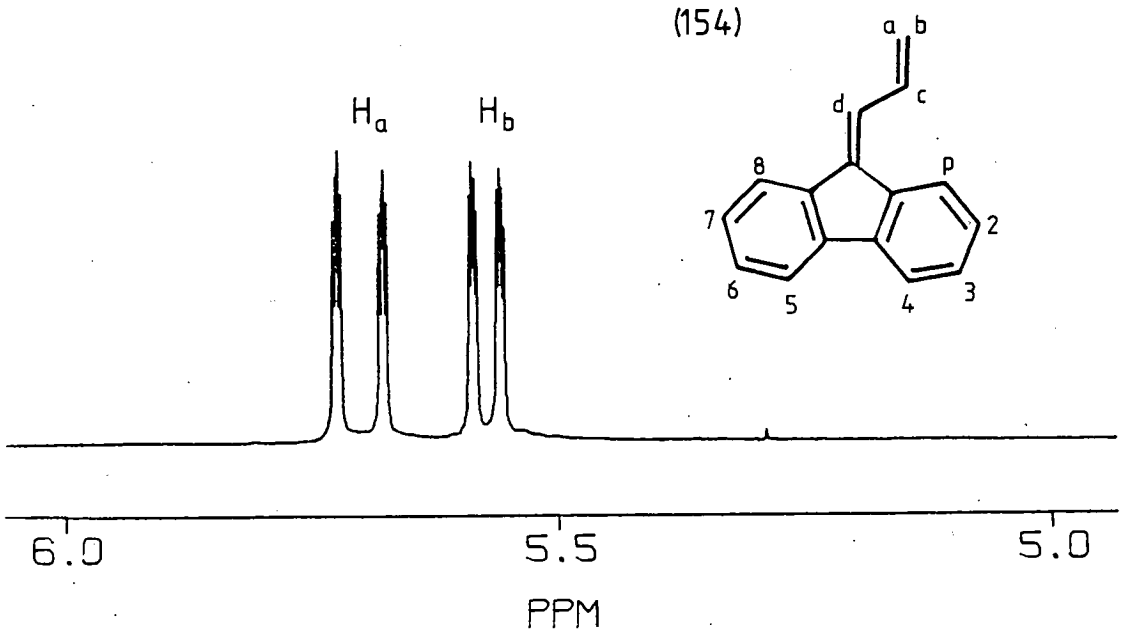


in the 360 MHz ^{1}H n.m.r. spectrum in comparison with a 17 Hz coupling exhibited by the E isomer.

9-Allenylfluorene (129) readily gave a near quantitative yield of dibenzo-6-vinylfulvene (154) by method III. The 360 MHz ^{1}H n.m.r. spectrum (fig. 30) shows the terminal proton

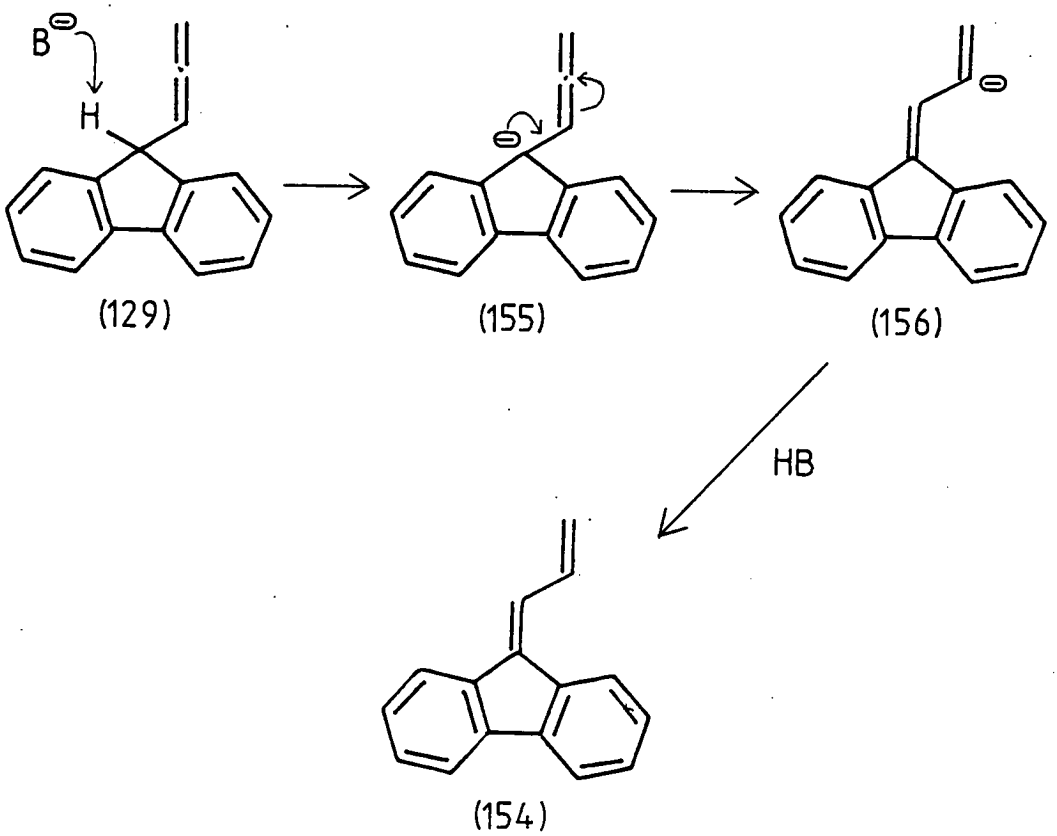
FIGURE 30





(154)

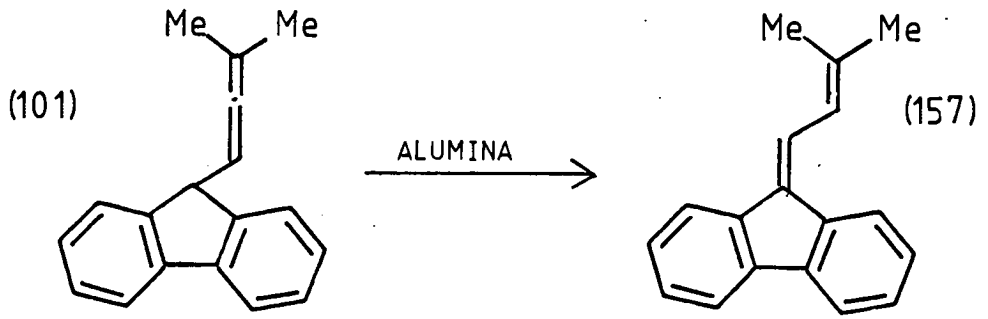
H_a at 5.7δ coupled to H_b (J=1.0Hz), H_c (J=16.1Hz, trans) and H_d (J=1.7Hz). H_b is coupled to H_a (1.0Hz), H_d (1.5Hz) and to H_c (9.8Hz, cis). H_c and H_d are deshielded in comparison with most olefinic protons due to the highly conjugated nature of the molecule, and so appear as multiplets (with the expected couplings) at 7.54 and 7.17δ respectively. H_c is more deshielded than H_d due to proximity to a benzene ring of the fluorene system. H_p of the fluorene is similarly deshielde by the proximity of the vinyl system. The reaction probably proceeds by the mechanism shown below in which the base removes the acidic fluorene C-9 proton to give the anion (155) which rearranges via the more conjugated anion (156) to give the product (154) on reprotonation.



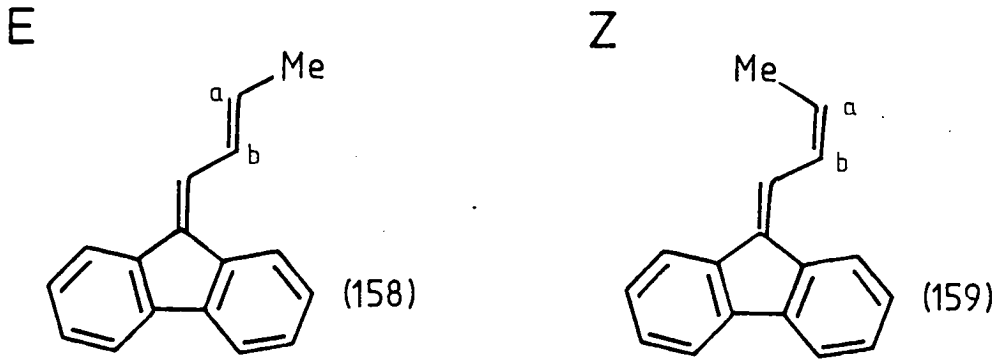
(129) (155) (156)

(154)

Reaction of 9-(3'-methylbuta-1',2'-dienyl)fluorene (101) proceeded similarly to give debenzo-6-(2'-methylprop-1'-enyl)fulvene (157).

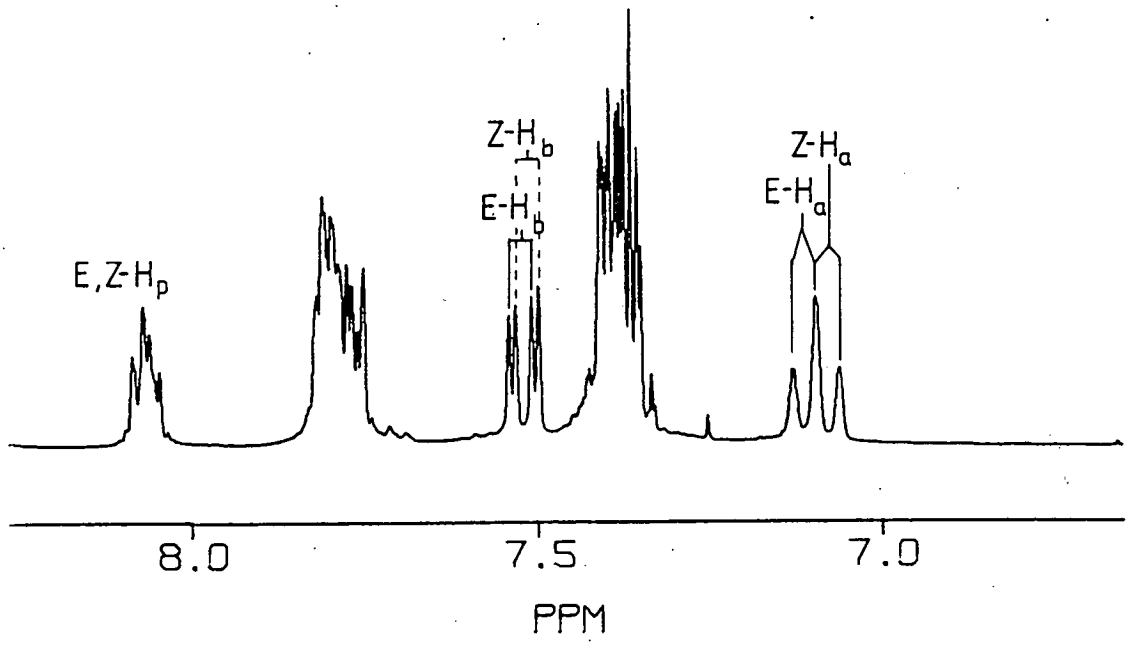


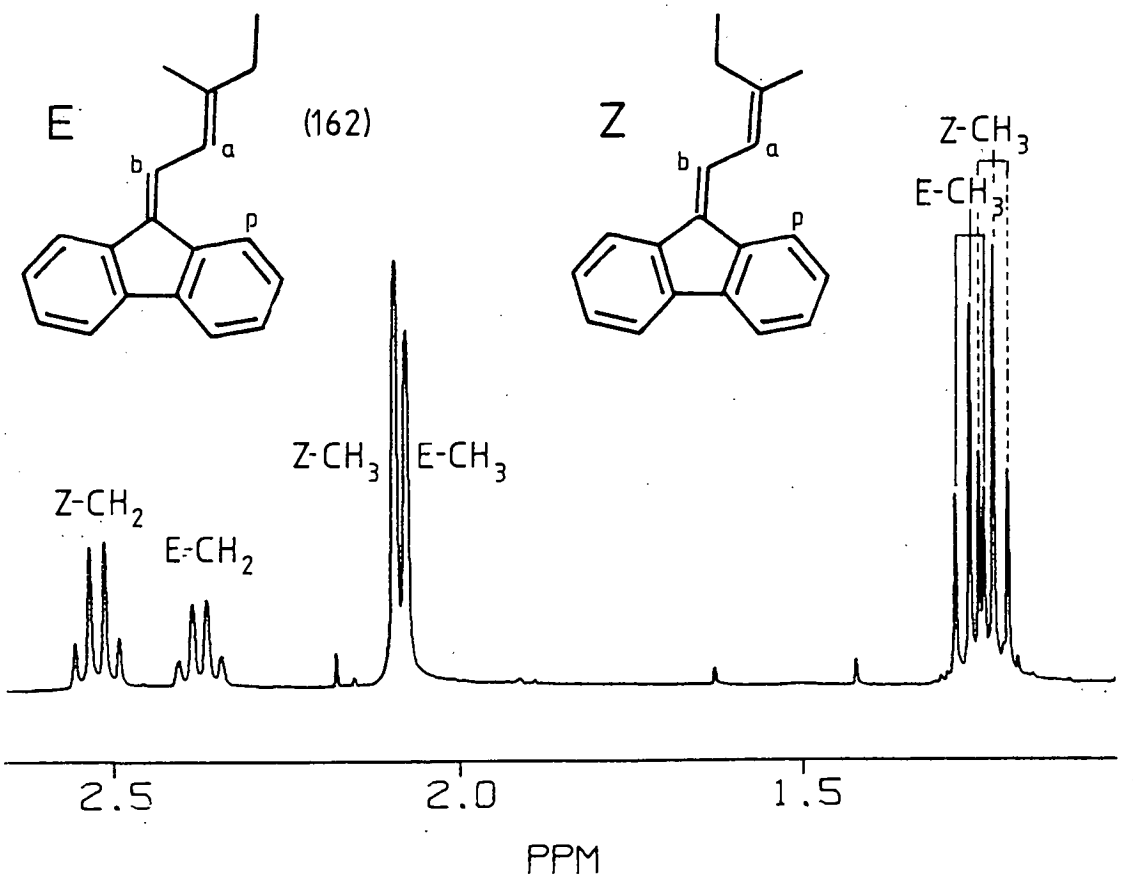
The possibility of obtaining E and Z isomeric products arises where the substituents differ on carbon-3' of the allene fragment. With 9-(buta-1',2'-dienyl)fluorene (130) method III gave E and Z-dibenzo-6-(prop-1'-enyl)fulvene (158 and 159) in th ratio 1:5 as shown by the 360 MHz spectrum of the mixture (which could not be separated). The assignment of a Z configuration

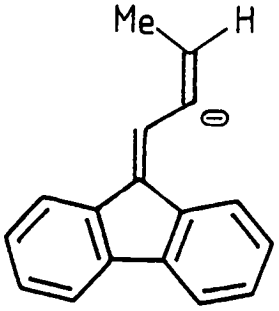


to the major isomer is based on the size of coupling observed for H_a to H_b. The major isomer shows a 10.8 Hz (cis) coupling, the minor isomer a 13.8 Hz (trans) coupling. The preferential formation of the less thermodynamically stable Z isomer under these mild conditions suggests that the intermediate ion prefers to adopt conformation (160) rather than (161) because of steric hindrance between the methyl group and the fluorene system and that reprotonation takes place on the side remote from the methy group.

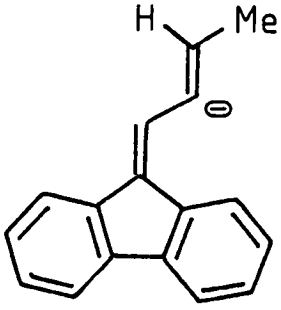
FIGURE 31


E,Z-Hp
Z-Hb
E-Hb
Z-Ha
E-Ha
8.0
7.5
7.0
PPM


E
(162)
Z
b
a
p
Z-CH3
E-CH3
Z-CH2
E-CH2
2.5
2.0
1.5
PPM



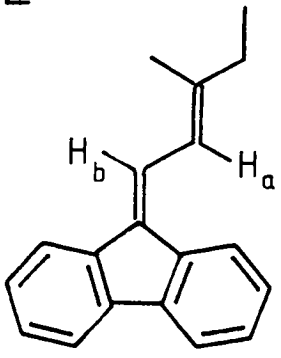
(160)



(161)

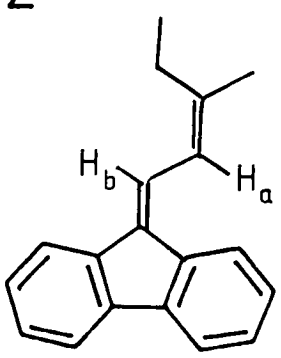
Attempts to purify the 9-(3'-methylpenta-1',2'-dienyl) fluorene (103), prepared in the synthesis of 9-(1'-methyl-1'-ethylprop-2'-ynyl)fluorene (p. 28), by alumina chromatography converted the allene into a 1:1 mixture of E and Z-dibenzo-6-(2'-methylbut-1'-enyl)fulvene (162 and 163) obtained as a bright yellow solid with a wide melting point range (92-97°). The two compounds in this mixture, which could not be separated, were identified from the 360 MHz ^{1}H n.m.r. spectrum (fig. 31). Decoupling experiments were used to assign resonances to each isomer and to assign E and Z configurations. Irradiation of

E



(162)

Z



(163)

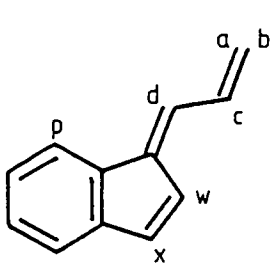
the methylene quartet at 2.37δ collapses the methyl triplet at 1.25δ to a singlet and sharpens the methyl resonance at 2.07δ to a clear doublet revealing coupling to H_a (J = 1.3Hz).

Similarly irradiation of the methylene quartet at 2.52δ collapse the methyl triplet at 1.22δ to a singlet and sharpens the methyl group resonance at 2.09δ to a clear doublet (J = 0.7Hz). On the basis of this smaller long range coupling to H_a the latter set of resonances are assigned to the Z isomer, and the former to the E isomer. The apparent 'triplet' at 7.09δ is in fact the doublets for H_a of both the E and Z isomers partially coinciding. The doublet at 7.11δ is assigned to H_a for the E isomer since it shows the 1.3Hz coupling. Irradiating at this frequency collapses the doublet at 7.52δ to a singlet and so this resonance is assigned to H_b for the E isomer. Similarly the doublets at 7.07δ and 7.51δ are assigned as the resonances for H_a and H_b of the Z isomer.

4.2 Rearrangements of Acetylenic Derivatives of Indene

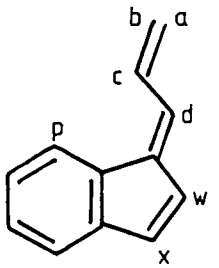
Reaction of 3-propargylindene (24) by method I (heating under reflux, 15 minutes) had previously been carried out by Truslove[22] but identification of the product(s) was uncertain since high resolution (360 MHz) proton n.m.r. spectroscopy was not available. The product of the reaction is a mixture of E and Z-1,2-benzo-6-vinylfulvene (30 and 31) in the ratio 9:1.

E



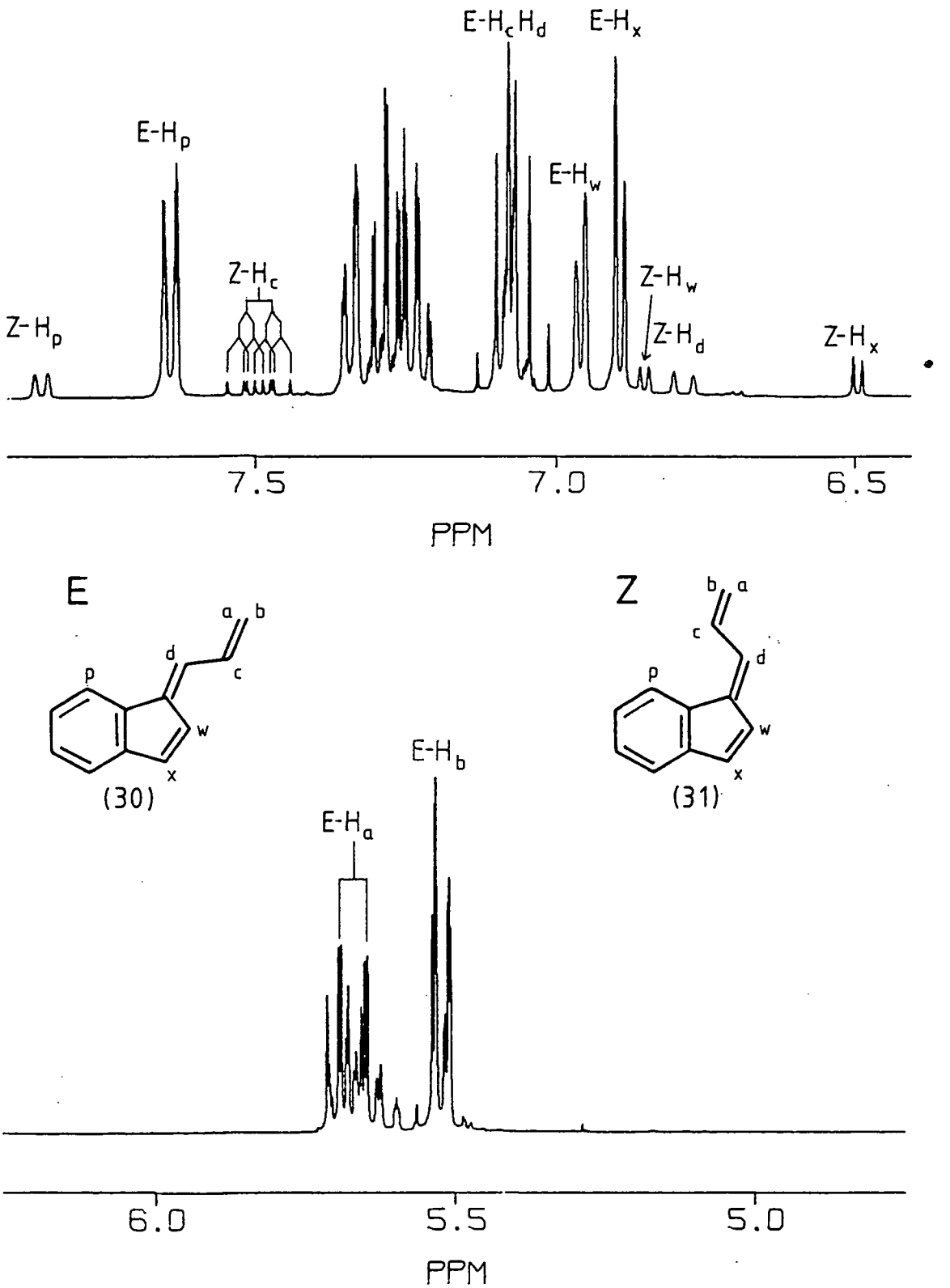
(30)

Z



(31)

FIGURE 32


E-H$_c$H$_d$
E-H$_x$
E-H$_p$
E-H$_w$
Z-H$_c$
Z-H$_w$
Z-H$_p$
Z-H$_d$
Z-H$_x$
7.5
7.0
6.5
PPM
E
a
b
d
c
p
w
x
(30)
Z
b
a
c
d
p
w
x
(31)
E-H$_b$
E-H$_a$
6.0
5.5
5.0
PPM

Only the major component of the mixture had previously been identified, it is assigned the E configuration on the basis of the proton chemical shifts of H_c and H_p for each isomer. For the Z isomer those two protons resonate at higher frequency due to the proximity of the benzene ring and the vinyl group, each deshields the nearest proton on the other group. H_c (E isomer) resonates at 7.07δ but for the Z isomer H_c is at 7.49δ. The effect on H_p is smaller but still clear. In the E isomer H_p resonates at 7.65δ and H_p (Z isomer) is at 7.85δ (fig. 32). These products are the most thermodynamically most stable rearrangement products of propargyl indene (p. 12) formed via the allene (124). A possible mechanism is shown below. Removal of a propargylic proton by base and then reprotonation gives 3-allenylindene. Removal of an indenyl proton by base gives the anion (164) which rearranges and reprotonates to give the vinylbenzofulvene product (30). This reaction is analogous to that observed for the 9-allenyl-fluorenes as described earlier (p. 55). Assignment of the

