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REACTIONS OF POLYCYCLIC QUINODIMETHANES
AND RELATED COMPOUNDS

by

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A Thesis submitted to the
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partial fulfilment of the
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of DOCTOR of PHILOSOPHY.

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SUMMARY

The thesis describes the use of polycyclic quinodimethanes and related compounds as reactive intermediates in the synthesis of polycyclic aromatic and heterocyclic systems, some of which are novel.

Following a general introduction (Chapter I), Chapter II describes the reactions of 5,6-chrysaquinodimethane to give dimers, and its reactions with various dienophiles; including 1,4-naphthoquinone, with which it gives a novel ring system. Chapter III describes the reaction of 9,10-phenanthraquinodimethane with 1,4-naphthoquinone and attempts to synthesise 6,12-chrysaquinone from chrysene. The reactions of 9,10-anthraquinodimethane with various dienophiles are described (Chapter III) while Chapter IV describes the reactions of 9-methyleneanthrone and 10-methyl-10-hydroxyanthrone with dimethyl acetylenedicarboxylate and diethyl azodicarboxylate. Chapter V describes the reactions of 1,1-diphenylethylene with various dienophiles to give novel adducts; and Chapter VI describes the preparation of endo-adducts of anthranol.

ACKNOWLEDGMENTS

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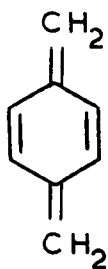
CHAPTER I

Introduction

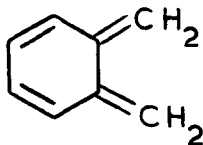
Quinodimethanes are aromatic compounds in which both oxygen atoms of a quinone have been replaced by methylene groups. Although little known before 1955, much interest has since been shown in these highly reactive compounds as indicated by the number of papers published in this field in the last decade. The highly reactive nature of these compounds (which is of value in synthetic chemistry) means that normally they are encountered only as reactive intermediates, although a few have been isolated.

Early work on the chemistry of quinodimethanes has been adequately reviewed by L. A. Errede and M. Szwarc¹ who were mainly interested in polymerisation studies on p-quinodimethane (p-xylylene) (I) and by J.M. Tedder² who briefly reviewed the chemistry of o-quinodimethane (II) as well as that of p-quinodimethane. The para- and ortho-quinodimethanes are normally encountered only as reactive intermediates, though p-quinodimethane is relatively stable in solution at low temperatures;³ o-quinodimethane is less stable and has not been isolated. Calculated resonance energies for (I) and (II) (29 and 34 kcal. respectively) imply that the elusiveness of these entities is due more to their high reactivity than to any inherent instability. The spectra and diamagnetism of p-quinodimethane

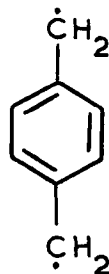
show that it exists as such rather than a diradical (III).^{4,5}



I

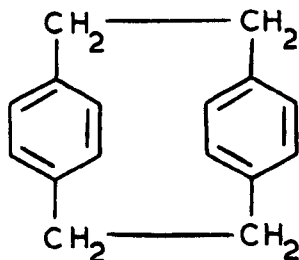


II

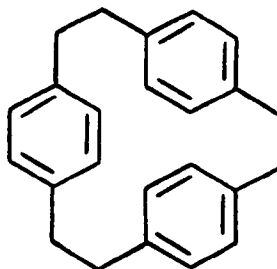


III

Pyrolysis of the o- and p-methylbenzyltrimethylammonium hydroxides^{6,7} and the reaction of magnesium with the o- and p-methoxymethylbenzyl chlorides⁸ give the o- and p-quinodimethanes; and p-quinodimethane is also formed on pyrolysis of p-xylene,⁹ and o-quinodimethane by the pyrolysis of 2,5-dihydrobenzo[b]thiophene-1,1-dioxide,¹⁰ by the reaction of magnesium with o-xylylene dichloride,⁸ by the action of alkali on 2-toluene-p-sulphonamidoisindoline,¹¹ by the reaction of zinc with o-xylylene dibromide,¹² and by isomerisation of cis-4-octene-1,7-diyne.¹³



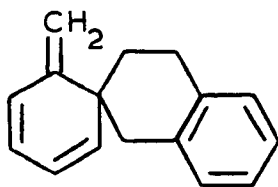
IV



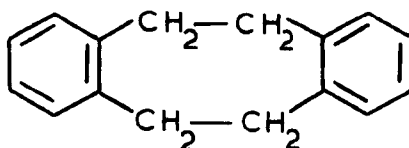
V

Depending on the reaction conditions the quinodimethanes give

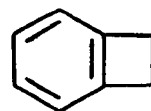
either linear polymers,² or various dimers. The polymerisation of p-quinodimethane has been fully studied;¹ it also gives co-polymers with, e.g. sulphur dioxide¹⁴ and phosphorus trichloride.¹⁵ Dimerisation of p-quinodimethane gives paracyclophane (IV) and the trimer (V) can also be obtained. o-Quinodimethane dimerises to the spiran (VI), or to 1,2,5,6-dibenzocyclo-octadiene (VII); it also isomerises to benzocyclobutene (VIII).



VI

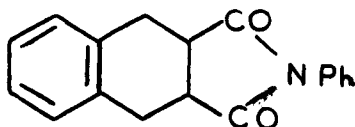


VII

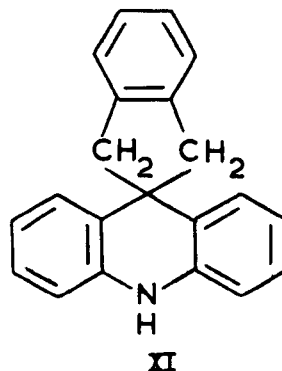
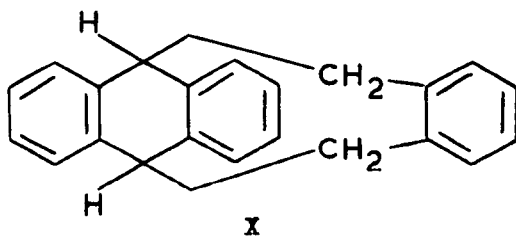


VIII

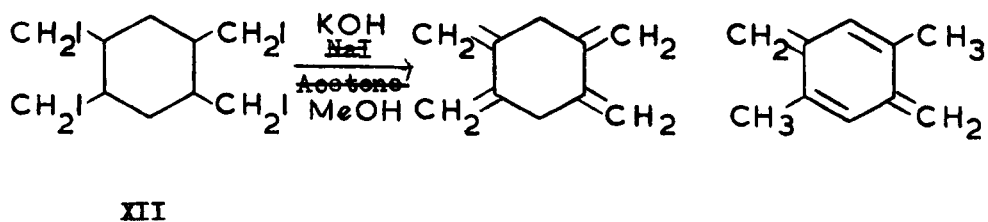
Although o-quinodimethane itself has not been isolated or even obtained in solution, its presence in these reactions may be inferred from the formation of the expected Diels-Alder adducts (IX) and (X), reactions not shown by benzocyclobutene,^{10,16} and other Diels-Alder adducts have been prepared;^{12,17} with acridine it does not give the expected adduct but the spiran (XI).



IX



Various paracyclophanes have been obtained using reactive p-quinodimethane intermediates; of particular interest is the formation of octafluoro[2,2]paracyclophane, formed by pyrolysis of 2,3,4,6-tetrafluoro-4-methylbenzyltrimethylammonium hydroxide:¹⁸ and the formation of a methyl-substituted paracyclophane from the non-aromatic compound (XII) as follows:

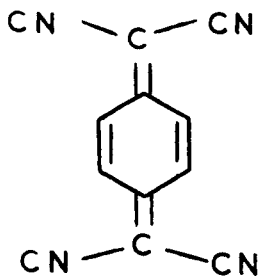


Pyrolysis of pentamethylbenzyltrimethylammonium hydroxide gives as intermediates both the corresponding o- and p-quinodimethanes, which

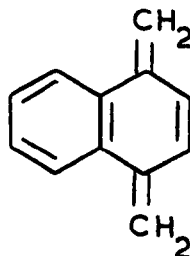
give a mixture containing polymer, a paracyclophane and the o-quinodimethane octadiene dimer, octamethyldibenzocyclo-octadiene.¹⁹

Several p-quinodimethanes with substituents on the exocyclic carbon atoms (7 and 8) have been obtained; pyrolysis of 1,4-bis(bromo-difluoromethyl)benzene over zinc gives 7,7,8,8-tetrafluoroquinodimethane which immediately polymerises.²⁰ The corresponding tetrachloroquinodimethane obtained by pyrolysis of 1,4-bis(trichloromethyl)benzene over copper is more stable, existing as a yellow solid at -78° .²¹ Even more stable is 7,7,8,8-tetracyanoquinodimethane,²² m.p. $293-296^{\circ}$ (XIII): this compound and its derivatives^{23,24} are strong Lewis acids forming charge-transfer complexes with many electron-rich compounds;²⁵ these complexes are claimed to have the highest electrical conductivity known for organic compounds.²³ Other stable 7,7,8,8-tetrasubstituted quinodimethanes have been prepared by the same workers.²⁶

The corresponding o-quinodimethanes have not been obtained though α,α -dibromo-o-quinodimethane has been postulated in the reaction of sodium iodide with $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-o-xylene,²⁷ and α,α,α' -tribromo-o-quinodimethane has been postulated when the same starting material is heated with potassium *t*-butoxide.²⁸

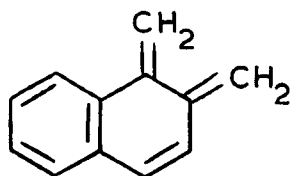


XIII

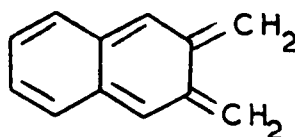


XIV

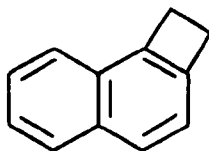
Benzoquinodimethanes have been postulated in several reactions; pyrolysis of 4-methyl-1-naphthyltrimethylammonium hydroxide gives the benzo-p-quinodimethane (XIV) which dimerises to anti[2,2]paracyclonaphthene.²⁹ Pyrolysis of 1,4-dimethylnaphthalene also gives (XIV) which under these circumstances polymerises.^{29a} The benzo-o-quinodimethanes (XVI) and (XVII) have been postulated in the formation of the naphthocyclobutenes (XVII) and (XVIII) from the corresponding naphthosulphones, as shown by the formation of the expected Diels-Alder adducts with maleic anhydride and N-phenylmaleimide;^{30,31} a diphenyl-naphthocyclobutene has been prepared in a similar fashion.³²



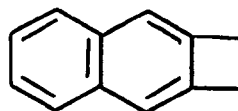
XV



XVI

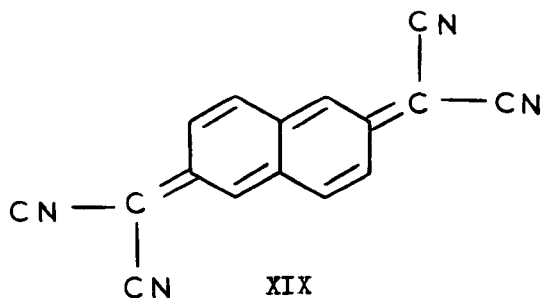


XVII

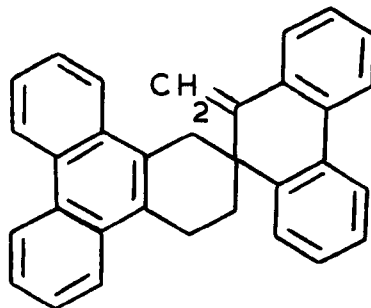
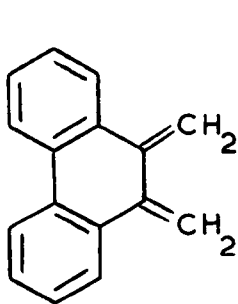


XVIII

In addition the stable 11,11,12,12-tetracyano-2,6-naphthoquinodimethane (XIX), m.p. $> 420^{\circ}$ has been prepared,²⁴ having similar properties to 7,7,8,8-tetracyanoquinodimethane previously mentioned.

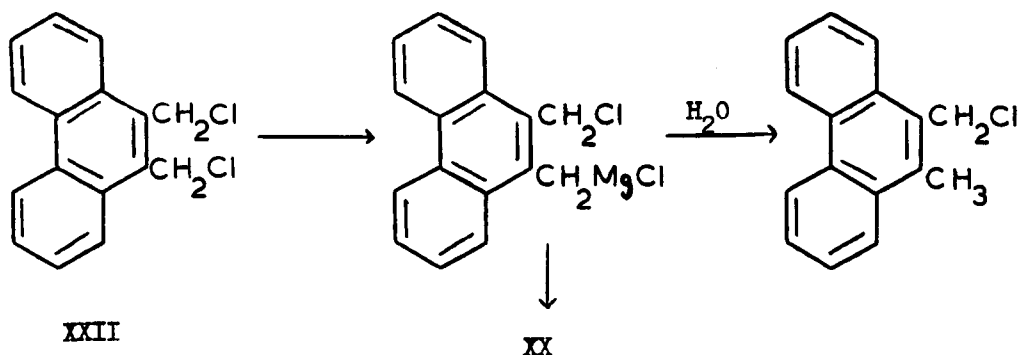


9,10-Phenanthraquinodimethane (XX) was first postulated as a reaction intermediate by Gardner and Sarrafizadeh³³ when they thermally decomposed trimethyl-10-methyl-9-phenanthrylmethylammonium hydroxide to give a polymer and a compound which they formulated as the spirocyclic dimer (XXI). Millar and Wilson³⁴ confirmed and extended this work;



in addition to obtaining as major product a non-volatile mixture of the spirocyclic dimer and polymeric material, they obtained a distillate which they trapped at -78° in ethanol. This distillate apparently

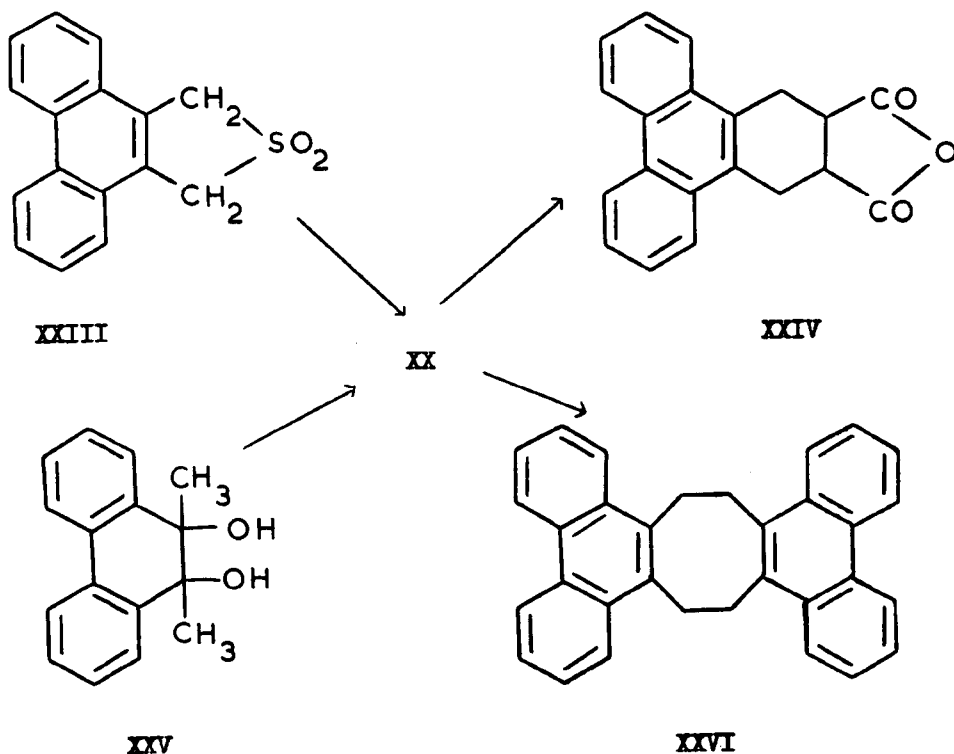
contained the monomeric quinodimethane (XX), since with hydrogen chloride at -78° it gave 9-chloromethyl-10-methylphenanthrene. In addition, Millar and Wilson used several methods, employed with success for the monocyclic quinodimethanes (I) and (II), for generating 9,10-phenanthraquinodimethane; reaction of 9,10-bis(chloromethyl)phenanthrene (XXII) with magnesium in diethyl ether or tetrahydrofuran gave an oxygen-containing polymer and an ether. Also isolated from this reaction (which consumed one molar equivalent of metal) was 9-chloromethyl-10-methylphenanthrene. These products presumably arise as shown:



Thermal decomposition of 1,3-dihydrophenanthro[9,10c]thiophen-1,1-dioxide (XXIII) in boiling diethyl phthalate gave (XX) since in the presence of maleic anhydride it gave the adduct (XXIV) which was subsequently dehydrogenated and decarboxylated to triphenylene.^{34,35}

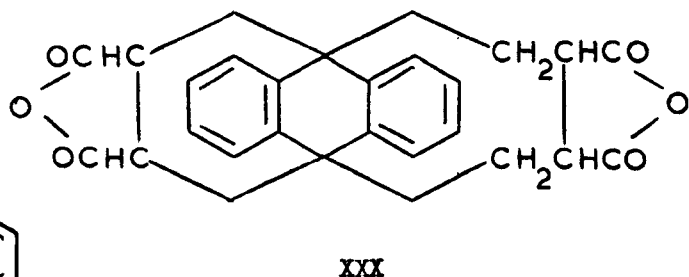
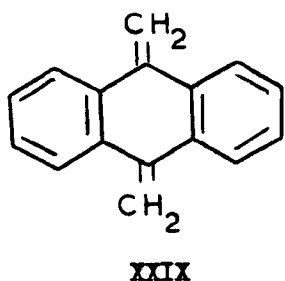
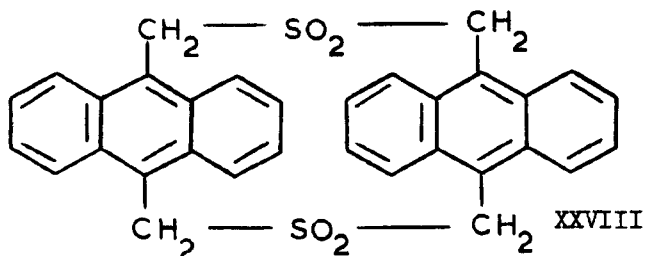
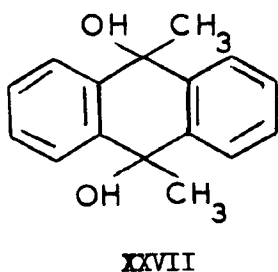
Millar and Wilson also obtained the adduct (XXIV) by dehydration of the diol (XXV) in boiling diethyl phthalate in the presence of maleic

anhydride. This method has an advantage over previous methods in that the diol is easily available from the corresponding quinone.

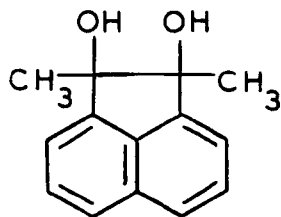


Working independently at about the same time, Stille and Foster³⁶ by pyrolysis of the diol (**XXV**) over alumina, obtained (depending on the temperature) polymeric 9,10-phenanthraquinodimethane, 9,10-dimethylphenanthrene, and 9-methylfluorene. An attempt to obtain the adduct (**XXIV**) by dehydration of the diol (**XXV**) in boiling acetic anhydride in the presence of maleic anhydride was unsuccessful. Like

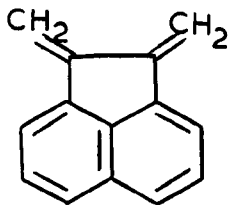
Millar and Wilson, Stille and Foster by pyrolysis of the sulphone in the presence of maleic anhydride obtained the adduct (XXIV). Heating the sulphone on its own in diethyl phthalate gave the cyclic dimer (XXVI) which was also obtained by heating at 275° the spirocyclic dimer (XXI) which was obtained by reaction of 9,10-bis(iodomethyl)-phenanthrene with sodium iodide in acetone.



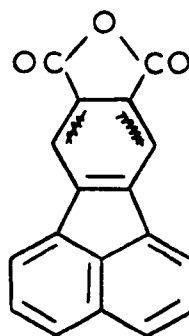
Pyrolysis of the diol (XXVII) and the sulphone (XXVIII) in boiling diethyl phthalate in the presence of maleic anhydride gave an adduct for which Millar and Wilson³⁴ suggested the structure (XXX), derived by reaction of maleic anhydride with 9,10-anthraquinodimethane (XXIX).



XXXI

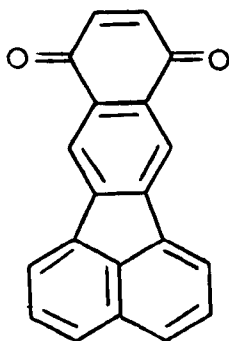


XXXII

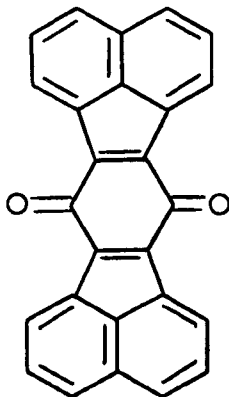


XXXIII

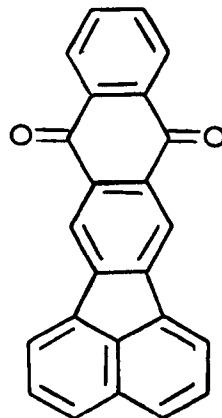
In addition to the chemistry of the true quinodimethanes, a quasi-quinodimethane, 7,8-dimethylenecyclohexa-1,3-diene (XXXII) has been described. Reaction of trans-7,8-dimethylacenaphthene-7,8-diol (XXXI) in acetic acid gave a hydrocarbon which is probably polymeric dimethylenecyclohexa-1,3-diene.³⁷ Campbell and Gow³⁸ allowed the intermediate to react with various dienophiles by heating trans-7,8-dimethylacenaphthene-7,8-diol (XXXI) in acetic anhydride in the presence of the dienophiles. (Use of the cis isomer in the diene reaction gave only a red polymer). Reaction with maleic anhydride gave the adduct (XXXIII); depending on the molar proportions reaction with benzoquinone gives either (XXXIV) or (XXXV). The reaction with 1,4-naphthoquinone gives the adduct (XXXVI).



XXXIV

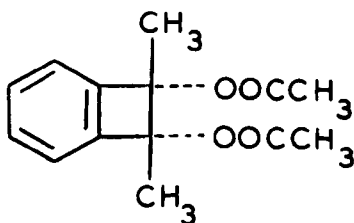


XXV

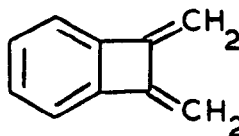


XXXVI

Pyrolysis of the diol diacetate at 300° (XXXVII) gives 1,2-dimethylenebenzocyclobutene (XXXVIII), which is not very stable, polymerising at room temperature after a few hours.³⁹



XXXVII



XXXVIII

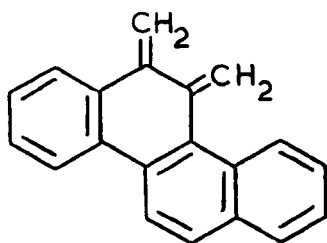
The work described in this thesis is concerned with studies on quinodimethanes derived from chrysene and phenanthrene (Chapter 2) and anthracene (Chapter 3) by dehydration of the dimethyl diols and with Diels-Alder-type reactions of the cognate compounds,

9-methyleneanthrone (Chapter 4), 1,1-diphenylethylene (Chapter 5) and anthrone (Chapter 6).

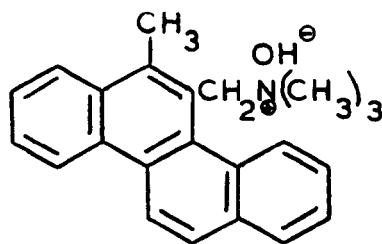
CHAPTER II

Quinodimethanes Derived from Chrysene and Phenanthrene

The initial aim of the work with 5,6-chrysaquinodimethane (XXXIX) was to follow the pattern of work with 9,10-phenanthraquinodimethane, i.e. to use various methods to generate 5,6-chrysaquinodimethane, to prove its existence by trapping it with maleic anhydride and to obtain if possible various types of dimer. The two methods devised to give 5,6-chrysaquinodimethane were the dehydration of the 5,6-dimethyldiol (XLI) and the thermal decomposition of the quaternary ammonium hydroxide (XL) or its isomer.



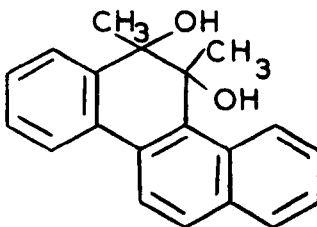
XXXIX



XL

Chrysene was oxidised using sodium dichromate to 5,6-chrysaquinone⁴⁰ which was treated with excess methylmagnesium iodide to give 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene (XLI).⁴¹ A few modifications were made in the work-up of the crude product which resulted in slightly

improved yield and purity.

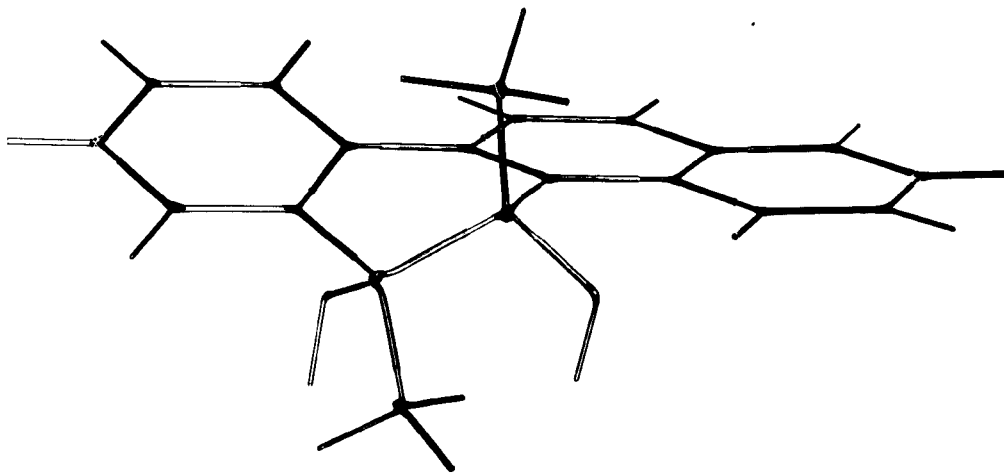


XLI

By comparison with the analogous preparation of the corresponding phenanthrenediol (XXV) it has been claimed that the chrysenediol should have the trans configuration.⁴² While it is true that phenanthraquinone does react with Grignard reagents to give invariably the trans isomers,⁴³ this is not necessarily so with 5,6-chrysaquinone, as here steric factors not present in the phenanthrene system might have some effect.

Infrared spectroscopy shows that in carbon tetrachloride solutions, at concentrations from 0.0025 molar to 0.04 molar, two peaks were present, the weaker at 3595 cm.^{-1} , the stronger at 3560 cm.^{-1} . When a plot of absorption against molar concentration was made two straight lines are found, both of which pass through the origin. In chloroform, at concentrations of up to 0.2 molar, a shift in the frequency of these peaks is seen, to 3620 and 3590 cm.^{-1} (the peak at 3620 cm.^{-1} appearing as a shoulder); in addition, at these higher concentrations a bulge begins to appear, centre c. 3440 cm.^{-1} . In the solid state (i.e. Nujol Mull) two peaks of comparable intensity are shown at 3550 and 3460 cm.^{-1} .

These peaks could be assigned as follows: the peak at 3460 cm.^{-1} (in solid state) being due to intermolecular hydrogen bonding, which is



5,6-Dimethyl-5,6-dihydro-5,6-dihydroxychrysene XLI
showing the two methyl groups in pseudo axial
positions and the two hydroxyl groups in pseudo
equatorial positions.

beginning to appear in solution at concentrations above 0.1 molar (c. 3440 cm.^{-1}). The peak at 3560 cm.^{-1} is due to intramolecular hydrogen bonding, dilution making no difference, its frequency varying slightly in the solid state and in a different solvent. This leaves the peak at 3595 cm.^{-1} which is due to free hydroxyl.

Although these factors initially seem to indicate that the diol is intramolecularly hydrogen-bonded and hence not a trans diol, consideration of Dreiding Models reveals that for one trans conformation, intramolecular hydrogen bonding is possible. This conformation is one in which both methyl groups are in the pseudo equatorial positions (see photograph); in this conformation the interatomic distance between the oxygen atom of one hydroxyl group and the hydrogen atom of the other is 3.0\AA (intramolecular hydrogen bonding requires an approach of less than 3.4\AA).⁴⁴ As a trans configuration would be in accord with the comparable phenanthrene diols it seems likely that 5,6-dimethyl-5,6-dihydro-5,6-dihydroxyehrysene has the trans conformation shown.

The n.m.r. spectrum of this diol could possibly be regarded as giving further support for this trans conformation. This spectrum shows two methyl singlets at 8.33 and 8.51 τ , indicating that these two methyl groups are in slightly different environments, as they would be in the two pseudo axial positions. If the diol had a cis configuration, one of the methyl groups would be in a pseudo axial position and the other would be in a pseudo equatorial position, differences of environment which might be expected to show up as a larger shift than 0.18 τ .

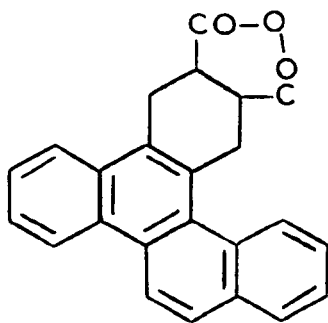
Two other points of interest are observed in the n.m.r. spectrum;

the first is a singlet peak at 2.04τ , due to the two protons at positions 11 and 12 which must hence be identical. Presumably the degree of twist in the molecule caused by the hydrogenated substituents at positions 5 and 6, and the substituents themselves causes these protons (which in chrysene are not identical, giving multiplet peaks at 1.33 and 2.22τ ⁴⁵) to have absolutely identical environments.

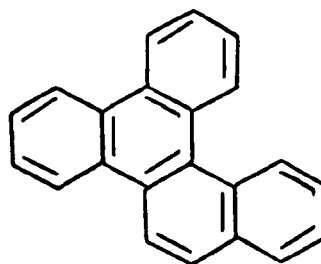
The other point of interest is that the n.m.r. spectrum also shows a multiplet peak centred at 0.68τ due to the proton at position 4. This represents a considerable downfield shift as in fully aromatic 5,6-disubstituted chrysene compounds, e.g. 5-methyl-6-chloromethyl-chrysene and 5-methyl-6-ethoxymethylchrysene (see later), the comparable proton is centred at c. 1.20τ . Hence it seems unlikely that this downfield shift is due in any way to an adjacent methyl group in a pseudo equatorial position which there is not if the postulated trans conformation is correct. The only other explanation could be then that this downfield shift is due in some way to the adjacent hydroxyl group in a pseudo equatorial position. Unfortunately as far as is known, no work has been done on similarly placed hydroxyl groups. The shift is not due to hydrogen bonding of the hydroxyl group with the adjacent aromatic system as this would involve the π -electrons as a whole and not one proton.

Proof that the dehydration of the dimethyl diol (XLI) gives 5,6-chrysaquinodimethane (XXXIX) came when the dimethyl diol was heated in boiling diethyl phthalate in the presence of maleic anhydride to give 5,6-benzo-1',2',3',4'-tetrahydrochrysene-2',3'-decarboxylic anhydride (XLII) m.p. 323° , in 29% yield. Precise control of quantity and time

of heating was found to be essential for maximum yield. From the anhydride (XLII) the corresponding dicarboxylic acid, m.p. 135-6° was prepared, which on heating above its m.p. readily dehydrated to regenerate the anhydride. Both these compounds showed a typical 5,6-disubstituted chrysene chromophore in the U.V.; c.f. 5,6-dimethylchrysene.⁴⁶



XLII

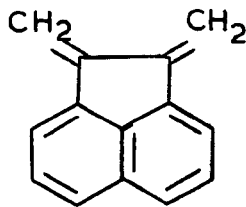


XLIII

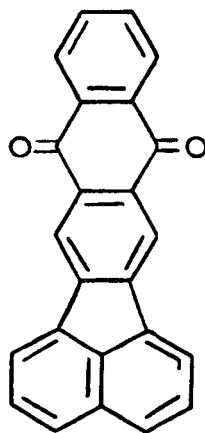
Final proof of the 5,6-benzochrysene structure came by the simultaneous decarboxylation and dehydrogenation of the anhydride (XLII) by boiling it in alkaline ferricyanide solution³⁸ to give, in low yield, 5,6-benzochrysene with identical ultraviolet chromophore to that given.⁴⁷

When the dimethyl diol (XLI) was heated on its own in boiling diethyl phthalate in the expectation of obtaining either polymeric or dimeric material, no such product was obtained, implying that although presumably the 5,6-chrysaquinodimethane (XXXIX) was liberated, in the absence of dienophiles it reacted reversibly with water to give the unchanged diol which was recovered on cooling.

It was at this stage that the emphasis of this work began to change when it was realised that the reaction of suitable dienophiles with 5,6-chrysaquinodimethane (or any other polycyclic quinodimethane) could have definite synthetic possibilities as Campbell and Gow³⁸ had shown much earlier in their studies on the quasi-quinodimethane (XXXII) (see Chapter 1, p. 11).

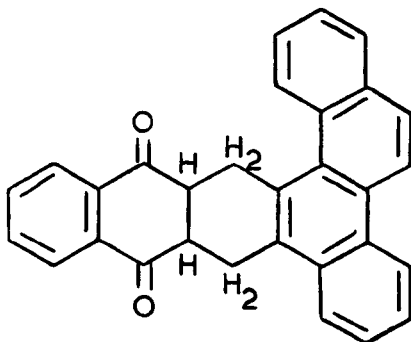


XXXIII

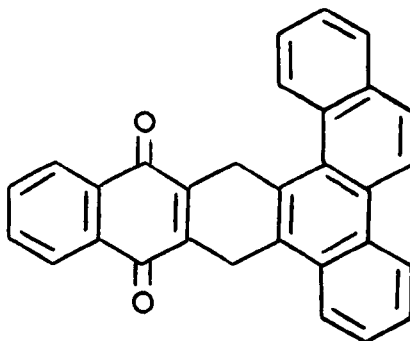


XXXVI

The dehydration of the 5,6-dimethyldiol (XLI) in boiling diethyl phthalate in the presence of 1,4-naphthoquinone gave 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (XLV) m.p. 322-324°, in a 56% yield⁴⁸ via the intermediate (XLIV) whose bridgehead hydrogen atoms have been oxidised during the reaction, but whose two methylene groups have not been, unlike the corresponding reaction between the quasi-quinodimethane (XXXII) and 1,4-naphthoquinone in boiling acetic anhydride to give the fully aromatic (XXXVI).



