THE STUDY OF SOME

POLYCYCLIC AROMATIC HYDROCARBONS.

T H E S I S

presented by

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———

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CONTENTS.

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I wish to record my sincere thanks and gratitude to Dr. E. Clar, under whose guidance this work was carried out, for his teaching and encouragement throughout the past three years.

My thanks are also recorded to the Department of Scientific and Industrial Research for a Maintenance Allowance awarded during sessions 1953-54 and 1954-55, and to the Salters' Company, London, for a Salters' Scholarship awarded for session 1955-56.

All the micro-analyses listed were carried out by Mr. J.M.L. Cameron and his staff in the Chemistry Department, and I am indebted to them all for this service.

The phosphorescence spectra shown on page 51 were very kindly recorded by Messrs. Rütgerswerke A.G. of Castrop-Rauxel, Germany, to whom I express my thanks.

INTRODUCTION.

For many years there has been some controversy on the relation of Kekulé structures to the stability of aromatic hydrocarbons.

As early as 1941, it was predicted by Clar[2] that no benzenoid hydrocarbon, for which there was no Kekulé structure, would exist in a stable form, thus implying that Kekulé structures were of paramount importance in considering the stability of hydrocarbons.

With the increase in our knowledge of theoretical chemistry, and in particular of the molecular-orbital and valence-bond treatments of organic molecules, the opinion grew that Kekulé structures were unreal and, at the most, of statistical significance only. Indeed this

tenet has received universal acceptance.

However, in 1950, Longuet-Higgins[3] supported the
importance of Kekulé structures from a quantum-mechanical
standpoint. He did not restrict his observations to
benzenoid hydrocarbons, but considered other hydrocarbons
for which no classical structure could be written, and
pointed out the interest which would be attached to
attempts to prepare hydrocarbons of this type.

Clar and Stewart[1] attempted to prepare the hydrocarbon
triangulene, which has no Kekulé structure, and found that,
in support of Clar's prediction[2] they were unable to
prepare the parent triangulene from its hydrogenated
derivatives by the usual methods of dehydrogenation,
since polymeriðation occured in the dehydrogenation due to
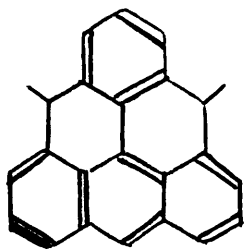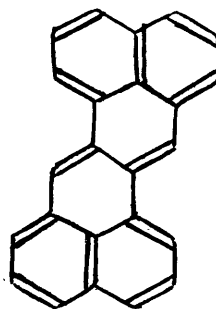
triangulene   zethrene

the intermediate formation of a reactive diradical.

Later, in 1955, Clar, Lang, and Schultz-Kiesow[18]
prepared the hydrocarbon 4:5-10:11-dibenztetracene, named

zethrene for convenience. Although this hydrocarbon has
nine possible Kekulé structures, these all contain the
same two double-bonds in the central region of the
molecule. In other words, zethrene is a hydrocarbon
which has only one Kekulé structure in a part of the
molecule, but the properties of zethrene are typical
of aromatic hydrocarbons.

It would appear then, that for a benzenoid hydrocarbon
to be typically aromatic,it must have at least one
Kekulé structure.

In order to increase our experimental knowledge
on the significance of Kekulé structures, attempts were
made to prepare two other hydrocarbons which have no
Kekulé structure. These were 4:5-7:8-dibenzpentacene and
4:5-6:7-dibenztetracene.
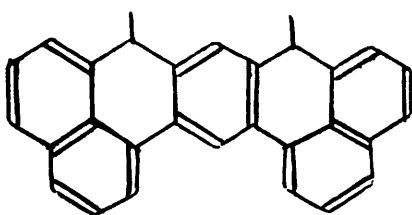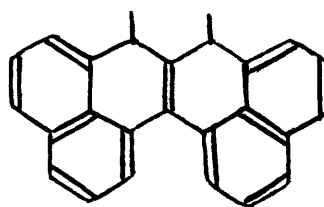
4:5-7:8-dibenzpentacene   4:5-6:7-dibenztetracene

The work on 4:5-7:8-dibenzpentacene derivatives (described in Part 1 of this Thesis) gave further proof that Kekulé structures do play an important part in considering the stability of an aromatic hydrocarbon.

No satisfactory conclusion was reached in the study of 4:5-6:7-dibenztetracene derivatives (described in Part 2 of this Thesis) because of a number of unexpected difficulties which caused the work to be abandoned.

In Part 3 of this Thesis is described a study of the unusual hydrocarbon dinaphtho-azulene.
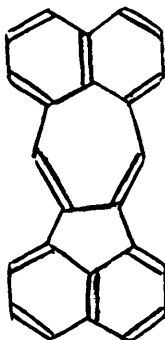
dinaphtho-azulene

Formerly, this hydrocarbon was thought to be zethrene, but this was shown to be erroneous, by Clar, Lang, and Schultz-Kieson[18]. The study of dinaphtho-azulene was initially taken up to elucidate its structure, but some other interesting properties of the hydrocarbon were

investigated.

Dinaphtho-azulene has only one Kekulé structure in the central region of the molecule and this is sufficient to render the hydrocarbon stable. The hydrocarbon is not entirely benzenoid, so that it is not surprising that it is not a typical aromatic hydrocarbon.
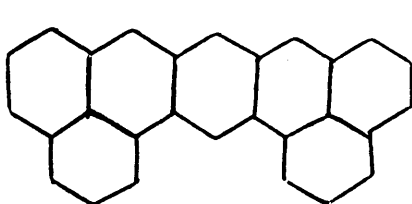
------oOo-------

P A R T   1.

4:5-7:8-DIBENZPENTACENE.

INTRODUCTION.

4:5-7:8-Dibenzpentacene has the carbon skeleton (I).
It is not possible to write a classical (Kekulé) structure
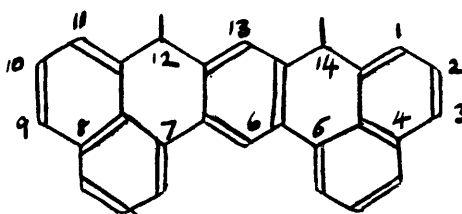
(I)   (II)

for the parent hydrocarbon, and for this reason it is
expected, like triangulene (III)[1]to be a diradical
(e.g. (II)) which may be stable under certain conditions
or which, more likely, will be highly reactive and
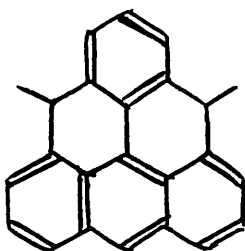
(III)

polymerise immediately on formation.

It was proposed in this work to prepare hydrogenated
derivatives of 4:5-7:8-dibenzpentacene and to study the
behaviour of these hydrocarbons in dehydrogenation
experiments, attempting to find whether the parent
hydrocarbon could be isolated in a stable form or whether,
as in the case of triangulene, dehydrogenation would
lead to the formation of reactive diradicals and hence
to polymerisation.

These studies would give still further data on the
general applicability of Clar's prediction[2].

--------oOo--------

DISCUSSION.

The route to 4:5-7:8-dibenzpentacene derivatives began with the chlorination of m-xylene, and the separation, from the mixture of chloro- compounds, of 4:6-dichloro-m-xylene (IV)[4]. Some difficulty was experienced in the repetition of the literature method for the preparation of this compound and suitable modifications had to be introduced. Dichloro-m-xylene

$$(IV) \xrightarrow{HNO_3} (V) \xrightarrow[OH^-]{KMnO_4}$$

(IV)   (V)

$$(VI) \xrightarrow{PCl_5} (VII)$$

(VI)   (VII)
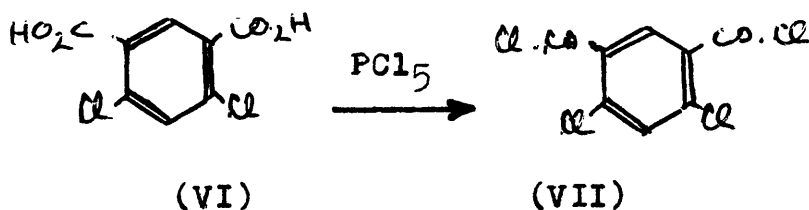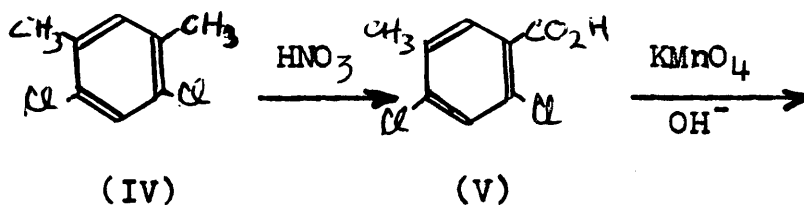
was oxidised firstly to 4:6-dichloro-<u>m</u>-toluic acid (V)[5] using nitric acid, and this in turn was oxidised to 4:6-dichloro-<u>iso</u>-phthalic acid (VI)[5] with alkaline permanganate. This acid was converted to the corresponding acid chloride (VII) by treatment with phosphorus pentachloride.

The crude acid chloride was dissolved in methylene chloride with two molecular equivalents of naphthalene, and by the addition of anhydrous aluminium chloride at room temperature, condensation was brought about very smoothly to give 1:3-dichloro-4:6-di-(1-naphthoyl)-benzene (VIII). The use of methylene chloride as solvent ensured substitution in the 1-position of naphthalene.

(VIII)   (IX)
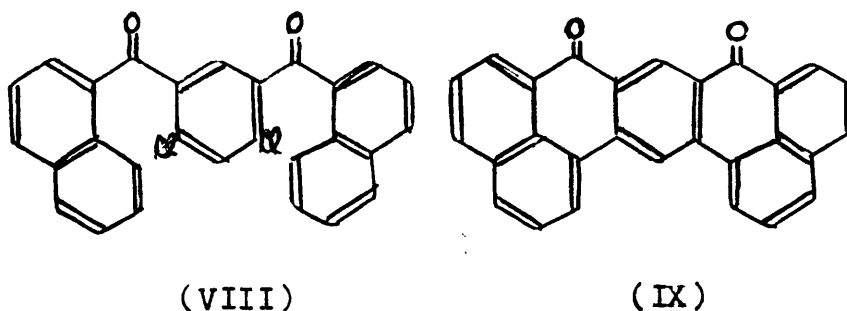
Cyclisation of this diketone to 4:5-7:8-dibenz-pentacene-12:14-quinone (IX) was best achieved by boiling the diketone in quinoline with a slight excess of

solid potassium hydroxide. If solid sodium hydroxide
was used in this cyclisation, the time taken to complete
the reaction increased from eight hours to thirty hours,
with corresponding loss in yield because of some
decomposition brought about by the sustained high temperature.
Again, cyclisation of the diketone (VIII) was brought
about very rapidly in boiling, strong, alcoholic potassium
hydroxide solution, but the resulting quinone (IX) was
very easily split under these extremely alkaline
conditions to give a dicarboxylic acid, which was one of
three possible isomers (X),(XI), or (XII).

(X)   (XI)   (XII)
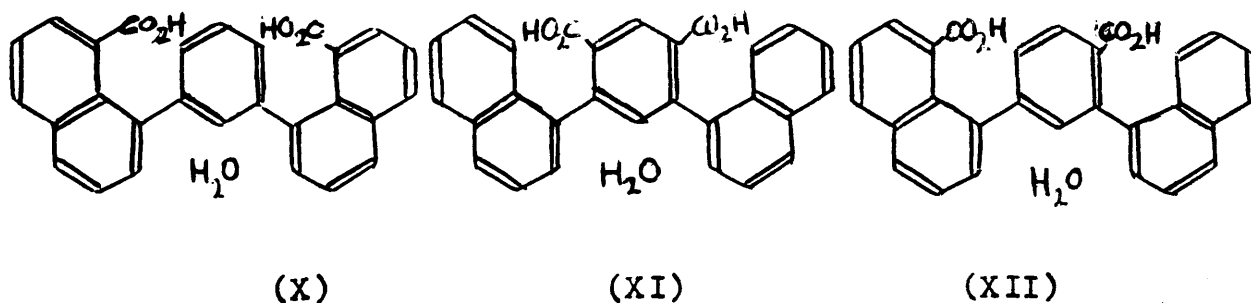
The quinone (IX) did not give a coloured vat on
treatment with alkaline sodium hydrosulphite solution.
This was as expected, since it is impossible to write
a classical formula for the corresponding hydroquinone

of (IX), and thus, by an extension of Clar's prediction[2],
no true vat of the quinone (IX) would exist under the
experimental conditions used to produce a vat.

Some difficulty was experienced in finding a
suitable method for reducing the quinone (IX) to a
hydrocarbon. It was unaffected by the zinc dust fusion
technique of E. Clar[6], and by refluxing in xylene
solution with red phosphorus and constant boiling
hydriodic acid at atmospheric pressure.

However, by treatment with red phosphorus and
hydriodic acid in a sealed tube at 200°, the quinone (IX)
could be reduced (in poor yield) to a hexahydrodibenz-
pentacene (4:5-7:8-dibenz-1:2:3:9:10:11-hexahydropentacene)
(XIII).

(XIII)

(XIV)

(XVI)

(XVII)
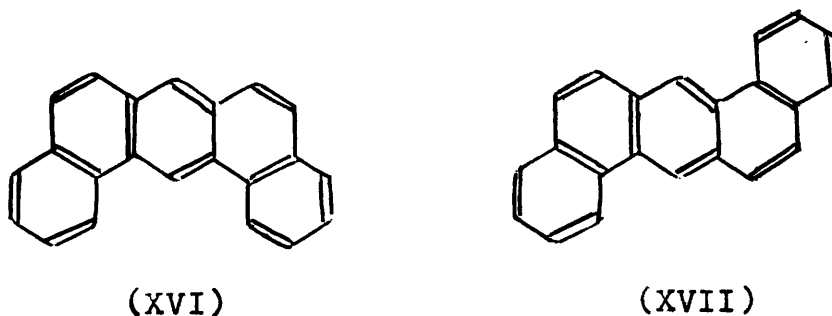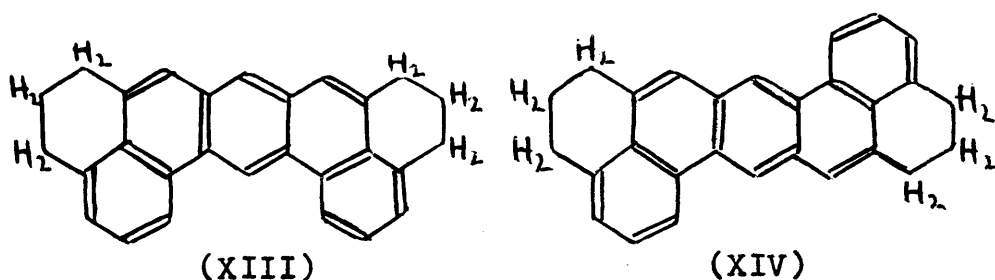
The structure of this hydrocarbon was proved
conclusively by an examination of its ultra-violet
absorption spectrum (page 17). This spectrum is very
similar to that of 1:14-7:8-dibenz-2:3:4:9:10:11-hexa-
hydropentacene (XIV)[7], which similarity is expected
by analogy with the two isomeric dibenzanthracenes (XVI)
and (XVII) whose absorption spectra are also very
similar[8,9]. The structure (XV) for the new hydrocarbon
is excluded, since (XV) would show tetracene-like
absorption bands with absorption taking place well into
the visible region.
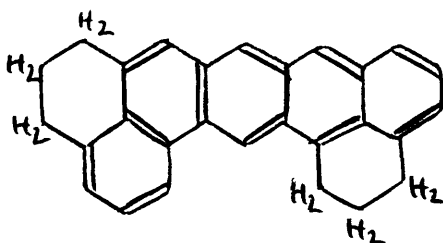
(XV)

The hydrocarbon did not form a maleic anhydride
adduct when it was refluxed in xylene solution with
maleic anhydride nor when it was refluxed in maleic
anhydride alone.

The solution of the hydrocarbon in trichlorobenzene

was not decolourised by refluxing for several hours in the presence of 20% palladised charcoal, this implying that the boiling point of trichlorobenzene (213°) is not sufficiently high to dehydrogenate the hydrocarbon catalytically.

Attempts were then made to prepare 4:5-7:8-dibenz-pentacene (II) from its hexahydro- derivative (XIII) by dehydrogenation on 20% palladised charcoal at 310°. The technique consists of subliming the hydrogenated hydrocarbon through the heated catalyst at reduced pressure (usually around 10^{-3} mm.) and in a stream of carbon dioxide (air-free[10]). The method has been successfully used in the preparation of very sensitive and reactive hydrocarbons like hexacene[11] or 1:2-benzhexacene[12], and was preferred for this reason to chemical methods of dehydrogenation.

Several samples of the hexahydro- derivative (XIII) were sublimed into the catalyst but were adsorbed completely on it, and no substance could be sublimed out of the catalyst even when the temperature was raised to 500°.

The efficiency of the catalyst was proved both before and after each of these experiments by the

dehydrogenation of 9:10-dihydroanthracene to pure anthracene in good yield.

Since a dimer of dibenzpentacene would have sublimed from the catalyst at least in part at the high temperature and low pressure used in the dehydrogenation experiments, it was concluded that complete polymerisation had occured, indicating the intermediate formation of a reactive diradical of the type (II).

This result bears out the findings of Clar and Stewart[1] in their work on triangulene derivatives, and is taken to be further support to the prediction[2] that a hydrocarbon having no Kekulé structure will not exist in a stable form.

-------oOo-------

log ε

200   300   400

wavelength (mμ) ⟶
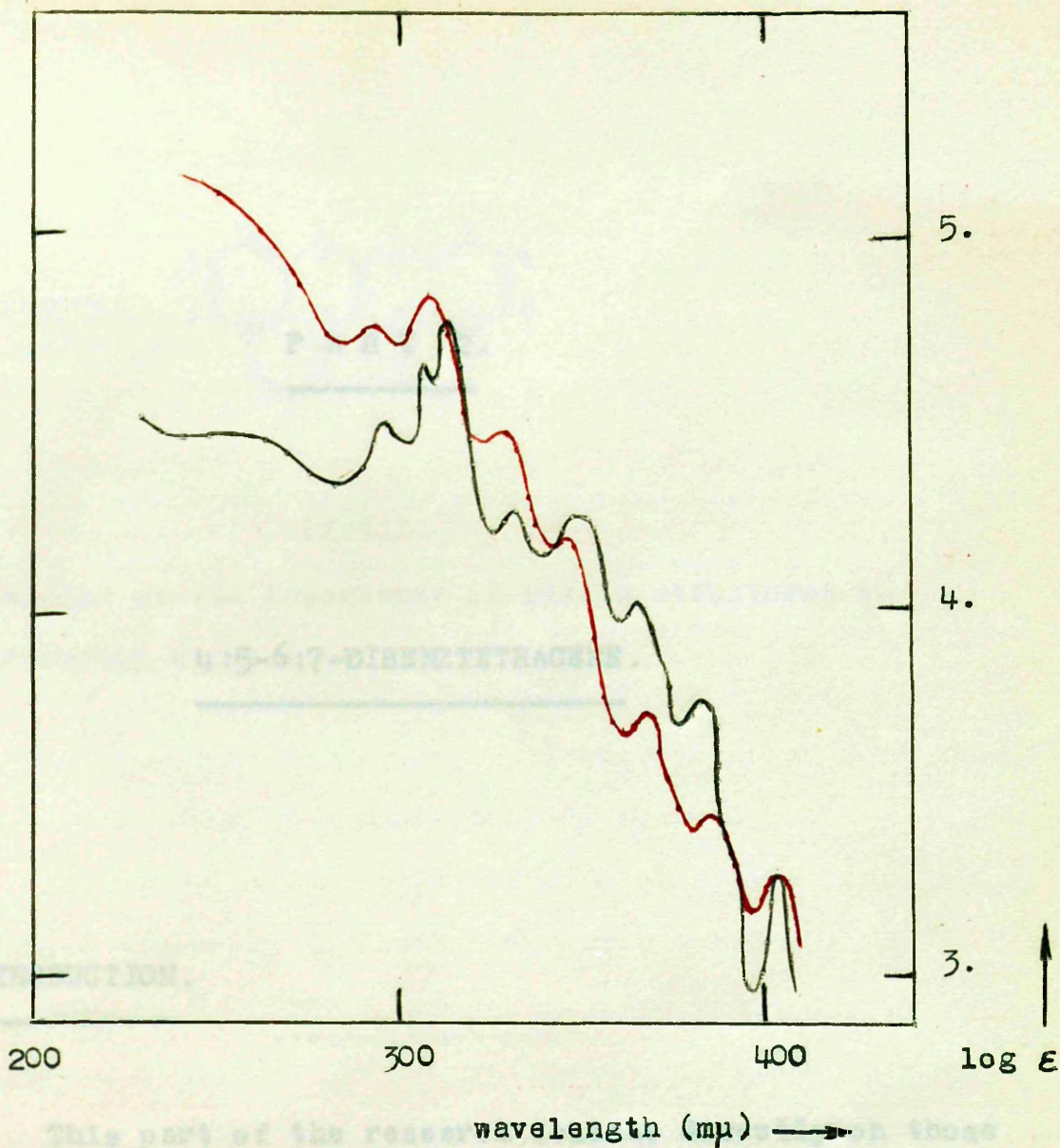
———— 1:14-7:8-dibenz-2:3:4:9:10:11-hexahydropentacene in alcohol.

