THE FORMATION OF AROMATIC HYDROCARBONS AT HIGH TEMPERATURES

A THESIS

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by

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To

My Mother

SUMMARY

In an attempt to obtain experimental evidence which might make possible a better understanding of the complex reactions involved in the formation of polycyclic aromatic hydrocarbons at high temperatures, a series of relatively simple aromatic hydrocarbons labelled with ^{14}C have been pyrolysed at 700°.

The pyrolysis of [1-^{14}C]naphthalene at 700° has given a tar from which 1,1'-binaphthyl and the isomeric 1,2'-, and 2,2'-binaphthyl, and the condensed hydrocarbons 10,11-, and 11,12-benzofluoranthene were isolated and radioassayed. All were found to have activity corresponding, within experimental error, to two labelled carbon atoms. It is concluded that C-H fission gives naphthyl radicals, which react with naphthalene to yield binaphthyls and that cyclodehydrogenation of the binaphthyls leads to the benzofluoranthenes. Some 3,4-benzopyrene was also detected; it is suggested that some hydrogenation of the naphthalene occurs, and that the 3,4-benzopyrene is formed following cleavage of a saturated C-C bond in this hydrocarbon.

[1-^{14}C]Styrene was synthesised and pyrolysis at 710° gave a tar from which nine compounds were isolated in sufficient quantity and purity for radiochemical analysis. Four of these have been degraded to determine the distribution of the activity, and the results are discussed with reference to the number of labelled carbon atoms found.

[3-^{14}C]Indene was synthesised and pyrolysed at 700°. Six compounds were isolated and subjected to radiochemical assay. All were found to have activity corresponding approximately to two labelled carbon atoms. It is concluded that the 1,2-bond as well as 1,8-bond

undergoes rupture to give three "primary" radicals which then undergo "dimerisation" and other transformations to give the major products.

Nine compounds were isolated from the tar obtained following the pyrolysis of n-[α-^{14}C]propylbenzene and subjected to radiochemical assay. Some of these compounds were partially degraded to locate the position of their activities. The mechanisms for their formation are discussed with reference to the number of labelled carbon atoms found.

β-[α-^{14}C]Methylstyrene has also been synthesised and pyrolysed at 700°. Ten compounds were isolated and submitted to radioassay. Five of these were partially degraded to locate the position of activity and the results are discussed with reference to the number of labelled carbon atoms found. It is concluded that β-methylstyrene serves as a precursor of indene and propylbenzene, and that the major products are formed by reaction of the primary decomposition products derived from indene and propylbenzene.

In general, the data presented in this thesis lead to the conclusion that C-C double bonds and aromatic rings are relatively stable at high temperatures; but many C-C single bonds and C-H bonds are readily ruptured at high temperatures to give radicals and that these radicals then abstract hydrogen, or add to double bonds or take part in radical substitution reactions, or interact with another radical, to give a wide variety of products including many polycyclic aromatic hydrocarbons. It has been shown that

(i) benzene is formed by cleavage of the side chain followed by hydrogen abstraction, and to a small extent by synthesis from side chains derived from two or more molecules;

(ii) benzyl radicals, and to some extent phenyl and methyl radicals, serve as precursors of toluene; and that phenethyl radicals serve as precursor of styrene;

(iii) a chain-resynthesis mechanism operates during the formation of naphthalene;

(iv) a mechanism involving styryl radicals (or phenethyl radicals) is the major route to phenanthrene; and the formation of chrysene involves the combination of C_6-C_2 and C_6-C_4 units, or of two C_6-C_3 units, depending on the relative abundances of these units in the reaction zone.

STATEMENT

The research work embodied in this thesis has been carried out in the Department of Organic Chemistry, University of Adelaide, Adelaide, under the guidance of Professor G.M. Badger. The extent of information derived from the existing literature has been indicated in the body of the thesis at appropriate places giving the sources of information. The work is original and has not been submitted in part or full for any diploma or degree in this or any other university.

S.D. JOLAD 26/1/66.

1966

ACKNOWLEDGEMENTS

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INTRODUCTION

Polycyclic aromatic hydrocarbons are known to be formed at high temperatures from aliphatic hydrocarbons or from simple aromatic hydrocarbons. In recent years there has been considerable interest in the mode of formation of these hydrocarbons at high temperatures, and recently a tracer method has proved of value in investigating the mechanisms postulated for the formation of these hydrocarbons.

The purpose of this investigation was to obtain experimental evidence which might make possible a better understanding of the mechanisms involved in the formation of these hydrocarbons at high temperatures by the pyrolysis of relatively simple aromatic hydrocarbons labelled with ^{14}C (Table 1).

TABLE 1.

COMPOUNDS PYROLYSED

Type	Compound	Temperature °C
$C_6 - C_4$	[1-^{14}C] Naphthalene	700°
$C_6 - C_2$	[1-^{14}C] Styrene	710°
$C_6 - C_3$	[3-^{14}C] Indene	710°
$C_6 - C_3$	_n_-[α-^{14}C] Propylbenzene	700°
$C_6 - C_3$	β-[α-^{14}C] Methylstyrene	700°

A suitable temperature (700°) was chosen for the pyrolytic experiments in the present investigation; this was based on the following:

(i) The combustion temperature of cigarettes and of pipe tobacco is near this temperature[1], or higher.

(ii) Many carbon-carbon single bonds and carbon-hydrogen bonds are readily ruptured at 650°-850° to give radicals.

(iii) A recent quantitative study on the effect of temperature on thermal degradation suggests that maximum yields of polycyclic hydrocarbons are obtained in the vicinity of 700°.[2]

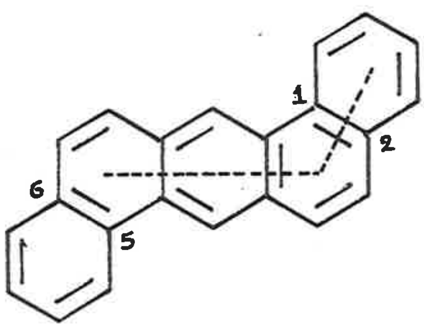
CHAPTER 1.

CARCINOGENIC HYDROCARBONS

Chemical cancer research can be said to have been begun when Percival Pott[3] in 1775 published his paper on the relation of a form of "occupational cancer" to a carcinogen, namely soot. More than hundred years later a group of industrial and occupational carcinogenic agents came to be recognised namely: tar[4], pitch[4], shale oil[5], certain dyestuffs, and so on. The discovery that certain polynuclear hydrocarbons can evoke malignant tumours in animal tissues opened a new field for the investigation of the incidence of cancer. The discovery was the outcome of the realisation at the early part of the present century that individuals in specific occupations involving prolonged exposures to coal tar products tended to show an abnormally high incidence of skin cancer, which sometimes developed several years after the period of exposure. The actual production of cancer in experimental animals by prolonged application of a specific coal-tar fraction was first achieved by two Japanese scientists, Yamagiwa and Ichikawa[6] in 1915, and later by Tsutsui[7] in 1918. Since then the view that the 'pathological' conditions caused by coal-tar cannot be due to mechanical injury, but must be 'associated with chemical injury', has been accepted.

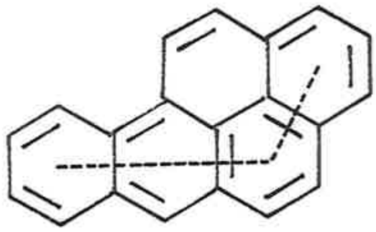
The first essential clue was provided in the year 1921 by Bloch and Dreifus[8] in Zurich, who found that the cancer-producing material was present in the higher boiling fraction of a tar as a neutral organic compound free from sulphur, nitrogen, arsenic, or other metals, forming a stable complex with picric acid and probably belonging to the class of polycyclic hydrocarbons. Passey[9] in 1922, proved the carcinogenicity of soot experimentally. Later, British investigators[10] were able to demonstrate experimentally that cancer can be induced in experimental animals by definite organic compounds and the hunt then began to isolate the cancer-producing compound or compounds.

The second vital clue[11], that the fluorescence spectra of the carcinogenic mixture resembled that of 1,2-benzanthracene, stimulated work on the synthesis of related compounds which finally led Kennaway and Hieger[12] in 1930, at the Royal Cancer Hospital, London, to the discovery of the first pure chemical entity to manifest pronounced carcinogenic properties namely, 1,2:5,6-dibenzanthracene (I).



(I)

With the fluorescence spectrum as 'the single thread that led all through this labyrinth', Cook and coworkers[13] in 1933, isolated from two tons of coal tar from Beeton gas-works a compound which is mainly responsible for its carcinogenic properties. They showed by synthesis that this compound was then unknown 3,4-benzopyrene (II). Later work has shown that the high-boiling gas-works tars may contain as much as 1.5 per cent 3,4-benzopyrene.



(II)

With the knowledge that two hydrocarbons had such dramatic properties in producing cancer when painted on to the skin of mice, the search began for other pure chemical compounds with similar properties. In recent years 3,4-benzopyrene (II) and very many polycyclic aromatic hydrocarbons have been shown to be widely distributed in human environment, having been identified in carbon blacks[14], in processed rubber[15], in atmospheric dust[16], in human hair wax[17], in oysters and barnacles taken from polluted water[18], in icelandic smoked food[19], in the soot from a smoked-sausage factory[20], in snuff[21], in tobacco[22], in the air from garages[23], in the smoke and tar from curing kilns[24], in petrol and diesel exhausts[25-28], coal gas[29], starch soots[30], and soot from a smoking chamber[31]. The following are some of the most important factors which make a very distinct contribution to the causation of 'spontaneous' cancer.

COAL TAR

There is abundant evidence that cancer of the skin can be induced in man by industrial exposures to coal tar and pitch. The first detailed investigations into the nature of the carcinogenic substance in coal tar were made by Bloch and Dreifuss[8] who found that it is concentrated in the fraction b.p. 370°-440°. The fraction was found to give malignant tumours. Tumours were also produced with the fractions b.p. 300°-400°, and with coal tar pitch. These observations on the cancer-producing activity of coal tar have been repeatedly confirmed and extensively investigated[32]. Four additional carcinogens and more recently naphtho-2',1'-3,4-pyrene (VII) have since been isolated from coal tar (Table 2). The activity of the last mentioned compound (VII) is not yet known. 3,4-Benzofluoranthene (IV), the carcinogenic power of which has been established only recently[38], was found to be more abundant than 3,4-benzopyrene in coal tar.

TOBACCO AND CIGARETTE SMOKE

The problem of the possible relationship between tobacco smoking and the incidence of lung cancer is one of the most topical issues in cancer research today. The mortality from cancer of the lung has

TABLE 2.

CARCINOGENS IN COAL TAR

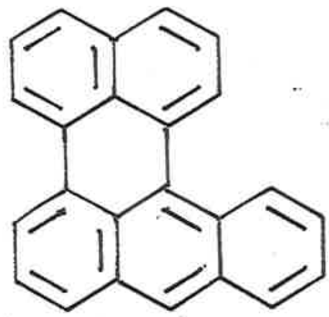
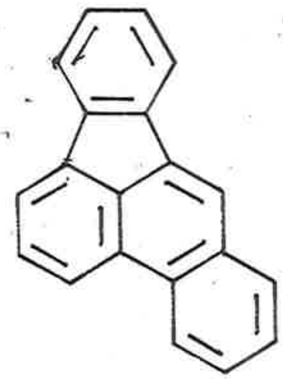
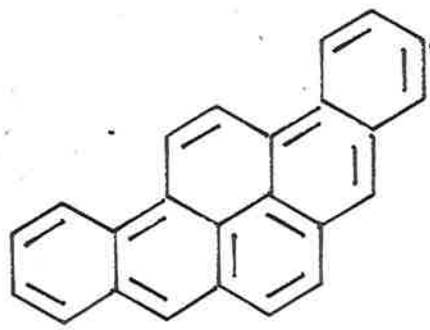
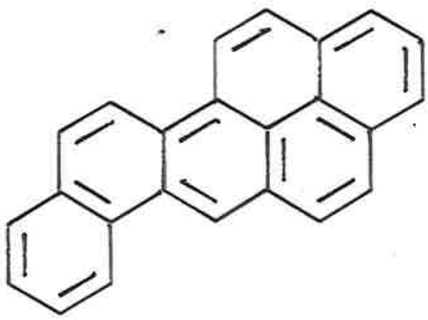
Compound	Structure	
1,2-Benzoperylene[33]		(III)
3,4-Benzofluoranthene[34]		(IV)
3,4:9,10-Dibenzopyrene[35]		(V)

TABLE 2, contd.

Compound	Structure
3,4:8,9-Dibenzopyrene[36]	 (VI)
Naphtho-2',1'-3,4-pyrene[37]	 (VII)

been steadily increasing since 1900 and the present weight of statistical evidence implicates excessive smoking as the principal factor in the increased incidence of lung cancer. The recent report[39] of the Advisory Committee to the Surgeon General of the U.S. Public Health Service states categorically: "Cigarette smoking is associated with an increased chance of developing lung cancer in men; the magnitude of the effect of cigarette smoking far outweights all other factors".

A wide range of compounds of many types have been shown to be present in tobacco and it is now considered as a very complex mixture of chemical components: the major groups are, hydrocarbons (aliphatic and alicyclic), terpenes and isoprenoid hydrocarbons, alcohols, phenols, esters, sterols, aldehydes, ketones, acids, alkaloids and inorganic minerals. During smoking (the temperature of the burning zone reaches approximately 880° [40]) many of these tobacco constituents undergo extensive reactions involving oxidation, dehydrogenation, cracking, rearrangement, condensation etc. It is thus not surprising that some 500 different compounds have been identified in cigarette smoke.

Seven polycyclic compounds (Table 3) isolated from cigarette smoke have been shown to be carcinogenic in laboratory animals. The other carcinogens known to be present in tobacco smoke are, with the exception of 3,4:9,10-dibenzopyrene (V), much less potent than 3,4-benzopyrene (II) and they are present in smaller amounts. It has been shown[43] that some polycyclic hydrocarbons although not

TABLE 3.

CARCINOGENS IN CIGARETTE SMOKE

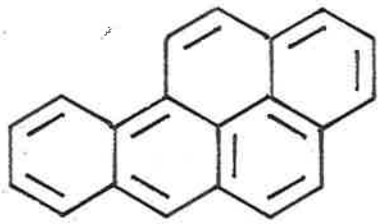
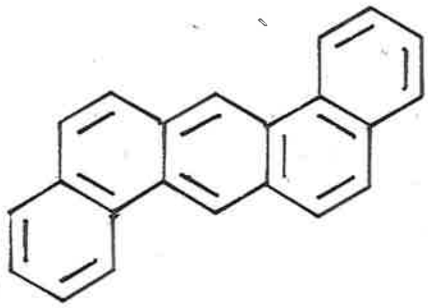
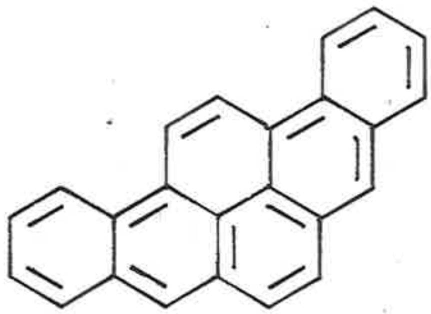
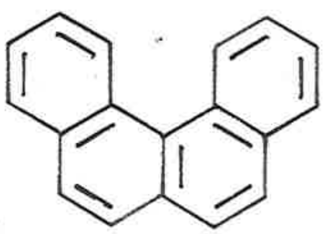
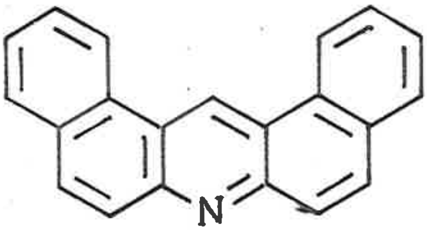
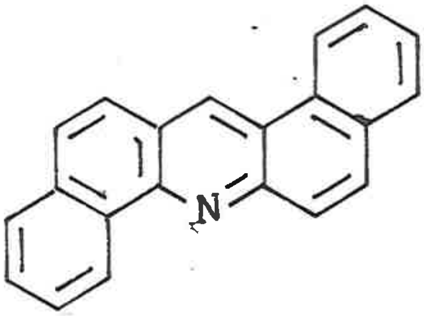
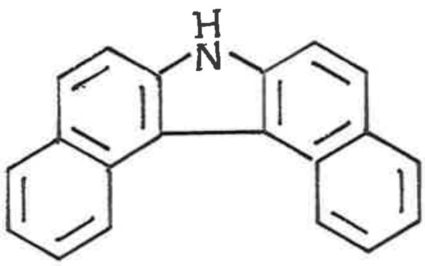
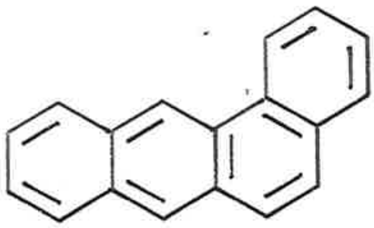
Compound	Structure	
3,4-Benzopyrene[41]		(II)
1,2:5,6-Dibenzanthracene[41]		(I)
3,4:9,10-Dibenzopyrene[41]		(V)
3,4-Benzophenanthrene[41]		(VIII)

TABLE 3. contd.

Compound	Structure	
1,2:7,8-Dibenzoacridine[42]		(IX)
1,2:5,6-Dibenzoacridine[42]		(X)
3,4:5,6-Dibenzocarbazole[42]		(XI)

themselves carcinogenic, can enhance the cancer-producing properties of the carcinogens even when present in minute concentrations. For example, 1,2-benzanthracene (XII), identified in cigarette smoke, is known to be a strong initiator though a very weak carcinogen[44].



(XII)

The carcinogenic activity of cigarette tar has been investigated experimentally and it has been shown[45] that it is a weak carcinogen. However, chemical investigation of cigarette tar has shown the presence of several carcinogenic polycyclic hydrocarbons including those listed in Table 4. Although some of these hydrocarbons are regarded as potent carcinogens, the low concentration of 3,4-benzopyrene is insufficient to account for the carcinogenic activity of the tar. While some of the activity may be derived from carcinogens, the presence of relatively large amounts of benzofluoranthenes in the tar may be of great importance.

ATMOSPHERIC POLLUTION[57]

There is considerable evidence supporting the view that

TABLE 4.

CARCINOGENS IN CIGARETTE TAR

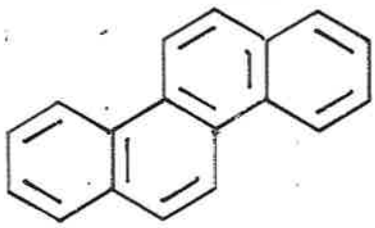
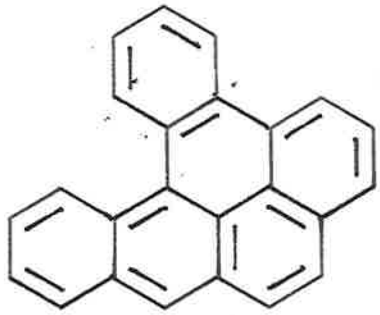
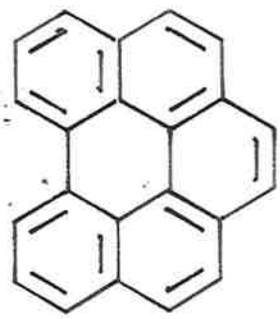
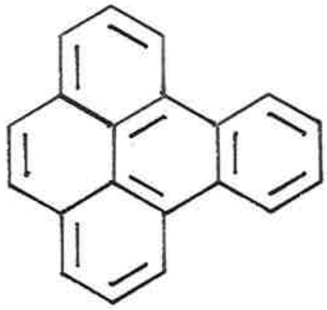
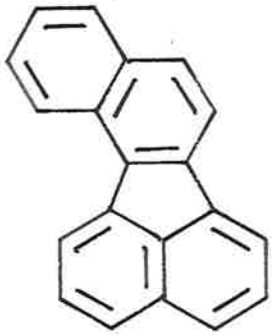
Compound	Structure
1,2:5,6-Dibenzanthracene[46]	(I)
3,4-Benzopyrene[47]	(II)
1,2-Benzanthracene[48]	(XII)
3,4:9,10-Dibenzopyrene[49]	(V)
3,4-Benzofluoranthene[50]	(IV)
3,4:8,9-Dibenzopyrene[51]	(VI)
Chrysene[52]	 (XIII)
1,2:3,4-Dibenzopyrene[53]	 (XIV)
1,12-Benzoperylene[54]	 (XV)

TABLE 4, contd.

Compound	Structure	
1,2-Benzopyrene[55]		(XVI)
10,11-Benzofluoranthene[56]		(XVII)

atmospheric pollution makes a contribution to the incidence of lung cancer[58,59]. The carcinogenic activity of various samples of atmospheric dust in cities has been demonstrated on many occasions[57,60,61] and 3,4-benzopyrene (II) and several other polycyclic hydrocarbons have been identified as constituents. In Table 5 are listed hydrocarbons detected in urban air[62]. The extent of the difference between urban and rural areas in this respect is shown[63] by the observation that there was six times as much smoke and ten times as much 3,4-benzopyrene in the atmosphere of the former than of the latter. These hydrocarbons present in the atmosphere are produced by the incomplete combustion of various organic materials; the most common sources are smoke from chimneys[64], waste products from industrial processes, petroleum vapours in streets conjested with traffic, diesel buses, cement dust in the vicinity of building operations etc. The exhaust gases of petrol and diesel engines[25-28] play a major role. They contain not only 3,4-benzopyrene (II), but also a wide range of aromatic hydrocarbons some of which are carcinogenic. Similarly several hydrocarbons have been identified in air from garages[23], and in smoke from curing kilns[24].

Following the discovery that carcinogenic tars can be produced artificially by the pyrolysis of many organic materials, and by passing acetylene and isoprene with hydrogen through a heated tube[10], a large number of compounds of many types (Table 6) have been pyrolysed at high temperatures and the tars have been examined. The pyrolysis of some of these compounds has been repeated and extensively investigated by

TABLE 5.

ORGANIC CONSTITUENTS OF TOWN AIR*

Individual Compounds	
Acenaphthene	Ethane
Acenaphthylene	Ethylene
Acetylene	Fluoranthene
Acrolein	Fluorene
Anthanthrene	*n*-Hexane
Anthracene	Methane
Azulene	2-Methylnaphthalene
1,2-Benzanthracene	3-Methylpyrene
Benzene	Naphthalene
1,2-Benzopyrene	*n*-Pentane
3,4-Benzopyrene	*iso*-Pentane
n-Butane	2,2-Dimethylpropane
iso-Butane	Perylene
Chrysene	Phenanthrene
Coronene	Pyrene
1,2:9,10-Dibenzonaphthacene	Toluene
4,9-Dimethylpyrene	

TABLE 5, contd.

Groups of Compounds	
Acids	Ketones
Alcohols	Peroxides
Aldehydes	Phenols
Epoxides	Pyridine compounds
Gasoline	Sulphur compounds
Glycols	Tar acids
Hydrocarbons (gaseous)	Xylenes
Hydrocarbons (unsaturated)	

* From [62].

TABLE 6.

COMPOUNDS PYROLYSED

Compound pyrolysed	Temperature °C	Reference
Acenaphthene	-	65
Acetylene	700°	10,66
Anthracene	700°, 950°	67
	700° - 750°	68
Benzene	700°	69
Benzene and anthracene	700° - 750°	67
Benzene and naphthalene	730° - 750°	70
Benzene and phenanthrene	730° - 750°	70
Benzene and pyrene	750°	71
Buta-1,3-diene	700°	72
Buta-1,3-diene and pyrene	700°	72
Butylbenzene	300° - 900° at 50° interval	73_{a-b}
n-Decane	700°	74
Diarylmethanes	970°, 1000°	75
w,w'-Diphenylalkanes	550° - 700° at 50° interval	76

TABLE 6, contd.

Compound pyrolysed	Temperature °C	Reference
Dotriacontane	700°	77
Ethylbenzene	700°	73a
Ethylene	Diffusion flame	78
Fluorene	700° - 750°	79
Indene	700°	80
Methane	Diffusion flame	78
1-Methylnaphthalene	725° - 750°	81
2-Methylnaphthalene	725° - 750°	81,82
Naphthalene	700°, 850°	83,84
Petrol	700°	85
Phenanthrene	700°, 850°	86,87
1-Phenylbuta-1,3-diene	550°, 700°	88
1,4-Phenylbutylnaphthalene	360°, 600°, 700°	89
Propylbenzene	700°	73a
"Schroeter Tar" (formed from tetralin and aluminium chloride)		
Stigmasterol	700°, 750°	77,41
Styrene	710°	91
Tetralin	700°	92
"Iso-octane" (2,2,4-trimethylpentane)		

TABLE 6. contd.

Compound pyrolysed	Temperature °C	Reference
Toluene	700°	73a
3-Vinylcyclohexene	700°	94
o-Xylene	925°	75
p-Xylene	1065 ± 5	75

modern techniques in order to understand the mode of formation of aromatic hydrocarbons during tar formation. 3,4-Benzopyrene (II) and other polycyclic aromatic hydrocarbons were found in almost all pyrolyzates.

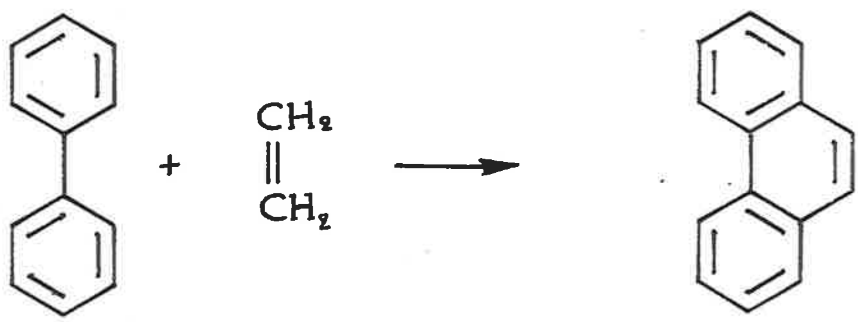
CHAPTER 2

MECHANISM OF THE FORMATION OF CARCINOGENS AND OTHER HYDROCARBONS

2.1 GENERAL

It appears from the foregoing that many organic materials can give rise to carcinogenic compounds by high temperature processes, sometimes involving incomplete combustion. For example, the "primary" tar obtained by heating coal at 300° - 450° consists mainly of paraffins, cycloparaffins, olefins and phenols, and has slight carcinogenic activity; but the "secondary" tar obtained at elevated temperatures (600°-800°) contains a greater proportion of polycyclic

(XVIII)



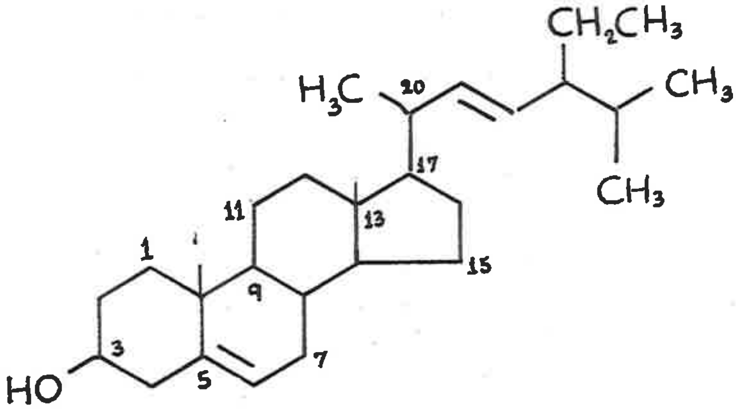
(XIX)

(XX)

hydrocarbons and is much more carcinogenic[10]. Mantel and Hansel[95] pyrolysed some "primary" tar products, namely, diphenylmethane, diphenyl and ethylene and 1,8-dimethylnaphthalene under laboratory conditions to give fluorene (XVIII), phenanthrene (XIX) and acenaphthene (XX) all of which have been isolated from "secondary" tars.

Similarly shale oil becomes carcinogenic after being heated[96]. Most of the carcinogenic compounds identified in cigarette smoke tar are not present in the native tobacco leaf, but are formed by pyrolysis at the high temperature (880°) of burning cigarettes[97]. The pyrolysis of stigmasterol (XXI), a tobacco constituent, at 750° has been shown to produce 3,4-benzopyrene and pyrene[41]. In a recent investigation the pyrolysis of stigmasterol at 700° was found to give a tar in which 50 products were identified in addition to 3,4-benzopyrene (0.59%) and pyrene (6.0%)[77]. Benzene, naphthalene, phenanthrene and chrysene were among the other major constituents of the stigmasterol tar. Similar pyrolysis of dotriacontane (XXII), another tobacco constituent, at 700° also gave a tar from which 43 compounds, including 3,4-benzopyrene (0.126%), were identified[77].

The pyrolysis of pyridine and nicotine gave dibenzo[a,j]acridine (IX)



(XXI)

$CH_3CH_2.[CH_2]_{28}.CH_2CH_3$

(XXII)

and dibenzo[a,h]acridine (X), both of which are carcinogenic[98]. The pyrolysis of "cigarettes" made from vegitable fibres and spinach also resulted in the formation of 3,4-benzopyrene[99]. Cigarette paper consists essentially of cellulose, and this has also been shown to produce 3,4-benzopyrene[100].

The occurrence of carcinogens and other hydrocarbons in soot, in the exhaust gases of automobiles, in certain petroleums, in carbon blacks, and in 'Schroetor tar' can likewise be attributed to high temperature reactions involving incomplete combustion. Experimentally the high temperature pyrolysis of simple hydrocarbons such as acetylene[66], butadiene[72], butylbenzene[73a-b], tetralin[92] and condensed hydrocarbons such as phenanthrene[86,87], and anthracene[67,68] have been shown to give rise to tars containing a wide range of polycyclic aromatic hydrocarbons, including those having carcinogenic activity.

2.2 MODE OF FORMATION

The pyrolysis of hydrocarbons at elevated temperatures is known to proceed through a variety of chain mechanisms[101], and several hypotheses have been advanced to explain the formation of polycyclic hydrocarbons at high temperatures.

(a) BERTHELOT'S HYPOTHESIS

Berthelot[102] proposed that the pyrolysis of hydrocarbons involves a primary degradation to acetylene, the ultimate product, which then polymerises in part into benzene and other aromatic hydrocarbons. His hypothesis has been supported by many workers[103-106].

The pyrolysis of acetylene has recently been studied at 530° and 700°.[66] Ethylbenzene, xylene, indene, naphthalene and pyrene were found in the 530° tar. At the higher temperature highly condensed products such as fluorene, fluoanthene, 3,4- and 11,12-benzofluoranthene, 2,3-o-phenylenepyrene, and 3,4-benzopyrene were identified. The amounts of indene and naphthalene were smaller in the 700° tar than in that formed at 530° and it has been suggested that these compounds undergo further transformations at the higher temperatures. Indeed this has been confirmed by the independent pyrolysis of indene[80] and naphthalene[83,84].

It is important to note, however, that the presence of acetylene has been reported in very few examples of pyrolytic decomposition[74,85]. On the contrary, on many occasions, hydrogen, methane and ethylene were observed in the gaseous products[107]. As the addition to an olefinic linkage proceeds more rapidly than addition to an acetylenic bond[108], ethylene, which is formed in large amounts in all pyrolysis[107] seems to be a more reasonable intermediate.

(b) BUTADIENE HYPOTHESIS

A suggestion that butadiene is the ultimate degradation product in the pyrolysis of hydrocarbons and that this compound serves as the precursor of aromatic hydrocarbons found in the tar was based on Staudinger's observation[109] that the pyrolysis of butadiene at 800° gave a tar of which 30% was benzene and 25% naphthalene. Jones[110], and more recently Weizmann[111] followed this lead, stressing the idea that conjugate unsaturation rather than acetylene was the necessary precursor in the formation of aromatic hydrocarbons. According to Weizmann, polycyclic hydrocarbons were assumed to be synthesised by successive Diels-Alder additions involving both olefins and butadiene. Thus phenanthrene and anthracene would be formed by an addition of buta-1,3-diene (XXIII) to naphthalene, pyrene by dimerisation of styrene or tetramerisation of buta-1,3-diene[111] and triphenylene,

$$CH_2 = CH - CH = CH_2$$

(XXIII)

chrysene, 3,4-benzophenanthrene and 1,2-benzanthracene by condensation of butadiene with phenanthrene.

The pyrolysis of butadiene has recently been investigated at 550° [112] and 700° [72]. At the lower temperature, cyclohexene, cyclohexadiene and C_8 aromatic compounds were formed, but at the higher temperature complete conversion of acyclic and alicyclic components to aromatic compounds occurred. Thus, benzene (41%), toluene (15%) and other condensed products were obtained. Methane and ethylene were observed among gaseous products.

It has been suggested that cyclohexene (obtained by reaction of buta-1,3-diene and ethylene) and 3-vinylcyclohexene (obtained by dimerisation of buta-1,3-diene) and the radicals derived from these compounds by hydrogen abstraction from the reactive allylic positions could be important intermediates in the formation of observed products. The dimerisation of butadiene is known to give 4-vinylcyclohexene[113], and it is important to note that the products obtained by the pyrolysis of 3-vinylcyclohexene[94] and of butadiene show a striking resemblance. On these results it seems likely that the

Diels-Alder reaction may play an important role in some pyrolyses at high temperatures.

In order to test the adequacy of the above hypothesis proposed by Weismann *et al.*[111], in which the polycyclic hydrocarbons were assumed to be synthesised by successive Diels-Alder additions of buta-1,3-diene, Badger *et al.*[72] recently pyrolysed a mixture of buta-1,3-diene and pyrene. A very small increase in the yield of benzopyrenes over those obtained from butadiene alone indicates that this reaction cannot be an important synthetic route. The pyrolysis of a mixture of naphthalene and butadiene[114] furnished additional evidence for the relative unimportance of the diene reaction, since the yield of phenanthrene showed only an insignificant increase over that obtained following the pyrolysis of the pure chemical.

Finally, it is important to note that butadiene is formed from most hydrocarbons under pyrolytic conditions[115]; but the relative activation energies for the diene addition (*ca.* 28 k cal./mole) and for radical addition (*ca.* 2.5 k cal./mole)[116] would suggest that resynthesis proceeds by radical reactions rather than by molecular condensation.

(c) CH_2 AND CH RADICALS

The suggestion that CH_2 and CH fragments serve as precursors of polycyclic hydrocarbons was put forward by Bone and Coward[117], but there is no other evidence to support it.

