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QUINONE DEHYDROGENATION OF ARENES AND STUDY OF QUINODIMETHANE ANALOGUES

by

© A. S. KWESI AIDOO

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

Spring, 1971

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

"QUINONE DEHYDROGENATION OF ARENES AND STUDY OF QUINODIMETHANE ANALOGUES"

submitted by A. S. KWESI AIDOO in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Supervisor

External Examiner

Date. November 19th 1970

To Yaw, my elder brother

ABSTRACT

The reactions of a number of methyl substituted aromatic compounds with tetra-chloro-o-benzoquinone (TOQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) have been examined as an extension of general quinone dehydrogenation of hydroaromatics.

These reactions were found to lead to adduct formation between the arenes and quinones. The type of adduct formed depended on the quinone and the arene involved. The adducts formed by TOQ were either dioxoles or dioxins; whilst DDQ formed mono quinol ethers, or Diels-Alder adducts by reaction at the cyano substituted double bond. Formation of some of these adducts has been rationalised as involving quinodimethane intermediates.

Dehydrogenation in the pleiadene series in general resulted in adduct formation, but in one case in transannular phenyl participation in quinone dehydrogenation; and in another, unexpectedly, in direct oxidation of aryl methylene to a ketone.

As an extension of the interest in quinodimethanes, novel radical anions have been generated in the acepleiadylene series. These radical anions have in their hydrocarbon framework the elements of o-quinodimethane.

ACKNOWLEDGEMENTS

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The people of Alberta, and the Chemistry Department for this opportunity to broaden my outlook.

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CHAPTER I

REVIEW OF QUINONE DEHYDROGENATION

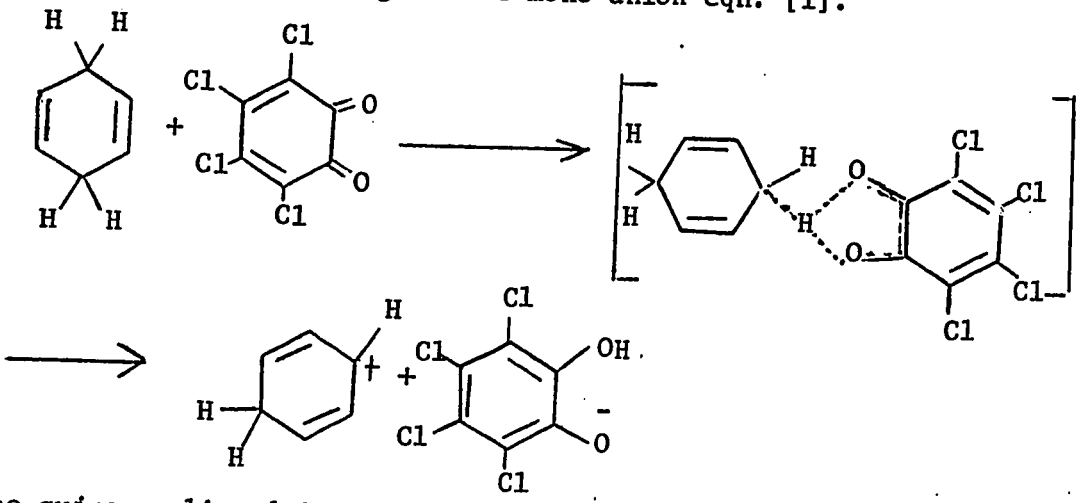
INTRODUCTION

Quinone dehydrogenation has been employed in (i) the introduction of double bonds in natural products (mainly steroids); (ii) aromatisation of hydroaromatics; (iii) oxidation of phenols, and allylic, benzylic, and propargylic alcohols; and (iv) dehydrogenation of polymers formed from olefins and dienes to give polyacetylenes.

The dehydrogenating power of quinones is dependent on the substituents. Electron withdrawing substituents increase the dehydrogenating power of quinones (e.g. CN, Cl), and electron donating substituents decrease in the dehydrogenating power. These same changes in substitution similarly affect the redox potential of a quinone, and there is a linear free energy relationship between redox potential and reactivity in dehydrogenation - i.e. the higher the potential of a quinone the greater is its dehydrogenating power. Table I (1) shows some quinones with their redox potentials E_o and their relative rates of dehydrogenation of 1,2-dihydronaphthalenes at 100° and Table II (2) gives the redox potential of some other quinones.

From Table I it is seen that tetrachloro-o-benzoquinone is a far more powerful dehydrogenating agent compared with its para-isomer, chloranil, than would be expected from a comparison of

redox potentials. This is attributed to strong hydrogen bonding in the transition state leading to the mono anion eqn. [1].



[1]

Of the quinones listed in Tables I and II, 2,3-dichloro-5,6-dicyano-1, 4-benzoquinone (DDQ), and tetrachloro-o-benzoquinone (TOQ) and chloranil have been used most often in dehydrogenation reactions, because of their higher redox potentials. Most of the discussion will be on dehydrogenation using these three quinones, though the present work was done with DDQ and TOQ.

TABLE I

Relative Rates of Dehydrogenation of

1, 2-Dihydronaphthalene at 100°

Quinone	Eo	Relative Rate
Choranil	0.70	1
3, 3',5,5'-Tetrachloro-4, 4'-diphenoquinone	ca 1.0	1100
Tetrachloro-o-benzoquinone	0.87	4200
2, 3-Dichloro-5, 6-dicyano-1, 4-benzoquinone	ca 1.0	5500

TABLE II

Redox Potentials of Quinones

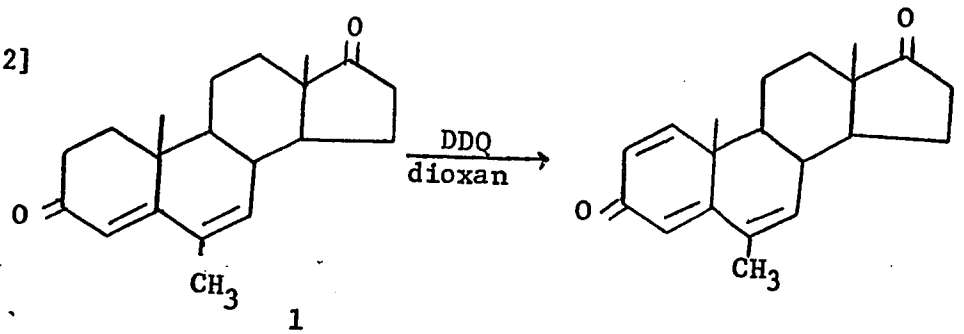
Quinone	E_o pH=0(H_2O)	E_1 (CH_3CN)	E_o 95% EtOH in HCl, 25°
DDQ	1.0	0.51	
TOQ			0.870
Chloranil	0.452	0.01	0.703
Trichloro-p-benzoquinone	0.486	-0.08	0.726
2,6-Dichloro-p-benzoquinone	0.475	-0.18	0.748
Chloro-p-benzoquinone	0.466	-9.34	0.736
Methyl-p-benzoquinone	0.339	-0.58	0.656
Tetramethyl-p-benzoquinone	0.220	-0.84	0.466
P-Benzoquinone	0.433	-0.51	0.711
1,4-Naphthaquinone	0.224	-0.71	

E_1 = One electron reduction potential

Dehydrogenation of Natural Products

Since the review by Jackman (1) on the use of quinone for dehydrogenation, a host of Δ^4-3-keto-steroids, saturated 3-keto-steroids and other steroids have been dehydrogenated using DDQ. A comprehensive review of these up to 1964 is given by Walker and Hiebert (2). Dehydrogenation of the steroids have received considerable attention because their dehydro compounds, the products of such dehydrogenations, are found to possess desirable biological activity. The dehydrogenation of Δ^4-keto-steroids under neutral or weakly acid conditions give $\Delta^{1,4}$,-3-keto steroids whilst in the presence of strong acids, usually hydrogen chloride, they give $\Delta^{4,6}$-3-keto steroids, and small amounts of $\Delta^{1,4,6}$-3-keto-steroids.

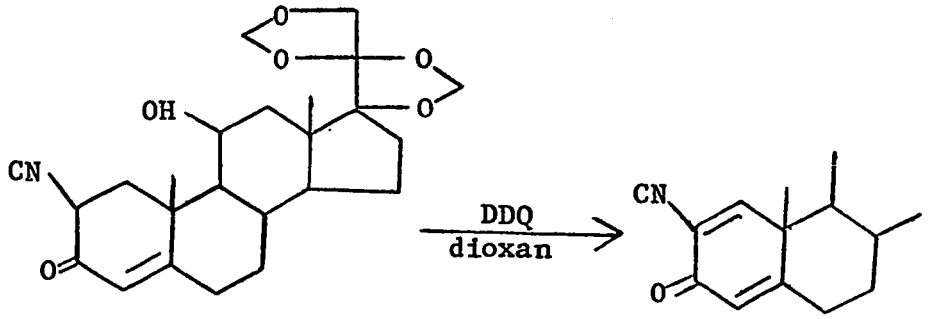
[2]



1 2

Burn, Petrow and Weston (3) obtained 6-methylcholestra-1,4,6-trien-3-one 2 by dehydrogenation of 6-methylcholestra-4,6-dien-3-one 1 with DDQ in refluxing dioxan, eqn. [2]. Orr and co-workers (4) have also dehydrogenated 2-cyanohydrocortisone 3 to 2-cyanoprednisolone 4 with DDQ in dioxan using benzoic acid as catalyst, eqn. [3].

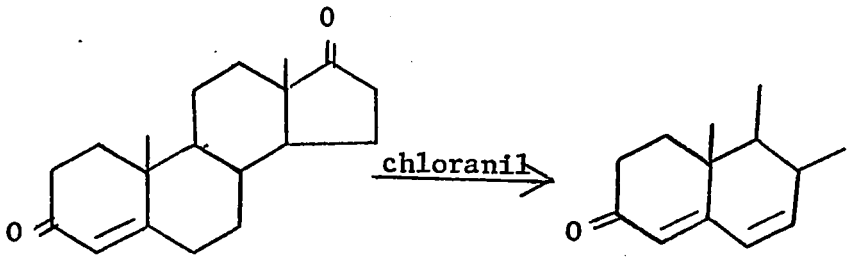
[3]



3 4

Examples that give the 4,6-diene instead of the 1,4-diene are dehydrogenations of androst-4-ene-3,17-dione 5, and 6-fluoro-9 β-, 10α-pregn-4-ene-3, 20-dione 7.

[4]



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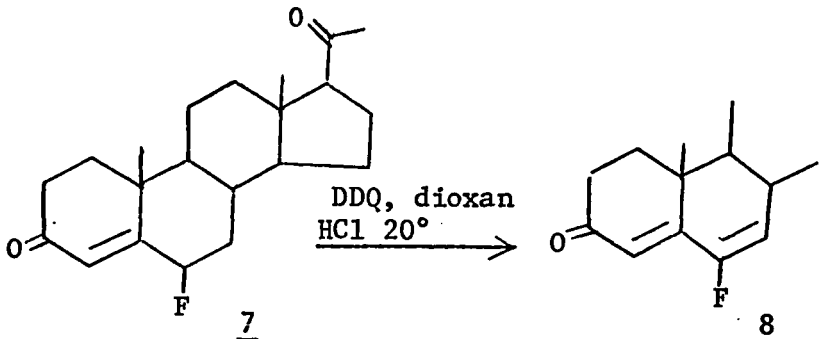
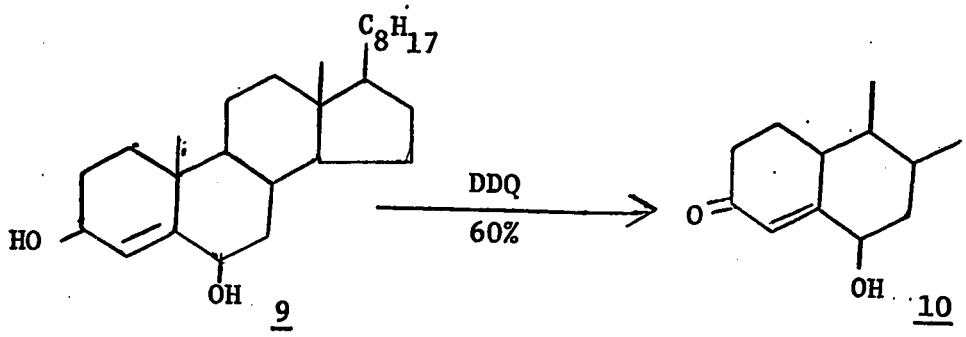
[5]



7 8

DDQ dehydrogenation of Δ^4-3-hydroxy-steroids leads to the enenones; for example, 3β, 6β-dihydroxycholest-4-ene 9 is converted to 6β-hydroxycholest-4-en-3one 10 (6).

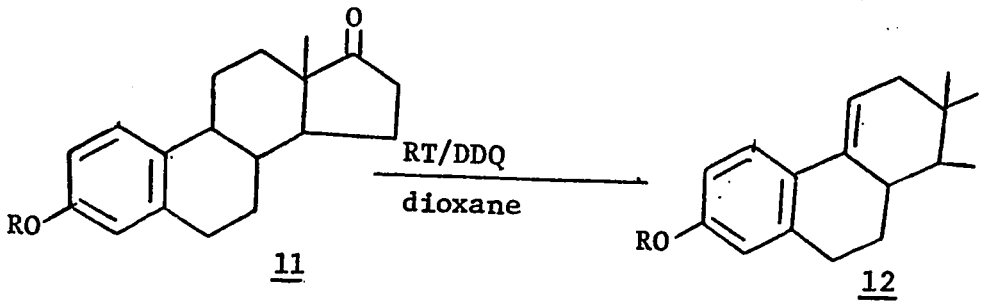
[6]



9 10

Recently Brown, Findlay, and Turner (7) have dehydrogenated oestrone (R=H) and its methyl ether ($R=CH_3$) to give 9(11)-dehydro derivatives in yields of 67% and 70% respectively; eqn. [7]

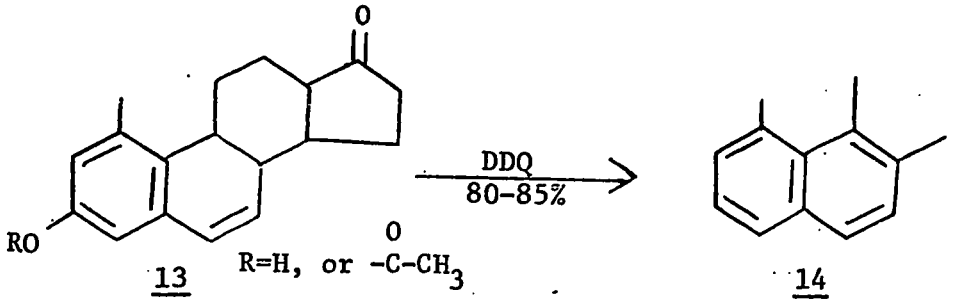
[7]



11 12

They have also converted the dehydro compound 13 to the A/B-aromatic steroids 14, eqn. [8].

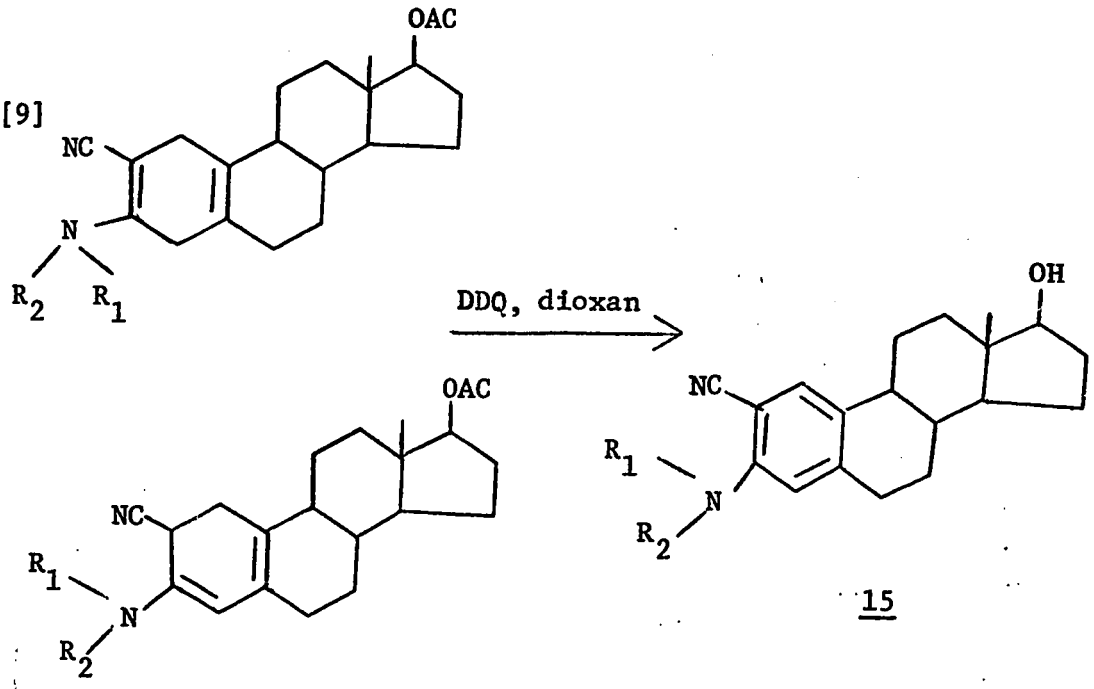
[8]



13 14

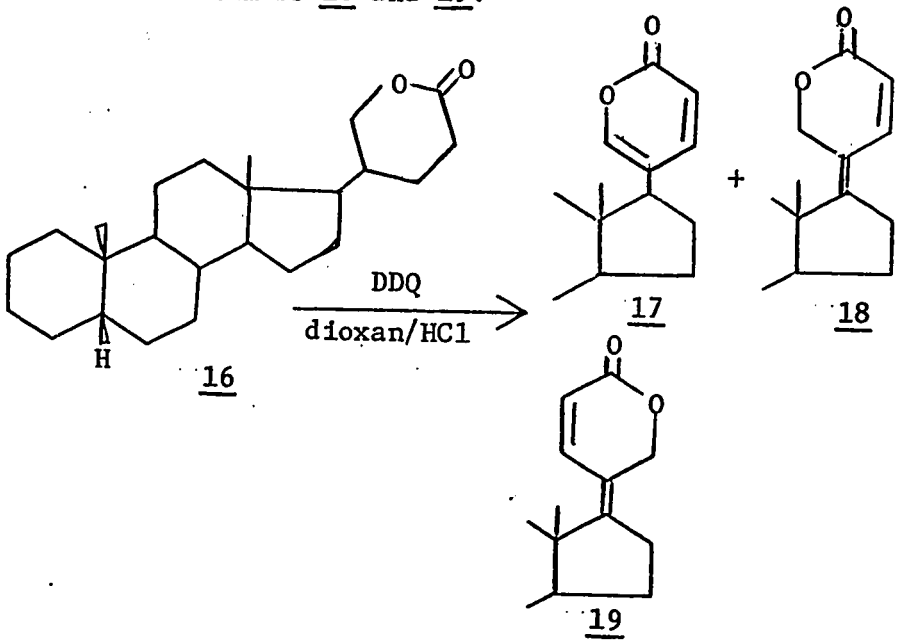
Other examples involving aromatisation are the preparations of the fertility control substances, 2-cyano-3-aminoestratrienes, 15 eqn. [9] (8).

[9]



Sarel, Shelon, and Yanuka (9) have converted 5β, 14α-buta-20(22)-enolide 16 a steroidal βα-unsaturated δ-lactone to the α-pyrone 17, with DDQ in presence of p-toluenesulfonic acid. In the presence of hydrogen chloride gas, however, 17 was obtained together with its isomers 18 and 19.

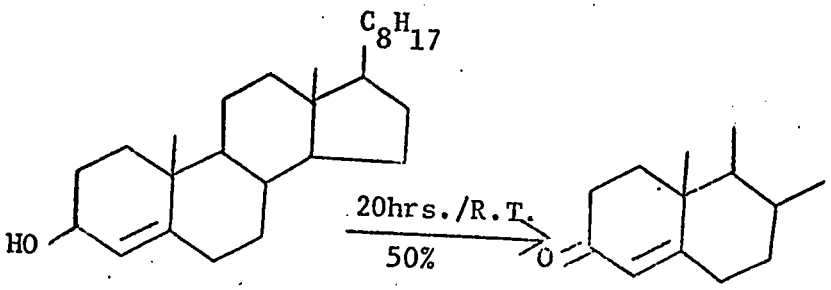
[10]



In addition to above examples Walker and Hiebert list over 230 different steroids that have been dehydrogenated using DDQ. Most of these appear under patents and are summarised in the Chemical Abstracts.

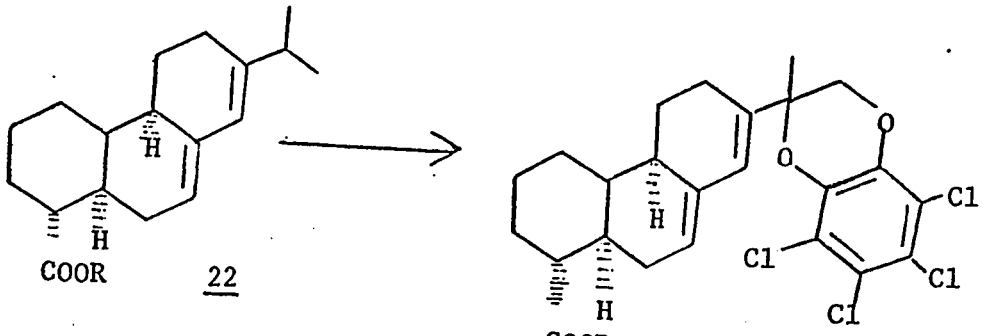
Tetrachloro-o-benzoquinone has not been used in dehydrogenation of natural products as much as DDQ. Examples found are in dehydrogenation of lanost-4-enol 20 to lanost 4-en-3-one, 21 (10) and of abietic acid 22 and limonene 24 which resulted in adduct formation, (11).

[11]



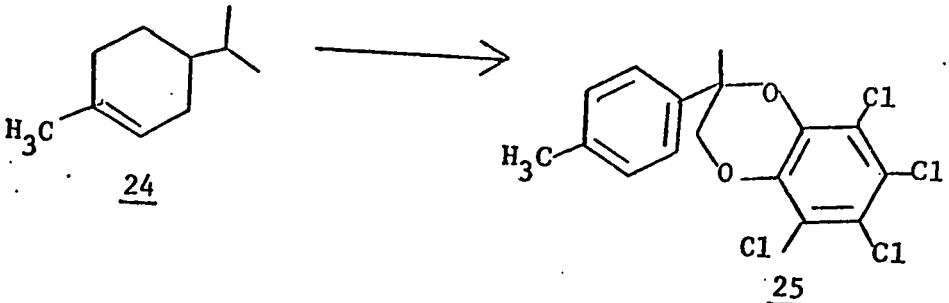
20 21

[12]



22 23

[13]



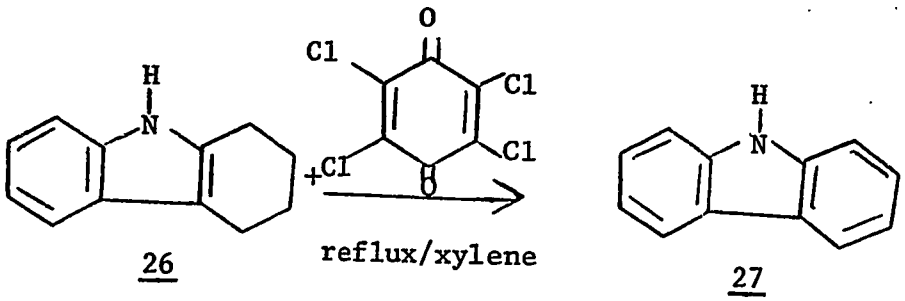
24 25

Dehydrogenation of Hydroaromatics

The major work on quinone dehydrogenation of hydroaromatics was done by the group of Braude, Linstead, Jackman, and co-workers and this will be discussed in detail under the "mechanism of quinone dehydrogenation." However, some applications will be discussed here.

Barclay and Campbell (12) dehydrogenated a series of di-, tetra-, and hexahydrocarbazoles using chloranil in refluxing xylene and obtained yields of 75 - 90%, e.g. eqn. [14].

[14]

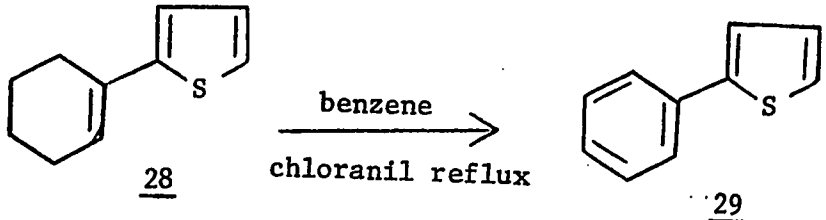


26 27

In this and other dehydrogenations of hydroheterocyclic compounds it is thought the hetero atom lone pair provides considerable driving force for the hydride abstraction (see mechanism), since the cationic intermediates in these would be much more stable than the carbonium ion resulting from carbocyclic compounds. Jackman (1) lists a series of nitrogen containing hydroaromatics such as dihydro derivatives of quinoline, isoquinoline and hydroporphins) that can be aromatised with quinones. 2-Phenylthiophene 29 has been obtained in 87% yield by refluxing chloranil and 2-(1-cyclohexenyl)-thiophene 28 in benzene (13). When this dehydrogenation was done with sulfur only 4% of 29 was obtained.

This is an example of the advantages quinone dehydrogenation has over other dehydrogenation methods.

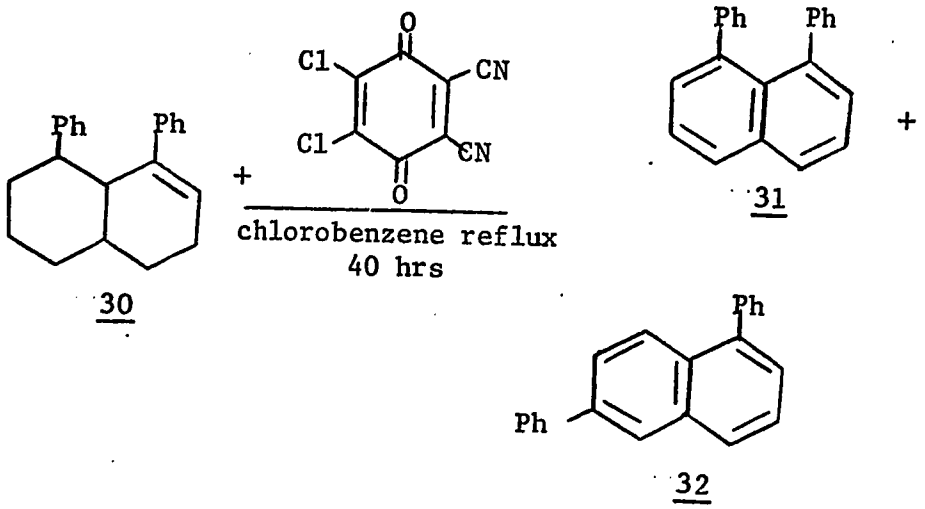
[15]



28 29

House and Bashe (14) dehydrogenated 1,8-diphenyl-$\Delta^{1,2}$-octalin 30 to give the expected product 1,8-diphenylnaphthalene 31 and a rearranged product 1,6-diphenylnaphthalene 32 using DDQ.

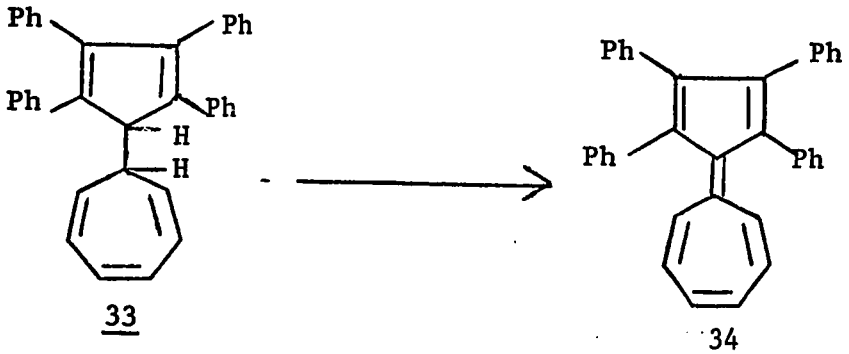
[16]



30 31 32

Dehydrogenation of 7-[2,3,4,5,-tetraphenyl-cyclo-pentadien-(2,4)-yl-(1)]-cycloheptatri-1,3,5-ene 33 to tetraphenylsesquifulvalene 34 is accomplished with chloranil in carbon tetrachloride in 64% yield.

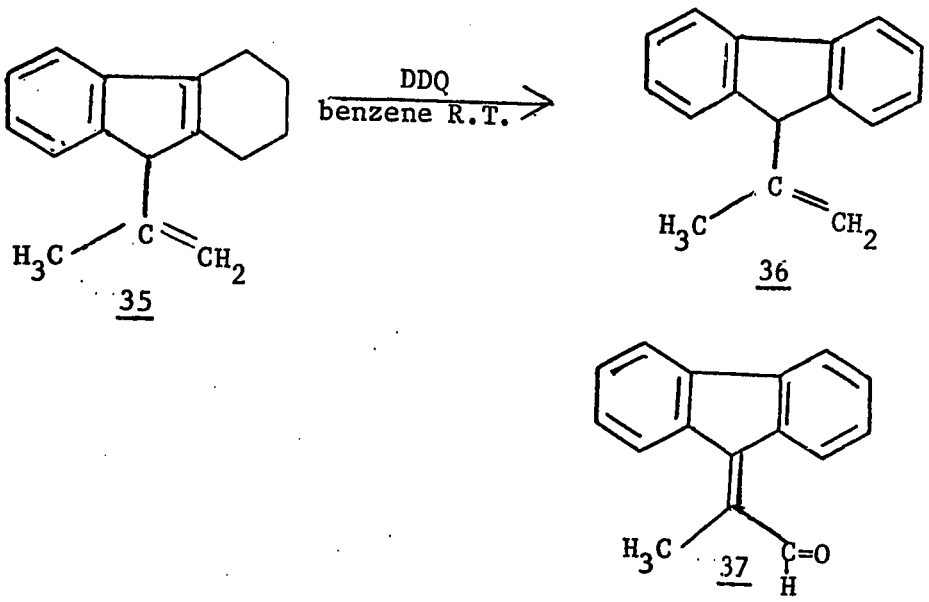
[17]



33 34

Sadler and Stewart (16) treated 9-isopropenyl-1,2,3,4-tetrahydrofluorene 35 with excess of DDQ in benzene at room temperature and obtained in addition to the expected product 9-isopropenyl fluorene 36, the aldehyde 37, which became the major product when the mixture was heated under reflux. Aldehydes were also obtained with a series of arylpropenes.

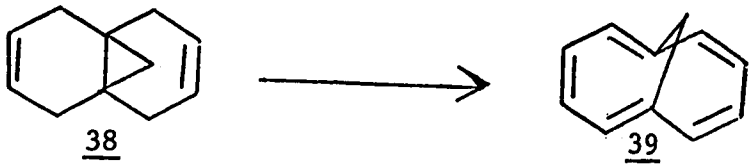
[18]



35 36 37

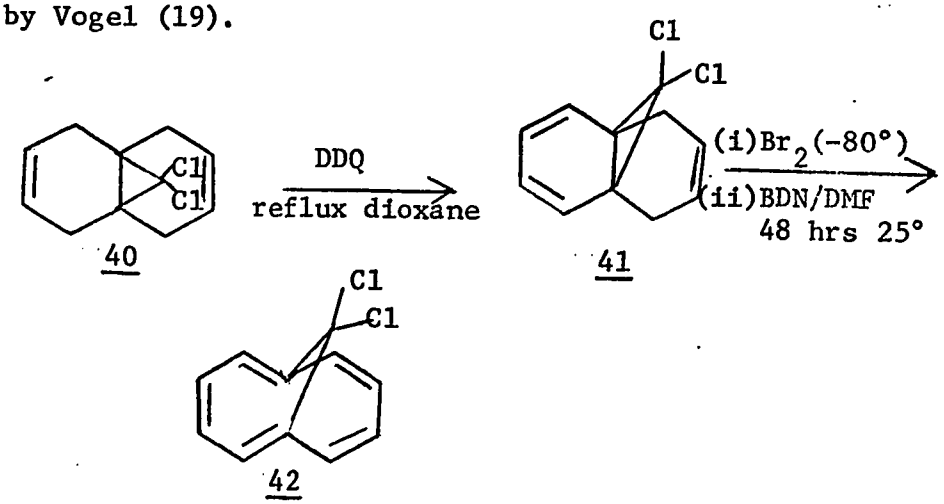
Recently Nelson and Untch (17) have employed DDQ in an improved synthesis of 1,6-methano-[10]-annulene, by refluxing 38 with 2.5 moles of DDQ in dioxan. Yield of 33 was

90%. This is a marked improvement on the 50% yield obtained by Vogel (18). The 11,11-dichloro derivative 40 could only be

[19] 

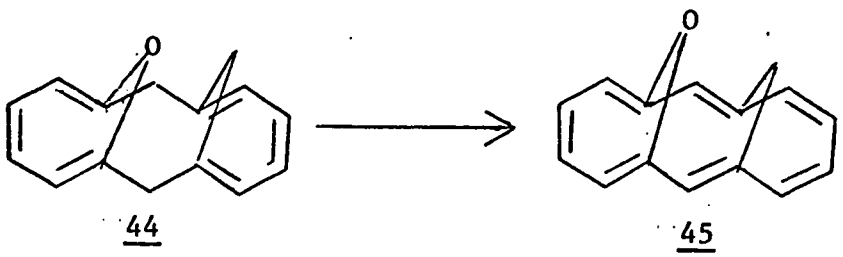
38 39

dehydrogenated to norcaradiene 41, which on bromination and treatment with diazabicyclononene (DBN) gave the dichloroannulene 42 in an overall yield of about 50% from 40. This was obtained in only 6% yield by Vogel (19).

[20] 

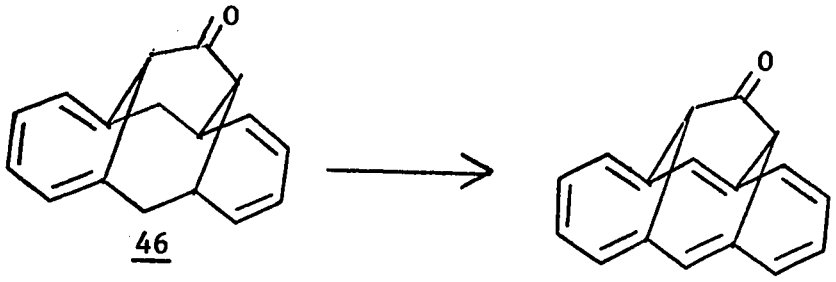
40 41 42

Following this discovery by Nelson and Untch, Vogel (20) has used DDQ in the synthesis of (14)-annulenes, 45, 47, 49, and the α-ketone 51 in yields of over 90%.

[21] 

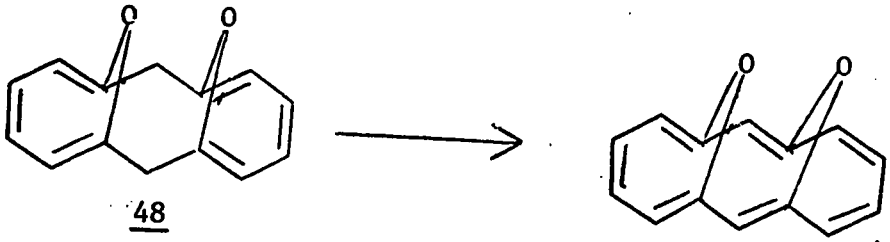
44 45

[22]



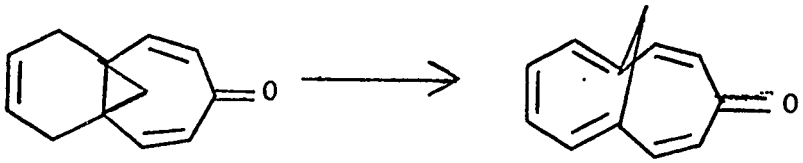
46 47

[23]



48 49

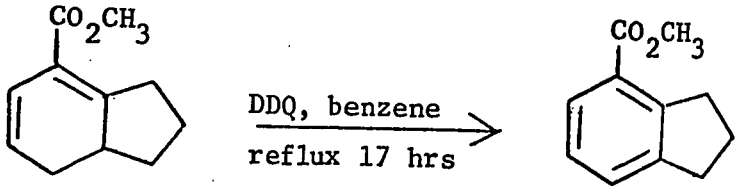
[24]



50 51

House and Cronin (21) have dehydrogenated the diene ester 52 to methylindan-4-carboxylate 53, in 87% yield by refluxing with DDQ in benzene, whilst Maloney (22) has converted the dihydro

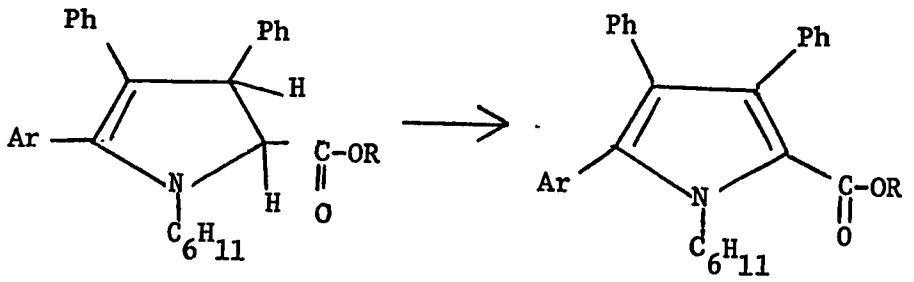
[25]



52 53

compounds 54, 56 to the pyrroles 55 and 57 respectively in 70 - 75% yield using chloranil in chlorobenzene.

[26]

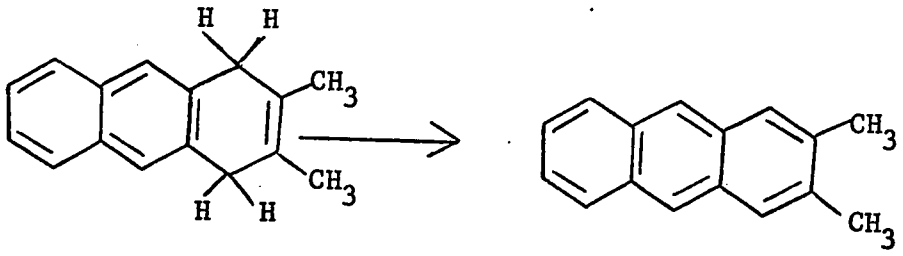


54 Ar = p-bibphenyl, R = CH_3 55

56 Ar = Ph R = iPr 57

Wolthuis (23) has used chloranil in the synthesis of some methylsubstituted anthracenes; an example is shown in eqn. [27].

[27]

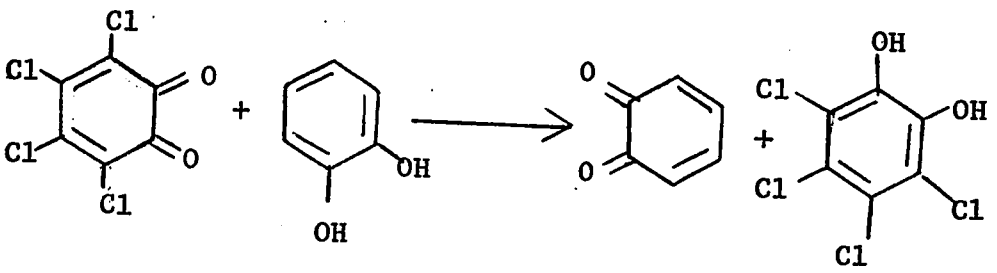


In the present work, it was found the o-chloranil gave a better yield and purer product than chloranil (see experimental of Chapter II).

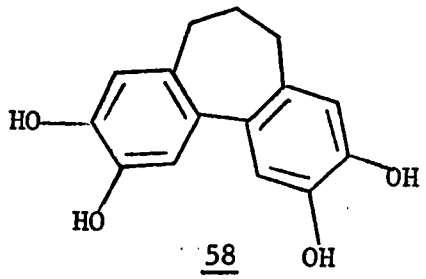
Oxidation of phenols, quinols, allylic, benzylic and propargylic alcohols

Quinols of lower redox potential are easily oxidized to quinones by higher potential quinones like TOQ. Catechol is

oxidized to 1,2-benzoquinone eqn. [28]. Other examples are

[28] 

oxidation of the bridged dihydrobiphenyl 58 and the benzotropolone 60 to the quinones 59 (25) and 61 (26).



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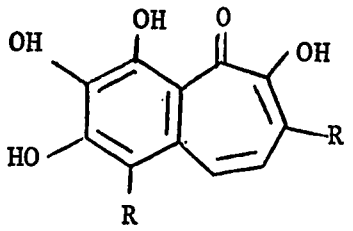

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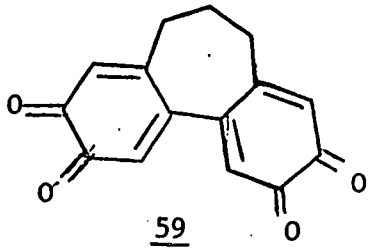

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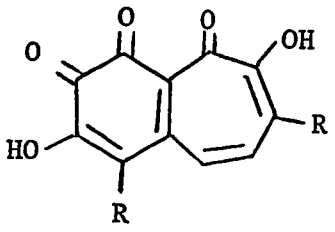
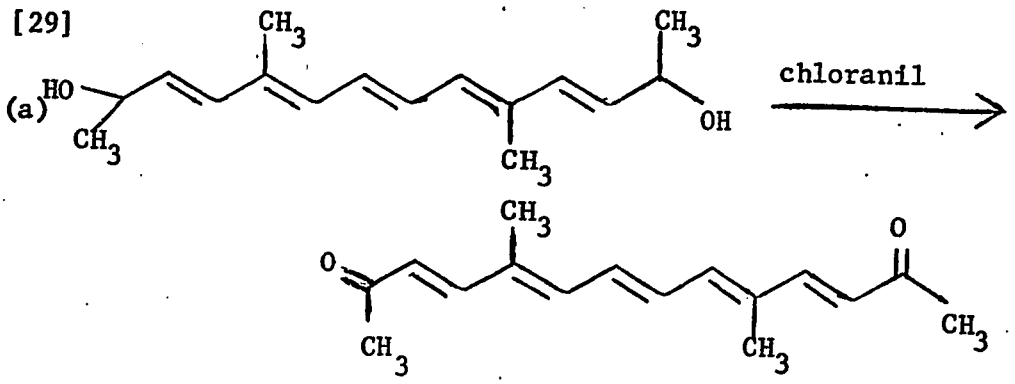


61

Allylic, benzylic, and propargylic alcohols are oxidized to aldehydes and ketones. An example using DDQ has already been given, (see eqn. [16]). Other examples using chloranil and o-chloranil (TOQ) are given below (27).

[29]



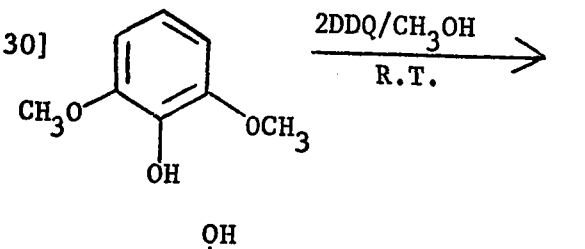
(b) $MeCH = CHCH = CH-CH_2OH \xrightarrow{TOQ} MeCH = CHCH = CHCHO$

(c) $PhCh_2OH \xrightarrow{TOQ} PhCHO$

(d) $PhC{\equiv}CC(OH)CH{=}CHPh \xrightarrow{TOQ} PhC{\equiv}CC(=O)CH{=}CHPh$

Phenols have been dehydrogenated mainly with DDQ. The products obtained are dependent on the nature of the phenol; but usually lead to oxidative coupling, eqns. [30] and [31], (28) or intramolecular cyclisation, eqns. [32] (29) and [33] (30).

[30]



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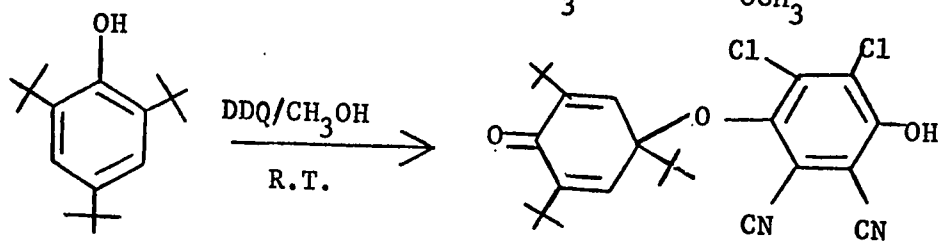
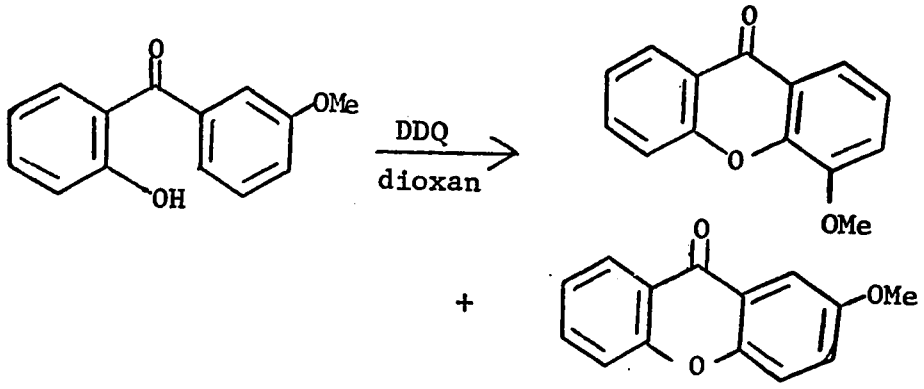


[32]



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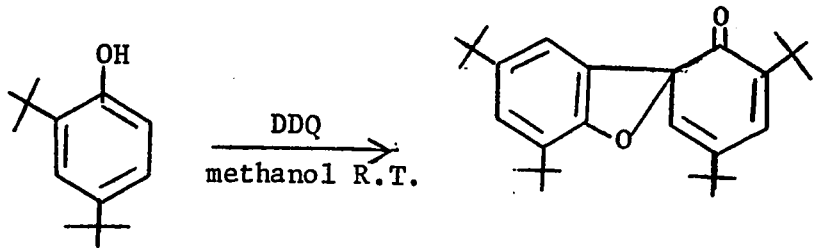
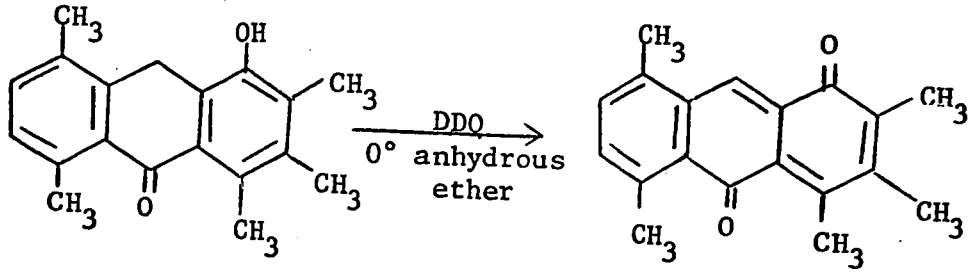


Of interest is the synthesis of the ana-anthraquinone 63 by the oxidation of 4-hydroxy-1,2,3,5,8-pentamethylanthrone 62 with DDQ; though the product could not be obtained pure except in very dilute solutions it represents the first time that ana-anthraquinone system has been prepared (31).

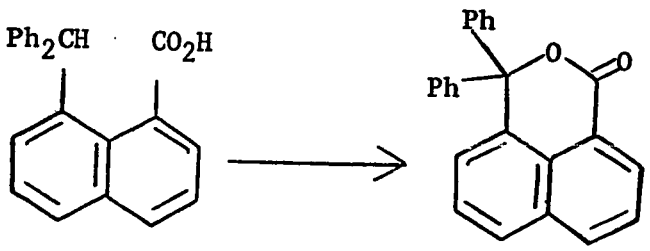
[34]



62 63

Cyclodehydrogenations, as described above for phenols, lead to formation of lactones and cyclic ethers when the substrates are carboxylic acid and benzylic alcohols respectively, eqns. [35] and [36] (32).

[35]



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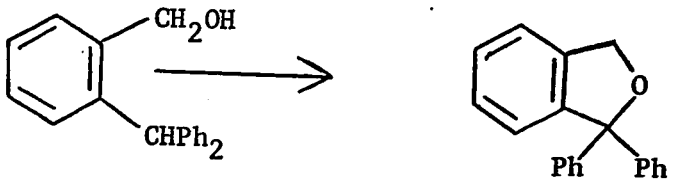
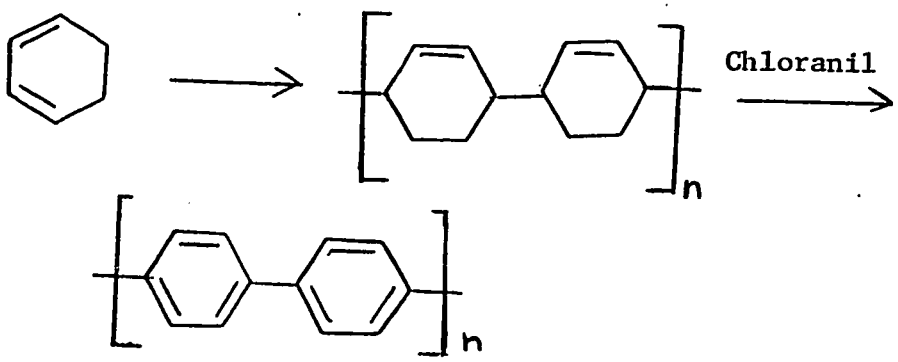


Quinone dehydrogenation of polymers formed from dienes and olefins

Polymers formed from cis-butadiene, styrene, and chlorostyrene have been reported to be dehydrogenated by TOQ and chloranil in benzene and chlorobenzene to give polyacetylenes (33, 34) whilst the polymer formed from cyclohexa-1,3-diene is oxidized by chloranil to give polybenzene, eqn. [37] (35).

[37]



Mechanism of Quinone Dehydrogenation

Braude, Linstead, Jackman and co-workers have done most of the work on the mechanistic study of quinone dehydrogenations. They found that in the dehydrogenation of 1,4-dihydronaphthalene (36):

(i) The reaction is essentially bimolecular, first order with respect to the quinone, and first order with respect to the dihydronapthalene.

(ii) Reaction is faster in polar solvents than in non-polar solvents; radical producing agents such as light and peroxides are without influence on reaction rate, and no coupling products derived from the hydrocarbon are obtained.

(iii) Reactivity of the quinones is enhanced by electron-attracting substituents and reduced by electron-donating substituents. The rate constants, as well as the energies of activation can be correlated with the redox potentials of the quinones, and o-quinones are more reactive relative to p-quinones than expected from their potentials (see Table I).

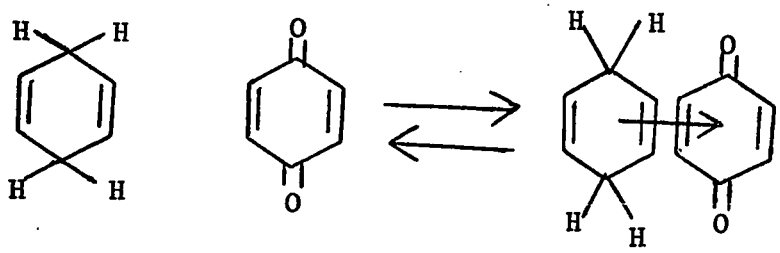
(iv) With quinones of low potentials (e.g. 9.10-phenathraquinone Eo = 0.471 volts) the reactions exhibit marked product catalysis which is due to the quinol formed. Similar catalytic effects are observed with other weak proton donors which form molecular complexes with quinones (e.g. p-nitrophenol), and with strong proton donors ($HClO_4$).

These observations have been rationalised as follows: The reactions proceed through a two-step ionic mechanism involving

a rate determining transfer of a hydride ion from the hydrocarbon to the quinone, followed by rapid proton transfer between the resulting conjugate acid of the aromatic hydrocarbon and the quinol anion, eqn. [38].

[38] $RH_2 + Q \xrightarrow[\text{slow}]{} RH^+ + QH^- \xrightarrow[\text{fast}]{} R + QH_2$

It is thought that this first rate-determining step is sometimes preceded by formation of a charge-transfer complex, eqn. [39].



Evidence for such a charge transfer complex is found in complexes formed by DDQ with macromolecular compounds like poly(N,N-dimethylaminostyrene) where ultraviolet and infrared spectra show normal charge transfer bands (37). Such charge transfer complex formation is made use of in photo-conductive materials for zerography or for photoplastic registration (38).

Catalysis by proton donors is ascribed to formation of the conjugate acid of the quinone, i.e. the quinol cation QH^+ which has an even higher affinity for anionoid hydrogen than the quinone eqn. [40].

[40]

$$Q + HX \xrightarrow{\text{fast}} QH^{+} + X^{-}$$

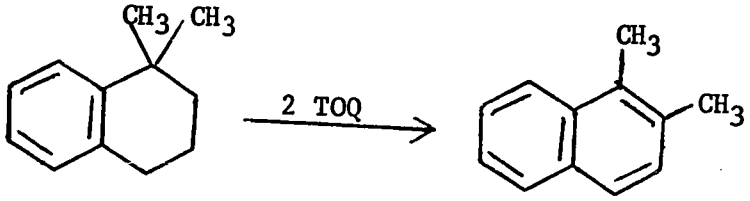
$$RH_2 + QH^{+} \xrightarrow{\text{slow}} RH^{+} + QH_2$$

$$X^{-} + RH^{+} \xrightarrow{\text{fast}} R + HX$$

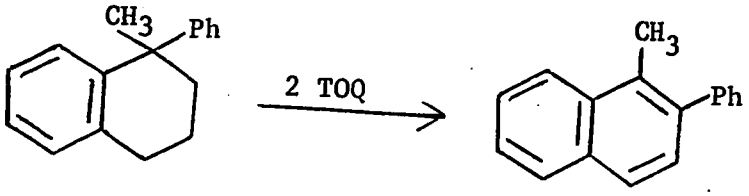
The observations above make it unlikely that a free radical chain mechanism, as proposed by Waters (39) is involved, though they do not rule out completely a homolytic mechanism.