———— 4:5-7:8-dibenz-1:2:3:9:10:11-hexahydropentacene in alcohol. Bands:- 294, 309, 330, 346, 366, 386, 405.

P A R T 2.

4:5-6:7-DIBENZTETRACENE.

INTRODUCTION.

This part of the research follows directly on those studies described in Part 1. It concerned the attempts to prepare and study the hydrocarbon 4:5-6:7-dibenztetracene which has no Kekulé structure and which, in consequence, was expected to be an unstable diradical, for instance (XVIII).

The object was, as in Part 1, to supplement our
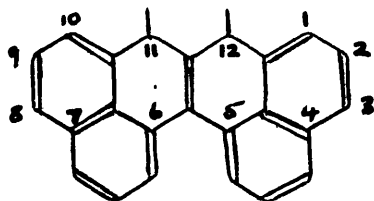
(XVIII)

knowledge on the importance of Kekulé structures to
hydrocarbon stability.

-------oOo-------

DISCUSSION.

The proposed route to hydrogenated derivatives of
4:5-6:7-dibenztetracene fell naturally into three
preparative stages. These were as follows.

The first stage concerned the preparation of the
dicarboxylic acid di-(1-naphthyl)-methylmalonic acid (XXIII)
and of some other compounds derived from it.

The second stage dealt with the attempted cyclisation
of these compounds to derivatives of 4:5-6:7-dibenz-
tetracene (e.g. (XXVI)), while the last stage was the
attempted reduction of the cyclisation products thus
obtained to give hydrogenated derivatives of the
dibenztetracene.

While the first stage was eventually carried out
in fairly good yield, the last two stages gave many
unexpected problems, as a result of which the work was
finally abandoned as being non-specific in its outcome.

Preparation of di-(1-naphthyl)-methylmalonic acid (XXIII).

Using the method of Schmidlin and Massini[13],
di-(1-naphthyl)-chloromethane (XX) was prepared from
1-bromonaphthalene, via 1-naphthylmagnesium bromide and
di-(1-naphthyl)-carbinol (XIX):-

2 [structure: naphthyl-MgBr] + HCO₂Et ⟶ [structure: di-(1-naphthyl)-carbinol with OH]

(XIX)

HCl gas ⟶ [structure: di-(1-naphthyl)-chloromethane with Cl] (XX) + EtOMg.CH(CO₂Et)(CO₂Et) (XXI) ⟶ [structure: dicarboxylic ester] (XXII)
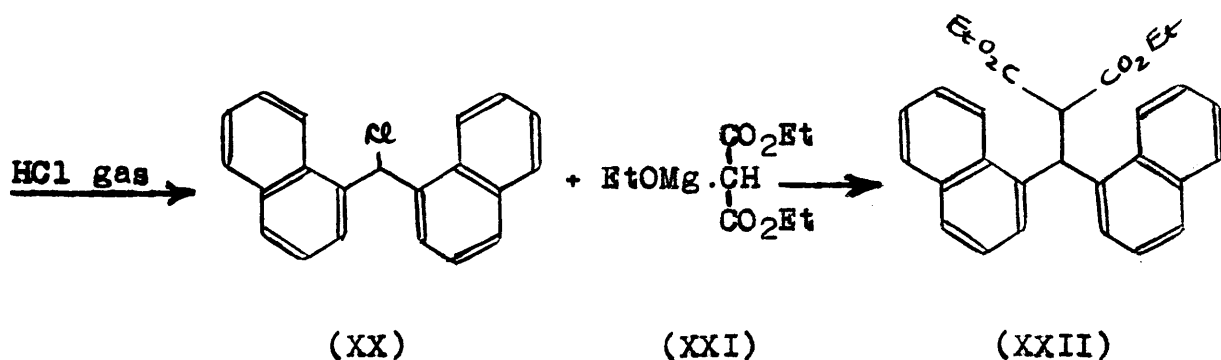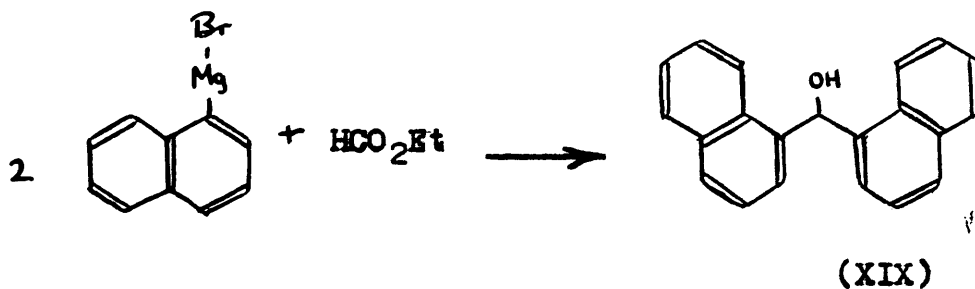
Magnesio-malonic ester (XXI) was prepared[14] and
condensed with di-(1-naphthyl)-chloromethane in benzene
solution to give the dicarboxylic ester (XXII). This was

saponified in alcoholic potassium hydroxide solution
to produce di-(1-naphthyl)-methylmalonic acid (XXIII).
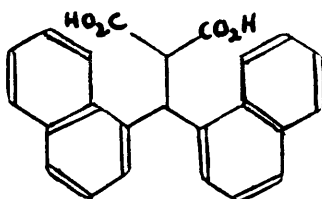
(XXIII)

This dicarboxylic acid was the main starting material
in the attempted synthesis of 4:5-6:7-dibenztetracene.
The overall yield of acid from bromonaphthalene was
84% of theoretical.

Two other compounds were utilised in the attempted
synthesis, though to a much less extent than the
dicarboxylic acid. The first of these was the acid chloride
(XXIV), derived from the acid (XXIII) by the action of
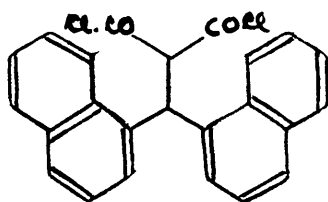
(XXIV)
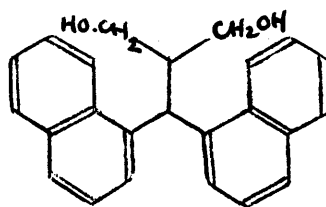
(XXV)

thionyl chloride. The second was the dihydric alcohol (XXV) which was obtained by reduction of the acid (XXIII) with lithium aluminium hydride in ether solution.

Cyclisations and Reductions.

Three main products are theoretically possible from the intramolecular ring-closure and oxidation of the dicarboxylic acid (XXIII), depending on the positions attacked in the naphthalene nuclei by the two carboxyl groups. These three products are (XXVI), (XXVII), and (XXVIII). However, it was expected that ring-closure
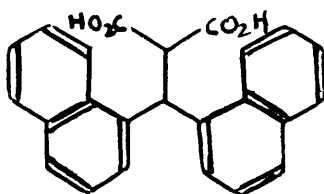
(XXIII)
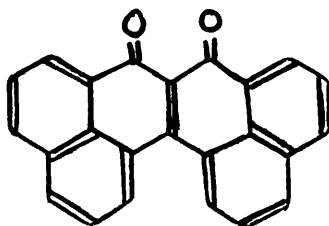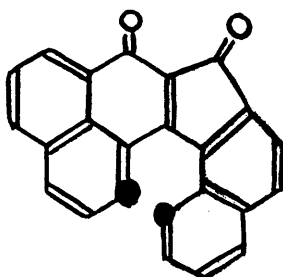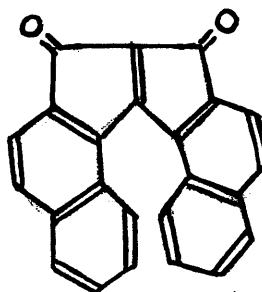
(XXVI)   (XXVII)   (XXVIII)

to the indenone (XXVII), containing one five-membered
ring, would be energetically less favourable than ring-
closure to the required quinone (4:5-6:7-dibenztetracene-
11:12-quinone) (XXVI), because of the possibility of
steric interference between the hydrogen atoms marked
with dots in the formula (XXVII). The other possibility,
the "double indenone" (XXVIII), containing two five-
membered rings, is almost certainly excluded for this
same reason.

A variety of attempts were made to cyclise the
dicarboxylic acid and its derivatives; a number of
different products were obtained and studied, some of
which were identified as arising from decomposition of
starting materials.

Concentrated sulphuric acid dissolved the
dicarboxylic acid (XXIII) to give a green solution, which
on heating changed through yellow (at ca. 80°) to red-
brown (at ca. 100°), these colour changes probably being
due to successive ring-closures taking place, although
sulphonation may also take place simultaneously, since
neither dilution nor neutralisation of the sulphuric acid
solution made it possible to isolate anything of value
from this reaction.

The dicarboxylic acid was unaffected by polyphosphoric acid at fairly low temperature (80°) nor by standing in liquid hydrogen fluoride at atmospheric temperature, since the unchanged dicarboxylic acid could be recovered in each case. With polyphosphoric acid at higher temperatures, however, (170°), the extent of decomposition of the dicarboxylic acid was judged by the pronounced odour of naphthalene subliming from the reaction mixture, and by the fact that perinaphthenone (XXIX) was

(XXIII)

(XXIX)

(XXX)

(XXXI)

$+CO_2$
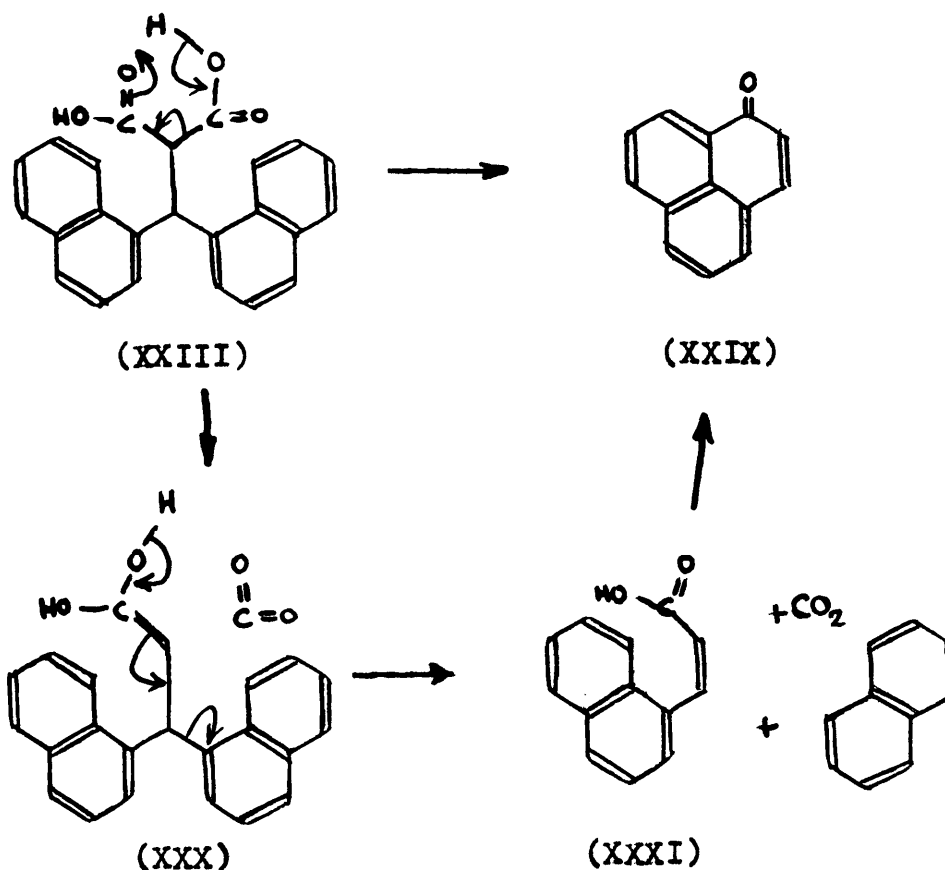
isolated after the reaction.

Decomposition of the dicarboxylic acid to naphthalene and perinaphthenone can be easily explained by the initial thermal decarboxylation of the dicarboxylic acid (XXIII) via the intermediate (XXX), followed by elimination of naphthalene to give (XXXI). This acid (XXXI) would then cyclise to perinaphthenone (XXIX).

The decarboxylation ((XXIII) ⟶ (XXX)) no doubt takes place by the cyclic mechanism shown: the elimination reaction ((XXX) ⟶ (XXXI)) is also postulated as following an established mechanism.

Perinaphthenone was also isolated after treatment of the dicarboxylic acid chloride (XXIV) with anhydrous aluminium chloride in benzene solution. (In nitrobenzene solution this reaction led only to material of high molecular weight, insoluble in xylene, and only sparingly soluble in nitrobenzene).

When the dihydric alcohol (XXV) was treated with polyphosphoric acid, decomposition (with generation of naphthalene) was again observed, together with the production of polymeric material from the intermolecular condensation of the alcohol. Even with the relatively mild reagent liquid hydrogen fluoride, this alcohol

split, yielding naphthalene and a substance which
probably had the structure (XXXIII).

(XXV)   (XXXII)
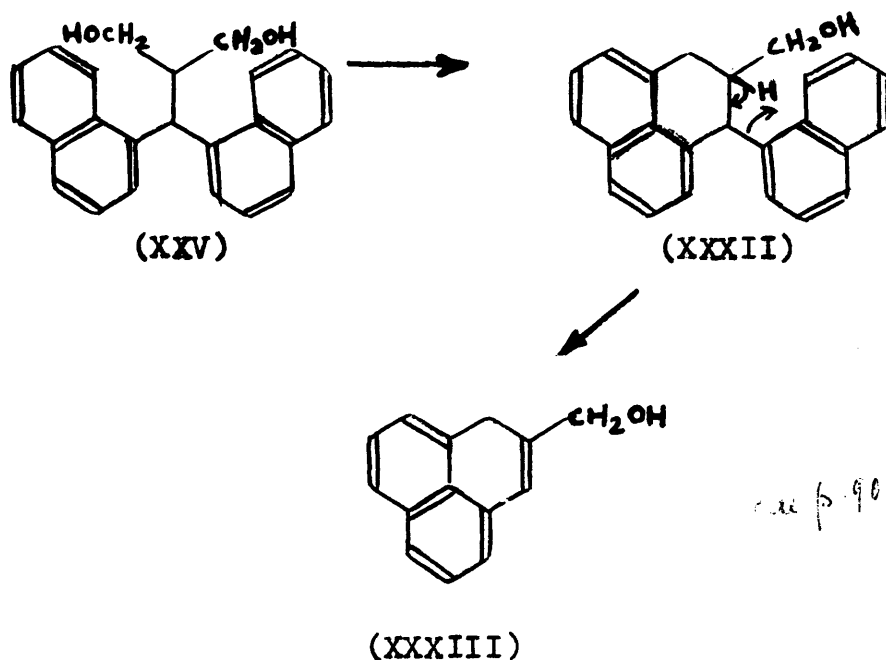
(XXXIII)

The mechanism of the reactions leading to
naphthalene and (XXXIII) would no doubt be as indicated
above. The half-cyclised alcohol (XXXII) was not
isolated, but must certainly have been an intermediate
in the reaction sequence.

When the dicarboxylic acid (XXIII) was heated for a
short time in an aluminium chloride - sodium chloride
(5:1) melt, the reaction product was almost completely

insoluble in benzene. The black, insoluble residue was
judged to be decomposition products, while the benzene
soluble fraction was chromatographed on alumina, but
yielded nothing of value.

The aluminium chloride - sodium chloride melt was
repeated on the dicarboxylic acid, but using an
equimolecular mixture of the two reagents. Using this
less vigorous melt, there was again produced a large
quantity of decomposition products, but there was also
produced a small amount of benzene soluble material which
was chromatographed on alumina; its behaviour on
chromatography indicated that it might have been a
hydrocarbon. To take advantage of this most unusual
result, the fusion was repeated with the addition of
a small amount of zinc dust. This latter was added to try
to increase the degree to which simultaneous ring-closure
and reduction had taken place. Again there was a great
deal of decomposition, and a very small amount of
non-crystallisable, benzene soluble substance produced.
Although this substance appeared to be a hydrocarbon, it
was not found possible, even on rechromatography, to
purify it sufficiently to enable any investigation of its
structure to be carried out. The amount obtained (impure)

was no more than a few milligrams.

In another attempt to obtain simultaneous cyclisation and reduction, the dicarboxylic acid (XXIII) was treated with red phosphorus and hydriodic acid in a sealed tube at 200°. Again, there was considerable darkening and decomposition to naphthalene, but it was possible to isolate a small amount of oil which was almost certainly a mixture of hydrocarbons, but which could not be induced to crystallise. The crude oil was dehydrogenated with 20% palladised charcoal at 200° (atmospheric pressure) and gave up approximately three moles of hydrogen. By subliming the residue out of the catalyst, a second hydrocarbon was obtained whose absorption bands in benzene solution were at 444 and 416 mμ. These bands are very close to the characteristic absorption bands of peropyrene (XXXIV) (443·5 and 415·5 mμ in benzene[15]) and on this basis we could say that the dehydrogenated material did, in fact, contain some of this hydrocarbon.

It is fairly easy to explain the production of a peropyrene derivative in this reaction. The dicarboxylic acid (XXIII) is firstly decomposed to perinaphthenone (see pages 24, 25) which undergoes reductive dimerisation to peropyrene (XXXIV) (Clar[15]) and subsequent

over-reduction to its hydrogenated derivative (for example(XXXV)).

(XXXIV)   (XXXV)
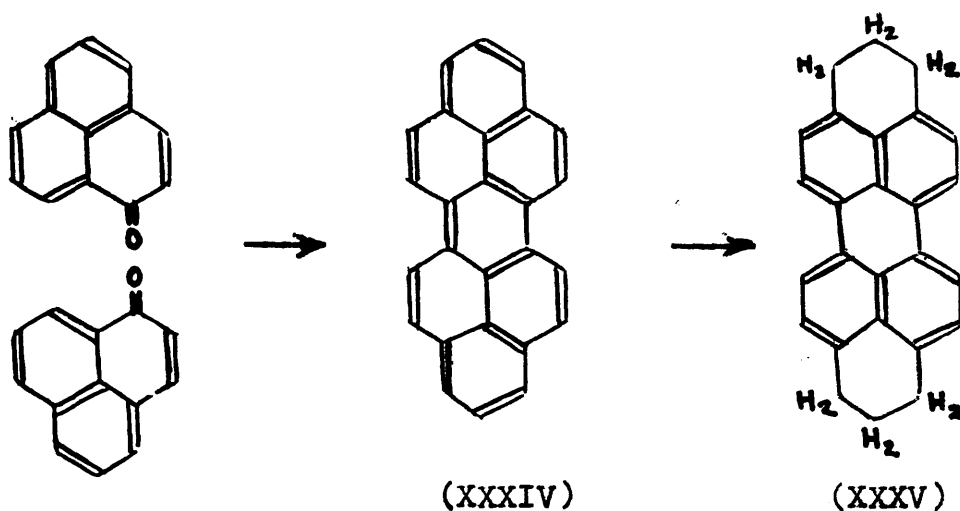
Up till now, we have only discussed those reactions which have led to more or less complete decomposition of starting materials. We will now discuss three different cyclisation products, two of which offered interesting prospects and were therefore investigated to some extent.

