Dehydrogenation of 7,12-Dihydropleiadene Compounds with High Potential Quinones

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Dehydrogenation with high potential quinones has been extended to dihydro derivatives of nonaromatic hydrocarbons using 7,12-dihydropleiadenes as models. Reaction of 7-phenyl-7,12-dihydropleiadene with high potential quinones resulted in dehydrogenative cyclization whereas preparative scale and rate studies in 9-aryl-9,10-dihydroanthracenes gave no evidence of aryl participation during quinone dehydrogenation due to geometrical restrictions on this system.

Utilisant les dihydro-7,12 pléiadènes comme modèles, on a étendu aux dérivés dihydrogénés des hydrocarbures non aromatiques la méthode de déshydrogénation faisant appel aux quinones à haut potentiel. La réaction du phényl-7 dihydro-7,12 pléiadène avec de telles quinones provoque une cyclisation déshydrogénante; par ailleurs des études tant préparatives que cinétiques sur des aryl-9 dihydro-9,10 anthracènes n'ont fourni aucune preuve que les restrictions géométriques imposées à ce système provoquent une participation du groupe aromatique au cours de ces déshydrogénations.

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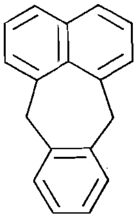
Dehydrogenation of hydroaromatic compounds with high potential quinones is an important reaction widely used in synthetic schemes and in the oxidation of natural products (1). A substantial part of the driving force for the two-step ionic mechanism, proceeding by initial hydride transfer to the quinone is thought to be provided by the net resonance energy gain in both the quinone (acceptor) and the hydroaromatic compound (donor) which is thereby aromatized (2). In previous publications (3, 4) we demonstrated that aralkyl groups may react further with quinones often with surprising ease (*e.g.* 9,10-dimethylanthracene and 7,12-dimethylbenzanthracene) giving rise to cyclic and acyclic quinol ethers some of which are plausibly interpreted as arising via the intermediacy of para-quinodimethane intermediates. We report studies of the reaction of high potential quinones on derivatives of 7,12-dihydropleiadene (**1**), the parent compound of which, pleiadene (**2**) is expected not to exhibit substantial resonance stabilization (5, 6). Compounds **1** had the added interest of containing a potential ortho-quinodimethane moiety which could be expected to result from quinone dehydrogenation. The results on these systems extend the range of quinone dehydrogenation, limited to hydroaromatic donors hitherto, and also one compound proved ideal for testing predictions of cyclodehydrogenation.



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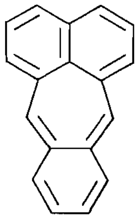

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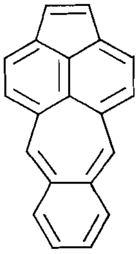

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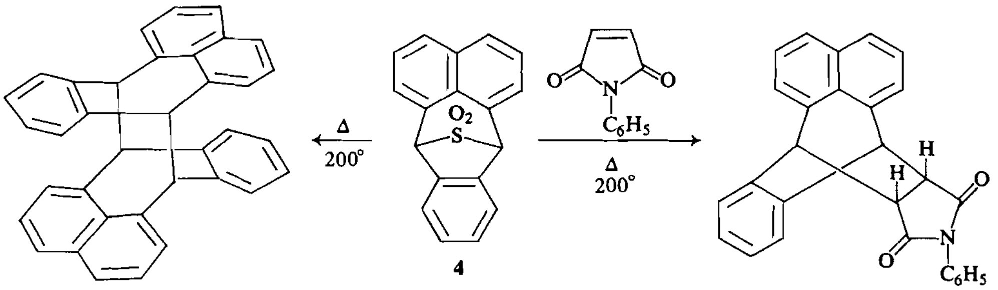
7,12-Dihydropleiadene as Donors

Pleiadene has been generated in solution by Cava and Schlessinger by the elimination of sulfur dioxide from 7,12-dihydropleiadene-7,12-sulfone (**4**) both thermally and photochemically (see eq. 1) and by dehalogenation of 7,12-dibromo-7,12-dihydropleiadene with zinc or copper bronze at moderate temperatures (7). Pleiadene, in contrast to acepleiadylene (**3**) cannot be regarded as a peripherally conjugated system, and consequently exhibits a greater degree of ortho-quinodimethane character than **3** and dimerized readily to **5** in solution or could be trapped with *N*-phenylmaleimide in a Diels–Alder reaction to form **6**, however, only at higher temperatures.

Reaction of **1** (8) with 2 equiv of tetrachloro-



[1]

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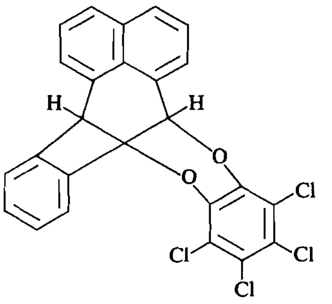
1,2-benzoquinone (TOQ) in refluxing chlorobenzene readily gave compound **7**. Examination of the products of the reaction of quinones with alkenes by Horner and Merz (9) and in our own work with arenes (3, 4) have shown that products may be formed of types **8**, **9**, and **10** from ortho quinones (*e.g.* TOQ) and of types **11** and **12** from para quinones such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).



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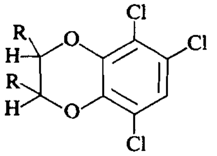

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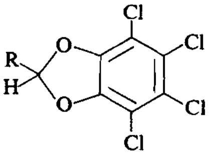

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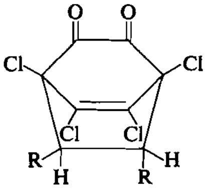

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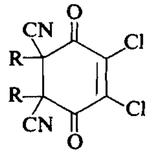

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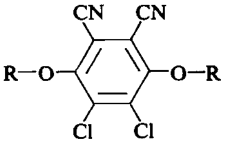

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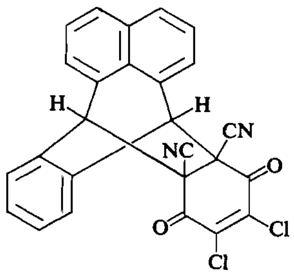
Compounds of types **8** and **9** are white or pale yellow solids the i.r. spectra of which exhibit strong and characteristic ether bands in the region 1420–1450 cm^{-1} due to tetrachlorobenzodioxan and tetrachlorobenzodioxole moieties (10). Adducts of type **10** are formed when TOQ acts as a diene and are characteristically bright yellow and exhibit strong α-diketone i.r. bands near 1680 cm^{-1}. In adducts of type **11** DDQ acts as a dienophile at the more reactive (nitrile substituted) double bond, an assumption which has recently been justified by X-ray analysis of a DDQ adduct of 1,3,5,5-tetramethylcyclohexa-1,3-diene (11).

Compound **7**, $C_{24}H_{12}Cl_4O_2$ showed a benzodioxan absorption at 1454 cm^{-1} but no hydroxyl or ketone absorption.

