SYNTHESES
of
POLYCYCLIC AROMATIC HYDROCARBONS.

THESIS

presented by

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Publications.

The following papers have been, or are about to be, published by E. Clar and D.G. Stewart. Reprints are enclosed at the end.

1. Aromatic Hydrocarbons. Part LIX. 1:2:3:4-Dibenzopyrene.
   J., 1951, 687.
2. Aromatic Hydrocarbons. Part LXI. Pentaphene.
   J., 1951, 3215.
3. Aromatic Hydrocarbons. Part LXIII. Resonance Restriction and the Absorption Spectra of Aromatic Hydrocarbons.
   J.Amer.Chem.Soc., 1952, *74*, 6235.
4. Aromatic Hydrocarbons. Part LXIV. 2:3-6:7-Dibenzofluoranthene.
   J., 1952, 4783.
5. Aromatic Hydrocarbons. Part LXV. Triangulene Derivatives.
   J.Amer.Chem.Soc. Received 24 Nov.,1952.
6. Aromatic Hydrocarbons. Part LXVII. Triangulene Derivatives II.
   Received May, 1953.

CONTENTS

Summary.

The Kekulé structures of benzenoid hydrocarbons have, according to the valency-bond treatment of L. Pauling, a statistical significance only, while the molecular-orbital theory dispenses with them entirely.

The synthesis of a hydrocarbon with no Kekulé structure, named for simplicity triangulene, was attempted to find out how far these assumptions are justified. Dehydrogenation of dodecahydrotriangulene and hexahydrotriangulene, and a study of the reduction of triangulenequinone indicated that triangulene is an unstable diradical which polymerises as soon as it is formed. It can therefore be concluded that a hydrocarbon which lacks a Kekulé structure possesses no aromatic character.

While investigating triangulene, a new synthesis of pentaphene was discovered, which is superior to the earlier synthesis in that no isomeric hydrocarbons are formed.

As coeranthrene and naphthanthrene have skeletons closely related to that of triangulene, these compounds and their derivatives were prepared and used for comparison purposes.

To arrive at a fuller understanding of the aromatic state it is necessary to ascertain if a single Kekulé structure is sufficient to lend aromatic character to a

benzenoid ring system. The hydrocarbon, zethrene in which the two central double bonds are fixed when formulated in terms of classical structures, has been synthesised. Its properties are so extraordinary that it must be concluded that zethrene is not a true aromatic hydrocarbon and that it has a pronounced tendency to assume a structure in which two localised electrons are surrounded by a closed system of conjugated double bonds.

From these experimental facts the following definition is proposed: aromatic resonance demands the participation of at least two Kekulé structures in which no double bond is isolated and which are of similar energy.

The unusual properties of perinaphthenone, e.g., its solubility in hydrochloric acid, have been attributed to its assuming a structure in which the external carbon atoms are joined by a system of alternating double bonds. Further investigation of this phenomenon has resulted in the production of stable free radicals derived from perinaphthenone, in which a lone electron is localised at the central carbon atom.

Symmetrical tribenzoperinaphthene has been synthesised, and although attempts to form the corresponding free radical were unsuccessful, the isolation of tribenzoperinaphthylium salts was accomplished.

A hydrocarbon obtained as a by-product in a preparation of hexahydrotriangulene was identified as 2:3-benzofluoranthene and, from a study of its absorption spectrum and the application of the Anellation Principle of E. Clar, it was predicted that the red hydrocarbon, obtained in the ring-closure of 9-phenyl-1:2-benzanthracene to 1:2-3:4-dibenzopyrene, was 2:3-6:7-dibenzofluoranthene. This hydrocarbon was therefore synthesised from 5-phenylnaphthacene and the prediction proved to be correct.

5-Benzylnaphthacene was prepared to demonstrate further the tautomerism between the methylacenes and the methylene-dihydroacenes. From a study of the absorption spectrum of this hydrocarbon it appears that there is present an appreciable proportion of the methylene form, 9-benzylidene-9:10-dihydronaphthacene. Attempts to separate the two tautomers, however, were not successful.

Finally, the initial steps of an unambiguous synthesis of 1:9-5:10-diperinaphthyleneanthracene were carried out. Although the final reduction to the hydrocarbon proved to be difficult, a product, which is probably the hydrocarbon, was obtained.

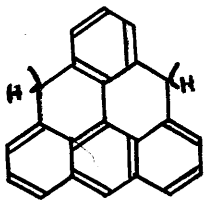
Throughout these investigations, the absorption spectra of many of the compounds were studied, and they were invaluable in the assigning of correct structures. The Anellation Principle of E. Clar was extended and new anellation series were found.

Discussion.

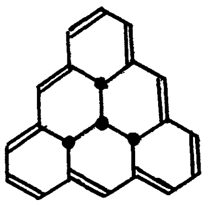
The Significance of Kekulé Structures (1).

The Kekulé structures of benzenoid hydrocarbons are, according to the valency-bond treatment of L. Pauling (2), of statistical importance only, in that each structure contributes towards the normal state of the molecule to a certain fixed percentage, depending on its stability. The molecular-orbital treatment dispenses with Kekulé structures entirely and has on occasion even denied their having any significance at all.

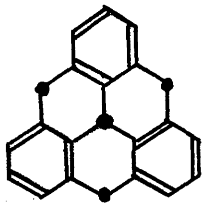
In order to find out how far these assumptions are justified, the synthesis of a hydrocarbon, which has been named triangulene, was attempted. Triangulene cannot be formulated in any way to give a Kekulé structure and therefore it must be, according to classical structural theory, a diradical (I), which would be quite unstable and would polymerise immediately.



I



II

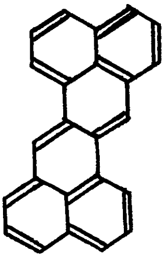


III

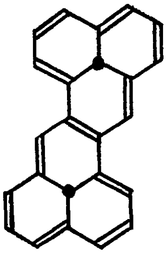
However, considering the symmetrical structure (II) from the standpoint of quantum mechanics and the principle of resonance stabilisation, it is possible that the molecule could acquire a certain stability by the combination of the 4 π electrons (indicated by dots) to form a non-localised molecular-orbital system with an external closed polyene system as shown. Similarly, the symmetrical "excited" structure (III) could form a stable molecule.

However, the experimental results, which will be described in detail later, indicate that triangulene is an unstable diradical which polymerises as soon as it is formed. Thus it is concluded that a hydrocarbon which lacks a Kekulé structure has no aromatic character. No other system of trigonal symmetry with a uniform distribution of paired electrons in molecular-orbitals over the whole ring system seems to exist. This excludes the existence of m-quinonoid and similar systems which cannot be expressed in terms of classical structures. This result was predicted by Clar (3) from the standpoint of classical structural chemistry and later by Longuet-Higgins (4) from the quantum mechanical standpoint.

In order to arrive at a definition of the atomatic state, it is necessary to ascertain if a single Kekulé structure is sufficient to lend aromatic character to a benzenoid ring system. This was accomplished by synthesising the hydrocarbon, zethrene, which, according to the classical structure (IV), consists of an upper and lower naphthalene complex and two central double bonds which are fixed and can only promote electron transfer of a low order such as is found in the polyenes.



IV

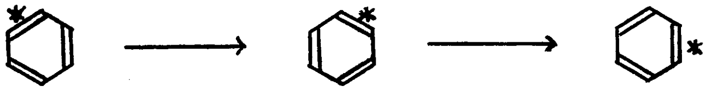


V

The properties of zethrene, e.g., its absorption spectrum, its ability to form salts with weak acids and its ease of reduction, are so extraordinary that it must be concluded that the hydrocarbon has a pronounced tendency to assume the structure (V), which has two localised electrons (indicated by dots) at the central carbon atoms and an external 8-shaped closed polyene system. This system is capable of forming three Kekulé structures as is the case for naphthalene.

The conclusion from these experiments is that a benzenoid hydrocarbon with only one Kekulé structure has no aromatic character and that it tends to assume a form which is capable of forming more Kekulé structures, even though a bond between two π-electrons is thereby partly sacrificed.

Aromatic resonance therefore demands the participation of at least two Kekulé structures, in which no double bond is isolated and which are of similar energy. The Kekulé structures of benzenoid hydrocarbons are, in effect, the transition states in the passage of a π-electron (*) through the ring system.



It should be noted that no experimental evidence has been obtained to support the idea that Dewar and other structures with long linkages, participate in the ground state of the normal aromatic hydrocarbon. These structures are only formed on excitation with light or by the action of strong acids, e.g., concentrated sulphuric acid, perchloric acid and $HAlCl_4$.

The molecular-orbital theory and this new definition of the aromatic state are compatible, if it is accepted that the π-electron pairs in the various levels cannot move independently of one another through the ring system, but must form Kekulé structures as transition states.

The Anellation Principle of E. Clar (21,22,23).

The absorption spectra of aromatic hydrocarbons have been resolved into three classes of bands by E. Clar (22 to 26) according to their behaviour under various physical conditions. The three classes have been termed α-, β-, and para-bands.

a). The para-bands, which shift to the red with a decrease in temperature, are the long wave bands in the spectra of anthracene and the higher acenes and the second group of bands in benzene and naphthalene. The para-bands shift strongly to the red on linear anellation in the acene series and slightly to the violet on angular anellation in the phene series (positive and negative anellation effect (24)). A considerable increase or decrease in reactivity, e.g., photo-oxidation and addition of maleic anhydride, is associated with these shifts and the para-bands are therefore attributed to an electronic transition from the ground state to an excited para- or Dewar form. In the acenes, the intensities of the para-bands lie between $\log \varepsilon = 3.5 - 4.3$.

b). The α-bands, which are less intense, shift slightly to the violet with decreasing temperatures. A strong shift to the red, which is accompanied by an increase in the reactivity of the central nucleus is obtained on anellation in the phene series. In the acene series, a similar shift is obtained on linear or angular anellation. The bands are the first group in the absorption spectra of benzene, naphthalene and the phenes. For anthracene and the higher acenes they are hidden, or partly hidden by the more intense para-bands. The intensities of the α-bands lie between log $\epsilon = 2 - 3$.

c). The β-bands, which are the most intense group of bands and which lie more in the ultraviolet, shift considerably to the red with decreasing temperatures. They show the same anellation effect as the -bands and it has been found that for uniplanar aromatic hydrocarbons, the ratio of the frequencies of the α- and β-bands is constant, viz. -

$$V_\alpha : V_\beta = \left(\frac{1}{2^2} - \frac{1}{3^2}\right) : \left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 1 : 1.35$$

The intensities of the β-bands lie in the region log $\epsilon = 5$.

From a study of the absorption spectra of aromatic hydrocarbons, E. Clar has shown that the wavelengths of the absorption bands can be calculated from the simple relationship $\lambda = K^2/R$, where K, which is called the Order Number of the hydrocarbon, is a simple function of the number of π electrons in it and R is a constant which can be related to Rydberg's Constant.

For example, when the α-bands of the phene series (benzene, naphthalene, phenanthrene, tetraphene, pentaphene and hexaphene) are compared, the similarity in type is striking. Moreover, an even closer relationship is apparent between each second group of bands. The wavelength of the first α-band of the above hydrocarbons can be calculated from $\lambda_\alpha = K^2/R_\alpha$ where $R_\alpha = 2194600$ cm^{-1} and the Order Numbers (K) equal $7\frac{1}{2}$, 8, $8\frac{1}{2}$, 9, $9\frac{1}{2}$ and 10 respectively (22).

In the same way the first band of the β-absorption of the phenes and acenes can be calculated from $\lambda_\beta = K^2/R_\beta$ where K has the same value for the hydrocarbons listed above and is equal to $8\frac{1}{2}$, 9, $9\frac{1}{2}$ and 10 for anthracene, tetracene, pentacene and hexacene. The constant R_β for this series is equal to 2962700 cm^{-1} and it is readily seen that the constants R_α and R_β are in the ratio

$$\left(\frac{1}{2^2} - \frac{1}{3^2}\right) : \left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 1 : 1.35$$

The significance of the Order Number (K) is that, with its help, the two constants R_α and R_β can be related to Rydberg's Constant (R) by the following simple equations:-

$$\frac{1}{\lambda_\alpha} = \bar{\nu}_\alpha = \frac{Z^2}{K^2} \cdot R \left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{ and } \frac{1}{\lambda_\beta} = \bar{\nu}_\beta = \frac{Z^2}{K_2} \cdot R \left(\frac{1}{2^2} - \frac{1}{4^2}\right).$$

where the Nuclear Charge (Z) = 12, which is double the

Nuclear Charge of carbon = 6. Both the above equations are comparable with Moseley's Equation for the calculation of the frequencies of the characteristic X-ray lines of the elements.

$$\nu = (Z - \sigma)^2 . R . \left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

where Z = Nuclear Charge = atomic number of the element

σ = The screening constant, which is approximately constant throughout any given series

R = Rydberg's Constant

n and m are integers.

In the acene series, the wavelength of the first para-band is calculated from the equation $\lambda = Kp^2/Rp$, where $Rp = 1712800\ \text{cm}^{-1}$. In this series, however, the Order Number (Kp) does not have the same value as the Order Number (K) used in the calculation of the wavelengths of the first β-bands of the acenes, but is equal to 6, 7, 8, 9, 10 and 11 for benzene, naphthalene, anthracene, tetracene, pentacene and hexacene. The relationship between the two Order Numbers is given by the equation:

$$Kp = 2K - 9.$$

This Principle and its theoretical implications have been developed and extended by E. Clar, and other anellation series have been found, e.g.,

i) the para-bands of the perylenes,

ii) the para-bands of the pyrenes,

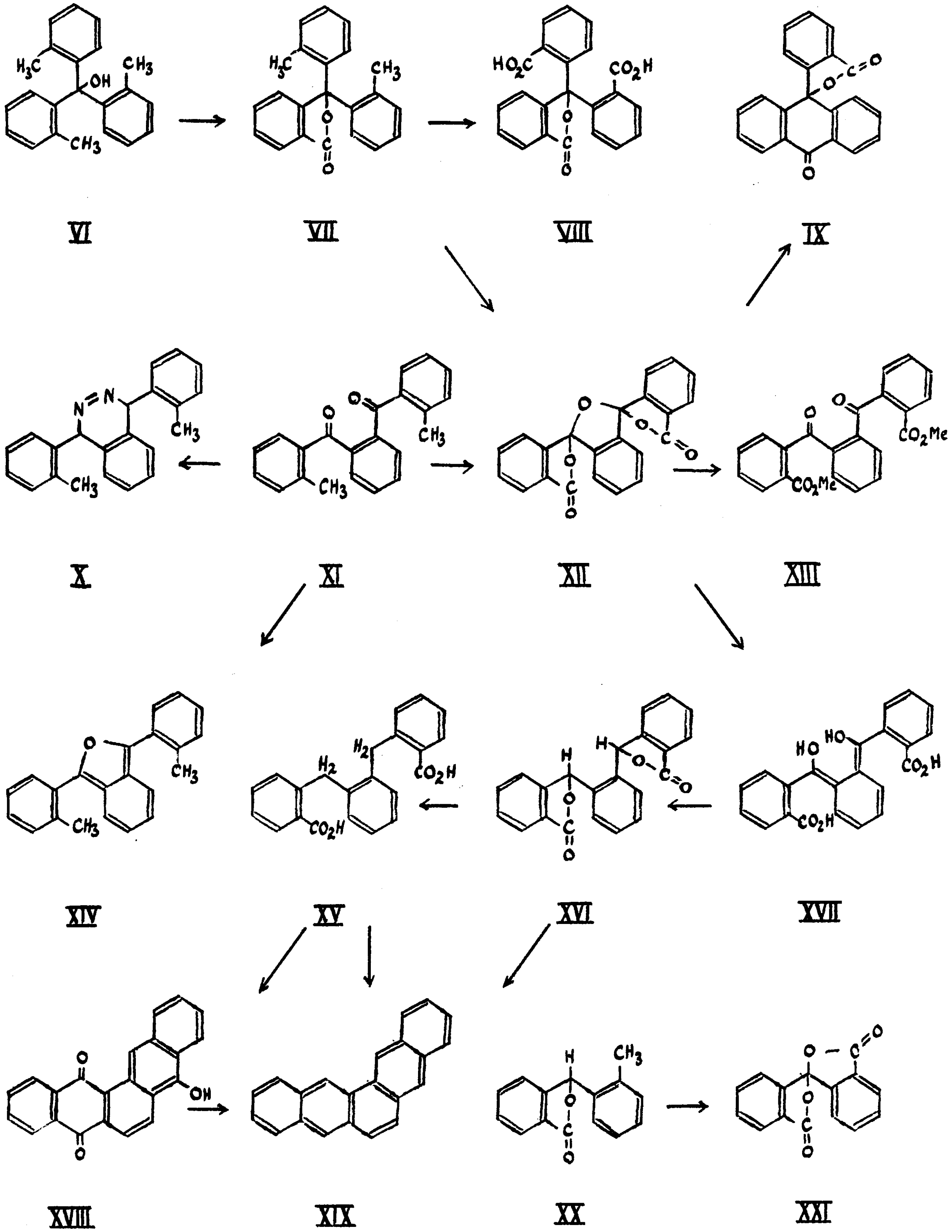
iii) the para-bands of the peropyrenes.

In the present work, the absorption spectra of new hydrocarbons which have been synthesised have been studied and where applicable have been fitted into the Anellation Principle, thereby giving new anellation series.

The Synthesis of Pentaphene (5).

Compounds having the triangulene skeleton have been synthesised (Weisz *et alia*, (6)(7)) and their method was first adopted. These authors have claimed that the two products of different melting point, obtained from the reaction of *o*-tolylmagnesium bromide with phthalic anhydride, have the phthalide constitution. The higher melting (m.p. 176°) has now been synthesised by the oxidation of tri-*o*-tolylcarbinol (VI) with dilute nitric acid and is without doubt di-*o*-tolylphthalide (VII). The properties of tri-*o*-tolylcarbinol prepared by us agree with those described for samples prepared by different methods (8)(9).

We have found, however, that the second product (m.p. 128-131°) prepared by Weiz *et alia* (6)(7) is a mixture of the phthalide (VII) and 1:2-di-*o*-toluoylbenzene (XI) and that the tendency to form the latter is so pronounced that even the reaction of *as*-phthaloyl chloride with *o*-tolylmagnesium bromide yields mostly the diketone (XI) and only a little phthalide (VII). Mono-*o*-tolylphthalide (XX) and 2-*o*-toluoylbenzoic acid were obtained as by-products, both of which gave benzophenone-2:2'-dicarboxylic acid dilactone (XXI) on oxidation with alkaline potassium permanganate solution.


VI
VII
VIII
IX
X
XI
XII
XIII
XIV
XV
XVI
XVII
XVIII
XIX
XX
XXI

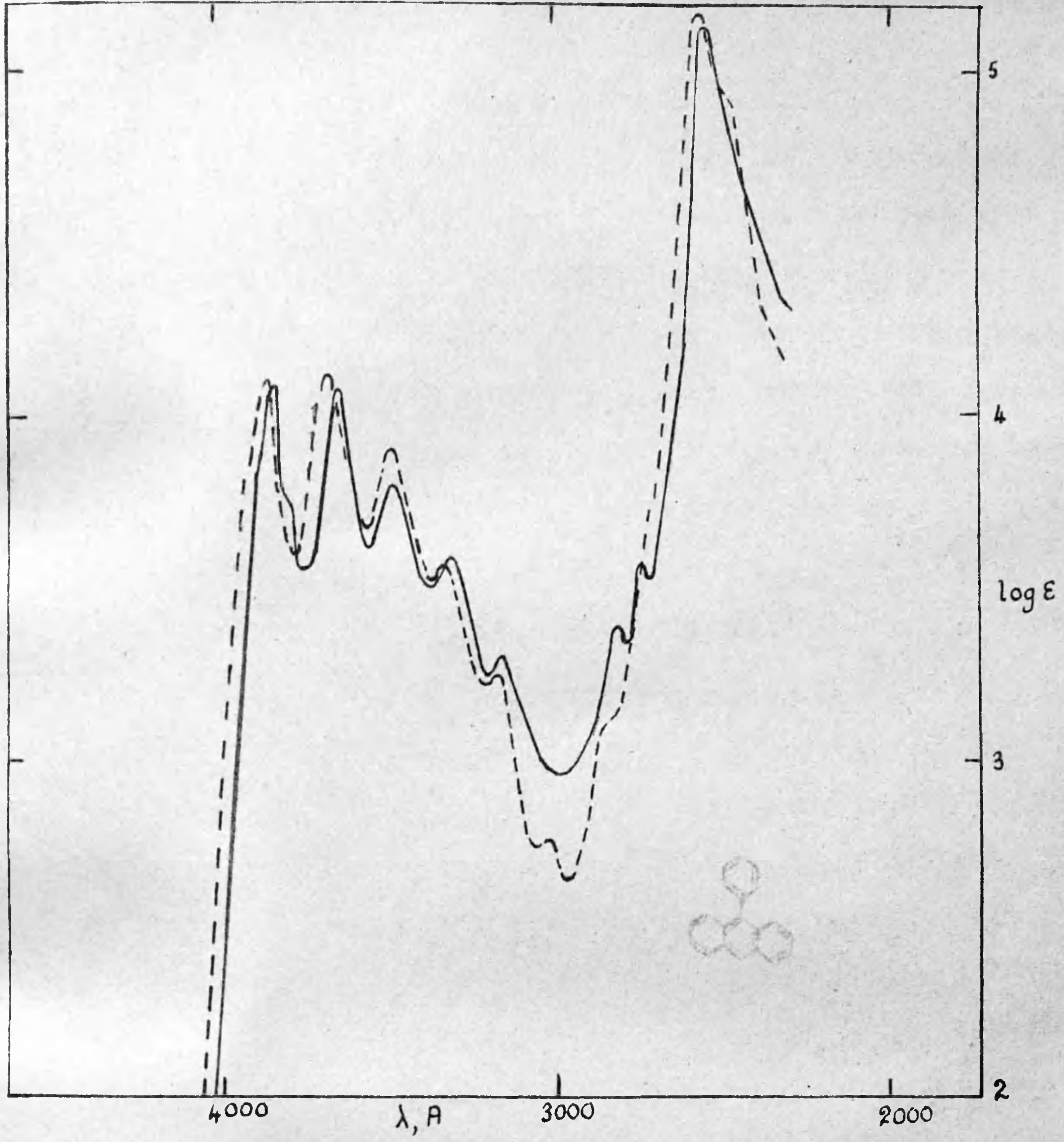
The structure of the diketone (XI) was proved by its condensation with hydrazine hydrate to give 1:4-di-o-tolylphthalazine (X). This reaction also proved a method of isolating the pure phthalide (VII) from the mixture (m.p. 128-131°), as the azine remained in the alcoholic solution, while the phthalide crystallised out unchanged. A good qualitative test for the presence of the diketone (XI) is the reduction with zinc dust in acetic acid which yields a yellow blue-fluorescent solution of the isobenzofuran (XIV). The interesting properties of the corresponding diphenyl compound were studied in detail by Guyot and Catel (10).

The pure diketone (XI) melted at 146°; when mixed with an equal amount of the pure phthalide (VII), a melting point of 125-128° was observed, which corresponds with the m.p. of the second alleged phthalide (Weisz *et alia*, (6)(7)).

The diketone (XI) was oxidised with dilute nitric acid under pressure or alternatively in two stages, *viz.*, first with dilute nitric acid solution and then with alkaline potassium permanganate solution, to a dicarboxylic acid which crystallised from acetic acid as the dispiran (XII). Similar oxidations of the phthalide (VII) gave, owing to a rearrangement which is the reverse of the benzilic acid rearrangement, good yields of the dispiran (XII) with only a small proportion of the unrearranged dicarboxylic acid (VIII). The latter could not be crystallised but owing to its solubility in acetic acid, the pure dispiran (XII) was readily obtained by oxidation of the mixture of (VII) and (XI) resulting from the Grignard reaction of phthalic anhydride with o-tolylmagnesium bromide, and crystallisation from acetic acid.

The dispiran (XII), when heated with copper powder at 350°, gave on sublimation a compound which proved to be 9-(o-carboxyphenyl)oxanthranol lactone (IX). The formation of this compound, whose properties agree with those of a sample prepared by Scholl and Donat (11), can be explained by a ring-closure, such as takes place in the formation of (IX) from 2-(o-carboxybenzoyl)benzophenone (LIX). When the dispiran (XII) was submitted to the zinc dust fusion procedure of Clar (12) a product was obtained whose structure could not be established, although its absorption spectrum, shown in Fig.1, compared with that of 9-phenylanthracene, proves it to be an anthracene derivative.

It is noteworthy that the melting points of the dispiran (XII) correspond exactly with that of the triphenylmethane-2:2':2"-tricarboxylic acid of Weisz and



—— Anthracene derivative in alcohol. Band maxima in A: 3840, 3650, 3470, 3300, 3150; 2820, 2720; 2540.

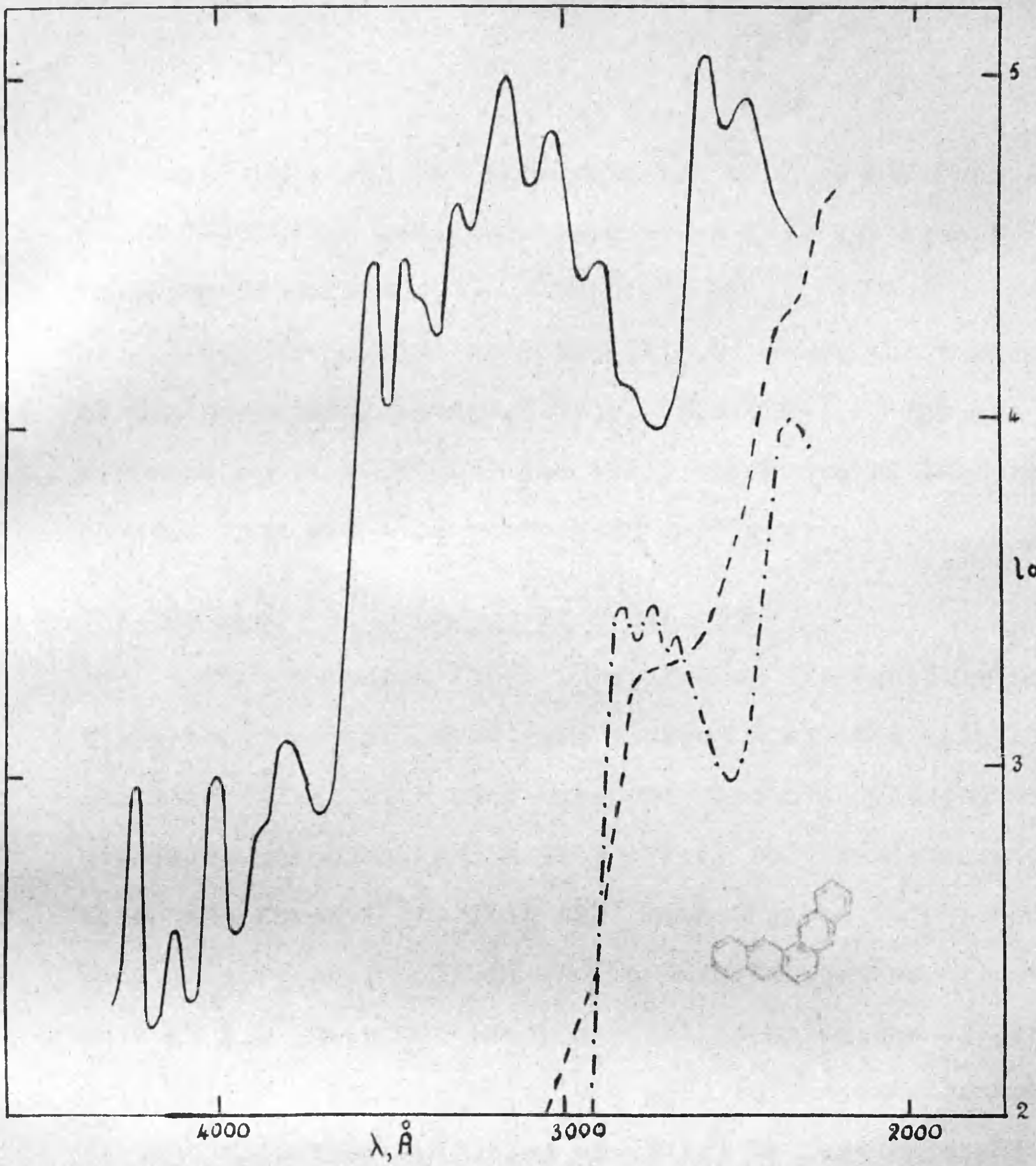
- - - 9-Phenylanthracene in alcohol. Band maxima in A: 3840, 3675, 3465, 3305, 3160, 3020; 2555.

FIG. 1.

Korczyn (6) and that the melting points of their methyl esters are also very similar. It is possible that the compounds analysed by these authors were the dispiran (XII) and its methyl ester (XIII), formed by rearrangement as described above. However, as they undoubtedly obtained compounds with the triangulene skeleton, the material used in further condensations must have contained the tricarboxylic acid.

The dispiran (XII) was reduced quantitatively with zinc dust and dilute sodium hydroxide solution to the double phthalide (XVI). In the initial stages of this reduction a transitory red colour is developed which disappears after five or ten minutes' boiling. The red colour is obviously due to the formation of the intermediate stage (XVII) containing an o-quinonoid structure. Further reduction of the diphthalide (XVI) with hydriodic acid and red phosphorus gave the acid (XV) and also, due to a simultaneous ring closure, pentaphene (XIX). Ring closure of the acid (XV) with concentrated sulphuric acid gave the reddish-brown 8-hydroxypentaphene-5:14-quinone (XVIII). When (XV) and (XVIII) were submitted to the zinc dust fusion procedure of Clar (12), pentaphene (XIX) was obtained.

This preparation of pentaphene is simpler and more



——— Pentaphene (**XIX**) in alcohol. Band maxima in A: 4235, 4120, 3990, 3790; 3560, 3450, 3290; 3145, 3020, 2895; 2575, 2450.

-·-·-· o-Di-(3-phthalidyl) benzene (**XVI**) in alcohol. Band maxima in A: 2820, 2750, 2680; 2350.

- - - - Disodium salt of 1:2-di-o-carboxybenzyl benzene (**XV**) in water. Band maximum at 2700 A.

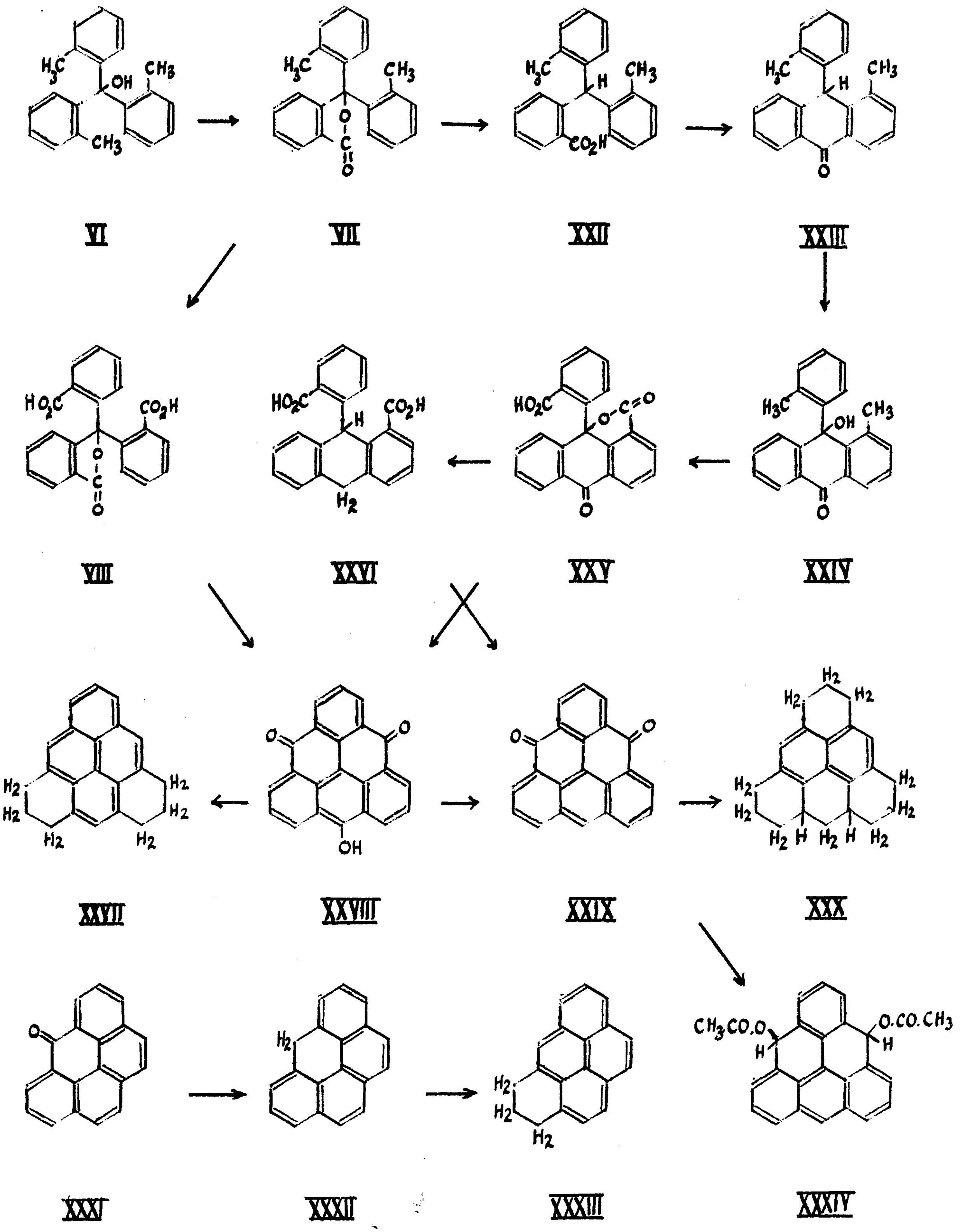
FIG. 2.

efficient than the earlier synthesis of Clar and John (13) which involves a laborious separation from the accompanying dihydropentacene.

The absorption spectrum (Fig.2) shows the purity of the pentaphene obtained (c.f. Clar (14)). The absorption spectra of (XV) and (XVI) which are of the simple benzene type are also reproduced in Fig.2.

The Synthesis of Triangulene Derivatives.

The phthalide (VII), prepared by the oxidation of tri-o-tolylcarbinol (VI), was reduced quantitatively to the acid (XXII) with zinc dust and alcoholic potassium hydroxide solution, which is contrary to the statement by Weisz and Korczyn (6) that this method gives poor yields. Ring closure of (XXII) in a zinc chloride-sodium chloride melt at 210° gave the anthrone (XXIII) which was oxidised with dilute nitric or selenious acid to the oxanthranol (XXIV). Further oxidation of (XXIV) by heating at 210° with nitric acid under pressure gave a mixture of an unidentified by-product, which did not contain nitrogen, and the lactone acid (XXV). The mixture was readily separated by crystallisation from acetic acid, and reduction of the acid (XXV) with zinc dust and sodium hydroxide solution yielded a product, which was proved to be the


VI
VII
XXII
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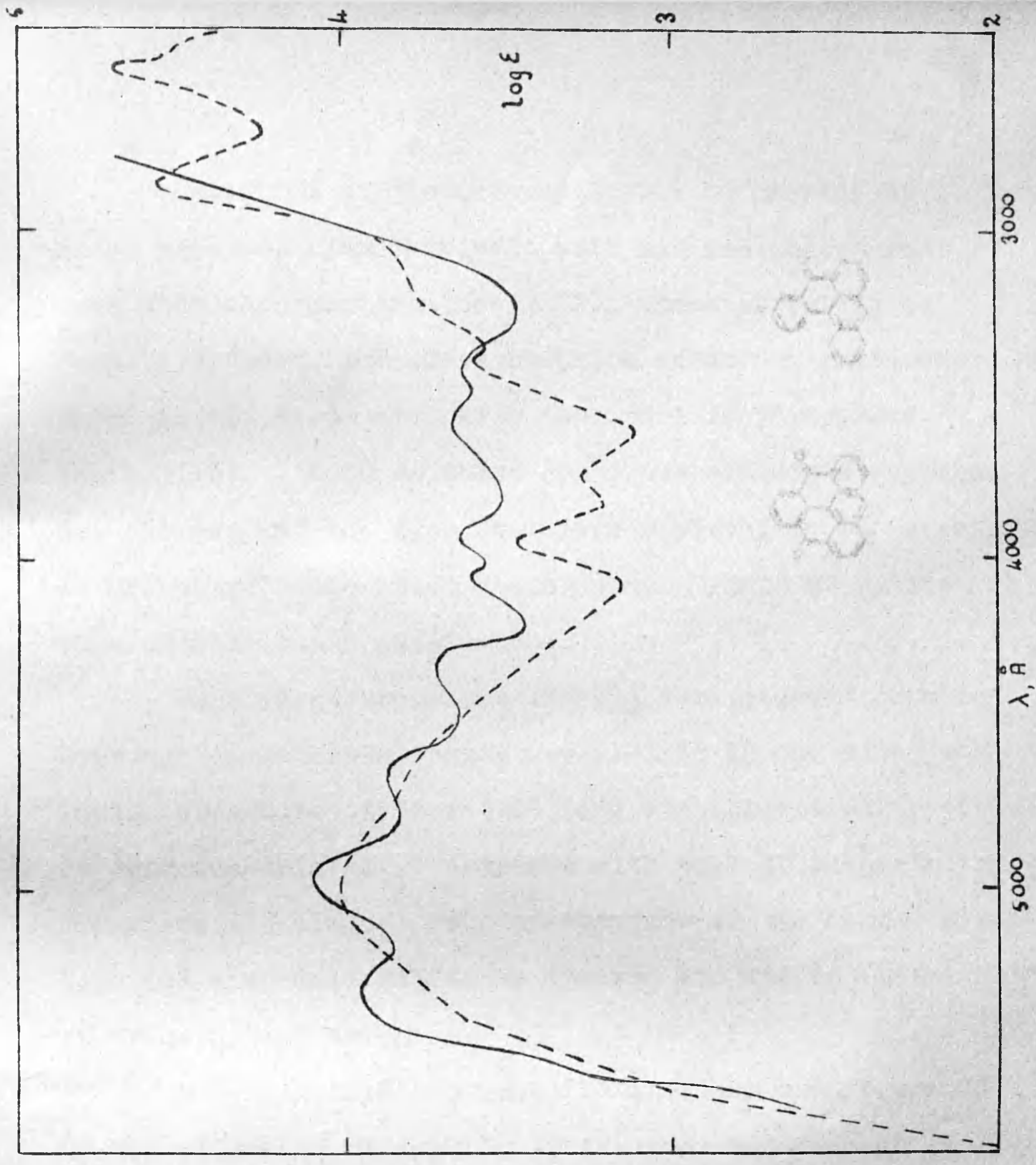
XXVI
XXV
XXIV
XXVII
XXVIII
XXIX
XXX
XXXI
XXXII
XXXIII
XXXIV
H3C
OH
CH3
O-C=O
H
CO2H
HO2C
H2
CH3CO.O
O.CO.CH3

dihydroanthracene derivative (XXVI) by its absorption spectrum which was of the simple benzene type.