1.   By the action of benzoyl chloride and a small
amount of concentrated sulphuric acid on the dicarboxylic
acid (XXIII) there was produced, together with
considerable decomposition, an interesting cyclisation
product, which was not characterised. The crude product
was reduced by the zinc dust fusion method of E. Clar[6]
and by repeated chromatography on alumina, there was
obtained a bright yellow hydrocarbon, $C_{24}H_{16}$. (The
molecular formula of 4:5-6:7-dibenz-11:12-dihydrotetracene
(XXXVI) is also $C_{24}H_{16}$).
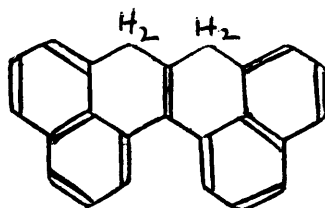
(XXXVI)

Surprisingly, this hydrocarbon was identical with a
hydrocarbon obtained later, in those studies reported in
Part 3 of this Thesis. The hydrocarbon is therefore
discussed fully in Part 3 (page 40), where evidence is also
given from which it was concluded that this hydrocarbon
$C_{24}H_{16}$ was not 4:5-6:7-dibenz-11:12-dihydrotetracene.

2.   The most promising ring-closure method used was to treat a solution of the dicarboxylic acid (XXIII) in dry nitrobenzene with phosphorus pentoxide at 130°. This yielded a very basic material $C_{24}H_{12}O_2$, giving a red-violet solution both in concentrated sulphuric acid and concentrated hydrochloric acid. This great basicity (solubility in concentrated hydrochloric acid) was an expected property of the required 4:5-6:7-dibenztetracene-11:12-quinone (XXVI) by analogy with _meso_-benzanthrone (XXIX), which is slightly basic and soluble in concentrated hydrochloric acid.
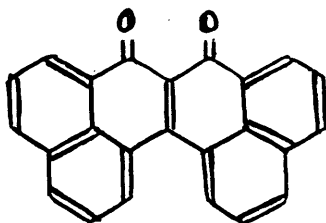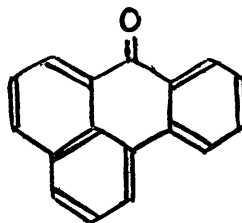
(XXVI)   (XXIX)

The product $C_{24}H_{12}O_2$ (isomeric with the required dibenztetracene-quinone) was not very stable, and decomposed considerably on sublimation and on chromatography on alumina.

It could not be satisfactorily reduced by the zinc

dust fusion technique[6], nor by refluxing for twenty
hours with red phosphorus and hydriodic acid.

When treated with red phosphorus and hydriodic acid
in a sealed tube at 200°, and the resulting dark solid
extracted with benzene and chromatographed on alumina,
there was obtained a small amount of colourless solid,
probably highly hydrogenated hydrocarbon. This solid,
however, failed to sublime at 350° and 10^{-2} mm. pressure,
and cannot therefore have had a molecular weight of the
order 300 (the approximate molecular weight of a
hydrocarbon of the dibenztetracene series). It is
possible, from this, to say that it may have been
polymeric material.

3.   It was found that using phosphorus pentoxide in
nitrobenzene solution to cyclise the dicarboxylic acid (XXIII)
sometimes yielded an isomer of the product obtained in
2, above ($C_{24}H_{12}O_2$) but which was not soluble in
concentrated hydrochloric acid, and gave a green solution
in concentrated sulphuric acid. The experimental
details of the experiments leading to these totally
different isomers were, to all observation, alike in all
details.

It was not found possible to characterise this new isomer, partly because its preparation was beyond prediction, and thus the amount of material available was small.

General Survey of the Attempted Synthesis.

The dicarboxylic acid (XXIII), being a substituted malonic acid, was readily decarboxylated, and in particular, did so under most of the conditions necessary to produce normal ring-closure, and to an extent beyond that expected.

Where cyclisation did occur, it did not proceed in one specific direction (to the dibenztetracene-quinone (XXVI)) but rather led to at least three different products, only one of which had the expected properties of the quinone (XXVI). This compound, however, was not very stable, and could not be reduced conveniently to a hydrogenated derivative of 4:5-6:7-dibenztetracene.

For these reasons, bearing in mind that the primary object of the attempted synthesis was to study a hydrocarbon having no Kekulé structure, this synthesis was abandoned in favour of the attempted synthesis of

4:5-7:8-dibenzpentacene (which also has no Kekulé
structure). This work has already been described in
Part 1 of this Thesis.

-------oOo-------

P A R T   3.

THE GREEN HYDROCARBON $C_{24}H_{14}$.

INTRODUCTION.

Under certain conditions, fumaryl chloride (XL)
condenses with naphthalene in the presence of anhydrous
aluminium chloride to yield a dark brown condensation
product which can be reduced to a bright yellow
hydrocarbon $C_{24}H_{16}$. Dehydrogenation of this gives a
green hydrocarbon $C_{24}H_{14}$ of unusually high basicity,

which gives a salt with even the weak acid, acetic acid[16].

After lengthy studies of this extraordinary and highly interesting hydrocarbon[16, 17], it was assigned the structure 4:5-10:11-dibenztetracene (XLI) or, for convenience, zethrene (from its Z-like arrangement of aromatic units).
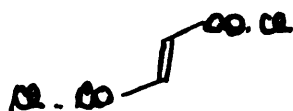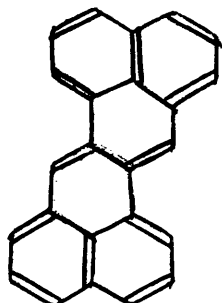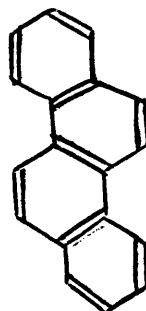
(XL)   (XLI)   (XLII)

In order to verify the assignment of this formula, however, Clar, Lang, and Schultz-Kiesow[18] recently prepared the hydrocarbon zethrene (XLI) from chrysene (XLII) by a less ambiguous synthesis than the original, and found it to be a red hydrocarbon, not unusually basic, and certainly not identical in any way with the above mentioned green hydrocarbon. It then became necessary to assign a new structure to the green hydrocarbon, and this was the chief object of the work described in the following pages.

The problem was attacked in two main ways.

Firstly, most of the original work was repeated and reviewed (in some instances leading to different conclusions) and the products obtained by the original workers were submitted to further studies and analyses. From this it was possible to propose a new formula for the green hydrocarbon. The new formula satisfies all the main demands of the experimental evidence.

Secondly, some preliminary attempts were made to prepare the green hydrocarbon (assuming it to have the new structure proposed) by a less ambiguous route than the original.

-------oOo-------

DISCUSSION.

Depending on the reaction temperature, fumaryl chloride (XL) condenses with naphthalene in the presence of anhydrous aluminium chloride to give two different products. The original work on these two compounds[16, 17] led to their both being assigned structures related to zethrene (XLI).

(a) Low Temperature Condensation.

Previous Work.

If the reaction between fumaryl chloride and naphthalene is carried out at around 0°, 1:2-di-(1-naphthoyl)-ethylene (XLIII) is produced, which adds bromine to give 1:2-dibromo-1:2-di-(1-naphthoyl)-ethane (XLIV)[16]. Ring-closure of this dibromo- compound by short treatment in an aluminium chloride - sodium chloride (5:1) melt yields a product which can be extracted with alkaline sodium

hydrosulphite solution as its deep blue vat. On
oxidation of the vat with air, the resulting substance is
isomeric with zethrene-quinone (XLV), and was in fact
assigned this structure[16].
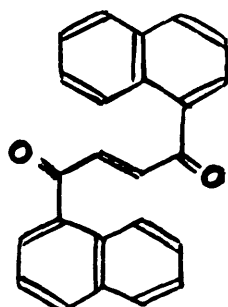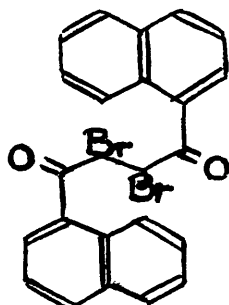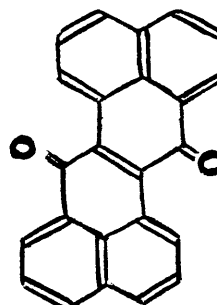
(XLIII)   (XLIV)   (XLV)

Recent Studies.

The above work was repeated and verified, the only
alteration being an improvement brought about in the
yield in the aluminium chloride - sodium chloride melt,
by using an equimolecular mixture of the two chlorides
instead of the ratio 5:1.

The ring-closure product obtained from this melt
was submitted to Clar's zinc dust fusion technique[6] and
this gave a hydrocarbon $C_{24}H_{16}$ isomeric with dihydro-
zethrene (XLVI) and with the yellow hydrocarbon mentioned
in the introduction (page 36). It was distinct from these
last two, but was identical with the hydrocarbon $C_{24}H_{16}$

obtained in the attempted synthesis of 4:5-6:7-dibenz-
tetracene (page 30) from the dicarboxylic acid (XXIII).
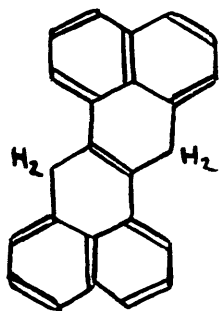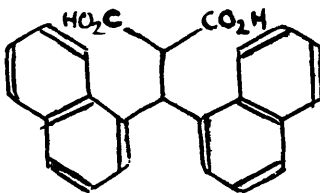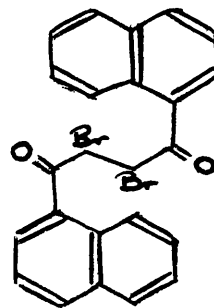
(XLVI)   (XXIII)   (XLIV)

In order that the dibromo- compound (XLIV) and the
dicarboxylic acid (XXIII) should lead to the same
hydrocarbon, rearrangement must take place during the
cyclisation of one or the other, or both. The medium
used to cyclise the dicarboxylic acid (benzoyl chloride -
sulphuric acid) would seem less likely to induce
migration than that used to cyclise the dibromo-
compound (aluminium chloride - sodium chloride melt).

The new hydrocarbon $C_{24}H_{16}$ was dehydrogenated
over palladised charcoal, and did not give the red
zethrene of Clar, Lang, and Schultz-Kiesow,[18] and hence
cyclisation of the dibromo- compound (XLIV) did not lead
to the quinone (XLV) as previously reported.
Dehydrogenation gave a new green hydrocarbon (not obtained

pure) whose absorption spectrum (page 44) was not typical of polycyclic aromatic hydrocarbons containing only six-membered rings. This dehydrogenation also established that the new hydrocarbon $C_{24}H_{16}$ was not related to the <u>basic</u> green hydrocarbon. (See introduction, page 36, and (b), page 45).

It is highly unlikely that the hydrocarbon $C_{24}H_{16}$ was 4:5-6:7-dibenz-11:12-dihydrotetracene (XXXVI) which,
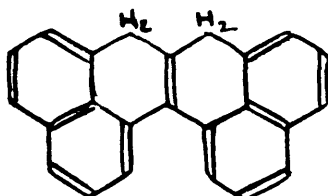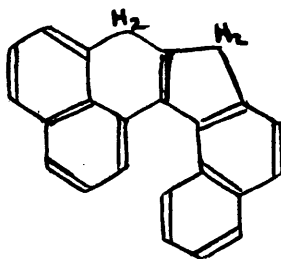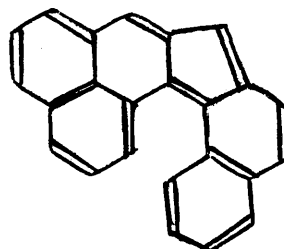
   (XXXVI)   (XLVII)   (XLVIII)

in any case, would be expected to dehydrogenate to an unstable diradical (page 18).

It is possible that this new hydrocarbon may have had the structure (XLVII); this formula is certainly not precluded by its absorption spectrum (page 43) which is similar to the dinaphthylethylene type. The dehydrogenation product would then be (XLVIII).

No conclusive proof of these formulae has been found.
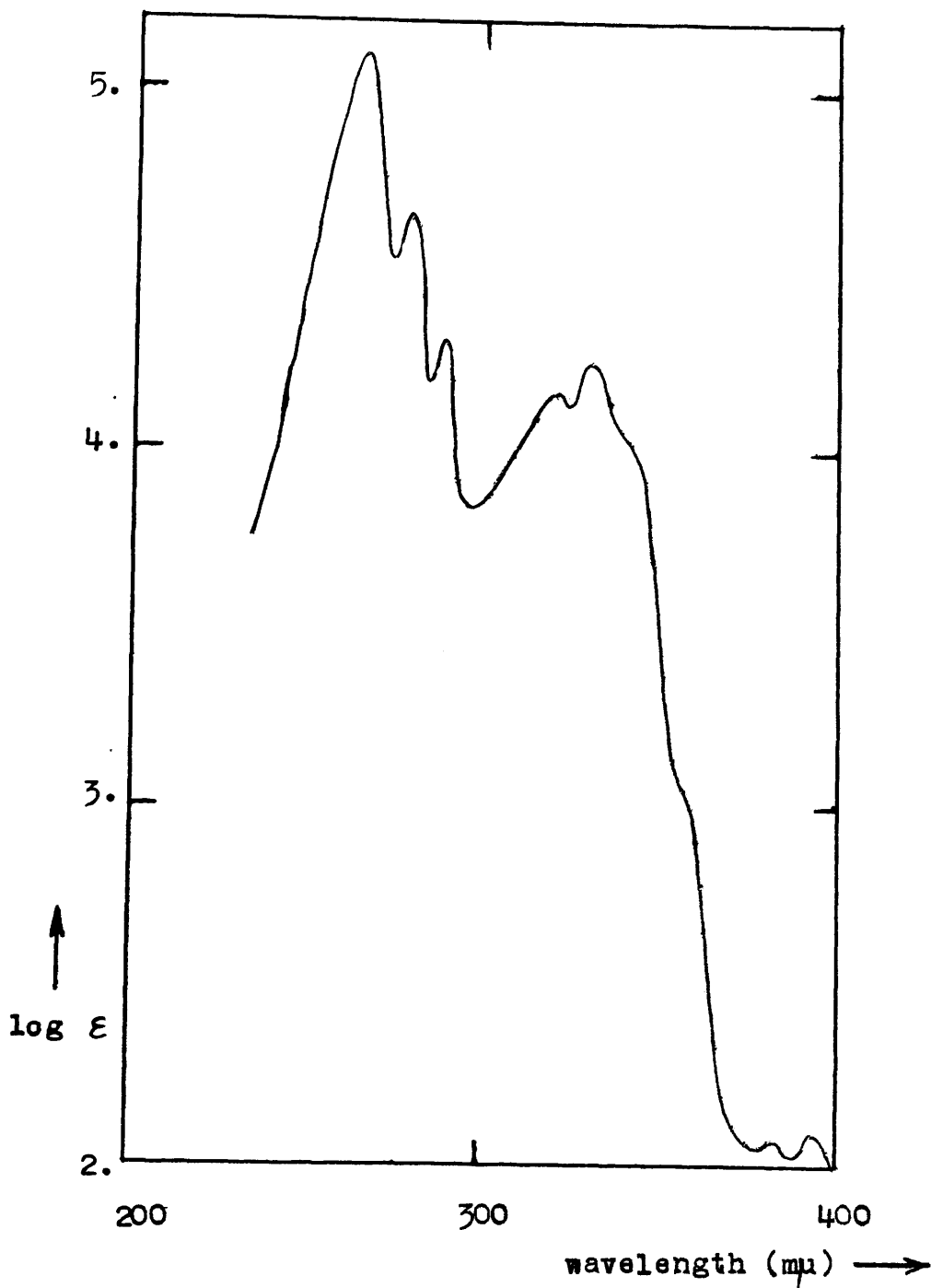
$C_{24}H_{16}$ (structure indefinite), in alcohol.

Bands:- 265, 279, 288, 320, 330, 342, (383, 393).
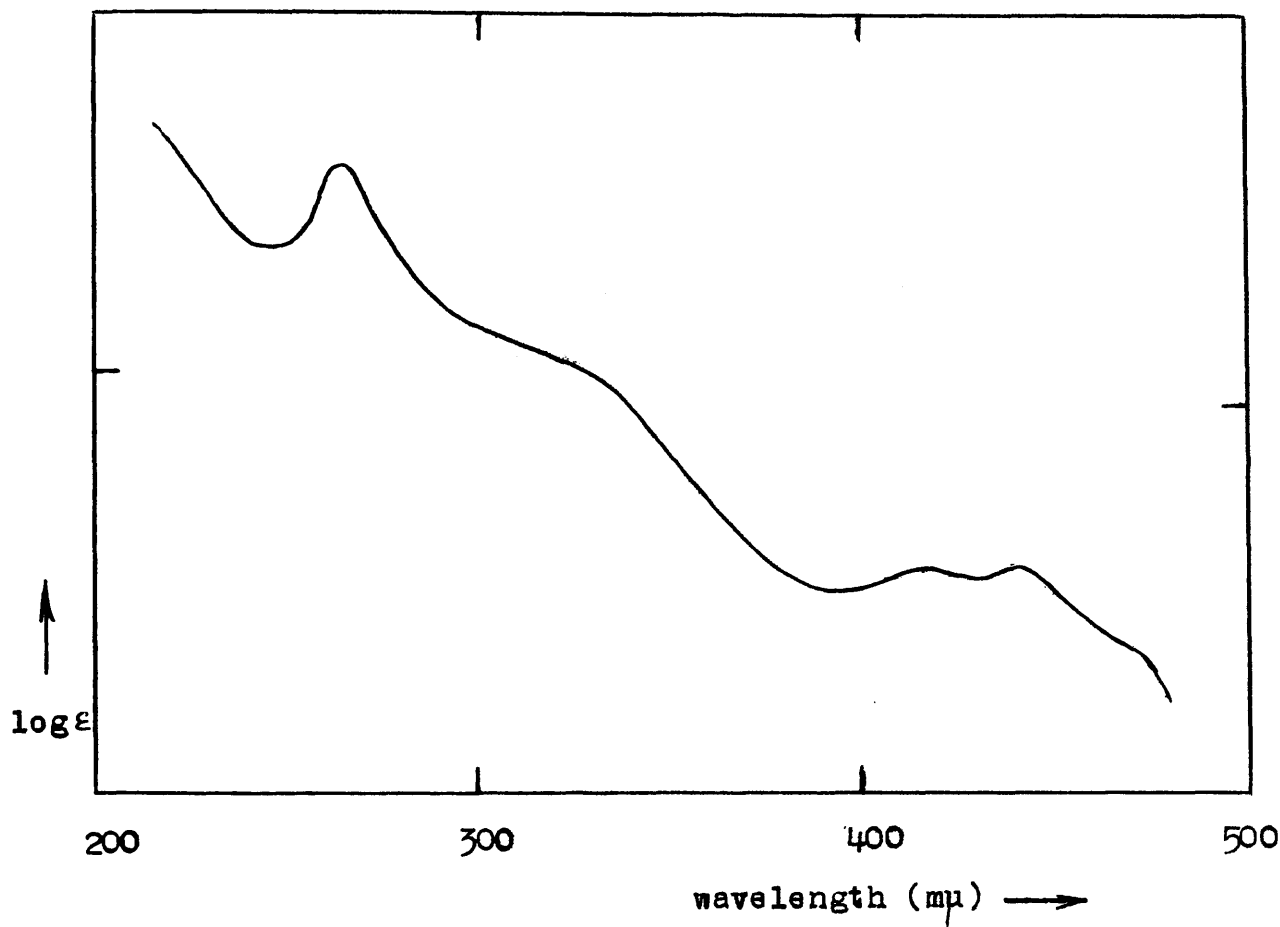
Product of <u>dehydrogenation of $C_{24}H_{16}$ (unknown ε)</u> in alcohol. Bands:- 265, 416, 440.

