THE FORMATION OF AROMATIC HYDROCARBONS

AT

HIGH TEMPERATURES

A THESIS

PRESENTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

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To

MY WIFE

CONTENTS

SUMMARY

Polycyclic aromatic hydrocarbons are known to be
formed at high temperatures from aliphatic hydrocarbons
or from simple aromatic hydrocarbons.   In an attempt to
elucidate the mechanisms of formation of these compounds,
and in particular the carcinogenic hydrocarbons, the
pyrolysis products of relatively simple hydrocarbons have
been examined, and mechanisms for their formation suggested.

The pyrolysis of n-decane at 700°C has given a tar
in which fifty-two compounds have been identified.   The
mechanisms of their formation are discussed.

Some of these mechanisms have been confirmed by
radiochemical analysis of the products obtained in the
pyrolysis of [1-^{14}C]tetralin and [β-^{14}C]butylbenzene.

[1-^{14}C]Tetralin has been synthesised and pyrolysed
at 700°C.   Twenty-one compounds have been isolated in
sufficient purity and quantity for radiochemical analysis.
The mechanisms for their formation are discussed with
reference to the number of labelled carbon atoms.

[β-^{14}C]Butylbenzene has been synthesised and
pyrolysed at 700°C.   Eighteen compounds have been isolated
and subjected to radiochemical assay.   Some of these
compounds have been partially degraded to locate the
position(s) of their activities.   It has been shown that,

at least to some extent, the formation of benzene in this
pyrolysis involves the resynthesis of the side chain,
that some toluene is formed by methylation of benzene or
by recombination of phenyl and methyl radicals, and that
at least three mechanisms are involved in the formation
of styrene.   The results obtained following isolation
and degradation of phenanthrene and chrysene have shown
that the mechanism involving phenethyl radical is the
major route to phenanthrene, and that the formation of
chrysene involves a combination of a C_6-C_4 and a C_6-C_2
unit.   It has been found that the formation of the
carcinogenic hydrocarbon 3,4-benzopyrene (benzo[a]pyrene)
(I) proceeds in accord with the hypothesis proposed
earlier.
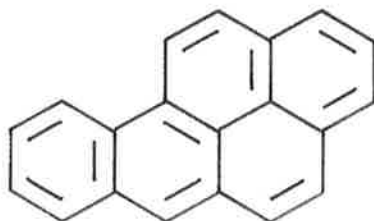
(I)

The optimum thermal conditions have been determined
for the formation of fifteen polycyclic hydrocarbons on
examining the tars obtained following pyrolysis of
n-butylbenzene over a range of temperatures varying from
300°-900°C at 50° intervals.   These results have shown

that maximum yields of polycyclic hydrocarbons are obtained
in the vicinity of 700°C, a temperature originally chosen
for the present investigation.

STATEMENT

The work described in this thesis is part of a
more extensive investigation conducted by a number of
other workers in this Department, but incorporates no
material which has been accepted for the award of any
other degree or diploma in any University and, to the
best of my knowledge and belief, contains no material
previously published or written by another person,
except when due reference is made in the text.

(J. Novotný)

ACKNOWLEDGEMENTS

INTRODUCTION

Since the discovery of the carcinogenic activity of certain polycyclic aromatic hydrocarbons, many new hydrocarbons have been tested for this effect.[1]

The most frequently reported carcinogen has been 3,4-benzopyrene (I), but other polycyclic hydrocarbons are known to be of comparable activity.   In addition to
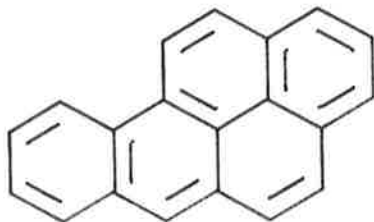
(I)

3,4-benzopyrene, the chief hydrocarbons of this nature encountered in the present investigation were 1,2:5,6-dibenzanthracene (II), 3,4:8,9-dibenzopyrene (III),
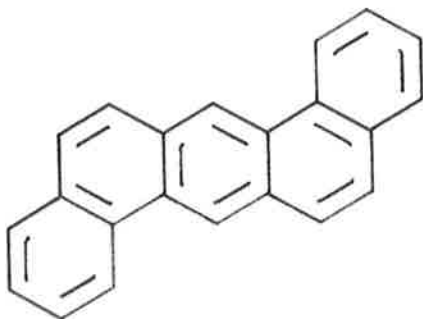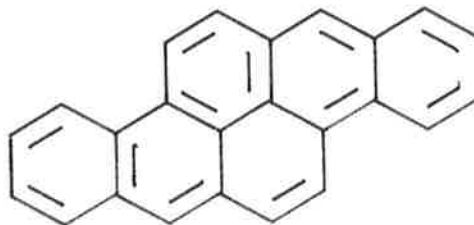
(II)   (III)

3,4:9,10-dibenzopyrene (IV), 3,4-benzofluoranthene (V),
and 10,11-benzofluoranthene (VI).
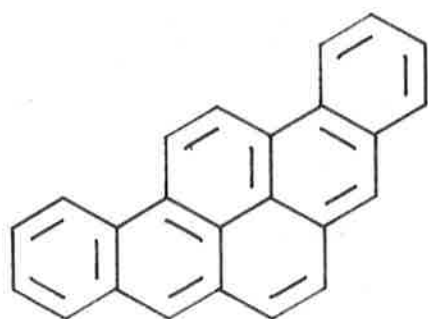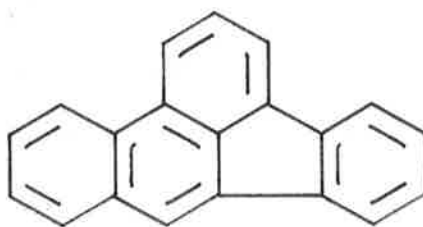
(IV) (V)
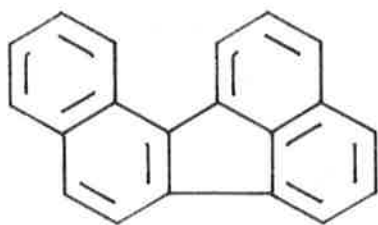
(VI)

The work carried out was concerned with tars
formed by pyrolysis of [1-^{14}C]tetralin, n-decane, and
[δ-^{14}C]butylbenzene at 700°C, and with those obtained
on pyrolysis of n-butylbenzene over a range of temperatures
from 300-900°C at 50 degree intervals. The temperature

chosen in the first three pyrolyses was 700°C, which
lies between the combustion temperatures of cigarette
and pipe tobacco,[2] and is approximately the temperature
at which coal decomposes, with the evolution of large
amounts of hydrogen.[3]   Both oil obtained by
distillation of shale,[3] and tars produced from acetylene[4]
and isoprene[4,5] at this temperature, had carcinogenic
properties.

The pyrolysis of the radioactive hydrocarbons in
the present investigation was designed to test the
hypothesis put forward for the formation of polycyclic
hydrocarbons and in particular, 3,4-benzopyrene.[6]
The pyrolysis of n-decane was carried out to determine
the nature and extent of carcinogenic hydrocarbon formation
from an aliphatic straight chain compound, and the pyrolyses
of n-butylbenzene to investigate the optimum thermal
conditions for the formation of polycyclic hydrocarbons
at the high temperatures involved.

It has been known for many years that tar can
produce cancer, but no systematic attempts to identify the
particular compounds responsible for this effect was possible
until the experimental production of cancer in lower animals
became a practical method.[7]

CHAPTER 1

CARCINOGENIC HYDROCARBONS

1.1 OCCURRENCE

The first experimental inducing of tumours by
the products of coal distillate was accomplished in 1915
by Yamagiwa and Ichikawa,[8] and the first investigation
into the chemical basis of tar cancer production was
carried out by Bloch and Dreifuss,[9] who concluded from
their observations that the substance responsible must be
a high boiling, neutral, non-nitrogenous compound, which
forms a stable complex with picric acid.   The production
of strongly carcinogenic tars by pyrolysis of isoprene,[4,5]
or acetylene[4] in a current of hydrogen, showed that the
agent present in these tars must be a hydrocarbon.
Moreover, the powerful fluorescence of these tars and of
other carcinogenic mixtures such as gas-works tar,[10] shale
oil,[11,12] refined mineral oils,[12,13] heated petroleum,[4]
pyrolysis products of cholesterol,[14] yeast,[4] skin,[4]
muscle[15] and hair,[15] and products obtained by the action
of aluminium chloride on tetralin,[16] suggested that this
cancer-producing hydrocarbon was a polycyclic aromatic
compound.   The fact that the fluorescence spectra
of the carcinogenic mixtures resembled

that of 1,2-benzanthracene (VII),[17] stimulated work on the synthesis of related compounds which finally led to the discovery of the first pure chemical entity to manifest pronounced carcinogenic properties, namely
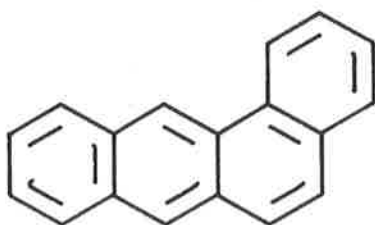
(VII)

1,2:5,6-dibenzanthracene (II).[15]

With the fluorescence spectrum as "the single thread that led through this labyrinth", the Royal Cancer Hospital research team in London began in the spring of 1930 the fractionation of two tons of pitch from the Becton gasworks, and by the autumn of 1931 by elimination of unwanted materials had reduced this to 7 grams of yellow crystalline powder which on further fractionation resulted in the isolation of the crystalline hydrocarbon, 3,4-benzopyrene (I).[16] This hitherto unknown hydrocarbon was found to be a powerful carcinogen and was recognised to be responsible for the strong characteristic fluorescence of the coal tar pitch.

Coal tar has been the most extensively investigated material of known carcinogenic potency,[19] and from it, other

carcinogenic hydrocarbons were later isolated.   These included

1,12-benzoperylene (VIII),[20] 3,4-benzofluoranthene (V),[21]

3,4:9,10-dibenzopyrene (IV),[22] 3,4:8,9-dibenzopyrene (III),[23]

and most recently naphtho-2',1'-3,4-pyrene (IX)[24] the

activity of which is as yet unknown.

3,4-Benzofluoranthene, the carcinogenic power of which has

been established only recently,[25] was found to be more

abundant than 3,4-benzopyrene in coal tar.[21]
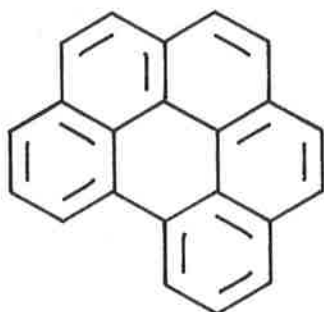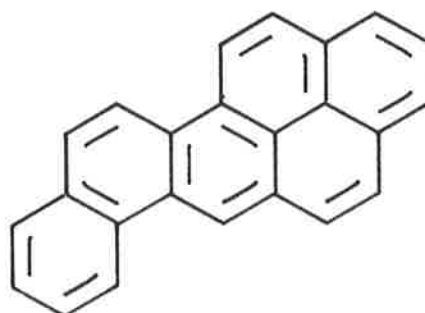
(VIII)   (IX)

A reinvestigation of shale oil and of mineral oil

fractions did not result in the isolation of any other

carcinogen of high potency[26] although fractions other than

that containing 3,4-benzopyrene, were found to be carcinogenic.

Chemical investigations of cigarette tar have

shown the presence of several carcinogenic polycyclic

hydrocarbons including 3,4-benzopyrene,[27]

1,2:5,6-dibenzanthracene,[28] 3,4:9,10-dibenzopyrene,[29]

3,4:8,9-dibenzopyrene,[30] 1,2:3,4-dibenzopyrene,[31]

3,4-benzofluoranthene,[32] 10,11-benzofluoranthene,[33] 1,12-benzoperylene,[34] 1,2-benzopyrene (X),[35] chrysene (XI),[36] and 1,2-benzanthracene.[37]
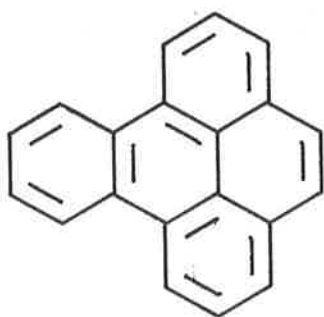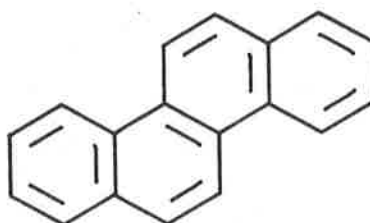
(X)   (XI)

Although some of these hydrocarbons are regarded as major initiating carcinogens they are present in such small amounts that they cannot alone account for the known biological activity of tobacco smoke condensate.[38]   Other carcinogens, as yet unidentified, or cancer promoting substances, or both, must be present.   Smoke phenols[39] and bases[40] have been established as co-factors in carcinogenesis caused by smoke polycyclic hydrocarbons.   The discovery of appreciable amounts of free radicals in cigarette smoke[41] led to the proposal that they were possibly involved in the carcinogenic process.[42]

The polynuclear hydrocarbons identified in tobacco smoke are present in relatively small quantities, but it has been shown[38] that some polynuclear hydrocarbons, although

rather weak complete carcinogens, are relatively potent
initiators even in minute concentrations.

1,2-Benzanthracene, for example, is known to be a strong
initiator though a weak carcinogen,[43] and a similar
observation was made with 2,3-(o-phenylene)pyrene (XII).[44]
On this basis, Wynder and Hoffmann[38] suggested that some
weak or even non-carcinogenic polynuclear hydrocarbons
in tobacco tar might contribute to its carcinogenic activity
by acting as initiators.
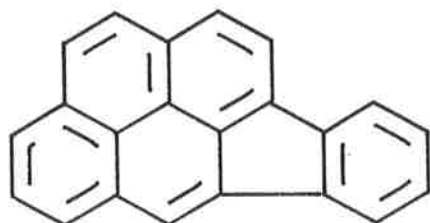
(XII)

The other main source of carcinogenic polycyclic
hydrocarbons in human environment are the atmospheric
pollutants, and a considerable amount of investigation
has been carried out on them.   Soot, an experimentally[45,46]
and clinically recognised carcinogen, is a major component
of smoke entering the atmosphere.[47]   A product of
incomplete combustion of most organic materials, soot has
carcinogenic properties and these are presumably due to
the presence of certain polycyclic aromatic hydrocarbons.[48,48]
The exhaust products of the internal combustion engine have

been examined by several groups of workers,[48-52] and a broad range of aromatic polycyclic hydrocarbons was found in the products from both petrol[48,51,52] and diesel[49,50,52] engines.   Further examination of the air from garages,[53] smoke and tar from curing kilns,[54] and rural and urban air[55] has added several hydrocarbons to those already identified.

Investigation of carbon blacks,[56] oysters and barnacles taken from polluted water,[57] human hair wax,[58] coal gas,[59] coffee soots,[60] Icelandic smoked food,[61] processed rubber,[62] soot from a smoked sausage factory,[63] snuff,[64] tobacco,[65] starch soots,[66] and soot from a smoking chamber[67] revealed the presence of 3,4-benzopyrene and other polycyclic aromatic hydrocarbons in these materials.

It has recently been reported[68] that benzopyrenes are common and relatively abundant constituents of soils. The carcinogenic 3,4-benzopyrene and its almost inactive 1,2-isomer have been identified spectroscopically in rural soil samples, where the possibility of industrial contamination is almost non-existent.   Even in the soil of tundras north of the arctic circle, 1 microgram of benzopyrene per 100 grams of soil could be detected.

Tars produced by the pyrolysis of hydrocarbons have not been extensively investigated by modern techniques although it has been shown that the pyrolyses of dicetyl,[69] tobacco hydrocarbons,[70] solid[71] and liquid[72] aliphatic

hydrocarbons produce tars containing 3,4-benzopyrene and other less carcinogenic hydrocarbons. The pyrolysis of methane, ethylene, and acetylene in diffusion flames was shown to yield a range of polycyclic hydrocarbons, including 3,4-benzopyrene.[73]

An examination of tars produced by the pyrolysis of naphthalene,[74] a mixture of pyrene and benzene,[75] α- and β-methylnaphthalene,[76] phenanthrene,[77] fluorene,[78] anthracene,[78] a mixture of anthracene and benzene,[79] acenaphthene,[80] and mixtures of naphthalene and benzene,[81] and phenanthrene and benzene,[81] yielded a large number of hydrocarbons not previously reported as pyrolytic products. These investigations will be more fully discussed in the next chapter.

The tar produced by the action of aluminium chloride on tetralin[82] has been reinvestigated and the products obtained by pyrolysis of 1,4'-phenylbutylnaphthalene,[83] styrene,[84] 1-phenylbuta-1,3-diene,[85,86] tetralin,[87] indene,[88] acetylene,[89] toluene,[80] ethylbenzene,[90] propylbenzene,[80] and butylbenzene,[80] buta-1,3-diene,[86] a mixture of buta-1,3-diene with pyrene,[81] benzene,[92] 4-vinylcyclohexene,[83] [α-^{14}C]ethylbenzene,[84] 2,2,4-trimethylpentane,[85] petrol,[86] anthracene,[87] phenanthrene,[87] and naphthalene[88] have been analysed and the yields of individual components determined. With few exceptions, 3,4-benzopyrene and other

carcinogenic hydrocarbons were found in almost all
pyrolysates.

1.2   MODE OF ACTION

The first direct interaction of 3,4-benzopyrene
with dermal constituents was noticed by Miller,[99] and
her initial results were greatly extended by Heidelberger
and his associates by using both carcinogenic[100] and
biologically inactive[101] ^{14}C-labelled polycyclic
hydrocarbons.   Following a single topical application
of various hydrocarbons to the skin of mice, a certain
degree of correlation was found between the amount of
protein-bound ^{14}C, and the respective carcinogenicities
toward this tissue.   It was found in the case of
[9,10-^{14}C]1,2:5,6-dibenzanthracene that irreversible binding
took place between the carcinogen, or its metabolite, and
the nucleoproteins, particulate or soluble proteins, but not
nucleic acids.   Furthermore, it was shown[100,102] that as no
radioactivity was extractable, essentially all the
radioactive material was combined chemically with both the
original denatured protein and the polypeptides derived
therefrom.   In an extension of these studies,[103] the
presence of 2-phenylphenanthrene-3,2'-dicarboxylic acid
(XIII) was demonstrated[104] in mouse skin

treated with 1,2:5,6-dibenzanthracene, indicating that
the K-region, i.e., the 3,4-bond, was involved in covalent

COOH
COOH
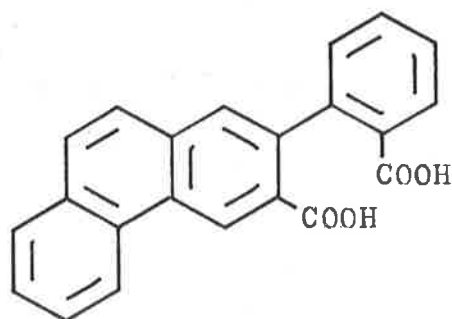
(XIII)

bonding.[105]   That the binding occurred through peptide
bonds involving one or both carboxyl groups was shown by
hydrazinolysis of the proteins, which resulted in the
removal of the dicarboxylic acid metabolite as an equal
mixture of dihydrazide and cyclic monohydrazide.[105], [106]

By means of fluorescence spectroscopy at low
temperatures similar results were later obtained[107]
using the extracts of the skin of mice which had been
painted with 3,4-benzopyrene.   The fluorescence spectra
of the solutions produced on hydrazinolysis of the
extracted proteins, showed a similarity to the spectra of
substituted chrysene and 1,2-benzanthracene derivatives.
This was in agreement with the theory[108] that the carcinogenic
hydrocarbons attach themselves to proteins by certain pairs
of adjacent carbon atoms known as " K regions ".   Figure 1.1

shows the K regions of 3,4-benzopyrene and the compounds
which might have been detected in the latter study.
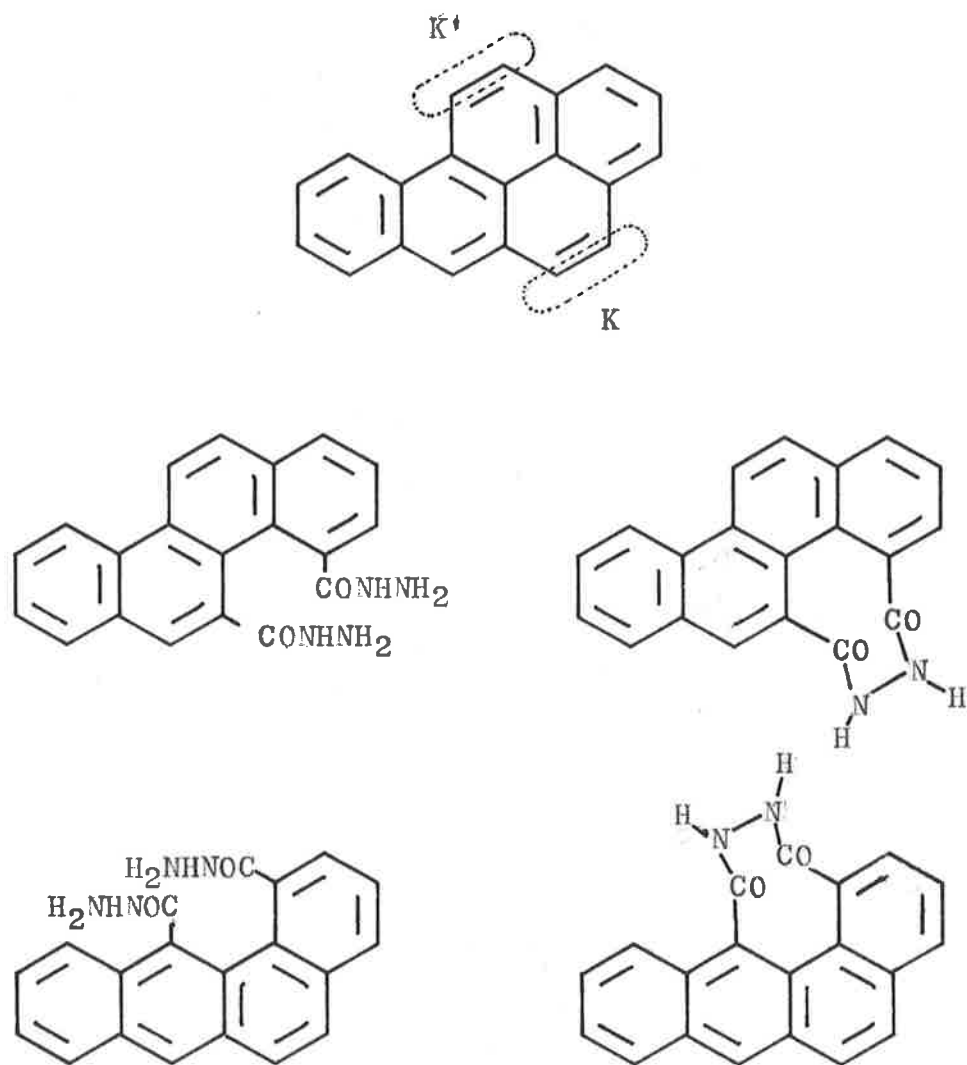
Figure 1.1

Systematic exploration with various [14]C- and
[3]H-labelled hydrocarbons[101,102] showed, however, the
existence of products which would indicate exceptions

to the binding-carcinogenicity correlation and this led
Heidelberger[110] and Miller[111] to the conclusion that
covalent bonding might be a necessary, but not sufficient,
prerequisite for tumour induction.

While Wiest and Heidelberger[109] had previously
claimed that timedependent binding of hydrocarbons in
mouse skin occurred solely with proteins, the possibility
of hydrocarbon-nucleic acid binding was not eliminated.
The recent report of firmly bound ^{14}C-labelled
1,2:5,6-dibenzanthracene (II) and 1,2:3,4-dibenzanthracene (XIV)
to desoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
was the first example,[112] but other cases of such bonding
have since appeared in the literature[113]. The mode of
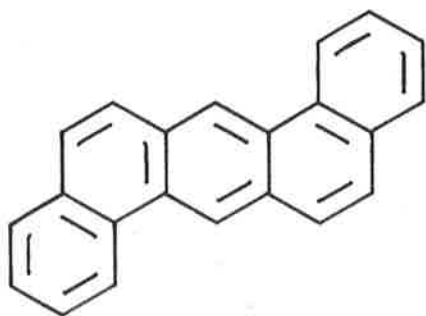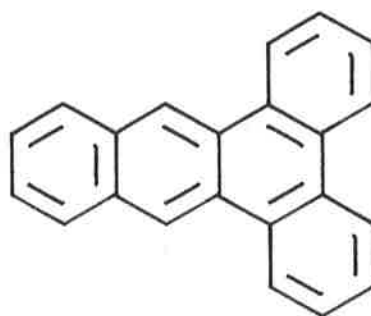
(II)   (XIV)

association of the hydrocarbons with the nucleic acids
has not yet been established; but it seems likely that
purely physicochemical bonding would be detected by the
methods used in the above studies.[113]

In an attempt to relate the characteristics of the active centres of the aromatic hydrocarbons to carcinogenic activity, several theories have been put forward. In the majority of these, the carcinogenic effect is associated with the reactivity of the phenanthrene type double bond (the K region) and the mesoanthracene positions (the L region) of these compounds.

In a series of classical papers, Schmidt[114] first suggested a relationship between the reactivity, π-electron density and carcinogenic activity of the polycyclic aromatic hydrocarbons.

A more refined modification of his theory was provided by Svartholm[115] who correlated carcinogenic activity with the ability of the K region to undergo addition reactions, determined on the basis of the total π-electron distribution in the molecule. The cellular reaction leading to carcinogenesis may then be pictured as a chemical reaction as shown in (XV).[116]

That the K region is a chemically reactive double bond was indicated by the reaction of polycyclic hydrocarbons with osmium tetroxide, forming well defined crystalline complexes which, on hydrolysis, yield the corresponding cis-diols. It has been shown that in polycyclic hydrocarbons this reaction involves the 9,10-phenanthrene-like double bond exclusively.

Quantitative studies by Badger[117] indicated that with
the exception of substituted 1,2-benzanthracenes,
increasing reactivity of any series of carcinogenic
hydrocarbons toward osmium tetroxide followed the
order of their increasing carcinogenic activity.
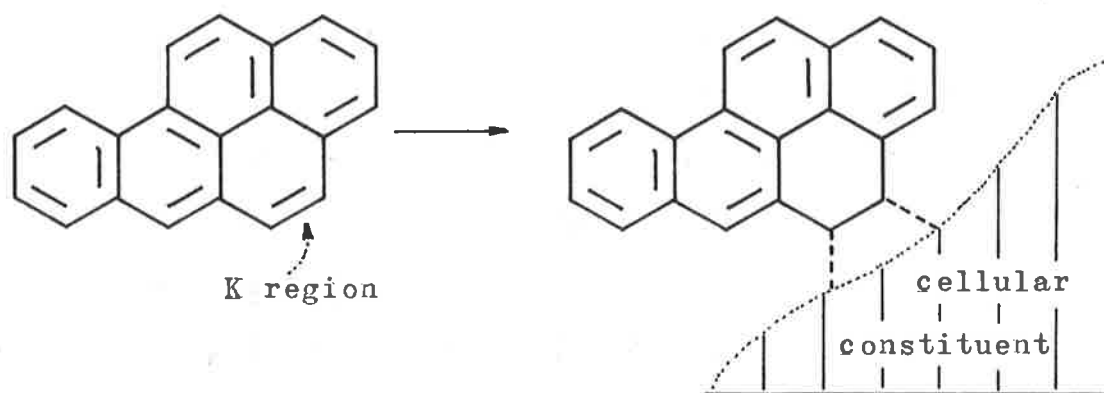
(XV)

Considerable extension of these ideas was due to
the work of Pullman and Daudel[108] who by using more precise
wave mechanical methods, found a correlation between the
carcinogenicity and various indices[116] that have been
developed to characterise the electronic properties of
the K region in these hydrocarbons. Several weaknesses
which later became apparent in the theory[119] led to the
development of new indices characterising not only the
K, but also the L regions and of the metabolically reactive
centre of the molecule—the so called M region (XVI).

These new indices have been also used to estimate the rate

(XVI)
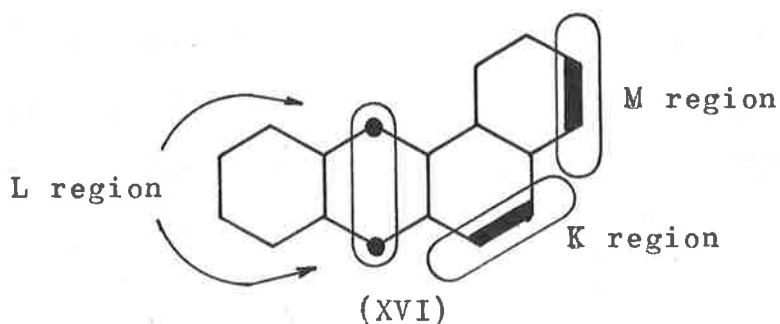
constants[20] of the formation of protein complexes with
the K region or L region of the hydrocarbon.[21]   In both
these theories, considerable reactivity of the K region and
slight reactivity of the L region, insofar as this region
exists, are simultaneously considered as a necessary and
sufficient condition for carcinogenic activity.

Starting from the experimentally proved[23]
Szent-Györgyi concept of the semiconductivity of proteins,[22]
Mason[24] suggested a theory of initiation of carcinogenic
processes, based upon the theory that an electron is
transferred from the protein to the hydrocarbon-a concept
which has recently been criticised by Pullman.[25]

Other theories have been suggested[26] to account
for the carcinogenic effect of polycyclic hydrocarbons,
but all can be divided into two groups.   The first
group contains all the theories considering the
reactivity of a certain part of the hydrocarbon as a

criterion of carcinogenicity, and the second contains theories considering magnitudes decisive for an easy transfer of the electron to the hydrocarbon from the biological substrate.

CHAPTER 2

PYROLYTIC REACTIONS OF HYDROCARBONS

2.1 EARLY INVESTIGATIONS

The first systematic studies of the products
obtained from the pyrolysis of hydrocarbons were carried
out on acetylene by Berthelot[127] more than a hundred years
ago, when analytical techniques other than distillation
and crystallisation were unknown. The early work on the
pyrolysis of aliphatic hydrocarbons resulting in the
formation of aromatic compounds, and the speculations on
the mechanism of the reactions involved have been
thoroughly reviewed by Egloff[128] and by Hurd.[129] Most of
the work discussed in these monographs was carried out
before 1900, and there seems to be some uncertainty about
(a) the purity of starting materials which were likely
to contain sulphur compounds - known to act as chain-
transfer agents, and (b) the actual temperature of the
pyrolyses as this was reported in many instances as "red
heat," "bright red heat," or "dull red heat."

All data on the free radical reactions involved
in the decomposition of simple hydrocarbons until June 1953
have been summarised by Steacie,[130] and the kinetics of these

reactions by Trotman-Dickenson.[131]   Other review articles
worthy of particular mention are those contained in
references [132] and [133], and the annual reviews published
by Haensel and Sterba,[134] Appell and Berger,[135] and
Berger and deRosset.[136]

The results of the work of the early investigators
led to the following conclusions:

(a) Paraffinic hydrocarbons are generally more stable to
pyrolytic reactions than the corresponding olefins.
Except under severe conditions, methane and ethane are
recovered unchanged in these reactions.

(b) Olefins undergo polymerisation at relatively low
temperatures; at higher temperatures both polymerisation
and decomposition are important.

(c) Acetylene is less stable to heat than ethylene.
It has been reported that acetylene begins to decompose
at 450° in a glass tube, while ethylene remains unchanged
up to 615°C.[128,129]

(d) Benzene can react with ethylene and acetylene under
pyrolytic conditions to give styrene and polycyclic hydrocarbons.

(e) The majority of reactions of aromatic compounds
containing an alkyl side chain involves the decomposition of
the side chain and the formation of longer chains capable
of cyclising to aromatic structures.

Futher investigations have confirmed and extended

most of the early work, although modern interpretation of
the results is very different from that of the early
investigators.

Recent developments in the study of the mechanism
of the pyrolytic decomposition of hydrocarbons include the
use of gas-liquid chromatography, isotope exchange and
radiotracer techniques. Contact times of the reactions
have been shortened in order to identify the primary
products. The relevant mechanisms of thermal decompositions
are considered below.

2.2   PYROLYSIS OF PARAFFINS

In spite of the considerable amount of work that
has been done on the kinetics of the thermal decomposition of
paraffins, the mechanism of these reactions still remains
a matter of controversy. Until recently the opinion held
by many workers was that the pyrolysis of paraffins takes
place by two concurrent processes, one molecular in character,
the other an unbranched free radical chain mechanism.[137]
The addition of sufficient quantity of an inhibitor such as
nitric oxide or propylene has been assumed to halt the
radical chain process without affecting the rate of the
supposed molecular reaction.

The molecular mechanism for the fully inhibited

reaction was, however, incompatible, with the results of
recent mass spectrometric experiments,[138] isotope
exchange experiments,[139] and detailed analytical studies.[140]
These results indicated that the fully inhibited reaction
involved free radicals, and was presumably a modification
of that radical chain system which must now be assumed to
account for the whole of the inhibited pyrolysis.   Despite
the fact that the nature of the initiation and termination
steps is uncertain there seems to be general agreement on
the chain propagating process in the uninhibited reaction
of ethane,[141] propane,[142] and n-butane,[143],[144]

The unimolecular initiation process is considered
to involve a scission of a carbon-carbon bond with the
production of two radicals.   The rupture of a carbon-
hydrogen bond is regarded a less likely initiation step of
the reaction chains since the pre-exponential rate parameter
associated with this process must be at least 10^5 times
larger than the pre-exponential parameters associated with
the rupture of the much weaker carbon-carbon bonds.[145]

The radicals produced can then react by:

(a) disproportionation;

$$RCH_2CH_2CH_2\overset{\bullet}{CH_2} \longrightarrow RCH_2CH_2CH\text{=}CH_2 + H \qquad (1)$$

$$RCH_2CH_2CH_2\overset{\bullet}{CH_2} \longrightarrow RCH_2CH\text{=}CH_2 + \overset{\bullet}{CH_3} \qquad (2)$$

$$RCH_2CH_2CH_2\overset{\bullet}{CH_2} \longrightarrow RCH\text{=}CH_2 + CH_3\overset{\bullet}{CH_2} \qquad (3)$$

$$RCH_2CH_2CH_2\overset{\bullet}{C}H_2 \longrightarrow RCH_2\overset{\bullet}{C}H_2 + CH_2{=}CH_2 \tag{4}$$

$$RCH_2\overset{\bullet}{C}H_2 + R'CH_2\overset{\bullet}{C}H_2 \longrightarrow RCH{=}CH_2 + R'CH_2CH_3 \tag{5}$$

(b) hydrogen abstraction;

$$RCH_2\overset{\bullet}{C}H_2 + R'CH_2CH_3 \longrightarrow RCH_2CH_3 + R'\overset{\bullet}{C}HCH_3 \tag{6}$$

$$\longrightarrow RCH_2CH_3 + R'CH_2\overset{\bullet}{C}H_2 \tag{7}$$

(c) recombination;

$$RCH_2\overset{\bullet}{C}H_2 + R'CH_2\overset{\bullet}{C}H_2 \longrightarrow RCH_2CH_2CH_2CH_2R' \tag{8}$$

$$RCH_2\overset{\bullet}{C}H_2 + H \longrightarrow RCH_2CH_3 \tag{9}$$

James and Steacie[145] demonstrated that an ethyl
radical could abstract hydrogen from C_7 hydrocarbons at
a rate increasing in the order: heptane, hept-1-ene,
hept-1-yne.   Rice and Vanderslice[146] showed that methyl
radicals could abstract tertiary hydrogen faster than
secondary hydrogen, and secondary faster than primary.

Methane was pyrolysed at 1000°-1100°C by Germain,[147]
both pure and in the presence of 50% nitrogen or hydrogen.
Nitrogen behaved as an inert gas, but hydrogen caused a
decrease in decomposition.   The activation energy was
found to be 87 kcal./mole in all three reactions,
suggesting that the rate controlling step was the same,
and that only the concentration of the chain initiating
radicals was effected by dilution.

Heath[148] reasoned that chain propagation steps were
not involved in the thermal decomposition of methane at these
temperatures since he found that hydrogen did not inhibit the
reaction.   His activation energy of 93 kcal./mole suggested
that the controlling step was a free radical split to
methylene.   Skinner[149] found a higher activation energy,
101 kcal./mole, in his shock tube experiments and postulated
a rupture of the carbon-hydrogen bond with the formation of a
methyl radical and a hydrogen atom as the primary step in the
decomposition of methane.   Another interesting decomposition
reaction of methane was its degradation at 2000-5000°C by
intense millisecond light pulses.[150]

An extension of Skinner's shock tube experiments[151]
showed that ethane decomposed into methyl radicals with an
activation energy of 79.3 kcal./mole.

n-Hexane[152] was thermally cracked at temperatures
varying from 290 to 412°C in a tubular reactor internally
illuminated with ultraviolet light.   Mercury vapour in the
reactor, activated by the radiation, provided an initiating
source for the radical chains.   The hexyl radicals either
dimerised or decomposed to lower molecular weight olefins
and alkyl radicals.   Hexene, which is thermally stable under
the experimental conditions was not detected, indicating that
the decomposition of hexyl radicals by carbon-hydrogen cleavage

did not occur.

A new technique applied for the first time to thermal decomposition of hydrocarbons was the use of a ballistic piston.[153]   n-Hexane was decomposed at pressures of up to 115.000 lb./in.^{2} and the most significant observation was the low activation energy, 8.4 kcal./mole.

Hexadecane was heated in the presence of ^{60}Co γ radiation and high energy mixed radiation from a nuclear reactor.[154]   n-Pentane and 2-methylbutane were cracked at 480°C in the presence of γ radiation.[155]   In neither case was the product distribution substantially affected by radiation, and it was concluded[154] that the chain reactions are not new reactions but ordinary thermal free radical reactions unaltered by radiation.

2.3   PYROLYSIS OF OLEFINS

The olefins studied during the past few years may be conveniently divided into three groups containing the following:

(a) no allylic carbon-hydrogen and no allylic
     carbon-carbon bonds, i.e., ethylene;

(b) allylic carbon-hydrogen bonds but no allylic
     carbon-carbon bonds;

(c) both allylic carbon-hydrogen and allylic
     carbon-carbon bonds.

From the information available on the pyrolytic decomposition of ethylene, it appears that polymerisation is the important reaction at temperatures below 600°C, while at higher temperatures both decomposition and polymerisation are important.[156]

The primary reaction in the decomposition of ethylene has been the subject of a number of investigations.[156-159] For some time there was no agreement as to whether the decomposition proceeded (a) by an elimination of molecular hydrogen or (b) by a scission to vinyl radicals and hydrogen atoms. It was shown by Cvetanović[158] that the initial decomposition proceeds predominantly by (10), a fact confirmed later by Kebarle,[159] who has, however, found that the reaction (11) also occurs but only to the extent of about 4% of the total decomposition.

$$CH_2=CH_2 \longrightarrow CH\equiv CH + H_2 \qquad (10)$$

$$CH_2=CH_2 \longrightarrow CH_2=\overset{\bullet}{C}H + H \qquad (11)$$

The primary decomposition of propylene and but-2-ene, compounds containing only allylic carbon-hydrogen bonds, was studied most recently by Kebarle and Avrahami.[160,161] These workers have shown that propylene[160] decomposed by three primary reactions (12)-(14) and that no molecular elimination of hydrogen took place. It is significant that although the

difference in bond

$$CH_3CH=CH_2 \longrightarrow \overset{\bullet}{C}H_2CH=CH_2 + H \qquad (89\%) \qquad (12)$$

$$CH_3CH=CH_2 \longrightarrow \overset{\bullet}{C}H_3 + \overset{\bullet}{C}H=CH_2 \qquad (11\%) \qquad (13)$$

$$CH_3CH=CH_2 \longrightarrow cyclopropane \qquad (0.2\%) \qquad (14)$$

dissociation energies $D(C_2H_5-CH_3)-D(C_3H_5-H)$ was 16 kcal./mole

reaction (13) still occurred. The isomerisation to

cyclopropane was similar to the rearrangement of but-1-ene

to methylcyclopropane, observed by Cvetanović.[162]

Two primary reactions (15) and (16) were observed in

the decomposition of but-2-ene.[161] Approximately 5/7 of

the but-2-ene decomposed by path (15) and 2/7 by path (16), and

the rearrangement to methylcyclopropane, reaction (17),

occurred to a very minor extent, if at all.

$$CH_3CH=CHCH_3 \longrightarrow \overset{\bullet}{C}H_2CH=CHCH_3 + H \qquad (15)$$

$$CH_3CH=CHCH_3 \longrightarrow \overset{\bullet}{C}H_3 + \overset{\bullet}{C}H=CHCH_3 \qquad (16)$$

$$CH_3CH=CHCH_3 \longrightarrow methylcyclopropane \qquad (17)$$

The initial step in the pyrolysis of olefins

containing a straight chain of at least four carbon atoms

(with the exception of but-2-ene, discussed above) is

believed to involve (α) the scission of the allylic carbon-

carbon bond with the formation of two radicals as in (18)-(21),

$$RCH_2CH_2CH_2CH_2CH=CH_2 \longrightarrow RCH_2CH_2\overset{\bullet}{CH_2} + \overset{\bullet}{CH_2}CH=CH_2 \quad (18)$$

$$RCH_2CH_2CH_2CH=CHCH_3 \longrightarrow RCH_2\overset{\bullet}{CH_2} + \overset{\bullet}{CH_2}CH=CHCH_3 \quad (19)$$

$$RCH_2CH_2CH=CHCH_2CH_3 \longrightarrow R\overset{\bullet}{CH_2} + \overset{\bullet}{CH_2}CH=CHCH_2CH_3 \quad (20)$$

$$\longrightarrow RCH_2CH_2CH=CH\overset{\bullet}{CH_2} + \overset{\bullet}{CH_3} \quad (21)$$

or (β) the rupture of the carbon-hydrogen bond in the allylic position with the formation of a radical and a hydrogen atom, as in (22)-(26).

$$RCH_2CH_2CH_2CH_2CH=CH_2 \longrightarrow RCH_2CH_2CH_2\overset{\bullet}{CH}CH=CH_2 + H \quad (22)$$

$$RCH_2CH_2CH_2CH=CH-CH_3 \longrightarrow RCH_2CH_2\overset{\bullet}{CH}CH=CH-CH_3 + H \quad (23)$$

$$\longrightarrow RCH_2CH_2CH_2CH=CH-\overset{\bullet}{CH_2} + H \quad (24)$$

$$RCH_2CH_2CH=CHCH_2CH_3 \longrightarrow RCH_2\overset{\bullet}{CH}CH=CH-CH_2CH_3 + H \quad (25)$$

$$\longrightarrow RCH_2CH_2CH=CH\overset{\bullet}{CH}CH_3 + H \quad (26)$$

The dissociation energy of the allylic carbon-carbon bond in an olefin is at least 15 kcal./mole smaller than that of any other carbon-carbon bond in the molecule, [165] and the scission of this bond should therefore be the primary step in the pyrolysis of these compounds.

The possible fate of the alkyl radicals in the pyrolytic reactions has been mentioned in the previous section. The allylic radicals formed in (20) and (21) could further decompose to give butadiene and an alkyl radical as shown in (27) and (28).

$$\overset{\bullet}{C}H_2CH=CHCH_2CH_3 \longrightarrow \overset{\bullet}{C}H_2CH=CH\overset{\bullet}{C}H_2 + \overset{\bullet}{C}H_3 \quad (27)$$

$$RCH_2CH_2CH=CH\overset{\bullet}{C}H_2 \longrightarrow R\overset{\bullet}{C}H_2 + \overset{\bullet}{C}H_2CH=CHCH_2 \quad (28)$$

The allylic radicals formed in (19), or (20) and (21), could react further by loss of allylic hydrogen atom to give butadiene as in (29) and substituted butadiene respectively, as shown in (30) and (31).

$$\overset{\bullet}{C}H_2CH=CHCH_3 \longrightarrow \overset{\bullet}{C}H_2CH=CH\overset{\bullet}{C}H_2 + H \quad (29)$$

$$\overset{\bullet}{C}H_2CH=CHCH_2CH_3 \longrightarrow \overset{\bullet}{C}H_2CH=CHCHCH_3 + H \quad (30)$$

$$RCH_2CH_2CH=CH\overset{\bullet}{C}H_2 \longrightarrow RC\overset{\bullet}{H}CH=CH\overset{\bullet}{C}H_2 + H \quad (31)$$

A similar situation will exist in further reactions of allylic radicals obtained in (22)-(26). The most likely reaction to occur for instance with radical obtained in (22) will be either the scission of a carbon-carbon bond as shown in (32) or of a carbon-hydrogen bond as shown in (33) with the formation of butadiene or of substituted butadiene. Analogous reaction schemes may be devised for branched chain olefins, which will result in alkyl substituted butadienes. The presence of butadiene or its alkyl derivatives in almost all pyrolytic reactions[164] may well be due to this type of reaction.

$$RCH_2CH_2CH_2\overset{\bullet}{C}HCH=CH_2 \longrightarrow RC\overset{\bullet}{H}_2 + CH_2=CHCH=CH_2 \quad (32)$$

$$RCH_2CH_2CH_2\overset{\bullet}{C}HCH=CH_2 \longrightarrow RCH_2CH_2CH=CHCH=CH_2 + H \quad (33)$$

The pyrolysis of polyenes represents an even more complex problem, because addition and polymerisation

processes can be expected to compete.[130] Aromatisation
of buta-1,3-diene was investigated at 550[105] and 700°C.[91,105]
At the lower temperature, cyclohexene, cyclohexadiene
and C_8 aromatic compounds were formed. At the higher
temperature, complete conversion of acyclic and alicyclic
components to aromatic compounds had occurred and benzene,
toluene and polycyclic compounds were observed among the
products. The postulated intermediate in the latter
case, 4-vinylcyclohexene,[93,105] gave a pyrolysis pattern
similar to that of buta-1,3-diene.

The hydrocarbon bicyclo[2,2,2]octa-2,5,7-triene (XVII),
known as "barrelene" on account of its barrel shaped
electron cloud, thermally decomposed at 350°C to benzene
and acetylene.[106]
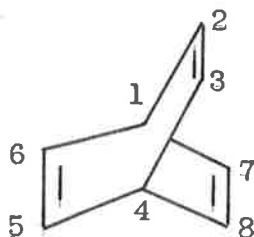
(XVII)

2.4   PYROLYSIS OF ACETYLENES

The pyrolysis of acetylenic compounds has not been

extensively investigated, but it has been shown that
inducing of polymerisation with acetylene occurred less
readily than it did with ethylene.[167]   It appeared from
the shock wave studies on acetylene using mass spectrometry
that polymerisation took place _via_ a dimer,[168,169]
presumably vinylacetylene, and both the dimer and higher
polymers appeared to have reached "equilibrium" with
acetylene.   A sharp drop in the concentration of these
polymers was observed at a later stage, which was
correlated with the formation of carbon after an induction
period.[169]

        The thermal hydrocracking pattern of acetylene was
surveyed by Coats and Anderson[170] over the range 500-900°C.
They pyrolysed acetylene for 2 to 10 minutes in the presence
of deuterium and $^2H_2$-acetylene in the presence of hydrogen.
Products were analysed by mass spectrometry.   At
500-800°C the former reactants gave principally benzene,
the latter $^2H_6$-benzene.   Methane formation was first
observed at 600°C and became a principal reaction at
800°C.   In spite of the attractive design of the experiment,
it failed to support a satisfactory mechanism for the
formation of methane, or of its precursor, the methyl radical.

        Gas chromatography in addition to other types of
chromatography has revealed a rich pattern of pyrolysis
products in a thermal decomposition of acetylene.[89]

Nineteen different compounds have been identified.

2.5   PYROLYSIS OF AROMATIC HYDROCARBONS

Aromatic hydrocarbons having an alkyl side chain
will be considered in more detail in Chapters 3 and 5,
and this section deals mainly with the pyrolysis of
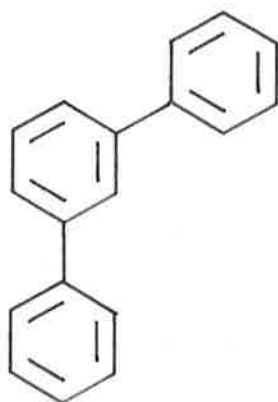compounds having no side chain.

The simplest and most investigated representative
of this class of compounds is benzene.   When benzene
was pyrolysed at 700°C[82] much of the initial material
was recovered unchanged and the major transformation
products were biphenyl (XVIII), p-terphenyl (XIX),
m-terphenyl (XX), and triphenylene (XXI).
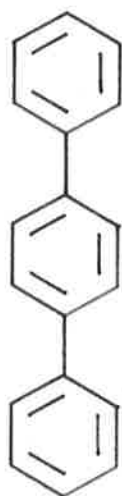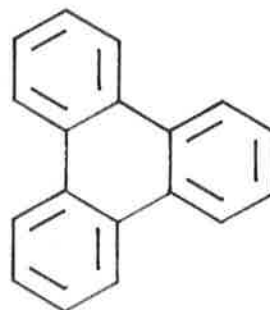
(XVIII)   (XIX)   (XX)   (XXI)

It seemed certain that the fission of carbon-hydrogen

bonds in benzene took place, giving phenyl radicals, which then reacted with benzene molecules to give biphenyl, and that further phenylation (and cyclodehydrogenation where necessary) gave the other compounds named. The fission of the benzene ring occurred to only a very small extent. Benzene[71] heated to 1200°C in helium for 4 milliseconds gave, however, acetylene and diacetylene. Apparently the primary reaction was ring rupture yielding an unstable six-carbon chain which immediately dissociated to two- and four-carbon fragments.