The dark blue 12-hydroxytriangulene-4:8-quinone (XXVIII) was obtained from the lactone acid (XXV) or the crude unrearranged dicarboxylic acid (VIII) by heating at 120° with concentrated sulphuric acid and copper powder, and its properties agreed with those of a sample prepared by Weisz and Korczyn (6). It is a strong acid giving deep blue solutions in alkalis, in basic solvent, e.g., pyridine and in sodium acetate solution, and must be largely ionic in character, for on acetylation by heating in acetic anhydride a deep red solution is obtained, as would be expected for the covalent acetoxytriangulene quinone. The acetyl derivative, however, is unstable and hydrolyses very readily (cf. Weisz and Muller, (7)).

A short reduction of 12-hydroxytriangulene-4:8-quinone (XXVIII) with zinc dust in sodium hydroxide solution, followed by reoxidation with a stream of oxygen, gave the red triangulene-4:8-quinone (XXIX), which was also prepared by the ring closure of the dihydroanthracene derivative (XXVI) with concentrated sulphuric acid. The absorption spectrum of the quinone (XXIX) is reproduced in Fig.3 compared with that of coeranthrone (LXI) to which it is closely related.



——— Triangulene-4:8-quinone (XXIX) in benzene. Band maxima in A: 5340, 4980, 4650, 4340; 4080, 3950; 3600 3430.

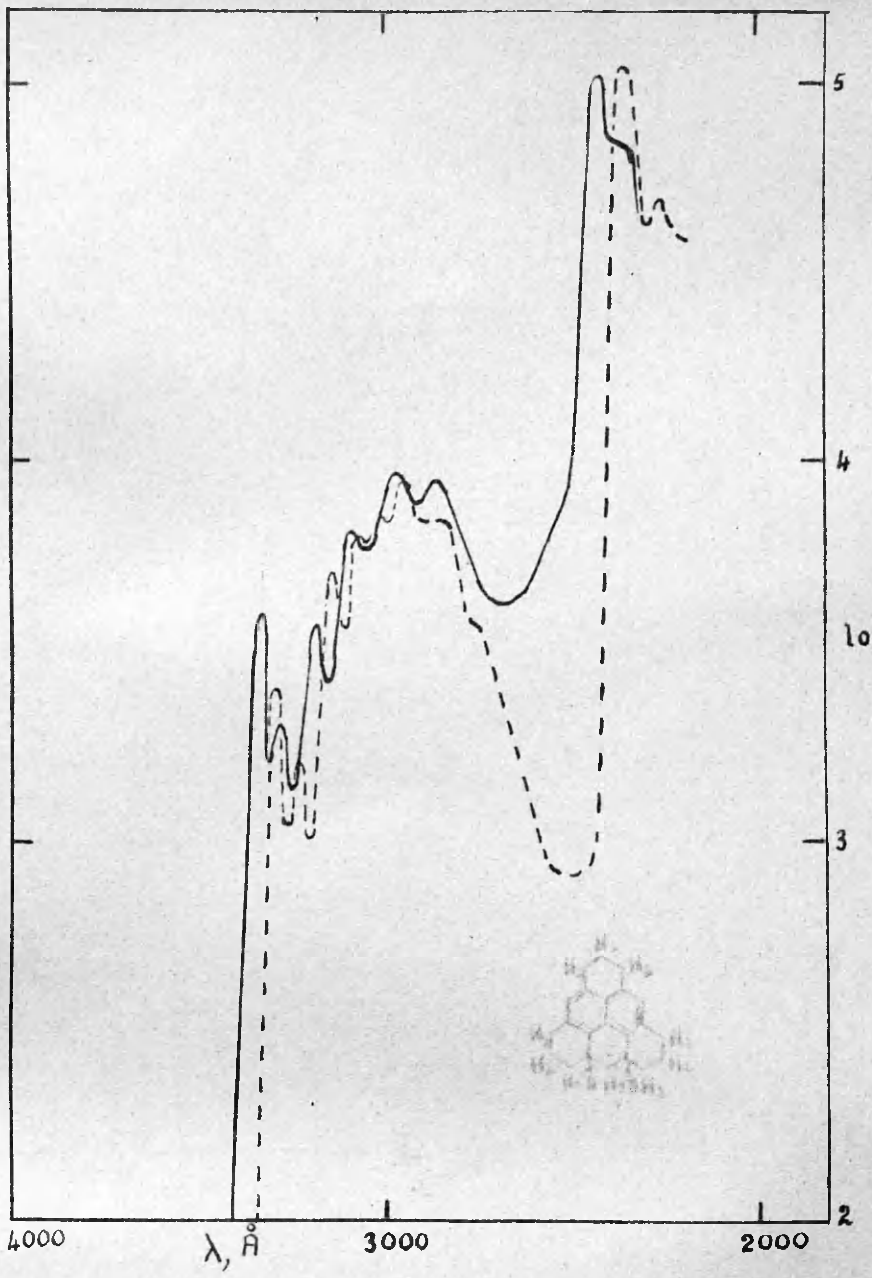
- - - - Coeranthrone (LXI) in alcohol. Band maxima in A: 4970; 3930, 3740; 3280, 3140; 2840 ; 2500.

Fig.3.

Reduction of the quinone (XXIX) by heating at 210° under pressure with hydriodic acid and red phosphorus gave dodecahydrotriangulene (XXX), whose structure is readily deduced from its absorption spectrum, which is shown in Fig.4 compared with that of hexahydropyrene (XLVII)(15). Both of these compounds contain a naphthalene complex and the fine structure apparent in the spectra is probably due to their having a more rigid structure than unsubstituted naphthalene.

Hexahydrotriangulene (XXVII) was prepared from 12-hydroxytriangulene-4:8-quinone (XXVIII) by the zinc dust fusion procedure of Clar (12), and its absorption spectrum is reproduced in Fig.5 compared with that of 2:3-trimethylenepyrene (XXXIII). Both spectra are of the simple pyrene type and the small shifts to the red are due to the addition of trimethylene bridges.

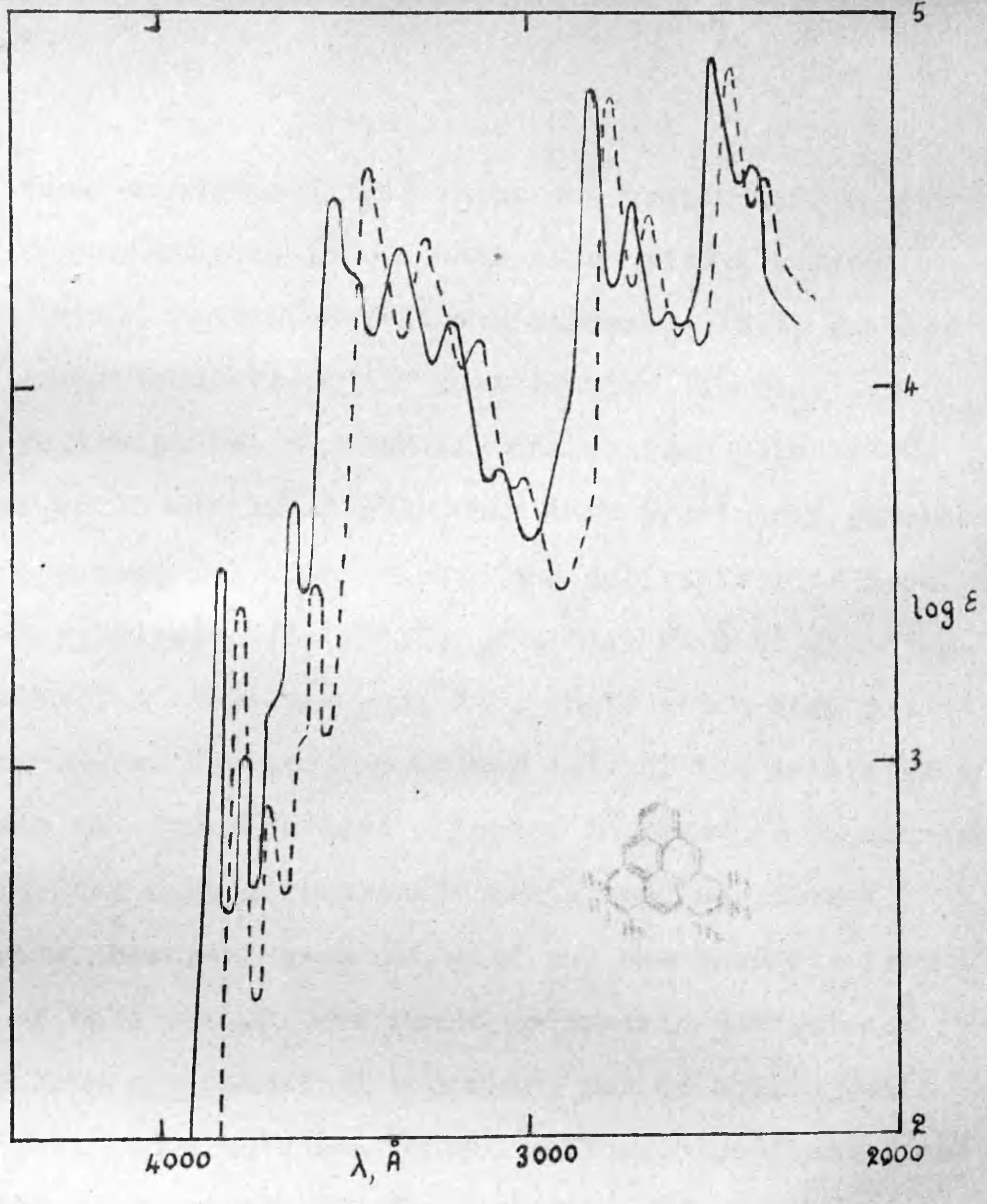
2:3-Trimethylenepyrene (XXXIII) has been prepared by the reduction of naphtho-(2':7'-1:8)-anthrone-10 (XXXI) with hydriodic acid and red phosphorus (16), or more conveniently by the zinc dust melt of Clar. Chromatographic purification (alumina) of the crude product gave a colourless compound (m.p. 112-113°) and it is probable that the yellow product (m.p. 107-108°) obtained by Scholl and Meyer (16) contained a small percentage of anthanthrene.



——— Duodecahydrotriangulene (XXX) in alcohol. Band maxima in A: 3350, 3280, 3180; 3060, 2950, 2860; 2420.

------- Hexahydropyrene (XLVII) in heptane. Band maxima in A: 3300, 3240, 3150; 3100, 3025, 2975, 2875; 2350, 2250.

FIG. 4



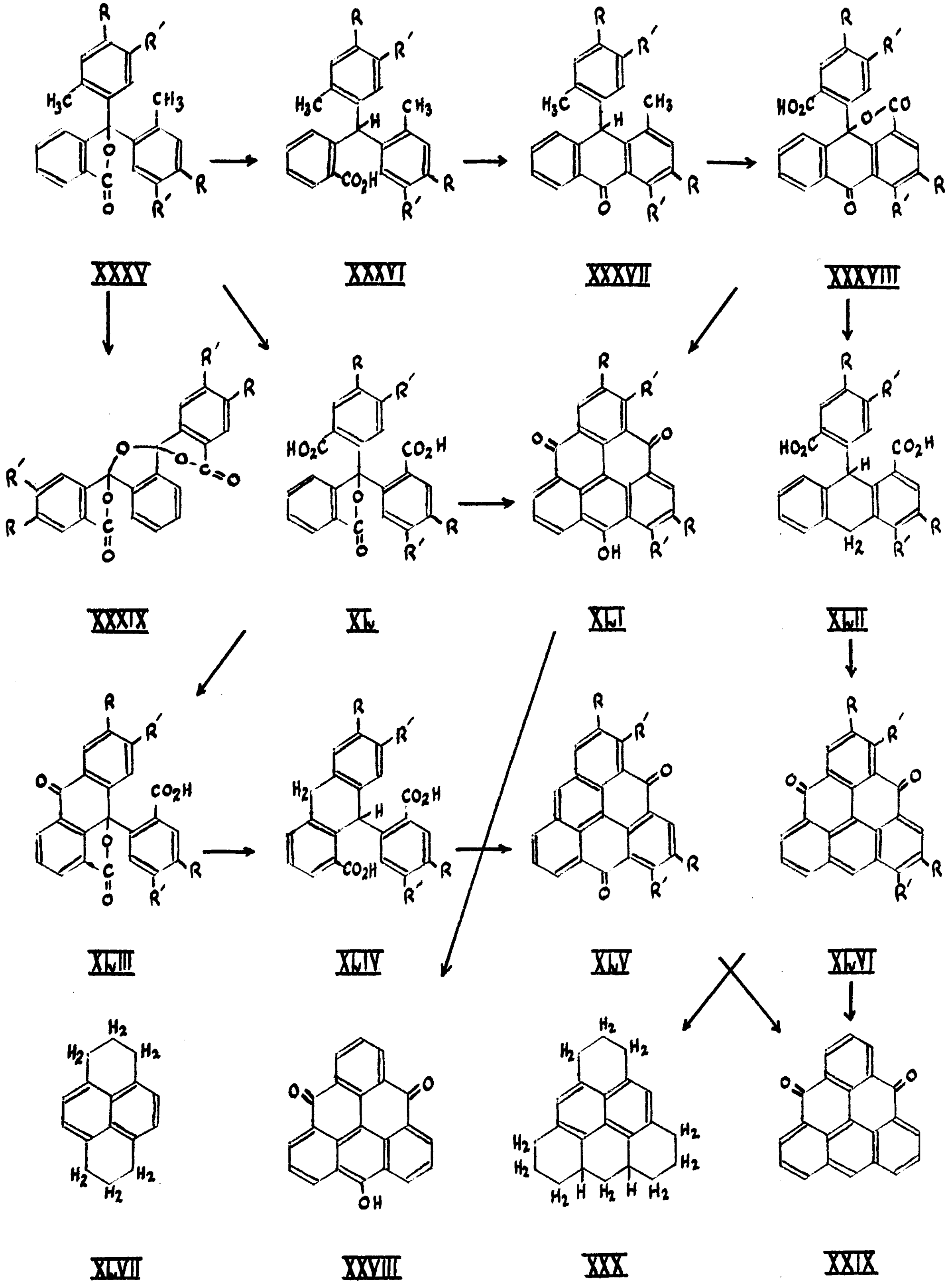
———— Hexahydrotriangulene (XXVII) in alcohol. Band maxima in A: 3830, 3765, 3625; 3515, 3350, 3200, 3070; 2815, 2700, 2590; 2480, 2380.

-------- 2:3-Trimethylenepyrene (XXXIII) in alcohol. Band maxima in A: 3780, 3700, 3575; 3430, 3270, 3130, 3010; 2770, 2660, 2550; 2445, 2345.

Fig. 5.

Naphthanthrone (XXXI) which was prepared from pyrene by a benzanthrone type condensation with glycerol (cf. Vollmann, Becker, Corell and Streeck, (17)), was obtained after chromatographic purification (alumina) as bright yellow plates or needles, the melting point (252-253°) of which was 10° higher than that previously reported.

A second route to triangulene derivatives is from the di-m-xylylphthalide (XXXV; $R = CH_3$, $R' = H$) and di-p-xylylphthalide (XXXV; $R = H$, $R' = CH_3{}'$) which were prepared by Weisz, Spitzer and Melzer (18) by the interaction of xylene and sym-phthaloyl chloride in presence of aluminium chloride, carbon disulphide being used as solvent. The yields, however, were not good and the products from a repeat of this method were found to contain o-diketones derived from sym-phthaloyl chloride, for on boiling with acetic acid and zinc dust, bright yellow, blue-fluorescent solutions were obtained. The formation of these o-diketones is due to the reactive xylenes combining with the sym-phthaloyl chloride, before isomerisation to the as-phthaloyl chloride by the action of aluminium chloride (19) can take place. In support of this it has been shown (20) that a similar reaction with the very reactive hydrocarbon, mesitylene, yields 81% o-diketone.


XXXV
XXXVI
XXXVII
XXXVIII
XXXIX
XL
XLI
XLII
XLIII
XLIV
XLV
XLVI
XLVII
XXVIII
XXX
XXIX

To overcome this difficulty, a complex of as-phthaloyl chloride with excess aluminium chloride was first formed (19) and the powdered solid added to the xylene. The phthalides (XXXV) obtained by this method were free from o-diketones and the yields were greatly improved.

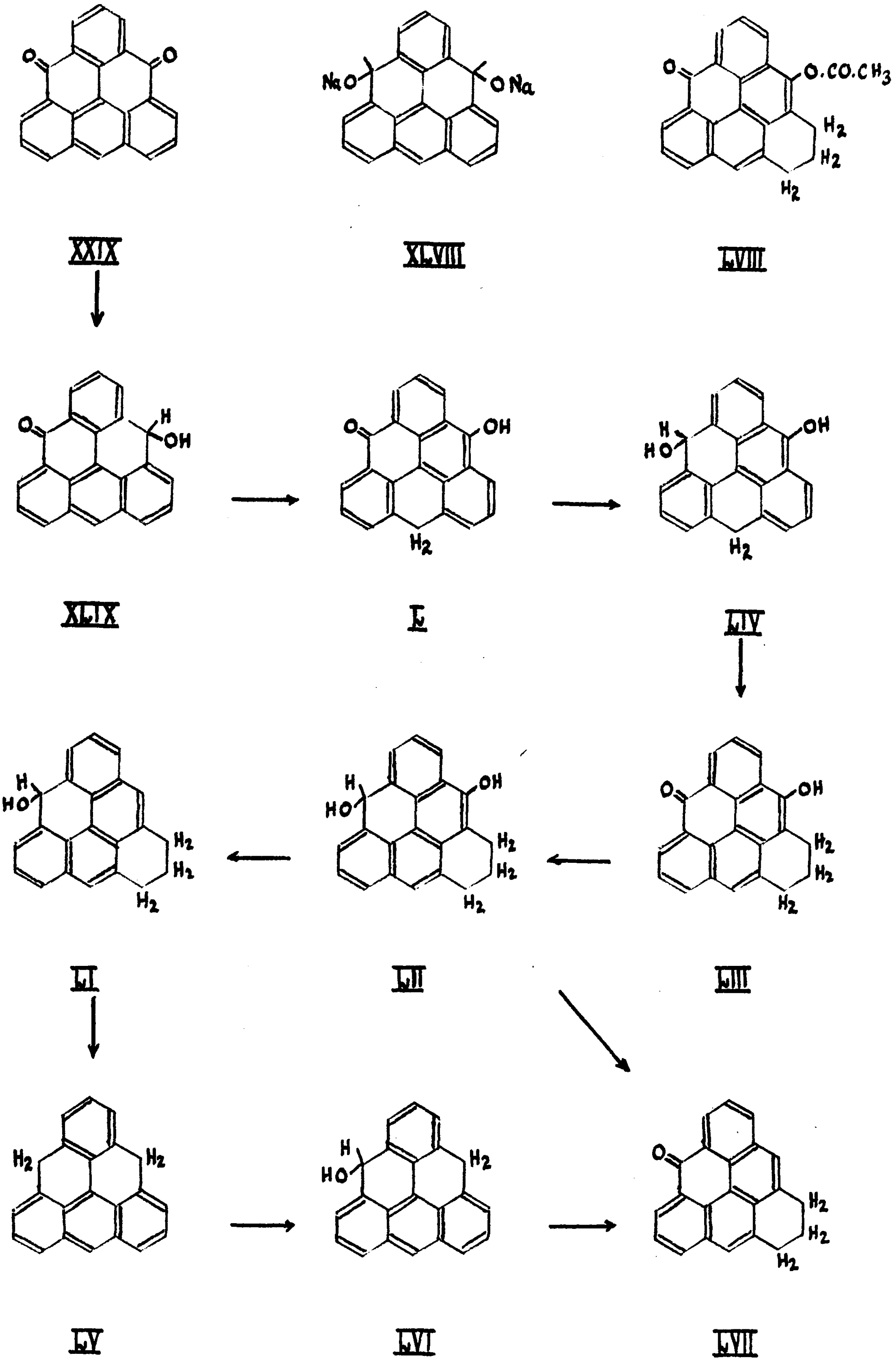
Oxidation of the phthalides (XXXV), first with nitric acid followed by alkaline potassium permanganate solution, resulted in a rearrangement which is completely analogous to that which occurs during the oxidation of di-o-tolylphthalide (VII), and the dispirans (XXXIX) were obtained. As was expected, decarboxylation of these dispirans by heating with copper powder at 350° yielded 9-(o-carboxyphenyl)oxanthranol (IX). The acetic acid mother liquors from the crystallisations of the dispirans gave on concentration and dilution with water viscous products which could not be crystallised but which mainly consisted of the unrearranged acids (XL).

The phthalides (XXXV) were reduced quantitatively to the acids (XXXVI), which were ring closed to the anthrones (XXXVII). Oxidation of these in two stages gave the lactone acids (XXXVIII) which on reduction yielded the dihydroanthracene derivatives (XLII). The structures of the latter were proved by their absorption spectra which are of the simple benzene type. The dark red triangulene quinone dicarboxylic acids (XLVI) were prepared from (XLII) by heating with concentrated sulphuric acid, a little m-nitrobenzene sulphonic acid being added to take up excess hydrogen. These acids (XLVI) were converted (a) to triangulene-4:8-quinone (XXIX), by vacuum sublimation from copper powder, and (b) to dodecahydrotriangulene (XXX) by reduction with hydriodic acid and red phosphorus under pressure and distilling the crude reduction product in a vacuum from soda lime.

To utilise the crude unrearranged acids (XL), the following steps were carried out, (a) XL —— XLI —— XXVIII and (b) XL —— XLIII —— XLIV —— XLV —— XXIX. In the first route (a), the acids (XL) were heated in concentrated sulphuric acid with copper powder at 150°, and dark blue products (XLI) were obtained, whose properties agreed with those of samples prepared by Weisz *et alia* (18). These were purified by thorough extraction with boiling acetic acid and were decarboxylated to 12-hydroxytriangulene-4:8-quinone (XXVIII) by boiling in quinoline with a copper chromite catalyst.

The intermediate stages of the second route (b) showed little tendency to crystallise and could not be obtained in an analytically pure state. However, the proposed structures are in agreement with the properties of the compounds isolated. The acids (XL) when heated at 150° with concentrated sulphuric acid gave colourless compounds (XLIII) which were reduced to the colourless dihydroanthracene derivatives (XLIV). Ring closure of (XLIV) followed by decarboxylation of the resulting dark red triangulene quinone dicarboxylic acids (XLV) as above yielded the well-defined triangulene-4:8-quinone (XXIX).

When hexahydrotriangulene (XXVII) was dehydrogenated by subliming it over a palladium-charcoal catalyst (27, 28, 29) at 310° in a vacuum, it was absorbed completely into the catalyst and no sublimate was obtained. The activity of the catalyst was carefully tested before and after the application of the hydrocarbon by the dehydrogenation of 9:10-dihydroanthracene (m.p. 105°) and in all cases pure anthracene was obtained. Even when the catalyst was heated to 500° in a vacuum no sublimate was obtained and as a dimeride of triangulene would have sublimed under such conditions, it must therefore be assumed that polymerisation was complete. A similar result was obtained when hexahydrotriangulene (XXVII) was dehydrogenated in trichlorobenzene with a palladium-charcoal catalyst at 200°. Here the absorption spectrum of 4:8-dihydrotriangulene (LV) was observed as an intermediate stage of dehydrogenation, but owing to immediate polymerisation no absorption of triangulene became visible.


XXIX
NaO
ONa
XLVIII
O.CO.CH3
H2
LVIII
H
OH
XLIX
L
HO
LIV
LI
LII
LIII
LV
LVI
LVII

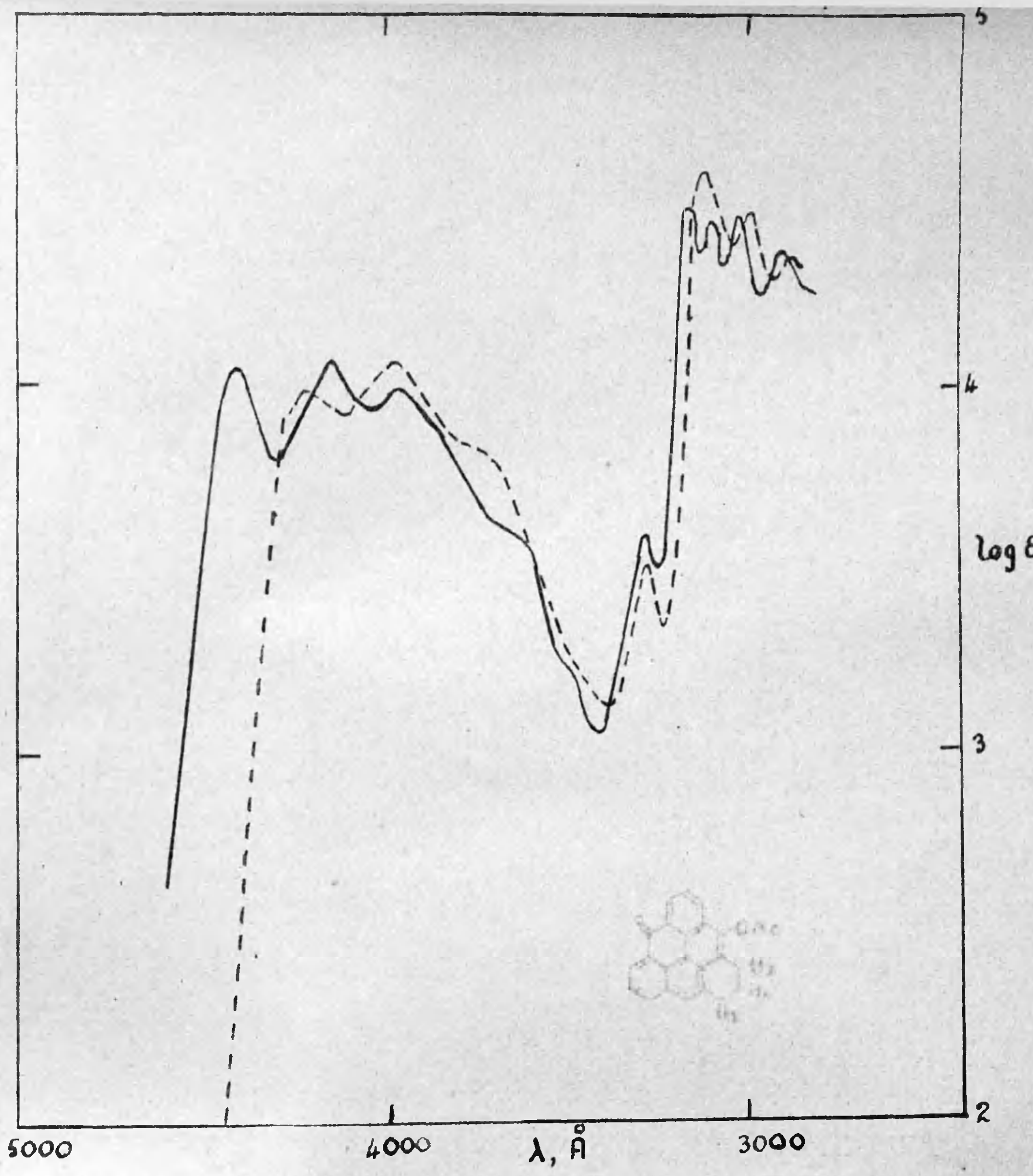
Another attempt to obtain triangulene by dehydrogenation was made using dodecahydrotriangulene (XXX). When this hydrocarbon was melted with a palladium-charcoal catalyst under pure carbon dioxide (30 to 33) at 200° a brisk evolution of hydrogen was observed which when collected corresponded roughly to the formation of hexahydrotriangulene (XXVII). On heating at 250° a new evolution of hydrogen was observed, but at a greatly reduced rate. After five hours, high vacuum sublimation of the residue yielded only some hexahydrotriangulene (XXVII) and no other triangulene derivative was detected.

The complete polymerisation of triangulene under conditions in which even the most reactive aromatic hydrocarbons, such as hexacene (34, 35) and 1:2-benzhexacene (36) can be prepared, indicates that triangulene is an unstable diradical. As has already been stated, the interpretation of this result is that Kekulé structures are of paramount importance when considering the stability of aromatic hydrocarbons.

This view is further supported by the results obtained from the reduction of triangulene-quinone (XXIX). A superficial observation suggests that triangulene-quinone forms a blue-green vat with alkaline sodium dithionite solution which dyes cotton green and which, after oxidation, changes to red. If this were a true vat, it would be derived from the diradical formula (XLVIII). However the analysis of the blue sodium salt shows that it contains only one atom of sodium and it must therefore be derived from the formula (XLIX). The "vat" therefore results from the reduction of one carbonyl group only and does not prove that triangulene-quinone has quinonoid properties. Moreover acidification of the blue-green "vat" with acetic acid gives the free, violet-blue hydroxy compound, which has properties similar to those of coeranthronol (11) as would be expected from the formula (XLIX).

Further reduction of triangulene-quinone (XXIX) with zinc dust and sodium hydroxide solution gave, after the acidification of the greenish-yellow solution, a brown product, the acetate (LVIII) of which has an absorption spectrum (Fig.6) closely related to those of naphtho-(2':7'-1:8)anthrone (XXXI) and 1:2:3:8-tetrahydro-8-keto-triangulene (LVII) (Fig.7). The compound must therefore have the structure (LIII). Its formation can be explained by the reduction of the second carbonyl group to give (LIV), followed by the migration of three hydrogen atoms to give (LIII), a rearrangement which seems to be typical for triangulene derivatives of this kind.

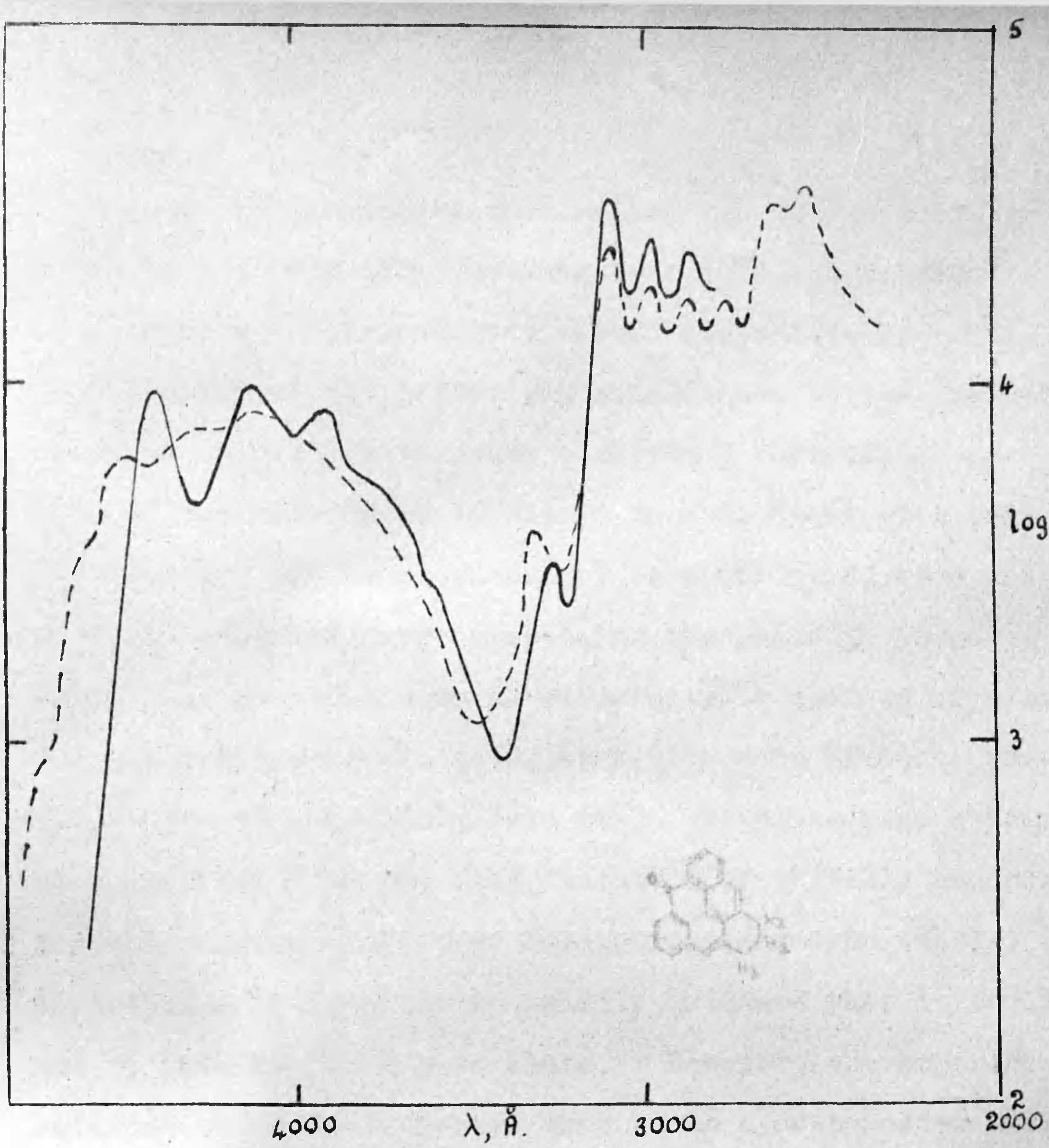
Prolonged treatment with zinc dust and sodium hydroxide solution reduced triangulene-quinone (XXIX) to



——— 1:2:3:8- Tetrahydro-4-acetoxy-8-ketotriangulene (LVIII) in benzene. Band maxima in Å: 4395, 4140, 3940; 3270; 3150, 3090, 3010, 2880.

------ Naphtho-2'7'-1;8-anthrone (XXXI) in benzene. Band maxima in Å: 4160, 3950; 3250; 3070, 2970.

Fig. 6.



——— 1:2:3:8-Tetrahydro-8-ketotriangulene (LVII) in benzene. Band maxima in A: 4400, 4190, 3930; 3275; 3110, 3000, 2880.

------ 1:2:3:8-Tetrahydro-8-ketotriangulene (LVII) in alcohol. Band maxima in A: 3320; 3100, 2980, 2875, 2770; 2535.

Fig. 7.

(LII) and (LI), which on sublimation ina vacuum lost water to give 4:8-dihydrotriangulene (LV) and 1:2:3:8-tetrahydro-8-ketotriangulene (LVII) respectively. The constitution of the latter was established by its absorption spectrum (Fig.7) which bears a striking resemblance to that of naphthanthrone (XXXI). In accordance with this formulation, the compound cannot be acetylated, does not show any phenolic properties being insoluble in strong alkali and is reduced to an autoxidisable product with zinc dust in boiling acetic acid, as in the case of benzanthrone.

4:8-Dihydrotriangulene (LV), which was also obtained as a by-product in the zinc dust melt of (XXVIII) and during the dehydrogenation of hexahydrotriangulene (XXVII) in trichlorobenzene, is so readily oxidised that it could not be obtained in a pure state. However, the experimental evidence obtained indicates that it is a deep yellow hydrocarbon with absorption bands at 4630A and 4440A. The oxidation product, which is formed during purification, is 1:2:3:8-tetrahydro-8-ketotriangulene (LVII) and, as the carbinol (LVI) is the most probable intermediate stage, the formation of (LVII) is a remarkable example of the above-mentioned rearrangement. (LIII), (LV) and (LVII) were also obtained by the reduction of triangulene-quinone (XXIX) with zinc dust in acetic acid.

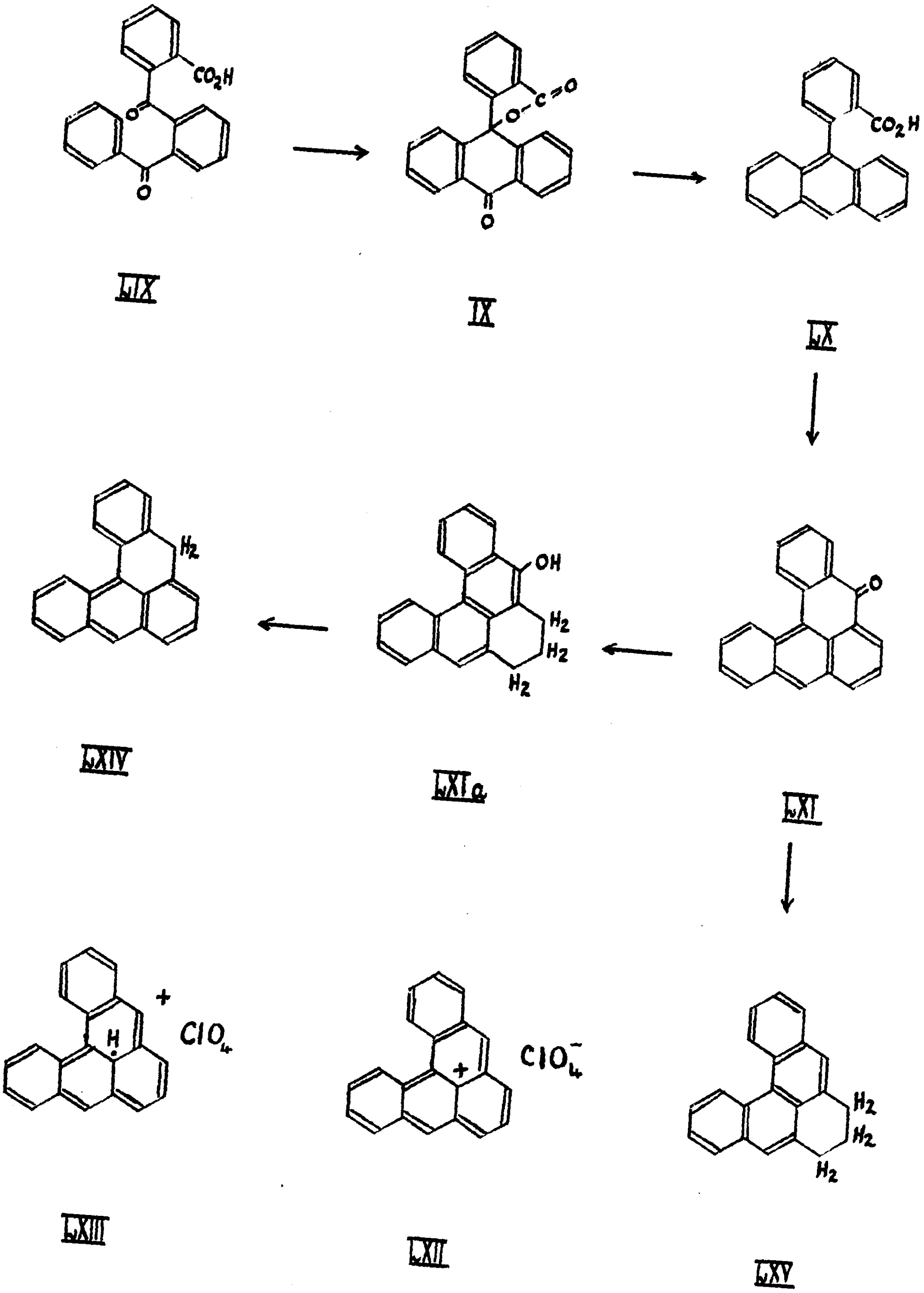
The only derivative of 4:8-dihydrotriangulene (LV), which can be obtained by the direct reduction of triangulene-quinone (XXIX), is the diacetate (XXXIV). Since it only contains two hydroaromatic H atoms, no rearrangement to a trimethylene compound is possible. As would be expected for a derivative of 4:8-dihydrotriangulene (LV), it readily oxidises in air and decomposes on heating.