(b)   Condensation at ca. 80°

Previous Work.

When no temperature control is applied, fumaryl
chloride condenses with naphthalene in the presence of
anhydrous aluminium chloride to give an approximately
5% yield of a brown condensation product, to which
was assigned the structure (IL)[16]. This, on reduction
by Clar's zinc dust fusion technique[6] leads to a bright
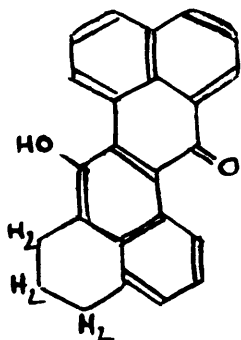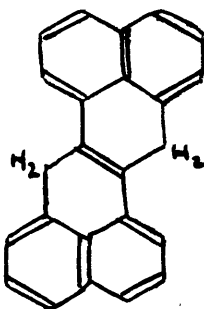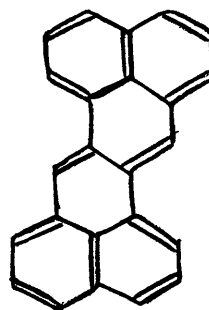
(IL)   (XLVI)   (XLI)

yellow hydrocarbon $C_{24}H_{16}$ (assigned the formula (XLVI))[16]
which can be dehydrogenated over palladised charcoal to
the basic green hydrocarbon $C_{24}H_{14}$ (assigned the structure
zethrene (XLI)[16]) the main subject of these studies.

The chief support for the structure (XLI) (apart
from the method of preparation) came from two sources,

one theoretical, the other experimental:-

Zethrene, as written in the formula (XLI) has nine Kekulé structures, all of which involve the two conjugated double-bonds in the central region of the molecule. It was postulated[16] that the unusual properties of the hydrocarbon thought to be zethrene (basicity etc.) were best explained by the molecule (XLI) existing in classical equilibrium with the molecule (L), in which two π-electrons are localised in the positions of the dots (formula (L)) and the remainder of the molecule existing as an 8-shaped <u>aromatic</u> system. The basicity

  (XLI)   (L)   (LI)
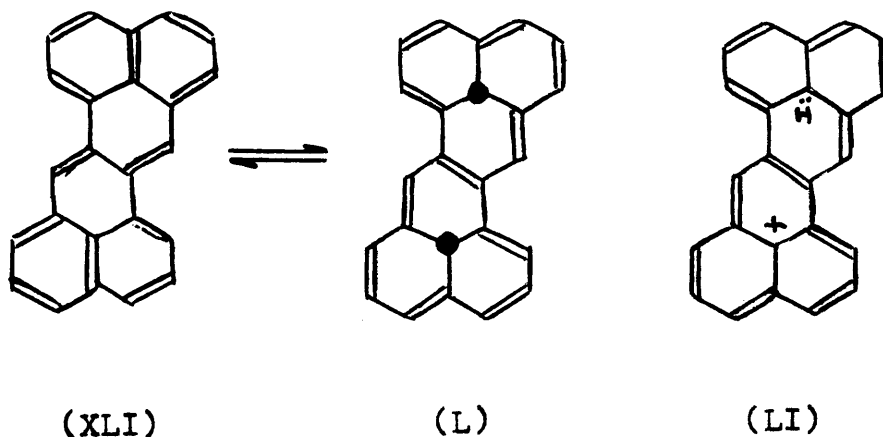
of the hydrocarbon could then be explained by the easy formation, in acid solutions, of the cation (LI).

The second chief piece of evidence derived from the

further reduction of the dihydro- derivative $(C_{24}H_{16})$
with red phosphorus and hydriodic acid at atmospheric
pressure. This was reported to yield a hexahydrozethrene
$C_{24}H_{20}$, to which was ascribed the structure (LII)[17]. It
can be seen that the hydrocarbon having this structure
would have an absorption spectrum very similar to that
of chrysene (XLII), and this was, in fact, the case with
the newly found hydrocarbon $C_{24}H_{20}$, this being taken,
therefore to support the zethrene structure.
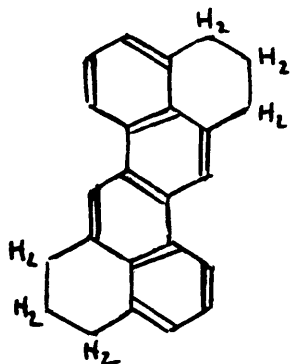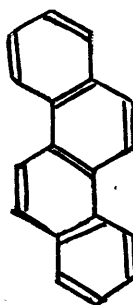
(LII)   (XLII)

Recent Studies.

The condensation of fumaryl chloride with naphthalene
was repeated, with little change from the original method.

The condensation product thus obtained was insoluble
in most organic solvents, but it could be recrystallised

(always with some decomposition) from 1:2:4-trichloro-benzene, when analysis gave the molecular formula $C_{24}H_{14}O_2$. A diacetyl derivative was formed ($C_{28}H_{18}O_4$) by dissolving the condensation product in boiling glacial acetic acid.

The most important experimental evidence concerning the structure of these compounds was derived from the reduction of the condensation product with red phosphorus and hydriodic acid in a sealed tube at 200°. From this reduction there was obtained a mixture of two hydrocarbons, $C_{24}H_{22}$ and $C_{24}H_{26}$. Each of these could be dehydrogenated over palladised charcoal to the basic green hydrocarbon, thus establishing their inter-relation. The hydrocarbon $C_{24}H_{22}$ was therefore an octahydro-derivative, and $C_{24}H_{26}$ was a dodecahydro- derivative.

Stewart[17] reported the formation of a hexahydro-derivative (page 47), and the properties of his hexahydro-and the new octahydro- derivative are compared in Table 1. It can be seen that they are without doubt the same hydrocarbon. (Stewart reports the results of only one micro-analysis of his hydrocarbon). The absorption spectrum of the octahydro- derivative is compared with that of chrysene on page 50, and the similarity between the

T A B L E 1.

	Stewart's $C_{24}H_{20}$	Octahydro- $C_{24}H_{22}$
Melting Point (uncorrected)	205-206°	208°
Colour in concentrated sulphuric acid	Violet, orange fluorescence.	Violet, becoming red-violet, red fluorescence.
Absorption Maxima (mμ) (in alcohol)	372,(361·5),354 (344), 335, 313, 300·5,(289),277, 267, 259	372, 354, 333, 313, 301, 276, 267, 223.
C and H (%) Found.	93·3; 6·9	1st:92·81; 7·26 2nd:93·08; 7.00
Calctd.	for $C_{24}H_{20}$ 93·5; 6·5	for $C_{24}H_{22}$ 92.85; 7·15
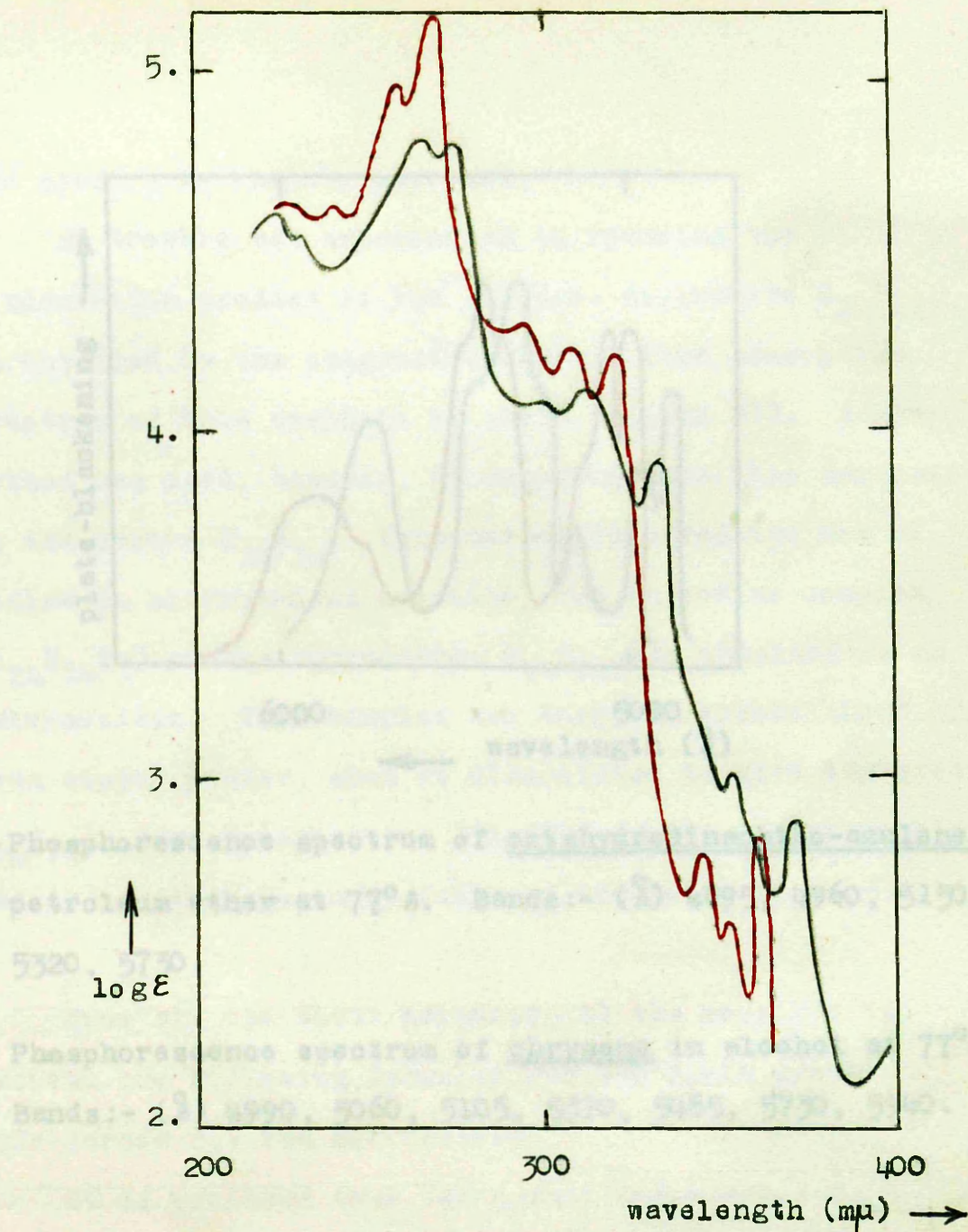
Chrysene in dioxan.

Octahydrodinaphtho-azulene in alcohol.

Bands:- 223, 266.5, 276, 301, 313, 333, 354, 372.
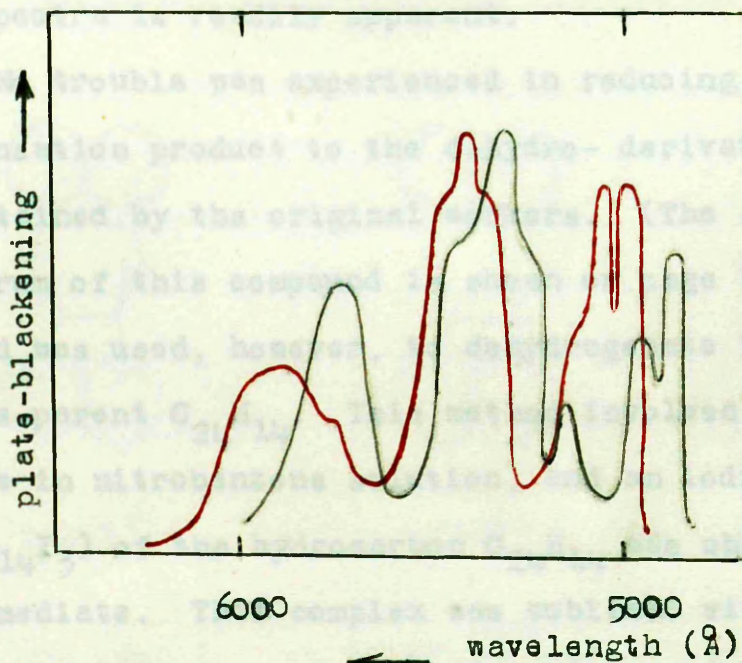
——— Phosphorescence spectrum of <u>octahydrodinaphtho-azulene</u> in petroleum ether at 77°A. Bands:- (Å) 4895, 4960, 5150, 5320, 5730.

——— Phosphorescence spectrum of <u>chrysene</u> in alcohol at 77°A. Bands:- (Å) 4990, 5060, 5105, 5370, 5485, 5730, 5940.

two spectra is readily apparent.

No trouble was experienced in reducing the condensation product to the dihydro- derivative $C_{24}H_{16}$ as obtained by the original workers. (The absorption spectrum of this compound is shown on page 67). A new method was used, however, to dehydrogenate this derivative to the parent $C_{24}H_{14}$. This method involved the use of iodine in nitrobenzene solution, and an iodine complex $(C_{24}H_{14}I_3)$ of the hydrocarbon $C_{24}H_{14}$ was obtained as an intermediate. This complex was sublimed either alone or from copper powder, when it dissociated to give the green $C_{24}H_{14}$. Some interest was attached to the iodine complex, and it is discussed more fully in the Notes (page 61).

From all the above evidence, it was possible to propose the following formulae for the basic green hydrocarbon and its derivatives.

It is proposed that the parent hydrocarbon $C_{24}H_{14}$ was a dinaphtho-azulene, 1:3-5:7-(1':8'-1":8"-)-dinaphtho-azulene (LIII). Its dihydro- derivative $C_{24}H_{16}$ was (LIV), the condensation product (LV), and the diacetyl condensation product (LVI). The properties of the octahydro- derivative $C_{24}H_{22}$ were best explained by the formula (LVII), and thus

the dodecahydro- derivative was (LVIII).
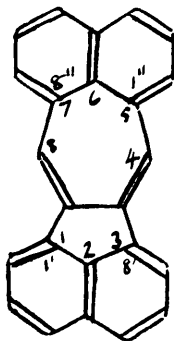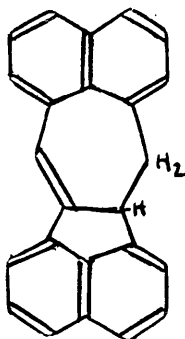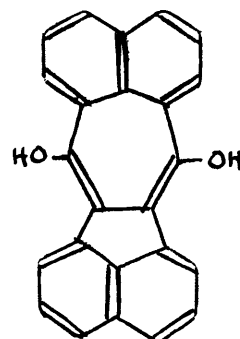
(LIII)   (LIV)   (LV)
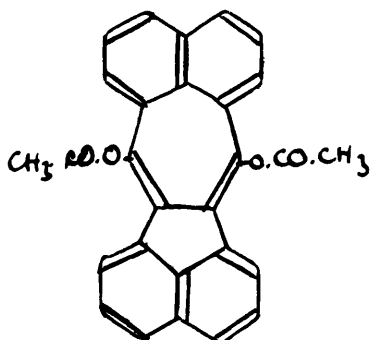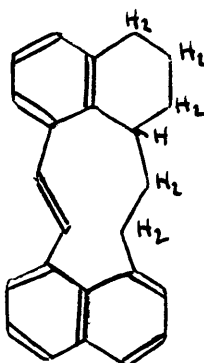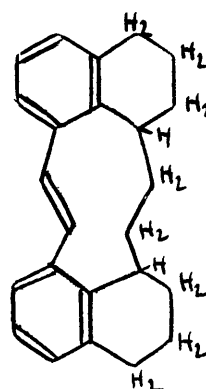
(LVI)   (LVII)   (LVIII)

Supporting Evidence.

From the behaviour of the dinaphtho-azulene derivatives on chromatography and sublimation, there is no possible doubt that they contain 24 carbon atoms, and not 12 or 48.

Considering the mode of formation of these derivatives, (from fumaryl chloride and naphthalene) it is reasonable to assume that the molecule is made up of two naphthalene molecules, with the four carbon atoms of the fumaryl chloride residue arranged between these two. The various feasible ways in which this can be done would lead to the following hydrocarbons:- (a), (b), (c), (d), and (LIII).
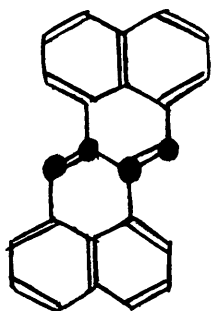
(a)
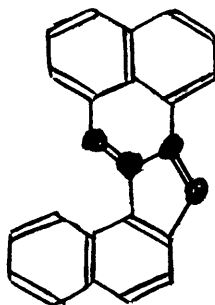
(b)
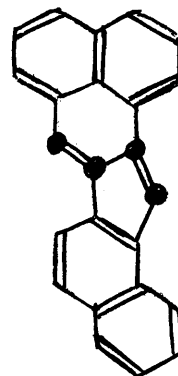
(c)
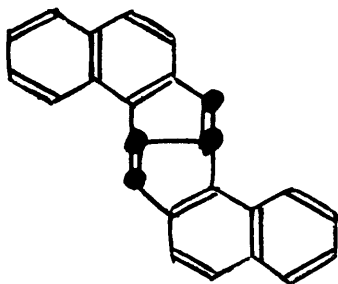
(d)
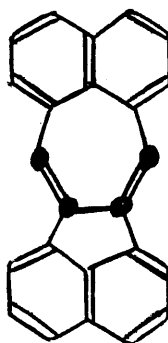
(LIII)
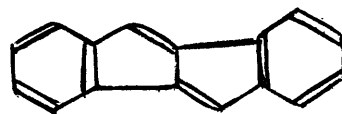
(e)

Of these, (a) is known (zethrene)[18]. The
hydrocarbons (b) and (c) would not show the unusual pro-
perties exhibited by the basic green hydrocarbon. The
dinaphthopentalene (d) would not differ greatly from the
dibenzpentalene (e), whose properties are quite different
from those of the basic green hydrocarbon[19]. By
elimination, then, the structure (LIII) would seem
correct, and this can be explained and supported in
several points.

Formation.

The mode of formation of an azulene structure in
the condensation reaction must be that the fumaryl
chloride does not attack the naphthalene as in Fig. 1, but
follows the reaction scheme shown in Fig. 2.

Fig. 1.

Fig. 2.

