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THE FORMATION OF AROMATIC HYDROCARBONS AT HIGH TEMPERATURES

A THESIS
PRESENTED FOR THE DEGREE OF
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by

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CONTENTS

SUMMARY

In an attempt to study the mode of formation of polycyclic aromatic hydrocarbons in cigarette smoke, pyrolyses of stigmasterol and dotriacontane have been undertaken. Both these compounds have been isolated from tobacco, and were chosen as representatives of the various sterols and paraffinic hydrocarbons present in processed tobacco. Complex tars containing more than fifty compounds were obtained, and the mechanisms for the formation of these are discussed. The relative concentrations of some of the polynuclear hydrocarbons present in both tars have been compared with those in cigarette tar.

Many terpenes have been identified in tobacco, and such compounds are known to undergo thermal cracking to isoprene when subjected to pyrolysis. Isoprene is an important constituent of tobacco smoke, and it was thought that this compound may be a precursor to the polycyclic hydrocarbons found in cigarette tars. The pyrolysis of isoprene at 700° was therefore investigated and many aromatic compounds were identified in the resulting tar. Mechanisms for the formation of many of these compounds are discussed.

The pyrolysis of phenanthrene at 700° and 850° has given tars in which seven and thirteen aromatic compounds respectively have been identified. Mechanisms for the formation of these compounds are postulated, with special reference to the formation of anthracene by rearrangement of the intermediate tetrahydrophenanthrene.

Finally, the pyrolysis of anthracene has been investigated at 700° and 950°. The tar produced at 700° contained ten polycyclic hydrocarbons, all of which were probably formed by the scission of carbon-hydrogen bonds to give anthryl radicals, followed by further reaction with anthracene. The tar produced at 950° was much more complex and twenty five aromatic hydrocarbons were identified. It is suggested that phenanthrene, the major constituent of the tar, is formed *via* tetrahydroanthracene and tetrahydrophenanthrene. It is also suggested that the complexity of the tar is due to scission of the saturated carbon-carbon bonds in the hydrogenated intermediates, followed by further reaction of the fragments.

STATEMENT

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

Jillian K. Donnelly.
July, 1965.

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to Professor G. M. Badger, to whom this work owes its inception and direction, and to Dr. T.M. Spotswood, whose previous experience in this field was invaluable.

I should also like to thank Mr. W.W. Reid, Chief Scientist of W.D., and H.O. Wills (Australia) Ltd., for gifts of dotriacontane and a mixture of long-chain hydrocarbons isolated from tobacco; Dr. K. Lang for gifts of samples of benzonaphthofluoranthenes; Dr. J. Novotny for many helpful practical suggestions; and other members of this Department for their ready assistance whenever required.

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INTRODUCTION

During recent years evidence has accumulated inferring a causal relationship between cigarette smoking and lung cancer. This inference is based on statistical, clinical and laboratory evidence.[1, 2] The report of the Advisory Committee to the Surgeon General of the U.S. Public Health Service[3] states categorically: "Cigarette smoking is causally related to lung cancer in men; the magnitude of the effect of cigarette smoking far outweighs all other factors". Accepting this causal hypothesis, it can be said that cigarette smoking causes lung cancer, either through the direct carcinogenic action of smoke, or by a more indirect mode of action, such as making the individual susceptible to some other specific carcinogenic agent in the environment,[4] *e.g.*, atmospheric pollution.[5]

There is some evidence supporting the view that atmospheric pollution may be an important factor in the causation of lung cancer. For example, a number of independent workers have established that urban dwellers have a higher incidence of lung cancer than rural inhabitants.[6] This is consistent with results of Commins,[7] who found that the concentration of polycyclic hydrocarbons, including 3,4-benzopyrene, was much lower in rural than in urban areas. These facts indicate that lung cancer may be caused, at least to some extent, by the action of various carcinogenic hydrocarbons in the atmosphere.

The polycyclic aromatic hydrocarbons present in the atmosphere are produced by the incomplete combustion of various organic materials; the most common sources are smoke from chimneys and exhaust gases from motor vehicles. Benzene extracts of vehicular exhaust tars have been shown to produce skin cancers in mice,[8] and the analysis of such tars has shown the presence of 3,4-benzopyrene and other carcinogenic hydrocarbons on several occasions. The most complete analysis of the exhaust products from an automobile operating under normal city driving conditions is that reported by Hoffmann and Wynder,[10] and it seemed of interest to compare their results with those obtained by the controlled pyrolysis of petrol, under nitrogen, at 700°.[11] The two tars were found to be remarkably similar; this similarity was of great importance, for mechanisms postulated for pyrolytic reactions (carried out at 700° under nitrogen) can now logically be extended to cover reactions involving incomplete combustion of complex materials.

Despite the evidence concerning the relationship between atmospheric pollution and lung cancer, it is generally accepted that lung cancer is caused through the direct carcinogenic action of cigarette smoke.[3] However there are two plausible ways in which the effects of cigarette smoking and atmospheric pollution may reinforce each other.

The carcinogenic hydrocarbons in the atmosphere are adsorbed on carbon particles[12(a)] and thereby inactivated: Cooper[12(b)] suggests that non-aqueous solvents, such as pyridine, present in tobacco smoke, may elute these carcinogens from the carbon particles retained in the lungs, thus bringing them into an active state. It has also been suggested that the carcinogens in the atmosphere may act as tumour initiators, and that tumours are produced as a result of the promoting activity of the cigarette tar. The promoting action of tobacco smoke condensate has in fact been demonstrated by Gillhorn.[13]

The direct carcinogenic activity of tobacco smoke has been demonstrated by the production of tumours following application of the condensate to the skin of mice and rabbits, and by subcutaneous injection in rats.[14] The identification of 3,4-benzopyrene and other polycyclic carcinogens in tobacco smoke has been reported so often that the individual papers are too numerous to list. The controlled pyrolysis of tobacco extracts[15] has also given a carcinogenic tar containing polycyclic aromatic hydrocarbons. There have been several suggestions regarding the actual precursors of such compounds in tobacco; Lam[16] investigated the pyrolysis of paraffinic hydrocarbons, and more recently, terpenes[17] have been considered to be important precursors to the carcinogenic hydrocarbons. However, Gilbert and Lindsey[18] have investigated the thermal decomposition of many of the major constituents of tobacco, including lignin, cellulose, pectins, etc., and found that 3,4-benzopyrene was present in the tars obtained from each compound. Indeed, it now seems likely that the incomplete combustion of almost any organic compound would give tars containing polycyclic aromatic hydrocarbons. It thus appears that these compounds arise in cigarette smoke as a result of the incomplete combustion of tobacco as a whole; no individual constituent is alone responsible for their formation. Consequently the pre-extraction of tobacco to remove certain compounds[19] seems futile, as there are so many other constituents present which would produce the polycyclic carcinogens at the high temperatures involved in smoking.

It might be stressed at this stage that the pyrolyses of all types of tobacco produce carcinogenic hydrocarbons, and that these compounds have been identified in the smoke condensates of cigarettes, pipe tobacco and cigars. However, results of more than twenty studies show conclusively that cigar and pipe smokers run a lesser risk of developing lung cancer than cigarette smokers, although the risk is greater than for non-smokers.[20] It is generally agreed that this is due to the fact that cigar and pipe smokers rarely inhale the tobacco smoke. Statistical data from Hammond and Horn indicate that the very heavy smoker has a sixtyfold increase in the risk of developing lung cancer over the non-smoker.

Because of the evidence pointing to the causation of lung cancer by the direct carcinogenic action of cigarette smoke, it is of great importance to determine what compounds are responsible for this carcinogenicity, and also their mode of formation from tobacco. It has been estimated that the total concentration of known carcinogenic hydrocarbons cannot account for more than 3% of the biological activity of cigarette smoke condensate.[22] It is apparent then that additional unknown carcinogens or cocarcinogens must be present in the tar.

In an attempt to find the important carcinogenic fractions of cigarette smoke condensate, Wynder and Hoffmann[22] divided the tar into various fractions which were then applied individually to the test animals.

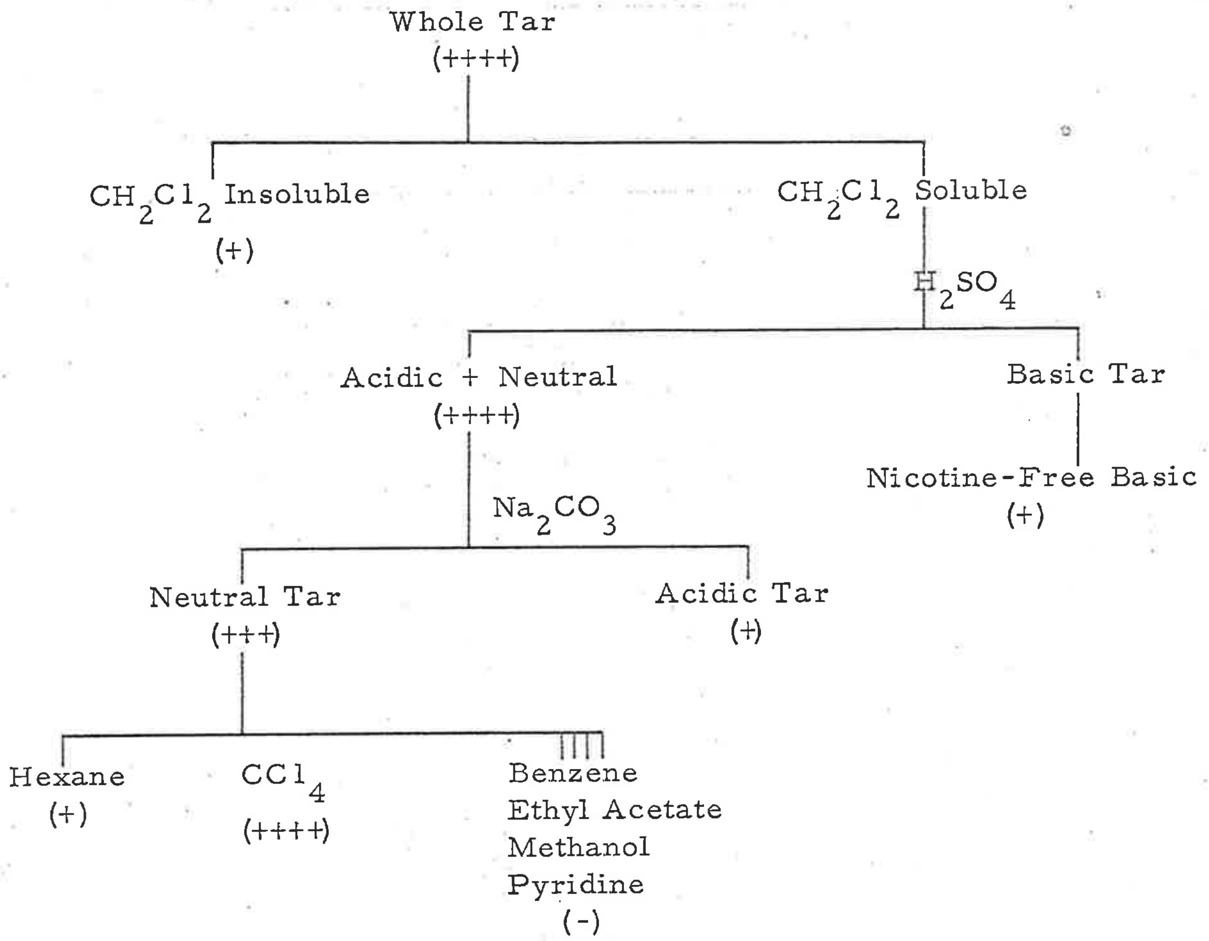


Fig. 1. Cigarette Tar Fractionation
(+) Relative Biological Activity

It will be noted that most of the activity was confined to the acidic and neutral tar. However, the sum of the activities of the isolated fractions may be considerably less than that of the total tar, since some components, although noncarcinogenic themselves, may act as cocarcinogens or promoters. There has been much speculation regarding the importance of the polycyclic hydrocarbons in cigarette tar because of their low concentrations and apparent inability to account for any significant degree of carcinogenic activity of the tar. However Wynder and Hoffmann[22] have carried out an experiment which demonstrates conclusively the fundamental importance of these carcinogens in cigarette tar. They removed the carbon tetrachloride fraction (which contained the polycyclic hydrocarbons) and recombined the remainder of the condensate. Biological testing over fifteen months revealed almost 100% reduction in the number of tumours observed. It is unlikely that the material lost any biological activity during the chemical separation, since in a previous study,[23] the tar was separated and recombined with no resultant loss in activity.

From these experiments, it appears that the carcinogenic aromatic hydrocarbons act as initiating agents, and certain other constituents, from both the neutral and acidic fractions, act as promoters or cocarcinogens. The term "cocarcinogen" was introduced by Shear[24] in 1938, and describes a noncarcinogenic agent which is capable of greatly enhancing the activity of a carcinogen. There is considerable evidence for the presence of cocarcinogens in cigarette smoke condensate. The phenolic fraction is important in this respect, since if this fraction is removed from tobacco smoke tar, the remaining condensate loses virtually all of its short-term activity.[22] A number of phenolic constituents have been characterised in cigarette smoke,[25] phenol itself being present in the highest concentration; the phenolic fraction constitutes 9-10% of tobacco smoke condensate, and approximately 10% of this fraction are phenols. The capacity of phenol to produce tumours in mice in areas previously treated with subcarcinogenic quantities of dimethylbenzanthracene has been demonstrated many times in mice of various sources and strains.[26] No tumours were observed if the initial treatment with dimethylbenzanthracene was omitted. Boutwell and Bosch[26] found that certain structural requirements were necessary for the retention of this carcinogenic activity of phenolic compounds. For example, at least one unsubstituted position ortho to the phenolic group was found to be essential, and although monomethyl substituted phenols retained full activity, the presence of larger aliphatic groups resulted in a decrease in activity. Hoffman and Wynder[22] have confirmed Boutwell's results of the promoting activity of phenol using 9,10-dimethyl-1,2-benzanthracene and 3,4-benzopyrene as initiators. Further evidence of the cocarcinogenic nature of the phenolic fraction has been provided by Roe,[27] who demonstrated the promoting activity for this whole fraction using dimethylbenzanthracene as initiator.

Both oleic and lauric acids are potent tumour promoters for mouse skin when applied with sufficient frequency,[28] and such long-chain acids are known to be present in the acidic fraction of cigarette smoke condensate.[29] A further observation which may be of considerable importance in determining the total activity of the tar is that some polycyclic aromatic hydrocarbons, themselves either very weak or inactive carcinogens, can initiate tumours under the influence of noncarcinogenic promoters. For example, 1,2-benzanthracene, which is present in significant quantity in cigarette smoke, is almost inactive by itself, but can initiate carcinogenesis under the influence of croton oil as promoter.[3]

Besides promoting agents present in the tar, there may be unknown carcinogenic compounds, particularly aromatic polycyclics, contributing to the observed activity. Recently it was found that 3,4:8,9-dibenzopyrene and 3,4:9,10-dibenzopyrene, both present in cigarette smoke, are active carcinogens,[31,32] and there may be many more such compounds which are carcinogenic, but as yet, have not been adequately tested. Included in this group is the large number of alkyl-substituted hydrocarbons present in cigarette tars. Many of these may be active carcinogens, for it is known that an alkyl substituent in a favourable position in 1,2-benzanthracene, for example, gives rise to a potent carcinogen,[24,33] although the parent compound itself is almost inactive.

One final factor in the discrepancy between the biological activity of the tar and the concentration of known carcinogens is the underestimation of polynuclear hydrocarbons in analysis. Hoffman and

Wynder[34] estimated the loss of 3,4-benzopyrene during separation to be of the order of 40%, by calculating the loss of a known amount of 3,4-benzopyrene-5-^{14}C, added prior to the separation. They assumed that other polycyclics would suffer similar losses; in fact, Commins[35] has demonstrated that losses may be considerably greater than this for some compounds, especially those of lower molecular weight than 3,4-benzopyrene.

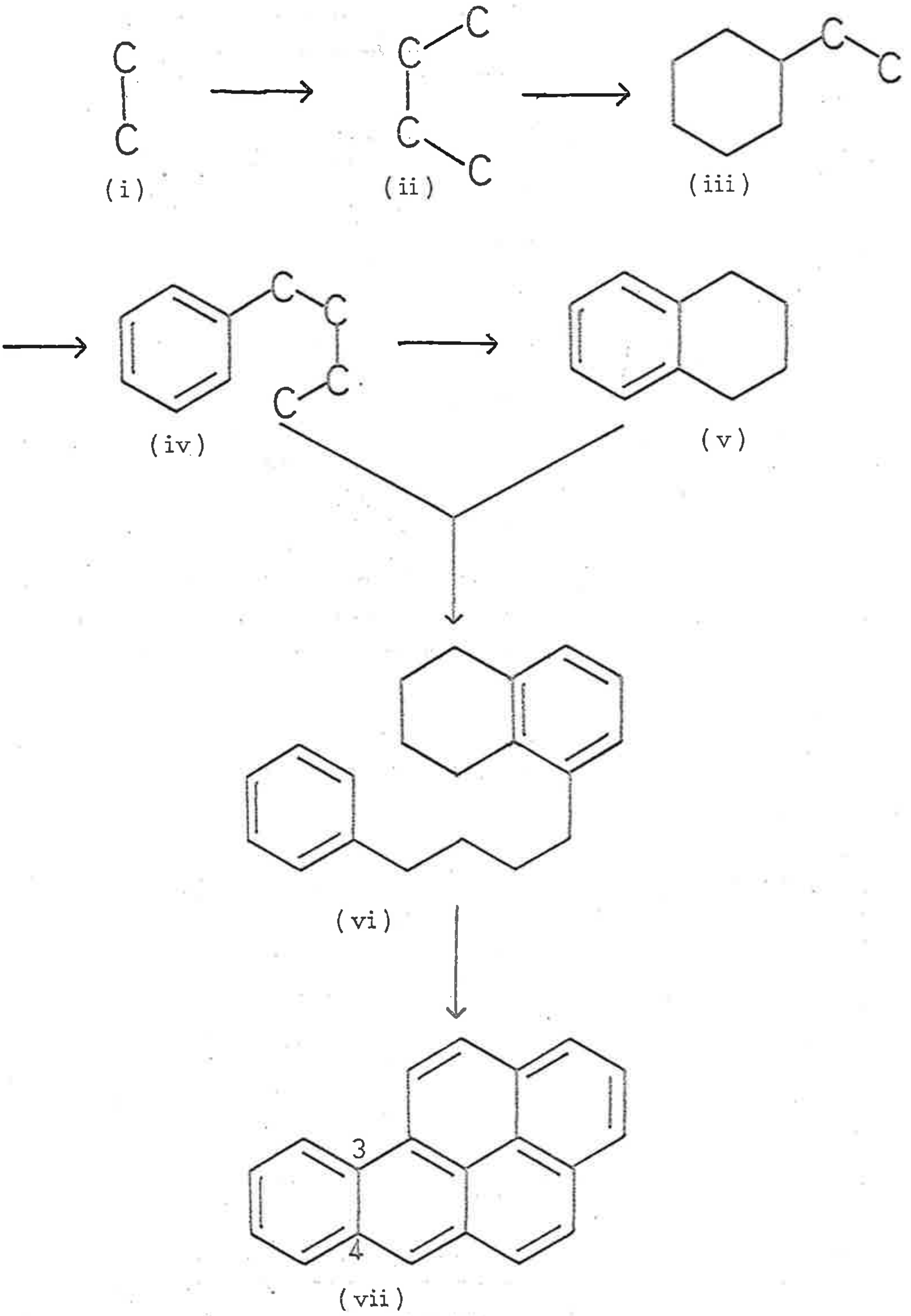
It seems therefore that there are many factors contributing to the total activity of cigarette tar, and the activities of individual constituents are not additive. It appears that the carcinogenic aromatic hydrocarbons, although present in relatively low concentrations, act as initiating agents and are therefore responsible, either directly or indirectly, for the carcinogenic nature of the tar.

	INITIATOR	+	PROMOTER	⟶	CANCER
1.	Carcinogenic hydrocarbons		Phenols		
2.	Hydrocarbons e.g. 1,2-benzanthracene which are initiators only under the influence of a promoter.		Long-chain acids.		
3.	Alkyl-substituted polycyclics.		Unknown or unidentified compounds.		
4.	Unknown or unidentified compounds.				

It is interesting to note that compounds in concentrations as low as 1 microgram can act as initiators in mice; and a single application of 1 microgram of initiator, such as 3,4-benzopyrene, followed by repeated applications of a promoting agent will induce tumours.[36,37] The concentration of initiators in cigarette smoke condensate is therefore of primary importance in determining the total activity of the tar.

In order to study the processes involved in the formation of polycyclic aromatic hydrocarbons during smoking, individual constituents of processed tobacco have been selected, and the pyrolysis of these materials investigated. This work is part of a much more extensive investigation of the mode of formation of aromatic hydrocarbons at high temperatures which has been conducted by a number of workers in this Department during the past eight years.

The observation that the carcinogenic hydrocarbons which occur in human environment are formed only at high temperatures led to the inception of this work. As a working hypothesis, it was assumed initially[38] that 3,4-benzopyrene (vii) may be formed by the series of reactions (i - vii) and that cracking, diene syntheses, dehydrogenations and cyclodehydrogenations would be the most important reactions.


(i)
(ii)
(iii)
(iv)
(v)
(vi)
3
4
(vii)

This hypothesis implied that 3,4-benzopyrene would be formed by the pyrolysis of any of the intermediate compounds; however, it did not presuppose that complex molecules need necessarily break down to a two-carbon unit before resynthesis. To test this hypothesis, several possible intermediate compounds$^{\text{Table 1}}$ have been pyrolysed at 700°, and the resulting tars analysed. The pyrolyses of some related compounds have also been studied, and much information concerning the mode of formation of the polycyclic hydrocarbons has been obtained. To provide more rigorous confirmation of many of the mechanisms proposed, and especially that suggested for the formation of 3,4-benzopyrene, some suitable precursors labelled with carbon-14 (compounds marked with an asterisk in Table 1) have been subjected to pyrolysis. The compounds isolated from the resulting tars were submitted to radiochemical assay. The activities were calculated as relative molar activities,[39] which are linearly proportional to the number of labelled carbon atoms per molecule. It has therefore been possible to verify conclusively certain mechanisms, and to discount others, by calculating the theoretical activity of a compound expected by a certain route, and comparing the experimentally observed activity with the calculated value. Chemical degradation of the labelled compound to determine the precise positions of radioactivity has also proved invaluable in mechanistic studies. It must be emphasised that many polycyclic compounds arise as a result of more than one mechanism, but the major route can often be determined on the basis of the radiochemical analyses.

TABLE 1

Compounds Pyrolysed at 700°

Type	Possible Intermediate	Other Compounds
C_2	Acetylene[40]	
C_4	Butadiene[41]	Isoprene[42]
C_6		Benzene[43]
C_6-C_1		Toluene[44]
C_6-C_2	Vinylcyclohexene[45]	
	Styrene*[46,47]	
	Ethylbenzene*[44,48]	
C_6-C_3		Indene*[49,50]
		Propylbenzene[44]
C_6-C_4	Butylbenzene*[44,51]	Naphthalene*[52]
	Tetralin*[53,54]	
	Phenylbutadiene[55]	
C_6-C_4; C_6-C_4	Phenylbutylnaphthalene[56]	
C_5		2,2',4-Trimethylpentane[57]
C_{10}		n-Decane[58]
C_{32}		Dotriacontane[59]

*Compounds labelled with C^{14}.

As a result of these studies it must be concluded that the mode of formation of 3,4-benzopyrene represented by (i-vii) is an important route to this compound at high temperatures. Mechanisms of the formation of other polycyclic hydrocarbons have also been established with much certainty, and these will be discussed in the following chapters of this thesis.

It was decided initially to pyrolyse the various compounds at 700°, because previous results had indicated that carcinogenic tars were produced from paraffins,[60] shale oils[60] and petroleums[61] at approximately this temperature. However 700° is considerably below the temperatures recorded for coal tar pyrolysis, the internal combustion engine and for the burning cigarette. It therefore seemed important to determine the optimum temperatures for the formation of polycyclic aromatic hydrocarbons, particularly 3,4-benzopyrene; n-butylbenzene was consequently pyrolysed over a range of temperatures from 300° to 900°, and the resulting tars analysed.[62] The yield of each hydrocarbon was plotted against the temperature of pyrolysis, and the optimum temperature for the formation of each was obtained. The optimum temperatures for the formation of the polycyclic compounds were all close to 700°; the range being from 660° for 1,2-benzanthracene to 740° for the more highly condensed compounds such as the benzofluoranthenes, and 2,3-(o-phenylene) pyrene.

Several suggestions have been advanced on the possible precursors of polycyclic aromatic hydrocarbons in burning tobacco, but no mechanisms for their formation have been proposed. In an attempt to study the mode of formation of these compounds during smoking, some individual constituents of processed tobacco, which seemed probable precursors of aromatic hydrocarbons, have been pyrolysed at 700°. The resulting tars have been analysed, and mechanisms for the formation of the compounds obtained have been postulated. Table 2 lists the known carcinogenic polynuclear hydrocarbons that have been identified in cigarette smoke condensate, and also in the tars produced by the pyrolyses of stigmasterol, dotriacontane and isoprene.

TABLE 2

Carcinogenic Hydrocarbons detected in cigarette smoke.

Compound	Relative Carcinogenic Activity
3,4-Benzopyrene	+++
3,4:8,9-Dibenzopyrene	+++
3,4:9,10-Dibenzopyrene	+++
1,2:4,5-Dibenzopyrene	+++
1,2:5,6-Dibenzanthracene	+++
3,4-Benzofluoranthene	++
10,11-Benzofluoranthene	++
Chrysene	+
1,2-Benzanthracene	+
1,2-Benzopyrene	+
1,12-Benzofluoranthene	+
11,12-Benzofluoranthene	+

Relative Carcinogenic Activity to Mouse Skin:

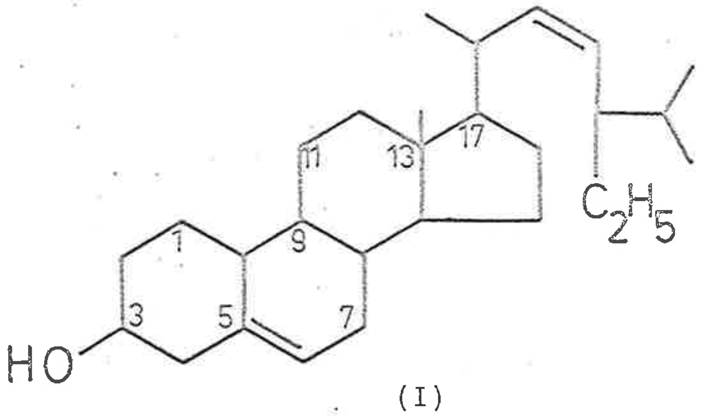
+++ high ++ moderate + weak to very weak.

CHAPTER 1

PYROLYSIS OF STIGMASTEROL

Tobacco is a complex mixture of hydrocarbons, alcohols, esters, sterols, aldehydes, ketones, acids, phenols, alkaloids, carbohydrates and other materials. During smoking, many of these materials would be expected to undergo pyrolysis to give tars containing polycyclic aromatic hydrocarbons, including those possessing carcinogenic activity. It is not surprising therefore, that tobacco smoke condensates have been found to be carcinogenic for several animal species,[14,63] and the presence of 3,4-benzopyrene and other carcinogens has been demonstrated on many occasions.[64,65]

In an attempt to study the processes which occur during smoking, individual constituents of processed tobacco have been selected and the pyrolysis of these materials investigated. Tobacco contains a number of sterols, the most important being stigmasterol (I), and β- and γ- sito sterol,[29] all 3β -hydroxy sterols possessing $\Delta^{5,6}$ unsaturation. The average level of sterols in various grades and types of tobacco is of the order of 0.29% of the dry weight of the tobacco leaf.[66] Stigmasterol has been chosen as the representative of this group, and its pyrolysis at 700° has been examined. The other members of this group would be expected to give essentially the same products in comparable yields on pyrolysis.



(I)

TABLE 1.1

COMPOSITION OF TAR FOLLOWING PYROLYSIS OF STIGMASTEROL AT 700°

Fraction	Compound	Percentage (w/w) in Tar	Method of Identification*
-	Methane	P≠	i.r.
-	Ethylene	P	i.r.
-	Propylene	P	i.r.
-	Acetylene	P	i.r.
(a)	Isoprene	0.002	r.t.
(a)	Cyclopentane	0.231	r.t.
(a)	Pentane	0.007	r.t.
(a)	Hexane	P	r.t.
(a)	Cyclohexane	0.042	r.t.
(a)-(c)	Benzene	11.68	r.t.,i.r.,u.v.
(a)-(d)	Toluene	7.91	r.t.,i.r.,u.v.

(c)	Ethylbenzene	0.105	r.t.
(b)-(d)	*p*, *m*-Xylene	1.12	r.t.,i.r.
(b)-(d)	Styrene	1.71	r.t.,i.r.
(d)	α-Methylstyrene	0.09	r.t.
(d) (e)	Indene	1.36	r.t.,i.r.
(e)	Tetralin	0.14	r.t.,i.r.
(e),2,3	Naphthalene	12.35	r.t.,u.v., mixed m.p.
(e),2,3	1-, 2-Methylnaphthalene	3.96	r.t.,u.v.
(e),3	Biphenyl	0.67	r.t.,u.v., mixed m.p.
3, 4	Acenaphthylene	1.6	u.v.
4, 5	Fluorene	0.9	u.v.
5-15	Phenanthrene	12.1	u.v., mixed m.p.
10-15	Alkylphenanthrenes	2.1	u.v.,n.m.r.
7-16	Anthracene	4.2	u.v., mixed m.p.
12-20	Pyrene	6.0	u.v., mixed m.p.
18-20	Alkylpyrene	P	u.v.
15-24	Fluoranthene	4.1	u.v., mixed m.p.
21-23	Alkylfluoranthene	P	u.v.
22-25	2,2'-Binaphthyl	0.2	u.v.
22-26	1,2-Benzanthracene	0.08	u.v.
23-28	1,2-Benzofluorene	0.37	u.v.
24-30	2,3-Benzofluorene	0.49	u.v.
26-38	Chrysene	13.2	u.v., mixed m.p.

Alkylchrysene	P	u.v., n.m.r.
10,11-Benzofluoranthene	0.07	u.v.
1,2:5,6-Dibenzanthracene	0.04	u.v.
1,2-Benzopyrene	0.28	u.v., mixed m.p.
Perylene	0.09	u.v.
3,4-Benzopyrene	0.59	u.v., f.s., mixed m.p.
Alkyl-3,4-Benzopyrene	P	u.v.
11,12-Benzofluoranthene	0.11	u.v.
3,4-Benzofluoranthene	0.13	u.v., mixed m.p.
1,12-Benzoperylene	0.08	u.v.
Picene	5.10	u.v., mixed m.p.
2,3-(_o_-Phenylene) pyrene	0.40	u.v., m.p.
Anthanthrene	0.09	u.v.
1,2:4,5-Dibenzopyrene	0.02	u.v.
3,4:8,9-Dibenzopyrene	0.01	u.v., f.s.
3,4:9,10-Dibenzopyrene	0.04	u.v., f.s.
Losses, unidentified material, water, etc.		

* r.t. - retention-time ratio
i.r. - infrared spectroscopy
u.v. - ultraviolet spectroscopy
f.s. - fluorescence spectroscopy
n.m.r. - nuclear magnetic resonance spectroscopy.

†P - present in tar, but yield undetermined.

RESULTS AND DISCUSSION

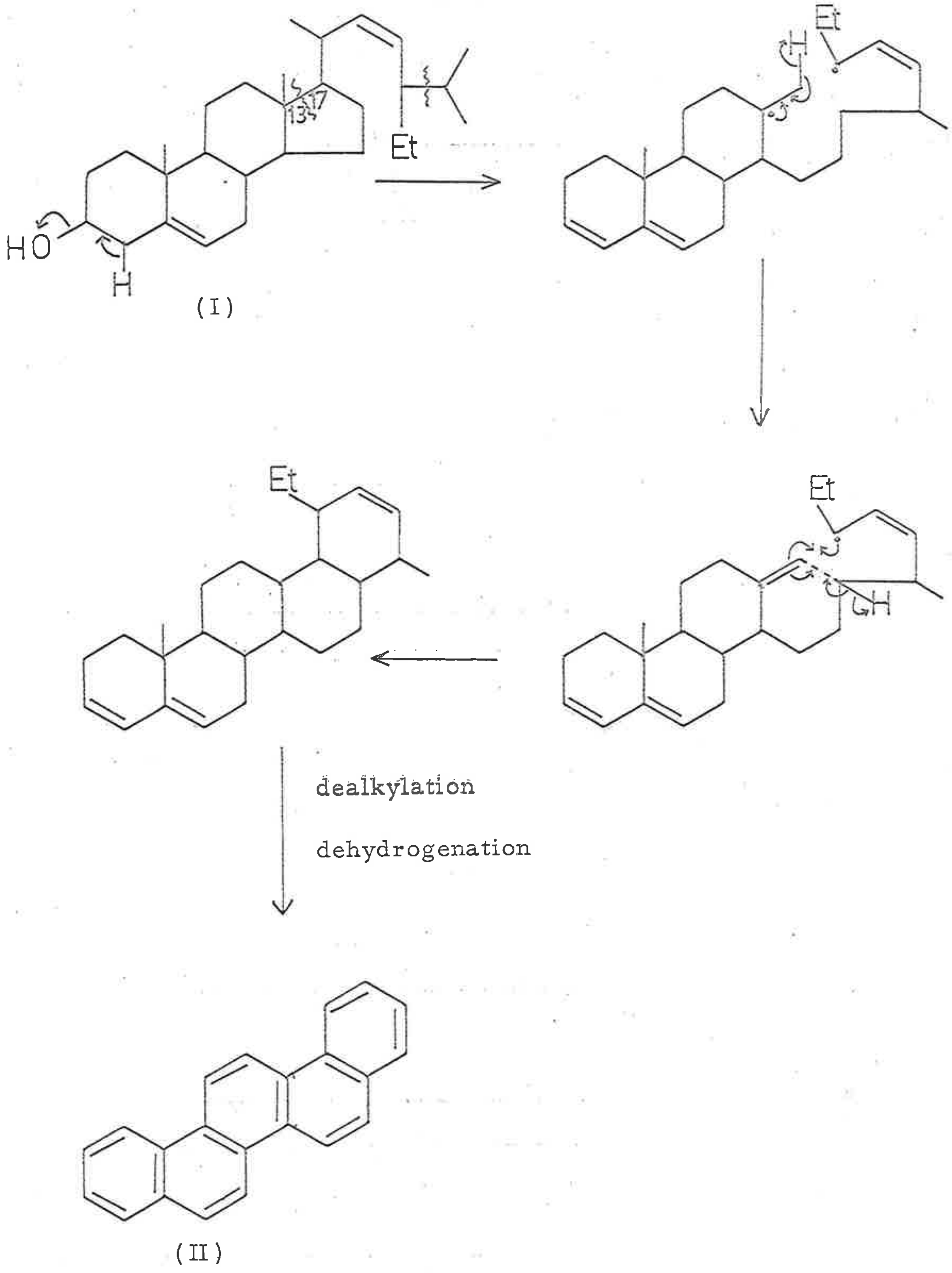
The pyrolysis was carried out by passing the stigmasterol vapour, with nitrogen, through a silica tube packed with porcelain chips at 700°. Methane, ethylene, propylene and acetylene were detected in the exit gases, and the tar (obtained in 23% yield) was collected and analysed by chromatography and spectroscopy. The various compounds identified have been listed in Table 1, which also gives the percentages of each in the tar and the methods of identification used. It will be seen that benzene, naphthalene, phenanthrene and chrysene were the major constituents.

The mechanisms of formation of many aromatic hydrocarbons produced by the pyrolysis of simple compounds have been reviewed by Badger.[67] The compound initially breaks down under the pyrolytic conditions to smaller fragments which subsequently undergo resynthesis to the polycyclic aromatic hydrocarbons. The mechanism of formation of many of the polynuclear compounds from stigmasterol, however, would not be expected to involve pyrosynthesis from small degradation fragments. As there are several rings already present in the molecule, initial cracking into small radicals, followed by recombination and cyclisation, would be relatively unimportant. On the other hand, simple dehydrogenation of the expected polynuclear primary radicals could lead to many of the polycyclic aromatic compounds identified in the tar.

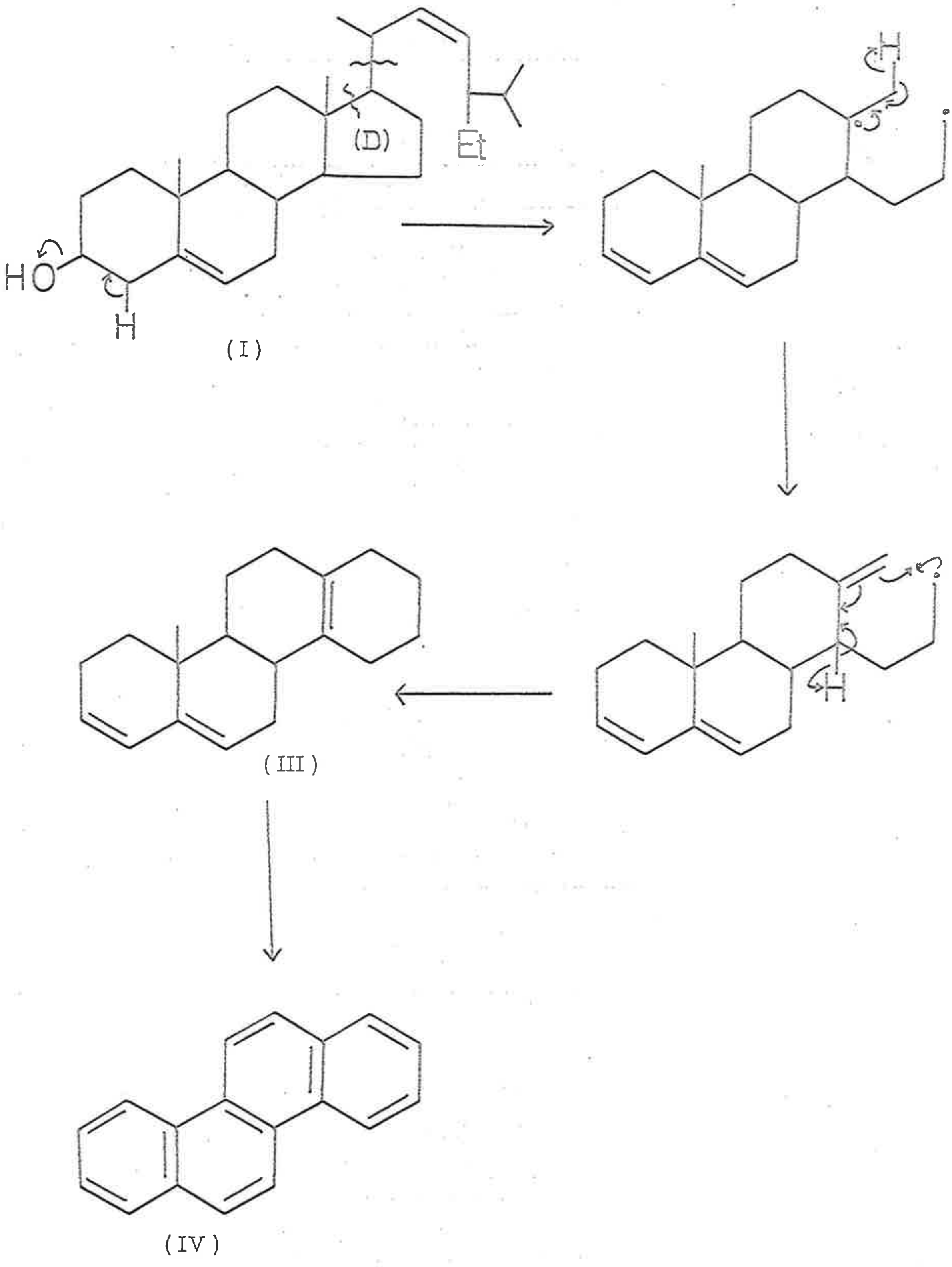
The five-membered ring (D) is the most highly strained in the steroid system, and would therefore be expected to break with more facility than the six-membered rings. It seems likely that the 13-17 carbon-carbon bond would undergo scission most readily, as C_{13} is tetrasubstituted and C_{17} trisubstituted. Scission of the 3-hydroxyl group would also be expected to occur fairly readily, and combination of this with a hydrogen radical in the reaction zone would yield water, which was in fact found in the tar. Thus picene(II)(5.1% of the tar) could conceivably be formed as shown in equation (1.i).

Chrysene (IV) is probably formed in a similar way to picene. The formation of chrysene requires complete scission of the side-chain : this must occur very readily as chrysene was obtained in almost three times the yield of picene. Indeed, chrysene was found to be the major compound formed in this pyrolysis.

The migration of methyl groups in steroid reactions has been reported on many occasions,[68] and the isomerisation of alkyl groups has also been observed during pyrolysis of aromatic hydrocarbons.[69] It would not be surprising if the methyl group on C_{13} migrated to C_{14} at the high temperatures involved. This provides another possible route

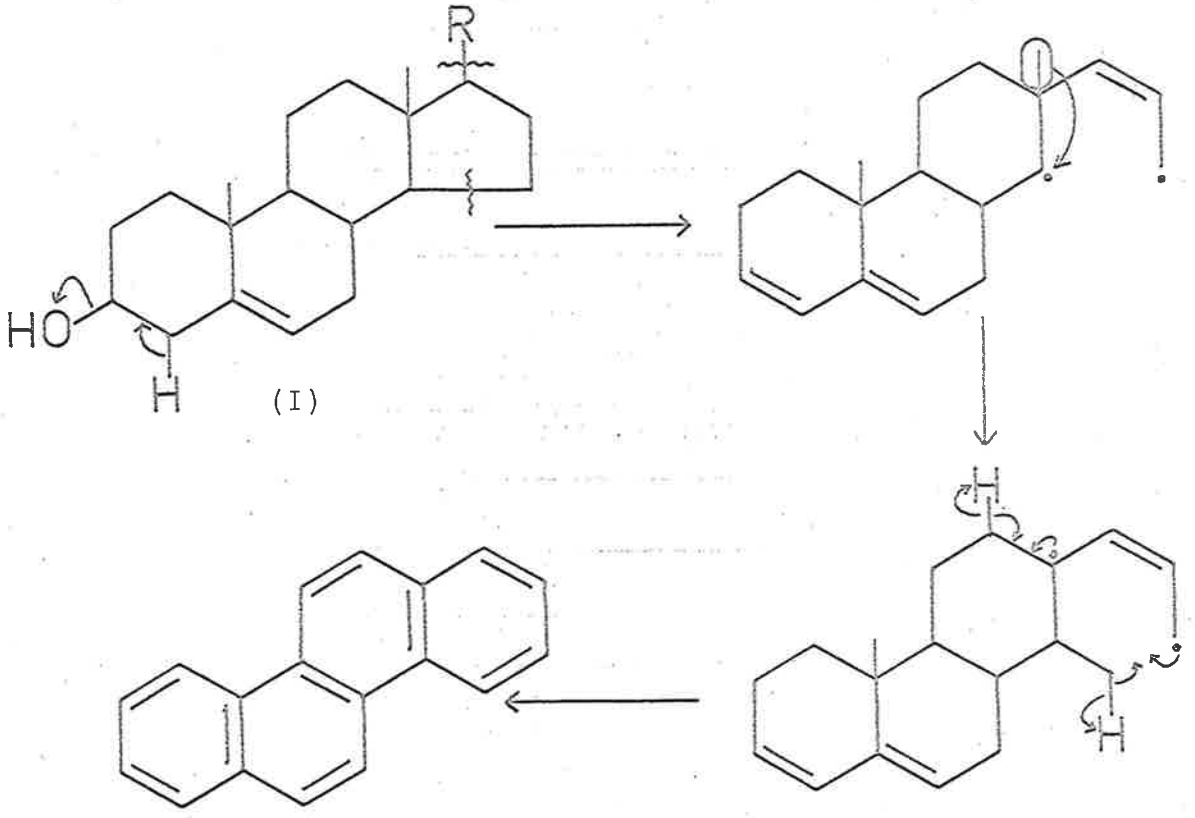


equation (1.i)



equation (1.ii)

to the formation of a six-membered ring (D). The route leading to chrysene is shown in equation (1.iii), and picene could be formed in an analogous way, but this alternative mechanism does not seem as probable as that outlined in equations (1.i) and (1.ii).

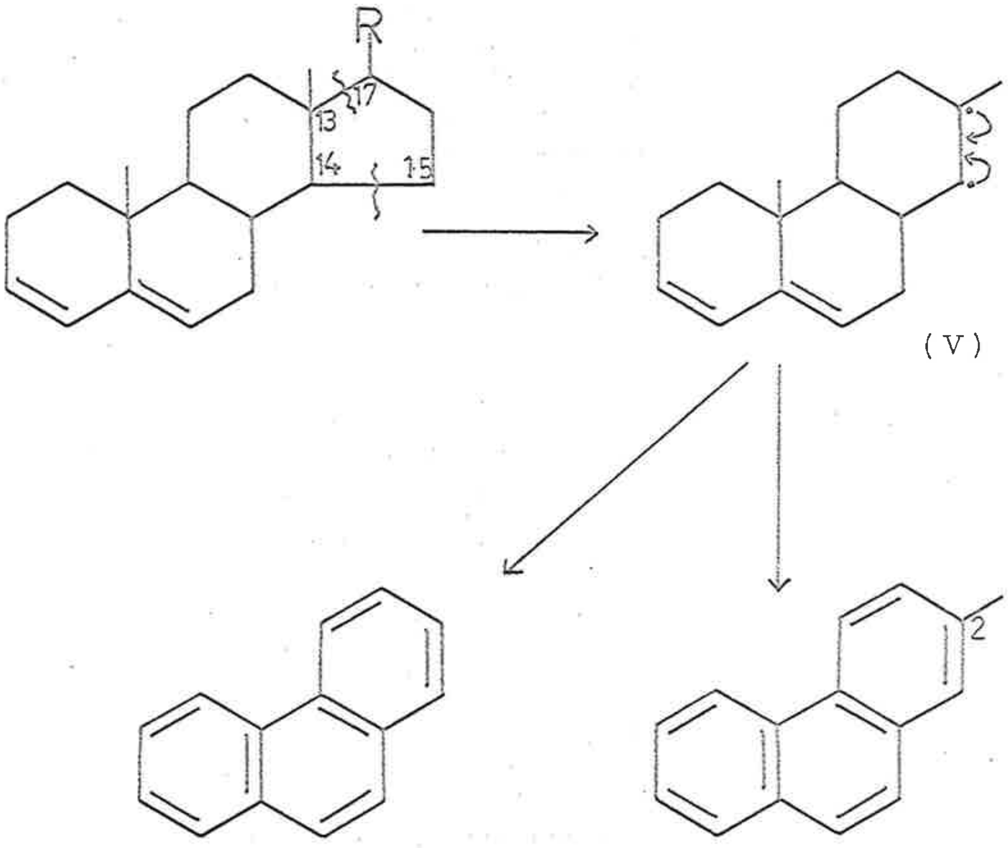


(I)

(IV)

equation (1.iii)

Phenanthrene (VI) was also formed in considerable yield; this could be formed as a result of scission of the 13-17 and 14-15 carbon-carbon bonds, as in equation (1.iv). Several substituted phenanthrenes were also found in the tar. These were not characterised but would most likely include the 2-methyl- (VII), 1,2-dimethyl- and 1,2-c-penteno-derivatives. Alkyl derivatives of pyrene, chrysene, fluoranthene and 3,4-benzopyrene were also detected in the tar, but not in as high a yield as the substituted phenanthrenes.

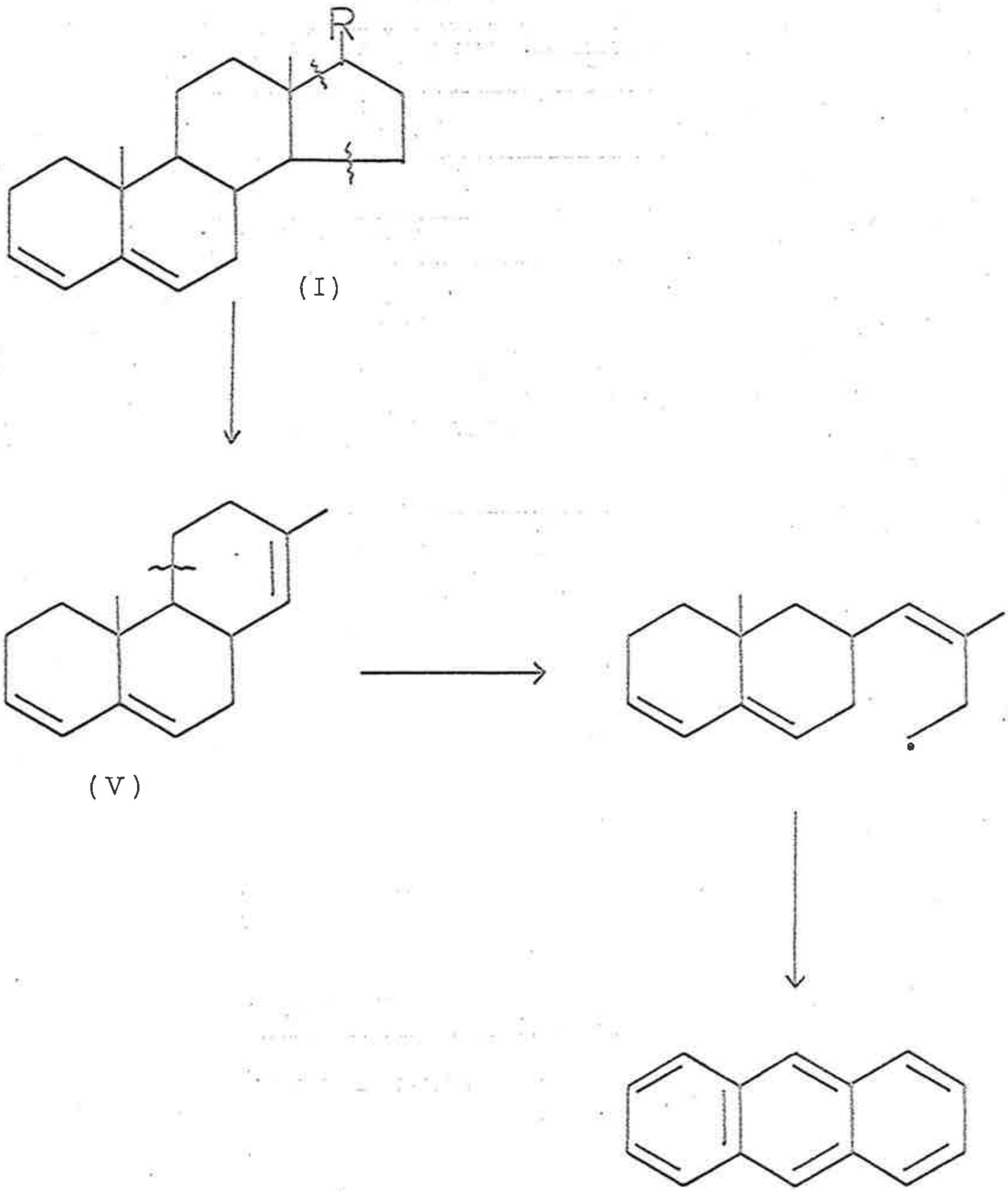


(V)

(VI)

(VII)

equation (1.iv)



(I)

(V)

(VIII)

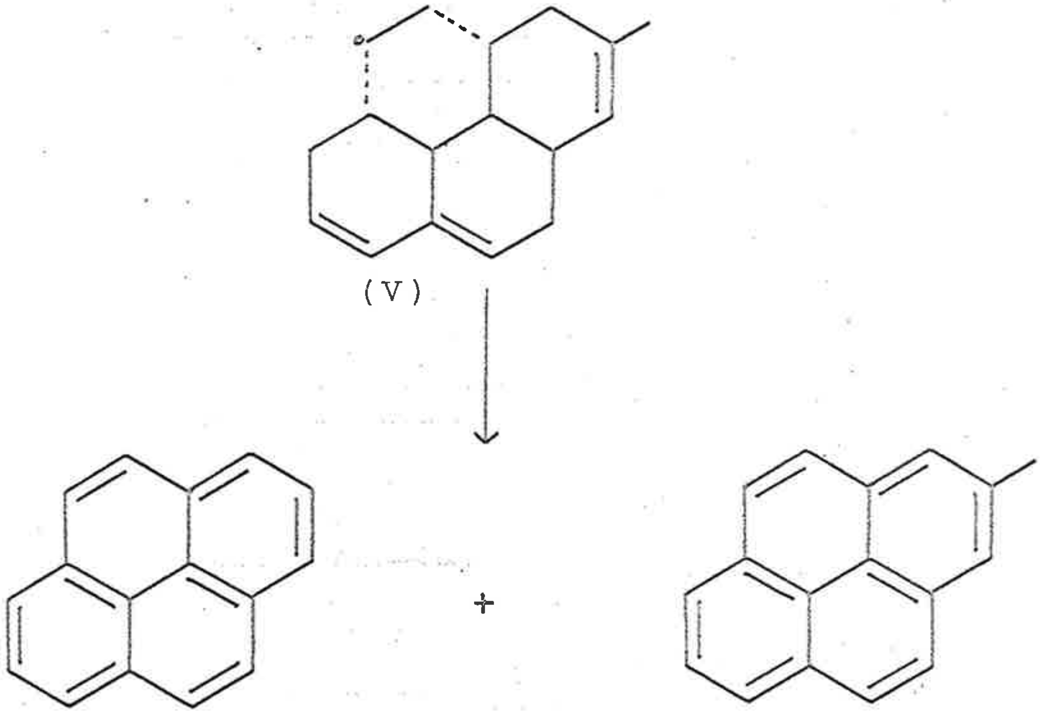
equation (1.v)

Thermal rearrangement of the hydrophenanthrene intermediate (V) could account for the anthracene (VIII) found in the tar, as illustrated by equation (1.v). Indeed, this mechanism probably represents the major route to anthracene in the present pyrolysis. A hydrogenated phenanthrene nucleus is present in the starting molecule, and, as shown in Chapter 4 such systems are almost certainly the intermediates in the phenanthrene ⟶ anthracene rearrangement.[70]

It has been shown that pyrene is formed during pyrolysis of phenanthrene,[70] presumably by attack of a C_2 unit on a hydrogenated phenanthrene intermediate. It can therefore be assumed that pyrene (IX) and alkylpyrenes (X) are formed in a similar way in the present pyrolysis, as in equation (1.vi).

