THE FORMATION OF AROMATIC HYDROCARBONS

AT HIGH TEMPERATURES.

A THESIS

PRESENTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE

ORGANIC CHEMISTRY DEPARTMENT

OF THE

UNIVERSITY OF ADELAIDE

by

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ACKNOWLEDGMENTS.

STATEMENT

The study of "The Formation of Aromatic Hydrocarbons at High Temperatures", as a whole, is being carried out by several workers in the Organic Chemistry Department of the University of Adelaide; however, this thesis contains no material previously submitted for a degree in any University, either by myself, or by any other person, except where due reference is made.

<div style="text-align: right;">

Ronald W.L. Kimber.

1959.

</div>

PUBLICATIONS

Most of the work in this thesis has been published in the following papers:

1. The Formation of Aromatic Hydrocarbons at High Temperatures. Part I. Introduction. *J. Chem. Soc.*, 1958, 2449.

2. The Formation of Aromatic Hydrocarbons at High Temperatures. Part II. An Examination of "Schroeter Tar". *J. Chem. Soc.*, 1958, 2453.

3. The Formation of Aromatic Hydrocarbons at High Temperatures. Part III. The Pyrolysis of 1-4'-Phenylbutylnaphthalene. *J. Chem. Soc.*, 1958, 2455.

4. The Formation of Aromatic Hydrocarbons at High Temperatures. Part VI. The Pyrolysis of Tetralin. *J. Chem. Soc.*, in the press.

5. The Formation of Aromatic Hydrocarbons at High Temperatures. Part VII. The Pyrolysis of Indene. *J. Chem. Soc.*, in the press.

CONTENTS

CHAPTER I

INTRODUCTION

The aim of the work described in this thesis was to investigate the mode of formation of aromatic hydrocarbons at high temperatures by pyrolysis of simpler hydrocarbons. It was hoped that a greater understanding of the complex reactions which takes place during tar formation would be gained from this work.

In particular, the mechanism of the formation of the carcinagenic hydrocarbon 3:4-benzopyrene, at high temperatures, has been examined.

General Discussion

It has been known for some years, from studies of the composition of coal tar formed in gas works' retorts and coke ovens, that various pyrolytic processes occur during the formation of the tar, which are dependant to a large extent on the temperature at which the tar is formed.

For example, low temperature tars (i.e. 425-550°) and "Primary" tar (tar which is first formed in the retort at low temperatures) consist mainly of paraffin

hydrocarbons, cycloparaffins, olefins, and phenols. At
higher temperatures (600-800°) these compounds are
dehydrogenated, rearranged, and condensed to give a
"Secondary" tar containing a greater amount of aromatic
polycyclic hydrocarbons.   Evidence of this has been given
by various workers.   Mantel and Hansen[1] have shown that
diphenylmethane, diphenyl and ethylene, and 1:8-dimethyl-
naphthalene, all of which are present in "Primary" retort
tar, when pyrolysed under similar conditions in the
laboratory give fluorene, phenanthrene and acenaphthene
(reactions 1, 2, and 3), all of which have been isolated
from "Secondary" (i.e. high temperature) retort tars.

$$\text{......... (3)}$$
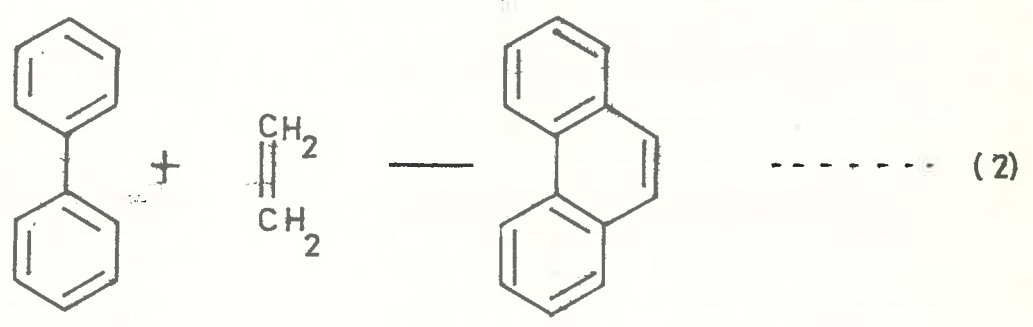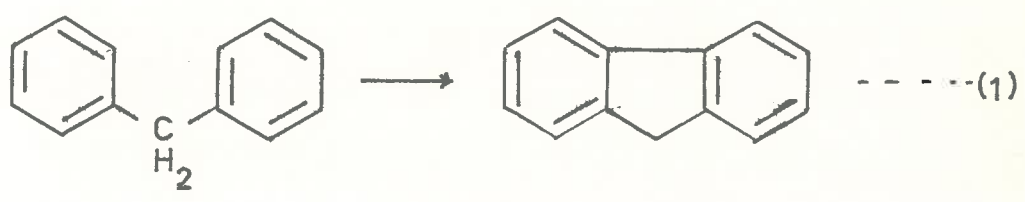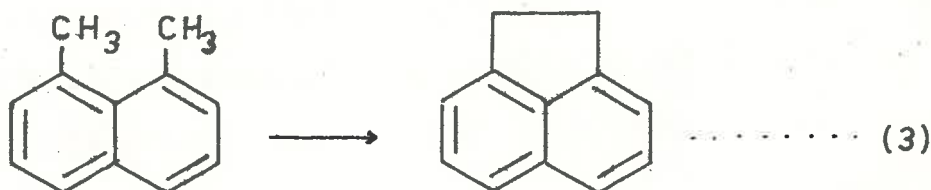
Several workers have suggested that the formation of polycyclic compounds involves the initial breakdown of complex molecules to more simple ones. Groll[2] assumes that the breakdown continues right down to acetylene before resynthesis commences. He suggests that the primary intermediate from which all the higher hydrocarbons are eventually formed is the diradical of acetylene. On the other hand, Weizmann et al.[3] assume that butadiene (or derivatives of it) is the fundamental unit. Their suggestion is that the resynthesis follows almost entirely a Diels-Alder type addition and is based on the results of various workers[4,5,6] (e.g. Hague and Wheeler have shown evidence of the formation of butadiene and butylene from the pyrolysis of ethylene at low temperatures, while at higher temperatures reasonable yields of benzene and naphthalene were obtained. - reaction 4).

$$\text{CH}_2=\text{CH} \longrightarrow \text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH} \longrightarrow + \text{CH}_2=\text{CH}$$

$$\longrightarrow \qquad \cdots\cdots\cdots\quad (4)$$
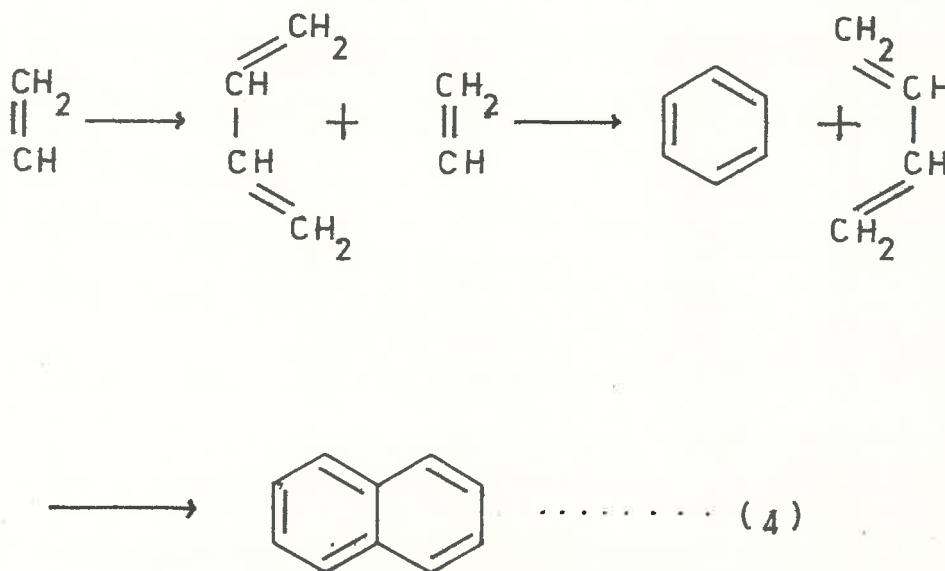
Weizmann extends this to explain the presence of
phenanthrene, anthracene, 1:2-benzanthracene, and
triphenylene by Diels-Alder addition of butadiene to
naphthalene and phenanthrene, in his pyrolysis of a
hydrocarbon oil.   At first glance this mechanism seems
very reasonable.   Closer examination, however, shows it
to be relatively unlikely.   As Diels-Alder addition to
the very reactive 9:10 bond of phenanthrene would be
expected to occur very readily, the yield of triphenylene
should be quite large.   Not only is the yield in this
case small, but also in the pyrolysis of butylbenzene,

which gives a large yield of phenanthrene, very little triphenylene[7] is obtained.   Furthermore, Weizmann also suggests that pyrene is formed from tetramerisation of butadiene, or dimerisation of styrene (reaction 5).
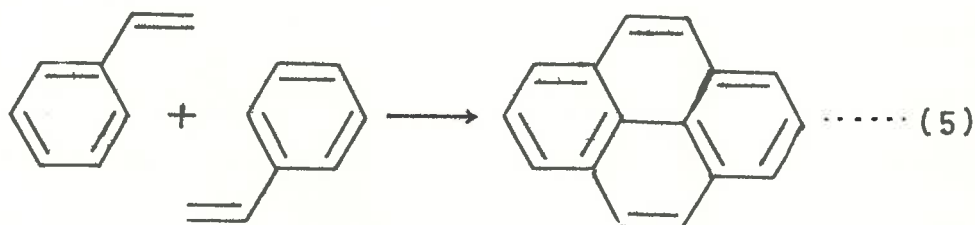
This has been shown to be most unlikely by Badger and Buttery[8], who have pyrolysed styrene and obtained only a very small amount of pyrene.

Only in pyrolyses where butadiene can easily be formed, (e.g. the pyrolysis of 1-phenylbuta-1:3-diene[9]) is much triphenylene found.   Even here the yield is not high, and the suggestion is that triphenylene is formed by free radical attack of a butadienyl radical (formed by fission of the carbon-carbon bond between the ring and the butadienyl side-chain) on the 9-position of phenanthrene, followed by cyclisation, rather than by a Diels-Alder mechanism.

Steiner[10] says the condensation of naphthalene and

butadiene gives a small yield of phenanthrene. One
would then expect to obtain large yields of naphthalene
compared with phenanthrene. However, the pyrolysis of
propylbenzene[7] and ethylbenzene[7] give greater yields of
phenanthrene.

It would seem, therefore, that even when butadiene
can be readily formed from carbon-carbon fission or by
dehydrogenation (e.g. from butane) Weizmann's proposed
mechanism seems most unlikely. Where the formation of
butadiene does not involve the breaking of a benzene ring
(as it is very stable to pyrolysis[11]) a Diels-Alder type
addition could play some part. In this regard the
pyrolysis of butadiene by Murphy and Duggan[12] gives only
a small yield of styrene.

Quite apart from these considerations, the results
as judged from the pyrolysis of complex hydrocarbon oils
must surely be open to question. Much interaction will
undoubtedly occur not only among the products of cracking,
but also of the original components.

The addition of ethylene (or acetylene diradicals)
to hydrocarbons to form higher aromatics also seems
improbable (e.g. chrysene, or 1:2-benzanthracene and
ethylene to give 3:4-benzopyrene) from evidence gained
from the pyrolysis of tetralin and of indene (Chapter IV).

Interpretation of Results

Care must be taken when evaluating results obtained from pyrolyses in order to arrive at the most likely mechanisms. The following points should be especially remembered:

(1) When considering the yield of a certain product as a guide to a mechanism, it is necessary to take into account;

(a) the ease of thermal breakdown of the substance pyrolysed compared with that of the particular product in question;

and, (b) the stability of a particular compound of the pyrolysate to further breakdown, or its tendency to react with other molecules; e.g. the absence of phenylbutadiene[9], butylbenzene, and tetralin from most high temperature pyrolyses does not mean that these molecules take no part as intermediates in the synthesis of higher hydrocarbons, due to their ease of dehydrogenation, cyclisation, etc.

(ii) Mechanisms which are the most likely at room temperature, and in low temperature reactions, need not

necessarily apply at high temperatures. At these
temperatures, the molecules are in a highly excited state
and the usually greater reactivities of some positions
in a molecule are likely to be less apparent. It should
be noted too, that steric factors will probably hold
greater sway than electrical effects at these elevated
temperatures.

The Formation of 3:4-Benzopyrene at High Temperatures

The carcinogenic hydrocarbon 3:4-benzopyrene was
isolated from coal tar in 1933 by Cook et al.[13]
Immediately, this was considered to be the cause of
certain "industrial" cancers. In recent years, however,
3:4-benzopyrene and other polycyclic hydrocarbons have
been identified in domestic soot[14], in the soot from a
smoked meat factory[15], in atmospheric dust[16], in
processed rubber[17], in carbon blacks[18], in exhaust gases
of petrol and diesel engines[19], in coal gas[20], in human
hair wax[21], in snuff[22], in tobacco[23], and in cigarette
and tobacco smoke[24]. This widespread occurrence in
everyday enviroment has obvious implications in connection
with the incidence of cancer among the general population,
and it seems important to determine the origin and mode

of formation of such carcinogenic hydrocarbons.

The carcinogenic hydrocarbons in the human enviroment appear to be formed mainly at high temperatures. Low temperature tars have been found to be only slightly carcinogenic, whereas high temperature tars, produced from the same coal, are far more active[25]. Similarly certain petroleums[25], and oil[26] have only become carcinogenic after pyrolysis. The pyrolysis of cholesterol[27], skin[25], yeast[25], isoprene[25,28], acetylene[25], dicetyl[29] and of aliphatic hydrocarbons[30] from tobacco all give tars which are carcinogenic, or from which have been isolated numerous polycyclic aromatic hydrocarbons.

The formation of aromatic hydrocarbons from aliphatic or simpler aromatic compounds, at high temperatures has not been extensively studied. The evidence that is available, however, suggests that the most important reactions may involve:

(i) Cracking, with the formation of free radicals which then undergo termination reactions with themselves or propogation reactions with neutral molecules;

(ii) Dehydrogenation; and

(iii) Cyclodehydrogenation.

A series of such reactions is probably involved in the formation of molecules such as 3:4-benzopyrene, and a feasible route (reactions I - VII) has been proposed as a working hypothesis.
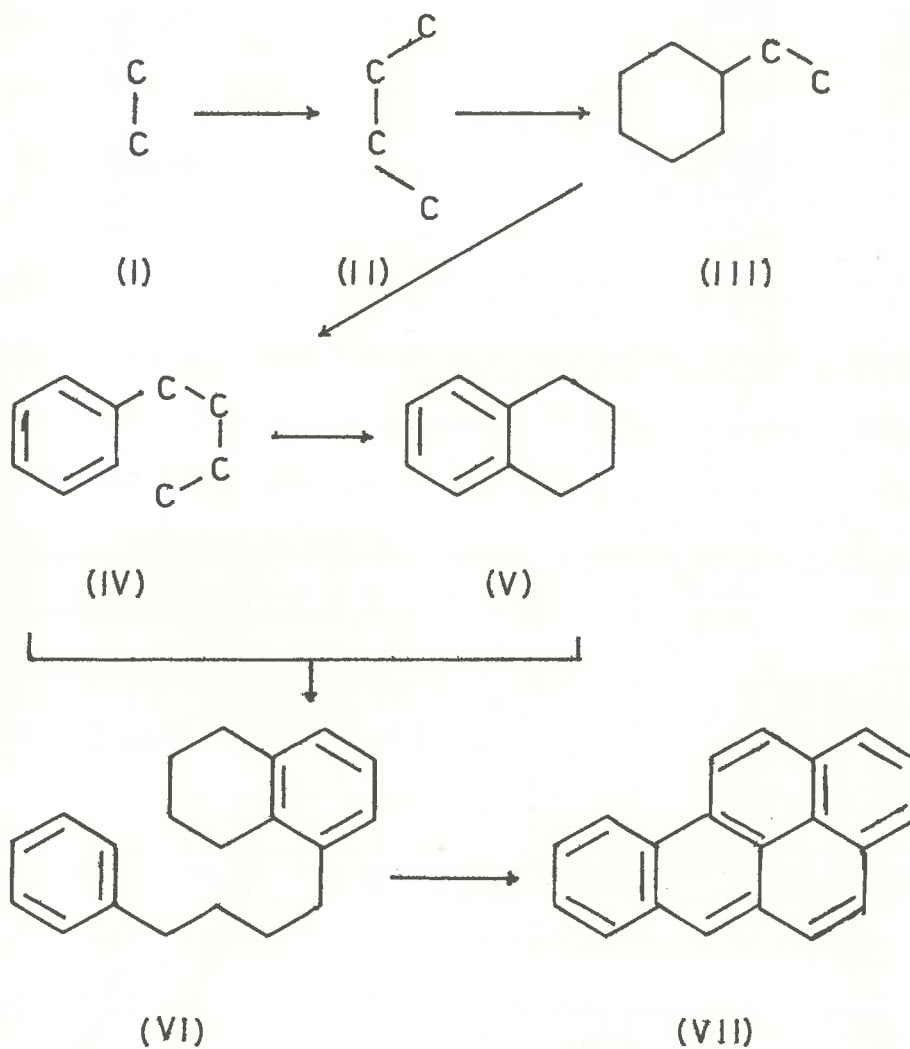
This mechanism presupposes that the benzopyrene will be formed by pyrolysis of any of the intermediate compounds. Pyrolysis of representatives of these intermediates has in every instance produced a tar in which 3:4-benzopyrene could be detected; viz. acetylene[31], styrene[8], ethylbenzene[7], 1-phenylbuta-1:3-diene[9], butylbenzene[7], tetralin (Chapter IV), and 1-4'-phenylbutylnaphthalene (Chapter III).

The degree of hydrogenation of these intermediates would be expected to alter the yield of a given product, and also in some instances, the nature of the products formed by pyrolysis of a compound and its analogous hydrogenated compound. This is borne out by experiment (e.g. phenylbutadiene[9] gives a large yield of naphthalene, while butylbenzene[7] gives less naphthalene, but a much wider range of alkylbenzenes.) The reactions (6) and (7) also occur.

$$\cdots\cdots\cdots (6)$$

$$\cdots\cdots (7)$$
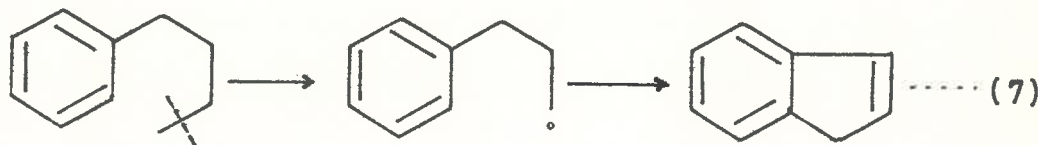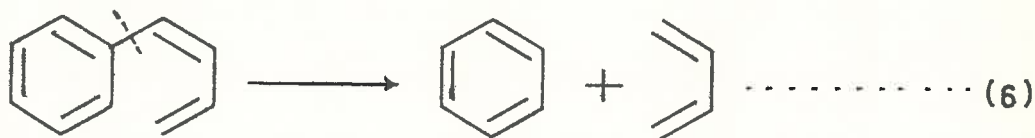
Generally it may be said that where polycyclic compounds are formed merely by cyclisation of the intermediates as such, then the degree of hydrogenation may not be important; but if cracking occurs prior to cyclisation, intermediates with varying degrees of hydrogenation will give rise to different products from cracking, and hence different cyclisation products.

The available evidence, small though it is, does support the view that benzopyrene is formed from simpler units by a stepwise synthesis. The pyrolysis of acetylene (I) is known to give a number of aromatic hydrocarbons[32] and has been shown recently to contain 3:4-benzopyrene[31]. Acetylene and small amounts of vinylacetylene have been detected in tobacco smoke[33]. The pyrolysis of ethylene also gives butadiene (see General Discussion). Butadiene is said to undergo reaction with itself to give vinylcyclohexene[34], and the pyrolysis of butadiene gives some styrene, ethylbenzene, and naphthalene, together with a small amount of tetralin[12]. A clue to the nature of the final steps of the synthesis is provided by the reaction of aluminium chloride on tetralin[35]. The complex tar so formed, becomes carcinogenic when heated[36], and has now been shown

to contain a relatively large amount of 3:4-benzopyrene
(see Chapter II).   6-4'-Phenylbutyltetralin is known to
be a major constituent of the tar[35], and it has been
suggested that some 5-4'-phenylbutyltetralin may also be
present which could readily give 3:4-benzopyrene by
cyclodehydrogenation[37].

While this mechanism was considered useful as a
working hypothesis, it was not suggested that this would
be the only mechanism operating.   Other routes could
involve the reaction of a C_2 unit (e.g. ethylene) and
chrysene or 1:2-benzanthracene; pyrene and a C_4 unit;
various arrangements of two C_6 - C_4 units with initial
attack at different positions; etc.   Evidence does
suggest, however, that ethylene and chrysene, and ethylene
and 1:2-benzanthracene are not important reactions
(Chapter IV); nor can a reaction between a C_4 unit and
pyrene be of general importance as such a reaction would
give rise to 1:2-benzopyrene.   This is rarely found in
pyrolysis reactions, and then only in small yield.
3:4-Benzopyrene could also be formed by breakdown of
larger molecules (e.g. dicetyl[29]) or from two C_{10}
hydrocarbons, such as n-decane[38], by cyclodehydrogenation.

Recent work suggests that styrene may not play a

very important part in the proposed stepwise formation
of 3:4-benzopyrene, as it has been shown to be relatively
stable to pyrolysis; _i.e._ at 550° the reported[39] recovery
of styrene is 99%; at 625°, 95.5%[40]; while at 710°
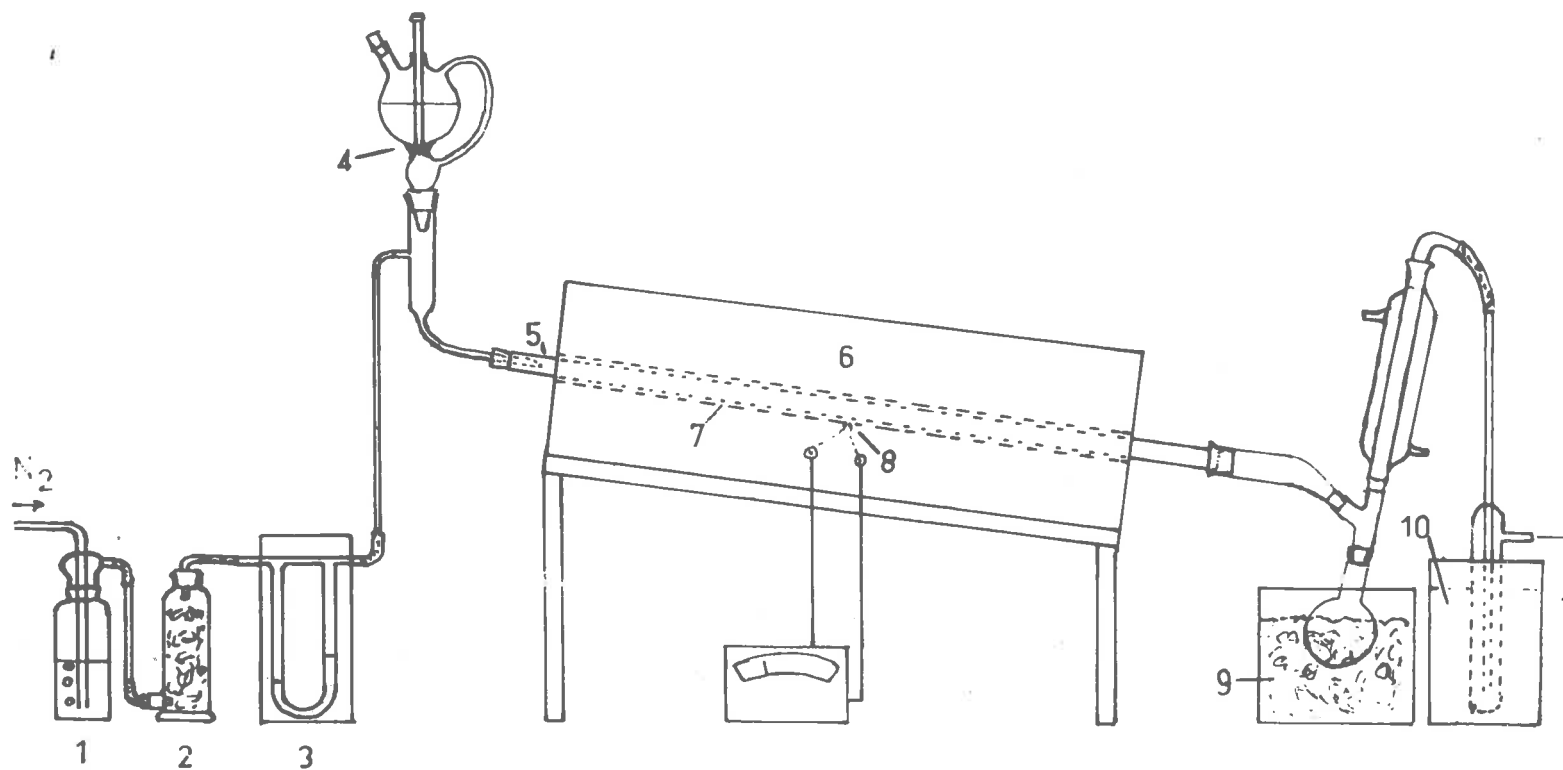approximately 20% is recovered[8].

It must be emphasised that generally it cannot be
stated that the pyrolysis of a compound invariably
proceeds through initial cracking to a fundamental unit,
followed by resynthesis. In fact, this would appear to
be the exception rather than the rule (except perhaps for
aliphatic compounds). The degree and the nature of the
cracking will vary from one compound to another. It
would appear generally, therefore, that cracking,
dehydrogenations, cyclodehydrogenations, etc. all proceed
together. The extent to which cracking occurs before
resynthesis will depend largely on the stability of the
radicals so formed, and on the available reactive species
with which they can react.

The experimental section of this chapter describes
some of the general methods and techniques used in this
work.

EXPERIMENTAL.

The Furnace (Fig. 1·1).-   This consisted of a silica
tube (3 ft. x 1 in. i.d.) wound along its length with
25 s.w.g. nichrome wire having a total resistance of 90
ohms.   A calibrated chromel-alumel thermocouple was
inserted through a hole bored near the centre of the tube.
The tube was mounted along the centre of a pressed
asbestos-board box (3 x 1 x 1 ft.) filled with
"vermiculite".   The material to be pyrolysed was led
through a second silica tube (3 ft. 6 in. x ¾ in. i.d.)
which just fitted into the heated tube.   The furnace
was inclined at an angle of 10^0 to the horizontal to
facilitate collection of the products.   The material to
be pyrolysed was led into the furnace using the device
shown in Fig. 1·1.   The arrangement of the tar collection
apparatus is also shown in this diagram.

Chromatography.-   (i) Gas-liquid partition
chromatography.   The low boiling fractions of the
earlier pyrolyses were examined on the machine built in
this laboratory[41].   However, a Griffin and George Vapour
Phase Chromatograph (Mk. II), adapted to collect
fractions[42], was used in the later work.

PYROLYSIS APPARATUS.

1. H_2SO_4 4. Needle valve   7. Heating tube   10. Dry-ice trap
2. $CaCl_2$ 5. Silica tube   8. Thermocouple
3. Flow-metre   6. Furnace   9. Ice bath
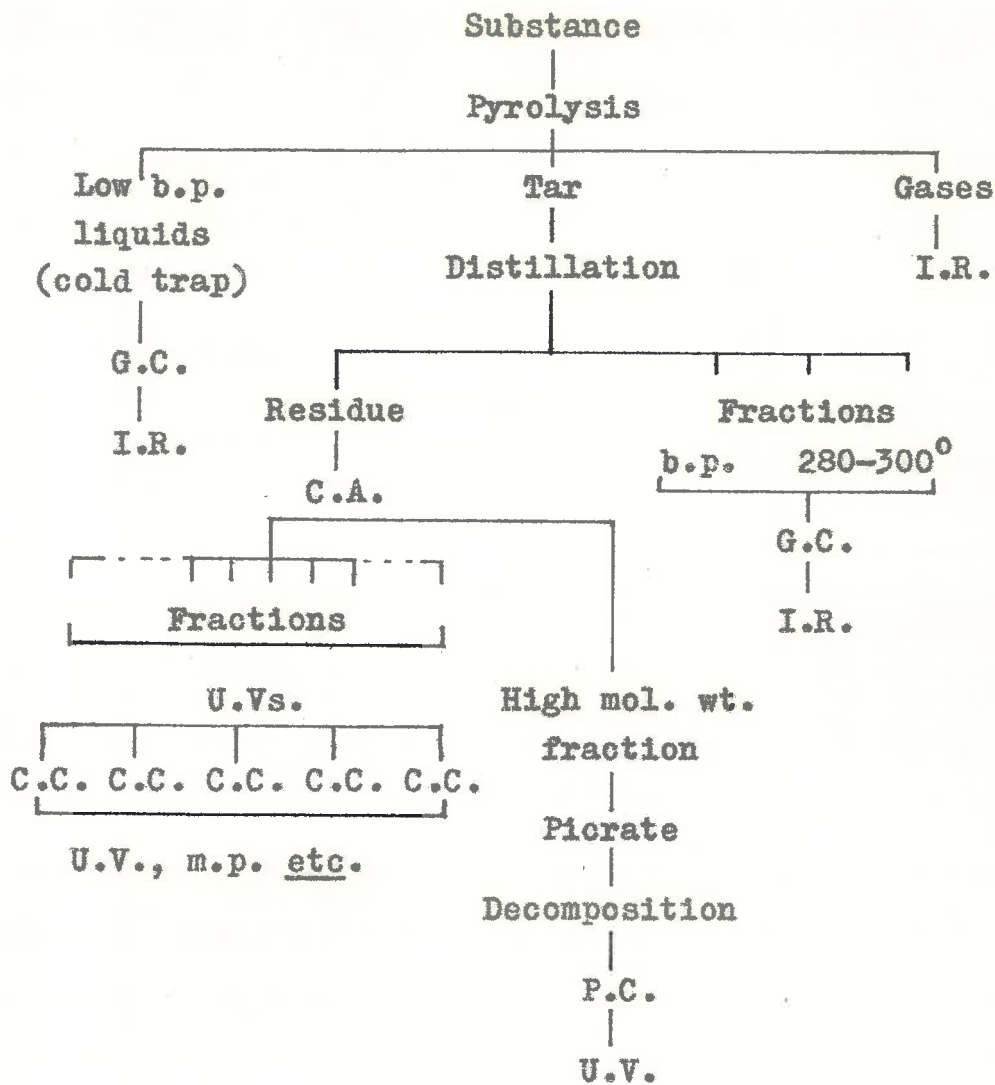
Fig. 1.1.

(ii) <u>On alumina</u>.   B.D.H. alumina activated at 200^0 was generally used, however, in the last pyrolysis, <u>viz.</u> indene, Spence alumina, which is more active, was used. Hexane and/or benzene were generally used as solvents and/or elutants.   The benzene used was thiophen-free while the hexane had been fractionally distilled.

(iii) <u>Paper chromatography</u>.   The partially acetylated paper required was made by the method of Spotswood[43,44].   (This technique was only fully developed very recently and was available only for the examination of the products from the tetralin and indene pyrolyses).

(iv) <u>Chromatography on cellulose acetate columns</u>. Whatman's Standard cellulose powder was acetylated by stirring with benzene, acetic anhydride, and sulphuric acid, also by the method of Spotswood[44].   (This technique was developed in time only for use in the indene pyrolysis).

<u>Identification of Products</u>.-   Generally the following sequence of operations has been found best when attempting to analyse a complex tar.   (It is shown schematically in Fig. 1·2).

The substance was pyrolysed and the products

Substance
|
Pyrolysis

Low b.p.   Tar   Gases
liquids
(cold trap)   Distillation   I.R.

|
G.C.
|
I.R.   Residue   Fractions
                 b.p.   280–300°
        C.A.
                       G.C.
     Fractions
                       I.R.

      U.Vs.   High mol. wt.
                   fraction
C.C. C.C. C.C. C.C. C.C.
                   Picrate
U.V., m.p. etc.
                  Decomposition
                     P.C.
                     U.V.

I.R. = Infrared spectra;   U.V. = Ultraviolet spectra;
G.C. = Gas-liquid chromatography;   C.A. = Column
alumina chromatography;   C.C. = Cellulose acetate
chromatography;   P.C. = Acetylated paper chromatography.