Basicity.
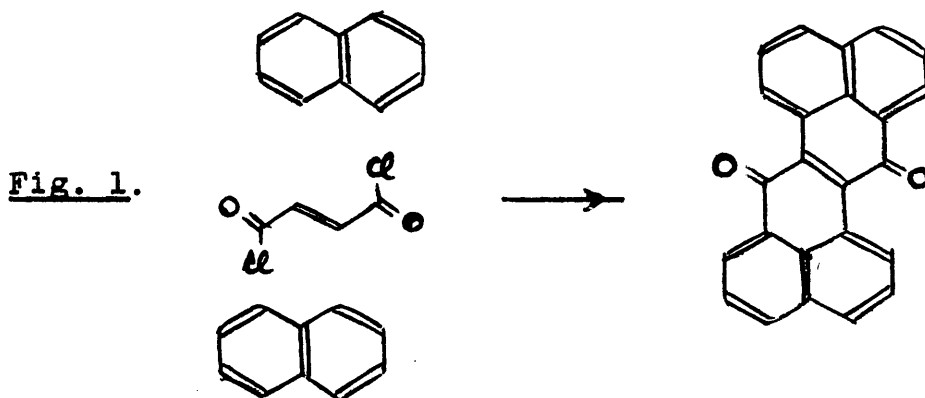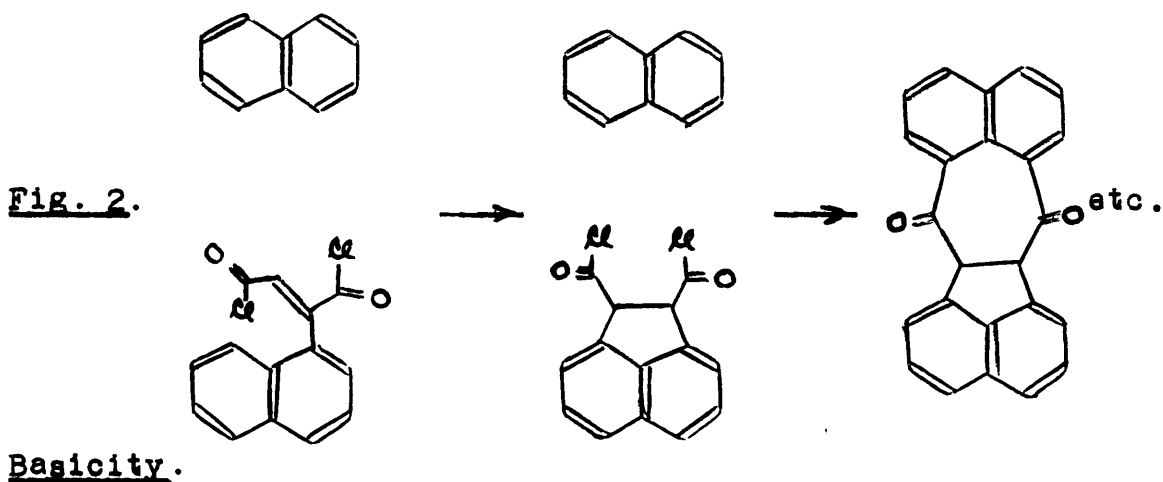
Azulene itself is basic, and thus it is not unreasonable to expect that the hydrocarbon (LIII) would also be basic. Two important differences arise in this respect.

Firstly, azulene is soluble only in concentrated mineral acids, and may be recovered from these on dilution. The dinaphtho-azulene (LIII) gives salts with even aqueous acetic acid.

Secondly, the widely accepted view on the formation of azulenium salts involves the cation (LIX), or better, (LX)[20], in acid solutions. No cation of this type can be formulated for the dinaphtho-azulene (LIII), since the 1-position of the azulene part of the molecule (calculated

in azulene to be the most basic) is occupied. The
salts of dinaphtho-azulene may be of the type (LXI).
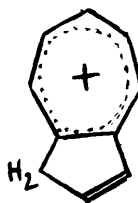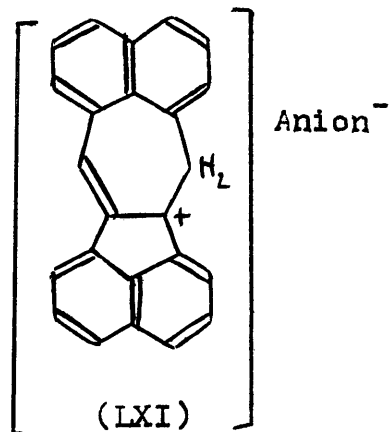
(LIX)   (LX)   (LXI)

Absorption Spectra.

The absorption spectrum of the dinaphtho-azulene (LIII)
(page 69) cannot be related to that of any known
polycyclic aromatic hydrocarbon, nor indeed does it even
resemble any of these in type. The absorption spectrum
of azulene also differs markedly from the usual type of
aromatic hydrocarbon spectrum, and although this absence
of typical spectrum may not be taken as positive proof
for the structure (LIII), it nevertheless does not
preclude this structure. Fusion of two naphthalene
residues to the azulene molecule would produce a completely
unpredictable change in the absorption spectrum of azulene.

Hydrogenated Derivatives.

The absorption spectrum of the octahydro- derivative
(LVII) is closely related to that of chrysene. (These
spectra are compared on page 50). It will be noted that
the molecule of the octahydro- derivative has the same
degree of conjugation (in formal double-bonds) as the
molecule of chrysene (XLII), and provided that the
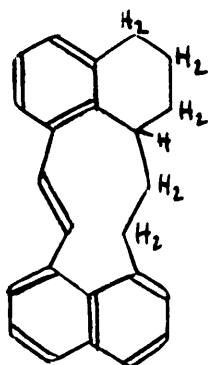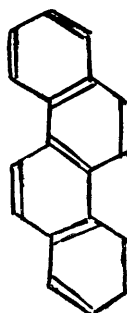
(LVII)   (XLII)

molecule (LVII) is held approximately planar, this could
account for the great similarity in absorption spectra.

The phosphorescence spectrum of (LVII) is compared
with that of chrysene on page 51. It can be seen that the
spectrum of the octahydro- derivative is at a lower
wavelength than that of chrysene, which would not be the
case in a substituted chrysene; this therefore establishes

that the green hydrocarbon $C_{24}H_{14}$ does not contain the
four-ring chrysene system, as is the case in zethrene (XLI).

Dehydrogenation of the octahydro- and dodecahydro-
derivatives to the parent $C_{24}H_{14}$ (LIII) involves the
formation of a carbon-carbon bond, but this reaction
finds analogy in the case of di-m-xylylene (LXII), which
on dehydrogenation over palladised charcoal results in
the formation of a new carbon-carbon bond to yield
pyrene (LXIII)[21]. Further, cyclodecane (LXIV) can be
converted to azulene by treatment with hot alumina,
followed by dehydrogenation on palladised charcoal[22].
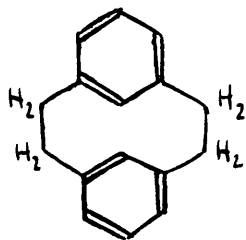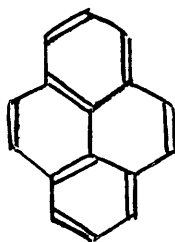
(LXII)   (LXIII)   (LXIV)

The absorption spectrum of the dodecahydro-
derivative (LVIII) is shown on page 68.

Maleic Anhydride Adduct

When maleic anhydride was added to a solution of dihydrodinaphtho-azulene in nitrobenzene and in the presence of iodine, three molecules of maleic anhydride were combined with one molecule of dinaphtho-azulene. Two of the anhydride molecules combined by addition and subsequent dehydrogenation (to give (LXV)) and the third molecule added, giving the endocyclic tri-maleic anhydride adduct (LXVI).
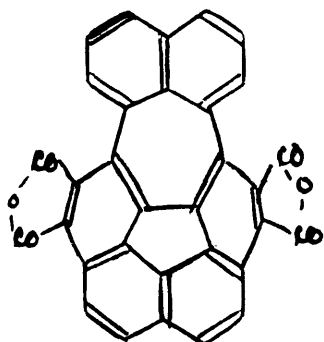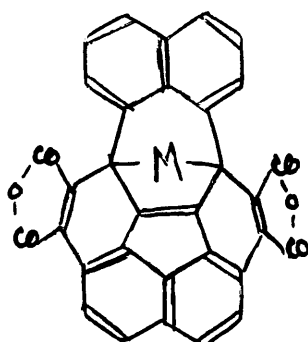
(LXV)   (LXVI)
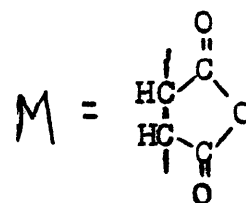
While all the available evidence indicated that the formula (LIII) was correct for the green hydrocarbon, conclusive proof was considered necessary. Some attempts were made to synthesise the hydrocarbon by another route, and these attempts are discussed below (page 64).

N O T E S.

1. **The iodine complex $C_{24}H_{14}I_3$.**

By adding iodine to a solution of dihydrodinaphtho-
azulene (LIV) in boiling nitrobenzene, dehydrogenation
occured and an iodine-containing substance $C_{24}H_{14}I_3$ was
obtained.

From studies of the absorption spectrum of this
substance (page 70) it could be shown that the iodine was
complexed and not combined, since the addition of an
excess of iodine to the solution of $C_{24}H_{14}I_3$ caused an
increase in the intensity of the absorption bands due to
this substance. The excess iodine served therefore to
displace the equilibrium:-

$$2 \; C_{24}H_{14} \quad + \quad 3 \; I_2 \quad \rightleftharpoons \quad 2 \; C_{24}H_{14}I_3$$
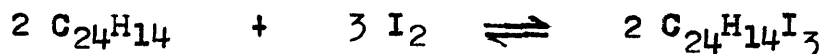
2. **Paramagnetism.**

Approximately one in eightyof the molecules of
dinaphtho-azulene are paramagnetic at room temperature[23],

as found by paramagnetic micro-wave absorption[23]. This
unusual property is almost certainly due to the
molecule's existing to some extent in a triplet state
at room temperature. The intensity of absorption bands
due to singlet-triplet transitions is normally of the
order $\varepsilon = 1$, and therefore the high wavelength
absorption bands of dinaphtho-azulene (intensity of the
order $\varepsilon = 1000$) are more likely correlated to a
triplet-triplet transition. The intensity of these
bands fit very well with the fact that one molecule in
eighty is paramagnetic.

3.   <u>Other dinaphtho-azulenes</u>.

Fumaryl chloride condensed with 1-methylnaphthalene
in the same way as with naphthalene. By the usual
series of reactions, dimethyldinaphtho-azulene (LXVII) was
obtained. It was hoped that the directing influence of the
methyl groups would lead to higher yields of hydrocarbon,
and thus facilitate further studies. The yield in the
condensation reaction was indeed higher, but dimethyl-
dinaphtho-azulene was far less stable than dinaphtho-
azulene, and decomposed considerably on sublimation, so

that no weight was attached to these studies.
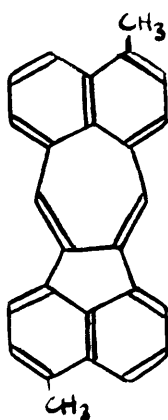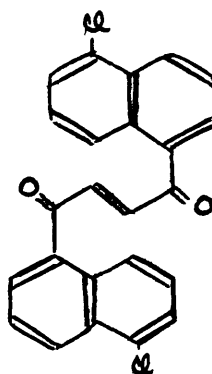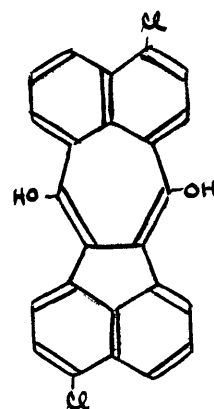
(LXVII)   (LXVIII)   (LXIX)

Under the usual experimental conditions, fumaryl
chloride was condensed with 1-chloronaphthalene. Instead
of the normal condensation, however, the diketone
(LXVIII) resulted, corresponding to the diketone (XLIII)
(page 39). Condensation at high temperature would be
necessary to produce the dichlorodinaphtho-azulene
derivative (LXIX).

The introduction of two chlorine atoms into the
dinaphtho-azulene molecule should produce an increase
in the proportion of molecules existing in the triplet
state[24], and hence in the degree of paramagnetism.

--------oOo--------

ATTEMPTED SYNTHESIS.

It was proposed to attempt a synthesis of dinaphtho-azulene by a more specific route than the original - as indicated in the reaction scheme :-

(LXX)   (LXXI)   (LXXII)
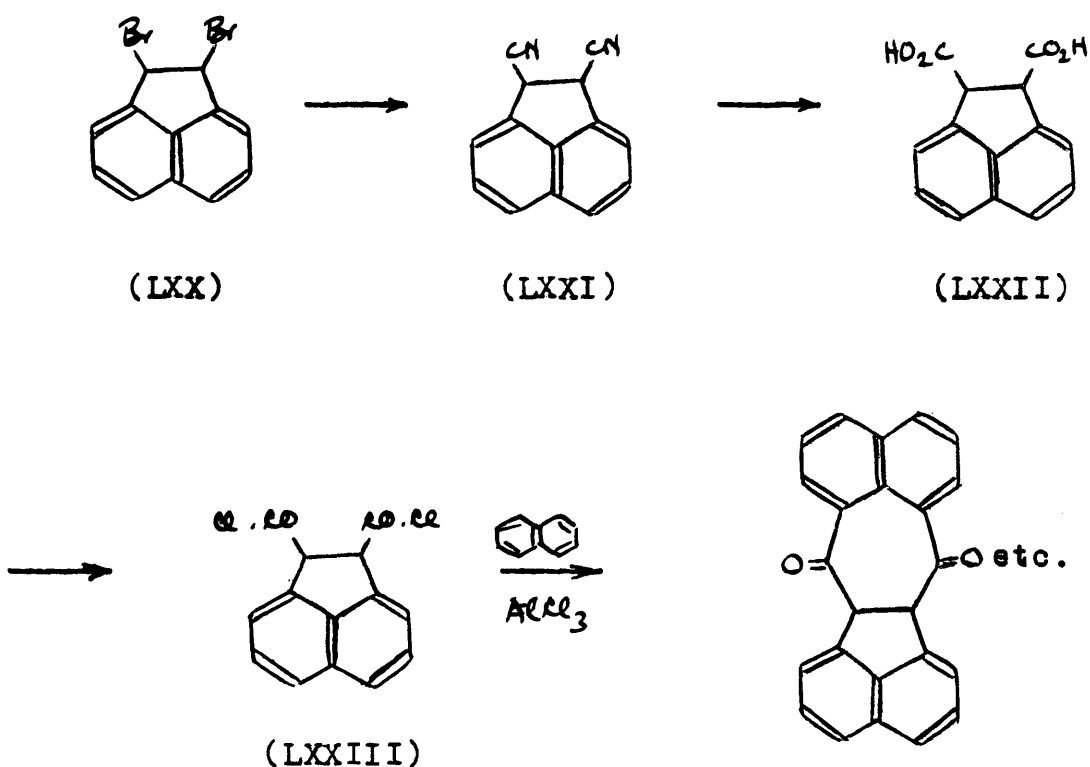
(LXXIII)

Dibromo acenaphthene (LXX) was prepared[25] from acenaphthylene, and attempts were made to prepare the nitrile (LXXI) from it. Hydrolysis would give the

acid (LXXII) which could be converted to its acid chloride (LXXIII).

Dibromoacenaphthene was treated with potassium cyanide and with cuprous cyanide under varying conditions, without any replacement of bromine by nitrile groups. In the same way, lithium metal could not be induced to react with the two bromine atoms, indicating unusually strong carbon-bromine linkages.

A second attempt was made, starting from bromomaleic anhydride (LXXIV)[26]. It was hoped thus to synthesise 1-naphthylmaleic anhydride (LXXV), from which acenaphthene-1:2-dicarboxylic acid (LXXII) could be prepared:-

(LXXIV) $\longrightarrow$ (LXXV) $\xrightarrow[\text{(b)AlCl}_3]{\text{(a) HBr}}$ etc.
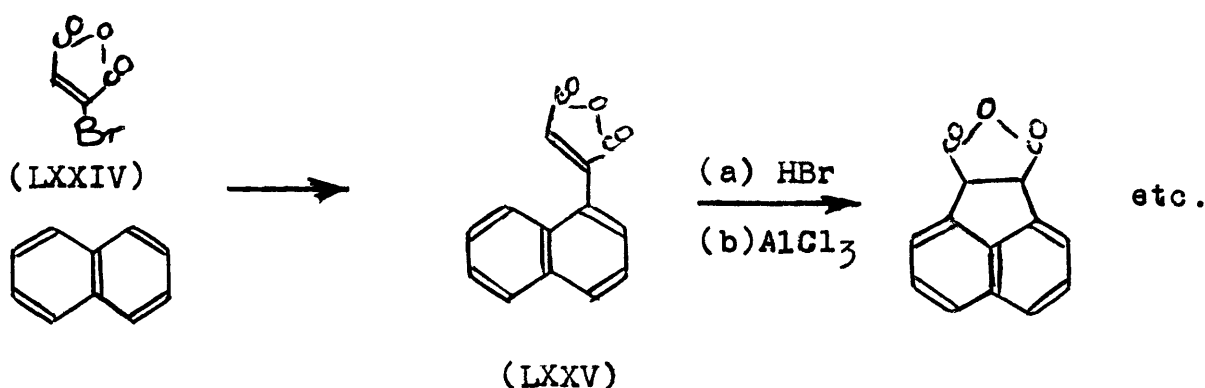
Naphthalene and bromomaleic anhydride (LXXIV) were dissolved in tetrachloroethane, and anhydrous aluminium chloride added to the mixture. It was found that the

anhydride grouping reacted more readily than the bromine
atom, and acylation occured. The ketonic, acidic
material obtained did not contain bromine ($C_{14}H_{10}O_3$) and
had an equivalent weight (sodium hydroxide titration) of
around 220. This indicated that it was probably a
mixture of the two naphthoylacrylic acids (LXXVI) and
(LXXVII)[27], formed from the Friedel-Crafts reaction by
acylation and subsequent removal of bromine. No
satisfactory mechanism can be advanced for the bromine
removal.
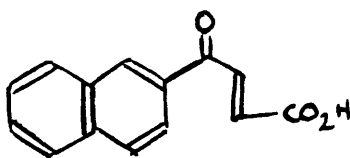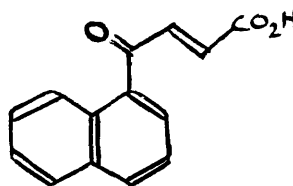
(LXXVI)   (LXXVII)