Experiments on the phenylation of pyrene have shown that 3-phenylpyrene is the major isomer obtained.[71] Cyclodehydrogenation of this compound (equation (1.vii)) would account for the 2,3-(o-phenylene)-pyrene (XI) found in the tar.

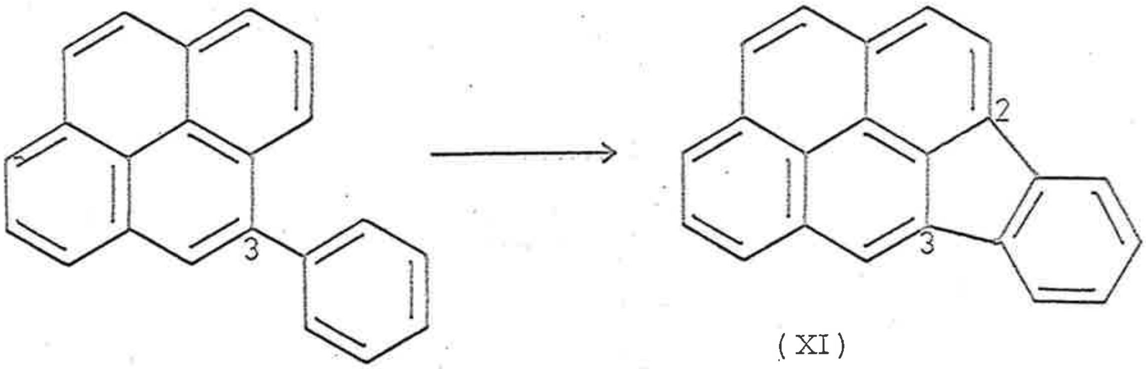
Scission of ring (C) in stigmasterol would lead to a bicyclic intermediate (XII), from which naphthalene (XIII) and tetralin (XIV) could be formed by dehydrogenation. 3,4-Benzopyrene (XVI) could be formed by combination of tetralin and the C_6-C_4 radical (XV) (equation (1.viii)) as originally proposed by Badger et al.[38] Considerable


(V)

(IX)

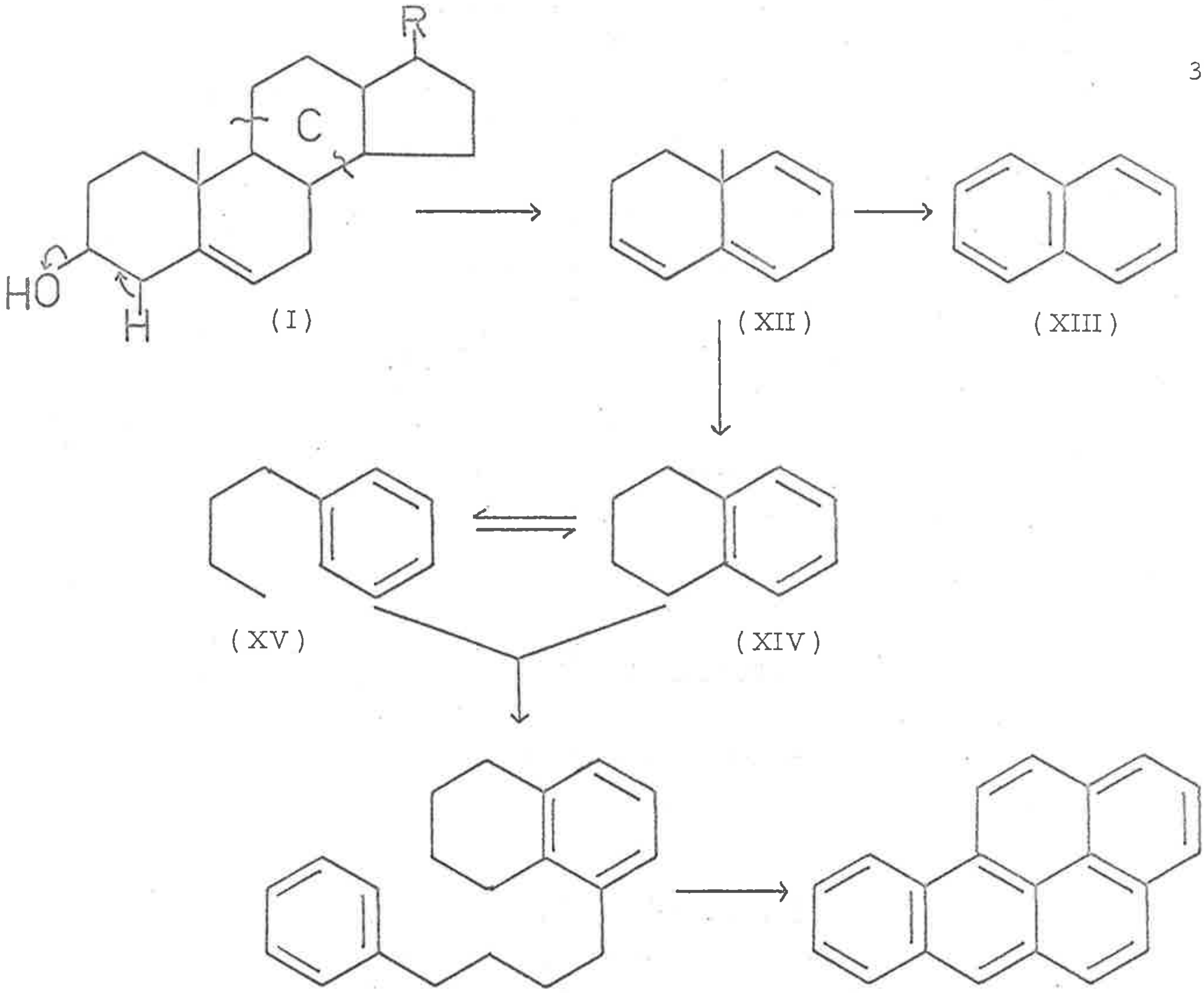
(X)

equation (1.vi)



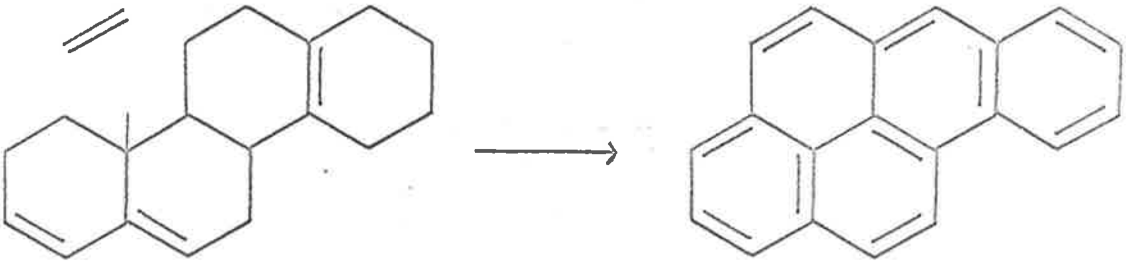
(XI)

equation (1.vii)



(I) (XII) (XIII) (XV) (XIV) (XVI)

equation (1.viii)



(III) (XVI)

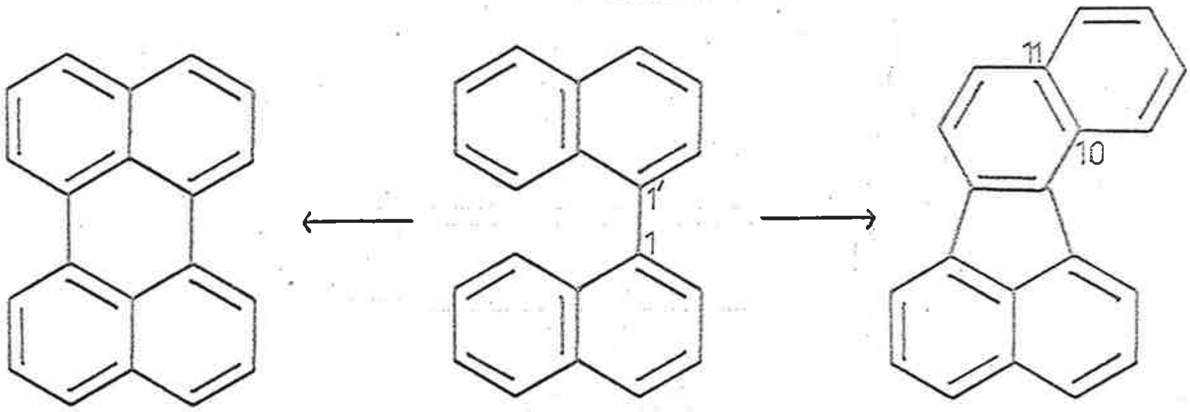
equation (1.ix)

evidence has now accumulated that this mechanism does represent a major route to 3,4-benzopyrene in many pyrolyses.

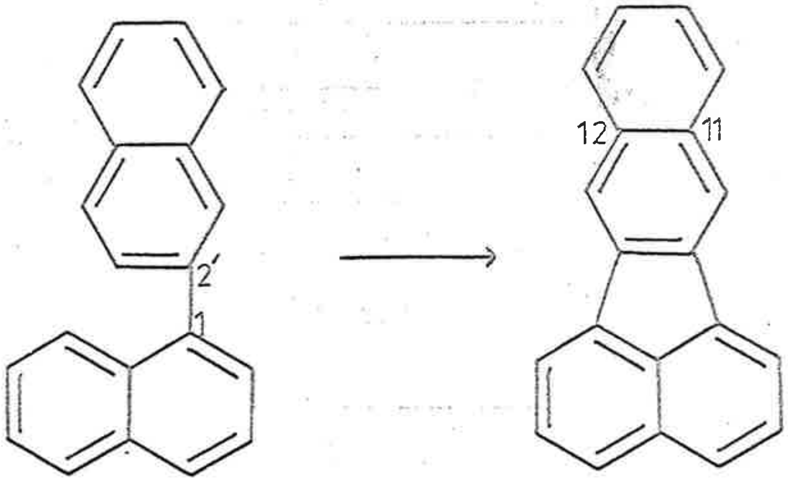
An alternative mechanism for the formation of 3,4-benzopyrene can be proposed for this pyrolysis. Since exceptionally large amounts of chrysene and its hydrogenated precursors were present in the reaction zone, it is expected that attack of a C_2 unit on an intermediate such as (III), followed by dehydrogenation, would give rise to 3,4-benzopyrene (equation (1.ix)).

The combination of 1- and 2-naphthyl radicals with naphthalene would result in the formation of binaphthyls (XVII), (XVIII) and (XIX). Cyclodehydrogenation of binaphthyls is known to give 10,11-benzofluoranthene (XX), 11,12-benzofluoranthene (XXI) and perylene[52] (XXII), and it is reasonable to assume that these compounds are formed by the same mechanism in the present pyrolysis. Further condensation of 2,2'-binaphthyl (XIX) is not possible and this isomer was isolated from the tar.

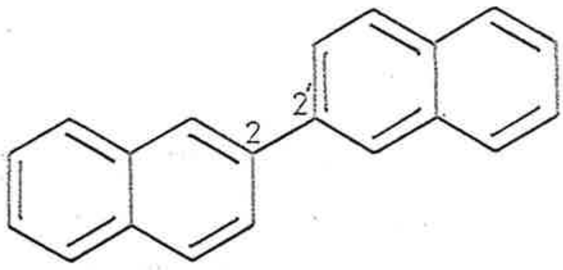
As phenanthrene was one of the major polycyclic products found in the tar, the phenylation of this compound would be expected to occur to a significant extent. No phenylphenanthrenes were detected in the tar, but a considerable amount of the carcinogenic 3,4-benzofluoranthene (XXIII) was isolated. This could be formed by the cyclodehydrogenation



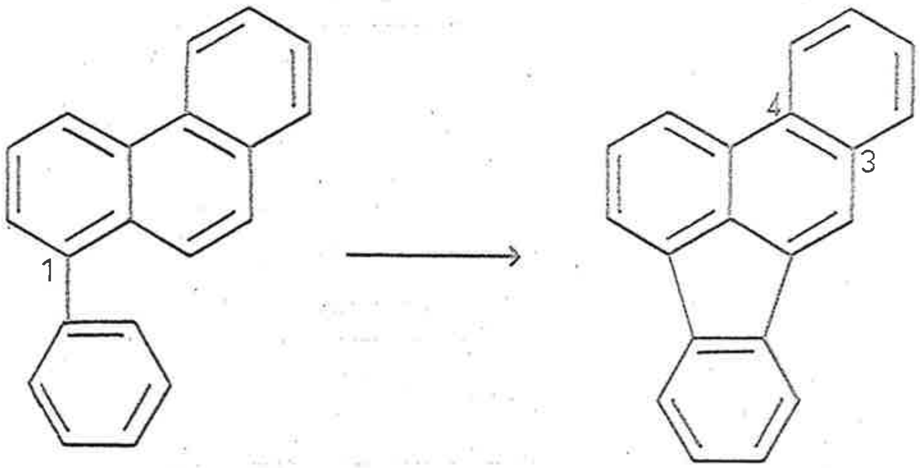
(XXII) (XVII) (XX)



(XVIII) (XXI)

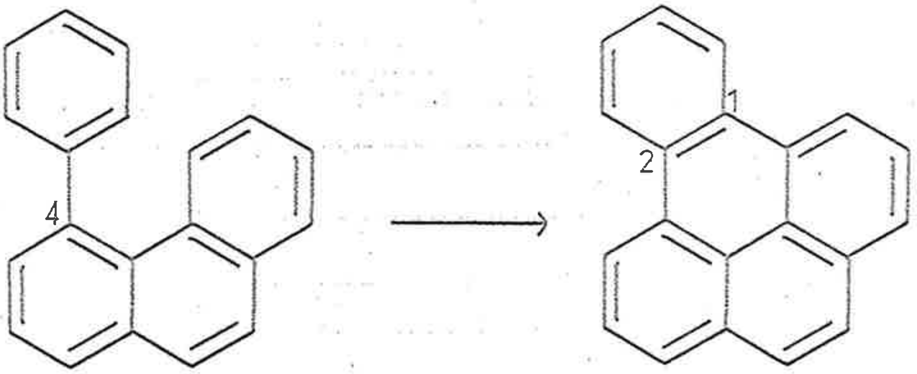


(XIX)



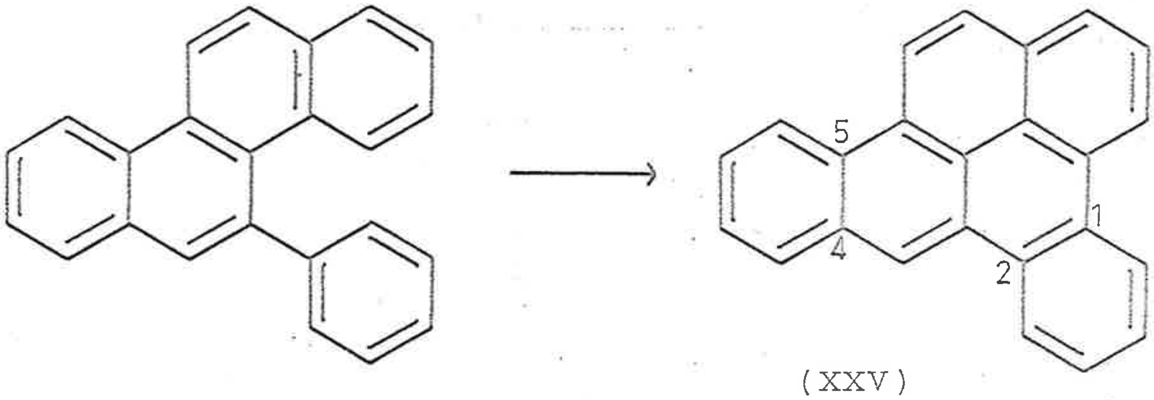
(XXIII)

equation (1.x)



(XXIV)

equation (1.xi)



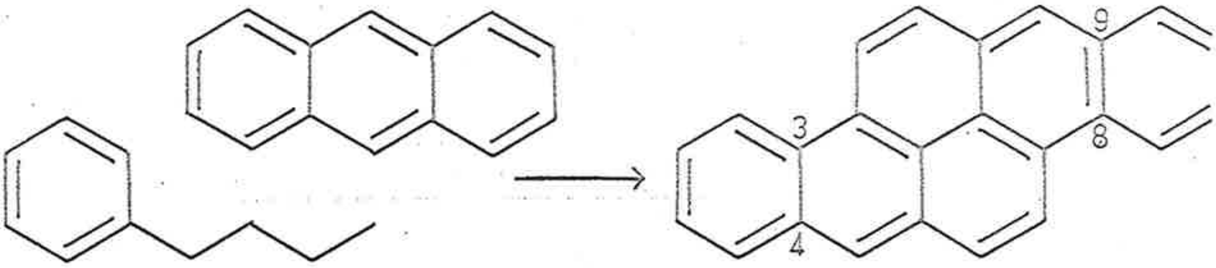
(XXV)

equation (1.xii)

of 9- or 1-phenylphenanthrene (equation (1.x)). Phenylation of phenanthrene would also be expected to give some of the 4-phenyl isomer, cyclodehydrogenation of which could account for the 1,2-benzopyrene (XXIV) formed.

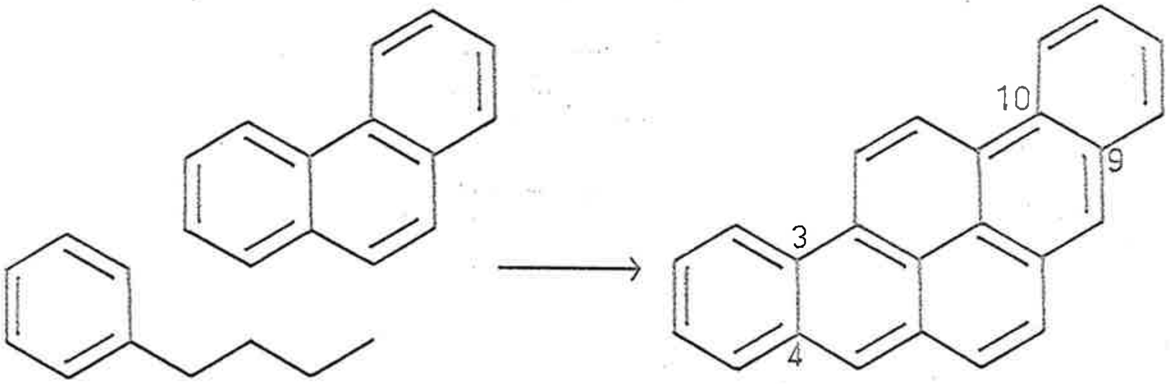
Similarly, the phenylation of chrysene (the major product in the tar) followed by cyclodehydrogenation, would give 1,2:4,5-dibenzopyrene (XXV) (equation (xii)).

The two other dibenzopyrenes identified could be formed by a mechanism similar to that proposed for 3,4-benzopyrene. Thus, 3,4:8,9-dibenzopyrene (XXVI) could be formed by the interaction of a C_6-C_4 unit with anthracene (equation (1.xiii)), while the interaction of the same unit with phenanthrene would account for the formation of 3,4:9,10-dibenzopyrene (XXVII) (equation (1.xiv)). An alternative mechanism for the formation of 3,4:9,10-dibenzopyrene involving attack of a C_2 unit on a hydrogenated picene intermediate (equation (1.xv)) may operate in this pyrolysis, since picene was formed in such high yield. An analogous mechanism with chrysene has already been suggested for 3,4-benzopyrene (equation (1.ix)), and attack of two C_2 units on the hydrochrysene intermediate would account for the anthanthrene (XXVIII) formed in the tar (equation (1.xvi)).



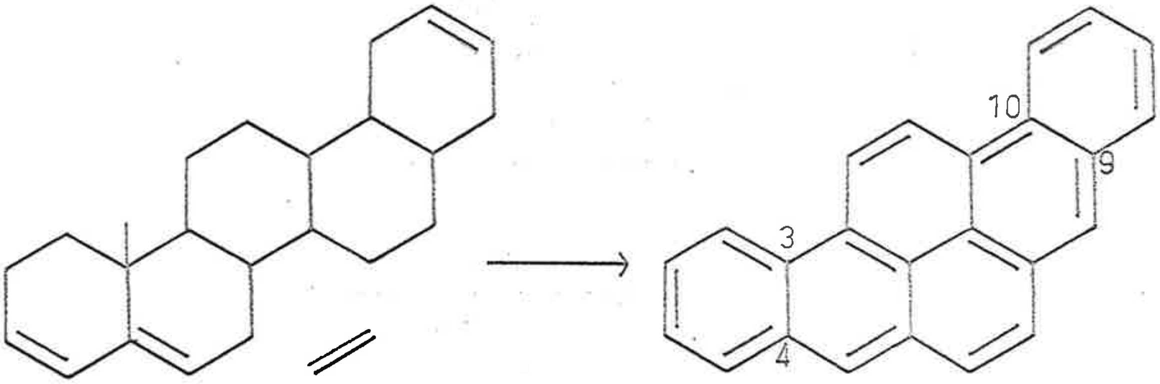
(XXVI)

equation (1.xiii)



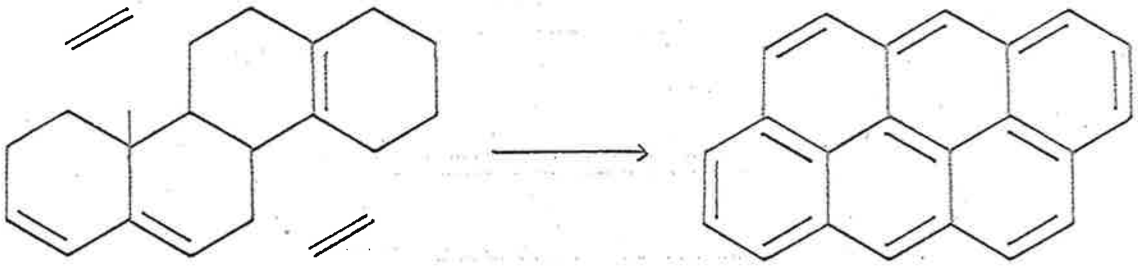
(XXVII)

equation (1.xiv)



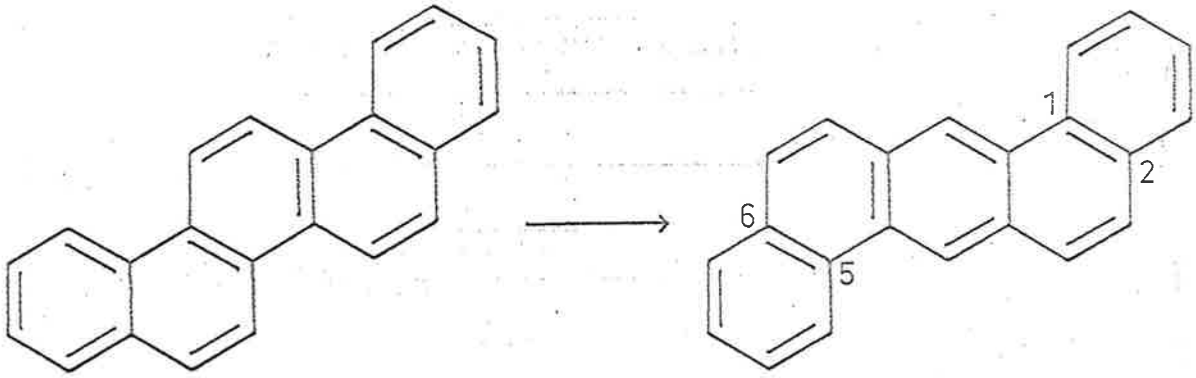
(XXVII)

equation (1.xv)



(III) (XXVIII)

equation (1.xvi)



(II) (XXIX)

equation (1.xvii)

In the pyrolyses of low molecular weight compounds, 1,2:5,6-dibenzanthracene (XXIX) is envisaged as arising by the interaction of methylnaphthyl radicals. However, it seems more likely in the present pyrolysis that this compound is formed by the thermal rearrangement of picene (equation (1.xvii)). The catalytic isomerisation of 1,2:5,6-dibenzanthracene and picene is known[73] and it would be feasible to expect it to occur thermally.

EXPERIMENTAL

(a) General

Stigmasterol

A commercial sample (Fluka) was recrystallised from ethanol to constant melting point. The resulting stigmasterol had m.p. 168-169° (lit.[74] 168°), $[\alpha]_D^{20}$ - 48.5° (lit.[74] -48°).

Pyrolysis

The pure stigmasterol (40.0g) was contained in a reservoir fitted with a needle valve and enclosed in an air-bath maintained at 170-180° (Fig. 1.1.) The liquid hydrocarbon was vaporized at 7g/hr. by dropping directly into a silica tube (33 x 5/8" i.d.) packed with porcelain chips, maintained at 700° in an electrically heated furnace. The vapour was carried through the tube with a stream of oxygen-free nitrogen, purified by passing through solutions of vanadylsulphate and zinc amalgam in dilute sulphuric acid, concentrated sulphuric acid and finally potassium hydroxide. The resulting tar was collected in a series of traps containing ice-salt, CO_2-ethanol and liquid air. Samples of the exit gases were collected in an evacuated gas-cell at intervals and examined by infrared spectroscopy.

The same pyrolysis apparatus was used for the pyrolyses of all solids, the temperature of the air-bath being maintained slightly above the melting point of the particular compound. The furnace used was that designed originally for the pyrolysis of acetylene;[40] the external silica tube was re-wound with three separate lengths of nichrome wire, for better control of the temperature. The internal silica tube was fitted with quartz joints at both ends, to enable direct heating when blocking occurred, and to eliminate leakage from the system. A chromel-alumel thermocouple (calibrated against a standard platinum-rhodium thermocouple*) directly connected to a pyrometer (0-1200°C, ext. res. 2.5 Ω , res. 746.6 Ω) with an auto-compensated cold junction, was used to measure the temperature gradients in the pyrolysis tube: Temperature gradients for pyrolyses at 700° and 950° are shown graphically, in Fig. 1.2.

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* Kindly lent by the S.A. Railways.

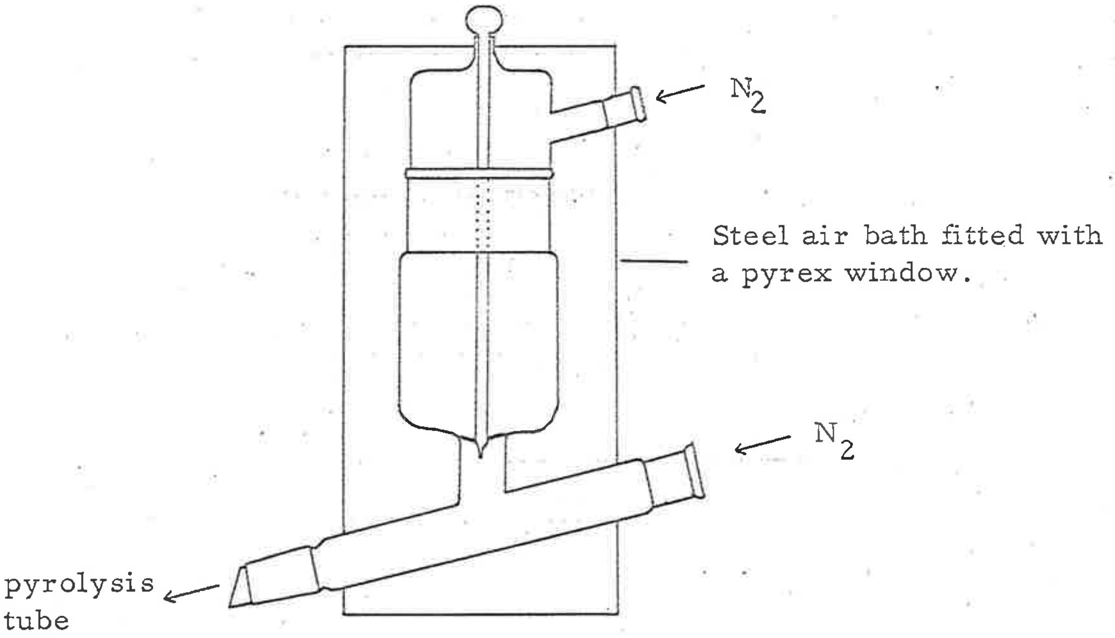

FIGURE 1.1. - Apparatus used for the introduction of solids to the pyrolysis tube.

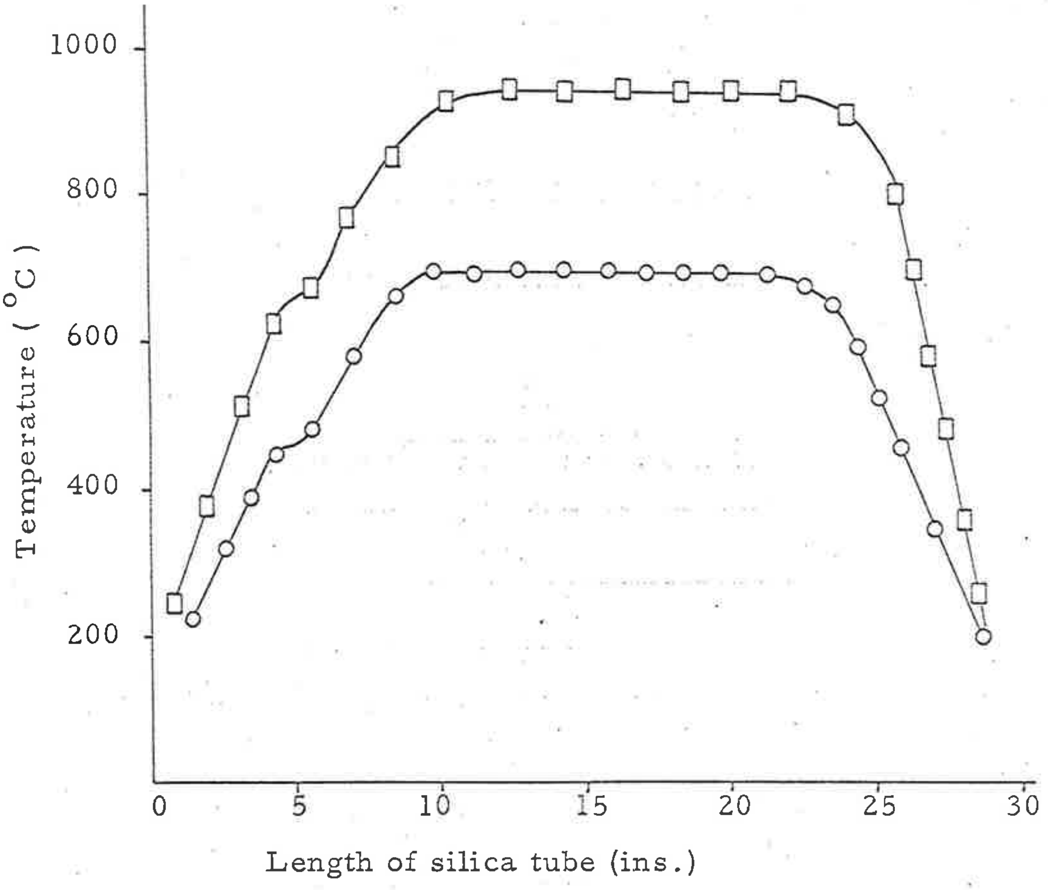

FIGURE 1.2. - Temperature gradients in the pyrolysis tube.

Analysis of the Stigmasterol tar

The tars collected from the ice-salt, CO_2-ethanol and liquid air traps were combined and distilled under reduced pressure to give five main fractions (a) - (e), and a residue (f). The pyrolysis tube and the porcelain chips were washed with boiling chloroform, the solution filtered to remove carbon, and the chloroform removed using a rotatory evaporator. The resulting tar was added to the residue (f) to give a total yield of 9.3g (23%). Fractions (a) - (e) were examined by gas-liquid chromatography and the components identified by retention-time ratios relative to benzene, and when possible by infrared spectroscopy. The residue (f) was divided into two equal portions and the detailed analysis carried out on one of these. The tar was first chromatographed on a column of Spence alumina (500g) using hexane, hexane containing increasing amounts of benzene, benzene and finally ethanol as eluants. The resulting fractions (90 x 200 ml) were examined by ultraviolet spectroscopy, and on this basis some were recombined to give 20 main fractions. These were then rechromatographed on columns of partially acetylated cellulose;[75] some were further purified by thin layer chromatography using partially acetylated cellulose as adsorbent.[76]

Gas-Liquid Chromatography

A Griffin and George Mark II vapour phase Chromatograph, modified to collect samples[77] was used. Apiezon L supported on celite (40-80 mesh, 1:4 w/w) was used as stationary phase, and dry nitrogen as carrier gas. This apparatus was used to collect samples only when the volume of the fraction was very small (less than 2cc). In all other cases, individual compounds were collected using a Beckman Megachrom Preparative Gas Chromatograph (column dimensions: 48' x 5/8" i.d.). Apiezon J supported on C-22 Firebrick (42-60 mesh) was used as stationary phase, and dry nitrogen as carrier gas. A Perkin-Elmer Model 800 Gas Chromatograph was also used in some pyrolyses. Apiezon L (15% by weight) supported on chromosorb W (80-100 mesh) was used as stationary phase, (column dimensions: 3' x 1/8") and dry nitrogen as carrier gas. The composition of each fraction was determined from the areas under the peaks (height x width at half-peak height)..

Chromatography on Alumina

The residue from the distillation was chromatographed on a column of Spence alumina (100 grams to 1 gram of tar), using hexane, hexane containing increasing amounts of benzene, benzene, and finally ethanol as eluants. The residue was introduced onto the column as solid adsorbed on an equal weight of alumina.

Chromatography on Partially Acetylated Cellulose

(1) Columns

The fractions obtained by chromatography on alumina were re-chromatographed on columns of partially acetylated cellulose. The cellulose powder was acetylated by the method of Spotswood,[75] using equal quantities of 92% sulphuric acid and 72% perchloric acid as catalyst. The solvent system used was ethanol : toluene : water (17 : 4: 1, v/v).

Thin-Layers

The separation of polycyclic aromatic compounds by thin-layer chromatography, using partially acetylated cellulose as adsorbent,[76] has found extensive application in this work. The acetylated cellulose (150 mesh) was prepared in the same way as that used for columns, and applied to the plates in a suspension of methanol or ethanol to give a 250 µ layer. The plates were developed by the ascending technique in a saturated chamber using methanol : ether : water (4 : 4: 1, v/v) as solvent system. The separated compounds, readily visible under ultra-violet light, were removed from the plates, extracted from the acetylated cellulose and identified by spectroscopy.

"Dry-Columns"

This technique was developed towards the end of this work, and was used only in the analysis of the isoprene tar. Dry-column chromatography, which is a preparative chromatographic technique with the resolvability of thin-layer chromatography, has been described by Loev and Snader[78] using alumina as adsorbent. Acetylated cellulose has proved to be a most satisfactory packing for such columns, and separations of the polycyclic compounds were comparable with those achieved on thin-layers. The columns (45 cm x 1 cm i.d.) were slowly packed with dry acetylated cellulose powder (150 mesh) under a steady pressure of nitrogen. The mixture of polycyclics was adsorbed on a small quantity of acetylated cellulose, this added to the column and covered with a little more adsorbent. Both ethanol : toluene : water (17 : 4: 1, w/w) and methanol : ether : water (4 : 4 : 1, w/w) proved satisfactory solvent systems. The solvent head was maintained at about 1 cm, and the separated compounds obtained either by cutting the column and extracting the compound from the adsorbent, or by continued elution.

Solvents used for chromatography were redistilled, and all columns were protected from light by wrapping with black paper. It is known that aromatic hydrocarbons decompose under daylight - type fluorescent lamps and also sunlight,[79] and by protecting the columns losses were kept at a minimum.

Ultraviolet Spectra

These were determined using an Optica CF_4 recording spectrophotometer, and a Perkin-Elmer Model 137 U.V. spectrophotometer. 95% Ethanol was generally used as solvent, but when the compound was not sufficiently soluble in this, benzene was used.

Infra-red Spectra

These were determined using a Perkin-Elmer 237B grating infrared spectrophotometer. The spectra were determined either as gases (the exit gases from the pyrolyses) or as liquid films.

Fluorescence Spectra

These were determined on a Farrand Model 104242 spectrofluorimeter, using 95% ethanol as solvent.

Calculations of Yields

All of the lower boiling hydrocarbons were analysed by gas-liquid chromatography, and yields calculated from the VPC spectra as described above (average of 3 runs). The yields of the remaining compounds were calculated from their ultraviolet spectra. The calculation was carried out by using a table of extinction coefficients showing the contribution of a solution containing 1 µg/ml of a compound to the optical density at the maxima.

Where difficultly separable mixtures were obtained the relative concentrations 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.

When possible, compounds were isolated and their relative amounts determined by direct weighing. The gravimetric values were in quite good agreement with those obtained by calculation from spectra.

Melting Points

All melting points were determined on a Zeiss hot stage microscope apparatus.

(b) Details of Identification

Methane, Ethylene, Propylene and Acetylene

Samples of the exit gases were collected and examined by infrared spectroscopy. Methane was identified by its complex series of absorption bands in the 7.3 - 8.5 μ region; ethylene by its band system in the 9.8 - 11.2 μ region; propylene in the 5.6 - 6.3 μ region; and acetylene by its spectrum in the 13.5 - 14.0 μ region.[80]

Isoprene, Pentane, Cyclopentane, Hexane and Cyclohexane

These compounds were all identified in fraction (a) by comparison of their retention-time ratios with those of authentic specimens. A sample of fraction (a) decolourised bromine water and alkaline potassium permanganate.

Benzene

Isolated from fractions (a), (b) and (c) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.25, 3.31, 4.31, 4.53, 5.11, 5.51, 5.70, 6.00, 6.31, 6.54, 6.76, 7.20, 8.52 and 9.67 μ, in agreement with an authentic sample.

Toluene

Isolated from fractions (a), (b), (c), and (d) by gas-liquid chromatography. The infrared absorption spectrum (liquid film) showed maxima at 3.29, 3.42, 3.48, 3.65, 3.86, 5.15, 5.39, 5.55, 5.76, 6.23, 6.68, 6.85, 7.25, 8.26, 8.48, 9.25, 9.60, 9.71, 11.16, 13.74 and 14.42 μ, in agreement with an authentic specimen.

Ethylbenzene

Identified in fraction (c) by comparison of its retention-time ratio with that of an authentic specimen.

p-Xylene and m-Xylene

Peaks were observed in the gas-liquid chromatograms of distillation fractions (b), (c) and (d) corresponding to either p-xylene or m-xylene. In the infrared spectrum maxima due to the meta-isomer occurred at 6.20, 8.54, 8.64, 9.79, 10.1, 11.0, 11.4, 12.95, and 13.68 μ; maxima due to the para-isomer at 6.14, 9.6, and 12.55 μ. Many other peaks were also observed which were common to both isomers.

Styrene

Isolated from distillation fraction (d), (and identified in fractions (b) and (c)) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.22, 3.27, 5.46, 6.21, 6.70, 6.90, 7.05, 7.74, 8.30, 9.22, 9.80, 10.09, 11.0, 12.90, and 14.37 μ, in agreement with an authentic specimen.

α-Methylstyrene

Identified in distillation fraction (d) by comparison of its retention-time ratio with that of an authentic specimen.

Indene

Isolated from fraction (e), and identified in fraction (d), by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.21, 3.39, 3.51, 5.10, 5.18, 5.40, 6.24, 6.50, 6.92, 7.24, 7.40, 7.59, 7.82, 8.17, 8.32, 8.55, 8.62, 8.94, 9.40, 9.84, 10.54, 10.90, and 11.60 μ.

Tetralin

Isolated from fraction (e) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.30, 3.42, 3.52, 3.70, 5.20, 5.61, 5.85, 6.40, 6.71, 6.90, 7.31, 8.30, 9.07, 9.28, 9.62, 9.74, 11.14, 11.57, and 13.58 μ.

Naphthalene

Isolated from fraction (e) by gas-liquid chromatography, and from fractions (2) and (3) by chromatography on a column of partially acetylated cellulose. The ultraviolet spectrum showed maxima at 248, 257, 266, 275, 285, and 311 mμ; and the sample had m.p. and mixed m.p. 78-80°.

1- and 2-Methylnaphthalene

Isolated from fraction (e) by gas-liquid chromatography, and from (2) and (3) by chromatography on partially acetylated cellulose.

The mixture of isomers showed ultraviolet absorption maxima at 224, 272, 278, 283, 287, 291, 294, 306, 312, and 319 mμ.

Biphenyl

Identified in fraction (e), and isolated from fraction (3) by chromatography on partially acetylated cellulose. Its ultraviolet absorption spectrum showed a maximum at 249 mμ. It had m.p. and mixed m.p. 69-70°.

Acenaphthylene

Isolated from fractions (3-4) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 229, 258, 266, 276, 309, 323, 334, and 340 mμ, in agreement with an authentic specimen.

Fluorene

Isolated from fractions (4-5) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima 260, 290, and 301 mμ, in agreement with an authentic specimen.

Phenanthrene

A mixture of phenanthrene, anthracene, and alkylphenanthrenes crystallised from fractions (5-15). The components were separated by chromatography on partially acetylated cellulose. The phenanthrene had m.p. and mixed m.p. 98-99°; its ultraviolet spectrum showed maxima at 243, 252, 275, 282, 294, 310, 317, 324, 331, 339, and 346 mμ, in agreement with an authentic specimen.

Alkyl-phenanthrenes

(Possibly 2-methyl-, 1,2-dimethyl- and 1,2-_c_-penteno-phenanthrene).

Separated from phenanthrene and anthracene by chromatography on a column of partially acetylated cellulose. Thin-layer chromatography on acetylated cellulose resolved the mixture into three components. The ultraviolet absorption spectrum of the mixture was the same general shape as phenanthrene, except that the maxima were shifted to longer wavelengths. As the absorption spectra of the alkyl-phenanthrenes are very similar,[81] it was not possible to identify the three compounds present. The n.m.r. spectrum showed peaks in the region τ, 7.5-7.8 confirming the presence of alkyl substituents.

Anthracene

Isolated by chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 246, 253, 308, 323, 339, 357, and 377 mμ, in agreement with an authentic specimen; and the sample had m.p. and mixed m.p. 215-216°.

Pyrene

Isolated from fractions (12-20) by chromatography on acetylated cellulose. The ultraviolet spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335, 351, 358, 364, and 373 mμ, in agreement with an authentic specimen; and the sample had m.p. and mixed m.p. 145-147°.

Alkylpyrene

Eluted prior to pyrene on a column of partially acetylated cellulose, and completely separated from this compound by thin-layer chromatography. Its ultraviolet spectrum showed maxima at 243, 255, 264, 278, 309, 321, and 338.5 mμ, suggesting an alkylpyrene, but no further identification was possible.

Fluoranthene

Isolated from fractions (15-24) following chromatography on acetylated cellulose. Its ultraviolet spectrum showed maxima at 236, 253, 263, 273, 278, 282, 309, 323, 342, and 360 mμ in agreement with an authentic sample. It had m.p. and mixed m.p. 105-107°.

Alkylfluoranthene

Separated from fluoranthene by thin-layer chromatography on partially acetylated cellulose. An extract gave an ultraviolet absorption curve having the same general shape as that from fluoranthene, but shifted to longer wavelengths. Insufficient material was available for further identification.

2,2'-Binaphthyl

Identified in fractions (22-25) by chromatography on both columns and thin films of acetylated cellulose; its ultraviolet spectrum showed maxima at 255, and 309 mμ, in agreement with an authentic sample.

1,2-Benzanthracene

Identified in fractions (22-26) following chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 227, 256, 268, 278, 289, 300, 315, 326, 341, 358, 365, 374, and 384 mμ, in agreement with an authentic sample.

1,2-Benzofluorene

Identified in fractions (23-28) after chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 229, 238, 253, 257, 262, 274, 286, 294, 303, 316, and 340 mμ, in agreement with an authentic specimen.

2,3-Benzofluorene

Identified in fractions (24-30) following chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 225, 264, 273, 285, 304, 317, 325, 333, and 340 mμ, in agreement with an authentic specimen.

Chrysene

Isolated from fractions (26-38) by crystallisation; it had m.p.

and mixed m.p. 254-255°. Its ultraviolet absorption spectrum showed maxima at 242, 259, 267, 283, 294, 306, 320, 344, 351, and 363 mμ, in agreement with an authentic specimen.

Alkylchrysene

Identified by chromatography of a sample of the crude chrysene on thin layers of acetylated cellulose. The ultraviolet spectrum showed maxima at 244, 260, 272, 285, 297, 308, 323, 354, and 365 mμ, indicating a methylchrysene. The n.m.r. spectrum showed a peak at $\tau = 7.9$ confirming the presence of an alkyl substituent.

10,11-Benzofluoranthene

Identified in fractions (35-36) following chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 241, 282, 293, 309, 318, 333, 345, 365, 376, and 383 mμ, in agreement with an authentic specimen.

1,2:5,6-Dibenzanthracene

Identified in fractions (33-43) by chromatography on both columns and thin films of acetylated cellulose. An extract showed maxima at 221, 230, 288, 298, 319, 335, and 348 mμ, in agreement with an authentic specimen.

1,2-Benzopyrene

Isolated from fractions (35-50) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 238, 258, 268, 278, 289, 305, 317, 333, and 366 mμ, in agreement with an authentic specimen. A sample had m.p. and mixed m.p. 174-176°.

Perylene

Identified in fractions (36-46) by chromatography on partially acetylated cellulose (both columns and plates). The ultraviolet absorption spectrum showed maxima at 245, 253, 263, 367, 386, 407, and 435 mμ, in agreement with an authentic specimen.

3,4-Benzopyrene

Isolated from fractions (40-55) by chromatography on acetylated cellulose. It had m.p. and mixed m.p. 174-176°. The ultraviolet absorption spectrum showed maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385, and 404 mμ; and its fluorescence spectrum showed maxima at 397, 422, 448, and 478 mμ. Both spectra were identical with those given by an authentic specimen.

Alkyl-3,4-benzopyrene

Identified in fractions (50-55) by thin-layer chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum was the same general shape as that of 3,4-benzopyrene, but shifted to longer wavelengths. It showed maxima at 300, 351, 371, 384, 390, and 410 mμ. Insufficient material was available for any further identification.

3,4-Benzofluoranthene

Isolated from fractions (45-57) by chromatography on partially acetylated cellulose, it had m.p. and mixed m.p. 161-163°. The absorption spectrum showed maxima at 239, 256, 266, 276, 290, 294, 301, 320, 339, 351, and 369 mμ, in agreement with an authentic specimen.

11,12-Benzofluoranthene

Identified in fractions (44-56) after chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 238, 247, 269, 283, 297, 309, 361, 380, and 402 mμ, in agreement with an authentic specimen.

1,12-Benzoperylene

Identified in fractions (54-60) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 268, 276, 289, 300, 315, 325, 330, 345, 363, and 383 mμ, in agreement with an authentic specimen.

Picene

Isolated from fractions (59-70) by crystallisation, it had m.p. and mixed m.p. 361-363°. The absorption spectrum showed maxima at 258, 275, 286, 302, 313, 328, 357, 364, and 376 mμ, in agreement with an authentic specimen.

2,3-(o-Phenylene)pyrene

Isolated from fractions (60-72) by chromatography on columns and plates of partially acetylated cellulose, it had m.p. 159-160° (lit.[82] 163°). The ultraviolet absorption spectrum showed maxima at 251, 261, 275, 292, 304, 315, 360, 376, 385, and 407 mμ, in agreement with Badger and Spotswood.[44]

Anthanthrene

Identified in fractions (65-75) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 233, 256, 259, 308, 365, 382, 402, 407, 422, and 431 mμ, in agreement with an authentic specimen.

1,2:4,5-Dibenzopyrene

Identified in fractions (70-86) after chromatography on a column of partially acetylated cellulose, followed by thin-layer chromatography. The absorption spectrum showed maxima at 294, 306, 327, 343, 360, 378, 396, and 416 mμ, in agreement with reported values.[83]

3,4:9,10-Dibenzopyrene

Identified in fractions (75-86) by chromatography on both columns and plates of partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 234, 242, 273, 283, 296, 315, 331, 353, 373, and 393 mμ; and the fluorescence spectrum maxima at 428, 456, 489, and 520 mμ, both in agreement with an authentic specimen.

3,4:8,9-Dibenzopyrene

Identified in fractions (75-86) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 289, 301, 314, 379, 401, 424, and 452 mμ, in agreement with recorded values.[83] The fluorescence spectrum showed maxima at 449, 475, and 512 mμ in agreement with the literature.[84]

CHAPTER 2

PYROLYSIS OF DOTRIACONTANE

Considerable interest has been shown in the aliphatic hydrocarbons present in tobacco. The percentages of the major hydrocarbons of processed tobacco[85] are listed in Table 2.1, and Fig. 2.1 shows a gas chromatogram* of the mixture of paraffins isolated from a particular tobacco.

TABLE 2.1

Paraffins	% Composition
C_{27} + iso	7.780
C_{29} + iso	9.260
C_{30} + iso	9.004
C_{31} + iso	36.56
C_{32} + iso	16.84
C_{33} + iso	16.60

The amount of the total paraffinic fraction present in tobacco varies considerably, but is of the order of 0.32%[66] of the dry weight of the tobacco.

The compound chosen for the present study was dotriacontane ($C_{32}H_{66}$), a representative of the paraffinic hydrocarbons present in

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* Kindly supplied by Mr. W.W. Reid, Chief Scientist of W.D. and H.O. Wills (Australia) Ltd.

tobacco, and its pyrolysis at 700° has been investigated.

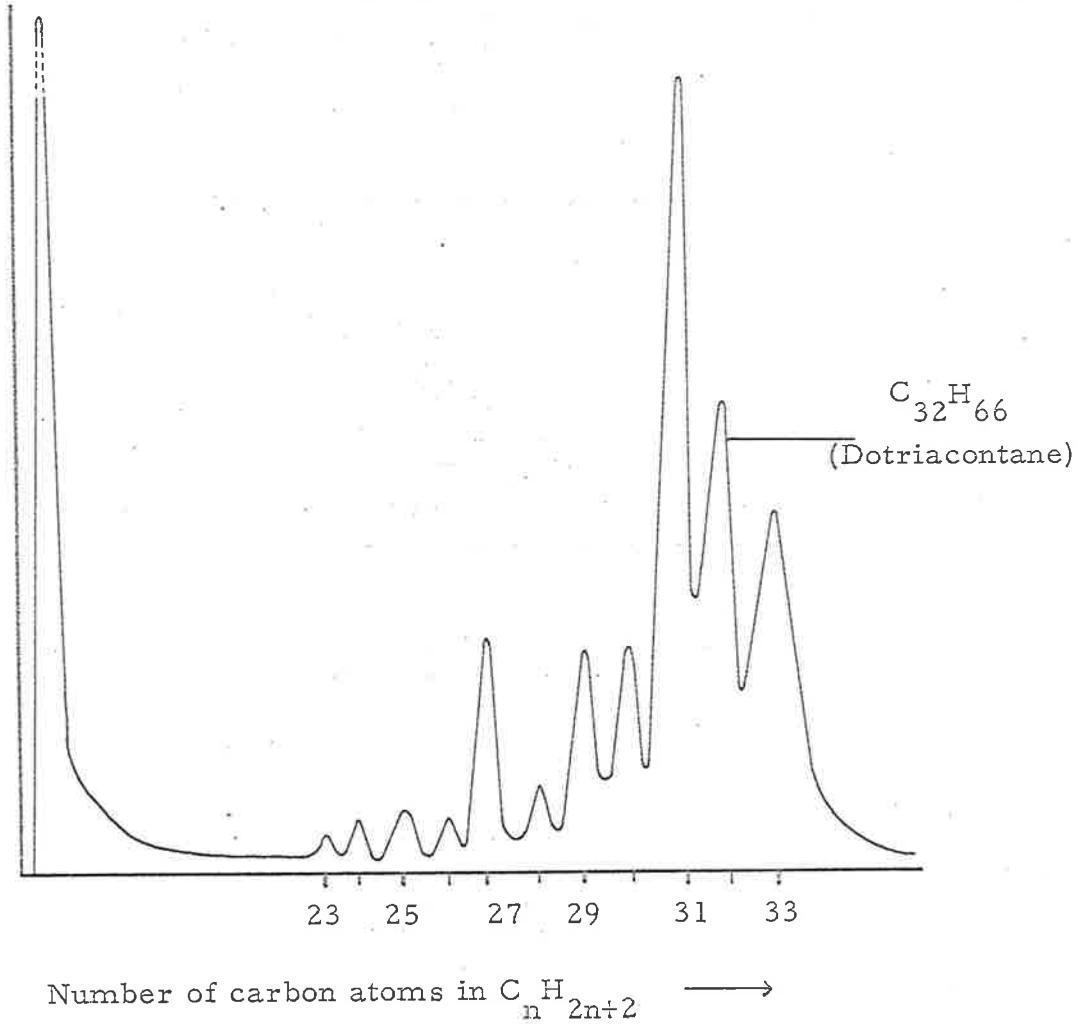


Figure 2.1. - Vapour Phase Chromatogram of Tobacco Hydrocarbons.