Pyrolysis of fused ring aromatic hydrocarbons with two to four nuclei either in a tube filled with porcelain fragments heated at 750°C, or on electrically heated wire, yielded more highly condensed systems. With non-substituted hydrocarbons such as naphthalene (XXII),[74] phenanthrene (XXIII),[77] and anthracene (XXIV),[78] direct nuclear condensation took place under these conditions.
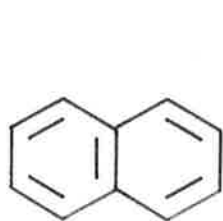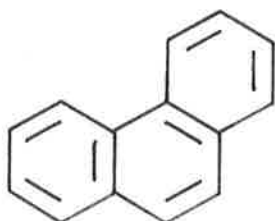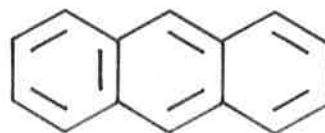

(XXII)   (XXIII)   (XXIV)

On the other hand, with methyl substituted aromatic

- 34 -

hydrocarbons such as $\underline{\alpha}$- and $\underline{\beta}$-methylnaphthalenes[76]
and acenaphthene (XXV),[80] the molecules were joined
preferentially through the methyl and methylene groups.
One of the reactions in the pyrolysis of fluorene (XXVI)[78]
is enlargement of the ring, yielding
1,2:7,8-dibenzochrysene (XXVII) as the main product as
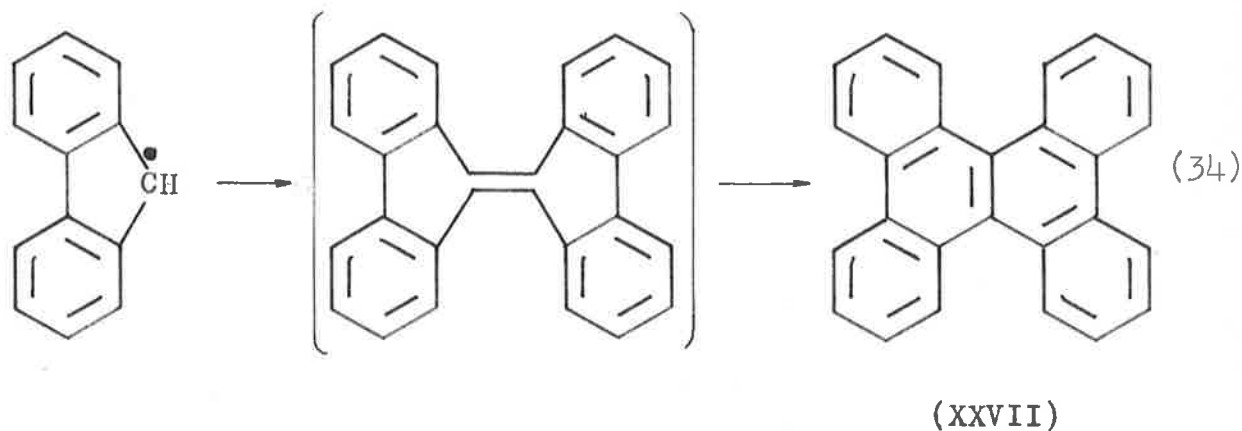shown in (34).   It is likely that the aromatic compounds
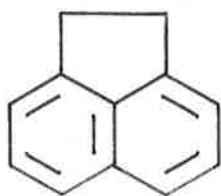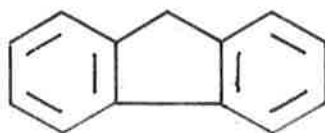
(XXV)   (XXVI)

with four or more rings that occur in coal tar pitch
are formed from lower aromatic compounds by pyrolytic
condensation during coking.[172]

(34)

(XXVII)

2.6 THE MODE OF FORMATION OF POLYCYCLIC HYDROCARBONS
IN PYROLYTIC REACTIONS

The pyrolysis of hydrocarbons at elevated
temperatures is known to proceed through a variety
of chain mechanisms.[173]   At temperatures below 700°C
kinetic data and the analysis of the products, when the
heated gases were passed over metallic mirrors, have
indicated that the primary chain carriers are
C_nH_{2n+1} radicals and hydrogen atoms[174] and other
radical carriers have been identified in mass
spectrometric studies.   At much higher temperatures,
especially above 2200°C, shock tube studies indicate
that a large variety of radicals is involved.   Indeed
at 3200°C, a considerable percentage of the material
present is in the form of molecular fragments.
Spectrophotometric studies have demonstrated the
occurrence of C_2 and C_3 units.   Rapidly sampled mass
spectra of acetylene subjected to shock waves showed the
presence of fragments as high as C_8H, along with a host of
lower molecular species.[169]

Several hypotheses have been suggested to account
for the formation of polycyclic hydrocarbons at high
temperatures taking into account these types of chain
propagation steps.

(a) <u>Acetylene Hypothesis of Berthelot.</u>- Berthelot[175]
proposed that the pyrolysed hydrocarbon was first
decomposed to acetylene and that different polycyclic
hydrocarbons were formed by polymerisation of these
two-carbon units. Later a similar view was held
by Groll[176] who suggested that the primary intermediate
from which all the higher hydrocarbons were formed was
the diradical of acetylene. More recently this concept
has found support from Bonnet and Neukomm,[177] and Falk
and Steiner.[56] Although this hypothesis is difficult
to disprove, it has been shown on many occasions[178]
that hydrogen, methane, and ethylene are the main products
of pyrolytic decomposition, whereas the presence of
acetylene was reported in very few cases.[179] In the
light of facts known to date there seems to be no need
to postulate acetylene as the exclusive precursor of
polycyclic hydrocarbons although exact details of their
formation are still unknown. As the addition to an
olefinic linkage proceeds more rapidly than addition to
an acetylenic bond,[167] ethylene, which is formed in
large amounts in all pyrolyses,[178] seems to be a more
reasonable intermediate.

(b) <u>CH$_2$ and CH Radicals.</u>- The suggestion that CH$_2$ and
CH fragments serve as precursors of polycyclic hydrocarbons
was put forward by Bone and Coward.[180]

(c) <u>Butadiene Hypothesis</u>.-   The concept that butadiene
or alkylated butadienes are the precursors of thermal
aromatisation was based on Staudinger's observation[181]
that butadiene when pyrolysed at 800°C yielded a
tar containing 30% benzene, and 25% naphthalene.
Jones[182] and more recently Weizmann[183] followed this lead,
stressing the idea that conjugate unsaturation was a
necessary factor in the formation of aromatic hydrocarbons
at high temperatures.   According to Weizmann, polycyclic
hydrocarbons were formed by a series of Diels-Alder
additions involving both olefins and butadienes.
Thus phenanthrene (XXIII) and anthracene (XXIV) would
be formed by an addition of buta-1,3-diene (XXVIII)
to naphthalene (XXII), whereas triphenylene (XIX),
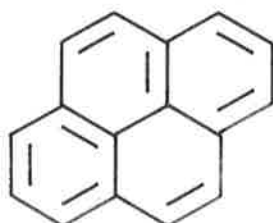
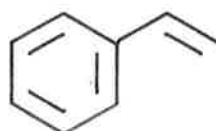$$CH_2=CH-CH=CH_2$$

(XXVIII)

chrysene (XI), 3,4-benzophenanthrene (XXIX), and
1,2-benzanthracene (VII) by condensation of butadiene
with phenanthrene.   Furthermore, Weizmann has
suggested that pyrene (XXX) was formed either by
dimerisation of styrene (XXXI), or tetramerisation
of buta-1,3-diene.[183]
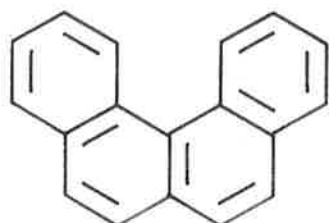
(XXIX)   (XXX)   (XXXI)

There are several objections to this mechanism.
The distribution of the products should be governed by
the relative activity of the carbon-carbon double bonds
in the substrate.   On the basis of the above theory
the yields of triphenylene should be larger than those of
either chrysene, 1,2-benzanthracene, or 3,4-benzophenanthrene;
chrysene and 1,2-benzanthracene are, however, produced in
larger amounts than triphenylene.[184]   The formation of
1,2-benzopyrene, furthermore, should be preferred to that
of 3,4-benzopyrene; however, the reverse was found.[185]
Naphthalene should always be formed in larger amounts than
phenanthrene; however, the pyrolysis of propylbenzene,[90]
and ethylbenzene[90] yielded more phenanthrene.   In
addition, only a small amount of pyrene was obtained in
the pyrolysis of styrene,[84] and a different mechanism must,
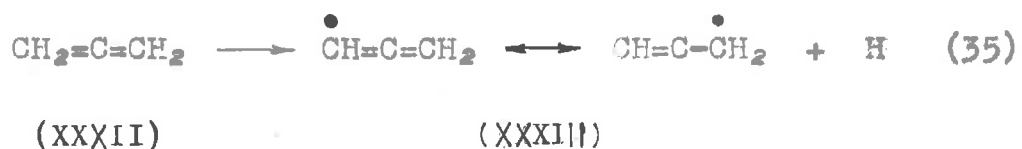therefore, operate.

Although buta-1,3-diene is formed from almost all

types of hydrocarbons under pyrolytic conditions[164] the
relative activation energies for the diene addition
(ca. 28 kcal.) and for radical addition (ca. 2.5 kcal.)[131]
would suggest that the resynthesis proceeds by radical
rather than molecular condensation.

The pyrolysis of a mixture of pyrene and
buta-1,3-diene[91] and a mixture of naphthalene and
butadiene[186] furnished additional evidence for the relative
unimportance of the diene reaction since the yields of
benzopyrenes and phenanthrene showed only an insignificant
increase over those obtained in the pyrolyses of pure
products.

(d) Formation of Aromatic Hydrocarbons from C₂ Fragments.-
In this concept,[187] which has not gained wide acceptance,
it was proposed that thermal abstraction of hydrogen from
allene (XXXII), a product obtained by Szwarc[188] in the
pyrolysis of propylene at 686-872°C, and low pressures,
yielded the resonance stabilised propadienyl radical (XXXIII)
as shown in (35).   It was suggested, that 1,2 shift of

$$CH_2=C=CH_2 \longrightarrow \overset{\bullet}{C}H=C=CH_2 \longleftrightarrow CH=C-\overset{\bullet}{C}H_2 + H \quad (35)$$

(XXXII)   (XXXIII)

hydrogen occured at high temperatures yielding the
fragment (XXXIV) which is both a free radical and a carbene

moiety.   Its dimerisation should give rise to benzene.

$$\overset{\bullet}{C}H=CH-CH: \quad \longleftrightarrow \quad :CH-CH=\overset{\bullet}{C}H$$

(XXXIV)

2.7   WORKING HYPOTHESIS

It was initially assumed by Badger[*] that
polycyclic hydrocarbons were formed by a step-wise
synthesis from two-carbon fragments.   Cracking, with the
formation of free radicals undergoing termination ractions
with other radicals or propagation reactions with neutral
molecules, dehydrogenation, and cyclodehydrogenation were
considered to be the most important reactions.   A series
of such reactions would be involved in the formation of
3,4-benzopyrene as shown in Figure 2.1.   The details of
the conversion and the degree of hydrogenation of the
intermediates were not specified, but it was considered that
reasonable intermediates would be ethylene or acetylene for (XXXV),
buta-1,3-diene or vinylacetylene for (XXXVI), styrene,
ethylbenzene or 4-vinylcyclohexene for (XXXVII),
1-phenylbuta-1,3-diene, n-butylbenzene or tetralin for
(XXXVIII) and (XXXIX), and 1-4'-phenylbutylnaphthalene or
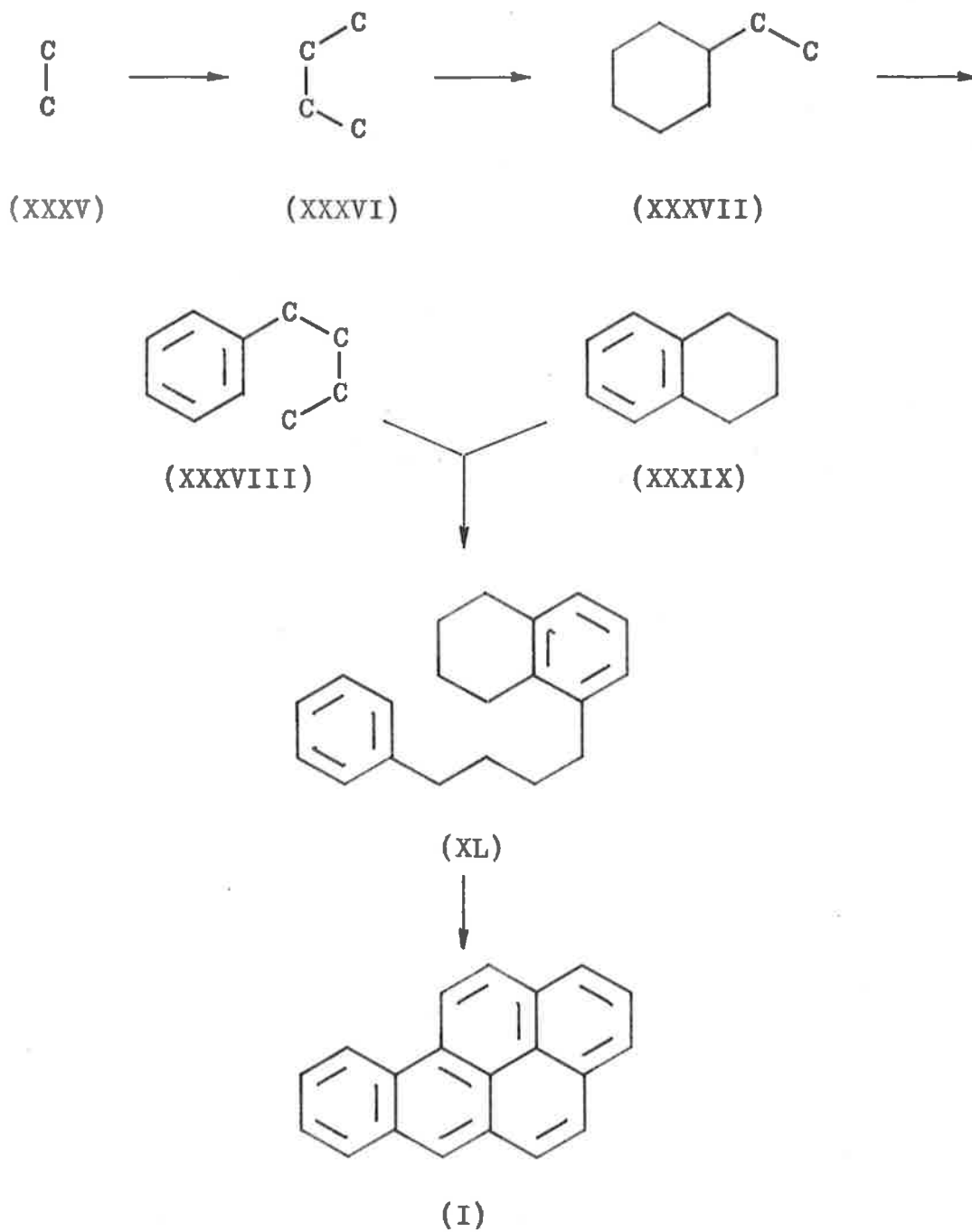5,4'-phenylbutyltetralin for (XL).

Figure 2.1

The participation of an intermediate such
as (XXXIX) in the formation of 3,4-benzopyrene was
supported by the fact that when tetralin was treated
with aluminium chloride it gave a complex mixture
known as "Schrœter tar," which became carcinogenic
after being heated, and was shown to contain
3,4-benzopyrene.[88]   Since 6,4'-phenylbutyltetralin
was a major constituent of the mixture,[189] some
5,4'-phenylbutyltetralin (XL) could also have been
formed, and its absence might have been due to its
rapid conversion to 3,4-benzopyrene, which was actually
isolated.   Similarly 1,4'-phenylbutylnaphthalene,
belonging to the same group of intermediates (XL),
has been shown to give 3,4-benzopyrene on pyrolysis.[83]

Pyrolysis of acetylene,[89] buta-1,3-diene,[91]
styrene,[94] ethylbenzene,[90] 4-vinylcyclohexene,[95]
n-butylbenzene,[90] n-decane (Chapter 4),
1-phenylbuta-1,3-diene,[85] naphthalene,[96] and tetralin[86]
have been shown to yield 3,4-benzopyrene.   Moreover,
other compounds (toluene,[90] n-propylbenzene,[90] indene,[88]
and 2,2,4-trimethylpentane[95]), which are not direct
intermediates in the scheme (XXXV) - (I), have been found
to give some 3,4-benzopyrene on pyrolysis.

The third step in the hypothesis was further
supported by the fact that the yields of 3,4-benzopyrene,

obtained in the pyrolyses of simple alkylbenzenes,
were found to decrease in the following order:
n-butylbenzene (XXXVIII); n-propylbenzene, easily
converted to (XXXVIII); ethylbenzene (XXXVII); and
toluene, which gave only a negligible amount of
3,4-benzopyrene.

The possibility of the formation of
3,4-benzopyrene by reaction of a C_2 unit (such as
ethylene) with chrysene or 1,2-benzanthracene has been
discarded on the basis of the fact that the pyrolysis
of indene,[88] for example, gave only a small amount of
3,4-benzopyrene, although the yields of chrysene were
high, and ethylene was present in the exit gases.

Conversely, it appeared, from the early experimental
evidence, that a reaction involving a C_4 unit (such as
buta-1,3-diene) and a pyrene precursor might be an important
step in the formation of 3,4-benzopyrene, in addition to
that represented by (XXXV) → (I). The ratio of pyrene
to 3,4-benzopyrene was found to be low for tetralin[88] and
indene[88] tar, but relatively high for most of the other
compounds examined. This was best explained by assuming,
that both mechanisms operate to a varying degree, depending
on the nature of the compound pyrolysed.

Dimerisation of buta-1,3-diene is known to yield
4-vinylcyclohexene,[100] and two vinylcyclohexene radicals

(XLI) could give a hydropyrene (XLII).   Dehydrogenation
of (XLII) would give pyrene (XXX); an addition of another
molecule of buta-1,3-diene to (XLII) followed by
dehydrogenation would give 3,4-benzopyrene (I).

(XLI)   (XLII)   (XXX)

(I)
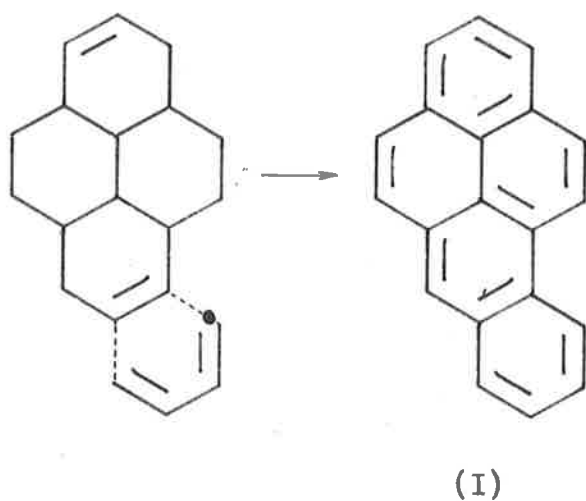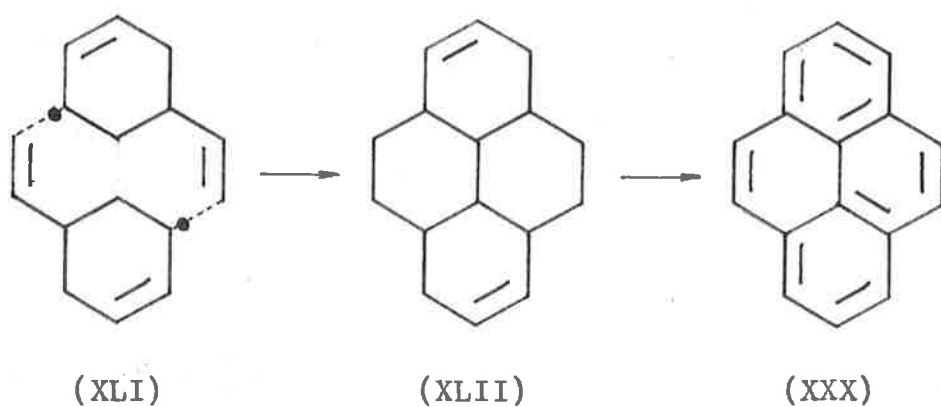
CHAPTER 3

THE PYROLYSIS OF [1-^{14}C]TETRALIN

3.1 INTRODUCTION

A detailed analysis of the tar obtained from the pyrolysis of tetralin at 700°C has already been reported,[86] and satisfactory mechanisms for the formation of the various polycyclic aromatic hydrocarbons have been suggested. These mechanisms have been based on the reactions of primary radicals which would form on scission of the weakest carbon-carbon or carbon-hydrogen bonds in tetralin, and on the relative ratio of yields of the different products. In postulating such mechanisms account has also been taken of the relative amounts of a polycyclic compound formed by the pyrolysis of different intermediates.[191] Reasonable mechanisms have been proposed for the formation of many of the compounds which have been identified, but few of these mechanisms can be said to be firmly established. To provide a firmer basis for these studies, [1-^{14}C]tetralin has been pyrolysed.

[1-^{14}C]Tetralin was prepared by cyclisation of [carboxy-^{14}C]phenylbutyric acid, followed by reduction of the [1-^{14}C]tetralone. The labelled tetralin was pyrolysed as previously described,[86] and the resulting tar separated

into its constituents by a combination of distillation,
chromatography on alumina, partition chromatography on
partially acetylated cellulose and gas-liquid
chromatography.

3.2   RESULTS AND DISCUSSION

Twenty-one compounds or their derivatives were
isolated from the tar in sufficient quantity and purity
for radiochemical analysis.   The activities were calculated
as relative molar activities which are linearly proportional
to the number of labelled carbon atoms per molecule.[192]
The results are summarised in Table 3.1, which lists all
the compounds isolated together with the number of labelled
carbon atoms found.   Other compounds formed in this
pyrolysis[86] could not be isolated in sufficient amount, or
in suitable purity, for radiochemical analysis.

By analogy with other compounds for which
determinations are available (Table 3.2), it seems likely
that the values of the dissociation energies (in kcal./mole)
for the carbon-carbon and carbon-hydrogen bonds in tetralin
(XXXIX) are approximately equal to the figures given in the
diagram (XLIII).   Since the 1,2- and 3,4-bonds in tetralin
are at least 15 kcal./mole weaker than normal aliphatic
carbon-carbon bonds,[202] the scission of one of these bonds
should be the first step of the pyrolysis.   This would

Table 3.1

CONSTITUENTS OF TAR OBTAINED BY PYROLYSIS OF $[1-^{14}C]$TETRALIN

Compound	Labelled C Atoms
Acenaphthene	1.35
Anthracene	0.84
1,2-Benzanthracene	1.61
Benzene	0.01
3,4-Benzofluoranthene	1.76
10,11-Benzofluoranthene	1.94
11,12-Benzofluoranthene	1.94
2,3-Benzofluorene	1.46, 1.52
3,4-Benzophenanthrene	1.44
3,4-Benzopyrene	1.96
1,1'-Binaphthyl	2.05
2,2'-Binaphthyl	2.04
Chrysene	1.67
Ethylene	0.27
Indene	0.70
Naphthalene	1.00
Perylene	1.91
Phenanthrene	0.84, 0.74
2-Phenylnaphthalene	0.95
Styrene	0.56
Toluene	0.32

Table 3.2

R-R' BOND DISSOCIATION ENERGIES OF HYDROCARBONS

R	R'	H Method	D(R-R') kcal./mole	Reference	CH$_3$ Method	D(R-R') kcal./mole	Reference	C$_2$H$_5$ Method	D(R-R') kcal./mole	Reference	n-C$_3$H$_7$ Method	D(R-R') kcal./mole	Reference	n-C$_4$H$_9$ Method	D(R-R') kcal./mole	Reference
C$_6$H$_5$-	α		102	103		89	103		91	130		88	130		87	130
						91	130									
C$_6$H$_5$CH$_2$-	α		77.5	104,105		63	199	α	57.5	200	α	65	201		57.5	130
	β		77	196					62	130		59	130			
	γ		88.1	197												
	α		85	198												
o-CH$_3$C$_6$H$_4$CH$_2$-	α		74	194		58	130		58	130						

Methods used: α pyrolysis

β electron impact

γ photobromination

result in a diradical (XLIV) whose further reactions could
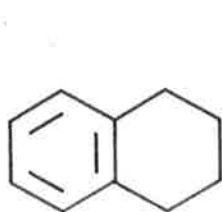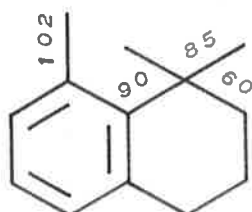

(XXXIX)   (XLIII)

be inferred from the products.   The diradical could
decompose in two competetive ways to give diradicals (XLV)
and (XLVI) as shown in (36) and (37).   Gordon and Smith[203]
have shown that hydrocarbon free radicals with a general
structure $R\dot{C}HCH_2CH_2R'$, where R, R' are alkyl groups or
hydrogen atoms, will eliminate a molecule of hydrogen at
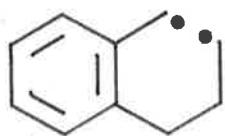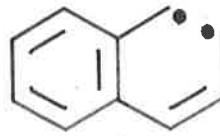a rate competetive with the breaking of a carbon-carbon bond.

$$CH_2=CH_2 \quad + \qquad\qquad (36)$$

(XLIV)   (XLV)

$$H_2 \quad + \qquad\qquad (37)$$
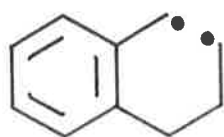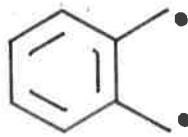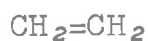
(XLIV)   (XLVI)

The diradical (XLVI) is resonance stabilised at each end

and its spatial configuration would favour cyclisation since both methylene groups are very close to each other. The 1,2-dihydronaphthalene (XLVIII) thus obtained would dehydrogenate under the experimental conditions to give naphthalene (XXII).

The same products could also be obtained by a different mechanism. The loss of a benzylic hydrogen atom from tetralin by (38) should be an endothermic

(XXXIX)   H +   (XLVII)   (38)
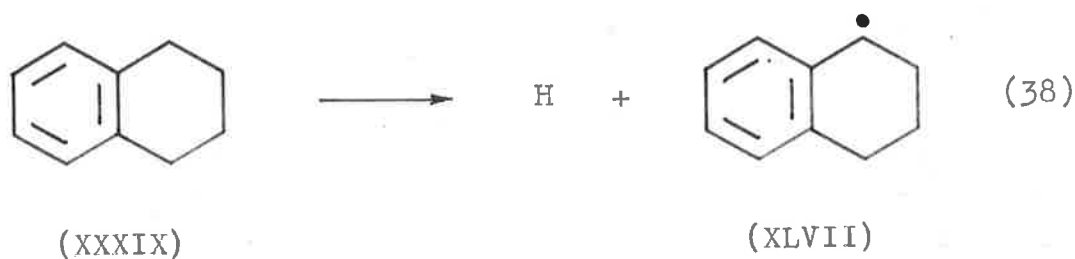
reaction requiring about 85 kcal./mole. The bond dissociation energy of the carbon-hydrogen bond adjacent to the free radical position in (XLVII) is very much lower, being approximately 37 kcal./mole,[204] and the formation of 1,2-dihydronaphthalene (XLVIII) by (39) would occur much more readily than the original carbon-hydrogen fission (38).

(XLVII)   H +   (XLVIII)   (39)
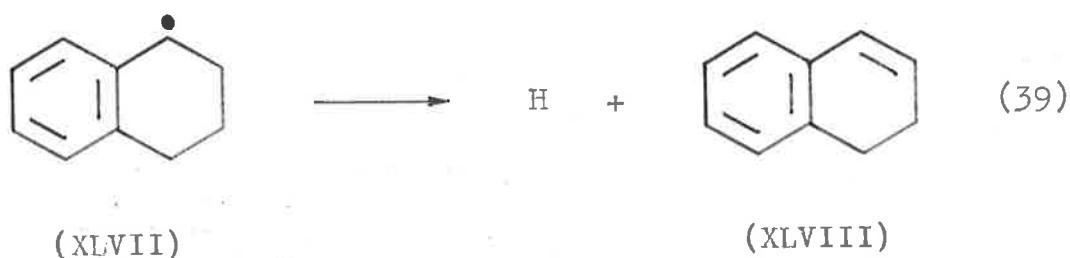
The hydrogen atom could act as a chain carrier (40), and

the overall process would probably require less energy than
the unimolecular decomposition of tetralin, discussed above.
Although both these mechanisms are in accord with the
activity found for naphthalene - the main product of the
pyrolysis - the second mode of formation seems to be
preferred on theoretical grounds.   That
1,2-dihydronaphthalene is an intermediate in the formation of
this compound is supported by the recent work of Wilshire,[205]

(XXXIX)   (XLVII)
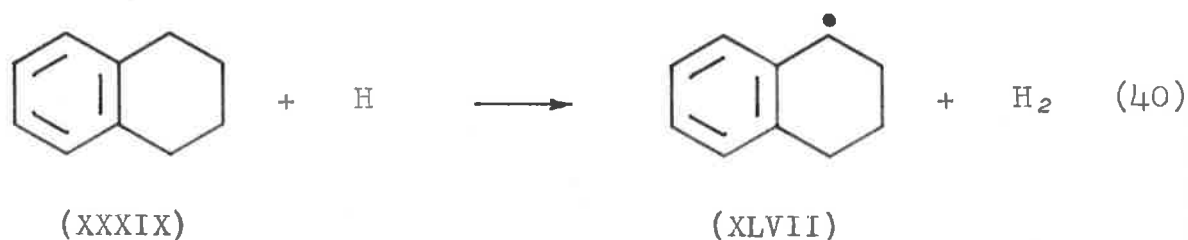
who pyrolysed tetralin at 650° and 700°C under slightly
milder conditions.   Thus in his experiments, tetralin was
recovered in 4.4% yield whereas under our conditions only
1.4% of the starting material was found.[66]   In his
pyrolysis a fraction which emerged slightly before
naphthalene in a gas-liquid chromatogram gave a peak which
could not be clearly separated from that of naphthalene,
and therefore could not be directly identified.   However,
its position in the gas chromatogram, and the fact that it
was formed in greater amount when tetralin was pyrolysed at
650°C, strongly suggested that it was in fact
1,2-dihydronaphthalene.[205]

As expected, the naphthalene isolated in our experiments was found to have radioactivity corresponding to one labelled carbon atom.

The pyrolysis of tetralin[66] yields 1,1'-, 1,2'-, and 2,2'-binaphthyls and the pyrolysis of naphthalene has been reported to give the same compounds,[74] suggesting that they may be formed by a similar mechanism. Further scission of a carbon-hydrogen bond in (XLVII) would give an α- or β-naphthyl radical and, as previously postulated,[86;101] combination of these radicals in the three possible ways would lead to 1,1'-binaphthyl (XLIX), 1,2'-binaphthyl (L), and 2,2'-binaphthyl (LI). Subsequent cyclodehydrogenation would give perylene (LII), 10,11-benzofluoranthene (VI), and 11,12-benzofluoranthene (LIII) (Figure 3.1).

It was found experimentally that 1,1'-binaphthyl, 2,2'-binaphthyl, perylene, 10,11-benzofluoranthene and 11,12-benzofluoranthene all had activity equivalent, within experimental error, to two labelled carbon atoms. These results therefore support the naphthyl radical hypothesis, and the mode of formation of these hydrocarbons seems to be beyond dispute.

The energy of activation for the breaking of an aliphatic carbon-carbon bond where an olefinic bond is simultaneously formed has been shown to be about 33 kcal./mole.[206] Thus the radical (XLVII) can decompose in two ways represented either by equation (39) or (41).
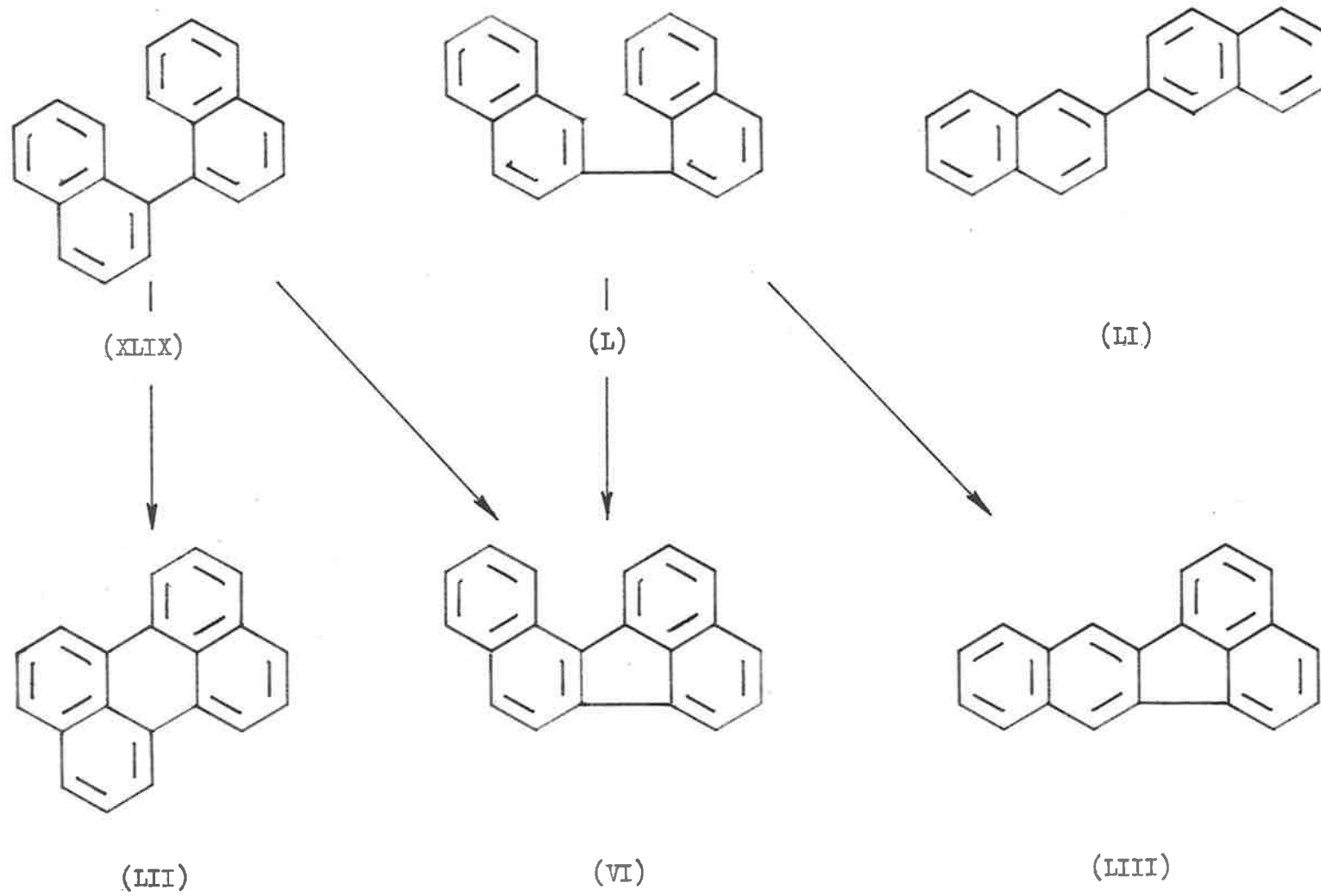
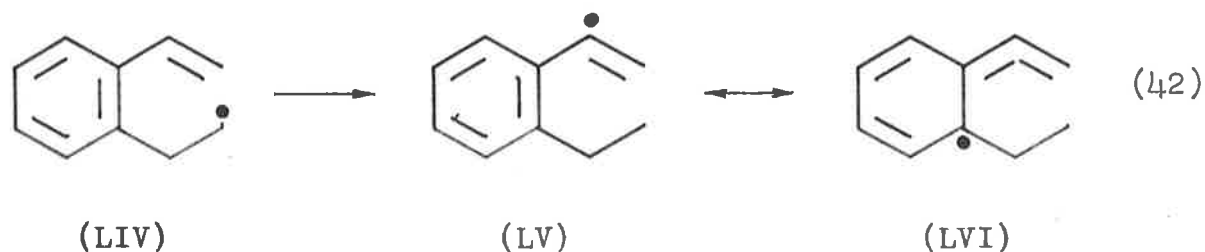(XLIX)   (L)   (LI)

(LII)   (VI)   (LIII)

Figure 3.1

The resulting radical (LIV) can isomerise by intraradical abstraction to give a new radical (LV) as shown in (42). This radical is also stabilised by resonance and as shown

(XLVII)   (LIV)   (41)

(LIV)   (LV)   (LVI)   (42)
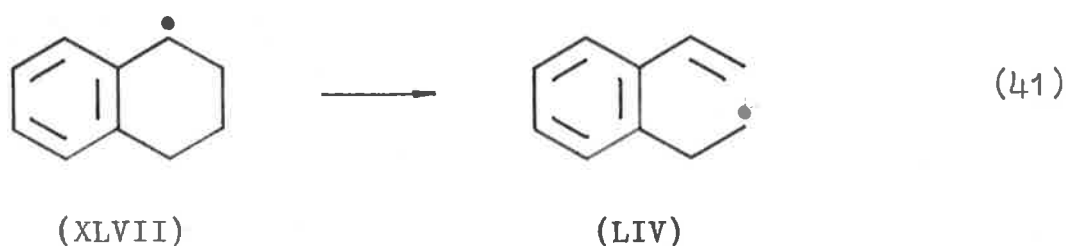
in (43), its other canonical form (LVI) may lose a methyl radical to give (LVII) which could be an important

(LVI)   (LVII)   (LVIII)   (43)
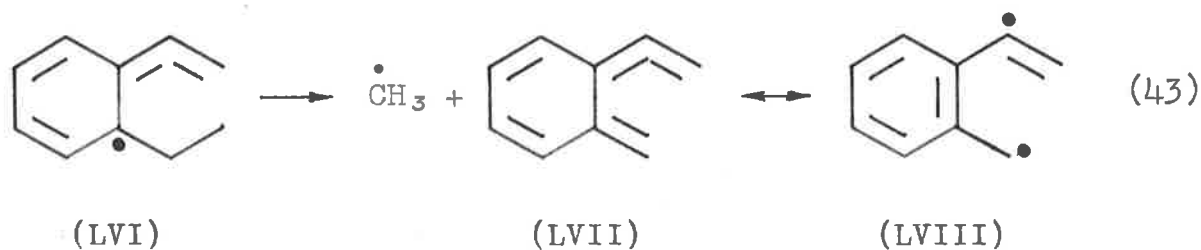
intermediate in the formation of indene, chrysene, 1,2-benzanthracene, 3,4-benzophenanthrene, and 1,2-, 2,3-, and 3,4-benzofluorenes if the resonance form (LVIII) is important.   The loss of ethylene from (LIV) would give another significant intermediate (LIX) as shown in (44).

(LIV) (LIX)
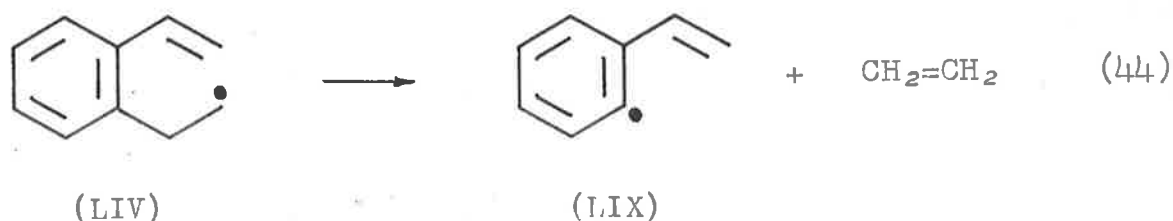
By a similar process, the diradical (XLIV) can presumably isomerise by intraradical abstraction to give radicals (LX) and (LXI) by equations (45) and (46). The

(XLIV) (LX) (45)

(XLIV) (LXI) (46)
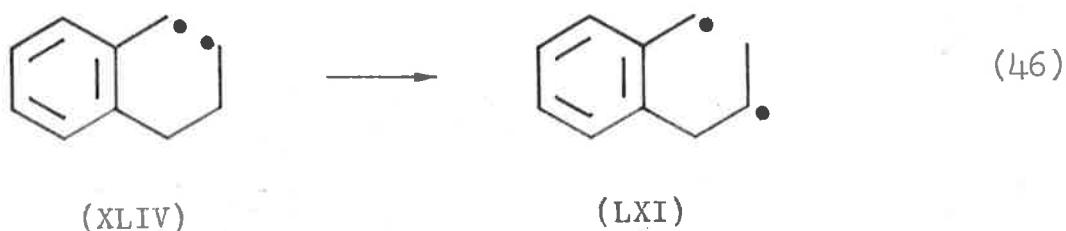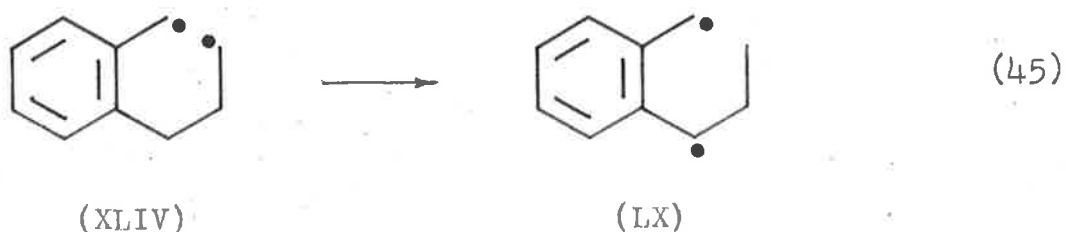
diradical (LX), also stabilised by resonance in each benzylic position, may lose a methyl radical to give (LXII) by equation (47), and the diradical (LXI) could lose a molecule of propylene to give (LXIII) by equation (48).

(LX) (LXII) + CH₃ (47)

(LXI)   (LXIII)   + $CH_3CH=CH_2$ (48)
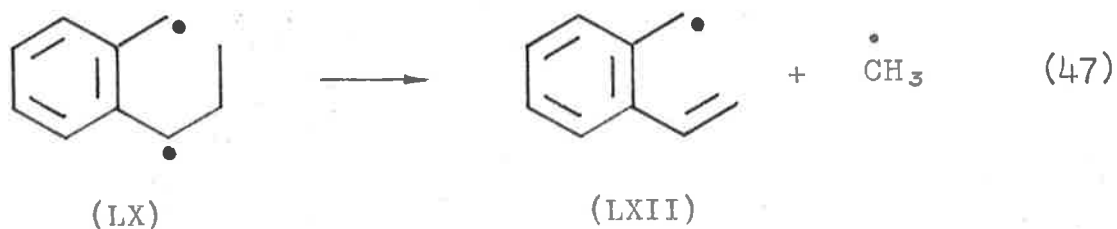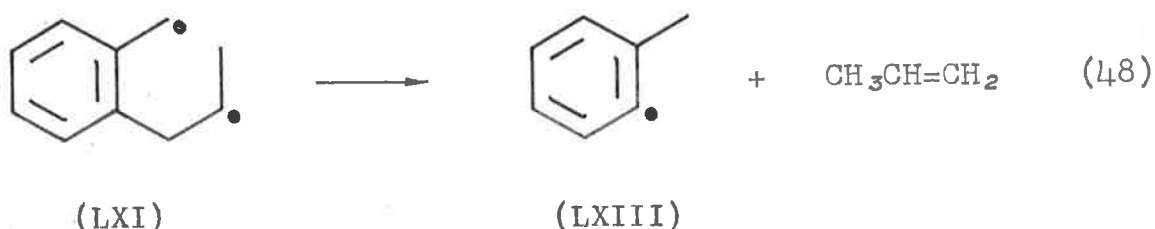
In a similar way, scission of the carbon-carbon bond
joining the α-carbon atom with the benzene nucleus must occur
at least to some extent to explain some of the experimental
results.   The diradical formed (LXIV) would undergo
fragmentation of the aliphatic chain in various ways to give
the intermediates (LIX) and (LXV-LXVII) by equations (49)-(53).
Figure 3.2 summarises all the possible pathways leading to
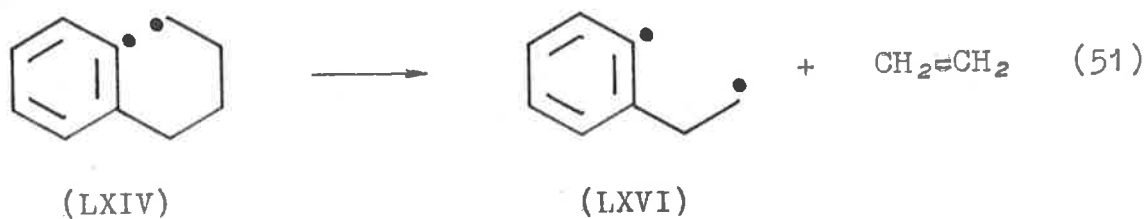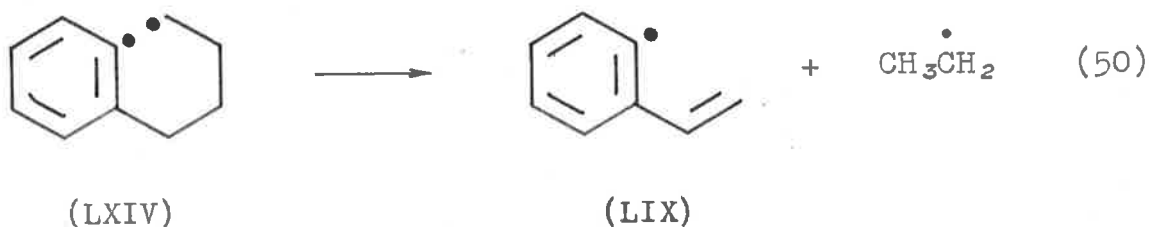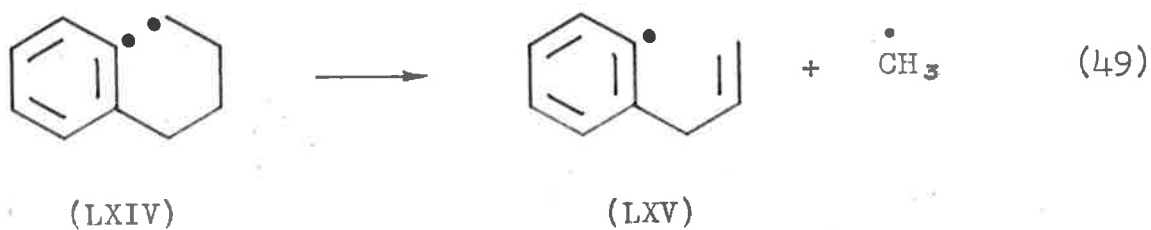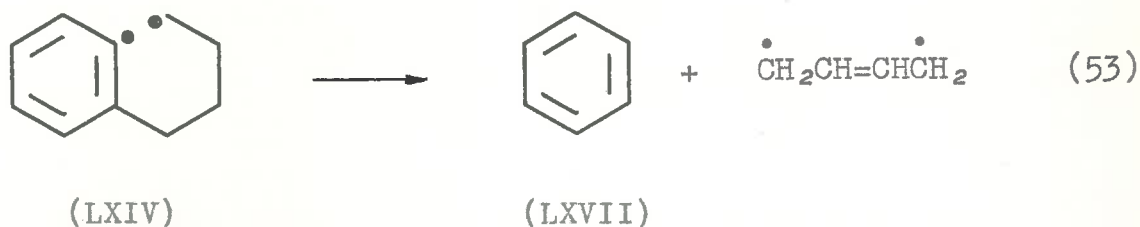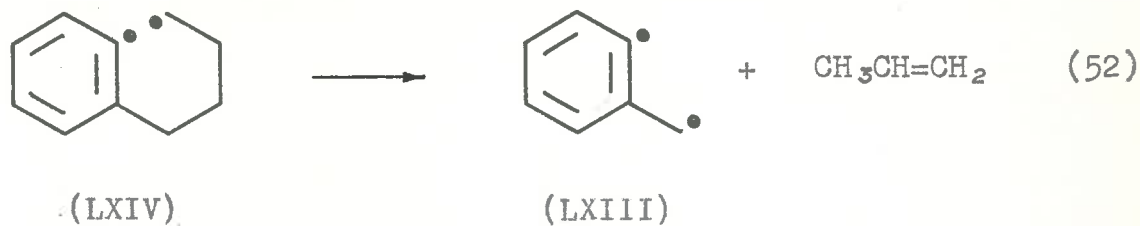
(LXIV)   (LXV)   + $\overset{\bullet}{C}H_3$ (49)

(LXIV)   (LIX)   + $CH_3\overset{\bullet}{C}H_2$ (50)

(LXIV)   (LXVI)   + $CH_2=CH_2$ (51)

(LXIV)   (LXIII)

$$\text{(LXIV)} \longrightarrow \text{(LXIII)} + CH_3CH=CH_2 \qquad (52)$$

(LXIV)   (LXVII)

$$\text{(LXIV)} \longrightarrow \text{(LXVII)} + CH_2CH=CHCH_2 \qquad (53)$$

the more important intermediates together with the expected activities of the fragments. Figure 3.3 surveys the activities of the aliphatic portions obtained in these reactions.

In accordance with the above mechanisms, the benzene formed in this pyrolysis was found to be practically inactive. This underlines the relative unimportance of the reaction path C (Figure 3.2, page 58). In the same way, the styrene isolated was found to contain 0.56 labelled carbon atoms and the intermediate (LIX), with an activity equivalent to 0.5 active atoms, could account for all the styrene formed.