XLIV



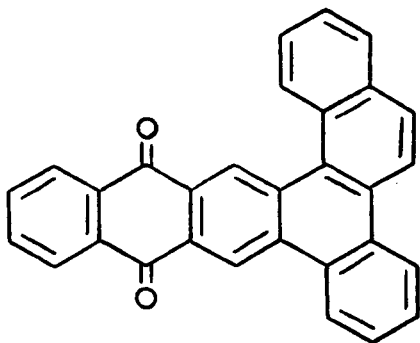
XLV

The structure of the adduct (XLV) is established by analysis, and the presence of a 5,6-dimethylchrysene type chromophore, as well as by its n.m.r. spectrum, which shows a singlet peak due to methylene protons at 8.33 τ .

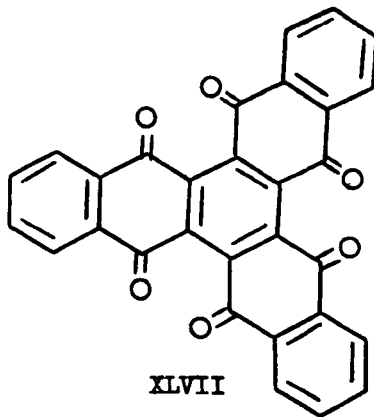
The infrared spectrum shows an interesting very strong absorption band at 707 cm.^{-1} which is attributed to the out-of-plane deformation absorption of the four adjacent aromatic C-H bonds on the terminal ring adjacent to the p-quinone ring.⁴⁷ (See the analogous case of 4,5-benzodiphenyltho[2',3':1,2][2'',3'':7,8]pyrene-1',4':1'',4''-diquinone in Chapter 3, p.87). The frequency of this band is outside that normally attributed to four adjacent aromatic C-H bonds (770 to 735 cm.^{-1}) although analogous shifts do occur with, e.g. anthrone (710 cm.^{-1}),

bianthron-9-yl (690 cm.^{-1}), 9,10-anthraquinone (692 cm.^{-1}) and methyleneanthrone. In addition to the band at 707 cm.^{-1} , 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone also shows strong bands at 742 and 754 cm.^{-1} due to the other two terminal rings containing four adjacent aromatic C-H bonds.

The reaction between the 5,6-dimethyldiol and 1,4-naphthoquinone in other solvents was also investigated: no reaction occurred in boiling acetic anhydride. A 3% yield of the adduct (XLV) was obtained in boiling diphenyl ether and 5% yield when the reactants were heated in boiling nitrobenzene for 15 minutes, indicating that a fairly high temperature is required for dehydration to take place.



XLVI

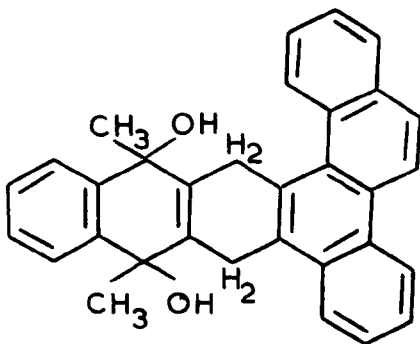


XLVII

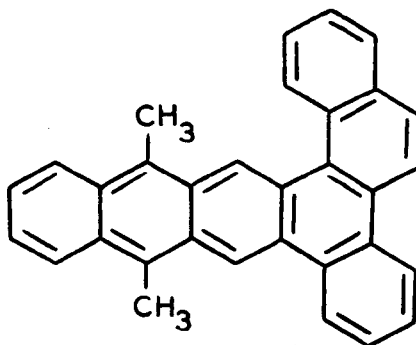
Heating for longer times in nitrobenzene did not give the fully aromatic quinone (XLVI) as hoped, but on one occasion 48 hours heating gave trinaphthylene-5,18:6,11:12,17-triquinone (XLVII) as shown by comparison with authentic material prepared by heating 1,4-naphthoquinone in nitrobenzene containing acetic acid and pyridine.⁴⁹

This triquinone is of interest in that its infrared spectrum shows two quinone peaks at 1678 and 1650 cm^{-1} presumably due to the close proximity of adjacent oxygen atoms, forcing these to be non-planar; a strong absorption is also shown at 686 cm^{-1} due to the terminal four adjacent aromatic C-H bonds. In another experiment a mixture of the triquinone (XLVII) and the hydrogenated quinone (XLV) was obtained after 8 hours.

Attempts to dehydrogenate the hydrogenated quinone (XLV) using 10% palladium-charcoal, either by heating the quinone with Pd/C in 1-methylnaphthalene for 24 hours, or by heating the quinone with Pd/C at 300-320° for 4 hours, have both failed, as did heating the quinone with 2,3-dicyano-4,5-dichlorobenzoquinone in xylene for 18 hours.



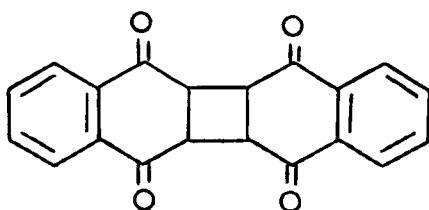
XLVIII



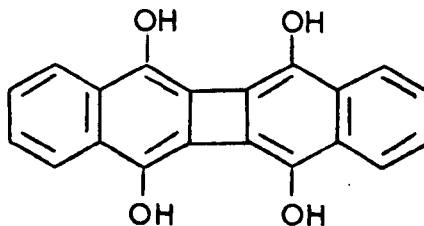
XLVIX

An approach to the fully aromatic system corresponding to (XLVIX) was tried by reacting the quinone with excess methylmagnesium iodide in the expectation of obtaining the diol (XLVIII) which it was

hoped would readily dehydrate to give 6,11-dimethyl-3,4-benzonaphtho-[1',2':1,2]naphthacene (XLVIX). Unfortunately the quinone failed to react with excess of methylmagnesium iodide in ether, ether-benzene or in di-n-butyl ether.

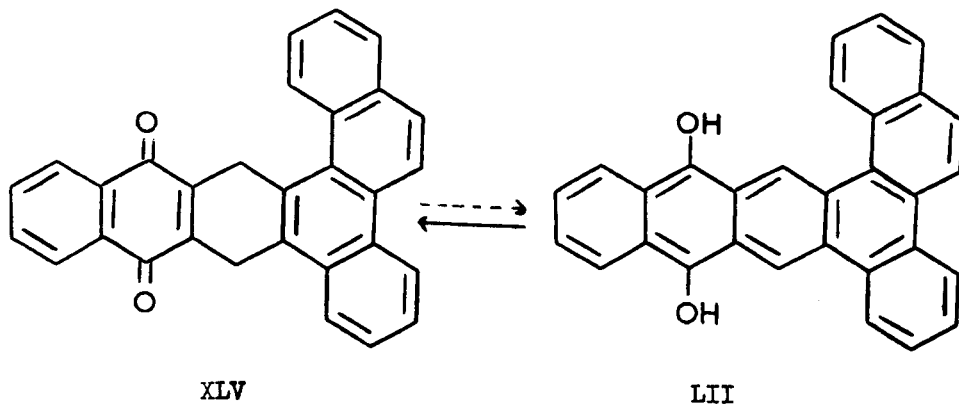


L

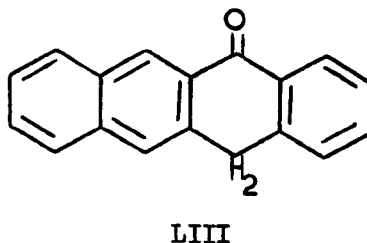


LI

Another approach (based on the enolisation of the photodimer (L) to the tetrahydroxydibenzobiphenylene (LI)⁵⁰) in which it was hoped that treatment of the hydrogenated quinone (XLV) with sodium hydroxide solution followed by acidification would give the fully aromatic diphenolic compound (LII) was tried. When dilute sodium hydroxide solution was added to a solution of the quinone in boiling dioxan, the colour immediately changed from yellow to an intense dark green suggesting that enolisation had taken place. On cooling, however, this intense colour faded and unchanged quinone began to separate out, and eventually all the quinone was recovered, indicating that the quinone is more stable than the diphenolic form.



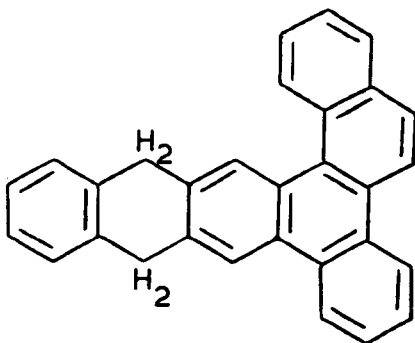
This is in accord with the trend for the stability of dihydro forms to increase in the linear polycyclic series,⁵¹ e.g. 1-naphthol is stable whereas anthrone is the more stable form of the tautomer anthrone-anthranol. In the naphthacene series the ketonic form (LIII) is so stable that it can only be transformed with the aid of alcoholic potash into the enol form which is so unstable that it cannot be isolated in a pure state.



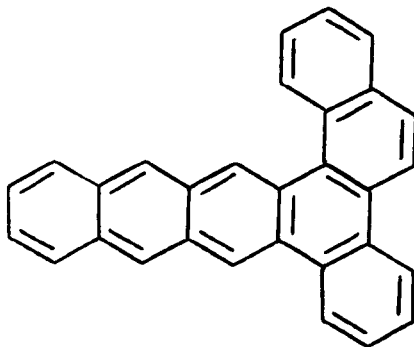
Reduction of the quinone (XLV) was achieved using the zinc-dust melt method⁵² in which a mixture of quinone, sodium chloride and zinc dust with moist zinc chloride was fused at 200-210° and the

melt heated with continuous stirring, eventually to give a solid which was chromatographed.

Two hydrocarbons in variable yields have been obtained in this way, one of which is 6,11-dihydro-3,4-benzonaphtho[1',2':1,2]-naphthacene (LIV) which was obtained in one experiment only. Other similar experiments gave the fully aromatic 3,4-benzonaphtho[1',2':1,2]-naphthacene (LV) which was also obtained when heating was continued for longer periods.



LIV



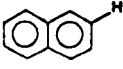
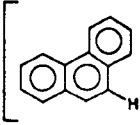
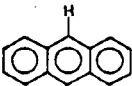
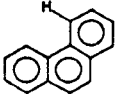
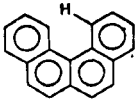
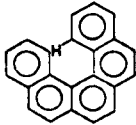
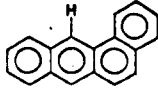
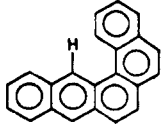
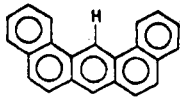


LV

6,11-Dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene (LIV) is a yellow solid, m.p. 135-136°, whose ultraviolet spectrum exhibits the expected chromophore for a suitably disubstituted 5,6-benzochrysene derivative.

Before considering the n.m.r. spectrum of this hydrocarbon it is necessary to consider, as essential background, work which has been done in elucidating the n.m.r. spectra of complex polycyclic hydrocarbons. Martin has classified aromatic protons into the different types as shown in Table 1 (reproduced from ⁵²) and has

TABLEAU 1. NATURE DES DIFFERENTS TYPES DE PROTONS AROMATIQUES ET SYMBOLES CORRESPONDANTS.

Type d'hydrogène	Dénomination	Symbole
Hydrogènes non angulaires		
	H sur noyau isolé	H- φ
	H du type α -naphthalénique	H- α
	H du type β -naphthalénique	H- β
	H du type <i>méso</i> phénanthrénique	H- $\alpha\beta$
	H du type <i>méso</i> anthracénique	H- γ
Hydrogènes angulaires		
	H ang. du type phénanthrénique	H- α_3
	H ang. du type benzo[c]phénanthrénique	H- α_4
	H ang. du type dibenzo[c,g]phénanthrénique	H- α_5
	H ang. <i>méso</i> anthracénique du type phénanthrénique	H- γ_3
	H ang. <i>méso</i> anthracénique du type benzo[c]phénanthrénique	H- γ_4
	H ang. <i>méso</i> anthracénique deux fois phénanthrénique	H- $\gamma_{3,3}$
Cette liste n'est, bien entendu, nullement limitative.		

assigned values to the various chemical shifts of these different types as seen in Table 2 and Figure 1 which have been found by recording the n.m.r. spectra of various polycyclic aromatic hydrocarbons.⁴⁵

Table 2

Chemical shifts of different types of aromatic protons

Non-angular protons	Chemical shift at 60 Mc (CDCl_3)	
	in c/s (TMS = 0)	τ values (TMS = 0)
H- (benzene)	singlet at 436	2.73
H- β (naphthalene)	multiplet, centre at 445	2.58
H- $\alpha\beta$ (phenanthrene)	singlet at 463	2.28
H- α (naphthalene)	multiplet, centre at 467	2.22
H- γ (anthracene)	singlet at 503	1.62
Angular protons		
H- $\alpha 5$ (dibenzo[c,g]phenanthrene)	multiplet, centre at 511	1.49
H- $\alpha 3$ (phenanthrene)	multiplet, centre at 520	1.31
H- $\gamma 3$ (benzo[a]anthracene)	singlet at 544	0.96
H- $\alpha 4$ (benzo[c]phenanthrene)	multiplet, centre at 549	0.85

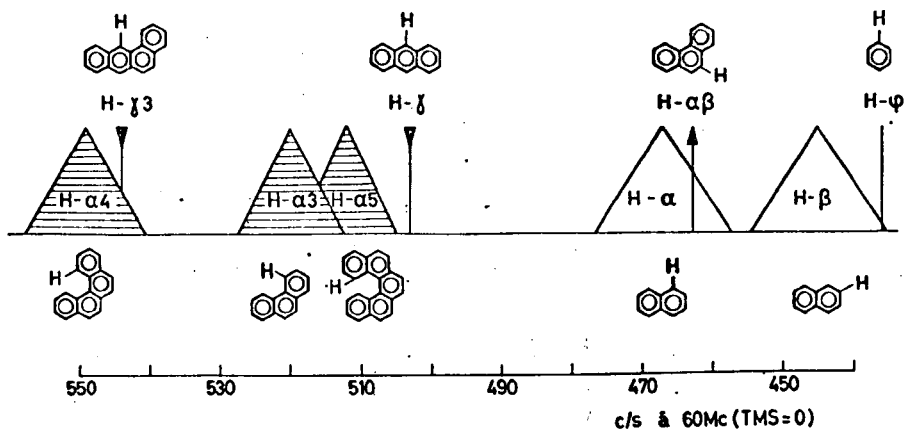


FIGURE 1

These chemical shifts are not meant to be arbitrary but are meant as a guide only as various factors tend to alter these values slightly depending on the hydrocarbon under consideration, as well as the solvent used, although according to Martin this does not make much difference. One value, not given by Martin, is for $H-\gamma_{3,3}$ for which a value has been given as 0.03τ .⁵⁴ An illustration of the different types of protons in a single hydrocarbon given by Martin is of 4-phenyl-dibenzo[b,1]chrysene (Figure 2).

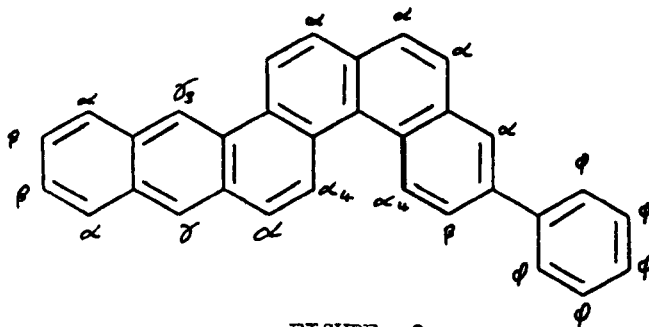
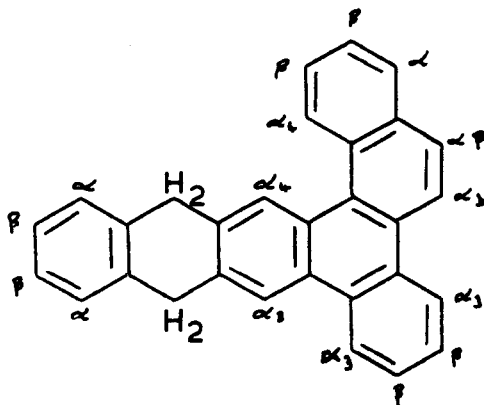


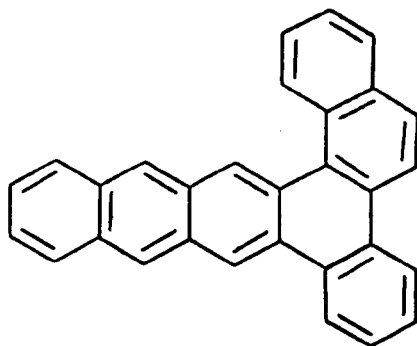
FIGURE 2

As can be seen, the meso-phenanthrene proteins are given as H- α protons rather than H- $\alpha\beta$; this is often found in similar hydrocarbons.

Unfortunately, the n.m.r. spectrum of 6,11-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene (LIV) does not fully conform to all that has been said above. The presence of four methylene protons at 5.83 τ fully confirms the dihydro nature of this hydrocarbon. The aromatic region shows a complex multiplet between 1.90 and 2.73 τ (3 H- α + 6 H- β) on which was possibly superimposed a singlet at 2.30 τ (H- $\alpha\beta$). A multiplet was also shown between 1.20 and 1.55 τ (3H- $\alpha\beta$) on which was superimposed two singlets at 1.25 τ (H- α_4) and 1.45 τ (H- α_3). In addition a multiplet was shown, centre 1.05 τ (H- α_4). These assignments can be seen in the following figure.



As can be seen from the τ values given for the two H-a4 protons these are not only different from each other, but also upfield from the value normally assigned to H-a4 protons (0.85 τ). This could be explained by the effect of the adjacent methylene group on the ring current of the aromatic portion of the molecule. (The difference in the upfield shifts, i.e. 0.85 to 1.25 τ (0.4 τ) for the singlet H-a4 at C₁₂ and to 1.05 τ (0.2 τ) for the multiplet H-a4 at C₁ being explained by the falling off of this effect with distance). As far as can be seen the H-a3 proton at C₅ is shifted upfield from 1.31 τ to 1.45 τ , i.e. only 0.14 τ .

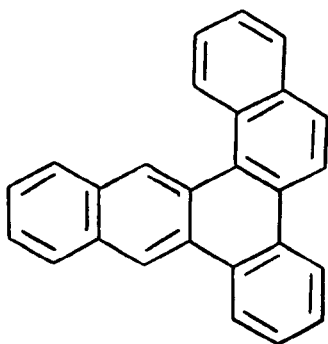


LV

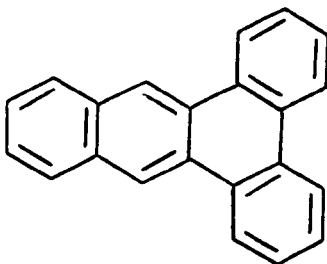
Dehydrogenation of 6,11-dihydro-3,4-benzonaphtho[1',2':1,2]-naphthacene (LIV) with Pd/C at 300° gave 3,4-benzonaphtho[1',2':1,2]-naphthacene (LV) which, as already mentioned, is the product usually obtained, in variable yields, 15 to 25%, when 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (XLV) was reduced by using the zinc dust melt method.⁵² When the quinone was reduced by aluminium cyclohexanolate⁵³ at 160° the yield of 3,4-benzonaphtho[1',2':1,2]naphthacene increases with the time of the reduction, e.g.

to 25% after 60 hours.

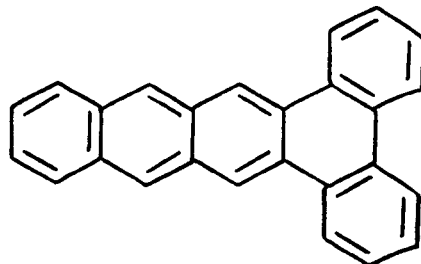
For a while, there was some doubt if this hydrocarbon had the fully aromatic structure or not; for this reason attempts were made unsuccessfully to dehydrogenate it further by heating it for several hours at 300° with Pd/C and by heating it with 2,3-dichloro-5,6-dicyanobenzoquinone in boiling xylene. Although the Pd/C dehydrogenation might not be expected to work due to the fact that at high temperatures the higher linear polyacenes tend to give stable hydrogenated derivatives,⁵⁶ the fact that the low temperature attempt failed using 2,3-dichloro-5,6-dicyanobenzoquinone, which is a more powerful oxidising agent than chloranil, indicates that the hydrocarbon is fully aromatic.



LVI



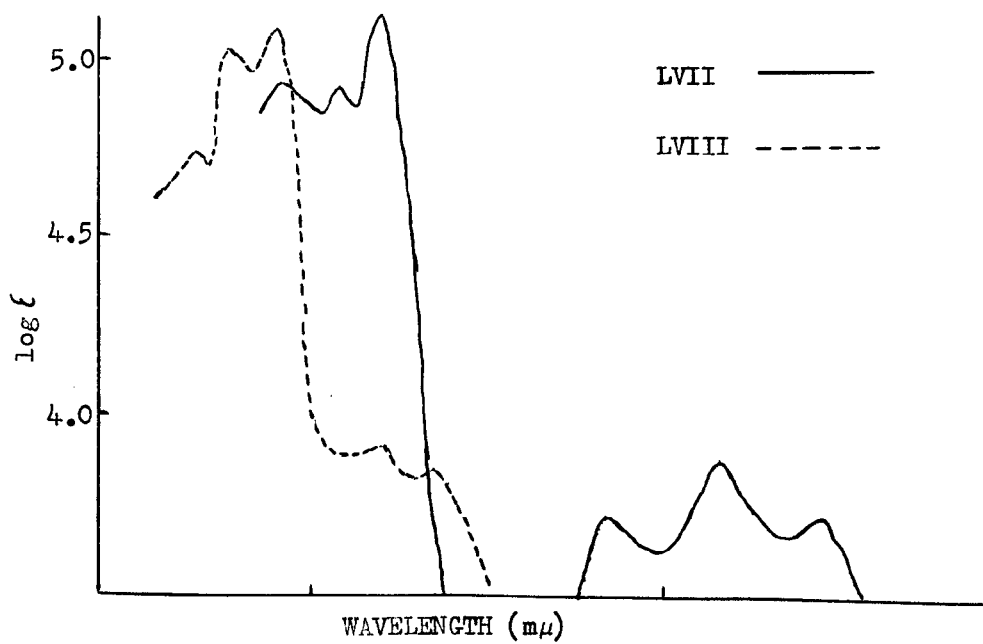
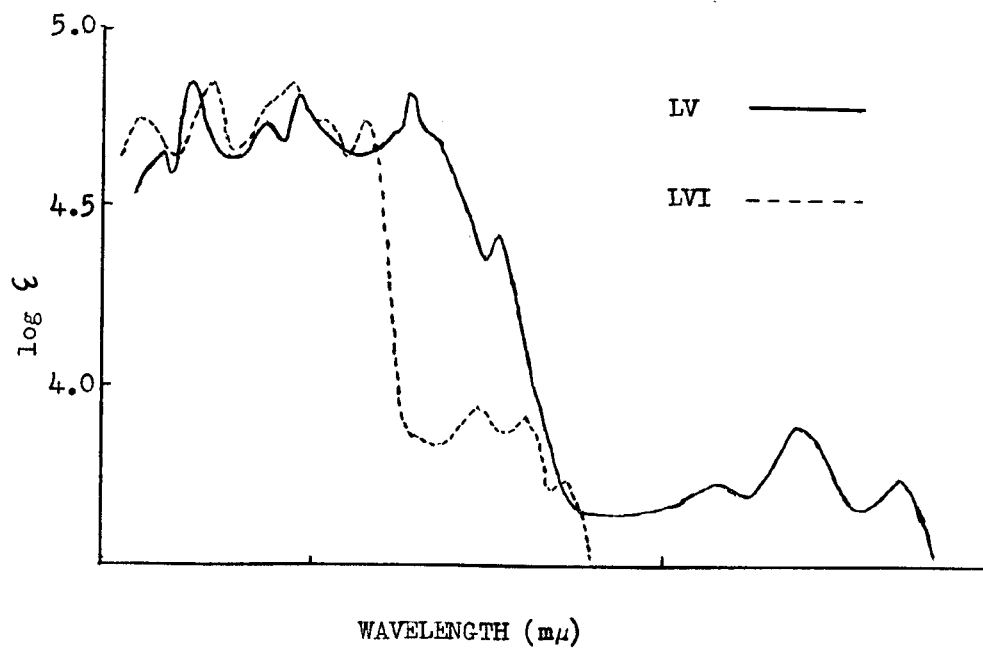
LVII



LVIII

Comparison of the ultraviolet spectrum of 3,4-benzonaphtho-[1',2':1,2]naphthacene with those of 1,2:10,11-dibenzotriphenylene (LVI), 10,11-benzotriphenylene (LVII) and 1,2:3,4-dibenzonaphthacene (LVIII) is interesting and informative.

As can be seen by comparing the spectra of 10,11-benzotriphenylene



with that of 1,2:3,4-dibenzonaphthacene, the addition of another ring has caused a bathochromic shift of the first peak in the Group I band from 286 $m\mu$ to 318 $m\mu$ and in the Group II band from 349 to 441 $m\mu$. When the spectra of 1,2:10,11-dibenzotriphenylene is compared with that of 3,4-benzonaphtho[1',2':1,2]naphthacene it is seen that in the Group I band the bathochromic shift is from 315 to 323 $m\mu$ only whereas in the Group II band the shift is from 376 to 465 $m\mu$, in addition to which there is an 'anomalous' peak at 353 $m\mu$ having $\log_{10} \epsilon$ 4.42, which could belong to either the Group I or the Group II band. Badger⁵⁵ gives values for Group I of $\log_{10} \epsilon$ 4.5 to 5.2 and for Group II of 3.6 to 4.1, but instances are known of Group II values as high as 4.82.

If the bathochromic shifts of these two sets of hydrocarbons are compared it will be seen that the shifts for the Group II bands are comparable indicating that in both instances an extension of the aromatic system by one ring has taken place. With this in mind it would seem certain that the peak at 353 $m\mu$ belongs to the Group I band as only then could the Group I bathochromic shifts of the two sets be comparable, and hence the fully aromatic character of 3,4-benzonaphtho[1',2':1,2]-naphthacene seems assured.

It has been found⁵⁸ that a comparison can be made between the values expressed in wave numbers of the longest ultraviolet absorption bands of a series of polycyclic aromatic hydrocarbons and the minimum number of quinonoid rings contained in their molecules. It was found that the hydrocarbons fell into a series of groups related to the

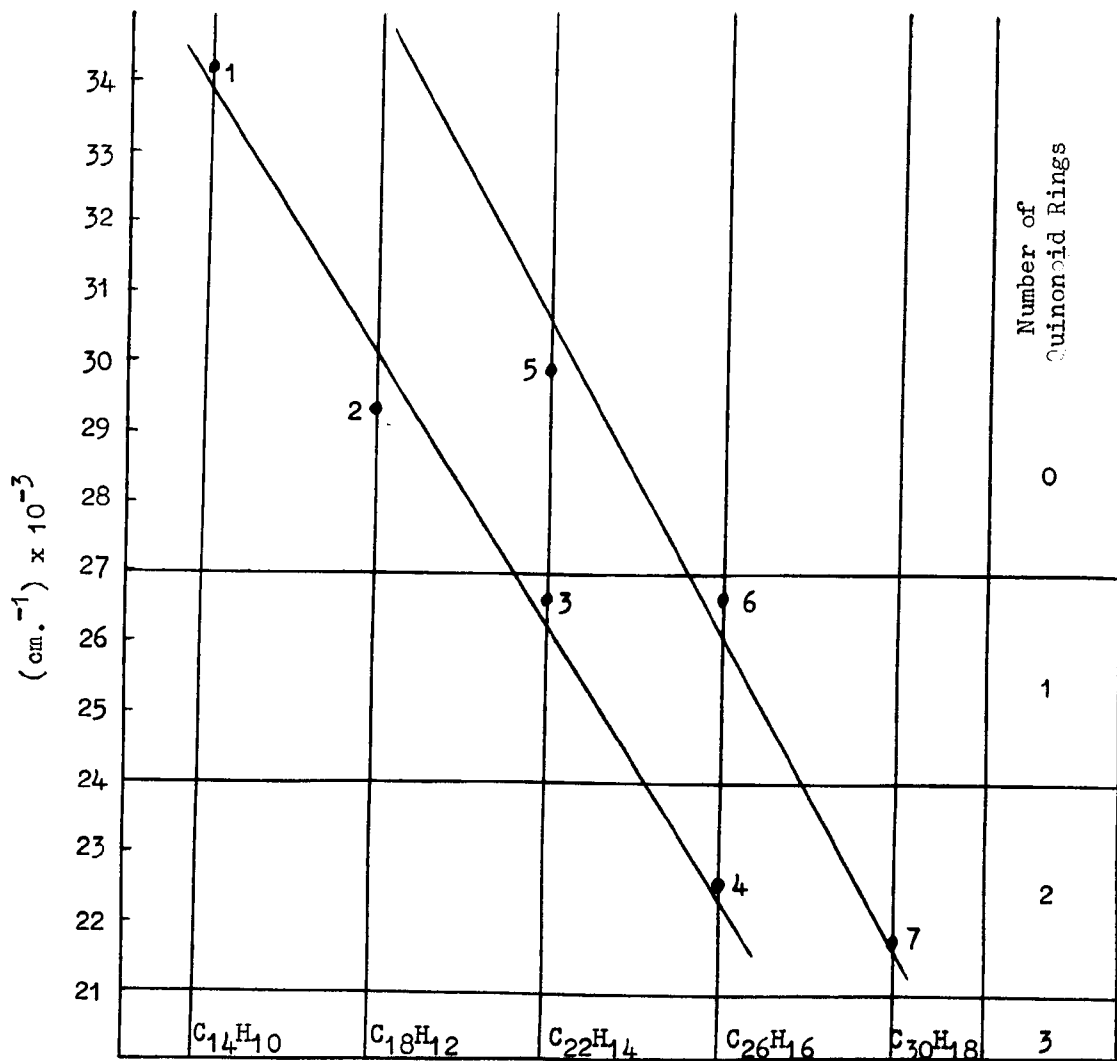


FIGURE 3

1. Phenanthrene; 2. Triphenylene;
3. 10,11-Benzotriphenylene (LVII);
4. 1,2:3,4-Dibenzonaphthacene (LVIII);
5. 5,6-Benzochrysene (XLIII);
6. 1,2:10,11-Dibenzophenylene (LVI);
7. 3,4-Benzonaphtho[1',2':1,2]naphthacene (LV).

number of quinonoid rings. In addition it was shown that for different series of hydrocarbons the values of the maxima of the longest ultraviolet absorption bands lie on approximately straight diagonal lines.

In Figure 3 a similar plot has been made for the series 5,6-benzochrysene, 1,2:10,11-dibenzotriphenylene, 3,4-benzonaphtho[1',2':1,2]naphthacene as well as a comparison plot of the series, phenanthrene, triphenylene, 10,11-benzotriphenylene, 1,2:3,4-dibenzo-naphthacene.

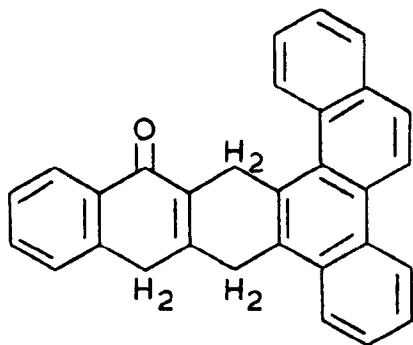
The plot in addition to showing that both series lie on parallel straight lines (confirming the aromatic character of 3,4-benzonaphtho[1',2':1,2]naphthacene) also shows that this hydrocarbon falls in the region given for hydrocarbons having two quinonoid rings, which it can only possess if it is fully aromatic.

3,4-Benzodinaphtho[1',2':1,2]naphthacene is a yellow sublimable solid which can be recrystallised and has m.p. 265 - 267°: it gives a 2,4,7-trinitrofluorenone complex.

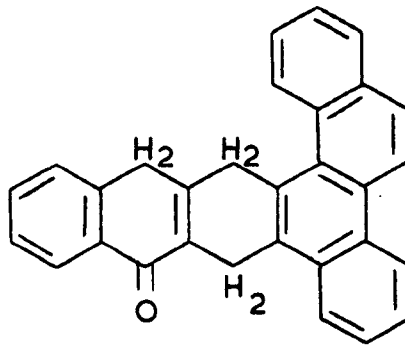
In addition to the successful reductions of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone, other reductive methods were tried. Reduction using the zinc dust, pyridine, acetic acid method⁵⁹ in which a solution of a quinone in pyridine is reduced with zinc dust and acetic acid, was unsuccessful.

Davies and Porter⁶⁰ found that stannous chloride reduction of polycyclic p-quinones gave anthones which could then be reduced to the corresponding hydrocarbon using zinc/sodium hydroxide, claiming that this method gave better yields than other methods, e.g. those of Clar.

Reduction of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone using stannous chloride gave either (LIX) or its isomer (LX) in 62% yield; which, could not be determined. This compound had m.p. $230-233^{\circ}$ if heated fairly rapidly; if heated more slowly it began to melt at 230° but then resolidified to give yellow needles, finally melting $312-315^{\circ}$, indicating that oxidation had occurred to the starting quinone. When this compound was heated with zinc dust, sodium hydroxide and toluene, it dissolved in the sodium hydroxide solution to give, on acidification, unchanged naphthene.