Lam has pyrolysed aliphatic tobacco hydrocarbons at various temperatures; no aromatics were detected following pyrolysis at 600°,[16] but eleven polycyclic compounds were identified at 700° and 800°.[16, 86] It is interesting to note that pyrolysis of a tobacco extract resulted in the formation of some alkyl-substituted polycyclics,[87] whereas no such compounds were formed from the aliphatic hydrocarbons. Similar results were obtained in the present pyrolysis; no alkyl-substituted polycyclics were isolated. However, these were obtained in considerable amounts from the pyrolyses of both stigmasterol and isoprene, and it is reasonable to conclude that such precursors in the tobacco may be responsible for the alkyl derivatives in cigarette smoke.

TABLE 2.2

COMPOSITION OF TAR FOLLOWING PYROLYSIS OF DOTRIACONTANE AT 700°

Fraction	Compound	% in Tar	Method of Identification
-	Methane	P	i.r.
-	Ethylene	P	i.r.
-	Propylene	P	i.r.
-	Acetylene	P	i.r.
a	Pentane	0.04	r.t.
a	Hexane	0.03	r.t.
a, b, c	Benzene	34.0	r.t., i.r.
a, b, c, d	Toluene	22.6	r.t., i.r.
c	Ethylbenzene	0.20	r.t.
c, d	p-, m-Xylene	1.92	r.t., i.r.
c, d	Styrene	7.03	r.t., i.r.
c, d	α -Methylstyrene	1.08	r.t.
d	n - Decane	0.41	r.t.
d, e	Indene	1.5	r.t., i.r.
e	Tetralin	0.9	r.t., i.r.
e, 2, 3	Naphthalene	13.2	r.t., u.v., mixed m.p.
e, 2	1-, 2-Methynaphthalenes	3.98	r.t., u.v.
2- 3	Biphenyl	2.0	u.v., mixed m.p.
3- 5	Acenaphthylene	1.44	u.v.
4- 6	Fluorene	0.68	u.v.
4- 8	Phenanthrene	1.80	u.v., mixed m.p.

5- 8	Anthracene	0.42	u.v., mixed m.p.
7-13	Pyrene	0.96	u.v., mixed m.p.
8-13	Fluoranthene	0.47	u.v., mixed m.p.
12-14	2,2'-Binaphthyl	0.15	u.v.
12-16	1,2 -Benzanthracene	0.05	u.v.
13-16	1,2 -Benzofluorene	0.31	u.v.
13-17	2,3 -Benzofluorene	0.36	u.v.
15-18	Chrysene	0.52	u.v., mixed m.p.
16-18	10,11-Benzofluoranthene	0.03	u.v.
17-21	1,2 -Benzopyrene	0.24	u.v., mixed m.p.
20-22	Perylene	0.02	u.v.
18-25	3,4 -Benzopyrene	0.126	u.v.,f.s., mixed m.p.
21-25	11,12-Benzofluoranthene	0.08	u.v.
21-25	3,4 -Benzofluoranthene	0.07	u.v., mixed m.p.
24-27	1,12-Benzoperylene	0.05	u.v.
25-28	Picene	0.02	u.v.
25-26	2,3-(o-Phenylene) pyrene	0.17	u.v.,m.p.
26-28	Anthanthrene	0.03	u.v.
27-28	1,2:4,5-Dibenzopyrene	P	u.v.
27-29	3,4:8,9-Dibenzopyrene	0.006	u.v.,f.s.
27-29	3,4:9,10-Dibenzopyrene	0.008	u.v.,f.s..
1	Dotriacontane	1.03	r.t., mixed m.p.
	Losses, unidentified material, etc.	2.1	

RESULTS AND DISCUSSION

The pyrolysis was carried out as described in Chapter 1. Methane, ethylene, propylene and acetylene were detected in the exit gases, and the tar (obtained in 21% yield) was analysed by chromatography and spectroscopy. The various compounds identified (45 in all) have been collected in Table 2.2. Benzene, toluene, naphthalene and styrene were found to be the major components of the tar.

By analogy with other compounds for which determinations are available, it seems likely that the carbon-carbon bonds in dotriacontane all have bond dissociation energies of about 70 K.cals.,[88] and would therefore be expected to break with approximately equal facility. Radical formation by the scission of a carbon-hydrogen bond may also be important at high temperatures, the bond dissociation energy for this process being about 100 K.cals. These radicals can then react by disproportionation, hydrogen abstraction or recombination, and thus many different primary and secondary radicals would be produced. It is impossible to predict which radicals would be of most importance in the breakdown of dotriacontane, because the initial scission of both carbon-carbon and carbon-hydrogen bonds is assumed to be a more or less random process.

It is interesting to note that the tar obtained from this pyrolysis was remarkably similar to those obtained from n-decane[58] and 2,2,4-trimethylpentane.[57] A small amount of n-decane was actually found in the tar, indicating that dotriacontane does in fact break down, at least to some extent, to a C_{10} unit, which could be the precursor of many polycyclic compounds, including 3,4-benzopyrene.

Combination of the primary radicals with a hydrogen atom in the reaction zone would give the corresponding saturated compounds (equation (2.i)); and methane, pentane, hexane and decane were found among the products.

$$R - \dot{C}H_2 + H^\bullet \longrightarrow R{-}CH_3 \qquad \text{(equation (2.i))}$$

Either disproportionation of a primary fragment, or recombination with another radical would produce olefins (equations (2.(ii)-(2.(vi)), and ethylene and propylene were identified in the exit gases.

$$CH_3 - CH_2 - \dot{C}H_2 \longrightarrow CH_3 - CH = CH_2 + H^\bullet \qquad \text{(2.(ii)}$$
$$CH_3 - CH_2 - \dot{C}H_2 \longrightarrow CH_2 = CH_2 + \dot{C}H_3 \qquad \text{(2.(iii)}$$
$$CH_3 - \dot{C}H_2 \longrightarrow CH_2 = CH_2 + H^\bullet \qquad \text{(2.(iv)}$$

$$CH_3 - \dot{C}H_2 + R\text{-}CH_2 - \dot{C}H_2 \longrightarrow CH_2 = CH_2 + R\text{-}CH_2 - CH_3 \quad (2.(v)$$

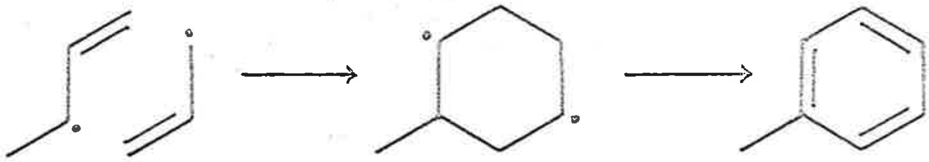
$$CH_3 - CH_2 - \dot{C}H_2 + R\text{-}CH_2 - \dot{C}H_2 \longrightarrow CH_3 - CH = CH_2 + R\text{-}CH_2 - CH_3 \quad (2.(vi)$$

Hydrogen abstraction from a vinyl radical would give rise to acetylene, which was also detected in the exit gases.

The mechanisms of formation of the aromatic compounds cannot be suggested with certainty as there are probably various mechanisms of equal importance all contributing to the formation of any particular compound. However, from the results of pyrolyses of simpler hydrocarbons, some of the more likely routes can be discussed.

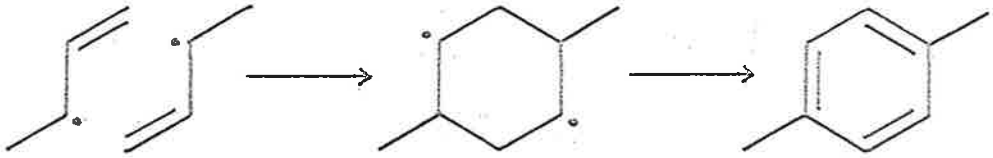
Benzene is known to be formed by the pyrolysis of acetylene,[40] ethylene and propylene,[90] and some of the benzene produced in the present pyrolysis could arise from these precursors. Some could also be formed by reaction of ethylene with a C_4 unit, or by the cyclisation of a hexyl radical followed by dehydrogenation. Benzene was the major constituent of the tar (obtained in 34% yield) and the above mechanisms all probably contributed to its formation.

Toluene (I) was also formed in considerable yield, most likely as a result of dimerisation of a propyl and butyl radical. Similarly, dimerisation of two butyl radicals would account for the p-xylene (II) found in the tar.



(I)

equation (2.vii)



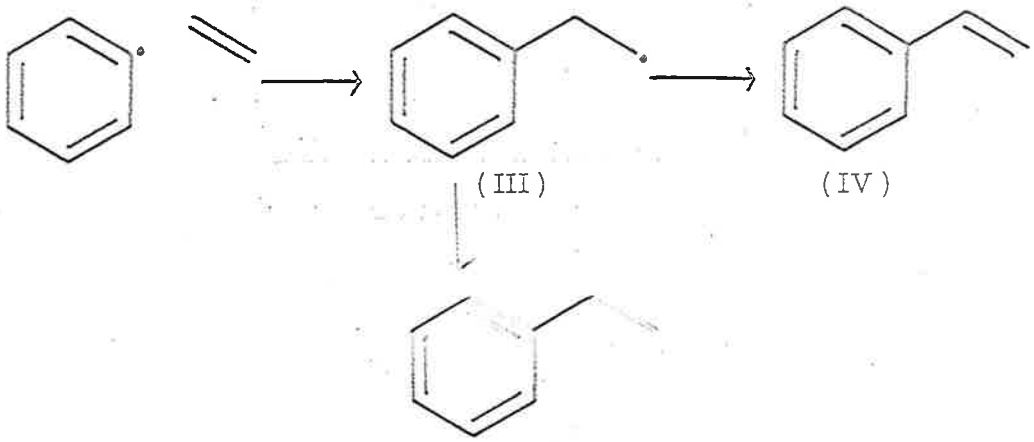
(II)

equation (2.viii)

The high yield of styrene (IV) is of interest, as it was also found to be among the major products in the pyrolyses of 2,2,4-trimethylpentane and decane. As benzene was formed in exceptionally high yields in all three pyrolyses, it seems likely that the styrene is largely formed from phenyl radicals and ethylene. The intermediate radical (III) produced could alternatively gain a proton to form ethylbenzene (V), although hydrogen abstraction appears to be a more favorable process since ethylbenzene was produced only in small yield.

Such addition of small primary units to phenyl radicals probably represents the most important route to many of the compounds found in the tar. For example, a phenyl and a propyl radical could give either α-methylstyrene (VI) or indene (VII), while reaction with a C$_4$

unit would account for the tetralin (VIII) and naphthalene (IX) formed.



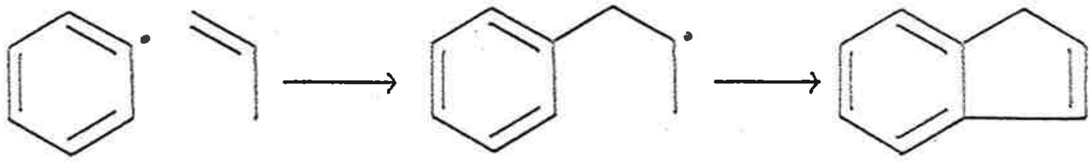
equation (2.ix)

The methylation of naphthalene would give both 1- and 2-methylnaphthalenes; these compounds could alternatively be formed by attack of a C_4 unit on toluene. (equation (2.xiii)).

Acenaphthene (XI) was one of the first polycyclic compounds to be prepared by pyrolytic dehydrogenation: Berthelot[91] reported its formation after the passage of 1-ethylnaphthalene through a hot tube, and a mixture of ethylene and naphthalene[92] under similar conditions also gave rise to this compound. Acenaphthene itself was not detected in the tar, but it is known to undergo ready dehydrogenation at high temperatures to acenaphthylene[93] (XII), which was obtained in significant yield.

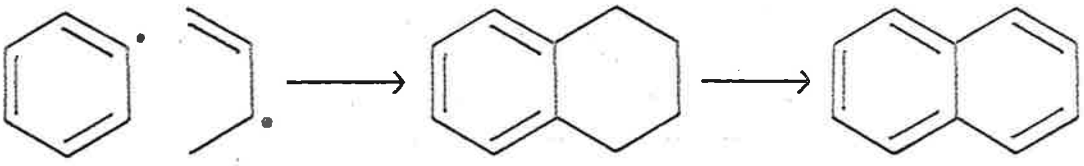
(VI)

equation (2.x)



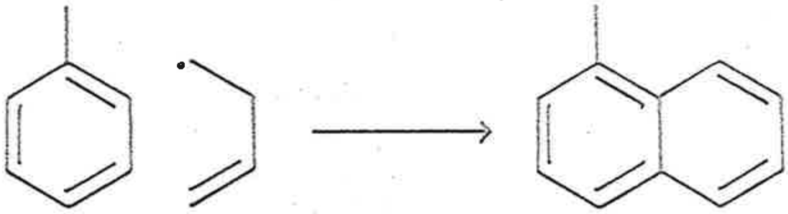
(VII)

equation (2.xi)



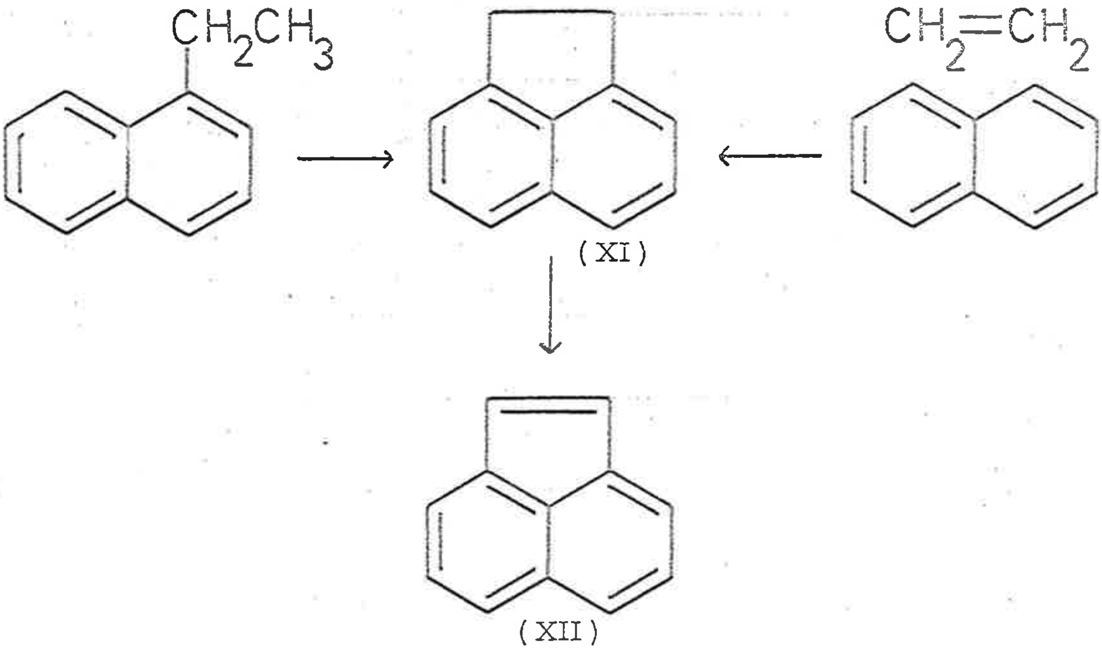
(VIII) (IX)

equation (2.xii)



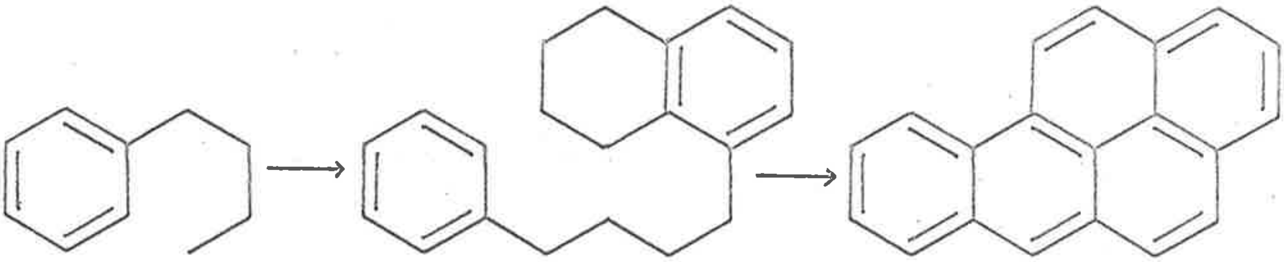
(X)

equation (2.xiii)



C_6C_4 units have been regarded as vital intermediates in the formation of many polycyclic hydrocarbons, including 3,4-benzopyrene (XIII), and the pyrolyses of such compounds as butylbenzene[44] and tetralin[53] have been investigated. The pyrolysis of radioactive C_6-C_4 units[51,54] has produced 3,4-benzopyrene with the expected number of labelled carbon atoms required if it were formed by the following scheme[38] (equation (2.(xiv)).

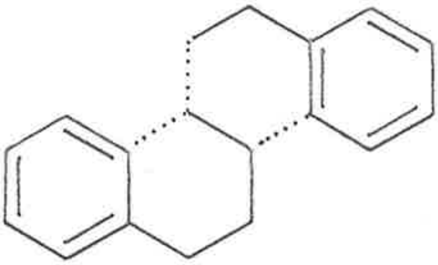
It was suggested initially[38] that C_2 units could undergo stepwise synthesis to C_6C_4 units, or alternatively, that complex hydrocarbons could undergo cracking to a C_{10} hydrocarbon which would then cyclise to the required C_6-C_4 unit. Evidence that C_{10} units were produced during the pyrolysis of dotriacontane has been supplied by the identification of n-decane in the tar; and the high yield of naphthalene is also significant. It is suggested then, that 3,4-benzopyrene is produced by the above mechanism in the present pyrolysis, either directly from a C_{10} unit formed on initial cracking, or by the pyrosynthesis of a C_6-C_4 unit from smaller fragments.



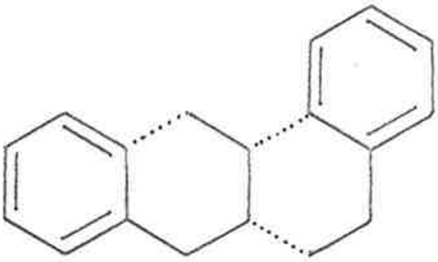
(XIII)

equation (2.xiv

C_6-C_4 units have also been shown to be important in the formation of chrysene (XIV) and 1,2-benzanthracene (XV), and many other polycyclic compounds, the mechanisms of which are discussed elsewhere in this thesis.



(XIV)



(XV)

As sterols and aliphatic hydrocarbons are both important constituents of cigarette tobacco, it is interesting to compare the relative concentrations of some of the polynuclear hydrocarbons found in the stigmasterol and dotriacontane tars, with those in cigarette smoke condensate.[94] Figure 2 is an attempt to compare the tars from the three sources. Pyrene has been chosen as an internal standard and the yields of other compounds have been recorded relative to this hydrocarbon.

Apart from the large amount of chrysene formed from stigmasterol, the three tars are remarkably similar, and it therefore seems likely that the sterols and paraffins present in tobacco may well contribute significantly to the polycyclic aromatic hydrocarbons present in tobacco smoke.

The actual amounts of known polycyclic aromatic carcinogens found in cigarette smoke condensate are insufficient to account for the carcinogenic activity of the tar. Cocarcinogens are certainly present[95]; and in addition, alkyl-substituted polycyclic hydrocarbons may contribute substantially to the carcinogenicity of the tar. Many alkyl derivatives have been identified in cigarette tars (and also in the stigmasterol tar), but the positions of the alkyl substituents have not been determined; neither has their carcinogenic activity. Although 1,2-benzanthracene,

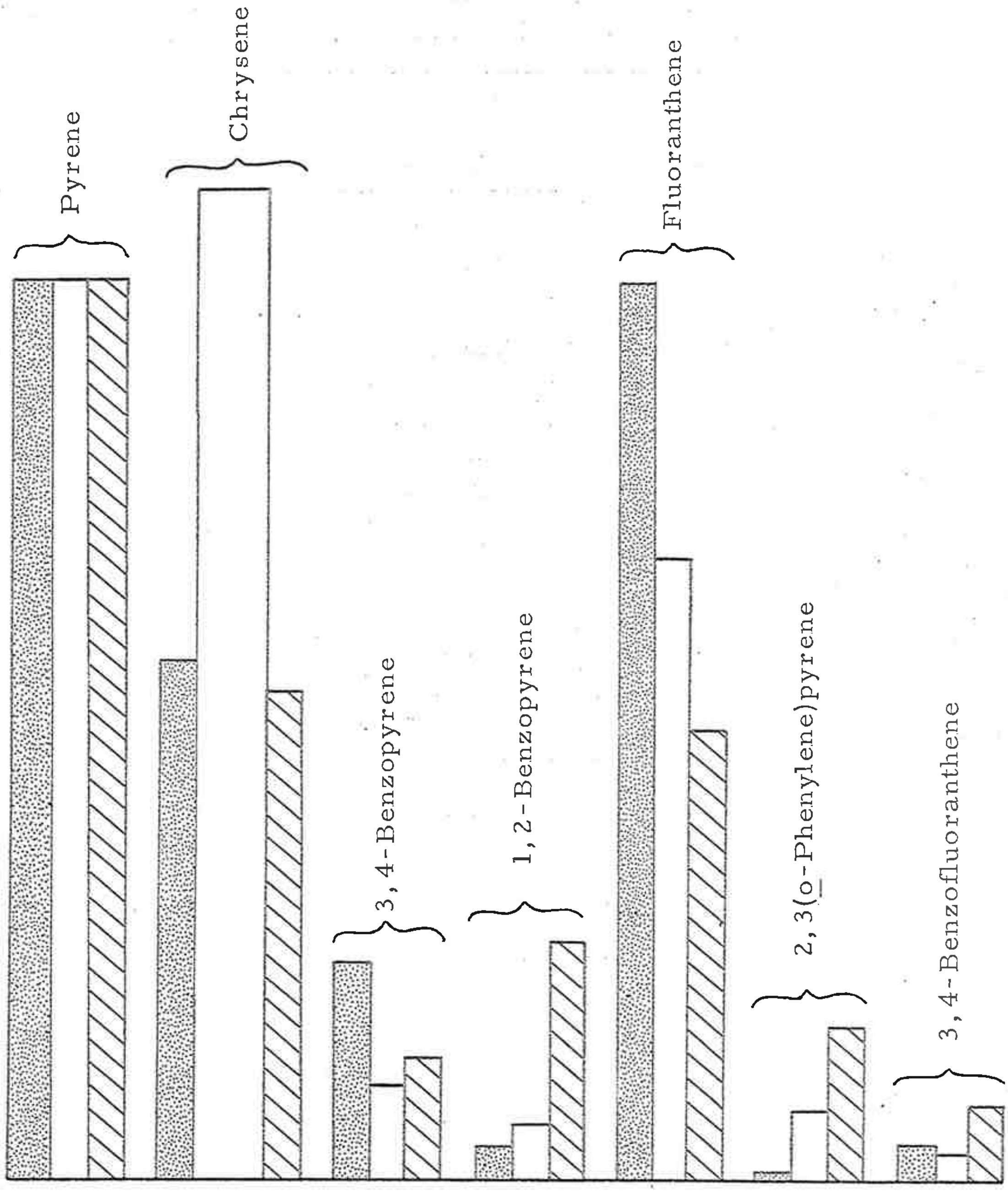


FIGURE 2.2. - Comparison of tars obtained by the pyrolyses of stigmasterol and dotriacontane at 700°, and from cigarette smoke condensate. Areas of bars represent yields relative to pyrene.

▒ Tobacco smoke condensate

□ Stigmasterol tar

▨ Dotriacontane tar

for example, is an inactive compound, a methyl substituent in a favourable position gives rise to a potent carcinogen.[33] These alkyl derivatives may therefore be most important in determining the total activity of the cigarette tar.

The maximum temperature of the burning zone of a cigarette has been shown to be 880°,[96] but there is some conjecture whether polycyclic aromatic hydrocarbons are produced at the maximum, or just before this temperature zone.[15] The results of pyrolysis of butylbenzene over a range of temperatures from 300-900° at 50° intervals[62] indicated that optimum temperatures for the formation of polycyclic hydrocarbons are in the range 660-740°. In particular, the optimum temperature for 3,4-benzopyrene formation was found to be 710°. It thus appears that the polycyclic aromatic hydrocarbons in tobacco smoke may be formed in the zone before the maximum.

EXPERIMENTAL

(a) General

Dotriacontane

A commercial sample (Lights) was twice recrystallised from ethanol and then further purified by zone-refining. The resulting dotriacontane had m.p. 70.3° (lit.[97] 70.3°) and contained no impurities which could be detected by gas-liquid chromatography.

Pyrolysis

The pure dotriacontane (10.0g) was contained in a reservoir maintained at 90-100°; other details were the same as for the pyrolysis of stigmasterol (Chapter 1).

Analysis of Tar

The tar (4.2g, 21%) was distilled to give five main fractions (a) - (e), and a residue (f). Fractions (a) - (e) were examined by gas-liquid chromatography and the components identified by retention-time ratios relative to benzene, and when possible by infrared spectroscopy. The residual tar (f), 0.7g, was chromatographed on a column of Spence alumina, using hexane, hexane-benzene, benzene and ethanol as eluants. The resulting fractions (120 x 100 ml) were collected and examined by ultraviolet spectroscopy. On this basis, some fractions were combined to give 30 main fractions. These were rechromatographed on both columns and thin-layers of partially acetylated cellulose.

(b) Details of Identification

Methane, Ethylene, Propylene and Acetylene

Samples of the exit gases were collected in a gas cell for infrared analysis. Methane was identified by its characteristic band system in the 7.3-8.5 µ region; ethylene by its complex series of absorption bands in the 9.0-11.2 µ region; propylene in the 5.6-6.5 µ region; and acetylene by its characteristic spectrum in the 13.5-14.5 µ region.[80]

Pentane and Hexane

These two compounds were identified in fraction (a) by comparison of their retention-time ratios with those of authentic specimens.

Benzene

Isolated from fractions (a), (b) and (c) by gas-liquid chromatography. The infrared absorption spectrum (liquid film) showed maxima at 3.25, 3.31, 4.31, 4.53, 5.10, 5.51, 5.70, 6.00, 6.31, 6.54, 6.76, 7.20, 8.52 and 9.67 µ, in agreement with an authentic specimen.

Toluene

Isolated from fractions (a) - (d) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.29, 3.42, 3.48, 3.65, 3.86, 5.15, 5.39, 5.55, 5.76, 6.23, 6.68, 6.85, 7.25, 8.26, 8.48, 9.03, 9.25, 9.60, 9.71, 11.16, 13.74, and 14.42 µ, in agreement with an

authentic specimen.

Ethylbenzene

Identified in fraction (c) by comparison of its retention-time ratio with that of an authentic specimen.

p-*Xylene* and m-*Xylene*

Peaks were observed in the gas-liquid chromatograms of distillation fractions (c) and (d) corresponding to either *p*- or *m*-xylene. The infrared spectrum showed the presence of both compounds. Maxima due to the *para*-isomer occurred at 6.14, 9.6 and 12.5 μ, while the *meta*-isomer showed maxima at 6.20, 8.54, 8.64, 9.79, 10.1, 11.0, 11.4, 12.95 and 13.68 μ. Many other peaks were also observed which were common to both isomers.

Styrene

Isolated from distillation fractions (c) and (d) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 2.40, 3.22, 3.27, 5.08, 5.30, 5.46, 5.76, 5.90, 6.10, 6.21, 6.31, 6.50, 6.70, 6.90, 7.05, 7.48, 7.58, 7.74, 8.30, 8.46, 8.65, 9.02, 9.22, 9.80, 10.09, 11.0, 11.90, 12.90 and 14.37 μ, in agreement with an authentic specimen.

α-Methylstyrene

Identified in fractions (c) and (d) by comparison of its retention-time ratio with that of an authentic sample.

n-Decane

Identified in distillation fraction (d) by comparison of its retention-time ratio with that of an authentic specimen.

Indene

Isolated from distillation fractions (d) and (e) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.25, 3.46, 3.60, 6.24, 6.50, 6.92, 7.24, 7.40, 7.58, 7.68, 7.82, 8.20, 8.34, 8.62, 8.94, 9.40, 9.84, 10.92, 11.60, 12.06, 13.02, 13.92 and 14.42 μ, in agreement with an authentic specimen.

Tetralin

Isolated from fraction (e) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.31, 3.42, 3.53, 3.69, 5.20, 5.42, 5.63, 5.86, 6.28, 6.40, 6.72, 7.30, 8.31, 8.54, 9.08, 9.62, 11.14, 11.57, 13.60 and 14.32 μ, in agreement with an authentic specimen.

Naphthalene

Isolated from fraction (e) by gas-liquid chromatography, and from (2-3) by chromatography on alumina. The ultraviolet absorption spectrum showed maxima at 248, 257, 266, 275, 285 and 311 mμ; and it had m.p. and mixed m.p. 78-80°.

1- and 2-Methylnaphthalene

Identified in distillation fraction (e) by gas-liquid chromatography, and isolated from fraction (2) by chromatography on alumina. The mixture of isomers showed ultraviolet absorption maxima at 224, 272, 283, 287, 291, 294, 306, 312 and 319 mμ. The predominance of the 2-isomer was inferred from the shape of the curve.

Biphenyl

Isolated from fractions (2-3) by chromatography on partially acetylated cellulose. It had m.p. and mixed m.p. 69-70°; and ultraviolet absorption maximum at 249 mμ.

Acenaphthylene

Isolated from fractions (3-5) by chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 229, 258, 266, 276, 309, 323, 334 and 340 mμ in agreement with an authentic specimen.

Fluorene

Isolated from fractions (4-6) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 260, 290 and 301 mμ in agreement with an authentic sample.

Phenanthrene

Isolated from fractions (4-8) by chromatography on partially acetylated cellulose. A sample had m.p. and mixed m.p. 98-99°, and λmax. 243, 252, 275, 282, 294, 310, 317, 324, 331, 339 and 346 mμ, in agreement with an authentic specimen.

Anthracene

Isolated from fractions (5-8) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 246, 253, 308, 323, 339, 357 and 377 mμ, in agreement with an authentic specimen; and it had m.p. and mixed m.p. 215-216°.

Pyrene

Isolated from fractions (7-13) by chromatography on partially acetylated cellulose. A sample had m.p. and mixed m.p. 145-147°; and u.v. absorption maxima at 231, 241, 253, 263, 274, 306, 319, 335, 351, 358, 364 and 373 mμ in agreement with an authentic specimen.

Fluoranthene

Isolated from fractions (8-13) by chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 236, 253, 263, 273, 278, 282, 288, 309, 323, 342 and 360 mμ in agreement with an authentic specimen; and a sample had m.p. and mixed m.p. 105-107°.

2,2'-Binaphthyl

Identified in fractions (12-14) after chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 255 and 309 mμ in agreement with an authentic specimen.

1,2-Benzanthracene

Identified in fractions (12-16) following chromatography on acetylated cellulose. The ultraviolet spectrum showed maxima at 227, 256, 268, 278, 289, 300, 315, 326, 341, 358, 365, 374 and 384 mμ in agreement with an authentic specimen.

1,2-Benzofluorene

Identified in fractions (13-16) following chromatography on acetylated cellulose. The ultraviolet spectrum showed maxima at 229, 238, 253, 257, 262, 274, 286, 294, 303, 316 and 340 mμ in agreement with an authentic sample.

2,3-Benzofluorene

Identified in fractions (13-17) after chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 255, 264, 273, 285, 304, 317, 325, 333 and 340 mμ, in agreement with an authentic specimen.

Chrysene

Isolated from fractions (15-18) by chromatography on partially acetylated cellulose. A sample had m.p. and mixed m.p. 253-254°; and u.v. maxima at 242, 259, 267, 283, 294, 306, 320, 344, 351 and

363 mμ, in agreement with an authentic specimen.

10,11-Benzofluoranthene

Identified in fractions (16-18) after chromatography on acetylated cellulose. The ultraviolet spectrum showed maxima at 241, 282, 293, 309, 318, 333, 345, 365, 376 and 383 mμ, in agreement with an authentic sample.

1,2-Benzopyrene

Isolated from fractions (17-21) by chromatography on acetylated cellulose; ultraviolet absorption maxima occurred at 238, 258, 268, 278, 289, 305, 317, 333 and 366 mμ, in agreement with an authentic specimen; and it had m.p. and mixed m.p. 173-175°.

Perylene

Identified in fractions (20-22) following chromatography on both columns and thin-layers of acetylated cellulose. An extract showed absorption maxima at 245, 253, 263, 367, 386, 407 and 435 mμ, in agreement with an authentic specimen.

3,4-Benzopyrene

Isolated from fractions (18-25) by chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385 and 404 mμ; and its fluorescence spectrum maxima at 397, 422, 488 and 478 mμ, both in agreement with an authentic specimen. It had m.p. and mixed m.p. 174-176°.

1, 12-Benzoperylene

Identified in fractions (24-27) after chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 268, 276, 289, 300, 315, 325, 330, 345, 363 and 383 mμ, in agreement with an authentic specimen.

11, 12-Benzofluoranthene

Identified in fractions (21-25) following chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 238, 247, 269, 283, 297, 309, 361, 380 and 402 mμ, in agreement with an authentic sample.

3, 4-Benzofluoranthene

Isolated from fractions (21-25) by chromatography on acetylated cellulose, it had m.p. and mixed m.p. 161-163°. The absorption spectrum showed maxima at 239, 256, 266, 276, 290, 294, 301, 320, 339, 351 and 369 mμ, in agreement with an authentic specimen.

Picene

Identified in fractions (25-28) after chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 258, 275, 286, 302, 313, 328, 357, 364 and 376 mμ, in agreement with an

authentic specimen.

2,3-(o-Phenylene) pyrene

Isolated from fractions (25-26) by chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 251, 261, 275, 292, 304, 315, 360, 376, 385 and 407 mμ, in agreement with Badger and Spotswood;[44] and a sample had m.p. (lit. 163°[82]) 158-160°.

Anthanthrene

Identified in fractions (26-28) by chromatography on acetylated cellulose. The absorption spectrum showed maxima at 233, 256, 259, 295, 308, 365, 382, 402, 407, 422 and 431 mμ, in agreement with an authentic specimen.

1,2:4,5-Dibenzopyrene

Detected in fractions (27-28) after chromatography on a column of acetylated cellulose followed by thin-layer chromatography. An extract showed u.v. maxima at 294, 306, 327, 343, 360, 378, 396 and 416 mμ, in agreement with the literature.[83]

3,4:8,9-Dibenzopyrene

Identified in fractions (27-29) by chromatography on partially acetylated cellulose; it had a much lower R_F than the other components of these fractions and was cleanly separated. The ultraviolet spectrum showed maxima at 289, 301, 314, 379, 401, 424 and 452 mμ, in agreement with recorded values;[83] and the fluorescence spectrum showed maxima at 449, 475 and 512 mμ in agreement with the literature.[84]

3,4:9,10-Dibenzopyrene

Identified in fractions (27-29) by chromatography on both columns and plates of acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 234, 242, 273, 283, 296, 315, 331, 353, 373 and 393 mμ; and the fluorescence spectrum maxima at 428, 456, 489 and 520 mμ, both in agreement with an authentic specimen.

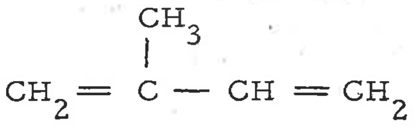
CHAPTER 3

PYROLYSIS OF ISOPRENE

It has been shown for stigmasterol that complete skeletal breakdown into small fragments, followed by resynthesis to polycyclics, is unlikely, and that many compounds are apparently formed by simple rearrangements and cyclodehydrogenations of high molecular weight precursors. On the other hand, it has been established that when polyisoprenoids are pyrolysed, isoprene constitutes 50 - 67% of the total products,[98] and isoprene may therefore be an important precursor to the polycyclic hydrocarbons found in cigarette smoke. Many terpenes, including phytadienes ($C_{20}H_{38}$), carotenes ($C_{40}H_{56}$) and solanesol, a pentaterpenoid alcohol, have been isolated and identified in tobacco;[29] and isoprene is an important constituent of cigarette smoke.[29] It seems likely that complex terpenes would decompose mainly to isoprene at 750°, the mean temperature of the burning zone of a cigarette.[99] In fact, solanesol has been reported[100] to break down directly to dipentene and isoprene on pyrolysis.

As early as 1913 it was found that the pyrolysis of isoprene at 700-800° gives an aromatic tar,[101] and Kennaway[60] later demonstrated the strongly carcinogenic properties of such a tar. More recently, isoprene has been pyrolysed at 600° to give a tar containing 0.1%

3,4-benzopyrene;[17] but analysis for other compounds was not attempted. Isoprene has therefore been pyrolysed at 700°, the resulting tar analysed for aromatic hydrocarbons, particularly for those known to be carcinogenic, and mechanisms of formation of some of these are discussed.



$$CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH=CH_2$$

Isoprene

TABLE 3.1

COMPOSITION OF TAR FOLLOWING PYROLYSIS OF ISOPRENE AT 700°

Fraction	Compound	% in Tar	Method of Identification
	Methane	P	i.r.
	Ethylene	P	i.r.
	Propylene	P	i.r.
	Acetylene	P	i.r.
a, b	Butadiene	0.32	r.t.
a, b	Isoprene	0.65	r.t.
a, b	Cyclopentene	0.15	r.t.
a - e	Benzene	15.54	r.t., i.r.
b - f	Toluene	22.18	r.t., i.r.
d	Ethylbenzene	P	r.t.
c - f	*p*-, *m*-Xylene	15.42	r.t., i.r.
d - g	Styrene	5.53	r.t., i.r.
f - h	α-Methylstyrene	0.89	r.t., i.r.
f - h	*m*-, *p*-Methylstyrene	0.86	r.t., i.r.
f - h	*m*-, *p*-Cymene	4.56	r.t., i.r.
f - h	*m*-, *p*-Methyl-α-methylstyrene	0.42	r.t., i.r.
g, h	Indene	1.63	r.t., i.r.
g, h	Tetralin	0.79	r.t.
g, h, l	Naphthalene	8.36	r.t., u.v., mixed m.p.
h, l	1-, 2-Methylnaphthalene	3.60	r.t., u.v.
h, l	Biphenyl	0.76	r.t., u.v., mixed m.p.

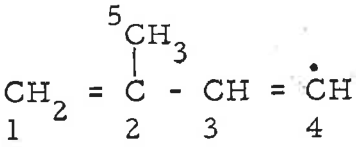
h, 1	4,4'-Dimethylbiphenyl	0.41	r.t., u.v.
h, 1	Bibenzyl	0.10	r.t.
h, 1-3	Acenaphthylene	1.02	r.t., u.v.
h, 2-4	Fluorene	1.03	r.t., u.v.
2,3	2-Phenylnaphthalene	0.19	u.v.
2- 7	Phenanthrene	3.42	u.v., mixed m.p.
5- 7	Methylphenanthrene	0.74	u.v., n.m.r.
3- 7	Anthracene	0.62	u.v., mixed m.p.
6-10	Pyrene	1.68	u.v., mixed m.p.
8-10	Methylpyrene	0.87	u.v., n.m.r., m.p.
8-12	Fluoranthene	1.01	u.v., mixed m.p.
10-12	Alkylfluoranthene	P	u.v.
11-13	2,2'-Binaphthyl	0.29	u.v.
11-13	1,2-Benzanthracene	0.30	u.v.
11-13	Triphenylene	0.08	u.v.
12-14	1,2-Benzofluorene	0.32	u.v.
13-15	2,3-Benzofluorene	0.63	u.v.
14-19	Chrysene	1.21	u.v., mixed m.p.
19	Alkylchrysene	0.36	u.v.
19-21	2,3-Benzofluoranthene	P	u.v.
15-21	1,2-Benzopyrene	0.49	u.v., mixed m.p.
17-24	3,4-Benzopyrene	0.65	u.v., mixed m.p.

23-24	Alkyl-3,4-benzopyrene	P	u.v.
19-21	Perylene	0.09	u.v.
16-21	10,11-Benzofluoranthene	0.12	u.v.
19-24	11,12-Benzofluoranthene	0.18	u.v.
19-24	3,4-Benzofluoranthene	0.10	u.v., mixed m.p.
21-24	1,2:5,6-Dibenzanthracene	0.09	u.v.
22-24	4,5-(*o*-Phenylene)fluoranthene	0.01	u.v.
22-26	1,12-Benzoperylene	0.36	u.v., mixed m.p.
24-27	7,10-Benzofluoranthene	0.11	u.v., mixed m.p.
25-27	Picene	0.02	u.v.
22-26	2,3-(*o*-Phenylene) pyrene	0.22	u.v., m.p.
25-28	Anthanthrene	0.13	u.v.
28-30	3,4-Benzotetraphene	0.03	u.v.
26-30	1,2:4,5-Dibenzopyrene	0.03	u.v.
28-30	1,2:3,4-Dibenzopyrene	0.02	u.v.
28-30	3,4:9,10-Dibenzopyrene	0.04	u.v.
28-30	3,4:8,9-Dibenzopyrene	0.02	u.v.
	Losses, resins, and unidentified material.	1.4	

RESULTS AND DISCUSSION

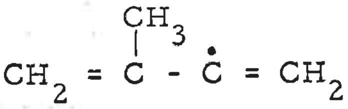
The pyrolysis was carried out by passing the isoprene vapour, with nitrogen, through a silica tube packed with porcelain chips at 700°. Methane, ethylene, propylene and acetylene were detected in the exit gases. The tar (obtained in 50.2% yield) was collected and analysed by chromatography and spectroscopy. The various compounds identified have been listed in Table 3.1.; toluene, benzene, p-xylene and m-xylene were the major constituents of the tar.

Hydrogen abstraction from isoprene would lead to radicals (I)-(IV), and these must be major components in the reaction zone. The 2-5 carbon-carbon bond would be expected to have a low dissociation energy, and would therefore undergo scission to form the butadienyl radical (V). The formation of many of the compounds found in the tar can be explained by reactions of these five primary radicals.



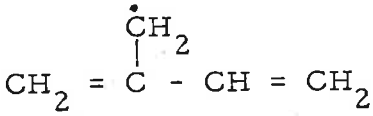
$\underset{1}{CH_2} = \underset{2}{\overset{{}^{5}CH_3}{C}} - \underset{3}{CH} = \underset{4}{\dot{C}H}$

(I)



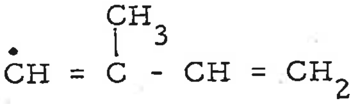
$CH_2 = \overset{CH_3}{C} - \dot{C} = CH_2$

(II)



$CH_2 = \overset{\dot{C}H_2}{C} - CH = CH_2$

(III)



$\dot{C}H = \overset{CH_3}{C} - CH = CH_2$

(IV)

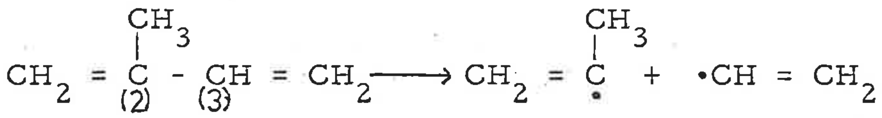
$CH_2 = \dot{C} - CH = CH_2$

(V)

The dimerisation of isoprene, (the reaction of radicals (I)-(IV) with another molecule of isoprene, or with each other) followed by dehydrogenation, would give six possible products, all of which were isolated from the tar. These compounds are *p*-methyl-α-methylstyrene (VI), *m*-methyl-α-methylstyrene (VII), *m*-xylene (VIII), *m*-methylstyrene (IX), *p*-xylene (X) and *p*-methylstyrene (XI). The total yield of these dimerisation products was almost 17%, a considerable proportion of the tar.

Hydrogenation of the double bond in *p*- and *m*-methyl-α-methylstyrene (VI and VII) would give *p*- and *m*-cymene (XII and XIII) respectively, (equations (3.i) and (3.ii)), and these compounds were also produced in considerable yield.

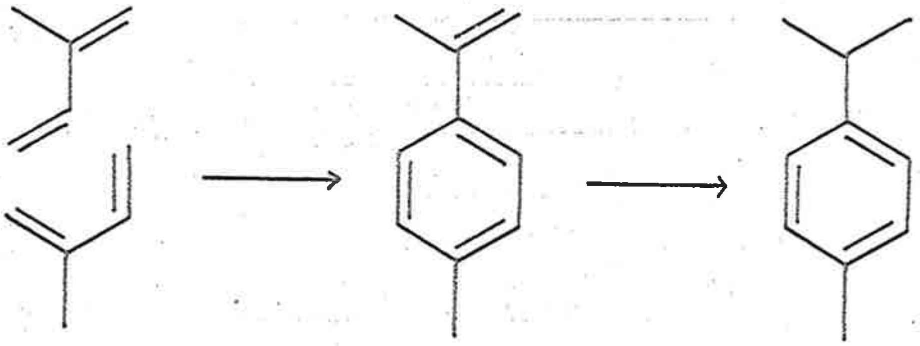
Scission of the 2-3 carbon-carbon bond in isoprene would give C_2 and C_3 units, which could then react with other constituents in the reaction zone to form the required compounds. Propylene, ethylene and acetylene were all identified in the exit gases, indicating that such units were in fact present in the reaction zone.



$$\mathrm{CH_2 = \underset{(2)}{\overset{\overset{CH_3}{|}}{C}} - \underset{(3)}{CH} = CH_2 \longrightarrow CH_2 = \underset{\bullet}{\overset{\overset{CH_3}{|}}{C}} + \cdot CH = CH_2}$$

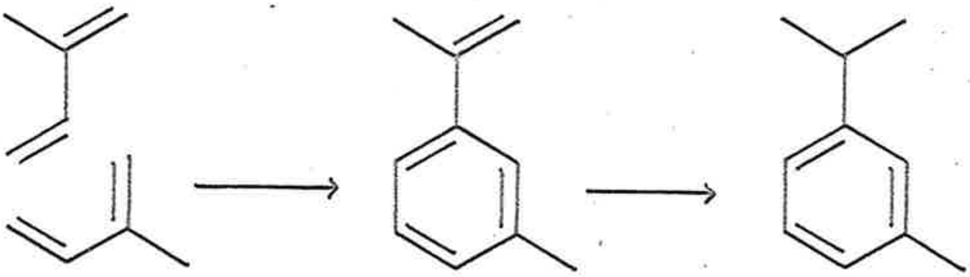
...equation (3.v).

Toluene (XIV) was the major constituent of the tar and would



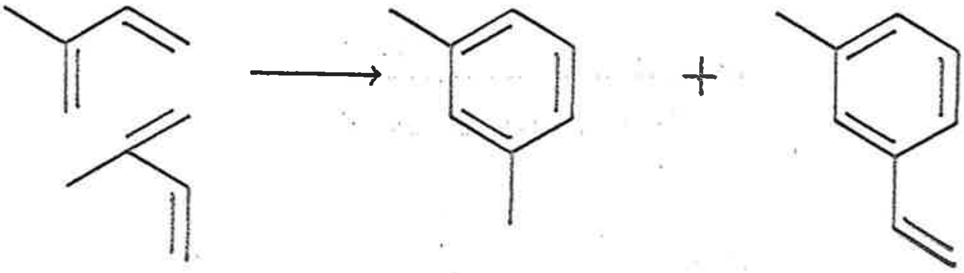
(VI)

(XII) equation (3.i)



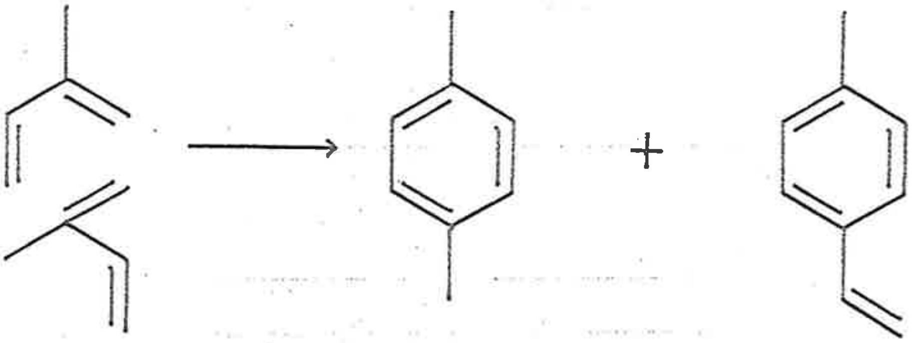
(VII)

(XIII) equation (3.ii)



(VIII)

(IX) equation (3.iii)



(X)

(XI) equation (3.iv)

probably be formed by reaction of a C_2 unit with an isoprene radical, or isoprene itself, as shown in equation (3.vi).

(XIV)

equation (3.vi)

Similarly, reaction of the butadienyl radical (V) with a C_2 unit would be a feasible route to benzene (XV) (equation (3.vii)).

(XV)

equation (3.vii)

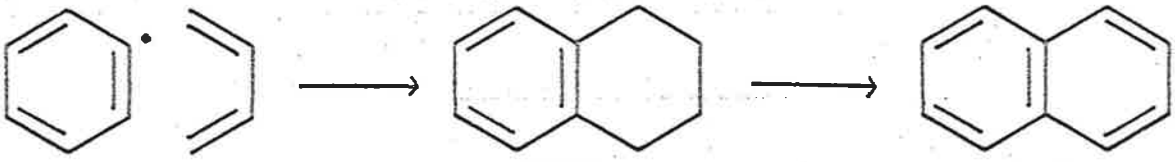
α-Methylstyrene (XVI) could be formed by reaction of the butadienyl radical with isoprene, followed by dehydrogenation as in equation (3.viii), while the dimerisation of two butadienyl radicals would account for the styrene (XVII) formed (equation (3.ix)). The trace of ethylbenzene detected in the tar could arise following hydrogenation of the double bond in styrene.

Attack of a C_3 unit on a phenyl radical, followed by cyclodehydrogenation, would yield indene (XVIII) (equation (3.x)), and an analogous reaction between a phenyl and butadienyl radical would give tetralin (XIX) on cyclisation. Subsequent dehydrogenation of tetralin would account for the naphthalene (XX) found in the tar (equation (3.xi)).

(XVI) equation (3.viii)

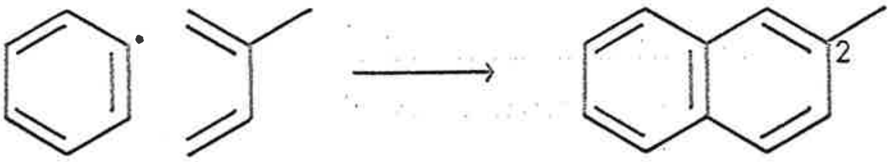
(XVII) equation (3.ix)

(XVIII) equation (3.x)



(XIX) (XX)
equation (3.xi)

2-Methylnaphthalene (XXI) could similarly be formed by attack of isoprene (or radical) on a phenyl radical (equation (3.xii)), while reaction between a benzyl radical and butadiene would give the 1-methyl isomer (XXII) (equation (3.xiii)). As ultraviolet spectroscopy showed a predominance of 2-methylnaphthalene, reaction (3.xii) must have occurred to a greater extent than reaction (3.xiii).

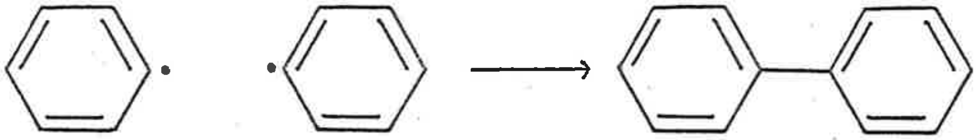


(XXI) equation (3.xii)

(XXII) equation (3.xiii)

Biphenyl (XXIII), and its 4,4'-dimethyl derivative (XXIV), would presumably be formed by the following schemes (equations (3.xiv) and (3.xv)), and bibenzyl (XXV) by the dimerisation of two benzyl radicals (equation (3.xvi)).