In contrast **1** reacted with DDQ to give compound **13**, $C_{26}H_{12}N_2Cl_2O_2$ in 47% yield, the formation of which can plausibly be interpreted by initial dehydrogenation of **1** to **2** followed by Diels–Alder addition to the nitrile substituted bond of DDQ. Compound **13** showed i.r. bands



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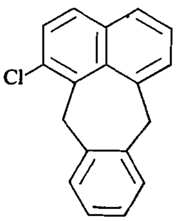

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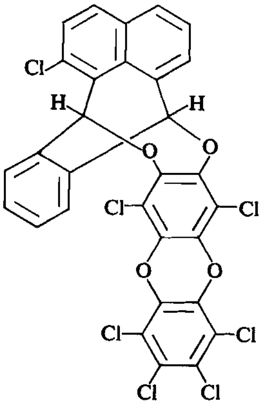
at 1705 (C=O) and 2250 cm^{-1} (C≡N) and the n.m.r. spectrum showed, besides aryl protons, a singlet at 5.05 δ (2H) demonstrating the equivalence of the 7- and 12-protons and therefore the symmetry of the molecule. (The signals of the corresponding protons in **7** are shifted by the adjacent oxygens into the aromatic region.)

Evidently 7,12-dihydropleiadene, lacking the driving force available to hydroaromatic donors, is still dehydrogenated readily by the two different quinones.

Cava and Schlessinger have convincingly demonstrated that Diels–Alder addition products of **2**, *e.g.* **6**, have the *exo* configuration illustrated (7). Accordingly we have assigned the *exo* configuration to **13** and tentatively assigned the conformation of **7** as *exo* as shown.

In contrast to the formation of **7** reaction of 1-chloro-7,12-dihydropleiadene (**14**) with TOQ gave rise to two isomeric products to which structures **15** and **16** were assigned the composition which corresponded to $C_{30}H_{10}Cl_4O_4$, *i.e.* 1:2 pleiadene:quinone $-2HCl$. Compound **15** showed two strong ether bands in the i.r. at 1420 (=C—O—C) and 1445–1453 cm^{-1} (=C—O—C=) and no C=O bands, the 7- and 12-protons as in the case of **7** appeared in the aromatic region in the n.m.r. The isomer **16** was a bright yellow solid the i.r. spectrum of which showed bands due to both tetrachlorobenzodioxan (1445 cm^{-1}) and α-diketone (1680 cm^{-1}). The n.m.r. spectrum showed, in addition to aryl protons, two singlets at 5.26 and 6.31 δ (1H each) unambiguously assigned to the 7- and 12-pleiadene bridge protons since the corresponding adduct prepared from 1-chloro-7,7,12,12-tetradeuteropleiadene lacked these signals. In addition a doublet at 6.26 δ (J = 10.6 Hz), unaffected by the deuteration, was shown to be an aromatic proton by double irradiation experiments. It is tentatively assigned to the C-6 proton, adjacent to a carbonyl group in the proposed structure **16**.



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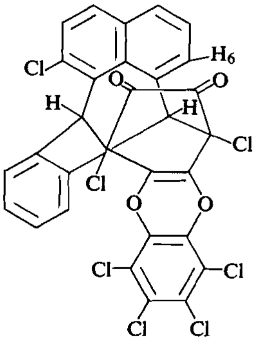

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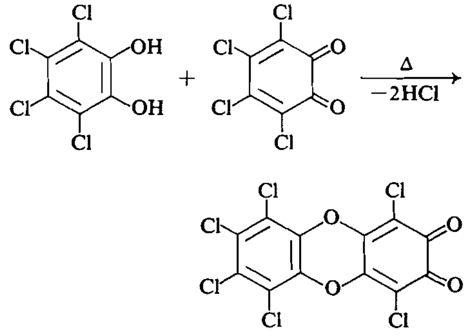
Compound **14** is far less reactive than **1** because the electron-withdrawing 1-chloro substituent in **14** so deactivates the potential hydride ion at the benzylic positions, that higher reaction temperatures and longer reaction times are required for dehydrogenation. A similar sensitivity to electron-withdrawing substituents reflected in the Hammett ρ value of −2.5 has been observed in the dihydronaphthalene series (12). Under these forcing conditions TOQ undergoes a preceding reaction with the corresponding quinol to form **17** (see eq. 2).

[2]



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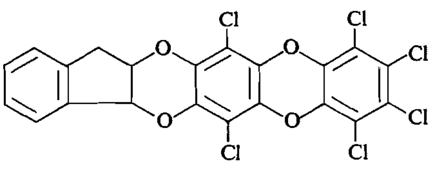
Compound **17** prepared independently (13) was allowed to react with **14** and gave rise to both compounds **15** and **16**.

In view of the reactions discussed above, the formation of **15** and **16** can be envisaged as involving similar reaction paths to those implied in the formation of **7** and **13** respectively, *i.e.* via an acyclic quinol ether to form **15** and by addition to 1-chloropleiadene to form **16**.



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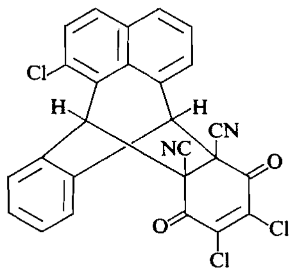
Indane, which like **14** requires forcing conditions to react with TOQ, similarly affords compound **18** (14). Compound **14** reacted with DDQ to give adduct **19**, $C_{26}H_{11}Cl_3N_2O_2$ similar to **13**.

Substitution of an alkyl group at the 7-position of 1-chloro-7,12-dihydropleiadene has a pronounced effect on the course of reaction with TOQ. The major product obtained from the 7-methyl derivative **21** was a pale yellow solid, $C_{31}H_{12}Cl_8O_4$, corresponding to the addition of 2 mol of TOQ and the elimination of H_2 and HCl. The product shows two distinct tetrachloroquinol ether bands at 1420 and 1445 cm^{-1} and is formulated as **20**. Supporting evidence for dehydrogenation into the methyl group of **21** to form the methylene compound followed by addition of TOQ to form the cyclic quinol ether is provided by reaction of **22** to form adduct **23**, $C_{25}H_{11}Cl_5O_3$, which shows a strong quinol ether absorption at 1423 cm^{-1}. In addition the methylene compound **24** forms **20** by reaction with 2 mol of TOQ. Reaction of the second quinone molecule results in substitution of the 1-chlorine by the quinone oxygen to form the cyclic ether.



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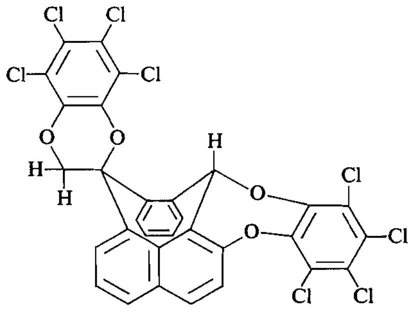

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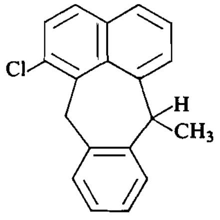

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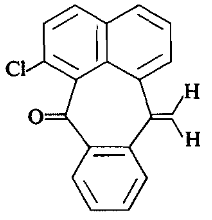

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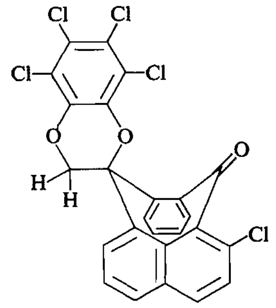