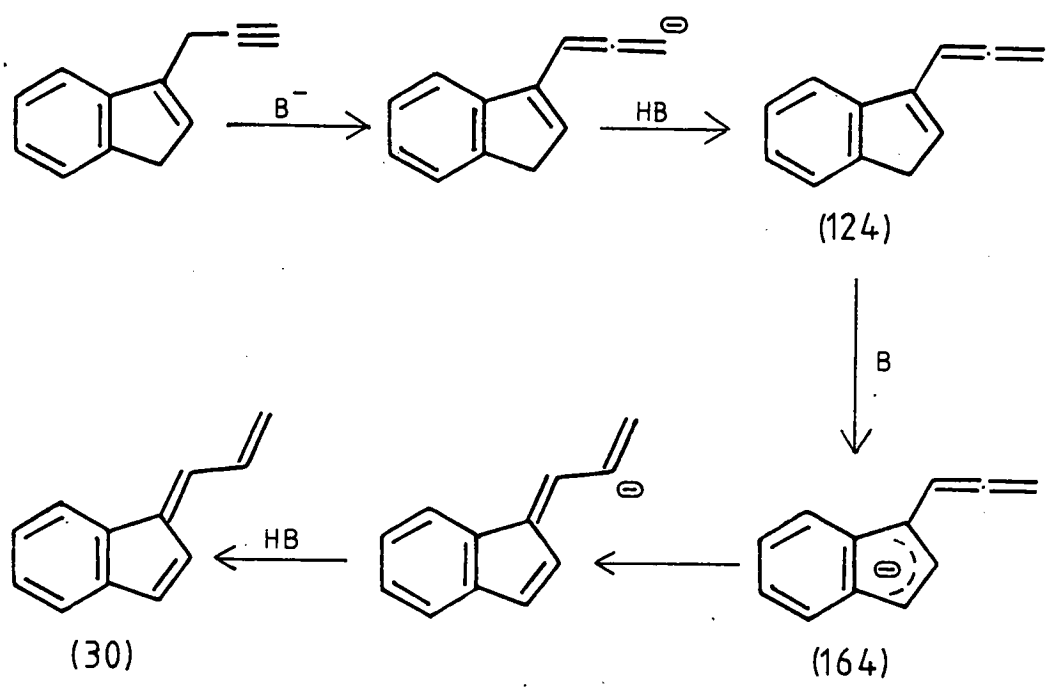


FIGURE 33

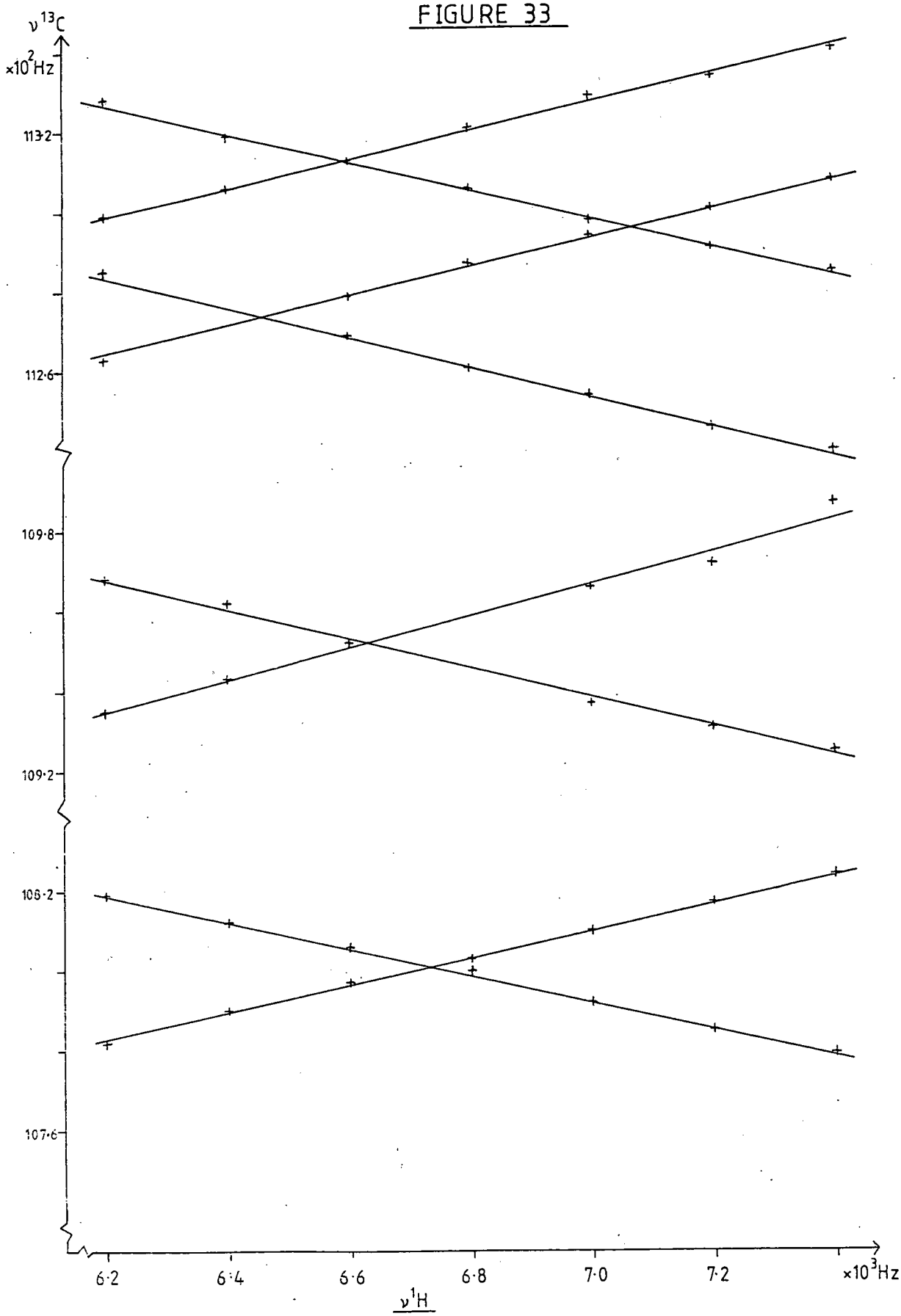

ν 13C
×10² Hz
113·2
112·6
109·8
109·2
108·2
107·6
6·2
6·4
6·6
6·8
7·0
7·2
×10³ Hz
ν 1H

FIGURE 34

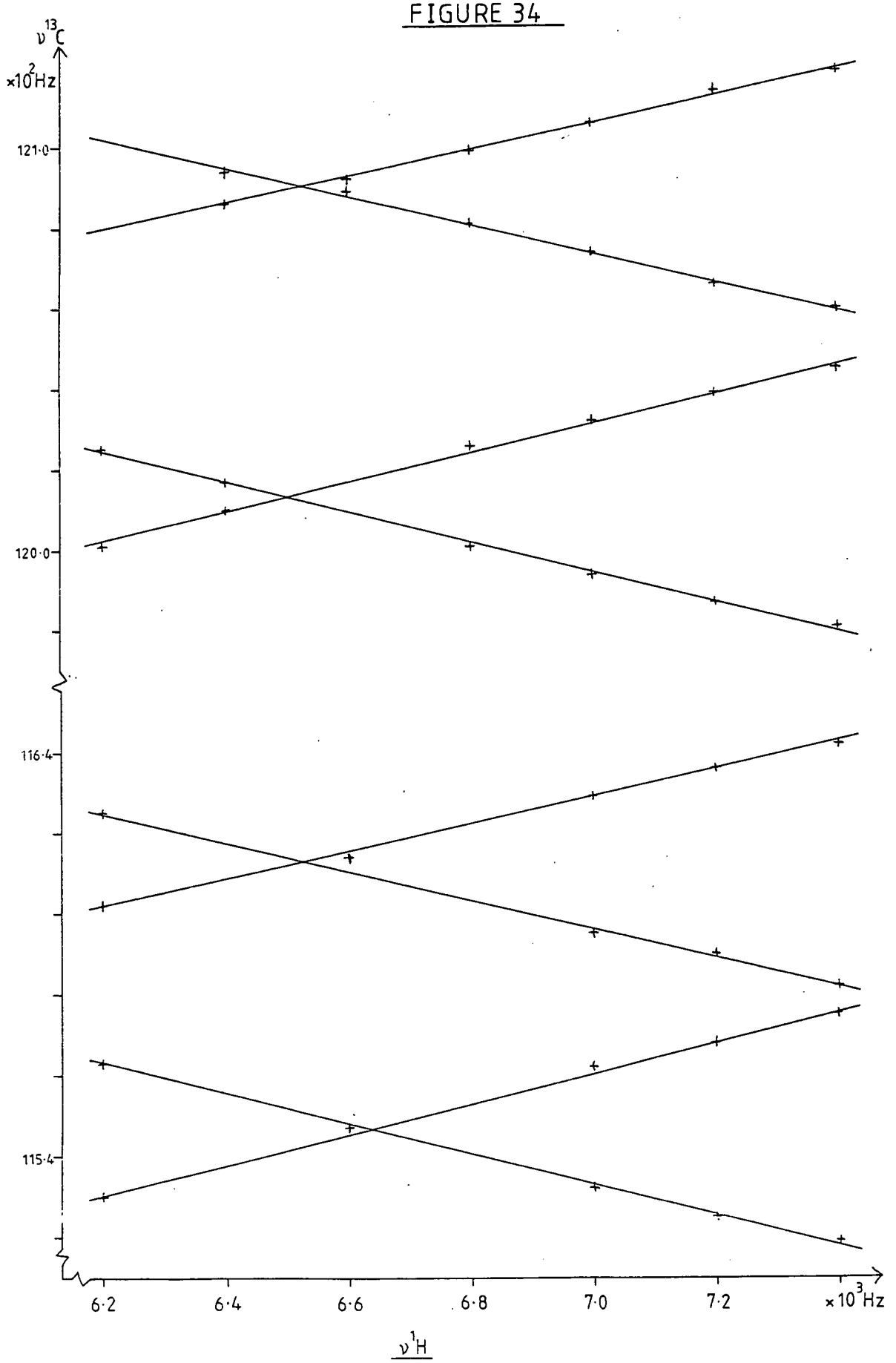

$\nu^{13}C$
$\times 10^2$ Hz
121·0
120·0
116·4
115·4
6·2
6·4
6·6
6·8
7·0
7·2
$\times 10^3$ Hz
ν^1H

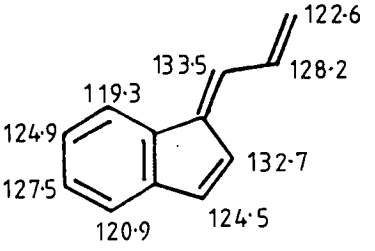
TABLE 5

^{13}C Frequencies from Single Frequency Decoupling Experiments

^{13}C (δ) (^{1}H bb decoupled) \ ^{1}H decoupling frequency*	6200	6400	6600	6800	7000	7200	7400
119.3	10782 10819	10790 10812	10797 10806	10800 10803	10792 10810	10785 10817	10824 10779
120.9	10935 10968	10943 10962	10952	†	10937 10966	10931 10972	10925 10987
122.6 (CH_2)	-	-	-	-	-	-	-
124.5	11263 11285	†	11269 11279	11261 11287	11253 11294	11246 11301	11240 11308
124.9	11299 11329	11306 11319	11313	11306 11321	11298 11329	11291 11334	11285 11341
127.5	11530 11563	†	11547	†	11532 11562	11525 11568	11519 11575
128.2	11602 11625	†	11614	†	11595 11629	11590 11636	11582 11642
132.7	12061 12025	12010 12017	†	12001 12026	11994 12032	11987 12039	11981 12045
133.5	†	12086 12094	12089 12092	12081 12099	12074 12106	12066 12114	12060 12119

* Frequency offset from 3987Hz (0δ) † More than two resonances present

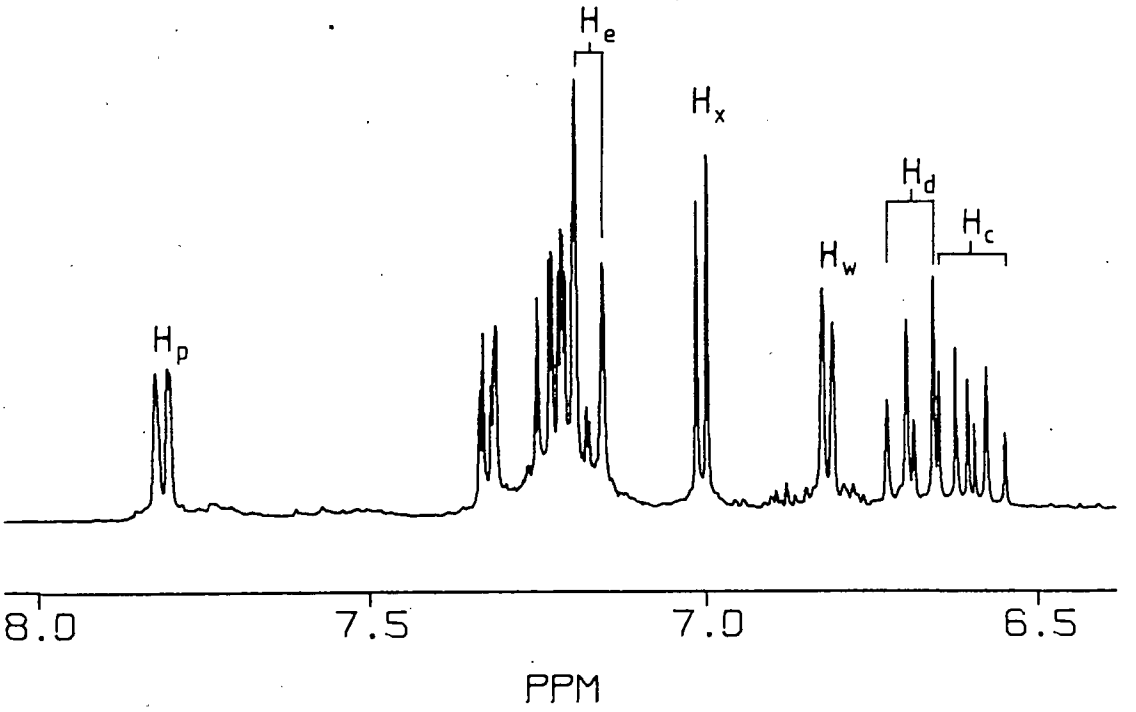
^{13}C Assignments

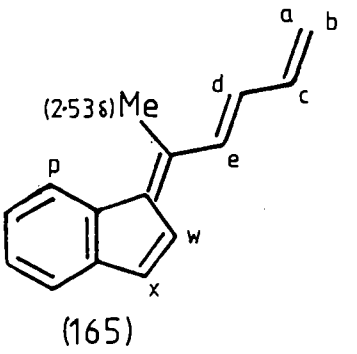


^{13}C resonances of the major (E) isomer was accomplished by the method of Feeney and Bridsal[73]. A series of single frequency off resonance proton decoupled spectra with different decoupling frequencies was obtained. For carbon atoms with one proton attached a doublet is obtained in the ^{13}C spectrum. Plotting the frequencies of the peaks in the doublet against proton decoupling frequency produces a pair of straight lines which intersect at the frequencies of the proton and the correspondingly bonded carbon. The proton and ^{13}C resonances of the molecule can thus be correlated. For the benzofulvene (30) the results obtained from the experiments are given in Table 5 and the graphs shown in figures 33 and 34 .

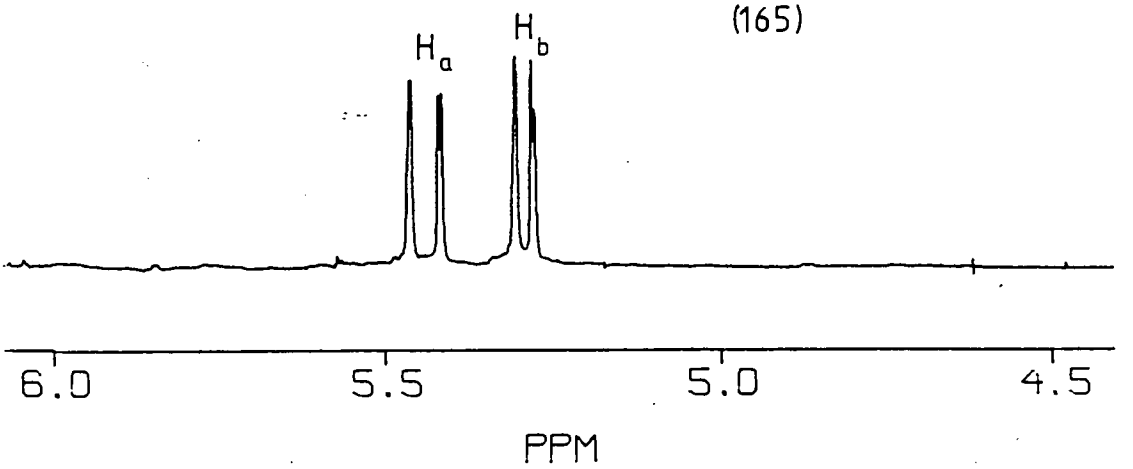
The rearrangement of E and Z-3-(1'-methylpent-2'-en-4'-ynyl)indene (120 and 119) by method I gave a mixture of compounds in the ratio 1.2:1 together with unreacted acetylene. Chromatography on alumina enabled the major component of the mixture, E-1,2-benzo-6-methyl-6-(E-buta-1',3'-dienyl)fulvene (165) to be isolated, the minor product, Z-1,2-benzo-6-methyl-6-(E-buta-1',3'-dienyl)fulvene (166) was not separated from unreacted acetylene but was clearly identified in the 360 MHz spectrum of the mixture. These two compounds have been obtained previously,[22] but their configuration could not be clearly established from the 100 MHz proton n.m.r. and infra-red spectra, it was suggested they might be the E,Z and Z,Z isomers. The 360 MHz n.m.r. spectra of these molecules however, permits certain assignment of configuration since coupling constants and chemical shifts for all the protons can be assigned. Both isomers show trans coupling

FIGURE 35

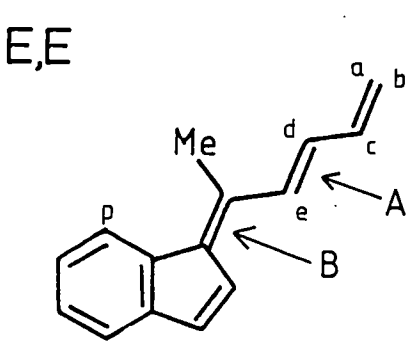




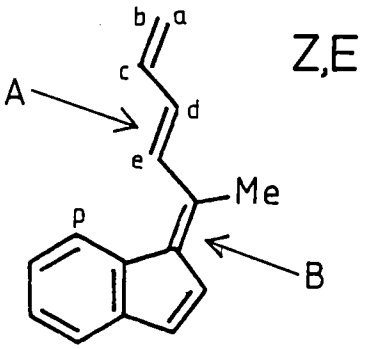
(165)



between H_e and H_d (14.6Hz) and thus both isomers have E configuration about bond A. The major isomer (fig. 35) has



(165)



(166)

the methyl protons resonating as a singlet at 2.53δ in contrast to the minor isomer where the methyl protons are not so deshielded appearing at 2.41δ. Since both isomers have the same configuration about bond A this difference can be attributed to proximity of the methyl group to the benzene ring in the case of the major isomer i.e. E configuration. The major isomer is thus E,E, the minor Z,E. H_c for the major isomer (fig. 35) is a multiplet at 6.6δ showing coupling to H_a (J = 16.7 Hz, trans), H_b (10.1 Hz, cis) and H_d (10.5Hz). H_d for this molecul resonates at 6.68δ and shows couplings to H_e at 7.17δ (J = 14.6 Hz) and to H_c (10.5Hz). These couplings for H_c and H_d are shown in the successive splitting diagram shown below.
The intensities of the peaks actually observed vary from those in the diagram due to the proximity of the two resonances.

FIGURE 36

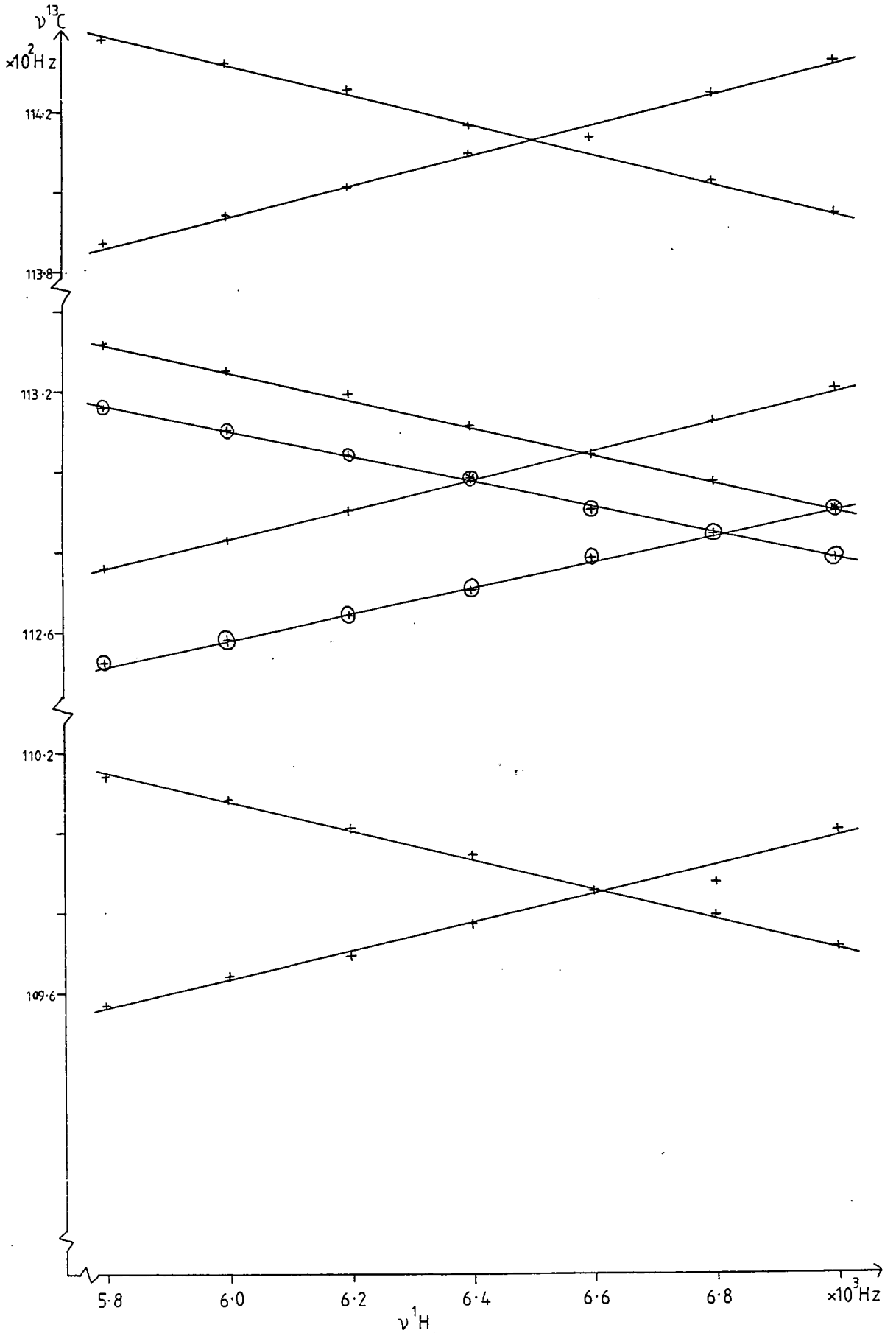

$\nu^{13}C$
$\times 10^2$ Hz
114·2
113·8
113·2
112·6
110·2
109·6
5·8
6·0
6·2
6·4
6·6
6·8
$\times 10^3$ Hz
ν^1H