Reaction between styrene and the butadienyl radical (V), followed by cyclodehydrogenation would account for the acenaphthylene (XXVI)

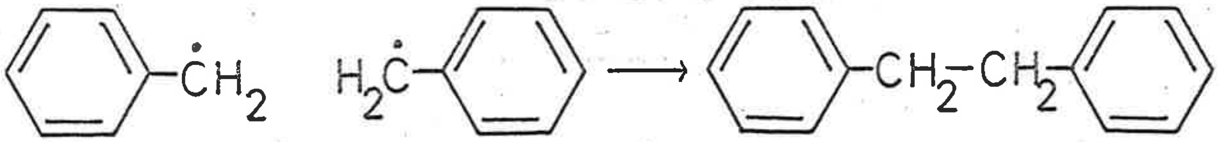


(XXIII)

equation (3.xiv)

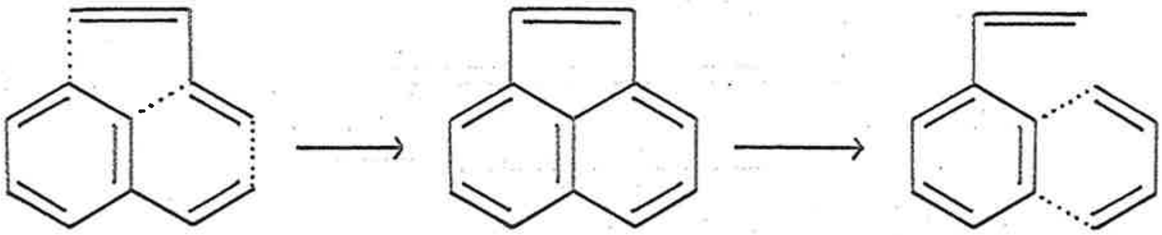
(XXIV)

equation (3.xv)



(XXV)

equation (3.xvi)



(XXVI)

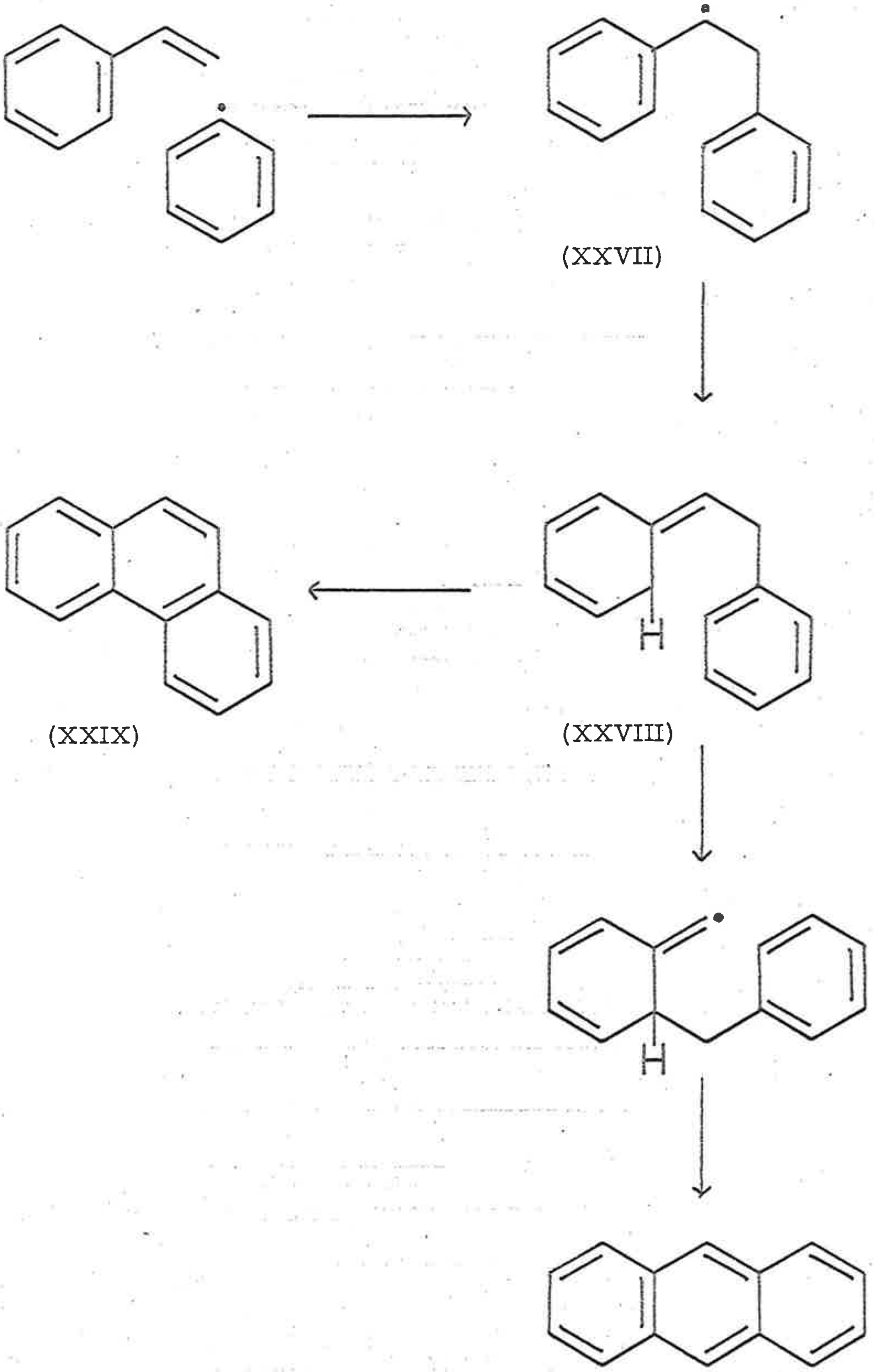
equation (3.xvii)

found in the tar (equation (3.xvii)).

The activity of the phenanthrene isolated from the tars following pyrolysis of (1 - ^{14}C) tetralin,[54] (δ - ^{14}C) butylbenzene and (α - ^{14}C) ethylbenzene[48] indicates that the most favourable route to phenanthrene (XXIX) involves attack of a phenyl radical on styrene. This mechanism would also be expected to be important in the present pyrolysis, as styrene was obtained in considerable yield. As previously suggested by Badger,[67] proton addition to the radical (XXVII) provides an alternative route to bibenzyl (XXV), while rearrangement of (XXVIII) would lead to the formation of anthracene (XXX) (equation (3.xviii)). The reaction between a butadienyl radical and naphthalene may also contribute to the formation of phenanthrene and anthracene in this pyrolysis (equation (3.xix)).

Similarly, the attack of an isopropenyl radical on naphthalene would produce methylphenanthrenes, which were obtained in significant yield.

Two mechanisms seem probable for the formation of pyrene in this pyrolysis. The first involves the dimerisation of styrene; and the methylpyrene isolated could be formed by the analogous reaction of styrene with a methylstyryl radical. However, it must be admitted that the pyrolysis of styrene[46] gave only a small yield of pyrene. Some



(XXVII)

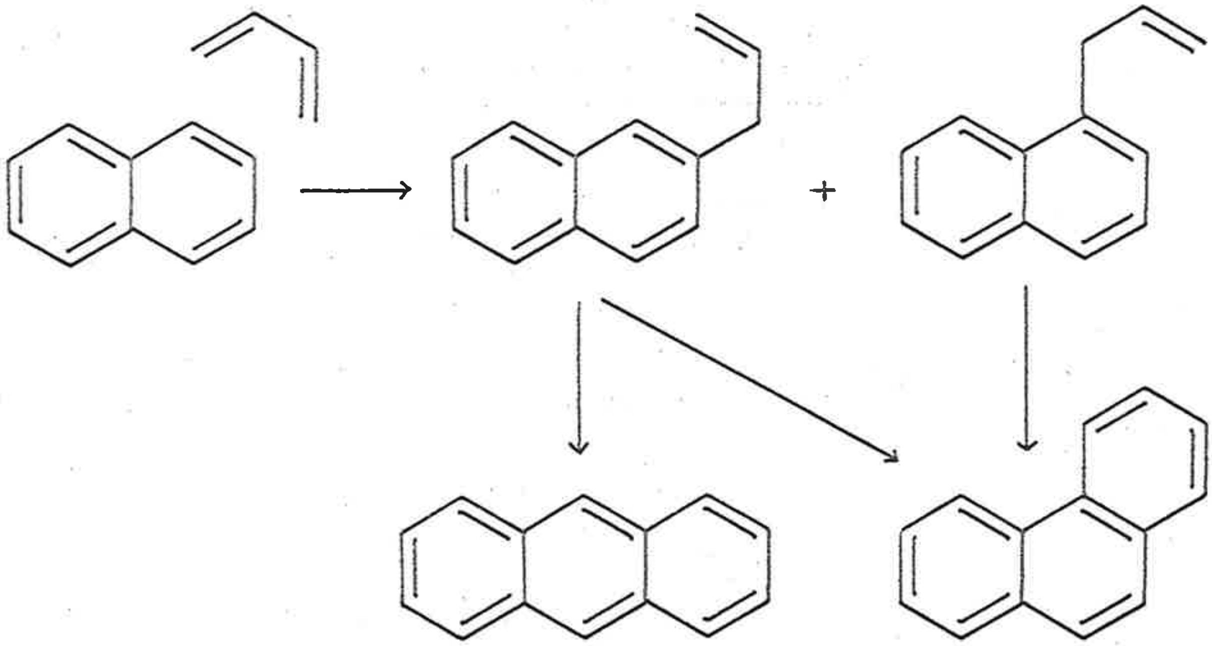
(XXVIII)

(XXIX)

(XXX)

equation (3.xviii)

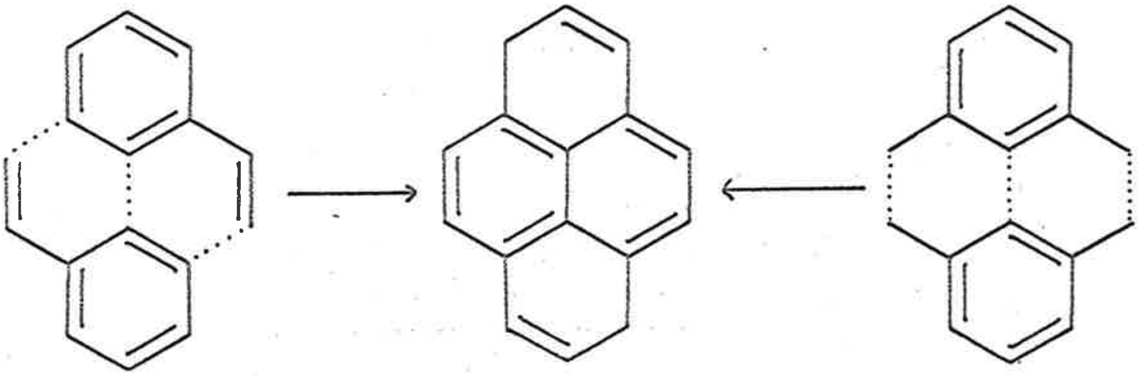
pyrene could also be formed from m-xylene, which was obtained in considerable yield, and the pyrolysis of m-xylene is known to produce pyrene.[102]



(XXX)

(XXIX)

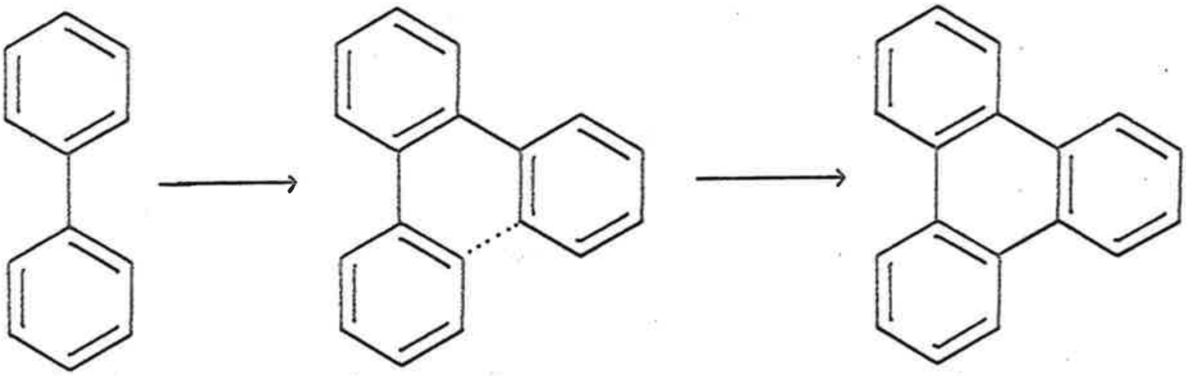
equation (3.xix)



(XXXI)

equation (3.xx)

The phenylation of aromatic compounds, followed by cyclodehydrogenation, provides a convenient route to many more highly condensed compounds. For example, the attack of a phenyl radical on benzene gives biphenyl (XXIII), and further phenylation of this compound would be expected to yield triphenylene (XXXII), in addition to the *m*- and *p*-terphenyls.



(XXIII)

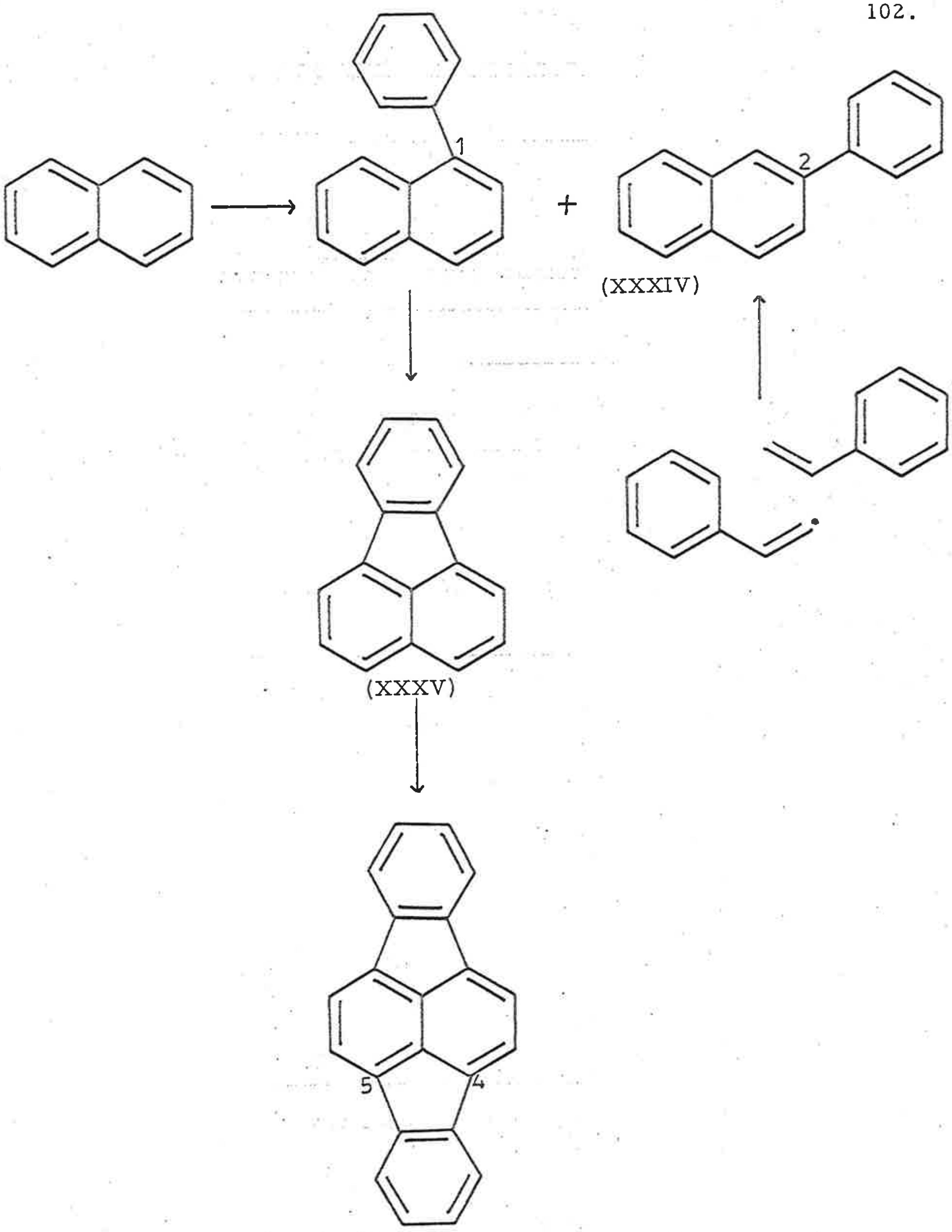
(XXXII)
equation (3.xxi)

Similarly, the phenylation of toluene (or a benzyl radical) in the 2-position, followed by cyclisation, provides a route to fluorene (XXXIII) (equation (3.xxii)). An alternative mechanism for the formation of fluorene involves the reaction of butadiene with indene.

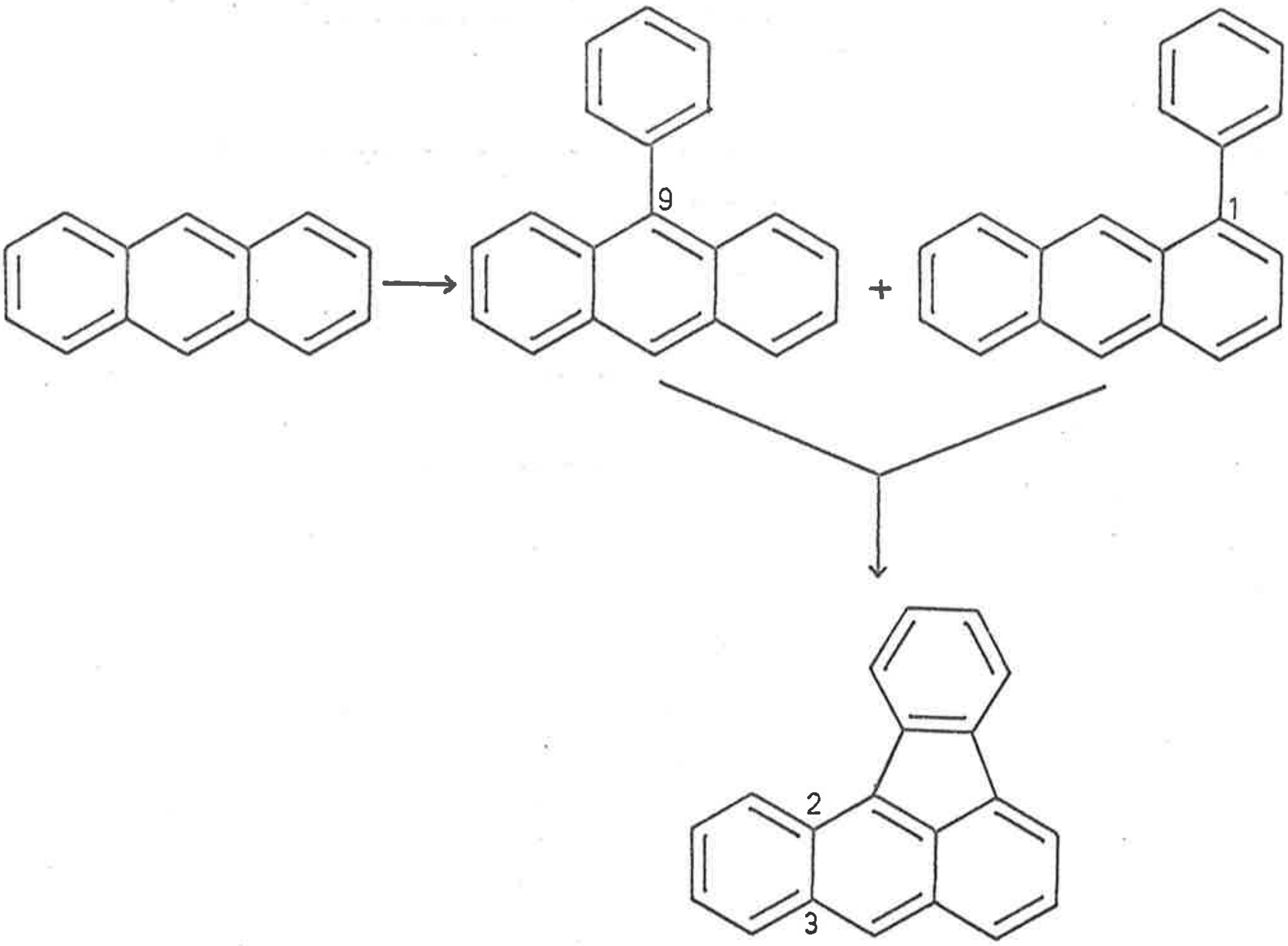
(XXXIII) equation (3.xxii)

Attack of a phenyl radical on naphthalene gives both 1- and 2-phenylnaphthalenes.[103] The 1-phenyl isomer can undergo cyclodehydrogenation to fluoranthene (XXXV), but further condensation is not possible for 2-phenylnaphthalene (XXXIV); the latter compound was detected in the tar, together with a relatively large yield of fluoranthene. The pyrolysis of a mixture of benzene and naphthalene[72] has in fact been found to produce fluoranthene in significant yield. The dimerisation of two styryl radicals[46] could also provide a path to 2-phenylnaphthalene. 4,5-(o-Phenylene)fluoranthene (XXXVI) was also detected in the tar, and this would presumably arise by cyclodehydrogenation of 4-phenylfluoranthene (equation (3.xxiii)).

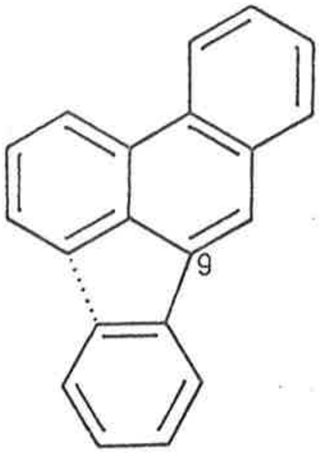
A phenyl radical can attack anthracene at three different positions, and experiments on the phenylation of anthracene[104] have shown the relative reactivities to be in the order $9 \gg 1 > 2$. Phenylation of anthracene would thus give mainly 9-phenylanthracene (XXXVII), which would yield 2,3-benzofluoranthene (XXXVIII) on cyclodehydrogenation. The same compound would also be expected to be formed from 1-phenylanthracene, and it was detected in trace amounts in the tar.



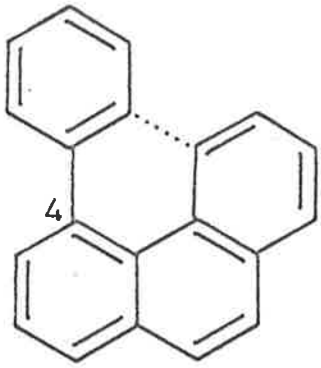
equation (3.xxiii)



(XXXVIII) equation (3.xxiv)



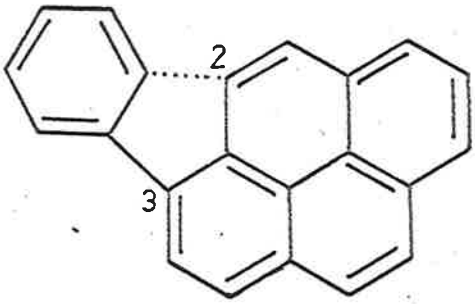
(XXXIX)



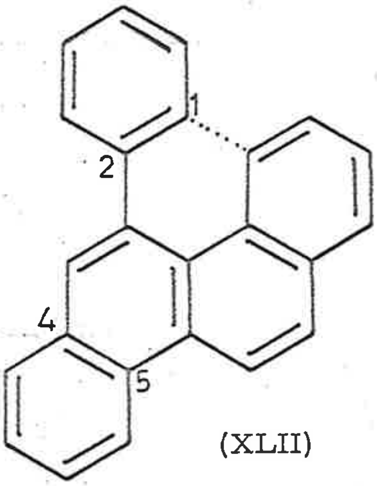
(XL)

Phenylation of phenanthrene gives a complex mixture of the five possible phenylphenanthrenes, and it has been found experimentally that the yields obtained are in the order 9 > 4 > 1 ≫ 3 > 2.[105] Thus 9-, 4- and 1-phenylphenanthrenes would be expected to be formed in the greatest yields, and these compounds can all undergo cyclodehydrogenation to more highly condensed polycyclics. Both the 9- and 1-isomer would give 3,4-benzofluoranthene (XXXIX), while 4-phenylphenanthrene would condense to form 1,2-benzopyrene (XL), as in equations (1.x) and (1.xi). Further condensation of 2- or 3-phenylphenanthrene is not possible; however, these compounds were not found in the tar.

The phenylation of pyrene followed by cyclodehydrogenation would produce 2,3-(o-phenylene) pyrene (XLI), as discussed in Chapter 1; and the formation of 1,2:4,5-dibenzopyrene (XLII) could proceed by cyclodehydrogenation of either 1- or 12-phenylchrysene.

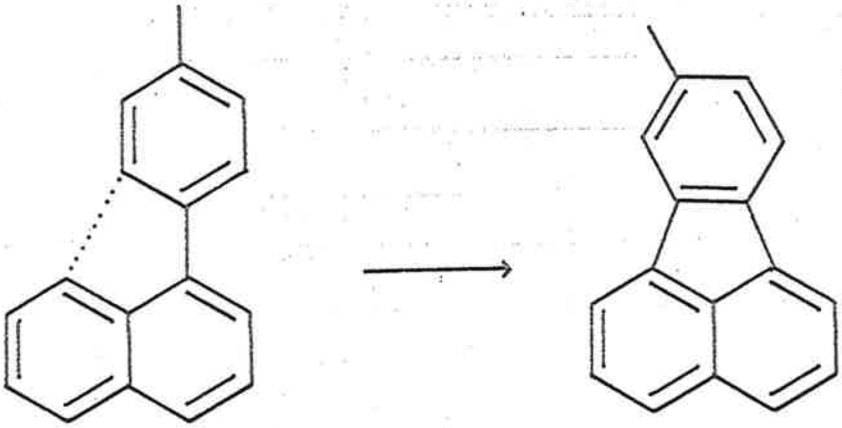


(XLI)



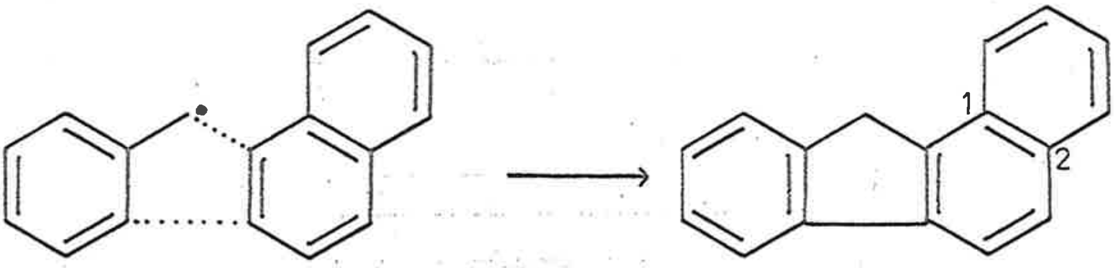
(XLII)

As toluene was the major product of the pyrolysis, a high concentration of radicals derived by hydrogen abstraction from toluene would be expected to be present in the reaction zone. Hence reaction of a radical, such as the 4-methylphenyl radical, with naphthalene, followed by cyclodehydrogenation, would account for the methylfluoranthene (XLIII) detected in the tar (equation (3.xxv)).



(XLIII) equation (3.xxv)

Similarly, both 1,2-benzofluorene (XLIV) and 2,3-benzofluorene (XLV) could be formed by reaction of a benzyl radical with naphthalene (equations (3.xxvi) and (3.xxvii)). 1,2-Benzanthracene (XLVI) could conceivably be formed by reaction of a benzyl radical with 1- and 2-methylnaphthalene (equation (3.xxviii)), and chrysene (XLVII) by a similar mechanism (equation (3.xxix)). This mechanism represents one of many possible routes to chrysene, and others have been discussed previously.[49, 54]

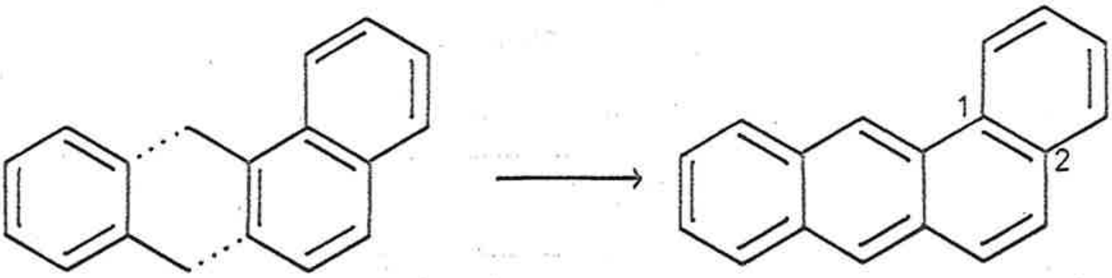


(XLIV)

equation (3.xxvi)

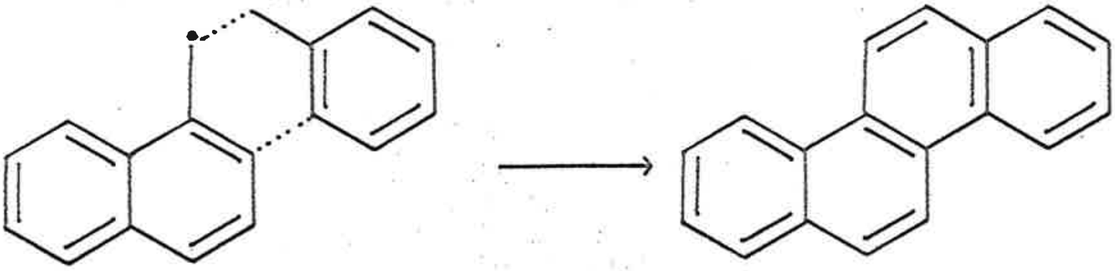
(XLV)

equation (3.xxvii)



(XLVI)

equation (3.xxviii)

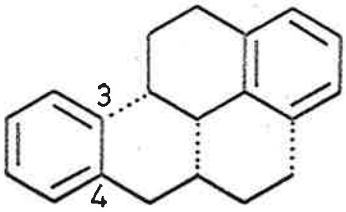


(XLVII)

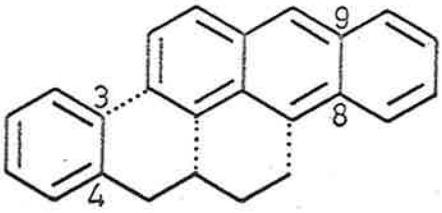
equation (3.xxix)

Comparison of the yields of 1,2-benzopyrene and 3,4-benzopyrene produced by the pyrolysis of butadiene,[41] with those obtained from butadiene plus pyrene[41] under the same conditions, has shown that the Diels-Alder addition of butadiene to pyrene is not an important route to the benzopyrenes. The mechanism of formation of 3,4-benzopyrene (XLVIII) discussed in Chapter 2 (equation(2.xiv)) has gained considerable support from experiments using labelled precursors,[67] and could well be important in this pyrolysis. Analogous mechanisms can be postulated for the formation of 1,2:3,4-dibenzopyrene (XLIX), 3,4:9,10-dibenzopyrene (L), and 3,4:8,9-dibenzopyrene (LI), all of which have been found to be potent carcinogens.

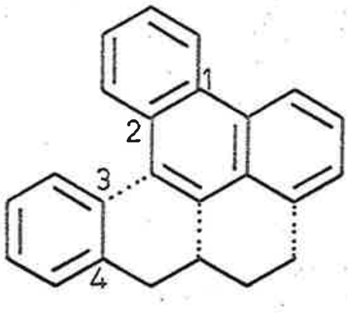
It has been suggested[58] that 1,12-benzoperylene (LII) could be formed by the addition of a C_2 unit to the 1,12 positions of perylene. There is some doubt about the feasibility of this reaction as benzyne was found not to add across these positions;[106] but maleic anhydride certainly adds to the 1,12 positions.[107] Moreover, the perylene (or radical) in the reaction zone would be in an excited state, and it is possible that the C_2 unit could add to this excited moiety, if not to perylene itself. An alternative mechanism involving the reaction of phenanthrene with a $C_6 - C_2$ unit may also operate to some extent (equation (3.xxxi)).



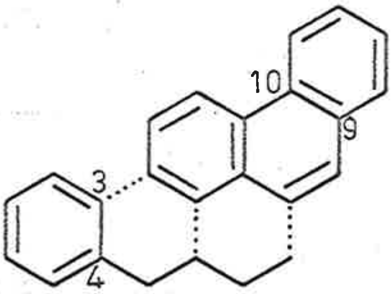
(XLVIII)



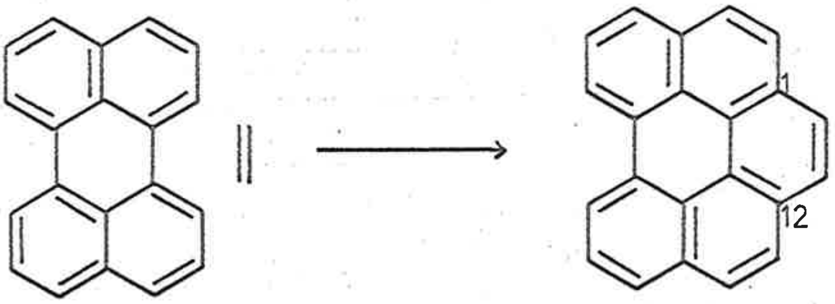
(LI)



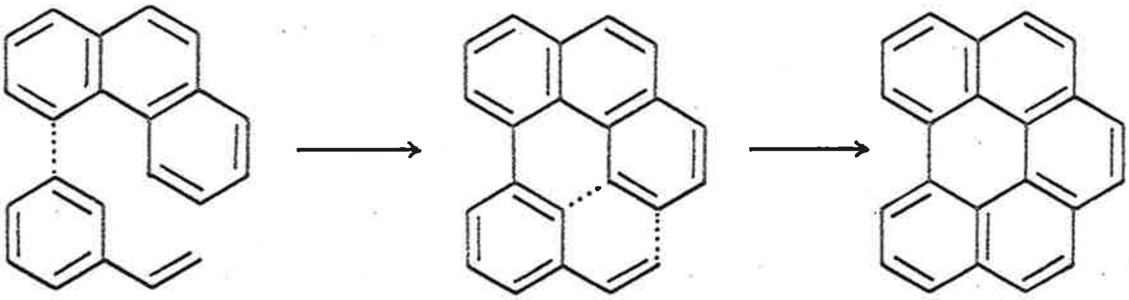
(XLIX)



(L)

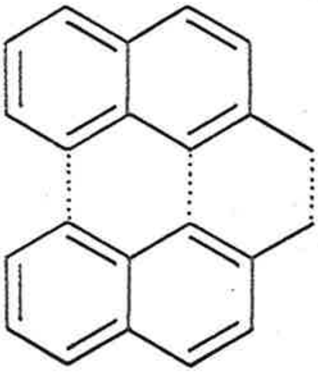


(LII)
equation (3.xxx)

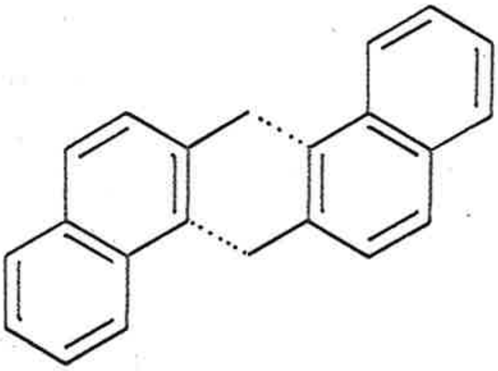


(LII)
equation (3.xxxi)

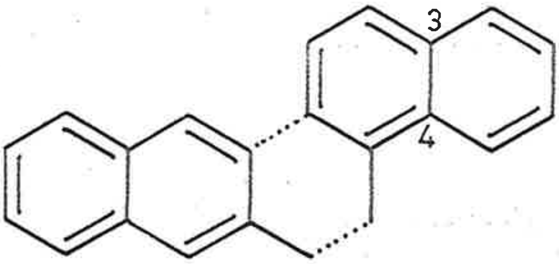
Lijinsky and Raha[108] have shown that 1,12-benzoperylene, 1,2:5,6-dibenzanthracene (LIII) and 3,4-benzotetraphene (LIV) are formed following pyrolysis of 2-methylnaphthalene, and this could well be an important route to these compounds in the present pyrolysis. These workers suggest that the 1-methylnaphthalene necessary for the formation of 3,4-benzotetraphene (LIV) was present as impurity in the starting material. However, the methylnaphthalenes are known[69] to isomerise at high temperatures, and this seems to be a more likely source of the 1-isomer. Picene (LV) and anthanthrene (LVI) can also be visualized as forming from methylnaphthalenes, although a mechanism analogous to that in equation (3.xxxi) may be postulated for picene (equation (3.xxxii)).



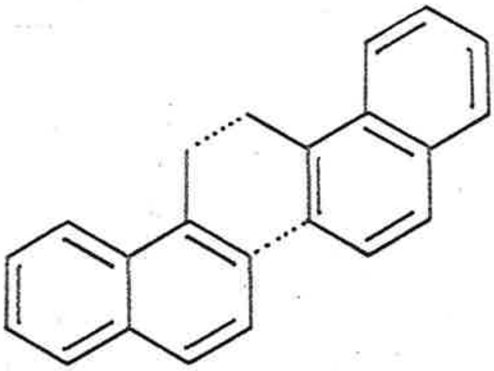
(LII)



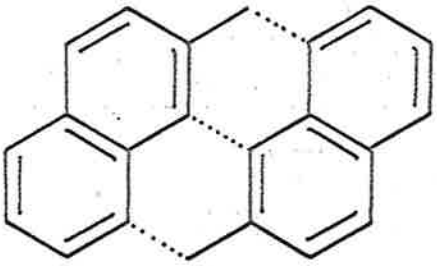
(LIII)



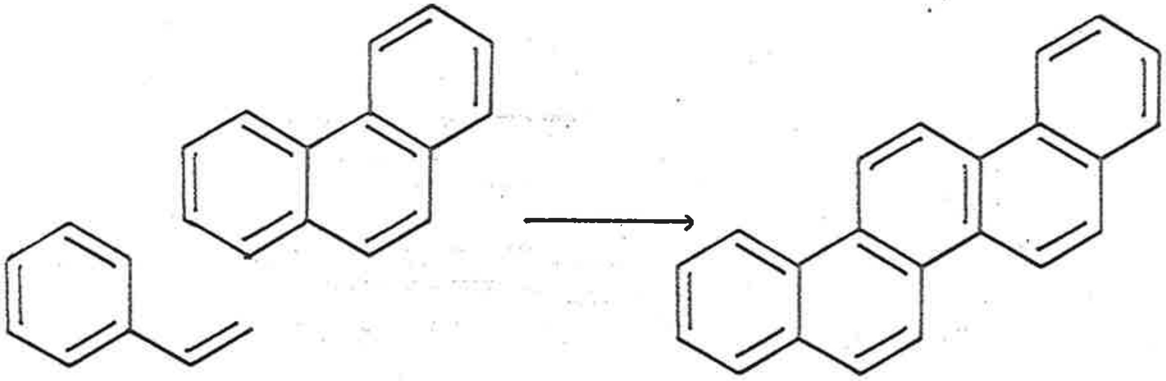
(LIV)



(LV)

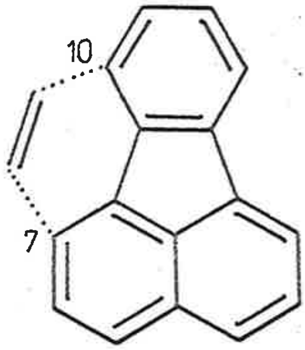


(LVI)

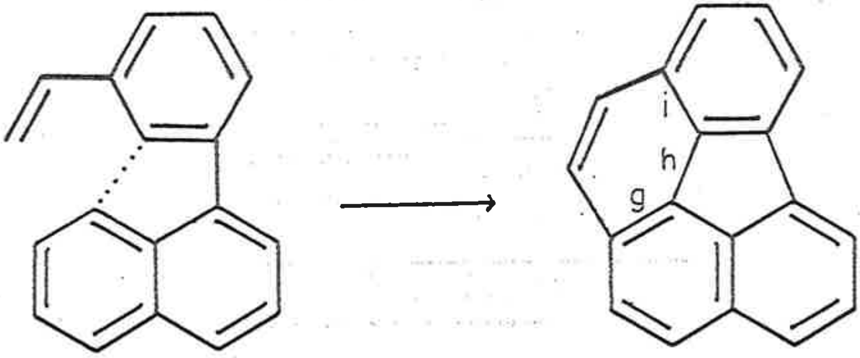


(LV) equation (3.xxxii)

The addition of a C_2 unit to fluoranthene would account for the formation of 7,10-benzofluoranthene (LVII), but this reaction would probably be energetically unfavourable, and an alternative mechanism is suggested (equation (3.xxxiii)). This involves attack of a C_6C_2 unit on naphthalene, followed by cyclodehydrogenation.



(LVII)



(LVII)

equation (3.xxxiii)

However the former mechanism may become important at very high temperatures (e.g. the temperature of petrol combustion) as 7, 10-benzofluoranthene is often found in polluted air and gasoline exhaust condensates. It is interesting that higher yields of 1, 12-benzoperylene, and also of coronene (both of which may be formed by C_2 addition to perylene) are also found in these sources.

EXPERIMENTAL

(a) General

Isoprene

A Commercial sample (Fluka) was purified by fractional distillation. The fraction b.p. 34 - 35°, n_D^{20} 1.422 (lit.[109] n_D^{20} 1.42158) contained no impurities which could be detected by gas-liquid chromatograph

Pyrolysis

Isoprene (100g) was vapourised at 7g/hour and passed with oxygen free nitrogen (1 ml/sec) through a silica tube (36" x 1" i.d.), packed with porcelain chips, which was maintained at 700° in an electrically heated furnace. The resulting dark brown tar (50.18g) was collected in a series of traps containing ice-salt, CO_2 - ethanol and liquid air. Samples of the exit gases were collected at intervals and examined by infrared spectroscopy.

Analysis of Tar

The tar (50.18g, 50.2%) was distilled to give seven main fraction (a) - (g), and a residue (h), 10.99g. Fractions (a) - (g) were examined by gas-liquid chromatography and peaks corresponding to butadiene, isoprene, cyclopentene, benzene, toluene, ethylbenzene, p- and m-xylenes, styrene, α-methylstyrene, m- and p- methyl - α-methylstyrenes, indene, tetralin, naphthalene, 1- and 2-methylnaphthalenes, biphenyl, 4,4'-biphenyl, bibenzyl, acenaphthylene and fluorene were observed. The identity of these compounds was usually confirmed by infrared or ultraviolet spectroscopy.

Half of the residue (h) was chromatographed on a column of Spence alumina (600g) by dissolving the whole residue in chloroform, adding alumina, removing the solvent on a rotatory evaporator and adding half the adsorbed residue to the column. Hexane, hexane-benzene, benzene and finally ethanol were used as eluants, and 140 x 250 ml fractions were collected. On the basis of their ultraviolet spectra these fractions were recombined to give 30 main fractions, which were rechromatographed on columns and thin-layers of partially acetylated cellulose. Some compounds were further purified by chromatography on dry columns of acetylated cellulose.

(b) Details of Identification

Methane, Ethylene, Propylene and Acetylene

Samples of the exit gases were collected in a gas cell for infrared analysis. The composition of the exit gases remained constant during the pyrolysis, and the individual gases were identified by their characteristic band systems : methane in the 7.3-8.5 μ region; ethylene in the 9.8-11.5 μ region; propylene in the 5.6-6.3 μ region; and acetylene by its spectrum in the 12.5-14.5 μ region.[80]

Butadiene, Isoprene and Cyclopentene

Identified in fractions (a) and (b) by comparison of retention-time ratios with those of authentic specimens.

Benzene

Isolated from fractions (a) - (e) by gas-liquid chromatography. The infrared absorption spectrum (liquid film) showed maxima at 3.25, 3.31, 4.31, 4.53, 5.10, 5.41, 5.62, 5.90, 6.52, 6.75, 7.13, 8.48 and 9.62 μ, in agreement with an authentic specimen.

Toluene

Isolated from fractions (b) - (f) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.29, 3.42, 3.48, 3.65, 3.86, 5.15, 5.39, 5.55, 5.76, 6.23, 6.68, 6.85, 7.25, 8.26, 8.48, 9.25, 9.60, 9.71, 11.16, 13.74 and 14.41 μ, in agreement with an authentic specimen.

Ethylbenzene

Detected in fraction (d) by comparison of its retention-time ratio with that of an authentic specimen.

p-Xylene and m-Xylene

Isolated from fraction (d), (and identified in fractions (c) - (f)) by gas-liquid chromatography. The infrared spectrum (liquid film) was complex, and showed many peaks common to both isomers, and some due to the individual compounds. The spectrum was identical with that obtained from a 1:1 mixture of authentic samples of p- and m-xylene.

Styrene

Isolated from distillation fraction (d), (and identified in fractions (d) - (g)) by gas-liquid chromatography. The infrared spectrum showed maxima at 3.22, 3.27, 5.46, 6.21, 6.70, 6.90, 7.05, 7.74, 8.30, 8.48, 8.92, 9.02, 9.22, 9.80, 10.09, 11.0, 11.9, 12.90 and 14.37 µ, in agreement with an authentic specimen.

α-Methylstyrene

Isolated from fraction (g) (and identified in fractions (f) and (h)) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3.22, 3.33, 4.36, 5.16, 5.36, 5.60, 5.87, 5.96, 6.14, 6.40, 6.73, 6.98, 7.35, 7.76, 7.96, 8.60, 9.41, 9.82, 10.00, 10.52, 11.24, 12.82 and 13.16µ, in agreement with the literature.[110]

m-Methylstyrene and p-Methylstyrene

Isolated from fraction (g), and also identified in fractions (f) and (h) by gas-liquid chromatography. The infrared spectrum (liquid film) was complex, and the presence of both isomers was established by comparison of the maxima with literature values.[111]

m-Cymene and p-Cymene

Isolated from fractions (g) and (h), and identified in fraction (f), by gas-liquid chromatography. The infrared spectrum showed the presence of both compounds. Comparison of this spectrum with spectra of authentic compounds in varying ratios gave the ratio m-cymene : p-cymene c 1:1. Maxima at 11.15, 11.38, 11.71, 11.84, 11.77 and 14.22 μ may be assigned to the meta isomer, and maxima at 9.79, 10.44, 10.65, 11.22, 11.60 and 11.96 μ, to the para isomer. There were also many other peaks which are common to both isomers.

m-Methyl-α-methylstyrene and p-Methyl-α-methylstyrene

Isolated from fraction (h), and also identified in fractions (f) and (g), by gas-liquid chromatography. The infrared spectrum was almost identical with that of p-methyl-α-methylstyrene,[112] but showed some additional peaks which were probably due to the meta isomer. (The infrared spectrum of m-methyl-α-methylstyrene has not been recorded).

Indene

Isolated from distillation fraction (h) by gas-liquid chromatography The infrared spectrum (liquid film) showed maxima at 3.26, 3.46, 3.60, 6.24, 6.50, 6.92, 7.24, 7.40, 7.58, 7.68, 7.82, 8.20, 8.35, 8.96, 9.40, 9.84, 10.54, 10.90, 11.60, 12.08, 13.02, 13.70 and 14.40 μ, in agreement with an authentic specimen.

Tetralin

Identified in fractions (g) and (h) by comparison of its retention-time ratio with that of an authentic specimen.

Naphthalene

Identified in distillation fractions (g) and (h) by retention-time ratio, and isolated from fraction (l) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 248, 257, 266, 275, 285 and 311 mμ ; a sample had m.p. and mixed m.p. 78 - 80°.

1- and 2-Methylnaphthalene

Identified in distillation fraction (h) by retention-time ratio, and isolated from fraction (l) by chromatography on partially acetylated cellulose. The mixture of isomers showed ultraviolet absorption maxima at 224, 272, 278, 283, 287, 291, 294, 306, 312 and 319 mμ, and the shape of the curve suggested the predominance of the 2-isomer.

Biphenyl

Identified in distillation fraction (h) by comparison of its retention-time ratio with that of an authentic sample ; and isolated from fraction (l) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed a maximum at 249 mμ; and it had m.p. and mixed m.p. 68 - 70°.

4,4' - Dimethylbiphenyl

Identified in distillation fraction (h) by comparison of its retention-time ratio with that of an authentic sample; also identified in fractio (1) by chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed a maximum at 255 mμ.

Bibenzyl

Identified in distillation fraction (h) by retention-time ratio, and also in fraction (1) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 255, 260 and 266 mμ, in agreement with an authentic specimen.

Acenaphthylene

Isolated from fractions (1) - (3) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 229, 258, 266, 276, 309, 323, 334 and 340 mμ in agreement with an authentic specimen.

Fluorene

Isolated from fractions (2) - (4) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 260, 290 and 301 mμ, in agreement with an authentic sample.

2- Phenylnaphthalene

Identified in fractions (2) and (3) by chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 250 and 285 mμ, in agreement with recorded values.[113]

Phenanthrene

Isolated from fractions (2) - (7) by chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 243, 252, 275, 282, 294, 310, 317, 324, 331, 339 and 346 mμ, in agreement with an authentic specimen. A sample had m.p. and mixed m.p. 96 - 98°.

Methylphenanthrene

Isolated from fractions (5) - (7) by chromatography on a column of partially acetylated cellulose. The ultraviolet spectrum was the same general shape as that of phenanthrene, but shifted to longer wavelengths. The nuclear magnetic resonance spectrum confirmed the presence of a methyl group (τ , 7.6).

Anthracene

Isolated from fractions (3) - (7) following chromatography on partially acetylated cellulose. The u.v. spectrum showed maxima at 246, 253, 308, 323, 339, 357 and 377 mμ, in agreement with an authentic specimen; and a sample had m.p. and mixed m.p. 215 - 216°.

Pyrene

Isolated from fractions (6) - (10) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335, 351, 358, 364 and 373 mμ, in agreement with an authentic specimen; and it had m.p. and mixed m.p. 145 - 147°.

Methylpyrene

Isolated from fractions (8) - (10) by chromatography on a column of partially acetylated cellulose. Its ultraviolet spectrum (maxima at 243, 255, 264, 278, 310, 322 and 339 mμ) and m.p. (137 - 139°) suggested a methylpyrene, and this was confirmed by n.m.r. spectroscopy. (τ, 7.3).

Fluoranthene

Isolated from fractions (8) - (12) by chromatography on partially acetylated cellulose. The u.v. spectrum showed maxima at 236, 253, 263, 273, 278, 282, 309, 323, 342 and 360 mμ, in agreement with an authentic specimen. A sample had m.p. and mixed m.p. 105 - 107°.

Alkylfluoranthene

Detected in fractions (10) - (12) by chromatography on a column of partially acetylated cellulose, followed by thin-layer chromatography. The ultraviolet absorption spectrum showed maxima at 280, 285, 291, 311, 327, 346 and 364 mμ, but insufficient material was available for further identification.

2,2'-Binaphthyl

Identified in fractions (11) - (13) by chromatography on both columns and thin-layers of acetylated cellulose. An extract showed maxima at 254 and 308 mμ, in agreement with an authentic specimen.

1,2-Benzanthracene

Identified in fractions (11) - (13) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 227, 256, 268, 278, 289, 300, 315, 326, 341, 358, 365, 374 and 384 mμ, in agreement with an authentic sample.

Triphenylene

Identified in fractions (11) - (13) by chromatography on a column of acetylated cellulose, followed by thin-layer chromatography. An extract showed u.v. absorption maxima at 250, 257, 275, 286, 316, 330 and 341 mμ, in agreement with an authentic specimen.

1,2-Benzofluorene

Identified in fractions (12) - (14) after chromatography on acetylated cellulose. The ultraviolet spectrum showed maxima at 229, 238, 253, 257, 262, 274, 286, 294, 303, 316 and 340 mμ, in agreement with an authentic specimen.

2,3-Benzofluorene

Identified in fractions (13) - (15) after chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 255, 264, 273, 285, 304, 317, 325, 333 and 340 mμ, in agreemen with an authentic sample.

Chrysene

Isolated from fractions (14) - (19) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 242, 259, 267, 283, 294, 306, 320, 344, 351 and 363 mμ, and it had m.p. and mixed m.p. 253 - 255°.

Alkylchrysene

Identified in fraction (19) by chromatography on a column of acetylated cellulose followed by thin-layer chromatography. An extract showed maxima at 244, 261, 272, 286, 297, 309, 324, 354 and 365 mμ; but insufficient material was available for further identification.

2,3-Benzofluoranthene

Identified in fractions (19) - (21) by chromatography on both columns and thin films of partially acetylated cellulose. An extract showed maxima at 256, 308, 346, 363 and 427 mμ, in agreement with recorded values.[83]

1,2-Benzopyrene

Isolated from fractions (15) - (21) by chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 238, 258, 268, 278, 289, 305, 317, 333 and 366 mμ, in agreement with an authentic specimen; and it had m.p. and mixed m.p. 175 - 177°.

3,4-Benzopyrene

Isolated from fractions (17) - (24) by chromatography on partially acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385 and 404 mμ, in agreement with an authentic specimen; a sample had m.p. and mixed m.p. 174 - 176°.

Alkyl-3,4-benzopyrene

Detected in fractions (23) and (24) following chromatography on columns and thin-films of partially acetylated cellulose. The ultraviolet absorption spectrum had the same general shape as that of 3,4-benzopyrene, but *para*-bands were shifted to longer wavelengths; maxima occurred at 300, 351, 370, 384, 390 and 410 mμ.

Perylene

Identified in fractions (19) - (21) following chromatography on columns and thin layers of acetylated cellulose. An extract showed absorption maxima at 245, 253, 263, 367, 386, 407 and 435 mμ, in agreement with an authentic specimen.

10,11-Benzofluoranthene

Identified in fractions (16) - (21) following chromatography on acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 241, 282, 293, 309, 318, 333, 345, 365, 376 and 383 mμ, in agreement with an authentic specimen.

11,12-Benzofluoranthene

Identified in fractions (19) - (24) after chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 238, 269, 283, 297, 309, 361, 380 and 402 mμ, in agreement with an authentic specimen.

3,4-Benzofluoranthene

Isolated from fractions (19) - (24) by chromatography on acetylated cellulose. A sample had m.p. and mixed m.p. 161 - 163°, and showed absorption maxima at 239, 256, 266, 276, 290, 294, 301, 320, 339, 351 and 369 mμ in agreement with an authentic specimen.

1,2:5,6-Dibenzanthracene

Identified in fractions (21) - (24) by chromatography on both columns and thin films of acetylated cellulose. An extract showed ultraviolet maxima at 231, 288, 298, 319, 335, 348, 374 and 383 mμ, in agreement with an authentic sample.

4,5-(o-Phenylene) fluoranthene

Identified in fractions (22) - (24) by chromatography on acetylated cellulose followed by thin-layer chromatography. An extract showed maxima at 253, 262, 272, 368, 380, 387, 402 and 411 mμ, in agreement with an authentic specimen.

1, 12-Benzoperylene (≡ benzo(ghi) perylene)

Isolated from fractions (22) - (26) by chromatography on acetylated cellulose followed by "dry chromatography". A sample had m.p. and mixed m.p. 271 - 273°; and its ultraviolet spectrum showed maxima at 268, 276, 289, 300, 315, 325, 330, 345, 363, 383 and 406 mμ in agreement with an authentic specimen.

7, 10-Benzofluoranthene (≡ benzo(ghi) fluoranthene)

Isolated from fractions (24) - (27) by rechromatographing certain fractions on a dry column of partially acetylated cellulose. A sample had m.p. and mixed m.p. 146 - 148°, and absorption maxima at 233, 245, 251, 260, 282, 291, 330.5, 346, 378, 398 and 420 mμ, in agreement with an authentic sample.