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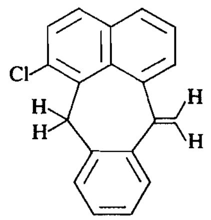
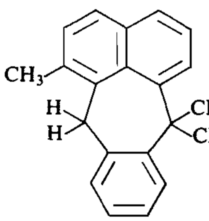
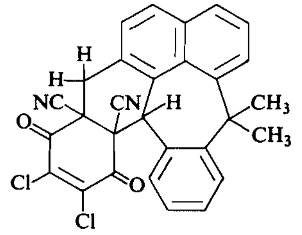




24 **25**



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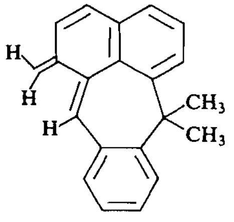
Reaction of 1,7,7-trimethyl-7,12-dihydropleiadene (**25**) with DDQ gave compound **26** $C_{29}H_{18}N_2Cl_2O_2$. The i.r. spectrum was typical of a Diels–Alder adduct of DDQ to the nitrile substituted double bond such as **13** and **19** and the n.m.r. spectrum showed the 7-methyl groups intact at 1.6 and 1.9, an AB quartet (J = 16 Hz) at 3.85 and 4.20 due to the methylene protons, and the methine singlet at 5.20 δ. Formation of **26** presumably involves Diels–Alder addition of DDQ to the reactive intermediate **27** which contains an ortho quinodimethane moiety and would resemble **2** in its reactivity towards dienophiles. Product **26** resembles those obtained from **22** and **24** with DDQ which gave **28** $C_{27}H_9Cl_3O_2N_2$, and **29**, $C_{27}H_{11}Cl_3N_2O_2$, respectively. In



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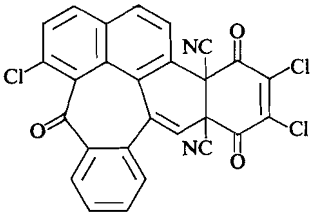

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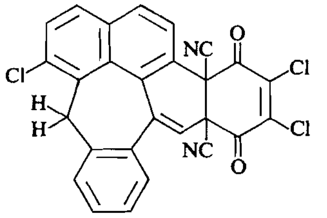

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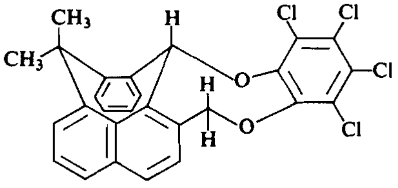
the case of **28** and **29** however the initial Diels–Alder addition products undergo further dehydrogenation to aromatize the naphthalene moiety. A corresponding subsequent dehydrogenation does not take place in the case of **26** since this would result in formation of a high energy ortho-quinodimethane structure. Compound **29** shows an AB quartet in the n.m.r. spectrum due to the C-12 methylene proton at 4.4 δ $J = 16$ Hz.

Compound **25** reacted with TOQ in refluxing benzene to give a white solid $C_{27}H_{18}Cl_4O_2$, the n.m.r. spectrum of which like **26** showed the 7-methyl groups unaffected at 1.8 and 2.05 δ and an AB quartet (2H) centered at 5.95 and 6.56 δ ($J = 16$ Hz) corresponding in chemical shift to a methylene bonded to oxygen. Since the i.r. spectrum showed a strong quinol ether absorption at 1405 cm^{-1} and no hydroxyl absorption this compound is formulated as **30**.



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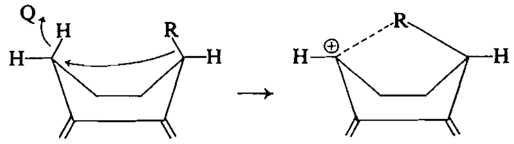
Thus the 1-methyl group in **25** shows a reactivity towards quinones comparable with that of methylnaphthalenes and 9-methylanthracene which also form quinol ethers under comparable conditions (3, 4).

Quinone Dehydrogenation of 9-Aryl-9,10-dihydroanthracenes and 7-Aryl-7,12-dihydropleiadenes

(i) Anthracene Models

The general quinone dehydrogenation reaction involves in the rate-determining initial step a hydride transfer from the donor (an arene or hydroaromatic compound) to the acceptor (quinone) with the concomitant generation of an electron deficient carbon (1, 2). It follows that in model compounds with a suitable geometry some degree of participation by a neighboring group could be anticipated (see eq. 3) and in the limit dehydrogenative cyclization could result.

[3]



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As a first approach we have examined the dehydrogenation with some high potential quinones of some 9-aryl-9,10-dihydroanthracenes since their geometry is reasonably well defined (15). 9,10-Dihydroanthracene, and its 9-phenyl, 9-*p*-tolyl, and 9-*p*-anisyl derivatives reacted with TOQ (in benzene at moderate temperatures) to give the corresponding anthracenes quantitatively. The rates of these reactions could be followed conveniently by a spectrokinetic procedure (16) by observing the rate of disappearance of the red quinone. Individual reactions obeyed the second order rate law strictly and the rate data obtained are summarized in Table 1.

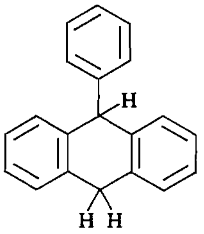
9-Phenyl, 9-*p*-tolyl, and 9-*p*-anisyl-9,10-dihydroanthracenes have reaction rates with TOQ very close to that of 9,10-dihydroanthracene when allowance is made for the statistical factor of 2. 9,10-Dihydroanthracenes adopt a quasi-boat conformation of the central ring and a 9-aryl substituent adopts the quasi-axial position preferentially so as to minimize interactions with the flanking benzene rings. Inspection of models suggests that the quasi-axial hydrogen atom at the 10-position is correctly disposed with respect to the aromatic rings of the anthracene structure to provide maximum stabilization of the incipient carbonium ion, in contrast to the quasi-equatorial hydrogen atom which is unfavorably oriented. We therefore make the reasonable

TABLE 1. Kinetic data for reaction of 9-aryl-9,10-dihydroanthracenes with tetrachloro-1,2-benzoquinone in 1,2-dichlorobenzene

		Arrhenius parameters	
Donor	Second order rate constant (80°)	E (kcal mol^{-1})	Log$_{10}$ B
9,10-Dihydroanthracene	$3.10 \pm 0.20 \times 10^{-1}$	12.06 ± 0.17	6.95
9,10-Dihydro-9-phenylanthracene	$1.37 \pm 0.04 \times 10^{-1}$	14.55 ± 0.58	8.15
9,10-Dihydro-9-*p*-tolylanthracene	$1.56 \pm 0.05 \times 10^{-1}$	13.48 ± 0.47	7.45
9,10-Dihydro-9-*p*-anisylanthracene	$1.75 \pm 0.12 \times 10^{-1}$	13.43 ± 0.23	7.65

assumption that the quasi-axial hydrogen atoms are potential hydride ions in the anthracene series.

In view of the known sensitivity of the quinone dehydrogenation reaction to substituent electronic effects in the dihydronaphthalene series (Hammett $\rho = -2.5$) (12) one would have anticipated a greater spread in the relative reactivities as reflected in the reaction rates, had hydride abstraction occurred at the 9-position.