Further evidence in favour of a carbonium ion intermediate is found in the dehydrogenation of 1,1-disubstituted-tetralins (40) in which there occurs a Wagner-Meerwein rearrangement to form the 1,2-substituted product with no loss of the migrating group eqns. [41], [42], and [43]. The ease of reaction

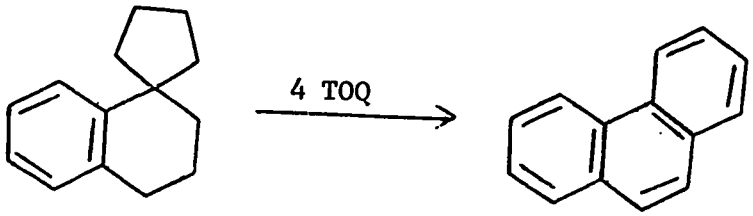
[41]



[42]

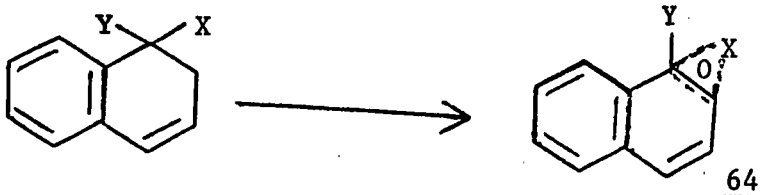


[43]



may be correlated with relative migratory aptitude of the groups at the 1-position indicating the formation of a carbonium ion 64 (a). If the reaction took place by a free radical mechanism

[44]

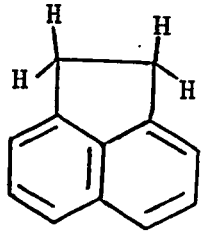


64(a) O = +
(b) O = •

then the formation of free radical intermediate 64 (b) must be postulated. Whilst an aryl migration could proceed by a free-radical, an alkyl migration is extremely unlikely.

Jackman and Thompson (41) have measured the rates of reaction of series of 6- and 7-substituted 1,2-dihydronapthalenes and found these rates correlate with Hammett σ-values of the substituents. They found ρ= -2.5, which is indicative of a high sensitivity of hydroaromatic donors toward changes in substitution.

Trost (42) has studied the mechanism of dehydrogenation of acenaphthene and its deuterated derivatives 65, 66, 67 and 68 with TOQ and DDQ and observed a net cis elimination decreasing with increase in solvent polarity; large isotope effect



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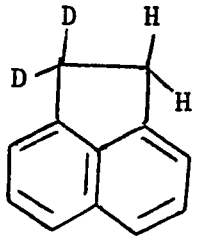

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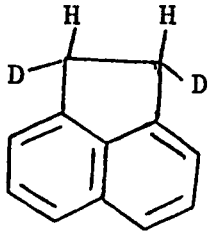

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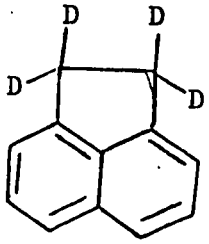


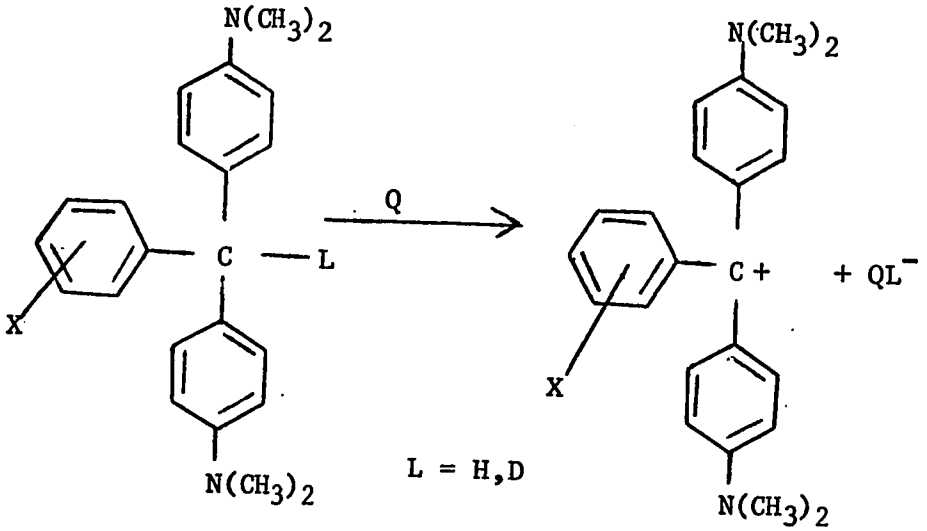
68

(k_H/k_D = 3.49 - 4.14); lack of 1,2-shifts of deuterium or hydrogen. These observations are interpreted as supporting the intermediacy of a classical carbonium ion. The high K_h/K_d value indicates a considerable amount of single C-H bond breakage with hydride abstraction as the rate-determining step. The net cis elimination is accounted for by initial ion-pair formation and partial collapse of the ion pair to products before dissociation.

Lown (43) has also observed high isotope effect in the dehydrogenation of 9,9,10,10-tetradeuteroanthracene, where K_H/K_D of 5 is recorded.

Lewis, Perry, and Grinstein (44) have observed very high K_H/K_D values for quinone oxidation of leucotriphenylmethane dyes eqn. [45]. A value of 14.7 was observed for chloranil at

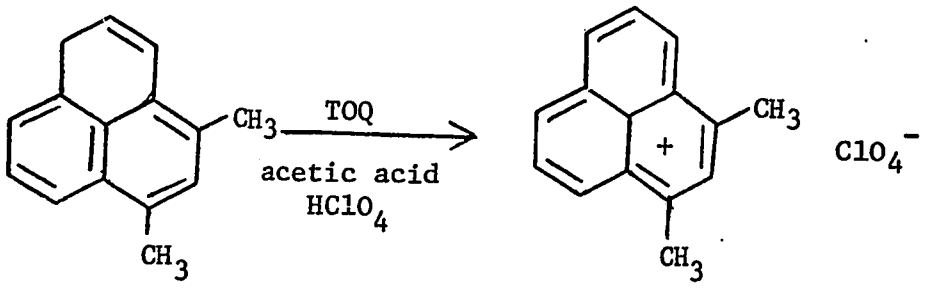
[45]

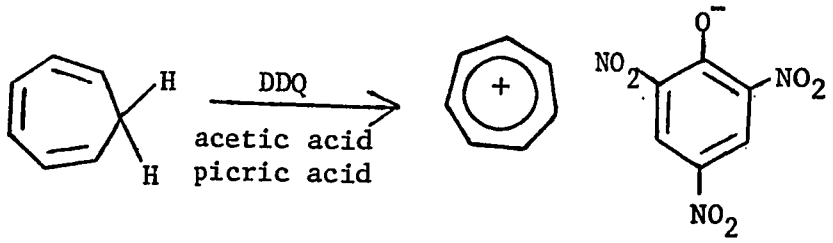


69 70

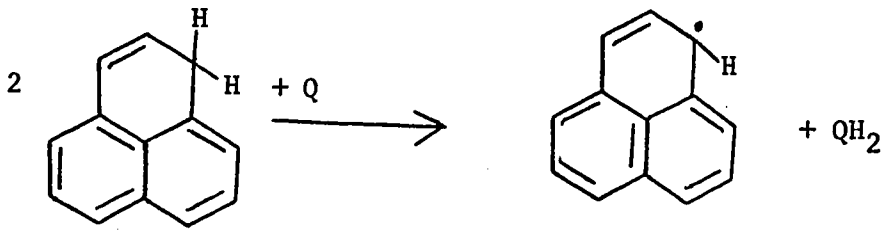
14.88°, and 6.96 for DDQ at 25° in acetonitrile. These values are explained as arising from tunnelling in the hydride-transfer reaction, and are reported to be of the same order as for oxidation of some triphenylmethanes by carbonium ions.

Generation of carbonium ion 70 by quinones also supports the hydride ion abstraction mechanism. Reid and co-workers (45, 46, and 47) have generated a few of these and trapped them as their chlorate or picrate salts:

[46] 

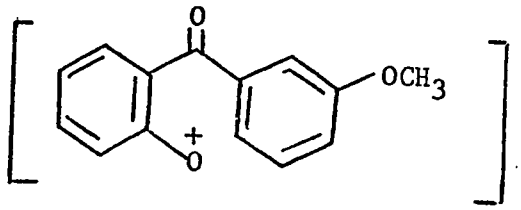
[47] 

However Reid and co-workers (46) also found that in absence of strong acid perinaphthalene reacted at room temperature in both polar and non-polar solvents with quinones to give the perinaphthyl radical eqn. [48]. This indicates that quinones can dehydrogenate

[48] 

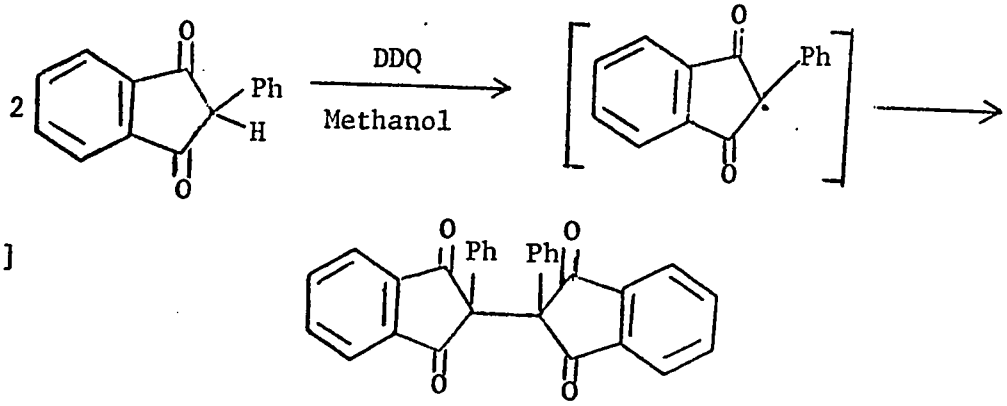
both by a homolytic and a heterolytic mechanism.

A homolytic mechanism has been used by Becker (28, 30, 48) to account for products obtained in the oxidation of phenols and enolisable ketones, see eqns. [30], [31], [33], and [49].



71

Lewis and co-workers (29) on the other hand have observed that though 2-hydroxy-3'-methoxybenzophenone (see eqn. [32]) was not cyclised by aqueous alkaline ferricyanide, it was readily cyclised by DDQ. They postulate the formation of phenoxonium ion 71 resulting from hydride abstraction from the 2-hydroxy group as the intermediate.

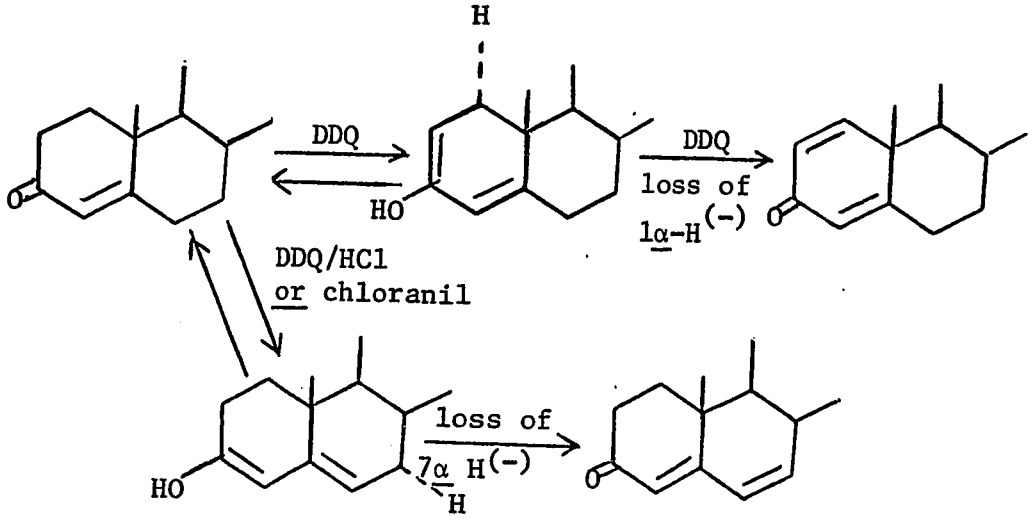


[49]

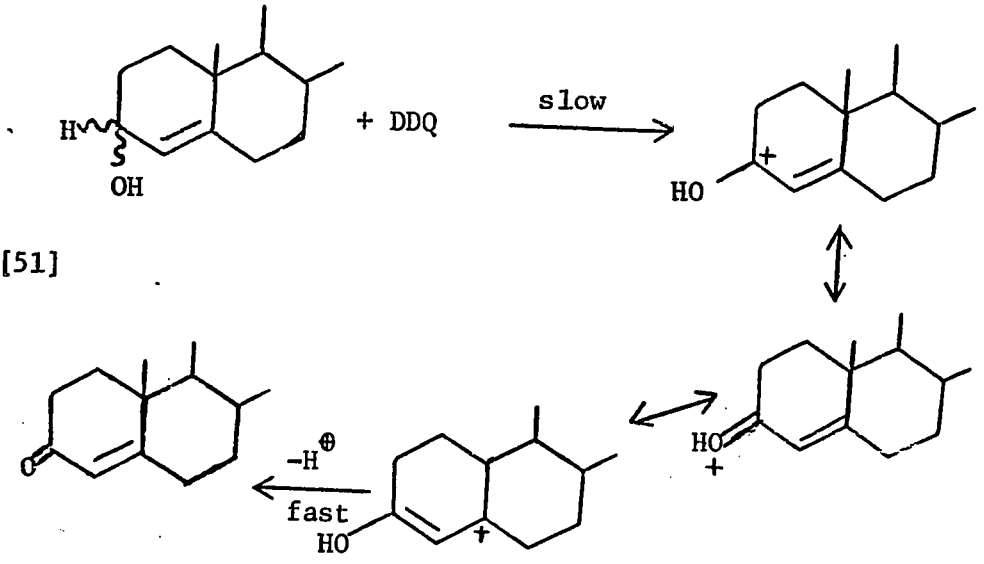
They also cite the fact that oxidation of 4-methoxy-2,6-di-t-butylphenol by DDQ to give the same product - 2,6-di-t-butyl-quinone - as the oxidation of 4-benzyloxy-2,6-di-t-butylphenol by Ce^{4+}, Fe^{3+} or IO_4^- in acid solution as further support for phenoxonium-ion participation in certain DDQ oxidations.

In dehydrogenation of Δ^4-3-keto steroids and Δ^4-3-hydroxy steroids the accepted mechanism is the hydride abstraction (49, 50). Δ^4-3-keto steroids are said to go through their enols as shown in eqn. [50], and the Δ^4-3-hydroxy-steroids are dehydrogenated via mechanism shown in eqn. [51].

[50]



[51]



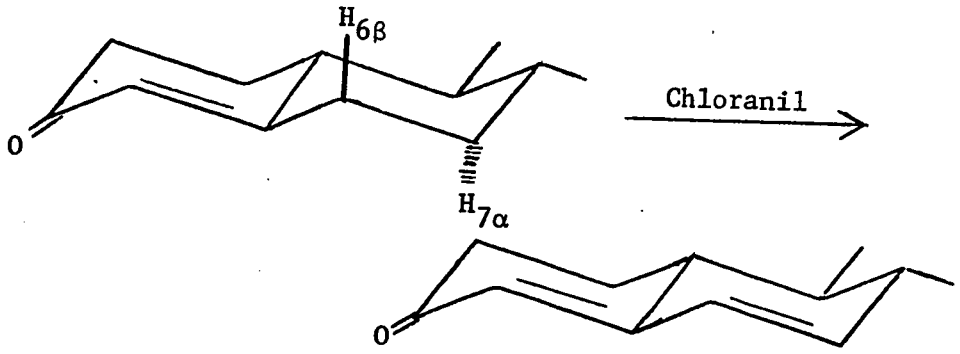
Burstein and Ringold (50) found in the kinetic study of the oxidation of a series of Δ^4-3-hydroxy-steroids with DDQ, found the same kind of rate dependence on solvent polarity; high deuterium isotope effect; and absence of acceleration of rate by radical initiators (e.g. benzoyl peroxide); as was found for hydroaromatics.

In summary: quinone dehydrogenation in hydroaromatics and steroids proceeds via overall hydride transfer as the rate determining step, whilst the comparable reaction with phenols, some enolisable ketones, and at least one hydroaromatic, by quinones do not necessarily require ionic mechanism, and could be explained in terms of a homolytic hydrogen transfer.

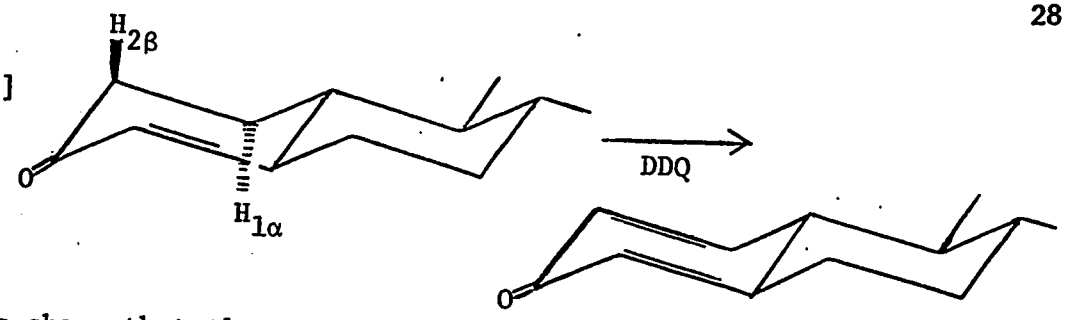
Stereochemistry of Quinone Dehydrogenation

Most of the work has been done in the steroid field. It has been shown that the dehydrogenation of Δ^4-3-keto-steroids with chloranil and DDQ to the corresponding 4,6-dien-3-ones (see eqn. [4]), and the 1,4-dien-3-ones (see eqn. [2]), involved the 6β, 7α (49, 51, 52) and 1α, 2β (53, 54) hydrogens respectively, using deuterium and tritium isotopes in these positions:

[52]



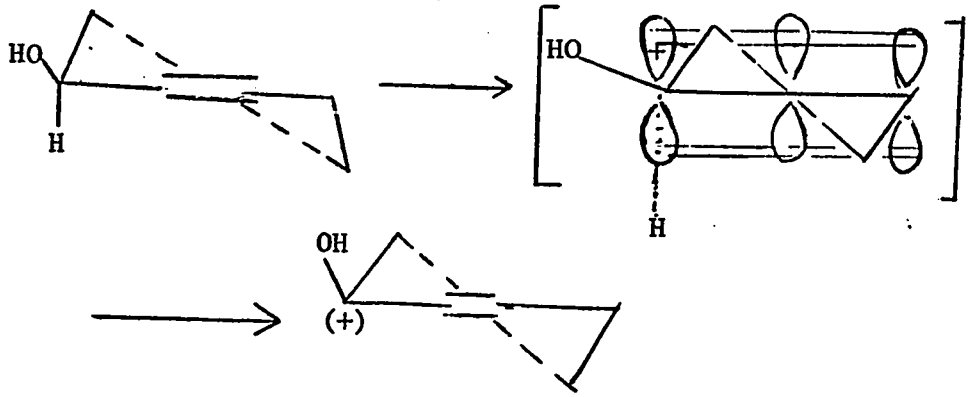
[53]



This shows that the quinone dehydrogenation of steroidsrequire the hydrogen being removed to be in the trans-diaxial position to one another.

In Δ^4-3-hydroxy steroids Burnstein and Ringold (50) found that the pseudoequatorial 3α-hydroxy compound reacted with DDQ more than six times as rapidly as the corresponding pseudo-axial 3α -hydroxy (3β -H) isomer. This is due to the fact that in the rate determining step the hydrogen being removed is axial; by virtue of its being essentially perpendicular to the double bond, the axial hydrogen will remain in continual overlap with the π-electrons of the double bond, thus minimizing the energy of the transition state eqn. [54]. In other words stereoelectronic effects favour the removal of the axial hydrogen rather than the equatorial hydrogen (see later discussion on cyclodehydrogenation).

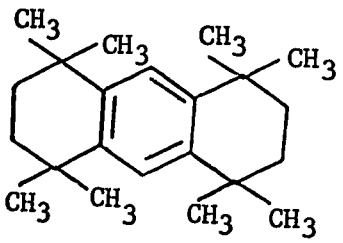
[54]



Such a conformational dependence of reactivity of donors towards quinones has also been observed in the dehydrogenation of tetralin, indane, and benzocycloheptene (43). Tetralin and indane react much more readily than benzocycloheptene. This is attributed to the fact that in indane and tetralin the incipient carbonium ion is stabilised by the benzene ring due to the coplanarity of the carbonium ion centre with the benzene ring. In benzocycloheptene no such resonance stabilisation is possible since the conformation of the molecule does not allow coplanarity of the incipient carbonium ion centre with the benzene ring. This sequence of reactivity of these three hydrocarbons parallels the reactivity of their 1-chlorides in solvolysis.

Limits of Quinone Dehydrogenation

Quinone dehydrogenation requires that the hydrogen being removed as the hydride ion be in the benzylic or allylic position. It is therefore impossible to aromatise such saturated hydrocarbons like decalin to napthalene, or to dehydrogenate carbocyclic compounds which are substituted in benzylic positions, for example quinones have no effect on the octamethyloctahydroanthracene 72 (55).



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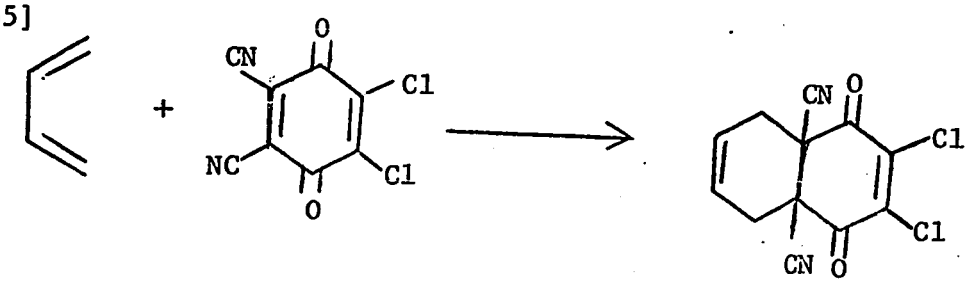
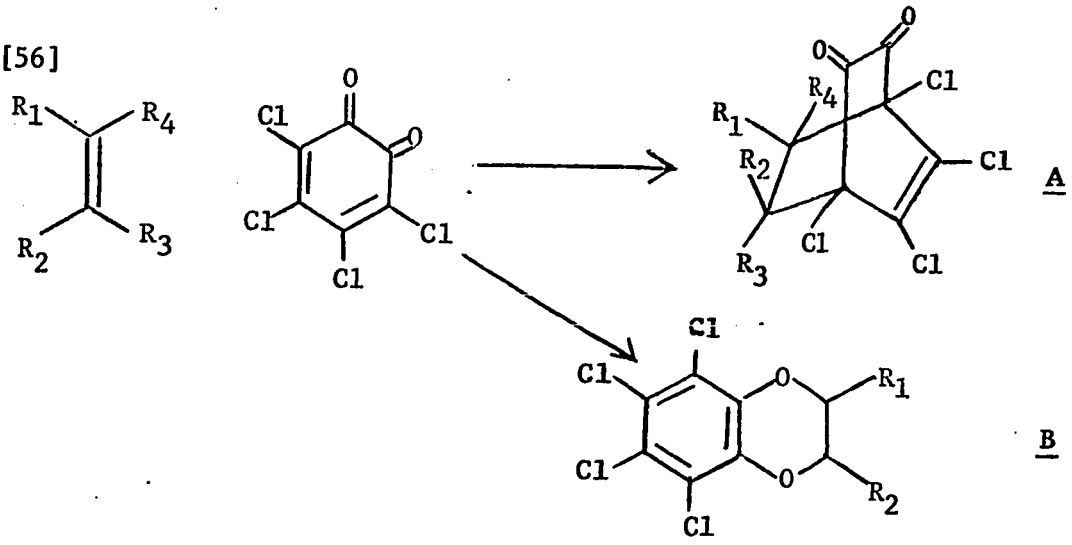
Quinone dehydrogenation of hydroaromatics is likened to unimolecular solvolysis of say alkyl halides; the potential hydride ion being analogous to the leaving group in the normal solvolytic reaction. In this anaolgy dehydrogenation is the counterpart of elimination (E_1). Just as elimination is but one of the number of reactions that can accompany unimolecular solvolysis, so it is with quinone dehydrogenation. Some of these other reactions that can occur e.g. replacement reaction can overshadow dehydrogenation. Quinones can also act as dienophile or dienes eqns. [55] and [56] and therefore if either the substrate, or the intermediate or the product contains a double bond or a diene then Diels-Alder adduct formation would supercede dehydrogenation as the main reaction.

[55]

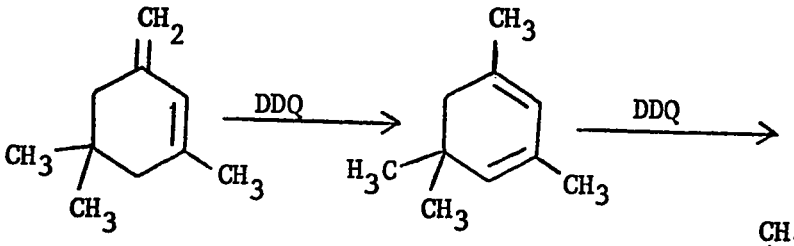


[56]

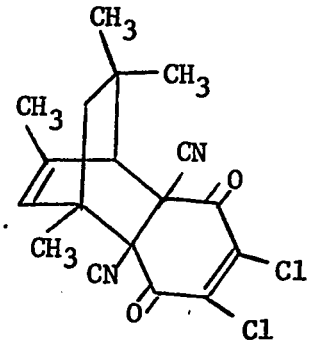


DDQ adduct formation has been found in dehydrogenation of 1,5,5-trimethyl-3-methylenecyclohexene (56) which isomerise to 1,1,3,5-tetramethylcyclo-hexa-2,4-diene which then adds to DDQ to form the adduct 73. The side of the quinone to which addition occurs was determined by X-ray structure analysis to be the least hindered and most activated side i.e. the side to which the cyano-groups are attached eqn. [57]. Asato and Kiefer (57) found that DDQ dehydrogenated 2,3-dimethylbut-2-ene to the 2,3-dimethyl-1,3 butadiene, which then added to DDQ to form the adduct 74. The intermediacy of the diene was confirmed by carrying out the reaction in the presence of tetracyanoethylene (TCNE) during which the known adduct 75 was formed eqn. [58].

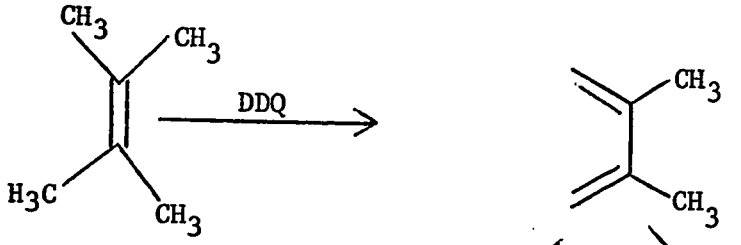
In addition to these adduct formations DDQ is very sensitive to hydrolysis by moisture, and hydrocyanic acid is evolved. It is therefore essential that DDQ be used under anhydrous conditions. It also is not very soluble in many of the solvents that are used in quinone dehydrogenation and the hydroquinone formed during these dehydrogenations is much less soluble, so that if the required product is also insoluble in the solvent employed in the reaction then a purification problem arises.


CH2
CH3
CH3
CH3
DDQ
CH3
H3C
CH3
CH3
DDQ

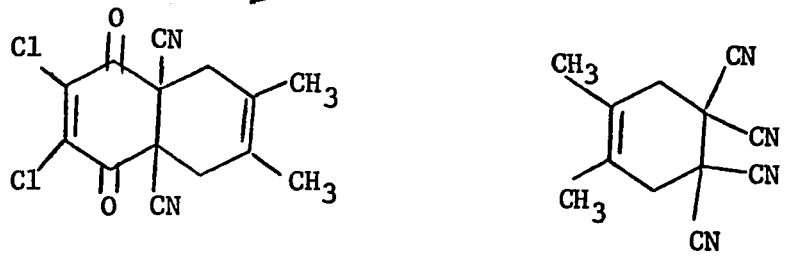
[57]


CH3
CH3
CH3
CN
O
CH3
CN
Cl
O
Cl

73


CH3
CH3
H3C
CH3
DDQ
CH3
CH3

[58]

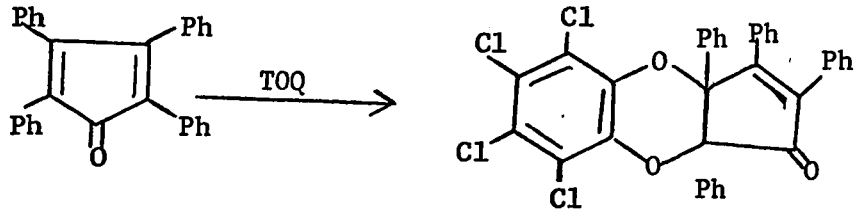

DDQ
TCNE
Cl
O
CN
CH3
Cl
O
CN
CH3
CH3
CN
CN
CN
CH3
CN

74

75

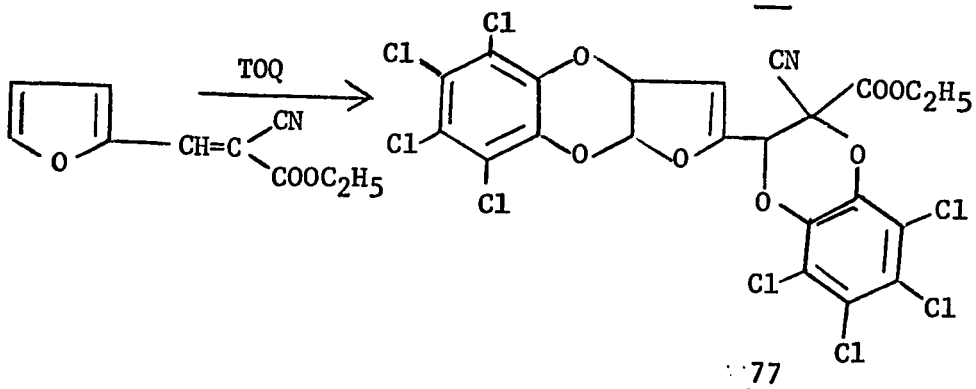
TOQ has been reported to form adducts of type A (eqn. [56]) with butadiene, styrene (58), and cyclopentadiene (59), whilst it forms type B adducts with tetracyclone (60) eqn. [59]; 2-vinyl-furans (61) (eqn. [60]), and stilbene (62) to name some examples. Ansell and Leslie (63) found that 2,3-dimethylbutadiene reacted with TOQ to form adduct 78 which added to another molecule of the diene to form the two isomeric adducts 79 and 80.

[59]



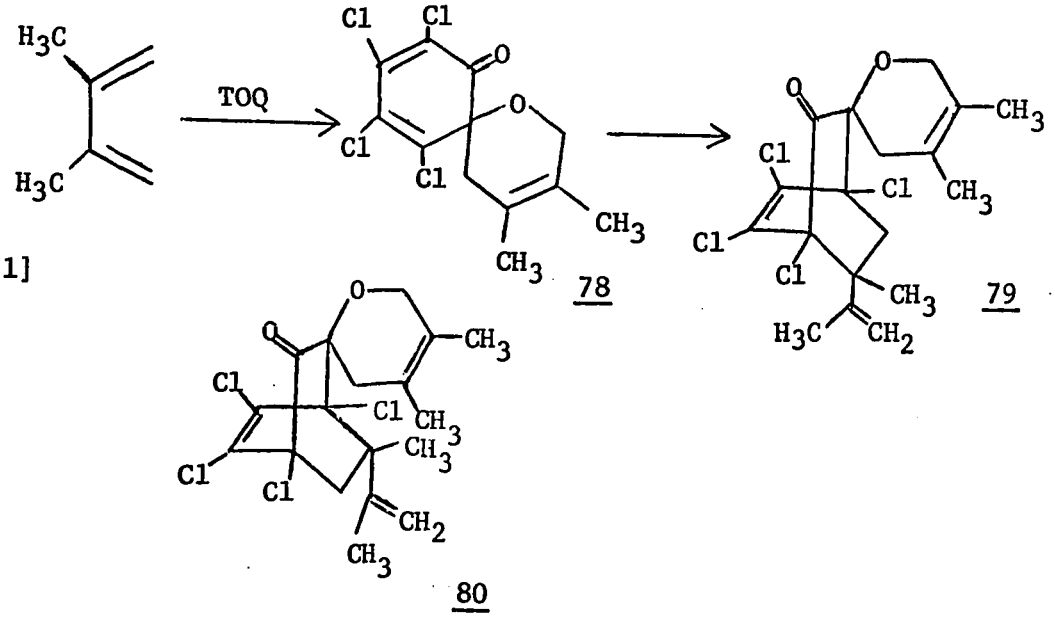
76

[60]



77

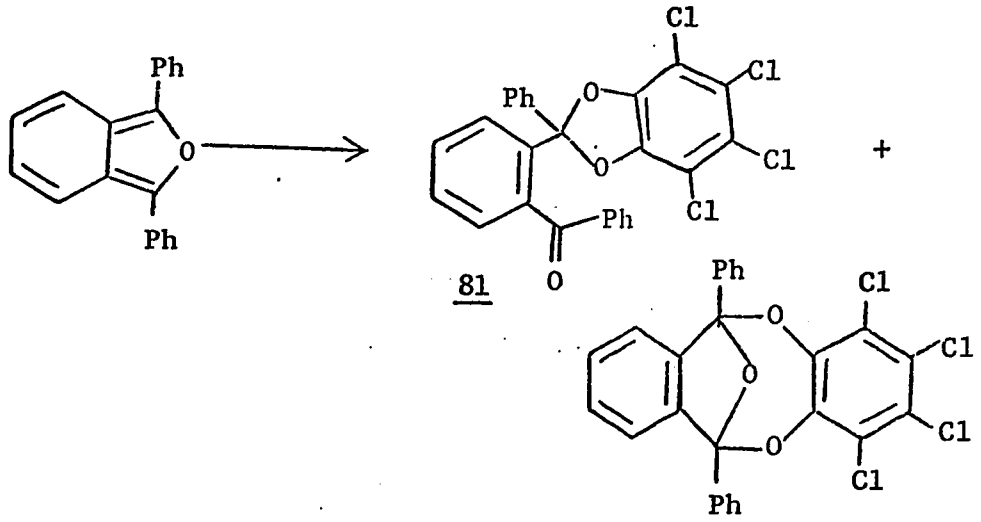
[61]



80

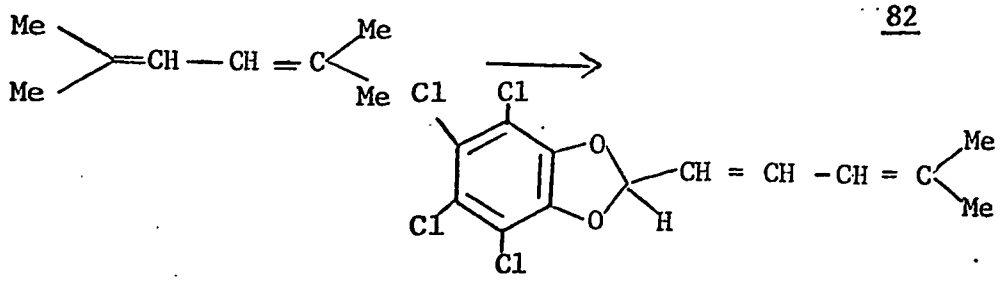
Horspool and co-workers (64) and Friedrichsen (65) have found that TOQ added to substituted benzofuran and naphtho(2,3-C) furan to give benzodioxoles (eqn. [62]). Similar type adducts were also formed by TOQ with hexadiene (66) (eqn. [63]) and 6-methoxy-1-tetrolone (67, 68), (eqn. [64]).

[62]



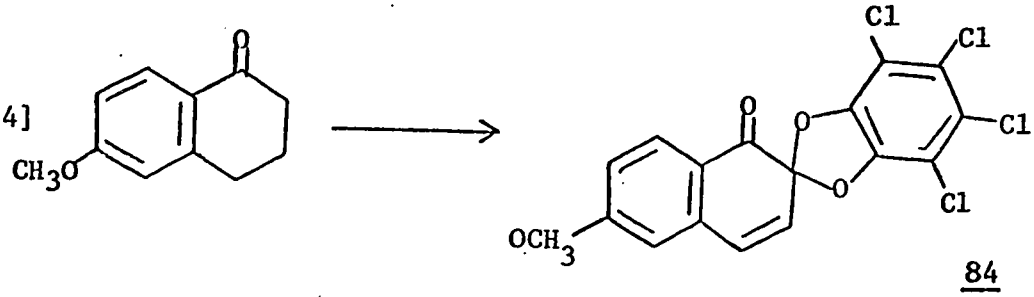
81 + 82

[63]



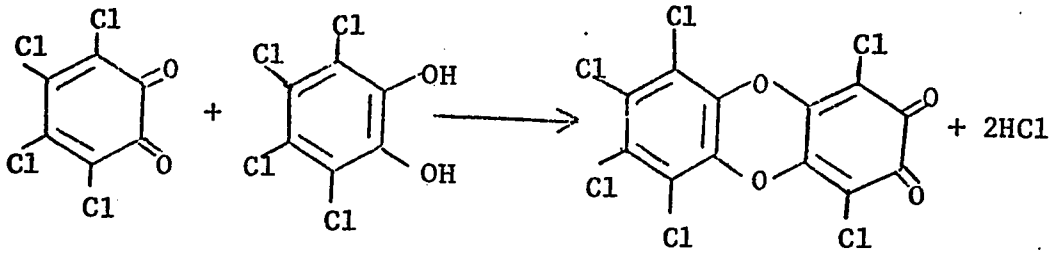
83

[64]



84

In addition to the benzodioxole 79 Friedrichsen isolated another adduct 82. These ether adducts form by TOQ have characteristic carbon-oxygen infrared absorption bands. The benzodioxin type adducts like 76 show absorption bands within the region 1420-1430 cm^{-1}, whilst the benzodioxoles, for example adduct 81, absorb at 1440-1455 cm^{-1} (65). TOQ also reacts with its hydroquinone to form a hexachloro compound, with production of hydrogen chloride which may lead to acid-catalysed reaction of the donor, see eqn. 65.

[65] 

Though all these disadvantages beset quinone dehydrogenation it has advantages over the other dehydrogenation methods - selenium dioxide, selenium, palladium on charcoal, and sulfur dehydrogenations - in that it is homogeneous, and that in the dehydrogenation of carbocyclics it provides a unique method of aromatizing rings containing quarternary carbon atoms (eqn. [41]) without the loss of carbon atoms. This is not true for selenium, or palladium on charcoal dehydrogenation (1). The conditions of quinone dehydrogenation are mild temperatures 0°-125° for 5 minutes to two hours, compared with Pd/C, or sulfur dehydro-

genations which are performed at 200°-350° for prolonged periods. Sealed tubes are not required and the reaction can often be carried out in a simple flask. Also in sulfur containing compounds, the catalysts in catalyic dehydrogenation can be easily poisoned and dehydrogenation inhibited, whilst no such poisoning has been reported for quinones. By a judicious choice of quinone (DDQ, TOQ, chloranil, phenanthrenequinone, 3,3',5,5'-tetrachloro-4,4'-diphenoquinone etc.) and of solvent (benzene, chlorobenzene, dioxan, ether, methanol, t-butanol) and the right reaction time, it is possible to dehydrogenate a variety of compounds by quinones.

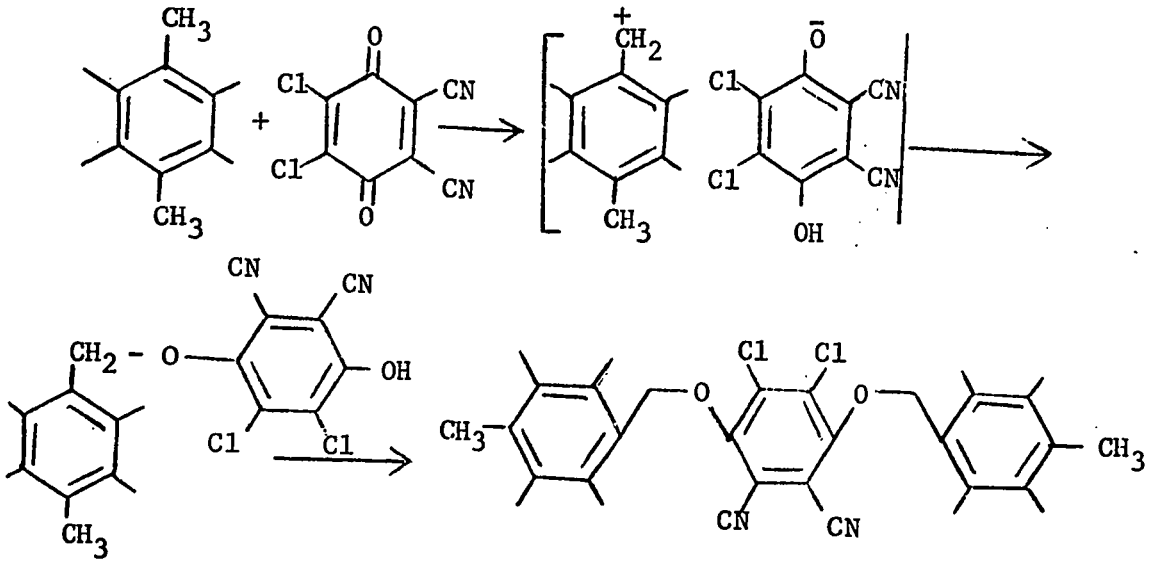
CHAPTER II

Quinone Dehydrogenation of Arenes

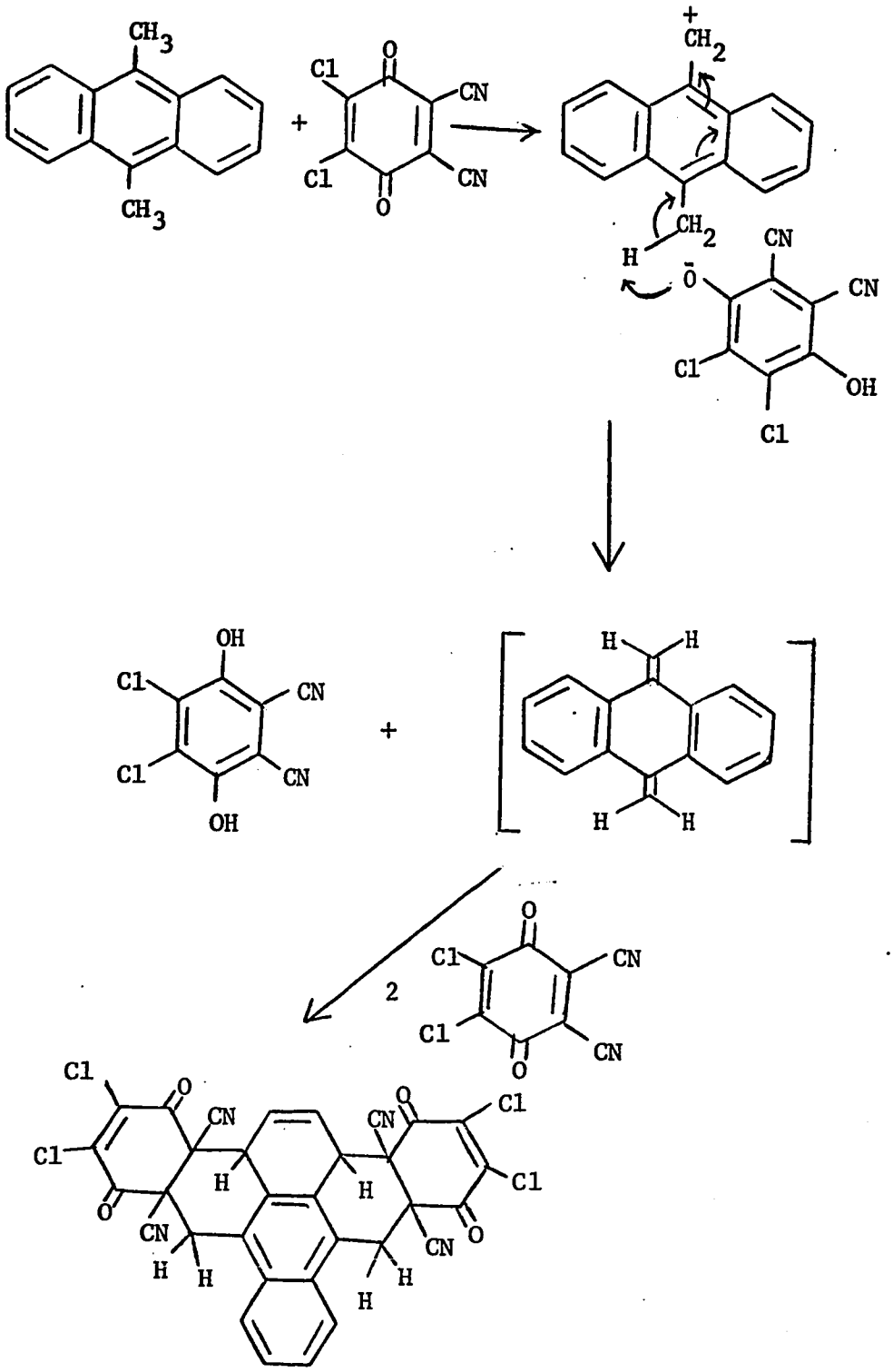
Jackman in his review on "Hydrogenation-Dehydrogenation Reaction" had stated that aliphatic side chains are inert under conditions where five and six-membered rings are rapidly dehydrogenated; as a consequence quinone may be used specifically to aromatise structures without affecting alkyl side chains.

The objective of this work was to test the validity of this claim, for preliminary studies (69) had shown that such arenes formed could be further attacked by quinones in the side chain; abstracting a hydride ion followed by either (i) substitution by the quinone; or the quinol anion formed (see scheme I) or (ii) formation of Diels-Alder adducts which could be most plausibly explained by involvement of quinodimethane intermediates, as illustrated in scheme II.

Scheme I



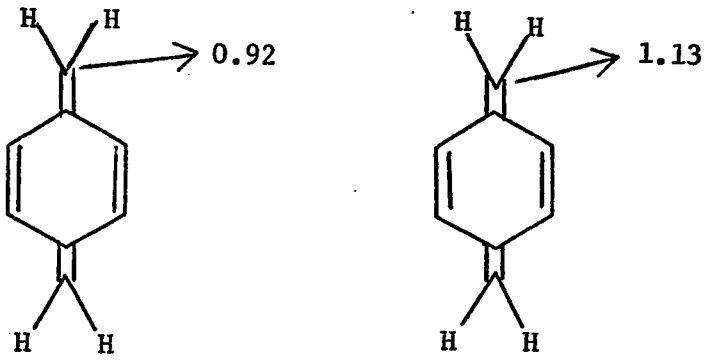
Scheme II


CH3
CH3
Cl
O
CN
Cl
CN
O
+
CH2
CH2
H
O
CN
CN
Cl
OH
Cl
OH
Cl
CN
Cl
CN
OH
+
H
H
H
H
2
O
Cl
CN
Cl
CN
O
Cl
Cl
O
CN
CN
O
Cl
Cl
O
CN
CN
O
H
H
H
H
H
H
H

Quinodimethanes have attracted the attention of theoreticians, and their free valence and bond order have been calculated (72-75). These calculations show very high free valence for the terminal methylene carbons, and there is little difference in this value between the ground state singlet and excited state triplet (Figure 1); thus these species would be expected to be very reactive.

Figure 1

Molecular diagram of p-xylylene



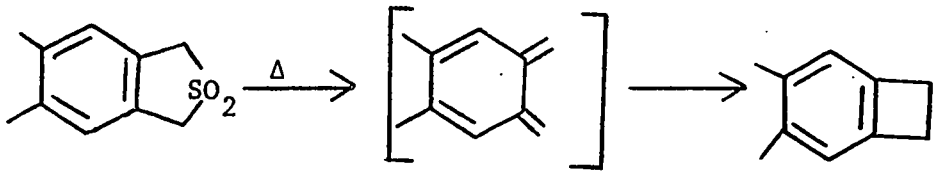
Ground State
Singlet

Excited State
Triplet

This predicted reactivity is borne out in the ease of dimerisation and polymerisation of unsubstituted quinodimethanes at ambient temperatures (76, 77); however at low temperatures (-78°) and low pressures, p-xylylene - generated by the pyrolysis of p-xylene - is stable in hexane or toluene solutions up to a concentration of 0.12 mole (77). Williams, Pearson, and Levy (78) have also prepared benzoquinodimethane, 1,4-naphthaquinodimethane and 9,10-anthraquinodimethane by pyrolytic cleavage of their

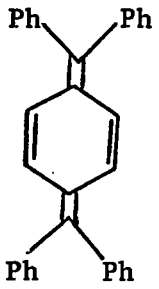
corresponding paracyclophanes and measured their nuclear magnetic resonance spectra at -80°.

Quinodimethanes have also been postulated as intermediates in the formation of cyclobutenes (79-84), e.g. benzocyclobutene, by the pyrolysis of their corresponding dihydrothiophene dioxides (see eqn. [66]). Further examples of reactions for which

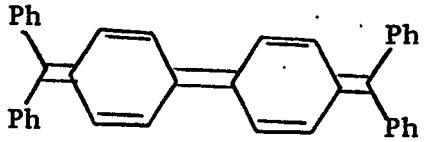
[66] 

the intermediacy of quinodimethanes is proposed are: (i) the thermal decomposition of certain trimethylammonium hydroxides (83, 86, 88, 89, 90) e.g. trimethyl-10-methyl-9-phenanthryl ammonium hyrdroxides; (ii) dehydration of 9,10-methylanthracene-9,10-diol (83); (iii) polycondensation of xylene dibromides by transition metals in water suspension (91); and (iv) the action of magnesium and Grignard reagents on certain benzyl ether (92).

Until recently the stable quinodimethanes known were tetraphenyl substituted p-xylylenes, the Chichibabin hydrocarbons (76,) e.g. 85 and 86. Hertler and co-workers have prepared and studied the properties of 7,7,8,8-tetracyanoquinodimethane 87 (93-95) and 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethane 88 (96). Also Gompper, Wagner and Kutter (97, 98) have prepared a whole series of 7,7,8,8-tetra-substituted p-xylylenes, as part of their

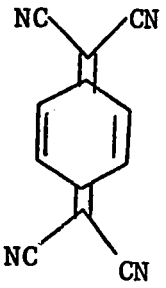


85

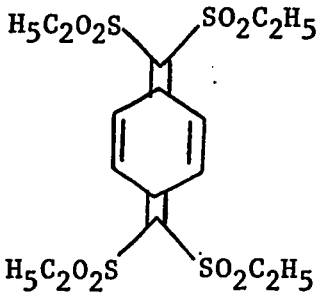


86

study of ketene derivatives. Compound 87 has received such attention within the past three years that over fifty papers have



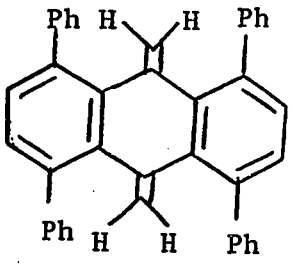
87



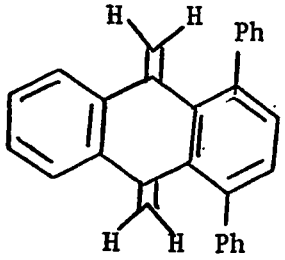
88

been published on its crystal structure, salt formations, and polymer initiation.

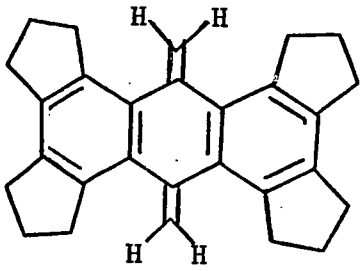
More significantly within the past three years the syntheses of the first stable unsubstituted quinodimethanes 89, 90 (99) and 91 (100) have been reported.



89



90



91

With the findings of the preliminary report (69), the present work was undertaken (i) to study the behavior of various arenes with quinones as an extension of the general quinone dehydrogenation reaction; (ii) to determine the structural features that lead to: (a) substitution of the hydride ion abstracted by the quinol anion generated, (b) elimination of a proton to give quinodimethanes.

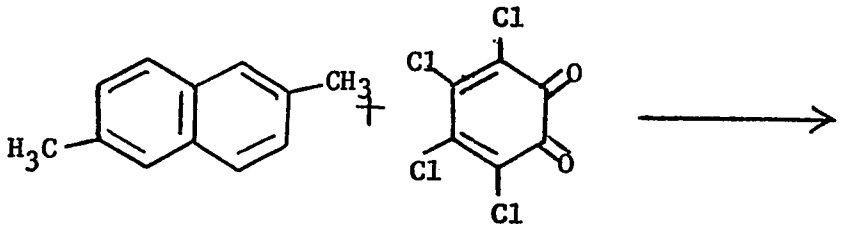
RESULTS AND DISCUSSION

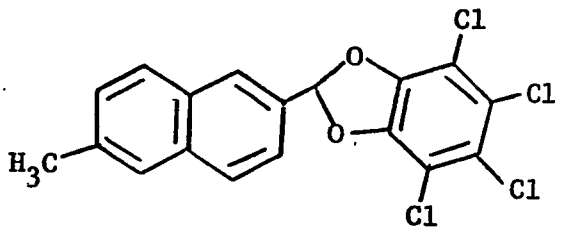
Reaction of Dimethylnaphthalenes with Tetrachloro-o-benzoquinone (TOQ)

The first arenes that were examined were the 1,4-; 1,2-; 1,5-; 2,3-; and 2,6-dimethylnaphthalenes. These dimethylnaphthalenes were chosen because they had the methyl substitutions in such positions to each other as to make it possible for them to form quinodimethanes.