The intramolecular cyclisation of the intermediates (LXII) and (LXV) would give the radicals (LXVIII) and (LXIX), which could either accept hydrogen to give hydrindene (LXX) or lose hydrogen to give indene (LXXI). The former hydrocarbon was not isolated from the tar obtained by the

Figure 3.2

[(XXXIX); 1*C]

A   B   C

[(XLIV); 1*C]   [(XLVII); 1*C]   [(LXIV); 1*C]

(36)   (48)   (47)   (41)   (50)   (49)   (52)

CH_2CH_2 CH_3 CH_3CH_2 CH_3 $CH_3CH=CH_2$

[0*C]   [0*C]   [(LIV); 1*C]   [0.5*C]   [0.5*C]   [0.5*C]

(43)   (44)   (53)   (51)

$CH_3CH=CH_2$ CH_3 CH_2CH_2 $CH_2=CHCH=CH_2$ CH_2CH_2

[0.5*C]   [0*C]   [0.5*C]   [1*C]   [0.5*C]
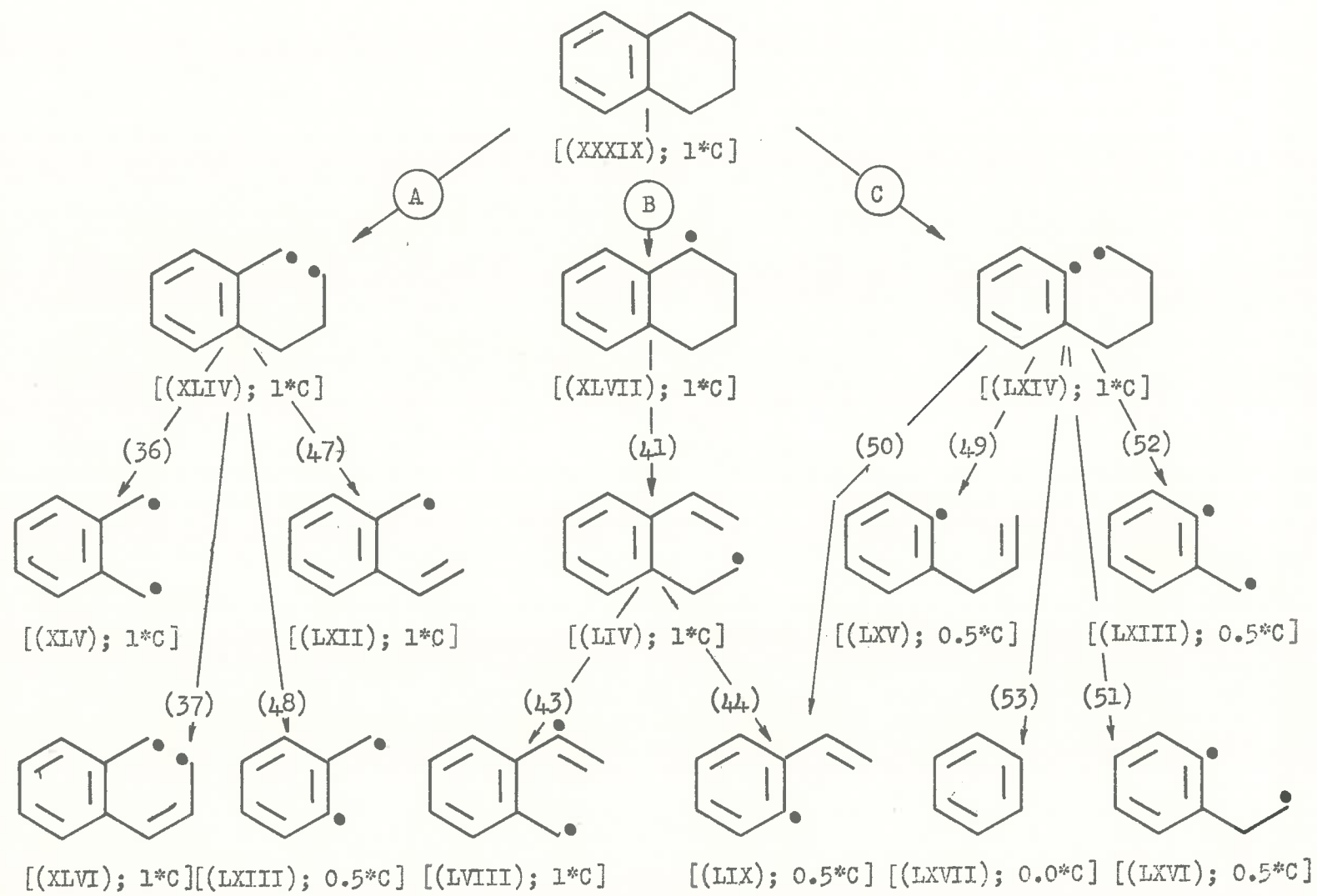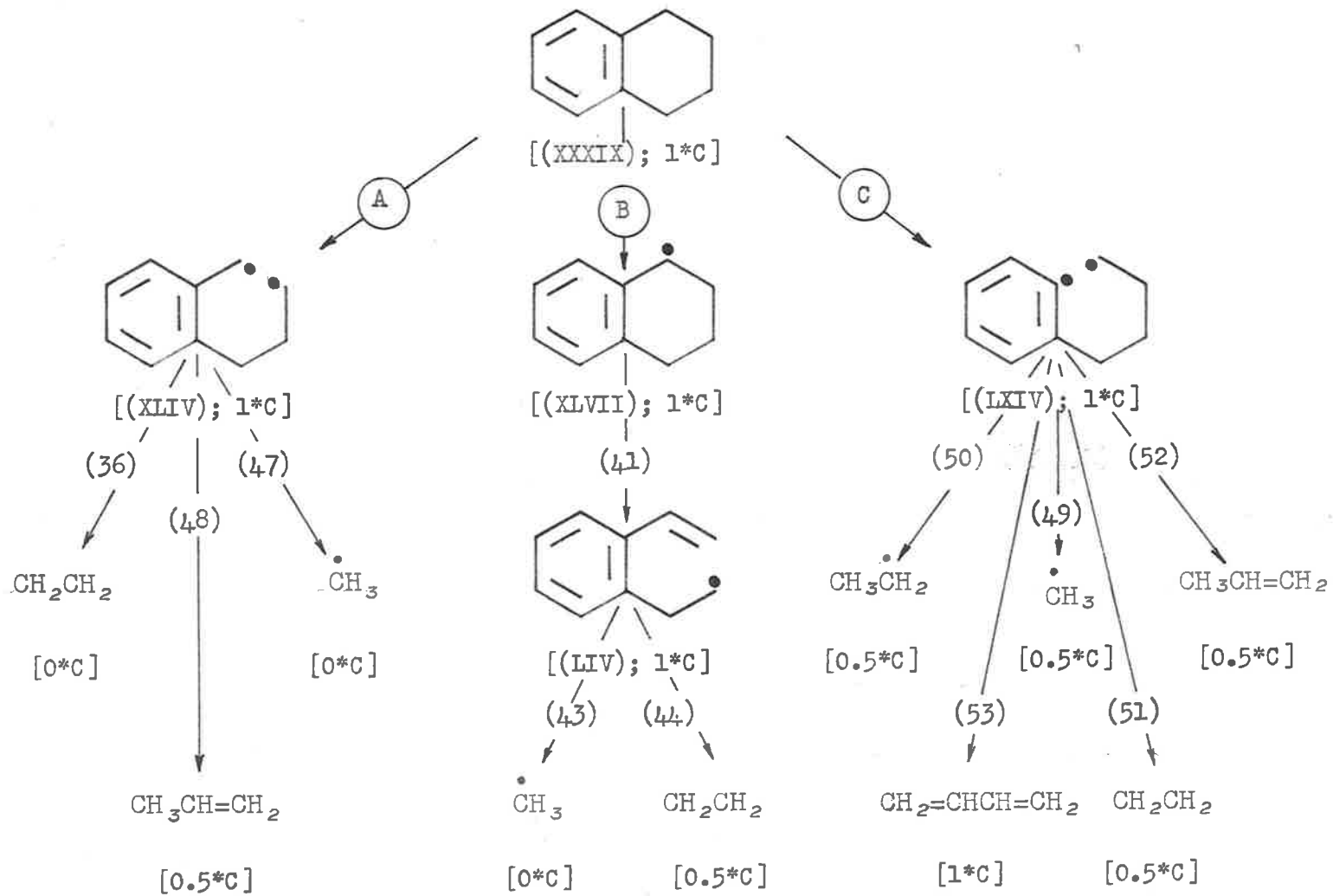
<u>Figure 3.3</u>

pyrolysis under discussion, but its presence was detected
under the milder conditions from Wilshire's pyrolysis.[205]
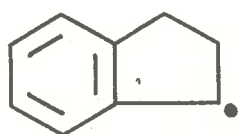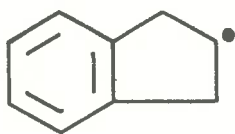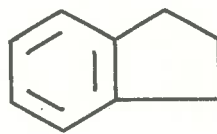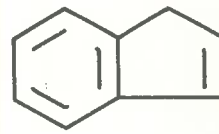
(LXVIII)   (LXIX)   (LXX)   (LXXI)

Indene, one of the major products of the pyrolysis, would be
expected to have 0.75 labelled carbon atoms according to
the above scheme, and this was borne out by the fact that
experimentally, the indene was found to have 0.70 labelled
atoms.

Toluene formed directly from the intermediate (LXIII)
would have an activity of 0.5 labelled carbon atoms.   The
figure found experimentally is lower than this (0.32) and
hence some toluene must be formed from phenyl radicals or
benzene and from methyl radicals derived from the saturated
ring in tetralin.   The benzene found was practically
inactive, and methyl radicals which are generated according
to the scheme proposed (Figure 3.3, page 59) by path A in the
formation of (LXII) and by path B in the formation of (LVIII)
would also be expected to be inactive.   Some methyl
radicals, which could be obtained in the formation of (LXV)
by path C would, however, be active to an extent of
0.5 labelled carbon atoms, but as already mentioned, this

reaction path would be of smaller importance.   Thus by assuming that about a third of the toluene formed would originate by this mechanism, the activity of toluene could be effectively accounted for.

Acenaphthene (XXV) was not isolated from the tar obtained in the earlier pyrolysis of tetralin[66] but acenaphthylene (LXXII) which is believed to be formed from this compound on dehydrogenation at the high temperatures involved, is found in tars obtained following pyrolysis of many simple hydrocarbons.   The most reasonable mechanism
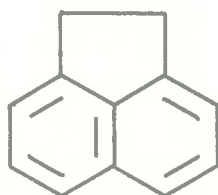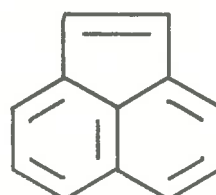
(XXV)   (LXXII)

for its formation would seem to be the addition of ethylene to a naphthyl radical in the α-position, followed by cyclisation with the elimination of one molecule of hydrogen (54).   The ethylene formed by scission of carbon-carbon bonds would be expected to have an average
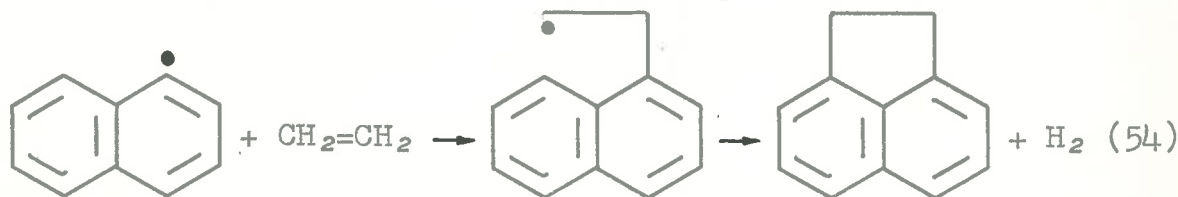
activity of 0.33 labelled atoms (Figure 3.3, page 59), so that the isolated acenaphthene on this basis should have 1.33 labelled atoms. Experimentally, the acenaphthene was found to have 1.35 labelled atoms thus suggesting that the mechanism is correct. The ethylene present in the exit gases was found to have 0.27 labelled atoms. Within the limits of experimental error, this is in agreement with the expected activity for ethylene, namely 0.33 labelled carbon atoms.

Two reasonable mechanisms can be suggested for the formation of 2-phenylnaphthalene (XXXIV) in this pyrolysis. The first would involve an attack of a phenyl radical on a naphthalene precursor, and the second would involve the dimerisation of two styryl radicals or their equivalent.[84] The addition of styrene to (LIX) appears to be a possible way of obtaining 2-phenylnaphthalene (LXXIII) in this pyrolysis (55). Both mechanisms would be expected to yield

(55)

(LXXIII)
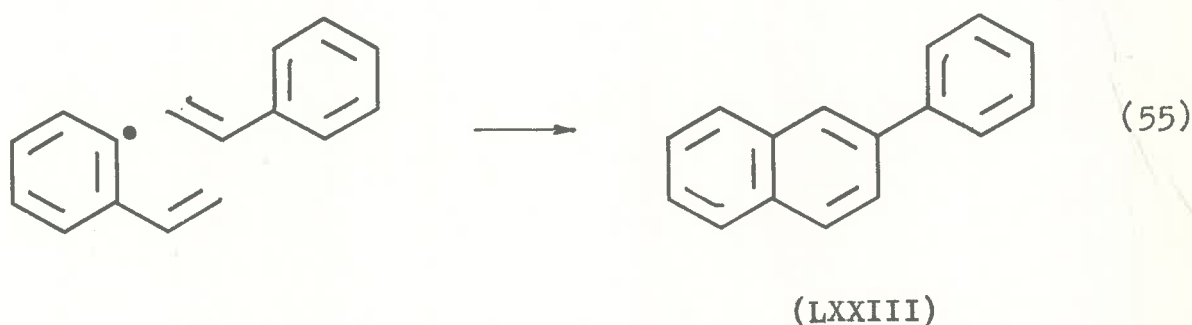
a product with an average activity of 1.0 labelled carbon atom, and experimentally 0.95 labelled atoms were found. It is,

therefore, impossible to decide between these two routes on the basis of the present activity studies. On the other hand, if the mechanism involving a direct phenylation of naphthalene is important, the formation of 1-phenylnaphthalene (LXXIV) and hence fluoranthene (LXXV) by cyclodehydrogenation would also be expected unless isomerisation of 1- to 2-phenylnaphthalene occurred to a significant extent. Experimentally, it was shown that much less fluoranthene than 2-phenylnaphthalene is formed. Thus a direct phenylation of naphthalene followed by cyclodehydrogenation of the resulting 1-phenylnaphthalene could not be an important process in the formation of fluoranthene, and is unlikely to be of any importance even in the formation of 2-phenylnaphthalene. This is in agreement with the results obtained from the pyrolysis of 1-phenylnaphthalene at 700°C, where it was shown[207] that fluoranthene is formed only in trace amounts.

(LXXIV)   (LXXV)
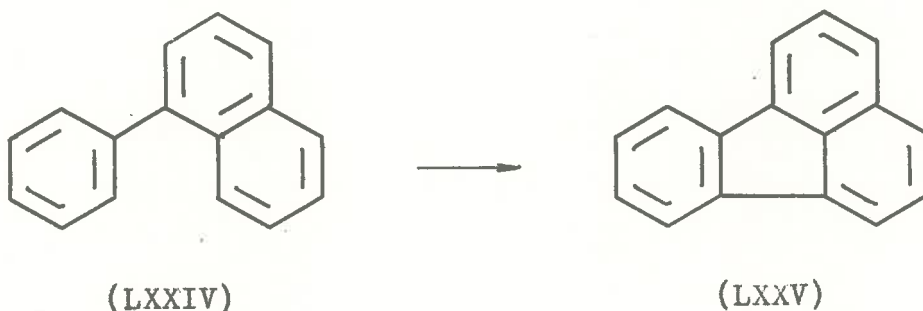
Chrysene (XI) and 1,2-benzanthracene (VII) are known to be formed from indene at high temperatures[88] and this fact may explain, at least to some extent, their

presence in other pyrolytic tars where indene is formed as a major product. To account for this, Wilshire[205] pyrolysed hydrindene (LXX) at 700°C in an attempt to trace any possible intermediates in the formation of these compounds. Indene (LXXI) was the major product (54.6%) together with toluene (6.1%) and benzene (0.87%), and the high boiling residue, formed in 13.4% yield, contained chrysene, 1,2-benzanthracene and a trace of naphthacene (LXXVI). Although the conditions of the experiment were
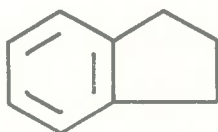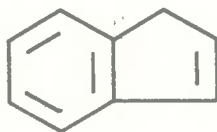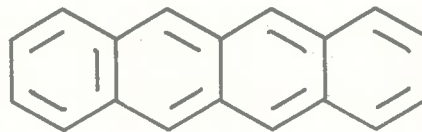
(LXX)   (LXXI)   (LXXVI)

mild enough to allow recovery of 25% of the starting material, no products such as o-methylstyrene which could be related to possible radical intermediates were detected. As a result of this experiment, Wilshire concluded that the formation of chrysene and of 1,2-benzanthracene does not require fission of the five-membered ring of indene.

The first step in his proposed mechanism for the formation of chrysene requires the attack of a 1-indenyl radical at the 2-position of another molecule of indene to give the radical intermediate (LXXVII). Intramolecular cyclisation involving the remaining 2-indenyl position leads

to a radical (LXXVIII).   This highly unstable intermediate,
a substituted 1,3-diphenylcyclobutane, would be expected to
undergo decomposition in two competetive ways based on the
direction of the collapse of the cyclobutane ring, namely
decomposition, as shown by the arrows in (LXXVIII) leading
to the aromatic diolefin (LXXIX), or the alternative mode
of ring collapse to regenerate two molecules of indene.
Thermal cleavage of the cyclobutane ring containing activated
substituents is known to occur at temperatures as low as
450°C.[206]   The diolefin (LXXIX) would not survive at 700°C
and its most obvious reaction would be its conversion to
chrysene (XI), presumably _via_ transannular interaction of the
diradical formed by the loss of hydrogen from the benzylic
positions, followed by dehydrogenation.
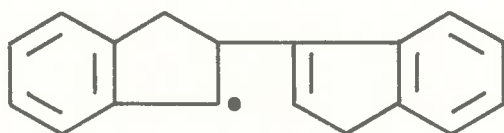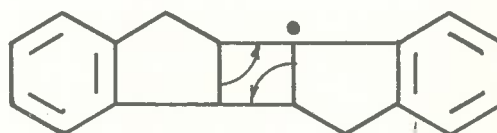
(LXXVII)   (LXXVIII)
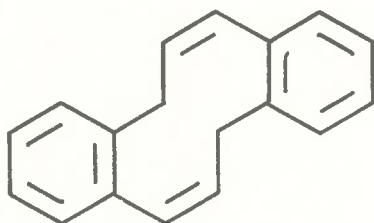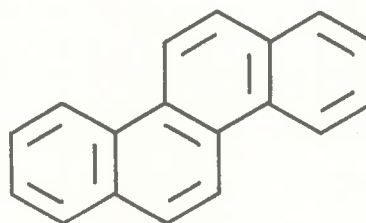
(LXXIX)   (XI)

The formation of 1,2,benzanthracene can be explained

by a similar mechanism the first step of which involves
the attack of an 2-indenyl radical at the 2-position of
another indene molecule, with the formation of the radical
(LXXX), and eventually the diolefin (LXXXI).   The fact
that the 2-indenyl radical requires more energy for its
formation than the 1-isomer, is reflected in the lower
proportion of 1,2-benzanthracene.

(LXXX)   (LXXXI)
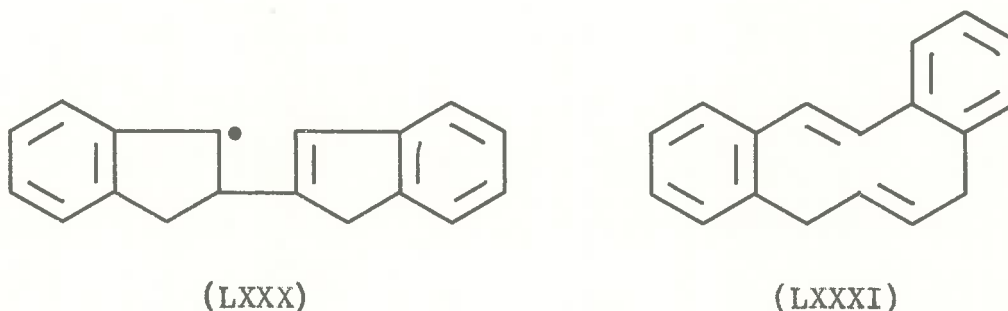
A similar scheme cannot, however, account for the
formation of 3,4-benzophenanthrene (XXIX) without the
participation of some rearrangement step as yet uncertain.[205]

(XXIX)
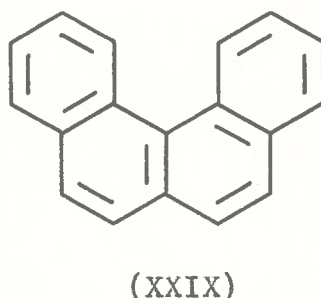
If these were the only mechanisms in the formation of
chrysene and 1,2-benzanthracene, the activities of these
compounds should amount to twice the activity of indene.

In fact, the activities found in both products are higher than this.   There is no reason to discard the possibility of the existence of this reaction path, but as indene is formed on cyclisation of one of the intermediates suggested in Figure 3.2, page 58, these fragments may combine directly to form the required products.   Thus chrysene may be formed from two C_6-C_3 units (LXXXII) or from a C_6-C_4 and a C_6-C_2 unit (LXXXIII) or from two C_1-C_6-C_2 units (LXXXIV). Suitable intermediates would be (LXV) for a C_6-C_3 unit, (XLIV), (XLVI), (LXIV) or (LIV) for a C_6-C_4 unit, (LIX) and (LXVI) for a C_6-C_2 unit and (LVIII) or (LXII) for a C_1-C_6-C_2 unit.   If only one mechanism is involved, one would expect
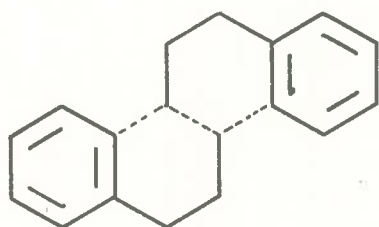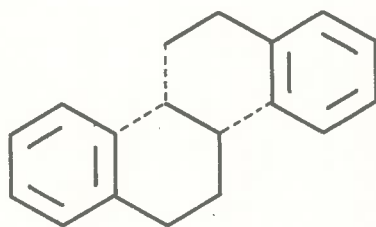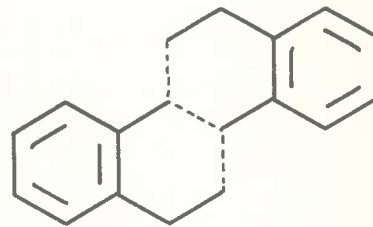
(LXXXII)   (LXXXIII)   (LXXXIV)

the chrysene formed to have 1.0 labelled atoms (LXXXII), 1.5 labelled atoms (LXXXIII) and 2.0 labelled atoms (LXXXIV), or 1.67 labelled atoms if formed entirely and in equal amounts from fragments (LVIII), (LXII) and (LXV), the only intermediates which could give rise to the formation of indene.   As the isolated chrysene was found to have 1.67 labelled atoms, it is possible that the last mentioned

reaction path could be the only mechanism operating.
However, the activity of indene would then be expected to be
0.83 labelled atoms and experimentally it was found to be
equivalent to 0.70 active carbon atoms.   It is hoped to
settle this problem by pyrolysis of suitably labelled indene
and successfully degrading the products formed.

1,2-Benzanthracene could be formed in a similar way
from a C_1-C_6-C_2 unit and a C_6-C_3 unit (LXXXV), which would
give the hydrocarbon with 1.5 labelled atoms.   Alternatively,
it could be formed from a C_6-C_4 unit and a C_6-C_2 unit (LXXXVI),
or from two C_1-C_6-C_2 units (LXXXVII), yielding
1,2-benzanthracene with 1.5 and 2.0 labelled carbon atoms
respectively.   It could also arise from two molecules of
indene by the procedure previously described, with the
expected activity of 1.67 labelled atoms.   As the isolated
hydrocarbon was found to have an activity equivalent to 1.61
active carbon atoms, it is impossible from the present work
to decide between these mechanisms.

(LXXXV)   (LXXXVI)   (LXXXVII)
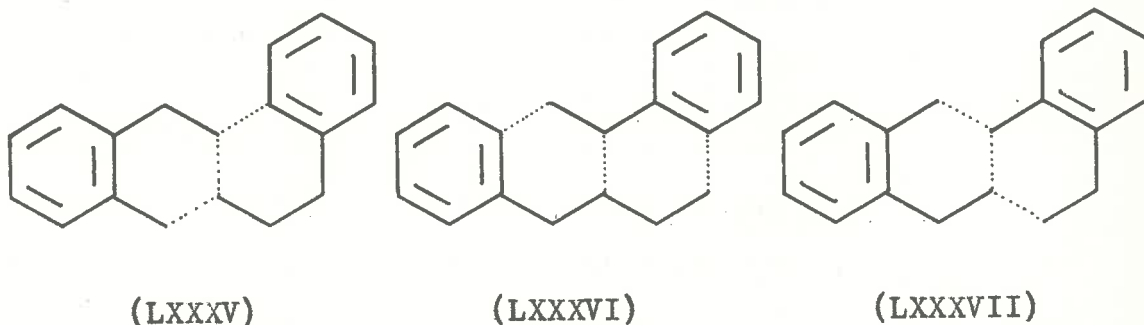
In a similar manner, 3,4-benzophenanthrene (XXIX)

could be formed with an expected activity of 1.5 labelled

atoms from a $C_1-C_6-C_3$ unit and a C_6-C_2 unit (LXXXVIII) or

with an activity of 2.0 labelled atoms from either a

$C_1-C_6-C_2$ unit and a C_6-C_3 unit (LXXXIX), or from $C_1-C_6-C_1$ and

C_6-C_4 units (XC).   The 3,4,benzophenanthrene isolated from
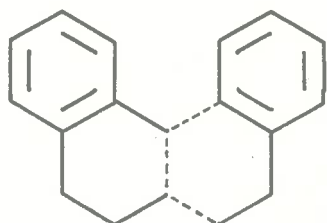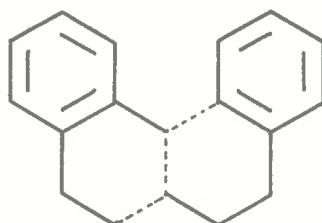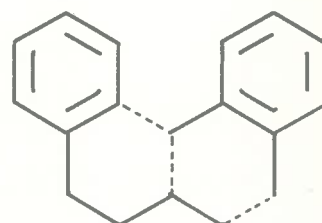
       (LXXXVIII)   (LXXXIX)   (XC)

the [$1-^{14}C$]tetralin tar had 1.44 labelled carbon atoms,

indicating that the route depicted by (XC) is less

significant.   This is supported by the finding that

although 3,4-benzophenanthrene was isolated only in tars

obtained following the pyrolysis of indene and tetralin, the

yield of this hydrocarbon in the indene tar was more than

twice that found in the tetralin tar.

       Indene can also be suggested as a possible precursor

of 1,2-, 2,3- and 3,4-benzofluorenes - hydrocarbons which are

formed in their highest yields in the tars obtained following

pyrolysis of indene[88] and to a smaller extent in other

pyrolyses.[209]   This seems to indicate that the primary

radicals which give rise to indene on one hand, or are

obtained by the thermal decomposition of indene on the

other, must play an important part in the formation of these hydrocarbons. Thus a reaction involving a C_6-C_2 unit and a $C_1-C_6-C_2$ unit (XCI) would give 2,3-benzofluorene (the only hydrocarbon of the above group which could be isolated in the present pyrolysis in sufficient quantity and purity for radiochemical assay) having 1.5 labelled atoms. Formation from C_6-C_2 and C_6-C_3 units (XCII) would give 2,3-benzofluorene having 1.0 labelled atoms, whereas formation from a $C_1-C_6-C_1$ unit and a $C_2-C_6-C_1$ unit (XCIII) would give 2,3-benzofluorene having 2.0 labelled atoms. In addition, three similar mechanisms can be postulated which
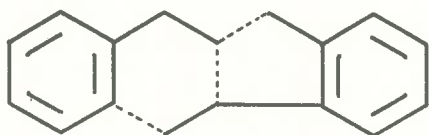
(XCI)
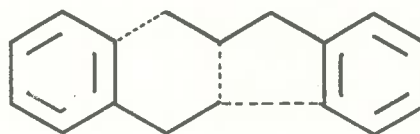
(XCII)
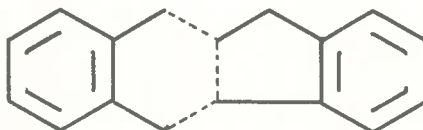
(XCIII)

involve primary radicals derived from tetralin, but not from indene, all of which would give the hydrocarbon with 1.5 labelled atoms (XCIV-XCVI). At present it seems likely that all these routes may be involved.
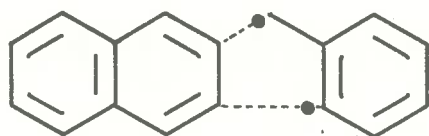
(XCIV)   (XCV)

(XCVI)

In the pyrolysis of $[g\text{-}^{14}C]$ethylbenzene,[94] evidence was adduced that phenanthrene (XXIII) must be largely formed by the attack of a phenyl radical on a $C_6\text{-}C_2$ unit such as styrene, followed by cyclodehydrogenation.   The affinity of phenyl radicals for styrene appears to be very high as the yields of phenanthrene are considerably higher than those of styrene in the pyrolysis of ethyl- and n-butylbenzene.[90]   A small yield of benzene and phenanthrene in the pyrolysis of active tetralin suggests that this reaction is of general importance.   According to the scheme shown below (55) and (56), the phenanthrene

(LXIII)   (XCVII)   (XXIII) $+$ H_2 (55)

(56)

(LXIII)   (XCVIII)   (XXIV)
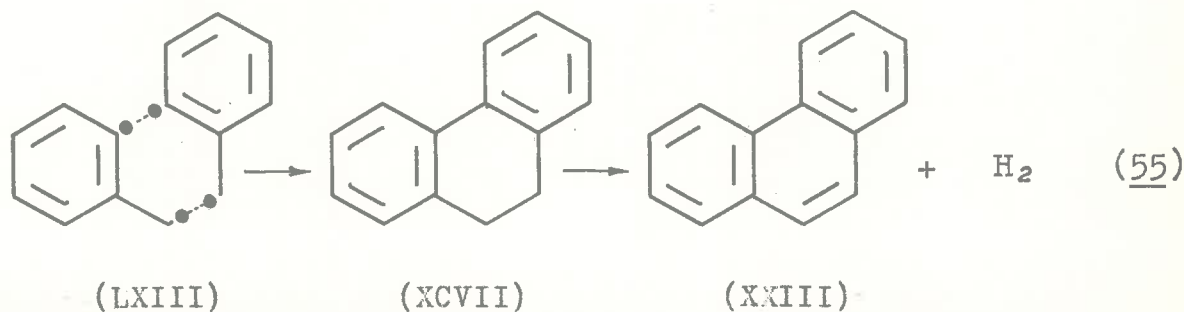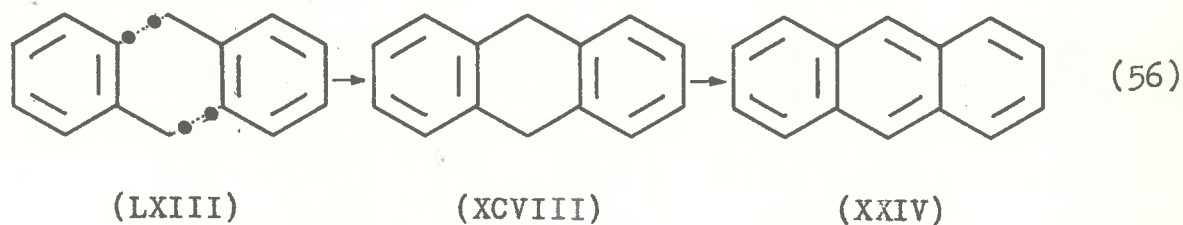
isolated should have an activity of 0.5 labelled atoms, but was found experimentally to possess an activity equivalent to ca. 0.8 active atoms.   The dimerisation of (LXIII) would give either 9,10-dihydrophenanthrene (XCVII) or 9,10-dihydroanthracene (XCVIII).   On a loss of one molecule of hydrogen, phenanthrene (XXIII) and anthracene (XXIV), each having 1.0 labelled atoms, would be obtained from these products.   The observed results and activity for phenanthrene, 0.8 active carbon atoms, can therefore be accommodated if both mechanisms operate.

The anthracene (XXIV) was also found to have 0.84 labelled atoms.   The possibility of its formation by rearrangement of phenanthrene[210] had to be rejected as a result of recent data obtained from the pyrolysis of phenanthrene,[97] and the addition of a C_4 unit to a naphthalene type intermediate seems to be unlikely. However, the addition of a phenyl radical to (XLV), or dimerisation of two intermediates as in (LXIII), would give radical (XCIX) or 9,10-dihydroanthracene (XCVIII) respectively. The radical (XCIX) would eventually yield anthracene by cyclodehydrogenation.   This path to anthracene has an

analogy in the work of Errede and Cassidy,[211] who subjected
o-methyldiphenylmethane to a fast flow pyrolysis and
obtained anthracene in good yield.

(XCIX)   (XXIV)
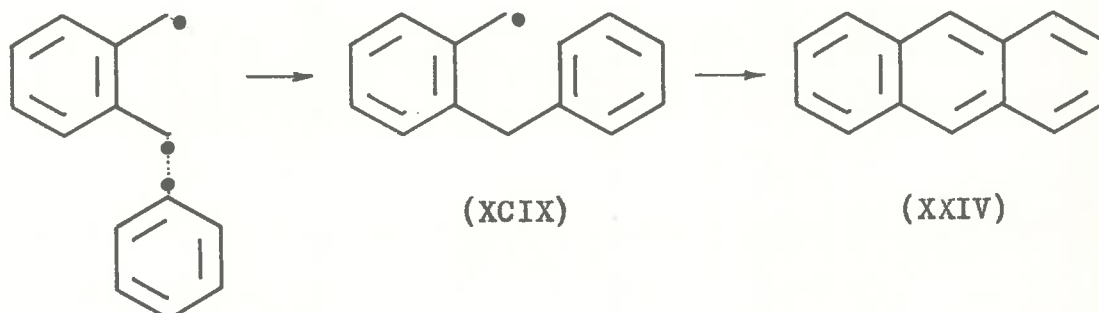
The pyrolysis of [α-14C]ethylbenzene[94] gave
3,4-benzofluoranthene (V) having one labelled carbon atom.
This result provided strong evidence for a mechanism
involving phenylation of phenanthrene, itself formed from
phenyl radicals and a C_6-C_2 unit such as styrene.
However, the yield of phenanthrene in the pyrolysis of
tetralin is small (0.15% of the tar) and it seems unlikely
that this mechanism is important in this case.   The
phenanthrene obtained from the pyrolysis of [1-14C]tetralin
was found to have 0.8 labelled atoms, and if the above
mechanism does operate, the derived 3,4-benzofluoranthene
should also have 0.8 labelled atoms.   In fact, however,
this hydrocarbon, when obtained from [1-14C]tetralin, was
found to have ca. 1.76 labelled atoms, and another process
must be operating.   The formation of 3,4-benzofluoranthene
from two C_6-C_4 units (C) would certainly be of much more
importance in the pyrolysis of tetralin than in the pyrolysis

of ethylbenzene.   This route would lead to
3,4-benzofluoranthene having 2.0 labelled atoms.   The
results can again be accommodated if it is assumed that
both mechanisms operate, the latter predominating.

(C)   (V)
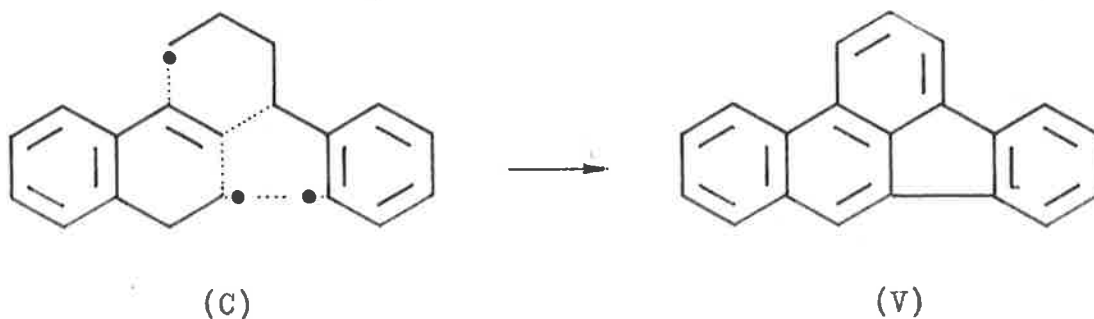
The formation of 3,4-benzopyrene (I) from two C_6-C_4
units (CI) has also been postulated,[86] and considerable
evidence is now available concerning the importance of this
process in the pyrolysis of simpler hydrocarbons.
3,4-Benzopyrene formed by such a mechanism would have an
activity of 2.0 labelled carbon atoms.   Actually, the
product isolated was found to have 1.96 labelled atoms so
that the suggested mechanism must provide the main route to
this hydrocarbon.

(CI)   (I)
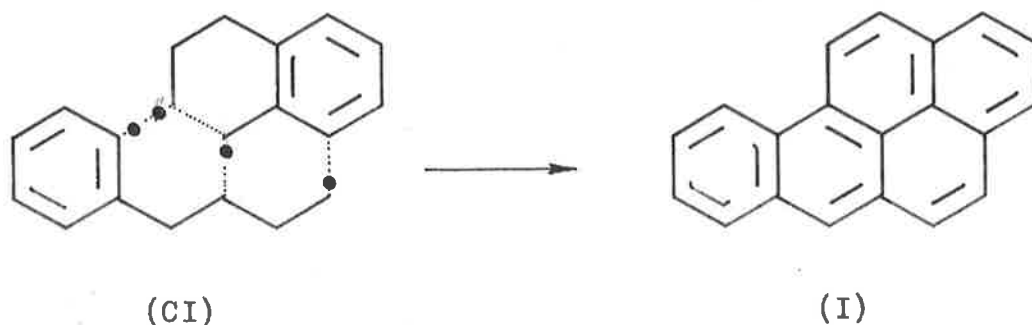
The observed activity could also be explained by
assuming that the formation of 3,4-benzopyrene (I) takes
place by an attack of (LXIII) or a benzyl radical on a
phenalenyl (perinaphthenyl) radical (CII), followed by
cyclodehydrogenation.   Both benzyl and perinaphthenyl
radicals were shown to be formed during the pyrolysis of
hydrocarbons,[212] and their apparent stability may be another

(CII)   (I)
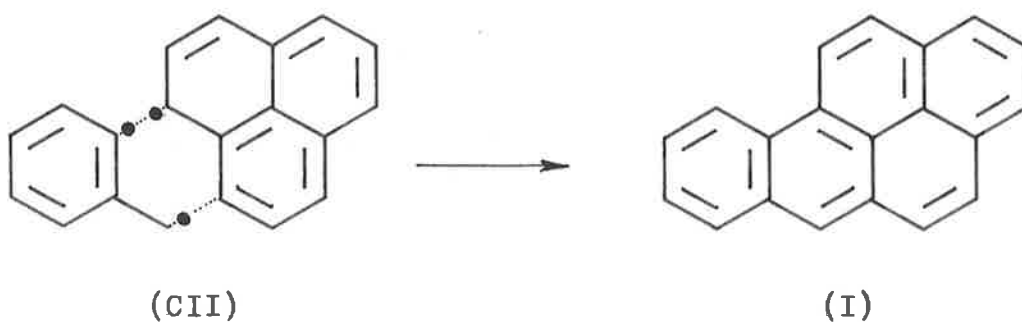
significant factor in an assessment of their importance in
the formation of 3,4-benzopyrene.

CHAPTER 4

THE PYROLYSIS OF n-DECANE

4.1   INTRODUCTION

The original hypothesis proposed for the formation of the carcinogen 3,4-benzopyrene (I) in pyrolytic reactions suggested that this hydrocarbon might be formed by a stepwise synthesis from a two-carbon unit such as ethylene or acetylene (Chapter 2, page 41).   It also allowed for the possibility that complex hydrocarbons need not necessarily break down to two-carbon fragments before resynthesis, and that the C_2-C_4 units required for the formation of 3,4-benzopyrene could arise by cyclisation of a C_{10} hydrocarbon such as n-decane or from a higher hydrocarbon such as dicetyl, by cracking followed by cyclisation.   The pyrolysis of n-decane over a chromia-alumina catalyst[2,3] gave benzene, toluene, ethylbenzene, o-xylene, propylbenzene, butylbenzene and naphthalene; and 3,4-benzopyrene was formed in the pyrolysis of dicetyl,[69] and of the waxy paraffins found in tobacco leaf.[70]   The present pyrolysis was carried out to establish to what extent carcinogenic hydrocarbons are formed at high temperatures from a straight chain alkane, such as n-decane.

4.2   RESULTS AND DISCUSSION

The pyrolysis was carried out by passing the n-decane vapour, in a stream of nitrogen through a silica tube packed with porcelain chips and maintained at 700°C. Methane, ethylene, acetylene, propylene and but-1-ene were detected in the exit gases.   The tar (obtained in 13.9% yield) was collected and analysed as previously described. The various compounds identified are summarised in Table 4.1, which also gives the percentage of each component of the tar, and the methods used for its identification.

Table 4.1

COMPOSITION OF TAR OBTAINED BY PYROLYSIS OF n-DECANE AT 700°C

Fraction	Compound	Percentage in Tar	Method of Identification *
-	Methane	-	I.R.
-	Ethylene	-	I.R., dibromo derivative
-	Propylene	-	I.R., dibromo derivative
-	But-1-ene	-	I.R., dibromo derivative
-	Acetylene	-	I.R.
a	Butane	0.04	R.T.
a	Pentane	0.06	R.T.
a	Hexane	0.06	R.T.
a,b	Cyclohexane	0.29	R.T.
a,b,c	Benzene	43.9	R.T., I.R., U.V.

Table 4.1   (Continued)

Fraction	Compound	Percentage in Tar	Method of Identification[*]
a,b,c	Toluene	13.8	R.T., I.R., U.V.
c	p- and m-Xylene	1.95	R.T., I.R.
c	Styrene	6.86	R.T., I.R.
c	α-Methylstyrene	1.25	R.T., I.R.
c,2	Indene	1.48	R.T., I.R., U.V.
c,2,3	Tetralin	1.37	R.T., I.R.
c,2-4	Naphthalene	13.2	R.T., U.V., mixed m.p.
c,2,3	1- and 2-Methylnaphthalene	4.30	R.T., U.V.
2,3	Biphenyl	2.04	R.T., U.V., mixed m.p.
3	Diphenylmethane	0.94	R.T., I.R.
3	Bibenzyl	0.42	R.T.
3-7	Acenaphthylene	1.33	U.V.
5-9	Fluorene	0.73	U.V.
5-7	2-Phenylnaphthalene	0.23	U.V.
5-10	Phenanthrene	1.86	U.V., mixed m.p.
5-10	Anthracene	0.04	U.V.
8-25	Pyrene	0.90	U.V., mixed m.p.
10-26	Fluoranthene	0.53	U.V., mixed m.p.
25-30	2,2'-Binaphthyl	0.17	U.V.
25-35	1,2-Benzanthracene	0.02	U.V.
25-35	Triphenylene	0.05	U.V.
25-35	1,2-Benzofluorene	0.20	U.V.

Table 4.1 (Continued)

Fraction	Compound	Percentage in Tar	Method of Identification*
25-35	3,4-Benzofluorene	0.09	U.V.
25-39	2,3-Benzofluorene	0.29	U.V.
31-39	Chrysene	0.53	U.V., mixed m.p.
36-39	10,11-Benzofluoranthene	0.017	U.V.
36-59	1,2-Benzopyrene	0.122	U.V., mixed m.p.
36-59	3,4-Benzopyrene	0.108	U.V., mixed m.p.
40-48	Perylene	0.015	U.V.
40-59	3,4-Benzofluoranthene	0.032	U.V., mixed m.p.
40-59	11,12-Benzofluoranthene	0.075	U.V.
49-68	1,12-Benzoperylene	0.039	U.V.
60-68	2,3-(o-Phenylene)pyrene	0.146	U.V.
60-86	7,10-Benzofluoranthene	Trace	U.V.
60-86	Picene	0.030	U.V.
69-77	Coronene	0.007	U.V.
69-86	Anthanthrene	Trace	U.V.
78-100	1,2:4,5-Dibenzopyrene	0.006	U.V.
87-100	1,2:3,4-Dibenzopyrene	Trace	U.V.
87-100	3,4:9,10-Dibenzopyrene	Trace	U.V.
	Resins, losses and unidentified material	0.5	

* I.R. = Infrared spectroscopy

U.V. = Ultraviolet spectroscopy

R.T. = Retention time ratio

The values of bond dissociation energies listed in Table 4.2 indicate that the scission of the central carbon-carbon bond in n-decane should be a process involving the lowest activation energy (57). The dissociation energies of the carbon-carbon bonds between carbon atoms 4 and 5 or 3 and 4 in n-decane do not differ a great deal from that of the central bond and the scission of these bonds would therefore be expected to occur with comparable ease (58) and (59). The bond energies of the remaining carbon-carbon bonds, which are 3-4 kcal./mole higher than those mentioned above, will presumably be the reason why the scission of these bonds would occur to a correspondingly smaller extent (60) and (61).

$$CH_3CH_2CH_2CH_2CH_2-CH_2CH_2CH_2CH_2CH_3 \rightarrow 2\ CH_3CH_2CH_2\overset{\bullet}{C}H_2CH_2 \qquad (57)$$

$$CH_3CH_2CH_2CH_2-CH_2CH_2CH_2CH_2CH_2CH_3 \rightarrow CH_3(CH_2)_2\overset{\bullet}{C}H_2+CH_3(CH_2)_4\overset{\bullet}{C}H_2 \quad (58)$$

$$CH_3CH_2CH_2-CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \rightarrow CH_3CH_2\overset{\bullet}{C}H_2+CH_3(CH_2)_5\overset{\bullet}{C}H_2 \quad (59)$$

$$CH_3CH_2-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \rightarrow CH_3\overset{\bullet}{C}H_2+CH_3(CH_2)_6\overset{\bullet}{C}H_2 \qquad (60)$$

$$CH_3-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \rightarrow \overset{\bullet}{C}H_3+CH_3(CH_2)_7\overset{\bullet}{C}H_2 \qquad (61)$$

Thus the radicals initially formed at high temperatures would be the primary n-alkyl radicals, methyl to nonyl. These radicals could be expected to react in three different ways:

(a) abstraction of a hydrogen atom from other molecules or combination with other radical;

Table 4.2

R-R' BOND DISSOCIATION ENERGIES OF HYDROCARBONS

R	R'		H D(R-R') kcal./mole	Reference		CH$_3$ D(R-R') kcal./mole	Reference		CH$_3$CH$_2$ D(R-R') kcal./mole	Reference		n-C$_3$H$_7$ D(R-R') kcal./mole	Reference		n-C$_4$H$_9$ D(R-R') kcal./mole	Reference
		Method			Method			Method			Method			Method		
CH$_3$-	α		101-102	173,204	α	83-85	204	α	82	130	α	79	130	α	78	130
	β															
	γ															
C$_2$H$_5$-	α		97	204	α	82	130	α	82	130		79	130		78	130
	β		98	173				γ	78	214						
	γ		96	214												
n-C$_3$H$_7$-	α		95	130	α	79	130		79	130		76	130		75	130
	γ		100	214												
n-C$_4$H$_9$-	α		94	130	α	78	130		78	130		75	130		74	130
	γ		101	214												

Methods used: α pyrolysis; β electron impact; γ photobromination

(b) decomposition to smaller fragments; and

(c) isomerisation to different radicals.

The first reaction path would be expected to afford the corresponding saturated hydrocarbons, and methane, n-butane, n-pentane, and n-hexane were found among the products. It seems likely that ethane and n-propane were also formed in the pyrolysis, but were not detected in the exit gases on account of their much smaller concentrations compared with that of methane.

The second route would be the main source of ethylene in this pyrolysis, as it is known[137,215] that long chain hydrocarbon radicals will thermally decompose according to equation (62), yielding a molecule of ethylene and a free radical containing two carbon atoms less than the original radical. Thus:

$$RCH_2 - \overset{\bullet}{CH_2} \longrightarrow R^{\bullet} + CH_2{=}CH_2 \tag{62}$$

where R is an alkyl group or a hydrogen atom. Ethylene could be the precursor of acetylene, a small amount of which was detected in the exit gases.

There is no universal agreement on the question of isomerisation of alkyl radicals.[216,217] It has been shown that up to 500°C, isomerisation is not competetive with normal decomposition of n-propyl,[218] n-butyl,[216,217] isobutyl,[219,220] and s-butyl[219] radicals, and is of minor importance in the case of isopropyl[221,222] radicals,

although results of the experiments of Kerr and
Trotman-Dickenson[217] have been interpreted to favour
isomerisation of n-butyl and isobutyl radicals.   There
are, however, indications that the isomerisation of n-alkyl
radicals with more than four carbon atoms[223-225] is an
important reaction even as low as 150°C.[226]   The position
of the unpaired electron in the isomerised radical would
govern the nature of the fragments formed on its
decomposition.   Thus n-pentyl radical would isomerise into
radicals in which the unpaired electron is situated on any
of the carbon atoms 2, 3 or 4.   These radicals will then
decompose according to equations (63)-(65) to afford
propylene and but-1-ene, in addition to methyl and ethyl
radicals.

$$CH_3CH_2\overset{\bullet}{C}H_2CHCH_3 \longrightarrow CH_3CH=CH_2 + CH_3\overset{\bullet}{C}H_2 \qquad (63)$$

$$CH_3CH_2\overset{\bullet}{C}HCH_2CH_3 \longrightarrow CH_3CH_2CH=CH_2 + \overset{\bullet}{C}H_3 \qquad (64)$$

$$CH_3\overset{\bullet}{C}HCH_2CH_2CH_3 \longrightarrow CH_3CH=CH_2 + CH_3\overset{\bullet}{C}H_2 \qquad (65)$$
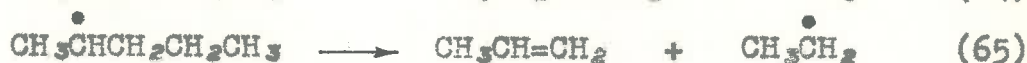
Since the number of n-pentyl radicals formed in the
primary reaction is larger than that of other n-alkyl radicals
(page 80), it follows that the secondary reactions of this
radical will be of greater importance than those of any other
such radical.   The most important decomposition product of
the isomerised radicals will thus be propylene, followed by
but-1-ene, pent-1-ene etc.   The concentrations of propylene
and but-1-ene would thus be larger than those of other

alk-1-enes, and it is therefore not surprising that
propylene and but-1-ene have been identified in the exit
gases.   The decomposition of ethyl, propyl, and butyl
radicals formed as primary fission products, or as secondary
products on decomposition of isomerised radicals, should
further increase the concentrations of ethylene, propylene
and but-1-ene.

Benzene is known to be formed by the pyrolysis of
ethylene or acetylene,[88,227] and some of the benzene found
in the present pyrolysis could be formed in this way.   As
shown above, the concentrations of propylene and but-1-ene
in the reaction zone would be expected to be high and the
most of the benzene (LXVII), toluene (CIII) and p-xylene
(CIV) could well arise from these products by reactions
shown in equations (66)-(68).   These reactions could also
account for the presence of cyclohexane, formed on
hydrogenation of (CV), but they cannot explain the presence

$$\text{(CV)} \longrightarrow \text{(LXVII)} \qquad (66$$

(CV)   (LXVII)

$$\longrightarrow \text{(CIII)} \qquad (67$$

(CIII)

(68)

(CIV)
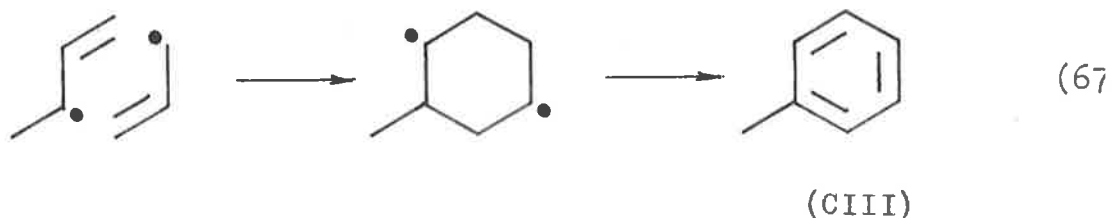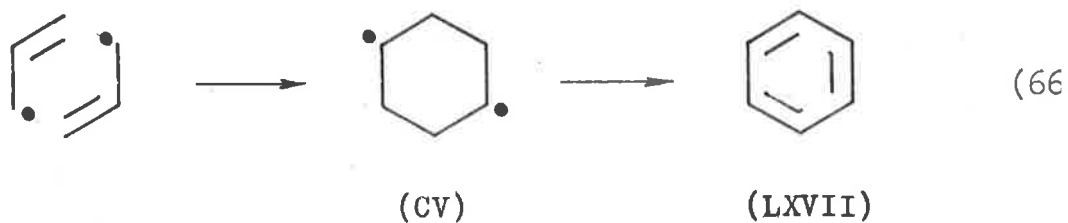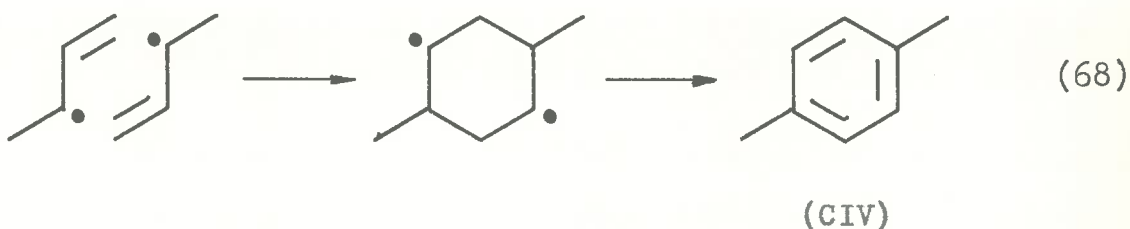
of m-xylene in the tar.