Fig. 1·2.

collected in the manner shown in Fig. 1·1.   Samples of
the exit gases were examined by infrared analysis.   Some
of the low boiling products which were not collected with
the main bulk of the tar, were condensed in a dry-ice/
ethanol trap.   Gas-liquid chromatography of this
material enabled provisional identification from retention
times.   This was confirmed by collection of the fractions
and infrared spectroscopy.   The main bulk of the tar was
distilled and divided into two or three fractions up to
b.p. 280-300°, the components of which were identified
by gas-liquid chromatography and infrared spectroscopy.
The residue was chromatographed on alumina and eluted with
mixtures of hexane and benzene (from pure hexane to pure
benzene).   Ultraviolet spectra of the fractions enabled
many to be combined to give between 5 and 10 main
fractions (e.g. phenanthrene fraction, 1:2-benzanthracene
fraction, chrysene fraction, 3:4-benzopyrene fraction,
etc.).   These were in turn chromatographed (as a whole,
or in part) on columns of cellulose acetate, and the
products identified by their ultraviolet spectrum or
melting point.   The yields were calculated from the
weights of these fractions or from their ultraviolet
spectra.   The very high molecular weight compounds,

which remained on the alumina column, were stripped off with ether, picrates made, and after decomposing with ammonium hydroxide, paper chromatographed.

Occasionally the chromatography on cellulose acetate needed to be followed by paper chromatography to effect a better separation. When a large amount of any one compound was present it was usually most effective to recrystallise this separately and to add the mother liquors to the rest of the fraction for examination as described above.

Ultraviolet Spectra.- These were usually determined in 95% ethanol, using, for the work in Chapters II and III a Hilger Uvispeck Spectrophotometer, and for the work in Chapter IV an Optica CF_4 Spectrophotometer recording instrument, and compared with published curves.

Infrared Spectra.- These were determined with a Grubb-Parsons double-beam instrument. Liquid samples were examined as such, and solids as solutions in carbon tetrachloride. The spectra were compared with published curves, or curves obtained from authentic specimens.

Fluorescence Spectra.- The following apparatus (Fig. 1·3, 1·4, and 1·5), although inexpensive, was found
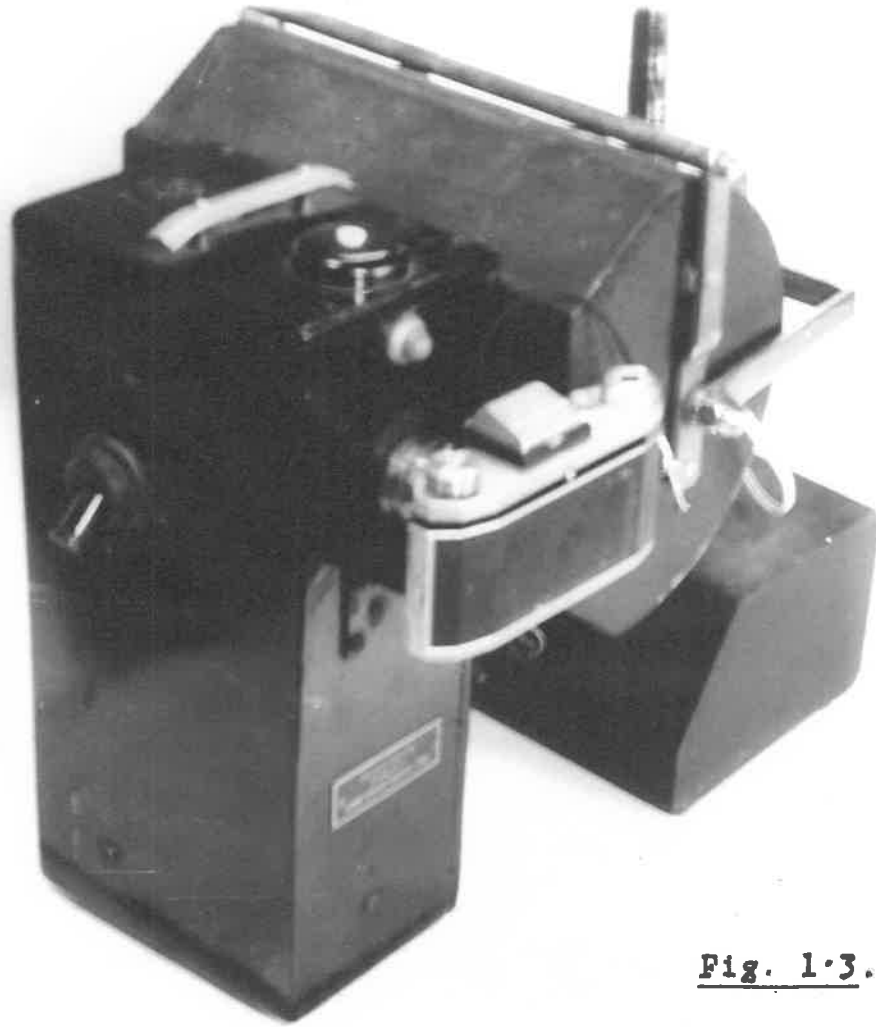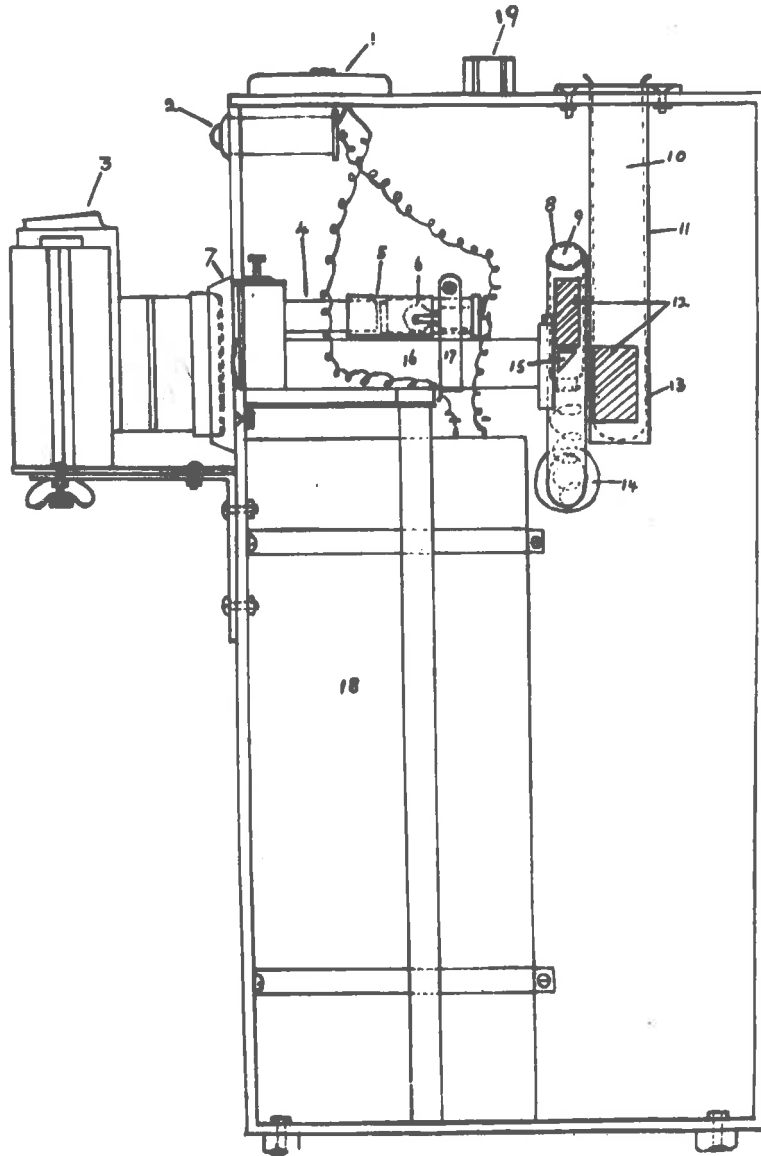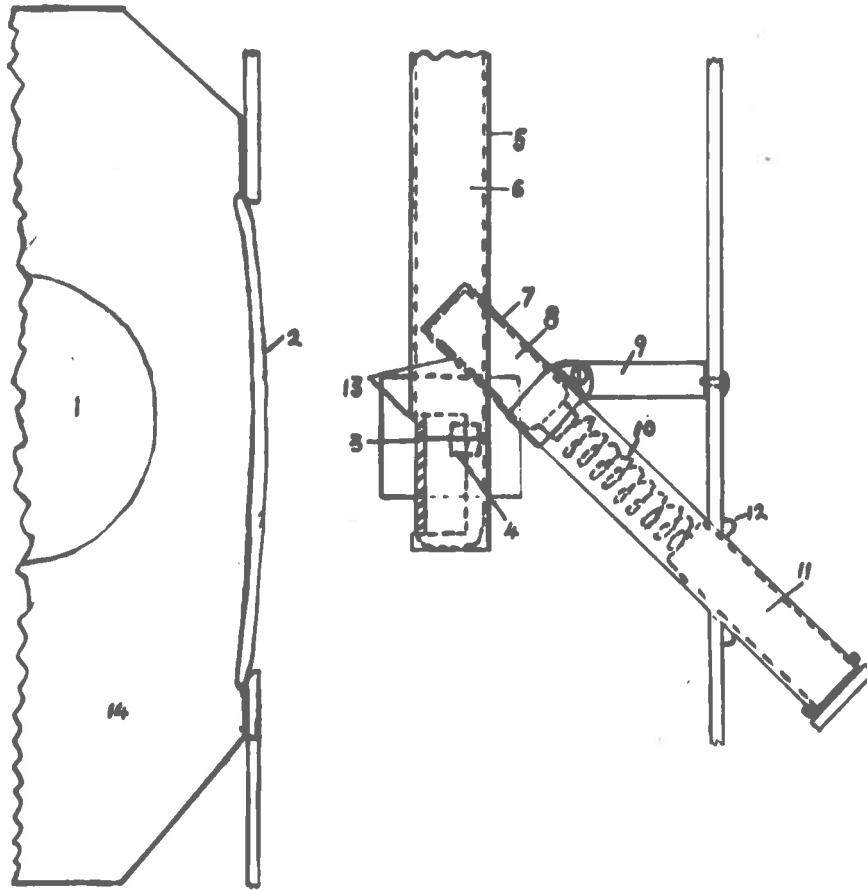
Fig. 1·3.

FLUORESCENT SPECTROPHOTOMETER.

INSIDE SIDE VIEW

1. Press Button
2. Indicator Light
3. Camera
4. Scale Tube
5. Rubber Sleeve
6. Scale Lamp
7. Rubber Seal

8. Standard Tube Holder
9. Standard Tube
10. Unknown Tube
11. Unknown Tube Holder
12. Windows
13. Aluminium Foil
14. Rubber Grommet

15. Prism
16. Spectrometer
17. Clamp
18. Battery
19. Handle

Fig. 1·4.

END VIEW SECTION

1. Ultraviolet Lamp
2. Wood's Glass Filter
3. Slit
4. Prism
5. Unknown Tube Holder
6. Unknown Tube
7. Standard Tube Holder

8. Standard Tube
9. Clamp
10. Spring
11. Standard Removing Plug
12. Rubber Grommet
13. Windows
14. U.V. Lamp Holder

Fig. 1·5.

to be very convenient and efficient.

A direct vision, prism, hand spectroscope, calibrated from 400-700 mμ in 10 mμ divisions was used. A model, having a prism fitted to cover half of the slit was used, so that unknown and standard solutions could be examined simultaneously (Fig. 1·4). Provision was made, by a push-button switch, for the scale to be illuminated momentarily by light from a bezzle lamp attached to the scale tube by a rubber tube. The light was diffused by frosted glass plates contained in this tube.

A camera ("Praktica" Fx2, 35 mm. with a Meyer Optik Gorlitz 2·9 lens of 50 mm. focal length), fitted with a 2 dioptre supplementary lens was mounted directly in front of the eyepiece, but outside the light-proof box which housed most of the apparatus. A rubber seal provided a light-proof connection between the camera lens and the inside of the box. The excitation radiation was provided by an enclosed 125 watt mercury lamp fitted to the outside of the box (Fig. 1·5). The Wood's glass bulb restricts the radiation to mainly the 3650 A$^{\circ}$ mercury line. The visible light still transmitted was almost completely removed by a further Wood's glass filter, which was used as a window to the optical box.

The instrument was calibrated against mercury, neon, hydrogen, and sodium lines. In the 400 mμ region the expected accuracy is within 1 mμ, and in the 500 mμ region within 5 mμ. Standards for comparing known spectra with unknown ones were contained in screw-capped glass phials of 4 c.c. capacity, which were supported in a metal tube inclined at 45° and directly over the comparison prism of the spectrometer. The tube had a window in the upper end in order to allow the incident light to reach the solution and the emitted rays to reach the slit. The standards contained the amount of fluorescent substance which would give approximately the brightest spectrum; e.g. 3:4-benzopyrene, $5x10^{-4}$ mole/l.; anthracene, 10^{-3} mole/l., and 1:2-benzanthracene $5x10^{-4}$ mole/l.

The unknown was contained in a pyrex test tube supported in another metal tube with a window cut so that the incident light, emitted at right angles, passed directly through the slit. Aluminium foil was used as reflectors behind both standard and unknown solutions, to increase the intensity of radiation.

The solvent used was usually benzene, but unknowns were always examined in the same solvent as the standard materials. With solutions of the above concentration,

TABLE 1·1.   MAXIMA (mμ) OF FLUORESCENCE BANDS OF
3:4-BENZOPYRENE.

Weigert[a] (acetone)	Chalmers[b] (alcohol)	Schoental[c] (light petroleum)	Cardon[d] (benzene)	Present Work. (benzene)
–	394	–	–	398 weak, B[*]
404	404·5	403	–	404 strong, N.
410	410	408	410	409 weak, N.
417	417	415	413	417 weak, N.
427	429	427	–	427 strong, B.
–	434	431	432	433 strong, B.
–	–	437	–	437 v. weak, N.
455	456	454	455	456 strong, B.
485	–	–	–	485 weak, B.

[*] B = Broad band;   N = Narrow band.

[a] Weigert and Mottram, Nature, 1940, 145, 895.

[b] Chalmers, Biochem. J., 1938, 32, 271.

[c] Schoental and Scott, J. Chem. Soc., 1949, 1683.

[d] Cardon, Alvord, Rand, and Hitchcock, Brit. J.
    Cancer, 1956, 10, 485.

TABLE 1·2.　　　　MAXIMA (mμ) OF FLUORESCENCE BANDS

OF PERYLENE.

Radulescu[a] (benzene)	Radulescu[a] (heptane)	Schoental[b] (light petroleum)	Present Work. (benzene)
446	440	438	445 B
475	465	465	475 B
505	498	497	502 B
537·5	535	–	536 B

[a] Radulescu and Dragulescu, Bul. Soc. chim. Romania, 1935, 17, 9, 26, 35.

[b] Schoental and Scott, J. Chem. Soc. 1949, 1683.

a spectrometer slit-width of 0·01 in., and an exposure
of 1 min. at $\underline{f}$2·9, with Kodak Tri-X or Ilford HPS film
was usually satisfactory.   The scale was illuminated
for approximately 0·5 sec.

   With this appartus, 3:4-benzopyrene (5×10^{-4} mole/l.
in benzene) gave a fluorescence spectrum showing
considerable fine structure.   The positions of the maxima
of the fluorescence bands are given in Table 1·1, which
records the values obtained by previous workers.   With
weaker or impure solutions only the strong bands were
normally detected.

   Perylene showed maxima as recorded in Table 1·2.

CHAPTER II

AN EXAMINATION OF "SCHROETER TAR"

When tetralin is treated with aluminium chloride at low temperature, a complex mixture ("Schroeter tar") is obtained[35]. Some of the distillation fractions have been found to be carcinogenic[36a]. Hieger[36b] showed that the fluorescence spectrum of the distilled tar was similar to that of other carcinogenic tars obtained from gasworks, and the pyrolysis of acetylene, yeast, muscle, hair, etc., and the presence of 3:4-benzopyrene has been presumed for many years. Schroeter's analysis of the tar showed that the mixture contained octahydroanthracene, octahydrophenanthrene, 6-4'-phenylbutyltetralin (I) and 2:6'-ditetralyl[35]. Cook and Hewett[37] have suggested that it may also contain some 5-4'-phenylbutyltetralin (II), which could conceivably give the carcinogenic hydrocarbon 3:4-benzopyrene (IV) by cyclodehydrogenation.
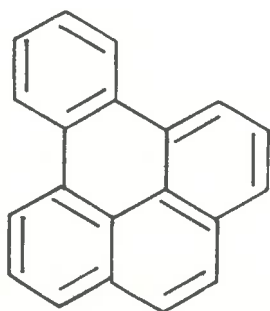
The distillation fractions of "Schroeter Tar" have now been examined for 3:4-benzopyrene. Several of the crude fractions gave diffuse fluorescence spectra corresponding to the fluorescence spectrum of this
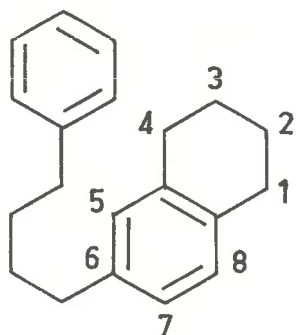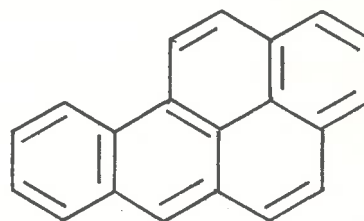
(I)
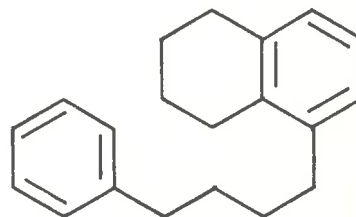
(II)

(III)

(IV)

hydrocarbon.   Chromatography on alumina gave 3:4-benzo-
pyrene from two fractions.   The 6-4'-phenylbutyltetralin
fraction, b.p. 230-240°/15 mm., was found to contain a
small amount of the benzopyrene, but the higher fraction,
b.p. 205-240°/0·5 mm., which approximately corresponds
to the fraction which Kennaway[36a] showed to be the most
carcinogenic, has been found to contain as much as 4%

3:4-benzopyrene. A small amount of perylene was also found, but no conclusive evidence of 1:2-benzopyrene (III), despite the fact that this might be expected following cyclodehydrogenation of 6-4'-phenylbutyltetralin (I). Another hydrocarbon, which was not identified, was isolated from the highest fraction b.p. 245-300°/1 mm.

An attempt was made to detect 5-4'-phenylbutyl-tetralin (II) in "Schroeter Tar", but without success. Careful fractionation of the fraction b.p. 230-240°/15 mm., using a spinning band column gave 6-4'-phenylbutyltetralin (I) and 2:6'-ditetralyl in agreement with Schroeter[35]; but the 5-isomer, if present, could not be separated. Gas-liquid chromatography also afforded no separation of isomers. Oxidation of a portion of the same fraction with potassium permanganate, esterification of the resulting acid with diazomethane, followed by chromato-graphy, gave 1:2:4-tricarbomethoxybenzene as the only product, and no 1:2:3-tricarbomethoxybenzene (which would be formed by the oxidation of II.) could be detected.

These experiments do not eliminate the possibility that a small amount of 5-4'-phenylbutyltetralin (II) may be present. If it is present, it would be expected to cyclodehydrogenate to 3:4-benzopyrene under pyrolytic

conditions, and it was thought that it may be easier to detect this transformation. The fraction b.p. $230-240^{\circ}/$ 15 mm. from which essentially all the 3:4-benzopyrene had been removed, was accordingly pyrolysed at 360° and 600°. At the lower temperature only a trace of 3:4-benzopyrene was detected. Pyrolysis at 600° gave a complex tar containing a considerable amount of low boiling products. Analysis by distillation, gas-liquid chromatography, and chromatography on alumina enabled positive identification of naphthalene, 2-methylnapthalene, and 2-ethylnaphthalene. Compounds with gas-liquid chromatographic retention times corresponding to toluene, ethylbenzene, styrene, propyl-benzene, and other unidentified simple products were also observed. A compound having a phenanthrene-type ultra-violet absorption spectrum was isolated and 2:2'-di-naphthyl was also found in reasonable yield. 3:4-Benzo-pyrene was again present in only trace amounts; but perylene was isolated in 0·125% yield.

This work has therefore failed to show the presence of 5-4'-phenylbutyltetralin (II). Nevertheless, this does seem to be the most reasonable intermediate for the formation of the 3:4-benzopyrene in "Schroeter Tar". The explanation may be that the 5-4'-phenylbutyltetralin

is formed, and is so readily converted into 3:4-benzo-
pyrene that the intermediate cannot be isolated.

It remained to be determined whether the proposed
cyclodehydrogenation is brought about by the catalytic
action of the aluminium chloride, or occurs during the
distillation in the subsequent working up of the
product. Undistilled "Schroeter Tar" was therefore
examined. Cold sulphuric acid extraction of the
undistilled tar, followed by chromatography on alumina
of the benzene extract, gave a yellow hydrocarbon,
apparently 1":2":3":4":5':6':7':8'-octahydro-8:9-
benzonaphtho-(2':3'-3:4)pyrene (VII), but no 3:4-benzo-
pyrene. The melting point and fluorescence spectrum of
the octahydrobenzonaphthopyrene agree with the
literature[45]. There is a slight difference in the
ultraviolet absorption spectrum (Fig. 2·1), and the
spectrum of the compound isolated here, more closely
resembles that of 3:4-benzopyrene, with a bathochromic
shift of approximately 15 mμ, than previously reported.
Dehydrogenation with palladium-charcoal gave 3:4-benzo-
8:9-(2'-3'-naphtho)pyrene (VIII) whose melting point,
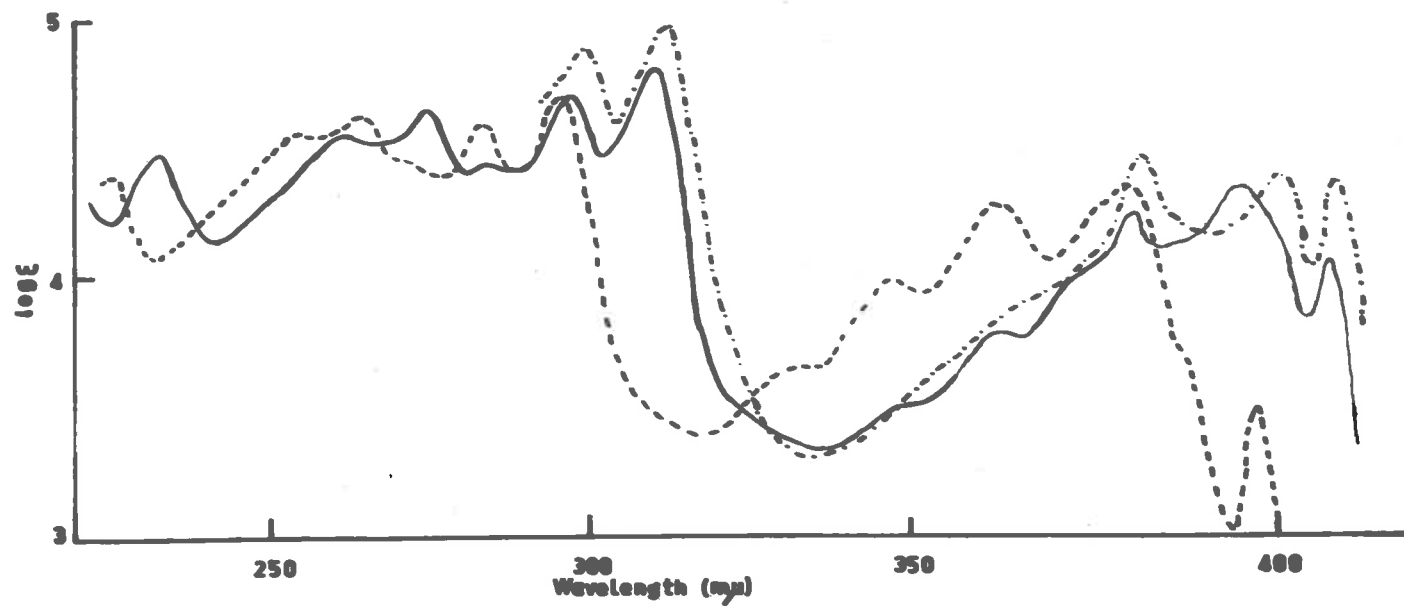fluorescence, and ultraviolet spectra (Fig. 2·2) was
in agreement with the literature[45].

Fig. 2.1.   1":2":3":4":5':6':7':8'-Octohydro-8:9-bensonaphtho-(2':3'-3:4)pyrene(?)
(This work: ———), and Grove (—·—·);   3:4-bensopyrene (– – –).
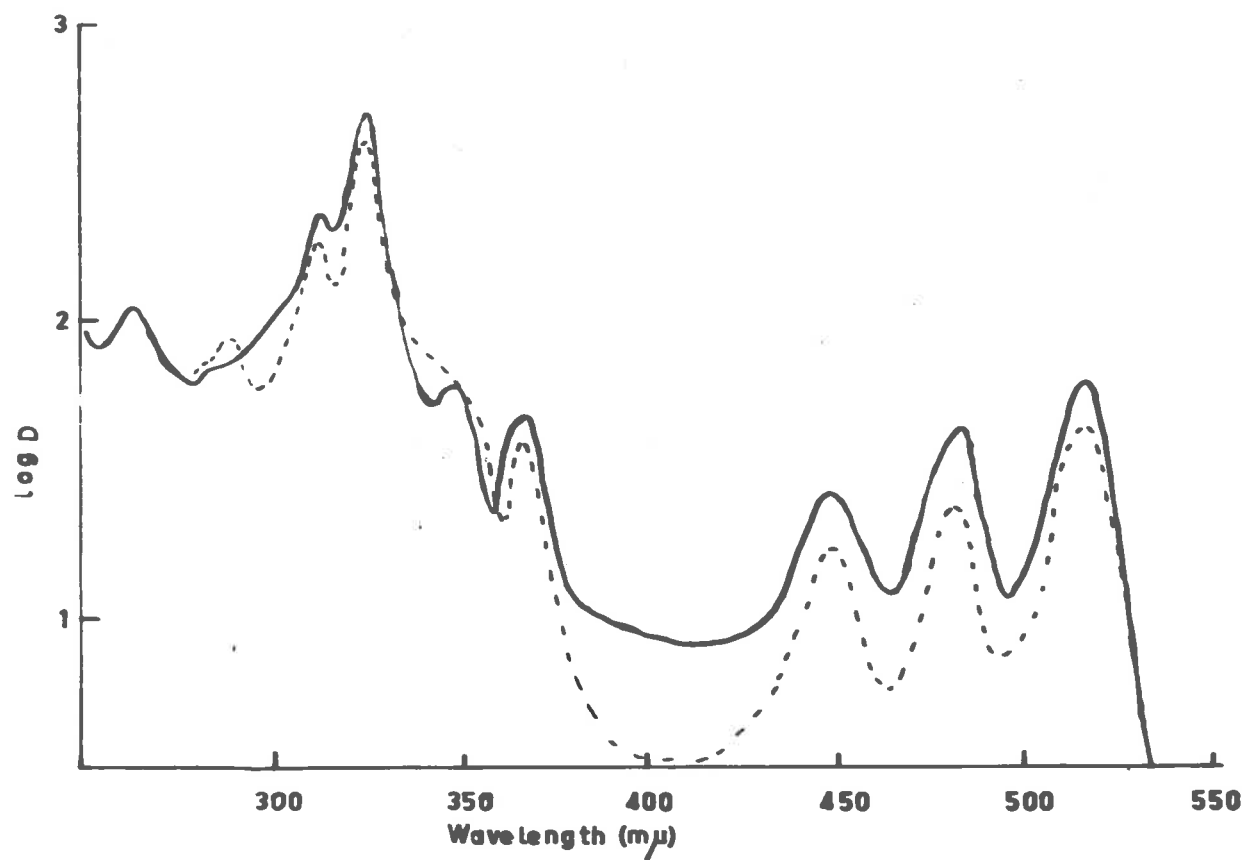
Fig. 2.2.   3:4-Benzo-8:9-(2':3'-naphtho)pyrene   (This work: ——);
                     (Grove: - - - -).

(V)

(VI)

(VII)

(VIII)
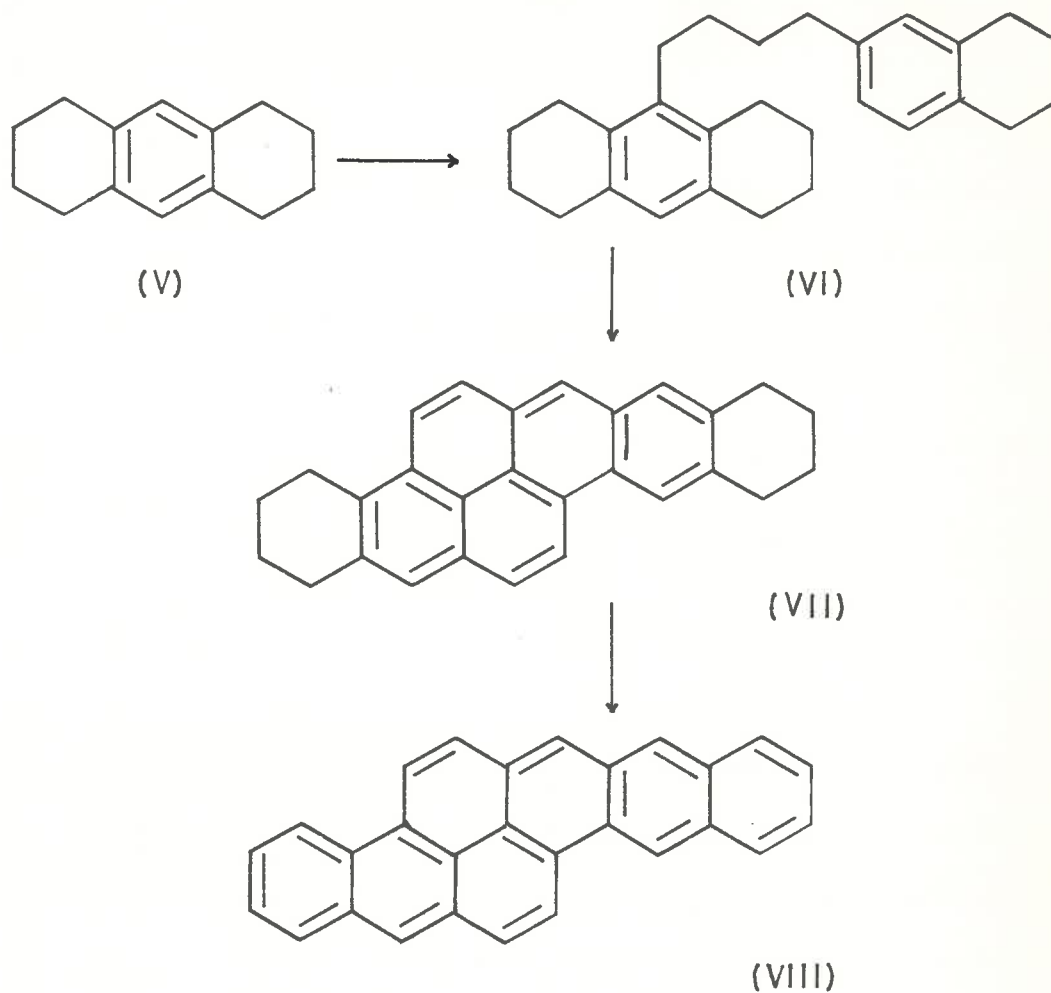
Grove[45] gives evidence that the octahydrobenzo-
naphthopyrene is the unidentified yellow compound found
by Schroeter[35] from the action of aluminium chloride on
octahydroanthracene (V).   In the present work this

compound could then be formed by the same mechanism
(V, VI, VII) suggested by Grove. (cf. the proposed
tetralin to 3:4-benzopyrene mechanism).

The material not extracted with sulphuric acid (see
fraction B2 Fig. 2·3) was distilled, but only small
amounts of 3:4-benzopyrene and perylene were detected
after chromatography on alumina. Similarly, distillation
of the early liquid fractions following chromatography of
the sulphuric acid-soluble material (fraction B4 Fig. 2·3)
gave very little 3:4-benzopyrene.