-------oOo-------
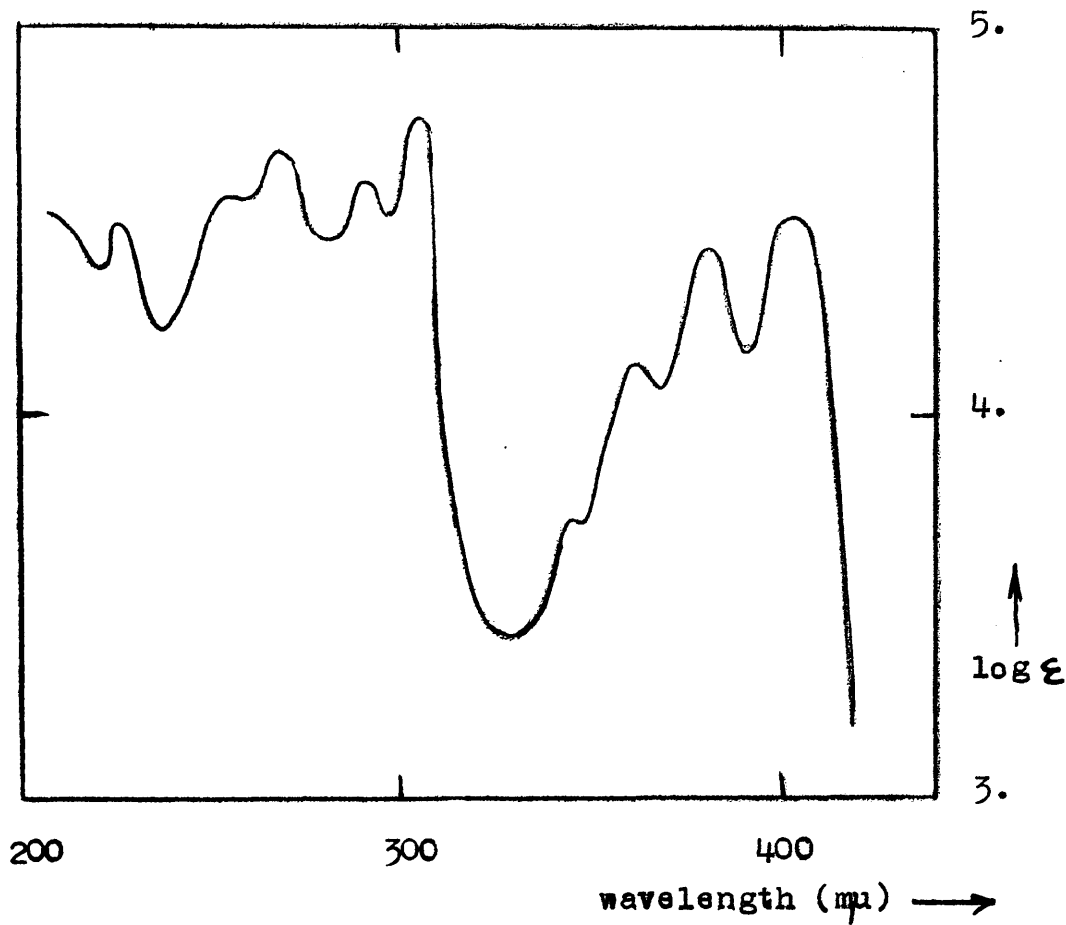
Dihydrodinaphtho-azulene in alcohol. Bands :- 229,
270, 291, 304, 340, 360, 379, 400.
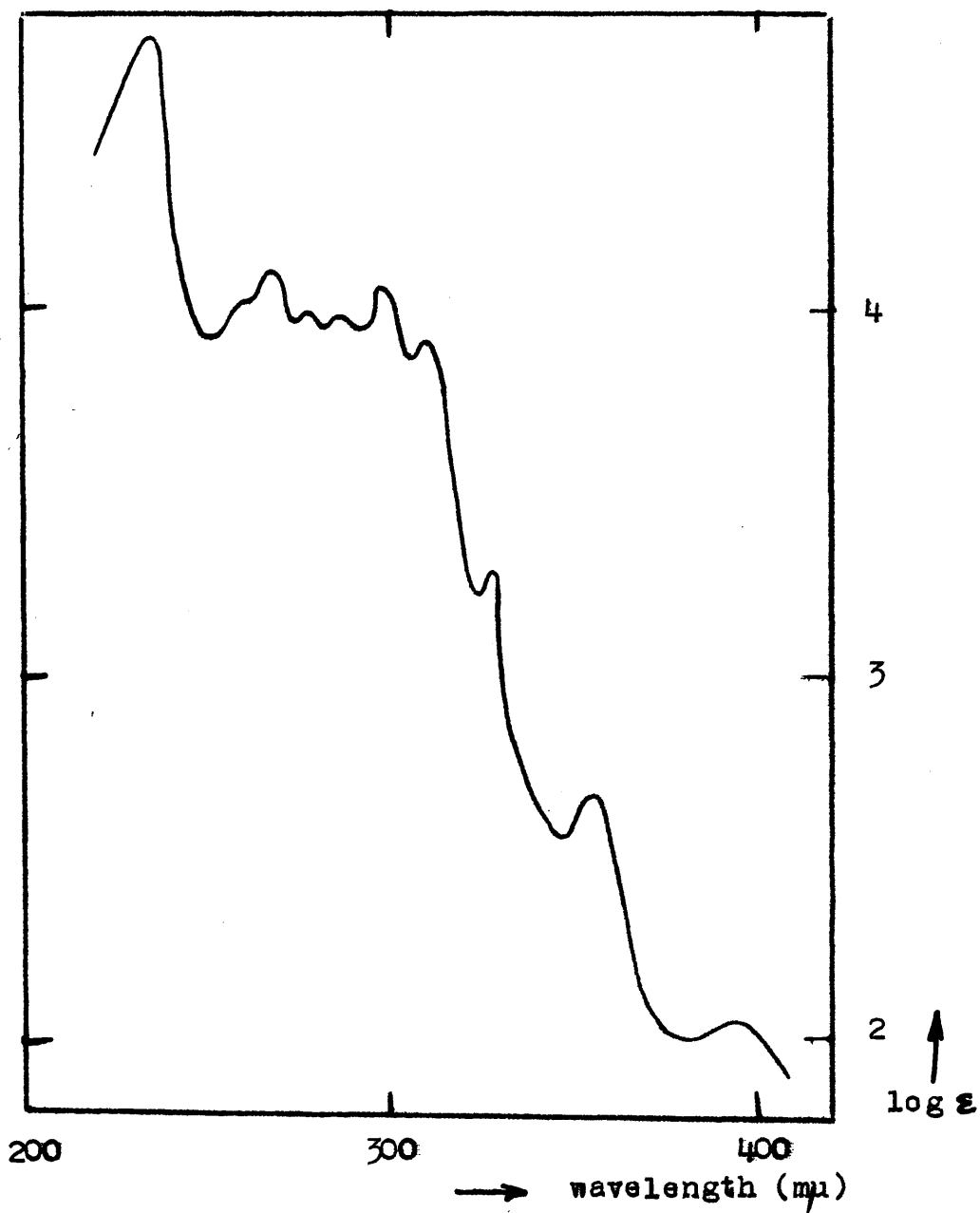
Dodecahydrodinaphtho-azulene in alcohol.

Bands:- 234 , 267 , 297 , 308 , 328 , 355 .
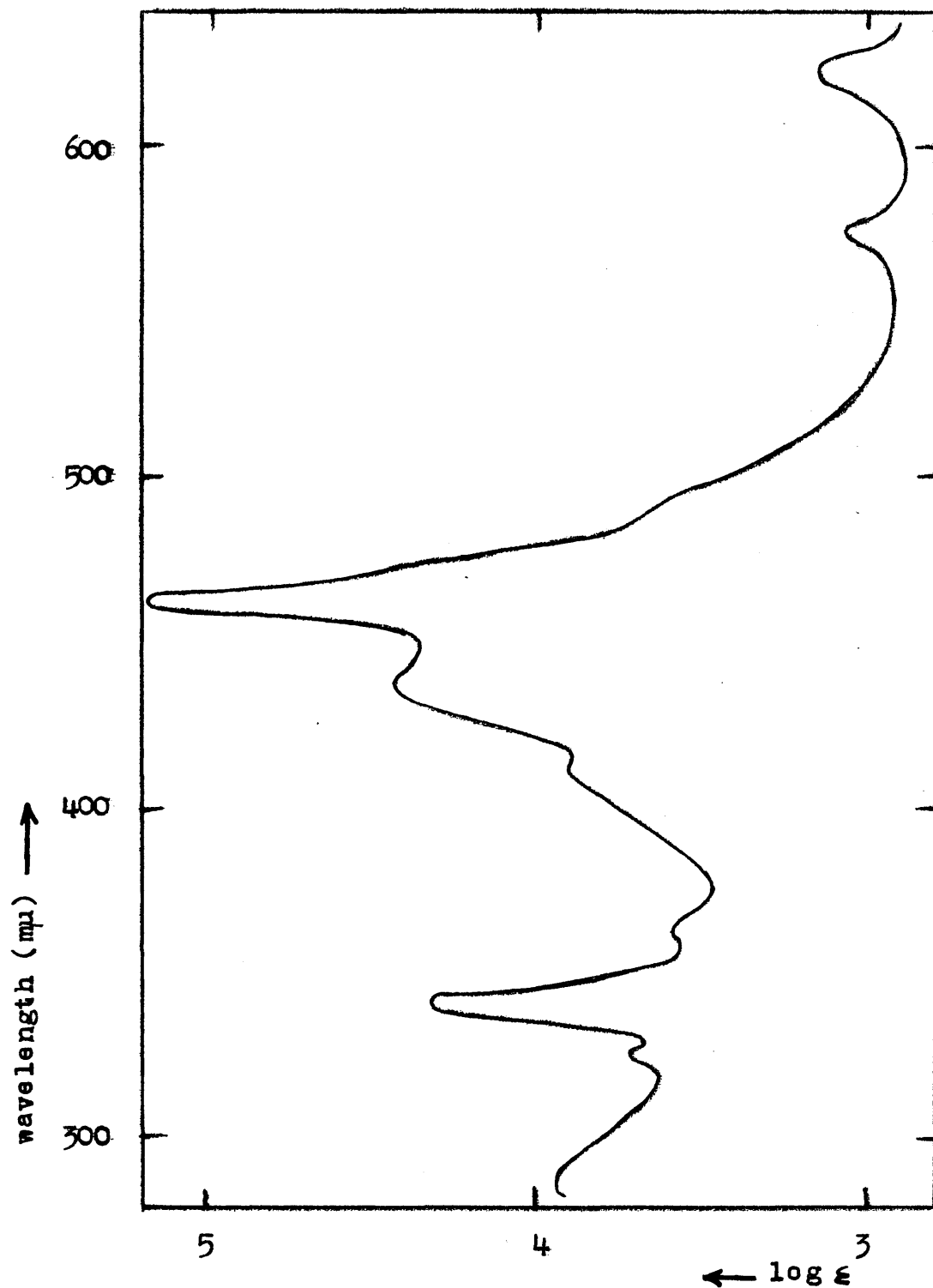
Dinaphtho-azulene in benzene.   Bands:- 284, 327, 342,
360, 414, 436, 461, 573, 622.
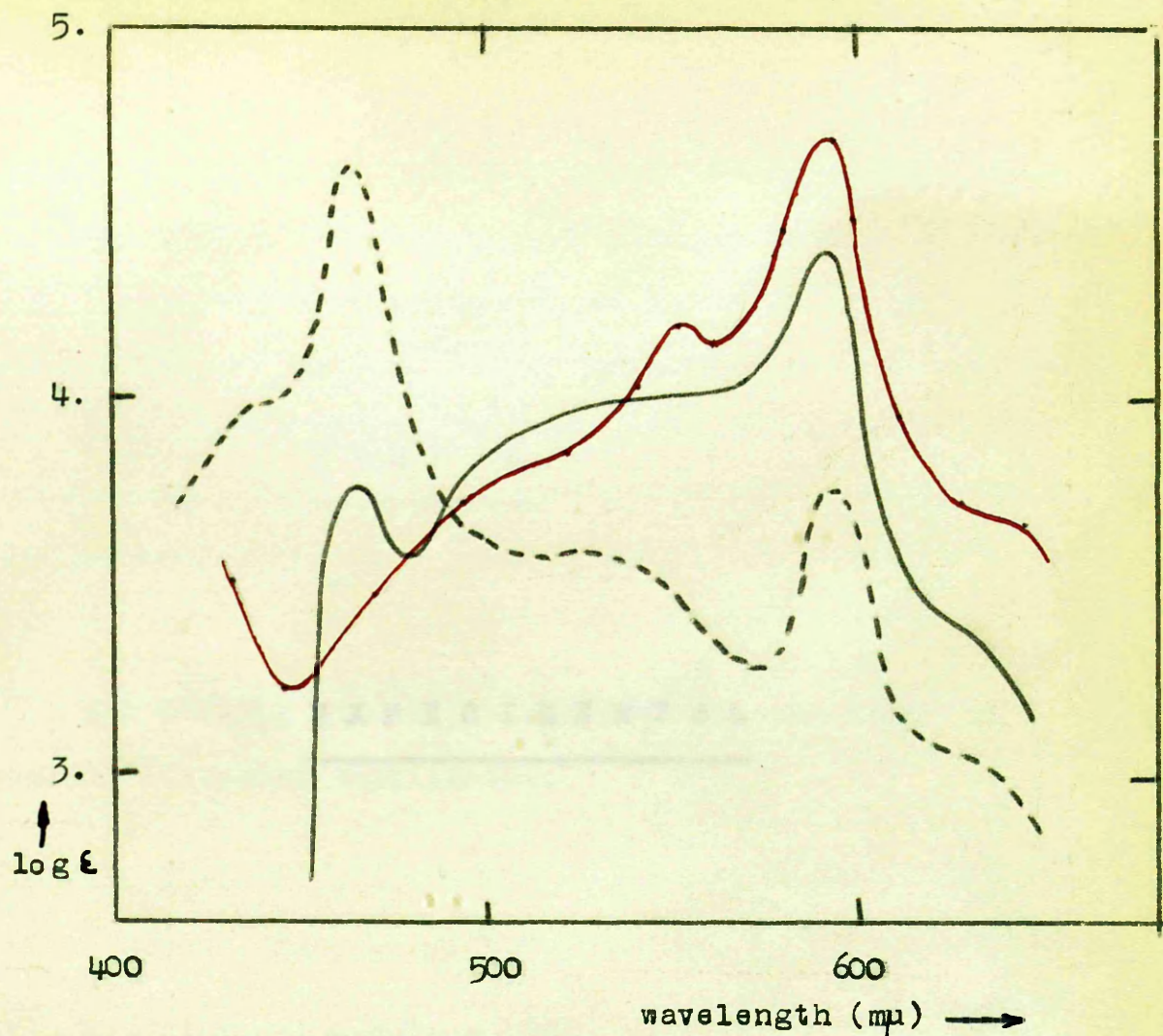
Dinaphtho-azulene/iodine complex ($C_{24}H_{14}I_3$) in nitrobenzene.

‑ ‑ ‑ ‑ ‑ ‑ $C_{24}H_{14}$ + 0·3 atoms iodine.

———— $C_{24}H_{14}$ + 3 atoms iodine.

—— $C_{24}H_{14}$ + 6 atoms iodine.

Bands:- (peak at 462 due to dinaphtho-azulene) 550, 590.

(All solutions were 1.99×10^{-4} M. with respect to $C_{24}H_{14}$,

and log ε was calculated on this basis).

EXPERIMENTAL

P A R T   1.

All melting points are uncorrected, and taken in sealed, evacuated capillaries.

1.   4:6-Dichloro-m-xylene (1V).

This was prepared by a method based on that of Claus and Burstert[4].

Iodine (20 g.) was added to m-xylene (200 g.) and the solution cooled to 0° and chlorinated directly at that temperature till the contents of the reaction vessel formed a semi-crystalline mass (ca. 8 hours). (Over-chlorination occured easily at this stage to give 2:4:6-trichloro-m-xylene). The mass was dissolved in chloroform (200 ml.), washed with water and dilute

sodium thiosulphate solution, dried (calcium chloride),
and distilled. The fraction distilling between 215 and
240° consisted almost entirely of 4:6-dichloro-m-xylene.
This distilled as a heavy oil which readily crystallised
in large plates in the receiver. It was recrystallised
from ethanol, m.p. 67°. (Literature, 68°). Yield, 60 g.
or 17% theoretical.

2.   4:6-Dichloro-m-toluic acid (V).

4:6-Dichloro-m-xylene (50 g.) was added to a mixture
of water (800 ml.), concentrated nitric acid (1200 ml.)
and manganese dioxide (0.5 g.), and the whole refluxed
for 7 days. On cooling, white needles of the toluic acid
crystallised out from the solution, and some unchanged
dichloro-m-xylene solidified on the bottom of the flask.
The white needles were filtered off and the unchanged
dichloro-m-xylene refluxed with fresh dilute nitric acid
(as above) for a further 4 days, when cooling gave more
white needles of dichloro-m-toluic acid. m.p. 168°.
(Literature 170°). Yield, 50 g. or 88% theoretical.

3.   4:6-Dichloro-iso-phthalic acid (VI).

4:6-Dichloro-m-toluic acid (50 g.) was dissolved in
dilute sodium hydroxide solution (500 ml.) and diluted

to 1.5 litres with water. The solution was boiled in a
large enamelled iron pot with efficient mechanical
stirring, and potassium permanganate (50 g.) added in
10 g. portions, each portion being added when the colour of
the previous portion had been discharged. The solution
was then boiled for a further half hour, and excess
permanganate destroyed by the addition of a little ethanol.
The solution was cooled, filtered, and the residue of
manganese salts extracted three times with boiling
water (500 ml. each time). The combined filtrates
were evaporated to 500 ml. and acidified with
concentrated hydrochloric acid, when white needles of
4:6-dichloro-iso-phthalic acid were obtained, m.p. 255°.
(Literature 280°). Recrystallisation from ethanol gave
long white needles, m.p. 280°. Yield, 50 g. or 85%
theoretical.

4. 4:6-Dichloro-iso-phthalic acid chloride (VII).

4:6-Dichloro-iso-phthalic acid (50 g.) was
powdered and mixed dry with phosphorus pentachloride
(90 g.). A vigorous reaction set in and only
intermittant stirring was necessary. Within 1 hour,
the reaction had subsided, and the resulting solution was

heated on the steam-bath for a further half hour. The
generated phosphorus oxychloride was distilled off under
reduced pressure, and the last traces removed by
distillation of petroleum ether (b.p. 100-120°) (100 ml.)
from the mixture. The crude, gummy 4:6-dichloro-iso-
phthalic acid chloride (VII) was used crude in the
following reaction.

5.   1:3-Dichloro-4:6-di-(1-naphthoyl)-benzene (VIII).

The acid chloride (VII) (from 50 g. acid (VI)) was
dissolved in methylene chloride (150 ml.) with
naphthalene (55 g.), and anhydrous aluminium chloride
(60 g.) was added over 1½ hours. During the vigorous
reaction the solution changed from brown to red. The
mixture was shaken over-night, poured into ice and
hydrochloric acid, and the solvent and excess
naphthalene steam distilled off, leaving a brown oil
which solidified on cooling and could be ground in a mortar
(58 g. crude).

A sample was recrystallised from benzene:ethanol:
water (2:4:1) as white needles, m.p. 157°. (Found:
C, 73.92; H, 3.69; Cl, 15.74 $C_{28}H_{16}O_2Cl_2$ requires C, 73.86;
H, 3.54; Cl, 15.57%). Colour in concentrated

sulphuric acid, orange, and on heating, yellow.

6.   4:5-7:8-Dibenzpentacene-12:14-quinone (IX).

(a)   Potassium hydroxide in quinoline.

The crude diketone (VIII) (10 g.) was refluxed in quinoline (50 ml.) with potassium hydroxide pellets (2.5 g.) for 8 hours and poured into dilute hydrochloric acid (400 ml.). The aqueous liquors were decanted off, and the tarry mass boiled with water (300 ml.) then with dilute ammonia solution (300 ml.), again using decantation to remove the aqueous solutions. On cooling, the dark tar solidified and was ground in a mortar with ethanol (10 ml.). Yield (crude) 8.5 g.

Chromatography on alumina using benzene and chloroform (1:1) as eluant gave brown needles, which were sublimed twice at 300° and 10^{-2}mm. pressure. This gave orange needles of the quinone (IX), softening at 280°, m.p. 342°. (Found: C, 87.83; H, 3.87 $C_{28}H_{14}O_2$ requires C, 87.94; H, 3.69%). Colour in concentrated sulphuric acid, red with very faint orange fluorescence.

(b)   Potassium hydroxide in alcohol.

Strong alcoholic potassium hydroxide solution was

prepared by evaporation of a 10% solution till the boiling point rose to 140°.

The diketone (VIII) (5 g.) was added to this, and heated for ½ minute at 140°. The mixture was cooled and poured into water. The insoluble material (0.5 g. crude) was the quinone (IX) and could be washed with water and purified as above (a). The alkaline solution was acidified with hydrochloric acid and the resulting white solid filtered off and recrystallised twice from aqueous acetic acid (1:1). White needles of a dinaphthylbenzene dicarboxylic acid, m.p. 153°. (Found: C, 76.74; H, 4.85 $C_{28}H_{18}O_4 \cdot H_2O$ requires C, 77.05; H, 4.62%). Colour in concentrated sulphuric acid violet, fading rapidly to brown, and on heating becoming pale red.

7.   4:5-7:8-Dibenz-1:2:3:9:10:11-hexahydropentacene.(XIII).

The quinone (IX),(1 g., chromatographed) was ground together with red phosphorus (0.34 g.) and added to constant boiling hydriodic acid (10 ml.) in a large Carius tube. The sealed tube was heated at 200° for 8 hours. The contents were extracted with benzene, and the benzene solution well washed with water and sodium

hydrosulphite solution, and dried. Chromatography on
alumina, using petroleum ether (b.p. 60-80°) containing
30% benzene as eluant, gave yellow needles of the
hexahydro- derivative (XIII), softening at 197°,
m.p. 215°. (Found: C, 93.85; H, 6.23 $C_{28}H_{22}$ requires
C, 93.81; H, 6.19%). In concentrated sulphuric acid it
dissolved very slowly giving a brown-green solution
with red fluorescence, and on heating became olive green
with red fluorescence.