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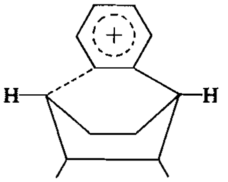

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It is apparent therefore that hydride abstraction occurs at the 10-position in this series of hydroaromatic donors (a conclusion which is borne out by experiments in the dihydropleiadene series described below) and we may also conclude that the axial 9-substituent does not participate in the removal of the hydride ion by bridging to the cationic center as in **33**.

We infer from the rate data that the geometry of the quasi-boat in the anthracene series is such that the 9-aryl substituent is not in a suitable position for this kind of interaction.

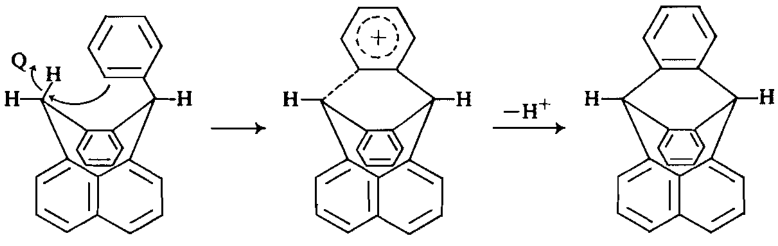
(ii) Pleiadene Models

The experience of the quinone dehydrogenation of the pleiadene system outlined in preceding sections and an examination of molecular models suggested that the geometry of this system in contrast to the anthracene case might be suitable to allow attack of a 7-arylsubstituent at the cationic center generated at the 12-position by hydride abstraction leading to dehydrogenative cyclization as illustrated in eq. 4. 7-Phenyl-7,12-dihydropleiadene (**34**) reacted with TOQ in benzene to give the bridged hydrocarbon **36** as the sole product. Evidently aryl attack as represented by **35** is so effective with this molecular geometry as to prevent loss of the 7-proton from the carbonium ion with formation of a 7-phenylpleiadene.

Recently Lansbury and coworkers (17) have prepared a similar compound **38** in an attempted dehydration of the alcohol **37** and this reaction must proceed by a similar mechanism once the cationic center has been generated at position 12 (see eq. 5).

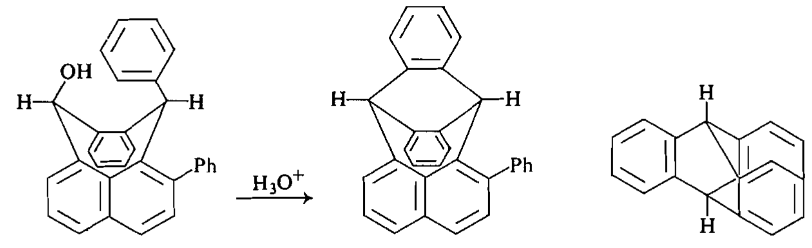
7-Phenyl-7,12-dihydropleiadene (**34**) also reacted with DDQ to give pure **36**. Compound **36** is completely unreactive towards further reaction with either TOQ or DDQ, a result which is in accordance with the observed lack of reactivity of the bridgehead hydrogens in trypticene **39**. This may be attributed to the inability of an incipient carbonium ion generated from **36** or **39** to attain coplanarity with the aryl rings despite the additional flexibility allowed in **36** by the

[4]



34 **35** **36**

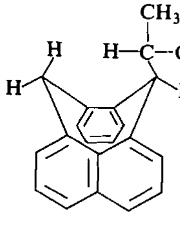
[5]



37 38 39

introduction of another fused aromatic ring compared with 39.

Reaction of 7-isopropyl-7,12-dihydropleiadene (40) with TOQ gave compound 41, similar in structure to 7 and 15. The n.m.r. spectrum of 41 shows bands characteristic of an intact isopropyl group and also reveals an absence of absorption characteristic of the 7,12-protons in 40. A strong quinol ether absorption at 1455 cm^{-1} and the absence of carbonyl absorption support structure 41.



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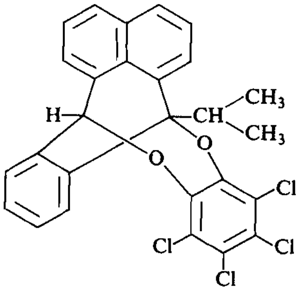


41

The results obtained with the 9,10-dihydro-9-arylanthracenes lead one to expect the 12-axial proton in 40 to be the potential hydride ion in the first step of the reaction since Lansbury has shown the isopropyl group in 40 adopts a pseudo-axial conformation. Had 1,5-hydride shift occurred from the isopropyl group in 40 such as occurs in the dehydration of 42 studied by Lansbury (see eq. 6 (17)), one would have expected a final product of addition of TOQ to the isopropenyl or isopropylidene group such as 23 to have resulted. We conclude that, unlike the rapid dehydrogenative cyclization in 34 to form 36, 41 results from collapse of the quinol anion to the initially formed carbonium ion which prevents a 1,5-transannular hydride shift, and that a second dehydrogenation step involving participation by the quinol hydroxyl results in the formation of 41.

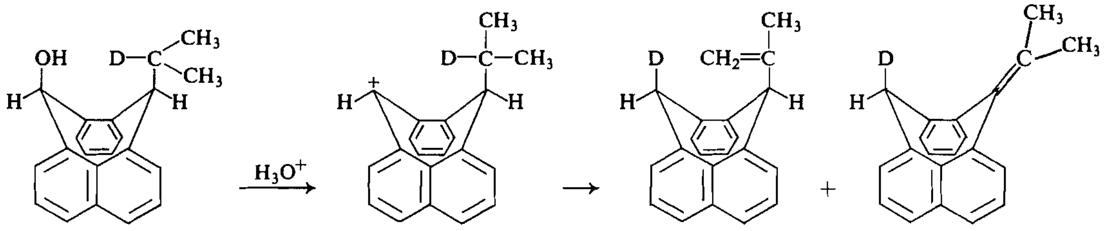
Experimental

Melting points were determined on a Fisher–Johns apparatus and are uncorrected. The i.r. spectra were recorded on a Perkin–Elmer model 421 spectrophotometer, and only the principal, sharply defined peaks are reported. The n.m.r. spectra were recorded on Varian A-60 and A-100 analytical spectrometers. The spectra were measured on approximately 10–15% (w/v) solutions in $CDCl_3$, with tetramethylsilane as a standard. Line positions are reported in p.p.m. from the reference. Mass spectra were determined on an Associated Electrical Industries MS-9 double focusing high resolution mass spectrometer. The ionization energy, in general, was 70 eV. Peak measurements were made by comparison with perfluorotributylamine at a resolving power of 15 000. Kieselgel DF-5 (Camag, Switzerland) and Eastman Kodak precoated sheets were used for t.l.c. Microanalyses were carried out by Dr. C. Daesslé, Organic Microanalysis Ltd., Montreal, Quebec and by Mrs. D. Mahlow of this Department. Values for carbon microanalysis of some adducts were unacceptable owing to difficulties in combustion of high molecular weight compounds. In such cases an accurate peak measurement by mass spectrometry was performed.

1-Chloro-7,12-dihydropleiadene

1-Chloro-7,12-dihydropleiadene was prepared from 1-chloro-7,12-dihydropleiadene-7,12-dione by the method of Cava and Schlessinger (7). The crude product was

[6]



42 43 44

purified by chromatography on alumina using hexane as eluent. Crystallization from hexane gave white needles, m.p. 116–119° (lit. 117–119° (7)).