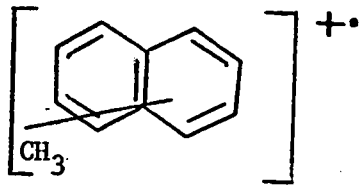
Reaction of the dimethylnaphthalenes with about two molar equivalents of TOQ gave benzodioxole adducts as illustrated in eqn. [67] for 2,6-dimethylnaphthalene. 1,2-Dimethylnaphthalene gave about 2:3 mixture 2-(1-methylnaphthyl-2)-, and 2-(2-methylnaphthyl-1)-4,5,6,7-tetrachlorobenzo-1,3-dioxole; as evidenced by the presence of two singlets at 2.4 and 2.6 ppm integrating for three protons, in the nuclear magnetic resonance spectrum. These adducts showed strong ether bands in the region 1440 - 1455 cm^{-1} and 1415 - 1420 cm^{-1}. Their nuclear magnetic resonance spectra showed the C_2-methine proton has been shifted downfield to aromatic region by the adjacent oxygen atoms. In their mass spectra was a strong peak at m/e=142; corresponding to 93. Such fragmentation is typical of aromatic acetals (101).

[67]





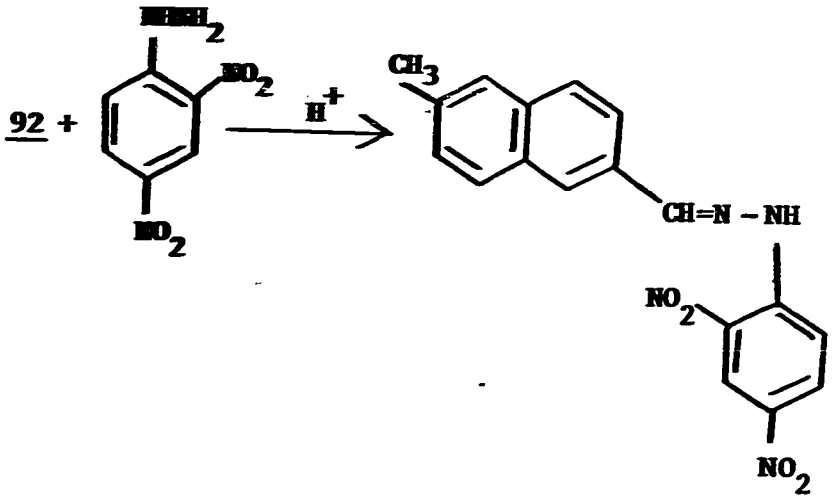
92



93

At the time the benzodioxole structure was assigned to these adducts Kasturi and Arunachalam (67) reported isolation of benzodioxole adduct from dehydrogenation of tetralone using TOQ (see eqn. [64]). Since then many more benzodioxoles have been reported and these have been already discussed in chapter one. Similar types of adduct were also formed with nitrogen heterocycles (70), for example, 2-methylquinoxaline reacted with two molar equivalents of TOQ in refluxing benzene to give 2-(2-quinoxalino)-4,5,6,7-tetrachlorobenzo-1,3-dioxole. The adduct 92 was found to give positive test with precipitation of the orange solid of 2,4-dinitrophenylhydrazone derivative of the 6-methylnaphthaldehyde (eqn. [68]). Other adducts gave similar orange precipitation.

[68]

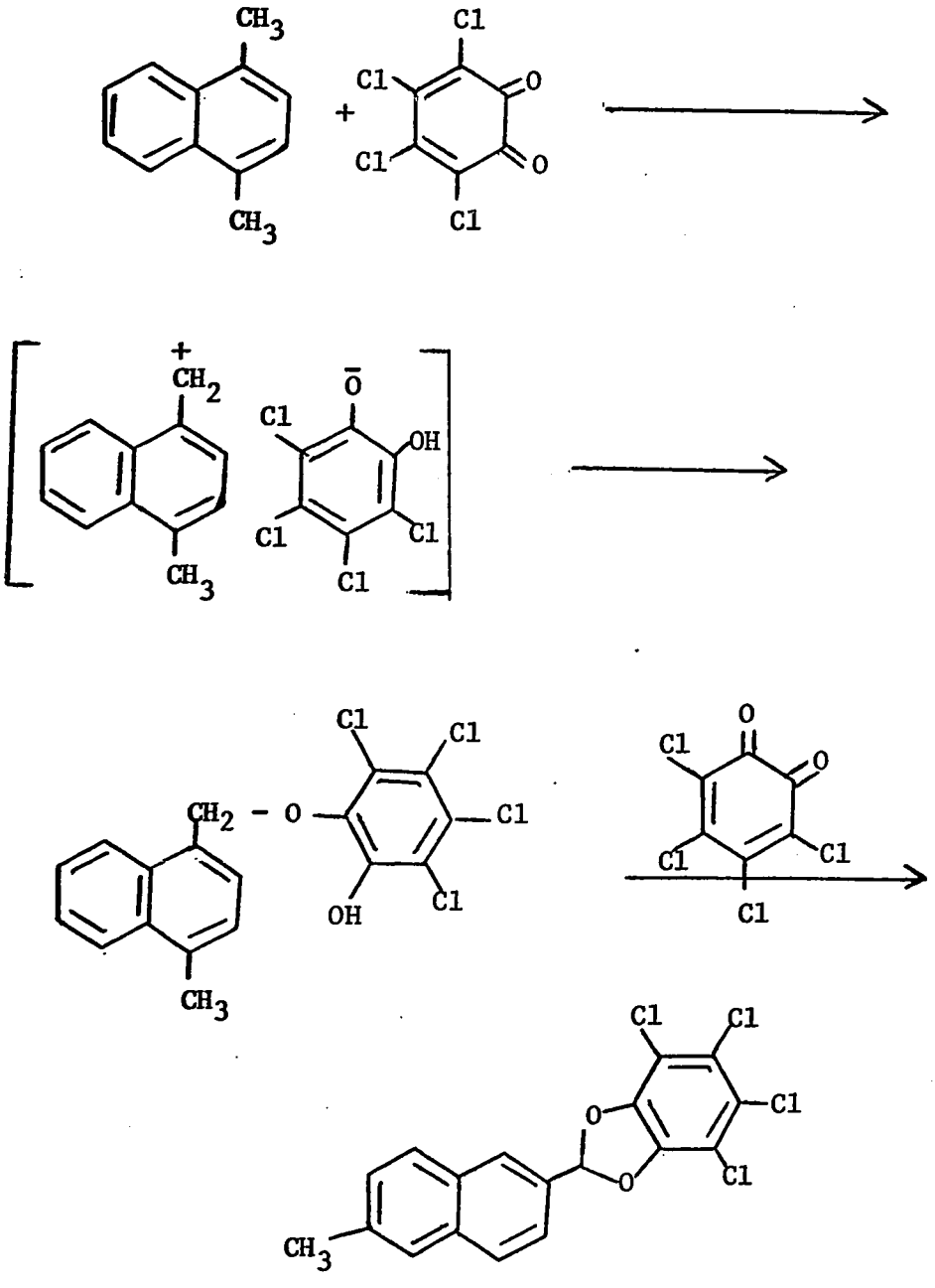


92

94

It was thought that the other methyl group in dimethylnaphthalenes would react further to give 1:2 naphthalene to quinone adducts, but even when the quinone to dimethylnaphthalene was increased to 4:1, only the 1:1 adduct was formed in quite an increased yield. This inertness of the second methyl group may be due to electron withdrawing nature of the acetal group. Quinone dehydrogenation as already discussed are very sensitive to substituent effect. This sensitivity to substituents in naphthalene series was confirmed when an attempt was made to dehydrogenate 4-methyl-1-nitronaphthalene. The substrate was recovered in about 80% yield after refluxing it with two molar equivalents of TOQ in chlorobenzene for 72 hours.

A possible mechanism for the formation of the benzodioxoles is illustrated in Scheme III, for 1,4-dimethylnaphthalene.



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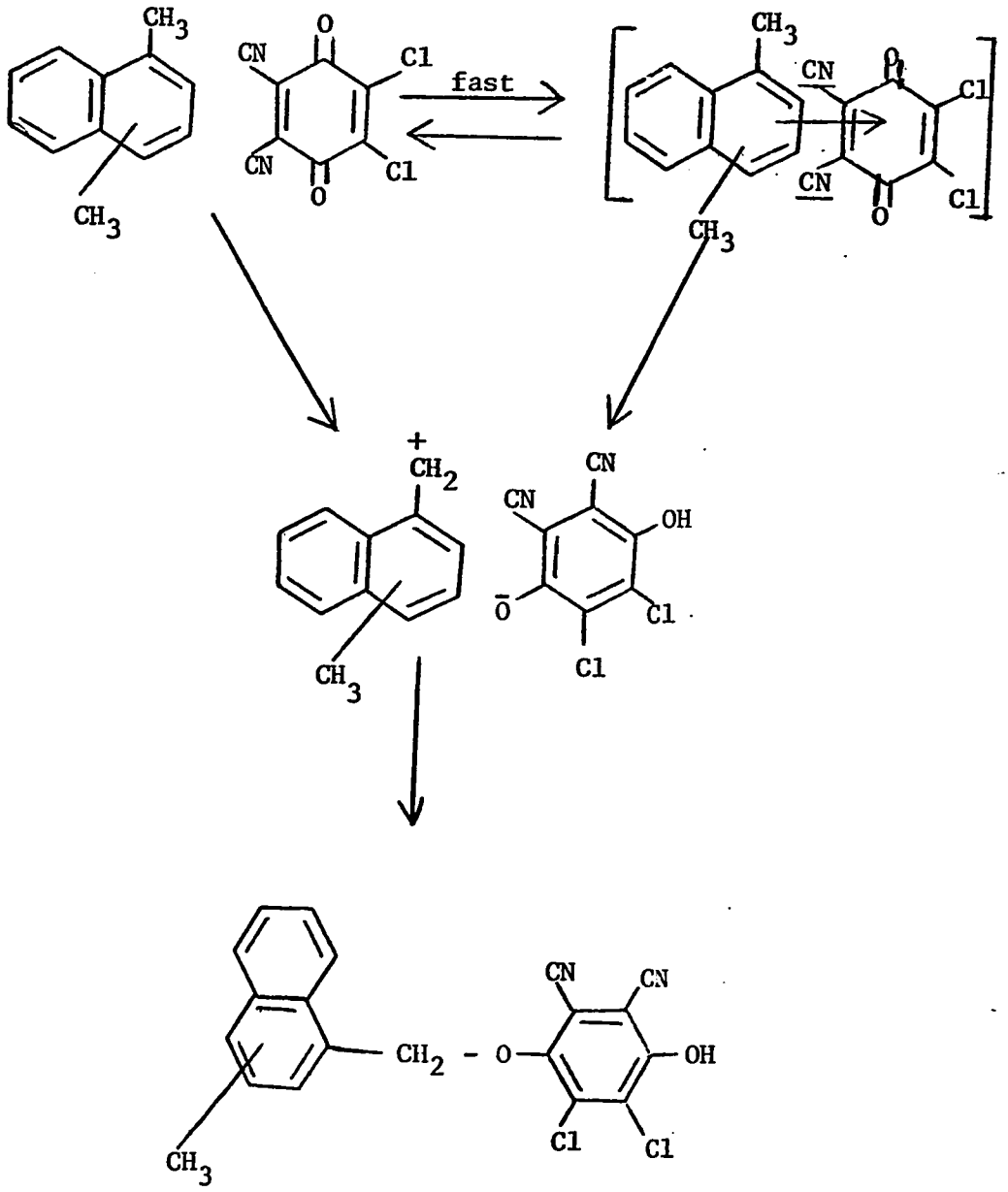
Similar adducts have been obtained from reactions of methylbenzene with DDQ (71). The formation of these adducts is rationalised as shown in Scheme IV. Formation of the charge transfer complex was

Scheme IV

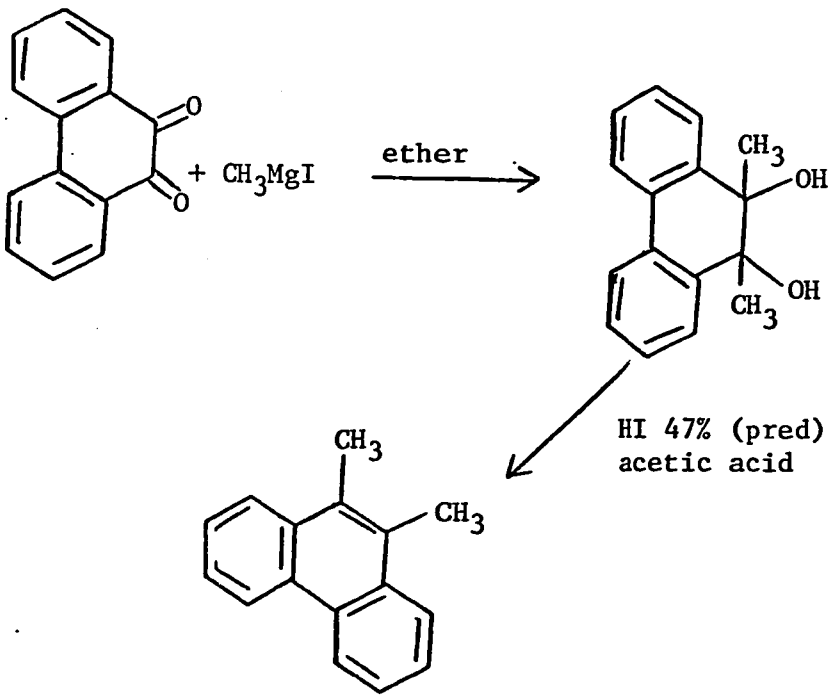


indicated by formation of beautiful colored solutions on addition of the hydrocarbons solution to the quinone. All the other dimethylnaphthalenes listed also gave colored solutions but only the 1,2- and 1,4-dimethylnaphthalenes were studied fully. The decay of these complexes by hydride transfer from the dimethylnaphthalene to the quinone gives an ion pair, which collapses to form the quinol mono ether.

Preparation of 9,10-Dimethylphenanthrene

9,10-Dimethyl-9,10-dihydroxy-9,10-dihydrophenanthrene was prepared according to the method of Zincke and Tropp (102); this was then refluxed with hydriodic acid and red phosphorus in acetic acid to give dimethylphenanthrene in fairly good yield, see Scheme V.

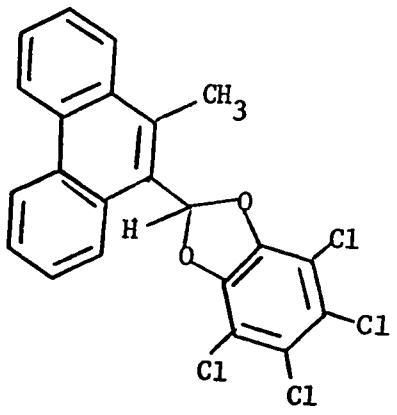
Scheme V



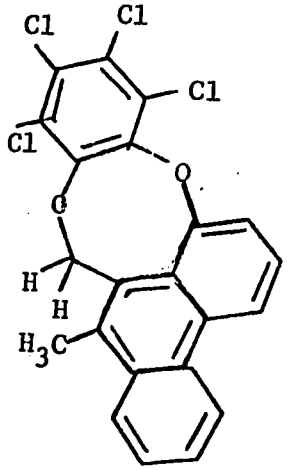
Reaction of 9,10-Dimethylphenanthrene with TOQ and DDQ

The dimethylnaphthalenes reacted with TOQ thermally to give the then novel mono benzodioxoles and with DDQ to give the quinol mono ethers. On the other hand 9,10-dimethylanthracene reacted with TOQ to give a benzodioxin, and with DDQ to give a Diels-Alder adduct, both products proposed as arising from quinodimethane intermediate (69). It was of interest to determine where the change over from substitution to elimination takes place. With this in view 9,10-dimethylphenanthrene was reacted with both TOQ and DDQ.

Reaction of 9,10-dimethylphenanthrene with two molar equivalents of TOQ gave two products, which were separated on BDH alumina. The first product, to which structure 98 was assigned, was a white insoluble powder. It showed in its infrared spectrum ether absorption at 1456 and 1447 cm^{-1}. When 98 was treated with dilute hydrochloric acid in refluxing aqueous acetone, 10-methylphenanthrene-9-carboxaldehyde was obtained confirming the dioxole structure assigned. Structure 99 was assigned to the second product.



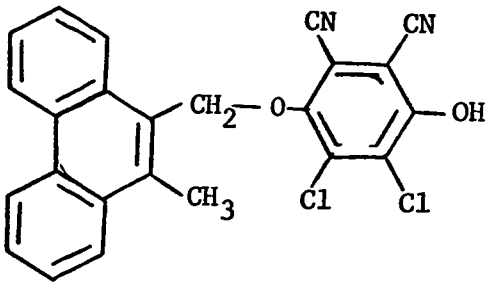
98



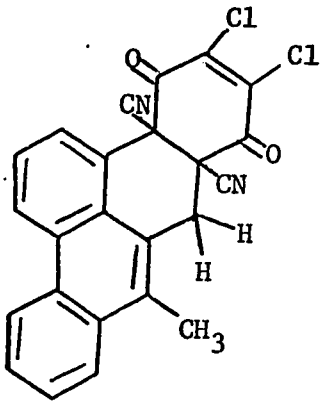
99

This adduct showed in its infrared spectrum absorptions at 1450 cm^{-1} and 1418 cm^{-1} for ether bands. Its nuclear magnetic resonance exhibited a singlet at 2.76 ppm for the methyl group and another singlet at 5.10 ppm for the methylene proton. Analogous product have been observed in the dehydrogenation of 7-methyl-7,12-dihydropleiadne.

Reaction of 9,10-dimethylphenanthrene with DDQ gave mainly the quinol mono ether 100, which showed broad hydroxyl absorption in its infrared at 3215 cm^{-1}. In addition to this a small amount of yellow compound was also isolated to which structure 101 was tentatively assigned. This adduct showed carbonyl absorption



100



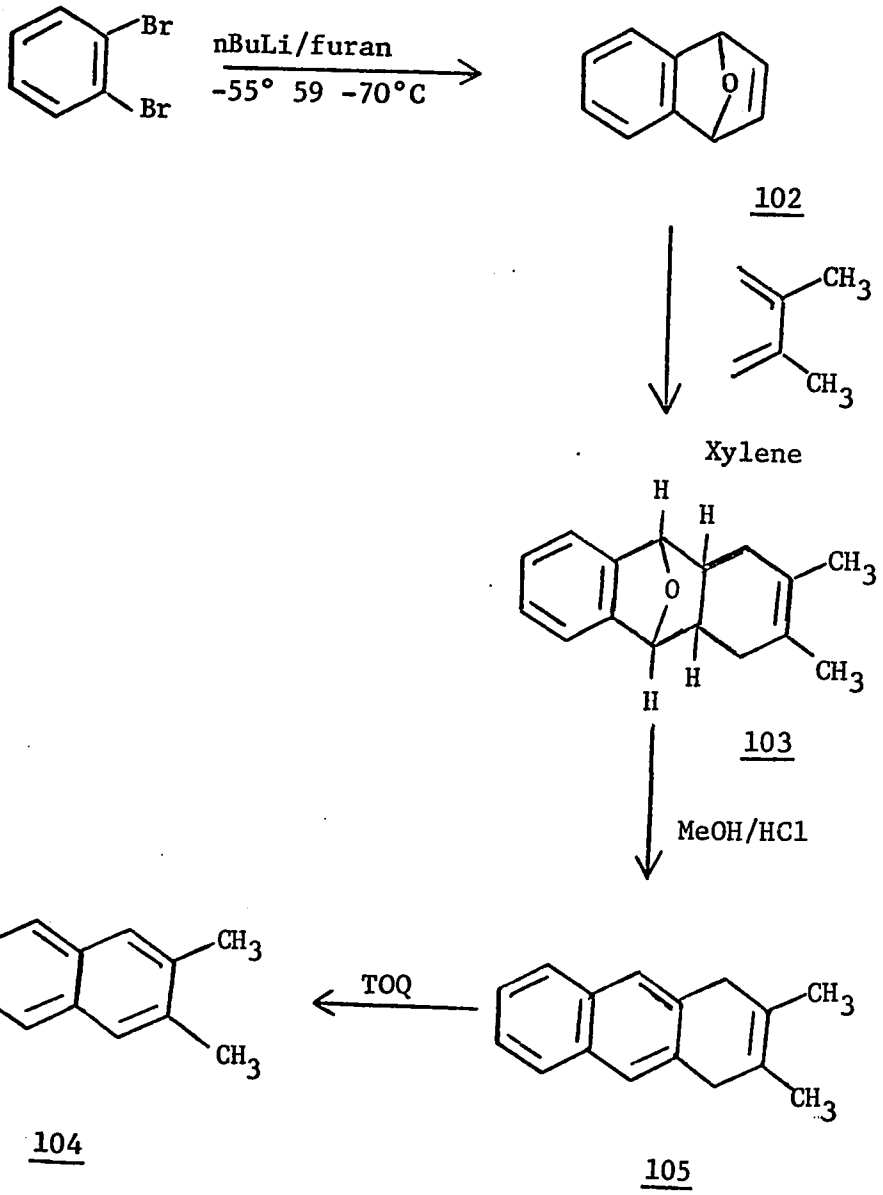
101

at 1718 cm^{-1}. Unfortunately the only solvent in which this compound was soluble sufficiently for nuclear magnetic resonance spectrum was dimethylsulfoxide-d_6 (DMSO-d_6) which absorbed at the same position as the aryl methyl group. Similar type adduct was formed by 1,4-dimethylanthrancene.

Preparation of 1,4-Dimethyl- and 2,3-Dimethylanthracene

These two compounds were prepared according to the method of Wolthuis (23), as sketched out in Scheme VI for 2,3-dimethyl-

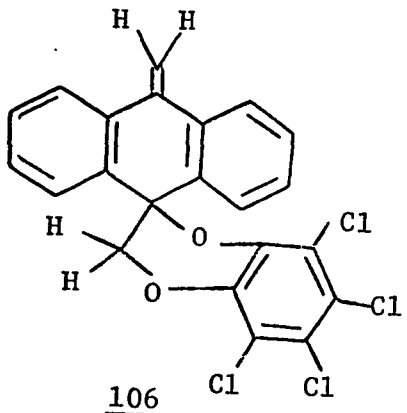
Scheme VI



anthracene. Benzyne was generated from o-dibromobenzene with n-butyllithium in presence of furan which reacted with it to give 1,4-dihydro-1,4-epoxynaphthalene, 102. Compound 102 underwent Diels-Alder reaction with 2,3-dimethyl-1,3-butadiene in refluxing xylene to give the epoxyhydroanthracene 103. (For the preparation of 1,4-dimethylanthracene trans, trans-2,4-hexadiene was used instead of 2,3-dimethyl-1,3-butadiene.) Dehydration of compound 103 gave 2,3-dimethyl-1,4-dihydroanthracene (104), which was treated with one molar equivalent of TOQ to give 2,3-dimethyl-anthracene.

Reaction of Methylanthracenes with TOQ

Dehydrogenation of dimethylnaphthalenes with TOQ has given benzodioxole adducts, and from 9,10-dimethylphenanthrene has been obtained a benzodioxole and adduct 99. However with 9,10-dimethylanthracene benzodioxin adduct 106 was formed (69). It was thought

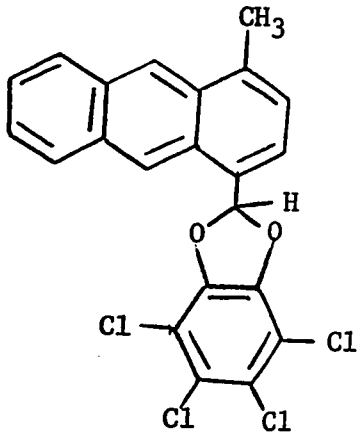


106

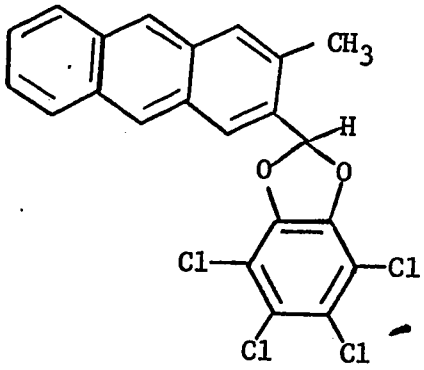
that other methylanthracenes may then lie on the boderline between benzodioxole and benzodioxin formation. In fact it might be possible

to isolate both types of products from say 1,4-dimethylanthracene.

Reaction of 1,4- and 2,3-dimethylanthracenes with two molar equivalents of TOQ however gave benzodioxoles 107 and 108 respectively; no benzodioxin adduct was formed in either reaction.

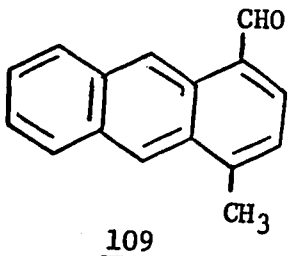


107

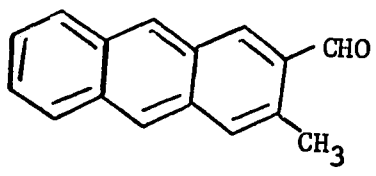


108

These adducts all showed ether absorptions around 1450 and 1425 cm^{-1} in their infrared spectra. Their nuclear magnetic resonance showed one methyl group still unaffected. Further confirmation of the benzodioxole structure was obtained by hydrolysis of the adducts to give their corresponding methylanthracene-carboxaldehydes, 109 and 110.



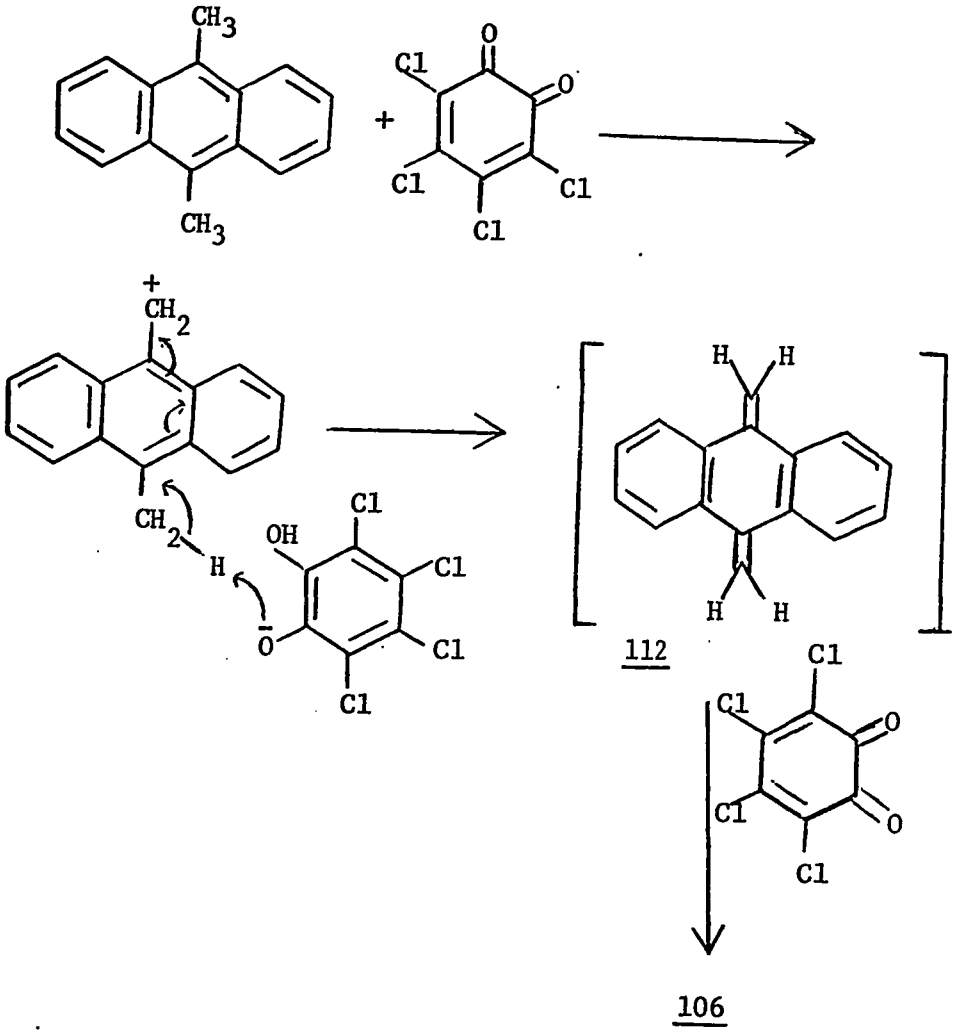
109



110

When 9,10-dimethylanthracene 111 was refluxed with two molar equivalents of TOQ in chlorobenzene the same adduct (106) was obtained, in a much improved yield (58.7%), as when the reaction was performed in benzene (18%). The formation of adduct 106 is proposed to go through the mechanism as illustrated in Scheme VII. A hydride abstraction at the C_9-methyl is followed

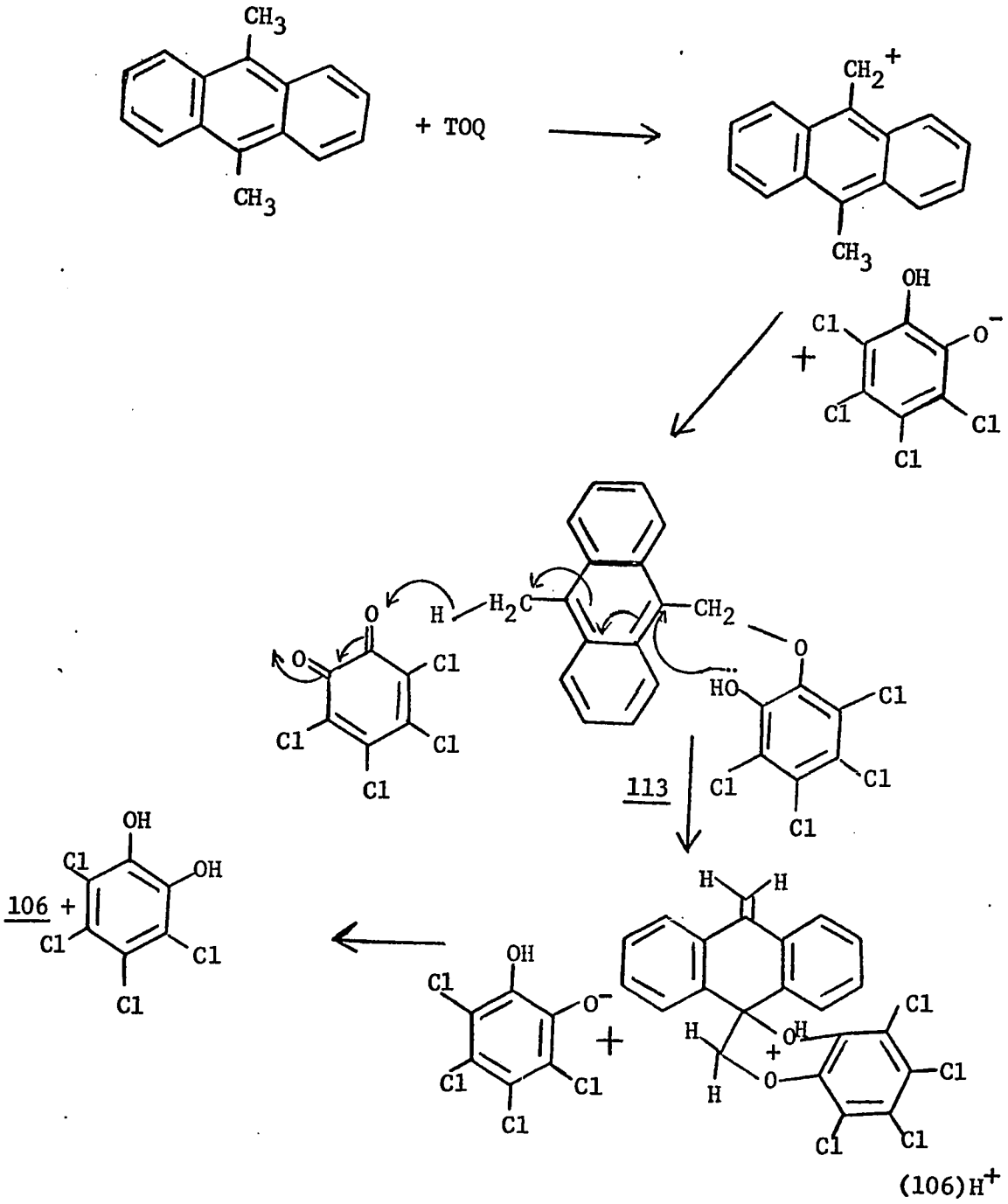
Scheme VII



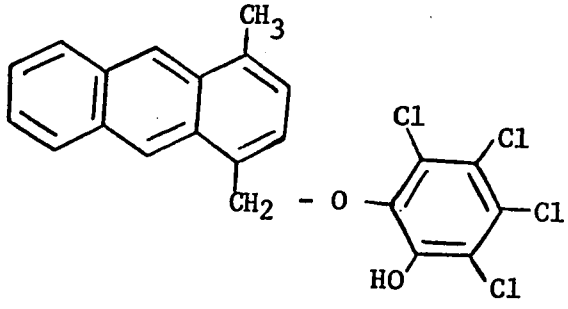
by elimination of a proton at C_{10}-methyl to form the quinodimethane 112, which then adds to TOQ to give adduct 106.

Another mechanism that may account for the formation of adduct 106 is as follows (Scheme VIII): A hydride abstraction

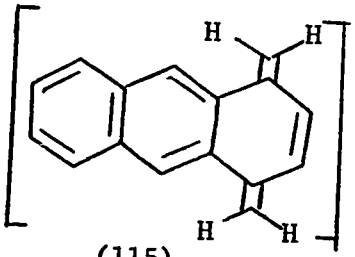
Scheme VIII



at C_9-methyl gives an ion pair which collapses to form the quinol mono ether 113. The hydroxy of the quinol moiety then participates in hydride abstraction at C_{10}-methyl group to give again an ion pair. This time a transfer of proton from (106)H^+ to the quinol anion gives 106. This mechanism cannot be ruled out completely, however, the first mechanism is preferred. If Scheme VIII were the mechanism, one would have expected some benzodioxole adduct to be formed as in the other methylanthracenes. A second hydride abstraction at C_9 would be expected to be more facile as this would be stabilised by the adjacent oxygen. Also if the quinol moiety can participate in the way it does in this second mechanism one would expect a similar adduct for 1,4-dimethylanthracene as for 9,10-dimethylanthracene. Assuming the first mechanism for the formation of adduct 106, the lack of formation of similar adduct by 1,4-dimethylanthracene may be due to the lower stability of 1,4-anthraquinodimethane (115) than 9,10-anthraquinodimethane. Thus whilst the latter is formed in preference to the quinol ether 113 in 9,10-dimethylanthracene, the quinol ether 114 is formed in



114



(115)

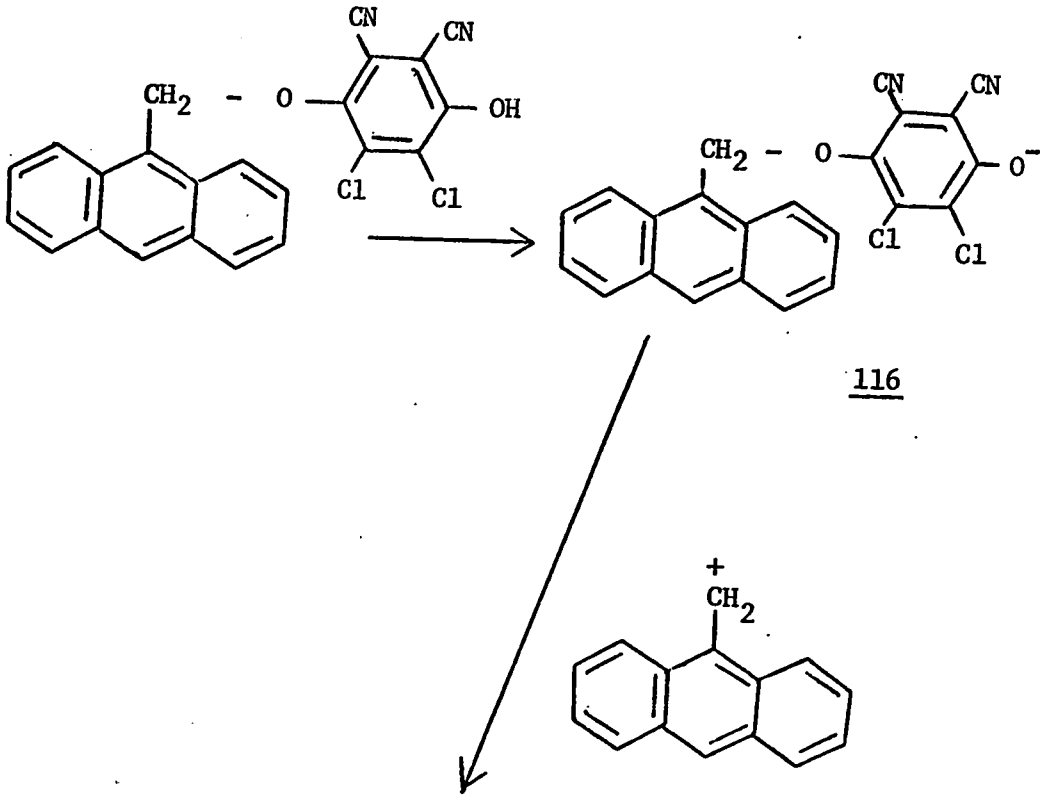
preference to the quinodimethane (115) in the case of 1,4-dimethylanthracene, resulting in different adducts for 1,4- and 9,10-dimethylanthracene.

It has also been found in the dimethylnaphthalene series that the second methyl group was unaffected even when excess quinone was used. This observation makes the second mechanism (Scheme VIII) unlikely, as the third step in this mechanism involves a dehydrogenation at the second methyl group.

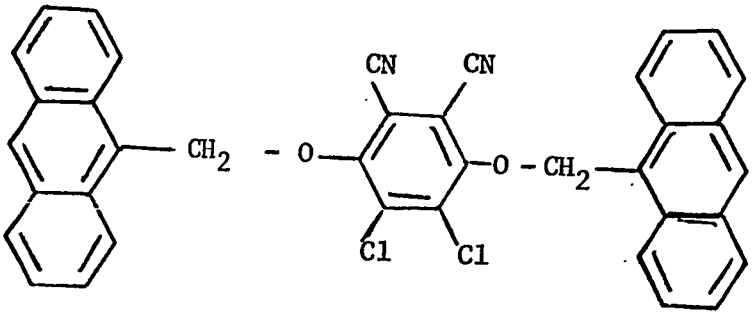
Reaction of Methylanthracenes with DDQ

9-Methylanthracene reacted with about two molar equivalents of DDQ in refluxing benzene to give a bright yellow fibrous solid. This adduct showed in its infrared spectrum characteristic ether and nitrile bands at 1425 (40) and 2216 cm^{-1} respectively. Structure 117 was assigned to this adduct by analogy with similar adduct obtained in the reaction of 2,2-dimethyl indane (40). Similar type adduct have subsequently been reported for reaction of durene and pentamethylbenzene (71) with DDQ. Formation of compound 117, may be rationalized as suggested by Foster and Horman (71) by loss of a proton from the quinol mono ether first formed to give the quinol mono ether anion (116) which then attacks the carbonium ion resulting from hydride abstraction of the 9-methylanthracene, as illustrated in Scheme IX.

Scheme IX



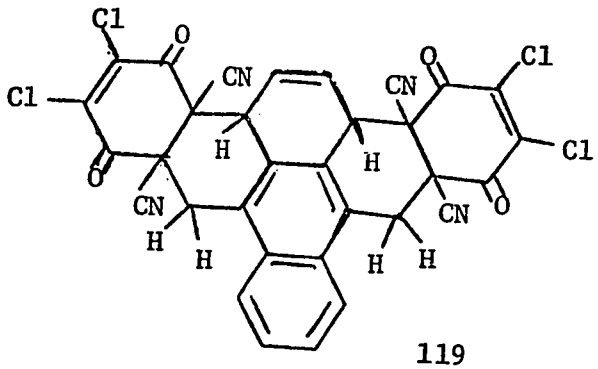
116



117

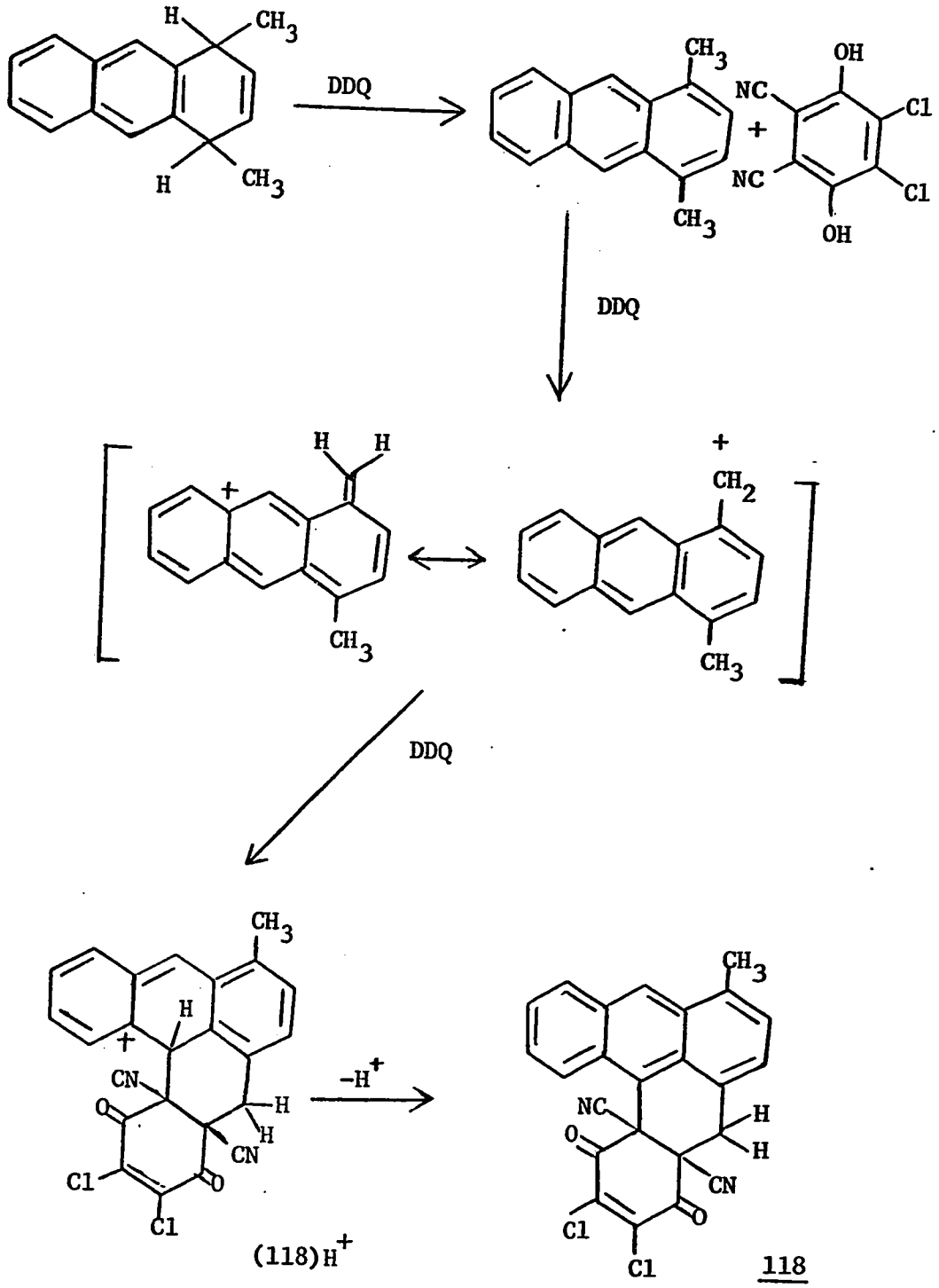
In contrast, 1,4-dimethylanthracene on refluxing with three molar equivalents of DDQ in chlorobenzene gave an adduct, which showed a carbonyl absorption at 1715 cm^{-1}. The nuclear magnetic resonance spectrum showed at 2.75 ppm a singlet for one unaffected methyl group; and a quartet at 4.32, 4.00 ppm for two proton with coupling constant of 15Hz. Structure 118 was assigned to this adduct. This same adduct was formed by 1,4-dimethyl-1,4-dihydroanthracene with four molar equivalents of DDQ in chlorobenzene. The formation of compound 118 in this reaction is rationalised as follows: The usual hydride abstraction gives the carbonium ion intermediate, the principal resonance structures of which are shown in Scheme X. This ion then adds to a quinone to give $(118)H^{+}$. Transfer of proton from this species to the quinol anion gives adduct 118.

2,3-Dimethylanthracene reacted with three molar equivalents of DDQ to give a complex mixture of products which could not be separated. 9,10-Dimethylanthracene on the other hand reacted with three molar equivalents of DDQ to give adduct 119 (69) as already illustrated in Scheme II.



119

Scheme X



(118)H+

118

Reaction of 9,10-Dibenzylanthracene with TOQ

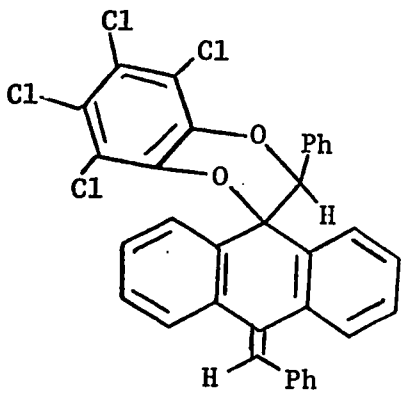
In the preceding discussions the formation of adducts from 9,10-dimethylanthracenes with both DDQ and TOQ have been rationalised as involving the intermediacy of anthraquinodimethane. A confirmation of this would be to prepare a quinodimethane and study its reaction with DDQ and TOQ. Preparation of 9,10-anthraquinodimethane itself requires a special apparatus and time did not permit construction of such an apparatus. A search through the literature revealed that the debromination of 9,10-bis-(dibromobenzhydryl)-anthracene gave in addition to polymeric materials a small amount of the monomeric 9,10-dibenzylidene-9,10-dihydroanthracene (103, 105). It was thought that it might be possible to isolate this monomer in quinone dehydrogenation of 9,10-dibenzylanthracene.

9,10-Dibenzylanthracene was prepared according to the method of Lippmann and Fritsch (104) by refluxing anthracene and benzylchloride in carbon disulfide in presence of aluminum chloride.

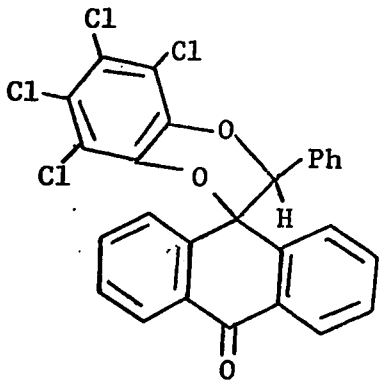
Reaction of 9,10-dibenzylanthracene with one or two molar equivalents of TOQ in refluxing o-dichlorobenzene formed adduct 120, no quinodimethane was isolated. The infrared spectrum exhibited characteristic benzodioxin absorption at 1427 cm^{-1} and a carbon-carbon double bond stretching at 1512 cm^{-1}.

The structure was confirmed by ozonolysis of 120 obtaining compoung 121, which showed a carbonyl absorption at 1668 cm^{-1}, and ether absorption at 1432 cm^{-1}. Similar type compound had been

obtained in the ozonolysis of adduct obtained from 9,10-dimethylanthracene and 5,12-dimethylbenzanthracene (69).



120

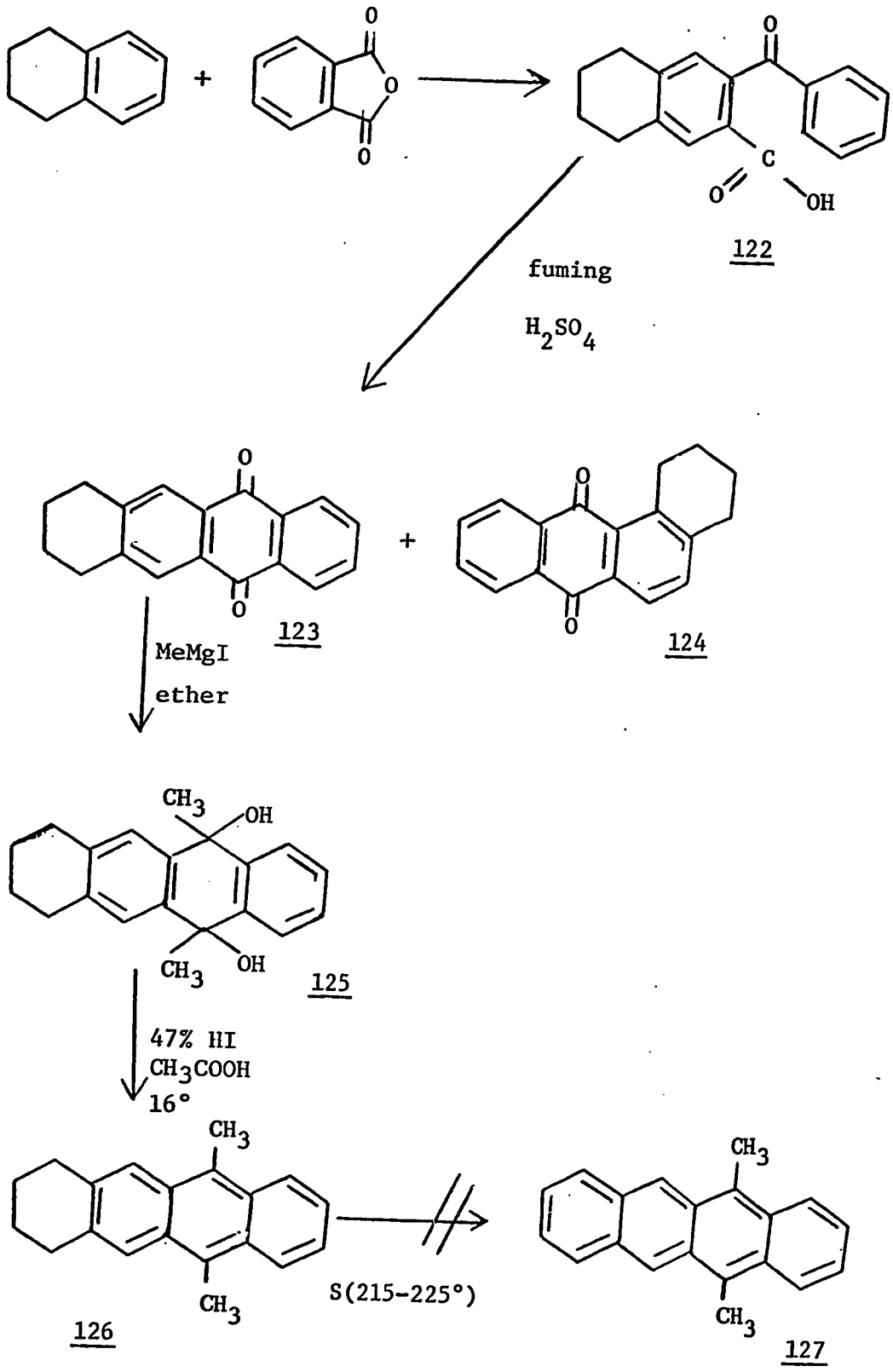


121

Attempted Preparation of 5,12-dimethylnaphthacene

The method that was used in this attempted synthesis is illustrated in Scheme XI. The keto-acid 122, obtained by condensation of tetralin with phthalic anhydride in presence of aluminum chloride (106), was cyclised to give the two isomeric quinones 123 and 124. Fractional crystallisation from benzene gave pure 2,3-tetralanthraquinone 123. This was then added to methylmagnesium iodide in ether to give the dihydroxy compound 125, which was treated with hydriodic acid in acetic acid to give hydrocarbon 126. Attempt to dehydrogenate compound 126 with sulfur only gave charred product.

Scheme XI

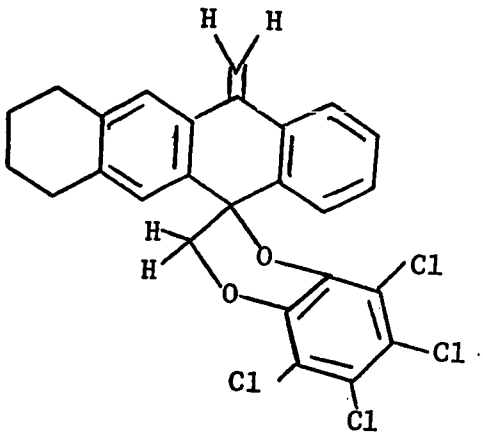

O
O
O
+
O
C
O
OH
122
fuming
H_2SO_4
O
O
123
+
O
O
124
MeMgI
ether
CH_3
OH
CH_3
OH
125
47% HI
CH_3COOH
16°
CH_3
CH_3
126
S(215-225°)
CH_3
CH_3
127

Reaction of 5,12-Dimethyl-7,8,9,10-tetrahydronaphthacene with TOQ

It was originally intended to react 5,12-dimethylnaphthacene with TOQ, but as already discussed this could not be prepared. The same product had been obtained when 9,10-dimethylanthracene and 9,10-dimethyl-9,10-dihydroanthracene were reacted with three and four molar equivalents of TOQ respectively (69). 5,12-Dimethyl-7,8,9,10-tetrahydronaphthacene should then give the same product as would have been given by 5,12-dimethylnaphthacene if reacted with appropriate amount of TOQ.

Reaction of 5,12-dimethyl-7,8,9,10-tetrahydronaphthacene with 4 molar equivalent of TOQ gave a complex mixture. After repeated chromatography a yellow solid was isolated. The mass spectrum of this compound showed a parent peak at m/e=502, for $C_{26}H_{18}Cl_4O_2$, and its infrared exhibited ether absorption as 1418 cm^{-1} and carbon-carbon double bond asborption at 1552 cm^{-1}. The carbon carbon double bond in adduct 106 from 9,10-dimethylanthracene absorbed at 1550 cm^{-1}.

Structure 128 is assigned tentatively to this adduct. Evidently the 5,12-methyl groups in 5,12-dimethyl-7,8,9,10-tetrahydronaphthacene are more reactive toward TOQ than the hydrogens at 7, 8,9,10 positions. This is in direct contrast to the claim of Jackman discussed at the beginning of this chapter.



128

EXPERIMENTAL

Throughout this work melting points were determined on Fisher-Johns apparatus and are uncorrected.

Infrared spectra were recorded with a Perkin—Elmer model 421 spectrophotometer, and only the principal well defined peaks are reported.

Nuclear magnetic resonance spectra (n.m.r.) were recorded on Varian A-60 and A-100 analytical spectrometers. The spectra were measured on approximately 10-15% (w/v) solutions in appropriate deuterated solvents with tetramethylsilane as reference. Line positions are reported in parts per million from the reference.