Several mechanisms can be suggested for the formation of styrene (XXXI).   Addition of a butenyl radical to butadiene (obtained from but-1-ene either by a molecular elimination of hydrogen, or by an abstraction of a hydrogen atom from its allylic position by a free radical, followed by loss of a hydrogen atom) would give an intermediate which could afford styrene on dehydrogenation as shown in equation (69).   In view of the very high yield of benzene, however, it seems likely that the styrene is largely formed from phenyl radicals and ethylene (70); and a similar mechanism involving phenyl radicals and propylene would account for the presence of the indene in the tar (71). In a similar way g-methylstyrene (CVI) could be formed by a recombination of s-propyl and a phenyl radical, followed by dehydrogenation (72).

(69)

(XXXI)

$$\text{(70)}$$

(XXXI)

$$\text{(71)}$$

(LXXI)

$$\text{(72)}$$

(CVI)
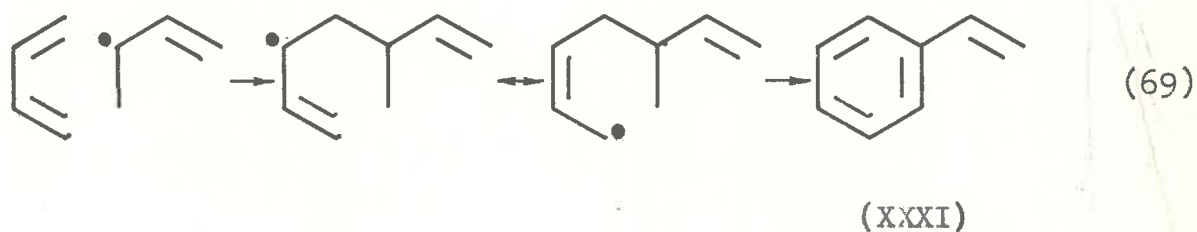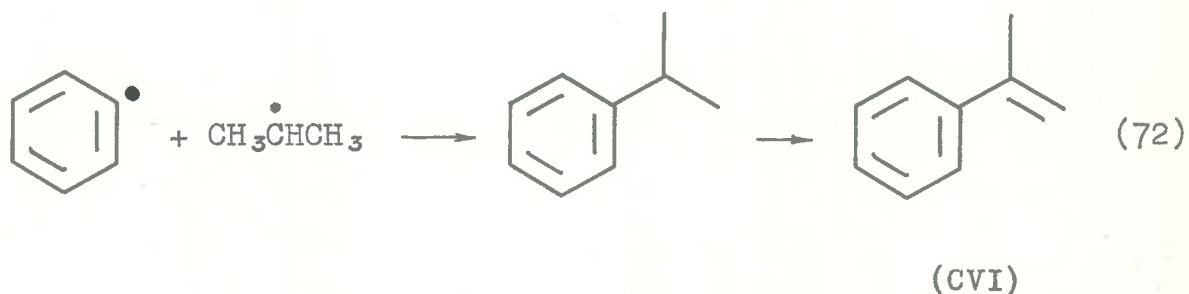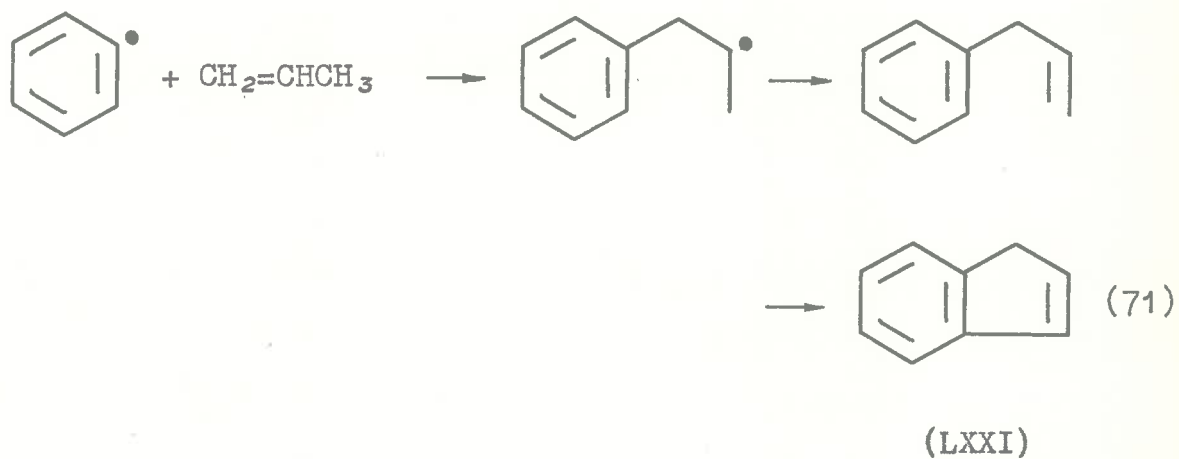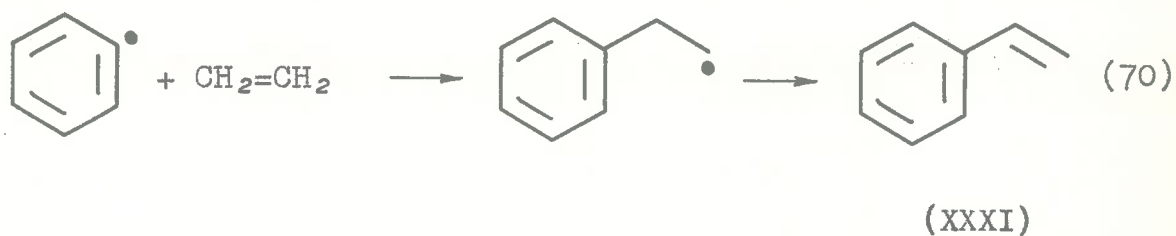
The pyrolysis of benzene is known to give a high yield of biphenyl and a little triphenylene.[92] The high yield of benzene in the present pyrolysis therefore suggests that the biphenyl is formed by the phenylation of benzene, or by recombination of two phenyl radicals. Further phenylation of biphenyl would be expected to give small amount of o-terphenyl (CVII), and hence triphenylene (XXI)

on cyclodehydrogenation (73).[92,226]

(CVII)   (XXI)   (73)
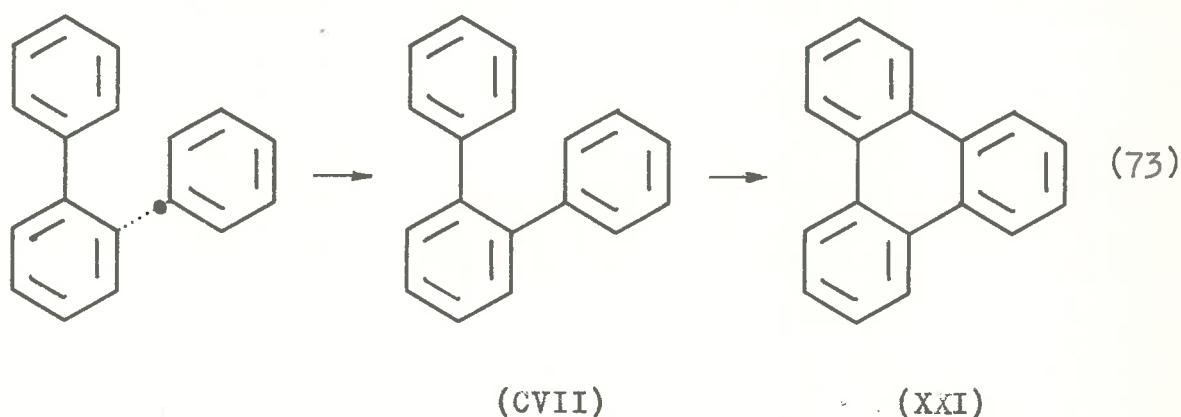
Bibenzyl is most probably formed by dimerisation of two benzyl radicals, in a way analogous to the formation of biphenyl from two phenyl radicals. The most likely mechanism for the formation of diphenylmethane would be by recombination of a phenyl and of a benzyl radical. A reaction of the latter with benzene could give the radical (CVIII), an appropriate intermediate in the formation of fluorene (XXVI) on cyclodehydrogenation as shown in (74).

(CVIII)   (XXVI)   (74)
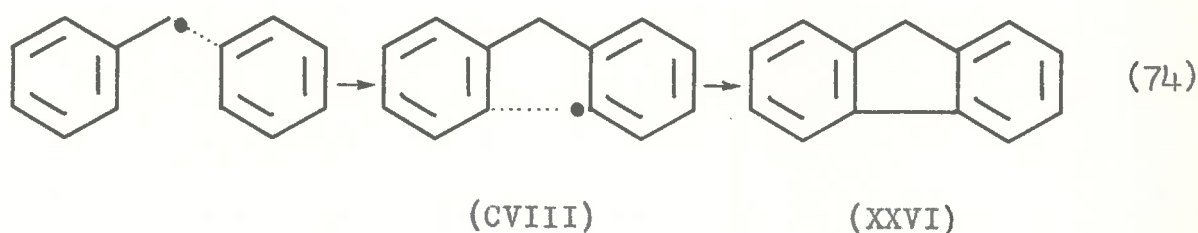
The large yield of naphthalene in this pyrolysis is noteworthy, but not unexpected from a C_{10} hydrocarbon.[213] Tetralin seems to be the likely intermediate in the

formation of naphthalene and a small amount of tetralin was also found in the tar. As already mentioned, the carbon-carbon fission of n-decane would give methyl radicals which would react with naphthalene to give the methylnaphthalenes found in the tar. Moreover, acenaphthylene, 2-phenylnaphthalene, fluoranthene, 2,2'-binaphthyl, perylene, 10,11-benzofluoranthene, and 11,12-benzofluoranthene, all of which were identified in the tar, would be expected to arise from suitable naphthalene intermediates as previously postulated.[229,230]

The presence of 1,12-benzoperylene (VIII), and of a very small amount of coronene (CIX) in the tar is of interest, especially as the latter hydrocarbon has not previously been identified in a tar produced at a temperature as low as 700°C. 1,12-Benzoperylene was reported to be one of the products obtained in the pyrolysis of 2-methylnaphthalene.[231] The primary reaction to be expected in the pyrolysis of the latter compound would be the abstraction of one of the naphthalylic hydrogen atoms resulting in the formation of 2-naphthylmethyl radicals (CX), which is a process analogous to the formation of benzyl radicals during the pyrolysis of toluene.[90] Dimerisation of such radicals would yield 1,2-di-β-naphthylethane (CXI) which could give 1,12-benzoperylene on cyclodehydrogenation. That this is the actual mechanism for the formation of 1,12-benzoperylene is borne out of the fact that

1,2-di-β-naphthylethane (CXI) and
1,2-di-β-naphthylethylene (CXII) were found in the tar
following pyrolysis of 2-methylnaphthalene carried out under
slightly milder conditions.[76]   By analogy to the above,
a satisfactory mechanism for the formation of
1,12-benzoperylene in the pyrolysis of n-decane would
firstly involve the following possibilities:

    (a)   methylation of a naphthalene intermediate such
           as (CXIII) which has been proposed in the
           formation of naphthalene from butylbenzene,[90]

    (b)   β-methylation of naphthalene to give (CXIV) and

    (c)   addition of ethylene to (CIII).

        Cyclodehydrogenation of products formed by processes
(a), (b) and (c) would result in the formation of
1,12-benzoperylene as shown in (75)-(77).

(CIX)

(CX)

(CXI)

(CXII)

(75)

(76)

(CXIII) (VIII) (CXIV)

+ 2 CH₃ →

+ CH₂=CH₂ →

(77)
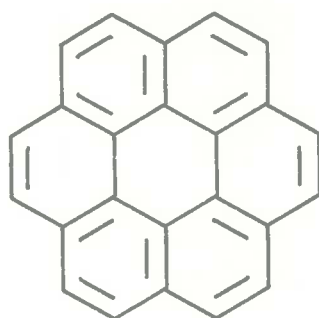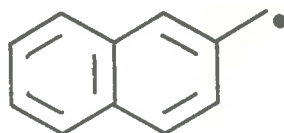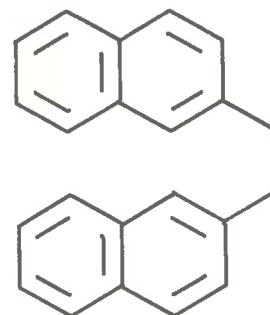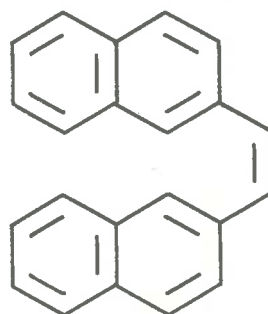
(CXIII) (VIII)
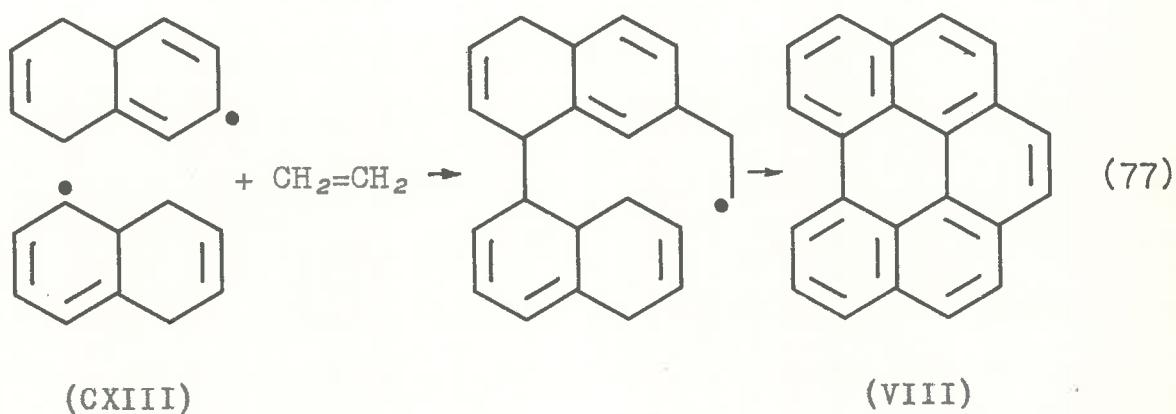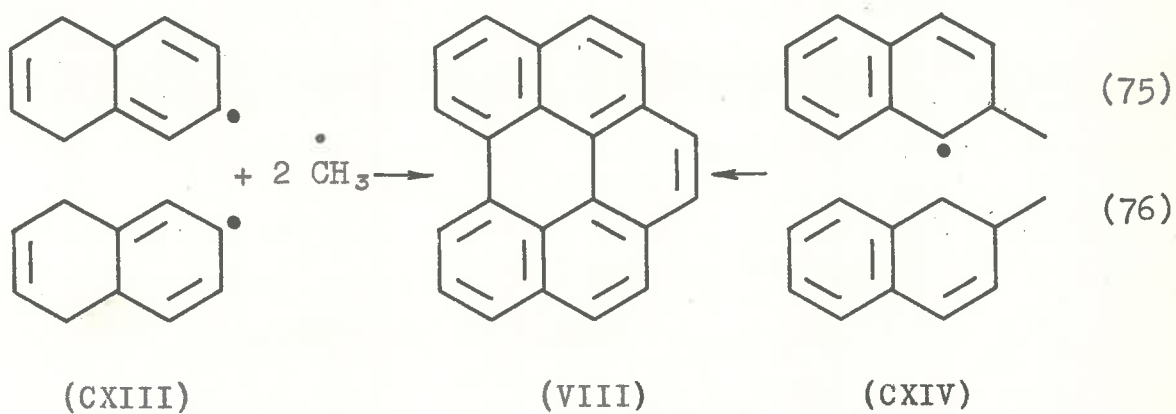
Coronene could be similarly formed by an addition of two molecules of ethylene to (CXIII) followed by cyclodehydrogenation (78).

+ 2 CH₂=CH₂ →

(78)

(CXIII) (CIX)
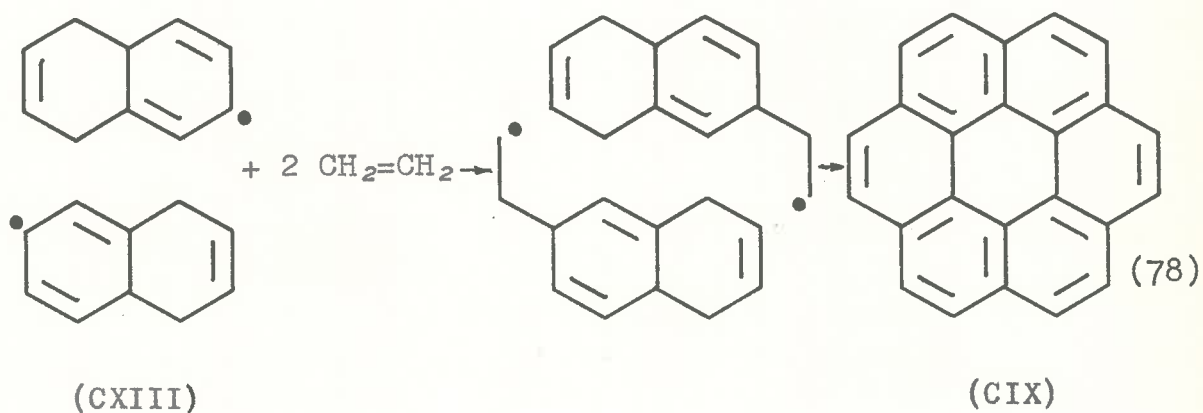
Picene (CXV) and anthanthrene (CXVI) could be formed
for the reasons described in connection with
methylnaphthalenes from intermediates (CXVII) and (CXVIII).
Methylation of naphthalene in the α-position would give the
intermediate (CXVII) and two such intermediates would give
the picene skeleton on dimerisation (79).   In a similar
way methylation of (CXIII) in the other possible canonical
form would give (CXIX) which would give anthanthrene on
dimerisation, followed by cyclodehydrogenation (80).

(CXVII)   (CXV)

(79)

(CXVIII)   (CXVI)   (CXIX)

(80)
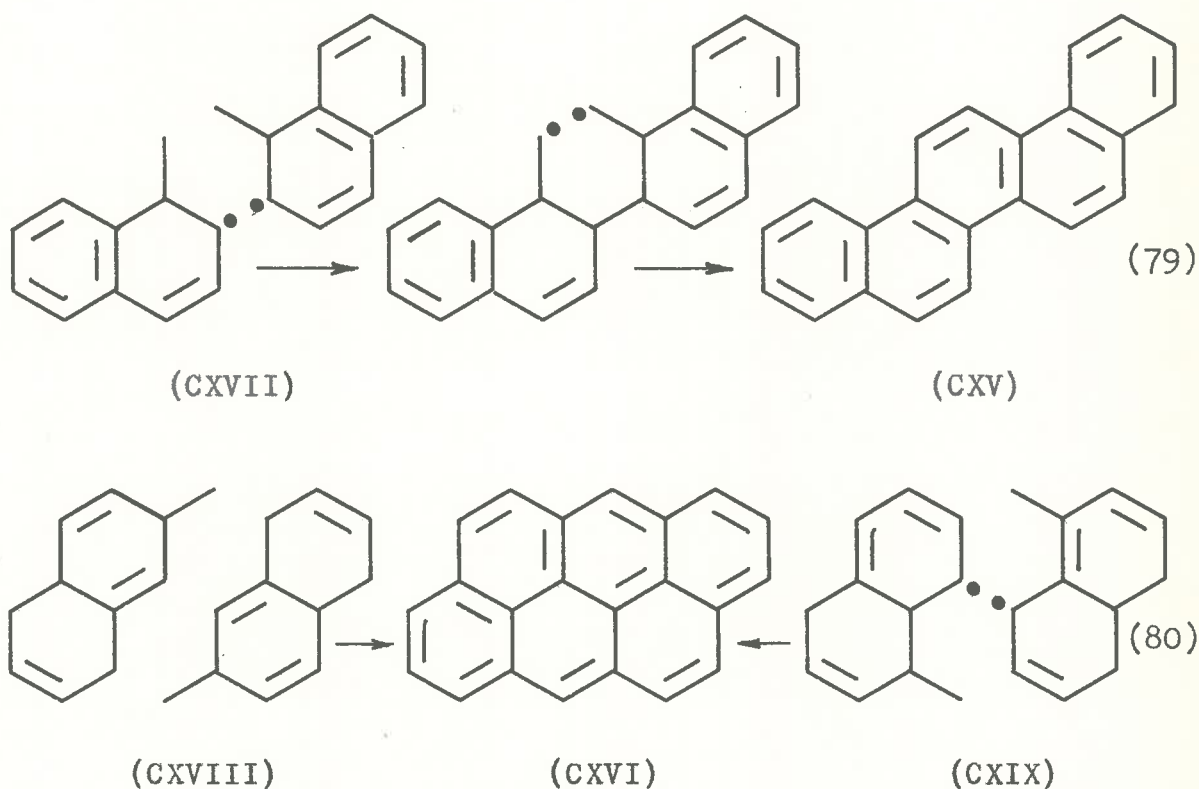
The probable mode of formation of 3,4-benzopyrene,
namely from two C_6-C_4 units, or from a perinaphthenyl and
a benzyl radicals has been already discussed in some detail.

In an analogous way 3,4:8,9-dibenzopyrene (III) (which was
not detected in the tar from this pyrolysis) could be formed
by interaction of a C_6-C_4 unit with anthracene, followed by
cyclodehydrogenation (81).   1,2:3,4-Dibenzopyrene (CXX)
could be formed from phenanthrene and a C_6-C_4 unit (82), and
3,4:9,10-dibenzopyrene (IV) could arise from the same
intermediates (83).

(III)   (81)

(CXX)   (82)

(IV)   (83)
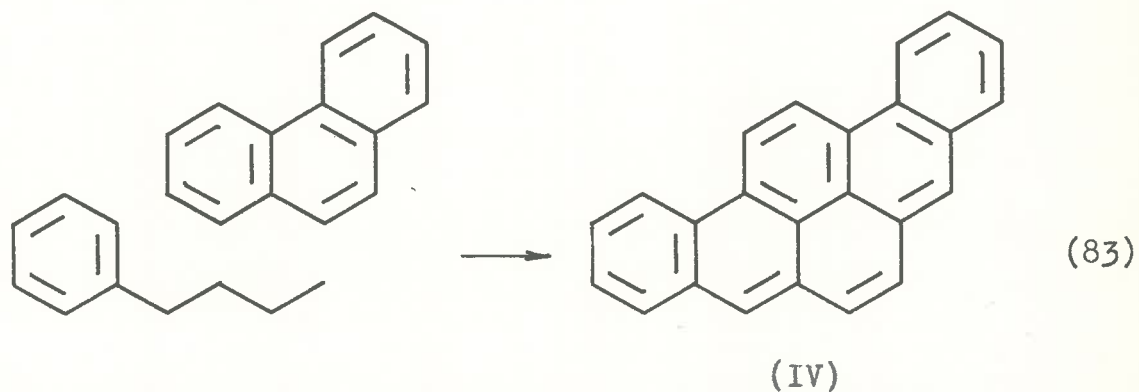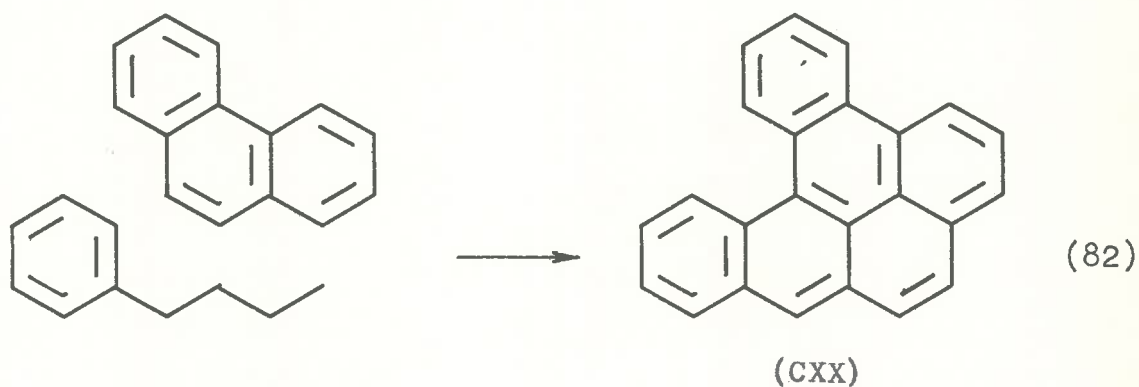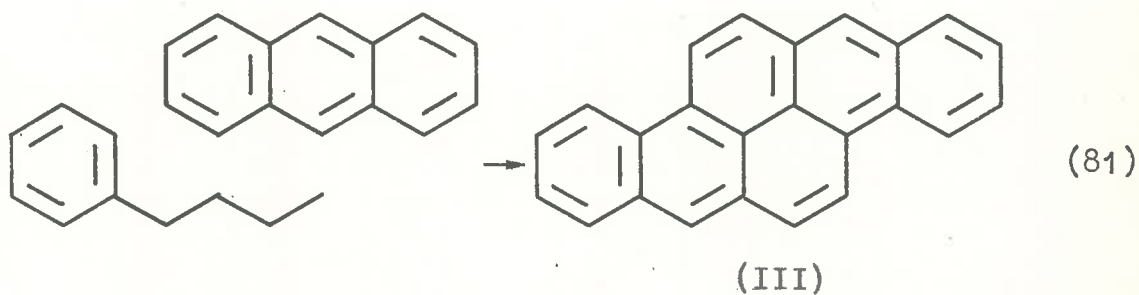
1,2:4,5-Dibenzopyrene (CXXI) could be formed in a
similar way (84), but the most reasonable mechanism for its
formation would seem to be the phenylation of chrysene,
followed by cyclodehydrogenation (85).

(84)

(CXXI)

(85)
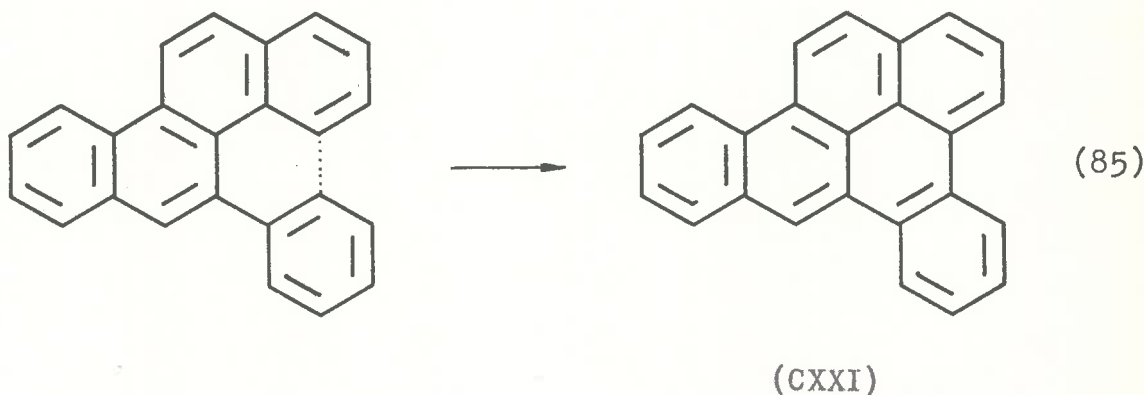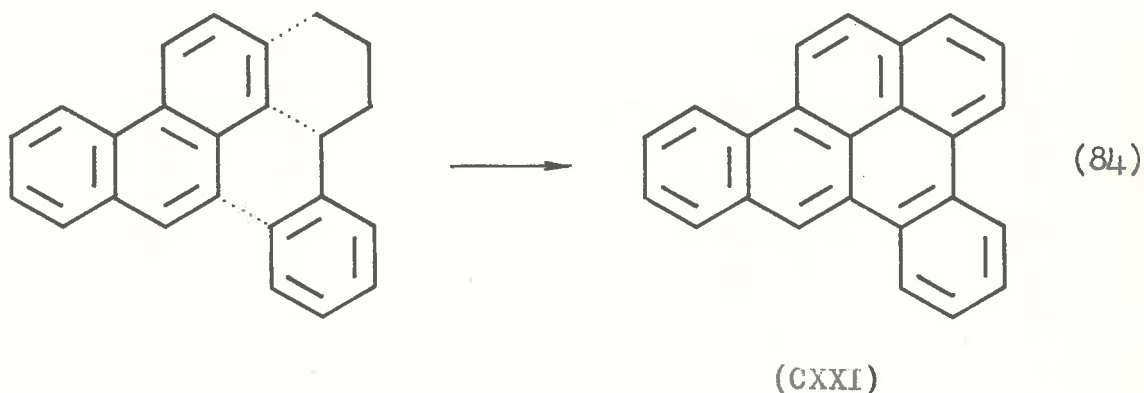
(CXXI)

The formation of the four dibenzopyrenes mentioned
above could also be formulated as a reaction of a benzyl
radical with an intermediate (CXXII) obtained in the
cyclisation of 1-benzylnaphthalene (which being a
benzoperinaphthenyl radical would be expected to be
extremely stable). Thus the formation of

3,4:8,9-dibenzopyrene could be represented as (CXXIII), and
that of 1,2:3,4-, 1,2:4,5-, and 3,4:9,10-dibenzopyrenes as
(CXXIV), (CXXV), and (CXXVI) respectively.
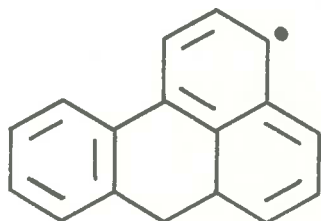
(CXXII)
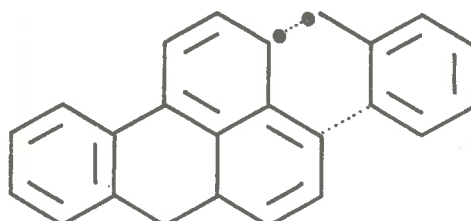
(CXXIII)
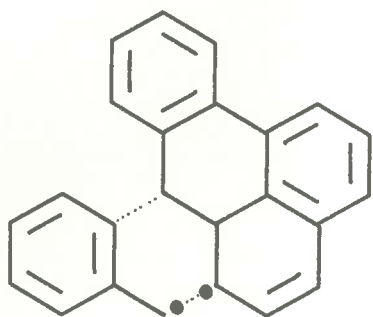
(CXXIV)
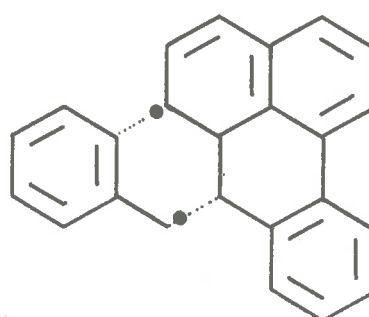
(CXXV)
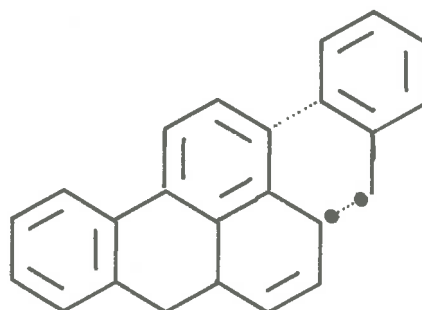
(CXXVI)

CHAPTER 5

THE PYROLYSIS OF [δ-¹⁴C]BUTYLBENZENE

5.1   INTRODUCTION

The tars obtained on pyrolysis of many different organic compounds have been examined for polycyclic aromatic hydrocarbons as part of a comprehensive study to determine their mode of formation.[6,191]   The pyrolysis of n-butylbenzene, for example, has been shown to give a complex tar containing at least forty-two compounds, most of which have been satisfactorily identified, and their relative abundance determined.[90]   Satisfactory mechanisms have been proposed for the formation of many of the compounds which have been identified; but few of these mechanisms can be said to be firmly established.   To obtain further evidence for these mechanisms, we have decided to carry out the pyrolysis of [δ-¹⁴C]butylbenzene.

[δ-¹⁴C]Butylbenzene was prepared by reaction of cinnamaldehyde (CXXVII) with methyl-¹⁴C iodide, followed by reduction of the 2-hydroxy-4-phenyl[1-¹⁴C]but-3-ene (CXXVIII), dehydration of the 2-hydroxy-4-phenyl[1-¹⁴C]butane (CXXIX), and hydrogenation of the product (CXXX) to give [δ-¹⁴C]butylbenzene (CXXXI). The labelled butylbenzene was pyrolysed as previously

described[90] and the resulting tar separated into its
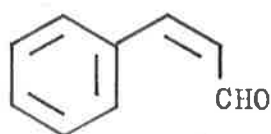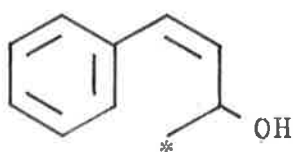
(CXXVII)   (CXXVIII)   (CXXIX)
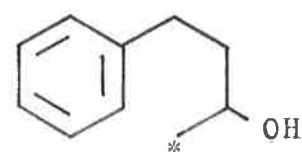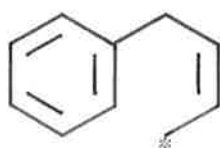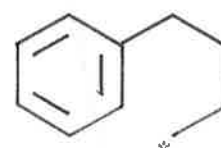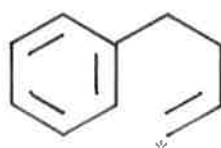
(CXXX)   (CXXXI)

constituents using gas-liquid chromatography and
chromatography on alumina and on acetylated cellulose.

5.2   RESULTS AND DISCUSSION

On treatment of the tar, eighteen compounds or their
derivatives were isolated in sufficient quantity and purity
for radiochemical analysis.   The activities were calculated
as relative molar activities, which are linearly proportiona
to the number of labelled carbon atoms per molecule.[192]
The results are summarised in Table 5.1, which lists all the
compounds isolated, together with the number of active
carbon atoms found.   It also lists the number of labelled
carbon atoms found in degradation products of the compounds

isolated.   Other compounds formed in this pyrolysis[00]
could not be isolated in sufficient amount, or in sufficient
purity, for radiochemical analysis.

Table 5.1

CONSTITUENTS OF TAR OBTAINED BY PYROLYSIS OF $[\delta-^{14}C]$BUTYLBENZEN

Compounds	Degradation Products	Labelled C Atoms
Benzene		0.13
Toluene		0.12
	Benzoic acid	0.11
	Carbon dioxide	0.07
	Benzene	0.03
Styrene		0.29
	Benzoic acid	0.16
	Carbon dioxide	0.02
	Benzene	0.15
Naphthalene		1.00
Biphenyl		0.27
Fluorene		0.22
Phenanthrene		0.55
	2,2'-Biphenic acid	0.53
	Carbon dioxide	0.18
	Biphenyl	0.36

Table 5.1 (Continued)

Compounds	Degradation Products	Labelled C Atoms
Anthracene		0.82
Pyrene		1.96
Fluoranthene		0.92
1,2-Benzanthracene		1.15
Chrysene		1.18
	Chrysa-1,2-quinone	1.18
	o-(2-Naphthyl)benzoic acid	1.14
	2-Phenyl-1-naphthoic acid	1.16
	Carbon dioxide	0.01
	2-Phenylnaphthalene	1.13
2,3-Benzofluorene		1.24
3,4-Benzopyrene		1.92
	3,4-Benzopyrene-6,7-quinone	1.92
	Carbon dioxide	0.87
	Chrysene	1.12
3,4-Benzofluoranthene		0.62
3,4-Benzotetraphene		2.16
2,3-(o-Phenylene)py- rene		2.21
1,2-Benzopyrene		2.0

The initial decomposition of aromatic compounds containing an alkyl side chain is believed to proceed by a carbon-carbon scission rather than carbon-hydrogen scission, with the exception of toluene (cf. the dissociation energies of the appropriate bonds in Figure 3.2, page 58). In the thermal decomposition of n-butylbenzene, the scission of the carbon-carbon bond resulting in the formation of a benzyl radical (CXXXII) and an n-propyl radical by equation (86) should be the most favoured process. However, the direct formation of a phenyl radical (CXXXIII) may well compete with the formation of a benzyl radical since it seems likely that with increasing length of the side chain, concentration of the thermal excitation energy in the bond linking the side chain to the bulky aromatic nucleus would lead to preferential scission according to equation (87).[90]

$$C_6H_5CH_2CH_2CH_2CH_3 \longrightarrow C_6H_5\overset{\bullet}{C}H_2 + CH_3CH_2\overset{\bullet}{C}H_2 \qquad (86)$$

$$(CXXXII)$$

$$C_6H_5CH_2CH_2CH_2CH_3 \longrightarrow C_6H_5{}^{\bullet} + CH_3CH_2CH_2\overset{\bullet}{C}H_2 \qquad (87)$$

$$(CXXXIII)$$
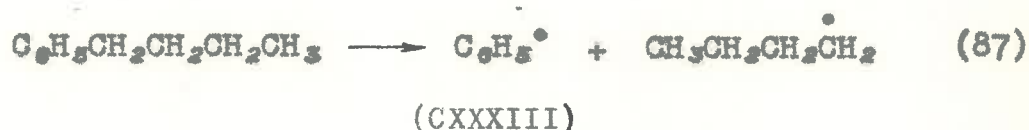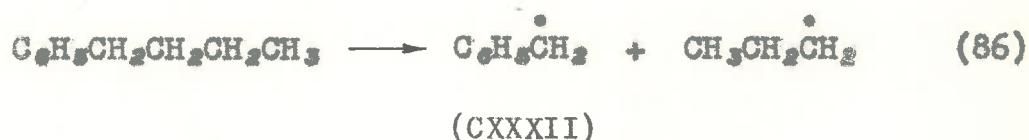
Random carbon-carbon scission of the side chain of n-butylbenzene would give rise to other radicals, equations (88) and (89), but these reactions are considered to be less important.

$$C_6H_5CH_2CH_2CH_2CH_3 \longrightarrow C_6H_5CH_2\overset{\bullet}{C}H_2 + CH_3\overset{\bullet}{C}H_2 \qquad (88)$$

(CXXXIV)

$$C_6H_5CH_2CH_2CH_2CH_3 \longrightarrow C_6H_5CH_2CH_2\overset{\bullet}{C}H_2 + \overset{\bullet}{C}H_3 \qquad (89)$$
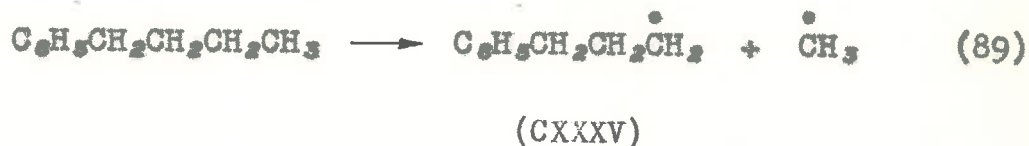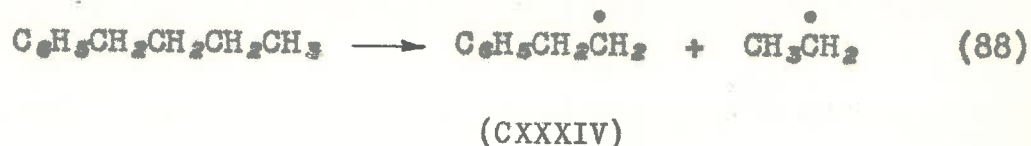
(CXXXV)

The most important hydrogen abstraction reactions
will be those occurring between any of the radicals
(CXXXII)-(CXXXV) and the starting material, and these would
be expected to occur preferentially at the α-carbon atom as
shown in equation (90), with abstraction at the other carbon
atoms being of minor importance by analogy with the known
rates of reaction at allylic and paraffinic carbon atoms.[131]

$$C_6H_5CH_2CH_2CH_2CH_3 + R^\bullet \longrightarrow C_6H_5\overset{\bullet}{C}HCH_2CH_2CH_3 + RH \qquad (90)$$
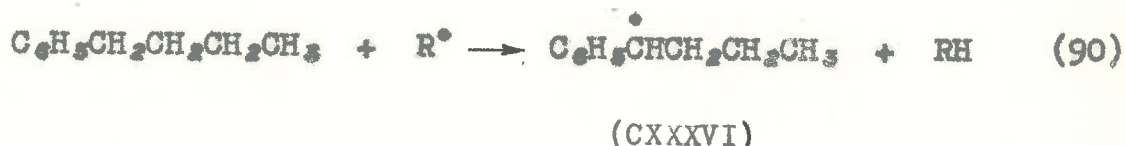
(CXXXVI)

($R^\bullet$ represents any radical or a hydrogen atom).

The radical (CXXXVI) will therefore be a major
primary reaction product, and radicals or compounds formed
from it by disproportionation will be of importance.   The
most probable reaction would appear to be the loss of a
hydrogen atom to give an unsaturated compound as shown in
equation (91) and loss of methyl or ethyl radicals by
equations (92) and (93).   The last two processes would
require an activation energy of ca. 20 kcal./mole, whereas

the loss of hydrogen atom would require an activation energy of the order of 40 kcal./mole.[31]

$$C_6H_5\overset{\bullet}{C}HCH_2CH_2CH_3 \longrightarrow C_6H_5CH=CHCH_2CH_3 + H \qquad (91)$$

(CXXXVII)

$$C_6H_5\overset{\bullet}{C}HCH_2CH_2CH_3 \longrightarrow C_6H_5CH=CHCH_3 + \overset{\bullet}{C}H_3 \qquad (92)$$

(CXXXVIII)

$$C_6H_5\overset{\bullet}{C}HCH_2CH_2CH_3 \longrightarrow C_6H_5CH=CH_2 + CH_3\overset{\bullet}{C}H_2 \qquad (93)$$

(XXXI)
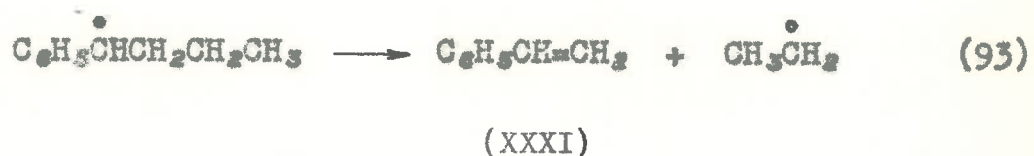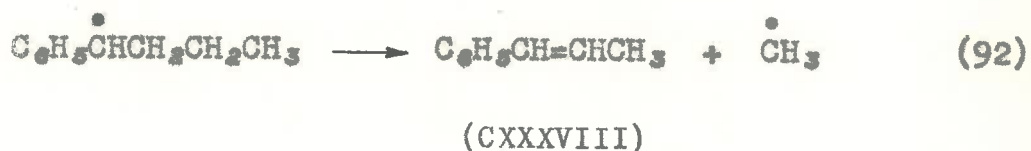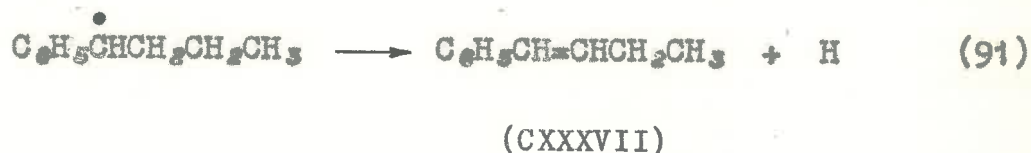
A futher mode of decomposition in which the entire side chain is removed as shown in equation (94) is of importance; but this leads to similar products as the decomposition already discussed.

$$C_6H_5\overset{\bullet}{C}HCH_2CH_2CH_3 \longrightarrow C_6H_5^{\bullet} + CH_2=CHCH_2CH_3 \qquad (94)$$

(CXXVIII)
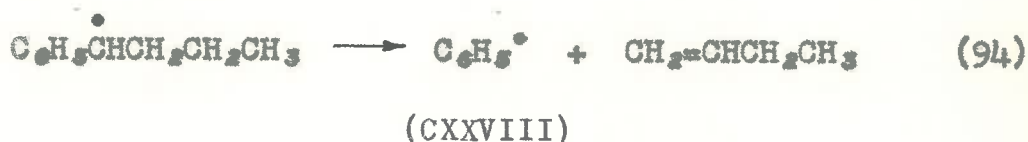
Random abstraction of hydrogen atoms from the alkyl side chain would give similar products, leading to olefinic compounds containing the same number of carbon atoms, or less.

Figure 5.1 summarises all the possible pathways leading to the more important intermediates, together with the expected activities of the fragments. Figure 5.2

[(CXXXI);1*C]

(87) (86) (90) (88) (89)

[(CXXXIII);0.0*C] [(CXXXII);0.0*C] [(CXXXVI);1*C] [(CXXXIV);0.0*C] [(CXXXV);0.0*C]

(91) (92) (93) (94)

[(XXXI);0.0*C] [(CXXXVIII);0.0*C] [(CXXXVII);1*C] [(CXXXIII);0.0*C] [(CXXXII);0.0*C]

Figure 5.1

[(CXXXI); 1*C]

(87)   (86)   (90)   (88)   (89)

$CH_3CH_2CH_2CH_2$ $CH_3CH_2CH_2$ [(CXXXVI); 1*C] CH_3CH_2 CH_3

[1*C]   [1*C]   [1*C]   [1*C]   [1*C]

(92)   (93)   (94)

CH_3 CH_3CH_2 $CH_2=CHCH_2CH_3$ $CH_2=CH_2$

[1*C]   [1*C]   [1*C]   [0.0*C]
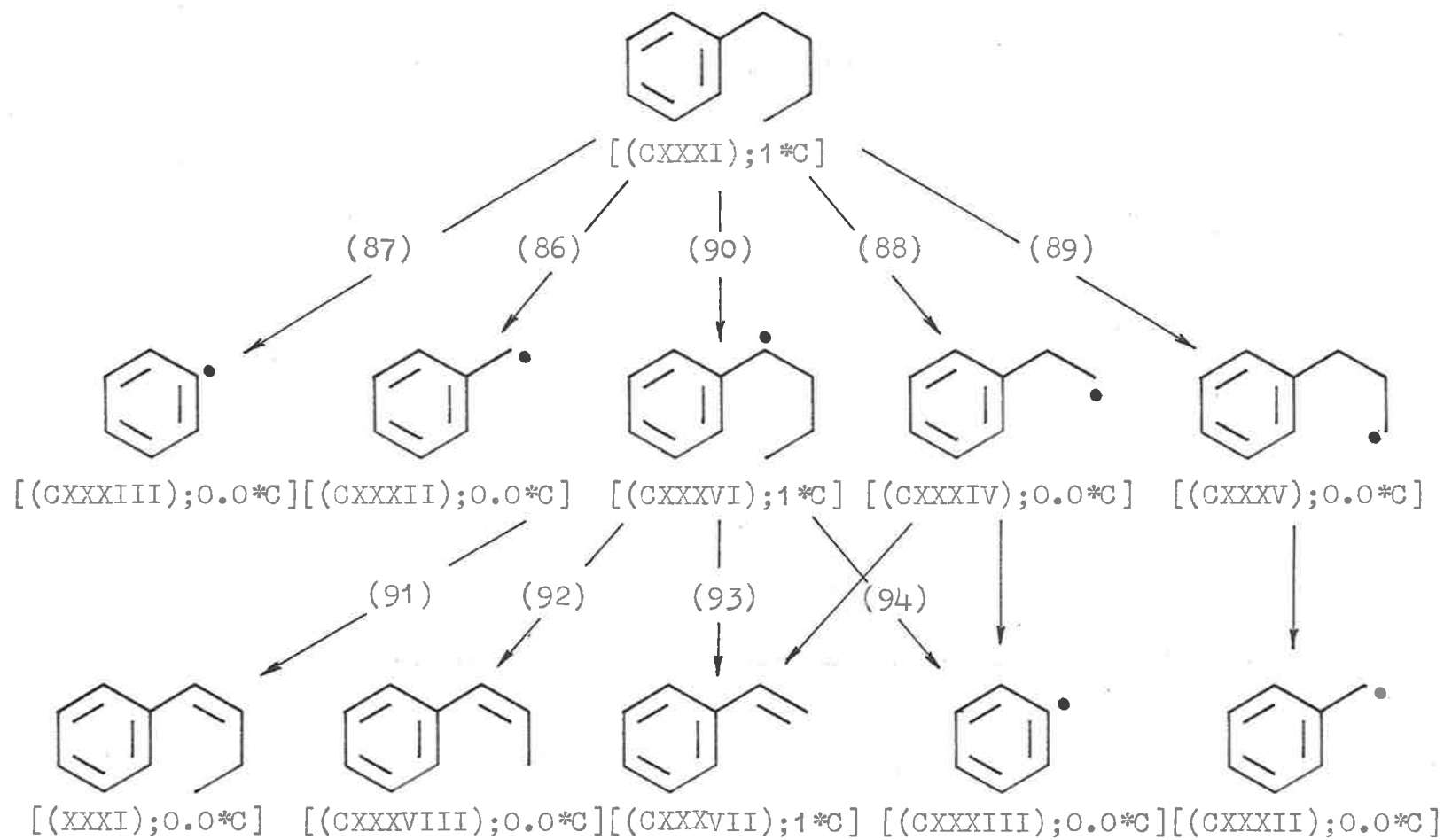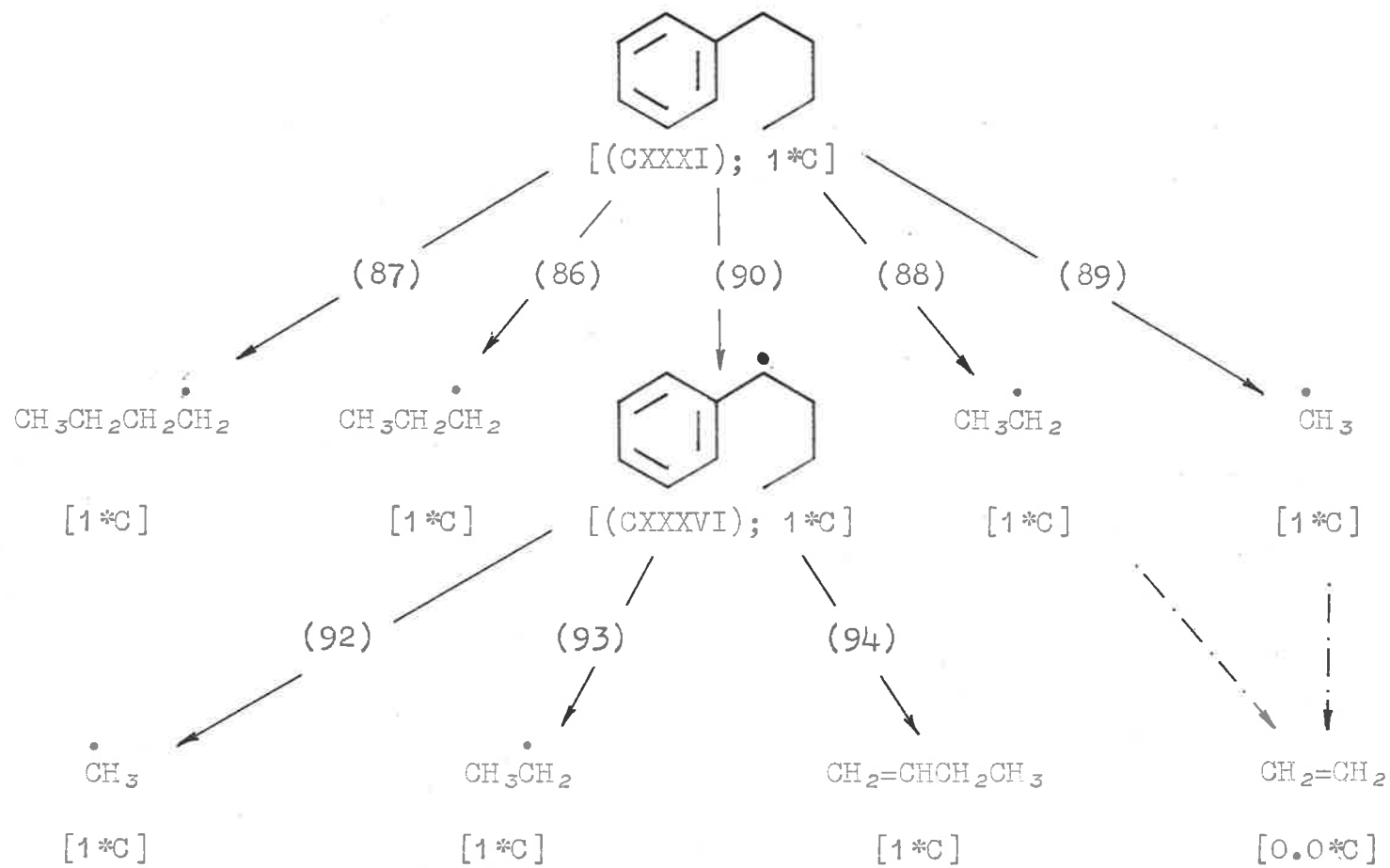
Figure 5.2

surveys the activities of the aliphatic portions obtained in these reactions.