7,12-Dihydropleiadene

7,12-Dihydropleiadene was prepared from 1-chloro-7,12-dihydropleiadene by a modification of the method of Cava and Schlessinger (7). A mixture of 25 g (0.095 mol) 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 h. 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. Recrystallization from hexane gave 20 g (91.8% yield) of 7,12-dihydropleiadene, m.p. 115–117° (lit. 113–114° (7), 116° (8)).

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

A solution of 4 g (0.017 mol) of 7,12-dihydropleiadene in 50 ml of dry chlorobenzene was added to a solution of 10 g (0.041 mol) of tetrachloro-1,2-benzoquinone in 250 ml of chlorobenzene and the mixture heated under reflux for 72 h. The solvent was removed *in vacuo*, the residue taken up in benzene and subjected to chromatography on BDH alumina using (1:1) benzene:hexane as eluent. The main fraction consisted of a buff-white solid recrystallized from benzene, m.p. 266–268°, 4.3 g (52.4% yield) of 7.

Anal. Calcd. for $C_{24}H_{12}Cl_4O_2$ (mol. wt. 471.9593): C, 60.78; H, 2.56; Cl, 29.90. Found (471.9594 (mass spectrum)): C, 61.26; H, 2.51; Cl, 29.05.

The i.r. spectrum ν_{max}($CHCl_3$): 1454 cm^{-1} (C—O—C); n.m.r. spectrum δ_{TMS}($CDCl_3$): 7.1–8.2 (m, aryl, C-7 and -12 protons).

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

A solution of 5 g (0.022 mol) of 7,12-dihydropleiadene in dry chlorobenzene was added to a solution of 10 g (0.044 mol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 350 ml of chlorobenzene and the mixture refluxed for 30 min during which time a brown solid separated. Refluxing was continued for a further 1½ h, 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 **13** 4.7 g (47.1% yield) m.p. >300°.

Anal. Calcd. for $C_{26}H_{12}N_2Cl_2O_2$ (mol. wt. 454.0276): N, 6.16; Cl, 15.42. Found (454.0275 (mass spectrum)): N, 6.08; Cl, 15.31.

The i.r. spectrum ν_{max}(Nujol mull): 1705 (C═O), 2250 cm^{-1} (C≡N); n.m.r. spectrum δ_{TMS}((CD_3)$_2$SO): 5.05 (2H, s, C-7 and -12 protons), 7.1–8.2 (m, 10H, aromatic protons).

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

A solution of 3.01 g (9 mmol) of 1-chloro-7,12-dihydropleiadene in 100 ml of dry *o*-dichlorobenzene was added to a solution of 8.36 g (0.0336 mol) of tetrachloro-1,2-benzoquinone in 300 ml of *o*-dichlorobenzene and the mixture refluxed for 48 h. The solvent was removed *in vacuo* (0.05 mm) and the residual solid taken up in benzene and subjected to chromatography on acid washed alumina. Elution with benzene gave **16**, 1 g, (13% yield) m.p. 280–281°.

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.

Mass Spectrum Calcd. for $C_{30}H_{10}{}^{35}Cl_6{}^{37}ClO_4$ (M^+-1): 680.8369. Found: 680.8372.

The i.r. spectrum ν_{max}($CHCl_3$)(Nujol): 1680 (C═O) 1454 cm^{-1} (—C—O—C); n.m.r. spectrum δ_{TMS}($CDCl_3$): 5.26 and 6.31 (1H each, s, C-7 and -12 pleiadene bridge protons), these signals disappear in the analogous compound obtained from 1-chloro-7,7,12,12-tetradeuteropleiadene, 6.26 (1H, d, J = 10.6 Hz ortho coupling, C-6(?) aromatic proton. Irradiation at 7.45 causes collapse of the 6.26 signal to a singlet, 7.0–8.0 (8H, m, aromatic protons).

Further elution with chloroform gave **15** 1.2 g (20% yield), m.p. >300°.

Anal. Calcd. for $C_{30}H_{11}Cl_7O_4$: Cl, 36.03. Found: Cl, 35.62.

The i.r. spectrum ν_{max}($CHCl_3$): 1420 (—C—O—C—), 1445–1453 cm^{-1} (—C═C—O—C); n.m.r. spectrum δ_{TMS}($CDCl_3$): 6.7–8.2 (m, aromatic, C-7 and -12 bridge protons).

Reaction of 1-Chloro-7,12-dihydropleiadene with Hexachloro-ortho-quinopyrocatechin Ether

A solution of 0.61 g (25 mmol) of 1-chloro-7,12-dihydropleiadene in 50 ml of dry chlorobenzene was added to a solution of 2.09 g (50 mmol) of hexachloro-ortho-quinopyrocatechin ether (13) in 300 ml of warm chlorobenzene and the mixture refluxed for 72 h. The solvent was removed *in vacuo* and the residue dissolved in benzene and subjected to chromatography on BDH alumina using benzene as eluant to give a bright yellow solid, m.p. >300°, 0.5 g (29.4% yield).

Mol. Wt. Calcd. for $C_{30}H_{11}Cl_7O_4$: 679.8480. Found (mass spectrum): 679.8470.

The i.r. spectrum ν_{max}($CHCl_3$): 1672 (—CO—CO—) 1452 cm^{-1} (C═C—O—C═C). This compound proved to be identical with adduct **16** obtained above.

Further elution with chloroform gave a violet compound 0.43 g (25.3% yield) the i.r. spectrum of which in $CHCl_3$ showed bands at 1453 and 1422 cm^{-1} (—C—O—C) and which proved to be identical with adduct **15** obtained above.

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

Aluminum chloride (2.7 g, 0.02 mol) and 0.84 g (0.02 mol) of lithium aluminum hydride were added to ether at 0°. To this mixture was added with stirring 2.54 g (8 mmol) of 1-chloro-7,12-dihydropleiadene-7,12-dione and the mixture stirred for 45 min, 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 BDH alumina to give 2 g of 1-chloro-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-tetradeutero-7,12-dihydropleiadene with Tetrachloro-1,2-benzoquinone

A solution of 0.5 g (1.86 mmol) of 1-chloro-7,7,12,12-tetradeutero-7,12-dihydropleiadene in 25 ml of *o*-dichlorobenzene was added to a solution of 1.05 g (4.26 mmol) of tetrachloro-1,2-benzoquinone in 50 ml of *o*-dichlorobenzene and the mixture refluxed for 48 h. 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 D-**16** m.p. 280–281°.

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

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

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

A solution of 4 g (15 mmol) of 1-chloro-7,12-dihydropleiadene in 75 ml of dry chlorobenzene was added to a solution of 10 g (0.044 mol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 350 ml of chlorobenzene and the mixture heated under reflux for 2 h. 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 **19** as bright yellow crystals in m.p. 270°, 3.8 g (51.2% yield).

Anal. Calcd. for $C_{26}H_{11}Cl_3N_2O_2$ (mol. wt. 487.9886): C, 63.95; H, 2.25; Cl, 21.52; N, 5.73. Found: 487.9888 (mass spectrum): C, 63.35; H, 2.39; Cl, 21.39; N, 5.64.