Mass spectra were determined with an A.E.I. MS9 double-focusing high-resolution mass spectrometer. Peak measurements were made by comparison with perfluorotributylamine at a resolving power of 15000.

Thin layer chromatography (t.l.c.) was performed with Kieselgel DF-5 (Camag. Switzerland) and Eastman-Kodak precoated silica and alumina sheets. Grade 1 B.D.H. alumina and silica gel and Mallinckrodt silicic acids were used for column chromatography.

Elemental analysis were carried out by Mrs. D. Mahlow of this department.

The solvents used were dried over sodium and distilled.

Reaction of Dimethylnaphthalenes with Tetrachloro-o-benzoquinone

A solution of 3 g (0.019 moles) of a dimethylnaphthalene in 20 ml of dry chlorobenzene was added to a solution of 10 g (0.041 mole) of tetrachloro-o-benzoquinone in 130 ml of dry chlorobenzene. The mixture was heated under reflux for 48 hours, allowed to cool and the solvent removed *in vacuo*. The residue was subjected to chromatography on B.D.H. alumina using 1:1 benzene/hexane mixture as eluant. The principal fraction consisted of a white microcrystalline solid after washing with hot hexane to remove some unreacted dimethylnaphthalene, and was purified by sublimation of 200°/0.3 mm. giving the pure compound, 2(X-methyl-Y-naphthyl)-4,5,6,7-tetrachlorobenzo-1,3-dioxole.

The analytical and spectra data on these compounds are listed in Tables III and IV.

Control Reaction of 1,5-Dimethylnaphthalene with Tetrachloro-o-benzoquinone

A solution of 1.52 g (10 mmoles) of 1,5-dimethylnaphthalene in 30 ml of chlorobenzene was added to a solution of 9.76 g (40 mmoles) of tetra chloro-o-benzoquinone in 150 ml of chlorobenzene. The mixture was refluxed for 48 hours, the solvent removed *in vacuo*, the residue dissolved in benzene and the solution was run down a column of B.D.H. alumina to give 2.1 g (52% yield) of the same product as for the above experiment. 2,3-Dimethylnaphthalene also gave the mono benzodioxole when reacted with four molar

TABLE III

Spectroscopic Data of 2-(x-Methyl-y-naphthyl)-4,5,6,7-tetrachlorobenzo-1,3-dioxoles

		Infrared Spectrum $\nu_{max}(CHCl_3)$ cm^{-1} (-O-C-O-C-)		Nuclear Magnetic Resonance* $\delta_{Tms}(CDCl_3)$	
				Arylmethyl	Aromatic Protons $+C_2$-proton
No.	X Y				
1	1 2	1455	1415	2.4 (3H,S)	7.2-8.1 (7H,m)
2	2 1			2.6	
4	4 1	1450	1420	2.70 (3H,S	7.25-8.30 (7H,m)
5	5 1	1445	1415	2.72 (3H,S)	7.20-8.25 (7H,m)
3	3 2	1450	1440	2.60 (3H,S)	7.20-8.20 (7H,m)
6	6 2	1450	1415	2.55 (3H,S)	7.25-8.20 (7H,m)

* S = singlet; m = multiplet

Table IV

2-(X-Methylnaphthyl-y)-4,5,6,7-tetrachlorobenzo-1,3-dioxoles

No	X	Y	Yield %	Melting Point	Analysis Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl	Mol. wt. ($C_{18}H_{10}{}^{35}Cl_4O_2$) Calcd.	Found (mass spectrum)
1	2											
2	1		22	101-102°	54.00	2.52	35.46	53.87	2.43	35.21	397.9437	397.9430
4	1		12	183°	54.00	2.52	35.46	54.03	2.40	35.90	397.9437	397.9438
5	1		29	210°	54.00	2.52	35.46	53.92	2.25	35.53	397.9437	397.9434
3	2		29	172-174°	54.00	2.52	35.46	53.85	2.76	33.59	397.9437	397.9434
6	2		33	179-181°	54.00	2.52	35.46	54.00	2.48	35.50	397.9437	397.9438

equivalents of TOQ, in 68% yield.

Preparation of 4-Methyl-1-nitronaphthalene

This compound was prepared in 40% yield according to the method of Thompson (105).

m.p. 70-72° (lit. (105) 71-2°).

Attempted reaction of 4-Methyl-1-nitronaphthalene with Tetrachloro-o- benzoquinone

A solution of 0.375 g (2 mmoles) of 4-methyl-1-nitronaphthalene in 25 ml of chlorobenzene was added to a solution of 0.98 gm (4 mmoles) of tetrachloro-o—benzoquinone in 150 ml of chlorobenzene and the mixture refluxed for 72 hours. The 4-methyl-1-nitronaphthalene was recovered in 80% yield.

Reaction of 1,4-dimethylnaphthalene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 3.1 g (0.02 moles) of 1,4-dimethylnaphthalene in 50 ml of dichloroethane was added to a solution of 9 g (0.04 moles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 250 ml of dichloroethane, and the mixture refluxed for 8 hours. The solution was allowed to cool, where upon a reddish brown solid separated out of solution. It was collected, washed with chloroform, and recrystallised from acetone benzene to give 5.2 g (68% yield) of a monoquinol ether, m. p. 165-167°.

Anal. Calcd. for $C_{20}H_{12}Cl_2N_2O_2$: C, 62.82, H, 3.40, Cl, 18.32 N, 7.33

Found: C, 62.65; H, 3.07; Cl, 18.29; N, 7.26

Infrared spectrum ν_{max}(Nujol mull) 3210 cm^{-1} (broad band O-H); 2240 cm^{-1} (C≡N).

Nmr spectrum δ_{TMS}(acetone-d_6): 2.66 (3H, singlet methyl proton); 5.56 (2H, singlet, -CH_2-O); 7.3-8.2 (6H, aromatic protons).

Reaction of 1,2-Dimethylnaphthalene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 3.12 g (0.02 moles) of 1,2-dimethylnaphthalene in 30 ml of dichloroethane was added to a solution of 9.04 g (0.04 moles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 250 ml of dichloroethane and the mixture refluxed for 18 hours, cooled and the solid formed collected, washed with chloroform and crystallised from acetone/benzene to give 2.3 g (30.1% yield) of a mixture of (1-methylnaphthyl-2)-methyl- and (2-methylnaphthyl-1)-methyl-quinol mono ethers. m.p. 168-170°.

Anal. Calcd. for $C_{20}H_{12}Cl_2N_2O_2$: C, 62.82; H, 3.14; Cl, 18.32; N, 7.33

Found: C, 62.55; H, 2.97, Cl, 18.42, N, 7.65

Infrared spectrum ν_{max}(Nujol): 3280 cm^{-1} (broad band O-H); 2242 cm^{-1} (C≡N)

N.m.r. spectrum δ_{TMS}(acetone-d_6): 2.73, 2.85 (3H, overall, singlets, methyl protons) 5.78, 5.90 (2H overall, singlets, -CH_2-O-); 7.3-8.3 (6H, multiplets aromatic protons).

9,10-Dimethyl, 9,10-Dihydroxy-9,10-dihydro-phenanthrene

This compound was prepared in 64% yield by the method of Zincke and Tropp (102) m.p. 163-166° (lit. (102) 164°).

9,10-Dimethylphenanthrene

9,10-Dimethyl-9,10-dihydroxy-9,10-dihydrophenanthrene 2 gm (0.083 mole) was dissolved in 100 ml of glacial acetic acid and treated with 3 gm of red phosphorus and 7 ml of 47% hydriodic acid. The mixture was refluxed for 2 hours, allowed to cool, poured into ice water, the solid removed by filtration and the latter extracted with ether. The ether solution was dried and the solvent removed to give colourless solid which was dissolved in hexane and subjected to chromatography on B.D.H. alumina to yield 1.16 gm (67%) of 9,10-dimethylphenanthrene m.p. 138-140° (lit. (102) 138°).

Reaction of 9,10-Dimethylphenanthrene with Tetrachloro-o-benzoquinone

A solution of 2.1 g (10 mmoles) of 9,10-dimethylphenanthrene in 75 ml of benzene was added to a solution of 4.90 g (20 mmoles) of tetrachloro-o-benzoquinone in 150 ml of benzene. The mixture was heated under reflux for 96 hours, cooled, concentrated to 50 ml, and subjected to chromatography on B.D.H. alumina using benzene/hexane (1:3) as eluant to give 1.0 g (22.3% yield) of 98).

m.p. 297-299°C.

Anal. Calcd. for $C_{22}H_{12}Cl_4O_2$: C, 58.92, H, 2.68, Cl, 31.25.
Found: C, 58.96, H, 2.63, Cl, 30.60

Mol. wt. Calcd. 447.9593. Found (mass spectrum) 447.9589.

Infrared spectrum ν_{max}(Nujol): 1456-1447 cm^{-1} (O-C-O-C)

Further elution with benzene gave 0.52 g (11.6%) of pale yellow solid 99. m.p. 240-245°.

Anal. Calcd. for $C_{22}H_{12}Cl_4O_2$: C, 58.92, H, 2.68, Cl, 31.25
Found: C, 58.81, H, 2.63, Cl, 31.29

Mol. wt. Calcd. for $C_{22}H_{12}{}^{35}Cl_3{}^{37}ClO_2$: 449.9562
Found: (mass spectrum): 449.9564

Infrared spectrum $\nu_{max}(CHCl_3)$ 1450, 1418 cm^{-1} (C-OC-)

N.m.r. $\delta_{TMS}(CDCl_3)$: 2.76 (3H, singlet methyl protons); 5.10 (2H, singlet $-C\underline{H}_2-O-$); 7.16-8.30 (7H, multiplet aromatic protons).

Hydrolysis of 2-(10'-Methylphenanthyl-9'-)-4,5,6,7-tetrachlorobenzo-1,3-dioxole (98)

2-(10'-methylphenathyl-9'-)4,5,6,7-tetrachlorobenzo-1,3-dioxole (67 mg, 0.15 mmoles) was dissolved in 20 ml of hot acetone and 10 ml of 6N hydrochloric acid added to it. The mixture was refluxed for 12 hours, it was poured into water, and extracted with ether. The ether solution was washed with water, dried (Na_2SO_4) and solvent removed. The residue was dissolved in benzene and subjected to chromatography to give 0.020 g (60.6%) of 10-methyl-phenanthrene-9-carboxaldehyde. m.p. 112-115°.

Mol. wt. Calcd. for $C_{16}H_{12}O$: 220.0887

Found (mass spectrum): 220.0887

Infrared spectrum $\nu_{max}(CHCl_3)$:1683 cm^{-1} (C=O).

Reaction of 9,10-Dimethylphenanthrene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 1.03 g (5 mmoles) of 9,10-dimethylphenanthrene in 50 ml of benzene was added to a solution of 3.39 gm (15 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of hot benzene; and the mixture refluxed for 3 hr. The solvent was removed, the filtrate concentrated to about 50 ml and hexane added to it to yield 1.4 g (64.9%) of the quinol mono ether 100.

mp. 250-252°.

Anal. Calcd. for $C_{24}H_{14}Cl_2N_2O_2$: C, 66.67; H, 3.24; Cl, 16.20; N, 6.48

Found: C, 66.55; H, 3.28; Cl, 16.05, N, 6.10.

Mol. wt. Calcd. for $C_{24}H_{14}{}^{35}Cl_2N_2O_2$: 432.

Found (mass spectrum); 432.

Infrared spectrum $\nu_{max}(CCl_4)$ 3125 cm^{-1} (broad O-H), 2250 cm^{-1} (C=N): 1445 cm^{-1} (C-O-C)

N.m.r. spectrum $\delta_{tms}(CDCl_3)$: 2.8 (3H, singlet methyl protons); 5.25 (2H, singlet, $C\underline{H}_2$-O-);7.23 to 8.70 (8H, multiplet, aromatic proton).

Addition of acetone to the solid that precipitated out of the reaction mixture during refluxing gave 0.019 g of a yellow solid 101, m.p.>300.

Mol. wt. Calcd. for $C_{24}H_{12}{}^{35}Cl_2N_2O_2$: 430.0277

Found: 430.0270.

Infrared spectrum ν_{max}(Nujol): 1718 cm^{-1} (C=O).

1,4-Epoxy-1,4-dihydronaphthalene

This compound was prepared in 65% yield according to the method of Wolthius (23), m.p. 54-56° (lit (23) 56°).

2,3-Dimethyl-9,10-epoxy-1,4,9,10-9a,10a-hexahydroanthracene

This compound was prepared in 75% yield according to the method of Wolthius (23) m.p. 108-110°, (lit. (23) 108.8-109°).

2,3-Dimethyl-1,4-dihydroanthracene

This compound was prepared in 50% yield by the method of Wolthius (23), m.p. 186-187° (lit. (23) 189-190°).

2,3-Dimethylanthracene

A solution of 1.56 g (7.5 mmoles) of 2,3-dimethyl-1,4-dihydro-anthracene in 20 ml of chlorobenzene was added to a solution of 1.83 g (7.5 mmoles) of tetrachloro-o-benzoquinone and the mixture refluxed for 45 min. The solution was allowed to cool, whereupon 2,3-dimethylanthracene crystallised out of solution. This was collected, washed with hexane and dried to give 1.02 g (66%) of product. m.p. 249-250° (lit. (23) 250°).

1,4-Dimethyl-9,10-epoxy-1,4,9,10,9a,10a-hexahydroanthracene

This compound was prepared in 63% yield from 1,4-epoxy-1,4-dihydroanaphthalene and trans-trans-1,4-dimethyl-1,4-butadiene according to the general method of Wolthuis. m.p. 73-75°.

Mol. wt. Calcd. for $C_{16}H_{18}O$: 226.

Found (mass spectrum, ms 2): 226.

N.m.r. $\delta_{Tms}(CDCl_3)$: 1.2 (6H, doublet J-6Hz methyl protons); 1.5 (2H, pair of doublet 9a,10a protons); 2.13 (2H poorly resolved multiplet 1,4-methine protons); 5.07 (2H, singlet 9,10 protons); 5.6 (2H, singlet, $C_{21}C_3$-olefinic protons); 7.1 (4H, weakly split singlet, aromatic protons).

1,4-Dimethyl-1,4-dihydroanthracene

This was prepared in 52% yield according to the method of Wolthius (23). m.p. 73-74°.

Mol. wt. Calcd. for $C_{16}H_{16}$: 208.

Found (mass spectrum (M.S.2)): 208.

1,4-Dimethylanthracene

A mixture of 1.02 g (5mmoles) of 1,4-dimethyl-1,4-dihydroanthracene and 1.22 gm (5 mmoles) of tetrachloro-o-benzoquinone in 100 ml of chlorobenzene was refluxed for 1 hour; the solvent removed, the residue dissolved in benzene and run down a column of B.D.H. alumina to give 0.65 g (65% yield) of 1,4-dimethylanthracene. m.p. 72-73°, [lit. (109) 74°; (110) 76°].

Reaction of 2,3-Dimethylanthracene with Tetrachloro-o-benzoquinone

A solution of 0.311 g (15 mmoles) of 2,3-dimethylanthracene in 40 ml of chlorobenzene was added to a solution of 0.735 g (30 mmoles) of tetrachloro-o-benzoquinone in 150 ml of chlorobenzene and the mixture refluxed for 48 hours. The solvent was then removed in vacuo and the residue dissolved in benzene and subjected to chromatography over B.D.H. alumina using benzene/hexane (1:1) as eluant. Recrystallisation of the resulting solid from benzene gave 0.60 g (91.3% yield) of pale yellow solid, 108. m.p. 215°.

Anal. Calcd. for $C_{22}H_{12}Cl_4O_2$: C, 58.91; H, 2.68; Cl, 31.25

Found: C, 58.75; H, 2.55; Cl, 31.23

Mol. wt. Calcd. 447.9591. Found (mass spectrum): 447.9598.

Infrared spectrum $\nu_{max}(CCl_4)$: 1447, 1425 cm^{-1} (-C-O-C-)

Hydrolysis of 2-(3'-Methyl-2'-anthryl)-4,5,6,7-tetrachlorobenzo-1,3-dioxole

Adduct 108 (0.67 g, 2 mmoles) was dissolved in 25 ml of hot acetone, and treated with 10 ml of 6N hydrochloric acid and the mixture refluxed for 12 hours. The solution was concentrated and poured into water and extracted with ether; the ether extract was washed with 10% sodium bicarbonate solution and then water, dried (Na_2SO_4) and solvent removed to give 0.25 g (75.7% yield) 3-methylanthracene-2-carboxaldehyde. m.p. 205-210°.

Mol. wt. Calcd. for $C_{16}H_{12}O$: 220.0887

Found (mass spectrum): 220.0886.

Infrared spectrum $\nu_{max}(CHCl_3)$: 1687 cm^{-1} (C=O).

Reaction of 1,4-Dimethylanthracene with Tetrachloro-o-benzoquinone

A solution of 0.315 g (15 mmoles) in 30 ml of chlorobenzene was added to a solution of 0.732 gm (30 mmoles) of tetrachloro-o-benzoquinone in 150 ml of chlorobenzene and the mixture refluxed for 48 hours. The solvent was taken off and the residue dissolved in benzene and subjected to chromatography on acid washed alumina to give 2-(4'-methylanthryl-1')-4,5,6,7-tetrachlorobenzo-1,3-dioxole (0.52 g, 77.4% yield) as pale yellow solid. m.p. 252-255°.

Anal. Calcd. for $C_{22}H_{12}Cl_4O_2$: C, 58.91; H, 2.68; Cl, 31.25

Found: C, 58.63; H, 2.75, Cl, 30.98.

Mol. wt. Calcd: 447.9591. Found (mass spectrum): 447.9602.

Infrared spectrum $\nu_{max}(CHCl_3)$: 1450 cm^{-1} 1425 cm^{-1} 1425 cm^{-1} (C-O-C).

Reaction of 9,10-Dimethylanthracene with Tetrachloro-o-benzoquinone

A solution of 2.06 g (10 mmoles) of 9,10-dimethylanthracene in 50 ml of chlorobenzene was added to a solution of 4.88 g (20 mmoles) of tetrachloro-o-benzoquinone in 150 ml of chlorobenzene. The mixture was refluxed for 48 hours and the solvent removed *in vacuo*. The residue was dissolved in benzene and subjected to chromatography on B.D.H. alumina, using 1:3 benzene/hexane as eluant to give a pale yellow solid. Recrystallisation from benzene/hexane gave 2.63 g (58.7% yield) of pale yellow crystalline solid 106, m.p. 239-241°.

Infrared spectrum $\nu_{max}(CHCl_3)$: 1422 cm^{-1}(C-O-C) 1550 cm^{-1} (C=C).
N.m.r. spectrum $\delta_{Tms}(CDCl_3)$: 5.80 (2H, singlet, vinyl protons);
3.94 (2H, singlet, $-C\underline{H}_2-O$);
The infrared spectrum, nuclear magnetic spectrum and melting point showed this compound to be the same as the compound which was obtained when the reaction was performed in benzene (69).

Reaction of 9-Methylanthracene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 1 g (0.0052 mole) of 9-methylanthracene in 5 ml of benzene was added to a solution of 2.4 g (0.0106 mole) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 45 ml of hot benzene. The mixture was refluxed 10 minutes, during which time a brown solid separated. The mixture was refluxed for 2 hours, cooled, and the solid collected by filtration. The major product was insoluble in chloroform, methanol acetonitrile, dimethylsulfoxide, and benzene and was purified by soxhlet extraction of the impurities with methanol, leaving a bright yellow solid (1.1 g 34.6% yield) 117 m.p. 215° (decomp.).

Anal. Calcd. $C_{38}H_{22}Cl_2N_2O_2$: C, 74.87, H, 3.61, Cl, 11.66; N, 4.61.
Found: C, 74.74; H, 3.88; Cl, 11.98; N, 4.42.
Infrared spectrum ν_{max}(KBr disk) 1425 cm^{-1}(C-O-C) 2216 cm^{-1} (C≡N).

Adduct 117 (0.227 g, 0.36 mmole) was refluxed with a mixture of 5 ml of 57% hydriodic acid and 3 ml of water for 8 hours. White crystals of 9-iodomethylanthrancene (45 mg) m.p. 65-66°, which

had sublimed into the condenser were removed and dried in vacuo. This solid, without further purification, was dissolved in 10 ml of anhydrous ether, treated with a suspension of 85 mg of lithium aluminum hydride in 10 ml of anhydrous ether, and stirred for four hours. The mixture was cooled, decomposed with water, the organic layer separated dried ($MgSO_4$), and the ether removed to give yellow crystals of 9-methylanthracene, m.p. 74-75°; mixed m.p. with authentic 9-methylanthracene 74-75°.

Reaction of 1,4-Dimethyl-1,4-dihydro-anthracene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 0.94 g (4.5 mmoles) of 1,4-dimethyl-1,4-dihydro-anthracene in 50 ml of chlorobenzene was added to a solution of 4.070 g (22 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of warm chlorobenzene, and the mixture refluxed for 30 minutes, cooled, and the solid formed removed. The solvent from the filtrate was removed in vacuo, the residue dissolved in benzene and subjected to chromatography on silicic acid (pH=4) to yield 0.8 g (41%) of 118, as reddish brown solid. m.p. 264-266°.

Anal. Calcd. for $C_{24}H_{12}Cl_2N_2O_2$: C, 66.97; H, 2.80, Cl, 16.28, N, 6.51.
Found: C, 66.58; H, 2.79, Cl, 15.94, N, 6.32.

Mol. wt. Calcd. 430.0277. Found (mass spectrum): 430.0274.

Infrared spectrum ν_{cm}^{-1} ($CHCl_3$): 1715 cm^{-1} (C=O).

N.m.r. spectrum δ_{Tms}($CDCl_3$):2.75 (3H, singlet, aryl methyl group) 4.32, 4.00 (2H, quartet J=15 Hz, methylene protons).

Reaction of 1,4-Dimethylanthracene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 0.210 g (1 mmole) of 1,4-dimethylanthracene in 25 ml of chlorobenzene was added to a solution of 0.68 g (3 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of chlorobenzene and the mixture refluxed for 30 minutes. The solvent was removed *in vacuo*, the residue dissolved in benzene and subjected to chromatography on silicic acid to give 0.14 g (32.6% yield) of a reddish brown solid which was found to be identical in all respects to the adduct obtained from 1,4-dimethyl-1,4-dihydroanthracene above.

9,10-Dibenzylanthracene

This compound was prepared in 40% yield by the method of Lippmann and Fritsch (103), and was purified by chromatography of a benzene solution on B.D.H. alumina. m.p. 245° (lit. (103) 248°).

Reaction of 9,10-Dibenzylanthracene with Tetrachloro-*o*-benzoquinone

A solution of 1.80 g (5 mmoles) of 9,10-dibenzylanthracene in *o*-dichlorobenzene was added to a solution of 3.7 g (15 mmoles) of tetrachloro-*o*-benzoquinone in 100 ml of dichlorobenzene and the mixture refluxed for 48 hours. The solvent was removed *in vacuo* the residue dissolved in benzene and subjected to chromatography on B.D.H. alumina using benzene/hexane (1:2) as eluant to give a white solid. Further recrystallisation from benzene gave 2.3 g (76.6%) of 120. m.p. 262-264°.

Anal. Calcd. for $C_{34}H_{20}Cl_4O_2$: C, 68.00; H, 3.33; Cl, 23.33.

Found: C, 67.34; H, 3.46; Cl, 23.51

Mol. wt. Calcd. 600.0219. Found (mass spectrum) 600.0210

Infrared spectrum $\nu_{max}(CHCl_3)$: 1427 cm^{-1} (C-O-C); 1512 cm^{-1} (C=C).

N.m.r. spectrum $\delta_{Tms}(CDCl_3)$: 5.08 (1H, singlet, =C^{ph}_H) 6.4-8.3 (19H, multiplet, aromatic protons + O-C^{ph}_H)

Ozonolysis of the Adduct from 9,10-Dibenzylanthracene and Tetrachloro-o-benzoquinone

Adduct 120 (0.6 g, 1 mmole) was dissolved in chloroform (100 ml) and a slow stream of ozone (from a Welsbach T-23 ozonator) was passed through the solution for 45 minutes the effluent gas being passed through a solution of potassium iodide. The reaction mixture was subjected to steam distillation, until all chloroform had distilled over and for 30 minutes more. A yellow solid separated from the water in the distillation flask; this solid was collected and recrystallised from benzene to give 121, 0.31 g (59% yield) as pale yellow solid. m.p. 300-305°.

Mol. wt. Calcd. ($C_{27}H_{14}Cl_4O_2$): 525.9699. Found (mass spectrum) 525.9711.

Infrared spectrum $\nu_{max}(CHCl_3)$: 1668 cm^{-1} (C=O) 1432 cm^{-1} (C-O-C).

O-(Tetroyl-2)benzoic Acid

This compound was prepared in 90% yield by the method of Fieser (106) m.p. 152-153° (lit (106) 153-155°).

2,3-Tetralanthraquinone

This compound was prepared in 33% yield according to the method of Schroeter (107). M.p. 210-213° (lit. (107) 211°).

5,12-Dihydroxy-5,12-dimethyl-7,8,9,10-tetrahydronaphthacene

2,3-Tetralanthraquinone (8 g, 0.031 moles) was added gradually to methyl magnesium iodide (prepared from 4 g of magnesium and 24 g of methyl iodide in 100 ml of anhydrous ether). The complex was stirred for 3 hours, decomposed with ice and ammonium chloride, the ether layer dried (Na_2SO_4) and concentrated at 15° to give white crystalline solid. m.p. 193-196°.

Mol. wt. Calcd. ($C_{20}H_{22}O_2$): 294.1620. Found (mass spectrum): 294.1620.

Infrared spectrum $\nu_{max}(CHCl_3)$: 3578,3536 cm^{-1} (C-H)

N.m.r. spectrum $\delta_{Tms}(CDCl_3)$: 1.58 (6H, Singlet, methyl protons); 1.87, 2.86 (8H, multiplets C_7,C_8,C_9,C_{10} protons); 7.23 to 8.1 (6H, multiplet, aromatic protons).

To filtrate from above was added petroleum ether and kept in a freezer for two days to give a light yellow solid which turned out to be isomeric to the white crystals above. m.p. 150-152°.

Mol. wt. Calcd. ($C_{20}H_{22}O_2$): 294.1620. Found (mass spectrum): 294.1620.

Infrared spectrum $\nu_{max}(CHCl_3)$: 3580, 3405 cm^{-1} (broad) (O-H).

N.m.r. spectrum $\delta_{Tms}(CDCl_3)$: 1.82 (6H, singlet, methyl protons); 2.23, 2.8 (8H, multiplet, (C_7,C_8,C_9,C_{10} protons); 7.17 to 7.87

(6H, aromatic protons). Total yield was 5.6 g (62.4%).

5,12-Dimethyl-7,8,9,10-tetrahydronaphthacene

A solution of 2 g (68 mmoles) of 5,12-dihydroxy-5,12-dimethyl-7,8,9,10-tetrahydronaphthacene in 50 ml of glacial acetic acid was cooled to 15° and treated with 10 ml of 25% hydroiodic acid, the temperature dropped to about 10°. The mixture was stirred for 30 minutes, at 10°, and for 6 hours at room temperature. It was poured into ice, and the solid formed collected. This solid was extracted with benzene and the benzene solution run down a column of B.D.H. alumina to give a bright yellow solid, (0.3 g, 17% yield). m.p. 135°.

Mol. wt. Calcd. ($C_{20}H_{20}$): 260.1565. Found (mass spectrum): 260.1568.

N.m.r. spectrum $\delta_{Tms}(CDCl_3)$: 1.95 (4H, multiplet, C_7, C_8, C_9, C_{10}, quasi-equatorial protons); 3.05 (10H, singlet with broad base, C_7,C_8,C_9,C_{10} quasi-axial protons and methyl protons); 7.15-8.30 (6H, multiplet, aromatic protons).

Attempted preparation of 5,12-Dimethylnaphthacene

A mixture of 0.52 g (2 mmoles) of 5,12-dimethyl-7,8,9,10-tetrahydronaphthacene and 0.05 g of sulfur was heated in an oil bath at 215-225° for 2 hours. The mixture was extracted with benzene, and solvent removed, no solid was left. Variation of time and temperature of the reaction all yielded nothing but charred substance from which

nothing could be extracted. The preparation was abondoned.

Reaction of 5,12-Dimethyl-7,8,9,10-tetrahydronaphthacene with Tetrachloro-o-benzoquinone

A solution of 0.13 g (0.5 mmole) of 5,12-dimethyl-7,8,9,10-tetrahydronaphthacene in 5 ml of chlorobenzene was added to a solution of 0.490 g (2 mmoles) in 50 ml of chlorobenzene and the mixture refluxed for 2 hours. The solvent was removed in vacuo; the residue dissolved in benzene and subjected to chromatography on B.D.H. alumina to give 0.035 g (13.9% yield) of a yellow solid 128. m.p. darkens at 230°, melts beyond 300°.

Anal. Calcd. for $C_{26}H_{18}Cl_4O_2$: Cl, 27.89

Found: Cl, 27.36

Mol. wt. Calcd. 502.0063. Found (mass spectrum) 502.0050

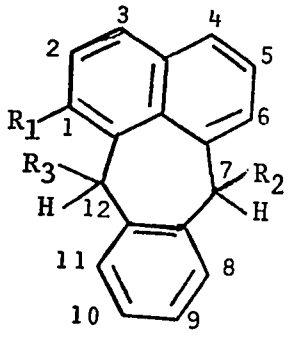
Infrared spectrum $\nu_{max}(CHCL_3)$: 1418 cm^{-1} (C-O-C-O) 1552 cm^{-1} (C=C).

CHAPTER III

DEHYDROGENATION OF DIHYDROPLEIADENE COMPOUNDS

In Chapter II it was found that quinone dehydrogenation of some arenes e.g. 9,10-dimethylanthracene gave adducts which could be plausibly explained by a mechanism involving quinodimethanes as intermediates. It was therefore decided to investigate further quinone dehydrogenation with donors that contained potential quinodimethanes, in the hope of developing the quinodimethane generation by quinones from substituted aromatic hydrocarbons.

7,12-Dihydropleiadenes 129 were chosen because the parent hydrocarbon pleiadene 131 contains within its framework the elements of an o-quinodimethane system 130 fused across the peri positions of naphthalene. It was expected that 131 could result from quinone



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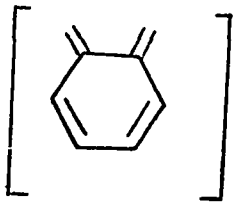

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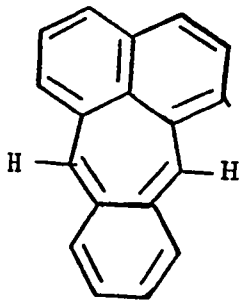
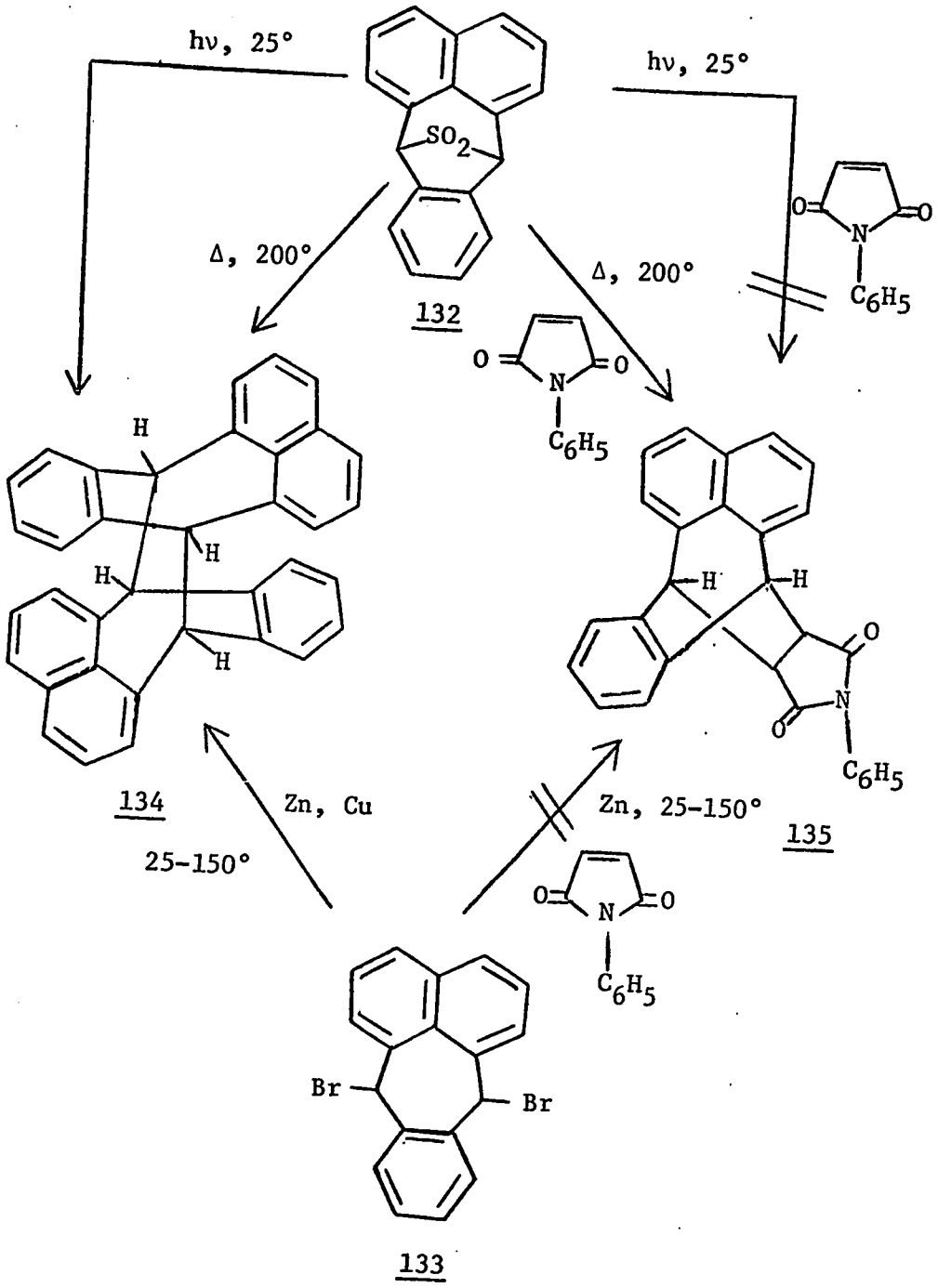


131

dehydrogenation of 129. Pleiadene would not be expected to be aromatic. A conjugated π-electron system is called aromatic if it shows neither strong first-order nor second-order double-bond fixation (111). Calculations of bond orders for pleiadene show it to have a degree of localised first-order effect (111). It would therefore be expected to be non-aromatic, and could be predicted to behave more as a quinodimethane, and its adducts with DDQ and TOQ could be studied. A second reason for choosing 129 was that its conformation proved ideal for studying transannular aryl, methyl, and hydride participation in quinone dehydrogenation.

Compounds containing pleiadene framework were first prepared by Fieser and Fieser (112-116), and Rieche and co-workers (117-118) by condensation of 2-naphthol with phthalic anhydride in the presence of aluminum chloride or sulfuric acid. Fieser proposed the name "Pleiadene" for the planar parent hydrocarbon, though the compounds he prepared were the 7,12-dihydro-derivatives. Pleiadene itself was first generated and trapped by Cava and Schlessinger (119), both thermally and photolytically from 7,12-dihydropleiadene-7,12-sulphone 132 as well as by copper or zinc debromination of 7,12-dibromo-7, 12-dihydropleiadene, 133. This parent hydrocarbon proved to be highly reactive as an o-quinodimethane (o-xylylene) and dimerised easily unless trapped by dienophiles as shown in Scheme XII.

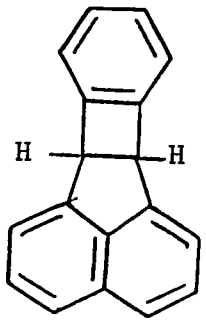
Scheme XII


hν, 25°
hν, 25°
SO2
Δ, 200°
Δ, 200°
132
O
N
O
C6H5
H
H
H
H
134
Zn, Cu
25-150°
Zn, 25-150°
135
Br
Br
133

Recently Kolc and Michl (120) have generated thermally (230 - 240°) 131 from 136, which then dimerised to 134. Irradiation of 136 in glass- forming solvents (e.g. 3-methylpentane) at low temperatures (77° K) also generated 131, which here too dimerised on allowing the solution to warm up to room temperature.

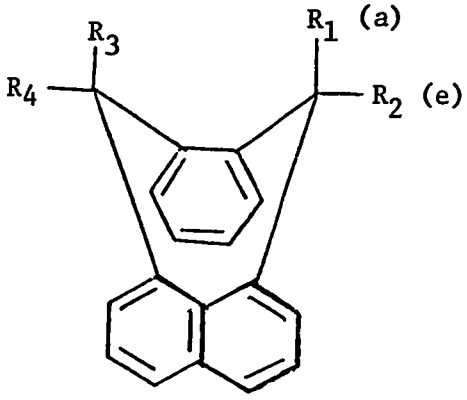
Unlike the parent hydrocarbon, pleiadene, which is unstable, 7,12-dihydropleiadenes (DHPs) are stable molecules. By virtue of their fused aryl rings, the seven-membered ring in DHPs is confined to a "half-boat" conformation 137. The inversion of this ring can produce, (i) an identical species, (ii) an enantiomeric conformer, or (iii) a diastereoisomeric conformer, depending on the substitutions at 1,7,8, and 12 positions, see eqn. [71].

[70]



136

$\xrightarrow[\text{or UV (77°K)}]{\Delta(230\text{-}240°)}$ 131 ⟶ 134



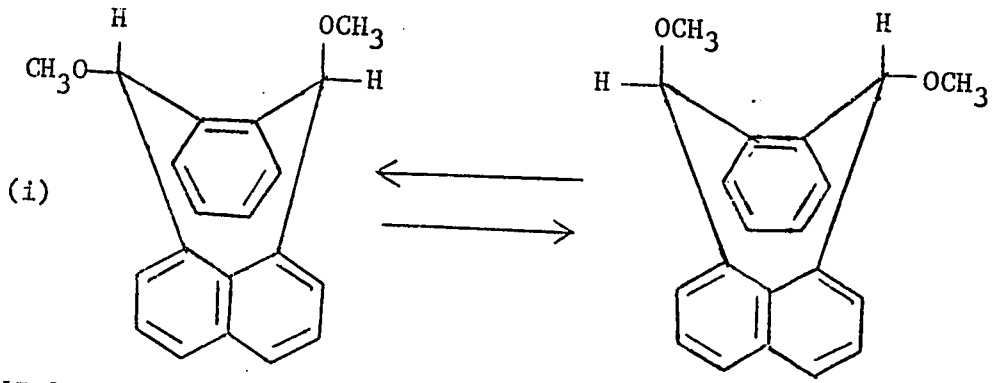
(a) = axial

(e) = equatorial

137

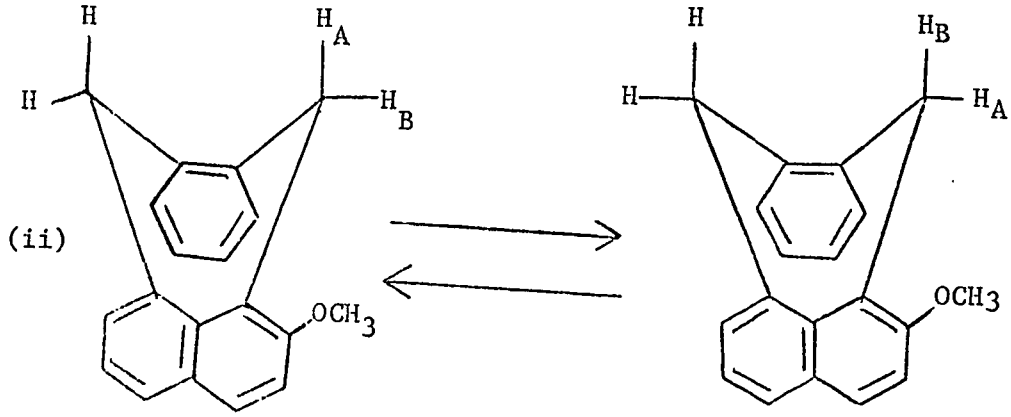
Within the past ten years, Lansbury and his co-workers (121-131) have synthesised a number of 7,12-dihydropleiadenes, and measured their nuclear magnetic resonance spectra over a range of temperatures. From the study of these spectra they determined the free energy barriers (ΔF) for inversions; the conformational preferences (axial, or equatorial) of various substitutents at the 7-position; the effects of various buttressing substituents at 1,6,8 and 11 on ΔF, and magnetic non-equivalence of methylene groups at carbons 7, and 12; and effects of replacement of tetrahedral carbons on the ring by one or more trigonal carbons (e.g. $>C=O$, $>C=R_2$) on conformational stability.

(i)

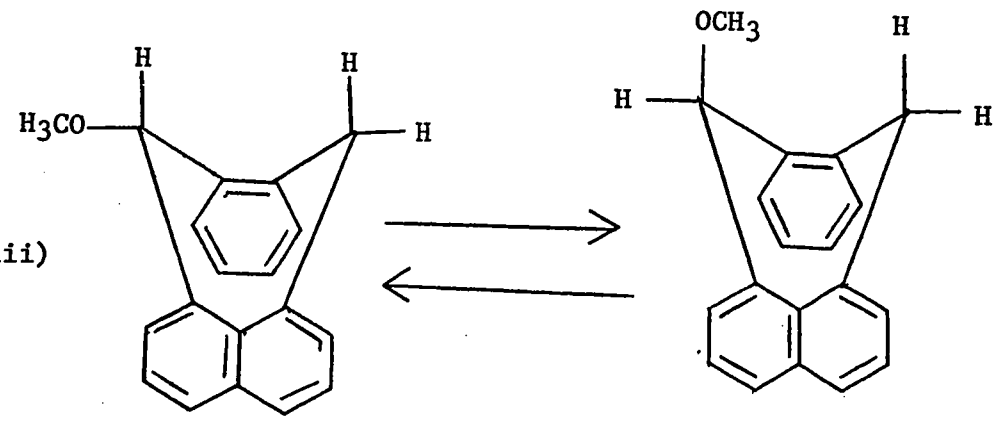


[71]

(ii)

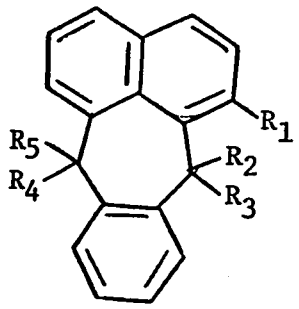


(iii)



RESULTS AND DISCUSSIONS

In these discussions a reference to a carbon position in an adduct refers to the numbering on 129. The 7,12-dihydropleiadenes employed in this study are listed below:



138 $R_1=R_2=R_3=R_4=R_5=H$

139 $R_1=Cl, R_2=R_3=R_4=R_5=H$

140 $R_1=Cl, R_2=R_3=R_4=R_5=D$

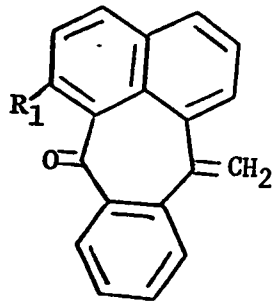
141 $R_1=Cl$, $R_4=CH_3$; $R_2=R_3=R_5=H$

142 $R_1=H$, $R_4=CH_3$; $R_2=R_3=R_5=H$

143 $R_1=H$, $R_4=i\text{-}Pr$, $R_2=R_3=R_5=H$

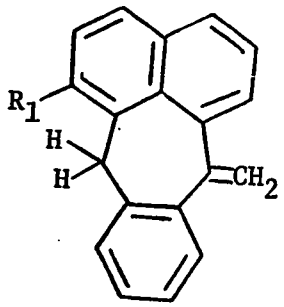
144 $R_1=H$, $R_4=Ph$, $R_2=R_3=R_5=H$

145 $R_1=R_4=R_5=CH_3$, $R_2=R_3=H$



146 R_1=H

147 R=Cl



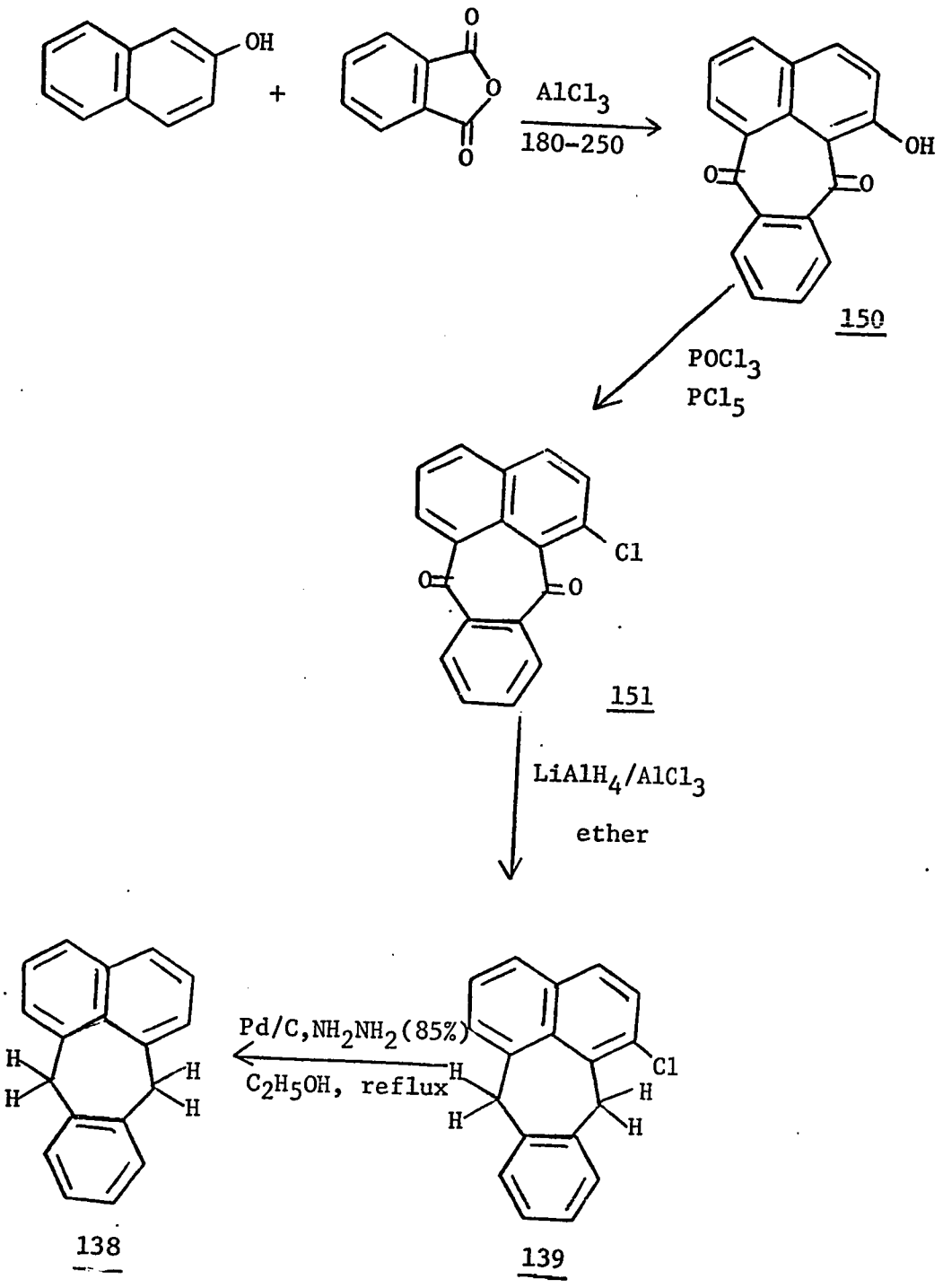
148 R_1=H

149 R_1=Cl

Preparation of 1-Chloro-7,12-Dihydropleiadene 11 and 7,12-Dihydropleiadene 138

The method used for the preparation of 1-chloro-7, 12-dihydropleiadene and 7,12-dihydropleiadene is illustrated in scheme XIII. The first two steps in this scheme were performed according to the methods of Fieser (112), and the rest by the method of Cava and Schlessinger (119) with some modifications. 1-Hydroxy-7,12-dihydropleiadene-7,12-dione 150 was prepared in 70% yield by condensing β-naphthol with phthalic anhydride in the presence of aluminum chloride at 180-250°. Compound 150 was then treated with phosphoryl chloride and phosphorus pentachloride to give the chloro-compound 151.

Scheme XIII


OH
+
O
O
O
AlCl3
180-250
OH
O
O
150
POCl3
PCl5
Cl
O
O
151
LiAlH4/AlCl3
ether
Pd/C,NH2NH2(85%)
C2H5OH, reflux
H
H
H
H
H
H
Cl
H
H
138
139

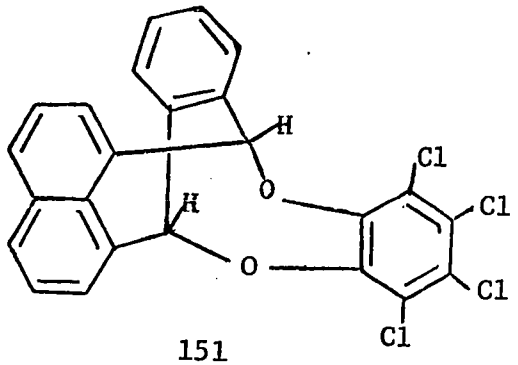
Though the method of Cava was satisfactory for the preparation of small scale samples of 139 it was found that, scaling up proportionally to obtain the amount needed for the present work meant using large quantities of ether and lithium aluminum hyrdride (LAH) which were difficult to handle at room temperature. It was found that if the ether was maintained around 0°, a fair amount of LAH, and aluminum chloride could be added to it gradually without causing the solution to boil. It was also found that it was not necessary to use the molar amounts of LAH and $AlCl_3$ recommended by Cava and Schlessinger. Instead of using a Soxhlet apparatus to extract the 1-chloro-7, 12-dihydropleiadene-7-12-dione 151 into the reaction pot which took over 3 days to dissolve it all, it was found that a gradual addition of 151 to the ethereal suspension of LAH and $AlCl_3$ and stirring the mixture overnight was adequate and gave yields of 66-70% of 139.

The same difficulty of quantities was faced on large scale preparation of 138. The amount of palladium on charcoal (Pd/C) needed had to be reduced to make the preparation safe. Also the proportionate amount of alcohol, and hydrazine hydrate (85%) as recommended by Cava and Schlessinger was not required.

Reaction of 7,12-Dihydropleiadene 138 with Tetrachloro-o-benzoquinone (TOQ)

Reaction of 138 with two molar equivalents of TOQ in refluxing dry chlorobenzene gave a white crystalline solid,

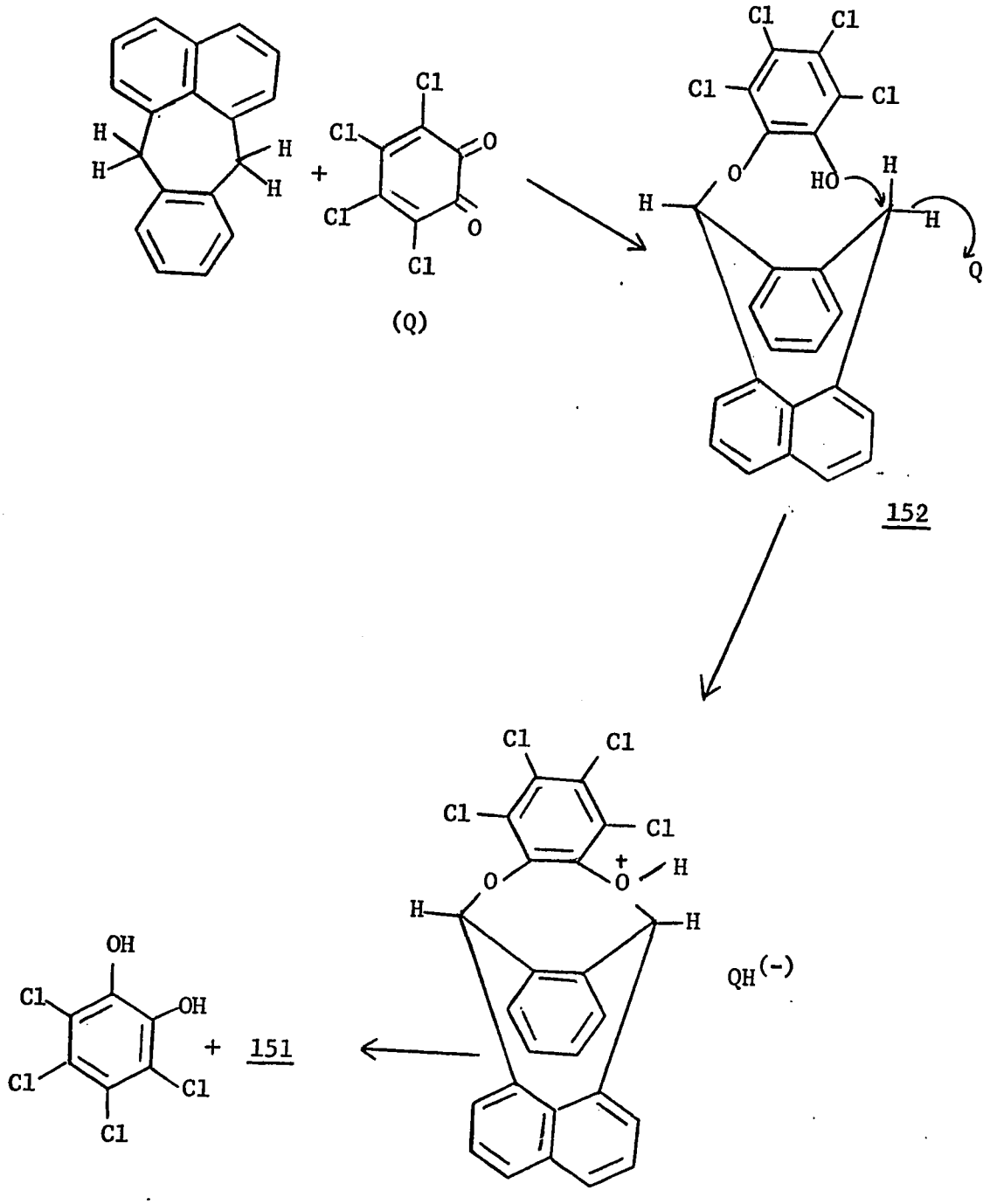
$C_{24}H_{12}Cl_4O_2$, corresponding to 1:1 TOQ to 138 adduct minus one hydrogen molecule; assigned to structure 151. Compound 151 showed an ether absorption band at 1454 cm^{-1}, but no hydroxyl or carbonyl stretching band, in the infrared; whilst in the nuclear magnetic resonance spectrum all signals appeared in the aromatic region. The signal of the two hydrogens at the bridgehead have been moved downfield relative to the signal of the corresponding hydrogen atoms in adduct 157 by the deshielding effect of the adjacent oxygen atoms.