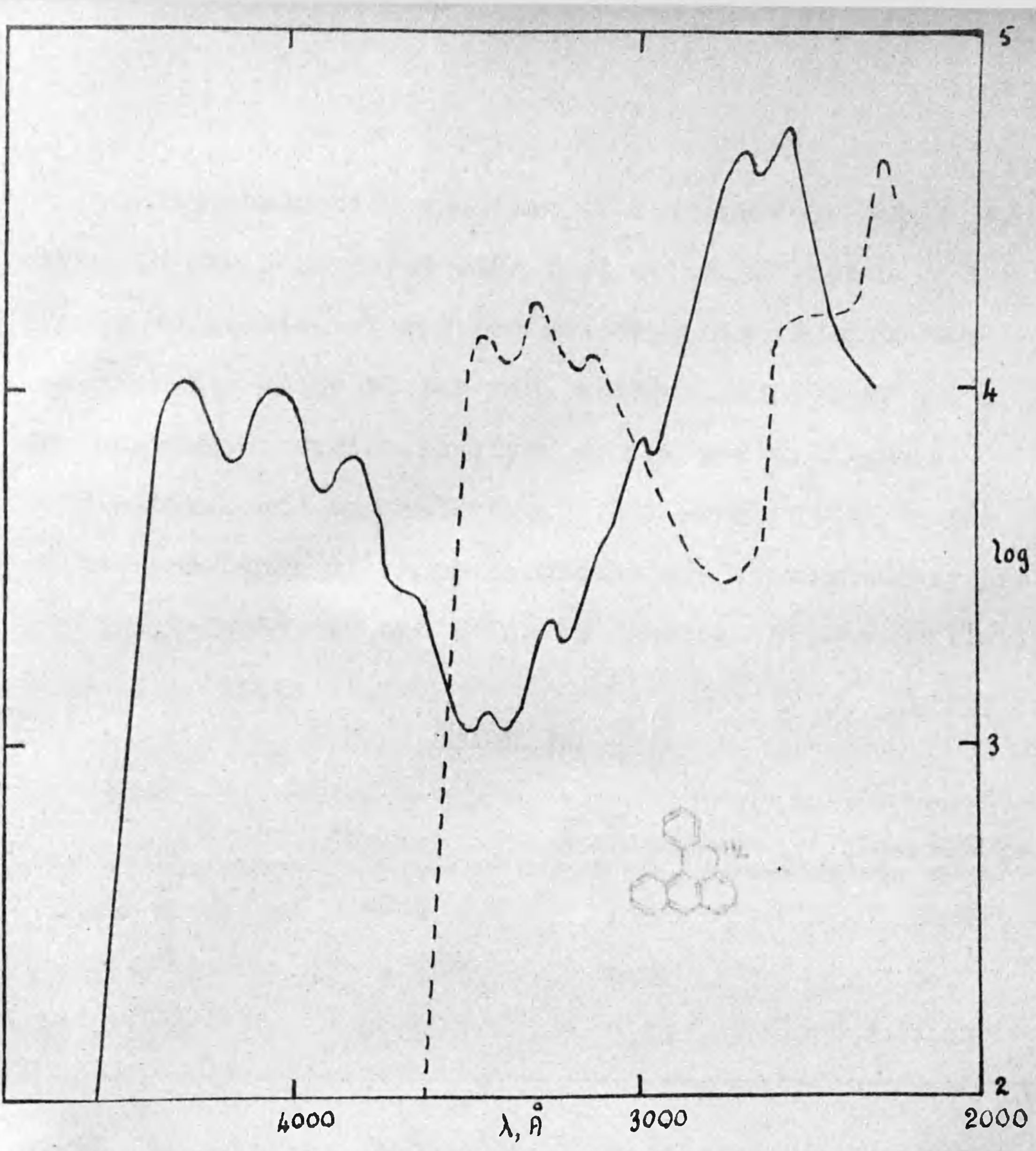
The above results indicate that a compound, which is derived from the 4:8-dihydrotriangulene structure (LV) has a strong tendency to rearrange to a more stable system if this is at all possible. Moreover, no compound having a structure similar to that of (XLVIII) could be detected, so that it must again be concluded that triangulene is an unstable diradical.

The Synthesis of Coeranthrene (26).

Coeranthrone (LXI) was prepared by Scholl and Donat (11), and the method used in this synthesis is essentially that described by these authors. J.W. Cook (37) has shown that benzophenone-2:2'-dicarboxylic acid anhydride (XXI) reacts with phenylmagnesium bromide to give the acid (LIX). The latter, on treatment with concentrated sulphuric acid, is ring-closed to the lactone (IX), which is reduced with zinc dust in ethanolic potassium hydroxide solution to the anthracene derivative (LX). Coeranthrone (LXI) was obtained by Scholl and Donat from the latter by treating with concentrated sulphuric acid, but it was found that this condensation is better carried out using 100% orthophosphoric acid as condensing agent. This last step is a slight modification of the method used by Bradsher and Vingiello (38).

In the same way as benzanthrone yields 9-hydroxy-1:10-trimethylene phenanthrene (Clar and Furnari, 39), reduction of coeranthrone (LXI) with zinc dust in dilute sodium hydroxide solution gives 2-hydroxy-1:10-trimethylene-3:4-benzophenanthrene (LXIa), which on heating in a vacuum splits out a molecule of water to give coeranthrene (LXIV).


CO₂H
O
O
O–C=O
O
CO₂H
LIX
IX
LX
H₂
OH
H₂
H₂
H₂
O
LXIV
LXIa
LXI
+
ClO₄
H
ClO₄⁻
+
H₂
H₂
H₂
LXIII
LXII
LXV



—— Coeranthrene (LXIV) in alcohol.   Band maxima in A: 4230, 4040, 3830, 3650; 3240, 2990; 2690, 2570.

------ *meso*-Benzanthrene in alcohol.   Band maxima in A: 3440, 3290, 3120; 2500; 2280.

Fig. 8.

The absorption spectrum of coeranthrene (LXIV) is shown in Fig.8 compared with that of benzanthrene. The linear anellation of one benzene ring has produced the considerable shift to the red, which is expected, and a new anellation series is given by the series diphenyl, benzanthrene and coeranthrene. The wavelengths of the first para-bands of these compounds are approximately proportional to 6^2, 7^2 and 8^2 as is required by the anellation principle (Table I).

Table I.

	Diphenyl	Benzanthrene	Coeranthrene
λ in A	2500	3440	4280
Rp (cm^{-1})	147×10^4	do.	do.
$Kp = \sqrt{\lambda Rp}$	6.06	7.11	7.93

Since coeranthrene (LXIX) has 20 π-electrons, its first para-band should be at the same wavelength as the first para-band of perylene (4340A) which also has 20 π-electrons and which fits more accurately into the anellation series. This slight divergency in the spectrum of coeranthrene from the calculated value is probably due to the hydrocarbon being non-planar, owing to the overlapping of the hydrogen atoms. This explanation is supported by the fact that the ratio of the frequencies of the α - and β-bands ($V_\alpha : V_\beta$)

is equal to 1 : 1.26, which is considerably lower than the constant value (1 : 1.35) found for uniplanar hydrocarbons in which there is no overlapping of hydrogen atoms and consequently no loss in resonance energy, e.g., anthracene and pyrene (26).

Another new anellation series is given by diphenyl, benzanthrone (Fig.18) and coeranthrone (LXI) (Fig.3) in which the methylene group is replaced by a carbonyl group. The π-electrons in the latter contribute towards the aromatic resonance system so that an additional red shift equivalent to half a benzene ring is produced. The wavelengths of the first para-bands of these compounds are thus proportional to 6^2, $(7\frac{1}{2})^2$, and $(8\frac{1}{2})^2$. (See Table II).

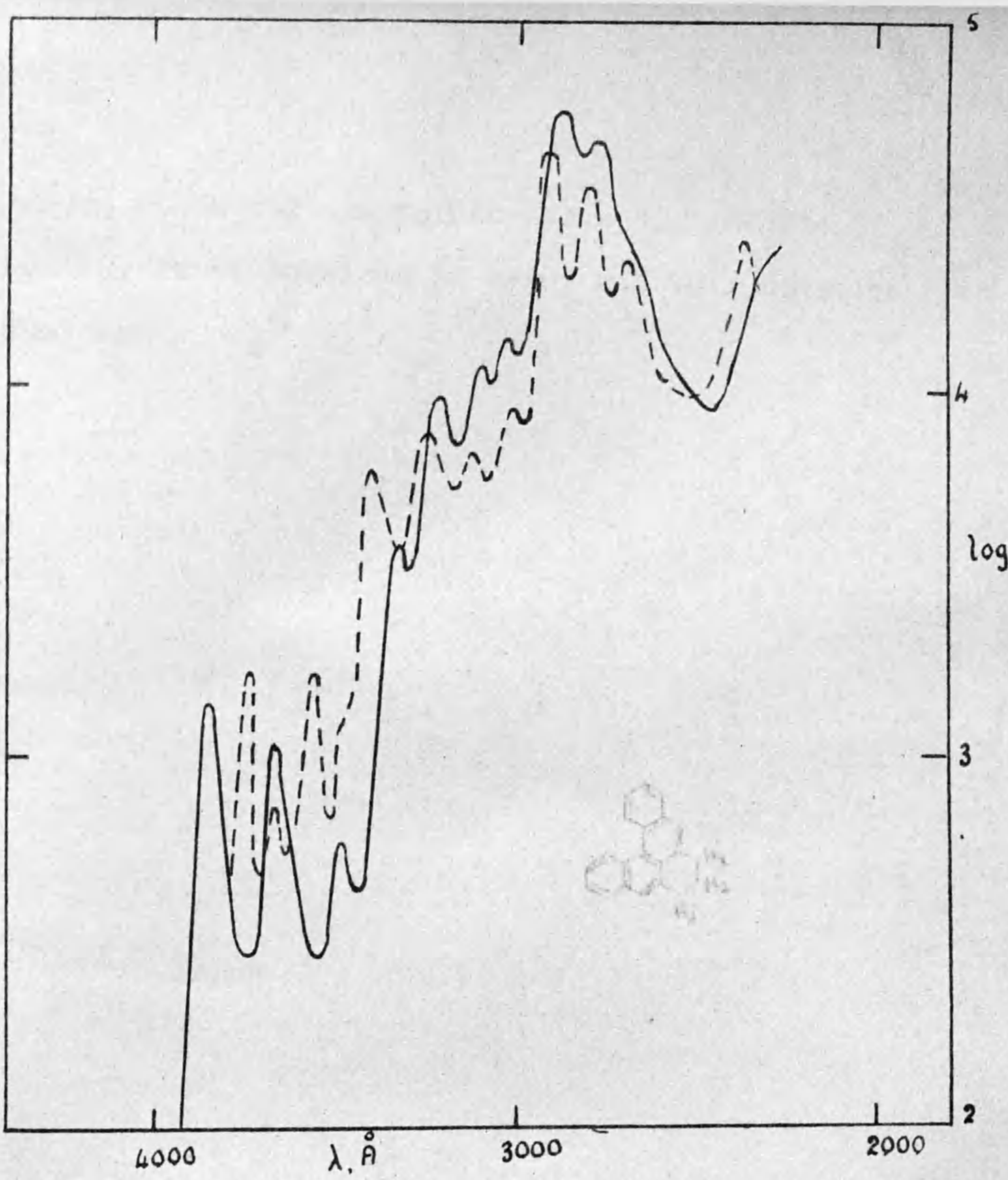
Table II

	Diphenyl	Benzanthrone	Coeranthrone
λ in A	2500	3950	4970
Rp (cm^{-1})	147×10^4	do.	do.
$Kp = \sqrt{\lambda Rp}$	6.06	7.62	8.55

The deviation of coeranthrone from the anellation principle, which is small, indicates a slight distortion only of its molecular plane.

Reduction of coeranthrone (LXI) with hydriodic acid and red phosphorus yields 1:10-trimethylene-3:4-benzophenanthrene (LXV), the absorption spectrum of which is shown in Fig.9 compared with that of naphtho-(2':7'-1:8)-anthrene (XXXII). Both spectra are very similar to that of 3:4-benzophenanthrene, the shifts to the red being due to the methylene group and the trimethylene bridge respectively. As would be expected, the ratios ($V_\alpha : V_\beta$) are rather low (1 : 1.33 and 1 : 1.28 respectively) and are considerably different for these hydrocarbons (26).

When coeranthrene (LXIV), which is readily photo-oxidised, is exposed to sunlight in the presence of oxygen, the initial yellow, blue-fluorescent solution is quickly decolourised and a colourless solution with a violet fluorescence is obtained. When a warm solution of selenium dioxide in acetic acid is added to an acetic acid solution of coeranthrene (LXIV), containing a few drops of perchloric acid, dark brown needles begin to crystallise out almost at once. As this compound is rather unstable and is readily hydrolysed, it could not be recrystallised, but there is little doubt that it is either coeranthrylium perchlorate (LXIII) or coeranthrenium perchlorate (LXII), both of which are possible stages in the oxidation of coeranthrene (LXIV) with selenium dioxide. It will be noticed that, in this case, a strong acid is required to give this reaction. For <u>sym</u>-tribenzoperinaphthene (XCVII)



———— 1:10-Trimethylene-3:4-benzophenanthrene (LXV) in alcohol. Band maxima in A: 3830, 3640, 3470; 3320, 3210, 3080, 3010; 2870, 2780.

------- Naphthanthrene (XXXII) in alcohol. Band maxima in A: 3750, 3690, 3565; 3410, 3260, 3120, 3020; 2910, 2800, 2700; 2360.

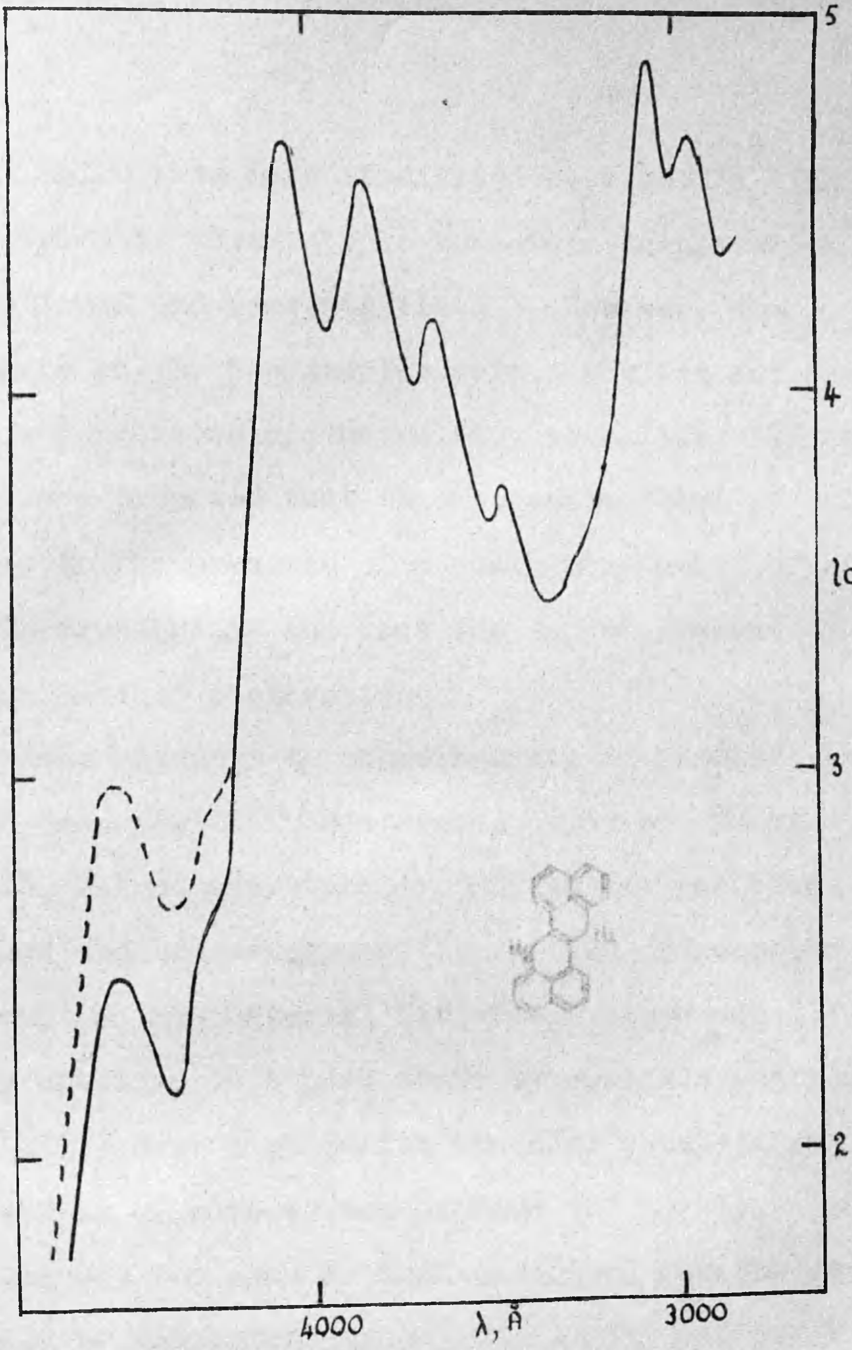
FIG. 9.

however, where the ion formed has a high degree of symmetry, it is possible to carry out this reaction with weaker acids.

The Synthesis of Zethrene (40).

Prior to the experiments described in this work, a great amount of work had been done by Clar and his co-workers (unpublished) on the synthesis of zethrene (IV). Many routes to the zethrene skeleton had been investigated but with little success. It now appears that the method originally developed by Clar is the best way of obtaining derivatives of zethrene, despite the fact that the yields are very poor (5 to 10%). Powdered aluminium chloride is added to a solution of fumaroyl chloride and naphthalene in benzene at such a rate that the mixture refluxes gently. If cooling is applied during the addition no useful material is obtained. After the usual decomposition of the reaction mixture and extraction of the tarry by-products with hot xylene, a dark brown, rather insoluble compound is isolated which can be acetylated and to which the structure (LXVI) has been assigned.

When this compound (LXVI) is reduced by means of Clar's zinc dust melt, the yellow hydrocarbon 7:14-dihydrozethrene (LXVII) is obtained, the absorption spectrum of which is shown in Fig.10. While examining this compound it was noted that the intensity of the absorption band at 4505A is not constant but depends on the method of purification of the sample. Chromatographic purification gives



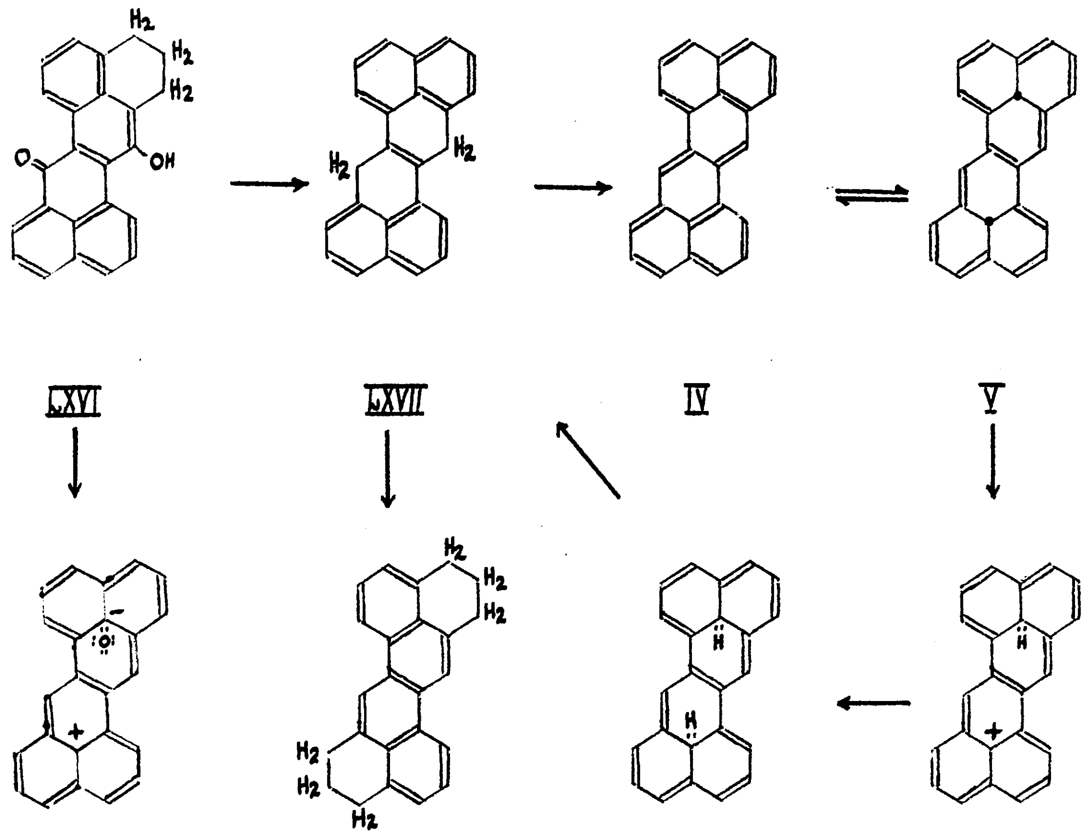
——— 7:14-Dihydrozethrene (LXVII) in benzene. Band maxima in Å: 4505, 4250; 4045, 3835, 3640, 3470; 3070, 2940.

Fig. 10.

a sample in which this band (indicated by a broken line in the spectrum) is more intense than in a sample which has been sublimed and recrystallised. However, the melting points of the two samples were identical and on admixture no depression of the melting point was obtained. It is therefore proposed that the absorption band at 4505A is due to the presence of a small percentage of an isomeric dihydrozethrene and that the amount present depends on the mode of preparation.

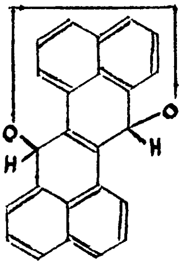
Previous attempts to dehydrogenate dihydrozethrene (LXVII) had been partially successful (Clar and Hopkins, unpublished), but no analytically pure sample had been obtained, and the unusual properties of the hydrocarbon had cast doubt on the material isolated. Zethrene (IV) was finally obtained in a pure state by subliming dihydrozethrene (LXVII) over a palladium charcoal catalyst at 310° in a stream of pure carbon dioxide (30 to 33). The apparatus was the same as that described for the dehydrogenation of hexahydrotriangulene (XXVII) and every precaution was taken to prevent the hydrocarbon coming in contact with oxygen.

By this method zethrene (IV) is obtained as a bluish-green sublimate, which crystallises from trichlorobenzene in glistening green plates which carbonise

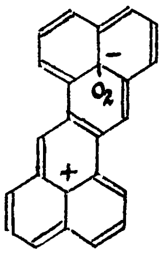


LXVI LXVII IV V

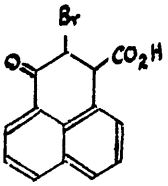
LXVIII LXIX LXX LXXI



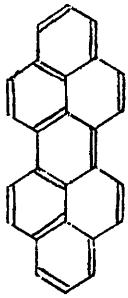
LXXII



LXXIII



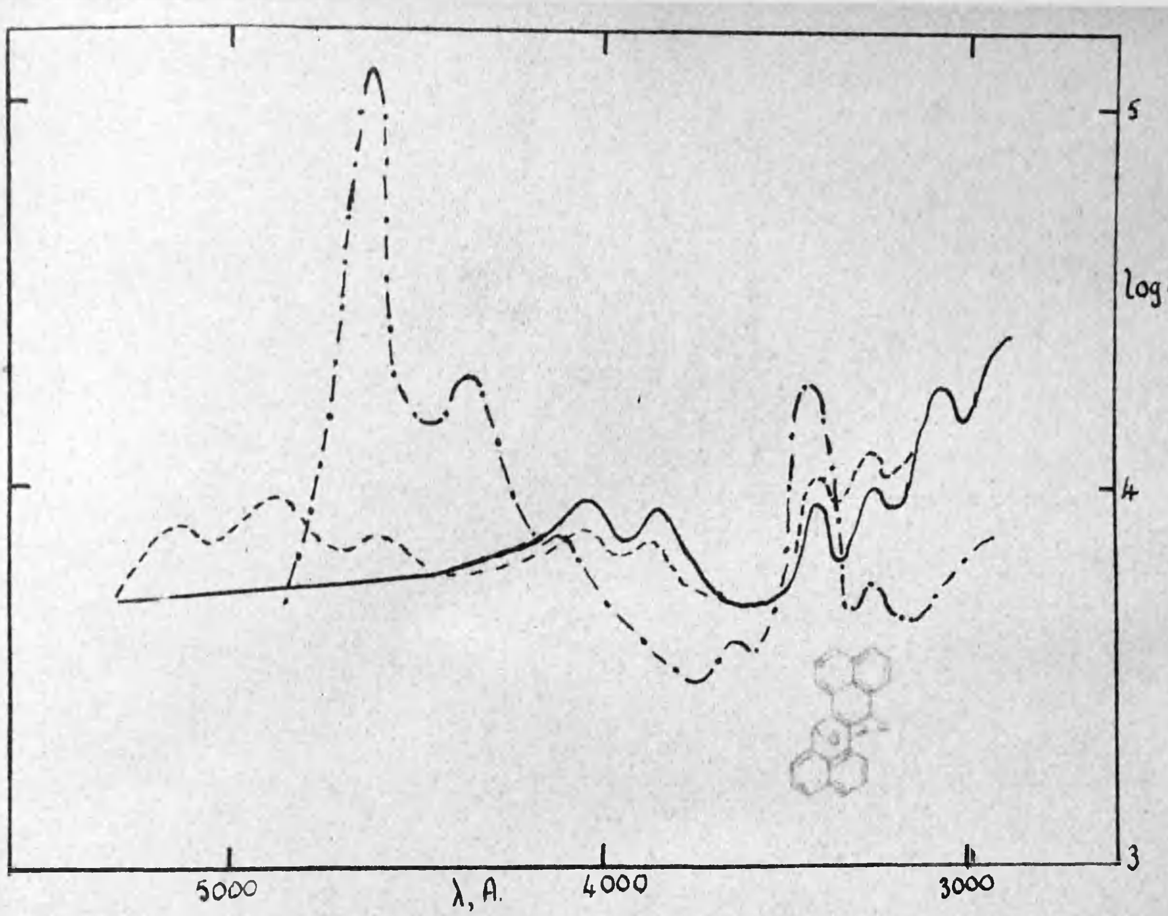
LXXIV



LXXV

without melting at high temperatures. In neutral organic solvents such as benzene it dissolves to give greenish yellow solutions which on exposure to light decompose to give a dark brown insoluble polymer. If oxygen is bubbled through the solution during irradiation, however, photo-oxidation takes place and from the absorption spectrum (Fig.11) of the solution so produced, it appears that two photo-oxides are formed (LXXII and LXXIII). Thus the absorption bands at 4040A and 3840A are attributed to the photo-oxide (LXXII) whose structure is closely related to that of dihydrozethrene (LXVII) (c.f. Fig.10), while those at 3405A, 3250A and 3060A are attributed to the polar structure (LXXIII) (c.f. zethrenium oxide (LXVIII), Fig.12). The photo-oxides are unstable and on boiling with palladium-charcoal (Fig.11) or by passing the solution through a column of activated alumina they are readily converted to zethrenium oxide (LXVIII).

Zethrenium oxide (LXVIII) is obtained as a by-product in the reduction of (LXVI) to dihydrozethrene (LXVII) and crystallises from acetic anhydride as dark red prisms. It cannot be acetylated and does not enolise, even when boiled with strong ethanolic potassium hydroxide solution. It dissolves readily in strong acids, such as phosphoric and hydrochloric acids, to give violet solutions, which on dilution with water are decomposed, the red oxide being

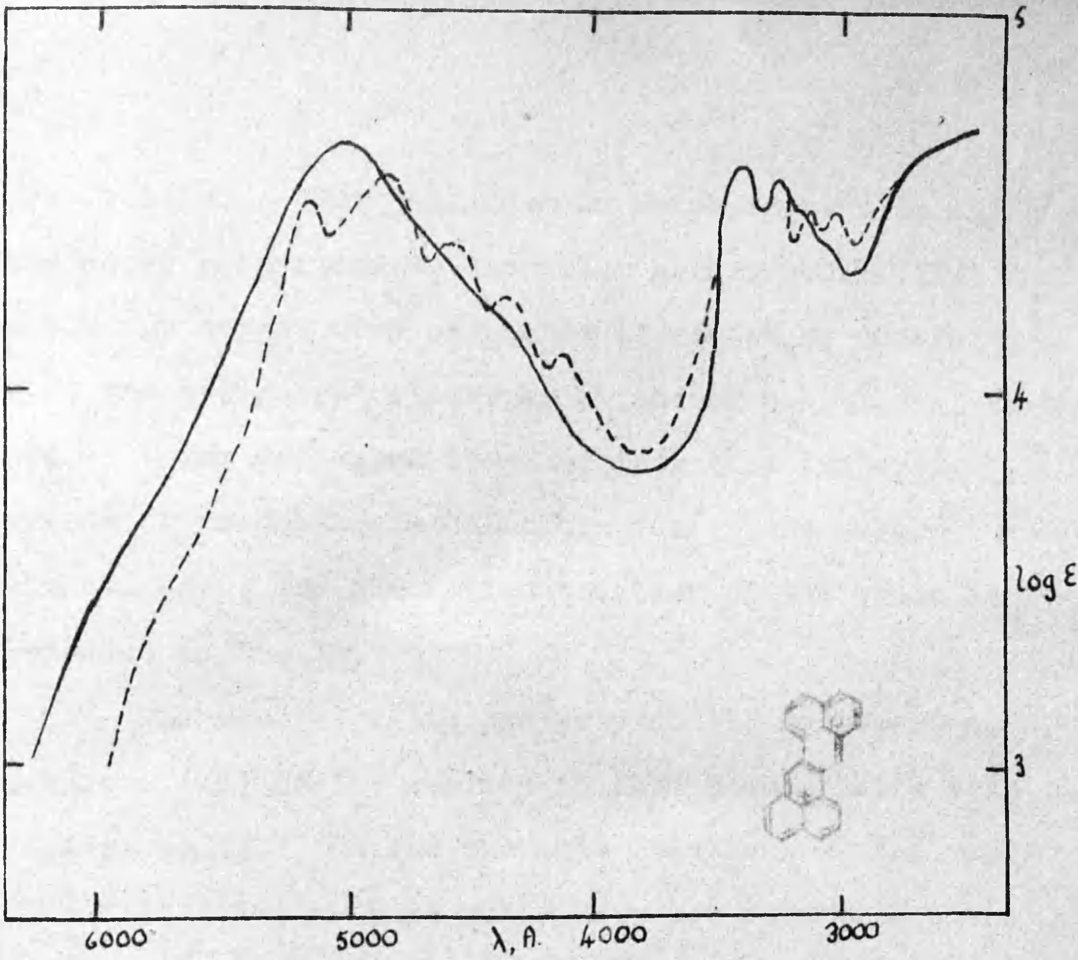


——— Zethrene peroxide (LXXII) in benzene. Band maxima in A: 4040, 3840; 3405, 3250, 3060.

-------- Zethrene peroxide (LXXII) after boiling with Pd/C. Band maxima in A: 5160, 4870, 4600, 4360; 4040, 3840; 3405, 3250, 3060.

-·-·-·-· Zethrene (IV.) in benzene. Band maxima in A: 4610 4360; 4120; 3600; 3420, 3270.

Fig. 11.



———— Zethrene oxide (LXVIII.) in alcohol. Band maxima in A: 5000; 3390, 3250, 3120, 3000.

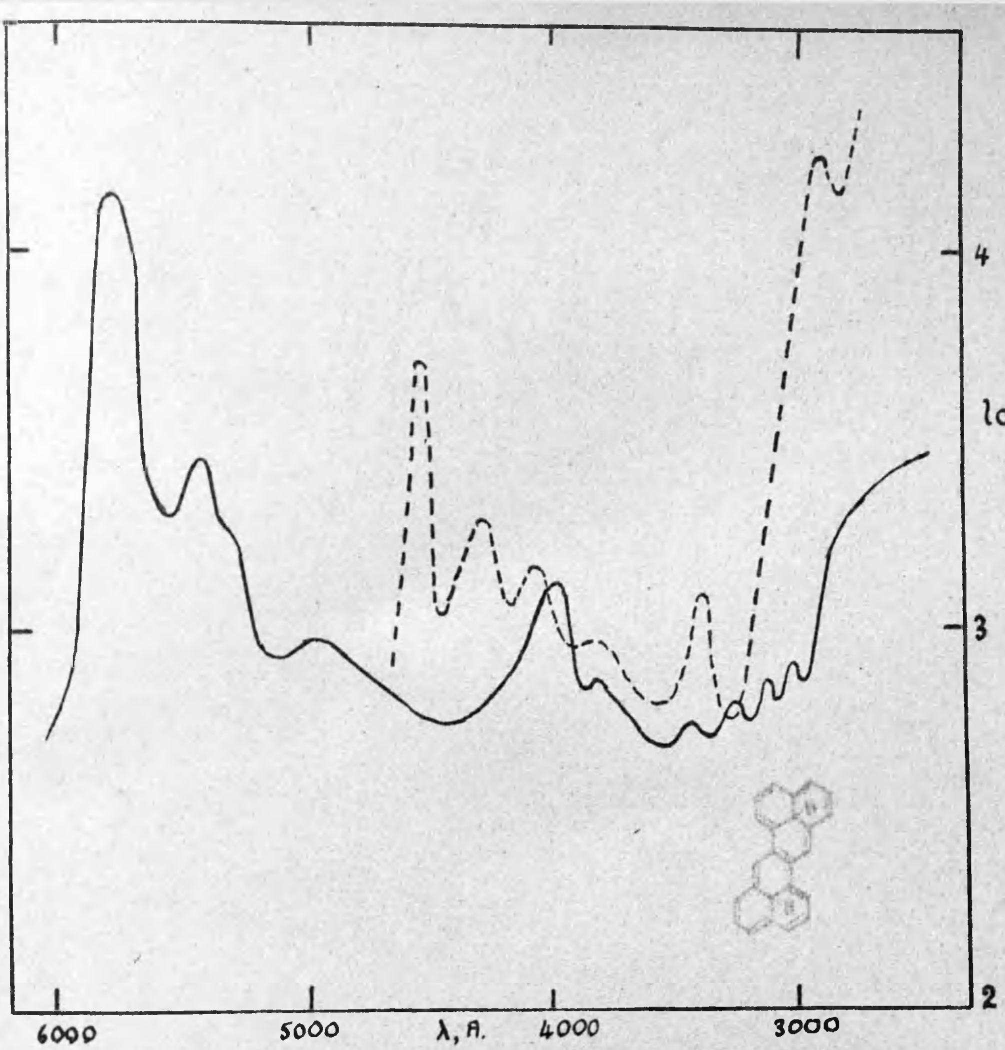
- - - - - - Zethrene oxide (LXVIII.) in benzene. Band maxima in A: 5160, 4870, 4600, 4360, 4140; 3405, 3265, 3125, 3010.

Fig.12.

precipitated. The only formula which appears to satisfy the above properties is the polar structure (LXVIII) in which the oxygen atom completes its octet by combining with the two paired electrons at one of the central carbon atoms. The framework then consists of a conjugated system of double bonds which can form three Kekulé structures. The absorption spectrum of the oxide is reproduced in Fig.12.

The most striking property of the hydrocarbon, zethrene (IV) is its ability to form stable salts with the weakest acids. Unlike the acid solutions of the oxide (LXVIII), dilution with water does not decompose these zethrenium salts. The absorption spectra of these salts are very similar to one another (Fig.13 and Fig.22) and all have an intense absorption band at 5800A. This salt formation of the hydrocarbon and the similarity of the absorption spectra of the salts are attributed to the formation of the common cation (LXXI). Solutions of zethrenium salts can also be produced by dihydrozethrene (LXVII), by treating the hydrocarbon with an acid oxidising agent such as chromium trioxide or selenium dioxide.

All the zethrenium salts are very readily reduced, for example with stannous chloride, sodium dithionite or zinc dust in acetic acid, to give yellow solutions with a



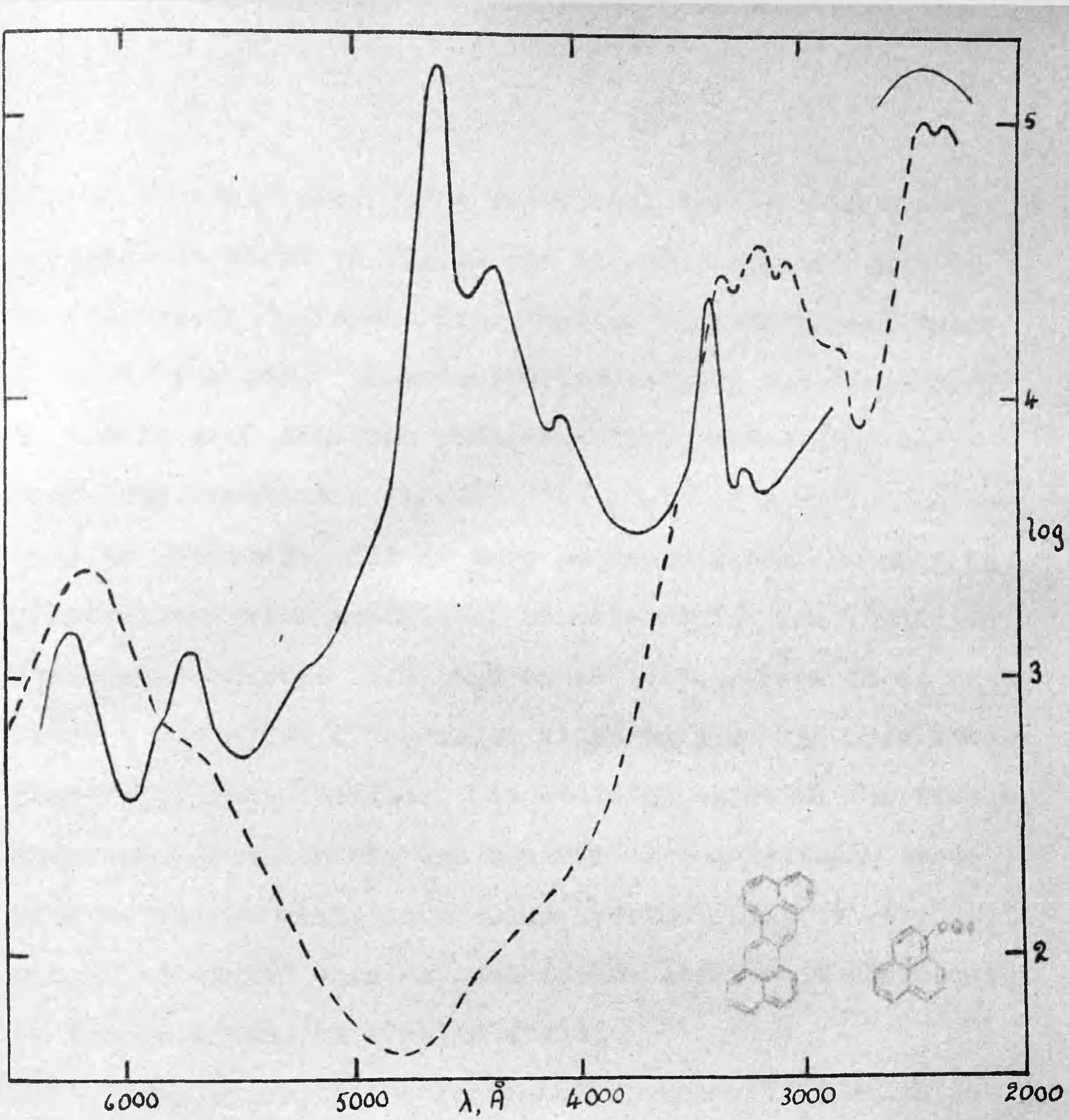
——— Zethrenium-acetate (LXXI) in 90% acetic acid.