FIGURE 37

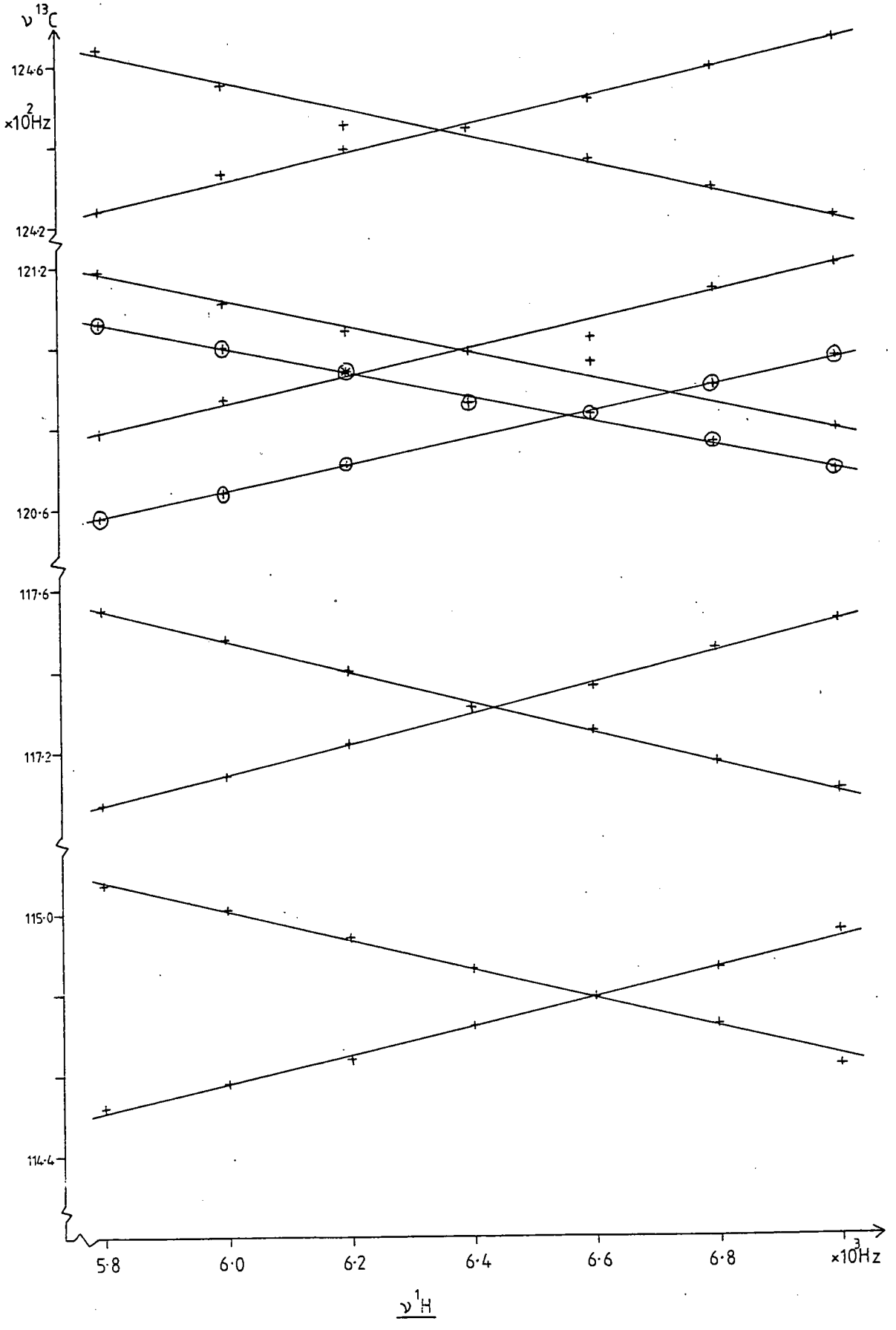

ν 13C
124·6
×10²Hz
124·2
121·2
120·6
117·6
117·2
115·0
114·4
5·8
6·0
6·2
6·4
6·6
6·8
×10³Hz
ν 1H

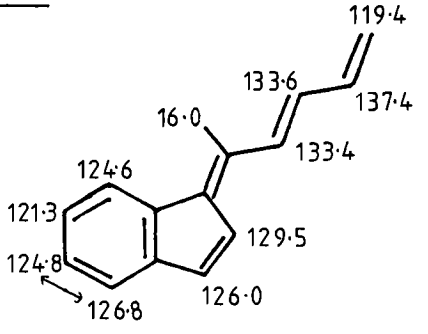
TABLE 6

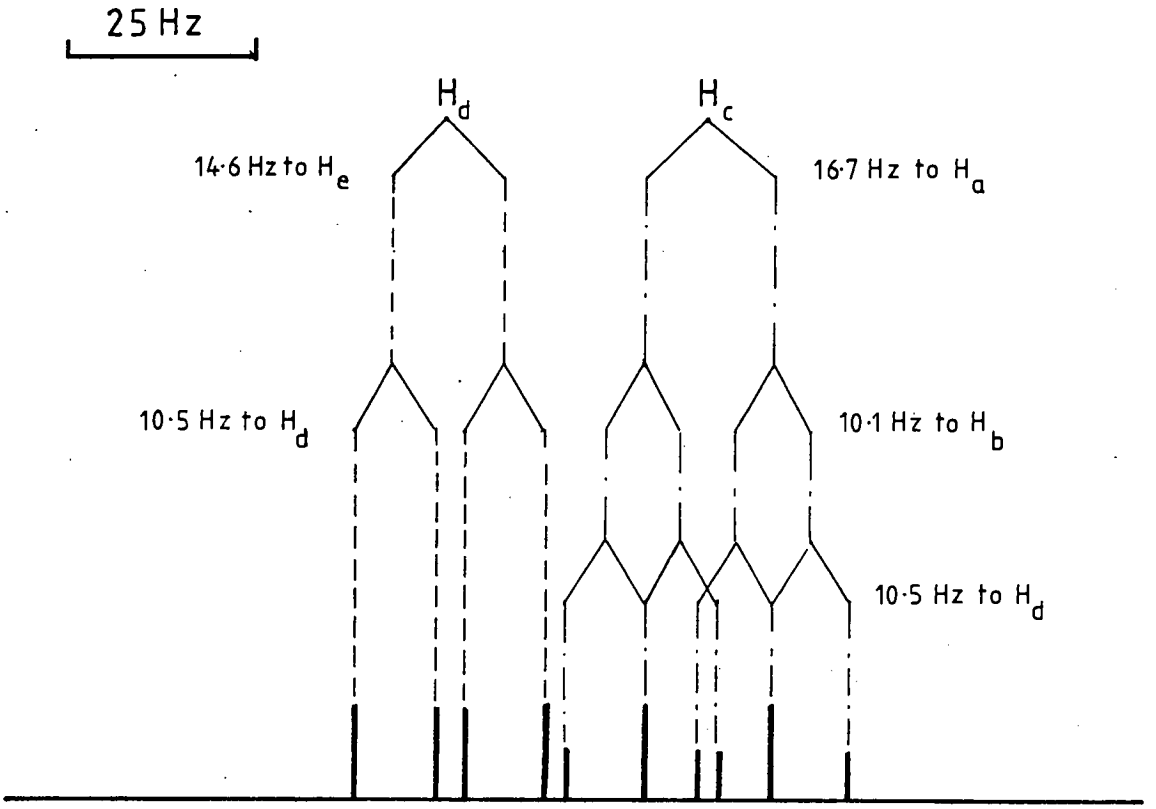
^{13}C Frequencies from Single Frequency Decoupling Experiments

^{13}C (δ) (^{1}H bb decoupled) \ ^{1}H decoupling frequency*	5800	6000	6200	6400	6600	6800	7000
121.3	10957 11014	10964 11008	10969 11001	10977 10994	10985	10979 10987	10971 11000
124.6	11252 11316	11258 11310	11264 11304	11270 11298	11278 11290	11284	11278 11290
124.8	11276 11332	11283 11325	11290 11319	11298 11311	11304	11297 11312	11290 11320
126.0	11387 11438	11394 11432	11401 11425	11409 11416	11413	11402 11424	11394 11432
126.8	11452 11507	11458 11501	11464 11494	11472 11486	11479	11472 11486	11462 11495
129.5	11707 11755	11714 11748	11722 11740	11731	11725 11736	11717 11745	11710 11752
133.4	12058 12106	12064 12100	12071 12094	12086	12083	12076 12090	12069 12097
133.6	12079 12119	12087 12111	12094 12104	12097	12096 12102	12114	12079 12120
137.4	12424 12464	12433 12455	12439 12445	12444	12436 12451	12429 12459	12422 12466

* Frequency offset from 3987Hz (0δ)

^{13}C Assignments





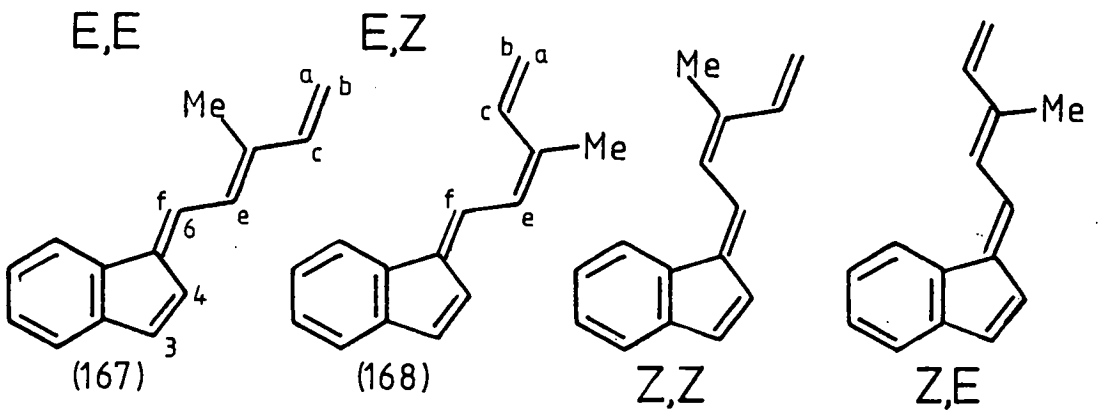
The minor (Z,E) isomer shows the same couplings for H_c,H_d and H_e but H_e and H_p for this molecule resonate at higher frequency than for the E,E isomer confirming the Z configuration about bond B, H_e and H_p are deshielded by proximity to the benzene ring and to the olefinic chain respectively.

As in the previous reaction the products obtained are the most highly conjugated (thermodynamically stable) rearrangement products.

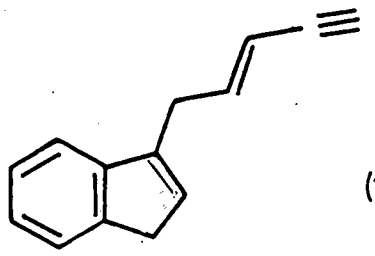
Assignment of carbon resonances was accomplished by the same method used previously (p. 60). The results are tabulated (Table 6) and the graphs shown in figures 36 and 37.

The rearrangment of Z-3-(3'-methylpent-2'-en'4'-ynyl) indene (119) by method I gave a mixture of all four possible geometric isomers of 1,2-benzo-6-(2'-methylbuta-1',3'-dienyl) fulvene. The two minor isomers were present in only trace

amounts, and the two major isomers have been identified as E-1,2-benzo-6-(E-2'-methylbuta-1',3'-dienyl)fulvene (167) and E-1,2-benzo-6-(Z-2'-methylbuta-1',3'-dienyl)fulvene (168) present in the ratio 1.6:1. Assignment of the E,E configuration to the most abundant isomer is based on the following evidence. H_e appears as a broad doublet at 6.77δ which is consistent with

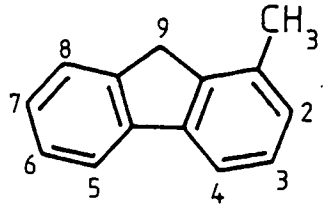


the E configuration at bond B by comparison with the spectra of the products of the preceding arrangement. If the molecule had Z configuration at this bond then H_e would be expected to resonate at ca. 7.5-7.8δ due to the deshielding effect of the benzene ring. Similarly the H_c resonance occurring at 6.58δ indicates E configuration about bond A. The Z configuration here would result in considerable deshielding caused by proximity to C-6 of the fulvene system. The second most abundant isomer has the E,Z configuration because H_e resonates at a similar frequency to (167) but H_c resonates at 7.23δ i.e. is considerably deshielded in comparison to H_c for (167). The H_c resonance is not readily apparent in the spectrum of the mixture since it is obscured by indene aromatic proton resonances. Irradiating at 7.23δ does however collapse the H_a, and H_b resonances to singlets revealing the presence of the obscured H_c resonance.

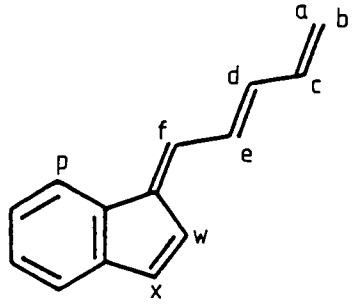


(121)

The rearrangement of E-3-(pent-2'-en-4'-ynyl) indene (121) by method I gave the expected benzofulvene type products as well as others. This compound, which can be regarded as the parent molecule of those of the two previous rearrangements gave a large quantity of polymer from which two fractions were obtained by preparative thin layer chromatography. The first fraction contained an unidentified product which retained the pentenynyl unit and another unidentified minor component. The second fraction contained three products, 1-methylfluorene (169) and E-1,2-benzo-6-(E-2'-buta-1',3'-dienyl)fulvene (170) in the ratio 1:3 and a small amount (≲ 10%) of Z-1,2-benzo-6-(E-2'-buta-1',3'-dienyl)fulvene (171).

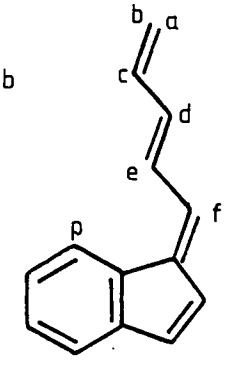


(169)



E,E

(170)



Z,E

(171)

FIGURE 38

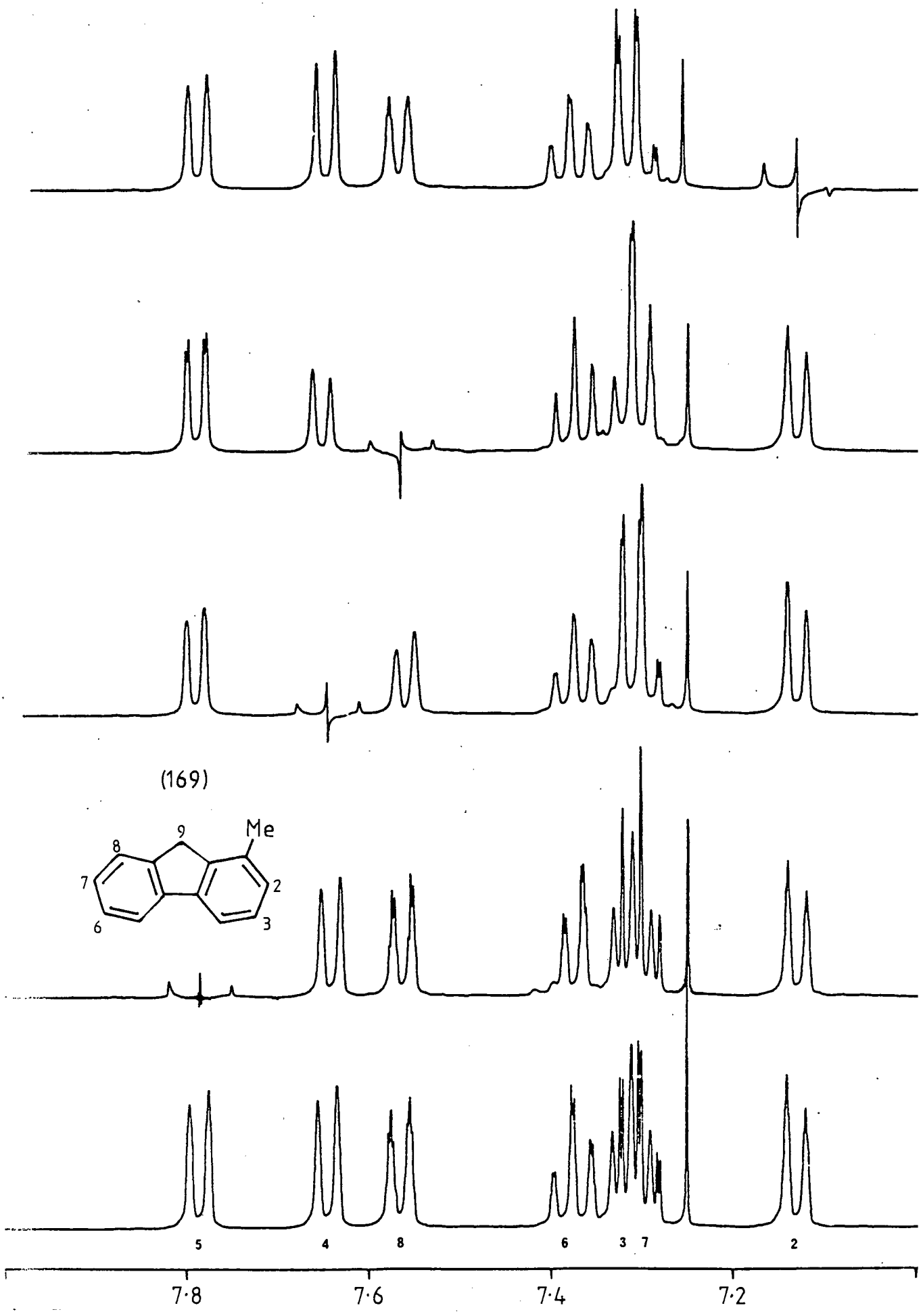
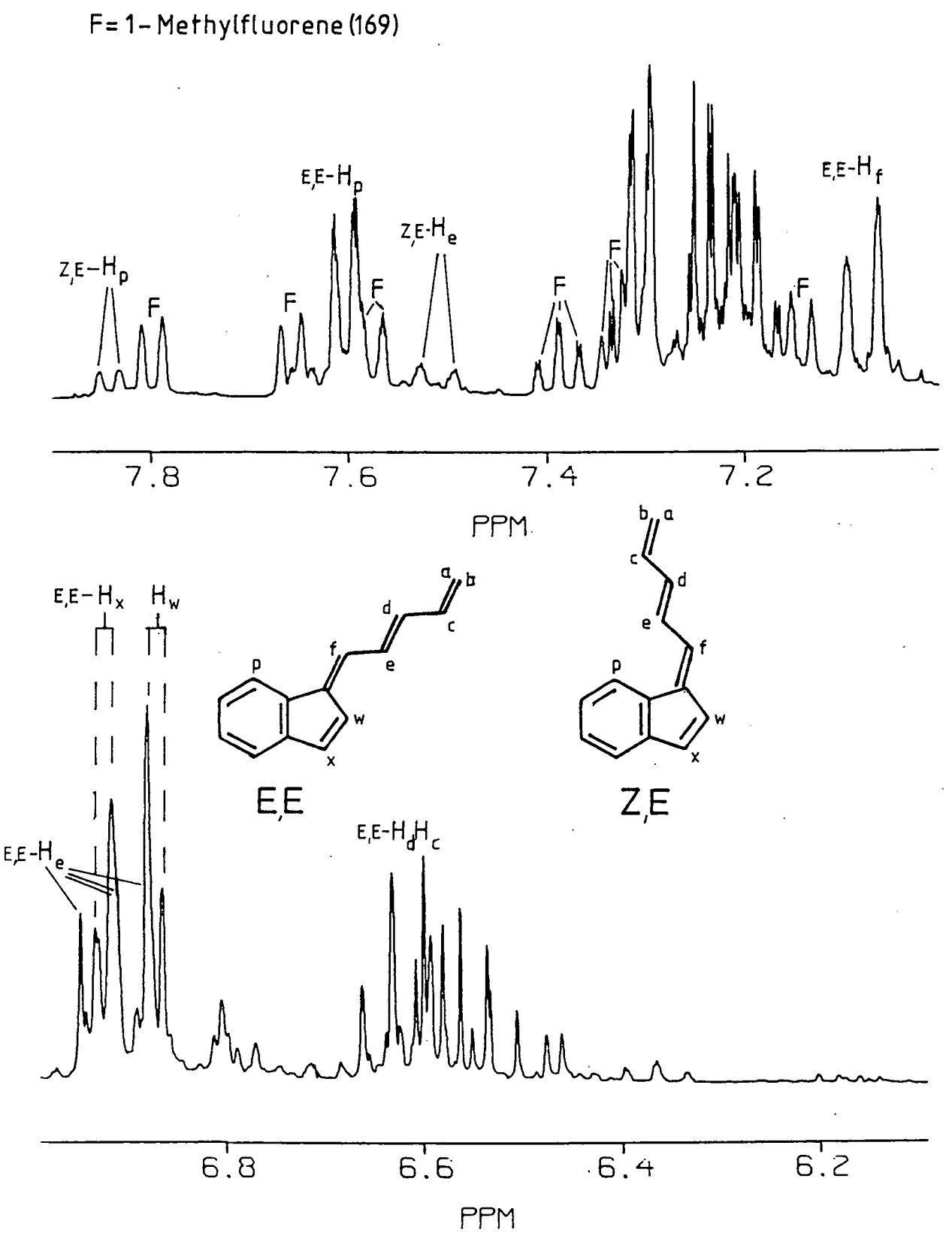


FIGURE 39


F= 1- Methylfluorene (169)
Z,E-Hp
E,E-Hp
Z,E-He
E,E-Hf
F
7.8
7.6
7.4
7.2
PPM
E,E-Hx
Hw
E,E-He
E,E-Hd,Hc
E,E
Z,E
6.8
6.6
6.4
6.2
PPM

The 1-methylfluorene proton resonances in the 360 MHz n.m.r. spectrum of the mixture were identified by comparison with those of an authentic sample whose aromatic proton resonances are shown (fig. 38) with the decoupling experiments which were carried out to assign them. Irradiating at CH-2 simplifies the CH-3 resonance to a doublet. Irradiating at CH-8 simplifies the CH-7 resonance to a doublet and removes the fine (meta) coupling of the CH-6 resonance. Similarly irradiating at the CH-5 resonance converts the CH-6 resonance to a doublet and removes the meta coupling on the CH-7 resonance. Finally irradiating at the CH-4 resonance simplifies the CH-3 resonance to a doublet.

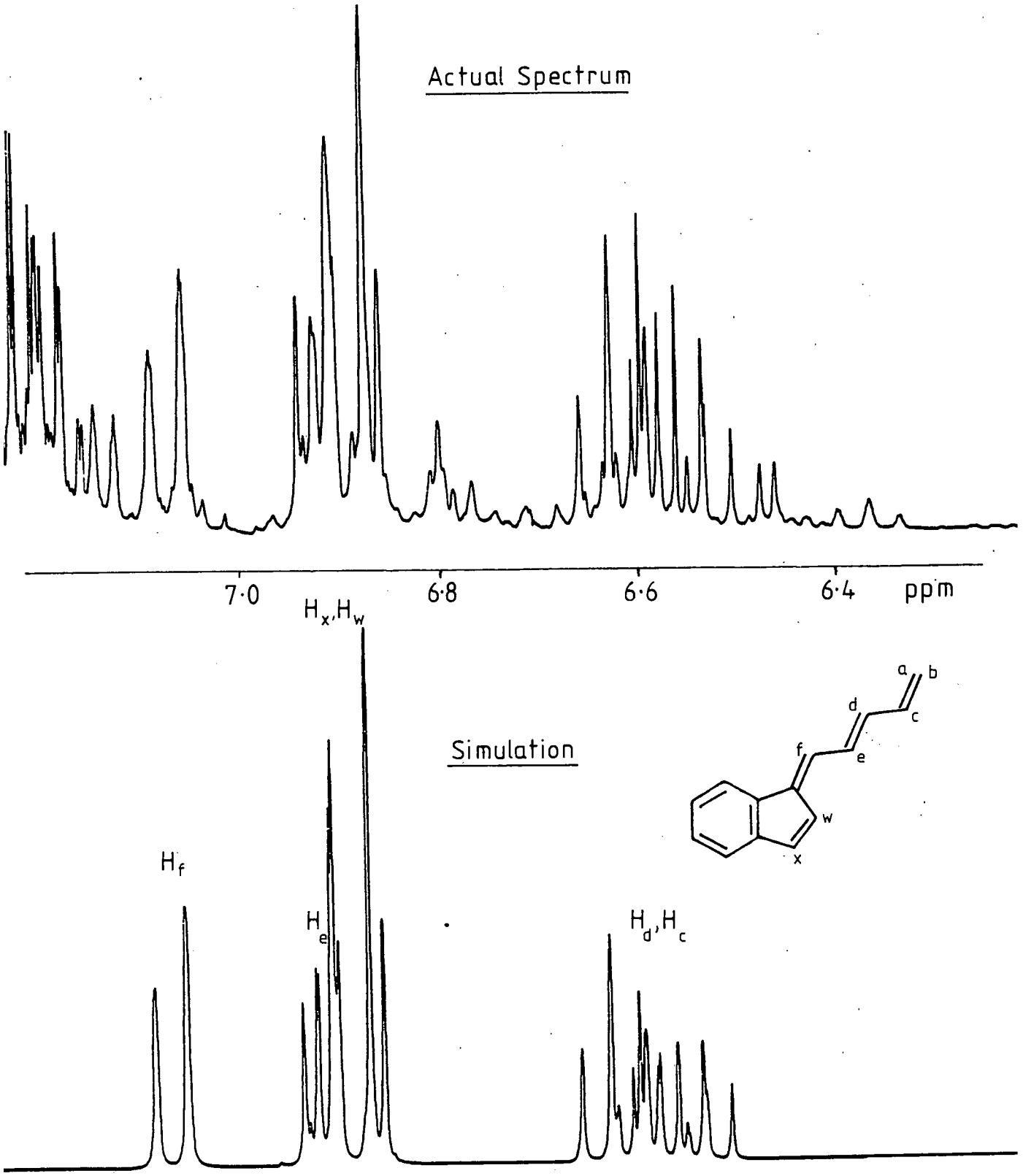
The benzofulvenes were identified in the mixture (fig.39) by analogy with the spectra of the products of the preceding rearrangements. The major isomer shows similar resonances and coupling patterns for protons a,b,c and d as E-1,2-benzo-6-methyl-6-(E-buta-1',3'-dienyl)fulvene (165) (fig.35) but the pattern for the c and d resonances shows a greater number of lines than would be expected for simple first order couplings. Accordingly a spectrum simulation was carried out on a Bruker Aspect 2000 computer using the program PANIC (1982 version). This program can simulate up to a nine spin system, eight were considered for this simulation i.e. protons a,b,c,d,e,f, w and x. The proton chemical shifts were estimated from the line positions in the experimental spectrum.