Picene

Identified in fractions (25) - (27) after chromatography on partially acetylated cellulose. The ultraviolet spectrum showed maxima at 232, 256, 274, 284, 301, 312 and 326 mμ, in agreement with an authentic specimen.

2, 3-(o-Phenylene) pyrene

Isolated from fractions (22) - (26) after chromatography on a column of acetylated cellulose followed by thin-layer chromatography. An extract showed absorption maxima at 251, 261, 275, 292, 304, 315, 360, 376, 385 and 407 mμ. A sample had m.p. 158 - 160° (lit.[82] 163°).

Anthanthrene

Identified in fractions (25) - (28) after chromatography on partially acetylated cellulose. The absorption spectrum showed maxima at 233, 256, 259, 295, 308, 365, 382, 402, 407, 422 and 431 mμ, in agreement with an authentic specimen.

1, 2:4, 5-Dibenzopyrene

Identified in fractions (26) - (30) after chromatography on acetylated cellulose, followed by dry chromatography. The absorption spectrum (in benzene) showed maxima at 294, 306, 327, 343, 360, 378, 396 and 416 mμ, in agreement with the literature.[83]

3, 4-Benzotetraphene

Identified in fractions (28) - (30) after chromatography on a dry column of acetylated cellulose. The absorption spectrum showed maxima at 248, 277, 287, 304, 318, 332, 345, 363, 382 and 390 mμ, in agreement with an authentic specimen.

1, 2:3, 4-Dibenzopyrene

Identified in fractions (28) - (30) after rechromatographing certain fractions on a dry column of acetylated cellulose. The absorption spectrum showed maxima at 240, 253, 261, 271, 289, 301, 315, 331, 359, 379 and 402 mμ, in agreement with the literature.[83]

3,4:9,10-Dibenzopyrene

Identified in fractions (28) - (30) following chromatography on a dry column of partially acetylated cellulose. The absorption spectrum showed maxima at 233, 242, 273, 283, 296, 315, 331, 353, 373 and 393 mμ, in agreement with an authentic sample.

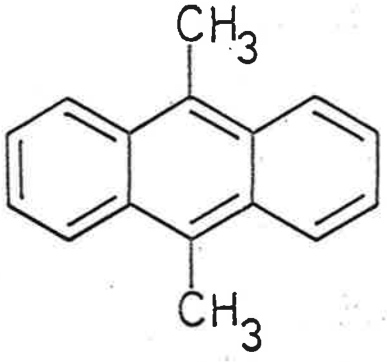
3,4:8,9-Dibenzopyrene

Identified in fractions (28) - (30) after chromatography on a column of acetylated cellulose. The absorption spectrum showed maxima at 291, 301, 314, 379, 401, 424 and 452 mμ, in agreement with recorded values.[83]

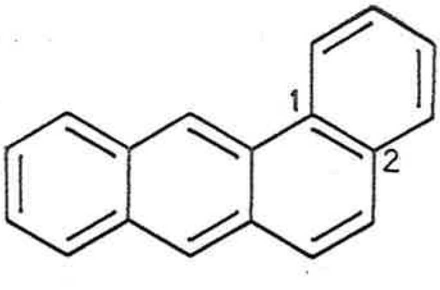
CHAPTER 4

PYROLYSIS OF PHENANTHRENE

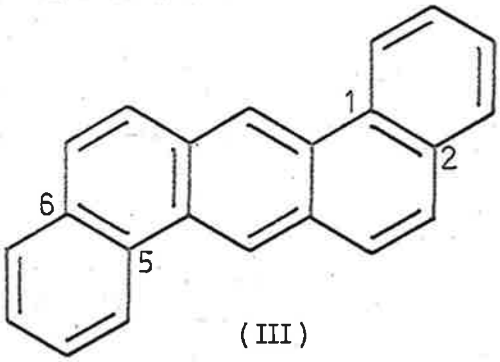
Anthracene is a common constituent of tars obtained by pyrolysis of aliphatic hydrocarbons, alkylbenzenes, and other simple organic molecules; it is also present in cigarette smoke condensates, vehicular exhaust tars, and air pollutants. Although anthracene itself has no carcinogenic activity,[114] the introduction of methyl groups to certain positions does lead to active compounds. For example, 9,10-dimethylanthracene (I) has been found to be carcinogenic when tested by application to the skin of mice; this compound is in fact, the simplest carcinogen known in the polycyclic series.[115] 1,2-Benzanthracene (II) also has slight activity,[116] and many of its simple derivatives are active carcinogens.[117] 1,2:5,6-Dibenzanthracene (III) was the first pure polycyclic aromatic hydrocarbon to produce tumours as a result of skin painting experiments on mice.[118]



(I)



(II)



(III)

The mechanism of formation of the anthracene nucleus is therefore very important in any study of the formation of carcinogenic hydrocarbons. As a result of extensive investigations of such a study in these laboratories, mechanisms for the formation of many aromatic compounds have been proposed; some have been unequivocally established by using compounds labelled with ^{14}C.[119] Prior to experiments with radioactive precursors, two mechanisms were regarded as important for the formation of anthracene. These were the interaction of two benzyl radicals, and attack of a C_4 unit on naphthalene or tetralin (equations 4 (i), (ii)).

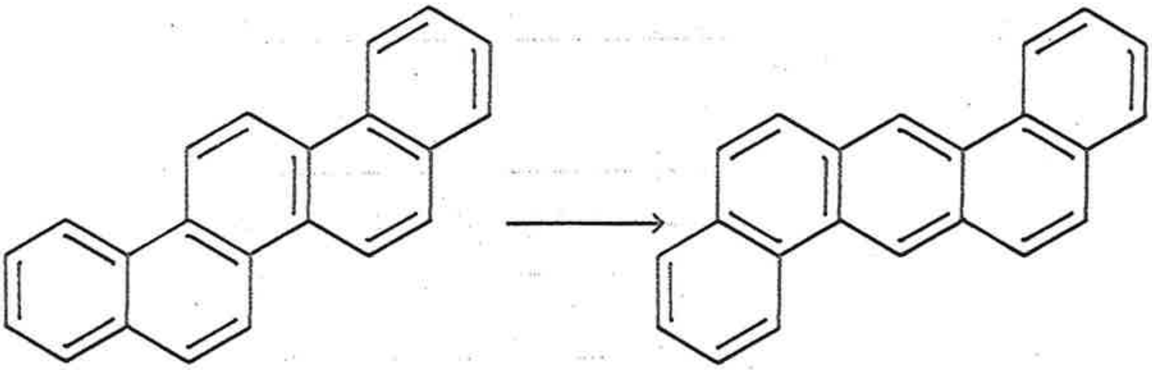
equation 4(i)

equation 4(ii)

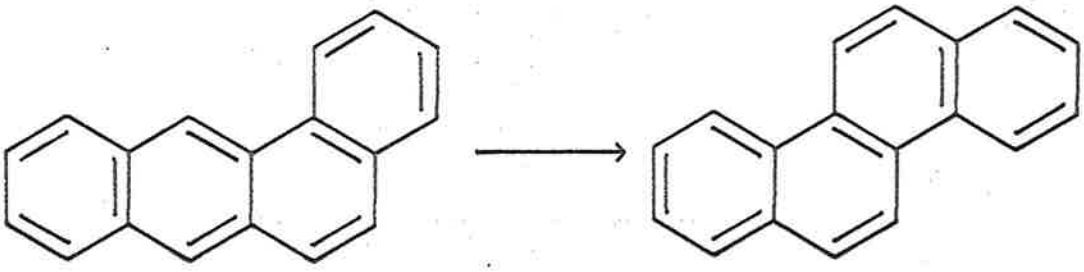
The radioactivity of anthracene isolated after pyrolysis of (1 - ^{14}C) tetralin,[54] however, has shown that neither of these two mechanisms can operate to any significant extent. Nevertheless, these experiments did reveal an interesting fact : in each case, the anthracene isolated contained the same number of labelled carbon atoms as the phenanthrene. The possibility of another mechanism for anthracene formation therefore became apparent : the thermal rearrangement of phenanthrene.

In 1927, Orlow[120] reported that some anthracene was formed by pyrolysis of phenanthrene in a stream of hydrogen. This appears to be the only example of thermal isomerisation, but it must be accepted with caution since Orlow gave no details of purification of the phenanthrene used. (Commercial phenanthrene is invariably contaminated with anthracene, which is very difficult to remove completely). Catalytic rearrangements of several polycyclic hydrocarbons have been reported in the literature, including those of picene (IV) to 1,2:5,6-dibenzanthracene (III)[73] (equation (4.iii)), 1,2-benzanthracene (II) to chrysene[121] (V) (equation 4.iv), and 10-methyl - 1,2-benzanthracene to 6-methylchrysene.

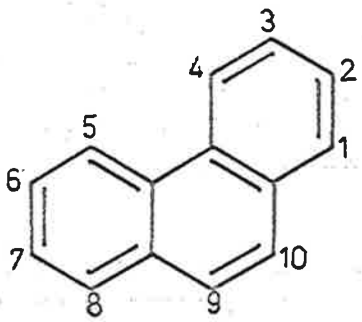
From the evidence available, the proposed hypothesis seemed probable, and certainly worth investigating. Pure phenanthrene (VI) was consequently pyrolysed at 700°, and at 850°, in a stream of nitrogen. The resulting tars were analysed for aromatic hydrocarbons.



(IV) (III) equation (4.iii)



(II) (V) equation (4.iv)



(VI)

RESULTS AND DISCUSSION

Table 4.1 lists the various compounds which were detected in each of the tars produced at 700° and 850°. The percentage composition of the tars, and the percentage yield of each hydrocarbon from phenanthrene, are given in the Table.

TABLE 4.1.

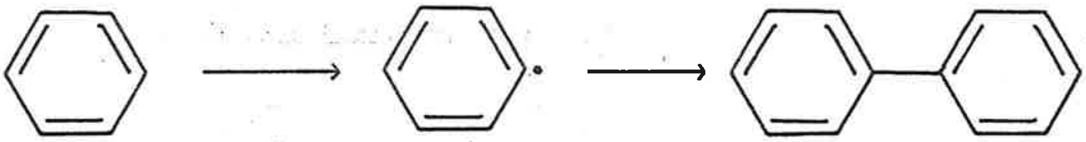
COMPOSITION OF TARS PRODUCED BY PYROLYSIS OF PHENANTHRENE

Compound	Percentage (w/w) in Tar		Percentage yield from Phenanthrene		Method of Identification
	700°	850°	700°	850°	
Ethylene	-	P	-	P	i.r.
Carbon	-	-	2.0	19.5	
9,10-Dihydrophenanthrene	0.52	1.0	0.5	0.3	u.v.
1,2,3,4-Tetrahydrophenanthrene	-	0.7	-	0.2	u.v.
Naphthalene	-	6.8	-	2.0	u.v., mixed m.p.
Phenanthrene	88.3	20.3	85.9	6.1	u.v., mixed m.p.
Anthracene	-	16.8	-	5.0	u.v., mixed m.p.
Pyrene	-	13.4	-	4.0	u.v., mixed m.p.
2,2'-Biphenanthryl	3.5	8.5	3.4	2.6	u.v., m.p.

Biphenanthryl, m.p. 175°	1.25	3.2	1.2	0.9	u.v.,m.p.
Biphenanthryl, m.p. 212°	1.98	3.6	1.9	1.0	u.v.,m.p.
2,3:8,9-Dibenzoperylene	2.1	10.6	2.0	3.3	u.v.,m.p.
2,3:10,11-Dibenzoperylene	1.87	10.0	1.8	2.9	u.v.,m.p.
Benzonaphthofluoranthene	-	P	-	P	u.v.
2,3-(o-Phenylene)pyrene	-	4.6	-	1.4	u.v.,m.p.

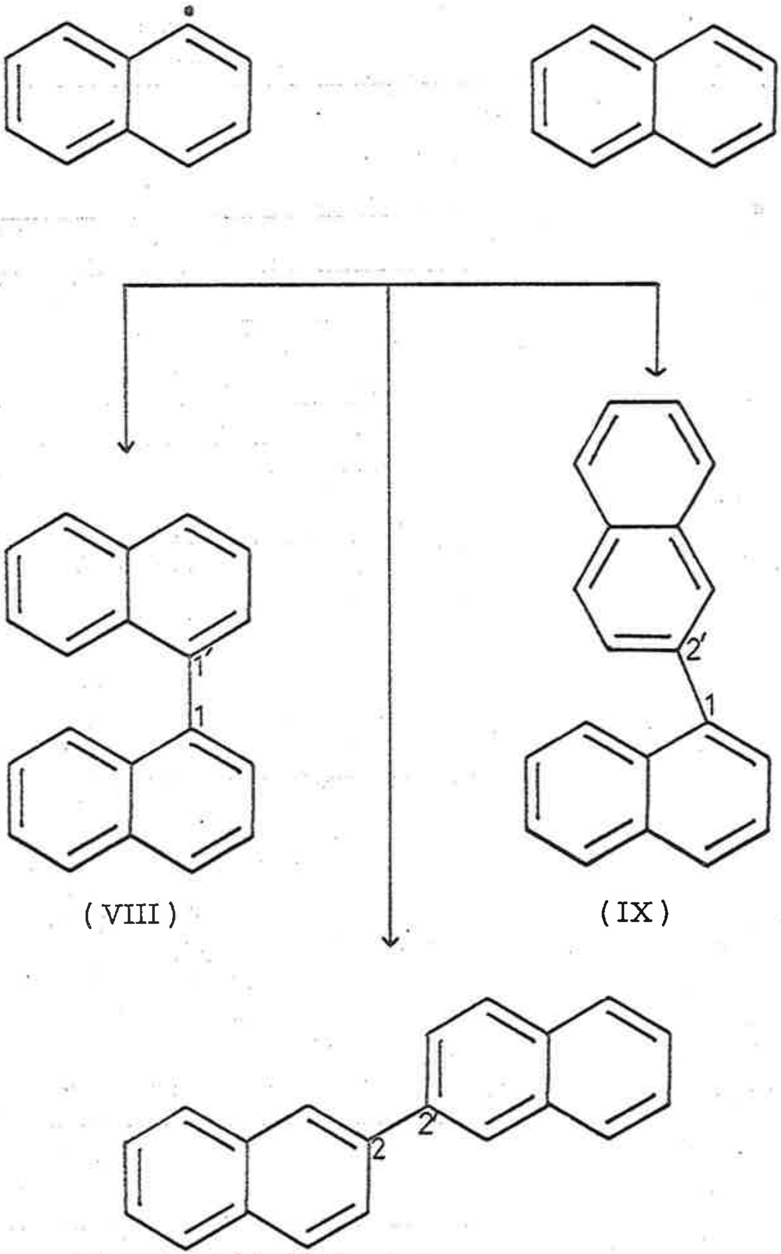
From the Table it can be seen that no anthracene was formed at the lower temperature. Phenanthrene is apparently fairly stable at 700°, since most of it was recovered unchanged. It was therefore decided to repeat the pyrolysis at 850° to determine whether the rearrangement would occur when more energy was supplied to the system. Indeed, anthracene was found to be the major product. The tar produced at 700° was qualitatively similar to that obtained by Lang, Buffleb and Kalowy.[123]

The pyrolysis of unsubstituted aromatic compounds at 700° has been found to yield mainly the corresponding dimers, together with any possible condensation products. Benzene, for example, produces biphenyl (VII) in high yield[43] (equation (4.vii)); and binaphthyls (VIII, IX, X) are the major products from the pyrolysis of naphthalene[52] (equation (4.viii)). Cyclodehydrogenation of the binaphthyls would lead



(VII)

equation (4.vii)



(VIII)

(IX)

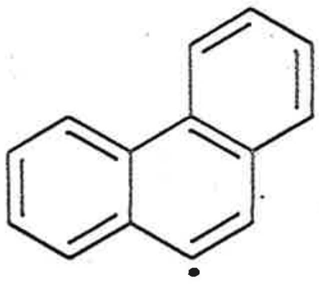
(X)

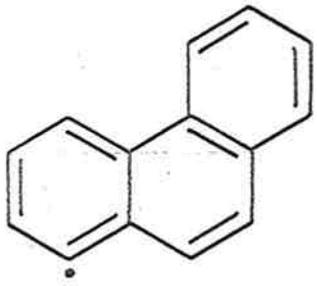
equation (4.viii)

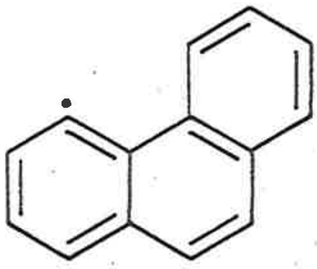
to benzofluoranthenes, and finally perylene, and these compounds were all present in the tar.

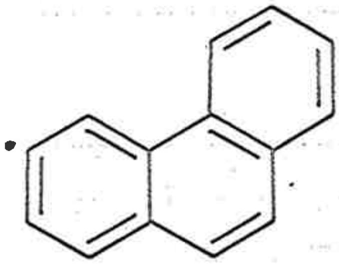
The primary process involved in the pyrolysis of any unsubstituted polycyclic hydrocarbon is thus apparently carbon-hydrogen scission to give an aryl radical and a hydrogen atom. This is not surprising, as the bond dissociation energy of a carbon-hydrogen bond is much lower than that of a carbon-carbon bond in an aromatic ring. Aryl radicals may then react with other radicals, or with molecules of the aromatic hydrocarbon, to form biaryls, some of which may undergo cyclodehydrogenation to more condensed hydrocarbons. The compounds detected in the tar produced at 700° can be explained in this way.

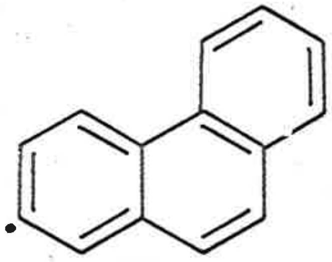
The pyrolysis of phenanthrene is more complex than that of either benzene or naphthalene, since carbon-hydrogen scission may occur at any of the 1-, 2-, 3-, 4- or 9- positions to give five alternative phenanthryl radicals (XI - XV).


(XI)


(XII)


(XIII)

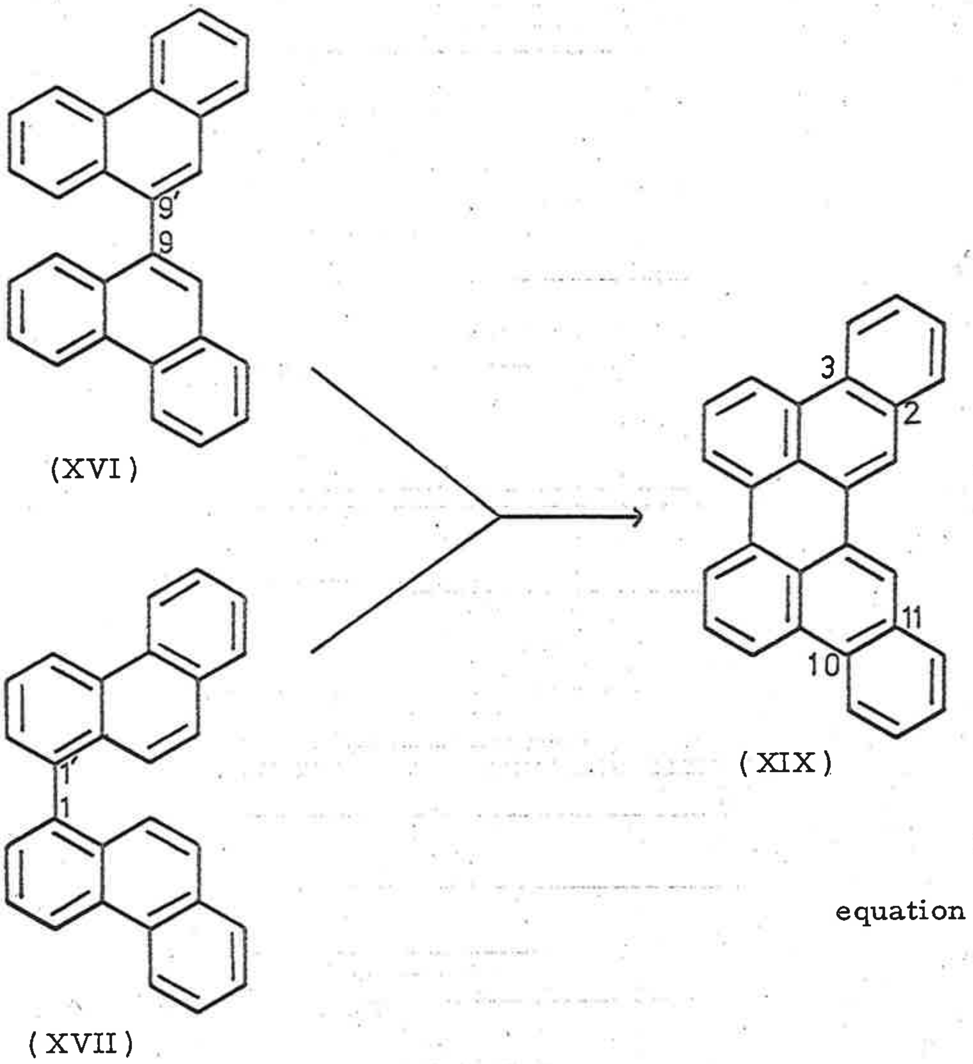

(XIV)


(XV)

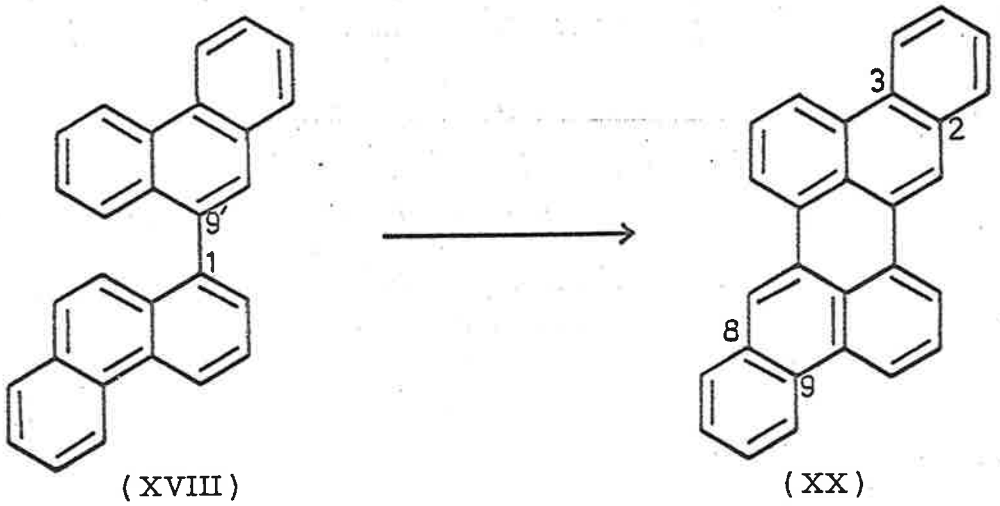
In a study of the phenylation of phenanthrene, Beckwith and Thompson[124] described the 4-position as too sterically hindered to allow attack by phenyl radicals. Recently, however, it was shown that 4-phenylphenanthrene is in fact an important phenylation product.[105] This has subsequently been confirmed by Beckwith.[125] In the pyrolysis of phenanthrene, no products resulting from attack of a 4-phenanthryl radical on phenanthrene were observed. It seems that a phenanthryl radical (or phenanthrene) is sterically prohibited from entering the 4-position, although a phenyl radical is not. An alternative explanation arises from the fact that the hydrogen atoms in the 4- and 5- positions are splayed with respect to each other. This bond-angle and vertical deformation of the carbon-hydrogen bonds would relieve the strain caused by overcrowding of the hydrogen atoms.[126] If a substituent were introduced to either of these positions, the deformation would become much more pronounced. Thus, if a 4-phenanthryl radical did attack phenanthrene the resulting dimer would certainly be nonplanar. Further condensation would therefore be unlikely; the biphenanthryl may subsequently undergo disproportionation in the reaction zone to its original radicals.

The 4-phenanthryl radical may thus be considered as unimportant in the discussion of formation of the compounds found in the tar. The other radicals would be expected to react with a molecule of phenanthrene, or with another radical, to form biphenanthryls. The reactivities of the various positions in phenanthrene (excluding the 4-position) towards phenyl radicals have been found to be in the order 9 > 1 > 3 > 2.[124] If it is supposed that this order also applies to attack of phenanthryl radicals on phenanthrene, then 9,9'-biphenanthryl (XVI), 1,9'-biphenanthryl (XVIII) and 1,1'-biphenanthryl (XVII) would be expected major products. Although none of these compounds was detected in the tar, their condensed forms, 2,3:10,11-dibenzoperylene (XIX) and 2,3:8,9-dibenzoperylene (XX) were isolated in appreciable yields.

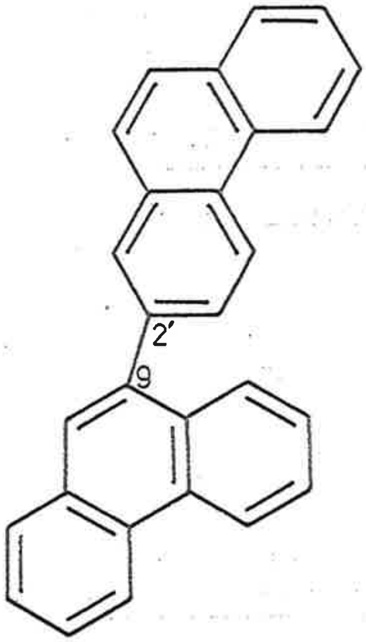
Similarly, biphenanthryls involving the 1- or 9- position and the 2- or 3- position (e.g. XXI, XXII) were not detected; but all these would be expected to undergo cyclodehydrogenation to give either 3,4-benzonaphtho(1,2'-11,12)fluoranthene (XXIII) or 3,4-benzonaphtho(2,1'-11,12)fluoranthene (XXIV).



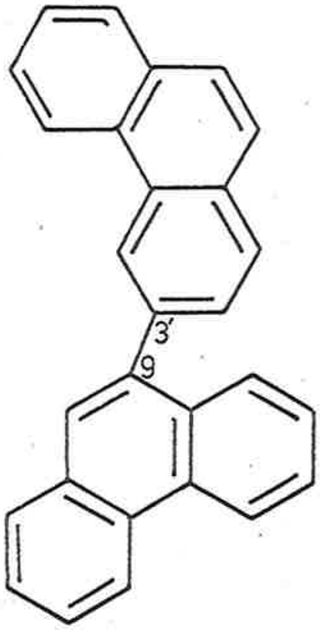
equation (4.ix)



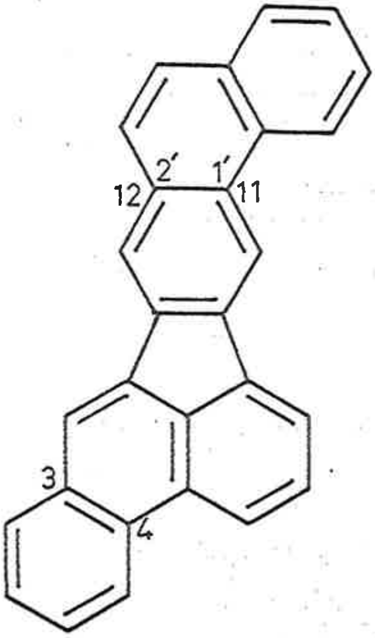
equation (4.x)



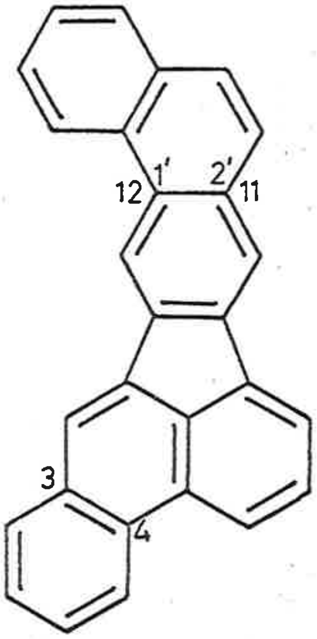
(XXI)



(XXII)



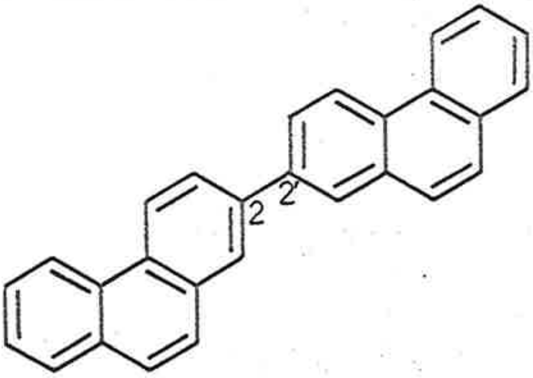
(XXIII)



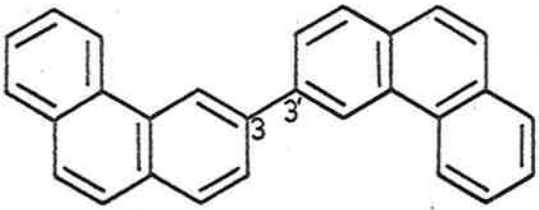
(XXIV)

A substance believed to be benzonaphthofluoranthene (XXIII) or (XXIV), or indeed, a mixture of both, was identified by absorption spectroscopy in the tar produced at 850°. The absorption spectrum was found to be very similar to the spectra given by related compounds (Figure 4.1.).

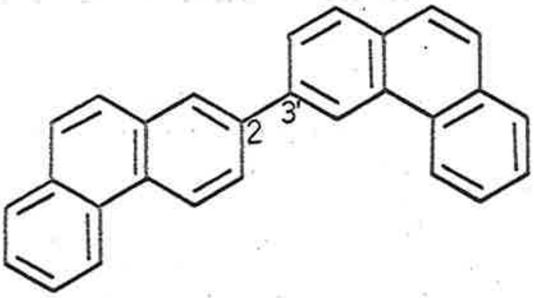
The remaining possible dimers of phenanthrene, 2, 2'-biphenanthryl (XXV), 2, 3'-biphenanthryl (XXVII) and 3, 3'-biphenanthryl (XXVI), were detected as such in both tars; cyclodehydrogenation to more condensed compounds is prohibited with these isomers.



(XXV)



(XXVI)



(XXVII)

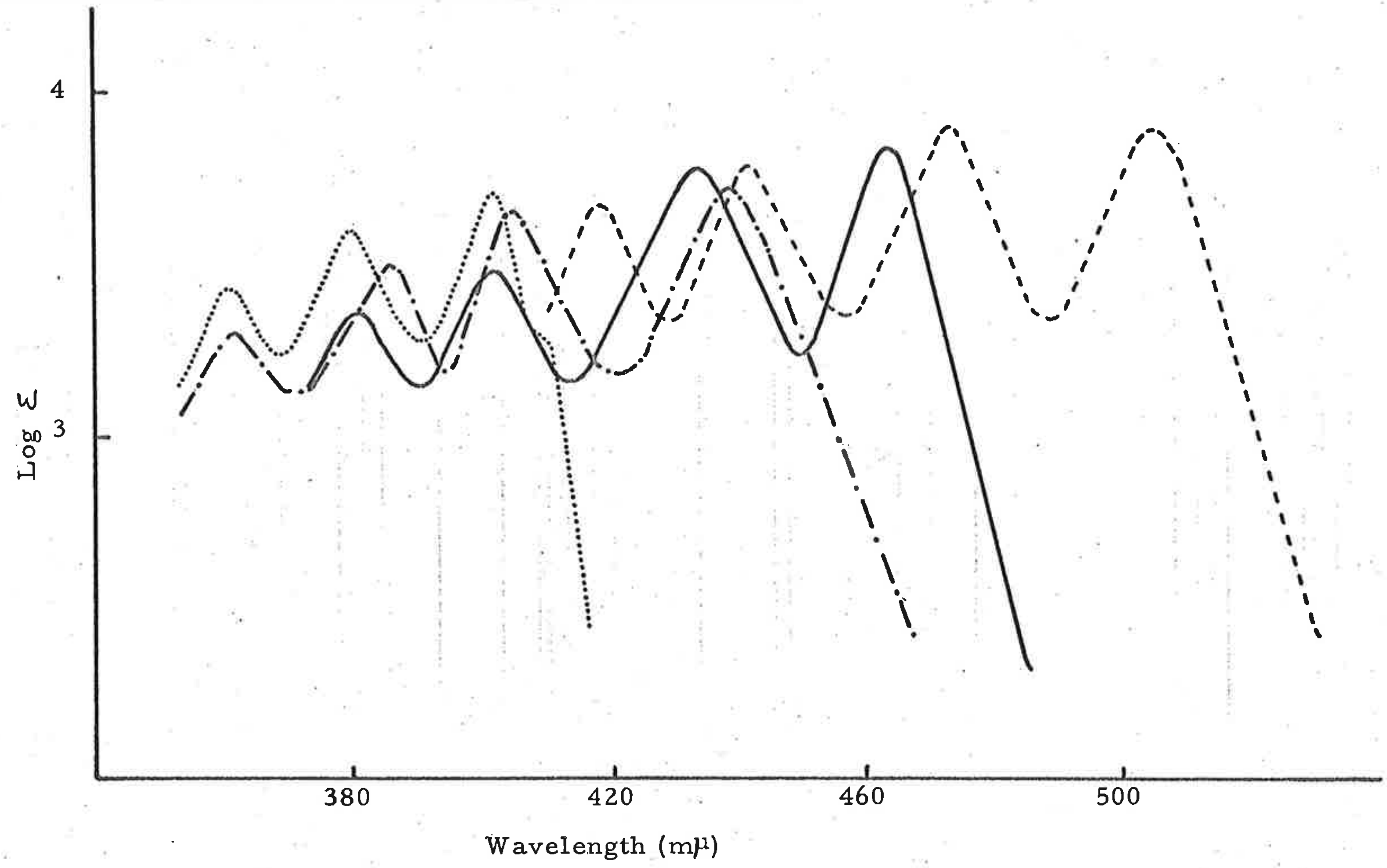


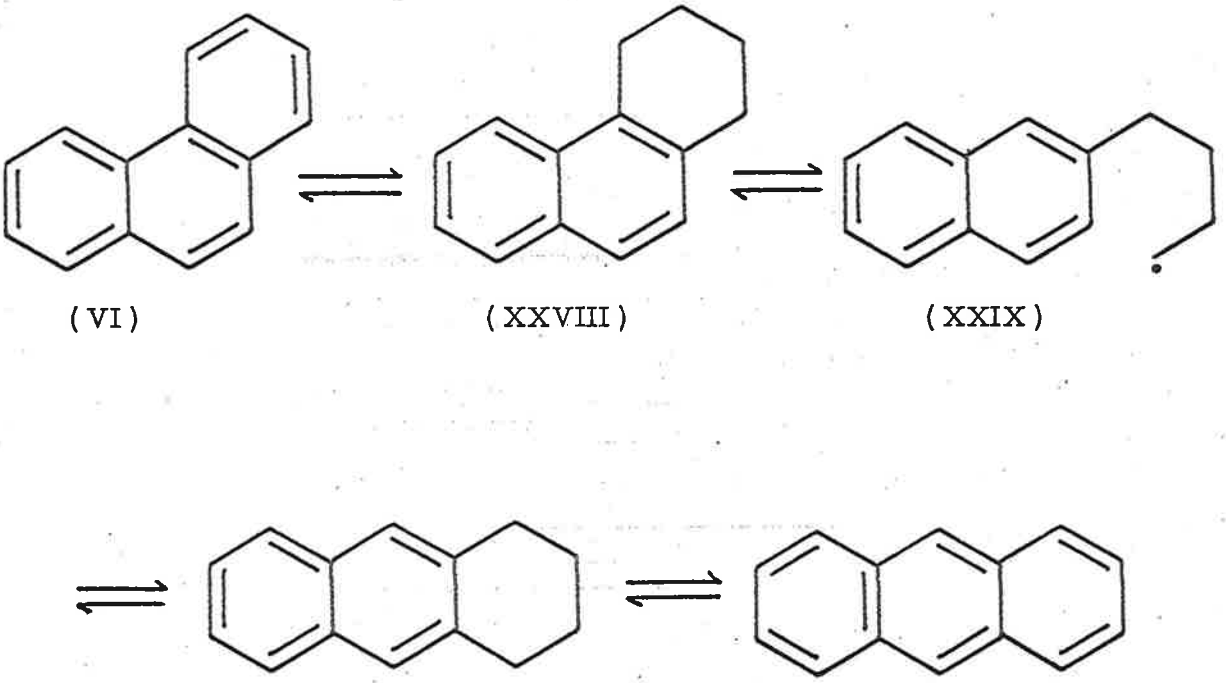
FIGURE 4.1. - Absorption spectra of fluoranthene derivatives in benzene (*para* bands only[83]).

——— (XXIII) or (XXIV); - - - - 2,3-benzonaptho(2'3'-11,12)fluoranthene;

-·-·-·- naphtho(2'3'-11,12)fluoranthene; ········ 11,12-benzofluoranthene.

The aim of this experiment was to investigate the possibility of the thermal rearrangement of phenanthrene to anthracene. Although no anthracene was found in the tar produced at 700°, it was in fact formed in considerable yield at 850°.

The rearrangement is unlikely to be direct, but is more likely to proceed through hydrogenated derivatives of phenanthrene (equation(4.xi)) Both 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene were detected in the high temperature tar, lending support to the proposed hypothesis.



(VI) (XXVIII) (XXIX)

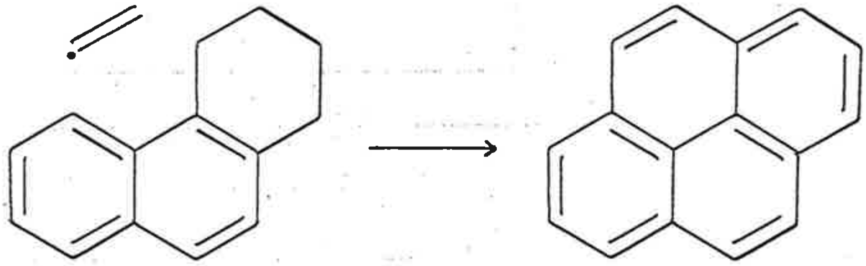
(XXX) (XXXI)

equation (4.xi)

Saturated carbon-carbon bonds would undergo cleavage much more readily than aromatic carbon-carbon bonds,[88] and it is significant that the rearrangement proceeds only at the higher temperature where there is a relatively high hydrogen concentration. Further evidence for rearrangement through hydrogenated derivatives is provided by the fact that passage of phenanthrene through a red-hot tube (temperature ≏ 750°) in an atmosphere of hydrogen does yield anthracene,[120] whereas under similar conditions in a nitrogen atmosphere, no such rearrangement occurs. In the latter case, there would apparently be insufficient hydrogen in the reaction zone to produce hydrophenanthrenes in significant yield. Pyrolysis at 850°, however, leads to markedly increased yields of condensation products, and consequently a higher concentration of hydrogen would be available for hydrogenation.

The presence of naphthalene in the tar produced at 850° also supports this rearrangement mechanism. The naphthalene is presumably formed by complete removal of the saturated carbon atoms from any of the intermediates (XXVIII), (XXIX) or (XXX).

The presence of pyrene (XXXII) as one of the major components of the higher temperature tar is rather surprising, and indicates the remarkable facility with which this compound must be formed from phenanthrene, or more likely, a hydrogenated phenanthrene. The most reasonable mechanism involves attack of a C_2 unit on the hydrophenanthrene (equation (4.xii)); scission of the saturated carbon atoms from another molecule of tetrahydrophenanthrene would account for the formation of the C_2 unit. That such cleavage does occur is supported by the identification of ethylene in the exit gases:



(XXXII)

equation (4.xii)

It is interesting to note that this mechanism has not been well accepted in the past, because the 4-position of phenanthrene was thought to be unfavourable for attack.[124] However, as mentioned previously, recent experimental work on phenylation[105] has shown that this is not so; and molecular orbital theory predicts the reactivities of the five positions in phenanthrene to be in the order 9 > 1 > 4 > 3 > 2.[127] Thus, attack of a C_2 unit at the 4-position can now be regarded as a probable mechanism for the formation of pyrene.

Owing to experimental difficulties, the present pyrolysis was not conducted under precisely the same conditions as those previously carried out in these laboratories. The silica pyrolysis tube was not packed with porcelain chips, and the residence time of the compound unde going pyrolysis would therefore be considerably less than if the tube were packed. Consequently, compounds in packed tubes would have more time for reaction to occur, and would therefore react more extensively than in an empty tube. Considering also the very much greater concentration of hydrogen radicals produced by pyrolysis of substituted aromatic and aliphatic compounds, as compared with the much more stable phenanthrene, it seems probable that the rearrangement of phenanthrene to anthracene may well occur during pyrolysis *at 700°* of the former group of compounds.

It is reasonable to conclude that the phenanthrene - anthracene rearrangement does occur at high temperatures, provided there is sufficient hydrogen to form the tetrahydro intermediate. Such hydrogenation reactions (in contrast to dehydrogenation reactions, which are known to occur extensively in pyrolyses) may well be important in the formation of polycyclic hydrocarbons formed during pyrolysis of benzene and naphthalene.

EXPERIMENTAL

(a) General

Phenanthrene

"Pure" phenanthrene (Rütgerswerke) was further purified by treatment with maleic anhydride, and then by treatment with sodium.[128] Most of the anthracene was removed by refluxing 70g of phenanthrene with 20g of maleic anhydride in 130 ml xylene under nitrogen for 24 hours. The mixture was filtered, the filtrate extracted with sodium hydroxide and the solvent removed from the organic layer by distillation. The residue was stirred under nitrogen for three hours with 1.0g sodium. The product was distilled in vacuo, then recrystallized three times from 30% benzene in ethanol; it was finally purified by zone-refining. The resulting pure phenanthrene had m.p. 98 - 99°. A sample was chromatographed on a column of partially acetylated cellulose; all the fractions were examined by ultraviolet spectroscopy, but no impurity (in particular, no anthracene) could be detected in any fraction.

Pyrolysis

The apparatus used for the pyrolysis was the same as that described in Chapter 1. In this pyrolysis experiment however, the silica pyrolysis tube was not packed with porcelain chips. (Preliminary experiments using a packed tube proved unsatisfactory, since extensive blocking occurred). The pure phenanthrene (20g) was contained in a reservoir maintained at c. 150^{o}, and introduced directly into the empty pyrolysis tube at 7g/hr. The tube was maintained at the required temperature (700^{o} of 850^{o}) by means of an electrically heated furnace, and the vapour was carried through the tube with a stream of oxygen-free nitrogen. The resulting tar was collected in a series of traps containing ice-salt, solid CO_2 - ethanol and liquid air. Samples of the exit gases were collected at intervals and examined by infrared spectroscopy.

Analysis of 700^{o} Tar

No methane or ethylene could be detected in the exit gases by infrared spectroscopy. The tar (19.2g, 96%) was distilled under reduced pressure to give two main fractions, A and B. Fraction A was chromatographed on a column of Spence alumina, using hexane for elution. The resulting fractions (30 × 200 ml) were examined by ultraviolet and fluorescence spectroscopy. Phenanthrene was found to be the major constituent, but a trace of dihydrophenanthrene was detected. No anthracene could be detected in any fraction.

Fraction B (2.3g) was chromatographed on a column of Spence alumina (300g) using hexane, hexane containing increasing amounts of benzene, benzene, and finally ethanol, as eluants. The fractions

(30 x 250 ml) were examined by ultraviolet spectroscopy and those having similar spectra were combined to give six main fractions. Each of thes six fractions was rechromatographed on thin-layers, and then on columns of partially acetylated cellulose.

Summary of Fractions:- The compounds identified in the six main fractions obtained by chromatography on alumina are summarised below:

Fraction	Compound
1	9,10-dihydrophenanthrene, phenanthrene.
2	2,2'-biphenanthryl, 2,3'-biphenanthryl, 3,3'-biphenanthryl.
3	2,2'-biphenznthryl, 2,3'-biphenanthryl, 3,3'-biphenanthryl.
4	2,2'-biphenanthryl, 2,3'-biphenanthryl, 3,3'-bipnenanthryl, 2,3:8,9-dibenzoperylene.
5	2,3:8,9-dibenzoprylene, 2,3:10,11-dibenzoperylene.
6	2,3, 10,11-dibenzoperylene.

Analysis of 850° Tar

A small amount of ethylene was detected in the exit gases by infrared spectroscopy. The tar (5.9g, 29%) was analysed as above with th exception that the preliminary distillation was omitted. A considerable amount of carbon (3.9g) was formed during the pyrolysis. The fractions collected by chromatography on alumina were recombined on the basis of their ultraviolet and fluorescence spectra to give ten main fractions. These were subsequently rechromatographed on both thin layers and columns of partially acetylated cellulose.

Summary of Fractions:- The compounds identified in each of the 10 main fractions are summarised below:

Fraction	Compound
1	9,10-dihydrophenanthrene, 1,2,3,4-tetrahydrophenanthrene.
2	naphthalene.
3	phenanthrene.
4	phenanthrene, anthracene.
5	anthracene, phenanthrene, pyrene.
6	pyrene
7	2,2'-biphenanthryl, 2,3'-biphenanthryl, 3,3'-biphenanthryl.
8	2,3:8,9-dibenzoperylene, 2,3:10,11-dibenzoperylene.
9	2,3:10,11-dibenzoperylene.
10	benzonaphthofluoranthene.

(b) Details of Identification

All the compounds detected in the tar produced at 700° were also present in the tar produced at 850°. The same methods of identification were used for both tars; the following details refer to the tar formed by pyrolysis at 850°.

Ethylene

This was detected in the exit gases by its infrared spectrum in the 10-11 μ region. Maxima occurred at 10.03, 10.12, 10.22, 10.30, 10.53, 10.76, 10.84, 11.06 and 11.13 μ.[80]

9, 10-Dihydrophenanthrene

The ultraviolet absorption spectrum showed maxima at 264, 289 and 299 mμ, in agreement with the literature.[129]

1, 2, 3, 4-Tetrahydrophenanthrene

The ultraviolet absorption spectrum showed maxima at 230, 284, 308, 315 and 325 mμ, in agreement with the literature.[130]

Naphthalene

Isolated after chromatography on a column of partially acetylated cellulose, the naphthalene had m.p. 79 - 80°, not depressed by admixtur with an authentic specimen. The ultraviolet absorption spectrum showe maxima at 248, 257, 266, 275, 285 and 311 mμ, in agreement with that of an authentic specimen.

Phenanthrene

Isolated after chromatography on alumina and on acetylated cellulose, the phenanthrene had m.p. and mixed m.p. 98 - 99°. The ultraviolet absorption spectrum showed maxima at 243, 252, 275, 282, 294, 310, 317, 324, 331, 339 and 346 mμ, in agreement with that of an authentic sample.

Anthracene

This was eluted from the alumina column in the same fractions as phenanthrene. Further chromatography of these fractions on acetylated cellulose gave anthracene, m.p. and mixed m.p. 215 - 216°. The ultraviolet absorption spectrum showed maxima at 246, 253, 308, 323, 339, 357 and 377 mμ, in agreement with that of an authentic specimen.

Pyrene

The first pyrene-containing fractions from the alumina column were contaminated with small amounts of phenanthrene. Further chromatography (of fraction 6) on a column of acetylated cellulose gave pyrene, m.p. and mixed m.p. 145 - 146°. The ultraviolet absorption spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335 and 364 mμ, in agreement with an authentic sample.

2,2'-Biphenanthryl

Isolated by chromatography on a column of acetylated cellulose, 2,2'-biphenanthryl had m.p. 306 - 307° in agreement with the literature.[123] The ultraviolet absorption spectrum spectrum showed maxima at 280, 296 and 315 mμ, in agreement with published figures.[123]

2,3'-Biphenanthryl and 3,3'-Biphenanthryl

Isolated following chromatography on a column of partially acetylated cellulose, the biphenanthryls had m.p. 212° and 175°, in good agreement with those reported by Lang, Buffleb and Kalowy.[123] The biphenanthryl, m.p. 212°, gave an absorption spectrum with maxima at 245, 265, 282 and 318.5 mμ. The spectrum of the isomeric biphenanthryl showed maxima at 250, 269, 280, 295 and 316 mμ. These absorption spectra are in good agreement with those reported for these compounds.[123]

2,3:10,11-Dibenzoperylene

The 2,3:10,11-dibenzoperylene isolated by chromatography on a column of partially acetylated cellulose had m.p. 330 - 332° (lit.[83] 329 - 332°). The ultraviolet spectrum showed maxima at 288, 302, 392, 414 and 440 mμ, in good agreement with the literature.[83]

2,3:8,9-Dibenzoperylene

Isolated following chromatography on a column of acetylated cellulose, the 2,3:8,9-dibenzoperylene had m.p. 339 - 341° (lit.[83] 343°). The ultraviolet absorption spectrum showed maxima at 291, 304, 365.5, 386, 408 and 434 mμ, in agreement with the literature.[83]

2,3(o-Phenylene)pyrene

Isolated after chromatography on acetylated cellulose, it had m.p. 158 - 159° and λ max. 251, 261, 275, 292, 304, 315, 360, 376, 385 and 407 mμ, in good agreement with Badger and Spotswood.[44] Long wavelength bands reported at 422 and 431 mμ for this compound[45] are due to anthanthrene impurity.

Benzonaphthofluoranthene

Isolated after chromatography on acetylated cellulose. Thin-layer chromatography could not resolve the substance into the two isomers. However these would be very difficult to separate, and owing to the very small amount isolated, no further identification was possible. The absorption spectrum (in benzene) showed maxima at 320, 334, 354, 373, 400, 432 and 460 mμ.

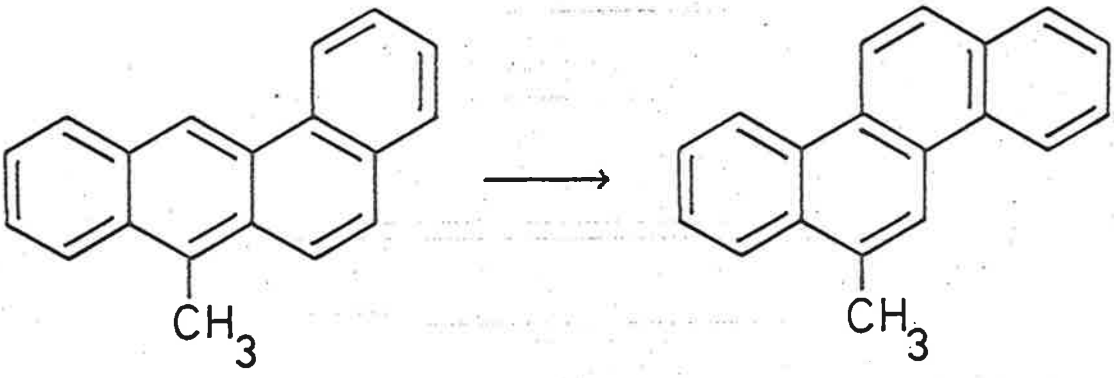
CHAPTER 5.

PYROLYSIS OF ANTHRACENE

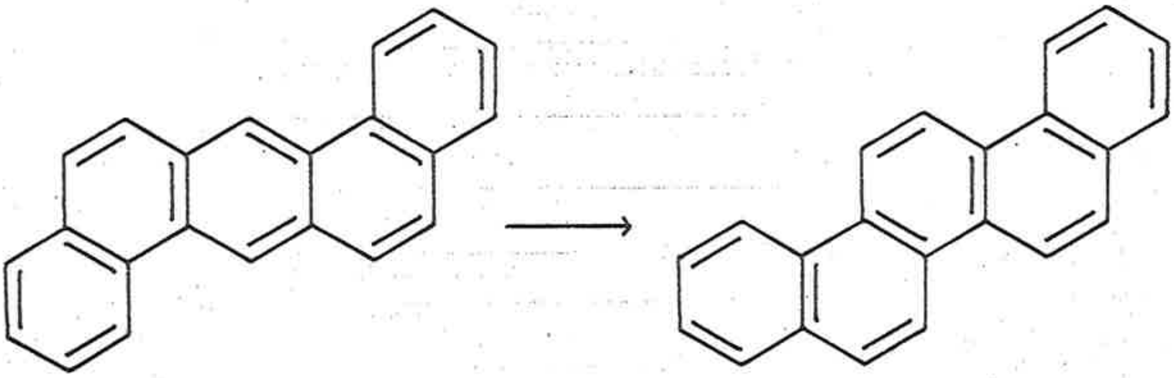
In the preceding Chapter it was shown that some anthracene is produced by the pyrolysis of phenanthrene, and that the anthracene detected following many pyrolytic reactions may be formed by this thermal rearrangement reaction. It was suggested that the rearrangement is not a direct one, but proceeds via 1,2,3,4-tetrahydrophenanthrene and 1,2,3,4-tetrahydroanthracene. If this is so, then the pyrolysis of anthracene would be expected to yield some phenanthrene.

The catalytic rearrangement of 10-methyl - 1,2-benzanthracene (I) to 6-methylchrysene[122] (II) was the first directly demonstrable conversion of an anthracene into a phenanthrene nucleus; and the catalytic isomerisation of 1,2,5,6-dibenzanthracene (III) to picene (IV)[121] also involves this conversion. The reversibility of the latter rearrangement was subsequently established,[131] and it seems possible that a hydrogenated intermediate may also be important in these catalytic reactions.

It is not suggested that the formation of phenanthrene from anthracene is an important route to this compound in pyrolytic reactions of simple hydrocarbons; in fact, results of experiments using radioactive precursors[48,54,51] have established that phenanthrene is mainly formed by way of a bibenzyl radical intermediate. Pure anthracene was pyrolysed at 700° and at 950° to verify further the proposed phenananthrene anthracene rearrangement through hydrogenated intermediates.

