SYNTHESIS AND PROPERTIES OF TRICYCLIC [10]ANNULENES

A thesis submitted in accordance with the requirements of the University of London for the degree of

DOCTOR OF PHILOSOPHY

by

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The work described in this thesis was carried out at Imperial College of Science and Technology under the supervision of Professor C.W. Rees and Dr. C.J. Moody. No part of it is concurrently being submitted for any other degree.

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Thanks are also due to Imperial College for the use of their facilities and to the Science and Engineering Research Council for providing a Research Studentship.

R. McCarey

To my parents

for helping me through it all.

Abstract

The evolution of [10]annulenes from transient intermediates to stable isolable compounds is reviewed with particular regard to the importance of transannular interactions.

The preparation of 5,7a-dihydro-7a-methyl-1H-inden-1-one has been improved. The conversion of the adduct of its enol ether, 3-methoxy-3a-methyl-3aH-indene, with dimethyl acetylenedicarboxylate into the tricyclic [10]annulene, 7b-methyl-7bH-cyclopent[cd]indene (1) has been shown to be an effective route, but unsuitable for large scale work.

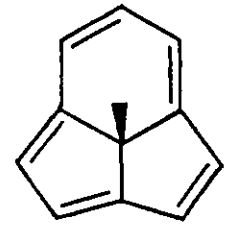
The structures of the [4+2] and [8+2] adducts of 3-methoxy-3a-methyl-3aH-indene with N-phenylmaleimide and maleic anhydride have been unambiguously assigned. New adducts with 2-chloroacrylonitrile and 2-chloroacryloyl chloride have been obtained, and used to prepare monosubstituted [10] annulenes and the versatile tricyclic ketone, 2a-methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2H-cyclopent[cd]inden-2-one respectively. This ketone has been converted into the annulene (1) by way of base induced fragmentation of its arenesulphonylhydrazones, and into the tetraenone, 2a,7b-dihydro-7b-methyl-2H-cyclopent[cd]inden-2-one, by removal of the elements of methanol. This tetraenone contained no substantial proportion of the "phenolic" tautomer, 7b-methyl-7bH-cyclopent[cd]inden-2-ol. Its conversion into the annulene (1) by reduction and elimination of water represents the best method so far for the synthesis of

this aromatic system.

A new 3a<u>H</u>-indene, 3-(trimethylsiloxy)-3a-methyl-3a<u>H</u>-indene, has been prepared and its use as an annulene precursor investigated. Attempts to prepare 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]inden-1-ol from its [8+2] adduct with dichloroketene were not successful.

The chemical properties of the annulene (1) were explored, particular attention being given to its thermal rearrangement and its reactions with dienophiles and electrophiles. In the reaction with chlorosulphonyl isocyanate, a ring expansion gave <u>N</u>-chlorosulphonyl-2,9b-dihydro-9b-methyl-1<u>H</u>-indeno[1,7-<u>cd</u>]azepin-1-one, a new 12π-system which showed some evidence of antiaromaticity.

The adduct of 3-(trimethylsiloxy)-3a-methyl-3a<u>H</u>-indene with benzoquinone was converted into a derivative of 9c-methyl-9c<u>H</u>-cyclopenta[<u>jk</u>]fluorene. The unsubstituted hydrocarbon itself, a benzo fused [10]annulene, was prepared from 7b-methyl-7b<u>H</u>-cyclopent-[<u>cd</u>]indene-1,2-dicarboxaldehyde, and its properties studied. The effects of benzo fusion are discussed in relation to recent related literature.



(1)

Contents

1 Introduction

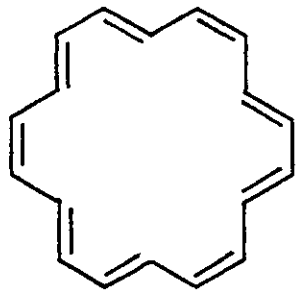
The term annulene is applied to the series of cyclic unsaturated hydrocarbons, $C_{2n}H_{2n}$, composed of a ring of (CH) units. The best known member of this series is [6]annulene (benzene). Its stability, the wide occurrence of its derivatives in nature and its tendency to undergo substitution rather than addition reactions is in marked contrast to cyclooctatetraene which has polyolefinic properties[1] and cyclobutadiene which has only a fleeting existence under ordinary conditions.[2]

These differences in properties are predicted by the molecular orbital theory of Hückel. His famous 4n+2 rule states that a planar monocyclic system containing 4n+2 out of plane π-electrons possesses a greater thermodynamic stability than a corresponding linear π-system and that the 4n π-electron cyclic systems possess no such stability.[3]

The proposal of this rule has prompted extensive experimental research to determine its validity. In this respect, Sondheimer and his co-workers were successful in preparing a series of the higher ring annulenes containing 12 to 30 carbon atoms which showed an alternation in properties in agreement with Hückel.[4] This is illustrated with [18]annulene (2) and [16]annulene (3).

Perhaps surprisingly, [18]annulene (2) was found to be not particularly stable and gave addition rather than substitution reactions, although by using mild

enough conditions, it could be nitrated,[5] acetylated,[5] brominated[6] and formylated.[6]



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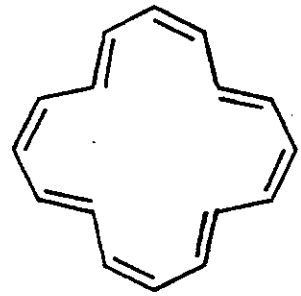


(3)

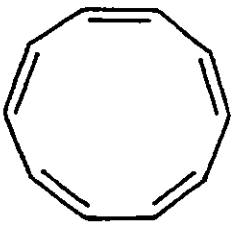
As stability is influenced by kinetic factors, it is not a satisfactory criterion for aromaticity; better is the phenomenon of ring current,[7,8] which is a measure of the delocalisation of the electrons and which can be measured readily by n.m.r.

[18]Annulene (2) did not give a satisfactory n.m.r. spectrum at room temperature due to rapid conformational inversions, but at -60°C the outer protons were observed to be strongly deshielded at δ9.28 and the inner protons were strongly shielded at δ-2.99. Conversely, [16]annulene (3), at -110°C, gave resonances for the outer protons at δ5.40 and the inner protons at δ10.43 showing a paramagnetic ring current to be present in an applied magnetic field.[4a]

One of the concepts characterising aromaticity is that of bond length equalisation. For annulenes higher than (2), the limit of Hückel's rule is reached, as manifested by significant bond alternation.[4] However,

recent calculations indicate that as the size of the annulene increases, there is a gradual transition from bond equalisation to bond alternation and that there may be some bond alternation, albeit small, even in [10]annulenes.[9]

In the series of annulenes prepared by Sondheimer, [10]annulene was notably absent. For the monocyclic [10]annulenes, the configurations (4) - (7) may be considered.



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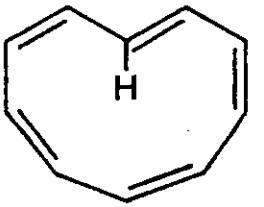

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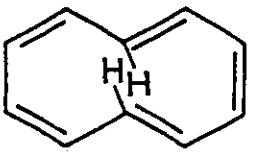

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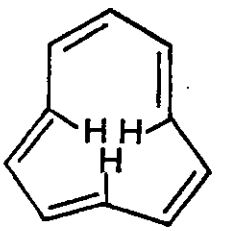
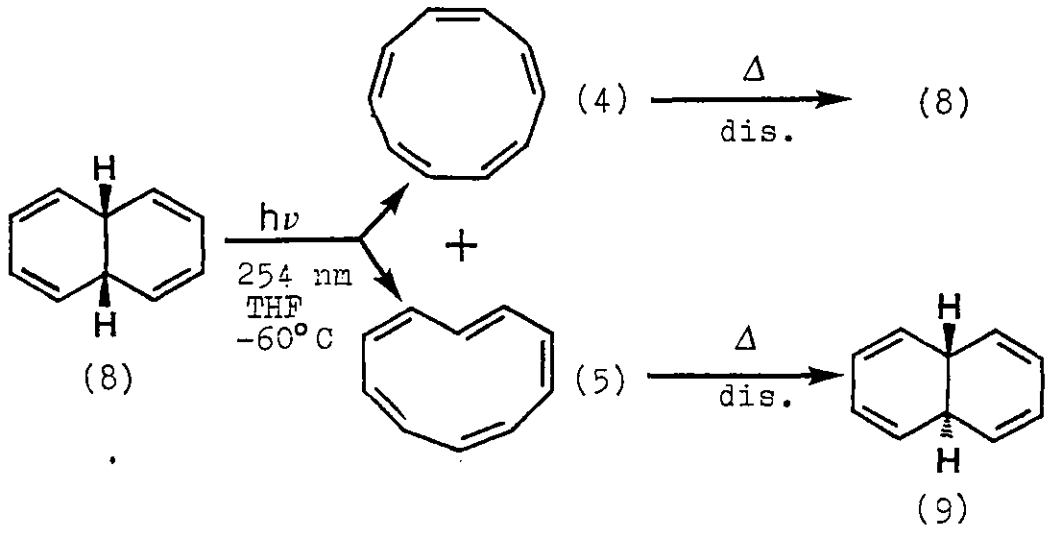


(7)

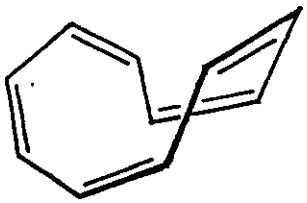
Following experiments demonstrating the intermediacy of [10]annulenes,[10] the isomers (4) and (5) were isolated by Masamune and co-workers.[11] The best preparative method was the low temperature photolysis of the cis-dihydronaphthalene (8) under carefully controlled conditions.

The resulting annulenes were separated and purified by low temperature column chromatography.[11]



However, neither of the annulenes (4) or (5) showed any evidence of a ring current and both gave only olefinic proton resonances in the n.m.r. spectrum. Furthermore, their u.v. spectra showed incomplete conjugation of the double bonds. When the all cis-annulene (4) was allowed to warm to room temperature, it reverted to the cis-dihydronaphthalene (8) by a thermally allowed disrotatory electrocyclic process with a half life of 47 minutes at 6°C. Similarly, the mono-trans-annulene (5) gave the trans-dihydronaphthalene (9) with a half life of 22 minutes at -25°C.[11]

In an elegant piece of work, structures (4a) and (5a) were assigned to be the most favoured conformations of these annulenes to explain the temperature variation of the proton and carbon-13 n.m.r. spectra,[11] and a theoretical treatment predicts these structures to be energetically the most favoured.[12]



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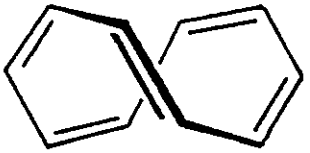
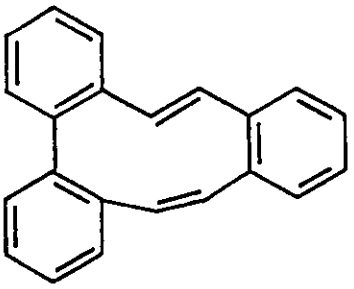


(5a)

Thus the monocyclic annulenes isolated by Masamune and co-workers do not possess the fully conjugated 10π-electron system of interest. Their non planar conformations were not surprising since planarity requires the imposition of either severe bond angle strain and / or non bonding repulsive interactions. For the all cis-compound (4), a planar conformation necessitates internal bond angles of 144° and there is unfavourable eclipsing of the external hydrogens. Non bonding interactions involving internal hydrogens are involved for the configurations (5), (6) and (7).

To construct a system which has a sufficiently planar 10π-system for complete cyclic conjugation, it was necessary to build constraints into the structure. The tribenzo-fused system (10) has been prepared by Sondheimer and co-workers but was found not to be planar.[4a] Even if it were, it is probable that the three benzene rings would cause so much perturbation of the system that the contribution of the inner 10π-ring to the overall electronic structure of the compound would be insignificant. The compound (11) with cyclohexenyl residues in place of the benzene rings was too unstable to be isolated.[4a]



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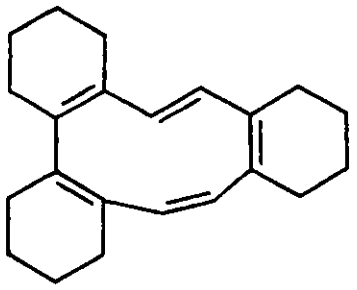

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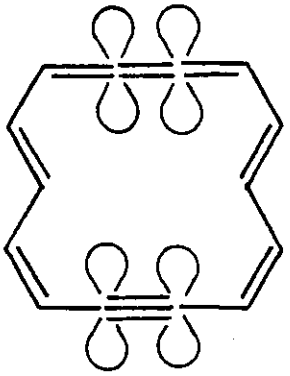

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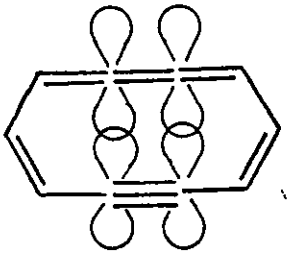
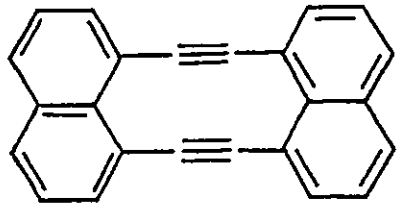


(13)

Although the dehydro [14]annulene (12) and similar higher annulenes have been prepared,[13] attempts to synthesise a dehydro [10]annulene have not been successful. The bis-dehydro [10]annulene (13) is expected to be planar but is unlikely to be isolable owing to instability caused by interactions of the in-plane π-electrons.[14] Attempts to prepare the model compound (14) resulted only in the isolation of zethrene (15) and dehydrogenation of the solvent occurred.[4a] Similarly, attempts to prepare dibenzo-1,2,6,7-bis-dehydro-[10]annulene (16) were not successful and one of the products isolated was a benz[a]anthracene derivative.[15]

On this basis, the annulene (13) would be expected to give naphthalene rapidly.



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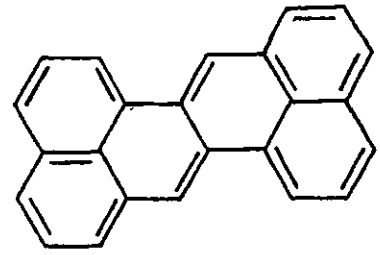

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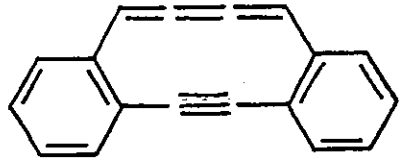

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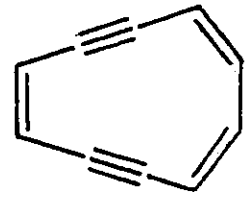
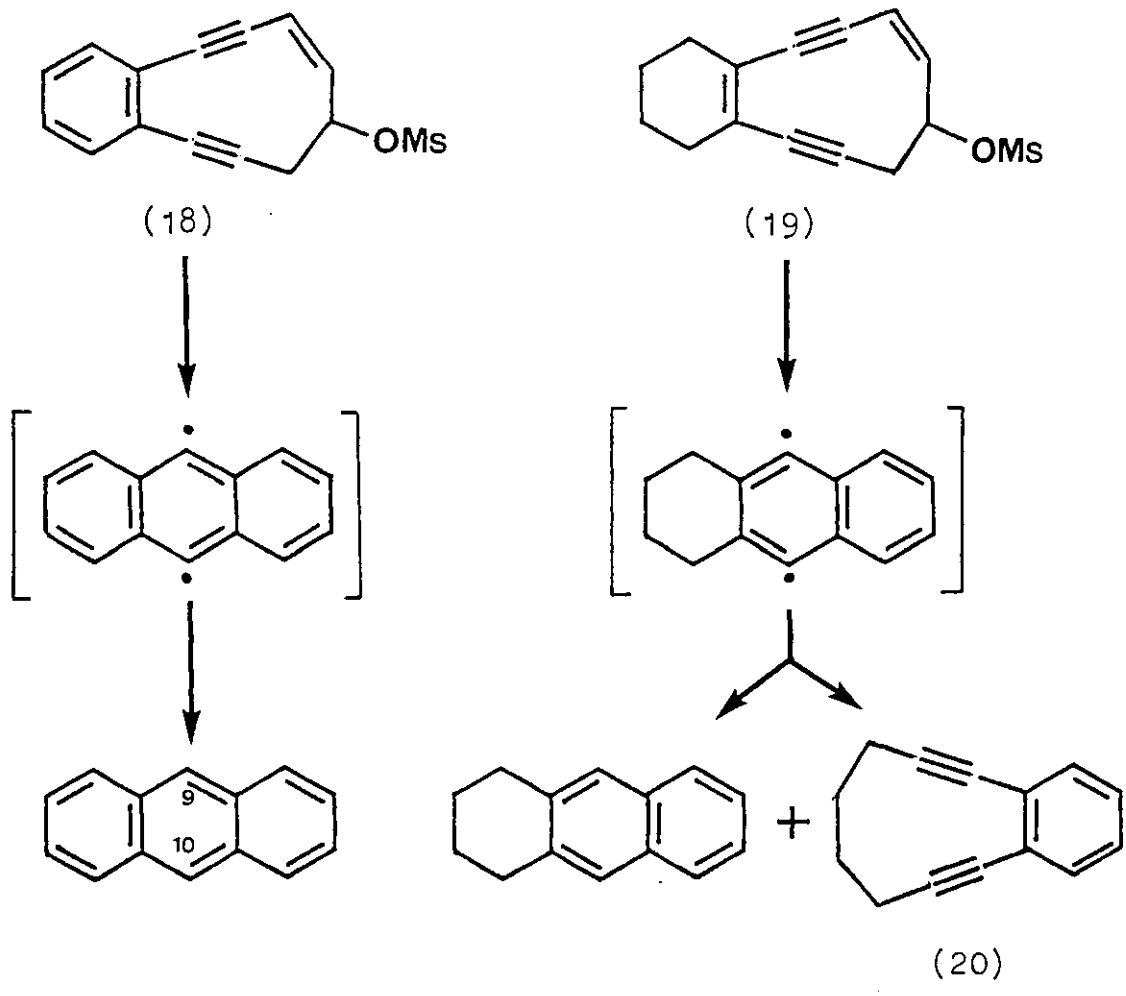
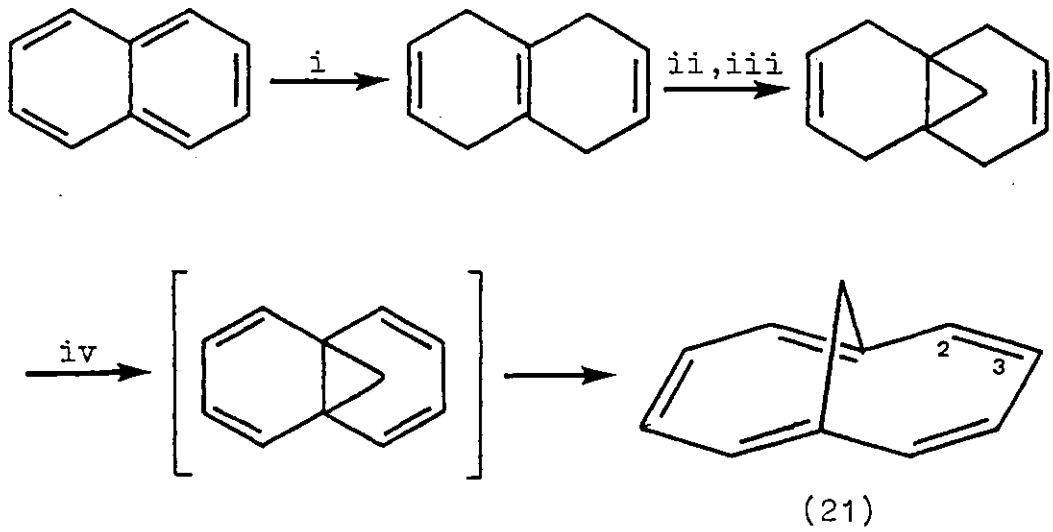


(17)

Following the above work, Masamune attempted the synthesis of derivatives of the annulene (17) which were expected to possess less repulsion between the in-plane π-electrons than the isomer (13).[10c] However, treatment of the mesylates (18) and (19) with a variety of bases gave anthracene and 1,2,3,4-tetrahydroanthracene respectively. In the case of the mesylate (18), phenanthrene was sometimes a minor byproduct and when a deuterated solvent was used for the reaction, deuterium was incorporated into the 9- and 10-positions of the anthracene.[10c] These observations support the diradical intermediate shown. In the case of the mesylate (19), a byproduct was the diacetylene (20) which may have been formed by opening of the diradical intermediate.[10c]



The problem of transannular reactions in the [10]annulenes was neatly overcome by Vogel, by connection of the 1- and 6-positions of the di-trans-isomer (6) with a methano bridge. The resulting 1,6-methano[10]annulene (21) was synthesised from naphthalene[16] (Scheme 1) and showed the characteristics of an aromatic compound. It undergoes electrophilic substitution reactions and in the proton n.m.r. spectrum, the methylene protons appear upfield of tetramethylsilane at δ-0.5 due to the diamagnetic ring current induced in the system by the applied magnetic field.[17]

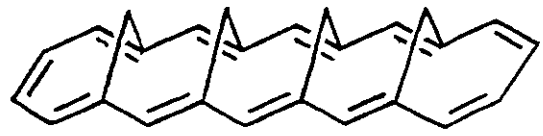


(21)

SCHEME 1

Reagents: i, Na-EtOH-NH_3; ii, $CHCl_3$-$KOBu^t$; iii, Na-Hg; iv, DDQ

A large number of derivatives of this compound has been prepared with various bridging groups and peripheral substitution, and also its higher "homologues" upto the [22]annulene (22).[17]



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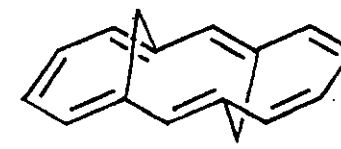
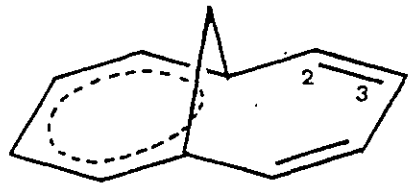


(23)

Although the methano bridge in the annulene (21) causes arching of the molecule so that the periphery is not planar,[18] the compound (22) still has some aromatic properties despite the presence of four such bridges.[17b]

The results of Vogel lead to the conclusion that the overall planarity of the π-system is less important in determining the extent of delocalisation than torsional angles between neighbouring double bonds which reach a maximum value of 34° in (21).[18] When large torsional angles are present, aromaticity is destroyed. For example, complete delocalisation in the anti-bis-methano[14]annulene (23) is disrupted by torsional angles greater than 70°. As a result, it is unstable and its methylene protons resonate at δ1.88 and δ2.48 in the n.m.r. spectrum showing the absence of a ring current.

Although there is no doubt that the annulene (21) has the structure shown, a substantial amount of evidence has amassed to support the view that a large proportion of the ring current which causes the upfield shift of the methylene protons in the n.m.r. spectrum arises from a 1,6-bonding interaction which gives a certain amount of 6π-delocalisation as depicted by (24).[19]

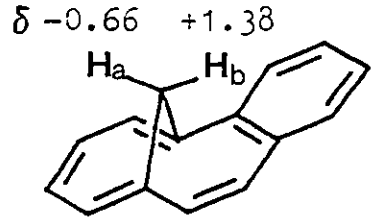


(24)

It is necessary to invoke this homoaromatic interaction to explain the electronic[20,21] and photoelectron[22] spectra, and a bond order of 0.4 between the 1- and 6-positions has been estimated.[20] A theoretical treatment predicts the system to be intermediate between naphthalene

and a true [10]annulene, and that the [22]annulene (22) would show no aromatic properties if transannular interactions were absent.[23] Measurements of the positional reactivity of the annulene (21) in detritiation and desilylation reactions show the 2-position to be much more reactive than the 3-position in electrophilic substitution reactions.[24] Only by invoking structures such as (24) as having a significant contribution, can these results be explained.[24]

Perhaps the most striking evidence is shown by the annelated compounds (25a) and (26a). The proton n.m.r. spectrum of compound (25a) shows H_a to resonate upfield of tetramethylsilane but H_b not to be under the influence of much ring current.[25] Similar effects are observed for compound (26a).[26] Thus, structures (25b) and (26b) may be better representations of these compounds.



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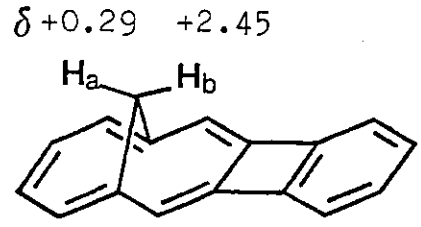

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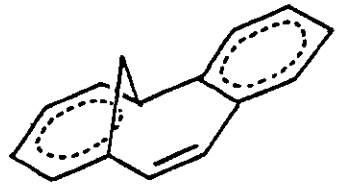

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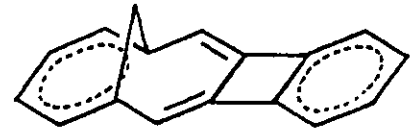
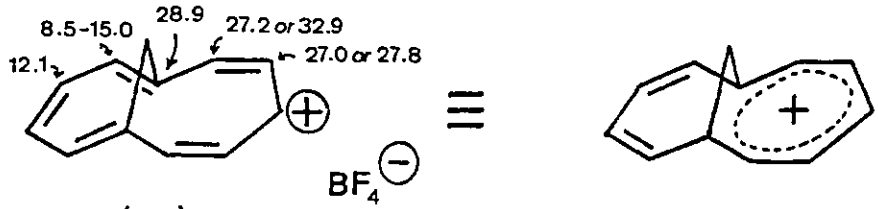


(26b)

A homoaromatic interaction has also been demonstrated in the cation (27). Its carbon-13 n.m.r. spectrum is similar to that of the benzotropylium ion (28) and shows the positive charge density to lie mainly in the right hand ring as shown.[27] If there were no interaction across the 10π-system, a comparable positive charge would be expected to reside on all the peripheral positions.



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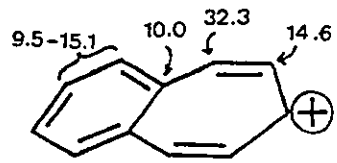


(28)

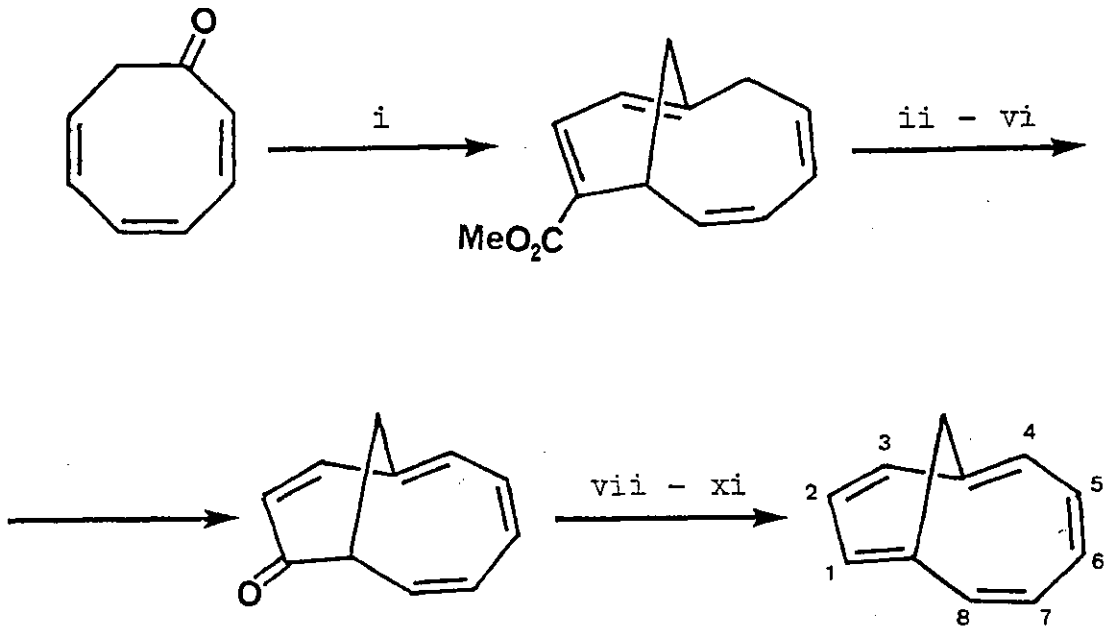
The figures given are downfield chemical shift differences in the carbon-13 spectrum relative to the uncharged hydrocarbon

The above results show that the annulene (21) studied by Vogel cannot be regarded as a true Hückel annulene in which the delocalisation is entirely around the periphery. Calculations predict that although the 1,6-interaction in a [10]annulene is bonding, the 1,5-interaction is not and that the 1,5-methano[10]annulene (29) should possess little homo-interaction.[28]

1,5-Methano[10]annulene bears the same relation to azulene as 1,6-methano[10]annulene does to naphthalene. The interaction in azulene itself is calculated to be

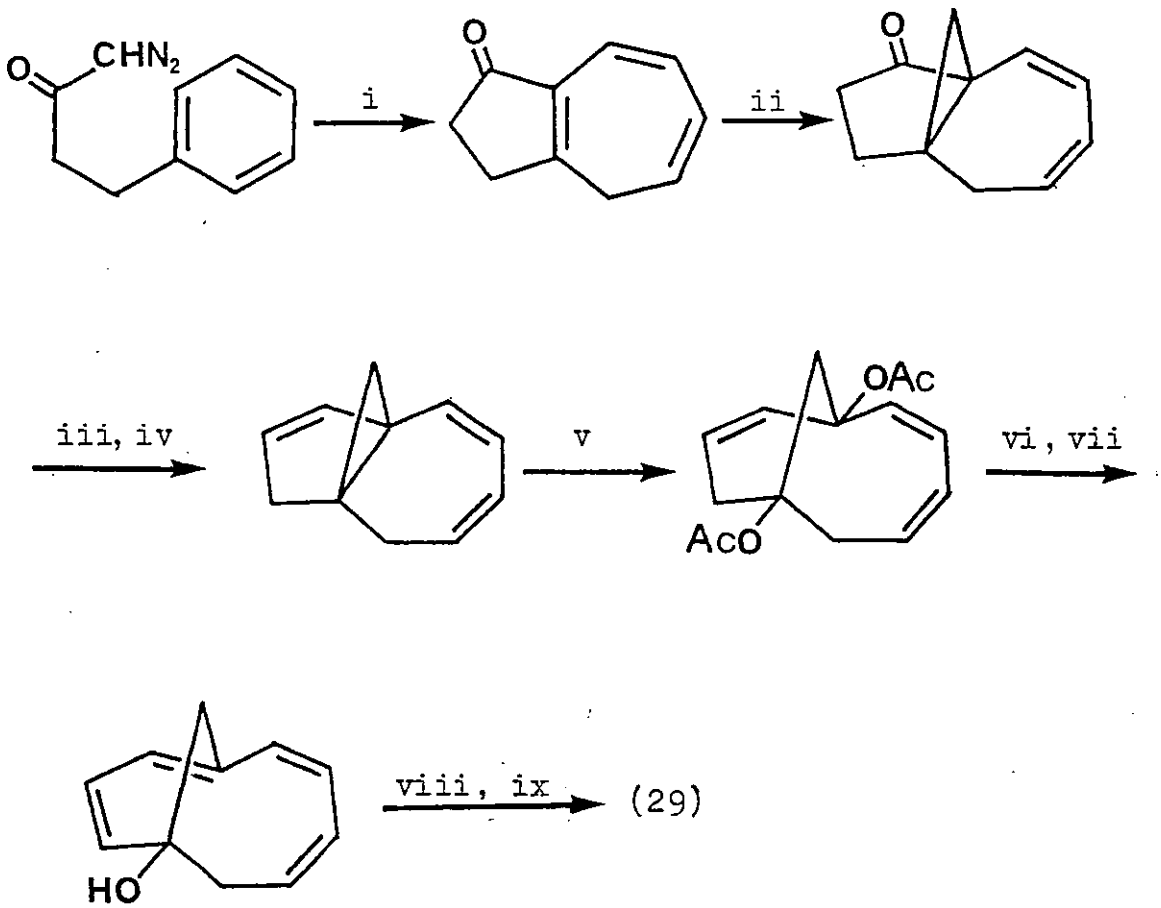
small[28] but its blue colour and large dipole moment show the interaction to be present. 1,5-Methano [10] annulene was first synthesised by Masamune and Brooks in 1977 (Scheme 2)[29] and later by Scott and co-workers (Scheme 3).[30]

Syntheses of 1,5-Methano [10] annulene



(29)

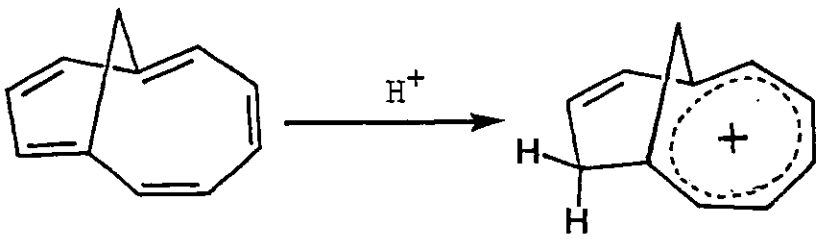
SCHEME 2 Reagents: i, $(MeO)_2\overset{O}{\underset{\ominus}{P}}CHCH=CHCO_2Me$-THF; ii, $Pr^i{}_2NLi$; iii, O_2; iv, $(EtO)_3P$; v, $LiAlH_4$; vi, $NaIO_4$; vii, $Bu^i{}_2AlH$, -78°C; viii, $PhCO_2H$-PPh_3-$MeO_2CN=NCO_2Me$, 0°C; ix, OH^-; x, $4\text{-}O_2NC_6H_4N=C=O$; xi, 300°C.



SCHEME 3 Reagents: i, CuCl-PhBr, 180°C; ii, $\bar{C}H_2\overset{+}{S}OMe_2$ DMSO, 75°C; iii, $TsNHNH_2$-MeOH, 25°C; iv, MeLi-Et_2O, 25°C; v, $Pb(OAc)_4$-C_6H_6-AcOH; vi, $Pb(OAc)_2$-PPh_3-Na_2CO_3; vii, MeLi-Et_2O; viii, MsCl-NEt_3-CH_2Cl_2, 0°C; ix, $KOBu^t$-Bu^tOH, 25°C

The annulene (29) has aromatic properties despite the considerable torsional strain anticipated; the torsional angles between neighbouring double bonds reach a maximum of 42°.[31] The presence of a ring current causes the methylene protons to appear in the n.m.r. spectrum upfield of tetramethylsilane at δ-0.50 and δ-0.95.[29] Even in this compound, the presence of some transannular interaction has been demonstrated and has led to the use

of the name, homoazulene.[32] The introduction of a methoxy substituent into the 1-position causes a greater effect on the band frequencies in the electronic spectrum than if the substituent is elsewhere; this behaviour is also shown by azulene.[32] The similarity with azulene is also shown by the e.s.r. spectrum of its radical anion where the main hyperfine coupling is to the proton at position-6 in both compounds.[31] Protonation of 1,5-methano-[10]annulene occurs exclusively at the 1-position to give the stable homotropylium ion (30).[31]

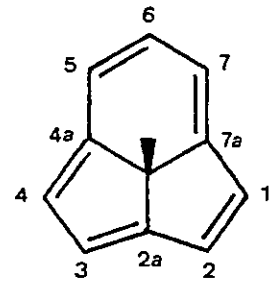


(29) (30)

Although the evidence shows a transannular interaction to be present in the annulene (29), unlike the 1,6-interaction encountered in Vogel's compound (21), that between the 1- and 5-positions causes a charge displacement in the molecule and a considerable change in properties may be brought about by an interaction of only a small magnitude.

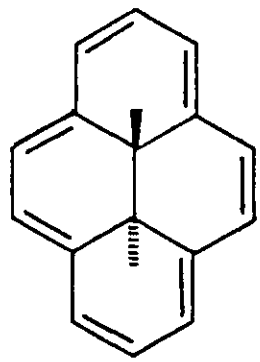
A bridged [10]annulene in which the geometry is such that any transannular interaction is probably even less significant is 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (1). The interatomic distance between the 4a- and 7a-positions has

been calculated to be 2.55 Å,[33] much longer than the transannular distance of 2.26 Å encountered in 1,6-methano-[10]annulene (21).[18] Paquette and co-workers have estimated that mutually canted homoconjugated carbon atoms can still interact at distances upto 2.45 Å, but above this value, the interaction falls off rapidly.[34]

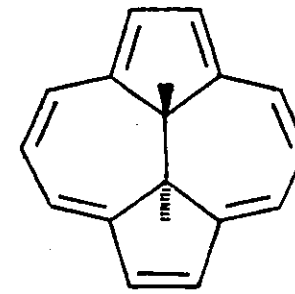


(1)

The tricyclic [10]annulene (1) is derived from the hypothetical monocyclic system (7) by replacement of the three internal hydrogen atoms with a single bridging carbon atom. It is related to the 14π-dihydropyrene (31), extensively studied by Boekelheide,[35] and the isomeric system (32).[36] Both of the annulenes (31) and (32) have been shown to be strongly diatropic aromatic compounds.[35,36]

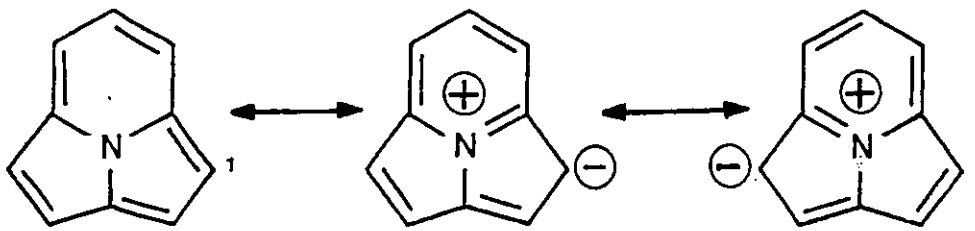


(31)



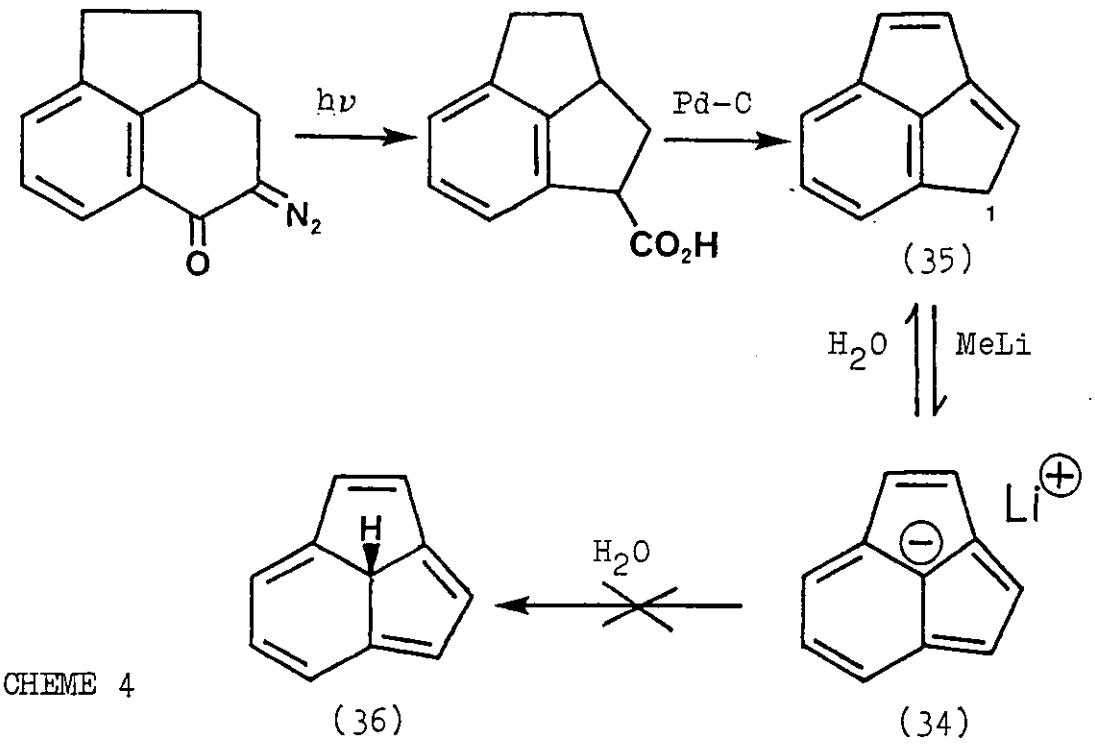
(32)

A compound with the same periphery as the annulene (1) is [3,2,2]cyclazine (33).[37] Although this is a stable aromatic compound, the contribution of the lone pair of electrons from the nitrogen atom has a marked effect on its electronic structure and its properties may be ascribed to the fusion of a pyridinium cation and one of two azacyclopentadienyl anions rather than to its 10π-periphery. Hence, electrophilic substitution takes place predominantly at the 1-position.[37]



(33)

Isoelectronic with [3,2,2]cyclazine is the anion (34) which has been synthesised as its lithium salt[38] (Scheme 4). Not surprisingly, quenching of the anion (34) with water does not give the annulene (36) but the more stable benzenoid hydrocarbon, 1H-cyclopent[cd]indene (35).[38] Also, when the anion was treated with deuterium oxide, a product deuterated specifically at the 1-position was obtained.[39] It is therefore considered unlikely that the annulene system could be prepared by alkylation of the anion (34) but nevertheless, this represents an interesting experimental challenge.



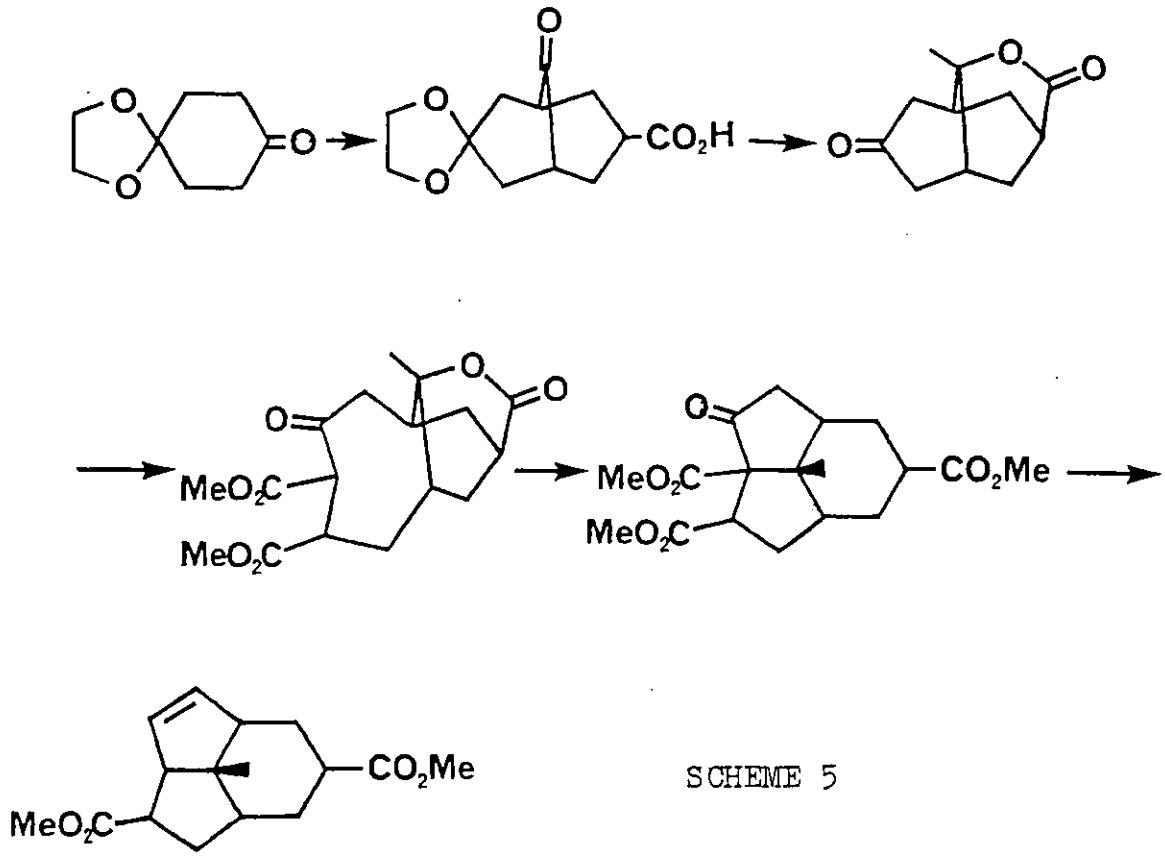
SCHEME 4

Due to the high mobility of the hydrogen atom, either in acid-base reactions or by sigmatropic shifts, it is probable that the isolation of compound (36) would be prevented by its facile rearrangement to the more stable 1H-isomer (35). For this reason, synthetic approaches to the annulene have concentrated on the compound with the bridgehead methyl group (1). The methyl group has a low tendency to undergo sigmatropic migration and is readily introduced.

Few reports of attempted synthesis of the annulene (1) have appeared in the literature. This may be because the methods that are frequently used in the preparation of annulenes are not applicable. Thus, acetylenic precursors, as used for the preparation of large ring annulenes such as [18]annulene,[4] cannot be utilised and there is no valence isomer which will rearrange into the annulene (1). The

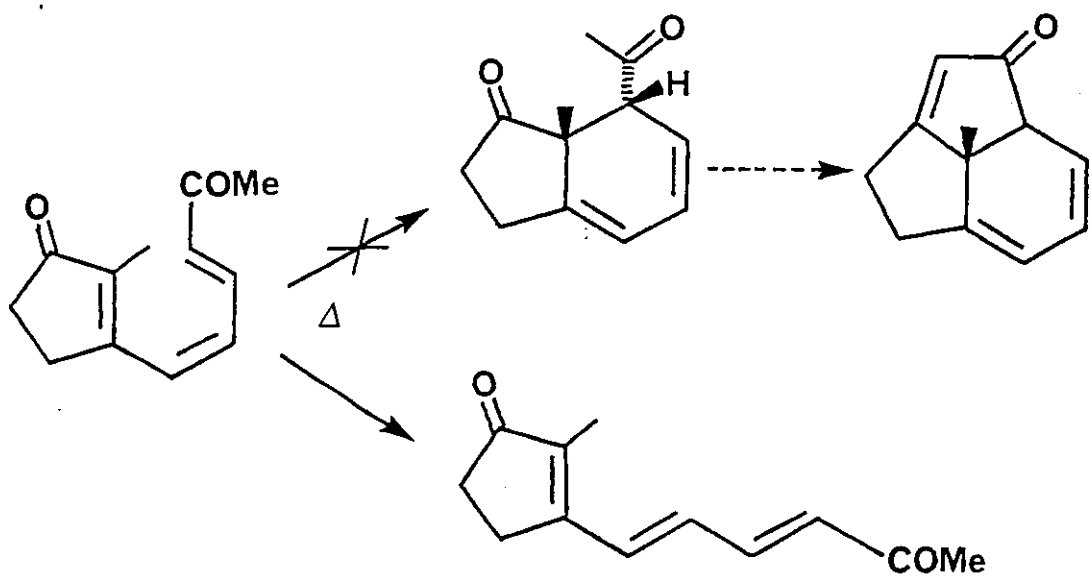
rearrangement of a suitable valence tautomer has been used in the preparation of 1,6-methano[10]annulene (21),[16] the dihydropyrene (31)[35] and the monocyclic [10]annulenes, (4) and (5).[4] Therefore a more classical approach, such as those used in the synthesis of 1,5-methano[10]annulene (29)[29,30] has to be used.

An attempt to synthesise the annulene (1) in which the carbon skeleton was constructed by a transannular reaction gave a virtually fully saturated system in which introduction of the necessary unsaturation was not achieved (Scheme 5).[40] The difficulties incurred in introducing unsaturation into strained systems were probably not fully appreciated when this synthesis was undertaken.



SCHEME 5

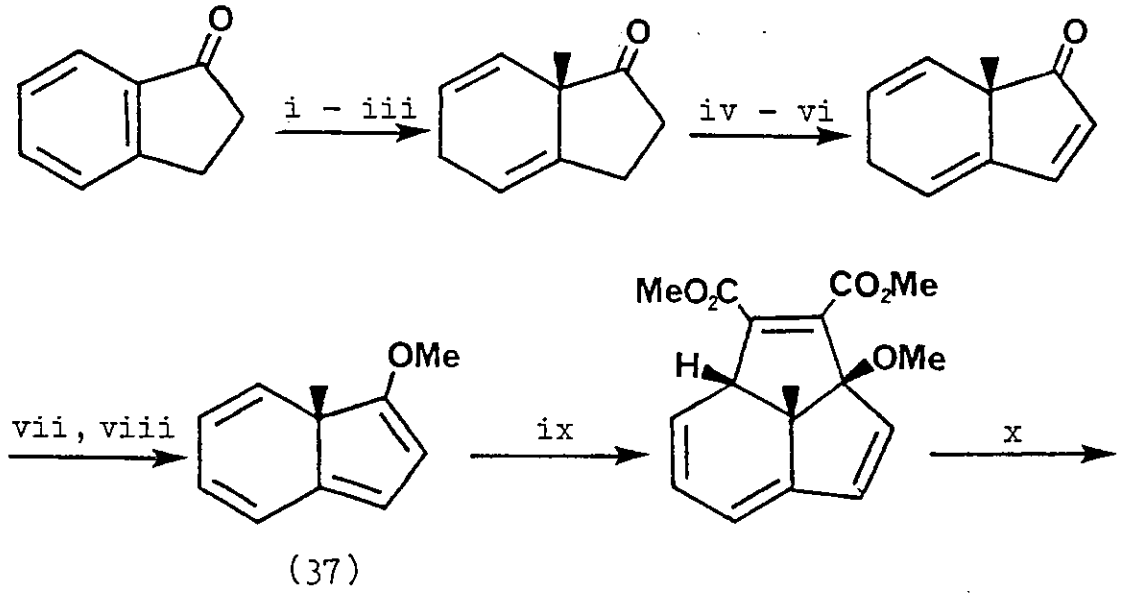
An attempt by Bradbury to prepare the system was thwarted when the required electrocyclic ring closure failed; a cis-trans isomerisation occurred instead (Scheme 6).[41]



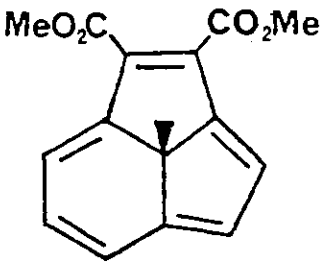
SCHEME 6

The breakthrough came in 1980; during an investigation of the chemical properties of the 3aH-indene derivative (37) Tuddenham discovered that its reaction with the dienophile, dimethyl acetylenedicarboxylate proceeded by an [8+2] cycloaddition reaction[42b] and that the elimination of methanol from the resulting adduct provided a derivative of the desired system (Scheme 7).[42c]

The diester (38) was a bright yellow fluorescent oil and the resonance of the central methyl group at δ-1,34 showed that the 10π-periphery could sustain a diamagnetic ring current in an applied magnetic field.[42c]



(37)



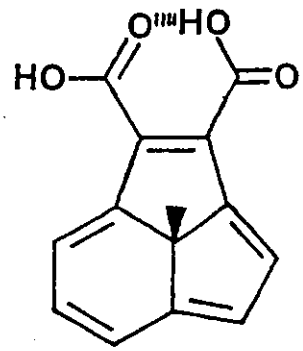
(38)

SCHEME 7

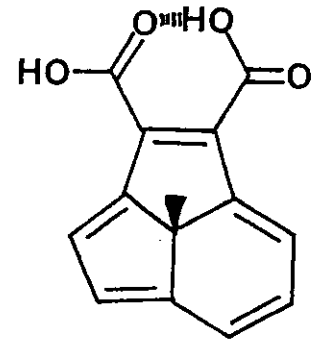
Reagents: i, K-Bu^{t}OH-THF-NH_3, -78°C; ii, LiBr-THF; iii, MeI-H_2O-THF; iv, Pr_2^{i}NLi-THF, -78°C; v, PhSeBr-THF, -78°C; vi, H_2O_2-THF, 0 → 25°C; vii, KH-18·Crown·6-DME, -15°C; viii, $MeOSO_2F$; ix, MeO_2C-C≡C-CO_2Me; x, H_2SO_4-MeOH, 0°C or TsOH-C_6H_6, 80°C

X-Ray crystallographic analysis of the dicarboxylic acid (39) obtained by base hydrolysis of the diester (38) showed the periphery was nearly planar with little variation of bond lengths.[42c] The central carbon atom was out of plane and maintained its tetrahedral geometry. Some shortening of the bonds connecting the central carbon atom to the periphery was observed[42c] and hence it is unlikely that any atom larger than the carbon atom could be accommodated as a bridging group in this 10π-system. It was unfortunate that accurate bond lengths could not be measured from the

crystallographic analysis; the crystal structure was disordered because either of the two diastereoisomeric forms (39a) and (39b) occupy a given site in the crystal lattice.[42c]

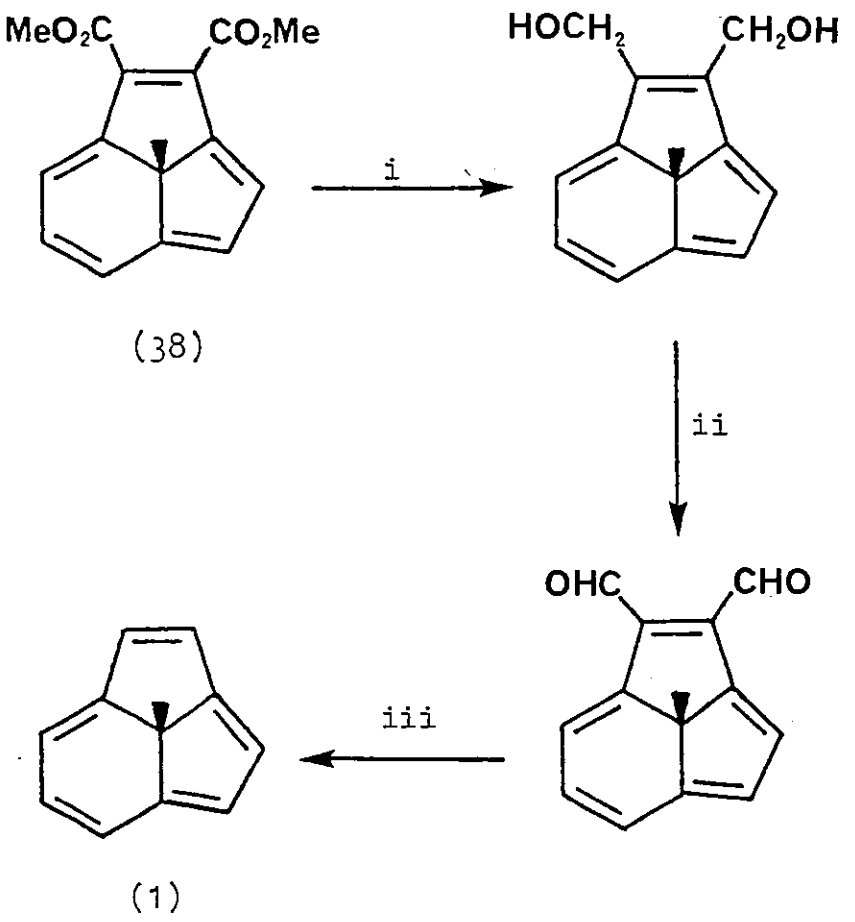


(39a)



(39b)

Attempts to decarboxylate the acid (39) to give the parent system (1) were not successful since the vigorous conditions necessary for decarboxylation were not compatible with the stability of the system.[42a,d] However, Tuddenham eventually showed that it was possible to prepare the parent annulene by conversion of the diester (38) into the corresponding dialdehyde and subsequent decarbonylation with tris(triphenylphosphine)rhodium(I) chloride (Scheme 8), although only a very small quantity of the annulene (1) was prepared and it was contaminated with triphenylphosphine.[42d]



(38)

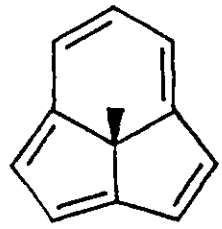
(1)

SCHEME 8 Reagents: i, $LiAlH_4$-Et_2O, 25°C; ii, DDQ-C_6H_6, 80°; iii, $Rh(PPh_3)_3Cl$-C_6H_6, 80°C

2 Discussion

2.1 The Synthesis of 7b-Methyl-7b*H*-cyclopent[*cd*]indene (1)

The aim of this project was to study the chemistry of the [10]annulene, 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) and a variety of its derivatives, in order to gain some understanding of the nature of its novel 10π-periphery.



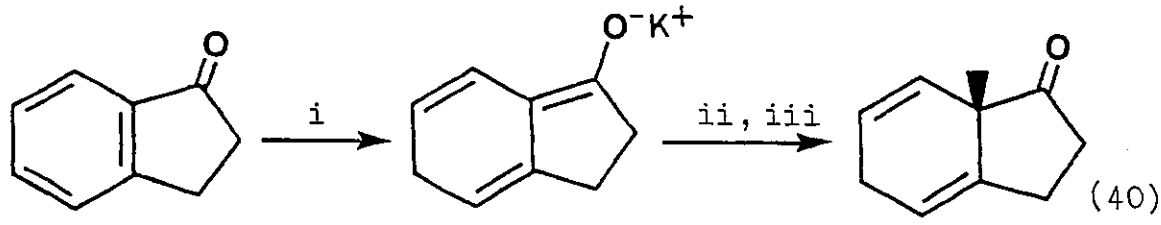
(1)

The synthesis pioneered by Tuddenham (Schemes 7 and 8) was the only successful approach to the system at the time this work started and it was decided to modify his route so that sufficient of the annulene could be prepared to allow for a thorough study of its properties. The key step of the synthesis involves the construction of the carbon skeleton by means of an [8+2]cycloaddition reaction of a suitable dienophile to a 3a*H*-indene derivative. This theme has been maintained throughout the present work and it was necessary to prepare precursors of the required 3a*H*-indenes in appreciable quantities. Therefore, considerable attention has been given to the early stages of the synthesis.

2.1.1 The Birch Reduction and Methylation of 1-Indanone

The Birch reduction of 1-indanone has been studied

by Narisada and Watanabe,[43] and later by Tuddenham[42a,b] (Scheme 9). Potassium metal was added to a solution of 1-indanone in liquid ammonia containing tert-butanol and tetrahydrofuran. Between 2.2 and 4 equivalents of methyl iodide were used in the subsequent methylation.[42a,b, 43]

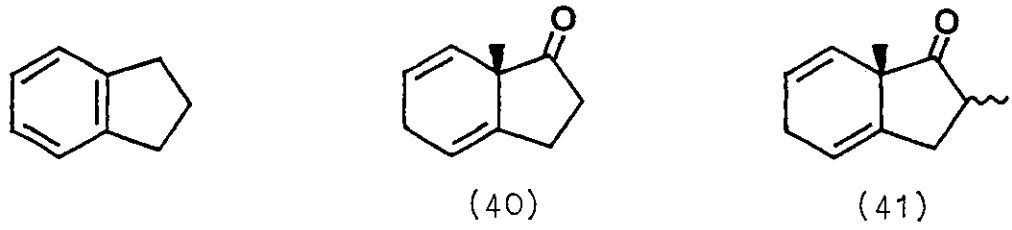


(40)

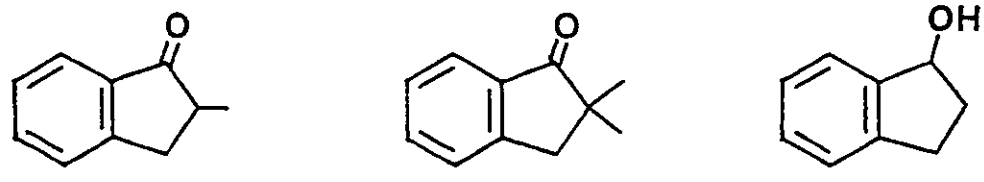
SCHEME 9

Reagents: i, K-Bu^{t}OH-THF-NH_3, -78°C; ii, LiBr-THF, -78°C; iii, MeI-H_2O-THF, -33°C

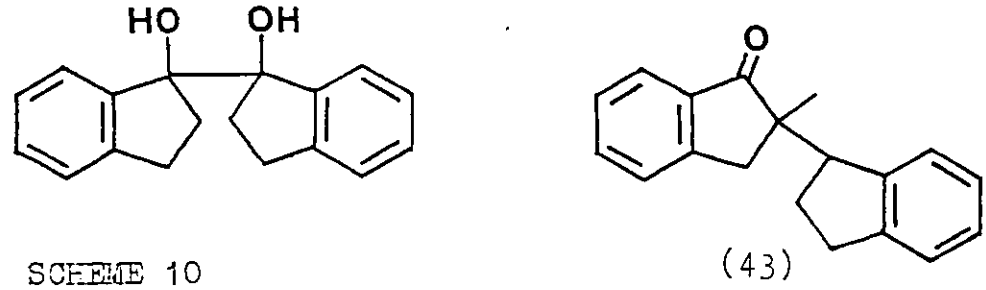
In our hands, these conditions gave rise to the many products shown in Scheme 10 which were separated mainly by chromatography.



(40) (41)



(42)



SCHEME 10

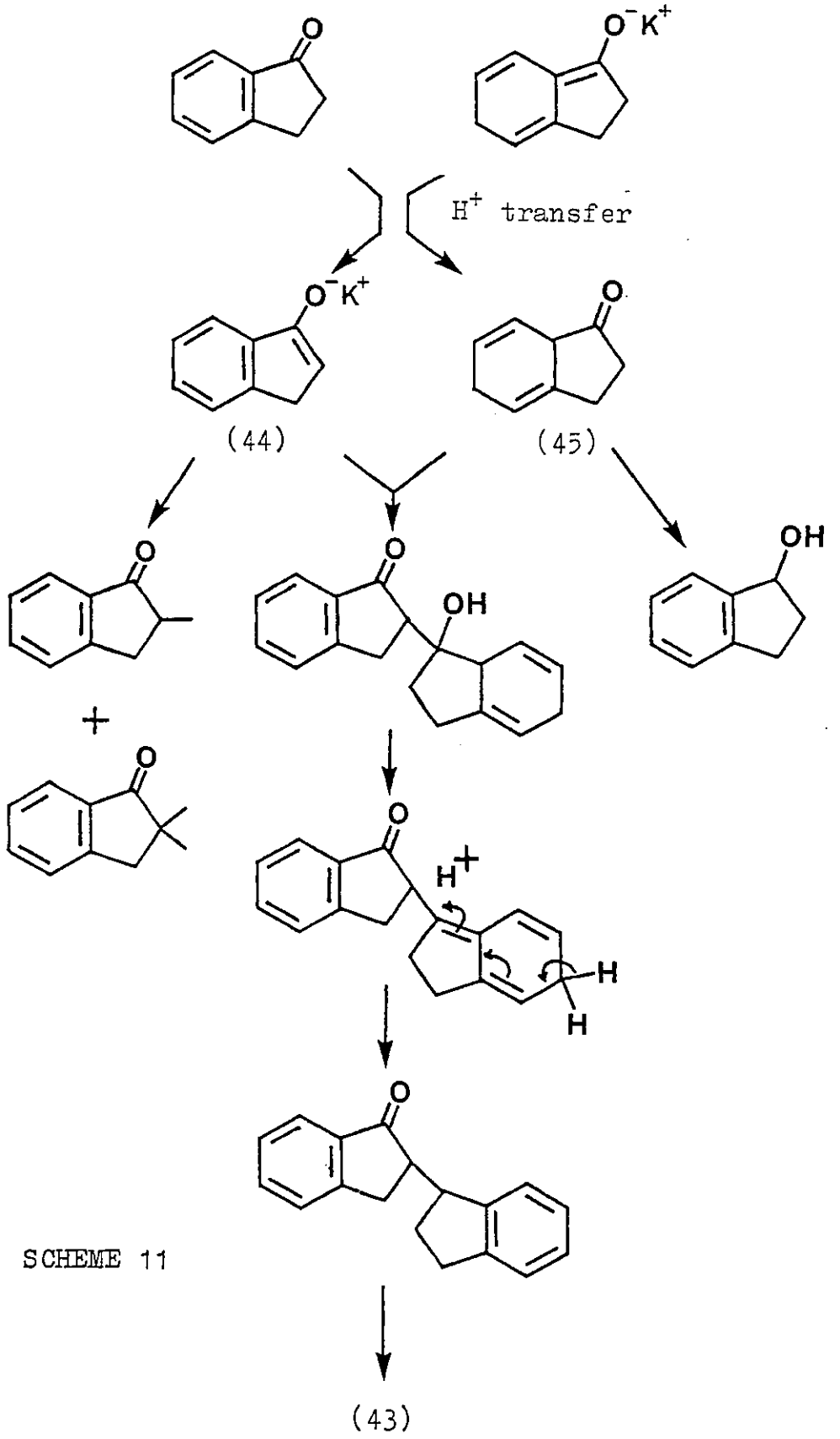
(43)

Considerable overmethylation occurred when 2.2 equivalents of methyl iodide were used and the required dienone was obtained in only 18% yield. The overmethylated dienone (41) and 2,2-dimethylindanone (42) were major byproducts. 2,2-Dimethylindanone (42) was particularly undesirable since it could not be fully separated from the required dienone (40). These two compounds have identical chromatographic characteristics and appear to give an azeotrope on distillation. When a mixture of them is distilled, an initial fraction containing 80% of the dienone (40) is followed by pure dimethylindanone. It was since found that the methylation was sufficiently efficient that only just over one equivalent of methyl iodide was needed and that the yield of (40) was then improved to 40%. No O-methylated products were isolated from any of the reactions.