The simulated spectrum was compared directly with the experimental spectrum and shows good agreement with the actual numbers of lines and line intensities observed. The resulting chemical shifts and coupling constants are given in Table 7 below.

Table 7

Proton	Shift (δ)	Coupling(s) (Hz)
a	5.43	1.8, 17.1 (to b and c)
b	5.30	1.8, 9.5 (to a and c)
c	6.56	17.1, 9.5, 10.7 (to a,b and d)
d	6.64	10.7, 13.7 (to c and e)
e	6.91	13.7, 11.7 (to d and f)
f	7.08	11.7, 0.5, 1.0 (to d,w and x)
w	6.87	0.5, 5.2 (to f and x)
x	6.92	1.0, 5.2 (to f and w)

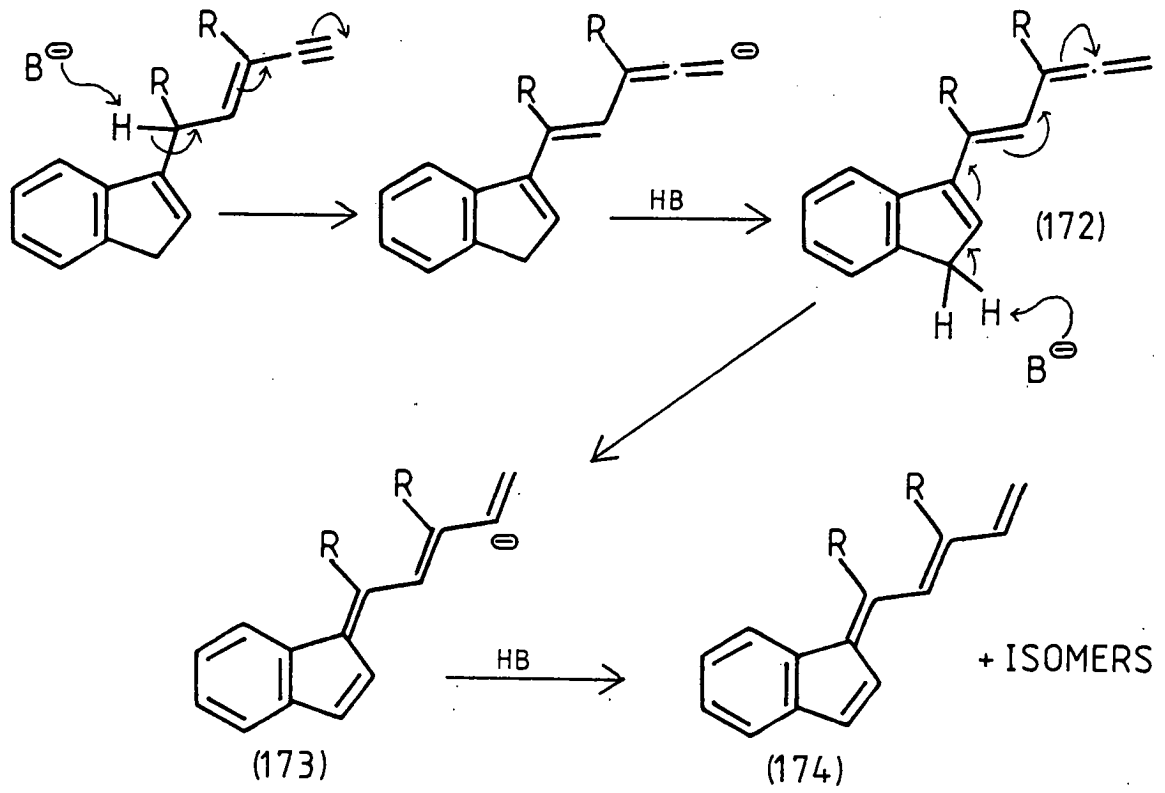
FIGURE 40


Actual Spectrum
7·0
6·8
6·6
6·4
ppm
Simulation
H_x, H_w
H_f
H_e
H_d, H_c
a
b
c
d
e
f
w
x

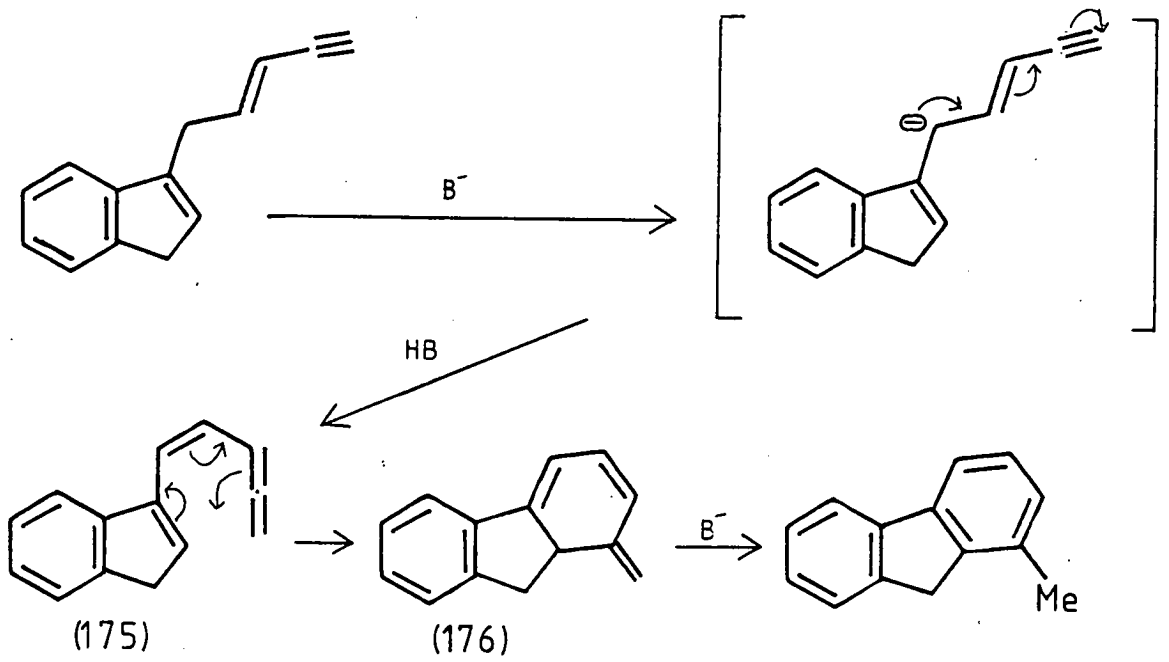
Part of the actual spectrum with the simulated spectrum printed below it is shown in figure 40. The assignment of an E configuration about the C_d to C_e bond is based on the size of the coupling between H_e and H_d which is 13.7Hz (i.e. trans). E configuration about the benzofulvene exocyclic double bond is based on the position of the H_e resonance. In this molecule it occurs at 6.92δ c.f. 7.17δ for H_e in E-1,2-benzo-6-methyl-6-(E-buta-1',3'-dienyl)fulvene (165) whereas in Z-1,2-benzo-6-methyl-6-(E-buta-1',3'-dienyl)fulvene (166) this proton resonates at higher frequency (7.63δ) due to proximity of the benzene ring.

The resonances for the minor isomer were in the main obscured by the resonances for the other compounds in the mixture. However resonances are clearly visible at 5.36 (H_b), 5.45 (H_a), 7.53 (H_e) and 7.84 (H_p) δ. Since H_e and H_p resonate at higher frequency for this isomer than for the E,E isomer (indicating proximity of the benzene ring and the conjugated side chain) and since H_e shows a 13Hz (trans) coupling to H_d this isomer is assigned the Z,E configuration.

The mechanism of the three preceding rearrangements can be considered as simply an extension of the mechanism proposed for the rearrangement of 3-propargylindene (p.59). Action of base produces an intermediate allene (172) which further rearranges to give a highly conjugated species such as (173) which leads to the product(s) (174). The production of 1-methylfluorene (169) in the rearrangement of E-3-(pent-2'-en-4'-ynyl)indene (121) is readily explained by the mechanism



shown below in which the allene (175) formed by action of base cyclises thermally (or by base) to give (176) which then aromatises to give the final product.



This reaction is analogous to that of hepta-1,6-diyne which gives toluene on reaction with base (p.14).

Experimental

5.1 Introduction

Gas-liquid Chromatography

A Pye 105 automatic preparative chromatograph fitted with a flame ionisation detector was used for preparative work and a Griffin and George D6 chromatograph fitted with a gas density balance detector was used for analytical work. The columns were packed with 5% N.P.G.S. on Chromosorb P80-100 mesh and nitrogen was used as the carrier gas.

Thin Layer Chromatography

Analytical thin layer chromatography was carried out on "Polygram" alumina coated (0.2 mm), plastic plates from Machery Nagel and Co. or on silica coated (0.2 mm, Merck Type 60G), glass plates. Preparative thin layer chromatography was carried out on alumina, or silica coated glass plates using a 1 mm layer of Merck Type 60G silica or Type 60G (E) alumina. Light petroleum or light petroleum/ether mixtures were used as eluants.

Column Chromatography

Alumina chromatography was carried out using Spence Type H basic alumina and silica chromatography was carried out using Fisons 60-120 mesh 'Silica for Chromatography.' Light petroleum or light petroleum/ether mixtures were used as eluants.

Infra-red Spectroscopy

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

Mass Spectroscopy

Mass spectra were obtained using an AEl MS-902 double focussing instrument. Exact masses of parent peaks were obtained by peak matching, giving results normally within 10 p.p.m. of the calculated values.

Nuclear Magnetic Resonance Spectroscopy

Proton n.m.r. spectra were recorded on a Varian HA 100 spectrometer (CW) or a Bruker WH 360 spectrometer (FT). Chemical shifts are given in parts per million (δ) relative to tetramethylsilane as internal standard.

Carbon-13 n.m.r. spectra were recorded on a Varian CFT-20 (20MHz) or on a Bruker WH-360 (90.56MHz) spectrometer using $CDCl_3$ as solvent and internal standard (δ $\underline{C}DCl_3$=76.9 p.p.m.). Chemical shifts are given in parts per million relative to tetramethylsilane.

Spectra (^1H and ^{13}C) obtained on the WH 360 spectrometer are denoted thus:- $^1H^*$ or $^{13}C^*$.

Materials

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

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

Dry tetrahydrofuran was prepared by boiling tetrahydrofuran under reflux, under nitrogen, with calcium hydride for 1 h and then distilling into bottles containing activated molecular seive.

Light petroleum refers to the fraction of b.p.30-40°C and was distilled before use.

2-Bromohex-3-en-5-yne and 1-bromo-3-methylpent-2-en-4-yne were kindly supplied by Dr.N.J. Truslove and were redistilled before use.

Indan-2-one was steam distilled before use to give white crystals m.p.51-54°, lit. m.p.58°.

Indene (BDH) was purified by passing through alumina and kept in the refrigerator before use.

But-3-yn-2-ol supplied as a 50% solution in water was treated with anhydrous potassium carbonate until two layers formed and the upper layer of but-3-yn-2-ol was further dried over more potassium carbonate before use.

5.2 Preparation of Starting Materials

In all cases the structures of the compounds were confirmed by their ^{1}H n.m.r. spectra.

5.2.1 2-Methylindene (87) was prepared by a Grignard reaction. Indan-2-one (40 g, 0.36 mol) dissolved in dry ether (150 ml) was added slowly to an ethereal solution of methyl magnesium bromide (0.4 mol) at such a rate as to allow gentle refluxing of the ether. After heating under reflux for a further 0.5 h, the cooled mixture was poured carefully onto ice/water. Dilute hydrochloric acid was added with stirring until both

layers were clear, the ether layer was removed and the aqueous layer extracted with more ether (4x100 ml). The combined ether extracts were dried, and the ether removed to give 2-methylindan-2-ol which was heated under reflux for 1 h with phosphorus pentoxide (30 g) in dry benzene (400 ml). The benzene solution was decanted and the benzene removed. The product appeared slightly wet and no light petroleum was added and the solution dried over magnesium sulphate. Filtering the solution and removal of the petrol, followed by distillation under reduced pressure gave 2-methylindene (69%, b.p.90-98°/30 mm lit. b.p. 62-65°/20 mm[60]).

5.2.2 3-Methylindene (88) was prepared as described by Truslove[22]. Sodium (5.75 g, 0.25 mol) was dissolved in liquid ammonia (500 ml) with a little ferric nitrate present to catalyse formation of sodamide. Indene (29 g, 0.25 mol) was then added dropwise with vigorous stirring and the mixture then stirred for a further 1 h. Methyl bromide (19.25 g, 0.4 mol) was added dropwise and the ammonia allowed to evaporate overnight. The residue was then extracted into ether (2x200 ml) and the ether extracts dried and then distilled to remove the ether. Distillation of the residue gav 3-methylindene (75% b.p.76-80°/15 mm, lit. b.p.198.5° [60]).

5.2.3 Indan-1-one (177) was prepared by intramolecular Friedel-Crafts acylation. 3-Phenylpropionic acid (100 g, 0.67 mol) and excess of thionyl chloride (130 ml) were heated under reflux for 2 h. Unreacted thionyl chloride was removed under reduced pressure and the acid chloride distilled (137-139°/29 mm).

The acid chloride was then dissolved in carbon disulphide (500 ml) and aluminium trichloride (64 g, 0.34 mol) was added in small portions with stirring. After heating under reflux for 1 h the mixture was poured onto ice, the carbon disulphide layer removed and the aqueous layer extracted with more carbon disulphide (2x100 ml). The combined extracts were distilled to remove the carbon disulphide and the residue steam distilled to give indan-1-one (65% m.p.37-40° lit.42° [60]).

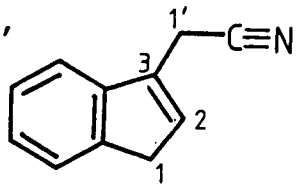
5.2.4 3-Cyanomethyl indene (143) was prepared by the method of Thorpe and Ingold[57]. Ethyl indan-1-ylidenecyanoacetate was first prepared from indan-1-one (19 g, 0.14 mol), ethyl-cyanoacetate (16 g, 0.14 mol) and diethylamine (6.5 g) which were stirred overnight at 45-50°C. After cooling for 1 h the crystals of ethyl indan-1-ylidenecyanoacetate were filtered off and recrystallised from ethanol (11.5 g, 40.5%, m.p.95-98°, lit. m.p. 104°[57]).

The ester was hydrolysed to the corresponding acid by pouring the finely powdered ester (2 g) into boiling 4M aqueous sodium hydroxide (8 ml), removing the heat source, and shaking to obtain a clear red solution. (Occasionally further gentle warming was required). The mixture was then cooled rapidly in water and then in ice to precipitate the sodium salt. The free acid was obtained by dissolving the sodium salt in water (400 ml), with gentle warming, filtering the solution and acidifying the filtrate with dilute hydrochloric acid. Yields of up to 1 g (58% based on the ester) of indan-1-ylidenecyanoacetic acid were fairly consistently obtained provided that the ester was not overheated when

mixed with the alkali (m.p.190-195°, lit. m.p.203° (dec)[57]).

The acid obtained above was decarboxylated by sublimation through the vapour phase pyrolysis apparatus described in Section 5.6. The acid (0.5 g) yielded a mixture (0.25 g) of products shown by its $^{1}H^{*}$ n.m.r. spectrum to consist of 3-cyanomethylindene (143), E-1-cyanomethyleneindane (145) and 1-cyanomethylindene (147) in the ratio 10:1:3. Crystallisation of this mixture at -78° from a mixture of ether and light petroleum (1:5) gave 3-cyanomethylindene (20%), a liquid at room temperature.

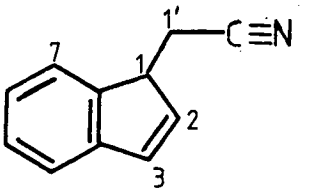
3-Cyanomethylindene (143)



^{1}H n.m.r. ($CDCl_3$) δ: 3.38 (m, 2H, $C\underline{H}_2$-1), 3.62 (m, 2H, $C\underline{H}_2$-1'), 6.56 (m, 1H, =C$\underline{H}$), 7.1-7.56 (m, 1H, Ar$\underline{H}$). Assignment of $C\underline{H}_2$ resonances based on data presented later (Section 6.13; p.108).

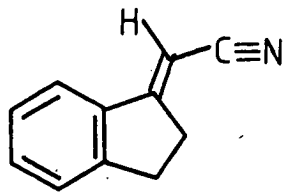
$^{13}C^{*}$ n.m.r. (p.p.m.): 16.9 (CH_2-1'), 37.7 (CH_2-1), 116.9 (C≡N), 118.3, 124.0, 125.5, 126.3, 131.9 (aromatic and olefinic CH), 132.9, 142.5, 143.9 (aromatic and olefinic C).

1-Cyanomethylindene (147)



$^{1}H^{*}$ n.m.r. ($CDCl_3$) δ: 2.52, 2.66 (two d of d, J=16.8, 7.8Hz, 2H, $C\underline{H}_2$), 3.67 (bt, J=7.8Hz, 1H, C$\underline{H}$-1), 6.46 (d of d, J=5.6, 1.8Hz, 1H, =C$\underline{H}$-2), 6.89 (d of d, J=5.6, 1.2Hz, 1H, =CH-3), 7.2-7.4 (m, 3H, Ar$\underline{H}$), 7.46 (d, J=7.1Hz, 1H, C$\underline{H}$-7).

5.2.5 E-1-Cyanomethyleneindane (146) was prepared by the method of Bell and Spanswick[56]. Indan-1-ylidenecyanoacetic acid (0.5 g, 0.0025 mol) was heated in the presence of a few drops of piperidine and the residue extracted into ether (50 ml). After removal of the ether the product was recrystallized twice from ethanol to give E-1-cyanomethyleneindane (33%, m.p.70-71°C lit. m.p.68-69°C[56]).



^{1}H n.m.r. ($CDCl_3$) δ: 3.03 (bs, 4H, 2xCH_2), 5.59 (m, 1H, =CH), 7.13-7.54 (m, 4H, ArH).

^{13}C n.m.r. (p.p.m.): 24.6 (CH_2), 31.1 (CH_2), 85.5 (=CH), 117.8 (C≡N), 121.2, 125.6, 126.9, 131.4, (aromatic CH), 137.8, 149.3 (aromatic C), 167.0 (olefinic C).

5.2.6 But-3-yn-1-ol

Preparation of the compound was attempted by several different methods in an effort to improve upon the yield given by the route described by Schulte and Reiss[61], which employs sodium acetylide and ethylene oxide, however only their method gave satisfactory results.

A Sodium Acetylide and Ethylene Oxide

Liquid ammonia (1.5 l) containing ferric nitrate (0.5 g) was saturated with a stream of acetylene gas dried by passing through concentrated sulphuric acid. Acetylene passage was continued whilst sodium (35.4 g, 1.5 mol) was added in small pieces and continued for a further 1.5 h. Ethylene oxide (100 ml, 2 mol) was added quickly and the

acetylene passage continued for a further 1.5 h after which the gas inlet was replaced by a nitrogen bubbler. The reaction was then kept under reflux, under nitrogen, for 8.5 h and left under nitrogen overnight. The resulting mixture was hydrolysed by the careful addition of solid ammonium chloride (91 g, 1.7 mol), and the remaining ammonia evaporated off. Extraction of the residue into ether (3x250 ml), drying of the extracts and removal of the solvent, followed by distillation of the residue gave but-3-yn-1-ol in varying yields (10-43% b.p. 68-74°/63 mm, lit. b.p.127-129°/724 mm [61]) as a colourless liquid.

An attempt to carry out the reaction with sodium acetylide suspended in ether instead of ammonia failed to produce any product.

B Propargyl zinc bromide and formaldehyde

Propargyl zinc bromide was prepared by the method of Gaudemar [62]. Propargyl bromide (1 ml) was added to zinc (16.3 g, 0.25 mol) and dry tetrahydrofuran (25 ml), under nitrogen, to start the reaction and then the mixture was cooled and maintained between -10° and -15°. Propargyl bromide (30 g, 0.25 mol) in dry tetrahydrofuran (100 ml) was then added dropwise over a 2 h period.

Addition of paraformaldehyde (7.5 g, 0.25 mol of formaldehyde) and warming to 40° for 24 h yielded no product on work up.

The reaction was repeated using formaldehyde gas generated by the method of Adams and Noller [63]. Para-

formaldehyde (15 g, two fold excess) was depolymerised by heating at 180-200°C and the gas produced was passed into a solution of propargyl zinc bromide (0.25 mol) in dry tetrahydrofuran (125 ml). 2.2M Methanolic hydrogen chloride (120 ml) was added to hydrolyse the complex and the mixture then neutralised with sodium methoxide. Distillation gave the desired alcohol in low yield (5%).

C Propargyl aluminium bromide and formaldehyde

Propargyl aluminium bromide was prepared by the method of Läuger, Prost and Charlier[64] as described later (p78) but reaction with paraformaldehyde produced only a trace of product (<2%).

5.2.7 Pent-4-yn-1-ol was prepared as described by Vogel[8]. Freshly distilled tetrahydrofurfuryl alcohol (102 g, 97 ml, 1 mol) and dry pyridine (87 g, 89 ml, 1.1 mol) were placed in an ice cooled flask and freshly distilled thionyl chloride (125 g, 76.5 ml, 1.05 mol) was added dropwise with stirring, the temperature being kept between 60° and 80°C. The mixture was then stirred at room temperature for 4 h, extracted with ether (7x100 ml), the ether removed by distillation, and the remaining product washed with water (3x50 ml), dried and distilled, to give tetrahydrofurfuryl chloride (42%, 51 g, 40°/12 mm).

This product (50 g) was added dropwise over a period of 30 minutes to a suspension of sodamide prepared from sodium (33.6 g, 1.46 mol, 3.5 equivalents) in liquid ammonia (750 ml) containing ferric nitrate (0.4 g). The mixture

was stirred for 1 h and then solid ammonium chloride (77 g, 1.46 mol) was cautiously added. The ammonia was allowed to evaporate overnight and the residue extracted with ether (10x125 ml). After removal of the ether the product was distilled under reduced pressure to give pent-4-yn-1-ol (b.p. 60-63°/20 mm, 86.5%) as a colourless liquid.

5.2.8 2-Methylpent-4-yn-2-ol was prepared by the method of Läuger, Prost and Charlier[64]. Aluminium turnings (7.3 g, 0.268 mol) were prepared by cutting the metal foil into small pieces which were etched in boiling methylene chloride and then dried in an oven at 100°C. These were then placed in a round bottomed flask fitted with stirrer, condenser and dropping funnel, and kept under a nitrogen atmosphere. Dry tetrahydrofuran (20 ml) and a little mercuric chloride were added and the mixture stirred for a few minutes to produce some amalgam on the aluminium surface. Propargyl bromide (47.6 g, 0.4 mol) in dry tetrahydrofuran (20 ml) was added dropwise, the temperature being kept near room temperature by cooling the reaction flask with water and ice. After the reaction had apparently ceased the mixture was warmed for 0.5 h at 30-35°C to complete the reaction. Dry acetone (23.2 g, 0.4 mol) in dry ether (50 ml) was then added dropwise with ice/water cooling and reaction again completed by warming at 30-35°C for 0.5 h. The reaction mixture was then dripped onto stirred ice (200 g), causing a vigorous reaction, and stirring was continued for 3 h. The organic layer was removed and the aqueous layer extracted twice with ether (2x200 ml). The combined organic layers were washed

with water until the water was neutral, then dried and the ether removed. Distillation (under nitrogen) of the residue gave 2-methylpent-4-yn-2-ol (b.p.116-118°C as lit.[64], 35%) as a colourless liquid.

5.2.9 Pent-4-yn-2-ol was prepared similarly from propargyl bromide and acetaldehyde.

Acetaldehyde was obtained by gentle distillation of paraldehyde (40 ml) with concentrated sulphuric acid (1 ml) and water (1 ml). The still head temperature was kept below 35°C and the acetaldehyde was collected in an ice cooled receiver.

Reaction of the acetaldehyde (0.4 mol) with propargyl aluminium bromide (0.4 mol) gave pent-4-yn-2-ol (50%, b.p. 80-81°/110 mm, lit. b.p. 78-79°/110 mm[64]), as a colourless liquid.