151

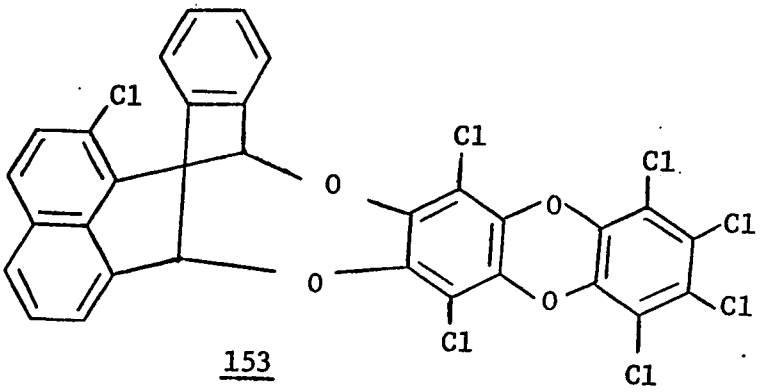
The formation of 151 is rationalized as shown in Scheme XIV. When the reaction was stopped after 1 hour of refluxing, a white crystalline solid could be isolated which showed a strong hydroxyl absorption at 3600 cm^{-1} and ether band at 1454 cm^{-1}, the chlorine analysis of which agreed with intermediate 152. However, if the reaction is allowed to go to completion, none of this hydroxyl containing compound is isolated. It is tentatively proposed therefore that formation of 151 goes through the quinol ether 152. Such a two step mechanism for addition of TOQ has been proposed for the formation of adducts 81 and 82 (65), see eqn. [62].

Scheme XIV

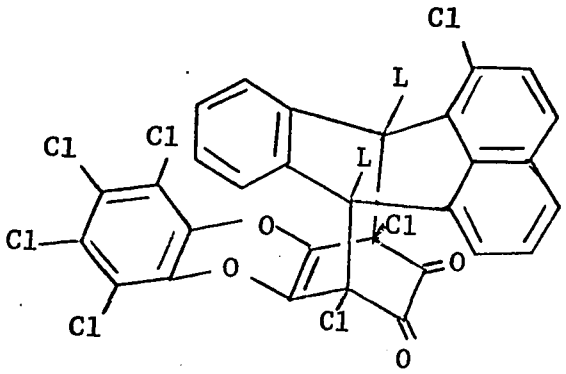

H
H
H
H
+
Cl
Cl
Cl
O
O
Cl
(Q)
Cl
Cl
Cl
Cl
O
HO
H
H
H
Q
152
Cl
Cl
Cl
Cl
O
+
O
H
H
H
QH(-)
OH
Cl
OH
+
151
Cl
Cl
Cl

Reaction of 1-chloro-7,12-dihydropleiadene 11 with TOQ

Unlike 138, 1-chloro-7,12-dihydropleiadene did not react with TOQ in chlorobenzene, however in refluxing o-dichlorobenzene under nitrogen it gave with TOQ two isomeric products, both corresponding to $C_{30}H_{10}Cl_7O_4$ (1:2 pleiadene to quinone-2HCl). Structures 153 and 154 were assigned to these adducts. The



153



L = H 154

L = D 155

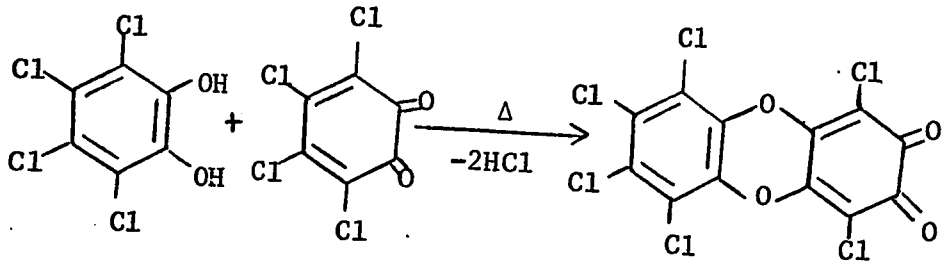
production of hydrogen chloride was confirmed by passing the evolved gases through silver nitrate solution when silver chloride was precipitated. Adduct 153, a violet powder, showed ether bands in the infrared at 1420 cm^{-1} (=C-O-C=), and 1445-1453 cm^{-1} (=C-O-C-)

and no carbonyl band. The bridgehead hydrogens as in the case of 151 appeared in the aromatic region in the nuclear magnetic resonance spectrum.

The adduct 154, on the other hand, was a bright yellow crystalline solid; the infrared spectrum of which showed both ether (1445 cm^{-1}) and α-diketone (1680 cm^{-1}) bands. The nuclear magnetic resonance spectrum showed two singlets 5.26 and 6.31 ppm (1H each) which were assigned to the C_7,C_{12} bridge protons. The corresponding adduct 155, formed from 7,7,12,12-tetradeutero-pleiadene 140, showed no signals at these positions; confirming the assignment of the above signals to the bridge-head protons. Also a doublet (1H) at 6.26 (J=10.6Hz), unaffected by deuteration was shown to be an aromatic proton by double irradiation experiments. This was tentatively assigned to the C_6 proton which, from models, is flanked by one of the carbonyl groups of α-diketone moiety.

The higher reaction temperature required for the reaction of 139, as compared with 138, is attributed to the deactivation by the 1-chloro substituent of the benzylic positions, making a hydride abstraction from these positions energetically unfavourable. Such sensitivity of quinone dehydrogenation to electron-withdrawing substituents has already been discussed for 1,2-dihydronaphthalenes in Chapter I. Under the conditions of the reaction it is considered that TOQ undergoes a preceding reaction with the corresponding quinol to form 156, (eqn. [72]).

[72]



156

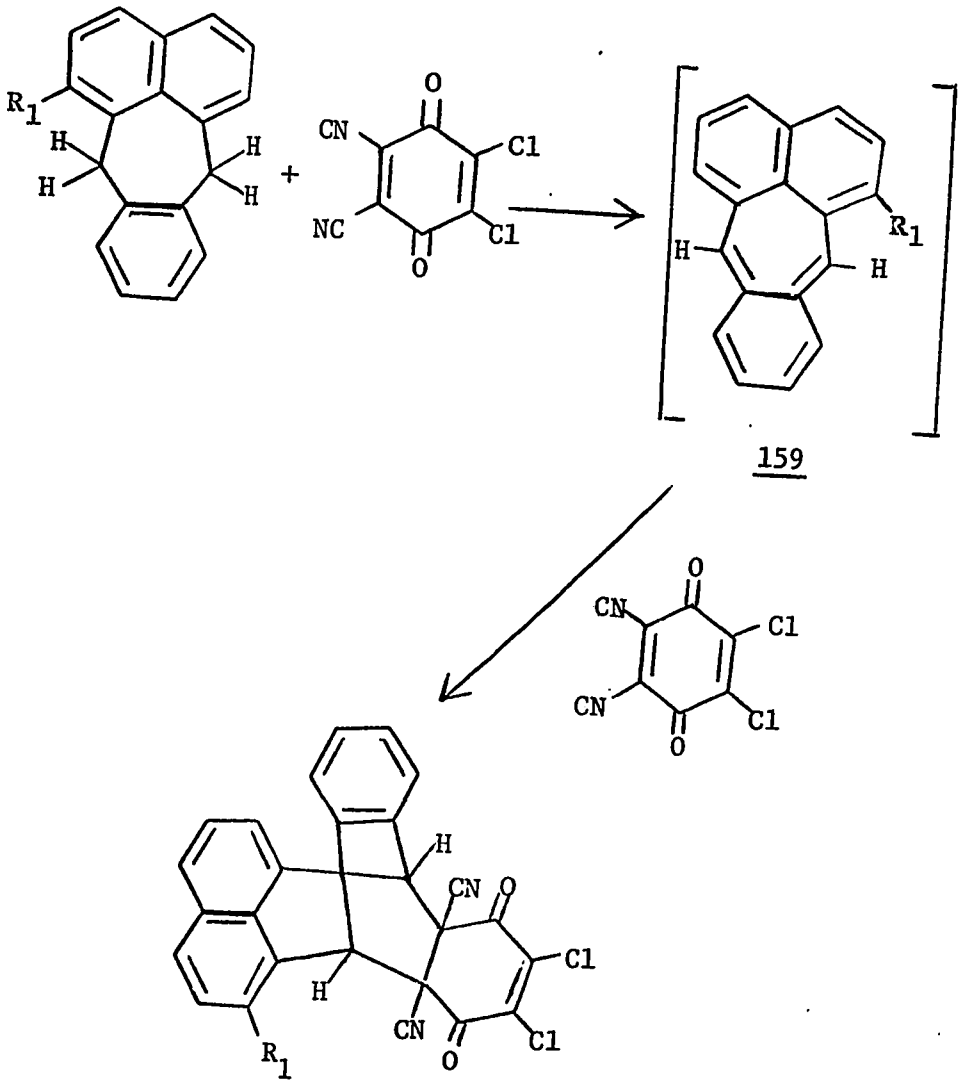
Compound 156 was therefore prepared, according to the method of Jackson and McLaurin (132), and allowed to react with 139 to give both compounds 153 and 154 in agreement with the above proposals.

Reaction of DDQ with 7,12-dihydropleiadene, and 1-chloro-7,12-dihydropleiadene

Whilst 138 and 139 reacted with TOQ under different conditions to give different adducts, with DDQ however both reacted with two molar equivalents in refluxing chlorobenzene to give bright yellow adducts 157 and 158 in yields of about 50% respectively. Both adducts exhibited in their infrared spectra carbonyl bands around 1700 cm^{-1} and nitrile bands between 2240-2250 cm^{-1}. The nuclear magnetic spectrum of 157 showed beside aryl protons a singlet of 5.05 ppm (2H) attributed to the C_7,C_{12} protons. The equivalence of these protons demonstrates the symmetry of the molecule. Compound 158 which is unsymmetrical exhibited two singlets at 5.15 and 5.64 (1H, each) for the C_7,C_{12} protons. Formation of 157 and 158 is interpreted as arising from initial dehydrogenation

of the dihydro compounds to give 159, followed by a Diels-Alder addition to the cyano-substituted bond of DDQ.

Scheme XV



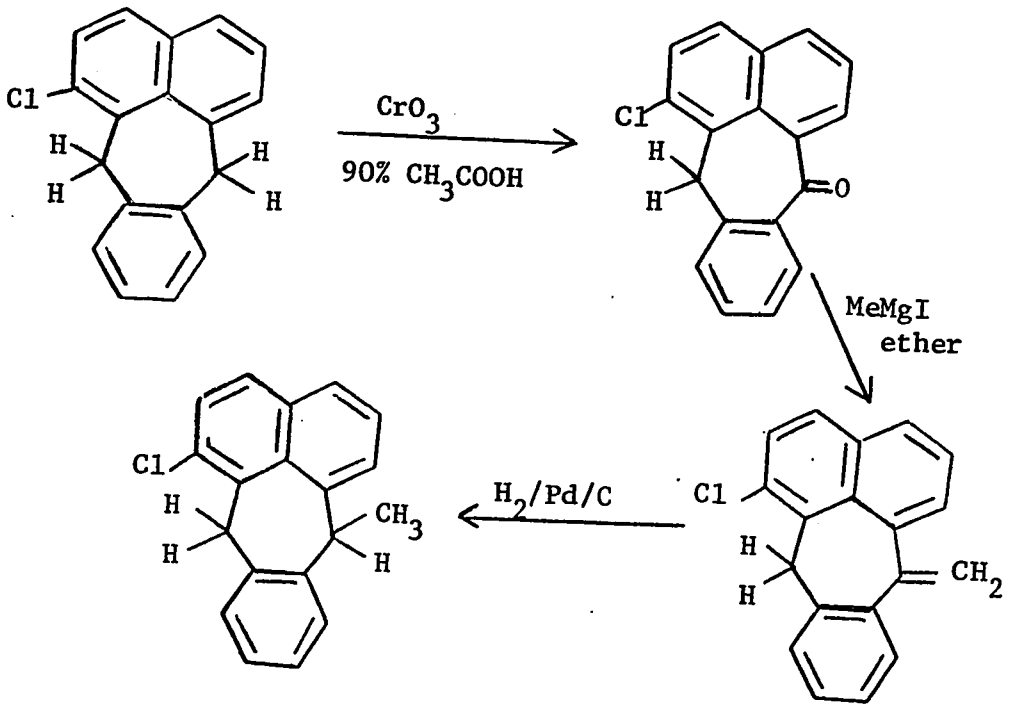
157 R_1 = H

158 R_1 = Cl

Preparation of 1-chloro-7-methyl-7,12-dihydropleiadene

1-Chloro-7-methyl-7,12-dihydropleiadene 141 was prepared by the scheme below:

Scheme XVI

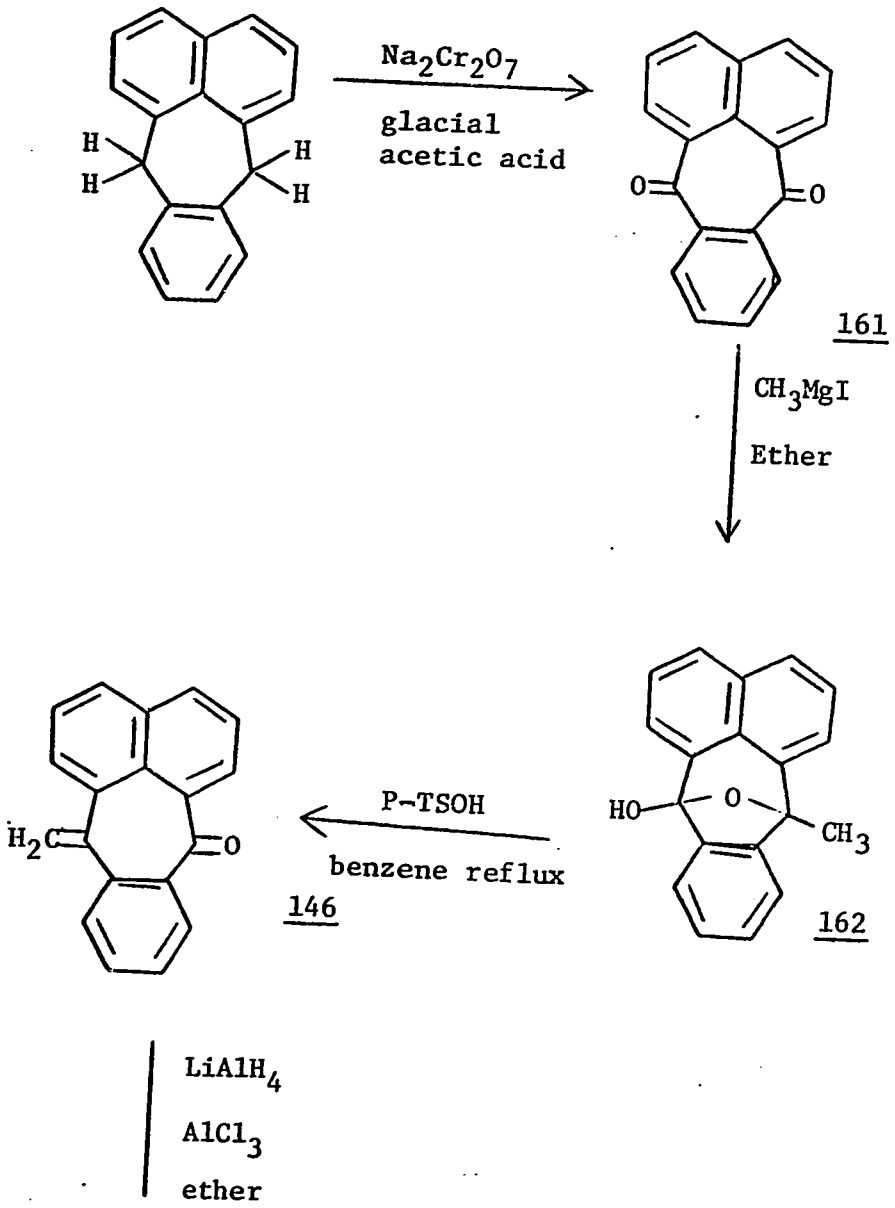


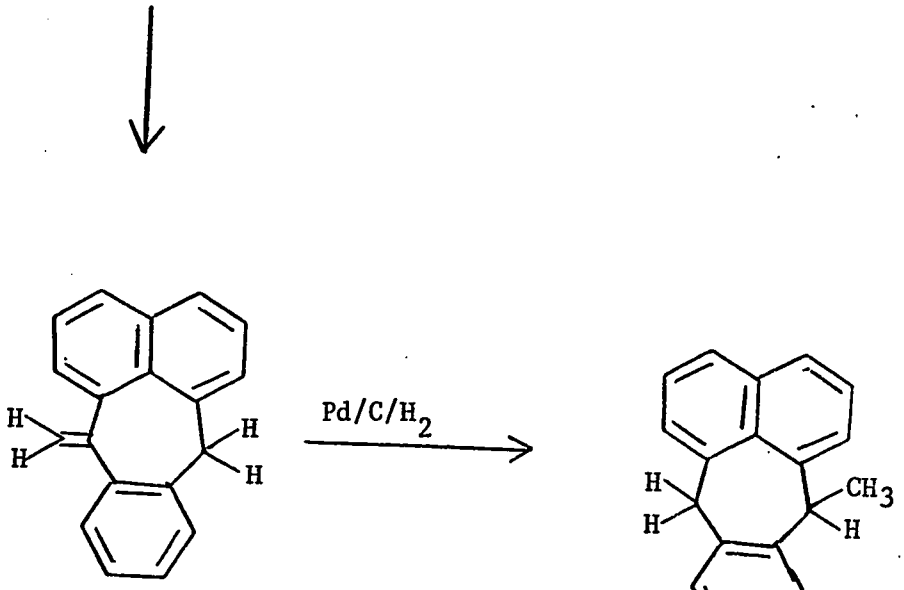
1-Chloro-7,12-dihydropleiadene, with slightly over 1 molar equivalent of chromium trioxide, is preferentially oxidized at C_7 to give 1-chloro-7,12-dihydropleiadene-7-one 160 (132), which was then added to methylmagnesium iodide to give 149. Catalytic hydrogenation of 149 at one atmosphere gave 141.

Preparation of 7-Methyl-7,12-dihydropleiadene

The method used in the preparation of 7-methyl-7,12-dihydropleiadene is shown in Scheme XVII.

Scheme XVII





148 142

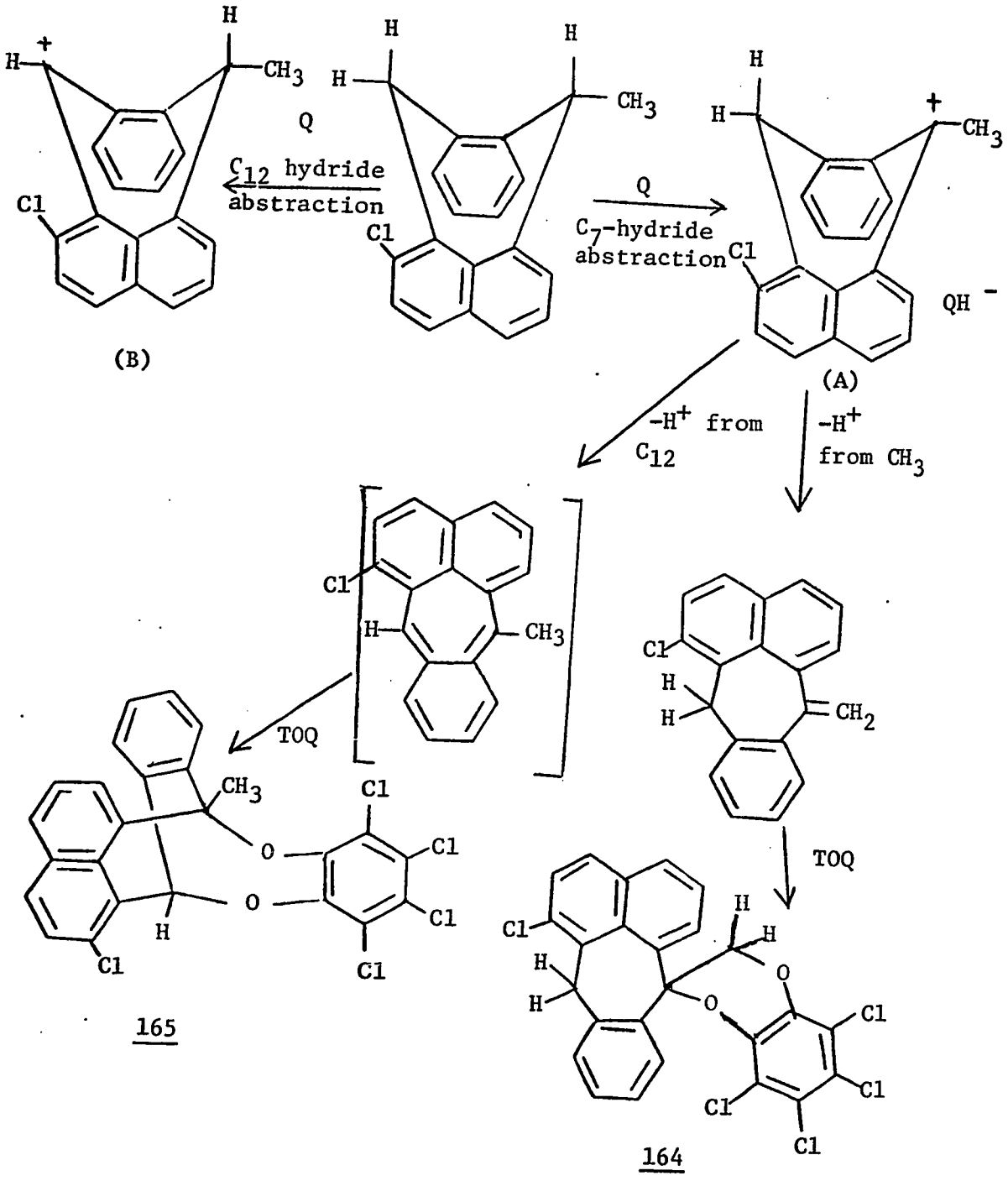
Oxidation of 7,12-dihydropleiadene with sodium dichromate in glacial acetic acid gave the diketone 161 (128). Reaction of 161 with methylmagnesium iodide gave 7,12-epoxy-7-12-dihydro-12-methylpleiadene-7-ol 162, which on treatment with a catalytic amount of p-toluenesulfonic acid in refluxing benzene gave 7-methylene-7,12-dihydropleiadene-12-one 146. Lithium aluminum hydride/aluminum chloride reduction of 146 yielded 148 which was further subjected to catalytic hydrogenation to give 142. When 1-chloro-7,12-dihydropleiadene-7,12-dione was used instead of 7,12-dihydropleiadene-7,12-dione in the second step of Scheme XVI, and the sequence followed through the third step, 1-chloro-7-methylene-7,12-dihydropleiaden-12-one 147 was obtained.

Reaction of 1-chloro-7-methyl-7,12-dihydropleiadene 141 with TOQ

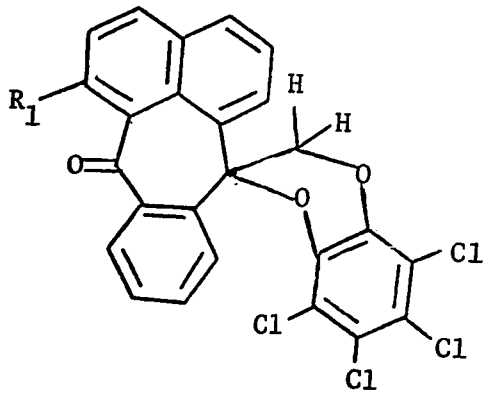
Lansbury and Lacher (126) have found that 7-methyl-7,12-dihydropleiadene exists mainly in the conformer with the C_7-methyl group in the equatorial position. This conformational preference could be assumed for 141 since the 1-chloro-substituent would not be expected to affect the conformation at C_7. Hydride abstraction from 141 would be expected to be energetically more favourable at the C_7 benzylic position for the hydrogen here is axial, and virtually perpendicular to the benzene ring. The transition state energy would be expected to be minimised by resonance stabilisation of the incipient carbonium ion. Secondly the methyl group which is electron donating would be expected to stabilise the carbonium ion generated next to it. Thirdly, due to the electron-withdrawing 1-chloro substituent adjacent to C_{12}, the C_{12}-axial proton would be less available as a hydride ion than the C_7-axial proton. One would therefore expect intermediate (A) formed rather than (B) as illustrated in Scheme XVII. Loss of proton from (A) could either lead to 1-chloro-7-methylene-7,12-dihydropleiadene 147, or 7-methylpleiadene 163, both of which could then add TOQ to give 164 and 165 respectively. Adduct 165 is similar to adduct formed from 7,12-dihydropleiadene and TOQ, the properties of which were known; but compound of type 164 had not been observed in the pleiadene series. It was therefore thought desirable to find pleiadene compounds that might give adducts similar to 164 with TOQ, so that their properties could be studied in anticipation of

formation of 164 from 1-chloro-7-methyl-7,12-dihydropleiadene. 1-Chloro-7-methylene-7,12-dihydropleiadene-12-one 147 and 1-chloro-7-methylene-7,12-dihydropleiadene were chosen since these had olefinic double bonds in the 7 positions which would be expected to add to TOQ readily.

Scheme XVIII



Reaction of 1-chloro-7-methylene-7,12-dihydropleiadene-12-one 147 with two equivalents of TOQ gave adduct 166 $C_{25}H_{11}Cl_5O_3$, the infrared spectrum of which showed benzodioxin band at 1423 cm^{-1} and carbonyl absorption at 1685 cm^{-1}, corresponding to the carbonyl absorption in the starting material. When the reaction was performed with 7-methylene-7,12-dihydropleiadene-12-one 146 a similar adduct 167 ($C_{25}H_{12}Cl_4O_3$) was obtained, which also had its carbonyl group absorbing at the same position as that of 146 (1650 cm^{-1}). This shows that the C_{12} carbonyl group remained intact during the reactions.



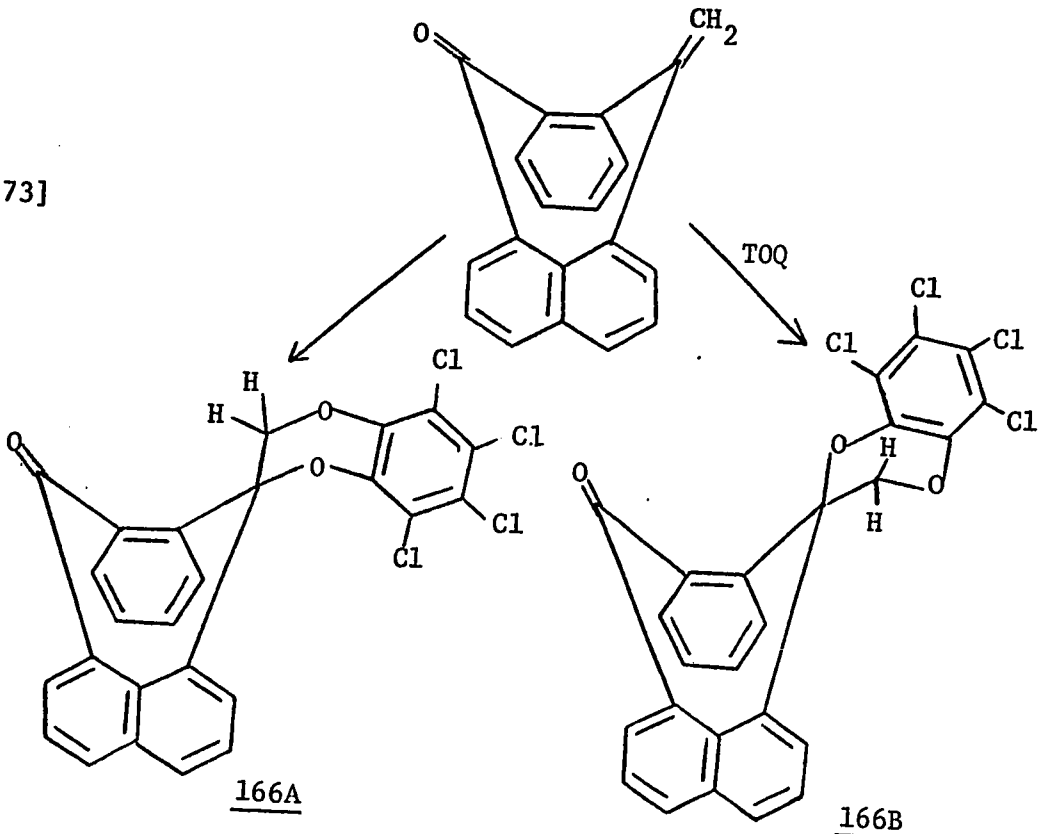
166 R = Cl

167 R_1 = H

The nuclear magnetic spectrum of the adduct 166 showed two sets of quartets centered at 4.68 and 5.43 ppm for the C_{19} methylene protons. This is attributed to the existence of two diastereoisomeric conformers arising from two modes of addition of the quinone to the double bond in 147. In one case the quinone adds so that the methylene group is in the quasi-equatorial position (166B) and in the second case with the methylene group in

the quasi-axial position (166A).

[73]

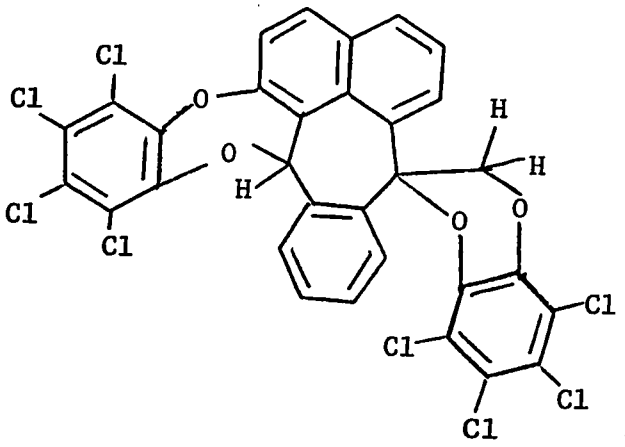


166A 166B

Owing to the trigonal carbon at the C_{12} position the barrier to ring inversion of one conformer into the other is increased relative to 7,12-dihydropleiadene (121), making it possible to observe absorption of each conformer in the nuclear magnetic resonance spectrum. Lansbury and co-workers (129) have shown that substituents at C_7 of the dihydropleiadenes when in the axial position absorb at lower fields in nuclear magnetic resonance spectrum than when equatorial. The quartet at 4.63 ppm (J=15) is therefore assigned to structure 166B, and the quartet at 5.43 ppm (J=13Hz) to structure 166A. Adduct 167 also exhibited

the same phenomenon.

With 1-chloro-7-methylene-7,12-dihydropleiadene 149, TOQ gave a light yellow adduct $C_{31}H_{12}Cl_8O_4$, corresponding to 1:2 pleiadene to quinone minus H_2 and HCl. Structure 168 was assigned to this adduct.



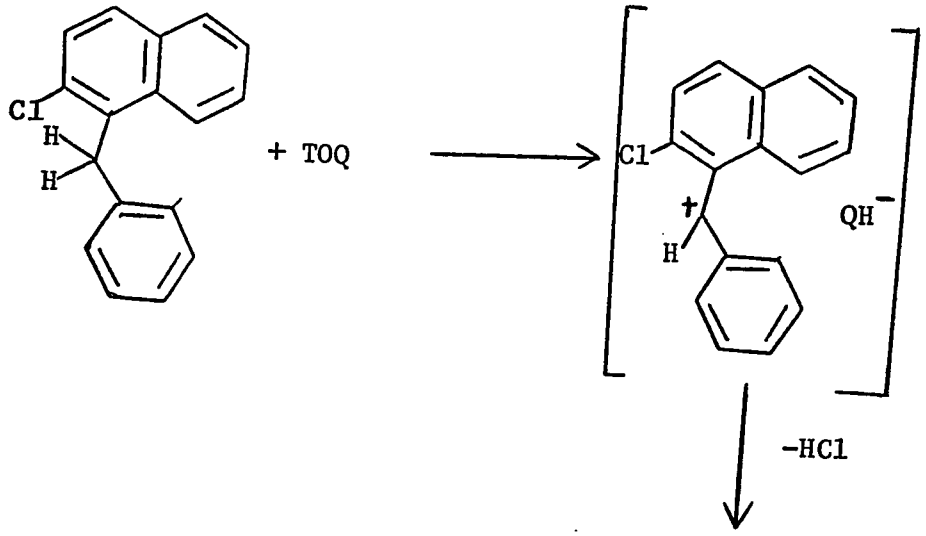
168

Compound 168 shows two distinct tetrachloroquinol ether bands at 1420 and 1445 cm^{-1}, in the infrared spectrum.

Reaction of 1-chloro-7-methyl-7,12-dihydropleiadene 141 with two equivalents of TOQ in o-dichlorobenzene also gave adduct 168. The production of 168 from both 141 and 149 shows that the dehydrogenation of 141 is into the methyl group at 7 position.

The addition of the second quinone molecule across 1 and 12 positions of the pleiadene possibly involves a hydride abstraction at C_{12} followed by ion pair formation and then a nucleophilic aryl substitution at C_1 of the chlorine, enhanced by the cationic center generated at the 12 position, Scheme XIX.

Scheme XIX

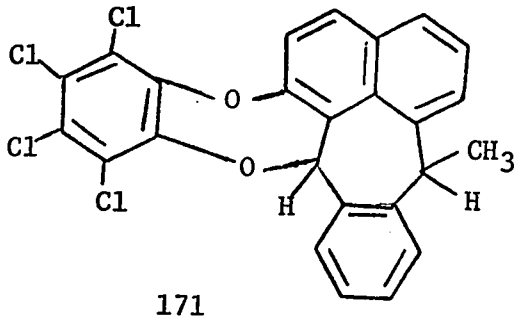


168

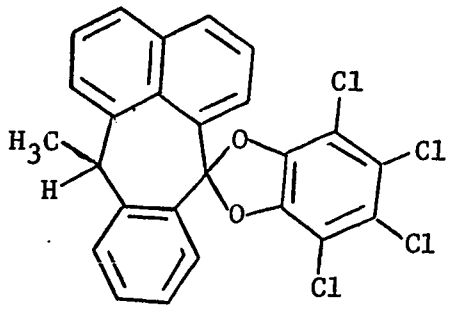
The lability of the chlorine at C_1 of dihydropleiadenes has been observed by Fieser in the conversion of 1-chloro-7,12-dihydropleiadene-7,12-dione 151 to 1-hydroxy-7,12-dihydropleiadene-7,12-dione 150 by treating a solution of 151 in pyridine and alkali with potassium permanganate (112). Attempts to confirm that it is the chlorine at 1 position that is removed as hydrogen chloride by preparing the 1-bromo derivative 169 was unsuccessful. Treatment of 1-hydroxy-7,12-dihydropleiadene-7,12-dione with phosphorus tribromide to obtain 1-bromo-7,12-dihydropleiadene-7,12-dione 170 needed for synthesis of 169 resulted in unretractable tars.

Reaction of 7-methyl-7,12-dihydropleiadene with TOQ

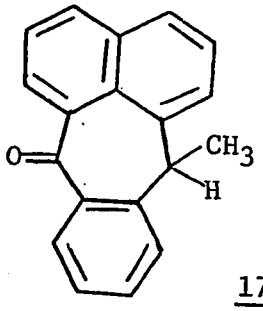
7-Methyl-7,12-dihydropleiadene reacted with two molar equivalents of TOQ to give an adduct, $C_{25}H_{14}Cl_4O_2$, corresponding to 1:1 pleiadene to quinone with loss of a hydrogen molecule. The nuclear magnetic resonance spectrum showed the C_7-methyl and methine protons of pleiadene still intact; (1.94, 3-H doublet J_{AB}=7Hz; 5.95, 1H quartet J_{AB}=7Hz). It also showed absorption bands at 1446 and 1452 cm^{-1} in the infrared, and no hydroxy or carbonyl absorption. These properties would fit both structures 171 and 172



171



172



173

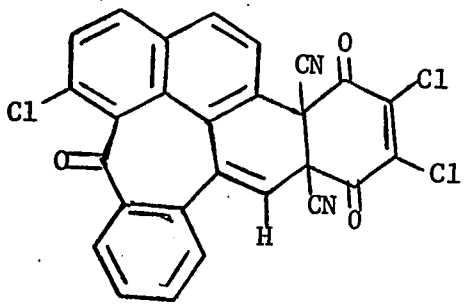
Compound 172, however is a ketal and would be expected to hydrolyse easily in presence of acid to give the ketone 173. When the adduct was treated with concentrated hydrochloric acid in aqueous acetone and the mixture refluxed for 36 hours, the adduct was recovered

unchanged. Structure 171 was therefore tentatively assigned to the adduct. The hydride abstraction of C_{12} rather than C_7 of 142 suggests that steric effect rather than electronic effect is predominating. Since as already noted, the hydrogen at C_7 is in the axial position, it would be expected to be easily removed as a hydride, as the incipient carbonium ion would be stabilised both by the benzene ring and the methyl group. However the product of the reaction shows no hydride was abstracted from the C_7 position. This is attributed to the methyl group hindering the approach of the quinone at this position, resulting in preferential attack at the C_{12} position.

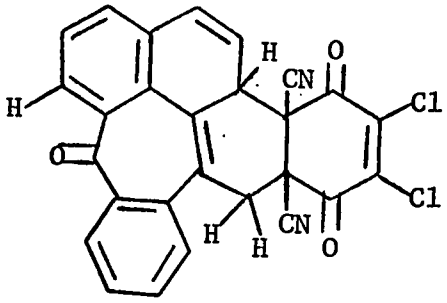
Reaction of 1-Chloro-7-methyl-7,12-dihydropleiadene with DDQ

The reaction of 1-chloro-7-methyl-7,12-dihydropleiadene with TOQ has been found to dehydrogenate into the methyl group at the C_7 position. The structure of the adduct formed was the same as the adduct from 149, the suspected intermediate. It was therefore found necessary to examine first the reaction of DDQ with 147 and 149, in anticipation of DDQ also dehydrogenating 142 into the methyl group.

Reaction of 1-chloro-7-methylene-7,12-dihydropleiadene-12-one with two molar equivalents of DDQ in refluxing chlorobenzene gave a yellow ochre adduct $C_{27}H_9Cl_3N_2O_3$ to which the structure 174 was assigned. Compound 174 showed carbonyl absorptions at 1736 and 1705 cm^{-1} for the quinone portion and at 1680 cm^{-1} for the carbonyl at C_{12}.



174

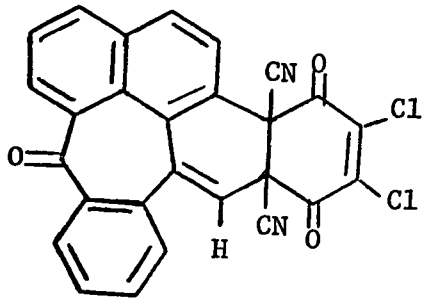


175

The formation of 174 is proposed to proceed by first the quinone addition to the diene system, formed by the methylene group and the adjacent double bond of the naphthalene portion, to give 175, followed by quinone dehydrogenation to give 174. The vinyl proton in 174 appears as two singlets at 6.45, and 6.70 in the nuclear magnetic resonance spectrum. The appearance of two singlets is tentatively attributed to the presence of stereoisomeric adducts, resulting from the two possible modes of addition of DDQ to the diene system, either with the cyano groups on the same face of the pleiadene framework or on the opposite face to the C_{12} carbonyl group.

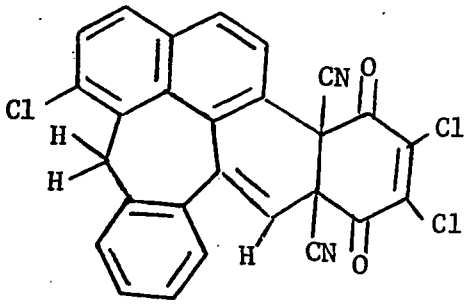
7-Methylene-7,12-dihydropleiadene-12-one 146 also reacted with two mole equivalents of DDQ to give a similar adduct as the 1-chloro compound. This adduct 176 showed in the infrared spectrum in addition to the quinone carbonyl stretching bands another

carbonyl band at 1650 cm^{-1} corresponding to absorption of the carbonyl group in 146.



176

1-Chloro-7-methylene-7,12-dihydropleiadene reacted with 2 molar equivalents of DDQ to give adduct 177 ($C_{27}H_{11}Cl_3N_2O_2$) which showed an AB quartet at 4.15, 4.63 (J_{AB}=15Hz) for the methylene protons at the C_{12} position. The electron-withdrawing effect



177

of the C_1 chlorine possibly is responsible for the addition of the quinone to the diene system first rather than abstracting a hydride from the C_{12} position.

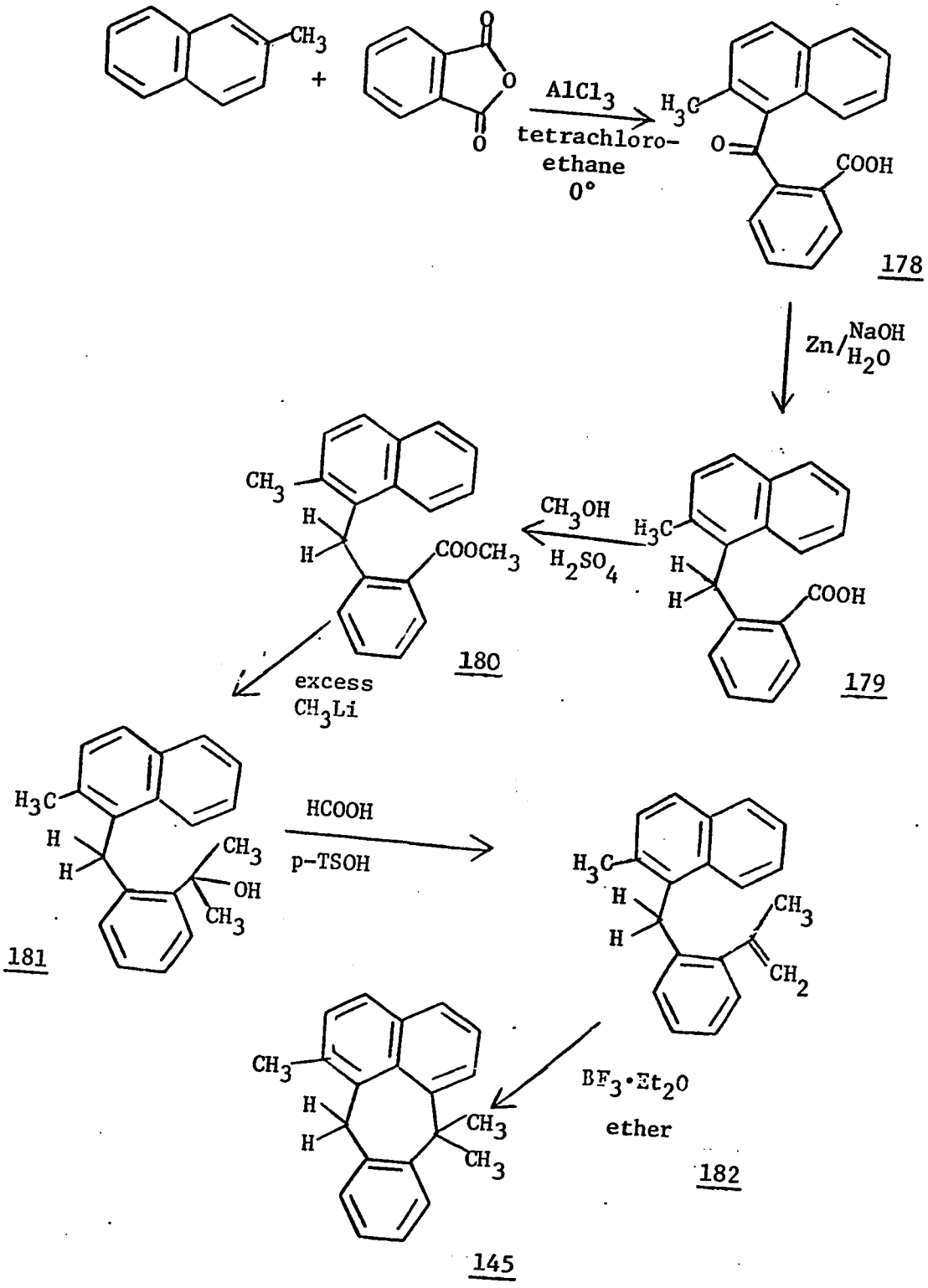
Reaction of 1-chloro-7-methyl-7,12-dihydropleiadene with three molar equivalents of DDQ in refluxing chlorobenzene gave the same adduct as the one obtained from 149. The presence of the chlorine at the C_1 position inhibits the hydride abstraction taking place preferentially at C_7. This leads to dehydrogenation into the methyl group to give 149. Diels-Alder addition of DDQ to the diene system generated followed by dehydrogenation, as already discussed, gives 177. Here again the sensitivity of quinone dehydrogenation to substituent effects is demonstrated.

Preparation of 1,7,7-trimethyl-7,12-dihydropleiadene 145

The synthesis of 145 had previously been sketched out but no experimental details were given (124). The method used in the present work is shown in Scheme XX.

2-(2'-Methylnaphthoyl-1')benzoic acid 178 was prepared by condensation of 2-methylnaphthalene with phthalic anhydride in tetrachloroethane at 0° in presence of aluminum chloride (113). Reduction of 178 with zinc and aqueous sodium hydroxide (113), gave 2-(2'-methyl-naphthylmethyl-1')benzoic acid 179; which was refluxed with excess methanol in presence of catalytic amount of sulfuric acid to give its methyl ester 180. Treatment of this ester with excess methyllithium in ether gave the tertiary alcohol 181; dehydration of which gave 2-[1-(2'-isopropenyltolyl-1')-] methylnaphthalene 182. Intramolecular Friedel-Crafts condensation of 182 in presence of boron trifluoride-etherate in ether (48%)

Scheme XX

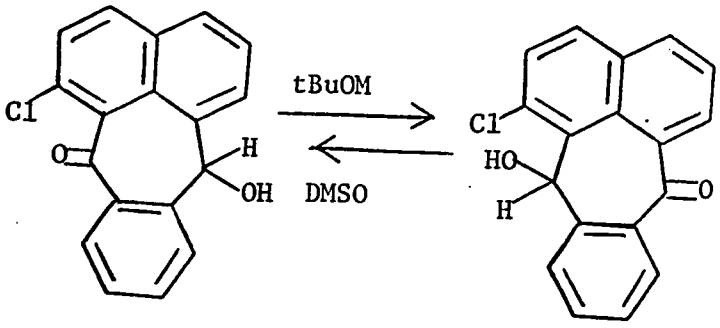

CH3
+
O
O
O
AlCl3
tetrachloro-
ethane
0°
H3C
O
COOH
178
Zn/NaOH
H2O
CH3
H
H
COOCH3
180
CH3OH
H2SO4
H3C
H
H
COOH
179
excess
CH3Li
H3C
H
H
CH3
OH
CH3
181
HCOOH
p-TSOH
H3C
H
H
CH3
CH2
BF3·Et2O
ether
182
CH3
H
H
CH3
CH3
145

gave 1,7,7-trimethyl-7,12-dihydropleiadene 145.

Reaction of 1,7,7-trimethyl-7,12-dihydropleiadene with TOQ and DDQ

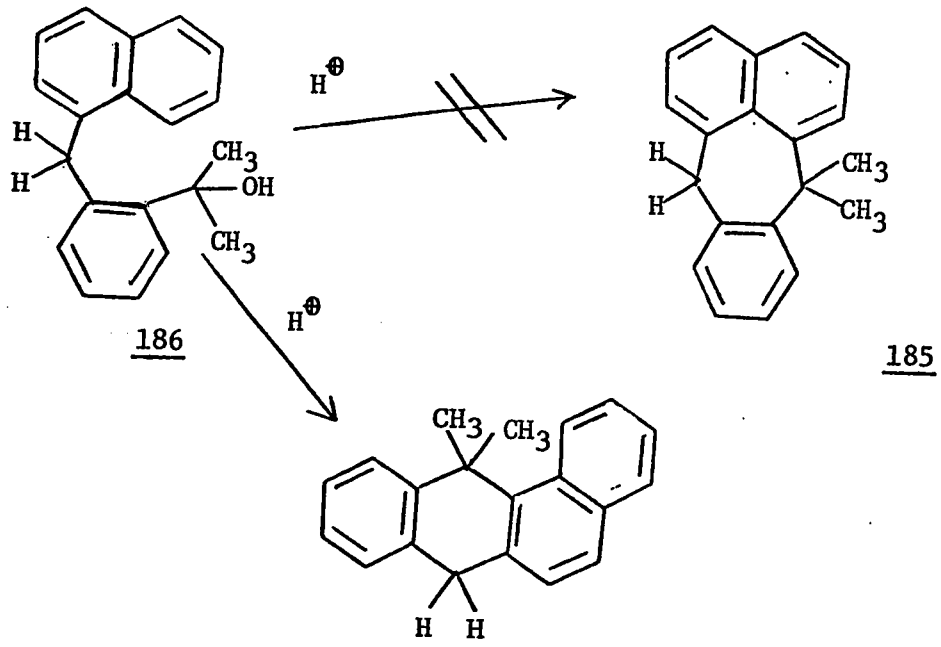
The dehydrogenation of 1,1-disubstituted dihydronaphthalenes with quinones has led to Wagner-Meerwein rearrangement to give the 1,2-disubstituted naphthalenes (40). Also Lansbury and Saeva (128) have found that 1-chloro-7-hydroxy-12(7H)-pleiadenone 183 rearranges by intramolecular 1,4-hydride migration to 1-chloro-12-hydroxy-7(12H)-pleiadenone 184 when treated with alkali metal t-butoxides in dimethylsulfoxide, eqn. [74].

[74]



183 184

It was therefore considered of interest to find out whether quinone dehydrogenation of pleiadene would be accompanied by 1,4-methyl migration. The compound needed for this study was 7,7-dimethyl-7,12-dihydropleiadene 185. However Lansbury (124) found that treatment of the alcohol 186 led to cyclisation at the 2 position of the napthalene to give the dihydrobenzanthracene 187, rather than at the 8-position to give the expected dihydro-

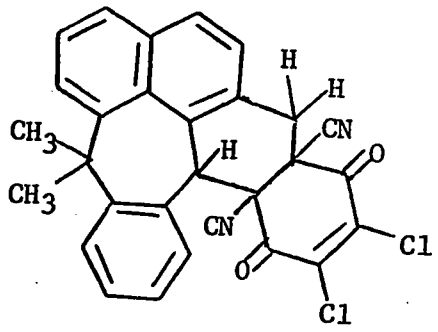


186 185 187

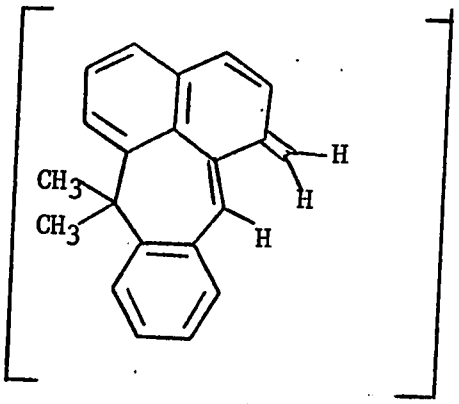
pleiadene. To prevent cyclisation at the 2-position therefore the 2-methyl substituted alcohol 181 was used for the synthesis.

Reaction of 145 with DDQ gave adduct 188, $C_{29}H_{18}N_2Cl_2O_2$. The nuclear magnetic resonance spectrum showed the 7-methyl groups intact at 1.6 and 1.9 ppm, and an AB quartet at 3.85 and 4.20 (J_{AB}=16Hz). The infrared spectrum exhibited carbonyl and cyano absorption bands at 1718 and 2225 cm^{-1} respectively, typical of a Diels-Alder adduct of DDQ to the nitrile substituted double bond (69).

The formation of 188 possibly involves a Diels-Alder addition of DDQ to the intermediate 189 which contains an o-quinodimethane moiety and would be expected to be very reactive towards dienophiles like DDQ.

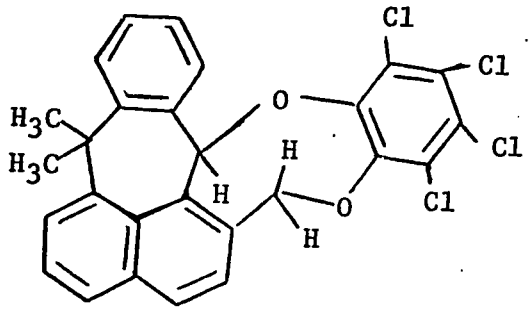


188



189

When compound 145 was refluxed in benzene with two molar equivalents of TOQ, a grey solid ($C_{27}H_{18}Cl_4O_2$) 190 was obtained; the nuclear magnetic resonance spectrum like that of 188 showed the 7-methyl groups intact at 1.8 and 2.05 ppm, and an AB quartet at 5.95 and 6.56 (J_{AB}=16Hz) corresponding in chemical shift to an aryl methylene bonded to oxygen (11). The infrared showed a strong quinol ether absorption at 1405 cm^{-1} typical of such dioxa-eight membered ring systems (65).



190

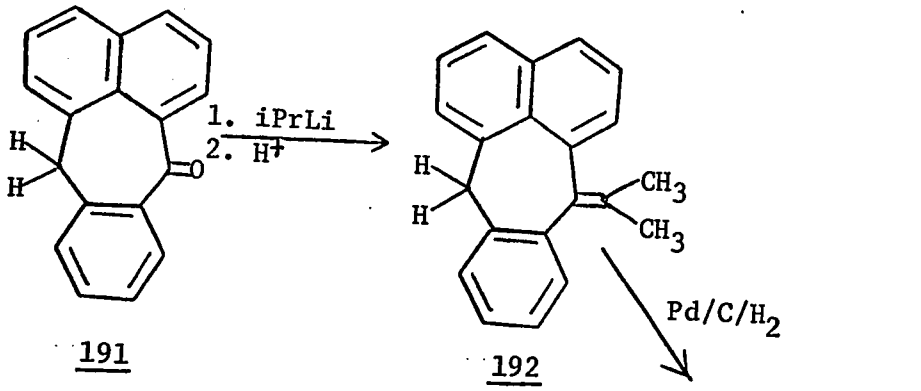
It will be recalled that reaction of 1-chloro-7-methyl-7,12-dihydropleiadene with TOQ led to a product with the C_1-chlorine removed. The formation of 188 and 190 are further examples of enhanced reactivity of groups in the 1-position adjacent to the generated cationic centres in 7,12-dihydropleiadene systems.