Band maxima in A: 5800 , 5440 , 4960 ; 4040 , 3830 ; 3430 , 3260 , 3150 , 3020 .

- - - - - - - Zethrenium-hydride (LXX) in 90% acetic acid.

Band maxima in A: 4555, 4300 , 4070 , 3840 ; 3375, 2895.

Fig. 13.



——————— Zethrene (IV) in benzene. Band maxima in A: 6220, 5730; 4610, 4360; 4140; 3420, 3270; 2450.

- - - - - - - - - Acetoxyperinaphthyl (LXXXIV) in ether. Log. ε obtained by inspection.

Band maxima in A: 6130; 3340, 3180, 3050; 2420, 2350.

Fig. 14.

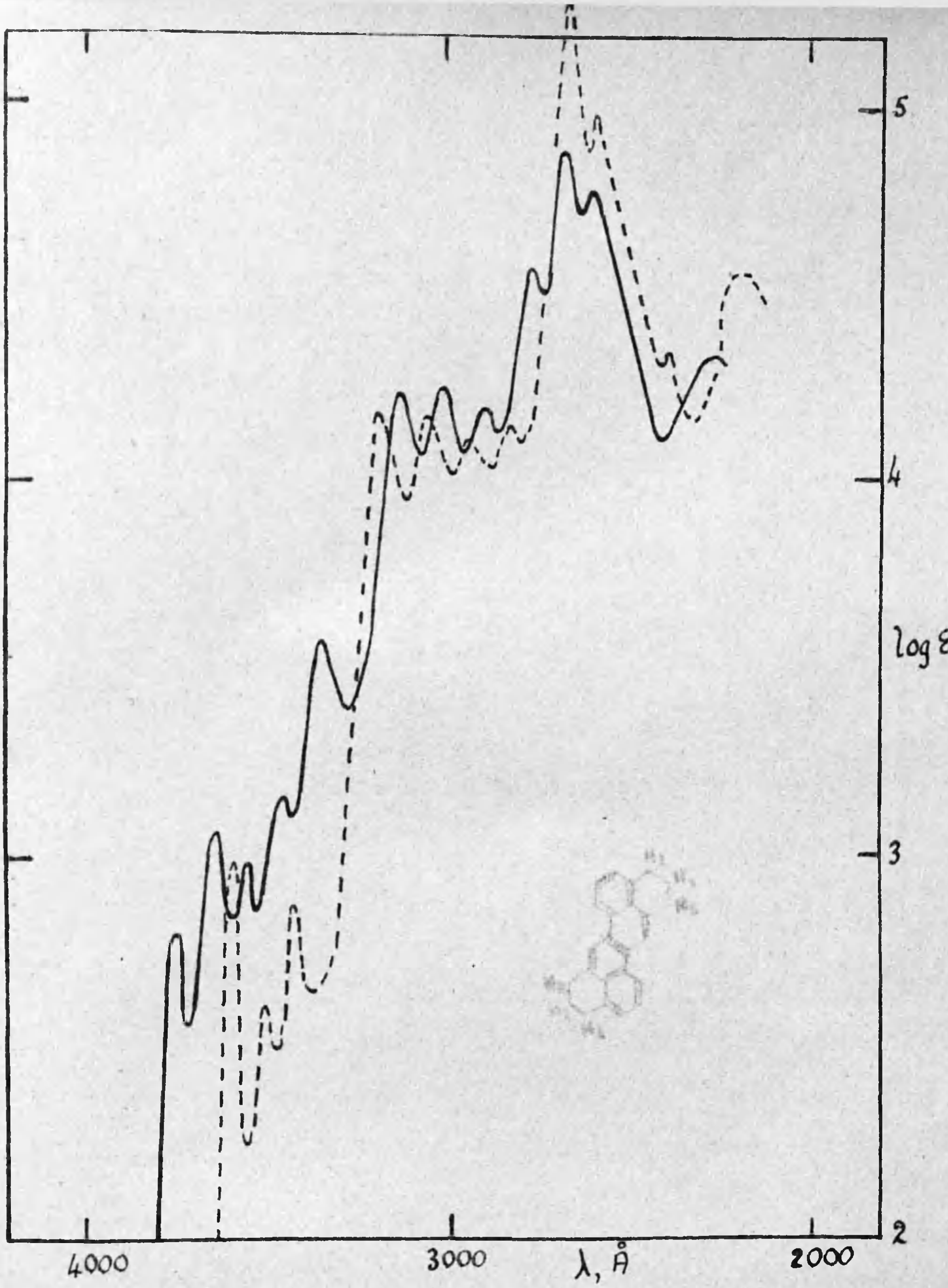
violet fluorescence. The absorption spectrum of such a solution is shown in Fig.13 and it will be noted that it is completely different from that of 7:14-dihydrozethrene (LXVII) (Fig.10). However, after boiling for five hours in acetic acid solution with zinc dust, conversion to 7:14-dihydrozethrene (LXVII) (50% yield of purified material) is obtained. It is very probable therefore that the primary reduction product of the zethrenium ion (LXXI) is zethrenium hydride (LXX) and on refluxing there is a gradual migration of hydrogen atoms to give the more stable dihydrozethrene (LXVII). As would be expected for such a structure in which the two central carbon-hydrogen bonds must be rather weak, zethrenium hydride (LXX) is very quickly oxidised when exposed to the air and it could not be isolated pure in a solid state.

The absorption spectrum of zethrene (IV) which is shown in Fig.14 bears no resemblance to that of any known aromatic hydrocarbon. Extensive spectroscopic investigations by Clar (unpublished) have suggested that the bands at 6220A and 5730A are due to the central structure (V) while the intense peak at 4610A is due to the polyene structure (IV). In other words, the hydrocarbon, zethrene (IV) exists to a certain extent in the central form (V) with two localised π-electrons surrounded by an 8-shaped aromatic system of double bonds which can assume three

Kekulé structures. The unusual properties of the hydrocarbon can therefore be attributed to the strong tendency to form such a structure and it will also be noted that the properties of the zethrene derivatives LXVIII, LXXIII, LXXI and LXX are best explained when similar structures are postulated.

In contrast to the ease with which zethrene is reduced, 7:14-dihydrozethrene (LXVII) requires to be refluxed with hydriodic acid and red phosphorus for two weeks before it is completely reduced to hexahydrozethrene (LXIX). This colourless hydrocarbon has an absorption spectrum which is closely related to that of chrysene (Fig.15), the shift to the red being due to the two trimethylene bridges. The unquestionable chrysene character of this hydrocarbon is important in that it provides convincing proof of the Z-shaped structure of zethrene and its derivatives.

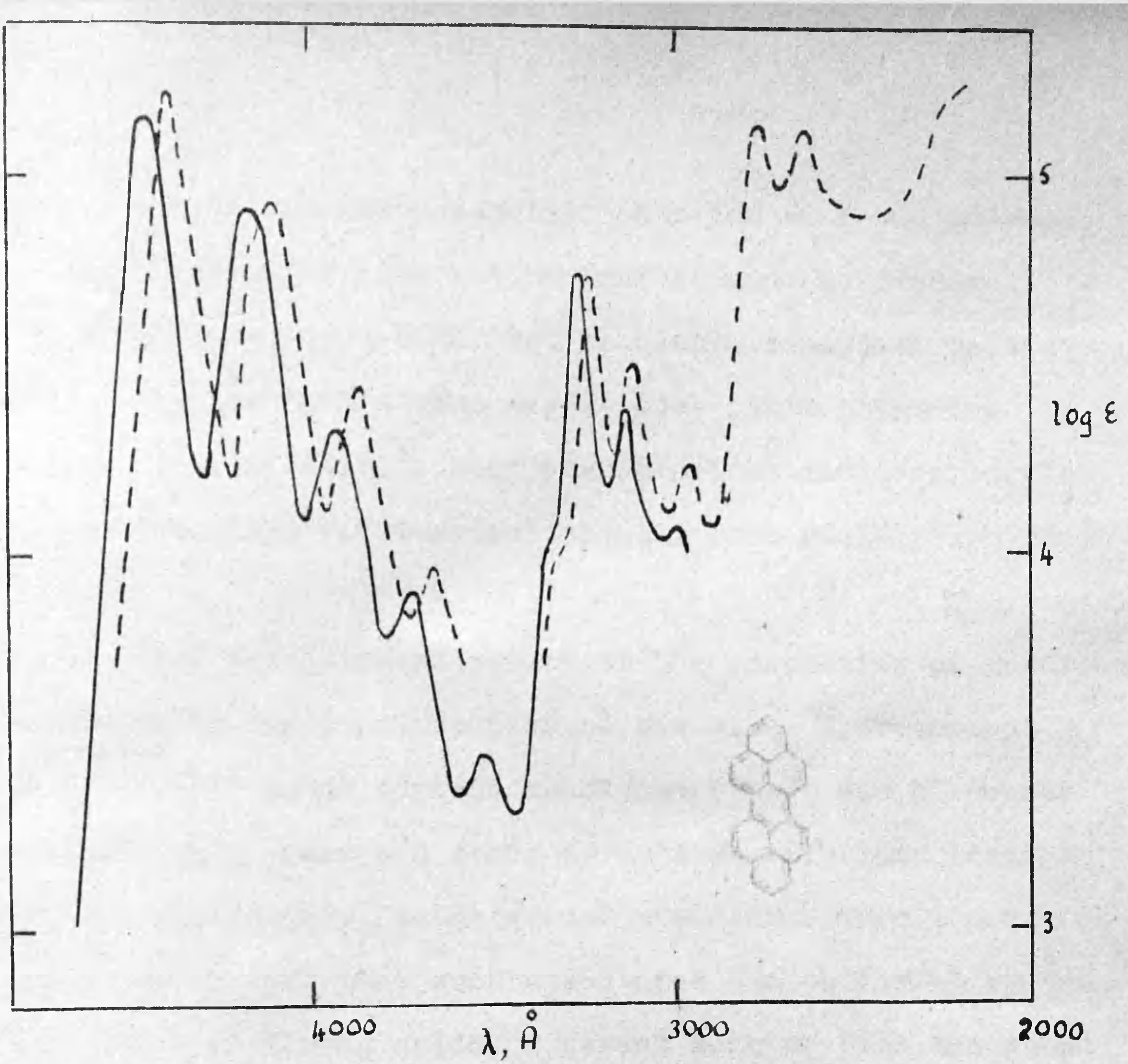
In an attempt to prepare the zethrene skeleton from naphthalene and dibromosuccinyl chloride (Clar and Collier, unpublished), a yellow hydrocarbon was isolated which at the time could not be identified. On repeating the reaction, the same hydrocarbon was obtained from the zinc dust melt and its properties and absorption spectrum (Fig. 16) proved it to be peropyrene (LXXV). The formation of this hydrocarbon can be explained by the interaction of



——— Hexahydrozethrene (LXIX) in alcohol. Band maxima in A: 3720, 3615, 3540, 3440, 3350; 3130 3005, 2890, 2770; 2670, 2590.

------- Chrysene in alcohol. Band maxima in A: 3600, 3510, 3435; 3190, 3060, 2950, 2830; 2670, 2590; 2410, 2200.

Fig. 15.



——— Peropyrene (LXXV) in benzene. Band maxima in A: 4435, 4155, 3920, 3710, 3520; 3260, 3120, 2990.

------ Peropyrene in alcohol. Band maxima in A: 4365, 4100, 3860, 3660; 3235, 3090, 2950; 2770, 2640.

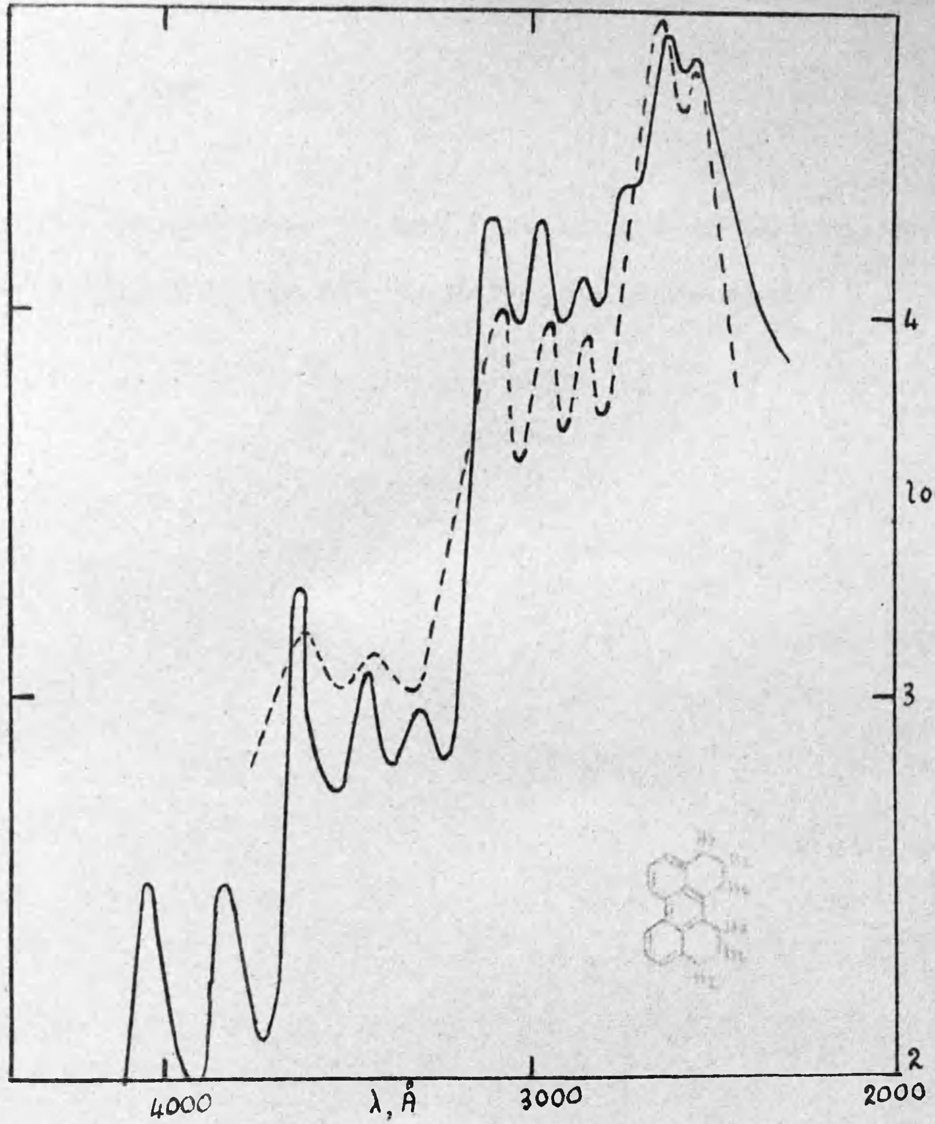
FIG. 16.

one molecule of dibromosuccinyl chloride with one molecule of naphthalene to give the perinaphthenone derivative (LXXIV) which, when submitted to Clar's zinc dust melt, will dimerise in the same way as does perinaphthenone (LXXXI) itself (41). Dehydrobromination and decarboxylation subsequent to dimerisation will then yield peropyrene (LXXV).

The above investigation of the properties of zethrene (IV) led to the consideration of how other hydrocarbons would behave under certain conditions. It was of course assumed that Dewar and other structures with long linkages do not participate in the ground state of a normal aromatic hydrocarbon, but that such structures can be formed by the influence of strong acids. Recent work by Clar has shown that the green solution, formed by perylene (LXXVI) in concentrated sulphuric acid and in benzene solution with anhydrous aluminium chloride, rapidly changes to violet due to the addition of a proton to the structure (LXXVII). On analogy with the reduction of zethrenium salts (LXXI), it was therefore predicted that perylene (LXXVI) under these conditions would be readily reduced and that an unstable central dihydroperylene (LXXVIII) would be formed.

When a solution of perylene (LXXVI) in benzene was boiled for ten minutes with aluminium chloride and zinc dust, rapid colour changes occurred and, after decomposition and purification, a colourless, violet-fluorescent hydrocarbon was isolated, the properties of which were identical with those of hexahydroperylene (LXXIX) (42). The production of this hydrocarbon under such conditions can be explained by the reduction of the central structure (LXXVII) (or better, the perylenium salt) to give the central dihydroperylene (LXXVIII), which being unstable, will rapidly convert to the hexahydroperylene (LXXIX) by hydrogen migration to the framework.

The absorption spectrum of the hexahydroperylene isolated is reproduced in Fig.17 and it is at once obvious that the hydrocarbon consists mainly of the phenanthrene derivative (LXXIX). However, the two absorption bands at 4040A and 3830A can only be due to the presence of approximately 5% of the anthracene derivative (LXXX), which would also explain the bright violet fluorescence of the solution and of the crystals of the hydrocarbon. In Fig.17, the absorption spectrum of hexahydroperylene according to Hua-Chih and Conrad-Billroth (43) is also shown. The melting point of the sample used by these authors is the same as that of our sample, but as these authors have not examined the spectral region in which the bands at 4040A and 3830A occur, the possibility that their sample did contain the anthracene derivative (LXXX) cannot be excluded.

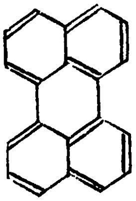


——— Hexahydroperylene (LXXIX)(Clar & Stewart) in alcohol. Band maxima in A: 4040, 3830; 3620, 3440, 3290; 3105 2980, 2860, 2750; 2640, 2550.

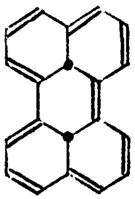
-------- Hexahydroperylene (Hua-Chih & Conrad-Billroth) in hexane. Band maxima in A: 3630, 3450; 3080, 2950, 2850; 2640, 2550.

Fig. 17.

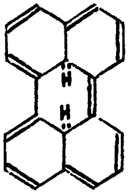
Apart from differences in the fine structure and solvents used, the two spectra are in very good agreement.



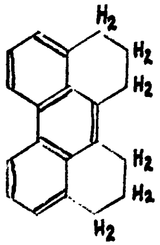
LXXVI



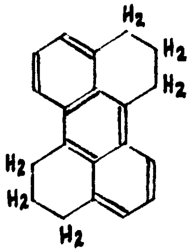
LXXVII



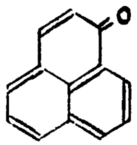
LXXVIII



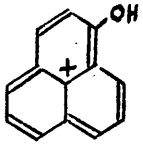
LXXIX



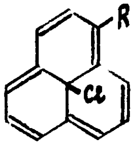
LXXX



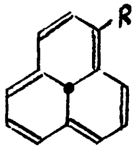
LXXXI



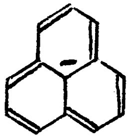
LXXXII



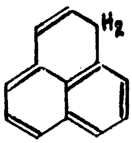
LXXXIII



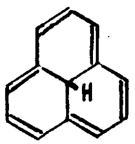
LXXXIV



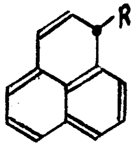
LXXXV



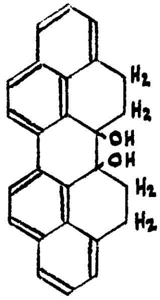
LXXXVI



LXXXVII



LXXXVIII



LXXXIX

The Synthesis of Perinaphthyl Radicals.

It has been pointed out by Clar (44) that benzenoid hydrocarbons containing an odd number of carbon atoms cannot be fully aromatic, but must contain an extra hydrogen atom. Examples of this type of hydrocarbon are benzanthrene and coeranthrene (LXIV). The methylene groups of such hydrocarbons are very reactive as is shown by their ready condensation with maleic anhydride (45) and by their sensitivity to oxygen. Another hydrocarbon of this type is perinaphthene (LXXXVI), which was first synthesised by Lock and Gergely (46) and later by Boekelheide and Larrabbee (47). It resembles fluorene in its ability to form a lithium salt and exchange reactions have shown it to be more acidic than triphenylmethane. Such properties are probably due to the high degree of resonance in the symmetrical mesomeric anion (LXXXV) to which the hydrocarbon can give rise by the loss of a proton. In a somewhat similar way, the solubility of perinaphthenone (LXXXI) in hydrochloric acid (Cook and Hewett, 48) and its ability to form stable complexes with various reagents, e.g., antimony pentachloride, ferric chloride and ferricyanic acid (Silbermann and Barkow, 49), must be due to resonance stabilisation of the symmetrical cation (LXXXII).

The pronounced tendency to assume a structure in which the outer carbon atoms are linked by a system of conjugated double bonds suggested that the reaction of perinaphthenone (LXXXI) with acid chlorides, such as acetyl- and benzoyl chlorides, would give rise to compounds having the structure (LXXXIII). It was found that perinaphthenone (LXXXI), prepared by the method of Fieser and Hershberg (50) reacted readily with acid chlorides to give yellow compounds, which were not isolated, as attempted crystallisation resulted in explosive decomposition, probably due to polymerisation. If a solution of such a compound is treated with an active metal, such as zinc dust or magnesium activated with iodine, in order to remove the chlorine atom, a deep blue or bluish-green solution is obtained. There is little doubt that the blue colour is due to the formation of acetoxy- (LXXXIV; $R = CH_3.CO.O^-$) and benzoyloxy-perinaphthyl ($R = C_6H_5.CO.O^-$) in which an unpaired electron is localised at the central carbon atom and the outer framework of carbon atoms is linked by a system of conjugated double bonds. The solutions are photo-oxidisable but if light is excluded and the solutions cooled to 0^oC, they can be kept without decomposition for weeks.

A remarkable property of these solutions is that on cooling strongly (-30^o), colourless solutions are obtained, but the blue colour is regenerated when the solutions are allowed to come to room temperature. This can be explained by a reversible polymerisation in which the radicals (LXXXIV) link together by weak bonds between the central carbon atoms. The linkages will only be stable at low temperature and will rupture when the temperature rises. On the other hand, if the blue solutions are heated, for example in benzene, an irreversible polymerisation or dimerisation takes place and the blue colour cannot be restored. This is attributed to the unpaired electron gaining sufficient energy to enter the carbon framework, so forming a radical (LXXXVIII), which will combine immediately with a similar radical. The bond formed in this combination is a normal covalent bond and the reaction is not reversible.

The blue solutions were obtained in a spectrally pure state by passing the cold solution through a cooled column of activated alumina under pressure. Some decomposition occurs during this purification, but clear, blue eluates are obtained free from unreated perinaphthenone (LXXXI) and peropyrene (LXXIII), the latter being formed by the condensing action of the active metals.

The absorption spectrum of acetoxyperinaphthyl (LXXXIV; R = $CH_3.CO.O^-$) is shown in Fig.14 compared with that of zethrene (IV) and the similarity between them is readily seen. The theory that the absorption bands of zethrene at 6220A and 5730A are due to the central structure (V), which one can consider as being a combination of two perinaphthyl radicals (LXXXIV; R = H), is supported by the obvious relationship of these bands with the absorption band of acetoxyperinaphthyl at 6130A. Furthermore, the intense absorption band at 4610A in the zethrene spectrum is completely missing in the spectrum of acetoxyperinaphthyl and a deep minimum is observed in this region. This is as expected and is consistent with the proposal that the band at 4610A is due to the polyene structure (IV).

When anhydrous hydrogen chloride was passed into a cooled solution of perinaphthenone (LXXXI) in methyl alcohol, a dark precipitate was obtained which was filtered off and dried in a vacuum. On treating this precipitate in ether with activated magnesium, a dark green solution was obtained, which on passing through an alumina column yielded a clear blue eluate of the methoxyperinaphthyl (LXXXIV; $R = MeO^-$). If during the initial reaction the alcoholic solution is not cooled but is allowed to warm up, a dark green solution is obtained and from the precipitate methoxyperinaphthyl can be extracted. The formation of the radical in this reaction is probably due to disproportionation of the intermediate (LXXXIII; R = MeO$^-$). The solution of the methoxyperinaphthyl is less stable than those of the above radicals, but in contrast to the latter, it gives, with dilute acids, violet-coloured solutions in the same way as does zethrene (IV).

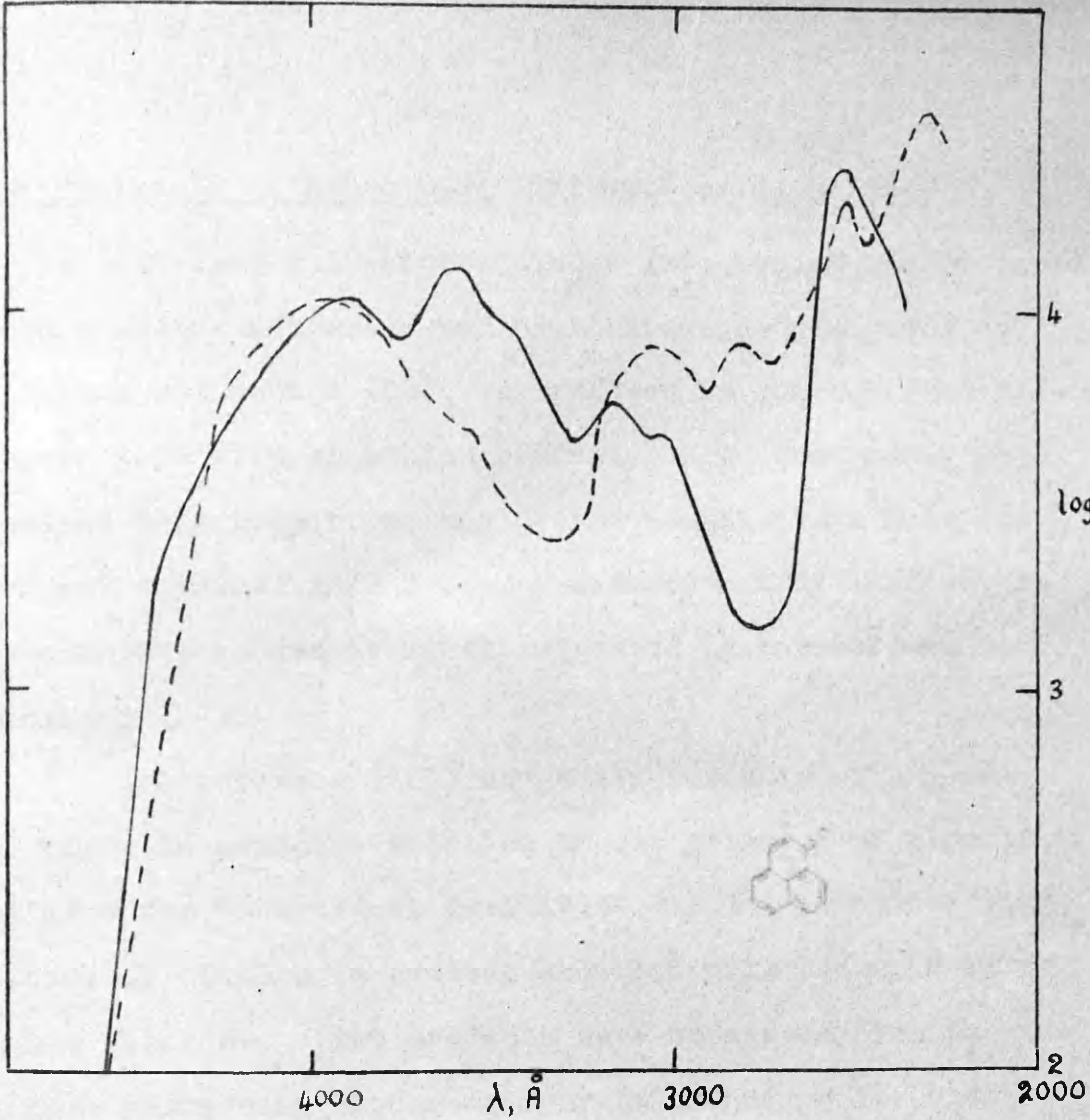
The stability of the perinaphthyl radicals in contrast to other short-lived aryl-radicals can only be explained by the localisation of an unpaired π -electron at the central carbon atom. This excludes the participation of all possible Kekulé structures, for there are only two Kekulé structures for (LXXXIV; R = H) and eighteen for (LXXXVIII; R = H), in which the unpaired electron is in the carbon framework. The latter will only occur as transition states in an irreversible polymerisation, e.g., when the solutions are heated. This means that only the two Kekulé structures (LXXXIV; R = H) or the eighteen structures (LXXXVIII; R = H) are in a state of unrestricted resonance with each other and that the transition from (LXXXIV) to (LXXXVIII) necessitates the overcoming of an energy barrier.

The above results are in harmony with the theory which has been advanced to explain the properties of zethrene (IV). They also provide a probable explanation of the sensitivity to oxygen of perinaphthene (LXXXVI) and other hydrocarbons with an odd number of carbon atoms. It appears likely that there is a tendency for perinaphthene (LXXXVI) to assume a structure (LXXXVII) which has an external system of conjugated double bonds. In such a structure (and also in zethrenium hydride (LXX)), the direction of the bonds of the central carbon atom will be greatly distorted from the normal tetrahedral configuration and the carbon-hydrogen bond will be weakened. It is therefore suggested that the sensitivity of the hydrocarbon is due to the formation of the central structure (LXXXVII). Another experimental fact which supports this proposal that a hydrogen atom can migrate through the system, with the central form as an intermediate, is that only one methylperinaphthene has been obtained from various syntheses (51, 52, 53, 54).

A new method of preparing perinaphthene (LXXXVI) was attempted, by the reduction of perinaphthenone (LXXXI) in dilute sodium hydroxide solution with zinc dust. Only a small amount of the hydrocarbon was obtained and this was treated in acetic acid, containing a little perchloric acid, with a warm solution of selenium dioxide in acetic acid. Dark brown crystals of the perinaphthylium perchlorate were obtained, but the compound was unstable and decomposed readily.

The yield of hydrocarbon was poor owing to the formation of a colourless by-product, which was insoluble in alkali and was extracted with xylene from the zinc dust after filtration. The compound, which crystallises from acetic anhydride unchanged, melts with decomposition at 257° and is clearly a dimeride of perinaphthenone. The structure (LXXXIX) has been assigned to the compound and its non-acetylation is attributed to steric hindrance. The dimerisation of perinaphthenone (LXXXI) to peropyrene (LXXV) during reduction has been demonstrated by Clar (41).

The absorption spectrum of perinaphthenone (LXXXI), which is shown in Fig.18, is closely related to that of benzanthrone with which it is compared.



—— Perinaphthenone (LXXXI) in alcohol. Band Maxima in A:
3920, 3620, 3160; 2555.

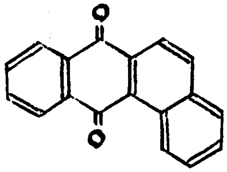
------ *meso*-Benzanthrone in alcohol. Band maxima in A:
3950; 3060, 2830; 2530, 2300.

Fig. 18.

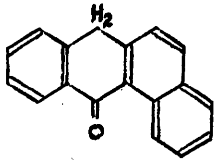
The Synthesis of 2:3-5:6-8:9-Tribenzoperinaphthene.

1:2-Benz-9:10-anthraquinone (XC), which was prepared from phthalic anhydride and naphthalene as described by Groggins and Newton (55), was reduced in concentrated sulphuric acid with aluminium powder. J.W. Cook (56), who devised this reduction, has proved conclusively that the product obtained is 1:2-benz-9-anthrone (XCI) and not the 10-anthrone as was at first suggested by Barnett and Matthews (57).

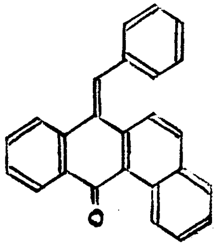
The anthrone (XCI) condensed smoothly with benzaldehyde in pyridine solution in the presence of piperidine to give the benzylidene derivative (XCII), which was ring-closed by boiling in benzene solution with powdered aluminium chloride. Two products were separated from the reaction mixture by chromatography (alumina). The orange-yellow product gave the typical reactions of a benzanthrone, but was rather resistant to reduction, being recovered unchanged after boiling in pyridine-acetic acid solution with zinc dust for one hour. A comparison of the absorption spectrum of this compound with that of naphtho-(1':3'-1:9)-anthrone (C) (Fig.19) (58) shows that there is a strong shift to the red which can only be due to the linear anellation of a benzene ring. The compound is therefore



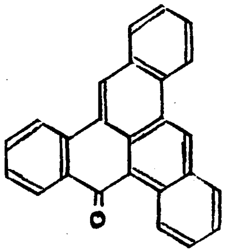
XC



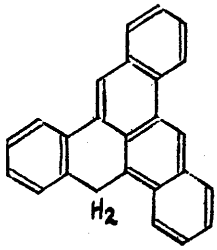
XCI



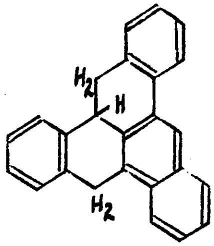
XCII



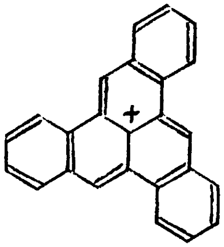
XCIII



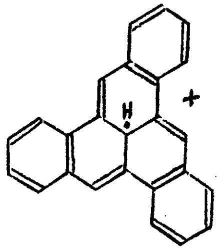
XCVII



XCIV



XCV



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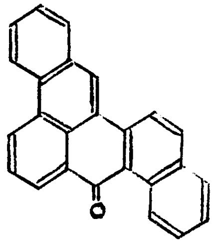
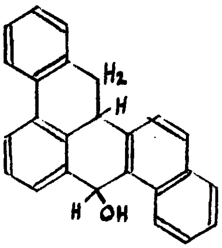
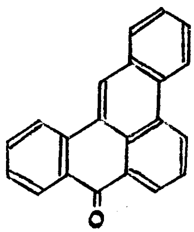


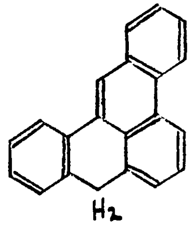
XCVIII



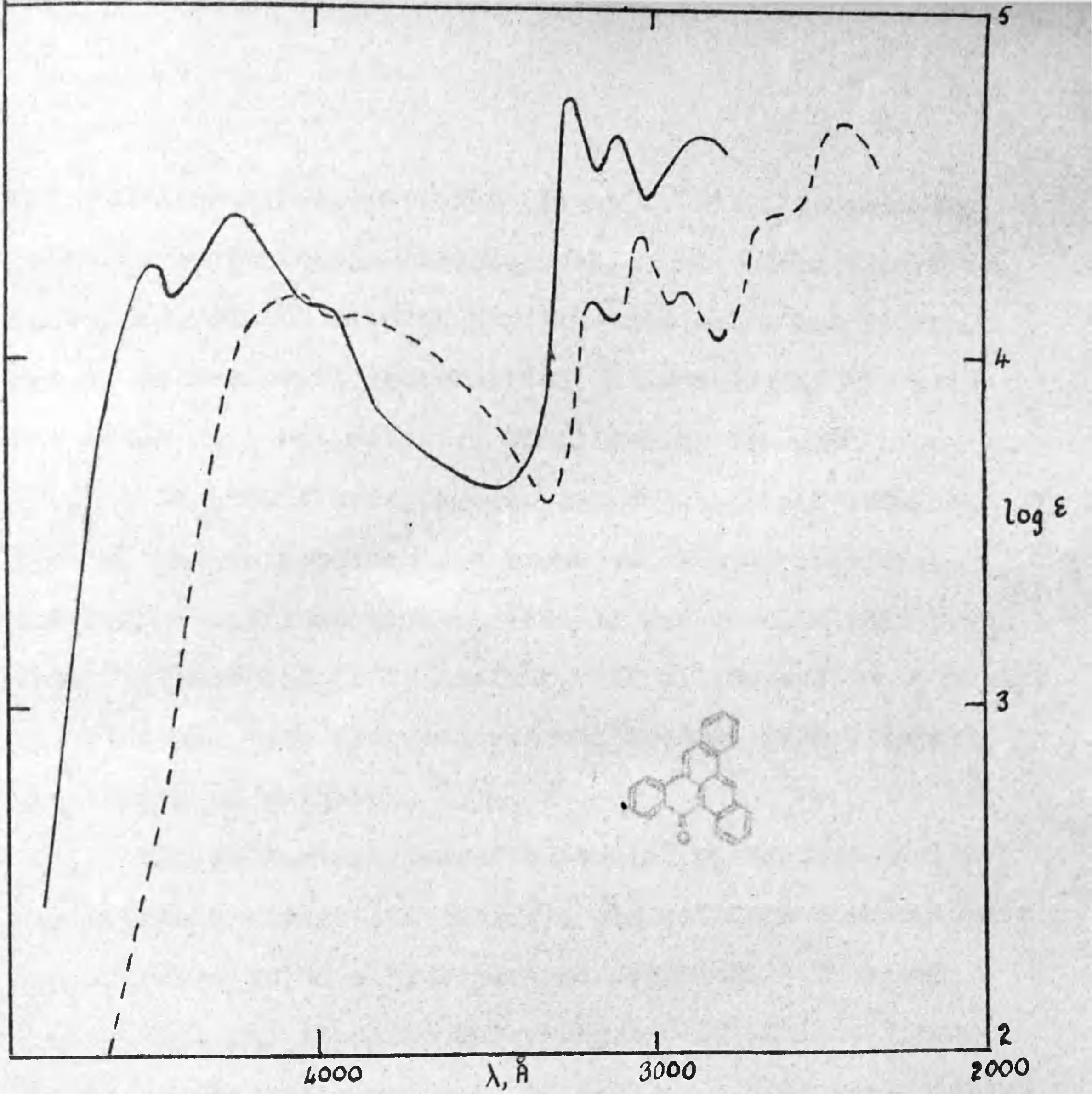
XCIX



C



CI



——— Tribenzoperinaphthenone (XCIII) in benzene. Band maxima in A: 4520, 4260; 3260, 3120, 2860.