52.10 E-Pent-2-en-4-yn-1-ol was prepared by the method of Heilbron, Jones and Sondheimer[65]. Epichlorohydrin (69.4 g, 0.75 mol) was added slowly with stirring, under a nitrogen atmosphere, to sodium acetylide (1.5 mol) in liquid ammonia (1.5 l) prepared as described previously (p.75). The mixture was stirred under reflux for a further 7 h and then left to stand overnight. More ammonia was added to make the volume up to 1 litre and then ammonium chloride (82.5 g, 1.54 mol) was added cautiously, with stirring. The ammonia was evaporated off and the residue extracted into ether (3x250 ml). After removal of the ether the product was distilled under reduced pressure to give E-pent-2-en-4-yn-

1-ol (26%, b.p.65-70°/12 mm, lit.71-73°/19 mm[65]). The E configuration of the double bond was confirmed by the ^1H n.m.r. spectrum.

5.3 Preparation of Acetylenic and Allenic Halides

These compounds were stored at -10° to reduce decomposition and their structures were confirmed by their ^1H n.m.r. spectra.

5.3.1 Propargyl bromide was prepared as described by Birch and McAllan[66]. Propargyl alcohol (96 g, 1.0 mol) and pyridine (36 ml) were placed in a flask fitted with magnetic stirrer, dropping funnel and calcium chloride guard tube. Phosphorus tribromide (52 ml) was added dropwise over 1.5 h, keeping the temperature at about -15°C (acetone/dry ice). Distillation directly from the flask under reduced pressure gave propargyl bromide (60-65%, b.p.24°/80 mm, lit. b.p. 35°/130 mm[66]) as a colourless liquid.

5.3.2 2-Bromobut-3-yne was prepared by the method of Black, Landor, Patel, and Whiter[67]. Triphenylphosphite dibromide (0.4 mol) was prepared by dropping bromine (64 g, 0.4 mol) into triphenylphosphite (124 g, 0.4 mol) with ice cooling, mechanical stirring, and with the exclusion of moisture. But-3-yn-2-ol (14.3 g, 0.2 mol) in pyridine (23 g) was added dropwise with mechanical stirring and ice cooling and the resulting mixture then stirred for 3 h at room temperature. The mixture was then filtered with suction and the filtrate distilled under reduced pressure to give 2-bromobut-3-yne (30-40%, b.p. 25°/35 mm lit. b.p. 43-45°/100 mm) as a

colourless liquid which darkened on standing.

5.3.3 1-Bromo-3-methylbuta-1,2-diene was prepared as described by Landor, Patel and Whiter[68]. 2-Methylbut-3-yn-2-ol (50 g, 0.6 mol), hydrobromic acid (48% w/w, 125 ml), cuprous bromide (25 g, 0.17 mol) and diglyme (6 g) were placed in a stoppered conical flask and allowed to stand overnight. The upper organic layer was then removed and washed with 48% hydrobromic acid (3x25 ml). The aqueous layer was extracted with light petroleum (3x25 ml) and the petrol extracts washed with hydrobromic acid (3x25 ml). The combined organic layers were dried over magnesium sulphate and the petrol removed. Distillation under reduced pressure gave 1-bromo-3-methylbuta-1,2-diene (68% b.p. 25°/15 mm, lit. b.p. 53-54°/60 mm[68]).

5.3.4 1-Bromobut-3-yne was prepared by the method of Nakada, Yura and Murayama[69]. Phosphorus tribromide (41 g, 0.15 mol) in dry ether (20 ml) was added dropwise, with stirring, to but-3-yn-1-ol (24 g, 0.034 mol) and pyridine (15 g) in dry ether (40 ml), under nitrogen at a temperature of -10 to -20°C. The reaction mixture was then stirred for a further 5 h, and left to stand overnight. The mixture was then poured onto ice, the ether layer removed and the aqueous layer extracted with ether (2x25 ml). The combined organic extracts were washed with 5% hydrochloric acid (100 ml), 5% sodium carbonate solution (100 ml) and then dried over anhydrous sodium carbonate. The mixture was filtered and after removing the ether the product was distilled, under nitrogen, to give 1-bromobut-3-yne (21% b.p.103-105°, lit.

b.p. 108-109.5°/723 mm [70]).

5.3.5 1-Bromopent-4-yne was prepared by the method of Black, Landor, Patel and Whiter [67]. Pent-4-yn-1-ol (30.3 g, 0.36 mol) in pyridine (23 ml) was added slowly with ice cooling and stirring to triphenylphosphite dibromide (335 g, 0.5 mol) prepared as described before (p.80) and the mixture stirred for 3 h. The mixture was then filtered and the filtrate distilled under reduced pressure to give 1-bromopent-4-yne (30% b.p. 25-30°/15 mm, lit. b.p.38-44°/30 mm [22]).

5.3.6 2-Bromopent-4-yne was prepared by the method of Nakada, Yura and Murayama [69]. Phosphorus tribromide (6.6 g, 0.024 mol) in dry ether (20 ml) was added dropwise with stirring to pent-4-yn-2-ol (5.04 g, 0.06 mol) and pyridine (2.4 g) in dry ether at -10° to -20°C. After stirring for a further 0.5 h the mixture was poured onto ice the ether layer removed and the aqueous layer extracted into ether (2x25 ml). The combined ether extracts were washed with 5% hydrochloric acid (100 ml), 5% sodium carbonate solution (100 ml) and dried over anhydrous sodium carbonate. The mixture was then filtered and the ether was removed to give 2-bromopent-4-yne (54%) which was used without further purification due to its instability.

5.3.7 2-Bromo-2-methylpent-4-yne was prepared from 2-methylpent-4-yn-2-ol (6 g, 0.06 mol) by the method described above for 2-bromopent-4-yne. The crude product (10 g) contained an unidentified impurity as shown by the ^{1}H n.m.r. spectrum. All attempts to purify the compound resulted

in rapid polymerisation and so it was used subsequently without distillation.

5.3.8 1-Bromo-3-methylpenta-1,2-diene was prepared as by Landor, Patel and Whiter[68]. 3-Methyl-1-pentyn-3-ol (60 g, 0.6 mol), cuprous bromide (25 g), diglyme (6 g) and hydrobromic acid (48% w/w, 125 ml) were left to stand overnight in a stoppered flask. The organic layer was removed and the aqueous layer extracted with petrol (3x50 ml). The combined organic extracts were dried and the petrol removed. Distillation under reduced pressure gave 1-bromo-3-methylpenta-1,2-diene (73.5%, b.p.46-48°/15 mm, lit. b.p.51-52.5°/24 mm[68]) as a colourless liquid.

5.3.9 E-1-Bromopent-2-en-4-yne was prepared from pent-2-en-4-yn-1-ol (0.183 mol, 15 g) by the method of Nakada, Yura and Murayama[69] as given for the preparation of 2-bromopent-4-yne. Distillation under nitrogen at atmospheric pressure gave the desired product (32% b.p. 140°, lit. b.p.43°/25 mm[69]) with some loss due to polymerisation.

5.3.10 1-Iodohex-5-yne was prepared by the method of Barbier and Hügel[71].

1-Chlorohex-5-yne[72] was prepared by adding 1-bromo-4-chlorobutane (25 g, 0.146 mol) dropwise to a suspension of sodium acetylide (0.146 mol) in liquid ammonia (500 ml). After stirring the reaction mixture for 7 h and then allowing the ammonia to evaporate overnight, water (500 ml) was added and the mixture extracted with ether (3x250 ml). The extracts were dried and the ether removed to give the crude product

(12.2 g, 72%) which was used without purification.

The 1-chlorohex-5-yne (12 g) was heated under reflux for 48 h in acetone (150 ml) with sodium iodide (20 g). The solid was filtered off and most of the acetone removed on a rotary evaporator. The resulting product was distilled under reduced pressure to give 1-iodohex-5-yne (96% b.p.62°/9 mm, lit. b.p. $70^{\circ}/12$ mm [72]).

5.4 Preparation of Acetylenic Derivatives of Fluorene

Propargyl fluorene (97) has been prepared in low yield [22] by the reaction of 9-fluorenyl sodium, prepared in liquid ammonia, with propargyl bromide but 9,9-dipropargyl fluorene (96) is the major product. Attempts to react 2-bromobut-3-yne, 2-bromo-2-methylbut-3-yne or 2-bromo-2-methylpent-4-yne with 9-fluorenylsodium in a similar manner all failed probably due to elimination reactions of these secondary and tertiary halides under basic conditions.

The following general method using 9-fluorenyl lithium was successful in most of the preparations attempted.

5.4.1 General Method

Phenyl lithium was first prepared by adding bromobenzene (7.85 g, 0.05 mol) in dry ether (25 ml) to freshly cut small pieces of lithium (0.7 g, 0.1 mol) in dry ether (80 ml) at such a rate as to maintain gentle refluxing. (The reaction was carried out under nitrogen). After addition of the bromobenzene solution was complete, the mixture was heated under reflux for a further 0.75 h and then filtered quickly

through a glass wool plug to remove unreacted lithium which was then weighed to give the quantity of phenyl lithium that had been produced. A molar equivalent of fluorene in dry ether (250 ml) was then added dropwise giving a deep orange-red solution of 9-fluorenyl lithium. The alkynyl halide (one molar equivalent or slight excess) in dry ether (50 ml) was then added slowly and the mixture stirred at room temperature for 1-2 h. Water was then added, the ethereal layer removed, the aqueous layer extracted with more ether (2x150 ml) and the combined ether extracts washed with saturated salt solution, dried and the ether removed. Chromatography on alumina eluting with light petroleum or light petroleum-ether mixtures gave monosubstituted 9-alkynyl fluorenes as pale yellow or colourless liquids or white crystals. In some cases other products were observed (see below).

5.4.2 Characterisation of products

The molecular formulae were confirmed by elemental analysis or exact mass measurement of the parent peak in the mass spectrum. Structures were confirmed by i.r. and n.m.r. spectra.

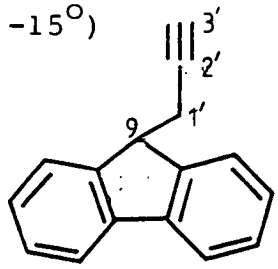
Details of the individual compounds are summarised below.

4.3 9-Propargylfluorene (97)

Halide: propargyl bromide Yield: 65%

M.p.: 39-41° (light petroleum at -15°)

lit. 41° [54]



^{1}H n.m.r. (CCl_4), δ (p.p.m.): 1.94 (t, J=2Hz, 1H, ≡C<u>H</u>), 2.60 (d of d, J=7Hz, 2Hz, 2H, C<u>H</u>$_2$), 3.96 (t, J=7Hz, 1H, C<u>H</u>), 7.06-7.4 (m, 4H, Ar<u>H</u>), 7.54-7.7 (m, 4H, Ar<u>H</u>).

^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.): 22.9 (CH_2), 45.4 (CH), 69.6 (≡CH), 82.4 (-C≡), 119.6, 124.3, 126.7, 127.3 (aromatic CH), 140.5, 145.5 (aromatic C)

I.r. (cm^{-1}): 3300 (s) ≡CH, 2120 (m) C≡C, 760 (s), 740 (s).

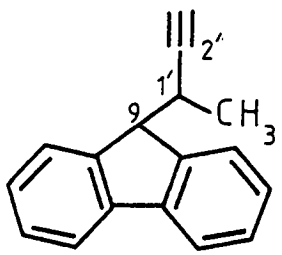
Analysis: found C, 93.9; H, 5.8%

$C_{16}H_{12}$ requires C, 94.2; H, 5.8%.

5.4.4 <u>9-(1'-Methylprop-2'-ynyl)fluorene</u> (99)

Halide: 2-bromobut-3-yne Yield: 35%

M.p.: 51-54°



^{1}H N.m.r. (CCl_4), δ (p.p.m.): 0.59 (d, J=7Hz, 3H, C<u>H</u>$_3$), 2.09 (d, J=3Hz, 1H, ≡C<u>H</u>), 3.24 (m, 9 lines intensities 1:2:4:6:6:6:4:2:1 due to coincidences in couplings from other protons J=7Hz, 3Hz, 3Hz, 1H, C<u>H</u>-1'), 4.09 (d, J=3Hz, 1H, C<u>H</u>-9), 7.02-7.38 (m, 5H, Ar<u>H</u>), 7.5-7.7 (m, 2H, Ar<u>H</u>), 7.8-7.94 (m, 1H, Ar<u>H</u>).

^{13}C N.m.r. ($CDCl_3$), δ (p.p.m.): 14.6 (CH_3), 28.7 (CH-1') 50.7 (CH-9), 69.6 (≡CH), 87.9 (-C≡), 119.6, 123.9, 125.4, 126.7, 126.8, 127.3 (aromatic CH, two lines are for two carbons), 141.5, 141.6, 144.0, 144.6 (aromatic C).

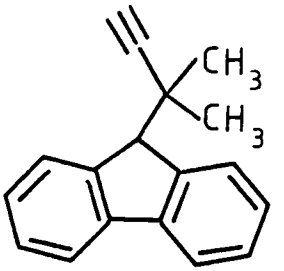
I.r. (cm^{-1}) (nujol): 3315 (s) ≡CH, 2110 (w) C≡C, 740 (s).

M.s. (m/e): 218.110887 (M^+, $C_{17}H_{14}$ requires 218.109545), 165.

5.4.5 9-(1',1'-Dimethylprop-2'-ynyl)fluorene (100)

Halide: 1-Bromo-3-methylbuta-1,2-diene Yield: 21%

M.p.: 77-79° (ethanol)



^{1}H N.m.r. (CCl_4), δ(p.p.m.): 1.10 (s, 6H, 2xCH_3), 2.24 (s, 1H, ≡C$\underline{H}$), 4.0 (s, 1H, C$\underline{H}$), 7.04-7.36 (m, 4H, Ar$\underline{H}$), 7.64-7.84 (m, 4H, Ar$\underline{H}$).

^{13}C N.m.r. ($CDCl_3$), δ(p.p.m.): 26.4 (2xCH_3), 34.8 ($C(CH_3)_2$), 55.5 (CH), 69.7 (≡CH), 92.4 (-C≡), 119.4, 126.2, 126.5, 127.4 (aromatic CH), 142.0, 144.1 (aromatic C).

I.r.: (cm^{-1}) (nujol): 33100 (s) ≡CH, 740 (s).

Analysis: found C, 93.2; H, 6.8%

$C_{18}H_{16}$ requires C, 93.1; H, 6.9%

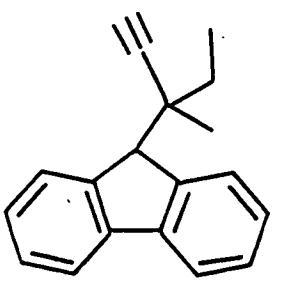
M.s. (m/e): 232 (M^+), 217, 180, 165.

The ^{1}H n.m.r. spectrum of the crude reaction mixture shows the presence of the above 9-(1',1'-dimethylprop-2'-ynyl) fluorene and 9-(3'-methylbuta-1',2'-dienyl) fluorene (101) (see p.103) in the ratio 2:1. Chromatography on basic alumina allowed separation of the acetylene and converted the allene to dibenzo-6-(2'-methylprop-1'-enyl) fulvene (137) (see p.112).

5.4.6 9-(1'-Ethyl-1'-methylprop-2'-ynyl) fluorene (102)

Halide: 1-bromo-3-methylpenta-1,2-diene Yield: 11.3%

M.p.: 96-98° (methanol)



^{1}H n.m.r. ($CDCl_3$), δ(p.p.m.): 0.86 (s, 3H, C-C$\underline{H}_3$), 1.11 (t, J=7Hz, 3H, CH_2 C$\underline{H}_3$), 1.10-1.86 (m, 2H, C$\underline{H}_2$ [prochiral]), 2.34 (s, 1H, ≡C$\underline{H}$),

4.12 (s, 1H, C<u>H</u>), 7.10-7.42 (m, 4H, Ar<u>H</u>), 7.6-7.78 (m, 3H, Ar<u>H</u>), 7.88-8.0 (m, 1H, Ar<u>H</u>).

^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.): 9.32 ($CH_2\underline{C}H_3$) 23.0 (C-$\underline{C}H_3$), 31.3 (CH_2), 39.4 (C-1'), 53.6 (CH), 71.1 (≡CH), 90.7 (≡C-), 119.2, 119.4, 126.2, 126.4, 127.3 (aromatic CH), 141.8, 142.2, 143.5 (aromatic C).

I.r. (cm^{-1}) (nujol): 3295 (s) ≡CH, 2100 (w) C≡C, 735 (s).

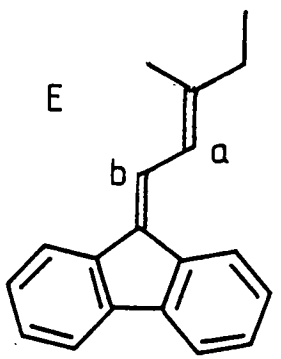
Analysis: found C, 92.8; H, 7.4%

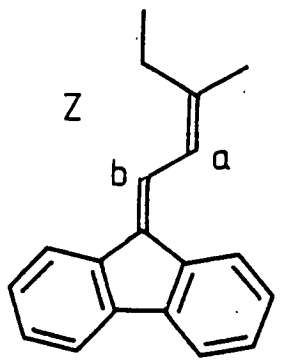
$C_{19}H_{18}$ requires C, 92.6; H, 7.4%

M.s. (m/e): 246 (M^+), 217, 165.

The ^{1}H n.m.r. spectrum of the crude reaction product showed resonances attributable to the allene 9-(3'-methylpenta-1,2-dienyl)fluorene (103) by comparison with those of the product of pyrolysis of the above acetylene (p.103). Chromatography on alumina separated the acetylene and converted the allene to an equimolar mixture (9%) of E and Z dibenzo-6-(2'-methylbut-1'-enyl)fulvene (162 and 163) which was isolated as a bright yellow solid.

<u>E and Z Dibenzo-6-(2'-methylbut-1'-enyl)fulvene (162 and 163)</u>





m.p.: 92-97° (ethanol, yellow needles)

^{1}H* n.m.r. ($CDCl_3$), δ (p.p.m.): E isomer: 1.25 (t,

J=7.5Hz, 3H, CH_2 $C\underline{H}_3$), 2.07 (bs, 3H, $C\underline{H}_3$), 2.37 (q, J=7.5Hz, 2H, $C\underline{H}_2$), 7.11 (d of d, J=12, 1.3Hz, 1H, $\underline{H}_a$), 7.3-7.4 (m, 5H, Ar$\underline{H}$), 7.52 (d, J=12Hz, 1H, $\underline{H}_b$), 7.7-7.8 (m, 3H, Ar$\underline{H}$), 8.04-8.08 (m, 1H, $\underline{H}_p$).

(a) Irradiating the quartet at 2.37 collapses the triplet at 1.25 to a singlet and sharpens the broad singlet at 2.07 to a doublet J=1.3Hz.

(b) Irradiating the d of d at 7.11 collapses the doublet at 7.52 to a singlet.

$^1H^*$ n.m.r. ($CDCl_3$), δ(p.p.m.): Z isomer:- 1.22 (t, J=7.5Hz, 3H, CH_2 $C\underline{H}_3$), 2.09 (bs, 3H, $C\underline{H}_3$), 2.52 (q, J=7.5Hz, 2H, $C\underline{H}_2$), 7.07 (bd, J=12Hz, 1H, $\underline{H}_a$), 7.3-7.4 (m, 5H, Ar$\underline{H}$), 7.51 (d, J=12Hz, $\underline{H}_b$), 7.7-7.8 (m, 3H, ArH), 8.04-8.08 (m, 1H, $\underline{H}_p$).

(a) Irradiating the quartet at 2.52 collapses the triplet at 1.22 to a singlet and sharpens the broad singlet at 2.09 to a doublet J=0.7Hz.

(b) Irradiating the doublet at 7.07 collapses the doublet at 7.51 to a singlet.

I,r. (cm^{-1}) (nujol): 1630 s (C=C), 775 s, 730 s

Analysis: found C, 92.4; H, 7.4%

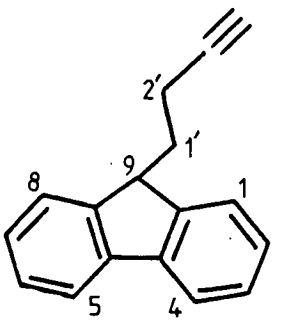
$C_{19}H_{18}$ requires C, 92.6; H, 7.4%

M.s. (m/e): 246 (M^+), 217, 165.

5.4.7 9-(But-3'-ynyl)fluorene (104).

Halide: 1-bromobut-3-yne Yield: 25%

M.p.: 35-37° (ethanol)



^1H* n.m.r. ($CDCl_3$), δ(p.p.m.): 1.96 (t, J=2.6Hz, 1H, ≡C<u>H</u>), 2.045 (t of d, J=7.5, 2.6Hz, 2H, C<u>H</u>$_2$ -2'), 2.24 (d of t, J=7.5, 6.0Hz, 2H, C<u>H</u>$_2$ -1'), 4.13 (t, J=6.0Hz, 1H, C<u>H</u>), 7.31 (t of d, J=7.2, 1.3Hz, 2H, <u>H</u>$_2$, <u>H</u>$_7$ or <u>H</u>$_3$, <u>H</u>$_6$), 7.37 (t with fine structure, J=7Hz, 2H, <u>H</u>$_2$, <u>H</u>$_7$ or <u>H</u>$_3$, <u>H</u>$_6$), 7.53 (d with fine structure, J=7Hz, 2H, <u>H</u>$_1$, <u>H</u>$_8$ or <u>H</u>$_4$, <u>H</u>$_5$), 7.75 (d, J=7.1Hz, 2H, <u>H</u>$_1$, <u>H</u>$_8$ or <u>H</u>$_4$, <u>H</u>$_5$).

^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.): 14.8 (CH_2), 31.8 (CH_2), 46.0 (CH), 68.8 (≡CH), 83.9 (-C≡), 119.7, 124.1, 126.8, 127.0 (aromatic CH), 140.9, 146.1 (aromatic C).

I.r. (cm^{-1}) (nujol): 3300 s (≡CH), 2120 w (C≡C), 735 s.

Analysis: found C, 93.6; H, 6.6%

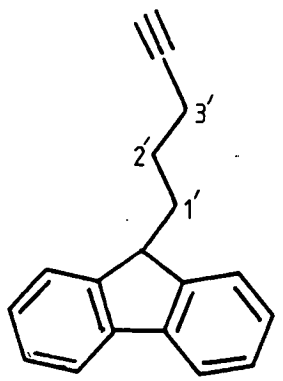
$C_{17}H_{14}$ requires C, 93.5; H, 6.5%

m.s. (m/e): 218 (M^+), 203, 178, 165.

4.8 9-(Pent-4'-ynyl)fluorene (105)

Halide: 1-bromopent-4-yne Yield: 38%

M.p.: 43-44° (ethanol) lit.m.p. 43° [54]



^1H n.m.r. (CCl_4), δ (p.p.m.): 1.1-1.46 (m, 2H, C<u>H</u>$_2$-2'), 1.74 (t, J=3Hz, 1H, ≡C<u>H</u>), 1.9-2.24 (m, 4H, C<u>H</u>$_2$-1', C<u>H</u>$_2$-3'), 3.88 (t, J=6Hz, 1H, C<u>H</u>), 7.04-7.48 (m, 6H, Ar<u>H</u>), 7.54-7.72 (m, 2H, Ar<u>H</u>).

^{13}C n.m.r. ($CDCl_3$): δ (p.p.m.): 18.4 (CH_2), 24.0 (CH_2), 31.6 (CH_2), 46.7 (CH), 69.4 (≡CH), 83.9 (-C≡), 119.6, 124.0,

126.7, 126.8 (aromatic CH), 140.9, 146.8 (aromatic C).

I.r. (cm^{-1}) (melt): 3300 s (≡CH), 3060 s, 2930 s, 2860 s, 2120 m (C≡C), 740 s.

Analysis: found C, 92.8; H, 6.8%

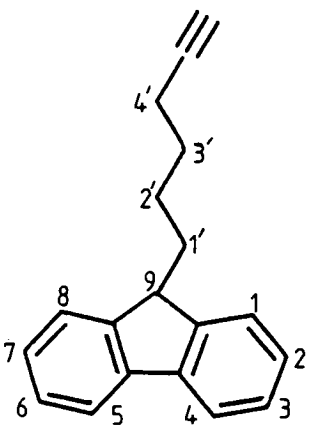
$C_{18}H_{16}$ requires C, 93.1; H, 6.9%

m.s. (m/e): 232 (M^+), 217, 204, 191, 178, 165.