The decomposition products thus obtained cannot, however, account for the formation of the polycyclic hydrocarbons. The presence of large amounts of naphthalene in the pyrolysis of n-butylbenzene[80] (21% of the tar) may be explained by assuming either that chain resynthesis proceeds to an appreciable extent with the formation of the phenbutenyl radical (CXXXIX), equation (95), or that hydrogen abstraction from the δ-position in n-butylbenzene is an important reaction yielding a phenbutyl radical (CXL), by equation (96). Cyclodehydrogenation of both (CXXXIX) and (CXL) would give naphthalene with an expected activity of one labelled carbon atom, and this has been confirmed by the experiment since the figure found was 1.00 labelled atoms.

$$(95)$$

(CXXXIX)

$$(96)$$

(CXL)
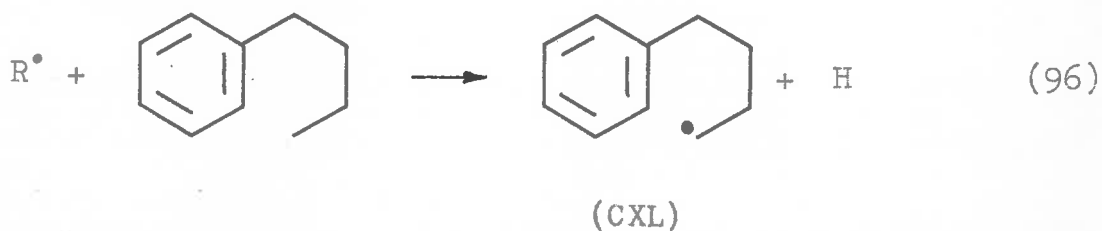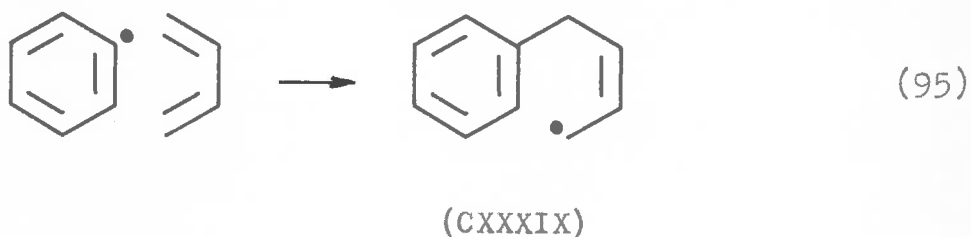
The scission of the carbon-carbon single bonds in
[δ-^{14}C]butylbenzene would yield the inactive radicals
(CXXXII)-(CXXXV).   Abstraction of a hydrogen atom from
butylbenzene by a phenyl radical (CXXXIII), as indicated in
equation (90), would therefore give inactive benzene.
However, the benzene found had an activity corresponding to
0.13 labelled carbon atoms, so that some of the benzene
must be formed by resynthesis of the fragments derived from
the alkyl chain.   Benzene formed from C_2, or C_2 and C_4 units
would be expected to have 1.5 labelled carbon atoms, so
approximately 8-9% of the benzene found in the tar must be
formed in this way.   As expected, biphenyl, which must be
formed by the phenylation of benzene, was found to have
0.27 labelled carbon atoms.

In an analogous way, abstraction of a hydrogen atom
by a benzyl radical (CXXXII), would give inactive toluene;
but the toluene was found to have an activity equivalent to
0.12 carbon atoms.   Oxidation of toluene afforded benzoic
acid (0.11 labelled carbon atoms), which was decarboxylated
to give benzene (0.03 labelled atoms) and carbon dioxide
(0.07 labelled atoms).   Thus the activity of the side
chain in toluene was approximately twice the activity of the
benzene nucleus.   A second mechanism, likely to involve
the methylation of benzene or the recombination of phenyl
and methyl radicals, must be operating.   If all the carbon
atoms in the side chain of butylbenzene are assumed to be

equally available for the methylating process, they have an
average activity of 0.25 labelled atoms.   The benzene found
in the tar had 0.13 labelled carbon atoms and the toluene
formed in this way would therefore have 0.38 labelled carbon
atoms, with the side chain having twice the activity of the
ring system.   The magnitude and distribution of activities
in toluene may therefore be accommodated by assuming that
about 70% of toluene is formed from inactive benzyl radicals
by hydrogen abstraction, and about 30% by the methylation of
benzene.

Abstraction of a hydrogen atom from butylbenzene by
a phenethyl radical (CXXXIV) would give ethylbenzene.   This
is known to be formed in this pyrolysis,[90] but could not be
isolated in sufficient quantity for radiochemical analysis.
However, the loss of a hydrogen atom from (CXXXIV), or more
likely, the loss of an ethyl radical from (CXXXVI) as shown
in (93), would give inactive styrene (XXXI).   Styrene is
one of the more abundant constituents of the tar (2.7% of the
tar[90]), and was satisfactorily isolated for radiochemical
analysis.   It was found to have 0.29 labelled carbon atoms.
Oxidation of the styrene gave benzoic acid (0.16 labelled
atoms), and this was decarboxylated to benzene (0.15 labelled
atoms) and carbon dioxide (0.02 labelled atoms).   Thus
about half the activity of the styrene is located in the
benzene ring and nearly all the remainder in the β-carbon
atom of the side chain.   Again, therefore, it seems certain

that a portion of the styrene must be formed by a second
mechanism, not involving the inactive phenethyl radicals.
The chain resynthesis from an ethylene molecule and a phenyl
radical, followed by elimination of a hydrogen atom cannot be
an important reaction since both α- and β-carbon atoms should
then have the same activity and in addition, the activity of
the benzene residue should be smaller than that of the side
chain.   A likely mechanism could involve the dimerisation
of two C_4 units such as butadiene, obtainable, for example,
from the products of equations (87) or (94), to give
vinylcyclohexene (CXLI),[93] which would then lose hydrogen to
give styrene as shown in (97).   Styrene formed in this way

$$(97)$$

(CXLI)   (XXXI)
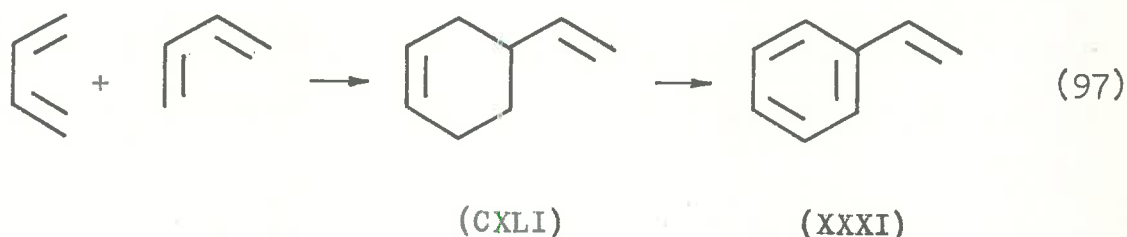
would be expected to have 2.0 labelled carbon atoms (1.5 labels
on the benzene ring, none on the α-carbon atom and 0.5 on the
β-carbon atom).   A second possible mechanism for the
formation of styrene would involve the reaction of toluene,
or a benzyl radical with a methyl radical, followed by
dehydrogenation.   The distribution of the labelled atoms in
toluene is known, and the activity of the methyl radicals
must average 0.25 labelled atoms, so that any styrene formed

in this way would be expected to have 0.35 labelled carbon atoms (0.03 in the benzene ring, 0.07 on the α-carbon atoms and 0.25 on the β-carbon atoms).   Assuming that these three mechanisms are responsible for the total yield of styrene in this pyrolysis, about 60% of the styrene must be formed from inactive phenethyl radicals, about 10% from the dimerisation of two C_4 units, and about 30% from toluene (or benzyl) and methyl radicals.

Three reasonable mechanisms can be postulated for the formation of phenanthrene (XXIII).   The first, equation (98), would involve the interaction of two benzyl radicals to give bibenzyl (CXLII), followed by cyclodehydrogenation.   The second, equation (99), would involve reaction of a phenyl radical with a C_6-C_2 unit, such as styrene, followed by cyclisation.   The third, equation (100), would involve raction of naphthalene, or its possible precursors in this pyrolysis,[90] with a C_4 unit, followed by cyclodehydrogenation.

(98)

(99)

(100)
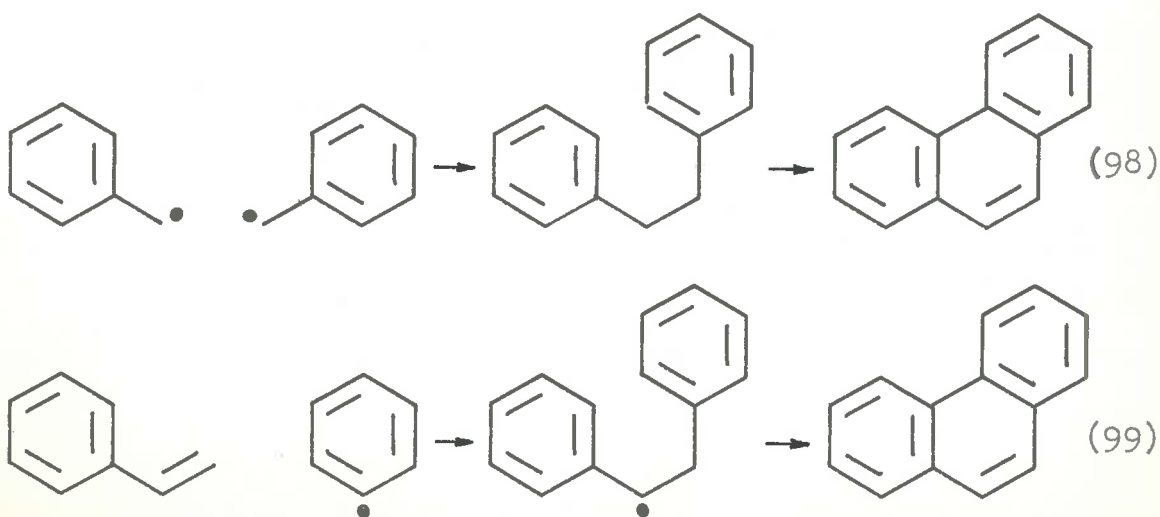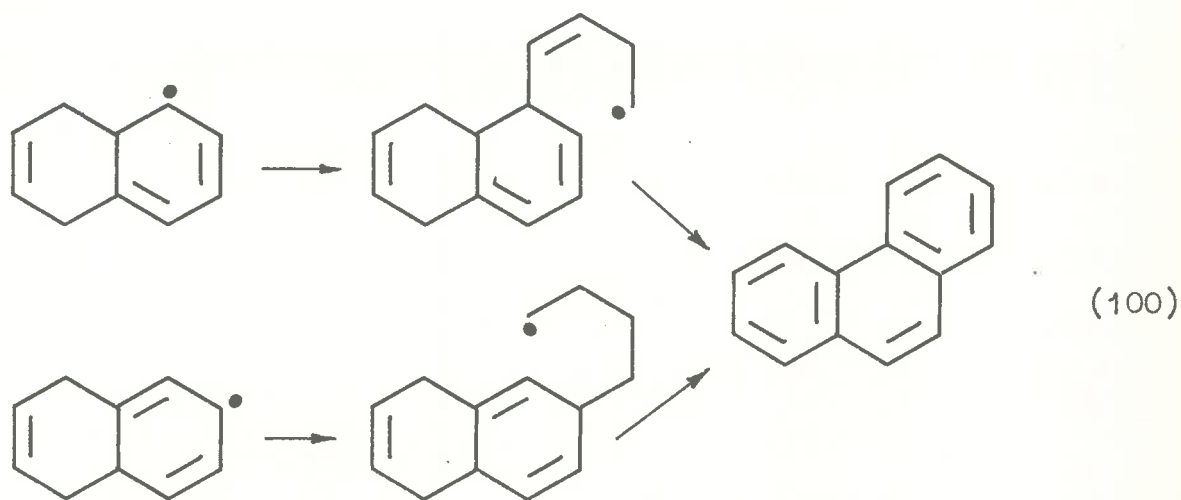
The phenanthrene isolated in the pyrolysis of [α-^{14}C]ethylbenzene was shown to be formed predominantly by the second mechanism. In the pyrolysis of [δ-^{14}C]butylbenzene, any phenanthrene produced by the first route would be expected to have 0.24 labelled carbon atoms, with ca. 0.03 labels distributed between each group of the positions 1-4 and 5-8 in phenanthrene, and ca. 0.07 labels on each of the carbon atoms 9 and 10, as shown in (CXLIII). These figures follow from the results obtained with toluene. Similarly, any phenanthrene produced by the second route would be expected to have 0.42 labelled carbon atoms - 0.13 active carbon atoms from benzene, and 0.29 from styrene. Of this ca. 0.29 labelled atoms would be found in the "biphenyl part" and ca. 0.13 distributed between the two meso-carbon atoms as shown in (CXLIV).

Finally, phenanthrene formed by (100) would be expected to have 2.0 labelled carbon atoms (CXLV).
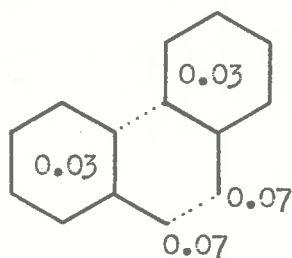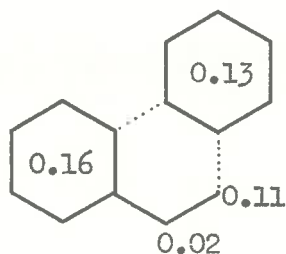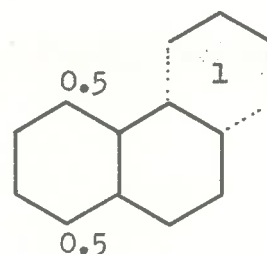
(CXLIII)   (CXLIV)   (CXLV)

The phenanthrene isolated in the present pyrolysis
was found to have 0.55 labelled carbon atoms.   Oxidation
of phenanthrene gave 2,2'-biphenic acid, which had 0.53
labelled atoms, and decarboxylation gave biphenyl (0.36) and
carbon dioxide (0.18 labelled atoms) as shown in (101).

0.55 *C   0.53 *C   0.36 *C   0.18 *C
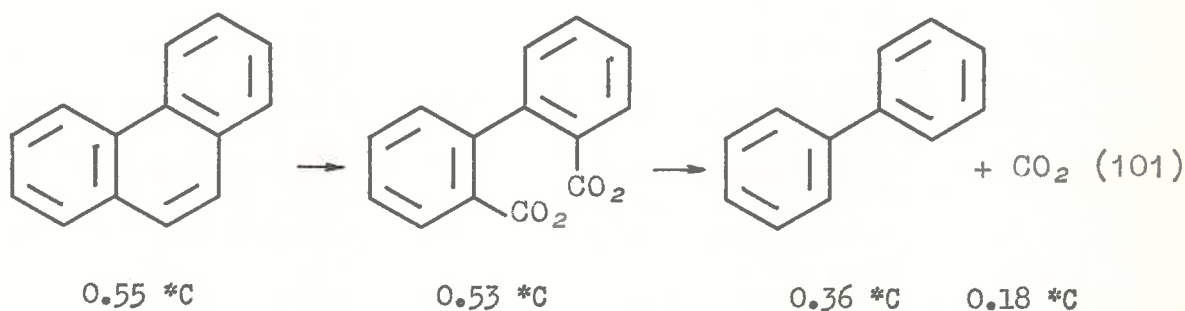
This distribution is quite unlike that expected from the
first route, and this process can therefore be rejected as
a major contributor.   The distribution is similar to that
expected from the second route, and it may be concluded,
therefore, that this process is important in the formation
of phenanthrene.   It seems likely, however, that the third
route may also operate to a small extent, thereby increasing

the activity of the phenanthrene isolated.

The mode of formation of anthracene could involve dimerisation of two benzyl radicals, or addition of a C_4 unit to a naphthalene precursor - a method analogous to the third route suggested for the formation of phenanthrene, and other reactions already discussed in some detail in Chapter 3. A decision on the preferred route cannot be made on the basis of the present results, and to explain the observed figure of 0.82 labelled atoms for anthracene, two or more routes must be involved.

More than one route may also be involved in the formation of pyrene from butylbenzene (Chapter 2, page 43). The dimerisation of two C_4 units, for example, and the further dimerisation of the resulting C_6-C_2 compound (e.g. vinylcyclohexene) would give pyrene having 4.0 labelled carbon atoms. But if it is formed from two C_6-C_2 units such as styrene, or from phenethyl radicals, then its activity would be equivalent to ca. 0.58 labelled atoms or less. The experimental figure of 1.96 labelled carbon atoms suggests that both processes may operate.

Earlier work[90,94] has suggested that hydrocarbons such as fluoranthene, 3,4-benzofluoranthene, and 2,3-(o-phenylene)pyrene might be formed predominantly by the phenylation of precursors of naphthalene, phenanthrene, and pyrene respectively, followed by cyclodehydrogenation (CXLIII)-(CXLV). Phenylation of a suitable naphthalene

precursor would be expected to give fluoranthene (CXLVI)
having 1.13 labelled atoms (naphthalene 1.00; benzene 0.13);
the fluoranthene isolated was found to have 0.92 labelled
atoms.   The phenylation of an appropriate phenanthrene
precursor (and subsequent cyclodehydrogenation) would be
expected to lead to 3,4-benzofluoranthene (CXLVII) having
0.68 labelled atoms (phenanthrene 0.55; benzene 0.13); the
material isolated had 0.62 labelled atoms.   Similarly the
phenylation of a suitable pyrene precursor would be expected
to lead to 2,3-(o-phenylene)pyrene (CXLVIII) having
2.09 labelled atoms (pyrene 1.96; benzene 0.13); and the
material isolated had 2.21 labelled atoms.   These results

(CXLVI)   (CXLVII)   (CXLVIII)
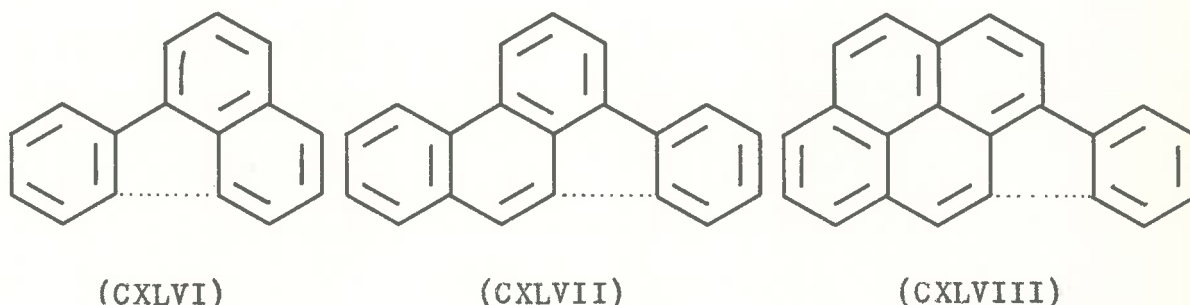
are therefore in agreement with the postulation that these
are the major routes to the hydrocarbons in question.

          Two fluorenes were isolated in the present study and
subjected to radiochemical analysis.   If fluorene (XXVI)
is formed from toluene by phenylation followed by cyclisation
as shown in (102), then it should have about 0.25 labelled
carbon atoms (toluene 0.12; benzene 0.13).   In fact the
fluorene was found to have 0.22 labelled atoms so this route

seems to be confirmed.

(102)
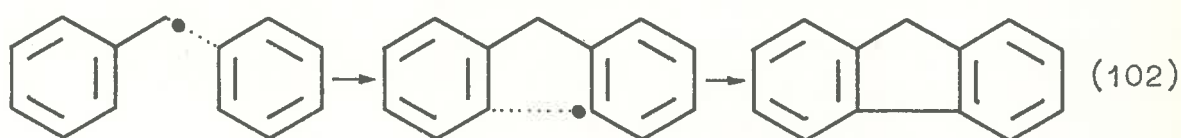
(XXVI)

Similarly, the formation of 2,3-benzofluorene (CXLIX) from toluene and a naphthyl radical, followed by cyclodehydrogenation (103) would give a product having 1.12 labelled carbon atoms, and experimentally 1.24 labelled atoms were found.   An alternative route involving methylation of 2-phenylnaphthalene would give a product of somewhat greater activity, and this latter route may well be important.   2,3-Benzofluorene could also be formed from fluorene and a C_4 unit.   This would give a product having 1.22 labelled carbon atoms.

(103)
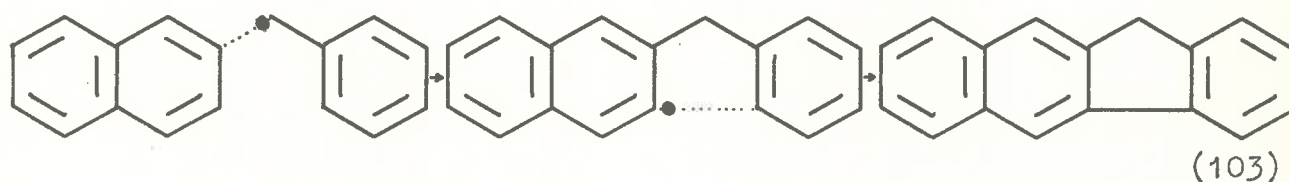
(CXLIX)

It was suggested previously[88,94] that chrysene (XI) could be formed from two C_6-C_3 units (LXXXII), from two C_1-C_6-C_2 units (LXXXIV), or from a C_6-C_4 and a C_6-C_2 unit (LXXXIII).   The latter route which is equivalent to

an attack on naphthalene by phenethyl radicals, would be expected to give chrysene having <u>ca</u>. 1.29 labelled carbon atoms (butylbenzene 1.00; styrene 0.29); and the average distribution would be approximately as shown in (CL). The chrysene isolated in the pyrolysis of [$\underline{6}$-^{14}C]butylbenzene was found to have 1.18 labelled carbon atoms, and this is in reasonable agreement with the expected activity. The distribution of the labelled carbon atoms was ascertained by degrading chrysene by oxidation to give chrysa-1,2-quinone (CLI), which was found to have 1.18 labelled atoms. Alkali fusion of the quinone gave <u>o</u>-(2-naphthyl)benzoic acid (CLII, 1.14 labelled atoms) and 2-phenyl-1-naphthoic acid (CLIII, 1.16 labelled atoms). Decarboxylation of the former acid gave carbon dioxide (0.01 labelled atoms) and 2-phenylnaphthalene (LXXIII, 1.13 labelled atoms). The expected activity of 2-phenylnaphthalene derived from (CL) would be equivalent to 1.22 labelled carbon atoms. It is therefore concluded that the route indicated by (LXXXIII) must be an important one in the formation of chrysene from butylbenzene.
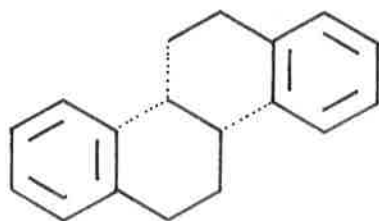
(LXXXIII)
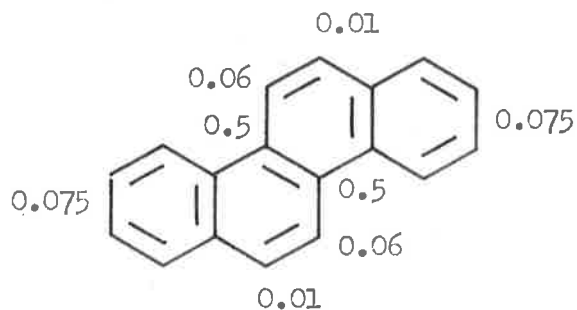
(CL)
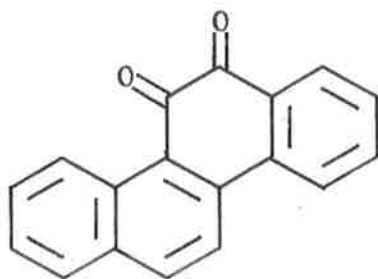
(CLI)
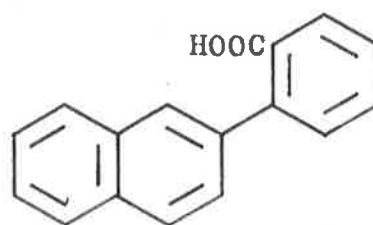
(CLII)
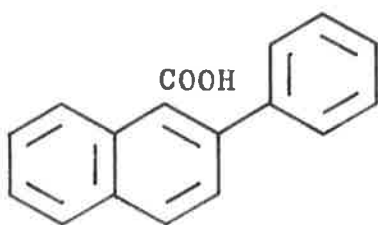
(CLIII)
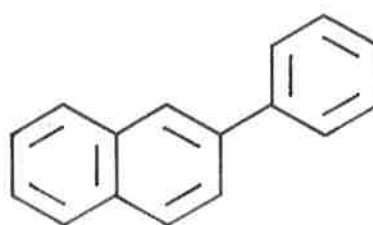
(LXXIII)

1,2-Benzanthracene (VII) could also be formed from a C_6-C_4 unit and a C_6-C_2 unit (as in LXXXVI), or from naphthalene and a phenethyl radical. The latter mechanism would give 1,2-benzanthracene having 1.29 labelled carbon atoms. The hydrocarbon isolated from the tar had 1.15 labelled atoms, and it seems that this route may be the preferred one. A somewhat similar mechanism would explain the activity found for 3,4-benzotetraphene (2.16 labelled atoms). The reaction of a C_6-C_2 unit with a $C_4-C_6-C_4$ unit, for example (CLIV), would be expected to give 3,4-benzotetraphene having 2.29 labelled carbon atoms.
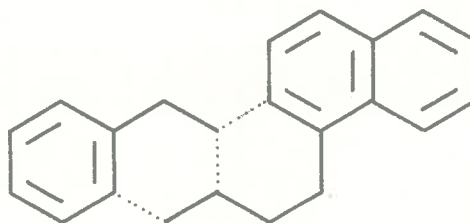
(LXXXVI)   (CLIV)

The mode of formation of the carcinogenic hydrocarbon 3,4-benzopyrene (I) is of special interest.   As a working hypothesis, it was suggested[e] that this hydrocarbon could be formed from two C_6-C_4 units as in equation (104), and subsequent work has tended to confirm this view.[191,230] This implies that 3,4-benzopyrene formed in the present pyrolysis should have 2.0 labelled carbon atoms, distributed as in (CLV).   In fact, the hydrocarbon isolated was found to have 1.92 labelled atoms, and the distribution was determined by degradation by firstly oxidising 3,4-benzopyrene to 3,4-benzopyrene-6,7-quinone (CLVI; found, 1.92 labelled atoms).   This was then oxidised and decarboxylated (carbon dioxide, 0.87 labelled atoms) to give chrysene (1.12 labelled atoms).   The results are therefore in agreement with the proposed mechanism by equation (104).

(104)

(I)
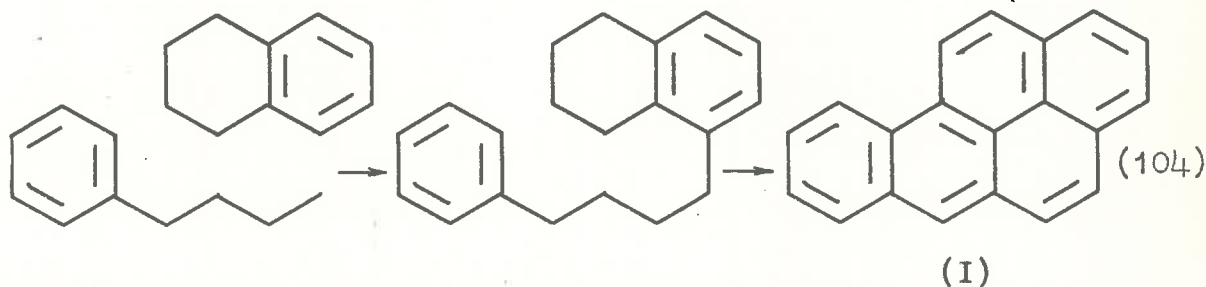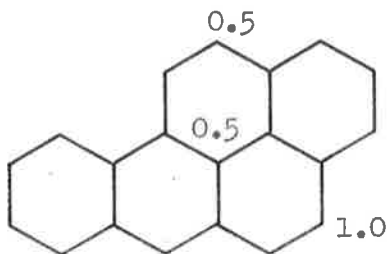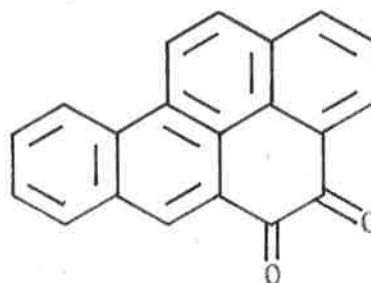
(CLV)   (CLVI)

It was previously suggested that 3,4-benzopyrene (I) could also be formed by a combination of benzyl and perinaphthenyl radicals as shown in (CLVII), followed by cyclodehydrogenation.
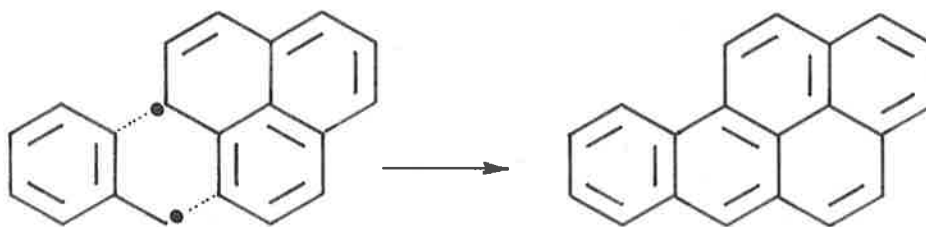
(CLVII)   (I)

Although this proposition seemed attractive since both benzyl and perinaphthenyl radicals have been identified during the pyrolysis of various hydrocarbons,[212] the distribution of activity in 3,4-benzopyrene, if formed by this method, would differ from the distribution expected by the previous hypothesis shown in (CLV). The activity of the toluene (and thus that of the benzyl radical) is known to be 0.12 active carbon atoms (0.07 in the side chain and

0.03 in the ring). Assuming that the perinaphthenyl
radical is formed by an addition of a C_3 unit to naphthalene
(or an appropriate precursor) as shown in (CLVIII) the
distribution of the labels in the perinaphthenyl radical due
to the naphthalene contribution may be calculated. This
is shown in (CLIX). The distribution of activity in the
C_3 unit will depend on its mode of formation. If formed
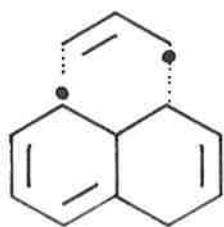
(CLVIII)
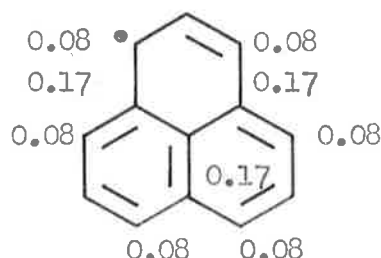
(CLIX)

by addition of ethylene to methyl radicals, each of the
carbon atoms would have an activity equivalent to 0.25
active atoms; if, on the other hand, it is obtained
directly from the side chain, its activity is likely to be
equivalent to 1 active carbon atom - distributed between
the terminal carbon atoms of the C_3 unit. Assuming that
both these mechanisms operate to an equal degree in the
formation of a C_3 unit, the total distribution of activity
in perinaphthenyl radical (CLX), and hence in
3,4-benzopyrene (CLXI), may be calculated. This
distribution is quite different from that obtained on
degradation of 3,4-benzopyrene, and in the pyrolysis of

[*δ*-¹⁴C]butylbenzene this mode of formation, therefore, cannot be of great importance. This mechanism can, nevertheless, explain the unequal distribution of labels between the carbons 6 and 7, and the rest of the 3,4-benzopyrene molecule.
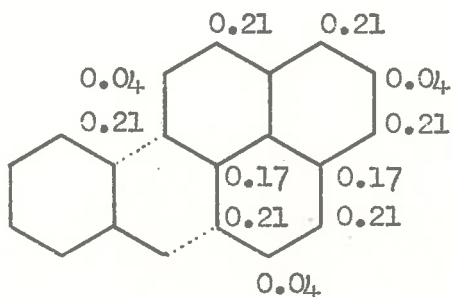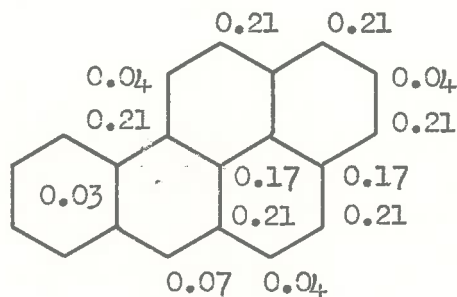
(CLX)   (CLXI)

1,2-Benzopyrene (X) could also be formed in a similar way from two C_6-C_4 units (CLXII). This implies that 1,2-benzopyrene isolated following the pyrolysis of [*δ*-¹⁴C]butylbenzene should have 2.00 labelled carbon atoms.
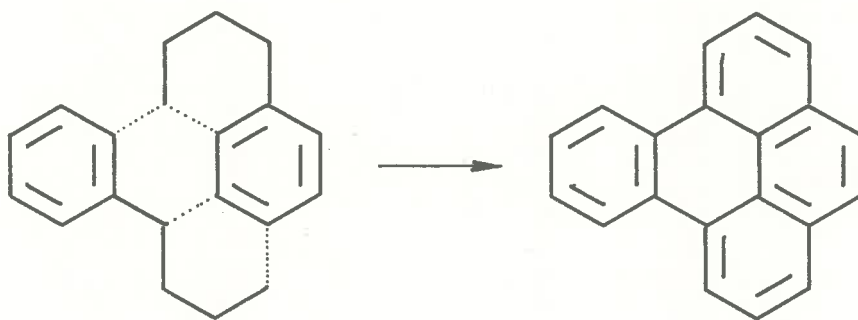
(CLXII)   (X)

The material isolated was in fact found to have activity corresponding to 2.0 labelled atoms, and it may be concluded therefore that the route suggested for the formation of this hydrocarbon is probably an important one.

CHAPTER 6

THE PYROLYSES OF n-BUTYLBENZENE OVER A RANGE OF TEMPERATURES FROM 300-900°C AT 50° INTERVALS

6.1   INTRODUCTION

The formation of polycyclic hydrocarbons in pyrolytic reactions is dependent on temperature.   The original purpose of this investigation was, therefore, to search for the best thermal conditions for the formation of 3,4-benzopyrene;   the decision to include all polycyclic hydrocarbons with three or more five- or six-membered rings was arrived at later.   It was hoped that some information might be obtained about the conditions required for the formation of coronene - a hydrocarbon which is found in relatively large quantities in polluted atmosphere, but which has not been isolated from tars obtained below and at 700°C, except in the pyrolysis of n-decane (cf. Chapter 4).

n-Butylbenzene was the hydrocarbon of choice since its behaviour in pyrolytic reactions at 700°C was known[20] and since it was easily obtainable in pure state.   Equal amounts of this hydrocarbon have been pyrolysed as described before, varying the temperatures from 300-900°C at 50° intervals.

6.2   RESULTS AND DISCUSSION

The results are summarised in Table 6.1.   The first
column of this table indicates the temperature of the
pyrolysis.   The yields of tar in grams, and as a
percentage, obtained following pyrolysis of five grams of
n-butylbenzene, are given in the second and third columns of
the table.   The remaining part of the table is devoted to
the yields of hydrocarbons which have been identified in the
tars.   Fifteen polycyclic hydrocarbons were systematically
studied over the whole range of temperatures.   The presence
of naphthalene, and of 2,3- and 3,4-benzofluorenes in the tars
was also noted, but the yields of these compounds were not
calculated.   Two sets of values appear with each
hydrocarbon, for each temperature, in the table.   The first
indicates the amount of hydrocarbon as a percentage of tar
formed at a particular temperature whereas the other figure
is the amount of hydrocarbon expressed as a percentage of
the starting material.

By plotting the yields of tars formed from a constant
weight (5 g. in each experiment) against the temperature,
a graph was obtained which showed that the yields of tar did
not change appreciably until 500°C, but decreased rather
rapidly from 500-800°C remaining almost constant at still
higher temperatures (Figure 6.1).   Any small variation in
temperature within the middle range would therefore have a

Table 6.1

Temperature in °C	Tar formed in grams	Tar formed in percent	Naphthalene	Acenaphthylene	Fluorene	Phenanthrene	Anthracene	Pyrene	Fluoranthene	1,2-Benzanthracene	3,4-Benzofluorene	2,3-Benzofluorene	Chrysene	10,11-Benzofluoranthene	1,2-Benzopyrene	3,4-Benzopyrene	3,4-Benzofluoranthene	11,12-Benzofluoranthene	1,12-Benzoperylene	2,3-(o-Phenylene)pyrene
300	4.044	80.9																		
350	4.136	82.7																		
400	3.990	79.8				0.009			Trace											
						0.007			Det.											
450	4.198	84.0	Det.		Trace	0.018			0.001		Det.	Det.					Trace			
					Det.	0.015			0.001								Det.			
500	3.535	70.7	Det.		Trace	0.067			0.008		Det.	Det.	Trace	Trace			0.002			
					Det.	0.047			0.006				Det.	Det.			0.001			
550	3.249	65.0	Det.	0.023	0.004	0.394	0.006	0.005	0.043	Trace	Det.	Det.	0.084	0.0005			0.003			
				0.015	0.0025	0.256	0.004	0.003	0.028	Det.			0.013	0.0003			0.002			
600	2.152	43.0	Det.	0.106	0.012	2.994	0.080	0.046	0.133	0.012	Det.	Det.	0.182	0.007	0.004	0.003	0.015	0.001		
				0.046	0.005	1.287	0.034	0.020	0.057	0.005			0.078	0.003	0.002	0.001	0.006	0.0004		
650	1.325	26.5	Det.	0.067	0.120	5.644	0.214	0.131	0.128	0.135	Det.	Det.	0.836	0.020	0.007	0.027	0.020	0.015	0.009	0.007
				0.018	0.032	1.496	0.057	0.035	0.034	0.036			0.222	0.005	0.002	0.007	0.005	0.004	0.002	0.0015
700	0.534	10.7	Det.	0.876	0.627	13.645	0.551	0.438	0.743	0.162	Det.	Det.	1.564	0.100	0.124	0.164	0.161	0.111	0.107	0.044
				0.094	0.067	1.460	0.059	0.047	0.080	0.017			0.167	0.011	0.013	0.018	0.017	0.012	0.011	0.005
750	0.333	6.7	Det.	0.219	0.502	13.232	0.754	0.692	2.664	0.127	Det.	Det.	1.402	0.132	0.111	0.197	0.411	0.063	Trace	0.080
				0.015	0.037	0.886	0.051	0.046	0.178	0.009			0.094	0.009	0.007	0.013	0.028	0.004	Det.	0.005
800	0.025	0.5			Trace	15.848	Trace	1.572	4.448	0.836			2.600	0.248	0.203	0.396	0.541	0.121		
					Det.	0.079	Det.	0.008	0.022	0.004			0.013	0.001	0.001	0.002	0.003	0.0006		
850	0.015	0.3				5.319		1.126	31.913				0.853				0.533			
						0.016		0.003	0.009				0.0026				0.0016			
900	0.009	0.18				4.740		0.644	1.911				Trace				Trace			
						0.008		0.001	0.003				Det.				Det.			

TAR
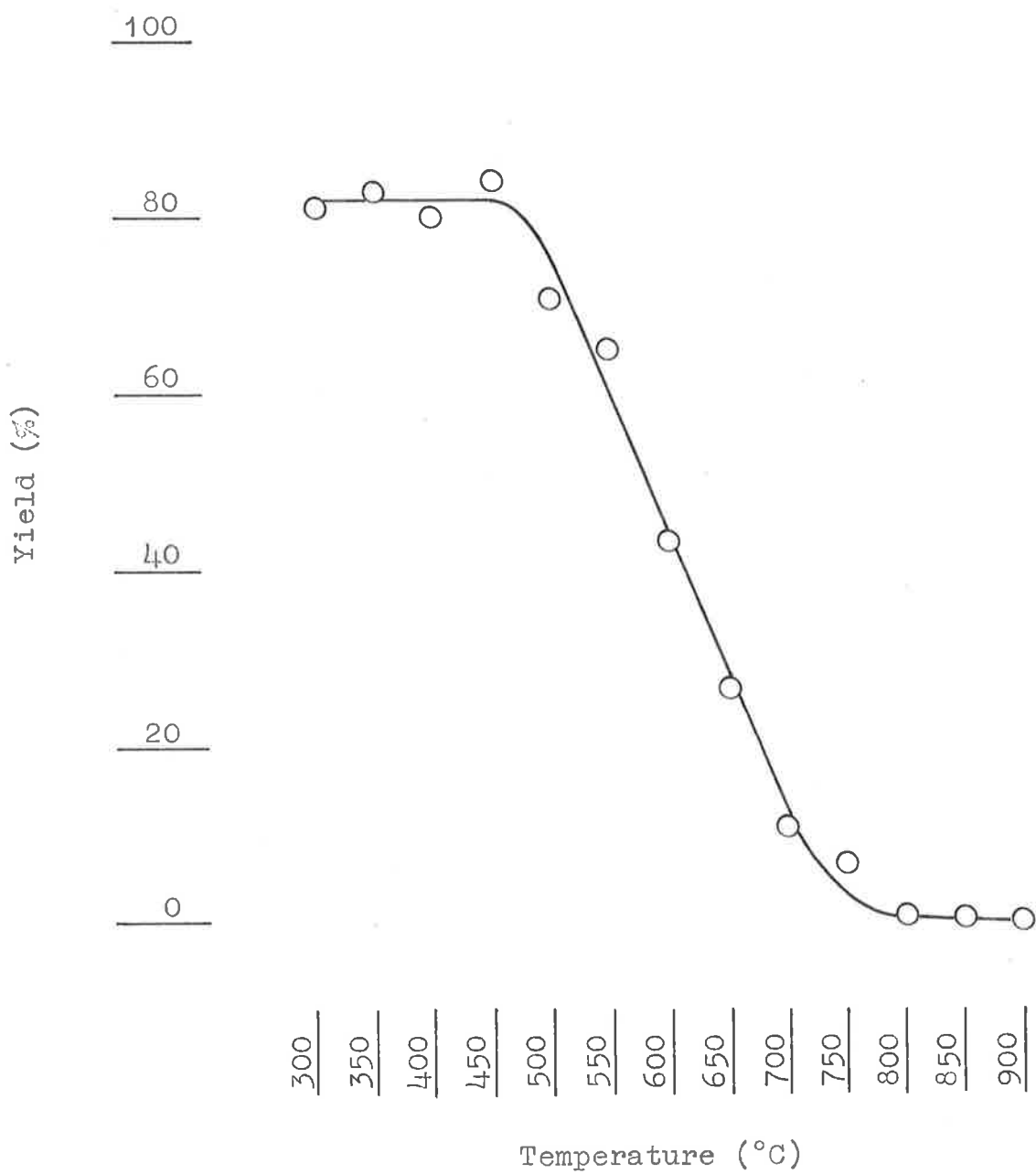
Figure 6.1

marked influence on the yields of tar.

The separation of the hydrocarbons and their quantitative determination is described in the Experimental.

Phenanthrene was the major product in this investigation, followed by chrysene and fluoranthene. All these hydrocarbons have been detected over a wide range of temperatures from 400-900°C for phenanthrene and fluoranthene and from 500-900°C for chrysene. By plotting the yields of phenanthrene against the temperature a curve was obtained (Figure 6.2) from which the optimum temperature for the formation of phenanthrene was determined. The point of intersection of the two straight lines obtained by extrapolating the slopes of the sides of this curve, lies in the vicinity of 660°C.

Similar curves were obtained, and optimum temperatures determined, for the remaining hydrocarbons. These are summarised in Figures 6.3-6.6 and in Table 6.2, respectively. With the exception of the values at 650°C for acenaphthylene and at 650° and 700°C for fluoranthene and 3,4-benzofluoranthene (which seem to be low), the curves are presented without further comment.