LIX



LX

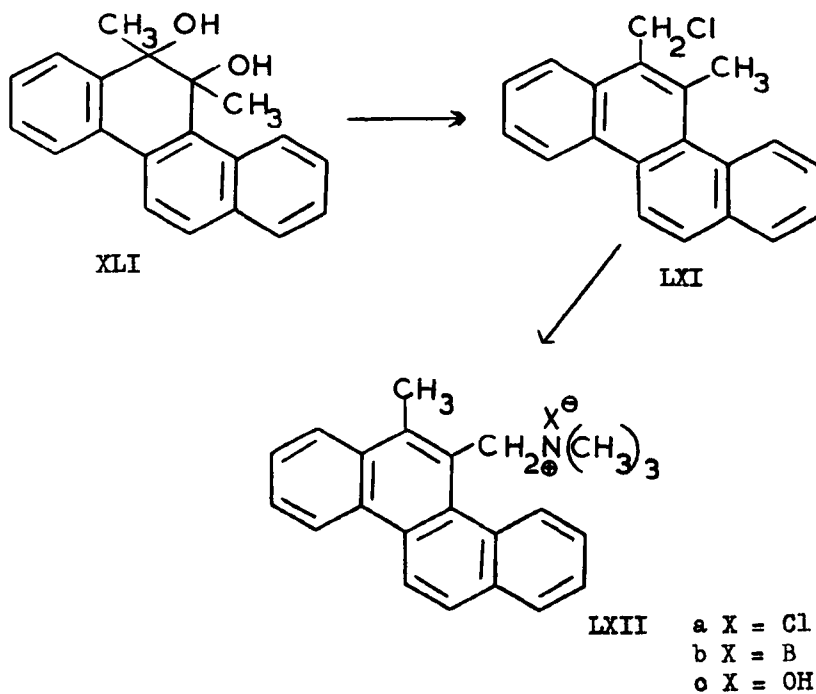
When lithium aluminium hydride was used to reduce 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone, a ketone was again obtained in good yield, m.p. $220-225^{\circ}$; and no hydrocarbon product was isolated.

The reaction of 5,6-chrysaquinodimethane with p-benzoquinone was next investigated by heating a mixture of 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene and excess of the benzoquinone in boiling

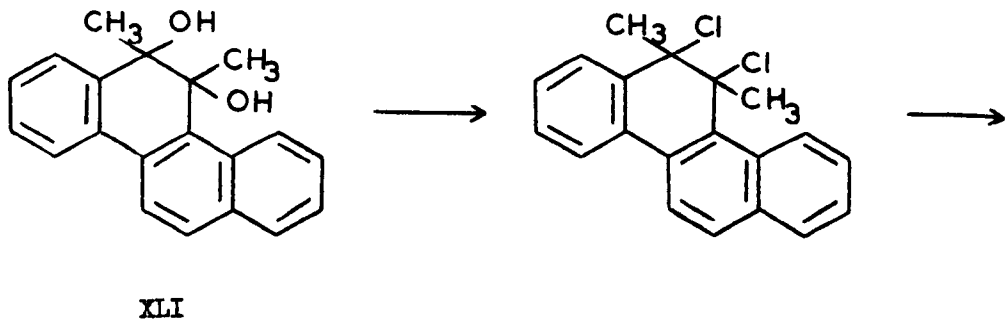
nitrobenzene or diethyl phthalate but the expected product could not be isolated.

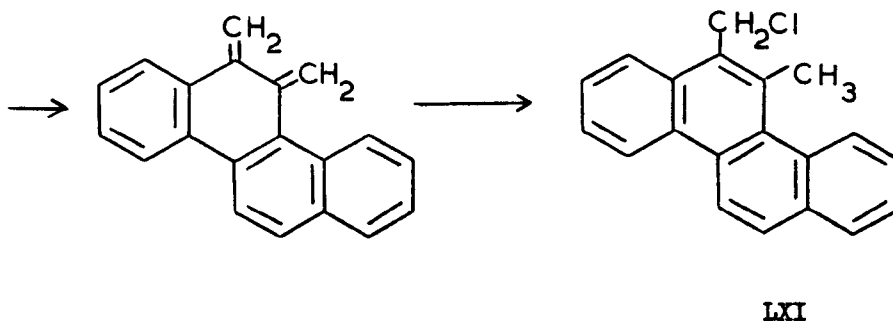
The failure of these reactions with benzoquinone and with 1,4-naphthoquinone in boiling nitrobenzene as opposed to the success with maleic anhydride and 1,4-naphthoquinone in boiling diethyl phthalate seems to indicate that a temperature considerably higher than 200° is required for the thermal dehydration of 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene to give 5,6-chrysaquinodimethane. This temperature is somewhat higher than the temperature at which many dienophiles decompose, e.g. dimethyl acetylenedicarboxylate and diethyl azodicarboxylate. A good illustration of this is the reaction with dimethyl acetylenedicarboxylate; in boiling diethyl phthalate no reaction other than decomposition of the dienophile occurs. If the reaction was attempted in nitrobenzene, only after long heating was any product obtained and then not only in such low yield (8% based on the crude material) but also so impure that further investigation was deemed profitless, though an ultraviolet spectrum did indicate that the product had a 5,6-disubstituted chrysene chromophore rather than a 5,6-benzochrysene chromophore.

At the same time as the initial reaction of 5,6-chrysaquinodimethane with maleic anhydride was being investigated, work was started on the synthesis of the quarternary ammonium hydroxide (LXIIc) as follows:



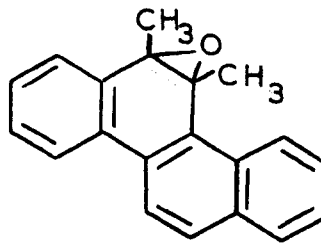
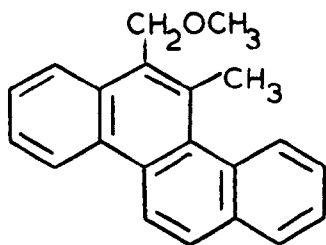
The reaction of 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene (XLI) with thionyl chloride gave a crude product which when heated lost hydrogen chloride; the reaction probably proceeds via the following mechanism as with the corresponding phenanthrene compounds.³⁵





The crude product was used in unsuccessful attempts to secure the quaternary ammonium chloride (LXIIa).

With hot ethanol the crude chloromethyl compound gave 6-ethoxymethyl-5-methylchrysene (LXIII). The structure of this compound was established by analysis of its n.m.r. spectrum which showed a methyl singlet at 6.91τ . It has been shown that for 1-methylphenanthrene, the methyl singlet is at 6.90τ ⁶¹ whereas for 9-methylphenanthrene, it is at 7.18τ ,⁵⁴ these positions can be regarded as corresponding respectively to the 5 and 6 positions in chrysene, hence showing that the structure is that of the 5-methyl compound (LXIII).



In a cognate study, when the dimethyldiol (XLI) was treated with hydrogen chloride,⁴¹ instead of the expected epoxide (LXIV), 5-methyl-6-chloromethylchrysene (LXI) was obtained. The 5-methyl structure was assigned on the position of the methyl singlet at 6.88 τ (cf. the ethoxymethyl chrysene (LXIII)). Soon after, a paper⁴² was published containing not only the preparation of 5-methyl-6-chloromethylchrysene (LXI) and its 5-chloromethyl isomer but details of the ⁵assignment of these structures based on the position of the methyl singlets at 6.90 and 7.15 τ respectively, but without giving any firm evidence other than that "in 5,6-dimethylchrysene the two methyls give singlets at 7.15 τ (5-methyl) and 7.40 τ (6-methyl)." (No other details of the n.m.r. spectrum of (LXI) and its isomer are given). In addition the preparation of the two methoxyether isomers is given as by heating the two chloromethyl isomers in boiling methanol!

The reaction of 5-methyl-6-chloromethylchrysene with sodium ethoxide in boiling ethanol gave 5-methyl-6-ethoxychrysene (LXIII) identical with that previously prepared, thus confirming the original structural assignment for (LXIII).

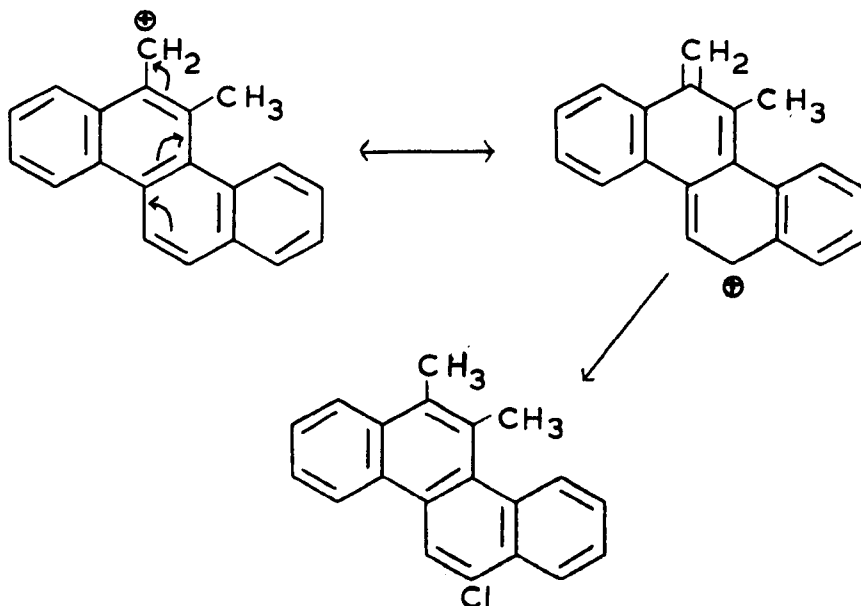
The aromatic regions in the n.m.r. spectra of the 6-ethoxy and 6-chloromethyl compounds are very similar in pattern, showing multiplets due to the three H- α 3 protons at C, 4, 11 and 12; a multiplet at 1.5 - 1.7 τ (or 1.69 - 1.9 τ) respectively for the proton at C7 and multiplets due to the remaining protons (2 H- α + 4 H- β).

In other experiments designed to obtain the epoxide (LXIV), 5-methyl-6-chloromethylchrysene (LXI) was again obtained and in some

experiments very small yields of a 5,6-dimethylchlorochrysene compound m.p. 144° were obtained. Analysis and the Lassigne test show beyond all doubt that this compound has the formula $C_{20}H_{15}Cl$ while the n.m.r. spectrum shows two singlets at 7.18 (5-methyl) and 7.37 τ (6-methyl) while the aromatic region is divided into three parts, corresponding to 4, 1 and 4 protons respectively. So that the compound has a 5,6-dimethylchrysene structure with a chlorine atom substituted in the aromatic nucleus.

For the 6-ethoxy and 6-chloromethyl compounds multiplets due to 6 protons (2 H- α + 4 H- β) are seen in the region c. 1.90 - 2.5 τ , whereas in the same region this chloro-compound has a multiplet (2.25 - 2.55 τ) due to 4 protons, probably indicating the presence of 4 H- β protons only. In addition, a multiplet (one proton) is shown (1.80 to 2.0 τ) comparable to those for the 6-ethoxy and 6-chloromethyl compounds and hence probably due to the proton at C7 leaving only five positions to be accounted for, those at C, 1, 4, 10, 11 and 12. Four of the protons in these positions show a multiplet (1.3 - 1.7 τ), three of these protons could be those at C, 1, 10 and 12, (i.e. 3 H- α) as compared with the 6-ethoxy and 6-chloromethyl compounds leaving only the two positions at C, 1 and 12 to be accounted for. This multiplet may possibly contain a singlet peak suggesting that the chlorine atom is at position C12.

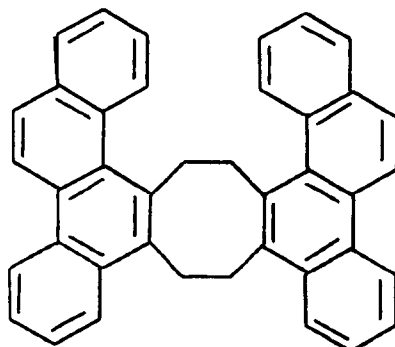
A possible mechanism starting from the 6-chloromethyl compound (LXI) is shown which could explain substitution of chlorine in the 12 position, is shown below.



Hewett⁴¹ describes the formation of a dimer, molecular weight 540, m.p. 260° when 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene (XLI) was heated with hydriodic acid in acetic acid but did not assign a structure. In the present work this reaction was re-investigated. Instead of recrystallising the product which precipitated on cooling, the whole organic product (after neutralisation) in benzene solution was chromatographed to give two products, one similar to that described by Hewett, having m.p. 260° (from benzene) and after sublimation, m.p. 270° . Hewett had found that analysis of this compound corresponded to $C_{20}H_{16}$, i.e. a hydrogenated dimer.

Analysis of our material is in agreement with $C_{20}H_{14}$, i.e. an unhydrogenated dimer. The absence of a vinylic frequency in

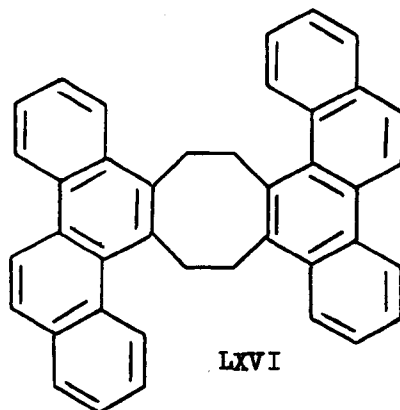
the infrared spectrum together with a typical 5,6-disubstituted
chrysene chromophore rules out the possibility of this material being
a spirodimer.



LXV

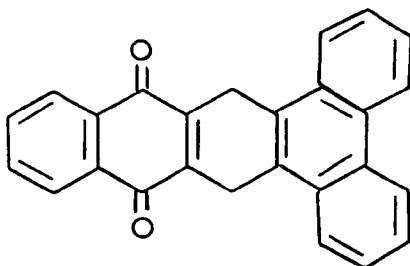
The n.m.r. spectrum shows that the dimer has structure (LXV). This is shown by the presence of two singlets due to four protons each at 6.91 and 7.18 τ , values indicating that the two sets of methylene groups are in an environment similar to the 5-methyl and 6-methylchrysene environment respectively. This can only be so without splitting if the dimer has structure (LXV) as if it had the isomeric structure (XLVI) there would be no longer two singlets but two sets of doublets.

The other product obtained may be the isomer (LXVI). This compound has a very ill-defined m.p., melting over a range 85-105°, repeated recrystallisation gave a microscopic yield of colourless rods, m.p. 121-2° having the same spectroscopic characteristics as the more widely melting material. As yet, satisfactory analyses have not been obtained; also we are still awaiting results of molecular weight determinations. The ultraviolet spectrum indicates a typical 5,6-disubstituted chrysene chromophore though two of the minor peaks differ slightly in frequency from that of the other isomer (LXV). The infrared spectrum shows the presence of four adjacent aromatic C-H as well as that of two adjacent aromatic C-H, the other isomer (LXV) only showed the four adjacent aromatic C-H. The n.m.r. spectrum shows the presence of two doublets centred at 7.05 and 7.26 τ respectively, in accord with the structure (LXVI).



In view of the success of the reaction of 5,6-chrysaquinodimethane with 1,4-naphthoquinone in boiling diethyl phthalate it was decided to investigate the corresponding reaction of 9,10-phenanthraquinodimethane (XX) with 1,4-naphthoquinone in the expectation of preparing the

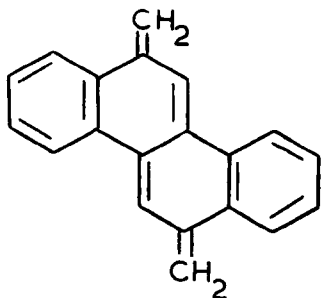
unknown 5,12-dihydro-1,2:3,4-dibenzonaphthacene-6,11-quinone (LXVII).



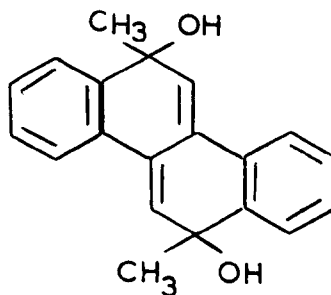
LXVII

The route to 9,10-phenanthraquinodimethane (XX) used was that of Millar and Wilson³⁵ (see Chapter 1, p. 10). 9,10-Phenanthraquinone with methylmagnesium iodide gave trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyphenanthrene (XXV). When a mixture of this diol and 1,4-naphthoquinone was heated in boiling diethyl phthalate, on one occasion only, a very small quantity of quinone (LXVII) was obtained having m.p. 326° and the expected 9,10-phenanthrene type chromophore. This quinone showed a strong peak at 718 cm.⁻¹ which can be attributed to the out-of-plane deformation absorption of the four adjacent aromatic C-H bonds, on the terminal ring adjacent to the p-quinone ring: (see p. 20). Satisfactory analyses could not be obtained.

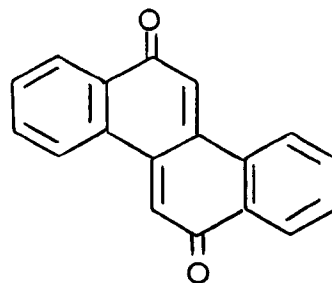
At the same time as the work with 5,6-chrysaquinodimethane was started it was thought desirable to examine the reactions of 6,12-chrysaquinodimethane (LXVIII) which it was thought could be obtained by the dehydration of the 6,12-dimethyl diol (LXIX), preparable from the 6,12-chrysaquinone (LXX).



LXXVIII

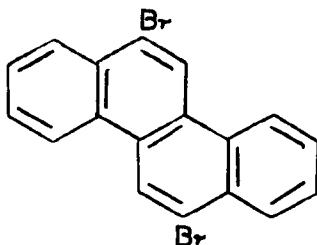


LXXIX

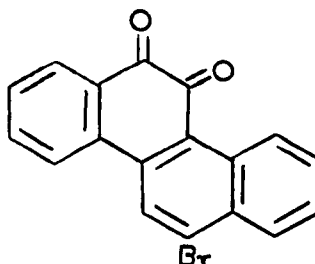


LXX

The only route to the quinone recorded is rather long and starts from benzil⁶² so four possible new routes to this quinone from chrysene were examined. None proved successful.



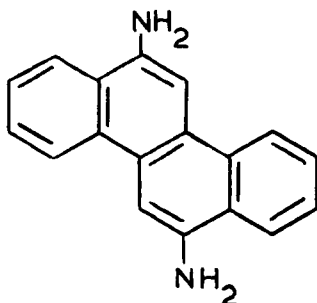
LXXI



LXXII

a) It has been reported that the oxidation of 6,12-dibromochrysene (LXXI) gives a quinone, of unspecified structure.⁶³ Bromination of chrysene gave 6,12-dibromochrysene in an almost quantitative yield. Oxidation using either sodium dichromate or chromic acid in acetic acid gave a product shown to be mainly 12-bromo-5,6-chrysaquinone (LXXII).⁶⁴

b) 6,12-Dibromochrysene was heated with silver acetate in glacial acetic acid in the hope of obtaining the diacetyl derivative of 6,12-dihydroxychrysene; no reaction occurred.

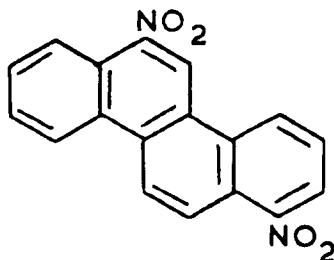


LXXVII

c) The next route to be considered was an adaption of that due to Newman and Cathcart⁶⁵ who prepared 6-hydroxychrysene from 6-aminochrysene by heating it in a sealed tube with 10% sulphuric acid. It is claimed that when chrysene is nitrated using fuming nitric acid and the product reduced with sodium polysulphide that 6,12-diaminochrysene (LXXVII) is obtained.⁶⁶ When a product prepared as described was treated with 10% sulphuric acid in a sealed tube at 220° it gave a product which with lead dioxide did not give 6,12-chrysaquinone (LXX) (as 6,12-dihydroxychrysene would do⁶²) but instead gave a green crystalline solid, m.p. 210° and not identified.

With reference to the nitration of chrysene, it was found that the product obtained was more complex than indicated in the literature and was probably a mixture. The reaction product can be recrystallised from pyridine;⁶⁵ the considerable portion insoluble in pyridine

(m.p. $> 350^{\circ}$) and having a good infrared spectrum was examined. This infrared spectrum showed, in the aromatic region, strong peaks at 760 (four or three adjacent aromatic C-H), 775 (three adjacent aromatic C-H), 818 (two adjacent aromatic C-H) and 890 cm.^{-1} (single aromatic C-H) indicating possibly 1,6-dinitrochrysene (LXXIV), although the presence of nitro groups tends to shift aromatic bands towards higher frequencies making it difficult to make definite assignments.



LXXIV

The structure (LXXIV) is in accord with the predictions of Dewar et al.⁶⁷ concerning the mono-nitration of chrysene, that nitration is most likely to take place at the 6-position and next at the 1-position. Evidence for the formation of tri-nitrochrysenes was also obtained.

d) The next approach to be tried was also based on the work of Newman and Cathcart⁶⁵ who treated chrysene with chlorosulphonic acid to give 6-chrysenesulphonic acid, whose sodium salt with potassium hydroxide at 300° gave 6-hydroxychrysene. When a solution of chrysene in tetrachlorethane was treated with $2\frac{1}{2}$ equivalents of chlorosulphonic

acid at $0-5^{\circ}$, a disulphonylchloride of chrysene, m.p. 206° , was obtained in 37% yield. The infrared spectrum of this compound shows, in the aromatic region, a strong peak at 755 cm.^{-1} (four adjacent aromatic C-H), as well as a complex pattern of moderate peaks at 898, 847, 828, 780, 745, and 732 cm.^{-1} , which make it difficult to make an assessment of the substitution pattern of this compound other than to assume that the initial substitution was at the 6-position. This disulphonyl chloride is extremely resistant to hydrolysis, though this is not uncommon in polycyclic sulphonyl chlorides,⁶⁸ as indicated not only by its stability towards steam distillation but also by its stability to hot aqueous potassium hydroxide.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are therefore corrected.

Infrared absorption spectra were measured with a Perkin Elmer 221 spectrophotometer and with a Unicam S.P. 200 G spectrophotometer.

Ultraviolet absorption spectra were measured with a Unicam S.P. 700 spectrophotometer.

Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Perkin Elmer 60 megacycle instrument.

Microanalyses were carried out by Drs. G. Weiler and F. B. Straus of Oxford, and by Mr. J. Boulton in the Department of Chemistry, University of Keele.

5,6-Chrysaquinone

This compound was prepared by oxidation of chrysene in glacial acetic acid with sodium dichromate according to the method of Graebe and Hönigsberger,⁴⁹ m.p. 238-240° (lit.⁴⁰ m.p. 239.5°, 83%).

5,6-Dimethyl-5,6-dihydro-5,6-dihydroxychrysene (XLI).

The method used is a modification of that due to Hewett.⁴¹ To a Grignard solution prepared from methyl iodide (65.0 g., 0.456 mole), and magnesium turnings (11.0 g., 0.452 mole), in anhydrous ether (450 ml.) finely powdered 5,6-chrysaquinone (19.0 g., 0.074 mole) was added in small portions with stirring and ice cooling. After heating under reflux with stirring for 1 hr., the reaction mixture was cooled and then poured into ammonium chloride and ice. Evaporation of the ethereal layer gave a solid, separated from the aqueous layer by filtration. The filtrate was extracted with chloroform (2 x 150 ml.) and the extract added to a solution of the solid in chloroform (400 ml.). This chloroform solution was stirred with warm saturated sodium bisulphite solution (2 x 150 ml.), separated, washed with water, dried (MgSO₄) and the solvent removed to give product m.p. 130-140°, (18.5 g.). Recrystallisation from carbon tetrachloride gave 14.7 g. (69%), m.p. 153-5° (lit.⁴¹ m.p. 151-155°). Further recrystallisation from 95% ethanol gave colourless needles, m.p. 157-9°.

Found: C, 82.5; H, 6.2%

Calc. for C₂₀H₁₈O₂: C, 82.7; H, 6.3%

λ_{\max} : 265 m μ ($\log_{10} \epsilon$ 4.49), 275 (4.62), 321 (4.18) in ethanol.

ν_{\max} (KBr disc): 3550 cm.⁻¹ (free OH), 3460 (OH, intramolecular hydrogen bonded), 828, 818 (two adjacent aromatic C-H), 758 and 751 (four adjacent aromatic C-H).

The n.m.r. spectrum (CDCl₃) showed two singlets at 8.51 and 8.33 τ (methyl groups), a broad diffuse peak with centre at 7.33 τ (hydroxyl groups), multiple peaks between 1.95 and 2.67 τ corresponding to 9 aromatic protons including a singlet peak at 2.04 τ (2 protons) (3 H- α + 4 H- β + 2 H- $\alpha\beta$) and a multiple peak centre 0.68 τ (one proton) (probably at C4).

1',2',3',4'-Tetrahydro-5,6-benzochrysene-2',3'-dicarboxylic anhydride.
(XLII).

5,6-Dimethyl-5,6-dihydro-5,6-dihydroxychrysene (0.7 g., 0.0024 mole,) was added to a solution of maleic anhydride (0.4 g., 0.0041 mole), in redistilled diethyl phthalate (1.5 ml.) and the resulting solution heated under reflux for 10 min. On cooling, colourless needles separated, m.p. 315-6° (0.25 g., 29%). Recrystallisation from glacial acetic acid gave a product, m.p. 323°. Increasing the quantities used led to diminished yields; increasing the reaction time also gave lower yields of adduct.

Found: C, 81.5; H, 4.7%

Required for C₂₄H₁₆O₃: C, 81.8; H, 4.6%

λ_{\max} : 222 m μ ($\log_{10} \epsilon$ 4.45), 276 (4.94), 307 (3.93), 321 (3.97), 344 (3.97) in ethanol.

ν_{\max} (KBr disc.): 1855 cm^{-1} , 1838, 1778 (C=O , anhydride), 927 (C-O , anhydride), 824 (two adjacent aromatic C-H), 760 (four adjacent aromatic C-H).

1',2',3',4'-Tetrahydro-5,6-benzochrysene-2',3'-dicarboxylic acid.

1',2',3',4'-Tetrahydro-5,6-benzochrysene-2',3'-dicarboxylic anhydride (0.55 g.), was dissolved in hot 50% sodium hydroxide solution (20 ml.), and this solution filtered while hot. On cooling, the solution was acidified with dilute sulphuric acid to give a solid (0.4 g., 73%), which was recrystallised from methanolic ethyl acetate to give colourless needles (m.p. 135-136°, then resolidifying with final m.p. 323-5°).

Found: C, 71.2; H, 5.2%

Required for $\text{C}_{24}\text{H}_{18}\text{O}_4$, 2 H_2O : C, 70.9; H, 5.4%

λ_{\max} (Ethanol) 222 $\text{m}\mu$ ($\log_{10} \epsilon$ 4.46), 276 (4.92), 307 (3.91), 321 (3.99) and 344 (3.98).

ν_{\max} (Nujol): 1745 and 1715 cm^{-1} (C=O , dicarboxylic acid).

Thermal decomposition of 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene.

A solution of the diol (1.0 g.), in redistilled diethyl phthalate (3 ml.) was heated under reflux for ten minutes. Removal of the solvent and chromatography of the residue give the diol (0.5 g.).

5,6-Benzochrysene (XLIII).

1',2',3',4'-Tetrahydro-5,6-benzochrysene-2',3'-dicarboxylic

anhydride (0.5 g., 0.0014 mole) was dissolved in hot 10% sodium hydroxide (40 ml.), and the solution filtered. To this hot solution was added potassium ferricyanide (4.5 g.) in water (20 ml.) and the resulting solution was heated under reflux for 3 hr., during which time solid was precipitated. On cooling the suspension was poured into water; filtration and drying of the solid so obtained gave a solid (160 mg.) contaminated with inorganic material. This solid was extracted with benzene and the solvent removed to give a solid (85 mg.), which was dissolved in a small volume of benzene, and placed on an alumina column (12.5 cm. x 2.5 cm.). Elution with a mixture of "60/80" petroleum, 60%, and benzene, 40%, gave a solid (26 mg.). Recrystallisation from 95% ethanol gave colourless rods (13 mg., 2%) of 5,6-benzochrysene, m.p. 114.5-116° (lit⁴⁶ m.p. 114.5-116°).

λ_{\max} : 278 m μ , 287, 312, 321 and 339 in ethanol.

lit λ_{\max} :⁴⁷ 277 m μ , 286, 308, 321 and 334 in ethanol.

ν_{\max} (KBr Disc): 858 cm.⁻¹ (singlet aromatic C-H), 814 (two adjacent aromatic C-H), 761 (four adjacent aromatic C-H), 750, 742, 717, 709.

5,12-Dihydro-3,5-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (XLV).

5,6-Dimethyl-5,6-dihydro-5,6-dihydroxychrysene (1.0 g., 0.0028 mole) was added to a solution of 1,4-naphthoquinone (0.68 g., 0.0035 mole) in warm diethyl phthalate (25 ml.), and the resulting solution heated under reflux for 5 min. (towards the end of this period violent bumping occurred). The solid precipitated on cooling was washed with excess ether, and dried to give dark orange needles, m.p. 317-9°.

(0.80 g., 56%). Recrystallisation from toluene gave orange needles, m.p. 322-324°, of the quinone. It dissolved in concentrated sulphuric acid to give a dark green solution.

Found: C, 87.5; H, 4.4%

Required for $C_{30}H_{18}O_2$: C, 87.8; H, 4.4%

λ_{\max} (in dioxan): 222 m μ ($\log_{10} \epsilon$ 4.67, 275 (4.92), 338 (4.36), 350 (4.39), 442 (3.82).

ν_{\max} (KBr Disc): 2941 cm.⁻¹ (CH₂), 2874 (CH₂), 1674 (C=O, quinone), 1588 (C=C, aromatic), 1291 (quinone), 957, 816 (two adjacent aromatic C-H), 754, 742 (four adjacent aromatic C-H), 707 (four adjacent aromatic C-H, in terminal ring next to p-quinone ring).

The n.m.r. spectrum (benzene) shows a singlet at 8.33 τ (methylenes between aromatic functions).

When the two reactants were heated together in solvents other than diethyl phthalate either the adduct was not obtained or it was obtained in much reduced yield.

Heating under reflux in acetic anhydride for 2½ hr. did not give the desired adduct. 5,12-Dihydro-3,4-benzonaphtho[1',2':1,2]-naphthacene-6,11-quinone was obtained in 3% yield when 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene and 1,4-naphthoquinone were heated together in diphenyl ether for ten minutes, and in 5% yield after reaction in boiling nitrobenzene for 15 min.

Attempted preparation of 3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (XLVI).

- a) A solution of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]-naphthacene-6,11-quinone (0.47 g.) in methyl-naphthalene (15 ml.) containing 10% palladium charcoal (0.27 g.) was boiled for 24 hrs. After filtration, cooling of the filtrate gave yellow needles (0.25 g.) of the unchanged quinone.
- b) 5,12-Dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (65 mg.), was thoroughly ground with 10% palladium-charcoal (100 mg.) and the mixture heated under nitrogen at 320-350° for 3 hr. The mixture was then heated at 320-350°/0.1 mm. in a microsublimation apparatus; yellow crystals of starting material were recovered.
- c) A solution of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene (0.23 g.) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (0.20 g.) in sulphur-free xylene (40 ml.) was heated under reflux for 18 hrs. On cooling, unchanged 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene (0.12 g.) separated. The filtrate was washed with 10% sodium hydroxide solution (2 x 20 ml.) and then with water: evaporation of the dried xylene solution gave more unchanged starting quinone.
- d) 5,6-Dimethyl-5,6-dihydro-5,6-dihydroxychrysene (1.0 g., 0.0028 mole) and 1,4-naphthoquinone (2.0 g., 0.103 mole) in nitrobenzene (10 ml.) were heated under reflux for 6 hrs. On cooling no precipitate separated, so a mixture of ether and petroleum was added, which did not precipitate any solid either. The low boiling solvents were removed and the

nitrobenzene solution heated under reflux for a further 42 hrs. On cooling excess ether was added to the reaction mixture to precipitate a green solid, m.p. $> 340^{\circ}$ (0.61 g.). Sublimation at $400^{\circ}/0.1$ mm gave golden yellow rods, m.p. $> 340^{\circ}$ of trinaphthylene-5,18:6,11:12,17-triquinone, identical (I.R. spectrum) with authentic material.

Found: C, 77.4; H, 2.6%

Calculated for $C_{30}H_{12}O_6$: C, 76.9; H, 2.6%

ν_{\max} (Nujol): 1690 and 1673 cm^{-1} (C=O, quinone), 1595 (C=C, aromatic), 1283, 1260, 1168, 973, 782, 757, 723, 719, and 687 (four adjacent aromatic C-H, in ring next to quinone ring).

Trinaphthylene-5,18:6,11:12,17-triquinone (XLVII)

1,4-Naphthoquinone (1.0 g.), in nitrobenzene (2.5 ml.), with pyridine (0.5 g.) and glacial acetic acid (0.7 g.) was heated under reflux for 1 hr. On cooling, trinaphthylene-5,18:6,11:12,17-triquinone (0.76 g., 76%) separated.⁴⁹

Attempted enolisation of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]-naphthacene-6,11-quinone (XLV) to 6,11-dihydroxy-3,4-benzonaphtho[1',2':1,2]naphthacene (LII).

A solution of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (80 mg.) in dioxan (60 ml.) and water (10 ml.) was heated under reflux with stirring, under nitrogen. To this solution was added a freshly boiled 10% sodium hydroxide solution; a colour change from the original yellow to an intense dark green immediately took place;

this green solution was heated under reflux with stirring for 4 min. and then allowed to cool. As the temperature of the solution dropped, yellow solid began to separate with a corresponding diminution of the green colour. Filtration gave a product, m.p. $315-9^{\circ}$ (60 mg.) with I.R. identical with starting material. Acidification of the filtrate with 15% hydrochloric acid (40 ml.) precipitated more starting material (10 mg.).

Attempted preparation of 6,11-dimethyl-6,11-dihydroxy-5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene (XLVIII).

a) To a Grignard solution prepared from magnesium (0.46 g., 0.018 mole) methyl iodide (3.5 g., 0.020 mole), and ether (30 ml.), was added ether (100 ml.) and benzene (100 ml.), and to this solution was added 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (200 mg., 0.00068 mole) in small portions. The reaction mixture was heated under reflux with stirring for 4 hrs. to give a deep reddish-brown solution, which was cooled and poured into dry ammonium chloride and ice. Filtration gave the unchanged quinone.

b) A Grignard solution was prepared from magnesium (0.60 g., 0.025 mole), methyl iodide (3.9 g., 0.027 mole) and ether (50 ml.), and then the diethyl ether was replaced by dibutyl ether (150 ml.). To the resulting solution was added 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]-naphthacene-6,11-quinone (1.0 g., 0.0024 mole) in small portions, and the reaction mixture heated under reflux with stirring for 7 hrs. On cooling the reaction mixture was poured onto ammonium chloride and ice;

filtration gave the unchanged quinone (0.98 g.).

Attempted reduction of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone using zinc dust, pyridine and acetic acid.