------- Naphtho-1':3'-1:9-anthrone (C) in alcohol. Band maxima in A: 4040; 3180, 3030, 2900; 2410.

Fig. 19.

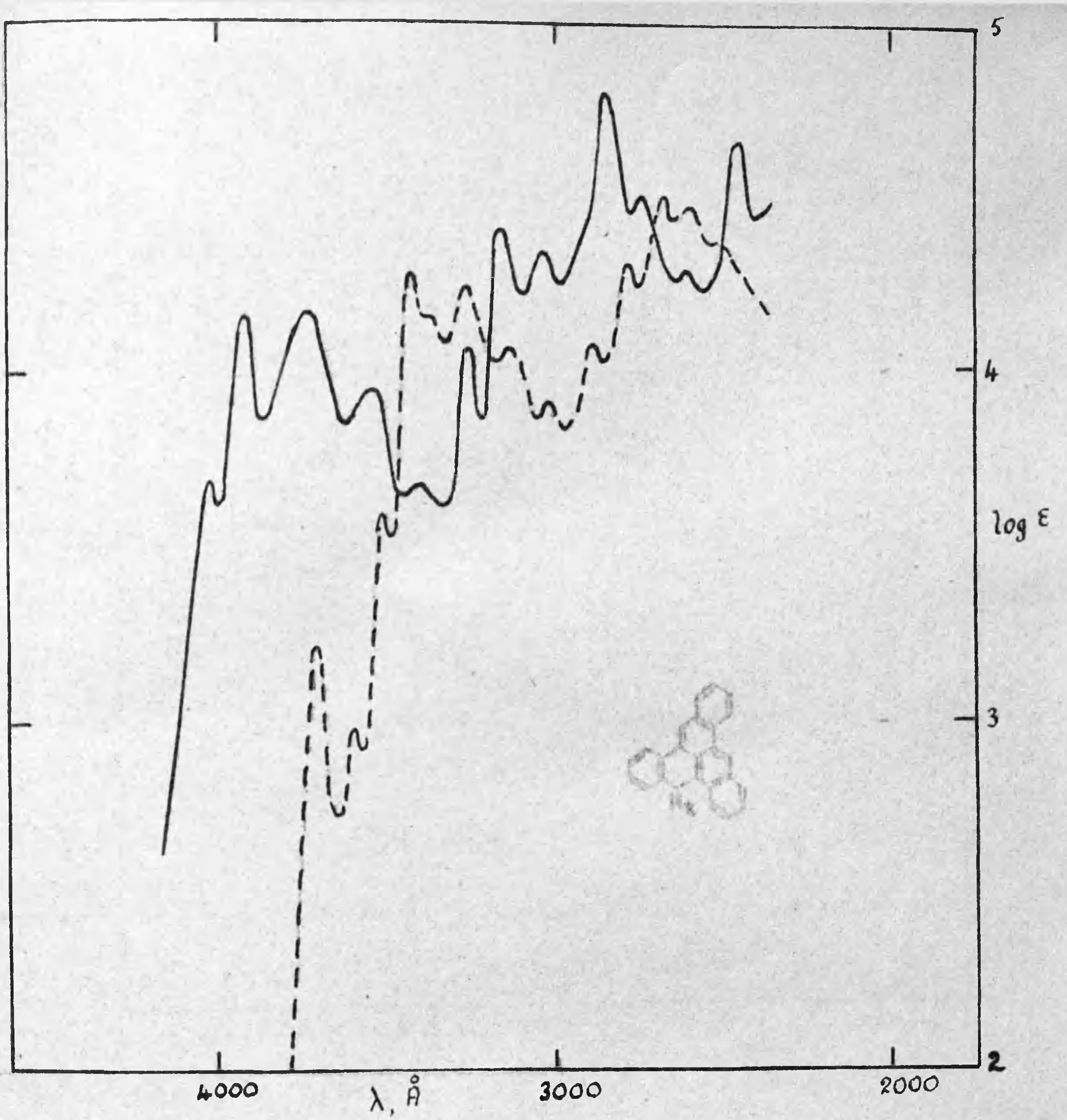
2:3-5:6-8:9-tribenzoperinaphthenone (XCIII), because the isomeric benzanthrone (XCVIII), which one could expect to be formed, cannot account for this red shift and it would not be so resistant to reduction. When perchloric acid was added to a hot solution of tribenzoperinaphthenone (XCIII) in acetic acid, a deep red solution was obtained from which, on cooling, red-brown needles crystallised. The tribenzoperinaphthenone (XCIII) was readily recovered from the perchlorate by heating with dilute sodium hydroxide solution and this reaction was utilised to purify larger quantities of material.

The colourless, non-fluorescent by-product, which was obtained along with (XCIII), did not form a perchlorate and appeared to be a hydrogenated compound. It seems likely that the isomeric benzanthrone (XCVIII) is formed in the condensation and that it acts as a hydrogen acceptor. The structure (XCIX) is assigned to explain its non-fluorescence and its insolubility in dilute sodium hydroxide. Its inability to form an acetyl derivative when boiled with acetic anhydride must be due to steric hindrance.

Reduction of tribenzoperinaphthenone (XCIII) with hydriodic acid and red phosphorus gives, depending on the time of reaction, either 2:3-5:6-8:9-tribenzoperinaphthene (XCVII) or dihydro-2:3-5:6-8:9-tribenzoperinaphthene (XCIV) as the main product. The absorption spectrum of tribenzoperinaphthene (XCVII) is shown in Fig.20, compared with that of naphtho-(1':3'-1:9)anthrene (CI) (58). The similarity in the shape of the curves and strong shift to the red of the para-bands, as is required by the anellation principle for the linear anellation of a ring, confirms that the structure is as assigned.

The absorption spectrum of the dihydrotribenzoperinaphthene (XCIV) is shown in Fig.21 compared with that of 2-phenylnaphthalene (59, 60). As the hydrocarbon (XCIV) can be considered as a substituted 2-phenylnaphthalene the shift to the red is to be expected, while the fine structure which is apparent is probably due to its having a more rigid structure. The corresponding hydrocarbon (c.f. XCIX) from the isomeric benzanthrone (XCVIII) could not have a spectrum of this type as the aromatic complexes in the molecule are diphenyl and naphthalene.

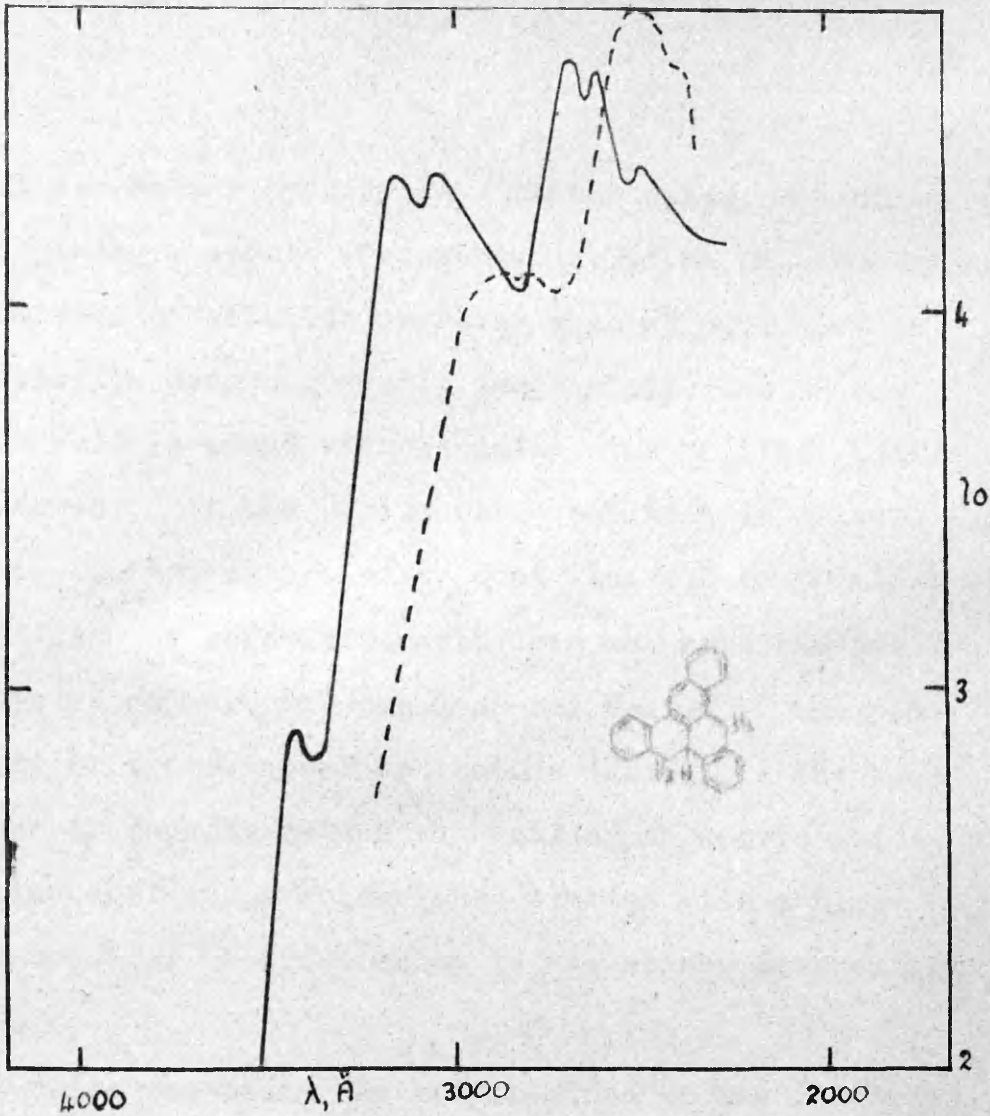
When a solution of tribenzoperinaphthene (XCVII) is heated in acetic acid in contact with air, a deep violet-blue colour develops which is not stable, as over-oxidation to tribenzoperinaphthenone (XCIII) readily occurs. When a small quantity of a strong acid such as perchloric acid is added and a stream of oxygen is passed through the hot acetic acid solution, a stable blue solution is obtained which, on cooling, yields violet-blue crystals. The



——— Tribenzoperinaphthene (**XCVII**) in alcohol. Band maxima in A: 4020; 3930, 3730, 3540; 3260, 3160, 3040; 2840 2740; 2460.

- - - - Naphtho-1':3'-1:9-anthrene (**CI**) in alcohol. Band maxima in A: 3695, 3590, 3500; 3410, 3250, 3110, 3010; 2870, 2760; 2660, 2580.

FIG. 20.



——— Dihydrotribenzoperinaphthene (XCIV) in alcohol. Band maxima in A: 3420; 3160, 3050; 2690, 2610.

------- 2-Phenylnaphthalene in alcohol. Band maxima in A: 2880; 2510.

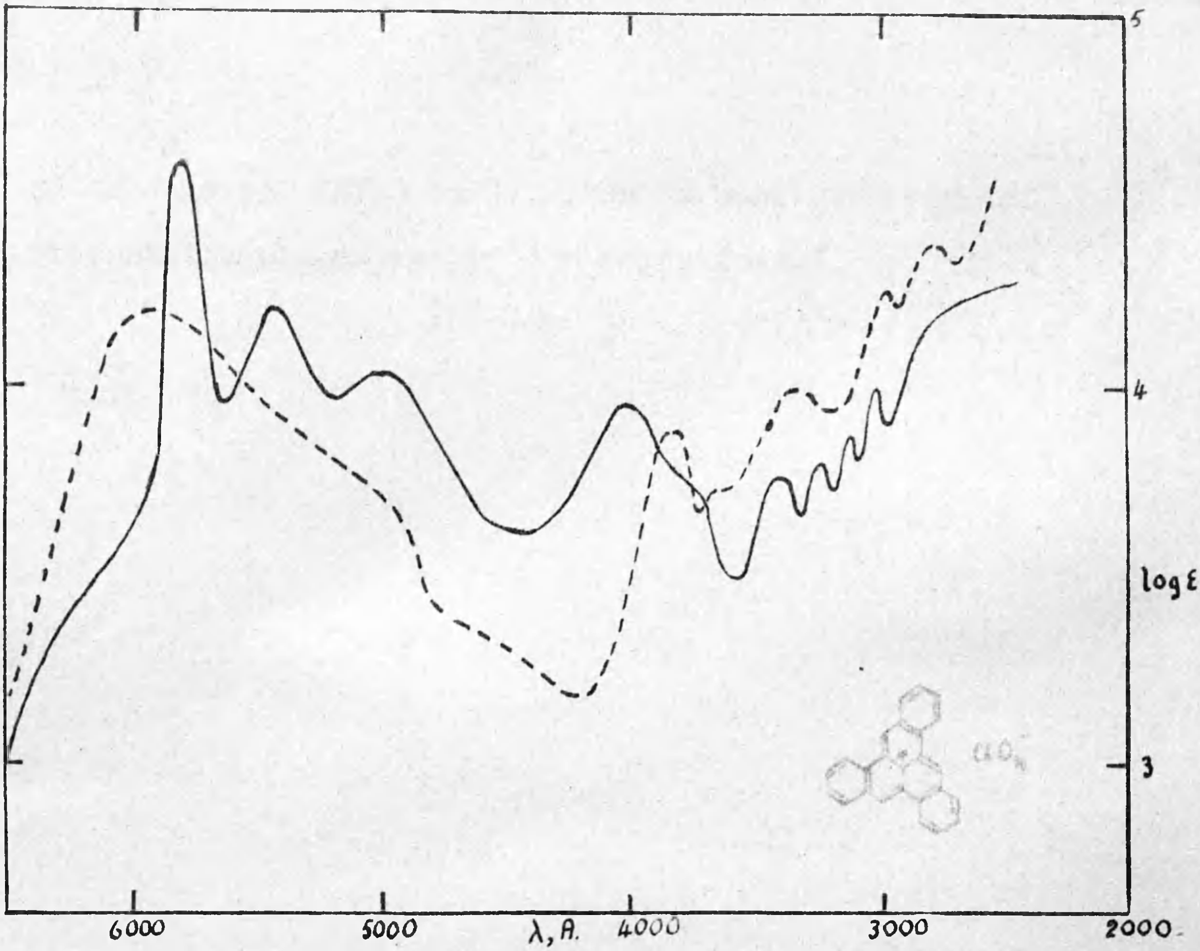
Fig. 21.

product is readily hydrolysed with hot water, but dissolves giving a stable violet-blue solution in nitromethane. The addition of alkalies or bases, such as pyridine, to this solution decolourises it immediately, but if perchloric acid is added without delay, the original colour is restored. If the decolourised solution is allowed to stand in contact with air for some time (15 to 30 minutes), the addition of perchloric acid does not give the initial violet-blue colour, but the deep red colour of the perchlorate of tribenzoperinaphthenone (XCIII). The blue compound is rapidly reduced by boiling in acetic acid with zinc dust and a colourless solution with a blue fluorescence is obtained which is not stable but readily oxidises.

These reactions can be explained by the following mechanism: the hydrocarbon (XCVII) is readily oxidised to the radical salt (XCVI) or to the cation (XCV), but if the acid is weak, e.g., acetic acid, further oxidation occurs and tribenzoperinaphthenone (XCIII) is obtained. If the salt (XCVI) or (XCV) is treated with alkali a colourless compound is formed which, when left in contact with air, is oxidised to (XCIII). Immediate addition of perchloric acid, however, reforms the cation (XCVI) or (XCV) as before. The ease with which these salts (XCVI) or (XCV) are reduced to an oxidisable product is completely analogous to the preparation of zethrenium hydride (LXX) from the zethrenium salts (LXXI). This mechanism is in complete harmony with the theory (which has already been advanced to explain the abnormal properties of other compounds), that compounds of this type have a pronounced tendency to assume structures having an external aromatic system of double bonds. In this case the highly symmetrical, mesomeric cation (XCVI) or (XCV) is formed, in which the positive charge is located at the central carbon atom.

A violet-blue compound with properties similar to those of the perchlorate described above is precipitated when a few drops of bromine are added to a cold solution of the hydrocarbon (XCVII) in benzene. Here it is suggested that a bromine atom replaces a hydrogen atom and the compound so formed ionises in polar solvents such as nitromethane to give the cation (XCV). The absorption spectrum of tribenzoperinaphthylium perchlorate is shown in Fig.22 compared with that of zethrenium sulphate and the similarity between the two spectra is readily seen.

Finally it was observed that dihydrotribenzoperinaphthene (XCIV) was stable to boiling in acetic acid in contact with air. If, however, a little selenium dioxide is added to the hot solution, the deep violet-blue colour



——— Zethrenium-sulphate (LXXI) in sulphuric acid (2%), water (49%) and alcohol (49%) Band maxima in A: 5800, 5430, 4950; 4040; 3410, 3250, 3130, 3025.

--------- Tribenzoperinaphthylium perchlorate (XCVI) in acetic acid (50%) and hydrochloric acid (50%). Band maxima in A: 5960; 3820; 3600, 3550, 2960, 2780.

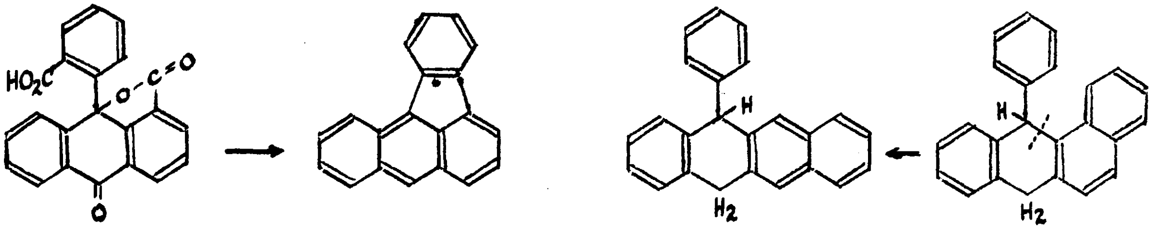
FIG. 22.

of the cation (XCVI) or (XCV) is at once obtained (cf., preparation of coeranthrylium perchlorate).

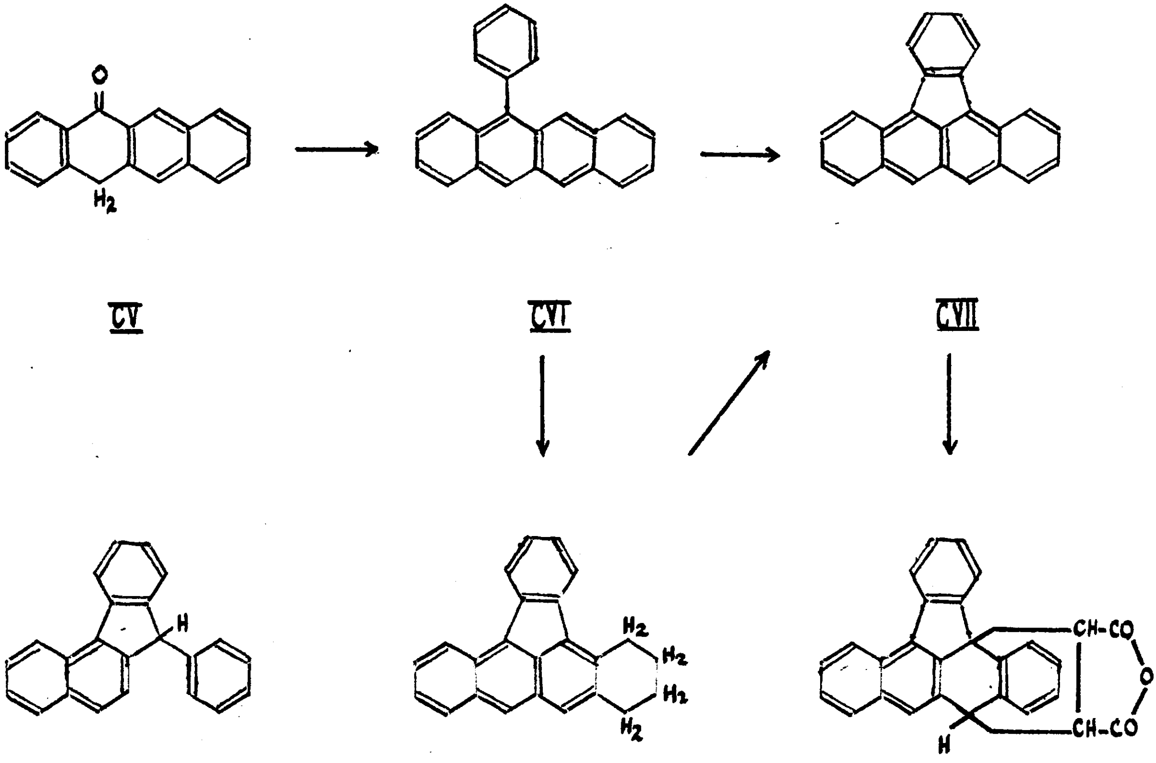
The Syntheses of Benzofluoranthenes (61).

During the chromatographic purification (alumina) of a reaction product, in the preparation of hexahydrotriangulene (XXVII) from a crude sample of 12-hydroxytriangulene-4:8-quinone (XXVIII), a yellow hydrocarbon (m.p. 143-144^{o}) was isolated which gave a yellow solution in concentrated sulphuric acid, changing to violet on standing. At first the hydrocarbon could not be identified, but when shortly after 2:3-benzofluoranthene (CII) was synthesised almost simultaneously by Stubbs and Tucker (62) and by Campbell and Marks (63), its properties and absorption spectrum were found to be identical with those of the new hydrocarbon.

The formation of 2:3-benzofluoranthene (CII), as a by-product in the preparation of hexahydrotriangulene (XXVII), can be attributed to the presence of a small amount of uncondensed material (XXV) which, when submitted to the zinc dust melt, is decarboxylated and ring-closed to 2:3-benzofluoranthene (CII) by the splitting out of the lactone group. This reaction is analogous to the preparation of rubicene (Scholl and Meyer, 64) by the zinc dust distillation of 9:10-diphenyl-9:10-dihydroxyanthracene-1:5-dicarboxylic acid dilactone.



XXV   CII   CIII   CIV



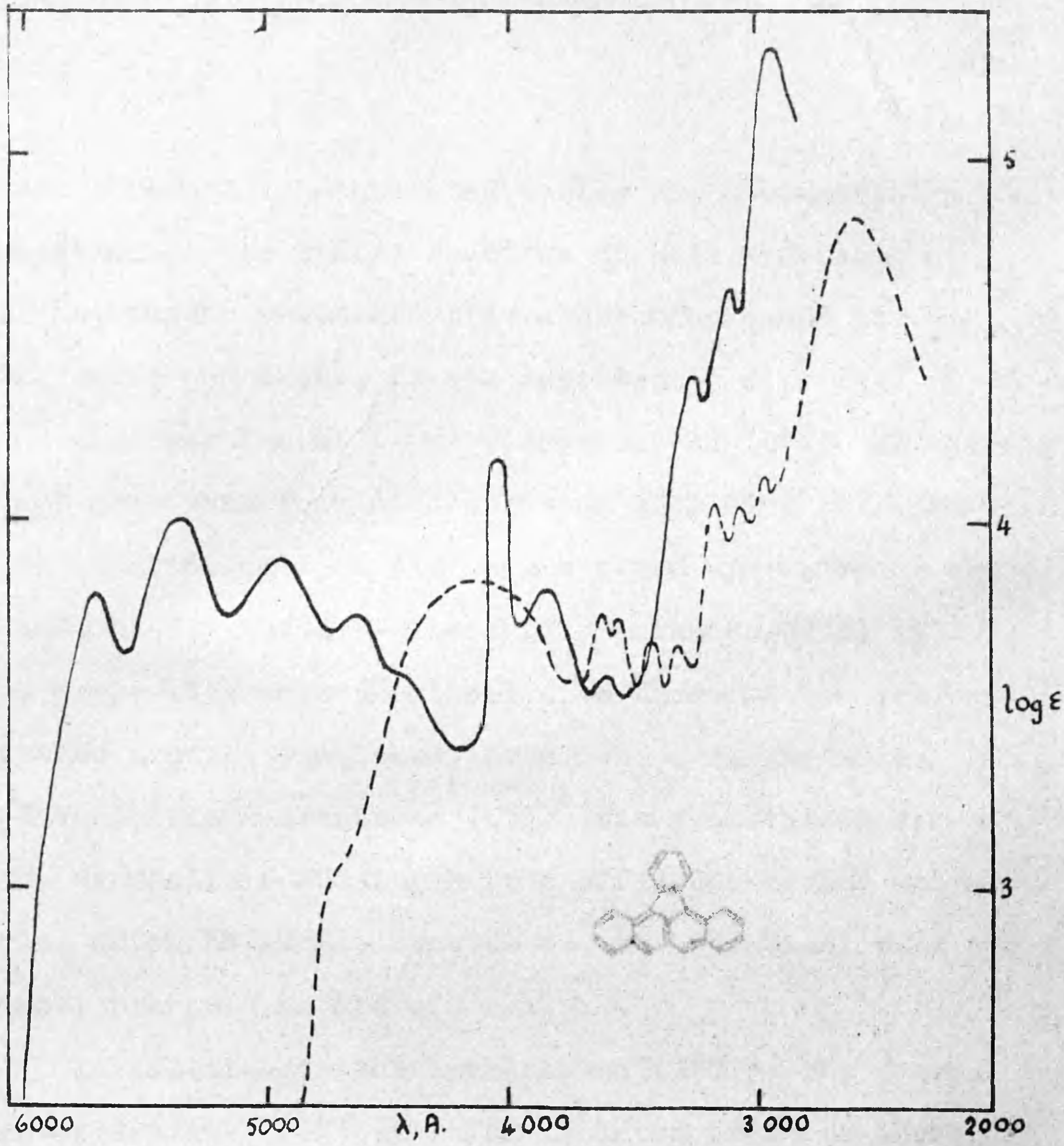
CV   CVI   CVII

CVIII   CIX   CX

The absorption spectrum of 2:3-benzofluoranthene (CII) is shown in Fig.23 and it is readily seen that the general shape of the curve is similar to that of fluoranthene (Clar, 65). The loss in fine structure of the spectrum and the slight deviation from the anellation principle (see Table III) is probably due to distortion of the plane of the molecule by the overlapping of the hydrogen atoms in the 1' and 13 positions.

It was also noted that the absorption spectrum of 2:3-benzofluoranthene (CII) bore a remarkable resemblance to that of a red condensation product (Fig.23) isolated by Clar and Stewart (66) as a by-product in the ring-closure of 9-phenyl-1:2-benzanthracene to 1:2:3:4-dibenzopyrene with aluminium chloride. Moreover, when the shift to the red of approximately 70A due to using benzene as a solvent in place of ethyl alcohol (c.f., Fig.16) was taken into account and the anellation principle of E. Clar was applied, the calculations indicated that the red by-product was 2:3-6:7-dibenzofluoranthene (CVII) and the following synthesis was therefore devised to check this prediction.

5-Keto-5:12-dihydronaphthacene (CV), which was prepared from naphthacene-5:12-quinone by a modification of Fieser's method (67), was treated with phenylmagnesium bromide and 5-phenylnaphthacene (5-phenyltetracene) (CVI) was obtained direct from the reaction mixture as the inter-



——— Dibenzofluoranthene (CVII) in benzene. Band maxima in A: 5710, 5330, 4940, 4630; 4080, 3850, 3630; 3230, 3090, 2925.

-------- 2:3-Benzofluoranthene (CII) in alcohol. Band maxima in A: 4280; 3620, 3570, 3450, 3285; 3150, 3030, 2955; 2570.

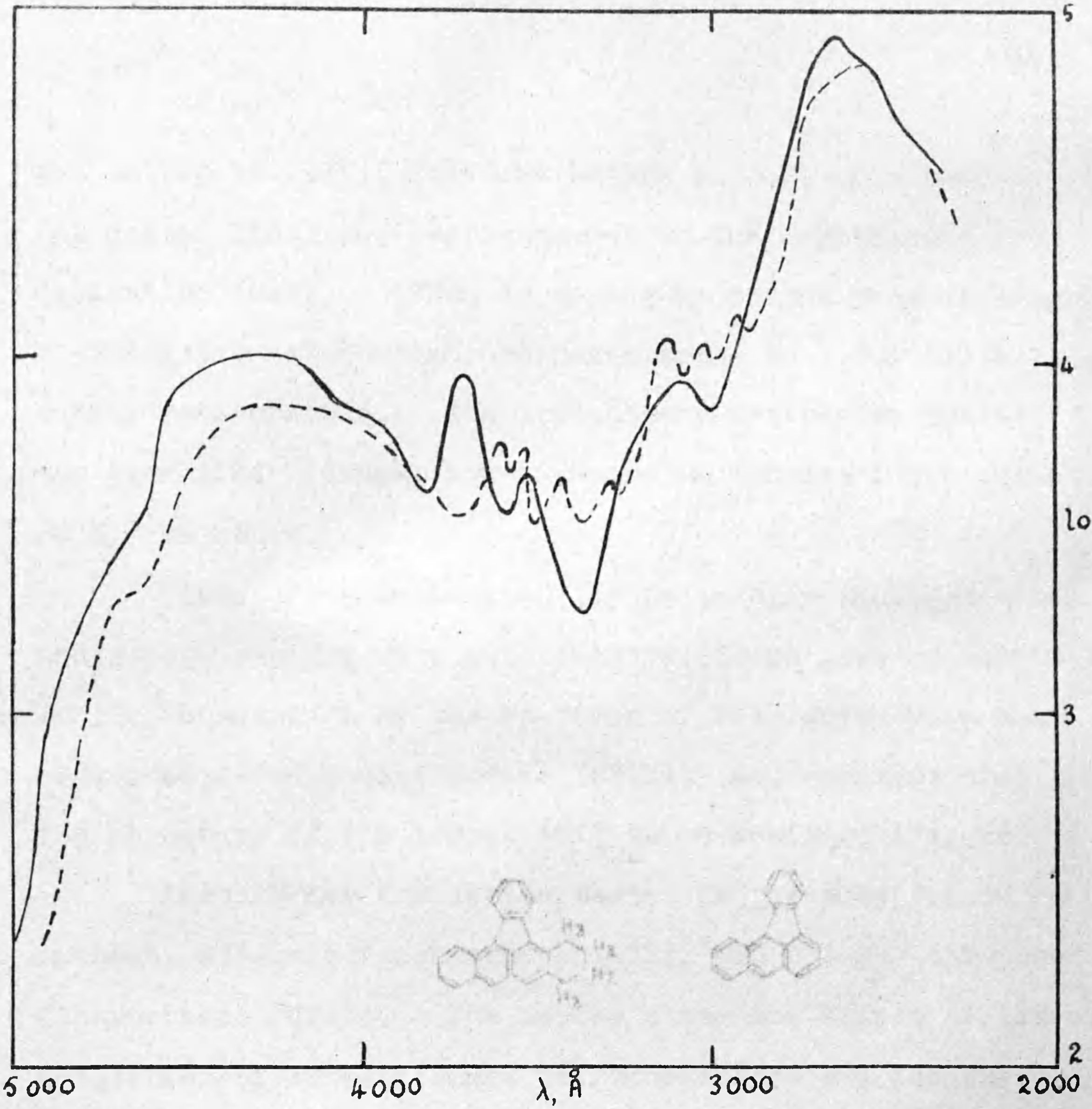
FIG. 23.

mediate carbinol is dehydrated during the decomposition. Examination of the visual spectrum of this hydrocarbon (CVI) in benzene revealed three absorption bands at 4860A, 4550A and 4280A, as was expected.

Condensation of 5-phenylnaphthacene (CVI), by heating for not more than four minutes in an aluminium chloride-sodium chloride melt at 110°, gave a red hydrocarbon, which was undoubtedly 2:3-6:7-dibenzofluoranthene (CVII) and whose properties were identical with those of the red condensation product previously obtained. Furthermore, 2:3-6:7-dibenzofluoranthene (CVII) was synthesised by Dr. N. Campbell of Edinburgh by a different method and a sample, which he kindly sent to us, was identical with our product, prepared as above.

In addition to the hydrocarbon (CVII), its tetrahydro-derivative (CIX) was also isolated from the above condensation. This hydrocarbon (CIX) is readily dehydrogenated to dibenzofluoranthene (CVII) by sublimation from a palladium-charcoal catalyst and its structure is easily deduced from its absorption spectrum as it is very similar to that of 2:3-benzofluoranthene (CII) (Fig.24).

The formation of dibenzofluoranthene (CVII) during the preparation of dibenzopyrene from 9-phenyl-1:2-benzanthracene (66), can be explained by the hydrogenation of



——— Tetrahydrodibenzofluoranthene (CIX) in alcohol. Band maxima in A: 4300; 3700, 3520; 3080; 2640.

- - - - 2:3-Benzofluoranthene (CII) in alcohol. Band maxima in A: 4280; 3620, 3570, 3450, 3285; 3150, 3030, 2955; 2570.

FIG. 24

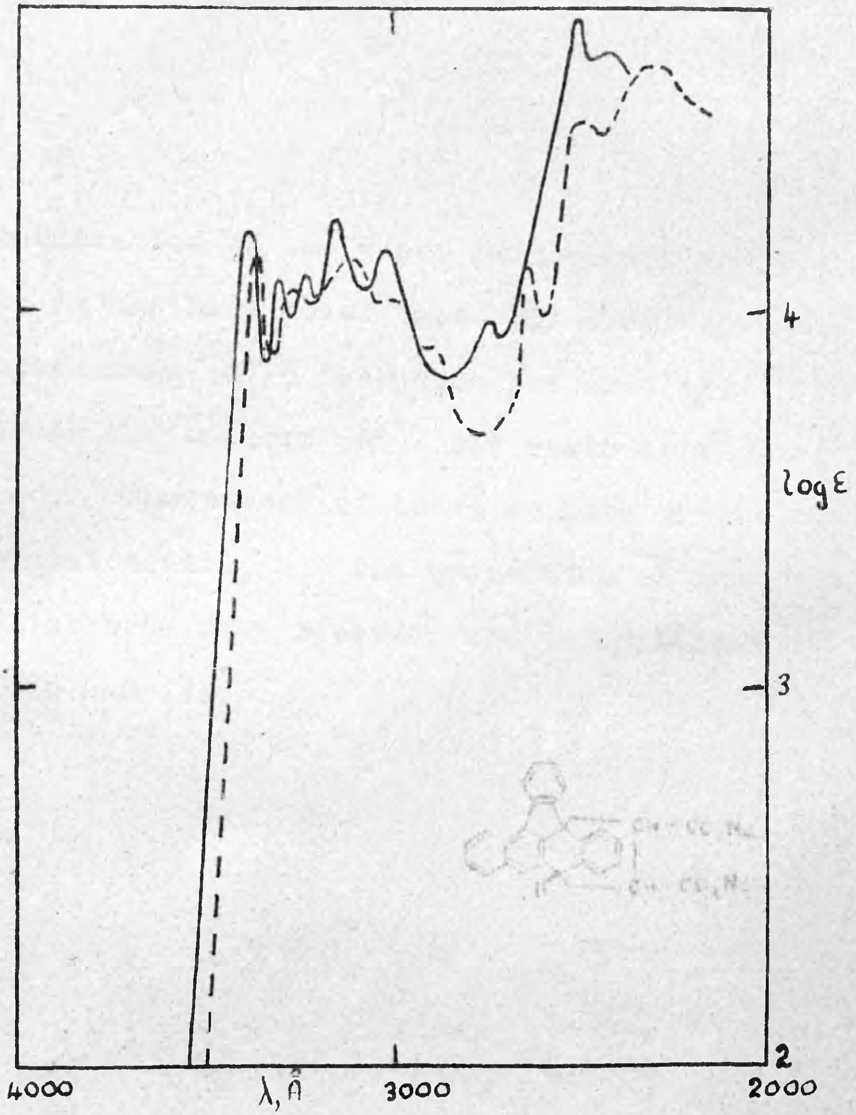
the latter to (CIV), followed by the rupture of a bond (at dotted line) and rearrangement to the naphthacene derivative (CIII). This is analogous to the rearrangement of 1:2:3:4:5:6:7:8-octahydrophenanthrene to 1:2:3:4:5:6:7:8-octahydroanthracene. The naphthacene derivative (CIII) may then lose hydrogen and condense to dibenzofluoranthene (CVII) as above.

Dibenzofluoranthene (CVII) is readily photo-oxidised and reacts rapidly with maleic anhydride to give an adduct (CX). Comparison of the spectrum of the latter with that of 9-phenyl-3:4-benzofluorene (CVIII) (68) confirms that the structure of the adduct (CX) is as assigned (Fig.25).

Another new anellation series is given by fluoranthene, 2:3-benzofluoranthene (CII), and 2:3-6:7-dibenzofluoranthene (CVII). The series shows the effect of linear anellation of benzene rings to fluoranthene and the wavelengths of the first para-bands are proportional to 7^2, 8^2 and 9^2 as is required by the anellation principle (Table III).

Table III.

	Fluoranthene	Benzofluoranthene	Dibenzofluoranthene
λ in A	3585	4280	5640
Rp (cm^{-1})	147×10^4	147×10^4	147×10^4
$Kp = \sqrt{\lambda Rp}$	7.26	7.93	9.11



——— Disodium salt of the maleic anhydric adduct of dibenzofluoranthene (**CX**) in water. Band maxima in A: 3365, 3295, 3220; 3140, 3005; 2740; 2510, 2420.

-------- 9-Phenyl-3:4-benzofluorene (**CVIII**) in alcohol. Band Maxima in A: 3360, 3270; 3130, 3000; 2640; 2500 2320.

FIG. 25.

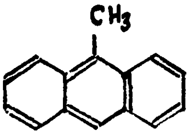
Since publication of the paper on dibenzofluoranthene (CVII), it has been found that this hydrocarbon and 5-phenylnaphthacene (CVI) have been prepared by Dufraisse, Etienne and Bucourt (69), but again by a different method. The report of these authors gives little experimental detail, but the properties of the hydrocarbons which have been reported are in agreement with those of our samples.

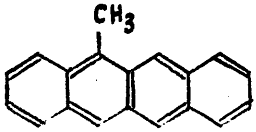
The Synthesis of Benzylnaphthacene.

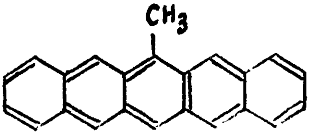
In the acene series, it is generally recognised that, as the series is ascended, the central ring becomes less benzenoid and more quinonoid in character. The keto-enol tautomerism of the phenols is a good example of this phenomenon and, in the higher members of the series, the keto-form is more stable so that they exist almost entirely as ketones with anthrone-type structures, e.g., 5-keto-5:12-dihydronaphthacene (CV). The increasing stability of the acene-quinones and the study of their reduction-oxidation potentials also supports this idea (70).

Tautomerism between methylacenes and methylene-dihydroacenes has frequently been postulated to account for the side-chain reactivity of aromatic compounds and the isolation of 6-methylene-6:13-dihydropentacene (CXVI) (Clar and Wright, 71) has given weight to the theory. As the anellation principle requires a gradual change in the properties of the members of the acene series, it was therefore inferred that 5-methylnaphthacene (CXIII), 9-methylanthracene (CXI), 1-methylnaphthalene and toluene would also contain the corresponding methylene form but in decreasing proportions.