PHENANTHRENE
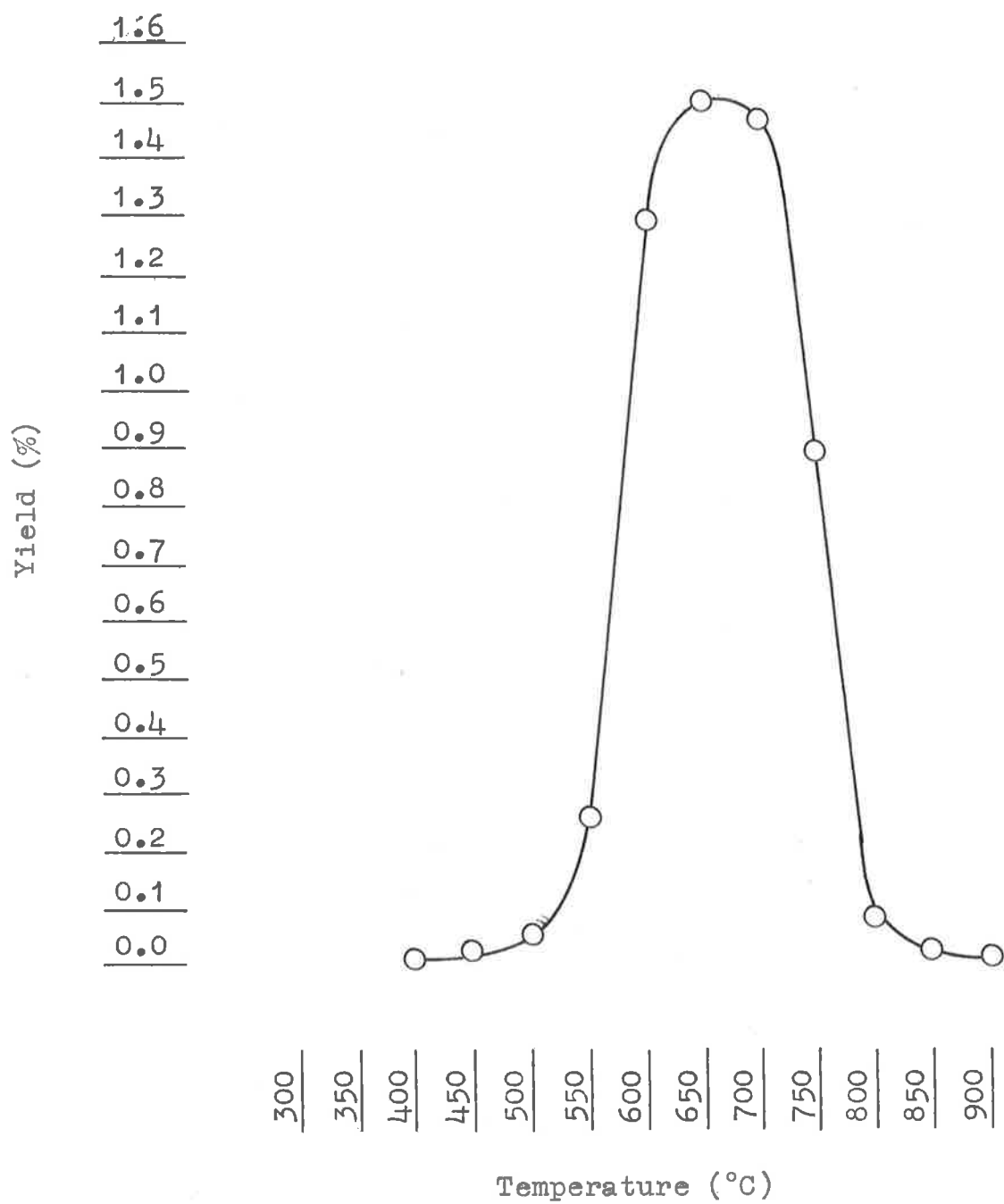
Figure 6.2
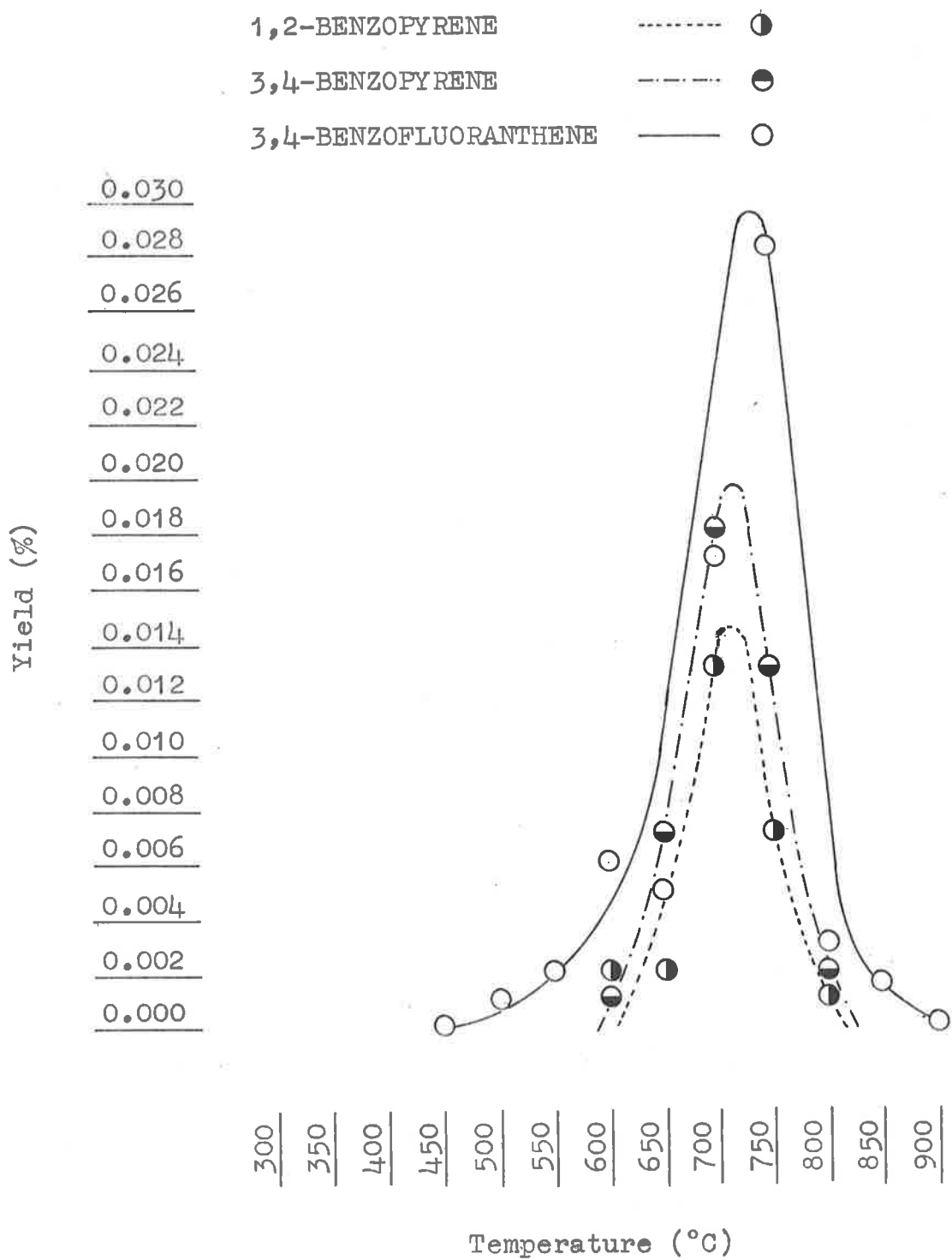
Figure 6.3
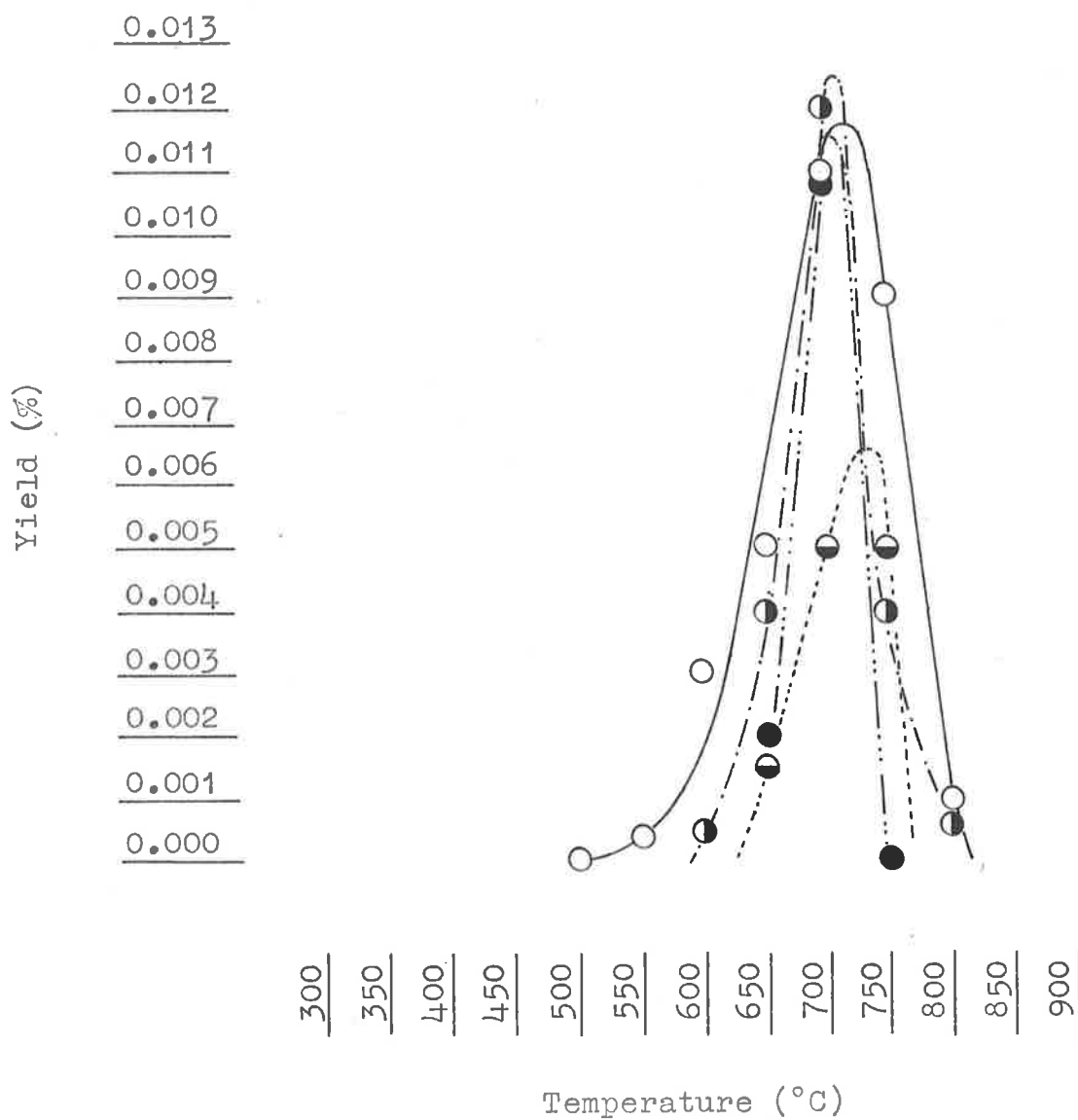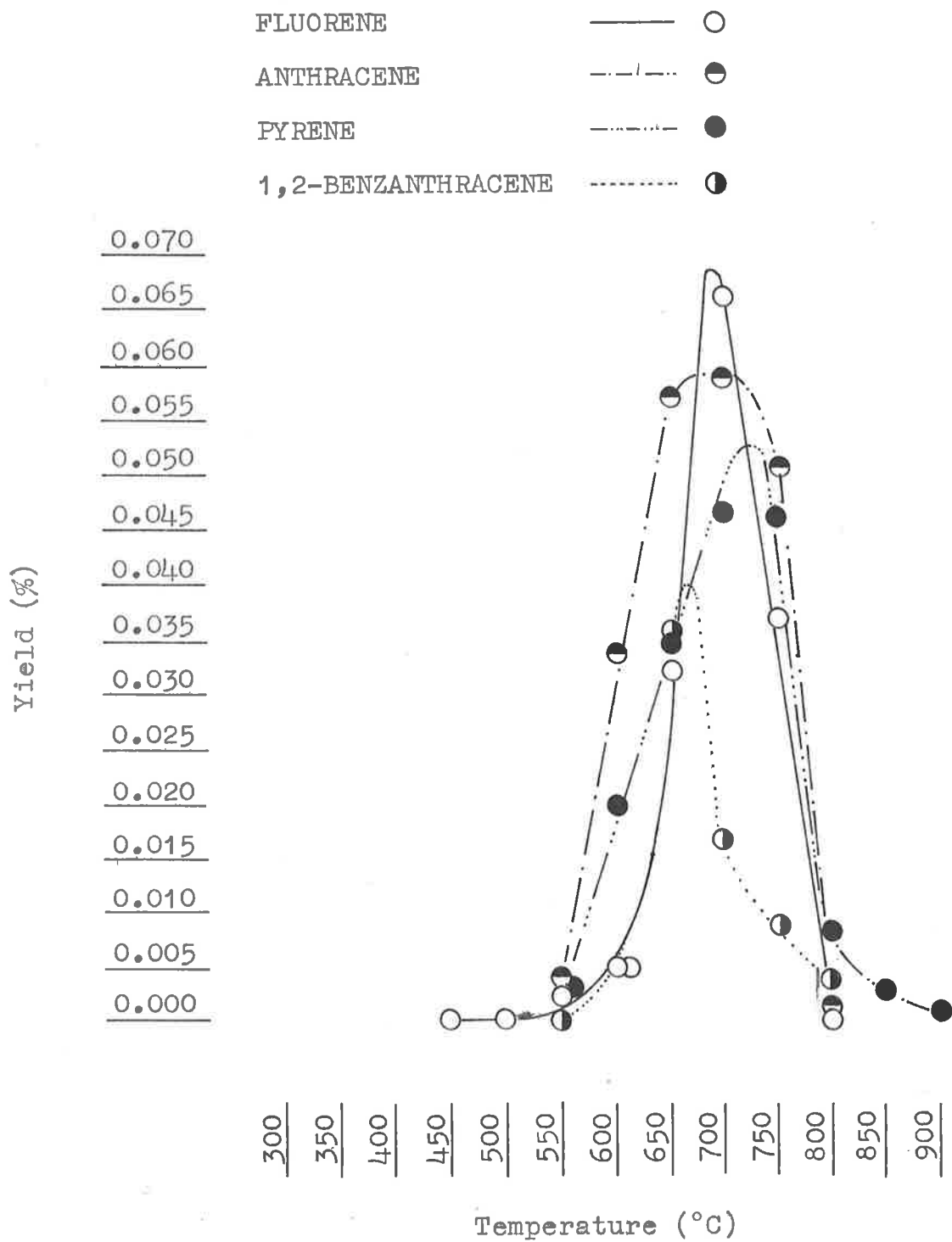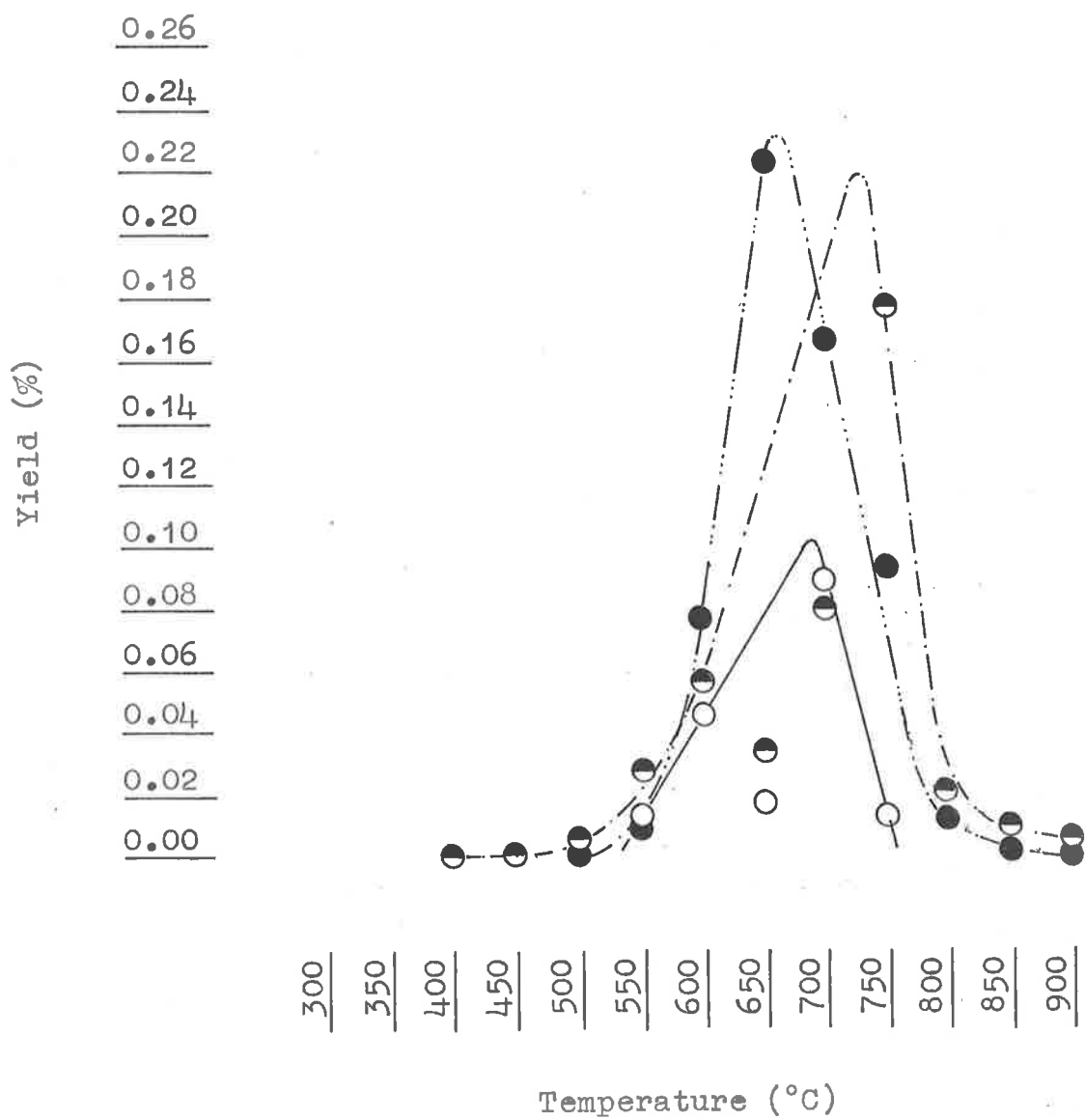
Figure 6.4

Figure 6.5

Figure 6.6

Table 6.2

OPTIMUM TEMPERATURES FOR THE FORMATION OF POLYCYCLIC AROMATIC
HYDROCARBONS IN THE PYROLYSIS OF n-BUTYLBENZENE

Temperature	Hydrocarbon
660°C	1,2-Benzanthracene
	Chrysene
	Phenanthrene
690°C	Acenaphthylene
	Anthracene
	Fluorene
710°C	1,2-Benzopyrene
	3,4-Benzopyrene
720°C	10,11-Benzofluoranthene
	11,12-Benzofluoranthene
	1,12-Benzoperylene
730°C	3,4-Benzofluoranthene
	Fluoranthene
740°C	2,3-(o-Phenylene)pyrene
	Pyrene

CHAPTER 7

EXPERIMENTAL

7.1   INTRODUCTION

The experiments are described in the same order as they were carried out, and any variations in the experimental procedure will be mentioned.

7.2   PYROLYSIS APPARATUS

The pyrolysis apparatus (see Figure 7.1) consisted of two concentric tubes.   The outer silica tube (3 ft. × 1 in. internal diameter) was wound with 25 s.w.g. Nichrome wire (resistance 90 ohms), and mounted along the centre of a pressed asbestos-board box (3 × 1 × 1 ft.) filled with "vermiculite".   The material to be pyrolysed was passed through an inner silica tube (3 ft. 6 in. × $\frac{3}{4}$ in. internal diameter).   The inner tube was packed with porcelain chips. The temperature of the furnace was controlled by a Variac transformer and was initially adjusted to 700°C, using a calibrated chromel-alumel thermocouple inside the inner tube. The temperature during the pyrolysis was controlled to give constant reading on a second chromel-alumel thermocouple inserted through a small hole bored near the centre of the

PYROLYSIS APPARATUS

Dry N$_2$
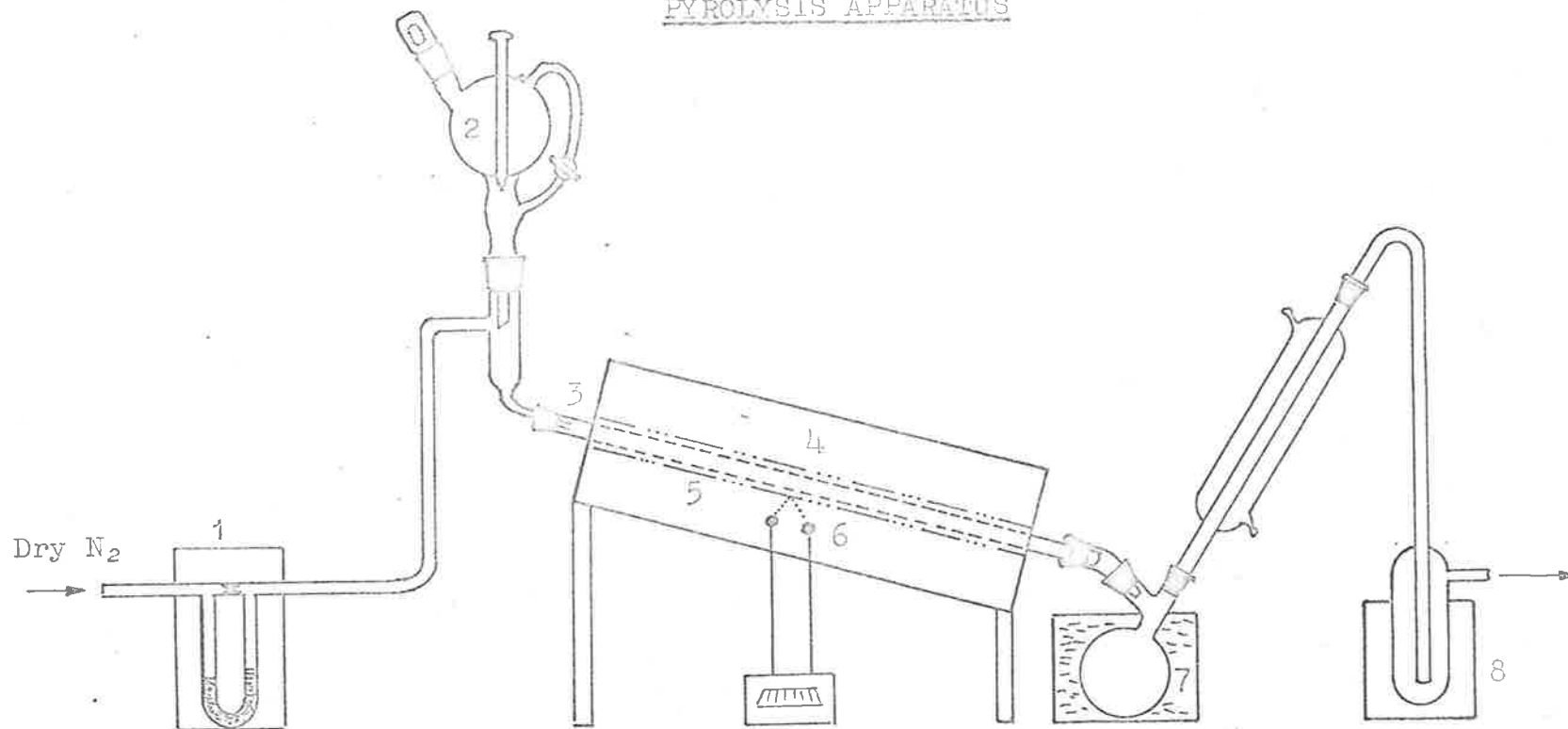
1 Flow meter   3 Silica tube   5 Outer tube   7 Ice-salt bath

2 Needle-valve 4 Furnace   6 Thermocouple 8 Dry-ice bath

Figure 7.1

outer tube, corresponding to a temperature of 700°C inside the inner tube. The whole furnace was inclined at an angle of approximately 15° to the horizontal to facilitate the collection of products.

The material to be pyrolysed was introduced directly into the pyrolysis tube from a dropping funnel fitted with a needle-valve to control the rate of addition. In the pyrolysis of 4-vinylcyclohexene, the material was first introduced into a flash evaporator to avoid the risk of pre-polymerisation. The flash evaporator used was a Pyrex tube kept at 360°C in a bath of Wood's metal.

All pyrolyses were carried out under nitrogen, dried by successive passage through concentrated sulphuric acid, potassium hydroxide and calcium chloride traps. The pyrolysis products were collected in a receiving flask fitted with a water condenser, followed by two traps containing solid carbon dioxide-ethanol mixtures and one trap containing liquid air.

7.3   ANALYTICAL TECHNIQUES

Gas-Liquid Partition Chromatography.- A Griffin and George vapour-phase chromatographic apparatus (Mark II), modified to collect samples[232] was used in the isolation of compounds boiling below 260°C. Either Apiezon L supported on Celite (40-80 mesh, 1:4 w/w) or Silicone 30 supported on

Celite (40-80 mesh, 1:4 w/w) was used as stationary phase depending on the sample to be analysed, and dry nitrogen as carrier gas.   The identity of individual compounds was established where possible by infrared spectroscopy and by retention time ratios, but where the amount of compound present was insufficient to allow further identification, the latter procedure alone was employed.

The relative amounts of the components in the fractions were determined from the areas under the peaks (height × width at half peak height).

The above-mentioned apparatus was used to collect samples only when the volume of the fraction amounted to less than 1 c.c. per component.   In all other cases individual compounds were collected using a Beckman Megachrom. Apiezon J supported on firebrick (C-22, 3:7 w/w) was used as stationary phase and dry nitrogen as carrier gas.

Chromatography on Alumina.-   The residue obtained on distillation of the tar was chromatographed on a column of Spence alumina using 100 g. of alumina per gram of tar.   All eluents used were redistilled and dried, hexane, thiophen- free benzene and chloroform being the main solvents required. The best resolution of components was obtained by introducing the residue, adsorbed on an equal amount (w/w) of alumina, on to the column.

Paper Chromatography.- The partially acetylated paper used was prepared by the method of Spotswood.[233,234] The papers were developed with a mixture of ethanol-toluene-water (17:4:1; v/v) by the descending technique. Fluorescent compounds were located by observation with ultraviolet light, and non-fluorescent compounds by spraying the chromatogram with a 2% solution of tetrachlorophthalic anhydride in a mixture of acetone and chlorobenzene (10:1; v/v) followed by examination with ultraviolet light. Under these conditions many non-fluorescent compounds gave spots varying in colour from bright yellow to orange, while the fluorescent spots remained distinguishable.

Chromatography on Columns of Partially Acetylated Cellulose.- The cellulose powder used was acetylated by the method of Spotswood.[234] The solvent systems used for elution were ethanol-benzene-water (17:4:1; v/v) and/or ethanol-toluene-water (17:4:1; v/v). The compounds were introduced on to the column in the same solvent system used for development. It was found that good resolution of a mixture of hydrocarbons having a reasonable difference in R_f values, was obtained using 100 g. of acetylated cellulose per 100 mg. of the mixture.

Thin Layer Chromatography.- Thin layer chromatography on alumina, silica gel, and partially acetylated cellulose[235] was employed prior to the use of the

appropriate column chromatography in the latter experiments.
The plates (20 x 20 cm.), prepared using a "Desage"
spreading device adjusted to give a layer of 275 μ
thickness, were developed by the same solvent systems as the
corresponding columns.

Ultraviolet Spectra.-   These were determined in
95% ethanol, using an Optica CF₄ recording spectrophotometer.

Infrared Spectra.-   These were determined either
on a Grubb Parsons Model S₄ double beam spectrophotometer or
on a Perkin-Elmer Model 137 Infracord spectrophotometer.
The measurements were made as solutions in carbon
tetrachloride or as liquid films.

Fluorescence Spectra.-   These were determined on
a Farrand Model 104242 spectrofluorimeter.   The best
resolution was usually obtained using hexane as solvent.

Identification of Products.-   The products isolated
by chromatography on partially acetylated cellulose or
acetylated paper, were identified mainly by comparison of
their ultraviolet, infrared, and fluorescence spectra with
those of authentic specimens or with published spectral
data where suitable standards were not available.[230]
Where possible, the identity of a compound was confirmed by
determining its melting point and mixed melting point.

<u>Quantitative Determination of Products</u>.— The
relative amounts of the compounds present in the pyrolysis
products were determined by direct weighing; however, for
relatively small amounts or for mixtures which could be
separated only with difficulty, the measurement of the
intensities of suitable peaks in the ultraviolet absorption
spectra was preferred. The calculation was carried out
by using a table of extinction coefficients showing the
contribution to the optical density at the maxima of a
solution containing 1 μg./c.c. of a compound. Table 7.1
lists the values which were determined under the
experimental conditions by Spotswood[237] and extended in the
present investigation. The relative concentrations of
unseparated mixtures were determined from the absorption
curve of the mixture by solving the simultaneous equations
obtained for the optical density at two or more points of
the spectrum.

The general scheme for the separation of a
pyrolysis product is shown in Figure 7.2.

<u>Melting Points</u>.— All melting points, with the
exception of samples in evacuated capillaries, were
determined on a Zeiss hot stage microscope.

<u>Radioactive Assay</u>.— Specimens were assayed for
radioactivity, with an end-window counter, as infinitely
thick, solid samples of 1 cm.^{2} cross-sectional area,[94] and

Table 7.1

CONTRIBUTIONS TO THE OPTICAL DENSITY OF SOLUTIONS CONTAINING 1 μg./c.c. OF A COMPOUND

Compound	Wavelength (mμ)	Optical Density	Compound	Wavelength (mμ)	Optical Density
Acenaphthylene	323	0.055	Perylene	406	0.084
	334	0.026		434	0.120
	340	0.027	1,2-Benzopyrene	317	0.088
Fluorene	260	0.116		333	0.150
	301	0.059	3,4-Benzopyrene	365	0.092
Phenanthrene	252	0.362		385	0.105
	275	0.075		404	0.013
	282	0.058	3,4-Benzofluoranthene	294	0.084
	294	0.078		301	0.160
Anthracene	253	1.05		351	0.036
	323	0.006	11,12-Benzofluoranthene	297	0.170
	339	0.011		309	0.210
	357	0.023		380	0.044
	377	0.031		402	0.047
Pyrene	274	0.260	1,12-Benzoperylene	289	0.126
	306	0.050		300	0.175
	319	0.140		363	0.062
	335	0.260		384	0.083
Fluoranthene	236	0.250	2,3-(o-Phenylene)pyrene	304	0.132
	263	0.065		316	0.118
	278	0.108		361	0.059
	288	0.220		378	0.050
1,2-Benzanthracene	278	0.305		386	0.042
	289	0.402	Anthanthrene	233	0.281
2,3-Benzofluorene	255	0.232		307	0.292
	264	0.310		430	0.256
	317	0.090	Coronene	302	0.736
	340	0.032		339	0.175
Chrysene	267	0.640			
	320	0.057			
10,11-Benzofluoranthene	318	0.125			
	333	0.053			
	365	0.031			
	383	0.052			

GENERAL SCHEME FOR THE SEPARATION OF A PYROLYSIS PRODUCT

Pyrolysis product

Distillation

b.p. < 260°C   b.p. > 260°C

b.p. < 260°C branch:

gas-liquid chromatography

→ infrared spectra / ultraviolet spectra

b.p. > 260°C branch:

alumina chromatography

- gas-liquid chromatography → infrared spectra / ultraviolet spectra
- cellulose acetate column chromatography
- deactivated alumina → Residue (Picrate) → deactivated silica gel → Residue

cellulose acetate column chromatography →
- ultraviolet spectra, m.p., mixed m.p., fluorescence spectra
- paper chromatography
- cellulose acetate column chromatography

counting rates were corrected for background and dead time
of the instrument. The counting equipment consisted of
an EKCO automatic scaler type N530D, in conjunction with
an EKCO probe unit type N 558 and an EW 3H Geiger tube.

7.4 PYROLYSIS OF [1-^{14}C]TETRALIN

Radioactive Assay.- Specimens were assayed for
radioactivity using the method previously described.[94]
The statistical counting error was calculated as standard
deviations for each series of counts and, with the exception
of benzene, was not greater than 2%.

[carboxy-^{14}C]Phenylbutyric Acid.- Barium
[^{14}C]carbonate (12.0 mc; 166.8 mg.) was diluted with inactive
barium carbonate (6.04 g.) and placed in a flask attached
to a vacuum line. The carbon dioxide evolved on addition
of sulphuric acid to the solid was condensed in a flask
cooled in liquid air, and then dried by distillation from
a bath maintained at -80°C. A Grignard reagent, prepared
from 1-bromo-3-phenylpropane[238] (6.18 g.), magnesium (0.75 g.)
and anhydrous ether (50 c.c.), was diluted with benzene
(20 c.c.) and the reaction flask attached to the vacuum line,
cooled in liquid air and the system evacuated. The flask
was then warmed to -20°C, using a bath of solid carbon
dioxide-ethanol and allowed to equilibrate for 10 min.
The solution was stirred magnetically and the ^{14}C carbon

dioxide introduced into the reaction flask. When most of
the carbon dioxide had reacted, the bath temperature was
lowered over a period of 15 min. to -70°C with continued
stirring. The excess carbon dioxide was re-condensed and
the reaction flask removed from the line. The Grignard
complex was decomposed with 20% sulphuric acid (20 c.c.) at
-20°C, and the aqueous layer extracted with ether. The
combined organic layers were extracted with 10% aqueous
sodium hydroxide (3 × 25 c.c.) and the resulting solution
treated dropwise with concentrated sulphuric acid. The
acidified mixture was extracted with ether (2 × 25 c.c.),
washed with water, dried over magnesium sulphate and the
ether evaporated. Recrystallisation of the residue from
light petroleum (b.p. 30-40°C) gave [carboxy-^{14}C]phenylbutyric
acid (2.8 g.).

[1-^{14}C]Tetralone.- Phosphorus pentachloride (5 g.)
was added over a period of one minute to a stirred ice-cold
solution of the above acid in benzene (10 c.c.). The
mixture was then warmed to boiling and heated under reflux
(5 min.), cooled to -15°C and stannous chloride (5 c.c.) in
benzene (5 c.c.) added dropwise with the temperature
maintained below 0°C. Stirring was continued (45 min.)
and a mixture of ice and concentrated hydrochloric acid
added. The whole was then heated under reflux with
vigorous stirring (1 hr.), cooled, the organic layer
separated and the aqueous phase extracted with benzene (3 ×

15 c.c.).   The combined organic solution was washed
successively with water, 10% aqueous sodium carbonate,
water, aqueous sodium chloride and dried over calcium
sulphate.   Evaporation of the solvent in a stream of dry
air gave crude [1-^{14}C]tetralone.

[1-^{14}C]Tetralin.-   A mixture of the above tetralone,
"AnalaR" acetic acid (8 c.c.), 70% perchloric acid (9 drops),
and 5% palladium on charcoal (2 g.) was hydrogenated for
10 hr. at a pressure of 50 lb./in.^{2} in a Cook and Son's
low-pressure hydrogenator adapted for semimicro work.   The
catalyst was removed by filtration through a sintered glass
funnel, and washed with ethanol (5 c.c.).   The filtrate
was made alkaline with sodium hydroxide solution and extracted
with ether (2 x 10 c.c.).   The ethereal extract was washed
with water, dried and evaporated, the residue diluted with
purified inactive tetralin (25 g.), and the mixture
distilled.   Further quantities of inactive tetralin were
added from time to time, until the residue on testing was
found to be inactive.   At this stage half the distillate
(approx. 50 g.) was diluted with inactive tetralin to give
[1-^{14}C]tetralin (500 g.) b.p. 207-208°C, n_D^{21} 1.5404 (lit.,[230]
n_D^{20} 1.5402) which on Van Slyke-Folch oxidation gave barium
carbonate which was collected for radioactive assay (Found:
relative molar activity x 10^{-2}, 22.2 ± 0.24).

Degradation of [1-^{14}C]Tetralin.-   A mixture of

[1-^{14}C]tetralin (1 g.) and nitric acid (d. 1.2; 200 c.c.) was heated under reflux (12 hr.). Solid nitration products which separated on cooling were removed by filtration and the mother liquor extracted with potassium carbonate solution. The alkaline solution was acidified and continuously extracted with ether (12 hr.). Evaporation of the solvent and recrystallisation of the residue from water gave phthalic acid, m.p. 212-213°C (Found: relative molar activity $\times$ 10^{-2}, 21.5 $\pm$ 0.06; ^{14}C requires 22.2).

Pyrolysis of [1-^{14}C]Tetralin.- [1-^{14}C]Tetralin (500 g.) was pyrolysed under similar conditions to those described for the inactive compound.^{88} The active tetralin was vaporised (6 drops/min.) and passed in a stream of nitrogen (1 c.c./sec.) through the pyrolysis tube maintained at 700°C. The exit gases were passed through liquid air traps and then through bromine water. The pyrolysate (295 g.) was combined with chloroform washings from the pyrolysis tube (12 g. after the removal of chloroform), and the whole distilled to give fractions (a) b.p. 20-85°C/760 mm. (10 g.); (b) b.p. 85-100°C/760 mm. (15 g.); (c) b.p. 100-170°C/760 mm. (9 g.); (d) b.p. 95-100°C/20 mm. (255 g.); (e) b.p. 100-110°C/20 mm. (10.3 g.); and (f) a residue (87 g.).

Analysis.- Separation of the components of the various fractions was effected by gas-liquid chromatography,

chromatography on activated alumina and on columns of
partially acetylated cellulose, as previously described.[88]
Products obtained following chromatography on partially
acetylated cellulose often contained traces of resinous
material.   This was removed by repeating the chromatography
on alumina, or by the inclusion of a $2\frac{1}{2}$-5 cm. layer of
alumina at the base of the column of acetylated cellulose.

Fractions (a), (b), (c), (d), and (e).-   Fractions
(a) and (b) were examined by gas-liquid chromatography and
shown to contain benzene and toluene.   Fraction (c) was
found to contain benzene, toluene, ethylbenzene, styrene,
indene, and naphthalene.   Fractions (d) and (e) were found
to contain almost entirely naphthalene.

Examination of Residue.-   The residue (f) was
dissolved in chloroform, adsorbed on alumina (1 kg.) and the
solvent removed in vacuo.   The resulting solid mixture was
then added to a column (150 × 10 cm.) of alumina (7 kg.)
using hexane.   Elution with hexane (75 l.) gave 1 l.
fractions which were recombined on the basis of their
fluorescence spectra to give new fractions 1-20.   Further
elution of the column with mixed solvents gave the following
additional fractions: hexane-benzene (1:10, v/v; 16 l.),
fractions 21-27; hexane-benzene (1:4, v/v; 18 l.);
fractions 28-35; hexane-benzene (1:2, v/v; 20 l.),

fractions 36-44; hexane-benzene (1:1, v/v; 10 l.), fractions
45-48; and chloroform (15 l.), fractions 49-50. Using
the techniques described below, the following pure substances
or their derivatives were isolated for radiochemical
analysis.

ISOLATION AND RADIOCHEMICAL ANALYSIS

Ethylene.-   The liquid condensed in the liquid-air
trap (ca. 20 g.) was allowed to warm gradually (12 hr.) and
the gas evolved bubbled through bromine water using a sintered
glass bubbler.   The resulting solution was made alkaline
with potassium hydroxide, extracted with ether, and the
ethereal solution dried over calcium chloride.   Evaporation
of the ether and distillation of the residue gave ethylene
dibromide, b.p. 127-129°C/756 mm.   A sample was oxidised
by the Van Slyke-Folch technique and the resulting barium
carbonate collected for radioactive assay (Found: relative
molar activity x 10^{-2}, 6.1 ± 0.05; $1^{0}C$ requires 22.2).

Benzene.-   Isolated from fraction (a) by gas-
liquid chromatography using a Beckman Megachrom and shown to
be identical with an authentic specimen by infrared
spectroscopy.   Van Slyke-Folch oxidation gave barium
carbonate which was collected for radioactive assay (Found:
relative molar activity x 10^{-2}; 0.2 ± 0.06).

Toluene.-   Isolated from fraction (a) by gas-
liquid chromatography.   Its infrared spectrum was identical
with that of an authentic specimen.   The barium carbonate
obtained on oxidation was subjected to radiochemical assay
(Found: relative molar activity x 10^{-2};   7.1 ± 0.09;   1 $^{\bullet}$C
requires 22.2).

Styrene.-   Fraction (c) was fractionated through
a 10 cm. Vigreux column and all distillate boiling below
150°C, was collected and subjected to gas-liquid
chromatography in the Megachrom.   The product collected was
shown by infrared spectroscopy, to be almost pure styrene.
A sample was oxidised to barium carbonate which was collected
for radioactive assay (Found: relative molar activity x 10^{-2},
12.5 ± 0.18;   1 $^{\bullet}$C requires 22.2).

Indene.-   The residue from the redistillation of
fraction (c) was chromatographed using a Griffin and George
chromatograph and the indene collected, with a special
collecting attachment.[232]   Van Slyke-Folch oxidation gave
barium carbonate which was collected for radioactive
assay (Found: relative molar activity x 10^{-2}, 15.4 ± 0.28;
1 $^{\bullet}$C requires 22.2).

Naphthalene.-   A sample of fraction (d) was
recrystallised from ethanol to give naphthalene, m.p.
80-80.5°C, which was subjected to radioactive assay (Found:

relative molar activity × 10^{-2}, 22.2 ± 0.08;   1$^\bullet$C requires 22.2).

Acenaphthene.-   Removal of the solvent from fraction (g, 8) gave an almost colourless solid which on recrystallisation from light petroleum (b.p. 30-40°C) gave acenaphthene (ca. 100 mg.), m.p. 94-95°C, which was not depressed on admixture of an authentic sample.   The ultraviolet spectrum showed maxima at 228, 243 sh., 266, 280, 289, 301, 306 sh., 314, and 321 mμ, in agreement with the literature[240],[241] (Found: relative molar activity × 10^{-2}, 30.1 ± 0.07; 1$^\bullet$C requires 22.2).   This compound was not isolated in the pyrolysis of inactive tetralin.$^{\bullet\bullet}$

Phenanthrene.-   Fractions 11-13 (shown by ultraviolet spectroscopy to contain mixtures of phenanthrene, anthracene, and 2-phenylnaphthalene) were combined and evaporated.   The residue was heated under reflux with ethanol (50 c.c.) and nitric acid (1 c.c.) for 1.5 hr. Removal of the solvent gave a residue which was dissolved in benzene and chromatographed on alumina.   Elution with hexane, followed by evaporation, gave a colourless solid shown by ultraviolet and fluorescence spectroscopy to contain phenanthrene and 2-phenylnaphthalene.   Treatment of the solid with picric acid and recrystallisation of the product from benzene-hexane (1:2, v/v) gave phenanthrene picrate, m.p. 139-141°C (Found: relative molar activity ×

10^{-2}, 18.7 ± 0.15; 1⁜C requires 22.2). The picrate was decomposed by chromatography on alumina in hexane and the resulting phenanthrene recrystallised from ethanol to give plates, m.p. 97-98°C (Found: relative molar activity × 10^{-2}, 16.2 ± 0.21; 1⁜C requires 22.2).

Anthracene.- Further elution with benzene of the chromatogram obtained following oxidation of fractions 11-13 gave a fraction from which 9,10-anthraquinone crystallised. The solid was removed by filtration and washed with light petroleum (b.p. 30-40°C) to give 9,10-anthraquinone as needles, m.p. 284-285°C (sealed capillary) (Found: relative molar activity × 10^{-2}, 18.6 ± 0.07; 1⁜C requires 22.2).

2-Phenylnaphthalene.- This was isolated by chromatography of fraction 14 on a column of partially acetylated cellulose. On recrystallisation from light petroleum (b.p. 30-40°C), the product had m.p. 99-101°C and its ultraviolet absorption spectrum was in agreement with the data given in the literature[241] (Found: relative molar activity × 10^{-2}, 21.2 ± 0.28; 1⁜C requires 22.2).

1,1'-Binaphthyl.- The crude phenanthrene fraction (15-22) was rechromatographed on a column of acetylated cellulose to give 1,1'-binaphthyl, fluorene, and phenanthrene. The 1,1'-binaphthyl crystallised from hexane as colourless prisms, m.p. 159-160°C (Found: relative molar activity × 10^{-2}, 45.4 ± 0.1; 2⁜C requires 44.4).

2,2'-Binaphthyl.- Fraction 24 was recrystallised twice from ethanol to give 2,2'-binaphthyl, m.p. 184-185°C (Found: relative molar activity × 10^{-2}, 45.4 ± 0.19; 2°C requires 44.4).

2,3-Benzofluorene (11 H-Benzo[b]fluorene).- Fractions 26-28 were combined and chromatographed on acetylated cellulose. The resulting product was recrystallised from ethanol to give 2,3-benzofluorene as colourless plates, m.p. 204-206°C (Found: relative molar activity × 10^{-2}, 33.7 ± 0.1; 1°C requires 22.2).

A sample of crude 2,3-benzofluorene (1 g.) was heated under reflux with sodium dichromate (2 g.) in acetic acid (20 c.c.) for 2 hr. The mixture was poured into water, extracted with chloroform, dried, and the chloroform solution passed through a column of alumina. The first fractions gave 2,2'-binaphthyl as colourless plates, m.p. 185-186°C. Subsequent fractions gave 2,3-benzofluorenone which crystallised from ethanol as yellow needles, m.p. 150-151°C (Found: relative molar activity × 10^{-2}, 32.4 ± 0.1; 1°C requires 22.2).

1,2-Benzanthracene (benz[a]anthracene).- Chromatography of fraction 28 on partially acetylated cellulose, and recrystallisation of the product from ethanol gave 1,2-benzanthracene, m.p. 159-159.5°C (Found: relative molar activity × 10^{-2}, 35.9 ± 0.21; 2* requires 44.4).

3,4-Benzophenanthrene (benzo[c]phenanthrene.-
Crude 3,4-benzophenanthrene obtained from fractions 29-30
(1 g.) was oxidised with sodium dichromate (2 g.) in glacial
acetic acid (10 c.c.) by heating under reflux for 30 min.
The mixture was poured into water (15 c.c.) and continuously
extracted with cyclohexane (8 hr.).   The crude product
which separated after concentration of the solution, was
collected and recrystallised from cyclohexane.
3,4-Benzophenanthra-9,10-quinone formed red needles, m.p.
185-186°C (Found: relative molar activity x 10^{-2}, 32.0 ± 0.1;
1*C requires 22.2).

Chrysene.-   Recrystallisation, from ethanol, of
the residue from fraction 32, gave chrysene, m.p. 251-252°C
(Found: relative molar activity x 10^{-2}, 37.0 ± 0.74; 2*C
requires 44.4).

Perylene.-   A portion of fraction 34 was
chromatographed on partially acetylated cellulose.   Of the
19 fractions collected, the 6th and 7th were shown by
ultraviolet and fluorescence spectroscopy to contain
perylene.   Chromatography of these two fractions on
alumina, and recrystallisation of the product from ethanol
gave perylene, m.p. 270-271°C (sealed capillary).   The
sample was diluted with an equal quantity of inactive
perylene for radiochemical analysis (Found: relative molar
activity x 10^{-2}, 42.5 ± 0.53; 2* requires 44.4).

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<u>10,11-Benzofluoranthene</u> (<u>benzo[j]fluoranthene</u>).-
Fraction 35 was chromatographed in two parts on columns of
partially acetylated cellulose (25 × 7.5 cm.).   The
appropriate fractions were combined on the basis of their
ultraviolet and fluorescence spectra, and chromatographed on
alumina.   Further chromatography of the products on a
column of partially acetylated cellulose followed by
chromatography on alumina gave, after two recrystallisations
from ethanol, 10,11-benzofluoranthene, m.p. 160-161°C (Found:
relative molar activity × 10^{-2}, 43.1 ± 0.23; 2°C requires
44.4).

<u>11,12-Benzofluoranthene</u> (<u>benzo[k]fluoranthene</u>).-
A portion of fraction 37 was chromatographed on partially
acetylated cellulose and those fractions shown by their
ultraviolet and fluorescence spectroscopy to contain
11,12-benzofluoranthene, were combined and rechromatographed
on alumina.   Recrystallisation of the product from ethanol
gave 11,12-benzofluoranthene, m.p. 214-215°C (Found: relative
molar activity × 10^{-2}, 43.2 ± 0.23; 2°C requires 44.4).

<u>3,4-Benzofluoranthene</u> (<u>benz[e]acephenanthrylene</u>).-
Fractions 34-37 containing 3,4-benzofluoranthene were
combined and rechromatographed on acetylated cellulose.
Recrystallisation of the product from aqueous ethanol
(charcoal) gave 3,4-benzofluoranthene as colourless needles,
m.p. 165-166°C (Found: relative molar activity × 10^{-2},

38.3 ± 0.2; 1°C requires 22.2).

<u>3,4-Benzopyrene</u> (<u>benzo[a]pyrene</u>).- Chromatography
of the benzopyrene fractions on acetylated cellulose and
recrystallisation of the residue from ethanol and finally
from light petroleum (b.p. 30-40°C) gave 3,4-benzopyrene as
yellow needles, m.p. 175.5-176.5°C (Found: relative molar
activity × 10^{-2}, 43.3 ± 0.1; 2°C requires 44.4).

7.5 PYROLYSIS OF n-DECANE

<u>n-Decane</u>.- n-Decane (B.D.H. reagent) was purified
by fractional distillation over sodium. The fraction
b.p. 173-174°C, n_D^{18} 1.41279 (lit., n_D^{20} 1.41203, n_D^{25}
1.40967;[242] n_D^{20} 1.41189; n_D^{25} 1.40967.[243]) contained no
impurities which could be detected by gas-liquid
chromatography.

<u>Pyrolysis</u>.- n-Decane (100 g.) was vaporised at a
rate of 7 g./hr. by adding the liquid dropwise directly into
the pyrolysis tube, and the vapour carried in a stream of
nitrogen (1 c.c./sec.) through the tube which was maintained
at 700°C in an electrically heated furnace.[ε] The
resulting dark brown fluid tar (13.9 g.) and samples of the
exit gases were collected.

<u>Analysis</u>.- The tar was distilled at atmospheric
pressure and then under reduced pressure to give fractions

(<u>a</u>) b.p. 40-80°C/760 mm. (2.2 g.), (<u>b</u>) b.p. 80-100°C/760 mm. (3.1 g.), (<u>c</u>) b.p. 40-100°C/30 mm. (4.7 g.), and (<u>d</u>) a residue (3.9 g.).

Fractions (<u>a</u>)-(<u>c</u>) were examined by gas-liquid chromatography using Apiezon L supported on Celite (40-80 mesh; 1:4 w/w) as stationary phase and nitrogen as carrier gas. Peaks corresponding to butane, pentane, hexane, cyclohexane, benzene, toluene, <u>p</u>- and <u>m</u>-xylenes, styrene, <u>a</u>-methylstyrene, indene, tetralin, and naphthalene were observed.

The identities of the compounds were confirmed, where possible, by infrared and ultraviolet absorption spectroscopy and the composition of the fractions determined by standard methods.

The residue (<u>d</u>) was chromatographed on a column (25 × 3 cm.) of Spence alumina (200 g.) by dissolving the whole residue in chloroform, adding alumina (45 g.), evaporating the solvent on a water-bath and adding a quarter of the resultant material on to the column in the usual way. The dark brown layer of alumina containing the residue was covered with a layer of alumina (30 g.). Elution gave the following fractions each of 100 c.c.: hexane, fractions 1-24; hexane-benzene (1:12, v/v), fractions 25-48; hexane-benzene (2:11, v/v), fractions 49-57; hexane-benzene (3:10, v/v), fractions 58-72; hexane-benzene (4:9, v/v), fractions 73-84; hexane-benzene (5:8, v/v), fractions

85-90; benzene, fractions 91-94; and the remaining
fractions each of 250 c.c.: chloroform, fractions 95-97;
ethanol, fractions 98-99; and diethyl ether, fraction 100.
On the basis of their ultraviolet spectra these fractions
were recombined to give sixteen fractions.

Of the latter, fractions 1-3 were further examined
by gas-liquid chromatography, and the remainder by
chromatography on columns of partially acetylated cellulose
and on partially acetylated paper where appropriate.[233,234]
The following compounds were identified in the fractions
enumerated:

Fraction	Compound
2	Indene, tetralin, naphthalene, 1- and 2-methylnaphthalene, biphenyl.
3	Tetralin, naphthalene, 1- and 2-methylnaphthalene, biphenyl, diphenylmethane, bibenzyl, acenaphthylene.
4	Naphthalene, acenaphthylene.
5	Acenaphthylene, fluorene, 2-phenylnaphthalene, phenanthrene, anthracene.
6	Fluorene, phenanthrene, anthracene, pyrene, fluoranthene.
7	Pyrene, fluoranthene, methylpyrene, methylfluoranthene.

Fraction	Compound
8	Pyrene, fluoranthene, methylpyrene, methylfluoranthene, 2,2'-binaphthyl, 1,2-benzanthracene, triphenylene, 1,2-benzofluorene, 3,4-benzofluorene, 2,3-benzofluorene.
9	1,2-Benzanthracene, triphenylene, 1,2-benzofluorene, 3,4-benzofluorene, 2,3-benzofluorene, chrysene.
10	2,3-Benzofluorene, chrysene, 10,11-benzofluoranthene, 1,2-benzopyrene, 3,4-benzopyrene.
11	1,2-Benzopyrene, 3,4-benzopyrene, perylene, 3,4-benzofluoranthene, 11,12-benzofluoranthene.
12	1,2-Benzopyrene, 3,4-benzopyrene, 3,4-benzofluoranthene, 11,12-benzofluoranthene, 1,12-benzoperylene.
13	1,12-Benzoperylene, 7,10-benzofluoranthene, picene, 2,3-(o-phenylene)pyrene.
14	1,12-Benzoperylene, coronene, anthanthrene, methylpicene.
15	1,12-Benzoperylene, anthanthrene, methylpicene, 1,2:4,5-dibenzopyrene.
16	3,4:9,10-Dibenzopyrene, 1,2:4,5-dibenzopyrene, 1,2:3,4-dibenzopyrene.

DETAILS OF IDENTIFICATION

Methane.- Samples of the exit gases were collected in a gas cell for infrared analysis. Methane was identified from the characteristic band system in the 7.3-8.5 μ region (maxima at 7.36, 7.43, 7.52, 7.62, 7.66, 7.70, 7.78, 7.82, 7.88, 7.90, 7.94, 7.97, 8.05, 8.10, 8.17, and 8.22 μ).

Ethylene.- This was identified from the characteristic band system in the 9.0-11.5 μ region (maxima at 9.91, 10.01, 10.11, 10.21, 10.31, 10.40, 10.51, 10.75, 10.83, 10.92, 11.02, 11.07, 11.16, and 11.25 μ). Its presence was confirmed by the isolation of 1,2-dibromoethane obtained on passing the exit gases through bromine water followed by gas-liquid chromatography of the bromo derivatives obtained. The infrared spectrum of the 1,2-dibromoethane was identical with that of an authentic specimen.

Propylene.- This was identified in the exit gases by its infrared spectrum in the 6.0-6.5 μ region. Its presence was confirmed by the isolation of 1,2-dibromopropane by the procedure described for ethylene. The infrared spectrum of the 1,2-dibromopropane was identical with the published data.[44]

But-1-ene.- Isolated as 1,2-dibromobutane, using the same procedure as for ethylene. The infrared spectrum

of the 1,2-dibromobutane was identical with that of an
authentic specimen.

Acetylene.- This was identified in the exit gases
by its characteristic absorption in the 12.5-14.5 μ region.

Butane.- Identified in fraction ($\underline{a}$) by comparison
of the retention time ratio with that of an authentic
specimen.

Pentane.- Identified in fraction ($\underline{a}$) by comparison
of the retention time ratio with that of an authentic
specimen.

Cyclohexane.- Identified in fractions ($\underline{a}$) and ($\underline{b}$)
by comparison of the retention time ratio with that of an
authentic specimen.

Benzene.- Isolated from fractions ($\underline{a}$), ($\underline{b}$), and
($\underline{c}$) by gas-liquid chromatography. The infrared spectrum
(liquid film) showed maxima at 3.25, 3.31, 4.31, 4.53, 5.10,
5.51, 5.70, 6.00, 6.31, 6.54, 6.76, 7.20, 8.52, and 9.67 μ.

Toluene.- Isolated from fractions ($\underline{a}$), ($\underline{b}$), and
($\underline{c}$) by gas-liquid chromatography. The infrared spectrum
(liquid film) showed maxima at 3.29, 3.42, 3.48, 3.64, 5.14,
5.38, 5.55, 5.74, 6.22, 6.56, 6.69, 6.84, 7.26, 9.25, 9.70,
13.73, and 14.42 μ.

p- and m-Xylene.- Isolated from fraction ($\underline{c}$) by

gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.30, 3.42, 3.48, 3.64, 5.20, 5.32, 5.42, 5.63, 5.78, 6.24, 6.62, 6.73, 6.91, 7.30, 8.60, 8.92, 9.06, 9.58, 11.02, 11.31, 12.53, 12.98, 13.44, and 14.46 μ.