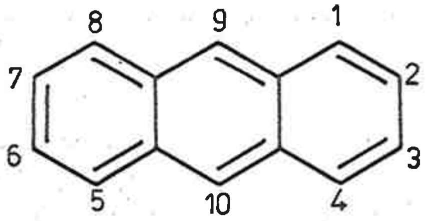


(I) (II) equation (5.i)



(III) (IV) equation (5.ii)

It is interesting to examine the results of the pyrolysis of *n*-butylbenzene over a range of temperatures[62] with reference to the formation of anthracene and phenanthrene. Phenanthrene was identified in tars produced at temperatures as low as 400°, while anthracene was not formed until 550°. The yields of anthracene were always considerably less than those of phenanthrene, and it is particularly noticeable that high yields of anthracene were parallelled by high yields of phenanthrene. These results are consistant with the formation of anthracene from phenanthrene.



Anthracene

TABLE 5.1.

COMPOSITION OF THE TARS FOLLOWING PYROLYSIS OF ANTHRACENE AT 700° AND 950°.

Compound	Percentage (w/w) in Tar		Percentage yield from Anthracene		Method of Identification
	700°	950°	700°	950°	
9, 10-Dihydroanthracene	0.08	0.15	0.08	0.04	u.v.
Anthracene	88.9	0.77	87.1	0.20	u.v., mixed m.p.
9, 9'-Bianthryl	0.9	0.59	0.88	0.15	u.v., mixed m.p.
1, 1'-Bianthryl	1.5	0.44	1.47	0.11	u.v., m.p.
2, 2'-Bianthryl	4.7	1.81	4.6	0.46	u.v., m.p.
1, 2:11, 12-Dibenzoperylene	0.6	0.39	0.59	0.10	u.v.
Bisanthrene	P	0.05	P	0.13	u.v.
2, 3-Benzonaphtho(2', 3' - 11, 12)fluoranthene	1.1	0.29	1.10	0.08	u.v., mixed m.p.
Benzonaphthofluoranthene, m.p. 240-241°	0.9	0.24	0.88	0.06	u.v., mixed m.p.
Benzonaphthofluoranthene, m.p. 227-228°	0.6	0.09	0.59	0.03	u.v., m.p.
1, 2, 3, 4-Tetrahydro-anthracene	-	0.20	-	0.05	u.v.
Naphthalene	-	3.9	-	0.10	u.v., mixed m.p.
Acenaphthylene	-	4.89	-	1.3	u.v., mixed m.p.
Phenanthrene	-	42.07	-	10.8	u.v., f.s., mixed m.p.

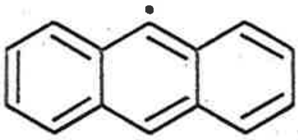
Pyrene	-	24.95	-	6.4	u.v., f.s., mixed m.p.
Fluoranthene	-	7.34	-	1.9	u.v., mixed m.p.
1,2-Benzopyrene	-	1.02	-	0.26	u.v.
Perylene	-	0.59	-	0.15	u.v.
11,12-Benzofluoranthene	-	0.25	-	0.06	u.v.
10,11-Benzofluoranthene	-	0.35	-	0.09	u.v.
3,4-Benzofluoranthene	-	0.59	-	0.25	u.v.
3,4-Benzopyrene	-	1.59	-	0.41	u.v., f.s., mixed m.p.
Anthanthrene	-	0.39	-	0.10	u.v.
2,3-(o-Phenylene)pyrene	-	3.13	-	0.80	u.v., m.p.
Coronene	-	2.10	-	0.54	u.v., mixed m.p.
3,4:8,9-Dibenzopyrene	-	0.54	-	0.14	u.v., f.s.
3,4:9,10-Dibenzopyrene	-	0.45	-	0.10	u.v., f.s., m.p.
Carbon	-	0.83	-	16.0	
Methane	-	P	-	P	i.r.
Ethylene	-	P	-	P	i.r.

RESULTS AND DISCUSSION

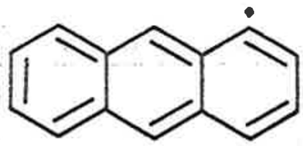
The results of the analyses of the tars produced by the pyrolyses of anthracene at 700° and 950° are given in Table 5.1.; this gives the percentage composition of the tars, and also the percentage yield of each hydrocarbon from anthracene. No methane, ethylene, carbon or phenanthrene were detected following the pyrolysis at 700°, but these compounds were formed in large amounts at 950°. In fact, anthracene is very stable at 700°, and 89% was recovered unchanged. No compounds resulting from carbon-carbon bond fission of anthracene were formed at this temperature.

The major primary process expected in the pyrolysis of anthracene would be the scission of a carbon-hydrogen bond to give an anthryl radical. The bond-dissociation energy of a C - H bond in benzene is 102 K.cals/mole,[88] and that for anthracene would be expected to be of similar value. Carbon-hydrogen scission can occur at the 9, 1 or 2 positions, giving rise to three alternative anthryl radicals (V, VI, VII), which would then be expected to react with a molecule of anthracene, or with each other, to form bianthryls.

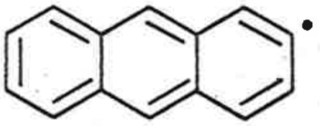
The calculated free valence figures for the different positions in anthracene[132] suggest that the relative reactivities should be in the order 9 > 1 > 2. Experiments on the phenylation[133] and benzylation of



(V)



(VI)



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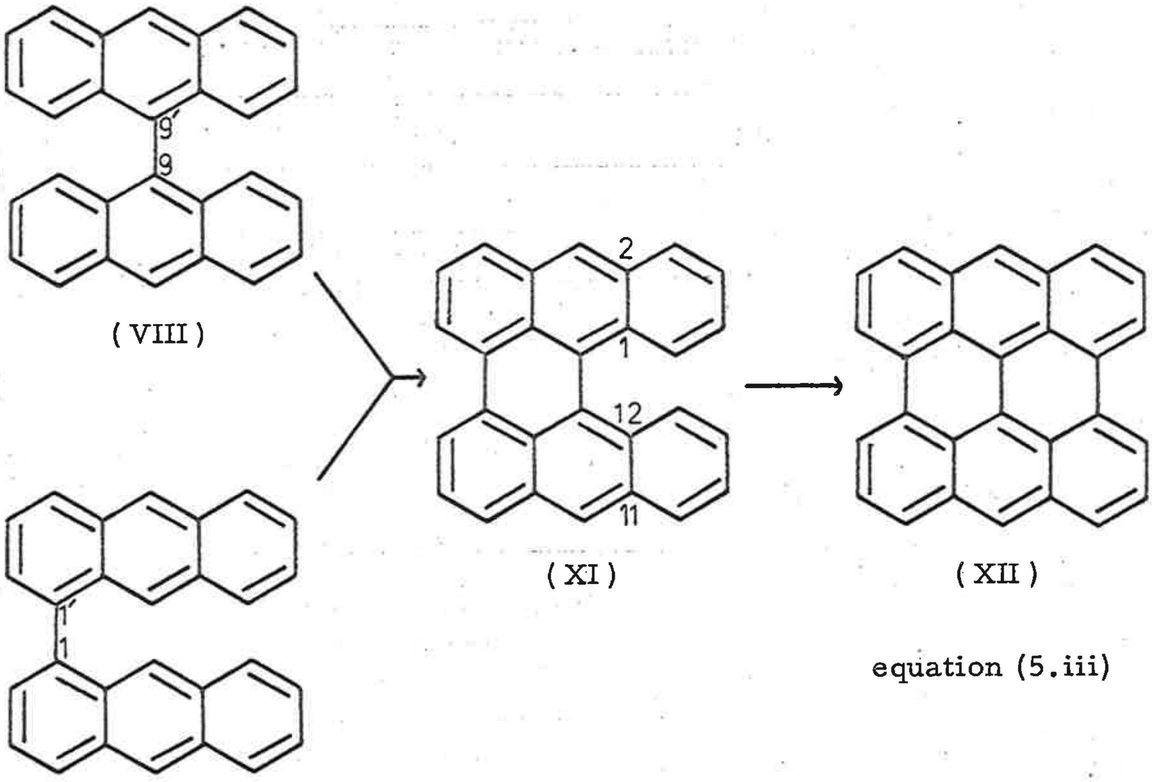


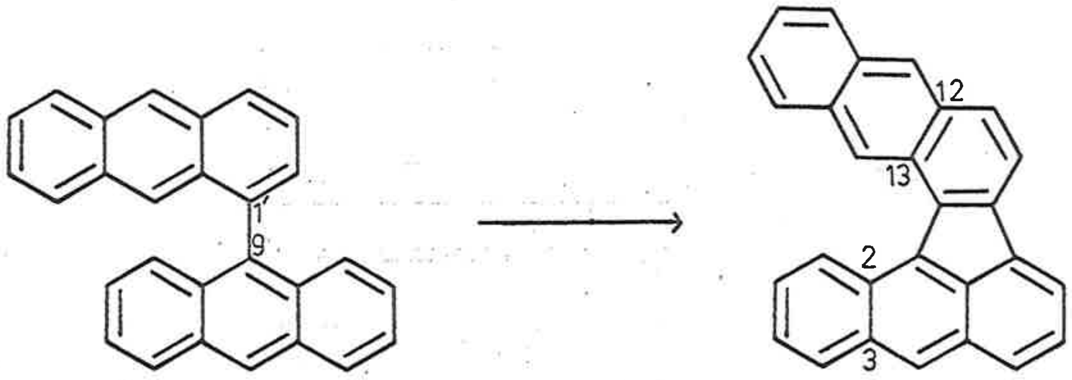
(VIII)

(IX)

(XI)

(XII)

equation (5.iii)



(X)

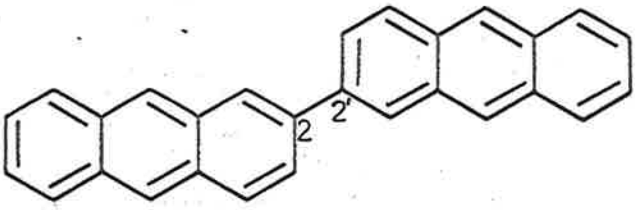
(XIII)

equation (5.iv)

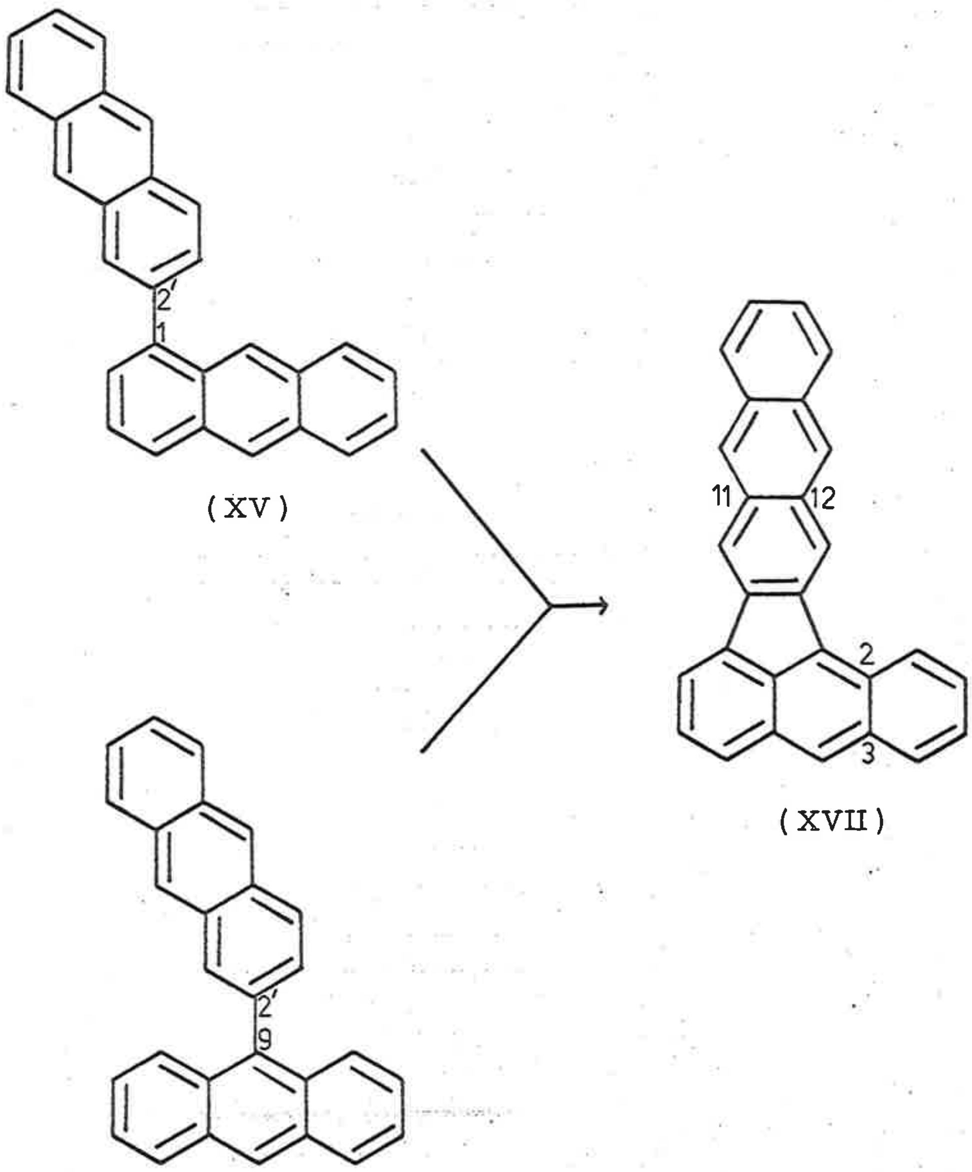
anthracene support this view.

It would therefore be expected that 9, 9'-bianthryl, (VIII) 1, 1'-bianthryl (IX) and 1, 9'-bianthryl (X) be formed in the greatest yields. Small amounts of 9, 9'-bianthryl and the 1, 1'-isomer were identified in both the tars, but both of these compounds could undergo cyclodehydrogenation to form more highly condensed polycyclics. Both 9, 9'-bianthryl and 1, 1'-bianthryl would be expected to condense to 1, 2:11, 12-dibenzoperylene (XI), and subsequent cyclodehydrogenation of this compound would yield bisanthrene (XII). Both of these compounds were identified in the tars. 1, 9'-Bianthryl (X) was not detected, but this would be expected to undergo cyclodehydrogenation to 2, 3-benzonaphtho-(2'3'-12, 13)fluoranthene (XIII), and the three isomeric benzonaphthofluoranthenes were all isolated. The bianthryl (X) might also be expected to yield 1, 2:7, 8-dibenzoperylene, but this was not detected. It would appear from the yields obtained that cyclodehydrogenation to a 5-membered ring giving a fluoranthene derivative is energetically more favourable than condensation to a six membered ring. It is significant that the pyrolysis of naphthalene at 700° gave seven times as much benzofluoranthene as perylene,[52] suggesting again that the condensation to a 5-membered ring is favoured.

The remaining bianthryls which could be formed are 2, 2'-



(XIV)



(XV)

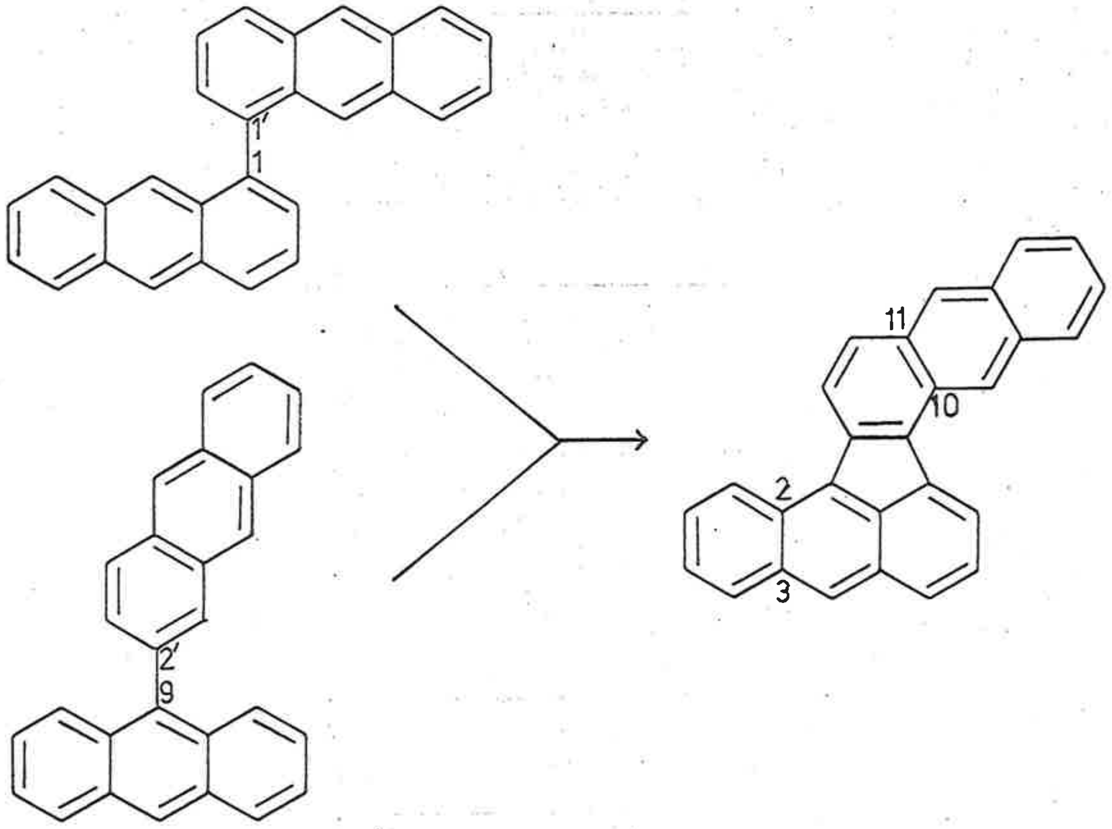
(XVI)

(XVII)

equation (5.v)

bianthryl (XIV), 1,2'-bianthryl (XV) and 2,9'-bianthryl (XVI). Of these, only the 2,2'-isomer cannot undergo cyclodehydrogenation and this compound was obtained in considerable yield in both tars. Both 1,2'-bianthryl and 2,9'-bianthryl would be expected to readily condense to 2,3-benzonaphtho(2',3'-11,12)fluoranthene (XVII); which was isolated from the tars.

1,2'-Bianthryl (XV) could alternatively condense to form 2,3-benzonaphtho(2'3'-12,13)fluoranthene (XIII).

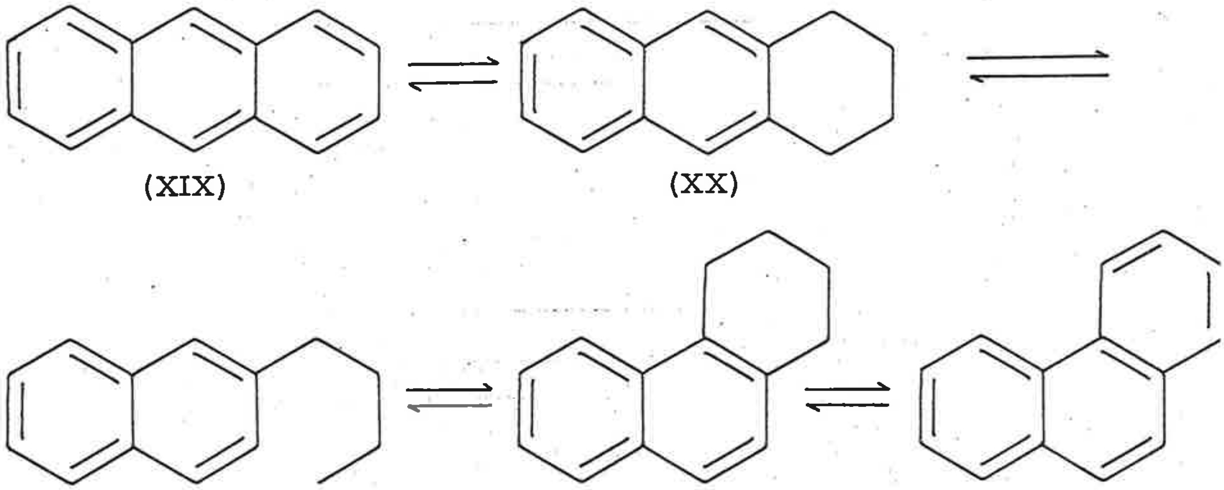


The third benzonaphthofluoranthene isomer (XVIII) could be formed by an alternative condensation of either 1, 1' -bianthryl (IX), or 2, 9' -bianthryl (XVI). The orientation of only one (XVII) of the three isomers has been established.

The formation of anthryl radicals and the cyclodehydrogenation reactions described above involve the liberation of hydrogen atoms. As a result, some anthracene was reduced, and 9, 10 -dihydroanthracene was detected in both tars; in addition 1,2,3,4 -tetrahydroanthracene was also detected in the tar produced at 950°.

The tar produced at 950° was much more complex than that formed at 700°, which was largely unchanged anthracene. Very little anthracene survived the pyrolysis at 950°, however, and the detection of methane and ethylene in the exit gases indicated that ring fission had occurred. It can be seen from Table 5.1. that phenanthrene was in fact the major component of the tar, and its mechanism of formation from anthracene now seems almost certain to proceed via the tetrahydro intermediates.

Hydrogen appears to be an essential requirement for the rearrangement, and it seems that insufficient hydrogen was present in the reaction zone during pyrolysis at 700° to enable a significant amount of tetrahydroanthracene to be formed. However, at 950°, this intermediate must have been formed in considerable yield.



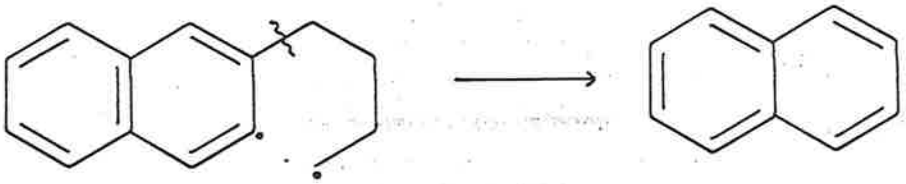
(XIX) (XX)

(XXI) (XXII) (XXIII)

equation (5.vii)

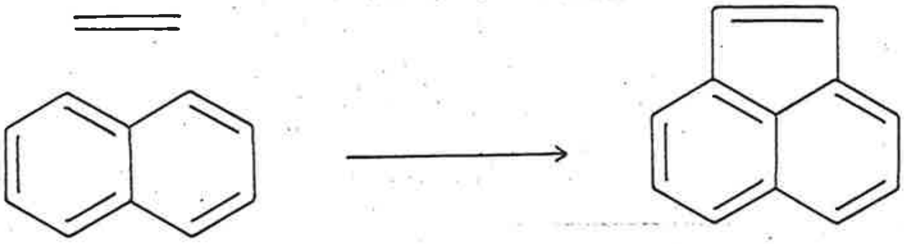
Scission of the side-chain of the butylnaphthalene radical (XXI) proposed in equation (5. vii) would occur with great facility (dissociation energy c 60 - 80 Kcals/mole) to yield naphthalene (XXIV), and this compound was isolated from the 950° tar.

The acenaphthylene (XXV) isolated could conceivably be formed by attack of a C_2 unit on naphthalene, or by ring fission of the tetrahydrophenanthrene intermediate (XXII) followed by cyclodehydrogenation.



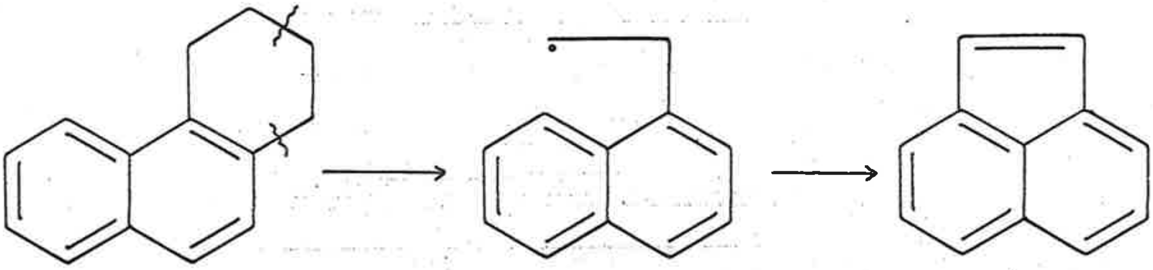
(XXI) (XXIV)

equation (5.viii)



(XXV)

equation (5.ix)

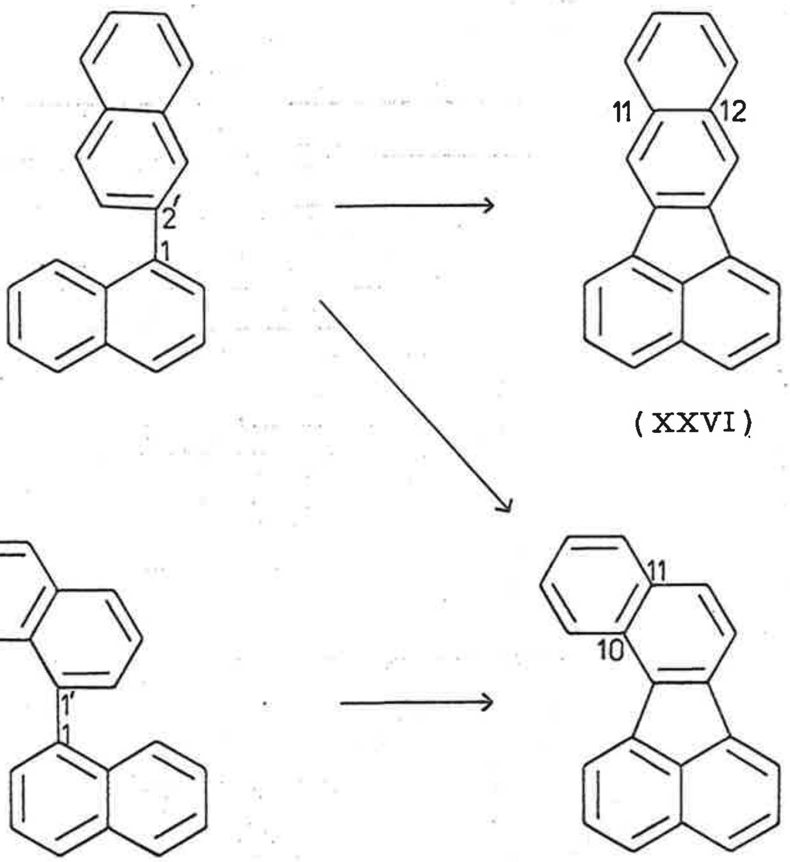


(XXII) (XXV)

equation (5.x)

The phenylation of phenanthrene, followed by cyclodehydrogenation could account for the formation of 3,4-benzofluoranthene, as suggested in equation (1.x). Two other isomers of benzofluoranthene (XXVI and XXVII), which were obtained in much lower yields, are almost certainly formed from naphthyl radicals, via the corresponding binaphthyl intermediate (equation (5.xi)). Perylene (XXVIII) may also be formed from a binaphthyl, (the 1,1'-isomer),as it must be in the pyrolysis of naphthalene.[52] However, as perylene constituted only 0.01% of the total tar obtained by pyrolysing naphthalene, it seems unlikely to be formed in this way in the anthracene pyrolysis. An alternative mechanism involves anthracene itself (equation (5.xii)), and perylene has in fact been synthesised by the reaction of anthracene with two C_3 units.[135]

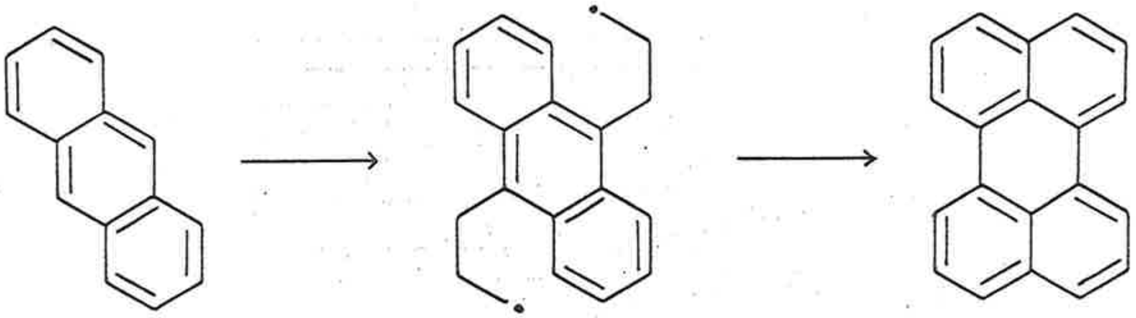
This same intermediate could also lead to the formation of 1,2-benzopyrene (XXIX) by the alternative cyclisation; cyclodehydrogenation of 4-phenylphenanthrene would also lead to 1,2-benzopyrene, as in equation (1.xi).



(XXVI)

(XXVII)

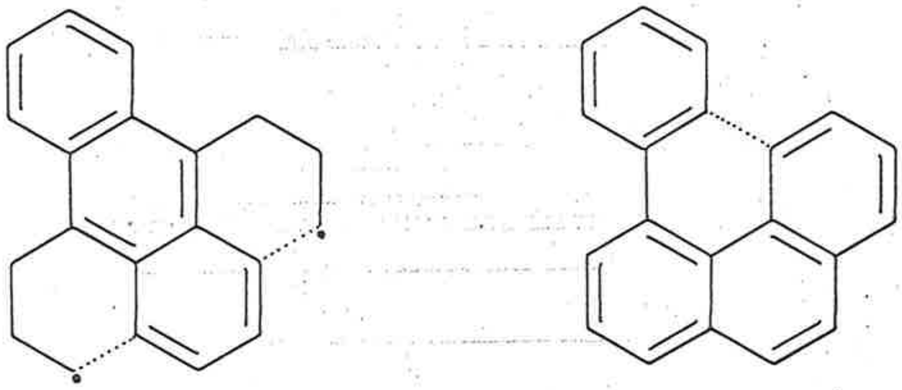
equation (5.xi)



(XIX)

(XXVIII)

equation (5.xii)



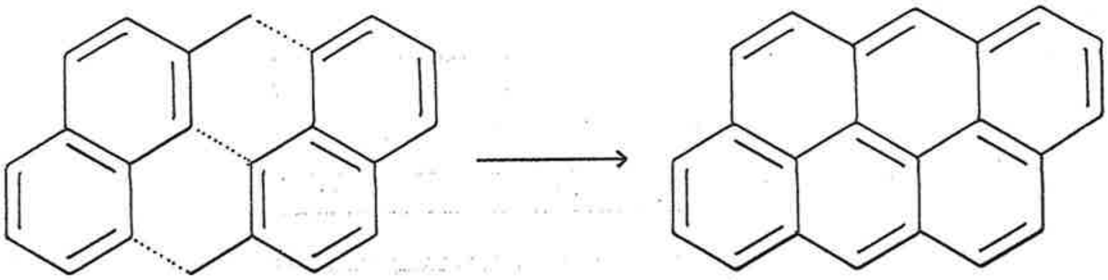
(XXIX)

The mechanism described earlier for the formation of 3,4-benzopyrene seems feasible in the present pyrolysis, as do the somewhat similar mechanisms for 3,4:8,9-dibenzopyrene and 3,4:9,10-dibenzopyrene discussed in Chapter 1.

The saturated carbon-carbon bonds in tetrahydroanthracene and tetrahydrophenanthrene would undergo scission with approximately equal facility. Thus the 2-methylnaphthyl radical would be expected to be present in the reaction zone. Combination of two such radicals may lead to the formation of anthanthrene (XXX).

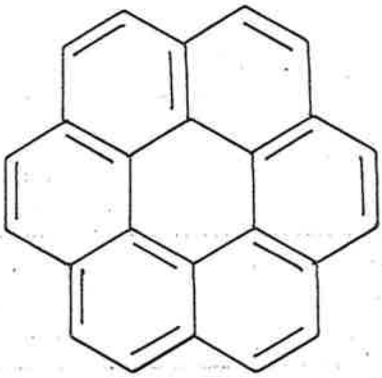
The presence of coronene (XXXI) in the tar produced at 950° is noteworthy. Coronene has been identified in exhaust condensates and in polluted air, often in relatively high concentrations. However, its presence in tars obtained by the pyrolysis of simple compounds at 700°

(*e.g.* the work of Badger *et al*. and Lang and Buffleb) has not often been reported. In most cases the analysis of tobacco smoke has failed to reveal the presence of coronene, although it has been reported in low concentrations on a few occasions. When the temperatures involved in pyrolysis experiments, combustion of petrol in motor vehicles, and in burning cigarettes are considered, it becomes apparent that coronene formation is temperature dependent.



(XXX)

equation (5.xiii)



(XXXI)

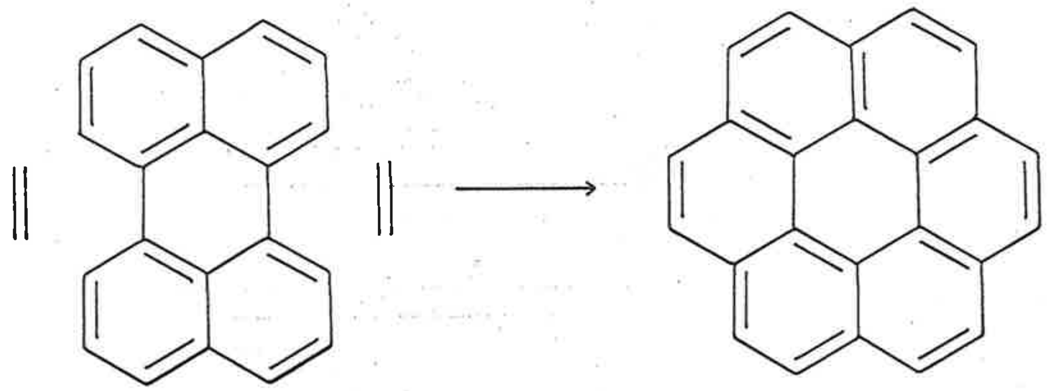
TABLE 5.2.

Heating Process	Temperature (°C)	Amount of Coronene formed
Pyrolysis	700°	-
Burning cigarettes[99]		
(i) Mean temperature	750°	Small
(ii) Surface temperature	900°	
Petrol combustion[136]		
(i) Mean temperature*	2,000	Large
(ii) Maximum temperature	3,000	

*Depends on the conditions of knocking, air/fuel ratio, etc.

It seems therefore that coronene is formed only if the temperature exceeds a certain minimum, probably about 900°. Evidence supporting this has been provided by Lam,[137] who found that the tar obtained by pyrolysing tobacco hydrocarbons at 850° did not contain coronene; but the tar obtained after heating at 950° did contain this hydrocarbon.

Very little information is available concerning the mode of formation of coronene, since this was the first pyrolysis to produce the compound in significant yield. However, it appears that the process must be one of considerable energy since it occurs only at very high temperatures. The addition of a C_2 unit to a polycyclic compound is known to involve high energies, and such a mechanism may be postulated for the formation of coronene (equation (5.xiv)). More high-temperature work is required before the mode of pyrosynthesis of coronene can be established with certainty.



(XXXI)

equation (5.xiv)

EXPERIMENTAL

(a) General

Anthracene

"Pure" anthracene (Fluka) was further purified by recrystallisation from ethanol followed by sublimation in vacuo. The sublimed material was dissolved in dimethylsulphoxide,[138] the solution cooled to 80°, and the solid collected. This was then recrystallised from ethanol, ethylene glycol,[139] and finally twice more from ethanol. The resulting pure anthracene formed beautiful lustrous plates, m.p. 218°, and showed an intense violet fluorescence in the solid state. A sample of the purified product was chromatographed on a column of partially acetylated cellulose, and the fractions examined by ultraviolet and fluorescence spectroscopy. No impurities (e.g. no phenanthrene) could be detected in any fraction.

Pyrolysis

The pyrolysis was carried out as described for phenanthrene (Chapter IV) except that the anthracene resevoir was maintained at c. 230-240°.

Analysis of 700° tar

No methane or ethylene could be detected in the exit gases by infrared spectroscopy. The tar (19.6g, 98%) was distilled under reduced pressure to give two main fractions, A and B.

Fraction A was chromatographed on a column of Spence alumina, using hexane for elution, and the resulting fractions (30 x 250 ml) were examined by ultraviolet and fluorescence spectroscopy. Anthracene was found to be the major constituent, but a small amount of 9,10-dihydroanthracene was detected.

Fraction B (2.16g) was chromatographed on a column of Spence alumina (250g) using hexane, hexane containing increasing amounts of benzene, benzene, and finally ethanol as eluants. Each fraction (25 x 250 ml) was examined by ultraviolet spectroscopy, and those having similar spectra were combined to give six main fractions. These were then rechromatographed on both thin-layers and columns of partially acetylated cellulose.

Summary of Fractions: The compounds identified in the six main fractions are summarised below:

Fraction	Compound
1	Anthracene
2	Anthracene, Bianthryls.
3	Bianthryls.
4	1,2:11,12-Dibenzoperylene, Bisanthrene.
5	Benzonaphthofluoranthene, m.p. 240°.
6	Benzonaphthofluoranthene, m.p. 240°. Benzonaphthofluoranthene, m.p. 227°. 2,3-Benzonaphtho(2'3'-11,12)-fluoranthene.

Analysis of 950° Tar

Ethylene and methane were detected in the exit gases by infrared spectroscopy. The resulting tar, which contained much carbon, was dissolved in chloroform and filtered. The carbon residue, together with the carbon removed from the pyrolysis tube, was extracted with chloroform (Soxhlet) for 6 hr. The chloroform solutions were combined and the solvent removed by distillation under reduced pressure. The residue (5.11g) was chromatographed on a column of Spence alumina (550g) using hexane-benzene, benzene and ethanol as eluants. The resulting fractions (80 x 200 ml) were combined on the basis of their absorption spectra to give 13 main fractions. These were then rechromatographed on thin-layers and columns of partially acetylated cellulose.

Summary of Fractions:

Fraction	Compound
1	9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene
2	naphthalene, acenaphthylene
3	phenanthrene, anthracene
4	phenanthrene, anthracene, pyrene
5	pyrene, fluoranthene
6	bianthryls
7	1,2-benzopyrene, perylene, 10,11-benzofluoranthene, 11,12-benzofluoranthene

Fraction	Compound
8	3,4-benzofluoranthene, 3,4-benzopyrene
9	1,2:11,12-dibenzoperylene, bisanthrene
10	anthanthrene, 2,3-(o-phenylene) pyrene
11	3,4:8,9-dibenzopyrene, 3,4:9,10-dibenzopyrene
12	benzonaphthofluoranthenes
13	coronene.

(b) Details of Identification

The same methods of identification were used for the compounds in both tars. The following details refer to the compounds identified in the tar produced by the pyrolysis of anthracene at 950°.

Methane and Ethylene

Samples of the exit gases were collected and examined by infrared spectroscopy. Methane was identified by its spectrum in the 7.3-8.5 μ region (maxima at 7.41, 7.48, 7.67, 7.78, 7.81, 7.86, 7.93, 8.04, 8.10 and 8.16 μ); and ethylene by its spectrum in the 10-11 μ region (maxima at 9.91, 10.01, 10.11, 10.21, 10.31, 10.40, 10.51, 10.75, 10.84, 11.0 and 11.08 μ).[80]

9,10-Dihydroanthracene

The ultraviolet absorption spectrum showed maxima at 252, 264 and 271 mμ, in agreement with an authentic specimen.

1,2,3,4-Tetrahydroanthracene

The ultraviolet absorption spectrum showed maxima at 230, 275, 285, 298, 310 and 324 mμ, in agreement with the literature.[81]

Naphthalene

Isolated following chromatography on a column of acetylated cellulose. A sample had m.p. and mixed m.p. 79-80°, and u.v. maxima at 248, 257, 266, 275, 285 and 311 mμ, in agreement with an authentic specimen.

Acenaphthylene

Isolated after chromatography on acetylated cellulose, the acenaphthylene had m.p. 94-95°, not depressed by admixture with an authentic specimen. The ultraviolet absorption spectrum showed maxima at 229, 258, 266, 276, 309, 323, 334 and 340 mμ, in agreement with an authentic specimen.

Phenanthrene

Isolated after chromatography on columns of alumina and acetylated cellulose, the phenanthrene had m.p. and mixed m.p. 97-98°. The ultraviolet absorption spectrum showed λmax 243, 252, 275, 282, 294, 310, 317, 324, 331, 339 and 346 mμ; and the fluorescence spectrum showed maxima at 350, 363 and 383 mμ, both in agreement with an

authentic specimen.

Anthracene

Isolated after chromatography on acetylated cellulose, the anthracene had m.p. and mixed m.p. 215-216°. The ultraviolet spectrum showed maxima at 246, 253, 308, 323, 339, 357 and 377 mμ, in agreement with an authentic specimen.

Pyrene

Isolated after chromatography on acetylated cellulose, the pyrene had m.p. and mixed m.p. 145-146°. The u.v. spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335 and 364 mμ, and the fluorescence spectrum maxima at 385 and 395 mμ, both in agreement with an authentic specimen.

Fluoranthene

Isolated after chromatography on acetylated cellulose. A sample had m.p. and mixed m.p. 106-108°, and u.v. absorption maxima at 236, 253, 263, 273, 278, 282, 288, 309, 323, 342 and 360 mμ, in agreement with an authentic specimen.

Perylene

Identified by chromatography on a column of acetylated cellulose, followed by thin-layer chromatography. An extract showed maxima at 245, 253, 263, 367, 386, 407 and 435 mμ, in agreement with an authentic specimen.

1,2-Benzopyrene

Identified by chromatography on both columns and thin-layers of acetylated cellulose. An extract showed maxima at 238, 258, 268, 278, 289, 305, 317 and 333 mμ, in agreement with an authentic specimen.

3,4-Benzopyrene

Isolated after chromatography on partially acetylated cellulose, the 3,4-benzopyrene had m.p. and mixed m.p. 174-176°. The ultraviolet spectrum showed maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385 and 404 mμ, and the fluorescence spectrum maxima at 397, 422, 448 and 478 mμ, both in agreement with an authentic specimen.

10,11-Benzofluoranthene

Identified by ultraviolet spectroscopy following chromatography on acetylated cellulose: λ max. 241, 282, 293, 309, 318, 333, 345, 365, 376 and 383 mμ, in agreement with an authentic specimen.

3,4-Benzofluoranthene

Identified by chromatography on a column of acetylated cellulose followed by thin-layer chromatography. An extract showed maxima at 239, 256, 266, 276, 290, 294, 301, 320, 339, 351 and 369 mμ, in agreement with an authentic specimen.

11, 12-Benzofluoranthene

Identified by ultraviolet spectroscopy following chromatography on acetylated cellulose: λ max. 238, 269, 283, 297, 309, 361, 380 and 402 mμ, in agreement with an authentic sample.

Anthanthrene

Identified after chromatography on a column of acetylated cellulose followed by thin-layer chromatography. An extract showed maxima at 233, 256, 259, 295, 308, 365, 382, 401, 407, 421 and 431 mμ, in agreement with an authentic specimen.

2, 3-(o-Phenylene)pyrene

Isolated following chromatography on acetylated cellulose, this had m.p. 158-159° (lit.[82] 163°). The ultraviolet absorption spectrum showed maxima at 251, 261, 275, 292, 304, 315, 360, 376, 385 and 407 mμ, in good agreement with Badger and Spotswood.[44] Long wavelength bands reported at 422 and 431 mμ for this compound are probably due to anthanthrene impurity.

3, 4:9, 10-Dibenzopyrene

This was identified after repeated chromatography on columns of acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 234, 242, 273, 283, 286, 315, 331, 353, 373 and 393 mμ, and its fluorescence spectrum maxima at 428, 456, 489 and 520 mμ, both in agreement with an authentic specimen.

3,4:8,9-Dibenzopyrene

Isolated after chromatography on partially acetylated cellulose, this had m.p. 303-305° (lit.[84] 308°). This compound had a much lower R_F than the other components in the same fraction, and was clearly separated. The ultraviolet absorption spectrum showed maxima at 291, 301, 314, 379, 401, 424 and 452 mμ, in agreement with recorded values.[83] The fluorescence spectrum showed maxima at 449, 475 and 512 mμ, in agreement with the literature.[84]

Coronene

Isolated following chromatography on partially acetylated cellulose, the coronene had m.p. and mixed m.p. 436-438°. The ultraviolet spectrum showed maxima at 293, 305, 317, 320, 325, 336, 341, 348, 355, 369, 378, 381, 388, 397, 402, 410, 419 and 427 mμ, in agreement with an authentic specimen.

9,9'-Bianthryl

Isolated after chromatography on acetylated cellulose, the 9,9'-bianthryl had m.p. and mixed m.p. 310-312°. The ultraviolet absorption spectrum (95% ethanol) showed maxima at 253.5, 316, 333, 349.5, 369.5 and 388.5 mμ, in agreement with an authentic sample; in benzene it showed maxima at 252, 317, 334, 350, 370 and 393 mμ, in agreement with the literature.[140] An authentic specimen was prepared by the method of Bell and Waring.[141].

2,2'-Bianthryl

Isolated following chromatography on acetylated cellulose. The ultraviolet spectrum (benzene) showed maxima at 284, 304, 317, 355, 388 and 402 mμ, in agreement with the literature;[142] it had m.p. and mixed m.p. 367-369° (lit.[142] 369-371°).

1,1'-Bianthryl

Isolated after chromatography on acetylated cellulose, the 1,1'-bianthryl had m.p. 319-320° (lit.[141] 321-322°). The ultraviolet absorption spectrum (95% ethanol) showed maxima at 254, 316, 329.5, 345, 365 and 383 mμ, in agreement with an authentic specimen prepared by the decarboxylation of 1,1'-bianthryl - 2,2'-dicarboxylic acid.

1,2:11,12-Dibenzoperylene

Identified following chromatography on acetylated cellulose; the ultraviolet spectrum (benzene) showed maxima at 300, 313, 353, 446, 478, 516 and 558 mμ, in agreement with recorded values.[83]

Bisanthrene

Identified following chromatography on acetylated cellulose; the spectrum in the visible region showed maxima at 399, 424, 555, 602 and 662 mμ, in agreement with the literature.[143]

2,3-Benzonaphtho(2',3'-11,12)fluoranthene

Isolated following chromatography on acetylated cellulose, this had m.p. 319-320°, not depressed by admixture with an authentic specimen, kindly presented by Dr. K. Lang. The absorption spectrum showed maxima at 284, 298, 357, 380, 416, 441, 472 and 505 mμ, in agreement with the authentic specimen.

2,3-Benzonaphtho(2',3'-10,11)fluoranthene and 2,3-Benzonaphtho-(2'3'-12,13)fluoranthene

(i) The first isomer isolated following chromatography on partially acetylated cellulose had m.p. 240-241°, not depressed by admixture with a specimen of benzonaphthofluoranthene presented by Dr. K. Lang. The absorption spectrum showed maxima at 320, 349, 375, 414, 438, 465, 535 and 570 mμ, in agreement with Dr. Lang's specimen.

(ii) The second isomer eluted from the column of acetylated cellulose had m.p. 227-228° in agreement with that recorded for the isomeric benzonaphthofluoranthene.[142] The ultraviolet absorption spectrum showed maxima at 298, 380, 388, 396, 420, 445, 474, 525 and 560 mμ, in agreement with the literature.[142]

TABLE 5.3.

Contributions to the Optical Density of solutions containing 1 µg/ml.

(Calculated from recorded extinction values).

Compound	(mµ)	O.D. (1 µg/ml)
9, 10-Dihydroanthracene	264	0.0061
	271	0.0061
1, 2, 3, 4-Tetrahydroanthracene	230	0.5126
	254	0.0135
	265	0.0219
	275	0.0282
	286	0.0275
	319	0.0022
	323	0.0038
Benzonaphthofluoranthene m.p. 241-242°	320	0.048
	438	0.035
	465	0.039
	535	0.0071
	620	0.0022
Benzonaphthofluoranthene m.p. 227-229°	276	0.184
	298	0.142
	420	0.021
	445	0.041
	477	0.039
	610	0.0015

Bisanthene	300.5 399 424 603 662.5	0.138 0.0197 0.0338 0.050 0.138

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Thin-layer chromatography using partially acetylated cellulose as adsorbent

The separation of polycyclic aromatic hydrocarbons by chromatography on acetylated paper (and also on columns of partially acetylated cellulose) has been described by SPOTSWOOD[1,2], and the technique has since found extensive application. The method suffers from the disadvantage that different batches of acetylated paper, and of acetylated cellulose, have somewhat different characteristics. It has now been found that polycyclic aromatic hydrocarbons can also be satisfactorily separated by thin-layer chromatography using acetylated cellulose. No adhesive is required to prepare a satisfactory plate. The separated compounds, readily visible under ultraviolet light, can be scraped from the plates and identified by spectroscopy.

This method has the advantage that a large batch of acetylated cellulose can be prepared and used for the preparation of a great many plates over a prolonged period. Reproducible results can be obtained with a given batch of acetylated cellulose, and it may also be noted that the acetylated cellulose can be recovered and used again.

It is to be hoped that good quality acetylated cellulose will become commercially available; if distinguished by a batch number, this would facilitate the comparison of R_F values determined in different laboratories.

TABLE I

Compound	R_F
3:4-Benzopyrene	0.105
3:4-Benzofluoranthene	0.150
3:4; 9:10-Dibenzopyrene	0.217
11:12-Benzofluoranthene	0.230
Perylene	0.342
1:2; 4:5-Dibenzopyrene	0.497
1:2; 3:4-Dibenzopyrene	0.559

Table I lists the R_F values obtained for several polycyclic aromatic hydrocarbons, the solvent system being methanol–ether–water (4:4:1).

Experimental

Whatman's cellulose chromatography powder (200 g) was acetylated by SPOTSWOOD's method[2] using a mixture of thiophen-free benzene (1700 ml) and acetic anhydride (800 ml) containing 92 % sulphuric acid (4 g) and 72 % perchloric acid (4 g).

A suspension of acetylated cellulose (35 g) in methanol or ethanol (60 ml) was applied to glass plates (20 cm × 20 cm) using a "Desaga" thin-layer spreading device, adjusted to give a 250 μ layer. The resulting plates were dried in air; compounds under test were applied in the usual way in 0.5 % solution; and the plates were developed by the ascending technique in a saturated chamber, the best results being obtained when the chromatography was carried out in an air-conditioned room (68°F). The solvent systems methanol–ether–water (4:4:1) and toluene–ethanol–water

(4:17:1) both proved satisfactory, but the former was found to be preferable as it gave more compact spots.

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Note

Similar results were described by T. WIELAND, G. LÜBEN AND H. DETERMAN, *Experientia*, 18 (1962) 430, on September 15th, 1962, and it is unlikely that these had reached Australia when this paper was sent off (October 24th, 1962).

THE EDITOR

THE FORMATION OF AROMATIC HYDROCARBONS AT HIGH TEMPERATURES*

XV. THE PYROLYSIS OF 2,2,4-TRIMETHYLPENTANE (" ISO-OCTANE ")

By G. M. Badger,† Jillian K. Donnelly,† and T. McL. Spotswood†

[*Manuscript received July 5, 1962*]

Summary

The pyrolysis of 2,2,4-trimethylpentane (" iso-octane ") at 700 °C has given a tar in which 30 different aromatic compounds have been identified. Mechanisms for the formation of these compounds are discussed.

I. Introduction

The cancer-producing hydrocarbon 3,4-benzopyrene was first isolated from coal tar (Cook, Hewett, and Hieger 1933), but it has since been identified in soot, in the atmospheric " dust " of cities, in the exhaust gases of petrol and diesel engines, in some smoked food, and to a small extent in cigarette and tobacco tar (see Badger, Kimber, and Spotswood 1960). Other carcinogenic and non-carcinogenic polycyclic aromatic hydrocarbons have also been shown to be widely distributed in human environment.

These polycyclic aromatic hydrocarbons all seem to be formed from a variety of organic materials by processes involving incomplete combustion and high temperatures. Earlier papers from these laboratories (Badger *et al.* 1958; Badger and Buttery 1958; Badger and Spotswood 1959, 1960*a*, 1960*b*, 1960*c*; Badger and Kimber 1960*a*, 1960*b*; Badger and Novotny 1961*a*, 1961*b*) have described attempts to determine the modes of formation of these compounds by the pyrolysis of relatively simple molecules, some of which may be intermediate products. These have included simple unsaturated compounds (acetylene, butadiene, vinylcyclohexene), aromatic compounds (benzene, alkylbenzenes, styrene, phenylbutadiene), and indene and tetralin.

In modern cities an increasing proportion of 3,4-benzopyrene and of other polycyclic compounds in the atmosphere must be derived from the incomplete combustion of petroleum products. The nature of the products obtained by the pyrolysis of an ordinary " petrol " would therefore be of interest, more especially for comparison with those obtained by analysis of urban air. The pyrolysis of petrol is at present being investigated, and the present paper reports the results of a study of the pyrolysis of 2,2,4-trimethylpentane (" iso-octane "). This compound, which is the standard for an octane rating of 100, has been chosen as a representative of the large number of alkanes which constitute a considerable proportion of petrol.

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* For Part XIV of this series, see *J. Chem. Soc.* **1961**: 3407.