(d) HURD'S HYPOTHESIS

The possible formation of aromatic hydrocarbons from C_3-fragments has also attracted attention in recent times. In the pyrolysis of propylene, Szwaro[118] demonstrated that allene was a product, and postulated the formation of an allyl radical in the first step. Hurd and coworkers[119], however, extended this idea to explain the large production of aromatic hydrocarbons obtained on heating propylene. They proposed that thermal abstraction of hydrogen from allene would give a resonance-stabilised propadienyl radical, followed by facile isomerisation into a radical-carbene, trimethine (also stabilised by resonance), by 1,2-shift of hydrogen. Dimerisation of two such fragments would then be expected to give benzene.

$$CH_2 = CH - CH_3 \longrightarrow CH_2 = CHCH_2\cdot \longrightarrow$$

$$CH_2 = C = CH_2 \longrightarrow \cdot CH = C = CH_2 + H\cdot$$

$$\downarrow\uparrow$$

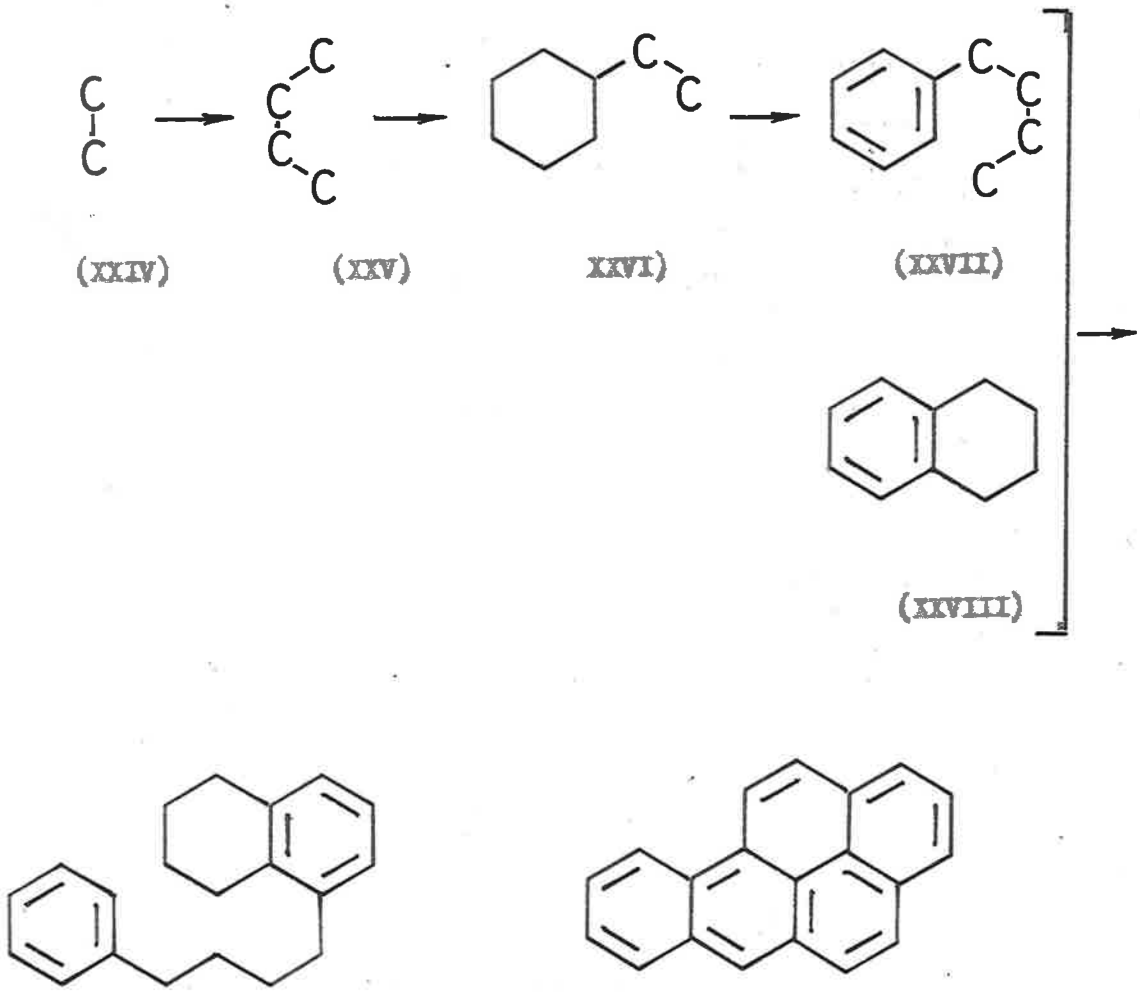
$$:CH - CH = CH\cdot \rightleftharpoons \cdot CH = CH - CH:$$

$$2\ C_3H_3 \longrightarrow C_6H_6$$

A similar hypothesis has also been advanced by these authors[119] to explain the formation of benzene and its small amount of activity from [1-^{14}C]toluene. However, this particular hypothesis for the formation of benzene and other aromatic hydrocarbons by way of C_3-unit has not been generally accepted, and there is no other evidence to support it.

(e) BADGER'S HYPOTHESIS

Admittedly based on rather meager experimental observations by earlier workers, Badger *et al.*[120], proposed an explanation for the formation of 3,4-benzopyrene and other polycyclic aromatic hydrocarbons.



(XXIX) (XI)

Figure 1

Essentially, the proposal involves a stepwise process as shown in figure 1. This hypothesis originated from the early observation that the tar produced by the pyrolysis of acetylene[10,121] at 700° has considerable cancer-producing power, and gave a fluorescence spectrum similar to that given by 3,4-benzopyrene. A more recent re-investigation of the pyrolysis of acetylene[66] showed the presence of 3,4-benzopyrene to the extent of 2%, and many other hydrocarbons. This hypothesis presupposed that 3,4-benzopyrene could be formed by the pyrolysis of any of the possible intermediate compounds, viz., acetylene or ethylene for the C_2-unit, butadiene or vinylacetylene for the C_4 unit, styrene, ethylbenzene or vinylcyclohexene for the C_6-C_2 unit, tetralin, butylbenzene or phenylbutadiene for the C_6-C_4 unit, and phenylbutyl-naphthalene for the C_6-C_4, C_6-C_4 unit.

To test the validity of the above hypothesis several possible intermediate compounds (Table 7) have been pyrolysed, 3,4-benzopyrene has been identified in every case. The pyrolysis of other compounds, viz., toluene, propylbenzene, and indene (which are not direct intermediate compounds in the proposed hypothesis) have also been found to give some 3,4-benzopyrene.

Evidence for the feasibility of the third step in the mechanism proposed has been provided by the pyrolysis of simple alkylbenzenes. Butylbenzene, having a C_6-C_4 structure, gave the highest yield of 3,4-benzopyrene. The pyrolysis of [1-^{14}C]tetralin[122] and [δ-^{14}C]butylbenzene[123] also provided further evidence on the mode of formation of 3,4-benzopyrene. The product isolated from the [1-^{14}C]tetralin tar and [δ-^{14}C]butylbenzene tar was found to have 1.96 and 1.92 labelled carbon atoms respectively. It seems therefore that the postulated mechanism provides an important route to 3,4-benzopyrene.

TABLE 7

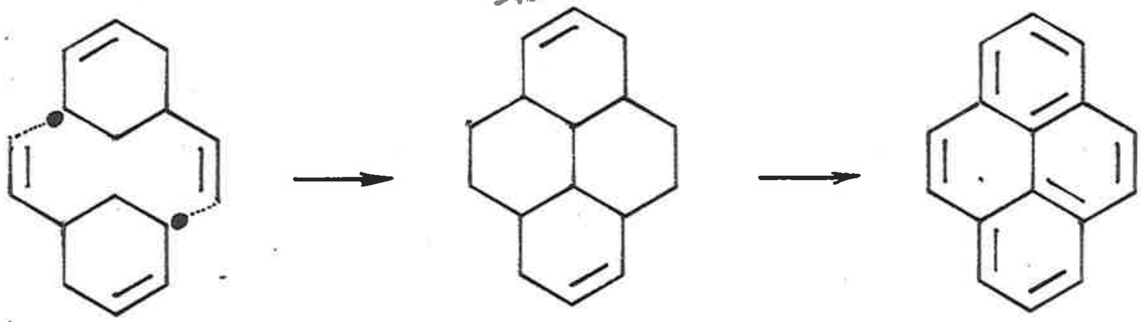
COMPOUNDS PYROLYSED AT 700°

Type	Compound
C_2	Acetylene[66]
C_4	Buta-1,3-diene[72]
C_6	Benzene[69]
C_6-C_1	Toluene[73a]
C_6-C_2	Ethylbenzene[73a]
	Styrene[91]
	Vinylcyclohexene[94]
C_6-C_3	Propylbenzene[73a]
	Indene[80]
C_6-C_4	Butylbenzene[73a]
	Tetralin[92]
	Phenylbutadiene[88]
C_6-C_4, C_6-C_4	Phenylbutylnaphthalene[89]

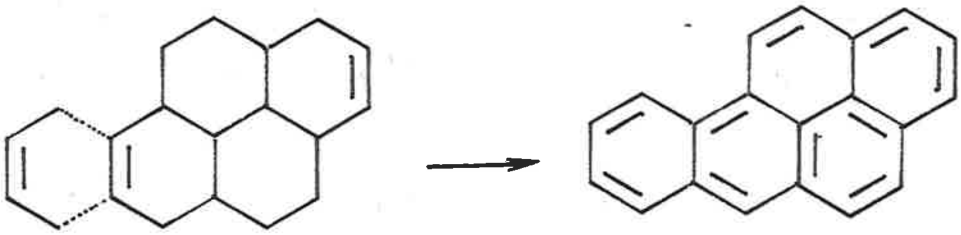
Evidence for the participation of (XXIX) in the final step

(XXIX → II) of the above mechanism has been provided by two critical experimental observations. First, the pyrolysis of "Schroeter tar", a complex mixture obtained by the action of aluminium chloride on tetralin gave a product which was shown to contain 3,4-benzopyrene. In this process it has been suggested that 3,4-benzopyrene might have been formed by the rapid conversion of 5,4'-phenylbutyltetralin, which was not actually isolated, but which was presumed to be present. Secondly, the pyrolysis of 1,4'-phenylbutylnaphthalene, the dehydrogenated analogue of (XXIX) and belonging to the same group of intermediates, has also been shown to give 3,4-benzopyrene.

Two alternative mechanisms for the formation of 3,4-benzopyrene have also been suggested. The first would involve the dimerisation of C_6-C_2 units, followed by another C_4 unit. For example, the dimerisation of two vinylcyclohexene radicals (XXX) would give hydropyrene (XXXI). Dehydrogenation of this at high temperatures would give a pyrene (XXXII), or addition of another molecule of butadiene followed by dehydrogenation would give 3,4-benzopyrene. This mechanism for the formation of 3,4-benzopyrene from C_6-C_2 unit has not been confirmed since the pyrolysis of styrene, the one having similar C_6-C_2 structure, gave only a small amount of pyrene and 3,4-benzopyrene.

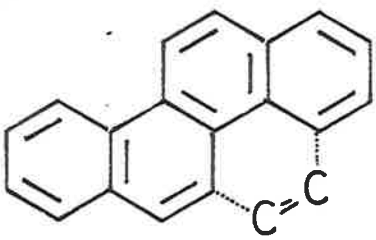


(XXX) (XXXI) (XXXII)

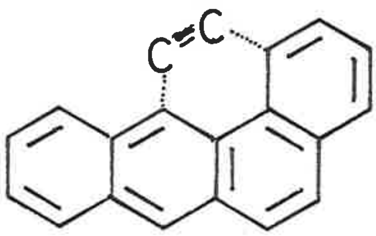


(XXXIII) (II)

The second possibility of the formation of 3,4-benzopyrene would involve the reaction of a C_2 unit (such as ethylene) with chrysene (as in XXXIV) or 1,2-benzanthracene (as in XXXV). However, this mechanism has been precluded as an important route in the formation of 3,4-benzopyrene on the basis of the fact that the pyrolysis of indene gave only a small amount of 3,4-benzopyrene although the yields of chrysene were high, and ethylene was present in the exit gases.



(XXXIV)



(XXXV)

CHAPTER 3

PYROLYTIC REACTIONS OF HYDROCARBONS

Since the discovery of benzene by Faraday[124] in 1825 from the condensate of a gas made by the pyrolysis of fish oils, and the thermal formation of aromatic hydrocarbons from simple unsaturated aliphatic compounds by Berthelot[102], many other hydrocarbons and related compounds have been produced by pyrolytic processes. This work has led to the development of ideas on the reaction mechanisms involved in these processes.

The first systematic work on the pyrolysis of hydrocarbons was carried out by Berthelot[102] at a time when analytical techniques other than distillation and crystallisation were unknown. His work has been repeated and extended by many other workers using improved techniques, and it may be pointed out that the results obtained before the introduction of new techniques such as chromatography, gas-liquid chromatography, ultraviolet and infrared spectroscopy need to be accepted with care. The purity of the starting materials is often suspect, as is the identity of some of the products; and the temperature of the pyrolysis was often described simply as "red heat", "dull red heat", or "bright red heat".

Early speculations on the mechanisms of the reactions involved were thoroughly reviewed in the monographs by Egloff[125] and by Hurd[126]. All data on the free radical reactions involved in the decomposition of simple hydrocarbons have been summarised by Steacie[127], and the kinetics of these reactions by Trotman-Dickenson[116]. Other review articles worthy of particular mention are those contained in references (128) and (129), and the annual reviews published by Haensel and Sterba[130].

The relevant mechanisms for the thermal decomposition of certain hydrocarbons are discussed below.

3.1 PYROLYSIS OF PARAFFINS

Paraffins have been shown to undergo pyrolytic rupture or cracking in the range of 500 -700° to yield a mixture of smaller molecules, some unsaturated (alkenes) and some saturated (alkanes) hydrocarbons of shorter chain length, and the products obtained from a given paraffin depend on: (i) the structure of the paraffin, (ii) the pressure under which the pyrolysis is carried out; and (iii) the presence or absence of catalyst. The cracking preferentially ruptures carbon-carbon rather than carbon-hydrogen bonds because the energy required to break the C-C bond is about 59 K cal./mole, whereas the C-H bond energy is about 87 K cal./mole.

Methane, the simplest member of this class, is exceptionally stable thermally (it decomposes into carbon and hydrogen at temperatures above 1000°), but the higher alkanes undergo both dehydrogenation and rupture of the side chain, usually with the formation of methane. Generally, C-C bond fission predominates over dehydrogenation as the chain length increases. In the pyrolysis of n-butane, for example, dehydrogenation to butene occurs to a minor extent and the predominating reaction is the fission of the chain with the formation of methane and ethane.

$$CH_3CH_2CH_2CH_3 \longrightarrow \begin{cases} CH_3CH_2CH = CH_2 + H_2 & \text{(12 parts)} \\ CH_3CH = CH_2 + CH_4 & \text{(50 parts)} \\ CH_2 = CH_2 + CH_3CH_3 & \text{(38 parts)} \end{cases}$$

In spite of the considerable amount of work that has been done on the kinetics of the thermal decomposition of paraffins, the mechanism of the reaction is still obscure. Until recently many workers have held the opinion that the pyrolysis of paraffins takes place by two concurrent processes, one molecular in character, the other an unbranched free-radical chain mechanisms. The addition of a 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[132]. It is now known that the molecular mechanism for the fully inhibited reaction is, however, incompatible with results of recent mass spectrometric experiments[133], isotope exchange experiments[134], and detailed analytical studies[135]. These results indicate that the fully inhibited reaction also involves free radicals and is variant of the uninhibited reaction mechanism. It is now agreed that the free radical process accounts for the whole of the uninhibited reaction. There is still some disagreement in connection with the initiation and termination steps, but there is general agreement on the chain propagating processes in the uninhibited thermal decomposition of ethane[136], propane[137], and butane[138,139].

The primary process in the thermal decomposition of paraffins seems to involve the rupture of a carbon-carbon bond to give two radicals. These radicals then undergo various reactions as follows.

(a) Disproportionation

$$RCH_2CH_2CH_2CH_2\cdot \longrightarrow RCH_2CH_2CH=CH_2 + H\cdot$$
$$\longrightarrow RCH_2CH=CH_2 + CH_3\cdot$$
$$\longrightarrow RCH=CH_2 + CH_3CH_2\cdot$$
$$\longrightarrow RCH_2CH_2\cdot + CH_2=CH_2$$
$$RCH_2CH_2\cdot + R'CH_2CH_2\cdot \longrightarrow RCH=CH_2 + R'CH_2CH_3$$

(b) Hydrogen abstraction

$$RCH_2CH_2\cdot + R'CH_2CH_3 \longrightarrow RCH_2CH_3 + R'\dot{C}HCH_3$$
$$\longrightarrow RCH_2CH_3 + R'CH_2CH_2\cdot$$

(c) Recombination

$$RCH_2CH_2\cdot + R'CH_2CH_2\cdot \longrightarrow RCH_2CH_2CH_2CH_2R'$$
$$RCH_2CH_2\cdot + H\cdot \longrightarrow RCH_2CH_3$$

The terminating step of recombination of radicals is very fast, but under pyrolytic conditions the radicals are so diluted with hydrocarbons that collision with hydrocarbons is much more frequent than collision with another radical.

In the pyrolysis of ethane[136] the initiating reaction is the splitting of the molecule into two methyl radicals, while the chain terminating step is the combination of two ethyl radicals at high pressure and abstraction of hydrogen by ethyl radicals at lower pressure.

Initiation reaction:

$$CH_3CH_3 \longrightarrow CH_3\cdot + CH_3\cdot$$

Chain termination reaction:

$$CH_3CH_2\cdot + CH_3CH_2\cdot \longrightarrow CH_3CH_2CH_2CH_3 \quad \text{or}$$

$$\longrightarrow CH_3CH_3 + CH_2 = CH_2 \quad \text{at high pr.}$$

$$CH_3CH_2\cdot + H\cdot \longrightarrow CH_3CH_3 \quad \text{at low pr.}$$

Similarly, the primary process in the thermal decomposition of propane[137] is the dissociation of the molecule into a methyl radical and an ethyl radical and these radicals can then react:

$$CH_3CH_2CH_3 \longrightarrow CH_3\cdot + CH_3CH_2\cdot$$

$$CH_3CH_2\cdot + CH_3CH_2CH_3 \longrightarrow CH_3CH_3 + CH_3CH_2CH_2\cdot$$

$$CH_3CH_2CH_3 + H\cdot \longrightarrow H_2 + CH_3CH_2CH_2\cdot$$

$$CH_3CH_2CH_3 + CH_3\cdot \longrightarrow CH_4 + CH_3CH_2CH_2\cdot$$

$$CH_3CH_2CH_2\cdot \longrightarrow CH_3\cdot + CH_2 = CH_2$$

$$\longrightarrow H\cdot + CH_3CH = CH_2$$

The most important chain terminating step in the pyrolysis of propane seems to be the combination of a methyl radical and a propyl radical.

The initiating reaction in the thermal decomposition of butane[139] has been postulated by Sagert and Laidler to be the breakdown into ethyl radicals. Another possible reaction is by scission into methyl and propyl radicals. However, Trotman-Dickenson[116] has estimated that the dissociation energy for this process is some 4 K cal./mole^{-1} higher than for the scission into two ethyl radicals. Hence it seems likely that the split into two ethyl radicals will predominate.

In the hydrogen abstraction reaction the "availability" of a hydrogen has been shown to depend on its environment. Rice and Vanderslice[140], for example, showed that the activation energy for the reaction of methyl radicals with primary hydrogen atoms in paraffin hydrocarbons is greater than that with secondary hydrogen atoms, and the reaction with secondary hydrogen atoms has a greater activation energy than with tertiary hydrogen atoms.

3.2 PYROLYSIS OF OLEFINS

The thermal decomposition of the hydrocarbons of this series differs sharply from that of the hydrocarbons of paraffin series in that the allylic C-H bond fission is also an important initiating step. Olefins generally are more stable than the corresponding paraffins, and the thermal resistance increases as the double bond is moved nearer the centre of the molecule, but decreases as the chain is lengthened or branched. The olefins studied during the past few years may be conveniently divided into three categories containing the following:

(A) without allylic C-H and C-C bonds,

(B) with allylic C-H bond, but no allylic C-C bond,

and (C) with allylic C-H and C-C bonds.

The thermal decomposition of ethylene, the simplest member of the class (A), has been studied by quite a number of workers[141-144] particularly in connection with the primary decomposition reaction. For some time there was some uncertainty whether the decomposition is proceeded (i) by an elimination of molecular hydrogen, or (ii) by a scission to vinyl radicals and hydrogen atoms. It was shown by Cvetanovic[143] that the initial decomposition step in the thermal decomposition of ethylene is the formation of acetylene and hydrogen (equation (1)), and that this is followed by the polymerisation and hydrogenation of the acetylene. Later, this mechanism was supported by Kebarle[144], who, however, found that reaction (2) also occurs, but only to the extent of about 4% of the total decomposition.

$$CH_2 = CH_2 \longrightarrow CH \equiv CH + H_2 \qquad \ldots\ldots(1)$$

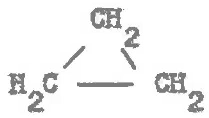
$$CH_2 = CH_2 \longrightarrow CH_2 = CH\cdot + H \qquad \ldots\ldots(2)$$

Compounds containing only allylic C-H bonds, for example, propylene and 2-butene, have been studied by Kebarle and

Avrahami[145,146]. These workers have shown that propylene[145] decomposed by three primary reaction ((3), (4), and (5)) and that no molecular elimination of hydrogen took place.

$CH_3CH = CH_2 \longrightarrow \cdot CH_2CH = CH_2$ 89% ......(3)

$CH_3CH = CH_2 \longrightarrow \cdot CH_3 + \cdot CH = CH_2$ 11% ......(4)

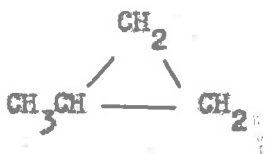
$CH_3CH = CH_2 \longrightarrow$  0.2% ......(5)

It is interesting that although the bond dissociation energy difference $D(C_2H_3 - CH_3) - D(C_3H_5 - H)$ is 16 K cal./mole[147], reaction (4) still occurred to a significant extent. The isomerisation to cyclopropane occurred to a much lesser extent.

Similarly, the primary reactions in the pyrolysis of 2-butene[146] have been shown to be:

$CH_3CH = CHCH_3 \longrightarrow \cdot CH_2CH = CHCH_3 + H\cdot$ ......(6)

$CH_3CH = CHCH_3 \longrightarrow \cdot CH_3 + \cdot CH = CHCH_3$ ......(7)

$CH_3CH = CHCH_3 \longrightarrow$  ......(8)

Approximately 70% of 2-butene decomposed by route (6), 30% by path (7) and the last reaction (8) occurred to a very insignificant extent.

For a considerable time it was believed that the olefins decompose only by cleavage of allylic C-H bonds. However, comparatively recently, Lossing _et al._[148] showed that molecules like 1-butene decompose by breaking not only allylic C-H bond (as in equations (9)-(13)) but also of a allylic C-C bond (as in equations (9a)-(13a)). In both cases one of the weak bonds in the β-position to the double bond breaks, resulting in the formation of the resonance stabilised allyl or methallyl radicals. The allylic C-C bonds in olefins have bond dissociation energies at least 15 K cal./mole smaller than that of any other C-C bond in the molecule, and hence the rupture of this bond seems to be favoured.

$$RCH_2CH_2CH_2CH_2CH = CH_2 \longrightarrow R(CH_2)_3\dot{C}HCH = CH_2 + H\cdot \quad (9)$$

$$\longrightarrow RCH_2CH_2CH_2\cdot + \dot{C}H_2CH = CH_2 \quad (9a)$$

$$\longrightarrow R(CH_2)_2\dot{C}HCH = CHCH_3 + H\cdot \quad (10)$$

$$\longrightarrow R(CH_2)_3CH = CHCH_2\cdot + H\cdot \quad (11)$$

$$\longrightarrow RCH_2CH_2\cdot + \cdot CH_2CH = CHCH_3 \quad (10a)$$

$$RCH_2CH_2CH = CHCH_2CH_3 \longrightarrow RCH_2\dot{C}HCH = CHCH_2CH_3 + H\cdot \quad (12)$$

$$\longrightarrow RCH_2CH_2CH = CH\dot{C}HCH_3 + H\cdot \quad (13)$$

$$\longrightarrow RCH_2\cdot + CH_2CH = \dot{C}HCH_2CH_3 \quad (11a)$$

$$\longrightarrow RCH_2CH_2CH = CHCH_2\cdot + CH_3\cdot \quad (12a)$$

The primary radicals formed in these reactions could decompose further either by the loss of allylic hydrogen, or by the rupture of the allylic C-C bond. For example, the allyl radicals formed in (11a) and (12a) could decompose by the rupture of a C-C bond in the allylic position to give butadiene and an alkyl radical as shown in (14) and (15).

$$\dot{C}H_2CH = CHCH_2CH_3 \longrightarrow \dot{C}H_2CH = CH\dot{C}H_2 + \dot{C}H_3 \;\ldots\ldots(14)$$

$$RCH_2CH_2CH = CHCH_2 \longrightarrow R\dot{C}H_2 + \dot{C}H_2CH = CHCH_2 \quad ......(15)$$

Similarly, the radicals formed in (10a), (11a) and (12a) could also decompose by the loss of C-H bond in the allylic position to give butadiene as in (16) and substituted butadiens as shown in (17) and (18).

$$\dot{C}H_2.CH = CHCH_3 \longrightarrow \dot{C}H_2CH = CH\dot{C}H_2 + H. \quad ......(16)$$

$$\dot{C}H_2CH = CHCH_2CH_3 \longrightarrow \dot{C}H_2CH = CH\dot{C}HCH_3 + H. \quad ...(17)$$

$$RCH_2CH_2CH = CH\dot{C}H_2 \longrightarrow RCH_2\dot{C}HCH = CH\dot{C}H_2 + H. \quad .(18)$$

The allylic radicals obtained in ((9)-(13)) display the same weakness towards thermal rupture at allylic positions with the formation of butadiene or of substituted butadienes.

The presence of butadiene or its alkyl derivatives in almost all pyrolytic reactions[115] may well be due to this type of reactions.

3.3 PYROLYSIS OF AROMATIC HYDROCARBONS

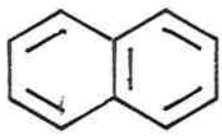
Aromatic hydrocarbons as pyrolytic source materials for other arenes fall into two categories: those with and those without side chains.

(A) Unsubstituted aromatic hydrocarbons

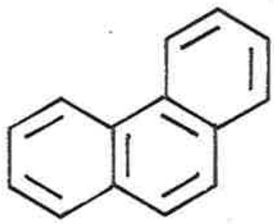
Benzene is more stable thermally than toluene, and its mode of decomposition is dramatically different. Berthelot[102] and many other workers[149-153] studied the pyrolysis of benzene in the early years, but more significant studies have been by Badger and Novotny[69].

They pyrolysed benzene by passing its vapour with nitrogen through a silica tube maintained at 700°. This will be discussed in detail as a comparative study in Chapter 4.

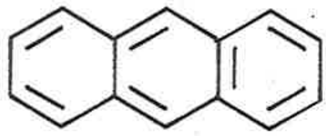
The pyrolysis of fused ring aromatic hydrocarbons, for example, naphthalene (XXXVI), phenanthrene (XXXVII), anthracene (XXXVIII) gave highly condensed systems. The pyrolysis of naphthalene will also be discussed in Chapter 4. The pyrolysis of phenanthrene has been reported earlier by Lang[87]. More recently Badger and coworkers pyrolysed phenanthrene[86] in nitrogen at 700° and 850° and anthracene[67] in nitrogen at 700° and 950°.



(XXXVI)



(XXXVII)



(XXXVIII)

The formation of most of the hydrocarbons found in these tars have been explained in a similar way as in the pyrolysis of benzene[69] and naphthalene[83]. However, it is interesting to note that in the pyrolysis of phenanthrene at 700°, much of the phenanthrene was recovered unchanged and no anthracene was detected; but at 850°, a much smaller recovery of phenanthrene was observed, a greater proportion of condensed hydrocarbons was obtained, and a considerable yield of anthracene was obtained. Similarly, in the pyrolysis of anthracene at 700°, most of the starting material was recovered, and no phenanthrene was obtained. On the other hand very little anthracene survived the pyrolysis at 950°, a much wider range of aromatic hydrocarbons was formed, and an excellent yield of phenanthrene was obtained. It seems certain that some hydrogenation must have occurred at the higher temperature, and fission of the resulting tetrahydrophenanthrene (XXXIX) or tetrahydroanthracene (LX) intermediates would account for the rearrangement of phenanthrene to anthracene or vice versa, as shown in figure 2, and of other condensed hydrocarbons which were present in very small amounts. The formation of naphthalene in these pyrolysis furnishes additional support for this view.

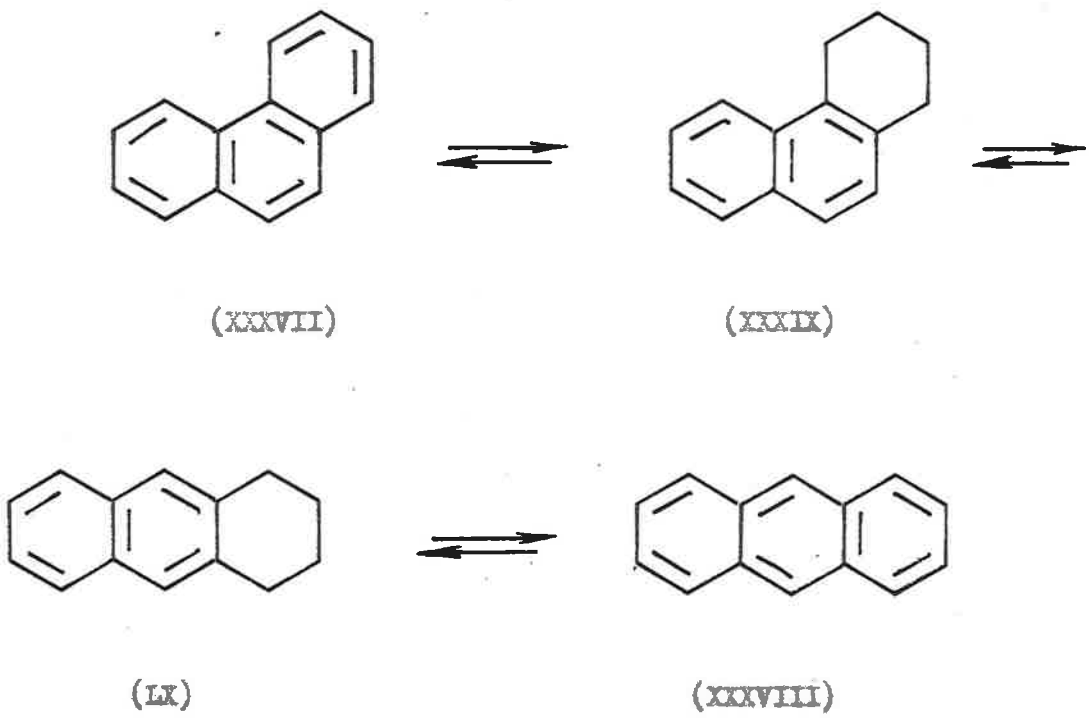
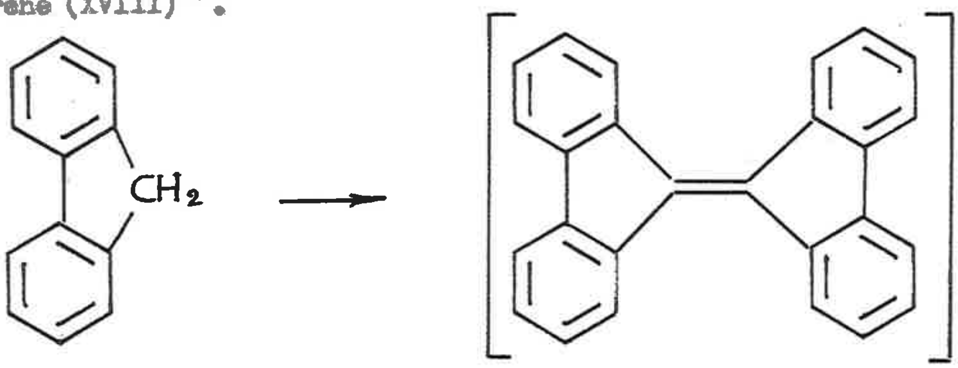


Figure 2

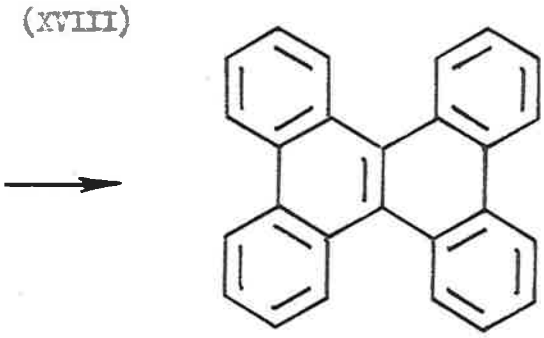
It is noteworthy that Orlow[154] first observed the phenanthrene → anthracene rearrangement following the passage of phenanthrene through a red-hot tube (about 750°), in presence of hydrogen.

In the pyrolysis of methyl substituted hydrocarbons such as 1- and 2-methylnaphthalenes[81,82] and acenaphthene[65], the molecules were coupled preferentially through the methyl or methylene groups. However, Lijinsky and Raha[82] have reported that in the formation of most of the products in the pyrolysis of 2-methylnaphthalene, the methyl group was, apparently, lost.

Another example is the expansion of the ring, yielding 1,2:7,8-dibenzochrysene (LXI) as the main product in the pyrolysis of fluorene (XVIII)[79].



(XVIII)



(LXI)

(B) Substituted aromatic hydrocarbons.

Although unsubstituted aromatic hydrocarbons are remarkably resistant to pyrolysis, alkylbenzenes are dramatically different. For example, toluene, a typical member of this class, is much less stable thermally than benzene and it decomposes in an entirely different fashion. The pyrolysis of toluene was first studied by Berthelot[102] in the early years, and his work has been repeated and extended by many other workers[75,155,156] using improved techniques. Many of the fundamental processes have been elucidated, but there is still considerable disagreement as to details except perhaps that the toluene initially breaks down to hydrogen and benzyl radicals. The methyl C-H bond in toluene has a bond dissociation energy (77.5 K cal./mole)[157] at least 20 K cal./mole smaller than that of any "aromatic" C-H bond, and hence the rupture of this bond seems to be favoured. The bond dissociation energy for the C-C bond linking methyl group to the benzene ring is uncertain, but may be near 87 K cal./mole[158]. Hence the rupture of this C_6H_5-CH_3 bond may also be expected. Thus the primary decomposition products of toluene in the reaction zone should be H., $C_6H_5CH_2$. , C_6H_5. , and CH_3. .

In a recent investigation the pyrolysis of toluene[73a] at 700° was found to give a tar in which 23 products were identified in addition to large amount of unchanged toluene and the formation of the major products of the pyrolysis has been explained by reactions of these primary decomposition products. It has been suggested that the most likely route to (i) benzene is simply by cleavage of the C_6H_5-CH_3 bond, and to some extent by the interaction of two methyl radicals to give ethylene and hence benzene, (ii) bibenzyl by the union of two benzyl radicals, (iii) fluorene by the union of phenyl and benzyl radicals followed by cyclodehydrogenation, (iv) phenanthrene by the cyclisation of bibenzyl or of stilbene or, more likely, by the combination of phenyl and styryl radicals followed by cyclodehydrogenation of the adduct (figure 3), and (v) anthracene by the union of phenyl and styryl radicals to give an intermediate radical (LXII) as in (iv) followed by rearrangement as shown in figure 3.

More recently Hurd and coworkers[119] have pyrolysed [1-^{14}C]toluene at 825° (hot contact time, 24 sec.) and proposed an explanation for the formation of labelled benzene, naphthalene, anthracene, and phenanthrene found in the tar.

Essentially, their proposal involves fragmentation of the benzyl radical in the manner of a reverse diene synthesis into C_4- and C_3- resonance stabilised radicals followed by isomerisation of the C_3 fragment to a radical-carbene, trimethine (also stabilised by resonance), by 1,2-shift of hydrogen and dimerisation of two such fragments into benzene having two labelled carbon atoms as shown in figure 4.