Styrene.-   Isolated from fraction (c) by gas-liquid chromatography.   The infrared spectrum (liquid film) showed maxima at 3.20, 3.25, 5.10, 5.30, 5.50, 5.70, 5.90, 6.11, 6.22, 6.31, 6.52, 6.70, 6.90, 7.08, 7.50, 7.60, 7.73, 8.32, 8.50, 8.68, 9.06, 9.26, 9.78, 10.10, 11.00, 11.91, 12.90, and 14.40 μ.

α-Methylstyrene.-   Isolated from fraction (c) by gas-liquid chromatography.   The infrared spectrum (liquid film) showed maxima at 3.22, 3.32, 4.35, 5.16, 5.36, 5.60, 5.86, 5.96, 6.14, 6.28, 6.40, 6.73, 6.98, 7.34, 7.42, 7.76, 7.96, 8.60, 9.40, 9.80, 10.02, 10.54, 11.26, 12.83, and 13.16 μ.

Indene.-   Isolated from fractions (c) and (d, 2) by gas-liquid chromatography.   The infrared spectrum (liquid film) showed maxima at 3.25, 3.46, 3.60, 6.24, 6.50, 6.92, 7.24, 7.40, 7.58, 7.68, 7.82, 8.20, 8.34, 8.62, 8.94, 9.40, 9.84, 10.56, 10.92, 11.60, 12.06, 13.02, 13.70, 13.92, and 14.42 μ.

Tetralin.-   Isolated from fractions (c) and (d, 2-3) by gas-liquid chromatography.   The infrared spectrum (liquid

film) showed maxima at 3.31, 3.42, 3.53, 3.69, 5.20, 5.42, 5.62, 5.85, 6.26, 6.40, 6.72, 6.90, 7.30, 8.31, 8.54, 9.08, 9.28, 9.62, 9.74, 11.14, 11.57, 13.60, and 14.32 μ.

Naphthalene.- Isolated from fractions (c) and (d, 2-4) by gas-liquid chromatography, and by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 248, 257, 266, 275, 285, and 311 mμ; m.p. and mixed m.p. 78-80°C.

1- and 2-Methylnaphthalene.- Isolated from fractions (c) and (d, 2-3) by gas-liquid chromatography. The ultraviolet spectrum showed maxima at 224, 272, 278, 283, 287, 291, 294, 306, 313, and 320 mμ. Attempts to separate the isomers by further gas-liquid chromatography were unsuccessful, but the predominance of the 2-isomer was inferred from the shape of the chromatogram.

Biphenyl.- Isolated from fractions (d, 2-3) by gas-liquid chromatography. The ultraviolet spectrum showed a maximum at 248 mμ in agreement with that of an authentic specimen; m.p. and mixed m.p. 69-70°C.

Diphenylmethane.- Isolated from fraction (d, 3) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.39, 3.40, 3.46, 3.52, 5.18, 5.58, 6.00, 6.08, 6.24, 6.34, 6.72, 6.92, 7.28, 7.42, 7.62, 7.86, 8.34, 8.50, 8.70, 9.08, 9.30, 9.70, 9.98, 10.62, 10.88,

11.18, 11.84, 12.32, 12.82, 13.50, and 14.30 μ.

Bibenzyl.- Identified in fraction ($\underline{d}$, 3) by comparison of its retention time ratio with that of an authentic specimen.

Acenaphthylene.- Isolated from fractions ($\underline{d}$, 3-7) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 229, 258, 266, 276, 309, 323, 334, and 340 mμ in agreement with those of an authentic specimen.

2-Phenylnaphthalene.- Identified in fractions ($\underline{d}$, 5-7) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 250 and 296 mμ in agreement with those given by an authentic specimen.

Fluorene.- Isolated from fractions ($\underline{d}$, 5-9) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 260, 290, and 301 mμ in agreement with those of an authentic specimen.

Phenanthrene.- Isolated from fractions ($\underline{d}$, 5-10) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 243, 252, 275, 282, 294, 310, 317, 324, 331, 339, and 346 mμ in agreement with those of an authentic specimen; m.p. and mixed m.p. 96-98°C.

Anthracene.- Isolated from fractions (d, 5-10) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 246, 253, 308, 323, 339, 357, and 377 mμ in agreement with those of an authentic specimen.

Pyrene.- Isolated from fractions (d, 8-25) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335, 351, 358, 364, and 373 mμ in agreement with those of an authentic specimen; m.p. and mixed m.p. 145-147°C.

Fluoranthene.- Isolated from fractions (d, 10-26) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 236, 253, 263, 273, 278, 282, 288, 309, 323, 342, and 360 mμ in agreement with those of an authentic specimen; m.p. and mixed m.p. 105-107°C.

2,2'-Binaphthyl.- Identified in fractions (d, 25-30) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 255 and 309 mμ in agreement with those of an authentic specimen.

1,2-Benzanthracene (benz[a]anthracene).- Identified in fractions (d, 25-35) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum had maxima at 227, 256, 268, 278, 289, 300, 315,

326, 341, 358, 365, 374, and 384 mμ in agreement with those
of an authentic specimen.

Triphenylene.- Identified in fractions ($\underline{d}$, 25-35)
by chromatography on partially acetylated cellulose. The
ultraviolet spectrum showed maxima at 250, 257, 275, 286,
316, 330, and 341 mμ in agreement with those of an authentic
specimen.

1,2-Benzofluorene (11 H-benzo[a]fluorene).-
Identified in fractions ($\underline{d}$, 25-35) by chromatography on
partially acetylated cellulose. The ultraviolet spectrum
showed maxima at 229, 238, 253, 257, 262, 274, 286, 294, 303,
316, and 340 mμ in agreement with those of an authentic
specimen.

3,4-Benzofluorene (7 H-benzo[e]fluorene).-
Identified in fractions ($\underline{d}$, 25-35) by chromatography on
partially acetylated cellulose. The ultraviolet spectrum
showed maxima at 230, 251, 262, 302, 311, 321, 329, and 337
mμ in agreement with those of an authentic specimen.

2,3-Benzofluorene (11 H-benzo[b]fluorene).-
Identified in fractions ($\underline{d}$, 25-39) by chromatography on
partially acetylated cellulose. Its ultraviolet spectrum
showed maxima at 255, 264, 273, 285, 304, 317, 325, 333, and
340 mμ in agreement with those of an authentic specimen.

Chrysene.- Isolated from fractions ($\underline{d}$, 31-39) by

chromatography on partially acetylated cellulose. The
ultraviolet spectrum showed maxima at 242, 259, 267, 283,
294, 306, 320, 344, 351, and 363 mμ in agreement with those
of an authentic specimen; m.p. and mixed m.p. 253-254°C.

10,11-Benzofluoranthene (benzo[j]fluoranthene).-
Identified in fractions (d, 36-39) by chromatography on
partially acetylated cellulose. The ultraviolet spectrum
showed maxima at 241, 282, 293, 309, 318, 333, 345, 365, 376,
and 383 mμ in agreement with those of an authentic specimen.

1,2-Benzopyrene (benzo[e]pyrene).- Isolated from
fractions (d, 36-59) by chromatography on partially
acetylated cellulose. The ultraviolet spectrum showed
maxima at 238, 258, 268, 278, 289, 305, 317, 333, and 366 mμ
in agreement with those of an authentic specimen; m.p. and
mixed m.p. 173-175°C.

3,4-Benzopyrene (benzo[a]pyrene).- Isolated from
fractions (d, 36-59) by chromatography on partially acetylated
cellulose. The ultraviolet absorption spectrum showed
maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385,
and 404 mμ in agreement with those of an authentic specimen;
m.p. and mixed m.p. 174-176°C.

Perylene.- Identified in fractions (d, 40-48) by
chromatography on partially acetylated cellulose. The
ultraviolet spectrum showed maxima at 245, 253, 263, 367,

386, 407, and 435 mμ in agreement with those of an authentic
specimen.

3,4-Benzofluoranthene (benz[e]acephenanthrylene).-
Isolated from fractions (d, 40-59) by chromatography on
partially acetylated cellulose.   The absorption spectrum
showed maxima at 239, 256, 266, 276, 290, 294, 301, 320, 339,
351, and 369 mμ in agreement with those of an authentic
specimen;   m.p. and mixed m.p. 160-163°C.

11,12-Benzofluoranthene (benzo[k]fluoranthene).-
Identified in fractions (d, 40-59) by chromatography on
partially acetylated cellulose.   The ultraviolet spectrum
showed maxima at 238, 247, 269, 283, 297, 309, 361, 380, and
402 mμ in agreement with those of an authentic specimen.

1,12-Benzoperylene (benzo[ghi]perylene).-
Identified in fractions (d, 49-68) by chromatography on
partially acetylated cellulose.   The absorption spectrum
showed maxima at 268, 276, 289, 300, 315, 325, 330, 345, 363,
and 383 mμ in agreement with those of an authentic specimen.

7,10-Benzofluoranthene (benzo[ghi]fluoranthene).-
Identified in fractions (d, 60-68) by chromatography on
partially acetylated cellulose.   The ultraviolet spectrum
showed maxima at 233, 245, 251, 260, 282, 291, 331, 348, 378,
398, and 420 mμ in agreement with those of an authentic
specimen.

Picene.- Identified in fractions (d, 60-86) by chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 232, 256, 274, 284, 301, 312, and 326 mμ in agreement with those of an authentic specimen.

2,3-(o-Phenylene)pyrene (indeno[1,2,3-cd]pyrene).- Identified in fractions (d, 60-68) by chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 259, 269, 277, 292, 304, 315, 360, 376, 385, 402, 422, and 431 mμ in agreement with those of an authentic specimen.

Coronene.- Identified in fractions (d, 69-77) by chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 267, 278, 289, 292, 297, 301, 316, 323, 328, 332, 338, and 344 mμ in agreement with those of an authentic specimen.

Anthanthrene (dibenzo[def-mno]chrysene).- Identified in fractions (d, 69-86) by chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 233, 256, 259, 295, 308, 365, 382, 402, 407, 422, and 431 mμ in agreement with those of an authentic specimen.

1,2:4,5-Dibenzopyrene (naphtho[1,2,3,4-def]chrysene).- Identified in fractions (d, 78-100) by chromatography on

partially acetylated cellulose. The absorption spectrum
showed maxima at 241, 247, 251, 271, 291, 303, 324, 339, 354,
370, and 372 mμ in agreement with those of an authentic
specimen.

1,2:3,4-Dibenzopyrene (dibenzo[def,p]chrysene).-
Identified in fractions (d, 87-100) by chromatography on
partially acetylated cellulose, followed by chromatography
on partially acetylated paper. The absorption spectrum
showed maxima at 262, 269, 290, 303, 315, 331, 355, 363, 372,
and 402 mμ in agreement with those of an authentic specimen.

3,4:9,10-Dibenzopyrene (benzo[rst]pentaphene).-
Identified in fractions (d, 87-100) by chromatography on
partially acetylated cellulose, followed by chromatography
on partially acetylated paper. The absorption spectrum
showed maxima at 232, 242, 273, 283, 296, 315, 331, 353, 373,
and 393 mμ in agreement with those of an authentic specimen.

7.6   PYROLYSIS OF [δ-^{14}C]BUTYLBENZENE

Radioactive Assay.-   Specimens were assayed for
radioactivity as previously described.[94]   The counts per
min. were determined by recording five readings per sample,
each of 5 min. duration.   All assays were repeated three
times, either with a new sample, or with the original sample
repacked.   The statistical counting error was calculated as

standard deviations for each series of counts and (with the
exception of fluorene) was not greater than 1%.   Samples
for counting were prepared by the "pellet" technique,[245]
using, when necessary, the modifications previously
described.[94]   Van Slyke-Folch oxidations were carried out
as described in the literature.[246]

2-Hydroxy-4-phenyl[1-^{14}C]but-3-ene.-   This was
prepared by vacuum line technique.   Two ampoules, one of
methyl-^{14}C iodide (1.5 mc, 45.3 mg.) and one of inactive
methyl iodide (4.23 g., 1.86 c.c.) and a three-necked flask,
containing magnesium (0.725 g.), anhydrous ether (50 c.c.),
and anhydrous benzene (25 c.c.), fitted with a low
temperature condenser and a pressure-equalised dropping
funnel, containing freshly distilled cinnamaldehyde[247]
(4.4 g., 10% excess), were attached to the vacuum line
(see Figure 7.3), and the system evacuated.   The active
methyl iodide was transferred to the ampoule containing the
inactive material, and the mixture was then allowed to warm
until it had completely distilled into the three-necked
flask.   When the formation of the Grignard complex was
complete (0.5 hr.) the cinnamaldehyde was introduced
dropwise.   Decomposition of the complex was effected by
the slow addition of aqueous ammonium chloride [AnalaR
ammonium chloride (2.8 g.) in 10 c.c. of water].   When the
addition was complete, the solution was stirred for an
additional 30 min.   The ether layer was decanted and the

aqueous layer extracted continuously with ether (16 hr.).
The combined ether extracts were dried over calcium sulphate
and the solvent evaporated in a current of dry air.   The
2-hydroxy-4-phenyl[1-^{14}C]but-3-ene[248] (4.4 g., 98%) was
obtained as an oil, b.p. 89-90°C/2 mm.

2-Hydroxy-4-phenyl[1-^{14}C]butane.-   The above butene
(4.4 g.) in absolute ethanol (5 c.c.) and glacial acetic
acid (5 drops) was hydrogenated over Adams' catalyst[249]
(120 mg.) for 16 hr.   The resulting
2-hydroxy-4-phenyl[1-^{14}C]butane[248] (4.4 g., 100%) was
obtained as a colourless viscous oil, b.p. 80-82°C/2 mm.

[δ-^{14}C]Butylbenzene.-   A mixture of the above
hydroxyphenylbutane (4.4 g.) and phosphoric acid (85%;   3 c.c.)
was heated under reflux for 2 hr.   The ethereal solution
of the product was washed successively with water,
5% aqueous sodium hydroxide, water, dried over magnesium
sulphate, and the ether evaporated.   The unsaturated
compound was then hydrogenated in the same way as before,
and the resulting [δ-^{14}C]butylbenzene distilled.   Inactive
butylbenzene was added and the distillation continued to
give [δ-^{14}C]butylbenzene, b.p. 182-183°C, n_D^{17} 1.4930
(lit.,[250] n_D^{15} 1.4921, n_D^{20} 1.4936).   Gas-liquid
chromatography of a sample of the distillate revealed no
impurities.   Van Slyke oxidation gave barium carbonate
which was collected for radioactive assay (Found: relative

To high vacuum
pumping system

1 Pressure-equalised dropping funnel;   2
Stirrer capsule (magnet sealed in teflon);
3 Low temperature condenser;   4 Magnetic stirrer;   5 Manometer;   6 Pirani vacuum gauge;
7 Manifold;   8 Graduated ampoule for liquids;   9 Storage flask for carbon dioxide.
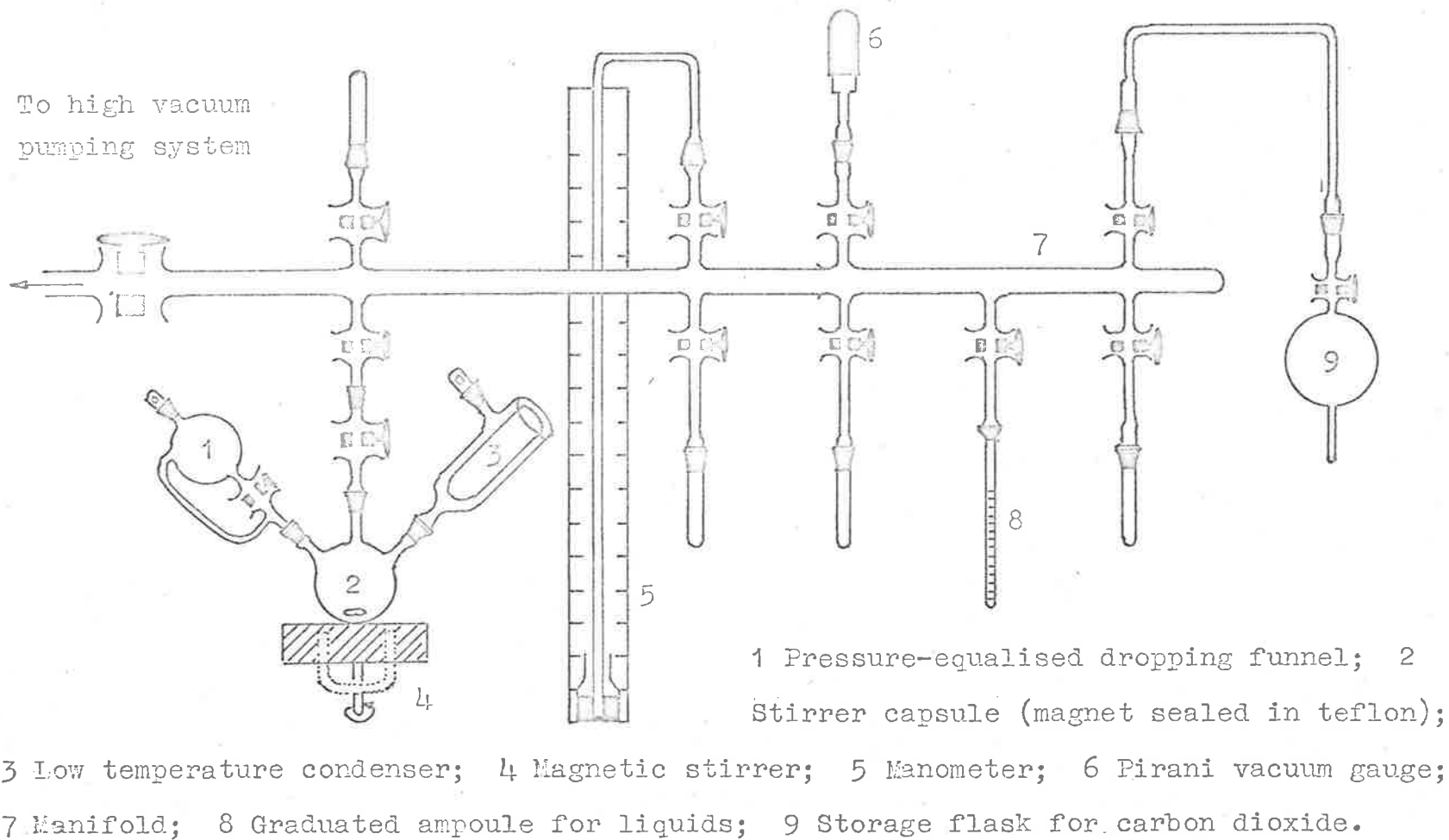
Figure 7.3

molar activity x 10^{-2}, 63.1 ± 0.28).

Butylbenzene.- Inactive butylbenzene was prepared
from butyric acid via butyryl chloride, followed by reaction
with benzene by the Friedel-Crafts method and reduction of
the resulting butyrophenone by the Huang-Minlon modification
of the Wolff-Kishner reaction.

Pyrolysis of [δ-^{14}C]Butylbenzene.-
[δ-^{14}C]Butylbenzene (100 g.) was vaporised at a rate of
7 g./hr. and passed in a stream of nitrogen (1 c.c./sec.)
through a silica tube maintained at 700°C as previously
described.[8],[85] The resulting semi-solid dark brown tar
(51.8 g.) was distilled to give fractions (a) b.p. 60-90°C/
760 mm. (13.7 g.), (b) b.p. 90-120°C/760 mm. (11.8 g.), (c)
b.p. 60-100°C/30 mm. (1.1 g.), (d) b.p. 100-130°C/30 mm.
(8.4 g.), and (e) a residue (13.04 g.).

Analysis.- Separation of the components of the
various fractions was effected by gas-liquid chromatography,
chromatography on activated alumina and on columns of
partially acetylated cellulose, as previously described.[80]
Radioactive assay could only be carried out on pure
compounds obtained in sufficient quantities to allow the
accuracy of the determination to be unaffected by dilution.
Usually not less than 5-10 mg. were required.

Fractions (a), (b), and (c).- Fraction (a) was

shown by gas-liquid chromatography to contain benzene and toluene. Fraction (b) was found to contain mainly benzene, toluene, and styrene; and fraction (c), mainly styrene. The compounds were separated and identified as described below.

Fraction (d).- Fraction (d) was chromatographed on a column of Spence alumina (1000 g.). Elution with hexane gave fifty fractions each of 500 c.c. On the basis of their fluorescence and ultraviolet spectra, these fractions were recombined to give five fractions. Naphthalene (fractions 1-8), biphenyl (fractions 9-10), and fluorene (fractions 17-20) were isolated by the technique described below for the individual compounds.

Examination of Residue.- The residue (e) in chloroform, was added to alumina (200 g.) and the solvent evaporated. The resulting mixture was then added on to the top of a column of alumina (1500 g.) and elution gave the following fractions each of 500 c.c.: hexane, fractions 1-39; benzene-hexane (sp. gr. 0.695), fractions 40-49; benzene-hexane (sp. gr. 0.700), fractions 50-55; benzene-hexane (sp. gr. 0.710), fractions 56-67; benzene-hexane (sp. gr. 0.720), fractions 68-79; benzene-hexane (sp. gr. 0.730), fractions 80-91; benzene-hexane (sp. gr. 0.740), fractions 92-99; chloroform, fractions 100-109; ethanol, fractions 110-117; and diethyl ether, fractions 118-120. On the

basis of their fluorescence and ultraviolet spectra these
fractions were recombined to give fourteen fractions.
By the technique described below, the following pure
substances or their derivatives were isolated from eight of
these fractions: from fractions 13-18, phenanthrene and
anthracene; fractions 22-39, pyrene and fluoranthene;
fractions 40-55, fluoranthene, 1,2-benzanthracene,
1,2-benzopyrene, and chrysene; fractions 56-59,
2,3-benzofluorene; fractions 60-63, 3,4-benzopyrene;
fractions 64-83, 3,4-benzopyrene and 3,4-benzofluoranthene;
fractions 96-99, 3,4-benzotetraphene; and fractions 100-120,
2,3-(o-phenylene)pyrene.

ISOLATION AND RADIOCHEMICAL ANALYSIS

Benzene.- This was isolated from fractions (a) and
(b) using a Megachrom preparative gas-liquid chromatograph.
The infrared spectrum of the product was identical with that
given by an authentic specimen. Van Slyke-Folch oxidation
gave barium carbonate which was collected for radioactive
assay (Found: relative molar activity $\times 10^{-2}$, 8.3 ± 0.06;
1 $^{\bullet}C$ requires 63.1).

Toluene.- Isolated from fractions (a) and (b) by
gas-liquid chromatography. Its infrared spectrum was
identical with that of an authentic specimen. The barium
carbonate obtained by oxidation was submitted to radioactive

assay (Found: relative molar activity × 10^{-2}, 7.8 ± 0.05; 1°C requires 63.1). Oxidation of the toluene (362 mg.) was effected by heating under reflux with potassium permanganate (1.242 g.) in water (20 c.c.) for 8 hr. The cold solution was acidifies with dilute hydrochloric acid and extracted continuously with ether (16 hr.), the ether removed by distillation, and the residue recrystallised from water (charcoal). The resulting benzoic acid was obtained as colourless needles, m.p. 122-122.5°C, and submitted to radioactive assay (Found: relative molar activity × 10^{-2}, 7.4 ± 0.04; 1°C requires 63.1). The benzoic acid (65 mg.) was decarboxylated in a stream of carbon dioxide-free nitrogen by heating under reflux with copper bronze (45 mg.) and freshly distilled quinoline. The exit gas was bubbled through a 4% solution of barium hydroxide in a two-necked flask protected with a potassium hydroxide tube. The resulting barium carbonate was collected and subjected to radioactive assay (Found: relative molar activity × 10^{-2}, 4.4 ± 0.02; 1°C requires 63.1). The residue from the decarboxylation was distilled to give two fractions. Gas-liquid chromatography of the first gave benzene, which was oxidised and converted into barium carbonate for radiochemical analysis (Found: relative molar activity × 10^{-2}, 2.0 ± 0.05; 1°C requires 63.1).

Styrene.- This was isolated from fractions (b) and (c) by gas-liquid chromatography using a Megachrom unit.

The infrared spectrum was identical with that of an authentic specimen. Van Slyke-Folch oxidation gave barium carbonate which was collected for radioactive assay (Found: relative molar activity $\times 10^{-2}$, 18.5 ± 0.16; 1*C requires 63.1). Oxidation of the styrene (120 mg.) in glacial acetic acid (6 g.) was effected by warming the solution to 85°C and adding hydrogen peroxide (50%; 2 g.) over a period of 5 min. The mixture was heated with stirring (1 hr.) and the warm solution poured into water (9 c.c.). The solution was basified to pH 10.5 with 25% aqueous sodium hydroxide with warming and stirring, and acidified with concentrated hydrochloric acid to pH 2.5. Continuous extraction with ether, removal of the solvent, and recrystallisation of the residue from water (charcoal) gave benzoic acid as needles, m.p. 120-121°C. The product was diluted (1:2) with inactive material and subjected to radioactive assay (Found: relative molar activity $\times 10^{-2}$, 11.6 ± 0.05; 1*C requires 63.1). The diluted benzoic acid (30 mg.) was decarboxylated in a stream of carbon dioxide-free nitrogen by heating under reflux with copper bronze (20 mg.) and freshly distilled quinoline (4 c.c.) for 2 hr. The carbon dioxide evolved was absorbed in a 4% solution of barium hydroxide as in the case of toluene oxidation, and the resulting barium carbonate subjected to radioactive assay (Found: relative molar activity $\times 10^{-2}$, 1.3 ± 0.00; 1*C requires 63.1).

Napthalene.- This was isolated from fractions (d, 1-8) following chromatography on alumina. Recrystallisation from ethanol and finally from light petroleum (b.p. 30-40°C) gave the naphthalene as plates, m.p. 80-80.5°C (Found: relative molar activity x 10^{-2}, 63.1 ± 0.12; 1 *C requires 63.1).

Biphenyl.- This was isolated from fractions (d, 9-10) following chromatography on alumina. Recrystallisation thrice from ethanol gave plates, m.p. 67-68°C. The product was diluted with inactive biphenyl (1:1) and subjected to radioactive assay (Found: relative molar activity x 10^{-2}, 17.1 ± 0.06; 1 *C requires 63.1).

Fluorene.- Isolated from fractions (d, 17-20) following chromatography on alumina. Repeated crystallisation from ethanol gave plates, m.p. 115-116°C (3 mg.), which were diluted with inactive material (30 mg.) for radioactive assay (Found: relative molar activity x 10^{-2}, 15.4 ± 1.32; 1 *C requires 63.1).

Anthracene.- Chromatography of fractions (e, 13-18) on alumina, followed by chromatography on acetylated cellulose, gave a mixture (2.0 g.) of anthracene and phenanthrene. Oxidation[251] of this was effected by heating under reflux with ethanol (50 c.c.) and concentrated nitric acid (1 g.) for 1.5 hr. The orange-yellow product was dissolved in a minimum amount of benzene and

chromatographed on a small column of alumina using hexane
and benzene as eluents.   Ten fractions each of 250 c.c.
were collected: hexane, fractions 1-7;   and benzene,
fractions 8-10.   The first five fractions contained
phenanthrene;   and anthraquinone was isolated from fractions
7 and 8.   After two recrystallisations from ethanol,
anthraquinone was obtained as fine needles, m.p. 287-288°C
(evacuated capillary) (Found: relative molar activity × 10^{-2},
51.7 ± 0.13; ^{14}C requires 63.1).

Phenanthrene.-   Phenanthrene obtained above was
practically pure.   It was recrystallised from ethanol to
give needles, m.p. 98-99°C, and subjected to radioactive
assay (Found: relative molar activity × 10^{-2}, 34.8 ± 0.15;
^{14}C requires 63.1).   A solution of phenanthrene (0.3 g.)
in glacial acetic acid (8 g.) was warmed to 85°C and
hydrogen peroxide (50%;   4 g.) added over a period of 10 min.
The mixture was heated with stirring (1 hr.), and the warm
solution poured into water (12 c.c.).   The mixture was
basified to pH 10.5 with 25% aqueous sodium hydroxide with
warming and stirring;   and acidified with concentrated
hydrochloric acid to pH 2.5.   Continuous extraction with
ether (16 hr.), removal of the solvent and recrystallisation
of the yellow crystalline residue from aqueous acetic acid
(charcoal) gave 2,2'-biphenic acid as needles, m.p. 230-231°C.
The product was submitted to radioactive assay (Found:
relative molar activity × 10^{-2}, 33.7 ± 0.13; ^{14}C requires

63.1). Decarboxylation of the 2,2'-biphenic acid (0.08 g.) was effected by heating under reflux in freshly distilled quinoline (6 c.c.) with copper bronze (0.05 g.) for 3 hr. in a stream of carbon dioxide-free nitrogen. The gas was bubbled through a 4% aqueous solution of barium hydroxide and the resulting barium carbonate collected for radioactive assay (Found: relative molar activity $\times 10^{-2}$, 11.3 ± 0.05; 1$^{\bullet}$C requires 63.1). The residue was acidified with hydrochloric acid and continuously extracted with ether (15 hr.). Removal of the ether and recrystallisation of the residue using light petroleum (b.p. 30-40°C) gave biphenyl as plates, m.p. 66-67°C. The product was oxidised by the Van Slyke-Folch method, collected and assayed as barium carbonate (Found: relative molar activity $\times 10^{-2}$, 22.9 ± 0.1; 1$^{\bullet}$C requires 63.1).

Pyrene.- This was isolated from fractions (e, 22-39) by chromatography on acetylated cellulose, followed by chromatography on alumina. The crude product (0.5 g.) was dissolved in nitrobenzene (35 c.c.) and bromine (0.64 c.c., 25% excess) added. The mixture was warmed to 150°C over a period of 30 min., and maintained at this temperature for 15 min. The product was collected, washed with benzene (5 c.c.), dried, and recrystallised twice from nitrobenzene to give 3,5,8,10-tetrabromopyrene as yellow needles, m.p. 400-401°C (evacuated capillary) (Found: relative molar activity $\times 10^{-2}$, 123.3 ± 0.41; 2$^{\bullet}$C requires

126.2).

Fluoranthene.- Isolated from fractions (e, 22-55)
by chromatography on acetylated cellulose, followed by
chromatography on alumina. Recrystallisation from ethanol
gave pale yellow needles, m.p. 106-107°C (Found: relative
molar activity × 10^{-2}, 58.1 ± 0.16; $1^{\ast}C$ requires 63.1).

1,2-Benzanthracene (benz[a]anthracene).- Crude
1,2-benzanthracene (0.1 g.) was isolated from fractions
(e, 40-55) by chromatography on acetylated cellulose, followed
by chromatography on alumina. The product was oxidised by
heating with sodium dichromate (0.2 g.) in acetic acid (3 c.c.)
on a water-bath for 10 min. Chromatography of the
resultant solid on alumina using hexane and benzene, and
recrystallisation of the product from methanol, gave
1,2-benzanthraquinone as orange-yellow needles, m.p. 166-167°C
(Found: relative molar activity × 10^{-2}, 72.3 ± 0.16; $1^{\ast}C$
requires 63.1).

Chrysene.- This was isolated by chromatography of
fractions (e, 40-55) on acetylated cellulose, followed by
chromatography on alumina. Recrystallisation from ethanol
gave plates, m.p. 254-255°C (Found: relative molar activity ×
10^{-2}, 74.6 ± 0.27; $1^{\ast}C$ requires 63.1). A mixture of the
labelled chrysene (50 mg.), inactive chrysene (180 mg.),
sodium dichromate (1.08 g.) and acetic acid (10 c.c.), was
heated under reflux (2 hr.) and then poured into water

- 180 -

(12 c.c.).[252]   The product was collected and purified by chromatography on a column of alumina (17 × 4 cm.) using benzene and chloroform as eluents; 12 fractions each of 250 c.c. were collected: benzene, fractions 1-5; and chloroform, fractions 6-12.   On the basis of their ultraviolet absorption spectra fractions 7-11 were combined, the solvent removed by distillation and the red residue recrystallised from toluene.   Chrysa-1,2-quinone was obtained as long red prisms, m.p. 240-241°C, and subjected to radiochemical assay (Found: relative molar activity × 10^{-2}, 74.7 ± 0.12; 1 °C requires 63.1).   The chrysaquinone (50 mg.) was diluted with inactive quinone (300 mg.), intimately mixed with lead dioxide (490 mg.), and the mixture added with stirring to potassium hydroxide (1.4 g.) and water (0.5 c.c.) maintained at 225-235°C in an oil-bath.[252]   After the addition (10 min.), the melt was maintained at 225-235°C for 0.5 hr.   The cooled mass was extracted with water, the filtrate acidified with hydrochloric acid, and continuously extracted with ether (5 hr.).   The solvent was evaporated and the residue crystallised from aqueous acetic acid (charcoal).   The crude yellow product was again recrystallised from acetic acid to give o-(2-naphthyl)benzoic acid (α-chrysenic acid) as colourless needles, m.p. 189-190°C.   The product was subjected to radioactive assay (Found: relative molar activity × 10^{-2}, 71.9 ± 0.78).   The mother liquors were evaporated and the

residue heated with a little water and excess barium
hydroxide added.   The residual barium hydroxide was removed
as barium carbonate by treatment with carbon dioxide.   The
resulting solution was concentrated to give the barium salt
of the acid which was collected and treated with hydrochloric
acid.   2-Phenyl-1-naphthoic acid was obtained as a light
brown crystalline powder, m.p. 111-113°C.   This acid (8 mg.)
was diluted with inactive material (20 mg.) and subjected to
radiochemical assay (Found: relative molar activity x 10^{-2},
73.4 ± 0.75; $1^{\bullet}C$ requires 63.1).   The labelled
o-(2-naphthyl)benzoic acid (100 mg.) was decarboxylated by
heating under reflux with copper bronze (50 mg.) and freshly
distilled quinoline (3 hr.) in a stream of carbon dioxide-free
nitrogen.   The carbon dioxide formed was bubbled through
a 4% solution of barium hydroxide in a two-necked flask
fitted with a potassium hydroxide tube.   The barium
carbonate formed was collected and assayed (Found: relative
molar activity x 10^{-2}, 0.01 ± 0.00).   The residue was
acidified with hydrochloric acid and continuously extracted
with ether (15 hr.).   The ether was evaporated and the
residue recrystallised from aqueous ethanol (charcoal) to
give 2-phenylnaphthalene as colourless plates, m.p.
103-104°C.   The active hydrocarbon was diluted with inactive
material (1:3) and assayed (Found: relative molar activity x
10^{-2}, 71.1 ± 2.68).

1,2-Benzopyrene (benzo[e]pyrene).-   Isolated from
fractions (e, 40-55) by chromatography on acetylated
cellulose.   On recrystallisation from ethanol, prisms of
1,2-benzopyrene (5 mg.), m.p. 175-177°C were formed.   The
product was diluted with inactive material (25 mg.) and
submitted to radiochemical assay (Found: relative molar
activity x 10^{-2}, 126.5 ± 0.71; $2^{\oplus}$ requires 126.2).

2,3-Benzofluorene (11 H-benzo[b]fluorene).-   This
was obtained by chromatography of fractions (e, 56-59) on
acetylated cellulose.   Recrystallisation from ethanol gave
plates, m.p. 206-207°C (Found: relative molar activity x 10^{-2},
78.2 ± 0.14; 1°C requires 63.1).

3,4-Benzopyrene (benzo[a]pyrene).-   Isolated
following chromatography of fractions (e, 60-83) on alumina
followed by chromatography on acetylated cellulose.   The
material was recrystallised from ethanol and finally from
light petroleum (b.p. 30-40°C) to give yellow needles, m.p.
176-177°C (Found: relative molar activity x 10^{-2}, 121.1 ±
0.16; 2°C requires 126.2).

A solution of labelled 3,4-benzopyrene (0.992 g.,
0.0040 mole) in pure dry benzene (24 c.c.) was treated with
osmium tetroxide (1 g., 0.0040 mole) and pure pyridine
(0.627 g., 0.56 c.c., 0.0080 mole), and the mixture allowed
to stand at room temperature for three days.[253]   The
resulting complex was collected, dissolved in methylene

dichloride (100 c.c.) and shaken for 2 hr. with 5N aqueous
sodium hydroxide (100 c.c.) and aquous 1M mannitol (30 c.c.).
The product was filtered using filter aid and the solid
extracted in a Soxhlet extractor with methylene dichloride.
The combined methylene dichloride solutions were washed,
dried and evaporated to give a crude amorphous powder (0.7 g.).
This was further oxidised with sodium dichromate (0.9 g.) in
water (3 c.c.) and acetic acid (90 c.c.) by heating under
reflux for 0.5 hr.   The mixture was poured into water, the
resulting precipitate collected and purified by
chromatography on a column of alumina (90 x 5 cm.).   Elution
with chloroform gave 18 fractions each of 500 c.c.   The
first fractions (3-4) contained unchanged 3,4-benzopyrene
(identified by its ultraviolet absorption spectrum).   The
following fractions (9-12) gave a yellow compound which on
recrystallisation from acetone formed orange yellow needles
(5 mg.), m.p. 291-292°C.   A sample gave a carmine red
solution in concentrated sulphuric acid, and the infrared
spectrum showed a single strong carbonyl stretching band at
6.10 μ.[254,255]   Its ultraviolet spectrum was identical
with that of 3,4-benzopyrene-5,10-quinone.[255]   The final
fractions (14-18) were evaporated and the residue
recrystallised from toluene to give
3,4-benzopyrene-6,7-quinone as dark red needles, m.p. 248-
249°C (lit.,[254,255] 253-254°C).   This compound was
submitted to radiochemical assay (Found: relative molar

activity $\times 10^{-2}$, 121.1 ± 1.03; 2*C requires 126.2).

This active quinone (182 mg.) was dissolved in glacial acetic acid (15 c.c.) and warmed to 85°C on a water-bath. Hydrogen peroxide (50%; 15 c.c.) was added in three equal portions, the second after 3 hr. and the third after 24 hr. The cooled mixture was poured into excess water and the yellow solid (71 mg.) collected and decarboxylated. (Attempts to purify this dicarboxylic acid by crystallisation and by partition chromatography on silica gel without heavy loss of material were unsuccessful. In one run a small amount of the alkali-insoluble mesobenzanthrone-3,4-dicarboxylic anhydride was isolated and identified by its m.p. and from its infrared and ultraviolet spectra.[254])

Decarboxylation of the crude dicarboxylic acid (60 mg.) was effected by heating under reflux in freshly distilled quinoline with copper bronze (30 mg.) for 2 hr. under a stream of carbon dioxide-free nitrogen. The carbon dioxide liberated was bubbled through a 4% solution of barium hydroxide in a two-necked flask fitted with a potassium hydroxide tube. The barium carbonate was collected and assayed (Found: relative molar activity $\times 10^{-2}$, 54.6 ± 0.18; 1*C requires 63.1). The residue was acidified with hydrochloric acid and continuously extracted with ether (16 hr.). Evaporation of the ether and recrystallisation of the residue from ethanol gave chrysene

as colourless plates, m.p. 251-253°C.   The hydrocarbon was diluted with inactive material (1:2) and assayed (Found: relative molar activity x 10^{-2}, 70.6 ± 1.51;   1^{14}C requires 63.1).

3,4-Benzofluoranthene (benz[e]acephenanthrylene).- This was isolated from fractions (e, 64-83) by repeated chromatography on acetylated cellulose and on alumina.   The product was recrystallised from ethanol to give needles, m.p. 165-166°C (8 mg.), and diluted with inactive material (32 mg.) for radioactive assay (Found: relative molar activity x 10^{-2}, 39.4 ± 0.12;   1^{14}C requires 63.1).

3,4-Benzotetraphene (benzo[b]chrysene).-   This was isolated from fractions (e, 96-99) by chromatography on acetylated cellulose, followed by chromatography on alumina. Crystallisation from benzene gave pale yellow needles, m.p. 288-291°C (1 mg.).   The hydrocarbon was diluted with inactive material (24 mg.) and subjected to radioactive assay (Found: relative molar activity x 10^{-2}, 136.4 ± 1.09; 2^{14}C requires 126.2).

2,3-(o-Phenylene)pyrene (indeno[1,2,3-cd]pyrene).- This was obtained from fractions (e, 100-120) by repeated chromatography on acetylated cellulose and on alumina. Two crystallisations from ethanol afforded yellow plates, m.p. 162-163°C (6 mg.).   The product was diluted with

inactive material (24 mg.) and subjected to radiochemical
assay (Found: relative molar activity $\times 10^{-2}$, 139.7 ± 0.35;
2$\cdot$C requires 126.2).

7.7 PYROLYSIS OF n-BUTYLBENZENE AT VARIOUS TEMPERATURES

n-Butylbenzene.- The butylbenzene was prepared
as previously described.[20] It contained no impurities
which could be detected by gas-liquid chromatography.

Pyrolysis of n-Butylbenzene.- The following was
carried out over a range of temperatures from 300-900°C at
50° intervals. n-Butylbenzene (5 g.) was vaporised at a
rate of 7 g./hr. and passed in a stream of nitrogen through
a silica tube packed with porcelain chips and maintained at
the required temperature. The resulting tar was collected
and combined with the residue obtained on extracting the
pyrolysis tube and the packing with chloroform after each
experiment.

Analysis.- The tars thus obtained were analysed
by chromatography on alumina, chromatography on partially
acetylated cellulose and by thin layer chromatography.
In each pyrolysis the entire tar, was adsorbed on alumina
(10 g.) and the mixture placed on to the top of a column
of alumina (15 × 3.5 cm.; 100 g.) and chromatographed as
previously described. Although the presence of simpler

aromatic hydrocarbons such as naphthalene was observed, the
analyses of tars were restricted to polycyclic aromatic
hydrocarbons containing three or more condensed five- or
six-membered rings with the exception of 2,3- and
3,4-benzofluorenes.   A complete separation of these
compounds was often difficult and the estimation of their
yields from absorption spectra of their mixtures was
unreliable because of the similarity of their spectra.

300°C.-   The tar (4.044 g., 80.9%) was
chromatographed on alumina (100 g.) as described above.
Elution with hexane and mixtures of hexane and chloroform
gave 41 fractions.   These fractions were combined on the
basis of their ultraviolet absorption spectra and, where
necessary, chromatographed on columns of partially acetylated
cellulose.   No compounds containing three or more fused
aromatic rings could be detected in the resulting fractions.

350°C.-   The tar (4.136 g., 82.7%) was
chromatographed on alumina (100 g.) as above.   Elution
with hexane followed by mixtures of hexane and chloroform
gave again 41 fractions, some of which were combined and
chromatographed on columns of acetylated cellulose.   No
compounds containing three or more fused aromatic rings could
be detected in the resulting fractions.

400°C.-   The tar (3.990 g., 79.8%) was
chromatographed on alumina (100 g.) as described above.

Elution gave the following fractions (each of approximately
100 c.c.): hexane, fractions 1-10; and 250 c.c. portions
containing mixtures of hexane and chloroform the composition
of which is shown in brackets; fractions 11-12 (24:1, v/v;
sp. gr. 0. 698); fractions 13-14 (23:2, v/v; sp. gr. 0.731);
fractions 15-16 (22:3, v/v; sp. gr. 0.764); fractions 17-18
(21:4, v/v; sp. gr. 0.797); fractions 19-20 (20:5, v/v;
sp. gr. 0.830); fractions 21-22 (19:6, v/v; sp. gr. 0.863).
The appropriate fractions were combined on the basis of
their ultraviolet absorption spectra and chromatographed on
columns of partially acetylated cellulose. By this method
phenanthrene was isolated from fractions (2-3), and
fluoranthene from fractions (11-12).

450°C.- The tar (4.198 g., 84.00%) was
chromatographed on alumina (100 g.) as described above.
Elution gave the following fractions (each of approximately
100 c.c.): hexane, fractions 1-19; and mixtures of hexane and
chloroform as above, fractions 20-22 (24:1, v/v); fractions
23-24 (23:2, v/v); fractions 25-26 (22:3, v/v); fractions
27-30 (21:4, v/v); and fractions 31-34 (20:5, v/v). The
appropriate fractions were combined on the basis of their
ultraviolet absorption spectra and chromatographed on
columns of partially acetylated cellulose. The following
compounds were identified in the fractions enumerated:
naphthalene (2-3), fluorene (5-6), phenanthrene (5-7),
fluoranthene (11-14), 3,4-benzofluorene (20-22),

2,3-benzofluorene (22-25), and 3,4-benzofluoranthene (27-29).

500°C.- The tar (3.535 g., 70.70%) was
chromatographed on alumina as described above. Elution
gave the following fractions (each of approximately 100 c.c.):
hexane, fractions 1-25; and mixtures of hexane and chloroform
as above, fractions 26-28 (24:1, v/v); fractions 29-30
(23:2, v/v); fractions 31-33 (22:3, v/v); fractions
34-36 (21:4, v/v); fractions 37-38 (20:5, v/v); fractions
39-40 (19:6, v/v); fractions 41-43 (18:7, v/v); fractions
44-46 (17:8, v/v); fractions 47-49 (16:9, v/v); and fractions
50-51 (15:10, v/v). The appropriate fractions were
combined on the basis of their ultraviolet absorption spectra
and chromatographed on columns of acetylated cellulose. The
following compounds were identified in the fractions
enumerated: naphthalene (2-3), fluorene (5-6), phenanthrene
(5-7), fluoranthene (12-17), 3,4-benzofluorene (18-27),
2,3-benzofluorene (26-31), chrysene (32-35),
10,11-benzofluoranthene (32-35) and 3,4-benzofluoranthene
(32-35).

550°C.- The tar (3.249 g., 64.98%) was
chromatographed on alumina (100 g.) as described above.
Elution gave the following fractions (each of approximately
100 c.c.): hexane, fractions 1-24; and mixture of hexane
and chloroform as above, fractions 25-27 (24:1, v/v);
fractions 28-30 (23:2, v/v); fractions 31-33 (22:3, v/v);

fractions 34-35 (21:4, v/v); fractions 36-38 (20:5, v/v); fractions 39-40 (19:6, v/v); fractions 41-43 (18:7, v/v); fractions 44-46 (17:6, v/v); fractions 47-48 (16:9, v/v); fractions 49-51 (15:10, v/v); and fractions 52-54 (14:11, v/v). On the basis of their ultraviolet absorption spectra some of these fractions were combined and chromatographed on columns of partially acetylated cellulose. The following compounds were identified in the fractions enumerated: naphthalene (1-2), acenaphthylene (3-4), fluorene (5-6), phenanthrene (5-8), anthracene (6-8), pyrene (9-14), fluoranthene (13-19), 3,4-benzofluorene (30-33), 2,3-benzofluorene (30-33), 1,2-benzanthracene (30-33), chrysene (30-38), 10,11-benzofluoranthene (34-38), and 3,4-benzofluoranthene (34-38).

600°C.- The tar (2.152 g., 43.04%) was chromatographed on alumina (100 g.) as above. Elution gave the following fractions (each of approximately 100 c.c.): hexane, fractions 1-41; and mixtures of hexane and chloroform as above, fractions 42-45 (24:1, v/v); fractions 46-48 (23:2, v/v); fractions 49-50 (22:3, v/v); fractions 51-53 (21:4, v/v); fractions 54-55 (20:5, v/v); fractions 56-57 (19:6, v/v); fractions 58-59 (18:7, v/v); fractions 60-62 (17:8, v/v); fractions 63-64 (16:9, v/v); fractions 65-67 (15:10, v/v); and fractions 68-70 (14:11, v/v). On the basis of their ultraviolet spectra, appropriate fractions were combined and examined by chromatography on cellulose. The

following compounds were identified in the fractions
enumerated: naphthalene (2-3), acenaphthylene (4-5),
fluorene (6-7), phenanthrene (6-12), anthracene (6-14),
pyrene (14-41), fluoranthene (19-41), 3,4-benzofluorene
(42-47), 2,3-benzofluorene (48-51), 1,2-benzanthracene
(48-53), chrysene (48-53), 10,11-benzofluoranthene (54-58),
1,2-benzopyrene (54-58), 3,4-benzopyrene (54-58),
3,4-benzofluoranthene (54-58) and 11,12-benzofluoranthene
(54-58).

650°C.-   The tar (1.325 g., 26.5%) was
chromatographed on alumina (100 g.) as described above.
Elution gave the following fractions (each of approximately
100 c.c.): hexane, fractions 1-53; and 250 c.c. portions
containing mixtures of hexane and benzene the composition of
which is shown in brackets; fractions 54-56 (24:1, v/v);
fractions 57-59 (23:2, v/v); fractions 60-61 (22:3, v/v);
fractions 62-64 (21:4, v/v); fractions 65-66 (20:5, v/v);
fractions 67-69 (19:6, v/v); fractions 70-71 (18:7, v/v);
fractions 72-74 (17:8, v/v); fractions 75-76 (16:9, v/v);
fractions 77-79 (15:10, v/v); fractions 80-81 (14:11, v/v);
fractions 82-84 (13:12, v/v); fractions 85-86 (12:13, v/v);
fractions 87-89 (11:14, v/v); fractions 90-92 (10:15, v/v);
fractions 93-95 (9:16, v/v); fractions 96-98 (8:17, v/v);
fractions 99-100 (7:18, v/v); and with chloroform, fractions
101-106.   On the basis of their ultraviolet spectra some
of these fractions were combined and chromatographed on

columns of acetylated cellulose. The following compounds
were identified in the fractions enumerated: naphthalene
(2-3), acenaphthylene (5-6), fluorene (8), phenanthrene
(9-20), anthracene (10-22), pyrene (21-42), fluoranthene
(37-60), 3,4-benzofluorene (63-64), 2,3-benzofluorene (66-68),
1,2-benzanthracene (66-68), chrysene (66-71),
10,11-benzofluoranthene (72-76), 1,2-benzopyrene (72-76),
3,4-benzopyrene (72-76), 3,4-benzofluoranthene (71-79),
11,12-benzofluoranthene (77-79), 1,12-benzoperylene (77-82),
and 2,3-(o-phenylene)pyrene (80-86). Traces of other
polycyclic aromatic hydrocarbons were detected (perylene,
dibenzopyrenes), but their yields were not determined.

700°C.- The tar (0.534 g., 10.70%) was
chromatographed on alumina (100 g.) as above. Elution
gave the following fractions (each of approximately 100 c.c.):
hexane, fractions 1-44; and mixtures of hexane and chloroform
as above, fractions 45-47 (24:1, v/v); fractions 48-50
(23:2, v/v); fractions 51-53 (22:3, v/v); fractions 54-56
(21:4, v/v); fractions 57-59 (20:5, v/v); fractions 60-61
(19:6, v/v); fractions 62-64 (18:7, v/v); fractions 65-67
(17:8, v/v); fractions 68-70 (16:9, v/v); fractions 71-73
(15:10, v/v); fractions 74-76 (14:11, v/v); fractions 77-78
(13:12, v/v); fractions 79-81 (12:13, v/v); fractions 82-84
(11:14, v/v); fractions 85-87 (4:6, v/v); fractions 88-90
(3:7, v/v); fractions 91-93 (2:8, v/v); fractions 94-96
(1:9, v/v); and with chloroform, fractions 97-100. On

the basis of their ultraviolet absorption spectra some of
these fractions were combined and chromatographed on
columns of acetylated cellulose. The following compounds
were identified in the fractions enumerated: naphthalene
(2-3), acenaphthylene (5-12), fluorene (5-12), phenanthrene
(5-53), anthracene (13-53), pyrene (22-53), fluoranthene
(45-53), 3,4-benzofluorene (45-53), 2,3-benzofluorene (45-53),
1,2-benzanthracene (45-53), chrysene (45-65),
10,11-benzofluoranthene (45-65), 1,2-benzopyrene (45-65),
3,4-benzopyrene (59-65), 3,4-benzofluoranthene (59-65),
11,12-benzofluoranthene (66-74), 1,12-benzoperylene (66-74),
and 2,3-(o-phenylene)pyrene (66-74). Traces of other
polycyclic hydrocarbons were detected
(1,2:5,6-dibenzanthracene, perylene, dibenzopyrenes), but
their yields were not calculated.