5.4.9 9-(Hex-5'-ynyl)fluorene (106)

Halide: 1-iodohex-5-yne Yield: 22%

M.p. 20-21° lit. oil [54]



^1H* n.m.r. ($CDCl_3$) δ (p.p.m.): 1.38 (m, 2H, CH_2-2'), 1.57 (quintet, J=7.2Hz, 2H, CH_2-3'), 1.97 (t, J=2.7Hz, 1H, ≡CH), 2.08 (m, 2H, CH_2-1'), 2.17 (t of d, J=7.2, 2.7Hz, 2H, CH_2-4'), 4.04 (t, J=5.9Hz, 1H, CH), 7.34-7.45 (2t, J=7.5Hz, 4H, H_2,H_3,H_6,H_7), 7.58 (d, J=7.5Hz, 2H, H_1,H_8 or H_4,H_5), 7.82 (d, J=7.5Hz, 2H, H_1,H_8 or H_4,H_5).

^{13}C n.m.r. ($CDCl_3$) δ (p.p.m.): 17.9 (CH_2), 24.6 (CH_2), 28.4 (CH_2), 32.2 (CH_2), 47.0 (CH), 68.2 (≡CH), 84.1 (-C≡), 119.5, 124.0, 126.6 (aromatic CH, line at 126.6 for 4 CH), 140.8, 147.0 (aromatic C).

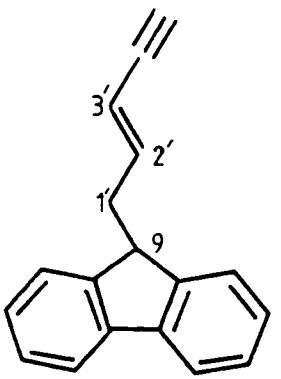
I.r. (cm^{-1}) (melt): 3300 s (≡CH), 3060 s, 2940 s, 2860 s, 740 s.

m.s. (m/e): 246.142489 (M^+, $C_{19}H_{18}$ requires 246.140844), 178, 165.

5.4.10 E-9-(Pent-2'-en-4'-ynyl)fluorene (107)

Halide: E-1-bromopent-2-en-4-yne Yield: 13% (silica chromatography)

M.p.: 58-63° (isopropanol)

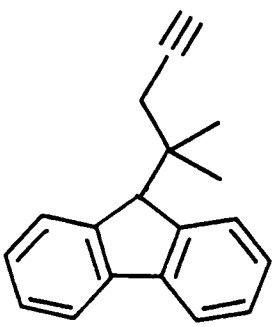


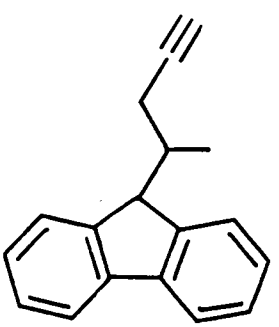
^{1}H n.m.r. ($CDCl_3$), δ(p.p.m.): 2.70 (t and d, J=7Hz, 1.5Hz, 3H, CH_2 and ≡CH), 3.95 (t, J=7Hz, 1H, CH-9), 5.40 (d with fine structure, J=17Hz (trans), 1H, CH-3'), 6.15 (d of t, J=17Hz, 7Hz, 1H, CH-2'), 7.14-7.56 (m, 6H, ArH), 7.68-7.78 (m, 2H, ArH).

^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.): 36.7 (CH_2), 46.5 (CH), 76.2 (≡CH), 82.0 (-C≡), 110.9 (=CH), 119.8, 124.3, 126.8, 127.1 (aromatic CH), 140.8 (aromatic C), 143.2 (=CH), 146.0 (aromatic C).

m.s. (m/e): 230.109433 (M^+, $C_{18}H_{14}$ requires 230.109545), 165.

5.4.11 Attempted Preparation of 9-(1',1'-Dimethylbut-3'-ynyl)fluorene (109) and 9-(1'-Methylbut-3'-ynyl)-fluorene (108).





Neither 2-bromopent-4-yne nor 2-bromo-2-methylpent-4-yne could be made to react with 9-lithiofluorene even after heating under reflux for 7 h in the case of 2-bromopent-4-yne.

5.5 Acetylenic Derivatives of Indene

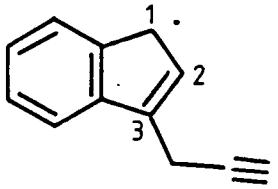
The preparation of these compounds was accomplished either by phase transfer catalysed reaction between the alkynyl halide and the indene in the presence of potassium hydroxide (method A) or alternatively treating the halide with the sodium salt of the indene in liquid ammonia (method B). All these compounds were colourless or pale yellow oils.

Method A: The indene and an equimolar or slight excess of the alkynyl halide were added to aqueous potassium hydroxide (50 g, 50%) and benzyltrimethylammonium chloride (0.2 g). The mixture was then vigorously stirred at room temperature, and in some cases with gentle warming, until reaction was complete as shown by ^{1}H n.m.r. spectroscopy. The reaction mixture was then diluted with water and extracted into light petroleum (2x125 ml). The combined organic extracts were dried, the solvent removed, and the residue was purified by chromatography on alumina or silica or by preparative g.l.c.

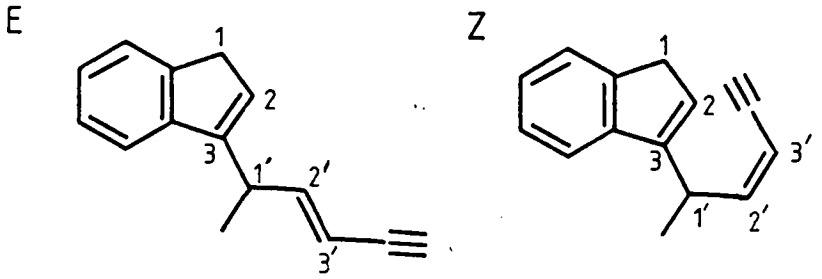
Method B: Sodamide was prepared by dissolving sodium (0.06 mol) in liquid ammonia (300 ml) in the presence of a little ferric nitrate. The indene (1 molar equivalent) was added and the mixture stirred for 1 h to prepare the indenyl anion. The alkynyl halide (1.1 molar equivalent) was then added dropwise with stirring and the ammonia allowed to evaporate. Water was then added and the mixture extracted into ether (3x150 ml). The ether extracts were dried, the solvent removed, and the products purified by chromatography on silica or alumina.

5.5.1 3-Propargylindene (24) was prepared from indene and propargyl bromide by method A (7 h at room temperature). Chromatography on silica gave 3-propargyl indene (39%) identical with that obtained previously [22].

^{1}H n.m.r. ($CDCl_3$), δ (p.p.m.): 2.08 (t, J=3Hz, 1H, ≡C<u>H</u>), 3.20 (bs, 2H, C<u>H</u>$_2$-C≡), 3.32 (bs, 2H, C<u>H</u>$_2$-1), 6.36 (t, J=2Hz, C<u>H</u>-2), 7.0-7.5 (m, 4H, Ar<u>H</u>).



5.5.2 E and Z-3-(1'-Methylpent-2'-en-4'-ynyl) indene (117 and 118)



These compounds were obtained (25%) as a mixture in the ratio 2.2:1 from E and Z-2-bromohex-3-en-5-yne and indene by method A (3 h at room temperature). Purification was effected by chromatography on alumina. The ^{1}H n.m.r. spectrum is in agreement with that reported previously.[22]

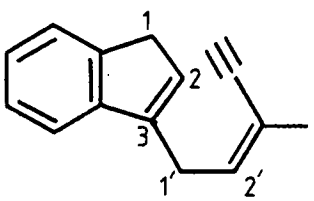
^{1}H n.m.r. ($CDCl_3$), δ (p.p.m.): E isomer:- 1.34 (d, J=7Hz, 3H, C<u>H</u>$_3$), 2.60 (d, J=2.5Hz, 1H, ≡C<u>H</u>), 3.22 (bs, 2H, C<u>H</u>$_2$), 3.50 (m, J=7Hz, 1H, C<u>H</u>-1'), 5.40 (d of d of d, J=16Hz, 1Hz, 1Hz, 1H, C<u>H</u>-3'), 6.14 (bs, 1H, C<u>H</u>-2), 6.32 (d of d, J=16Hz, 7Hz, 1H, C<u>H</u>-2'), 6.9-7.5 (m, 4H, ArH).

Z isomer:- 1.40 (d, J=7Hz, 3H, $C\underline{H}_3$), 3.06 (d, J=2.5 Hz, 1H, $\equiv C\underline{H}$), 3.25 (bs, 1H, $C\underline{H}_2$), 4.10 (m, 1H, $C\underline{H}$-1'), 5.41 (d of d, J=11Hz, 2.5Hz, 1H, $C\underline{H}$-3'), 5.89 (bt, J=11Hz, 1H, $C\underline{H}$-2'), 6.14 (bs, 1H, $C\underline{H}$-2), 6.9-7.5 (m, 4H, Ar$\underline{H}$).

5.5.3 Z-(3'-Methylpent-2'-en-4'-ynyl)indene (119) was prepared together with a trace of the E isomer from indene and 1-bromo-3-methylpent-2-en-4-yne by method A (4 h at room temperature). The Z isomer (63%) was isolated by recrystallisation from methanol.

m.p. 38-41° lit. m.p. 42-43°

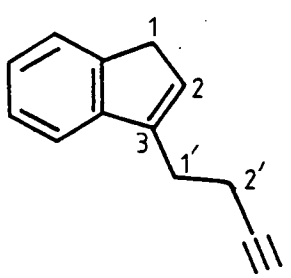
^{1}H n.m.r. ($CDCl_3$), δ (p.p.m.):



1.91 (bs, 3H, $C\underline{H}_3$), 3.08 (s, 1H, $\equiv C\underline{H}$), 3.28 (bs, 2H, $C\underline{H}_2$-1), 3.49 (bd, J=7Hz, 2H, CH_2-1'), 5.98 (bt, J=7Hz, 1H, $C\underline{H}$-2'), 6.14 (bs, 1H, $C\underline{H}$-2), 7.0-7.4 (m, 4H, Ar$\underline{H}$).

5.5.4 3-(But-3'-ynyl)indene (113) was prepared from indene and 1-bromobut-3-yne by method B. Chromatography on alumina gave the indene (45%). When method A was attempted the reaction mixture heated up rapidly on addition of the bromide and no product was isolated.

^{1}H n.m.r. (CCl_4), δ (p.p.m.): 1.81 (t, J=2Hz, 1H, $\equiv C\underline{H}$), 2.38-2.60 (m, 2H, $C\underline{H}_2$), 2.54-2.88 (m, 2H, $C\underline{H}_2$), 3.25 (m, 2H, $C\underline{H}_2$), 6.17 (m, 1H, $=C\underline{H}$), 6.96-7.40 (m, 4H, ArH).



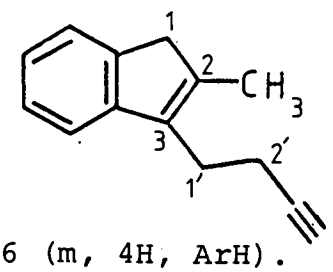
^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.): 17.2 (CH_2), 26.8 (CH_2), 37.5 (CH_2, C-1), 68.6 (≡CH), 83.9 (-C≡), 118.5 (olefinic CH), 123.6, 124.5, 125.8, 128.2 (aromatic CH), 142.2, 144.1, 144.7 (aromatic and olefinic C).

I.r. (cm^{-1}): 3300 s (≡CH), 3040 w, 2920 s, 2125 w (C≡C), 1615 w (C=C), 770 s, 720 s.

m.s. (m/e): 168.094475 (M^+, $C_{13}H_{12}$ requires 168.093896), 129, 115.

5.5.5 3-(But-3'-ynyl)-2-methylindene (114) was prepared from 2-methylindene and 1-bromobut-3-yne by method B. Chromatography on alumina gave the indene (25%).

^1H n.m.r. ($CDCl_3$), δ (p.p.m.): 1.88 (t, J=3Hz, 1H, ≡C<u>H</u>), 2.03 (s, 3H, C<u>H</u>$_3$), 2.34 (t of d, J=7Hz, 3Hz, 2H, C<u>H</u>$_2$-2'), 2.73 (t, J=7Hz, 2H, C<u>H</u>$_2$-1'), 3.20 (s, 2H, C<u>H</u>$_2$-1), 6.94-7.36 (m, 4H, ArH).

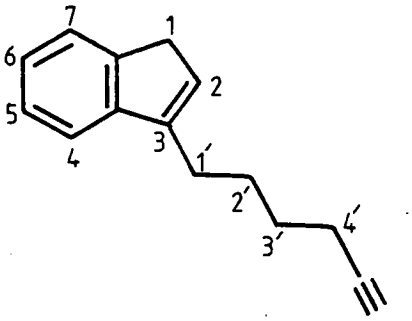


^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.): 13.8 (CH_3), 17.8 (CH_2), 24.4 (CH_2), 42.4 (CH_2, C-1), 68.4 (≡CH), 84.0 (-C≡), 117.7, 123.0, 123.5, 125.8 (aromatic CH), 135.1, 139.7, 142.3, 145.8 (aromatic and olefinic C).

I.r. (cm^{-1}): 3300 s (≡CH), 3040 (CH), 2920 s (CH), 2120 m (C≡C), 1630, 1605 m (C=C), 760 s, 720 s.

m.s. (m/e): 182.112080 (M^+, $C_{14}H_{14}$ requires 182.109545), 167, 143, 128, 115.

5.5.6 3-(Hex-5'-ynyl)indene (115) was prepared from indene and 1-iodohex-5-yne by method A (3 h at 60°). Chromatography on alumina gave the indene (65%).



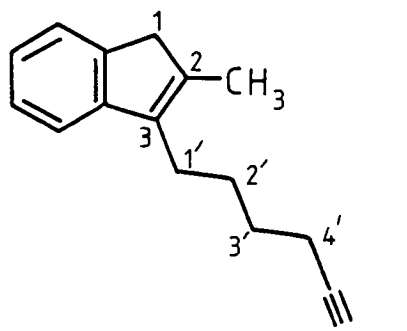
$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 1.69 (m, 2H, $C\underline{H}_2$-3'), 1.86 (m, 2H, $C\underline{H}_2$-2'), 1.99 (t, J=2.7Hz, 1H, ≡$C\underline{H}$), 2.30 (t of d, J=7.1Hz, 2.7Hz, 2H, $C\underline{H}_2$-4'), 2.61 (t of d, J=7.6Hz, 1.7Hz, 2H, $C\underline{H}_2$-1'), 3.36 (d, J=1.9Hz, 2H, CH_2-1), 6.25 (m, J=1.7Hz, 1H, =CH), 7.24 (t, J=7.3Hz, 1H, $\underline{H}_5$ or $\underline{H}_6$), 7.33 (t, J=7.3Hz, 1H, $\underline{H}_5$ or $\underline{H}_6$), 7.40 (d, J=7.3Hz, 1H, $\underline{H}_4$ or $\underline{H}_7$), 7.49 (d, J=7.3Hz, 1H, $\underline{H}_4$ or $\underline{H}_7$).

^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.): 18.1 (CH_2), 26.8 (CH_2), 27.0 (CH_2), 28.1 (CH_2), 37.5 (CH_2, C-1), 68.2 (≡CH), 84.2 (-C≡), 118.7, 123.5, 124.3, 125.8, 127.6 (aromatic and olefinic CH), 143.9, 144.3, 145.2 (aromatic and olefinic C).

I.r. (cm^{-1}): 3300 s (C≡CH), 3020 w (CH), 2940 s (CH), 2120 w (C≡C) 1610 w (C=C), 965 m, 770 s, 720 s.

m.s. (m/e): 196.124502 (M^+, $C_{15}H_{16}$ requires 196.125194), 181, 168, 129, 115.

5.5.7 <u>3-(Hex-5'-ynyl)-2-methylindene (116)</u> was prepared from 2-methylindene and 1-iodohex-5-yne by method A (7 h at 65°). Chromatography on alumina gave the indene (52%).



^1H n.m.r. ($CDCl_3$): δ (p.p.m.): 1.60 (m, 4H, 2x$C\underline{H}_2$), 1.88 (t, J=3Hz, 1H, ≡$C\underline{H}$), 2.01 (s, 3H, $C\underline{H}_3$), 2.17 (t of d, J=7Hz, 3Hz, 2H, $C\underline{H}_2$-4'), 2.50 (bt, J=7Hz, 2H, $C\underline{H}_2$-1'), 3.21 (s, 2H, $C\underline{H}_2$-1), 6.96-7.36 (m, 4H, Ar$\underline{H}$).

^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.): 13.9 (CH_3), 18.2 (CH_2),

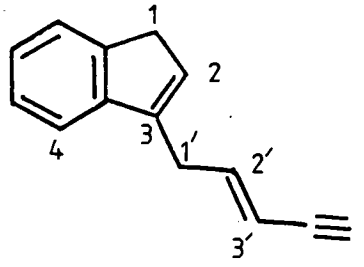
24.6 (CH_2), 27.6 (CH_2), 28.3 (CH_2), 42.5 (CH_2, C-1), 68.2 (≡CH), 84.3 (-C≡), 118.0, 123.0, 123.4, 125.9 (aromatic CH), 136.7, 138.3, 142.5, 146.5 (aromatic and olefinic C).

I.r. (cm^{-1}): 3300 s (≡CH), 3030 w (CH), 2940 s (CH), 2120 w (C≡C), 1610 w (C=C), 765 s, 720 s.

m.s. (m/e): 210.140030 (M^+, $C_{16}H_{18}$ requires 210.140844), 195, 143, 115.

5.5.8 E-3-(Pent-2'-en-4'-ynyl)indene (121) was prepared from indene and 1-bromopent-2-en-4-yne by method A (0.5 h at room temperature). Chromatography on silica gave the indene (25%).

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.81 (d, J=1.7Hz, 1H, ≡CH), 3.34 (d, J=1.7Hz, 2H, $C\underline{H}_2$-1), 3.38 (d of m, J=6.7Hz, 2H, CH_2-1'), 5.59 (d of m, J=15.9Hz, 1H, C<u>H</u>-3'), 6.26 (bs, 1H, C<u>H</u>-2), 6.46 (d of t, J=15.9Hz, 6.7Hz, 1H, C<u>H</u>-2'), 7.2-7.4 (m, 3H, Ar<u>H</u>), 7.44 (d, J=6.6Hz, 1H, H_4).

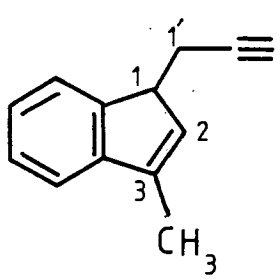


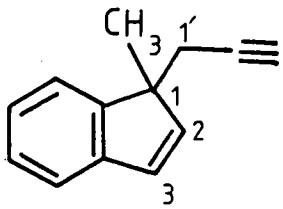
^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.): 31.3 (CH_2), 37.7 (CH_2), 76.4 (≡CH), 82.1 (-C≡), 110.3 (=CH), 119.0, 123.7, 124.7, 126.0, 129.6 (aromatic CH), 141.1 (aromatic C), 142.9 (=CH), 144.3, 144.6 (aromatic C).

I.r. (cm^{-1}): 3300 s (≡CH), 3020 m (CH), 2900 m (CH), 2100 w (C≡C), 1615 s, 1630 w (C=C), 957 s, 770 s, 720 s.

m.s. (m/e): 180.092230 (M^+, $C_{14}H_{12}$ requires 180.093896), 165, 115.

5.5.9 3-Methyl-1-propargylindene (111) and 1-Methyl-1-propargylindene (110)





These compounds were obtained from 3-methylindene (88) and propargyl bromide as a mixture, the proportions of each depending on the method of preparation.

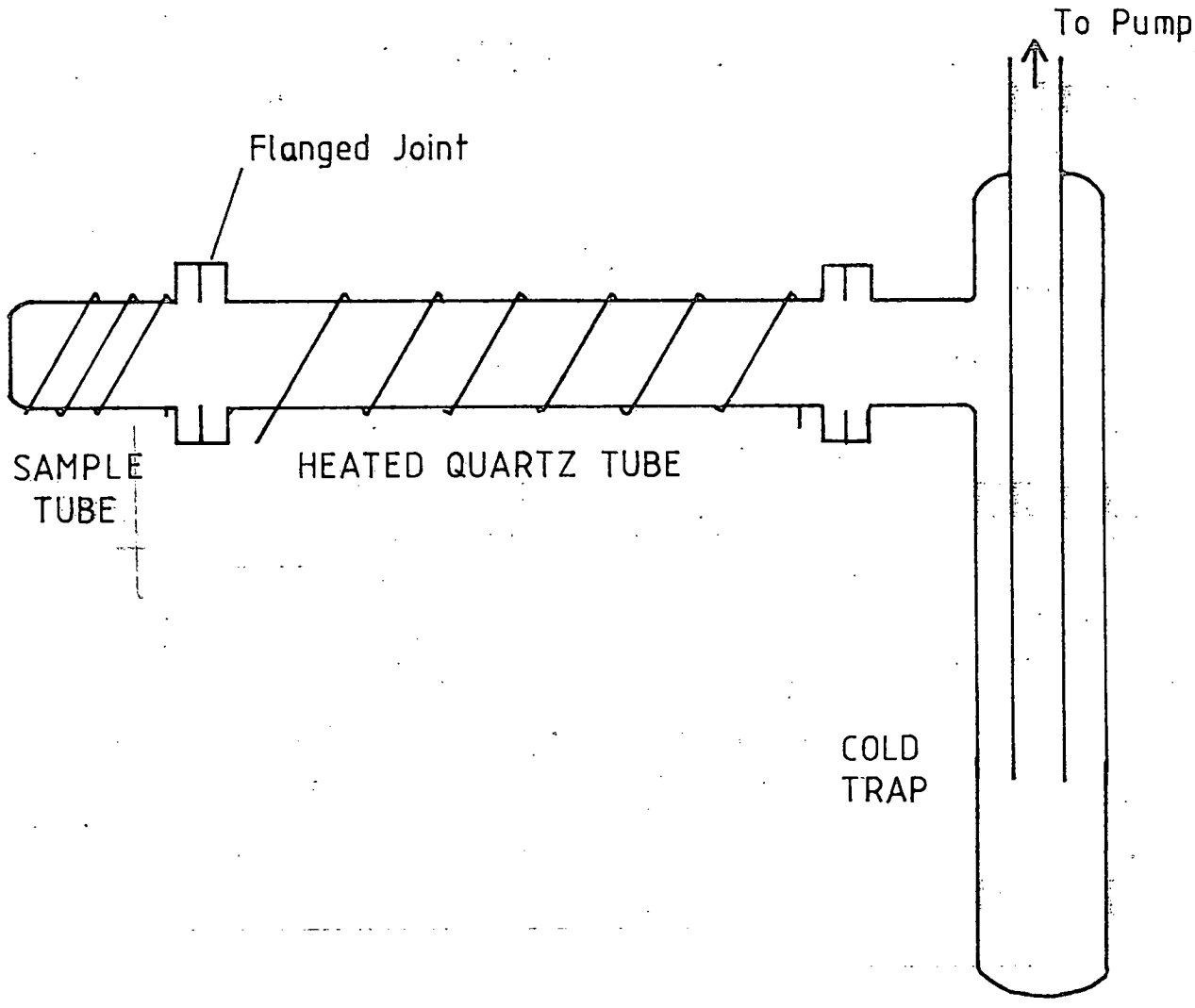
1. Method A: Stirring the reagents for 3 h at 70-75°C and removal of the unreacted 3-methylindene gave the two compounds (111) and (110) in the ratio 1:4 as shown by the ^{1}H n.m.r. spectrum. Silica chromatography, eluting with light petroleum, gave 1-methyl-1-propargyl indene (14%), and a small amount of 3-methyl-1-propargylindene.

2. Method B: The products (111) and (110) were obtained in the ratio 3:1. 3-Methyl-1-propargylindene (24%) was isolated from this mixture by preparative g.l.c. (5% N.P.G.S., 135°C).

3, Phenyl Lithium was used to generate the 3-methylindenyl anion by the method described on p.84 . The reaction with propargyl bromide produced a mixture of the compounds (111) and (110) in the ratio 4.5:1.

5.5.9.1 1-Methyl-1-propargylindene (110)

^{1}H n.m.r. ($CDCl_3$), δ (p.p.m.): 1.27 (s, 3H, $C\underline{H}_3$),



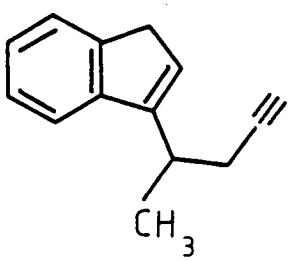
PYROLYSIS APPARATUS

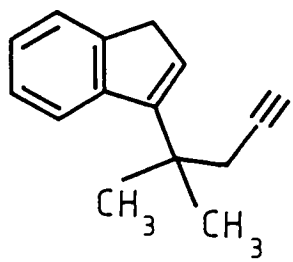
1.84 (t, J=3Hz, 1H, ≡C<u>H</u>), 2.23 (d of d, J=8Hz, 3Hz, 1H, from C<u>H</u>$_2$), 2.48 (d of d, J=8Hz, 3Hz, 1H, from C<u>H</u>$_2$), 6.39 (d, J=5Hz, 1H, <u>H</u>$_2$), 6.62 (d, J=5Hz, 1H, <u>H</u>$_3$), 7.0-7.4 (m, 4H, Ar<u>H</u>).