To a stirred suspension of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene (0.35 g.), and zinc dust (1.05 g.), in boiling pyridine (30 ml.), was added 5 ml. of 80% acetic acid during 30 min., and heating continued for a further 3 hrs. The initial colour of the suspension was yellow, this changed immediately on the addition of the acetic acid to a wine red; after all the acetic acid had been added the colour slowly reverted to the original yellow. On cooling, zinc was removed from the solution by filtration, the filtrate evaporated, and the residue taken up in toluene and chromatographed on an alumina column to give unchanged quinone (0.25 g.).

Reduction of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone using the zinc melt method.

a) To a finely ground mixture of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (1.0 g.) with zinc dust (1.0 g.), and sodium chloride (1.0 g.) was added moist zinc chloride (5.0 g.), and the mixture melted at 200-210°. The melt was then stirred continuously whilst the temperature was raised to and subsequently kept at 280° for 15 min., and then at 300-310° for 15 min. The cooled melt was then treated with dilute hydrochloric acid and the insoluble residue washed well with dilute ammonia solution and then with water.

The dried solid (0.71 g.), was placed on an alumina column (Woelm activity no. 1., wt. 100 g., 22 cm x 2.5 cm) in a benzene 1:9 benzene-'60°/80°' petroleum solution.

Elution with a 60/40 benzene-'60°/80°' petroleum mixture gave 300mg. of yellow rods, m.p. (rapid heating) 152-158°. Recrystallisation from chloroform gave yellow rods, m.p. 135-136° of 6,11-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene.

Found: C, 93.5; H, 5.3%

Required for $C_{30}H_{20}$: C, 94.7; H, 5.3%

λ_{max} (chloroform): 283 m μ ($\log_{10} \epsilon$ 4.77), 294 (4.73), and 327 (4.16).

This chromophore was identical with that of the 152-158° melting product.

ν_{max} (KBr Disc): 2940 and 2870 cm^{-1} (CH stretch, CH_2), 820 (two adjacent aromatic C-H), 758, 755, 745, 733 and 730 (four adjacent aromatic C-H).

The n.m.r. spectrum (in $CDCl_3$) showed a singlet at 5.83 (this singlet slightly broadened) (two methylene groups flanked by aromatic rings); a complex multiplet between 1.90 and 2.73 τ (3 H- α + 6 H- β) on which is superimposed a singlet at 2.30 τ (H- $\alpha\beta$); a complex multiplet between 1.20 and 1.55 τ (3 H- α_3) on which was superimposed two singlets at 1.25 τ (H- α_4) and 1.45 τ (H- α_3), in addition a multiplet was shown, centre 1.05 τ (H- α_4).

Elution with a 60/40 benzene-60°/80° petroleum mixture gave 95 mg. of a mixture of 6,11-dihydro-3,4-benzonaphtho[1',2':1,2]-naphthacene and 3,4-benzonaphtho[1',2':1,2]naphthacene.

Elution with a 90/10 benzene-diethyl ether mixture gave unchanged 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (160 mg.).

b) When a mixture of 5,12-dihydro-3,4-benzo[1',2':1,2]naphthacene-6,11-quinone (0.9 g.) with the corresponding quantities of zinc dust, sodium chloride and moist zinc chloride was heated at 300-310° for 1 $\frac{1}{4}$ hrs., and the treated product placed on an alumina column (Spence type '0', wt. 100 g., 19 x 2.5 cm.), the following results were obtained.

Elution with a 60/40 benzene-60°/80° petroleum mixture gave yellow solid, m.p. 255-262° (210 mg.). Recrystallisation from acetone gave then 3,4-benzonaphtho[1',2':1,2]naphthacene, m.p. 265-267°, as did sublimation at 280°/0.1 mm.

Found: C, 94.6; H, 4.7%

Required for C₃₀H₁₈: C, 95.2; H, 4.8%

λ_{\max} (dioxan): 255 m μ (log₁₀ ϵ 4.67), 261 (4.84), 268 (4.74), 284 (4.76), 294 (4.82), 323 (4.80), 353 (4.42), 413 (3.73), 439 (3.86) and 465 (3.75).

$\lambda_{\text{shoulder}}$: 313 (4.70), 337 (4.75).

ν_{\max} (KBr disc): 920, 913, 906, 890 and 887 (singlet aromatic C-H), 816 807 (two adjacent aromatic C-H), 767, 756, 748, 738, 730 (four adjacent aromatic C-H) and 693 cm.⁻¹.

When this compound was heated with Pd/C at 300° or with 2,3-dichloro-5,6-dicyanobenzoquinone in benzene unchanged 3,4-benzonaphtho[1',2':1,2]naphthacene was recovered.

Elution with a 10/90 diethyl ether-benzene mixture gave unchanged quinone, 350 mg.

c) A mixture of aluminium turnings (2.7 g.), mercuric chloride (0.15 g.) dry carbon tetrachloride (1.5 ml.) and dry cyclohexanol (50 ml.) was cautiously heated to give initially a vigorous exothermic reaction which required cooling. After this initial vigorous reaction, the mixture was heated with stirring until all the aluminium had reacted, giving aluminium cyclohexanolate. To the cooled reaction mixture was added 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (2.7 g.) and the suspension heated with stirring under reflux for 22 hrs. On cooling the reaction mixture was successively treated with glacial acetic acid (50 ml.) and concentrated hydrochloric acid (50 ml.) followed by water. The organic layer was separated, and washed with more water, and was then added to 300 ml. of methanol to precipitate a green solid (1.80 g.). This solid was dissolved in chloroform and this solution placed on an alumina column (Woelm activity No. 1, wt. 120 g., 25 cm. x 2.5 cm.).

Elution with a 60/40 benzene-petroleum mixture gave 3,4-benzonaphtho[1',2':1,2]naphthacene, (0.13g., 6%).

d) 5,12-Dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (2.2 g.) was added to aluminium cyclohexanolate (prepared as above) and the suspension heated with stirring under reflux for 60 hrs. On cooling, the reaction mixture was treated as above to give a solid (1.02 g.) which was dissolved in benzene and the solution placed on an alumina column (Woelm activity No. 1, wt. 100 g., 25 cm. x 2.5 cm.).

Elution using a 9:1 benzene-petroleum mixture gave 3,4-benzonaphtho[1',2':1,2]naphthacene (0.51 g., 25%).

2,4,7-Trinitrofluorenone complex of 3,4-benzonaphtho[1',2':1,2]naphthacene.

Hot saturated solutions of 3,4-benzonaphtho[1',2':1,2]naphthacene and 2,4,7-trinitrofluorenone in absolute ethanol-benzene were mixed with immediate formation of a red colour. On cooling red needles precipitated, m.p. 203-205°. Recrystallisation from absolute ethanol gave material m.p. 209-211°. A satisfactory analysis for C could not be obtained.

Found: C, 73.3; H, 3.3; N, 6.1%

Required for $C_{43}H_{23}N_3O_7$: C, 74.4; H, 3.3; N, 6.1%

Stannous chloride reduction of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]-naphthacene-6,11-quinone.

A solution of stannous chloride (4.0 g.) in concentrated hydrochloric acid (10 ml.) was added during 30 minutes with stirring to a solution, heated under reflux, of 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (1.0 g.) in a mixture of glacial acetic acid (100 ml.) and toluene (75 ml.). Heating and stirring was continued for a further 3 hours, concentration of the reaction mixture to approximately 100 mls. followed by cooling deposited material, m.p. 225-230°, (0.60 g., 62%). Recrystallisation from toluene gave yellow rods, m.p. 230-233° if heated rapidly, if very slowly heated, melting commenced at 230° with change of form to yellow needles, m.p. 313-5°.

Found: C, 90.8; H, 4.7%

Required for $C_{30}H_{20}O$: C, 90.9; H, 5.1%

λ_{\max} (Ethanol): 276, 341, 384 and 444 μ .

ν_{\max} (KBr disc): 2920 and 2845 cm^{-1} (CH stretch, CH_2) 1654 ($\text{C}=\text{O}$, aryl ketone), 1595 ($\text{C}=\text{C}$, aromatic), 1293 ($\text{C}-\text{O}$, ketone) 824 and 811 (two adjacent aromatic C-H), 753 and 726 (four adjacent aromatic C-H).

Lithium aluminium hydride reduction of 5,12-dihydro-3,4-benzonaphtho-
[1',2':1,2]naphthacene-6,11-quinone.

5,12-Dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (0.90 g.), was extracted (Soxhlet) into a suspension of lithium aluminium hydride (1.0 g.), in boiling tetrahydrofuran (200 ml.) during 17 hrs. Excess lithium aluminium hydride was decomposed by the careful addition of water followed by dilute hydrochloric acid. Tetrahydrofuran was removed from the dried organic layer to give a dark brown residue (0.65 g.), which was dissolved in toluene and the solution percolated through a short alumina column to give a yellow solution which was evaporated to give an orange solid (0.5 g.). This was recrystallised from benzene/light petroleum to give orange solid, m.p. $220-225^\circ$.

ν_{\max} (Nujol): 1670 ($\text{C}=\text{O}$, aryl ketone), 1598 ($\text{C}=\text{C}$, aromatic), 1285 ($\text{C}-\text{O}$, ketone), 958, 818 (two adjacent aromatic C-H), 758 (four adjacent aromatic C-H).

Attempted reduction of 5,6,11,12-tetrahydro-3,4-benzonaphtho[1',2':1,2]-
naphth-11(6)-one (LIX or LX).

The naphthone (0.5 g.), and zinc dust (0.5 g., activated by brief treatment with 0.1% aqueous copper sulphate) were boiled in 2 N sodium hydroxide solution (50 ml.) under toluene (20 ml.) for 16 hrs.

More toluene (75 ml.) was added and the aqueous layer separated from the hot solution. The toluene solution was washed with water, dried over magnesium sulphate, and decolourised by charcoal and the pale yellow solution concentrated to give starting material (30 mg.).

Acidification of the sodium hydroxide solution precipitated more starting material (0.28 g.).

Reaction of 5,6-chrysaquinodimethane with excess of p-benzoquinone.

1. A mixture of 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene (1.0 g., 0.0034 mole), and p-benzoquinone (3.0 g., 0.028 mole) in nitrobenzene (10 ml.) was heated under reflux for 6 hrs. On cooling a solid separated; this was filtered off and washed with ether (1.0 g.). Addition of excess ether to the nitrobenzene filtrate did not give further solid.

Treatment of the solid with hot ethanol left an insoluble black residue, m.p. $> 360^{\circ}$ (0.30 g.). This substance was extremely insoluble, and could not be sublimed even at $450^{\circ}/0.1$ mm. The infrared spectrum of this compound was very indistinct, showing a broad carbonyl peak between 1650 and 1675 cm^{-1} and very indistinct aromatic peaks.

Evaporation of the ethanolic solution gave quinhydrone.

2. 5,6-Dimethyl-5,6-dihydro-5,6-dihydroxychrysene (1.0 g., 0.0034 mole) was added to a suspension of benzoquinone (0.37 g., 0.0028 ml.) in diethyl phthalate (15 ml.) and the mixture boiled for 7 min. On cooling a solid deposited; ether was added to the suspension, and the suspension filtered to give an extremely insoluble quinone, whose infrared spectrum indicated two quinone peaks and rather vague aromatic peaks

(m.p. $> 350^{\circ}$; 0.10 g.).

Reaction of 5,6-chrysaquinodimethane with dimethyl acetylenedicarboxylate.

a) A mixture of 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene (1.0 g., 0.0034 mole) and dimethyl acetylenedicarboxylate (1.0 g., 0.0071 mole), in diethyl phthalate (6 ml.), was boiled for 4 min., when signs of decomposition began to show. On cooling and treating with excess ether a product did not precipitate; removal of diethyl phthalate and treatment of the residue with ether did not give any product other than unchanged 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene.

b) A mixture of 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene (1.0 g., 0.0034 mole) dimethyl acetylenedicarboxylate (1.2 g., 0.0085 mole) in nitrobenzene (3 ml.) was heated under reflux for 7 hrs. On cooling no solid precipitated, so excess ether was added to precipitate 0.09 g. of solid, m.p. $130-190^{\circ}$, showing the ultraviolet chromophore of 5,6-disubstituted chrysene.

Attempted preparation of 5,6-dimethylchrysene-5,6-oxide.

a) 5,6-Dimethyl-5,6-dihydro-5,6-dihydroxychrysene (5.0 g.), was dissolved in methanol (70 ml.) the solution cooled in ice and hydrogen chloride passed until the solution was saturated. During this time solid precipitated; this was filtered and washed with methanol and water and dried to give a product m.p. 145° (1.50 g., 30%). Recrystallisation from benzene/ $60^{\circ}/80^{\circ}$ petroleum gave needles, m.p. 158° , and further recrystallisation from carbon tetrachloride gave

5-methyl-6-chloromethylchrysene, m.p. 164° , (lit⁴² m.p. $164-5^{\circ}$).

Found: C, 82.5; H, 5.3%

Calculated for $C_{20}H_{15}Cl$: C, 82.6; H, 5.2%

ν_{\max} (KBr disc.): 1247 cm^{-1} , 1240, 824 (two adjacent aromatic C-H)
753 (four adjacent aromatic C-H).

The n.m.r. spectrum (in $CDCl_3$) showed a singlet at 6.90 τ (aromatic methyl group), a singlet at 5.76 τ (aromatic chloromethyl group), a multiplet between 2.00 and 2.50 τ (2 H- α + 4 H- β), a multiplet between 1.69 and 1.93 τ (proton at C7), and a multiplet between 1.21 and 1.53 τ (3 H- α 3).

b) When this reaction was repeated under seemingly identical conditions using 2 g. of the diol, a product was obtained (0.40 g.), which recrystallised from carbon tetrachloride to give solid, m.p. $135-8^{\circ}$, (0.3 g.). Further recrystallisation from acetone gave plates, m.p. $142-3^{\circ}$ of 12-chloro-5,6-dimethylchrysene.

Found: C, 82.5; H, 5.1%

Required for $C_{20}H_{15}Cl$: C, 82.6; H, 5.2%

λ_{\max} (in chloroform): 279 $m\mu$ ($\log_{10} \epsilon$ 4.86), 330 (3.91), 344 (3.91).

ν_{\max} (Nujol): 1197 cm^{-1} , 1030, 1007, 952, 858 (singlet aromatic C-H), 785, 747 (four adjacent aromatic C-H).

The n.m.r. spectrum (in $CDCl_3$) showed a singlet at 7.38 τ (methyl at C6) a singlet at 7.19 τ (methyl at C5), a multiplet 2.25-2.55 τ (4 H- β), a multiplet, 1.80-2.0 τ (probably proton at C7), and a multiplet, 1.3-1.7 τ (3 H- α 3 plus a proton possibly at C1).

5-Methyl-6-ethoxymethylchrysene (LXIII)

a) Sodium (0.18 g.) was added to a suspension of 5-methyl-6-chloromethylchrysene (0.4 g.) in absolute ethanol (30 ml.) and the suspension heated under reflux for 3 hrs. During this time the original chloromethyl compound dissolved while a small quantity of solid deposited. The hot suspension was filtered, and the filtrate on cooling gave needles of 5-methyl-6-ethoxymethylchrysene, (m.p. 144° ; 0.32 g., 75%). Recrystallisation from ethanol gave needles, m.p. 144° .

Found: C, 87.8; H, 6.9%

Required for $C_{22}H_{22}O$: C, 88.0; H, 6.7%

λ_{\max} (ethanol): 221 $m\mu$ ($\log_{10} \epsilon$ 4.41), 274 (4.88), 308 (3.91), 321 (4.04), 334 (4.01).

ν_{\max} (Nujol): 1110 cm^{-1} , 1090, 1072, 1006, 815 (two adjacent aromatic C-H), 755 (four adjacent aromatic C-H).

The n.m.r. spectrum (in $CDCl_3$) showed a triplet ($J = 7$ c.p.s.) centred at 8.70 τ ($-O-CH_2-\underline{CH_3}$), a singlet at 6.93 τ (aromatic methyl), a quartet ($J = 6$ c.p.s.) centred at 6.26 τ ($-O-\underline{CH_2}-CH_3$), a singlet at 4.90 τ (aromatic- $\underline{CH_2}-O$), a multiplet between 1.85 and 2.42 τ (2 Ha + 4 H- β), a multiplet between 1.5-1.7 τ (proton at C7), a multiplet between 1.1 and 1.4 τ (3H- α 3).

b) Thionyl chloride (11 ml.) was added to a solution of 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene (11.0 g.), in chloroform (250 ml.) over a period of 30 min. at room temperature. The resulting solution was then heated under reflux for 10 hr.; at the end of this time the chloroform was removed under reduced pressure to give a gum which was

heated on a steam bath for 30 min. (during which time much hydrogen chloride was evolved). Various solvents were used in an attempt to recrystallise the gum without success, except in the case of absolute ethanol which gave needles, m.p. 144° , of 5-methyl-6-ethoxymethylchrysene.

5,6-Chrysaquinodimethane dimers (LXV) and (LXVI).

5,6-Dimethyl-5,6-dihydro-5,6-dihydroxychrysene (1.0 g.) hydriodic acid (1 ml.) and acetic acid (25 ml.) were heated under reflux for 10 min. After cooling the suspension was poured into benzene and water and neutralised with excess of aqueous sodium bicarbonate. The benzene layer was separated, washed with sodium thiosulphate solution and then with water; most of the benzene was removed under reduced pressure from the dried solution. The concentrated solution was placed on an alumina column (Woelm activity No. 1; wt. 100 g., 22 cm. x 2.5 cm.).

Elution with a mixture of 60° - 80° petroleum (60%) and benzene (40%) gave a product m.p. $85-105^{\circ}$ (200 mg.). Recrystallisation from petroleum gave rods, m.p. $121-2^{\circ}$, (15 mg.) of dimer LXVI.

λ_{\max} (chloroform): 278 ($\log_{10} \epsilon$ 5.23), 319 (4.39), 322 (4.38).

ν_{\max} (Nujol): 818 cm.^{-1} (two adjacent aromatic C-H), 759 (four adjacent aromatic C-H).

The n.m.r. spectrum (in CS_2) showed a doublet, centre 7.26τ ($J = 19 \text{ c.p.s.}$) (two methylene groups), a doublet, centre 7.05τ ($J = 19 \text{ c.p.s.}$), a multiplet between 1.9 and 2.65τ (6 H- α + 8 H- β) and a multiplet between 1.30 and 1.70τ (6 H- α 3).

Sublimation of the material m.p. $85-105^{\circ}$ at 0.1 mm gave material

in all respects identical with dichryso[11',12':1,2][5'',6'':5,6]cyclo-octa-1,2:5,6-diene (LXVI), as given above, except that it had m.p. 73-105°.

Elution with benzene gave a product m.p. 250°, (230 mg); recrystallisation from benzene gave rods m.p. 260° (lit,⁴¹ m.p. 260°) of dichryso[11',12':1,2][11'',12'':5,6]cyclo-octa-1,2:5,6-diene (LXV).

Found: C, 94.1; 5.8%

Calculated for (C₂₀H₁₄)_n: C, 94.4; 5.6%

λ_{\max} (in chloroform): 278 m μ (log₁₀ 5.12), 329 (4.23), 33.7 (4.23).

ν_{\max} (Nujol): 754 and 748 cm.⁻¹ (four adjacent aromatic C-H).

The n.m.r. spectrum (in CS₂) showed a singlet at 7.18 τ (two methylene groups), a singlet at 6.91 τ (two methylene groups), and a complex multiplet between 1.34 and 2.75 τ (6 H- $\alpha\beta$ + 6 H- α + 8 H- β).

Mass spectrographic determinations reveal that both these dimers decompose to give a product, mass 240, probably chrysene.

9,10-Phenanthraquinone

This was prepared by the method of Wendland and Lalonde⁶⁹ and purified by the formation and decomposition of the sodium bisulphite addition compound; the product had m.p. 202-4° (lit⁶⁹ m.p. 204°).

Trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyphenanthrene (XXV).

This was prepared by the reaction of methylmagnesium iodide with 9,10-phenanthraquinone by the method of Gardner and Sarrafizadeh⁷⁰ m.p. 162° (lit⁷⁰ m.p. 164°). The n.m.r. spectrum (in CDCl₃) showed a singlet at 8.68 τ (two methyl groups), a singlet at 7.63 τ (hydroxyl

groups) and two symmetrical sets of multiplets (2.20-2.42 τ and 2.52-2.75 τ).

Reaction of trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyphenanthrene with 1,4-naphthoquinone.

Trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyphenanthrene (0.85 g., 0.0035 mole) was added to a warm solution of 1,4-naphthoquinone (0.58 g., 0.0036 mole) in diethyl phthalate (14 ml.) and the resulting solution was heated under reflux for 5 minutes. On cooling, no solid precipitated, so an excess of a mixture of ether and 60°/80° petroleum was added to precipitate a green crystalline solid, m.p. 326° (sub.), (50 mg.). An attempt at purification by sublimation led to a chemical change, as indicated by the appearance of a second quinone peak in the I.R. spectrum. Recrystallisation from toluene gave orange needles, m.p. 326° (sub.) of 5,12-dihydro-1,2:3,4-dibenzonaphthacene-6,11-quinone.

Found: C, 87.5; H, 4.4%

Required for $C_{26}H_{16}O_2$: C, 86.7; H, 4.5%

λ_{\max} (chloroform): 253, 281, 292 and 326 $m\mu$.

ν_{\max} (Nujol): 1685 (C=O, quinone), 1590 (C=C, aromatic), 1280 (C-O, quinone), 755 and 748 (four adjacent aromatic C-H), 718 (four adjacent aromatic C-H in terminal ring adjacent to p-quinone ring.).

6,12-Dibromochrysene (LXXI)

Bromine (40 g., 0.25 mole) was added during 1 hr to a stirred suspension of chrysene (22.8 g., 0.1 mole), in glacial acetic acid (200 ml.) containing a small quantity of iron wire. The suspension was

then stirred with heating under reflux for 6 hrs. with much evolution of hydrogen bromide. On cooling, the reaction mixture was poured onto ice and a 5% aqueous sodium hydroxide solution, the precipitated solid was washed successively with 5% sodium hydroxide solution, 10% sodium carbonate solution, and water, and gave on drying 6,12-dibromochrysene, m.p. 270-275°, (38.4 g., 99%). Recrystallisation from benzene gave needles, m.p. 283-286° (lit⁶³ m.p. 273°).

Found: C, 56.2; H, 2.5%

Calculated for $C_{18}H_{10}Br_2$: C, 56.0; H, 2.6%

ν_{\max} (Nujol): 1575 cm^{-1} (C=C, aromatic), 1510 (C=C, aromatic), 915, 865 (singlet aromatic C-H), 765, 758, 752 (four adjacent aromatic C-H), and 696.

Reaction of silver acetate with 6,12-dibromochrysene.

A suspension of 6,12-dibromochrysene (5.0 g., 0.013 mole), and silver acetate (4.1 g., 0.0245 mole), in glacial acetic acid (300ml.) was heated under reflux with stirring for 58 hrs: on cooling the starting materials were recovered.

Oxidation of 6,12-dibromochrysene.

A mixture of 6,12-dibromochrysene (20.0 g., 0.051 mole) and sodium dichromate (60.0 g., 0.2 mole), in glacial acetic acid (500ml.) was heated under reflux with stirring for 24 hrs. The reaction mixture was then allowed to cool to about 25° when it was filtered to give unchanged 6,12-dibromochrysene (15 g.). The filtrate was poured into excess water

to precipitate a yellow-red solid which was washed well with water and dried (3.1 g.). The infrared spectrum of this solid showed carbonyl frequencies at 1790, 1713 and 1663 cm^{-1} . This solid was suspended in a sodium hydroxide solution (1.0 g. in 80 ml. of water) and the suspension heated on a water bath for 1 hr. At the end of this time filtration gave a deep red solid which was washed well with water and dried to give quinone, m.p. 230-235° (1.87 g.). Repeated recrystallisation from toluene gave 12-bromo-5,6-chrysaquinone, m.p. 255-6° (lit⁶³ m.p. 249-250°).

Found: C, 64.4; H, 2.6%

Calculated for $\text{C}_{18}\text{H}_9\text{BrO}_2$: C, 64.1; H, 2.7%

ν_{max} (Nujol): 1695 cm^{-1} 1668 (C=O stretch, ortho-quinone), 1597 (C=C stretch, aromatic), 1570, 1300, 1280, 1182, 935, 863 (singlet aromatic C-H), 770, 753 (four adjacent aromatic C-H).

Nitration of chrysene^{65,66}

To a stirred suspension of chrysene (10 g.) in glacial acetic acid (250 ml.), containing concentrated sulphuric acid (10 ml.) was added at a temperature of 45-50°, fuming nitric acid over a period of 5½ hrs. The resulting mixture was then heated for 4 hrs. on a steam bath and on cooling it was poured into water (1500 ml.) to precipitate a mustard-yellow solid. This solid was filtered, and washed well with water, and finally dried at 120° to give a solid (m.p. 250° upwards, 13.7 g.).

To a stirred suspension of the above product (9.5 g.) in boiling ethanol (250 ml.) was added a solution of hydrated sodium sulphide

(80.0 g.) in the minimal quantity of water over a period of 5 min.

Immediately on the addition, the colour of the suspension changed from a yellow to dark brown. Heating was continued for 1 hr; at the end of this time the ethanol was removed and excess water added to the residue to give dark brown pellets, m.p. 255-258° (7.0 g., 81%). Recrystallisation from chlorobenzene gave yellow needles, m.p. 279-283° (lit⁶⁶ m.p. 284-286°).

ν_{\max} (Nujol): 3478 and 3415 cm^{-1} (NH stretch, primary NH_2).

The above amino-compound (5.0 g.) was heated with 10% sulphuric acid (35 ml.) in a sealed tube for 6½ hrs. at 220-225°. On cooling the reaction product was extracted with hot ethanolic potash solution to give a purple solution. Filtration gave unchanged starting material, (2.0g.). Acidification of the filtrate gave readily oxidisable solid (2.5 g.). When, however, a suspension of this solid in glacial acetic acid (200 ml.) containing lead dioxide (1.0 g.) was boiled for 30 min. no 6,12-chrysaquinone was obtained, instead a small quantity of solid, m.p. 210° (0.2 g.) was obtained.

Reaction of chrysene with chlorosulphonic acid.

To a well-stirred suspension of chrysene (5.0 g., 0.22 mole) in tetrachloroethane (50 ml.) was added chlorosulphonic acid (15.3 g., 0.13 mole) over a period of 1 hr., the temperature being maintained at 0-5°C. Initially as the drops of chlorosulphonic acid came in contact with the suspension a local purple colour was noted. As the addition proceeded the colour of the reaction mixture darkened to a deep brown. The reaction mixture was then stirred at 0-5° for a further 5 hrs. and then at room temperature

for 18 hrs. Excess ice-water was then added with vigorous stirring and ice cooling, after which tetrachloroethane was removed by steam distillation.

Filtration gave a pale green solid, m.p. $188-189^{\circ}$ (2.0 g.). Recrystallisation from dry benzene gave a chrysenebissulphonyl chloride, m.p. 206° , as an off-white solid.

Found: C, 50.7; H, 2.2%

Required for $C_{18}H_{10}Cl_2O_4S_2$: C, 50.9; H, 2.4%

λ_{\max} (in chloroform): 281 μ ($\log_{10} \epsilon$ 4.68), 331 (4.05).

ν_{\max} (Nujol): 1380 and 1370 cm^{-1} (SO_2Cl), 1175 (SO_2Cl), 898, 847, 828, 780, 755 (four adjacent aromatic C-H), 745, 732.

The filtrate from the steam distillation was neutralised with sodium bicarbonate; as no precipitation occurred, sodium chloride (100 g.), was added with stirring until all the sodium chloride had dissolved and a green gelatinous solid had precipitated out. This solid was filtered, and recrystallised from 120 ml. of water, the solution on cooling gave a green thixotropic gel, which was filtered with difficulty to give a green solid, (14.0 g. of hydrated sodium chrysenedisulphonate).

Reaction of sodium chrysene disulphonate with molten alkali.

A mixture of hydrated sodium chrysene-sulphonate (4.0 g.), with potassium hydroxide (25 g.), was heated under nitrogen so that the temperature was raised to 290° over 5 minutes and kept at this temperature for a further 15 minutes. The melt was allowed to cool to about 200° and the semi-molten material poured into 400 ml. of water, through which

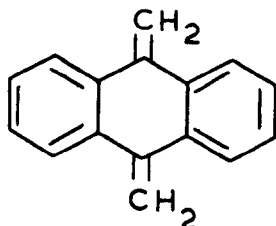
nitrogen was bubbling. The resulting solution was acidified, with ice cooling, with moderately concentrated sulphuric acid to precipitate a tan coloured solid, m.p. 220° (1.0 g.). Lassigne test of a sample indicated that sulphur was absent. Sublimation at $210/0.1$ mm. gave a white solid which very rapidly darkened, m.p. 220° .

This solid when boiled with glacial acetic acid containing lead dioxide did not give 6,12-chrysaquinone.

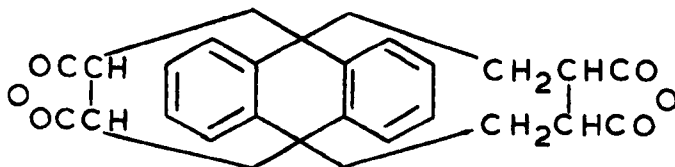
CHAPTER III

Reactions of 9,10-Anthraquinodimethane

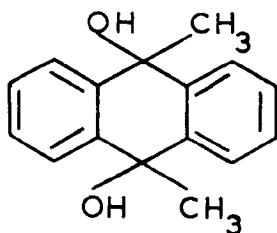
It was reported by Millar and Wilson³⁴ that the dehydration of cis-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (XXVII) in boiling diethyl phthalate gave 9,10-anthraquinodimethane (XXIX) which reacted in situ with two molecules of maleic anhydride to give an adduct, m.p. 360° ; the structure tentatively suggested for this was (XXX). This adduct was claimed to be identical with that obtained by heating tetrabenzo[2,2']paracyclophane (LXXV) with maleic anhydride, either in benzene,⁷¹ or in diethyl phthalate at 350° .³⁴ This adduct was also obtained when bi(anthracene-9,10-dimethylene)-disulphone was thermally decomposed in boiling diethyl phthalate in the presence of maleic anhydride.³⁴



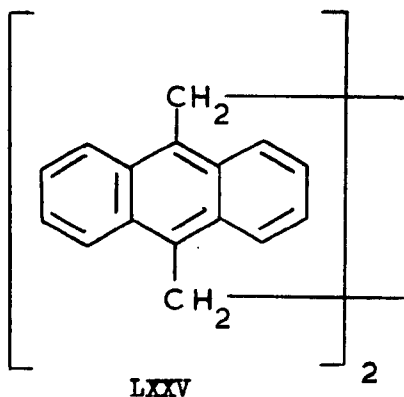
XXIX



XXX

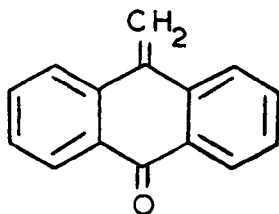


XXVII



LXXV

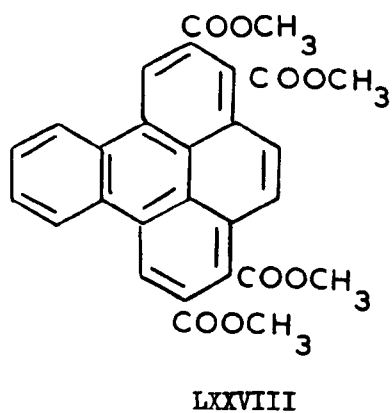
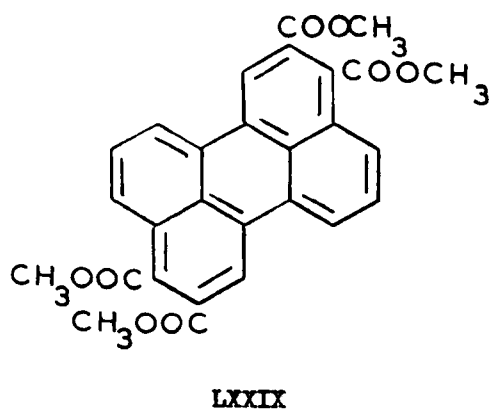
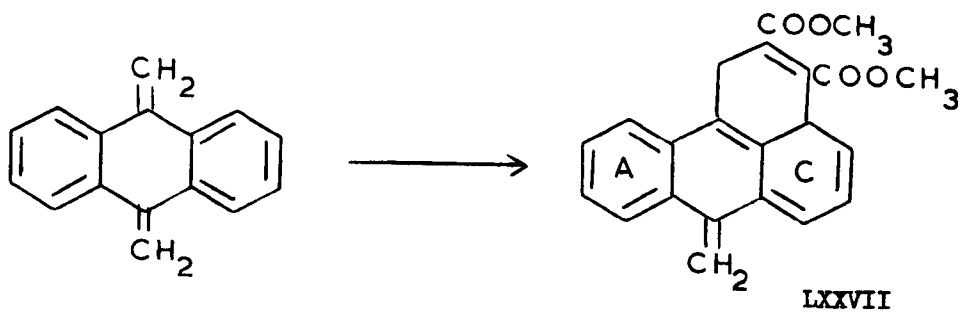
In the present work dehydration of cis- or trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene in boiling acetic anhydride liberated 9,10-anthraquinodimethane (XXIX) which also reacted with two molecules of maleic anhydride, this time to give an adduct, m.p. 230°. Use of models then showed that the interatomic distance between the extremities of the two methylene groups in 9,10-anthraquinodimethane is large and made it unlikely that a molecule of maleic anhydride could bridge them as in (XXX).



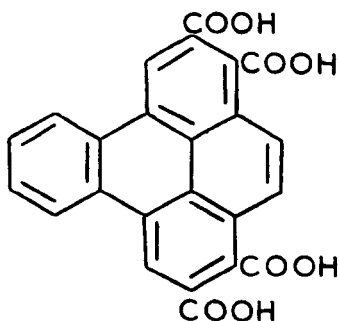
LXXVI

Earlier work⁷² (see also Chapter 4) had shown that with methyleneanthrone (LXXVI) dienophiles reacted by 1,4-addition to the diene system formed by the methylene group and one of the immediately adjacent Kekulé double bonds of a terminal benzenoid ring to give a benzanthrone derivative. It hence seemed likely that 9,10-anthraquinodimethane would react similarly with dienophiles.