Clar and Wright (71) have shown that the absorption spectrum of 9-methylanthracene (CXI) closely resembles that







CXI

CXIII

CXV

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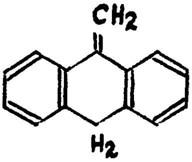
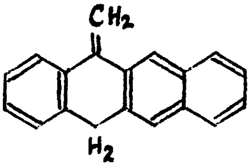
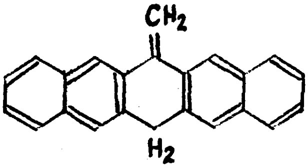


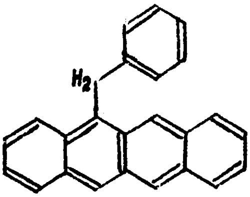




CXII

CXIV

CXVI



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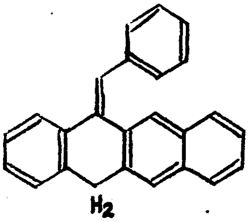


CXVII

CXVIII

of anthracene but this does not exclude the possibility that a small percentage of the weakly-absorbing methylene form (CXII) is present. 5-Methylnaphthacene (CXIII) has an absorption spectrum similar to that of naphthacene (tetracene), but the intensities of the absorption bands are lower than those of naphthacene. Clar and Wright attributed this lowering of the intensities to the presence of an appreciable amount of the methylene form (CXIV).

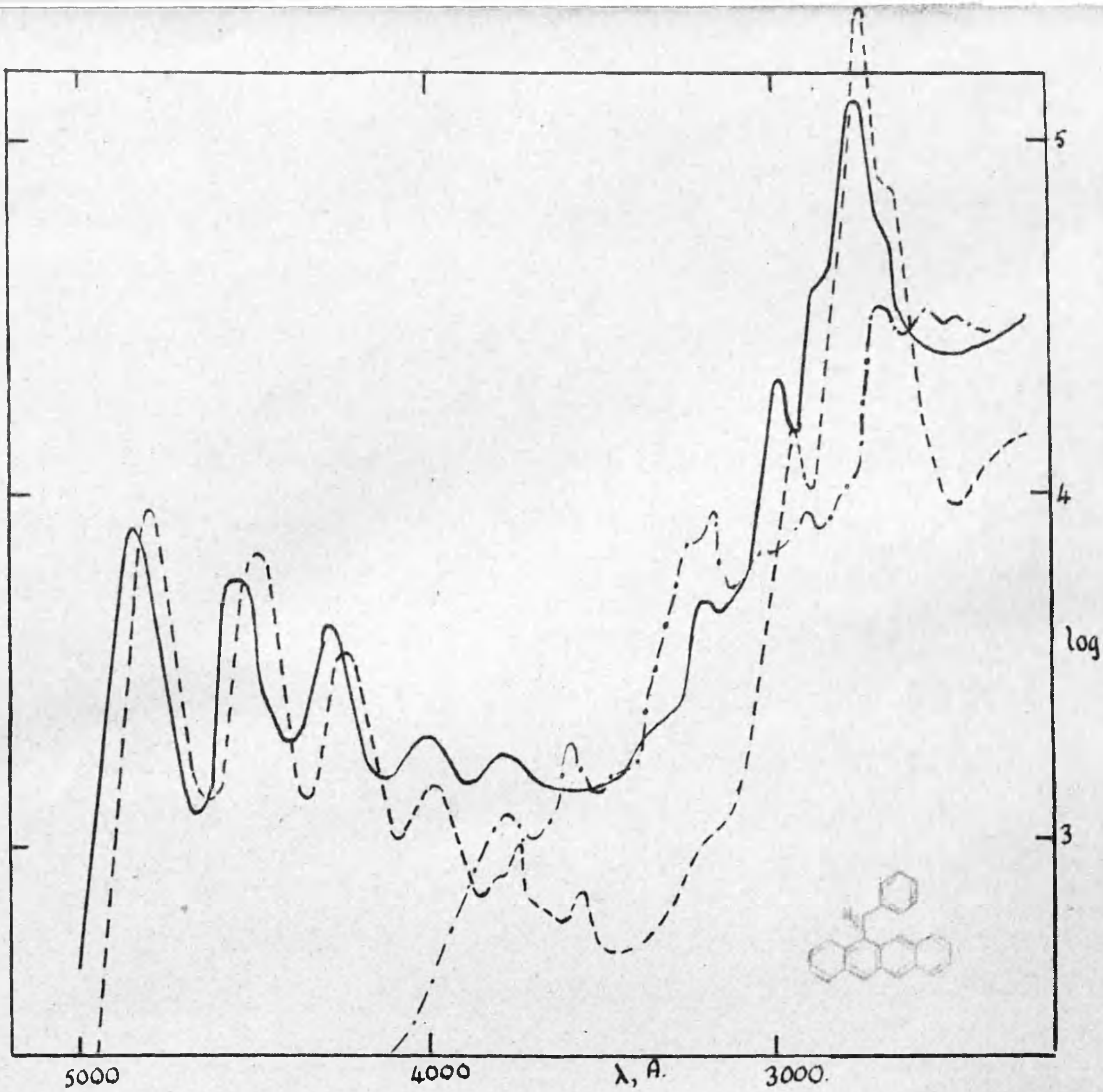
In the pentacene series, the absorption spectrum of the pale yellow 6-methylene-6:13-dihydropentacene (CXVI) bears no resemblance to that calculated for 6-methylpentacene (CXV) by applying the anellation principle of E. Clar. However, the para-bands of methylpentacene (CXV) were observed when a solution of the methylene form (CXVI) in 1-methylnaphthalene was heated to 200° with the exclusion of air. These bands slowly disappear as the solution cools.

From these facts it was predicted that 5-benzylnaphthacene (CXVII) would exist to a considerable extent in the methylene form (CXVIII). This hydrocarbon was prepared by the interaction of benzylmagnesium chloride and 5:12-dihydro-5-ketonaphthacene (CV), the carbinol, which is formed as an intermediate stage, being dehydrated during the decomposition of the reaction mixture. It was observed that when the yellow-orange hydrocarbon was heated in glacial acetic acid the solution became more red in colour and that, on cooling, this colour slowly faded.

The absorption spectrum of 5-benzylnaphthacene (CXVII) is shown in Fig.26 compared with that of 5-methylnaphthacene (CXIII) and 6-methylene-6:13-dihydropentacene (CXVI). It is at once noticed that the absorption bands of (CXVII) are less intense than those of methylnaphthacene (CXII) and that the minimum of the curve is not as deep. In addition, the band at 3770A cannot be explained by the benzylnaphthacene structure (CXVII). It was concluded that these deviations from the naphthacene-type spectrum must be due to the presence of a high percentage of the methylene form (CXVIII), which will have a spectrum very similar to that of methylene-dihydropentacene (CXVI).

Attempts were therefore made to separate the two tautomers, e.g., by careful crystallisation from various solvents, and to remove one tautomer, e.g., by reacting the acene form with maleic anhydride. The attempts were not successful and a different approach will have to be devised.

This work is of importance from the standpoint of resonance in aromatic hydrocarbons. Clar and Wright (71) have pointed out that as each member of the pairs of structures formulated contain the same number of double



——— 5-Benzyltetracene (CXVII) in alcohol. Band maxima in A: 4830, 4540, 4270, 4000; 3770; 3150, 2980, 2860; 2785.

- - - - - 5-Methyltetracene in alcohol. Band maxima in A: 4805, 4490, 4220, 3980; 3750, 3560; 2950; 2755, 2650.

-·-·-·-·- 6-Methylene-6:13-dihydro-pentacene (CXVI) in alcohol. Band maxima in A: 3770, 3585, 3420; 3175, 3020, 2900; 2690, 2570.

Fig. 26.

bonds as the other member, the energy difference between the methyl form and the methylene form must comprise the difference in resonance energy. Wave mechanical treatment predicts a decreasing difference in the resonance energy of these pairs of hydrocarbons with an increasing number of rings, until the difference becomes zero with an infinite number of rings (72). Hence the ratio between the methyl and methylene forms should never exceed 1 : 1. The isolation of pure 6-methylene-6:12-dihydropentacene (CXVI) by E. Clar has shown this prediction to be wrong and it is desirable to extend this work, if possible, to the naphthacene series.

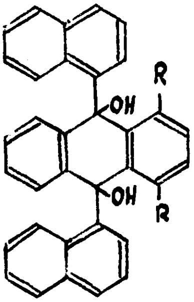
Finally, an attempt was made to ring-close benzylnaphthacene (CXVII) to 2:3-4:5-8:9-tribenzoperinaphthene by heating with aluminium chloride in benzene solution and in a melt with sodium chloride. In one experiment, a small quantity of deep-red crystals was obtained after chromatographic purification, and the visible spectrum of these was consistent with the linear anellation of a benzene ring to coeranthrene (LXIV). However, repeated attempts to obtain further samples of this compound were not successful and it was concluded that this hydrocarbon is too sensitive to be isolated by this method.

The Synthesis of 1:9:5:10-Diperinaphthyleneanthracene.

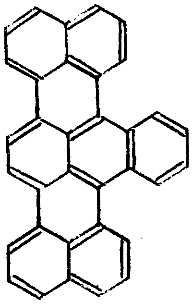
The condensation of 9:10-di-α-naphthyl-9:10-dihydroxy-9:10-dihydroanthracene (CXIX; R = H) by heating with aluminium chloride and a trace of pyridine at 110° yielded a greenish-blue hydrocarbon (Clar and Guzzi, 73). As both 7:8-benzoterrylene (CXX) and diperinaphthyleneanthracene (CXXV) are possible products in this reaction, the structure of this hydrocarbon was not certain and, at first, the latter formulation appeared to be the more likely as the 1:4-dimethyl-derivative of CXIX ($R = CH_3$) did not give a similar condensation product when heated with aluminium chloride.

This view, however, was erroneous and further work by Clar and Wright (74, 75) has proved that the hydrocarbon is 7:8-benzoterrylene (CXX). These authors, who improved the yield of the hydrocarbon by using an aluminium chloride-sodium chloride melt at 110° for the condensation, and by chromatographing (alumina) the reaction product, have shown that the dehydrochlorination of the 1:4-dichloro-derivative of (CXIX) (R = Cl) gives the same hydrocarbon as that obtained above.

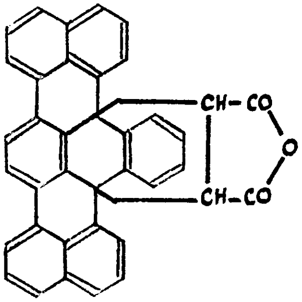
An examination of the absorption spectrum of the maleic anhydride adduct (CXXI) of the hydrocarbon, which was prepared by heating the hydrocarbon with excess maleic



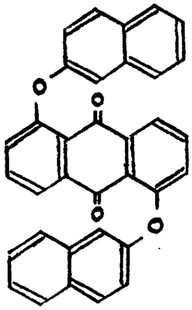
CXIX



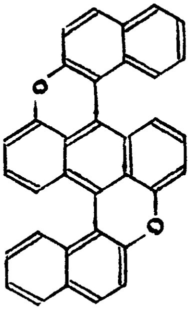
CXX



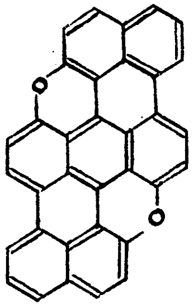
CXXI



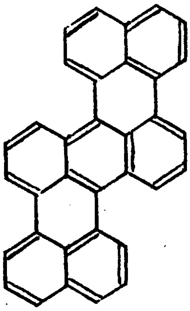
CXXII



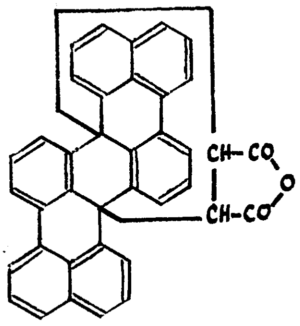
CXXIII



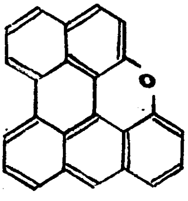
CXXIV



CXXV



CXXVI



CXXVII

anhydride at approximately 200°, provided further evidence that the structure is (CXX). The basic aromatic structure of the adduct (CXXI) is 2:3-2":3"-dibenzoterphenyl which is held in one plane by the rest of the molecule. As is required by the anellation principle, the parallel linear anellation of two benzene rings to the planar terphenyl structure increases the order number (K) by unity (cf., perylene) and consequently an anellation series, into which the adduct (CXXI) fits very well, is given by the para-bands of terphenyl, the adduct (CXXI), terrylene and 7:8-benzoterrylene (CXX) (76).

Although the above investigations established that the hydrocarbon, isolated by Clar and Guzzi (73), was 7:8-benzoterrylene (CXX), the isomeric 1:9-5:10-diperinaphthyleneanthracene (CXXV) was still unknown and the following unambiguous synthesis, based on unpublished work of E. Clar, was therefore devised.

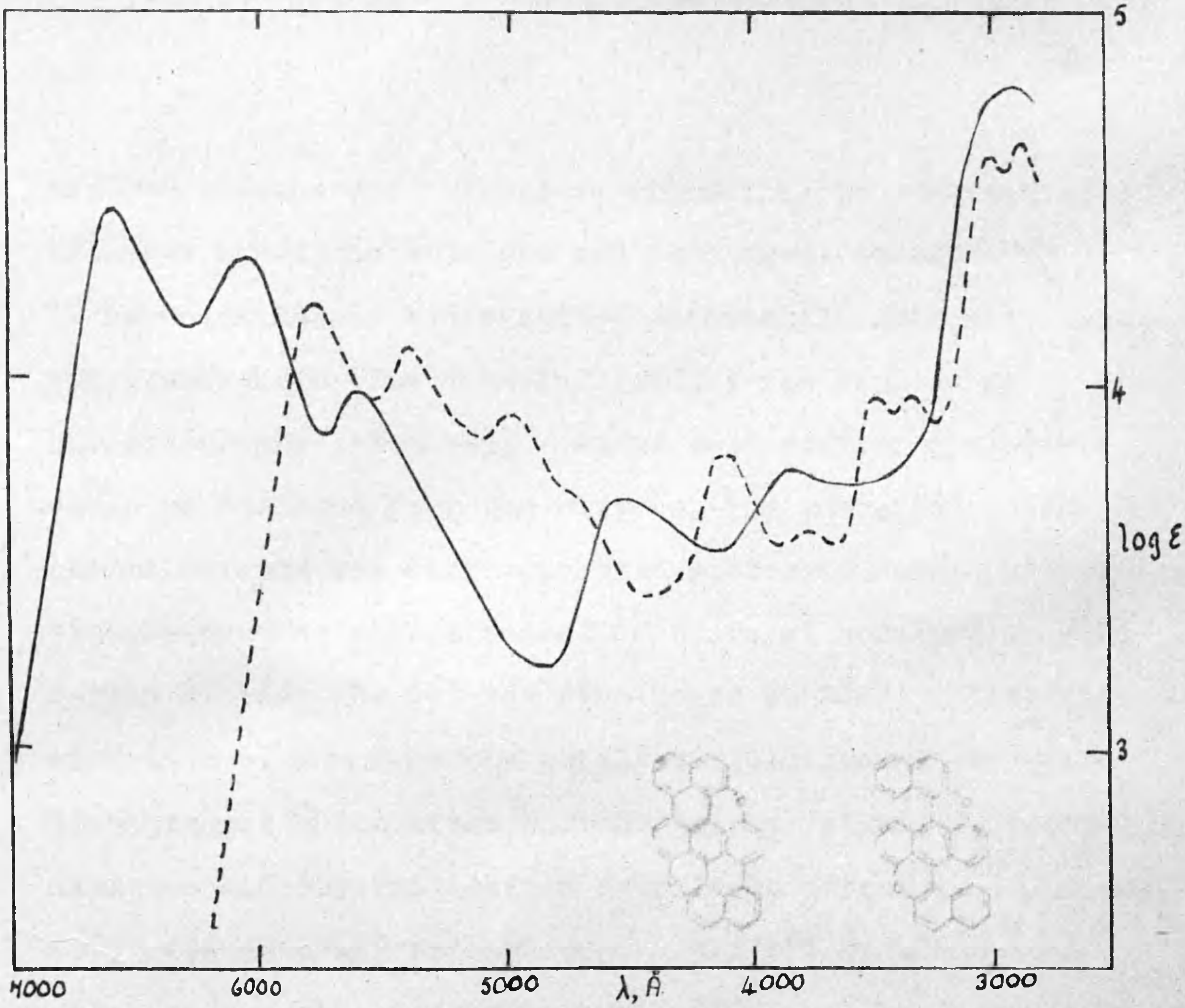
Fusion of 1:5-dichloroanthraquinone with β-naphthol and powdered potassium hydroxide at 145° yielded the bright yellow 1:5-di-β-naphthoxyanthraquinone (CXXII), whose properties agreed with those of samples prepared by other methods (77, 78). A peculiar property of this compound is that when the dry powder is exposed to light, the surface becomes tinged with orange, but the initial bright yellow colour is restored by standing for some time in the dark. This change can be effected many times without any apparent deterioration of the compound.

Condensation of the diether (CXXII) was carried out by heating in an aluminium chloride-sodium chloride melt at 185° for ten minutes and from the reaction mixture two compounds, (CXXIII) and (CXXIV), were isolated by chromatography (alumina).

The dark red by-product (CXXIII), whose formation is due to incomplete ring-closure, was converted to the blue compound (CXXIV) by further treatment with aluminium chloride. It was readily soluble in cold benzene and gave a violet-red solution with a red fluorescence, which photo-oxidised very rapidly.

The absorption spectra of these two compounds, (CXXIII) and (CXXIV), are compared in Fig.27 and the similarity in the shapes of the curves is at once obvious. It will also be noted that the formation of two new bands by the ring-closure of (CXXIII) to (CXXIV) produces a strong shift to the red, as would be expected from the anellation principle.

The dark blue material (CXXIV) is not readily reduced and the ether linkages are not broken either by Clar's zinc dust melt or by boiling with hydriodic acid



——— 8:2'-4:2''-Dioxido-1:9-5:10-diperinaphthyleneanthrscene. (CXXIV) in benzene. Band maxima in Å: 6600, 6050, 5600; 4550, 3940; 2900.

- - - - 1:2'-5:2''-Dioxido-9:10-di-α-naphthylanthracene. (CXXIII) in benzene. Band maxima in Å: 5760, 5370, 4850; 4090, 3840, 3470, 3310; 2990, 2860.

Fig. 27.

and red phosphorus. However, on heating in a sealed tube with 55% hydriodic acid and red phosphorus at 210° for 10 hours, a highly hydrogenated material is obtained, from which unreduced blue material (CXXIV) was removed by chromatography (alumina). As no well-defined compound could be isolated from the mixture, the gum obtained after chromatography was dehydrogenated without further purification by heating with a palladium-charcoal catalyst in pure carbon dioxide (30-33) for five hours at 230°. Sublimation in a vacuum from the catalyst yielded a non-crystalline product which after chromatography (alumina), resublimation and crystallisation from light petroleum (b.p. 60-80°) gave deep red prisms (m.p. 115-116°) of a compound which is probably the hydrocarbon (CXXV). The compound dissolved in benzene to give an orange solution with a green fluorescence, which when boiled with maleic anhydride decolourised very rapidly. The maleic anhydride adduct crystallised out as colourless needles, which is consistent with the structure (CXXVI), whose absorption spectrum will be very similar to that of benzanthrene, except that the intensities of the absorption bands will be higher.

Until analyses are obtained for the hydrocarbon and its maleic anhydride adduct and their absorption spectra fully examined, the main evidence, apart from its method of preparation, that this product is 1:9-5:10-diperinaphthyleneanthracene (CXXV), is based on its visual spectrum. When the latter was examined in benzene solution, sharp absorption bands were observed at 5090A, 4760A and 4460A.

The contribution of one oxygen bridge to a resonating aromatic system can be estimated by comparing the absorption spectra of 1:2-benzoperylene (74, 79) and 12:1'-oxido-1:2-benzoperylene (CXXVII) (80). The maxima of the para-bands of the hydrocarbon in benzene solution occur at 5220A, 4880A and 5620A, while those of the oxide (CXXVII) in benzene solution are at 6010A, 5570A and 5100A. Considering the first para-bands of these compounds, the bathochromic shift due to the addition of one oxygen bridge to the hydrocarbon is equal to 790A. Now assuming that the addition of two oxygen bridges to the hydrocarbon (CXXV) will produce a shift to the red equal to twice the amount estimated for the addition of one oxygen bridge, the first para-band of the hydrocarbon (CXXV) should occur at 5020A, as that of the blue compound (CXXIV) is at 6600A (Fig.27).

Although this estimated value of 5020A does not correspond exactly with the value (5090A) found for the first para-band of the red prisms (m.p. 115-116^{o}) in benzene solution, it does indicate that this compound is the hydrocarbon (CXXV), and the work now being carried out by Clar and Kelly at Glasgow is expected to verify this supposition.

EXPERIMENTAL.

EXPERIMENTAL.

(All melting points are uncorrected and were taken in evacuated capillaries. Microanalyses are by Miss R.H. Kennaway, Miss M.W. Christie and Mr. J.M.L. Cameron).

Synthesis of Pentaphene (5).

Reaction of Phthalic Anhydride with o-Tolylmagnesium Bromide. - Procedure was as described by Weisz and Korczyn (6). An 80% yield of colourless crystals (m.p. 126-130°) was obtained on crystallisation from acetic acid.

Tri-o-tolylcarbinol (VI).-o-Toluoyl chloride (65 g.) in anhydrous ether (50 c.c.) was slowly added to a solution of *o*-tolyl-lithium prepared from *o*-bromotoluene (207.5 g.) and "atomised" lithium (16.8 g.). After decomposing the mixture with dilute hydrochloric acid solution, the ethereal layer was concentrated and diluted with light petroleum (b.p. 40-60°). The crystals (110 g.) were recrystallised from light petroleum and yielded colourless needles (m.p. 105°) and a by-product (8%) (m.p. 240-242°). The carbinol (VI) dissolved readily in concentrated sulphuric acid to give an orange solution. The properties of the carbinol agree with those described for a sample prepared by a different method (8 and 9).

Di-o-tolylphthalide (VII). - The carbinol (VI) (75 g.), mixed with nitrobenzene (30 c.c.) was boiled in 20% nitric acid solution (1500 c.c.) for 16 hours, fumes of nitrogen oxides being evolved. After distilling off the nitrobenzene, the light-yellow solid obtained was extracted thoroughly with boiling dilute sodium hydroxide solution to remove over-oxidised material, washed well with water and crystallised first from glacial acetic acid and then from ethanol to give colourless plates (68 g.) (m.p. 174°) (Found: C, 83.7; H, 5.5. Calc. for $C_{22}H_{18}O_2$: C, 84.0; H, 5.8%). The phthalide (VII) gave an orange-red solution in concentrated sulphuric acid which changed first to orange, then to pale yellow. The melting point compares with that of the higher-melting phthalide (m.p. 176°) reported by Weisz and Muller (7).

Reaction of as-Phthaloyl Chloride with o-Tolylmagnesium Bromide. - o-Tolylmagnesium bromide, prepared from o-bromotoluene (140 g.) and magnesium (21 g.) in ether (350 c.c.), was added to as-phthaloyl chloride (70 g.) in benzene (300 c.c.). After the usual decomposition and separation of the aqueous layer, concentration of the organic layer gave colourless crystals (12.5 g.) of mono-(o-tolyl)phthalide (XX) (m.p. 262°), (Found: C, 79.6; H, 5.4. $C_{15}H_{12}O_2$ requires C, 80.3; H, 5.4%), which gave a colourless solution in concentrated sulphuric acid. The mother liquors, after extraction with dilute sodium hydroxide solution (10%) to remove 2-o-toluoylbenzoic acid (20 g.) were steam distilled and the resulting solid was crystallised from glacial acetic acid to give colourless crystals (m.p.125-129°) (73 g.). Further crystallisation, however, first from benzene and then from ethanol gave the pure 1:2-di-(o-toluoyl)benzene (XI) (m.p. 146°) (76% of mixture) (Found: C, 83.8; H, 5.5. $C_{22}H_{18}O_2$ requires C, 84.0; H, 5.8%) which gave a pale yellow solution in concentrated sulphuric acid. Hot acetic acid and zinc dust yielded a yellow solution of (XIV) which showed a strong blue fluorescence. Both by-products, mono-(o-tolyl)phthalide (XX) and 2-o-toluoylbenzoic acid, on oxidation with alkaline potassium permanganate solution and recrystallisation from concentrated nitric acid gave colourless crystals (m.p. 212°) which gave mixed m.ps. of 212° with an authentic sample of benzophenone-2:2'-dicarboxylic anhydride (XXI).

1:4-Di-o-tolylphthalazine (X). - The mixture (m.p. 125-129°) (1 g.) was dissolved in ethanol (15 cc.), hydrazine hydrate solution (100%) (0.18 cc.) added and the solution refluxed for one hour. Concentration yielded colourless plates (m.p. 174°) (0.2 g.) which gave a mixed m.p. of 174° with an authentic sample of di-o-tolylphthalide

(VII). Dilution of the mother liquors with water gave a white precipitate (0.75 g.) which on crystallisation from ethanol yielded colourless crystals (m.p. 162-163°) of 1:4-di-o-tolylphthalazine (X). (Found: N, 9.0. $C_{22}H_{18}N_2$ requires N, 9.0%). The azine gave a colourless solution in concentrated sulphuric acid.

Oxidation of 1:2-Di-o-toluoylbenzene (XI) and Di-o-tolylphthalide (VII) - (a) With dilute nitric acid solution at 210°.

The diketone (XI) (1 g.) was heated under pressure with 20% nitric acid solution at 210° for 10 hours. The solid obtained crystallised from acetic anhydride to give colourless needles of (XII) (m.p. 302-303°). The yield was theoretical.

(b) The phthalide (VII) gave, in the same way, 60% of (XII) (m.p. 302-303°) and from the mother liquor 35% of unrearranged dicarboxylic acid (VIII) derived from (VII). The latter formed a syrup which did not crystallise and gave on heating with concentrated sulphuric acid and copper powder the blue condensation product described by Weisz and Korczyn (6).

(c) With dilute nitric acid solution followed by alkaline potassium permanganate solution. The diketone

(XI) (15 g.) mixed with nitrobenzene (6 c.c.) was boiled for 48 hours with 20% nitric acid solution (250 c.c.). After distillation of the nitrobenzene, the solid obtained was dissolved in dilute sodium hydroxide solution and powdered potassium permanganate added till its colour persisted for 15 minutes. The filtrate was acidified and the precipitate crystallised from acetic anhydride, (15 g.) (m.p. 302-303°).

(d) A similar treatment of (VII) yielded 75% of (XII) (m.p. 302-303°) and 20% unrearranged dicarboxylic acid (VIII).

Oxidation of Mixture of (VII) and (XI). - Both methods of oxidation described above were applied to the mixture (m.p. 125-129°) of (VII) and (XI). Colourless needles (m.p. 302-303°) were obtained in both cases after crystallisation from acetic acid and acetic anhydride, the yields being 87% and 82% respectively. The products (m.p. 302-303°) from the above oxidations all proved to be dihydro-iso-benzofuran-1:3-bis-spiro-(3-phthalide) (XII) which sublimed in long colourless needles. (Found: C, 74.2, 74.3; H, 3.5, 3.2. $C_{22}H_{12}O_5$ requires C, 74.2; H, 3.4%). The dispiran (XII) dissolved slowly in concentrated sulphuric acid to give a colourless solution which on being heated changed to dark green.

1:2-Di-(o-carbomethoxybenzoyl)benzene (XIII). - The dispiran (XII) (1 g.) was suspended in anhydrous methanol and dry hydrogen chloride passed through the mixture for 10 minutes. On refluxing, the starting material was gradually dissolved and a crystalline deposit was obtained, which was filtered off and washed with methanol. Crystallisation from benzene gave colourless needles or rods (m.p. 160°) of the ester (Found: C, 71.6; H, 4.4. $C_{24}H_{18}O_6$ requires C, 71.6; H, 4.5%), which gave a colourless solution in concentrated sulphuric acid and was insoluble in aqueous alkalis.

9-(o-Carboxyphenyl)oxanthranol lactone (IX). - The dispiran (XII) (1 g.) was ground together with copper powder and the mixture heated at 350° till a quiet melt was obtained. Sublimation in a vacuum yielded large prisms, which crystallised from ethyl alcohol in prisms (m.p. 232-233°), which were identified as the lactone (IX). (Found: C, 80.6; H, 4.2. Calc. for $C_{21}H_{12}O_3$: C, 80.75; H, 3.9%). The compound gave a yellow green solution in concentrated sulphuric acid and its properties agreed with those described for a sample prepared by a different method (Scholl and Donat, (11)).

Zinc Dust Melt of Dispiran (XII). - The dispiran (XII) (1 g.), zinc dust (2 g.) and sodium chloride (1.5 g.)

were powdered together and moist zinc chloride (7.5 g.) was added. The mixture was melted and heated to 300° during fifteen minutes with constant stirring. When cold, the melt was decomposed with dilute acetic acid and the residue was filtered off, washed and sublimed in a vacuum. The sublimate crystallised from xylene in large colourless prisms (m.p. 193-194°) (Found: C, 89.9; H, 4.4. Calc. for $C_{22}H_{14}O$: C, 89.8; H, 4.8%), whose absorption spectrum (Fig.1) showed the compound to be an anthracene derivative.

o-Di-(3-phthalidyl)benzene (XVI). - The dispiran (XII) (20 g.) was dissolved in boiling caustic soda solution (15%) (200 c.c.) and zinc dust (20 g.) added during 2 hours. The initial yellow colour changed to a deep red which persisted for 10 minutes. After 3 hours, the hot solution was filtered directly into concentrated hydrochloric acid and the white precipitate crystallised from glacial acetic acid. Colourless needles (m.p. 211-212°) of the diphthalide (XVI) (Found: C, 77.1; H, 4.3. $C_{22}H_{14}O_4$ requires C, 77.2; H, 4.1%), were obtained, which gave a colourless solution in concentrated sulphuric acid. The yield was theoretical.

1:2-Di-(o-carboxybenzyl)benzene (XV). - The diphthalide (XVI) (13 g.), red phosphorus (6 g.) and hydriodic acid (55%) (60 c.c.) were covered with xylene (60 c.c.) and after being refluxed for 36 hours, the mixture was filtered. The solid obtained was extracted with xylene and then with hot sodium hydroxide solution. The aqueous layer from the filtrate was extracted with xylene, and the combined xylene fractions then extracted with hot sodium hydroxide solution. The alkaline solutions obtained were acidified with concentrated hydrochloric acid and the precipitate crystallised from glacial acetic acid to give colourless needles (10 g., 76%) (m.p. 242-243°) of 1:2-di-(o-carboxybenzyl) benzene (XV). (Found: C, 76.2; H, 5.2. $C_{22}H_{18}O_4$ requires C, 76.3; H, 5.2%).

8-Hydroxypentaphene-5:14-quinone (XVIII). - The acid (XV) (3 g.) was dissolved in concentrated sulphuric acid (30 c.c.) and heated at 120° for 10 minutes. The initial pale yellow colour changed to reddish-brown and then to dark green. The cold solution was poured into water and the reddish-brown precipitate obtained was recrystallised from nitrobenzene, and sublimed in a vacuum. Dark red needles (2.6 g.) (m.p. 349-351°) of 8-hydroxypentaphene-5:14-quinone (XVIII) (Found: C, 80.9; H, 3.5. $C_{22}H_{12}O_3$ requires C, 81.5; H, 3.7%) were obtained which gave with alkaline sodium dithionite solution a reddish-brown vat which lightens on standing.

Pentaphene (XIX). - (a) From the diphthalide (XVI). - In the preparation of the acid (XV), the xylene fractions, after extraction with dilute sodium hydroxide solution, were concentrated and pale yellow needles (2 g.) crystallised, m.p. 255-257° alone or mixed with an authentic sample of pentaphene. (Found: C, 94.3; H, 5.4. Calc. for $C_{22}H_{14}$: C, 94.9; H, 5.1%).

(b) From (XV) or (XVIII) by the zinc dust melt. - The compound (XV) or (XVIII) (1 part) was finely ground with zinc dust (1.2 parts) and sodium chloride (1.2 parts) and moist zinc chloride (7 parts) added. The temperature was raised with constant stirring to 300° during 15 minutes. The cold melt was decomposed with dilute acetic acid; the resulting solid was filtered off, dried and sublimed in a vacuum. Crystallisation of the sublimate from xylene gave yellow needles (m.p. 255-256°) which gave a mixed m.p. of 255-256° with a sample of pentaphene. The pentaphene was further purified by chromatography (alumina), benzene being used as eluant. The clear yellow, blue-fluorescent eluate gave on concentration pale yellow plates (m.p. 256-257°) which were insoluble in concentrated sulphuric acid.

Synthesis of Triangulene Derivatives.

Di-o-tolylphthalide (VII) - This compound was prepared from tri-o-tolylcarbinol (VI) as described.

2-(Di-o-tolylmethyl)benzoic acid (XXII). - Zinc dust (100 g.) activated with copper, was added in portions during 48 hours, to a boiling solution of the phthalide (VII) (40 g.) in 20% ethanolic potassium hydroxide (300 c.c.). After dilution with water (500 c.c.) the hot solution was filtered from the excess zinc dust which was thoroughly washed with hot water. After distilling off the alcohol the filtrate was acidified with concentrated hydrochloric acid, and a white crystalline precipitate (36.5 g., 91%) was obtained. Crystallisation from acetic acid or benzene gave clusters of small colourless needles, m.p. 239-240° (cf. Weisz and Korczyn, (6)) of the acid (XXII) which gave a pale yellow solution in concentrated sulphuric acid. (Found: C, 83.6; H, 6.1. Calc. for $C_{22}H_{20}O_2$: C, 83.5; H, 6.4%).

1-Methyl-9-(o-tolyl)-10-anthrone (XXIII). - The acid (XXII) (20 g.), zinc chloride (10 g.), and sodium chloride (20 g.) were heated with constant stirring to 220° and maintained at this temperature for 15 to 20 minutes. The cold melt was extracted with boiling hydrochloric acid solution and the solid obtained washed with hot ammonia to remove non-ring closed material. The anthrone (XXIII) (18 g., 96%) crystallised from acetic acid in colourless prisms, m.p. 181-182°. (Found: C, 88.4; H, 6.2. $C_{22}H_{18}O$ requires C, 88.6; H, 6.1%). The solution in concentrated sulphuric acid was yellow, changing to green on warming.

1-Methyl-9-(o-tolyl)oxanthranol (XXIV). - (a) With nitric acid solution. The anthrone (XXIII) (3 g.) mixed with nitrobenzene (3 c.c.) was refluxed with nitric acid solution (150 c.c.; d 1.1) for 36 hours. After removal of the nitrobenzene by steam distillation, the solid was filtered off, extracted with dilute sodium hydroxide solution and washed. The oxanthranol (3 g., 95%) crystallised from acetic acid or ethanol in colourless prisms which gave a red melt at 207-209°. (Found: C, 84.5; H, 5.7. $C_{22}H_{18}O_2$ requires C, 84.0; H, 5.8%). The compound gave a magenta solution in concentrated sulphuric acid which changed to blue and then to green on standing.

(b) With selenious acid solution. The anthrone (XXIII) (3 g.), selenium dioxide (5.5 g.) and water (15 c.c.) were heated for 10 hours at 220° in a sealed tube. The solid obtained was filtered off, washed and extracted with dilute sodium hydroxide. The residue (2.5 g.) crystallised from acetic acid in colourless prisms which were identical with the previous sample of the oxanthranol.

Di-(o-carboxyphenyl)phthalide (VIII). - This compound was obtained as a syrup in 35% yield along with dihydro iso-benzofuran-1:3-bis spiro-(3-phthalide) (XII) in the oxidation of di-o-tolylphthalide (VII). It could not be crystallised and the crude product was used for condensation.

9-(o-Carboxyphenyl)oxanthranol-1-carboxylic acid lactone (XXV). - The oxanthranol (XXIV) (3 g.) was heated under pressure in nitric acid solution (40 c.c., d 1.12) at 200° for 10 hours. Crystallisation from acetic acid gave first an unidentified by-product (0.7 g.) as yellow plates (m.p. 312-314°) (Found: C, 72.8, 72.7; H, 3.6, 3.3%), which gave a deep red solution with alkaline sodium dithionite. It dissolved yellow in concentrated sulphuric acid, and on addition of copper powder the solution changed to green. Concentration of the mother liquors and further crystallisation from acetic acid gave the lactone (XXV) as colourless plates (2 g.) which decomposed giving a red melt at 270-275°. (Found: C, 74.1; H, 3.4. $C_{22}H_{12}O_5$ requires C, 74.15; H, 3.4%). It gave a pale yellow solution in concentrated sulphuric acid which did not change on heating to 110°.

9-(o-Carboxyphenyl)-9:10-dihydroanthracene-1-carboxylic acid (XXVI). - Zinc dust was added in portions to a refluxing solution of the lactone (XXV) (1.75 g.) in 20% ethanolic potassium hydroxide (75 c.c.) and after 16 hours the diluted solution was filtered from excess zinc, which was washed with boiling water. After distilling off the ethanol, the hot filtrate was acidified with concentrated hydrochloric acid and the oily precipitate, on boiling for 10 minutes, crystallised. When cold, the product was filtered off, washed with ice-cold water and crystallised from acetic acid, colourless prisms (1.5 g.) (m.p. 269-270°) of the acid (XXVI) being obtained. (Found: C, 76.9; H, 4.7. $C_{22}H_{16}O_4$ requires C, 76.7; H, 4.7%).

12-Hydroxytriangulene-4:8-quinone (XXVIII). -

(a) From 9-(o-carboxyphenyl)oxanthranol-1-carboxylic acid lactone (XXV). The lactone (XXV) (1 g.) and copper powder (0.3 g.) were heated with concentrated sulphuric acid (10 c.c.) at 120° for 1 hour, a deep blue solution being obtained. After filtering hot through sintered glass, the cold solution was poured into water (40 c.c.) and the dark blue precipitate filtered off, washed and extracted several times with boiling acetic acid. Crystallisation from trichlorobenzene and o-toluidine gave microscopic blue needles of 12-hydroxytriangulene-4:8-quinone (XXVIII) which did not melt below 450° but sublimed with slight decomposition in a high vacuum (10^{-6} mm.). (Found: C, 81.9; H, 3.2. Calc. for $C_{22}H_{10}O_3$: C, 82.0; H, 3.1%). The yield was theoretical.

(b) From di-(o-carboxyphenyl)-phthalide (VIII). The crude dicarboxylic acid (VIII) (5 g.) was treated as above. The compound obtained (3.8 g.) proved to be identical with that above and its properties agreed with those described for a sample prepared by a different method (Weisz and Korczyn (6)). It dissolved giving blue solutions in concentrated sulphuric acid, in alkali, in basic solvents and in sodium acetate solution. The blue solution in pyridine when treated with acetic anhydride changed to red, the blue colour being regenerated on the addition of ammonia solution.