5.5.9.2 <u>3-Methyl-1-propargylindene (111)</u>

^{1}H n.m.r. ($CDCl_3$), δ (p.p.m.): 2.00 (t, J=3Hz, 1H, ≡C<u>H</u>), 2.11 (t, J=2Hz, 3H, C<u>H</u>$_3$), 2.25 (d of d of d, J=18Hz, 8Hz, 3Hz, 1H, from C<u>H</u>$_2$), 2.59 (d of d of d, J=18Hz, 8Hz, 3Hz, 1H, from C<u>H</u>$_2$), 3.52 (m, 1H, C<u>H</u>), 6.22 (m, 1H, =C<u>H</u>), 7.10-7.58 (m, 4H, Ar<u>H</u>).

5.5.10 <u>3-(1'-Methylbut-3'-ynyl)indene (122) and 3-(1',1'-Dimethylbut-3'-ynyl)indene (123)</u> could not be prepared by method A (heating 2-methyl-2-bromopent-4-yne with hydroxide solution produced the corresponding alcohol). Method B will not work because of reaction between the bromides and ammonia and so the phenyl lithium method (p 84) was attempted but no products were isolated .





5.6 Pyrolysis of Acetylenes

Samples (50 mg - 1 g) were passed through a hot (electrical heated), quartz tube (packed lightly with quartz wool), under

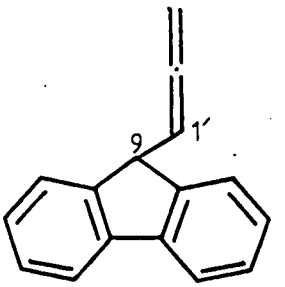
high vacuum (<0.005 mmHg), and collected in a trap cooled by ice water or liquid nitrogen. The products were obtained as pale yellow oils except in the case of 9,9'-bifluorenyl (128) which condensed as a solid immediately after the hot tube due to its high melting point. In all cases 90% or more of the sample passed through the hot tube leaving only a trace of tarry material behind.

5.6.1 Rearrangement of 9-Propargylfluorene (97)

Pyrolysis at 400° gave unchanged starting material. At temperatures from 500° to 650° pyrolysis gave fluorene, 9,9'-bifluorenyl (128) and 9-allenefluorene (129) in varying proportions (see Table 3). At 700° only fluorene and 9,9'-bifluorenyl were obtained. The allene could not be isolated from the reaction mixture by preparative g.l.c. and underwent rearrangement during chromatography on alumina (p.110) but was identified from the $^1H^*$ n.m.r. spectrum of the mixture by its distinctive resonances. 9,9'-Bifluorenyl was identified by comparison of its $^1H^*$ n.m.r. spectrum with that of an authentic sample kindly supplied by Professor N. Campbell and by a mixed melting point determination.

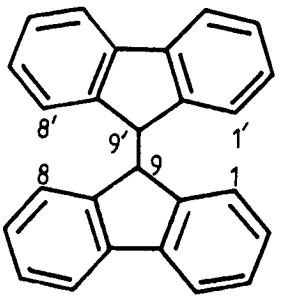
5.6.1.1 9-Allenylfluorene (129)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 4.49 (bd, J=8.1Hz, 1H, C<u>H</u>-9), 4.87 (d of d, J=6.6Hz, 2Hz, 2H, =C<u>H</u>$_2$), 5.15 (d of t, J=8.1Hz, 6.6Hz, 1H, C<u>H</u>-1'), 7-8 (m, 8H, Ar<u>H</u>).



5.6.1.2 9,9'-Bifluorenyl (128)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 4.83 (s, 2H, CH-9,9'), 6.96 (bs, 4H, CH-1,8,1',8'), 7.09 (t, J=7.7Hz, 4H, CH-2,7,2',7' or 3,6,3',6'), 7.27 (t, J=7.7Hz, 4H, CH-3,6,3',6' or 2,7,2',7'), 7.64 (d, J=7.7Hz, 4H, CH, 4,5,4',5').



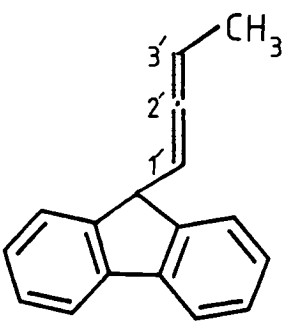
M.p.: isolated 236-238° (from carbon tetrachloride), authentic 236-238°, mixture 236-238°, lit.246° [60].

5.6.2 Rearrangement of 9-(1'-Methylprop-2'-ynyl)fluorene (99)

Pyrolysis at 500, 550 and 600° gave mixtures of fluorene, 9,9'-bifluorenyl (123) and 9-(buta-1',2'-dienyl)fluorene (130) (see Table 3). The allene (25%) was isolated from the mixture by preparative g.l.c. (5% N.P.G.S., 160°).

.6.2.1 9-(Buta-1',2'-dienyl)fluorene (130)

^1H n.m.r. (CCl_4) δ (p.p.m.): 2.74 (d of d, J = 6Hz, 3Hz, 3H, CH_3), 4.39 (bd, J=8Hz, 1H, CH-9), 4.86-5.34 (m, 2H, CH-1',3'), 7.7-7.76 (m, 8H, ArH).



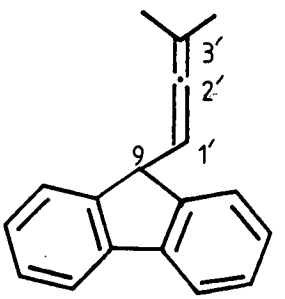
5.6.3 Rearrangement of 9-(1',1'-Dimethylprop-2'-ynyl)-fluorene (100)

Pyrolysis at 500, 550 and 600° produced mixtures of fluorene, 9,9'-bifluorenyl and 9-(3'-methylbuta-1',2'-dienyl)-fluorene (101) (see Table 3). The allene could not be

separated from the mixture containing fluorene but was identified from the ^1H n.m.r. spectrum of the mixture.

5.6.3.1 9-(3'-Methylbuta-1',2'-dienyl)fluorene (101)

^1H n.m.r. ($CDCl_3$), δ (p.p.m.): 1.75 (d, J=2Hz, 6H, 2xCH_3), 4.40 (d, J=8Hz, 1H, C<u>H</u>-9), 4.75-5.15 (m, J=8Hz, 2Hz, 1H, C<u>H</u>-1'), 7.1-7.8 (m, 8H, Ar<u>H</u>).

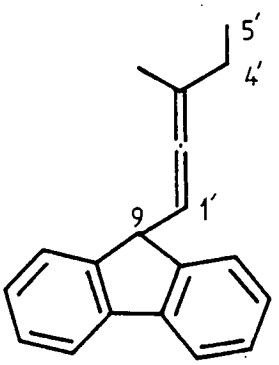


5.6.4 Rearrangement of 9-(1'-Ethyl-1'-methylprop-2'-ynyl)-fluorene (102)

Pyrolysis at 600° gave a mixture of fluorene and 9-methylfluorene in the ratio 1:2, as shown by comparison of the $^1H^*$ and $^{13}C^*$ n.m.r. spectra with published data[75] Pyrolysis at 500° produced a mixture of unreacted acetylene (35%), 9-(3'-methylpenta-1',2'-dienyl)fluorene (103) (35%), fluorene (4%), 9-methylfluorene (8%) and 9-9'-bifluorenyl (20%). The identification and proportions of each being deduced from the $^1H^*$ n.m.r. spectrum.

.6.4.1 9-(3'-Methylpenta-1',2'-dienyl)fluorene (103)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 1.13 (t, J=7.3Hz, 3H, C<u>H</u>$_3$-5'), 1.86 (d, J=2.7Hz, 3H, C<u>H</u>$_3$), 2.06 (q of d, J=7.3Hz, 2.9Hz, C<u>H</u>$_2$), 4.50 (d, J=8.3Hz, 1H, C<u>H</u>-9), 5.08 (m, 1H, C<u>H</u>-1'), 7-8 (aromatic C<u>H</u>).



5.6.5 Rearrangement of 9-(Pent-4'-ynyl)fluorene (105)

No reaction occurred at 500 or 600°. At 650° the product contained unreacted acetylene, fluorene and bifluorenyl in the ratio 3:2:1. Pyrolysis at 700° gave largely unidentified aromatic products together with fluorene and bifluorenyl in low yield.

5.6.6 Rearrangement of 9-(Hex-5'-ynyl)fluorene (106)

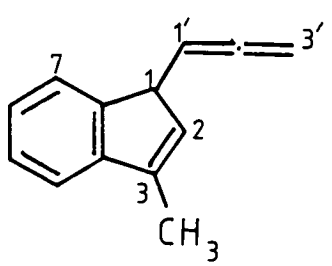
The compound did not react below 650°. At this temperature the product consisted largely of unreacted starting material with a little fluorene and bifluorenyl. At 700° unidentified aromatic compounds predominated together with fluorene and bifluorenyl in the ratio 12:1.

5.6.7 Rearrangement of 1-Methyl-1-propargylindene (110)

At 500° 1-methyl-1-propargylindene gave mostly unreacted starting material. At 550° the $^1H^*$ n.m.r. spectrum of the crude pyrosylate shows the presence of three compounds: 1-methyl-1-propargylindene, 1-allenyl-3-methylindene (132) and 3-allenyl-1-methylindene (133) present in the ratio 1:4.2:5. 1-Allenyl-3-methylindene (30%) was isolated pure by preparative g.l.c. (5% N.P.G.S. 130°).

.6.7.1 1-Allenyl-3-methylindene (132)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.15 (t, J=1.8Hz, 3H, $C\underline{H}_3$), 4.0 (m, 1H, $C\underline{H}$-1), 4.80 (d of m, J=6.6Hz, 2H, $C\underline{H}$-3'), 5.03 (d of t, J=6.6, 8.1Hz, 1H, $C\underline{H}$-1').

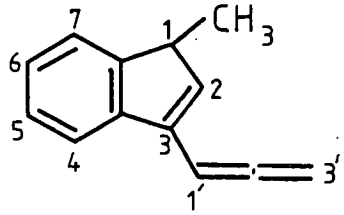


7.2-7.3 (m, 3H, Ar$\underline{H}$), 7.44 (d, J=7.3Hz, 1H, Ar$\underline{H}$-7).

$^{13}C^{*}$ n.m.r. ($CDCl_3$), δ (p.p.m.): 12.7 (CH_3), 48.4 (CH), 75.7 (=·=CH_2), 89.0 (HC=·=), 118.9, 123.5, 125.0, 126.7, 126.9, 132.6 (aromatic and olefinic CH), 139.6, 145.3, 146.9 (aromatic C), 209.3 (=C=).

5.6.7.2 3-Allenyl-1-methylindene (133)

$^{1}H^{*}$ n.m.r. ($CDCl_3$), δ (p.p.m.):



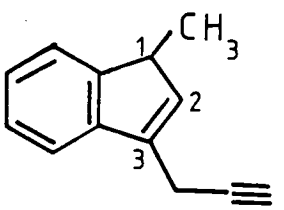
1.38 (d, J=7.6Hz, 3H, C$\underline{H}_3$), 3.55 (m, 1H, C$\underline{H}$-1), 5.24 (d of d of d, J=7.0Hz, 2.0Hz, 1.5Hz, 2H, C$\underline{H}_2$-3'), 6.38 (t of d, J=7.0Hz, 0.7Hz, 1H, C$\underline{H}$-1'), 6.41 (bs, 1H, C$\underline{H}$-2), 7.2-7.4 (m, 2H, $\underline{H}_5$, $\underline{H}_6$), 7.52 (d, J=7.3Hz, 1H, $\underline{H}_7$), 7.92 (d, J=7.4Hz, 1H, $\underline{H}_4$).

5.6.8 Rearrangement of 3-Methyl-1-propargylindene (111)

At 550° this compound gave a complex mixture containing five compounds which were identified from the $^{1}H^{*}$ n.m.r. spectrum of the mixture as follows: 3-methyl-1-propargylindene (46%), 1-methyl-3-propargylindene (112) (22%), 1-allenyl-1-methylindene (134) (12%), 1-allenyl-3-methylindene (132) (10%) and 3-allenyl-1-methylindene (133) (10%). No attempt was made to separate this mixture and the $^{1}H^{*}$ n.m.r. spectral data given below has been taken from that of the mixture.

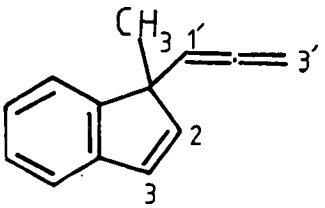
5.6.8.1 1-Methyl-3-propargylindene (112)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.):
1.33 (d, J=7.6Hz, $C\underline{H}_3$), 2.04 (t, J=2.4Hz, ≡C$\underline{H}$), 3.46 (m, C$\underline{H}$-1'), 3.56 (m-C$\underline{H}$-1), 6.45 (m, $C\underline{H}_2$-1').



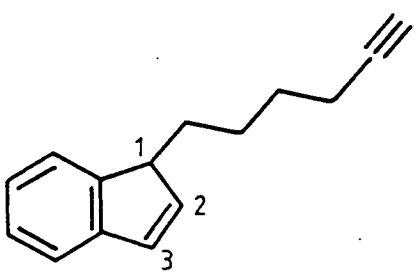
5.6.8.2 1-Allenyl-1-methylindene (134)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.):
1.42 (s, $C\underline{H}_3$), 4.87 (d of d, J=6.6Hz, 1.9Hz, $C\underline{H}_2$-3'), 5.09 (t, J=6.6Hz, C$\underline{H}$-1'), 6.37 (d, J=5.4Hz, C$\underline{H}$-2), 6.70 (d, J=5.4Hz, C$\underline{H}$-3).



5.6.9 Rearrangement of 3-(Hex-5'-ynyl)indene (115)

At 600° this compound gave mostly unreacted starting material with a small amount (<5%) of another compound, possibly 1-(Hex-5'-ynyl)indene (142) as indicated by resonances at 6.5 δ(d of d, J=6, 1Hz), and 6.85 (d of d, J=6, 1Hz) in the ^1H n.m.r. spectrum of the mixture. At 650° and 700° a complex mixture was produced which could not be separated and whose $^1H^*$ n.m.r. spectrum did not allow the identification of any possible products.



5.6.10 Rearrangement of 3-(Hex-5'-ynyl)-2-methylindene (116)

Pyrolysis at 600°, 650° and 700° produced complex

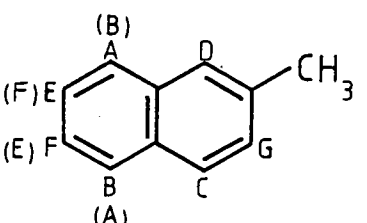
mixtures whose ^1H n.m.r. spectra showed resonances at 2.2, 3.3, 6.5δ attributable to 2-methylindene. It was not possible even to partially separate the mixtures.

5.6.11 Rearrangement of 3-(But-3'-ynyl)-2-methylindene (114)

At 600° unreacted starting material was largely obtained. Pyrolysis at 700° yielded a mixture of 2-methylnaphthalene (137) and 1,2-benzo-4-methylfulvene (138) together with polymeric material. On standing in solution at room temperature the benzofulvene was converted to a mixture of polymer and 2-methylnaphthalene. The naphthalene and benzofulvene were separated from polymer by preparative g.l.c. (5% N.P.G.S., 160°, 40%). The naphthalene was identified by comparison of the $^1H^*$ n.m.r. spectrum of the mixture with that of an authentic sample and the benzofulvene by analogy of the ^1H n.m.r. spectrum with that of benzofulvene[74].

5.6.11.1 2-Methylnaphthalene

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.):

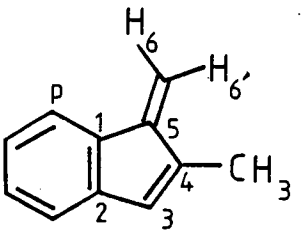


(2.52, s, $\underline{CH}_3$), 7.32 (d of d, J=8.4Hz, 1.8Hz, $\underline{H}_G$), 7.42 (quintet of d, J=7.0Hz, 1.5Hz, H_E, H_F), 7.61 (bs, $\underline{H}_D$), 7.74 (d, J=8.3Hz, $\underline{H}_C$, 7.75 (d, J=7.9Hz, $\underline{H}_B$ or $\underline{H}_A$), 7.79 (d, J=7.7Hz, $\underline{H}_A$ or $\underline{H}_B$).

5.6.11.2 1,2-Benzo-4-methylfulvene (138)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.):

2.14 (d, J=1.5Hz, $C\underline{H}_3$), 5.67 (bs, H_6), 6.00 (d, J=1.7Hz, $H_{6'}$),6.55 (m, H_3), 7.72 (m, 3xAr$\underline{H}$), 7.49 (d of d, J=7.3Hz, 1.1Hz, $\underline{H}_p$).



5.6.12 Rearrangement of 3-(But-3'-ynyl)indene (113)

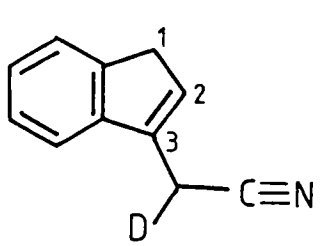
At 500° starting material was recovered virtually unchanged. Pyrolysing at 600° and 700° gave complex mixtures of products which could not be separated.

5.6.13 Rearrangement of O-Deuterioindan-1-ylidenecyanoacetic Acid (178)

Deuteration of indan-1-ylidenecyanoacetic acid (144) was effected by dissolving the acid (100 mg) in dry tetrahydrofuran (5 ml) in the pyrolysis inlet tube, and adding a twofold excess of deuterium oxide. The solution was then evaporated to dryness under reduced pressure, fitted to the pyrolysis apparatus and sublimed through as for the non deuterated compound (p.74). The ^1H n.m.r. spectrum shows a reduction of about 50% in the intensity of one of the CH_2 multiplets which was shown by $^{13}C^*$ n.m.r. to be the CH_2 of the acetonitrile function.

5.6.13.1 1'-Deuterio-3-cyanomethylindene (179)

^1H n.m.r. ($CDCl_3$), δ (p.p.m.): 3.4 (m, 2H, $C\underline{H}_2$-1), 3.6(m, 1H, C$\underline{H}$D-1'), 6.6 (m, 1H, =CH), 7.1-7.6 (m, 4H, Ar$\underline{H}$).



$^{13}C^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 16.6 (J=19.5Hz, CHD-1'), 37.7 (CH_2-1), 116.8 (CN), 118.3, 124.0, 125.5, 126.3, 131.9 (aromatic and

olefinic CH), 132.9, 142.5, 143.9 (aromatic and olefinic C).

5.6.14 Rearrangement of 3-Cyanomethylindene (143)

Pyrolysis at 600° gave unreacted starting material and 1-cyanomethylindene (147) (see p. 74) in the ratio 8:2.4 as shown by the ^{1}H n.m.r. spectrum.

5.6.15 Rearrangement of 9-(but-3'-ynyl)fluorene (104)

No reaction occurred at 500°. At 550° the product consisted largely of unreacted acetylene with a little fluorene. Pyrolysis at 600° gave a mixture of unidentified products containing some fluorene and unreacted acetylene.

5.7 Base Catalysed Rearrangement of Acetylenes and Allenes

Rearrangements of acetylenes were effected in one of two ways:-

I. Following the method of Truslove[22] the acetylene (0.1-0.5 g) was boiled under reflux in sodium ethoxide (50 ml, 2M), and the reaction followed by ^{1}H n.m.r. spectra. The reaction mixture was poured into water (50 ml) and the products extracted into petrol (3x50 ml). The organic extracts were combined, dried, and the solvent removed to give the crude products which were purified by chromatography on alumina.

II. Following the method of Ghera and Sprinzak[59] , the acetylene (0.1 g) was dissolved in 25 ml pyridine, cooled to -5°, and Triton B (benzyltrimethylammonium hydroxide, 0.1 ml, 40% solution in water) was added under a nitrogen atmosphere. A deep red/orange colour was produced indicating the formation of an anion. The reaction was then stirred for several hours at room temperature or heated under reflux for a short period. The mixture was poured into water and

extracted with ether (3x50 ml). The combined ether extracts were washed with dilute hydrochloric acid (100 ml, 10%) and then with aqueous sodium bicarbonate solution (100 ml, 10%). Drying the organic phase and removing the solvent gave the crude products, purified by alumina chromatography.

Allenes produced from the pyrolysis experiments (p.100) were readily rearranged by the following method:-

III. A solution of the allene or, where separation was not possible, of a mixture of the allene and acetylene (0.1-0.5 g) was stirred with basic alumina for 0.5 h. After filtering the mixture and washing the alumina with more solvent (ether or chloroform) the organic phases were combined and the solvent removed. The products were purified by chromatography on alumina.

The structures of the products of the above rearrangements were deduced from their $^{1}H^{*}$ n.m.r. spectra.

5.7.1 Rearrangement of 9-Propargylfluorene (97), 9-(1'-Methylprop-2'-ynyl)fluorene (99) and 9-(1',1'-Dimethylprop-2'-ynyl)fluorene (100)

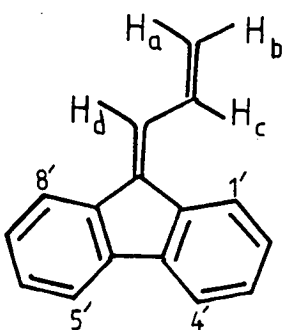
These compounds did not react with sodium ethoxide (method I) except after prolonged heating (>7 h) which produced some insoluble polymer. Method II also produced no reaction apart from polymer formation on prolonged heating.

5.7.2 Rearrangement of 9-Allenylfluorene (129)

On stirring with alumina (method III) 9-allenylfluorene (together with some fluorene) gave a virtually quantitative

yield of dibenzo-6-vinylfulvene (154) identified by its $^1H^*$ n.m.r. spectrum.

5.7.2.1 Dibenzo-6-vinylfulvene (154)

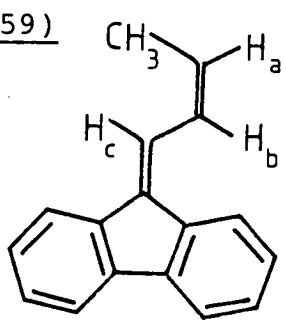


$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 5.60 (d of d of d, J=9.8Hz, 1.5Hz, 1.0Hz, 1H, $\underline{H}_b$), 5.70 (d of d of d, J=16.1Hz, 1.7Hz, 1.0Hz, 1H, $\underline{H}_a$), 7.17 (d, J=11.7Hz, 1H, $\underline{H}_d$), 7.26-7.38 (m, 4H, $\underline{H}$-2',3',6',7'), 7.54 (m, J=16.6Hz, 11.7Hz, 9.8Hz, 1H, $\underline{H}_c$), 7.67-7.74 (m, 3H, $\underline{H}$-4', 5', 8'), 7.94 (d, J=7.3Hz, 1H, $\underline{H}$-1').

5.7.3 Rearrangement of 9-(Buta-1',2'-dienyl)fluorene (130)

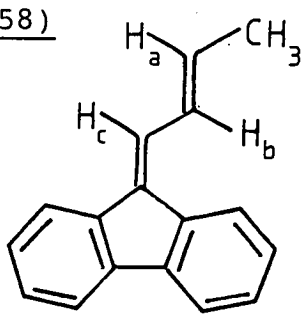
This allene rearranged readily (method III) to give a mixture of two compounds, E and Z-dibenzo-6-(prop-1'-enyl)-fulvene (158) and (159), in the ratios 1:5;E:Z as shown by the $^1H^*$ n.m.r. spectrum

5.7.3.1 Z-Dibenzo-6-(prop-1'-enyl)fulvene (159)



$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.04 (d of d, J=7.3Hz, 1.7Hz, 3H, $C\underline{H}_3$) 6.06 (d of q of d, J=10.8Hz, 7.3Hz, 1.3Hz, 1H, $\underline{H}_a$), 7-8 (m, 10H, Ar$\underline{H}$ and $\underline{H}_b$,$\underline{H}_c$).

5.7.3.2 E-Dibenzo-6-(prop-1'-enyl)fulvene (158)



$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.03 (d of d, J=6.9Hz, 1.5Hz, higher frequency d obscured by Z isomer, $C\underline{H}_3$), 6.23 (sextet, intensity ratio 1:3:4:4:3:1,

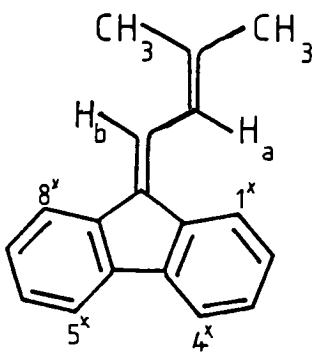
i.e. d of q, J=13.8Hz, 6.9Hz, 1H, $\underline{H}_a$), 7-8 (m, 10H, Ar$\underline{H}$ and $\underline{H}_b$,$\underline{H}_c$).