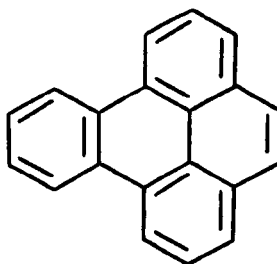
In order to establish the general pattern of the addition of dienophiles with 9,10-anthraquinodimethane, it was decided to liberate the latter in boiling nitrobenzene in the presence of excess dimethyl acetylenedicarboxylate in the expectation of obtaining a fully aromatic product whose structure could readily be determined. It was assumed that as with the reaction with maleic anhydride, this reaction would involve the addition of two molecules of dimethyl acetylenedicarboxylate which would not react simultaneously; but that addition of one molecule would give an intermediate (LXXVII) which would then react with a further molecule of dimethyl acetylenedicarboxylate to give a 4,5-benzopyrene derivative (LXXVIII). The assumption was made that the second molecule of dimethyl acetylenedicarboxylate is more likely to react with the diene system formed from the remaining unreacted methylene group and the adjacent double bond of the non-benzenoid ring, C, rather than the diene system incorporating a double bond from the adjacent benzenoid ring A (which would give the perylene derivative LXXX).



Experimentation showed that these presumptions were correct; reaction of 9,10-anthraquinodimethane with dimethyl acetylenedicarboxylate gave tetramethyl-4,5-benzopyrene-1,2,7,8-tetracarboxylate (LXXVIII) in 23% yield as yellow needles, m.p. 223° . Hydrolysis of the ester gave the pale yellow hydrated potassium salt of the tetracarboxylic acid (LXXX). Acidification of the salt gave the acid as a red solid. Attempts to recrystallise the acid gave always the dianhydride, also a red crystalline solid, m.p. $> 350^{\circ}$. Decarboxylation of the acid by soda-lime at $400-450^{\circ}$ gave 4,5-benzopyrene (LXXXI) in 25% yield, as confirmed by comparison of its ultraviolet spectrum with that of authentic material,⁷³ and thus confirming the structure of the original adduct, (LXXVIII).

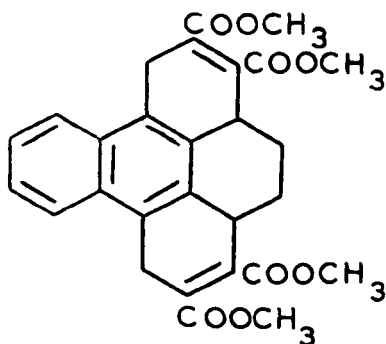


LXXX



LXXXI

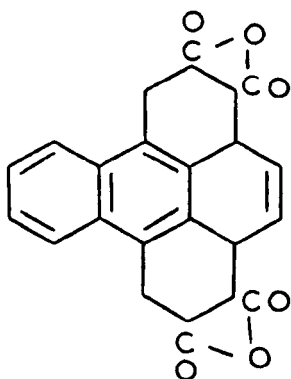
The reaction of 9,10-anthraquinodimethane with dimethyl acetylenedicarboxylate under non-reducing conditions, i.e. in boiling tetralin under an atmosphere of nitrogen, besides giving tetramethyl-4,5-benzopyrene-1,2:7,8-tetracarboxylate, (LXVIII) presumably by autoxidation, also gave, in low yield, a hydrogenated benzopyrene derivative which when heated with chloroanil in boiling xylene was aromatised to (LXXVIII). This hydrogenated benzopyrene derivative probably has structure (LXXXII) as indicated particularly by its ultraviolet spectrum which shows a substituted naphthalene chromophore.



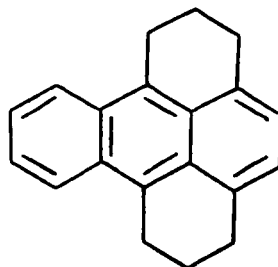
LXXXII

By analogy with these reactions with dimethyl acetylenedicarboxylate, the reaction of 9,10-anthraquinodimethane with maleic anhydride would be expected also to give a 4,5-benzopyrene derivative. The analytical data for both the adduct, m.p. 230° , prepared in acetic anhydride, and the adduct, m.p. 360° , prepared in diethyl phthalate³⁴ were identical. Repetition of the work of Millar and Wilson in order to establish the difference between the two adducts, showed that the reaction of 9,10-anthraquinodimethane with maleic anhydride in boiling diethyl phthalate did not give an adduct, m.p. 360° , but always gave, no matter what proportions of maleic anhydride were used, an adduct, m.p. 230° , identical in all respects with that obtained in acetic anhydride. Comparison of the infrared spectra of these two adducts, m.p. 360° and m.p. 230° , indicate that these do not have the same structure.

Analytical and spectroscopic data indicate that this adduct is 4,5-benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (LXXXIII) which was obtained in a 60% yield. An attempt to prepare the corresponding tetracarboxylic acid by dissolving the dianhydride in alkali followed by acidification resulted on recrystallisation in recovery of the dianhydride.



LXXXIII



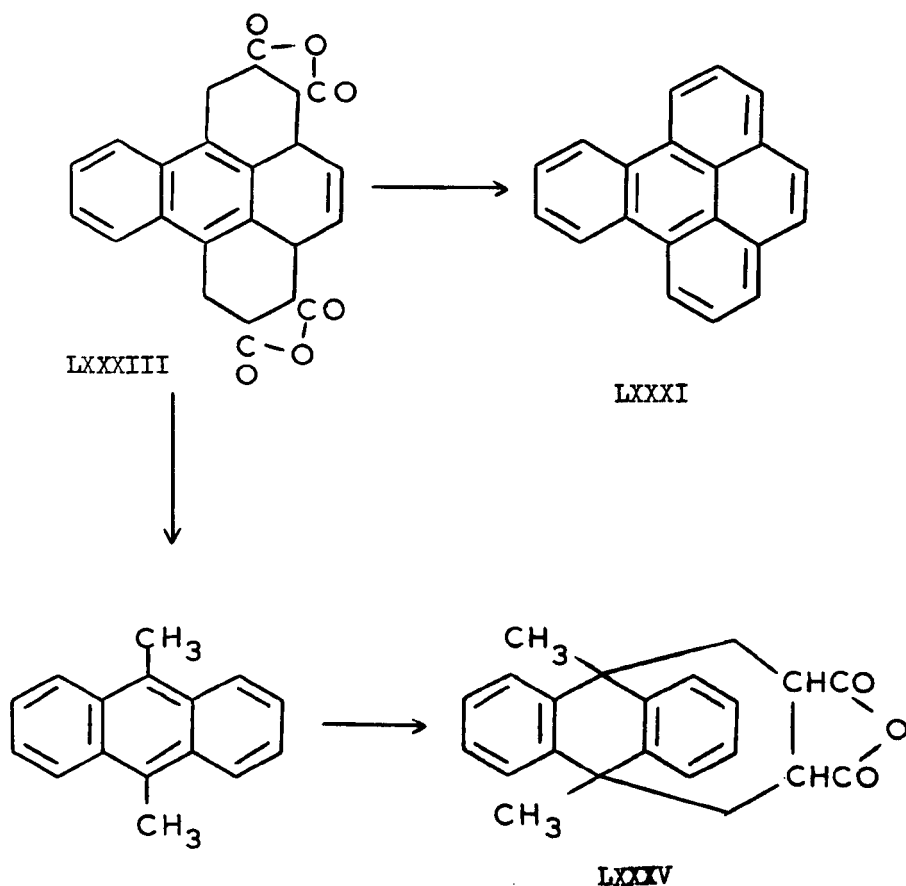
LXXXIV

Dehydrogenation of the dicarboxylic anhydride (LXXXIII) to give the fully aromatic 4,5-benzopyrene system proved to be more difficult than anticipated. Heating with chloroanil in boiling xylene even for 42 hrs. was ineffective, unchanged (LXXXIII) being recovered. An attempt to obtain 4,5-benzopyrene (LXXXI) directly by heating (LXXXIII) with alkaline potassium ferricyanide solution (see Chapter 2, p. 18) also resulted in recovery of unchanged dianhydride.

When the dicarboxylic anhydride was heated with soda-lime at 300°, a yellow product sublimed in 40% yield which was initially thought to be 4,5-benzo-1,2,3,6,7,8-hexahydropyrene (LXXXIV) but was subsequently shown to be 9,10-dimethylantracene by comparison

with authentic material. Possibly a retro-Diels-Alder reaction occurs to give 9,10-anthraquinodimethane which then protonates, the maleic anhydride being removed by the soda-lime.

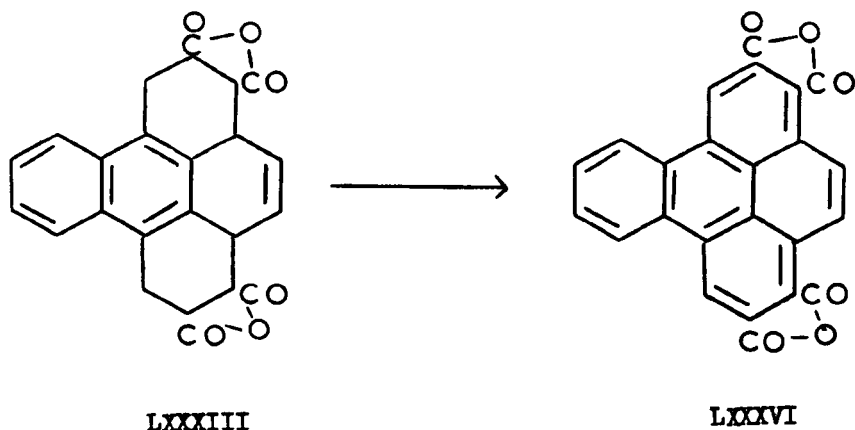
The action of hot phosphorus pentoxide on 1,2,3,6-tetrahydrophthalic anhydride derivatives results in the simultaneous elimination of carbon monoxide and water to give the corresponding aromatic hydrocarbons.⁷⁴ When 4,5-benzo-1,2,3,6,7,8,8a,10a-octa-hydropyrene-1,2:7,8-dicarboxylic anhydride was heated with excess of phosphorus pentoxide to 220°, a trace of material having the 4,5-benzopyrene (LXXXI) chromophore was obtained: but the yield was too low to afford substantial proof of the presence of a 4,5-benzopyrene skeleton in the dianhydride. When the phosphorus pentoxide-dianhydride mixture was quickly heated to 240°, rapid sublimation took place to give colourless needles of a product found (by comparison with an authentic specimen⁷⁵) to contain 9,10-dimethyl-9,10-dihydro-anthracene-9,10-endosuccinic anhydride (LXXXV), and in addition a small quantity of maleic anhydride was obtained. Again a retro-Diels-Alder Reaction took place to give maleic anhydride and 9,10-dimethylantracene which then reacted to give the endo adduct (LXXXV). Reaction of phosphorus pentoxide with the dianhydride in boiling xylene also gave a small quantity of 9,10-dimethylantracene.



Partially hydrogenated phthalic anhydride derivatives have been successfully dehydrogenated by heating with a mixture of palladium charcoal and sulphur.⁷⁶ When the dicarboxylic anhydride was so treated, at 300°, only 9,10-dimethylanthracene was formed.

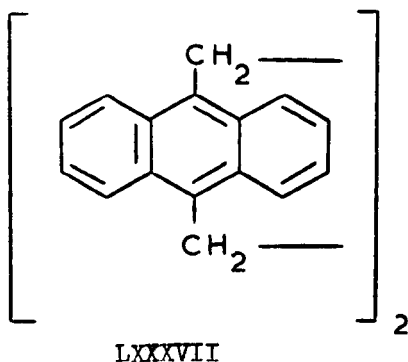
The 9,10-anthraquinodimethane-maleic anhydride adduct was finally successfully dehydrogenated by heating with sulphur at

200-220°, which gave 4,5-benzopyrene-1,2:7,8-dicarboxylic anhydride (LXXXVI) in 40% yield thus confirming the assigned structure of the 9,10-anthraquinodimethane-maleic anhydride adduct as 4,5-benzo-1,2,3,6,7,8,8a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (LXXXIII).



These reactions show clearly that 9,10-anthraquinodimethane, liberated from the readily available cis- or trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene, reacts with maleic anhydride and dimethyl acetylenedicarboxylate to give 4,5-benzopyrene derivatives.

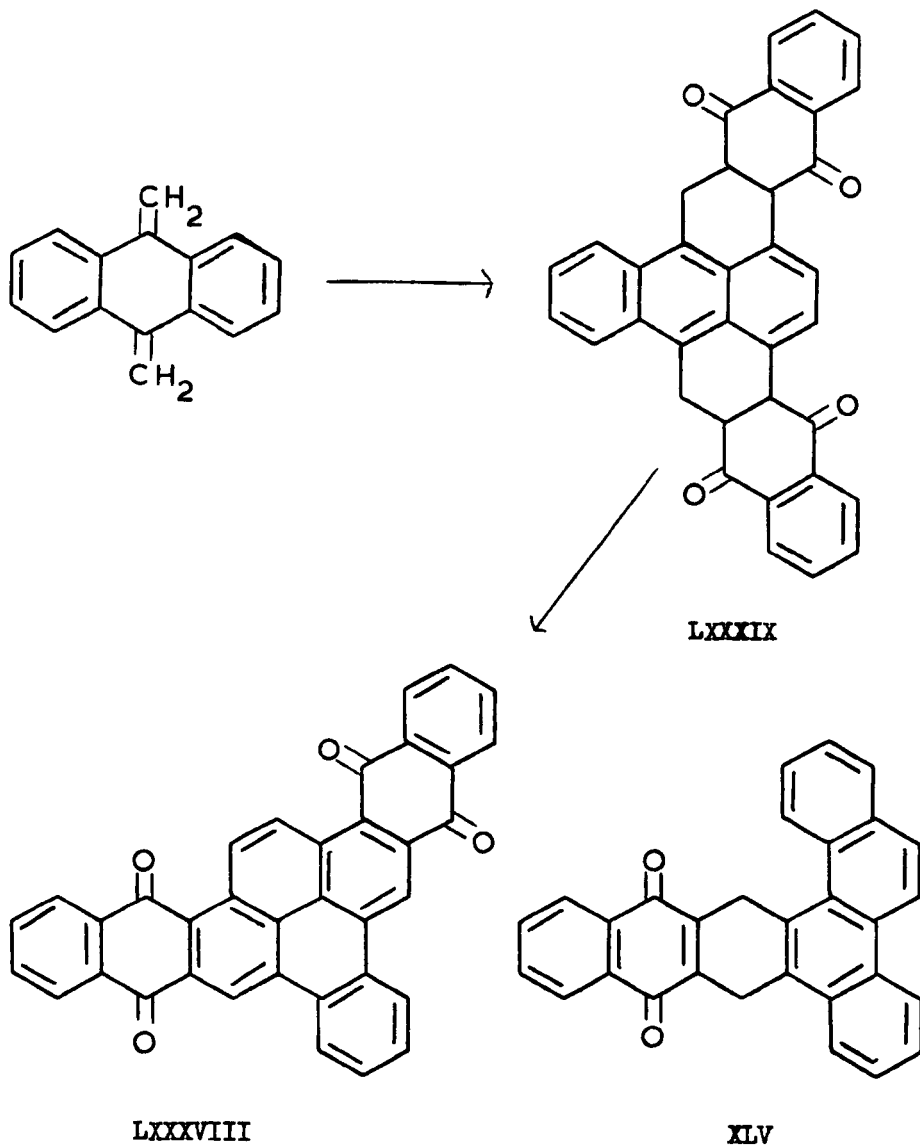
As other ethylenic and acetylenic dienophiles would also be expected to react in a similar way, this method affords a new and convenient route to 4,5-benzopyrene derivatives, which are otherwise inaccessible or only available via cumbersome routes.



The reaction of tetrabenzobis[2,2]paracyclophane (LXXXVII) with maleic anhydride was then investigated to see if in fact a 4,5-benzopyrene derivative was obtained. The reaction of anthracene with paraformaldehyde and hydrochloric acid gave 9,10-di(chloromethyl)-anthracene⁷⁷ which was treated with sodium iodide in acetone to give tetrabenzobis[2,2]paracyclophane⁷¹ (LXXXVII).

It is claimed that when tetrabenzobis[2,2]paracyclophane was reacted with maleic anhydride, either in benzene,⁷¹ or in diethyl phthalate,³⁴ a product, m.p. 360° was obtained. In the present work the product obtained, although having the analysis $C_{16}H_{12}$, $2 C_4H_2O_3$ had m.p. 250-260°. When this adduct (m.p. 250-260°) was heated with sulphur under the conditions whereby 4,5-benzo-1,2,3,6,7,8,8a-octahydropyrene-1,2:7,8-dicarboxylic anhydride was dehydrogenated,

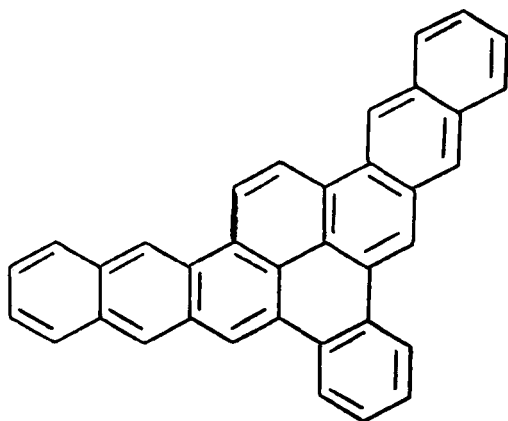
the fully aromatic 4,5-benzopyrene-1,2:7,8-dicarboxylic anhydride was not obtained, indicating that the initial adduct probably has not a 4,5-benzopyrene skeleton: its structure remains uncertain.



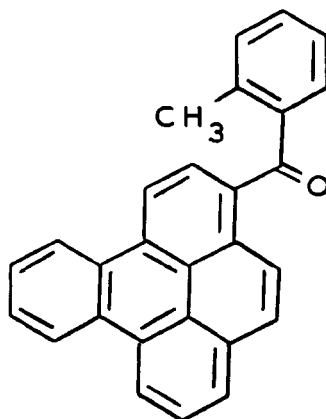
With 1,4-naphthoquinone in boiling nitrobenzene, 9,10-anthraquinodimethane (from cis- or trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene) gave (after 5 hrs.) 4,5-benzonaphtho[2',3':1,2][2'',3'':7,8]pyrene-1',4':1'',4''-diquinone (LXXXVIII) in 46% yield. If the reaction is stopped after 10 minutes, a mixture of (LXXXVIII) and its hydrogenated derivatives (e.g. LXXXIX), mainly the latter, is obtained, as shown by the 9,10-dimethylanthracene-type ultraviolet absorption spectrum of the mixture, and the low intensity of an absorption band at 707 cm.^{-1} (in the infrared spectrum). The progress of aromatisation may be followed by the increase in intensity of the very strong absorption band at 707 cm.^{-1} which is attributed to the out-of-plane deformation absorption of the four adjacent aromatic C-H bonds on the terminal rings adjacent to the p-quinone rings⁴⁸ (cf. 5,12-dihydro-3,4-benzonaphtho[1',2':1,2]naphthacene-6,11-quinone (XLV) Chapter 2, p.20 which also shows a strong absorption band at 707 cm.^{-1}). The diquinone also shows a strong absorption band at 762 cm.^{-1} , due to the four adjacent aromatic C-H bonds on the terminal ring not adjacent to the p-quinone rings, i.e. within the frequency range usually associated with the four adjacent aromatic C-H bonds (770 to 735 cm.^{-1}).

Reduction of the diquinone using zinc, pyridine and acetic acid⁵⁹ gave 4,5-benzodinaphtho[2',3':1,2][2'',3'':7,8]pyrene (XC) in 2% yield. A 9% yield of this hydrocarbon was obtained when the diquinone was reduced using the zinc dust melt method.⁵¹ The ultraviolet absorption spectrum of this hydrocarbon was identical with that given

by Clar and Zander⁷⁸ for the hydrocarbon obtained, with others, by pyrolysis of 8-(o-toluyl)-4,5-benzopyrene (XCI) at 420-440°. Clar and Zander had assigned the structure of this hydrocarbon as 4,5-benzodinanaphtho[2',3':1,2][2'',3'':7,8]pyrene (XC) by comparison of its ultraviolet absorption spectrum with that of dinaphtho[2',3':1,2]-[2'',3'':7,8]pyrene.



XC

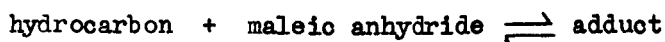


XCI

This present synthesis confirms the structure assigned by Clar and Zander to the hydrocarbon (XC) and also establishes the structure of the diquinone (LXXXVIII) showing that 9,10-anthraquinone-dimethane reacts with 1,4-naphthoquinone in exactly the same way as it

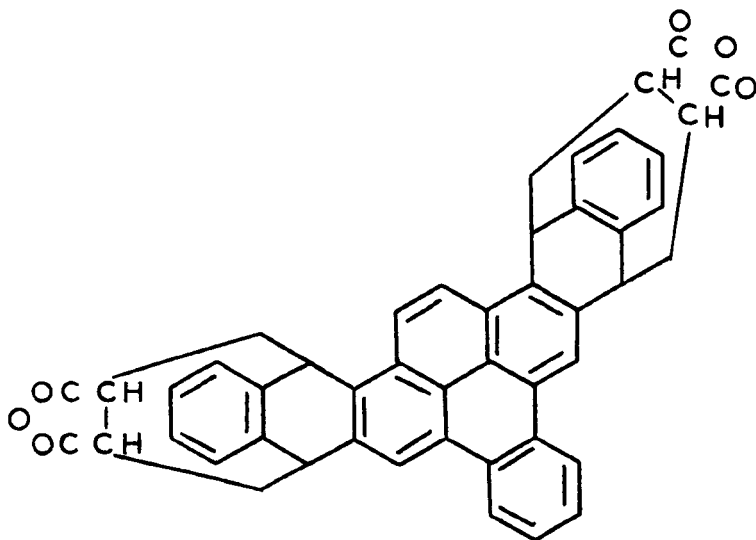
does with maleic anhydride and dimethyl acetylenedicarboxylate.

No mention was made by Clar and Zander of any derivatives of 4,5-benzodiphenyl[2',3':1,2][2'',3'':7,8]pyrene, such as the 2,4,7-trinitrofluorenone complex or an adduct with maleic anhydride. Attempts in the present work to make the 2,4,7-trinitrofluorenone complex failed, the hydrocarbon always precipitating out first from a solution of the two, a solution which incidently did not show the colouration characteristic of complex formation.⁷⁹ No adduct was obtained from the hydrocarbon and maleic anhydride when these were heated in xylene. When the hydrocarbon was heated in boiling maleic anhydride, an unstable adduct was obtained which showed an ultraviolet chromophore which is very similar to that found for the 4,5-benzopyrene-1,2:7,8-tetracarboxylic acid derivatives indicating that the adduct was probably (XCII). Attempts to recrystallise this adduct resulted in decomposition to the original components, thus confirming that the equilibrium of the reaction



lies far to the left.

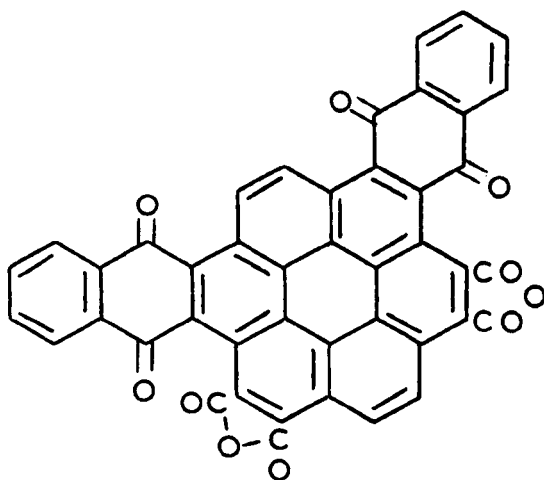
The diquinone (LXXXVII) was heated in boiling maleic anhydride, containing chloranil as aromatising agent, to give after repeated washings with hot xylene and ether, a product whose weight and infrared spectrum suggested that an almost quantitative reaction had taken place between the quinone (LXXXVII) and two molecules of maleic anhydride to give a derivative (CXIII) of the unknown diphenyl[2',3':1,2][2'',3'':5,6]coronene system.



XCII

Attempts to purify this product by recrystallisation, sublimation and treatment with hot alkali all led to recovery of starting materials suggesting that the product is not particularly stable, cf. (XCII).

It is of interest that the corresponding derivative of 1,2:5,6-dibenzo-coronene prepared from 1,2:4,5:7,8-tribenzopyrene and maleic anhydride decomposes into starting materials on heating with soda-lime.⁸⁰

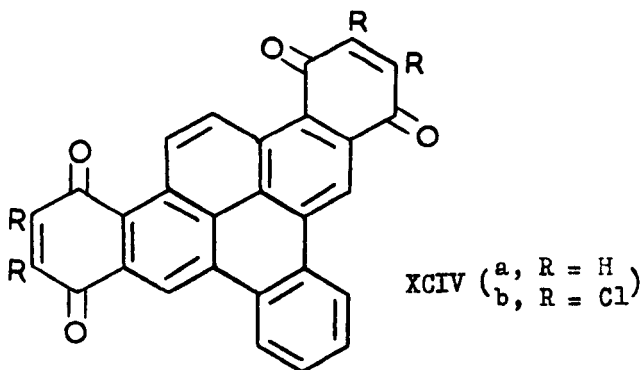


XCIII

The reaction of 9,10-anthraquinodimethane (from cis- or trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene) with excess of p-benzoquinone in boiling acetic anhydride gave 1,2:4,5:7,8-tribenzopyrene-1',4':1'',4''-diquinone (XCIVa) in 56% yield; in boiling

nitrobenzene a 43% yield was obtained. Although this diquinone was not reduced to the parent hydrocarbon, 1,2:4,5:7,8-tribenzopyrene, the structure is consistent with analytical and spectroscopic data as well as being in accord with the reaction of 9,10-anthraquinodimethane with other dienophiles.

Attempts to reduce the diquinone have all failed; apparently the only method successfully used for the reduction of terminal quinone rings in polycyclic systems has been the use of lithium aluminium hydride to give chrysene and 3,4-benzophenanthrene,⁶⁰ respectively. 1,2:4,5:7,8-Tribenzopyrene was not obtained when the diquinone was extracted into a refluxing solution of lithium aluminium hydride or when the diquinone was heated with a solution of lithium aluminium hydride in a tetrahydrofuran-dioxan mixture. Treatment of the diquinone by the zinc melt method⁵¹ also resulted in recovery of quinone, as did treatment with aluminium cyclohexanolate.⁵⁵



When cis-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene was heated with chloranil in xylene, in an attempt to prepare (XCIIIb), hydrogen chloride was evolved, but the product obtained formed coal-like lumps, insoluble in organic solvents, and whose infrared spectrum was featureless. When this reaction was attempted in acetic anhydride as solvent, a good yield of 1,4-diacetoxy-2,3,5,6-tetrachlorobenzene was obtained.

EXPERIMENTAL

Cis- and trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (XXVII).

The cis- and trans-isomers were prepared by the reaction of excess of methylmagnesium iodide with 9,10-anthraquinone by the method of Beckett and Lingard⁸¹ in 60% and 56% yield respectively.

Tetramethyl-4,5-benzopyrene-1,2,7,8-tetracarboxylate (LXXVIII).

a) cis- or trans-9,10-Dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (1.0 g., 0.0046 mole), and dimethyl acetylenedicarboxylate (1.40 g., 0.011 mole), in nitrobenzene (3.5 ml.) were heated under reflux for 2 hr. On cooling yellow needles separated, m.p. 313-319°; (0.47 g., 23%). Recrystallisation from glacial acetic acid gave yellow needles, m.p. 321°.

Found: C, 69.6; H, 4.2%

Required for C₂₈H₂₀O₈: C, 69.4; H, 4.2%

λ_{\max} (dioxan): 288 m μ (log₁₀ ϵ 4.84), 299 (4.79), 329 (4.34) and 340 (4.44).

ν_{\max} (KBr disc): 1725 and 1712 cm.⁻¹ (C=O, ester), 1434, 1331, 1287, 1240, 1204, 1163, 1083, 1015, 898 (singlet aromatic C-H), 776, 751 (four adjacent aromatic C-H).

b) When cis-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (1.0 g., 0.0046 mole) and dimethyl acetylenedicarboxylate (0.55 g.,

0.0043 mole), were heated under reflux in nitrobenzene (3.5 ml.) for 2 hr. as in (a); the only product identified was again tetramethyl-4,5-benzopyrene-1,2,7,8-tetracarboxylate (6%).

c) cis-9,10-Dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (1.0 g., 0.0046 mole) and dimethyl acetylenedicarboxylate (1.4 g., 0.011 mole) in acetic anhydride (5 ml.) were heated under reflux for 12 hr. on cooling tetramethyl-4,5-benzopyrene-1,2,7,8-tetracarboxylate separated, m.p. 321° , (50 mg., 3%).

Tetramethyl-4,5-benzo-3,6,8a,9,10,10a-hexahdropyrene-1,2,7,8-tetracarboxylate (LXXXII).

cis-9,10-Dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (2.0 g., 0.0088 mole) dimethyl acetylene-dicarboxylate (2.0 g., 0.016 mole) in tetralin (6.5 ml.) were heated under nitrogen under reflux for 45 min. On cooling, yellow needles separated, m.p. $310-315^{\circ}$, (40 mg.), identical in all respects with tetramethyl-4,5-benzopyrene-1,2,7,8-tetracarboxylate. Addition of excess of ether to the filtrate gave pale yellow rods, m.p. $196-198^{\circ}$ (185 mg., 9.5%). Recrystallisation from isopropanol gave rods, m.p. $202-204^{\circ}$.

Found: C, 68.6; H, 5.6%

Required for $C_{28}H_{26}O_8$: C, 68.5; H, 5.4%

λ_{\max} (ethanol): 204 $m\mu$ ($\log_{10} \epsilon$ 4.78), 230 (4.32), 287 (4.16).

ν_{\max} (KBr disc): 1740 cm^{-1} (C=O ester), 1640, 1439, 1285, 1257, 1207, 1180, 1130, 995, 895, 817, 758 (four adjacent aromatic C-H).

Dehydrogenation of tetramethyl-4,5-benzo-3,6,8a,9,10,10a-hexahydro-pyrene-1,2,7,8-tetracarboxylate (LXXXII).

Tetramethyl-4,5-benzo-3,6,8a,9,10,10a-hexahdropyrene-1,2,7,8-tetracarboxylate (0.50 g., 0.001 mole), and chloranil (0.55 g., 0.0022 mole), in sulphur-free xylene (35 ml.) were heated under reflux for 42 hr. On cooling, yellow needles of tetramethyl 4,5-benzopyrene-1,2,7,8-tetracarboxylate m.p. 315-318° (70 mg.) deposited. The filtrate was washed with ice-cold sodium bicarbonate solution, followed by water. Removal of xylene from the dried solution gave a residue which was treated with hot isopropanol to give more of the fully aromatic ester (total 120 mg., 24%).

Attempted dehydrogenation of tetramethyl 4,5-benzopyrene-1,2,7,8-tetracarboxylate.

Tetramethyl 4,5-benzopyrene-1,2,7,8-tetracarboxylate (0.5 g., 0.001 mole), and chloranil (0.275 g., 0.0011 mole), in sulphur-free xylene (40 ml.) were heated under reflux for 18 hr. On cooling, starting material separated (0.39 g., 78%).

4,5-Benzopyrene-1,2,7,8-tetracarboxylic acid (LXXX) and 4,5-benzopyrene-1,2,7,8-tetracarboxylic dianhydride (LXXXVI).

Tetramethyl 4,5-benzopyrene-1,2,7,8-tetracarboxylate (1.0 g., 0.002 mole), was suspended in a solution of potassium hydroxide (3.7 g., 0.065 mole), in aqueous ethanol (30 m. water, 50 ml. ethanol), and the suspension heated under reflux for 6 hr. During this time all

of the ester went into solution giving a claret-coloured solution showing intense fluorescence. On cooling, pale yellow needles of the potassium salt of the acid separated (0.60 g.). A portion of this salt was recrystallised from aqueous ethanol to give a pale yellow solid, m.p. $> 350^{\circ}$.

Found: C, 45.6; H, 2.2%

Required for $C_{24}H_8O_8K_4, 3H_2O$: C, 45.4; H, 2.2%

λ_{\max} (water): 288 m μ ($\log_{10} \epsilon$ 4.84), 299 (4.79), 329 (4.34) and 340 (4.44).

ν_{\max} (KBr disc): 1558 cm.⁻¹ (carboxylate), 1527, 1505, 1480, 1430, 1402, 1385, 1315, 909, 802, 754, 748 (four adjacent aromatic C-H).

The remainder of the salt, together with the filtrate from the recrystallisation was added to the original potash solution, to give a solution from which ethanol was removed. The aqueous residue was acidified with dilute hydrochloric acid to give a gelatinous reddish yellow precipitate which proved impossible to filter; boiling the solution did not cause coagulation. Removal of water under reduced pressure gave a residue which on treatment with boiling water gave a red solid (0.86 g., 97%). ν_{\max} (Nujol): 1710 cm.⁻¹ (C=O, carboxylic acid).

All attempts to recrystallise this acid as such failed, due to its extreme insolubility in low-boiling solvents. Recrystallisation from 1,2,4-trichlorobenzene gave 4,5-benzopyrene-1,2,7,8-tetracarboxylic dianhydride as red needles, m.p. $> 350^{\circ}$.

Found: C, 73.2; H, 2.2%

Required for $C_{24}H_{18}O_6$: C, 73.4; H, 2.1%

λ_{\max} (dioxan): 288 $m\mu$ ($\log_{10} \epsilon$ 4.84), 299 (4.79), 329 (4.34), and 340 (4.44).

ν_{\max} (KBr disc): 1825 and 1757 cm^{-1} (C=O anhydride), 1273, 1237, 1155, 932, 912, 890 and 883 (singlet aromatic C-H), 854, 848, 791, 771, 738 (four adjacent aromatic C-H).

4,5-Benzopyrene (LXXXI).

4,5-Benzopyrene-1,2,7,8-tetracarboxylic acid (100mg.) was ground with soda-lime (1.0 g.) and the mixture heated under nitrogen at 300-320° for 30 min. The mixture was then heated at 400-450°/0.1 mm for 5 hr., during which time a yellow solid (42 mg.) sublimed. This solid was placed onto an alumina column (Spence 'O', 13.0 cm. x 1.5 cm.) in benzene solution. Elution with 60°/80° petroleum 70%; benzene 30% mixture gave 4,5-benzopyrene, m.p. 167-172° (25% yield). Recrystallisation from benzene-ethanol gave yellow plates, m.p. 172-174° (lit⁷³ m.p. 178-179°).