It seems likely, therefore, that the 3:4-benzopyrene
in "Schroeter Tar" is not formed by the action of
aluminium chloride, but is formed by the heat of
distillation. It can also be said that the sulphuric
acid used here for extraction, in some way rearranges or
otherwise interferes with the precursor, and prevents the
formation of 3:4-benzopyrene even on heating. This was
supported by repeating the analysis on a smaller scale
and by chromatographing the tar on alumina instead of
extracting with sulphuric acid. As anticipated,
distillation of the appropriate fractions gave 3:4-
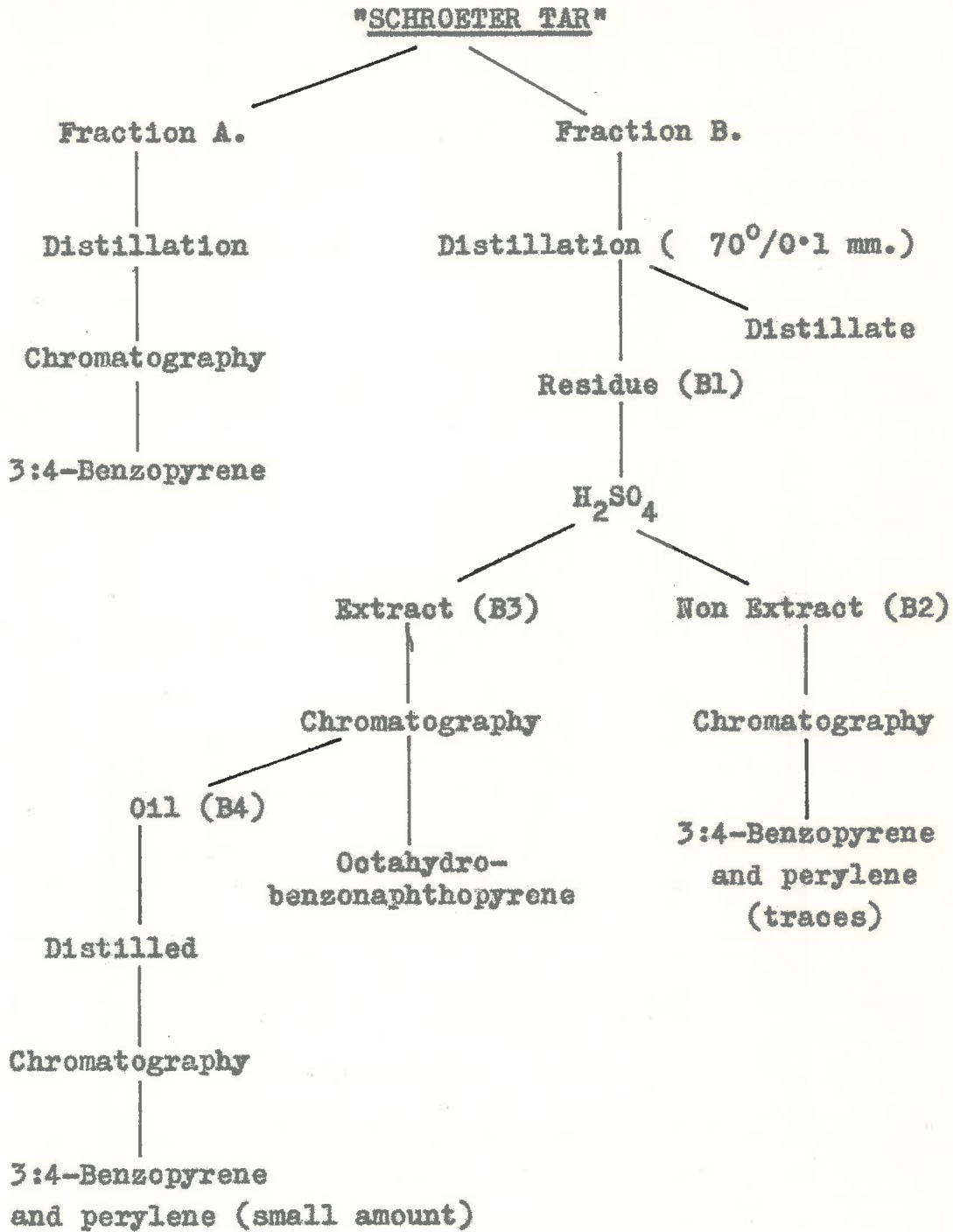benzopyrene, so confirming the above conclusions.

"SCHROETER TAR"

Fraction A.

Fraction B.

Distillation

Distillation (70°/0·1 mm.)

Distillate

Chromatography

Residue (B1)

3:4-Benzopyrene

H_2SO_4

Extract (B3)

Non Extract (B2)

Chromatography

Chromatography

Oil (B4)

3:4-Benzopyrene
and perylene
(traces)

Octahydro-
benzonaphthopyrene

Distilled

Chromatography

3:4-Benzopyrene
and perylene (small amount)

Fig. 2·3.

EXPERIMENTAL.

"Schroeter Tar".—   Tetralin (2·5 kg.) and aluminium chloride (50 g.) were stirred for 10 hr. at 50–70°. After pouring onto ice the tar produced was collected and distilled.   On removal of the lower boiling fractions containing benzene, tetralin, octahydroanthracene and octahydrophenanthrene[35] the following fractions were distilled: (i) b.p. 230–240°/15 mm. (280 g.); (ii) b.p. 205–240°/0·5 mm. (75 g.); and (iii) b.p. 245–300°/1 mm. (71 g.).   All fractions having b.p. greater than 120°/15 mm. showed fluorescence bands corresponding to 3:4–benzopyrene.

Analysis of Fraction (i).—   The crude tar (63 g.) from this fraction was chromatographed in hexane on alumina (40 x 5 cm.).   Elution with hexane (1 l.) brought through the bulk of the tar, mainly consisting of 6–4'–phenylbutyltetralin, which showed only a very faint fluorescence spectrum of 3:4–benzopyrene.   However, further elution with benzene–hexane (1:2), gave eight fractions (each of 70 c.c.) having fluorescence ranging from blue–violet in the early fractions, to green–blue, and then back to blue–violet in the later fractions.

Fractions 1, 2, 6, 7 and 8 showed strong fluorescence bands of 3:4-benzopyrene, and fractions 3, 4, and 5 somewhat weaker bands owing to quenching, together with three other bands which were identical with those of perylene. Removal of the solvent gave crude 3:4-benzopyrene (60 mg.). Recrystallisation from ethanol gave the substantially pure product as yellow needles, m.p. 174-176°, not depressed by admixture with an authentic sample (lit.[46] 176-177°). Its ultraviolet absorption spectrum (in ethanol) gave the following maxima (mμ) and log ϵ values (in parenthesis), in good agreement with the literature[46,47] 226 (4·40); 255 (4·58); 265 (4·65); 274 (4·44); 284 (4·62); 296 (4·73); 331 (3·65); 347 (4·04); 364 (4·30); 384 (4·37); 404 (3·50). A maximum at 434 mμ (2·78) was identical with that of perylene (lit.[48] 434 mμ). From the absorption spectrum this seems to be present in less than 1%.

Analysis of Fraction (ii).- The tar (55 g.) was chromatographed in hexane on alumina (35 x 5 cm.). Elution with hexane (2 l.) brought through the main product as a pale yellow oil with an intense violet fluorescence. Further elution with benzene-hexane (1:2) brought through a very broad yellow band which was

practically non fluorescent on the column, but which gave
a green-yellow fluorescence in solution. Eight fractions
(each of 175 c.c.) were collected and removal of the
solvent gave yellow crystals of crude 3:4-benzopyrene
(2·1 g.). Fractions 2 - 5, which contained most of the
material, were combined and recrystallised from ethanol.
A further three recrystallisations gave the substantially
pure product m.p. 174-175°, not depressed by admixture
with an authentic sample. (Found: C, 95·0; H, 5·0.
$C_{20}H_{12}$ requires C, 95·2; H, 4·8%). The trinitrobenzene
complex had m.p. 223-224° (lit. 226-227° corr.).
(Found: C, 67·15; H, 3·2. $C_{26}H_{15}N_{3}O_{6}$ requires C, 67·1;
H, 3·2%). Absorption spectroscopy showed perylene to
be present to the extent of less than 1%.

Analysis of Fraction (iii).- This fraction (71 g.)
was chromatographed as above. The fractions which were
eluted with benzene-hexane (1:2) (1·5 l.) were combined,
the solvent removed, and the residue extracted in benzene
with cold sulphuric acid[49]. The acid extract was poured
onto ice and extracted with benzene in a continuous
liquid extractor for 12 hr. After washing with sodium
bicarbonate solution, then water, and finally drying,
the benzene was evaporated. Chromatography on alumina,

and elution with benzene-hexane (1:2) gave several orange fractions which were evaporated. The residues were recrystallised from ethanol to give orange-brown prisms m.p. 255-257°. Its ultraviolet absorption spectrum had maxima at 220, 246, 255, 269, 297, 310, 323, 354, 374, 396, 422, 448, and 456 (infl.) mμ. (Fig. 2·4)

Attempted Isolation of 5:4'-Phenylbutyltetralin from "Schroeter Tar".- (1) By fractionation. An attempt was made to fractionate the crude tar (70 g., b.p. 230-240°/15 mm.) using a spinning band column. By plotting both boiling point and refractive indices of 2 c.c. fractions against the amount distilled, the distillate could be divided into three fractions: (a) the forerun (6 c.c.) b.p. 230-235°/15 mm.; (b) the main fraction (36 c.c.) (which had both a slowly rising boiling point, i.e. 136-140°/15 mm., and refractive index, η_D^{17} 1·5670-1·5720); and (c) a compound (24 c.c.) which solidified as colourless plates and identified by its m.p. 54-54·5° (Schroeter gives m.p. 53-54°) as 2:6'-di-tetralyl. Fraction (b) which still exhibited a pale violet fluorescence in visible light, and which was intensely violet in ultraviolet light, showed identical infrared spectra throughout the fraction.
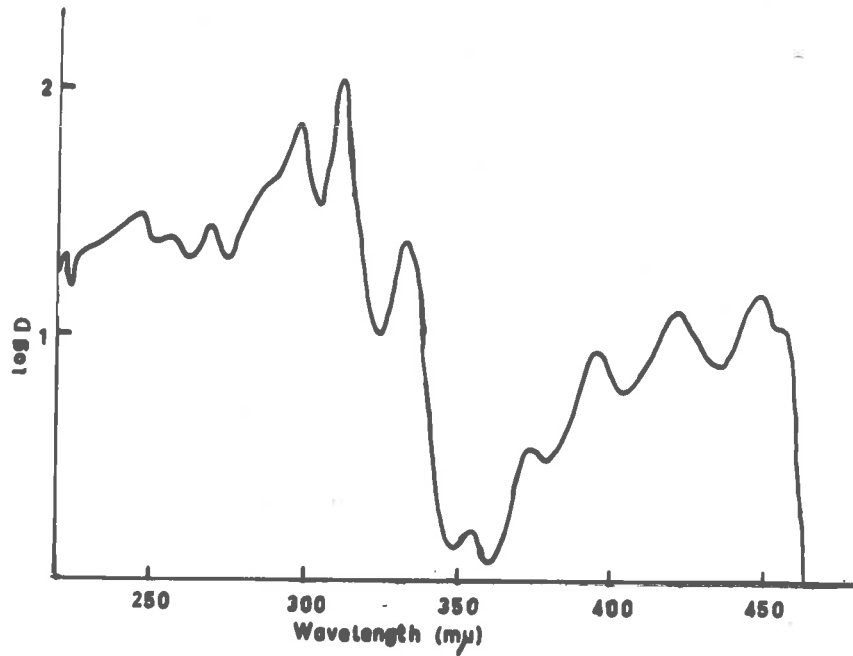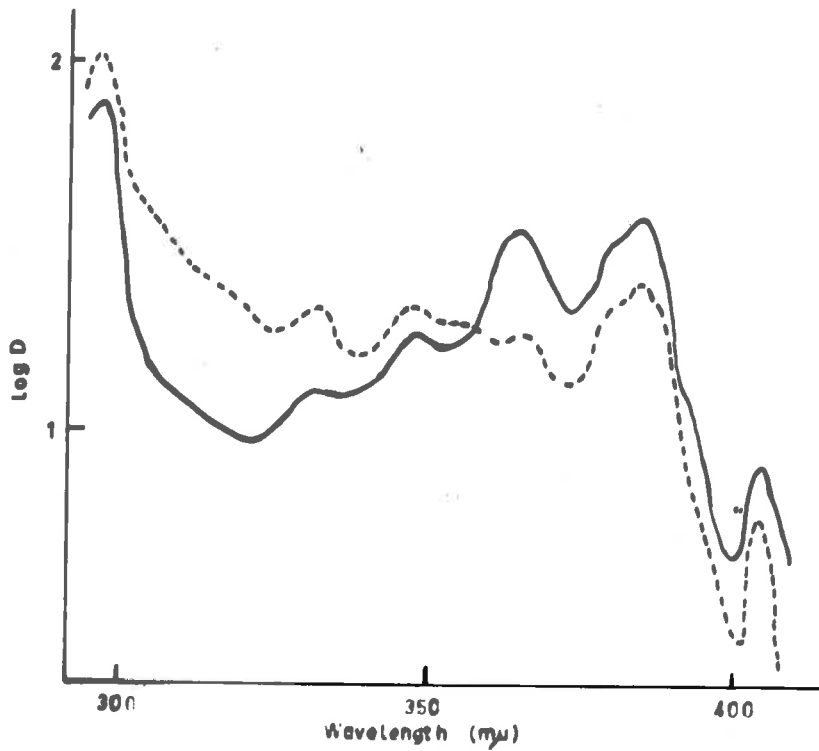
Fig. 2·4.   Unknown from fraction (iii).

Fig. 2·5.   3:4-Benzopyrene (authentic: ——);
(This work: - - -).

(ii) **By gas-liquid chromatography.** Gas-liquid chromatography, using both the instrument built in this laboratory[41] and a Griffin Vapour Phase Refractometer, of the fraction b.p. 230-240°/15 mm., failed to separate the two isomers of phenylbutyltetralin.

(iii) **By oxidation.** Oxidations with (a) potassium permanganate, and (b) chromium trioxide and acetic acid, were carried out on the redistilled tar, b.p. 230-240°/15 mm. (13 g. and 5·2 g. respectively) by the method of Schroeter[35], except that with (a) after acidification with sulphuric acid the mixture was extracted with ether, the ethereal solution dried, and then treated with diazomethane. However, the product was 1:2:4-tricarbomethoxybenzene and no 1:2:3-tricarbomethoxybenzene expected from oxidation of the α-isomer, could be detected in the resulting oily product.

With oxidation by method (b) no separation of 2:4-dinitrophenylhydrazones of the ketone(s) formed could be effected by chromatography in chloroform on kieselguhr and bentonite (1:4).

Pyrolysis Reactions.- (i) **Distillation.** The fraction (b) from the spinning band distillation (27 g.), which showed strong but diffuse fluorescence bands of

3:4-benzopyrene (Plate 2·1a) was chromatographed on alumina (40 x 5 cm.). Elution with hexane (800 c.c.) brought through the bulk of the material as a non-fluorescent (in visible light) colourless oil. Further elution with benzene-hexane (1:2) (8 fractions of 70 c.c.) gave 3:4-benzopyrene in the last three fractions, identified by its fluorescence (Plate 2·1b) and absorption spectra (Fig. 2·5) (maxima at 404, 384, 365, 347, and 332 mμ.). The calculated amount present from the absorption curve was less than 0.5 mg.

(ii) At 360°. Fraction (i) (2 g.) b.p. 230-240°/ 15 mm., from which the 3:4-benzopyrene had been removed by chromatography was refluxed for 1 hr. Chromatography of the product on alumina gave small amounts (ca. 0·5 mg.) of 3:4-benzopyrene and perylene, as estimated from the ultraviolet absorption spectrum. Three maxima (at 331, 316, and 299 mμ) suggested the presence of a small amount of 1:2-benzopyrene also.

(iii) At 600°. Fraction (i) from which the benzopyrene had been removed (20 g.) was vapourised at the rate of 1 drop/15 sec. and passed with nitrogen (1 c.c./sec.) through a silica tube (36 x 1 in.) packed with porcelain chips (⅛ - ¼ in.) heated to 600°.

Distillation of the resulting reddish-brown tar (15 g.) gave 8 fractions and a residue as follows:- F1, b.p. 80° (0.25 g.); F2, b.p. 80-120° (0.5 g.); F3, b.p. 80-110°/ 21 mm. (3 g.); F4, b.p. 110-120°/21 mm. (2.5 g.); F5, b.p. 120-140°/21 mm. (0.5 g.); F6, b.p. 100-150°/ 1.2 mm. (3 g.); F7, b.p. 150-180°/1.2 mm. (2 g.); F8, b.p. 180-220°/1.2 mm. (1 g.); and the residue (2 g.).

Gas phase chromatography* of fractions F1 and F2 gave peaks with retention times corresponding to toluene (0.1 g.), ethylbenzene (0.3 g.), styrene or o-xylene (0.25 g.), and n-propylbenzene (0.1 g.) (Table 2.1). (The amounts were calculated from the areas under the peaks). The third compound was found to decolourise bromine water.

Similarly, gas phase chromatography of fraction F3 gave four peaks, the last two of which corresponded to naphthalene and 2-methylnaphthalene. (Table 2.2). Collection of the fractions confirmed the presence of naphthalene (1.62 g.), m.p. and mixed m.p. 79-80°, and 2-methylnaphthalene (0.54 g.); its infrared spectrum showed maxima at 5.18, 5.38, 5.53, 5.66, 5.91, 6.08, 6.23, 6.98, 7.12, 7.28, 7.36, 7.55, 7.89, 8.10, 8.32, 8.53,

* The instrument built in this laboratory used here.

TABLE 2·1   FRACTION F1 & 2.

Column: Apiezon M on 100-150 mesh Celite;

Temperature 115°;   Inlet pressure 760 mm.;

Outlet pressure 760 mm.; N_2 flow rate, 2·5 l./hr.

UNKNOWN			STANDARD		
Peak.	RT	RTR	Inference	RT	RTR
1	6 mm.	1	Toluene	6·3 mm.	1
2	11 "	1·8	Ethylbenzene	11·4 "	1·8
3	14 "	2·7	o-Xylene or styrene	16·4 "	2·6
4	22·5 "		Propylbenzene(?)		

TABLE 2·2   FRACTION F 3.

Column: Apiezon L on 40-80 mesh Celite;

Temperature 192°;   Inlet pressure 423 mm.;

Outlet pressure 5 mm.; N_2 flow rate, 1·1 l./hr.

UNKNOWN			STANDARD		
Peak.	RT	RTR	Inference	RT	RTR
1	3·4	·5	Unknown -X		
2	5·3	·77	Unknown -Y		
3	6·75	1	Naphthalene	6·8	1
4	10·9	1·6	2 Me-naphthalene	11·0	1·6
5	12 (infl.)		1 Me-naphthalene(?)	12·1	

RT = Retention time.   RTR = Retention time ratio.

8·67, 8·76, 8·89, 9·64, 10·44, and 14·34 μ essentially
in agreement with the literature[50]. It also showed
maxima at 5·90, 6·85, 7·22, 7·42 (infl.), and 9·28 μ
probably indicative of 1-methylnaphthalene. This is
supported by the presence of a shoulder on the main peak
of the chromatography curve as expected for a mixture of
methylnaphthalenes. The unidentified compounds,
unknown -X (0·54 g.) and unknown -Y (0·27 g.) were
collected. Infrared analysis of unknown -X suggested
a mixture of two trisubstituted benzene compounds
containing some methyl substitution. This was indicated
by six absorption maxima at 5·09, 5·19, 5·25, 5·33,
5·42 and 6·02 μ from combination tone vibrations, and by
a peak at 3·54 μ denoting methyl absorption in the C - H
stretching region. There was insufficient of unknown -Y
for identification.

Fractions F4-5 showed the presence of naphthalene
(0·62 g.), methylnaphthalenes (1·25 g.), and 2-ethyl-
naphthalene (0·9 g.). The latter was collected, and
showed maxima in the infrared at 5·20, 5·42, 5·61, 5·85,
6·10, 6·23, 7·88, 8·30, 8·55, 8·67, 8·76, 8·89, 9·37
(infl.), 9·47, 9·81, 10·28 (infl.), 10·39, 10·56, 11·26,
11·73, 12·24, 12·79, and 13·11 μ in agreement with the
literature[50]. In the region 6·5 - 8 μ the maxima

corresponded with those of 1-ethylnaphthalene. A fourth gas phase chromatography fraction (0·07 g.) could not be identified.

Fraction F6 was chromatographed on alumina (3 x 15 cm.) in hexane. Elution with this solvent gave five fractions (each of 60 c.c.) all of which gave on evaporation of the solvent a white solid. Recrystallisation from ethanol gave fine colourless prisms m.p. 150-157°. Its ultra-violet absorption spectrum (Maxima at 250, 252, 276, 288, 300, 323, 340, and 358 mμ) suggested a phenanthrene derivative (Fig. 2·6), but it was not identified.

Chromatography of fractions F7-8 on alumina and elution with hexane and benzene-hexane (1:2), gave 2:2'-dinaphthyl (1 g.), (identified by m.p., mixed m.p., and ultraviolet spectrum). Trace amounts of 3:4-benzopyrene and perylene were indicated by fluorescence spectroscopy.

The residue was chromatographed on alumina in benzene to remove black intractable materials. The resulting eluant was treated with cold sulphuric acid[49] giving an extracted portion, F11, and a non-extracted portion, F12. Evaporation of the solvent from F11, followed by chromatography on alumina, gave perylene (20 mg.) shown by absorption spectroscopy (maxima at 245,
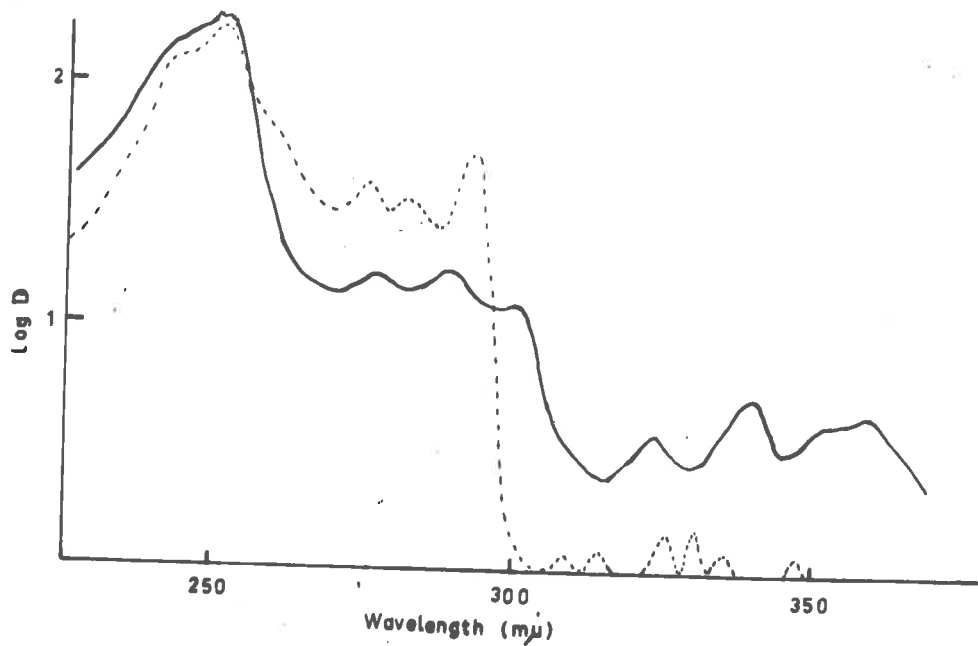
Fig. 2·6. Unknown compound from fraction F6 (————);
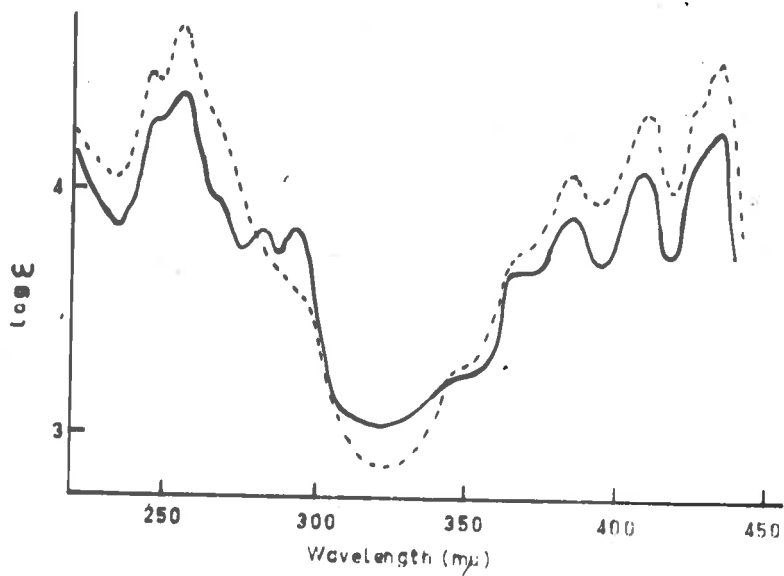Phenanthrene (– – –)

Fig. 2·7. Perylene from fraction F11 (————);
authentic (– – –).

252, 386, 408, 426 (infl.) and 435 mμ). (Fig. 2.7).
Its fluorescence spectrum also showed the presence of a
small amount (1 mg.) of 3:4-benzopyrene. Similar
treatment of F12 gave 2:2'-dinaphthyl (1 g.).
Recrystallisation twice from ethanol gave the pure product
m.p. 182-184° (lit.[51] 186° corr.) and showed maxima (mμ)
and log values (in parenthesis) at 231 (4.12), 254
(4.94), and 304 (4.25). (Found: C, 94.5; H, 5.5.
Calc. for $C_{20}H14$: C, 94.5; H, 5.6%).

Analysis of Undistilled "Schroeter Tar".- "Schroeter
Tar" prepared from tetralin (2 kg.) and aluminium chloride
(40 g.) was divided into two equal portions. Portion A
was distilled as above. Chromatography on alumina of
the appropriate fractions gave 3:4-benzopyrene (0.65 g.).

The tetralin and benzene were removed from portion
B by distillation up to a temperature not greater than
70°/0.1 mm. The residue (300 g.), in an equal amount
of benzene, was cooled to 0° and vigorously stirred while
sulphuric acid (200 c.c.) was added at such a rate that
the temperature did not rise above 5°. Stirring was
continued for 15 min. and the acid layer removed. The
extraction was repeated with 150, 100 and 50 c.c. lots
of acid. The combined extracts were added with stirring

to ice (1 kg.), extracted with four lots of benzene and the combined benzene extracts washed with water, sodium bicarbonate and water respectively, then finally dried over calcium chloride. The benzene was removed and the residual tar (17 g.) chromatographed in hexane on alumina (20 x 3 om.).

Elution with hexane brought through most of the product, and removal of the solvent gave a viscous oil B4 (Fig. 2·3). Further elution with benzene-hexane (1:2) gave a yellow compound (0·3 g.). Reorystallisation three times from cyclohexane gave 1":2":3":4":5':6':7':8'-octahydro-8:9-benzonaphtho-(2':3'-3:4) pyrene (?) as bright yellow plates m.p. 309-311° (silicone bath) (lit.[45] 320°). (Found: C, 92·8; H, 6·8. Calc. for $C_{28}H_{24}$: C, 93·3; H, 6·7%). Its fluorescence spectrum (Plate 2·1c) had maxima at 420, 445, 475, and 499 in agreement with the literature [45]. The ultraviolet absorption spectrum (in cyclohexane) showed maxima ($m\mu$) and log ϵ values (in parenthesis) at; 233 (4·49), 262 (4·56), 275 (4·66), 297 (4·72), 311 (4·84), 350 (3·69), 366 (3·80), 374 (4·25), 420 (4·36), 416 (4·06) in agreement with the literature [45], except the maximum at 420 $m\mu$. (Fig. 2·1).

The octahydrobenzonaphthopyrene (58 mg.) was dehydrogenated by refluxing it in p-cymene (10 c.c.) with 10% palladium-charcoal (50 mg.) for 6 hr. The red residue remaining after removal of the solvent was chromatographed on alumina in benzene. Recrystallisation from benzene gave 3:4-benzo-8:9-(2':3'-naphtho)pyrene as scarlet plates m.p. 334-337° (lit.[45] 338-339°). Its ultraviolet absorption spectrum and its fluorescence spectrum with maxima at 262, 311, 324, 348, 366, 448, 482 and 515 mμ (Fig. 2·2) and 528, 565 and 612 mμ (Plate 2·1d) respectively, were in agreement with the literature[45].

The material B2 (Fig. 2·3) not extracted by the sulphuric acid, was washed with sodium bicarbonate, water, dried, and distilled. The material b.p. 210°/0·9 mm. was removed, and the residue chromatographed on alumina. Some fractions showed the fluorescence bands of 3:4-benzopyrene and perylene. This was confirmed by ultra-violet absorption spectroscopy, and by their R_f values from chromatography on acetylated paper. It was estimated that only a small amount of each was present.

Distillation, chromatography and spectral analysis in a similar manner of the fractions b.p. 260-320°/19 mm. of the oil B4 (Fig. 2·1) also gave only a few mg. of 3:4-benzopyrene and perylene.
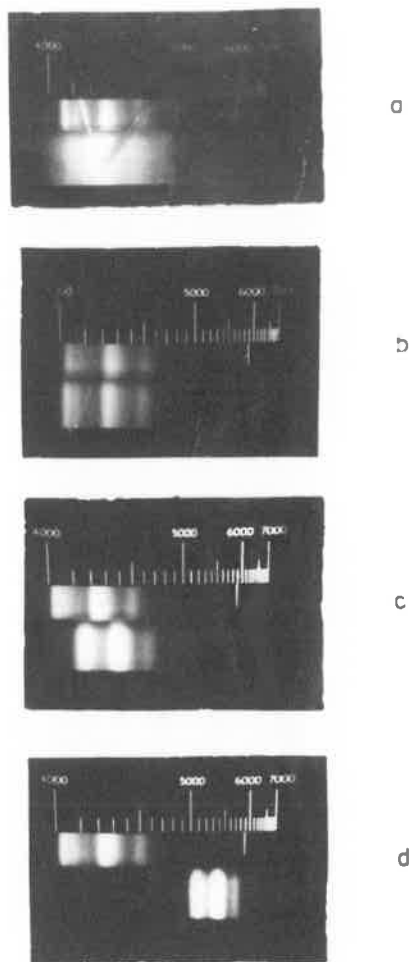
Plate 2·1. (a) Crude 3:4-benzopyrene fraction; (b)
purified 3:4-benzopyrene; (c) 1":2":3":
4":5':6':7':8'-octahydro-8:9-benzonaphtho-
(2':3'-3:4)pyrene(?); (d) 3:4-benzo-8:9-
(2':3'-naphtho)pyrene. (The upper spectra
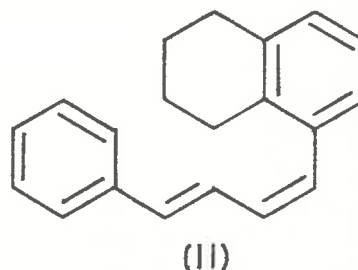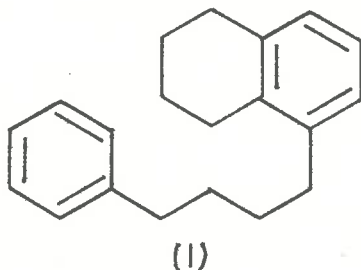are all 3:4-benzopyrene).

CHAPTER III

THE SYNTHESIS AND PYROLYSIS OF 1-4'-PHENYLBUTYLNAPHTHALENE AND RELATED COMPOUNDS.

### PART I.

The Pyrolysis of 1-4'-Phenylbutylnaphthalene.

5-4'-Phenylbutyltetralin (I) can be considered as a possible intermediate for the formation, at high temperatures, of 3:4-benzopyrene (see Chapters I and II). This could involve two mechanisms:-

(1) A primary cyclisation followed by dehydrogenation of the tetralin ring and the butyl linkage.

(2) Dehydrogenation of either the tetralin ring, or the butyl linkage, or both, to give 1-4'-phenylbutylnaphthalene (IV), or 1-4'-phenyl-buta-1:3-dienyltetralin (II), or 1-4'-phenyl-buta-1:3-dienylnaphthalene (III), followed by cyclisation.