Triangulene-4:8-quinone (XXIX). - (a) From 9-(o-carboxyphenyl)-9:10-dihydroanthracene-1-carboxylic acid (XXVI). The acid (XXVI) (1 g.) and the sodium salt of m-nitrobenzene sulphonic acid (0.5 g.) were added to concentrated sulphuric acid (15 c.c.) and the solution kept at room temperature for 2 hours. The initial light yellow colour of the solution rapidly changed to violet-red, a transitory green stage being observed. After pouring the solution into water (150 c.c.) and boiling, the red precitate was filtered off, washed and crystallised from nitrobenzene, red needles (0.8 g.) being obtained, which decomposed without melting at 310-320° to give a black residue. Triangulene-4:8-quinone (XXIX) (Found: C, 86.6; H, 3.3. $C_{22}H_{10}O_2$ requires C, 86.3; H, 3.3%) sublimed in a vacuum in dark red needles and gave a violet-red solution in concentrated sulphuric acid.

(b) From 12-Hydroxytriangulene-4:8-quinone (XXVIII). The blue compound (XXVIII) (1 g.) in dilute sodium hydroxide solution was reduced with zinc dust, till on exposure to air the blue colour did not reappear (after ca. 10 mins.). After filtering, oxygen was bubbled through the solution and the red precipitate obtained, filtered off, washed and crystallised from nitrobenzene, giving red needles of triangulene-4:8-quinone (XXIX).

1:2:3:5:6:7-Hexahydrotriangulene (XXVII). - The blue compound (XXVIII) (1 g.), zinc dust (1.2 g.) and sodium chloride (1.2 g.) were ground together and moist zinc chloride (7 g.) added. The mixture was melted and the temperature raised with constant stirring to 300° over 15 minutes. At 250° a deep red colour was observed, but this disappeared on further heating. The cold melt was decomposed with hot dilute acetic acid and the residue extracted with benzene, the solution obtained being chromatographed (alumina). Using light petroleum (b.p. 40-60°) as eluant, a colourless eluate with a violet fluorescence was obtained, which on concentration gave colourless needles (0.4 g.) (m.p. 175-176°) of hexahydrotriangulene (XXVII). (Found: C, 93.8; H, 6.2. $C_{22}H_{18}$ requires C, 93.6; H, 6.4%). It dissolved in concentrated sulphuric acid to give a yellow solution with a dark green fluorescence which changed to green on standing.

Dodecahydro-triangulene (XXX). - Triangulene-4:8-quinone (XXIX) (0.5 g.), red phosphorous (1 g.), potassium iodide (0.5 g.) and 55% hydriodic acid solution (10 c.c.) were heated together under pressure at 210° for 10 hours. Having diluted the mixture with water, the solid was filtered off, washed and extracted with benzene to give a solution which was dried and chromatographed (alumina). Elution with light petroleum (b.p. 40-60°) gave a colourless, non-fluorescent solution which on concentration and crystallisation from methanol, yielded clusters of colourless, silky needles (m.p. 162-163°) (0.25 g.) of dodecahydro-triangulene. (Found: C, 91.4; H, 8.35. $C_{22}H_{24}$ requires C, 91.6; H, 8.4%). The hydrocarbon which sublimed in a vacuum in needles did not dissolve readily in sulphuric acid, but on warming gave a crimson solution which on standing became yellow with a green fluorescence. A second colourless violet-fluorescent eluate was obtained with a light petroleum (b.p. 40-60°)-benzene mixture, which on concentration gave hexahydrotriangulene (XXVII) (m.p. 174-175°) (20 mg.).

Naphtho-(2':7'-1:8)-anthro-10-one (XXXI). - Crystallised naphthanthrone (XXXI) (1 g.) (m.p. 242-243°) prepared from pyrene as described by Vollmann, Becker, Corell and Streeck (17) was dissolved in benzene and chromatographed (alumina). Elution with benzene completely removed a colourless, violet-fluorescent band, and the second pale yellow band was washed through with a benzene-ether mixture. The pale yellow eluate yielded on concentration yellow elongated plates (m.p. 252-253°) (0.8 g.) of naphthanthrone (XXXI), (Found: C, 89.6; H, 4.3. Calc. for $C_{19}H_{10}O$, C, 89.7; H, 4.0%), which dissolved red in concentrated sulphuric acid.

2:3-Trimethylenepyrene (XXXIII). - Sodium chloride (2 g.) and moist zinc chloride (10 g.) were added to an intimate mixture of naphtho-(2':7'-1:8)-anthrone (XXXI) (1 g.) and zinc dust (2 g.). The mixture was melted and the temperature raised during 15 minutes to 300° with constant stirring. After decomposition of the cold melt with dilute acetic acid, the residue was filtered off, washed and dried. Chromatographic purification (alumina), with light petroleum (b.p. 40 - 60°) as eluant, yielded colourless crystals (0.8 g.) (m.p. 112-113°) of 2:3 trimethylenepyrene (Found: C, 94.4; H, 5.5. Calc. for $C_{19}H_{14}$, C, 94.2; H, 5.8%), which gave in concentrated sulphuric acid a yellow green-fluorescent solution which changed to dark green on standing.

Di-p-xylylphthalide (XXXV; R = H, R' = CH_3). - Powdered aluminium chloride (93 g.) and sym-phthaloyl chloride (93 g.) were heated at 100° for 10 hours, the mixture being well shaken at intervals. When cold, the resulting complex was powdered and slowly added to p-xylene (200 g.), the temperature of the reaction being kept below 20°. After 2½ hours, the deep red mixture was heated to 60° for 5 minutes and, after cooling, was poured into dilute hydrochloric acid containing crushed ice. The organic layer was separated, washed with hot water and excess p-xylene removed by steam distillation. The crystalline solid obtained was filtered off and extracted with dilute sodium hydroxide solution to remove 2-(2':5'-dimethylbenzoyl)-benzoic acid (26 g.), which was isolated from the alkaline filtrate by acidification with concentrated hydrochloric acid. The crude phthalide (116 g.; 74%), m.p. 175 - 176°, crystallised from ethyl alcohol or acetic acid in colourless prisms, m.p. 178 - 179° (Found: C, 84.3; H, 6.5. Calc. for $C_{24}H_{22}O_2$: C, 84.2; H, 6.5%), which gave a red solution in concentrated sulphuric acid.

Di-m-xylylphthalide (XXXV; R = CH_3, R' = H). - The complex formed as above from sym-phthaloyl chloride (101 g.) and aluminium chloride (101 g.) was added to m-xylene (200 g.) and the mixture kept at room temperature for ½ hour. Following the above procedure, 2-(2':4'-dimethylbenzoyl)benzoic acid (28 g.) and di-m-xylylphthalide (123 g.; 72%), m.p. 164 - 166°, were isolated. The phthalide crystallised from ethyl alcohol or acetic acid in colourless prisms, m.p. 167 - 168° (Found: C, 84.1; H, 6.3. Calc. for $C_{24}H_{22}O_2$: C, 84.2; H, 6.5%), which gave a red solution in concentrated sulphuric acid.

1:3-Dihydroisobenzofuran-1:3-bisspiro-(3-phthalide-5-carboxylic acid) (XXXIX; R = H, R' = COOH). - Di-p-xylylphthalide (50 g.) mixed with nitrobenzene (10 c.c.) was boiled in 20% nitric acid solution (800 c.c.) for 3 days, a catalytic amount of manganese dioxide being added. When the nitrobenzene was steam distilled off, a yellow solid was obtained which was filtered off, washed and extracted with dilute sodium hydroxide solution from unoxidised material (1 g.). Acidification of the alkaline filtrate gave a precipitate (50 g.) which was isolated, washed and completely oxidised by the following two methods:

(a). Powdered potassium permanganate was added to a boiling

solution of the partially oxidised material (25 g.) in sodium carbonate solution, till the permanganate colour was stable for 7 minutes. Excess potassium permanganate was destroyed by ethyl alcohol, and after filtering off the manganese dioxide, acidification with concentrated hydrochloric acid gave a white precipitate (25 g.).
(b). The partially oxidised material (3 g.) was heated under pressure at 200° in 20% nitric acid solution for 9 hours. The product (3 g.) was filtered off and washed with water. Crystallisation of these products from acetic acid gave colourless crystals (6 g. and 1 g. resp.) of *the spiro-compound* (Found: C, 64.6; H, 2.8. $C_{22}H_{12}O_9$ requires C, 64.9; H, 2.7%), which softened at 270° and gave a clear melt at 300°. It dissolved in concentrated sulphuric acid to give a colourless solution which changed to green on warming. Dilution of the acetic acid mother-liquors with water gave the unrearranged acid (XL) as a viscous oil (18 g. and 1.8 g. resp.) which could not be crystallised. It dissolved in concentrated sulphuric acid giving a colourless solution, which on heating to 150° with copper powder gave a deep blue solution.

1:3 *Dihydroisobenzofuran*-1:3-*bis*spiro-(3-*phthalide*-6-*carboxylic acid* (XXXIX; R = COOH, R' = H), Di-*m*-xylylphthalide (50 g.) was oxidised as described above.

Partially oxidised material (42 g. and 6 g.) gave, by methods (a) and (b), products which, on crystallisation from acetic acid, yielded colourless crystals (10 g. and 2 g.). Recrystallisation from nitrobenzene gave colourless needles, m.p. 357 - 358°, of the spiro-compound (Found: C, 64.6; H, 2.9. $C_{24}H_{12}O_9$ requires C, 64.9; H, 2.7%), which gave a colourless solution in concentrated sulphuric acid. Dilution of the acetic acid mother liquors with water gave the unrearranged acid (XL) as an oil (30 g. and 4 g. resp.) which could not be obtained in a crystalline state. It gave, with concentrated sulphuric acid and copper powder at 150°, a deep blue solution.

9-o-Carboxyphenyloxanthranol lactone (IX). - The spiro-compounds (XXXIX; R = H, R' = COOH; R = COOH, R' = H) (1 g.) were ground together with copper powder and the mixture heated at 350° till a quiet melt was obtained. Sublimation in a vacuum yielded large prisms, which crystallised from ethyl alcohol in prisms, m.p. 232 - 233°, which were identical with the sample of 9-o-carboxyphenyloxanthranol lactone (IX) obtained by the decarboxylation of dihydroisobenzofuran-1:3-bisspiro-(3-phthalide) (XII).

2-(Di-p-xylylmethyl)benzoic acid (XXXVI; R = H, R' = CH_3). - Di-p-xylylphthalide (50 g.) was dissolved in 20%

ethanolic potassium hydroxide solution (450 c.c.) and the solution refluxed for 48 hours, zinc dust (100 g.) activated with copper being added in portions at regular intervals. After diluting with water (500 g.) the hot solution was filtered from the zinc which was washed with boiling water. The solution was boiled to remove the ethyl alcohol and then acidified with concentrated hydrochloric acid, a colourless precipitate (48 g.) being obtained which was filtered off, washed and crystallised from acetic acid or ethyl alcohol. The colourless needles, m.p. 233 - 234°, of the acid (Found C, 83.6; H, 7.0. Calc. for $C_{24}H_{24}O_2$: C, 83.7; H, 7.0%), gave, in concentrated sulphuric acid, a colourless solution which changed to green on heating.

2-(<u>Di</u>-m-<u>xylylmethyl)benzoic acid</u> (XXXVI; $R = CH_3$, $R' = H$). - Following the procedure described above, di-<u>m</u>-xylylphthalide (50 g.) was reduced to the corresponding acid (45 g.), which crystallised from acetic acid or benzene in clusters of colourless needles, m.p. 230 - 232°. (Found: C, 83.2; H, 7.1. Calc. for $C_{24}H_{24}O_2$: C, 83.7; H, 7.0%). The acid gave a colourless solution in concentrated sulphuric acid.

1:4-<u>Dimethyl</u>-9-p-<u>xylylanthrone</u> (XXXVII; $R = H$; $R' = CH_3$). - The acid (45 g.) from di-<u>p</u>-xylylphthalide, zinc chloride (45 g.) and sodium chloride (9 g.) were ground together and heated to 220° with constant stirring. After 15 minutes, the dark green melt was allowed to cool, decomposed with dilute hydrochloric acid solution, washed and extracted with dilute ammonia. The yellow orange residue (41 g.) crystallised from acetic acid in colourless leaflets, m.p. 190 - 191°. The <u>anthrone</u> (Found: C, 88.5; H, 7.1. $C_{24}H_{22}O$ requires C, 88.3; H, 6.8%) gave a yellow solution in concentrated sulphuric acid, which changed to green on heating.

1:3-<u>Dimethyl</u>-9-m-<u>xylylanthrone</u> (XXXVII; $R = CH_3$, $R' = H$). - The acid (43 g.) from di-<u>m</u>-xylylphthalide was condensed and the product (40 g.) isolated as described above. Crystallisation from acetic acid gave prisms, m.p. 166 - 168°, of the <u>anthrone</u> (Found: C, 88.0; H, 6.5. $C_{24}H_{22}O$ requires C, 88.3; H, 6.8%) which gave a yellow solution in concentrated sulphuric acid.

9-<u>Phenyloxanthranol</u>-1:4:2':5'-<u>tetracarboxylic acid lactone</u> (XXXVIII; $R = H$, $R' = COOH$). - The anthrone (XXXVII; $R = H$, $R' = CH_3$) (40 g.) was mixed with nitrobenzene (8 c.c.) and refluxed with 20% nitric acid solution (450 c.c.) for 48 hours. After removal of the nitrobenzene by steam distillation, the product was filtered off, washed, dissolved in dilute sodium hydroxide solution and treated with powdered potassium permanganate, till the permanganate colour was stable to 10 minutes boiling. The hot filtrate from the manganese dioxide was acidified with hydrochloric acid and an oily precipitate was obtained which solidified after boiling for several minutes. The product (38 g.) was filtered off, washed with cold water and crystallised from nitrobenzene containing a little ethyl alcohol to give colourless crystals which decomposed giving a violet-blue sublimate at 330 - 340°. The lactone (Found: C, 64.5; H, 2.9. $C_{24}H_{12}O_9$ requires C, 64.9; H, 2.7%) gave a pale yellow solution in concentrated sulphuric acid, which was unchanged on heating. The addition of copper powder, however, gave at 150° a deep blue solution.

9-Phenyloxanthranol-1:3:2':4'-tetracarboxylic acid lactone (XXXVIII; R = COOH, R' = H). - The anthrone (XXXVII; R = CH_3, R' = H) (35 g.) was oxidised as above. The product (34 g.) crystallised from nitrobenzene containing a little acetic acid, in colourless needles, which decomposed giving a violet-blue sublimate at 335 - 340°. The lactone (Found: C, 64.7; H, 3.0. $C_{24}H_{12}O_9$ requires C, 64.9; H, 2.7%) gave a deep blue solution when heated at 150° with copper powder in concentrated sulphuric acid.

9:10-Dihydro-9-phenylanthracene-1:4:2':5'-tetracarboxylic acid (XLII; R = H, R' = COOH). - The lactone (XXXVIII; R = H, R' = COOH) (35 g.) was dissolved in boiling 15% sodium hydroxide solution, covered with a thin layer of octyl alcohol, and zinc dust, activated with copper, was added in portions at regular intervals. After refluxing for 24 hours, the octyl alcohol was distilled off and the non-fluorescent solution was filtered from the zinc, which was washed with hot water. Acidification of the filtrate with hydrochloric acid gave an oily precipitate which solidified after boiling for some time. The product (34 g.) was filtered off, washed and crystallised from nitrobenzene containing a little alcohol, to give colourless leaflets of the tetracarboxylic acid (Found: C, 66.6; H, 3.4. $C_{24}H_{16}O_8$ requires C, 66.7; H, 3.7%) which decomposed giving a red melt and sublimate at 340 - 345°.

9:10-Dihydro-9-phenylanthracene-1:3:2':4'-tetracarboxylic acid (XLII; R = COOH, R' = H). - The lactone (XXXVIII; R = COOH, R' = H) (30 g.) was reduced as described above. The product (30 g.) crystallised from concentrated hydrochloric acid in colourless crystals, which were found to contain water of crystallisation. (Found: C, 60.0; H, 4.8. $C_{24}H_{16}O_8.3H_2O$ requires C, 59.3; H, 4.6%). No alternative solvent could be found for crystallisation.

The tetracarboxylic acid softened at 240° and decomposed giving a red melt and sublimate at 310°.

Triangulene-4:8-quinone-7:11-dicarboxylic acid (XLVI; R = H, R' = COOH). - The tetracarboxylic acid (XLII; R = H, R' = COOH) (32 g.) and m-nitrobenzene sulphonic acid (sodium salt) (20 g.) were dissolved in concentrated sulphuric acid and the solution heated at 110 - 120° for 15 minutes. The initial pale yellow colour of the solution rapidly changed to red violet, an intermediate green stage being observed. The hot solution was diluted slowly with ice, the temperature being maintained at 110°, till a dark red solid began to crystallise. After cooling and diluting further with cold water, the crystalline precipitate was filtered off and thoroughly washed with hot water till free from sulphuric acid and sulphonated material. After extracting with hot acetic acid, the product (20 g.) was crystallised from o-toluidine, prolonged heating of the solution being avoided, and dark red crystals of the dicarboxylic acid (Found: C, 72.75; H, 2.75. $C_{24}H_{10}O_6$ requires C, 73.1; H, 2.6%) were obtained which did not melt below 400°. The violet red solution of the compound in alkali changed to green on the addition of sodium dithionite.

Triangulene-4:8-quinone-6:10-dicarboxylic acid (XLVI; R = COOH, R' = H). - The tetracarboxylic acid (XLII; R = COOH, R' = H) (25 g.) was condensed in sulphuric acid as above. The product (17 g.) could not be crystallised, due to its insolubility in organic solvents. To purify, the compound was extracted with nitrobenzene, acetic acid and acetone, dissolved in dilute ammonia, filtered and precipitated with concentrated hydrochloric acid. After filtering and washing, the compound was dried in a vacuum at 200° but it could not be freed from water. (Found: C, 66.9; H, 3.1. $C_{24}H_{10}O_6.2H_2O$ requires C, 67.0; 3.3%). The dicarboxylic acid which did not melt below 400°, gave a green solution in alkaline sodium dithionite.

7:11-Dicarbomethoxytriangulene-4:8-quinone (XLVI; R = H, R' = COOMe). - The silver salt of the dicarboxylic acid (XLVI; R = H, R' = COOH) (1 g.) was precipitated by the addition of silver nitrate solution to a hot neutral solution of the ammonium salt. After filtering off and washing, the dark red silver salt was dried, powdered and refluxed with methyl iodide solution, for 48 hours. When cold, the solid was filtered off and extracted with dilute sodium carbonate solution to remove unesterified material. The methyl ester crystallised from trichlorobenzene in dark red needles (0.6 g.), m.p. 289 - 290° (Found: C, 73.6; H, 3.5. $C_{26}H_{14}O_6$ requires C, 73.9; H, 3.3%) which gave a violet red solution in concentrated sulphuric acid and a green solution in boiling alkaline sodium dithionite.

6:10-Dicarbomethoxytriangulene-4:8-quinone (XLVI; R = COOMe, R' = H). - This compound was prepared from the dicarboxylic acid (XLVI; R = COOH, R' = H) (1 g.) by the above method. Crystallisation from trichlorobenzene gave dark red needles of the methyl ester (Found: C, 73.8; H, 3.5. $C_{26}H_{14}O_6$ requires C, 73.9; H, 3.3%) which did not melt below 360°.

Dodecahydrotriangulene (XXX). - The dicarboxylic acids (XLVI) (2 g.), red phosphorus (2 g.), potassium iodide (1 g.) and 55% hydriodic acid (20 c.c.) were heated under pressure at 210° for 10 hours. When cold, the reaction mixture was diluted with water and the product filtered off, washed with hot water, dried and ground with soda lime (4 g.). On heating in a vacuum a clear, greenish fluorescent oil distilled which gave a white solid on cooling. Chromatographic purification (alumina), with light petroleum (b.p. 40 - 60°) as eluant, gave a colourless, non-fluorescent solution, which on concentration and crystallisation from methyl alcohol, yielded clusters of colourless silky needles (0.6 g. and 0.4 g. resp.), (m.p. 162 - 163°), which gave no depression in melting point when admixed with a sample of dodecahydrotriangulene (XXX).

Triangulene-4:8-quinone (XXIX). - (a) From the dicarboxylic acids (XLVI). - The dark red dicarboxylic acids (XLVI) (1 g.) were ground with copper powder (3 g.), and the mixture heated in a vacuum (10^{-4} mm.) at 260 - 270° for 10 hours. The sublimate was crystallised from nitrobenzene and dark red needles (0.3 g. and 0.25 g. resp.) were obtained whose properties were identical with those of a sample of triangulene-4:8-quinone (XXIX) prepared by a different method.

(b) From the unrearranged acids (XL). - The crude unrearranged acids (XL) (20 g.) were dissolved in concentrated sulphuric acid (200 c.c.) and the solution heated at 140° for 15 minutes, a bright green colour being developed. Dilution with water gave a light violet precipitate which was filtered off, washed and dried. After crystallisation from acetic acid (charcoal), which yielded small amounts (2 g. and 2.25 g. respect.) of the dispirans (XXXIX), the mother liquors were diluted with water to give the crude lactone acids (XLIII) which were dissolved in 15% sodium hydroxide solution (150 c.c.) and refluxed for 24 hours, zinc dust being added at intervals. The colourless, non-fluorescent filtrates from the excess zinc dust gave on acidification with hydrochloric acid the dihydroanthracene derivatives (XLIV) (14 g. and 13 g. respect.) which could not be crystallised. On heating the latter in concentrated sulphuric acid (150 c.c.), containing m-nitrobenzene sulphonic acid (sodium salt) at 120° for 15 minutes, deep violet-red solutions were obtained which on dilution with water yielded the dark red triangulene quinone dicarboxylic acids (XLV) (10 g. and 8.5 g. respect.). These were extracted several times with boiling acetic acid, and the products thus obtained gave violet-red solutions in aqueous alkali, which changed to green on adding sodium dithionite. Decarboxylation was carried out as described above, small amounts (1 to 2 g.) only being used for each experiment. When larger amounts were used, more decomposition and carbonisation were apparent and the yields were lower. Crystallisation from nitrobenzene and resublimination yielded dark red needles of triangulene-4:8-quinone (XXIX).

12-Hydroxytriangulene-4:8-quinone (XXVIII). - Copper powder (3 g.) was added to solutions of the crude unrearranged acids (XL) (10 g.) (the lactone acids (XXXVIII) may also be used) in concentrated sulphuric acid (150 c.c.) and the temperature raised to 150°. After $\frac{1}{2}$ hour, the resulting deep blue solutions were filtered through sintered glass and diluted with water, the dark blue precipitates were filtered off, washed with hot water and extracted with boiling acetic acid. The properties of (XLI) prepared in this way were in agreement with those of samples prepared by Weisz *et alia* (18). The dark blue acids (XLI) (7.5 g.) were dissolved in quinoline (75 c.c.)containing copper chromite catalyst and on boiling for three hours the dark blue-green colour of the solution gradually changed to blue violet. The solutions, after concentration to 20 c.c., were acidified with concentrated hydrochloric acid and the dark blue precipitates of 12-hydroxytriangulene-4:8-quinone (XXVIII) were filtered off, washed and dried. The compound prepared in this way was identical with the samples from other methods.

Palladium-charcoal Catalyst (27, 28, 29). - Charcoal was heated in normal nitric acid solution until the fumes of oxides of nitrogen were no longer evolved. After standing for one hour, the charcoal was filtered off, washed with water and dried at 200° in a vacuum. The charcoal (6 g.) was stirred into a cold solution of palladious chloride (2 g.) in normal hydrochloric acid solution (13 c.c.) and while stirring mechanically, a 40% formalin solution (12 c.c.) was added. A cold solution of potassium hydroxide (12 g.) in water (12 c.c.) was added slowly to the mixture and the temperature was not allowed to rise above 5°. When the addition was complete, the temperature of the mixture was raised to 60° for ½ hour. The 20% palladium-charcoal catalyst was then filtered off, washed with dilute acetic acid and hot water and dried in a vacuum at 100°.

<u>Dehydrogenation of dodecahydrotriangulene</u> (XXX). - The hydrocarbon (XXX) (0.5 g.) and 20% palladium-charcoal (0.5 g.) were heated together in an air-free carbon dioxide atmosphere and the hydrogen evolved measured in a nitrometer. At 210°, a brisk evolution was observed and hydrogen (110 c.c.) was collected which roughly corresponds to the formation of hexahydrotriangulene (XXVII). On heating to 250°, hydrogen was again given off, but at a greatly reduced speed. After 5 hours the residue was heated in a vacuum and hexahydrotriangulene (XXVII) sublimed in small needles (40 mg.) (m.p. 173 - 175°). No other sublimate was obtained even when the temperature was raised to 500°.

<u>Dehydrogenation of hexahydrotriangulene</u> (XXVII). - (a) <u>By sublimation over palladium charcoal</u>.- Palladium charcoal (20%) (6 g.), prepared from granulated, metal-free charcoal, was mounted in a combustion tube. A slow current of air-free carbon dioxide was allowed to enter at one end, while a vacuum (1 mm.) was applied at the other. Prior to dehydrogenation, the catalyst was heated to 350° and the apparatus swept out till free from air. To test the

efficiency of the catalyst 9:10-dihydroanthracene (m.p.106°) (0.1 g.) was sublimed over it at 310° and a theoretical yield of anthracene (m.p. 212 - 214°) was obtained. The process was then repeated using hexahydrotriangulene (XXVII) (50 mg.) (m.p. 174°), but no sublimate was obtained, even when the catalyst was heated to 500°. The activity of the catalyst was retested as before and anthracene (m.p. 214°) was obtained. Similar results were obtained on repetition of the above series of reactions.

(b) By heating in trichlorobenzene with palladium-charcoal. - After palladium-charcoal (20%) (10 mg.) had been boiled with trichlorobenzene (15 c.c.) till no oxygen was detectable in the carbon dioxide passing over the surface of the mixture, hexahydrotriangulene (XXVII) (30 mg.) was introduced. The dehydrogenation was carried out before a spectroscope and in the hot reaction mixture a sharp absorption band at 4600 Å was seen to develop. On allowing the solution to cool to room temperature, however, a strong band at 4440 Å and a faint band at 4630 Å were observed, which disappeared on reheating the solution, the original band only being detectable. No other bands were observed during the course of the reaction. After boiling for 7 hours the solution was diluted with light petroleum (b.p. 40 - 60°) and chromatographed (alumina). Elution with light petroleum (b.p. 40 - 60°) and concentration yielded some unchanged hexahydrotriangulene (m.p. 172 - 174°) (4 mg.).

4:8 Dihydro-12-hydroxy-8-ketotriangulene (L). - Finely divided triangulene-4:8-quinone (XXIX) (0.1 g.) was added to 5% sodium hydroxide solution (15 c.c.) containing ethanol (10 c.c.). Sodium dithionite (0.1 g.) was introduced and the mixture refluxed till the solid was completely dissolved. The ethanol was then distilled from the green-blue solution, and on cooling, a dark blue solid crystallised out. This was filtered off, washed carefully with distilled water containing ammonia, and dried. Analysis showed it to be the sodium salt of (L), containing water of crystallisation. (Found: C, 77.0; H, 3.8; Na, 6.45. $C_{22}H_{11}O_2Na$ requires C, 80.0; H, 3.4; Na, 7.0. $C_{22}H_{13}O_3Na$ requires C, 75.9; H, 3.8; Na, 6.6%). To obtain the free hydroxy-compound the blue solution, prepared as above, was acidified with acetic acid, and a blue precipitate was obtained, which crystallised from acetic acid containing a little sodium dithionite in blue needles (85 mg.) of 4:8-dihydro-12-hydroxy-8-ketotriangulene (L) (Found: C, 85.5; H, 3.9. $C_{22}H_{12}O_2$ requires C, 85.7; H, 3.9%) which gave a violet-red solution in concentrated sulphuric acid. It dissolved readily in ethanol giving a blue solution which decolourised very rapidly on exposure to light. The addition of a little stannous chloride however rendered the solution stable.

1:2:3:8-Tetrahydro-12-hydroxy-8-ketotriangulene (LIII). - Zinc dust, activated with copper, was added in portions to a boiling 15% sodium hydroxide solution (60 c.c.) containing finely divided triangulene-4:8-quinone (XXIX) (1.5 g.). The green colour of the solution which developed rapidly, gradually changed to a pale greenish-yellow which however was not stable but became violet-blue on exposure to the air. After refluxing for 6 hours, the solution was filtered into hydrochloric acid giving a greenish-brown precipitate, which was filtered off, dried and sublimed in a vacuum. The reddish-brown sublimate was crystallised from xylene yielding light brown needles (0.7 g.) of 1:2:3:8-tetrahydro-12-hydroxy-8-ketotriangulene (LIII) (Found: C, 84.9; H, 4.65. $C_{22}H_{14}O_2$ requires C, 85.1; H, 4.55%), which decomposed giving a red melt at 220 - 225°. In aqueous alkali it gave a blue solution, which on the addition of sodium dithionite and boiling changed to green and then to yellow. The compound was acetylated by refluxing with acetic anhydride for 15 minutes and on cooling yellow needles of the acetate (LVIII) (Found: C, 81.6; H, 4.8. $C_{24}H_{16}O_3$ requires C, 81.8; H, 4.6%) were obtained which gave a red brown melt at 269 - 272°. In concentrated sulphuric acid, it gave a violet solution which on standing changed to magenta. Hydrolysis with ethanolic sodium hydroxide gave a blue solution.

1:2:3:8-Tetrahydro-8-ketotriangulene (LVII). - (a) From zinc dust melt of (XXVIII). - In the chromatographic purification of (XXVII) a second orange-red band was observed, a sample of which gave a sharp absorption band at 4405 Å in benzene and at 4440 Å in trichlorobenzene. On eluting with a benzene-ether mixture, the colour of the band changed to pale yellow and a yellow-green eluate was obtained which on concentration yielded yellow needles (m.p. 258 - 259°) of 1:2:3:8-tetrahydro-8-ketotriangulene (LVII). (Found: C, 89.3; H, 4.8. $C_{22}H_{14}O$ requires C, 89.8; H, 4.8%). The compound, which was insoluble in alkali, gave a brown solution in concentrated sulphuric acid, which on standing rapidly changed to dark red. Sublimation in a vacuum or recrystallisation from acetic anhydride did not alter its constitution.

(b) From the dehydrogenation of (XXVII) in trichlorobenzene. In the chromatogram of the reaction mixture, an orange-red band was observed as above. Elution again gave a yellow-green solution but the quantity present was too minute to be isolated. Spectroscopic tests however showed the presence of (LVII).

(c) From the zinc-sodium-hydroxide reduction of (XXIX). - The xylene mother liquors from the crystallisation of 1:2:3:8-tetrahydro-12-hydroxy-8-ketotriangulene (LIII) were concentrated and chromatographed (alumina). Elution with a benzene-ether mixture gave a yellow-green solution which yielded yellow needles (0.2 g.) (m.p. 258 - 259°), identical with the previous sample of (LVII).

(d) From the zinc-acetic acid reduction of (XXIX). - When zinc dust was added to boiling acetic acid (50 c.c.) containing triangulene-4:8-quinone (XXIX) (0.5 g.), a short-lived violet-blue solution was obtained which decolourised very rapidly. After refluxing for 5 hours, the clear yellow solution was concentrated and diluted with water containing sodium dithionite, giving a precipitate which was filtered off, washed, and sublimed in a vacuum from the excess zinc dust. Extraction of the sublimate with alkaline sodium dithionite gave a green solution from which was obtained a brown precipitate on acidification with acetic acid. This crystallised from xylene in light brown needles (0.1 g.) which proved to be identical with the previous sample of 1:2:3:8-tetrahydro-12-hydroxy-8-ketotriangulene (LIII).
The residue from the extraction was sublimed in a vacuum and crystallised from xylene (charcoal) to give yellow needles (0.3 g.) (m.p. 256 - 258°) of 1:2:3:8-tetrahydro-8-ketotriangulene (LVII).

4:8-*Diacetoxy*-4:8-*dihydrotriangulene* (XXXIV). - Triangulene-4:8-quinone (XXIX) (0.1 g.) was dissolved in acetic anhydride (20 c.c.) containing a little sodium dithionite and zinc dust was added. A light yellow solution with a green fluorescence was obtained which after boiling for 1 hour, was filtered from the zinc dust into a sodium dithionite solution. The acetic anhydride slowly hydrolysed to give a pale yellow precipitate of 4:8-*diacetoxy*-4:8-*dihydrotriangulene* (XXXIV) (Found: C, 79.9; H, 4.35. $C_{26}H_{18}O_4$ requires C, 79.2; H, 4.6%), which polymerised when crystallisation was attempted. The compound, which melted with decomposition at 160 - 170°, rapidly darkened to an orange-brown colour when exposed to air. In concentrated sulphuric acid, it gave a yellow green solution which quickly changed to brown.

The Synthesis of Coeranthrene.

9-o-Carboxyphenylanthracene (LX). - This compound was prepared from benzophenone-2:2'-dicarboxylic acid di-lactone (XXI) (20 g.) following the synthesis described by Scholl and Donat (11). Crystallisation of the product from acetic acid gave yellow needles (6 g.; overall yield, 25%), m.p. 241-242°, of (LX). Scholl and Donat give m.p. 242-243.5°.

Coeranthrone (LXI). - The method used for the condensation of (LX) was a modification of that described by Bradsher and Vingiello (38). When 9-*o*-carboxyphenylanthracene (LX) (6 g.) was heated in 100% orthophosphoric acid (250 c.c.) at 200° for two hours, a dark green solution was obtained which, after cooling and pouring into water, gave a red precipitate. This compound was extracted thoroughly with hot dilute ammonium hydroxide solution, sublimed in a vacuum and crystallised from acetic acid to give dark red needles (4.5 g.; 80%), m.p. 175-176° of coeranthrone (LXI), which gave a green solution in concentrated sulphuric acid. Scholl and Donat (11) give m.p. 178-179°. Coeranthrone (LXI) could not be purified by chromatography (alumina) for, during elution, a blue compound is formed on the column. This is probably due to the oxidation of coeranthrone (LXI) to coeranthronol, which is described as a dark blue compound (11).

Coeranthrene (LXIV). - Coeranthrone (LXI) (3 g.) was ground with zinc dust (5 g.) and the mixture added to 10% sodium hydroxide solution (100 c.c.) covered with a layer of octyl alcohol (15 c.c.). After refluxing for six hours, the octyl alcohol was distilled off, and the hot solution filtered from excess zinc dust into concentrated hydrochloric acid. The precipitate was collected, washed with hot water and dried in a vacuum. When the dry, powdered product (LXIVa) was heated in a vacuum, water was first given off and on further heating gave an orange-red sublimate which was dissolved in benzene and chromatographed. On developing the chromatogram with a benzene-light petroleum (b.p. 40-60°) mixture, a clear yellow eluate with a blue fluorescence was obtained which, after concentration and cooling, yielded large, orange-yellow plates (1 g.), m.p. 138-139° of coeranthrene (LXIV) (Found: C, 94.7; H, 5.2. $C_{21}H_{14}$ requires C, 94.7; H, 5.3%). The hydrocarbon dissolved readily in concentrated sulphuric acid to give a yellow solution which rapidly changed to green on standing. When the yellow-blue fluorescent solution of coeranthrene (LXIV) in alcohol was exposed to sunlight and oxygen passed through it, a colourless solution with a violet fluorescence was obtained.

Coeranthrenium Perchlorate (LXII) or Coeranthrylium Perchlorate (LXIII). - Analytically pure coeranthrene (LXIV) (0.1 g.) was dissolved in warm acetic acid (2 c.c.) containing a few drops of perchloric acid and to this was added a warm, filtered solution of selenium dioxide in acetic acid. Almost at once, brown needles began to crystallise and when the solution was cold, these were filtered off, washed with benzene and dried in a vacuum. The coeranthrenium perchlorate (LXII) or coeranthrylium perchlorate (LXIII) (Found: C, 69.9; H, 3.65. $C_{21}H_{13}O_4Cl$ requires C, 69.1; H, 3.6%. $C_{21}H_{14}O_4Cl$ requires C, 68.95; H, 3.9%) could not be purified further as it was rather unstable and hydrolysed very readily. When it was heated in a vacuum at 100°, the compound slowly decomposed giving a black residue.

1:10-Trimethylene-3:4-benzophenanthrene (dihydrocoeranthrene) (LXV). - Coeranthrone (LXI) (0.75 g.), red phosphorus (1.0 g.) and hydriodic acid (55%) (10 c.c.) were covered with a layer of xylene (10 c.c.) and after refluxing for 48 hours, the mixture was diluted with water and filtered, the excess phosphorus being well washed with hot xylene. After separating off the aqueous layer and washing with hot water, the xylene layer was dried and concentrated. Chromatographic purification (alumina), with a benzene-light petroleum (b.p. 40-60°) mixture as eluant gave a clear eluate, with a violet-blue fluorescence, which on concentration and recrystallisation from light petroleum (b.p. 40-60°) gave long flat colourless prisms (0.5 g.), m.p. 116-117°, of dihydrocoeranthrene (LXV) (Found: C, 94.1; H, 6.1. $C_{21}H_{16}$ requires C, 94.0; H, 6.0%). The hydrocarbon dissolved very slowly in concentrated sulphuric acid to give a greenish-yellow solution, which on warming changed to green.

The Synthesis of Zethrene.

7:14-Dihydrozethrene (LXVII). - This compound was synthesised by E. Clar (40), but a short description of the method is included for completeness. Finely ground aluminium chloride (133.5 g.) was added to a mixture of naphthalene (128 g.) and fumaroyl chloride (76.5 g.) (b.p. 58-59°/15 mm.) in benzene (250 c.c.) without cooling and at such a rate that the mixture refluxed gently. When the reaction, which was very vigorous, was complete the mixture was decomposed with ice and dilute hydrochloric acid solution. After boiling, the crude product was filtered off, washed with hydrochloric acid solution and thoroughly extracted with hot xylene till all tarry material was removed. The compound (LXVI) was finally isolated as a dark brown, rather insoluble material, which dissolved in concentrated sulphuric acid to give a blue solution and which could be acetylated. The yield is usually of the order of 10%.

The brown compound (LXVI) was reduced by submitting it to the zinc dust melt of E. Clar. 7:14-dihydrozethrene (LXVII) was obtained from the decomposed melt and crystallised from xylene as bright yellow plates, m.p. 234°. The hydrocarbon (LXVII) dissolved in concentrated sulphuric acid to give a red solution which rapidly changed to violet, with an orange fluorescence.

Chromatographic Purification of 7:14-Dihydrozethrene (LXVII). - The alumina, which was used, was specially treated to reduce oxidation of the hydrocarbon on the column to a minimum. Alumina, moistened with a little methyl alcohol, was heated at 300° in a muffle furnace for two hours and after cooling was reheated at 200° in a vacuum (10 mm.) for 3 hours. During the latter stage, pure carbon dioxide was introduced into the flask at intervals (15 mins.) and after a few minutes the system re-evacuated. Finally, the alumina was cooled slowly under pure carbon dioxide. Alumina prepared in this way was found to be very suitable for the chromatography of sensitive hydrocarbons such as coeranthrene (LXIV) and sym-tribenzoperinaphthene (XCVII). As dihydrozethrene (LXVII) tended to decompose if allowed to remain on the column too long, pressure was applied to the top of the column to hasten the elution.