750°C.- The tar (0.333 g., 6.70%) was
chromatographed on alumina (100 g.) as before. Elution
gave the following fractions (each of approximately 100 c.c.):
hexane, fractions 1-50; and mixtures of hexane and
chloroform as above, fractions 51-53 (24:1, v/v; sp. gr.
0.698); fractions 54-55 (23:2, v/v; sp. gr. 0.731);
fractions 56-57 (22:3, v/v; sp. gr. 0.764); fractions
58-60 (21:4, v/v; sp. gr. 0.797); fractions 61-63 (20:5,
v/v; sp. gr. 0.830); fractions 64-65 (19:6, v/v; sp. gr.
0.863); fractions 66-68 (18:7, v/v; sp. gr. 0.896);
fractions 69-70 (17:8, v/v; sp. gr. 0.929); fractions 71-73

(16:9, v/v; sp. gr. 0.962); fractions 74-76 (15:10, v/v; sp. gr. 0.995); fractions 77-79 (14:11, v/v; sp. gr. 1.028); fractions 80-82 (5:5, v/v; sp. gr. 1.077); fractions 83-85 (4:6, v/v; sp. gr. 1.160); and fractions 86-89 (3:7, v/v; sp. gr. 1.243). On the basis of their ultraviolet spectra some of these fractions were combined and chromatographed on columns of partially acetylated cellulose, followed, if necessary, by thin layer chromatography on partially acetylated cellulose. The following compounds have been identified in the fractions enumerated: naphthalene (2-4), acenaphthylene (6-10), fluorene (11-14), phenanthrene (11-31), anthracene (14-30), pyrene (29-55), fluoranthene (33-58), 3,4- and 2,3-benzofluorenes (56-61), 1,2-benzanthracene (56-61), chrysene (59-64), 10,11-benzofluoranthene (65-67), 1,2-benzopyrene (62-67), 3,4-benzopyrene (65-67), 3,4-benzofluoranthene (65-67), 11,12-benzofluoranthene (65-70), 1,12-benzoperylene (68-70), and 2,3-(o-phenylene)pyrene (68-70). Traces of other polycyclic hydrocarbons were detected (1,2:5,6-dibenzanthracene, dibenzopyrenes), but their yields were not determined.

800°C.- The tar (0.025 g., 0.50%) was chromatographed on alumina (100 g.) as in the previous experiments. Elution gave the following fractions (each of approximately 100 c.c.): hexane, fractions 1-63; and

mixtures of hexane and chloroform as above, fractions
64-79 (99:1, v/v);   fractions 80-81 (98:2, v/v);   fractions
82-84 (97:3, v/v);   fractions 85-87 (96:4, v/v);   fractions
88-89 (95:5, v/v);   fractions 90-92 (94:6, v/v);   fractions
93-94 (93:7, v/v);   fractions 95-97 (92:8, v/v);   fractions
98-99 (90:10, v/v);   fractions 102-102 (88:12, v/v);
fractions 103-104 (86:14, v/v);   fractions 105-107 (84:16,
v/v);   fractions 108-110 (82:18, v/v);   fractions 111-113
(80:20, v/v);   fractions 114-115 (78:22, v/v);   fractions
116-118 (73:27, v/v);   fractions 119-121 (65:35, v/v);
fractions 122-123 (54:46, v/v);   and fractions 124-128
(40:60, v/v).   On the basis of their ultraviolet and
fluorescence spectra some of these fractions were combined
and chromatographed on columns of partially acetylated
cellulose, followed by thin layer chromatography on
partially acetylated cellulose when necessary.

The following compounds were identified in the
fractions enumerated: fluorene (17), phenanthrene (17-32),
anthracene (23-24), pyrene (39-58), fluoranthene (54-80),
1,2-benzanthracene (76-85), chrysene (95-110),
10,11-benzofluoranthene (106-110), 1,2-benzopyrene (106-110),
3,4-benzopyrene (106-110), 3,4-benzofluoranthene (111-120)
and 11,12-benzofluoranthene (116-124).

850°C.-   The tar (0.015 g., 0.30%) was
chromatographed on a column of partially acetylated cellulose
and the following compounds were identified in the fractions

enumerated (each fraction of approximately 6 c.c.):
phenanthrene (20-25), pyrene (20-25), fluoranthene (21-25),
chrysene (33-40), and 3,4-benzofluoranthene (43-54). The
fractions 20-25 were combined and chromatographed on a
large column of acetylated cellulose. This procedure
afforded a complete separation of the three components.

900°C.- The tar (0.009 g., 0.18%) was
chromatographed on a column of partially acetylated cellulose
and the following compounds identified in the fractions
enumerated (each fraction of approximately 6 c.c.):
phenanthrene (19-22), pyrene (19-23), fluoranthene (20-23),
chrysene (31-36), and 3,4-benzofluoranthene (42-48).
A similar procedure to that outlined above resulted in the
determination of the yields of the first three components
of the mixture.

DETAILS OF IDENTIFICATION

Naphthalene.- Identified in tars obtained at
temperatures of 450-750°C by chromatography on alumina.
The ultraviolet absorption spectrum showed maxima at 248,
257, 266, 275, 285, and 311 mμ in agreement with those of
an authentic specimen.

Acenaphthylene.- Identified in tars obtained at

temperatures of 550-750°C, by chromatography on alumina
followed by chromatography on partially acetylated
cellulose.   The ultraviolet absorption spectrum showed
maxima at 229, 258, 266, 276, 309, 323, 334, and 340 mμ in
agreement with an authentic specimen.

Fluorene.-   Identified in tars obtained at
temperatures of 450-800°C, by chromatography on alumina
followed by chromatography on partially acetylated cellulose.
The ultraviolet absorption spectrum showed maxima at 260,
290, and 301 mμ in agreement with those of an authentic
specimen.

Phenanthrene.-   Identified in tars obtained at
temperatures of 400-900°C, by chromatography on alumina and
on partially acetylated cellulose.   The ultraviolet
absorption spectrum showed maxima at 243, 252, 275, 282,
294, 310, 317, 324, 331, 339, and 346 mμ in agreement with
those of an authentic specimen.

Anthracene.-   Identified in tars obtained at
temperatures of 550-800°C, by chromatography on alumina
followed by chromatography on partially acetylated cellulose.
The ultraviolet absorption spectrum showed maxima at 246,
253, 308, 323, 339, 357, and 377 mμ in agreement with those
of an authentic specimen.

Pyrene.-   Identified in tars obtained at

temperatures of 550-900°C, by chromatography on alumina and on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335, 351, 358, 364, and 373 mμ in agreement with those of an authentic specimen.

Fluoranthene.- Identified in tars obtained at temperatures of 400-900°C, by chromatography on alumina followed by chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 236, 253, 263, 273, 278, 282, 288, 309, 323, 342, and 360 mμ in agreement with those of an authentic specimen.

1,2-Benzanthracene (benz[a]anthracene).- Identified in tars obtained at temperatures of 550-800°C, by chromatography on alumina followed by chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 256, 268, 278, 289, 300, 315, 326, 341, 358, 365, 374, and 384 mμ in agreement with those of an authentic specimen.

3,4-Benzofluorene (7 H-benzo[c]fluorene).- Identified in tars obtained at temperatures of 450-750°C, by chromatography on alumina followed by chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 230, 251, 262, 302, 311, 321, 329, and 337 mμ in agreement with those of an authentic specimen.

<u>2,3-Benzofluorene</u> (<u>11</u> H-<u>benzo</u>[b]<u>fluorene</u>).-
Identified in tars obtained at temperatures of 450-750°C,
by chromatography on alumina and on acetylated cellulose.
The ultraviolet absorption spectrum showed maxima at 255,
264, 273, 285, 304, 317, 325, 333, and 340 mμ in agreement
with an authentic specimen.

<u>Chrysene</u>.-   Identified in tars obtained at
temperatures of 500-900°C, by chromatography on alumina and
on acetylated cellulose.   The ultraviolet spectrum showed
maxima at 242, 259, 267, 283, 294, 306, 320, 344, 351, and
363 mμ in agreement with those of an authentic specimen.

<u>10,11-Benzofluoranthene</u> (<u>benzo</u>[j]<u>fluoranthene</u>).-
Identified in tars obtained at temperatures of 500-800°C,
by chromatography on alumina and on acetylated cellulose.
The ultraviolet absorption spectrum showed maxima at 241,
282, 293, 309, 318, 333, 345, 365, 376, and 383 mμ in
agreement with those of an authentic specimen.

<u>1,2-Benzopyrene</u> (<u>benzo</u>[e]<u>pyrene</u>).-   Identified in
tars obtained at temperatures of 600-800°C, by
chromatography on alumina and on partially acetylated
cellulose.   The absorption spectrum showed maxima at 238,
258, 268, 278, 289, 305, 317, 333, and 366 mμ in agreement
with those of an authentic specimen.

<u>3,4-Benzopyrene</u> (<u>benzo</u>[a]<u>pyrene</u>).-   Identified in

tars obtained at temperatures of 600-800°C, by chromatography on alumina and on partially acetylated cellulose. The absorption spectrum showed maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385, and 404 mμ in agreement with those of an authentic specimen.

3,4-Benzofluoranthene (benz[e]acephenanthrylene).- Identified in tars obtained at temperatures of 450-900°C, by chromatography on alumina and on partially acetylated cellulose. The absorption spectrum showed maxima at 239, 256, 266, 276, 290, 294, 301, 320, 339, 351, and 369 mμ in agreement with those of an authentic specimen.

11,12-Benzofluoranthene (benzo[k]fluoranthene).- Identified in tars obtained at temperatures of 600-800°C, by chromatography on alumina and on partially acetylated cellulose. The absorption spectrum showed maxima at 238, 247, 269, 283, 297, 309, 361, 380, and 402 mμ in agreement with those of an authentic specimen.

1,12-Benzoperylene (benzo[ghi]perylene).- Identified in tars formed at temperatures of 650-750°C, by chromatography on alumina and on acetylated cellulose. The absorption spectrum showed maxima at 268, 276, 289, 300, 315, 325, 330, 345, 363, and 383 mμ in agreement with those of an authentic specimen.

2,3-(o-Phenylene)pyrene (indeno[1,2,3-cd]pyrene).-

Identified in tars formed at temperatures of 650-750°C, by chromatography on alumina and on acetylated cellulose. The absorption spectrum showed maxima at 259, 269, 277, 292, 304, 315, 360, 376, 385, 402, 422, and 431 mμ in agreement with those of an authentic specimen.

REFERENCES

1   Haddow, A., *Endeavour*, 1943, **2**, 27;   Haddow, A., and
    Kon, G.A.R., *Brit. Med. Bull.*, 1947, **4**, 314;   Haddow, A.,
    Brit. Med. Bull., 1947, **4**, 331;   Badger, G.M., *Brit. J.
    Cancer*, 1948, **2**, 309;   Badger, G.M., *Adv. Cancer Res.*,
    1954, **2**, 73;   Buu-Hoi, N.P., *Arzneimittelforsch.*, 1956,
    6, 251;   Haddow, A., *Brit. Med. Bull.*, 1958, **14**, 79;
    Hartwell, J.L., "Survey of Compounds Which Have Been
    Tested for Carcinogenic Activity," US Public Health
    Service Publication No 149, Washington, 1951;   Shubik, P.,
    and Hartwell, J.L., "Survey of Compounds Which Have
    Been Tested for Carcinogenic Activity." Supplement I,
    US Public Health Service Publication No 149, Washington,
    1957

2   Lam, J., *Acta Path. Microbiol.*, 1955, **36**, 503

3   Kennaway, E.L., *J. Ind. Hyg.*, 1924, **5**, 462

4   Kennaway, E.L., *Brit. Med. J.*, 1925, **ii**, 1

5   Kennaway, E.L., *J. Path. Bact.*, 1924, **27**, 233

6   Badger, G.M., Buttery, R.G., Kimber, R.W.L., Lewis, G.E.,
    Moritz, A.G., and Napier, I.M., *J. Chem. Soc.*, 1958,
    2449

7   Tsutsui, H., *Gann*, 1918, **12**, 17

8   Yamagiwa, K., and Ichikawa, K., *Mitt. med. Fak. Kaiserl.
    Univ., Tokyo*, 1915, **15**, 295;   *J. Cancer Res.*, 1918, **3**, 1

9   Bloch, B., and Dreifuss, W., *Schweiz. med. Woch.*, 1921,
    51, 1033

10 Deelman, H.T., *Z. Krebsforsch.*, 1922, **18**, 261

11 Leitch, A., *Brit. Med. J.*, 1922, **ii**, 1104

12 Twort, C.C., and Ing, H.R., *Lancet*, 1928, **1**, 752;

Z. Krebsforsch., 1928, 27, 308; Twort, C.C., and Fulton, J.D., J. Path. Bact., 1929, 32, 149; Z. Krebsforsch., 1932, 35, 543; Twort, C.C., and Twort, J.M., J. Ind. Hyg., 1931, 13, 204

13   Leitch, A., Brit. Med. J., 1924, 11, 941

14   Kennaway, E.L., and Sampson, B., J. Path. Bact., 1928, 31, 609

15   Cook, J.W., Hieger, I., Kennaway, E.L., and Mayneord, W.V., Proc. Roy. Soc., 1932, B 111, 455

16   Kennaway, E.L., Biochem. J., 1930, 24, 497

17   Hieger, I., Biochem. J., 1930, 24, 505

18   Cook, J.W., Hewett, C.L., and Hieger, I., J. Chem. Soc., 1933, 395

19   "The Coal Tar Data Book," Coal Tar Research Assoc., Leeds, 1953

20   Cook, J.W., and Percy, N., J. Soc. Chem. Ind., 1945, 64, 27

21   Kruber, O., and Oberkobusch, R., Chem. Ber., 1952, 85, 433

22   Schoental, R., Nature, 1957, 180, 606

23   Buu-Hoi, N.P., Nature, 1958, 182, 1158

24   Westrop, J.W., Naturwiss., 1962, 49, 280

25   Wynder, E.L., and Hoffmann, D., Cancer, 1959, 12, 1194

26   Cook, J.W., Carruthers, W., and Woodhouse, D.L., Brit. Med. Bull., 1958, 14, 132

27   Cooper, R.L., and Lindsey, A.J., Chem. and Ind., 1953 1205; Cooper, R.L., Lindsey, A.J., and Waller, R.F., Chem. and Ind., 1954, 1418; Cooper, R.L., and Lindsey, A.J., Brit. J. Cancer, 1955, 9, 304; Seelkopf, C.,

Z. Lebensm.-Untersuch., 1955, 218; Bonnet, J., and Neukomm, S., Helv. Chim. Acta, 1956, 39, 1724; Campbell, J.M., and Lindsey, A.J., Brit. J. Cancer, 1956, 10, 649; Alvord, E.T., and Cardon, S.Z., Brit. J. Cancer, 1956, 10, 498; Kuratsune, M., J. Nat. Cancer Inst., 1956, 16, 1485; Gilbert, J.A.S., and Lindsey, A.J., Brit. J. Cancer, 1956, 10, 642; Lettré, H., Jahn, A., and Hausbeck, C., Angew. Chem., 1956, 68, 212; Lyons, M.J., Nature, 1956, 177, 630; Latarjet, R., Cuzin, J.L., Hubert-Habart, M., Muel, B., and Royer, R., Bull. Cancer, 1956, 43, 180; Patton, H.W., and Touey, G.P., Analyt. Chem., 1956, 28, 1685; Philippe, R.J., and Hobbs, M.E., Analyt. Chem., 1956, 28, 2002; Wynder, E.L., Fritz, L., and Furth, N., J. Nat. Cancer Inst., 1957, 19, 361; Bonnet, J., and Neukomm, S., Oncologia, 1957, 10, 124; Van Duuren, B.L., J. Nat. Cancer Inst., 1958, 21, 1; Orris, L., Van Duuren, B.L., Kosak, A.I., Nelson, N., and Schmitt, F.L., J. Nat. Cancer Inst., 1958, 21, 557; Cardon, S.Z., Tobacco Sci., 1958, 2, 130; Bentley, H.R., and Burgan, J.G., Analyst, 1958, 83, 442; Ahlmann, J., Acta Path. Microbiol. Scand., 1958, 43, 379; Pietzsch, A., Naturwiss., 1958, 45, 445; Wynder, E.L., and Hoffmann, D., Cancer, 1959, 12, 1079; Wynder, E.L., and Hoffmann, D., Cancer, 1961, 14, 1306

[28] Van Duuren, B.L., J. Nat. Cancer Inst., 1958, 21, 1; Pietzsch, A., Naturwiss., 1958, 45, 445; Wynder, E.L., and Hoffmann, D., Cancer, 1961, 14, 1306

[29] Bonnet, J., and Neukomm, S., Helv. Chim. Acta, 1956, 39, 1724; Bonnet, J., and Neukomm, S., Oncologia, 1957, 10, 124

[30] Wynder, E.L., and Wright, G., Cancer, 1957, 10, 255; Lyons, M.J., and Johnston, H., Brit. J. Cancer, 1957, 11, 554

[31] Wynder, E.L., and Wright, G., Cancer, 1957, 10, 255;

Lyons, M.J., Nature, 1958, 182, 178

32 Wynder, E.L., and Wright, G., Cancer, 1957, 10, 255; Wynder, E.L., and Hoffmann, D., Cancer, 1959, 12, 1079; 1194

33 Wynder, E.L., and Hoffmann, D., Cancer, 1959, 12, 1079; 1194

34 Cooper, R.L., and Lindsey, A.J., Brit. J. Cancer, 1955, 9, 304; Van Duuren, B.L., J. Nat. Cancer Inst., 1958 21, 1; Van Duuren, B.L., and Nelson, N., Proc. Amer. Assoc. Cancer Res., 1958, 2, 353

35 Roffo, A.H., Z. Krebsforsch., 1939, 49, 588; Lettré, H., and Jahn, A., Naturwiss., 1955, 42, 210; Lyons, M.J., and Johnston, H., Brit. J. Cancer, 1957, 11, 554; Van Duuren, B.L., J. Nat. Cancer Inst., 1958, 21, 1; Orris, L., Van Duuren, B.L., Kosak, A.I., Nelson, N., and Schmitt, F.L., J. Nat. Cancer Inst., 1958, 21, 557; Ahlmann, J., Acta Path. Microbiol. Scand., 1958, 43, 379; Pietzsch, A., Naturwiss., 1958, 45, 445; Wynder, E.L., and Hoffmann, D., Cancer, 1959, 12, 1079

36 Lyons, M.J., and Johnston, H., Brit. J. Cancer, 1957, 11, 554; Van Duuren, B.L., and Nelson, N., Proc. Amer. Assoc. Cancer Res., 1958, 2, 353; Ahlmann, J., Acta Path. Microbiol. Scand., 1958, 43, 379; Pietzsch, Naturwiss., 1958, 45, 445; Wynder, E.L., and Hoffmann, D., Cancer, 1959, 12, 1079

37 Lettré, H., and Jahn, A., Naturwiss., 1955, 42, 210; Gilbert, J.A.S., and Lindsey, A.J., Brit. J. Cancer, 1956, 10, 642; Kuratsune, M., J. Nat. Cancer Inst., 1956, 16, 1485; Lyons, M.J., Nature, 1956, 177, 630; Bonnet, J., and Neukomm, S., Oncologia, 1957, 10, 124; Pietzsch, A., Naturwiss., 1958, 45, 445; Van Duuren, B.L., J. Nat. Cancer Inst., 1958, 21, 1; Wynder, E.L., and Hoffmann, D., Cancer, 1959, 12, 1079

38   Wynder, E.L., and Hoffmann, D., Cancer, 1961, 14, 1306

39   Roe, F.J.C., Salaman, M.H., and Cohen, J., Brit. J.
     Cancer, 1959, 13, 623

40   Wynder, E.L., and Wright, G., Cancer, 1957, 10, 255

41   Lyons, M.J., Gibson, J.F., and Ingram, D.J.E., Nature,
     1958, 181, 1003

42   Lyons, M.J., and Spence, J.B., Brit. J. Cancer, 1960,
     14, 703

43   Hadler, H.I., Darchun, V., and Lee, K., J. Nat. Cancer
     Inst., 1951, 23, 1383

44   Wynder, E.L., and Hoffmann, D., unpublished results,
     quoted in reference 38

45   Passey, R.D., Brit. Med. J., 1922, 11, 1112

46   Goulden, F., and Tipler, M.M., Brit. J. Cancer, 1949, 3,
     157

47   Clemo, G.R., and Miller, E.W., Chem. and Ind., 1955, 38;
     Lyons, M.J., and Johnston, H., Brit. J. Cancer, 1957,
     11, 60

48   Waller, R.E., Brit. J. Cancer, 1952, 6, 8; Stock, P.,
     and Campbell, J.M., Brit. Med. J., 1956, 11, 923;
     Falk, H.L., Kotin, P., and Markul, I., Cancer, 1958, 2,
     482

49   Kotin, P., Falk, H.L., and Thomas, M., Arch. Ind. Hyg.,
     1954, 9, 164; Kotin, P., Falk, H.L., and Thomas, M.,
     Arch. Ind. Health, 1955, 11, 113

50   Reuter, A., Johne, K.O., and Lieb, J., Z. analyt. Chem.,
     1958, 164, 335

51   Lyons, M.J., and Johnston, H., Brit. J. Cancer, 1957,
     11, 60; Lyons, M.J., Brit. J. Cancer, 1959, 13, 126;
     Lyons, M.J., Nat. Cancer Inst., Monograph 9, 1962, 193

52 Hoffmann, D., and Wynder, E.L., Cancer, 1962, 15, 93;
    Wynder, E.L., and Hoffmann, D., Cancer, 1962, 15, 103;
    Hoffmann, D., and Wynder, E.L., Nat. Cancer Inst.,
    Monograph 9, 1962, 91

53 Commins, B.T., Waller, R.E., and Lawther, P.J., Brit.
    J. Ind. Med., 1957, 14, 232

54 Tilgner, D.J., and Muller, K., Roczniky technologii i
    chemii zywności, 1957, 2, 21; See Kay, K., Analyt.
    Chem., 1959, 31, 633

55 Commins, B.I., Internat. J. Air Poll., 1958, 1, 14

56 Falk, H.L., and Steiner, P.E., Cancer Res., 1952, 12,
    30; Lindsey, A.J., Phillips, M.A., and Wilkinson, D.S.,
    Chem. and Ind., 1958, 1365

57 Koe, B.K., and Zechmeister, L., Arch. Biochem. Biophys.,
    1952, 41, 396; Cahmann, H.J., and Kuratsune, M.,
    Analyt. Chem., 1957, 29, 1312

58 Hougen, F.W., Chem. and Ind., 1954, 192

59 Gilbert, J.A.S., and Lindsey, A.J., Chem. and Ind.,
    1956, 927

60 Kuratsune, M., and Hueper, W.C., J. Nat. Cancer Inst.,
    1958, 20, 37

61 Bailey, E.J., and Dungal, N., Brit. J. Cancer, 1958, 12,
    348

62 Falk, H.L., Steiner, P.E., Goldfein, S., Breslow, A.,
    and Hykes, R., Cancer Res., 1951, 11, 318

63 Sulman, E., and Sulman, F., Cancer Res., 1946, 6, 366;
    Beránková, Z., and Sula, J., Časopis lékařů českých,
    1953, 92, 195; Chem. Abs., 1955, 49, 592; Bailey,
    E.J., and Dungal, N., Brit. J. Cancer, 1958, 12, 348

64 Campbell, J.M., and Cooper, R.L., Chem. and Ind., 1955
    64; Campbell, J.M., and Lindsey, A.J., Chem. and

Ind., 1957, 951

65   Campbell, J.M., and Lindsey, A.J., _Brit. J. Cancer_,
      1956, _10_, 649

66   Davies, W., and Wilmhurst, J.R., _Brit. J. Cancer_, 1960,
      _14_, 295

67   Kolšek, J., Perpar, M., and Žitko, M., _Mikrochim. Acta_,
      1959, 299

68   Blumer, M., _Science_, 1961, _134_, 474; See Selected
      Abstracts, _Angew. Chem. internat. Edit._, 1962, _1_, 222

69   Lam, J., _Acta Path. Microbiol. Scand._, 1956, _39_, 198

70   Lam, J., _Acta Path. Microbiol. Scand._, 1955, _37_, 421;
      1956, _39_, 207

71   Wright, G.F., and Wynder, E.L., _Proc. Amer. Assoc. Cancer
      Res._, 1955, _2_, 55; 1956, _2_, 159

72   Falk, H.L., and Steiner, P.L., _Cancer Res._, 1952, _12_, 30

73   Arthur, J.R., Commins, B.T., Gilbert, J.A.S., Lindsey,
      A.J., and Napier, D.H., _Combustion and Flame_, 1958, _2_,
      267

74   Lang, K.F., Buffleb, H., and Kalowy, J., _Chem. Ber._,
      1957, _90_, 2888

75   Lang, K.F., and Buffleb, H., _Chem. Ber._, 1957, _90_, 2894

76   Lang, K.F., and Buffleb, H., _Chem. Ber._, 1958, _91_, 2866

77   Lang, K.F., Buffleb, H., and Kalowy, J., _Chem. Ber._,
      1960, _93_, 303

78   Lang, K.F., Buffleb, H., and Kalowy, J., _Chem. Ber._,
      1961, _94_, 523

79   Lang, K.F., and Buffleb, H., _Chem. Ber._, 1961, _94_, 1075

80   Lang, K.F., and Zander, M., _Chem. Ber._, 1961, _94_, 1871

81   Lang, K.F., and Buffleb, H., _Chem. Ber._, 1962, _95_, 1049

82 Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1958, 2453

83 Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1958, 2455

84 Badger, G.M., and Buttery, R.G., J. Chem. Soc., 1958, 2458

85 Badger, G.M., and Spotswood, T.M., J. Chem. Soc., 1959, 1635

86 Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1960, 266

87 Spotswood, T.M., J. Chem. Soc., 1960, 4427

88 Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1960, 2746

89 Badger, G.M., Lewis, G.E., and Napier, I.M., J. Chem. Soc., 1960, 2825

90 Badger, G.M., and Spotswood, T.M., J. Chem. Soc., 1960, 4420

91 Badger, G.M., and Spotswood, T.M., J. Chem. Soc., 1960, 4431

92 Badger, G.M., and Novotny, J., J. Chem. Soc., 1961, 3400

93 Badger, G.M., and Novotny, J., J. Chem. Soc., 1961, 3403

94 Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1961, 3407

95 Badger, G.M., Donnelly, Jillian K., and Spotswood, T.M., Austral. J. Chem., 1962, 15, 605

96 Badger, G.M., Donnelly, Jillian K., and Spotswood, T.M., Austral. J. Chem., 1963, 16, 392

97 Badger, G.M., Donnelly, Jillian K., and Spotswood, T.M., unpublished results

98 Badger, G.M., Jolad, S.D., and Spotswood, T.M.,

unpublished results

99 Miller, E.C., Cancer Res., 1951, 11, 100

100 Wiest, W.G., and Heidelberger, C., Cancer Res., 1953, 13, 250

101 Oliverio, V.T., and Heidelberger, C., Cancer Res., 1958, 18, 1094

102 Bhargava, P.M., and Heidelberger, C., Proc. Amer. Assoc. Cancer Res., 1954, 1, 5

103 Heidelberger, C., and Davenport, G.R., Proc. Amer. Assoc. Cancer Res., 1956, 2, 117; Heidelberger, C., and Moldenhauer, M.G., Cancer Res., 1956, 16, 442

104 Bhargava, P.M., Hadler, H.I., and Heidelberger, C., J. Amer. Chem. Soc., 1955, 77, 2877

105 Bhargava, P.M., and Heidelberger, C., J. Amer. Chem. Soc., 1956, 78, 3671

106 Heidelberger, C., "Carcinogenesis. Mechanism of Action," Ciba Foundation Symposium, J. and A. Churchill, Ltd., London, 1959, p. 179

107 Daudel, P., Muel, B., Lacroix, G., and Prodi, G., J. Chim. phys., 1962, 263

108 Pullman, A., and Pullman, B., "Cancérisation par les substances chimiques et structure moléculaire," Masson and Cie, Paris, 1955; Daudel, R., Adv. Chem. Phys., 1958, 1, 165

109 Woodhouse, D.L., Brit. J. Cancer, 1955, 9, 418

110 Somerville, A.R., and Heidelberger, C., Cancer Res., 1961, 21, 591; Davenport, G.R., Abell, C.W., and Heidelberger, C., Cancer Res., 1961, 21, 599; Abell, C.W., and Heidelberger, C., Cancer Res., 1962, 22, 931

111   Miller, E.C., and Miller, J.A., J. Natl. Cancer Inst.,
       1955, 15, 1571

112   Heidelberger, C., and Davenport, G.R., Acta Unio
       Internat. contre Cancrum, 1961, 47, 55

113   Brookes, P., and Lawley, P.D., Brit. Empire Cancer
       Campaign, Annual Report, 1962, 40, 45

114   Schmidt, O., Z. phys. Chem., 1938, B 39, 59; 1939,
       B 42, 83; Schmidt, O., and Schmidt, H., Z. phys.
       Chem., 1939, B 44, 185; Schmidt, O., Z. phys. Chem.,
       1939, B 44, 194; Schmidt, O., Naturwiss., 1941, 29,
       146

115   Svartholm, N., Arkiv Kemi, Min., Geol., 1942, A 15, 1;
       Chem. Abs., 1942, 36, 6414

116   Arcos, J.C., and Arcos, M., Fort. Arzneimittelforsch.,
       1962, 4, 407

117   Badger, G.M., J. Chem. Soc., 1949, 456; 1950, 1809

118   Coulson, C.A., Adv. Cancer Res., 1953, 1, 1; Badger,
       G.M., Adv. Cancer Res., 1954, 2, 73; Pullman, A.,
       and Pullman, B., Adv. Cancer Res., 1955, 3, 117

119   Badger, G.M., Brit. J. Cancer, 1948, 2, 309

120   Daudel, R., Adv. Chem. Phys., 1958, 1, 165; Chalvet,
       O., Daudel, R., and Moser, C., Cancer Res., 1958, 18,
       1033

121   Woodhouse, D.L., Brit. J. Cancer, 1954, 8, 346;
       Heidelberger, C., and Moldenhauer, M.G., Cancer Res.
       1956, 16, 442

122   Szent-Györgyi, A., Nature, 1941, 148, 157; Evans, M.G.,
       and Gergely, J., Biochim. Biophys. Acta, 1949, 3, 188

123   Cardew, M.H., and Eley, D.D., Discuss. Faraday Soc.
       1959, 27, 115

124   Mason, R., *Nature*, 1958, *181*, 820; *Brit. J. Cancer*, 1958, *12*, 469; *Discuss. Faraday Soc.*, 1959, *27*, 129

125   Pullman, A., and Pullman, B., *Nature*, 1962, *196*, 228

126   Nagata, C., Fukui, K., Yonezawa, T., and Tagashira, Y., *Cancer Res.*, 1955, *15*, 233; Koutecký, J., and Zahradník, R., *Cancer Res.*, 1961, *21*, 457

127   Berthelot, M., *Ann. Chim. Phys.*, 1866, *9*, 445; *Bull. Soc. chim. France*, 1866, *6*, 272

128   Egloff, G., "The Reactions of Pure Hydrocarbons," Reinhold, New York, 1937

129   Hurd, C.D., "The Pyrolysis of Carbon Compounds," Reinhold, New York, 1929

130   Steacie, E.W.R., "Atomic and Free Radical Reactions," Reinhold, New York, 2nd. ed., 1954

131   Trotman-Dickenson, A.F., "Gas Kinetics," Butterworths, London, 1955

132   "Reactions of Free Radicals in the Gas Phase," Special Publication No. 9, The Chemical Society, London, 1957

133   "Hydrocarbons," *Discuss. Faraday Soc.*, 1951, *10*

134   Haensel, V., and Sterba, M.J., *Ind. Eng. Chem.*, 1948, *40*, 1660; 1949, *41*, 1914; 1950, *42*, 1739; 1951, *43*, 2016; 1952, *44*, 2073; 1953, *45*, 2034; 1954, *46*, 1888

135   Appell, H.R., and Berger, C.V., *Ind. Eng. Chem.*, 1955, *47*, 1842; 1956, *48*, 1566; 1957, *49*, 1478; 1958, *50*, 1330

136   deRosset, A.J., and Berger, C.V., *Ind. Eng. Chem.*, 1959, *51*, 1075; 1960, *52*, 711; 1961, *53*, 680

137   Stubbs, F.J., and Hinshelwood, C.N., *Proc. Roy. Soc.*, 1950, *A*, *200*, 458

138   Eltenton, G.C., *J. Chem. Phys.*, 1947, 15, 455

139   Kuppermann, A., and Larson, J.G., *J. Chem. Phys.*,
      1960, 33, 1264

140   Purnell, J.H., and Quinn, C.P., *Nature*, 1961, 189, 656;
      J. Chem. Soc., 1961, 4128

141   Laidler, K.J., and Wojciechowski, B.W., *Proc. Roy. Soc.*,
      1961, A, 260, 91;   103

142   Laidler, K.J., Sagert, N.H., and Wojciechowski, B.W.,
      Proc. Roy. Soc., 1962, A, 270, 242;   254

143   Purnell, J.H., and Quinn, C.P., *Proc. Roy. Soc.*, 1962,
      A, 270, 267

144   Sagert, N.H., and Laidler, K.J., *Canad. J. Chem.*, 1963,
      41, 838;   848

145   James, D.G.L., and Steacie, E.W.R., *Proc. Roy. Soc.*,
      1958, A, 244, 289;   297

146   Rice, F.O., and Vanderslice, T.A., *J. Amer. Chem. Soc.*,
      1958, 80, 291

147   Germain, J.E., and Vaniscotte, C., *Bull. Soc. chim.*
      France, 1958, 319

148   Kevorkian, V., Heath, C.E., and Boudart, M., *J. Phys.*
      Chem., 1960, 64, 964

149   Skinner, G.B., and Ruehrwein, R.A., *J. Phys. Chem.*,
      1959, 63, 1736

150   Nelson, L.S., and Lundberg, J.L., *J. Phys. Chem.*,
      1959, 63, 433

151   Skinner, G.B., and Sokoloski, E.M., *J. Phys. Chem.*,
      1960, 64, 1028

152   Norrish, R.G.W., and Purnell, J.H., *Proc. Roy. Soc.*,
      1958, A, 243, 435

153 Longwell, P.A., and Sage, B.H., J. Chem. Eng. Data, 1960, 5, 322

154 Lucchesi, P.J., Baeder, D.L., and Longwell, J.P., Proc. 5th World Petroleum Congress, New York, 1959, quoted in reference 136

155 Hoare, M.F., Garbett, T.A., and Pegg, R.E., Proc. 5th World Petroleum Congress, New York, 1959, quoted in reference 136

156 Arai, S., and Shida, S., J. Chem. Phys., 1963, 38, 694

157 LeRoy, D.J., and Steacie, E.W.R., J. Chem. Phys., 1941, 9, 829; 1942, 10, 676; Callear, A.B., and Robb, R.C., Discuss. Faraday Soc., 1954, 17, 21; Okabe, H., and McNesby, J.R., J. Chem. Phys., 1962, 36, 601

158 Cvetanović, R.J., and Callear, A.B., J. Chem. Phys., 1955, 23, 1182; Callear, A.B., and Cvetanović, R.J., J. Chem. Phys., 1956, 24, 873

159 Kebarle, P., J. Phys. Chem., 1963, 67, 716

160 Avrahami, M., and Kebarle, P., J. Phys. Chem., 1963, 67, 354

161 Kebarle, P., and Avrahami, M., J. Chem. Phys., 1963, 38, 700

162 Cvetanović, R.J., and Doyle, L.C., J. Chem. Phys., unpublished results, quoted in reference 160

163 LeRoy, D.J., and Steacie, E.W.R., J. Chem. Phys., 1944, 12, 117; Collin, J., and Lossing, F.P., Canad. J. Chem., 1957, 35, 778

164 Egloff, G., and Hulla, G., Chem. Rev., 1944, 35, 279

165 Gil-Av, E., Shabtai, J., and Steckel, F., J. Chem. Eng. Data, 1960, 5, 98; Ind. Eng. Chem., 1960, 52, 31

166 Zimmerman, H.E., and Paufler, R.M., J. Amer. Chem. Soc.,

1960, 82, 1514

167   Greene, E.F., Taylor, R.L., and Patterson, W.L.,
       J. Phys. Chem., 1958, 62, 233; Aten, C.F., and
       Greene, E.F., Combustion and Flame, 1961, 5, 55

168   Bradley, J.N., and Kistiakowsky, G.B., J. Chem. Phys.,
       1961, 35, 264

169   Tsang, W., Bauer, S.H., and Waelbroeck, F., J. Phys.
       Chem., 1962, 66, 282

170   Coats, F.H., and Anderson, R.C., J. Phys. Chem., 1959,
       63, 1340

171   Slysh, R.S., Diss. Abs., 1960, 21, 144; Slysh, R.S.,
       and Kinney, C.R., J. Phys. Chem., 1961, 65, 1044

172   Lang, K.F., Buffleb, H., and Zander, M., Angew. Chem.,
       Internat. Ed., 1963, 2, 158

173   Cowperthwaite, M., and Bauer, S.H., J. Chem. Phys.,
       1962, 36, 1743

174   Lossing, F.P., Ingold, K.U., and Henderson, I.H.S.,
       J. Chem. Phys., 1954, 22, 621

175   Berthelot, M., Ann. Chim. Phys., 1866, 9, 445; 471;
       1867, 12, 143; 1869, 16, 144; Bull. Soc. chim.
       France, 1874, 22, 437

176   Groll, H.P.A., Ind. Eng. Chem., 1933, 25, 784

177   Bonnet, J., and Neukomm, S., Oncologia, 1957, 10, 124

178   Badger, G.M., and Buttery, R.G., J. Chem. Soc., 1958,
       2458; Badger, G.M., and Spotswood, T.M., J. Chem. Soc.,
       1959, 1635; Badger, G.M., and Kimber, R.W.L., J. Chem.
       Soc., 1960, 266; Spotswood, T.M., J. Chem. Soc., 1960,
       4427; Badger, G.M., and Kimber, R.W.L., J. Chem. Soc.,
       1960, 2746; Badger, G.M., and Spotswood, T.M., J. Chem.
       Soc., 1960, 4420; 4431; Badger, G.M., and Novotny, J.,

J. Chem. Soc., 1961, 3400; 3403; Badger, G.M., and
Kimber, R.W.L., J. Chem. Soc., 1961, 3407; Badger,
G.M., Donnelly, Jillian K., and Spotswood, T.M.,
Austral. J. Chem., 1962, 15, 605; Badger, G.M., Kimber,
R.W.L., and Novotny, J., Austral. J. Chem., 1962, 15,
616; Badger, G.M., Donnelly, Jillian K., and Spotswood,
T.M., Austral. J. Chem., 1963, 16, 392; Badger, G.M.,
and Novotny, J., Austral. J. Chem., 1963, 16, 613; 623

179   Badger, G.M., Donnelly, Jillian K., and Spotswood, T.M.,
Austral. J. Chem., 1963, 16, 392; Badger, G.M., and
Novotny, J., Austral. J. Chem., 1963, 16, 613

180   Bone, W.A., and Coward, H.F., J. Chem. Soc., 1908, 93,
1197

181   Staudinger, H., Endle, R., and Herold, J., Ber., 1913,
46, 2466

182   Jones, D.T., J. Chem. Soc., 1915, 107, 1582; J. Soc.
Chem. Ind., 1917, 36, 3

183   Weizmann, C., Bergmann, E., Huggett, W.E., Steiner, H.,
Sulzbacher, M., Parker, D., Michaelis, K.O., Whincup,
S., and Zimkin, E., Ind. Eng. Chem., 1951, 43, 2312;
Weizmann, C., Bergmann, E., Boyd-Barrett, H.S.,
Steiner, H., Sulzbacher, M., Holker, J.R., Mandel, E.,
Porges, J., and Rowley, D., Ind. Eng. Chem., 1951, 43,
2318

184   Badger, G.M., and Spotswood, T.M., J. Chem. Soc., 1959,
1635; Badger, G.M., and Kimber, R.W.L., J. Chem. Soc.,
1960, 266; Spotswood, T.M., J. Chem. Soc., 1960, 4427;
Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1960,
2746; Badger, G.M., Lewis, G.E., and Napier, I.M.,
J. Chem. Soc., 1960, 2825; Badger, G.M., and
Spotswood, T.M., J. Chem. Soc., 1960, 4420; 4431;
Badger, G.M., and Novotny, J., J. Chem. Soc., 1961, 3403;

Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1961, 3407; Badger, G.M., Donnelly, Jillian K., and Spotswood, T.M., Austral. J. Chem., 1962, 15, 605; Badger, G.M., and Novotny, J., Austral. J. Chem., 1963, 16, 613

[185] Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1958, 2453; 2455; Badger, G.M., and Buttery, R.G., J. Chem. Soc., 1958, 2458; Badger, G.M., and Spotswood, T.M., J. Chem. Soc., 1959, 1635; Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1960, 266; Spotswood, T.M., J. Chem. Soc., 1960, 4427; Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1960, 2746; Badger, G.M., Lewis, G.E., and Napier, I.M., J. Chem. Soc., 1960, 2825; Badger, G.M., and Spotswood, T.M., J. Chem. Soc., 1960, 4420; 4431; Badger, G.M., and Novotny, J., J. Chem. Soc., 1961, 3403; Badger, G.M., and Kimber, R.W.L., J. Chem. Soc., 1961, 3407; Badger, G.M., Donnelly, Jillian K., and Spotswood, T.M., Austral. J. Chem., 1962, 15, 605; Badger, G.M., and Novotny, J., Austral. J. Chem., 1963, 16, 613

[186] Steiner, H., and Goodmann, H., unpublished results, quoted in reference [183]

[187] Hurd, C.D., Macon, A.R., Simon, J.I., and Levetan, R.V., J. Amer. Chem. Soc., 1962, 84, 4509

[188] Szwarc, M., J. Chem. Phys., 1949, 17, 284

[189] Schroeter, G., Ber., 1924, 57, 1990

[190] Ziegler, K., and Wilms, H., Annalen, 1950, 567, 1; Ziegler, K., Sauer, K., Bruns, L., Froitzheim-Kühlhorn, H., and Schneider, J., Annalen, 1954, 589, 122

[191] Badger, G.M., Kimber, R.W.L., and Spotswood, T.M., Nature, 1960, 187, 663

[192] Birch, A.J., Massy-Westropp, R.A., Rickards, R.W., and

Smith, H., J. Chem. Soc., 1958, 360

193   Szwarc, M., and Williams, D., J. Chem. Phys., 1952, 20, 1171

194   Szwarc, M., J. Chem. Phys., 1948, 16, 128

195   Horrex, C., and Miles, S.E., Discuss. Faraday Soc., 1951, 10, 187

196   Schissler, D.O., and Stevenson, D.P., J. Chem. Phys., 1954, 22, 151

197   Schwegler, E.W., Scheraga, H.A., and Van Artsdalen, E.R., J. Chem. Phys., 1951, 19, 135; Anderson, H.R., Scheraga, H.A., and Van Artsdalen, E.R., J. Chem. Phys., 1953, 21, 1258

198   Price, S.J., Canad. J. Chem., 1962, 40, 1310

199   Szwarc, M., J. Chem. Phys., 1949, 17, 431

200   Leigh, C.H., and Szwarc, M., J. Chem. Phys., 1952, 20, 403

201   Leigh, C.H., and Szwarc, M., J. Chem. Phys., 1952, 20, 407

202   Smith, S.R., and Gordon, A.S., J. Phys. Chem., 1961, 65, 1124

203   Gordon, A.S., and Smith, S.R., J. Chem. Phys., 1961, 34, 331

204   Knox, B.E., and Palmer, H.B., Chem. Rev., 1961, 61, 247

205   Wilshire, J.F.K., Austral. J. Chem., 1962, 15, 538

206   Brinton, R.K., J. Chem. Phys., 1958, 29, 781

207   Sweeting, J.W., and Wilshire, J.F.K., Austral. J. Chem., 1962, 15, 89

208   Bailey, W.J., Cunov, C.H., and Nicholas, L., J. Amer. Chem. Soc., 1955, 77, 2787

209   Badger, G.M., Nat. Cancer Inst., Monograph 9, 1962, 1

210   Orlow, N.A., Ber., 1927, 60, 1950

211   Errede, L.A., and Cassidy, J.P., J. Amer. Chem. Soc.,
      1960, 82, 3653

212   Bennett, J.E., Proc. Chem. Soc., 1961, 144

213   Herington, E.F.G., and Rideal, E.K., Proc. Roy. Soc.,
      1945, A, 184, 447; Hoog, H., Verheus, J., and
      Zuiderweg, F.J., Trans. Faraday Soc., 1939, 35, 993;
      Rozenberg, L.M., Doklady Akad. Nauk S. S. S. R., 1950,
      73, 719

214   Cottrell, T.L., "The Strengths of Chemical Bonds,"
      Butterworths, London, 1954, pp. 272; 275

215   Stubbs, F.J., and Hinshelwood, C., Proc. Roy. Soc.,
      1950, A, 201, 18

216   McNesby, J.R., and Jackson, W.M., J. Chem. Phys., 1963,
      38, 692

217   Kerr, J.A., and Trotman-Dickenson, A.F., J. Chem. Soc.,
      1960, 1602

218   Jackson, W.M., and McNesby, J.R., J. Amer. Chem. Soc.,
      1961, 83, 4891

219   McNesby, J.R., Drew, C.M., and Gordon, A.S., J. Chem.
      Phys., 1956, 24, 1260

220   Gordon, A.S., and McNesby, J.R., J. Chem. Phys., 1960
      33, 1882

221   Heller, C.A., and Gordon, A.S., J. Phys. Chem., 1958,
      62, 709

222   Jackson, W.M., and McNesby, J.R., J. Chem. Phys., 1962,
      36, 2272

223   Kossiakoff, A., and Rice, F.O., J. Amer. Chem. Soc.,
      1943, 65, 590

224   Sefton, V.B., and LeRoy, D.J., Canad. J. Chem., 1956,
        34, 41

225   Gordon, A.S., and McNesby, J.R., J. Chem. Phys., 1959,
        31, 853

226   Wijnen, M.H.J., J. Amer. Chem. Soc., 1961, 83, 3752

227   Cullis, C.F., Minkoff, G.J., and Nettleton, M.A.,
        Trans. Faraday Soc., 1962, 58, 1117

228   Copeland, P.G., Dean, R.E., and McNeil, D., J. Chem.
        Soc., 1960, 1687

229   Copeland, P.G., Dean, R.E., and McNeil, D., J. Chem.
        Soc., 1960, 1689

230   Badger, G.M., Kimber, R.W.L., and Novotny, J., Austral.
        J. Chem., 1962, 15, 616

231   Lijinsky, W., and Raha, C.R., J. Org. Chem., 1961, 26,
        3566

232   Napier, I.M., and Rodda, H.J., Chem. and Ind., 1958,
        1319

233   Spotswood, T.M., J. Chromatog., 1959, 2, 90

234   Spotswood, T.M., J. Chromatog., 1960, 3, 101

235   Badger, G.M., Donnelly, Jillian K., and Spotswood, T.M.,
        J. Chromatog., 1963, 10, 397

236   Friedel, R.A., and Orchin, M., "Ultraviolet Spectra
        of Aromatic Compounds," John Wiley and Sons, New York,
        1951; Clar, E., "Aromatische Kohlenwasserstoffe,"
        Springer, Berlin, 1952; Thomas, J.F., Tebbens, B.D.,
        Sanborn, E.N., and Cribbs, J.M., Internat. J. Air
        Poll., 1960, 2, 210; Sawicki, E., Hauser, T.R., and
        Stanley, T.W., Internat. J. Air Poll., 1960, 2, 253

237   Spotswood, T.M., PhD Thesis, Adelaide, 1959

238   Nystrom, R.F., and Brown, W.G., J. Amer. Chem. Soc.,

1947, 69, 2548

239 "Beilsteins Handbuch der organischen Chemie," 4th ed.,
5, 492, Springer, 1922

240 Jones, R.N., J. Amer. Chem. Soc., 1945, 67, 2127

241 Friedel, R.A., and Orchin, M., "Ultraviolet Spectra
of Aromatic Compounds," John Wiley and Sons, New York,
1951

242 Shepard, A.F., Henne, A.L., and Midgley, T., J. Amer.
Chem. Soc., 1931, 53, 1948

243 Forziati, A.F., Glasgow, A.R., Willingham, C.B., and
Rossini, F.D., J. Res. Natl. Bur. Standards, 1946, 36,
129; Chem. Abs., 1946, 40, 4341

244 Eckstein, B.H., Scheraga, H.A., and Van Artsdalen, E.R.,
J. Chem. Phys., 1954, 22, 28

245 Popják, G., Biochem. J., 1950, 46, 560

246 Calvin, M., Heidelberger, C., Reid, J.C., Tolbert, B.M.,
and Yankwich, P.E., "Isotopic Carbon. Techniques in
its Measurement and Chemical Manipulation." John
Wiley and Sons, New York, 1949

247 Grummitt, O., and Becker, E.I., J. Amer. Chem. Soc.,
1948, 70, 149

248 Kenyon, J., Partridge, S.M., and Phillips, J., J. Chem.
Soc., 1936, 85

249 Adams, R., Voorhees, V., and Shriner, R.L., Org. Synth.,
1928, 8, 92

250 Timmermans, J., and Martin, F., J. Chim. phys., 1928,
25, 411

251 O'Connor, W.F., and Moriconi, E.J., Ind. Eng. Chem.,
1953, 45, 277

252   Graebe, C., and Hönigsberger, F., Annalen, 1900, 311, 257

253   Cook, J.W., and Schoental, R., J. Chem. Soc., 1948, 170

254   Moriconi, E.J., Rakoczy, B., and O'Connor, W.F., J. Amer. Chem. Soc., 1961, 83, 4618

255   Moriconi, E.J., Rakoczy, B., and O'Connor, W.F., J. Org. Chem., 1962, 27, 2772

Badger, G. M. & Novotny, J. (1961). 661. The formation of aromatic hydrocarbons at high temperatures. Part XII. The pyrolysis of benzene. *Journal of the Chemical Society,* 3400-3402.

Badger, G. M. & Novotny, J. (1961). 662. The formation of aromatic hydrocarbons at high temperatures. Part XIII. The pyrolysis of 3-vinylcyclohexene. *Journal of the Chemical Society,* 3403-3407.

Badger, G. M. & Novotny, J. (1963). The formation of aromatic hydrocarbons at high temperatures. XVIII. The pyrolysis of n-Decane. *Australian Journal of Chemistry, 16*(4), 613-622.

Badger, G. M., Kimber, R. W. L. & Novotny, J. (1962). The formation of aromatic hydrocarbons at high temperatures. XVI. The Pyrolysis of (1-^{14}C] Tetralin. *Australian Journal of Chemistry, 15*(4), 616-625.

Badger, G. M. & Novotny, J. (1963). The formation of aromatic hydrocarbons at high temperatures. XIX. The pyrolysis of [δ- ^{14}C]Butylbenzene. *Australian Journal of Chemistry, 16*(4), 623-635.

Badger, G. M. & Novotny, J. (1963). Mode of formation of 3,4-benzopyrene at high temperatures. *Nature, 198*(4885), 1086.