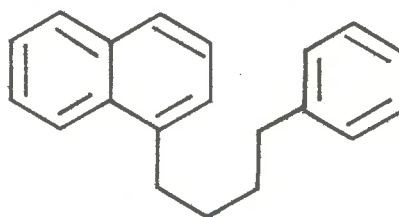(I)   (II)
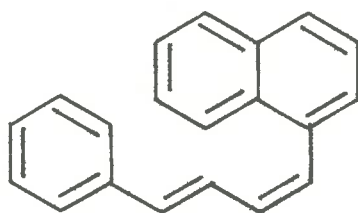
(III)
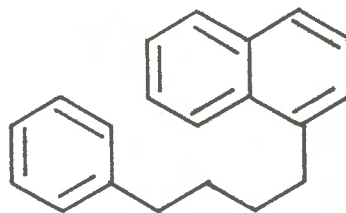
(IV a)
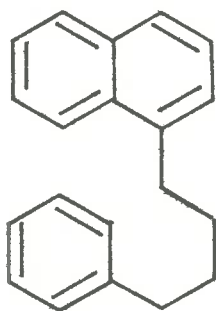
(IV b)

(IVc)

Cyclodehydrogenation clearly can take place in several ways, i.e. in the sense (IVa) to give 3:4-benzo-pyrene, in the sense (IVb) to give 1:1'-dinaphthyl or perylene, or in the sense (IVc) to give 1-phenylphenan-threne.

1-4'-Phenylbutylnaphthalene has now been synthesised and pyrolysed under varying conditions. All of the above cyclodehydrogenation products have been identified in the tars formed. Cyclodehydrogenation could conceivably occur so as to give compounds containing five membered

rings. However, none of these were found. When heated at 360°, 1-4'-phenylbutylnaphthalene was recovered essentially unchanged; however, ultraviolet and fluorescence spectra indicated that small amounts of 3:4-benzopyrene and perylene were present. On heating at 360° with palladium-charcoal as a catalyst the phenyl-butylnaphthalene gave a 63% yield of 1-phenylphenanthrene. Fluorescence spectra indicated the presence of only very small amounts of 3:4-benzopyrene and perylene. Similar results were found using activated charcoal itself except that the yield of 1-phenylphenanthrene (8%) was much lower, and the yield of perylene (0·3%) greatly increased. No 3:4-benzopyrene could be detected. However, refluxing phenylbutylnaphthalene at 360° with palladium-asbestos gave no 1-phenylphenanthrene, but did give a small amount of benzopyrene and perylene and another compound with a chrysene type ultrviolet absorption spectrum. If this were 6:7-dihydro-3:4-benzopyrene it would be expected to have a spectrum similar to 5-ethylchrysene. Although the main maximum (268 mμ) was the same as for 5-ethylchrysene the very impure nature of the isolated product precluded any definite identification.

The observation that using palladium-charcoal or

charcoal itself as a catalyst a far greater yield is
obtained of 1-phenylphenanthrene than the other cyclo-
dehydrogenation products (at 360^0) requires some comment.
The catalyst may be expected to increase the yields of
each possible cyclodehydrogenation product.   If the
dehydrogenation is a radical reaction (which is a reason-
able assumption at these temperatures), then the most
reactive positions will be those adjacent to the aromatic
rings[52]; viz. those shown by an asterisk in (V), (VI),
and (VII).   Cyclisation is then more likely to occur in
(VI) and (VII) as these involve an active position.   It
would also be expected that cyclisation to a naphthalene
nucleus (as with VII) would occur far more readily than
to a benzene nucleus (as with VI)[53].   On this reasoning
alone, then, the yields should be in the order (VII)>>(VI)
>(V).

Other factors are undoubtedly involved, including the
fact that the cyclisation of one ring only is required in
the formation of 1-phenylphenanthrene.   However, this
satisfactorily explains the yields with charcoal as
catalyst, and to a lesser extent with palladium-charcoal.
As the yields of perylene and 3:4-benzopyrene when pallad-
ium-asbestos was used were of the same order as those
obtained by the pyrolysis at 360^0 without any catalyst,

palladium-asbestos appears to be ineffective as a catalyst. The larger surface area of the charcoal may be involved in an explanation of this anomaly.

(V)

(VI)

(VII)
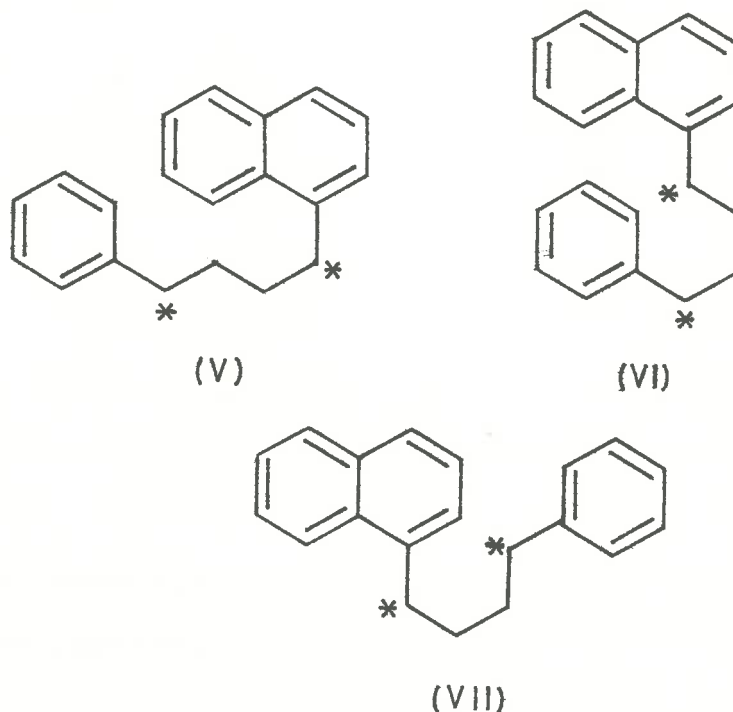
Pyrolysis of the phenylbutylnaphthalene at 600° was carried out by passing the liquid through a silica tube packed with porcelain chips heated in the electric furnace described in Chapter I. Low boiling substances produced by cracking (toluene, naphthalene, and 1-methylnaphthalene) were removed by distillation from the resulting tar. The residue was submitted to chromatography on alumina and the

various fractions analysed using ultraviolet and fluores-
cence spectra. These techniques showed the presence of
1:1'-dinaphthyl, pyrene, perylene and 3:4-benzopyrene in
small yield. The mechanism of the formation of these
compounds, except that of pyrene, which is obviously formed
by secondary reactions involving the substances produced
by cracking (e.g. styrene), have been discussed above.

The tar formed at 700° was shown, in the same way,
to contain similar products, but with a much larger yield
(40%) of naphthalene due to the greater amount of cracking
at the higher temperature. However, at 500° using an
unpacked pyrex tube unchanged starting material was mostly
recovered. A comparison of the products obtained and
their yields, in these pyrolyses, is given in Table 3·1.

For the synthesis of 1-4'-phenybutylnaphthalene,
ethyl β-benzoylpropionate was esterified with ethanol and
sulphuric acid, and then reduced with "copper chromite"
and hydrogen to ethyl-4-phenylbutyrate[*]. Further reduction

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[*] Adkins, Wojcik, and Covert[54] describe this reduction
as proceeding right through to the alcohol; however,
with the apparatus used (maximum pressure obtainable
was 2500 lbs./sq.in.) only the carbonyl function was
reduced.

## TABLE 3·1   PYROLYSIS PRODUCTS OF 1-4'-PHENYLBUTYLNAPHTHALENE.

Product	Yield %						
	360	360 (C)	360 (Pd/C)	360 (Pd/Asb.)	500 (Un-pack-ed)	600	700
Recovered	75	50	sa	50	70	–	–
Toluene, etc.	–	sa	sa	25	–	25	10
Naphthalene	–	5	–	–	–	2	40
1 Me-Naphthalene	–	sa(?)	–	–	–	27%	(?)
Dinaphthyl	–	–	–	–	–	0·4%	(?)
1-Phenyl-phenanthrene	–	7·5	63	–	–	–	–
Pyrene	–	–	–	–	–	0·2	–
Perylene	0·05	0·3	sa	0·04	–	0·06	(?)
3:4-Benzopyrene	0·05	–	sa(?)	0·08	(?)	0·2	0·1
F.S. 412, 438, 465.	–	–	–	sa	sa	sa	0·02
Unidentified	sa	sa	sa	12·5	sa	20	20

F.S. = Fluorescence Spectrum;

sa   = small amount.

with lithium aluminium hydride gave 4-phenylbutan-1-ol
in good yield.   This was converted to the bromide (VIII)
with phosphorus pentabromide or with phosphorous tribromide.
The tertiary alcohol (IX) was formed from the reaction of
the Grignard complex, or lithio-derivative, of the bromide,
and 1-tetralone.   Dehydration of the alcohol, which
occurred very readily, could conceivably give either a
compound with an endocyclic (X), or exocyclic (XIV) double
bond.   Ozonisation of the product, and examination of
the neutral fraction (presumably XII) by infrared
spectroscopy showed two carbonyl bands.   After treatment
with acidified 2:4-dinitrophenylhydrazine no carbonyl
bands could be detected.   However, regeneration of the
carbonyl compounds with pyruric acid gave a compound which
contained only one (aldehydic) carbonyl group.   Evidently
the action of the acidified 2:4-dinitrophenylhydrazine on
(XII) resulted in intramolecular dehydration to the
dinitrophenylhydrazone of the indene aldehyde (XII).   A
similar intramolecular dehydration to indene-2-aldehyde
has been reported by Braun and Zobel[55].

This evidence indicates that the unsaturated compound
is the dihydronaphthalene derivative (X).   Dehydrogenation
of this compound with palladium-charcoal in p-cymene gave
the desired phenylbutylnaphthalene (XI).

(VIII)   (IX)   (X)

(XI)   (XII)

(XIV)   (XIII)
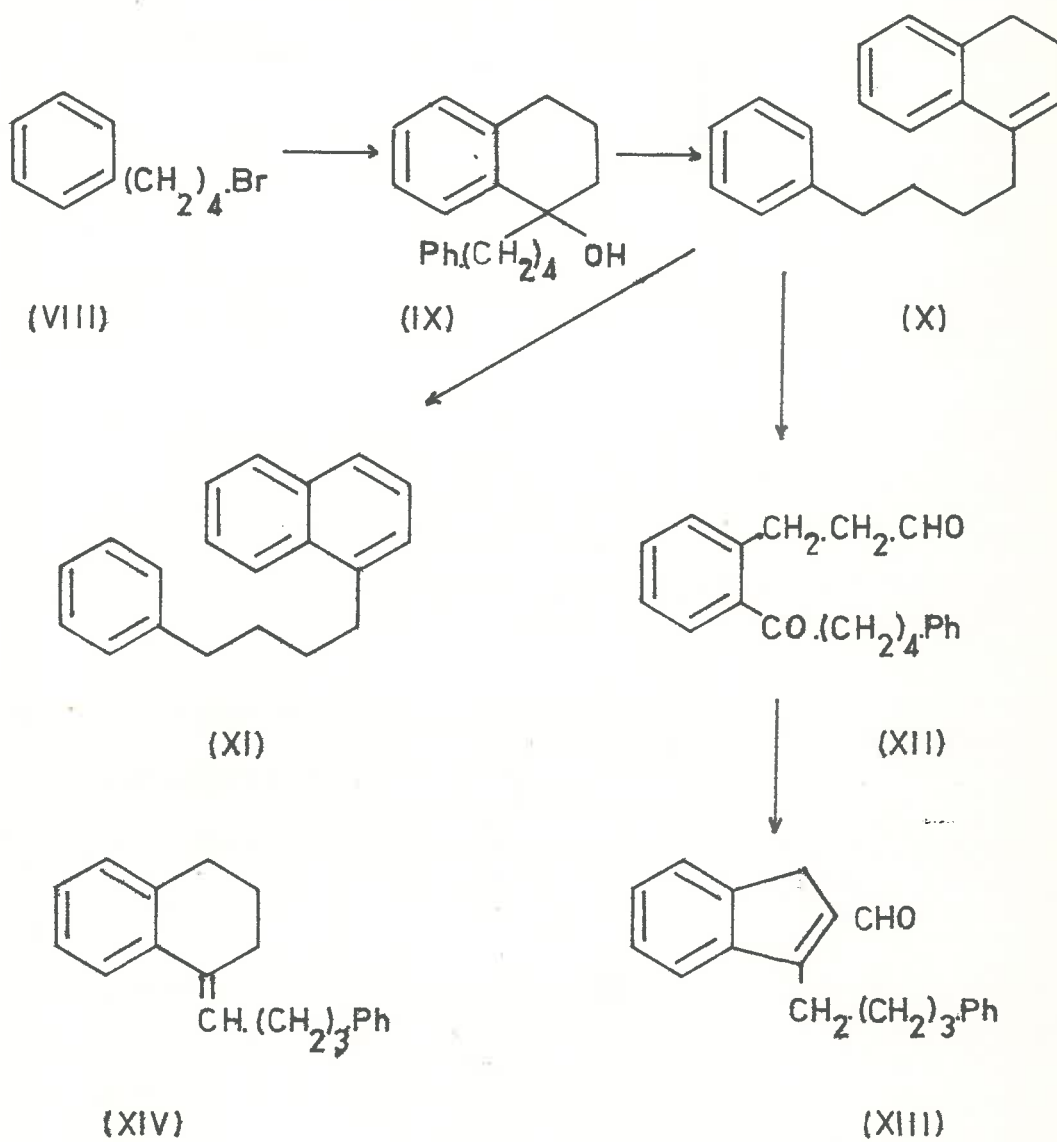
PART II.

The Pyrolysis of a Partially Dehydrogenated
1-4'-Phenylbutyldecalin* and 1-4'-Cyclohexylbutyldecalin.

As the proposed intermediate for the formation of
3:4-benzopyrene in "Schroeter Tar", i.e. 5-4'-phenylbutyl-
tetralin, contains a saturated ring adjacent to the
benzene ring when the molecule is arranged so that cyclo-
dehydrogenation would result in the formation of 3:4-
benzopyrene, it was thought desirable to examine compounds
with this ring hydrogenated.

A partially dehydrogenated 1-4'-phenylbutyldecalin*
and 1-4'-cyclohexylbutyldecalin have therefore been
synthesised and some pyrolysis experiments carried out.
Pyrolysis of the former at 600° gave, besides some low
boiling products, chrysene, and a small amount of 3:4-
benzopyrene and perylene.   No benzopyrene could be
detected in the tar produced by pyrolysis at 360°.
However, at 360° with palladium-charcoal as catalyst,
pyrolysis gave naphthalene, 1-4'-phenylbutylnaphthalene,
1-phenylphenanthrene and traces of perylene and 3:4-
benzopyrene.

* Actually a mixture with 1-4'-phenylbut-1-enyldecalin.

Unchanged starting material was recovered almost entirely from the pyrolysis of 1-4'-cyclohexylbutyldecalin at 360°.

(XV)　　　　　　　　　　(XVI)

(XVIII)　　　　　　　　(XVII)
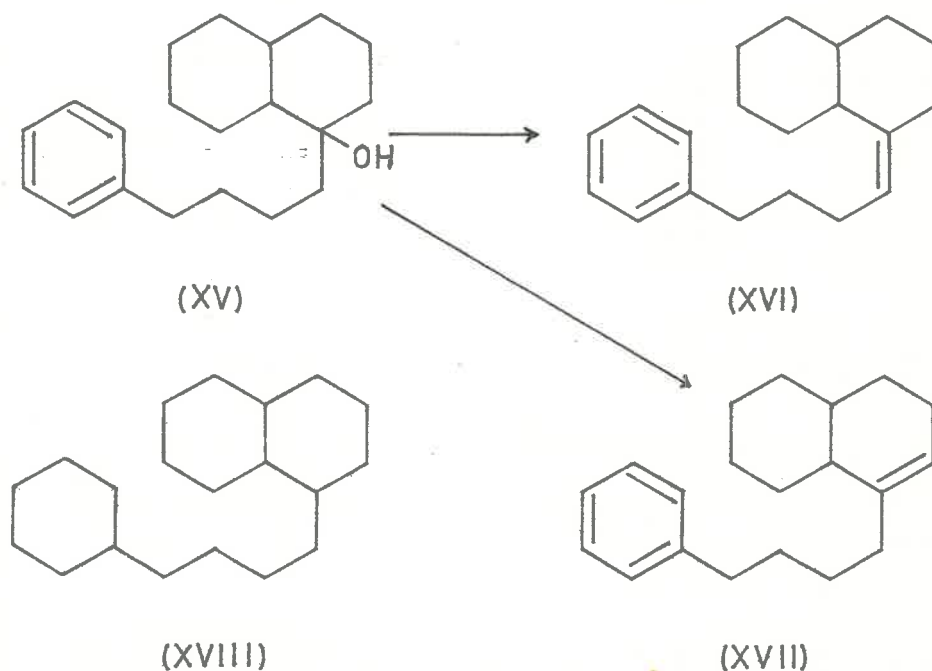
For the synthesis of (XVI) and (XVII) the lithio-derivative of phenylbutylbromide was added to 1-decalone to give the tertiary alcohol (XV).　Dehydration gave a mixture of (XVI) and (XVII) (shown by ozonisation). High pressure hydrogenation of 1-4'-phenylbutylnaphthalene with Raney nickel catalyst gave 1-4'-cyclohexylbutyldecalin (XVII).

PART III.

The Attempted Synthesis of 5-4'-Phenylbutyltetralin.

In view of the proposed formation of 3:4-benzopyrene from 5-4'-phenylbutyltetralin (XXIV) in "Schroeter Tar", it was considered important to try to obtain some of this hydrocarbon itself, for pyrolysis.

Many attempts to synthesis it were carried out. The scheme (XIX - XXIV) was tried exhaustively.
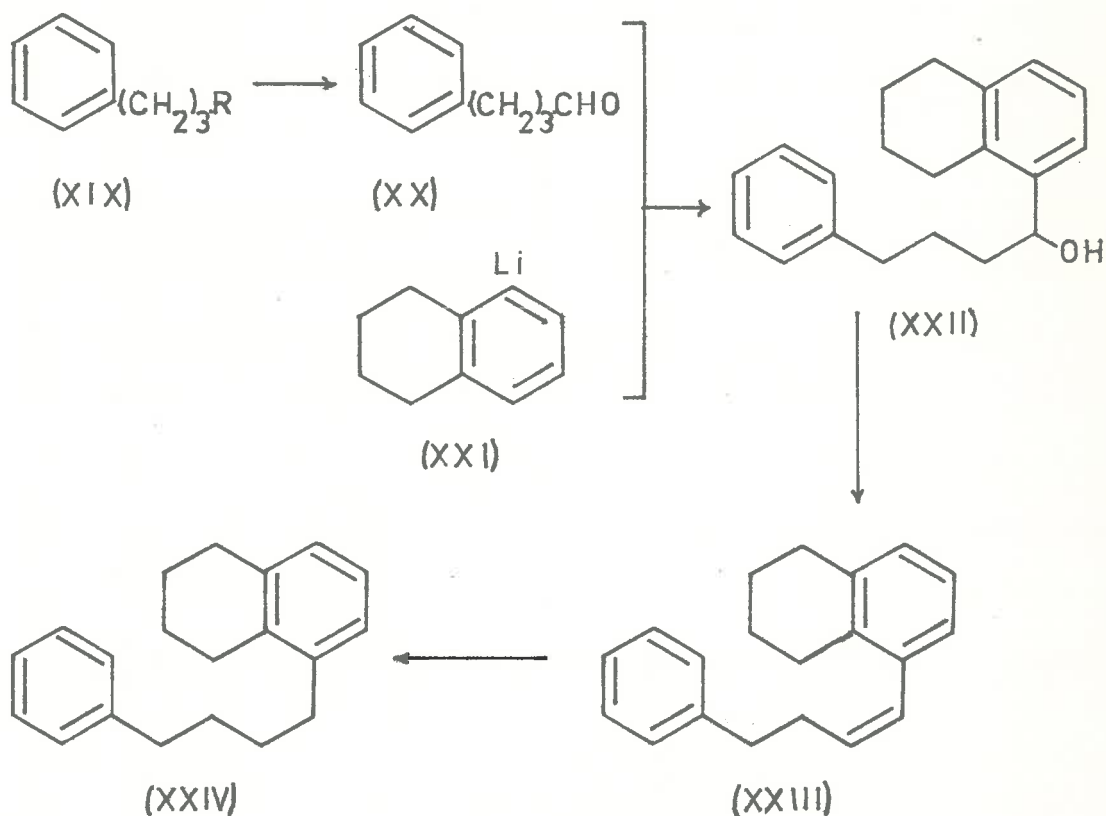
Phenylbutyraldehyde is quite unstable and soon polymerises in air, in contact with alkali, on heating in the presence of oxygen, etc., and is difficult to prepare and handle. Various oxidative and reductive methods were tried for its preparation. Oxidation of (XIX) (where R = CH_2OH) with sodium dichromate, chromium trioxide and pyridine[56], and dinitrogen tetroxide[57], all gave poor yields, while dehydrogenation over copper[58] at 220° gave after purification through the bisulphite compound a 40-50% yield (the best method). Where R = CH_2 Br nitration with silver nitrite[59] followed by reduction of the sodium salt gave very little aldehyde. Where R = COCl Rosenmund reduction with or without poisoning, and also reduction with lithium-tri-t.-butoxyaluminium hydride[60] gave poor yields.

Analyses of the compounds (XXII), (XXIII) and (XXIV) were very poor. Dehydration of the secondary alcohol did not remove all the oxygen. A mixture of the required compound with polymers formed by the action of excess lithium on the aldehyde seems probable, and the method was eventually abandoned.

The scheme (XXV - XXVII) was also tried. However, satisfactory yields of the starting material (XXV) could not be obtained. Hence this approach was also abandoned.
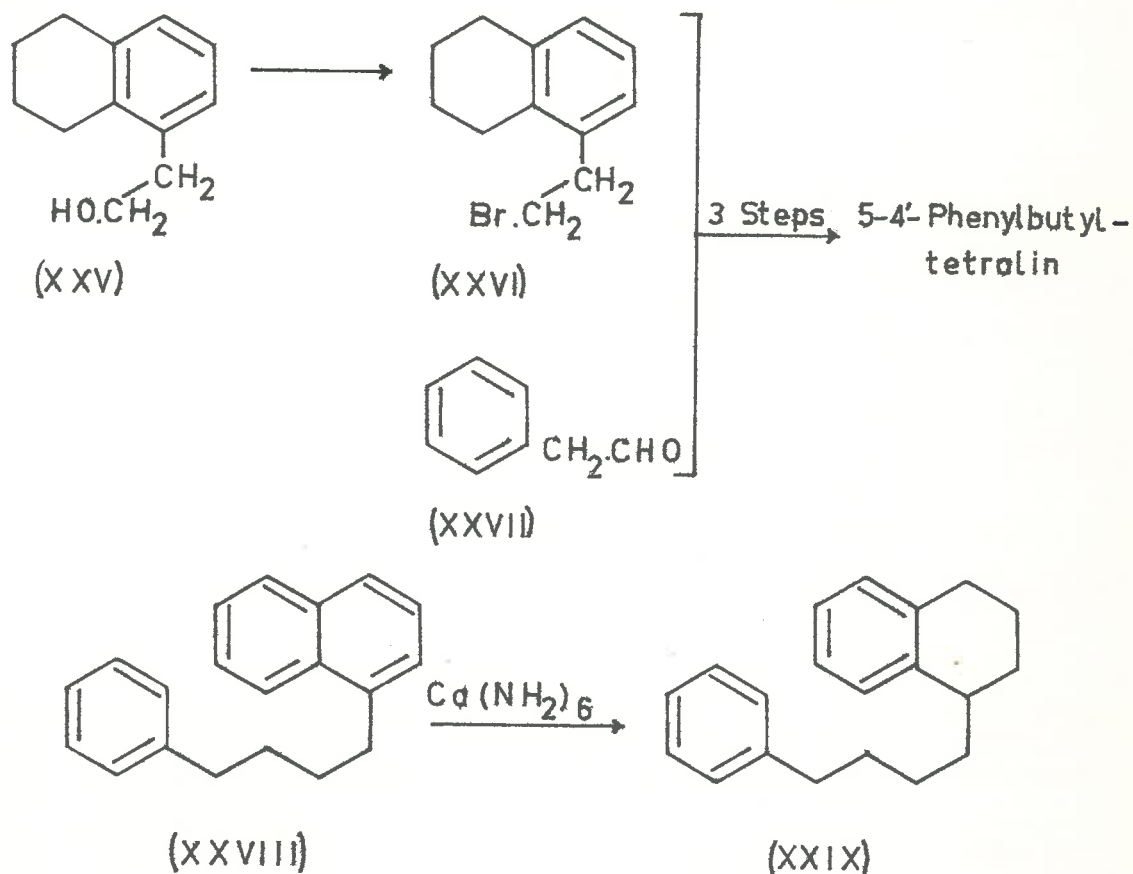
Boer and Duinker[61] have described the selective
reduction of alkylnaphthalenes to alkyltetralins with
calcium hexammine to give 3% reduction in the substituted
ring and 97% in the non-substituted.   However, reduction
of 1-4'-phenylbutylnaphthalene (XXVIII) in this way gave
1-4'-phenylbutyltetralin (XXIX).

Finally attempts were made to effect the condensation of the two parts of the molecule using 5-cyanotetralin (XXXI) and phenylpropylbromide (XXX) *via* the Grignard complex or *via* the lithium alkyl to give the ketone (XXXII). However, both gave unidentifiable products. Similarly condensation of 5-bromotetralin (XXXIV) and phenylbutyryl chloride (XXXIII) *via* the Grignard and cadmium complexes also gave the ketone (XXXII).
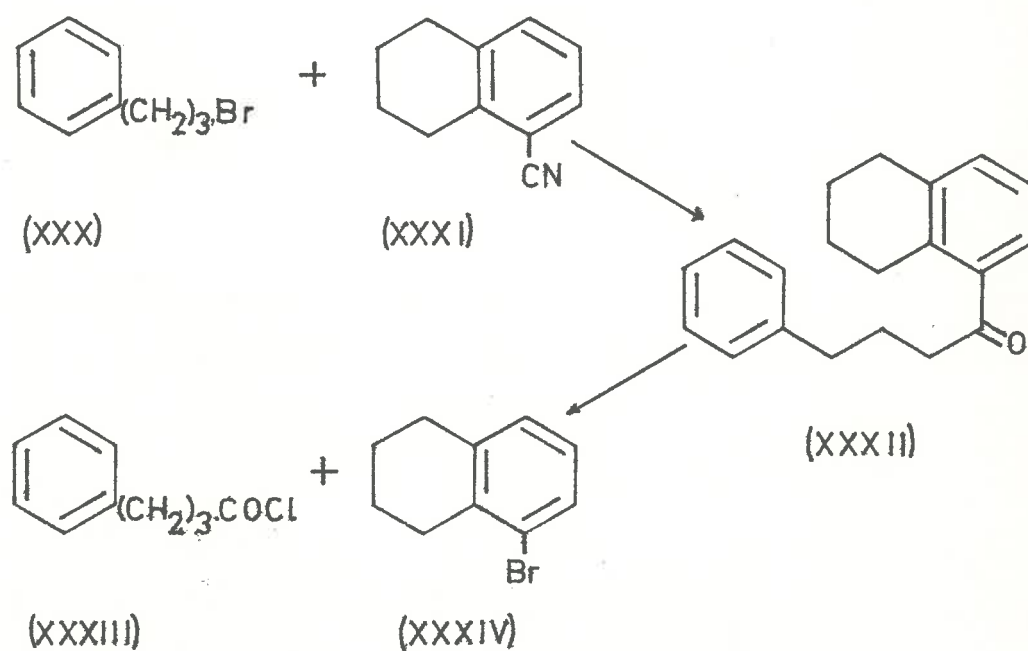
In this case a small amount of ketonic material was obtained, which however, showed four bands in the carbonyl region in the infrared, indicating a mixture.

As 3:4-benzopyrene is formed in "Schroeter Tar" only
after distillation (see Chapter II) it seems possible,
in this case, that some cyclodehydrogenation has occurred
during distillation of the product to give e.g. compounds
(XXXV) and (XXXVI).
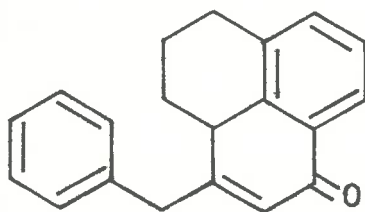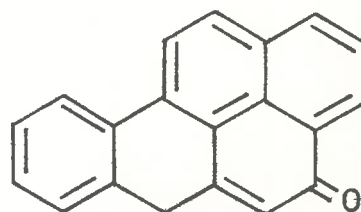
(XXXV)   (XXXVI)
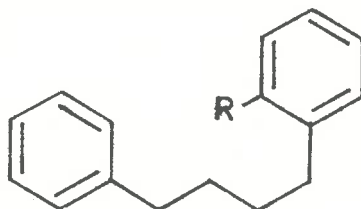
(XXXVII)

Another possible method of synthesis involving an
ortho-substituted diphenylbutane intermediate (XXXVII)
was considered.   However, it did not seem promising,
and was not attempted.

EXPERIMENTAL.

4-Phenylbutan-1-ol.-   Ethyl 4-phenylbutyrate
(100 g.) obtained from the reduction with hydrogen and
copper chromite of ethyl 3-benzoylpropionate[62], in ether
(100 c.c.) was added dropwise to a suspension of lithium
aluminium hydride (30 g.) in ether (500 c.c.).   The
reaction mixture was refluxed for 1 hr. and then carefully
decomposed with water and dilute sulphuric acid.   The
ethereal extract was dried, evaporated, and the alcohol
distilled as a colourless oil, (73 g., 96%), b.p. 124-
127°/9 mm. (Lit.[63] 140°/17 mm.) η_D^{24} 1·5188.   The phenyl-
urethane had m.p. 51-52° (Lit.[64] 51-52°).

4-Phenylbutyl Bromide.-   Method (i)   4-Phenyl-
butan-1-ol (50 g.) was added dropwise to phosphorus
pentabromide (120 g.).   After standing at room temperature
for ½ hr. the reaction mixture was heated on a water-bath
for 1 hr.   It was poured onto ice, the oil washed with
water, sodium bicarbonate solution, and water, and then
finally dried over anhydrous calcium sulphate.   Removal
of the ether and distillation of the residue gave 4-
phenylbutyl bromide (51·5 g., 76%), b.p. 132°/12 mm.,
(Lit.[63] 132°/12 mm.), $_D^{19}$ 1·5408.

Method (ii)   The alcohol (50 g.) was added slowly,
with stirring to a slight excess of phosphorus tribromide
(120 g.) contained in a three-necked flask fitted with a
mercury-sealed stirrer, dropping funnel, and drying tube.
After the addition was complete, the reaction mixture
was heated, with stirring, on the water-bath for 1-2 hr.
The crude material was worked up as in method (i) to give
the bromide (49 g., 72%).

1-Hydroxy-1-4'-phenylbutyltetralin.-   Method (i)
1-Tetralone (21 g.) was added dropwise to the Grignard
reagent prepared from 4-phenylbutyl bromide (30 g.) and
magnesium (4 g.) in ether (45 c.c.).   After refluxing
for ½ hr. the complex was decomposed by pouring onto ice
(70 g.) and 10% hydrochloric acid (100 c.c.).   The
ethereal solution was thoroughly washed with water, dried,
and the ether removed.   Distillation of the residue gave
three fractions;   (a) b.p. 80-100°/30 mm. (10 g.)
η_D^{25} 1.5040;   (b) b.p. 120-140°/30 mm. (12 g.);   and (c)
b.p. 170-172°/0.1 mm. (15 g., 37%).   Fraction (a) was
carefully fractionated in a Griffin and Tatlock semi-
micro distillation apparatus.   Infrared spectroscopy
and the refractive index of the constant boiling main
part of the distillate showed this to be n-butylbenzene.

Fraction (b) was mainly 1-tetralone, while fraction (c) on redistillation gave <u>1-hydroxy-1-4'-phenylbutyltetralin</u>, b.p. 170–172°/0·1 mm., η_D^{17} 1·5760, (Found: O, 5·5; $C_{20}H_{24}O$ requires O, 5·7%).

Method (ii)   20 Drops of a solution of the bromide (35 g.) in ether (50 c.c.), was added to a nitrogen flushed flask containing lithium wire (3·5 g.) in ether (75 c.c.).   When a slight milkiness of the solution developed, showing the reaction had commenced, the reaction mixture was cooled to -10° in a dry-ice/ethanol bath.   The remainder of the bromide solution was added, with stirring, over ½ hr. maintaining the internal temperature at -10°.   The stirring was continued for a further 2 hr. allowing the temperature to rise to 10° over this period. (<u>c.f.</u> butyllithium[65]).   To this solution was added dropwise tetralone (24 g.) in ether (25 c.c.) maintaining the temperature between 10–20°. After refluxing for ½ hr. and filtering the product through glass wool, it was worked up as in method (i).   Distillation gave 1-hydroxy-1-4'-phenylbutyltetralin (27 g., 57%), together with the same fore-runs as in the first method.