Formation of 188 and 190 are also in contrast to products formed from 1,2-dimethylnaphthalene with TOQ and DDQ (Chapter II), for whilst the products formed with 1,2-dimethylnaphthalene show no participation by adjacent methyl group, products 188 and 190 from 1,7,7-trimethyl-7,12-dihydropleiadene clearly shows participation of the 1-methyl group in the dehydrogenation. Such a difference may be due to a higher stabilisation of the cationic centre in 145 than in 1,2-dimethylnaphthalenes, due to the added stabilisation by the benzene ring. Methyl migration did not occur in either of the two reactions. This may be due to the initial ion pair formation preventing the participation of the C_7-methyl group in the dehydrogenation.

Preparation of 7-Isopropyl-7,12-dihydropleiadene

Lansbury and co-workers (124, 129) have reported two methods for the preparation of 143. The first was by isopropyllithium reaction with 7,12-dihydro-7(12H)-pleiadenone 191 to give the isopropylidene compound 192 which on subsequent catalytic hydrogenation gave 143 (Scheme XXI). In the present work however, the isopropyllithium reaction did not give the expected olefin 192, but a compound which had an isopropyl grouping (from its nmr),

Scheme XXI

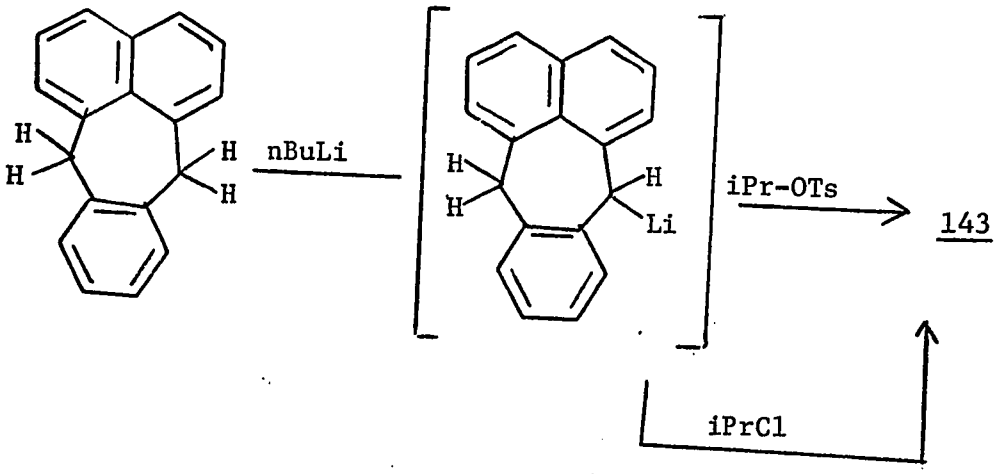


191 192 143

and also still had a carbonyl absorption band at 1650 cm^{-1} in its infrared. This compound was not studied any further.

The second method reported was the alkylation of 7-lithio-7,12-dihydropleiadene 193 prepared from 7,12-dihydropleiadene and n-butyllithium in ether with isopropyl tosylate, Scheme XXII. Repetition of this preparation gave no 7-isopropyl-7,12-dihydropleiadene, the starting material being recovered in over 95-98% yield. However when the isopropyl tosylate was replaced by isopropyl chloride, 143 was obtained in yields of 60-65%.

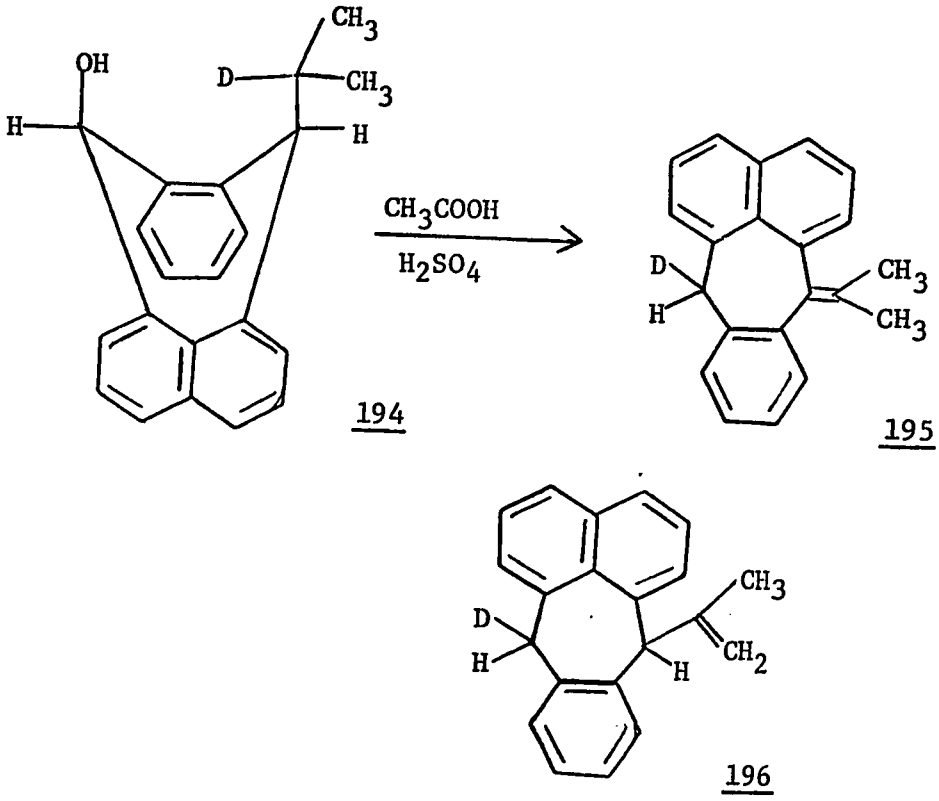
Scheme XXII



Reaction of 7-isopropyl-7,12-dihydropleiadene with TOO

Lansbury and co-workers (129) have established that 7-isopropyl-7,12-dihydropleiadene exists in the conformer in which the isopropyl group is overwhelmingly axial. They have also shown that the dehydration of 7-isopropyl-12-hydroxy-7,12-dihydropleiadene 194 is accompanied by a transannular 1,5-hydride shift to give 195 and 196. In earlier discussions it had been noted that the axial protons in 7,12-dihydropleiadenes are the potential hydride ions in the first step of quinone dehydrogenation. Since the isopropyl group at C_7 in 143 is known to be axial the C_{12} axial proton will be expected to be the potential hydride in quinone dehydrogenation of this compound. Should hydride abstraction be followed by 1,5 hydride shift from the isopropyl group then one

[75]

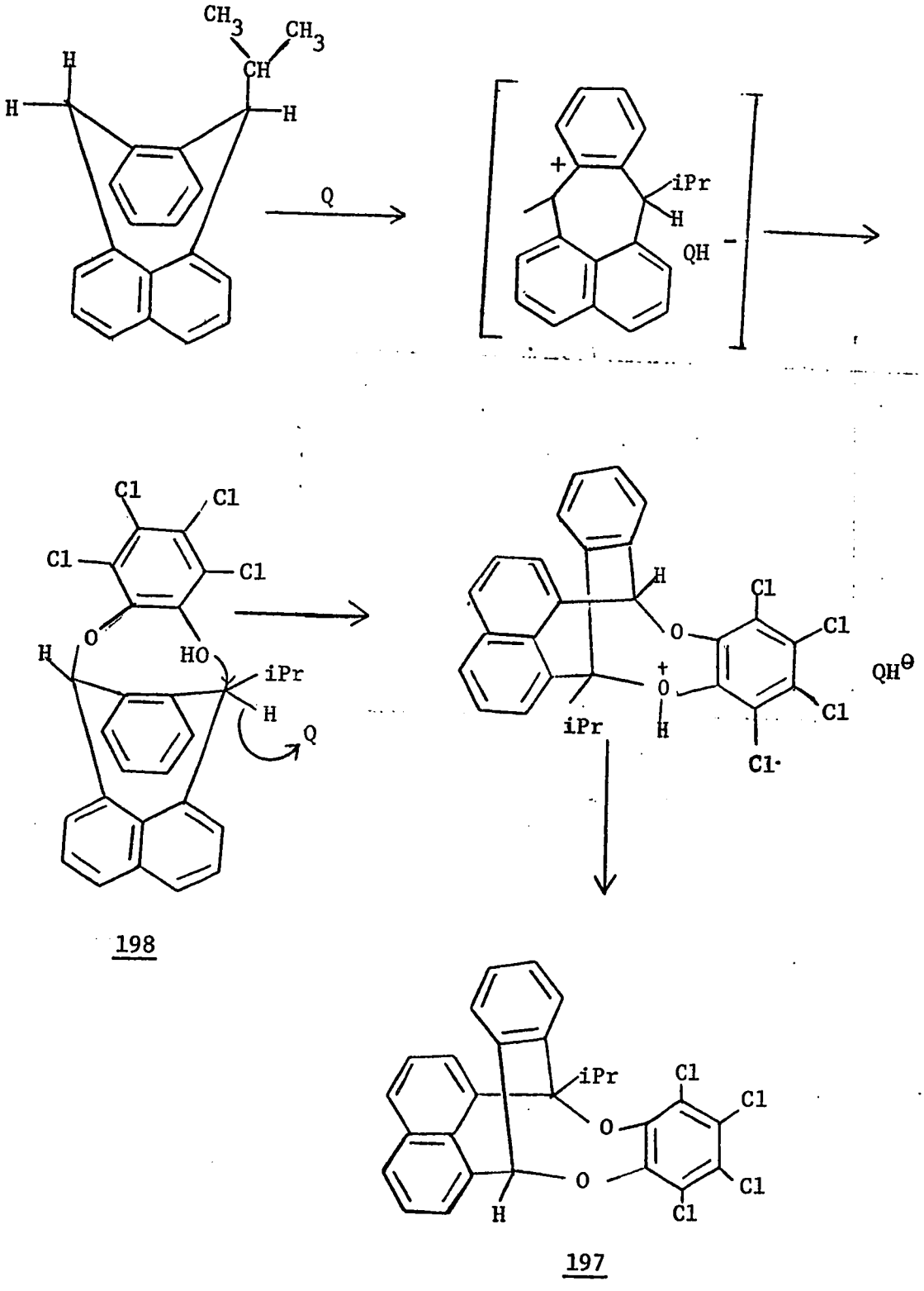


194 195 196

would have expected addition of TOQ to the isopropenyl of isopropylidene group in 195 and 196 to give adducts as have been found for 7-methylene compounds.

Reaction of 7-isopropyl-7,12-dihydropleiadene with two molar equivalents of TOQ gave compound 197, similar in structure to 151. The nuclear magnetic resonance spectrum of 197 shows that the isopropyl group is intact, and signals due to the C_{12} protons in 143 were absent; and its infrared spectrum showed strong ether absorption at 1455 cm^{-1}, and no carbonyl or hydroxyl absorptions. The formation of 197 is proposed to proceed by the mechanism shown below:

Scheme XXIII



198

197

The initially formed ion pair collapses to form 198 which prevents a 1,5-transannular hydride shift. A second dehydrogenation involving participation of the quinol hydroxyl results in the formation of 197.

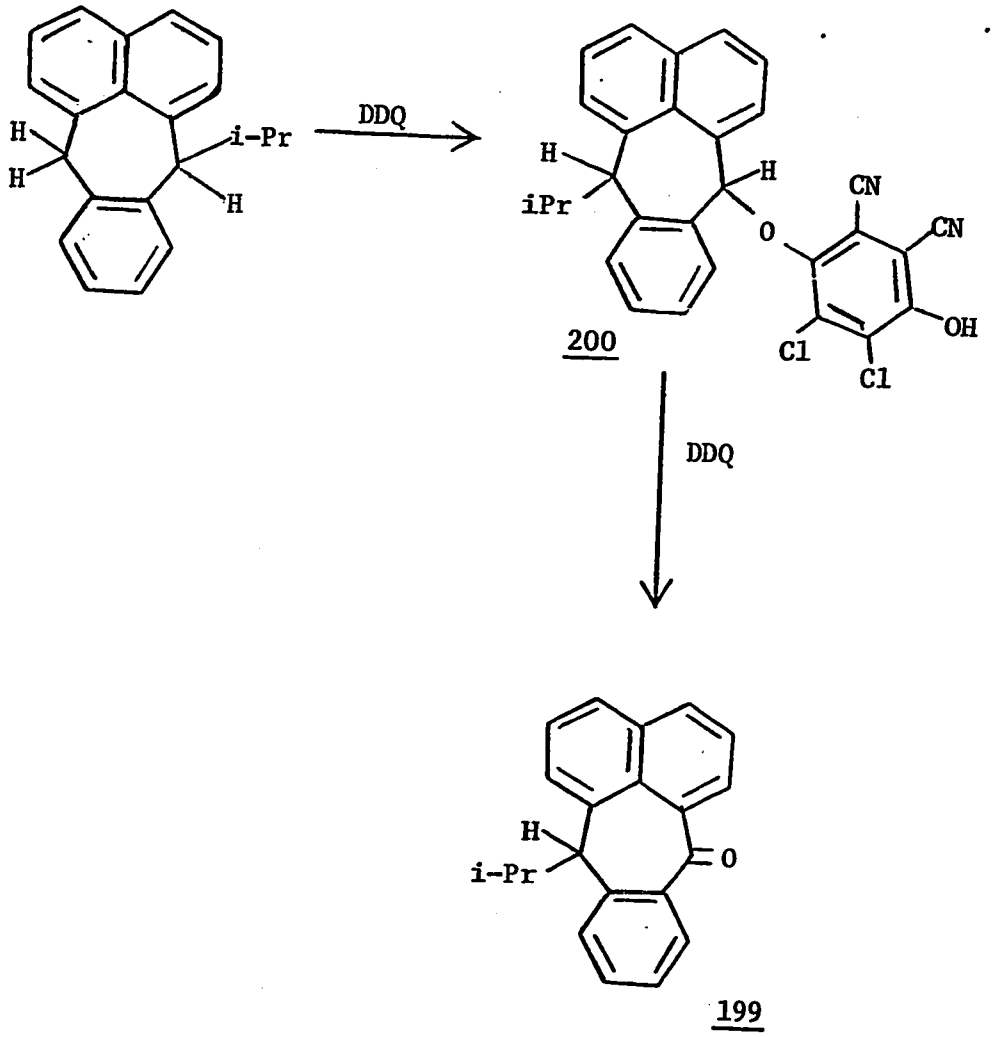
The formation of 197 by 7-isopropyl-7,12-dihydropleiadene (C_7-H equatorial) and the inability of 7-methyl-7,12-dihydropleiadene (C_7-H axial) to form a similar adduct suggests that for the second dehydrogenation step to take place at the C_7 position, the C_7 proton should be in the equatorial position. It is further proposed that in this second step the pleiadene framework exists in the planar conformation, since diaxially substituted dihydropleiadenes with a boat conformation have been found to be too compressed to exist (121). Models also show that in the planar conformation the molecule is well set up for participation of the hydroxyl group of the quinol ether moiety in the hydride removal at C_7 position.

Reaction of 7-Isopropyl-7,12-dihydropleiadene with DDQ

Reaction of 7-isopropyl-7,12-dihydropleiadene 143 with 2-molar equivalents of DDQ led unexpectedly to oxidation of the C_{12} methylene to give 7-isopropyl-12(7H)pleiadene-one 199. The assignment of the structure was confirmed by independent synthesis of 199 by chromium trioxide oxidation of 143 (129). In the literature there is a mention of direct oxidation of a hydrocarbon to give carbonyl containing compounds using DDQ (16), (see eqn. [18]). The mechanism of this oxidation is not clear. It may be proceeding

by formation first of the quinol ether 200, which unlike the quinol ether 198 formed from TOQ is unable to participate in any trans-annular dehydrogenation. It therefore reacts with another molecule of quinone to give the ketone, (see Scheme XXIV).

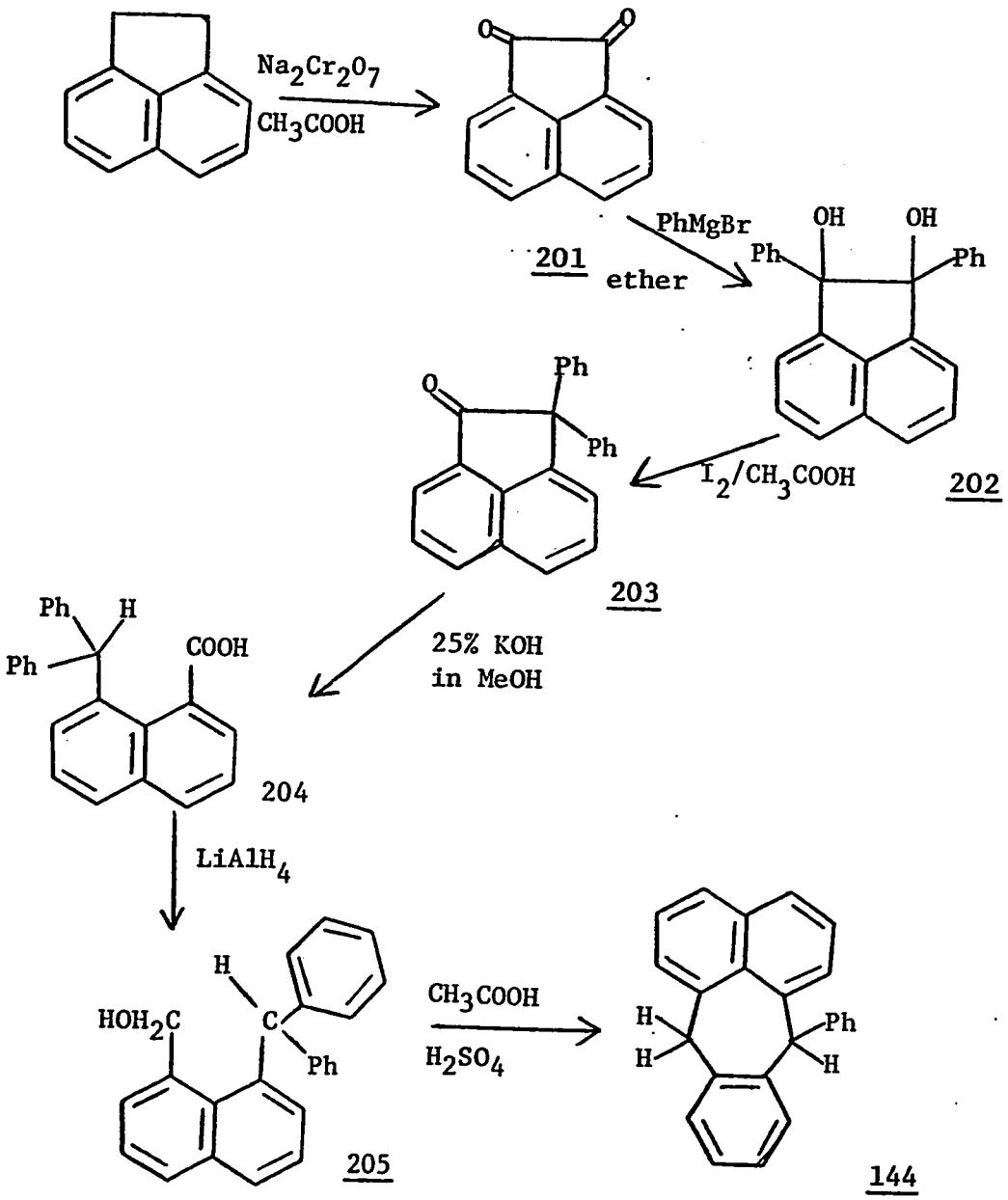
Scheme XXIV



Preparation of 7-phenyl-7,12-dihydropleiadene

The preparation of 7-phenyl-7,12-dihydropleiadene was accomplished by the scheme below:

Scheme XXV



Acenaphthaquinone 201 was prepared by chromic acid oxidation of acenaphthene (133). It was treated with phenyl magnesium bromide to give the diol 202, which underwent pinacol-pinacolone rearrangement to give 7,7-diphenylacenaphthenone 203. This compound on refluxing with 25% methanolic solution of potassium hydroxide gave the ring scission product 204 (134). Reduction of this acid with lithium aluminum hydride in ether gave 8-benzhydryl-1-hydroxymethylnaphthalene 205. Dehydrative cyclisation of 205 with catalytic amount of sulfuric acid in glacial acetic acid gave 7-phenyl-7,12-dihydropleiadene 144 (122).

Reaction of 7-phenyl-7,12-dihydropleiadene with DDQ and TOQ

Lown (43) has found that the reaction rates of 9-aryl-9,10-dihydroanthracenes with TOQ are similar, and very close to the reaction rate of 9,10-dihydroanthracene, when allowance is made for a statistical factor of 2 for the latter; see Table V. The 9,10-hydroanthracenes adopt a quasi-boat conformation of the central ring with the 9-substitutent preferentially in the quasi-axial position. It was assumed from inspection of models that the quasi-axial hydrogens were the potential hydrides, since they were disposed with respect to the aromatic rings of the anthracene structure to provide maximum stabilisation of the incipient carbonium ion. From the reaction rates mentioned above it had been inferred that the hydride abstraction did not take place at the 9 position, for in view of the known sensitivity of quinone dehydrogenation to substituent

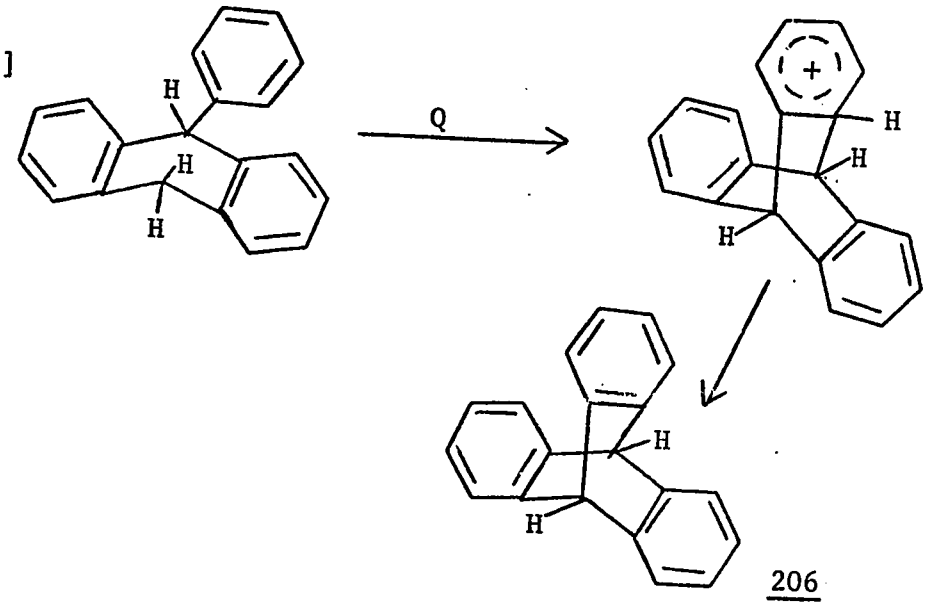
TABLE V

Kinetic Data for Reaction of 9-Aryl-9,10-Dihydroanthracenes with Tetrachloro-1,2-benzoquinone in 1,2-Dichlorobenzene

Donor	Second Order Rate Constant (80°)	Arrhenius Parameters E kcal-mole^{-1}	Log_{10} B
1. 9,10Dihydroanthracene	$3.10 \pm 0.20 \times 10^{-1}$	12.06 ± 0.17	6.95
2. 9,10Dihydro-9-phenylanthracene	$1.37 \pm 0.04 \times 10^{-1}$	14.55 ± 0.58	8.15
3. 9,10Dihydro-9-p-tolylanthracene	$1.56 \pm 0.05 \times 10^{-1}$	13.48 ± 0.47	7.45
4. 9,10-Dihydro-9-p-anisylanthracene	$1.75 \pm 0.12 \times 10^{-1}$	13.43 ± 0.23	7.65

electronic effects (Hammett's ρ=-2.5) (41) one would have anticipated a greater spread in relative rates, in the 9-aryl compounds studied. The products that were obtained from these reactions were the corresponding 9-arylanthracenes, which shows that no transannular participation by the aryl groups at the 9-position in the hydride ion abstraction at the 10-position took place. If this had been the case one would have expected trypticenes 206 to result.

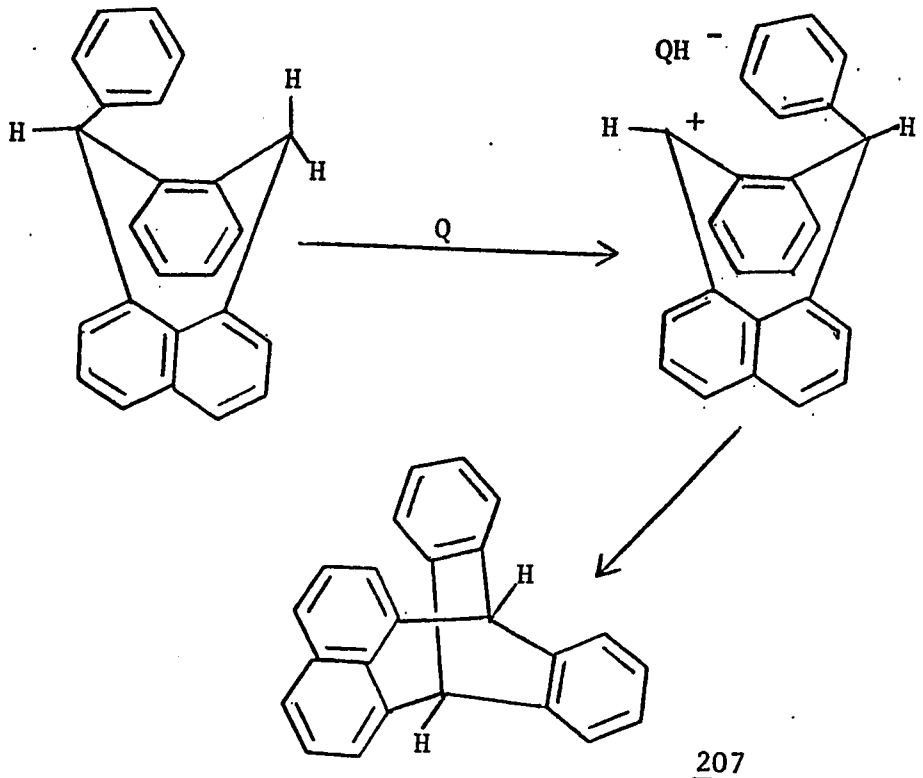
[76]



206

Lansbury has determined that 7-phenyl-7,12-dihydropleiadene exists in a conformer in which the C_7-phenyl group is in the axial position. As it has been noted many times in preceding discussions the 12-axial proton would therefore be the potential hydride in quinone reactions. Removal of this C_{12} axial proton could lead to a transannular phenyl group participation yielding eventually 207, Scheme XXVI.

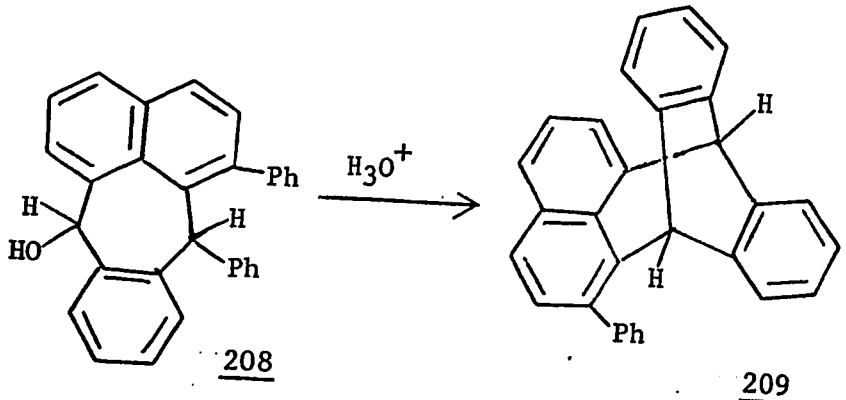
Scheme XXVI



207

The geometry of 7,12-dihydropleiadene system makes this dehydrogenative cyclisation a rather attractive proposition for study. Spatial proximity of the "hinged" carbons is greater here than in dihydroanthracenes, thus transannular phenomena are more likely in 7,12-dihydropleiadenes than in dihydroanthracenes. Lansbury and co-workers (131) have isolated a compound 209 in the attempted dehydration of 1,12-diphenyl-7-hydroxy-7,12-dihydropleiadene 208, eqn. [76], an added incentive.

[76]



208 209

Reaction of 144 with 3 molar equivalents of TOQ gave the expected product 207, $C_{24}H_{16}$, which showed in its nuclear magnetic resonance spectrum in addition to the aromatic signals, a singlet at 5.45 for the C_7,C_{12}, protons. The same product was obtained on reacting 144 with 2 molar equivalents of DDQ in refluxing benzene.

EXPERIMENTAL

1-Hydroxyl-7,12-dihydropleiadene-7,12-dione

This compound was prepared in 70% by the method of Fieser. m.p. 198-199° (lit. (112) 198°).

1-Chloro-7-12,-dihydropleiadene-7,12-dione

This compound was prepared by the method of Fieser from 1-hydroxy-7,12-dihydropleiadene in 67%. m.p. 164-166° (lit. (112) 165°).

1-Chloro-7,12-dihydropleiadene

1-Chloro-7,12-dihydropleiadene was prepared by modification of the method of Cava and Schlessinger (119). Anhydrous ether (1 liter) in a 3 liter 3-necked flask fitted with a condenser and stirrer was cooled to 0°. Lithium aluminum hydride (9.52 g; 0.25 mole was added to it gradually, followed by 33.2 gm (0.25 mole) of aluminum chloride, all the time keeping the temperature around 0°. 1-Chloro-7,12-dihydropleiadene-7,12-dione (25 g, 0.086 moles), well powdered, was then added with stirring to the mixture during 40 minutes. The mixture was stirred at room temperature for 12 hours, then gently refluxed for 2 hours. The pot was then cooled again to 0° and the ether solution carefully decanted onto ice and the ether separated. The complex left in the flask was decomposed with ice and dilute sulfuric acid and extracted with

ether. The ether solutions were mixed, washed with water, dried (Na_2SO_4) and evaporated *in vacuo* to give a brown solid. This was dissolved in hexane and passed down a column of alumina to give 139 as white needles. Yield: 15.6 g (69%). m.p. 116-119° (lit. (119) 117-119°).

7,12-Dihydropleiadene

7,12-Dihydropleiadene was prepared from 1-chloro-7,12-dihydropleiadene by a modification of the method of Cava and Schlessinger (119). A mixture of 25 g (0.095 mole) of 1-chloro-7,12-dihydropleiadene, 5 g of 10% palladium on charcoal, 100 ml of 85% hydrazine hydrate and 1000 ml of 95% ethanol was refluxed for 1 hour. The filtered solution was concentrated to ca 100 ml, acidified with 2 N hydrochloric acid and the solid product collected, washed repeatedly with water and dried. Recrystallisation from hexane gave 20 g (91.8% yield) of 7,12-dihydropleiadene m.p. 115-117°. (lit. (119), 116°).

Reaction of 7,12-Dihydropleiadene with Tetrachloro-1,2-benzoquinone

A solution of 4 g (0.017 mole) of 7,12-dihydropleiadene in 50 ml of dry chlorobenzene was added to a solution of 10 g (0.041 mole) of tetrachloro-1,2-benzoquinone in 250 ml of chlorobenzene and the mixture heated under reflux for 72 hours. The solvent was removed *in vacuo*, the residue taken up in benzene and subjected to chromatography on B.D.H. alumina using (1:1)

benzene:hexane as eluant. The main fraction consisted of a buff-white solid recrystallised from benzene to give 4.3 g (52.4% yield) of 151. m.p. 266-268°.

Anal. calcd. for $C_{24}H_{12}Cl_4O_2$: C, 60.78; H, 2.56; Cl, 29.90

Found: C, 61.26; H, 2.51; Cl, 29.65

Mol. wt. Calcd.: 471.9593. Found (mass spectrum): 471.9594

Infrared spectrum: $\nu_{max}(CDCl_3)$ 1454 cm^{-1} (C-O-C)

N.m.r. $\delta_{Tms}(CDCl_3)$: 7.1-8.2 (multiplet; aryl, C_7 and C_{12} protons).

Reaction of 1-Chloro-7,12-dihydropleiadene with Tetrachloro-1,2-benzoquinone

A solution of 3.01 g (11.4 mmoles) of 1-chloro-7,12-dihydropleiadene in 100 ml of dry o-dichlorobenzene was added to a solution of 8.36 g (0.0336 mole) of tetrachloro-1,2-benzoquinone in 300 ml of o-dichlorobenzene and the mixture refluxed for 48 hours. The solvent was removed in vacuo (0.05 mm/Hg) and the residual solid taken up in benzene and subjected to chromatography on acid washed alumina. Elution with benzene gave 1 g of 154 (13% yield). m.p. 295-300°.

Anal. Calcd. for $C_{30}H_{11}Cl_7O_4$: C, 52.94; H, 1.62; Cl, 36.03

Found: C, 53.05; H, 2.05; Cl, 36.48

Mol. wt. Calcd. for $C_{30}H_{10}{}^{35}Cl_6{}^{37}ClO_4$ (M^+-1): 680.8369

Found: 680.8372

Infrared spectrum $\nu_{max}(CHCL_3)$, (Nujol) 1672 cm^{-1} (C=O), 1454, 1422 cm^{-1} (C-O-C)

N.m.r. Spectrum: $\delta_{TMS}(CDCL_3)$: 5.26 and 6.31 (1H each, singlets

C_7 and C_{12} protons, these signals disappear in the analogous adduct obtained from 1-chloro-7,7,12,12-tetradeuteropleiadene); 6.26 (1H doublet, J=10.6 Hz ortho coupling, C_6 aromatic proton. Irradiation of 7.45 causes collapse of this signal to a singlet); 7.0-8.0 (8H, multiplet, aromatic protons).

Further elution with chloroform gave 1.2 g of 153 (20% yield) m.p. >300°.

Anal. Calcd. for $C_{30}H_{11}Cl_7O_4$: C, 52.94; H, 1.62; Cl, 36.02
Found: C, 52.82; H, 2.04; Cl, 35.62

Infrared Spectrum $\nu_{max}(CHCl_3)$: 1420 (C-O-C), 1445-1453 cm^{-1} (-C=C-O-C).

N.m.r. Spectrum $\delta_{Tms}(CDCl_3)$: 6.7-8.2 (multiplet, aromatic C_7, C_{12} bridge protons).

1-Chloro-7,7,12,12-tetradeutero-7,12-dihydropleiadene

Aluminum chloride (2.7 g, 0.02 mole) and 0.84 g (0.02 mole) of lithium aluminum hydride were added to ether at 0°. To this mixture was added with stirring 2.45 g (8.7 mmoles) of 1-chloro-7,12-dihydropleiadene-7,12-dione and the mixture stirrred for 45 minutes, decomposed with ice, the ether layer washed with water and dried (Na_2SO_4), and the ether removed *in vacuo* to give a slightly yellow solid. The latter was chromatographed on B.D.H. alumina to give 2 g (85.6%) of 7,7,12,12-tetradeutero-7,12-dihydropleiadene. m.p. 119-121°.

Mol. wt. Calcd. for $C_{18}H_9D_4Cl$: 268.0876. Found (mass spectrum) 268.0879.

Reaction of 1-Chloro-7,7,12,12-tetradeuteropleiadene with tetrachloro-1,2-benzoquinone

A solution of 0.5 g (1.86 mmole) of 7,7,12,12-tetradeuteropleiadene in 25 ml of o-dichlorobenzene was added to a solution of 1.05 g (4.26 mmole) of tetrachloro-1,2-benzoquinone in 50 ml of o-dichlorobenzene and the mixture refluxed for 48 hours. The solvent was removed in vacuo and the residue subjected to chromatography using benzene as eluant to give 0.3 g (29.4% yield) of 155. m.p. 295-296°.

Mol. wt. Calcd. for $C_{30}H_9D_2O_4{}^{35}Cl_6{}^{37}Cl$: 683.8581. Found: (mass spectrum) 683.8576.

Infrared spectrum ν_{max}(Nujol): 1660 cm^{-1} (C=O), 1445 cm^{-1} (-C-O-C=C-O).

N.m.r. spectrum $\delta_{Tms}(CDCl_3)$: 6.28 (1H, d. J=10.4 Hz C_6 proton); 7.2-8.1 (8H multiplet, rest of aromatic protons).

Hexachloro-o-quino pyrocatechin Ether

This compound was prepared in 69% yield according to the method of Jackson and McLaurin. m.p. 299-301° (lit (132) 300°).

Reaction of 1-chloro-7,12-dihydropleiadene with hexachloro-o-quinopyrocathechin ether

A solution of 0.61 g (25 mmole) of 1-chloro-7,12-dihydropleiadene in 50 ml of dry o-dichlorobenzene was added to a solution of 2.09 g (50 mmole) of hexachloro-o-quinopyrocatechin ether 156 in 300 ml of warm o-dichlorobenzene and the mixture refluxed for 72 hours. The solvent was removed in vacuo and the residue dissolved

in benzene and subjected to chromatography on B.D.H. alumina using benzene as eluant to give a bright yellow solid 0.5 g (29.4%). m.p. >300°.

Mol. wt Calcd. for $C_{30}H_{11}Cl_7O_4$: 679.8480.

Found (mass spectrum): 679.8470.

Infrared spectrum $\nu_{max}(CHCl_3)$: 1672 cm^{-1} (C=O) 1452 cm^{-1} (C=C-O-C=C).

This compound proved to be identical with adduct 154 obtained above.

Further elution with chloroform gave a violet compound 0.43 g (25.3% yield).

Infrared spectrum ν_{max} ($CHCl_3$) 1453, 1422 cm^{-1} (-C-O-C).

This compound proved to be identical to adduct 153 obtained above.

Reaction of 7,12-dihydropleiadene with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 5 g (0.022 moles) of 7,12-dihydropleiadene in dry chlorobenzene was added to a solution of 10 g (0.044 mole) of benzene and the mixture refluxed for 30 minutes during which time a brown solid separated. Refluxing was continued for a further 1 1/2 hours, the mixture cooled and the solid collected and washed with benzene. The filtrate was concentrated in vacuo, benzene added whereupon a yellow solid separated which was collected and washed with benzene yielding 157, 4.7 g (47.1% yield). m.p. 300°.

Anal Calcd. for $C_{26}H_{12}N_2Cl_2O_2$: C, 68.73; H, 2.64; Cl, 15.42, N, 6.16

Found: C, 68.24; H, 2.76; Cl, 15.31; N, 6.08.

Mol. wt. Calcd.: 454.0276. Found (mass spectrum): 454.0275.

Infrared spectrum ν_{max} (Nujol mull) 1705 cm^{-1} (C=O) 2250 cm^{-1} (C=N).

N.m.r. spectrum δ_{Tms} ($(CD_3)_2SO$): 5.05 (2H, singlet C_7 and C_{12} protons), 7.1-8.2 (10H, multiplet, aromatic protons).

Reaction of 1-Chloro-7,12-dihydropleiadene with 2,3-Dichloro-5,6-dichloro-1,4-benzoquinone

A solution of 4 g (15 mmole) of 1-chloro-7,12-dihydropleiadene in 75 ml of dry chlorobenzene was added to a solution of 10 g (0.044 mole) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 350 ml of chlorobenzene and the mixture heated under reflux for 2 hours. The insoluble quinol which separated from the reaction mixture was collected and the filtrate concentrated in vacuo. The residual solid was taken up in chloroform and subjected to chromatography on silica gel with benzene/chloroform (2:1) as eluent giving 158 as bright yellow crystals, 3.8 g (51.2% yield).

m.p. 270-272°.

Anal. Calcd. for $C_{26}H_1Cl_3N_2O_2$: C, 63.95; H, 2.25; Cl, 21.52; N, 5.73

Found: C, 63.35; H, 2.39; Cl, 21.39; n, 5.64.

Mol. wt. Calcd.: 487.9886. Found (mass spectrum): 487.9888.

Infrared spectrum ν_{max} (Nujol mull) 1700, 1715 (sh) cm^{-1} (C=O); 2246 cm^{-1} (C≡N).

N.m.r. spectrum δ_{Tms} ($(CD_3)_2SO$): 5.15 (1H, singlet, C_7 proton); 5.64 (1H, singlet C_{12} proton); 7.2-8.2 (9H, multiplet, aromatic protons).

1-Chloro-7(12H)-pleiadenone

1-Chloro-7(12H)-pleiadenone was prepared from 1-chloro-7,12-dihydropleiadene in 72% yield by the method of Lansbury and Saeva (128). m.p. 162-164°. [lit. (128) 163-164°].

1-Chloro-7-methylene-7,12-dihydropleiadene

A stirred suspension of 10 g (0.036 m) of 1-chloro-7 (12H) pleiadenone in 200 ml of anhydrous ether was treated dropwise with a solution of methyllithium in ether added through a serum cap until a pink coloration persisted. The mixture was stirred for 2 hours, then poured unto ice and acidified with dilute hydrochloric acid. The ether layer was separated, washed with water and dried (Na_2SO_4). The ether was removed *in vacuo*, the residual solid dissolved in hexane and purified by chromatography on B.D.H. alumina to give 6 g (60.4%) of 1-chloro-7-methylene-7,12-dihydropleiadene 149.

1-Chloro-7-methyl-7,12-dihydropleiadene

1-Chloro-7-methylene-7,12-dihydropleiadene 5.52 g was dissolved in 250 ml of 95% ethanol and hydrogenated over 1.5 g of 5% palladium on charcoal at atmospheric pressure giving 5.5 g (99%) of 1-chloro-7-methyl-7,12-dihydropleiadene. m.p. 95°.

Anal. Calcd. for $C_{19}H_{15}Cl$: C, 82.60; H, 4.71; Cl, 12.69

Found: C, 82.02; H, 4.77, Cl, 12.67.

Mol. wt. 292.0655 found (mass spectrum): 292.0653.

N.m.r. spectrum δ_{Tms} ($CDCl_3$): 1.80 (3H, doublet $C_7-C\underline{H}_3$); 4.6-4.97

(3H, multiplet C_7 and C_{12} protons); 7.05-7.70 (9H, multiplet, aromatic protons).

7,12-Dihydropleiadene-7,12-dione

7,12-Dihydropleiadene-7,12-dione was prepared in 93% from 7,12-dihydropleiadene by the method of Cava and Schlessinger (119). m.p. 166-168° (lit. 168° (119)).

7,12-Epoxy-12-methyl-7,12-dihydropleiadene

7,12 Dihydropleiadene-7,12-dione (20 g, 77 mmoles) was added during 30 minutes to a stirred solution of methyl magnesium iodide (prepared from 6 g of magnesium and 30 g of methyl iodide in 200 ml of anhydrous ether). After addition was completed, stirring was continued for 12 hours. The complex was decomposed with cold saturated ammonium chloride solution, the ether layer washed with water dried (Na_2SO_4) and concentrated to give 19.6 g (92.3%) of 162. m.p. 186-188°, (lit. (135) 184-186°).

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.21, H, 5.11

Found: C, 82.96, H. 508

Mol. wt. Calcd. 274.0994. Found (mass spectrum): 274.0996.

7-Methylene-7,12-dihydropleiaden-12-one

A catalytic amount of p-toluenesulfonic acid was added to a solution of 13.7 g (0.05 moles) of 7,12-epoxy-7-methyl-7,12-dihydropleiadene-7-ol in 400 ml benzene and the mixture refluxed for 8 hours. After cooling, the solution was washed successively

with water, 10% sodium bicarbonate, and water; dried and concentrated to give 10 g (85%) of 146. m.p. 155-157°, (lit. (135) 154-156°).

Anal. Calcd. for $C_{19}H_{12}O$: C, 89.06, H, 4.69

Found: C, 89.09; H, 4.77.

Mol. wt. Calcd. 256.0888. Found (mass spectrum): 256.0888.

7-Methylene-7,12-dihydropleiadene

7-Methylene-7,12-dihydropleiaden-12-one (2.6 g, 0.01 mole) was added during 5 minutes to a mixture of 1.2 g (0.03 mole) of lithium aluminum hydride and 4.4 g (0.03 mole) of aluminum chlride in 125 ml of anhydrous ether at 0-5°. The mixture was stirred at room temperature for 1 hour and decomposed by pouring into ice and dilute sulfuric acid. The ether layer was washed with water, dried ($MgSO_4$), and evaporated in vacuo to give 1.4 g (58.3%) of a yellow oil, which solidified on standing. m.p. 56-58°, (lit. (124) 58-59°).

7-Methyl-7,12-dihydropleiadene

7-Methylene-7,12-dihydropleiadene (4.24 g, 0.0175 m) was dissolved in ethylacetate and hydrogenated over 1.0 g of palladium on charcoal at atmospheric pressure to give 3.95 g (92.5%) of 142. m.p. 106-108° (lit. (125) 104-106°).

1-Chloro-7,12-epoxy-7-methyl-7,12-dihydropleiaden-12-ol

1-Chloro-7,12-dihydropleiadene-7,12-dione (10 g, 34 mmole) was added during 30 minutes to a stirred solution of methyl magnesium iodide (prepared from 15 g of methyl iodide and 3 g of

magnesium in 200 ml of anhydrous ether). After addition was completed, stirring was continued for 8 hours and worked up in the usual way with saturated aqueous ammonium chloride to give 6.2 g (59% yield) of 1-chloro-7,12-epoxy-7-methyl-7,12-dihydropleiaden-7-ol as a white solid. m.p. 205-207°.

Anal. Calcd. for $C_{19}H_{13}ClO_2$: C, 74.03; H, 4.22; Cl, 11.36
Found: C, 74.00; H, 4.28; Cl, 11.47.

Infrared spectrum $\nu_{max}(CHCl_3)$: 3560, 3360 cm^{-1} (O-H) 1450 cm^{-1} (C-O-C).

N.m.r. $\delta_{Tms}(CDCl_3)$: 2.2 (3H, singlet $C\underline{H}_3$); 4.95 (1H, singlet $O\underline{H}$); 7.0-8.0 (9H, multiplet, aromatic protons).

1-Chloro-7-methylene-7,12-dihydropleiaden-12-one

1-Chloro-7,12-epoxy-12-methyl-7,12-dihydropleiaden-12-ol (6.2 g, 20 mmole) was dissolved in 100 ml of benzene, a catalytic quantity of p-toluenesulfonic acid added, and the mixutre refluxed for 8 hours; allowed to cool and washed successively with 10% aqueous sodium bicarbonate and water. The benzene layer was dried ($MgSO_4$) and solvent removed in vacuo to give 1-chloro-7-methylene=7,12-dihyrdropleiaden-12-one (5.3 g, 91.4% yield). m.p. 169-171°.

Anal. Calcd. for $C_{19}H_{11}ClO$: C, 78.61; H, 3.79; Cl, 12.07
Found: C, 78.64; H, 3.79; Cl, 12.01

Infrared spectrum ν_{max} $(CDCl_3)$: 1685 cm^{-1} (C=O).

N.m.r. spectrum δ_{Tms} $(CDCl_3)$: 5.65, 5.45 (2H, pair of doublets, J= 1.5 Hz, methylene protons); 7.25-7.85 (9H, multiplet, aromatic protons).

Reaction of 1-Chloro-7-methylene-7,12-dihydropleiaden-12-one with Tetrachloro-1,2-benzoquinone

A solution of 1.45 g (5 mmole) of 1-chloro-7-methylene-7, 12-dihydropleiaden-12-one in 75 ml of dry dichlorobenzene was added to a solution of 2.44 g (0.01 mole) of tetrachloro-1,2-benzoquinone in 125 ml of dichlorobenzene and the mixture refluxed for 24 hours. The solvent was removed *in vacuo* and the residue titurated with benzene and recrystallized from benzene to give 1.3 g of 166. The mother liquor was subjected to chromatography on B.D.H. alumina to give an additional 0.5 g of 166 making a total yield of 67.4%. m.p. 292-293°.

Anal. Calcd. for $C_{25}H_{11}Cl_5O_3$: C, 56.16; H, 2.07; Cl, 32.77

Found: C, 56.24; H, 2.07; Cl, 32.69.

Mol. wt. Calcd. 533.9153, Found (mass spectrum) 533.9150.

Infrared spectrum $\nu_{max}(CHCl_3)$, 1685 cm^{-1} (C=0) 1423 cm^{-1} (-C-O-C-).

N.m.r. spectrum $\delta_{Tms}(CDCl_3)$ 4.50, 4.86; 5.26, 5.58 (2H, two sets of quartets, C_7 methylene protons J=15; 12.5) 7.3-8.1 (9H, aromatic protons).

Reaction of 7-Methylene-7,12-dihydropleiaden-12-one with Tetrachloro-1,2-benzoquinone

A solution of 1.28 g (0.005 mole) of 7-methylene-7,12-dihydropleiaden-12-one in 50 ml of chlorobenzene was added to a solution of 2.44 g (0.01 mole) of tetrachloro-1,2-benzoquinone in chlorobenzene, and the mixture refluxed for 72 hours. The chlorobenzene was removed under reduced pressure, and the

residue treated with benzene and resulting white solid collected, recrystallisation from benzene gave 1.7 g (68%) of 167. m.p. 290-291°.

Anal. Calcd. for $C_{25}H_{12}Cl_4O_3$: C, 60.00; H, 2.40;, Cl, 2800
Found: C, 60.08; H, 2.43; Cl, 27.98

Mol. wt. Calcd. 499.9543. Found (mass spectrum): 499.9540.

Infrared spectrum ν_{max} ($CHCl_3$): 1650 cm^{-1} (C=O), 1415 cm^{-1} (-C-O-C).

N.m.r. spectrum δ_{Tms} ($CDCl_3$): 4.57, 4.62, 5.21, 5.55 (2H two sets of quartets, C_7 methylene protons J=15 cps); 7.2-8.5 (10H, aromatic protons).

Reaction of 1-Chloro-7-methylene-7,12-dihydropleiadene with Tetrachloro-o-benzoquinones

A solution of 0.552 g (0.002 mole) of 1-chloro-7-methylene-7,12-dihydropleiadene in 50 ml of chlorobenzene was added to a solution of tetrachloro-1,2-benzoquinone (0.976 g, 0.004 mole in 150 ml of chlorobenzene and the mixture was heated under reflux for 24 hours. The chlorobenzene was removed in vacuo, benzene added to the residue and the resulting solid removed. Recrystallisation from benzene gave 0.73 g (50.1%) of pale yellow fibrous solid m.p. >300°.

Anal. Calcd. for $C_{31}H_{12}Cl_8O_4$: C, 51.09; H, 1.65; Cl, 38.47
Found: C, 51.26; H, 1.82; Cl, 38.59

Mol. wt. Calcd. 727.8248. Found (mass spectrum): 727.8233.

Infrared spectrum ν_{max} (Nujol mull): 1447, 1423 cm^{-1} (-C-O-C).

Reaction of 1-Chloro-7-methyl-7,12-dihydropleiadene with Tetrachloro-o-benzoquinone

A solution of 0.556 g (2 mmoles) of 1-chloro-7-methyl-7,12-dihydropleiadene in dry chlorobenzene was added to a solution of 0.976 g (4 mmoles) of tetrachloro-o-benzoquinone in 150 ml of dichlorobenzene and the mixture refluxed for 10 hours. The solvent was removed in vacuo and the residual solid purified by chromatography on B.D.H. alumina using hexane:benzene (2:1) as eluant to give 0.13 g (8.9% yield) of 168. m.p. 298°-300°.

Anal. Calcd. for $C_{31}H_{12}Cl_8O_4$: C, 51.10 H, 1.65; Cl, 38.47

Found: C, 51.71, H, 1.65, Cl, 37.83.

Mol. wt. Calcd. 727.8248. Found (mass spectrum) 727.8436.

Infrared spectrum $\nu_{max.}$ ($CHCl_3$) 1447 cm^{-1} 1421 cm^{-1} (C-O-C).

Reaction of 7-Methyl-7,12-dihydropleiadene with Tetrachloro-o-benzoquinone

A solution of 0.61 g (2.5 mmoles) of 7-methyl-7,12-dihydropleiadene in 30 ml of chlorobenzene was added to a solution of 1.22 g (5 mmoles) of tetrachloro-o-benzoquinone in 150 ml of chlorobenzene and the mixture refluxed for 48 hours. The solvent was removed in vacuo; the residue was dissolved in benzene and subjected to chromatography on B.D.H. alumina using hexane:benzene (1:1) as eluant to give 0.82 g (67.5% yield) of white solid, (171). m.p. 207-209°.

Anal. Calcd. for $C_{25}H_{14}Cl_4O_2$: C, 61.72; H, 2.88; Cl, 28.80
Found: C, 61.54; H, 2.87; Cl, 28.93
Mol. wt. Calcd.: 485.9750. Found (mass spectrum): 485.9745.
Infrared spectrum ν_{max} ($CDCl_3$): 1446, 1452 cm^{-1} (-O-C-O-C).
N.m.r. spectrum δ_{Tms}($CDCl_3$): 1.94 (3H, doublet, J=7Hz C_7 methyl protons). 5.95 (1H, quarter J=7Hz, C_7 methine proton).

Reaction of 1-Chloro-7-methylene-7,12-dihydropleiadene-12-one with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 1.45 g (5 mmoles) of 1-chloro-7-methylene-7,12-dihydropleiadene-12-one in 100 ml of chlorobenzene was added to a solution of 2.26 g (10 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of chlorobenzene and the mixture heated under reflux for 6 hours. The quinol formed was removed and filtrate concentrated to give a yellow ochre solid which was recrystallised from chloroform to give 1.77 g (67.3% yield) of 174. m.p. 225-228°.

Anal. Calcd. for $C_{27}H_9Cl_3N_2O_3$: C, 63.02; H, 1.75; Cl, 20.43, N, 5.45
Found: C, 62.31; H, 1.74; Cl, 20.54; N, 5.50.
Mol. wt. Calcd.: 513.9680. Found (mass spectrum): 513.9682.
Infrared spectrum ν_{max} (Nujol mull): 1736, 1705 cm^{-1} (C=O of quinone); 1680 cm^{-1} (C=O at C_{12}).
N.m.r. spectrum δ_{Tms}($(CD_3)_2SO$): 6.45, 6.7 (1H, two singlets vinyl proton); 6.95-8.4 (8H, multiplet, aromatic protons).