λ_{\max} (ethanol): 237 $m\mu$, 267, 278, 289, 305, 316, 331, 365, corresponding to that given by Clar.⁸²

4,5-Benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2,7,8-dicarboxylic anhydride (LXXXIII).

a) When cis- or trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxy-anthracene (1.0 g., 0.0046 mole) and maleic anhydride (2.1 g., 0.021 mole)

in acetic anhydride (5 ml.) were heated under reflux for 30 min. Adding excess of ether to the cooled solution gave a cream solid, m.p. 230° , (0.3 g.). Evaporation of the filtrate under reduced pressure and subsequent treatment of the gum-like residue with ether gave a further 0.7 g., m.p. $225-227^{\circ}$ (60% total yield). Recrystallisation from benzene or toluene gave colourless crystals of the anhydride, m.p. 230° .

Found: C, 72.0; H, 4.3%, M, 443

Required for $C_{24}H_{16}O_6$: C, 72.0; H, 4.0%, M, 400

λ_{\max} (in dioxan): 215 $m\mu$ ($\log_{10} \epsilon$ 4.78), 270 (4.29), 298 (4.07).

ν_{\max} (KBr disc): 1851 and 1770 cm^{-1} (C=O, anhydride), 1453 ($-CH_2-$), 1375, 1222, 1070, 930, 767.

b) When equimolar proportions of cis-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene and maleic anhydride were heated under reflux in acetic anhydride, the only product isolated was again 4,5-benzo-1,2,3,6,7,8,8a,10a-octahdropyrene-1,2:7,8-dicarboxylic anhydride in 10% yield.

c) cis-9,10-Dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (1.0 g., 0.0046 mole), and maleic anhydride (2.1 g., 0.021 mole) in diethyl phthalate (2.5 ml.) were heated under reflux for ten minutes. Treatment of the cooled solution with ether precipitated a solid m.p. $225-230^{\circ}$, (0.86 g., 52%). Spectroscopic data showed this to be identical with 4,5-benzo-1,2,3,6,7,8,8a,10a-octahdropyrene-1,2:7,8-dicarboxylic anhydride prepared in acetic anhydride.

Use of the molar proportions used by Millar and Wilson,³⁴ i.e. cis-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene.

(1.0 g., 0.0046 mole) and maleic anhydride (0.5 g., 0.0050 mole) failed to give any product other than 4,5-benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride.

Attempted preparation of 4,5-benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-tetracarboxylic acid.

4,5-Benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (0.3 g., 0.0014 mole) was dissolved in hot 10% aqueous sodium hydroxide solution (20 ml.), and the cooled filtrate was acidified with dilute hydrochloric acid to give a gelatinous unfilterable precipitate. Extraction with ethyl acetate (2 x 50 ml.) followed by removal of the ethyl acetate from the dried solution gave a residue, which on recrystallisation from isopropanol gave the anhydride, m.p. 230° , (0.15 g.).

Aromatisation of 4,5-benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (LXXXIII).

4,5-Benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (0.4 g., 0.0018 mole) was ground with sulphur (0.2 g., 0.0063 mole), and the mixture was heated at $200-220^{\circ}$, under nitrogen, for 5 hr. until the evolution of hydrogen sulphide had ceased. The black product was boiled with an excess of dilute sodium hydroxide solution, filtered hot and the cooled filtrate acidified with dilute sulphuric acid to give, after filtration, 0.20 g. Recrystallisation from 1,2,4-trichlorobenzene gave red needles, m.p. $>350^{\circ}$, of 4,5-benzopyrene-1,2:7,8-tetracarboxylic anhydride as shown by spectroscopic comparison with

authentic material.

The material insoluble in the sodium hydroxide solution, after drying, was extracted with benzene. Removal of benzene from the resulting solution gave material (20 mg.) having the ultraviolet chromophore of 9,10-dimethylantracene.

Unsuccessful attempts to aromatise 4,5-benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride.

1. Using chloranil. - 4,5-Benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (1.0 g., 0.0046 mole) and chloranil (3.10 g., 0.123 mole) in sulphur-free xylene (45 ml.) were heated under reflux with stirring for 42 hr. On cooling no solid separated, so the xylene was removed to give a residue which was washed well with excess of ether to give starting material (0.6 g.).
2. Using alkaline ferricyanide solution. - A solution of 4,5-benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (1.0 g., 0.0046 mole) in hot aqueous 10% sodium hydroxide solution (30 ml.) was added to a solution of potassium ferricyanide (9.0 g. in 40 ml. water). The resulting solution was then heated under reflux with stirring for six hr. during which time solid separated: this solid proved to be wholly inorganic.

The filtrate was acidified with dilute sulphuric acid to give a gelatinous precipitate which could not be filtered, so the suspension was extracted with chloroform (2 x 100 ml.). Removal of the chloroform from the dried solution gave solid, m.p. 120-130° (0.9 g.).

Recrystallisation from isopropanol gave starting material, m.p. 228° .

3. Using soda-lime. - 4,5-Benzo-1,2,3,6,7,8,8a,10a-octahdropyrene-1,2:7,8-dicarboxylic anhydride (2.0 g., 0.0092 mole) was thoroughly ground with soda-lime (10 g.) and the mixture heated, under nitrogen, for $2\frac{1}{2}$ hr., during which time a yellow solid sublimed (0.59 g.). Recrystallisation from $60^{\circ}/80^{\circ}$ petroleum gave m.p. $178-181^{\circ}$ (0.42 g., 41%). Mixed m.p. with authentic 9,10-dimethylantracene showed no depression.

λ_{\max} (ethanol): 261 m μ , 266, 384, 407.

It gave a 2,4,7-trinitrofluorenone complex prepared by mixing hot saturated equimolar solutions of 9,10-dimethylantracene and 2,4,7-trinitrofluorenone in absolute ethanol; a deep red colour immediately developed, and the red complex precipitated, m.p. $217-218^{\circ}$. Recrystallisation from benzene gave red needles, m.p. $220-2^{\circ}$.

Found: C, 66.4; H, 3.4; N, 8.1%

Required for $C_{29}H_{19}N_3O_7$: C, 66.8; H, 3.7; N, 8.1%

9,10-Dimethyl-9,10-dihydro-anthracene-9,10-endosuccinic anhydride (LXXXV) was prepared by reacting 9,10-dimethylantracene with maleic anhydride in boiling xylene to precipitate the 9,10-endo-derivative, m.p. $312-313^{\circ}$ (sealed tube), recrystallisation from xylene gave colourless rods, m.p. $316-317^{\circ}$ (sealed tube, uncorrected), lit⁷⁵ m.p. 333° .

Found: C, 79.4; H, 5.4%

Calculated for $C_{20}H_{16}O_3$: C, 79.0; H, 5.3%

4. Using a palladium-charcoal-sulphur mixture. - 4,5-Benzo-1,2,3,6,7-8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (0.5 g., 0.0023 mole) was ground with 10% palladium-charcoal (0.3 g.) and sulphur (0.5 g., 0.016 mole) and the mixture heated at 300-310° for 5 min. The cooled product was extracted with boiling dilute sodium hydroxide solution; filtration followed by acidification with dilute sulphuric acid gave only inorganic material. The material insoluble in sodium hydroxide solution was dried and extracted with hot chloroform (2 x 50 ml.). Chloroform was removed and the residue taken up in benzene and the solution passed through an alumina column to give material, containing sulphur, whose ultraviolet spectrum showed the 9,10-dimethylantracene chromophore.

5. Using phosphorus pentoxide. - (a) 4,5-Benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (0.7 g., 0.0032 mole), and phosphorus pentoxide (1.0 g.), were well mixed and the mixture heated under nitrogen for 1 hr. at 160°, during which time a slight darkening was observed. The temperature was then raised to 200-220°; immediately the mixture turned black. On cooling the black residue was extracted with benzene (3 x 30 ml.), to give a bright yellow solution from which benzene was removed to give a black residue (5 mg.) with the ultraviolet chromophore of 4,5-benzopyrene.

Other attempts were made to improve upon the yield of 4,5-benzopyrene, without success, by altering the reaction conditions. However, two other products were obtained as described in the following sections.

b) A mixture of 4,5-benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic anhydride (0.5 g., 0.0023 mole) and phosphorus

pentoxide (0.5 g.), in dry xylene (30 ml.) were heated under reflux with stirring for 2 hrs. After filtration, the filtrate was extracted with dilute sodium hydroxide solution, washed well with water and dried (MgSO_4). Removal of xylene then gave a residue, (30 mg.) with the 9,10-dimethylantracene chromophore.

c) When the mixture of 4,5-benzo-1,2,3,6,7,8,8a,10a-octahydropyrene-1,2:7,8-dicarboxylic dianhydride (0.9 g., 0.0041 mole), and phosphorus pentoxide (2.0 g.), was heated rapidly to and subsequently kept at 240° for 15 min., sublimation took place rapidly to give colourless needles. In addition a small quantity of liquid condensed above the sublimate. On cooling, the liquid solidified to give solid, m.p. 54° (40 mg.), shown to be maleic anhydride. (Mixed m.p. and infrared spectra).

The sublimate (0.15 g.) was resublimed to give needles m.p. $310-312^\circ$ (sealed tube) identical with those of 9,10-dimethyl-9,10-dihydro-anthracene-9,10-endosuccinic anhydride (LXXXV) as shown by infrared spectral comparison.

9,10-Di(chloromethyl)anthracene

This was prepared by Miller's method,⁷⁷ by passing hydrogen chloride through a solution of anthracene and paraformaldehyde in dioxan, and isolated as yellow needles, m.p. $251-255^\circ$ (60%), lit⁷⁷ m.p. $255-260^\circ$.

Tetrabenzo[2,2]paracyclophane (LXXXVII).

This was prepared by Golden's method,⁷¹ in which 9,10-di(chloromethyl)-anthracene was extracted (Soxhlet) into a refluxing solution of sodium

iodide in acetone. The resulting red-brown suspension was filtered hot to give an orange precipitate which was purified by extraction (Soxhlet) with chloroform until the extract was colourless: filtration while hot then gave orange crystals of tetrabenzo[2,2]paracyclophane. Recrystallisation from chloroform gave analytically pure material.

Found: C, 93.6; H, 6.0%

Calculated for $C_{32}H_{24}$: C, 94.0; H, 5.9%

λ_{\max} (chloroform): 258 $m\mu$ ($\log_{10} \epsilon$ 4.86), 282 (4.26), 386 (3.52) and 426 (3.21).

Reaction of tetrabenzo[2,2]paracyclophane with maleic anhydride.

a) In benzene.⁷¹

Tetrabenzo[2,2]paracyclophane (0.5 g.) was extracted (Soxhlet) into a refluxing solution of maleic anhydride (1.0 g.) and the solution was then refluxed for 16 hr. Filtration of the cold solution gave a pale cream solid m.p. 250-260° (0.24 g.), which on extractive crystallisation (Soxhlet) from benzene gave a pale cream solid adduct, m.p. 250-260°.

Found: C, 71.7; H, 4.2%

Calculated for $C_{24}H_{16}O_6$: C, 72.0; H, 4.0%

ν_{\max} (in Nujol): 1830 and 1770 cm^{-1} ($C=O$, anhydride), 748 (four adjacent aromatic C-H).

b) In diethyl phthalate.³⁴

A mixture of tetrabenzo[2,2]paracyclophane (0.5 g.) and maleic anhydride (0.375 g.) in diethyl phthalate (2.5 ml.) was boiled for 5 min.,

during which time the hydrocarbon lost its orange colour to give a pale cream solid; addition of ether then deposited the adduct, m.p. 250-260° (0.51 g.) having an infrared spectrum identical with a sample prepared as described above.

Attempted dehydrogenation of the tetrabenz[2,2]paracyclophane-maleic anhydride adduct.

The above adduct (0.5 g.) was ground with sulphur (0.25 g.) and the mixture was heated at 200-220° under nitrogen for 8 hr. The black product was boiled with an excess of dilute sodium hydroxide solution, filtered while hot and the cooled filtrate acidified with dilute sulphuric acid to give a green gelatinous precipitate (0.10 g.).

λ_{\max} (chloroform): 269 m μ .

4,5-Benzodimaphtho[2',3':1,2][2'',3'':7,8]pyrene-1',4':1'',4''-diquinone. (XXXVIII)

cis-9,10-Dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (1.0 g., 0.0046 mole), and 1,4-naphthoquinone (1.4 g., 0.0097 mole), in nitrobenzene (4 ml.) were heated under reflux for 15 min. during which time solid precipitated. The cooled suspension was filtered, washed with ether and dried to give a burnt orange solid, (1.16 g., 54%), probably a mixture of 4,5-benzodimaphtho[2',3':1,2][2'',3'':7,8]pyrene-1',4':1'',4''-diquinone and its hydrogenated derivatives, as shown by spectroscopic data.

λ_{\max} (dioxan): 270 m μ , 390, 410., i.e. similar to a 9,10-dimethyl-anthracene chromophore.

ν_{\max} (Nujol): 762 cm.⁻¹ (strong) and 707 (weak).

This intermediate hydrogenated mixture (1.0 g.), in nitrobenzene (20 ml.) was heated under reflux for 5 hr. On cooling solid precipitated, which was washed well with ether, dried to give 4,5-benzodinanaphtho[2',3':1,2][2'',3'':7,8]pyrene-1',4':1'',4''-diquinone, m.p. > 360° (0.86 g., 46%). This product was sufficiently pure for subsequent reactions.

A sample for analysis was purified in the following way: on sublimation, at 300-320°/0.1 mm, tarry material sublimed out leaving red solid. At 420-440°/0.1 mm the red solid sublimed, showing some contamination with decomposition products. The sublimed material was then extracted (Soxhlet) into dry benzene for 22 hrs. and the extract filtered to give red needles, m.p. > 360°. I.R. identical with unpurified material.

Found: C, 84.1; H, 3.2%

Required for C₂₆H₁₆O₄: C, 84.4; H, 3.2%

λ_{\max} (in chloroform): 285 m μ (log₁₀ ϵ 4.78), 379 (4.46), 448 (4.36) and 610 (4.01).

$\lambda_{\text{shoulder}}$: 311 m μ (log₁₀ ϵ 4.57), and 338 (4.46)

ν_{\max} (KBr disc): 1670 cm.⁻¹ (C=O, quinone), 1590 (C=C, aromatic), 1290 and 1280 (C-O, quinone), 843 (single aromatic C-H), 808, 803, 783, 762 (four adjacent aromatic C-H bonds, in ring not next to the quinone rings), 726, and 707 (four adjacent aromatic C-H bonds, in the terminal rings adjacent to the quinone rings).

4,5-Benzodinanaphtho[2',3':1,2][2'',3'':7,8]pyrene (XC).

a) To a finely ground mixture of 4,5-benzodinanaphtho[2',3':1,2]-

[2",3":7,8]pyrene-1',4':1",4"-diquinone (1.5 g.), with zinc dust (3.0 g.), and sodium chloride (2.0 g.), was added moist zinc chloride (3.5 g.), and the mixture melted at 200-210°. The melt was then stirred continuously whilst the temperature was raised to, and subsequently kept, at 300-310° for 20 min. The cooled melt was then treated with dilute hydrochloric acid, the insoluble residue was washed well with dilute ammonia solution and then well with water. The dried solid (1.6 g.), was extracted (Soxhlet) into toluene (700 ml.) for 66 hrs. to give a green fluorescent solution. The volume of this solution was reduced by half under reduced pressure, and the concentrated solution diluted with 60°/80° petroleum in the ratio 70% toluene, 30% petroleum and was percolated through an alumina column (150 g., 35 cm. x 2.5 cm.) followed by a mixture of benzene 70%, petroleum 30%. Evaporation of solvent under reduced pressure gave 4,5-benzodiphenyl[2',3':1,2]-[2",3":7,8]pyrene (0.12 g., 9%).

λ_{\max} (in chloroform): 262 m μ ($\log_{10} \epsilon$ 4.72), 301 (4.89), 321 (4.74), 351 (4.42), 374 (4.48), 390 (4.26), 415 (4.47) and 444 (4.54).

$\lambda_{\text{shoulder}}$: 290 ($\log_{10} \epsilon$ 4.72).

Clar⁷⁸ gives

λ_{\max} (in benzene): 301 m μ ($\log_{10} \epsilon$ 5.10), 318 (4.74).

(in 1,2,4-trichlorobenzene): 376 (4.71), 390 (4.40), 415 (4.65), 443 (4.87), 493 (3.01).

ν_{\max} (KBr Disc): 883 and 870 cm.⁻¹ (singlet aromatic C-H), 807 (two adjacent aromatic C-H), 758, 732 (four adjacent C-H).

The hydrocarbon gives a blue solution in concentrated sulphuric acid.

b) To a stirred suspension of 4,5-benzodinanaphtho[2',3':1,2]-[2'',3'':7,8]pyrene-1',4':1'',4''-diquinone (4.0 g.), and zinc dust (10 g.) in refluxing pyridine (100 ml.) was added during 2 hrs. 80% acetic acid (100 ml.). Heating was continued for a further 6 hrs. On cooling the suspension was poured into a large excess of water to give a solid; the dried solid was extracted (Soxhlet) with boiling xylene. Percolation through an alumina column gave 4,5-benzodinanaphtho[2',3':1,2]-[2'',3'':7,8]pyrene (60 mg., 2%).

Attempted preparation of derivatives of 4,5-benzodinanaphtho[2',3':1,2]-[2'',3'':7,8]pyrene (XC).

a) 2,4,7-Trinitrofluorenone derivative.

A solution of 4,5-benzodinanaphtho[2',3':1,2]-[2'',3'':7,8]pyrene (20 mg.) in boiling xylene (20 ml.) was filtered into a hot solution of 2,4,7-trinitrofluorenone (14 mg.) in xylene (2 ml.). The resulting solution did not darken immediately and on cooling deposited crystals of the hydrocarbon.

b) Maleic anhydride derivative (XCII)

1. 4,5-Benzodinanaphtho[2',3':1,2]-[2'',3'':7,8]pyrene (50 mg.) was heated in boiling xylene (30 ml.) for 1 hr. until all had dissolved, and maleic anhydride (22 mg., 2.05 eq.), was added, dissolving immediately. The resulting solution was heated under reflux for 2 hr.; on cooling, the hydrocarbon precipitated.

2. A mixture of 4,5-benzodinanaphtho[2',3':1,2]-[2'',3'':7,8]pyrene (47 mg.) and maleic anhydride (2.0 g.), was heated under reflux for

2 hr. At the end of this time, the hot reaction mixture was poured into hot xylene (30 ml.) and the resulting suspension filtered. The solid was washed with hot xylene and finally with much ether, and dried to give a green solid (54 mg., 80%).

λ_{max} (chloroform): 282 m μ , 294, 337, 353.

cf. the 1,2:7,8-substituted 4,5-benzopyrene chromophore.

Attempted recrystallisation (e.g. from acetic anhydride) led to recovery of the maleic anhydride and hydrocarbon.

Attempted preparation of dinaphtho[2',3':1,2][2'',3'':5,6]coronene-1',4':1'',4''-diquinone-7,8:11,12-dicarboxylic anhydride (XCIII).

A mixture of 4,5-benzodinaphtho[2',3':1,2][2'',3'':7,8]pyrene-1',4':1'',4''-diquinone (1.0 g., 0.0046 mole) and maleic anhydride (25.0 g.), was heated under reflux for 15 min. Chloranil (3.5 g., 0.014 mole) was then added to the mixture and heating was continued for a further 2½ hrs. The hot reaction mixture was then poured into hot xylene and the precipitate filtered and washed repeatedly with hot xylene, followed by much ether to give 1.36 g., (99%).

λ_{max} (Nujol): 1840 and 1770 cm.⁻¹ (C=O, anhydride), 1667 (C=O, quinone), 1608 and 1588 (C=C, aromatic), 841, 770, 758, 722, 707 (four adjacent aromatic C-H, in ring next to quinone).

Sublimation at 380°/0.1 mm. gave the starting quinone, as did recrystallisation from 1,2,4-trichlorobenzene. When the reaction product was boiled with sodium hydroxide solution, 'decomposition' into the starting materials also occurred.

1,2:4,5:7,8-Tribenzopyrene-1',4':1'',4''-diquinone (XCIVa).

a) cis-9,10-Dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (1.0 g., 0.0046 mole), benzoquinone (6.0 g., 0.055 mole), quinol (0.001 g.), in acetic anhydride (7 ml.) was heated under reflux for 4 hr. On cooling, the solid was washed well with ether to give dark orange solid, m.p. $> 350^{\circ}$ (0.96 g., 56%). Recrystallisation from nitrobenzene gave orange needles m.p. $> 350^{\circ}$.

Found: C, 81.6; H, 3.0%

Required for $C_{28}H_{12}O_4$: C, 81.55; H, 2.9%

ν_{\max} (Nujol): 1670 cm^{-1} (C=O stretch, quinone), 1602 (C=C, aromatic), 1285 (C-O, quinone), 1105, 848 (two adjacent aromatic C-H), and 758 (four adjacent aromatic C-H).

b) The same product was also obtained (43% yield) when cis-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (1.0 g.) and benzoquinone (6.0 g.), were heated under reflux in nitrobenzene (30 ml.) for 4 hr.

Attempted preparation of 1,2:4,5:8,9-tribenzopyrene by reduction of 1,2:4,5:8,9-tribenzopyrene-1',4':1'',4''-diquinone.

a) To a finely ground mixture of 1,2:4,5:8,9-tribenzopyrene-1',4':1'',4''-diquinone (1.0 g.), with zinc dust (2.0 g.), and sodium chloride (2.0 g.), was added moist zinc chloride (3.5 g.), and the mixture melted at $200-210^{\circ}$. The melt was then stirred continuously whilst the temperature was raised to and subsequently kept at $300-310^{\circ}$ for 20 min. The cooled melt was then treated with dilute hydrochloric acid, the insoluble residue was washed well with dilute ammonia solution and then

with water. The dried solid (0.84 g.) was extracted (Soxhlet) into boiling xylene, the solution diluted with 60°/80° petroleum in 1:1 ratio and then percolated through an alumina column (100 g.) to give unchanged diquinone.

Increasing the reaction time failed to give 1,2:4,5:8,9-tribenzopyrene.

b) 1,2:4,5:8,9-Tribenzopyrene-1',4':1'',4''-diquinone (1.0 g.), was extracted (Soxhlet) into a solution of lithium aluminium hydride (2.0 g.), in boiling tetrahydrofuran (300 ml.), for 48 hrs., leaving undissolved quinone in the Soxhlet thimble (0.64 g.). Excess of lithium aluminium hydride was decomposed with water, followed by dilute hydrochloric acid (100 ml.). Tetrahydrofuran was removed by distillation leaving dark solid and an aqueous solution; these were extracted with benzene, until the aqueous solution lost its colour, and the dried benzene solution evaporated to give solid (180 mg.). Attempted recrystallisation from xylene showed that 130 mg. was insoluble; tests showed that this material was inorganic, and the material soluble in xylene was found to be unchanged quinone. The material insoluble in benzene gave more unchanged quinone (0.23 g.).

c) 1,2:4,5:8,9-Tribenzopyrene-1',4':1'',4''-diquinone (0.57 g.) was added in small portions over 30 min. to a stirred solution of lithium aluminium hydride (2.0 g.) in tetrahydrofuran (150 ml.). The resulting suspension was heated with stirring under reflux for 8 hrs., after which dioxan (75 ml.) was added, and heating continued for a further 20 hrs. On cooling, excess lithium aluminium hydride was decomposed

with water; the addition of water also precipitated much solid, which was filtered off and treated with dilute hydrochloric acid; most of the solid dissolved, leaving unchanged starting quinone (0.47 g.).

The original filtrate was acidified with dilute hydrochloric acid precipitating a solid (50 mg.) shown to be unchanged quinone. Evaporation of this acidified filtrate also gave unchanged quinone.

d) A mixture of aluminium turnings (2.0 g.), mercuric chloride (0.05 g.), dry carbon tetrachloride (1.5 ml.), and dry cyclohexanol (40 ml.) was cautiously heated to give initially a vigorous exothermic reaction which required cooling. After this initial vigorous reaction, the mixture was heated with stirring until all the aluminium had dissolved to form aluminium cyclohexanolate. To the cooled reaction mixture was added 1,2:4,5:8,9-tribenzopyrene-1',4':1'',4''-diquinone (1.0 g.), and the suspension heated under reflux with stirring for 24 hr. The cooled reaction mixture was treated with glacial acetic acid (40 ml.), filtered and the solid treated with concentrated hydrochloric acid (40 ml.) and the remaining solid washed well with water, and dried to give the quinone (0.6 g.).

Reaction of 9,10-anthraquinodimethane with chloranil

a) In acetic anhydride

A mixture of trans-9,10-dimethyl-9,10-dihydro-9,10-dihydroxy-anthracene (1.0 g., 0.0046 mole), and chloranil (3.0 g., 0.012 mole), in acetic anhydride (20 ml.) was heated under reflux for 2 hrs. On cooling, a green solid precipitated, (2.81 g.); washing with much ether gave

2.15 g. Recrystallisation from glacial acetic acid gave green needles m.p. 242° (sub.) (0.90 g.). Sublimation at $170^{\circ}/0.2$ mm. gave colourless rods, of 1,4-diacetoxy-2,3,5,6-tetrachlorobenzene, m.p. 245° (sub.) lit.⁸³ m.p. 245° (sub.).

Found: C, 36.2; H, 1.8%

Calculated for $C_{10}H_6Cl_4O_4$: C, 36.2; H, 1.8%

ν_{\max} (KBr disc): 1772 cm.^{-1} (C=O, ester), 1414, 1387, 1372, 1187, 1153, 1015, 928, 839, 723.

The n.m.r. spectrum (CF_3COOH) shows a singlet peak at 7.97τ (CH_3COO).

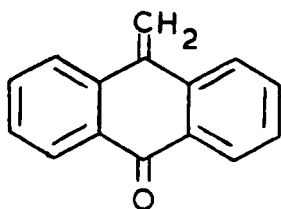
b) In nitrobenzene

A mixture of cis-9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene (1.0 g., 0.0046 mole) and chloranil (2.0 g., 0.080 mole) in nitrobenzene (10 ml.) was heated under reflux for 16 hr. until evolution of HCl ceased. Cooling followed by filtration and gave a shiny black solid, m.p. $> 350^{\circ}$ (1.43 g.) which showed a very indistinct infrared spectrum. This solid was insoluble in concentrated sulphuric acid, and organic solvents. Extraction (Soxhlet) with boiling 1,2,4-trichlorobenzene until the extract was colourless (after 24 hrs.) gave a solution which on dilution with $60^{\circ}/80^{\circ}$ petroleum gave a black solid also with a very indistinct spectrum.

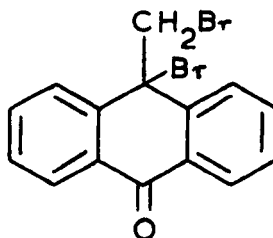
CHAPTER IV

Studies on 9-Methyleneanthrone

9-Methyleneanthrone is the sole example of a stable quinonemethide having an unsubstituted methylene group.⁸⁴ This stability is due to the fact that in methyleneanthrone both the methylene and carbonyl functions are situated on the central anthracene ring, preventing these groups from reacting as in ortho-quinonemethides. The comparative isolation of the ethylenic bond from the carbonyl group in this molecule is shown by its typically olefinic behaviour in adding a molecule of bromine to give the dibromide (XCV).



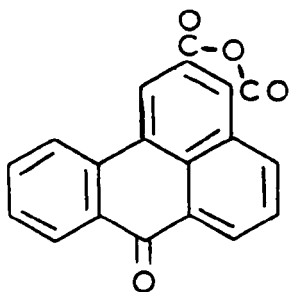
LXXVI



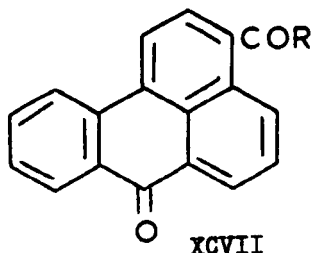
XCV

As a result 1,4-addition occurs when dienophiles react with the diene system formed from the ethylenic bond and one of the Kekulé double bonds of an adjacent benzene ring to give a benzanthrone derivative.

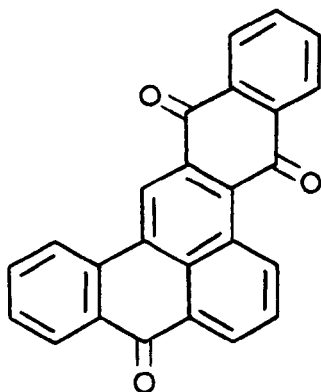
The reaction of methyleneanthrone with ethylenic dienophiles has been surveyed in the literature;^{72,85,86} when these reactions take place in oxidising solvents, the products are fully aromatic, e.g. the reaction with maleic anhydride in nitrobenzene (XCVI). With acetylenic compounds of the type $\text{HC}\equiv\text{CCOR}$, similar behaviour is observed⁸⁷ to give compounds of the type (XCVII). Methyleneanthrone also reacts with quinones,^{85,86} e.g. with 1,4-naphthoquinone (XCVIII) is obtained.



XCVI



XCVII



XCVIII

The intention of the present work was to react methyleneanthrone with diethyl azodicarboxylate to obtain a new ring system; and also with

dimethyl acetylenedicarboxylate, and to investigate by means of n.m.r. the structure of the previously-known reaction product of methyleneanthrone with two molecules of maleic anhydride.

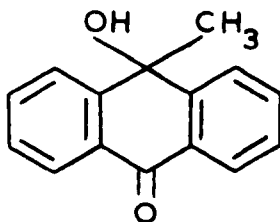
Anthrone with formaldehyde in the presence of piperidine yields methyleneanthrone. Two variants of procedure are given in the literature. Initially the method described by Clar⁸⁵ was followed (in which a suspension of anthrone in boiling ethanol containing formaldehyde is treated with a little piperidine until all the anthrone has dissolved, to give methyleneanthrone on cooling); this method worked well occasionally, but usually a complex product not containing methyleneanthrone was obtained. Clar records that the method of Barnett and Matthews⁸⁸ sometimes gave yellow resin; on the one occasion that this method (which involved the addition of formaldehyde solution to a suspension of anthrone in boiling ethanol containing piperidine) was used it gave methyleneanthrone satisfactorily, although others preparing methyleneanthrone in the same way have run into difficulties. In this context it is of significance that when an attempt was made to react methyleneanthrone with malononitrile in ethanol containing piperidine, 9,10-anthraquinone was obtained, presumably by peroxide oxidation of methyleneanthrone.

The n.m.r. spectrum of methyleneanthrone in CDCl_3 is as expected, showing a singlet peak at 3.67τ due to the exomethylene group and multiplet peaks between 1.51 and 2.67τ which fall into three distinct groups. The first between 1.51 and 1.76τ is due to the two protons, H-a immediately adjacent to the carbonyl group;

of. anthrone 1.58 - 1.77 τ ; the second between 1.86 and 2.11 τ is due to the two H- α , adjacent to the exomethylene group; whereas the third between 2.11 and 2.71 τ is due to the four H- β protons.

The capricious preparation of methyleneanthrone led to investigation of the use of 10-methyl-10-hydroxyanthrone (XCIX) as a suitable substitute capable of generating methyleneanthrone in situ; as 5,6-dimethyl-5,6-dihydro-5,6-dihydroxychrysene and 9,10-dimethyl-9,10-dihydro-9,10-dihydroxyanthracene were used to generate 5,6-chrysaquinodimethane and 9,10-anthraquinodimethane.

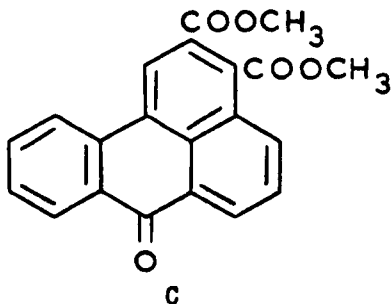
The reaction of methylmagnesium iodide with a four-fold excess of 9,10-anthraquinone gave 10-methyl-10-hydroxyanthrone⁸⁹ (XCIX) whose n.m.r. spectrum showed a singlet peak at 8.30 τ (methyl), a peak at 6.68 τ (hydroxyl) and multiplet peaks between 1.87 and 2.58 τ due to the aromatic protons, the carbonyl group causing less chemical shift on the adjacent aromatic protons than in the case of methyleneanthrone and anthrone.



XCIX

A report⁹⁰ that treatment of 10-methyl-10-hydroxyanthrone in boiling acetic acid containing oxalic acid gave methyleneanthrone in unspecified yield was investigated but it was found that a crude product containing a small proportion only of methyleneanthrone was obtained.

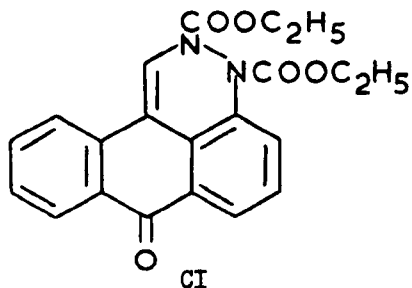
With dimethyl acetylenedicarboxylate in boiling acetic anhydride, 10-methyl-10-hydroxyanthrone gave dimethyl benzy[de]anthrone-2,3-dicarboxylate (C) as yellow needles in 39% yield, a 33% yield being obtained when methyleneanthrone was used in boiling acetic acid, demonstrating that 10-methyl-10-hydroxyanthrone is a suitable substitute for methyleneanthrone in such reactions.



The fact that other acetylenic dienophiles give the fully aromatic system has already been noted by Irving and Johnson⁸⁷ and

presumably dehydrogenation of the initial adduct occurs by abstraction of hydrogen by excess of the acetylenic dienophile. Evidence for the structure of (C) was conclusive, being supported by analysis and ultraviolet and n.m.r. spectroscopy. The ultraviolet spectrum of (C) is very similar to that of benz[de]anthrone-2,3-carboxylic anhydride (XCVIII) (see later).

The n.m.r. spectrum of interest showing besides the expected singlets at 5.89 and 5.93 τ (two methyl ester groups), a complex pattern in the aromatic region. Two H- α 3 protons can be seen, one unsplit at 1.22 τ , due to the proton at C1, this singlet ester is only shifted downfield by 0.11 τ from the normal H- α 3 position, as compared with the downfield shift of 0.73 τ for the corresponding H- α 3 proton in methyl phenanthrene-3-carboxylate.⁶¹ The other H- α 3 proton at C11 is seen as a subsplit doublet, centre 1.25 τ . The rest of the spectrum is seen as two multiplets due to two sets of three protons each, one multiplet (2.05 - 2.50 τ) due to the 3 H- β protons at C5, 9 and 10, while the other multiplet (1.50 - 1.90 τ) is due to the protons at C4, 6 and 8. The H- α and H- β protons at C5 and C6 being shifted downfield from their normal positions by the group at C3, this shift diminishing with distance, while the protons at C6 and C8 fall in the same region as the corresponding protons in methyleneanthrone.