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II. Results and Discussion

The pyrolysis was carried out by passing the trimethylpentane vapour, with nitrogen, through a silica tube packed with porcelain chips, at 700 °C. Methane and ethylene were detected in the exit gases, and the tar (obtained in 24% yield) was collected and analysed by distillation, gas–liquid chromatography, chromatography on alumina and on acetylated cellulose, chromatography on acetylated paper, and by infrared, ultraviolet, and fluorescence spectroscopy. The various compounds identified have been collected in Table 1 which also

Table 1

COMPOSITION OF THE TAR FOLLOWING PYROLYSIS OF 2,2,4-TRIMETHYLPENTANE AT 700 °C

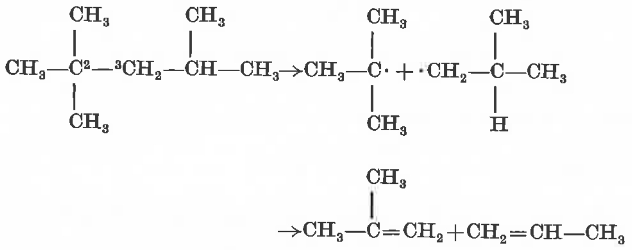
Fraction	Compound	Percentage in Tar	Method of Identification*
—	Methane	—	I.R.
—	Ethylene	—	I.R.
a, *b*, *c*	Benzene	43·8	R.T., I.R.
a, *b*, *c*, *d*, *e*	Toluene	9·52	R.T., I.R.
d, *e*	Ethylbenzene	0·29	R.T., I.R.
c, *d*	*p*-Xylene	1·23	R.T., I.R.
c, *d*, *e*	Styrene	8·47	R.T., I.R.
e	Indene	0·75	R.T.
e, 1	Naphthalene	18·2	R.T., U.V., mixed m.p.
e, 1	1- and 2-Methylnaphthalenes	1·49	R.T., U.V.
2, 3	Acenaphthylene	1·24	U.V., mixed m.p.
2, 3, 4, 5, 6	Phenanthrene	2·44	U.V., mixed m.p.
4, 5	Anthracene	1·11	U.V.
5, 6, 7	Pyrene	2·10	U.V., mixed m.p.
6, 7, 8	Fluoranthene	0·97	U.V., mixed m.p.
7	2,3-Benzofluorene	0·08	U.V.
7, 8, 9	1,2-Benzanthracene	0·82	U.V., mixed m.p.
9, 10, 11	Chrysene	1·44	U.V., mixed m.p.
10, 11, 12	Perylene	0·19	U.V.
10, 11, 12	1,2-Benzopyrene	0·93	U.V.
13	1,2,5,6-Dibenzanthracene	0·08	U.V.
12, 13, 14	3,4-Benzopyrene	0·81	U.V., F.S., mixed m.p.
12, 13	3,4-Benzofluoranthene	0·35	U.V.
14	4,5-(*o*-Phenylene)fluoranthene	0·16	U.V.
13	10,11-Benzofluoranthene	0·09	U.V.
14	11,12-Benzofluoranthene	0·09	U.V.
14, 15	1,12-Benzoperylene	0·07	U.V.
14, 15	Anthanthrene	0·24	U.V.
15, 16	2,3-(*o*-Phenylene)pyrene	0·65	U.V.
15, 16	3,4,9,10-Dibenzopyrene	0·095	U.V., F.S.
14, 15, 16	3,4,8,9-Dibenzopyrene	0·19	U.V., F.S., m.p.
16	3,4-Benzotetraphene	0·35	U.V.
	Resins, losses and unidentified material	1·76	
		100	

* I.R., infrared spectroscopy; U.V., ultraviolet spectroscopy; F.S., fluorescence spectroscopy; R.T., retention time ratio.

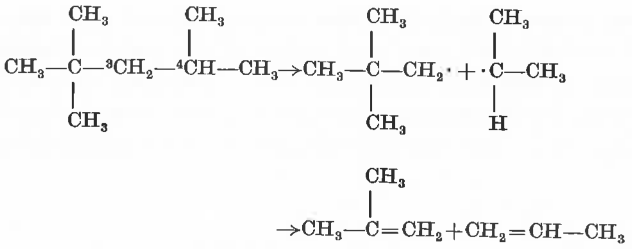
gives the percentage of each in the tar and the methods of identification used. It may be noted that benzene, naphthalene, toluene, and styrene were found to be *major* components of the tar.

There can be little doubt that the reactions leading to the formation of all these aromatic compounds are predominantly radical in nature. However, before the possible mode of formation of the individual compounds can be discussed, the probable nature of the primary fragmentation of 2,2,4-trimethylpentane must be considered.

As a matter of fact the carbon–carbon bonds in trimethylpentane would all be expected to have bond dissociation energies of about 75–78 kcal/mole, and all would therefore be expected to break with approximately equal facility (Steacie 1954). By analogy with other work of this field scission of the 2,3-bond (eqn. (1)) would be expected to give two primary radicals, and then propene and 2-methylpropene. Scission of the 3,4-bond would also yield two primary radicals, and then propene and 2-methylpropene (eqn. (2)). The primary radicals formed by scission of the 1,2 (or 2,6 or 2,7)-bond would also be expected to give 2-methylpropene and propene (eqn. (3)); and the scission of the 4,5 (or 4,8)-bond would give a methyl radical and a primary radical which would be expected to undergo further scission to propene and 2-methylpropene (eqn. (4)). It seems likely therefore that propene and 2-methylpropene radicals may be important units in the formation of the aromatic compounds actually found in the tar. It is also noteworthy that 2-methylpropene is known to undergo pyrolytic dissociation into equal proportions of propene and methane (Molera and Stubbs 1952); and the pyrolysis of propene is known to yield mainly methane, ethylene, and hydrogen (Ingold and Stubbs 1951). The formation of polycyclic compounds by step-wise processes from a two-carbon unit may also be an important process.

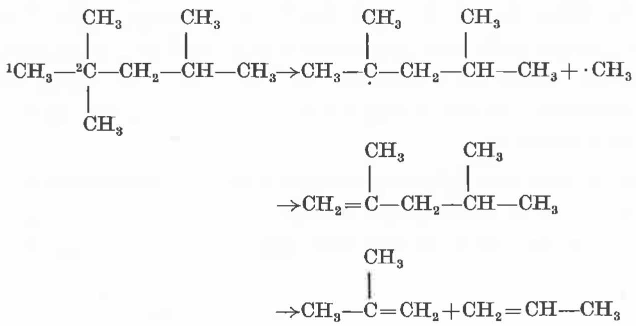


$$CH_3—\overset{CH_3}{\underset{CH_3}{C^2}}—{}^3CH_2—\overset{CH_3}{CH}—CH_3 \rightarrow CH_3—\overset{CH_3}{\underset{CH_3}{C\cdot}} + \cdot CH_2—\overset{CH_3}{\underset{H}{C}}—CH_3$$
$$\rightarrow CH_3—\overset{CH_3}{C}=CH_2+CH_2=CH—CH_3 \qquad (1)$$



$$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—{}^3CH_2—{}^4\overset{CH_3}{CH}—CH_3 \rightarrow CH_3—\overset{CH_3}{\underset{CH_3}{C}}—CH_2\cdot + \cdot\overset{CH_3}{\underset{H}{C}}—CH_3$$
$$\rightarrow CH_3—\overset{CH_3}{C}=CH_2+CH_2=CH—CH_3 \qquad (2)$$

Some of the benzene could be formed by the combination of three two-carbon units, as is certainly the case in the pyrolysis of acetylene (Badger, Lewis, and Napier 1960) and of some other compounds. In the pyrolysis of trimethylpentane, however, it seems likely that the propene radical may have such a high concentration in the reaction zone that much of the benzene could be formed by the combination of two such units (eqn. (5)). Similarly the combination of a propene radical with a 2-methylpropene radical would account for the formation of the toluene (eqn. (6)); and the combination of two 2-methylpropene radicals

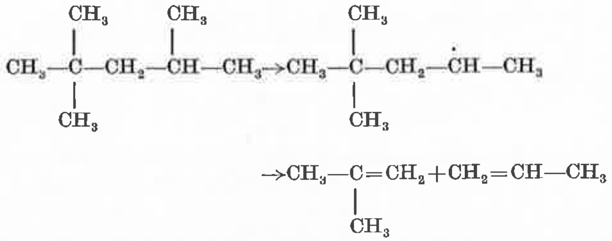


$$ {}^{1}CH_3-{}^{2}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3 \rightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\cdot}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3+\cdot CH_3 $$

$$ \rightarrow CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3 $$

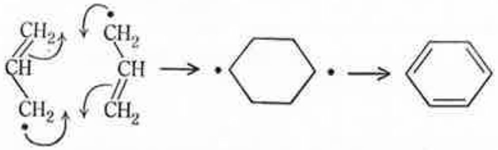
or

$$ \rightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2+CH_2=CH-CH_3 \qquad (3) $$



$$ CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3 \rightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\dot{C}H-CH_3 $$

$$ \rightarrow CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2+CH_2=CH-CH_3 \qquad (4) $$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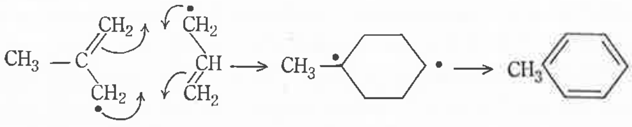
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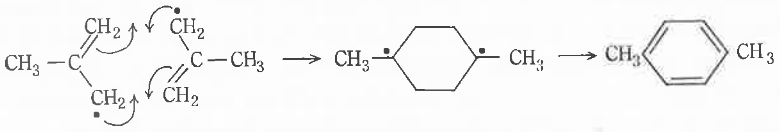
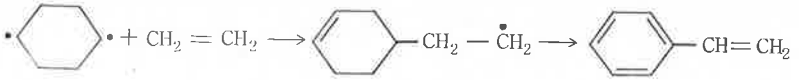

(7)

would account for the relatively large amount of *p*-xylene formed in this pyrolysis (eqn. (7)). Neither *m*-xylene nor *o*-xylene could be formed by mechanisms of this nature, and these latter compounds could not be detected among the products.

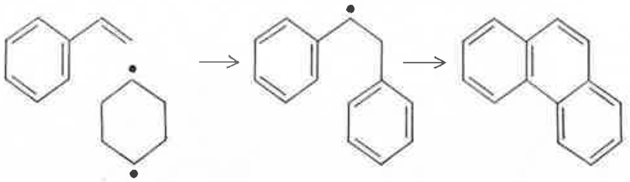
The intermediates suggested by equations (5), (6), and (7) would also be expected to undergo reaction, at least to some extent, with other constituents of the mixture in the reaction zone. Reaction of the benzene intermediate (eqn. (5)) with ethylene, for example, would be expected to give C_6–C_2 compounds such as styrene and ethylbenzene, both of which were found among the products (eqn. (8)). 3-Vinylcyclohexene is also a possible product, but this compound has already been shown to be readily converted into a variety of products at high temperatures (Badger and Novotny 1961*b*). Reaction of the benzene intermediate with propene, followed by scission of a methyl radical, would also be expected to yield styrene. It might be thought that this latter mechanism would also yield a little propylbenzene. No propylbenzene was detected among the products, but some indene was identified, and this could be formed by a very similar mechanism.



(8)

The high yield of compounds having a C_6–C_2 structure is especially noteworthy, for such substances have been shown to be important building blocks in the preparation of many polycyclic aromatic hydrocarbons (Badger and Buttery 1958 ; Badger and Spotswood 1960*a* ; Badger and Novotny 1961*b*).

Chain-lengthening has been demonstrated on many occasions. The interaction of a C_6–C_2 unit, such as a styryl radical, with ethylene would be expected to yield a C_6–C_4 unit and hence naphthalene ; and naphthalene was found in large amounts among the products. Similarly the interaction of a styryl radical with propene would be expected to yield both 1- and 2-methylnaphthalenes ; and interaction of a styryl radical with benzene, or styrene with the benzene intermediate, would be expected to yield phenanthrene (eqn. (9)). This mechanism has been firmly established as an important route to phenanthrene following the pyrolysis of [α-^{14}C]ethylbenzene (Badger and Kimber 1961).

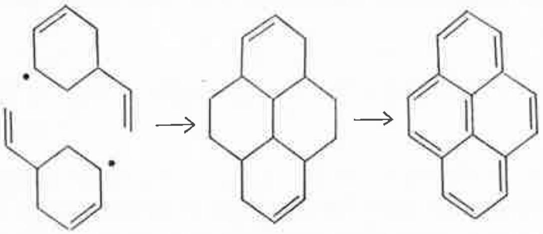


(9)

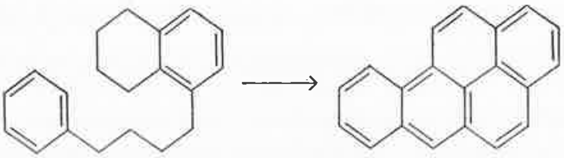
The formation of 1,2-benzanthracene can be rationalized by assuming the interaction of a C_6–C_4 unit with a C_6–C_2 unit ; but several other possibilities also exist. Similarly chrysene could be formed from two C_6–C_3 units, and in this connection it may be noted that indene has been found to yield large amounts of chrysene on pyrolysis, together with some 1,2-benzanthracene and other hydrocarbons (Badger and Kimber 1960*b*). The pyrolysis of propylbenzene also yields some chrysene, 1,2-benzanthracene, and many other hydrocarbons (Badger and Spotswood 1960*a*).

The interaction of two C_6–C_2 units (for example two vinylcyclohexene radicals) could account for the presence of the relatively large amount of pyrene found in the tar (eqn. (10)). The interaction of two C_6–C_4 units would similarly account for the presence of the carcinogenic hydrocarbons 3,4-benzopyrene (eqn. (11)) and 3,4-benzofluoranthene (eqn. (12)), as well as 1,2-benzopyrene (eqn. (13)).

The proposed mechanism for the formation of 3,4-benzopyrene in pyrolytic reactions (eqn. (11)) was first suggested by Badger *et al.* (1958) and considerable evidence has now accumulated that this does represent a major route to this hydrocarbon (Badger, Kimber, and Spotswood 1960). Somewhat similar mechanisms seem equally feasible for the formation of 3,4,8,9-dibenzopyrene and 3,4,9,10-dibenzopyrene. Thus, interaction of a C_6–C_4 unit with phenanthrene (present to the extent of 2·44% in the final tar) would be expected to give 3,4,9,10-dibenzopyrene (eqn. (15)); and interaction of a C_6–C_4 unit with anthracene (present to the extent of 1·11% in the final tar) would be expected to give 3,4,8,9-dibenzopyrene (eqn. (14)).



(10)



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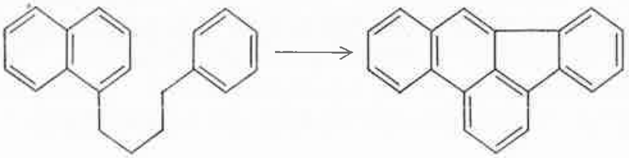

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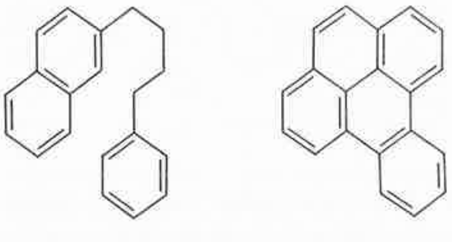
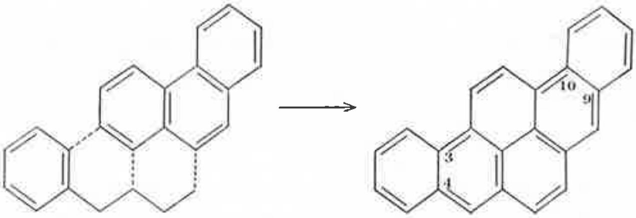


(13)

The tar obtained from the pyrolysis of trimethylpentane is remarkable for the absence of biphenyl, in spite of the fact that large amounts of benzene were formed. It seems likely therefore that in this particular reaction environment any phenyl radicals formed must undergo preferential reaction by abstraction of hydrogen. Mechanisms for the formation of polycyclic hydrocarbons involving the attack of a phenyl radical on some aromatic system, and which have been entirely reasonable in some other pyrolyses, therefore, seem to be precluded for the present pyrolysis. The formation of fluoranthene by the phenylation of naphthalene, followed by dehydrogenation, may therefore be precluded, although reaction of naphthalene with the benzene *intermediate* may still be possible. An alternative route to fluoranthene could involve the direct interaction of two C_6–C_2 units, followed by cyclodehydrogenation. 1,1′-Binaphthyl was also found to be absent from the tar, and it might therefore be concluded that the perylene present could not be formed by cyclodehydrogenation of the binaphthyl (as is undoubtedly the case in some other pyrolyses: see Lang, Buffleb, and Kalowy 1957). An alternative mechanism would seem to involve the attack of a molecule of anthracene by two propene radicals, followed by cyclodehydrogenation (eqn. (16)).



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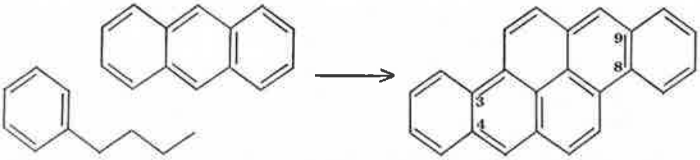

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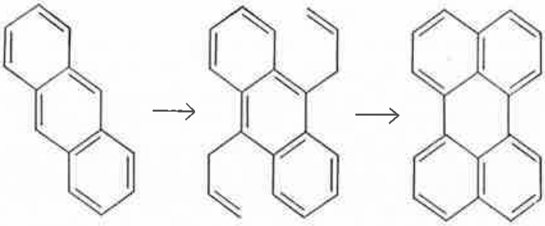

(16)

No similar mechanism can however be drawn to account for the presence of 10,11-benzofluoranthene and of 11,12-benzofluoranthene and it must be concluded that these compounds are derived, as expected, from hydrogenated precursors related to 1,2′-, 1,1′-, and 2,2′-binaphthyls (cf. Lang, Buffleb, and Kalowy 1957). Similarly it seems likely that 1,2,5,6-dibenzanthracene and 1,12-benzoperylene must be produced from 2-methylnaphthalene or its equivalent. Lijinsky and Raha (1961) have shown that these hydrocarbons are indeed formed following pyrolysis of 2-methylnaphthalene.

III. EXPERIMENTAL

(a) *General*

Material for Pyrolysis.—2,2,4-Trimethylpentane (B.D.H.) was distilled and the fraction b.p. 99·0–99·5 °C collected. It had $n_{\mathrm{D}}^{18}=1\cdot3920$ (lit. $n_{\mathrm{D}}^{20}=1\cdot3916$), and no impurity could be detected by gas–liquid chromatography.

Pyrolysis.—The pyrolysis tube consisted of a silica tube packed with porcelain chips ($\frac{3}{8}$–$\frac{1}{4}$ in.) (Badger *et al.* 1958). The trimethylpentane (100 g) was introduced directly into the pyrolysis tube using a dropping funnel with a needle-valve and passed with nitrogen (0·5 c.c./sec) through the tube which was kept at 700 °C. The resulting tar (24 g) was collected in a series of traps containing solid CO_2-ethanol mixtures, and liquid air. The gaseous products were found to decolourize Br water and alkaline permanganate, and samples were collected for i.r. spectroscopy.

Analysis of Tar.—The tar was distilled to give the following fractions : (*a*) b.p. 85 °C (5·12 g) ; (*b*) b.p. 85–90 °C (3·01 g) ; (*c*) b.p. 90–100 °C (3·81 g) ; (*d*) b.p. 100 °C/20 mm (1·72 g) ; (*e*) b.p. 120–130 °C/20 mm (4·07 g), and (*f*) a residue (6·44 g).

Fractions (*a*)–(*e*) were examined by gas–liquid chromatography, and peaks corresponding to benzene, toluene, ethylbenzene, *p*-xylene, styrene, indene, naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene were observed. The identity of these compounds was confirmed by i.r. or u.v. spectroscopy.

The residue (*f*) was chromatographed on Spence alumina, using hexane, hexane–benzene, benzene, and finally ethanol as eluants. The fractions were examined spectrofluorometrically, and the fractions having similar fluorescence spectra were combined. The combined fractions (1–17) were rechromatographed on partially acetylated cellulose and on partially acetylated paper (Spotswood 1960).

Gas–liquid Chromatography.—A Griffin and George Mark II VPC apparatus was used, modified to collect samples (Napier and Rodda 1958). Apiezon L supported on Celite (40–80 mesh, 1 : 4 w/w) was used as stationary phase, and nitrogen as carrier gas. The composition of each fraction was determined from the areas under the peaks (height × width at half-peak height). The components of fraction (*d*) were collected for infrared analysis using this apparatus ; but the components of fractions (*a*), (*b*), (*c*), and (*e*) were collected using a Beckman Megachrome with nitrogen as carrier gas.

Spectroscopy.—The i.r. spectra were determined on the liquid film using a Perkin–Elmer Infracord. U.V. spectra were determined in 95% ethanol using an Optica CF_4 recording spectrophotometer. Fluorescence spectra were obtained using a Farrand recording spectrofluorimeter.

(b) *Details of Identification*

Methane and Ethylene.—Samples of the exit gases were collected and examined by i.r. spectroscopy. Methane was identified by its spectrum in the 7·3–8·5 μ region (maxima at 7·41, 7·48, 7·67, 7·78, 7·81, 7·86, 7·93, 8·04, 8·10, 8·16 μ), and ethylene by its spectrum in the 10–11 μ region (maxima at 9·94, 10·03, 10·12, 10·22, 10·31, 10·53, 10·76, 10·84, 11·0, and 11·08 μ).

Benzene.—Isolated from fractions (*a*), (*b*), and (*c*) by gas–liquid chromatography, its i.r. absorption spectrum (liquid film) showed maxima at 3·23, 3·29, 5·11, 5·51, 6·54, 6·75, 9·65, and 14·82 μ, in agreement with an authentic specimen.

Toluene.—Isolated from fractions (*a*)–(*e*) by gas–liquid chromatography. The i.r. spectrum (liquid film) showed maxima at 3·29, 3·42, 6·25, 6·68, 6·85, 7·25, 8·48, 9·25, 9·71, 13·74, and 14·42 μ, in agreement with an authentic specimen.

Ethylbenzene.—Identified in fractions (*d*) and (*e*) by gas-liquid chromatography, and isolated from (*d*) by this method. The i.r. spectrum (liquid film) showed maxima at 3·37, 3·41, 3·79, 5·15, 5·55, 6·23, 6·66, 6·88, 7·26, 7·52, 8·04, 8·48, 9·00, 9·17, 9·40, 9·70, 10·36, 11·06, 11·87, 12·7, 12·96, 13·4, and 14·36 μ, in agreement with an authentic specimen.

p-*Xylene*.—Isolated from fraction (*d*) by gas-liquid chromatography. The i.r. spectrum (liquid film) showed maxima at 3·30, 3·42, 5·29, 6·14, 6·58, 6·87, 7·25, 8·20, 8·90, 9·06, 9·58, 9·78, and 12·59 μ, in agreement with an authentic specimen.

Styrene.—Isolated from fractions (*c*) and (*d*), and also identified in (*e*), by gas–liquid chromatography. The i.r. spectrum (liquid film) showed maxima at 3·22, 3·27, 5·46, 6·21, 6·70, 6·90, 7·05, 7·74, 8·30, 9·22, 9·80, 10·09, 11·0, 12·90, and 14·37 μ, in agreement with an authentic specimen.

Indene.—This was identified in fraction (*e*) by gas–liquid chromatography by comparison of its retention time ratio with that of an authentic specimen.

Naphthalene.—This was isolated from fraction (*e*) by gas–liquid chromatography, and from fraction 1 by chromatography on a column of partially acetylated cellulose. It had m.p. 79–80 °C not depressed by admixture with an authentic specimen. Its u.v. absorption spectrum showed maxima at 248, 257, 266, 275, 285, and 311 mμ, in agreement with an authentic specimen.

1- and 2-Methylnaphthalenes.—Gas–liquid chromatography of fraction (*e*) gave a peak having the same retention time ratio as that for 1- and 2-methylnaphthalenes. Chromatography of fraction 1 on partially acetylated cellulose gave a mixture of 1- and 2-methylnaphthalenes. The u.v. spectrum was of the same general appearance as those of the authentic specimens, and showed maxima at 312 and 319 mμ characteristic of 1- and 2-methylnaphthalene respectively.

Acenaphthylene.—Isolated from fractions 2 and 3 by chromatography on a column of partially acetylated cellulose, it had m.p. 94–95 °C, not depressed by admixture with an authentic specimen. Its u.v. spectrum showed maxima at 229, 258, 266, 276, 309, 323, 334, and 340 mμ, in agreement with an authentic specimen.

Phenanthrene.—Isolated from fractions 2–6 by chromatography on a column of partially acetylated cellulose, it had m.p. 97–99 °C, not depressed by admixture with an authentic specimen. Its u.v. spectrum showed maxima at 243, 252, 275, 282, 294, 310, 317, 324, 331, 339, and 346 mμ, in agreement with an authentic specimen.

Anthracene.—Isolated from fractions 4 and 5 by chromatography on acetylated cellulose, its u.v. spectrum showed maxima at 246, 253, 308, 323, 339, 357, and 377 mμ, in agreement with an authentic specimen.

Pyrene.—Isolated from fractions 5, 6, and 7 by chromatography on acetylated cellulose, it had m.p. 145–146 °C, not depressed by admixture with an authentic specimen. Its u.v. spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335, and 364 mμ, in agreement with an authentic specimen.

Fluoranthene.—Isolated from fractions 6, 7, and 8 by chromatography on acetylated cellulose it had m.p. 106–108 °C, not depressed by admixture with an authentic specimen. Its u.v. spectrum showed maxima at 236, 253, 263, 273, 278, 282, 288, 309, 323, 342, and 360 mμ, in agreement with an authentic specimen.

2,3-Benzofluorene.—Identified in fraction 7 following chromatography on a column of acetylated cellulose and on acetylated paper. An extract showed maxima at 255, 264, 273, 285, 304, 317, 325, 333, and 340 mμ, in agreement with an authentic specimen.

1,2-Benzanthracene.—Isolated from fractions 7, 8, and 9 following chromatography on acetylated cellulose, it had m.p. 156–158 °C, not depressed by admixture with an authentic specimen. Its u.v. spectrum showed maxima at 222, 227, 256, 268, 278, 289, 300, 315, 326, 341, 358, 365, 374, and 384 mμ, in agreement with an authentic specimen.

Chrysene.—Isolated from fractions 9, 10, and 11 by chromatography on acetylated cellulose, it had m.p. and mixed m.p. 253–255 °C. Its u.v. spectrum showed maxima at 242, 259, 267, 283, 294, 306, 320, 344, 351, and 363 mμ, in agreement with an authentic specimen.

Perylene.—Identified in fractions 10, 11, and 12 following chromatography on acetylated cellulose and on acetylated paper. An extract from the paper chromatogram showed the typical long wavelength maxima of perylene at 367, 386, 407, and 435 mμ, but the full spectrum was not obtained.

1,2-Benzopyrene.—Identified in fractions 10, 11, and 12 by chromatography on acetylated cellulose followed by acetylated paper. An extract showed maxima at 238, 258, 268, 278, 289, 305, 317, and 333 mμ, in agreement with an authentic specimen.

1,2,5,6-Dibenzanthracene.—Identified in fraction 13 by chromatography on acetylated cellulose followed by acetylated paper. An extract showed maxima at 221, 230, 276, 288, 298, 319, 335, and 348 mμ, in agreement with an authentic specimen.

3,4-Benzopyrene.—Isolated from fractions 12, 13, and 14 by chromatography on a column of acetylated cellulose, it had m.p. 173–176 °C not depressed by admixture with an authentic specimen. Its u.v. spectrum showed maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385, and 404 mμ, and its fluorescence spectrum maxima at 397, 422, 448, and 478 mμ. Both spectra were identical with those given by an authentic specimen.

3,4-Benzofluoranthene.—Isolated from fractions 12 and 13 by chromatography on a column of acetylated cellulose, its u.v. spectrum showed maxima at 239, 256, 276, 290, 294, 301, 339, 351, and 369 mμ, in agreement with an authentic specimen.

10,11-Benzofluoranthene.—Identified in fraction 13 by chromatography on a column of acetylated cellulose followed by chromatography on acetylated paper using an extended development time. An extract showed maxima at 293, 309, 318, 333, 345, 365, 376, and 383 mμ, in agreement with an authentic specimen.

11,12-Benzofluoranthene.—Identified in fraction 14 by chromatography on acetylated cellulose and then on acetylated paper. An extract showed maxima at 238, 247, 269, 283, 297, 309, 361, 380, and 402 mμ, in agreement with an authentic specimen.

1,12-Benzoperylene.—Isolated from fractions 14 and 15 by chromatography on acetylated cellulose. Its u.v. spectrum showed maxima at 268, 276, 289, 300, 315, 325, 345, 363, and 383 mμ, in agreement with an authentic specimen.

4,5-(o*-Phenylene)fluoranthene.*—Identified in fraction 14 by chromatography on acetylated cellulose followed by acetylated paper. An extract showed maxima at 253, 262, 272, 368, 380, 387, 402, and 411 mμ, in agreement with an authentic specimen.

Anthanthrene.—Identified in fractions 14 and 15 by chromatography on acetylated cellulose, followed by acetylated paper. An extract showed maxima at 233, 256, 259, 295, 308, 365, 382, 402, 407, 422, and 431 mμ, in agreement with an authentic specimen.

2,3-(o*-Phenylene)pyrene.*—Identified in fractions 15 and 16 by chromatography on acetylated cellulose followed by acetylated paper. An extract showed maxima at 251, 261, 277, 292, 304, 315, 360, 376, 385, 402, 408, 422, and 431 mμ, in good agreement with recorded values (Lang, Buffleb, and Kalowy 1957).

3,4,8,9-Dibenzopyrene.—Isolated from fractions 14, 15, and 16 by chromatography on acetylated cellulose. It had a much lower R_F than the other components of these fractions, and was clearly separated. The material isolated had m.p. 300–305 °C (lit. 308 °C) and its absorption spectrum (in benzene) showed maxima at 291, 301, 314, 379, 401, 424, and 452 mμ, in good agreement with recorded values (Clar 1952). Its fluorescence spectrum showed maxima at 449, 475, and 512 mμ, in good agreement with the literature (Lyons and Johnston 1957).

3,4,9,10-Dibenzopyrene.—Identified in fractions 15 and 16 by chromatography on acetylated cellulose followed by acetylated paper. An extract showed absorption maxima at 234, 242, 273, 283, 296, 315, 331, 353, and 393 mμ, in agreement with recorded figures (Clar 1952), and fluorescence maxima at 428, 456, 489, and 520 mμ, in agreement with an authentic specimen.

3,4-Benzotetraphene.—Identified in fraction 16 by chromatography on acetylated cellulose followed by acetylated paper. An extract showed maxima at 248, 277, 287, 304, 318, 332, 345, 363, 382, and 390 mμ, in agreement with an authentic specimen.

IV. ACKNOWLEDGMENTS

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THE FORMATION OF AROMATIC HYDROCARBONS AT HIGH TEMPERATURES*

XVII. THE PYROLYSIS OF A PETROL

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[*Manuscript received January* 4, 1963]

Summary

The pyrolysis of a premium grade petrol at 700°C has given a tar in which 46 different aromatic compounds have been identified. The relative concentrations of some of the polynuclear hydrocarbons present have been compared with those obtained from the analysis of vehicular exhaust tars.

I. Introduction

There is a close statistical relationship between cigarette smoking and the incidence of cancer of the lung, and most investigators have concluded that the relationship is causal.[1] However, there is some evidence that atmospheric pollution may also be an important factor.[2,3] Urban dwellers, for example, have a higher incidence of lung cancer than rural inhabitants.[4] In this connection it is noteworthy that the concentration of polycyclic aromatic hydrocarbons (including the carcinogenic 3,4-benzopyrene) is much higher in the atmosphere of cities than in rural areas.

The polycyclic aromatic hydrocarbons present in the atmosphere are produced by the incomplete combustion of various organic materials; the most common sources include domestic and industrial smoke, and the exhaust products from petrol and diesel engines. It is significant that benzene extracts of vehicular exhaust products have been shown to produce skin tumours in mice,[5] and the analysis of exhaust tars has shown the presence of 3,4-benzopyrene and of other carcinogenic hydrocarbons.[6,7]

It therefore seemed of interest to pyrolyse an ordinary petrol under the same conditions previously used for the pyrolysis of benzene,[8] styrene,[9] butylbenzene,[10]

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* For Part XVI of this series, see *Aust. J. Chem.* **15**: 616.

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Aust. J. Chem., 1963, **16**, 392–400

tetralin,[11] and other compounds, and to analyse the resulting tar for polycyclic aromatic hydrocarbons, particularly the carcinogenic hydrocarbons.

II. Results and Discussion

The pyrolysis was carried out by passing the petrol vapour, with nitrogen, through a silica tube packed with porcelain chips, at 700°C. Methane, ethylene, propylene, and acetylene were detected in the exit gases, and some carbon was deposited in the pyrolysis tube. The tar, obtained in 37·3% yield was collected and analysed by distillation, gas-liquid chromatography, chromatography on alumina and on acetylated cellulose, chromatography on acetylated paper, and by infrared, ultraviolet, fluorescence, and n.m.r. spectroscopy. Table 1 lists the compounds identified, together with the percentage of each in the tar, and the methods of identification used.

Several other compounds (total yield, 0·23%) were detected in the tar, but these were not identified. Five were low-boiling compounds and were detected by gas-liquid chromatography, but could not be collected for identification because of their small volume. These compounds had retention time ratios (relative to benzene) of 0·206, 0·286, 0·349, 0·429, and 0·508.

The main constituents of the tar (see Table 1) were benzene, toluene, naphthalene, and *m*-xylene. The high yields of toluene (21·6%) and *m*-xylene (5·10%), the relatively high yields of *o*- and *p*-xylene and mesitylene, and the presence of so many alkyl derivatives of polycyclic hydrocarbons, are remarkable. However, as all commercial petrols are complex mixtures of aromatic and aliphatic substances, any attempt to postulate modes of formation for the constituents of the tar would be unprofitable.

The most complete analysis of the exhaust products from an automobile operating under normal city driving conditions is that reported by Hoffmann and Wynder,[7] and it is of interest to compare their results with those now obtained by the controlled pyrolysis of petrol.

Figure 1 is an attempt to compare the tars from the two sources. Pyrene has been chosen as an internal standard, and the yields of other compounds are recorded relative to that of this hydrocarbon.

Within the limits of experimental error, and bearing in mind the probable differences between the petrols used in the two countries, the two tars may be seen to show many similarities. Much more 3,4-benzopyrene was found in the petrol tar, however; and although coronene was found to be a major constituent of the tar from the automobile exhaust it could not be identified in the petrol tar.

The difference in the pyrene/3,4-benzopyrene ratios is difficult to explain. The rate of pyrolysis could be important, as could the temperatures of the two processes; and the relative stabilities of the two hydrocarbons could greatly affect the observed result.[12] It is interesting to note, however, that the increase

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TABLE 1

COMPOSITION OF THE TAR OBTAINED BY PYROLYSIS OF PETROL AT 700°C

Fraction	Compound	% in Tar	Method of Identification*
—	Methane	—	i.r.
—	Ethylene	—	i.r.
—	Acetylene	—	i.r.
—	Propylene	—	i.r.
a, *b*, *c*	Benzene	23·89	r.t., i.r.
a, *b*, *c*	Toluene	21·57	r.t., i.r.
b, *c*	Ethylbenzene	0·20	r.t.
b, *c*, *d*	*p*-Xylene	2·55	r.t., i.r.
b, *c*, *d*	*m*-Xylene	5·10	r.t., i.r.
b–*f*	*o*-Xylene	1·68	r.t., i.r.
b–*f*	Styrene	3·36	r.t., i.r.
d	*n*-Propylbenzene	0·10	r.t.
d	Ethyltoluene(?)	0·19	r.t.
c, *d*, *e*	Mesitylene	1·36	r.t., i.r.
c, *d*, *e*	Indene	1·77	r.t., i.r.
d	Tetralin	0·34	r.t.
d, *e*, 1	Naphthalene	14·02	r.t., u.v., mixed m.p.
d, *e*, 2	1-, and 2-Methylnaphthalenes	3·06	r.t., u.v.
e, 3	Biphenyl	0·80	r.t., u.v.
4	Acenaphthylene	1·04	u.v., mixed m.p.
5, 6, 7	Phenanthrene	2·91	u.v., mixed m.p.
5	Fluorene	0·31	u.v.
6	Anthracene	0·73	u.v., mixed m.p.
7, 8, 9	Pyrene	3·81	u.v., mixed m.p.
14	Alkylpyrene	0·05	u.v., n.m.r.
9	2,2′-Binaphthyl	0·18	u.v.
8, 9, 10	Fluoranthene	1·92	u.v., mixed m.p.
10	Alkylfluoranthene	0·02	u.v.
10, 11	2,3-Benzofluorene	0·50	u.v.
11, 12	1,2-Benzanthracene	0·69	u.v., mixed m.p.
12, 13, 14	Chrysene	1·01	u.v., mixed m.p.
14	Alkylchrysene	Trace	u.v.
13	Triphenylene	0·06	u.v.
15, 16	Perylene	0·06	u.v.
15, 16, 17	1,2-Benzopyrene	1·09	u.v., mixed m.p.
15	1,2:5,6-Dibenzanthracene	0·07	u.v.
16, 17	10,11-Benzofluoranthene	0·10	u.v.
16, 17, 18, 19	3,4-Benzopyrene	1·42	f.s., u.v., mixed m.p.
18	Alkyl-3,4-benzopyrene	Trace	u.v.
18	3,4-Benzofluoranthene	0·08	u.v.
18	4,5-(*o*-Phenylene)fluoranthene	0·01	u.v.
19, 20	11,12-Benzofluoranthene	0·29	u.v.
19, 20	1,12-Benzoperylene	0·32	u.v., m.p.
21	Dimethylpicene	0·05	u.v., n.m.r.
20, 21	Anthanthrene	0·23	u.v.

* r.t., retention time ratio; i.r., infrared spectroscopy; u.v., ultra violet spectroscopy; f.s., fluorescence spectroscopy; n.m.r., nuclear magnetic resonance spectroscopy.

Table 1 (*Contnued*)

Fraction	Compound	% in Tar	Method of Identification*
21, 22, 23	2,3-(*o*-Phenylene)fluoranthene	0·31	u.v., mixed m.p.
22, 23, 24	3,4:9,10-Dibenzopyrene	0·09	u.v., f.s., mixed m.p.
23, 24	3,4:8,9-Dibenzopyrene	0·04	u.v., f.s.
22	1,2:4,5-Dibenzopyrene	0·04	u.v., m.p.
24	3,4-Benzotetraphene	0·04	u.v.
	Losses, resins, and unidentified material	3	

in the amount of 3,4-benzopyrene obtained from pyrolysed petrol tar as compared with pyrolysed iso-octane tar (1·4 from 0·8),[13] is almost parallel to the increase when petrol and iso-octane are used as fuels in a motor vehicle.[14]

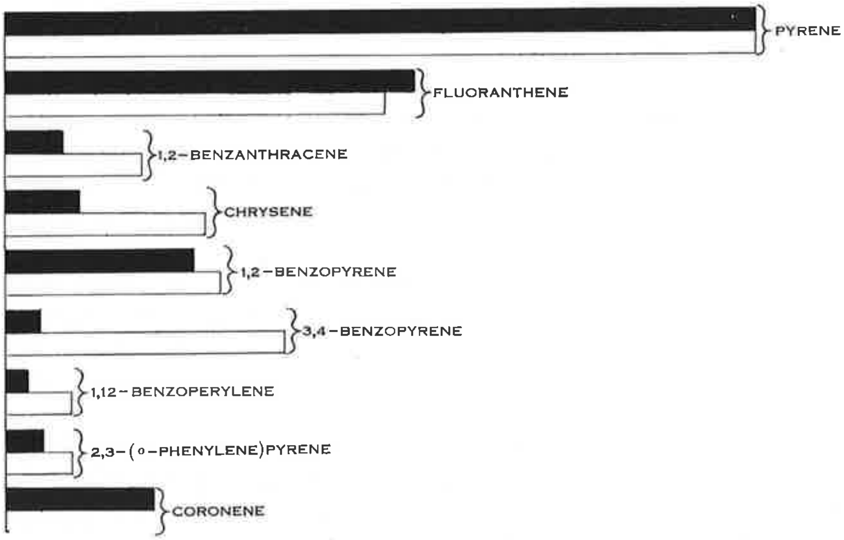

Fig. 1.—Comparison of tars obtained by the pyrolysis of petrol at 700°C, and from the exhaust of an automobile.[7] Bars represent yields relative to pyrene in each case. The black bars represent the automobile exhaust tar.

Large amounts of coronene were found in the exhaust tar, and this hydrocarbon has been identified in urban air, often in relatively high concentrations.[15] It has not been found in the tars obtained by the pyrolysis of individual compounds at 700°C.[8–11] It has sometimes, but not always, been found in low concentration in

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cigarette tar.[16] These differences in concentration are of some interest, and it seems that the temperatures reached in the various processes may be important.

From Table 2 it is seen that significant amounts of coronene are formed only when very high temperatures are involved. Further evidence has been provided by Lam,[18] who found that the tar obtained by pyrolysing tobacco hydrocarbons at 850°C did not contain coronene; but the tar obtained after heating at 970°C did contain this hydrocarbon. A probable factor contributing to the large amount of coronene found in urban air could be the greater stability and lower volatility of this hydrocarbon compared to other polynuclear hydrocarbons.[12] Some substances, such as 3,4-benzopyrene and pyrene, are well known to be susceptible to oxidation and photo-oxidation.

TABLE 2

Heating Process	Temperature (°C)	Amount of Coronene Formed
Pyrolysis of simple compounds[8–11]	700	—
Burning cigarettes[16]		
(i) Mean temperature	750	Small
(ii) Surface temperature	900	
Petrol combustion[17]		
(i) Mean temperature*	2 000	Large
(ii) Maximum temperature	3 000	

* Depends on the conditions of knocking, air/fuel ratio, etc.

Finally it may be noted that the following compounds, which have been identified in the tar obtained by pyrolysing petrol, have been reported to be carcinogenic; 1,2-benzanthracene; chrysene; 1,2:5,6-dibenzanthracene; 3,4-benzopyrene; 3,4-benzofluoranthene; 2,3-(*o*-phenylene)pyrene; 3,4:9,10-dibenzopyrene; and 3,4:8,9-dibenzopyrene.

Many of these carcinogens are ubiquitously present in urban atmosphere and may be of some importance in the incidence of cancer of the lung.

III. EXPERIMENTAL

(*a*) *General*

Material for Pyrolysis.—A premium grade petrol (b.p. 35–200°C, octane rating 93) was used without preliminary distillation or purification.

Pyrolysis.—The petrol was pyrolysed under similar conditions to those described for 2,2,4-trimethylpentane.[13] The petrol (100 g) was introduced directly into the pyrolysis tube at a rate of 7 g/hr, and passed with nitrogen (0·5 ml/sec) through the tube which was kept at 700°C. The resulting tar was combined with chloroform washings of the pyrolysis tube, and

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the whole (37·3 g) was distilled to give the following fractions (*a*) b.p. 90°C (4·51 g); (*b*) b.p. 90–100°C (5·69 g); (*c*) b.p. 100–140°C (9·88 g); (*d*) 100°C/20 mm (2·99 g); (*e*) 120–140°C/20 mm (6·99 g); (*f*) residual tar (7·17 g).

Fractions (*a*)–(*e*) were examined by gas-liquid chromatography, and peaks corresponding to benzene, toluene, ethylbenzene, *p*-, *m*-, and *o*-xylenes, styrene, n-propylbenzene, ethyltoluene, mesitylene, indene, tetralin, naphthalene, 1- and 2-methylnaphthalenes and biphenyl were observed. In most cases, the identity of these compounds was confirmed by infrared or ultraviolet spectroscopy.

The residue (*f*) was chromatographed on Spence alumina, using hexane, hexane–benzene, benzene, and finally ethanol, as eluants, and 150 × 250 ml fractions were collected. These fractions were examined spectrofluorimetrically, and on this basis some were combined. The combined fractions (24 in all) were rechromatographed on partially acetylated cellulose and on partially acetylated paper.[19]

Gas-liquid Chromatrography.—A Griffin and George Mark II V.P.C. apparatus, modified to collect samples[20] was used. Apiezon L supported on Celite (40–80 mesh, 1: 4 w/w) was used as stationary phase, and dry nitrogen as carrier gas. The composition of each fraction was determined from the areas under the peaks (height × width at half peak height). The individual fractions were collected using a Beckman Megachrome unit and nitrogen as carrier gas. The identity of the components was established by infrared spectroscopy and retention-time ratios.

Spectroscopy.—Infrared spectra were determined on a Perkin–Elmer model 137 Infracord spectrophotometer. The spectra were determined either in the gas phase (the exit gases from the pyrolysis), or as liquid films. Ultraviolet spectra were determined in 95% ethanol using an Optica CF_4 recording spectrophotometer. Fluorescence spectra were obtained using a Farrand recording spectrofluorimeter.

(*b*) *Details of Identification*

Methane, Ethylene, Propylene, and Acetylene.—Samples of the exit gases were collected and examined by infrared spectroscopy. Methane was identified by its spectrum in the 7·3–8·5 μ region (maxima at 7·41, 7·48, 7·67, 7·78, 7·81, 7·86, 7·93, 8·04, 8·10, and 8·16 μ); ethylene by its spectrum in the 10–11 μ region (maxima at 9·94, 10·03, 10·12, 10·22, 10·31, 10·53, 10·76, 10·84, 11·0, and 11·08 μ); propylene in the 5·4–6·3 μ region (maxima at 5·4, 5·55, 6·05, 6·15, and 6·28 μ); and acetylene by its spectrum in the 13·5–14·0 μ region (intense maximum at 13·67 μ).

Benzene.—Isolated from fractions (*a*), (*b*), and (*c*) by gas-liquid chromatography. Its infrared absorption spectrum (liquid film) showed maxima at 3·29, 3·80, 4·21, 4·41, 5·00, 5·41, 5·60, 5·89, 6·51, 6·76, 7·13, 8·50, and 9·61 μ in agreement with an authentic specimen.

Toluene.—Isolated from fractions (*a*)–(*c*) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3·29, 3·42, 3·48, 3·65, 3·86, 5·15, 5·39, 5·55, 5·76, 6·23, 6·68, 6·85, 7·25, 8·26, 8·48, 9·03, 9·25, 9·60, 9·71, 11·16, 13·74, and 14·42 μ, in agreement with an authentic specimen.

Ethylbenzene.—Identified in fractions (*b*) and (*c*) by gas-liquid chromatography by comparison of its retention time ratio with that of an authentic specimen.

p-*Xylene and* m-*Xylene.*—Peaks were observed in the gas-liquid chromatography of distillation fractions (*b*), (*c*), and (*d*) corresponding to either *p*-xylene or *m*-xylene. The infrared spectrum showed the presence of both compounds. Comparison of this spectrum with spectra of authentic compounds in varying ratios gave the ratio *m*-xylene to *p*-xylene = 2 : 1. Maxima due to the *meta*-isomer occurred at 6·20, 8·54, 8·64, 9·79, 10·1, 11·0, 11·4, 12·95, and 13·68 μ, while the *para*-isomer showed maxima at 6·14, 9·6, and 12·5 μ. There were also many other peaks observed which were common to both isomers.

[19] Spotswood, T. M. (1960).—*J. Chromatagr.* **3**: 101.

[20] Napier, I. M., and Rodda, H. J. (1958).—*Chem. & Ind.* **1958**: 1319.

o-Xylene and Styrene.—Peaks were observed in the gas-liquid chromatography of distillation fractions (*b*)–(*f*) which corresponded to either *o*-xylene or styrene. A complex infrared spectrum showing maxima of both these compounds, gave the ratio styrene to *o*-xylene = 2 : 1.

n-Propylbenzene and Ethyltoluene (?).—Two compounds were detected by gas-liquid chromatography of distillation fraction (*d*), and the retention time ratios corresponded to those of authentic specimens of n-propylbenzene and an ethyltoluene, respectively. Insufficient material was present to allow further identification.

Mesitylene.—Isolated from distillation fractions (*c*), (*d*), and (*e*) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3·39, 3·68, 5·83, 6·21, 6·34, 6·79, 7·05, 7·26, 7·68, 9·62, 11·93, and 14·52 μ in agreement with an authentic specimen.

Indene.—Isolated from distillation fractions (*c*), (*d*) and (*e*) by gas-liquid chromatography. The infrared spectrum (liquid film) showed maxima at 3·22, 3·27, 5·46, 6·21, 6·70, 6·90, 7·05, 7·74, 8·30, 9·22, 9·80, 10·09, 11·0, 12·90, and 14·37 μ, in agreement with an authentic specimen.

Tetralin.—Identified in fraction (*d*) by gas-liquid chromatography, by comparison of its retention time ratio with that of an authentic specimen.

Naphthalene.—Isolated from fractions (*d*) and (*e*) by gas-liquid chromatography, and from fraction 1 obtained by chromatography on a column of alumina. Its ultraviolet absorption spectrum showed maxima at 248, 257, 266, 275, 285, and 311 mμ, in agreement with an authentic specimen; and it had m.p. and mixed m.p. 78–80°C.

1- and 2-Methylnaphthalenes.—Gas-liquid chromatography of fractions (*d*) and (*e*) gave a peak having the same retention time ratio as that for the methylnaphthalenes, Fraction 2 from the alumina column gave a mixture of both these compounds. The ultraviolet absorption spectrum showed maxima at 312 and 319 mμ, characteristic of 1- and 2-methylnaphthalene respectively, and also suggested the predominance of the 2-isomer.

Biphenyl.—Identified in fraction (*e*), and isolated from fraction 3 by chromatography on a column of alumina. The ultraviolet absorption spectrum showed a maximum at 250 mμ, in agreement with an authentic specimen. It had m.p. and mixed m.p. 69–70°C.

Acenaphthylene.—Isolated from fraction 4, it had m.p. 94–95°C, not depressed by admixture with an authentic specimen. Its ultraviolet spectrum showed maxima at 229, 258, 266, 276, 309, 323, 334, and 340 mμ, in agreement with an authentic specimen.

Phenanthrene.—Isolated from fractions 5, 6, 7 by chromatography on a column of partially acetylated cellulose, it had m.p. 98–99°C, not depressed by admixture with an authentic specimen. Its ultraviolet spectrum showed maxima at 243, 252, 275, 282, 294, 310, 317, 324, 339, and 346 mμ, in agreement with an authentic specimen.

Fluorene.—Identified in fraction 5 by chromatography on a column of partially acetylated cellulose. Its ultraviolet absorption spectrum showed maxima at 260, 290, and 301 mμ, in agreement with an authentic specimen.

Anthracene.—Isolated from fraction 6 by crystallization. A sample showed maxima at 246, 253, 308, 323, 339, 357, and 377 mμ in agreement with an authentic specimen; it had m.p. and mixed m.p. 215–216°C.

Pyrene.—Isolated from fractions 7, 8 and 9 by chromatography on a column of partially acetylated cellulose. Its ultraviolet spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335, 351, 358, 364, and 373 mμ, in agreement with an authentic specimen and it had m.p. and mixed m.p. 146–147°C.

Methylpyrene.—Isolated from fraction 14 by chromatography on a column of partially acetylated cellulose. Its ultraviolet absorption spectrum showed maxima at 243, 255, 264, 278, 310, 322, and 339 mμ, suggesting an alkyl pyrene. This was confirmed by nuclear magnetic resonance spectroscopy; aromatic protons absorbed in the region τ, 1·8–2·3, while a peak at $\tau = 7{\cdot}3$, which integrated for ratio 3 : 9, was attributed to methyl protons. A melting point of 138–140°C suggested that the methyl group was in the 4 position. (Reported m.p. of 4-methylpyrene is 142·5–143·5°C).[21]

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[21] Clar, E. (1952).—"Aromatische Kohlenwasserstoffe."—(Springer–Verlag: Berlin.)

2,2′-Binaphthyl.—Identified in fraction 9 by chromatography on acetylated cellulose, followed by paper chromatography. An extract showed maxima at 254 and 308 mμ in agreement with an authentic specimen.

Fluoranthene.—Isolated from fractions 8, 9, and 10 by chromatography on a column of partially acetylated cellulose. Its ultraviolet spectrum showed maxima at 236, 253, 263, 273, 278, 282, 309, 323, 342, and 360 mμ, in agreement with an authentic specimen. It had a melting point 105–106°C, which was not depressed by admixture with an authentic specimen.

Alkylfluoranthene.—Detected in fraction 10 by chromatography on a column of partially acetylated cellulose. Its ultraviolet absorption spectrum was the same general shape as that of fluoranthene, but shifted to longer wavelengths, and the maxima occurred at 279, 285, 290, 311, 326, 345, and 362 mμ.

2,3-Benzofluorene.—Identified in fractions 10 and 11 by chromatography on partially acetylated cellulose, followed by chromatography on acetylated paper. Its ultraviolet spectrum showed maxima at 225, 264, 273, 285, 304, 317, 325, 333, and 340 mμ, in agreement with an authentic specimen.

1,2-Benzanthracene.—Isolated from fractions 11 and 12 following chromatography on partially acetylated paper. Its ultraviolet spectrum showed maxima at 222, 227, 256, 268, 278, 289, 300, 315, 326, 341, 358, 365, 374, and 384 mμ, in agreement with an authentic specimen. It had m.p. 156–158°C, not depressed by admixture with an authentic specimen.

Chrysene.—Isolated from fractions 12, 13, and 14 by chromatography on acetylated cellulose, it had m.p. and mixed m.p. 254–255°C. Its ultraviolet spectrum showed maxima at 242, 259, 267, 283, 294, 306, 320, 344, 351, and 363 mμ, in agreement with an authentic specimen.

Alkylchrysene.—Identified in fraction 14 by chromatography on acetylated cellulose followed by paper chromatography. A sample showed maxima at 244, 260, 272, 285, 297, 308, 323, 353, and 364 mμ; but insufficient material was available for further identification.

Triphenylene.—Identified in fraction 13 following chromatography on acetylated cellulose. A sample showed maxima at 250, 257, 275, 286, 316, 330, and 341 mμ, in agreement with an authentic specimen.

Perylene.—Identified in fractions 15 and 16 by chromatography on acetylated cellulose, followed by paper chromatography; an extract showed maxima at 245, 253, 263, 367, 386, 407, and 435 mμ, in agreement with an authentic specimen.