Attempts to make a <u>p</u>-nitrobenzoate, 3:5-dinitrobenzoate, and a <u>p</u>-bromophenacyl ester failed.

<u>3:4-Dihydro-1-4'-phenylbutylnaphthalene</u>.-   The
above alcohol (8 g.) in ethanol (100 c.c.) and sulphuric
acid (1 c.c.) was refluxed for 1 hr. and the reaction
mixture poured into a large volume of cold water.   The
oil which separated, was removed, dried, and distilled to
give an almost quantitative yield of 3:4-<u>dihydro-1-4'-</u>
<u>phenylbutylnaphthalene</u>, b.p. 174-176°/0·1 mm., η_D^{23} 1·5809,
(Found: C, 91·6; H, 8·6. $C_{20}H_{22}$ requires C, 91·6; H,
8·4%).   The oil exhibited a blue-violet fluorescence in
ultraviolet light.

<u>Determination of the Position of the Double Bond</u>.-
Ozonisation of the dehydrated alcohol (2 g.) in ethyl
acetate (15 c.c.) and after the addition of ethanol
(20 c.c.), decomposition of the ozonide with 10% palladium/
charcoal and hydrogen gave a viscous residue on removal
of the solvent.   Treatment with sodium bicarbonate
removed a small amount of acid formed.   Infrared
absorption spectroscopy of the unextracted position showed
two bands in the carbonyl region (5·80 and 5·93), one
corresponding to a aldehydic and the other to a ketonic
group.   The 2:4-dinitrophenylhydrazone, considered as
being 3-4'-<u>phenylbutylindene-2-aldehyde dinitrophenyl-</u>
<u>hydrazone</u> crystallised from chloroform as fine red prisms,
m.p. 210-211° (Found: C, 68·4; H, 5·3; N, 12·4; O, 14·2;

$C_{26}H_{23}N_4O_4$ requires C, 68·6; H, 5·1; N, 12·3; O, 14·05%).
Infrared absorption spectroscopy showed no carbonyl
groups present in the 2:4-dinitrophenylhydrazone.
However, on regenerating some of the carbonyl compound
by heating the derivative with pyruvic acid at 100° for
7-8 hr.[66] only the aldehydic band (5·84μ) was shown.

1-4'-Phenylbutylnaphthalene.- The above hydrocarbon
(14 g.), 10% palladium/charcoal (4·25 g.) and p-cymene
(70 c.c.) were heated under reflux in an atmosphere of
nitrogen for 5 hr. The initial heating was carefully
controlled as the early part of the reaction was very
vigorous due to the elimination of hydrogen. The liquid
was filtered off, and the catalyst thoroughly washed with
boiling benzene. The solvents were removed by distilla-
tion, and the dehydrogenated product distilled under
vacuum. Redistillation gave 1-4'-phenylbutylnaphthalene
(12·5 g.), as a viscous oil, b.p. 164-6°/0·3 mm., and
345-350°/760 mm., η_D^{22} 1·5990 (Found: C, 92·0; H, 8·0.
$C_{20}H_{20}$ requires C, 92·3; H, 7·7%). The absorption
spectrum in cyclohexane showed maxima (log ε in parenthesis)
at: 226 (4·75); 240 (3·32) infl.; 264 (3·56) infl.;
273 (3·78); 283 (3·81); and 290 (3·52). (See Fig. 3·1).
The phenylbutylnaphthalene exhibited a pale blue
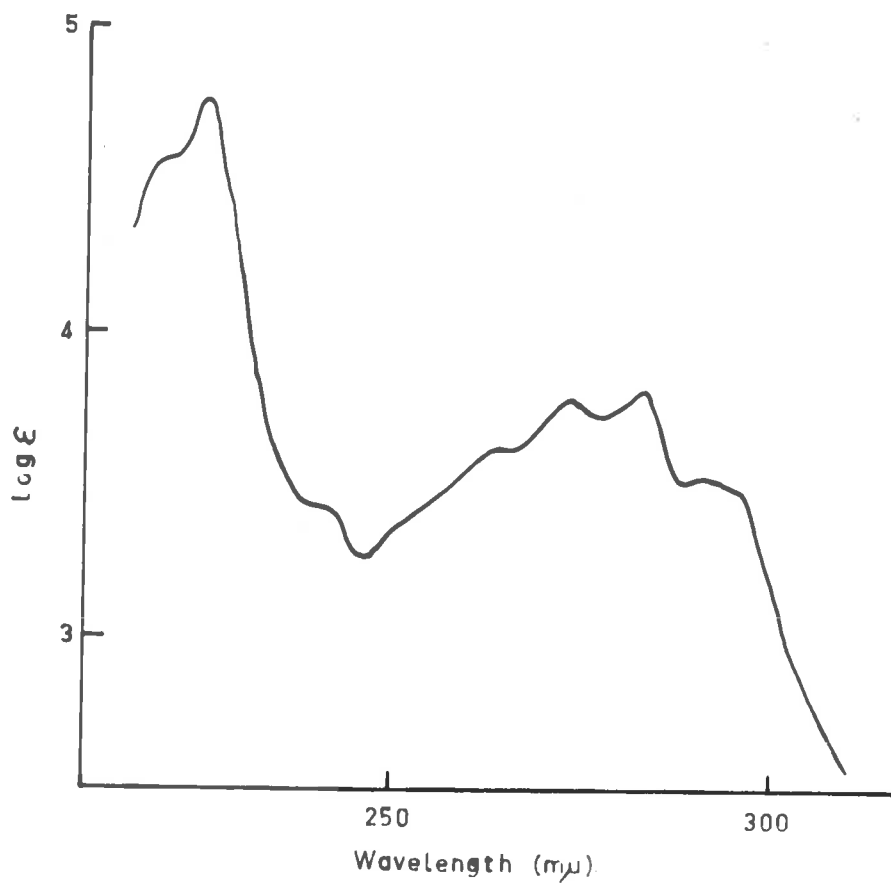
Fig. 3·1. 1-4'-Phenylbutylnaphthalene.

fluorescence in ultraviolet light.

Pyrolysis of 1-4'-Phenylbutylnaphthalene.-

(i) At 360°. Phenylbutylnaphthalene (2 g.) was refluxed for 20 hr. during which the colour of the liquid changed from pale yellow to reddish-green. The product which exhibited a deep green-yellow fluorescence was chromatographed on activated alumina (20 x 2½ cm.). Elution with hexane brought through unchanged phenyl-butylnaphthalene (1·5 g.). Further elution with benzene-hexane (1:1) yielded fractions containing a very small amount of yellow crystalline material. Fluorescence spectra taken of these fractions showed five bands identical with those of an authentic specimen of 3:4-benzopyrene and four corresponding to those of perylene (Plate 3·1a). The fractions combined were extracted with cold concentrated sulphuric acid[26] and after further chromatography, gave a very impure sample of 3:4-benzo-pyrene (less than 1 mg.). Its absorption spectrum showed maxima at 365, 384, and 405 mμ only (Fig. 3·3). Literature values in this region are 364, 384, and 404 mμ.

(ii) At 360° with palladium-charcoal. Phenyl-butylnaphthalene (2 g.) and 5% palladium-charcoal (0·5 g.) were heated under reflux for 5 hr. After 2 hr. the

temperature of the refluxing vapour had decreased to 200° apparently due to the presence of low boiling products formed by cracking. However, after a further 2 hr. the temperature had returned to 360°. The reaction mixture was filtered from the catalyst, which was washed well with boiling benzene. After removal of the solvent, chromatography on activated alumina (20 x 2½ cm.) was carried out in hexane. Elution with hexane gave fractions which on removal of the solvent gave a white solid (1·25 g.). This was identified as 1-phenyl-phenanthrene, prisms, m.p. 78-79° (lit.[67] 78-79°) (Found: C, 94·6; H, 5·75. Calc. for $C_{20}H_{14}$: C, 94·5; H, 5·5%). The picrate had m.p. 117-118° (lit.[67] 117-118°). (Found: N, 8·8. Calc. for $C_{20}H_{14}C_6H_3N_3O_7$: N, 8·7%). The ultraviolet absorption curve (Fig. 3·2) is of the type expected. Further elution of the column with benzene-hexane (1:2) gave seven fractions, each of 70 c.c., two of which showed faint 3:4-benzopyrene bands in its fluorescence spectrum (Plate 3·1b). However, after cold sulphuric acid extraction, the fractions did not give any maxima of 3:4-benzopyrene on submission to ultraviolet absorption spectroscopy. Quite strong fluorescence bands corresponding to those of perylene suggested that
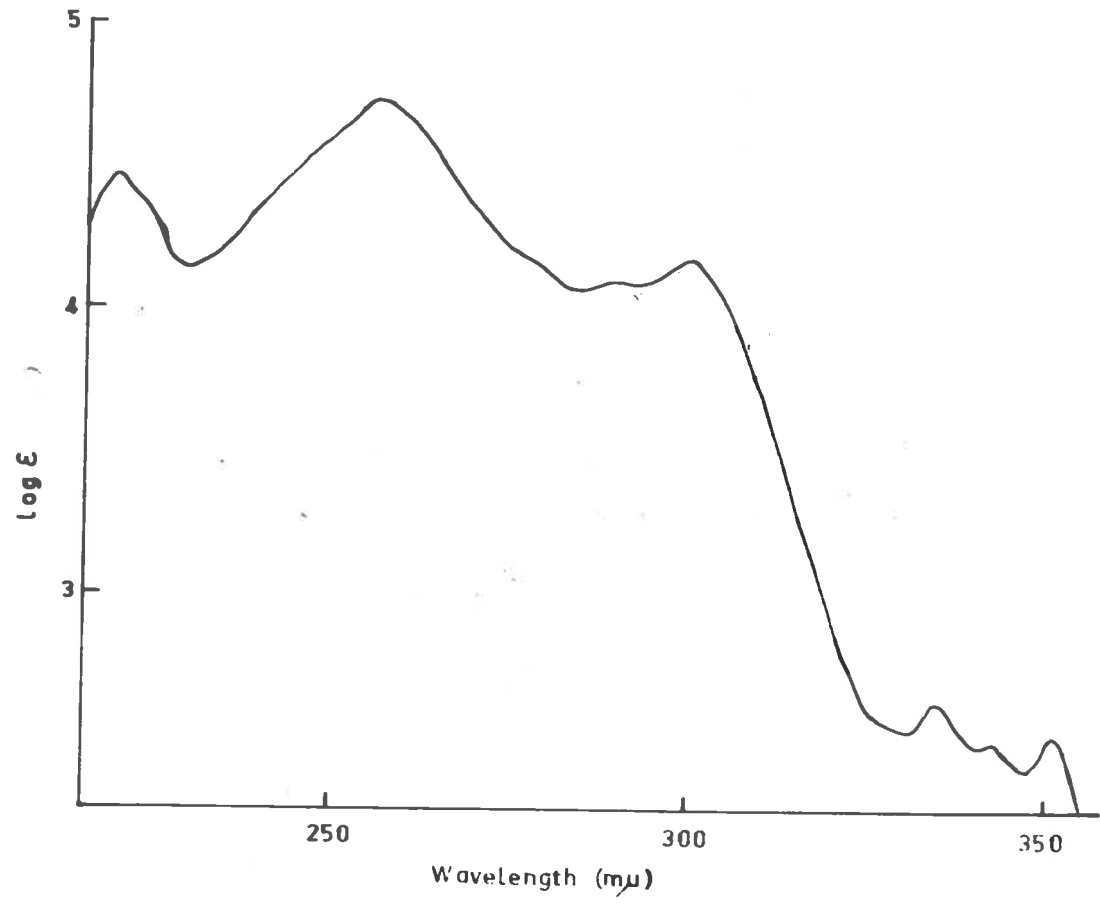
Fig. 3·2.   1-Phenylphenanthrene.

a small amount of this was present (Plate 3·1b).

(iii) At 360° with palladium-asbestos. Method (ii) was repeated using 5% palladium-asbestos catalyst. After removal of the low boiling products (0·5 c.c.) by distillation, the residue was chromatographed on alumina. Elution with hexane brought through mainly recovered starting material. However, the later fractions contained, on removal of the solvent, small amounts of a white solid, which had fluorescence spectral bands (in benzene) at 415, 440, and 475 mμ, and had a chrysene type ultraviolet absorption spectrum. Elution with benzene-hexane (1:2) gave an impure mixture of 3:4-benzopyrene and perylene identified by their ultraviolet absorption maxima at 364, 384, and 406 and 434 mμ (Fig. 3·4) respectively, and by their fluorescence spectra. About 1 mg. of each was present. (Estimated from the absorption spectrum).

(iv) At 360° with activated charcoal. Repetition of method (ii) using only activated charcoal as catalyst gave naphthalene (100 mg.), identified by m.p. and mixed m.p. Chromatography of the residue and elution with hexane gave on removal of the solvent 1-phenylphenanthrene
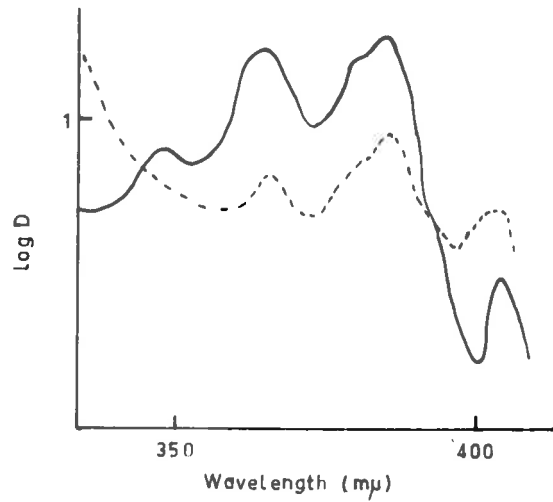
Fig. 3.3.   3:4-Benzopyrene from pyrolysis
             of 1-4'-phenylbutylnaphthalene
             at 360° (- - -).
             (Authentic: ———).
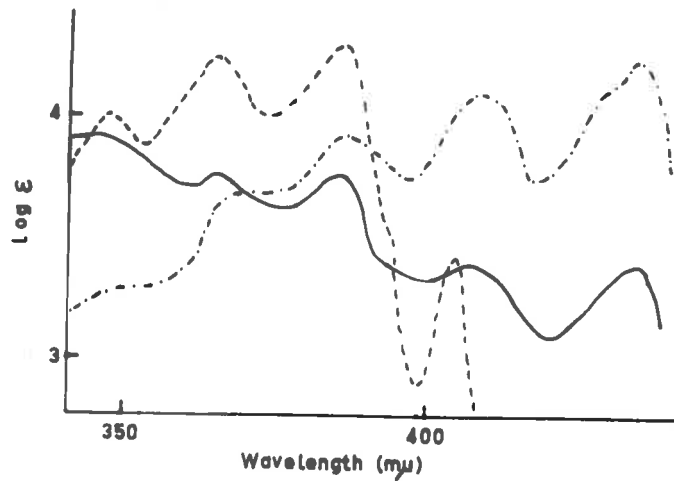
Fig. 3.4.   3:4-Benzopyrene from pyrolysis
             at 360° with palladium/asbestos
             (———).   Authentic 3:4-
             benzopyrene (- - -), and
             perylene (-·-·).

(150 mg.), m.p. 78-79°, mixed m.p. with sample obtained from (ii), 78-79°.   Elution with benzene-hexane (1:2) brought through an intensely blue band which on removal of the solvent, yielded perylene (6 mg.), m.p. 265° (lit.[46] 265).   This was confirmed by its fluorescence spectrum (Plate 3·1c).

(v) <u>At 600°</u>.   The phenylbutylnaphthalene (5 g.) was vapourised at the rate of 1 drop every 15 secs. and passed with nitrogen (1 c.c./sec.) through a silica tube (36 x 1 in.) packed with porcelain chips (⅜ - ¼ in.) heated to 600° in a special electrically heated furnace (see Chapter I).   The resulting red non-viscous tar, which contained some crystalline material, was distilled to remove the low boiling products;   to give fractions (a) and (b).   Fraction (a) (1·25 g.), b.p. 110-120°, was shown by infrared spectroscopy and refractive index, to be mainly toluene.   The colourless solid, which crystallised from fraction (b), b.p. 90-120°/28 mm., was sublimed from the rest of the fraction, and on recrystallisation from ethanol, gave naphthalene (0·1 g.), m.p. 80°, which was not depressed on admixture with an authentic sample.   After redistillation, the yellow liquid, forming the remainder of the fraction, was

identified by its infrared and ultraviolet spectra as
1-methylnaphthalene (1·3 g.).   The picrate had m.p.
140-142°, and mixed m.p. 140-142°.

The residue (1·5 g.) after distillation, was
dissolved in a minimal amount of a mixture of benzene
and hexane and chromatographed on a column of activated
alumina (20 x 2½ cm.).   Elution with hexane brought down
a blue fluorescent band in five fractions (70 c.c. each).
Further elution with benzene-hexane (1:1) gave two more
fractions from an orange fluorescent band, and then
elution with pure benzene eluted a yellow fluorescent
band in two more fractions.   Examination of the
fluorescence spectra of the nine fractions showed diffuse
bands in the 3:4-benzopyrene region (400-450 mμ) in
fractions 3 to 6.   Rechromatography of these fractions
(3-6) combined, followed by extraction with cold sulphuric
acid[49], of the fractions shown by their fluorescence
spectra to contain probably 3:4-benzopyrene, and further
chromatography of this extract gave a pale yellow solution
on elution with benzene-hexane (1:2).   This solution
fluoresced blue, both in visible and ultraviolet light.
Examination of the fluorescence spectrum showed three
bands at high wavelength (445, 475 and 502 mμ) as well as

those of 3:4-benzopyrene (Plate 3·1d). A reasonable
separation of the 3:4-benzopyrene from the contaminant
was effected by chromatography on alumina (30 x 5 cm.)
and elution, under vacuum, with hexane. Elution with
6-8 litres of hexane brought through a pale violet
fluorescent first fraction, which was followed, on elution
with 5 litres more of hexane, by a blue fluorescent band.
Finally, the remainder of the fluorescent (violet)
material on the column came through with another 4 litres
of hexane. On removal of the solvent, and after yet
another chromatographic run on each of the latter two
fractions, small amounts of crystalline material were
isolated. The first fraction showed four maxima of 3:4-
benzopyrene and three maxima of perylene on ultraviolet
spectroscopy. (Fig. 3·5). (The maxima of perylene
were at 386, 408, 434 mμ). The estimated amount of
perylene present from the absorption curve was 3 mg.
Confirmation of this was given by comparison of the
fluorescence spectrum with that of a sample of authentic
perylene (Plate 3·1e). The ultraviolet absorption
spectrum of the second yellow crystalline fraction
(10 mg.) was identical with that recorded for 3:4-benzo-
pyrene[46,47]. (Fig. 3·6). It had m.p. 170-172°, mixed
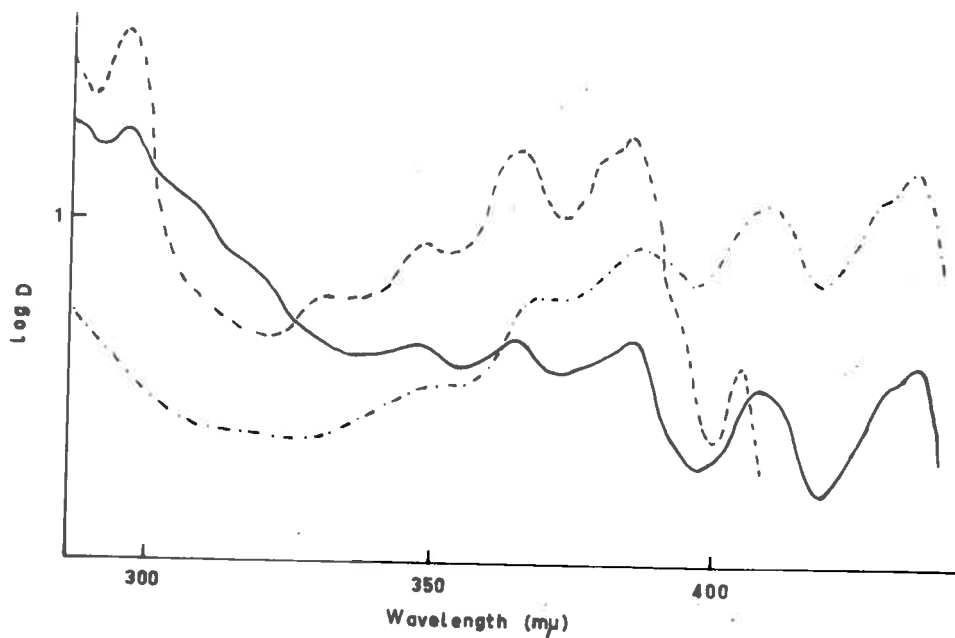
Fig. 3·5. 3:4-Benzopyrene and perylene from pyrolysis at 600°.
(———). Authentic 3:4-benzopyrene (– – –)
and perylene (– – –).
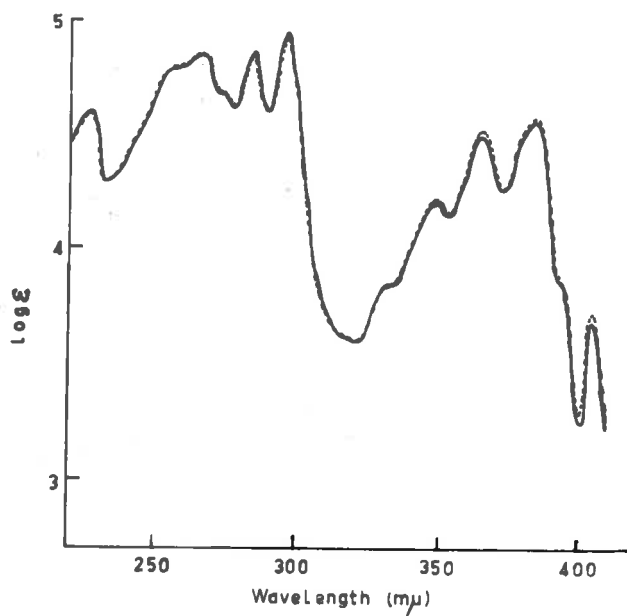
Fig. 3·6. 3:4-Benzopyrene from pyrolysis
at 600° (———).
Authentic (– – –).

m.p. 171-174°, (lit. 176-177^{o46}). The picrate which could not be obtained in a pure state, had m.p. greater than 180° (lit. 198^{o46}).

Fractions 1 and 2 of the original chromatogram were combined and rechromatographed with hexane as elutant. The first fractions gave, on removal of the solvent, a yellow liquid from which crystallised a white solid. This was washed free of oily material with cold ethanol, and recrystallisation from ethanol gave white prisms of 1:1'-dinaphthyl (20 mg.), m.p. 143-146°, mixed m.p. 145-147°. The ultraviolet absorption spectrum had maxima at (authentic in parenthesis) 221 (220), 283 (283), and 293 (294 mμ)[68]. Further elution of the chromatogram with benzene-hexane (1:2) gave a pale blue fluorescent solution, which on fluorescence spectrophotographic examination, showed very faint diffuse bands similar to those of pyrene. The ultraviolet absorption spectrum showed maxima at (authentic values in parenthesis), 240 (241), 259 (261), 272 (272), 304 (305), 319 (318), 335 (334 mμ) corresponding to those of pyrene[46]. The estimated amount of pyrene was less than 10 mg. Examination of the fractions 7-9 of the original chromatogram gave no further identifiable products.

(vi) <u>At 700°</u>.   The phenylbutylnaphthalene was
pyrolysed in the same manner as at 600°, and the resulting
tar chromatographed on alumina.   Elution with benzene-
hexane (1:3), benzene-hexane (1:1), and finally with pure
benzene gave 12, 8, and 10 fractions (each of 70 c.c.)
respectively.   Fluorescence spectral examination of these
fractions showed no distinctive bands in fractions 1-13,
however, fractions 14-24 showed bands in the 3:4-benzo-
pyrene region.   The remaining fractions showed bands of
higher wavelength.

Removal of the solvent from fractions 1 and 2 gave
a yellow solid, which after two recrystallisations from
ethanol, was identified as naphthalene (2 g.).   It had
m.p. 80°, not depressed by admixture with an authentic
sample.   Cold sulphuric acid extraction of fractions
14-24, followed by chromatography on alumina of the main
blue-violet band, gave a yellow solid (5 g.), whose
ultraviolet absorption maxima corresponded with those of
3:4-benzopyrene (Fig. 3.7).   However, this could not be
obtained sufficiently pure to take an accurate melting
point.   Small amounts of perylene were probably present.
This was shown by faint characteristic bands in
fluorescence spectral photographs.

Fractions 25-30 were combined, and rechromatographed

on alumina.   Elution with benzene-hexane (1:2) eluted
blue-violet, blue, and finally yellow bands from the
column.   The fluorescence spectra showed that fractions
1-3 contained small amounts of 3:4-benzopyrene, while
fractions 4-6 showed bands at 412, 438, and 465 mμ,
(Plate 3·1f), and the remaining fractions showed very
intense bands at 470, 500, and 540 mμ (plate 3·1g).
Ultraviolet absorption spectroscopy of the second fraction
still showed six 3:4-benzopyrene maxima, together with a
further six (222, 242, 250, 274 (infl.) 310 and 326 mμ)
maxima of an unidentified compound or compounds (Fig. 3·8).
The third fraction was too impure for any identification
of the compound to be made.

(vii) At 500°.   The phenylbutylnaphthalene (5 g.)
was passed through an empty pyrex tube, heated to 500°
in the special electrically heated furnace, as in the
previous runs at 600° and 700°.   Chromatography on
alumina (30 x 4 cm.) of the resulting tar, and elution
with cyclohexane, gave mainly starting material
(refractive index and ultraviolet spectra).   Fluorescence
spectra of the subsequent fractions, eluted with benzene-
cyclohexane (1:2), failed to indicate the presence of any
3:4-benzopyrene.
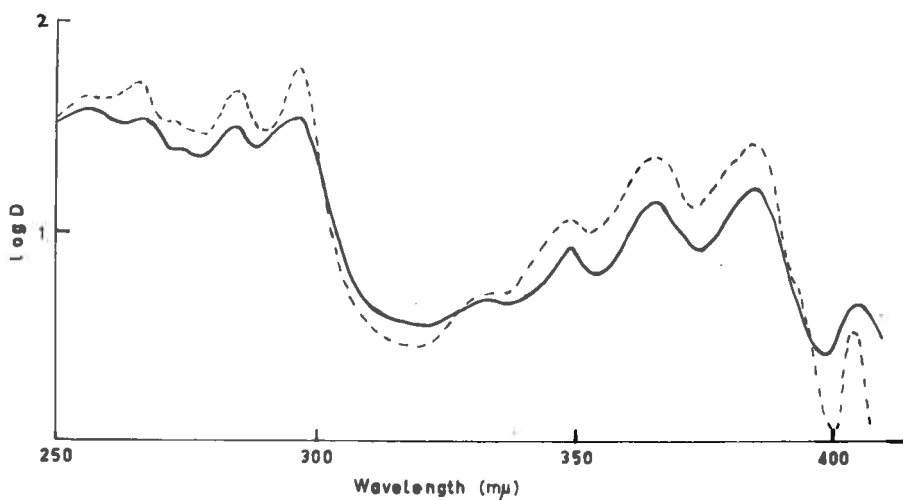
Fig. 3·7.   3:4-Benzopyrene from pyrolysis at 700° (——).
             Authentic (- - -).
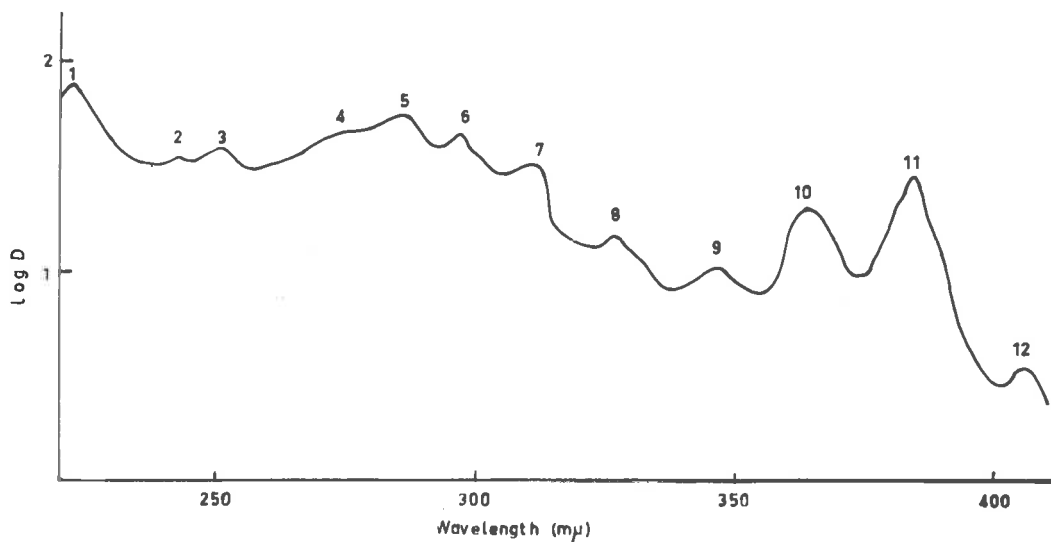
Fig. 3·8.   3:4-Benzopyrene from pyrolysis at 700° (peaks 5, 6, 9,
             10, 11, and 12).   Unknown (peaks 1, 2, 3, 4, 7, 8).

1-Hydroxy-1-4'-phenylbutyldecalin.-   4-Phenylbutyl
bromide (20 g.) in ether (30 c.c.) was added to lithium
wire (2 g.) in ether (50 c.c.) by the method described
for 1-hydroxy-1-4'-phenylbutylnaphthalene. 1-Decalone[69]
(14 g.) in ether (20 c.c.) was added dropwise to the
resulting lithio compound.   After working up as usual,
distillation gave three fractions: (a) b.p. 68-104°/
12 mm. (3 g.); (b) b.p. 104-130°/12 mm. (2 g.) and (c)
b.p. 179-185°/0·7 mm. (17 g., 63·5%).   Redistillation
of fraction (c) gave 1-hydroxy-1-4'-phenylbutyldecalin
as a viscous colourless oil, b.p. 186-188°/1 mm.
η_D^{16} 1·5383 (Found: C, 84·2; H, 10·5; O, 5·8. $C_{20}H_{30}O$
requires C, 83·9; H, 10·5; O, 5·6%).   Fraction (a)
on redistillation was identified as largely n-butylbenzene
while (b) was mainly recovered starting material.

Dehydration of 1-hydroxy-1-4'-phenylbutyldecalin.-
The above alcohol (17 g.) was dehydrated by refluxing in
ethanol (75 c.c.) and concentrated sulphuric acid (3 c.c.)
for 1½ hr.   The reaction mixture was poured into water
(800 c.c.), extracted twice with ether, dried, the solvent
removed, and distilled.   Redistillation gave a colourless
non-viscous oil (14 g., 88%) b.p. 168-170°/0·8 mm.,
η_D^{12} 1·5400 (Found: C, 89·3; H, 10·5. $C_{20}H_{28}$ requires

C, 89·6; H, 10·4%); $\lambda_{max.}$ (log$\mathcal{E}$) in ethanol 222 infl.
(3·25), 227 (3·55), 248 infl. (2·32), 252 (2·38), 258
infl. (2·30, 261 (2·38), 269 (2·38).

Position of unsaturation.-   The above unsaturated
compound was ozonised and worked up as for the correspond-
ing dihydrophenylbutylnaphthalene.   The resulting
neutral fraction gave a 2:4-dinitrophenylhydrazone of
indefinite m.p.   The mixture could not be separated by
chromatography on a bentonite-Kieselguhr column.

Pyrolysis of the above mixture.-   (1) At 360° with
palladium-charcoal.   The above mixture of unsaturated
compounds (2 g.) was refluxed with 10% palladium-charcoal
for 5 hr. in an atmosphere of nitrogen.   During this
time, the reaction mixture developed a green-yellow
fluorescence.   The product was filtered from the catalyst,
which was washed well with boiling benzene.   On removal
of the solvent the residue was chromatographed on alumina
(20 x 3 cm.).   Elution with hexane (4 fractions of
60 c.c.) brought through a violet fluorescent band.   The
first of these fractions contained most of the product
(1·5 g.).   Distillation of this fraction gave a trace of
naphthalene m.p. 80°, and an oil b.p. 182-186°/0·5 mm.

which was identified by its absorption spectrum (maxima at 226, 262, 272, 283, and 294 mμ) and refractive index (η_D^{18} 1.5973) as 1-4'-phenylbutylnaphthalene.