8. Apparatus for dehydrogenation over heated
                                    palladised charcoal.

(a) Preparation of catalyst.

A charcoal block was crushed in a mortar and
suitable pieces (diameter ca. 2 - 4 mm.) were
separated manually. Metallic palladium was deposited
on these by the usual method of reducing palladium
chloride with formalin [29].

(b) Assembly.

The catalyst thus prepared was introduced into a
long glass combustion tube (ca. 3 feet long by ½ inch
bore) so that it occupied the central 9 inches of the

tube, being held there by plugs of glass wool. The
catalyst was heated in these experiments by an
electrically heated wire wound inside an asbestos
paper sheath, and controlled by a rheostat callibrated
to give the required temperatures.

9.   Dehydrogenation of 4:5-7:8-dibenz-1:2:3:9:10:11-
hexahydropentacene (XIII).

The hexahydro- derivative (XIII) (30 mg.) was
sublimed in a current of air-free carbon dioxide[10] into
the palladised charcoal catalyst at 310° and 10^{-3}mm.
pressure, but was completely absorbed in it. The
temperature was raised to 500°, but no sublimate was
obtained from the catalyst.

The efficiency of the catalyst was tested both
before and after this experiment by the dehydrogenation
of 9:10-dihydroanthracene to anthracene in good yield.

The complete testing of the catalyst and
dehydrogenation of the hexahydro- derivative (XIII) was
repeated several times with identical results.

-------oOo-------

P A R T   2.

1.   Di-(1-naphthyl)-chloromethane.(XX).

As prepared by Schmidlin and Massini, **Ber.**, **42**, 2381.

2.   Di-(1-naphthyl)-methylmalonic acid (XXIII).

Di-(1-naphthyl)-chloromethane (30 g.) in 400 ml. of dry

benzene was added to a solution of magnesio-malonic ester in

benzene (200 ml.). This latter was prepared according to the

method of Lund[14], from 7.5 g. of magnesium.

The mixture was refluxed for 30 hours[x], cooled, and excess

magnesio-malonic ester destroyed by shaking with 500 ml. of

dilute sulphuric acid. The benzene solution was then shaken

with dilute sodium carbonate solution, washed with water and

dried over magnesium sulphate; the benzene was distilled off

leaving a semi-crystalline mass which consisted mainly of

di-(1-naphthyl)-methylmalonic ester. (Recrystallisation of

a portion of this from ethanol gave ivory needles, m.p. 113°.
Analysis: Found: C, 78.77; H, 5.76. $C_{28}H_{26}O_4$ requires
C, 78.85; H, 6.15%).

The crude ester was then hydrolysed by boiling for 6
hours with 500 ml. of 15% alcoholic potassium hydroxide
solution, after which most of the alcohol was removed by
distillation. 400 ml. of water was added and the remainder
of the alcohol distilled off azeotropically. The resulting
aqueous solution was diluted to 1 litre, filtered, cooled
and acidified with concentrated hydrochloric acid,
precipitating white needles of the   required dicarboxylic
acid (XXIII), which was then filtered off, washed with
water and dried. Yield, 32 g., or 84% theoretical.

The acid was recrystallised from glacial acetic acid,
as white needles, m.p. 238° containing one molecule of
water of crystallisation. (Found: C, 74.30; H, 5.35.
$C_{24}H_{18}O_4.H_2O$ requires C, 74.21; H, 5.19%).

The dicarboxylic acid dissolved slowly in concentrated
sulphuric acid giving a bluish-green solution, which on
warming to 80° became yellow, and at 100° changed to red.

* If the condensation time was much shortened, the
unreacted di-(1-naphthyl)-chloromethane remained in solution
and reacted with ethanol in the subsequent hydrolysis

reaction to give a water insoluble precipitate of
di-(1-naphthyl)-methyl ethyl ether. This recrystallised
from ethanol in fawn rhombs, m.p. 125°.[13] (Found: C, 88.26;
H, 6.63. $C_{23}H_{20}O$ requires C, 88.44; H, 6.45%).

3. Attempted cyclisation of di-(1-naphthyl)-methylmalonic acid (XXIII) using liquid hydrogen fluoride.

The dicarboxylic acid (XXIII) (0.3 g.) was added to
liquid hydrogen fluoride (ca. 15 ml.) in a polyethylene
vessel and allowed to stand for 24 hours. The hydrogen
fluoride was then allowed to evaporate and the residue
washed out with water, filtered, and recrystallised from
glacial acetic acid. White needles, m.p. 230°. It was
identified as starting material by mixed melting point
determination with an authentic sample of the dicarboxylic
acid.

4. Attempted cyclisation using polyphosphoric acid. Preparation of the polyphosphoric acid slurry.

Phosphorus pentoxide (37.2 g.) was added to 85%
phosphoric acid (24 ml.) and the mixture heated on the
steam-bath for 2 hours [28].

(a) The dicarboxylic acid (XXIII) (1.g.) was added to the
polyphosphoric acid slurry and the mixture heated on the
steam-bath for two hours, then poured into water and
extracted with benzene. The benzene solution was extracted
with 5% sodium hydroxide solution, then evaporated to
dryness. There remained only a small gummy residue.
Acidification of the alkaline extract gave 0.8 g. of
starting material, identified by mixed melting point with
an authentic sample.

(b) The dicarboxylic acid (XXIII) (1.g.) was added to the
polyphosphoric acid slurry and the whole heated, with
stirring, to 100°. When the temperature was further raised
to 150°, a green colour developed which changed to brown
at 170°. The mixture was cooled and poured into water and
extracted with benzene as before. (Further extraction of
this benzene solution with dilute alkali and subsequent
acidification of the alkaline layer gave no precipitate
of starting material). The brown benzene layer was
evaporated to dryness and the residue recrystallised from
benzene/petroleum ether (b.p. 60-80°). This gave a small
amount of perinaphthenone (m.p. 142°) identified by mixed
melting point with an authentic sample.

5.   Attempted cyclisation using an aluminium chloride -
     sodium chloride melt.

Powdered anhydrous aluminium chloride (10 g.) and
sodium chloride (2 g.) were melted together and cooled.
The dicarboxylic acid (XXIII) (1 g.) was added and the
whole remelted for 3 minutes, (maximum temperature, 160°).
The cooled mass was poured into ice and hydrochloric acid,
filtered, boiled with dilute ammonia solution, and
filtered again. The residue was extracted with benzene,
but most failed to dissolve. The benzene solution was
chromatographed on alumina, using benzene as eluant, but
no crystallisable material was obtained. A narrow dark
band at the top of the column was washed out by the
addition of ½% methanol to the benzene, but no crystallisation
was obtained from the resulting dark solution.

6.   Attempted cyclisation/reduction by modifications
     of 5, using an equimolecular mixture of aluminium
     chloride - sodium chloride.

The dicarboxylic acid (XXIII) (2 g.) was fused for
5 minutes in a mixture of anhydrous aluminium chloride
(17.8 g.) and sodium chloride (4 g.), the maximum
temperature being 140°. The melt was decomposed by pouring

into ice and hydrochloric acid, and the resulting solid filtered off, boiled with dilute ammonia solution, filtered off again and dried. It was then extracted thoroughly with benzene (insoluble residue remained, 1.4 g.) and chromatographed on alumina. Using petroleum ether (b.p. 60-80°) containing 40% benzene as eluant, a small amount of sticky yellow material was obtained, which, although not obtained crystalline, was expected to be a hydrocarbon from its behaviour on chromatography.

The melt was repeated on a further 2 g. of dicarboxylic acid with the addition of zinc dust (2 g.). After working up in the usual manner, a further small amount of hydrocarbon was obtained. The two samples were united and rechromatographed on alumina, but it was not possible to crystallise them. The yield (ca. 0.01 g.) rendered the method of no value.

7.   Attempted cyclisation/reduction using hydriodic acid
        and red phosphorus in a sealed tube.

The dicarboxylic acid (XXIII) (1 g.), red phosphorus (0.21 g.) and 55% hydriodic acid (10 ml.) were heated in a large sealed Carius tube at 200° for 4 hours. After opening, the resulting solid was filtered off, extracted

well with ether and the ether extract washed with water
and dilute sodium carbonate solution, and dried over
calcium chloride. The ether was then evaporated, leaving
an oily residue which distilled over a wide range of
temperature at 10^{-2}mm. pressure giving a yellow
fluorescent oil. Colourless crystals in the condenser
used to distil the oil had the characteristic odour of
naphthalene, and were identified as such by comparison
with an authentic sample.

The oil (0.5 g.) was dehydrogenated at 200°
(atmospheric pressure) by 20% palladised charcoal, and
gave up the equivalent of 6 atoms of hydrogen per molecule
of hydrogenated derivative. The dehydrogenation product
was sublimed out from the palladised charcoal as a sticky
yellow solid which was washed with a little ether. Its
absorption bands in the visible region of the spectrum
were at 444 mμ and 416 mμ (in benzene),(peropyrene has
characteristic absorption bands at 444 and 416 mμ in
benzene). There was insufficient material for full
characterisation, but the presence of these absorption
bands indicated that the dehydrogenation product contained
some peropyrene.

8. Preparation of the acid chloride of di-(1-naphthyl)-methylmalonic acid.

The dicarboxylic acid (XXIII) (5.g.) was refluxed with thionyl chloride (100 g.) till the acid dissolved (2 hours) then for a further hour. (This large excess of thionyl chloride (60 times theoretical) was necessary to prevent superheating). The excess thionyl chloride was distilled off, and the last traces removed by the addition of dry benzene and distillation of this, latterly under reduced pressure. The residual oil solidified on standing and was used crude in the following reactions.

9. Attempted cyclisation of the acid chloride (XXIV).

(a) Using aluminium chloride in nitrobenzene solution.

The acid chloride (XXIV)(from 5 g. dicarboxylic acid (XXIII)) was dissolved in nitrobenzene (10 ml.) and powdered anhydrous aluminium chloride (10 g.) added. A very vigorous reaction set in and cooling was applied to keep the temperature below 100°. The mixture was poured into ice and hydrochloric acid and the nitrobenzene steam-distilled off leaving a dark green solid, insoluble in both xylene and nitrobenzene, and judged to be material of high molecular weight.

(b)   Using aluminium chloride in benzene solution.

The crude acid chloride (XXIV) (from 2 g. dicarboxylic acid (XXIII)) was dissolved in benzene (5 ml.) and powdered anhydrous aluminium chloride (3 g.) added. The mixture was shaken for 2 hours at room temperature, poured into ice and hydrochloric acid and the benzene distilled off as its water azeotrope. The solid was filtered off, dried, extracted with dry benzene and chromatographed on alumina. A trace of non-crystalline yellow material was washed through with benzene, and when $\frac{1}{2}\%$ methanol was added to the benzene, a red solution was washed out of the column, which was evaporated to small bulk. This could be extracted with hydrochloric acid, and on standing of this acid solution there was obtained yellow needles of perinaphthenone, m.p. 138-142°, identified by mixed melting point with an authentic sample.

The amount of benzene insoluble material obtained (0.9 g.) rendered the method useless.

10.   Preparation of the dihydric alcohol (XXV).

The dicarboxylic acid (XXIII) (2 g.) was dissolved in ether (300 ml.) and added slowly to lithium aluminium hydride (2 g.) in ether (100 ml.). No vigorous reaction

ensued. The mixture was refluxed for 3 hours, then
ethanol (20 ml.) was added, followed by water (40 ml.)
then dilute sulphuric acid (60 ml.). The ether layer
was separated off and the aqueous layer extracted with
ether. The united ether solutions were washed with
dilute sodium carbonate solution, dried over anhydrous
sodium sulphate and evaporated to dryness. The resulting
solid was best recrystallised from benzene, m.p. 138°.
Yield 1.3 g. or 74% of theoretical. (Found: C, 83.02;
H, 6.94. $C_{24}H_{22}O_2$ requires, C, 84.17; H, 6.48%).

In concentrated sulphuric acid the alcohol dissolved
readily giving a green solution which, on heating,
changed through red (at 80°) to dark green (at 160°).

11. Attempted cyclisation of the dihydric alcohol (XXV).

(a) Using polyphosphoric acid.

The dihydric alcohol (XXV) (0.6 g.) was added to a
slurry of polyphosphoric acid (prepared from 13 g.
phosphorus pentoxide and 8 ml. 85% phosphoric acid) and
the temperature raised slowly to 130°, when a strong odour
of naphthalene was detected. The mixture was cooled,
poured into water and the resulting solid filtered off.
It was insoluble in benzene and failed to sublime at 200°

and 0.5 mm. pressure, and was judged to be polymeric material from the inter-molecular condensation of the alcohol or its decomposition products.

(b) <u>Using liquid hydrogen fluoride</u>.

The alcohol (XXV) (1. g.) was treated with liquid hydrogen fluoride for 24 hours. The hydrogen fluoride was then allowed to evaporate and the resulting brown solid sublimed (150°, 0.5 mm. pressure) when two different products were obtained. The first sublimed extremely quickly and was identified as naphthalene by mixed melting point with an authentic sample. The second sublimed at 280° and could be recrystallised from benzene/petroleum ether (b.p. 80-100°) in small white needles m.p. 168-170°. (Found: C, 83.78; H, 6.28 . $C_{14}H_{12}O$ requires C, 85.68; H, 6.16%)

<u>12. Cyclisation of the dicarboxylic acid (XXIII) using benzoyl chloride.</u>

The dicarboxylic acid (5 g.) was dissolved in benzoyl chloride (30 ml.) and nitrobenzene (20 ml.), and the mixture held at 100°. Concentrated sulphuric acid (ca. 0.5 ml.) was added dropwise, and the temperature

allowed to rise to 200°. When all the sulphuric acid had
been added, the mixture was evaporated to 30 ml. and
60 ml. glacial acetic acid added. This gave a precipitate
which was filtered off, boiled in dilute ammonia solution,
filtered off again and dried. The product was extremely
soluble in xylene, and could not satisfactorily be
crystallised for analysis. It was submitted crude to
reduction. Yield (crude) 3 g. or 65% theoretical.

The method was repeated several times on twice this
scale.

13. Reduction of the condensation product obtained in 12 above, by zinc dust melt.[6]

The crude cyclisation product (3 g.) from the above
cyclisation was powdered with 7 g. zinc dust and 5 g.
sodium chloride. Zinc chloride (20 g.) was added,
followed by 0.2 ml. water. The mixture was fused and the
temperature raised to a maximum of 310°. On cooling to
100°, dilute acetic acid (100 ml.) was added, the mass
broken up and filtered off. The residue was boiled with
concentrated hydrochloric acid to remove excess zinc dust,
filtered, washed with dilute ammonia solution and dried.

The crude reduction product thus obtained was

extracted with benzene and chromatographed on alumina using petroleum ether (b.p. 60-80°) plus 30% benzene as eluant, but failed to crystallise. It was always found necessary to rechromatograph the product on active, methanol washed alumina, when a small amount of yellow hydrocarbon was obtained. From a total of 12 g. of crude cyclisation product, there was obtained 0.02 g. (ca. 0.2% theoretical) of yellow hydrocarbon, m.p. 228 - 229°. (Found: C, 94.40; H, 5.48 $C_{24}H_{16}$ requires C, 94.70; H, 5.30%).

This same hydrocarbon was obtained in the studies discussed in Part 3, (page 40, experimental page 100), as a colourless compound. The repeated chromatography to which this <u>yellow</u> compound was submitted failed to remove the yellow colour; also the ultra-violet absorption spectrum of the yellow sample showed two peaks in the visible (at 450 and 425 mµ in alcohol) not shown in the spectrum of the colourless sample. The absorption spectrum of the colourless sample was taken to be the better, and is in consequence the one shown (page 43).

14. <u>Cyclisation of the dicarboxylic acid (XXIII) using</u>
    <u>phosphorus pentoxide in nitrobenzene.</u>

The dicarboxylic acid (XXIII) (5 g.) was dissolved in

nitrobenzene (50 ml.) and the solution heated to 130°.
With vigorous mechanical stirring, phosphorus pentoxide
(15 g.) was added in 3 g. portions, the colour of the
solution changing to green, then violet, then brown.
The entire reaction took about 10 minutes. The mixture
was treated with water (100 ml.) and the nitrobenzene
steam-distilled off. The dark residue was filtered off,
boiled with dilute ammonia solution, filtered off again
and dried. Weight of crude material obtained, 4.1 g.

Recrystallisation of a portion twice from xylene
gave red-brown needles, m.p. 270 - 280°(d). The dark
nature of this compound did not enable a sharp melting
point to be observed. (Found: C, 86.77; H, 3.74.
$C_{24}H_{12}O_2$ requires C, 86.74; H, 3.64%). Colour in
concentrated sulphuric acid, red-violet.

The product was soluble in concentrated hydrochloric
acid, giving a red-violet solution.

The method was repeated several times on twice this
scale.

The isomeric $C_{24}H_{12}O_2$ (see discussion, page 33) gave
Found: C, 86.99; H, 4.04 $C_{24}H_{12}O_2$ requires C, 86.74;
H, 3.64%)   m.p. 270 - 280°(d).
Colour in concentrated sulphuric acid, green.

15. Attempted reduction of this cyclisation product (14).

(a) Zinc Dust Melt[6].

The crude cyclisation product (5 g.) was powdered with zinc dust (10 g.) and sodium chloride (10 g.) Zinc chloride (40 g.) was added, followed by 0.3 ml. water. The mixture was fused and the temperature raised to a maximum of 310°. On cooling, the mass was treated with hot dilute hydrochloric acid (100 ml.) to remove excess zinc, and filtered off. The residue was further treated with boiling dilute ammonia solution, filtered off, and dried.

The resulting product was only sparingly soluble in benzene, and gave a violet solution in concentrated sulphuric acid. It was identified as consisting almost entirely of starting material by mixed melting point determination with an authentic sample.

(b) Red phosphorus and hydriodic acid at atmospheric pressure.

The cyclisation product (1 g.), recrystallised from xylene, was dissolved in xylene (20 ml.), then red phosphorus (4 g.) and constant boiling hydriodic acid (60 ml.) added. The mixture was set refluxing and a drop of the xylene layer tested from time to time in concentrated

sulphuric acid to observe the rate of disappearance of
starting material, which gave a violet solution in the
acid. After a total of 20 hours, the mixture was cooled,
diluted with water, filtered, and the red phosphorus residue
extracted with boiling xylene. The united xylene layer
and extract were washed well with water and alkaline
sodium hydrosulphite solution to remove iodine. The
xylene was evaporated to small bulk, diluted with benzene
and chromatographed on alumina. Using benzene as eluant,
a small amount of non-crystalline colourless material was
obtained. A dark red band at the top of the column was
partly washed out (benzene containing ½% methanol as
eluant) and was composed mostly of starting material
(identified by comparison with an authentic sample)
together with decomposition products.

(c) Red phosphorus and hydriodic acid in a sealed tube.

The crude cyclisation product (4.75 g.), red
phosphorus (3.35 g.) and constant boiling hydriodic acid
(20 ml.) were heated together in a large sealed Carius
tube for 12 hours at 200°. After opening of the tube, the
dark solid was filtered off, dried, and extracted with
benzene. This benzene solution was washed with alkaline

sodium hydrosulphite solution, dried, evaporated to small
bulk, and chromatographed on alumina, when, using
petroleum ether (b.p. 60-80°) containing 20% benzene as
eluant, there was obtained ca. 0.07 g. of colourless
solid, which on attempted sublimation, formed a glass and
failed to sublime at 350° and 10^{-2}mm. pressure.

On further elution of the column a trace of brown
solid was obtained, which failed to crystallise and was
not investigated further.

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P A R T   3.

1.   1:2-di-(1-naphthoyl)-ethylene (XLIII).