This mechanism was thought to explain the small amount of labelled benzene (0.033 labelled atom) isolated following the

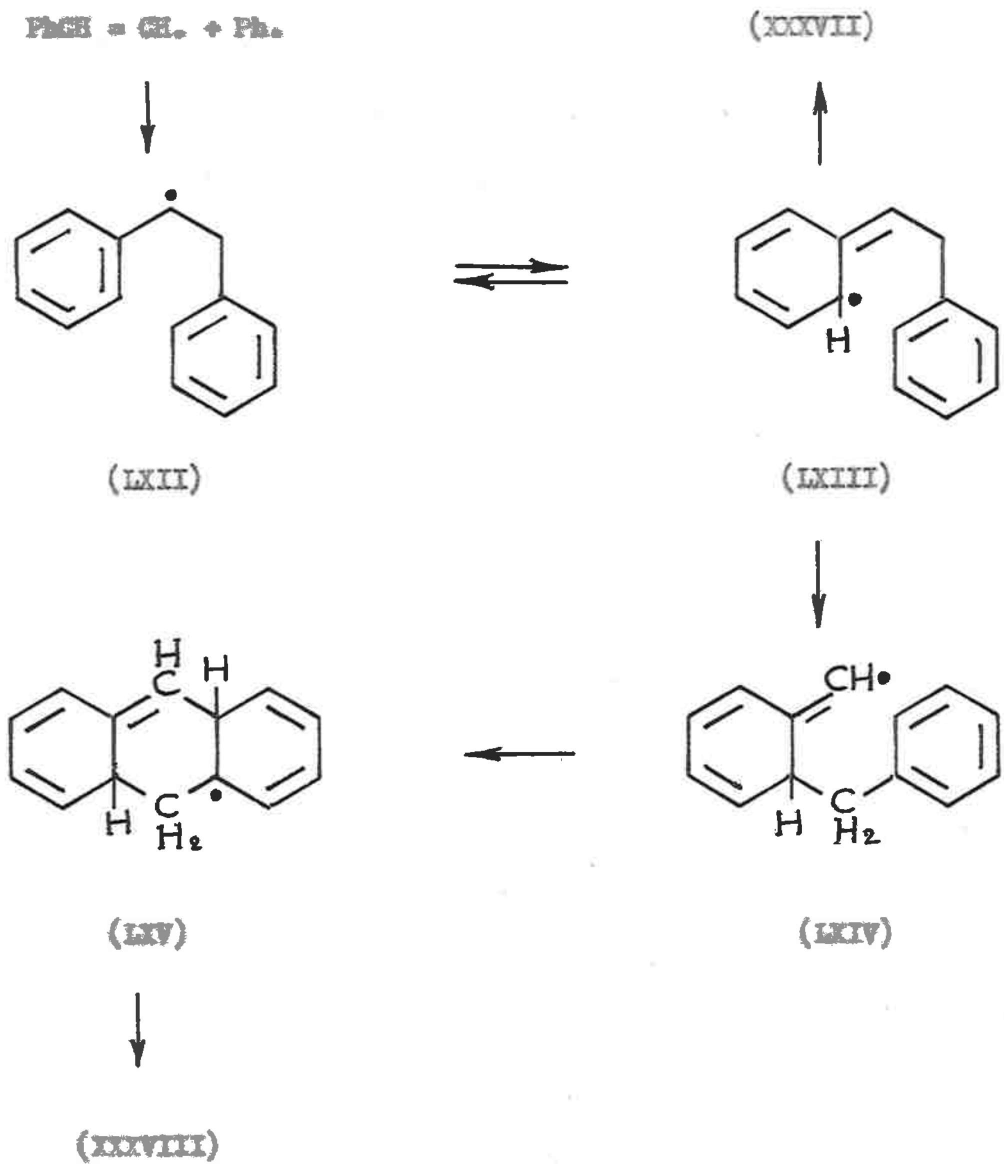


Figure 3

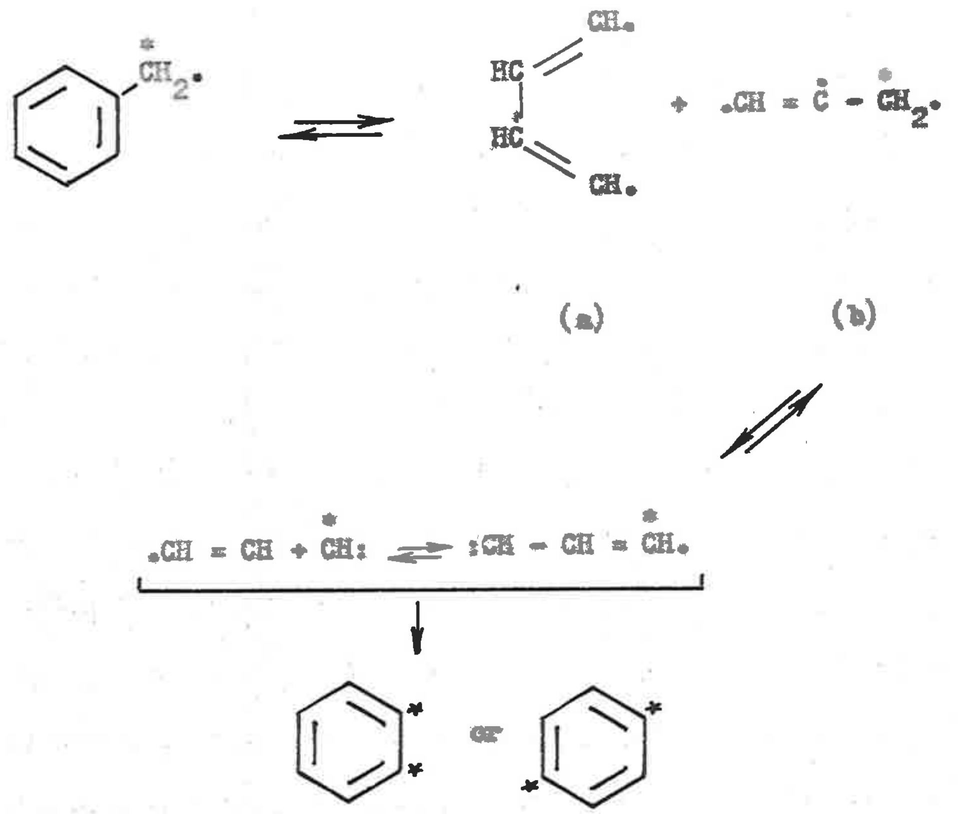
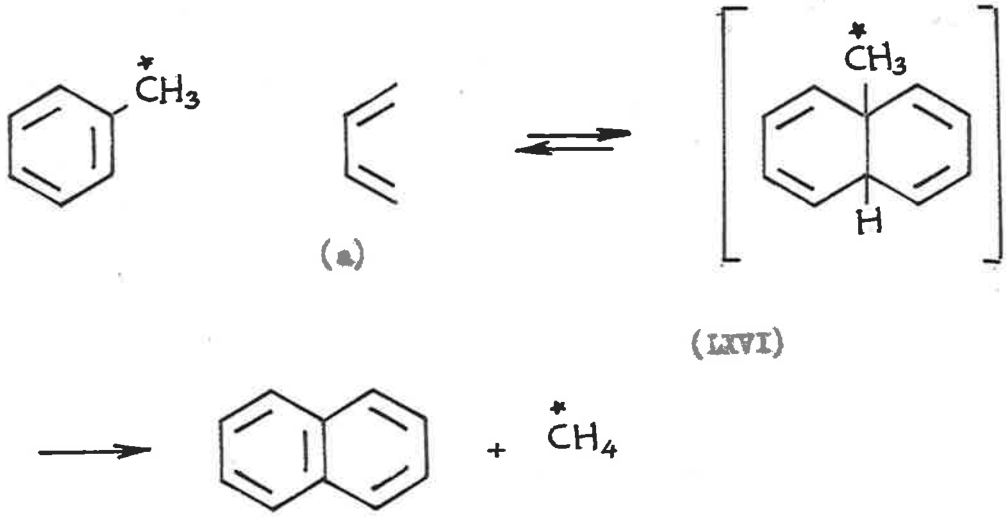


Figure 4

pyrolysis of [1-^{14}C] toluene. This small amount of active benzene could, however, be formed equally well as indicated above, i.e. by the interaction of two methyl radicals to give ethylene, and hence benzene.

Similarly a diene mechanism was suggested[119] to explain the formation of naphthalene (0.176 labelled atom) which arises from

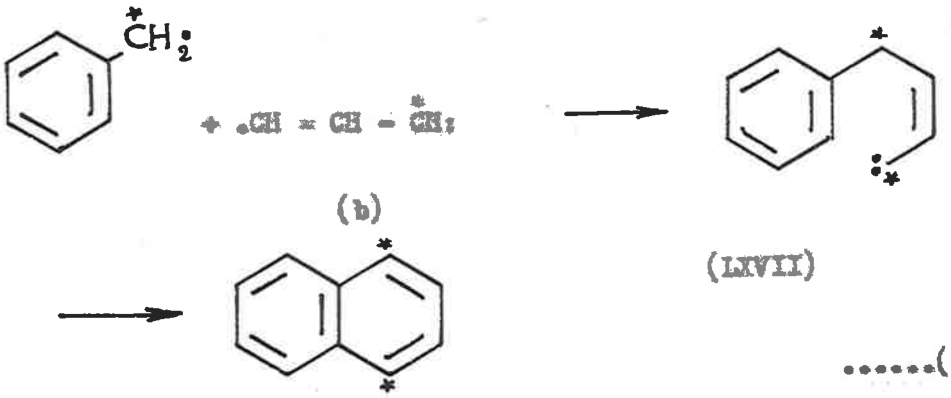
$[1-^{14}C]$toluene. This would involve reversible addition of a C_4 fragment (a) to toluene followed by irreversible loss of methane to give unlabelled naphthalene (equation (19)).



(a) (LXVI) (XXXVI)

.......(19)

Another route has also been suggested by these workers that the reaction of benzyl radical with C_3 fragment (b) would give naphthalene having two labelled carbon atoms (equation (20)).



(b) (LXVII) (XXXVI)

.......(20)

The anthracene isolated by Hurd and coworkers[119] following the pyrolysis of [1-^{14}C]toluene was found to have 1.91 labelled atoms. This result is in good agreement with the mechanisms involving two labelled benzyl radicals, for example, by rearrangement from bibenzyl as shown in figure 3. These workers, however, interpreted their results in a different manner. This involves a modified Errede's mechanism in which the benzyl radical attacks ortho to the methyl substituent or another benzyl radical, followed by cyclisation as shown in figure 5.

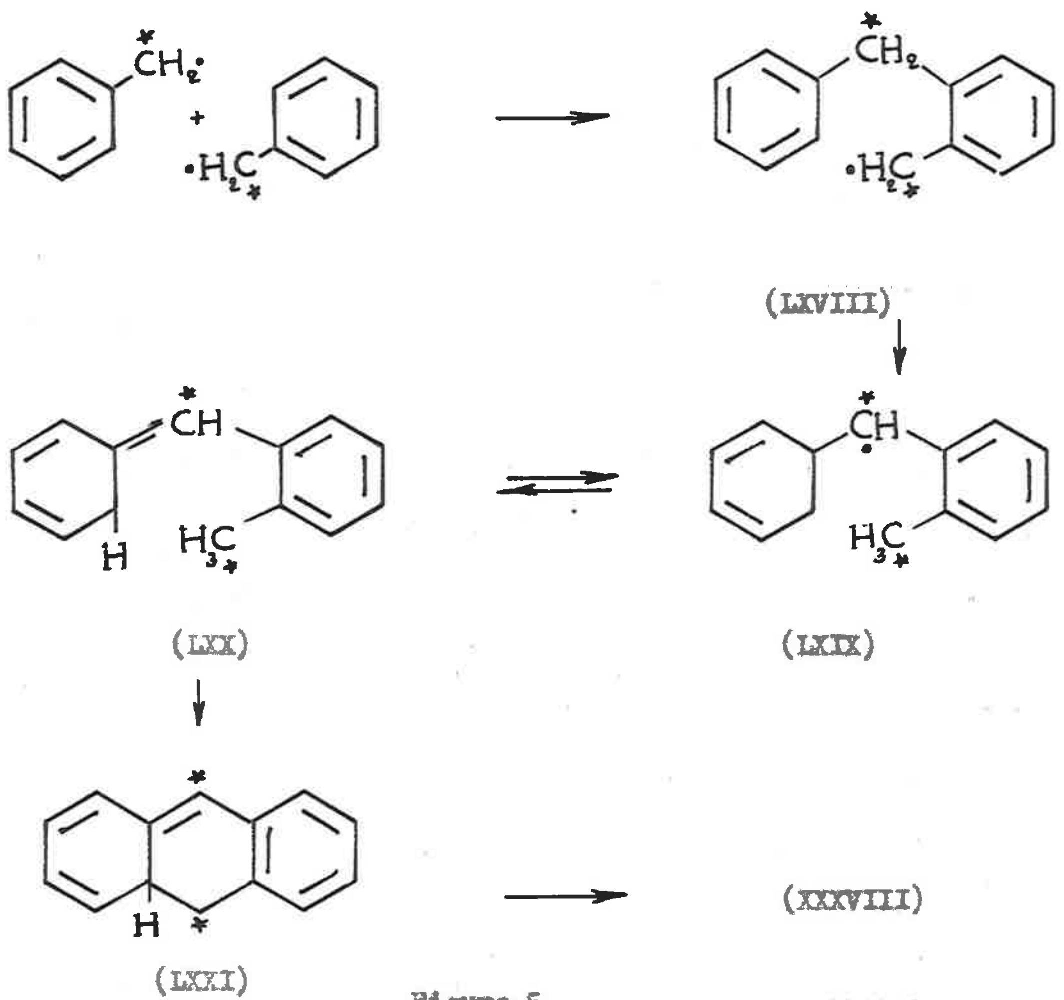


Figure 5

Similarly the phenanthrene activity of 1.71 labelled carbon atoms supports the generally accepted mechanism involving bibenzyl as an intermediate as shown in figure 3.

The Hurd mechanism[119] for the formation of benzene and naphthalene by way of C_3- and C_4-fragments has not been generally accepted. Considerable evidence is accumulating on the relative stability of the aromatic rings at temperatures around 650 -850° and it is known that hydrogen atoms produced by C-H fission can reduce aromatic rings so that fission of the resulting saturated C-C bonds could well occur. In other words some labelled benzene and naphthalene would be expected if any reduced toluene or benzene is formed and then ruptured. The formation of phenanthrene and anthracene in the pyrolyses of anthracene[67] and phenanthrene[86] respectively and also the formation of naphthalene in these pyrolyses supports this latter view.

The pyrolysis of aromatic hydrocarbons with higher alkyl side chains such as ethyl, propyl, and butyl will be reviewed in connection with the present investigation.

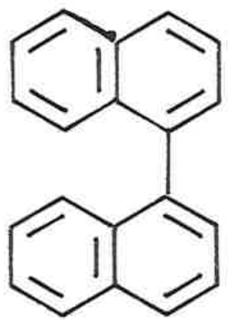
CHAPTER 4

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

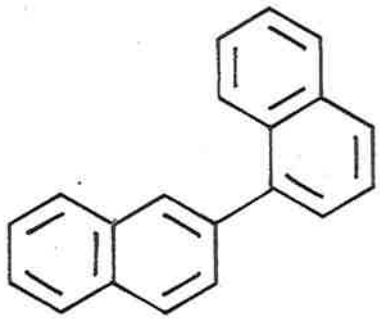
4.1 INTRODUCTION

Naphthalene is an important constituent of the tars obtained by the pyrolysis (at 700°) of acetylene, butadiene, paraffin hydrocarbons, alkylbenzenes, and of tetralin and related compounds (Table 8). 1,1'-Binaphthyl (LXXII), and the isomeric 1,2'- (LXXIII) and 2,2'- (LXXIV) binaphthyls, have also been detected in many of these tars, and it has been suggested that these hydrocarbons are formed by reaction of naphthyl radicals with naphthalene[73a,84,92]. The condensed hydrocarbons perylene (LXXV), 10,11-benzofluoranthene (XVII) and 11,12-benzofluoranthene (LXXVI) have similarly been detected in many of these tars, and it is reasonable to suggest that they are formed from the corresponding binaphthyls by cyclodehydrogenation.

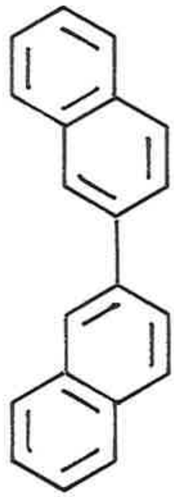
The binaphthyls, and the three condensed hydrocarbons, were all detected by Lang and Buffleb[84] in the tar obtained following the pyrolysis of naphthalene at 800°. Moreover, all these hydrocarbons have been found in the tar produced by the pyrolysis of tetralin[92]. More recently, the pyrolysis of [1-^{14}C]tetralin[122] has also been reported, and labelled 1,1'-binaphthyl (LXXII), 2,2'-binaphthyl (LXXIV), perylene (LXXV), 10,11-benzofluoranthene (XVII) and 11,12-benzofluoranthene (LXXVI) were isolated from the resulting tar. All showed radioactivity corresponding, within experimental



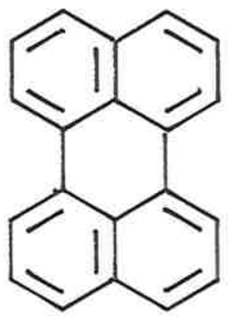
(LXXII)



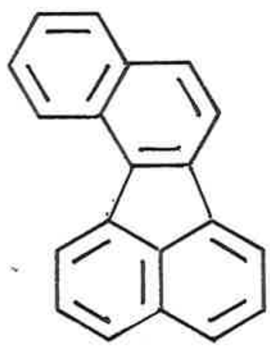
(LXXIII)



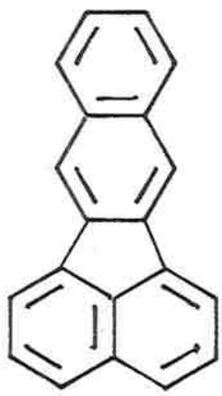
(LXXIV)



(LXXV)



(XVII)



(LXXVI)

TABLE 8

NAPHTHALENE OBTAINED FOLLOWING PYROLYSIS

OF SIMPLE HYDROCARBONS

Hydrocarbon pyrolysed	Percentage naphthalene in resulting tar
Acetylene[66]	12.00
"Iso-octane"[93]	18.20
Buta-1,3-diene[72]	14.00
Styrene[91]	6.10
3-Vinylcyclohexene[94]	13.16
Indene[80]	4.60
Tetralin[92]	74.40
_n_-Decane[74]	13.20
Toluene[73a]	0.042
Ethylbenzene[73a]	4.54
Propylbenzene[73a]	3.43
Butylbenzene[73a]	21.00

error, to two labelled carbon atoms. It may also be noted that in a related investigation[159] naphthyl radicals were generated at much lower temperatures (by decomposition of naphthylsulphonyl chlorides or photochemically from 1-iodonaphthalene) and allowed to react with naphthalene. Binaphthyls, perylene and benzofluoranthenes were obtained. As a further contribution to the study of the mode of formation of the binaphthyls (LXXII-LXXIV) and the condensed hydrocarbons (LXXV, XVII, LXXVI), the pyrolysis of [1-^{14}C]naphthalene has been undertaken.

4.2 RESULTS

Before studying isotopically-labelled naphthalene, the pyrolysis of ordinary naphthalene was first investigated to establish the conditions for pyrolysis, the nature of the products, and to determine their percentage in the tar.

The pyrolysis was carried out at 700° using the apparatus described in Chapter 9.1. Naphthalene, as a liquid, was introduced dropwise into the pre-heated silica tube, and nitrogen was used as carrier gas. The exit gases were examined by infrared spectroscopy. The resulting tar was collected and analysed by distillation, chromatography on alumina and chromatography on acetylated cellulose. The products were isolated and identified by spectroscopy and whenever possible by m.p. and mixed m.p.

The percentage composition of the resulting tar is given in Table 9. Most of the naphthalene was recovered unchanged, but 1,1'-, 1,2'- and 2,2'-binaphthyls were formed in significant amounts; the condensed hydrocarbons perylene, 10,11-benzofluoranthene and 1,12-benzofluoranthene were formed in smaller amounts. No methane or ethylene could be detected in the exit gases. Surprisingly, some

3,4-benzopyrene was also detected in the tar.

TABLE 9

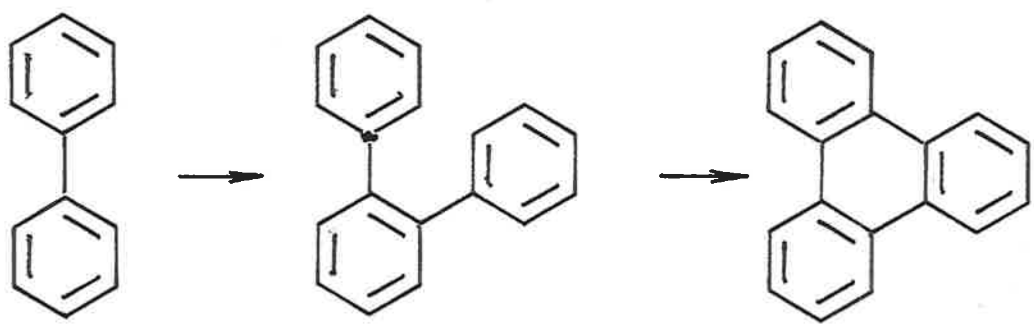
PERCENTAGE COMPOSITION (w/w) OF TAR OBTAINED BY PYROLYSIS OF NAPHTHALENE AT 700° AND THE NUMBER OF LABELLED CARBON ATOMS IN EACH CONSTITUENT OF THE TAR

Compound	Percentage in tar	Labelled C. atoms
Naphthalene	86.21	1.00
1,1'-Binaphthyl	0.76	2.00
1,2'-Binaphthyl	1.90	2.01
2,2'-Binaphthyl	2.18	2.00
Perylene	0.011	
10,11-Benzofluoranthene	0.041	1.93
11,12-Benzofluoranthene	0.037	1.95
3,4-Benzopyrene	Trace	

The pyrolysis was then repeated using [1-^{14}C]naphthalene, and most of the products were isolated in sufficient quantity and purity for radiochemical analysis. Perylene (LXXV) and 3,4-benzopyrene, however, could not be isolated in sufficient quantity for this purpose. The activities were calculated as relative molar activities, which are linearly proportional to the number of labelled carbon atoms per molecule[160], and the results are summarised in Table 9.

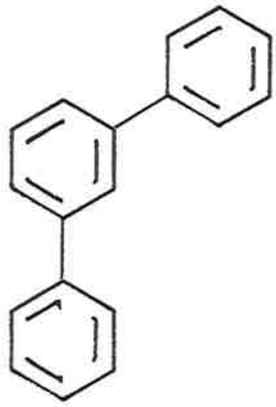
4.3 DISCUSSION

The pyrolysis of benzene was carried out by Badger et al.[69] by passing its vapour with nitrogen through a silica tube maintained at 700°. Most of the initial material was recovered unchanged and the major product was biphenyl (LXXVII). The only other substances formed in relatively large amounts were m-terphenyl (LXXVIII), p-terphenyl (LXXIX), triphenylene (LXXX); and a few polycyclic compounds were also identified. It seemed certain that the major process involves carbon-hydrogen fission to give phenyl radicals which then react with benzene to yield biphenyl (LXXVII), or with biphenyl to yield o-terphenyl (LXXXI) and m-terphenyl (LXXVIII), and p-terphenyl (LXXIX), and cyclodehydrogenation of (LXXXI) would give triphenylene (LXXX).



(LXXVII) (LXXXI) (LXXX)

(LXXIX)



(LXXVIII)

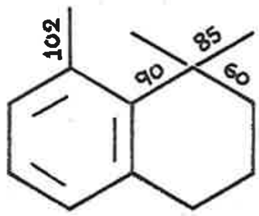
It has also been suggested that some hydrogenation may occur during the pyrolysis of benzene, and that fission of the resulting cyclohexene or cyclohexane would account for the methane and ethylene formed and several hydrocarbons (fluorene, phenanthrene, anthracene, fluoranthene, chrysene, and 3,4-benzofluoranthene) detected in the tar. It has already been indicated in Chapter 3.3 that the presence of hydrogenated hydrocarbons in tars produced by the pyrolysis of phenanthrene[86] and anthracene[67] has been confirmed. It is therefore possible that the carbon-carbon bond fission products arise from reduced benzene molecules rather than from the aromatic ring itself. As mentioned earlier, saturated carbon-carbon bonds are certainly much weaker than aromatic carbon-carbon bonds.

The pyrolysis of naphthalene at 700° has now given similar results.

The major process clearly involves carbon-hydrogen bond fission to give naphthyl radicals, which then react with naphthalene to yield 1,1'-binaphthyl (LXXII), 1,2'-binaphthyl (LXXIII), and 2,2'-binaphthyl (LXXIV). The condensed hydrocarbons 10,11-benzofluoranthene (XVII), 11,12-benzofluoranthene (LXXVI), and perylene (LXXV) are evidently formed from the binaphthyls by further carbon-hydrogen fission; that is by cyclodehydrogenation. The number of labelled carbon atoms in the binaphthyls and in the benzofluoranthenes isolated following the pyrolysis of [1-^{14}C]naphthalene are all consistent with this view. The mode of formation of these hydrocarbons must now be considered as established beyond dispute.

No methane or ethylene could be detected in the exit gases following the pyrolysis of naphthalene. However, the presence of little 3,4-benzopyrene in the tar shows that cleavage of the ring system does occur to some extent.

The results of the present investigation have shown that the major process in the pyrolysis of naphthalene involves the cleavage of carbon-hydrogen bonds, and considerable quantities of free hydrogen must therefore be present in the reaction zone. Under these conditions it would be conceivable for some hydrogenation to occur, and that some tetralin may be formed during the pyrolysis, of naphthalene. Most of this tetralin would, no doubt, be dehydrogenated to naphthalene; but the saturated carbon-carbon bonds in tetralin would also be expected to undergo ready cleavage (the approximate values of the dissociation energies (in K cal./mole) for the C–C and C–H bonds in tetralin are shown in the diagram (LXXXII)). It is therefore suggested that the 3,4-benzopyrene detected in the



(LXXXII)

tar obtained by the pyrolysis of naphthalene is formed as outlined in figure 6 and not by any fission of aromatic carbon-carbon bonds.

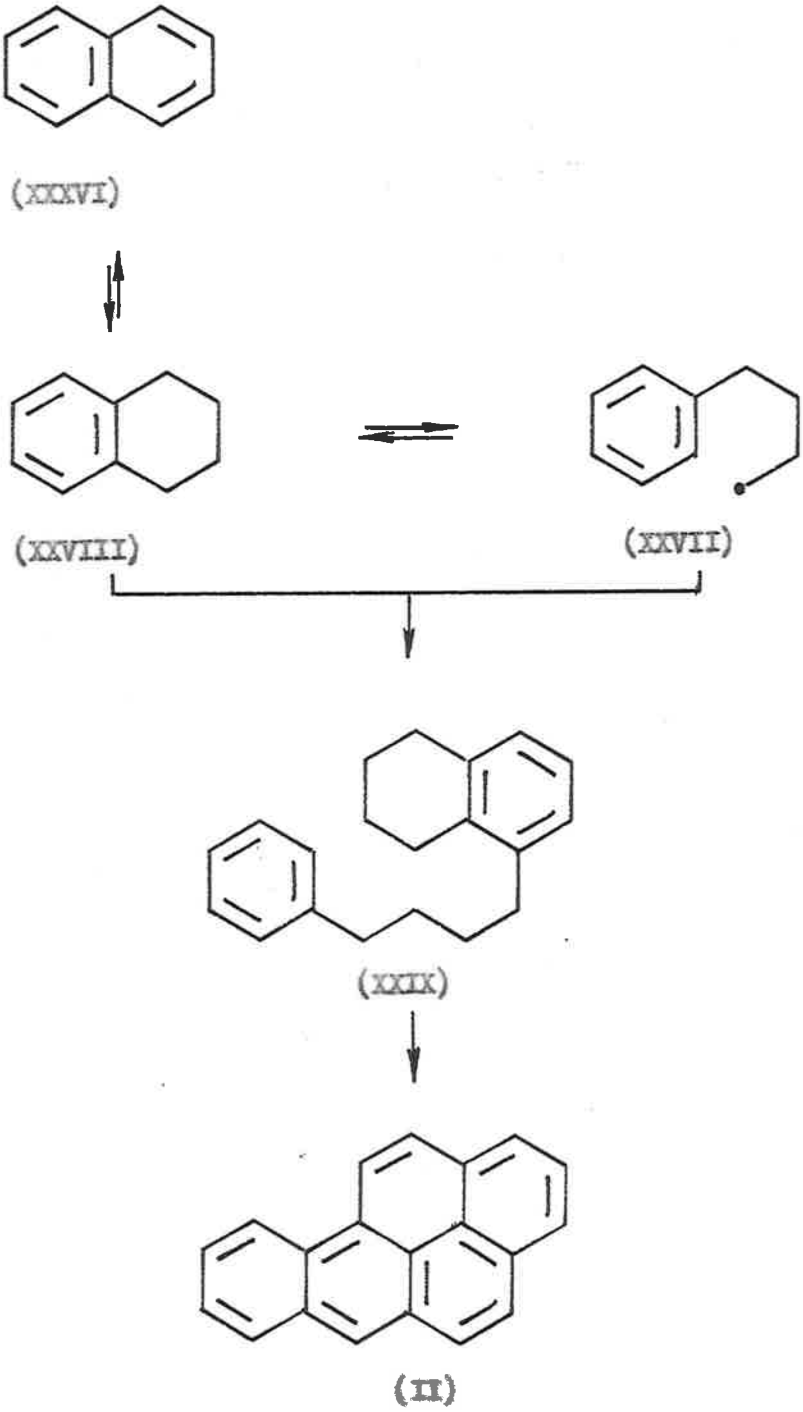


Figure 6

CHAPTER 5

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

5.1 INTRODUCTION

Styrene, a typical alkenylbenzene, is one of the most important constituents of the tars obtained by the pyrolysis (at 700°) of alkylbenzenes, 3-vinylcyclohexene, iso-octane, tetralin, and related compounds (Table 10). The thermal decomposition of styrene was first studied by Berthelot[161] by passing its vapour through a porcelain tube at "bright red heat", and the products were found to be benzene and acetylene. A 99% recovery of styrene has been reported following heating to 550°[162] and a 95.3% recovery after heating at 625°[163,164]. More recently, Badger and coworkers made a detailed analysis of the tar obtained by pyrolysing styrene at 710° and identified fifteen compounds. Plausible mechanisms were designed to explain the formation of these compounds on the considerations of the "primary" radicals expected following scission of the weakest C-H and C-C bonds and on the relative yields of the various hydrocarbons in these tars. To provide a means of checking mechanistic considerations regarding the pyrolysis of styrene, a tracer method using carbon-14 in the side chain of styrene has been investigated. Accordingly the pyrolysis of [1-^{14}C]styrene has now been studied.

5.2 RESULTS

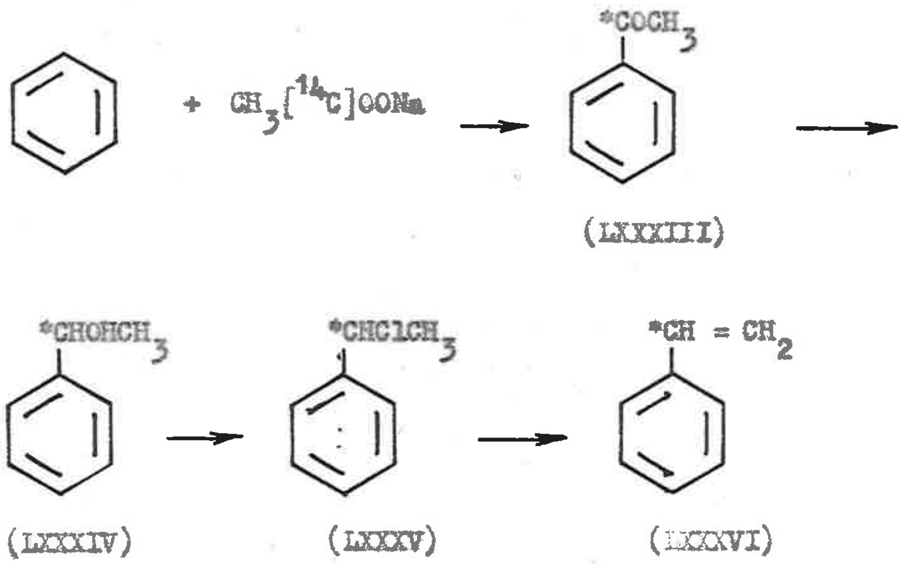
[1-^{14}C]Styrene was synthesised by the following route. A Friedel-Crafts reaction between benzene and [1-^{14}C]sodium acetate in the presence of aluminium chloride gave [carbonyl-^{14}C]acetophenone (LXXXIII) in 81.6% yield[165]. Reduction of (LXXXIII) with Raney nickel in aqueous alcoholic sodium hydroxide afforded

TABLE 10

STYRENE OBTAINED FOLLOWING PYROLYSIS OF HYDROCARBONS

Hydrocarbon pyrolysed	Styrene in resulting tar %
Tolene[73a]	0.1
Ethylbenzene[73a]	9.9
Propylbenzene[73a]	14.7
Butylbenzene[73a]	2.7
3-Vinylcyclohexene[94]	3.14
Iso-octane[93]	8.47
Tetralin[92]	0.86
n-Decane[74]	0.86
Dotriacontane[77]	7.03

1-phenyl [1-^{14}C]ethanol (LXXXIV) in 92.7% yield[166]; treatment with concentrated hydrochloric acid gave the corresponding chloro compound 1-chloro-1-phenyl [1-^{14}C]ethane (LXXXV) in 85.6% yield; and finally ~~dehydrogenation~~ dehydrohalogenation in boiling quinoline gave the required [1-^{14}C]styrene (LXXXVI) in 75.6% yield.



(*) indicates ^{14}C

This labelled styrene was diluted with purified inactive styrene (approximately 1:50) from a commercial source to provide the stock supply of [1-^{14}C]styrene used in all subsequent experiments.

No impurities were detected by gas-liquid chromatography of this styrene, which had an infrared spectrum and refractive index identical with that of pure unlabelled styrene.

The isotopic purity of the styrene was confirmed by oxidation to benzoic acid and subsequent decarboxylation to benzene. The benzoic acid (relative molar activity, 6.25×10^{-2}) and carbon dioxide (relative molar activity, 6.24×10^{-2}) obtained on decarboxylation had almost the same activity as the original styrene (relative molar activity, 6.81×10^{-2}), and the label is thereby shown to be exclusively in the 1-position of the side chain.

[1-^{14}C]Styrene was pyrolysed, as previously described for the inactive compound[91], by passing its vapour with oxygen-free nitrogen, through a pre-heated (710°) silica tube filled with porcelain chips. The gaseous products were identified as methane and ethylene. The resulting liquid tar was analysed by a combination of distillation, gas-liquid chromatography, chromatography on alumina and on acetylated cellulose. Nine compounds were isolated in sufficient quantity and purity for radiochemical analysis. Four of these have been degraded to determine the distribution of the activity. The results for these compounds are summarised in Table 11, which gives the number of labelled carbon atoms for each compound and for some degradation products. Activities were calculated as relative molar activities[160] which are linearly proportional to the number of active carbon atoms per molecule.

5.3 DISCUSSION

According to the previous discussion based on the consideration of bond dissociation energies of various types of C-C and C-H bonds (Table 12), the energy required to break the C-C single bond is approximately the same order as that required to break the C-H bonds,

TABLE 11

Compound	Degradation Products	Labelled C Atoms
Benzene		0.086
Toluene		0.70
	Benzoic acid	0.66
	Carbon dioxide (from decarboxylation of benzoic acid)	0.65
	Benzene	0.01
Ethylbenzene		0.97
	Benzoic acid	0.86
	Carbon dioxide (from decarboxylation of benzoic acid)	0.85
	Benzene	0.02
Styrene		1.00
Indene		1.38
Naphthalene		2.04
2-Phenylnaphthalene		1.94
Phenanthrene		0.99
	2,2'-Biphenic acid	1.00

(contd.)

TABLE 11, contd.