The residue remaining after distillation (100 mg.), partially solidified. It was identified by absorption and fluorescence spectroscopy, as essentially 1-phenyl-phenanthrene (absorption maxima at 258, 290, 302, 334, 342 and 350 mμ).

Further elution of the column with benzene-hexane (1:2) brought through a blue band. Removal of the solvent, and examination of the very small amount of residue by fluorescence spectroscopy, showed faint bands of perylene and 3:4-benzopyrene. However, the presence of impurities was shown by the diffuse nature of the bands and the presence of other bands (Plate 3.1h). This was supported by absorption spectroscopy which showed maxima at 364, and 384 mμ identified with 3:4-benzopyrene, and at 407 and 434 mμ identified with perylene. The estimated amount of these present, derived from the absorption curve, was less than 1 mg.

(ii) <u>At 600°</u>. The mixture (5 g.) was passed with nitrogen (1 c.c./sec.), at the rate of 1 drop every 15 secs., through a silica tube packed with porcelain chips

($\frac{3}{8}$ - $\frac{1}{4}$ in.) heated at 600°. Distillation of the non-viscous reddish tar obtained, gave several low boiling fractions (total, 2·3 g.), up to b.p. 115°/15 mm. and a residue (1 g.). Gas-liquid chromatography of the low boiling fractions gave retention times corresponding to benzene, toluene, ethylbenzene, styrene, butylbenzene (?), naphthalene and 1- and 2-methylnaphthalene.

The residue was chromatographed on alumina (25 x 3 cm.). Elution with hexane brought through chrysene m.p. 250-252° (lit.[46] 255-256 corr.). Its absorption spectrum was essentially in agreement with the literature[46]. (Fig. 3·9). The trinitrobenzene complex had m.p. 192-194° (lit.[70] 192-194). Further elution of the column with benzene-hexane (1:2) gave some fractions which had diffuse 3:4-benzopyrene type fluorescence spectra. Treatment of the residues after removal of the solvent with cold sulphuric acid[49] followed by further chromatography of the extract gave 3:4-benzopyrene, identified by its ultraviolet absorption maxima at 254, 266, 284, 296, 331, 347, 364, 384 and 404 (Fig. 3·10), and a very weak band of perylene at 434 mμ.

(iii) At 360°. No benzopyrene could be detected in the product after refluxing the mixture (2 g.) under
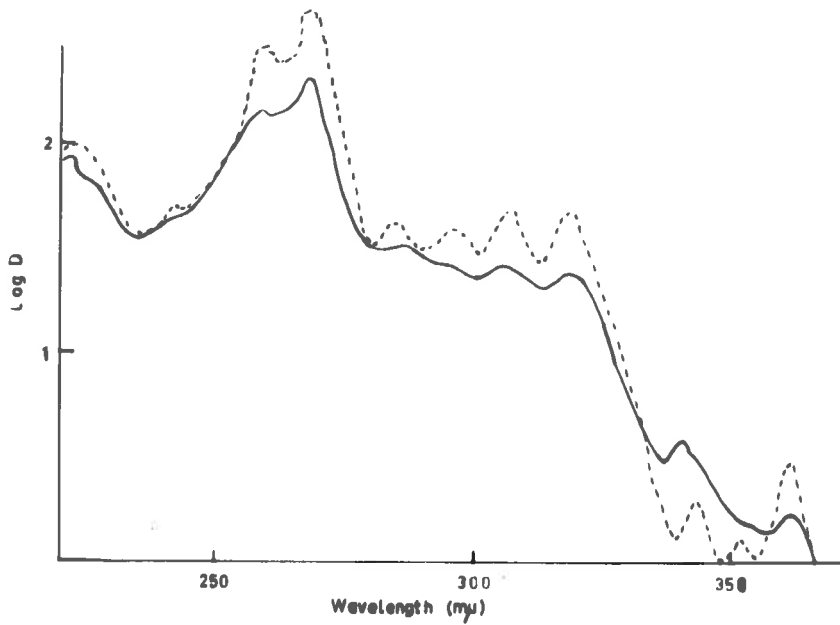
Fig. 3·9. Chrysene (This work: ——). (Authentic: – – –).
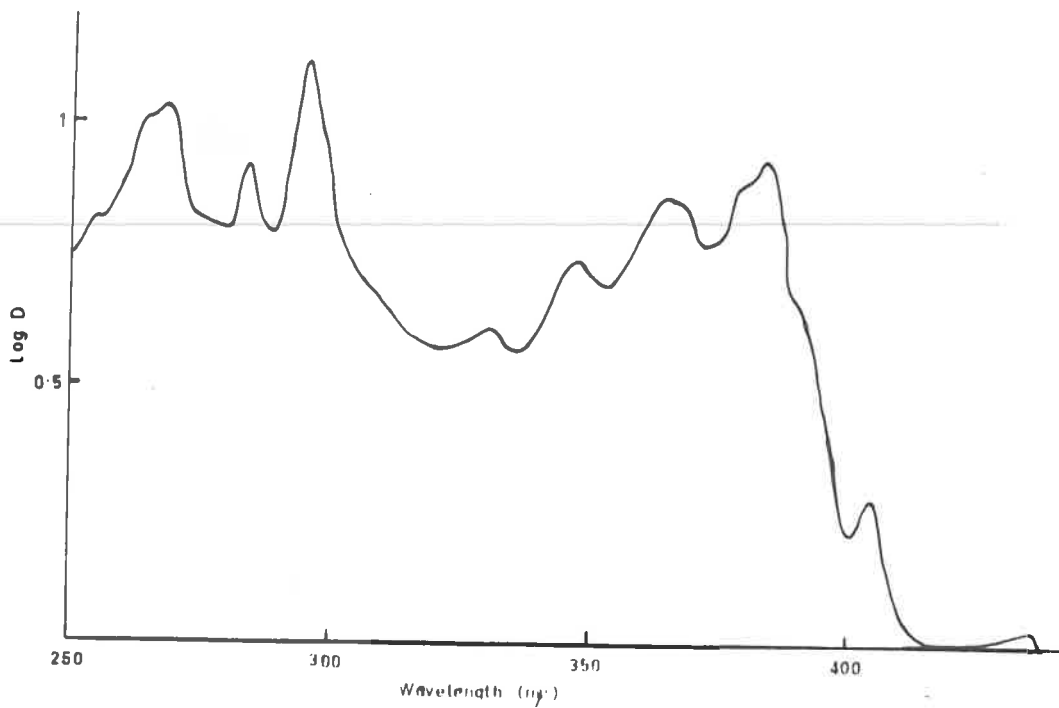
Fig. 3·10. 3:4-Benzopyrene from pyrolysis a mixture of partially dehydrogenated 1-4'-phenylbutyldecalins. (Impure).

nitrogen for 20 hr.

1-4'-Cyclohexylbutyldecalin.- 1-4'-Phenylbutyl-
tetralin (10 g.) in a mixture of tetralin (20 c.c.) and
cyclohexane (200 c.c.) was hydrogenated in a bomb (1·5 l.),
using W7 Raney-nickel (2·5 g.) as a catalyst. An initial
hydrogen pressure of 110 atmospheres was used and the
temperature raised to 200° in 1½ hr. This was maintained
for a further 15 min., and the bomb allowed to cool. The
reaction mixture was filtered from the catalyst, the
catalyst washed with boiling ethanol, and the combined
solutions distilled in vacuo to remove the solvents.
Distillation of the residue gave 1-4'-cyclohexylbutyl-
decalin (8 g., 78%) as a colourless oil b.p. $142-144^{\circ}/$
0·05 mm., η_{D}^{12} 1·4983 (Found: C, 87·1; H, 12·7. $C_{20}H_{26}$
requires C, 87·0; H, 13·0%). The pure material had a
pale blue fluorescence in ultraviolet light.

Pyrolysis of 1-4'-Cyclohexylbutyldecalin.- The
cyclohexylbutyldecalin (1 g.) was refluxed for 7 hr.
However, no identifiable material was recovered other
than the starting material, which constituted almost the
entire product.

Attempted Synthesis of 5-4'-Phenylbutyltetralin.-

Method (i)   To the 5-lithiotetralin, in an
atmosphere of nitrogen, prepared from 5-iodotetralin
(10 g.) by the method for the preparation of phenyl-
lithium[65], phenylbutyraldehyde (6 g.) was added dropwise
with stirring.   The product was worked up in the usual
way, and distilled to give fraction (a) (1·5 g.) b.p.
96-97°/20 mm.; fraction (b) (2 g.) b.p. 153-155°/20 mm.
and fraction (c) (4 g.) b.p. 196-200°/0·5 mm.   A residue
(1·5 g.) remained.   Fraction (a) was identified as
tetralin and fraction (b) as mainly iodotetralin.
Fraction (c) was twice redistilled to give 4'-hydroxy-
5-4'-phenylbutyltetralin (?), b.p. 189-190°/0·08 mm.,
η_D^{22} 1·5744 (Found: C, 86·2; H, 8·7; O, 5·6. $C_{20}H_{24}O$
requires C, 85·7; H, 8·6; O, 5·7%).   However, vigorous
dehydration in ethanol with sulphuric acid, followed by
hydrogenation using Raney-nickel as catalyst gave a
compound containing approximately 1% oxygen.

Method (ii)   (a) Preparation.   A current of dry
ammonia gas (5 l./hr.) was passed for 4 hr. into a stirred
suspension of ground calcium (4 g.) in a solution of 1-4'-
phenylbutylnaphthalene (6 g.) in ether (75 c.c.) cooled
in ice.   The ethereal solution was filtered off and the

filter cake decomposed with water and hydrochloric acid. This was extracted with ether and the combined ethereal solutions dried over calcium chloride. The ether was removed and the residue distilled to give fractions (a) b.p. 167-175°/0·1 mm; and fraction (b) b.p. 175-177°/ 0·1 mm. Redistillation of (a) gave 1-4'-phenylbutyl-tetralin (2·5 g.) b.p. 178-180°/1 mm., η_D^{22} 1·5760 (Found: C, 90·9; H, 8·7. $C_{20}H_{24}$ requires C, 90·9; H, 9·1%). Analysis of fraction (b) showed incomplete reduction.

(b) Proof of structure. The reduced product above (2·5 g.) in water (100 c.c.) was heated with vigorous stirring on a water-bath and potassium permanganate (25 g.) added over 4 hr. When the oxidation was complete, the manganese dioxide was filtered off, the filtrate acidified with sulphuric acid, and extracted with ether in a continuous liquid extractor for 12 hr. Evaporation of the ether gave a white solid (0·5 g.). Esterification with diazomethane, followed by gas-liquid chromatography of the product, and comparison of retention times with authentic samples showed it to be essentially dimethyl-phthalate.

Method (iii) 5:5'-Ditetralyl-cadmium in benzene (20 c.c.) was prepared from magnesium (0·6 g.), 5-bromo-tetralin (5 g.) and cadmium chloride (2·5 g.), by the

method of Cason[71].   To this solution (cooled to 10°),
was added, during three minutes, a benzene solution
(5 c.c.) of phenylbutyryl chloride (4·3 g.), the
temperature being kept below 40°.   The mixture was
stirred at $25-35^o$ for 2 hr. and then poured onto ice and
sulphuric acid, washed with sodium bicarbonate solution,
brine, and finally dried and distilled.   A product
(4·5 g.) b.p. $210-260^o/1$ mm. was obtained.   The first
part (0·5 g.) of which formed a 2:4-dinitrophenylhydrazone
derivative.   Its infrared spectrum showed bands in the
carbonyl region at 5·59, 5·68, 5·75, 5·85 and 5·93 μ.
The remainder of the distillate showed bands at 5·50,
5·59, 5·68, 5·85, and 5·93 μ.
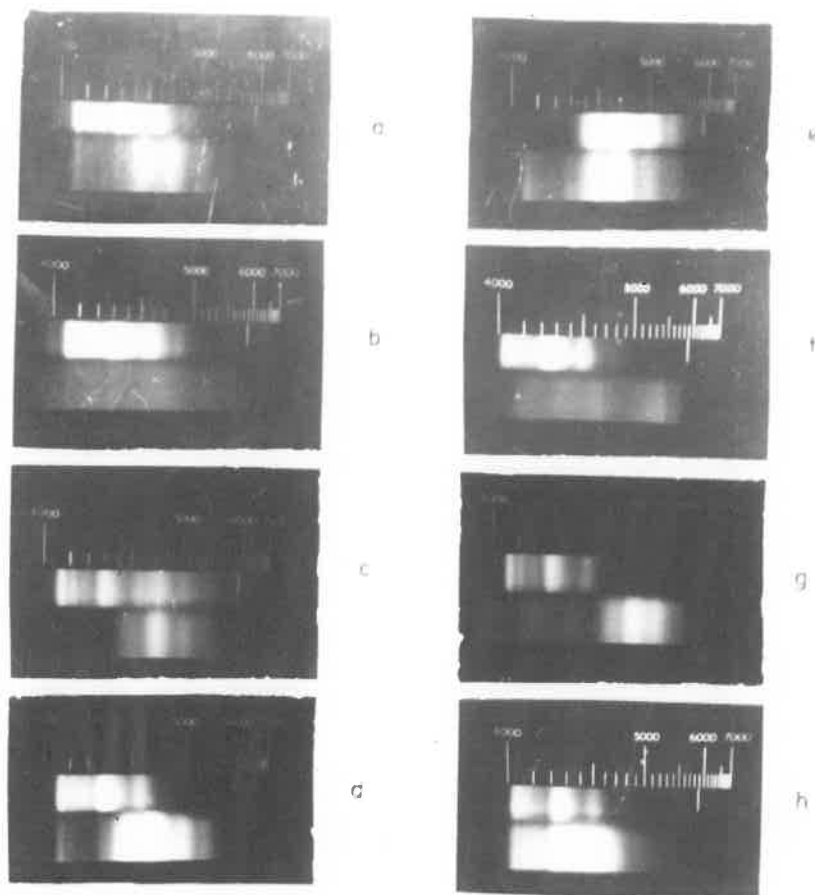
Plate 3·1. (a) 3:4-benzopyrene and perylene from
pyrolysis at 360°; (b) 3:4-benzopyrene(?)
from pyrolysis with Pd/C; (c) perylene
from pyrolysis with charcoal; (d) & (e)
perylene and 3:4-benzopyrene from pyrolysis
at 600°; (f) unknown compound; (g)
unknown compound; (h) 3:4-benzopyrene from
pyrolysis at 600° of 1-4'-phenylbutyl-
decalin. (For a, b, d, f, g, & h, the
upper spectra are 3:4-benzopyrene; for c,
a mixture of 3:4-benzopyrene and perylene;
and for e, perylene).

CHAPTER IV

THE PYROLYSIS OF TETRALIN AND INDENE.

Tetralin

Tetralin is a possible intermediate in the formation of 3:4-benzopyrene at high temperatures, and the pyrolysis of this compound is therefore of interest (see Chapter I). Graebe showed that the pyrolysis of tetralin by passing it through a red hot tube gave naphthalene[72]. Benzene and homologues of benzene were reported following pyrolysis between 580-650°[73,74]; however, it has also been reported that at 700° naphthalene alone is formed[74]. When superheated, tetralin is said to give chrysene[75]. A complete analysis of the products formed by pyrolysing tetralin at 700° has been undertaken.

The pyrolysis was carried out by passing tetralin vapour, with nitrogen, through a silica tube filled with porcelain chips. It gave some gaseous products, among which methane and ethylene were identified. The semi-solid tar also obtained (in 72·5% yield), was collected and analysed by chromatography on alumina, gas-liquid partition chromatography, chromatography on acetylated paper[43], and by spectroscopy. The compounds detected,

TABLE 4·1.   **PYROLYSIS PRODUCTS OF TETRALIN.**

Product	Yield (g. & %) of tar[a]		How Identified[b]
Methane	?	–	I.R.
Ethylene	?	–	I.R.
Benzene	1·6,	(2·28%)	R.T., I.R.
Toluene	0·6,	(0·86%)	R.T., I.R.
Ethylbenzene	0·24,	(0·34%)	R.T., I.R.
Styrene & o-xylene	0·6,	(0·86%)	R.T., I.R.
Indene	2·6,	(3·72%)	R.T., I.R.
Tetralin	1·0,	(1·43%)	R.T., I.R.
Naphthalene	52·0,	(74·4%)	mixed m.p.
1-,&2-Me-naphthalene(?)	0·1,	(0·14%)	R.T., I.R.
Diphenyl(?)	0·015,	(0·02%)	R.T.
Unknown -X	0·015,	(0·02%)	
2-Phenylnaphthalene	0·095,	(0·14%)	R_f, U.V.
Phenanthrene	0·11,	(0·16%)	U.V.
Anthracene	0·2,	(0·29%)	U.V., F.S.
1:1'-Dinaphthyl(?)	0·07,	(0·1%)	U.V.
1:2'-Dinaphthyl	0·40,	(0·57%)	U.V.
2:2'-Dinaphthyl	0·93,	(1·33%)	U.V., mixed m.p.

TABLE 4·1. (Cont.)

Product	Yield (g. & %) of tar[a]	How Identified[b]
1:2-Benzofluorene	0·03, (0·04%)	U.V.
Fluoranthene	0·03, (0·04%)	U.V.
3:4-Benzophenanthrene	0·56, (0·79%)	R_f, U.V.
1:2-Benzanthracene	1·82, (2·60%)	U.V., F.S.
Pyrene	0·01, (0·01%)	R_f, U.V., F.S.
Chrysene	2·4, (3·43%)	U.V., mixed m.p. & analysis.
Perylene	0·18, (0·25%)	U.V., F.S.
11:12-Benzofluoranthene	0·19, (0·27%)	R_f, U.V.
3:4-Benzopyrene	0·12, (0·17%)	R_f, U.V., F.S.
Loses & unidentified	6 (9%)	
	72·5g. (100%)	

a. i.e. weight obtained from 100 g. of tetralin.

b. R.T. = Retention time.

U.V. = Ultraviolet spectra.

I.R. = Infrared spectra.

F.S. = Fluorescence spectra.

their yeilds, and the manner in which they were identified are given in Table 4·1.

As expected, naphthalene is the major product, being formed by dehydrogenation of tetralin. It has been postulated (Chapter I) that tetralin, together with a $C_6 - C_4$ compound would give a C_{20} intermediate which by cyclodehydrogenation could give 3:4-benzopyrene. It may be noted that no $C_6 - C_4$ compounds have been found, but this does not exclude this as an intermediate in the formation of 3:4-benzopyrene in this tar as it would probably react to give further products. (In this connection it may be noted that no butylbenzene[7] or 1-phenylbuta-1:3-diene[9] remained unchanged after pyrolysis at 700°).

Bond dissociation energies of the carbon-carbon single bonds in the hydrogenated ring of tetralin will be similar (i.e. approximately 80 kcal./mole) and hence scissions will be expected to occur equally readily to give rise to the following primary radicals: (1) $C_6H_5\cdot$, (2) $C_6H_5\cdot CH_2\cdot$, (3) $C_6H_5\cdot CH_2CH_2\cdot$, (4) $C_6H_5\cdot CH_2CH_2CH_2\cdot$, (5) $C_6H_5\cdot CH_2CH_2CH_2CH_2\cdot$, (6) $CH_3\cdot C_6H_4\cdot CH_2\cdot$, (7) $CH_3CH_2\cdot C_6H_4\cdot CH_2\cdot$, (8) $CH_3CH_2\cdot C_6H_4\cdot CH_2CH_2\cdot$, and (9) $CH_3CH_2CH_2\cdot C_6H_4\cdot CH_2\cdot$, together with their counterparts with the electrons localised on alternative carbon atoms.

Reaction of radicals (1), (2), (3), and (6) with hydrogen accounts for the presence of benzene, toluene, ethyl-benzene, and o-xylene, while styrene is readily obtained by dehydrogenation of ethylbenzene. The absence of the corresponding products from the other radicals suggest that they readily cyclise, or that further scission of carbon-carbon bonds occur to give shorter chain products together with methane or ethylene. Indene would be formed by cyclisation of radicals (4) or (7). However, the pyrolysis of propyl benzene gives very little indene[7].

2-Phenylnaphthalene could be formed by phenyl radical attack on naphthalene or by dimerisation of styrene as suggested by Badger and Buttery[8]. A direct radical attack on naphthalene would be expected to give 1-phenylnaphthalene as the major product, but this could not be detected. However, this compound has a very unspecific ultraviolet absorption spectrum, and although somewhat similar curves were found, no definite conclusions could be drawn. Fluoranthene is known to be formed by cyclodehydrogenation of 1-phenylnaphthalene[77]. This probably accounts for the small yield of fluoranthene found in the tar.

The phenanthrene could have been formed either from diphenyl and ethylene or from two benzyl radicals

indicated by reaction (1). The latter could also give rise to anthracene as indicated by reaction (2).
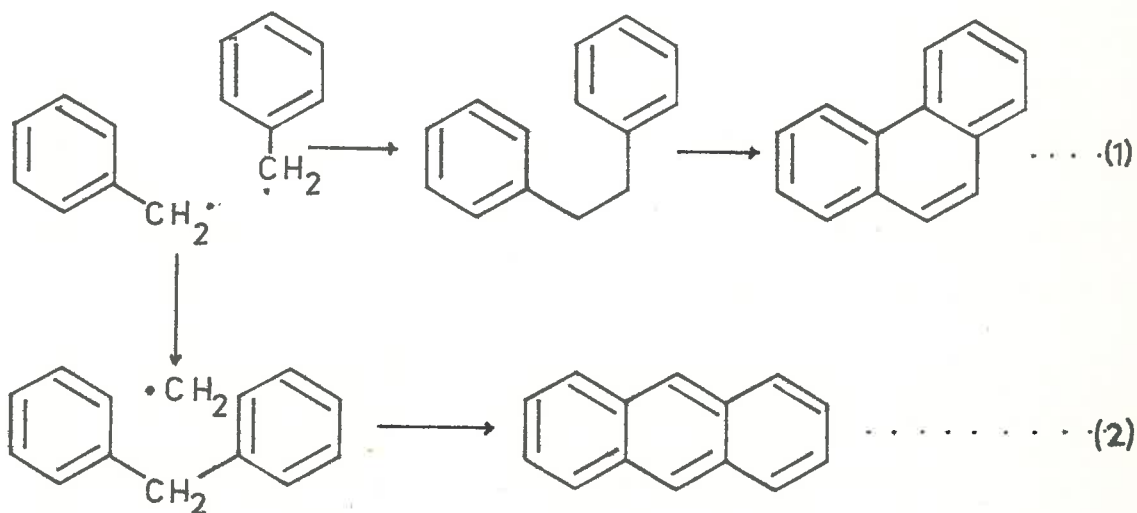
The stability of benzyl radicals[78] suggests that reactions involving it as an intermediate could be expected.

Dimerisation of naphthalene, or of tetralin followed by dehydrogenation, would give the dinaphthyls. At high temperatures steric factors will have more influence than electrical effects. This together with the fact that both 1:1'- and 1:2'-dinaphthyl can cyclise to give other compounds is perhaps the reason for the larger yield of 2:2'-dinaphthyl.

1:2-Benzofluorene could be formed by benzyl radical attack on naphthalene followed by ring closure as

indicated by reaction (3), or in a similar manner as
proposed from indene (see below).
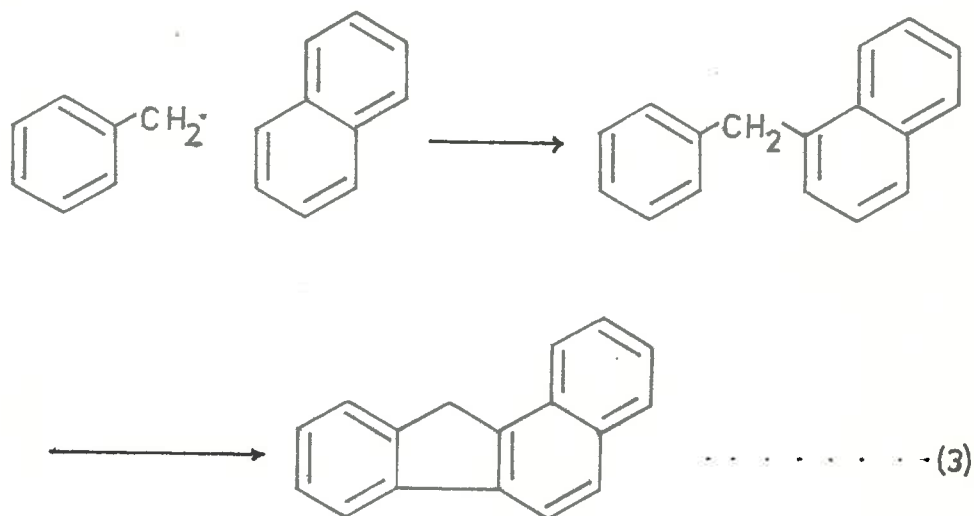
The pyrolysis of indene has been reported to give
large quantities of chrysene[79].   The chrysene detected,
could be formed in this way.   A reinvestigation of the
pyrolysis of indene, at 700° (see below), has shown also,
the presence of 1:2-benzanthracene and 3:4-benzophenan-
threne, and it seems more likely, taking into consideration
the larger relative yield of chrysene compared with 1:2-
benzanthracene and 3:4-benzophenanthrene, that from
tetralin, its formation would involve the radicals,
$C_6H_5 \cdot CH_2CH_2CH_2 \cdot$, and $CH_3CH_2 \cdot C_6H_4 \cdot CH_2 \cdot$, before cyclisation

to indene has occurred.   Combination of these radicals
can occur in the ways (I - IV).   Therefore chrysene,
1:2-benzanthracene, 3:4-benzophenanthrene, and
triphenylene could all conceivably be formed.
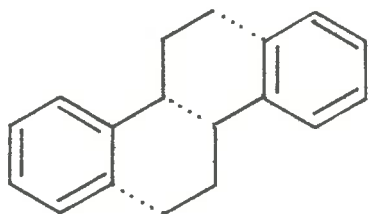
(I a)
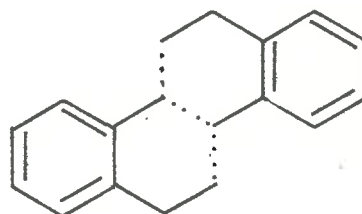
(I b)
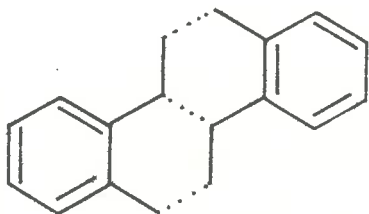
(I c)
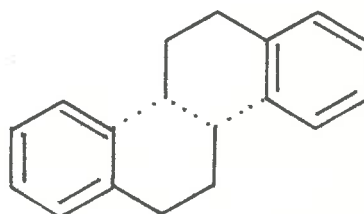
(I d)
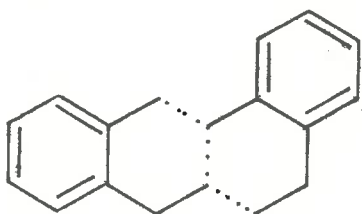
(II a)
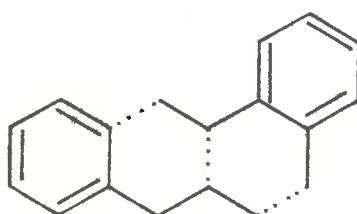
(II b)
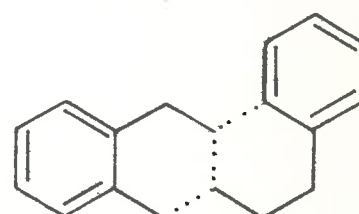
(II c)
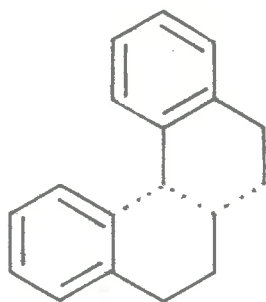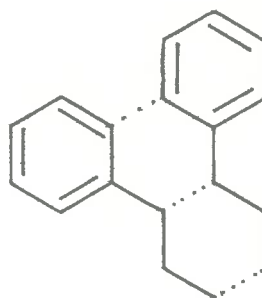
(III)   (IV)

However, no triphenylene has been found.   Various factors
may be involved in an explanation of this apparent anomaly.
Firstly, benzyl radicals are known to be relatively
stable[78].   One can imagine that when arranged in the
sense (Ib and IIa) the reaction could involve two
substituted benzyl radicals reacting to give a
disubstituted dibenzyl which could then cyclodehydrogenate
to give chrysene and 1:2-benzanthracene respectively.
Similarly, when arranged in the sense (Ic, IIb, IIc, and
III) the reaction could involve a substituted benzyl and
another radical.

The remaining arrangements all involve two units
with three-carbon side-chains.   Secondly, therefore,
one can imagine that these longer side-chains will move
around more rapidly under pyrolysis conditions than their

heavier parent rings. Hence one can reasonably suppose that ω,ω' side-chain attack is less likely to occur as often as ω side-chain attack on a more slowly moving parent ring. Nevertheless, it seems likely that ω,ω' attack is the most reasonable mechanism for the formation of triphenylene as (i) dinuclea attack will be retarded due to steric factors, and (ii)α,α' attack to give o-terphenyl as intermediate would certainly cyclise to give triphenylene. One would then expect to find very little triphenylene. The ratio of 4:3:1 of the yields of chrysene : 1:2-benzanthracene : 3:4-benzophenanthrene is as expected from the above, provided each possible combination has approximately equal possibility of occurring.

The very small amount of pyrene present may be formed from phenanthrene and ethylene, or possibly from two molecules of styrene. Pyrolysis of 1:1'-dinaphthyl with palladium-charcoal, is known to give perylene[80] and this is probably the intermediate in its formation here.

11:12-Benzofluoranthene is probably formed from 1:2'-dinaphthyl by cyclodehydrogenation as shown by reaction (4).

$$\cdots \cdots (4)$$
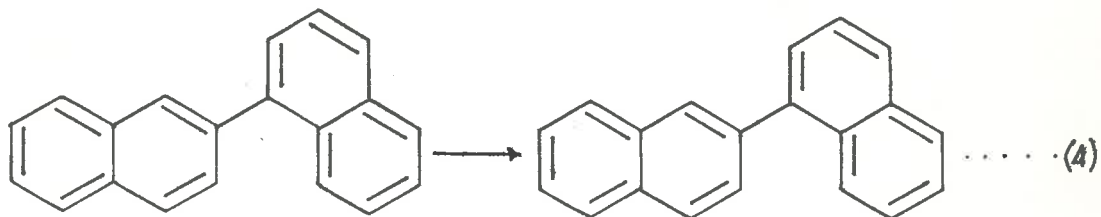
3:4-Benzopyrene may be formed from the proposed
intermediate (V); however, considering the relatively

(V)   (VI)   (VII)
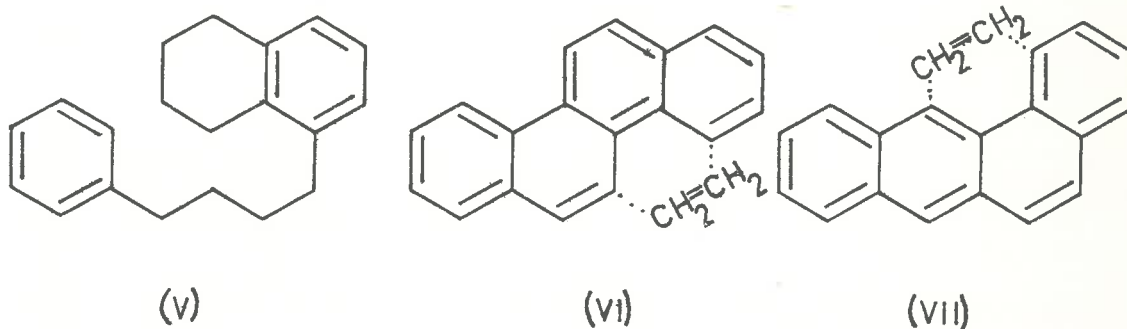
large yields of chrysene and 1:2-benzanthracene, it may
be more reasonable to suppose that the benzopyrene is
formed from ethylene and these compounds as indicated by
(VI) and (VII).   Evidence from the indene work, however,
indicates that the latter are not likely mechanisms
(see below).

Indene

The pyrolysis of indene by passing it through a red hot tube in the hands of Spilker[79], gave chrysene (15%) with indene (75%) recovered. A thorough analysis with more modern techniques was considered advisable, especially in view of the possibility of the formation of 1:2-benzanthracene and 3:4-benzophenanthrene from indene at high temperatures.