The i.r. spectrum ν_{max}(Nujol mull): 2246 (C≡N), 1700, 1715(sh) cm^{-1} (C=O); n.m.r. spectrum δ_{TMS}-($(CD_3)_2SO$): 5.15 (1H, s, C-7 proton), 5.64 (1H, s, C-12 proton), 7.2–8.2 (9H, m, aromatic protons).

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

A solution of 0.556 g (2 mmol) of 1-chloro-7-methyl-7,12-dihydropleiadene in dry chlorobenzene was added to a solution of 0.976 g (4 mmol) of the quinone in 150 ml of dichlorobenzene and the mixture refluxed for 10 h. The solvent was removed *in vacuo* and the residual solid purified by chromatography on BDH alumina using hexane:benzene (2:1) as eluent to give 0.13 g (8.9% yield) of **20**, m.p. 286–289.

Anal. Calcd. for $C_{31}H_{12}Cl_8O_4$ (mol. wt. 727.8248): C, 51.10; H, 1.65; Cl, 38.47. Found (727.8237 (mass spectrum)): C, 51.71; H, 1.65; Cl, 37.03.

The i.r. spectrum $\nu_{max}(CHCl_3)$: 1445, 1420 cm^{-1} (—C—O—C).

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

A stirred suspension of 10 g (0.036 mol) of 1-chloro-7-pleiadenone in 200 ml 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 h, then poured on to ice, and acidified with dilute hydrochloric acid. The ether layer was separated, washed with water and dried ($NaSO_4$). The ether was removed *in vacuo*, the residual solid dissolved in hexane and purified by chromatography on BDH alumina giving 1-chloro-7-methylene-7,12-dihydropleiadene (**24**) 6 g (60.4% yield). The latter (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% yield) of 1-chloro-7-methyl-7,12-dihydropleiadene (**21**), m.p. 95°.

Anal. Calcd. for $C_{19}H_{15}Cl$ (mol. wt. 292.0655): Cl, 12.59. Found (292.0653 (mass spectrum)): Cl, 12.40.

The n.m.r. spectrum $\delta_{TMS}(CDCl_3)$: 1.80 (3H, d, CH_3), 4.6–4.97 (3H, m, C-7 and -12 protons), 7.05–7.70 (9H, m, aromatic protons).

1-Chloro-7,12-epoxy-7,12-dihydro-7-methylpleiaden-12-ol

1-Chloro-7,12-dihydropleiadene-7,12-dione (10 g, 34 mmol) was added during 20 min to a stirred solution of methyl magnesium iodide (prepared from 15 g of methyl iodide, 3 g of magnesium, and 200 ml of anhydrous ether). After completed addition, stirring was continued for 8 h and worked-up in the usual way with saturated aqueous ammonium chloride giving 6.2 g (59% yield) of 1-chloro-7,12-epoxy-7,12-dihydro-12-methylpleiaden-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.

The i.r. spectrum $\nu_{max}(CHCl_3)$ 3560, 3360 cm^{-1} (OH), 1450 cm^{-1} (—C—O—C); n.m.r. spectrum $\delta_{TMS}(CDCl_3)$: 2.2 (3H, s, CH_3), 4.95 (1H, s, OH), 7.0–8.0 (9H, m, 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, 2 mmol) was dissolved in 100 ml of benzene, a catalytic quantity of *p*-toluenesulfonic acid added, and the mixture refluxed for 8 h, allowed to cool, and washed successively with 10% aqueous sodium hydrogen carbonate and water. The benzene layer was removed and dried ($MgSO_4$). Removal of the solvents *in vacuo* gave 1-chloro-7-methylene-7,12-dihydropleiaden-12-one (**22**), m.p. 169–171°, 5.3 g (91.4% yield).

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.

The i.r. spectrum $\nu_{max}(CHCl_3)$ 1685 cm^{-1} (C=O); n.m.r. spectrum $\delta_{TMS}(CDCl_3)$: 5.65, 5.45 (2H, pair of doublets, J = 1.5 Hz, methylene protons), 7.25–7.85 (9H, m, 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 mmol) 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 mol) of tetrachloro-1,2-benzoquinone in 125 ml of dichlorobenzene and the mixture refluxed for 24 h. The solvent was removed *in vacuo* and the residue triturated with benzene and recrystallized from benzene to give 1.3 g, m.p. 292–293° of **23**. The mother liquor was subjected to chromatography on BDH alumina to give an additional 0.5 g of **23** making a total yield of 67%.

Anal. Calcd. for $C_{25}H_{11}Cl_5O_3$ (mol. wt. 533.9153): C, 56.16; H, 2.07; Cl, 32.77. Found (533.9150 (mass spectrum)): C, 56.24; H, 2.07; Cl, 32.69.

The i.r. spectrum $\nu_{max}(CHCl_3)$, 1685 (C=O), 1423 cm^{-1} (—C—O—C—).

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 mmol) of 1-chloro-7-methylene-7,12-dihydropleiadene in 25 ml of benzene was added to a solution of 0.904 g (4 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 200 ml of benzene and the mixture refluxed for 10 h, cooled, and filtered. Concentration of the filtrate gave a brick-red solid purified by recrystallization from benzene to give **29**, 0.68 g (68% yield), m.p. 242–245° (dec.).

Anal. Calcd. for $C_{27}H_{11}Cl_3N_2O_2$ (mol. wt. 499.9888): C, 64.80; H, 2.20; Cl, 21.00. Found (499.9886 (mass spectrum)): C, 64.79; H, 2.37; Cl, 20.95.

The i.r. spectrum ν_{max}(Nujol mull): 1718 (C═O); 2250 cm^{-1} (CN), n.m.r. spectrum $\delta_{TMS}((CD_3)_3SO)$: quartet centered at 4.4 (2H, C-12 bridge protons J_{AB} = 15 Hz broad lines), 6.1, 6.47 (1H, singlets, vinyl proton), 6.95–8.5 (8H, aromatic protons).

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

To a stirred solution of 6.5 g of methyl-2-[2′-methyl-1′naphthylmethyl]benzoate in ether (prepared by treating the acid with methanol in the presence of a catalytic quantity of sulfuric acid), was added excess of a solution of methyllithium in ether. The mixture was poured on to ice, acidified with 2 *N* hydrochloric acid, and the ether layer separated and dried ($MgSO_4$). Evaporation of the solvent gave 1-[2′-(1″-hydroxy-1″-methylethyl)tolyl]-2-methylnaphthalene 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 h. 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)-2-methylnaphthalene as a white crystalline solid identified by its n.m.r. spectrum $\delta_{TMS}(CDCl_3)$: 2.25 (3H, s, isopropenyl protons), 2.40 (3H, s, aryl methyl protons), 4.50 (2H, s, bridge methylene protons), 5.15, 5.40 (2H, m, isopropenyl vinylic protons), 6.40–8.0 (9H, m, aromatic protons). The latter was dissolved in 50 ml of anhydrous ether, treated with 25 ml of boron trifluoride-etherate in ether (48%) and the mixture stirred for 2 h. The reaction mixture was decomposed with ice, the ether layer removed, washed with water, and dried ($MgSO_4$). Evaporation of the solvent gave a brown solid purified by chromatography on BDH alumina to give 2.5 g (40% yield overall from the ester) of 1,7,7-trimethyl-7,12-dihydropleiadene (**25**), m.p. 165–166°.