Compound	Degradation Products	Labelled C Atoms
	Carbon dioxide (from decarboxylation of 2,2'-biphenic acid)	0.53
	Biphenyl	0.11
Chrysene		2.92
	Chrysa-1,2-quinone	2.90
	o-(2-Naphthyl)benzoic acid	2.58
	Carbon dioxide (from decarboxylation of o-(2-naphthyl)benzoic acid	0.53
	2-Phenylnaphthalene	2.07

TABLE 12

BOND DISSOCIATION ENERGIES

Bond	Bond dissociation energy K cal./mole
C-H	100
C-C double bond	140
C-C single bond linking ethylenic group to the benzene ring	110

and that a much greater energy would be required to break the C-C double bond or the aromatic ring. This leads to the conclusion that the "primary" radicals formed in the pyrolysis of styrene arise by random C-H scission in the side chain and ring and by C-C bond (linking ethylenic group to the benzene ring) scission, according to equations (21) and (22).

$$C_6H_5\overset{*}{C}H = CH_2 \longrightarrow C_6H_5\cdot + \cdot\overset{*}{C}H = CH_2 \qquad \text{......(21)}$$

$$\left.\begin{array}{l} C_6H_5\overset{*}{C}H = CH_2 \xrightarrow{a} C_6H_5\overset{*}{C}H = CH\cdot + H\cdot \\ \qquad\qquad\qquad \xrightarrow{b} C_6H_5\overset{*}{\underset{\cdot}{C}} = CH_2 + H\cdot \\ \qquad\qquad\qquad \xrightarrow{c} \cdot C_6H_4\overset{*}{C}H = CH_2 + H\cdot \end{array}\right] \qquad \text{......(22)}$$

The bonds cleaved are of comparable strength, and random formation of the radicals would be expected. In addition, methyl radicals must be present in the reaction zone (in view of the presence of methane in the exit gases) and are probably formed mainly from the styrene side chain.

The formation of the major products following the pyrolysis of [1-^{14}C]styrene can be explained by reasonable reactions (chain propagating and chain terminating) of these primary decomposition products, namely, phenyl, vinyl, and styryl radicals, and the results of the radiochemical analysis presented here provide a method of investigating possible alternative modes of formation.

Benzene is an important and major product of the pyrolysis of [1-^{14}C]styrene and could plausibly be formed simply by cleavage of the $C_6H_5 - \overset{*}{C}H = CH_2$ bond according to equation (21) followed by hydrogen abstraction by the phenyl radical. Benzene formed in this way should be devoid of radioactivity; the presence of an activity corresponding to 0.086 labelled atoms in the benzene isolated suggests that a small percentage may be formed by resynthesis from smaller active fragments. Formation from three labelled vinyl radicals $\cdot\overset{*}{C}H = CH_2$, for example, would give benzene with three labelled atoms, and if approximately 3% of the benzene were formed in this way, the observed activity would be obtained. It is concluded, therefore, that the major route to benzene in this pyrolysis is by cleavage of the olefinic side chain.

Toluene is also a major constituent of the pyrolysate and its mode of formation is of importance because benzyl radicals, the most important precursors of toluene in the pyrolysis of [α-^{14}C]ethylbenzene[167], n-[α-^{14}C]propylbenzene and [δ-^{14}C]butylbenzene[123], are not formed in the primary decomposition process in this pyrolysis.

It has been suggested[91] that reaction between a labelled styryl radical $C_6H_5\overset{*}{C}H = CH\cdot$ and an unlabelled phenyl radical followed by hydrogenation to give bibenzyl, and subsequent cleavage (the central bond of bibenzyl has a very small bond dissociation energy, 47 K cal./mole) to two benzyl radicals (equation (23)) may be an important route to toluene. Equally plausible is hydrogenation of styrene to ethylbenzene, followed by cleavage to a labelled benzyl radical and an unlabelled methyl radical, and subsequent hydrogen abstraction according to equation (24); or union of a methyl radical and a phenyl radical according to equation (25).

$$C_6H_5\overset{*}{C}H = CH\cdot + C_6H_5\cdot \longrightarrow C_6H_5\overset{*}{C}H = CHC_6H_5$$

$$C_6H_5\overset{*}{C}H_2\cdot + C_6H_5CH_2\cdot \longleftarrow C_6H_5\overset{*}{C}H_2 - CH_2C_6H_5$$

$$\downarrow$$

$$C_6H_5\overset{*}{C}H_3 + C_6H_5CH_3 \qquad \ldots\ldots(23)$$

$$C_6H_5\overset{*}{C}H = CH_2 \longrightarrow C_6H_5\overset{*}{C}H_2CH_3 \longrightarrow$$

$$C_6H_5\overset{*}{C}H_2\cdot + CH_3\cdot \longrightarrow C_6H_5\overset{*}{C}H_3 \qquad \ldots\ldots(24)$$

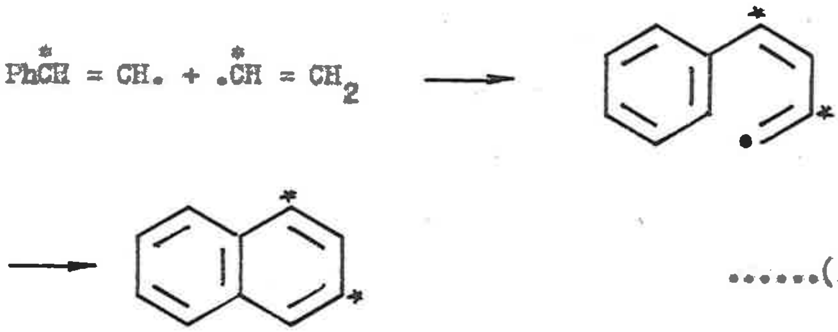
$$C_6H_5\cdot + CH_3\cdot \longrightarrow C_6H_5CH_3 \qquad \ldots\ldots(25)$$

Formation according to equation (23) would give toluene with 0.54 labelled atoms; according to equation (24), 0.86 labelled atoms; and finally according to equation (25), less than 0.5 labelled atoms depending on the activity of the methyl radicals. These figures follow from the results with benzene and ethylbenzene.

The toluene isolated following the pyrolysis of [1-^{14}C]styrene showed activity corresponding to 0.70 labelled carbon atoms. Oxidation of the toluene gave benzoic acid (0.66 labelled atoms). This on decarboxylation gave benzene (0.01 labelled atoms) and carbon dioxide (0.65 labelled atoms). The side chain in the toluene therefore had almost all the activity, providing strong evidence that formation according to equation (24) must be a major route in this pyrolysis with formation according to equations (23) and (25) providing significant alternative pathways.

Ethylbenzene must certainly be formed almost exclusively by hydrogenation of styrene, as in equation (24). Oxidation of ethylbenzene (0.97 labelled atoms) to benzoic acid (0.86 labelled atoms) and decarboxylation to benzene of low activity (0.02 labelled atoms) gave a distribution of activity very similar to that of the parent styrene, and it is unlikely that any other route to this compound is of importance in the present pyrolysis.

Naphthalene (XXXVI) was an important constituent of the pyrolysate and must have arisen by a process of chain resynthesis, most probably by a reaction between the primary decomposition products namely, a labelled styryl radical $C_6H_5\overset{*}{C}H = CH\cdot$ and a labelled ethylene or vinyl radical $\cdot\overset{*}{C}H = CH_2$, followed by ring closure and dehydrogenation. This would be expected to lead to naphthalene, according to equation (26), with 2.0 labelled atoms, in excellent agreement with the experimental figure of 2.04.

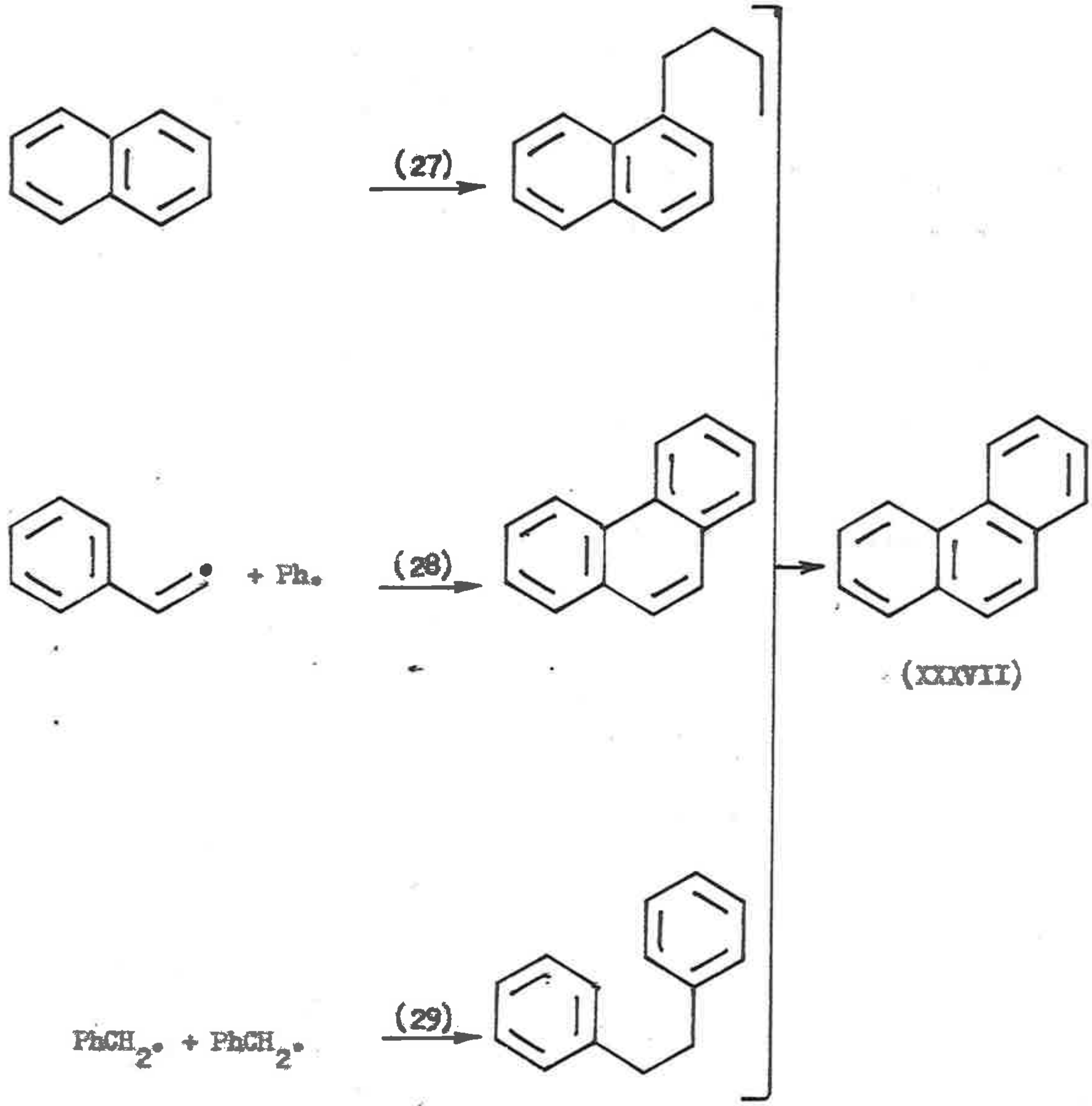


......(26)

(XXXVI)

Phenanthrene (XXXVII) is the major component of the pyrolysate[91], and must have been formed mainly by reactions involving the primary decomposition products.

Three reasonable mechanisms have previously been suggested as important routes to phenanthrene in other papers in this series. Equation (27) would involve the union of a C_6-C_4 unit (such as naphthalene) and a C_4 unit (from two vinyl radicals). Equation (28) would involve the interaction of a phenyl radical and styrene (or styryl radical) followed by cyclisation. Equation (29) would involve the interaction of two benzyl radicals to give bibenzyl, followed by cyclodehydrogenation.

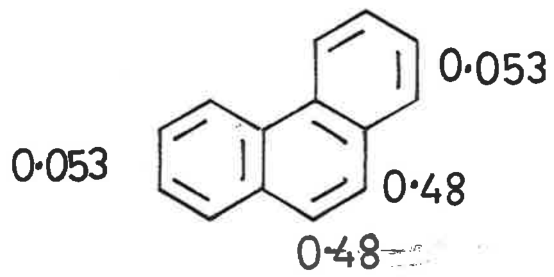


(XXXVII)

In the pyrolysis of [1-^{14}C]styrene, any phenanthrene produced by the first pathway would be expected to have 4.04 labelled atoms, with 2.04 labelled atoms in the C_6-C_4 unit (i.e. naphthalene) and 2.0 labelled atoms from a C_4 unit (i.e. from two ethylene residues).

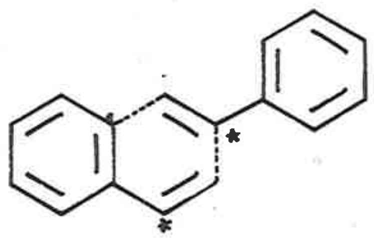
Similarly formation of phenanthrene according to equation (28) would lead to phenanthrene with 1.08 labelled atoms (from styrene, 1.0, and benzene, 0.08). Finally, formation according to equation (29) would lead to phenanthrene with 1.4 labelled carbon atoms of twice the activity of toluene isolated in this pyrolysis.

The experimental figure of 0.99 labelled atoms is clear evidence in favour of formation from a phenyl radical and styrene according to equation (28). Further, oxidation to 2,2'-biphenic acid (1.00 labelled atoms) and subsequent decarboxylation to biphenyl (0.11 labelled atoms) and carbon dioxide (0.53 labelled atoms) indicated a distribution of activity in good agreement with the expected values (LXXXVII).

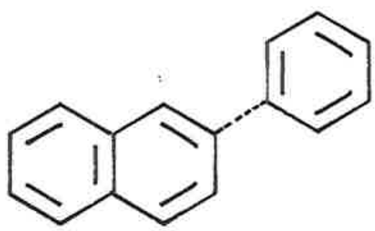


(LXXXVII)

2-Phenylnaphthalene is formed in significant yield on pyrolysis of styrene, and its mode of formation is of interest since it is rarely formed following the pyrolysis of hydrocarbons. Unfortunately, the two most likely mechanisms of formation, from a styryl radical and styrene (as in LXXXVIII) and from naphthalene and a phenyl radical (as in LXXXIX) would give 2-phenylnaphthalene with 2.0 and 2.12 labelled atoms respectively and no decision between these two mechanisms is possible from the present results. However, if the mechanism involving phenylation of naphthalene is important, the formation of 1-phenylnaphthalene and hence fluoranthene (by cyclodehydrogenation) (the pyrolysis of benzene and naphthalene is known to give 1- and 2-phenylnaphthalene and fluoranthene) would also be expected, unless, of course, isomerisation of 1- to 2-phenylnaphthalene occurred to a significant extent; but no fluoranthene is formed following the pyrolyses of styrene. The 2-phenylnaphthalene isolated showed activity corresponding to 1.94 labelled atoms, in agreement with the two possible mechanisms.



(LXXXVIII)

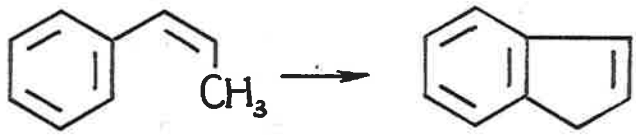


(LXXXIX)

The formation of indene (LLX) in this pyrolysis is equally important in connection with possible routes to chrysene since the latter compound is known to be formed in high yield on pyrolysis of indene at 700°[80].

The most likely route to this compound would appear to be by reaction between styrene (or a styryl radical) and a methyl radical followed by cyclodehydrogenation according to equation (30).

$$C_6H_5CH = CH\cdot + \cdot CH_3 \longrightarrow$$



......(30)

(LIX)

The expected activity of indene would depend on the origin of the methyl radicals, and two reactions could be of major importance (equation (31) and (32)).

$$C_6H_5\overset{*}{C}H = CH_2 \longrightarrow C_6H_5\cdot + \cdot\overset{*}{C}H = CH_2 \longrightarrow$$

$$C_6H_6 + \overset{*}{C}H_2 = CH_2 \longrightarrow \overset{*}{C}H_3 - CH_3 \longrightarrow \cdot\overset{*}{C}H_3 + \cdot CH_3 \quad ......(31)$$

$$C_6H_5\overset{*}{C}H = CH_2 \longrightarrow C_6H_5\overset{*}{C}H_2CH_3 \longrightarrow C_6H_5\overset{*}{C}H_2\cdot + CH_3 \quad ......(32)$$

Formation according to these equations would give methyl radicals with activity corresponding to 0.5 labelled atoms and no labelled atoms respectively. Thus, indene formed as above should have an activity between 1.0 and 1.5 labelled atoms. The observed value of 1.38 labelled atoms suggests that methyl radicals (hence methane) are formed mainly from ethylene as in equation (31).

Alternatively, reaction between benzyl radicals and ethylene or a vinyl radical may also be an important route to this compound in view of the relatively high yield of toluene[91].

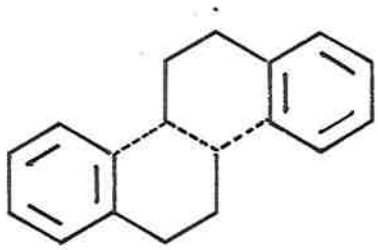
Chrysene is one of the most common products of the pyrolysis of hydrocarbons and several mechanisms of formation are of importance in other pyrolysis in this series[80,92,93].

It has been suggested that chrysene could be formed

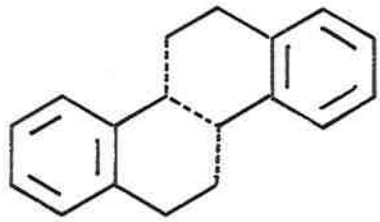
(i) from two C_6-C_3 units (as in LLXI),

(ii) from two C_1-C_6-C_2 units (as in LLXII) or

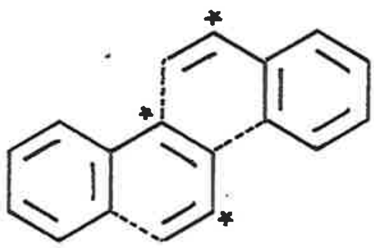
(iii) from a C_6-C_4 and a C_6-C_2 unit (as in LLXIII).



(LLXI)



(LLXII)

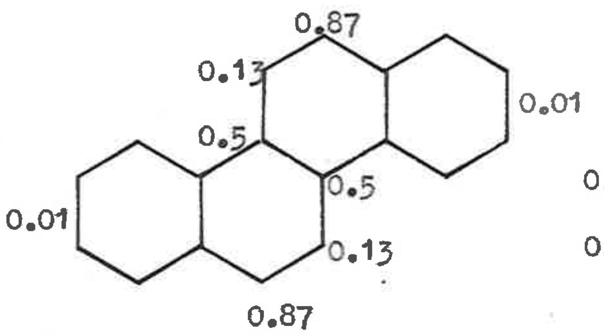


(LLXIII)

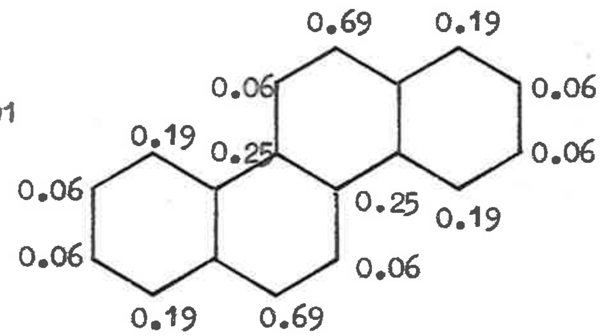
Mechanisms involving dimerisation of two C_6-C_3 units or two C_1-C_6-C_2 units derived from indene or its precursors, are unlikely to be of great importance in the present pyrolysis as indene is only a minor constituent of the pyrolysate. However, mechanisms involving a C_6-C_4

unit and a C_6-C_2 unit are highly probable in view of the high yield of naphthalene and the presence of large amounts of styrene and styryl radicals in the reaction zone.

If it is assumed that the C_6-C_4 unit involved is also the precursor of naphthalene the expected distribution of activity is given by (LLXIV), and if naphthalene itself, by (LLXV).

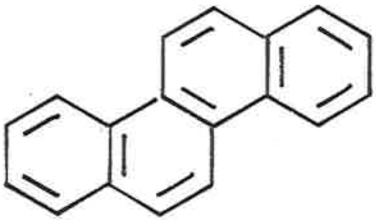


(LLXIV)

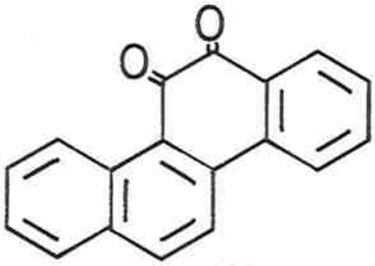


(LLXV)

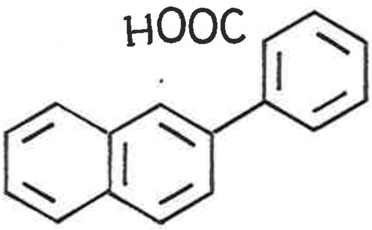
The present experimental results cannot decide between these possibilities, but the general features of the distribution of activity in the two inner rings have been confirmed by degradative studies. Oxidation of chrysene (XIII; 2.92 labelled atoms) with sodium dichromate in acetic acid gave chrysa-1,2-quinone (LLXVI; 2.90 labelled atoms) and alkali fusion of (LLXVI) gave 2-(o-naphthyl) benzoic acid (LLXVII; 2.58 labelled atoms). Decarboxylation of (LLXVII) gave 2-phenylnaphthalene (LLXVIII; 2.07 labelled atoms) and carbon dioxide (0.53 labelled atoms).



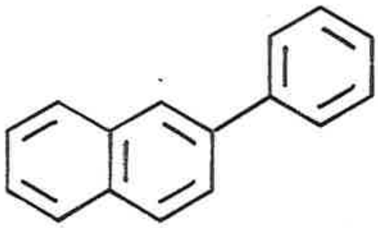
(XIII)



(LLXVI)



(LLXVII)



(LLXVIII)

The distribution of activity is not in particularly good agreement with either (LLXIV) or (LLXV) and other mechanisms of formation must also be of importance.

CHAPTER 6

THE PYROLYSIS OF $[3-^{14}C]$INDENE

6.1 INTRODUCTION

It has long been known[168] that chrysene is formed in good yield from indene by passing its vapour through a red hot tube. Recently it has been shown[80] that the pyrolysis of indene at 700° also gives significant amounts of benzofluorenes and 1,2-benzanthracene in addition to chrysene. It has been suggested that all these hydrocarbons are formed by the "dimerisation" of the radicals expected following scission of the weakest carbon-carbon bond in indene. The data reported in this chapter records an extension of the above work to indene containing carbon-14 at the 3-position, to provide further evidence for the mechanisms of these transformations.

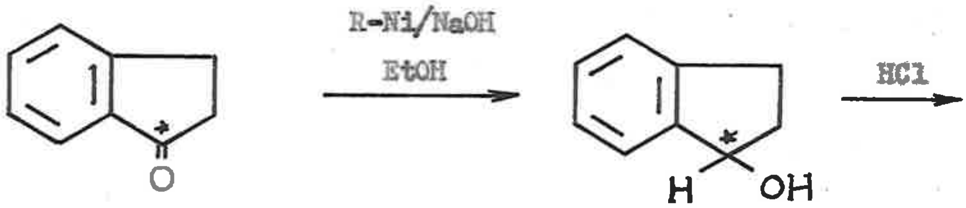
6.2 RESULTS

$[3-^{14}C]$Indene was conveniently prepared in satisfactory yield by the following route.

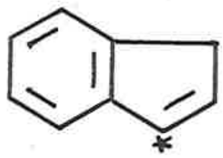
The Grignard reagent of β-phenylethylbromide (LLXIX) was treated with radioactive carbon dioxide under usual vacuum line technique to give [carboxy-^{14}C]hydrocinnamic acid (LLXX). Subsequent treatment of this acid (LLXX) with thionyl chloride followed by anhydrous aluminium chloride in carbon disulphide
cyclodehydrohalogenation
medium brought about cyclodehydrogenation, and yielded

[carbonyl-^{14}C]indanone (LLXXI). This was hydrogenated under atmospheric pressure with Raney nickel in aqueous alcoholic sodium hydroxide to give [1-^{14}C]indanol (LLXXII). Dehydration of (LLXXII) in boiling hydrochloric acid gave the required [3-^{14}C]indene (LLXXIII).

(LLXIX) (LLXX)



(LLXXI) (LLXXII)



(LLXXIII)

This radioactive indene was appropriately diluted with pure inactive indene. The infrared spectrum of this mixture was identical with that of pure unlabelled indene. No impurities could be detected by gas-liquid chromatography.

The diluted active indene was then pyrolysed under conditions similar to those previously used[80] except that the pyrolysis tube was not packed with porcelain chips. An empty tube was used to avoid the blocking of the tube (with carbon and chrysene) obtained under packed-tube conditions. Under these empty-tube conditions some indene survived the pyrolysis; the major product was chrysene, and only a few other compounds could be isolated for radiochemical analysis.

The results are summarised in Table 13, which lists the compounds (isolated from the tar), degradation products of chrysene, and their radiochemical values. The activities were calculated as relative molar activities, which are linearly proportional to the number of labelled carbon atoms per molecule.

6.3 DISCUSSION

Using the calculated bond orders[169] for indene it is possible to obtain approximate bond dissociation energies for the carbon-carbon bonds, and hence to predict which bonds are most likely to rupture at high temperature to yield radicals. In a previous paper[80] it was suggested that the carbon-carbon double bond in the five membered ring has a bond dissociation energy of 138 K cal./mole, and the carbon-carbon single bond, linking this conjugated double bond to the benzene ring, has a bond dissociation energy of 108 K cal./mole.

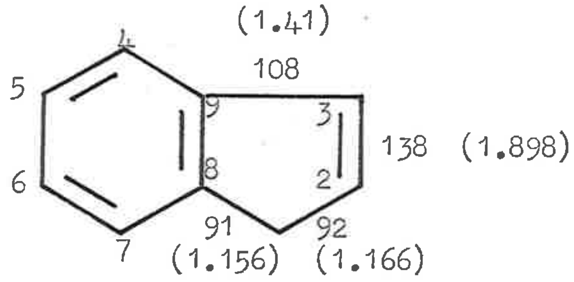
TABLE 13

CONSTITUENTS OF THE TAR OBTAINED BY

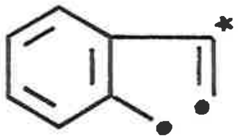
THE PYROLYSIS OF [3-^{14}C]INDENE

Compound	Degradation Products	Labelled C Atoms
2,3-Benzofluorene		1.92
1,2-Benzofluorene		1.87
1,2-Benzanthracene		1.86
Chrysene		1.86
	Chrysa-1,2-quinone	1.86
	o-(2-Naphthyl)benzoic acid	1.55
	Carbon dioxide (from o-(2-naphthyl)benzoic acid)	0.15
	2-Phenylnaphthalene	1.27
10,11-Benzofluoranthene		1.89
11,12-Benzofluoranthene		1.85

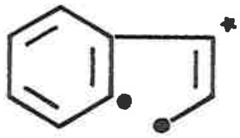
The remaining two carbon-carbon single bonds in the five membered ring (i.e. 1,2- and 1,8-bonds) have a bond dissociation energy of approximately 90 K cal./mole. These two bonds should therefore undergo ready scission at 700° to give three important "primary" radicals.



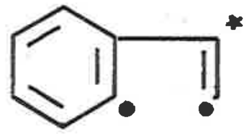
(LLXXIV)



(LLXXV)

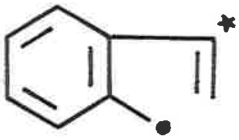


(LLXXVI)

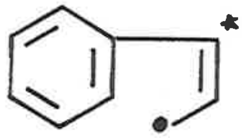


(LLXXVII)

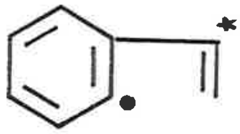
It seems unlikely that these diradicals will be stable for any length of time. It is possible that in the case of (LLXXV), the diradical may react very quickly with hydrogen radicals to give the relatively stable benzyl radical (LLXXVIII). Similarly, in the case of diradicals (LLXXVI) and (LLXXVII), one or other part may undergo a termination reaction with hydrogen radicals to give the more stable mono-radicals (LLXXIX) and (LLXXX).



(LLXXVIII)



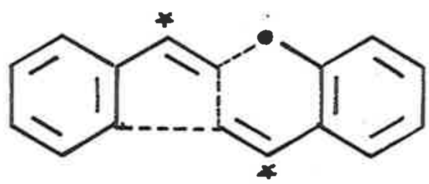
(LLXXIX)



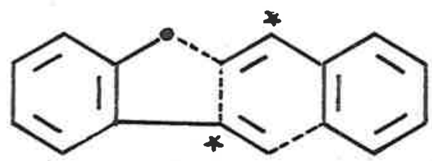
(LLXXX)

As previously postulated[80], the major products of the pyrolysis can be explained by suitable reactions involving these "primary radicals", and the radiochemical analyses provide data for the examination of this hypothesis.

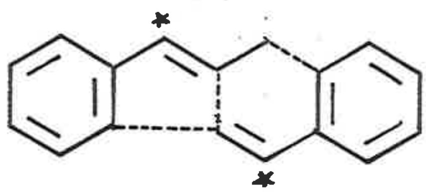
The union of a radical of type (LLXXVIII) or (LLXXIX) with one of type (LLXXX), for example, would be expected to yield 2,3-benzofluorene (LLXXXIa-e) having two labelled carbon atoms. Similarly, a radical of type (LLXXVIII) or (LLXXIX) could combine with one of type (LLXXX) in a different fashion to yield 1,2-benzofluorene (LLXXXIIa-g) with two labelled carbon atoms.



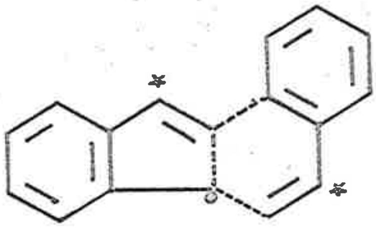
(LLXXXIa)



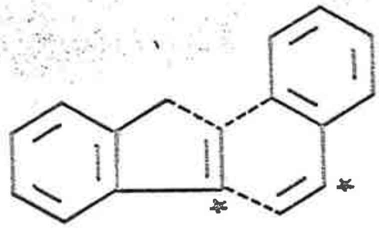
(LLXXXIb)



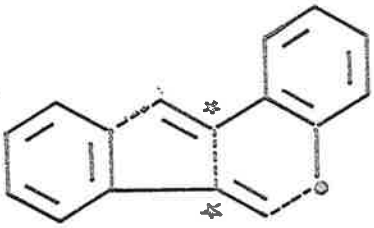
(LLXXXIc)



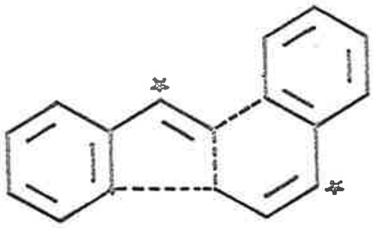
(LLXXXIIa)



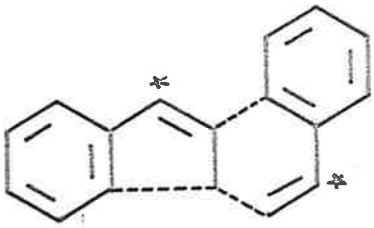
(LLXXXIIb)



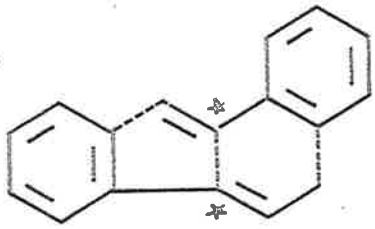
(LLXXXIIc)



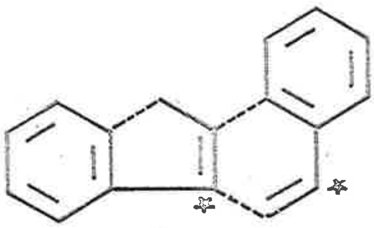
(LLXXXIId)



(LLXXXIIe)



(LLXXXIIf)



(LLXXXIIg)

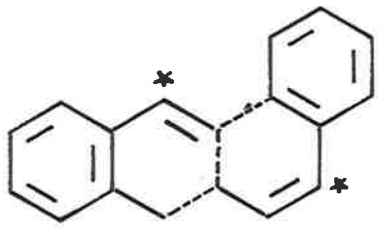
Of these (LLXXXIa), (LLXXXIb), (LLXXXIIa) and (LLXXXIIc) involve the most reactive benzyl radical-double bond attack. The others either do not involve benzyl-type radicals or double bonds or both, and hence would not be expected to play as important a part in the formation of these compounds.

Experimentally 2,3-benzofluorene and 1,2-benzofluorene were found to have 1.92 and 1.87 labelled carbon atoms. It may be pointed out that the thermal rearrangement of $[3-^{14}C]$indene to $[1-^{14}C]$indene will undoubtedly occur during the pyrolysis via the intermediate allylic radical leading to some activity appearing in the 1-position. Consequently, radicals of type (LLXXX) should have an activity less than 1.0 labelled atoms, and mechanisms involving these radicals probably account for the significant deviations from 2.0 labelled atoms in the compounds isolated.

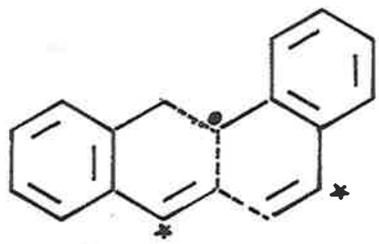
Similarly, 1,2-benzanthracene activity of 1.86 labelled carbon atoms, virtually twice that of the starting indene, supports the idea that 1,2-benzanthracene arises following the "dimerisation" by suitable "primary" radicals, as illustrated by (LLXXXIIIa-c). (LLXXXIIIb) involves the most reactive benzyl radical-double bond attack.

Formation from C_6-C_4 and C_6-C_2 (LLXXX) units may account for the activity being significantly less than that corresponding to two labelled atoms. Such mechanisms are known to be of importance in other pyrolyses in this series.

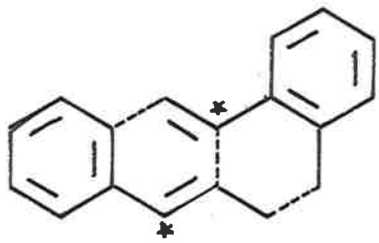
Chrysene formed following the pyrolysis of ethylbenzene[73a],



(LLXXXIIIa)



(LLXXXIIIb)

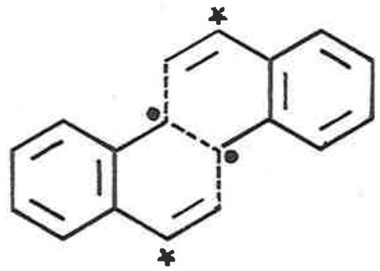


(LLXXXIIIc)

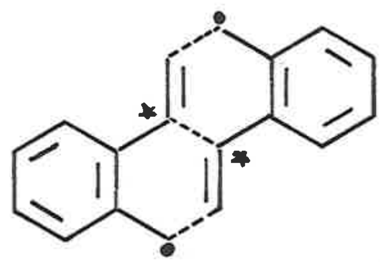
styrene[91], butylbenzene[73a] and tetralin[92] seems to be formed predominantly by combination of a C_6-C_4 unit (such as naphthalene) with a C_6-C_2 unit (such as styrene). Mechanisms involving the "dimerisation" of these two units cannot be of great importance in the present pyrolysis since styrene was only a minor constituent of the pyrolysate[80]. In the pyrolysis of indene[80], however, chrysene was formed in very high yield, and there is little doubt that it is formed by "dimerisation" of the primary radicals mentioned above.