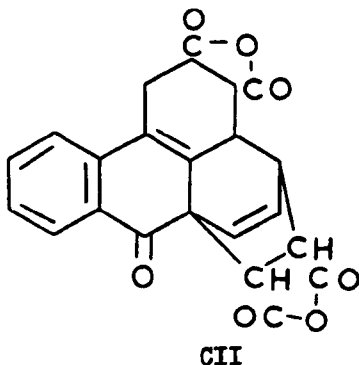


The reaction of 10-methyl-10-hydroxyanthrone with diethyl azodicarboxylate in boiling acetic anhydride gave diethyl-2,3-dihydro-7H-dibenzo[deh]phthalaz-7-one-2,3-dicarboxylate (CI) as yellow needles, m.p. 180-182°, in 29% yield. Infrared spectroscopy established the absence of -NH- groups and the ultraviolet spectrum is similar to that of dimethyl benz[de]anthrone-2,3-dicarboxylate (C) suggesting that the structure is (CI).

The n.m.r. spectrum in CDCl₃, showed a quartet, centre 8.65 τ ($J = 6$ c.p.s.) due to the two ester methyl groups having a difference in chemical shift equal to the coupling constants. A quintet, centre 5.64 τ was also shown, due to the two ester methylene groups again having a difference in chemical shift equal to the coupling constants. In the aromatic region is shown a multiplet between 1.45 and 1.75 τ due to the protons immediately adjacent to the carboxyl group on which is superimposed a singlet at 1.75 τ due to the proton

at C1, and a multiplet between 2.03 and 2.60 τ due to the remaining protons (1 H- α + 4 H- β). As can be seen, there is a considerable downfield shift for the proton at C1 as compared with the vinylic protons in methyleneanthrone (at 3.67 τ), for which simple parallels are not apparently available.

Hydrolysis of the ester (CI) under mild conditions followed by acidification gave material not containing nitrogen, suggesting a complete breakup of the heterocyclic ring system. The presence of a red solid soluble in water, before acidification, does suggest that the destruction of the heterocyclic system occurs during acidification.



When Clar heated methyleneanthrone with maleic anhydride in acetic acid he claimed to obtain a di-adduct, to which he assigned structure (CII). When, in the present work, this reaction was repeated under Clar's conditions, yellow needles of benz[de]anthrone-2,3-carboxylic anhydride (XCVI) precipitated in 4% yield. Treatment

of the filtrate with excess of ether gave an impure material which on recrystallisation gave a very small yield (3%) of product having the same melting point as Clar's adduct. Unfortunately this adduct was not sufficiently soluble in suitable solvents for its structure to be examined by means of n.m.r. spectroscopy. When 10-methyl-10-hydroxy-anthrone was used, a larger yield of the mono-adduct¹ was obtained, of improved m.p. (323°) (Clar gives m.p. 310°), but no di-adduct was isolated.

EXPERIMENTAL

Anthrone

This was prepared by the method of Meyer⁹¹ by the reduction of 9,10-anthraquinone with tin and hydrochloric acid, giving anthrone, m.p. 154° (lit⁹¹ m.p. 154-155°) (75%).

The n.m.r. spectrum in (CDCl₃) showed a singlet at 5.7 τ (methylene group), a multiplet 2.40 - 2.70 τ (2 H-α + 4 H-β) and a multiplet, 1.55 - 1.70 τ (2 H-α, adjacent to the carbonyl group).

9-Methyleneanthrone (LXXVI)

This compound was prepared as follows:

- a) By the method of Barnett and Matthews⁸⁸ in which formaldehyde was added to a suspension of anthrone in refluxing methanol containing piperidine. The anthrone gradually dissolved during 5 min.; after a further 10 min. heating colourless needles of methyleneanthrone separated.
- b) By the method of Clar⁸⁶ in which piperidine was added to a refluxing solution of anthrone and formaldehyde in ethanol. After heating under reflux for 20 min. crystals of methyleneanthrone began to separate, m.p. 140-3°. Repeated recrystallisation from ethanol gave rods, m.p. 145-7°. lit⁸⁶ m.p. 148°.

Found: C, 87.3; H, 4.9%

Calculated for $C_{15}H_{10}O$: C, 87.4; H, 4.9%

λ_{\max} (ethanol): 234 $m\mu$ ($\log_{10} \epsilon$ 4.59), 262 (4.18), 276 (4.20), 352 (3.76).

ν_{\max} (Nujol): 1660 cm^{-1} (C=O, aryl ketone), 1600 (C=C, aromatic), 1315 (C-O, ketone), 932, 923 (C=CH₂), 782 and 676.

The n.m.r. spectrum (CDCl₃) showed a singlet 3.67 τ (vinylic protons), a multiplet between 2.11 and 2.71 τ (due to the H- β protons at C2, 3, 6 and 7), a multiplet between 1.86 and 2.11 τ (due to the two protons at C1 and 8, immediately adjacent to the exo-methylene group), and a multiplet between 1.51 and 1.76 τ (due to the two protons at C4, 5 immediately adjacent to the carbonyl group).

On several occasions methyleneanthrone was not obtained from the above reaction, instead a resin was obtained.

10-Methyl-10-hydroxy-9-anthrone (XCIX)

This compound was prepared by a modification of the method of Julian et al.⁸⁹

A solution containing 0.25 mole of methylmagnesium iodide in ether (150 ml.) was added dropwise into a stirred suspension of 9,10-anthraquinone (100 g., 0.123 mole) in benzene (375 ml.) during 2 hrs. The reaction mixture was poured onto ice and ammonium chloride, and the product left overnight (during which time all the ether evaporated). The resulting suspension was filtered, and the organic layer separated and dried (MgSO₄). The residual solid was repeatedly extracted with ether and these extracts dried. Solvent was removed from the dried

organic extracts to give a solid which, recrystallised from diethyl ether 60°/80° petroleum mixture, gave 10-methyl-10-hydroxyanthrone, m.p. 152-3° (lit m.p. ⁸⁹ 154°) (23 g., 51%).

Reaction of 10-methyl-10-hydroxyanthrone with oxalic acid.

This was carried out by the method of Heymann and Trowbridge⁹⁰ in which a solution of oxalic acid (2 g.) and 10-methyl-10-hydroxyanthrone (1 g.), in glacial acetic acid (10 ml.) was boiled for 30 seconds and then poured into excess cold water. The resulting yellow solid (0.90 g.) was shown by its infrared spectrum to be a mixture containing only a small proportion of methyleneanthrone.

Dimethylbenz[de]anthrone-2,3-dicarboxylate (C)

a) A mixture of methyleneanthrone (1.0 g., 0.0048 mole), and dimethyl acetylenedicarboxylate (1.0 g., 0.0070 mole), in acetic acid (20 ml.) were heated under reflux for 1½ hr. On cooling a yellow solid precipitated, m.p. 210-213° (0.55 g., 33%). Recrystallisation from ethanol gave yellow microneedles, m.p. 215-216°.

Found: C, 72.5; H, 4.1%

Required for C₂₁H₁₄O₅: C, 72.8; H, 4.0%

λ_{\max} (ethanol solution): 240 m μ (log₁₀ ϵ 4.62), 273 (4.40), 286 (4.13), 311 (3.75), 394 (4.05).

ν_{\max} (Nujol): 1738 and 1710 cm.⁻¹ (C=O, ester groups), 1665 (C=O, aryl ketone), 1270 (C-O), 785, 773, 765, 747 and 697.

The n.m.r. spectrum (in CDCl₃) showed singlets at 5.89 and

5.93 τ (ester methyl groups), a multiplet between 2.05 - 2.50 τ (3 H- β at C5, 9, 10), a multiplet, 1.50 - 1.90 τ (protons at C4, 6, 8), a subsplit doublet, centre 1.25 τ (H- α 3, at C11), and a singlet at 1.22 τ (H- α 3 at C1).

b) 10-Methyl-10-hydroxy-9-anthrone (1.0 g., 0.0045 mole), and dimethyl acetylene dicarboxylate (1.05 g., 0.0074 mole), in acetic anhydride (10 ml.) were heated under reflux for 5 hr. On cooling a yellow solid precipitated m.p. 213-215° (0.60 g., 39%); spectroscopic data identical with that given above.

Diethyl-2,3-dihydro-7H-dibenzo[deh]phthalaz-7-one-2,3-dicarboxylate (CI).

A mixture of 10-methyl-10-hydroxy-9-anthrone (2.0 g., 0.0089 mole), and diethyl azo-dicarboxylate (1.9 g., 0.011 mole), in acetic anhydride (10 ml.) was heated under reflux for 2 hr. On cooling, no solid precipitated, so the acetic anhydride was removed under reduced pressure to give a gum-like residue. This on trituration with ether gave solid m.p. 165-175° (1.55 g.). Recrystallisation from ethanol gave m.p. 180-2° (1.0 g., 29%).

Found: C, 66.8; H, 4.9; N, 7.2%

Required for $C_{21}H_{18}N_2O_5$: C, 66.7; H, 4.8; N, 7.4%

λ_{\max} (ethanol): 236 $m\mu$ ($\log_{10} \epsilon$ 4.54), 287 (4.06), 316 (4.03) 398 (4.04).

ν_{\max} (Nujol): 1750 and 1730 cm^{-1} (C=O, ester), 1646 (C=O, aryl ketone), 1598 (C=C, aromatic), 758 (three adjacent aromatic C-H), 745 and 697 (four adjacent aromatic C-H).

The n.m.r. spectrum (CDCl_3) showed a quartet, centre 8.65 τ ($J = 6$ c.p.s.) (two ester methyl groups), a quintet, centre 5.64 τ ($J = 6$ c.p.s.), a multiplet between 2.03 and 2.60 τ (1 H- α + 4 H- β), a singlet at 1.75 τ (proton at C1), and a multiplet between 1.45 and 1.75 τ (two protons immediately adjacent to the carbonyl group).

Hydrolysis of diethyl-2,3-dihydro-7H-dibenzo[deh]phthaz-7-one-2,3-dicarboxylate (CI).

The ester (1.0 g.) was added to 2 M sodium hydroxide solution in ethanol (prepared by the addition of water to ethanolic sodium ethoxide (40 ml.) at 25°). A deep red colouration developed immediately as the ester dissolved; the solution was left under nitrogen at 25° for 22 hr. At the end of this time a red almost gum-like solid was observed; attempts to filter this solid failed, so water (40 ml.) was added to dissolve all the red solid giving a deep red solution. Acidification using dilute hydrochloric acid, with ice cooling, precipitated a solid (0.70 g.), but analysis of this indicated that it did not contain nitrogen.

1,2,3,3a,4,6a-Hexahydrobenz[de]anthrone-2,3-carboxylic anhydride-4,6a-endosuccinic anhydride (CII).

(Reaction of methyleneanthrone with excess of maleic anhydride.)

A mixture of methyleneanthrone (1.0 g., 0.0048 mole) and maleic anhydride (1.0 g., 0.011 mole) in glacial acetic acid (3 ml.)

was heated under reflux for 30 min. On cooling, yellow needles of benz[de]anthrone-2,3-carboxylic anhydride m.p. 310° (lit⁸⁶ m.p. 310°) (40 mg., 3%).

The filtrate was treated with excess ether and gave a product (0.42 g.), melting from 100° upwards; the infrared spectrum showed that this material was a gross mixture. Recrystallisation from an acetic acid-xylene mixture gave solid, m.p. 196° (lit m.p. 192°) (70 mg., 4%) of the diadduct.

This compound was not soluble in CS_2 or CDCl_3 and not sufficiently soluble in CF_3COOH to give an n.m.r. spectrum.

Benz[de]anthrone-2,3-carboxylic anhydride (XCVI).

(Reaction of 10-methyl-10-hydroxyanthrone with excess of maleic anhydride.)

A mixture of 10-methyl-10-hydroxyanthrone (1.0 g., 0.0045 mole), and maleic anhydride (1.0 g., 0.011 mole), in acetic anhydride (10 ml.) was heated under reflux for 40 min. On cooling yellow needles of benz[de]anthrone-2,3-carboxylic anhydride deposited, m.p. $323-4^{\circ}$ (lit⁸⁶ m.p. 310°) (0.13 g., 9%).

Found: C, 76.15; H, 2.65%

Calculated for $\text{C}_{19}\text{H}_8\text{O}_4$: C, 76.0; H, 2.7%

λ_{max} (in ethanol): 240 m μ ($\log_{10} \epsilon$ 4.53), 273 (4.40) and 400 (4.04).

ν_{max} (Nujol): 1845 and 1775 cm^{-1} (C=O, anhydride) 1663 (C=O, aryl ketone), 898 (anhydride), 791 (three adjacent aromatic C-H), and 747 (four adjacent aromatic C-H).

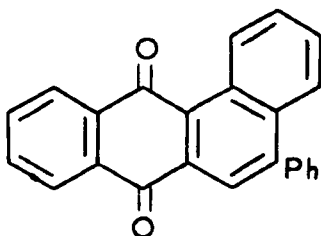
Attempted preparation of 9-dicyano-9,10-anthraquinodimethane.

To a solution of methyleneanthrone (0.5 g., 0.0024 mole) in boiling ethanol (75 ml.) was added malononitrile (0.48 g., 0.0072 mole) and piperidine (3 drops). The resulting solution was then heated under reflux for 1 hr., and on cooling precipitated 9,10-anthraquinone (0.25 g.) as shown by spectral comparison with authentic material.

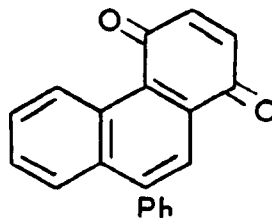
To a solution of methyleneanthrone (0.25 g.) in boiling ethanol (35 ml.) was added piperidine (2 drops) and the solution heated under reflux for 1 hr. On cooling 9,10-anthraquinone (0.03 g.) separated; on condensation of the filtrate to 10 ml. a mixture of methyleneanthrone and 9,10-anthraquinone separated.

CHAPTER V

Diels-Alder Reactions of 1,1-Diphenylethylene

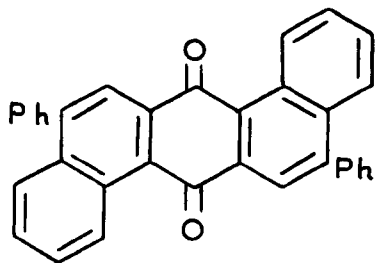


CII

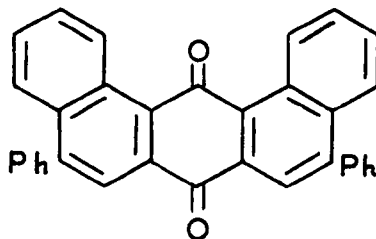


CIII

It has been reported⁹² that when a mixture of 1,1-diphenylethylene and *p*-benzoquinone is heated, brisk reaction occurs to give quinhydrone, no other product being isolated. As 1,4-naphthoquinone reacts with 1,1-diphenylethylene to give 5-phenyl-1,2-benzo-9,10-anthraquinone (CII) in a 20% yield,⁹³ it was decided to investigate the reaction of 1,1-diphenylethylene with benzoquinone in boiling nitrobenzene in the hope of obtaining 9-phenyl-1,4-phenanthraquinone (CIII).



CIV

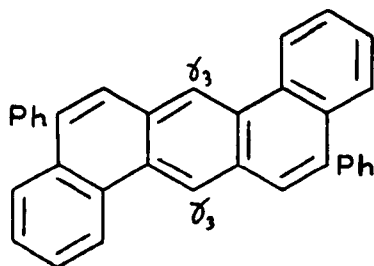


CV

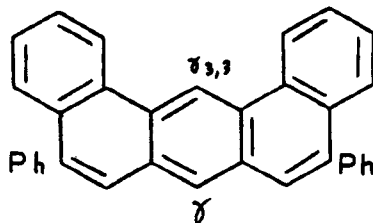
A mixture of 1,1-diphenylethylene with a three-molar excess of benzoquinone was heated in nitrobenzene for 5 hr. to give instead of the expected mono-adduct, a di-adduct $C_{34}H_{20}O_2$ in 19% yield which could be one of two dibenzanthraquinones (CIV) or (CV). Unfortunately, spectroscopic methods were not of much use in determining which structure the di-adduct possessed, as e.g. although the infrared spectrum was extremely clear-cut and simple, showing frequencies at 701 and 768 $cm.^{-1}$ for five and four adjacent aromatic C-H's respectively and at 843 $cm.^{-1}$ for singlet aromatic protons, these are applicable for both structures. Likewise with the ultraviolet chromophore as the major peaks in the chromophores of 1,2:5,6 and 1,2:7,8-dibenzanthracene differ by only 5 $m\mu$.

The proportions of 1,1-diphenylethylene and benzoquinone chosen may seem rather peculiar to give a diadduct but in fact these proportions were subsequently found to give the best practical yield of pure di-adduct. Decreasing the proportion of benzoquinone led to a diminished yield of the di-adduct whereas increasing the proportion

of benzoquinone gave impure product which could not be easily purified. Other solvents were also tried; in ethanol an impure product was obtained as was the case in dimethylformamide; no reaction occurred in toluene.



CVI



CVII

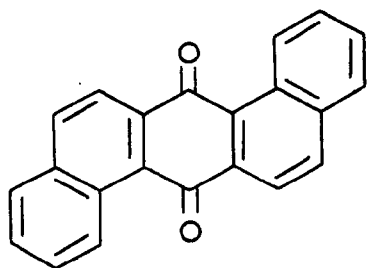
Reduction of the di-adduct using aluminium cyclohexanolate⁵⁵ gave, in 34% yield, a colourless crystalline hydrocarbon, m.p. 283°, which could have one of the two structures (CVI) or (CVII). Use of n.m.r. spectroscopy established that the hydrocarbon is in fact 1,2:5,6-dibenzo-3,7-diphenylanthracene (CVI) hence establishing that the di-adduct is 1,2:5,6-dibenzo-3,7-diphenyl-9,10-anthraquinone (CIV). The key factor is that the n.m.r. spectrum in CDCl₃ showed a singlet peak due to two H-γ protons at 0.93 τ (see Chapter 2, p. 27), the corresponding protons in 1,2:5,6-dibenzanthracene are reported as giving singlet peaks at either 0.87 τ⁵⁴ or 0.90 τ⁴⁵. If the structure had been

of the 1,2:7,8-dibenzanthracene type (CVII) this would have shown singlet peaks due to one H- γ _{3,3} proton and one H- γ proton which in 1,2:7,8-dibenzanthracene are positioned at 0.03 τ and 1.75 τ respectively.⁵⁴ The rest of the n.m.r. spectrum is consistent with structure (CVI) and showed multiple peaks centred at 1.17 τ due to two H- α ₃ protons, a singlet peak at 2.20 due to two H- α β protons, a singlet peak at 2.50 τ (ten H ϕ protons) and multiple peaks between 1.93 and 2.53 τ (2H- ~~α~~ and 4 H- β protons).

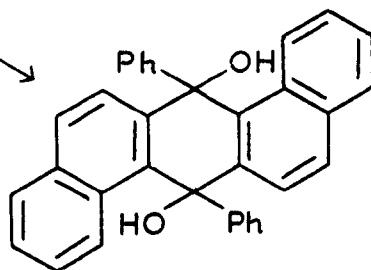
A red crystalline 2,4,7-trinitrofluorenone derivative of 1,2:5,6-dibenz-3,7-diphenylanthracene was prepared, m.p. 264°.

Cook reported that 1,2:5,6-dibenzanthracene reacts with difficulty to give a 9,10-endo-maleic anhydride adduct.⁹⁴ In view of our own experience that the dimethyl acetylenedicarboxylate adduct with anthranol was more stable than the maleic anhydride adduct (see Chapter 6) it was decided to try to make the dimethyl acetylenedicarboxylate adduct of (CVI) by heating the two components together in tetralin at 200°, unfortunately without success.

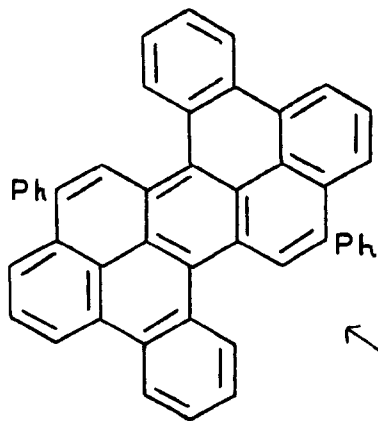
It was thought that the quinone (CIV) could be used to synthesise the little-known tetrabenzoperopyrene system (CX) by the following sequence of reactions:



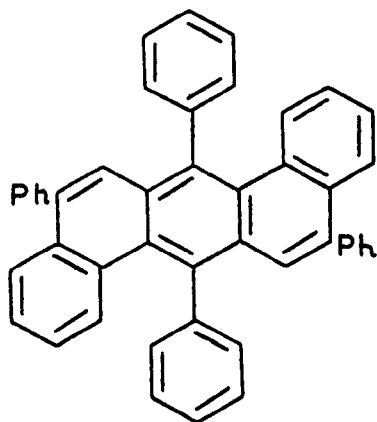
CIV



CVIII



CX



CVIX

This tetrabenzopyrene system without the two phenyl substituents has been obtained when benzanthrone is boiled with phosphorus oxychloride.⁹⁵

The reaction of excess of phenyl-lithium with the quinone (CIV) gave the tetraphenyl-diol (CVIII) as indicated by the disappearance of the carbonyl absorption band and the appearance of a hydroxyl absorption band. This diol was not purified, but the crude product was reduced directly by heating a suspension of the diol in glacial acid containing hydriodic and hypophosphorus acids for 24 hr. (a modification of the method due to Dickermann et al.⁹⁶) followed by column chromatography to give 1,2:5,6-dibenzo-3,7,9,10-tetraphenylanthracene (CVIX) as a pale yellow crystalline solid, m.p. $> 350^{\circ}$ in overall yield of 29% from the diphenyl quinone (CIV).

The two phenyl substituents at the 9- and 10-positions cannot be in the same plane as the rest of the molecule due to steric factors, this is shown by the fact that (CVIX) does not form either a 2,4,7-trinitrofluorenone complex or a 9-dicyanomethylene-2,4,7-trinitrofluorenone complex, though these substituents cause a bathochromic shift of 17 $m\mu$ (the 3,7-diphenyl substituents cause a shift of only 13 $m\mu$).

The effect of the angle of twist of these two phenyl substituents to the rest of the molecule can also be seen in the n.m.r. spectrum of this compound, which shows a multiplet (2.20 - 2.80 τ) on which is superimposed two singlets at 2.4 and 2.5 τ probably corresponding to the two different sets of phenyl substituents in the 9,10- and 3,7-positions

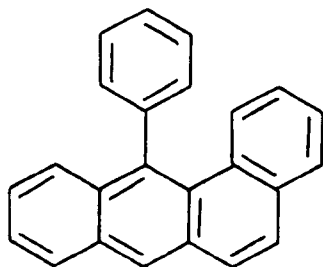
respectively; the anisotropic effect of the phenyl substituents at positions 9 and 10 causing an upfield shift for the adjacent H- α 3 and H- α β protons.

When 1,2:5,6-dibenzo-3,7,9,10-tetraphenylanthracene (CVIX) was treated with aluminium chloride and selenium in benzene or when 1,2:5,6-dibenzo-9,10-dihydro-9,10-dihydroxy-3,7,9,10-tetraphenylanthracene was treated with aluminium chloride in benzene, a yellow solid, m.p. 130-133°, was obtained in good yield. Several factors indicated that this hydrocarbon was a hydrogenated derivative, e.g. its low m.p., its 'non-tetrabenzoperopyrene' ultraviolet chromophore and its n.m.r. spectrum which showed a singlet at 8.6 τ after extensive drying and sublimation. Hence attempts were made to dehydrogenate this hydrocarbon, by heating it with 10% palladium-charcoal, by heating it with 2,3-dichloro-5,6-dicyano-p-benzoquinone, and by heating it at 420° with copper, but in each instance unchanged starting hydrocarbon was recovered.

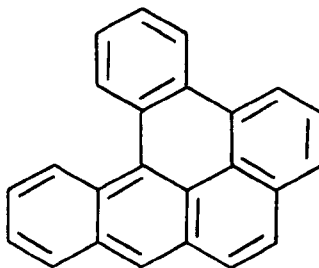
It now seems reasonably certain that this hydrocarbon is fully aromatic but so strongly solvated with petroleum (so strongly that sublimation or heating with copper fails to remove it) that it is difficult to make an accurate assessment of either the ultraviolet or n.m.r. spectra.

Very recently a paper⁹⁷ has appeared which throws doubt on the validity of the original assumption that cyclodehydrogenation of 1,2:5,6-dibenzo-3,7,9,10-tetraphenylanthracene (CVIX) or 1,2:5,6-dibenzo-9,10-dihydro-9,10-dihydroxy-3,7,9,10-tetraphenylanthracene

(CVIII) would necessarily give a tetrabenzoperopyrene system (CX).

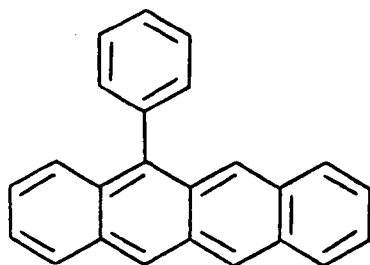


CXI

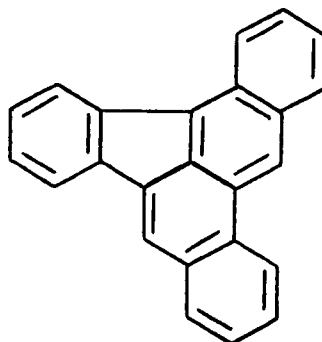


CXII

Lavit-Lamy and Buu-Hoi⁹⁷ examined the cyclodehydrogenation of (CXI) and found that instead of giving (CXII) as had been claimed⁹⁸ a rearrangement of the benzanthracene system took place as indicated by the appearance of the side-product (CXIII) and that the hydrocarbon given as (CXII) was in fact (CXIV).

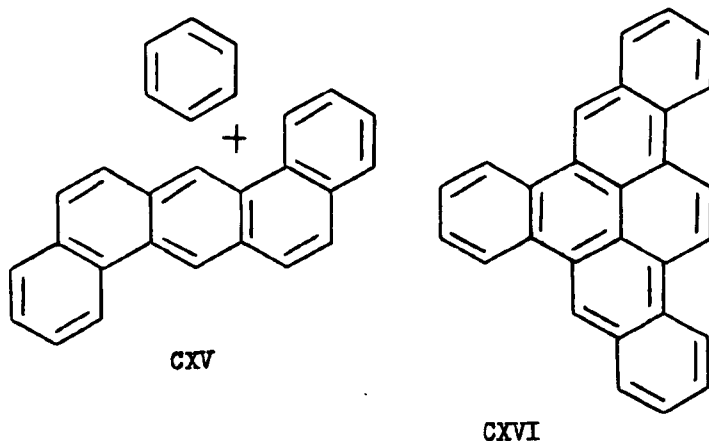


CXIII

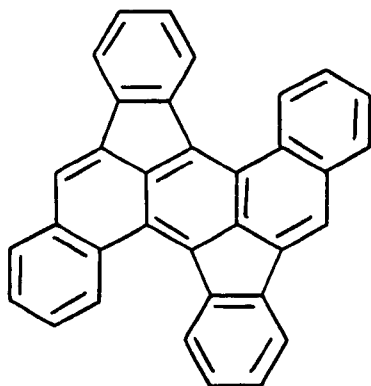


CXIV

Other instances of rearrangements of polycyclic systems are known, e.g. when 1,2:5,6-dibenzanthracene (CXV) is condensed with benzene⁹⁹ the product is (CXVI).

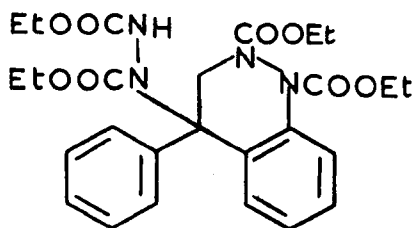


In view of these rearrangements it is not therefore surprising that the tetrabenzoperopyrene system (CX) was not obtained from either (CVIII) or (CVIX). It is difficult to make any predictions concerning the structure of the hydrocarbon so obtained as too many uncertainties are present, though it could (assuming no structural rearrangements) have the structure (CXVII), cyclodehydrogenation occurring between the two phenyl substituents in the 9,10-positions and adjacent benzene rings.

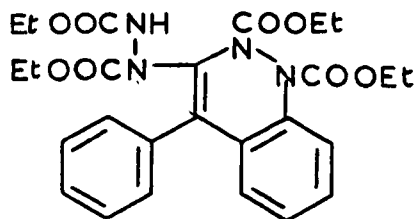


CXVII

It has been claimed that when 1,1-diphenylethylene is heated with diethyl azodicarboxylate that the di-adduct (CXVIII) m.p. 175° is formed.¹⁰⁰



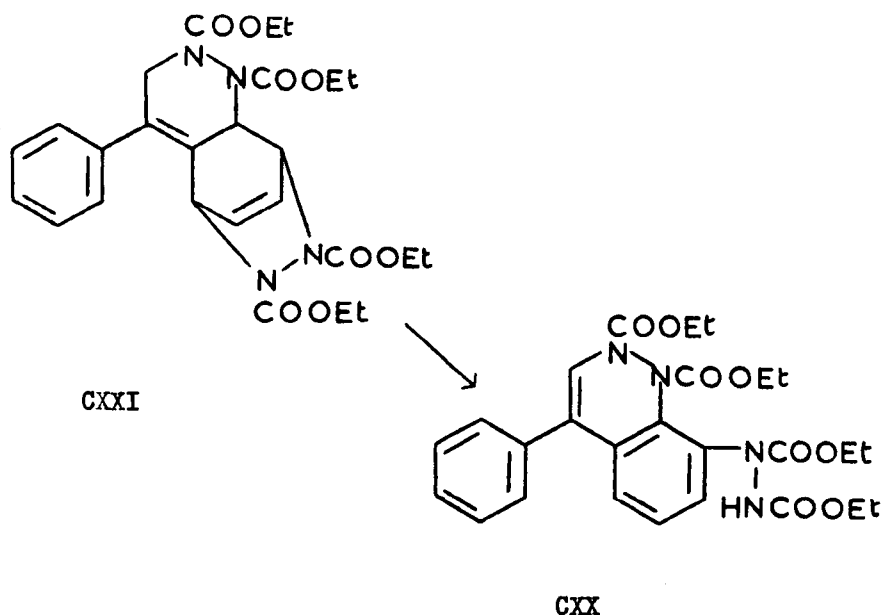
CXVIII



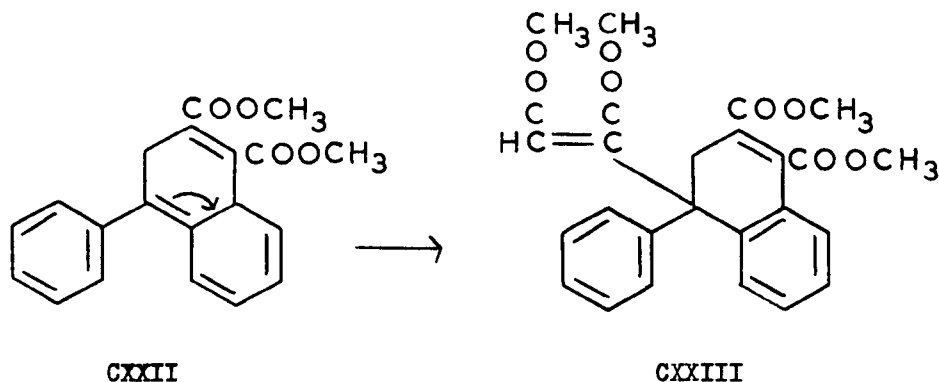
CXIX

When in the present work, 1,1-diphenylethylene was heated with diethyl azodicarboxylate under seemingly identical conditions, the only product obtained was a di-adduct, m.p. 165°, having a

formula $C_{26}H_{30}N_4O_8$ (i.e. containing two hydrogen atoms less than for (CXVIII)) and having an n.m.r. spectrum which showed 9 aromatic protons and 20 non-aromatic protons. This data is compatible with the structure (CXX) or its isomer which could have been obtained by aromatisation of the possible initial di-adduct (CXXI) which then underwent aromatisation, though the possibility of structure (CXIX) cannot be ruled out.



When attempts were made to hydrolyse the adduct, m.p. 165° , by methods¹⁰⁰ described for degradative hydrolysis of (CXVIII) which gave crystalline products, only intractable gums were obtained, indicating that the previously reported adduct, m.p. 175° (CXVIII) is not the same as the di-adduct obtained in the present work.



When 1,1-diphenylethylene and dimethyl acetylenedicarboxylate were heated together at 100° , a di-adduct $C_{26}H_{24}O_8$, m.p. 155° , was obtained. The n.m.r. spectrum shows a singlet at 4.50τ (olefin proton), and two singlets at 6.76 and 6.60τ (one proton each), these two singlets could be due to a methylene group with its two protons in slightly different environments. This spectrum suggests that the di-adduct has the structure (CXXIII). The formation of this adduct could be explained in terms of a normal Diels-Alder addition of one molecule of dimethyl acetylenedicarboxylate with 1,1-diphenylethylene to give (CXXII) which then reacts with a second molecule of dimethyl acetylenedicarboxylate by means of an Ene reaction¹⁰¹ with a shift of a double bond to reform the original ring (a mechanism similar to that postulated for the formation of the adduct (CXVIII)¹⁰⁰). Attempts to hydrogenate this adduct have so far failed.

EXPERIMENTAL

1,2:5,6-Dibenzo-3,7-diphenyl-9,10-anthraquinone (CIV).

A mixture of 1,1-diphenylethylene (2.0 g., 0.011 mole) and p-benzoquinone (3.0 g., 0.028 mole) in nitrobenzene (10 ml.) was heated under reflux for 5 hr. On cooling, solid deposited which after filtration was washed well with ether to give a product, m.p. $> 350^{\circ}$, (0.95 g., 19%). Recrystallisation from toluene gave orange red rods, m.p. $> 350^{\circ}$.

The above proportions of reactants gave the best yield of the pure quinone. Larger proportions of 1,1-diphenylethylene gave diminished yields of pure quinone; larger proportions of benzoquinone gave increased yields but of very impure quinone.