In an early reaction, a minor byproduct was the unusual unsymmetrical dimer (43) which probably arose from a condensation reaction between reduced and unreduced material. One possible mechanism is illustrated in Scheme 11, and if such a proton transfer is involved, the intermediates (44) and (45) could also give methylated indanones and 1-indanol respectively.

These unwanted reactions would be favoured by the presence of an excess of indanone in the reaction mixture. To avoid this, the order of addition of the reagents was altered. The indanone in tetrahydrofuran containing tert-butanol was added to a preformed solution of potassium in liquid ammonia. The yield of the required dienone was then increased, consistently to over 50%. Table 1

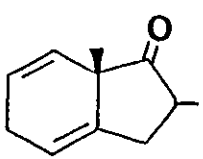
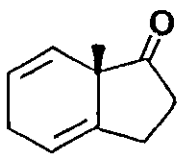
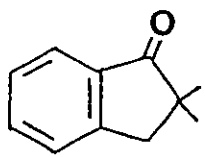
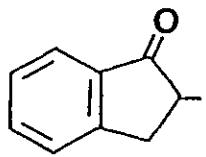
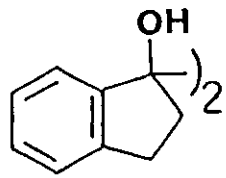
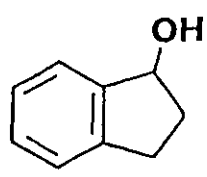
summarises the results of using a variety of conditions.



SCHEME 11

(43)

TABLE 1 Product Distribution in the Reduction and Methylation of 1-Indanone

Conditions	Equivalents of methyl iodide	Yields %						
		 (41)	 (40)	 (42)				
Potassium added to the indanone solution	2.2	22	15	19	1	7	12	*
"	1.7	38	30	14	← not measured →			
"	1.05	13	40	9	2	8	13	
Indanone added to the preformed potassium solution	1.05	3	53	1	2	12	10	**

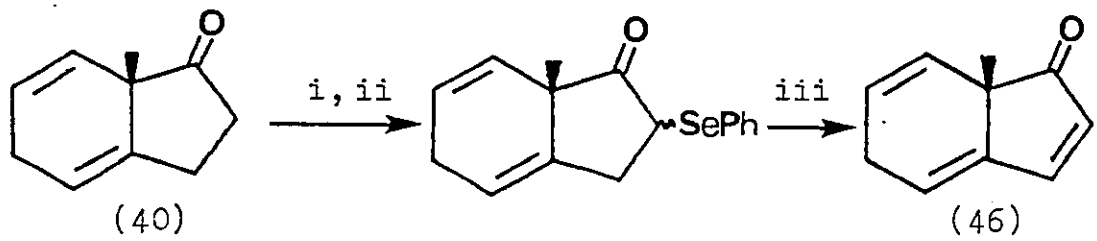
* 5% of the dimer (43) was isolated in one instance under these conditions

** 6% of indane was also isolated

The reduction of 118 g of 1-indanone has been accomplished in one reaction. On this scale, chromatographic work-up is impracticable, both in terms of time and cost. Distillation of the crude product mixture through an efficient fractionating column gave dienone that was pure enough for the next stage of the synthesis.

2.1.2 The Preparation of the Trienone, 5,7a-Dihydro-7a-methyl-1H-inden-1-one (46)

The introduction of the necessary extra unsaturation (Scheme 12) was troublesome.



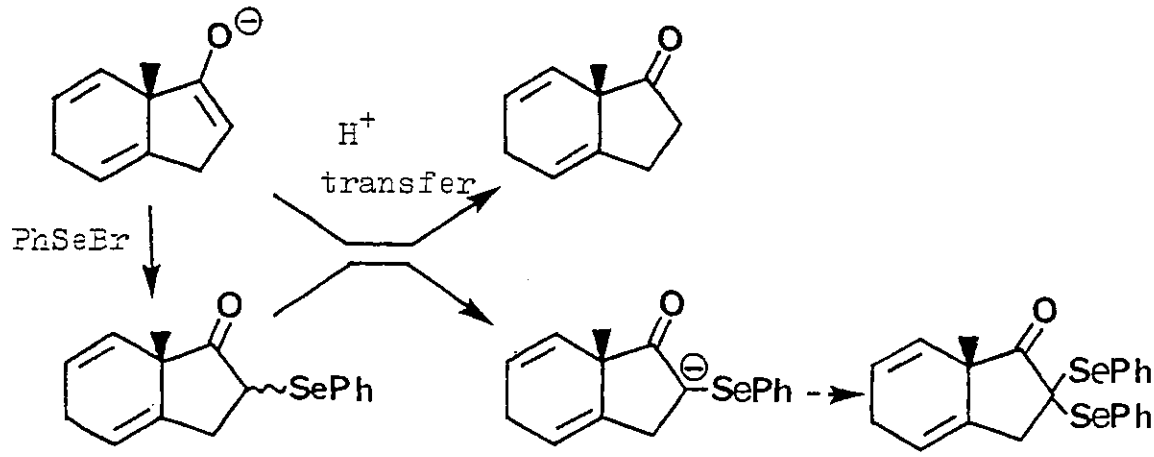
(40) (46)

SCHEME 12

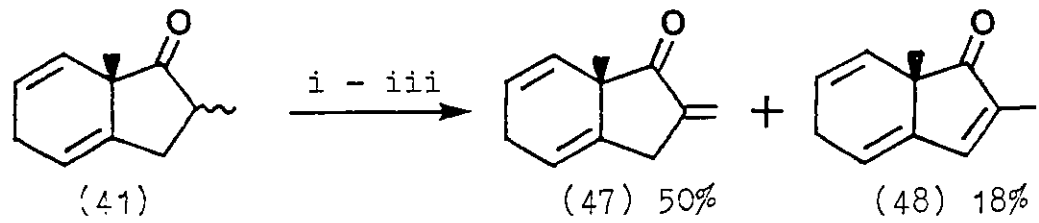
Reagents: i, $LiNPr^i_2$ - THF, -78°C; ii, PhSeBr-THF, -78°C; iii, H_2O_2-H_2O-THF, 0 → 25°C

Although in some small scale reactions, yields of the trienone (46) approaching 60% have been reported,[42a] the yield for the conversion is more frequently in the range 25 - 40% and considerable amounts of starting material were always recovered. The main cause of the low yields was found not to be the oxidation, as previously thought,[42a] and the use of alternative oxidants gave no improvement (see Table 2). The problem was eventually

found to be an acid-base reaction during the phenylselenation (Scheme 13). Two pieces of evidence support this reasoning. Firstly, n.m.r. analysis showed that the crude selenide was a mixture of at least eight compounds. A yield of the selenide was unobtainable since it could not be efficiently separated from other compounds in the mixture. Secondly, when the overmethylated dienone (41) was subjected to the same reaction conditions, no starting material was recovered and a respectable yield of two products was isolated (Scheme 14). In this example, the selenide has no acidic proton and an acid-base reaction cannot occur.



SCHEME 13



SCHEME 14 Reagents: i - iii, as for Scheme 12.

The major product (47) was an unstable oil which rapidly polymerised on standing. Its structure was established by examination of the proton n.m.r. spectrum which showed the five olefinic protons and only one methyl group.

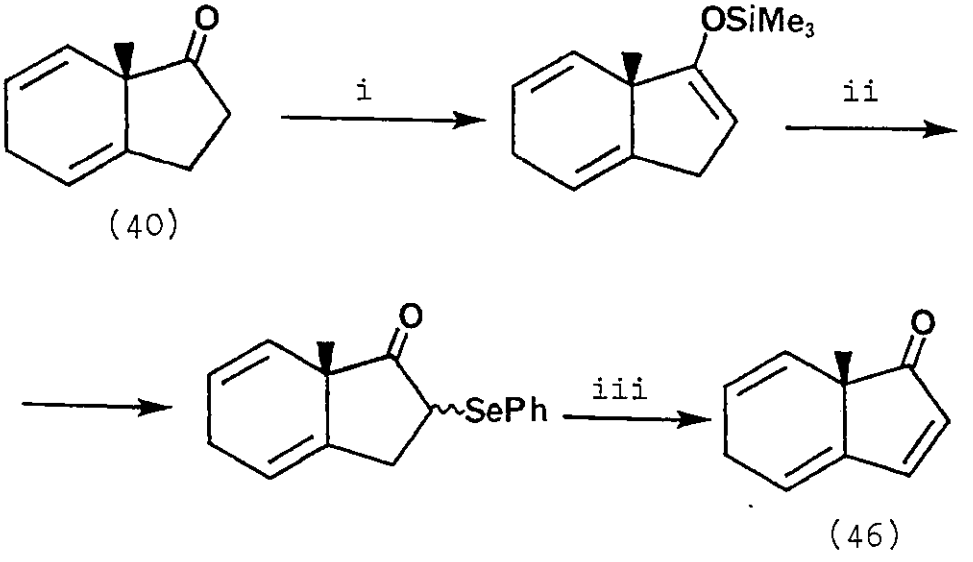
Numerous unsuccessful attempts to improve the preparation of the trienone (46) by adjustment of the reaction conditions are summarised in Table 2. A method involving preparation of the selenide by treatment of the dienone (40) with phenylselenyl chloride in refluxing ethyl acetate[44] gave, after oxidation, only 7% yield of the required trienone.

The absence of recovered starting material when the enolate was trapped with chlorotrimethylsilane prior to the phenylselenation was promising, but the trimethylsilylation was not a clean reaction. It was subsequently found that the dienone could be converted in good yield into its trimethylsilyl enol ether by treatment with chlorotrimethylsilane and triethylamine in acetonitrile containing sodium iodide.[47] This method has the advantages that the reagents are cheap and isolation of the product is simple. Large quantities of the trimethylsilyl ether were thus made easily and converted into the selenide by treatment with phenylselenyl bromide in tetrahydrofuran at -78°C.[48] The selenide prepared in this way was virtually pure (n.m.r.). Oxidation with hydrogen peroxide then gave the trienone (46) in an overall yield of over 50%. Scheme 15 illustrates this improved procedure.

TABLE 2 Variation of the Standard Conditions of Scheme 12 in the Preparation of the Trienone (46)

Alteration to the standard conditions	Yield of trienone (46) %	Yield of recovered dienone (40) %
Two phase oxidation: H_2O_2-H_2O-CH_2Cl_2[45]	27	13
Two phase oxidation: TsN·Cl·Na-H_2O-CH_2Cl_2-$PhMe_3N^+Cl^-$ (cat.)[44]	20	23
Oxidation with m-Cl·C_6H_4·CO_3H-THF-Et_2NH[46]	22	*
Inverse addition of the enolate to phenylselenyl bromide	29	21
Inverse addition of the enolate to phenylselenyl chloride	20	33
Addition of hexamethylphosphoramide (HMPA) with the phenylselenyl bromide	34	29
Enolate trapped with chlorotrimethylsilane at room temperarature, then selenation at -90°C	31	0

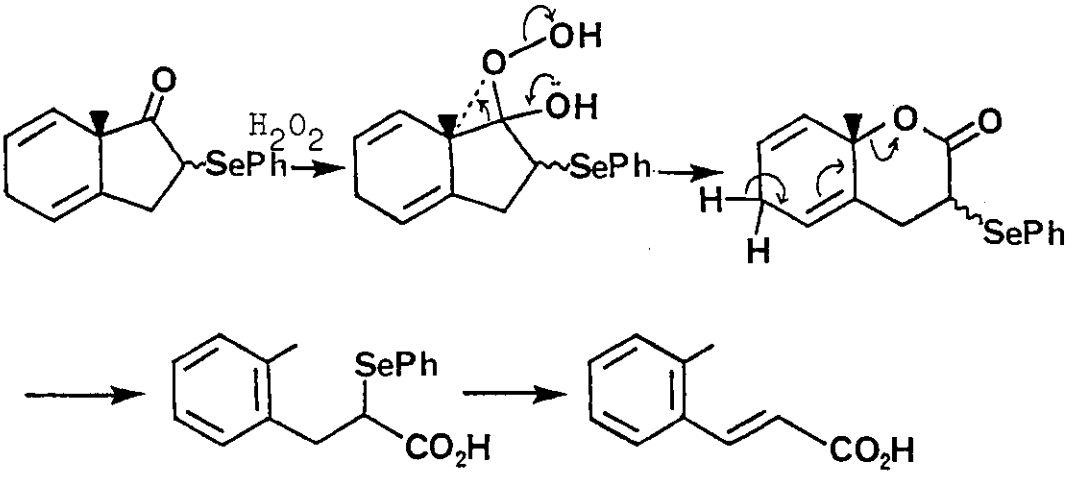
* Yield unknown owing to contamination with unoxidised selenide



SCHEME 15

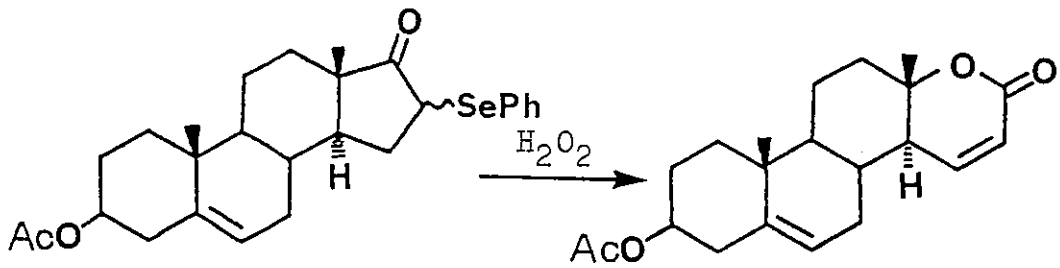
Reagents: i, Me_3SiCl-NaI-Et_3N-CH_3CN, 40°C; ii, PhSeBr-THF, -78°C; iii, H_2O_2-H_2O-pyridine-THF, 5°C

Pyridine has been used as a buffer in selenide oxidations[45] and although its inclusion appears to give no direct yield improvement, the oxidation becomes more controllable since an induction period which can be encountered in the highly exothermic reaction is eliminated. A byproduct of the oxidation is 2-methyl-*trans*-cinnamic acid which is probably formed by way of a competing Baeyer-Villager oxidation of the selenide or selenoxide (Scheme 16).



SCHEME 16

This byproduct was not formed by overoxidation of the trienone (46); the trienone was stable to the reaction conditions. Furthermore, if the oxidation of the trienone did give a cinnamic acid, it would be expected to be of cis-stereochemistry. These findings are contrary to the explanation of Sharpless and co-workers that formation of the lactone (49) from a comparable oxidation was an overoxidation of the enone they wanted.[44] The Baeyer-Villager reaction had probably occurred before the selenoxide elimination.

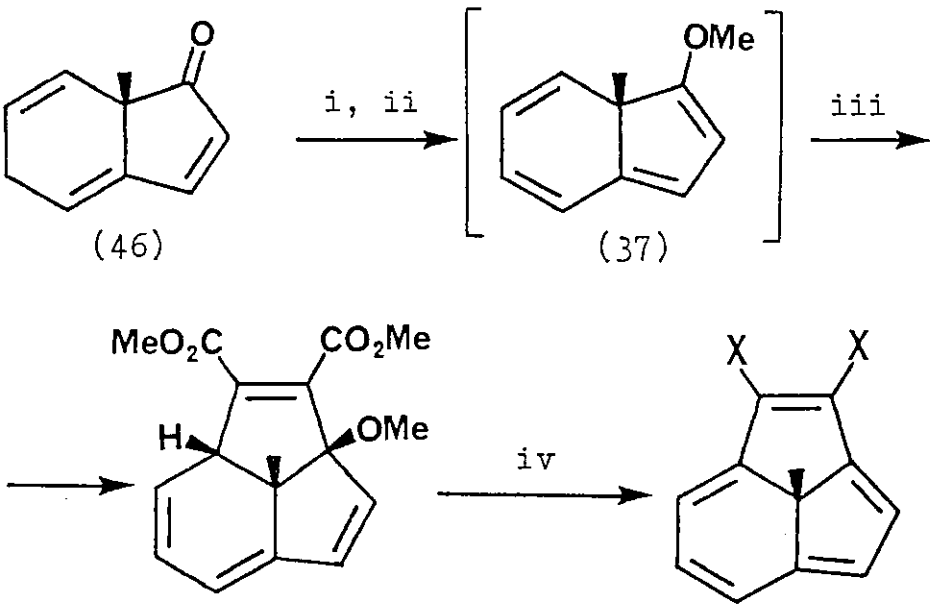


(49)

The trienone (46), a pale yellow oil was isolated by chromatography and could be further purified by a rapid bulb to bulb distillation under nitrogen.

2.1.3 The Adduct of 3-Methoxy-3a-methyl-3aH-indene (37) with Dimethyl Acetylenedicarboxylate and its Conversion into 7b-Methyl-7bH-cyclopent[cd]indene (1)

Conversion of the trienone (46) into the annulene derivative (38) was accomplished by the procedure of Tuddenham (Scheme 17).[42a-c]



SCHEME 17

(38) X = CO_2Me
(50) X = CH_2OH
(51) X = CHO
(1) X = H

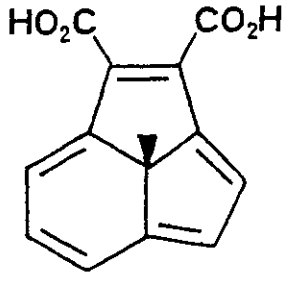
Reagents: i, KH-18-Crown-6-DME, -23°C; ii, $MeOSO_2F$; iii, $MeO_2C-C\equiv C-CO_2Me$; iv, H_2SO_4-MeOH, 0°C or TsOH-C_6H_6, 80°C

The cycloaddition reaction was quite slow and was preferentially done at slightly above room temperature. As well as the acidic catalysts used by Tuddenham,[42a,c,d] the base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) also effected the aromatisation in high yield.

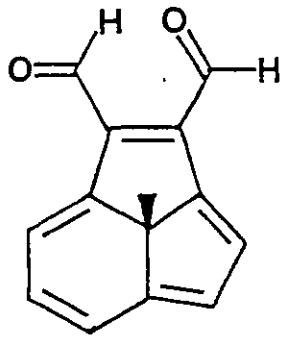
The reduction of the diester (38) into the diol (50) was straightforward, but the product was sensitive and therefore immediately oxidised to the dialdehyde (51). Tuddenham used 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[49] for this oxidation but found that isolation of the product was difficult.[50] Barium manganate has been reported to be a good reagent for the oxidation of benzylic alcohols.[51] Treatment of the diol (50) with an excess of barium manganate in refluxing

dichloromethane afforded the required dialdehyde (51) in a yield of 66% based on the diester (38). This dialdehyde is a stable orange-red solid; its bridgehead methyl group resonates at δ-1.12 in the proton n.m.r. spectrum.

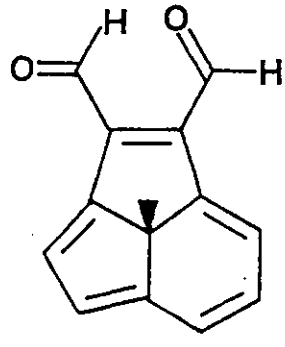
The disorder in the crystal structure of the dicarboxylic acid (39) has been attributed to strong intramolecular hydrogen bonding.[42a] Since such hydrogen bonding cannot be present in the dialdehyde, a crystal structure determination was undertaken.[52] Unfortunately, the same kind of disorder was present and atomic co-ordinates could not be determined accurately. A given site in the crystal was found to be occupied by either of the two structures (51a) or (51b) in a 60 : 40 ratio. Therefore, intramolecular hydrogen bonding is not a necessary criterion for the presence of disorder. The crystal structure data for the dialdehyde (51) are presented in Appendix 1.



(39)

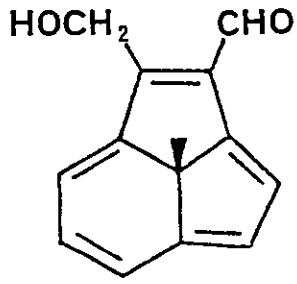


(51a)

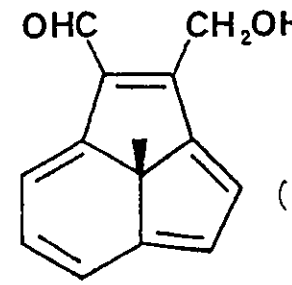


(51b)

If the diol (50) is oxidised with barium manganate at room temperature or below, a 2 : 1 mixture of the two isomers (52a) and (52b) could be isolated. It was surprising that these compounds exist as shown rather than as isomeric lactols, but this explains why the oxidation gives a dialdehyde. Similar oxidation of the corresponding benzene derivative gave a lactone.[53] The open forms are probably favoured for isomers (52a) and (52b) because the five membered ring to which the functional groups are attached will bestow some extra angle strain on the lactol.

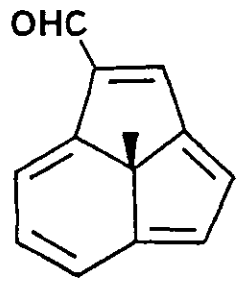


(52a)

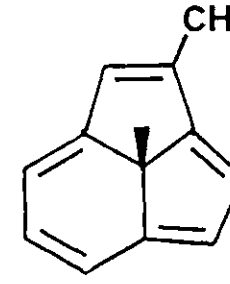


(52b)

Decarbonylation of the dialdehyde (51) with tris(triphenylphosphine)rhodium(I) chloride proceeded smoothly and in high yield in refluxing benzene.[54] The monoaldehydes (53a) and (53b) were intermediates in this reaction and were isolated as an inseparable 5 : 4 mixture when only one equivalent of the reagent was used.



(53a)



(53b)

A byproduct from the decarbonylation reaction is triphenylphosphine which is very difficult to separate from the annulene (1) by physical means. However, it could be removed chemically by final treatment of the reaction mixture with methyl iodide at room temperature; this converts the triphenylphosphine to a salt and leaves the annulene untouched. Chromatography then gives the annulene completely free from triphenylphosphine, as shown by the absence of an ion at m/e 185 due to the diphenylphosphinium ion, Ph_2P^+, in the mass spectrum.

The parent annulene (1) is a free running bright yellow oil which is volatile and can be readily distilled under reduced pressure. It has a green fluorescence in daylight. On exposure to air at room temperature, it slowly undergoes oxidative polymerisation manifested by an increase in viscosity, and it is best stored in solution at low temperature or under nitrogen below its freezing point. An analytical sample prepared by a method yet to be discussed (Section 2.1.7) has m.p. 13°C. The solid is pale yellow and waxy in appearance. A sharp absorption at 450 nm in the electronic spectrum accounts for the yellow colour. Fig. 1 illustrates the spectrum and shows that it has a much greater resemblance to that of 1,5-methano[10]annulene than that of 1,6-methano[10]annulene. This is probably because of the significant transannular interaction in the latter. Compared to the unsubstituted annulene (1), the diester (38) shows a bathochromic shift of about 30 nm owing to the effect of the substituents. A compilation of electonic spectral data for a number of derivatives of the annulene (1) is given in Appendix 2.

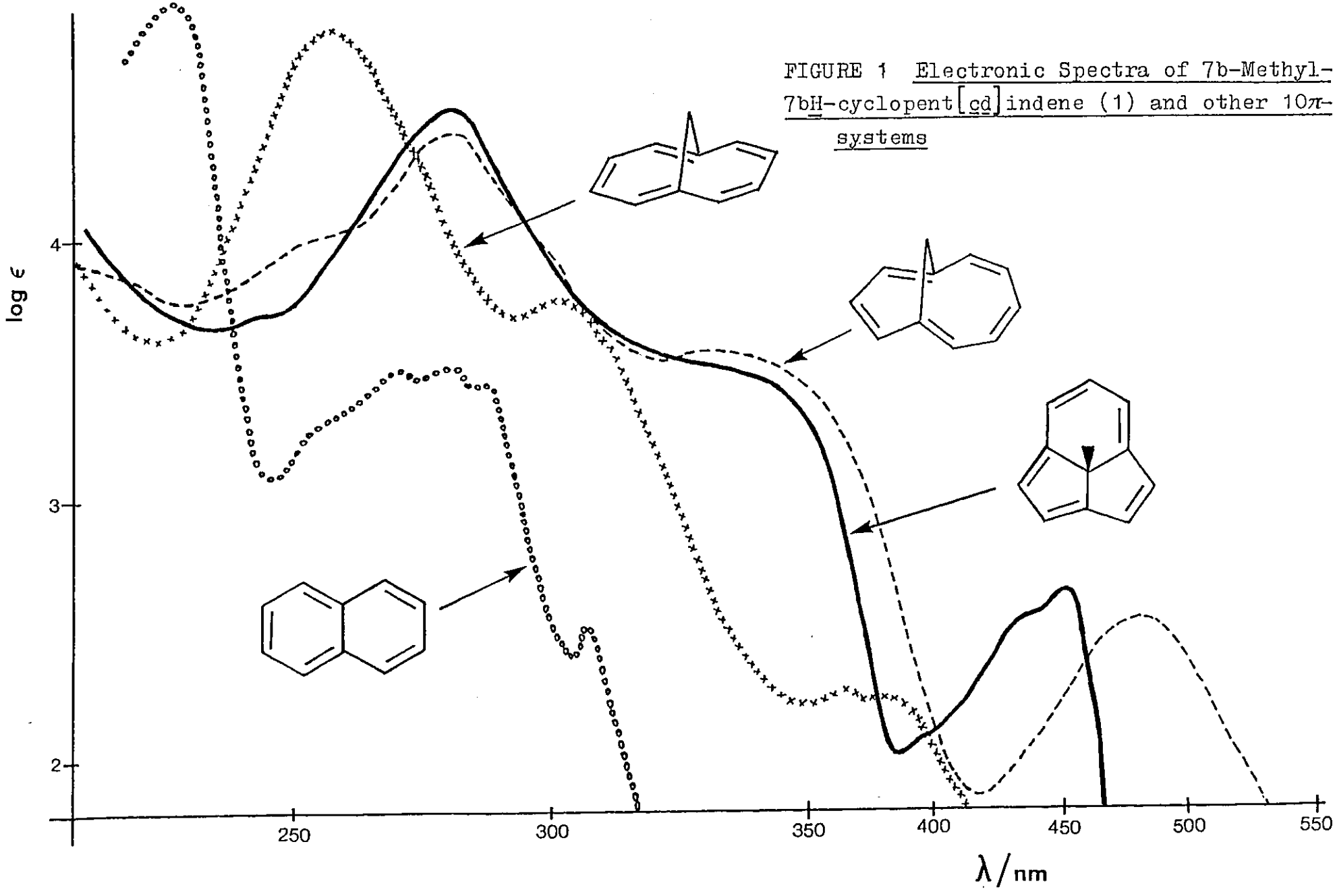
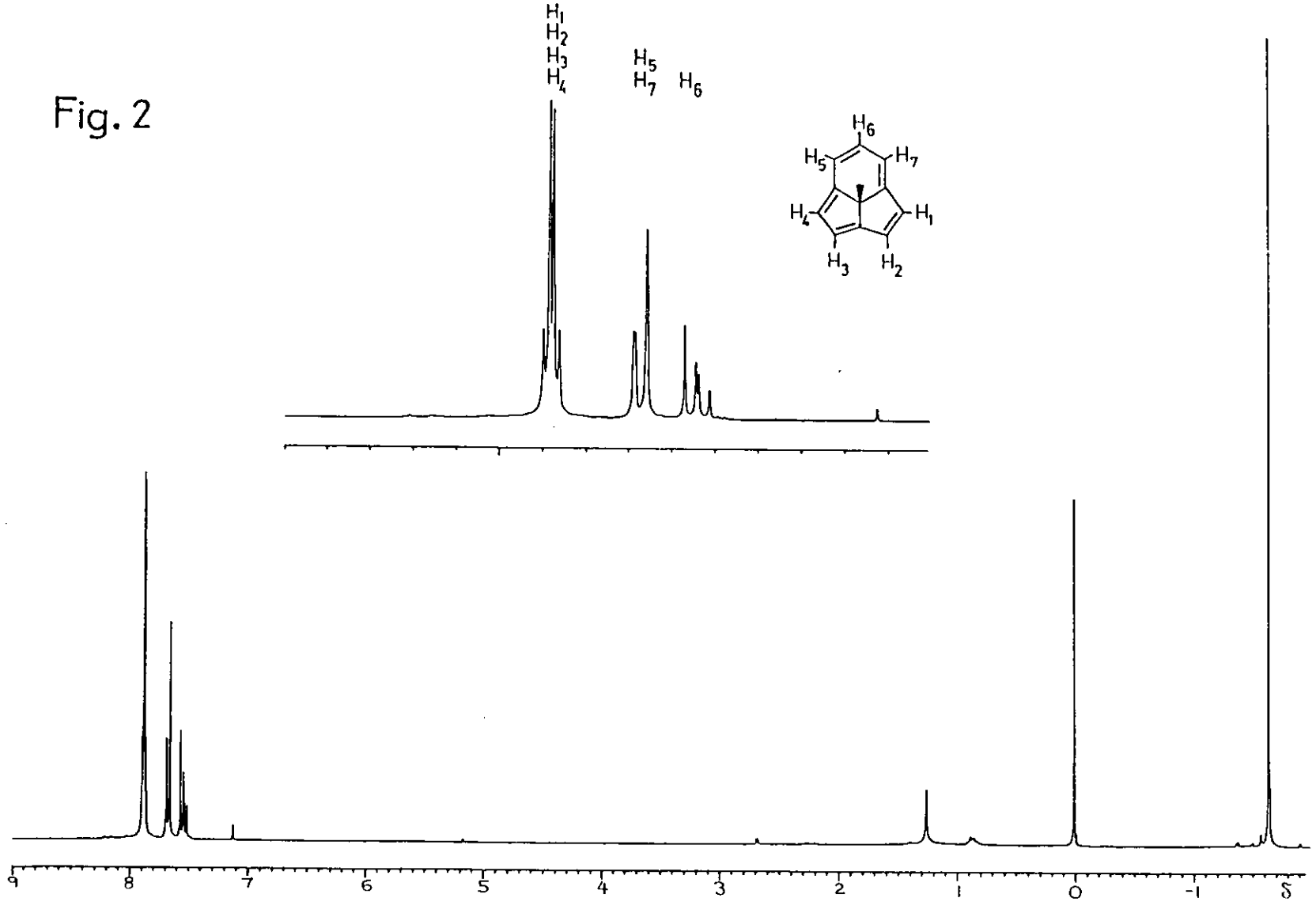


FIGURE 1 Electronic Spectra of 7b-Methyl-7bH-cyclopent[cd]indene (1) and other 10π-systems

Fig. 2



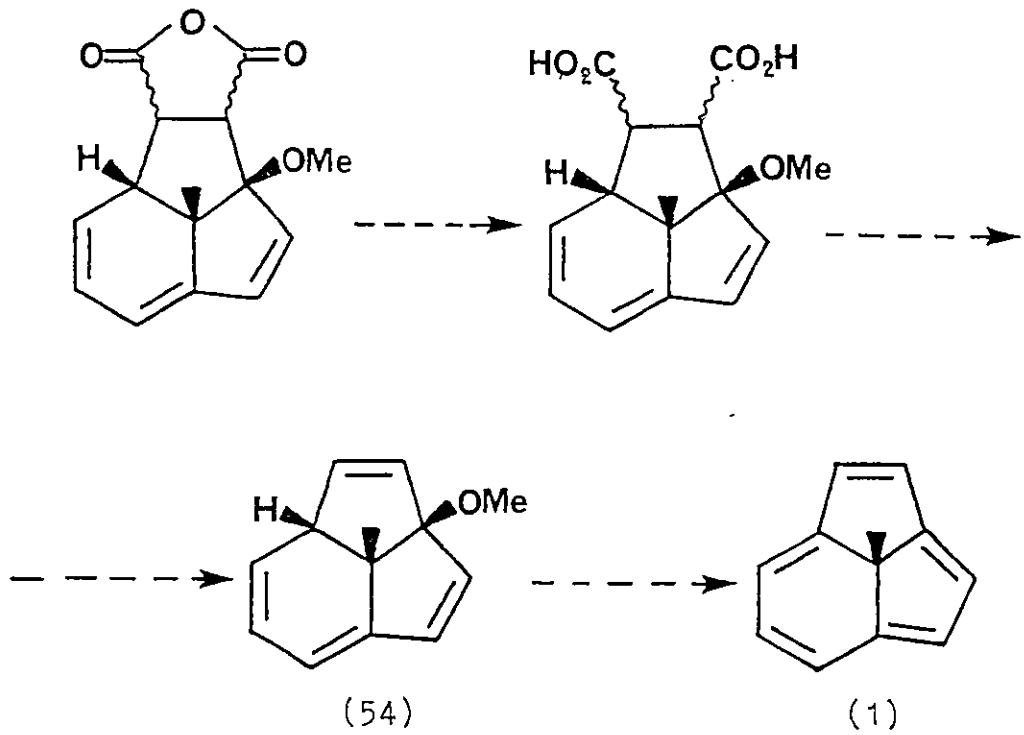
The proton n.m.r. spectrum of the parent annulene (1) shows a methyl singlet at δ-1.67 and the aromatic protons are in the range δ7.4 - 8.2. The spectrum, illustrated in Fig. 2 supports the symmetrical structure of the compound. A compilation of the proton n.m.r. data for a number of derivatives of the annulene (1) is given in Appendix 3. The carbon-13 n.m.r. spectrum and the chemical properties of this annulene are discussed later in this thesis (Sections 2.1.6 and 2.2 respectively).

A severe disadvantage of the above route to the annulene is that the expense of the rhodium reagent, of which two equivalents are necessary, precludes the preparation of substantial quantities of the parent system. Unfortunately, reagents which are reported to give catalytic decarbonylation of aldehydes were not suitable. Bis(1,2-bisdiphenylphosphinoethane)rhodium(I) chloride, $[Rh(dppe)_2Cl]$,[55] bis(1,3-bisdiphenylphosphinopropane)rhodium(I) chloride, $[Rh(dppp)_2Cl]$,[55] and bis(triphenylphosphine)tetraphenylporphyrinatoruthenium(II), $[Ru(tpp)(PPh_3)_2]$,[56] all decomposed during the attempted decarbonylation and very little of the dialdehyde was consumed. The rhodium reagents were prepared by a combination of literature methods[57,58] and the ruthenium complex was kindly supplied by Dolphin.

2.1.4 The Adducts of 3-Methoxy-3a-methyl-3aH-indene (37) with Maleic Anhydride and N-Phenylmaleimide

The problem above prompted a reinvestigation of the use of maleic anhydride as the dienophile in the trapping of the 3a*H*-indene derivative (37). It was proposed that

electrolytic oxidative bis-decarboxylation of the dicarboxylic acids derived by hydrolysis of the [8+2] adducts would give an immediate precursor (54) of the parent annulene (1) (Scheme 18).

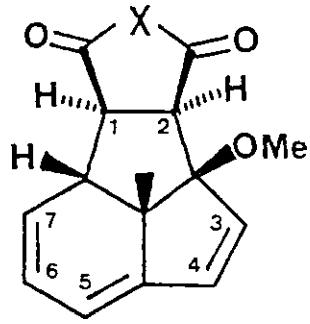


(54) (1)

SCHEME 18

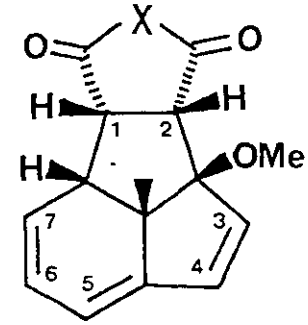
Tuddenham reported that the cycloaddition of maleic anhydride with the 3a<u>H</u>-indene (37) gave a complex mixture of adducts in poor yield.[42a,b] The cause of the low yields was possibly the ease of hydrolysis of the adducts on silica during chromatography. Inclusion of a small amount of acetic anhydride in the eluant facilitated chromatographic purification and at room temperature a mixture of adducts could then be isolated in good yield (65%). After heating this mixture on a steam bath, it could be separated by further chromatography into two components. These could be ascribed as [8+2] adducts from the close resemblance of their proton n.m.r. spectra to those of the known [8+2] adducts of <u>N</u>-phenylmaleimide.[42a,b] It was found that for both

maleic anhydride and N-phenylmaleimide, the less polar and more polar [8+2]adducts were formed in a 2 : 3 ratio. A matter of concern had been the assignment of the stereochemistry of these [8+2]adducts. Tuddenham quoted a coupling constant of 1.9 Hz for H-6 to H-7 in the less polar N-phenylmaleimide adduct which could not be adequately explained and led to doubts about the structure of the compound.[42a] The n.m.r. spectrum of the corresponding maleic anhydride adduct was interpreted but gave a normal coupling of 9 Hz for H-6 to H-7. Comparison of the spectra of these two compounds revealed that the resonance containing the 1.9 Hz coupling in the N-phenylmaleimide adduct was that of H-5 and that its previous assignment as H-6 was incorrect. This small coupling is that between H-5 and H-7. By careful examination of the multiplet in the spectrum due to H-6 and H-7, a normal coupling constant of 10 Hz for H-6 to H-7 could be revealed.



(55a) X = NPh
(55b) X = O

exo-



(56a) X = NPh
(56b) X = O

endo-

The alteration of the assignments of the spectra not only verifies the structure of the adducts but nullifies

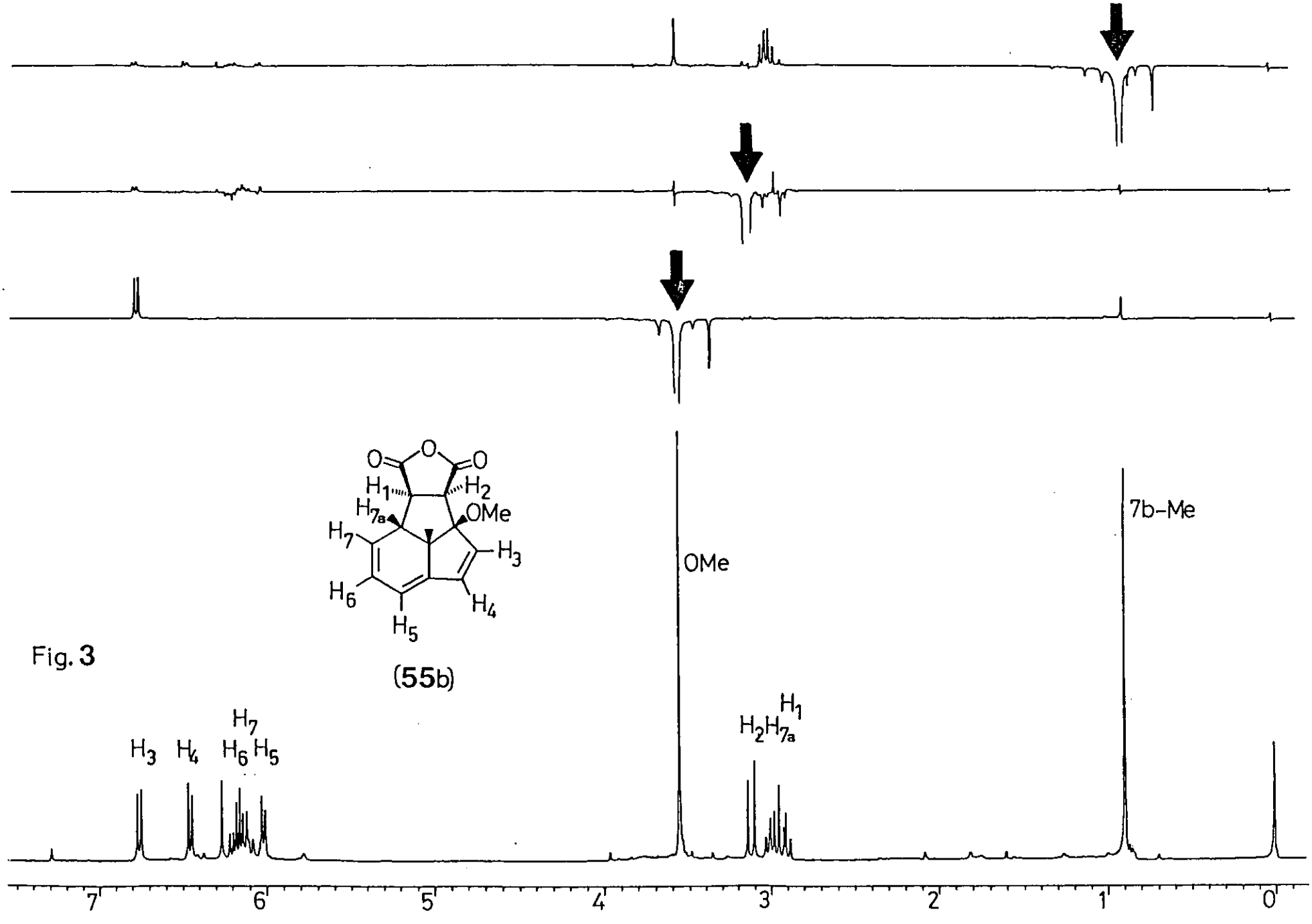

H1
H2
H7a
OMe
H7
H3
H6
H4
H5
(55b)
OMe
7b-Me
H3
H4
H7
H6
H5
H1
H2H7a
7
6
5
4
3
2
1
0

Fig. 3

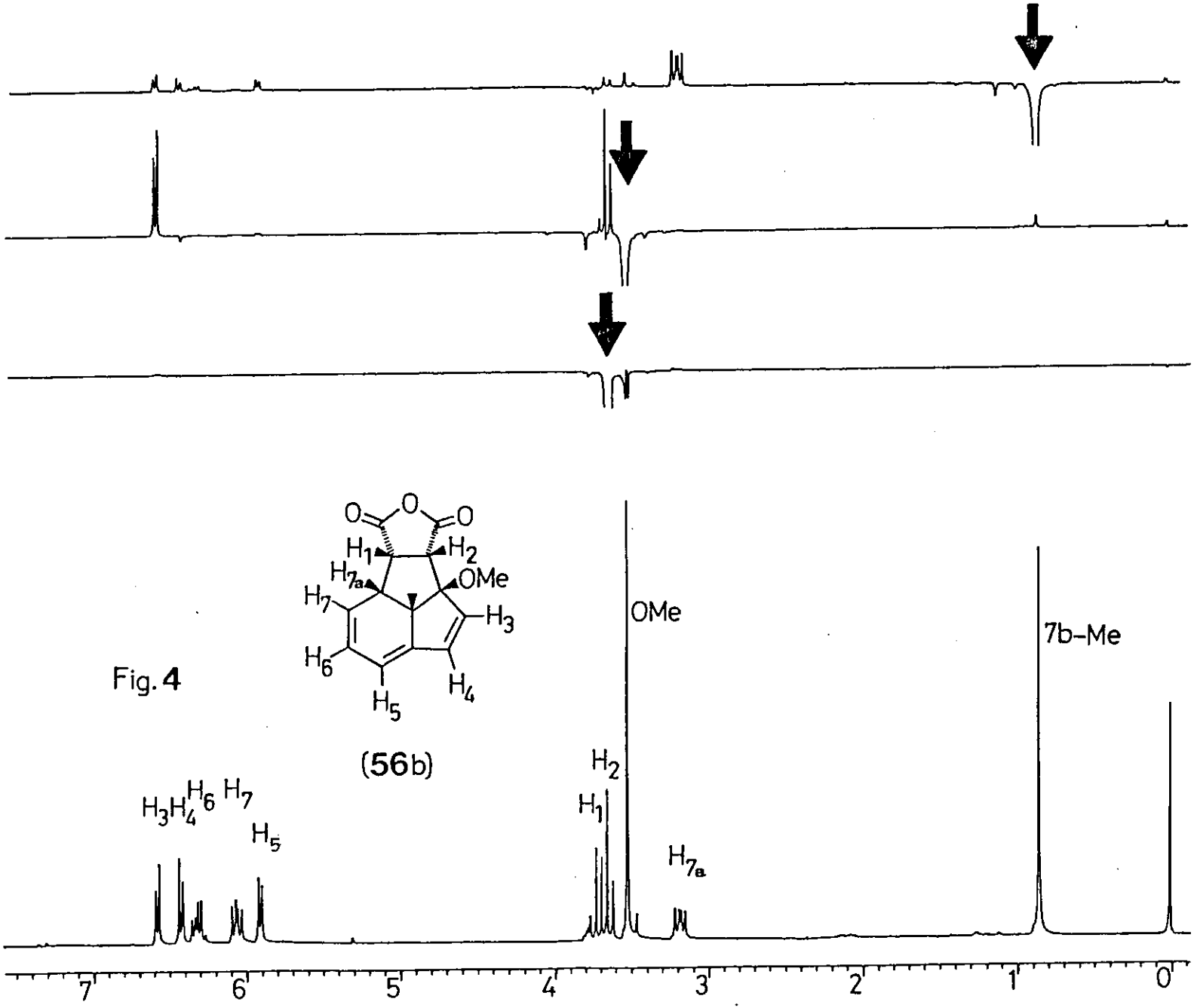
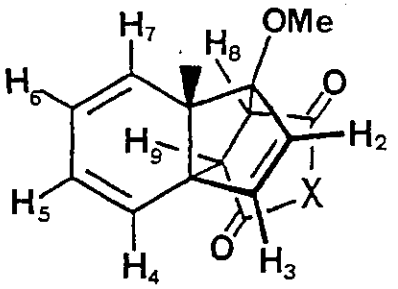

O
O
O
H1
H2
H7a
OMe
H7
H3
H6
H4
H5
(56b)
OMe
7b-Me
H2
H1
H7a
H3 H4 H6 H7
H5
7
6
5
4
3
2
1
0

Fig. 4

the argument of Tuddenham based on the coupling constants for assignment of the less polar product as the endo-isomer (56a).[42a] To assign the stereochemistry of these adducts, the nuclear Overhauser effect (n.O.e.) technique was used. This showed the previous assignments of stereochemistry were incorrect and that the less polar adducts are of exo-sterochemistry (ie. 55a and 55b). The measurements were made on the maleic anhydride adducts since these have the clearer spectra. Irradiation of the protons of the methoxy group gave an enhancement of the signal for H-2 only in the more polar isomer in which H-2 and the methoxy group must be in a cis-relationship. Both isomers showed the expected strong enhancement of H-7a when the methyl group was irradiated, confirming their cis-relationship. Figs 3 and 4 illustrate the nuclear Overhauser effects obtained.

It is known that the [8+2] N-phenylmaleimide adducts are derived by a thermal rearrangement of an initial [4+2]-adduct at about 90°C.[42a,b] For the maleic anhydride adduct, the rearrangement occurs at about room temperature, making it difficult to isolate the [4+2]maleic anhydride adduct. A reasonable sample of the compound was prepared by keeping the product below room temperature throughout the work-up. Solvents were removed at 0°C using a rotary evaporator attached to a cold trap and high vacuum pump, and the chromatography column was cooled by a jacket of ice-water. The proton n.m.r. spectrum of the initial adduct was very similar to that of the stable initial adduct of N-phenyl-maleimide. The initial maleic anhydride adduct rearranges to the [8+2]adducts with a half life of about 10 min at

35°C. The initial [4+2]adducts (57a and 57b) were shown to be of the expected endo-stereochemistry by n.O.e. measurements on the N-phenylmaleimide adduct (57a). Fig. 5 illustrates the results obtained. Irradiation of the methoxy group gave strong enhancements of the signals due to H-2 and H-8, and lesser enhancements of H-7 and the bridgehead methyl group. When H-8, as determined by this experiment was irradiated, enhancement of the signal for H-7 was observed, confirming the endo-stereochemistry. If the stereochemistry were exo-, an enhancement of the signal for H-2 would have been expected instead. Further confirmation was that irradiation of H-9 gave approximately equal enhancements of H-4, H-5, H-6 and H-7. Molecular models show H-9 to be close and equidistant from these four protons only in an endo-isomer.



(57a) X = NPh
(57b) X = O

The non-interconvertibility of the [8+2]adducts by heat was taken as evidence for a dissociation-recombination mechanism for the thermal rearrangement of the [4+2]adducts.[42a] This mechanism is strongly supported by trapping experiments. When the [4+2]maleic anhydride adduct (57b) is warmed in the presence of N-phenylmaleimide,

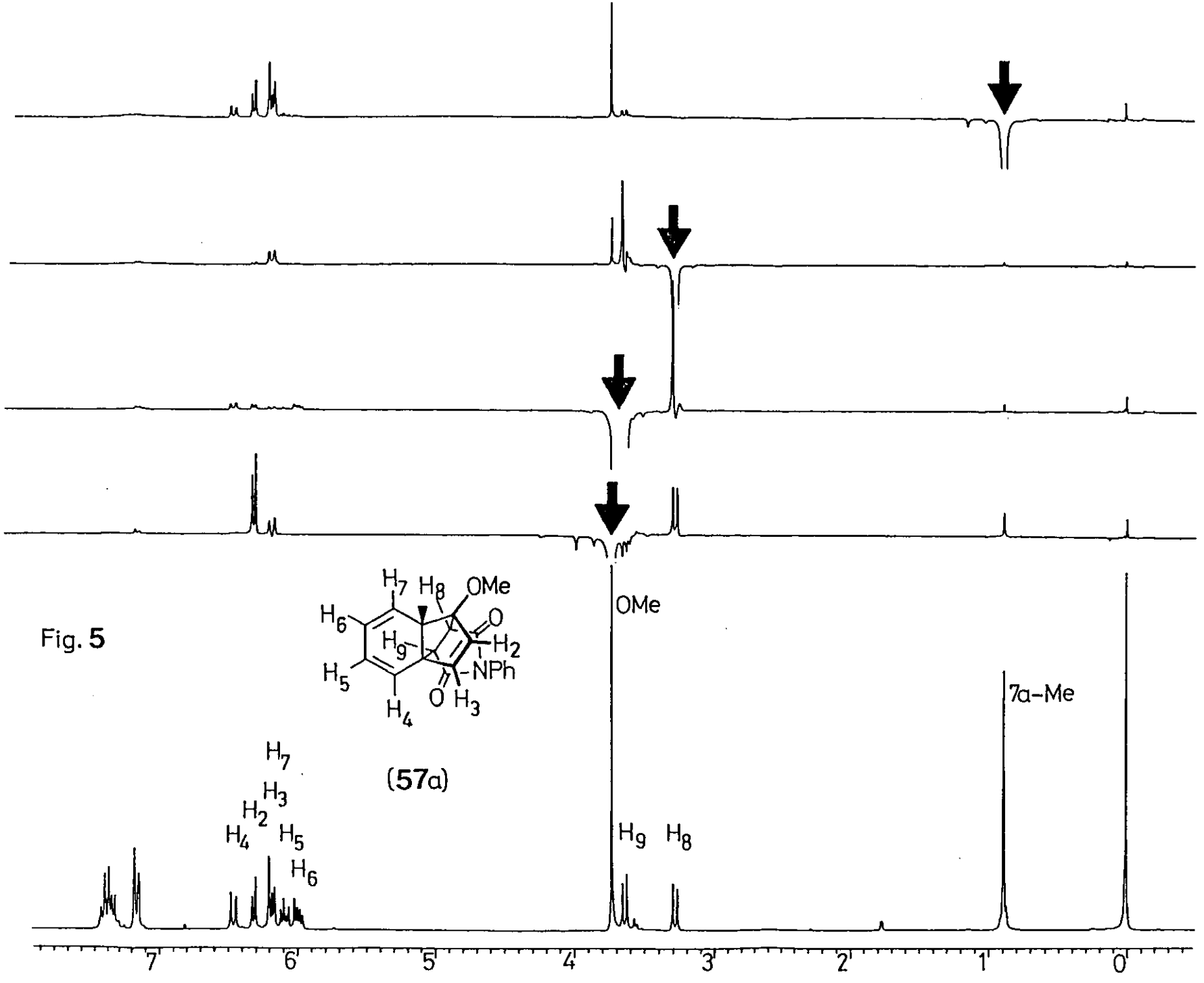

H7 H8 OMe
H6
H9
H2
H5
NPh
O
H4
O H3
OMe
7a-Me
H7
H3
H2
H4
H5
H6
H9 H8
7
6
5
4
3
2
1
0

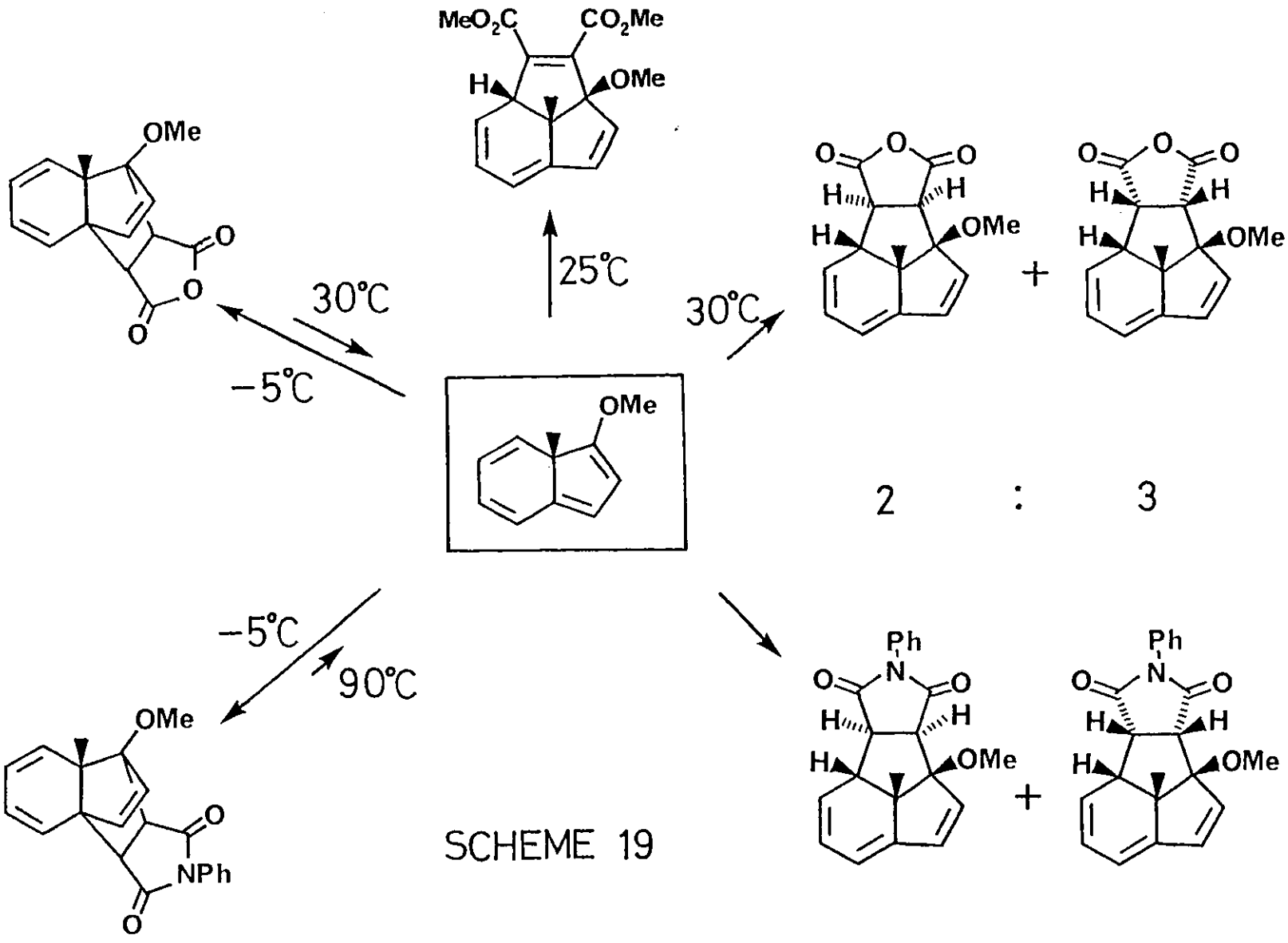
Fig. **5**

(**57a**)

the [4+2] N-phenylmaleimide adduct (57a) is formed. The [8+2] dimethyl acetylenedicarboxylate (DMAD) adduct was formed when either of the [4+2]adducts (57a) or (57b) were heated in the presence of DMAD at 110°C and 40°C respectively. These experiments show that the 3aH-indene (37) is an intermediate in the rearrangement process and therefore support a dissociation-recombination mechanism. In a complementary experiment, the [4+2]adduct (57b) was warmed in ether in the presence of cyclopentadiene. Here it is the maleic anhydride that is trapped and a bright yellow solution of the 3aH-indene (37) remained. Scheme 19 illustrates the processes involved and the approximate temperatures at which the transformations occur.

In an attempt to add phenyl vinyl sulphoxide to the 3aH-indene (37), the [4+2]adduct (57a) was heated in the presence of a large excess of this dienophile in the hope that the 3aH-indene generated at a relatively high temperature would be trapped as required. However, no new adduct was formed and one of the [8+2]N-phenylmaleimide adducts was isolated from the resulting mixture. Had phenyl vinyl sulphoxide given an [8+2]adduct, a facile elimination of phenylsulphenic acid could have given the tetraene (54) directly.[59]

Unfortunately, attempts to use the maleic anhydride adducts as annulene precursors were unsuccessful. When the dicarboxylic acid salts obtained from a solution of a mixture of [8+2]adducts in methanolic potassium hydroxide was electrolysed using a platinum anode, or when a solution of the anhydrides in aqueous pyridine containing triethylamine was electrolysed,[60,61] none of the required product was


MeO2C
CO2Me
H
OMe
25°C
OMe
O
O
O
30°C
−5°C
30°C
H
OMe
+
OMe
2 : 3
−5°C
90°C
OMe
NPh
Ph
N
+
SCHEME 19

detected in the resulting mixture although starting material was consumed. The failure of this method was probably the consequence of the presence of a conjugated triene in the molecule. Quoted oxidation potentials[62] (Table 3) indicate that a conjugated triene may take up electrons more readily than a carboxylate group. Furthermore, no example has been located in the literature of the successful bis-decarboxylation of a compound containing conjugated double bonds apart from one example in which benzene is the product.[63]

TABLE 3 Oxidation Potentials[62]

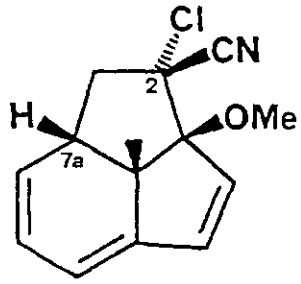
Discharge of carboxylate	+0.8 to +2.5 V
Ethylene	+2.90 V
1,3-Butadiene	+1.84 V
1,3,5-Cycloheptatriene	+1.13 V

Further attempts to utilise these adducts were discontinued when work with dienophiles derived from acrylic acid started to show much promise.

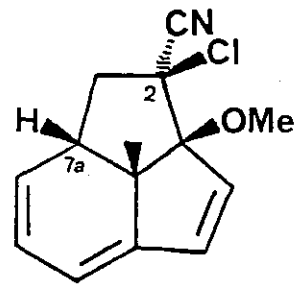
2.1.5 The Adducts of the 3aH-Indene (37) with 2-Chloroacrylonitrile; Their Reactions and Conversion into the Annulene (1)

The commercially available dienophile, 2-chloroacrylonitrile was just sufficiently reactive to add to the 3aH-indene (37). The reaction mixture had to be heated to about 60°C and a mixture of adducts was formed. Separation by column chromatography gave first a 55% yield of a mixture

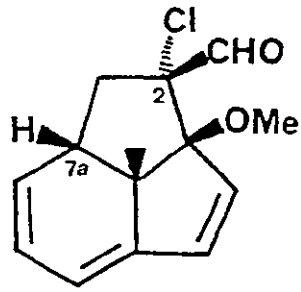
of the [8+2]adducts (58a) and (58b) in a 3 : 1 ratio.



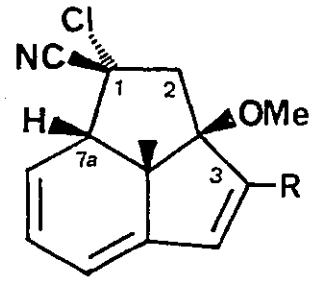
(58a)



(58b)



(59)



(60a) R = H
(60b) R = Me

The structure of these adducts was assigned on the basis of n.m.r. which showed a pattern of olefinic proton resonances very similar to that of [8+2]adducts already described. Coupling between the protons originating from the dienophile and the bridgehead proton, H-7a, confirmed the regiochemistry. When this mixture of stereoisomers was cooled in ice, the major isomer (58a) crystallised selectively leaving an oil enriched in the minor isomer (58b). The relative stereochemistry at C-2 was determined by n.O.e. measurements on the aldehyde (59) (Fig. 6) which was prepared by reduction of the adduct (58a) with

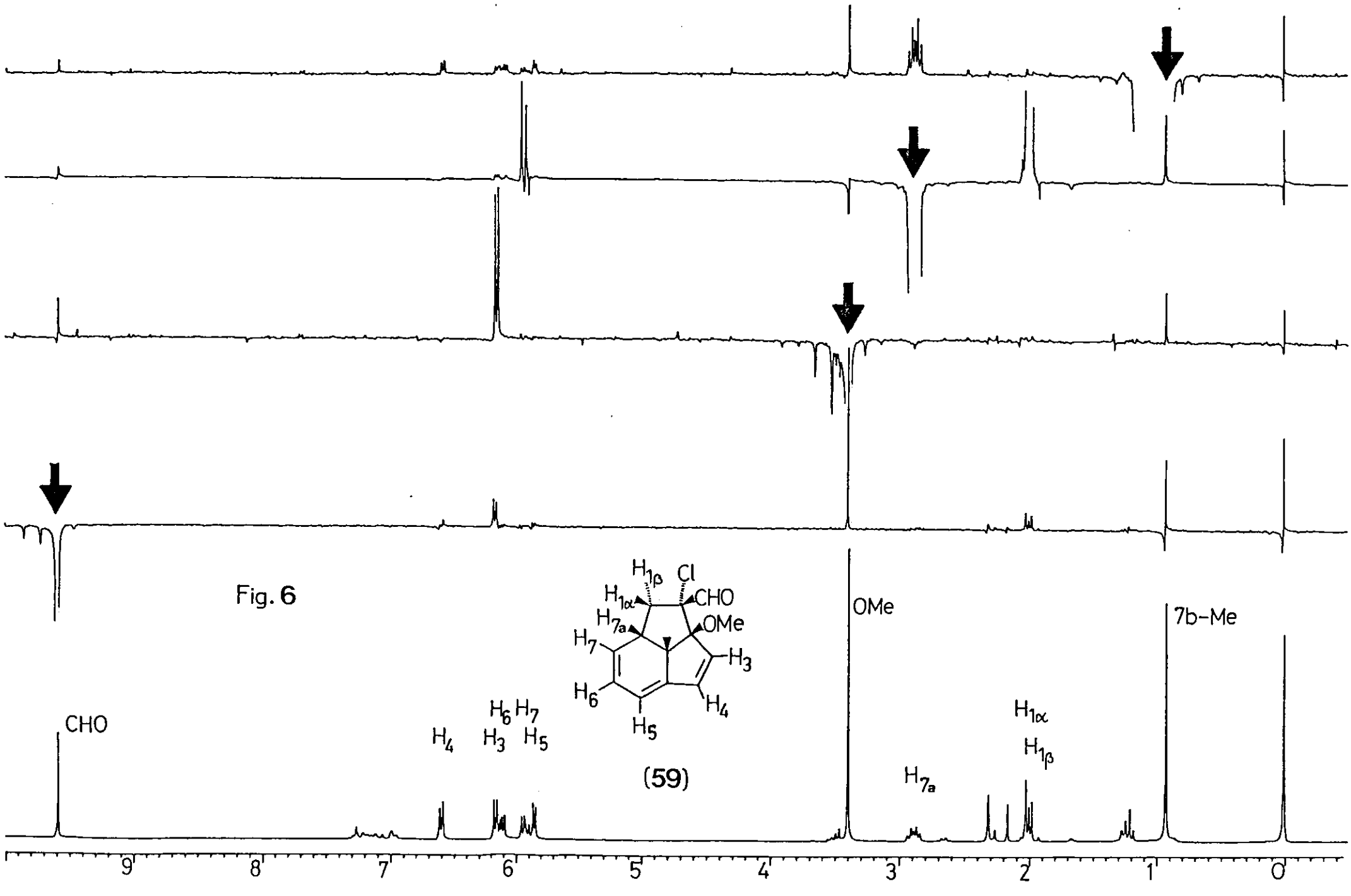

CHO
H4
H6 H7
H3 H5
OMe
H7a
H1α
H1β
7b-Me
9
8
7
6
5
4
3
2
1
0

Fig. 6

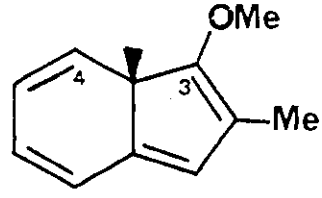
H1β
Cl
H1α
CHO
H7a
OMe
H7
H3
H6
H4
H5

(59)

diisobutylaluminium hydride (DibalH). A small enhancement of the aldehyde proton resonance was observed on irradiation of either H-7a or the central methyl group. This would not be expected if the stereochemistry at C-2 was reversed.