The "dimerisation" of two radicals of type (LLXXVIII) (as in (LLXXXIVa-b) or of type (LLXXIX) (as in (LLXXXIVc-d) would give chrysene having two labelled atoms. Of these (LLXXXIVa) and

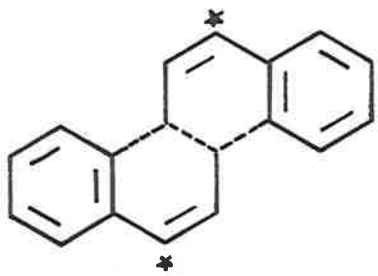
(LLXXXIVb) involve the most reactive benzyl radical-double bond attack.



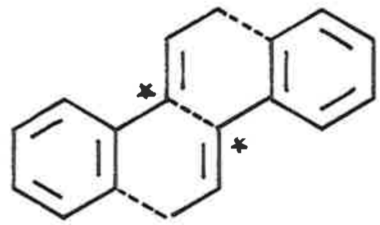
(LLXXXIVa)



(LLXXXIVb)

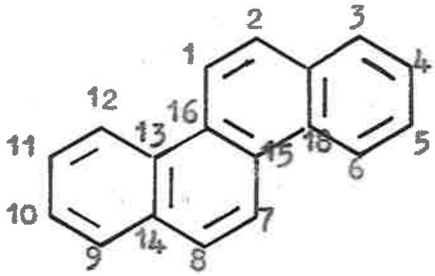


(LLXXXIVc)



(LLXXXIVd)

The chrysene actually isolated showed activity corresponding to 1.86 labelled carbon atoms; and the chrysa-1,2-quinone (LLXVI) obtained by sodium dichromate oxidation had almost similar activity. This was degraded to o-(2-naphthyl)benzoic acid (LLXVII; found 1.55 labelled atoms), which on decarboxylation, gave 2-phenylnaphthalene (LLXVIII; found 1.27 labelled atoms) and carbon dioxide (0.15 labelled atoms).



(LLXXXV)

From these results it seems that some activity resides at the 1- and 7-positions as well as in the 2- and 8-positions, and that activity (presumably) resides at the 15- and 16-positions. The activity at the 2-, 8-, 15- and 16-positions (LLXXXV) is explained by participation of the mechanisms illustrated by (LLXXXIVa-b).

Activity at the 1- and 7-positions cannot be explained in this way; but chrysene with labelled carbon atoms in these positions would be formed by the union of a C_6-C_4 unit (such as naphthalene) and a C_6-C_2 unit (such as styrene). Formation in this way may also account for the activity of the chrysene isolated being significantly less than that corresponding to two labelled atoms. Similar mechanisms of formation are known to be of major importance in other pyrolysis in this series[122,123,167].

Naphthalene is known to be formed in this pyrolysis[80], but it was not isolated in the present experiment. However, the presence of 10,11- and 11,12-benzofluoranthene in the tar shows that naphthalene was formed; as previously shown[83] these hydrocarbons must have formed from two naphthalene units.

CHAPTER 7

THE PYROLYSIS OF n-[α-^{14}C]PROPYLBENZENE

7.1 INTRODUCTION

As a part of a comprehensive scheme to determine the mode of formation of polycyclic aromatic hydrocarbons in tars, many different organic compounds have been pyrolysed and reasonable mechanisms for the formation of the various polycyclic aromatic hydrocarbons have been suggested. Some theoretically possible mechanisms have been excluded as major routes to some compounds by consideration of the relative yields; but in other cases two or more mechanisms have seemed equally probable. In the pyrolysis of alkylbenzenes, namely, toluene[73a], ethylbenzene[73a], propylbenzene[73a], and butylbenzene[73a], it has been suggested that all these hydrocarbons undergo C-C or C-H bond fission to give various "primary" radicals, which then undergo secondary reactions, and the yields of higher polycyclic hydrocarbons varied with the nature of the aliphatic side chain. More recently pyrolysis of ^{14}C labelled hydrocarbons has proved of value in investigating similar mechanisms in the pyrolysis of [1-^{14}C]toluene[119], [1-^{14}C]ethylbenzene[167], [1-^{14}C]tetralin[122], [δ-^{14}C]butylbenzene[123], [1-^{14}C]naphthalene[83], [-^{14}C]styrene, and [3-^{14}C]indene, and as a further contribution to these studies n-[α-^{14}C]propylbenzene has now been synthesised and pyrolysed at 700°.

7.2 RESULTS

The required *n*-[α-^{14}C]propylbenzene (LLXXXVII) was conveniently prepared in satisfactory yield (69%) by the Friedel-Crafts reaction of benzene and [1-^{14}C]sodium propionate, followed by Clemmensen's reduction of the resulting [*carbonyl*-^{14}C]propiophenone (LLXXXVI, 77.9%).

$$C_6H_6 + CH_3CH_2[^{14}C]OONa \xrightarrow{AlCl_3} C_6H_5\overset{*}{C}OCH_2CH_3$$

(LLXXXVI)

$$\xrightarrow{Zn/HCl} C_6H_5\overset{*}{C}H_2CH_2CH_3$$

(LLXXXVII)

The *n*-[α-^{14}C]propylbenzene thus obtained was appropriately diluted with ordinary purified propylbenzene. The infrared spectrum and refractive index of this mixture were identical with that of pure *n*-propylbenzene. A sample examined by gas-liquid chromatography showed no impurity.

Radioassay of the *n*-[α-^{14}C]propylbenzene was made in the same way as previously described, using Van Slyke-Folch oxidation reagent to produce carbon dioxide which was precipitated as barium carbonate and counted. Two determinations of radioactivity of *n*-[α-^{14}C]propylbenzene gave values of relative molar activity, 8.27×10^{-2} and 7.98×10^{-2}, or an average of 8.12×10^{-2}.

In order to demonstrate that none of the ^{14}C was in the other positions of the side chain and six-membered ring of the synthetic product, a small sample of n-[α-^{14}C]propylbenzene was oxidised to benzoic acid and then decarboxylated. This benzoic acid (relative molar activity, 8.34 x 10^{-2}) and carbon dioxide (relative molar activity, 8.24 x 10^{-2}) had almost the same activity as n-[α-^{14}C]propylbenzene; the label is thereby shown to be exclusively in the α-position. The resulting benzene was oxidised to carbon dioxide by the Van Slyke-Folch oxidation method; this CO_2 had no activity, hence the six carbons of the ring had no activity.

The n-[α-^{14}C]propylbenzene was then pyrolysed at 700° under conditions similar to those used for the inactive compound[73a], and the resulting tar separated into its constituents by different techniques for radiochemical assay. Nine compounds were isolated from the tar in sufficient quantity and purity for radiochemical analysis. Some of these have been degraded to determine the distribution of the activity. The activities were calculated as previously described[160]. The results are summarised in Table 14, which lists the number of labelled carbon atoms found for all the compounds isolated and some degradation products. Other compounds known to be formed in this pyrolysis[73a] could not be isolated in sufficient amount or in suitable purity for radiochemical analysis.

7.3 DISCUSSION

The initial decomposition of aromatic compounds containing an

TABLE 14

CONSTITUENTS OF TAR OBTAINED BY PYROLYSIS OF

n-[α-^{14}C]PROPYLBENZENE

Compound	Degradation Products	Labelled Carbon Atoms
Benzene		0.0486
Toluene		0.722
	Benzoic acid	0.732
	Carbon dioxide	0.67
	Benzene	0.041
Ethylbenzene		0.76
Styrene		0.89
	Benzoic acid	0.547
	Carbon dioxide	0.512
	Benzene	0.012
Indene		1.01
Naphthalene		1.73
Phenanthrene		0.90
	2,2'-Biphenic acid	0.88
	Biphenyl	0.052
	Carbon dioxide	0.82
2,3-Benzofluorene		2.22
Chrysene		2.30
	Chrysa-1,2-quinone	2.30

(contd.)

TABLE 14, contd.

Compound	Degradation Products	Labelled Carbon Atoms
	o-(2-Naphthyl)benzoic acid	1.60
	Carbon dioxide	0.31
	2-Phenylnaphthalene	1.244

alkyl side chain is believed to proceed by a C-C scission rather than C-H scission, with the exception of toluene. In propylbenzene the energy required to break the C-C bond is approximately 60-80 K cal./mole, whereas the C-H bond energy is 90-100 K cal./mole and the initial decomposition of propylbenzene at higher temperature would therefore be expected to occur predominately by fission of a side chain C-C bond to give the following "primary" radicals (equations (33a-c)). The fission could occur in more than one place to give rise to other radicals, but scission according to equation (33c) is considered to be less important.

$$Ph\overset{*}{C}H_2CH_2CH_3 \longrightarrow Ph\cdot + \cdot\overset{*}{C}H_2CH_2CH_3 \qquad \ldots\ldots(33a)$$

$$\longrightarrow Ph\overset{*}{C}H_2\cdot + \cdot CH_2CH_3 \qquad \ldots\ldots(33b)$$

$$\longrightarrow Ph\overset{*}{C}H_2CH_2\cdot + \cdot CH_3 \qquad \ldots\ldots(33c)$$

Similarly, the abstraction of a hydrogen atom (particularly from the α-carbon atom of propylbenzene) by any radical, and the

~~and the~~ decomposition products of the resulting propylbenzene radical (secondary radical) are also important.

$$Ph\overset{*}{C}H_2CH_2CH_3 + R\cdot \longrightarrow Ph\overset{*}{\underset{\cdot}{C}}HCH_2CH_3 + RH \qquad \ldots\ldots(34a)$$

$$Ph\overset{*}{\underset{\cdot}{C}}HCH_2CH_3 \longrightarrow Ph\overset{*}{C}H = CHCH_3 + H \qquad \ldots\ldots(34b)$$

$$\longrightarrow Ph\overset{*}{C}H = CH_2 + CH_3 \qquad \ldots\ldots(34c)$$

It has been suggested that the saturated $\alpha\beta$-bond in propylbenzene is ruptured preferentially to give a benzyl radical and a two-carbon fragment (equation (33b)) i.e. ethyl radical. However, the direct formation of a phenyl radical and a propyl radical (equation(33a)) 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 rupture according to equation (33a). This suggestion was based on Szwarc's work, and on the experimental observation that the pyrolysis of ethylbenzene[73a] and butylbenzene[73a] gave benzene in greater yield than toluene, while the pyrolysis of propylbenzene[73a] gave a greater yield of toluene than benzene. Similarly, the yield of bibenzyl from propylbenzene was greater than that ~~of~~ from either ethylbenzene or butylbenzene, while the yield of biphenyl from ethyl and butylbenzene was greater than that from propylbenzene. It seems clear, therefore, that Ph· , $Ph\overset{*}{C}H_2\cdot$, $\cdot CH_2CH_3$, and $\cdot\overset{*}{C}H_2CH_2CH_3$ are the important "primary" radicals in the pyrolysis of propylbenzene.

$$PhC^{*}H_2CH_2CH_3 \longrightarrow PhC^{*}H_2\cdot + \cdot CH_2CH_3 \quad \text{major}$$

$$\longrightarrow Ph\cdot + \cdot C^{*}H_2CH_2CH_3 \quad \text{minor}$$

Benzene is one of the major products of the pyrolysis of n-propylbenzene and could be formed by scission of the $C_6H_5-C^{*}H_2CH_2CH_3$ bond, according to equation (33a), followed by hydrogen abstraction. Benzene formed in this way should be devoid of radioactivity. The rupture of the $C_6H_5C^{*}H_2-CH_2CH_3$ bond, according to equation (33b), followed by a loss of a hydrogen atom would also give an unlabelled ethylene and hence an unlabelled benzene. Experimentally, the benzene isolated following the pyrolysis of n-[α-^{14}C]propylbenzene was found to have 0.048 labelled carbon atoms. This small amount of labelled benzene could be formed in several ways. For example, the labelled methyl radicals produced by the fission of the $C_6H_5-C^{*}H_3$ bond could interact to give ethylene and hence benzene.

Toluene is also a major constituent of the pyrolysate. It has been suggested in earlier papers in this series that benzyl radicals, $C_6H_5CH_2\cdot$, serve as the precursors of toluene found in the tar. However, the direct reaction between a methyl radical and a phenyl radical (or benzene) and hence toluene may well compete with the formation of toluene from benzyl radicals since the ethyl radicals arising according to the equation (33b) may either react as such or lose a hydrogen atom to form ethylene, or abstract a hydrogen atom to form ethane, and the latter would be expected to undergo ready scission to give an unlabelled methyl radicals (35a-c).

$$Ph\overset{*}{C}H_2CH_2CH_3 \longrightarrow Ph\overset{*}{C}H_2\cdot + \cdot CH_2CH_3 \qquad ......(33b)$$

$$Ph\overset{*}{C}H_2\cdot \longrightarrow Ph\overset{*}{C}H_3$$

$$\cdot CH_2CH_3 \longrightarrow CH_2 = CH_2 + H\cdot \qquad ......(35a)$$

$$\longrightarrow CH_3 - CH_3 \qquad ......(35b)$$

$$\longrightarrow CH_3\cdot + CH_3\cdot \qquad ......(35c)$$

Some labelled methyl radicals may also be produced by random scission of the propyl radical according to equation (36a-c).

$$\cdot\overset{*}{C}H_2CH_2CH_3 \longrightarrow \overset{*}{C}H_2 = CH_2 + CH_3 \qquad ......(36a)$$

$$\longrightarrow \overset{*}{C}H_3 - CH_3 \qquad ......(36b)$$

$$\longrightarrow \overset{*}{C}H_3\cdot + CH_3\cdot \qquad ......(36c)$$

However, the low proportion of ethylbenzene in the pyrolysis of n-propylbenzene suggests that the ethyl radicals undergo further scission to methyl radicals according to equation (35c) (or ethylene according to equation (35b)) and finally either form a stable compound methane or react with a phenyl radical (or benzene) to form toluene.

As the phenyl radicals are unlabelled, any toluene formed in this pyrolysis would be expected to be unlabelled, or partially labelled, depending on the activity of the methyl radicals (or methane). On the other hand, if the toluene were formed from benzyl radicals, then it should have one labelled carbon atom.

As the toluene found was 72% (0.72 labelled carbon atoms) as active as n-[α-^{14}C]propylbenzene, it follows that approximately 70% of it was formed according to equation (33b) and about 30% by the methylation process. Similar results have also been obtained in the pyrolysis of [δ-^{14}C]butylbenzene. Oxidation of toluene gave benzoic acid (0.73 labelled atoms), which was decarboxylated to benzene (0.04 labelled atoms) and carbon dioxide (0.67 labelled atoms). The distribution is quite similar to that expected from the latter route involving benzyl radicals and it may be concluded, therefore, this process is an important one in the formation of toluene.

Ethylbenzene could be isolated from the tar in sufficient quantity for radiochemical analysis. Three reasonable mechanisms can be postulated for the formation of this compound from n-propylbenzene. The first would involve the direct interaction of an unlabelled phenyl radical with an unlabelled ethyl radical (primary decomposition products) and hence give unlabelled ethylbenzene (equation (37)). The second possible mechanism would involve the interaction of a benzyl radical (or toluene) with a methyl radical (equation (38)). The activity of toluene is known (see above), so any ethylbenzene formed in this way would be expected to have 0.72 labelled atoms, or more depending on the activity of methyl radicals (or methane). The third mechanism would involve the abstraction of a hydrogen atom by a phenethyl radical (equation (39)) or styryl radical (equation (40)) to give ethylbenzene having one labelled carbon atom, or 0.89 labelled atoms (*i.e.* the activity of styrene).

$$C_6H_5\cdot + \cdot CH_2CH_3 \longrightarrow C_6H_5CH_2CH_3 \qquad \ldots\ldots(37)$$

$$C_6H_5\overset{*}{C}H_2\cdot + \cdot CH_3 \longrightarrow C_6H_5\overset{*}{C}H_2CH_3 \qquad \ldots\ldots(38)$$

$$C_6H_5\overset{*}{C}H_2CH_2\cdot + \cdot H \longrightarrow C_6H_5\overset{*}{C}H_2CH_3 \qquad \ldots\ldots(39)$$

$$C_6H_5\overset{*}{C}H = CH_2 + 2H \longrightarrow C_6H_5\overset{*}{C}H_2CH_3 \qquad \ldots\ldots(40)$$

The ethylbenzene isolated showed activity corresponding to 0.76 labelled atoms, providing strong evidence that formation according to equation (38) is a major route in this pyrolysis with formation according to equation (40) providing significant alternative pathway.

The pyrolysis of alkylbenzenes has been shown to yield styrene in good yield and it is significant that among these hydrocarbons and other simpler aromatic hydrocarbons studied so far the highest yield of styrene was obtained from *n*-propylbenzene. One could assume, therefore, that styrene must have been formed mainly by reactions involving the primary decomposition products.

It has been shown in earlier papers from these laboratories that the successive loss of hydrogen from ethylbenzene would give styrene (equation (41)). Thus, the formation of styrene depends on ethylbenzene and *vice versa*. Any styrene formed in this way would be expected to have an activity corresponding to the activity of ethylbenzene.

$$C_6H_5CH_2CH_3 \longrightarrow C_6H_5\dot{C}HCH_3$$
$$\longrightarrow C_6H_5CH = CH_2 \qquad \ldots\ldots(41)$$

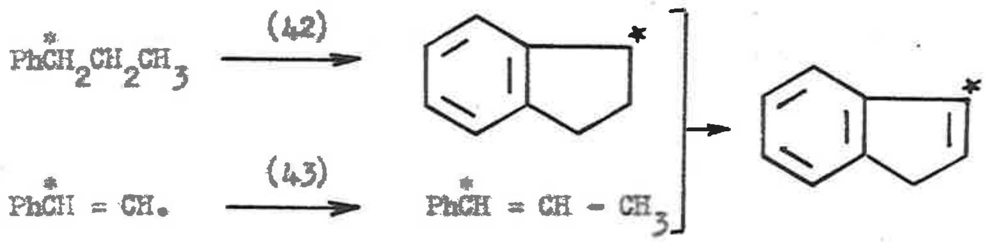
Formation according to equation (34a-c) would also yield styrene with 1.0 labelled atom.

The isolated styrene was found to have activity corresponding to 0.89 labelled atoms. Chromic acid oxidation gave benzoic acid (0.53 labelled atoms) which was decarboxylated to carbon dioxide (0.51 labelled atoms) and benzene (0.012 labelled atoms). Thus, about one third the activity of the styrene was located in the β-carbon atom and the rest in the α-carbon atom of the side chain. It is clear, therefore, that styrene must have formed predominately by a mechanism involving benzyl radicals (or toluene), and methyl radicals, followed by dehydrogenation.

The activity of toluene is known and if all the side chain carbon atoms in propylbenzene are equally available for the methylating process, they have an average of 0.33 labelled atoms; so any styrene formed in this way would be expected to have 1.0 labelled atoms. It is therefore concluded that this route must be an important one in the formation of styrene from n-propylbenzene.

Indene obtained in this pyrolysis seems to be formed by a cyclodehydrogenation process (equation (42)) with 1.0 labelled atom.

Another likely route to this compound (as mentioned in the pyrolysis of [1-^{14}C]styrene) would appear to be from a styryl radical (or styrene) and a methyl radical followed by cyclodehydrogenation (equation (43)). The expected activity of the product according to this pathway should be 1.22 labelled atoms (assuming 0.33 labelled atoms is the average activity of the methyl radicals).

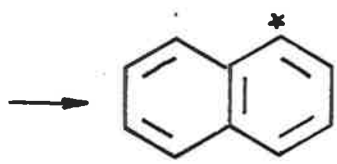


The observed figure of 1.01 labelled atoms for the indene isolated from this pyrolysis suggests that the former route operates predominately.

Naphthalene is a very common product of the pyrolysis of hydrocarbons, and a chain resynthesis mechanism has been suggested to account for the formation of this compound.

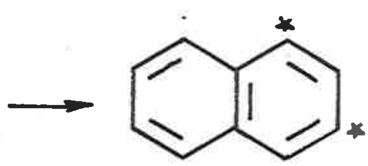
Several possible mechanisms can be postulated for the formation of naphthalene. Reaction of a labelled phenethyl radical with an ethylene molecule would be expected to give a phenbutyl radical and hence a labelled naphthalene (equation (44)). The activity of ethylbenzene is known; so any naphthalene formed in this way would be expected to have 0.76 labelled atoms plus the activity of the ethylene. Similarly, reaction of a labelled styrene molecule with a labelled ethyl radical (derived from ethylbenzene) would give a phenbutyl radical and hence naphthalene (equation (45)). The activity of styrene and ethylbenzene is known; so any naphthalene formed in this way would be expected to have 1.65 labelled atoms. An alternate route to naphthalene involving a labelled benzyl radical and a labelled propyl radical to give a doubly-labelled phenbutyl radical and hence doubly-labelled naphthalene (equation(46)). Another possible mechanism for the formation of naphthalene would involve the reaction of a labelled phenpropyl radical with a methyl radical followed by cyclodehydrogenation (equation (47)). Any naphthalene formed in this way would be expected to have 1.33 labelled atoms (assuming 0.33 labelled atoms is the average activity of the methyl radicals.

$$C_6H_5\overset{*}{C}H_2CH_2\cdot + CH_2 = CH_2 \longrightarrow C_6H_5\overset{*}{C}H_2CH_2CH_2CH_2$$



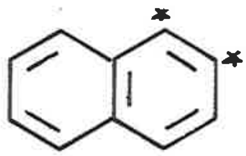
......(44)

$$C_6H_5\overset{*}{C}H = CH_2 + \cdot\overset{*}{C}H_2CH_3 \longrightarrow C_6H_5\overset{*}{C}HCH_2\overset{*}{C}H_2CH_3$$

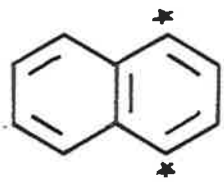


......(45)

$$C_6H_5\overset{*}{C}H_2\cdot + \cdot\overset{*}{C}H_2CH_2CH_3 \longrightarrow C_6H_5\overset{*}{C}H_2\overset{*}{C}H_2CH_2CH_3$$

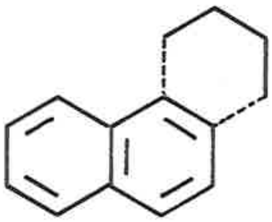
$\longrightarrow$  ......(46)

$$C_6H_5\overset{*}{C}H_2CH_2CH_2\cdot + \overset{*}{C}H_3\cdot \longrightarrow C_6H_5\overset{*}{C}H_2CH_2CH_2\overset{*}{C}H_3$$

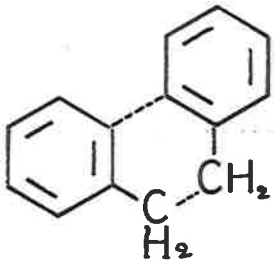
$\longrightarrow$  ......(47)

As the isolated naphthalene was found to have 1.73 labelled atoms, it is possible that all these mechanisms may play a part, with predominance according to the equation (45).

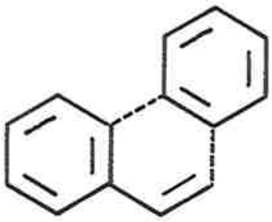
Phenanthrene is the major constituent of the pyrolysate[73a] and this may be formed (i) from a C_6-C_4 and a C_4 unit (as in LLXXXVIII), (ii) from two benzyl radicals (as in LLXXXIX), or (iii) by the union of a phenyl radical and a styryl radical (or styrene) (as in LLLX). However, mechanisms according to (LLXXXIX) and (LLLX) are highly probable in view of the presence of large proportion of benzyl radicals and the high yield of styrene.



(LLXXXVIII)



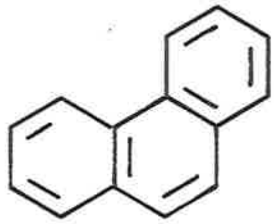
(LLXXXIX)



(LLLX)

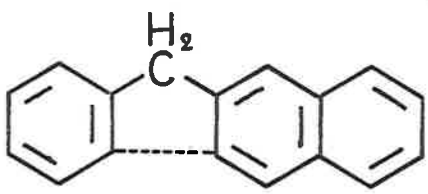
Formation according to (LLXXXIX) would lead to phenanthrene with 1.44 labelled atoms or twice the activity of toluene, and according to (LLLX) with 0.94 labelled atoms (benzene, 0.048, styrene, 0.89).

The phenanthrene activity of 0.90 labelled atoms supports the idea that phenanthrene arises following attack of a styryl radical on benzene (as in LLLX). Oxidative degradation of the phenanthrene isolated, followed by decarboxylation of the resulting biphenic acid (0.88 labelled atoms) and carbon dioxide having 0.82 labelled atoms. The distribution is in good agreement with the expected values.



(LLLXI)

2,3-Benzofluorene is formed in significant yield on pyrolysis of propylbenzene and two most likely routes may be suggested to explain its activity. The combination of a C_6-C_3 unit (such as indene) with a C_6-C_2 unit (such as styrene) (as in LLXXXIa-c) would give 2,3-benzofluorene having 1.90 labelled atoms (styrene, 0.89, indene, 1.01). Similarly, the formation of 2,3-benzofluorene from benzyl radical (or toluene) and naphthalene followed by cyclodehydrogenation (as in LLLXII), would give a product having 2.45 labelled atoms.



(LLLXII)

The 2,3-benzofluorene isolated showed activity corresponding to 2.22 labelled atoms, in agreement with the ~~later~~ latter route. It seems likely, however, that the former route may also operate to a small extent, thereby decreasing the activity of the 2,3-benzofluorene isolated.

Chrysene is a common product of the pyrolysis of many hydrocarbons and three possible routes are suggested to explain the mechanisms of formation of this compound in other pyrolyses in this series[122,123,167].

Mechanisms involving dimerisation of two C_6-C_3 units (LLXXXIVc-d) or two C_1-C_6-C_2 units (LLXXXIVa-b) (derived from indene or its precursors), would yield chrysene with two labelled atoms (or twice the activity of indene), whereas mechanisms involving a C_6-C_4 unit (such as naphthalene) and C_6-C_2 unit (such as styrene) (LLXIII) would yield chrysene with 2.62 labelled atoms.

The isolated chrysene had an activity corresponding to 2.30 labelled atoms. Oxidation of this chrysene gave chrysa-1,2-quinone (2.30 labelled atoms) which was fused with alkali to give o-(2-naphthyl)benzoic acid (LLXVII; 1.60 labelled atoms). Decarboxylation of (LLXVII) gave 2-phenylnaphthalene (LLXVIII; 1.24 labelled atoms) and carbon dioxide (0.31 labelled atoms).

It seems therefore that some activity resides at the 1- and 7-positions as well as 2- and 8-positions (LLXXXV). The activity expected in the 2-phenylnaphthalene derived from (LLXIII) is uncertain as the distribution of activity in naphthalene isolated in the present pyrolysis is uncertain. However, the general features of the distribution of activity in chrysene suggests that it must have formed according to (LLXIII).

CHAPTER 8

THE PYROLYSIS OF β-[α-^{14}C]METHYLSTYRENE

8.1 INTRODUCTION

An analysis of the tars obtained following the pyrolysis of indene[80] and propylbenzene[73a] has previously been reported, and possible mechanisms by which some of the compounds could be formed have been discussed. The probable role of C_6-C_3, C_1-C_6-C_2, and C_6-C_2 fragments in giving rise to chrysene, 1,2-benzanthracene and benzofluorenes from indene has been explained. Similarly, it has been pointed out that the saturated αβ-bond in propylbenzene is preferentially ruptured to give a benzyl radical and a two-carbon fragment. It has also been suggested that the direct formation of a phenyl radical and a propyl radical may compete with the formation of a benzyl radical. Experiments on which these conclusions are based have been discussed in Chapters 6 and 7. To confirm these findings a possible intermediate compound, namely, β-methylstyrene, labelled with ^{14}C in the α-position, has now been synthesised, and pyrolysed at 700°.

8.2 RESULTS

β-[α-^{14}C]Methylstyrene was synthesized essentially as described for the synthesis of [1-^{14}C]styrene. The starting material [carbonyl-^{14}C] propiophenone (LLXXXVI) was converted in a series of reactions to the corresponding alcohol (LLLXIII, 87.6%) and chloride (LLLXIV, 92.17%). Final dehydrohalogenation in boiling quinoline gave the desired β-[α-^{14}C]methylstyrene (LLLXV) in excellent yield (88.9%).

$$CH_3CH_2\overset{*}{C}OONa + Bz \xrightarrow{AlCl_3} Ph\overset{*}{C}OCH_2CH_3$$

(LLXXXVI)

$$\xrightarrow[87.6\%]{R\text{-}Ni/NaOH} Ph\overset{*}{C}HOHCH_2CH_3 \xrightarrow[92.17\%]{conc.\ HCl} Ph\overset{*}{C}HClCH_2CH_3$$

(LLLXIV)

$$\xrightarrow[88.9\%]{Quinoline} Ph\overset{*}{C}H{=}CHCH_3$$

(LLLXV)

The β-[α-^{14}C]methylstyrene thus obtained was diluted with 120 ml. of ordinary purified β-methylstyrene. The infrared spectrum and refractive index of this mixture was identical with that of pure β-methylstyrene. No impurities were detected by gas-liquid chromatography.

The radioactivity of this hydrocarbon was determined on a sample by converting it to a solid dibromide before counting. The β-[α-^{14}C]methylstyrene was found to have relative molar activity of 8.94×10^{-2}.

In order to locate the position of the carbon atom, a small sample of the β-[α-^{14}C]methylstyrene was oxidised to benzoic acid which was then decarboxylated. The relative molar activities of the benzoic acid (8.01×10^{-2}) and carbon dioxide (7.92×10^{-2}) confirmed that activity was confined to the α-position of the side chain.

A sample of unlabelled β-methylstyrene was first pyrolysed (making use of previously described procedures) to establish the conditions for pyrolysis, the nature of the products, and to determine their percentage in the tar.

A summary of the analytical results is given in Table 15.

The pyrolysis was then repeated using labelled β-methylstyrene. Most of the compounds were isolated in sufficient quantity and purity and submitted to radiochemical assay, the activities being expressed as relative molar activities[160] (which are linearly proportional to the number of labelled carbon atoms per molecule). Some of these compounds were then degraded to determine the distribution of activity. The results are summarised in Table 16 which gives the number of labelled carbon atoms for each compound, and for some of the degradation products.

8.3 DISCUSSION

The formation of the major products following the pyrolysis of [3-^{14}C]indene at 700° has been explained by mechanisms involving "dimerisation" of the primary radicals expected following the scission of the 1,2- and 1,8- bonds in the indene molecule (Chapter 6). Similarly, a detailed analysis of the tar obtained following the pyrolysis of n-[α-^{14}C]propylbenzene has been discussed in Chapter 7,

TABLE 15

COMPOSITION OF TAR FOLLOWING PYROLYSIS OF β-METHYLSTYRENE AT 700°

Compound	Percentage in Tar	Method of identification
Methane	-	I.R.
Ethylene	-	I.R.
Benzene	9.75	R.T., I.R., U.V., dinitro derivative
Toluene	18.32	R.T., I.R., U.V., dinitro derivative
Ethylbenzene	4.5	R.T., I.R.
Styrene	12.6	R.T., I.R., dibromo derivative
Indene	1.7	R.T., I.R.
Naphthalene	7.98	R.T., U.V., mixed m.p., picrate derivative
Phenanthrene	7.15	U.V., mixed m.p.
Anthracene	0.034	U.V.
2,3-Benzofluorene	3.03	U.V., mixed m.p.
1,2-Benzofluorene	0.084	U.V.
1,2-Benzanthracene	3.51	U.V., mixed m.p.
Chrysene	17.23	U.V., mixed m.p.
10,11-Benzofluoranthene	0.006	U.V.
3,4-Benzopyrene	Trace	U.V.
High b.p. tar	10.56	

R.T. = Retention time ratio; U.V. = Ultraviolet spectroscopy;
I.R. = Infrared spectroscopy

TABLE 16

CONSTITUENTS OF TAR OBTAINED BY PYROLYSIS OF

β-[α-^{14}C]METHYLSTYRENE

Compound	Degradation products	Labelled Carbon Atoms
Benzene		0.001
Toluene		0.613
	Benzoic acid	0.562
	Carbon dioxide	0.554
	Benzene	0.013
Ethylbenzene		0.822
	Benzoic acid	0.458
	Carbon dioxide	0.476
	Benzene	0.01
Styrene		0.973
	Benzoic acid	0.582
	Carbon dioxide	0.570
	Benzene	0.011
Indene		1.01
Naphthalene		1.18
Phenanthrene		0.932
	2,2'-Biphenic acid	0.91
	Carbon dioxide	0.878
	Biphenyl	0.014

(contd.)

TABLE 16 (contd.)

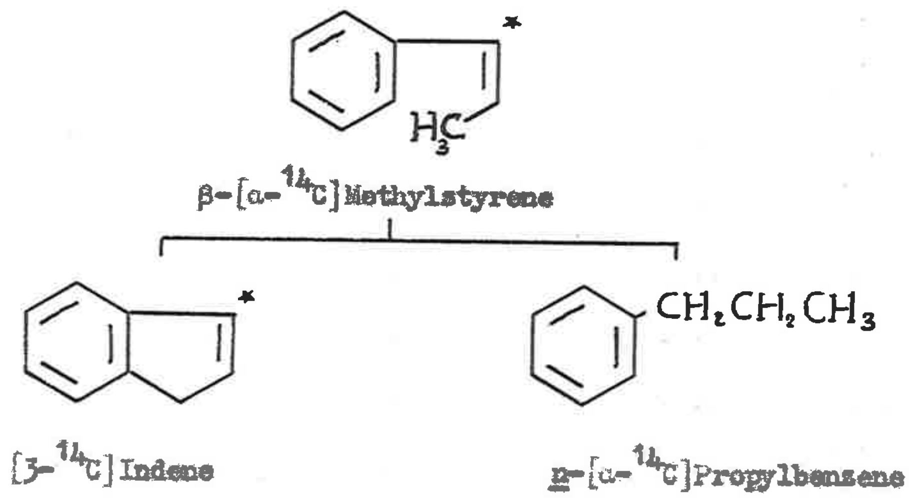
Compound	Degradation products	Labelled Carbon Atoms
2,3-Benzofluorene		1.792
1,2-Benzanthracene		1.875
Chrysene		1.823
	Chrysa-1,2-quinone	1.825
	α-Chrysenic acid	1.422
	Carbon dioxide	0.098
	2-Phenylnaphthalene	1.17

and possible mechanisms for the formation of the various aromatic hydrocarbons have been suggested. These mechanisms were based on the primary radicals expected following (i) the preferential rupture of the saturated cβ-bond (as in equation 33b) and (ii) the direct formation of a phenyl radical and a propyl radical (as in equation 33a).

$$C_6H_5\overset{*}{C}H_2CH_2CH_3 \longrightarrow C_6H_5\overset{*}{C}H_2\cdot + \cdot CH_2CH_3 \qquad ......(33b)$$

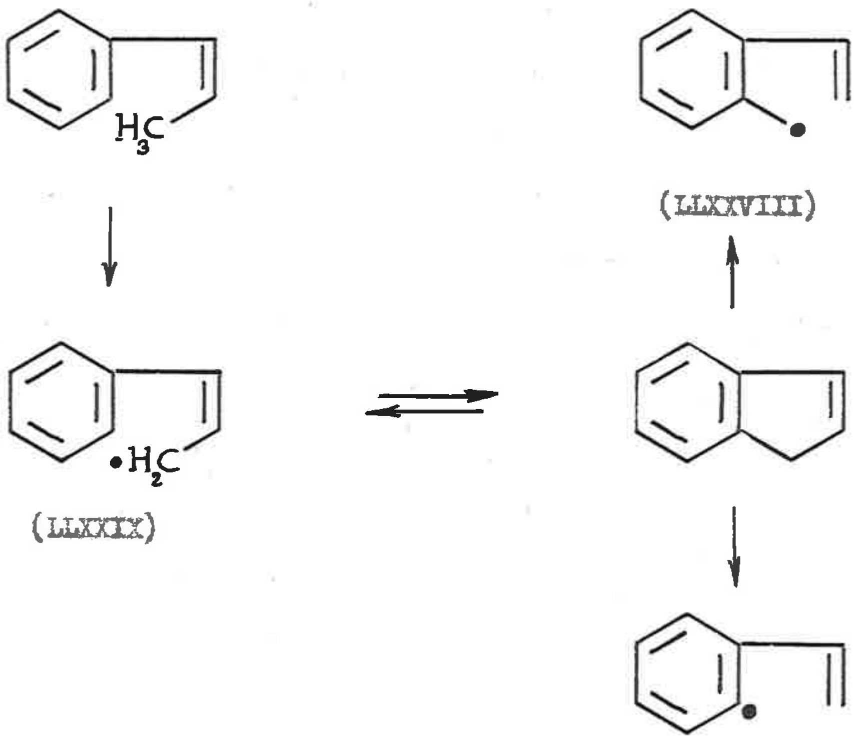
$$\longrightarrow C_6H_5\cdot + \cdot\overset{*}{C}H_2CH_2CH_3 \qquad ......(33a)$$

The β-methylstyrene may be looked upon as a precursor of indene and propylbenzene and the formation of the major products following the pyrolysis of β-[α-^{14}C]methylstyrene can be explained by reasonable reactions of the primary decomposition products derived from indene and propylbenzene.