Reaction of 7-Methylene-7,12-dihydropleiadene-12-one with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 0.770 g (3 mmoles) of 7-methylene-7,12-dihydropleiadene-12-one in 50 ml chlorobenzene was added to a solution of 1.356 g (6 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 200 ml of warm dry chlorobenzene, and the mixture heated under reflux for 3 hours. The solvent was removed in vacuo and the residue treated with benzene to give a bright yellow solid. Recrystallisation from benzene gave 1.123 g (78% yield) of 176. m.p. 226-228°.

Anal. Calcd. for $C_{27}H_9Cl_2N_2O_3$: C, 67.50; H, 2.08; Cl, 14.58; N, 5.83
Found: C, 68.23; H, 2.43; Cl, 14.15; N, 5.78.

Mol. wt. Calcd.: 480.0079. Found (mass spectrum): 480.0079.

Infrared spectrum ν_{max} ($CDCl_3$): 1720 cm^{-1} (C=O for quinone moiety) 1660 cm^{-1} (C=O at C_{12}).

N.m.r. spectrum δ_{Tms} [$(CD_3)_2SO$]: 6.55, 6.78 (1H, singlets C_{19}-methine proton); 7.1-8.5 (9H, aromatic protons).

Reaction of 1-Chloro-7-methylene-7,12-dihydropleiadene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 0.552 g (2 mmoles) of 1-chloro-7-methylene-7,12-dihydropleiadene in 25 ml of benzene was added to a solution of 0.904 g (4 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 20 ml of benzene and the mixture refluxed for 10 hours, cooled and solid formed removed. Concentration of filtrate gave a brick-

red solid, purified by recrystallisation from benzene to give 177, 0.68 g (68% yield). m.p. 242-245° (decomposition).

Anal. Calcd. for $C_{27}H_{11}Cl_3N_2O_2$: C, 64.8; H, 2.20; Cl, 21.00; N, 5.60
Found: C, 64.79; H, 2.37; Cl, 20.95; N, 5.56
Mol. wt. Calcd.: 499.9888. Found (mass spectrum): 499.9886.
Infrared spectrum ν_{max} ($CHCl_3$): 1718 cm^{-1} (C=O); 2250 cm^{-1} (C≡N).
N.m.r. spectrum δ_{Tms} ($(CD_3)_2SO$): 4.15, 4.63 (2H, quartet (broad lines) J=15 Hz, C_{12}-bridge protons): 6.1, 6.47 (1H, two singlets, vinyl proton); 6.95-8.5 (8H, aromatic protons).

Reaction of 1-Chloro-7-methyl-7,12-dihydropleiadene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 0.420 g (1.5 mmoles) of 1-chloro-7-methyl-7,12-dihydropleiadene in 50 ml of chlorobenzene was added to a solution of 1.02 g (4.5 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of chlorobenzene and the mixture refluxed for 2 hours. The solid formed was removed and the solvent from filtrate removed in vacuo. The residue was dissolved in benzene and subjected to chromatography on silicic acid (pH 7) to give brick-red solid 0.63 g (84% yield) of 177. m.p. 242-243°.
Infrared spectrum ν_{max} ($CHCl_3$): 1718 cm^{-1} (C=O); 2250 cm^{-1} (C≡N).

This compound was found to be identical with the compound obtained from 1-chloro-7-methylene-7,12-dihydropleiadene.

2-(2'-Methylnaphthoyl-1')benzoic acid

This compound was prepared together with its isomer 2-(6'-methylnaphthoyl-1')benzoic acid in 3:1 ratio in overall yield of 93%, according to the method of Fieser and Fieser (113).

2-(2'-Methyl-1'-naphthylmethyl)benzoic acid

This compound was prepared together with its isomer 2-(6'-methyl-1'-naphthylmethyl)benzoic acid in 70% yield from the mixture of 2-(2'-methylnaphthoyl-1') benzoic acid according to the method of Fieser and Fieser (113).

Methyl-2-(2'-methyl-1'-naphthylmethyl)benzoate

A mixture of 50 g of 2-(2'-methyl-1'-naphthylmethyl)-benzoic acid and 2-(6'-methyl-1'-naphthylmethyl)benzoic acid was suspended in 500 ml of methanol and catalytic amount of concentrated sulfuric acid added to it. The mixture was refluxed for 16 hours, concentrated to about 100 ml and 200 ml of water added to it, then extracted with ether. The ether solution was washed successively with water, 10% sodium bicarbonate solution and water, dried (Na_2SO_4) and solvent removed to give 40 g (76% yield) of a brown oil (mixture of the two benzoates). This oil was extracted with petroleum ether (30-60°), and the petroleum ether kept in refrigerator overnight. Pure methyl-2-(2'-methyl-1'-naphthylmethyl)-benzoate crystallised out of solution. m.p. 85-88°.

Anal. Calcd. for $C_{21}H_{22}O$: C, 86.90; H, 7.59

Found: C, 86.67; H, 7.41

Infrared spectrum ν_{max} ($CHCl_3$): 1715, 1723 (C=O).

N.m.r. spectrum δ_{Tms} ($CDCl_3$): 2.46 (3H, singlet, Ar-CH_3); 3.97 (3H, singlet, -O-CH_3); 4.87 (2H, singlet $\begin{matrix}Ar\\Ar\end{matrix}>CH_2$); 7.0-8.2 (9H, aromatic protons).

1,7,7-Trimethyl-7,12-dihydropleiadene

To a stirred solution of 6.5 g of methyl-2-(2'-methyl-1'-naphthylmethyl-1')benzoate in ether was added excess of a solution of methyllithium in ether. The mixture was poured on to ice, acidified with 2N hydrochloric acid and the ether layer separated and dried ($MgSO_4$). Evaporation of the solvent gave 1-(2'-(1"-hydroxy-1"-methylethyl)toly)-2-methylnaphthalene 181 as a yellow oil. The oil was dissolved in 100 ml of formic acid containing a catalytic amount of p-toluenesulfonic acid and the mixture heated on the steam bath for 3 hours. The solution was diluted with water extracted with ether and the ether layer separated and washed with 10% sodium hydrogen carbonate solution then water and dried ($MgSO_4$). Evaporation of the solvent gave a yellow oil, chromatography of which on alumina gave 1-(2'-isopropenyltolyl-1') 2-methylnaphthalene (182) as a white crystalline solid identified by its nuclear magnetic resonance spectrum, δ_{Tms} ($CDCl_3$) 2.25 (3H, singlet, isopropenyl methyl protons); 2.40 (3H, singlet, aryl methyl proton); 4.50 (2H, singlet, bridge methylene protons). 5.15.-5.40 (2H, multiplet, isopropenyl vinyl protons) 6.40-8.00 (9H, multiplet, aromatic protons). The latter

was dissolved in 50 ml of anhydrous ether, treated with 25 ml of borontrifluoride-etherate in ether (48%) and the mixture stirred for 2 hours. The reaction mixture was decomposed with ice, the ether layer was washed with water and dried ($MgSO_4$). Evaporation of the solvent gave a brown solid purified by chromatography on B.D.H. alumina to give 2.5 g (40% yield overall from the ester) of 1,7,7,-trimethyl-7,12-dihydropleiadene 145. m.p. 165-166°.

Anal. Calcd. for $C_{21}H_{20}$: C, 92.64; H, 7.36

Found: C, 92.62; H, 6.70

N.m.r. spectrum δ_{Tms} ($CDCl_3$): 1.74 (6H singlet, C_7 methyl groups); 2.73 (3H, singlet, C_1 methyl protons), 4.18 (2H, singlet, C_{12} methylene protons); 7.00-8.00 (9H, multiplet, aromatic protons).

Reaction of 1,7,7-Trimethyl-7,12-dihydropleiadene with Tetrachloro-o-benzoquinone

A solution of 0.34 g (1.25 mmoles) of 1,7,7-trimethyl-7,12-dihydropleiadene in 25 ml of dry benzene was added to a solution of 0.61 g (2.5 mmole) of tetrachloro-o-benzoquinone in 125 ml of benzene. The mixture was refluxed for 48 hours, cooled and concentrated to give a grey solid, which on further recrystallisation from benzene gave 0.263 g (41% yield) of 190. m.p. 197-199°.

Anal. Calcd. for $C_{27}H_{18}Cl_4O_2$: C, 63.02; H, 3.50; Cl, 27.24

Found: C, 63.48; H, 3.45; Cl, 27.12

Infrared spectrum ν_{max} ($CHCl_3$): 1405 cm^{-1} (C-O-C-).

N.m.r. spectrum δ_{Tms} ($CDCl_3$): 1.8 (3H, singlet, C_7 equatorial

CH_3); 2.05 (3H, singlet, C_7 axial CH_3); 5.95, 6.56 (2H, AB quartet, J_{AB}=16 Hz, C_1 methylene protons); 7.2-8.3 (9H, multiplet, aromatic protons).

Reaction of 1,7,7-trimethyl-7,12-dihydropleiadene with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 0.34 g (1.25 mmoles) of 1,7,7-trimethyl-7,12-dihydropleiadene in 25 ml of benzene was added to 0.565 g (2.5 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of benzene and the mixture refluxed for 30 minutes, during which time the hydroquinone separated as a brown solid. The solution was refluxed for a further 1 1/2 hours, cooled and filtered. Concentration of the filtrate to about 50 ml deposited bright orange-red crystals. Recrystallisation from benzene gave 0.531 g (85.6% yield) of 188. m.p. 209-212°.

Anal. Calcd. for $C_{29}H_{18}Cl_2N_2O_2$: C, 70.17; H, 3.63; Cl, 14.11, N, 5.64

Found: C, 70.33; H, 3.41; Cl, 14.03, N, 5.37

Mol. wt. Calcd.: 496.0746. Found (mass spectrum): 496.0753.

Infrared spectrum ν_{max} ($CHCl_3$): 1718 (C=O), 2225 cm^{-1} (C≡N).

N.m.r. spectrum δ_{Tms} ($CDCl_3$): 1.60 (3H, singlet, C_7 equatorial CH_3); 1.90 (3H, singlet, C_7 axial CH_3) 3.85, 4.20 (2H, AB quartet J_{AB}=16 Hz C_1-methylene protons), 5.20 (1H, singlet, C_{12} methine); 7.20-8.30 (9H, multiplet, aromatic protons).

7-Isopropyl-7,12-dihydropleiadene

7,12-Dihydropleiadene (6.9 g, 0.03 mole) was dissolved in 150 ml of anhydrous ether in a pressure bottle under an atomosphere of nitrogen and 14 ml of 2.25 M n-butyllithium in hexane added to it gradually with stirring. The bottle was securely stoppered and the complex stirred magnetically for 2 hours. After cooling the mixture to -20°, 2.6 g (0.033 mole) of isopropylchloride in 10 ml of anhydrous ether was added with stirring and under nitrogen. The bottle was stoppered again and the contents stirred at room temperature for 8 hours. The complex was decomposed with ice and the ether layer dried (Na_2SO_4) and the solvent removed to give a thick yellow oil. This oil was treated with a hot methanolic solution of 2,4,7-trinitro-9-fluorenone when only the unreacted starting material formed a complex, which was removed by filtration. The solvent was removed from the filtrate and the residual oil extracted with hexane and the extract subjected to chromatography on B.D.H. alumina using hexane as eluant to give 4.9 g (60% yield) of 143 as a yellow oil.

Anal. Calcd. for $C_{21}H_{20}$: C, 92.61, H, 7.39

Found: C, 92.57, H, 7.52

N.m.r. spectrum δ_{Tms} ($CDCl_3$): 0.8-1.05 (6H, multiplet, CH ($C\underline{H}_3$)$_2$): 2.55 (1H, multiplet, $C\underline{H}$ (CH_3)$_2$); 3.6 (1H, doublet J_{AB}=10.5 Hz, C_7 bridge proton); 3.84, 5.14 (2H, quartet J_{AB}= 16 Hz, C_{12} bridge protons)1 7.0-7.83 (10H, multiplet, aromatic protons).

N.m.r. spectrum was the same as the one reported by Lansbury (129).

Reaction of 7-isopropyl-7,12-dihydropleiadene with tetrachloro-1,2-benzoquinone

A solution of 1.7 g (6.25 mmole) of 7-isopropyl-7,12-dihydropleiadene in 75 ml of dry chlorobenzene was added to a solution of 3.20 g (0.0120 mole) of tetrachloro-1,2-benzoquinone in 125 ml of chlorobenzene and the mixture refuluxed for 72 hours. The solvent was removed in vacuo and the residue dissolved in benzene and subjected to chromatography on B.D.H. alumina using 1:1 hexane/benzene as eluant to give 1.56 g (49% yield) of 197. m.p. 160-165°.

Anal. Calcd. for $C_{27}H_{18}Cl_4O_2$: C, 63.02; H, 3.50; Cl, 27.24

Found: C, 62.89; H, 3.62; Cl, 27.29

Mol. wt. Calcd.: 514.0063. Found (mass spectrum): 514.0050.

Infrared spectrum ν_{max} ($CHCl_3$): 1455 cm^{-1}, (C-O-C).

N.m.r. spectrum δ_{Tms} ($CDCl_3$): 0.5-1.5 (6H, multiplet $CH(CH_3)_2$); 1.87 (1H, multiplet, aromatic protons).

Reaction of 7-isopropyl-7,12-dihydropleiadene with 2,3-dicyano-5,6-dicyano-1,4-benzoquinone

A solutionof 0.82 g (0.003 mole) of 7-isopropyl-7,12-dihydropleiadene in 50 ml of benzene was added to a solution of 1.36 g (0.006 mole) of 2,3-dichloro-5,6-dicynao-1,4-benzoquinone in 125 ml of benzene and the mixture refluxed for 1 hour. The quinol formed was removed and the filtrate concentrated to about 15 ml. A yellow solid crystallised out on addition of hexane to

the solution. Recrystallisation from benzene/hexane gave 0.52 g (60.6% yield) of 7-isopropyl-7,12-dihydropleiadene-12-one. m.p. 188-189°. N.m.r. spectrum δ_{TMS} ($CDCl_3$): 0.5, 0.72 (6H pair of doublets isopropyl methyl protons); 1.9 to 2.6 (1-H multiplet isopropyl methine proton); 3.52 (1-H, doublet J_{AB}=11Hz, C_7-methine proton); 7.15-8.4 (10H multiplet aromatic protons).

Infrared spectrum ν_{max} ($CHCl_3$) 1647 cm^{-1} (-C=O at C_{12}).

Preparation of 7-Isopropyl-12(7H)-pleiadenone

7-Isopropyl-12(7H)-pleiadenone was prepared according to the method of Lansbury, Lacher and Saeva from 7-isopropyl-7,12-dihydro-pleiadene. Yield was 75%. m.p. 187-190°, [lit. (128) 188-190°].

1,2-Acenaphthaquinone

This compound was prepared from acenaphthene according to the method of Maxwell and Allen (133) in 45% yield. m.p. 243-246° [lit. (133) 243-245°].

1,2-Dihydroxy-1,2-diphenyl-acenaphthene

1,2-Dihydroxy-1,2-diphenyl-acenaphthene was preapred accroding to the method of Bachmann and Chu (134) in 52% yield. m.p. 154-156° [lit. (134) 154.3-155.3°].

7,7-Diphenylacenaphthenone

This compound was prepared in 80% yield from 1,2-dihydroxyl-1,2-diphenyl-acenaphthene according to the method of Bachmann and Chu (134). m.p. 171-172 [lit. 171.2-173.4°].

8-Benzhydryl-1-naphthoic acid

This compound was prepared in 75% yield from 7,7-diphenyl-acenaphthenone according to the method of Bachmann and Chu (134) m.p. 224-227° (lit. (134) 226°).

1-(8-Benzyhydryl)-naphthyl carbinol

This compound was prepared from 8-benzhydryl-1-naphthoic acid in 72% according to the method of Lansbury (122). m.p. 168-170° (lit. 168.5-169°).

7-Phenyl-7,12-dihydropleiadene

7-Phenyl-7,12-dihydropleiadene 144 was prepared from 1-(8-benzyhydryl)naphthylcarbinol by the method of Lansbury in 80% yield. m.p. 180-181°, (lit. (122) 179-179.5°).

Reaction of 7-Phenyl-7,12-dihydropleiadene with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

A solution of 1.53 g (5 mmole) of 7-phenyl-7,12-dihydro-pleiadene in 25 ml of benzene was added to a solution of 2.26 g (0.01 mole) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of benzene and the mixture refluxed for 8 hours, then concentrated to about 20 ml and chromatographed on B.D.H. alumina using hexane/benzene (3:1) as eluant. Crystallisation of the resulting solid in benzene gave 0.81 g (53.3% yield) of 207. m.p. 271-273°.

Anal. Calcd. for $C_{24}H_{16}$: C, 94.73; H, 5.27

Found: C, 94.67; H, 5.45.

Mol. wt. Calcd.: 304.1252. Found (mass spectrum): 304.1250.
N.m.r. spectrum: δ_{Tms} ($CDCl_3$) 5.16 (2H, singlet C_7 C_{12} protons); 6.95-7.67 (14H, multiplet, aromatic protons).

Reaction of 7-Phenyl-7,12-dihydropleiadene with Tetrachloro-1,2-benzoquinone

A solution of 1.53 g (5 mmole) of 7-phenyl-7,12-dihydropleiadene in 50 ml of dry benzene was added to a solution of 3.66 g (15 mmole) of tetrachloro-1,2-benzoquinone in 125 ml of benzene and the mixture refluxed for 72 hours. The solution was concentrated *in vacuo* to a small volume and chromatographed on B.D.H. alumina using hexane/benzene as eluant. Recrystallisation of the main fraction from benzene gave 1.22 g of 207 (80.3% yield). m.p. 272°.

Anal. Calcd. for $C_{24}H_{16}$: C, 94.73; H, 5.27
Found: C, 94.53; H, 5.66.

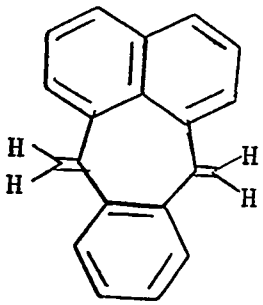
N.m.r. spectrum δ_{Tms} ($CDCl_3$): 5.16 (2H, singlet C_7, C_{12} bridge protons); 6.95-7.67 (14H, multiplet, aromatic protons).

CHAPTER IV

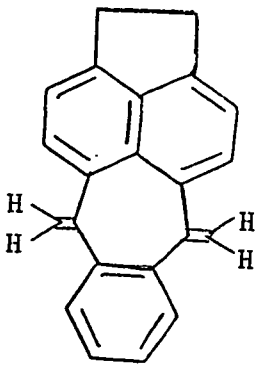
A. Quinodimethane Analogues in the Pleiadene and Acepleiadene Series

The possible intermediacy of 9,10-anthraquinodimethane 112 in the dehydrogenation of 9,10-dimethylanthracene suggested that analogues of this species in the pleiadene (210), and acepleiadene (211) could be prepared. The preparation of these species could be used as a means of testing theoretical predictions of whether they are quinodimethanes or dienes. For these compounds to be quinodimethanes they must possess planar structures. In this conformation they would be expected, as unsubstituted, unhindered, quinodimethanes, to be very reactive, and dimerise or polymerise readily.

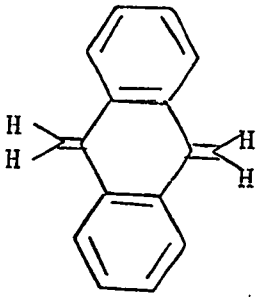
On the other hand should compounds 210 and 211 exist in the boat conformation, as their parent hydrocarbon dihydropleiadene, then they would exhibit diene properties and be stable enough to allow isolation.



210



211



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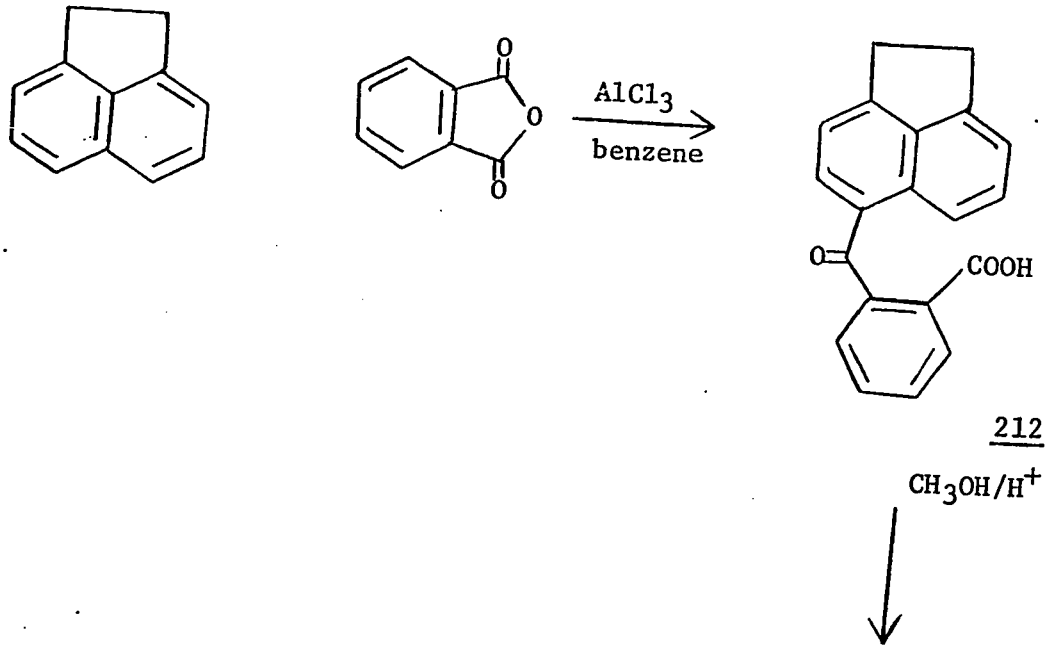
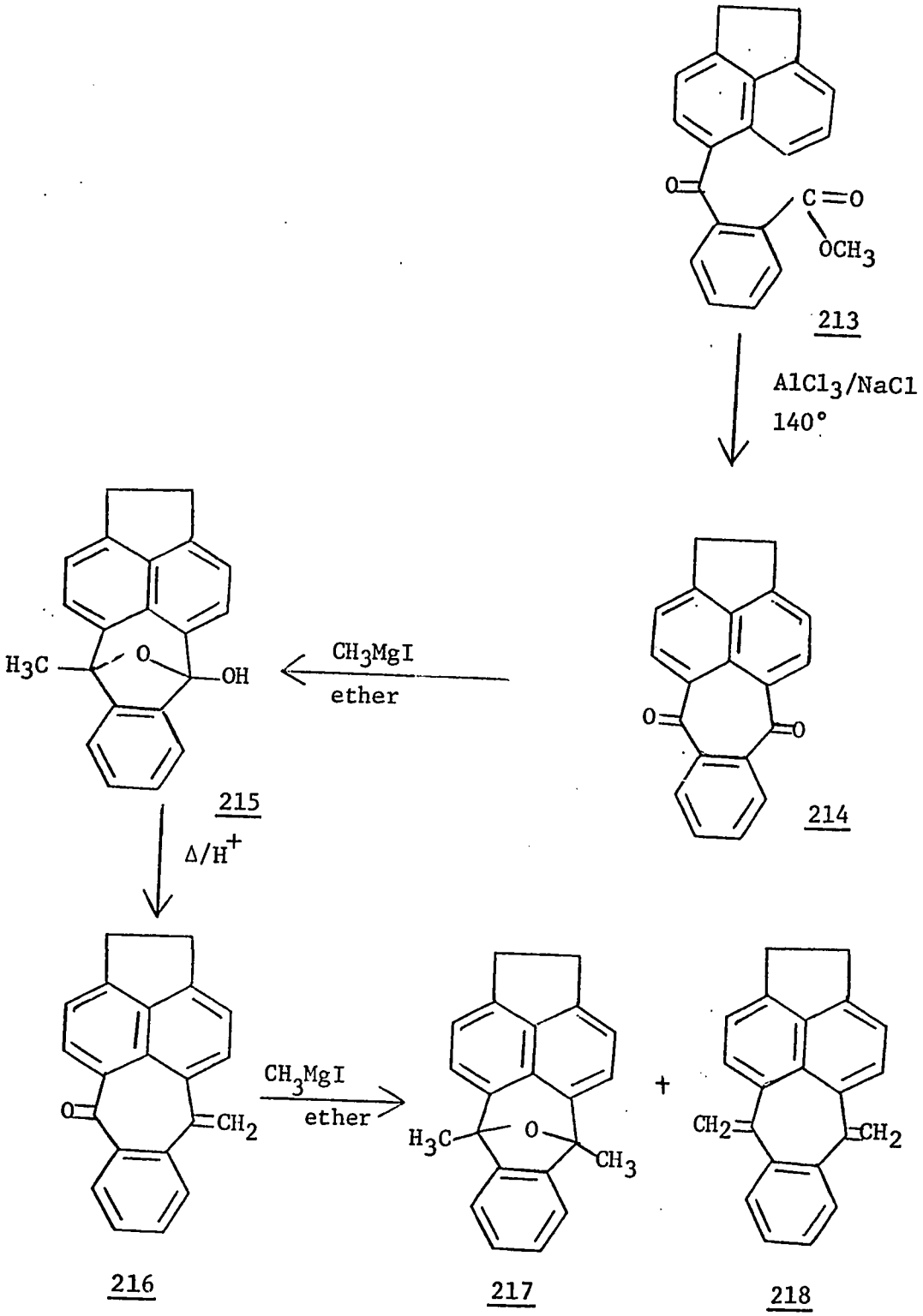
RESULTS AND DISCUSSION

Synthesis of 5,12-Dimethylene-5,10-dihydroacepleiadene

The keto-acid 212, prepared by condensation of acenaphthene with phthalic anhydride in the presence of aluminum chloride, was refluxed with methanol to give the methyl ester 213. This ester underwent intramolecular condensation when heated with aluminum chloride and sodium chloride to give 5,12-dihydroacepleiadene-5,12-dione 214 (136), see Scheme XXVII. Compound 214 was then added to methyl magnesium iodide in ether to give 5-methyl-5,12-epoxy-5,12-dihydroacepleiaden-12-ol 215, which was dehydrated to give 5-methylene-5,12-dihydroacepleiaden-12-one 216. Treatment of 216 with methyl magnesium iodide in ether gave a mixture of 217 and 218, which were separated by chromatography on a silicic acid column.

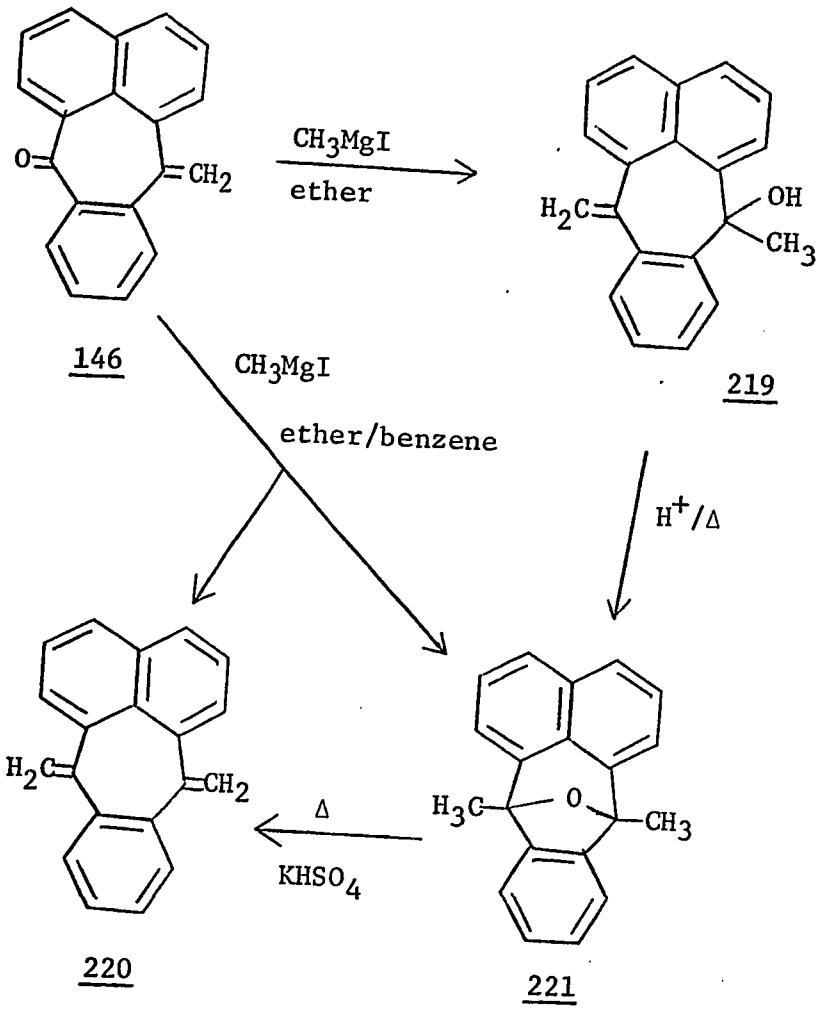
SCHEME XXVII




O
C=O
OCH3
213
AlCl3/NaCl
140°
O
O
214
CH3MgI
ether
H3C
O
OH
215
Δ/H+
O
CH2
216
CH3MgI
ether
H3C
O
CH3
217
+
CH2
CH2
218

Synthesis of 7,12-Dimethylene-7,12-dihydropleiadene

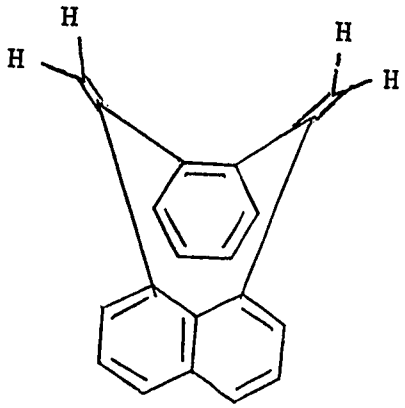
SCHEME XXVIII



When compound 146 was added to methylmagnesium iodide in ether and the mixture stirred at room temperature and worked up only 7-hydroxy-7-methyl-12-methylene-7,12-dihydropleiadene 219 was isolated (see Scheme XXVIII). This reaction has been reported recently not to proceed under these conditions (135). On the other hand when 146 was added to methylmagnesium iodide in ether/benzene and the mixture refluxed, a mixture of 7,12-dimethyl-7,12-epoxy-7,12-dihydropleiadene 221 and 7,12-dimethylene-7,12-dihydropleiadene 220 were obtained. The preparation of 7,12-dimethylene-7,12-dihydropleiadene has been reported recently employing a similar route indicated above (135).

Some Properties of 7,12-Dimethylene-7,12-dihydropleiadene and 5,10-Dimethylene-5,10-dihydroacepleiadene

The stability of these hydrocarbons leads to the conclusion that they lack coplanarity in the seven-membered ring and are neither aromatic nor quinodimethanes. They must behave in their reactions as dienes, and have conformation as illustrated in 222. 7,12-Dimethylene-7,12-dihydropleiadene 220 was quite hygroscopic. A solution of it in benzene left in the atmosphere gradually converted to 221, a reaction which could be followed readily by nuclear magnetic resonance; the appearance of a methyl absorption at 2.13 ppm indicated the formation of 221. The complete disappearance of 220 was shown by the absence of the methylene absorption at 5.22, 5.49 ppm. This conversion becomes very rapid when the solution was refluxed in presence of acids, e.g. p-toluenesulfonic acid. Compound 219 also was transformed readily by acids to 221. This ready



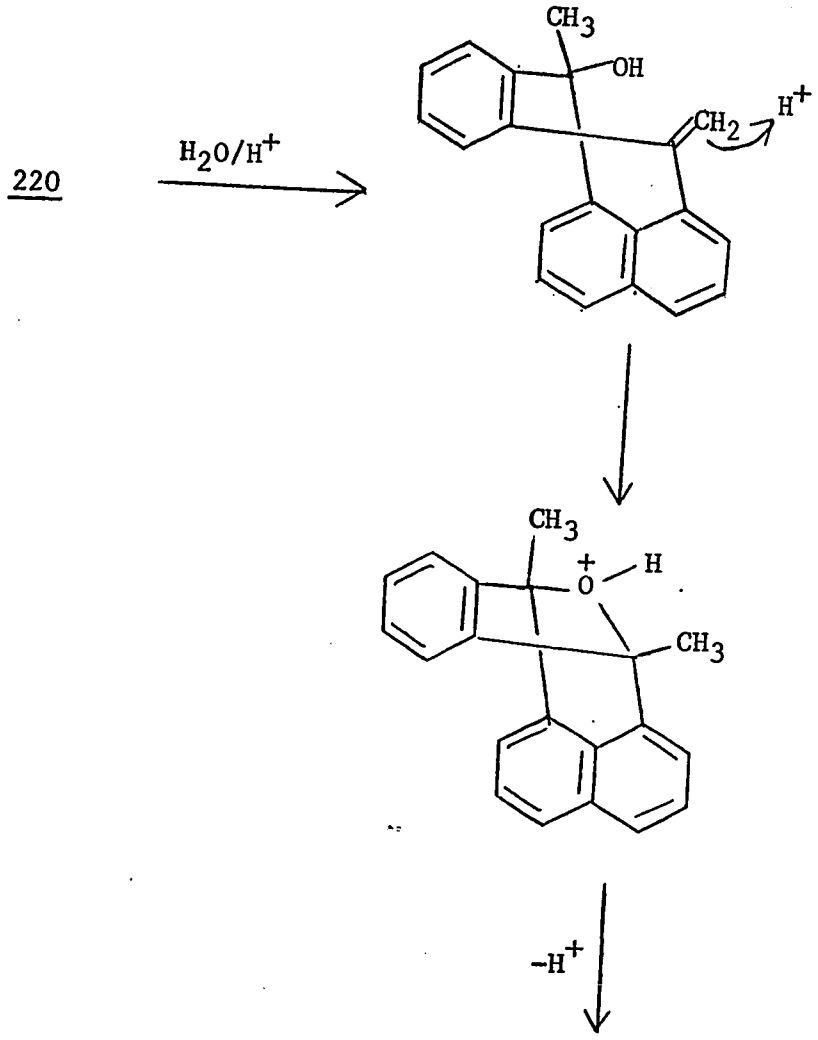
222

formation of 221 from both 219 and 220 made it impossible to dehydrate 221 to 220 using acids. Other unsuccessful attempts to dehydrate 221 was by treating a pyridine solution with p-toluenesulfonyl chloride or thionyl chloride. Compound 221 was dehydrated by heating with solid potassium hydrogen sulfate at 140° to give in quite good yield 220.

The facile ring closure observed in the formation of 221 is attributed to the geometry of the pleiadene system and to the conformational preference of the hydroxy group for axial position and the methyl for the equatorial position (129), see Scheme XXIX.

Another example of such transannular participation resulting from the geometry of pleiadene system and conformational preference of substituents at the bridge position is in the quinone dehydrogenation of 7-phenyl-7,12-dihydropleiadene already discussed in Chapter III.

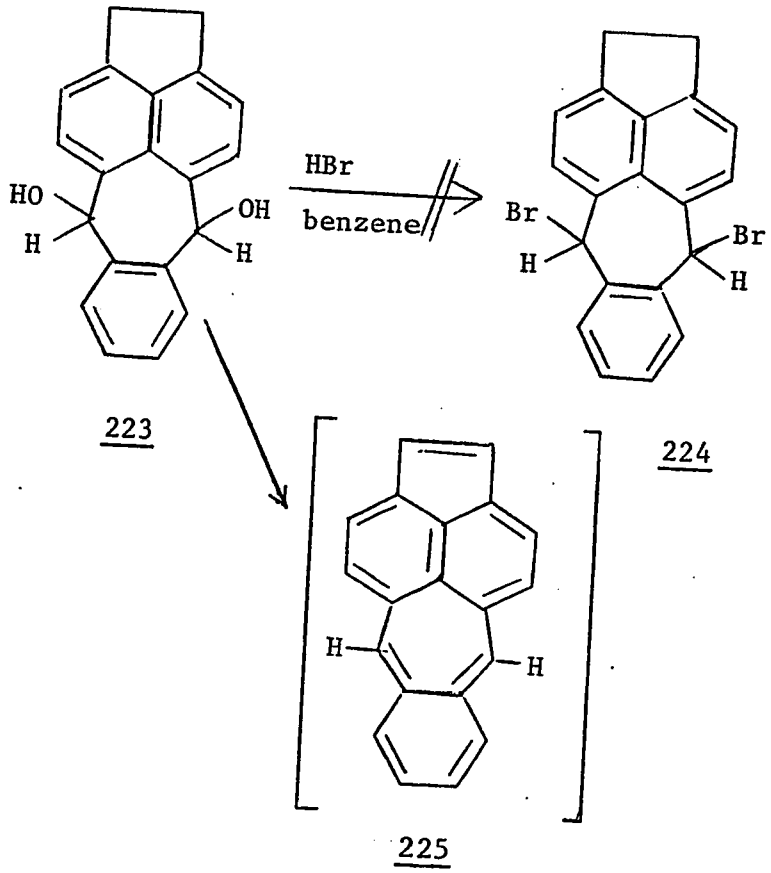
SCHEME XXIX



Cava and Schlessinger in their attempt to convert diol 223 to the corresponding dibromide 224, found that a deep blue solution of acepleiadylene 225 was generated instead by acid catalysed

dehydration (136). This compound could not be isolated in the solid state, it was unstable and on evaporation of solvent yielded a mixture

[77]

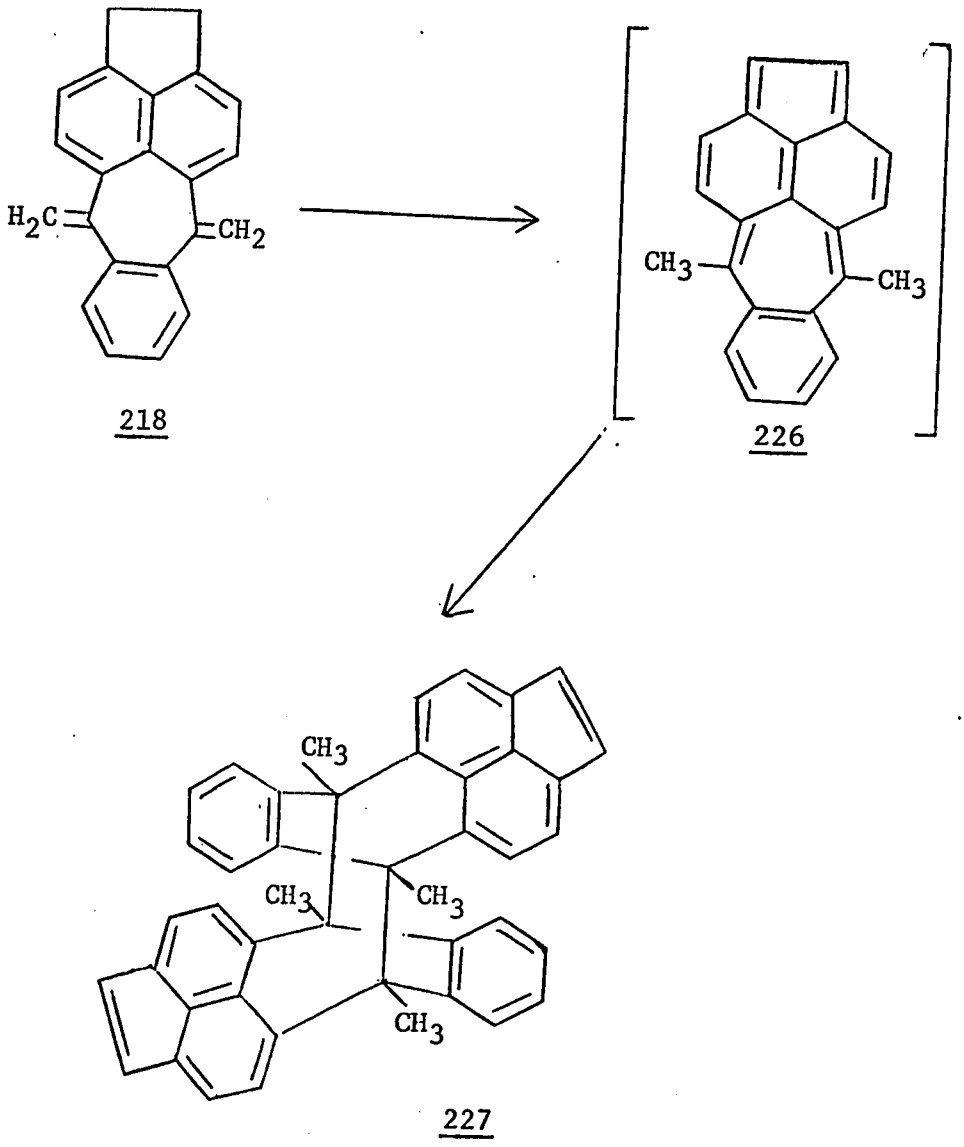


223 224 225

of polymers and a dimer. It was thought therefore that 5,10-dimethylene-5,10-dihydroacepleiadene under basic conditions may isomerise to 5,10-dimethylacepleiadylene, which may then dimerise to give 227, Scheme XXX. When a solution of potassium t-butoxide in dimethylsulfoxide was added to a solution of 218 in dimethyl-sulfoxide a deep greenish blue solution was obtained which showed absorption at λ_{max} = 248, 326, 354, 498, 625 mμ for the visible and ultra-violet spectrum. The absorption spectrum is

is characteristic of the acepleiadylene moiety. Attempts to isolate the dimer 227 after allowing the solution to sit for two days failed.

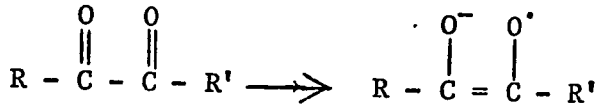
SCHEME XXX



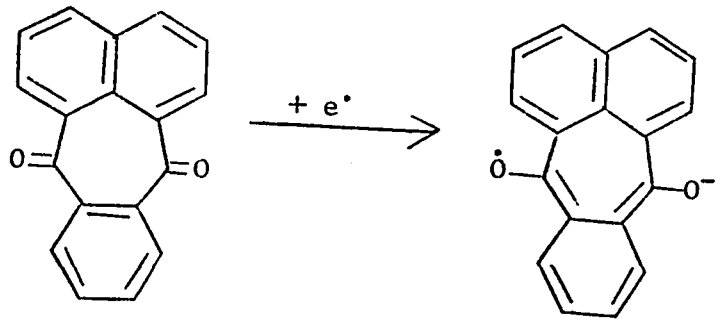
218 226 227

B. Generation of Radical Anions from Acepleiadene Derivatives

Our interest in generation of quinodimethane intermediates and the recognition that they could be generated from pleiadene (119) and acepleiadenes (136) made us look for other methods of achieving this conversion. Reduction of diones has been used as a means of generating semidione radical anions which have appreciable stability.

[78] 

Conceivably the analogous pleiadene and acepleidlylene semidione anion could be produced; these as illustrated in eqn. [79] for pleiadene would have in their hydrocarbon framework an o-quinodimethane moiety.

[79] 

161 228

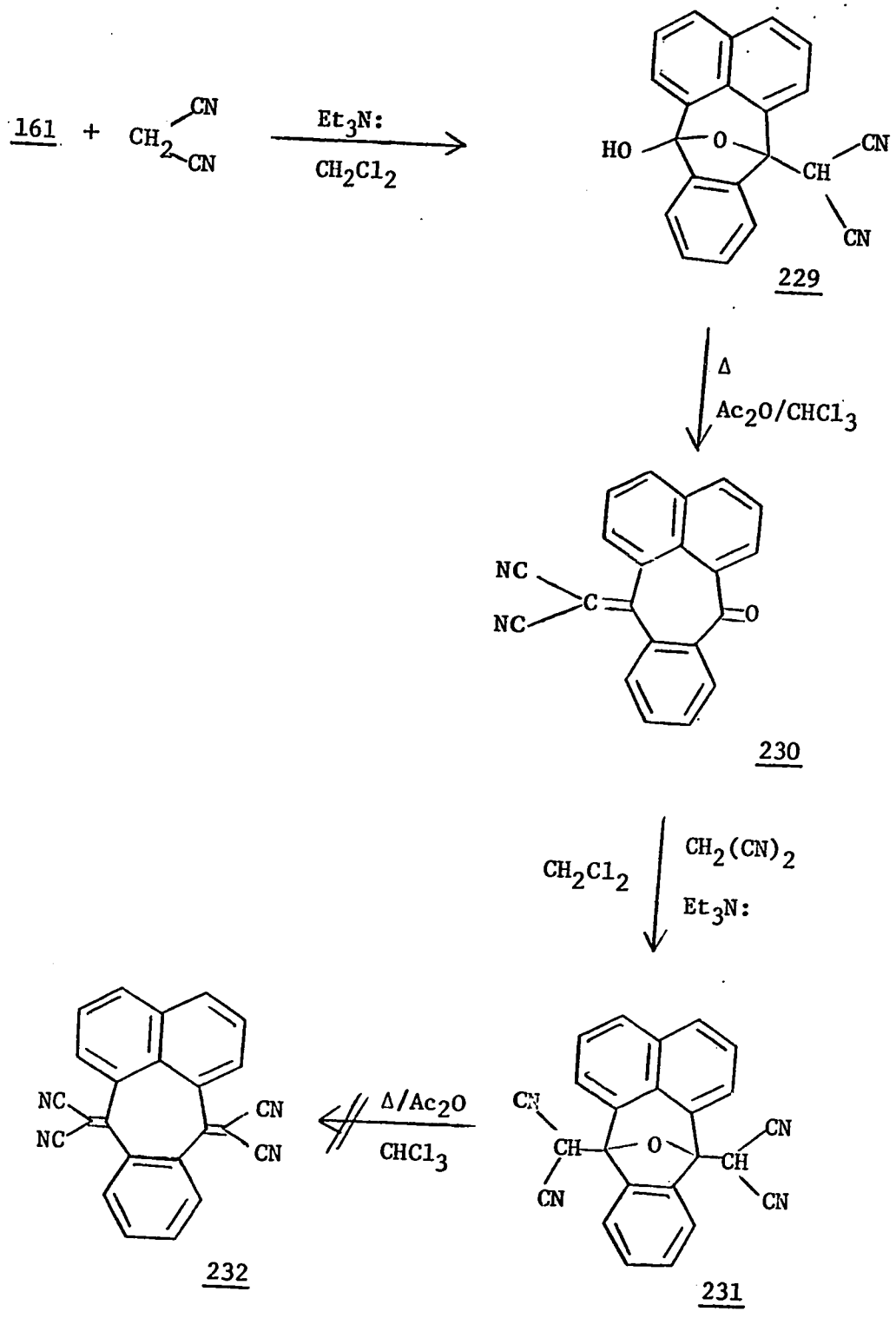
Attempt at Generation of Pleiadene Semidione Radical Anions

Russell and co-workers (137,138) have generated many semidiones anions by treatment of diones with potassium t-butoxide, or the enolate anion of propiophenone in dimethylsulfoxide solution.

Treatment of 7,12-dihydropleiadene-7,12-dione under these conditions failed to produce any free radical detectable by electron spin resonance. Also no radical was produced when 161 was treated with sodium hydroxide in acetonitrile solution. It was thought then this might be due to the instability of the semidione 228 relative to 161; and that if groups better able to support a negative charge were substituted for oxygens at the C_7 and C_{12} positions these might stabilise the radical enough to be detectable by electron spin resonance. Accordingly an attempt was made to synthesise 7,12-bis(dicyanomethylene)-7,12-dihydropleiadene 232 by the method outlined in Scheme XXXI.

Base catalysed condensation of the dione 161 with malonitrile produced the epoxy-alcohol 229, similar in structure to 215. Dehydration of 229 with acetic anhydride in chloroform solution gave 7-dicyanomethylene-7,12-dihydropleiaden-12-one 230. Further condensation of the latter compound with malonitrile gave the tetracyano-oxide 231, which resisted attempted dehydration to 232. Neither 230 nor 231 could be induced to form a radical anion, detectable by electron spin resonance, by the action of potassium t-butoxide, or the enolate anion of propiophenone in dimethylsulfoxide solutions.

SCHEME XXXI


161
CH2(CN)2
Et3N:
CH2Cl2
HO
O
CH
CN
CN
229
Δ
Ac2O/CHCl3
NC
NC
C
O
230
CH2Cl2
CH2(CN)2
Et3N:
NC
NC
CN
CN
232
Δ/Ac2O
CHCl3
CN
CH
O
CH
CN
CN
CN
231

Generation of Acepleiadylene Radical Anion

In contrast to 7,12-dihydropleiadene-7,12-iodne which failed to produce any detectable radical anion, 5,10-dihydroacepleiadene-5,10-dione 214 produced a very stable radical anion by the action of potassium tert-butoxide in dimethylsulfoxide.

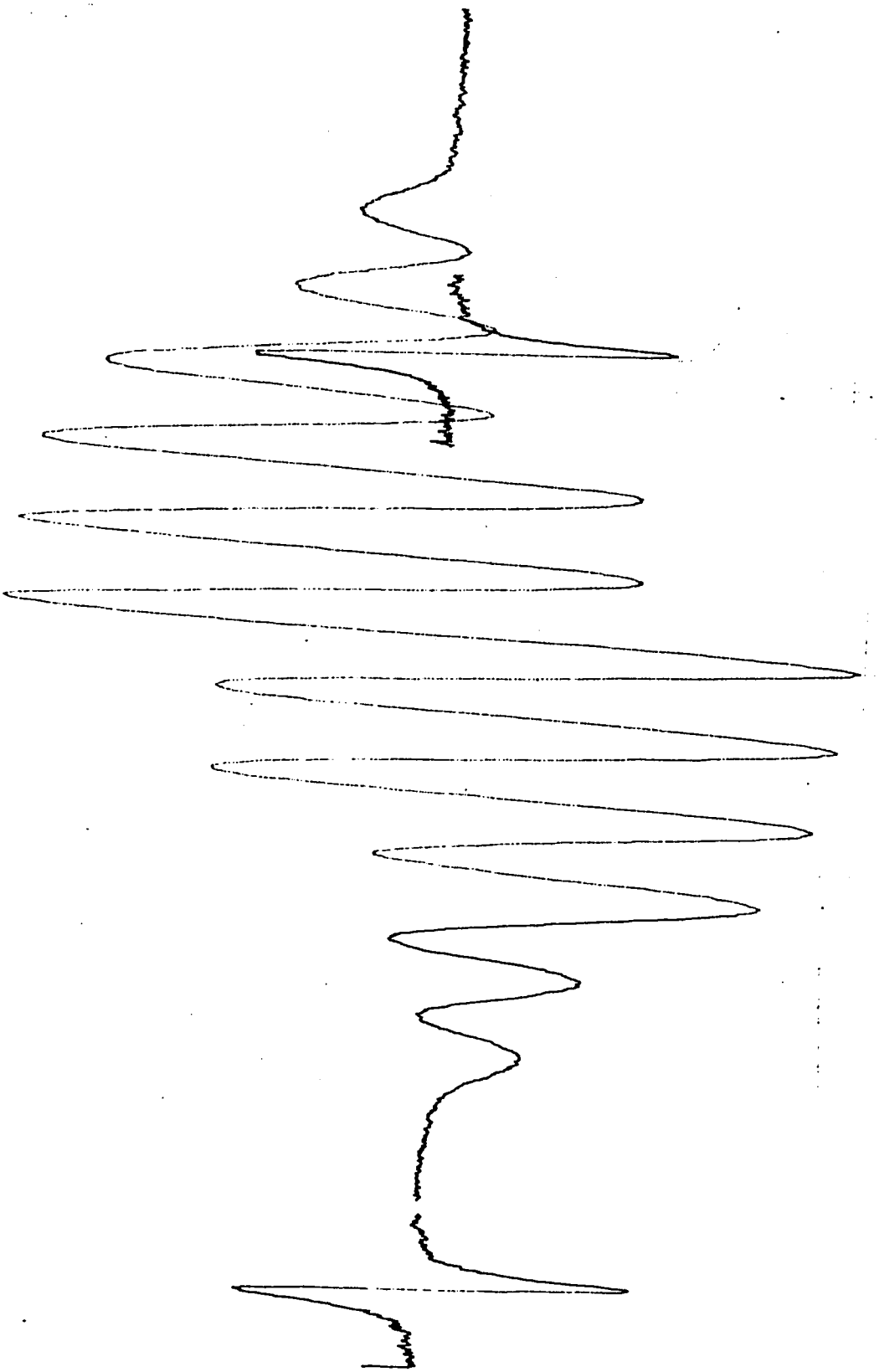
A solution of 214 in dimethylsulfoxide ($1x10^{-2}$ molar) was mixed with $2.5x10^{-2}$ molar solution of potassium tert-butoxide solution at ambient temperature to give a deep blue solution containing a paramagnetic species 233, which persisted for over 72 hr. The electron spin resonance examination showed an eleven line spectrum with overall splitting of 11.0 gauss (see Fig. II). This blue solution in dimethylsulfoxide showed absorption in the U.V. and visible region at λ_{max} = 342, 362(sh), 552, and 688 mμ, characteristic of an acepleiadylene structure (136).

The same electron spin resonance spectrum was obtained when $1x10^{-2}$ molar solution of 5,10-dihydroacyleiadylene-5,10-dione 235 in dimethylsulfoxide was treated with $2.5x10^{-2}$ molar solution of potassium tert-butoxide in dimethylsulfoxide.