Further elution of the column gave a mixture of the two adducts (60a) and (60b) in a 3 : 2 ratio. This mixture had an electronic spectrum (λ_{max} 305 nm) identical to that of (58a) showing the same conjugated triene to be present, but in the n.m.r. spectrum, the protons which originated from the dienophile were not coupled to H-7a. The stereochemistry was determined in the same way as was that of adduct (58a). The mixture was reduced with diisobutylaluminium hydride and n.O.e. measurements made on the resulting mixture of aldehydes (Figs 7 and 8). For both of the compounds in the mixture, irradiation of the aldehyde proton or the methoxyl methyl protons enhance the signal of the same one of the two protons at position-2. Thus, the aldehyde and methoxy groups must lie on the same side of the molecules.

The presence of the homologue (60b) can be explained by addition of the 2-chloroacrylonitrile to the overmethylated 3a<u>H</u>-indene (61).



(61)

Examination of the n.m.r. spectrum of the trienone starting material showed that it was not contaminated with

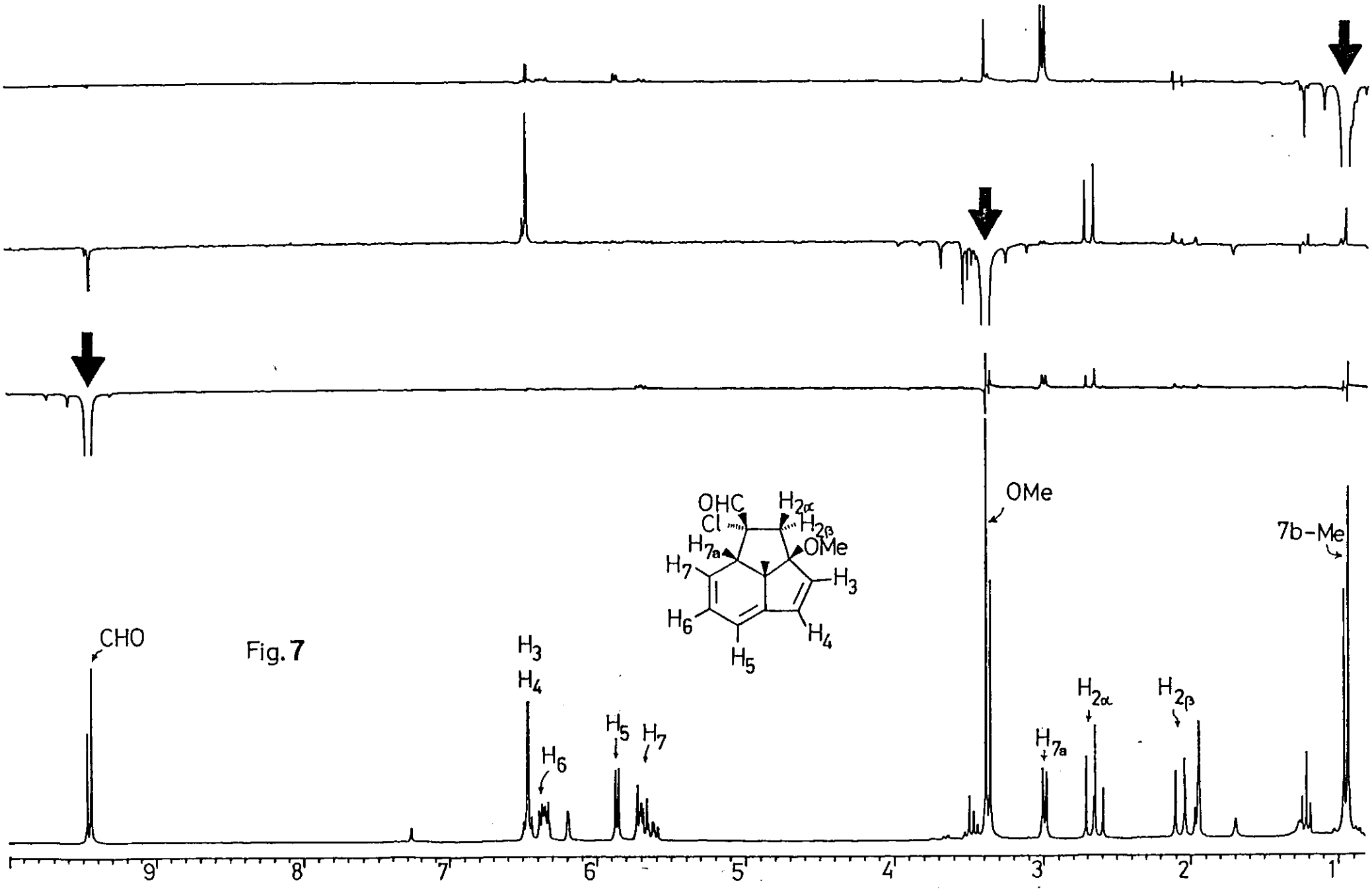

OHC
Cl
$H_{2\alpha}$
$H_{2\beta}$
H_{7a}
OMe
H_7
H_3
H_6
H_4
H_5
CHO
H_3
H_4
H_6
H_5
H_7
OMe
H_{7a}
$H_{2\alpha}$
$H_{2\beta}$
7b-Me
9
8
7
6
5
4
3
2
1

Fig. 7

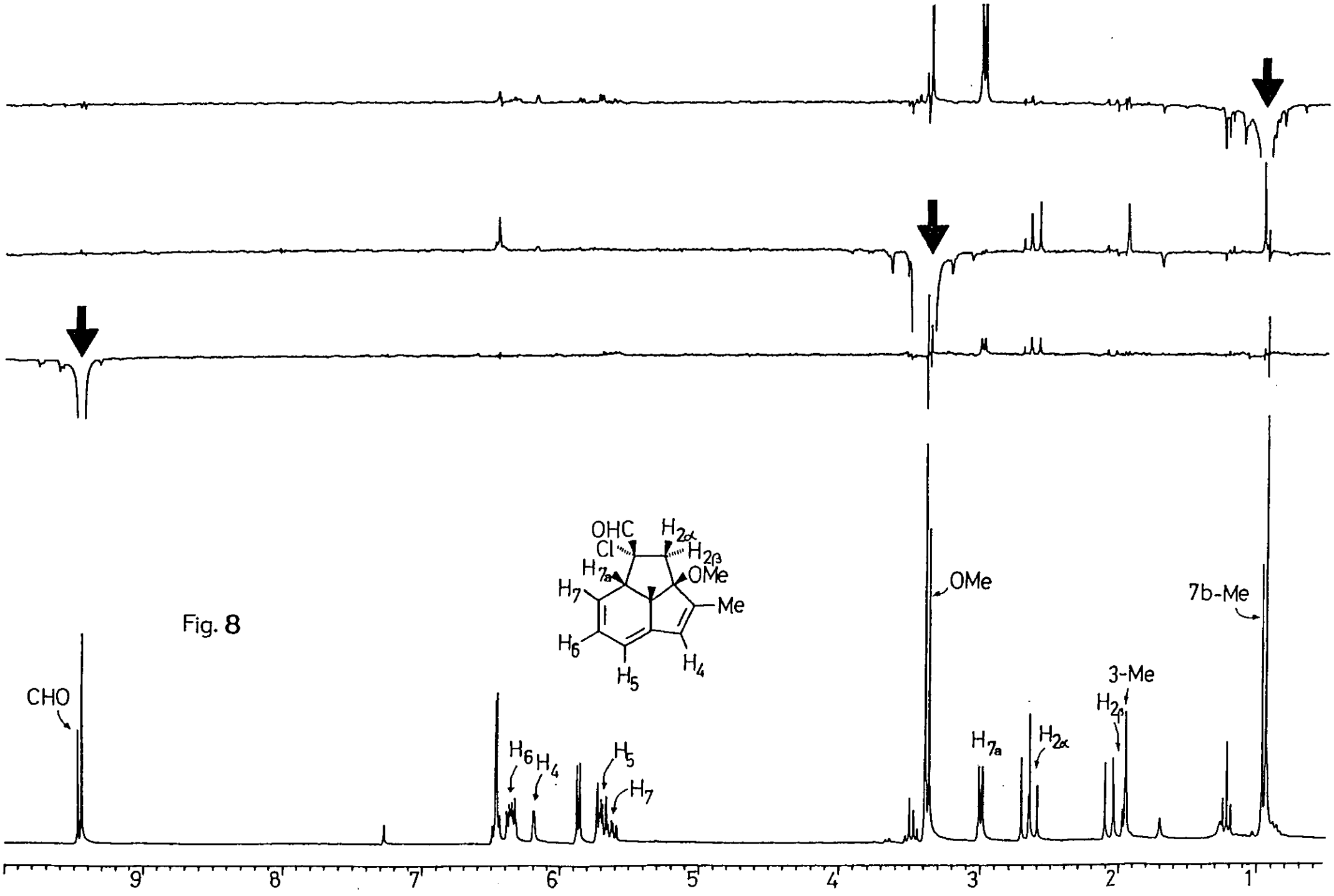
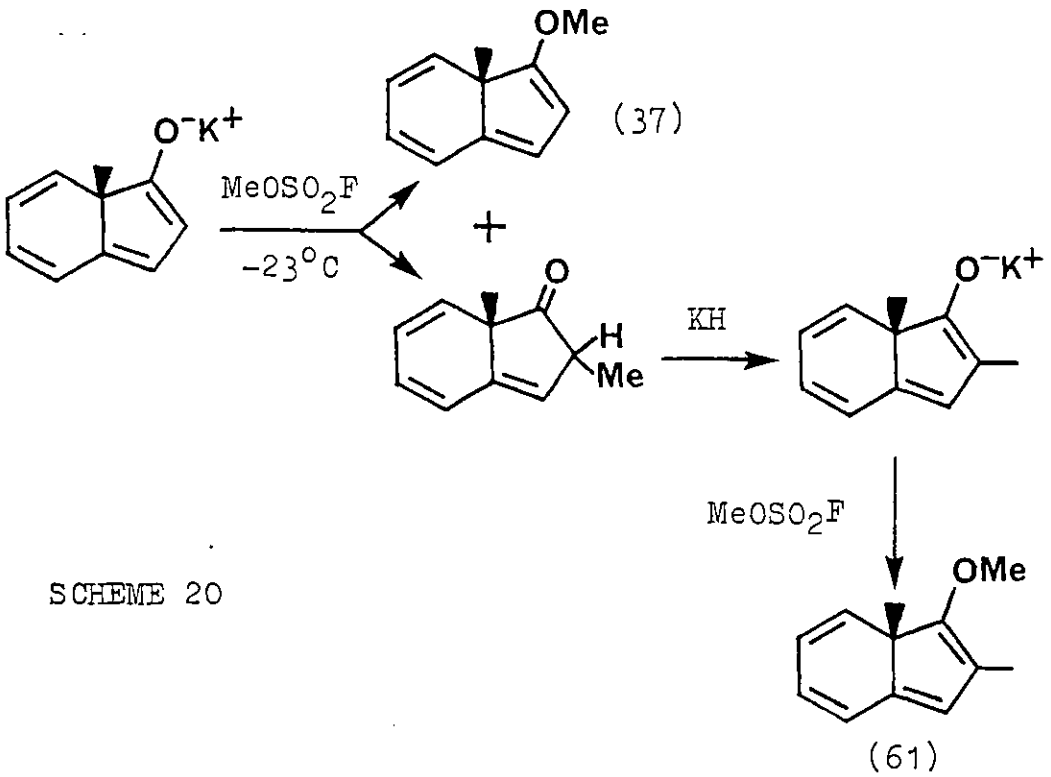

OHC
Cl
$H_{2\alpha}$
$H_{2\beta}$
H_{7a}
OMe
H_7
Me
H_6
H_5
H_4
CHO
H_6 H_4
H_5
H_7
OMe
H_{7a}
$H_{2\alpha}$
3-Me
$H_{2\beta}$
7b-Me
9
8
7
6
5
4
3
2
1

Fig. 8

any of its homologue (48) and hence the extra methyl group must have come from the methyl fluorosulphonate used. It was first thought that the indene (61) was derived from the normal indene (37) by an overmethylation with the excess of methyl fluorosulphonate present in the reaction mixture at the relatively high temperature required for the cycloaddition. In a further experiment, triethylamine was added to destroy excess methylating agent before the mixture was heated with the dienophile. Unexpectedly, the product distribution from the reaction was unchanged by this modification. Therefore, the indene (61) must have been formed by way of an initial C-methylation of the anion (Scheme 20).



SCHEME 20

The 3a<u>H</u>-indene (61) appears to react with 2-chloroacrylonitrile to give adduct (60b) exclusively; no homologues of adducts (58a) or (58b) were detected. This

unusual regiospecificity can be explained as a combination of two factors:

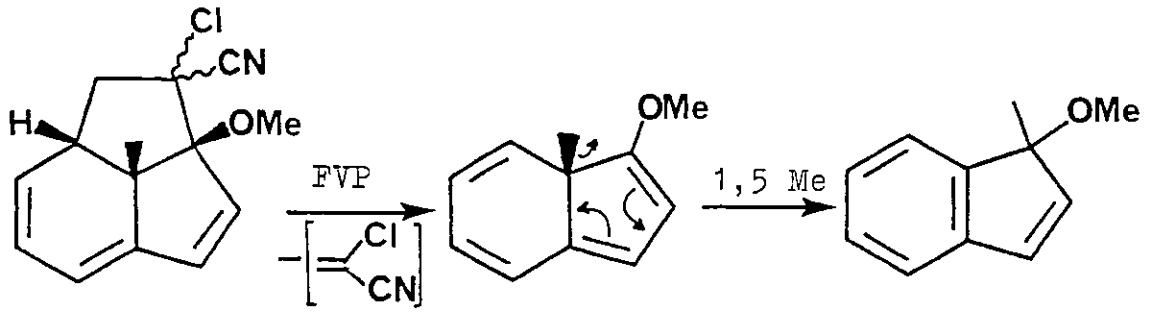
(i) steric repulsion between the extra methyl group and the bulky end of the dienophile

(ii) the hyperconjugative electron release of the extra methyl group is directed towards C-3 and not C-4, and it is C-3 that attaches to the electron deficient end of the dienophile.

If the explanation for the formation of the over-methylated 3a<u>H</u>-indene (61) is correct, it is to be expected that the adducts described previously were contaminated with overmethylated material. This was the case with the DMAD adduct since the mass spectra of annulenes derived from this adduct showed appreciable M+14 ions.

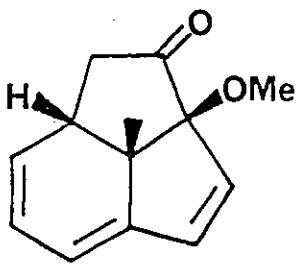
The mass spectra of the adducts (58a) and (58b) show strong ions due to loss of the dienophile. This led to an investigation of the thermolysis of these adducts to study the retro[8+2]cycloaddition reaction. When a mixture of the adducts (58a) and (58b) was heated, they were found to be stable and not interconverted (no change in isomer ratio) up to 200°C. Above this temperature, both isomers decomposed to undefined material. Under flash vacuum pyrolysis conditions with an oven temperature of 400°C, there was some retrocycloaddition and the resulting product was the 1<u>H</u>-indene (62). The recovered starting material was of unchanged isomer distribution so both isomers undergo the retrocycloaddition at about the same rate. When the oven temperature was increased to remove all of the starting material, a complex mixture of products was collected; this was probably a mixture of indenes resulting

from further rearrangements of the 1H-indene (62).



(58a)/(58b) (37) (62)

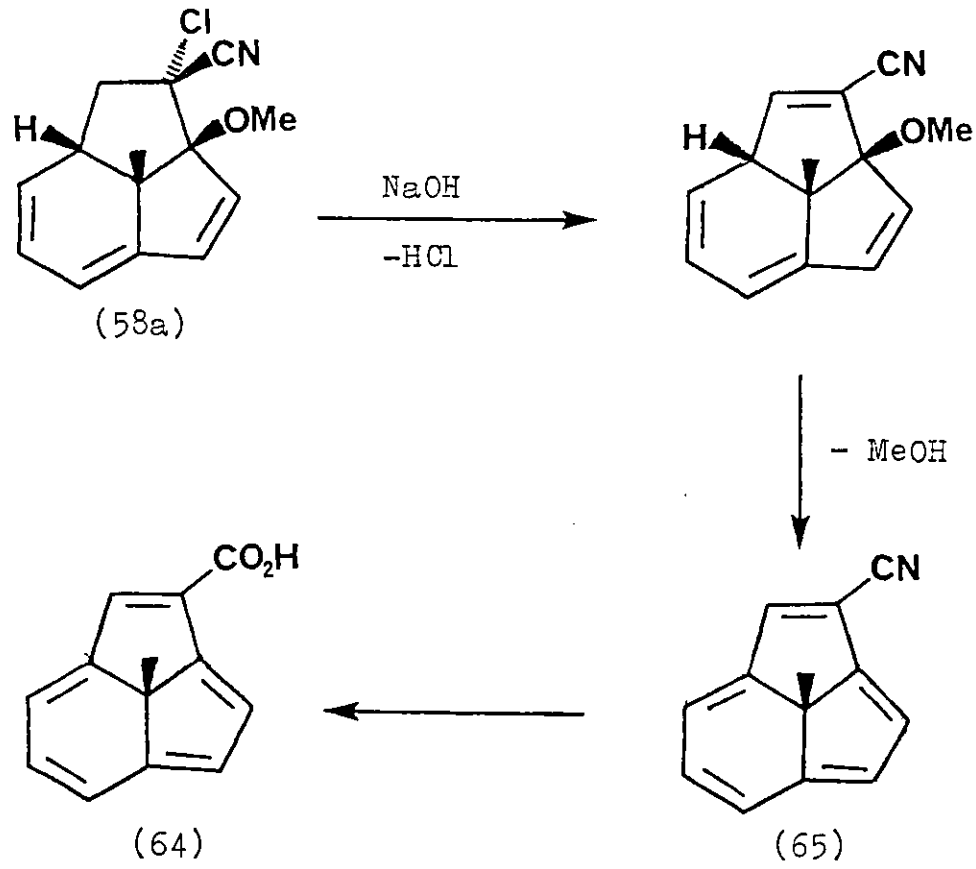
2-Chloroacrylonitrile has found much use as a ketene equivalent since hydrolysis of its adducts gives the required ketones directly. However, attempts to prepare the ketone (63) from adducts (58a) and (58b) were not successful.



(63)

Two sets of conditions are common for the conversion. The first, sodium sulphide in ethanol,[64,65,66] gave a mixture of products and the only compound that could be isolated was isomer (58b) of starting material. The second, sodium hydroxide in ethanol and dimethyl sulphoxide,[67,68] similarly gave this unreactive isomer of starting material but together with a small amount of yellow fluorescent material

which was found to be the acid (64), probably formed as shown in Scheme 21.

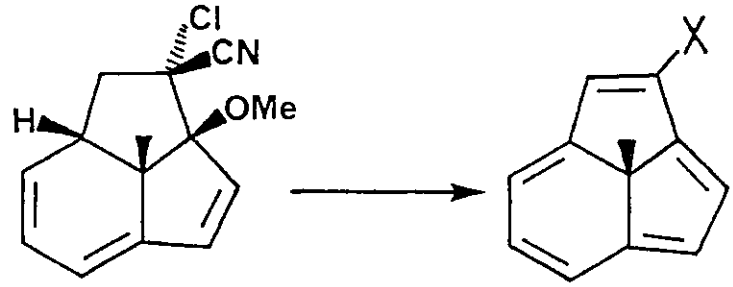


(58a) (64) (65)

SCHEME 21

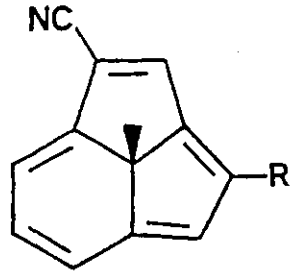
Other bases were tested in the hope of improving the yield of an annulene from adduct (58a) and the results are summarised in Table 4. The adduct (58b) was inert to all of these conditions. As the Table shows, 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU) is the best reagent of those tried for the preparation of a 2-monosubstituted annulene. It was best to use the reagent neat since the reaction was very slow in a solvent (benzene or toluene).

TABLE 4



base	product	yield
NaOH-DMSO-EtOH, 80°C	X = CO_2H (64)	26%
NaOMe-DMF, 60°C	X = CN (65)	3%
$KOBu^t$-C_6H_6, 80°C	X = $CONH_2$(66)	20%
NEt_3, 89°C	no reaction	
DBU, 110°C	X = CN (65)	74%

DBU also effected the conversion of the adducts (60a) and (60b) into the 1-substituted annulenes (67a) and (67b) respectively. The reaction in this case was more rapid than that with the adduct (58a).



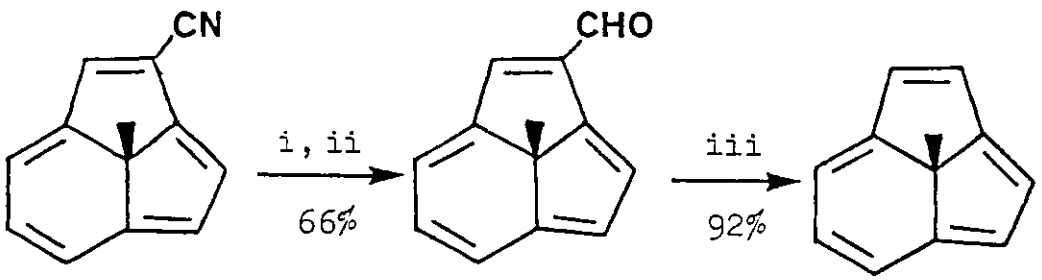
(67a) R = H
(67b) R = Me

The formation of 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene-2-carboxamide (66) by treatment of the adduct (58a) with potassium <u>tert</u>-butoxide was not expected. The reagent was not purified and it is probable that potassium hydroxide

present had caused the partial hydrolysis of the nitrile to give the amide.

The monocarboxylic acid (64) was wanted for X-ray crystallographic studies since its crystals were expected not to possess the disorder found with the diacid (39) and the dialdehyde (51). The nitrile (65) was hydrolysed only very slowly under acidic conditions and the acid was better prepared by alkaline hydrolysis. Although the acid is crystalline, crystals giving suitable X-ray diffraction data could not be obtained.

Conversion of the nitrile (65) into the parent system (1) was accomplished by reduction with diisobutylaluminium hydride to give the previously mentioned monocarboxaldehyde (53b) which was decarbonylated in high yield with one equivalent of tris(triphenylphosphine)rhodium(I) chloride (Scheme 22).



(65) (53b) (1)

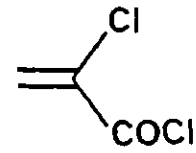
SCHEME 22 Reagents: i, Bu^i_2AlH - petrol, 20°C; ii, MeOH; iii, $Rh(PPh_3)_3Cl$-C_6H_6, 80°C

This route to the parent annulene has the advantage over the previous one that only half as much of the expensive rhodium reagent is needed. The overall yields of the two methods are comparable. However, another

route was needed to prepare the important tricyclic ketone (63) and to dispense with the use of the rhodium reagent altogether.

2.1.6 The Cycloaddition of the 3a*H*-Indene (37) with 2-Chloroacryloyl Chloride; Synthesis and Reactions of 2a-Methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2*H*-cyclopent[*cd*]inden-2-one (63)

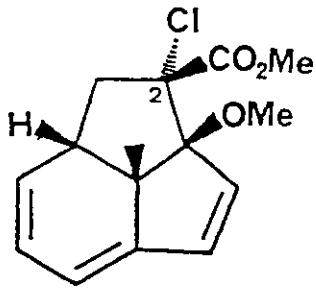
2-Chloroacryloyl chloride (68) is reported to be a highly reactive dienophile and a useful ketene equivalent.[69]



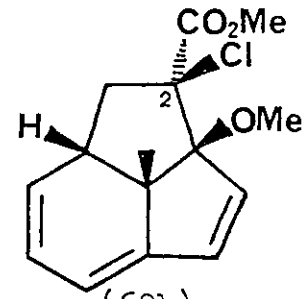
(68)

Unlike 2-chloroacrylonitrile, it is not commercially available but was easily prepared from methyl acrylate by the method of Marvel, Dec, Cooke and Cowan.[70]

When 2-chloroacryloyl chloride was added to a solution of the 3a*H*-indene (37) generated in the usual way, the colour of the indene was discharged by the time the mixture had warmed to 0°C showing the high reactivity of this dienophile. The resulting adduct was expected to be difficult to handle as it is an acid chloride and no attempt was made to isolate it. Instead, the mixture was treated with methanol and triethylamine to give the methyl ester. Work-up then gave the compound (69a) containing 1 part in 25 of the stereoisomer (69b). None of the other regioisomer was formed.



(69a)



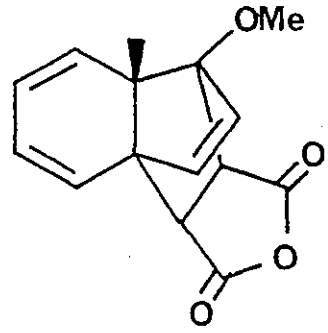
(69b)

The greater selectivity of 2-chloroacryloyl chloride than 2-chloroacrylonitrile reflects its greater reactivity. The observation that the more reactive dienophiles give better endo-selectivity in the Diels Alder reaction has been reported by Suguchi and co-workers.[71] A difference however is that whereas the endo-adduct is generally the more favoured isomer in Diels Alder reactions,[72] the major adducts (58a), (60a) and (69a) are all of exo-stereochemistry. It has been shown that for the comparable [6+4] cycloaddition reaction, endo-addition is disfavoured owing to antibonding secondary orbital interactions in an endo-transition state.[73] This is possibly also the situation in these [8+2] cycloaddition reactions.

The ester (69a) was also formed by heating the [4+2] adducts (57a) and (57b) in the presence of an excess of 2-chloroacryloyl chloride, followed by treatment with methanol. In these reactions, a greater proportion of isomer (69b) was formed, presumably since the cycloadditions are forced to proceed at a higher temperature which makes them less selective (Scheme 23).

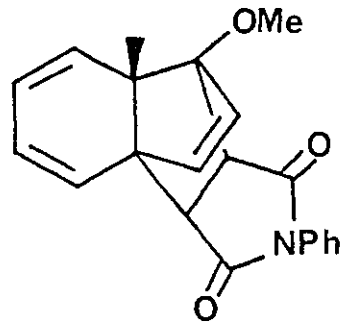
Reduction of the ester (69a) with diisobutylaluminium hydride gave an alcohol which on oxidation with chromium trioxide in pyridine was converted into the aldehyde (59) which had an n.m.r. spectrum identical to that of the

sample prepared by reduction of the 2-chloroacrylonitrile adduct (58a). This shows the stereochemistry at C-2 in the ester (69a) to be as shown.



i, ii → (69a) + (69b)

12 : 1



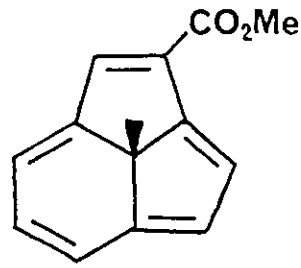
iii, iv → (69a) + (69b)

8 : 1

SCHEME 23

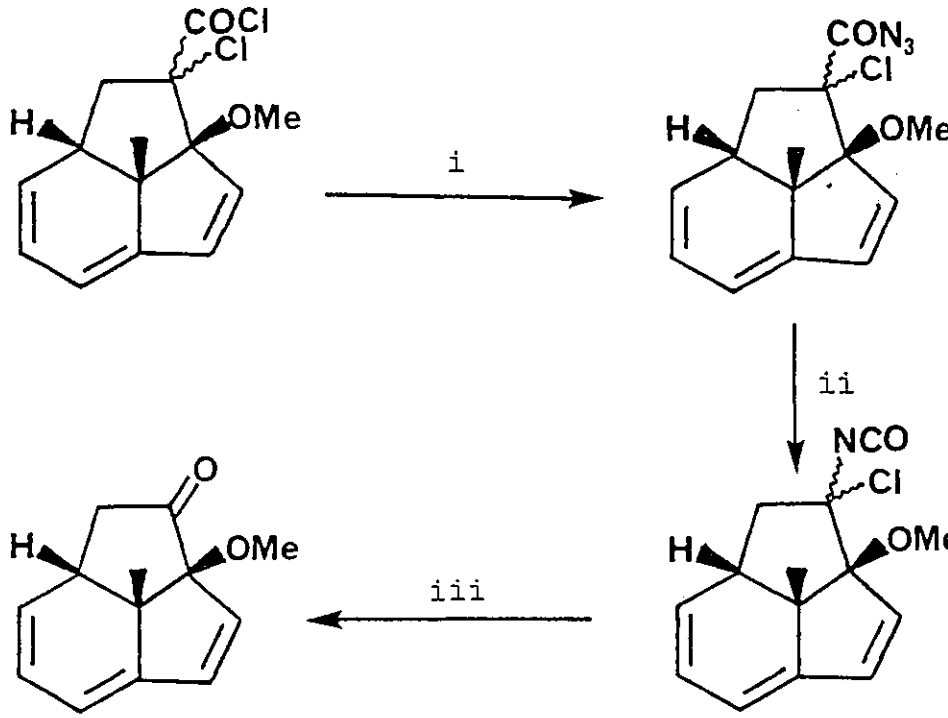
Reagents: i, $CH_2=C(Cl)COCl$-CH_2Cl_2-40°C; ii, MeOH; iii, $CH_2=C(Cl)COCl$ - toluene, 110°C; iv, MeOH, NEt_3

Treatment of the esters (69a) and (69b) with DBU gave only a low yield of the annulene (70) and the reaction was very slow. The recovered starting material from this reaction contained a higher proportion of the isomer (69b). Thus, compound (69b) is like adduct (58b) in its lack of reactivity.



(70)

The major part of the reaction mixture from the cycloaddition of the 3a<u>H</u>-indene (37) with 2-chloroacryloyl chloride was not treated with methanol but was treated so as to give the ketone (63) (Scheme 24). It was fortunate that the procedure developed by Corey and co-workers for this conversion[69] uses the same solvent (1,2-dimethoxyethane) as that required for the preparation of the 3a<u>H</u>-indene (37). This made possible the preparation of the ketone (63) from the trienone (46) without necessitating a change of solvent or the isolation of any of the intermediates.

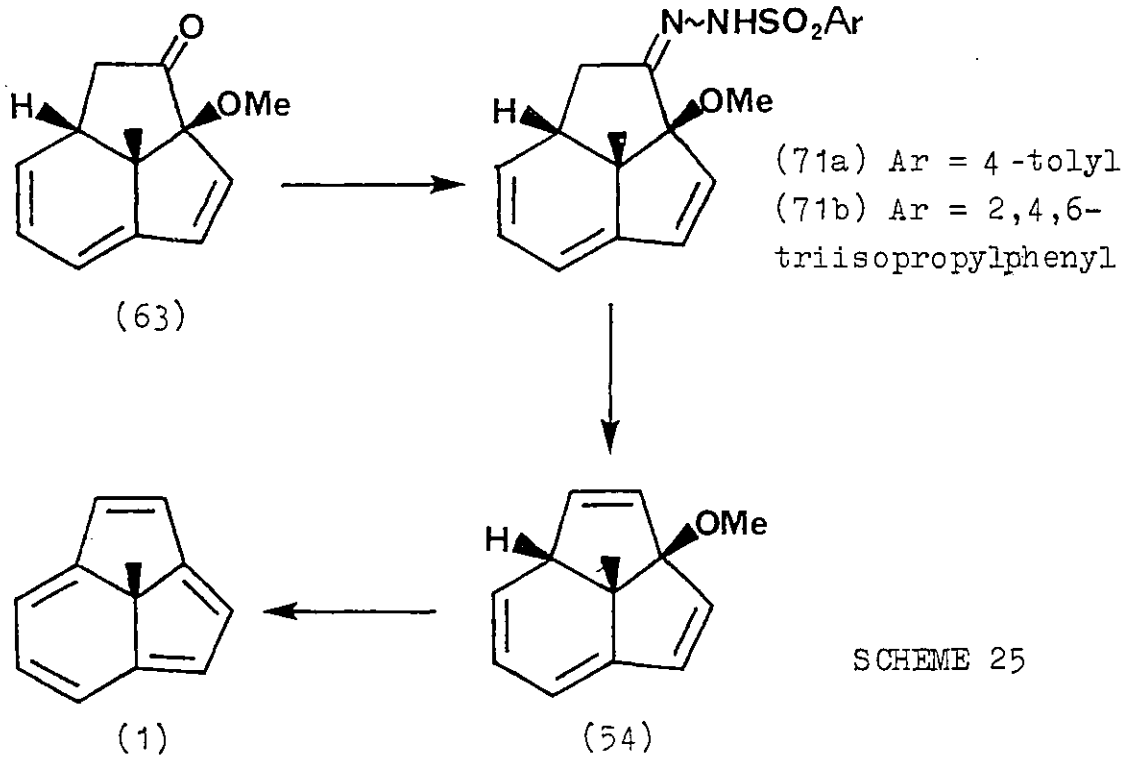


(63)

SCHEME 24 <u>Reagents:</u> i, NaN_3-DME, 20°C; ii, 80°C; iii, AcOH-H_2O-DME, 60°C

The reactions in this sequence could be readily followed by infrared spectroscopy. The yield of the tricyclic ketone (63) from the trienone (46) (48% after optimisation) was only slightly lower than the yield of the esters (69a) and (69b). If the methanolysis of the 2-chloroacryloyl chloride adducts is virtually quantitative, the conversion shown in Scheme 24 must also proceed in high yield.

The ketone (63) is a colourless oil with a carbonyl absorption at 1732 cm^{-1} and is of considerable value as a precursor of a variety of 1- and 2-substituted 7b-methyl-7b<u>H</u>-cyclopent[cd]indenes. Its conversion into the parent [10]annulene (1) has been accomplished by cleavage of an arenesulphonylhydrazone derivative with a strong base (Shapiro reaction),[74] followed by elimination of methanol from the resulting tetraene (54) (Scheme 25).



SCHEME 25

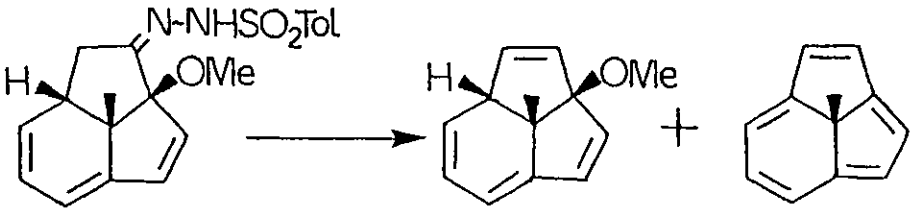
The hydrazone (71a) was prepared by heating the tricyclic ketone (63) with toluene-4-sulphonylhydrazine in refluxing benzene with azeotropic removal of the water formed in the reaction. The product was isolated by chromatography and could be separated into two isomers in a combined yield of 91%.

The best conditions found for the cleavage of the hydrazone (71a) was the use of a large excess of methyl lithium with benzene as the solvent. Table 5 lists the results obtained by using a variety of conditions. The hydrazones were insoluble in petrol and in ether so these solvents were not used.

Elimination of methanol from the tetraene (54) to give the parent annulene (1) was found to proceed to some extent in the strongly basic medium at room temperature. By heating the reaction mixture to 40°C, the conversion into the annulene could be taken to completion. Unfortunately, the annulene prepared in this way was contaminated with some olefinic hydrocarbon material which could not be removed by the usual methods. However, separation was achieved by column chromatography on silica impregnated with 10% silver acetate when the impurity is retarded to a greater extent than the annulene.

The tetraene (54) showed no tendency for spontaneous elimination of methanol and there was only a very slow reaction when it was heated with DBU at 110°C. It could be converted into the parent annulene by heating with methyl lithium in benzene but more convenient was the treatment with a catalytic amount of toluene-4-sulphonic acid in methylene chloride at room temperature which gave

TABLE 5 Shapiro Reactions of the Tosylhydrazone (71a)

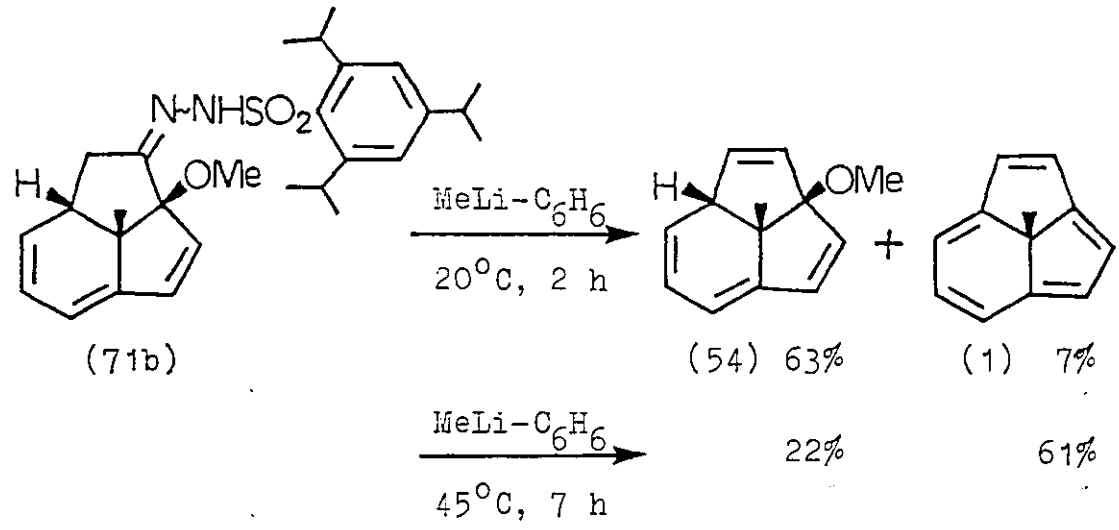


(71a) (54) (1)

Base	Solvent	Conditions	Yield of the tetraene (54)	Yield of the annulene (1)
MeLi	Benzene	20°C, 20 h	26%	17%
MeLi	"	40°C, 10 h	-	40%
MeLi	Tetrahydrofuran	20°C, 0.5 h	25%	14%
MeLi	1,2-Dimethoxyethane	40°C, 0.5 h	9%	33%
n-BuLi	Tetramethylethylene-diamine (TMEDA)	20°C, 1 h	trace	trace
t-BuLi	Benzene	20°C	0	0
KH - 18-Crown-6	1,2-Dimethoxyethane	-23°C → 20°C	0	0
LiN^iPr_2	Tetrahydrofuran	20°C	trace	4%

the annulene in 81% yield. The yield was lowered if the mixture was warmed due to the sensitivity of the annulene towards acids (see Section 2.2.8).

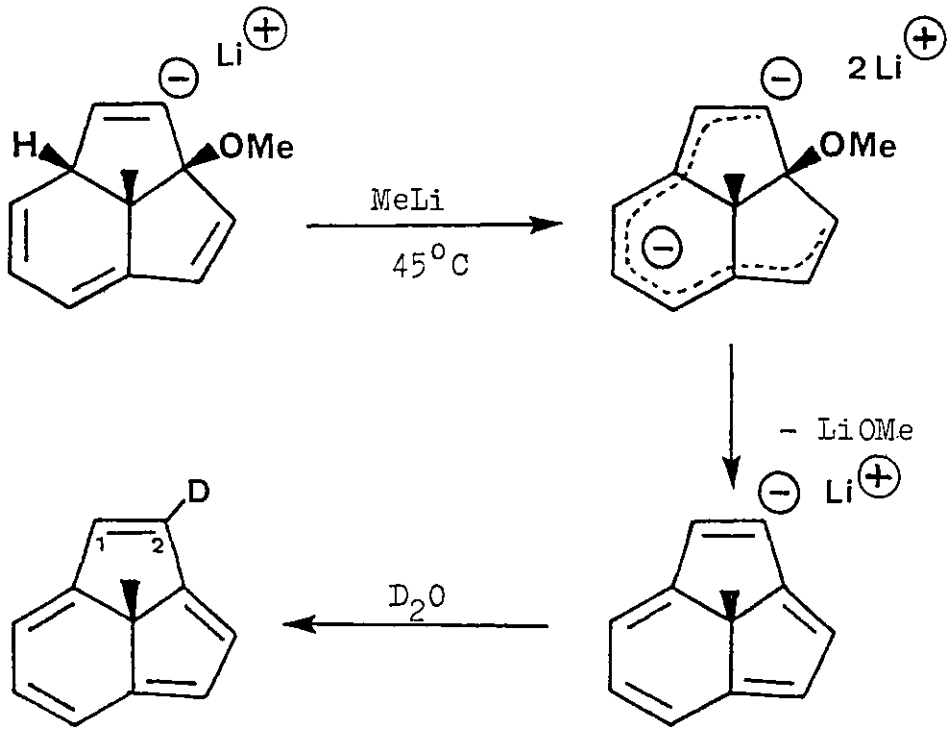
Since the yields for the cleavage of the hydrazone (71a) were only moderate, an improvement was looked for. It is reported that 2,4,6-triisopropylbenzenesulphonyl (trisyl)hydrazones undergo fragmentation under milder conditions than the corresponding tosylhydrazones.[75,76] The hydrazone (71b) was prepared at room temperature in 83% yield by treatment of the ketone (63) with the hydrazide reagent in dichloromethane containing Amberlite resin IR120(H) as catalyst.[77] This hydrazone gave much improved yields of the desired products on treatment with methyl lithium.



The Shapiro reaction is useful for the synthesis of deuterated olefins because the product of the reaction before work-up is a vinyl lithium compound.[78] When the room temperature reaction was quenched with deuterium oxide instead of normal water, a product specifically deuterated

in the 2-position was obtained. The extent of deuteration, determined by proton n.m.r., was 65 - 70%. Treatment of this product with toluene-4-sulphonic acid in dichloromethane gave the specifically 2-deuterated annulene (72). There was no evidence for any deuterium scrambling in this acid catalysed reaction.

When the Shapiro reaction was run at 45°C and then quenched with deuterium oxide, the annulene isolated directly was about 20% deuterated. This was determined by integration of the signals of its bis(4-phenyl-1,2,4-triazole-3,5-dione) adduct to be discussed (see Section 2.2.6). This deuterated annulene is possibly formed by way of a dianion as shown in Scheme 26. The low extent of deuteration is probably because the strongly basic anions involved, abstract protons from the solvent or from other substrate molecules to an appreciable extent at the higher temperature.



(72)

SCHEME 26

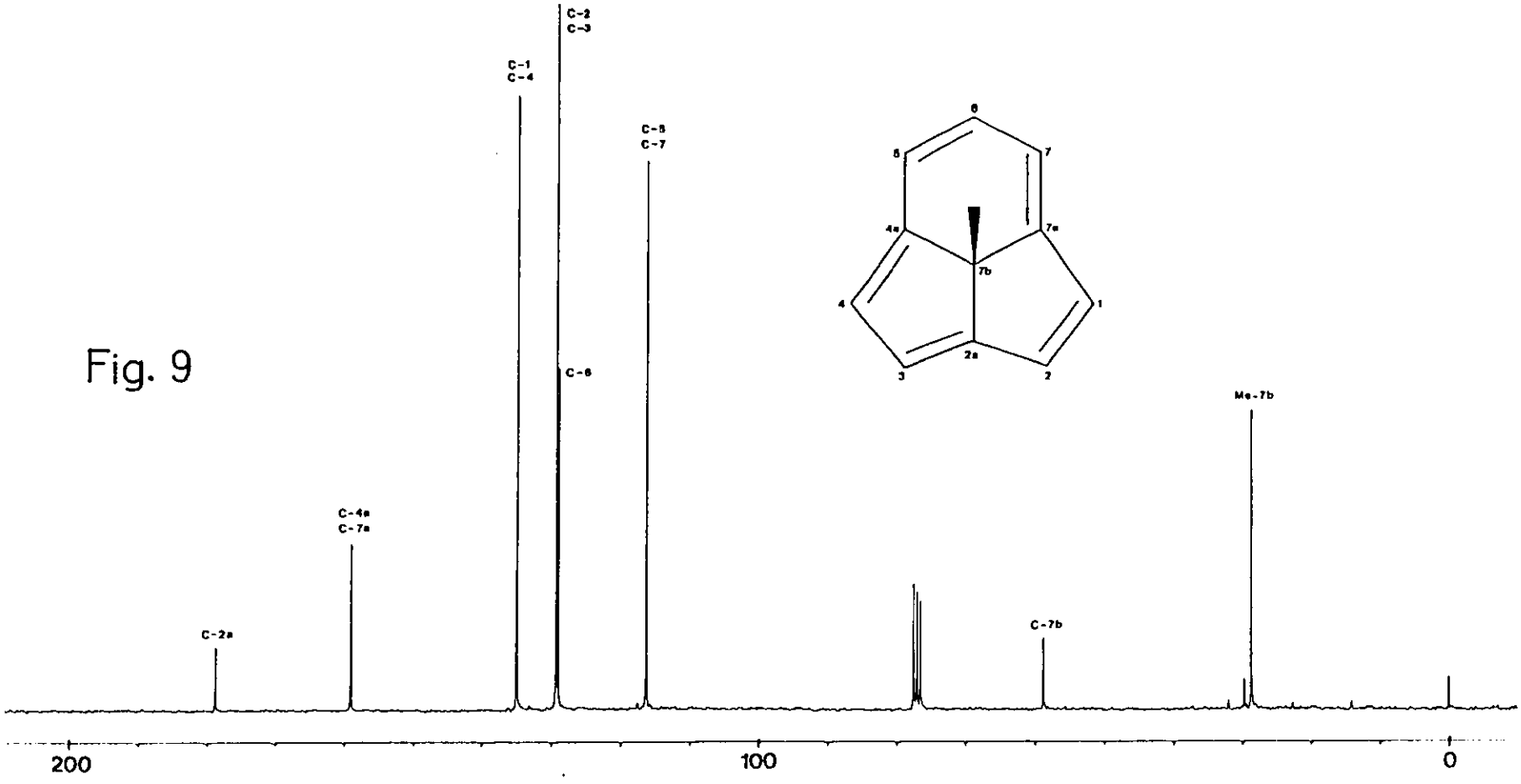
N.m.r. spectra were recorded for the deuterated annulene (72) so that the signals for the 1- and 2-positions could be distinguished. In the proton spectrum, the upfield half of the AB quartet at δ7.9 is reduced in intensity and a new line appears within the doublet of the downfield half. This new line is due to H-1 in the deuterated compound which gives a singlet because the coupling between hydrogen and deuterium is too small to observe. Thus, the downfield half of the AB quartet in the undeuterated annulene can be assigned as H-1 and H-4, and the upfield half as H-2 and H-3. More important is the effect in the carbon-13 broad band decoupled spectrum where the lines due to C-1 and C-2 are appreciably separated. For the 65% deuterated sample, two of the lines become split into two. These are the signals for C-1 and C-2a. The splitting is due to an isotope shift caused by the presence of the deuterium atom. The line due to C-2 and C-3 is reduced in intensity. This results from a combination of two factors:

(i) When C-2 is attached to a deuterium atom, the coupling causes its signal to become a 1 : 1 : 1 triplet.

(ii) In the deuterated compound, C-2 does not have the nuclear Overhauser enhancement that would occur if a proton were attached and it behaves as a quaternary carbon.

The carbon-13 spectrum of the parent annulene (1) could now be completely assigned and is illustrated in Fig. 9. The chemical shifts of the central carbon atom and the methyl group show little effect of the presence of a ring current. This is the result of the large chemical shift range in the carbon-13 spectrum which dwarfs a few

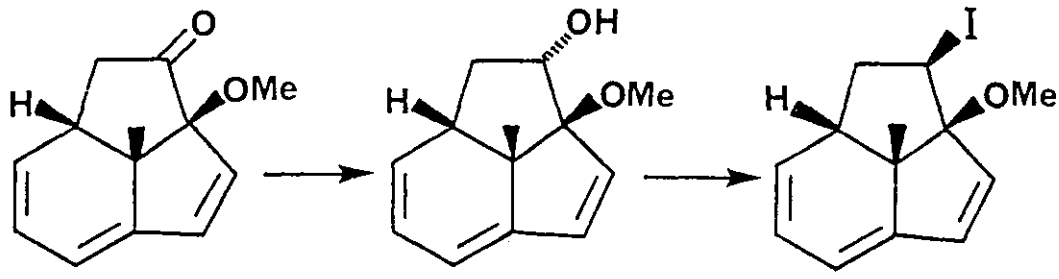
Fig. 9


C-2
C-3
C-1
C-4
C-5
C-7
C-6
C-4a
C-7a
C-2a
C-7b
Me-7b
8
5
7
4a
7a
7b
4
1
3
2a
2
200
100
0

parts per million shift that the ring current might bring about.[79] The unusual downfield shift of C-2a is probably the consequence of the strain at that position. Similar effects occur in comparable systems. For example, the ring junction carbon atom in indane (δ_C 144) resonates further downfield than that of the unstrained hydrocarbon tetralin (δ_C 137).[80]

A second use of the deuterated annulene (72) is in the interpretation of the n.m.r. spectra of compounds synthesised from it. This aspect will be discussed later (Section 2.2.8).

The successful use of the Shapiro reaction was all the more rewarding when attempts to prepare the parent annulene (1) from the tricyclic ketone (63) by dehydration of the alcohol (73) ran into problems. Reduction of the ketone (63) with sodium borohydride in ethanol gave a 61% yield of the alcohol (73). Its stereochemistry was deduced from coupling constants in its proton n.m.r. spectrum.



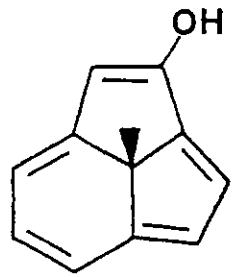
(63) (73) (74)

No recognisable products were formed when attempts were made to dehydrate the alcohol (73) using toluene-4-

sulphonic acid, thionyl chloride or phosphoryl chloride. Methyltriphenoxyphosphonium iodide (MTPI) is reported to be a good reagent for the preparation of primary and secondary alkyl iodides.[81] Treatment of the alcohol (73) with MTPI in hexamethylphosphoramide (HMPA) gave the iodide (74). Inversion of the stereochemistry at position-2 occurred in this reaction. Unfortunately, all attempts to dehydroiodinate this iodide failed. Aqueous sodium hydroxide with HMPA,[82] DBU and sodium methoxide in dimethylformamide all gave no reaction. This surprising resistance towards either elimination of hydrogen halide or nucleophilic displacement of the halogen was also found with the 2-chloroacrylonitrile adduct (58b) where the halogen atom had the same configuration.

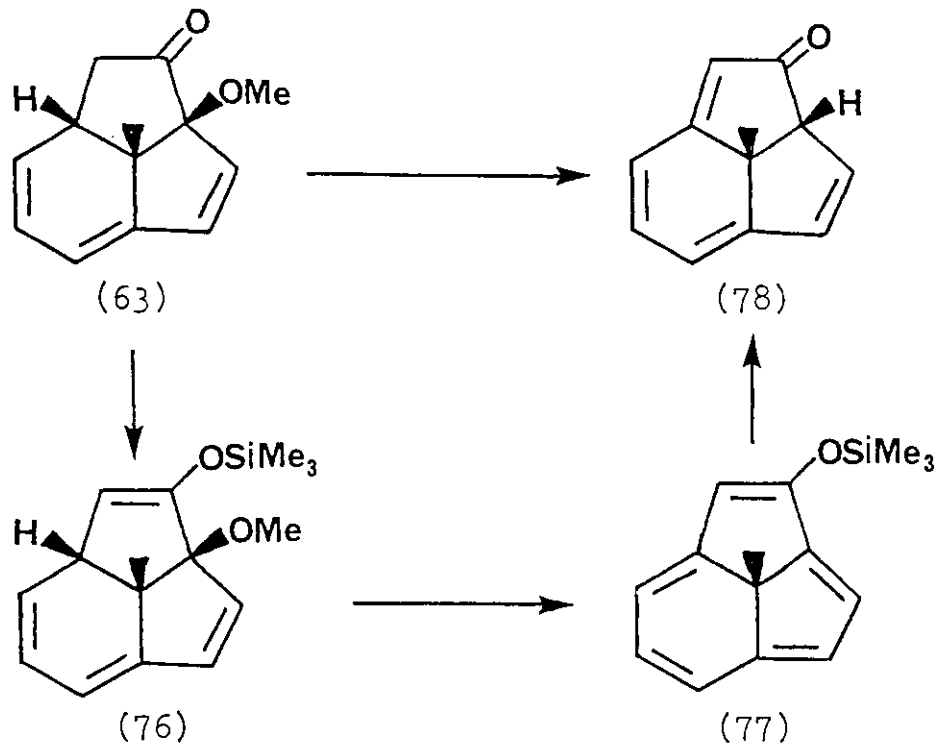
2.1.7 Synthesis and Properties of the Tetraenone, 7a,7b-Dihydro-7b-methyl-2H-cyclopent[cd]inden-2-one (78)

It was noticed that removal of the elements of methanol from the tricyclic ketone would formally give the hydroxyannulene (75). It was hoped to prepare this compound so that its properties could be compared to those of phenol



(75)

The initial idea was to treat the trimethylsilyl ether (76) with methyl lithium in the hope that elimination of methanol from the resulting enolate would occur in much the same way as it did in the reaction shown in Scheme 26. During the preparation of the trimethylsilyl ether (76) with the chlorotrimethylsilane - sodium iodide combination, a small amount of a yellow compound was also formed. A signal upfield of tetramethylsilane in the n.m.r. spectrum showed an annulene was present and therefore that elimination of methanol had occurred. By heating the reaction mixture and using an excess of reagents, the elimination could be taken to completion. Quenching of the reaction mixture with water immediately hydrolysed the trimethylsilyl ether to give the tetraenone (78), an orange-red oil in 81% overall yield (Scheme 27).



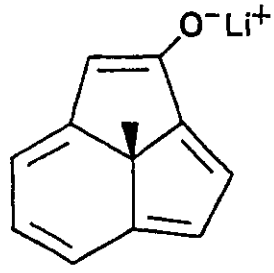
SCHEME 27

None of the "phenolic" tautomer (75) was detected in the tetraenone (78). There were no signals upfield of tetramethylsilane in the n.m.r. spectrum; the central methyl group of (78) resonated at $\delta_H(CDCl_3)$ 1.41 and the single methine proton resonance showed that (78) was the tautomer present. The infrared spectrum showed a carbonyl stretching vibration at 1692 cm^{-1} and no hydroxyl stretching vibration. It forms a mauve 2,4-dinitrophenylhydrazone, the n.m.r. spectrum of which was recorded to confirm that it had the expected structure.

The tetraenone (78) did not give deuterium exchange by shaking a carbon tetrachloride solution with deuterium oxide, even in the presence of acid at reflux. However, exchange did occur in this two phase system in the presence of a catalytic amount of tetra-n-butylammonium hydroxide after 2 h at 40°C. It did so exclusively at the 2a-position even though the anion could have deuterated also at C-1, C-4, C-5 or C-7. Deuterium exchange at the 2a-position was also complete on heating the tetraenone in dimethyl sulphoxide containing a trace of the same catalyst or within 1 hour in pyridine containing deuterium oxide at 50°C. In the latter mixture, no deuterium incorporation occurred in any of the other positions, even after overnight reflux. Since deuterium exchange had taken place, the keto-enol equilibrium must have been established assuming that kinetic protonation of the enolate is on oxygen. The absence of any appreciable amount of annulenol (<1%) in these polar solvents which would stabilise the enol form by hydrogen bonding[83] implies that the keto form must be much more energetically favoured

than the enol form.

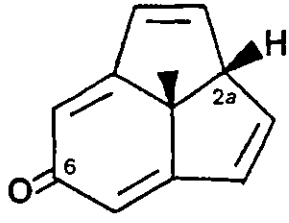
The trimethylsilyl ether (77) was a bright yellow oil which gave a signal in the n.m.r. spectrum at $\delta_H(CDCl_3)$ -1.50. As well as by the method in Scheme 27, it could be prepared in 74% yield by treatment of the tetraenone (78) with the chlorotrimethylsilane - sodium iodide combination. Treatment of this trimethylsilyl ether with one equivalent of methyl lithium[84] afforded a deep yellow solution of the anion (79) which gave an n.m.r. signal upfield of tetramethylsilane at δ_H(DME) -1.45. Therefore this ion can sustain a diamagnetic ring current. In the same solvent the methyl group of the trimethylsilyl ether (77) resonates at δ-1.62. When this solution of the anion (79) was quenched with a sodium acetate - acetic acid buffer or with acetic acid at low temperature, and the resulting mixture immmediately examined by n.m.r., only the tetraenone (78) could be detected. Since presumably the initial protonation was on oxygen, the rearrangement to the keto tautomer must be very rapid.



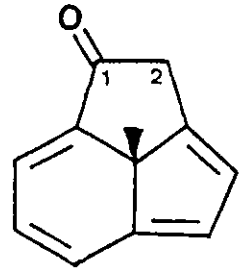
(79)

The behaviour of the tetraenone (78) is completely unlike the phenol-cyclohexadienone equilibrium which lies far on the side of phenol; the cyclohexadienone tautomer has

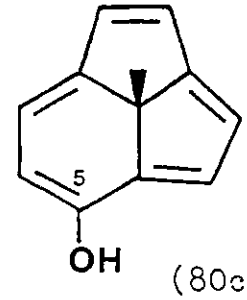
been isolated only recently at low temperature.[85] In the case of the annulenol (75) desribed here, it is apparent that the delocalisation energy of the annulene is insufficient to compensate both for the loss of carbonyl bond energy and the greater strain energy of the phenolic tautomer. This strain is relieved significantly only by protonation at the 2a-position and this explains why deuteration was not observed elsewhere. Calculations by Rzepa predicted independently that the isomer (78) is the most stable of those possible, and have shed light on the likely forms of the other possible annulenol isomers.[33] The 6-isomer is predicted to exist in a similar 2a<u>H</u>-tautomer (80a). For both the 1- and 5-isomers, ring junction protonation can occur only at the 4a- and 7a-positions and in doing so, not as much strain is relieved as for 2a-protonation. The somewhat surprising consequence of this is that the 2<u>H</u>-tautomer (80b) is predicted to be the most stable form of the 1-isomer and that the 5-isomer is most likely to exist in the annulenol form (80c).



(80a)



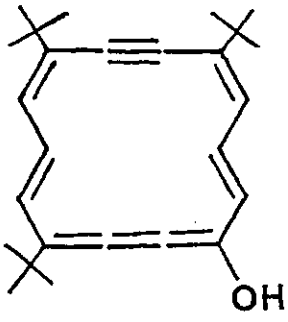
(80b)



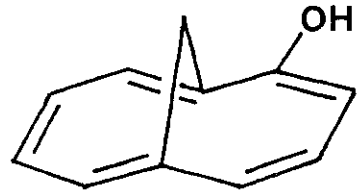
(80c)

It would of course be of interest to verify these predictions experimentally and attempts to synthesise the 1-isomer (80b) are given later (Section 2.1.9).

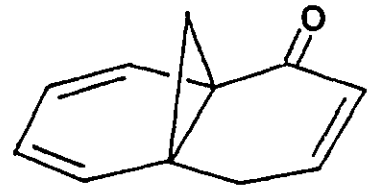
The above work on the 2-isomer is in accord with other approaches to annulenols in that the enol forms have not been isolated.[83,86,87] In attempts to prepare the bis-dehydro[14]annulenol (81a)[87] and 1,6-methano[10]annulen-2-ol (81b)[83] the enol forms were detected in solution spectroscopically. In the case of the enol (81b), attempted isolation gave only the ketone shown.



(81a)



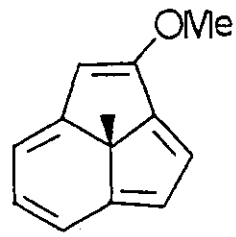
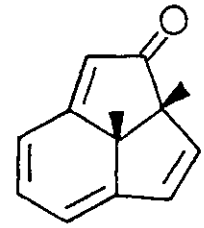
(81b)



Methylation of the tetraenone (78) on oxygen was the exclusive reaction when its potassium enolate was treated with methyl fluorosulphonate. When methyl iodide was the alkylating agent, methylation on oxygen was accompanied by carbon alkylation which occurred exclusively at the 2a-position (Table 6). Greatest selectivity for carbon alkylation resulted when the lithium enolate was used. Use of hydrogen bonding solvents gave a lesser

improvement in selectivity. With lithium hydroxide in aqueous ethanol, the reaction was very slow and the yield of products was low.

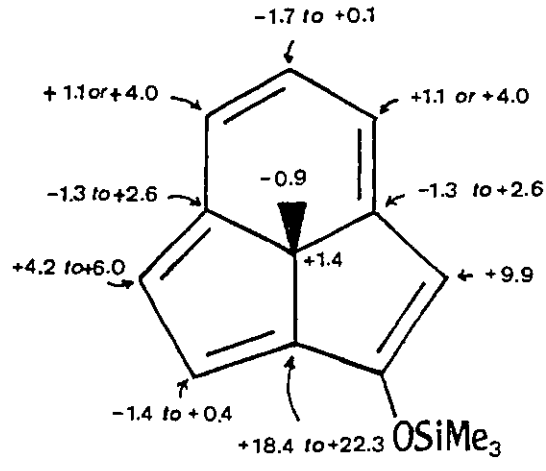
TABLE 6 Methylation of the Tetraenone (78)

Conditions	Products  (82)	 (83)
i, KH - 18-Crown-6 - DME, -23°C; ii, $MeOSO_2F$, -23°C	67%	0%
i, NaH-THF, 20°C; ii, MeI, 20°C	25%	40%
NaOH-EtOH-MeI, 50°C	21%	42%
NaOH-EtOH-H_2O-MeI, 50°C	19%	47%
i, NaH-THF, 20°C; ii, LiBr-THF, 20°; iii, MeI, 40°C	19%	59%
LiOH-EtOH-H_2O-MeI, 50°C	0.5%	20%

The tetraenone (83) is an orange-red oil similar to the unmethylated ketone (78) and in its n.m.r. spectrum, the central methyl group resonates at $\delta_H(CDCl_3)$ 1.47. The methoxy annulene (82), on the other hand, is a yellow oil and the central methyl group resonates at $\delta_H(CDCl_3)$ -1.50 in the n.m.r. spectrum. The resonance of the methoxyl

methyl at $\delta_H(CDCl_3)$ 4.30 is further downfield than that of anisole, $\delta_H(CDCl_3)$ 3.75, and probably reflects the greater number of carbon atoms over which the lone pair of electrons on oxygen can be delocalised in the annulene. It is interesting to compare the carbon-13 spectra of the trimethylsilyl ether (77) and the unsubstituted annulene (1). Fig. 10 gives the chemical shift differences observed and it can be seen that the greatest upfield shift and hence the greatest build up of charge is at the 2a-position. Assuming that this effect is even more pronounced in the enolate (79), it is even less surprising that deuteration and methylation should occur exclusively at the 2a-carbon atom.

FIG. 10

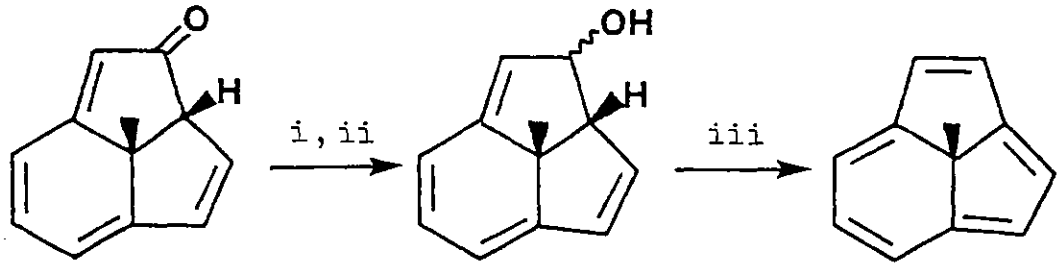


The figures given are $\delta_C(1) - \delta_C(77)$ in $CDCl_3$. Ranges are given where ambiguities in the assignment of the spectrum for compound (77) occur.