No prior work has been reported on the pyrolysis of β-methylstyrene, but it should be capable of pyrolytic change into the $C_6H_5CH{=}CHCH_2\cdot$ radical (LLXXIX) if it follows the pattern set by indene. Conceivably, radical (LLXXIX) might dimerise or cyclise to indene from which chrysene, benzanthracene and benzofluorene would be the predicted products. Offsetting this, however, is the fact that chrysene formation was important in the pyrolysis of indene and that only the five-membered ring were cleaved. This tendency for the formation of these products should be even more pronounced with β-methylstyrene in view of the facile rupture of the C-H bond in the allylic position to give (LLXXIX) followed by cyclodehydrogenation to give indene. But the saturated C-C bonds in the five-membered ring in indene would also be expected to undergo ready cleavage (the approximate bond dissociation energies for C-C bonds are shown in diagram (LLXXIV)) to give three important radicals (LLXXIX), (LLXXVIII), and (LLXXX) and dimerisation of any two of these would lead to chrysene, benzanthracene, and benzofluorene. This, indeed, is what was found to occur in the thermal decomposition of β-methylstyrene at 700°. Chrysene, 1,2-benzanthracene, 2,3- and 1,2-benzofluorene were all formed, but were present in smaller quantity than from indene.

The number of labelled carbon atoms in the 2,3-benzofluorene (1.792), 1,2-benzanthracene (1.875) and chrysene (1.823) isolated following the pyrolysis of β-[α-^{14}C]methylstyrene are all consistent with this view.



(LLXXVIII)

(LLXXIX)

(LLXXX)

It may be pointed out that the thermal rearrangement of the allylic radical will undoubtedly occur during pyrolysis, leading to some activity appearing in the 3-position. Consequently, radicals of type (LLXXX) should have an activity less than 1.0, and mechanisms involving these radicals probably account for the significant deviations from 2.0 labelled atoms in the compounds isolated. The pyrolysis of $[3-^{14}C]$indene at 700° has also given similar results.

Chrysene obtained following the pyrolysis of ethylbenzene[73a,167], styrene[91], butylbenzene[73a-b,123], and tetralin[92] seems to be formed predominantly by combination of C_6-C_4 and C_6-C_2 units. Mechanisms involving these units are also equally important in the present pyrolysis in view of the good yield of naphthalene and the presence of styrene or styryl radicals in the reaction zone. In the pyrolysis of β-methylstyrene, however, chrysene is formed in very high yield, and there is little doubt that it is formed by "dimerisation" of the primary radicals mentioned above.

To determine the distribution of activity in chrysene, a small sample was oxidised to chrysaquinone (LLXVI, 1.825 labelled atoms), which was then degraded to o-(2-naphthyl)benzoic acid (LLXVII, 1.422 labelled atoms). This on decarboxylation gave 2-phenylnaphthalene (LLXVIII, 1.17 labelled atoms) and carbon dioxide (0.098 labelled atoms). It is noteworthy that the distribution of activity in chrysene obtained in this pyrolysis is very similar to that obtained in the pyrolysis of [3-^{14}C]indene.

The isolation of chrysene, 1,2-benzanthracene, and benzofluorene as pyrolytic products following the pyrolysis of β-methylstyrene therefore supports the statement made in the Chapter 6 that a significant thermal weakness exists in indene at a 1,2-bond as well as 1,8-bond. It seems established, therefore, that all these products obtained from β-methylstyrene or indene come by way of dimerisation of any two of the radicals mentioned above.

The results of the present investigation have shown that the major process in the thermal decomposition of β-methylstyrene involves the cleavage of C-H bond in the allylic position, and considerable quantities of free hydrogen must therefore be present in the reaction zone. Under these conditions it would be conceivable for the hydrogenation of the double bond in the side chain to occur, and that propylbenzene may be formed during the pyrolysis of β-methylstyrene. The saturated C-C bonds in the side chain of the propylbenzene would also be expected to undergo ready cleavage as shown in equations (33a) and (33b). It is reasonable to assume, therefore, that the benzene, toluene, ethylbenzene, styrene, naphthalene, phenanthrene and anthracene detected in the tar obtained by the pyrolysis of β-methylstyrene are formed by the radicals derived from propylbenzene. It is significant that the pyrolysis of β-methylstyrene gave (i) toluene in greater yield than benzene and (ii) styrene in high yield. Similar results were also obtained following the pyrolysis of propylbenzene[73a].

The benzene obtained following the pyrolysis of β-[α-^{14}C]-methylstyrene was found to be practically inactive. It is concluded, therefore, that the major route to benzene in this pyrolysis is by rupture of the $C_6H_5—\overset{*}{C}H{=}CHCH_3$ bond followed by hydrogen abstraction. The cleavage of the $C_6H_5\overset{*}{C}H_2—CH_2CH_3$ bond followed by a loss of a hydrogen atom would also give an unlabelled ethylene, and hence unlabelled benzene.

The toluene was found to have 0.613 labelled atoms, and oxidation gave benzoic acid (0.562 labelled atoms), which on decarboxylation gave carbon dioxide (0.554 labelled atoms) and benzene (0.013 labelled atoms). These figures suggests that the toluene must be formed by the abstraction of hydrogen by benzyl radicals (derived from propylbenzene) and by the union of methyl radicals (some of which would be labelled and some unlabelled) derived from the alkyl chain and phenyl radicals (or benzene). The methyl radicals formed by chain breakdown would have an average activity of 0.33 labelled atoms, so it seems that a significant proportion (40%) of the toluene must be formed in this way.

Styrene is one of the major constituents of the tar. It was found to have an activity of 0.97 labelled atoms. Chromic acid oxidation gave benzoic acid (0.582 labelled atoms) and this was decarboxylated to carbon dioxide (0.57 labelled atoms) and benzene (0.011 labelled atoms). Thus, about 60% of the activity of the styrene was located in the α-carbon atom, and the remainder in the β-carbon atom of the side chain. It seems that the styrene must be formed by mechanisms involving reaction of a benzyl radical (or toluene) and a methyl radical followed by dehydrogenation. The distribution of labelled atoms in toluene is known (see above), and the activity of methyl radicals must average 0.33 labelled atoms, so any styrene formed in this way would be expected to have 0.94 labelled atoms in good agreement with the experimental value. Some styrene could be formed by the rupture of the $C_6H_5CH{=}CH—CH_3$ bond followed by hydrogenation. Styrene formed in this way would be expected to have 1.0 labelled atom (with no activity in the β-carbon atom).

Similarly, the ethylbenzene had 0.822 labelled atoms, virtually the same that of styrene isolated from the tar, and this provides strong evidence that ethylbenzene is formed by interaction of benzyl and methyl radicals. Oxidation of the ethylbenzene gave benzoic acid which had 0.458 labelled atoms, and decarboxylation gave carbon dioxide (0.476 labelled atoms) and benzene (0.01 labelled atoms). Although this distribution of activity in ethylbenzene is similar to that expected by the above route, it seems likely that other possible mechanisms (for example, interaction of unlabelled phenyl and ethyl radicals derived from propylbenzene) may operate to small extent, thereby decreasing the activity of the ethylbenzene isolated.

Naphthalene was also an important constituent of the tar obtained by the pyrolysis of β-methylstyrene. Four possible mechanisms have been suggested in Chapter 7 to explain the formation of naphthalene from propylbenzene. In this pyrolysis, mechanisms involving (i) phenethyl radical (0.822 labelled atoms) and ethylene would give naphthalene (equation (44)) with 0.822 labelled atoms or more depending on the activity of ethylene, and (ii) styrene (0.973 labelled atoms) and an ethyl radical (0.822 labelled atoms) would give naphthalene with 1.795 labelled atoms (equation (45)). Mechanisms involving (i) a benzyl radical (0.61 labelled atoms) and a propyl or allyl radical (1.0 labelled atom) would give naphthalene with 1.61 labelled atoms (equation (46)), and (ii) a $C_6H_5CH{=}CHCH_2\cdot$ or $C_6H_5CH_2CH_2CH_2\cdot$ radical (1.0 labelled atom) and a methyl radical (assuming 0.33 labelled atoms to be the average activity) would give naphthalene with 1.33 labelled atoms (equation (47)). Since the naphthalene was found to have 1.17 labelled atoms, it is reasonable to assume that it must be formed according to (47).

In earlier papers in this series, evidence was presented that the phenanthrene must be largely formed by a mechanism involving the reaction of phenyl and styryl radicals (as in LLLX) followed by cyclodehydrogenation. In the pyrolysis of β-[α-^{14}C]-methylstyrene, any phenanthrene produced by this route would be expected to have the same activity as styrene (i.e. 0.973 labelled atoms). An alternative route involving interaction of two benzyl radicals (as in LLXXXIX) followed by cyclodehydrogenation would give a somewhat more active product (i.e. 1.22 labelled atoms).

The phenanthrene isolated from the present tar showed activity corresponding to 0.932 labelled atoms, in agreement with the two possible mechanisms. Although no decision between these two mechanisms is possible, the present results favour the former route. Oxidation of the phenanthrene gave 2,2'-biphenic acid (0.91 labelled atoms) and this was decarboxylated to give biphenyl (0.014 labelled atoms) and carbon dioxide (0.878 labelled atoms).

Anthracene was also detected in the present pyrolysis but it could not be isolated in sufficient quantity and purity. It could be formed from phenanthrene by rearrangement[154,67,86] as shown in figure 2.

Only a very small amount of 10,11-benzofluoranthene and a trace of 3,4-benzopyrene could be detected in β-methylstyrene tar. As suggested earlier in this series, 10,11-benzofluoranthene (XVII) could arise by "dimerisation" of two naphthyl radicals followed by cyclodehydrogenation. Similarly, 3,4-benzopyrene could be formed by interaction of two C_6-C_4 units to give (XXIX) followed by cyclodehydrogenation. Alternative mechanisms for the formation of 3,4-benzopyrene have been discussed in Chapter 2.

CHAPTER 9

EXPERIMENTAL

9.1 INTRODUCTION

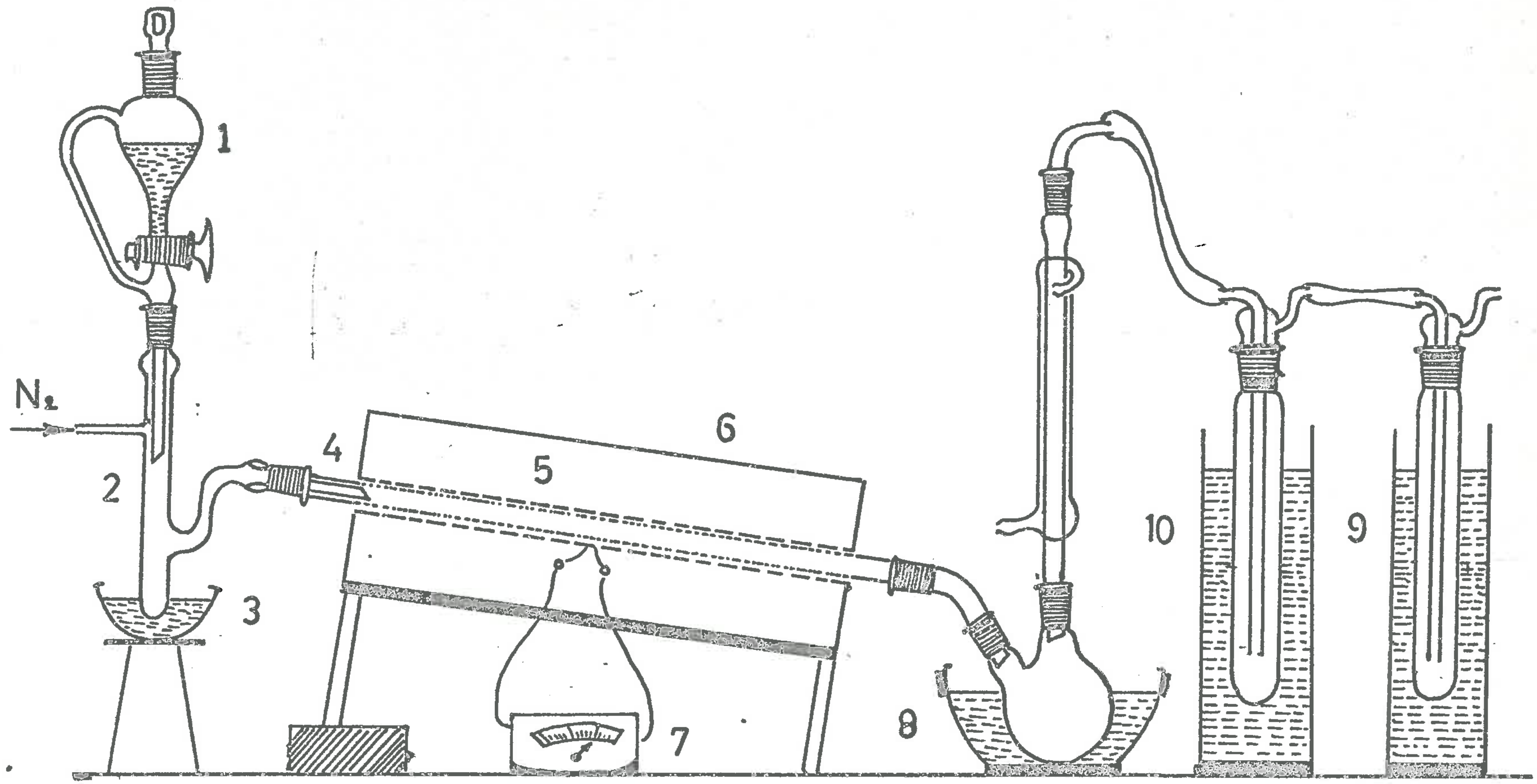
The experimental part of this chapter is presented in two sections. Section A describes in broad outline some of the general methods, techniques and apparatus used in this investigation. Section B presents in detail the synthesis, the pyrolysis and isolation of various compounds formed in the tar.

SECTION A

9.2 THE PYROLYSIS APPARATUS

The Furnace:

The furnace consisted of two silica tubes, the outer and inner. The outer silica tube (3ft. x 1in. internal diameter) was wound with 25 s.w.g. nichrome wire (total resistance 90 ohms) and mounted along the centre of a pressed asbestos-board box (3 x 1 x 1 ft) filled with "vermiculite". The material to be pyrolysed was passed through an inner silica tube (3ft. 5in. x 3/4in. internal diameter) packed with porcelain chips, which just fitted into an outer tube. The temperature of the furnace was controlled by a Variac transformer and was initially adjusted to 700°, using a calibrated chromel-alumel thermocouple inside the inner silica tube. The temperature



1. Pressure equallising dropping funnel
2. Flash evaporator
3. Woods-metal bath
4. Inner Silica tube
5. Outer Silica tube
6. Electric furnace
7. Thermocouple
8. Ice-salt bath
9. Liquid air bath
10. Dry-ice/Ethanol bath

Figure 7

during the pyrolysis was controlled to give a constant reading on a second chromel-alumel thermocouple inserted through a small hole bored near the centre of the outer silica tube, corresponding to a temperature of 700° inside the inner tube. The whole furnace was inclined to an angle of approximately 15 -20° to the horizontal to facilitate the collection of products (Figure 7).

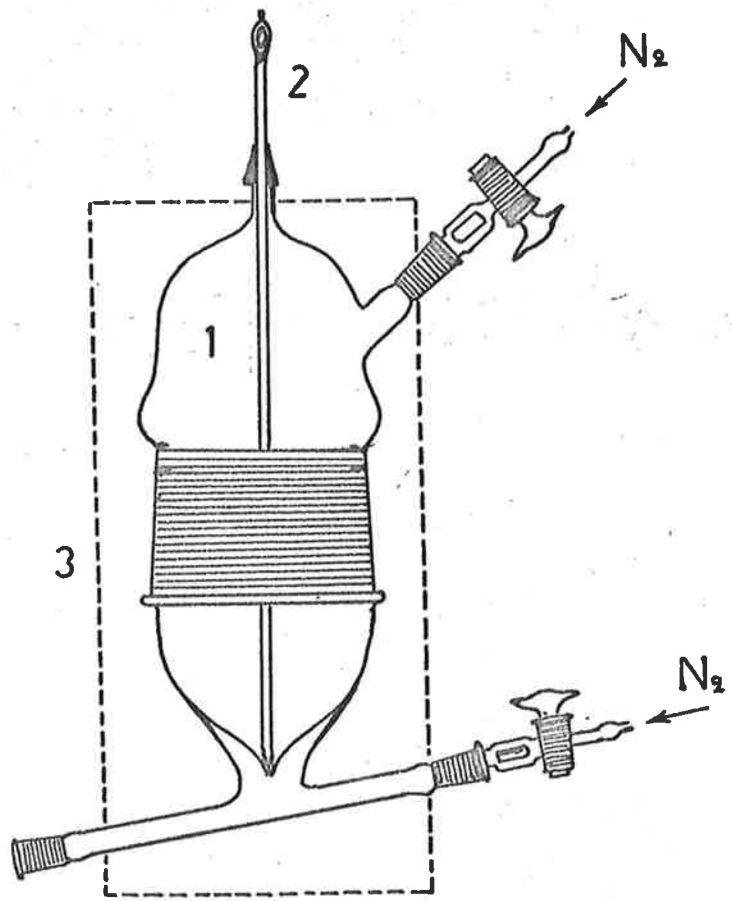
A smaller furnace, having the similar features as the above, was used for the pyrolysis of [1-^{14}C]naphthalene.

The Dropping Funnel:

With solid compounds, samples were melted initially at the desired temperature in a special dropping funnel and then introduced dropwise directly into the silica tube in an atmosphere of oxygen-free nitrogen. The dropping funnel consisted of a glass reservoir with an adjustable needle valve, an inlet tube for nitrogen and fitted to a silica tube. The whole reservoir was enclosed in an air-bath fitted with a small window (Figure 8).

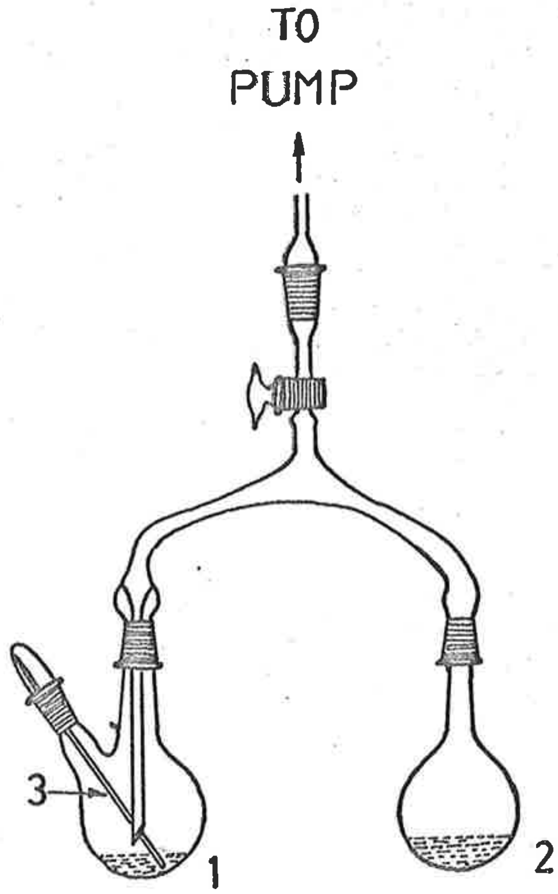
With liquid compounds, samples were vaporised initially (in order to avoid the risk of pre-polymerisation) at the desired temperature and the vapour was carried through the silica tube in a stream of oxygen-free nitrogen. The samples were vaporised in a pre-heated (Woods-metal bath) flash evaporator by the dropwise addition of the liquid from a pressure equalliaing dropping funnel (Figure 7).

Figure 8



1. Dropping funnel
2. Needle valve
3. Air-bath

Figure 9



1. Van-Slyke Folch oxidation reagent
2. Barium hydroxide (4%)
3. Capillary

All pyrolysis experiments were carried out under an atmosphere of oxygen-free nitrogen, dried by successive passage through concentrated sulphuric acid and potassium hydroxide towers. The pyrolysis products were collected in a round bottom flask (immersed in ice-salt bath) fitted with water condenser, followed by an ethanol-dry ice trap and two liquid air traps.

9.3 HIGH VACUUM SYSTEM

For the synthesis of carboxy-^{14}C labelled compounds from Ba[^{14}C]O_3, the reactions were carried out in a high vacuum system.

The apparatus consisted of a length of a wide-bore tubing (the manifold), along which were side tubes with taps for the connection of reaction vessels, etc. The end of the manifold led through a liquid air trap to an efficient pumping system. The essentials of a high-vacuum pumping system were a mechanical 'backing' pump connected via a liquid air trap to a mercury diffusion pump which in turn was connected to the apparatus. The pressure gauge (Pirani, for pressure $<10^{-3}$) was attached as shown in the figure 10. The whole vacuum manifold with reaction vessels were supported on a metal-rod framework.

9.4 RADIOACTIVE MATERIALS AND ASSAY

Radioactive Materials:

Before synthesising isotopically-labelled compounds for pyrolysis

Figure 10 Vacuum manifold with accessory apparatus.

1. Wide bore tap.
2. Pressure equalising dropping funnel.
3. Sulphuric acid (98%).
4. Barium carbonate.
5. Manometer.
6. Pirani vacuum gauge.
7. Low temperature condenser.
8. Cooling bath (Dry ice/ethanol).
9. Stirrer capsule (magnet sealed in teflon).
10. Magnetic stirrer.
11. Graduated ampoule for liquids.
12. Gas storage bulb.
13. Manifold.

P. To high vacuum pumping system.

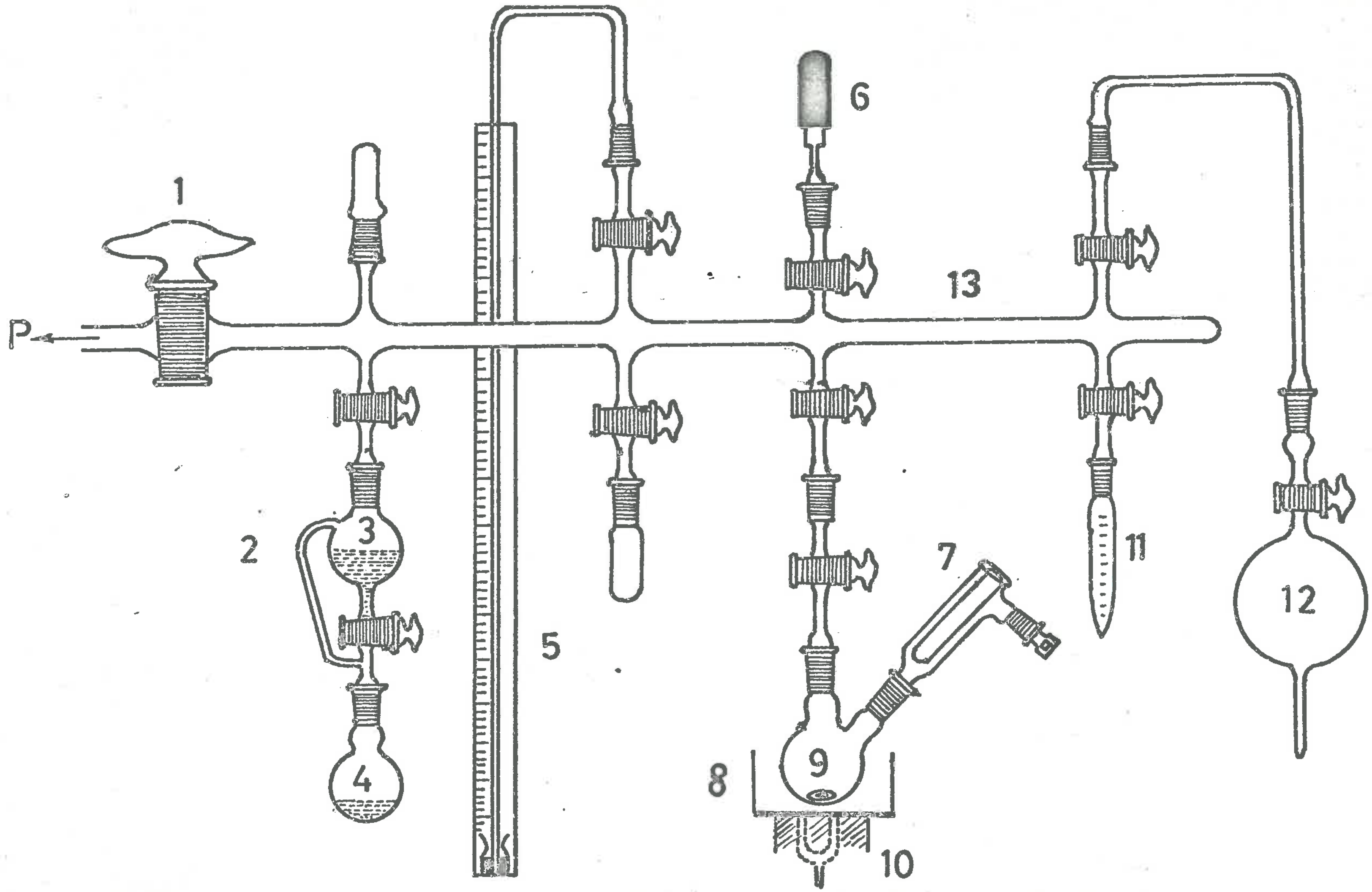


Figure 10 Vacuum manifold with accessory apparatus.

unlabelled compounds were first studied. The optimum conditions for each stage in the synthesis were worked out in practise runs using non-radioactive materials. The active compounds were then synthesised, appropriately diluted with pure inactive compounds and pyrolysed under conditions similar to those used for the inactive compounds.

Radioactive Assay:

Specimens were assayed for radioactivity, with an end-window counter, and infinitely thick, solid samples of 1 cm^2. cross-sectional area[170]; and counting rates were corrected for background and dead time of the instrument. The counting equipment consisted of an EKCO automatic scalar type N530D, in conjunction with an EKCO probe unit type N558 and an EW3H Geiger tube. The counts per minute were determined by recording five readings each of five minutes duration for each sample. All assays were usually repeated twice either with a new sample or with the original sample repacked. In this way errors due to differences in packing, and losses during dilution, were almost eliminated. The statistical counting error was calculated as standard deviations for each series of counts and was in no case greater than 1.5% (except for the practically inactive products).

The samples were prepared by the "pellet" technique[170]. With liquid compounds, samples were oxidised to carbon dioxide by the

Van Slyke-Folch oxidation reagent[171] in an apparatus shown in figure 9. The gas was absorbed in a 4% solution of barium hydroxide. The resulting barium carbonate was collected and subjected to radioactive assay.

9.5 ANALYTICAL TECHNIQUES

Gas-Liquid Partition Chromatography:

A Griffin and George vapour-phase chromatographic apparatus (Mark II) was used in the identification of compounds boiling below 260°. Apiezon L supported on Celite (40-60 mesh, 1:4 w/w) was used as stationary phase and nitrogen as carrier gas. Fractions were identified by comparison of retention times or of the ratio of their retention times to those of known substances under the same conditions. Individual components were then collected using a Beckman Megachrome. 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 high boiling residue obtained on distillation of the tar was initially chromatographed on a column of Spence alumina using 100 g. of alumina per gram of residue. Normally the residue was dissolved in chloroform and adsorbed on alumina. The resulting alumina was then placed on the top of a column of alumina which had been packed in hexane. The column was then eluted with hexane, then with hexane containing increasing concentration of benzene. Both these solvents were purified by washing with concentrated sulphuric acid, water, then dried and distilled.

Chromatography on Partially Acetylated Cellulose:

Whatman's chromatography cellulose powder was acetylated in a mixture of thiophen-free benzene, acetic anhydride and sulphuric acid according to the method of Spotswood[172].

The separations obtained by the thin layer chromatography on partially acetylated cellulose have been reproduced on a larger scale on columns of partially acetylated cellulose powder using the same solvent systems as those used in the thin layer chromatography. The most common solvent system used for the development of columns and also for the introduction of the compounds onto the column were ethanol-benzene-water (17:4:1 v/v) and/or ethanol-toluene-water (17:4:1 v/v). Approximately 100 g. of acetylated cellulose per 100 mg. of the mixture of hydrocarbons having a reasonable difference in R_f values was required for good separation.

Thin Layer Chromatography:

Thin layer chromatography on alumina, or on partially acetylated cellulose[173], etc., was used prior to the use of the appropriate column chromatography. The plates (20 x 8 cm.) were prepared using a "Desage" spreading device adjusted to give a layer of 275 μ thickness.

Ultraviolet Spectroscopy:

Ultraviolet spectra were determined in 95% ethanol using an Optica CF_4 recording spectrophotometer.

Infrared Spectroscopy:

The infrared spectra were determined using a Perkin-Elmer Model 137 Infracord spectrophotometer. The measurements were made as solutions in carbon tetrachloride or as liquid films.

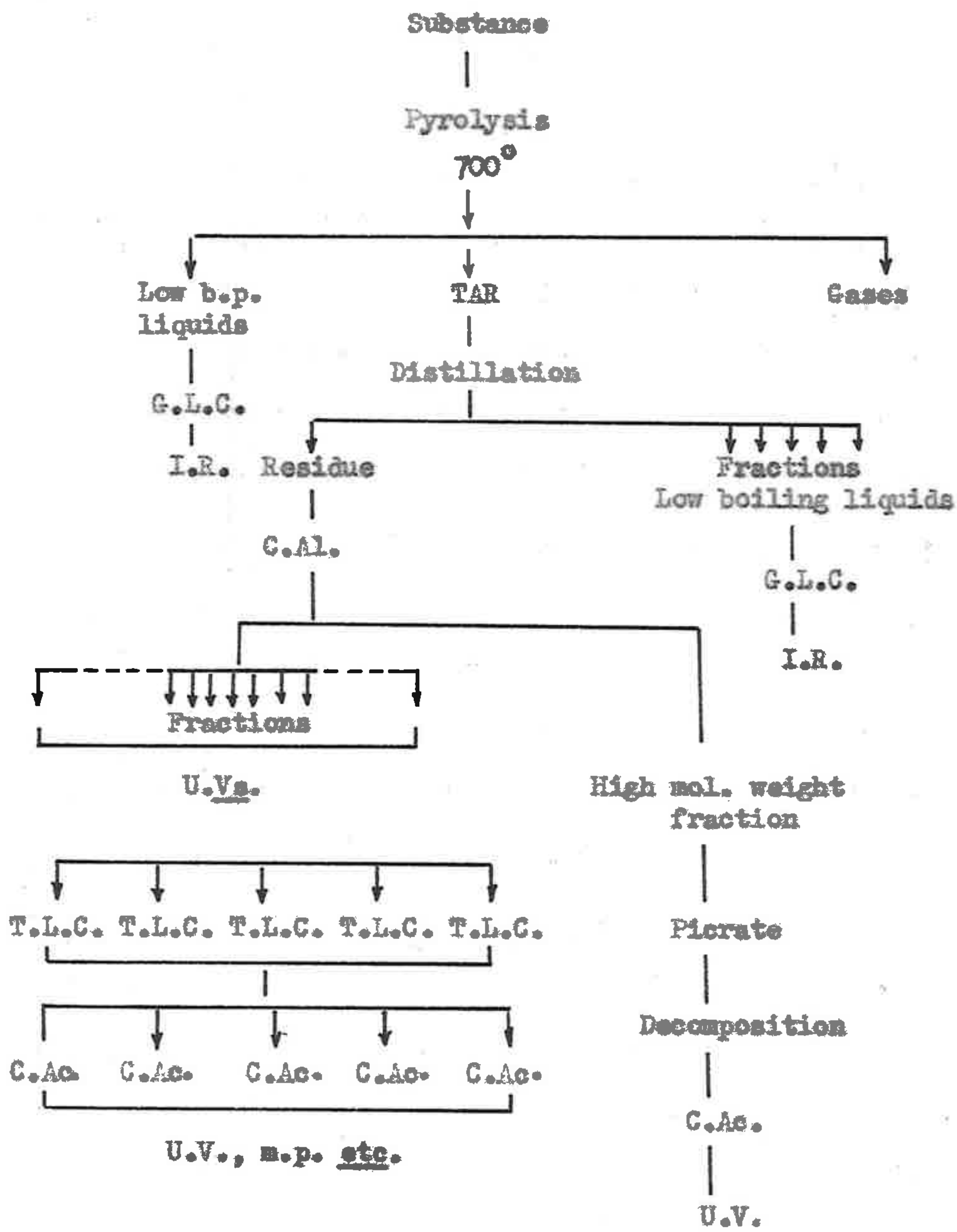
Identification of Products:

Samples of the exit gases were identified by infrared analysis. The products isolated by gas-liquid chromatography or by chromatography on alumina or partially acetylated cellulose were identified mainly by comparison of their ultraviolet or infrared spectra with curves obtained from authentic specimens, or with published curves where suitable standards were not possible. Some of the low boiling products were also identified by their retention times. In some cases, the identity of a compound was established by determining its melting point and mixed melting point. Where possible, the identity of a compound was confirmed by preparing a derivative.

A general scheme for the analysis of a complex tar is shown schematically in figure 11.

Quantitative Determination of Products:

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. The relative concentrations of the 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.



U.V. = Ultraviolet spectra; I.R. = Infrared spectra;

G.L.C. = Gas-liquid chromatography; T.L.C. = Thin layer chromatography;

C.Al. = Chromatography on alumina; C.Ac. = Chromatography on acetylated cellulose.

Figure 11

SECTION B

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

[1-^{14}C]Naphthalene:

The [1-^{14}C]naphthalene used was obtained by the pyrolysis of [1-^{14}C]tetralin[122]. The crude material (m.p. 78 -79°) was repeatedly recrystallised from ethanol; it then had m.p. 80.5°.

In order to check the purity of this sample, a small amount (100 mg.), in hexane, was run onto a column of alumina, and hexane used as eluant. Thirty fractions were collected and each was examined by ultraviolet spectroscopy; but no fraction showed any impurity. As a further check a small sample was examined by gas-liquid chromatography using Apiezon L supported on Celite (60 mesh, 1:4 w/w) as stationary phase and nitrogen as carrier gas (Griffin and George Mark II VPC apparatus). No impurity could be detected.