Anal. Calcd. for $C_{21}H_{20}$: C, 92.64; H, 7.36. Found: C, 92.62; H, 6.7.

The n.m.r. spectrum $\delta_{TMS}(CDCl_3)$: 1.74 (6H, s, C-7 methyl groups), 2.73 (3H, s, C, methyl group), 4.18 (2H, s, C-12 methylene protons), 7.00–8.00 (9H, m, aromatic protons). This compound has previously been reported but no experimental details were given (18).

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 mmol) of 1,7,7-trimethyl-7,12-dihydropleiadene in 25 ml of benzene was added to 0.565 (2.5 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of benzene and the mixture refluxed for 30 min during which time the hydroquinone separated as a brown solid. The solution was refluxed for a further 1½ h, cooled, and filtered. Concentration of the filtrate to *ca.* 50 ml deposited bright orange–red crystals of **26** purified by recrystallization from benzene 0.531 g (85.6% yield), m.p. 209–212°.

Anal. Calcd. for $C_{29}H_{18}N_2Cl_2O_2$ (mol. wt. 496.0746): C, 70.17; H, 3.63; Cl, 14.11. Found (496.0753 (mass spectrum)): C, 70.33; H, 3.41; Cl, 14.03.

The i.r. spectrum $\nu_{max}(CHCl_3)$: 1718 (C═O), 2225 cm^{-1} (C≡N); n.m.r. spectrum $\delta_{TMS}(CDCl_3)$: 1.6 (3H, s, C-7 equatorial CH_3), 1.9 (3H, s, C-7 axial CH_3), AB quartet centered at 3.85 and 4.20 (2H, q, J_{AB} = 16 Hz, C-12 CH_2), 5.20 (1H, s, C-12 methine proton), 7.20–8.30 (9H, m, aromatic protons).

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

A solution of 1.37 g (5 mmol) of 1-chloro-7-methylene-7,12-dihydropleiadene in 100 ml of chlorobenzene was added to a solution of 2.230 g (10 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of chlorobenzene and the mixture heated under reflux for 6 h. The filtered solution was concentrated to a small volume to give **28** as a yellow ocher solid, m.p. 225–228°, 1.77 g (67.3% yield).

Anal. Calcd. for $C_{27}H_9Cl_3O_3N_2$: Cl, 20.43; N, 5.45. Found: Cl, 21.65; N, 5.50.

The i.r. spectrum ν_{max}(Nujol mull): 1736, 1705 (C═O of quinone) 1680 cm^{-1} (C═O at C-12), n.m.r. spectrum $\delta_{TMS}((CD_3)_2SO)$: 6.45, 6.7 (1H, s, vinyl proton) 6.95–8.4 (8H, m, aromatic protons).

The appearance of two singlets for the vinyl protons is tentatively attributed to the presence of stereoisomeric adducts, resulting from the two possible modes of addition of DDQ to the diene system.

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

A solution of 0.34 g (1.25 mmol) 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 mmol) of tetrachloro-1,2-benzoquinone in 125 ml of benzene and the mixture heated under reflux for 48 h, cooled, and concentrated to *ca.* 25 ml yielding a gray solid which on crystallization from benzene gave **30**, m.p. 197–199°, 0.263 g (41% yield).

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.

The i.r. spectrum $\nu_{max}(CHCl_3)$: 1405 cm^{-1} (C—O—C); n.m.r. spectrum $\delta_{TMS}(CDCl_3)$: 1.8 (3H, s, C-7 equatorial CH_3), 2.05 (3H, s, C-7 axial CH_3), 5.95, 6.56 (AB quartet, J_{AB} = 16 Hz, C-19 CH_2 protons), 7.2–8.3 (9H, m, aromatic protons).

Synthesis of 9-Arylanthracenes and 9,10-Dihydro-9-arylanthracenes

The general method is described for 9-*p*-tolylanthracene and 9,10-dihydro-9-*p*-tolylanthracene.

(a) 9-p-Tolylanthracene

Anthrone (10 g, 0.0515 mol) was extracted with ether during 12 h into a refluxing solution of *p*-tolyl magnesium bromide (prepared from 26 g, 0.152 mol of *p*-bromotoluene, 3.7 g, 0.154 mol of magnesium turnings, and 100 ml of ether). The solution was cooled and hydrolyzed with aqueous ammonium chloride. The mixture was extracted with ether and the extract washed with (*a*) 2 *N* sodium hydroxide solution, (*b*) 2 *N* hydrochloric acid, (*c*) aqueous sodium hydrogen carbonate solution, and dried ($MgSO_4$). The filtered solution was concentrated to 75 ml and refluxed for 1 h, the solvent removed, and the residual oil heated at 100°/0.5 mm for 12 h. Recrystallization of the yellow solid residue from ethanol and chromatography on grade 1 alumina (BDH) in benzene afforded pure *p*-tolyl-

TABLE 2. 9-Arylanthracenes

9-Substituent	Melting point (°C)	Yield (%)	Formula	Observed C	Observed H	Calculated C	Calculated H	λ_{max}(mμ)	log ε
C_6H_5	155–157	80	$C_{20}H_{14}$	94.61	5.72	94.23	5.62	255 364.5 384	5.15 4.10 4.10
p-$CH_3C_6H_4$	145–147	29	$C_{21}H_{16}$	94.02	6.13	94.00	6.00	256 364 384	5.16 4.01 3.99
p-$CH_3OC_6H_4$	165–167	24	$C_{21}H_{16}O$	88.82	5.71	88.73	5.70	257 364 384	5.10 4.02 4.00

TABLE 3. 9,10-Dihydro-9-arylanthracenes

9-Substituent	Melting point (°C)	Yield (%)	Formula	Observed C	Observed H	Calculated C	Calculated H
C_6H_5	89	49	$C_{20}H_{16}$	93.73	6.31	93.80	6.30
p-$CH_3C_6H_4$	104–106	69	$C_{21}H_{18}$	93.33	6.91	93.30	6.70
p-$CH_3OC_6H_4$	130–132	24	$C_{21}H_{18}O$	88.33	6.31	88.10	6.30

anthracene in pale yellow needles, 4.0 g (29% yield), m.p. 145–147°.

(b) 9,10-Dihydro-9-p-tolylanthracene

Sodium (10 g) was added in small portions to a refluxing solution of 2 g (7.47 mmol) of 9-*p*-tolylanthracene in 150 ml of ethanol, until the solution no longer fluoresced in u.v. light. The solution was diluted with 600 ml of water and the resulting precipitate collected. Recrystallization from ethanol afforded 9,10-dihydro-9-*p*-tolylanthracene in colorless plates, m.p. 104–106°, 1.4 g (69% yield). The properties of other 9-arylanthracenes together with their 9,10-dihydro derivatives prepared by this method are summarized in Tables 2 and 3.

Preparative Scale Dehydrogenations

The general method is exemplified for 9,10-dihydro-9-*p*-tolylanthracene.