(77)

The tetraenone (78) could be readily converted into the parent annulene (Scheme 28). Reduction with diisobutylaluminium hydride in petrol gave a mixture of epimeric alcohols separable by chromatography. The less polar

isomer, a pale yellow crystalline solid is very unstable and rapidly polymerises to an insoluble substance on standing. The more polar isomer is a pale yellow oil. Neither isomer showed any tendency for spontaneous loss of water but both gave the annulene (1) rapidly by treatment with toluene-4-sulphonic acid in dichloromethane at room temperature. A consequence of the instability of the less polar epimer was that the best yield of the annulene (76% from the tetraenone) resulted when no attempt was made to isolate the alcohols. This procedure represents the best method so far for the synthesis of the parent annulene (1). A two gram sample has been prepared by this method and after chromatography and short path distillation at 100°C/ 3 mmHg, the product was analytically pure.



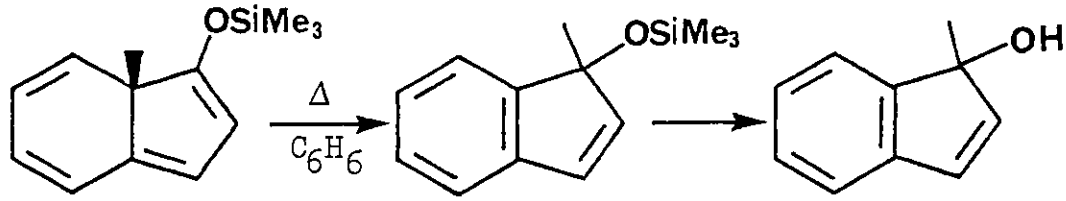
(78) (84) (1)

SCHEME 28 Reagents: i, Bu^i_2AlH-petrol, 0°C; ii, MeOH, 20°C; iii, $TsOH-CH_2Cl_2$, 20°C

2.1.8 Synthesis and Reactions of 3a-Methyl-3-(trimethylsiloxy)-3aH-indene (85)

The chlorotrimethylsilane - sodium iodide - triethylamine combination was also used with success for the preparation of the extended trimethylsilyl enol ether (85) from

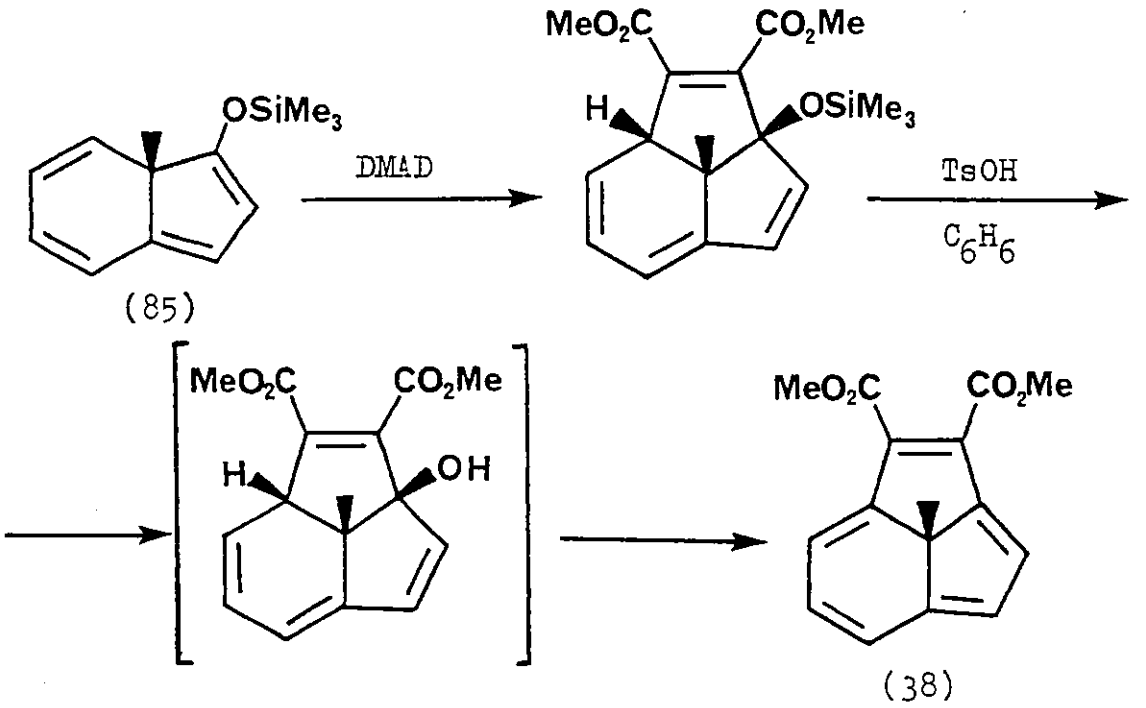
the trienone (46). This 3a$\underline{H}$-indene derivative could be isolated from the reaction mixture as an oxygen sensitive bright yellow oil. On heating it rearranged in a similar manner to the methoxy derivative (37) to give a 1$\underline{H}$-indene isomer. Removal of the trimethylsilyl group gave the known 1-methyl-1$\underline{H}$-inden-1-ol (87).[88]



(85) (86) (87)

The trimethylsilyl ether (85) behaves very similarly to the methoxyindene (37) in cycloaddition reactions. Thus with dimethyl acetylenedicarboxylate (DMAD), an adduct was formed which gave the annulene diester (38) after treatment with acid in an overall yield of 33% from the trienone (46). This route has the obvious advantage over that shown in Scheme 17 in that highly toxic and expensive reagents are avoided. A further improvement was the preparation of the trimethylsilyl ether (85) with trimethylsilyl trifluoromethanesulphonate in the presence of triethylamine.[89] In a one-pot reaction, the annulene diester (38) was then prepared in 54% yield from the trienone (46). The yield was later increased to 59% in a procedure whereby a partial work-up of the adduct was carried out prior to aromatisation with toluene-4-sulphonic acid in refluxing benzene. In this aromatisation, t.l.c. analysis showed the presence of a

polar intermediate and therefore that direct elimination of trimethylsilanol did not take place but rather hydrolysis of the trimethylsilyl group occurred first and was followed by elimination of the elements of water, as illustrated in Scheme 29.

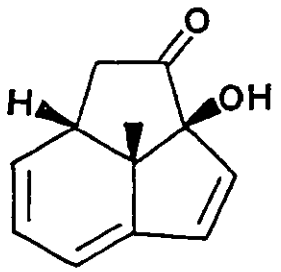


SCHEME 29

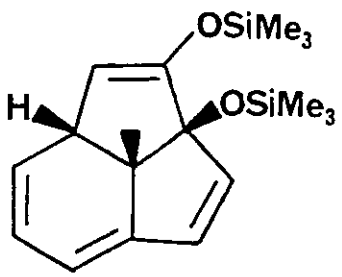
The annulene diester (38) prepared in this way solidified on cooling to give a yellow solid, m.p. 49 - 50°C which crystallised from petrol. When this ester was prepared from the methoxyindene (37), it did not solidify, most probably because of contamination by a homologue (see Section 2.1.5). The absence of such contamination by using the indene (85) represents another advantage of this method.

With 2-chloroacryloyl chloride the indene (85) gave an adduct which was treated as before to give the tricyclic ketone (88). Hydrolysis of the trimethylsilyl group

occurred during the acidic conditions used to hydrolyse the isocyanate intermediate and some potassium fluoride was added towards the end of this hydrolysis to ensure complete removal of the trimethylsilyl group. The reaction sequence only gave, at best, a 36% yield of the ketone (88) from the trienone (46), somewhat poorer than when the methoxyindene (37) was used.



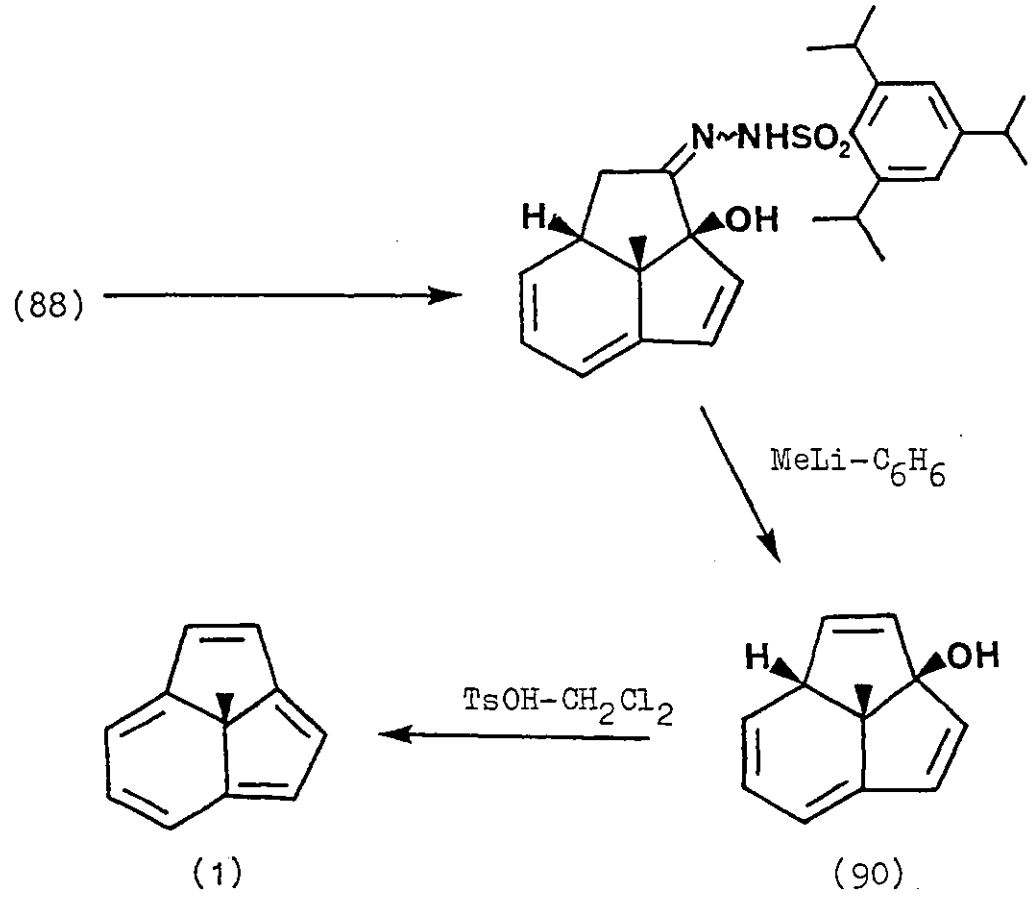
(88)



(89)

The ketone (88) is a colourless oil and was characterised as its orange 2,4-dinitrophenylhydrazone. Treatment with an excess of the sodium iodide - chlorotrimethylsilane combination in refluxing acetonitrile gave only the trimethylsilyl ether (89); none of the tetraenone (78) was formed. This result was unfortunate but showed that for the reaction of the ketone (63), the elimination does not involve an initial demethylation to give compound (89) as an intermediate. Such a demethylation is a possible process under these reaction conditions.[90]

The tricyclic ketone (88) could be converted into the annulene (1) by a route involving the Shapiro reaction (Scheme 30).

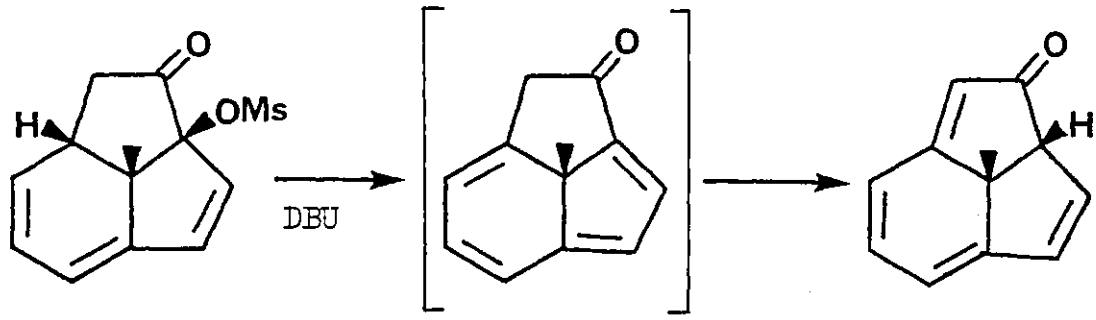


SCHEME 30

The hydrazone formation at room temperature was catalysed by Amberlite IR120(H) resin and gave a 95% yield of a mixture of isomers but the Shapiro reaction was sluggish and only one of the isomers reacted, even at elevated temperature. This outcome was presumably the consequence of the acidity of the hydroxyl group such that the fragmentation requires the formation of a trianion. The yield of the alcohol (90), an unstable solid, was only 35%. No annulene was formed in the reaction because the oxide ion (O^{2-}) is such a poor leaving group, but the usual acid catalysed elimination could be used. The overall yield of the parent annulene (1) from the ketone (88) was only 22%.

It was found subsequently that the ketone (88) could be converted into the tetraenone (78) by treatment with

methanesulphonyl chloride followed by DBU, but only in moderate yield (36%). The problem was not the elimination reaction but the formation of the mesylate. Clearly, the elimination reaction cannot give the tetraenone (78) directly. It must either proceed through the intermediate shown which rapidly tautomerises, or by elimination in the enol form of the mesylate so that the annulenol (75) is an intermediate.



(78)

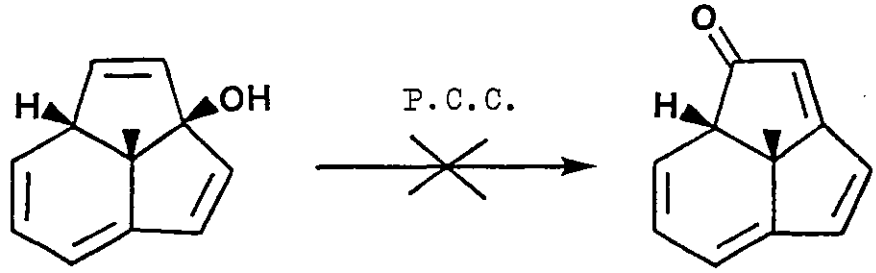
Therefore, although the 3a<u>H</u>-indene (85) showed promise as a precursor of annulenes, low yields mean that more work would be necessary before it could be used in an improved synthesis of the annulene (1).

2.1.9 The Attempted Synthesis of a Tautomer of 7b-Methyl-7b<u>H</u>-cyclopent[<u>cd</u>]inden-1-ol

The prediction that the 1-annulenol would exist as the 3a<u>H</u>-indene (80b) made it an attractive synthetic target but unfortunately the compound remains elusive.

In the first approach, it was hoped that treatment of the alcohol (90) with pyridinium chlorochromate would give the required product directly. Pyridinium chlorochromate has been used very successfully for oxidative

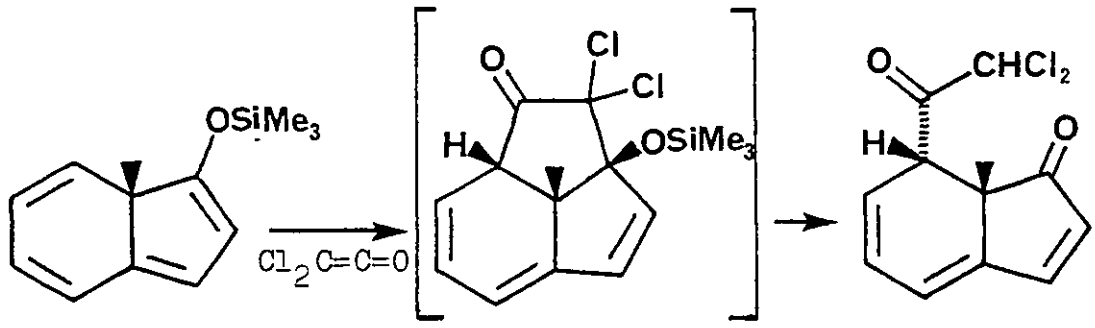
rearrangements of tertiary allylic alcohols to give enones,[91] but in this case the oxidation gave only baseline material (t.l.c.).



(90)

It was noticed that although 2-chloroacryloyl chloride is regarded as a ketene equivalent, the regiochemistry of its addition is opposite to that expected for ketene itself. During approaches to aza derivatives of the annulene (1), Gibbard discovered that chlorosulphonyl isocyanate reacts with the 3a$\underline{H}$-indene (37) by an [8+2] cycloaddition rather than in a [2+2] reaction more characteristic of this reagent.[92,93] For this reason, it was anticipated that dichloroketene would undergo a similar [8+2] cycloaddition.

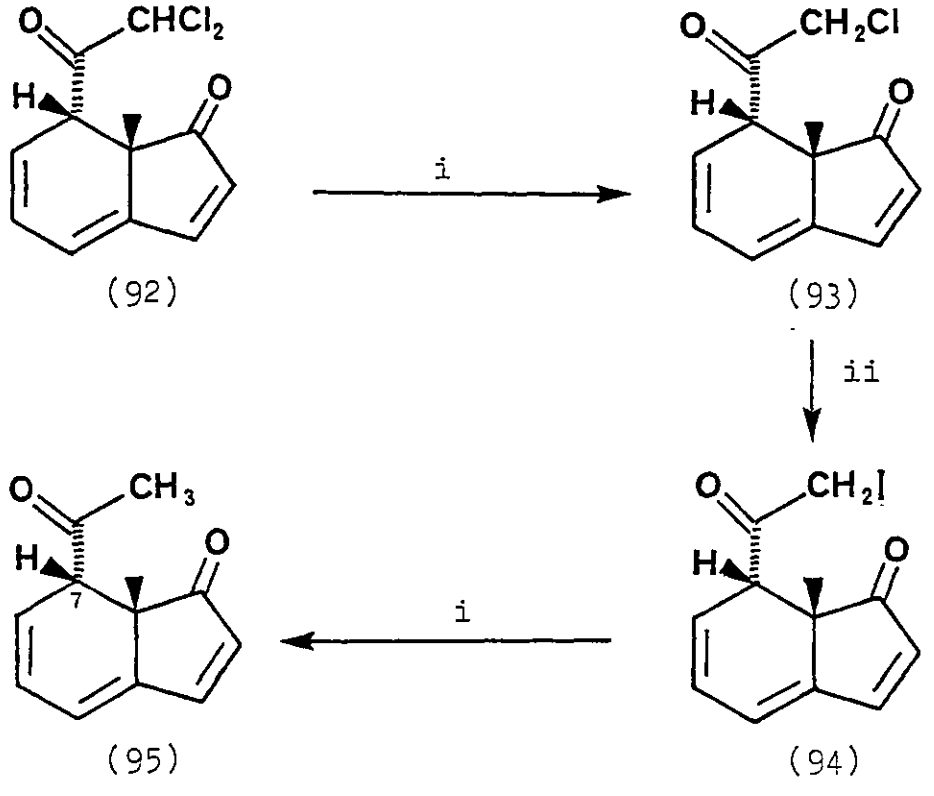
When dichloroacetyl chloride was added to a solution of the 3a$\underline{H}$-indene (85) containing an excess of triethylamine, the dichloroketene generated[94,95] reacted with the indene. Chromatographic work-up gave the compound (92) in moderate yield.



(85) (91) (92)

Attempts to isolate the adduct (91) were not successful although in one instance n.m.r. analysis of the crude product mixture prior to the chromatography showed that (92) was not present at that stage. During chromatography, the trienone (92) was seen as an orange band. When the orange solution which eluted from the column was evaporated, the solid which crystallised was only pale yellow and redissolved to give a nearly colourless solution. Addition of silica to this solution again regenerated the orange colour. It is likely that this colour was due to an enol form of (92) in which there is considerable conjugation.

Three steps were required to remove the chlorine atoms (Scheme 31).

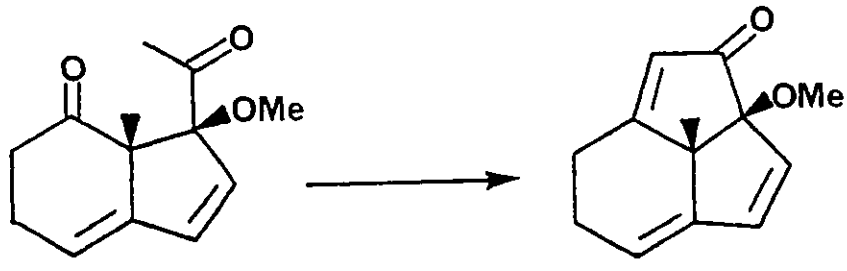


SCHEME 31 Reagents: i, $Bu^n_3SnH-C_6H_6$-AIBN, 80°C; ii, NaI-$(CH_3)_2CO$, 20°C

Reaction of compound (92) with tributyltin hydride[94,96] gave the chloroketone (93) but this product was not converted into compound (95) by treatment with an excess of the reagent; instead the product decomposed if conditions were forcing. In practice, the best yield of the monochloroketone (93) was obtained was obtained when much of the starting material remained unreacted. However, treatment of the chloroketone (93) with sodium iodide in acetone[97] gave the iodoketone (94) which could then be reduced in high yield with further tributyltin hydride.

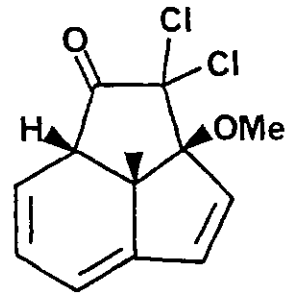
An attempt to bring the three steps together by addition of sodium iodide to a solution of tributyltin hydride in acetone was not successful; a complex mixture resulted. Zinc in acetic acid[98] was not successful for the reduction.

Unfortunately, all attempts to close the diketone (95) by an intramolecular aldol condensation were unsuccessful, presumably the result of a combination of the unreactivity of the unsaturated ketone and the acidity of the proton at the 7-position. Treatment with a variety of acidic or basic catalysts gave either no reaction or a complex mixture. The behaviour of the diketone (95) contrasts that of the diketone (96) which Lidert found to undergo a ready intramolecular aldol condensation with potassium hydroxide in methanol to give the annulene precursor (97).[99]



(96) (97)

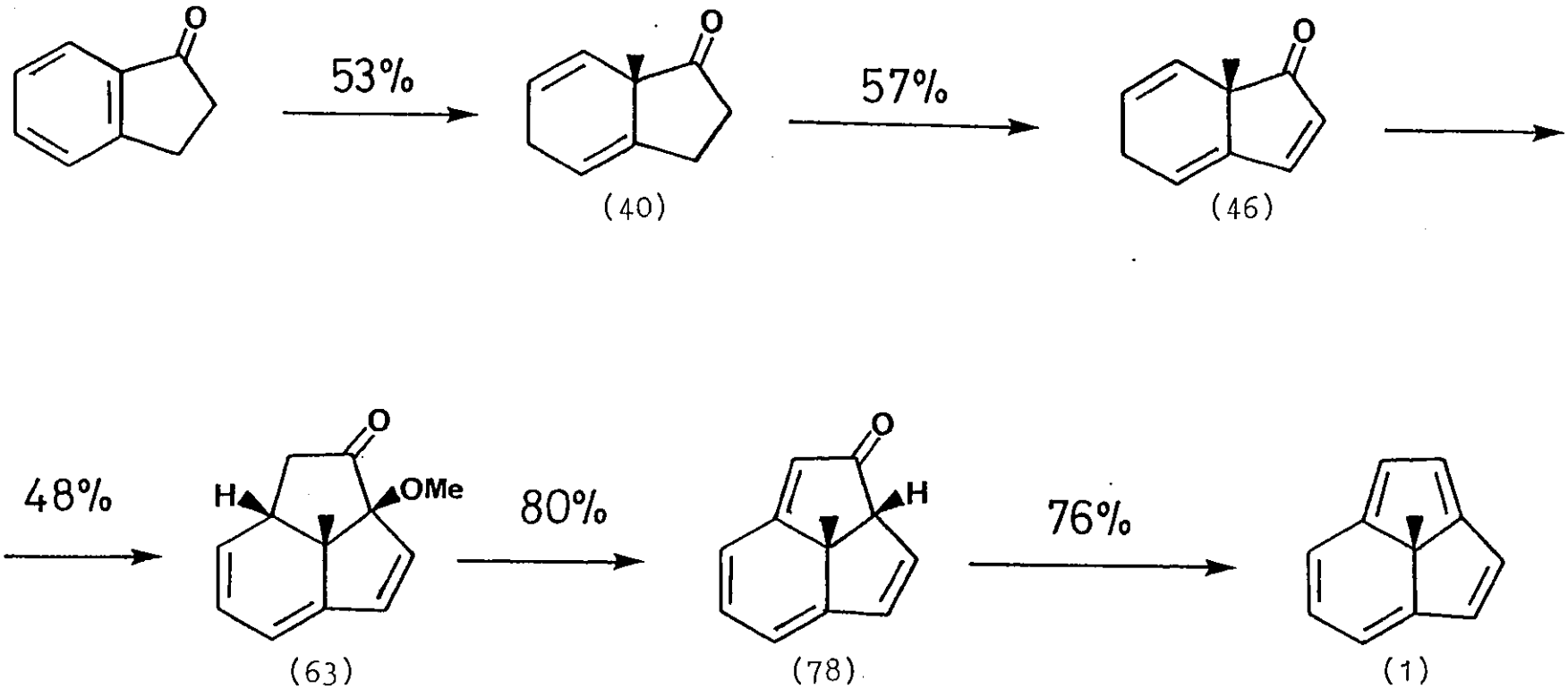
One solution to this problem would be to ensure that the adduct (91) does not ring-open but the adduct was too sensitive in this respect and so attention was turned to the methoxy-3a<u>H</u>-indene (37). Treatment of a solution of this indene generated in the usual way in 1,2-dimethoxy-ethane, with dichloroketene generated in <u>situ</u> as before, gave a complex mixture from which only a very impure sample of what was probably the required adduct (98) was isolated in low yield. The reaction was not pursued; it is likely that the conditions used were not appropriate for the preparation of the dichloroketene.



(98)

The third approach to the desired compound was the utilisation of the adduct of unexpected regiochemistry (60a) from the chloroacrylonitrile cycloaddition. However, attempts to hydrolyse this adduct failed, just as it did for the isomers (58a) and (58b). Treatment of a mixture of the adducts (60a) and (60b) with sodium hydroxide in ethanol and dimethyl sulphoxide gave surprisingly a clean reaction, but to give a mixture of the annulenes (67a) and (67b) in good yield. This elimination did not occur with sodium sulphide in ethanol, but the reaction gave a complex mixture.

The Best Current Route to 7b-Methyl-7bH-cyclopent[cd]indene

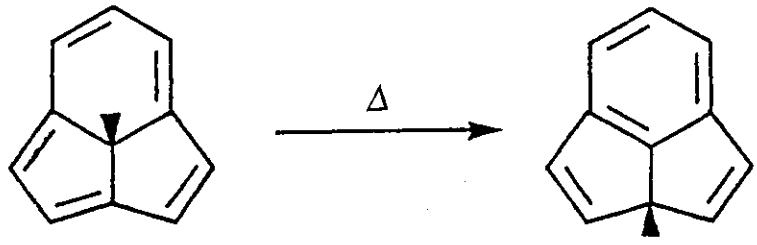


9% overall

2.2 The Chemical Properties of 7b-Methyl-7b*H*-cyclopent-[*cd*]indene (1)

2.2.1 Thermal Rearrangements

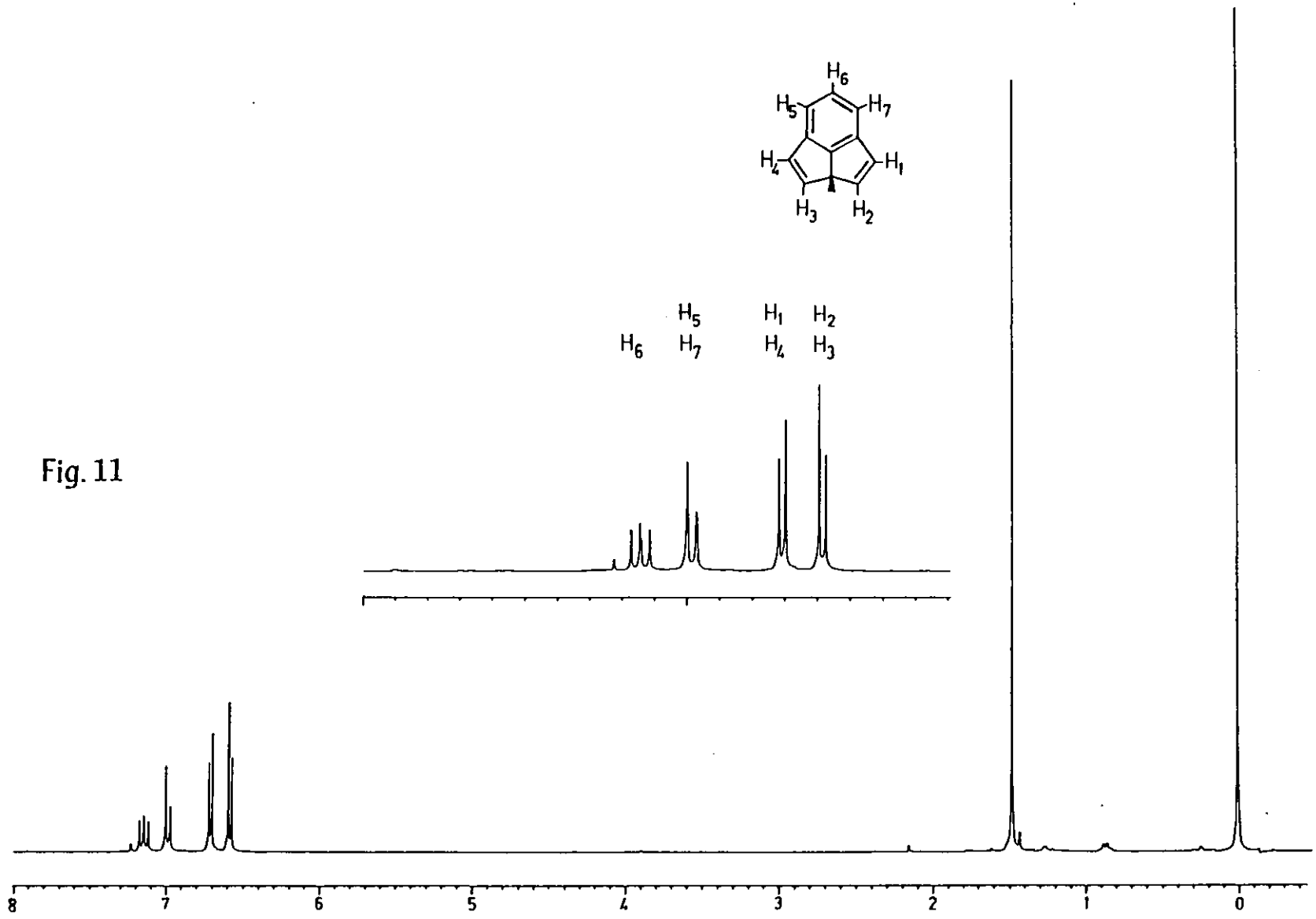
7b-Methyl-7b*H*-cyclopent[*cd*]indene (1) rearranges in boiling xylene to the 2a*H*-isomer (99) with a half life of 12 h.

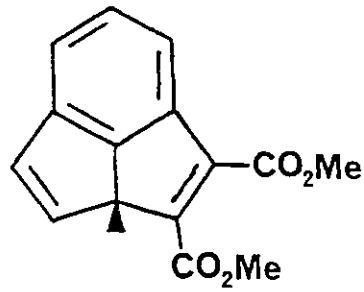


(1) (99)

When the reaction was followed by g.l.c., it was observed that the ratio of the amounts of (1) and (99) approached a constant ratio of 1 : 3 and that the product was then decaying at the same rate as the annulene was being converted into it. In order to identify the product, no attempt was made to take the reaction to completion; it was stopped after 24 h and a low yield of a mixture of compound (99) and starting material could be isolated. The symmetrical structure (99) was apparent from the proton n.m.r. spectrum (Fig. 11). The similarity of the u.v. spectrum of the 2a*H*-isomer (99) with that of the thermal rearrangement product of the diester (38) confirms that Tuddenham was correct with the assignment of his product as compound (100).[42a]

Fig. 11





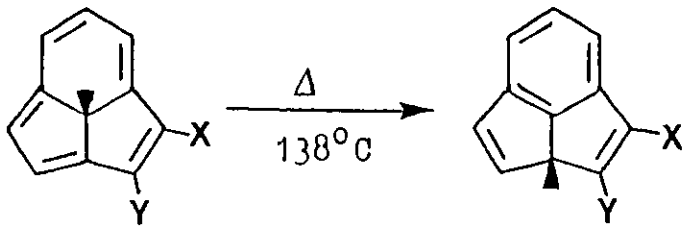
(100)

The rearrangement of the annulene(1) followed first order kinetics consistent with a concerted unimolecular [1,5]sigmatropic shift of the methyl group. Thus a plot of the logarithm of the proportion of the annulene remaining against time was linear. Furthermore, the rate of migration was unchanged when dimethyl sulphoxide was used as the solvent (at the same temperature) and therefore the rearrangement is apparently not subject to a solvent effect.

The rates were most conveniently measured by following the decrease in absorbance of the long wavelength band in the electronic spectrum. By this method, half-life determinations were made for a variety of derivatives and the results are given in Table 7. All the reactions gave good first order plots. An anomalous result was observed in the case of the dialdehyde (51). Under the conditions, this dialdehyde rapidly isomerised to a new annulene, probably a lactone which had a visible absorption maximum at 474 nm instead of at 498 nm. This new absorption then decayed with a half life of 2 h.

The introduction of any substituent into the 2-position of the annulene increases the rate of the rearrangement. The most electron withdrawing substituents have the greatest effect on the rate.

TABLE 7 Rate Measurements for the Thermal Rearrangement of Variously Substituted [10]Annulenes

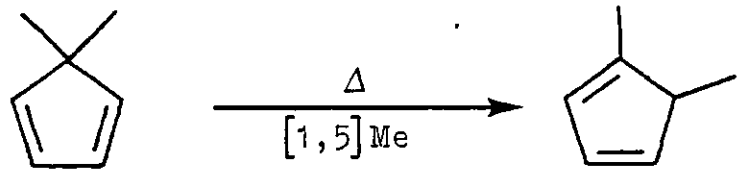


X	Y	compound number	$t_{\frac{1}{2}}$/h	k_{rel}	δ_H(7b-Me, $CHCl_3$)	λ_{max}(EtOH) /nm
H	H	(1)	12	1	-1.67	450
H	OMe	(82)	6.7	1.8	-1.50	459
H	CN	(65)	2.0	6.0	-1.52	470
CN	H	(67a)	6.4	1.9	-1.50	467
H	$CONH_2$	(66)	3.5	3.4	-1.47	471
H	CO_2H	(64)	2.0	6.0	-1.42	474
H	CO_2Me	(70)	1.9	6.3	-1.47	475
H	CHO	(53b)	1.1	11.0	-1.40	488
CO_2Me	CO_2Me	(38)	3.4	3.5	-1.34	472

The effects of perturbation of the 10π-system are reflected by a reduction of the ring current of the annulene causing a downfield shift of the signal for the central methyl group in the proton n.m.r. spectrum, and by a bathochromic shift of the long wavelength band in the electronic spectrum. These effects parallel the kinetic measurements and the variation in the rates may be explained in terms of the ground state energy of the annulene. However, a surprising result was the much faster rearrangement of the 2-nitrile (65) than the 1-nitrile (67a). This could be explained in terms of product stability; the 2-nitrile rearranges to a compound related to cinnamonitrile but the 1-isomer rearranges to a less stable cross conjugated product. However unusual results for 5-substituted annulene derivatives have led to a different explanation (see Section 2.2.8).

Rate measurements for the rearrangement of the parent annulene (1) were determined using decalin as the solvent at a variety of temperatures in the range 138 - 190°C. A plot of the logarithm of the rate constant against the reciprocal of the absolute temperature was linear, and from the slope of the graph, the activation energy for the rearrangement was calculated to be 32.7 ($\pm$1) kcal mol^{-1}. In comparison, the simpler [1,5]methyl shift shown below has an activation energy of 45 kcal mol^{-1}.[100] The greater ease of migration in the annulene is due to the extra driving force caused by formation of a benzene ring. It must be emphasised however that all the annulene derivatives rearrange much slower than the 3a<u>H</u>-indene derivatives (37) and (85) where there is no aromatic

stabilisation of the starting material (see also Section 2.2.8).



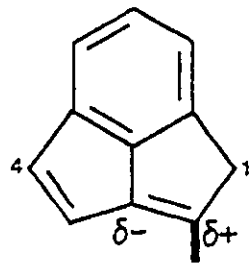
The pre-exponential factor, A, for the rearrangement of the annulene (1) was 4 x 10^{12} s^{-1}, and from it, a value of the activation entropy, $\Delta S^{\ddagger}$, of -9 ($\pm$4) J $mol^{-1}K^{-1}$ was calculated.* This value is small and negative as expected for a concerted sigmatropic shift.

It was thought that the yield of the rearrangement product (99) would improve if the reaction was rapid and done under dilute conditions since the decay of the product may be a polymerisation (cf. styrene and indene which have similar structures). Use of a high boiling solvent would give a fast reaction but removal of the solvent afterwards from the volatile hydrocarbon would constitute a problem. It seemed that flash vacuum pyrolysis (FVP) conditions should be ideal and this was indeed found to be the case. Distillation of the annulene at 0.3 mmHg twice up a tube heated to 400°C, gave, in 78% yield, a practically pure

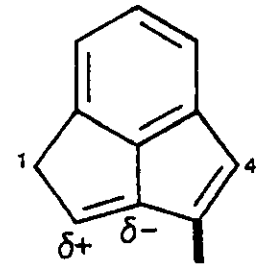
---

* From the equation $A = \frac{ekT}{h} e^{\Delta S^{\ddagger}/R}$ where e = 2.7, k = Boltzmann's constant, h = Planck's constant, and R = universal gas constant.[101]

sample of the 2a<u>H</u>-isomer (99), as a colourless oil with a strong bitter smell. In the hope of observing further products, the FVP was repeated at 700°C. The yellow oil which collected on the cold finger was chromatographed to give a 2 : 1 mixture of the 1<u>H</u>-isomers (101) and (102).



(101)



(102)

The structures were assigned by the similarity of the proton n.m.r. spectrum of the mixture with that of the known unsubstituted compound, 1<u>H</u>-cyclopent[<u>cd</u>]indene (35).[38] The minor isomer (102) showed a fine splitting of the methyl group signal, presumably owing to an allylic coupling to the proton at the 4-position and leading to its assignment as (102) in which such a coupling is expected. The n.m.r. spectrum of the mixture also showed the presence of a small amount of a compound having aromatic proton resonances, assignable to three adjacent protons but which were unusually downfield at δ7.4 - 7.9. This compound could be a naphthalene derivative, but it was not identified.

When the FVP was carried out at 600°C, the reaction was cleaner and a mixture of the isomers (101) and (102) was isolated in 76% yield. The ratio of the isomers was the same as before and may be an equilibrium ratio. That compound (101) is the major isomer is not surprising since

the fulvene type resonance (shown) places partial carbonium ion character on a tertiary carbon instead of a secondary carbon as is the case with isomer (102). The u.v. spectrum of the mixture of the 1H-isomers was very similar to that recorded for the unsubstituted compound (35)[38] confirming the identification.

The 1H-isomers are most probably formed from the 2aH-isomer (99) by a [1,5]methyl shift followed by a series of rapid [1,5]hydrogen shifts. The results of the FVP reactions implies a stability order of cyclopent[cd]indenes of

$$1H > 2aH > 7bH$$

The main contributing factor to the relative stability of the 1H-isomers is probably that they are planar whereas in the 2aH- and 7bH-isomers, a tetrahedral carbon atom at a ring junction causes distortion of the π-systems and resultant loss in resonance energy. The 1H-isomers are also stabilised by the fulvenoid resonance mentioned above. The stability order given above is different to that implied by the calculations of Streitwieser.[102] He calculated that the parent hydrocarbons follow the acidity order 2aH > 7bH > 1H. Since the acidities were determined by the differences in calculated energies between the hydrocarbons and the common anion (34),[102] it follows that the stabilities of the hydrocarbons were incorrectly calculated to be in the order 1H > 7bH > 2aH.

2.2.2 Photolysis

When a solution of the annulene (1) in petrol was

irradiated in a Rayonet reactor at 300 nm, a wavelength at which it absorbs strongly, no reaction occurred but a strong green fluorescence was emitted. The u.v. spectrum was recorded at intervals and did not change. After 15 hours, the petrol was removed and the residue was shown by its proton n.m.r. spectrum to be starting material. On irradiation at 254 nm, a small amount of the annulene was consumed after 24 hours, but no new products could be isolated. The annulene (1) can be regarded as essentially inert to photolysis.

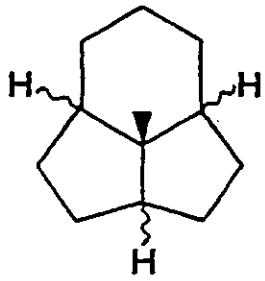
2.2.3 Hydrogenation

The annulene (1) was readily hydrogenated in ethanol over a catalyst of 5% palladium on charcoal at atmospheric pressure. Five equivalents of hydrogen were rapidly taken up to give fully saturated compound(s) (103), as a colourless oil with a minty smell. The proton n.m.r. spectrum supported the structure and the mass spectrum confirmed the extent of hydrogen uptake.

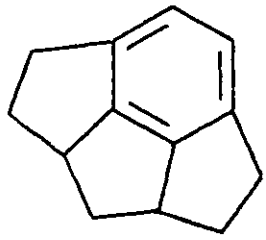
Following the observation in the literature that the tetracyclic hydrocarbon (104) is strained enough to be readily hydrogenated,[103] the related 2a-methyl-2a<u>H</u>-cyclopent-[<u>cd</u>]indene (99) was also hydrogenated. A rapid initial uptake of hydrogen was followed by a slow uptake. The mass spectrum showed products arising from the uptake of 2, 4, and 5 equivalents of hydrogen. These products are most likely to be (105), (106), and (107) respectively.

Thus, the effect of strain in these compounds is to make the normally inert benzene ring susceptible to hydrogenation. An X-ray study of the related hydrocarbon,

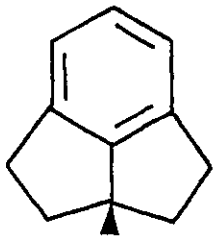
fluoradene (108) has shown that the trisubstituted benzene ring is considerably warped away from planarity.[104]



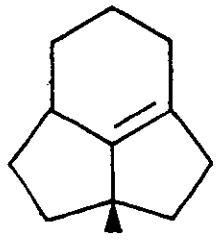
(103)



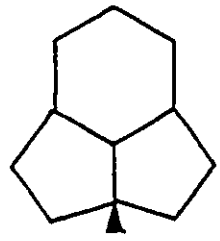
(104)



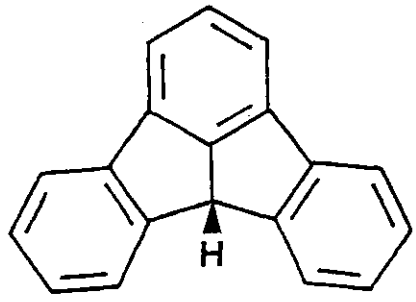
(105)



(106)



(107)



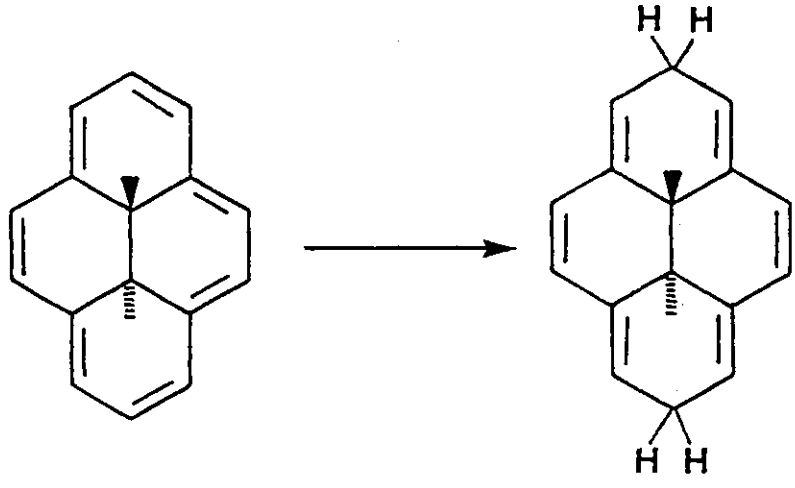
(108)

2.2.4 Electon Transfer Reactions

Like the 14π-system (31) studied by Boekelheide,[35b] the annulene (1) failed to form a picrate. When concentrated solutions of the two components in ethanol were mixed, the resulting solution was orange suggesting the formation of a charge transfer complex. However, no precipitate formed

and on concentration of the solution, the crystals which deposited were picric acid and the annulene remained in solution. The non-formation of a solid picrate is perhaps not too surprising since the angular methyl group would be expected to prevent the stacking of layers in a crystal.

Potassium metal was found to dissolve in a solution of the annulene (1) in tetrahydrofuran to give a deep red solution which was unstable and turned brown on standing. When a solution of the annulene was added to a solution of sodium in liquid ammonia, and the resulting orange mixture quenched with ammonium chloride, a mixture of olefinic hydrocarbons resulted and no products could be identified by examination of the 250 MHz proton n.m.r. spectrum. Under similar conditions, trans-10b,10c-dihydro-10b,10c-dihydropyrene (31) cleanly gave the symmetrical product (109).[35b]



(31) (109)

2.2.5 Lithiation

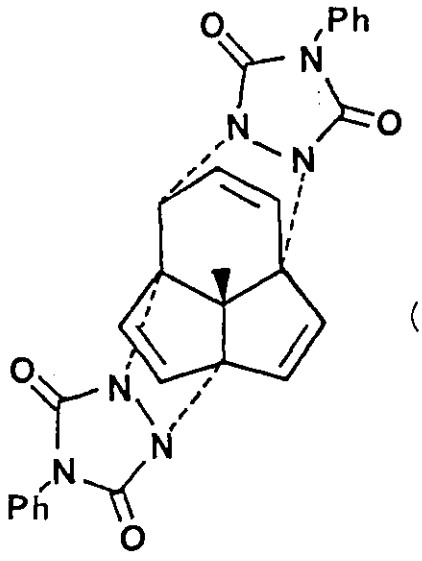
Attempts to lithiate the annulene (1) were not successful. There was no reaction with n-butyl lithium in petrol but when tetramethylethylenediamine was added,[105] the annulene was consumed to give a deep red solution.

After a quench with carbon dioxide in ether and acidification, no annulenecarboxylic acids could be detected. A yellow olefinic product was formed and its n.m.r. spectrum showed that a butyl group had been incorporated. No structure could be deduced for the product and it was probably a mixture. The annulene (1) reacted only very slowly with tert-butyl lithium in petrol at room temperature and, after carbonation, again no products could be identified.

2.2.6 Cycloaddition Reactions

In so far as the annulene (1) formally contains a cyclopentadienyl unit, it could undergo Diels Alder reactions. However, it did not give an adduct with an excess of dimethyl acetylenedicarboxylate or maleic anhydride in refluxing toluene, or with benzyne generated by thermolysis of benzenediazonium-2-carboxylate.[106] With tetracyanoethylene (TCNE), the annulene (1) gave reversible formation of a green charge transfer complex in solution. There was no adduct formation and even after heating the annulene with a large excess of TCNE in refluxing 1,2-dimethoxyethane, the annulene (1) was recovered unreacted. With the powerful dienophile, 4-phenyl-1,2,4-triazole-3,5-dione (PTAD), there was no reaction at room temperature, but in refluxing 1,2-dimethoxyethane the 2 : 1 adduct (110) was formed in 75% yield.

When only one equivalent of PTAD was used, half of the annulene was recovered unchanged; no 1 : 1 adduct was formed. Therefore the olefinic 1 : 1 adduct must be more reactive to PTAD than the annulene.



(110)

The structure of the 2 : 1 adduct was deduced from nuclear Overhauser effect measurements in the proton n.m.r. spectrum (Fig 12). Irradiation of the methyl group causes strong enhancement of all of the protons originating from the periphery of the annulene. This proves the methyl group is still in the central position and that the PTAD groups are both on the side of the molecule opposite to the methyl group. A molecular model shows that the PTAD units lie in nearly parallel planes and it is likely that the second PTAD molecule is guided into its position by association between the dienophile and the PTAD unit in the initial 1 : 1 adduct. Such an association has already been reported by Ginsburg in his work on propellanes[107] and on 1,6-methano-[10]annulene.[108] In the latter case, cycloaddition of the annulene with PTAD occurs at room temperature to give a mixture of 1 : 1 and 2 : 1 adducts. This behaviour is further evidence for the significance of a transannular interaction in 1,6-methano[10]annulene (21) as described in the Introduction.

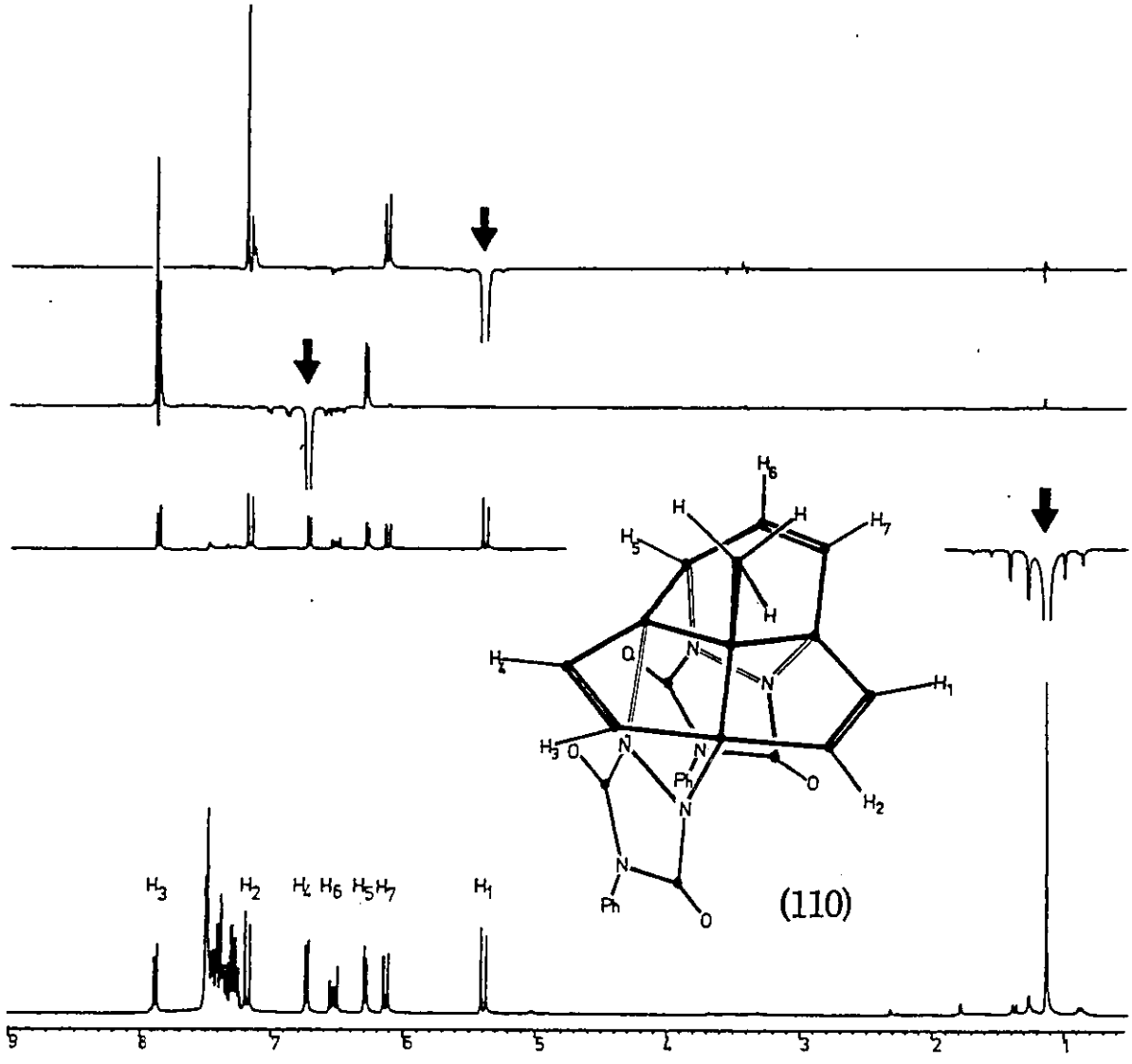
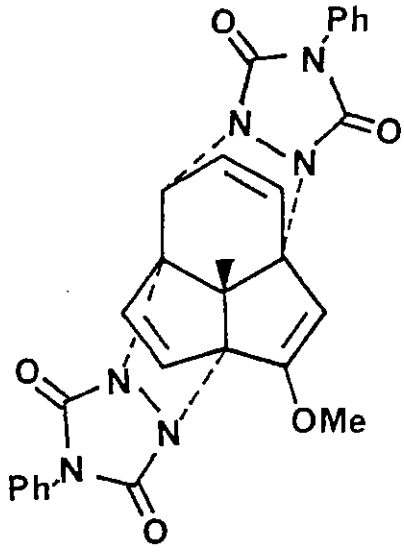


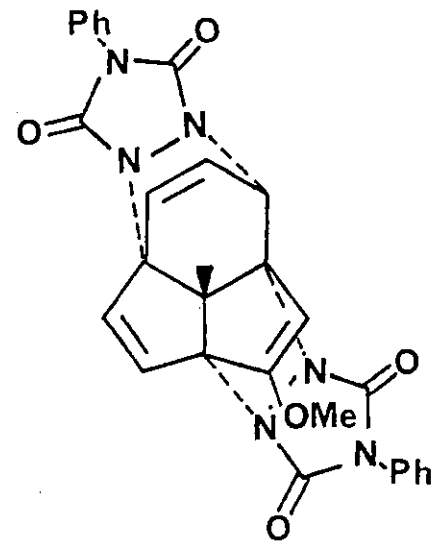
Fig. 12

Irradiation of the protons at positions 1 and 4, as determined from the spectrum of the 2 : 1 adduct (110) derived from deuterated annulene, gave enhancements of H-7 and H-5 respectively. This allows complete assignment of the spectrum of the adduct and proves that the deuterium was incorporated into the 2-position of the annulene (see Section 2.1.6).

The reactions of the electron rich annulenes (77) and (82) with PTAD were studied since it was thought that these were more likely to give 1 : 1 adducts. The 2-methoxyannulene (82) reacted with PTAD at room temperature to give a low yield of the 2 : 1 adduct (111). Its structure was deduced by comparison of its n.m.r. spectrum with that of adduct (110). None of the isomeric adduct (112) was detected and adduct (111) is probably preferred for steric reasons.

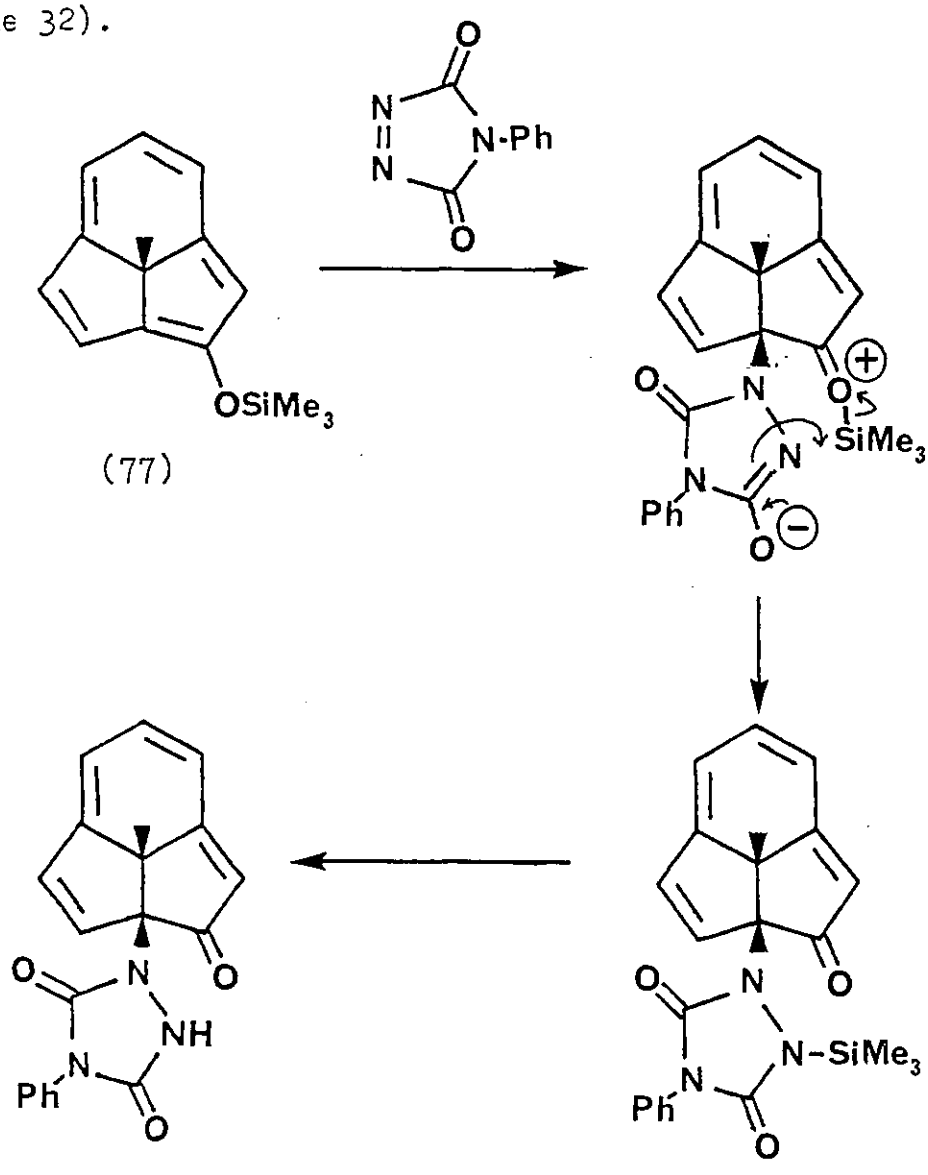


(111)



(112)

The trimethylsilyl ether (77) also reacted with PTAD at room temperature but the product was not a 2 : 1 adduct. After chromatographic work-up, the tetraenone (113), an orange-red solid, was isolated in 54% yield. The reaction presumably proceeds by electrophilic addition of the PTAD to the 2a-position followed by transfer of the trimethylsilyl group which is then hydrolysed off on work-up (Scheme 32).



(77)

(113)

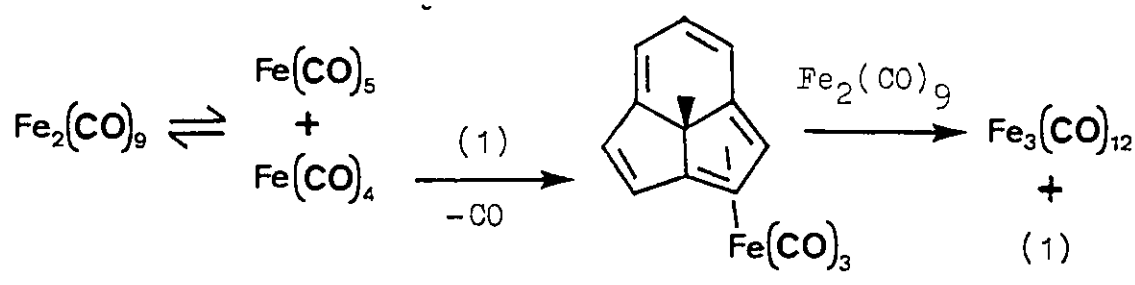
SCHEME 32

The resistance of the annulene (1) to undergo Diels Alder reactions is clear evidence for the aromatic delocalisation. A further reason for its resistance is probably that any adducts formed by addition of the electrophile to the face of the annulene opposite to the methyl group would be strained owing to the presence of trans-fused rings. Addition to the annulene on the same face as the methyl group would be disfavoured by steric repulsion from the methyl group.

The behaviour of the annulene (1) with chlorosulphonyl isocyanate and dichloroketene are discussed later, in Section 2.2.8.

2.2.7 Metal Complexes

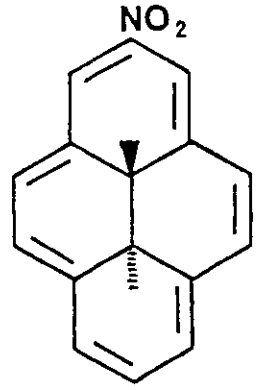
Preliminary results suggest that the annulene (1) resists complexation with metals. Apart from decomposition of the reagent, there was no reaction with chromium hexacarbonyl in a refluxing 3 : 1 mixture of di-n-butyl ether and tetrahydrofuran.[109a] With diiron nonacarbonyl in benzene at 50°C,[109b] the reaction mixture became dark green and triiron dodecacarbonyl could be isolated. No annulene was consumed but the triiron dodecacarbonyl did not form if the annulene was not included. Hence, the annulene catalyses the decomposition of the diiron nonacarbonyl and possibly involves an unstable iron tricarbonyl complex as shown below.



2.2.8 Electrophilic Substitution and Related Reactions

The annulene (1) undergoes substitution reactions with certain electrophilic reagents. With copper(II) nitrate in acetic anhydride[5,35b] at 0°C, a mixture of all four possible mononitrated products was formed. These compounds could not be separated by preparative layer chromatography but could with careful column chromatography, eluting only with petrol, when the mixture was separated into two bands which were analysed by n.m.r. The first band (orange) was a mixture of the 1- and 2-nitro derivatives and the second band (yellow) was a mixture of the 5- and 6-nitro derivatives. A full assignment of the n.m.r. spectra of the 1-, 5-, and 6-nitro derivatives was possible after examination of the spectrum of the product mixture derived by nitration of the deuterated annulene (72). The ratio of products is given in Table 8. No dinitrated products were detected and lowering of the reaction temperature did not alter the product composition. A test for copper(I) in the aqueous extracts from the work-up of the nitration was negative and therefore the copper(II) nitrate was not causing side reactions by acting as an oxidising agent.

The diester (38) also gave a mixture of mononitrated products under these conditions[42a] but the tetracyclic [14]annulene (31) gave only the symmetrical product (114).[35b]



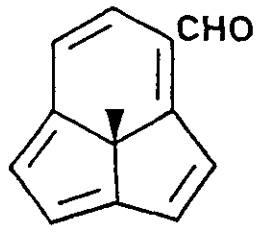
(114)

Reduction of the mixture of nitroannulenes derived from the annulene (1) with zinc in acetic anhydride gave a corresponding mixture of acetamidoannulenes (54% yield) as an unstable semi-solid. Reduction with zinc in acetic acid gave a complex mixture.

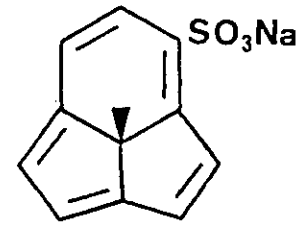
It is reported that mononitration of the related system, azulene, is better brought about using tetranitromethane in pyridine than the reagent system discussed above.[110] However, using this method, the annulene was consumed only slowly at room temperature to give dark baseline material (t.l.c.). After warming the mixture, the annulene was consumed completely and t.l.c. showed that only a trace of a mixture of nitro compounds had formed. Use of dimethyl sulphoxide as the solvent instead of pyridine gave the same result.

Acetylation of the annulene was accomplished by treatment with acetic anhydride in dichloromethane catalysed by boron trifluoride etherate.[5,35b] The reaction which was complete in three hours at room temperature was more selective than nitration and gave a higher yield of monoacetylated products in the ratio given in Table 8.

Formylation of the annulene with dichloromethyl n-butyl ether and tin(IV) chloride in dichloromethane[35b] at -78°C was more selective still and gave the 5-aldehyde (115) almost exclusively. The mauve 2,4-dinitrophenylhydrazone of (115) was isolated pure. It was unfortunate that the formylation went in low yield (28%) and hence that little use could be made of the product for the synthesis of other 5-substituted derivatives.



(115)



(116)

Sulphonation of the annulene (1) was also very selective. The annulene was consumed immediately when added to a solution of an excess of sulphur trioxide in dioxan[111] at 12°C. The product was isolated as its sodium salt, a yellow hygroscopic solid, the n.m.r. of which showed it was almost pure 5-monosulphonate (116). Traces of other products were present but none could be identified. The product was characterised as its S-benzylthiouronium salt.

Under the same conditions, 1,6-methano[10]annulene (21) gave disubstituted products[111] and it was necessary to use a deficiency of the reagent to achieve monosubstitution. This is further evidence for transannular bonding in 1,6-methano[10]annulene since methylated naphthalene derivatives also give disubstitution under these conditions.[112]

Measurements of the rates of the methyl migration in the 5-substituted annulenes (115) and (116) gave unexpected results. The aldehyde (115) rearranges in decalin at the same rate as the parent system (1) ($t_{\frac{1}{2}}$ 12 h at 138°C) whereas the 2-aldehyde (53b) rearranges much faster under the same conditions ($t_{\frac{1}{2}}$ 1.1 h at 138°C). An explanation for this is that the rate is increased when partial carbonium ion character is induced onto the terminus of migration of the methyl group at C-2a. In the 5-position, the aldehyde group

is too far from C-2a to have any inductive effect and cannot induce positive charge onto the 2a-position by a resonance effect. This also explains why the 2-nitrile (65) rearranged faster than the 1-nitrile (67a) and is probably a better explanation than that based on product stability mentioned in Section 2.2.1.