(a) Pyrolysis of [1-^{14}C]Naphthalene

The pyrolysis was carried out in a silica tube mounted in the furnace described earlier. The pure [1-^{14}C]naphthalene (25.0 g.) was contained in a reservoir fitted with a needle valve and enclosed in an air-bath maintained at about 120°. Before the pyrolysis run the tube was brought to the desired temperature (700°), and a stream of oxygen-free nitrogen allowed to pass through the tube at 1 ml./sec. [1-^{14}C]Naphthalene was then vaporised at 1 drop/12 sec. by dropping the liquid directly into an empty silica tube (33 x 5/8 in. internal diameter). When all the naphthalene had been introduced, the temperature was maintained and the carrier gas allowed to pass through the tube, for a further 30 minutes. The resulting tar was collected in a series of traps cooled in ice-salt, solid CO_2-ethanol, and liquid air.

During the pyrolysis samples of the exit gases were collected at intervals and examined by infrared spectroscopy. No methane or ethylene could be detected.

The whole pyrolysis was then repeated three more times under identical conditions and the tars combined.

(b) Analysis of Tar from [1-^{14}C]Naphthalene

The total yield of tar from 100 g. of [1-^{14}C]naphthalene was 93.12 g. This was carefully distilled under vacuum to give naphthalene (83.7 g.) and a black residue (7.5 g.).

The residue (7.5 g.) was dissolved in a little chloroform, alumina (80 g.) added, and the solvent then removed under reduced pressure. The resulting mixture was then placed on the top of a column of alumina (1.5 kg; 125 x 6 cm) which had been packed in hexane. The column was then eluted with hexane containing increasing concentration of benzene and 270 fractions, each of 500 ml., were collected. These fractions were examined by ultraviolet

TABLE 17

CHROMATOGRAPHY OF TAR FROM [1-^{14}C]NAPHTHALENE

Fraction	Original fractions	Solvent	Compounds identified
(a)	1-20	Hexane	Naphthalene
(b)	21-72	Hexane	1,1'-Binaphthyl
(c)	73-76	Hexane	1,1'-Binaphthyl 1,2'-Binaphthyl
(d)	77-101	Hexane:benzene (9:1 v/v)	1,2'-Binaphthyl
(e)	102-116	Hexane:benzene (9:1 v/v)	-
(f)	117-155	Hexane:benzene (8:2 v/v)	2,2'-Binaphthyl
(g)	156-180	Hexane:benzene (8:2 v/v)	-
(h)	181-202	Hexane:benzene (7:3 v/v)	Perylene 10,11-Benzofluoranthene 3,4-Benzopyrene
(i)	203-206	Hexane:benzene (7:3 v/v)	Perylene 10,11- and 11,12-Benzofluor-the
(j)	207-235	Hexane:benzene (6:4 v/v)	Perylene 11,12-Benzofluoranthene
(k)	236-270	Hexane:benzene (5:5 v/v)	-

spectroscopy, and then recombined to give 11 main fractions (a-k), as summarised in Table 17. Some of these fractions were rechromatographed on columns of partially acetylated cellulose. The individual compounds were then isolated, purified and submitted to radiochemical analysis as described below.

(c) Isolation and Radiochemical Analysis

Naphthalene.

Evaporation of the solvent from fraction (a), and recrystallisation of the colourless residue from ethanol gave naphthalene, m.p. 80.5°. A sample of the distillate was also recrystallised from ethanol to give naphthalene, m.p. 80.5°, which was submitted to radiochemical analysis.

Relative molar activity x 10^{-2},

Found: 22.3 ± 0.07

Calc.: 22.2 (for 1.0 $\overset{*}{C}$)

1,1'-Binaphthyl.

Solvent was evaporated from fraction (b), recrystallisation of the residue from ethanol gave 1,1'-binaphthyl m.p. 156°, not depressed by admixture with an authentic specimen (lit. m.p. 156°). Its ultraviolet absorption spectrum showed maxima at 285 and 295 mμ in good agreement with the literature[174].

Relative molar activity x 10^{-2},

Found: 44.5 ± 0.25

Calc.: 44.4 (for 2.0 $\overset{*}{C}$)

1,2'-Binaphthyl.

Evaporation of the solvent from fraction (d) under reduced pressure gave a semi-solid mass which solidified on cooling. Recrystallisation from light petroleum gave 1,2'-binaphthyl, m.p. 75 -76°, not depressed by admixture with an authentic specimen, m.p. 76°. Its ultraviolet absorption spectrum showed a maximum at 282 mμ, in good agreement with the literature[174].

Relative molar activity x 10^{-2},

Found: 44.8 ± 0.19

Calc.: 44.4 (for 2.0 $\overset{*}{C}$)

2,2'-Binaphthyl.

A portion of the residue obtained by evaporation of the solvent from fraction (e) was recrystallised from ethanol. The resulting 2,2'-binaphthyl was obtained as shining plates, m.p. 187°, not depressed by admixture with an authentic specimen (lit. m.p. 187 -188°). Its ultraviolet absorption spectrum showed maxima at 254 and 306 mμ in excellent agreement with the literature values[175].

Relative molar activity x 10^{-2},

Found: 44.6 ± 0.1

Calc.: 44.4 (for 2.0 $\overset{*}{C}$)

10,11-Benzofluoranthene.

Evaporation of the solvent from fraction (h) gave a crude yellow residue, which was dissolved in a little toluene and chromatographed on a column of partially acetylated cellulose (5 x 75 cm.) using ethanol:toluene:water (17:4:1 v/v). The fractions containing 10,11-benzofluoranthene (u.v. spectroscopy) were combined, the solvent removed, and the residue rechromatographed on alumina. 10,11-Benzofluoranthene was obtained as bright yellow needles, m.p. 165°, not depressed by admixture with an authentic specimen (lit. m.p. 165°). Its ultraviolet absorption spectrum showed maxima at 241, 282, 294, 307, 318, 333, 348, 365, 375 and 383 mμ in good agreement with the literature[176].

Relative molar activity x 10^{-2},

Found: 43.08 ± 0.061

Calc.: 44.4 (for 2.0 C*)

11,12-Benzofluoranthene.

Evaporation of the solvent from fraction (j) gave a crude residue which was dissolved in a little benzene, and chromatographed on a column of partially acetylated cellulose (5 x 75 cm.) using ethanol, benzene and water (17:4:1 v/v). 145 Fractions (each of 20 ml.) were collected. The fractions containing 11,12-benzofluoranthene (u.v. spectroscopy) were combined, solvent evaporated, and rechromatographed on alumina. Recrystallisation of the product gave 11,12-benzofluoranthene as pale yellow needles, m.p. 216°, not depressed by admixture with an authentic specimen (lit. m.p. 217°). Its ultraviolet absorption spectrum showed maxima at 269, 284, 297, 309, 362, 380, and 402 mμ in good agreement with the literature[176].

Relative molar activity x 10^{-2},

Found: 43.4 ± 0.093

Calc.: 44.4 (for 2.0 $\overset{*}{C}$)

Perylene.

Perylene was isolated from fractions (h), (i), and (j) following chromatography on a column of partially acetylated cellulose (5 x 75 cm.) using ethanol:toluene:water (17:4:1 v/v). Its absorption spectrum showed maxima at 253, 386, 409 and 436 mμ in good agreement with the literature. However, it could not be obtained pure in sufficient quantity for radiochemical analysis.

3,4-Benzopyrene.

This was isolated following chromatography of fraction (h) on acetylated cellulose (see above). The appropriate fractions were combined, evaporated, and the residue rechromatographed on alumina. The solvent was again evaporated and the residue taken up in 95% ethanol. Its ultraviolet absorption spectrum showed maxima at 255, 265, 274, 284, 297, 332, 348, 365, 379, 384 and 404 mμ in good agreement with those recorded for 3,4-benzopyrene[176].

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

(a) Synthesis of [1-^{14}C]styrene

[carbonyl-^{14}C]Acetophenone.

Sodium [carboxy-^{14}C]acetate (2.0 mc; 4.6 mg.) was scraped from the phial with a spatula into a 3-necked flask. The phial was rinsed with ten small portions of inactive anhydrous sodium acetate, and the washings were poured into the reaction vessel. More sodium acetate (Analar) was added to give total acetate (5 g.). Anhydrous aluminium chloride (33 g., 0.12 mole) and sodium-dried benzene (20 ml.) were added and the mixture was gently refluxed for 8 hours with stirring. It was then cooled, decomposed carefully with ice and excess concentrated hydrochloric acid and refluxed for 1 hour. The reaction mixture was then cooled, extracted with ether (1 x 100 ml., 2 x 50 ml.), the combined extracts washed with water, aqueous sodium hydroxide (10%) and again with water, dried ($CaCl_2$), the solvent evaporated and the residue distilled under reduced pressure to yield [carbonyl-^{14}C]acetophenone, b.p. 92°/16 mm (5.97 g., 81.6%).

1-Phenyl[1-^{14}C]ethanol.

A solution of [carbonyl-^{14}C]acetophenone (5.97 g., 0.05 mole) in 95% ethanol (8 ml.) was added to a solution of sodium hydroxide (5 g., 0.125 mole) in water (50 ml.) cooled to 15°. Raney nickel alloy (5 g.) was added portionwise with stirring at 15 -20° (external cooling) over a period of 30 minutes, and the mixture then stirred at room temperature for 1 hour. The nickel catalyst was removed by filtration, washed with ethanol, and the combined filtrate saturated with sodium chloride and extracted with ether (3 x 50 ml.). The combined ethereal extract was washed with water and dried ($MgSO_4$). The solvent was removed by distillation and the residue distilled under reduced pressure to give 1-phenyl [1-^{14}C]ethanol, b.p. 100°/16 mm. (5.63 g., 92.7%).

1-Chloro-1-phenyl[1-^{14}C]ethane.

A mixture of 1-phenyl[1-^{14}C]ethanol (5.63 g., 0.04 mole) and concentrated hydrochloric acid (38 g., Sp. g., 1.18) was shaken vigorously for 15 minutes, diluted with water (100 ml.), and extracted with ether (3 x 50 ml.). The combined ethereal extracts were washed with water, aqueous sodium hydroxide (10%), water, dried ($CaCl_2$), the solvent removed, and the residue distilled under reduced pressure to give 1-chloro-1-phenyl[1-^{14}C]ethane, b.p. 91 -92°/16 mm. (5.55 g., 85.6%).

[1-^{14}C]Styrene.

A mixture of 1-chloro-1-phenyl[1-^{14}C]ethane (5.55 g.) and freshly distilled quinoline (3.5 ml.) was refluxed gently for 30 minutes, cooled, decomposed with ice-cold dilute hydrochloric acid and extracted with ether (3 x 50 ml.). The combined ethereal extracts were washed with water, aqueous sodium hydroxide (10%), again with water, dried ($CaCl_2$), the solvent removed and the residue distilled under reduced pressure to yield [1-^{14}C]styrene, b.p. 54°/16 mm. (3.5 g., 76.6%).

The purified inactive styrene (10 g.) was added to the distillation flask and the mixture was distilled. More styrene was added from time to time, until 195 g. of distillate had been collected. The infrared spectrum of this diluted active styrene was identical with that of pure inactive styrene. No impurities could be detected by gas-liquid chromatography.

(b) Radioactivity of [1-^{14}C]Styrene

The radioactivity of the styrene was determined by conversion to the dibromide as follows: a solution of [1-^{14}C]styrene (0.1 ml.) in chloroform (0.1 ml.) was treated dropwise with a solution of bromine in chloroform (1:2 v/v) until the red colour persisted. The dibromide separated on evaporation of the solvent. Recrystallisation twice from dilute alcohol (charcoal) gave pure [1-^{14}C]styrene dibromide, m.p. 72 -73°, which was assayed radiochemically (Found: relative molar activity x 10^{-2}, 6.81 $\pm$ 0.028).

(c) Degradation of [1-^{14}C]Styrene

[1-^{14}C]Styrene (2.25 g.) was added to a solution of chromium trioxide (7.5 g.) in water (28 ml.) at 0°. Concentrated sulphuric acid (18 ml.) was added portionwise with stirring over a period of 1.5 hour, maintaining the temperature below 20°, the mixture was then refluxed gently for 2 hours. Crystals of benzoic acid which separated on cooling were filtered, washed with cold water, dissolved in 10% sodium hydroxide, boiled with Norite, filtered, the filtrate cooled and acidified with hydrochloric acid. Recrystallisation from water gave pure benzoic acid, m.p. 120°-121°.

Relative molar activity x 10^{-2},

Found: 6.25 ± 0.016

Calc.: 6.81 (for 1.0 $\overset{*}{C}$)

A sample of [carboxy-^{14}C]benzoic acid (210 mg.) was decarboxylated by refluxing with copper bronze (140 mg.) in freshly distilled quinoline (10 ml.) in a slow stream of CO_2-free nitrogen for 4 hours. The exit gases were bubbled through a 4% solution of barium hydroxide in a two-necked flask protected with a potassium hydroxide tube. The precipitated barium carbonate was collected, washed with hot water, acetone, dried and radioassayed.

Relative molar activity x 10^{-2},

Found: 6.24 ± 0.023

Calc.: 6.81 (for 1.0 $\overset{*}{C}$)

(d) Pyrolysis of [1-^{14}C]Styrene

The pyrolysis was carried out in a silica tube (40" x 1") packed with porcelain chips (3/8" x 1/4") as described earlier. Freshly redistilled [1-^{14}C]styrene (50 g.) was vaporised by dropwise addition (10 drops/min.; 10 g./hr.) to a flash evaporator immersed in a Woods-metal bath kept at 340^{o}, and the vapour carried by a stream of oxygen-free nitrogen into a silica tube maintained at 710^{o}. After all the styrene had been introduced the carrier gas was allowed to pass through the tube for a further 30 minutes. The resulting liquid tar was collected in a series of traps cooled in ice-salt, dry ice/ethanol, and liquid air. Samples of the exit gases were collected during the pyrolysis and methane and ethylene were identified by infrared spectroscopy.

The pyrolysis was then repeated twice more under identical conditions. In this way a total of 150 g. of [1-^{14}C]styrene was pyrolysed at 710^{o}.

(e) Analysis of Tar from [1-^{14}C]Styrene

A dark liquid tar (110.8 g.) was collected and a further quantity (1.7 g.) was obtained by washing the tube with hot chloroform and evaporating the solvent. An additional quantity (2 g.) of low boiling material was collected in a trap cooled in a dry ice/ethanol trap (Fraction A).

The combined tars (114.5 g., 76.3%) were distilled carefully under reduced pressure to give six main fractions. Fractions (A), (B), and (C) were examined by gas-liquid chromatography (Griffin and George VPC apparatus) and the major components separated using a Beckman Megachrome preparative gas chromatograph. Fractions (D), (E), and (F) were examined by chromatography on alumina and acetylated cellulose. The major compounds were isolated as described below.

The results are summarised in Table 18.

TABLE 18

Fraction	B.P.	Weight (g.)	Compounds isolated
A	-	2	Benzene Toluene
B	36 -48°/15 mm.	56.14	Benzene Toluene Ethylbenzene Styrene
C	40 -72°/5.5 mm.	6.2	Styrene Indene Naphthalene
D	72 -80°/3 mm.	4.2	Naphthalene
E	80 -160°/1.5 mm.	28.6	Phenanthrene Anthracene (detected)
F	residue	17.1	Chrysene 2-Phenylnaphthalene

(f) Isolation and Radiochemical Analysis

Benzene.

Isolated from fractions (A) and (B) by preparative gas-liquid chromatography. Redistillation gave pure benzene; the infrared spectrum was identical with that of an authentic sample. Van Slyke-Fol oxidation gave barium carbonate, which was assayed radiochemically.

Relative molar activity x 10^{-2},

Found: 2.27 ± 0.04

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

Toluene.

Isolated from fractions (A) and (B) by preparative gas-liquid chromatography. The infrared spectrum of the redistilled product was identical with that of an authentic specimen. Van Slyke-Folch oxidation gave barium carbonate which was assayed.

Relative molar activity x 10^{-2},

Found: 18.5

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

Degradation of toluene.

A sample of active toluene (500 mg.) was refluxed with a solution of potassium permanganate (2.0 g.) and sodium carbonate (0.25 g.) in water (40 ml.) for 4 hours and the reaction mixture was worked up in the usual manner. Recrystallisation of the product from water gave benzoic acid as colourless needles, m.p. 120°.

Relative molar activity x 10^{-2},

Found: 17.6 ± 0.03

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

The benzoic acid (100 mg.) was decarboxylated by refluxing with copper bronze (70 mg.) in freshly distilled quinoline (8 ml.) in a stream of CO_2-free nitrogen for 3 hours. The carbon dioxide evolved was absorbed in 4% barium hydroxide solution, the barium carbonate collected, dried, and assayed.

Relative molar activity x 10^{-2},

Found: 17.1 ± 0.04

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

The resulting benzene (collected in the cold trap at -70°) was oxidised by Van Slyke-Folch oxidation reagent, converted into barium carbonate and radioassayed.

Relative molar activity x 10^{-2},

Found: 0.27 ± 0.03

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

Ethylbenzene.

Isolated from fraction (B) by gas-liquid chromatography. Its infrared spectrum was identical with that of an authentic specimen. Van Slyke-Folch oxidation gave barium carbonate which was assayed radiochemically.

Relative molar activity x 10^{-2},

Found: 25.64 ± 0.016

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

Degradation of Ethylbenzene.

The active ethylbenzene (167 mg.) diluted with purified inactive ethylbenzene (376 mg.), was oxidised to benzoic acid by refluxing with potassium permanganate (2 g.), sodium carbonate (0.25 g.) and water (40 ml.) for 12 hours. Recrystallisation of the product from water gave benzoic acid as colourless needles, m.p. 122°.

Relative molar activity x 10^{-2},

Found: 22.73 ± 0.06

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

The active benzoic acid (130 mg.) was decarboxylated by refluxing with copper bronze (85 mg.) in freshly distilled quinoline (8 ml.) in a stream of CO_2-free nitrogen. The carbon dioxide evolved was bubbled through a 4% solution of barium hydroxide and the precipitated barium carbonate radioassayed.

Relative molar activity x 10^{-2},

Found: 22.41 ± 0.07

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

Styrene.

Isolated from fractions (B) and (C) by preparative gas-liquid chromatography. The activity was determined by conversion to the dibromide as described on page 145.

Relative molar activity x 10^{-2},

Found: 26.29 ± 0.061

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

Indene.

Isolated from fraction (C) by preparative gas-liquid chromatography; its infrared spectrum was identical with that of an authentic specimen. Van Slyke-Folch oxidation gave barium carbonate which was collected for radioactive assay.

Relative molar activity x 10^{-2},

Found: 36.36 ± 0.26

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

Naphthalene.

This was isolated from fraction (C) by preparative gas-liquid chromatography and from fraction (D) by chromatography on alumina. Two recrystallisations from ethanol gave naphthalene as colourless plates, m.p. and mixed m.p. 80°. Its ultraviolet spectrum was identical with that of an authentic specimen.

Relative molar activity x 10^{-2},

Found: 13.9 ± 0.23

Calc.: 13.6 (for 2.0 $\overset{*}{C}$)

2-Phenylnaphthalene.

Isolated from fraction (F) following chromatography on alumina. Distillation of the fractions containing 2-phenylnaphthalene under reduced pressure (b.p. 140°/15 mm.), followed by chromatography of the distillate on alumina, and recrystallisation of the product from ethanol (charcoal), gave 2-phenylnaphthalene as colourless needles, m.p. 101-102°. Its ultraviolet spectrum was identical with that of an authentic specimen.

Relative molar activity x 10^{-2},

Found: 13.2 ± 0.04

Calc.: 13.6 (for 2.0 $\overset{*}{C}$)

Phenanthrene.

Isolated from fraction (E) following chromatography on alumina and on partially acetylated cellulose using ethanol:benzene:water (17:4:1 v/v) as eluting solvent. Small amounts of anthracene contaminating phenanthrene were removed by refluxing with concentrated nitric acid (1 ml.) in ethanol (50 ml.) for 1½ hours. The orange-yellow residue obtained after removal of the solvent was dissolved in the minimum amount of benzene and chromatographed on a small column of alumina, using hexane and benzene as eluants. Fractions containing phenanthrene (u.v. spectroscopy) were combined, the solvent removed, and the residue recrystallised twice from ethanol to give phenanthrene as colourless needles, m.p. 99°.

Relative molar activity x 10^{-2},

Found: 6.74 ± 0.022

Calc.: 6.81 (for 1.0$\overset{*}{C}$)

Degradation of Phenanthrene.

A solution of active phenanthrene (0.6 g.) in glacial acetic acid (15 ml.) was heated to 85° in a water bath and hydrogen peroxide (7.0 ml., 50%) added portionwise over 10 minutes. The mixture was then heated at 85° for an hour with stirring and the warm solution poured into water (20 ml.). The aqueous solution was made alkaline (pH 10.5) with 25% aqueous sodium hydroxide, warmed with stirring, and then acidified to pH 2.5 with concentrated hydrochloric acid. After cooling the precipitate was dissolved in ether, the ethereal solution washed with water, the solvent removed, and residue crystallised twice from dilute ethanol (charcoal) to give colourless needles of 2,2'-biphenic acid, m.p. and mixed m.p. 230°.

Relative molar activity x 10^{-2},

Found: 6.80 ± 0.038

Calc.: 6.81 (for 1.0 $\overset{*}{C}$)

Decarboxylation of active 2,2'-biphenic acid (130 mg.) with copper bronze (90 mg.) in freshly distilled quinoline (8 ml.) gave carbon dioxide, converted into barium carbonate which was radioassayed.

Relative molar activity x 10^{-2},

Found: 3.64 ± 0.015

Calc.: 6.81 (for 1.0 $\overset{*}{C}$)

The residue from the decarboxylation was acidified (HCl) and extracted with ether. After removal of the solvent, the residue was recrystallised from ethanol. Biphenyl was obtained as colourless plates m.p. and mixed m.p. 65 -66°.

Relative molar activity x 10^{-2},

Found: 2.89 ± 0.014

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

Chrysene.

Isolated from fraction (F) by chromatography on alumina, followed by chromatography on partially acetylated cellulose using ethanol:benzene:water (17:4:1 v/v) as eluting solvent. Fractions containing chrysene were combined, the solvent removed and the residue twice recrystallised from an alcohol-benzene mixture (charcoal) to give chrysene as colourless plates, m.p. 253°.

Relative molar activity x 10^{-2},

Found: 19.9 ± 0.03

Calc.: 20.4 (for 3.0 $\overset{*}{C}$)

Degradation of Chrysene.

A mixture of active chrysene (100 mg.), pure inactive chrysene (100 mg.), sodium dichromate (1 g.) and glacial acetic acid (8 ml.) was heated under reflux for 2 hours and then poured into water (10 ml.).

The red precipitate was collected and recrystallised twice from glacial acetic acid to give red prisms of chrysa-1,2-quinone, m.p. 241°.

Relative molar activity x 10^{-2},

Found: 19.75 ± 0.08

Calc.: 20.4 (for 3.0 $\overset{*}{C}$)

This active chrysa-1,2-quinone (155 mg.) was diluted with a purified inactive sample (560 mg.), intimately mixed with lead dioxide (1 g.) and added portionwise with stirring to potassium hydroxide (2.8 g.) and water (1 ml.) maintained at 225°-235° in an oil bath over a period of 15 minutes. After the addition the melt was heated at 225°-235° for 45 minutes, slightly cooled, repeated extracted with hot water and filtered. The combined filtrates were boiled with charcoal, filtered, acidified with concentrated hydrochlori acid, and exhaustively extracted with ether. The ethereal extract was washed (water), the solvent removed and the residue twice crystallised from dilute acetic acid (charcoal) to give 2-(o-naphthyl)benzoic acid (α-chrysenic acid) as colourless needles, m.p. 188°.

Relative molar activity x 10^{-2},

Found: 68.16 ± 0.11

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

The labelled 2-(o-naphthyl)benzoic acid (100 mg.) was decarboxylated with copper bronze (50 mg.) in freshly distilled quinoline (7 ml.) for 3 hours under a gentle stream of CO_2-free nitrogen. The carbon dioxide formed was bubbled through a 4% solution of barium hydroxide. The barium carbonate was collected and assayed.

Relative molar activity x 10^{-2},

Found: 14.16 ± 0.14

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

Acidification of the quinoline residue, extraction with ether, removal of the solvent, and recrystallisation from aqueous ethanol (charcoal) gave 2-phenylnaphthalene as colourless plates, m.p. 103°.

Relative molar activity x 10^{-2},

Found: 54.56 ± 0.21

Calc.: 26.36 (for 1.0 $\overset{*}{C}$)

9.8 THE PYROLYSIS OF [3-^{14}C]INDENE

(a) Synthesis of [3-^{14}C]Indene

[carboxy-^{14}C]Hydrocinnamic acid.

Barium [^{14}C]carbonate (1.0 mc; 225 mg.) was transferred from a phial to a flask attached to a vacuum line through a pressure-equalising dropping funnel for concentrated sulphuric acid. The phial was rinsed with several portions of inactive barium carbonate, and the washings poured into the reaction vessel. More inactive barium carbonate was added to give total carbonate (7.775 g., 0.04 mole). The system was evacuated and the [14-C] carbon dioxide evolved by the dropwise addition of concentrated sulphuric acid (98%) was condensed in a liquid-air trap, dried by distillation from a dry ice-ethanol bath at -80° and again condensed in a liquid-air trap. The Grignard reagent, prepared separately from β-phenylethylbromide (8.0 g., 0.043 mole), magnesium (1.035 g., 0.043 mole) and anhydrous ether (40 ml.), was diluted with anhydrous benzene (15 ml.) and the flask attached to the vacuum line, then cooled with liquid air and the system evacuated. The flask was then warmed to -20° using a dry ice-ethanol bath, and allowed to equilibrate for 10 minutes. The solution was stirred (magnetic stirrer) vigorously, and the [^{14}C] carbon dioxide introduced slowly. When most of the carbon dioxide had reacted, the bath temperature was reduced over 15 minutes to -70° with continued stirring. Excess carbon dioxide was then recondensed using a liquid air trap and air was then introduced into the reaction flask. The flask was warmed to -20° and the Grignard complex decomposed with ice-cold 20% sulphuric acid, with stirring. The aqueous layer was extracted with ether (4 x 25 ml.) and the combined ethereal solution washed with water, and extracted with 10% sodium hydroxide (4 x 20 ml.). The alkaline solution was boiled with charcoal, filtered, cooled and acidified to give [carboxy-^{14}C]hydrocinnamic acid (3.71 g.). This was used without further purification for the next step.

[carbonyl-^{14}C]Indan-1-one.

A mixture of [carboxy-^{14}C]hydrocinnamic acid (3.71 g.) diluted with inactive pure hydrocinnamic acid (1.29 g.) and thionyl chloride (8.0 ml.) was gently refluxed on a water bath for 2 hours. Excess thionyl chloride was evaporated under reduced pressure and the residue treated with anhydrous carbon disulphide (25 ml.), and the solution cooled to 0°. Anhydrous aluminium chloride (5 g.) was added portionwise at intervals of 5 minutes with shaking, and the mixture allowed to stand at 0° for 15 minutes, then at room temperature for 30 minutes, and finally refluxed gently at 50 -55° for 3 hours. The mixture was then cooled and carefully decomposed with ice and hydrochloric acid, then refluxed for 45 minutes, cooled and extracted with ether (3 x 50 ml.). The combined ethereal extracts were washed with water, aqueous sodium carbonate (5%), dried ($CaCl_2$), the solvent evaporated, and the residue distilled under reduced pressure. The [carbonyl-^{14}C]indan-1-one was obtained as a colourless oil, b.p. 128 -130°/15 mm., which solidified on cooling (yield, 3.29 g.).

[carbinol-^{14}C]Indan-1-ol.

A mixture of [carbonyl-^{14}C]indan-1-one (3.29 g.), sodium hydroxide (0.12 g.), ethanol (20 ml.), W-4 Raney nickel (0.75 g.) and chloroplatinic acid (26 mg.) was hydrogenated under atmospheric pressure for 1.5 hours. The catalyst was removed, washed with alcohol, the filtrates treated with three volumes of saturated aqueous sodium chloride, and extracted with ether. The ethereal solution was washed with water, dried ($MgSO_4$), the solvent evaporated, and the residue distilled under reduced pressure. The [carbinol-^{14}C]indan-1-ol

(2.3 g.) was obtained as a colourless oil, b.p. 138°/16 mm.

[3-^{14}C]Indene.

A mixture of [carbinol-^{14}C]indan-1-ol (2.3 g.) and hydrochloric acid (2N., 20 ml.) was refluxed for 30 minutes, then cooled and extracted with ether (4 x 25 ml.). The combined ethereal solutions were washed with water, aqueous sodium hydroxide (10%), again with water, dried ($CaCl_2$), the solvent evaporated and the residue distilled under reduced pressure. [3-^{14}C]Indene (0.86 g.) was obtained as a colourless oil, b.p. 83-84°/16 mm.

Purified inactive indene was added to the reaction flask and distilled. More indene was added from time to time, until 60 g. of distillate had been collected. The infrared spectrum of this product was identical with that of pure indene. A sample examined by gas-liquid chromatography showed no impurity. A sample was oxidised by the Van Slyke-Folch method and the [^{14}C]carbon dioxide evolved was absorbed by 4% barium hydroxide. The resulting [^{14}C]barium carbonate was collected for radioactive assay (Found: relative molar activity x 10^{-2}, 58.65 ± 0.29).

(b) Pyrolysis of [3-^{14}C]Indene

The pyrolysis was carried out in an empty silica tube (40" x 1"). Freshly redistilled diluted [3-^{14}C]indene (50 g.) was vaporised at 7 g./hr. in a flash evaporator immersed in a Woods-metal bath kept at 340°, and the vapour carried by a stream of oxygen-free nitrogen into an empty silica tube maintained at 700°. The resulting tar was collected in a series of traps cooled in ice/salt, solid CO_2/ethanol, and liquid air.

The infrared spectrum of a sample of the exit gases showed the presence of methane and ethylene.

(c) Analysis of [3-^{14}C]Indene Tar

The resulting tar (40.9 g.) together with the chloroform washings from the pyrolysis tube was distilled to give indene (8.5 g.) and a residue (29.85 g.). This residue was dissolved in chloroform, alumina (800 g.) added and the solvent evaporated under vacuum. The resulting alumina was then placed on the top of a column of alumina (7 Kg., 63 x 3 in.) packed in hexane. Elution with hexane containing increasing amounts of benzene (finally with benzene) gave 200 fractions (each of 1 litre). For working up, these fractions were recombined on the basis of their ultraviolet spectra to give six main fractions (A-F) as summarised in Table 19. The individual compounds were then isolated either by further chromatography on alumina, or by chromatography on columns of partially acetylated cellulose, and submitted to radioactive assay.

(d) Isolation and Radioassay

2,3-Benzofluorene.

This was isolated from fractions A, B and C. Evaporation of

TABLE 19

CHROMATOGRAPHY OF TAR FROM [3-^{14}C]INDENE

Fraction	Original fractions	Compound identified
A	1-69	2,3-Benzofluorene 1,2-Benzofluorene
B	70-77	2,3-Benzofluorene Chrysene
C	78-125	2,3-Benzofluorene 1,2-Benzanthracene Chrysene
D	129-164	10,11-Benzofluoranthene 11,12-Benzofluoranthene 3,4-Benzofluoranthene 3,4-Benzopyrene Alkylchrysene Unknown X_1
E	165-188	Unknown X_2
F	189-200	-

the solvent from fraction A gave a crystalline residue which was dissolved in a small amount of benzene and chromatographed on acetylated cellulose using ethanol:benzene:water (17:4:1 v/v) as eluant; 78 fractions (each 30 ml.) were collected. The fractions (21-53) containing 2,3-benzofluorene (as determined by ultraviolet spectroscopy) were combined, the solvent evaporated and the residue rechromatographed on acetylated cellulose; 100 fractions (each 20 ml.) were collected. The product obtained by evaporation of the first 74 fractions was twice crystallised from ethanol (charcoal). 2,3-Benzofluorene was obtained as colourless plates, m.p. and mixed m.p. 206°.

Relative molar activity x 10^{-2},

Found: 112.6 ± 0.04

Calc.: 117.3 (for 2.0 $\overset{*}{C}$)

1,2-Benzofluorene.

This was isolated following rechromatography of fraction (A 21-53) on acetylated cellulose. Evaporation of the solvent from fractions 82-99 (each of 20 ml.) gave a product which was again rechromatographed on alumina, and finally recrystallised from ethanol (charcoal). 1,2-Benzofluorene was obtained as colourless plates (17 mg.), m.p. and mixed m.p. 182 -183°. It was diluted with pure inactive material (36 mg.) and submitted to radioactive assay.

Relative molar activity x 10^{-2},

Found: 109.7 ± 0.07

Calc.: 117.3 (for 2.0 $\overset{*}{C}$)

Chrysene.

This was isolated from fraction B and C but the main bulk was obtained from fraction C. Evaporation of the solvent from fraction C gave a residue, a portion of which was repeatedly recrystallised from benzene, then chromatographed on alumina using hexane and benzene. Final recrystallisation from benzene-ethanol gave chrysene as colourless plates, m.p. 255°.

Relative molar activity x 10^{-2},

Found: 109.5 ± 0.05

Calc.: 117.3 (for 2.0 $\overset{*}{C}$)

The degradation of chrysene was carried out as described earlier (see pyrolysis of [1-^{14}C]styrene). A mixture of labelled chrysene (2.0 g.), sodium dichromate (4.4 g.) and acetic acid (80 ml.) was refluxed for 2 hours and then worked up as usual to give chrysa-1,2-quinone as red prisms, m.p. 239-240°.

Relative molar activity x 10^{-2},

Found: 109.1 ± 0.02

Calc.: 117.3 (for 2.0 $\overset{*}{C}$)

A mixture of this chrysa-1,2-quinone (1 g.) and lead oxide (1.5 g.) was fused by adding portionwise to a solution of potassium hydroxide (4.2 g.) in water (1.5 ml.) at 225-235°. After the addition (15 minutes) the melt was maintained at 225-235° for 30 minutes, then cooled and worked up as usual. o-(2-Naphthyl)benzoic acid was obtained as colourless needles, m.p. 188-189°.

Relative molar activity x 10^{-2},

Found: 90.55 ± 0.2

Calc.: 117.3 (for 2.0 $\overset{*}{C}$)

The labelled o-(2-naphthyl)benzoic acid (page 164) (120 mg.) was decarboxylated in the usual way by refluxing for 3 hours with freshly distilled quinoline (8 ml.) in the presence of copper bronze (90 mg.) in a gentle stream of CO_2-free nitrogen to give carbon dioxide, isolated and assayed as barium carbonate.

Relative molar activity x 10^{-2},

Found: 9.09 ± 0.02

Calc.: 58.65 (for 1.0 $\overset{*}{C}$)

Working up the residue from the quinoline in the usual way gave 2-phenylnaphthalene as colourless plates, m.p. 103°.

Relative molar activity x 10^{-2},

Found: 74.33 ± 0.04

Calc.: 58.65 (for 1.0 $\overset{*}{C}$)

1,2-Benzanthracene.

The mother liquors obtained following the first crystallisation of the crude chrysene from benzene were evaporated to small volume and the chrysene which separated was removed. This process was repeated three times, and the resulting mother liquors then chromatographed on acetylated cellulose (35 x 2 in.) using ethanol:benzene:water (17:4:1 v/v) as eluant; 130 fractions (each of 20 ml.) were collected. Fractions 1-40 gave 2,3-benzofluorene. Evaporation of the solvent from fractions 41-102 and recrystallisation of the residue from ethanol-acetic acid (charcoal) gave 1,2-benzanthracene as colourless needles, m.p. and mixed m.p. 157-159°.

Relative molar activity x 10^{-2},

Found: 109.2 ± 0.08

Calc.: 117.3 (for 2.0 $\overset{*}{C}$)

10,11-Benzofluoranthene.