A crude sample of dihydrozethrene (LXVII) (0.5 g.) was dissolved in benzene (75 c.c.) and the solution added to the alumina column, which was then washed thoroughly with light petroleum (b.p. 60-80°). On eluting with benzene, a bright yellow band was developed which yielded a clear yellow eluate with a blue fluorescence. Concentration and crystallisation from benzene gave yellow plates (0.4 g.), m.p. 233-234° of dihydrozethrene (LXVII), which when admixed with a sample prepared by E. Clar gave no depression of the melting point. Spectroscopic examination, however, showed that the absorption band at 4505A had increased in intensity (see Fig.10).

Zethrene (IV). - The apparatus, which was used in this preparation, was the same as that described in dehydrogenation of hexahydrotriangulene (XXVII). 7:14-Dihydrozethrene (LXVII) (0.3 g.) was sublimed over the palladium-charcoal catalyst (20%) (6 g.), which was preheated to 310°, in a stream of pure carbon dioxide, and a dark bluish-green sublimate was obtained. After washing with cold benzene to remove unchanged dihydrozethrene (LXVII), crystallisation of the sublimate from trichlorobenzene in a carbon dioxide atmosphere yielded glistening green plates (160 mg.) of zethrene (IV) (Found: C, 95.3; H, 4.55. $C_{24}H_{14}$ requires C, 95.3; H, 4.7%) which carbonised without melting at high temperatures (ca. 350°). The hydrocarbon gave greenish-yellow solutions in benzene and carbon disulphide which when exposed to light decomposed rapidly to give an insoluble brown polymer.

Photo-oxidation of Zethrene (IV). - Zethrene (IV) (10 mg.) was dissolved in benzene and a stream of oxygen bubbled through the solution while it was exposed to light. In this case no polymer was formed and a clear, blue-fluorescent solution was obtained, whose absorption spectrum is shown in Fig.11.

Zethrene Oxide (LXVIII). - a). In the preparation of dihydrozethrene (LXVII). - This experiment was carried out by Clar and Hopkin (unpublished). The dark brown compound (LXVI) (3 g.) in pyridine (40 c.c.) was refluxed with zinc dust (7 g.) while acetic acid (20 c.c.) was run in, over three hours. More zinc dust (3 g.) was added at the end of each hour. The orange complex, which was precipitated by pouring the mixture into dilute acetic acid, was filtered off, washed and boiled with trichlorobenzene (20 c.c.) for 15 minutes. The filtered trichlorobenzene solution was diluted with benzene and extracted with phosphoric acid (d 1.75). The benzene solution after washing with water and concentration yielded dihydrozethrene (LXVII). The violet phosphoric acid extract was diluted with water and the resulting red precipitate crystallised from benzene to give red prisms, m.p. 270-272° of zethrene oxide (LXVIII) (Found: C, 90.7; H, 4.9. $C_{24}H_{14}O$ requires C, 90.5; H, 4.4%).

b). From the Photo-oxides of Zethrene. - A solution of the photo-oxides prepared as above was heated with a palladium-charcoal catalyst (20%) for 10 minutes. After cooling, the solution was chromatographed (alumina) and with a benzene-ether mixture as eluant, a clear red solution was obtained which on concentration yielded red prisms, m.p. 270-272°, of zethrene oxide (LXVIII) (Found: C, 89.5; H, 4.1. Calc. for $C_{24}H_{14}O$: C, 90.5; H, 4.4%). The properties of this compound were identical with those of the zethrene oxide isolated by Clar and Hopkin. The oxide dissolved readily in phosphoric acid (d 1.75), 50% sulphuric acid and concentrated hydrochloric acid to give violet solutions which, when diluted with water, decomposed, the oxide being precipitated. It showed no phenolic properties, as it was insoluble in alkalies and alcoholic potassium hydroxide solution and it was recovered unchanged after boiling with acetic anhydride. Reduction of the oxide (LXVIII) with zinc dust and acetic acid or with alkaline sodium dithionite solution gave a yellow solution which quickly re-oxidised on standing.

Zethrenium Salts (LXXI). - a). From Zethrene (IV). - Violet solutions, all of which had a sharp absorption band at 5800A, were obtained by dissolving zethrene (IV) in acids. The absorption spectra of two of these salt solutions (zethrenium acetate and zethrenium sulphate), are shown in Fig.13 and Fig.22. The solutions are quite stable and can be greatly diluted with water without decomposition in contrast to the acid solutions of zethrene oxide (LXVIII). When a few drops of perchloric acid were added to a solution of zethrene (IV) in acetic acid, dark violet crystals at once separated, which were filtered off, washed with benzene and dried. Zethrenium perchlorate (LXXI) (Found: C, 69.9; H, 4.0; Cl, 8.7. $C_{24}H_{15}O_4Cl$ requires C, 71.55; H, 3.75; Cl, 8.8%) could not be recrystallised as it was insoluble in organic solvents. It was stable to alkalies and was recovered unchanged from boiling pyridine.

b). From 7:14-Dihydrozethrene (LXXVII). - A warm aqueous solution of selenium dioxide was added to a solution of 7:14-dihydrozethrene (LXVII) (10 mg.) in acetic acid. A violet solution was obtained which showed a sharp absorption band at 5800A when its visual spectrum was examined.

A similar result was obtained when dilute chromic acid solution was added to a solution of the hydrocarbon in acetic acid.

Zethrenium Hydride (LXX) and its Isomerisation to 7:14-Dihydrozethrene (LXVII). - When zethrene (IV) (50 mg.) dissolved in acetic acid (90%) was boiled with zinc dust, the violet colour of the solution quickly disappeared, and a clear yellow solution with a violet fluorescence was obtained. This solution was unstable and quickly re-oxidised when allowed to cool. The reduced solution was stabilised, however, by adding a little stannous chloride and the absorption spectrum of zethrenium hydride (LXX), which is shown in Fig.13, was thus examined.

The solution of (LXX) in acetic acid was refluxed for 5 hours, small portions of zinc dust being added at intervals. After filtering off the excess zinc dust, the solution was evaporated to dryness in a vacuum and the residue sublimed in a vacuum. Chromatographic purification (alumina) of the sublimate, with benzene as eluant, yielded a clear yellow solution with a blue fluorescence which on concentration and crystallisation from benzene gave yellow plates, m.p. 233-234°, of 7:14-dihydrozethrene (LXVII) (26 mg.) (Found: C, 94.9; H, 5.6. Calc. for $C_{24}H_{16}$: C, 94.7; H, 5.3%) whose properties were identical with those of previous samples. A second red band in the chromatogram yielded on elution with a benzene-ether mixture a small quantity of zethrene oxide m.p. 269-272° (LXVIII).

<u>Hexahydrozethrene</u> (LXIX). - 7:14-Dihydrozethrene (LXVII) (0.1 g.), red phosphorus (3 g.) and 55% hydriodic acid (20 c.c.) were covered with a layer of xylene (20 c.c.) and the mixture refluxed. The reaction was followed spectroscopically and when the concentration of dihydro-

zethrene (LXVII) was greatly reduced (after ca. 2 weeks), the mixture was diluted with water and filtered from excess phosphorus, which was washed with hot xylene. After separating off the aqueous layer and washing with hot water, the xylene layer was dried, concentrated and chromatographed (alumina), light petroleum (b.p. 40-60°) being used as eluant. A colourless eluate with a bright violet fluorescence was obtained which after concentration and crystallisation from light petroleum (b.p. 60-80°) yielded colourless leaflets (60 mg.), m.p. 205-206°, of hexahydrozethrene (LXIX) (Found: C, 93.3; H, 6.9. $C_{24}H_{20}$ requires C, 93.5; H, 6.5%). The hydrocarbon did not dissolve readily in concentrated sulphuric acid but on warming gently a violet solution with an orange fluorescence was obtained. A very small amount of unreduced dihydrozethrene (LXVII) was recovered from the column on elution with benzene.

Peropyrene (LXXV). - When sym-dibromosuccinyl chloride (15.6 g.) (b.p. 99-101°/9 mm.), which was prepared from fumaroyl chloride and the theoretical quantity of bromine by refluxing in carbon tetrachloride for 24 hours, and naphthalene (12.8 g.) were treated with powdered aluminium chloride (13.4 g.), a very vigorous reaction occurred and as before no cooling was applied. When cold, the mixture was decomposed with ice and dilute hydrochloric acid solution and after boiling the crude product was filtered off, washed with benzene and methyl alcohol, and dried. The product, which was probably (LXXIV), was reduced by means of Clar's zinc dust melt and the residue from the decomposed melt was sublimed in a vacuum. The orange sublimate was dissolved in xylene and chromatographed (alumina), benzene being used to develop the chromatogram. A clear yellow eluate with a strong blue fluorescence was obtained which, when concentrated, yielded yellow plates, m.p. 365-368°, of peropyrene (LXXV) (Found: C, 95.7; H, 4.35. Calc. for $C_{26}H_{14}$: C, 95.7; H, 4.3%). The hydrocarbon gave a blue solution when dissolved in concentrated sulphuric acid.

<u>Hexahydroperylene</u> (LXXIX or LXXX). - Perylene (LXXVI) (1 g.) was ground together with zinc dust (5 g.) and aluminium chloride (10 g.) and the mixture added to benzene (200 c.c.). When the mixture was heated, the colour of the solution rapidly changed from green to violet, to red and finally to green. After boiling for 10 minutes, the mixture was decomposed with water, filtered from excess zinc dust which was washed with hot benzene. After separating the aqueous layer, the benzene solution was washed with dilute hydrochloric acid solution, concentrated and dried. Chromatographic purification (alumina)

with light petroleum (b.p. 40-60°) as eluant yielded a colourless solution with a strong violet fluorescence which gave on concentration colourless, violet fluorescent prisms (0.6 g.), m.p. 188-189° of hexahydroperylene (LXXIX) (Found: C, 93.1; H, 6.75. Calc. for $C_{20}H_{18}$: C, 93.0; H, 7.0%). The hydrocarbon was insoluble in cold concentrated sulphuric acid but gave on warming first a red solution and then a yellowish-brown one with a green fluorescence. Hua-Chih and Conrad-Billroth (43) gave the melting point of the sample which they used for spectroscopic examination as 189°. A little unchanged perylene (LXXVI) was recovered from the column on elution with benzene.

The Syntheses of Perinaphthyl Radicals.

Perinaphthenone (LXXXI). - The method used to prepare this compound was that described by Fieser and Hershberg (50) but with slight modifications. β-Naphthol (180 g.) was added in small portions over 30 minutes to a mixture of glycerol (450 g.), water (414 c.c.), concentrated sulphuric acid (608 c.c.) and m-nitrobenzene sulphonic acid (sodium salt) (225 g.) at 135°. After heating at 135-140° for a further 30 minutes and cooling, the reaction mixture was poured on to crushed ice and diluted to 5½ litres. When the tarry precipitate had settled, the yellow supernatant liquor was decanted and extracted with hot benzene. The tar was also thoroughly extracted with boiling benzene and after the combined extracts had been concentrated to approximately 1 litre, they were refluxed with activated charcoal for 20 minutes and filtered. The residue, when the remaining benzene had been removed, was distilled in a vacuum and a clear yellow distillate (b.p. 200°/3 mm.) (100 g.; 45%) was obtained which crystallised on cooling. Recrystallisation from a benzene-light petroleum (b.p. 80-100°) mixture gave elongated yellow prisms, m.p. 153-154°, of perinaphthenone (LXXXI) which dissolved readily in concentrated sulphuric acid to give a yellow solution with a green fluorescence.

Acetoxyperinaphthyl (LXXXIV; R = $CH_3.CO.O$). - When acetyl chloride (0.3 c.c.) was added to a solution of perinaphthenone (LXXXI) (0.1 g.) in anhydrous benzene, a slightly exothermic reaction occurred and, after cooling, a yellow solid crystallised from the solution. This compound, which probably is LXXXIII (R = $CH_3.CO.O$) was not purified as it tended to decompose with explosive violence when heated. After decanting the benzene, the yellow solid was dissolved in anhydrous ether, and magnesium turnings, activated by subliming a crystal of iodine through them, were added. On occasions, reaction occurred at once, but at other times the mixture had to be shaken gently for several minutes before the blue colour developed. A greenish-blue solution was thus obtained and examination of its visual spectrum showed that it was contaminated with peropyrene (LXXV) (sharp absorption bands at 4435A, 4155A and 3920A). The solution was obtained spectrally pure by cooling it to 0°C and passing it through a cooled column of alumina under pressure. Decomposition of the blue solution was observed on the column, but a clear blue solution free from perinaphthenone (LXXXI) and peropyrene (LXXV) was obtained. The absorption spectrum of such a solution is shown in Fig.14. The solution, which was decomposed when exposed to light and air, was quite stable when kept at 0° in the dark, but when it was cooled strongly (-35°), a colourless solution was obtained. However, on allowing this solution to warm to room temperature, the initial deep blue colour was regained. When the solution was heated in benzene, the blue colour rapidly disappeared and a pale yellow solution was obtained. Attempts to isolate the solid radical by evaporating the solvent in a vacuum without heating were not successful, a dark oil being obtained.

Benzoyloxyperinaphthyl (LXXXIV; $R = C_6H_5.CO.O$). - A pure blue solution of this radical was obtained from perinaphthenone (LXXXI) and benzoyl chloride as described above. This radical appeared to be slightly more stable to chromatography than the acetoxyperinaphthyl, but its properties were very similar to those of the latter.

Methoxyperinaphthyl (LXXXIV; $R = CH_3.O$). -

a). Anhydrous hydrogen chloride was slowly passed into a cold solution (0°) of perinaphthenone (LXXXI) (0.1 g.) in methyl alcohol and a yellowish-brown solid was precipitated. The precipitate, which was very readily hydrolysed, was filtered off, washed with methanol and dried in a vacuum. An ethereal solution of this compound, which is probably LXXXIII ($R = CH_3.O$), was treated with magnesium, activated with iodine. A dark bluish-green solution was obtained which was purified by passing it through a cooled column of alumina under pressure. The properties of the clear blue solution of methoxyperinaphthyl (LXXXIV; R = CH_3O), which was obtained, were very similar to those of the above radicals, but this radical was much less stable than the other two. However, in contrast to the other radicals, a solution of methoxyperinaphthyl gave a violet solution when treated with dilute acids.

b). Dry hydrogen chloride was passed into a solution of perinaphthenone (LXXXI) (0.1 g.) in methyl alcohol without cooling and a dark green solution was obtained. On cooling, a dark solid was obtained which was filtered off, washed with methyl alcohol and dried in a vacuum. Extraction of this solid with cold benzene yielded a greenish-blue solution which, on chromatographing as above, gave a blue solution of methoxyperinaphthyl (LXXXIV; R = CH_3O).

Perinaphthylium Perchlorate. - A hot solution of perinaphthenone (LXXXI) (10 g.) in xylene (50 c.c.) was added to a boiling dilute sodium hydroxide solution (5%) (200 c.c.) containing zinc dust (5 g.) which had been activated by the addition of a little copper salt. A deep blood-red colour immediately developed which disappeared after refluxing for 30 minutes. After removal of the xylene by steam distillation, the yellow solution was filtered into concentrated hydrochloric acid and the acidified solution cooled to 0°. A pale yellow solid was obtained which was filtered off, washed and sublimed in a vacuum to give perinaphthene (LXXXVI) (0.5 g.). The hydrocarbon was dissolved in acetic acid containing a few drops of perchloric acid and when a warm solution of selenium dioxide in acetic acid was added, dark brown crystals of perinaphthylium perchlorate were obtained, which were filtered off, washed with benzene and dried in a vacuum. This compound was very unstable and it was not possible to purify it.

On extracting the zinc dust with boiling xylene, a colourless, non-fluorescent solution was obtained which on concentration and crystallisation from toluene gave colourless needles (6 g.) of the <u>dimeride</u> (LXXXIX) (Found: C, 85.6; 85.5; H, 5.3, 5.4. $C_{26}H_{20}O_2$ requires C, 85.7; H, 5.5%). The compound, which was insoluble in alkali, decomposed to give a yellow melt at 256-257° and dissolved in concentrated sulphuric acid to give a bright yellow solution. It could not be sublimed, but was recovered unchanged after boiling for one hour with acetic anhydride. When the compound was melted with alcoholic potassium hydroxide solution it gave a purple dyestuff, which was very similar to that obtained from perinaphthenone (LXXXI).

The Synthesis of 2:3-5:6-8:9-Tribenzoperinaphthene.

1:2-Benz-9:10-anthraquinone (XC). - This compound was prepared as described by Groggins and Newton (55), the following conditions being used. Aluminium chloride (147 g.) was added with continuous stirring to naphthalene (65 g.) and phthalic anhydride (74 g.) in o-dichlorobenzene (b.p. 179°) at 0°. After the usual decomposition and removal of the solvent by steam-distillation, the crude 2-α-naphthoylbenzoic acid (130 g.) was dried and ring-closed by heating for 7 hours with continuous stirring in concentrated sulphuric acid (780 g.) at 75-80°. Boric acid (130 g.) was used to inhibit sulphonation. Pure 1:2-benz-9:10-anthraquinone (XC) (m.p. 167-168°) which gave an olive-green solution in concentrated sulphuric acid, was obtained by crystallisation from acetic acid.

1:2-Benz-9-anthrone (XCI). - The method used was that described by J.W. Cook (56). Aluminium powder (12.5 g.) was slowly added to the quinone (XC) (50 g.) in concentrated sulphuric acid (500 c.c.), the temperature being kept below 45° by occasional cooling. After 3 hours the orange-yellow solution was poured into water containing crushed ice and the precipitate, which was filtered off, was dried in a vacuum. No attempt was made to purify the anthrone (XCI) as it oxidised very readily.

10-Benzylidene-1:2-benzanthrone (XCII). - The anthrone (XCI) (48 g.), benzaldehyde (25 g.), pyridine (125 c.c.) and piperidine (1.25 c.c.) were boiled together for 4 hours. The solvent was then distilled off and the residue dried at 140° in a vacuum till free from benzaldehyde. The glass-like product was dissolved in benzene and thoroughly extracted with warm alkaline sodium dithionite solution, till the red vat of the quinone (XC) was no longer formed. After washing and drying, the benzene was removed and crystallisation from acetic acid gave yellow prisms (50 g.), m.p. 144-145°, of 10-benzylidene-1:2-benzanthrone (XCII) (Found: C, 90.1; H, 5.1. $C_{25}H_{16}O$ requires C, 90.3; H, 4.85%) which gave a magenta solution with no fluorescence in concentrated sulphuric acid.

2:3-5:6-8:9-Tribenzoperinaphthenone (XCIII). - Powdered aluminium chloride (50 g.) was added to a solution of (XCII) (10 g.) in benzene (150 c.c.), and the deep red solution refluxed for 30 minutes. After decomposition by pouring into dilute hydrochloric acid solution (1:1), containing crushed ice, the benzene layer was separated, washed and dried. Chromatographic purification (alumina) with benzene as eluant gave first a colourless, non-fluorescent solution, which on concentration and crystallisation from xylene yielded colourless prisms (3 g.), m.p. 276-

278° (Found: C, 89.7; H, 5.7. Calc. for $C_{25}H_{18}O$: C, 89.75; H, 5.4%). The compound, which is probably XCIX, sublimed without decomposition in a vacuum, crystallised unchanged in needles, m.p. 276-278°, after refluxing with acetic anhydride for one hour and gave a bright yellow, green fluorescent solution in concentrated sulphuric acid. It was insoluble in alkaline solution and did not form a perchlorate. Attempts to dehydrogenate (chloranil and palladium-charcoal) and to oxidise (selenium dioxide and chromic acid) were unsuccessful. The second yellow band in the chromatogram gave a clear yellow eluate which on concentration and crystallisation from acetic acid or benzene yielded orange-yellow needles (4 g.), m.p. 260-261°, of tribenzoperinaphthenone (XCIII) (Found: C, 91.0; H, 4.3. $C_{25}H_{14}O$ requires C, 90.9; H, 4.3%) which gave a violet-red solution with an orange fluorescence in concentrated sulphuric acid. The compound, which gave stable brown needles by the addition of a little bromine to its benzene solution, was not readily reduced and was recovered unchanged after boiling for one hour with zinc dust in pyridine and acetic acid.

2:3-5:6-8:9-<u>Tribenzoperinaphthenone Perchlorate</u>. - Perchloric acid (1 c.c.) in acetic anhydride (2 c.c.) was added to a boiling solution of (XCIII) (1 g.) in acetic acid. The initial clear yellow colour of the solution immediately changed to a deep red and dark reddish-brown needles began to crystallise out. When cold, the crystals were filtered off, washed with acetic acid and benzene and dried in a vacuum at 100°. The perchlorate (Found: Cl, 8.4. $C_{25}H_{15}O_5Cl$ requires Cl, 8.25) was readily hydrolysed and the tribenzoperinaphthenone (XCIII) recovered by warming with dilute alkaline solutions. The yields from these reactions were theoretical.

2:3-5:6-8:9-Tribenzoperinaphthene (XCVII). - Tribenzoperinaphthenone (XCIII) (1 g.), red phosphorus (2.5 g.) and potassium iodide were added to 55% hydriodic acid (25 c.c.) covered with a layer of xylene (25 c.c.). After refluxing for 48 hours, the mixture was diluted with water and the phosphorus filtered off from the hot solution. The xylene layer was separated off, washed thoroughly with warm alkaline sodium dithionite solution, concentrated and chromatographed (alumina). As the hydrocarbon was oxidisable, the column was protected against light and pressure was applied to the top. Using benzene as eluant, a pale yellow solution with a bright blue fluorescence was obtained which on concentration and crystallisation from benzene or methyl alcohol yielded pale yellow needles (0.6 g.), m.p. 253-255° of tribenzoperinaphthene (XCVII) (Found: C, 94.4; H, 5.2. $C_{25}H_{16}$ requires C, 94.9;

H, 5.1%). The hydrocarbon did not dissolve readily in concentrated sulphuric acid but on gently warming a violet-blue solution with a red fluorescence was obtained. A solution having the same colour was obtained by boiling the hydrocarbon in acetic acid in contact with air.

2:3-5:6-8:9-Tribenzoperinaphthenium Perchlorate (XCV) or (XCVI). - The hydrocarbon (XCVII) (0.2 g.) was dissolved in acetic acid (30 c.c.) containing perchloric acid (1 c.c.). A stream of oxygen was passed through the boiling solution, which rapidly changed to a deep violet-blue colour. After 15 minutes the solution was allowed to cool and violet-blue crystals of the perchlorate (XCV) or (XCVI) were obtained, which were filtered off, washed with dry benzene and dried in a vacuum over potassium hydroxide pellets (Found: C, 71.5; H, 3.9. $C_{25}H_{15}O_4Cl$ requires C, 72.4; H, 3.6%. $C_{25}H_{16}O_4Cl$ requires C, 72.2; H, 3.9%). When treated with water the blue solid was quickly decomposed and a yellow compound was obtained. The perchlorate was soluble in nitromethane giving a violet-blue solution with a red fluorescence, which became pale yellow on the addition of alkalies or basic solvents such as pyridine. The initial colour of the solution was restored, however, by the addition of perchloric acid. The addition of perchloric acid to the solution after it had been standing for some time (15-30 minutes) gave the deep red colour of the perchlorate of tribenzoperinaphthenone and not that of the hydrocarbon perchlorate (XCV). The perchlorate in acetic acid was rapidly reduced by boiling with zinc dust and a colourless solution with a blue fluorescence was obtained which re-oxidised on standing.

Dihydro-2:3-5:6-8:9-tribenzoperinaphthene (XCIV). -

Tribenzoperinaphthenone (XCIII) (1 g.) was reduced for 5 days, using the same conditions as in the preparation of tribenzoperinaphthene (XCVII). The reaction mixture was treated as already described and the concentrated xylene layer was chromatographed (alumina), with light petroleum (b.p. 40-60°) as eluant. A colourless non-fluorescent solution was obtained which on concentration and crystallisation from methyl alcohol gave pale yellow plates (0.5 g.), m.p. 178-180° of dihydrotribenzoperinaphthene (XCIV) (Found: C, 94.0; H, 5.7. $C_{25}H_{18}$ requires C, 94.3; H, 5.7%). The hydrocarbon did not dissolve in cold concentrated sulphuric acid but on heating a violet-blue solution with a red fluorescence was obtained. Boiling in acetic acid in contact with oxygen did not affect the compound, but the addition of a little selenium dioxide gave a violet-blue solution (cf., the preparation of coeranthrenium perchlorate (LXII)).

The Syntheses of Benzofluoranthenes.

2:3-Benzofluoranthene (CII). - An unpurified sample of 12-hydroxytriangulene-4:8-quinone (XXVIII) (2 g.) was reduced to hexahydrotriangulene (XXVII) by Clar's zinc dust melt. When the reaction product was chromatographed (alumina) with light petroleum (b.p. 60-80°) as eluant, a yellow band was developed which gave a clear yellow solution with a green fluorescence. Concentration and crystallisation from light petroleum (b.p. 60-80°) yielded yellow needles (60 mg.), m.p. 143-144° of 2:3-benzofluoranthene (CII) (Found: C, 94.7; H, 5.0. Calc. for $C_{20}H_{12}$: C, 95.2; H, 4.8%) which dissolved in concentrated sulphuric acid to give a yellow solution which rapidly changed to violet. The properties of this hydrocarbon agreed with those of the samples prepared by Stubbs and Tucker (62) and by Campbell and Marks (63).

5-Keto-5:12-dihydronaphthacene (CV). - This was prepared by the reduction of naphthacene-5:12-quinone, the method being a modification of that used by Fieser (67). A finely divided suspension of naphthacene-5:12-quinone (8 g.), obtained by precipitation from concentrated sulphuric acid with water, was heated in 4% sodium hydroxide solution (500 c.c.) to 95° and sodium dithionite (12 g.) added, giving a deep green solution. After several minutes, pale crystals separated, and the solution changed to a deep orange-brown colour. Two further portions (4 g.) of sodium dithionite were added at 15 minute intervals and the mixture boiled for one hour. The light brown precipitate, after filtration from the hot solution and washing, was crystallised from acetic acid, small amounts of naphthacene present being removed by the addition of a little maleic anhydride. The dark yellow needles of 5-keto-5:12-dihydronaphthacene (7 g.), m.p. 185-190°, gave an orange-red solution in concentrated sulphuric acid. Fieser (67) gives m.p. 196°, but states that it varies with the rate of heating.

5-Phenylnaphthacene (CVI). - Phenylmagnesium bromide, prepared by the addition of bromobenzene (15.7 g.) in anhydrous ether (50 c.c.) to magnesium turnings (2.5 g.), was added dropwise to a fine suspension of 5-keto-5:12-dihydronaphthacene (CV) (4 g.) in anhydrous benzene (50 c.c.). After refluxing for 30 minutes, the clear red-brown solution was decomposed with dilute hydrochloric acid solution and the mixture steam-distilled to remove solvents and diphenyl. Crystallisation of the resulting solid from benzene gave brownish-yellow crystals (3.75 g.), which on recrystallisation from acetic acid yielded orange-yellow prisms, m.p.187-188°, of 5-phenylnaphthacene (CVI) (Found: C, 94.6; H, 5.3.

$C_{24}H_{16}$ requires C, 94.7; H, 5.3%). The hydrocarbon, which sublimed in a vacuum in prisms, gave a green solution in concentrated sulphuric acid which changed to violet on standing.

1':2':3':4'-Tetrahydro-2:3-6:7-dibenzofluoranthene (CIX) and 2:3-6:7-dibenzofluoranthene (CVII). - 5-Phenylnaphthacene (CVI) (2 g.) was added to a sodium chloride (2 g.) - aluminium chloride (10 g.) melt at 110°. The initial dark green solution rapidly changed to red and when uniform (after approximately 2½ minutes) the melt was poured into hydrochloric acid solution (1:1). After filtering and washing thoroughly with dilute hydrochloric acid ammonia and water, the dark red precipitate was heated at 170-180° in a vacuum (1 mm.) and an orange-yellow sublimate was obtained. The sublimate, which gave a green solution in concentrated sulphuric acid, was extracted with cold benzene and crystallised from xylene in orange yellow plates which melted at 331-333° and gave a mixed m.p. of 332-333° with an authentic sample of naphthacene. The visual spectrum of the sublimate was identical with that of naphthacene. The residue after sublimation was dissolved in benzene and chromatographed (alumina), with a benzene-light petroleum (b.p. 40-60°) mixture as eluant. The first yellow band gave a yellow eluate with a green fluorescence, which yielded, on concentration, yellow needles (0.4 g.), m.p. 151-152°, of 1':2':3':4'-tetrahydro-2:3-6:7-dibenzofluoranthene (CIX) (Found: C, 93.8; H, 5.9. $C_{24}H_{18}$ requires C, 94.1; H, 5.9%). The hydrocarbon gave a yellow solution in concentrated sulphuric acid which changed to red on standing. A second dark red band gave on elution a violet-red solution which was sensitive to light and on prolonged exposure was decolourised. This red eluate gave on concentration and crystallisation from benzene stout red needles (0.8 g.), m.p. 216.5 - 217°, of 2:3-6:7-dibenzofluoranthene (CVII) (Found: C, 95.5; H, 4.7. $C_{24}H_{14}$ requires C, 95.3; H, 4.7%). The hydrocarbon was identical with the red condensation product from 9-phenyl-1:2-benzanthracene (Clar and Stewart, (61)) and with a sample kindly supplied by Dr. Neil Campbell. It gave a red-brown solution in concentrated sulphuric acid which changed to violet on standing.

Dehydrogenation of (CIX). - The tetrahydro-derivative (CIX) (0.1 g.) was mixed with a palladium-charcoal catalyst (20%) (0.1 g.) and heated at 180° for 5 minutes in an air-free, carbon dioxide atmosphere. The product was sublimed in a vacuum (1 mm.) and dark red needles were obtained. Crystallisation from benzene gave needles which melted at 213-216° and gave a mixed m.p. 214-216° with the sample of

2:3-6:7-dibenzofluoranthene obtained above. The visual spectrum was identical with that of the previous sample.

Maleic Anhydride Adduct (CX). - 2:3-6:7-Dibenzofluoranthene (CVII) (0.1 g.) was dissolved in benzene (1.5 c.c.) and excess maleic anhydride added. After refluxing for 5 minutes, the deep red colour was discharged and on cooling colourless needles were obtained. Crystallisation from acetic anhydride gave colourless needles of the adduct (Found: C, 84.0; H, 4.2. $C_{28}H_{16}O_3$ requires C, 84.0; H, 4.0%), which began to decompose at 256° and gave a clear red melt at 284°.

The Synthesis of Benzylnaphthacene.

5-Benzylnaphthacene (CXVII). - A solution of benzylmagnesium chloride, which was prepared by the interaction of benzyl chloride (10 c.c.) and magnesium (2.15 g.) in anhydrous ether (50 c.c.), was slowly added to a fine suspension of 5-keto-5:12-dihydronaphthacene (CV) (5.5 g.) in dry benzene (100 c.c.). After refluxing for 30 minutes, the clear orange-red solution, which was obtained, was decomposed with dilute hydrochloric acid solution and then steam-distilled to remove the solvents. An orange-yellow solid was obtained and crystallisation from acetic acid yielded yellow needles (6 g.), m.p. 180-181° of 5-benzylnaphthacene (CXVII) (Found: C, 94.1; H, 5.5. $C_{25}H_{18}$ requires C, 94.3; H, 5.7%). It was observed that when a solution of the yellow hydrocarbon in acetic acid was heated, the colour deepened to an orange-yellow, but the initial clear yellow solution was obtained on cooling. The hydrocarbon dissolved in concentrated sulphuric acid to give a dark green solution.

When a solution of the hydrocarbon in benzene was heated with a small amount of maleic anhydride, the yellow colour was not diminished at all. It was concluded that, as soon as the acene from (CXVII) reacted with maleic anhydride, the methylene form (CXVIII) isomerises to the acene form (CXVII) to maintain the equilibrium between the tautomers. This method of separating the tautomers was therefore abandoned.

Crystallisation of the hydrocarbon from various solvents, e.g., methanol, ethanol, benzene and light petroleum, was carried out in an attempt to isolate the methylene form (CXVIII), but without success.

Attempted Preparation of 2:3-4:5-8:9-Tribenzoperinaphthene. - 5-Benzylnaphthacene (CXVII) (1 g.) was added to a sodium chloride (1 g.) - aluminium chloride (5 g.) melt at 110°. The initial dark green colour quickly changed to dark brown and when the melt was uniform (after approximately 4 minutes), it was poured into dilute hydrochloric acid solution (1:1). After boiling the mixture, the precipitate was filtered from the hydrochloric acid solution which was deep violet in colour. After washing and drying, the solid was heated in a vacuum (1 mm.) at 170-180° and a small quantity of naphthacene (m.p. 333°) was obtained. The residue was dissolved in benzene and chromatographed (alumina), benzene being used to develop the chromatogram. At first a colourless eluate was obtained which on concentration yielded colourless crystals, m.p. 143-146°, of an unidentified compound which dissolved slowly in concentrated sulphuric acid to give a brownish-red solution. A second yellow band was developed which yielded a clear yellow eluate with a green fluorescence. On concentration a gum was obtained which could not be crystallised. An attempt was made to dehydrogenate this compound by subliming it from a palladium-charcoal catalyst (20%), but no identifiable product could be obtained. Finally, a small red band gave a deep violet-red eluate, which on concentration yielded a minute quantity of red needles. Repeated attempts to prepare more of this compound were unsuccessful.

The Synthesis of Diperinaphthyleneanthracene.

1:5-Di-β-naphthoxyanthraquinone (CXXII). - An intimate mixture of 1:5-dichloroanthraquinone (37 g.), β-naphthol (75 g.) and powdered potassium hydroxide (22 g.) was heated in an oil-bath at 145° for 2 hours. The melt, which at first was quite mobile, became more viscous as the reaction proceeded and finally a thick mass was obtained. The cold melt was powdered and thoroughly extracted with boiling dilute sodium hydroxide solution till the filtrate was colourless. After washing with water and drying, the yellow solid was crystallised from nitrobenzene and large yellow prisms (65 g.), m.p. 245-247°, of the dinaphthoxyanthraquinone (CXXII) (Found: C, 83.0, 82.8; H, 4.9, 4.3. Calc. for $C_{34}H_{26}O_4$: C, 82.9; H, 4.1%) were obtained. The melting point of a sample of this compound prepared by a different method (77) is given as 243-245°. The compound dissolved in concentrated sulphuric acid to give a violet-blue solution and gave a yellow vat when warmed with an alkaline sodium dithionite solution. When a powdered sample of this material was exposed to light, the colour of the surface changed to orange, but the initial bright yellow colour returned after storing in the dark for some time. This experiment was repeated several times, but the melting point and the properties of the sample did not change.

1:2'-5:2"-Dioxido-9:10-di-α-naphthylanthracene (CXXIII) and 8:2'-4:2"-Dioxido-1:9-5:10-diperinaphthylene-anthracene (CXXIV). - A mixture of dinaphthoxyanthraquinone (CXXII) (30 g.), sodium chloride (30 g.) and aluminium chloride (150 g.) was heated with constant stirring in an oil-bath at 180° for 10 minutes and then at 145° for 15 minutes. After cooling to 110°, the melt was decomposed by pouring it into dilute hydrochloric acid solution (1:1) containing crushed ice and the mixture was boiled for several minutes. The dark blue precipitate, which was obtained, was filtered off, extracted with warm alkaline sodium dithionite solution, washed with water and dried. Thorough extraction of the powdered solid with cold benzene yielded a dark blue solution which was filtered from undissolved material and chromatographed (alumina), pressure being applied to the column. With benzene as eluant, a brilliant violet-red solution with an orange fluorescence was obtained which on concentration and crystallisation from benzene yielded dark red prisms (4 g.), m.p. 255-256° of dioxido-dinaphthylanthracene (CXXIII) (Found: C, 88.9; H, 4.1. $C_{34}H_{18}O_2$ requires C, 89.1; H, 4.0%). The compound, which photo-oxidised rapidly, dissolved in concentrated sulphuric acid to give a violet-red solution. A second bright blue band in the chromatogram gave a clear blue eluate, which on concentration and crystallisation from xylene yielded small blue crystals (2 g.) of dioxido-diperinaphthyleneanthracene (CXXIV) (Found: C, 88.9; H, 3.6. $C_{34}H_{14}O_2$ requires C, 89.8; H, 3.1%). A further portion (15 g.) of this blue compound was obtained by extracting the undissolved material from the benzene extraction in a Soxhlet apparatus with xylene. This compound, which sublimed in a vacuum without decomposition, did not melt below 400° and dissolved in concentrated sulphuric acid to give a violet solution with a red fluorescence.

Condensation of (CXXIII) to (CXXIV). - The dark red by-product (CXXIII) (3 g.) was heated in an aluminium chloride (15 g.) - sodium chloride (3 g.) melt at 175° for 30 minutes. After cooling to 110°, the melt was decomposed and treated as above and a dark blue compound was isolated. Crystallisation from xylene gave blue crystals (2.5 g.) which were identical with the sample of (CXXIV) obtained above.

1:9-5:10-Diperinaphthyleneanthracene (CXXV). - A mixture of the blue compound (CXXIV) (0.75 g.), red phosphorus (1 g.), potassium iodide (0.5 g.) and hydriodic acid (55%) (10 c.c.) was heated in a sealed tube at 210°

for 10 hours. After diluting with water, the clear supernatant liquid was decanted from the light brown resin which was then washed with hot water and dissolved in benzene. Chromatographic purification (alumina) of the dried solution gave on elution with light petroleum (b.p. 60-80°), a pale yellow solution with a green fluorescence, which when concentrated yielded a gum. Repeated attempts to crystallise the latter were unsuccessful and eventually the crude material was used for dehydrogenation. After the gum (0.5 g.) had been heated at 230° for 5 hours with a palladium-charcoal catalyst (20%) (0.5 g.) in a pure carbon dioxide atmosphere, sublimation in a vacuum (1 mm.) gave a non-crystalline product which was dissolved in benzene and chromatographed (alumina). Pressure was applied to the top of the column and using benzene as eluant, an orange band was developed which gave a clear orange solution with a green fluorescence. Concentration and sublimation of the residue in a vacuum gave a dark red sublimate, which crystallised from light petroleum (b.p. 60-80°) as deep red prisms, m.p. 115-116°. This compound, which is probably diperinaphthyleneanthracene (CXXV), dissolved in concentrated sulphuric acid to give a dark green solution. When a benzene solution of the compound was heated with maleic anhydride it was decolourised rapidly and from the reaction mixture colourless needles, which are probably the adduct (CXXVI), were obtained. The visual spectrum of the alleged hydrocarbon (CXXV) in benzene was examined and sharp absorption bands were observed at 5090A, 4760A and 4460A.

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