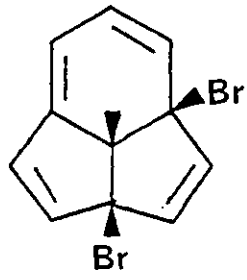
The rearrangement of the sulphonate (116) could not be followed in non-polar solvents owing to its insolubility. In diethylene glycol, this sulphonate rearranged surprisingly fast ($t_{\frac{1}{2}}$ 7 h at 138°C) but it was found that the parent annulene (1) rearranged just as fast in this solvent. Thus the rate of migration shows a slight solvent effect in that the reaction is accelerated by a protic solvent. These results suggest that there is some charge separation in the transition state of the migration and that the reaction is accelerated when this charge separation is stabilised.

Attempted benzoylation of the annulene (1) with benzoyl chloride and aluminium chloride[35b] was not successful. A complex mixture was formed and it is likely that the annulene is not compatible with the Lewis acid.

Attempted bromination of the annulene (1) using the conditions employed by Mitchell, Lai, and Williams for the monobromination of the [14]annulene (31)[113] was not very successful. After two days at room temperature with N-bromosuccinimide in dimethylformamide the mixture had appreciably darkened. Work-up gave a 10% recovery of starting material containing only a small amount of a new annulene; possibly the brominated material required.

In contrast, treatment with pyridinium bromide per-

bromide in benzene, as used successfully for the bromination of [18]annulene (2),[6] gave a clean reaction but did not give substitution products. Instead, the crystalline addition product (117) was formed (78%).



(117)

This product is most probably formed by electrophilic attack at the 2a-position. The resulting carbonium ion cannot lose a proton to return to an annulene and instead is trapped out at another bridgehead position by the excess of bromide present. The dibromide (117) could be converted back into the annulene (1) by treatment with activated zinc in ether. Hence, this dibromide is a potentially useful protected annulene and may for instance be used to prepare cycloadducts of the annulene not available directly.

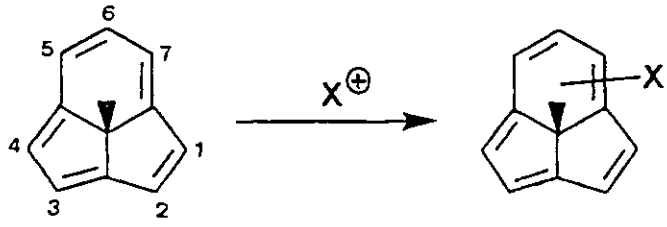
It is interesting to compare the reaction of 1,6-methano[10]annulene (21) with bromine when substitution does occur but the mechanism is one of addition followed by elimination of hydrogen bromide.[114]

With bromine in carbon tetrachloride, the annulene (1) was consumed but the reaction was not as clean as with pyridinium bromide perbromide and a mixture of products resulted, none of which were identified.

The dibromide (117) could also be prepared by treatment of the annulene (1) with copper nitrate in acetic

anhydride in the presence of excess lithium bromide. This reaction was done in the hope that an addition product of the annulene and nitryl bromide (NO_2Br) would be obtained.

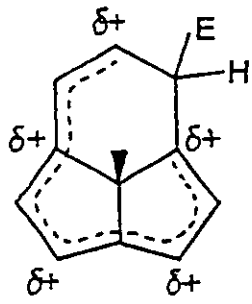
TABLE 8 Product Composition in Electrophilic Substitution Reactions of the Annulene (1)



Isomer	Percentage distribution				Yield
	1-	2-	5-	6-	
X = NO_2	40	5	40	15	41%
X = $COCH_3$	20	0	75	5	55%
X = CHO	4	0	93	3	28%
X = SO_3H			>95		70%

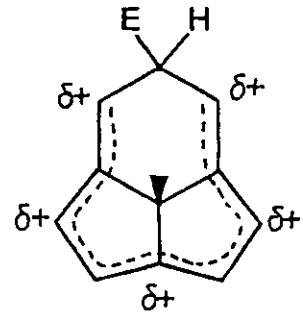
The preference for 5- and 1-substitution can be explained in terms of the carbocation intermediates involved. For example, the intermediate cation (118) for attack of the electrophile, E^+, at the 5-position should be more stable than the cation (119) for attack at the 6-position, in spite of the greater symmetry of (119), since the positive charge can be delocalised onto two tertiary positions in (118) but onto only one in (119). Similarly 1-substitution should be favoured over 2-substitution. That substitution occurs to a greater extent at the 6- than the 2-position is possibly due to the enhanced

symmetry of intermediate (119).



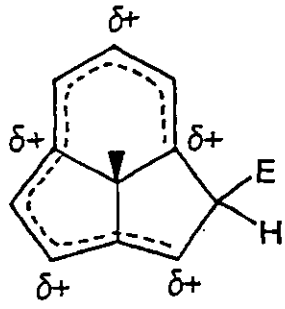
(118)

5-substitution

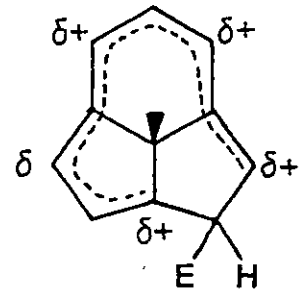


(119)

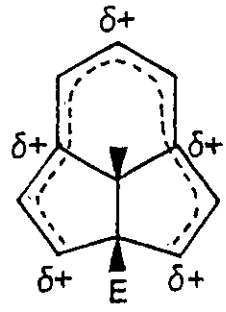
6-substitution



1-substitution



2-substitution



(120)

2a-addition

The intermediate (120) is stabilised by two tertiary centres, is symmetrical, and its formation relieves strain at the 2a-position. It is therefore to be expected that the 2a-position should be that favoured for attack by electrophiles and it is probable that reasonable yields for

substitution products only result when this addition is reversible, as for example with sulphonation where the reversibility is well known.

From the results above it can be concluded that the order of preference for attack of electrophiles is

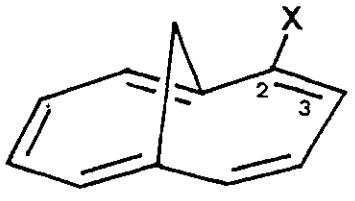
$$2a > 5 > 1 > 6 > 2$$

and it is further likely that the preference for bridgehead positions is

$$2a > 4a$$

Rzepa has calculated that the most favoured position for protonation of the annulene (1) is C-2a and that there should be little selectivity for other positions.[33]

It was obviously desirable to find other electrophiles which would give exclusive substitution at one position. Effenberger has reported that treatment of 1,6-methano-[10]annulene with the nitronium trifluoromethanesulphonate-collidine complex or with chlorosulphonyl isocyanate gave exclusively the 2-substituted products (121a) and (121b) whereas copper(II) nitrate gave a mixture of 2- and 3-substituted products.[115]



(121a) X = NO_2

(121b) X = $CONHSO_2Cl$

It is known however, that the 2-position of 1,6-methano[10]annulene is much the more reactive[24] and it was useful to test these electrophiles with our annulene system. Both reagents gave unexpected results. The complex formed from nitronium trifluoromethanesulphonate and collidine reacted slowly with the annulene (1) in refluxing dichloromethane to give a poor yield of mono-nitrated products. Examination of the product by n.m.r. showed it was a 2 : 1 mixture of the 6-isomer and the 2-isomer. These are the two isomers that are normally formed to the least extent. This unusual selectivity may be the result of steric control by the hindered reagent or a completely different mechanism (eg. electron transfer) may be operating.

With chlorosulphonyl isocyanate,[93] the single product formed was not the expected 5-substituted derivative but the less strained ring expanded adduct (122). This product is a deep red solid with a methyl resonance at $\delta_H(CDCl_3)$ 1.94. Hydrolysis with a two phase system of dichloromethane and aqueous sodium sulphite with sodium hydroxide gave the amide (123). This amide is an unstable deep green solid which gives mauve solutions. Its methyl resonance at $\delta_H(CDCl_3)$ 3.03 shows the presence of some paramagnetic ring current due to the 12π-periphery. The spectra (Fig 13) also show the upfield shift of the olefinic protons caused by this ring current. The formation of adduct (122) is explained by a [2+2] addition of the reagent to the annulene followed by a thermally allowed ten electron disrotatory ring opening as shown in Scheme 33.

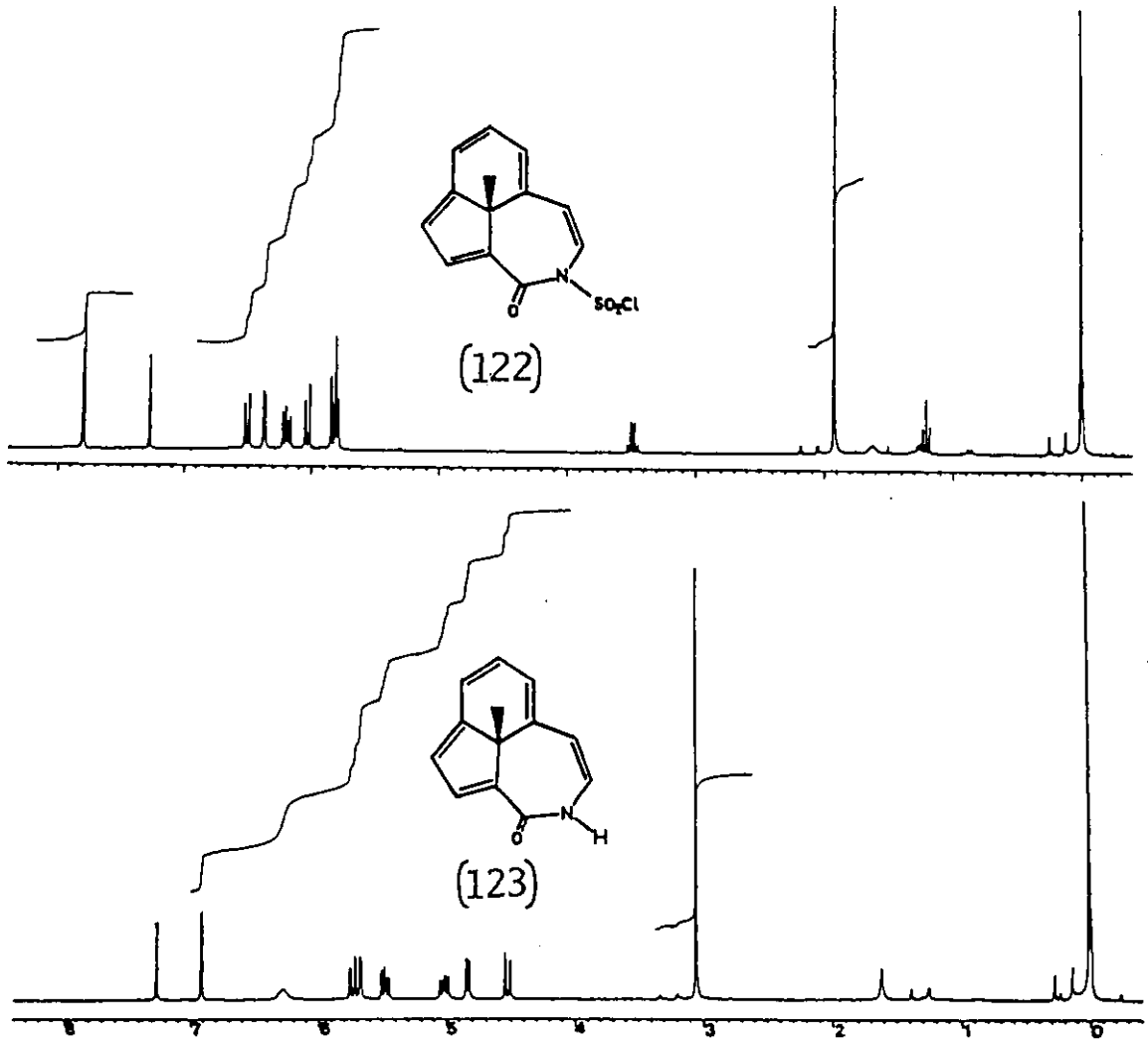
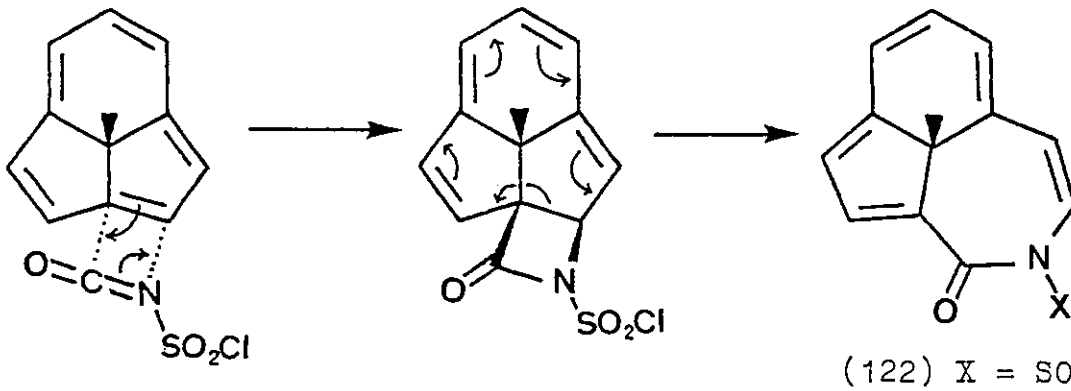


Fig. 13



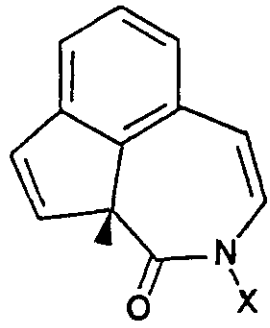
(122) X = SO_2Cl
(123) X = H

SCHEME 33

Electron withdrawal by the chlorosulphonyl group in compound (122) causes the lone pair of the nitrogen atom to be less available for contribution to the ring system than for compound (123), and consequently, compound (122) shows only a very small paratropic effect. The resistance to the formation of a 12π-system is apparent by the strongly basic conditions necessary for hydrolysis of the chlorosulphonyl group. It should be emphasised that the amide (123) only shows a small degree of antiaromaticity. The n.m.r. spectrum is much more sensitive to paramagnetic effects than diamagnetic effects. In a fully antiaromatic system, very large shifts are observed. For example, the methyl groups of the 16π-dianion of the tetracyclic [14]annulene (31) resonate at δ21.0 in the n.m.r. spectrum.[116]

The amide (123) rearranges by a [1,5] sigmatropic shift of the methyl group with a half life of less than ten seconds in refluxing xylene, just over one minute in refluxing toluene, and seventeen minutes in refluxing benzene. It is not surprising that the rearrangement is so fast since an aromatic product is formed from an antiaromatic starting material. The product of the

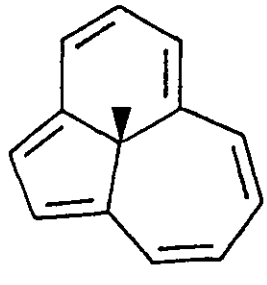
rearrangement (124) is a stable colourless crystalline solid.



(124) R = H
(125) R = SO_2Cl

When heated in refluxing toluene, the chlorosulphonyl compound (122) rearranged with a half life of 8.3 min. However, when this rearrangement was followed as usual by spectrophotometry, a small peak at 450 nm appeared. This absorption resulted from the presence of the annulene (1) and shows that the cycloaddition and ring opening in Scheme 33 are reversible. By addition of cyclohexene to the solvent to trap the liberated chlorosulphonyl isocyanate, the yield of annulene (1) was 42%. In the absence of cyclohexene, the major product was the expected aromatic compound (125) and traces of annulenamides were formed. These annulenamides must be formed by addition of the liberated chlorosulphonyl isocyanate to the annulene at a non-bridgehead position.

The indenoazepines (122) and (123) are the first examples of a tricyclic [5-6-7] system with a fully conjugated 12π-periphery. The parent hydrocarbon (126) would obviously be desirable.



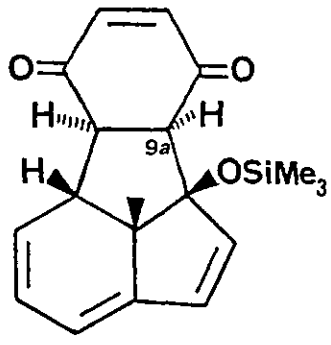
(126)

This hydrocarbon could in principle be prepared by the [2+2] addition of a suitable two carbon unit to the annulene (1). Unfortunately, the annulene (1) did not react with dichloroketene, prepared either by dehydrohalogenation of dichloroacetyl chloride or by zinc dehalogenation of trichloroacetyl chloride.[117] 1,5-Methano[10]annulene (29) reacted by [2+2] additions with tetracyanoethylene (TCNE),[118] dimethyl acetylenedicarboxylate (DMAD),[118] and benzyne.[119] With DMAD and benzyne, ring expansions occurred to give 12π-systems.[118,119] The failure of these 2π-components to react with the annulene (1) was mentioned in Section 2.2.6. Tetracyanoethylene is highly reactive and the probable reason why it did not react with the annulene (1) by a [2+2] reaction is that if it added from the same side as the methyl group there would be a severe repulsive interaction between one of the cyano groups and the methyl group. A [2+2]addition to the opposite side as the methyl group is unlikely since molecular models show that an adduct, if formed, would be highly strained.

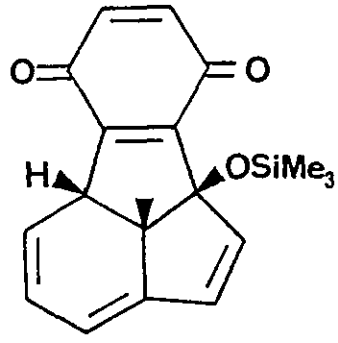
2.3 Synthesis and Properties of 9c-Methyl-9cH-cyclopenta-[jk]fluorene (130); a Benzo fused [10]annulene

There has been considerable effort to rationalise the effect of fusion of an annulene to another aromatic system.[120] Hence, it was desirable to prepare a derivative of the annulene (1) in which it is fused to an aromatic ring.

It was apparent that an [8+2] adduct of a 3aH-indene with benzoquinone would have the carbon framework of a benzo fused annulene. Addition of benzoquinone to a petrol solution of the 3aH-indene (85) gave a deep red solution. The colour was probably due to a charge transfer complex and slowly disappeared. Isolation of the resulting adduct was difficult and not always successful. After thorough removal of the solvent and the excess of reagents, chromatography gave a yellow substance in poor yield (10%) which was assigned the structure (127) on the basis of its n.m.r. spectrum supported by the n.O.e. measurements shown in Fig. 14. Irradiation of the protons of either the central methyl group or the trimethylsilyl group did not give the enhancement of the proton at the 9a-position that would be expected if the stereochemistry was endo.



(127)



(128)

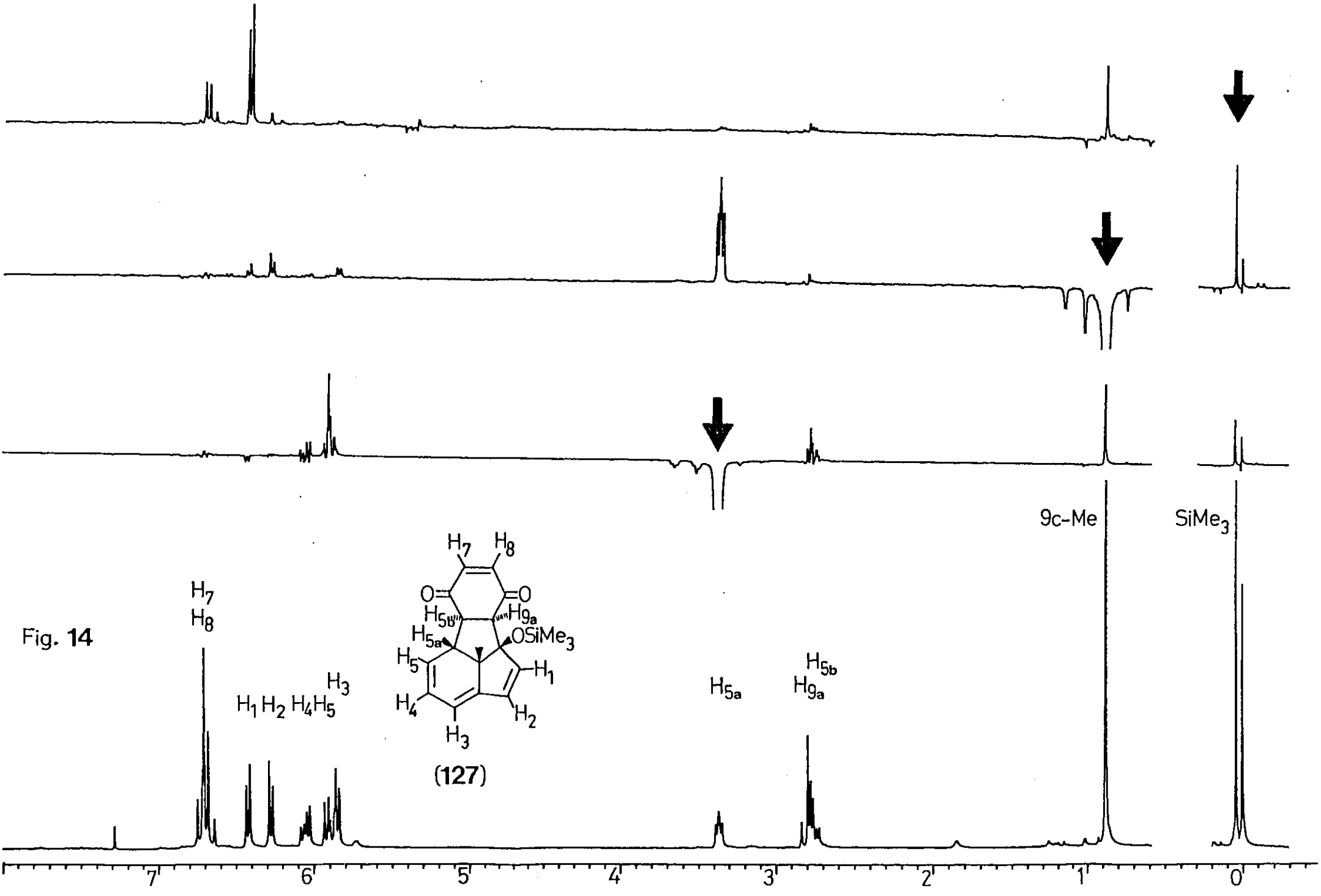
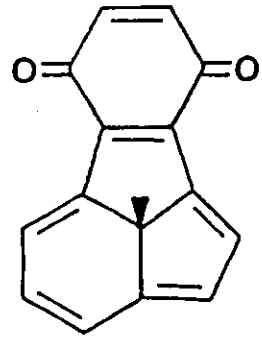

H7
H8
H1 H2 H4H5
H3
H5a
H5b
H9a
9c-Me
SiMe3
7
6
5
4
3
2
1
0

Fig. 14

H7
H8
O
O
H5b
H9a
H5a
OSiMe3
H5
H1
H4
H2
H3

(127)



(129)

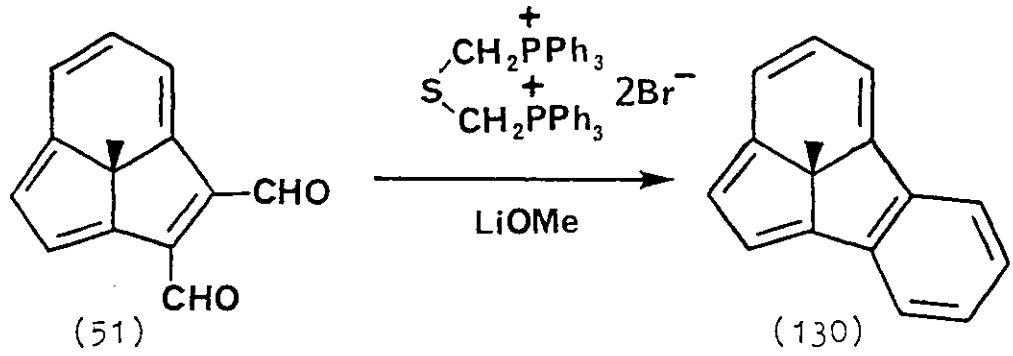
The instability of the adduct (127) in the presence of silica is presumably due to its facile tautomerisation into a hydroquinone, and the quinone (128) was often the only product that could be isolated (upto 24%). This quinone is probably formed by oxidation of the hydroquinone tautomer of the adduct (127) by the excess of benzoquinone present.

Elimination of the elements of trimethylsilanol from the quinone (128) by reaction with toluene-4-sulphonic acid in refluxing chloroform gave the purple annulenequinone (129) in 33% yield. The bridgehead methyl group in this annulene gave a signal in the n.m.r. spectrum at $\delta_H(CDCl_3)$ -1.01. Its position may be compared to that of the dialdehyde (51) $[\delta_H(CDCl_3)$ -1.12$]$.

Further work on the benzoquinone adduct was abandoned owing to the low yields and difficulties of isolation.

The hydrocarbon (130) was prepared by reaction of the dialdehyde (51) with thiodimethylenedi(triphenylphosphonium bromide) in the presence of lithium methoxide in

dimethylformamide at room temperature.[121]



(51) (130)

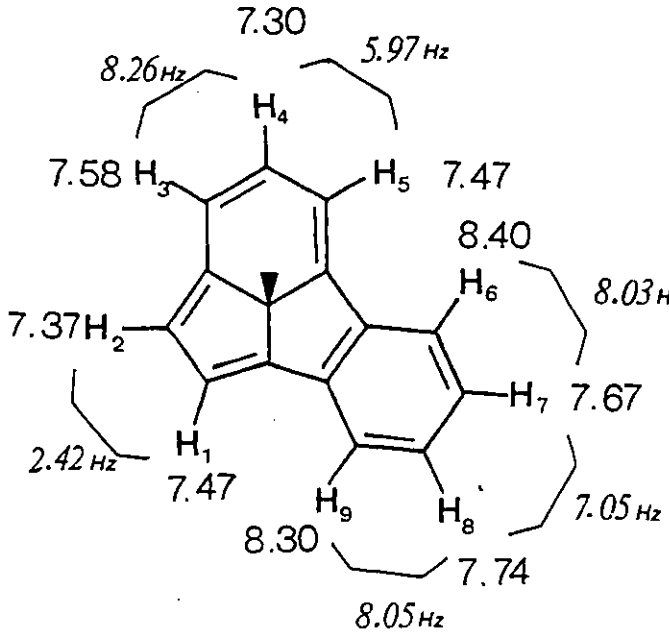
The process involves a double Wittig reaction followed by extrusion of sulphur and has previously been used by Vogel and co-workers for the preparation of a bridged [14]annulene from a dialdehyde precursor.[121]

After chromatography, the annulene (130) was isolated in 14% yield. The low yield, like those of other reactions involving bis-Wittig reagents,[26 121] probably results from the formation of an intermediate with a trans-double bond which cannot give the required product.

The annulene (130) is a surprisingly stable bright yellow solid which was recrystallised from petrol to give an analytical sample, m.p. 74 - 76°C. In the n.m.r. spectrum, the central methyl group resonates at $\delta_H(CDCl_3)$ -0.79 and the peripheral protons in the range δ7.30 - 7.58 for the protons of the 10π-ring and δ7.67 - 8.40 for the benzo ring. From these figures, it can be seen that the effect of benzo fusion is to shift the central methyl group downfield and the peripheral protons upfield relative to the unperturbed annulene (1). These shifts are the result of a reduced ring current in the benzo fused annulene. Similar effects have been observed in other systems.[120a-f] The upfield shift of the methyl group in (130) relative to the tetraene (54)

in which there can be no ring current is 1.80 ppm. The corresponding figure for the annulene (1) is 2.68 ppm. Thus, the benzo fused annulene (130) retains 67% of the ring current of (1).

Calculations by Günther have established a relationship in which the coupling constants in the benzo ring of a benzo fused annulene reflect the resonance energy of that annulene.[122] To apply his theory, it was necessary to obtain accurate coupling constants for the peripheral protons and this was done to sufficient accuracy ($\pm$0.04 ppm) from a resolution enhanced 400 MHz n.m.r. spectrum. The values obtained are illustrated in the diagram below. The chemical shift assignments were made on the basis of n.O.e. measurements which showed enhancements from H-5 to H-6 and from H-1 to H-9.



(130)

The measured coupling constants give a value, Q*, of 1.168. Günther's calculations predict a value of Q for a benzo

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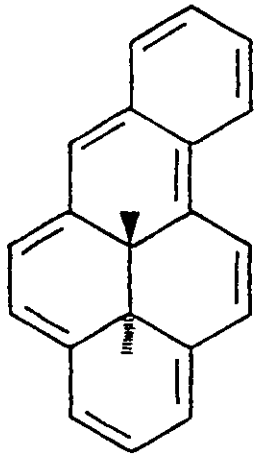
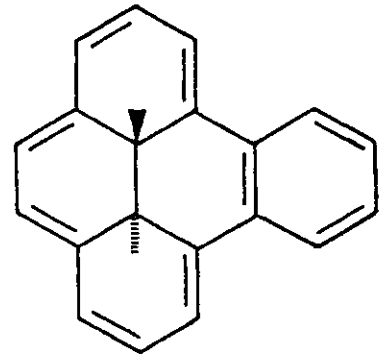
* Given by $Q = (0.104\ J_{6,7} - 0.12)/(0.104\ J_{7,8} - 0.12)$[122]

fused [10]annulene of 1.21 and for a benzo fused [14]annulene of 1.15.[122] Therefore, the measured values are in reasonable agreement with the theory of Günther bearing in mind that the system (1) will have less resonance energy than a pure "Hückel" 10π-system as a result of torsional strain.

It is interesting to compare the compounds (131) and (132) in which the coupling constants around the periphery are comparable to those for the system (130) suggesting a similar degree of imposed bond fixation, but in which reduction of the ring current is 50%.[120a,b]



(131)



(132)

Since the resonance energy is approximately inversely proportional to the size of the annulene,[7] the [10]annulene should have a greater resonance energy than a [14]annulene and therefore be less perturbed by benzo fusion. However, this effect may be cancelled by the reduction of resonance energy in the [10]annulene by torsional strain which is more significant than in the 14π-dihydropyrenes.

An X-ray crystal structure determination was undertaken to give further understanding of the bonding in (130).

Unlike the annulene derivatives previously studied, crystals of (130) were not disordered and furthermore, spontaneous resolution had occurred during crystallisation so that the crystal submitted was a single enantiomer. Accurate bond lengths could be determined and are given in Fig. 15. Distinct alternation of the bond lengths around the periphery of the tricyclic [10]annulene portion is caused by fusion of a benzene ring. There is only a small alternation of the bond lengths around the benzo ring. Just on this basis, it is surprising that so much ring current should still be retained but it was observed that the bond common to the [10]annulene and the benzo ring (C-5b - C-9a) is slightly longer than expected, 1.45 Å compared to 1.41 Å for the corresponding bond in naphthalene.[123] The lengthening of this bond is probably favoured since it relieves strain in the five membered ring. The result of the increased single bond character in the internal bond is that the compound (130) has significant [14]annulene character involving the entire periphery. Since ring current is greater in larger annulenes,[7] this effect will increase the ring current and may explain why such a large proportion of the ring current is retained in (130). On the basis of these results, some interesting predictions can be made. For example, the isomer (133) should possess less ring current, since lengthening of the bond common to the 6π- and 10π-systems does not relieve any strain. On the other hand, in the dibenzo fused derivative (134), benzo fusion would relieve strain in both five membered rings. The resulting appreciable 18π-contribution coupled with the opposing effects of the benzene rings, which mean that there would be

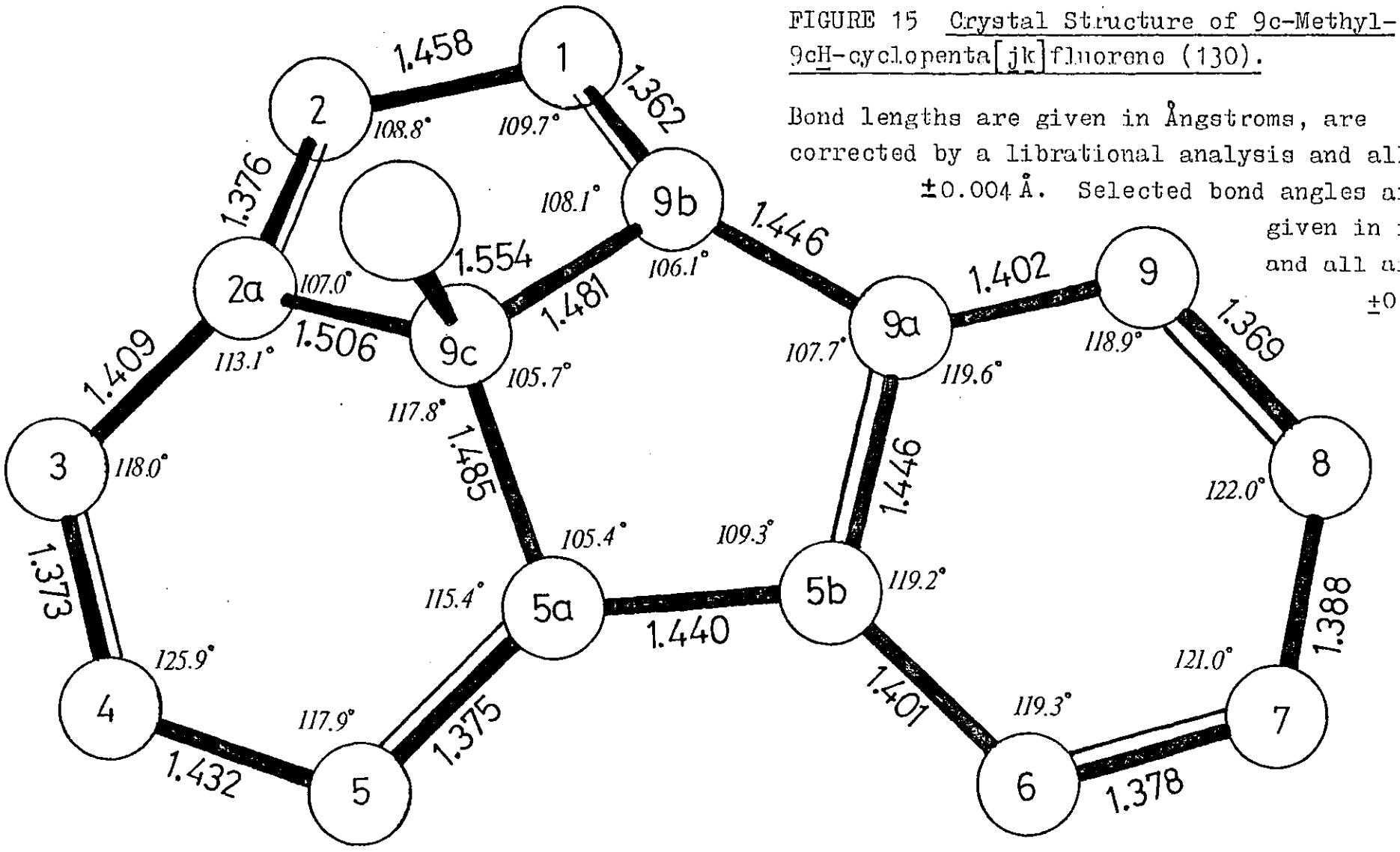
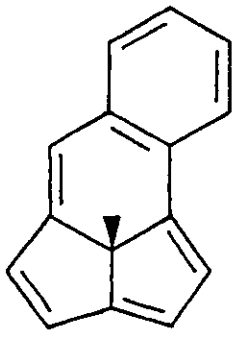


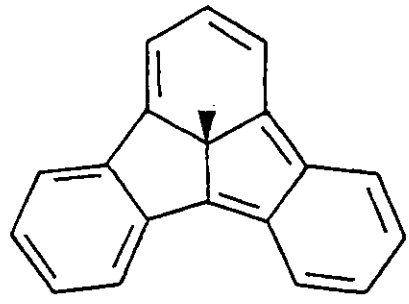
FIGURE 15 Crystal Structure of 9c-Methyl-9cH-cyclopenta[jk]fluorene (130).

Bond lengths are given in Ångstroms, are corrected by a librational analysis and all are ±0.004 Å. Selected bond angles are given in italics and all are ±0.3°.

no bond fixation in the 10π-system, might give a compound with more ring current than the parent annulene (1). Thus, the central methyl group in compound (134) may resonate at a value more negative than δ-1.67. In comparison, compound (135) retains 83% of the ring current of the unperturbed dihydropyrene (31).[120c]



(133)



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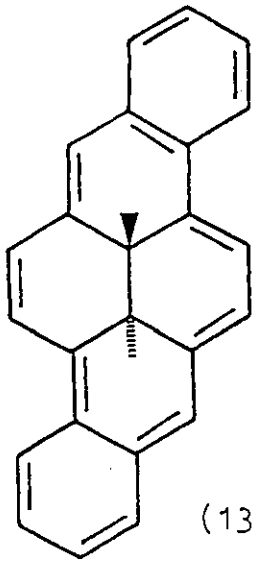
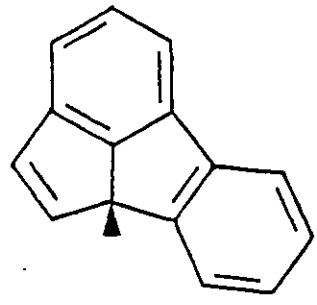


(135)



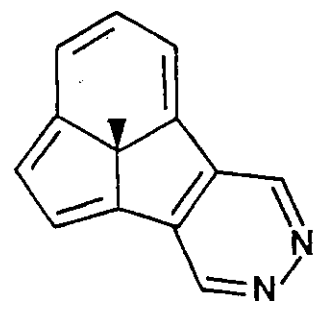
(136)

The benzo fused annulene (130) rearranges on heating in refluxing xylene to the known[124] 9bH-isomer (136) which is a colourless solid best purified by sublimation. The rearrangement is much faster than that of the unperturbed

annulene (1); its half life is 8.3 min in decalin at 138°C. Rate measurements at different temperatures in the range 110 - 138°C give a value of the activation energy for the rearrangement of (130) of 30 kcal mol^{-1}. This is 3 kcal mol^{-1} less than the value for the unperturbed system and further illustrates that benzo fusion has reduced the resonance energy in (1).

Apart from the thermal rearrangement, the chemistry of (130) contrasts with that of the annulene (1); (130) reacted with PTAD at 0°C but to give a complex mixture. Nitration with copper(II) nitrate in acetic anhydride was unsuccessful. The annulene was rapidly consumed but thin layer chromatography showed that no coloured products were formed.

Treatment of the dialdehyde (51) with hydrazine hydrate in ethanol at 0°C gave the pyridazino fused annulene (137). After chromatography on alumina, it was isolated as an unstable semi-solid in 90% yield. This heteroaromatic fused system has properties intermediate between those of the annulenes (1) and (130) since the pyridazine ring has less resonance energy than the benzene ring. The central methyl group resonates at $\delta_H(CDCl_3)$ -1.06 and the thermal rearrangement has a half life of 38 min at 138°C.



(137)

2.4 Conclusion

A number of methods are now available for the synthesis of the [10]annulene, 7b-methyl-7b*H*-cyclopent[*cd*]-indene (1), which involve the cycloaddition of a suitable acetylene equivalent to a 3a*H*-indene derivative. The best of these methods uses 2-chloroacryloyl chloride as the dienophile. In so far as the instability of the 3a*H*-indenes makes them good models for a critical test of dienophiles, 2-chloroacryloyl chloride may be regarded as one of the best ketene and acetylene equivalents available. The best current route to the annulene (1) (see Scheme at end of Section 2.1) has an overall yield of 9% from the readily available 1-indanone, and since it could be scaled up, it was possible to prepare sufficient of the annulene (1) for a thorough investigation of its properties.

Unless some important use is found for the annulene (1), it is unlikely that much would be gained by development of further routes directed specifically at the parent system (1). However, the routes described are limited to 1- and 2-substituted derivatives of the annulene. A method has yet to be developed for the synthesis of important symmetrical 6-substituted annulenes. The route recently developed by Lidert to the annulene (1)[99] has the advantage that it is more suited to variation of the bridgehead substituent since it does not involve a 3a*H*-indene derivative in which facile sigmatropic shift of the bridgehead group occurs if it is other than methyl.[125] However, his method has similar limitations with regard to variation of the peripheral substituents.

Studies of the stereochemistry of the [8+2] cyclo-

addition reactions of various dienophiles to the 3a<u>H</u>-indene (37) have shown that unlike the better known [4+2]-cycloaddition (Diels-Alder reaction), there is a preference for <u>exo</u>-addition and that this preference is greater for the more reactive dienophiles. Retro[8+2]cycloaddition has been achieved by flash vacuum pyrolysis of one of the adducts. The product was a 1<u>H</u>-indene, which shows that the only mode of thermal rearrangement of the 3a<u>H</u>-indene (37) in the vapour phase is a [1,5]sigmatropic shift of the methyl group.

The synthesis of the annulene has demonstrated the usefulness of silicon reagents and in particular the chlorotrimethylsilane - sodium iodide - triethylamine combination, both for the preparation of enol ethers and for the elimination of methanol. It was unfortunate that there were problems with the conversion of the trimethylsilyloxy substituted 3a<u>H</u>-indene (85) into the parent annulene (1) so that the best route still involves the use of the hazardous methyl fluorosulphonate.

The properties of the annulene (1) show that it can be classified as an aromatic compound but that its strain causes it to be reactive, particularly at the 2a-position. Relief of this strain is favoured, as shown by the complete tautomerisation of the 2-hydroxyannulene (75) into a ketone with the hydrogen exclusively at this 2a-position. The aromaticity of the annulene (1) is shown by its n.m.r. spectrum, its reluctance to undergo cycloaddition reactions, and by its electrophilic substitution reactions. The lack of specificity of its nitration is evidence against any transannular interaction but other electrophiles strongly favour the 5-position.

The central methyl group of the annulene (1) has been shown to be a useful probe for the effect of substituents. The use of chemical shifts of similarly cited methyl groups have been described for other annulenes, but the rate measurements for the [1,5] sigmatropic shift provides a new quantitative measure of the effects. More examples, in particular of 5- and 6-substituted derivatives, would be necessary to clarify fully how substituents affect the shift.

A ring expansion reaction observed with chlorosulphonyl isocyanate has allowed entry into the fully conjugated [5-6-7] ring system but so far the reaction is limited to this reagent.

Benzo fusion of the annulene (1) gives the expected reduction in diatropicity but to a lesser extent than expected. This has been explained in terms of the relief of strain that benzo fusion imparts and the significant 14π-character of the resulting ring system. Synthesis of other benzo fused and related derivatives of the annulene (1) would be desirable to gain a fuller understanding of the chemistry of conjugated π-systems.

3 Experimental

(a) Solvents and Reagents

Most of the reagents used were commercially available and were used without further purification unless otherwise indicated. References are given when reagents were prepared by literature procedures.

Petrol refers to light petroleum spirit, b.p. 40 - 60°C unless otherwise indicated.

Ether refers to diethyl ether.

Solvents for reactions were dried by the following procedures:

Hydrocarbon solvents were allowed to stand over activated alumina. Diethyl ether was allowed to stand over clean sodium wire for several days. Other ether solvents (tetrahydrofuran, 1,2-dimethoxyethane, and dioxan) were refluxed under nitrogen over potassium in the presence of benzophenone until a deep blue colour had formed and then distilled onto molecular sieves (type 4A). Chlorinated solvents were distilled from phosphorus pentoxide onto molecular sieves (type 4A). Acetonitrile and dimethylformamide were distilled from powdered calcium hydride onto molecular sieves (type 3A).

Diisopropylmine and chlorotrimethylsilane were supplied by the Aldrich Chemical Company and were distilled under nitrogen from powdered calcium hydride immediately before use.

Sodium hydride was supplied by the Aldrich Chemical Company as a 50% dispersion in oil and used as such.

Potassium hydride was supplied by Alfa Inorganics

as a 20 - 25% dispersion in oil. The amount required was weighed and the oil removed by washing with petrol (10 ml per gram of dispersion). When the solid had settled, the petrol was removed by pipette. This process was repeated and the last of the solvent was removed under vacuum. An atmosphere of nitrogen was finally introduced.

Methyl fluorosulphonate was supplied by Fluka A.G. Best results were obtained when it was distilled at atmospheric pressure before use. An efficient fume cupboard was used for all operations involving this material owing to its high toxicity and all apparatus which contacted this compound were washed with an aqueous solution of ammonia after use.

n-Butyl lithium, tert-butyl lithium, and diisobutyl-aluminium hydride were supplied as solutions in hexane by Aldrich Chemical Company and were used at the concentrations indicated. Methyl lithium refers to the methyl lithium - lithium bromide complex, supplied by Aldrich Chemical Company, and was used at the concentration indicated.

(b) Apparatus

All glassware used for reactions was dried in an oven at above 100°C for at least 4 h. When dry solvents and reagents were necessary, they were transferred using dry syringes with needles of the appropriate sizes.

(c) Chromatography

Unless indicated otherwise, chromatography refers to column chromatography on Merck silica gel H, type 60.

The mixture to be separated was pre-adsorbed by evaporation of a solution in dichloromethane onto the silica (2 g per gram of the mixture to be separated) and applied to the top of a column prepared from a suspension of the silica (15 g per gram of the mixture to be separated) in petrol. Pressure was applied by an aquarium pump operating at between 5 and 10 pounds per square inch.

Thin layer chromatography (t.l.c.) was used extensively as a qualitative analytical technique for the following of the progress of reactions, determination of the purity of compounds, and for the analysis of column eluant. Aluminium backed silica plates (Merck Kieselgel 60 F_{254}) were used. After elution, the plates were observed under ultra-violet light (254 nm) or developed with iodine vapour.

(d) Spectra

Infra-red spectra (i.r.) were recorded using a Perkin Elmer 298 spectrophotometer and calibrated against polystyrene at 1602 cm^{-1}. Spectra of solids were recorded as solutions in carbon tetrachloride and oils as thin films between sodium chloride plates. Abbreviations are: strong (s), medium (m), and weak (w). Only the principal peaks and those of particular significance are given.

Ultra-violet and visible spectra (u.v.) were recorded on a Unicam SP800B spectrophotometer and calibrated against Holmium glass at 360.9 and 453.2 nm. An abbreviation is shoulder (sh).

Proton nuclear magnetic resonance spectra (n.m.r.)

were recorded either on a Bruker WM250 spectrometer operating at 250 MHz, a Perkin Elmer R32 spectrometer operating at 90 MHz, or a Perkin Elmer EM360 spectrometer operating at 60 MHz. In one instance a ULIRS WH400 spectrometer operating at 400 MHz was used. All data quoted are for 250 MHz spectra unless indicated otherwise. Chemical shifts (δ_H) are given in parts per million relative to tetramethylsilane as an internal reference. Abbreviations used are singlet (s), doublet (d), triplet (t), quartet (m), multiplet (m), and broad (br.). Coupling constants ($\underline{J}$) quoted to one decimal place are $\pm$0.3 Hz.

Carbon-13 n.m.r. spectra were recorded on a Bruker WM250 spectrometer operating at 62.9 MHz and were fully proton decoupled. Chemical shifts (δ_C) are given in parts per million relative to tetramethylsilane as internal reference. Relative intensities of the signals are given in parentheses following the chemical shifts.

Low resolution mass spectra (m.s.) and accurate mass measurements were recorded using a VG Micromass 7070B mass spectrometer operating at 70 eV and using a direct insertion probe. Only the principal peaks are given.

(e) Other data

Melting points (m.p.) were measured using a Kofler hot stage apparatus and are uncorrected.

Micro-analyses were carried out in the organic micro-analytical laboratory under the supervision of Mr. K.I. Jones.

3.1 The Synthesis of 7b-Methyl-7bH-cyclopent[cd]indene (1)

3.1.1 The Birch reduction and methylation of 1-indanone

7a-Methyl-2,3,5,7a-tetrahydro-1H-inden-1-one (40)[42b]

(a) 1-Indanone (15.0 g) was reduced and methylated by the conditions described by Tuddenham.[42b] Work up involving chromatography on silica (Hopkin and Williams M.F.C., 500 g), eluting with petrol (b.p. 60 - 80°C) containing an increasing proportion of ether gave (i) 2,7a-dimethyl-2,3,5,7a-tetrahydro-1H-inden-1-one[42b] (41) (1.0 g, 6%). (ii) A mixture from which crystallised 2-(1-indanyl)-2-methyl-1-indanone (43) (0.72 g, 5%), m.p. 117.5 - 118.5°C (from petrol, b.p. 60 - 80°C) (Found: C, 87.09; H, 6.96. $C_{19}H_{18}O$ requires C, 86.99; H, 6.92%); $\nu_{max}(CCl_4)$ 1710 (s, C=O stretch), 1602 (m), and 1280 cm^{-1} (m); $\delta_H(CCl_4, 90\ MHz)$ 1.24 (3H, s, 2-Me), 1.7 - 2.45 (2H, m, 2 x H-2'), 2.5 - 3.0 (4H, m, 2 x H-3 and 2 x H-3'), 2.78 (1H, t, J 9 Hz, H-1'), 6.5 - 7.1 (4H, m, H-4', H-5', H-6' and H-7'), and 7.1 - 7.9 (4H, m, H-4, H-5, H-6 and H-7); m/e 262 (M^+), 247, 146, and 117 (100%). The residual liquid (4.8 g) was a 2 : 1 mixture of the title compound (18%) and 2,2-dimethyl-indanone (42) (9%). Distillation at 8 mmHg gave a 4 : 1 mixture of the title compound and 2,2-dimethylindanone which could not be purified further, followed by 2,2-dimethylindanone, pure by n.m.r. (iii) 2-Methyl-1-indanone (0.5 g, 3%). (iv) Bi-(1-hydroxy-1-indanyl) (0.4 g, 2.5%), m.p. 158 - 161°, (lit.,[126] m.p. 156 - 157°C). (v) 1-Indanol (1.1 g, 7%).

(b) To a stirred solution of potassium (100 g, 2.55 mol) in liquid ammonia (5 l) at -78° under nitrogen was added a

solution of 1-indanone (118 g, 0.89 mol) and tert-butanol (150 g, 2.03 mol) in dry tetrahydrofuran (400 ml) dropwise over 1 h. A solution of anhydrous lithium bromide (206 g, 2.34 mol) in dry tetrahydrofuran (600 ml) was added, followed after 0.5 h by a simultaneous rapid addition of 50% aqueous tetrahydrofuran (900 ml) and iodomethane (134 g, 0.94 mol). The external cooling was removed and the ammonia allowed to evaporate overnight. Water (2 l) was added and the mixture extracted with ether (3 x 800 ml). The combined ether extracts were washed with water (2 x 500 ml), dried (Na_2SO_4) and the solvent evaporated. The resulting oil was distilled and the fraction boiling in the range 85 - 95°C at 7 mmHg was collected giving a colourless oil (82.8g).

A sample of this oil (2.00 g) was chromatographed on silica, eluting with petrol containing an increasing proportion of ether to give (i) the title compound (1.70 g), (ii) 2-methyl-1-indanone (0.13 g), (iii) 1-indanone (0.13 g) and (iv) 1-indanol (0.10 g). The proportion of the title compound in the oil was 84% and hence the yield was 69.9 g (53%).

The distilled material was suitable for use in the preparation of 5,7a-dihydro-7a-methyl-1H-inden-1-one.

3.1.2 The preparation of 5,7a-dihydro-7a-methyl-1H-inden-1-one (46)

1 Via the lithium enolate of 7a-methyl-2,3,5,7a-tetrahydro-1H-inden-1-one

To a stirred solution of 7a-methyl-2,3,5,7a-tetrahydro-1H-inden-1-one (40) (84% pure; 32.7 g, 135 mmol) in dry tetrahydrofuran (200 ml) at -78°C under nitrogen was added a solution of lithium di-isopropylamide [prepared at 0°C from di-isopropylamine (17.6 g, 173 mmol) in dry tetrahydrofuran (100 ml) and n-butyl lithium solution (1.4 M; 108 ml, 150 mmol)] dropwise. After 0.5 h, a solution of phenyl selenyl bromide [prepared at 0°C by dropwise addition of bromine (15.0 g, 93 mmol) to a solution of diphenyl diselenide[127] (29.5 g, 94 mmol) in dry tetrahydrofuran (100 ml)] was added. The mixture was allowed to warm to room temperature and poured with stirring into hydrochloric acid (1 M, 1 l). The mixture was extracted with ether (3 x 100 ml), the combined extracts washed with water (100 ml), dried ($MgSO_4$) and the solvent evaporated. The crude selenide was dissolved in tetrahydrofuran (500 ml), pyridine (20 ml) added, the solution cooled to 5°C in an ice bath, and with stirring, aqueous hydrogen peroxide (25%; 60 ml, 400 mmol) was added dropwise so as to maintain the temperature between 5 and 10°C. The addition took ca. 1 h. The resulting mixture was poured into water (1 l) and the aqueous solution extracted with ether (3 x 300 ml). The combined ether extracts were washed with water (300 ml), dried ($MgSO_4$) and the solvent evaporated to give an oil

which was chromatographed on silica. Elution with petrol containing an increasing proportion of ether gave after a forerun of selenium containing material, (i) starting material (5.2 g). (ii) 5,7a-Dihydro-7a-methyl-1H-inden-1-one[42b] (7.82 g, 40%).

2 5,7a-Dihydro-2,7a-dimethyl-1H-inden-1-one (48)

This was carried out in the same way as the preparation of 5,7a-dihydro-7a-methyl-1H-inden-1-one above but using 2,7a-dimethyl-2,3,5,7a-tetrahydro-1H-inden-1-one (4.3 g, 27 mmol, a 1 : 1 mixture of diastereoisomers) to give an oil which after chromatography on silica, eluting with petrol containing an increasing proportion of ether gave (i) 7a-methyl-2-methylene-2,3,5,7a-tetrahydro-1H-inden-1-one (47) (2.1 g, 50%), an oil which polymerised on standing, ν_{max}(neat) 2960 (m), 1725 (s, C=O stretch), 1630 (m), 1260 (m), 1015 (m), and 704 cm^{-1} (m); δ_H(CCl_4, 90 MHz) 1.11 (3H, s, Me-7a), 2.6 - 2.8 (2H, m, 2 x H-5), 3.2 - 3.4 (2H, m, 2 x H-3), 5.48 (1H, br. s, $=CH_2$), 5.8 - 6.0 (3H, m, H-4, H-6 and H-7), and 6.10 (1H, br. s, $=CH_2$); m/e 160 (M^+). (ii) The title compound (0.8 g, 18%), a yellow oil, ν_{max}(neat) 2920 (m), 1700 (s, C=O stretch), 1450 (m), 1020 (m), and 705 cm^{-1} (m); δ_H($CDCl_3$) 1.20 (3H, s, Me-7a), 1.85 (3H, s, Me-2), 2.80 (1H, m, H-5, decoupling at δ5.88 gives d, J 22 Hz), 2.89 (1H, m, H-5, decoupling at δ5.88 gives d, J 22 Hz), 5.85 (1H, m, H-6, decoupling at δ2.85 gives d, J 10 Hz), 5.89 (1H, m, H-4, decoupling at δ2.85 gives s), 6.16 (1H, dd, $J_{5,7}$ 3 Hz, $J_{6,7}$ 10 Hz, H-7,

decoupling at δ5.88 gives d, J 3 Hz), and 7.35 (1H, s, H-3); m/e 260 (M^+).

3 Direct phenylselenation of 7a-methyl-2,3,5,7a-tetrahydro-1H-inden-1-one with phenylselenyl chloride

A solution of 7a-methyl-2,3,5,7a-tetrahydro-1H-inden-1-one (40) (0.58 g, 3.9 mmol) and phenylselenyl chloride[127] (0.76 g, 4.0 mmol) in ethyl acetate (15 ml) was refluxed 24 h. The mixture was washed with water (10 ml), then saturated sodium hydrogen carbonate solution (10 ml) and diluted with tetrahydrofuran (20 ml). Pyridine (0.5 ml) was added and the mixture was oxidised as above with hydrogen peroxide (30%, 5 ml). Work up as before involving chromatography gave (i) starting material (0.17 g) and (ii) 5,7a-dihydro-7a-methyl-1H-inden-1-one (46) (0.04 g, 7%).

4 Improved preparation of 5,7a-dihydro-7a-methyl-1H-inden-1-one (46)

Chlorotrimethylsilane (82 g, 0.75 mol) was added to a stirred solution of sodium iodide (115 g, 0.77 mol) in dry acetonitrile (600 ml) at room temperature under nitrogen. After 5 min, a mixture of 7a-methyl-2,3,5,7a-tetrahydro-1H-inden-1-one (40) (84% pure; 91g, 0.52 mol) and dry triethylamine (76 g, 0.75 mol) was added over 0.5 h and the mixture warmed by a water bath at 45°C for 2 h. The mixture was then extracted with petrol (4 x 150 ml). The combined extracts were evaporated and the residue distilled at 3 mmHg, collecting the fraction boiling in the range 82 - 85°C to give 3,3a-dihydro-3a-methyl-

3-(trimethylsiloxy)-1H-indene (117 g, 97%) as a mobile oil, (Found: C, 71.29; H, 9.44. $C_{13}H_{20}SiO$ requires C, 70.85; H, 9.15%); $\delta_H(CCl_4$, 90 MHz) 0.23 (9H, s, $SiMe_3$), 1.11 (3H, s, 3a-Me), 2.5 - 2.9 (3H, m), 2.9 - 3.3 (1H, m), 4.51 (1H, m, H-2), 5.2 - 5.6 (1H, m), 5.6 - 5.9 (1H, m), and 5.9 - 6.1 (1H, br d, J 10 Hz, H-4). A stirred solution of this trimethylsilyl ether (55 g, 0.25 mol) in dry tetrahydrofuran (300 ml) at -78°C under nitrogen was treated over 2 h with a solution of phenylselenyl bromide [prepared at 0°C from diphenyl diselenide[127] (39.3 g, 0.125 mol) and bromine (20.0 g, 0.125 mol) in dry tetrahydrofuran (300 ml)]. The resulting mixture was allowed to warm to -30°C over 1 h, poured into saturated sodium hydrogen carbonate solution and then extracted with ether (3 x 250 ml). The combined extracts were washed with water (500 ml), dried ($MgSO_4$) and the solvent evaporated to give the selenide (79.4 g); $\delta_H(CCl_4$, 90 MHz) 1.04 (3H, s, 7a-Me), 2.6 - 2.9 (3H, m), 3.0 - 3.3 (1H, m), 3.78 (1H, d, J 10 Hz, H-2), 5.4 - 5.8 (2H, m, H-4 and H-6), 5.85 (1H, br d, J 9 Hz, H-7), 7.1 - 7.4 (3H, m, Ph), and 7.4 - 7.6 (2H, m, Ph). This crude selenide was taken up in tetrahydrofuran (650 ml), pyridine (35g) added, the solution cooled to 5°C, and with stirring, hydrogen peroxide (30%; 85 g, 0.75 mol) was added dropwise so as to maintain the temperature between 5 and 10°C. Aqueous work-up and chromatography as before gave (i) a mixture (3.9g). (ii) The title compound (21.4g, 59% from the trimethylsilyl ether, 57% from the starting dienone).

During an earlier preparation from the dienone (40) (5.0 g), elution of the column with ether afforded

2-methyl-*trans*-cinnamic acid (0.97 g, 18%), m.p. 175 - 177°C (from chloroform - petrol, b.p. 60 - 80°C), (lit.,[128] m.p. 176 - 178°C); δ_H(2 : 1 d_6-acetone - D_2O, 90 MHz) 2.46 (3H, s), 6.48 (1H, d, *J* 16 Hz), 7.35 (3H, m, ArH), and 8.02 (1H, d, *J* 16 Hz).

5 Reaction of 5,7a-dihydro-7a-methyl-1*H*-inden-1-one with hydrogen peroxide

A solution of 5,7a-dihydro-7a-methyl-1*H*-inden-1-one (45) (0.16 g, 1.1 mmol) in tetrahydrofuran (5 ml) containing pyridine (0.15 g) was treated with aqueous hydrogen peroxide (30%; 1 ml, 8.8 mmol) and the mixture stirred at room temperature for 24 h. The mixture was poured into water (40 ml) and extracted with ether (30 ml). The ether solution was washed with water (2 x 30 ml), dried ($MgSO_4$) and the solvent evaporated to give an oil; its n.m.r. spectrum was identical to that of starting material.

3.1.3 The adduct of the 3a*H*-indene (37) with dimethyl acetylenedicarboxylate and its conversion into the annulene (1)

1 Generation of a solution of 3-methoxy-3a-methyl-3a*H*-indene (37) and its cycloaddition with dimethyl acetylenedicarboxylate

To a suspension of potassium hydride (from a dispersion in oil, 25%; 14.5g, 91 mmol) in dry 1,2-dimethoxyethane (30 ml) under nitrogen and cooled externally by a

cooling bath at -23°C was added with stirring, a solution of 18-Crown-6[129] (10 g, 38 mmol) in dry 1,2-dimethoxyethane (40 ml) followed by a solution of 5,7a-dihydro-7a-methyl-1H-inden-1-one (46) (5.0 g, 34 mmol) in dry 1,2-dimethoxyethane (30 ml). The resulting deep purple solution was stirred 0.5 h and methyl fluorosulphonate (3.7 ml, 46 mmol) added. The purple colour was discharged and to the resulting yellow solution of 3-methoxy-3a-methyl-3aH-indene (37) was added a solution of dimethyl acetylenedicarboxylate[130] (6.37 g, 45 mmol) in dry 1,2-dimethoxyethane (30 ml). The solution was allowed to warm to room temperature and then warmed in a water bath at 35°C. After 1 h, the reaction mixture was filtered through celite, the solvent removed under reduced pressure at room temperature and the residue chromatographed on silica. Elution with 30% ether in petrol gave dimethyl 7a,7b-dihydro-2a-methoxy-7b-methyl-2aH-cyclopent[cd]indene-1,2-dicarboxylate (7.1 g, 69%); spectral data were identical to those reported.[42a,b]

2 Dimethyl 7b-methyl-7bH-cyclopent[cd]indene-1,2-dicarboxylate (38)

(a) From dimethyl 7a,7b-dihydro-2a-methoxy-7b-methyl-2aH-cyclopent[cd]indene with toluene-4-sulphonic acid in refluxing benzene by the method of Tuddenham[42a,c,d] (82%).

(b) A solution of dimethyl 7a,7b-dihydro-2a-methoxy-7b-methyl-7bH-cyclopent[cd]indene-1,2-dicarboxylate (108 mg, 0.36 mmol) in petrol (b.p. 60 - 80°C) (10 ml)

containing 1,8-diazabicyclo[5.4.0]undec-7-ene (50 mg, 0.33 mmol) was refluxed under nitrogen for 35 h. The solvent was removed and the residue chromatographed. Elution with 30% ether in petrol gave the title compound (86 mg, 89%). Spectral data were identical to those reported.[42a,c,d]

3 7b-Methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene-1,2-dicarboxaldehyde (51)

A solution of dimethyl 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]-indene-1,2-dicarboxylate (38) (3.42 g, 12.7 mmol) in ether (100 ml) was added dropwise over 0.5 h to a stirred suspension of lithium aluminium hydride (1.85 g, 49 mmol) in dry ether (100 ml) under nitrogen at room temperature and the resulting brick-red mixture stirred at room temperature for 1.5 h. A solution of ethyl acetate (30 ml) in ether (100 ml) was added dropwise over 0.75 h and the mixture then poured with stirring into ice-water (500 ml). The mixture was filtered through celite and the residue washed with ether (300 ml). The aqueous layer was extracted with ether (4 x 250 ml), the combined ether layers dried ($MgSO_4$) and the solvent evaporated to give the crude diol (50) (2.59 g) as a yellow oil. To a solution of this oil in dichloromethane (100 ml) was added barium manganate[51] (15 g, 64 mmol) and the mixture refluxed 16 h. The cooled mixture was filtered through celite and the spent barium manganate washed with dichloromethane (2 x 25 ml). The filtrate and washings were combined, the solvent evaporated and the resulting

oil chromatographed on silica. Elution with 30% ether in petrol gave the title compound (51) (1.73 g, 66%) as an orange-red solid, m.p. 76 - 77°C (from cyclohexane) (Found: C, 79.92; H, 4.75. $C_{14}H_{10}O_2$ requires C, 79.99; H, 4.79%); $\nu_{max}(CCl_4)$ 2960 (m), 2924 (m), 2868 (m), 1680 (s, C=O stretch), 1448 (m), 1420 (m), 1230 (m), and 930 cm^{-1} (m); λ_{max}(EtOH) 217 (log ϵ 4.09), 242 (4.02), 318 (4.30), 375 sh (3.66), and 498 nm (3.30); $\delta_H(CDCl_3)$ -1.12 (3H, s, 7b-Me), 7.73 (1H, d, J 7 Hz, H-5), 7.84 (1H, dd, J 7 Hz, 8 Hz, H-6), 8.27 (1H, d, J 4Hz, H-4), 8.34 (1H, d, J 8 Hz, H-7), 8.44 (1H, d, J 4 Hz, H-3), and 10.82 (2H, s, ArCHO); $\delta_C(CDCl_3)$ 30.0 (0.71, 7b-Me), 59.8 (0.36, C-7b), 118.7 (0.92, C-5), 122.5 (0.69, C-7), 133.9 (0.20, C-2), 135.4 (1.00, C-3 or C-6), 136.2 (0.86, C-6 or C-3), 140.1 (0.18, C-1), 142.8 (0.99, C-4), 162.4 (0.22, C-4a or C-7a), 163.1 (0.32, C-7a or C-4a), 176.9 (0.18, C-2a), 187.7 (0.87, CHO), and 189.1 (0.97, CHO).