Evaporation of fraction D gave a yellow residue which was dissolved in a small amount of benzene and chromatographed on acetylated cellulose (32 x 2 in.) using ethanol:benzene:water (17:4:1 v/v) as eluant. Fractions 31-40 (each of 100 ml.) containing 10,11-benzofluoranthene as determined by ultraviolet spectroscopy were recombined, the solvent removed, and the residue rechromatographed on acetylated cellulose (26 x 1 in.). Appropriate fractions were combined, the solvent evaporated, and the residue crystallised from ethanol. 10,11-Benzofluoranthene (12 mg.) was obtained as fine yellow needles, m.p. 162-164°. It was diluted with inactive material (36 mg.) for radiochemical assay.

Relative molar activity x 10^{-2},

Found: 110.8 ± 0.1

Calc.: 117.3 (for 2.0 $\overset{*}{C}$)

11,12-Benzofluoranthene.

Isolated following chromatography of fraction (D, 41-50) followed by rechromatography on acetylated cellulose. Recrystallisation of the product from ethanol gave 11,12-benzofluoranthene (8 mg.), m.p. 213°, which was diluted with inactive material (32 mg.) and assayed.

Relative molar activity x 10^{-2},

Found: 108.6 ± 0.08

Calc.: 117.3 (for 2.0 C*)

9.9 THE PYROLYSIS OF n-[α-^{14}C]PROPYLBENZENE

n-Propylbenzene.

The ordinary n-propylbenzene used was repeatedly washed with 10% sulphuric acid (by volume) followed by water, 10% sodium carbonate, water, dried over potassium hydroxide and twice distilled over sodium through a fractionating column. The resulting n-propylbenzene (b.p. 157-160°) had an infrared spectrum and refractive index identical with that of an authentic specimen.

(a) Synthesis of n-[α-^{14}C]Propylbenzene

[carbonyl-^{14}C]Propiophenone.

A mixture of sodium propionate-1-^{14}C (10.2 mc/mM) diluted with ordinary freshly prepared sodium propionate (total propionate, 5.85 g., 0.061 mole), benzene (20 ml.) and anhydrous aluminium chloride (33 g., 0.247 mole) was gently refluxed with stirring for 8 hours. The reaction mixture was then thoroughly cooled and carefully decomposed with ice. Concentrated hydrochloric acid (75 ml.) was then added, and the mixture again refluxed for an hour. The reaction mixture was cooled, extracted with ether (1 x 100 ml., 3 x 50 ml.), the combined ether extracts washed with water, aqueous sodium hydroxide and again with water, dried ($CaCl_2$), the solvent evaporated and the residue distilled under reduced pressure to give [carbonyl-^{14}C]propiophenone, b.p. 110°/16 mm. (6.36 g., 77.9%).

n-[α-^{14}C]Propylbenzene.

A mixture of amalgamated zinc (prepared from 25 g. of mossy zinc and 5% mercuric chloride), [carbonyl-^{14}C]propiophenone (6.36 g.) and equal portions of water and concentrated hydrochloric acid (50 ml. each) was refluxed vigorously for 8 hours. 30 ml. portions of concentrated hydrochloric acid were added every 2 hours during the heating period. The reaction mixture was then cooled, the aqueous layer decanted and after dilution with an equal volume of water, was extracted with ether (3 x 100 ml.). The combined ethereal extracts were washed with water, 10% sodium hydroxide, water, dried ($CaCl_2$), the solvent evaporated and the residue distilled at atmospheric pressure. n-[α-^{14}C]Propylbenzene was obtained as colourless oil, b.p. 158-60° (4.76 g., 69.0%).

Without further purification this n-[α-^{14}C]propylbenzene was diluted with inactive purified propylbenzene (105 ml.). The infrared spectrum and refractive index of this mixture were identical with those of pure propylbenzene. No impurities were detected by gas-liquid chromatography.

(b) Radioactivity of n-[α-^{14}C]Propylbenzene

A sample of the diluted radioactive n-propylbenzene was oxidised as previously described, using Van Slyke-Folch oxidation reagent to produce carbon dioxide which was absorbed by 4% barium hydroxide. The precipitated barium carbonate was collected and assayed.

Two such determinations of radioactivity of n-[α-^{14}C]propylbenzene gave values of relative molar activity, 8.27×10^{-2} and 7.98×10^{-2}, or an average of 8.12×10^{-2}.

(c) Degradation of n-[α-^{14}C]Propylbenzene

(i) Oxidation.

A mixture of diluted n-[α-^{14}C]propylbenzene (1 ml.), potassium permanganate (6 g.), potassium hydroxide (1 g.) and water (60 ml.) was refluxed with stirring for 3 hours. It was then acidified with 8N sulphuric acid and refluxing and stirring were continued another 2 hours. The mixture was cooled, basified with solid sodium hydroxide, filtered hot, and the residue washed with little hot water, the combined filtrates concentrated, boiled with charcoal, filtered, acidified with 18N sulphuric acid and cooled in ice. The benzoic acid that separated was purified by crystallisation from water and then sublimation. Pure benzoic acid (m.p. 120-121°) thus obtained was subjected to radioassay.

Relative molar activity x 10^{-2},

Found: 8.34 $\pm$ 0.024

Calc.: 8.12 (for 1.0 $\overset{*}{C}$)

(ii) Decarboxylation.

A mixture of the above benzoic acid (100 mg.), copper bronze (70 mg.) and freshly distilled quinoline (7 ml.) was refluxed in a current of CO_2-free nitrogen for 4 hours. The [^{14}C]O_2 evolved was absorbed in a 4% solution of barium hydroxide to give the barium carbonate which was filtered, washed with water and little acetone, dried and subjected to radioassay.

Relative molar activity x 10^{-2},

Found: 8.24 $\pm$ 0.024

Calc.: 9.12 (for 1.0 $\overset{*}{C}$)

The resulting benzene, collected in a CO_2/ethanol trap, was oxidised by the Van Slyke-Folch oxidation reagent to give barium carbonate which was collected and assayed. This was found to be practically inactive, i.e. to have activity corresponding to the background activity.

(d) Pyrolysis of n-[α-^{14}C]Propylbenzene

A 100 ml. (87 g.) sample of the diluted n-[α-^{14}C]propylbenzene was vapourised (330-350°) at 7 g./hr. and the vapour passed with oxygen-free nitrogen through a silica tube maintained at 700° as previously described. The resulting dark brown liquid tar was collected in a series of traps cooled in ice-salt, dry ice-ethanol and liquid air.

The samples of the exit gases, collected during pyrolysis, showed the presence of methane and ethylene (infrared spectroscopy).

(e) Analysis of Tar from n-[α-^{14}C]Propylbenzene

The total yield of the tar from 87 g. of n-[α-^{14}C]propylbenzene was 65.6 g. (65.0%). This was carefully distilled under reduced pressure to give five main fractions.

Fractions A (collected in dry ice/ethanol trap during pyrolysis), B (collected in ice-salt bath during distillation) and C (collected in dry ice/ethanol trap during distillation) were examined initially by gas-liquid chromatography using a Griffin and George VPC apparatus, and the major components separated using a Beckman Megachrome preparative gas chromatograph.

Fractions D and E were processed by chromatography on alumina, and on acetylated cellulose.

The results are summarised in Table 20.

(f) Isolation and Radiochemical Analysis

Benzene.

This was isolated from fractions A, B, and C using a Megachrome

TABLE 20

Fraction	B.P.	Weight (g)	Compounds isolated
A	-	1.21	Benzene, Toluene
B	28 -65°/16 mm.	16.3	Benzene, Toluene, Styrene
C	28 -65°/16 mm.	21.9	Benzene, Toluene Ethylbenzene, Styrene
D	66 -140°/16 mm.	5.7	Indene, Naphthalene
E	High boiling residue	10.4	Phenanthrene, 2,3-benzofluorene, Chrysene

preparative gas-liquid chromatograph. The infrared spectrum of the redistilled product was identical with that given by an authentic specimen. Van Slyke-Folch oxidation gave $BaCO_3$ which was collected for radioactive assay.

Relative molar activity x 10^{-2},

Found: 0.394 ± 0.0479

Calc.: 8.12 (for 1.0 $\overset{*}{C}$)

Toluene.

Isolated from fractions A, B, and C by preparative gas-liquid chromatography. Redistillation gave pure toluene; the infrared spectrum was identical with that of an authentic specimen. Van Slyke-Folch oxidation gave active barium carbonate which was assayed.

Relative molar activity x 10^{-2},

Found: 5.86 ± 0.06

Calc.: 8.12 (for 1.0 $\overset{*}{C}$)

Degradation of toluene.

Oxidation of the toluene (1 g.) in water (60 ml.) was effected by refluxing with potassium permanganate (4 g.) and sodium carbonate (0.5 g.) for 8 hours). The resulting benzoic acid was crystallised from water and then sublimed; m.p. 122-123°.

Relative molar activity x 10^{-2},

Found: 5.95 ± 0.03

Calc.: 8.12 (for 1.0 $\overset{*}{C}$)

The active benzoic acid (120 mg.) was decarboxylated by refluxing with copper bronze (100 mg.) in freshly distilled quinoline (8 ml.), in a stream of CO_2-free nitrogen for 4 hours. The gas was bubbled through a 4% solution of barium hydroxide. The resulting barium carbonate was collected and radioassayed.

Relative molar activity x 10^{-2},

Found: 5.47 ± 0.028

Calc.: 8.12 (for 1 $\overset{*}{C}$)

The resulting benzene (collected in dry ice/ethanol trap) was oxidised, converted into barium carbonate and assayed.

Relative molar activity x 10^{-2},

Found: 0.333 ± 0.01

Calc.: 8.12 (for 1 $\overset{*}{C}$)

Ethylbenzene.

This was isolated from fraction C by gas-liquid chromatography using a Beckman Megachrome unit, and its infrared spectrum was identical with that of an authentic specimen. Van Slyke-Folch oxidation gave barium carbonate which was collected for radioactive assay.

Relative molar activity x 10^{-2},

Found: 6.17 ± 0.063

Calc.: 8.12 (for 1 $\overset{*}{C}$)

Styrene.

This was collected from fractions B and C (Beckman Megachrome apparatus) and redistilled under reduced pressure, b.p. 51°/16 mm. Its infrared spectrum was identical with that of an authentic specimen. Oxidation with Van Slyke-Folch oxidising reagent gave barium carbonate which was radioassayed.

Relative molar activity x 10^{-2},

Found: 7.22 $\pm$ 0.12

Calc.: 8.12 (for 1 $\overset{*}{C}$)

Degradation of Styrene.

Oxidation of styrene (1.12 g.) in water (14 ml.) and chromium trioxide (3.7 g.) was effected by cooling to 0° and adding concentrated sulphuric acid (9 ml.) over a period of 1.5 hour, maintaining the temperature below 20°. The mixture was then refluxed gently for 2 hours and worked up as described earlier (Chapter 9.7). Recrystallisation from water gave benzoic acid, m.p. 121-122°.

Relative molar activity x 10^{-2},

Found: 4.44 $\pm$ 0.015

Calc.: 8.12 (for 1 $\overset{*}{C}$)

The [carboxy-^{14}C]benzoic acid (100 mg.) was decarboxylated by refluxing with copper bronze (80 mg.) in freshly distilled quinoline (8 ml.) for 4 hours in a stream of CO_2-free nitrogen. The exit gases were absorbed in a 4% solution of barium hydroxide and the precipitated barium carbonate collected and assayed.

Relative molar activity x 10^{-2},

Found: 4.16 ± 0.024

Calc.: 8.12 (for 1 $\overset{*}{C}$)

The resulting benzene was converted into barium carbonate by the Van Slyke-Folch oxidation method and subjected to radioassay.

Relative molar activity x 10^{-2},

Found: 0.0985 ± 0.0335

Calc.: 8.12 (for 1 $\overset{*}{C}$)

Indene.

This was separated from fraction D and purified by redistillation. Its infrared spectrum and refractive index were identical with those of an authentic specimen. Van Slyke-Folch oxidation gave barium carbonate which was assayed radiochemically.

Relative molar activity x 10^{-2},

Found: 8.20 ± 0.01

Calc.: 8.12 (for 1 $\overset{*}{C}$)

Naphthalene.

The crude naphthalene obtained from fraction D was chromatographed on alumina using hexane as eluant. The naphthalene passed through first was purified by two crystallisations from ethanol and then sublimation.

Relative molar activity x 10^{-2},

Found: 14.03 ± 0.037

Calc.: 16.24 (for 2 $\overset{*}{C}$)

Phenanthrene.

Isolated from fraction E following chromatography and rechromatography on alumina using hexane as eluant. The appropriate fractions containing phenanthrene (contaminated with small amounts of anthracene) were combined and the solvent evaporated. A portion of the residue was then refluxed with ethanol (50 ml.) and concentrated nitric acid (1 ml.) for 1.5 hours. Removal of the solvent gave a residue which was dissolved in benzene and chromatographed on alumina using hexane as eluant. Fractions containing phenanthrene were combined (u.v. spectroscopy), the solvent removed, and the residue recrystallised from ethanol to give phenanthrene, m.p. and mixed m.p. 98°.

Relative molar activity x 10^{-2},

Found: 7.31 ± 0.025

Calc.: 8.12 (for 1 $\overset{*}{C}$)

Degradation of Phenanthrene.

Oxidation of phenanthrene (0.5 g.) in glacial acetic acid (12 ml.) with hydrogen peroxide (6 ml., 50%) was carried out under conditions similar to those described in Chapter 9.7. 2,2'-Biphenic acid was twice crystallised from dilute ethanol (charcoal) and had m.p. 227-229°.

Relative molar activity x 10^{-2},

Found: 7.14 ± 0.11

Calc.: 8.12 (for 1 $\overset{*}{C}$)

Decarboxylation of active 2,2'-biphenic acid (120 mg.) with copper bronze (100 mg.) in freshly distilled quinoline (8 ml.) gave carbon dioxide, isolated and assayed as barium carbonate.

Relative molar activity x 10^{-2},

Found: 6.65 ± 0.09

Calc.: 8.12 (for 1 $\overset{*}{C}$)

The residue was acidified with hydrochloric acid, extracted with ether, removal of the solvent, and recrystallisation from dilute ethanol gave biphenyl, m.p. 66-68°.

Relative molar activity x 10^{-2},

Found: 0.421 ± 0.03

Calc.: 8.12 (for 1 $\overset{*}{C}$)

<u>Chrysene</u>.

This was isolated from fraction E. Evaporation of the solvent from appropriate fractions gave a pale yellow residue which was repeatedly recrystallised from alcohol-benzene, washed with petroleum ether, then chromatographed on alumina using hexane and benzene. Final recrystallisation from ethanol gave pure chrysene, m.p. 253°.

Relative molar activity x 10^{-2},

Found: 18.7 ± 0.052

Calc.: 16.24 (for 2 $\overset{*}{C}$)

Degradation of Chrysene.

Degradation of chrysene was carried out under conditions similar to those described in Chapter 9.7.

Labelled chrysene (214 mg.) diluted with inactive pure chrysene (428 mg.) in glacial acetic acid (27 ml.) was oxidised by refluxing with sodium dichromate (2.7 g.) for 2 hours. Recrystallisation from ethanol-benzene (1:1 v/v) gave chrysa-1,2-quinone as bright red needles, m.p. 239-240°.

Relative molar activity x 10^{-2},

Found: 18.67 ± 0.021

Calc.: 16.24 (for 2 $\overset{*}{C}$)

An intimate mixture of active chrysaquinone (500 mg.) and lead dioxide (700 mg.) was fused with potassium hydroxide (2.0 g.) and water (0.7 ml.) at 225-235°. The melt was heated at this temperature for 45 minutes, cooled and worked up as usual. Recrystallisation from dilute acetic acid (charcoal) gave pure 2-(α-naphthyl)benzoic acid, m.p. 187-189°.

Relative molar activity x 10^{-2},

Found: 13.03 ± 0.093

Calc.: 8.12 (for 1 $\overset{*}{C}$)

The labelled 2-(α-naphthyl)benzoic acid (90 mg.) was decarboxylated by refluxing with copper bronze (70 mg.) and freshly distilled quinoline (6 ml.) for 3 hours in a slow stream of CO_2-free nitrogen. The carbon dioxide formed was bubbled through a 4% solution of barium hydroxide and the precipitated barium carbonate collected and assayed.

Relative molar activity x 10^{-2},

Found: 2.512 ± 0.027

Calc.: 8.12 (for 1 $\overset{*}{C}$)

The residue from the quinoline was cooled, acidified with concentrated hydrochloric acid, extracted with ether, the solvent removed and the residue recrystallised from dilute alcohol (charcoal) gave 2-phenylnaphthalene in colourless shining flakes, m.p. 103°.

Relative molar activity x 10^{-2},

Found: 10.10 ± 0.078

Calc.: 8.12 (for 1 $\overset{*}{C}$)

<u>2,3-Benzofluorene.</u>

This was isolated from the mother liquors obtained after removal of chrysene (see page 178). Evaporation of the solvent from the mother liquors gave a residue which was dissolved in small amounts of benzene and chromatographed on acetylated cellulose using ethanol:benzene:water (17:4:1 v/v) as eluant. The fractions containing 2,3-benzofluorene were combined, the solvent removed and the residue recrystallised from ethanol (charcoal) gave 2,3-benzofluorene as colourless plates, m.p. 205-206°.

Relative molar activity x 10^{-2},

Found: 18.03 $\pm$ 0.027

Calc.: 16.24 (for 2 $\overset{*}{C}$)

10.0 THE PYROLYSIS OF β-[α-^{14}C]METHYLSTYRENE

β-Methylstyrene.

This was prepared from propiophenone in a three-step synthesis as described below. It was purified by fractional distillation. The fraction b.p. 70-72°/15 mm., n_D^{17} 1.55, n_D^{22} 1.546 (lit.[177], n_D^{16} 1.5903) contained no impurities which could be detected by gas-liquid chromatography.

(a) Synthesis of β-[α-^{14}C]Methylstyrene

[carbonyl-^{14}C]Propiophenone.

For the preparation of this compound the procedure described in Chapter 9.9 was repeated using three ampoules of [1-^{14}C]sodium propionate (0.3 mc., 6.9 mg.).

1-Phenyl[1-^{14}C]propanol.

The above ketone (6.7 g., 0.05 mole) in absolute alcohol and aqueous sodium hydroxide (5 g. in 50 ml. water) was reduced with Raney nickel alloy (5 g.) and the product worked-up as usual. 1-Phenyl[1-^{14}C]propanol (5.96 g., 87.6%) was obtained as a colourless oil, b.p. 109-110°/15 mm.

1-Chloro-1-phenyl[1-^{14}C]propane.

The above alcohol (5.96 g.) and concentrated hydrochloric acid (35 ml.) was shaken vigorously for 20 minutes and on working-up the reaction mixture in the usual way, 1-chloro-1-phenyl[1-^{14}C]propane (6.24 g., 92.17%) was obtained as a colourless liquid, b.p. 100-102°/16 mm.

β-[α-^{14}C]Methylstyrene.

Freshly distilled quinoline (6 ml.) was added to the above chloro-compound (6.24 g.), and gently refluxed for 30-40 minutes and the mixture worked-up as described for the synthesis of [1-^{14}C]styrene. β-[α-^{14}C]Methylstyrene (4.2 g., 88.9%) was obtained as a colourless liquid, b.p. 70-72°/15 mm. (lit.[177], b.p. 176-177°).

This active β-methylstyrene (4.2 g.) was then diluted with 120 ml. of purified inactive β-methylstyrene. No impurities were detected by gas-liquid chromatography.

To determine the activity of this mixture a small sample was converted to the dibromide. The dibromide of β-[α-^{14}C]methylstyrene was prepared in a similar way as described for the preparation of the dibromide of [1-^{14}C]styrene. Two crystallisations from dilute alcohol (charcoal) gave pure colourless β-[α-^{14}C]methylstyrene dibromide, m.p. 64-65° (lit.[177], m.p. 66°), which was submitted to radioactive assay (Found: relative molar activity x 10^{-2}, 8.94 ± 0.05).

(b) Degradation of β-[α-^{14}C]Methylstyrene

Oxidation.

β-[α-^{14}C]Methylstyrene (2.5 g.) was added to a solution of chromium trioxide (7.5 g.) in water (28 ml.) at 0°. Concentrated sulphuric acid (18 ml.) was added with stirring over a period of 1.5 hours, maintaining the temperature below 20°. The mixture was then refluxed gently for two hours, and worked-up as described for the oxidation of [1-^{14}C]styrene. Recrystallisation from water gave benzoic acid, m.p. 123-124°, which was submitted to radioactive assay (Found: relative molar activity x 10^{-2}, 8.01 ± 0.018).

Decarboxylation.

Benzoic acid (200 mg.) was decarboxylated by heating in freshly distilled quinoline (6 ml.) with copper bronze (150 mg.).

The resulting carbon dioxide was precipitated as barium carbonate, which was radioassayed (Found: relative molar activity x 10^{-2}, 7.92 $\pm$ 0.016).

(c) Pyrolysis of β-[α-^{14}C]Methylstyrene

Both unlabelled β-methylstyrene and β-[α-^{14}C]methylstyrene samples were pyrolysed making use of the previously described procedure. β-[α-^{14}C]Methylstyrene (63 g.) was vaporised at 9 g./hr. in a flash evaporator immersed in a Woods-metal bath kept at 320-340°, and the vapour passed with oxygen-free nitrogen through a silica tube (40" x 1") packed with porcelain chips (3/8" x 1/4") and maintained at 700°. The resulting tar was collected in a series of cold traps.

Samples of the exit gases were collected in a gas cell during pyrolysis for infrared pyrolysis.

(d) Analysis of Tar from β-[α-^{14}C]Methylstyrene

The total yield of semi-solid dark brown tar from 63 g. of β-[α-^{14}C]methylstyrene was 42.6 g. (67.6%). This was carefully distilled under vacuum to give four main fractions. Fractions (A), (B), and (C) were initially examined by gas-liquid chromatography using a Griffin and George vapour-phase chromatographic apparatus, and the major components then separated using an Autoprep model A-700 preparative gas chromatograph. Fraction (D) was examined by chromatography on alumina and acetylated cellulose. The major components were isolated as described below.

The results are summarised in Table 21.

TABLE 21

Fraction	B.P.	Weight (g.)	Compounds isolated
A	Collected in EtOH/CO_2 trap.	8.2	Benzene, Toluene, Ethylbenzene, Styrene.
B	32-55°/16 mm.	6.8	Benzene, Toluene, Ethylbenzene, Styrene.
C	100-110°/16 mm.	5.0	Benzene, Toluene, Ethylbenzene, Styrene, Indene.
D	High boiling black residue.	21.5	Naphthalene Phenanthrene Anthracene* 2,3-Benzofluorene 1,2-Benzofluorene* 1,2-Benzanthracene Chrysene 10,11-Benzofluoranthene* 3,4-Benzopyrene*

(*) identified

(e) Identification, Isolation, and Radiochemical Analysis

Methane and ethylene.

During the pyrolysis, the gaseous products were collected in a gas cell from infrared analysis. Methane was identified by its spectrum in the 7.5-8.5μ region (maxima at 7.60, 7.78, 7.81, 7.85, 7.94, 8.04, 8.10, 8.17 and 8.30μ), and ethylene by its spectrum in the 10-11μ region (maxima at 10.0, 10.23, 10.29, 10.40, 10.51, 10.73, 10.81, and 11.0μ).

Benzene.

Isolated from fractions (A), (B), and (C) by an Autoprep model A-700 preparative gas-liquid chromatograph. This was identified by its retention time, and by its ultraviolet spectrum, and confirmed by its infrared spectrum (liquid film) which showed maxima at 3.20, 3.45, 3.61, 5.21, 5.50, 6.54, 6.75, 7.20, 9.60, and 14.81 in good agreement with an authentic specimen. It was further characterised by preparing a solid dinitro-derivative. Concentrated sulphuric acid (2 ml.) was added to benzene (0.2 ml.) followed by an equal volume of concentrated nitric acid and the mixture was heated for 15 minutes on a steam bath, and then poured onto ice (15-20 g.). The pale yellow flocculent m-dinitrobenzene that separated was recrystallised from dilute methanol. It then had m.p. and mixed m.p. 86-87°, and was subjected to radioassay.

Relative molar activity x 10^{-2},

Found: 0.014 ± 0.004

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

Toluene.

This was isolated from fractions (A), (B), and (C) using an Autoprep model A-700. It was identified by its retention time, by its ultraviolet spectrum and by its infrared spectrum (liquid film) which showed maxima at 3.30, 3.43, 3.65, 5.14, 5.40, 5.55, 6.25, 6.70, 6.86, 7.22, 9.25, 9.73, and 13.74μ. This was further characterised by preparing the dinitro derivative. Recrystallisation from dilute ethanol gave pale yellow 2,4-dinitrotoluene, m.p. and mixed m.p. 70-71°, which was submitted to radioassay.

Relative molar activity x 10^{-2},

Found: 5.48 ± 0.02

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

<u>Degradation of toluene.</u>

A sample (600 mg.) was oxidised by refluxing with potassium permanganate (2.2 g.) in water (40 ml.) for 8 hours. Recrystallisation from water (charcoal) gave benzoic acid, m.p. 120°, which was submitted to radioactive assay.

Relative molar activity x 10^{-2},

Found: 5.03 ± 0.02

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

The benzoic acid (150 mg.) was decarboxylated in boiling quinoline (7 ml.) with copper bronze (100 mg.) in a stream of CO_2-free nitrogen. The resulting carbon dioxide was precipitated as barium carbonate and counted.

Relative molar activity x 10^{-2},

Found: 4.95 ± 0.02

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

The benzene collected in an ethanol/dry ice trap was oxidised by the Van Slyke-Folch oxidation method and converted into barium carbonate for radioassay.

Relative molar activity x 10^{-2},

Found: 0.116 ± 0.01

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

<u>Ethylbenzene</u>.

Isolated from fractions (B) and (C) using an Autoprep model A-700. It was identified by its retention time and infrared spectrum (liquid film), which was identical with that of an authentic specimen (maxima at 3.40, 3.76, 4.30, 5.16, 5.51, 6.21, 6.86, 7.25, 7.50, 8.50, 8.98, 9.20, 9.40, 9.72, 10.39, 11.0, 12.5, and 13.4μ). Van Slyke-Folch oxidation gave barium carbonate which was assayed radiochemically.

Relative molar activity x 10^{-2},

Found: 7.35 ± 0.07

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

<u>Degradation of ethylbenzene</u>.

A sample (124 mg.) of radioactive ethylbenzene, diluted 5 times, was oxidised to benzoic acid by refluxing with potassium permanganate (2.3 g.), sodium carbonate (0.3 g.) and water (50 ml.) for 24 hours. Recrystallisation from water gave benzoic acid, m.p. 121°.

Relative molar activity x 10^{-2},

Found: 4.10 ± 0.05

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

The active benzoic acid (120 mg.) was decarboxylated in the usual way. The resulting carbon dioxide was precipitated as barium carbonate and assayed.

Relative molar activity x 10^{-2},

Found: 4.26 ± 0.04

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

Styrene.

Isolated from fractions (B) and (C), this was identified by its retention time, and the infrared spectrum (liquid film) was identical with that of an authentic specimen (maxima at 3.20, 5.25, 5.35, 5.55, 5.75, 6.00, 6.20, 6.31, 6.48, 6.71, 6.90, 7.15, 7.50, 7.68, 7.75, 8.35, 8.50, 8.68, 9.08, 9.25, 9.75, 11.0, and 11.9μ). The identity was confirmed by preparing its dibromo-derivative. Recrystallisation from dilute ethanol gave pure styrene dibromide, m.p. 73°, which was submitted to radioactive assay.

Relative molar activity x 10^{-2},

Found: 8.70 ± 0.04

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

Degradation of styrene.

Oxidation of the styrene (0.5 g.) with chromic acid (1.8 g.) in water (8 ml.) was effected by cooling to 0° and adding concentrated sulphuric acid (5 ml.) over a period of 1.5 hours. After the addition, the mixture was gently refluxed for 2 hours and worked-up as usual. Recrystallisation from water gave pure benzoic acid, m.p. 122-123°.

Relative molar activity x 10^{-2},

Found: 5.21 ± 0.014

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

Benzoic acid (100 mg.) was decarboxylated to give carbon dioxide, which was precipitated as barium carbonate and assayed.

Relative molar activity x 10^{-2},

Found: 5.10 ± 0.018

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

Indene.

Isolated from fraction (C), this was identified by its retention time. The infrared spectrum (liquid film) showed maxima at 3.26, 3.45, 3.60, 6.25, 6.48, 6.90, 7.25, 7.40, 7.60, 7.81, 8.18, 8.35, 8.60, 9.42, 9.85, 10.55, 10.9, 11.6, 12.1, 13.0, and 13.7μ. Van Slyke-Folch oxidation gave carbon dioxide which was assayed as barium carbonate.

Relative molar activity x 10^{-2},

Found: 9.03 ± 0.01

Calc.: 8.94 (for 1.0 $\overset{*}{C}$)

Naphthalene.

This was isolated by chromatography of fractions (D, 1-12) on alumina. Two crystallisations from ethanol gave colourless plates, m.p. and mixed m.p. 80°. Its ultraviolet spectrum in 95% ethanol showed maxima at 248, 256, 267, 275, 284, and 312 mμ in good agreement with an authentic specimen. It was further characterised by preparing the picrate (m.p. 149°). Radioassay of the naphthalene and the naphthalene picrate gave values of 10.72 ± 0.023, and 10.3 ± 0.04 relative molar activity x 10^{-2}, respectively, an average of 10.51 ± 0.03.

<u>Phenanthrene.</u>

Chromatography of fraction (D, 40-90) on alumina, followed by rechromatography, gave phenanthrene contaminated with a small amount of anthracene. This was removed by refluxing with concentrated nitric acid (1 ml.) in ethanol (50 ml.) for 90 minutes. Solvent removed and the orange-yellow residue (dissolved in a small amount of benzene) was chromatographed on a column of alumina using hexane and benzene as eluants. The earlier fractions containing phenanthrene were combined, the solvent removed, and recrystallisation of the residue from ethanol gave phenanthrene, m.p. and mixed m.p. 98-100°. Its ultraviolet spectrum showed maxima at 245, 252, 276, 283, 295, 309, 318, 324, 332, 340, and 346 mμ in agreement with an authentic specimen.

Relative molar activity x 10^{-2},

Found: 8.34 ± 0.01

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

Degradation of phenanthrene.

A sample (500 mg.) of active phenanthrene in acetic acid (12 ml.) at 85° was oxidised by adding hydrogen peroxide (6 ml., 50%) over a period of 10 minutes. The mixture was heated at 85° for 1 hour, with stirring, and the warm solution poured into water (20 ml.). On working-up the reaction mixture in the usual way, 2,2'-biphenic acid (m.p. 229°) was obtained as colourless needles.

Relative molar activity x 10^{-2},

Found: 8.14 $\pm$ 0.02

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

Decarboxylation of active 2,2'-biphenic acid (110 mg.) in quinoline (6 ml.) and copper bronze (70 mg.) gave carbon dioxide which was assayed as barium carbonate.

Relative molar activity x 10^{-2},

Found: 7.85 $\pm$ 0.01

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

From the quinoline residue, biphenyl (m.p. 67°) was isolated and assayed.

Relative molar activity x 10^{-2},

Found: 0.13 $\pm$ 0.005

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

Chrysene.

This was isolated from fractions (D, 91-154). Evaporation of the solvent gave a large amount of residue, which was repeatedly triturated with alcohol, warmed, and filtered. Two crystallisations of the small sample of the colourless residue from benzene gave almost pure chrysene as shining plates, m.p. and mixed m.p. 254-255°. Its ultraviolet spectrum showed maxima at 240, 258, 269, 283, 297, 308, 320, 342, and 361 mμ.

Relative molar activity x 10^{-2},

Found: 16.30 ± 0.02

Calc.: 17.88 (for 2.0 $\overset{*}{C}$).

<u>Degradation of chrysene.</u>

Oxidation of this active chrysene (720 mg.) in acetic acid (30 ml.) with sodium dichromate (3.24 g.) gave chrysa-1,2-quinone, which was recrystallised from acetic acid (m.p. 238-240°) and assayed.

Relative molar activity x 10^{-2},

Found: 16.32 ± 0.04

Calc.: 17.88 (for 2.0 $\overset{*}{C}$).

An intimate mixture of this labelled chrysa-1,2-quinone (525 mg.) with lead dioxide (735 mg.) was fused with aqueous potassium hydroxide (2.1 g. in 0.75 ml. water) at 225-235°. Recrystallisation of the product from dilute acetic acid gave <u>o</u>-(2-naphthyl)benzoic acid as colourless needles, m.p. 190-191°.

Relative molar activity x 10^{-2},

Found: 12.72 ± 0.04

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

Decarboxylation of the above labelled o-(2-naphthyl) benzoic acid (100 mg.) in quinoline (6 ml.) and copper bronze (60 mg.) gave carbon dioxide, which was assayed as barium carbonate.

Relative molar activity x 10^{-2},

Found: 0.83 ± 0.015

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

From the quinoline residue, 2-phenylnaphthalene was isolated and recrystallised from dilute ethanol (charcoal), m.p. 102-104°.

Relative molar activity x 10^{-2},

Found: 10.47 ± 0.05

Calc.: 8.94 (for 1.0 $\overset{*}{C}$).

2,3-Benzofluorene.

The combined mother liquors obtained following repeated trituration of the crude chrysene from ethanol were evaporated to small volume, chromatographed on alumina, and then rechromatographed on acetylated cellulose using ethanol:benzene:water (17:4:1 v/v); 175 fractions (each of 30 ml.) were collected. Crude 2,3-benzofluorene was isolated from the early fractions, and after two crystallisations from ethanol (charcoal) this separated as colourless plates, m.p. and mixed m.p. 206-208°. Its ultraviolet spectrum showed maxima at 255, 263, 285, 291, 303, 318, 325, 334, and 340 mμ in good agreement with an authentic specimen.

Relative molar activity x 10^{-2},

Found: 16.02 ± 0.02

Calc.: 17.88 (for 2.0 $\overset{*}{C}$).

1,2-Benzofluorene.

Some of the 2,3-benzofluorene fractions from the above chromatography on acetylated cellulose also showed maxima at 245, 259, 264, 294, 301, 315, 329, and 343 mμ, suggesting the presence of 1,2-benzofluorene. However, it could not be isolated in sufficient quantity and purity for radiochemical analysis.

1,2-Benzanthracene.

Evaporation of the solvent from the later fractions of the above chromatography on acetylated cellulose, and recrystallisation of the residue from ethanol-acetic acid (charcoal) gave 1,2-benzanthracene as colourless needles, m.p. and mixed m.p. 158-159°. Its ultraviolet absorption spectrum had maxima 238, 255, 258, 268, 279, 289, 302, 315, 324, 340, 360, 374, and 385 mμ in good agreement with an authentic specimen.

Relative molar activity x 10^{-2},

Found: 16.77 ± 0.02

Calc.: 17.88 (for 2.0 $\overset{*}{C}$).

10,11-Benzofluoranthene and 3,4-benzopyrene.

The last fractions (155 onwards) of the main chromatography on alumina were combined, the solvent evaporated, and rechromatographed on acetylated cellulose (using ethanol:benzene:water (17:4:1 v/v) as eluant) and showed the presence of 10,11-benzofluoranthene and 3,4-benzopyrene. The ultraviolet spectrum of 10,11-benzofluoranthene had maxima at 240, 282, 295, 306, 317, 333, 347, 365, 374, and 383 mμ in good agreement with the literature.[176] Similarly, fractions containing 3,4-benzopyrene showed maxima at 254, 264, 274, 285, 298, 332, 347, 365, 380, 384, and 405 mμ in substantial agreement with the literature.[176]

Neither of these two compounds could be obtained in sufficient quantity for radiochemical analysis.

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