A mixture of naphthalene (110 g.) anhydrous aluminium chloride (120 g.) and dry benzene (200 ml.) was cooled to 0° in a 2 litre flask. Fumaryl chloride (61 g.) was added dropwise over a period of 3 hours, the temperature being retained below 10°. A red colour developed. The mixture was poured into ice and hydrochloric acid, and the whole boiled. The benzene and excess naphthalene were steam-distilled off leaving a dark oil which partly solidified on cooling. The aqueous layer was decanted off and the oil washed by decantation with hot water. The tarry residue was shaken for a few hours with 350 ml. ether, when it crystallised and could be filtered off and

washed with ether, giving brown-yellow needles, a portion
of which was recrystallised from glacial acetic acid as
yellow needles, m.p. 141-143°. Yield, 31 g. or 11%
theoretical. Further identified by mixed melting point
determination with an authentic sample supplied by
Dr. E. Clar.

2.   1:2-Dibromo-1:2-di-(1-naphthoyl)-ethane (XLIV).

1:2-Di-(1-naphthoyl)-ethylene (XLIII) (25 g.) was
dissolved in glacial acetic acid (300 ml.) at 80°.
Bromine (18 g.) was dropped in slowly with stirring, and
the solution cooled, when the dibromo- derivative crystallised
out as pale brown needles. These were filtered off and
washed with ether, m.p. 173 - 175°. Yield, 32 g. or
87% theoretical. Further identified by mixed melting
point determination with an authentic sample supplied by
Dr. E. Clar.

3.   Cyclisation of (XLIV).

(a)   Using 5 aluminium chloride to 1 sodium chloride.

Powdered anhydrous aluminium chloride (100 g.) and
sodium chloride (20 g.) were melted together and allowed
to cool. The dibromo- derivative (XLIV) (10 g.) was added

and the whole remelted (maximum temperature 150°) for

3 minutes with efficient stirring. The mass was cooled,

decomposed by pouring into ice and concentrated hydrochloric

acid, and the resulting dark solid filtered off, boiled

with dilute ammonia solution, filtered off, and dried.

The cyclisation product was extracted from the crude

reaction product as its vat :-

The crude product was boiled with 500 ml. water

containing 10 ml. concentrated sodium hydroxide solution,

and sodium hydrosulphite (5 g.) was added gradually. The

solution, now deep blue, was filtered, and the residue

extracted three times more as above. The combined blue

filtrates were the solution of the vat. Air was blown in

till the vat was oxidised and the blue colour vanished.

The precipitated, crude quinone was filtered off and used

thus for reduction. Yield, 0.1 g. or 1.7% theoretical.

(b) <u>Using an equimolecular ratio of aluminium chloride -</u>

<u>sodium chloride.</u>

Powdered anhydrous aluminium chloride (8.9 g.) and

sodium chloride (4 g.) were melted together as above.

The dibromo- derivative (XLIV) (1 g.) was added and the

whole remelted, maximum temperature, 150°, for 10 minutes.

The initial bright red colour darkened to brown. The cyclisation product was worked up and extracted as above (3a). Yield, 0.1 g. or 17% theoretical.

4.   Reduction of the product obtained in 3 using zinc dust melt.[6]

The crude quinone (1.2 g.) was powdered with zinc dust (2 g.) and sodium chloride (2 g.). Anhydrous zinc chloride (8 g.) was added together with 0.1 ml. water, and the whole melted with stirring. The maximum temperature was 310°. On cooling, the mass was treated with hot dilute hydrochloric acid (100 ml.) as usual, filtered off, boiled with dilute ammonia solution, and filtered off and dried.

The crude reduction product was extracted with benzene and chromatographed on alumina. Using petroleum ether (b.p. 40-60°) containing 30% benzene as eluant, colourless crystals were obtained, m.p. 228 - 230°, giving no colour in concentrated sulphuric acid. (Found: C, 94.42; H, 5.35 $C_{24}H_{16}$ requires C, 94.70; H, 5.30%). Yield, 0.03 g. or ca. 27% theoretical. This hydrocarbon was shown to be identical with $C_{24}H_{16}$ obtained in Part 2 (see page 40) by mixed melting point determination, and by comparison of their absorption spectra.

5. Dehydrogenation of this hydrocarbon $C_{24}H_{16}$.

The hydrocarbon $C_{24}H_{16}$ (from 4 above) (6 mg.) was sublimed in a current of carbon dioxide through 20% palladised charcoal at 310° and 0.5 mm. pressure giving a green hydrocarbon. The amount obtained (estimated ca. 2 mg.) made it impossible to recrystallise this hydrocarbon for analysis. It was dissolved in alcohol and its absorption spectrum recorded, (at unknown ϵ).

6. Condensation product (leading to dinaphtho-azulene) (LV).

Naphthalene (130 g.) was dissolved in dry chlorobenzene (300 ml.) in a 2 litre flask, and fumaryl chloride (60 g.) added. A yellow colour developed. Powdered anhydrous aluminium chloride (140 g.) was added gradually with constant swirling of the contents of the flask over half an hour. During the course of the vigorous reaction, hydrogen chloride was evolved and the reactants, though very dark, became brown with green tinges. The reactants were heated for a further half hour on the water-bath, allowed to cool, and poured into ice and hydrochloric acid, then heated to ca. 90°. The mixture was diluted with one litre of water and transferred to a large (diameter 20 cm.) Buchner funnel and the solid

filtered off and washed with 1.5 litres of warm xylene. The residue was finally washed with ethanol and dried. Yield, from 11 to 15 g. or ca. 7% theoretical.

Recrystallisation of a portion from 1:2:4-trichloro-benzene gave red-brown needles, which did not melt below 450°, but the dark nature of the crystals did not enable any decomposition point to be observed. (Found: C, 85.00; H, 4.03 $C_{24}H_{14}O_2$ requires C, 86.20; H, 4.22%). Colour in concentrated sulphuric acid, deep blue with blood red fluorescence.

Boiling in the minimum quantity of glacial acetic acid gave brown needles of the diacetyl derivative (LVI). It was also difficult to determine the exact decomposition point of this compound because of its dark colour, but decomposition takes place ca. 234°. (Found; C, 80.98; H, 4.19 $C_{28}H_{18}O_4$ requires C, 80.40; H, 4.30%). Colour in concentrated sulphuric acid, deep blue with blood red fluorescence.

The above condensation reaction could be repeated between fumaryl chloride and 1-methylnaphthalene, with no variation in procedure. Yields however, increased to 15% theoretical. Colour in concentrated sulphuric acid was

deep blue with blood red fluorescence.

Condensation of fumaryl chloride with 1-chloronaphthalene,
to give 1:2-di-(5-chloro-1-naphthoyl)-ethylene (LXVIII).

Distilled 1-chloronaphthalene (231 g.) and fumaryl
chloride (105 g.) were dissolved in chlorobenzene (300 ml).
Anhydrous aluminium chloride (240 g.) were added gradually
and the temperature allowed to rise to ca. 90°. A deep
brown colour developed and the reactants were heated for
1 hour on the hot-plate. The mixture was cooled and
decomposed by pouring into ice and hydrochloric acid,
and heated to boiling point. Water (1 litre) was added
and the whole transferred to a large Buchner funnel and
the solid material filtered off and washed with xylene.
Recrystallisation of the dark material twice from
nitrobenzene, and once more from glacial acetic acid,
gave pale yellow needles, m.p. 226°. (Found: C, 70.94;
H, 3.58; Cl, 17.71 $C_{24}H_{14}O_2Cl_2$ requires C, 71.12;
H, 3.48; Cl, 17.50%). Colour in concentrated sulphuric
acid, deep violet, which on heating became green.

7. Dihydrodinaphtho-azulene (LIV).

The crude condensation product (LV) (10 g.) was

powdered with zinc dust (20 g.) and sodium chloride (20 g.).
Anhydrous zinc chloride (80 g.) was mixed with these and
water (0.3 ml.) added. The reactants were heated with
constant stirring to a maximum temperature of 310° at
which temperature there was vigorous effervescence, and
the neck of the flask was plugged lightly with cotton
wool to minimise loss by sublimation. When the melt had
become tranquil, (after about 5 minutes), the reactants
were allowed to cool to 100°, when boiling 20% aqueous
acetic acid (100 ml.) was added to dissolve most of the
zinc salts. The insoluble matter was filtered off and
treated with concentrated hydrochloric acid to remove
zinc dust, filtered again and boiled with dilute ammonia
solution, and finally filtered off and dried. Yield of
crude product, from 8 to 12 g.

The crude reduction product was sublimed in a current
of carbon dioxide at 250° and 0.5 mm. pressure, and the
dark yellow sublimate scraped out and washed with a little
ether. The yield of crude dihydrodinaphtho-azulene thus
obtained was variable, dependent on the variable composition
of the crude condensation product (LV), and ranged from
1 g. (ca.10% theoretical) to 0.2 g. (ca. 2% theoretical).

Recrystallisation from benzene or xylene, or

chromatography on alumina (using petroleum ether (b.p. 60-80°) containing 30% benzene as eluant) gave bright yellow plates, m.p. 236 - 237°. (Found: C, 94.84; H, 5.21 $C_{24}H_{16}$ requires C, 94.70; H, 5.30%). Colour in concentrated sulphuric acid, red, rapidly becoming violet on standing or heating.

This reduction method was repeated on the corresponding dimethyldinaphtho-azulene condensation product, yielding dihydrodimethyldinaphtho-azulene, m.p. 214°. Yield (best) 15% theoretical. Colour in concentrated sulphuric acid, violet.

8.   Dinaphtho-azulene (LIII).

Dihydrodinaphtho-azulene (LIV) (0.2 g.) (sublimed, ether washed material) was dissolved in boiling nitrobenzene (10 ml.) and iodine (5 g.) added. The excess iodine was driven off and the solution cooled and filtered. The residue was washed well with ether and dried; dec. above 200°. (Found: C, 44.76; H, 2.50 $C_{24}H_{14}I_3$ requires C, 42.07; H, 2.35%. Iodine; Found, 53.28. Required, 55.58%) Colour in concentrated sulphuric acid, violet.

The iodine complex was sublimed either alone or with the addition of a small amount of copper powder at 250° and

the green dinaphtho-azulene sublimed out. It was
recrystallised from xylene or 1:2:4-trichlorobenzene in
glistening, dark green platelets, which decomposed ca.300°,
but the decomposition point is indefinite because of the
dark colour of the crystals. Yield, 0.07 g. or 30%
theoretical. It dissolved in sulphuric, hydrochloric,
or acetic acid giving violet solutions, which could be
characterised by a very intense absorption band at
580 mμ.[16,17]

This dehydrogenation method was repeated on
dihydrodimethyldinaphtho-azulene, giving dark green plates
of dimethyldinaphtho-azulene (LXVI), again decomposing
ca. 300°. Colour in sulphuric, hydrochloric, or acetic
acid, also violet, with an intense absorption band at
601 mμ.

Considerable decomposition occured on sublimation
of dimethyldinaphtho-azulene.

9. The octahydro- and dodecahydro- derivatives

The crude condensation product (LV) (2.5 g.) was
ground together with red phosphorus (0.7 g.) and
introduced into a large Carius tube with constant boiling
hydriodic acid (10 ml.). The sealed tube was heated at

200° for 8 hours, and on opening, the contents were diluted with water and the dark solid mass broken up and filtered off. This mass was extracted several times with dry benzene (200 ml.) which was washed with alkaline sodium hydrosulphite solution, water, and then dried. The solution was evaporated to small bulk and chromatographed on alumina.

(a) Using petroleum ether (b.p. 40-60°) containing 5% benzene as eluant, colourless plates of the dodecahydro-dinaphth-azulene (LVIII) were obtained, m.p. 178 - 180°. The amount obtained was 0.02 g. (Found: C, 91.72; H, 8.13 $C_{24}H_{26}$ requires C, 91.64; H, 8.35%). Colourless in concentrated sulphuric acid, and on heating changed through green to red with red fluorescence.

(b) Using petroleum ether (b.p. 40-60°) containing 30% benzene as eluant, colourless plates of the octahydro-dinaphtho-azulene (LVII) were obtained (0.06 g.), m.p. 208°. (Found: C, 93.08, 92.81; H, 7.00, 7.26: $C_{24}H_{22}$ requires C, 92.85; H, 7.15%). In concentrated sulphuric acid it dissolved slowly giving a colourless solution which on standing or warming changed through violet to red with red fluorescence.

(c) Using petroleum ether (b.p.40-60°) containing 50%

benzene as eluant, yellow crystals of dihydrodinaphtho-
azulene (LIV) were obtained, m.p. 237°, and identified
by mixed melting point determination with an authentic
sample.

10. Dehydrogenation of the octahydro- and dodecahydro-
derivatives.

The octahydro- derivative (LVII) (0.015 g.) was
sublimed in a current of carbon dioxide through 20%
palladised charcoal at 310° and 0.1 mm. pressure. The
green dinaphtho-azulene (LIII) was produced and identified
by its characteristic formation of violet solutions in
common acids. The amount of dinaphtho-azulene obtained
was ca. 0.007 g.

The dodecahydro- derivative was dehydrogenated by
the same method with similar results.

11. Maleic anhydride adduct (LXVI).

Dihydrodinaphtho-azulene (LIV) (0.1 g.) was dissolved
in boiling nitrobenzene (10 ml.) with maleic anhydride
(5 g.) and iodine (20 mg.). The solution was refluxed
for 1 hour, poured into hot xylene (20 ml.), and the
precipitated solid filtered off and dried. The adduct

was recrystallised from nitrobenzene and washed well with
benzene.   Softens 220°, dec. above 250°.

(Found: C, 73.99, 72.98; H, 2.52, 3.15 $C_{36}H_{12}O_9$ requires
C, 73.47; H, 2.06%).

The equivalent weight of the adduct was determined
by dissolving in excess standard alkali and back-
titrating with standard acid. A pH meter (glass electrode)
was used to follow the titration, and a graph was constructed
showing the variation in pH throughout the titration.
The slope of the curve was fairly steep, and the
equivalence point was taken to lie near the steepest part.
Equivalent weight, Found, 94.5 - 98.5: Calculated for
the tri-adduct $C_{36}H_{12}O_9$, 98.06 .

12.   1:2-Dibromoacenaphthene (LXX).

This was prepared by the addition of bromine to
acenaphthylene (Blumenthal, **Ber**., **7**, 1093.)

13.   Attempted preparation of 1:2-dicyanoacenaphthene (LXXI).

(a) Cuprous cyanide (2 g.) dried at 110° was added to
dibromoacenaphthene (LXX) (3 g.) in 75 ml. of solvent
(dry ethanol, benzene, and xylene were used in succession)
and the mixture refluxed for one hour, after which the
solution was filtered from cuprous cyanide and

evaporated to dryness. In no case was there produced a nitrogen-containing material. The residue after evaporation was composed of starting material and bromoacenaphthylene (produced by elimination of hydrogen bromide from dibromoacenaphthene in boiling solvents [25]).

(b) Potassium cyanide replaced cuprous cyanide in the above, and no replacement of bromo- by nitrile- occured in benzene or xylene. In ethanol solution, there was produced a heavy oil which was distilled twice (b.p. 224° at 10^{-2}mm. pressure). The analysis results (C, 65.48; H, 4.98; Br, 24.21%) could not satisfactorily be ascribed to any structure. No nitrogen-containing derivative was isolated.

14. Attempted preparation of dilithium acenaphthene.

Dibromoacenaphthene (LXX) (3 g.) was added to lithium metal (0.2 g.) and 100 ml. dry solvent (ether, benzene, and xylene were used in succession) in a nitrogen atmosphere. The mixture was refluxed for from 4 to 8 hours in each case, but approximately the same weight of lithium was recovered, together with starting material.

15. Bromomaleic anhydride (LXXIV).

This was prepared by addition of bromine to
maleic anhydride giving dibromosuccinic anhydride,
followed by dehydrobromination (by the action of heat at
ca. 150°) to bromomaleic anhydride[26].

16. Attempted preparation of 1-naphthylmaleic anhydride
(LXXV).

Naphthalene (26 g.) and bromomaleic anhydride (LXXIV)
(35 g.) were dissolved in tetrachloroethane (100 ml.), and
anhydrous aluminium chloride (30 g.) was added over 1 hour,
with constant shaking and cooling to keep the temperature
below 20°. After shaking for a further hour, the
initially red solution became brown. The mixture was
poured into ice and hydrochloric acid and the solvent
and excess naphthalene steam-distilled off, leaving a
dark oil which solidified on cooling (10 g.). It was
dissolved with difficulty in a large amount of benzene
and on evaporation of the solution to small bulk, fawn
plates crystallised out, m.p. 155 - 156°. (Found: C, 74.27;
H, 4.54 calculated for $C_{14}H_{10}O_3$ C, 74.33; H, 4.46%)
Equivalent weight (titration with standard sodium
hydroxide) Found, 220. Calculated for a monocarboxylic

acid, 226.

β-(2-naphthoyl)-acrylic acid, m.p. 166 - 167°.

β-(1-naphthoyl)-acrylic acid, m.p. 148 - 149° [27].

From the above data, it was concluded that the acid $C_{14}H_{10}O_3$ was β-(2-naphthoyl)-acrylic acid, together with a little of the 1-naphthoyl- isomer.

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B I B L I O G R A P H Y .

1. Clar and Stewart, J.Amer.ChemSoc., 1953, 75, 2667;
    1954, 76, 3504.

2. Clar, "Aromatische Kohlenwasserstoffe", Springer-
    Verlag, Berlin, 1st Edition, 1941, p. 311.

3. Longuet-Higgins, J.Chem.Phys., 1950, 18, 265.

4. Claus and Burstert, J.pr.Chem., 1890, 41, 560 et seq.

5. Description and physical constants given - idem, loc.
    cit.

6. Clar, Ber.,1939, 72, 1645.

7. Clar, op. cit., 2nd Edition, p. 394.

8. Clar, op. cit., 2nd Edition, p. 204.

9. Clar and Lombardi, Gazzetta, 1932, 62, 541.

10. Tucker, Analyst, 1939, 64, 410; 1942, 67, 320; 1950,
    75, 170. Chem.and Ind., 1945, 270.

11. Clar, <u>Ber</u>., 1939, <u>72</u>, 1817; Marschalk, <u>Bull. Soc</u>. <u>chim</u>., 1939, (5), <u>6</u>, 1112.

12. Clar and Marschalk, ibid., 1950, <u>17</u>, 444.

13. Schmidlin and Massini, <u>Ber</u>., 1909, <u>42</u>, 2381.

14. Lund, ibid., 1934, <u>67</u>, 935.

15. Clar, ibid., 1943, <u>76</u>, 462.

16. Clar, private communication, published in outline in "Aromatische Kohlenwasserstoffe" 2nd Edition, p. 387 et seq.

17. Stewart, Ph.D. Thesis, Glasgow University, 1953.

18. Clar, Lang and Schultz-Kiesow, <u>Ber</u>., 1955, <u>88</u>, 1520.

19. Blood and Linstead, <u>J.C.S</u>., 1952, 2263.

20. Heilbronner, Plattner et al., <u>Helv.Chim.Acta</u>, 1952, <u>35</u>, 1036, 1049, 2170.

21. Baker, McOmie, and Norman, <u>J.C.S</u>., 1951, 1114.

22. Prelog and Schenker, <u>Helv.Chim.Acta</u>, 1953, <u>36</u>, 1181.

23. Forrester, private communication.

24. Kasha, <u>Discuss.Faraday Soc</u>., 1950, <u>9</u>, 17.

25. Blumenthal, <u>Ber</u>., 1874, <u>7</u>, 1093.

26. Kirchhoff, <u>Annalen</u>, 1894, <u>280</u>, 207.

27. Martin and Stoffyn, <u>Bull.Soc.chim.Belg</u>., 1950, <u>59</u>, 83.

28. Gilman, <u>J.Amer.Chem.Soc</u>., 1951, <u>73</u>, 5879.

29. Newman and Zahm, ibid., 1943, <u>65</u>, 1099.