4 Oxidation of 7b-methyl-7bH-cyclopent[cd]indene-1,2-dimethanol (50) with barium manganate at 0°C

A solution of the crude diol (50) (119 mg, 0.56 mmol) in dichloromethane (5 ml) was cooled in ice and treated with barium manganate (1.0 g, 4 mmol). After 2 h at 0°C, the mixture was filtered through celite, the solvent evaporated and the residue chromatographed on silica. Elution with petrol containing an increasing proportion of ether gave (i) the dialdehyde (51) (10 mg, 9%). (ii) A 2 : 1 mixture of 1-hydroxymethyl-7b-methyl-7bH-cyclopent[cd]indene-2-carboxaldehyde (52a) and

2-hydroxymethyl-7b-methyl-7bH-cyclopent[cd]indene-1-carboxaldehyde (52b) (51 mg, 43%), as an orange semi-solid; ν_{max}(neat) 3400 (m, OH stretch) and 1662 cm^{-1} (s, C=O stretch); λ_{max} 247 (log ϵ 4.22), 312 (4.54), 354 (3.85), and 491 nm (3.34); $\delta_H(CDCl_3)$ for (52a): -1.32 (3H, s, 7b-Me), 4.39 (1H, br. t, J 7 Hz, OH), 5.06 (1H, dd, J 7, 14 Hz, $-CH_2-$), 5.22 (1H, dd, J 7, 14 Hz, $-CH_2-$), 7.56 (1H, t, J, 7 Hz, H-6), 7.70 (1H, d, J 6.9 Hz, H-5), 8.01 (1H, d, J 7.7 Hz, H-7), 8.14 (1H, d, J 3.6 Hz, H-3 or H-4), 8.19 (1H, d, J 3.6 Hz, H-4 or H-3), and 10.53 (1H, s, CHO); for (52b): -1.32 (3H, s, 7b-Me), 4.20 (1H, br. t, J 7 Hz, OH), 5.20 (2H, m, $-CH_2-$), 7.64 (1H, d, J 6.9 Hz, H-5), 7.78 (1H, t, J 7 Hz, H-6), 7.96 (1H, d, J 7.0 Hz, H-7), 7.96 (1H, d, J 3.7 Hz, H-3 or H-4), 8.27 (1H, d, J 3.7 Hz, H-4 or H-3), and 10.61 (1H, s, CHO); m/e 212 (M^+), 197, 183, 164, 153, and 152. (iii) The starting diol (50) (14 mg, 12%).

5 7b-Methyl-7bH-cyclopent[cd]indene (1) (method 1)

A solution of 7b-methyl-7bH-cyclopent[cd]indene-1,2-dicarboxaldehyde (51) (456 mg, 2.16 mmol) in benzene (55 ml) containing tris(triphenylphosphine)rhodium (I) chloride (4.00 g, 4.32 mmol) was refluxed under nitrogen for 7 h. The reaction mixture was cooled to room temperature, iodomethane (3 ml) added, and the mixture stirred at room temperature for 2 h. The mixture was filtered and the residue washed with benzene until the filtrate was no longer coloured. The combined filtrate and washings were evaporated and the residue

chromatographed on silica. Elution with petrol gave 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (295 mg, 88%), as a yellow oil; spectral data are given later, in Section 3.1.7.

6 Decarbonylation of 7b-methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarboxaldehyde (51) with one equivalent of tris(triphenylphosphine)rhodium(I) chloride

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarboxaldehyde (51) (116 mg, 0.55 mmol) in benzene (20 ml) containing tris(triphenylphosphine)rhodium (I) chloride (511 mg, 0.55 mmol) was refluxed under nitrogen for 7 h. Work up as before and chromatography on silica, eluting with petrol containing an increasing proportion of ether gave (i) 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (9.5 mg, 11%). (ii) A 5 : 4 mixture of 7b-methyl-7b*H*-cyclopent[*cd*]indene-1-carboxaldehyde (53a) and 7b-methyl-7b*H*-cyclopent[*cd*]indene-2-carboxaldehyde (53b) (48 mg, 48%), as an orange oil; $\delta_H(CDCl_3)$ for (53a): -1.38 (3H, s, 7b-Me), 7.69 (1H, d, *J* 7.5 Hz, H-5), 7.77 (1H, t, *J* 7.5 Hz, H-6), 7.99 (1H, d, *J* 3.7 Hz, H-4), 8.08 (1H, d, *J* 7.5 Hz, H-7), 8.16 (1H, d, *J* 3.7 Hz, H-3), 8.24 (1H, s, H-2), and 10.50 (1H, s, C*H*O); spectral data for compound (53b) are given later, in Section 3.1.5.

7 Bis(1,2-bisdiphenylphosphinoethane)rhodium(I) chloride

A mixture of carbon monoxide and nitrogen was passed through a refluxing solution of tris(triphenyl-

phosphine)rhodium(I) chloride (137 mg, 0.15 mmol) and 1,2-bisdiphenylphosphinoethane (300 mg, 0.75 mmol) in toluene (5 ml) for 1 h. The resulting bright yellow solution was cooled to room temperature, petrol (3 ml) added, the precipitate collected and washed with cold toluene to give the title compound (101 mg, 72%), m.p. 215°C dec., (lit.,[57] m.p. 218 - 221°C).

8 Bis(1,3-bisdiphenylphoshinopropane)rhodium (I) chloride[58]

This was prepared in the same way as above from tris(triphenylphosphine)rhodium(I) chloride (148 mg, 0.16 mmol) and 1,3-bisdiphenylphosphinopropane[13] (300 mg, 0.73 mmol) to give the complex as a glass (121 mg, 80%).

9 Attempted decarbonylation of 7b-methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarboxaldehyde (51) using bis(1,2-bisdiphenylphosphinoethane)rhodium(I) chloride and bis(1,3-bisdiphenylphosphinopropane)rhodium(I) chloride

A slow stream of nitrogen was passed through a refluxing solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarboxaldehyde (51) (*ca.* 18 mg, 0.09 mmol) and the rhodium complex (*ca.* 15 mg, 0.016 mmol) in toluene (2 ml). After 1 h, a small amount of the monoaldehydes (53a) and (53b) were present (t.l.c.). More of these products were formed when the complex with the 1,3-bisdiphenylphosphinopropane ligands was used but insufficient was formed to enable the product to be isolated. Most of the dialdehyde

remained unreacted and a grey-black precipitate formed. No further reaction was observed after refluxing for longer periods.

10 Attempted decarbonylation of 7b-methyl-7b*H*-cyclopent-[*cd*]indene-1,2-dicarboxaldehyde with bis(triphenylphosphine)tetraphenylporphyrinato ruthenium(II)

A solution of the ruthenium complex (1.0 mg, 0.8×10^{-3} mmol) in dry dichloromethane (0.5 ml) was added to dry acetonitrile (6 ml) with stirring under nitrogen at room temperature. After addition of the dialdehyde (51) (25 mg, 0.12 mmol), a slow stream of carbon monoxide was passed through the solution and freshly distilled tri-*n*-butylphosphine (5 μl) added. The mixture became deep red. After 15 min, the dialdehyde had not been consumed and tetraphenylporphyrin was present (t.l.c.), indicating that the catalyst had decomposed.

3.1.4 The adducts of the 3a*H*-indene (37) with maleic anhydride and *N*-phenylmaleimide

1 The cycloaddition of 3-methoxy-3a-methyl-3a*H*-indene with *N*-phenylmaleimide

A solution of *N*-phenylmaleimide[132] (0.63 g, 3.6 mmol) in dry 1,2-dimethoxyethane (3 ml) was added to a solution of the 3a*H*-indene (37) in 1,2-dimethoxyethane, prepared as described in Section 3.1.3 from the trienone (46) (0.50 g, 3.4 mmol). The solution was allowed to

warm to room temperature and then filtered through celite. The solvent was removed under reduced pressure and the residue chromatographed on silica. Elution with 1 : 1 petrol - dichloromethane gave the endo-[4+2]-adduct (57a) (0.54 g, 47%), m.p. 99 - 100°C (from petrol, b.p. 60 - 80°C), (lit.,[42a] m.p. 91 - 93°C); $\delta_H(CDCl_3)$ 0.90 (3H, s, 7a-Me), 3.30 (1H, d, J 8.5 Hz, H-8), 3.65 (1H, d, J 8.5 Hz, H-9), 3.74 (3H, s, OMe), 6.00 (1H, dd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.9 Hz, H-6), 6.10 (1H, dd, $J_{5,6}$ 5.2 Hz, $J_{4,5}$ 9.0 Hz, H-5), 6.18 (1H, d, J 9.9 Hz, H-7), 6.19 (1H, d, J 6.0 Hz, H-3), 6.26 (1H, d, J 6.0 Hz, H-2), 6.43 (1H, d, J 9.0 Hz, H-4), and 7.1 - 7.5 (5H, m, Ph); assignments were made on the basis of n.O.e. measurements, illustrated in Fig 5.

2 Thermal rearrangement of the [4+2] N-phenylmaleimide adduct of 3-methoxy-3a-methyl-3aH-indene

The [4+2] adduct (57a) (195 mg) was heated to 110°C under vacuum (water pump) for 2 h. The resulting viscous oil was cooled to room temperature and chromatographed on silica. Elution with petrol containing an increasing proportion of 3 : 1 dichloromethane - ether gave (i) the exo-[8+2]adduct (55a) (66 mg, 34%); $\delta_H(CDCl_3)$ 0.91 (3H, s, 7b-Me), 2.82 (1H, dd, $J_{1,2}$ 10 Hz, $J_{1,7a}$ 7Hz, H-1), 2.98 (2H, m, H-2 and H-7a), 3.57 (3H, s, OMe), 6.01 (1H, d, J 5 Hz, H-5), 6.17 (2H, m, H-6 and H-7), 6.42 (1H, d, J 5Hz, H-4), 6.84 (1H, d, J 5 Hz, H-3), and 7.2 - 7.6 (5H, m, Ph). Irradiation at δ2.82 simplifies the multiplet at δ6.17 to give δ6.16 (1H, dd, $J_{5,6}$ 5 Hz, $J_{6,7}$ 10 Hz,

H-6) and δ6.18 (1H, d, $J_{6,7}$ 10 Hz, H-7). (ii) The endo-[8+2] adduct (56a) (89 mg, 46%); $\delta_H(CDCl_3)$ 0.92 (3H, s, 7b-Me), 3.20 (1H, dd, $J_{1,7a}$ 10 Hz, $J_{7,7a}$ 6.5 Hz, H-7a), 3.54 (1H, s, OMe), 3.56 (1H, d, J 9 Hz, H-2), 3.62 (1H, dd, $J_{1,2}$ 9 Hz, $J_{1,7a}$ 10 Hz, H-1), 5.90 (1H, d, J 5Hz, H-5), 6.16 (1H, dd, $J_{6,7}$ 9 Hz, $J_{7,7a}$ 6.5 Hz, H-7), 6.24 (1H, dd, $J_{5,6}$ 5 Hz, $J_{6,7}$ 9 Hz, H-6), 6.38 (1H, d, J 5 Hz, H-4), 6.60 (1H, d, J 5 Hz, H-3), and 6.9 - 7.5 (5H, m, Ph).

3 The cycloaddition of 3-methoxy-3a-methyl-3aH-indene with maleic anhydride

(a) The experiment was carried out as for the cycloaddition with N-phenylmaleimide but on twice the scale and substitution of the N-phenylmaleimide with maleic anhydride (0.45 g, 4.6 mmol). Chromatography on silica, eluting with petrol containing acetic anhydride (ca. 0.1%) and an increasing proportion of ether gave (i) a 1 : 1 mixture of the [4+2] adduct (57b) and the exo-[8+2] adduct (55b) (0.62 g). (ii) The endo-[8+2] adduct (56b) (0.52 g, 30%), as an oil (Found: m/e 258.0888. $C_{15}H_{14}O_4$ requires m/e 258.0892); $\nu_{max}(CCl_4)$ 1860 (m), 1782 (s), 1736 (m), 1740 (m), 1074 (m), and 916 cm^{-1} (s); λ_{max} 301 nm (log ε 3.88); $\delta_H(CDCl_3)$ 0.86 (3H, s, 7b-Me), 3.18 (1H, dd, $J_{1,7a}$ 9.9 Hz, $J_{7,7a}$ 6.4 Hz, H-7a), 3.52 (3H, s, OMe), 3.64 (1H, d, $J_{1,2}$ 9.8 Hz, H-2), 3.78 (1H, dd, $J_{1,2}$ 9.8 Hz, $J_{1,7a}$ 9.9 Hz, H-1), 5.91 (1H, d, $J_{5,6}$ 5.3 Hz, H-5). 6.06 (1H, dd, $J_{6,7}$ 9.0 Hz, $J_{7,7a}$ 6.4 Hz, H-7), 6.31 (1H, dd, $J_{5,6}$ 5.3 Hz, $J_{6,7}$ 9.0 Hz,

H-6), 6.41 (1H, d, J 5.6 Hz, H-4), and 6.57 (1H, d, J 5.6 Hz, H-3); m/e 258 (M^+), 160, and 145 (100%).

The mixture (i) (214 mg) was heated at 70°C under vacuum (water pump) for 15 min, and the resulting oil chromatographed as above to give (i) the exo-[8+2]adduct (55b) (121 mg, 20%), as an oil; $\nu_{max}(CCl_4)$ 1860 (m), 1782 (s), 1736 (m), 1076(m), and 912 cm^{-1} (s); $\delta_H(CDCl_3)$ 0.90 (3H, s, 7b-Me), 2.92 (1H, dd, $J_{1,2}$ 9.6 Hz, $J_{1,7a}$ 7.4 Hz, H-1), 2.98 (1H, dd, $J_{1,7a}$ 7.4 Hz, $J_{7,7a}$ 5.7 Hz, H-7a), 3.13 (1H, d, $J_{1,2}$ 9.6 Hz, H-2), 3.55 (3H, s, OMe), 6.02 (1H, d, $J_{5,6}$ 5.0 Hz, H-5), 6.11 (1H, dd, $J_{6,7}$ 9.1 Hz, $J_{7,7a}$ 5.7 Hz, H-7), 6.19 (1H, dd, $J_{5,6}$ 5.0 Hz, $J_{6,7}$ 9.1 Hz, H-6), 6.46 (1H, d, J 5.8 Hz, H-4), and 6.76 (1H, d, J 5.8 Hz, H-3); m/e 258 (M^+). (ii) The endo-[8+2]adduct (56b) (66 mg, 11%).

(b) The cycloaddition reaction was repeated on the same scale but the mixture was allowed to warm only to 0°C, filtered through celite and the solvent evaporated at 0°C and 2 mmHg. The residue was chromatographed as above but with a column cooled by a jacket of ice-water to give the endo-[4+2]adduct (57b) (1.00 g, 57%), as an unstable crystalline solid; $\delta_H(CDCl_3)$ 0.87 (3H, s, 7a-Me), 3.41 (1H, d, J 8.5 Hz, H-8), 3.71 (3H, s, OMe), 3.72 (1H, d, J 8.5 Hz, H-9), 6.02 (1H, dd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.0 Hz, H-6), 6.12 (1H, dd, $J_{4,5}$ 9.4 Hz, $J_{5,6}$ 5.2 Hz, H-5), 6.16 (1H, d, $J_{6,7}$ 9.0Hz, H-7), 6.26 (1H, d, J 6.0 Hz, H-3), 6.37 (1H, d, J 6.0 Hz, H-2), and 6.43 (1H, d, $J_{4,5}$ 9.4 Hz, H-4).

The endo-[4+2] adduct (57b) (0.81 g) was heated at 50°C under vacuum (water pump) for 30 min. Chromatography as above gave (i) the exo-[8+2] adduct (55b) (0.19 g, 23%). (ii) The endo-[8+2]adduct (56b) (0.28g, 35%).

4 Thermal rearrangement of the endo-[4+2]maleic anhydride adduct (57b) in the presence of N-phenylmaleimide

A solution of the endo-[4+2]maleic anhydride adduct (57b) (90 mg, 0.35 mmol) in dichloromethane (2 ml) containing N-phenylmaleimide (60 mg, 0.35 mmol) was refluxed for 15 min. The solvent was evaporated and the residue chromatographed on silica. Elution with petrol containing an increasing proportion of dichloromethane gave (i) a mixture of the exo-[8+2]-adduct (55b) and unreacted N-phenylmaleimide (55 mg). (ii) A 2 : 1 mixture of the endo-[4+2]N-phenylmaleimide adduct (57a) and the endo-[8+2]maleic anhydride adduct (56b) (29 mg).

5 Thermal rearrangement of the endo-[4+2]maleic anhydride adduct (57b) in the presence of dimethyl acetylenedicarboxylate

A solution of the [4+2]maleic anhydride adduct (57b) (29 mg, 0.11 mmol) in dichloromethane (0.5 ml) containing dimethyl acetylenedicarboxylate (50 mg, 0.35 mmol) was warmed to 40°C for 15 min. The resulting

mixture was cooled to room temperature, diluted with methanol (0.5 ml) and acidified with concentrated sulphuric acid (0.7 ml). The dark green mixture was poured into water (5 ml) and extracted with ether (5 ml). T.l.c. of the ether extract (silica, 30% ether in petrol) showed a characteristic yellow spot with a green fluorescence and of the same R_f value as an authentic sample of dimethyl 7b-methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarboxylate (38).

6 Thermal rearrangement of the [4+2]*N*-phenylmaleimide adduct (57a) in the presence of dimethyl acetylene-dicarboxylate

A solution of the [4+2]*N*-phenylmaleimide adduct (57a) (*ca* 1 mg) and dimethyl acetylenedicarboxylate (*ca* 20 mg) in toluene (0.25 ml) was refluxed for 10 min. T.l.c. of the resulting mixture (silica, 30% ether in petrol) showed one spot, but was inconclusive since the starting material and the dimethyl acetylenedicarboxylate adduct run coincidentally. The mixture was diluted with methanol (0.5 ml) and acidified with concentrated sulphuric acid (1 ml). The mixture was then poured into water (5ml) and extracted with ether (5 ml). T.l.c. showed that dimethyl 7b-methyl-7b*H*-cyclopent[*cd*]-indene-1,2-dicarboxylate (38) was present, by comparison with an authentic sample.

7 Thermal rearrangement of the [4+2] maleic anhydride adduct (57b) in the presence of cyclopentadiene

A solution of the [4+2] maleic anhydride adduct (57b) (121 mg, 0.47 mmol) in ether (5 ml) was treated with a solution of cyclopentadiene (31 mg, 0.47 mmol) in ether (5 ml) at 0°C. On warming to 30°C under nitrogen, the mixture became bright yellow and fluorescent. T.l.c (silica, 10% ether in petrol) showed the presence of 3-methoxy-3a-methyl-3a<u>H</u>-indene (37), as a fast running yellow spot which became colourless on exposure to the air after 30 sec.

8 Thermal rearrangement of the [4+2] <u>N</u>-phenylmaleimide adduct (57a) in the presence of phenyl vinyl sulphoxide

A solution of the [4+2] <u>N</u>-phenylmaleimide adduct (57a) (59 mg, 0.18 mmol) in toluene (3 ml) containing phenyl vinyl sulphoxide[59] (115 mg, 0.76 mmol) was refluxed for 1 h. T.l.c. of the resulting mixture showed only a mixture of [8+2] <u>N</u>-phenylmaleimide adducts by comparison with authentic samples. The solvent was evaporated and the residue chromatographed on silica. Elution with petrol containing an increasing proportion of ether gave (i) the <u>exo</u>-[8+2] <u>N</u>-phenylmaleimide adduct (55a) (17.2 mg, 29%). (ii) A mixture of phenyl vinyl sulphoxide and the <u>endo</u>-[8+2] <u>N</u>-phenylmaleimide adduct (56a).

9 Attempted electrolytic decarboxylation of acids from the [8+2]maleic anhydride adducts

a) In pyridine containing triethylamine

A solution of a 2 : 3 mixture of the [8+2]maleic anhydride adducts (55b) and (56b) (630 mg) in 10 : 1 pyridine - water (50 ml) containing triethylamine (0.5 ml) was electrolysed between two stationary platinum foil electrodes with a potential difference of 100 V and an initial current of 0.4 A. External cooling was employed to maintain the reaction mixture at about room temperature. Electrolysis was discontinued when the current had fallen to 0.15 A. The resulting dark brown mixture was diluted with water (100 ml) and extracted with petrol (2 x 80 ml). The combined petrol layers were washed with water (2 x 50 ml), dried ($MgSO_4$) and the solvent evaporated to give a yellow oil (73 mg). N.m.r. showed that this oil was a complex mixture.

b) In methanol

A 2 : 3 mixture of the [8+2]maleic anhydride adducts (55b) and (56b) (89 mg, 0.34 mmol) was dissolved in a solution of potassium hydroxide (0.10 g, 1.8 mmol) in water (1 ml) and methanol (9 ml). The stirred mixture was electrolysed between a platinum anode and a stainless steel cathode at 1.0 A and 50 V. External cooling was used to maintain the mixture at around room temperature. Electrolysis was discontinued when the baseline spot on t.l.c. (silica, ether) no longer darkened when exposed to iodine vapour. By this time, the current had fallen to 0.8 A. The mixture was acidified with dilute

hydrochloric acid and extracted with dichloromethane (2 x 25 ml). The combined dichloromethane layers were dried ($MgSO_4$) and the solvent evaporated to give an oil (46 mg). T.l.c. showed that this oil was a complex mixture.

3.1.5 The adducts of the 3a*H*-indene (37) with 2-chloroacrylonitrile; their reactions and conversion into the annulene (1)

1 The cycloaddition of 3-methoxy-3a-methyl-3a*H*-indene (37) with 2-chloroacrylonitrile

A solution of freshly distilled 2-chloroacrylonitrile (4.0 g, 46 mmol) in dry 1,2-dimethoxyethane (24 ml) was added to a solution of the 3a*H*-indene (37), prepared as described in Section 3.1.3 from the trienone (46) (3.0 g, 21 mmol). The mixture was heated in a water bath at 70°C for 1 h, filtered, the solvent evaporated, and the residue chromatographed on silica. Elution with petrol containing an increasing proportion of ether gave (i) a 3 : 1 mixture of (2aα,7aα,7bα)-2β-chloro-2a-methoxy-7b-methyl-2,2a,7a,7b-tetrahydro-1*H*-cyclopent[*cd*]indene-2α-carbonitrile (*exo*-adduct, 58a) and (2aα,7aα,7bα)-2α-chloro-2a-methoxy-7b-methyl-2,2a,7a,7b-tetrahydro-1*H*-cyclopent[*cd*]indene-2β-carbonitrile (*endo*-adduct 58b) (2.8 g, 55%); ν_{max} (neat) 2238 cm^{-1} (w, C≡N stretch); *m/e* 247 (M^+), 160, and 145. Cooling of this mixture to 0°C gave crystals of the *exo*-adduct (58a) (1.5 g), m.p. 82 - 84°C (from petrol, b.p. 60 - 80°C) (Found: C, 67.78; H, 5.69; N 5.62. $C_{14}H_{14}ClNO$ requires

C, 67.89; H 5.70, N 5.66%); λ_{max}(EtOH) 305 nm (log ϵ 3.84); δ_H($CDCl_3$) 0.92 (3H, s, 7b-Me), 1.88 (1H, dd, $J_{1\alpha,1\beta}$ 13.2 Hz, $J_{1\alpha,7a}$ 12.4 Hz, H-1α), 2.41 (1H, dd, $J_{1\alpha,1\beta}$ 13.2 Hz, $J_{1\beta,7a}$ 5.2 Hz, H-1β). 2.83 (1H, ddd, $J_{1\beta,7a}$ 5.2 Hz, $J_{1\alpha,7a}$ 12.4 Hz, $J_{7,7a}$ 5.8 Hz, H-7a), 3.55 (3H, s, 2a-OMe), 5.80 - 5.95 (2H, m, H-5 and H-7), 6.14 (1H, dd, $J_{5,6}$ 5.0 Hz, $J_{6,7}$ 9.0 Hz, unaffected by decoupling of H-7a, H-6), 6.57 (1H, d, $J_{3,4}$ 5.7 Hz, H-3 or H-4), and 6.71 (1H, d, $J_{3,4}$ 5.7 Hz, H-4 or H-3). The endo-adduct (58b) gives δ_H($CDCl_3$) 0.95 (3H, s, 7b-Me), 1.78 (1H, t, $J_{1\alpha,1\beta}$ and $J_{1\alpha,7a}$ 12.4 Hz, H-1), 2.61 (1H, dd, $J_{1\alpha,1\beta}$ 12.4 Hz, $J_{1\beta,7a}$ 5.5 Hz, H-1β), 2.71 (1H, ddd, $J_{1\beta,7a}$ 5.5 Hz, $J_{1\alpha,7a}$ 12.4 Hz, $J_{7,7a}$ 5.8 Hz, H-7a), 3.61 (3H, s, 2a-OMe), 5.80 - 5.92 (2H, m, H-5 and H-7), 6.12 (1H, dd, $J_{5,6}$ 5.0 Hz, $J_{6,7}$ 9.0 Hz, unaffected by decoupling of H-7a, H-6), 6.43 (1H, d, $J_{3,4}$ 5.7 Hz, H-3 or H-4), and 6.68 (1H, d, $J_{3,4}$ 5.7 Hz, H-4 or H-3).

(ii) A 3 : 2 mixture of (2aα,7aα,7bα)-1β-chloro-2a-methoxy-7b-methyl-2,2a,7a,7b-tetrahydro-1H-cyclopent-[cd]indene-1α-carbonitrile (60a) and (2aα,7aα,7bα)-1β-chloro-3,7b-dimethyl-2a-methoxy-2,2a,7a,7b-tetrahydro-1H-cyclopent[cd]indene-1α-carbonitrile (60b) (0.9 g, 17%), ν_{max}(neat) 2238 cm^{-1} (w, C≡N stretch); λ_{max}(EtOH) 305 nm; m/e 261 (M^+ of 60b), 247 (M^+ of 60a), 226, 212, 174, 160, 159, and 145; δ_H($CDCl_3$) of adduct (60a) 0.96 (3H, s, 7b-Me), 2.43 (1H, d, J 15.1 Hz, H-2β), 2.78 (1H, d, J 15.1 Hz, H-2α), 3.03 (1H, br. d, $J_{7,7a}$ 5.9 Hz, H-7a), 3.39 (3H, s, 2a-OMe), 5.83 (1H, d, $J_{5,6}$ 5.4 Hz, H-5), 5.90 (1H, dd, $J_{6,7}$ 9.2 Hz, $J_{7,7a}$ 5.9 Hz, becomes a doublet on decoupling of H-7a, H-7), 6.44 (2H, s, H-3 and H-4), 6.45 (1H, ddd,

$J_{5,6}$ 5.4 Hz, $J_{6,7}$ 9.2 Hz, $J_{6,7a}$ 0.9 Hz, the fine splitting is removed by decoupling of H-7a, H-6), and of adduct (60b) 0.99 (3H, s, 7b-Me), 1.93 (3H, s, 3-Me), 2.37 (1H, d, J 15.4 Hz, H-2β), 2.69 (1H, d, J 15.4 Hz, H-2α), 3.01 (1H, br. d, $J_{7,7a}$ 6.7 Hz, H-7a). 3.40 (3H, s, 2a-OMe), 5.69 (1H, d, $J_{5,6}$ 5.1 Hz, H-5), 5.83 (1H, dd, $J_{6,7}$ 9.3 Hz, $J_{7,7a}$ 6.7 Hz, H-7), 6.19 (1H, s, sharpened by decoupling of 3-Me, H-4), and 6.43 (1H, ddd, $J_{5,6}$ 5.1 Hz, $J_{6,7}$ 9.3 Hz, $J_{6,7a}$ 0.9 Hz, the fine splitting is removed by irradiation of H-7a, H-6).

2 (2aα,7aα,7bα)-2β-Chloro-2a-methoxy-7b-methyl-2,2a,7a,7b-tetrahydro-1H-cyclopent[cd]indene-2α-carboxaldehyde (59)

A solution of the exo-2-chloroacrylonitrile adduct (58a) (130 mg, 0.53 mmol) in dry tetrahydrofuran (5 ml) under nitrogen at room temperature was treated with a solution of diisobutylaluminium hydride (1 M; 1.0 ml, 1.0 mmol). The mixture was stirred 1.5 h. Methanol (1.5 ml) was then added, followed by water (2 ml). The resulting slurry was extracted with ether (2 x 30 ml), the combined extracts dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with 20% ether in petrol gave the title compound (36 mg, 28%), as an oil; $\delta_H(CDCl_3)$ 0.92 (3H, s, 7b-Me), 2.00 (1H, dd, $J_{1\alpha,1\beta}$ 13.9 Hz, $J_{1\beta,7a}$ 7.0 Hz, H-1β), 2.02 (1H, dd, $J_{1\alpha,1\beta}$ 13.9 Hz, $J_{1\alpha,7a}$ 11.4 Hz, H-1α), 2.89 (1H, ddd, $J_{1\beta,7a}$ 7.0 Hz, $J_{1\alpha,7a}$ 11.4 Hz, $J_{7,7a}$ 6.0 Hz, H-7a), 3.40 (3H, s, 2a-OMe), 5.84 (1H, d, $J_{5,6}$ 4.9 Hz, H-5), 5.92 (1H, dd, $J_{6,7}$ 9.2 Hz, $J_{7,7a}$ 6.0 Hz, H-7), 6.11

(1H, dd, $J_{5,6}$ 4.9 Hz, $J_{6,7}$ 9.2 Hz, H-6), 6.17 (1H, d, J 5.5 Hz, H-3), 6.60 (1H, d, J 5.5 Hz, H-4), and 9.60 (1H, s, CHO). See Fig. 6 for nuclear Overhauser effect results.

3 (2aα,7aα,7bα)-1β-Chloro-2a-methoxy-7b-methyl-2,2a,7a,7b-tetrahydro-1H-cyclopent[cd]indene-1α-carboxaldehyde and (2aα,7aα,7bα)-1β-chloro-3,7b-dimethyl-2a-methoxy-2,2a,7a,7b-tetrahydro-1H-cyclopent[cd]indene-1α-carboxaldehyde

A stirred solution of a 3 : 2 mixture of the 2-chloroacrylonitrile adducts (60a) and (60b) (204 mg, 0.82 mmol) in hexane (10 ml) and dry tetrahydrofuran (2 ml) at 0°C under nitrogen was treated with a solution of diisobutylaluminium hydride (1 M; 2.0 ml, 2.0 mmol). The mixture was stirred at room temperature for 2 h, methanol (2 ml) added and then water (4 ml) added. The mixture was filtered and the residue washed with ether (3 x 10 ml). The filtrate was extracted with ether (3 x 15 ml), the combined extracts and washings dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with 25% ether in petrol gave a 2 : 1 mixture of the title compounds (36 mg, 17%), as an oil; the aldehyde derived from adduct (60a) gives $\delta_H(CDCl_3)$ 0.93 (3H, s, 7b-Me), 2.07 (1H, d, J 14.0 Hz, H-2β), 2.68 (1H, d, J 14.0 Hz, H-2α), 3.00 (1H, br. d, $J_{7,7a}$ 6.4 Hz, H-7a), 3.39 (3H, s, OMe), 5.69 (1H, dd, $J_{6,7}$ 9.2 Hz, $J_{7,7a}$ 6.4 Hz, H-7), 5.87 (1H, d, $J_{5,6}$ 5.2 Hz, H-5), 6.36 (1H, ddd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.2 Hz,

$J_{6,7a}$ 1.1 Hz, the fine splitting is removed by decoupling of H-7a, H-6), 6.45 (1H, d, J 5.9 Hz, H-4), and 6.47 (1H, d, J 5.9 Hz, H-3); the aldehyde derived from adduct (60b) gives $\delta_H(CDCl_3)$ 0.96 (3H, s, 7b-Me), 1.94 (3H, s, 3-Me), 2.00 (1H, d, J 14.5 Hz, H-2β), 2.62 (1H, d, J 14.5 Hz, H-2α), 3.00 (1H, br. d, $J_{7,7a}$ 6.4 Hz, H-7a), 3.35 (3H, s, OMe), 5.61 (1H, dd, $J_{6,7}$ 9.2 Hz, $J_{7,7a}$ 6.4 Hz, H-7), 5.72 (1H, d, $J_{5,6}$ 5.2 Hz, H-5), 6.20 (1H, s, H-4), and 6.35 (1H, ddd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.2 Hz, $J_{6,7a}$ 1.1 Hz, the fine coupling is removed by decoupling of H-7a, H-6). See Figs. 7 and 8 for nuclear Overhauser effect results.

4 Melt pyrolysis of the 2-chloroacrylonitrile adducts (58a) and (58b)

A 2 : 3 mixture of the 2-chloroacrylonitrile adducts (58a) and (58b) (75 mg) was heated under nitrogen at 200°C for 15 min. The mixture became dark but its proton n.m.r. spectrum was unchanged. After further heating at 230°C for 15 min, the proton n.m.r. spectrum showed that considerable decomposition had occurred.

5 Flash vacuum pyrolysis of the 2-chloroacrylonitrile adducts (58a) and (58b)

(a) At 400°C

A 2 : 3 mixture of the 2-chloroacrylonitrile adducts (58a) and (58b) (94 mg) was distilled at 0.3 mmHg up a tube heated to 400°C. N.m.r. examination of the pyrolysate (90 mg) showed it to be a 2 : 3 : 1

mixture of the adducts (58a) and (58b), and 1-methoxy-1-methyl-1H-indene (62);[42a,b] δ_H($CDCl_3$, 60 MHz) 1.52 (3H, s, 1-Me), 2.94 (3H, s, OMe), 6.15 (1H, d, J 6 Hz, H-2), 6.65 (1H, d, J 6 Hz, H-3), and 7.0 - 7.4 (4H, m, ArH).

(b) At 500°C

A 2 : 3 mixture of the 2-chloroacrylonitrile adducts (58a) and (58b) (98 mg) was distilled at 0.3 mmHg up a tube heated to 500°C. N.m.r. examination of the pyrolysate (66 mg) showed it to be a 2 : 3 : 3 mixture of the adducts (58a) and (58b), and 1-methoxy-1-methyl-1H-indene (62), but other products were present to a small extent.

(c) At 550°C

A 2 : 3 mixture of the 2-chloroacrylonitrile adducts (58a) and (58b) (120 mg) was distilled at 0.3 mmHg up a tube heated to 550°C. N.m.r. examination of the pyrolysate (68 mg) showed that all starting material was consumed to give aromatic material of which only about 20% was the 1H-indene (62).

6 Reaction of the 2-chloroacrylonitrile adducts (58a) and (58b) with sodium sulphide

A solution of a 2 : 3 mixture of the 2-chloroacrylonitrile adducts (58a) and (58b) (125 mg, 0.50 mmol) in ethanol (3 ml) was treated with sodium sulphide (30%; 340 mg, 1.3 mmol) and the mixture stirred at room temperature for 16 h. The mixture was then poured into water (15 ml) and extracted with ether (2 x 20 ml). The

pale yellow combined extracts were dried (Na_2SO_4) and the solvent evaporated. T.l.c. (silica, 15% ether in petrol) showed that at least five compounds were present. The only material that was isolated by column chromatography was a 1 : 3 mixture of the unreacted adducts (58a) and (58b) (39 mg).

7 Reaction of the 2-chloroacrylonitrile adducts (58a) and (58b) with sodium hydroxide

A solution of a 2 : 3 mixture of the 2-chloroacrylonitrile adducts (58a) and (58b) (58 mg, 0.23 mmol) in ethanol (1.5 ml) and dimethyl sulphoxide (0.5 ml) containing sodium hydroxide (50 mg, 1.25 mmol) and a drop of water was purged with nitrogen and then refluxed for 2 h. The mixture was poured into water (30 ml), neutralised with acetic acid and extracted with dichloromethane (3 x 40 ml). The combined extracts were washed with water (50 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with petrol containing an increasing proportion of ether gave (i) the unreacted adduct (58b) (12.2 mg). (ii) 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene-2-carboxylic acid (64) (16.8 mg, 26%); spectral data are given later.

8 Reaction of the 2-chloroacrylonitrile adducts (58a) and (58b) with sodium methoxide

A solution of a 3 : 1 mixture of the 2-chloroacrylonitrile adducts (58a) and (58b) (58 mg, 0.23 mmol) in dimethylformamide (2 ml) containing sodium methoxide

(240 mg, 4.4 mmol) was heated at 60°C for 0.5 h. The dark mixture was poured into water (50 ml) and extracted with ether (3 x 20 ml). The combined extracts were washed with water (30 ml), dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with 20% ether in petrol gave a 4 : 1 mixture of the unreacted adduct (58b) and 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene-2-carbonitrile (65) (12 mg); spectral data for the annulene (65) are given later.

9 <u>Reaction of the 2-chloroacrylonitrile adduct (58a) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene-2-carbonitrile (65)</u>

A mixture of the adduct (58a) (1.06 g, 4.3 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1.0 g, 6.6 mmol) was stirred under nitrogen and heated at 110°C for 6 h. The resulting black viscous mixture was chromatographed on silica. Elution with 20% ether in petrol gave <u>7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene-2-carbonitrile (65)</u>, (0.57 g, 74%), as a mobile yellow oil (Found: <u>m/e</u> 179.0736. $C_{13}H_9N$ requires <u>m/e</u> 179.0735); ν_{max}(neat) 2224 (s, C≡N stretch), 1444 (m), 852 (s), 816 (m), 736 (m), and 686 cm^{-1} (s); λ_{max}(EtOH) 251 (log ϵ 3.87), 297 (4.66), 329 (3.84), and 470 nm (3.15); $\delta_H(CDCl_3)$ -1.56 (3H, s, 7b-Me), 7.60 (1H, t, <u>J</u> 7Hz, H-6), 7.70 (1H, d, <u>J</u> 7.0 Hz, H-5), 7.82 (1H, d, <u>J</u> 7.4 Hz, H-7), 7.90 (1H, s, H-3), 7.97 (1H, d, <u>J</u> 3.5 Hz, H-4), and 8.03 (1H, d, <u>J</u> 3.5 Hz, H-3); $\delta_C(CDCl_3)$ 28.6 (0.96, 7b-Me), 59.6 (0.26, C-7b), 101.7 (0.14, <u>C</u>N or C-2), 116.5 (0.16, C-2 or <u>C</u>N), 118.5 (0.85,

C-5), 121.0 (1.00, C-7), 130.5 (0.86, C-3 or C-6), 130.8 (0.87, C-6 or C-3), 136.4 (0.75, C-4), 139.6 (0.93, C-1), 157.3 (0.21, C-4a or C-7a), 159.5 (0.27, C-7a or C-4a), and 179.4 (C-2a); m/e 179 (100%, M^+), 178, 164, 152, and 151.

10 Reaction of the 2-chloroacrylonitrile adduct (58a) with potassium tert-butoxide; 7b-methyl-7bH-cyclopent[cd]indene-2-carboxamide (66)

A solution of the adduct (58a) (1.25 g, 5.0 mmol) in benzene (20 ml) containing potassium tert-butoxide (1.8 g, 16 mmol) was stirred and refluxed under nitrogen for 0.5 h. The dark brown mixture was poured into water (100 ml), acidified with acetic acid (2 ml) and extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with water (100 ml), dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with 20% ethyl acetate in ether afforded 7b-methyl-7bH-cyclopent[cd]indene-2-carboxamide (66) (0.20 g, 20%), as yellow needles, m.p. 150.5 - 155°C (from ethyl acetate) (Found: C, 78.92; H, 5.64; N, 7.07. $C_{13}H_{11}NO$ requires C, 79.16; H, 5.62; N, 7.10%); $\nu_{max}(CCl_4)$ 1678 cm^{-1} (C=O stretch); λ_{max}(EtOH) 245 sh (log ϵ 3.89), 299 (4.61), 333 (3.81), and 471 nm (3.06); $\delta_H(CDCl_3)$ -1.47 (3H, s, 7b-Me), 6.5 (2H, br., NH_2), 7.60 (1H, t, J 7 Hz, H-6), 7.74 (1H, d, J 7.2 Hz, H-5), 7.83 (1H, d, J 7.4 Hz, H-7), 8.05 (2H, AB system, $J_{3,4}$ 3.1 Hz, H-3 and H-4), and 8.28 (1H, s, H-1); m/e 197 (M^+), 160, 154, 153, 152, and 144.

11 Reaction of the 2-chloroacrylonitrile adducts (60a) and (60b) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

A 3 : 2 mixture of the 2-chloroacrylonitrile adducts (60a) and (60b) (239 mg, 0.97 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (200 mg, 1.3 mmol) was stirred under nitrogen and heated at 100°C for 20 min. The resulting dark viscous mixture was chromatographed on silica. Elution with 20% ether in petrol gave a 2 : 1 mixture of 7b-methyl-7b*H*-cyclopent-[*cd*]indene-1-carbonitrile (67a) and 3,7b-dimethyl-7b*H*-cyclopent[*cd*]indene-1-carbonitrile (67b) (74 mg, 43%), as a yellow oil; the mixture gives ν_{max}(neat) 2920 (m), 2220 (s, C≡N stretch), 1438 (m), 862 (s), 818 (s), 786 (m), and 706 cm^{-1} (s); *m/e* 193 (M^+ of 67b), 179 (M^+ of 67a, 100%), 178, 164, 152, and 151. $\delta_H(CDCl_3)$ for compound (67a): -1.50 (3H, s, 7b-Me), 7.51 (1H, d, *J* 6.8 Hz, H-5), 7.64 (1H, t, *J* 7 Hz, H-6), 7.76 (1H, d, *J* 7.3 Hz, H-7), 7.93 (1H, s, H-2), 8.01 (1H, d, *J* 3.6 Hz, H-4), and 8.10 (1H, d, *J* 3.6 Hz, H-3); for compound (67b): -1.44 (3H, s, 7b-Me), 2.76 (3H, s, 3-Me), 7.68 - 7.75 (3H, m, H-5, H-6 and H-4), 7.81 - 7.87 (1H, m, H-7), and 7.90 (1H, s, H-2), comparison with a computer simulation for an ABX system for H-5, H-6 and H-7 gives δ_A 7.70 (H-6); δ_B 7.71 (H-5); δ_X 7.85 (H-7); $J_{5,6}$ 6.5 Hz, $J_{6,7}$ 7.5 Hz, $J_{5,7}$ *ca*. 0.8 Hz and H-4 at δ7.71.

12 7b-Methyl-7b*H*-cyclopent[*cd*]indene-2-carboxylic acid (64)

A mixture of 7b-methyl-7b*H*-cyclopent[*cd*]indene-2-

carbonitrile (118 mg, 0.66 mmol) and a solution of sodium hydroxide (250 mg, 6.2 mmol) in water (5 ml) was stirred and refluxed under nitrogen. After 2 h, the mixture was poured into water (20 ml) and extracted with dichloromethane (2 x 30 ml). The extracts were discarded and the aqueous layer was acidified with sulphuric acid (6 M, 5 ml) and extracted with dichloromethane (3 x 30 ml). These extracts were washed with water (50 ml), dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with 50% ether in petrol afforded 7b-methyl-7b*H*-cyclopent[*cd*]indene-2-carboxylic acid (89 mg, 68%), as light orange crystals, m.p. 152 - 153.5°C (from petrol, b.p. 60 - 80°C) (Found: C, 78.85; H, 5.08. $C_{13}H_{10}O_2$ requires C, 78.77; H, 5.09%); $\nu_{max}(CCl_4)$ 3400 - 2300 (br. OH stretch), 1680 (s, C=O stretch), 1452 (m), 1274 (s), 1236 (s), 856 (m), and 688 cm^{-1} (s); λ_{max}(EtOH) 250 (log ϵ 3.89), 299 (4.62), 332 (3.82), 418 sh (2.15), and 474 nm (3.17); $\delta_H(CDCl_3)$ -1.40 (3H, s, 7b-Me), 7.59 (1H, t, *J* 7 Hz, H-6), 7.71 (1H, d, *J* 6.6 Hz, H-5), 7.91 (1H, d, *J* 7.3 Hz, H-7), 8.12 (1H, d, *J* 3.5 Hz, H-4), 8.23 (1H, d, *J* 3.5 Hz, H-3), 8.31 (1H, s, H-1), and 10.3 -12.0 (1H, br., CO_2H); $\delta_C(CDCl_3)$ 28.8 (0.85, 7b-Me), 60.2 (0.47, C-7b), 118.2 (1.00, C-5), 121.7 (0.99, C-7), 129.4 (0.30, C-2), 129.9 (0.73, C-3 or C-6), 131.8 (0.90, C-6 or C-3), 136.4 (0.82, C-4), 140.1 (0.91, C-1), 157.6 (0.28, C-4a or C-7a), 159.2 (0.43, C-7a or C-4a), 170.9 (0.41, CO_2H), and 180.2 (0.32, C-2a); *m/e* 198 (M^+), 153 (100%), and 152.

13 7b-Methyl-7b*H*-cyclopent[*cd*]indene-2-carboxaldehyde (53b)

To a solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene-

2-carbonitrile (65) (228 mg, 1.3 mmol) in petrol (10 ml), cooled in an ice bath and stirred under nitrogen was added a solution of diisobutylaluminium hydride in hexane (1 M; 3 ml, 3 mmol). After 15 min, methanol (0.5 ml) was added, followed by a solution of ammonium chloride (0.3 g) in water (2 ml) and the resulting mixture was stirred at room temperature for 2 h. The mixture was then poured into water (20 ml) and extracted with ether (3 x 25 ml). The combined extracts were dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with 20% ether in petrol gave (i) a highly coloured band (14 mg). (ii) 7b-Methyl-7bH-cyclopent[cd]indene-2-carboxaldehyde (53b) (154 mg, 66%), as an orange oil; ν_{max}(neat) 1666 (s, C=O stretch), 1522 (m), 1154 (m), 852 (s), 814 (m), 706 (m), and 682 cm^{-1} (m); λ_{max}(EtOH) 257 (log ϵ 4.07), 312 (4.51), 350 (3.85), and 488 nm (3.20); $\delta_H(CDCl_3)$ -1.41 (3H, s, 7b-Me), 7.57 (1H, t, J 7 Hz, H-6), 7.71 (1H, d, J 7.1 Hz, H-5), 7.90 (1H, d, J 7.5 Hz, H-7), 8.11 (1H, d, J 3.6 Hz, H-4), 8.16 (1H, d, J 3.6 Hz, H-3), 8.21 (1H, s, H-1), and 10.38 (1H, s, CHO); $\delta_C(CDCl_3)$ 28.7 (0.94, 7b-Me), 60.5 (0.26, C-7b), 118.7 (0.80, C-5), 122.5 (0.70, C-7), 130.2 (1.00, C-3 or C-6), 130.7 (0.94, C-6 or C-3), 134.5 (0.66, C-4), 137.3 (0.17, C-2), 140.7 (0.78, C-1), 157.7 (0.17, C-4a or C-7a), 159.2 (0.20, C-7a or C-4a), 179.4 (0.16, C-2a), and 188.3 (0.61, CHO). Treatment of this aldehyde with 2,4-dinitrophenylhydrazine in ethanol containing sulphuric acid gave an immediate precipitate of the 2,4-dinitrophenyl hydrazone, as brick red needles, m.p. 220 - 222°C (decomp.) (from 1 : 1

dimethylformamide - acetonitrile) (Found: C, 62.64; H, 3.87; N, 15.25. $C_{19}H_{14}N_4O_4$ requires C, 62.98; H, 3.89; N, 15.46%).

14 7b-Methyl-7b*H*-cyclopent[*cd*]indene (1) (method 2)

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene-2-carboxaldehyde (53b) (163 mg, 0.89 mmol) in benzene (20 ml) was treated with tris(triphenylphosphine)rhodium(I) chloride (850 mg, 0.92 mmol) and the mixture was stirred and refluxed under nitrogen for 6.5 h. The mixture was cooled to room temperature, iodomethane (1 ml) added and the stirring was continued for 1.5 h. The mixture was filtered and the residue was washed with benzene (2 x 5 ml). The combined filtrate and washings were evaporated and the residue chromatographed on silica. Elution with petrol gave 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (126 mg, 92%); spectral data are given later, in Section 3.1.7.

3.1.6 The use of 2-chloroacryloyl chloride (68); Synthesis and reactions of the tricyclic ketone, 2a-methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2*H*-cyclopent[*cd*]-inden-2-one (63)

1 The cycloaddition of 3-methoxy-3a-methyl-3a*H*-indene (37) with 2-chloroacryloyl chloride

a) Methyl (2aα,7aα,7bα)-2β-chloro-2a-methoxy-7b-methyl-2,2a,7a,7b-tetrahydro-1*H*-cyclopent[*cd*]indene-2α-carboxylate (69a)

A solution of 2-chloroacryloyl chloride[70] (4.2 g,

34 mmol) in dry 1,2-dimethoxyethane (10 ml) was added to a solution of the 3a*H*-indene (37), prepared as described in Section 3.1.3 and below from the trienone (46) (4.75 g, 32 mmol). The mixture was allowed to warm to 0°C, filtered and the residue washed with 1,2-dimethoxyethane (20 ml). The combined filtrate and washings (3.3% of) was treated with a mixture of methanol (2 ml) and triethylamine (1 ml) and the mixture was stirred at room temperature for 1 h. The solvent was evaporated and the residue chromatographed on silica. Elution with 20% ether in petrol gave the title ester (69a) containing 1 part in 25 of its isomer (69b) (145 mg, 48%), as an oil; $\delta_H(CDCl_3)$ 0.92 (3H, s, 7b-Me), 2.09 (1H, dd, $J_{1\alpha,1\beta}$ 14.0 Hz, $J_{1\alpha,7a}$ 12.4 Hz, H-1α), 2.22 (1H, dd, $J_{1\alpha,1\beta}$ 14.0 Hz, $J_{1\beta,7a}$ 5.5 Hz, H-1β), 2.79 (1H, ddd, $J_{1\alpha,7a}$ 12.4 Hz, $J_{1\beta,7a}$ 5.5 Hz, $J_{7,7a}$ 6.3 Hz, H-7a), 3.57 (3H, s, 2a-OMe), 3.76 (3H, s, CO_2Me), 5.80 (1H, d, J 5.2 Hz, H-5), 5.91 (1H, dd, $J_{7,7a}$ 6.3 Hz, $J_{6,7}$ 9.4 Hz, H-7), 6.08 (1H, dd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.4 Hz, H-6), 6.26 (1H, d, J 5.7 Hz, H-3 or H-4), and 6.54 (1H, d, J 5.7 Hz, H-4 or H-3); the minor isomer (69b) gives extra peaks at 0.87 (3H, s, 7b-Me), 3.05 (1H, ddd, H-7a), 3.44 (3H, s, 2a-OMe), 3.81 (3H, s, CO_2Me), 5.84 (1H, d, H-5), 6.49 (1H, d, H-3 or H-4), and 6.61 (1H, d, H-4 or H-3) m/e 280 (M^+), 160 (100%), and 145. The remainder of the solution of the adduct (96.7% of) was treated as described in part (b) below to give the ketone (63) (2.65 g, 42%).

(b) 2a-Methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2*H*-cyclopent[*cd*]inden-2-one (63)

To a mechanically stirred solution of potassium

hydride (from a dispersion in oil, 25%; 46 g, 0.23 mol) in dry 1,2-dimethoxyethane (100 ml) under nitrogen and cooled externally by a cooling bath at -23°C, was added a solution of 18-Crown-6 (37.5 g, 0.14 mol) in dry 1,2-dimethoxyethane (160 ml), followed by a solution of 5,7a-dihydro-7a-methyl-1H-inden-1-one (46) (18.7 g, 0.13 mol) in dry 1,2-dimethoxyethane (20 ml). After 0.5 h, freshly distilled methyl fluorosulphonate (12 ml, 0.15 mol) was added, followed by 2-chloroacryloyl chloride[70] (20.0 g, 0.16 mol). The solution was allowed to warm to 0°C, filtered and the residue washed with dry 1,2-dimethoxyethane (80 ml). Sodium azide (32 g, 0.48 mol) was added to the filtrate. The mixture was stirred in a sealed system at room temperature for 16 h, filtered and the filtrate refluxed for 2 h. The resulting dark brown mixture was cooled to room temperature, treated with 2 : 1 acetic acid - water (200 ml) and warmed at 60°C for 1 h. The cooled mixture was poured into water (1 l) and extracted with ether (4 x 250 ml). The combined ether layers were washed with water (500 ml), then saturated aqueous sodium hydrogen carbonate (2 x 500 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petrol gave the title ketone (12.5 g, 48%), as a colourless oil; ν_{max}(neat) 1732 (s, C=O stretch), 1114 (m), and 1052 cm^{-1} (m); λ_{max}(EtOH) 240 (log ϵ 3.43), 310 (3.75) and 342 nm sh (3.29); δ_H($CDCl_3$) 1.12 (3H, s, 7b-Me), 2.12 (1H, dd, J 11.8 Hz, 18.6 Hz, H-1), 2.50 (1H, dd, J 7.8 Hz, 18.6 Hz, H-1), 2.81 (1H, ddd, J 7.8 Hz, 11.8 Hz, 6.1 Hz, H-7a), 3.50 (3H, s,

2a-OMe), 5.88 (2H, m, H-5 and H-7), 6.02 (1H, dd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.4 Hz, H-6), 6.24 (1H, d, J 5.7 Hz, H-3 or H-4), and 6.47 (1H, d, J 5.7 Hz, H-4 or H-3); m/e 202 (M^+), 160, 159, 145 (100%), and 145.

2 Rearrangement of the [4+2] maleic anhydride adduct (57b) in the presence of 2-chloroacryloyl chloride

A solution of the [4+2] maleic anhydride adduct (57b) (128 mg, 0.50 mmol) in dichloromethane (2 ml) at 0°C was treated with 2-chloroacryloyl chloride (0.1 ml, 1.0 mmol). The mixture was refluxed for 20 min, methanol (0.5 ml) added, the solvent evaporated and the residue chromatographed on silica. Elution with 20% ether in petrol gave a 12 : 1 mixture of the esters (69a) and (69b) (30 mg, 22%)

3 Rearrangement of the [4+2] N-phenylmaleimide adduct (57a) in the presence of 2-chloroacryloyl chloride

A solution of the [4+2] N-phenylmaleimide adduct (57a) (33 mg, 0.10 mmol) in toluene (2 ml) containing 2-chloroacryloyl chloride (0.1 ml, 1.0 mmol) was refluxed for 15 min. The resulting pale yellow solution was cooled to room temperature and a mixture of methanol (0.3 ml) and triethylamine (0.2 ml) added. The mixture was stirred for 10 min, the solvent evaporated and the residue chromatographed on silica. Elution with 20% ether in petrol gave (i) an 8 : 1 mixture of the esters (69a) and (69b) (12 mg, 43%)

4 Conversion of the ester (69a) into the aldehyde (59)

A solution of the ester (69a) (83.2 mg, 0.30 mmol) in petrol (8 ml) was stirred at 0°C under nitrogen and treated with a solution of diisobutylaluminium hydride in hexane (1 M; 1 ml, 1.0 mmol). After 30 min, methanol (1.5 ml) was added followed by water (2 ml) and the mixture stirred at room temperature for 1 h. The mixture was then filtered, the residue washed with ether (2 x 20 ml) and the filtrate extracted with ether (2 x 30 ml). The combined washings and extracts were dried (Na_2SO_4), the solvent evaporated and the residue chromatographed. Elution with 60% ether in petrol gave (2aα,7aα,7bα)-2β-chloro-2a-methoxy-7b-methyl-2,2a,7a,7b-tetrahydro-1H-cyclopent[cd]indene-2α-methanol (51.4 mg, 69%), as an oil; ν_{max} 3440 (OH stretch), 2922 (m), and 1082 cm^{-1} (s); δ_H($CDCl_3$, 90 MHz) 0.95 (3H, s, 7b-Me), 1.49 (1H, dd, J 12 Hz, 14 Hz, H-1α), 2.14 (1H, dd, J 6 Hz, 14 Hz, H-1β), 2.3 (1H, br., OH), 2.85 (1H, dt, J 12 Hz, 6 Hz, H-7a), 3.49 (3H, s, OMe), 3.63 (2H, m, CH_2OH), 5.82 (1h, d, J 4 Hz, H-5), 6.00 (1H, dd, J 6 Hz, 8 Hz, H-7), 6.10 (1H, dd, J 4 Hz, 8 Hz, H-6), 6.49 (1H, d, J 6 Hz, H-3 or H-4), and 6.52 (1H, d, J 6 Hz, H-4 or H-3). A solution of this alcohol (39 mg, 0.155 mmol) in dichloromethane (5 ml) was treated with a solution prepared from powdered chromium trioxide (78 mg, 0.78 mmol) in pyridine (125 mg, 1.7 mmol) and dichloromethane (2 ml). After 10 min at room temperature, the solvent was removed, ether (10 ml) added, the mixture filtered and the residue washed with ether (2 x 5 ml). The combined filtrate and washings were concentrated and the residue chromatographed on silica.

Elution with 25% ether in petrol gave the aldehyde (59) (5.5 mg, 14 %); the proton n.m.r. spectrum was identical to that of a sample prepared from the 2-chloroacrylonitrile adduct (58a) as described in Section 3.1.5.

5 Methyl 7b-methyl-7b*H*-cyclopent[*cd*]indene-2-carboxylate (70)

A 25 : 1 mixture of the esters (69a) and (69b) (204 mg, 0.73 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (300 mg, 2.0 mmol) was heated at 110°C under nitrogen for 4 h. The resulting dark viscous mixture was chromatographed on silica. Elution with 20% ether in petrol gave (i) the title compound (19 mg, 12%), as a yellow oil; $\nu_{max}(CCl_4)$ 1718 (s, C=O stretch), 1444 (m), 1268 (m), 1222 (s), 1212 (s), and 1114 cm^{-1} (s); λ_{max}(EtOH) 251 (log ϵ 3.89), 302 (4.60), 336 (3.81), and 475 nm (3.16); $\delta_H(CDCl_3)$ -1.47 (3H, s, 7b-Me), 4.00 (3H, s, CO_2Me), 7.58 (1H, t, *J* 7.2 Hz, H-6), 7.71 (1H, d, *J* 7.2 Hz, H-5), 7.87 (1H, d, *J* 7.2 Hz, H-7), 8.08 (1H, d, *J* 3.4 Hz, H-4), 8.16 (1H, d, *J* 3.4 Hz, H-3), and 8.26 (1H, s, H-1). (ii) Starting material [6 : 1 ratio of the isomers (69a) and (69b), 34.0 mg].

6 Impregnation of silica H with silver acetate

Silver acetate (10 g) and silica H (90 g) was added with stirring to water (400 ml). The mixture was heated on a steam bath and was stirred until no more silver acetate remained on the surface of the mixture. The water was then evaporated under reduced pressure and the silica dried

by azeotropic removal of the water with benzene and then the solvent removed under high vacuum.

7 2a-Methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2H-cyclopent[cd]inden-2-one-toluene-4-sulphonylhydrazone (71a)

A solution of 2a-methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2H-cyclopent[cd]inden-2-one (63) (1.24 g, 6.1 mmol) and toluene-4-sulphonylhydrazine (1.21 g, 6.5 mmol) in benzene (15 ml) was refluxed under nitrogen for 3 h with an apparatus for azeotropic removal of the water formed. The solvent was evaporated from the cooled mixture and the residue chromatographed on silica. Elution with 3 : 3 : 4 ether - dichloromethane - petrol gave the toluene-4-sulphonylhydrazone (71a) (2.05 g, 91%), as a gum which became a white powder when triturated with ether.

In a separate experiment, more careful chromatography gave (i) a minor isomer (112 mg), m.p. 157 - 160°C (by diffusion of petrol into a dichloromethane solution) (Found: C, 65.21; H, 6.00; N, 7.65: S, 8.49. $C_{20}H_{22}N_2O_3S$ requires C, 64.84; H, 5.99; N, 7.56; S, 8.65%). (ii) A major isomer (234 mg), m.p. 172 - 175°C (by diffusion of petrol into a dichloromethane solution) (Found: C, 65.00; H, 6.07; N, 7.56; S, 8.64. $C_{20}H_{22}N_2O_3S$ requires C, 64.84; H, 5.99; N, 7.56; S, 8.65%).

8 Reaction of the toluene-4-sulphonylhydrazone (71a) with methyl lithium

(a) At room temperature

A stirred solution of the hydrazone (71a) (195 mg, 0.53 mmol) in benzene (10 ml) was cooled to 5°C under nitrogen and treated with a solution of methyl lithium in ether (2M; 5 ml, 10 mmol). The mixture was stirred at room temperature for 20 h and then water (1 ml) was added dropwise. The resulting slurry was poured into water (30 ml) and extracted with ether (3 x 30 ml), The combined extracts were dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with petrol gave impure 7b-methyl-7b*H*-cyclopent-[*cd*]indene (1) (70% pure by n.m.r.; 20 mg, 17%). Elution with 5% ether in petrol gave, after a forerun of aromatic material (39 mg), 4a,7b-dihydro-2a-methoxy-7b-methyl-2a*H*-cyclopent[*cd*]indene (54) (26 mg, 26%), as an oil (Found: *m/e* 186.1050. $C_{13}H_{14}O$ requires *m/e* 186.1045); ν_{max}(neat) 1076 (s), 724 (m), and 716 cm^{-1} (m); λ_{max}(EtOH) 309 nm (log ϵ 3.66); $\delta_H(CDCl_3)$ 1.01 (3H, s, 7b-Me), 3.31 (3H, s, OMe), 3.32 (1H, m, H-4a), 5.77 (3H, m, affected by decoupling at δ3.32, H-3, H-5 and H-7), 6.02 (1H, ddd, $J_{4a,6}$ 0.9 Hz, $J_{6,7}$ 5.2 Hz, $J_{5,6}$ 9.4 Hz, the small coupling is removed by irradiation at δ3.32, H-6), 6.07 (1H, dd, $J_{4,4a}$ 1.7 Hz, $J_{3,4}$ 5.6 Hz, the smaller coupling is removed by irradiation at δ3.32, H-4), 6.24 (1H, d, *J* 5.6 Hz, H-1 or H-2), and 6.31(1H, d, *J* 5.6 Hz, H-2 or H-1); $\delta_C(CDCl_3)$ 15.6 (1.00, 7b-Me), 49.6 (0.23, C-7b), 50.2 (0.86, OMe), 53.2 (0.56, C-4a), 100.4 (0.26, C-2a), 113.2 (0.78), 123.2 (0.71),

124.8 (0.75), 129.5 (0.80), 133.2 (0.81), 139.4 (0.73), 140.0 (0.65), and 150.5 (0.14, C-7a); m/e 186 (M^+) and 171 (100%).

The 7b-methyl-7bH-cyclopent[cd]indene (1) obtained in this reaction was purified by chromatography on silica impregnated with silver acetate (10% w/w). Elution with petrol gave first, the pure annulene (1), and then the contaminant.

(b) At 45°C

A stirred solution of the hydrazone (71a) (667 mg, 1.8 mmol) in benzene (40 ml) was cooled to 5°C under nitrogen and treated with a solution of methyl lithium in ether (2 M; 15 ml, 30 mmol). The mixture was then heated at 45°C for 10 h and then water (3 ml) was added dropwise. Work-up was on three times the scale of part (a) and chromatography was on silica impregnated with silver acetate (10% w/w). Elution with petrol gave 7b-methyl-7bH-cyclopent[cd]indene (1) (110 mg, 40%); spectral data are given later, in Section 3.1.6.