The pyrolysis was carried out in the same way as for tetralin. The gaseous products were found to contain, as usual, methane and ethylene. The solid tar also obtained (in 51.6% yield), was collected and analysed by chromatography on alumina, gas-liquid partition chromatography, chromatography on cellulose acetate[44] and on acetylated paper, and by spectroscopy. The compounds obtained and their yields, together with the manner in which they were identified are given in Table 4.2.

Chrysene was the major product, but was present in smaller quantity than expected from the literature[79].

Taking account of the bond orders of the carbon-carbon bonds in indene[81], approximate values for their bond dissociation energies can be obtained (VIII).

TABLE 4·2.   PYROLYSIS OF PRODUCTS OF INDENE.

Product	Yield (g. & %) of tar[a]		How Identified[b]
Methane	?	-	I.R.
Ethylene	?	-	I.R.
Benzene	2·6,	(5·4%)	R.T., I.R.
Toluene	0·4,	(0·83%)	R.T., I.R.
Styrene(?)	0·05,	(0·1%)	R.T.
Unknown -X	1·1,	(2·3%)	
Indene	3·12,	(6·5%)	R.T., I.R.
Naphthalene	2·9,	(4·6%)	R.T., mixed m.p.
Fluorene	0·01,	(0·02%)	U.V.
Phenanthrene	0·18,	(0·38%)	U.V., mixed m.p.
Anthracene	0·10,	(0·20%)	U.V., F.S.
3:4-Benzophenanthrene	1·1,	(2·3%)	R_f, U.V., mixed m.p.
Unknown -Y	0·25,	(0·52%)	
Pyrene	0·05,	(0·10%)	R_f, U.V., F.S.
Fluoranthene	0·13,	(0·27%)	U.V., F.S.
1:2-Benzofluorene	2·1,	(4·4%)	U.V.
2:3-Benzofluorene	2·15,	(4·5%)	R_f, U.V., mixed m.p.
3:4-Benzofluorene	0·5,	(1·0%)	U.V.

TABLE 4·2. (Cont.)

Product	Yield (g. & %) of tar[a]	How Identified[b]
1':2':3':4'-Tetrahydro-3:4-benzopyrene(?)	0·22, (0·46%)	U.V.
1:2-Benzanthracene	2·2, (4·6%)	R$_f$, U.V., F.S., mixed m.p.
Alkylchrysene	0·5, (1·1%)	U.V.
Chrysene	15·2, (31·7%)	R$_f$, U.V., mixed m.p.
3:4-Benzofluoranthene	0·004, (0·008%)	R$_f$, U.V., F.S.
10;11-Benzofluoranthene	0·005, (0·01%)	U.V.
11:12-Benzofluoranthene	trace	R$_f$, U.V., F.S.
3:4-Benzopyrene	0·001, (0·002%)	R$_f$, U.V., F.S.
Very high b.p. tar	7·5, (16%)	
Loses & unidentified	5·6, (11%)	
	48 g. (100%)	

a. i.e. weight obtained from 93 g. of indene.

b. R.T. = Retention time.

U.V. = Ultraviolet spectra.

I.R. = Infrared spectra.

F.S. = Fluorescence spectra.
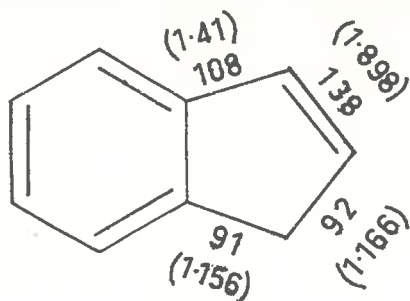
(VIII)

It would seem then that the carbon-carbon double bond
has a bond dissociation energy of ca. 138 kcal./mole,
and the carbon-carbon single bond linking this conjugated
double bond to the benzene ring, a bond dissociation
energy of ca. 108 kcal./mole.   The remaining two carbon-
carbon bonds in the five membered ring will have
dissociation energies of approximately 90 kcal./mole.
Ring fission would then be expected to give rise to the
primary free radicals (IX), (X), and (XI).
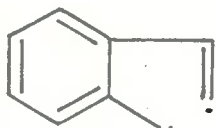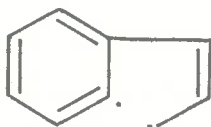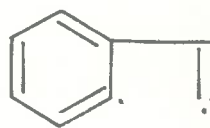
(IX)   (X)   (XI)

It seems unlikely that these diradicals will be stable
for any length of time.   One could imagine that in the
case of (IX), the diradical would react very quickly with

hydrogen radicals to give the relatively stable benzyl radical (XII). In the case of the diradicals (X) and (XI), one or other part could undergo termination reactions with hydrogen radicals to give the more stable mono-radicals (XIII) and (XIV).
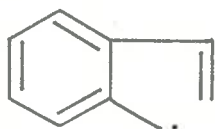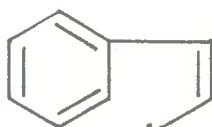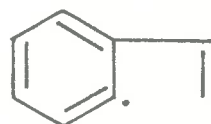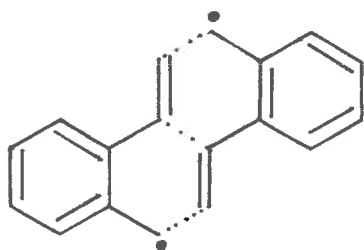
(XII)   (XIII)   (XIV)

Chrysene, 1:2-benzanthracene, and 3:4-benzophenanthrene could be expected to be formed from radicals (XII), and (XIII), by arrangement in the ways (XV), (XVI), and (XVII). The rate of addition of free radicals to unhindered double bonds is far greater than the rate of hydrogen abstraction from single bonds[82].
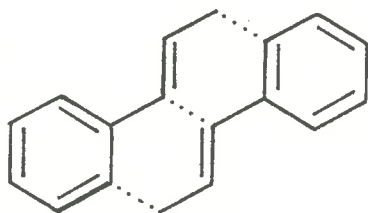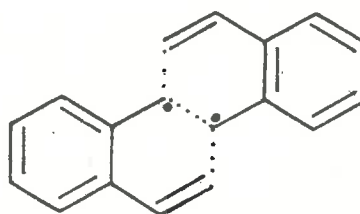
(XVa)   (XVb)
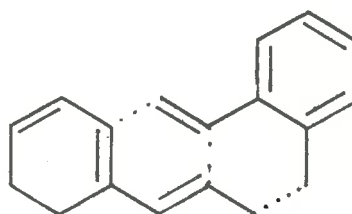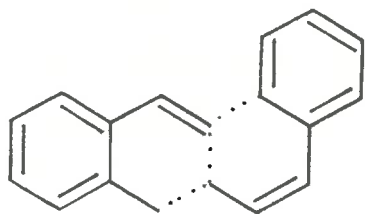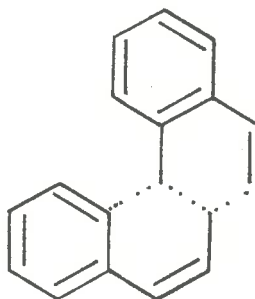
(XVc)
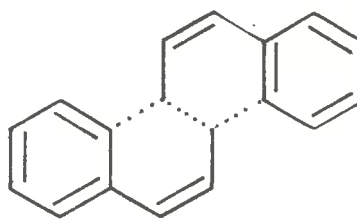
(XVd)
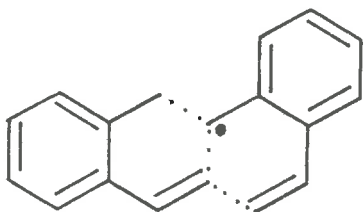
(XVIa)

(XVIb)

(XVIc)

(XVII)

Styrene is particularly reactive and the arrangements
(XVb), (XVc), (XVIa), (XVIb), (XVIc) and (XVII) all
involve this type of free radical attack. Of these (XVb)
and (XVc) both involve two benzyl-type radical to double

bond attacks, while (XVIa) involves one. The others either do not involve benzyl-type radicals or double bonds or both, and hence would not be expected to play as important a part in the formation of these compounds. Taking these effects into consideration, one would then expect the ratio of chrysene to 1:2-benzanthracene to be approximately 4:1 (i.e. as there are four benzyl radical-double bond attacks for the formation of chrysene, and one for the formation of 1:2-benzanthracene).

The mechanism for their formation, in the absence of the double bond, as proposed for the tetralin pyrolysis, supported the 4:3:1 ratio of the yields obtained of chrysene, 1:2-benzanthracene, and 3:4-benzo-phenanthrene. The presence of the radical-double bond attack would be expected to increase the yields of all of these compounds, and also taking into consideration the above special effects, the yields of chrysene would be expected to be increased the greatest amount. Experimentally the ratio of chrysene:1:2-benzanthracene : 3:4-benzophenanthrene was found to be 13:2:1.
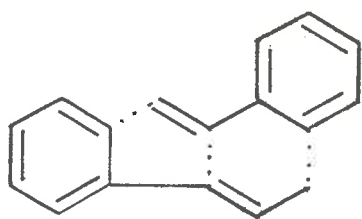
Radicals (XII) and (XIV), and (XIII) and (XVI) may also be arranged in various ways in order to form 1:2-, 2:3-, and 3:4-benzofluorene, (XVIII), (XIX), and (XX).
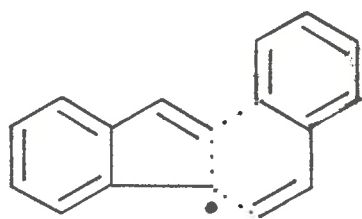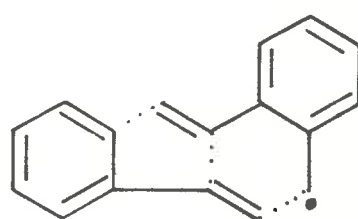
(XVIII a)
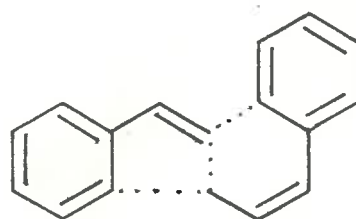
(XVIII b)

(XVIII c)

(XVIII d)
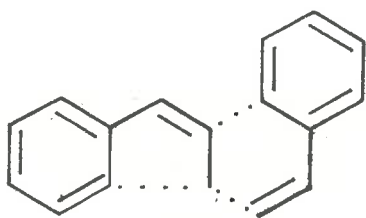
(XVIII e)
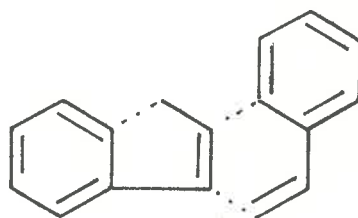
(XVIII f)
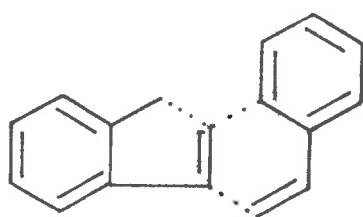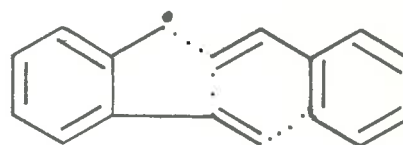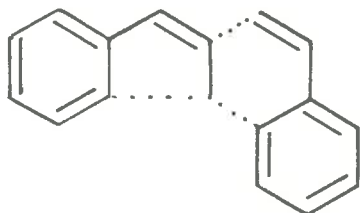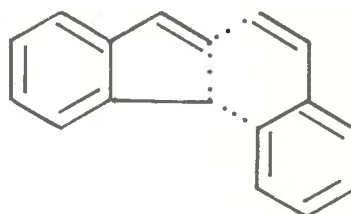
(XVIII g)

(XIX a)

(XIX b)

(XIX c)

(XX a)
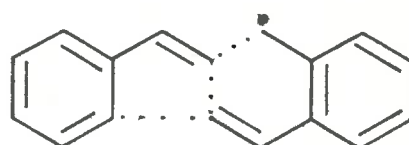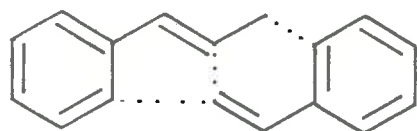
(XX b)
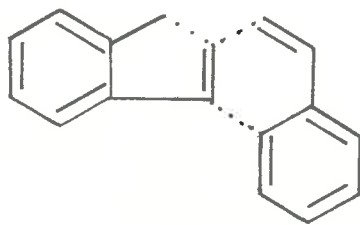
(XX c)
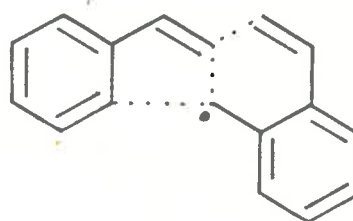
(XX d)

However, of these only those arranged in the sense
(XVIIIa), (XVIIId), (XIXa), (XIXc), and (XXd) involve
the most reactive benzyl radical–double bond attack. One
can then imagine that the ratios of the yields may be of
the order of 2:2:1.   In fact, experimentally it is
4:4:1.   This is not inconsistant with the theoretical

considerations, especially as there are doubtless other factors involved, and also the ultraviolet spectrum of 3:4-benzofluorene is not very easy to detect in mixtures with the other benzofluorenes.

The reaction of the styryl radical (XIV) with hydrogen would account for the small amount of styrene obtained. Secondary fission of this radical, involving the breaking of the carbon-carbon bond linking the ethylenic group to the benzene ring, would account for the benzene and some of the ethylene. (The pyrolysis of styrene[8] at 710° gives benzene in 6·4% yield). The toluene is also probably obtained through a secondary fission of the radical (XII), followed by reaction with hydrogen. Reaction between the benzyl radicals formed and benzene, would explain the presence of fluorene, and that between two benzyl radicals would account for the presence of the phenanthrene and anthracene (see above).

The fluoranthene may be formed from two $C_6 - C_2$ units, or from a $C_6 - C_3$ and a $C_6 - C_1$ unit, and probably goes through 1-phenylnaphthalene[77] as an intermediate (Reaction 1).

The very small amount of pyrene present could be formed in numerous ways (e.g. from styrene, m-xylene[83], etc.), but there is no evidence to support any particular

$$\cdots\cdots(1)$$
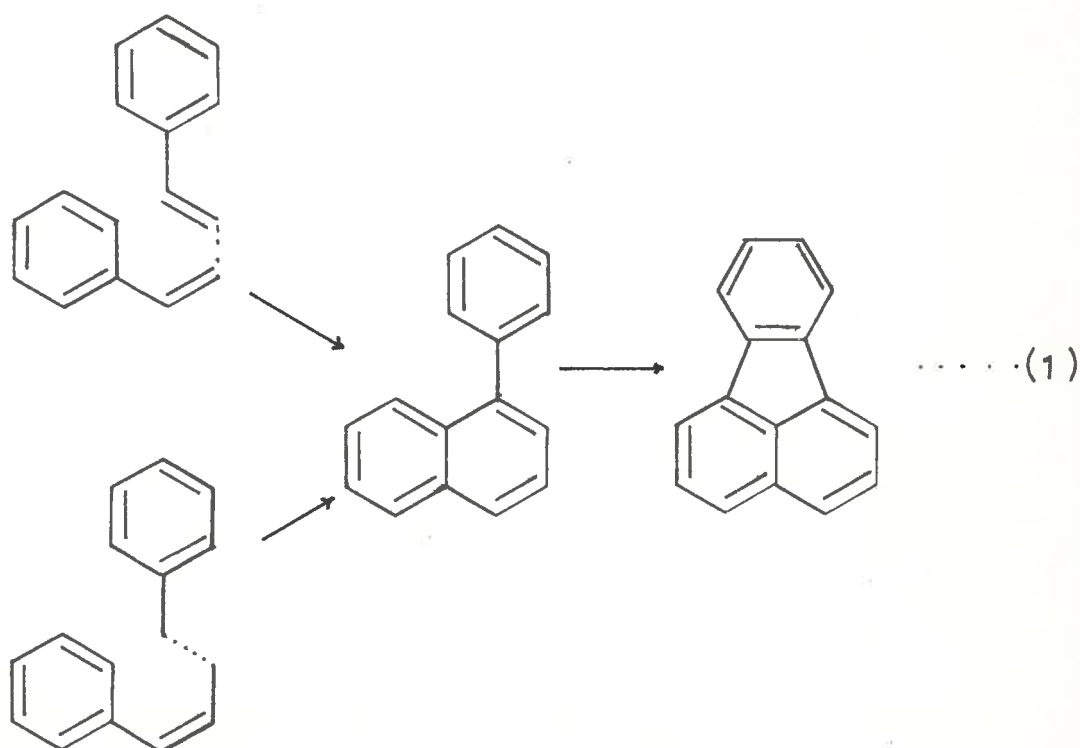
mechanism. The formation of naphthalene can only be explained if chain lengthening occurs, e.g. the attack of ethylene on the styryl radical (XIV), or even from a $C_6 - C_3$ unit and methane. The presence of a $C_6 - C_4$ hydrocarbon can then easily explain the presence of the very small amounts of 3:4-, 10:11-, and 11:12-benzofluoranthene and 3:4-benzopyrene by arrangement of two units as in (XXI), (XXII), (XXIII), and (XXIV).
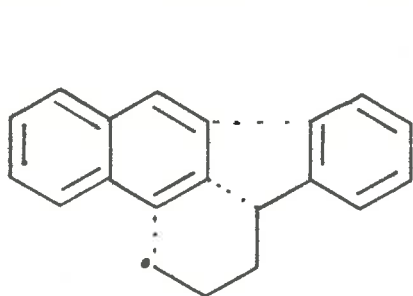
(XXI)
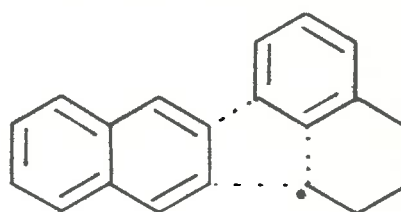
(XXII)
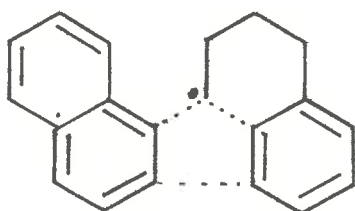
(XXIII)
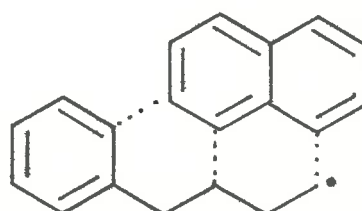
(XXIV)

It can be reasonably concluded, also, from this work that 3:4-benzopyrene is not formed in pyrolyses, at this temperature, from chrysene and a C_2 hydrocarbon (e.g. ethylene), or from 1:2-benzanthracene and a C_2 hydrocarbon. These hydrocarbons are all present in considerable amount, and should give a relatively large yield of 3:4-benzopyrene if it was formed to any significant extent by these mechanisms.

This indene-tar contained an unusually large amount of very high boiling material (16%) which could not be

identified.   Indene is known to undergo ready polymerisation on heating[84], and this probably accounts for a large proportion of the unidentified material.

EXPERIMENTAL.

Tetralin.- Technical tetralin (B.D.H.) was sulphonated and purified by the method of Schroeter[85]. The pure tetralin b.p. 100-101°/25 mm., η_D^{14} 1·5453 (lit.[86] η_D^{20} 1·5451), was shown to contain no naphthalene by gas-liquid chromatography.

Pyrolysis of Tetralin at 700°.- Tetralin (100 g.) was passed at the rate of 6 drops/min. with nitrogen (1 c.c./sec.) through a silica tube (36 x 1 in.) packed with porcelain chips (⅛ - ¼ in.) heated to 700° in the furnace previously described (see Chapter I). The semi-solid tar (70 g.) resulting, was collected and the gaseous products also formed, having first been passed through a trap cooled in a dry-ice/ethanol mixture were found to decolourise bromine water, and neutral and alkaline permanganate. Samples of the gaseous products were examined in the infrared spectrometer.

Analysis Techniques.- (1) Gas-liquid partition chromatography. The distillation fractions with b.p. up to 160°/0·3 mm. were examined by gas-liquid chromatography, using a Griffin and George vapour phase chromatographic apparatus (Mk.II) modified to collect

samples[42]. The column was packed with Apiezon-L
supported on Celite (40-80 mesh, B.S.S.; 1:4, w/w).
Varying conditions of temperature, pressure, and nitrogen
flow rate were used to suit the various fractions. The
compounds were collected and identified by infrared
spectroscopy and the percentage composition determined
from the areas under the peaks.

(ii) Chromatography on acetylated paper. All the
fractions collected from chromatography on alumina were
chromatographed on acetylated paper[43] using, ethanol-
toluene-water (17:4:1) as developing solvent. The
fractions containing essentially the same compounds, shown
by the positions of their spots under ultraviolet light,
were combined and rechromatographed on paper, using
larger amounts of material. After development with
methanol-ether-water (4:4:1), or with ethanol-toluene-
water (17:4:1) followed by thorough drying in an oven,
the fluorescent spots were cut out, extracted with 95%
ethanol, and ultraviolet spectra taken using an Optica
CF_4 Spectrophotometer recording instrument. The position
of non-fluorescent materials on the paper was found by
contact printing their position on Ilford Reflex Document
paper No. 50, using an ultraviolet light source emitting

90% of the 2537A$^{\text{o}}$ mercury line. The amounts present
were determined from their ultraviolet spectra by
comparison with optical densities of authentic spectra
of known concentration. Sometimes, spots required
rechromatographing on paper once or twice in order to
purify the compound.

Details of Chromatography.- The pyrolysis tube
and porcelain chips were washed with chloroform and the
residue (0·5 g.), after removal of the solvent, added to
the main bulk of the tar and the whole distilled to give
(a) b.p. 40-80$^{\text{o}}$/14 mm. (0·8 g.); (b) b.p. 90-95$^{\text{o}}$/14 mm.
(56 g.); and (c) the residue (9 g.). Fractions (a) and
(b) were submitted to gas-liquid chromatography (see
above). Fraction (a) was found to contain toluene,
ethylbenzene, styrene, o-xylene and indene; and fraction
(b) indene, tetralin and naphthalene. The essentially
crystalline residue was washed with cold benzene and the
pale yellow crystalline material (2 g.) remaining,
extracted in a hot Soxhlet apparatus with hexane.
Chromatography on alumina of the extracted product,
followed by paper chromatography on acetylated paper
showed it to be practically pure chrysene (see below).

The benzene washings were evaported to give a dark

residue (7 g.), which was taken up in a minimum quantity
of benzene-hexane (1:1) and chromatographed on alumina.
Elution with hexane gave fractions (70 c.c. each) 1 - 16,
with benzene-hexane (1:4) fractions 17 - 23, with benzene-
hexane (1:2) fractions 24 - 31, with benzene-hexane (1:1)
fractions 32 - 37, with benzene-hexane (2:1) fractions
38 - 41, with benzene fractions 42 - 45, and with benzene-
chloroform (1:1) fractions 46 - 49).   Fractions 1 - 21,
which were oily, were combined and distilled to give
fractions (d) b.p. 95-210°/19 mm. (0·5 g.); (e) b.p.
155-160°/0·3 mm. (0·2 g.); and (f) a residue (1·2 g.).
Gas-liquid chromtography of fraction (d) showed the
presence of naphthalene, 1- and 2-methylnaphthalene(?),
diphenyl(?) and unknown -X.

Paper chromatography and ultraviolet spectroscopy
was used to show that fraction (e) contained a mixture
of anthracene, phenanthrene, fluoranthene, pyrene and
2-phenylnaphthalene.   The residue (f) was chromatographed
on alumina and elution with light petroleum, hexane, and
benzene-hexane (1:4) gave 20 fractions (70 c.c. each),
the composition of which were determined by paper
chromatography and ultraviolet spectroscopy.   This
technique showed the presence of 1:1'-, 1:2'-, and 2:2'-
dinaphthyl, 2-phenylnaphthalene, 1:2-benzofluorene,

1:2-benzanthracene, and 3:4-benzophenanthrene. Fractions 22 - 49 of the original chromatogram were further analysed by paper chromatography and were found to contain perylene, chrysene, 11:12-benzofluoranthene and 3:4-benzopyrene.

Details of Identification.- Methane and ethylene. The gaseous products from the furnace were collected in a gas cell for infrared analysis. Methane was identified by its spectrum[50] in the 7·5-8·5 μ region (maxima at 7·61, 7·73, 7·77, 7·81, 7·85, 7·90, 7·94, 7·98, 8·05, 8·11, 8·17, 8·22, and 8·31 μ), and ethylene by its spectrum[50] in the 9·0-11·5 μ region (maxima at 9·33, 9·44, 9·53, 9·63, 9·72, 9·79, 9·83, 9·91, 10·01, 10·11, 10·20, 10·30, 10·51, 10·75, 10·83, 10·92, 11·00, 11·07, 11·16, 11·24, and 11·35 μ).

Benzene. The benzene (1·6 g.) was found in the dry-ice/ethanol trap together with a small amount of toluene (0·4 g.). Separation by gas-liquid chromatography gave pure benzene, shown by its infrared spectrum[50] (maxima at 2·40, 3·23, 5·05, 5·47, 6·65, 6·71, 7·18, 9·51, 9·62, 9·75, 12·82, 14·55, and 14·90 μ).

Toluene. This was identified by its infrared

spectrum[50] in the 2-8 μ region (maxima at 2·16, 2·31, 2·35, 2·47, 2·60, 2·74, 3·29, 3·31, 3·42, 3·48, 3·67, 3·90, 4·17, 4·45, 4·64, 5·04, 5·11, 5·14, 5·34, 5·38, 5·50, 5·55, 5·76, 6·85, and 7·29 μ).

Ethylbenzene.   This also was identified by its infrared spectrum; with maxima at 2·30, 2·70, 3·25, 3·32, 3·35, 3·41, 3·60, 3·78, 4·10, 4·30, 5·10, 5·31, 5·50, 5·71, 6·08, 6·85, 7·22, 7·48, 8·46, 8·62, 9·01, 9·20, 9·40, 9·70, and 11·03 μ, in agreement with the literature[50].

Styrene and o-xylene.   A mixture isolated by gas-liquid chromatography was shown to contain both styrene and o-xylene.   Styrene was identified by its infrared maxima at 2·12, 2·25, 2·41, 2·70, 3·26, 3·30, 3·61, 5·10, 5·29, 5·45, 5·70, 5·89, 6·10, 6·70, 6·88, 7·05, 7·20, 7·47, 7·57, 7·75, 8·30, 8·46, 8·65, 9·05, 9·25, and 11·00 μ, in agreement with the literature[50], and o-xylene by five maxima at 3·40 (infl.), 4·08, 4·27, 8·91, and 9·50 μ.   This fraction decolourised bromine water.

Indene.   This was identified by its maxima at 2·15, 2·32, 2·39, 2·52, 3·00, 3·26, 3·42, 3·58, 3·71, 3·82, 4·07, 4·86, 5·12, 5·20, 5·27, 5·36, 5·44, 5·54, 5·74,

5·90, 6·00, 6·86, 7·17, 7·35, 7·49, 7·61, 7·77, 8·57, 8·66, 8·90, 9·38, 10·59, 10·81, and 10·93 μ, in agreement with those obtained on an authentic specimen.

Tetralin. Recovered by gas-liquid chromatography of fraction (b) this was identified by its retention time and by its infrared spectrum.

Naphthalene. Obtained from fractions (b) and (d) this had m.p. and mixed m.p. 79-80°.

Methylnaphthalenes(?). Gas-liquid chromatography of fraction (d) gave a peak with a shoulder similar to that given by a mixture of authentic 1- and 2-methyl-naphthalene, and with the same retention times.

Diphenyl(?). A further small peak obtained by gas-liquid chromatography of fraction (d) had the same retention time as an authentic specimen of diphenyl.

2-Phenylnaphthalene. This was identified by its ultraviolet absorption spectrum of extracts of spots obtained in paper chromatograms of fractions (e) and (f). It had maxima at 250 and 287 mμ. The literature[87] gives maxima at 251 and 288 mμ.

Anthracene. Fraction (e) was recrystallised from

petroleum ether, and after sublimation, the product had an ultraviolet absorption spectrum having maxima at 252, 323, 339, 357, and 375 mμ with inflexions at 246, 352, and 371 mμ indicative of anthracene[46]. This was confirmed by its fluorescence spectrum (Plate 4·1a). A broad diffuse band in the 430 to 470 mμ region was caused by impurities.

Phenanthrene. Paper chromatography of the mother liquor of recrystallised fraction (e) (above) gave several spots. The ultraviolet absorption spectrum of the ethanol extract of one spot had maxima at 246 (infl.), 251, 274, 282, and 293 mμ indicative of phenanthrene[46].

Fluoranthene and pyrene. The extract of another spot had maxima at 233 (infl.), 236, 253 (infl.), 262, 272, 277, 282, 288, 309, 323, 342, and 360 mμ characteristic of fluoranthene[46]. Maxima at 242, 319, and 335 mμ suggested the presence of some pyrene. This was confirmed by its fluorescence spectrum.

1:1'-Dinaphthyl(?) and 1:2'-dinaphthyl. Paper chromatography of the fractions resulting from the chromatography of fraction (f) on alumina, gave several violet-blue spots of high R$_f$. One such spot when

extracted with ethanol had an ultraviolet absorption
spectrum with maxima at 219 and 283, with inflexions at
225 and 273 mµ identical with 1:2'-dinaphthyl[68].
However, another spot differed slightly, with maxima at
221, 272, and 283 with an inflexion at 292 mµ.   This
spectrum suggested a mixture of 1:1'-dinaphthyl and 1:2'-
dinaphthyl by comparison with the literature[68].   (Fig. 4·1)

2:2'-Dinaphthyl.   This was isolated mainly from
the original chromatogram on alumina.   Recrystallisation
from benzene-hexane (1:4) gave colourless plates m.p.
184-185°, mixed m.p. 184-186° and infrared and ultraviolet
absorption spectra identical with those for an authentic
sample.

3:4-Benzophenanthrene.   Chromtography on alumina
of fraction (f) gave by elution with light petroleum
several oily fractions which gave a broad intense blue
spot on acetylated paper.   Ultraviolet absorption
spectroscopy showed numerous maxima which could not be
identified with any one compound.   However, micro-
distillation of the oil b.p. 150-155°/0·05 mm., gave a
semi-solid product which formed a picrate.
Recrystallisation three times gave orange-red plates m.p.
118-121°.   After breaking down the complex with dilute
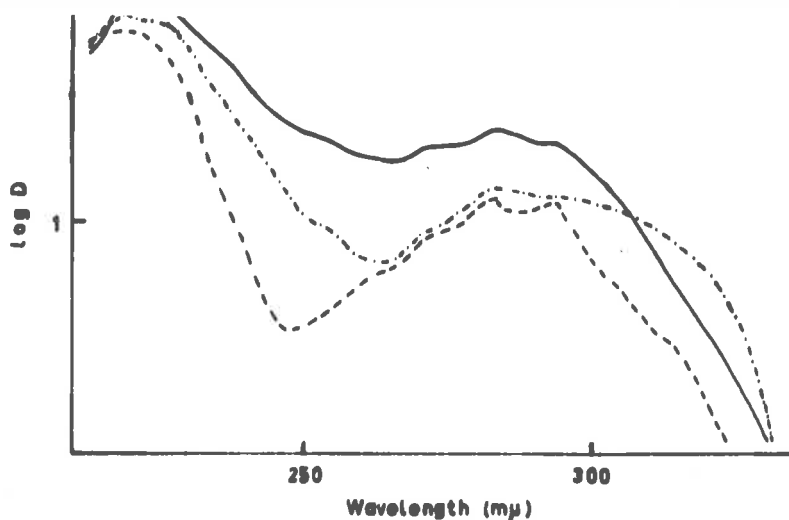
Fig. 4·1.   Mixture of 1:1'- and 1:2'-dinaphthyl from
tetralin pyrolysis (———); Authentic
1:1'-dinaphthyl (– – –), and 1:2'-
dinaphthyl (–·–·).
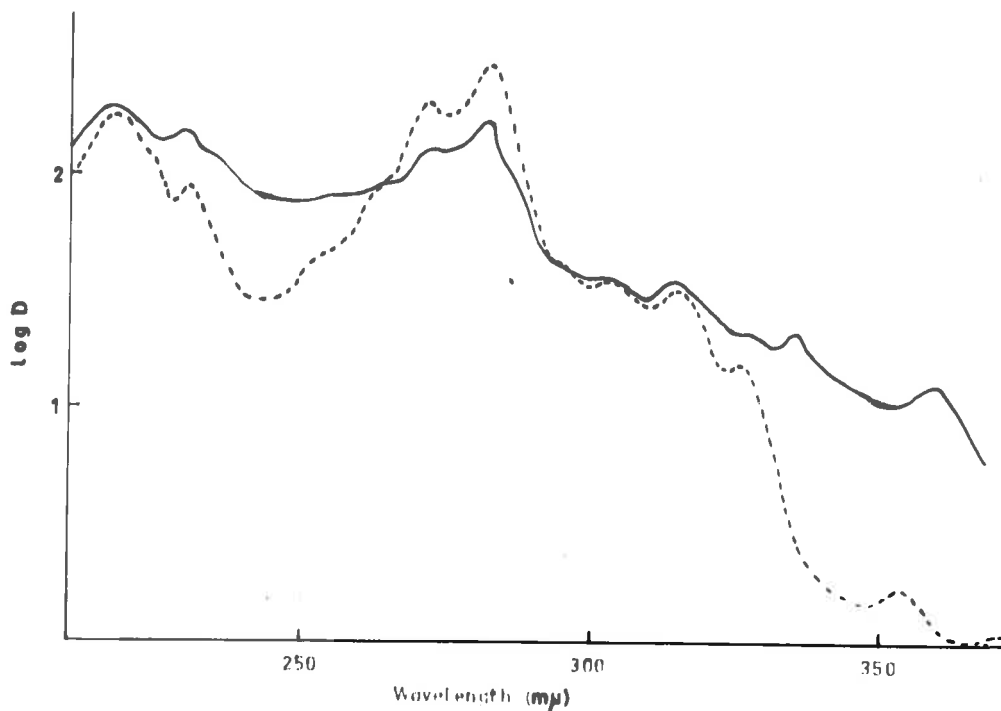
Fig. 4·2.   3:4-Benzophenanthrene from pyrolysis of tetralin (———).
Authentic (– – –).

ammonium hydroxide and extraction with ether, the product
was again paper chromatographed. The ultraviolet
absorption spectrum of the violet-blue spot had maxima
at 218, 230, 272, 282, 304 (infl.), 315, and 326 (infl.) mµ
indicative of 3:4-benzophenanthrene[46]. (Fig. 4·2).