Found: C, 88.9; H, 4.8%

Required for $C_{34}H_{20}O_2$: C, 88.7; H, 4.4%

λ_{\max} (chloroform): 309 m μ ($\log_{10} \epsilon$ 4.74), 410 (4.08), shoulder, 343 (4.09).

ν_{\max} (KBr Disc): 1655 cm. $^{-1}$ (C=O, quinone), 1272, 1230, 843 (singlet aromatic C-H), 768 (four adjacent aromatic C-H), 701 (five adjacent aromatic C-H).

If the filtrate from the preparation was allowed to stand for some time, crystals of quinohydrone appeared.

Other reactions of 1,1-diphenylethylene with p-benzoquinone.

a) In ethanol

A mixture of 1,1-diphenylethylene (2.0 g., 0.011 mole) and benzoquinone (6.0 g., 0.056 mole), in ethanol (60 ml.) was heated under reflux for 14 hr. On cooling, benzoquinone precipitated, the filtrate was steam distilled to give as residue a sticky solid which was filtered, dried and washed with much ether to give solid (0.28 g.). The infrared spectrum of this solid appeared to be that of impure di-adduct.

b) In toluene

When 1,1-diphenylethylene (1.0 g.) and benzoquinone (3.0 g.) were heated in boiling toluene (70 ml.) for 36 hr., only the starting materials were isolated.

c) In dimethyl-formamide

Diphenylethylene (1.5 g.), benzoquinone (2.5 g.) were heated in boiling dimethyl-formamide (60 ml.) for 60 hr. No solid precipitated on cooling, so solvent was removed under reduced pressure to give a gum which on treatment with ether gave a product (1.8 g.), whose infrared spectrum showed it to be a very impure quinone.

1,2:5,6-Dibenzo-3,7-diphenylanthracene (CVI).

A mixture of aluminium turnings (2.0 g.), mercuric chloride (0.1 g.), dry carbon tetrachloride (1.5 ml.) and dry cyclohexanol (50 ml.) was cautiously heated to give initially a vigorous

exothermic reaction which had to be cooled. After this initial vigorous reaction, the mixture was heated with stirring until all the aluminium had reacted giving aluminium cyclohexanolate. To the cooled reaction was added 1,2:5,6-dibenzo-3,7-diphenyl-9,10-anthraquinone (1.80 g.), and the suspension heated with stirring under reflux for 48 hr. On cooling, the reaction mixture was washed successively with glacial acetic acid (50 ml.), concentrated hydrochloric acid (50 ml.) and much water to give (after drying) a crude solid (1.2 g.). This solid was dissolved in chloroform and the solution placed on an alumina column (Woelm activity No. 1, wt. 80 g., 20 x 2.5 cm.).

Elution with 60/80° petroleum gave colourless rods, m.p. 293° (0.53 g., 34%). Recrystallisation from ethanol-benzene mixture gave colourless rods, m.p. 293°.

Found: C, 94.9; H, 5.1%

Required for $C_{32}H_{22}$: C, 94.85; H, 5.15%

λ_{\max} (in chloroform): 299 m μ ($\log_{10} \epsilon$ 4.81), 312 (4.86), 350 (4.21), 366 (4.19).

ν_{\max} (Nujol): 1590 cm.⁻¹ (C=C, aromatic), 1485 (C=C, aromatic), 903 (singlet aromatic C-H), 766 and 753 (four and five aromatic C-H), 698 (five aromatic C-H).

The n.m.r. spectrum (CDCl₃) showed a multiplet, 1.93 - 2.53 τ (2 H- α + 4 H- β), a singlet at 2.50 τ (10 H- ϕ), a singlet at 2.20 τ (2 H- $\alpha\beta$), a multiplet 1.05 - 1.25 τ (2 H- $\epsilon\delta$), and a singlet at 0.93 τ (2 H- $\gamma\delta$).

2,4,7-Trinitrofluorenone derivative.

This was prepared by mixing equimolar hot saturated solutions of 2,4,7-trinitrofluorenone and the hydrocarbon in absolute ethanol-benzene to give immediately a coloured solution which on cooling gave red microneedles, m.p. 261° . Recrystallisation from benzene-ethanol mixture gave red needles, m.p. 264° .

Found: C, 74.2; H, 3.6; N, 5.4%

Required for $C_{47}H_{27}N_3O_7$: C, 75.8; H, 3.6; N, 5.6%

Attempted preparation of a 9,10-endo-adduct of 1,2:5,6-dibenzo-3,7-diphenylanthracene with dimethyl acetylene dicarboxylate.

A mixture of the hydrocarbon (0.4 g., 0.001 mole) and dimethyl acetylenedicarboxylate (1.0 g., 0.008 mole) in tetralin (10 ml.), was heated under reflux for 10 hr. On cooling, no precipitate appeared, nor when the solution was treated with ether. On removal of the ether the solution was steam distilled to remove tetralin. Extraction of the contents of the residual flask with benzene and subsequent removal of benzene from the dried solution gave a gum which on trituration with ether gave unchanged hydrocarbon (0.2 g.).

1,2:5,6-Dibenzo-9,10-dihydro-9,10-dihydroxy-3,7,9,10-tetraphenyl-anthracene (CVIII).

To an ethereal solution of phenyl-lithium (prepared from lithium (0.4 g.) and bromobenzene (4.5 g.) under nitrogen) was added dry benzene (250 ml.) and ether removed by distillation.

1,2:5,6-Dibenzo-3,7-diphenyl-9,10-anthraquinone (3.0 g.) was added in small portions to the benzene solution and the reaction mixture stirred at reflux temperature for 3 hr. At the end of this time, steam distillation left as a residue a solid, m.p. $> 350^{\circ}$ (3.6 g.), which did not show a carbonyl absorption band in the infrared spectrum but did show the presence of hydroxyl groups at 3560 cm.^{-1} . This solid was considered pure enough for the next stage.

3,7,9,10-Tetraphenyl-1,2:5,6-dibenzanthracene

Crude 1,2:5,6-Dibenzo-9,10-dihydro-9,10-dihydroxy-3,7,9,10-tetraphenylanthracene (2.8 g.) was added with stirring to a solution of concentrated hydroiodic acid (6.0 ml.), and 50% hypophosphorus acid (36 ml.) in glacial acetic acid (350 ml.). The resulting suspension was then heated under reflux with stirring for 10 hr. cooling with a salt ice mixture followed by filtration gave a solid (1.90 g.). Removal by distillation of the majority of the acetic acid from the filtrate, followed by treatment of the residue with excess water gave solid (0.70 g.) apparently identical with that previously obtained. The combined product was taken up in chloroform; some solid remained undissolved (0.4 g.), whose I.R. indicated that it was unreacted starting material. The chloroform solution was placed in an alumina column, (Woelm activity No. 1, wt. 160 g., $34 \times 2.5\text{ cm.}$). Elution with benzene gave yellow needles, (m.p. $> 350^{\circ}$) (0.8 g., 29%). Recrystallisation from benzene, using charcoal, gave pale yellow needles, m.p. $> 350^{\circ}$.

Found: C, 95.1; H, 5.2%

Required for $C_{46}H_{30}$: C, 94.8; H, 5.2%

λ_{\max} 329 $m\mu$ ($\log_{10} \epsilon$ 4.81), 371 $m\mu$ (4.36), 388 (4.34), shoulder 317 (4.75) in chloroform.

ν_{\max} (Nujol): 1600 cm^{-1} (C=C aromatic), 1491 (C=C aromatic), 892 (singlet aromatic C-H), 773, 762, 755, 697 (five adjacent aromatic C-H).

The n.m.r. spectrum ($CDCl_3$) shows multiple peaks 2.20 - 2.80 τ on which there are superimposed two singlet peaks at 2.40 and 2.50 τ respectively.

Attempted preparation of the 2,4,7-trinitrofluorenone complex.

Equimolar hot saturated solutions of 2,4,7-trinitrofluorenone and the hydrocarbon in ethanol-benzene were added; no deep colour was observed. On cooling the solution, needles of the hydrocarbon were deposited. When on standing solvent was allowed to evaporate from the filtrate a few coloured crystals were observed.

Attempted preparation of the 9-dicyanomethylene-2,4,7-trinitrofluorene complex.

Hot solutions of the hydrocarbon and 9-dicyanomethylene-2,4,7-trinitrofluorene in chloroform were mixed; no immediate dark colour was observed, nor when the solution was allowed to cool. Removal of some of the chloroform did not give any coloured precipitate or solution; eventual evaporation of the remaining chloroform gave the starting materials.

Reaction of 1,2:5,6-dibenzo-3,7-diphenyl-9,10-anthraquinone with aluminium chloride and selenium.

To a solution of 1,2:5,6-dibenzo-3,7-diphenyl-9,10-anthraquinone (0.7 g.) in dry benzene (120 ml.) was added anhydrous aluminium chloride (2.0 g.) and selenium powder (0.9 g.) and the resulting suspension heated under reflux with stirring for 30 min. during which time the colour of the benzene solution became progressively darker. To the cooled reaction mixture was added, with vigorous stirring, dilute hydrochloric acid. After filtration, the benzene solution was washed well with water, dried over MgSO_4 , and most of the solvent removed.

The concentrated solution was placed on an alumina column (Woelm, activity No. 1, 45 g., 15 x 2.5 cm.).

Elution with a 60/40 benzene-60°/80° petroleum mixture gave yellow solid, m.p. 130-3° (0.45 g.).

The n.m.r. spectrum indicated the presence of petroleum in this solid, sublimation below 100°/0.1 mm failed to remove this solvent.

λ_{max} (chloroform): 281, 303, 326 and 344 μ .

Reaction of 1,2:5,6-dibenzo-9,10-dihydro-9,10-dihydroxy-3,7,9,10-tetraphenylanthracene with aluminium chloride.

The diol (0.5 g.) was suspended in dry benzene (150 ml.) and aluminium chloride (2.0 g.) added to the suspension, and the suspension heated under reflux with stirring with copious evolution of hydrogen

chloride for 3 hr. On cooling excess aluminium chloride was decomposed by dilute hydrochloric acid, the organic layer was separated, washed well with water, dried (MgSO_4) and most of the solvent removed to give a concentrated solution which was placed on an alumina column (Woelm activity No. 1., 12.5 x 2.5 cm.).

Elution with a 60/40-benzene-60°/80° petroleum mixture gave yellow solid, m.p. 130-133° (0.42 g.) identical in all respects with the solid prepared in the previous section.

Attempts were made to aromatise this compound as indicated in the following sections.

- a) The hydrocarbon (0.35 g.) was heated with 2,3-dichloro-5,6-dicyano-p-benzoquinone (1.0 g.) in dry benzene (70 ml.) under reflux for 24 hr. On cooling, more benzene (130 ml.) was added, and the benzene solution washed with 10% sodium hydroxide solution (3 x 50 ml) and then well with water, dried (MgSO_4), and the solvent removed to give unchanged starting material (0.30 g.).
- b) The hydrocarbon (0.10 g.) was thoroughly ground with 10% palladium charcoal (0.33 g.) and the mixture heated at 300-310° for 4 hr. Sublimation at 400°/0.2 mm gave unchanged hydrocarbon.
- c) The hydrocarbon (0.15 g.) was mixed with freshly reduced copper powder (3.0 g.), and the mixture heated at 420 - 440° for 1 hr. under a stream of carbon dioxide. During this time some yellow solid sublimed out; on cooling, the residue was extracted with chloroform to give unchanged starting material, as was the case with the sublimed

material.

Reaction of 1,1-diphenylethylene with diethyl azodicarboxylate.

1,1-Diphenylethylene (2.0 g., 0.011 mole) and diethyl azodicarboxylate (3.0 g., 0.018 mole) were heated together either at 70° (more conveniently at 100°) for 5 hr. during which time the reaction mixture became very viscous, solidifying to a clear hard glass, which was treated with excess ether to give solid, m.p. 163° (2.15 g., 0.37%). Recrystallisation from methanol gave m.p. 165°.

Found: C, 59.7; H, 6.0; N, 10.4%

Required for $C_{26}H_{30}N_4O_8$: C, 59.3; H, 5.8; N, 10.6%

ν_{\max} (KBr disc): 3280 cm^{-1} (NH), 1755 and 1713 (C=O, ester), 772 (three or four adjacent aromatic C-H) and 701 (five adjacent aromatic C-H).

The n.m.r. spectrum (in CDCl_3) showed a multiplet 8.5 - 9.1 τ (12 protons, four $\text{COOCH}_2\text{CH}_3$), a multiplet 5.5 - 6.1 τ (8 protons, four $\text{COOCH}_2\text{CH}_3$), a multiplet 2.5 - 3.0 τ (7 protons) on which is superimposed a singlet at 2.67 τ , and a multiplet 2.10 - 2.35 τ (two protons).

Hydrolysis of the 1,1-diphenylethylene-diethylazodicarboxylate adduct.

The adduct (3.5 g.) was added to hydrazine hydrate (15 ml.) and the suspension heated under reflux for 6 hr. After about 10 to 15 min. the solid adduct had gone to an oil, after $1\frac{1}{4}$ hr. this oil had all dissolved, after 3 hr., oil began to separate out. On cooling, more oil separated; the supernatant liquid was decanted off and the

oil triturated with a small quantity of methanol, without precipitating solid. The methanolic solution was added to the decanted liquid and the combined solution extracted with ethyl acetate (2 x 100 ml.). Solvent was removed from the dried organic extract to give a gum which was dissolved in a small quantity of benzene and the solution placed on an alumina column (Woelm Activity No. 1, 100 g., 22 x 2.5 cm.).

Elution with a benzene (40%) petroluem (60%) mixture gave a gum (0.41 g.) which could not be crystallised.
 ν_{\max} (gum): 770 cm.^{-1} (three or four adjacent aromatic C-H), and 694 (five adjacent aromatic C-H).

The n.m.r. spectrum (in CCl_4) showed a singlet at 2.60 (five H- ϕ), a multiplet, 2.0 - 2.31 τ (four protons), a multiplet, 1.4 - 1.5 τ (one proton), and a singlet at 0.87 τ (one proton).

Reaction of 1,1-diphenylethylene with dimethyl acetylenedicarboxylate

1,1-Diphenylethylene (2.0 g., 0.011 mole) and dimethyl acetylenedicarboxylate (3.2 g., 0.022 mole) were heated at $94-96^\circ$ for 48 hr. to give a gum. Treatment of the gum with ether gave solid, m.p. 153° (1.2 g., 23%). Recrystallisation from ethanol gave needles, m.p. 155° .

Found: C, 67.5; H, 5.4%

Required for $\text{C}_{26}\text{H}_{24}\text{O}_8$: C, 67.2; H, 5.3%

λ_{\max} (ethanol): 227 $\text{m}\mu$ ($\log_{10} \epsilon$ 4.31), 297 (4.12).

ν_{\max} (KBr Disc): 1735 and 1708 cm.^{-1} ($\text{C}=\text{O}$, ester), 1640, 1620, 1442, 1430, 1350, 1302, 1280, 1275, 1250, 1235, 1195, 1163, 1130, 1104, 1080, 1045, 993, 897, 876, 798, 770, 767, 755, 745, 735 and 698 (five adjacent

aromatic C-H).

The n.m.r. spectrum (in CDCl_3) showed a singlet at 6.76 τ (one proton), a singlet at 6.60 τ (one proton), singlets at 6.11, 6.20, 6.30 and 6.33 τ (four COOCH_3), a singlet at 4.50 τ (one olefinic proton), and singlets at 2.65 and 2.67 τ (nine aromatic protons).

This compound when exposed to sunlight turns yellow.

Reduction of the 1,1-diphenylethylene-dimethyl acetylenedicarboxylate adduct.

a) The di-adduct (0.7 g.), in absolute ethanol (150 ml.) was hydrogenated over 10% palladium charcoal at 50° and atmospheric pressure with an uptake of hydrogen (100 cc. at N.T.P.). Removal of most of the ethanol precipitated solid, m.p. 142-146° (0.5 g.). Recrystallisation from ethanol gave m.p. 144-146°.

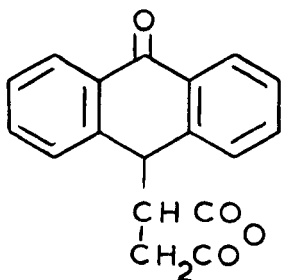
The n.m.r. spectrum of this adduct was identical with that of the original adduct.

b) The di-adduct (0.40 g.) in ethanol (150 ml.) was hydrogenated over platinum oxide (0.05 g.) at 50° with an uptake of hydrogen (55 cc. at N.T.P.). Removal of the bulk of ethanol gave solid identical with that in section (a).

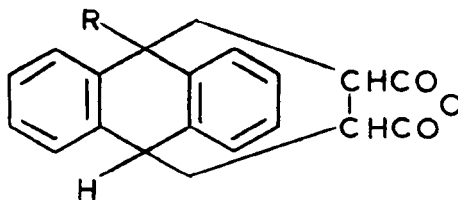
CHAPTER VI

Some Reactions of Anthrone

When Barnett et al.¹⁰² heated anthrone with maleic anhydride in di-*p*-tolylether the anthronyl adduct (CXXIV) was obtained and not the anthranol adduct (CXXVa, R = OH). Hydrolysis of the corresponding 9-substituted vicinal adducts (CXXVb, R = Cl) and (CXXVc, R = CH₃COO) gave anthrone and maleic anhydride (or acid).



CXXIV

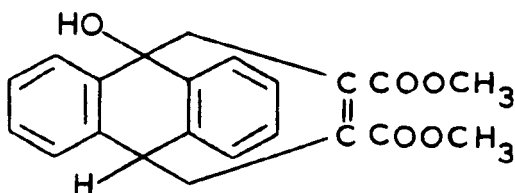


CXXV

Subsequent attempts to make such anthranol adducts from the corresponding methoxy- or acetoxy-adducts by treatment with hydroiodic acid have given the anthronyl adducts except in those cases where there is not a carbonyl group or other electron-withdrawing group on the bridgehead linkage immediately adjacent to the bridgehead hydroxyl.^{103,104,105} The only other instance of direct formation of

an anthranol adduct recorded is obtained when anthrone is heated with ethylene in dioxan or pyridine under pressure.^{103,104}

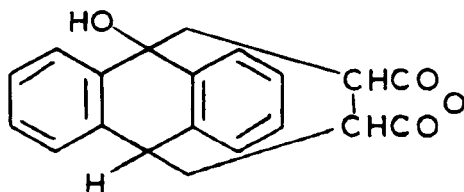
In the present work, when anthrone was heated under reflux in acetic acid with dimethyl acetylenedicarboxylate it was found to give dimethyl 9,10-dihydro-9-hydroxyanthracene-9,10-endo- α,β -maleate (CXXVI) as colourless rods, m.p. 215-218° in an 81% yield.



CXXVI

The evidence for this structure is conclusive, as the infrared spectrum shows the absence of a ketonic carbonyl frequency but shows the presence of hydroxyl. The hydroxyl group was shown to be non-phenolic by the ferric chloride test, while the ultraviolet spectrum showed a non-conjugated benzenoid chromophore. Further evidence for structure (CXXVI) was obtained from the n.m.r. spectrum in CF_3COOH which showed two singlet peaks at 5.98 and 6.03 τ due to the two methyl ester groups, a singlet peak at 4.33 τ due to the bridgehead proton (this assignment is not unreasonable in view of the fact that this proton is adjacent to two benzene rings and one double bond) and non-symmetrical multiplet peaks between 2.30 and 2.95 τ .

When (CXXVI) is heated at 230-240°, i.e. above its m.p., for 10 min., it was recovered unchanged showing that it is thermally more stable than the corresponding maleic anhydride adduct (CXXVII).



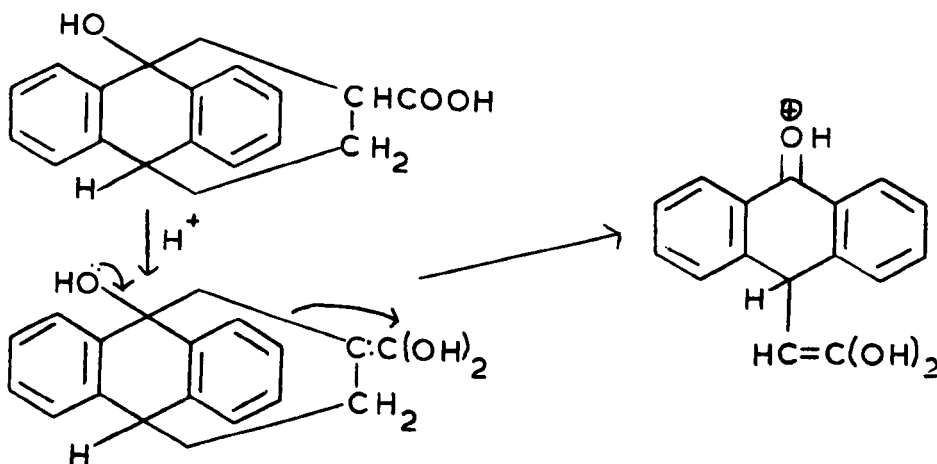
CXXVII

The reaction of anthrone with maleic anhydride in refluxing acetic acid for 30 min. gave the anthranol adduct (CXXVII) in 75% yield. Although the n.m.r. spectrum of this compound could not be obtained, due to its lack of solubility in non-interfering solvents, its structure is almost certainly as given. Quite apart from the obvious analogy with the dimethylacetylenedicarboxylate adduct (CXXVI), other evidence supports this structure, e.g. its infrared spectrum showed a hydroxyl peak shown to be non-phenolic by the ferric chloride test, and its ultraviolet chromophore is that of a non-conjugated benzenoid system.

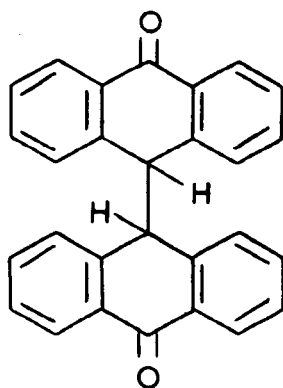
When instead of heating the reaction mixture of anthrone and maleic anhydride in acetic acid for 30 min., heating was continued for 4 hr., initially (CXXVI) was deposited but after a time this product redissolved. Removal of acetic acid and trituration of the residue with

ether gave the anthronyl adduct (CXXIV), m.p. 214-216° (lit¹⁰² m.p. 215°) in 31% yield. The structure of this adduct was confirmed by its n.m.r. spectrum in CF₃COOH.

The anthranol adduct (CXXVII) was found to melt between 165 and 175°, resolidifying about 175° to finally melt at 210-213°. To test whether this was due to rearrangement of (CXXVII) to (CXXIV), the former was heated at 230-240° under nitrogen for 10 min. to give on cooling (CXXIV). When (CXXIV) was heated under similar conditions, it was recovered unchanged showing that the rearrangement of (CXXVII) to (CXXIV) is irreversible. This rearrangement both in solution and thermally could occur by a similar mechanism to that suggested by Meek et al.¹⁰⁵ to explain why anthranol adducts could not be obtained by treatment of the corresponding methoxy adduct with hydriodic acid, as follows:



The reaction of anthrone with diethyl azodicarboxylate in boiling acetic acid for 1 hr. gave bianthron-9-yl (CXXVIII) in 60% yield, identical with authentic material prepared by oxidation of anthracene with concentrated nitric acid.¹⁰⁶ Likewise bianthron-9-yl was obtained in 70% yields in instances when anthrone was heated with tetracyanoethylene or chloranil, in boiling acetic acid.



CXXVIII

Bianthron-9-yl has also been reported as being formed in small quantities when anthrone reacts with ethylene under pressure in neutral solvents.¹⁰³ It has also been reported¹⁰⁷ that bianthron-9-yl is formed when anthrone is oxidised by air or other oxidising agents; so anthrone was heated in acetic acid to check whether the formation of bianthron-9-yl was due to aerial oxidation or to dehydrogenation by the dienophiles, diethyl azodicarboxylate, tetracyanoethylene and chloranil; it was found that not a trace of bianthron-9-yl was

formed suggesting that anthrone was dehydrogenated by the dienophiles.

It seems inexplicable that whereas maleic anhydride and dimethyl acetylenedicarboxylate react with anthrone to give stable adducts, other dienophiles should under seemingly identical conditions give bianthron-9-yl, especially as e.g. tetracyanoethylene is a much more powerful dienophile than either maleic anhydride or dimethyl acetylenedicarboxylate as shown by the comparison of the reactivities of various dienophiles with 9,10-dimethylanthrone.¹⁰⁸

To check whether the addition of maleic anhydride and dimethyl acetylenedicarboxylate to anthrone went via bianthron-9-yl dimethyl acetylenedicarboxylate was heated with bianthron-9-yl in acetic acid; but no products other than bianthron-9-yl were recovered from this reaction.

All that can be said is that with anthrone some dienophiles react to give adducts, whereas other dienophiles oxidise anthrone to bianthron-9-yl.

The fact that in bianthron-9-yl, the two anthracene segments lie at an angle of 90° to each other is apparent in the n.m.r. spectrum by the upfield shift of the four H- α protons, in the positions adjacent to the bridgehead linkage due to the anisotropic effect of the benzene rings in one anthracene segment on these protons in the other anthracene segment. These protons show as a multiplet at 3.05 - 3.21 τ , in addition, there are multiplets at 2.50 - 2.70 τ (8 H- β) and at 2.0 - 2.20 τ , due to the 4 H- α protons immediately adjacent to the two carbonyl groups (i.e. upfield from the corresponding

protons in anthrone and methyleneanthrone).

In addition to these reactions 'benzyne' was liberated in the presence of anthrone in an attempt to make the endo adduct, but no product other than anthrone was recovered from this reaction.

EXPERIMENTAL

Anthrone

This compound was prepared by the method of Meyer⁹¹ by the reduction of 9,10-anthraquinone with tin and hydrochloric acid, to give anthrone, m.p. 154° (lit m.p. ⁹¹ 154-155°).

The n.m.r. spectrum (in CDCl₃) shows a singlet at 5.7τ (methylene group), a multiplet 2.40 - 2.70τ (2 H-α + 4 H-β) and a multiplet 1.55 - 1.70τ (2 H-α adjacent to the carboxyl group).

Bianthron-9-yl (CXXVIII).

Bianthron-9-yl was prepared by the method of Barnett and Matthews¹⁰⁵ in which anthracene suspended in glacial acetic acid was oxidised with concentrated nitric acid. After 40 min. most of the anthracene had gone into solution and the remainder was removed by filtration. The clear filtrate was then heated under reflux for 1½ hr. during which time pure bianthron-9-yl crystallised out.

ν_{\max} (KBr disc): 1655 cm.⁻¹ (C=O, αβ, α'β unsaturated ketone), 1597, (C=C, aromatic) 1460, 1350, 1317, 1170, 1155, 933, 787, 736, 707, 691 (four adjacent aromatic C-H, next to carbonyl).

The n.m.r. spectrum (in CF₃COOH) showed a singlet at 5.39τ (bridgehead hydrogens), a multiplet, 3.05 - 3.21τ (4 H-α adjacent

to the bridgehead linkage), a multiplet 2.50 - 2.70 τ (8 H- β), and a multiplet 2.0 - 2.20 τ (4 H- α , adjacent to the carbonyl groups).

9,10-Dihydro-9-hydroxyanthracene-9,10-endo-succinic anhydride (CXXVII).

A mixture of anthrone (2.0 g., 0.010 mole) and maleic anhydride (2.0 g., 0.020 mole) in glacial acetic acid (10 ml.) were heated under reflux for 30 min. During this time colourless rods began to separate; cooling gave a product (2.26 g., 75%), m.p. 165-175 $^{\circ}$, resolidifying about 175 $^{\circ}$ to new crystals, finally melting at 210-213 $^{\circ}$. Recrystallisation from acetic acid gave needles, m.p.

Found: C, 73.8; H, 4.15%

Required for C₁₈H₁₂O₄: C, 73.95; H, 4.15%

ν_{\max} (KBr disc): 3420 cm.⁻¹ (hydroxyl), 1858, 1830 and 1775 (C=O, anhydride), 1461 (CH₂), 1077 (OH), 947 (anhydride), 769 and 756 (four adjacent aromatic C-H).

10-Anthrionylsuccinic anhydride (CXXIV).

A mixture of anthrone (1.0 g., 0.0052 mole) and maleic anhydride (1.0 g., 0.010 mole) in glacial acetic acid (20 ml.) were heated under reflux for 4 hr. On cooling, no solid separated, so the acetic acid was removed under reduced pressure. The gum-like residue was triturated with ether to give a crystalline solid, m.p. 214-6 $^{\circ}$ (lit¹⁰¹ 215 $^{\circ}$) (0.46 g., 31%).

ν_{\max} (KBr disc): 3080 cm^{-1} (aromatic C-H), 2925 (CH_2), 1860 and 1774 ($\text{C}=\text{O}$, anhydride), 1665 ($\text{C}=\text{O}$, $\alpha\beta$, $\alpha'\beta$ unsaturated ketone), 1598 ($\text{C}=\text{C}$, conjugated) 1462 ($-\text{CH}_2-$), 1405, 1318, 1206, 1058, 957, 937 (anhydride), 812, 761, 708, 682 (four adjacent aromatic C-H next to carbonyl).

The n.m.r. spectrum (in CF_3COOH) showed two doublets ($J = 8$ c.p.s.) centres at 7.70 and 7.52 τ ($\text{CH}-\underline{\text{CH}_2}-\text{CO}$), an octet ($J = 2$ c.p.s.), centre 6.10 τ ($\text{CH}-\underline{\text{CH}}-\text{CH}_2\text{CO}$), a doublet ($J = 3$ c.p.s.), centre 4.93 τ (bridgehead proton), a multiplet, 2.25 - 2.55 τ (2 H- α + 4 H- β), and a multiplet, 1.65 - 1.85 τ (2 H- α adjacent to carbonyl groups).

Effect of heat on 9,10-dihydro-9-hydroxyanthracene-9,10-endosuccinic anhydride (CXXVII).

The above compound was heated under nitrogen, at 230-240° (bath) for 10 min. The cooled product was recrystallised from ethanol to give 10-anthronylsuccinic anhydride, m.p. 214-6°.

Effect of heat on 10-anthronylsuccinic anhydride (CXXIV).

The above compound was recovered unchanged after heating under nitrogen, at 230-240° (bath) for 10 min.

Dimethyl-9,10-dihydro-9-hydroxyanthracene-9,10-endo- α,β -maleate (CXXVI).

A mixture of anthrone (1.0 g., 0.0052 mole), and dimethyl acetylenedicarboxylate (1.0 g., 0.0070 mole), in acetic acid (7 ml.) was heated under reflux for 5 hr. On cooling, colourless rods deposited

m.p. 215-218° (1.4 g., 81%). Recrystallisation from aqueous acetone gave a product of m.p. 220-222°.

Found: C, 71.4; H, 4.8%

Required for $C_{20}H_{16}O_5$: C, 71.4; H, 4.8%

ν_{\max} (KBr disc): 3460 cm^{-1} (hydroxyl), 1730 and 1681 (C=O, ester), 1630 (C=C, conjugated), 1445, 1429, 1267 (C-O-), 1233, 1207, 1177, 1120, 1070, 1055, 763 and 758 (four adjacent aromatic C-H).

The n.m.r. spectrum (in CF_3COOH) showed two singlets at 5.98 and 6.03 τ (two methyl ester groups), a singlet at 4.33 τ (bridgehead hydrogen), two multiplets, 2.78 - 2.93 τ and 2.30 - 2.52 τ due to four protons each.

The above compound was also prepared in 28% yield when anthrone and dimethyl acetylenedicarboxylate were heated under reflux in nitrobenzene for 50 min.

Effect of heat on dimethyl-9,10-dihydro-9-hydroxyanthracene-9,10-endo- α,β -maleate.

The above compound was recovered unchanged when it was heated under nitrogen, at 230-240° (bath) for 10 min.

Reaction of anthrone with diethyl azodicarboxylate in acetic acid.

When anthrone (1.0 g., 0.0052 mole) and diethyl azodicarboxylate (1.5 g., 0.0087 mole) in acetic acid (10 ml.) were heated under reflux for 1 hr. crystalline material began to be precipitated. On cooling more solid precipitated, m.p. 245-8°, (total 0.55 g.) shown by

spectroscopic data to be bianthron-9-yl.

Reaction of anthrone with tetracyanoethylene

When a mixture of anthrone (0.50 g., 0.0026 mole) and tetracyanoethylene (0.30 g., 0.0023 mole), in glacial acetic acid (8 ml.) was heated under reflux for 30 min., the initially yellow solution rapidly darkened to an intense green with separation of a crystalline solid. On cooling more solid precipitated, m.p. $260-2^{\circ}$, shown by spectroscopic data to be bianthron-9-yl, (0.36 g.). Recrystallisation from glacial acetic acid gave plates, m.p. $260-2^{\circ}$, whereas recrystallisation from acetone gave rods, m.p. $245-8^{\circ}$; both melting forms having same spectroscopic data.

When anthrone (1.0 g., 0.0052 mole), and tetracyanoethylene (0.6 g., 0.0046 mole), in glacial acetic acid (40 ml.) were heated under reflux for 96 hr. On cooling, bianthron-9-yl (0.96 g.) deposited.

Reaction of anthrone with chloranil.

Anthrone (0.5 g., 0.0026 mole) was added in small portions over 25 min. to a refluxing solution of chloranil (0.65 g., 0.0026 mole) in xylene (10 ml.) and the resulting solution heated under reflux for a further 25 min. during which time evolution of hydrogen chloride was noted. On cooling, a crystalline solid precipitated (0.38 g.) found to be bianthron-9-yl.

Effect of heating anthrone in acetic acid.

When anthrone (0.48 g.), was heated under reflux in glacial acetic acid (8 ml.) for 1 hr., no precipitation of bianthron-9-yl occurred. On cooling, unchanged anthrone separated.

Reaction of bianthron-9-yl with dimethyl acetylenedicarboxylate.

A mixture of bianthron-9-yl (1.0 g.) and dimethyl acetylenedicarboxylate (1.2 g.), in glacial acetic acid (35 ml.) were heated under reflux for 6 hr. During this time was noted a gradual darkening of the solution. On cooling, unchanged bianthron-9-yl (0.85 g.) was obtained.

Reaction of anthrone with 'benzyne'.

A solution of anthranilic acid (1.45 g., 0.0106 mole), in acetone (20 ml.) was added during 3 hr. to a refluxing solution of anthrone (2.0 g., 0.0104 mole) and amyl nitrite (1.3 g., 0.111 mole), in methylene chloride (40 ml.). After cooling volatile material was removed under reduced pressure to give a solid residue which was redissolved in methylene chloride. This solution was extracted with dilute potassium hydroxide solution, washed with water, dried, and the methylene chloride removed to give unchanged anthrone.

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