A mixture of 0.242 g (0.9 mmol) of 9,10-dihydro-9-*p*-tolylanthracene and 0.271 g (1.1 mmol) of tetrachloro-1,2-benzoquinone in 7 ml of benzene was heated under reflux for 8 h. The resulting mixture was passed down a column of grade 1 alumina and the column eluted with benzene. The evaporated eluent (0.23 g) had λ_{max} 255, 364, 384 mμ (log ε, 5.19; 4.01; 4.10). Pure 9-*p*-tolylanthracene has λ_{max} 256, 364, 384 mμ (log ε, 5.15, 4.01, 4.10). The product therefore contained 9-*p*-tolylanthracene (99.5%) and the overall yield of the latter was 94.5%.

Similarly 9,10-dihydro-9-phenylanthracene afforded 9-phenylanthracene (95% yield) and 9,10-dihydro-9-*p*-anisylanthracene afforded 9-*p*-anisylanthracene (92.5% yield).

Dehydrogenation Reaction Rate Studies

Materials

Pure 1,2-dichlorobenzene was dried over sodium and then distilled and had b.p. 177–178° at 750 mm. Commercial samples of tetrachloro-1,2-benzoquinone were purified by sublimation *in vacuo*.

Reaction Rates

The rates were determined by following spectrophotometrically the disappearance of the red quinone. The E_0 values were determined by graphical extrapolation. The experimental method used and detailed treatment of the rate data have been described previously (16). Values for the second order rate constants for reaction of the dihydroanthracenes with the quinone at 80° together with the Arrhenius parameters are summarized in Table 1.

A representative kinetic run at one temperature is recorded in Table 4. A summary of the rate constants for all the runs at different temperatures is given in Table 5. Unless otherwise stated the initial concentration of both the acceptor and the donor were 0.0100 *M* and 1,2-dichlorobenzene was the solvent.

Control Reaction Between Triptycene and Tetrachloro-1,2-benzoquinone

Reaction between 187 mg of triptycene and 429 mg of tetrachloro-1,2-benzoquinone in 5 ml of refluxing benzene for 8 days resulted in the recovery of unchanged triptycene, m.p. 250–252° in 81% yield, which set an approximate upper limit for any reaction as $k = 2 \times 10^{-6}$ $1\ mol^{-1}\ s^{-1}$.

TABLE 4. Dehydrogenation of 9-*p*-tolylanthracene by tetrachloro-1,2-benzoquinone at 73.10°

Time (min)	*E* (560 mμ)	10*k* ($l\ mol^{-1}\ s^{-1}$)
0	1.007	—
8	0.640	1.19
10	0.589	1.19
12	0.545	1.18
15	0.443	1.16
24	0.367	1.21
28	0.334	1.20
47	0.232	1.19

TABLE 5. Summary of rate constants*

9,10-Dihydroanthracene		9,10-Dihydro-9-phenylanthracene (0.00862 M)		9,10-Dihydro-9-p-tolylanthracene		9,10-Dihydro-9-p-anisylanthracene	
T^0	10^2k†	T^0	10^2k†	T^0	10^2k†	T^0	10^2k†
30.7	1.88	58.9	3.69	56.8	4.18	52.5	3.43
38.2	3.02	68.0	6.43	58.7	4.46	57.2	4.71
52.2	6.98	69.2	7.43	59.5	4.83	62.4	6.48
60.7	11.10	74.2	9.53	63.6	5.89	63.7	6.75
68.2	17.5	76.3	9.87	66.4	7.19	68.7	9.31
				73.1	11.90	71.5	10.7

*Initial concentrations of donors where different from 0.01 M are given in brackets.
†The units are l mol^{-1} s^{-1}.

7-Phenyl-7,12-dihydropleiadene

7-Phenyl-7,12-dihydropleiadene **34** was prepared from 1-(β-benzhydryl)naphthylcarbinol by the method of Lansbury in 80% yield, m.p. 180–181° (lit. m.p. 179–179.5) (19).

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

A solution of 1.53 g (5 mmol) of 7-phenyl-7,12-dihydropleiadene in 25 ml of benzene was added to a solution of 2.26 g (0.01 mol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 150 ml of benzene and the mixture refluxed for 8 h, then concentrated to about 20 ml and chromatographed on BDH alumina using hexane:benzene (3:1) as eluent. Crystallization of the resulting solid in benzene gave 0.81 g (53.3% yield) of **36**, m.p. 271–273°.

Anal. Calcd. for $C_{24}H_{16}$: C, 94.73; H, 5.27. Found: C, 94.67; H, 5.45.

The n.m.r. spectrum δ_{TMS}(CDCl$_3$): 5.16 (2H, s, C-7 and -12 protons); 6.95–7.67 (14H, m, aromatic protons).

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

A solution of 1.53 g (5 mmol) of 7-phenyl-7,12-dihydropleiadene in 50 ml of dry benzene was added to a solution of 3.66 g (15 mmol) of tetrachloro-1,2-benzoquinone in 125 ml of benzene and the mixture refluxed for 72 h. The solution was concentrated *in vacuo* to a small volume and chromatographed on BDH alumina using hexane:benzene as eluant. Recrystallization of the main fraction from benzene gave 1.22 g of **36**, (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.

This material was identical in every respect with that obtained in the preceding experiment.

7-Isopropyl-7,12-dihydropleiadene

7,12-Dihydropleiadene (6.9 g, 0.03 mol) was dissolved in 150 ml of anhydrous ether in a pressure bottle under an atmosphere 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 h. After cooling the mixture to −20°, 2.6 g (0.033 mol) of isopropylchloride in 10 ml of anhydrous ether was added from a syringe with stirring and under nitrogen. The bottle was stoppered again and the contents stirred at room temperature for 8 h. The complex was decomposed with ice and the ether layer dried (Na$_2$SO$_4$) 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 subjected to chromatography on BDH alumina using hexane as eluent to give **40** as a yellow oil. The n.m.r. spectrum δ_{TMS}(CDCl$_3$): 0.8–1.05 (6H, m, CH(CH_3)$_2$), 2.55 (1H, m, CH(CH$_3$)$_2$), 3.6 (1H, d, J_{AB} = 10.5 Hz, C-7 bridge proton), 3.84, 5.14 (2H, q, $J_{A'B'}$ = 16 Hz, C-12 bridge protons), 7.0–7.83 (10H, m, aromatic protons) (20).

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

A solution of 1.7 g (6.25 mmol) of 7-isopropyl-7,12-dihydropleiadene in 75 ml of dry chlorobenzene was added to a solution of 3.20 g (0.0120 mol) of tetrachloro-1,2-benzoquinone in 125 ml of chlorobenzene and the mixture refluxed for 72 h. The solvent was removed *in vacuo* and the residue dissolved in benzene and subjected to chromatography on BDH alumina using 1:1 hexane:benzene as eluent to give 1.56 g **41**, m.p. 160–165°.

Anal. Calcd. for $C_{27}H_{18}Cl_4O_2$ (mol. wt. 514.0063): Cl, 27.24. Found (514.0050 (mass spectrum)): Cl, 27.44.

The i.r. spectrum ν_{max}(CHCl$_3$): 1455, 1425 cm^{-1} (—C—O—C—); n.m.r. spectrum δ_{TMS}(CDCl$_3$): 0.5–1.5 (6H, m, CH(CH_3)$_2$), 1.87 (1H, m, J = 5 Hz, CH(CH$_3$)$_2$), 7.0–8.2 (8H, m, aromatic protons).

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