9 2a-Methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2H-cyclopent[cd]inden-2-one-2,4,6-triisopropylbenzenesulphonylhydrazone (71b)

A solution of 2a-methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2H-cyclopent[cd]inden-2-one (63) (4.05 g, 20 mmol) in dichloromethane (50 ml) containing Amberlite resin IR120(H) (5 g) was treated with a solution of purified 2,4,6-triisopropylbenzenesulphonylhydrazine

(6.60 g, 22 mmol) in dichloromethane (50 ml). The mixture was stirred at room temperature for 3 h, the solvent then evaporated under reduced pressure at room temperature and the residue chromatographed on silica. Elution with 1 : 1 : 2 dichloromethane - ether - petrol gave the 2,4,6-triisopropylbenzenesulphonylhydrazone (71b) (8.1 g, 83%), m.p. 174 - 177°C (by evaporation of a solution in 1 : 1 dichloromethane - petrol, b.p. 60 - 80°C) (Found: C, 69.33; H, 7.96; N, 5.72. $C_{28}H_{38}N_2O_3S$ requires C, 69.66; H, 7.93; N, 5.83%).

10 Reaction of the triisopropylbenzenesulphonylhydrazone (71b) with methyl lithium followed by deuterium oxide

(a) At room temperature

A stirred solution of the hydrazone (71b) (274 mg, 0.57 mmol) in dry benzene (10 ml) under nitrogen at room temperature was treated with a solution of methyl lithium in ether (2 M; 7.5 ml, 15 mmol) and the resulting mixture was stirred at room temperature for 2 h. The mixture was then treated with dropwise addition of deuterium oxide (99.7 atom %; 0.5 ml). After 5 min, the mixture was poured into water (30 ml) and the products extracted with ether (3 x 30 ml). The combined ether layers were dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with petrol gave 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (6 mg, 7%). Elution with 5% ether in petrol gave 4a,7b-dihydro-2a-methoxy-7b-methyl-2a*H*-cyclopent[*cd*]indene-3d (*ca*. 65% deuterium incorporation; 67 mg, 63%); $\delta_H(CDCl_3)$ as for an undeuterated sample except 5.77 (2.35H, m, H-3 of undeuterated compound, H-5

and H-7), 6.07 (1H, m, H-4; decoupling of H-4a at 3.03 gives a singlet and a doublet, J 5.6 Hz, the relative intensities of which are consistent with the extent of deuteration as 65 - 70%); $\delta_C(CDCl_3)$ as for undeuterated sample except for reduction of intensity of the lines at 129.5 (0.41, C-3) and 140.0 (0.33, C-4 of undeuterated compound, and a new line appears at 139.9 (0.67, C-4 of deuterated compound).

(b) At 45°C

A stirred solution of the hydrazone (71b) (980 mg, 2.0 mmol) in dry benzene (50 ml) under nitrogen at room temperature was treated with a solution of methyl lithium in ether (2 M; 27 ml, 54 mmol) and the mixture was stirred at 45°C for 7 h. Work-up was the same as for part (a) but on four times the scale to give (i) 7b-methyl-7b*H*-cyclopent-[*cd*]indene (193 mg, 61%); the extent of deuteration in the 2-position was *ca*. 20% - see preparation of the *4*-phenyl-1,2,4-triazole-3,5-dione adduct (see Section 3.2.6). (ii) 4a,7b-Dihydro-2a-methoxy-7b-methyl-2a*H*-cyclopent[*cd*]indene (54)(84 mg, 22%); the extent of deuterium incorporation was not determined for this sample.

11 Reaction of 4a-7b-dihydro-2a-methoxy-7b-methyl-2a*H*-cyclopent[*cd*]indene (54) with toluene-4-sulphonic acid

A solution of the tetraene (54) (52 mg) in dichloromethane (12 ml) at room temperature was treated with toluene-4-sulphonic acid (5 mg) and the mixture was stirred at room temperature for 3 h. The resulting solution was washed with saturated sodium hydrogen carbonate

solution (3 x 10 ml), then water (10 ml), the solvent evaporated and the residue chromatographed on silica. Elution with petrol gave 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]-indene (1) (35 mg, 81%).

A 65 - 70% deuterated sample of the tetraene (54) gave by this procedure, 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene-2<u>d</u>, 65 - 70% deuterium incorporation, $\delta_H(CDCl_3)$ -1.64 (3H, s, 7b-Me), 7.52 - 7.72 (3H, AB_2 system, J_{AB} 7 Hz, δ_A 7.57, H-6; δ_B7.69, H-5 + H-7), 7.90 (1.3H, d, <u>J</u> 3 Hz, H-3 + H-2 of undeuterated material), and 7.92 (2H, s + d, <u>J</u> 3 Hz, H-1 + H-4); $\delta_C(CDCl_3)$ 28.7 (0.67, 7b-Me), 58.8 (0.12, C-7b), 116.3 (1.00, C-5 + C-7), 129.0 (0.58, C-6), 129.3 (0.71, intensity reduced relative to undeuterated sample, C-2 + C-3), 134.87 (0.38, C-1 of deuterated compound), 134.92 (0.58, C-4 + C-1 of undeuterated compound), 159.2 (0.20, C-4a + C-7a), 178.8 (0.06, C-2a of deuterated compound), and 178.9 (0.04, C-2a of undeuterated compound). Full spectral data for the undeuterated annulene (1) are given in Section 3.1.7.

12 <u>(2aα,7aα,7bα)-2a-Methoxy-7b-methyl-2,2a,7a,7b-tetrahydro-1<u>H</u>-cyclopent[<u>cd</u>]inden-2β-ol (73)</u>

A stirred emulsion of 2a-methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2<u>H</u>-cyclopent[<u>cd</u>]inden-2-one (63) (622 mg, 3.1 mmol) in ethanol (10 ml) was treated with a solution of sodium borohydride (400 mg, 10.5 mmol) in ethanol (10 ml). After 0.5 h, the clear solution was poured into water (90 ml) and the product extracted with ether (3 x 60 ml). The combined ether layers were washed with water (50 ml), dried ($MgSO_4$), the solvent evaporated and the

residue chromatographed on silica. Elution with 40% ether in petrol gave the title compound (383 mg, 61%), as a viscous oil (Found: m/e 204.1156. $C_{13}H_{16}O_2$ requires m/e 204.1150); ν_{max}(neat) 3420 (OH stretch), 2964 (m), 2932 (m), 1448 (m), 1080 (s), 978 (m), and 728 cm^{-1} (m); λ_{max}(EtOH) 304 nm (log ϵ 3.89); δ_H($CDCl_3$) 0.84 (3H, s, 7b-Me), 1.05 (1H, ddd, $J_{1\alpha,1\beta}$ 10.8 Hz, $J_{1\alpha,2}$ 9.4 Hz, $J_{1\alpha,7a}$ 10.8 Hz, H-1α), 1.52 (1H, br. s, 2-OH), 2.22 (1H, ddd, $J_{1\alpha,1\beta}$ 10.8 Hz, $J_{1\beta,2}$ 6.0 Hz, $J_{1\beta,7a}$ 6.1 Hz, H-1β), 2.35 (1H, ddd, $J_{1\beta,7a}$ 6.1 Hz, $J_{1\alpha,7a}$ 10.8 Hz, $J_{7,7a}$ 6.1 Hz, H-7a), 3.45 (1H, s, 2a-OMe), 4.08 (1H, br., H-2), 5.75 (1H, d, $J_{5,6}$ 5.1 Hz, H-5), 5.86 (1H, dd, $J_{6,7}$ 9.2 Hz, $J_{7,7a}$ 6.1 Hz, H-7), 6.03 (1H, dd, $J_{5,6}$ 5.1 Hz, $J_{6,7}$ 9.2 Hz, H-6), 6.39 (1H, d, $J_{3,4}$ 5.7 Hz, H-3), and 6.61 (1H, d, $J_{3,4}$ 5.7 Hz, H-4); decoupling H-2 at δ4.08 affects the signal at 2.22 for H-1β but not that at 2.35 for H-7a; m/e 204 (M^+), 160 (100%), and 145.

13 Attempted direct dehydration of the alcohol (73)

A solution of the alcohol (73) (30.5 mg, 0.15 mmol) in pyridine (2 ml) was treated with phosphorus oxychloride (100 mg, 0.65 mmol) and the mixture stirred at room temperature. The mixture stayed colourless and a solid precipitated. T.l.c. showed only baseline; there was no starting material or the required olefin. Use of dimethylformamide as the solvent or thionyl chloride as the reagent gave similar results.

14 (2aα,7aα,7bα)-2α-Iodo-2a-methoxy-7a-methyl-2,2a,7a,7b-tetrahydro-1H-cyclopent[cd]indene (74)

A solution of the alcohol (73) (28.7 mg, 0.14 mmol) in dry hexamethylphosphoramide (0.5 ml) was treated with methyltriphenoxyphosphonium iodide (MTPI)[133] (186 mg, 0.41 mmol) and the resulting mixture was stirred overnight at room temperature. The mixture was then treated with sodium hydroxide solution (10% w/v; 5 ml) and stirred at room temperature for 1 h. The mixture was extracted with ether (3 x 5 ml), the combined extracts dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 10% ether in petrol gave the title compound (20.8 mg, 47%), as an oil (Found: m/e 314.0175. $C_{13}H_{15}IO$ requires m/e 314.0170); δ_H($CDCl_3$, 90 MHz) 0.99 (3H, s, 7b-Me), 1.72 (1H, ddd, $J_{1\alpha,1\beta}$ 14 Hz, $J_{1\alpha,2}$ 6 Hz, $J_{1\alpha,7a}$ 12 Hz, H-1α), 2.30 (1H, ddd, $J_{1\alpha,1\beta}$ 14 Hz, $J_{1\beta,2}$ 2 Hz, $J_{1\beta,7a}$ 6 Hz, H-1β), 2.91 (1H, dt, $J_{1\alpha,7a}$ 12 Hz, $J_{1\beta,7a}$= $J_{7,7a}$ 6 Hz, H-7a), 4.40 (1H, dd, $J_{1\alpha,2}$ 6 Hz, $J_{1\beta,2}$ 2 Hz, H-2), 5.79 (1H, d, J 5 Hz, H-5), 6.00 (1H, dd, $J_{7,7a}$ 6 Hz, $J_{6,7}$ 9 Hz, H-7), 6.06 (1H, dd, $J_{5,6}$ 5 Hz, $J_{6,7}$ 9 Hz, H-6), 6.28 (1H, d, J 6 Hz, H-3 or H-4), and 6.49 (1H, d, J 6 Hz, H-4 or H-3); m/e 314 (M^+), 160, and 145.

15 Attepted dehydroiodination of the iodo compound (74)

A mixture of the iodo compound (74) (17 mg, 0.05 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (50 mg, 0.3 mmol) in benzene (2 ml) was refluxed for 1 h. T.l.c. showed no reaction had taken place. Dimethylformamide (1 ml), sodium methoxide (150 mg) and sodium iodide (200 mg)

were added. After further reflux for 1 h, the mixture was poured into water (10 ml) and extracted with ether (3 x 5 ml). The combined extracts were dried ($MgSO_4$), the solvent evaporated and after chromatography, starting material (10 mg, 59%) was recovered.

3.1.7 Synthesis and reactions of the tetraenone, 2a,7b-dihydro-7b-methyl-2H-cyclopent[cd]inden-2-one (78)

1 2a,7b-Dihydro-7b-methyl-2H-cyclopent[cd]inden-2-one (78)

Chlorotrimethylsilane (14.5 ml, 120 mmol) was added to a solution of sodium iodide (17 g, 120 mmol) in dry acetonitrile (160 ml) at room temperature under nitrogen. A mixture of 2a-methoxy-7b-methyl-1,2a,7a,7b-tetrahydro-2H-cyclopent[cd]inden-2-one (63) (4.6 g, 22.7 mmol) and dry triethylamine (16.5 ml, 120 mmol) was then added and the mixture refluxed by external heating with an oil bath at 115°C. After 6 h, the yellow mixture was cooled in ice-water and water (150 ml) added. The mixture immediately became deep red and the product was extracted with ether (4 x 150 ml). The combined ether layers were washed with water (150 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petrol gave the title ketone (3.1 g, 80%), as an orange-red oil; ν_{max} (CCl_4) 2964 (m), 2924 (m), 1702 (s, C=O stretch), 1622 (ms), 1192 (m), 890 (m), 864 (m), 842 (m), and 678 cm^{-1} (m); λ_{max}(EtOH) 252 (log ϵ 4.34), 335 sh (3.11), and 446 nm (3.03); δ_H($CDCl_3$)

1.41 (3H, s, 7b-Me), 3.01 (1H, dd, J 2.2 Hz, 3.4 Hz, H-2a), 4.97 (1H, s, H-1), 5.71 (1H, d, J 5.2 Hz, H-5), 6.21 (1H, dd, J 2.2 Hz, 5.4 Hz, H-4; decoupling of H-2a at δ3.01 removes the smaller coupling; irradiation of H-3 at δ6.86 removes the larger coupling), 6.25 (1H, dd, J 5.2 Hz, 9.4 Hz, H-6), 6.39 (1H, d, J 9.4 Hz, H-7), and 6.86 (1H, dd, J 3.4 Hz, 5.4 Hz, H-3; decoupling of H-2a at δ3.01 removes the smaller coupling); $\delta_C(CDCl_3)$ 22.4 (0.93, 7b-Me), 52.4 (0.28, C-7b), 63.4 (0.89, C-2a), 113.5 (0.98), 114.7 (0.88), 119.6 (0.95), 132.5 (0.95), 132.8 (0.97), 143.8 (1.00), 163.8 (0.23, C-4a), 183.7 (0.18, C-7a), and 211.7 (0.11, C-2); m/e 170 (M^+), 155, 152, 151 (100%), 137, and 115.

Treatment of this ketone with 2,4-dinitrophenylhydrazine in ethanol acidified by sulphuric acid, for 2 h at room temperature gave a precipitate of the 2,4-dinitrophenylhydrazone (77%), as mauve needles, m.p. 180 - 182°C (from ethyl acetate)(Found: C, 61.97; H, 3.99; N, 15.98. $C_{18}H_{14}N_4O_4$ requires C, 61.71; H, 4.03; N, 15.99%); $\delta_H(CDCl_3)$ 1.31 (3H, s, 7b-Me), 3.67 (1H, m, 2aH), 5.47 (1H, s, H-1), 5.79 (1H, d, J 5.4 Hz, H-5), 6.24 (1H, dd, J 5.4 Hz, 9.5 Hz, H-6), 6.35 (2H, m, H-4 and H-7), 6.80 (1H, dd, J 3.4 Hz, 5.6 Hz, H-3), 7.96 (1H, d, J 9.6 Hz, H-6'), 8.28 (1H, dd, J 2.4 Hz, 9.6 Hz, H-5'), 9.10 (1H, d, J 2.4 Hz, H-3'), and 11.57 (1H, br. s, NH).

2 Deuteration of 2a,7b-dihydro-7b-methyl-2H-cyclopent-[cd]inden-2-one (78)

(a) Acidic conditions

A solution of the tetraenone (78) (100 mg) in

carbon tetrachloride (1 ml) was treated with deuterium oxide (99.7 atom %; 1 ml) and toluene-4-sulphonic acid (*ca.* 10 mg), and the mixture refluxed for 30 min. N.m.r. analysis of the organic layer showed that no exchange had taken place.

(b) Basic conditions (two phase)

The mixture from the above reaction was made alkaline with a solution of tetra-*n*-butylammonium hydroxide in methanol (25% w/v; *ca.* 0.1 ml) and warmed at 40°C for 2 h. The organic layer was removed and washed with deuterium oxide (1 ml). Evaporation of the solvent gave 2a,7b-dihydro-7b-methyl-2*H*-cyclopent[*cd*]inden-2-one-2a*d*, as an orange-red oil; δ_H($CDCl_3$; 90 MHz) 1.42 (3H, s, 7b-Me), 4.96 (1H, s, H-1), 5.71 (1H, d, *J* 5 Hz, H-5), 6.21 (1H, d, *J* 5 Hz, H-4), 6.25 (1H, dd, *J* 5 Hz, 9 Hz, H-6), 6.39 (1H, d, *J* 9 Hz, H-7), and 6.84 (1H, d, *J* 5 Hz, H-3).

(c) In dimethyl sulphoxide

A solution of the tetraenone (78) (65 mg) in d_6-dimethyl sulphoxide (1 ml) showed no peaks above tetramethylsilane in the n.m.r. spectrum. A solution of tetra-*n*-butylammonium hydroxide (25% w/v; 1 drop) was added and the mixture heated at 60°C for 1 h. The mixture darkened but its n.m.r. spectrum was unchanged. Deuterium oxide (0.1 ml) was added. After 30 min at room temperature, n.m.r. analysis showed that there was no deuterium exchange but after 1 h at 60°C, deuterium exchange of the 2a-position was complete.

(d) In pyridine

A solution of the tetraenone (78) (65 mg) in pyridine (0.5 ml) was treated with deuterium oxide (0.1 ml). N.m.r. analysis showed partial deuterium exchange had occurred after 30 min at room temperature and complete exchange of H-2a after 10 min at 50°C. The mixture was refluxed for 16 h but there was no further change in the n.m.r. spectrum.

3 7b-Methyl-2-(trimethylsiloxy)-7b*H*-cyclopent[*cd*]-indene (77)

Chlorotrimethylsilane (0.12 ml, 0.93 mmol) was added to a stirred solution of sodium iodide (137 mg, 0.93 mmol) in dry acetonitrile (1 ml) under nitrogen at room temperature. A mixture of the tetraenone (78) (127 mg, 0.75 mmol) and dry triethylamine (0.13 ml, 0.93 mmol) was then added. After 10 min at room temperature, the mixture was extracted with petrol (3 x 2 ml). The combined extracts were concentrated (to 2 ml), filtered, and the filtrate evaporated to give the title compound (128 mg, 74%), as a yellow oil; $\delta_H(CDCl_3)$ -1.51 (3H, s, 7b-Me), 0.42 (9H, s, $SiMe_3$), 7.25 (1H, s, H-1), 7.36 (1H, d, *J* 7.0 Hz, H-7), 7.50 (1H, t, *J* 7.0 Hz, H-6), 7.60 (1H, d, *J* 7.0 Hz, H-5), 7.63 (1H, d, *J* 3.1 Hz, H-4), and 7.79 (1H, d, *J* 3.1 Hz, H-3); $\delta_C(CDCl_3)$ 0.29 (1.00, $SiMe_3$), 29.6 (0.51, 7b-Me), 57.3 (0.10, C-7b), 112.2 (0.36, C-5 or C-7), 115.1 (0.41, C-7 or C-5), 125.0 (0.49, C-1), 128.9 (0.37), 129.9 (0.44), 130.7 (0.42), 156.4 (0.11), 158.8 (0.14), 159.7 (0.09), and 160.3 (0.12).

4 Attempted preparation of a solution of 7b-methyl-7b*H*-cyclopent[*cd*]inden-2-ol (75)

A solution of 7b-methyl-2-(trimethylsiloxy)-7b*H*-cyclopent[*cd*]indene (77) (57 mg, 0.25 mmol) in dry 1,2-dimethoxyethane (DME) (0.5 ml) in an n.m.r. tube was treated with a solution of methyl lithium in ether (1.5 M; 0.2 ml, 0.3 mmol). A deep yellow solution of the lithium enolate of the title compound resulted; δ_H(DME, 60 MHz) -1.45 (3H, s, 7b-Me), 6.92 (1H, s, H-1), 7.0 - 7.4 (4H, m), and 7.77 (1H, d, *J* 3 Hz, H-3); [the starting material gives δ_H(DME, 60 MHz) -1.62 (3H, s, 7b-Me), 7.26 (1H, s, H-1), 7.3 - 7.7 (4H, m), and 7.82 (1H, d, *J* 3 Hz, H-3)]. The solution was cooled to -78°C under nitrogen and treated with a neutral aqueous sodium acetate - acetic acid buffer. The resulting orange-red oil was immediately examined by n.m.r. which showed no signals upfield of tetramethylsilane.

The above preparation of the lithium enolate was repeated from the trimethylsilyl ether (77) (21 mg, 0.09 mmol). The solution was cooled to -78°C under nitrogen and treated with aqueous acetic acid (20% v/v; 0.1 ml, 0.3 mmol). The resulting orange-red mixture was immediately examined by n.m.r. which showed no signals upfield of tetramethylsilane and that the product was the tetraenone (78).

5 2-Methoxy-7b-methyl-7b*H*-cyclopent[*cd*]indene (82)

A solution of the tetraenone (78) (29.5 mg, 0.17 mmol) in dry 1,2-dimethoxyethane (1 ml) was added to

a stirred suspension of potassium hydride (from a dispersion in oil, 25%; 100 mg, 0.6 mmol) in dry 1,2-dimethoxyethane (2 ml) containing 18-Crown-6 (150 mg, 0.6 mmol) under nitrogen at -23°C. The mixture became yellow and then brown. After 15 min, methyl fluorosulphonate (0.1 ml, 1.2 mmol) was added to give a bright yellow solution. Addition of triethylamine (0.5 ml) destroyed the excess methyl fluorosulphonate. The mixture was filtered, the solvent evaporated and the residue chromatographed on silica. Elution with 10% ether in petrol gave 2-methoxy-7b-methyl-7bH-cyclopent[cd]indene (21.3 mg, 67%), as a bright yellow oil (Found: m/e 184.0887. $C_{13}H_{12}O$ requires m/e 184.0888); $\nu_{max}(CCl_4)$ 1464 (m), 1414 (m), 1338 (m), 1168 (m), and 1042 cm^{-1} (m); λ_{max}(EtOH) 234 sh (log ϵ 3.78), 291 (4.70), 326 (3.72), and 459 nm (2.96); $\delta_H(CDCl_3)$ -1.51 (3H, s, 7b-Me), 4.30 (3H, s, OMe), 7.25 (1H, s, H-1), 7.37 (1H, d, J 6.9 Hz, H-7), 7.54 (1H, t, J 6.9 Hz, H-6), 7.60 (1H, d, J 6.9 Hz, H-5), 7.65 (1H, d, J 3.4 Hz, H-4), and 7.91 (1H, d, J 3.4 Hz, H-3); m/e 184 (M^+, 100%), 169, and 141.

6 2a,7b-Dimethyl-2a,7b-dihydro-2H-cyclopent[cd]inden-2-one (83)

(a) From the sodium enolate of the tetraenone (78)

A solution of the tetraenone (78) (81 mg, 0.47 mmol) in dry tetrahydrofuran (1 ml) was added to a stirred suspension of sodium hydride (50% dispersion in oil; 90 mg, 1.9 mmol) in tetrahydrofuran under nitrogen at room temperature. Hydrogen was immediately evolved and iodomethane (0.25 ml, 4 mmol) was added to the deep yellow mixture. After

4 h at room temperature, the excess sodium hydride was destroyed by addition of methanol (0.5 ml) and the mixture then poured into water (20 ml). The product was extracted with ether (2 x 20 ml) and the combined ether layers were washed with water (20 ml), dried (Na_2SO_4) and the solvent evaporated. The residue was chromatographed on silica. Elution with petrol containing an increasing proportion of ether gave (i) 2-methoxy-7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (82) (22 mg, 25%). (ii) <u>The title compound (83)</u> (35 mg, 40%), as an orange-red oil; ν_{max}(neat) 2980 (m), 1694 (s, C=O stretch), 1620 (s), 1576 (m), 1074 (m), 870 (m), 854 (m), 778 (s), 668 (m), and 622 cm^{-1} (m); λ_{max}(EtOH) 252 (log ϵ 4.32), 335 sh (3.09), and 450 nm (2.98); $\delta_H(CDCl_3)$ 1.18 (3H, s, 2a-Me), 1.47 (3H, s, 7b-Me), 4.90 (1H, s, H-1), 5.55 (1H, d, <u>J</u> 5.2 Hz, H-5), 6.02 (1H, d, <u>J</u> 5.3 Hz, H-4), 6.13 (1H, dd, <u>J</u> 5.2 Hz, 9.5 Hz, H-6), 6.32 (1H, d, <u>J</u> 9.5 Hz, H-7), and 6.59 (1H, d, <u>J</u> 5.3 Hz, H-3); <u>m/e</u> 184 (M^+), 179, 156, 155, 141 (100%), and 115. (iii) Starting material (6 mg, 7.5%).

Treatment of the ketone (83) with 2,4-dinitrophenylhydrazine in ethanol acidified with sulphuric acid, for 1 h at 80°C followed by addition of a small quantity of water, gave <u>the 2,4-dinitrophenylhydrazone</u> (63%), as a red powder, m.p. 179 - 181°C (from nitromethane) (Found: C, 62.66; H, 4.52; N, 14.98. $C_{19}H_{16}N_4O_4$ requires C, 62.63; H, 4.43; N, 15.37%).

(b) <u>Using ethanolic sodium hydroxide</u>

A solution of the tetraenone (78) (39 mg, 0.23 mmol) in ethanol (2 ml) under nitrogen at 50°C was treated with

ethanolic sodium hydroxide (5% w/v; 0.5 ml, 1 mmol). To the deep yellow solution was added iodomethane (0.5 ml, 8.0 mmol). The deep yellow colour slowly discharged and a red solution resulted. The addition of reagents was repeated. After 1 h at 50°C, aqueous work up as for part (a) followed by chromatography on silica gave (i) 2-methoxy-7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (82) (9 mg, 21%). (ii) The title compound (83) (18 mg, 42%). (iii) Starting material (6 mg, 16%).

(c) <u>Using sodium hydroxide in aqueous ethanol</u>

This was carried out as for method (b) but ethanol was replaced with aqueous ethanol (50% v/v). Starting with the tetraenone (78) (80 mg) gave (i) 2-methoxy-7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (82) (17 mg, 19%). (ii) The title compound (83) (41 mg, 47%). (iii) Starting material (50 mg, 7%).

(d) <u>Using lithium hydroxide in aqueous ethanol</u>

A solution of the tetraenone (78) (39 mg, 0.23 mmol) and iodomethane (0.5 ml, 8.0 mmol) in ethanol (2 ml) was added to a solution of lithium hydroxide, prepared by dissolution of lithium (0.1 g, 14 mmol) in water (2 ml). The resulting mixture was refluxed under nitrogen for 4 h. More iodomethane (0.5 ml, 8.0 mmol) was then added and the mixture refluxed for a further 4 h. Work-up as for part (a) and chromatography on silica gave (i) 2-methoxy-7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (82) (0.2 mg, 0.5%). (ii) The title compound (83) (8.3 mg, 20%). (iii) Starting material (10.7 mg, 28%).

(e) Using the preformed lithium enolate of the tetraenone (78)

A solution of the tetraenone (78) (76 mg, 0.45 mmol) in dry tetrahydrofuran (1 ml) was added to a stirred suspension of sodium hydride (50% dispersion in oil; 80 mg, 1.7 mmol) in dry tetrahydrofuran (2 ml) at 0°C under nitrogen. After 10 min, a solution of lithium bromide (174 mg, 2.0 mmol) in dry tetrahydrofuran (2 ml) was added followed by iodomethane (0.5 ml, 8.0 mmol). After 3 h at room temperature, the excess sodium hydride was destroyed by addition of methanol (0.5 ml). Work-up as described in part (a) and chromatography on silica gave (i) 2-methoxy-7b-methyl-7b*H*-cyclopent[*cd*]indene (16 mg, 19%). (ii) The title compound (83) (49 mg, 59%).

7 7b-Methyl-7b*H*-cyclopent[*cd*]indene (method 4)

A stirred solution of the tetraenone (78) (3.08 g, 18 mmol) in petrol (100 ml) under nitrogen at 0°C was treated with a solution of diisobutylaluminium hydride in hexane (1 M; 18.2 ml, 18.2 mmol). The mixture immediately lightened to pale yellow. After 20 min at 0°C, methanol (20 ml) was added and the mixture stirred for 3 h at room temperature. The mixture was then filtered through celite and the residue washed with hot methanol (4 x 20 ml). The combined filtrate and washings were evaporated and the residue taken up in dichloromethane (100 ml). Toluene-4-sulphonic acid (1 g) was added and the mixture stirred for 15 min at room temperature. The mixture was then washed with saturated sodium hydrogen carbonate solution (100 ml), then water (100 ml), dried (Na_2SO_4), the

solvent evaporated and the residue chromatographed on silica. Elution with petrol gave 7b-methyl-7b*H*-cyclopent-[*cd*]indene (1) (2.11 g, 76%), as a yellow oil; an analytical sample was prepared by distillation, b.p. 95°C (oven) at 3 mmHg, m.p. 12 - 13°C (Found: C, 93.28; H, 6.59. $C_{12}H_{10}$ requires C, 93.46; H, 6.54%); ν_{max}(neat) 3055 (m), 2970 (m), 2920 (m), 2860 (w-m), 1574 (w-m), 1442 (m), 1376 (w-m), 1360 (w-m), 1338 (w-m), 1332 (m), 1292 (m), 1242 (m), 1036 (w-m), 940 (m), 840 (s), 830 (s), 768 (m), 722 (s), 684 (s), 656 (m), and 622 cm^{-1} (m); λ_{max}(EtOH) 249 sh (log ϵ 3.74), 282 (4.54), 335 sh (3.52), 398 sh (2.11), 439 sh (2.57), and 450 nm (2.64); $\delta_H(CDCl_3)$ -1.67 (3H, s, 7b-Me), 7.53 - 7.83 (3H, AB_2 system giving δ_A 7.57, H-6; δ_B 7.69, H-5 and H-7; J_{AB} 7 Hz), 7.89 - 7.92 (4H, AB system giving δ_A 7.90; δ_B 7.92; J_{AB} 3 Hz, H-1, H-2, H-3 and H-4); $\delta_C(CDCl_3)$ 28.7 (0.57, 7b-Me), 58.7 (0.13, C-7b), 116.2 (0.92, C-5 and C-7), 129.0 (0.52, C-6), 129.3 (1.00, C-2 and C-3), 134.9 (0.94, C-1 and C-4), 159.1 (0.23, C-4a and C-7a), and 178.7 (0.11, C-2a); *m/e* 154 (M^+), 153 (100%), 139, and 76.

8 2a,7b-Dihydro-7b-methyl-2*H*-cyclopent[*cd*]inden-2-ol (84)

A stirred solution of the tetraenone (78) (76 mg, 0.45 mmol) in petrol (5 ml) under nitrogen at 0°C was treated with a solution of diisobutylaluminium hydride in hexane (1 M; 0.5 ml, 0.5 mmol). After 20 min, methanol (0.5 ml) was added, followed by water (2 ml). After 1 h at room temperature, the mixture was filtered through celite and the residue was washed with hot methanol (4 x 5 ml). The combined filtrate and washings were poured

into water (50 ml) and the products extracted with ether (3 x 15 ml). The combined extracts were washed with water (30 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petrol gave unreacted tetraenone (78) (4 mg, 5%). Elution with 40% ether in petrol gave a less polar isomer of the title compound (25 mg, 32%), as an unstable pale yellow solid, m.p. 74 - 76°C (from cold petrol); $\delta_H(CDCl_3$, 60 MHz) 1.03 (3H, s, 7b-Me), 1.20 (1H, m), 3.37 (1H, d, J 10 Hz), 4.84 (1H, m), 4.96 (1H, m), 5.71 (1H, m), and 6.1 - 6.4 (4H, m). Elution with 60% ether in petrol gave a more polar isomer of the title compound (36 mg, 47%), as a pale yellow oil; ν_{max}(neat) 3340 (s, br., OH stretch) 1018 (s, C-O stretch), 854 (s), and 670 cm^{-1} (s); λ_{max}(EtOH) 232 (log ϵ 4.13) and 348 nm (3.40); $\delta_H(CDCl_3)$ 1.18 (3H, s, 7b-Me), 2.22 (1H, br. s, OH), 2.66 (1H, m, H-2a), 4.65 (1H, m, H-2), 4.89 (1H, d, J 2.5 Hz, H-1), 5.66 (1H, d, J 4.9 Hz, H-5), 6.08 (1H, dd, J 4.9 Hz, 9.9 Hz, H-6), 6.20 (2H, m, H-4 and H-7), and 6.54 (1H, dd, J 2.8 Hz, 5.3 Hz, H-3); m/e 172 (M^+), 157, 143, 129, 128 (100%), 127, and 115.

3.1.8 Synthesis and Reactions of 3a-Methyl-3-(trimethylsiloxy)-3aH-indene (85)

1 3a-Methyl-3-(trimethylsiloxy)-3aH-indene (85)

Chlorotrimethylsilane (0.16 ml, 1.3 mmol) was added to a stirred solution of sodium iodide (200 mg, 1.3 mmol) in dry acetonitrile (1 ml) under nitrogen. A mixture of the trienone (46) (150 mg, 1.03 mmol) and dry

triethylamine (0.17 ml, 1.3 mmol) was added and the resulting mixture was stirred at 35°C for 1 h. The product was extracted with petrol (3 x 3 ml) and the bright yellow combined extracts were concentrated under a reduced pressure of nitrogen at room temperature. The residue was chromatographed on silica. Elution with 5% ether in petrol gave the title compound (151 mg, 67%), as an unstable yellow oil; $\delta_H(CDCl_3)$ 0.28 (9H, s, $SiMe_3$), 1.31 (3H, s, 3a-Me), 5.05 (1H, d, J 2.6 Hz, H-2), 5.73 (1H, dd, J 5.1 Hz, 9.0 Hz, with other fine splittings, H-5 or H-6), 5.81 (1H, dd, J 5.1 Hz, 9.1 Hz with other fine splittings, H-6 or H-5), 6.13 (1H, m, H-1), and 6.24 (1H, d, with fine splittings, J 9.1 Hz, H-4 or H-7) and 6.31 (1H, d with fine splittings, J 9.0 Hz, H-7 or H-4).

2 Thermal rearrangement of 3a-methyl-3-(trimethylsiloxy)-3a*H*-indene (85)

A solution of the 3a*H*-indene (85) [prepared from the trienone (46) (122 mg) by the method described above] in benzene (5 ml) was refluxed under nitrogen for 15 min. The mixture was cooled to room temperature, the solvent evaporated and the residue chromatographed on silica. Elution with 5% ether in petrol gave 1-methyl-1-(trimethylsiloxy)-1*H*-indene (86) (65 mg, 37%), as an oil; $\delta_H(CDCl_3$, 90 MHz) 0.12 (9H, s, $SiMe_3$), 1.63 (3H, s, 1-Me), 6.36 (1H, d, J 6 Hz), 6.67 (1H, d, J 6 Hz), and 7.1 - 7.5 (4H, m)

To a solution of this trimethylsilyl ether (48 mg, 0.22 mmol) in tetrahydrofuran (2 ml) and water (0.5 ml) containing potassium fluoride (100 mg, 1.4 mmol) was added

a solution of tetra-n-butylammonium hydroxide in methanol (25% w/v; 2 drops) and the resulting mixture refluxed for 2 h. The mixture was then poured into water (10 ml) and the product extracted with ether (3 x 4 ml). The combined extracts were washed with water (10 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 40% ether in petrol gave 1-methyl-1H-inden-1-ol (87) (16 mg, 50%), as silky needles, m.p. 96 - 98°C (from cold petrol), (lit.,[88] m.p. 96 - 98°C); δ_H($CDCl_3$, 90 MHz) 1.59 (3H, s), 6.34 (1H, d, J 6 Hz), 6.63 (1H, d, J 6 Hz), and 7.1 - 7.5 (4H, m).

3 Dimethyl 7b-methyl-7bH-cyclopent[cd]indene-1,2-dicarboxylate (38) (see also Section 2.1.3)

(a) One pot procedure

A solution of the trienone (46) (200 mg, 1.37 mmol) in dry ether (2 ml) under nitrogen at 10°C was treated with dry triethylamine (0.20 ml, 1.5 mmol) and then with trimethylsilyl trifluoromethanesulphonate (0.26 ml, 1.4 mmol) and the mixture stirred for 1 h. Dimethyl acetylene-dicarboxylate (DMAD) (0.25 ml, 2.0 mmol) was added to the resulting yellow solution of the 3aH-indene (85) and the mixture was stirred at 35°C for 1 h. The solvent was evaporated and the residue taken up in methanol (1 ml). The solution was cooled in ice and concentrated sulphuric acid (1.5 ml) was added dropwise over 5 min. The mixture was stirred for 10 min and poured into ice-water (20 ml). The product was extracted with ether (3 x 10 ml); the combined ether layers were washed with water (20 ml),

dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petrol gave the annulene (38) (201 mg, 54%), as a yellow oil which solidified on cooling, m.p. 49 - 50°C (from petrol, b.p. 60 - 80°C) (Found: C, 71.22; H, 5.24. $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%).

(b) Improved yield procedure

The preparation of the trimethylsilyl ether (85) and its cycloaddition with DMAD were carried out in the same way as described above from the trienone (46) (400 mg, 2.74 mmol). The resulting solution was poured into water (30 ml) and the adduct extracted with ether (2 x 20 ml). The combined ether layers were washed with water (40 ml), dried (Na_2SO_4) and the solvent evaporated. The residue was taken up in benzene (25 ml), toluene-4-sulphonic acid (100 mg) added and the mixture refluxed under nitrogen for 5 h with an apparatus for azeotropic removal of the water formed in the reaction. The mixture was cooled, washed with saturated sodium hydrogen carbonate solution (20 ml) and then water (20 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petrol gave (i) the annulene (38) (307 mg, 42%). (ii) A viscous oil (197 mg) which was heated in refluxing benzene (5 ml) containing toluene-4-sulphonic acid (50 mg) to give more of the annulene (38) (128 mg, 17%) (total yield 435 mg, 59%).

4 2a-Hydroxy-7b-methyl-1,2a,7a,7b-tetrahydro-2H-cyclopent[cd]inden-2-one (88)

A stirred solution of the trienone (46) (1.0 g, 6.85 mmol) in dry 1,2-dimethoxyethane (25 ml) under nitrogen at 0°C was treated with dry triethylamine (1.25 ml, 9.4 mmol) and then trimethylsilyl trifluoromethanesulphonate (1.4 ml, 7.6 mmol). After 1 h, a solution of 2-chloroacryloyl chloride (950 mg, 7.6 mmol) in dry 1,2-dimethoxyethane (2 ml) was added. The yellow colour of the 3aH-indene was discharged and after 30 min, finely powdered sodium azide (2.0 g, 31 mmol) was added and the mixture stirred at room temperature for 6 h. The mixture was filtered and the filtrate refluxed for 2 h. The mixture was cooled to room temperature and 2 : 1 acetic acid - water (20 ml) was added. After 1 h at 55°C, potassium fluoride (4 g) was added. After a further 1 h at 55°C, the mixture was poured into water (150 ml) and the product extracted with ether (4 x 60 ml). The combined ether layers were washed with water (100 ml), then saturated sodium hydrogen carbonate solution (2 x 100 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 50% ether in petrol gave the title ketone (430 mg, 34%), as an oil; ν_{max}(neat) 3440 (s, br., OH stretch), 3045 (m), 2970 (m), 2930 (m), 1734 (s, C=O stretch), 1398 (m), 1216 (m), 1152 (m), 1042 (s), 872 (m), 772 (m), 734 (m), and 632 cm^{-1} (m); λ_{max}(EtOH) 307 (log ϵ 3.78), and 337 sh nm (3.45); $\delta_H(CDCl_3)$ 1.10 (3H, s, 7b-Me), 2.28 (1H, dd, J 12.0 Hz, 16.8 Hz, H-1), 2.47 (1H, dd, J 7.0 Hz, 16.8 Hz, H-1), 2.72 (1H, ddd, J 7.0 Hz, 8.0 Hz, 12.0 Hz, H-7a), 2.91 (1H, br. s, OH), 5.87 (2H, m, H-5 and

H-7), 5.97 (1H, d, J 5.2 Hz, H-3 or H-4), 6.06 (1H, dd, J 5.0 Hz, 8.9 Hz, H-6), and 6.50 (1H, d, J 5.2 Hz, H-4 or H-3); m/e 188 (M^+), 146 (100%, $M^+ - CH_2=C=O$), 145, and 131.

Treatment of this ketone with 2,4-dinitrophenylhydrazine in ethanol acidified with sulphuric acid for 16 h at room temperature gave a precipitate of the 2,4-dinitrophenylhydrazone (35%), as orange crystals, m.p. 225 - 227°C (from nitromethane) (Found: C,58.63; H, 4.35; N, 15.20. $C_{18}H_{18}N_4O_6$ requires C, 58.69; H, 4.38; N, 15.21%).

5 Reaction of the tricyclic ketone (88) with the chlorotrimethylsilane - sodium iodide - triethylamine combination

A mixture of the ketone (88) (193 mg, 1.0 mmol), triethylamine (0.52 ml, 4.0 mmol), chlorotrimethylsilane (0.50 ml, 4.0 mmol) and sodium iodide (600 mg, 4.0 mmol) in dry acetonitrile (6 ml) was refluxed under nitrogen for 1 h. The mixture was cooled to room temperature and extracted with petrol (3 x 10 ml). Evaporation of the solvent gave 2a,3-bis(trimethylsiloxy)-4a,7b-dihydro-7b-methyl-2aH-cyclopent[cd]indene (89) (265 mg, 75%); δ_H($CDCl_3$, 60 MHz) 0.18 (18H, s, 2 x $SiMe_3$), 3.20 (1H, dd, J 2 Hz, 6 Hz, H-4a), 4.50 (1H, d, J 2 Hz, H-4), 5.4 - 6.0 (3H, m, H-5, H-6 and H-7), 6.14 (1H, d, J 5 Hz, H-1 or H-2), and 6.30 (1H, d, J 5 Hz, H-2 or H-1).

Treatment of this product again with the reagents above but with vigorous reflux for 4 h gave only unreacted material (214 mg, 81% recovered). None of the annulene (77) was formed (t.l.c.).

6 4a,7b-Dihydro-7b-methyl-2aH-cyclopent[cd]inden-2a-ol (90)

A mixture of the tricyclic ketone (88) (234 mg, 1.24 mmol) and 2,4,6-triisopropylbenzenesulphonylhydrazine (408 mg, 1.36 mmol) in dichloromethane (6 ml) containing Amberlite resin IR120(H) (100 mg) was stirred at room temperature for 2 h. The cloudy mixture was dried with sodium sulphate and filtered. The solvent was evaporated and the residue chromatographed on silica. Elution with 1 : 1 : 2 ether - dichloromethane - petrol gave the 2,4,6-triisopropylbenzenesulphonylhydrazone (mixture of isomers; 554 mg, 95%), as a foam.

A solution of this hydrazone (200 mg, 0.43 mmol) in benzene (8 ml) was treated with a solution of methyl lithium in ether (1.3 M; 2.0 ml, 2.56 mmol) at 0°C under nitrogen and then for 1 h at room temperature. The mixture was cooled in ice-water and water (10 ml) added. The products were extracted with ether (2 x 10 ml), the combined organic layers washed with water (10 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petrol gave the title compound (26 mg, 35%), as an unstable solid, m.p. 88 - 90°C (from cold petrol) (Found: m/e 172.0884. $C_{12}H_{12}O$ requires m/e 172.0888); $\nu_{max}(CCl_4)$ 3610 (m, sharp, OH stretch), 3500 - 3000 (w, br., OH stretch), 3020 (m), 2960 (m), 1150 (m), 1056 (s, C-O stretch), and 624 cm^{-1} (s); λ_{max}(EtOH) 310 nm (log ϵ 3.65); $\delta_H(CDCl_3)$ 1.02 (3H, s, 7b-Me), 1.86 (1H, br.s, OH), 3.34 (1H, m, H-4a), 5.7 - 5.85 (3H, m, H-3, H-5 and H-7), 5.96 (1H, dd, $J_{4,4a}$ 1.8 Hz, $J_{4a,5}$ 5.8 Hz, H-4), 6.02 (1H, dd, $J_{6,7}$ 5.2 Hz, $J_{5,6}$ 9.2 Hz,

H-6), 6.18 (1H, d, J 5.5 Hz, H-3 or H-4), and 6.34 (1H, d, J 5.5 Hz, H-4 or H-3); m/e 172 (M^+), 157 (100%), 129, and 128. Elution with 35% ether in petrol gave an isomer of the starting hydrazone (71 mg, 36%). This isomer did not give any of the title compound after further treatment with excess methyl lithium at 40°C in benzene, but was recovered unreacted.

7 7b-Methyl-7bH-cyclopent[cd]indene (method 5)

A solution of the 2,4,6-triisopropylbenzenesulphonylhydrazone (100 mg, 0.53 mmol) of the tricyclic ketone (88) in benzene (5 ml) was treated with a solution of methyl lithium in ether (1.3 M; 3 ml, 3.9 mmol). After 2 h at room temperature, water (10 ml) was added and the tetraene (90) extracted with ether (3 x 20 ml). The ether layers were dried ($MgSO_4$) and the solvent evaporated. The residue was taken up in dichloromethane (2 ml) and acidified with toluene-4-sulphonic acid (15 mg). The mixture was stirred at room temperature for 3 h and then washed with saturated sodium hydrogen carbonate solution (2 ml). The solvent was evaporated and the residue chromatographed on silica. Elution with petrol gave 7b-methyl-7bH-cyclopent-[cd]indene (7.1 mg, 22%).

8 Conversion of the tricyclic ketone (88) into the tetraenone (78)

A stirred solution of the tricyclic ketone (88) (79 mg, 0.42 mmol) in pyridine (1 ml) was treated with methanesulphonyl chloride (0.3 ml, 3.7 mmol). After 1 h

at room temperature, the mixture was poured into water (20 ml) and ether (20 ml), and acidified with dilute sulphuric acid (2 M; 10 ml). The ether layer was removed and the aqueous layer extracted with ether (20 ml). The combined ether layers were washed with water (20 ml), dried (Na_2SO_4) and the solvent evaporated. The crude mesylate was taken up in carbon tetrachloride (2 ml) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (200 mg, 1.3 mmol) added. The mixture became warm and orange-red. Aqueous work-up as for the first part of this experiment and chromatography on silica gave the tetraenone (78) (26.0 mg, 36%)

In an earlier experiment, the mesylate was purified by chromatography on silica (eluting with 20% ether in petrol) and gave an oil (35% form the tricyclic ketone (88)); $\delta_H(CCl_4$, 90 MHz) 1.19 (3H, s, 7b-Me), 1.93 (1H, dd, J 11 Hz, 18 Hz, H-1α), 2.53 (1H, dd, J 8 Hz, 18 Hz, H-1β), and 5.8 - 6.7 (5H, m).

Treatment of this mesylate with DBU in carbon tetrachloride as above gave the tetraenone (78) (88% from the mesylate).

3.1.9 Attempted Synthesis of 7b-Methyl-7b*H*-cyclopent[*cd*]-inden-1-ol

1 Oxidation of 4a,7b-dihydro-7b-methyl-2a*H*-cyclopent-[*cd*]inden-2a-ol with pyridinium chlorochromate

A stirred solution of 4a,7b-dihydro-7b-methyl-2a*H*-cyclopent[*cd*]inden-2a-ol (90) (9.0 mg, 0.05 mmol) in dichloromethane (2 ml) at room temperature was treated

with pyridinium chlorochromate.[134] The mixture rapidly went brown. T.l.c. showed that the starting material was consumed but to give a complex mixture.

2 Cycloaddition of 3a-methyl-3-(trimethylsiloxy)-3a<u>H</u>-indene (85) with dichloroketene

A stirred solution of the trienone (46) (400 mg, 2.7 mmol) in dry ether (4 ml) at 0°C under nitrogen was treated with dry triethylamine (0.45 ml, 3.4 mmol) and then with trimethylsilyl trifluoromethanesulphonate (0.51 ml, 3.4 mmol). After 1 h at 0°C, more dry triethylamine (0.45 ml, 3.4 mmol) was added. The mixture was warmed to reflux and a solution of dichloroacetyl chloride (500 mg, 3.4 mmol) in petrol (4 ml) was added dropwise over 10 min. After further reflux for 30 min, the mixture was poured into water (20 ml) and the product extracted with ether (3 x 10 ml). The combined ether layers were washed with water (10 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petrol gave 7-dichloroacetyl-7,7a-dihydro-7a-methyl-1<u>H</u>-inden-1-one (92) (30 mg, 43%), as pale yellow prisms, m.p. 100 - 101°C (from dichloromethane - petrol) (Found: C, 55.90; H, 3.88; Cl, 27.34. $C_{12}H_{10}Cl_2O_2$ requires C, 56.06; H, 3.92; Cl, 27.58%); $\nu_{max}(CCl_4)$ 1712 (s, C=O stretch), 1122 (m), 1094 (m), 874 (m), and 624 cm^{-1} (m); λ_{max}(EtOH) 241 (log ϵ 3.84) and 338 nm (3.82); $\delta_H(CDCl_3)$ 1.12 (3H, s, 7a-Me), 4.09 (1H, dd, <u>J</u> 1.2 Hz, 6.9 Hz, H-7), 5.97 (1H, s, C<u>H</u>Cl_2), 6.13 (1H, d, <u>J</u> 5.3 Hz, H-4), 6.21 (1H, dd, <u>J</u> 6.9 Hz, 9.3 Hz, H-6), 6.45 (1H, ddd, <u>J</u> 1.2 Hz, 5.3 Hz, 9.3 Hz, H-5), 6.50 (1H, d, <u>J</u>

5.4 Hz, H-2) and 7.78 (1H, d, J 5.4 Hz, H-3); m/e 260-258-256 (1 : 6 : 9, M^+), 145 (100%, M^+-Cl_2CHCO), 117, 115, and 91.

3 Dechlorination of the dichloroketone (92) with tributyltin hydride

A solution of the dichloroketone (92) (264 mg, 1.03 mmol) in dry degassed benzene (10 ml) containing azoisobutyronitrile (AIBN) (50 mg, cat.) was added over 30 min to a refluxing solution of tributyltin hydride[94] (0.3 ml, 1.03 mmol) in dry degassed benzene (10 ml). The resulting mixture was refluxed for 5 h, the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petrol gave unreacted starting material (60 mg, 19%). Elution with 80% ether in petrol gave 7-chloroacetyl-7,7a-dihydro-7a-methyl-1H-inden-1-one (93) (139 mg, 52%, 65% based on unrecovered starting material), as a red oil (Found: m/e 222.0451. $C_{12}H_{11}O_2{}^{35}Cl$ requires m/e 222.0448); ν_{max}(neat) 1710 (s, C=O stretch), 1144 (m), 1092 (m), 874 (m), and 606 cm^{-1} (m); λ_{max}(EtOH) 237 (log ϵ 3.88), 287 sh (3.57), and 332 nm (3.83); $\delta_H(CDCl_3)$ 1.09 (3H, s, 7a-Me), 3.89 (1H, d, J 7.1 Hz, H-7), 4.09 (2H, ABq, J_{AB} 15.3 Hz, CH_2Cl), 6.10 (1H, d, J 5.4 Hz, H-4), 6.21 (1H, dd, J 7.1 Hz, 9.2 Hz, H-6), 6.41 (1H, dd, J 5.4 Hz, 9.2 Hz, H-5), 6.49 (1H, d, J 5.6 Hz, H-2) and 7.75 (1H, d, J 5.6 Hz, H-3); m/e 224-222 (1 : 2, M^+), 145 (100%, M^+-ClCH_2CO), 131, 117, 115, 102, and 91.

4 7-Acetyl-7,7a-dihydro-7a-methyl-1H-inden-1-one (95)

A solution of the chloroketone (93) (137 mg,

0.62 mmol) was added to a stirred solution of sodium iodide (460 mg, 3.1 mmol) in acetone (10 ml). After 1 h, the dark mixture was filtered and the filtrate diluted with ether (30 ml). The mixture was again filtered and the solvent evaporated. The residue was extracted with dichloromethane (5 x 2 ml). The combined extracts were filtered and the solvent evaporated to give the iodoketone (94) (177 mg, 91%) as a red oil; $\delta_H(CDCl_3$, 90 MHz) 1.07 (3H, s, 7a-Me), 3.89 (2H, ABq, J_{AB} 11 Hz, CH_2I), 4.04 (1H, d, J 7 Hz, H-7), 6.13 (1H, d, J 5 Hz, H-4), 6.22 (1H, dd, J 5 Hz, 9 Hz, H-6), 6.44 (1H, dd, J 5 Hz, 9 Hz, H-5), 6.52 (1H, d, J 6 Hz, H-2), and 7.77 (1H, d, J 6 Hz, H-3).

A solution of the iodoketone (94) (59 mg, 0.19 mmol) and tributyltin hydride (0.1 ml, 0.3 mmol) in dry degassed benzene (5 ml) containing azoisobutyronitrile (AIBN) (10 mg, cat.) was refluxed under nitrogen. After 30 min, the solvent was evaporated and the residue chromatographed on silica. Elution with ether gave the title compound (45) (29 mg, 83%), as an oil; ν_{max}(neat) 1696 (s, C=O stretch), 1352 (m), 824 (m), 734 (m), and 718 cm^{-1}(m); λ_{max}(EtOH) 235 (log ϵ 3.76), 282 (3.54), and 337 nm (3.80); $\delta_H(CDCl_3)$ 1.04 (3H, s, 7a-Me), 2.12 (3H, s, COMe), 3.60 (1H, d, J 6.7 Hz, H-7), 6.07 (1H, d, J 5.0 Hz, H-4), 6.20 (1H, dd, J 6.7 Hz, 9.0 Hz, H-6), 6.34 (1H, dd, J 5.0 Hz, 9.0 Hz, H-5), 6.49 (1H, d, J 5.3 Hz, H-2), and 7.71 (1H, d, J 5.3 Hz, H-3); m/e 188 (M^+), 145 (100%), 131, 117, and 115.

Treatment of this diketone with 2,4-dinitrophenylhydrazine in ethanol acidified by sulphuric acid for 2 h at room temperature, followed by cooling in ice, gave a

precipitate of the mono-2,4-dinitrophenylhydrazone (30%), as yellow-orange crystals, m.p. 161 - 162°C (from ethanol) (Found: C, 58.81; H, 4.42; N, 15.15. $C_{18}H_{16}N_4O_5$ requires C, 58.69; H, 4.38; N, 15.21%).

5 Attempted intramolecular aldol condensation of the diketone (95)

A stirred solution of the diketone (95) (15 mg, 0.07 mmol) in methanol (1 ml) was treated with a solution of potassium hydroxide in methanol (5% w/v; 1 ml, 0.9 mmol). An initial deep blue colour subsided and the resulting mixture was deep yellow-brown. After 5 min, a mixture of acetic acid (0.2 ml) and ether (8ml) was added. The mixture was washed with saturated sodium hydrogen carbonate solution (2 x 5 ml) and then water (10 ml), dried (Na_2SO_4) and the solvent evaporated. N.m.r. examination of the residue (14 mg) showed it was a complex mixture and its t.l.c. was mostly baseline.

Treatment of the diketone (95) with toluene-4-sulphonic acid in refluxing benzene also gave a complex mixture (t.l.c.). Treatment of the diketone (95) with sulphuric acid in methanol at room temperature also gave no recognisable products.

6 Cycloaddition of 3-methoxy-3a-methyl-3aH-indene (37) with dichloroketene

A solution of the 3aH-indene (37) in 1,2-dimethoxyethane was prepared as described in Section 3.1.3 from the trienone (46) (400 mg, 2.74 mmol). The mixture was

filtered and the filtrate treated with triethylamine (1.0 ml, 6.9 mmol). The mixture was warmed to 40°C and dichloroacetyl chloride (600 mg, 4.1 mmol) was added over 15 min. After a further 30 min, the mixture was poured into water (50 ml) and extracted with ether (3 x 20 ml). The combined ether extracts were washed with water (40 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with petrol containing an increasing proportion of ether gave complex mixtures and an oil (108 mg), the n.m.r. spectrum of which showed it to be a mixture of adducts. Attempts to isolate a pure adduct by further chromatography on silica were unsuccessful.

7 Attempted hydrolysis of the 2-chloroacrylonitrile adducts (60a) and (60b)

(a) With sodium hydroxide

A solution of a 3 : 2 mixture of the adducts (60a) and (60b) (12.2 mg, 0.05 mmol) in ethanol (0.5 ml) was added to a stirred solution of sodium hydroxide (20 mg, 0.05 mmol) in ethanol (0.5 ml) and dimethyl sulphoxide (0.3 ml) at reflux under nitrogen. After 15 min, all of the starting material was consumed (t.l.c.). The mixture was poured into water (10 ml) and the product extracted with ether (2 x 5 ml). The ether layers were washed with water (10 ml), the solvent evaporated and the residue chromatographed on silica. Elution with 20% ether in petrol gave a mixture of the annulenenitriles (67a) and (67b) (7.0 mg, 79%).

(b) With sodium sulphide

A solution of a 3 : 2 mixture of the adducts (60a) and (60b) (43.7 mg, 0.17 mmol) in ethanol (2 ml) was treated with sodium sulphide (30%; 130 mg, 0.5 mmol) and the mixture stirred at room temperature. After 6 h, the mixture was poured into water (10 ml) and extracted with ether (3 x 2 ml). The combined ether layers were washed with water (5 ml), dried (Na_2SO_4), and the solvent evaporated to give a yellow oil (29 mg), its n.m.r. spectrum showed it to be a complex mixture. Attempts to isolate a single compound by further chromatography on silica were not successful.

3.2 Reactions of 7b-Methyl-7bH-cyclopent[cd]indene (1)

3.2.1 Thermal rearrangements

1 Kinetic measurements

A solution of the annulene (ca. 5 mg) in distilled decalin (8 ml) under nitrogen was heated in the vapour of a suitable solvent (130 ml), boiling in the range 109 - 190°C. After the temperature of the annulene solution had stabilised (ca. 10 min), aliquots (2 ml) were withdrawn at intervals of 15 min - 2 h, and measurements made of the absorbance of the solution at the wavelength of the visible absorption maximum of the compound (450 - 500 nm). Graphs of the logarithm of the absorbance/initial absorbance against time were generally linear and the rate constant was determined by the slope of the graph. The results are presented in Table 7 (Section 2.2.1).

2 Thermal rearrangement of 7b-methyl-7b*H*-cyclopent[*cd*]-indene (1) in solution

(a) G.l.c. analysis

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (10.7 mg) in xylene (4 ml) was refluxed under nitrogen and the composition of the mixture analysed by g.l.c. (Squalene on Chromosorb P column, oven temperature 150°C) which showed formation of a new compound of shorter retention time. Relative percentages of the starting material and the product after given times are as follows: 0 h, 100, 0%; 2 h, 87, 13%; 3.7 h, 81, 19%; 5.8 h, 71, 29%; 7 h, 67, 33%; 10.2 h, 71, 29%; 29 h, 38, 62%; 48 h, 30, 70%; 70 h, 23, 76%. The earlier results give a half life value of the annulene (1) of 11.7 (±0.5) h.

(b) Preparative reaction

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (26 mg) in xylene (7 ml) was refluxed for 24 h. The solvent was removed by evaporation and the residue chromatographed on silica. Elution with petrol gave a 1 : 1 mixture (4.8 mg) of starting material (9%) and 2a-methyl-2a*H*-cyclopent[*cd*]indene (99) (9%); spectral data are given below.

3 Flash vacuum pyrolysis of 7b-methyl-7b*H*-cyclopent-[*cd*] indene (1)

(a) At 400°C

7b-Methyl-7b*H*-cyclopent[*cd*]indene (1) (33.0 mg) was distilled up a hot tube at 400°C and 2 mm Hg and the product

collected on a cold finger at -78°C. The product was isolated by removal of the coolant, washing of the cold finger with petrol (2 x 25 ml), and evaporation of the solvent under reduced pressure to give a pale yellow oil (28 mg) which contained 10% of unreacted starting material (n.m.r.). This oil was resubjected to the above conditions but at 3 mmHg to give 2a-methyl-2a*H*-cyclopent[*cd*]indene (99) (25.3 mg, 78%), as an oil; λ_{max}(EtOH) 258 (log ϵ 4.04), 318 sh (2.50), and 331 sh nm (2.41) nm; $\delta_H(CDCl_3)$ 1.48 (3H, s, 2a-Me), 6.59 (2H, d, *J* 5 Hz, H-2 + H-3), 6.70 (2H, d, *J* 5 Hz, H-1 + H-4), and 6.95 - 7.20 (3H, AB_2 system giving δ_A 6.14, H-6 and δ_B 5.99, H-5 + H-7; J_{AB} 7 Hz); $\delta_C(CDCl_3)$ 23.6 (0.16, C-2a), 118.5 (1.00), 129.7 (0.68, C-6), 131.8 (0.98), 142.5 (0.21, C-4a + C-7a), 145.1 (0.98), and 169.5 (0.07, C-7b).

(b) At 700°C

7b-Methyl-7b*H*-cyclopent[*cd*]indene (1) (28.4 mg) was distilled up a tube at 700°C and 0.2 mmHg The yellow pyrolysate was extracted with petrol (3 x 25 ml) and the solvent evaporated to give a yellow-brown oil (26.8 mg) which was chromatographed on silica. Elution with petrol and collection of the initial pale yellow band gave mainly a 2 : 1 mixture of 2-methyl-1*H*-cyclopent[*cd*]indene (101) and 3-methyl-1*H*-cyclopent[*cd*]indene (102) (18.0 mg, 62%), as an oil; $\delta_H(CDCl_3)$ 2.30 (3H x 1/3, fine d, 3-Me of (102)), 2.39 (3H x 2/3, s, 2-Me of (101)), 3.99 (2H, br. s, 1-CH_2), 6.4 - 7.0 (2H, m), and 7.1 - 7.4 (3H, m). A minor component was also present in the mixture giving $\delta_H(CDCl_3)$ 7.53 (1H, dd, *J* 7 Hz, 8 Hz), 7.68 (1H, d, *J* 7 Hz), and 7.80 (1H, d, *J* 8 Hz).

(c) At 600°C

7b-Methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (36.4 mg) was distilled up a tube at 600°C and 0.3 mmHg. The yellow pyrolysate was extracted with petrol (3 x 25 ml) and the solvent evaporated to give an orange oil which was chromatographed on silica. Elution with petrol and collection of the initial pale yellow band gave a 2 : 1 mixture of 2-methyl-1<u>H</u>-cyclopent[<u>cd</u>]indene (101) and 3-methyl-1<u>H</u>-cyclopent[<u>cd</u>]indene (102) (27.5 mg, 76%), as an oil; λ_{max}(EtOH) 227 (log ϵ 3.91). 249 sh (3.99), 258 (4.05), 263 (4.03), 274 sh (3.76), 317 (3.68), and 330 sh nm (3.54). A later bright yellow band from the column gave a mixture (8.8 mg).

3.2.2 Photolysis of 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (1)

1 At 300 nm

A solution of 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (1) (28.1 mg) in petrol (200 ml) was irradiated in a Rayonet reactor at 300 nm for 15 h at room temperature. The electronic spectrum of the mixture was unchanged. The solvent was evaporated and the residue chromatographed on silica. Elution with petrol gave starting material (27.7 mg, 99%).

2 At 254 nm

A solution of 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (1) (55.1 mg) in petrol (200 ml) was irradiated in a Rayonet reactor at 254 nm for 24 h at room temperature. The electronic spectrum of the mixture showed that 25 - 30% of

the starting material was consumed. Some solid had coated the walls of the reaction vessel. Evaporation of the solution gave a bright yellow oil (48.9 mg). This oil was chromatographed on silica. Elution with petrol gave a yellow oil (40.1 mg). Its n.m.r. spectrum showed that it was mainly starting material but some material with resonances in the range δ6.7 - 7.4 was present. No new products could be identified.

3.2.3 Hydrogenation

1 Hydrogenation of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1)

7b-Methyl-7b*H*-cyclopent[*cd*]indene (22.9 mg, 0.15 mmol) was introduced to a shaken suspension of 5% palladium on charcoal (55 mg) in ethanol (12 ml) under hydrogen at 750 mmHg and 16.1°C. Hydrogenation was complete in 0.5 h when 16.72 ml (0.75 mol, 5.0 equivalents) of hydrogen were taken up by the annulene. The reaction mixture was filtered through celite, the filtrate poured into water (100 ml), and the product extracted with petrol (3 x 50 ml). The combined petrol extracts were washed with water (50 ml), dried ($MgSO_4$), and the solvent evaporated to give decahydro-7b-methyl-1*H*-cyclopent[*cd*]indene (103) (14.1 mg, 58%), as a colourless oil (Found: *m/e* 164.1562. $C_{12}H_{20}$ requires *m/e* 164.1565); $\delta_H(CDCl_3)$ 1.13 (3H, s, 7b-Me) and 1.0 - 1.7 (17H, m); *m/e* 164 (M^+), 149, 136, 135, and 121.

2 Hydrogenation of 2a-methyl-2a*H*-cyclopent[*cd*]indene (99)

A solution of 2a-methyl-2a*H*-cyclopent[*cd*]indene (99) (*ca.* 8 mg) in ethanol (12 ml) was hydrogenated over

5% palladium on charcoal (11 mg) at 751 mmHg and 16.5°C. Accurate readings were not obtained for the quantity of hydrogen taken up but it was apparent that there was a fairly rapid uptake (*ca.* 30 min) followed by a much slower uptake. After 24 h, the mixture was filtered through celite and the solvent evaporated to give an oil. Mass spectrometry showed ions at *m/e* 158, 162, and 164 with corresponding M^+-15 ions at 143, 147, and 149.

3.2.4 Reactions involving electron transfer

1 Attempted preparation of a picrate of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1)

To a solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (17.6 mg, 0.114 mmol) in ethanol (0.5 ml) was added a hot solution of picric acid in ethanol (0.55 mmol/ml; 0.5 ml, 0.28 mmol). The resulting orange solution was warmed on a steam bath for 5 min and then cooled in ice. The crystals which separated were picric acid, m.p. 121 - 123°C. T.l.c. showed the solution to still contain the annulene and on dilution, the electronic spectrum of the mixture was that of a mixture of the starting materials.