1:2-Benzanthracene. Isolated by chromatography on
acetylated paper of fraction (f), this was identified by
its absorption maxima at 222, 228, 254, 258, 263, 278,
288, 300, 314, 325, 340, 359, 373, and 384 mµ and by its
fluorescence spectrum with bands at 408, 435, and 464 mµ
both in agreement with the literature[46]. (Plate 4·1b).

Chrysene. Recrystallisation of the crude product
from benzene gave pure chrysene m.p. and mixed m.p. 251-
252°. (Found: C, 94·9; H, 5·3. Calc. for $C_{18}H_{12}$:
C, 94·7; H, 5·3%). This was confirmed by ultraviolet
absorption spectroscopy with maxima at ($\log \varepsilon$ in
parenthesis) 220 (4·45), 241 (4·25), 259 (4·80), 268
(5·10), 283 (4·10), 295 (4·07), 307 (4·11), 320 (4·10),
343 (2·80), and 361 mµ (2·80).

Perylene. This was identified by its maxima at
245, 252, 385, 408, 426 (infl.), and 435 mµ in the ultra-
violet and by its fluorescence spectrum (Plate 4·1c), with

bands at 445, 475, and 502 mμ, both in agreement with the literature[46].

11:12-Benzofluoranthene. This compound had a slightly higher R_f than 3:4-benzopyrene on acetylated paper. Ultraviolet absorption spectroscopy of an extract had maxima at 220, 236, 246 (infl.), 268, 283, 296, 308, 360, 378, and 401 mμ in good agreement with the literature[46]. (Fig. 4·3).

3:4-Benzopyrene. Identified by its absorption maxima at 226, 255, 266, 274, 284, 296, 330, 364, 384, and 404 mμ (lit.[88]), this was confirmed by its characteristic fluorescence spectrum with bands at 398, 404, 409, 417, 427, 456, and 485. (Plate 4·1d).

Pyrolysis of Indene at 700°.— Indene (93 g.) η_D^{14} 1·5676, which contained no impurities (as shown by gas-liquid chromatography) was pyrolysed at 700° under similar conditions as for tetralin. (Some blocking of the silica tube occurred near the outlet end, and it was found necessary to heat frequently the portion protruding from the furnace with a Bunsen burner). The solid yellow-brown tar (44 g.) resulting was collected, and another quantity (1 g.) was obtained by washing the
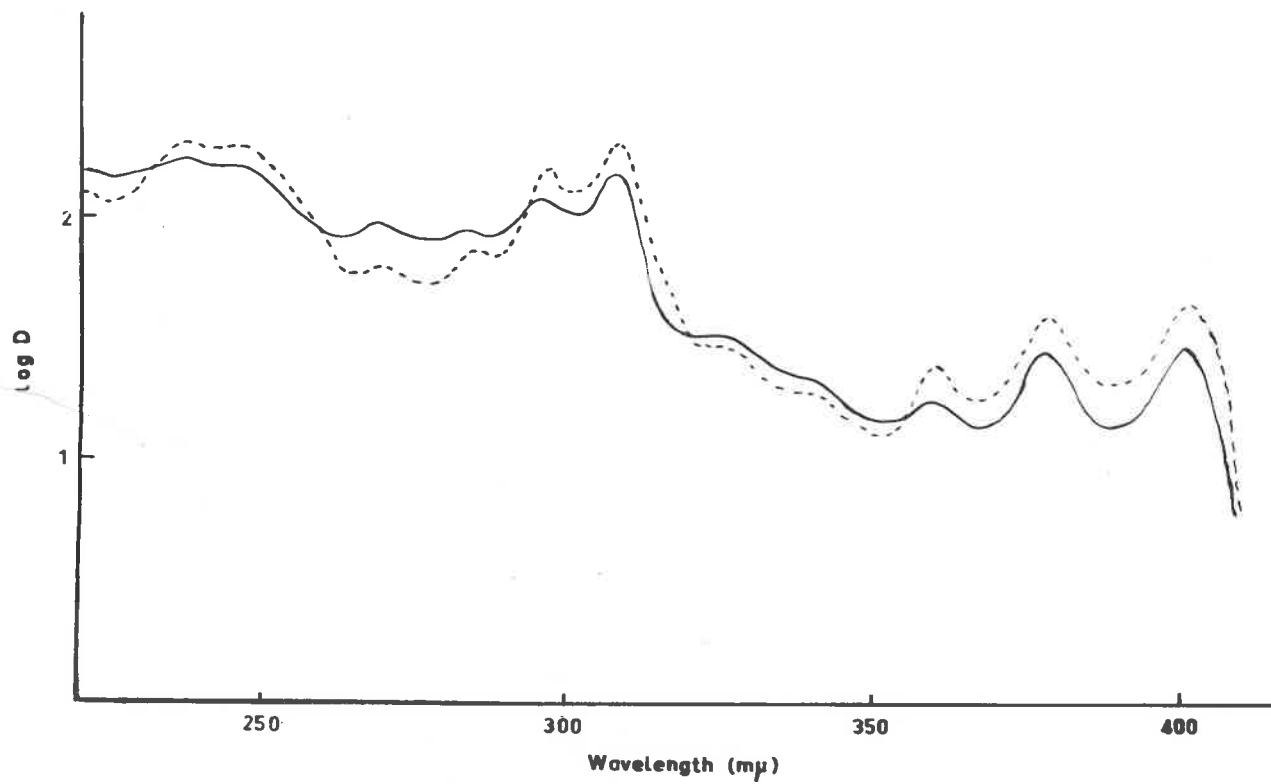
Fig. 4·3.   11:12-Benzofluoranthene from pyrolysis of tetralin
(———).   Authentic (– – –).

pyrolysis tube with boiling chloroform and evaporating the solvent. A further trap, cooled in a dry-ice/ethanol mixture condensed lower boiling products (3 g.) (fraction a). The exit gases decolourised bromine water and permanganate solutions. Samples of the gases were examined by infrared spectroscopy.

Distillation of the tar (bath temperature up to $220^{\circ}/50$ mm.) removed the low boiling products and gave residue (b). Redistillation gave the following fractions: (c) b.p. $90^{\circ}/25$ mm. (3 g.); and (d) b.p. $95-105^{\circ}/30$ mm. (4 g.).

Analysis Techniques.- These were similar to those used for the analysis of the tetralin tar. Separation of the low boiling products was carried out by gas-liquid chromatography, which were then identified from their infrared spectra. However, fractions of higher molecular weight, after a preliminary separation on alumina, were chromatographed on a cellulose acetate column[44] (45 x 3 cm.). Portions of the fractions (10-200 mg.) from alumina chromatography were chromatographed in ethanol-benzene-water (17:4:1) and eluted with the same solvent. (Where chrysene was predominant in a fraction, its low solubility precluded larger amounts than 10-20 mg. being

used).   The resulting fractions, after removal of the
solvent, were weighed, and identified by their ultraviolet
absorption spectra, and where practicable, by their
melting points.   These were confirmed in several cases
by their fluorescence spectra.   The percentage
compositions were determined, where possible,
gravimetrically, or where products were present in only
minute amounts, and in overlapping fractions, (i.e.
fractions containing more than one compound) from their
ultraviolet spectra.

Examination of Fractions (a), (c), and (d).-   These
fractions were analysed by gas-liquid chromatography.
Fraction (a) contained benzene (2·6 g.) and toluene
(0·4 g.); fraction (c) unknown -X (0·6 g.), indene
(2·3 g.) and naphthalene (0·1 g.); and fraction (d)
unknown -X (0·52 g.), indene (0·81 g.) and naphthalene
(2·6 g.).   Both fractions (c) and (d) contained a small
amount of material which had a retention time correspond-
ing to styrene.

Examination of Residue.-   The residue (fraction b)
was extracted with benzene-hexane (1:4) in a Soxhlet
apparatus.   A black tar (0·5 g.) (fraction e) remained.
The solvent was removed from the extracted product and a

slurry of the solid material (44·5 g.) in hexane, was
placed on top of a large column of alumina (70 x 5 cm.).
Development with hexane gave fractions 1 - 14; with
benzene-hexane (1:2), fractions 15 - 27; and with benzene,
fractions 28 - 31.   The column was then stripped of all
other material with ether, to give fraction (f) (10·5 g.)
and a black tar (2 g.).   (The latter was added to
fraction e).   The following fractions, which showed
similar ultraviolet absorption spectra, were combined:
i.e. fractions 1 - 5, (0·1 g.); 6 - 11, (0·11 g.);
12 - 14, (0·164 g.); 15 - 18 (1·22 g.); 19 - 21, (3·0 g.);
and 22 - 30, (11·08 g.).

Fractions 1 - 5 contained naphthalene, while fractions
6 - 11 contained oily material which could not be
identified.   Chromatography on a cellulose acetate
column of fractions 12 - 14 showed the presence of
phenanthrene, anthracene, and fluorene.   Similarly
phenanthrene, anthracene, 3:4-benzophenanthrene, pyrene(?)
and fluoranthene were identified from fractions 15 - 18,
and 1:2-, 2:3-, and 3:4-benzofluorene, 1':2':3':4'-
tetrahydro-3:4-benzopyrene(?), 3:4-benzophenanthrene, and
1:2-benzanthracene from fractions 19 - 21.   Three
recrystallisations from benzene of fractions 22 - 30 gave
chrysene, while the mother liquors, by chromatography on

cellulose acetate, were found to contain (in the order of elution from the column), 2:3-, and 1:2-benzofluorene, 1:2-benzanthracene, an alkylchrysene, 10:11-, and 11:12-benzofluorene, chrysene, 3:4-benzofluoranthene, and 3:4-benzopyrene.

Fraction (f) was recrystallised four times (from benzene), and the product (3 g.), although still yellow, shown by chromatography on acetylated paper to be almost pure chrysene. The combined mother liquors were chromatographed in benzene on alumina. Elution with benzene-hexane (1:1) gave eleven fractions (each of 70 c.c.), and with benzene, three further fractions (each of 175 c.c.). The column was then stripped with ether to give a further black tar (5 g.) (fraction g). Chromatography of a portion of the first eleven fractions combined, on cellulose acetate showed the presence of 1:2-, and 2:3-benzofluorene, 1:2-benzanthracene, and chrysene. Similarly the latter three fractions were shown to be mainly chrysene, together with a small amount of a compound unknown -Y.

The picrates of fractions (e) and (g) were decomposed with dilute ammonium hydroxide. The process was repeated and the product chromatographed on acetylated paper. However, no further apparently pure products

could be detected by ultraviolet absorption spectroscopy.

Details of Identification.- Methane and ethylene.
Samples of the exit gases were collected in a gas cell
for infrared analysis. Methane was identified by its
spectrum[50] in the 7·8-8·5 μ region (maxima at 7·62, 7·73,
7·77, 7·81, 7·86, 7·90, 8·00, 8·05, 8·10, 8·17, 8·24,
and 8·30 μ), and ethylene by its spectrum[50] in the 10-11·5 μ
region (maxima at 10·00, 10·11, 10·21, 10·31, 10·52,
10·75, 10·84, 10·94, 11·00, 11·09, 11·17, and 11·24 μ).

Benzene. Separated from toluene in fraction (a)
by gas-liquid chromatography benzene was identified[50]
by its retention time, and by its infrared maxima
(examined as vapour) at 2·40, 3·23, 5·06, 5·48, 6·65,
6·71, 7·18, 9·51, 9·63, 9·74, 12·82, 14·55, and 14·90 μ.

Toluene. This was identified[50] by its retention
time and confirmed by its infrared spectrum, which showed
(liquid film) maxima at 2·16, 2·31, 2·34, 2·47, 2·61,
2·74, 3·29, 3·31, 3·43, 3·48, 3·67, 3·90, 4·17, 4·46,
4·64, 5·03, 5·11, 5·14, 5·34, 5·39, 5·50, 5·55, 5·76,
6·85, and 7·29 μ.

Styrene(?). A very small peak from gas-liquid
chromatography of fraction (c) had a retention time

identical with that obtained for an authentic specimen.

Indene. Recovered in fractions (c) and (d) this
was identified by its retention time. The infrared
spectrum of a specimen collected was identical with that
of authentic indene.

Naphthalene. Isolated from fractions (b), (c), and
(d) this had m.p. and mixed m.p. 79·5–80°.

Unknown –X. One peak, with a small shoulder,
obtained by gas-liquid chromatography of fractions (c)
and (d) had a retention time almost identical with that
of n-propylbenzene. However, its infrared spectrum,
although showing bands at 4·99, 5·04, 5·19, 5·40, and
5·49 μ, typical of a monsubstituted benzene derivative,
could not be identified with any of the obvious mono-
substituted benzenes of similar boiling point. A strong
band at 4·40 μ suggested a disubstituted acetylene
derivative.

Phenanthrene. Isolated from fraction (b) this had
m.p. 99–100° and mixed m.p. 99·5–100°. Its identification
was confirmed by its ultraviolet absorption spectrum[46]
which had maxima at 221, 245 (infl.), 252, 276, 282, 295,
316, 324, 332, 339, and 346 mμ.

Fluorene. Some of the early fractions from chromatography on cellulose acetate of the phenanthrene fractions also showed maxima at 262 (infl.), 274 (infl.), 290, 294 (infl.), and 301 mµ, suggesting the presence of fluorene[89].

Anthracene. The next fraction from the column, although contaminated with phenanthrene, showed maxima at 252, 340, 353 (infl.), 358, 372 (infl.), and 377 mµ indicative of anthracene[46]. This was confirmed by its fluorescence spectrum with bands at 403, 429, and 455 mµ, (Plate 4·le) in agreement with the literature[90].

Fluoranthene. Isolated by chromatography of fractions 15 – 18 on cellulose acetate, this was identified by its ultraviolet absorption spectrum, with maxima at 230 (infl.), 236, 252, 262, 272, 276, 282, 287, 310, 321, 340, and 359 mµ, (Fig. 4·4) in good agreement with the literature[46]. This was confirmed by its fluorescence spectrum with diffuse bands at approximately 430–450, 465, 513, and 573 mµ (Plate 4·lf).

3:4-Benzophenanthrene.- This was isolated from fractions 15 – 18 and 19 – 21, and had m.p. 66–67·5° and mixed m.p. 66–67°. Its ultraviolet absorption spectrum
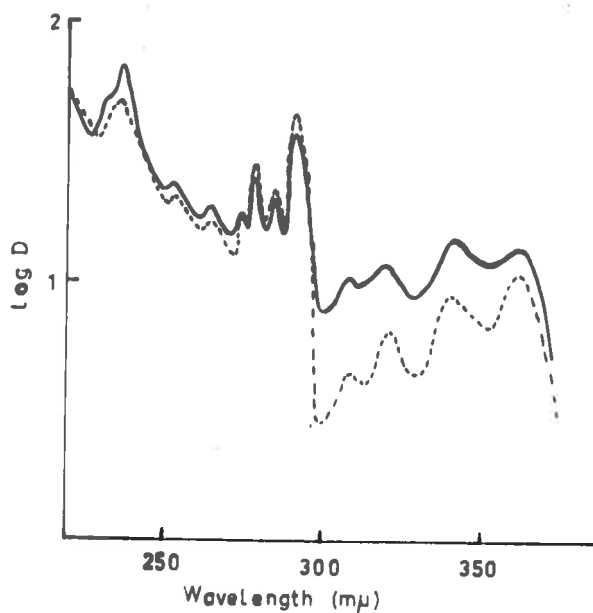
Fig. 4·4.   Fluoranthene from indene
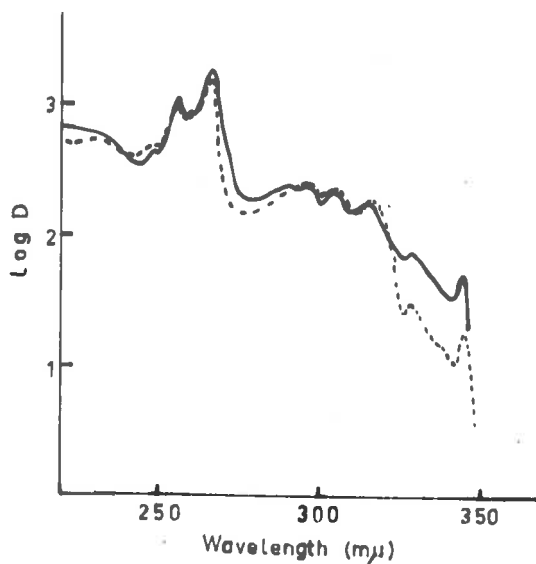pyrolysis (———);
Authentic (– – –).

Fig. 4·5.   1:2-Benzofluorene from
indene pyrolysis (———).
Authentic (– – –).

had maxima at 217, 227 (infl.), 229, 244 (infl.), 254
(infl.), 263 (infl.), 272, 282, 303, 316, 327, 354, and
372 mμ in agreement with the literature[46].

Pyrene(?).   Several of the fractions from chromato-
graphy on cellulose acetate of fractions 15 - 18 had
absorption maxima at 319 and 335 mμ suggesting the
presence of pyrene[46].   Its fluorescence spectrum,
although diffuse, had the same bands as an authentic
specimen (Plate 4·1g).

1:2-Benzofluorene.   Some of the early fractions
from chromatography of fractions 19 - 21, 22 - 30, and
of fraction (f) on cellulose acetate, showed ultraviolet
absorption maxima at 245, 254, 258, 263, 288, 294, 302,
315, 328, and 342 mμ indicative of 1:2-benzofluorene[89].
(Fig. 4·5).

2:3-Benzofluorene.   This was identified from the
same fractions by maxima[68] at 216, 255, 264, 274 (infl.),
285, 292 (infl.), 304, 313 (infl.), 317, 325, 333, and
340 mμ.   One specimen had m.p. 205-206° and mixed m.p.
207-208°. (lit.[91] 208-209°).

3:4-Benzofluorene.   Some of the 1:2-, and 2:3-
benzofluorene fractions from chromatography of fractions

19 - 21 on cellulose acetate, also had ultraviolet maxima at 230, 329, and 336 mμ (Fig. 4·6), suggesting the presence of 3:4-benzofluorene (lit.[68] values are 230, 250, 268, 298, 312, 320, 328, and 336 mμ).

1':2':3':4'-Tetrahydro-3:4-benzopyrene(?).   One fraction of the above chromatogram could not be obtained in a pure state.   It had maxima at 245, 266, 279, 303, 316, 330, 345, 358, 364 (infl.), 370, and 377 mμ suggesting a substituted pyrene (Fig. 4·7).   Literature[92] values for 1':2':3':4'-tetrahydro-3:4-benzopyrene are 228, 239, 247, 258, 268, 280, 304, 316, 329, 346, 358, 370, and 378 mμ.

1:2-Benzanthracene.   Found in various fractions, this was identified by its m.p., ultraviolet[46] and fluorescence spectrum, and by its R_f on cellulose acetate. One specimen, following micro-sublimation onto a microscope cover-slip, had m.p. and mixed m.p. 158-159° (Leitz hot-stage microscope) and light absorption maxima at 222, 238, 254 (infl.), 257, 268, 278, 288, 301, 314, 325, 340, 359, 374, and 384 mμ.

Unknown -Y.   An oily fraction (which may have been impure) obtained from chromatography of fraction (f) on
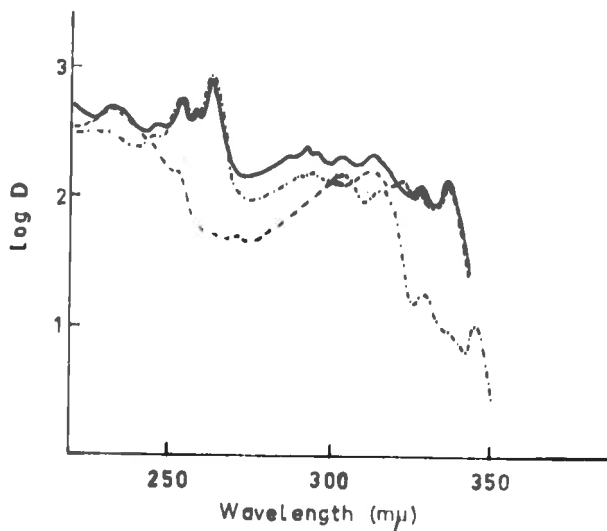
Fig. 4·6.   Mixture of 3:4- and 1:2-Benzofluorene
            from indene pyrolysis (———).
            Authentic 3:4-benzofluorene (- - -)
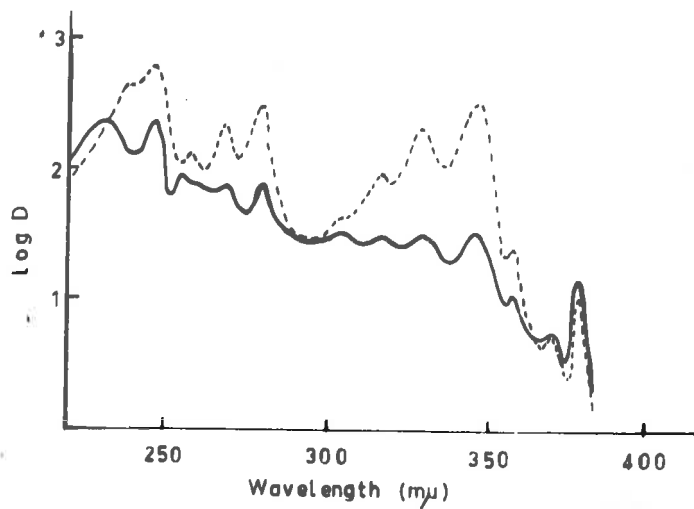   and 1:2-benzofluorene (—·—·).

Fig. 4·7.   1':2':3':4'-Tetrahydro-3:4-
            benzopyrene(?) (———).
            Authentic (- - -).

cellulose acetate had a high R_f value.   It showed absorption maxima at 247, 266 (infl.), 274, 281, 285, 303, 313, and 340 mμ.

Alkylchrysene.   Observed in fractions 22 - 30, its ultraviolet absorption spectrum had maxima at 260, 270, 282, 291, 296, 308, and 320 mμ suggesting an alkylchrysene.

Chrysene.   A specimen was recrystallised twice from benzene.   It had m.p. 251-252°, not depressed by admixture with an authentic sample.   Its light absorption had maxima[46] at 220, 241, 258, 268, 283, 296, 307, 320, 343, and 361 mμ.

10:11-Benzofluoranthene.   A yellow fluorescent band on the cellulose acetate column by chromatography of fractions 22-30, had a R_f value slightly higher than chrysene.   Its ultraviolet absorption spectrum had maxima at 292, 306, 317, 333, 364, 375, and 382 mμ (Fig. 4·8) in substantial agreement with the literature[46] for 10:11-benzofluoranthene.

11:12-Benzofluoranthene.   One of the first of the above fractions containing 10:11-benzofluoranthene also
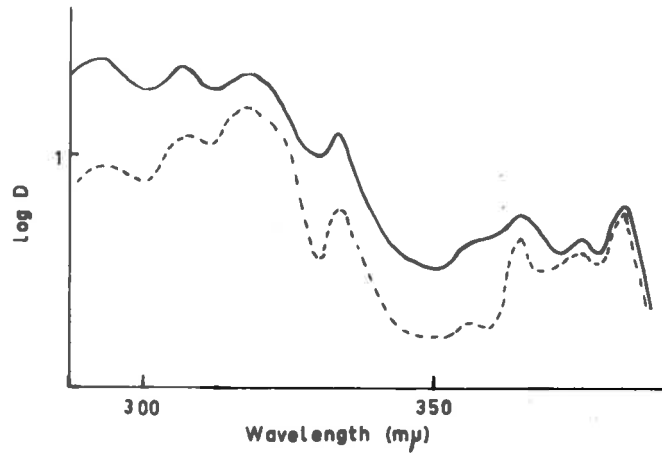
Fig. 4.8.   10:11-Benzofluoranthene from indene
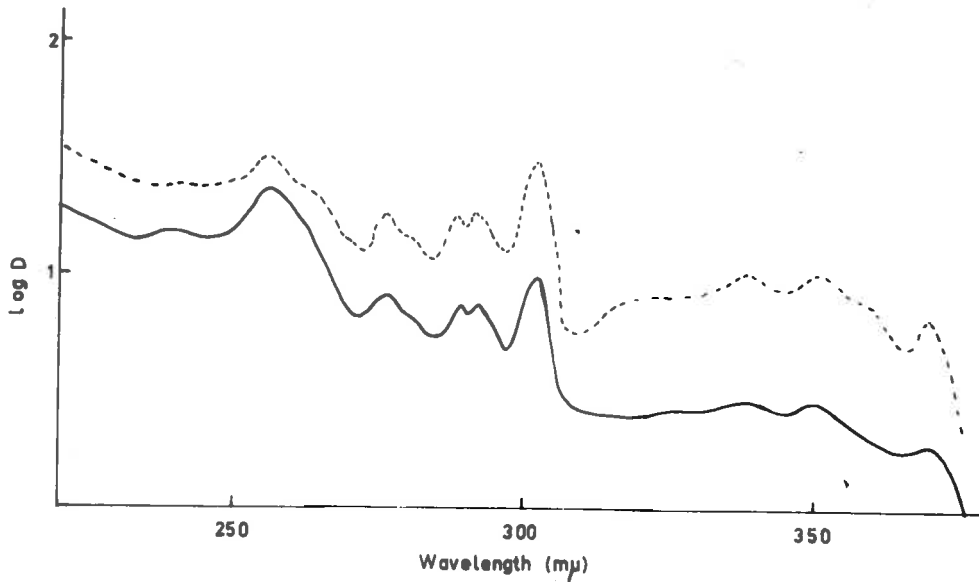   pyrolysis (———),
             Authentic (– – –).

Fig. 4.9.   3:4-Benzofluoranthene from indene pyrolysis (———).
             Authentic (– – –).

had maxima at 378 and 401 mμ in agreement with literature values for 11:12-benzofluoranthene in this region[46]. This was confirmed by its distinctive fluorescence spectrum which had bands at 409, 432, 467, and 500 mμ (Plate 4·1h) identical with those of an authentic specimen.

3:4-Benzofluoranthene.   A blue fluorescent compound having a slightly higher R_f on cellulose acetate than 3:4-benzopyrene, had light absorption maxima at 239, 256, 276, 281 (infl.), 289, 292, 302, 338, 350, and 369 mμ indicative of 3:4-benzofluoranthene[46]. (Fig. 4·9).   Its R_f and fluorescence spectrum were identical with an authentic specimen.

3:4-Benzopyrene.   Identified by its R_f on cellulose acetate, this had light absorption maxima at 226, 256, 265, 273, 284, 297, 331, 364, 381, 384, and 405 mμ in good agreement with the literature[88].   The identification was confirmed by its fluorescence spectrum, with bands at 404, 409, 417, 427, 456, and 485 mμ.
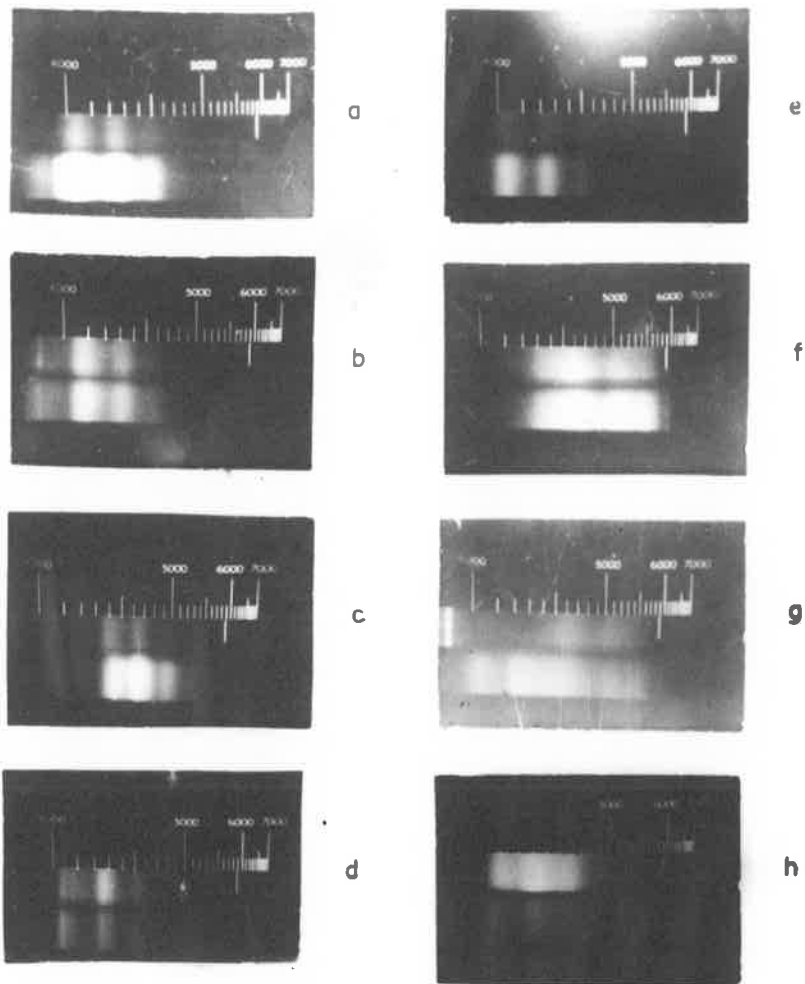
Plate 4·1. (a) Anthracene; (b) 1:2-benzanthracene;
(c) perylene; (d) 3:4-benzopyrene from the
tetralin pyrolysis; and (e) anthracene;
(f) fluoranthene; (g) pyrene; (h) 11:12-
benzofluoranthene from the indene pyrolysis
(Upper spectra are authentic specimens).

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SUMMARY

Some of the problems associated with the mode of formation of aromatic hydrocarbons at high temperature have been investigated. A feasible route to the formation of 3:4-benzopyrene in tars involving, two, four, six, ten, and twenty carbon units has been taken as a working hypothesis. This mechanism presupposes that 3:4-benzopyrene may be found by pyrolysis of any of these supposed intermediate compounds. The pyrolysis of 1-4'-phenylbutylnaphthalene (and related compounds), tetralin, and indene have been shown to contain 3:4-benzopyrene (together with twenty-five to thirty other compounds in the case of tetralin and indene), and a fraction of "Schroeter Tar", known to be strongly carcinogenic, has now been found to contain some 4% of 3:4-benzopyrene. These experiments, together with other very recent results in this field, have confirmed the suggestion that the most important reactions in pyrolytic synthesis involve cracking (with the formation of free radicals which then undergo further reaction), dehydrogenations, and cyclohydrogenations. However, the suggestion that diene synthesis also plays an important part has been shown to be most unlikely.

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