5.7.4 Rearrangement of 9-(3'-Methylbuta-1',2'-dienyl)-fulvene (101)

This compound rearranged readily (method III) to give dibenzo-6-(2'-methylprop-1'-enyl)fulvene (157), identified by its $^1H^*$ and $^{13}C^*$ n.m.r. spectra.

.7.4.1 Dibenzo-6-(2'-methylprop-1'-enyl)fulvene (157)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.04 (bs, 3H, C$\underline{H}_3$), 2.05 (bs, 3H, C$\underline{H}_3$), 7.04 (d of m, J=12.0Hz, 1H, $\underline{H}_a$), 7.27-7.37 (m, 4H, $\underline{H}$-2*,3*,6*,7*), 7.44 (d, J=12.0Hz, 1H, $\underline{H}_b$), 7.70-7.77 (m, 3H, $\underline{H}$-4*,5*,8*), 8.0 (d of d, J=5.9Hz, 2Hz, 1H, $\underline{H}$-1*).



Irradiating the H_a resonance collapses the H_b doublet to a singlet and sharpens the methyl resonances.

$^{13}C^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 18.4 (CH_3), 27.0 (CH_3), 119.4, 119.6, 119.7, 122.0, 123.4, 125.6, 126.57, 126.64, 127.1, 127.3 (aromatic and olefinic CH), 132.2, 137.5, 138.6, 140.0, 140.6, 143.8 (aromatic C).

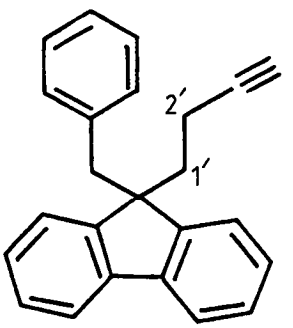
5.7.5 Rearrangement of 9-(But-3'-ynyl)fluorene (104)

This compound did not react by method II at room temperature but heating under reflux for 4 h produced 9-benzyl-9-(but-3'-ynyl)fluorene (150) in near quantitative yield (based on Triton B present). This compound was separated

from the starting material by chromatography on alumina, the starting material being eluted first.

5.7.5.1 9-Benzyl-9-(But-3'-ynyl)fluorene (150)

m.p. 88-90°.



^1H* n.m.r. ($CDCl_3$), δ (p.p.m.): 1.39 (m, 2H, $C\underline{H}_2$-2'), 1.78 (t, J=2.6Hz, 1H, ≡C$\underline{H}$), 2.46 (m, 2H, $C\underline{H}_2$-1'), 3.15 (s, 2H, $C\underline{H}_2$-benzyl), 6.68-6.70 (m, 2H, Ar$\underline{H}$-fluorene), 6.95-7.03 (m, 3H, Ar$\underline{H}$-fluorene), 7.27-7.32 (m, 6H, Ar$\underline{H}$-benzyl + one fluorene), 7.55-7.58 (m, 2H, Ar$\underline{H}$-fluorene).

Irradiating the $C\underline{H}_2$-2' resonance collapses the ≡CH and the $C\underline{H}_2$-1' resonances to singlets. Irradiating the $C\underline{H}_2$-1' resonance affects the $C\underline{H}_2$-2' resonance but not the ≡CH resonance.

^{13}C* n.m.r. ($CDCl_3$), δ (p.p.m.): 13.4 (CH_2), 37.8 (CH_2) 46.5 (CH_2 benzyl), 55.3 (aliphatic C), 67.7 (≡CH), 84.4 (-C≡), 119.8, 123.7, 126.0, 126.8, 127.1, 127.3, 130.3 (aromatic CH), 136.7, 140.9, 147.9 (aromatic C).

m.s. (m/e): 308 (M^+), 217, 202, 178, 165.

5.7.6 Rearrangement of 9-(Pent-4'-ynyl)fluorene (105)

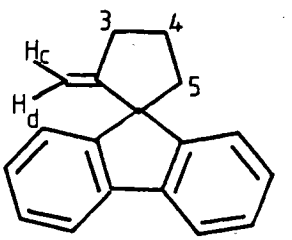
This compound did not react by method I after heating under reflux for 24 h. Using method II irreproducible results were obtained depending on the age of the Triton B. Using fresh Triton B no reaction had occurred after stirring at room temperature for 2 h. However after heating the

mixture under reflux for 1.5 h some reaction had occurred possibly forming the 9-benzyl-9-(pent-4'-ynyl)fluorene as indicated by the ^{1}H n.m.r. spectrum at the crude reaction product. This showed a singlet at 3.1δ (benzyl CH_2) and the aromatic region shows a similar structure to that of the benzylated 9-(but-3'-ynyl)fluorene (see above). No attempt was made to purify the product.

Using an older sample of Triton B, reaction occurred after 2 h at room temperature to give spiro[2-methylene-cyclopentane-1',9'-fluorene] (151) in 62% yield (after chromatography on alumina), identified by its ^{1}H n.m.r. spectru

5.7.6.1 Spiro[2-methylenecyclopentane-1 ,9'-fluorene] (151)

^{1}H n.m.r. ($CDCl_3$), δ (p.p.m.):
2.20 (m, 4H, 2x$\underline{CH_2}$-4,5), 2.86 (m, 2H, $\underline{CH_2}$-3), 4.42 (t, J=2Hz, 1H, $\underline{H_c}$), 4.78 (t, J=2Hz, 1H, $\underline{H_d}$), 7.14-7.42 (m, 6H, Ar$\underline{H}$), 7.62-7.76 (m, 2H, Ar$\underline{H}$).

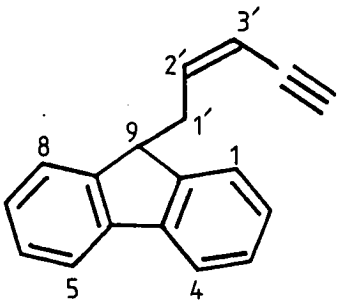


m.s. (m/e): 232.124976 (M^+, $C_{18}H_{16}$ requires 232.125194), 217, 215, 203, 191, 178, 165.

5.7.7 Rearrangement of E-9-(Pent-2'-en-4'-ynyl)fluorene (107)

This was attempted by method I, heating under reflux for 1.5 h. A large quantity of black tar was produced from which only one product was isolated, a trace of Z-9-pent-2'-en-4'-ynyl)fluorene (153). This may have been present initially in the starting material.

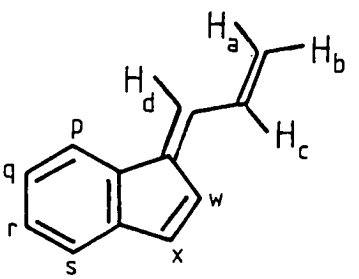
5.7.7.1 Z-9-(Pent-2'-en-4'-ynyl)fluorene (153)

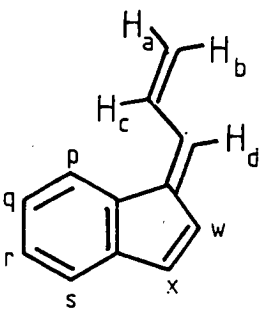


$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.70 (t, J=6.4Hz, 3H, $C\underline{H}_2$, ≡CH), 3.97 (t, J=6.4Hz, $C\underline{H}$-9), 5.83 (d of t, J= 13.2Hz, 6.5Hz, 1H, $C\underline{H}$-2'), 5.90 (d of d, J=13.2Hz, 0.9Hz, 1H, $C\underline{H}$-3'), 7.30 (t of d, J=7.4Hz, 1.2Hz, 2H, $\underline{H}_{2,7}$ or $\underline{H}_{3,6}$), 7.38 (t, J=7.4Hz, 2H, $\underline{H}_{2,7}$ or $\underline{H}_{3,6}$), 7.49 (bd, J=7.4Hz, 2H, $\underline{H}_{1,8}$ or $\underline{H}_{5.4}$), 7.75 (bd, J=7.4Hz, 2H, $H_{4,5}$ or $H_{1.8}$).

5.7.8 Rearrangement of 3-Propargylindene (24)

Method I, after heating under reflux for 15 minutes gave 55% yield of a mixture of E-1,2-benzo-6-vinylfulvene (30) and Z-1,2-benzo-6-vinylfulvene (31) in the ratio 9:1. These compounds were identified by their $^1H^*$ n.m.r. spectra.





5.7.8.1 E-1,2-Benzo-6-ynylfulvene (30)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 5.52 (d of d, J=8.8Hz, 1.8Hz, 1H, $\underline{H}_b$), 5.67 (d of d, J=15.8Hz, 1.8Hz, 1H, $\underline{H}_a$), 6.89 (d, J=5.5Hz, 1H, $\underline{H}_x$), 6.96 (bd, J=5.5Hz, 1H, $\underline{H}_w$), 7.07 (m, 2H, $\underline{H}_c$,$\underline{H}_d$), 7.2-7.3 (2x[t of d], J=7.0Hz, 1.5Hz, 2H, $\underline{H}_q$, $\underline{H}_r$), 7.34 (d of d of d, J=7.0Hz, 1.5Hz, 0.7Hz, 1H, $\underline{H}_s$),

7.65 (d of d of d, J=7.0Hz, 1.5Hz, 0.7Hz, 1H, $\underline{H}_p$).

$^{13}C^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 119.3 (CH_p), 120.9 (CH_s), 122.6 (CH_2), 124.5 (CH_x), 124.9 (CH_q), 127.5 (CH_r), 128.2 (CH_c), 132.7 (CH_w), 133.5 (CH_d), 136.6, 140.9, 142.7 (quaternary C).

Single frequency proton decoupled carbon-13 n.m.r. spectra (Table 5) were obtained using different proton decoupling frequencies in the region δ_H, at constant decoupler power. A graphical procedure was used to correlate the proton and protonated carbon shifts [73].

5.7.8.2 Z-1,2-Benzo-6-vinylfulvene (31)

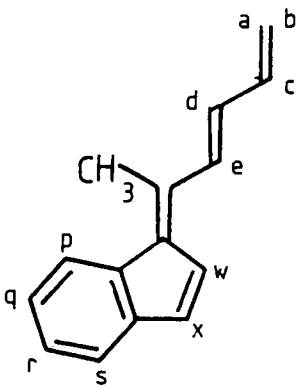
$^{1}H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): H_a,H_b not distinguished in mixture from those of the E isomer, 6.49 (d, J=5.3Hz, 1H, $\underline{H}_w$), 6.78 (d, J=11.6Hz, 1H, $\underline{H}_d$), 6.85 (d, J=5.3Hz, 1H, $\underline{H}_x$), $\underline{H}_q\underline{H}_r\underline{H}_s$ not distinguished in mixture, 7.49 (m, J=16.7Hz, 11.8Hz, 9.9Hz, 1H, $\underline{H}_c$), 7.85 (d, J=7.3Hz, 1H, $\underline{H}_p$).

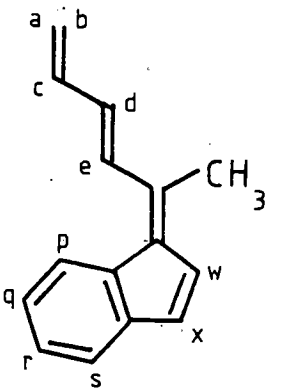
$^{13}C^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 121.0, 123.9, 124.4, 124.8, 131.2, 132.1, 133.1, 133.4 (CH-1 and quaternary Cs not apparent).

5.7.9 Rearrangement of E and Z-3-(1'-Methylpent-2'-en-4'-ynyl)indene (117), (118)

These compounds rearranged by method I after heating under reflux for 0.75 h to give E-1,2-benzo-6-methyl-6-(E-buta-1',3'-dienyl)fulvene (165) and Z-1,2-benzo-6-methyl-6-(E-buta-1',3'-dienylfulvene (166) in the ratio 1.2:1 together with unreacted E-acetylene. Chromatography on

alumina gave the pure E,E isomer (165) which eluted first and the Z,E isomer (166) as a mixture with unreacted acetylene.





5.7.9.1 E-1,2-Benzo-6-methyl-6-(E-buta-1',3'-dienyl) fulvene (165)

$^{1}H^{*}$ n.m.r. ($CDCl_3$), δ (p.p.m.), 2.53 (s, 3H, $\underline{CH}_3$), 5.29 (d of d, J=10.1Hz, 1.7Hz, 1H, $\underline{H}_b$), 5.44 (d of d, J= 16.7Hz, 1.7Hz, 1H, $\underline{H}_a$), 6.60 (d of d of d, sextet, J=16.7Hz, 10.5Hz, 10.1Hz, 1H, $\underline{H}_c$), 6.68 (d of d, J=14.6Hz, 10.5Hz, 1H, $\underline{H}_d$), 6.81 (d, J=5.7Hz, 1H, $\underline{H}_w$), 7.0 (d, J=5.7Hz, 1H, $\underline{H}_x$), 7.17 (d, J=74.6Hz, 1H, $\underline{H}_e$), 7.19 (t of d, J=7.2, 1.6Hz, 1H, $\underline{H}_q$ or $\underline{H}_r$), 7.22 (t of d, J=7.2Hz, 1.6Hz, 1H, $\underline{H}_q$ or $\underline{H}_r$), 7.31 (bd with fine structure, J 7Hz, 1H, $\underline{H}_s$), 7.81 (bd, J=7.2Hz, 1H, $\underline{H}_p$).

$^{13}C^{*}$ n.m.r. ($CDCl_3$), δ (p.p.m.): 16.0 (CH_3), 119.4 (CH_2), 121.3 (CH_q), 124.6 (CH_p), 124.8 (CH_r or CH_s), 126.0 (CH_x), 126.8 (CH_r or CH_s), 129.5 (CH_w), 133.4 (CH_e), 133.6 (CH_d), 136.0 (quaternary C), 137.4 (CH_c), 138.8, 140.1, 144.2 (quaternary C).

The assignment of ^{13}C resonances was achieved as in 5.7.8.1 by correlation with the proton resonances. See Table (6).

5.7.9.2 Z-1,2-Benzo-6-methyl-6-(E-buta-1',3'-dienyl)-fulvene (166)

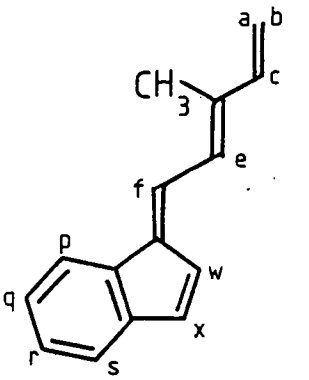
$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.41 (s, 3H, CH_3), 5.37 (d of d, J=10.3Hz, 1.9Hz, 1H, $\underline{H}_b$), 5.51 (d of d, J=15.9Hz, 1.9Hz, 1H, $\underline{H}_a$), 6.71 (d of d of d, sextet, J=15.9Hz, 10.3Hz, 10.6Hz, 1H, $\underline{H}_c$), 6.80 (d of d, J=14.6Hz, 10.6Hz, 1H, $\underline{H}_d$), 6.87 (d, J=5.6Hz, 1H, $\underline{H}_x$), 6.93 (d, J=5.6Hz, 1H, $\underline{H}_w$), 7.2-7.5 (m, $\underline{H}_q$,$\underline{H}_r$,$\underline{H}_s$), 7.63 (d, J=14.9Hz, 1H, $\underline{H}_e$), 7.88 (d of d, J=7Hz, 2.3Hz, 1H, $\underline{H}_p$).

5.7.10 Rearrangement of Z-3-(3'-Methylpent-2'-en-4'-ynyl)-indene (119)

This compound rearranged by method I after heating under reflux for 0.5 h to give a mixture (50%) of products. This was shown by $^1H^*$ n.m.r. to consist of all four possible geometric isomers of 1,2-benzo-6-(2'-methylbuta-1',3'-dienyl)fulvene. The two major isomers were E-1,2-benzo-6-(E-2'-methylbuta-1',3'dienyl)fulvene (167) and E-1,2-benzo-6-(Z-2'-methylbuta-1',3'-dienyl)fulvene (168) present in the ratio 1·6:1. The two other isomers were present in trace amounts only. This mixture could not be separated by chromatography on silica or alumina.

5.7.10.1 E-1,2-Benzo-6-(E-2'-methylbuta-1',3'-dienyl)fulvene (167)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.09 (d, J=1.2Hz, $C\underline{H}_3$), 5.23 (d, J=10.7Hz, $\underline{H}_b$), 5.29 (d, J=17.1Hz, $\underline{H}_a$), 6.58 (d of d of d, J=17.3Hz, 10.7Hz, 0.6Hz, $\underline{H}_c$), 6.77

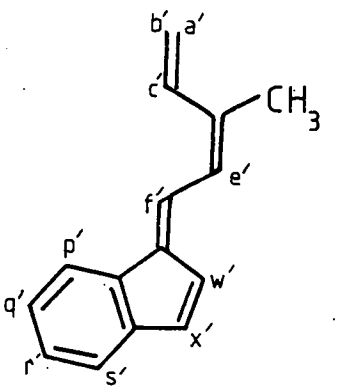


(bd, J=12.2Hz, $\underline{H}_e$), 6.90 (d, J=5.9Hz, $\underline{H}_x$), 6.91 (d, J=5.9Hz, $\underline{H}_w$), 7.14-7.24 (m, 2H, $\underline{H}_q$,$\underline{H}_r$), 7.28 (d of m, J 7Hz, $\underline{H}_s$), 7.39 (d of d, J=12.2Hz, 0.7Hz, $\underline{H}_f$), 7.64 (d of d, J 7Hz, 1.7Hz, $\underline{H}_p$).

Irradiating at H_c collapses the $\underline{H}_a$ and $\underline{H}_b$ resonances to singlets and simplifies H_e to two quartets (i.e. reveals the coupling to $\underline{CH}_3$).

Irradiating at H_e removes the small coupling at H_c and the coupling to the methyl resonance. It also sharpens H_a and changes the H_f resonance to a broad singlet. Irradiating at H_f affects H_w and collapses the H_e resonance to a broad singlet.

5.7.10.2 <u>E-1,2-Benzo-6-(Z-2'-methylbuta-1',3'-dienyl)-fulvene (168)</u>



$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.07 (d, J=1.0Hz, $\underline{CH}_3$), 5.36 (bd, J=11Hz, $\underline{H}_b$, , 5.46 (bd, J=17.1Hz, $\underline{H}_a$,), 6.71 (bd, J=12.2Hz, $\underline{H}_e$,), 6.90 (d, J=5.9Hz, $\underline{H}_x$,), 6.91, (J=5.9Hz, $\underline{H}_w$,), 7.14-7.25 (m, $\underline{H}_q$,,$\underline{H}_r$,,$\underline{H}_c$,), 7.28 (d of m, J 7Hz, $\underline{H}_s$,), 7.52 (bd, J=12.2Hz, $\underline{H}_f$,), 7.63 (d of d, J=8Hz, 1.7Hz, $\underline{H}_p$,).

Irradiating at $\underline{H}_e$, collapses the $\underline{H}_f$, resonance to a singlet and collapses the methyl resonance to a singlet. Irradiating at $\underline{H}_f$, collapses the $\underline{H}_e$, resonance to a singlet. Irradiating at 7.23δ ($\underline{H}_c$, centre) collapses the $\underline{H}_a$, and $\underline{H}_b$, resonances to singlets.

5.7.10.3 The methyl resonances of the other two isomers occur at 2.05 and 2.06δ. Irradiating at H_f or $H_{f'}$ affects the 2.05δ resonance indicating that H_e for this molecule lies between 7.3 and 7.6δ as would be expected since H_e for either of the two minor isomers will be deshielded by the benzene ring.

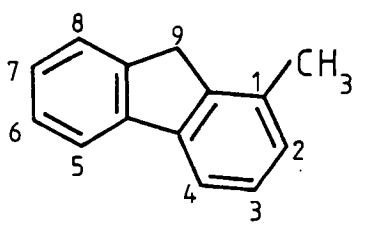
5.7.11 Rearrangement of E-3-(Pent-2'-en-4'-ynyl)indene (121)

This compound reacted by method I after heating under reflux for 0.5 h to give a mixture which contained a substantial proportion of polymer. Preparative thin layer chromatography on silica gave two fractions. Fraction I appeared to contain one major component in which the pentenyl group was retained and another minor product, Fraction 2 was shown by its $^1H^*$ n.m.r. spectrum to contain 1-methylfluorene (169), and E-1,2-benzo-6-(E-2'-buta-1',3'-dienyl)-fulvene (170) in the ratio 1:3 and a little Z-1,2-benzo-6-(E-2'-buta-1',3'-dienyl)fulvene (171).

The 1-methylfluorene resonances were identified from the spectrum of the mixture by comparison with a spectrum of an authentic sample kindly supplied by Professor N. Campbell and the resonances of the fulvenes by analogy with the spectra of the two preceeding rearrangements.

5.7.11.1 1-Methylfluorene (169)

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.): 2.43 (s, 3H, $C\underline{H}_3$), 3.79 (s, 2H, $C\underline{H}_2$), 7.13 (bd, J=7.6Hz, 1H, $\underline{H}_2$), 7.30, t of d, J=7.3Hz, 1.2Hz, 1H, $\underline{H}_5$),



7.31 (bt, J=7.6Hz, 1H, $\underline{H}_3$), 7.38 (t with fine structure, J=7.3Hz, 1H, H_6), 7.56 (d of t, J=7.3Hz, 1Hz, 1H, $\underline{H}_8$), 7.64 (bd, J=7.6Hz, 1H, $\underline{H}_4$), 7.78 (bd, J=7.6Hz, 1H, $\underline{H}_9$).

The assignment of the aromatic proton resonances is based on the following decoupling experiments:-

(a) Irradiating at H_5 collapses H_6 to a doublet and removes the small coupling on H_7.

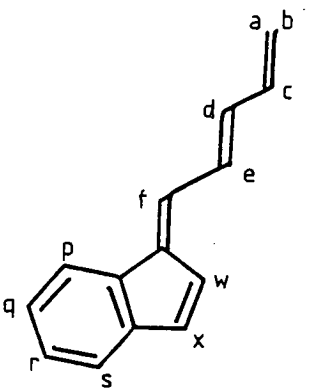
(b) Irradiating at H_4 collapses H_3 to a doublet.

(c) Irradiating at H_8 collapses H_7 to a doublet, removes fine structure from H_6 and sharpens H_5 to show fine structure.

(d) Irradiating at H_2 collapses H_3 to a doublet.

5.7.11.2 <u>E-1,2-Benzo-6-(E-2'-buta-1',3'-dienyl)fulvene (170)</u>

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.):



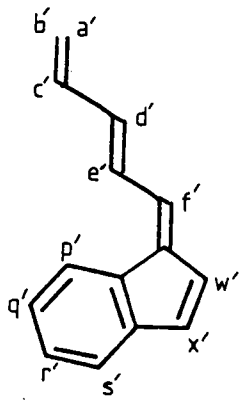
5.30 (d of d, J=9.7Hz, 2.0Hz, $\underline{H}_b$), 5.42 (d of d, J=16.5Hz, 1.9Hz, $\underline{H}_a$), 6.56 (d of d of d, sextet, J=16.2Hz, 10.7Hz, 10.8Hz, $\underline{H}_c$), 6.63 (d of d, J=13.7Hz, 10.8Hz, H_d), 6.87 (d, J=5.4Hz, $\underline{H}_w$), 6.92 (d, J=5.4Hz, $\underline{H}_x$), 6.92 (d of d, J=13.7Hz, 12.4Hz, $\underline{H}_e$), 7.07 (bd, J=12.4Hz, $\underline{H}_f$), 7.15-7.26 (m, $\underline{H}_q$,$\underline{H}_r$), 7.30 (d with fine structure, J 7.5Hz, $\underline{H}_s$), 7.60 (d with fine structure, J= 7.5Hz, $\underline{H}_p$).

5.7.11.3 <u>Z-1,2-Benzo-6-(E-2'-buta-1',3'-dienyl)fulvene (171)</u>

$^1H^*$ n.m.r. ($CDCl_3$), δ (p.p.m.):

5.36 (bd, J 9Hz, $\underline{H}_b$,), 5.45 (bd, J 16Hz, $\underline{H}_a$), H_c and H_d not readily apparent.

(d of d, J 11Hz, 14Hz, $\underline{H}_{d'}$), 7.53 (bt, J 13Hz, $H_{e'}$), 7.84 (bd, J 7Hz, $\underline{H}_{p'}$). Resonances due to $H_{f'}$, $H_{q'}$, $H_{r'}$ and $H_{s'}$, were obscured by resonances from (170).



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