2 Reaction of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) with potassium

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (19 mg) in dry tetrahydrofuran (1 ml) was treated with freshly cut potassium (50 mg) and the mixture stirred under nitrogen at room temperature. A red colour developed on the surface of the potassium. The solution became deep

red and all of the annulene was consumed (t.l.c.). On standing, the solution turned brown.

3 Birch reduction of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1)

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (29 mg, 0.19 mmol) in dry tetrahydrofuran (3 ml) was added to a stirred solution of sodium (*ca*. 5 mg, 0.22 mmol) in liquid ammonia (10 ml) under nitrogen at -33°C. The resulting orange mixture was treated with further sodium (*ca*. 5 mg, 0.22 mmol), and after 10 min, ammonium chloride (50 mg) was added. The resulting mixture was pale yellow. The ammonia was evaporated, the mixture poured into water (10 ml) and the products extracted with petrol (3 x 5 ml). The combined petrol layers were dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with petrol gave a pale yellow oil (22 mg). N.m.r showed this oil was a mixture and about 10% of the annulene was unreduced. No products could be identified. The mass spectrum showed that the oil was mainly a mixture of dihydro and tetrahydro products giving M^+ ions at *m/e* 156 and 158 respectively, and corresponding M^+-15 ions at *m/e* 141 and 143.

3.2.5 Attempted lithiation of 7b-methyl-7b*H*-cyclopent[*cd*]-indene (1)

A solution of *n*-butyl lithium in hexane (1.5 M; 0.2 ml, 0.3 mmol) was added to a stirred solution of tetramethylethylenediamine (0.1 ml) in petrol (1 ml) under nitrogen. After 10 min at room temperature, a solution of

7b-methyl-7b*H*-cyclopent[*cd*]indene (39 mg, 0.25 mmol) in petrol (2 ml) was added. The mixture immediately became deep red. After 1 h at room temperature, the mixture was poured into ether (20 ml) containing an excess of solid carbon dioxide. The mixture was acidified with acetic acid (0.2 ml), filtered, the solvent evaporated, and the residue chromatographed on silica. Elution with petrol gave starting material (0.6 mg, 2%). Elution with 30% ether in petrol gave a bright yellow oil (20 mg). N.m.r. showed this oil was a mixture of olefinic compounds and that the butyl group had been incorporated. There were no signals upfield of tetramethylsilane.

No reaction occurred when the tetramethylethylenediamine was omitted from the above experiment.

Treatment of the annulene (1) with an equivalent of *tert*-butyl lithium in petrol at room temperature for 3 h, followed by work-up as above, gave unreacted starting material (73%).

3.2.6 Cycloaddition reactions

1 With dimethyl acetylenedicarboxylate (DMAD)

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (39 mg, 0.25 mmol) and DMAD (180 mg, 1.25 mmol) in toluene (2 ml) was refluxed under nitrogen for 10 h. The solvent was then evaporated and the residue chromatographed on silica. Elution with petrol gave the starting annulene (1) (23 mg, 57%). No adducts could be isolated.

2 With maleic anhydride

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1)

(6.5 mg, 0.04 mmol) and maleic anhydride (54 mg, 0.55 mmol) in toluene (1 ml) was refluxed under nitrogen for 8 h. The solvent was then evaporated. N.m.r. analysis of the residue showed that it was mainly maleic anhydride and unreacted annulene (1). Resonances in the ranges 1.1 - 1.6, 3.0 - 3.5, and 5.6 - 7.0 were present but no product could be identified. This residue was chromatographed on silica. Elution with petrol gave the starting annulene (1) (3.2 mg, 50%).

3 With tetracyanoethylene

Tetracyanoethylene (57 mg, 0.44 mmol) was added to a solution of 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (1) (34 mg, 0.22 mmol) in dry 1,2-dimethoxyethane (5 ml). A dark green colour immediately developed and the electronic spectrum of the mixture showed a weak but very broad absorption band with a maximum at 650 nm. The mixture was refluxed under nitrogen for 2 h, poured into water (30 ml), and extracted with petrol (2 x 15 ml). The petrol layers were dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with petrol gave unreacted annulene (1) (28 mg, 82% recovered).

4 With benzyne

A stirred solution of 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]-indene (1) (49 mg, 0.32 mmol) in dry 1,2-dimethoxyethane (2 ml) containing benzenediazonium carboxylate[106] (200 mg, 1.4 mmol) was warmed under nitrogen to 45°C. After 12 h, the dark red mixture was poured into water (10 ml) and extracted with ether (3 x 3 ml). The ether extracts were dried, the solvent evaporated and the residue chromatographed on silica. Elution with petrol gave the annulene (1) (28 mg,

57%). Elution with dichloromethane gave products derived from the benzyne (98 mg).

5 With 4-phenyl-1,2,4-triazole-3,5-dione (PTAD)

(a) With 2 equivalents of PTAD

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (34 mg, 0.22 mmol) and PTAD[135] (78 mg, 0.44 mmol) in dry freshly distilled 1,2-dimethoxyethane (10 ml) was refluxed under nitrogen for 1 h. The solvent was then evaporated and the residue chromatographed on silica. Elution with 5 : 3 : 2 ether - petrol - dichloromethane gave the 2 : 1 adduct (110) (85 mg, 75%), as fine needles which decompose at 150°C without melting (from 1 : 1 : 1 ethyl acetate - ether - petrol) (Found: C, 66.59; H, 4.00; N, 16.59. $C_{28}H_{20}N_6O_4$ requires C, 66.66; H, 4.00; N, 16.66%); $\nu_{max}(CCl_4)$ 1794 (m), 1776 (m), 1724 (s), and 1408 cm^{-1} (s); λ_{max}(EtOH) 242 sh (log ϵ 3.96) and 290 sh nm (3.49); $\delta_H(CDCl_3)$ 1.13 (3H, s), 5.40 (1H, d, *J* 10.0 Hz, H-1)*, 6.13 (1H, d, *J* 9.0 Hz, becomes a singlet on decoupling at 6.53, H-7), 6.30 (1H, d, *J* 5.5 Hz, H-5), 6.53 (1H, dd, *J* 5.5 Hz, 9.0 Hz, H-6), 6.75 (1H, d, *J* 6.0 Hz, becomes a singlet on decoupling at 7.80, H-4)*, 7.20 (1H, d, *J* 10.0 Hz, becomes a singlet on decoupling at 5.40, H-2), 7.23 - 7.53 (10H, m, 2 x Ph), and 7.89 (1H, d, *J* 6.0 Hz, H-3). Signals marked with an asterix show a singlet within the doublet when the adduct is prepared from 2-deuterated starting material. See Fig. 12 for the n.O.e. results on which the above spectral assignments are based.

(b) With 1 equivalent of PTAD

Reaction of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (23.5 mg, 0.15 mmol) and PTAD (26.7 mg, 0.15 mmol) in 1,2-

dimethoxyethane (3 ml) as above gave the starting annulene (1) (11.4 mg, 49%) and the 2 : 1 adduct (110) (31.3 mg, 41%).

6 Reaction of 2-methoxy-7b-methyl-7bH-cyclopent[cd]indene (82) with 4-phenyl-1,2,4-triazole-3,5-dione (PTAD)

A solution of 2-methoxy-7b-methyl-7bH-cyclopent[cd]-indene (82) (19 mg, 0.10 mmol) in dichloromethane (2 ml) was treated with a solution PTAD (18 mg, 0.10 mmol) in dichloromethane (2 ml) and the mixture stirred at room temperature. After 15 min, the colour of the reagent was discharged. The solvent was evaporated and the residue chromatographed on silica. Elution with 60% ether in petrol gave the 2 : 1 adduct (111) (7.5 mg, 14%), as an unstable solid which decomposed without melting at 135°C (from petrol - dichloromethane); $\delta_H(CDCl_3)$ 1.12 (3H, s), 3.81 (3H, s, 2a-OMe), 4.90 (1H, s, H-1), 6.13 (1H, d, J 9.2 Hz, H-7), 6.30 (1H, d, J 5.4 Hz, H-5), 6.47 (1H, dd, J 5.4 Hz, 9.2 Hz, H-6), 6.72 (1H, d, J 5.9 Hz, H-4), 7.25 - 7.50 (10H, m, Ph), and 7.75 (1H, d, J 5.9 Hz, H-3).

7 Reaction of 7b-methyl-2-(trimethylsiloxy)-7bH-cyclopent[cd]indene (77) with 4-phenyl-1,2,4-triazole-3,5-dione (PTAD)

A solution of 7b-methyl-2-(trimethylsiloxy)-7bH-cyclopent[cd]indene (77) (25.0 mg, 0.11 mmol) in dichloromethane (1 ml) was treated with a solution of PTAD (18.9 mg, 0.11 mmol) in dichloromethane (1 ml) and the mixture stirred at room temperature. After 10 min, the solvent was evaporated and the residue chromatographed on silica. Elution with ether gave the urazole (113) (19.4 mg, 54%), as orange-red crystals, m.p. 223 - 225°C decomp. (from 1 : 1 : 1 petrol - ethyl acetate - dichloromethane) (Found: C, 69.41; H, 4.33; N, 12.11. $C_{20}H_{15}N_3O_3$ requires C, 69.56; H, 4.38; N, 12.17%);

$\delta_H(CDCl_3)$ 1.66 (3H, s, 7b-Me), 5.21 (1H, s, H-1), 5.68 (1H, d, J 5.0 Hz, H-5), 6.13 (1H, dd, J 5.0 Hz, 9.9 Hz, H-6), 6.32 (1H, d, J 5.4 Hz, H-4), 6.40 (1H, d, J 9.9 Hz, H-7), 6.70 (1H, d, J 5.4 Hz, H-3), and 7.3 - 7.5 (5H, m, Ph); the NH resonance was not located; m/e 345 (M^+), 330 (M^+-CH_3), 211 (M^+-PhNCONH), 183, 155, 141, and 119 (100%, $PhNCO^+$); M*(183 - 155) 131.3.

See Section 3.2.8 for the reactions of the annulene (1) with chlorosulphonyl isocyanate and dichloroketene.

3.2.7 Attempted preparation of a metal complex of the annulene (1)

1 Reaction of the annulene (1) with chromium hexacarbonyl

A solution of 7b-methyl-7bH-cyclopent[cd]indene (1) (43 mg, 0.31 mmol) in a mixture of dry tetrahydrofuran (10 ml) and dry di-n-butyl ether (30 ml) containing chromium hexacarbonyl (76 mg, 0.34 mmol) was rigorously degassed and refluxed under nitrogen in an apparatus which returned any sublimed reagent into the reaction vessel. After 3 h, the formation of a grey precipitate indicated decomposition of the reagent. The cooled mixture was filtered through celite, the solvent evaporated, and the residue chromatographed on silica. Elution with petrol gave unreacted annulene (1) (40 mg, 93% recovered).

2 Reaction of the annulene (1) with diiron nonacarbonyl

To a degassed solution of 7b-methyl-7bH-cyclopent-[cd]indene (1) (29 mg, 0.19 mmol) in benzene (2 ml) was added diiron nonacarbonyl (68 mg, 0.19 mmol). There was no reaction until the mixture was heated to 60°C. After 10 min reflux,

the mixture was dark green. Further diiron nonacarbonyl (100 mg, 0.27 mmol) was added and the mixture refluxed for a further 10 min. T.l.c. showed the annulene was not consumed and after evaporation of the solvent, the proton n.m.r. spectrum of the residue was that of the annulene (1). Chromatography on silica failed to separate the unreacted annulene (1) from the dark green triiron dodecacarbonyl which crystallised when a petrol solution of the product mixture was concentrated.

3.2.8 Reactions of the annulene (1) with electrophiles

1 Reaction with acids

(a) With sulphuric acid

Concentrated sulphuric acid (0.25 ml) was added to 7b-methyl-7b*H*-cyclopent[*cd*]indene (3.2 mg) at room temperature. The deep blue solution was quenched with water (0.5 ml). The blue colour was discharged and a dark green solid precipitated. The mixture was extracted with petrol (2 x 2 ml). The colourless extracts were concentrated and t.l.c. showed no material was present.

(b) With toluene-4-sulphonic acid

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (6.6 mg) in benzene (2 ml) containing toluene-4-sulphonic acid (5 mg) was refluxed under nitrogen. After 15 min, the mixture had become dark green and a precipitate started to form. Very little starting material remained after 2 h (t.l.c.).

2 Nitration of the annulene (1) with copper(II) nitrate

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (29.9 mg, 0.194 mmol) in acetic anhydride (2 ml) at 0°C was treated with powdered copper(II) nitrate trihydrate

(47 mg, 0.194 mmol) and the mixture was stirred. After 40 min, the mixture was poured into ice-water (10 ml) and extracted with ether (3 x 5 ml). The combined ether layers were washed with saturated sodium hydrogen carbonate solution (20 ml), dried ($MgSO_4$), the solvent evaporated, and the residue chromatographed on a long column of silica. Elution with petrol gave (i) a 10 : 1 mixture of 7b-methyl-1-nitro-7bH-cyclopent[cd]indene and 7b-methyl-2-nitro-7bH-cyclopent[cd]indene (6.7 mg, 17%), as an orange-red oil; $\nu_{max}(CCl_4)$ 1378 (m), 1338 (s), and 1304 cm^{-1}(s); λ_{max} (EtOH) 246 (log ϵ 4.18), 307 (4.11), 332 sh (3.88), 402 (3.75), and 485 nm (3.19); $\delta_H(CDCl_3)$ for the 1-nitro compound: -1.27 (3H, s, 7b-Me), 7.72 (1H, d, J 7.3 Hz, H-5), 7.89 (1H, t, J 7 Hz, H-6), 8.08 (1H, d, J 3.5 Hz, H-4), 8.23 (1H, d, J 7.5 Hz, H-7), 8.29 (1H, d, J 3.5 Hz, H-3), and 8.33 (1H, s, H-2). The signals for the 2-nitro compound are obscured by those of the 1-nitro compound except for 7.69 (1H, t, J 7 Hz, H-6), 7.81 (1H, d, J 7.3 Hz, H-5), and 8.01 (1H, d, J 7.6 Hz, H-7). The mixture gives m/e 199 (M^+), 182, 169, 153, and 152 (100%). (ii) A 2 : 1 mixture of 7b-methyl-5-nitro-7bH-cyclopent[cd]indene and 7b-methyl-6-nitro-7bH-cyclopent[cd]indene (9.1 mg, 24%), as a yellow-orange oil; $\nu_{max}(CCl_4)$ 1320 cm^{-1} (s); λ_{max}(EtOH) 248 sh (log ϵ 3.95), 275 (4.15), 315 (4.22), 376 (3.82), 444 sh (3.19), and 482 nm (3.07); $\delta_H(CDCl_3)$ for the 5-nitro compound: -1.32 (3H, s, 7b-Me), 7.71 (1H, d, J 8.2 Hz, H-7), 7.99 (1H, d, J 3 Hz, H-1), 8.14 (1H, d, J 3.3 Hz, H-2), 8.20 (1H, d, J 3.3 Hz, H-3), 8.48 (1H, d, J 8.2 Hz, H-6), and 8.50 (1H, d, J 3.3 Hz, H-4); for the 6-nitro compound: -1.35 (3H, s, 7b-Me), 8.00 (2H, d, J 3 Hz,

H-2 + H-3), 8.29 (1H, d, J 3.5 Hz, H-1 + H-4), and 8.62 (1H, s, H-5 + H-7).

Treatment of the first aqueous layer from the work-up of the above reaction with a saturated solution of 2,2′-biquinoline in ethanol did not give the purple colour expected if the copper(I) ion were present.

3 Nitration of 7b-methyl-7bH-cyclopent[cd]indene-2d (72)

The reaction was carried out by the procedure given above, but using 65% 2-deuterated annulene (72), and with reaction conditions of 2 h at -23°C and then 24 h at -18°C. The resulting mixture of mononitro-compounds was analysed by proton n.m.r. The same ratio of products was present as for the earlier experiment above. New signals appeared within the doublets at 8.00, 8.08, 8.29, and 8.50. These signals are for protons in the 1- and 4-positions and show the assignments given above are correct.

4 Attempted nitration of 7b-methyl-7bH-cyclopent[cd]indene with tetranitromethane

A stirred solution of 7b-methyl-7bH-cyclopent[cd]-indene (23 mg, 0.15 mmol) in pyridine (1 ml) at 0°C was treated with a solution of tetranitromethane in ethanol (10% v/v; 345 mg, 0.18 mmol). The mixture immediately became orange but there was little reaction (t.l.c.). The mixture was then warmed in a water bath at 40°C. It rapidly became very dark brown. T.l.c. showed some starting material was still present and that a trace of a mixture of nitro compounds had been formed. The dark coloured material was

baseline. Replacement of the pyridine and ethanol with dimethyl sulphoxide gave the same result.

5 Reduction of the nitroannulenes with zinc in acetic anhydride

A solution of a mixture of the nitro-7b-methyl-7b*H*-cyclopent[*cd*]indene derivatives from above (22.6 mg) in acetic anhydride (2 ml) was treated at room temperature with sodium acetate (100 mg) and zinc dust (200 mg). The mixture was stirred for 10 min, poured into water (30 ml) and extracted with ether (3 x 15 ml). The combined ether layers were washed with saturated sodium hydrogen carbonate solution (20 ml), dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petrol gave a mixture of acetamido derivatives of the annulene (1) (13.0 mg, 54%), as an unstable yellow semi-solid; $\delta_H(CDCl_3$, 90 MHz) -1.45 (3H, s, 7b-Me) and 7.4 - 8.0 (6H, m, ArH); *m/e* 211 (M^+), 169 (100%), and 168.

6 Acetylation of the annulene (1)

A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (10.1 mg) in dichloromethane (3 ml) was treated with acetic anhydride (0.25 ml) and two drops of boron trifluoride etherate. The mixture was stirred at room temperature for 3.5 h and then poured into water (10 ml). The dichloromethane layer was removed and the aqueous layer extracted with dichloromethane (10 ml). The combined organic layers were dried ($MgSO_4$), the solvent evaporated, and the residue chromatographed on silica. Elution with 15% ether in petrol

gave a 15 : 5 : 1 mixture of 5-, 1-, and 6-acetyl-7b-methyl-7b*H*-cyclopent[*cd*]indene (6.9 mg, 54%), as an orange oil; $\nu_{max}(CCl_4)$ 1672 cm^{-1} (s, C=O stretch); λ_{max}(EtOH) 305, 347, 450 sh, and 477 nm; $\delta_H(CDCl_3)$ for the 5-acetyl isomer: -1.47 (3H, s, 7b-Me), 2.87 (3H, s, $COCH_3$), 7.69 (1H, d, *J* 7.5 Hz, H-7), 7.93 (1H, d, *J* 3.3 Hz, H-1), 8.05 (1H, d, *J* 3.3 Hz, H-2 or H-3), 8.08 (1H, d, *J* 3.3 Hz, H-3 or H-2), 8.22 (1H, d, *J* 7.4 Hz, H-6), and 8.38 (1H, d, *J* 3.3 Hz, H-4); for the 1-acetyl isomer: -1.42 (3H, s, 7b-Me), 2.82 (3H, s, $COCH_3$), 7.67 (1H, d, *J* 6.8 Hz, H-5), 7.75 (1H, t, *J* 7 Hz, H-6), 7.97 (1H, d, *J* 3.3 Hz, H-4), 8.06 (1H, d, H-7), 8.12 (1H, d, *J* 3.3 Hz, H-3), and 8.27 (1H, s, H-2); for the 6-acetyl isomer: -1.44 (3H, s, 7b-Me), 2.81 (?) (3H, s, $COCH_3$), 7.90 (2H, d, *J* 3.3 Hz, H-2 + H-3), 8.14 (2H, d, *J* 3.3 Hz, H-1 + H-4), and 8.31 (2H, s, H-5 + H-7); *m/e* 196 (M^+, 100%), 181, and 153.

7 Formylation of the annulene (1)

A stirred solution of 7b-methyl-7b*H*-cyclopent[*cd*]-indene (1) (52 mg, 0.33 mmol) in dichloromethane (3 ml) containing dichloromethyl *n*-butyl ether[136] (100 mg, 0.64 mmol) was cooled to -78°C under nitrogen and treated with tin(IV) chloride (0.05 ml). The mixture immediately became dark blue. After 10 min, the mixture was poured into water (50 ml) and the mixture shaken until the blue colour was discharged. The products were extracted with ether (3 x 20 ml). The combined ether layers were washed with water (20 ml), dried ($MgSO_4$), the solvent evaporated, and the residue chromatographed on silica. Elution with petrol gave the starting annulene (1) (3 mg, 4% recovered). Elution with 20% ether

in petrol gave 7b-methyl-7b*H*-cyclopent[*cd*]indene-5-carboxaldehyde (115) (*ca*. 93% pure; contains 4% of the 1-carboxaldehyde (53a) and 3% of the 6-carboxaldehyde); $\delta_H(CDCl_3)$ -1.42 (3H, s, 7b-Me), 7.74 (1H, d, *J* 7.6 Hz, H-7), 7.96 (1H, d, *J* 3.4 Hz, H-1), 8.07 (1H, d, *J* 7.6 Hz, H-6), 8.08 (1H, d, *J* 3.4 Hz, H-2), 8.11 (1H, d, *J* 3.4 Hz, H-3), 8.40 (1H, d, *J* 3.4 Hz, H-4), and 10.43 (1H, s, C*H*O) [for the 6-isomer: -1.36 (3H, s, 7b-Me), 7.92 (2H, d, *J* 3.4 Hz), and 8.20 (2H, s, H-5 + H-7); an expected doublet, *J* 3.4 Hz and the aldehyde proton resonance were not located. Spectral data for the 1-carboxaldehyde (53a) are given earlier in Section 3.1.3. Spectral data for the 2-carboxaldehyde (53b) that was not detected in this product are given earlier in Section 3.1.5].

Treatment of this mixture of aldehydes with 2,4-dinitrophenylhydrazine in ethanol acidified with concentrated sulphuric acid at room temperature gave an immediate precipitate of hydrazones (81%). Repeated recrystallisation gave a pure isomer as mauve needles, m.p. 201.5 - 203.5°C (from 1 : 1 acetonitrile - dimethylformamide) (Found: C, 62.92; H, 3.93; N, 15.43. $C_{19}H_{14}N_4O_4$ requires C, 62.98; H, 3.89; N, 15.46%).

8 Sulphonation of the annulene (1)

Sulphur trioxide was freshly prepared by distillation from a mixture of concentrated sulphuric acid and phosphorus pentoxide, into an ice cooled receiver. A solution of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) (74 mg, 0.48 mmol) in dry dioxan was added to a stirred solution of sulphur trioxide (200 mg, 2.5 mmol) in dry dioxan (5 ml) at 12°C

under nitrogen. After 20 min, the mixture was poured into sodium carbonate solution (5% w/v; 40 ml) and the solution washed with dichloromethane (30 ml). The aqueous solution was evaporated to dryness and the residue extracted exhaustively with hot ethanol. Evaporation of the ethanol gave sodium 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene-5-sulphonate (116) (86 mg, 70%), as a hygroscopic yellow solid; δ_H(d_6-dimethyl sulphoxide) -1.69 (3H, s, 7b-Me), 7.66 (1H, d, <u>J</u> 7.6 Hz, H-7), 7.83 (1H, d, <u>J</u> 7.6 Hz, H-6), 7.94 (1H, d, <u>J</u> 3.4 Hz, H-1 or H-2), 7.99 (1H, d, <u>J</u> 3.4 Hz, H-2 or H-1), 8.01 (1H, d, <u>J</u> 3.4 Hz, H-3), and 8.23 (1H, d, <u>J</u> 3.4 Hz, H-4); there were only traces of other isomers present.

Treatment of this sodium salt with a solution of <u>S</u>-benzylthiouronium chloride in water acidified with dilute hydrochloric acid (0.1 M, 1 drop) at room temperature gave an immediate precipitate of the <u>S</u>-benzylthiouronium salt (70%), as yellow needles, m.p. 195 - 197°C (from water) (Found: C, 60.08; H, 5.04; N, 7.03; S, 16.22. $C_{20}H_{20}N_2S_2O_3$ requires C, 59.98; H, 5.04; N, 6.99; S, 16.01%).

9 <u>Attempted benzoylation of the annulene (1)</u>

A solution of 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene (1) (38.7 mg, 0.25 mmol) in dichloromethane (10 ml) was stirred and treated with benzoyl chloride (0.25 ml) and cyclohexene (0.5 ml) at room temperature. Freshly powdered aluminium chloride (35 mg, 0.25 mmol) was added. The mixture became deep blue. After 2 h, t.l.c. showed formation of only baseline material.

10 Attempted bromination of the annulene (1) with N-bromosuccinimide

A solution of 7b-methyl-7bH-cyclopent[cd]indene (1) (16.3 mg, 0.11 mmol) in dry dimethylformamide (1 ml) was treated with N-bromosuccinimide (18.9 mg, 0.11 mmol) and the mixture stirred at room temperature in the dark. After 48 h, the mixture was poured into water (100 ml) and extracted with petrol (3 x 2 ml). The combined extracts were dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with petrol gave starting material (3.5 mg) containing a small amount of a new compound; $\delta_H(CDCl_3)$ -1.52 (7b-Me) which could not be identified.

11 Attempted bromination of the annulene (1) with pyridinium bromide perbromide

A solution of 7b-methyl-7bH-cyclopent[cd]indene (1) (38 mg, 0.25 mmol) in benzene (10 ml) was treated with pyridinium bromide perbromide[137] (79 mg, 0.25 mmol) and the mixture stirred at room temperature. After 1 h, the colour of the reagent was discharged. The mixture was then washed with dilute sulphuric acid (1 M, 10 ml) followed by water (5 ml), dried (Na_2SO_4) and the solvent evaporated to give 2a,4a-dibromo-4a,7b-dihydro-7b-methyl-2aH-cyclopent[cd]indene (117) (60 mg, 78%), as pale yellow crystals, m.p. 123 - 124.5°C (from cold petrol) (Found: C, 45.99; H, 3.15. $C_{12}H_{10}Br_2$ requires C, 45.90; H, 3.21%); $\nu_{max}(CCl_4)$ 3060 (m), 1450 (m), 1372 (m), 1142 (m), 918 (s), 862 (ms), and 654 cm^{-1} (ms); λ_{max}(EtOH) 326 nm (log ϵ 3.46); $\delta_H(CDCl_3)$ 1.43 (3H,

s, 7b-Me), 5.80 (1H, br. d, J 5 Hz, H-7), 5.83 (1H, dd, J 5.1 Hz, 8.6 Hz, H-6), 5.97 (1H, dd, J 1.2 Hz, 8.6 Hz, H-5), 6.03 (1H, d, J 5.6 Hz), 6.17 (1H, d, J 5.8 Hz), 6.19 (1H, d, J 5.6 Hz), and 6.39 (1H, d, J 5.8 Hz); m/e 316-314-312 (1 : 2 : 1, M^+), 235-233 (1 : 1, M^+-Br), 154 (100%, M^+-2Br), 153, and 149.

12 Nitration of the annulene (1) with nitronium trifluoromethanesulphonate

A stirred suspension of nitronium trifluoromethanesulphonate[138] (36 mg, 0.18 mmol) in dichloromethane (2 ml) at 0°C under nitrogen was treated with collidine (23 mg, 0.19 mmol). After 30 min at room temperature, a solution of 7b-methyl-7bH-cyclopent[cd]indene (1) (28 mg, 0.18 mmol) in dichloromethane (2 ml) was added and the mixture refluxed for 4 h. The mixture was then cooled, the solvent evaporated, and the residue chromatographed on silica. Elution with petrol gave the starting annulene (1) (15 mg, 42% recovered). Elution with 5% ether in petrol gave a 2 : 1 mixture of 7b-methyl-6-nitro-7bH-cyclopent[cd]indene and 7b-methyl-5-nitro-7bH-cyclopent[cd]indene (2.3 mg, 5%); spectral data for these compounds are given earlier in this Section.

Replacement of the dichloromethane with acetonitrile gave no improvement.

13 Reaction of the annulene (1) with chlorosulphonyl isocyanate

A stirred solution of 7b-methyl-7bH-cyclopent[cd]indene (1) in dichloromethane (20 ml) at 0°C was treated with

chlorosulphonyl isocyanate (0.15 ml, 240 mg, 1.7 mmol). After 25 min at 0°C, the dark red mixture was poured with shaking into ice-water (100 ml). The aqueous layer was extracted with dichloromethane (30 ml). The combined dichloromethane layers were dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with petrol gave the starting annulene (1) (62 mg, 25%). Elution with 50% ether in petrol gave N-chlorosulphonyl-2,9b-dihydro-9b-methyl-1H-indeno[1,7-cd]azepin-1-one (122) (219 mg, 47%, 63% based on consumed starting material), as red flakes, m.p. 160 - 162°C (from petrol - dichloromethane) (Found: m/e 295.0075. $C_{13}H_{10}NO_3{}^{35}Cl$ requires m/e 295.0070); $\nu_{max}(CCl_4)$ 1712 (s, C=O stretch), 1690 (m, C=C-C=O), 1490 (m), 1410 (s, S=O), 1088 (s, S=O), 1134 (m), 1100 (m), 1030 (m), 1010 (m), 852 (m), 678 (m), 632 (s), and 614 cm^{-1} (m); λ_{max}(cyclohexane) 232 (log ϵ 4.05), 299 (4.42), and 484 nm (3.02); $\delta_H(CDCl_3)$ 1.93 (3H, s, 9b-Me), 5.79 (1H, d, J 5.8 Hz, H-5), 5.82 (1H, d, J 9.5 Hz, H-4), 6.03 (1H, d, J 9.5 Hz, H-3), 6.20 (1H, dd, J 5.8 Hz, 9.4 Hz, H-6), 6.37 (1H, d, J 2.9 Hz, H-8), 6.50 (1H, d, J 9.4 Hz, H-7), and 7.89 (1H, d, J 2.9 Hz, H-9); m/e 297-295 (1 : 2, M^+), 282-280 (1 : 2, M^+-CH_3), 254-252 (1 : 2, M^+-CH_3-CO), 231, 197, 196, 162, and 154 (100%).

14 Hydrolysis of the chlorosulphonamide (122)

A solution of the chlorosulphonamide (122) (101 mg) in dichloromethane (10 ml) was stirred with a mixture of aqueous sodium sulphite (5% w/v; 5 ml) and aqueous sodium hydroxide (5% w/v; 3 ml). After 5 h at room temperature, the aqueous layer was discarded and the dichloromethane

layer was washed with water (10 ml), dried (Na_2SO_4), the solvent evaporated, and the residue chromatographed on silica. Elution with 50% ether in petrol gave starting material (6 mg, 6% recovered). Elution with 80% ether in petrol gave 2,9b-dihydro-9b-methyl-1H-indeno[1,7-cd]azepin-1-one (123) (53 mg, 79%), as a dark brown-green solid (Found: m/e 197.0840. $C_{13}H_{11}NO$ requires m/e 197.0841); $\nu_{max}(CCl_4)$ 3420 (w), 3225 (m, NH stretch), 3090 (m), 2980 (m), 1669 (s, C=O stretch), 1628 (s, C=C-C=O), 1344 (m), and 912 cm^{-1} (s); λ_{max}(EtOH) 299 (log ϵ 3.72), 275 (4.11), 343 (3.41), and 550 br. nm (2.16); $\delta_H(CDCl_3)$ 3.06 (3H, s, 9b-Me), 4.53 (1H, d, J 10.2 Hz, H-4), 4.84 (1H, d, J 6.0 Hz, H-5), 5.02 (1H, dd, J 7.0 Hz, 10.2 Hz, H-3), 5.48 (1H, dd, J 6.0 Hz, 9.7 Hz, H-6), 5.68 (1H, d, J 2.5 Hz, H-8), 5.74 (1H, d, J 9.7 Hz, H-7), 6.3 (1H, br., NH), and 6.91 (1H, d, J 2.5 Hz, H-9); m/e 197 (M^+, 100%), 196, 182, and 154.

15 Thermal rearrangement of the amide (123)

A solution of the amide (123) (22.3 mg) in benzene (3 ml) was refluxed under nitrogen. After 7 h, the solvent was evaporated and the residue chromatographed on silica. Elution with ether gave 2,9a-dihydro-9a-methyl-1H-indeno-[1,7-cd]azepin-1-one (124) (18.4 mg, 83%), as colourless flakes, m.p. 142 - 143°C (from petrol - dichloromethane) (Found: C, 78.98; H, 5.59; N, 7.08. $C_{13}H_{11}NO$ requires C, 79.17; H, 5.62; N, 7.10%); $\nu_{max}(CCl_4)$ 3400 (w, sharp, free NH), 3220 (m, NH), 3100 (m, NH), 2970 (m), 1668 (s, C=O stretch), 1642 (s, C=C-C=O), 1372 (m), 1348 (ms), 1144 (m), 1054 (m), and 848 cm^{-1} (m); λ_{max}(EtOH) 270 sh (log ϵ 3.97), 274 (3.98), 286 sh (3.86), and 345 sh (2.11); m/e

197 (M^+, 100%), 196, 182 (M^+-CH_3), 178, 168, and 154.

16 Thermal rearrangement of the chlorosulphonamide (122)

(a) In the presence of cyclohexene

A solution of the chlorosulphonamide (122) (10.8 mg) in toluene (1.5 ml) and cyclohexene (0.5 ml) was refluxed under nitrogen for 15 min. The solvent was then evaporated and the residue chromatographed on silica. Elution with petrol containing an increasing proportion of ether gave (i) the annulene (1) (2.4 mg, 42%). (ii) Starting material (1.5 mg, 14%). (iii) The amide (124) (2.9 mg, 40%).

(b) In the absence of cyclohexene

A solution of the chlorosulphonamide (122) (27.0 mg) in toluene (1 ml) was refluxed under nitrogen for 30 min. The solvent was then evaporated and the residue chromatographed on silica. Elution with petrol containing an increasing proportion of ether gave (i) the annulene (1) (1.6 mg, 11%). (ii) N-Chlorosulphonyl-2,9a-dihydro-9a-methyl-1H-indeno[1,7-cd]azepin-1-one (125) (6.2 mg, 23%), as an oil; $\nu_{max}(CCl_4)$ 1736 (s, C=O stretch), 1422 (m), 1406 (s, S=O stretch), 1044(m), 1032 (m), 910 (s), 658 (s), and 626 cm^{-1} (m); λ_{max}(EtOH) 254 (log ϵ 4.05), 275 sh (3.95), 294 sh (3.71), and 326 sh nm (3.03); $\delta_H(CDCl_3)$ 1.49 (3H, s, 9a-Me), 6.64 (1H, d, J 9.3 Hz, H-3 or H-4), 6.79 (1H, d, J 5.8 Hz, H-8 or H-9), 6.88 (1H, d, J 5.8 Hz, H-9 or H-8), 6.92 (1H, d, J 9.3 Hz, H-4 or H-3), 7.17 (1H, X part of ABX system, H-5), and 7.39 (2H, AB part of ABX system, H-6 + H-7); m/e 297-295 (2 : 1, M^+), 254-252 (2 : 1, M^+-CH_3-CO), 231, 197 (100%), 196, 182, 173, and 154. (iii) Starting

material (3.7 mg). (iv) A 4 : 1 mixture of the amide (124) and annulenamides (7 mg), as a yellow solid; $\delta_H(CDCl_3)$ -1.44 and -1.46 (7b-Me of annulenamides); the products gave a yellow spot on t.l.c. which ran alongside an authentic sample of the annulenamide (66).

17 Reaction of the annulene (1) with dichloroketene

(a) A stirred solution of 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]-indene (1) (37 mg, 0.24 mmol) in petrol (5 ml) containing dichloroacetyl chloride (35 mg, 0.24 mmol) under nitrogen was warmed to 40°C and treated with dropwise addition of a solution of triethylamine (50 mg) in petrol (1 ml). After 1 h reflux, the solvent was evaporated and the residue chromatographed on silica. Elution with petrol gave starting material (26 mg, 70% recovered). No new products could be isolated.

(b) A stirred solution of 7b-methyl-7b<u>H</u>-cyclopent[<u>cd</u>]-indene (1) (53 mg, 0.34 mmol) in ether (10 ml) containing copper activated zinc[94] (350 mg) was refluxed under nitrogen and treated with dropwise addition of trichloroacetyl chloride (310 mg, 1.7 mmol) over 1 h. After 12 h reflux, the solvent was evaporated and the residue chromatographed on silica. Elution with petrol gave starting material (27 mg, 50% recovered). No new products could be isolated.

3.3 Synthesis and Properties of 9c-Methyl-9cH-cyclopenta-[jk]fluorene (130); a Benzo fused [10]Annulene

3.3.1 The adduct of the 3aH-indene (85) with benzoquinone

1 Cycloaddition of the 3aH-indene (85) with benzoquinone; isolation of the initial adduct (127)

A solution of 3a-methyl-3-(trimethylsiloxy)-3aH-indene (85) in petrol (15 ml) prepared as described in Section 3.1.8 from the trienone (46) (250 mg, 1.7 mmol), and treated with a solution of 1,4-benzoquinone (192 mg, 1.8 mmol) in dry tetrahydrofuran (5 ml). The mixture immediately became red but after 3 h at room temperature, it was pale yellow. The solvent was then evaporated and the residue heated at 60°C under vacuum (0.05 mmHg) for 1 h, and then chromatographed on silica. Elution with 60% ether in petrol gave the exo-adduct (127) (53 mg, 10%), as a yellow oil; ν_{max}(neat) 2960 (m), 1678 (s, C=O stretch), 1282 (m), 1264 (m), 1118 (m), 914 (m), 848 (s), and 756 cm^{-1}(m); λ_{max}(EtOH) 301 nm (log ϵ 3.84); δ_H($CDCl_3$) 0.05 (9H, s, $SiMe_3$), 0.89 (3H, s, 9c-Me), 2.76 (1H, dd, J 4.4 Hz, 9.2 Hz, H-5b), 2.80 (1H, d, J 9.2 Hz, H-9a), 3.37 (1H, br.t, J 5 Hz, H-5a), 5.85 (1H, d, J 5.0 Hz, H-3), 5.90 (1H, dd, J 5.7 Hz, 9.2 Hz, H-5), 6.04 (1H, dd, J 5.0 Hz, 9.2 Hz, H-4), 6.29 (1H, d, J 4.8 Hz, H-1 or H-2), 6.41 (1H, d, J 4.8 Hz, H-2 or H-1), 6.67 (1H, d, J 11.2 Hz, H-7 or H-8), and 6.72 (1H, d, J 11.2 Hz, H-8 or H-7); see Fig. 14 for n.O.e. results on which the stereochemical assignment is based; m/e 326 (M^+), 311, 236, 219, 203, and 167 (100%).

2 Cycloaddition of the 3a*H*-indene (85) with benzoquinone; isolation of the oxidised adduct (128)

A solution of 3a-methyl-3-(trimethylsiloxy)-3a*H*-indene (85) in petrol (20 ml) was prepared as described in Section 3.1.8 from the trienone (46) (300 mg, 2.05 mmol) and treated with a solution of 1,4-benzoquinone (230 mg, 2.05 mmol) in tetrahydrofuran (5 ml). After 2 h at room temperature, the solution was evaporated onto silica under reduced pressure at 40°C. The mixture darkened considerably during this pre-adsorption. The residue was chromatographed on silica. Elution with 50% ether in petrol gave 9c-methyl 6,9,9b,9c-tetrahydro-9b-(trimethylsiloxy)-5a*H*-cyclopenta-[*jk*]fluorene-6,9-dione (128) (160 mg, 24%), as a deep red oil; ν_{max}(neat) 1660 cm^{-1} (s, C=O stretch); λ_{max}(EtOH) 247 (log ϵ 4.19), 302 (3.67), and 472 nm (1.90); δ_H($CDCl_3$) 0.20 (9H, s, $SiMe_3$), 0.93 (3H, s, 9c-Me), 3.60 (1H, d, *J* 6.7 Hz, H-5a), 5.85 (1H, d, *J* 4.7 Hz, H-3), 6.09 (1H, dd, *J* 4.7 Hz, 9.2 Hz, H-4), 6.13 (1H, dd, *J* 6.7 Hz, 9.2 Hz, H-5), 6.41 (1H, d, *J* 5.3 Hz, H-1 or H-2), 6.48 (1H, d, *J* 10.0 Hz, H-7 or H-8), 6.60 (1H, d, *J* 5.3 Hz, H-2 or H-1), and 6.61 (1H, d, *J* 10.0 Hz, H-8 or H-7); decoupling at δ3.60 removed the smaller coupling at δ6.13; *m/e* 324 (M^+, 100%), 309, 296, 294, 281, 236, 235, and 234.

3 9,9c-Dihydro-9c-methyl-6*H*-cyclopent[*jk*]fluorene-6,9-dione (129)

A solution of 9c-methyl-6,9,9b,9c-tetrahydro-9b-(trimethylsiloxy)-5a*H*-cyclopenta[*jk*]fluorene-6,9-dione (128) (68 mg) in chloroform (3 ml) containing toluene-4-sulphonic acid (5 mg) was refluxed under nitrogen for

45 min. The cooled mixture was diluted with dichloromethane (30 ml) and washed with saturated sodium hydrogen carbonate solution (10 ml). The organic layer was dried ($MgSO_4$), the solvent evaporated, and the residue chromatographed on silica. Elution with 30% ether in petrol gave the title compound (129) (14 mg, 33%), as a dark mauve viscous oil (Found: m/e 234.0684. $C_{16}H_{12}O_2$ requires m/e 234.0681); ν_{max}(neat) 1650 (s, C=O stretch), 1589 (m), 1242 (m), 1072 (m), 852 (m), and 700 cm^{-1}(m); λ_{max}(EtOH) 275 (log ϵ 4.25), 295 (4.17), 374 (4.08), and 560 nm (3.67); $\delta_H(CDCl_3)$ -1.01 (3H, s, 9c-Me), 6.92 (2H, AB system, J 10.8 Hz, H-7 and H-8), 7.71 (1H, d, J 7.5 Hz, H-3), 7.81 (1H, t, J 7.5 Hz, H-4), 8.22 (1H, d, J 3.8 Hz, H-2), 8.32 (1H, d, J 7.5 Hz, H-5), and 8.39 (1H, d, J 3.8 Hz, H-1); m/e 234 (M^+, 100%), 206, 205, 188, 187, 163, and 152.

3.3.2 Synthesis and properties of 9c-methyl-9cH-cyclopenta[jk]fluorene (130)

1 9c-Methyl-9cH-cyclopenta[jk]fluorene (130)

A solution of 7b-methyl-7bH-cyclopent[cd]indene-1,2-dicarboxaldehyde (51) (450 mg, 2.14 mmol) in dry dimethylformamide (10 ml) was added to a stirred suspension of thiodimethylenedi(triphenylphosphonium bromide)[139] (1.6 g, 2.15 mmol) in dry dimethylformamide (20 ml) and the mixture treated with lithium methoxide (170 mg, 4.5 mmol). After 1 h at room temperature, a further portion of lithium methoxide (170 mg, 4.5 mmol) was added and after a further 1 h, the mixture was poured into water (200 ml). The product was extracted with ether (3 x 50 ml), the ether extracts washed with water (3 x 200 ml), dried (Na_2SO_4), the solvent

evaporated and the residue chromatographed on silica. Elution with petrol gave 9c-methyl-9cH-cyclopenta[jk]-fluorene (130) (62 mg, 14%), as yellow crystals, m.p. 74 - 76°C (from cold petrol) (Found: C, 94.21; H, 5.91. $C_{16}H_{12}$ requires C, 94.08; H, 5.92%); $\nu_{max}(CCl_4)$ 3060 (m), 2980 (m), 2925 (m), 2860 (w), 1440 (m), 1328 (m), 696 (m), and 632 cm^{-1} (ms); λ_{max}(EtOH) 311 (log ϵ 4.43), 400 br. (3.34), and 464 sh nm (2.82); $\delta_H(CDCl_3$, 400 MHz) -0.79 (3H, s, 7b-Me), 7.30 (1H, dd, $J_{3,4}$ 8.26 Hz, $J_{4,5}$ 5.97 Hz, H-4), 7.37 (1H, d, $J_{1,2}$ 2.42 Hz, H-2), 7.47 (1H, d, $J_{4,5}$ 5.97 Hz, H-5 and 1H, d, $J_{1,2}$ 2.42 Hz, H-1), 7.58 (1H, d, $J_{3,4}$ 8.26 Hz, H-3), 7.67 (1H, ddd, $J_{6,7}$ 8.03 Hz, $J_{7,8}$ 7.05 Hz, $J_{7,9}$ 1.19 Hz, H-7), 7.74 (1H, ddd, $J_{8,9}$ 8.05 Hz, $J_{7,8}$ 7.05 Hz, $J_{6,8}$ 1.21Hz, H-8), 8.30 (1H, ddd, $J_{8,9}$ 8.05 Hz, $J_{7,9}$ 1.19 Hz, $J_{6,9}$ 0.91Hz, H-9), and 8.40 (1H, ddd, $J_{6,7}$ 8.03 Hz, $J_{6,8}$ 1.21 Hz, $J_{6,9}$ 0.91 Hz, H-6); $\delta_C(CDCl_3)$ 23.6 (1.00, 9c-Me), 62.0 (0.22, C-9c), 113.6 (0.73), 119.2 (0.74), 123.9 (0.66), 124.7 (0.95), 124.9 (0.83), 126.4 (0.76), 128.2 (0.94), 128.6 (0.74), 131.1 (0.85), 139.2 (0.19), 144.7 (0.13), 153.0 (0.19), 159.0 (0.20), and 171.4 (0.18, C-9b); m/e 204 (M^+, 100%) and 189.

2 Thermal rearrangement of 9c-methyl-9cH-cyclopenta[jk]-fluorene (130)

(a) Kinetic measurements

The following rates were recorded for rearrangement of (130) in decalin: $t_{\frac{1}{2}}$ 8.3 ($\pm$0.4) min at 138°C, $t_{\frac{1}{2}}$ 15.2 ($\pm$0.5) min at 132°C, $t_{\frac{1}{2}}$ 64 ($\pm$2) min at 117°C, and $t_{\frac{1}{2}}$ 132 ($\pm$3) min at 109°C.

(b) Preparative reaction

A solution of 9c-methyl-9c*H*-cyclopenta[*jk*]fluorene (130) (13.4 mg) in xylene (3 ml) was refluxed under nitrogen for 3 h. The solvent was evaporated and the residue chromatographed on silica. Elution with petrol gave 9b-methyl-9b*H*-cyclopenta[*jk*]fluorene (136) (6.6 mg, 49%), as a colourless solid, m.p. 50 - 51°C (after sublimation at 75°C/0.1 mmHg) (lit.,[124] m.p. 53°C); δ_H($CDCl_3$, 90 MHz) 1.56 (3H, s, 9b-Me), 6.67 (1H, d, *J* 5 Hz), 6.90 (1H, d, *J* 5 Hz), 6.94 - 7.47 (5H, m), and 7.49 - 7.62 (2H, m).

3 Attempted nitration of 9c-methyl-9c*H*-cyclopenta[*jk*]-fluorene (130)

A solution of 9c-methyl-9c*H*-cyclopenta[*jk*]fluorene (130) (2 mg, 0.01 mmol) in acetic anhydride (0.3 ml) was treated with powdered copper(II) nitrate trihydrate (5 mg, 0.02 mmol) and the mixture stirred at 0°C. T.l.c. after 10 min showed only starting material and baseline. After 20 min, the mixture was shaken with water (5 ml) and the products extracted with ether (5 ml). No coloured products were extracted.

4 Reaction of 9c-methyl-9c*H*-cyclopenta[*jk*]fluorene with 4-phenyl-1,2,4-triazole-3,5-dione (PTAD)

A stirred solution of 9c-methyl-9c*H*-cyclopenta[*jk*]-fluorene (130) (12 mg, 0.06 mmol) in dichloromethane (1 ml) was treated with a solution of PTAD (10 mg, 0.06 mmol) in dichloromethane (1 ml) at 0°C. After 5 min, the annulene was consumed (t.l.c.) but the red colour of the reagent

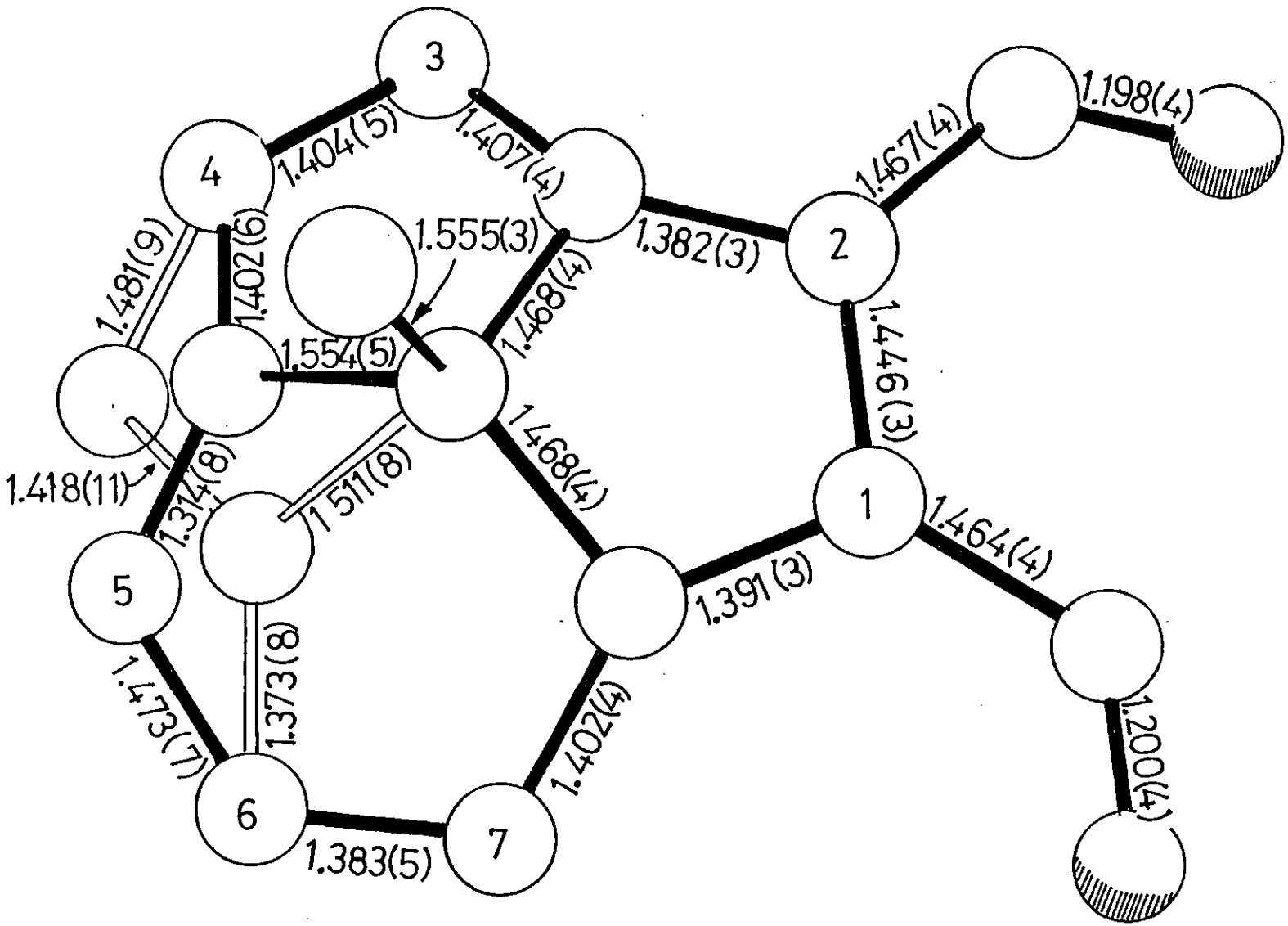
remained. The solvent was evaporated; the residue was a complex mixture (n.m.r.) in which no new products could be identified.

3.3.3 7,8-Diaza-9c-methyl-9cH-cyclopenta[jk]fluorene (137)

A solution of 7b-methyl-7bH-cyclopent[cd]indene-1,2-dicarboxaldehyde (51) (70 mg, 0.33 mmol) in ethanol (2 ml) was treated at 0°C with hydrazine hydrate (ca. 50 mg, 0.9 mmol). The reaction was instantaneous. The solvent was evaporated at room temperature and the residue chromatographed on alumina (basic, Brockmann grade 1). Elution with 10% ethyl acetate in dichloromethane gave the title compound (137) (62 mg, 90%), as a dark red semi-solid (Found: m/e 206.0845. $C_{14}H_{10}N_2$ requires m/e 206.0844); ν_{max}(neat) 2910 (m), 1458 (m), 1440 (m), 1380 (m), 1312 (m), 832 (m), and 732 cm^{-1}(m); λ_{max}(EtOH) 248 (log ϵ 3.91), 321 (4.25), 406 (3.34), and 478 sh nm (2.92); $\delta_H(CDCl_3)$ -1.06 (3H, s, 9c-Me), 7.56 (1H, dd, J 6.2 Hz, 8.3 Hz, H-4), 7.64 (1H, d, J 2.9 Hz, H-1 or H-2), 7.82 (1H, d, J 8.3 Hz, H-3), 7.86 (1H, d, J 6.2 Hz, H-5), 7.89 (1H, d, J 2.9 Hz, H-2 or H-1), and 10.09 (2H, AB system, H-6 and H-9); $\delta_C(CDCl_3)$ 27.4 (1.00, 9c-Me), 62.2 (0.32, C-9c), 119.5 (1.00, C-3), 121.7 (0.95, C-5), 130.8 (0.97, C-1 or C-4), 131.3 (1.00, C-4 or C-1), 132.1 (0.20, C-5b or C-9a), 134.7 (0.91, C-2), 133.1 (0.19, C-9a or C-5b), 148.4 (0.69, C-6 or C-9), 148.6 (0.75, C-9 or C-6), 151.1 (0.25, C-5a), 162.9 (0.24, C-2a), and 168,4 (0.19, C-9b); m/e 206 (M^+, 100%), 177, 163, and 152.

APPENDIX 1 Crystal Structure of 7b-Methyl-7bH-cyclopent-[cd]indene-1,2-dicarboxaldehyde (51)

The following diagrams give the bond lengths and bond angles in the title compound; standard deviations are given in parentheses. The unfilled bonds indicate the minor configurational isomer (40%) giving disorder in the crystal. Bond angles are only given for the major configuration.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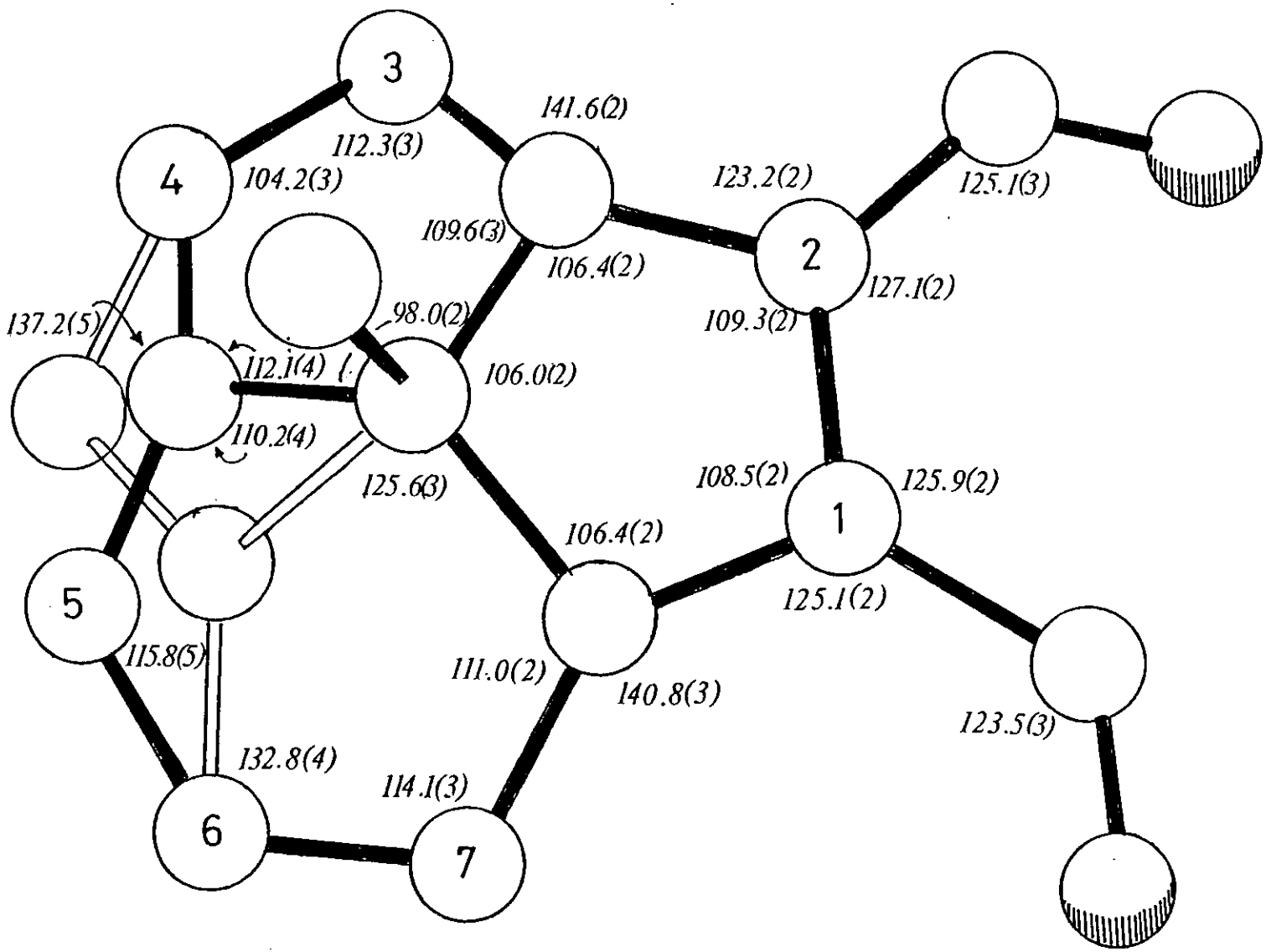
1.383(5)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98.0(2)
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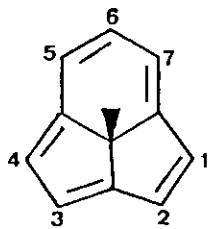
125.9(2)
106.4(2)
125.1(2)
115.8(5)
111.0(2)
140.8(3)
123.5(3)
132.8(4)
114.1(3)

APPENDIX 2 Compilation of Electronic Spectral Data of Derivatives of 7b-Methyl-7bH-cyclopent[cd]indene.

Wavelengths (in nm.) of the 4 principal bands in the spectra are given (log ϵ in parentheses). All spectra were measured of solutions in ethanol.

Substituents	Compound number	λ_{max}(log ϵ)							
none	(1)	249sh	(3.74)	282	(4.54)	335sh	(3.52)	450	(2.64)
2-OMe	(82)	234sh	(3.89)	291	(4.70)	326	(3.72)	459	(2.96)
2-CO_2Me	(70)	251	(3.89)	302	(4.60)	336	(3.81)	475	(3.16)
2-CN	(65)	251	(3.87)	297	(4.66)	329	(3.84)	470	(3.15)
2-$CONH_2$	(66)	245sh	(3.89)	299	(4.61)	333	(3.81)	471	(3.06)
2-CO_2H	(64)	250	(3.89)	299	(4.62)	332	(3.82)	474	(3.17)
2-CHO	(53b)	257	(4.07)	312	(4.51)	350	(3.85)	488	(3.20)
1-CO_2Me, 2-CO_2Me	(38)	262	(3.82)	305	(4.60)	336	(3.84)	471	(3.25)
1-CHO , 2-CHO	(51)	217sh	(4.09)	318	(4.30)	375sh	(3.66)	498	(3.30)

APPENDIX 3 Compilation of Proton n.m.r. data of Derivatives of 7b-Methyl-7bH-cyclopent[cd]indene



Typically $J_{1,2} \simeq J_{3,4} \simeq 3$ Hz

$J_{5,6} \simeq J_{6,7} \simeq 7$ Hz

Compound number	Chemical shift [$\delta_H(CDCl_3)$] or substituent							
	7b-Me	1	2	3	4	5	6	7
(1)	-1.67	7.92	7.90	7.90	7.92	7.69	7.57	7.69
(77)	-1.51	7.25	$-OSiMe_3$	7.79	7.63	7.60	7.50	7.36
(82)	-1.51	7.25	-OMe	7.91	7.65	7.60	7.54	7.37
(65)	-1.56	7.90	-CN	8.03	7.97	7.70	7.60	7.82
(67a)	-1.50	-CN	7.93	8.10	8.01	7.51	7.64	7.76
(67b)	-1.44	-CN	7.90	$-CH_3$	7.71	7.71	7.70	7.84
(66)	-1.47	8.28	$-CONH_2$	8.05	8.05	7.74	7.60	7.83
(64)	-1.40	8.31	$-CO_2H$	8.23	8.12	7.71	7.59	7.91
(70)	-1.47	8.26	$-CO_2Me$	8.16	8.08	7.71	7.58	7.87

Appendix 3 continued

Compound number	Chemical shift $[\delta_H(CDCl_3)]$ or substituent							
	7b-Me	1	2	3	4	5	6	7
(53a)	-1.38	-CHO	8.24	8.16	7.99	7.69	7.77	8.08
(53b)	-1.41	8.21	-CHO	8.16	8.11	7.71	7.57	7.90
(115)	-1.42	7.96	8.08	8.11	8.40	-CHO	8.07	7.74
	-1.36					8.20	-CHO	8.20
	-1.27	$-NO_2$	8.33	8.29	8.08	7.72	7.89	8.23
			$-NO_2$			7.81	7.69	8.01
	-1.32	7.99	8.14	8.20	8.50	$-NO_2$	8.48	7.71
	-1.35	8.29	8.00	8.00	8.29	8.62	$-NO_2$	8.62
	-1.42	$-COCH_3$	8.27	8.12	7.97	7.67	7.75	8.06
	-1.42	8.27	$-COCH_3$	(8.12)	(8.13)	7.74	7.60	7.90
	-1.47	7.93	(8.05)	(8.08)	8.38	$-COCH_3$	8.22	7.69
	-1.44	8.14	7.90	7.90	8.14	8.31	$-COCH_3$	8.31
(116)*	-1.69	(7.94)	(7.99)	8.01	8.23	$-SO_3Na$	7.83	7.66
(51)	-1.12	-CHO	-CHO	8.44	8.27	7.73	7.84	8.34
(52a)	-1.32	$-CH_2OH$	-CHO	(8.14)	(8.19)	7.70	7.56	8.01

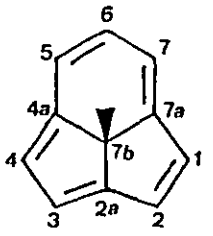
Appendix 3 continued

Compound number	Chemical shift $[\delta_H(CDCl_3)]$ or substituent							
	7b-Me	1	2	3	4	5	6	7
(52b)	-1.32	-CHO	$-CH_2OH$	(7.96)	(8.27)	7.64	7.78	7.96
(38)	-1.34	$-CO_2Me$	$-CO_2Me$	8.22	8.08	7.68	7.68	8.06

Figures in parentheses may be interchanged.

*d_6-Dimethyl sulphoxide as solvent.

APPENDIX 4 Compilation of Carbon-13 n.m.r. Data of some Derivatives of 7b-Methyl-7b<u>H</u>-cyclopent[<u>cd</u>]indene



Substituents	Compound number	Chemical shift [δ_C($CDCl_3$)]											
		7b-Me	C-7b	C-5	C-7	C-6	C-2	C-3	C-1	C-4	C-4a	C-7a	C-2a
none	(1)	29	59	116	116	129	129	129	135	135	159	159	179
2-$OSiMe_3$	(77)	30	57	(112)	(115)	(129)	-	(130)	125	(131)	156 - 160		
2-CN	(65)	29	60	118	121	(130)	-	(131)	140	136	(160)	(158)	179
2-CO_2H	(64)	29	60	118	122	(130)	-	(132)	140	136	(159)	(158)	180
2-CHO	(53b)	29	60	119	123	(130)	-	(131)	141	134	(159)	(158)	179
1-CO_2Me, 2-CO_2Me	(38)*	29	59	118	121	(133)	-	(134)	-	140	(161)	(160)	175
1-CHO , 2-CHO	(51)	30	60	119	122	(135)	-	(136)	-	143	(162)	(163)	177
1-CH=N-N=CH-2	(137)	27	62	120	122	131	-	131	-	135	163	151	168

Chemical shifts are given to the nearest part per million.
Chemical shifts for carbon atoms attached to functional groups are not given.
Figures in parentheses may be interchanged.
* The data for the ester (38)is taken from the thesis of Tuddenham.[42a]

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