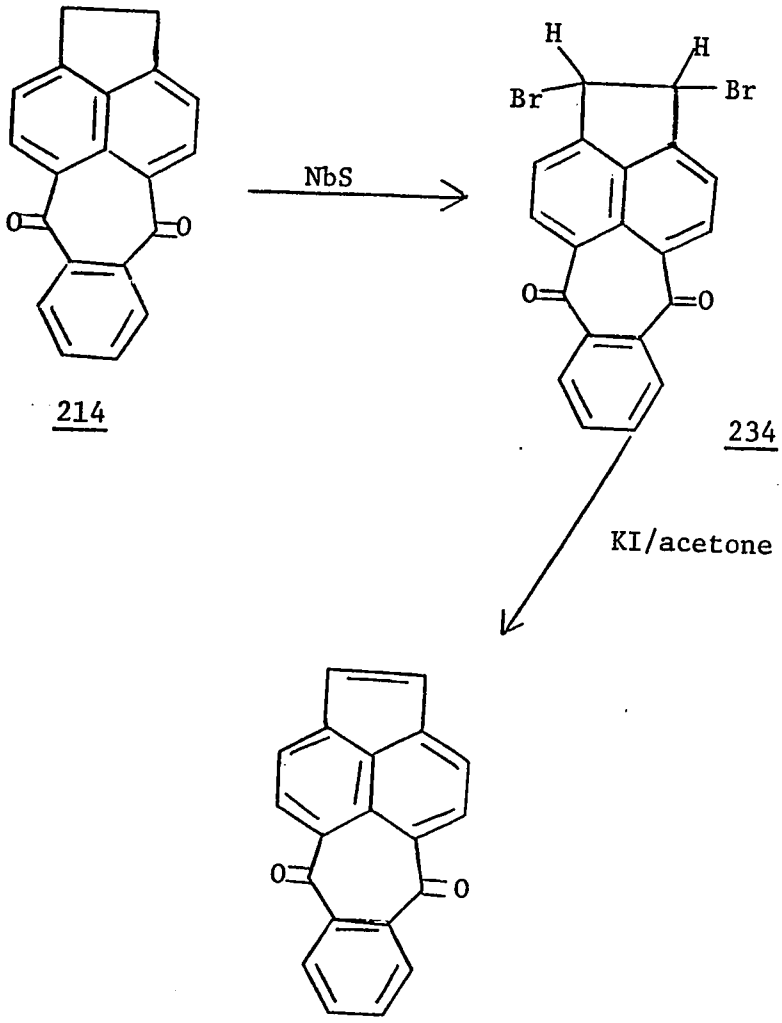
Compound 235 was prepared as illustrated in Scheme XXXII. 5,10-Dihydroacepleiadene-5,10-dione was treated with two molar equivalents of N-bromosuccinimide to give the dibromide 234, which was debrominated by treatment of its acetone solution with potassium iodide.

Figure II

First-derivative e.s.r. spectrum of Acepleiadylene-5,10-semidione anion formed from 5,10-Dihydroacepteiadene-5,10-dione ($1x10^{-2}$ M) in Dimethylsulfoxide Solution Containing Potassium tert-butoxide ($2.5x10^{-2}$ M) at ambient Temperature.



SCHEME XXXII



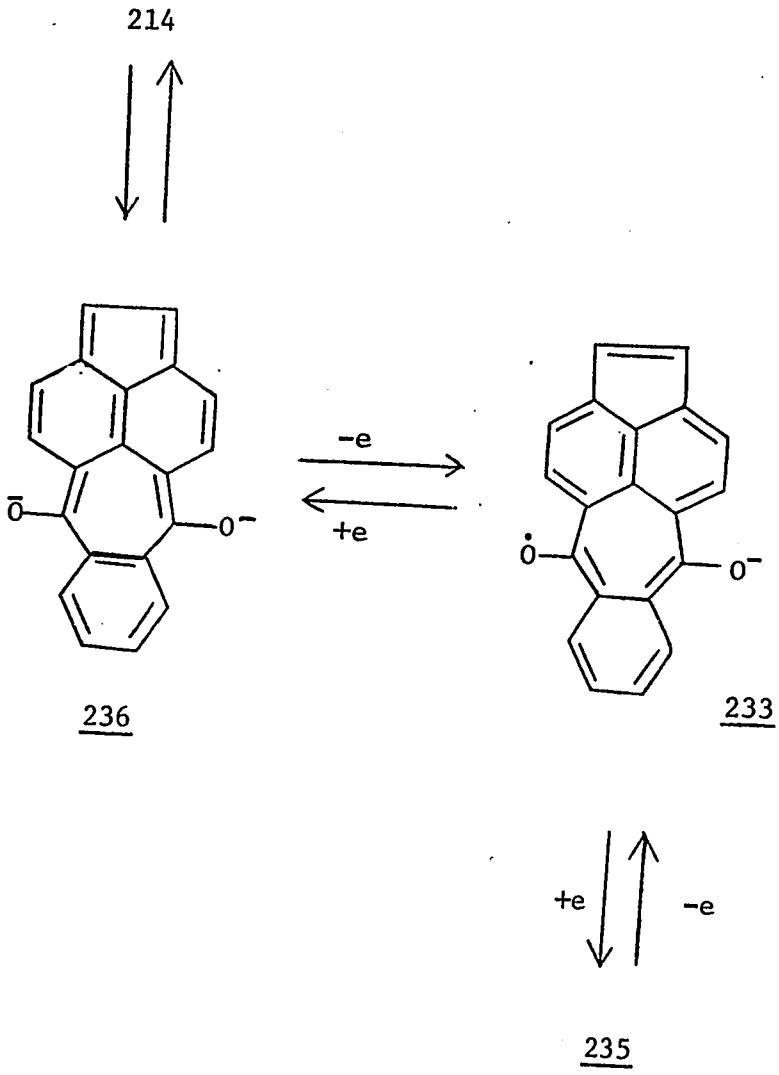
214

234

235

The formation of the radical anion 233 from both 214 and 235 may be rationalised as illustrated in Scheme XXXIII.

SCHEME XXXIII



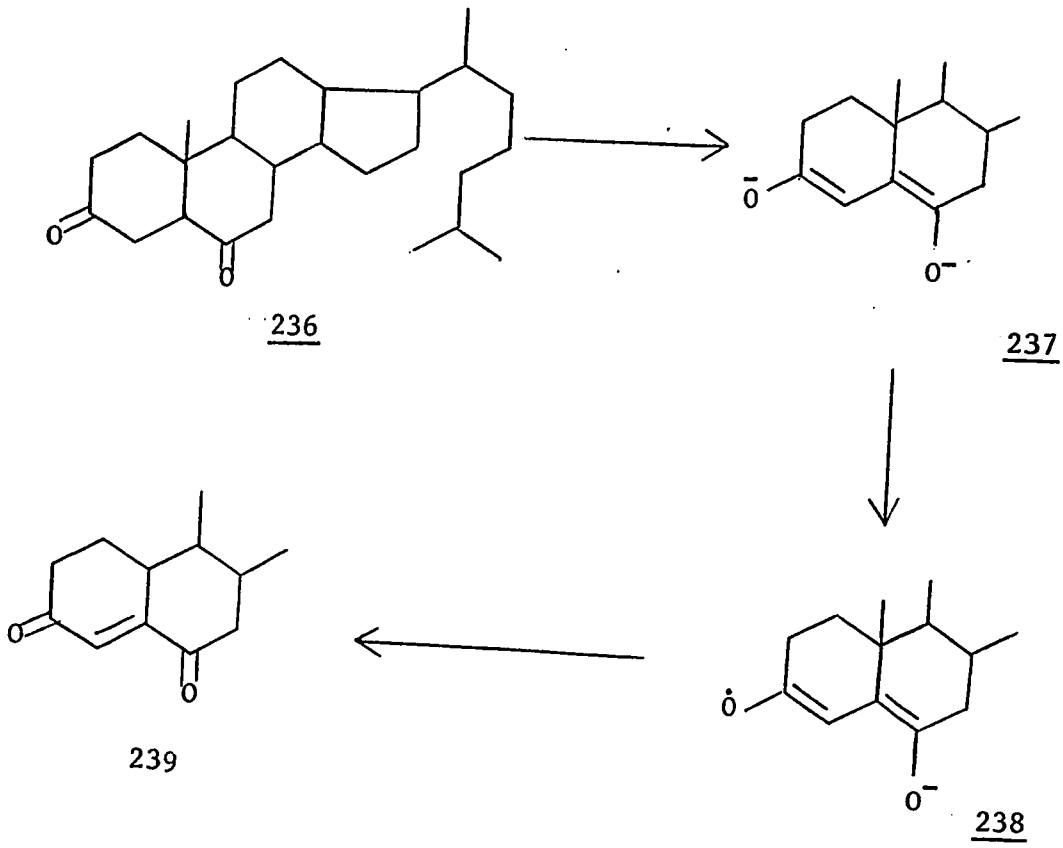
236 233 235

5,10-Dihydroacepleiadene-5,10-dione is converted to the dienolate ion 236 which reacts with oxygen to generate the anion radical 233. Finally, 233 is oxidized further to 235.

Dauben (139) has suggested the same mechanism to be operative in the conversion of cyclic 1,4-diketones, to corresponding

enediones, by shaking alkaline alcoholic solution of the diketones with air, (see Scheme XXXIV). The generation of the semidione anion

SCHEME XXXIV



236 237 238 239

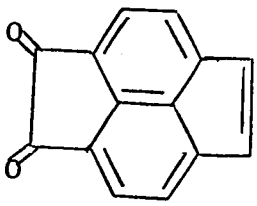
233 lends support to this mechanism.

When $1x10^{-3}$ molar solution of 214 in dimethylsulfoxide was mixed with a $2.5x10^{-3}$M solution of potassium tert-butoxide in dimethylsulfoxide the electron spin resonance spectrum obtained showed further splitting of the eleven lines obtained above (see Fig. III).

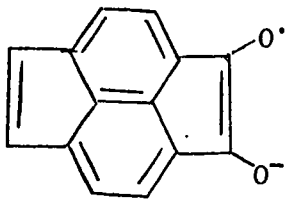
Further support for the structure of the radical ion was obtained by reduction of 5,10-dihydroacepleiadylene-5,10-dione with

potassium in 1,2-dimethoxyethane. The electron spin resonance spectrum obtained had the same gross features as that obtained from 5,10-dihydroacepleiadene-5,10-dione in dimethylsulfoxide, but differed in details as would be expected for radicals generated under two rather different conditions. The distribution of charges in an aromatic radical anion has been shown to be affected by the nature of the solvent (140-143). Trost and co-workers (144) found differences in the spectra of pyracyclosemiquinone anion 241 generated from 1,2-diketopyracene 240 by (i) potassium tert-butoxide reduction in dimethylsulfoxide, and (ii) irradiation of 1,2-dimethoxyethane solution in presence of sodium or potassium hydroxide. The spin density variation with solvents is assumed, to a first approximation,

[80]



240



241

to be affected only by localised complexes between solvent and polar substituents in the radical anion (141). In general as the solvating ability of the solvent increases the hyperfine splitting constants increase (145). Attempts were made to assign hyperfine splitting constants (a_H) to the protons of the acepleiadylene semidione anion, see Table VI. It must be emphasised that these assignments are very approximate, and do not give the correct a_H values. They represent the closest fit, of the experimental spectrum

Figure III

First-derivative e.s.r. spectrum of Acepleiadylene-5,10-semidione anion formed from 5,10-Dihydroacepleiadene-5,10-dione ($1x10^{-3}M$) in Dimethylsulfoxide Solution containing Potassium tert-butoxide ($2.5x10^{-3}M$) at ambient Temperature.

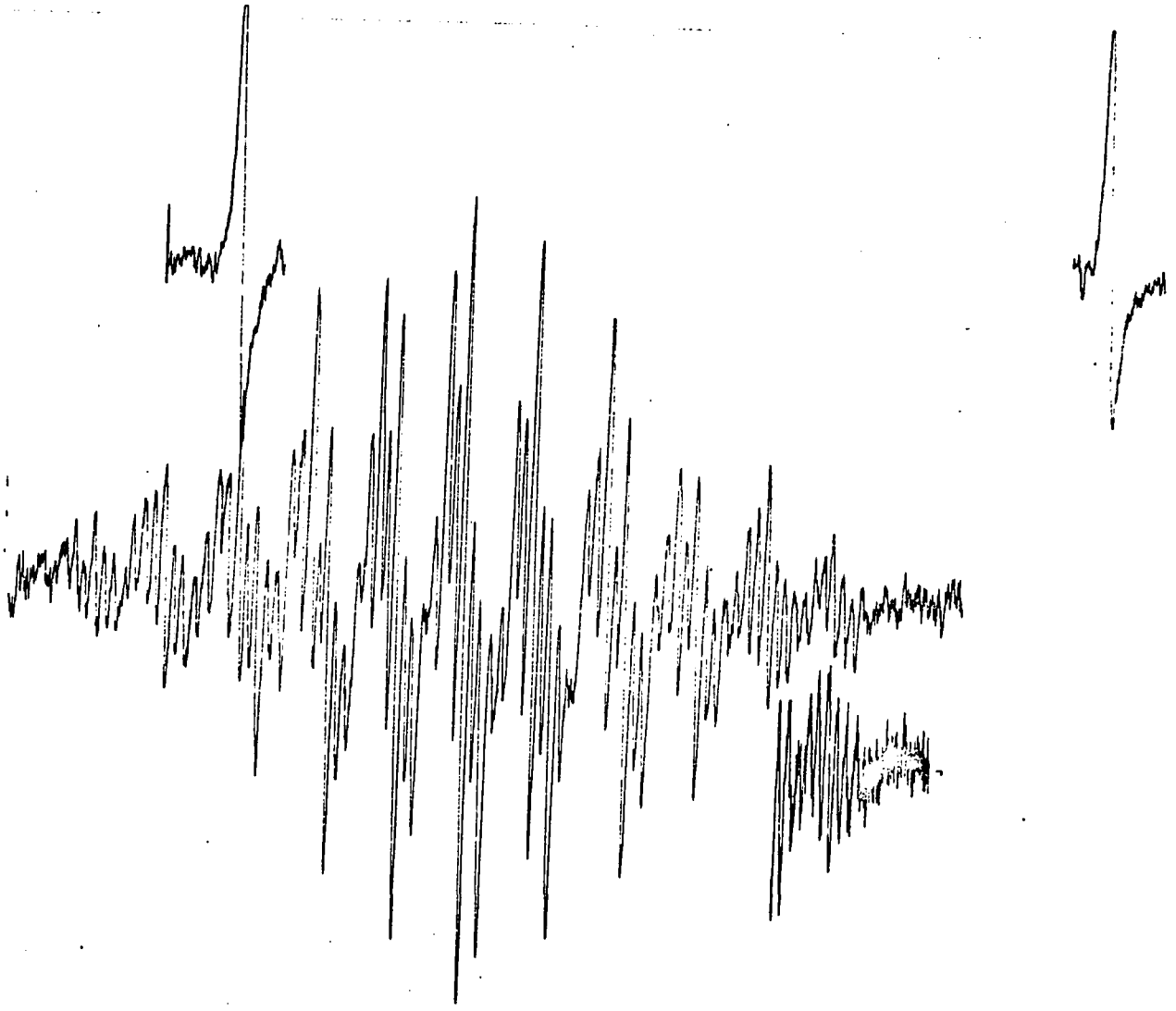
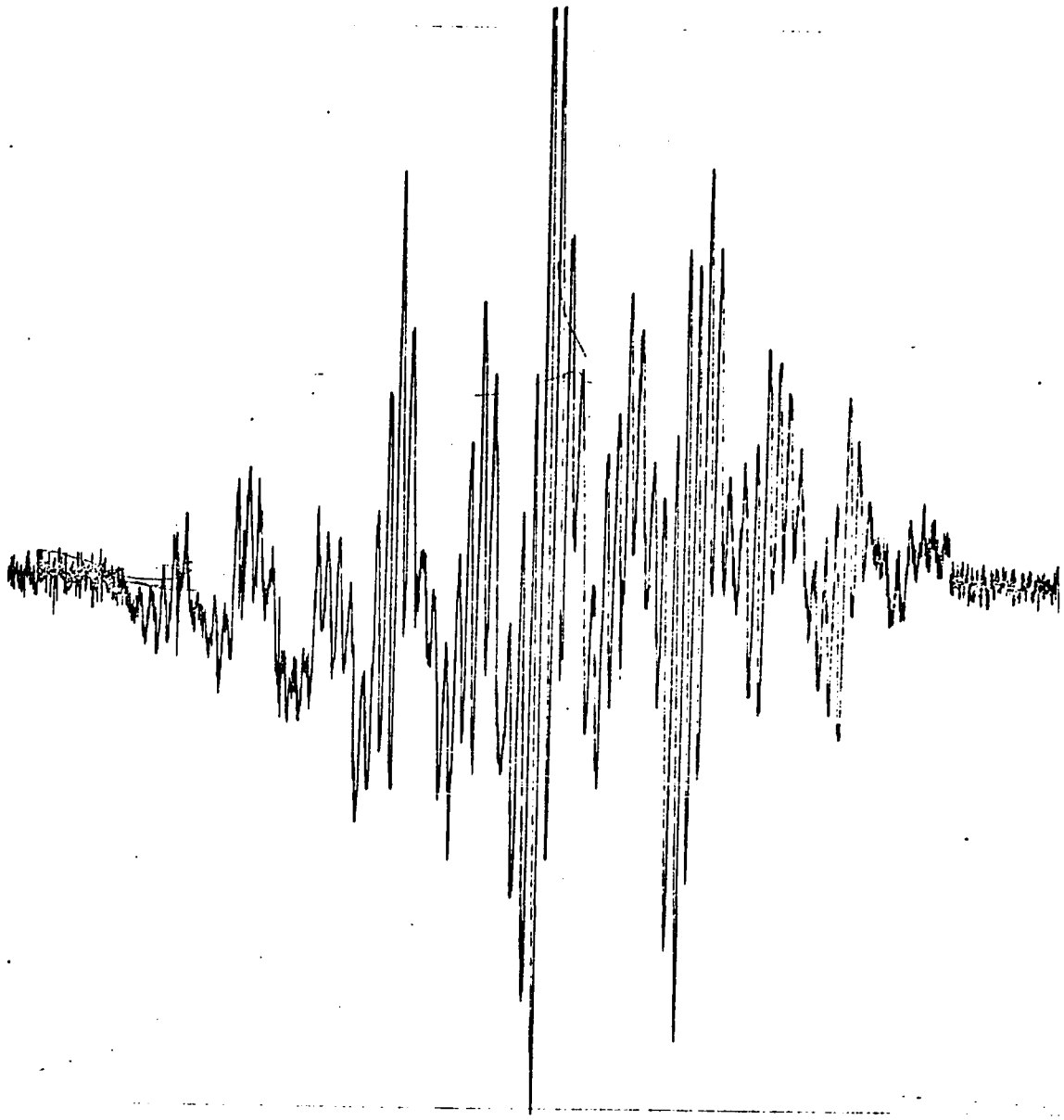
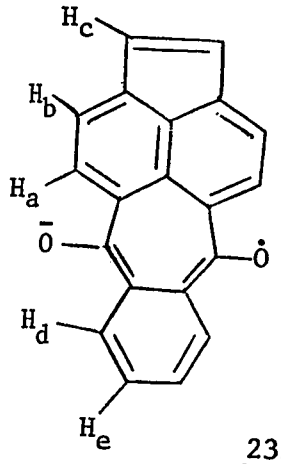


Figure IV

First-derivative e.s.r. spectrum of Acepleiadylene-5,10-semidione anion formed from 5,10-Dihydroacepleiadylene-5,10-dione by treatment with Potassium metal in 1,2-Dimethoxyethane.



that could be obtained by simulation of the spectrum. The decision as to which a_H value is assigned to which protons was based on a very rough calculation of the unpaired electron densities at each carbon atom (Table VI). Though these do not correlate directly to the a_H values assigned, they give a qualitative picture of the magnitudes of these splitting constants.



233

One of the most stable paramagnetic species is the superoxide anion $\cdot O\text{-}O^-$; and its organic derivatives are among the most stable radical anions known which possess an appreciable spin density on a carbon atom. The phenylogues of the superoxide, the semiquinones, are well known and have been examined exhaustively (146-151). The semidiones which are the vinylogues of the superoxides have been extensively studied by Russell and co-workers (137,138).

TABLE V

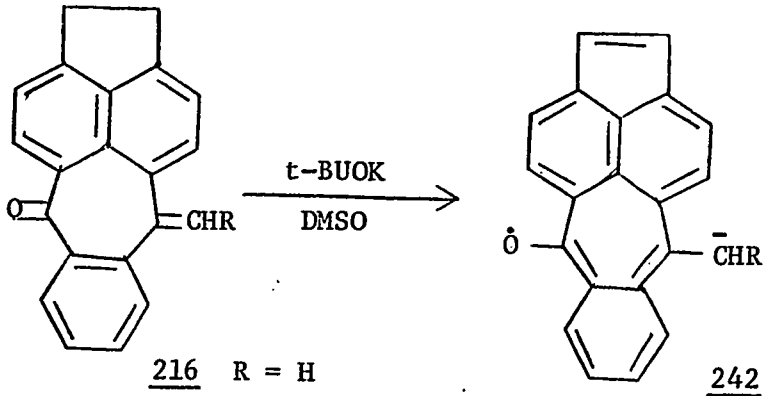
Hydrogen	Estimated Unpaired Electron Spin Density	Estimated Hyperfine Splitting Constant in gauss
a	0.09184	2.50
b	0.04319	1.11
c	0.06107	1.85
d	0.01865	0.30
e	0.01587	0.15

The 7,12-acepleiadylene semidione anion 233 represents an extension in this series. Its stability is undoubtedly due to the aromaticity of the acepleiadylene framework, thus the driving force for the formation of 233 from 214 and 235 is the gain in resonance energy of the acepleiadylene moiety. There are 18π-electrons in the periphery of this framework, which satisfies the Huckel's 4n+2 rule for aromaticity. The radical anion 233 is much more stable than the parent hydrocarbon generated by Cava and Schlessinger, by dehydration of 5,10-dihydroxy-5,10-dihydroacepleiadene (see eqn. [77]), which retained its blue color for only 40 mins. at room temperature. This new radical anion is particularly interesting because it has in its framework the elements of o-quinodimethane which we had set out to generate.

The facile formation of the radical anion 233 from 214 suggested examination of derivatives of 214 under similar conditions. Accordingly a $1x10^{-3}$ molar solution of 5-methylene-5,10-dihydro-acepleiaden-10-one 216 in dimethylsulfoxide was treated with

potassium tert-butoxide, to give a paramagnetic species whose electron spin resonance spectrum is shown in Fig. V. This spectrum is attributed to the radical anion 242.

[81]



216 R = H

243 R = Ph

242 R = H

244 R = Ph

5-Benzylidene-5,10-dihydroacepleiaden-12-one 243 was also found to give an electron spin resonance signal on treatment with potassium tert-butoxide in dimethylsulfoxide, as shown in Fig. VI. This spectrum is attributed to radical anion 244.

Compound 243 was prepared by the same sequence as for 216. Reaction of 5,10-dihydroacepleiadene-5,10-dione with benzylmagnesium chloride in ether gave the alcohol 245. Acid catalysed dehydration of 245 afforded 243.

The radical anions 242 and 244, are novel; they represent the first time to our knowledge radical anions of this type have been generated. An analogy in simple aromatic series would be generation of radical anions from p-quinomethides, e.g. 9-methyleneanthrone 246.

Figure V

First-derivative e.s.r. spectrum of 5-Methylene-5,10-dihydro-acepleiaden-12-one Radical Anion, formed from 5-Methylene-5,10-dihydroacepleiaden-12-one ($1x10^{-3}$ M) in Dimethylsulfoxide solution containing Potassium tert-butoxide ($2.5x10^{-3}$ M) at ambient Temperature.

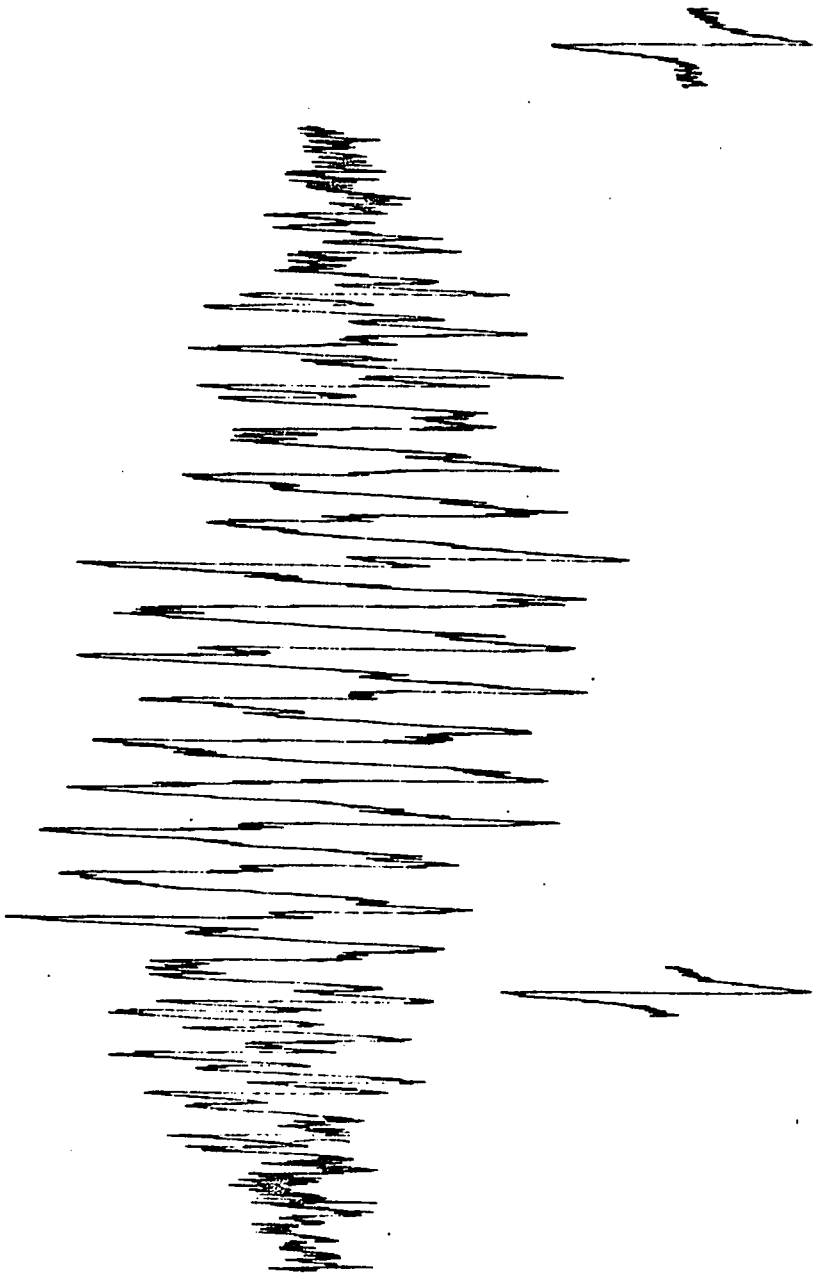
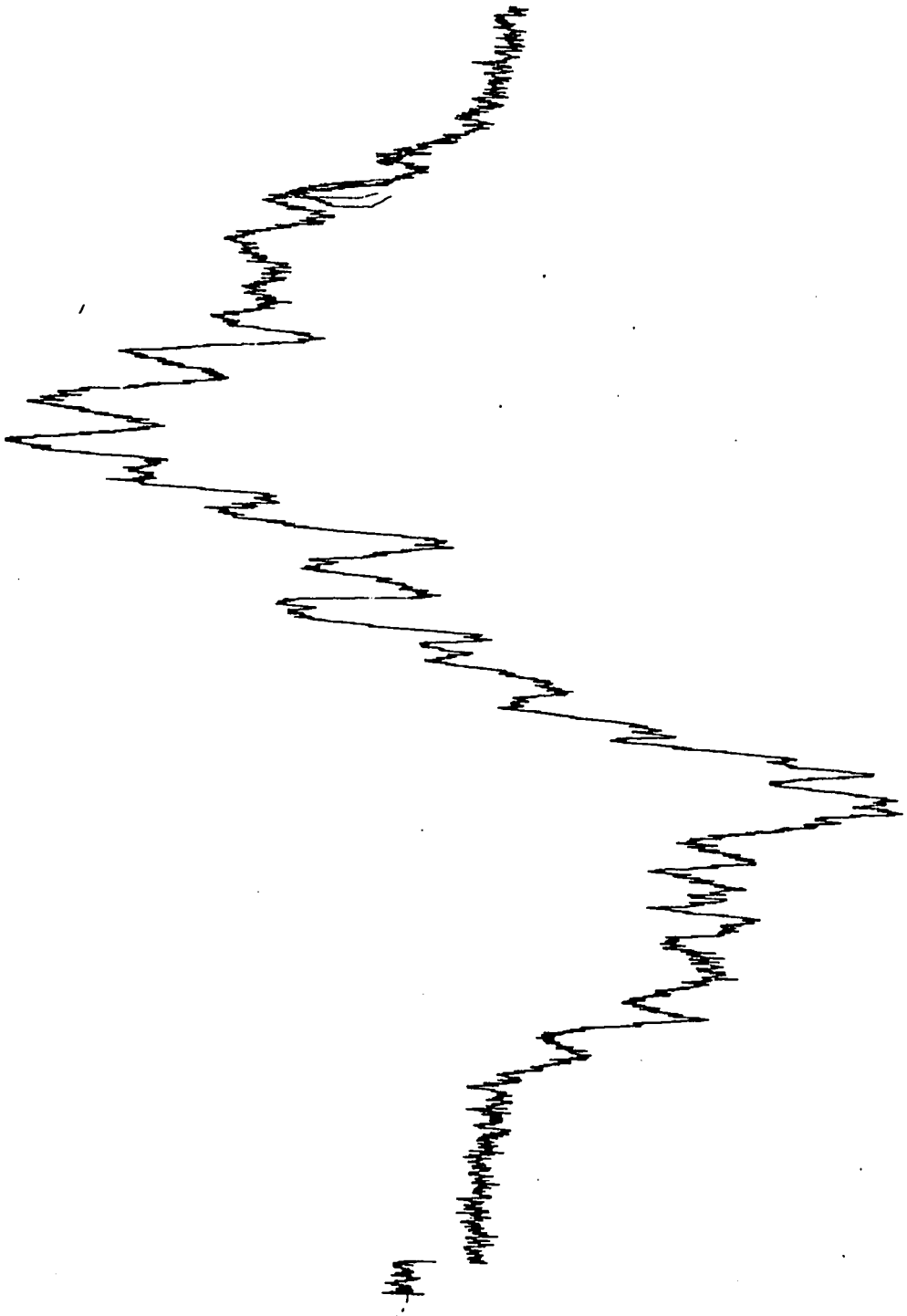
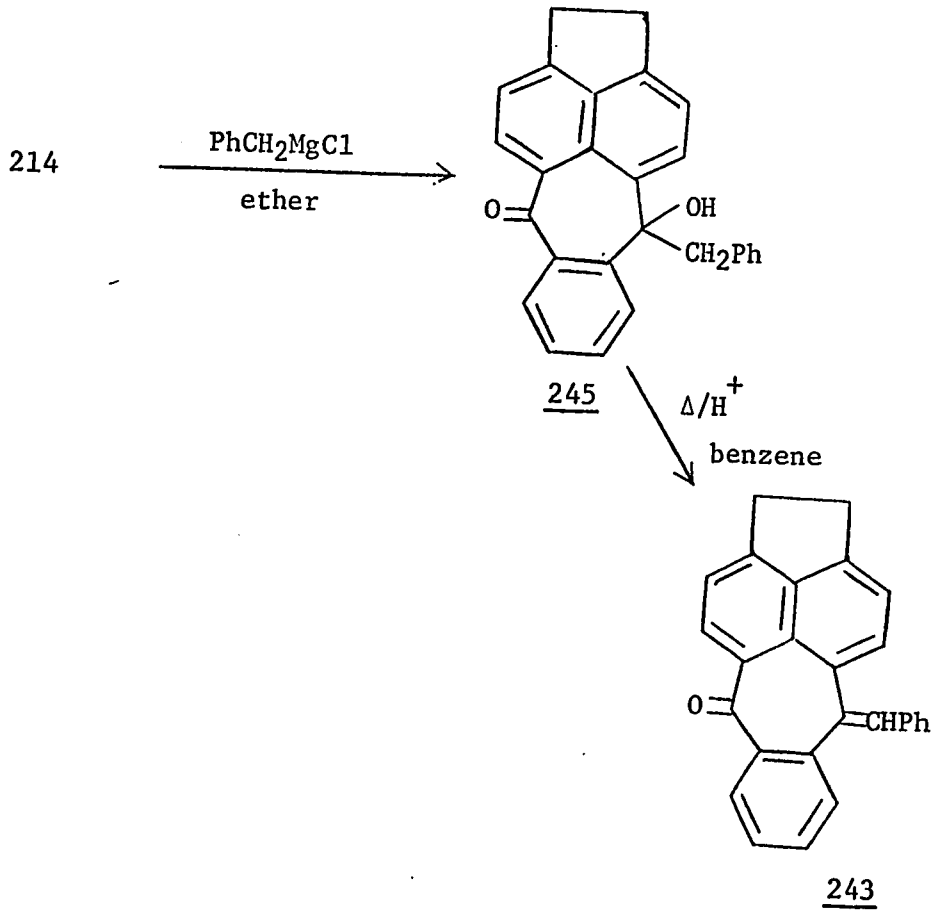


Figure VI

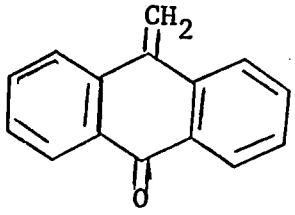
First-derivative e.s.r. spectrum of 5-Benzylidene-5,10-dihydro-acepleiaden-12-one Radical Anion, formed from 5-Benzylidene-5,10-dihydroacepleiaden-12-one ($3x10^{-3}$ M) in Dimethylsulfoxide solution containing Potassium tert-butoxide ($7.5x10^{-3}$ M) at ambient Temperature.



SCHEME XXXV



No such radical anion has been reported in the literature. The stability of these radicals generated above, as in 233, must be due to aromatic character of acepleiadylene framework.



246

SUMMARY

Quinone dehydrogenation of hydroaromatics has been extended to arenes.

In Chapter II, the reactions of DDQ and TOQ with methyl substituted aromatic compounds led to adduct formation. The reaction of dimethylnaphthalenes with DDQ gave monoquinol ethers; whilst with TOQ dioxoles were formed. Dioxoles were also formed by 1,4 and 2,3-dimethylanthracenes, and 9,10-dimethylpehnanthrene with TOQ.

The formation of these dioxoles have been rationalised as proceeding by two consecutive dehydrogenations at one methyl group. The inertness of the second methyl group towards quinone dehydrogenation has been attributed to the deactivating influence of the dioxole moiety.

9,10-Dimethylanthracene on the other hand formed adducts with both DDQ and TOQ which have been interpreted as involving the intermediacy of 9,10-anthraquinodimethane.

In general the reactivity of the methyl groups in these arenes towards quinones increased with the number of fused rings.

In Chapter III, quinodehydrogenation was extended to the dihydropleiadene compounds. Mostly, the reactions resulted in adduct formation. The adducts formed by DDQ have been rationalised as involving pleiadenes as intermediates, whilst those formed by TOQ have been rationalised as involving two consecutive quinone dehydrogenations.

In addition to adduct formation, cyclodehydrogenation, and direct oxidation of a methylene group to a ketone were also observed.

The various products formed have been explained on the basis of the geometry of the dihydropleiadene system and the conformational preference of substituents at the bridge-head positions.

In Chapter IV "quinodimethane analogues" of pleiadene and acepleiadene series have been prepared and found to be stable dienes. Also some novel acepleiadylene radical anions have been generated. The stability of these radicals have been attributed to the aromatic character of the acepleiadylene hydrocarbon framework.

EXPERIMENTAL

5-Methylene-5,10-dihydroacepleiaden-12-one

A suspension of 2.84 g (0.01 m) of 5,10-dihydropleiadene-5,10-dione in 50 ml of dry benzene was added to a Grignard reagent prepared from 4.3 g of magnesium and 22.5 g of iodomethane in 150 ml of anhydrous ether. The mixture was stirred for 30 mins; 70 ml of ether was distilled off and replaced by 50 ml of dry benzene. The reaction mixture was then refluxed overnight, cooled decomposed with ice and saturated ammonium chloride solution, organic layer dried ($MgSO_4$), and solvent removed *in vacuo* to give a light yellow solid, 215.

Infrared spectrum ν_{max} ($CHCl_3$): 3605, 3576 cm^{-1} (O-H).

N.m.r. δ_{TMS} ($CDCl_3$): 2.1 (3H, singlet methyl protons); 3.26 (4H, C_1,C_2 - protons).

Compound 215 without further purification was dissolved in benzene and a small amount of p-toluenesulfonic acid added to the solution. The mixture was refluxed for 4 hrs. cooled washed with water, sodium bicarbonate solution, and water; the benzene solution dried, concentrated and subjected to chromatography on B.D.H. alumina using benzene as eluent to give 1.5 gm (88.2%) of 216 as brilliant yellow solid, m.p. 202-205°.

Anal. Calcd. for $C_{21}H_{14}O$: C, 89.37; H, 4.96.

Found: C, 88.94; H, 4.95.

Mol. wt. calcd. 282.1045. Found (mass spectrum): 282.1040.

Infrared spectrum ν_{max} ($CHCl_3$): 1648 cm^{-1} (C = O).

N.m.r. spectrum δ_{TMS} ($CDCl_3$): 3.41 (4H, singlet, C_1 and C_2 protons); 5.42, 5.50 (2H, pair of doublets, J = 1.5 Hz, $=CH_2$); 7.2-8.4 (8H, aromatic protons).

Reaction of 5-Methylene-5,10-dihydroacepleiaden-12-one with Methylmagnesium Iodide

A methyl magnesium iodide was prepared from 2.4 g of magnesium and 14.5 g of iodomethane, in 100 ml of anhydrous ether; 2.0 g (0.007 M) of 5-methylene-5,10-dihydroacepleiaden-12-one was added to it a little at a time, with stirring. Stirring was continued for 8 hrs, the complex decomposed with ice and ammonium chloride; the ether layer dried (Na_2SO_4) and solvent removed to give a light yellow oil.

This oil was dissolved in benzene and subjected to chromatography on silicic acid (pH 7), using hexane as eluant to give 0.5 g (25.3% yield) of 218 as a light yellow oil, which solidified on standing, m.p. 85-87°.

Anal. calcd. for $C_{22}H_{16}$: C, 94.28; H, 5.72.

Found: C, 94.30; H, 5.78.

Mol. wt. Calcd. 280.1252. Found (mass spectrum): 280.1253.

N.m.r. spectrum δ_{TMS} ($CDCl_3$): 3.27 (4H, singlet, C_1,C_2 protons). 5.3, 5.56 (4H, a pair of doublet, J = 1.5 Hz, $=CH_2$); 7.05-7.65 (8H, multiplet, aromatic ring protons).

Further elution with benzene gave 0.7 g (33.6% yield) of 217, m.p. 222-224°.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.59, H, 6.04.

Found: C, 88.46; H, 6.12.

Mol. wt. Calcd.: 298.1357. Found: 298.1355.

N.m.r. spectrum δ_{TMS} ($CDCl_3$): 2.15(6H, singlet, methyl protons); 3.23

(4H, singlet, C_1,C_2 bridge protons); 7.05-7.43 (8H, multiplet, aromatic protons).

7-Hydroxy-7-methyl-7,12-dihydropleiaden-12-ene

7-Methylene-7,12-dihydropleiaden-12,-one (0.5 g, 19.5 mmoles) was added to a Grignard reagent (0.5 g and 3 g iodomethane in 30 ml of anhydrous ether), and stirred for 30 mins. The mixture was then refluxed gently for another 30 mins, stirring continued overnight, cooled, and the complex decomposed with ice and saturated solution of ammonium chloride. The ether layer was washed with water, dried ($MgSO_4$), and solvent removed to yield a gum which was titurated with hexane to give 0.41 g (77.3%) of crystalline solid, m.p. 114-116°.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.24; H, 5.88.

Found: C, 88.07; H, 5.90.

Mol. wt. Calcd.: 272.1201. Found (mass spectrum) 272.1200.

Infrared spectrum ν_{max} ($CHCl_3$): 3690, 3610, 3580 cm^{-1} (O-H).

N.m.r. spectrum δ_{TMS} ($CDCl_3$): 1.97 (3H, singlet, C_7-methyl protons); 5.6, 5.2 (2H, pair of doublets J_{AB} = 1.5 Hz, C_{12}-methylene protons); 7.3-8 (11H, multiplet, aromatic ring protons + O-H).

7-12-Dimethylene-7,12-dihydropleiadene and 7,12-Dimethy-7,12-epoxy-7,12-dihydropleiadene

7-Methylene-7,12-dihydropleiaden-12-one (1 g, 0.004 moles) was added with stirring over 30 mins. to a Grignard reagent, prepared from 1 g of magnesium and 6 g of iodomethane in 30 ml of anhydrous ether. Dry benzene (30 ml) was then added to the mixture and refluxed

with stirring overnight, cooled, and decomposed with ice and ammonium chloride solution. The organic layer was washed with water, dried, and solvent removed in vacuo to yield a gum. This gum was dissolved in benzene and subjected to chromatography on B.D.H. silica gel using hexane as eluant to give 26 mg (25% yield) of 220. M.p. 91-93° [lit. (135) 88-90)].

Infrared spectrum ν_{max} (CCl_4): 1625 cm^{-1} (C=C).

N.m.r. spectrum δ_{TMS} (CCl_4): 5.22, 5.49 (4H, a pair of doublets, J = 2Hz, $=CH_2$); 7.0-7.8 (10H, multiplet, aromatic protons).

Further elution with benzene gave 0.65 g (60% yield) of 221, m.p. 152-153°.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.24; H, 5.88.

Found: C, 88.13; H, 5.69.

Mol. wt. Calcd. 272.1201. Found (mass spectrum) 272.1200.

N.m.r. spectrum δ_{TMS} ($CDCl_3$): 2.13 (6H, singlet, methyl protons); 7.0-7.75 (8H, multiplet, aromatic protons).

Dehydration of 7,12-Dimethyl-7,12-epoxy-7,12-dihydropleiadene

A mixture of 1.4 g (5 mmoles) of 221, and 0.5 g of potassium hydrogen sulfate was heated in an oil bath at 140° for 15 mins. The mixture was cooled and extracted with hexane, and hexane solution subjected to chromatography on silicic acid (pH 7) to give 1.1 g (85% yield) of 220.

7-Dicyanomethane-12-hydroxy-7,12-epoxy-7,12-dihydropleiadene

7,12-Dihydropleiadene-7,12-dione 6.5 g (0.025 moles) and 10 g (0.15 moles) of malonitrile were mixed in 60 ml of dichloromethane,

and 2.5 ml of triethylamine was added dropwise to the mixture with shaking. The reaction mixture was allowed to stand for 10 mins, whereupon a white solid separated out of solution. This was collected by filtration washed thoroughly with dichloromethane, and crystallised from acetone to give 6.3 g (78% yield) of 229, m.p. 250°.

Anal. Calcd. for $C_{21}H_{12}N_2O_2$: C, 77.78; H, 3.70; N, 8.64.

Found: C, 77.76; H, 3.76; N, 8.54.

Mol. wt. Calcd. 324.0889. Found (mass spectrum) 324.0889.

Infrared spectrum ν_{max} (Nujol) 3690 cm^{-1} (O-H) 2225 cm^{-1} (C≡N).

N.m.r. spectrum δ_{TMS} ($CD_3C{=}O$): 5.67 (1H, $\underline{CH}\langle^{CN}_{CN}$); 7.25-8.20 (11H, multiplet, aromatic protons + O-H).

7-Dicyanomethylene-7,12-dihydropleiaden-12-one

7-Dicyanomethane-12-hydroxyl-7,12-epoxy-7,12-dihydropleiadene, 4 g (0.12 moles) was suspended in chloroform, and acetic anhydride added until the mixture was homogeneous. The mixture was then refluxed for 2 hr, concentrated and allowed to cool; the crystals formed collected by filtration and washed with ether. Yield was 3 g (81.7%), m.p. 230°.

Anal. Calcd. for $C_{21}H_{10}N_2O$: C, 82.35; H, 3.27; N, 9.15.

Found: C, 81.79; H, 3.30; N, 8.92.

Mol. wt. Calcd. 306.0793. Found (mass spectrums) 306.0794.

Infrared spectrum ν_{max} (Nujol): 1660 cm^{-1} (C=O) 2218 cm^{-1} (C=N).

7,12-Dis-(dicyanomethyl)-7,12-epoxy-7,12-dihydropleiadene

7-Dicyanomethylene-7,12-dihydropleiaden-12-one 1.55 g (0.005 moles) and 2 g (0.03 moles) of malonitrile were mixed in 20 ml

of dichloromethane, and the mixture treated dropwise with triethylamine until the mixture was homogeneous. On standing for 20 mins. with stirring white solid crystallised out of solution. This was collected and washed with acetone to give 1.34 g (76.1%) of 7,12-bis-(dicyanomethyl-7,12-epoxy-7,12-dihydropleiadene, m.p. 230-232°.

Anal. Calcd. for $C_{24}H_{12}N_4O$: C, 77.41; H, 3.23; N, 15.05.

Found: C, 76.93; H, 3.50; N, 14.70.

Mol. wt. Calcd: 372.1011. Found (mass spectrum) 372.1012.

Infrared spectrum ν_{max} (Nujol) 2105, 2178 cm^{-1} (C=N).

N.m.r. spectrum δ_{TMS} $(CD_3)_2SO$): 4.47 (2H, singlet - $\underline{CH}\begin{matrix}CN\\CN\end{matrix}$); 7.3-8.20 (10H, multiplet, aromatic protons).

1,2-Dibromo-5,10-dihydroacepleiacene-5,10-dione

N-Bromosuccinimide (5.34 g, 0.030 moles) was added to a refluxing solution of 4.26 g (0.015 moles) 5,10-dihydroacepleaidene-5,10-dione and benzoyl peroxide in carbon tetrachloride, over a period of 10 mins and refluxing was continued for an additional 1¼ hr. The succinimide was removed, and the mother liquor concentrated and cooled to give a dull yellow solid. This was further crystallised from carbon tetrachloride to give 6.5 g (98%) of 234, m.p. 200°.

Anal. Calcd. for $C_{20}H_{10}Br_2O_2$: C, 54.30; H, 2.26; Br, 36.20.

Found: C, 54.40; H, 2.27; Br, 36.41.

Mol. wt. Calcd.: 439.9047. Found (mass spectrum): 439.9046.

Infrared spectrum ν_{max} ($CHCl_3$) 1650 cm^{-1} (C=O).

N.m.r. spectrum δ_{TMS} ($CDCl_3$): 5.95 (2H, singlet, C_1,C_2 protons); 7.5-8.1 (8H, multiplet, aromatic protons).

5,10-Dihydroacepleiadylene-5,10-dione

1,2-Dibromo-5,10-dihydroacepleiadene-5,10-dione (3.08 g 0.07 moles) was dissolved in 300 ml of acetone, and 15 g of potassium iodide was added to the solution under nitrogen. The reaction mixture was refluxed for 3 hrs, cooled poured into sodium thiosulphate solution and extracted with chloroform. The chloroform layer was dried (Na_2SO_4) and solvent concentrated to give a red solid, which was recrystallised from methanol to give brick red flakes. Yield was 1.4 g (71%), m.p. 196-198°.

Anal. Calcd. for $C_{20}H_{10}O_2$: C, 85.11; H, 3.55.

Found: C, 84.87; H, 3.53.

Mol. wt. Calcd: 282.0681. Found (mass spectrum): 282.0678.

Infrared spectrum ν_{max} ($CHCl_3$): 1660 cm^{-1} (C=O).

N.m.r. spectrum: δ_{TMS} ($CDCl_3$): 7.05 (2H, singlet, C_1,C_2 protons); 7.55-8.40 (8H, multiplet, aromatic protons).

5-Benzylidene-5,10-dihydroacepleiaden-12-one

5,1-Dihydroacepleiadene-5,10-dione 2.84 g (0.001 moles) was added a little at a time to a Grignard reagent prepared from 2 g of magnesium and 13 g of benzylchloride in 200 ml of ether. 100 ml of the ether was distilled off and replaced by 100 ml of dry benzene and the mixture refluxed for 8 hrs. The complex was then decomposed with ice and saturated solution of ammonium chloride. The organic layer was dried (Na_2SO_4) and the solvent was removed in vacuo to give a brilliant yellow solid, 245 (from its infrared, and n.m.r.).

Infrared spectrum ν_{max} ($CHCl_3$): 3530 cm^{-1} (O-H) 1653 cm^{-1} (C=O).

N.m.r. spectrum δ_{TMS} ($CDCl_3$): 3.5 (4H, singlet, C_1,C_2 protons); 5.13 (2H, singlet, $-\underline{CH_2}-Ph$); 7.25-8.2 (13H, multiplet, aromatic protons).

This yellow solid, without further purification was dissolved in benzene, p-toluenesulfonic acid added to the solution and refluxed for 3 hrs. Worked up as for 216 gave 1.4 g (37.2% yield) of 5-benzylidene-5,10-dihydroacepleiaden-12-one, m.p. 182-184°.

Anal. Calcd. for $C_{27}H_{18}O$: C, 90.48; H, 5.24.

Found: C, 90.51; H, 5.24.

Infrared spectrum ν_{max} ($CHCl_3$): 1645 cm^{-1} (C=O).

N.m.r. spectrum δ_{TMS} ($CDCl_3$) 3.6 (4H, singlet, C_1,C_2 protons); 6.7 (1H, singlet, $=\underset{\underline{H}}{\overset{Ph}{<}}$); 6.87-84 (13H, multiplet, aromatic protons).

Electron Spin Resonance Determinations

(a) Generation of Radical Anion in Dimethylsulfoxide

The dimethylsulfoxide used was dried with sodium sulfate, distilled and kept standing on molecular sieve.

The radical anions were generated according to the method of Russell and Strom (152). Solutions of the diketones in dimethylsulfoxide were placed in one leg of an inverted U-cell; the potassium tert-butoxide in dimethylsulfoxide was placed in the other leg, and both solutions simultaneously deoxygenated by streams of prepurified nitrogen. After about 15-20 min of deoxygenation, the solutions were mixed by inverting the cell and the final solution was shaken into the sample cell, and the electron spin resonance spectrum recorded, using Varian V4500 with 12 in magnet, operating at 9.5 gigacycles. Fremy's salt in saturated sodium carbonate was used as

a calibration standard.

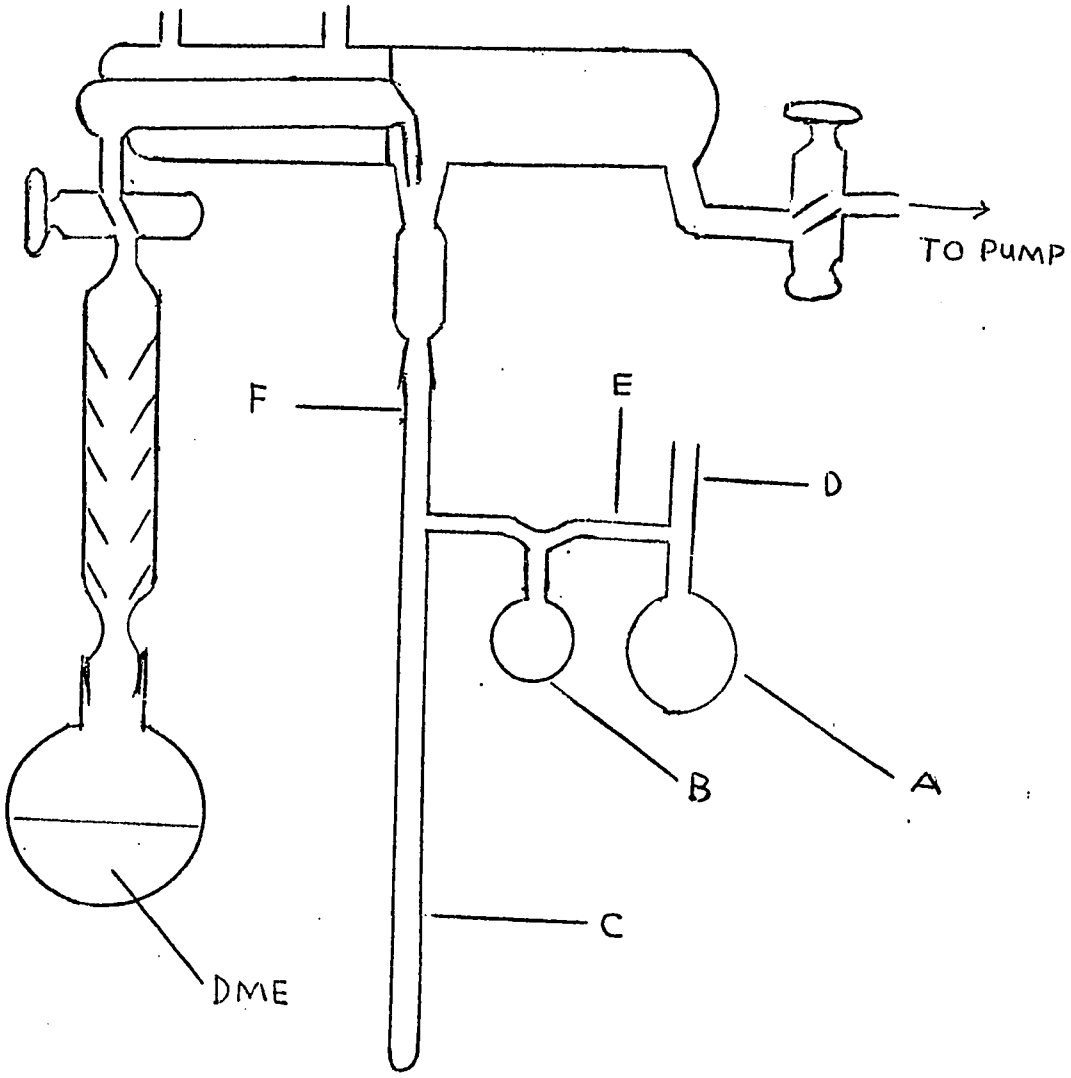
(b) Generation of Radical Anion by Reduction of 5,10-Dihydro-acepleiadylene-5,10-dione with Potassium in 1,2-Dimethoxyethane

The dimethoxyethane used was dried over sodium and distilled. It was kept standing on freshly-cut sodium.

The apparatus used is sketched in Fig. VII. About 6 mg of 235 was placed in the sample tube and the apparatus set up as shown in the diagram. Small pieces of freshly cut potassium was placed in bulb A, and the cell sealed off at D. The whole set-up was then evacuated and some potassium distilled into the bulb B. The cell was then sealed off at E. Dimethoxyethane was then distilled into the sample tube C, to dissolve the sample. The cell was then sealed off at F, allowed to cool and inverted to allow the solution to come into contact with the potassium for about 2 min. After about 15 min, the solution went blue, indicating the formation of the radical anion, and the electron spin resonance spectrum was recorded as for (a).

Figure VII

Diagram of Apparatus used in Generation of Acepleiadylene-5,10-semidione anion from 5,10-Dihydroacepleiadylene-5,10-dione by Reduction with Potassium metal in 1,2-Dimethoxy ethane.


TO PUMP
F
E
D
B
A
C
DME

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