1,2-Benzopyrene.—Isolated from fractions 15, 16, and 17 by chromatography on a column of acetylated cellulose, followed by rechromatographing certain fractions on a second column of acetylated cellulose. It had m.p. 176–177°C, not depressed by admixture with an authentic specimen; and a sample showed maxima at 238, 258, 268, 278, 289, 305, 317, 333, and 366 mμ in agreement with an authentic specimen.

1,2:5,6-Dibenzanthracene.—Identified in fraction 15 by chromatography on acetylated cellulose followed by paper chromatography. An extract showed maxima at 221, 230, 288, 298, 319, 335, and 348 mμ, in agreement with an authentic specimen.

10,11-Benzofluoranthene.—Identified in fractions 16 and 17 following chromatography on acetylated cellulose. Its ultraviolet spectrum showed maxima at 241, 282, 293, 309, 318, 333, 345, 365, 376, and 383 mμ, in agreement with an authentic specimen.

3,4-Benzopyrene.—Isolated from fractions 16–19 by chromatography on acetylated cellulose. It had m.p. 174–176°C, not depressed by admixture with an authentic specimen. Its ultraviolet absorption spectrum showed maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385, and 404 mμ, and its fluorescence spectrum showed maxima at 397, 422, 448, and 478 mμ. Both spectra were identical with those given by an authentic specimen.

Alkyl-3,4-benzopyrene.—Identified in fraction 18 by chromatography on acetylated cellulose and acetylated paper. An extract showed maxima at 300, 350, 370, 383, 389, and 410 mμ. Insufficient material was available for further identification, although the absorption maxima corresponded to those reported for 2-methyl-3,4-benzopyrene.[22]

[22] Friedel, R. A., and Orchin, M. (1951).—"Ultraviolet Spectra of Aromatic Compounds." (John Wiley: New York & London.)

3,4-Benzofluoranthene.—Identified in fraction 18 by chromatography on acetylated cellulose followed by acetylated paper. An extract showed maxima at 238, 247, 269, 283, 297, 309, 361, 380, and 402 mμ, in agreement with an authentic specimen.

1,12-Benzoperylene.—Isolated from fractions 19 and 20 by chromatography on a column of acetylated cellulose, it had m.p. 268–269°C (lit.[21] 273°C). Its ultraviolet spectrum showed maxima at 268, 276, 289, 300, 315, 325, 345, 363, and 383 mμ, in agreement with an authentic specimen.

4,5-(o-Phenylene)fluoranthene.—Identified in fraction 18 by chromatography on acetylated cellulose followed by acetylated paper. An extract showed maxima at 253, 262, 272, 368, 380, 387, 402, and 411 mμ, in agreement with an authentic specimen.

11,12-Benzofluoranthene.—Identified in fractions 19 and 20 by chromatography on acetylated cellulose; its ultraviolet spectrum showed maxima at 238, 269, 283, 297, 309, 361, 380, and 402 mμ, in agreement with an authentic specimen.

Dimethylpicene.—Isolated from fraction 21 by chromatography on a column of acetylated cellulose. A sample decomposed at 320°C when heated in an evacuated capillary tube. Its ultraviolet spectra showed maxima at 258, 278, 289, 304, 315, and 329 mμ, and was very similar to that of picene. Two methyl groups were detected by n.m.r. spectroscopy at τ, 7·3, but a full interpretation of the spectrum was not possible because of the sparing solubility of the sample.

Anthanthrene.—Identified in fractions 20 and 21 by chromatography on acetylated cellulose followed by paper chromatography. Its ultraviolet spectrum showed maxima at 233, 256, 259, 295, 308, 365, 382, 402, 407, 422, and 431 mμ, in agreement with an authentic sample.

2,3-(o-Phenylene)pyrene.—Isolated from fractions 21, 22, and 23 by chromatography on acetylated cellulose; it had m.p. 159–160°C (lit.[23] 163°C). Its ultraviolet spectrum showed maxima at 251, 261, 277, 292, 304, 315, 360, 376, 402, 408, 422, and 431 mμ, in agreement with the literature.[22]

1,2:4,5-Dibenzopyrene.—Isolated from fraction 22 by repeated chromatography on columns of acetylated cellulose. Its ultraviolet absorption spectrum showed maxima at 294, 306, 327, 343, 360, 378, 396, 416, and 437 mμ. These maxima correspond with the literature values for this compound,[21] except for the long-wavelength peak at 437 mμ. This was probably due to impurity. The melting point of 219–221°C is in fair agreement with the reported value of 225°C.[21]

3,4:9,10-Dibenzopyrene.—Isolated from fractions 22, 23, and 24 by repeated chromatography on columns of partially acetylated cellulose; it had m.p. 276–278°C, not depressed by admixture with an authentic specimen. Its ultraviolet absorption spectrum showed maxima at 234, 242, 273, 283, 296, 315, 331, 353, 373, and 393 mμ, and its fluorescence spectrum, maxima at 428, 456, 489, and 520 mμ, in agreement with an authentic specimen.

3,4:8,9-Dibenzopyrene.—Identified in fractions 23 and 24 by chromatography on acetylated cellulose. It had a much lower R_F than the other components of these fractions, and was clearly separated. Its ultraviolet absorption spectrum showed maxima at 291, 301, 314, 379, 401, 424, and 452 mμ, in agreement with recorded values.[21] Its fluorescence spectrum showed maxima at 449, 475, and 512 mμ, in agreement with the literature.[24]

3,4-Benzotetraphene.—Identified in fraction 24 by chromatography on acetylated cellulose, followed by paper chromatography. An extract showed maxima at 248, 277, 287, 304, 318, 332, 345, 363, 382, and 390 mμ, in agreement with an authentic specimen.

IV. ACKNOWLEDGMENTS

This work has been supported by a grant from the Damon Runyon Memorial Fund for Cancer Research Inc., and we are also grateful to the C.S.I.R.O. for a Scholarship awarded to one of us (J.K.D.).

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[23] Aitken, M., and Reid, D. H. (1956).—*J. Chem. Soc.* **1956**: 3487.

[24] Lyons, M. J., and Johnston, H. (1957).—*Brit. J. Cancer* **11**: 544.

THE FORMATION OF AROMATIC HYDROCARBONS AT HIGH TEMPERATURES

XXII.* THE PYROLYSIS OF PHENANTHRENE

By G. M. BADGER,† JILLIAN K. DONNELLY,† and T. M. SPOTSWOOD†

[*Manuscript received April* 22, 1964]

Summary

The pyrolysis of phenanthrene at 700° and at 850° has given tars in which 7 and 13 aromatic compounds have been identified respectively. Mechanisms for the formation of these compounds are discussed, with special reference to the formation of anthracene by rearrangement of the intermediate tetrahydrophenanthrene.

INTRODUCTION

In previous publications from these laboratories it has been shown that the pyrolysis of relatively simple aromatic and aliphatic hydrocarbons gives tars containing many different polycyclic aromatic hydrocarbons.[1] Mechanisms for the formation of many of these have been postulated, and a few mechanisms have been firmly established.[2,3,4] Anthracene has often been detected in these tars, but its mode of formation remains in doubt. It seemed possible that the anthracene could be formed from two benzyl radicals, or from naphthalene (or tetralin) and a C_4 unit. However, the radioactivity of the anthracene isolated following the pyrolysis of [α-^{14}C]ethylbenzene[2] and of [1-^{14}C]tetralin[3] has shown that neither of these routes can be important.

In 1927 Orlow[5] reported that the pyrolysis of phenanthrene in a stream of hydrogen leads to the formation of some anthracene. It seemed possible, therefore, that most of the anthracene encountered in our tars could have arisen from phenanthrene by thermal rearrangement. This view was supported by the observation that the anthracene isolated from the tar produced by the pyrolysis of [α-^{14}C]ethylbenzene contained the same number of labelled carbon atoms as the phenanthrene.[2] The anthracene and phenanthrene isolated from the tar produced by the pyrolysis of [1-^{14}C]tetralin were also found to contain the same number of labelled atoms.[3] On the other hand, Orlow did not give any details of the purification of his phenanthrene (and it is notoriously difficult to remove anthracene from phenanthrene), and separation techniques have been considerably developed since then. Moreover Lang,

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* Part XXI, *Aust. J. Chem.*, 1964, **17**, 778.

† Department of Organic Chemistry, University of Adelaide.

[1] Badger, G. M., *J. Nat. Cancer Institute*, 1962, Monogr. 9, 1.

[2] Badger, G. M., and Kimber, R. W. L., *J. Chem. Soc.*, 1961, 3407.

[3] Badger, G. M., Kimber, R. W. L., and Novotny, J., *Aust. J. Chem.*, 1962, **15**, 616.

[4] Badger, G. M., and Novotny, J., *Aust. J. Chem.*, 1963, **16**, 623.

[5] Orlow, N. A., *Ber. dt. chem. Ges.*, 1927, **60**, 1950.

Aust. J. Chem., 1964, **17**, 1138–46

Buffleb, and Kalowy[6] recently reported the results of the pyrolysis of phenanthrene. These authors were chiefly concerned with the substances of high molecular weight which were formed, and they did not discuss the question of the rearrangement of phenanthrene to anthracene. It therefore seemed of interest to pyrolyse *pure* phenanthrene, at 700° and at 850°, in a stream of nitrogen.

TABLE 1

COMPOSITION OF TAR FOLLOWING PYROLYSIS OF PHENANTHRENE

Compound	Percentage (w/w) in Tar		Percentage Yield from Phenanthrene		Method of Identification
	700°	850°	700°	850°	
Ethylene	—	detected	—	detected	i.r.
Carbon	—	—	2	19·5	
9,10-Dihydrophenanthrene	0·52	1·0	0·5	0·3	u.v.
1,2,3,4-Tetrahydrophenanthrene	—	0·7	—	0·2	u.v.
Naphthalene	—	6·8	—	2·0	u.v., mixed m.p.
Phenanthrene	88·3	20·3	85·9	6·1	u.v., mixed m.p.
Anthracene	—	16·8	—	5·0	u.v., mixed m.p.
Pyrene	—	13·4	—	4·0	u.v., mixed m.p.
2,2′-Biphenanthryl	3·5	8·5	3·4	2·6	u.v., m.p.
Biphenanthryl, m.p. 175°	1·25	3·2	1·2	0·9	u.v., m.p.
Biphenanthryl, m.p. 212°	1·98	3·6	1·9	1·0	u.v., m.p.
2,3 : 8,9-Dibenzoperylene	2·1	10·6	2·0	3·3	u.v., m.p.
2,3 : 10,11-Dibenzoperylene	1·87	10·0	1·8	2·9	u.v., m.p.
Benzonaphthofluoranthene	—	trace	—	trace	u.v.
2,3-(*o*-Phenylene)pyrene	—	4·6	—	1·4	u.v., m.p.

RESULTS

The pyrolyses were carried out by passing the phenanthrene vapour, with nitrogen, through an empty silica tube which had been preheated to the required temperature (700° or 850°). The exit gases were examined by infrared spectroscopy, and the tars were collected and analysed by distillation, chromatography on columns of alumina and of acetylated cellulose, thin-layer chromatography on acetylated cellulose, and by ultraviolet spectroscopy.

The compounds identified in the tars have been listed in Table 1; this gives the percentage composition of the tars and also the percentage yield of each hydrocarbon from phenanthrene. It will be noted that the tar produced by the pyrolysis of phenanthrene at 700° was qualitatively similar to that obtained by Lang, Buffleb, and Kalowy.[6]

DISCUSSION

The bond dissociation energies for various types of carbon–carbon and carbon–hydrogen bonds are known with some accuracy. The bond dissociation energy for

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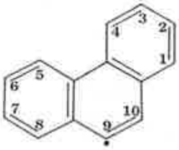
[6] Lang, K. F., Buffleb, H., and Kalowy, J., *Chem. Ber.*, 1960, **93**, 303.

carbon–carbon single bonds is *c.* 80 kcal/mole, and that for carbon–carbon double bonds is *c.* 125 kcal/mole.[7] Carbon–carbon bonds in aromatic rings are also very strong, much stronger than carbon–carbon single bonds. The bond dissociation energies for carbon–hydrogen bonds are intermediate, that for C_6H_5–H, for example, being 102 kcal/mole.[7] The major primary process expected in the pyrolysis of an *aromatic* hydrocarbon, therefore, should be the scission of a carbon–hydrogen bond to give a hydrogen atom and an aryl radical. These latter radicals would then be expected to react with other molecules of aromatic hydrocarbon, or with other radicals, to form biaryls and condensed hydrocarbons. The formation of most of the hydrocarbons found in the tars produced by the pyrolysis of benzene,[8] and of naphthalene,[9] has been explained in this way.



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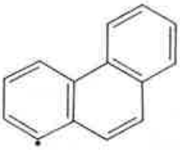

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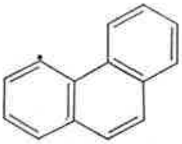

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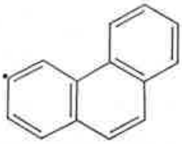

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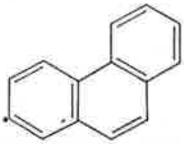

(V)

In the pyrolysis of phenanthrene, the scission of a carbon–hydrogen bond could give rise to five alternative phenanthryl radicals (I–V). The radical (III) would be formed but is sterically hindered and may therefore be unimportant; the remainder would all be expected to react with a molecule of phenanthrene, or with another phenanthryl radical, to form biphenanthryls.

Beckwith and Thompson[10] have determined the relative yields of the phenylphenanthrenes obtained by the phenylation of phenanthrene, and have concluded that the reactivities of the positions in phenanthrene towards phenyl radicals are in the order $9>1>3\simeq 2$. If it is supposed that this order applies for the attack of phenanthryl radicals on phenanthrene at high temperature, then 9,9′-biphenanthryl (VI), 1,1′-biphenanthryl (VII), and 1,9′-biphenanthryl (IX) might be expected. None of these compounds was found in the tar; however, further condensation would be expected to lead to 2,3 : 10,11-dibenzoperylene (VIII) and 2,3 : 8,9-dibenzoperylene (X), and these compounds were detected in tars formed both at 700° and at 850°.

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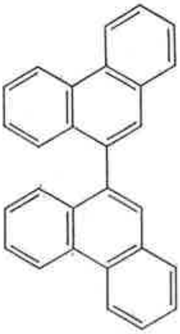
[7] Cottrell, T. L., "The Strengths of Chemical Bonds." 2nd Ed. (Butterworths: London 1958.)

[8] Badger, G. M., and Novotny, J., *J. Chem. Soc.*, 1961, 3400.

[9] Badger, G. M., Jolad, S. D., and Spotswood, T. M., *Aust. J. Chem.*, 1964, **17**, 778.

[10] Beckwith, A. L. J., and Thompson, M. J., *J. Chem. Soc.*, 1961, 73.

2,2′-Biphenanthryl (XI), a biphenanthryl, m.p. 175° (XII or XIII), and a biphenanthryl, m.p. 212° (XIII or XII), were identified in both tars; with these biphenanthryls further condensation is precluded.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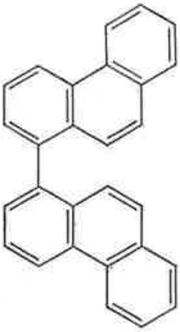
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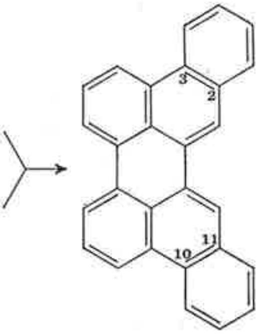

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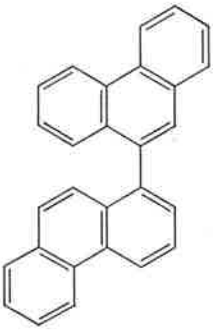
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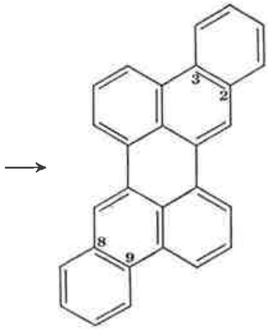

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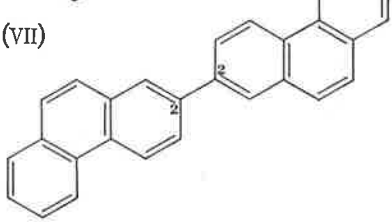

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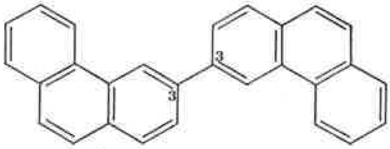

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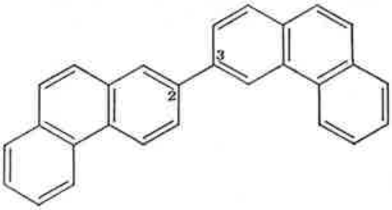
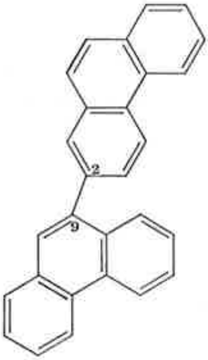


(XIII)

If the biphenanthryls derived from the phenanthryl radical (III) are omitted, the only remaining biphenanthryls are those involving the 9- or 1-position and the

2- or 3-position (e.g. XIV, XV): all these would be expected to undergo further condensation to give either 3,4-benzonaphtho[1′,2′-11,12]fluoranthene (XVI) or 3,4-benzonaphtho[2′,1′-11,12]fluoranthene (XVII). A substance believed to be benzonaphthofluoranthene (XVI or XVII) was identified by absorption spectroscopy in the tar produced by the pyrolysis of phenanthrene at 850°; but it was not identified in the 700° tar. The absorption spectrum of this compound (Fig. 1) was found to be very similar to the spectra given by related compounds.



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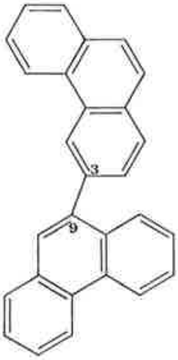

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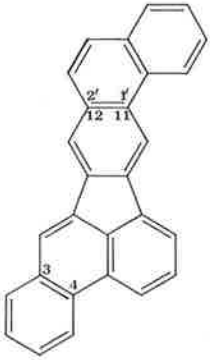

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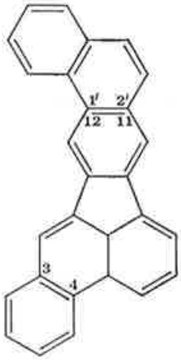

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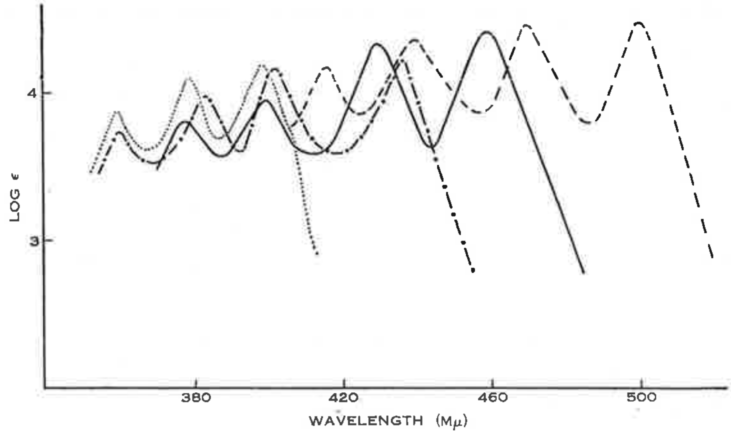

Fig. 1.—Absorption spectra of fluoranthene derivatives in benzene (*para* bands only[11]). ——— (XVI) or (XVII); — — — 2,3-benzonaphtho[2′,3′-11,12] fluoranthene; —·—·— naphtho[2′,3′-11,12]fluoranthene; ····· 11,12-benzofluoranthene.

The scission of carbon–hydrogen bonds to form phenanthryl radicals has another consequence: although the pyrolyses were carried out in a stream of nitrogen, a considerable amount of hydrogen must also be present in the reaction zone. In the

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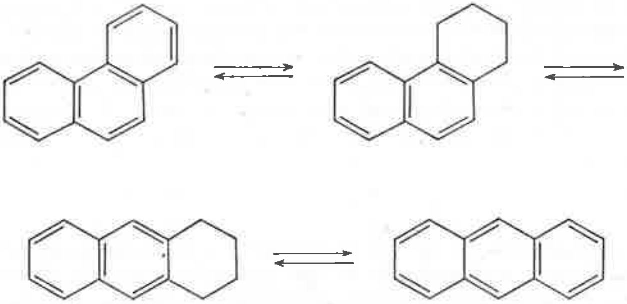
[11] Clar, E., "Aromatische Kohlenwasserstoffe." 2nd Ed. (Springer-Verlag: Berlin 1952.)

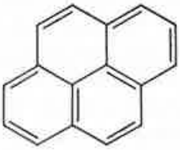
absence of more reactive "acceptors", some phenanthrene was reduced; 9,10-dihydrophenanthrene was identified in both tars, and 1,2,3,4-tetrahydrophenanthrene was identified in the tar produced by pyrolysis at 850°.

Most of the phenanthrene (85·9%) was recovered unchanged following pyrolysis at 700°, and no anthracene could be detected. At 850° there was a much smaller recovery of phenanthrene (6·1%); the yields of condensed hydrocarbons were greater; there was a bigger yield of carbon; more hydrocarbon was lost in the exit gases; and anthracene was formed in considerable yield.

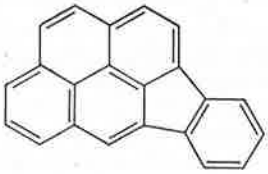
The *direct* rearrangement of phenanthrene to anthracene seems very unlikely. However, as hydrogenated phenanthrenes are certainly formed (especially at 850°) it is suggested that the rearrangement proceeds according to the following scheme:



Saturated carbon–carbon bonds would undergo cleavage much more readily than aromatic carbon–carbon bonds,[7] and it is significant that the rearrangement only proceeds to an appreciable extent in the pyrolysis at 850°, in the presence of a relatively high concentration of hydrogen. This mechanism is supported by the fact that naphthalene was also detected in the tar produced at 850°, presumably being formed by the complete removal of the saturated carbon atoms from the tetrahydrophenanthrene or tetrahydroanthracene intermediate. It may also be noted that Orlow[5] observed the phenanthrene→anthracene rearrangement following the passage of phenanthrene through a red-hot tube (*c.* 750°) *in an atmosphere of hydrogen.*



(XVIII)



(XIX)

Finally, reference may be made to the presence of pyrene (XVIII) in the tar produced by the pyrolysis of phenanthrene at 850°. A reasonable mechanism would involve the reaction of a hydrophenanthrene radical and a C_2 unit. The necessary C_2 unit could be derived by scission from another molecule of tetrahydrophenanthrene or tetrahydroanthracene. It is also of some interest that 2,3-(*o*-phenylene)pyrene

(XIX) was also identified in the 850° tar; as previously suggested[12] this could arise by the phenylation of pyrene followed by cyclodehydrogenation.

It is reasonable to conclude that the phenanthrene→anthracene rearrangement does occur at high temperatures provided there is sufficient hydrogen to produce the intermediate tetrahydrophenanthrene. In the preceding paper[9] of this series it was suggested that hydrogenated intermediates may also be important in the formation of some polycyclic compounds during the pyrolysis of benzene and of naphthalene.

EXPERIMENTAL

(a) *General*

Phenanthrene

"Pure" phenanthrene (Rütgerswerke) was further purified by treatment with maleic anhydride in boiling xylene, and then by treatment with sodium[13] (to remove traces of anthracene). The product was distilled *in vacuo*, then recrystallized three times from 30% ethanol in benzene, and finally purified by zone-refining. The resulting pure phenanthrene had m.p. 98–99°. A sample was submitted to chromatography on a column of acetylated cellulose; all the fractions were examined by ultraviolet spectroscopy, but no impurity (e.g. no anthracene) could be detected in any fraction.

Pyrolysis

The pure phenanthrene (20 g) was contained in a reservoir fitted with a needle valve and enclosed in an air-bath maintained at *c.* 150°. It was vaporized at 7 g/hr by dropping the liquid directly into an empty silica pyrolysis tube (33 by $\frac{5}{8}$ in. internal diameter). The tube was maintained at the required temperature (700° or 850°) by means of an electrically heated furnace, and the vapour was carried through the tube with a stream of oxygen-free nitrogen. The resulting tar was collected in a series of traps containing ice–salt, solid CO_2–ethanol, and liquid air. Samples of the exit gases were collected at intervals and were examined by infrared spectroscopy.

Analysis of 700° Tar

No methane or ethylene could be detected in the exit gases. The tar (19·2 g, 96%) was distilled under reduced pressure to give two main fractions, A and B. Fraction A was chromatographed on alumina using hexane for elution. The resulting fractions (30 × 200 ml) were examined by ultraviolet and fluorescence spectroscopy. Phenanthrene was found to be the major constituent, but a trace of tetrahydrophenanthrene was detected. No anthracene could be detected in any fraction.

Fraction B (2·3 g) was chromatographed on a column of Spence alumina (300 g) using hexane, hexane containing increasing amounts of benzene, benzene, and finally ethanol, as eluants. The fractions (30 × 250 ml) were examined by ultraviolet spectroscopy and those having similar spectra were combined to give six fractions. These six fractions were then re-chromatographed on thin layers, and then on columns, of partially acetylated cellulose. Fraction 1 contained 9,10-dihydrophenanthrene and phenanthrene; fraction 2, biphenanthryls; fraction 3, biphenanthryls; fraction 4, 2,3 : 8,9-dibenzopyrene and biphenanthryls; fraction 5, 2,3 : 8,9-dibenzoperylene and 2,3 : 10,11-dibenzoperylene; fraction 6, 2,3 : 10,11-dibenzoperylene.

Analysis of 850° Tar

A small amount of ethylene was detected in the exit gases. The tar (5·9 g, 29%) was analysed as above except that the preliminary distillation was omitted. Recombination of the fractions following chromatography on alumina gave ten main fractions: these were then

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[12] Badger, G. M., and Spotswood, T. M., *J. Chem. Soc.*, 1960, 4420.

[13] Feldman, J., Pantages, P., and Orchin, M., *J. Amer. Chem. Soc.*, 1951, **73**, 4341.

rechromatographed on thin layers[14] and on columns[15] of partially acetylated cellulose. Fraction 1 contained 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene; fraction 2, naphthalene; fraction 3, phenanthrene; fraction 4, phenanthrene and anthracene; fraction 5, anthracene, phenanthrene, and pyrene; fraction 6, pyrene; fraction 7, biphenanthryls; fraction 8, 2,3 : 8,9-dibenzoperylene and 2,3 : 10,11-dibenzoperylene; fraction 9, 2,3 : 10,11-dibenzoperylene; and fraction 10, benzonaphthofluoranthene.

Spectroscopy

Infrared spectra were determined in the gas phase using a Perkin–Elmer 137 Infracord spectrophotometer. Ultraviolet spectra were determined in 95% ethanol, or benzene, using an Optica CF4 recording spectrophotometer.

(*b*) *Details of Identification*

All the compounds detected in the tar produced at 700° were also present in the tar produced at 850°. The same methods of identification were used for both tars; the following details refer to the tar formed by pyrolysis at 850°.

Ethylene

This was detected in the exit gases by its infrared spectrum in the 10–11 μ region (maxima at 10·03, 10·12, 10·22, 10·30, 10·53, 10·76, 10·84, 11·06, and 11·13 μ).[16]

9,10-Dihydrophenanthrene

The ultraviolet absorption spectrum showed maxima at 264, 289, and 299 mμ in agreement with the literature.[17]

1,2,3,4-Tetrahydrophenanthrene

The ultraviolet absorption spectrum showed maxima at 230, 284, 308, 315, and 325 mμ in agreement with the literature.[18]

Naphthalene

Isolated after chromatography on a column of partially acetylated cellulose, the naphthalene had m.p. 79–80°, not depressed by admixture with an authentic specimen. The ultraviolet absorption spectrum showed maxima at 248, 257, 266, 275, 285, and 311 mμ in agreement with that of an authentic specimen.

Phenanthrene

Isolated following chromatography on alumina and on acetylated cellulose, the phenanthrene had m.p. and mixed m.p. 98–99°. The ultraviolet absorption spectrum showed maxima at 243, 252, 275, 282, 294, 310, 317, 324, 331, 339, and 346 mμ in agreement with that of an authentic specimen.

Anthracene

This was eluted from the alumina column in the same fractions as phenanthrene. Further chromatography of these fractions on acetylated cellulose gave anthracene, m.p. 215–216°, not depressed by admixture with an authentic specimen. The ultraviolet absorption spectrum showed maxima at 246, 253, 308, 323, 339, 357, and 377 mμ in agreement with that of an authentic specimen.

[14] Badger, G. M., Donnelly, J. K., and Spotswood, T. M., *J. Chromatogr.*, 1963, **10**, 397.

[15] Spotswood, T. M., *J. Chromatogr.*, 1960, **3**, 101.

[16] American Petroleum Inst. Res. Proj. 44, I.R. Spectral Data.

[17] Beaven, G. H., Hall, D. M., Lesslie, M. S., and Turner, E. E., *J. Chem. Soc.*, 1952, 854.

[18] Bavin, P. M. G., and Dewar, M. J. S., *J. Chem. Soc.*, 1955, 4479.

Pyrene

The first pyrene-containing fractions from the alumina column were contaminated with small amounts of phenanthrene. Further chromatography (of fraction 6) on a column of acetylated cellulose gave pyrene, m.p. 145–146°, not depressed by admixture with an authentic specimen. The ultraviolet absorption spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335, and 364 mμ in agreement with an authentic specimen.

2,2′-Biphenanthryl

Isolated by chromatography on a column of acetylated cellulose, 2,2′-biphenanthryl had m.p. 306–307° in agreement with the literature.[6] The ultraviolet absorption spectrum showed maxima at 280, 296, and 315 mμ in agreement with published figures.[6]

2,3′-Biphenanthryl and 3,3′-Biphenanthryl

Isolated following chromatography on a column of partially acetylated cellulose the biphenanthryls had m.p. 212° and 175° in good agreement with the m.p. reported by Lang, Buffleb, and Kalowy.[6] The biphenanthryl, m.p. 212°, gave an absorption spectrum with maxima at 245, 265, 282, and 318·5 mμ. The spectrum of the isomeric biphenanthryl, m.p. 175°, showed maxima at 250, 269, 280, 295, and 316 mμ. These absorption spectra are in good agreement with those reported[6] for the biphenanthryls.

2,3 : 10,11-Dibenzoperylene

Isolated following chromatography on a column of acetylated cellulose the 2,3 : 10,11-dibenzoperylene had m.p. 330–332° (lit.[11] 329–332°). The ultraviolet absorption spectrum showed maxima at 288, 302, 392, 414, and 440 mμ in good agreement with the literature.[11]

2,3 : 8,9-Dibenzoperylene

Isolated following chromatography on a column of acetylated cellulose the 2,3 : 8,9-dibenzoperylene had m.p. 339–341° (lit.[11] 343°). The ultraviolet absorption spectrum showed maxima at 291, 304, 365·5, 386, 408, and 434 mμ, in agreement with the literature.[11]

2,3(o-Phenylene)pyrene

Isolated following chromatography on acetylated cellulose it had m.p. 158–159° and $\lambda_{\text{max.}}$ 251, 261, 275, 292, 304, 315, 360, 376, 385, and 407 mμ in good agreement with Badger and Spotswood.[12] Long wavelength bands reported at 422 and 431 mμ for this compound[19] are due to anthanthrene impurity.

Benzonaphthofluoranthene (XVI or XVII)

Isolated following chromatography on acetylated cellulose. The ultraviolet absorption spectrum (in benzene) showed maxima at 320, 334, 354, 373, 400, 432, and 460 mμ.

ACKNOWLEDGMENTS

This work has been supported by the U.S. Public Health Service, National Institutes of Health (C6419), to whom we express our thanks. We also thank Dr. K. Lang for specimens of benzonaphthofluoranthenes.

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[19] Badger, G. M., and Novotny, J., *J. Chem. Soc.*, 1961, 3403.

THE FORMATION OF AROMATIC HYDROCARBONS AT HIGH TEMPERATURES

XXIII.* THE PYROLYSIS OF ANTHRACENE

By G. M. Badger,† Jillian K. Donnelly,† and T. M. Spotswood†

[*Manuscript received April* 22, 1964]

Summary

The pyrolysis of anthracene at 700° has given a tar containing ten polycyclic hydrocarbons all of which are probably formed by the scission of carbon–hydrogen bonds to give anthryl radicals followed by further reaction with anthracene. The pyrolysis of anthracene at 950° gave a much more complex tar in which 25 aromatic hydrocarbons have been identified. The major constituent was found to be phenanthrene. It is suggested that this is formed via tetrahydroanthracene and tetrahydrophenanthrene. It is also suggested that the complexity of the tar is due to the scission of the saturated carbon–carbon bonds in tetrahydroanthracene and tetrahydrophenanthrene, followed by further reaction of the fragments.

Introduction

The pyrolysis of phenanthrene has already been shown[1] to give some anthracene, and it seems likely that anthracene detected following many pyrolytic reactions may have been formed by this thermal rearrangement reaction. In the preceding paper[1] it was suggested that the rearrangement is not a direct one, but proceeds via 1,2,3,4-tetrahydrophenanthrene and 1,2,3,4-tetrahydroanthracene. If this is so then the pyrolysis of anthracene might also be expected to yield some phenanthrene. In order to examine this hypothesis, pure anthracene was pyrolysed at 700° and at 950°, and the resulting tars analysed.

Results

The pyrolyses were carried out by passing the anthracene vapour, with nitrogen, through an empty silica tube which had been preheated to the required temperature (700° or 950°). Samples of the exit gases were examined at intervals by infrared spectroscopy. The tars were collected and analysed by distillation, chromatography on columns of alumina and acetylated cellulose, thin-layer chromatography on acetylated cellulose, and by ultraviolet and fluorescence spectroscopy.

The results of the analyses are given in Table 1; this gives the percentage composition of the tars, and also the percentage yield of each hydrocarbon from anthracene. No carbon, methane, or ethylene were detected following pyrolysis at 700°, but these substances were formed in large amount following pyrolysis at 950°.

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* Part XXII, *Aust. J. Chem.*, 1964, **17**, 1138.

† Department of Organic Chemistry, University of Adelaide.

[1] Badger, G. M., Donnelly, Jillian K., and Spotswood, T. M., *Aust. J. Chem.*, 1964, **17**, 1138.

Aust. J. Chem., 1964, **17**, 1147–56

Discussion

The major primary process expected in the pyrolysis of anthracene should be the scission of a carbon–hydrogen bond to give an anthryl radical (cf.[1]). Three alternative anthryl radicals (I–III) could be formed; these would be expected to react with a molecule of anthracene, or with another anthryl radical, to form bianthryls.

Table 1

COMPOSITION OF TAR FOLLOWING PYROLYSIS OF ANTHRACENE

Compound	Percentage (w/w) in Tar		Percentage Yield from Anthracene		Method of Identification
	700°	950°	700°	950°	
9,10-Dihydroanthracene	0·08	0·15	0·08	0·04	u.v.
Anthracene	88·9	0·77	87·1	0·20	u.v., mixed m.p.
9,9′-Bianthryl	0·9	0·59	0·88	0·15	u.v., mixed m.p.
1,1′-Bianthryl	1·5	0·44	1·47	0·11	u.v., m.p.
2,2′-Bianthryl	4·7	1·81	4·6	0·46	u.v., m.p.
1,2:11,12-Dibenzoperylene	0·6	0·39	0·59	0·10	u.v.
Bisanthrene	trace	0·05	trace	0·13	u.v.
2,3-Benzonaphtho[2′,3′-11,12]fluoranthene	1·1	0·29	1·10	0·08	u.v., mixed m.p.
Benzonaphthofluoranthene, m.p. 240–241°	0·9	0·24	0·88	0·06	u.v., mixed m.p.
Benzonaphthofluoranthene, m.p. 227–228°	0·6	0·09	0·59	0·03	u.v., m.p.
1,2,3,4-Tetrahydroanthracene	—	0·20	—	0·05	u.v.
Naphthalene	—	3·9	—	0·10	u.v., mixed m.p.
Acenaphthylene	—	4·89	—	1·3	u.v., mixed m.p.
Phenanthrene	—	42·07	—	10·8	u.v., f.s.,* mixed m.p.
Pyrene	—	24·95	—	6·4	u.v., f.s., mixed m.p.
Fluoranthene	—	7·34	—	1·9	u.v., mixed m.p.
1,2-Benzopyrene	—	1·02	—	0·26	u.v.
Perylene	—	0·59	—	0·15	u.v.
11,12-Benzofluoranthene	—	0·25	—	0·06	u.v.
10,11-Benzofluoranthene	—	0·35	—	0·09	u.v.
3,4-Benzofluoranthene	—	0·59	—	0·25	u.v.
3,4-Benzopyrene	—	1·59	—	0·41	u.v., f.s., mixed m.p.
Anthanthrene	—	0·39	—	0·10	u.v.
2,3-(*o*-Phenylene)pyrene	—	3·13	—	0·80	u.v., m.p.
Coronene	—	2·10	—	0·54	u.v., mixed m.p.
3,4:8,9-Dibenzopyrene	—	0·54	—	0·14	u.v., f.s.
3,4:9,10-Dibenzopyrene	—	0·45	—	0·10	u.v., f.s., m.p.
Carbon	0·7	0·83	2·7	59·2	

* Fluorescence spectroscopy.

The calculated free valence figures for the different positions in anthracene[2] suggest that the relative reactivities should be in the order $9>1>2$, and experiments

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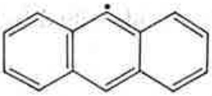
[2] Pullman, B. and Pullman, A., "Progress in Organic Chemistry." (Ed. J. W. Cook.) Vol. 4. (Butterworths: London 1958.)

on the phenylation and benzylation of anthracene support this view.[3,4,5] This being so it might be expected that 9,9′-bianthryl (IV), 1,1′-bianthryl (V), and 1,9′-bianthryl (VI) would be formed. Small amounts of 9,9′-bianthryl and of 1,1′-bianthryl were identified in both tars; but all these bianthryls might be expected to undergo further condensation (cyclodehydrogenation). 9,9′-Bianthryl (IV) and 1,1′-bianthryl (V), for example, would be expected to yield 1,2:11,12-dibenzoperylene (VII) and bisanthrene (VIII), both of which were identified in the tars. 1,9′-Bianthryl (VI) was not identified in the tars, but this would be expected to undergo cyclodehydrogenation to 2,3-benzonaphtho[2′,3′-12,13]fluoranthene (IX), and three isomeric 2,3-benzonaphthofluoranthenes were identified. This benzonaphthofluoranthene could also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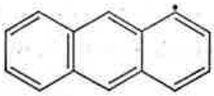
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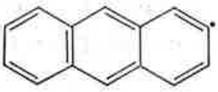
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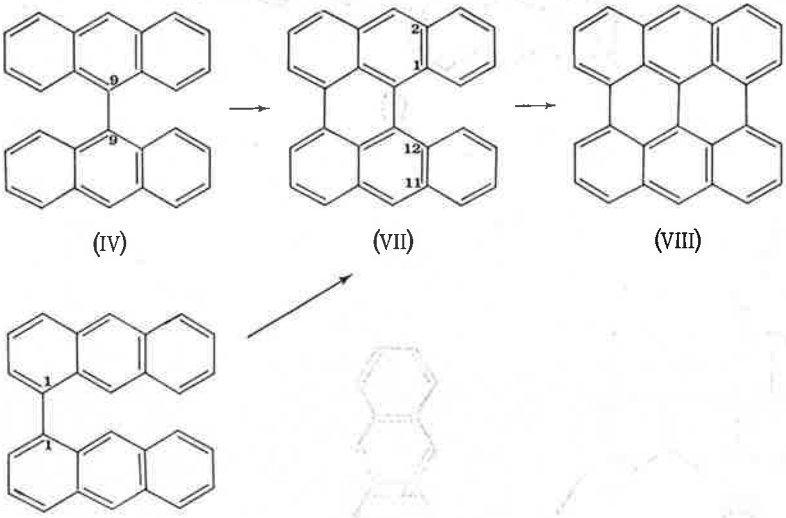
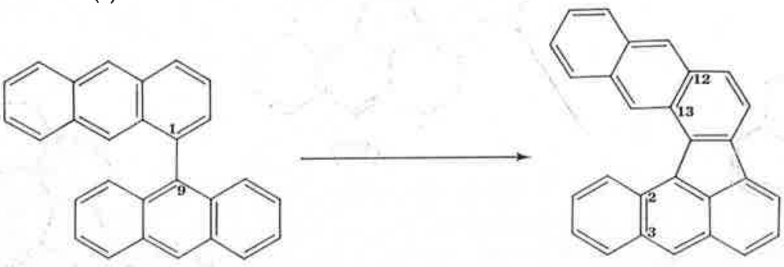


(IV) (VII) (VIII)

(V)



(VI) (IX)

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[3] Dickerman, S. C., and Vermont, G. B., *J. Amer. Chem. Soc.*, 1962, **84**, 4150.

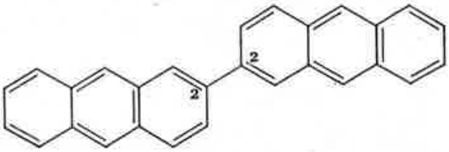
[4] Norman, R. O. C., and Waters, W. A., *J. Chem. Soc.*, 1958, 167.

[5] Beckwith, A. L. J., and Waters, W. A., *J. Chem. Soc.*, 1957, 1001.

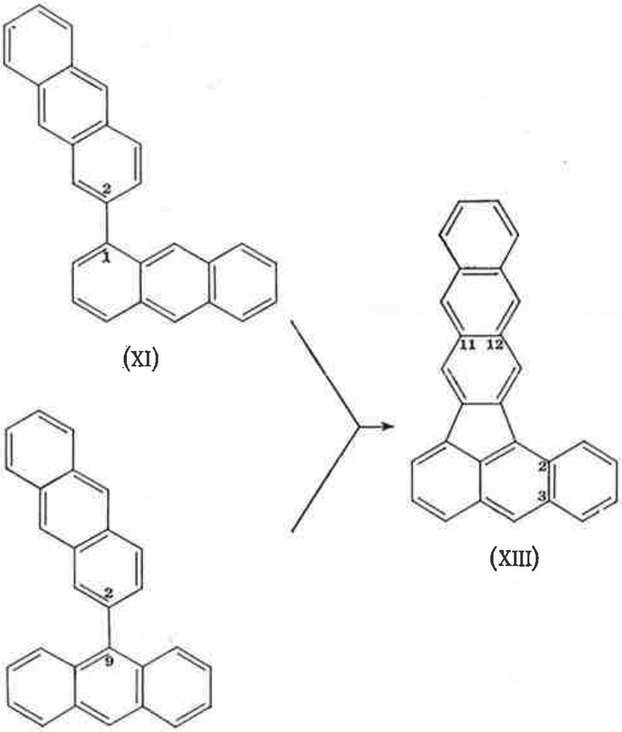
arise from 1,2′-bianthryl (XI). The bianthryl (VI) might also be expected to give some 1,2 : 7,8-dibenzoperylene, but this was not detected.

The remaining bianthryls are 2,2′-bianthryl (X), 1,2′-bianthryl (XI), and 2,9′-bianthryl (XII).

2,2′-Bianthryl (X) would certainly be expected, and this was identified in both tars; with this bianthryl further condensation is precluded.



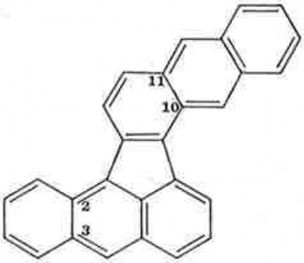
(X)



(XI)

(XII)

(XIII)



(XIV)

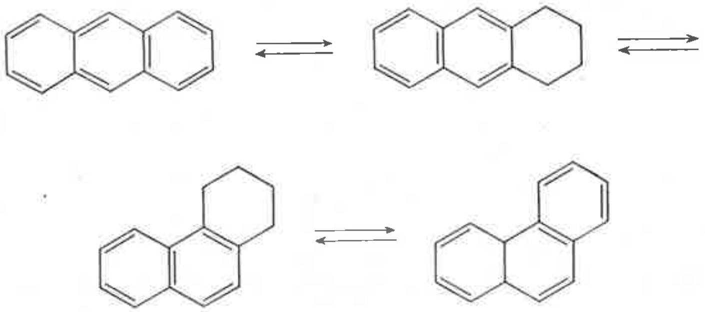
Both 1,2′-bianthryl (XI) and 2,9′-bianthryl (XII) would be expected to undergo ready dehydrogenation to 2,3-benzonaphtho[2′,3′-11,12]fluoranthene (XIII), and this compound was found in the tars.

Finally, it may be mentioned that 2,3-benzonaphtho[2′,3′-10,11]fluoranthene (XIV) could also be formed from 1,1′-bianthryl (V) and from 2,9′-bianthryl (XII) by cyclodehydrogenation. As stated above, three benzonaphthofluoranthenes were identified, but the orientation of only one (XIII) has been established.

All the processes detailed above involve the liberation of hydrogen atoms. In the absence of more reactive "acceptors", some anthracene was reduced; 9,10-dihydroanthracene was identified in both tars and, in addition, 1,2,3,4-tetrahydroanthracene was identified in the tar produced by the pyrolysis of anthracene at 950°.

Most of the anthracene (87·1%) was recovered unchanged following pyrolysis at 700°, and no phenanthrene could be detected in the tar. On the other hand, very little anthracene (0·20%) survived the pyrolysis at 950°. Much more carbon was formed, more hydrocarbon was lost in the exit gases, a much wider range of aromatic hydrocarbons was formed, and phenanthrene was formed in good yield.

It seems almost certain that the phenanthrene was formed indirectly via 1,2,3,4-tetrahydroanthracene and 1,2,3,4-tetrahydrophenanthrene as intermediates, as in the following scheme:



Hydrogen seems to be an essential requirement for the rearrangement, and it seems that insufficient hydrogen was present in the reaction zone during pyrolysis at 700° to enable a significant amount of tetrahydroanthracene to be formed. At 950°, however, it seems that this intermediate must be formed in good yield.

The carbon–carbon single bonds in tetrahydroanthracene and tetrahydrophenanthrene would be expected to undergo ready rupture to naphthalene and small fragments such as C_2 units. Naphthalene was identified in the 950° tar, and the other hydrocarbons identified in this tar clearly arise by further reaction of these C_2 units with other constituents in the reaction zone.

The presence of coronene in the tar produced at 950° is noteworthy. As previously pointed out,[6] this hydrocarbon seems to be formed only at very high temperatures and it is not normally present in the tars obtained by the pyrolysis of a variety of compounds at 700°.

Experimental

(*a*) *General*

Anthracene

"Pure" anthracene (Fluka) was further purified by recrystallization from ethanol followed by sublimation *in vacuo*. The sublimed material was dissolved in dimethylsulphoxide,[7] the solution cooled to 80°, and the solid collected. This was then recrystallized from ethanol, ethylene

[6] Badger, G. M., Donnelly, J. K., and Spotswood, T. M., *Aust. J. Chem.*, 1963, **16**, 392.

[7] Brit. Pat. 819,125 (*Chem. Abstr.*, 1961, **55**, 952).

glycol,[8] and ethanol (twice). The resulting pure anthracene formed beautiful lustrous plates, m.p. 218°, and showed an intense violet fluorescence in the solid state. A sample of the purified product was chromatographed on a column of partially acetylated cellulose and the fractions examined by ultraviolet and fluorescence spectroscopy. No impurities (e.g. no phenanthrene) could be detected in any fraction.

Pyrolysis

The pyrolysis was carried out as described for phenanthrene[1] except that the anthracene reservoir was maintained at *c.* 230–240°.

Analysis of 700° Tar

No methane or ethylene could be detected by infrared spectroscopy of the exit gases. The tar (19·6 g, 98%) was distilled under reduced pressure to give two fractions, A and B.

Fraction A was chromatographed on a column of Spence alumina, using hexane for elution, and the resulting fractions (30 × 250 ml) examined by ultraviolet and fluorescence spectroscopy. The greater part of this fraction was found to be anthracene, but a small amount of 9,10-dihydroanthracene was also detected.

Fraction B (2·16 g) was chromatographed on a column of Spence alumina using hexane, hexane containing increasing amounts of benzene, benzene, and finally ethanol as eluants. Each fraction was examined by ultraviolet spectroscopy, and fractions having similar spectra were recombined to give six main fractions. These were then rechromatographed on columns of partially acetylated cellulose. Fraction 1 contained anthracene; fraction 2, anthracene and bianthryls; fraction 3, bianthryls; fraction 4, 1,2:11,12-dibenzoperylene and bisanthrene; fraction 5, benzonaphthofluoranthene, m.p. 240°; and fraction 6, benzonaphthofluoranthene, m.p. 240°, benzonaphthofluoranthene, m.p. 227°, and 2,3-benzonaphtho[2′,3′-11,12]fluoranthene.

Analysis of 950° Tar

Ethylene and methane were detected by infrared spectroscopy of the exit gases. The resulting tar, which contained much carbon, was dissolved in chloroform and filtered. The carbon residue, together with the carbon removed from the pyrolysis tube, was extracted with chloroform (Soxhlet) for 6 hr. The chloroform solutions were combined and the solvent removed by distillation under reduced pressure. The residue (5·11 g) was chromatographed on a column of alumina using hexane, benzene, and then ethanol as eluants. The subsequent steps were then similar to those described under fraction B above. The combined fractions (13 in all) were rechromatographed on thin layers, and on columns of partially acetylated cellulose. Fraction 1 contained 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene; fraction 2, naphthalene and acenaphthylene; fraction 3, phenanthrene and anthracene; fraction 4, phenanthrene, anthracene and pyrene; fraction 5, pyrene and fluoranthene; fraction 6, bianthryls; fraction 7, 1,2-benzopyrene, perylene, 10,11-benzofluoranthene, and 11,12-benzofluoranthene; fraction 8, 3,4-benzofluoranthene and 3,4-benzopyrene; fraction 9, 1,2:11,12-dibenzoperylene and bisanthrene; fraction 10, anthanthrene and 2,3-(*o*-phenylene)pyrene; fraction 11, 3,4:8,9-dibenzopyrene and 3,4:9,10-dibenzopyrene; fraction 12, benzonaphthofluoranthenes and fraction 13, coronene.

Spectroscopy

Infrared spectra of exit gases were determined using a Perkin–Elmer 137 Infracord spectrophotometer. Ultraviolet spectra were determined in 95% ethanol, or in benzene, using an Optica CF4 recording spectrophotometer; and fluorescence spectra were examined in 95% ethanol using a Farrand recording spectrofluorimeter.

[8] Mikhailova, L. A., and Markovich, I. S., *Tr. Vses. Nauchn.-Issled. Inst. Khim. Reactivov.*, 1958, **22**, 130 (*Chem. Abstr.*, 1963, **58**, 4487).

(*b*) *Details of Identification*

The same methods of identification were used for the compounds in both tars. The following details refer to the compounds separated from the tars produced by the pyrolysis of anthracene at 950°.

Methane and Ethylene

Samples of the exit gases were collected and examined by infrared spectroscopy. Methane was identified by its spectrum in the 7·3–8·5 μ region (maxima at 7·41, 7·48, 7·67, 7·78, 7·81, 7·86, 7·93, 8·04, 8·10, and 8·16 μ), and ethylene by its spectrum in the 10–11 μ region (maxima at 9·91, 10·01, 10·11, 10·21, 10·31, 10·40, 10·51, 10·75, 10·84, 11·0, and 11·08 μ).[9]

9,10-Dihydroanthracene

The ultraviolet absorption spectrum showed maxima at 252, 264, and 271 mμ in agreement with an authentic specimen.

1,2,3,4-Tetrahydroanthracene

The ultraviolet absorption spectrum showed maxima at 230, 275, 285, 298, 310, and 324 mμ in agreement with the literature.[10]

Naphthalene

Isolated following chromatography on a column of acetylated cellulose, the naphthalene had m.p. 79–80°, not depressed by admixture with an authentic specimen. The ultraviolet spectrum showed maxima at 248, 257, 266, 275, 285, and 311 mμ in agreement with an authentic specimen.

Acenaphthylene

Isolated after chromatography on acetylated cellulose, the acenaphthylene had m.p. 94–95°, not depressed by admixture with an authentic specimen. The ultraviolet absorption spectrum showed maxima at 229, 258, 266, 276, 309, 323, 334, and 340 mμ in agreement with an authentic specimen.

Phenanthrene

Isolated after chromatography on columns of alumina and acetylated cellulose the phenanthrene had m.p. and mixed m.p. 97–98°. The ultraviolet absorption spectrum showed $\lambda_{\max}$ 243, 252, 275, 282, 294, 310, 317, 324, 331, 339, and 346 mμ in agreement with an authentic specimen; and the fluorescence spectrum showed maxima at 350, 363, and 383 mμ in agreement with an authentic specimen.

Anthracene

Isolated after chromatography on acetylated cellulose, the anthracene had m.p. 215–216°, not depressed by admixture with an authentic specimen. The ultraviolet spectrum showed maxima at 246, 253, 308, 323, 339, 357, and 377 mμ in agreement with an authentic specimen.

Pyrene

Isolated after chromatography on acetylated cellulose the pyrene had m.p. and mixed m.p. 145–146°. The ultraviolet spectrum showed maxima at 231, 241, 253, 263, 274, 306, 319, 335, and 364 mμ, and the fluorescence spectrum maxima at 385 and 395 mμ, both in agreement with those of an authentic specimen.

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[9] American Petroleum Inst. Res. Proj. 44, I.R. Spectral Data.

[10] Friedel, R. A., and Orchin, M., "Ultraviolet Spectra of Aromatic Compounds." (John Wiley: London 1951.)

Fluoranthene

Isolated by chromatography on acetylated cellulose, this had m.p. 106–108°, not depressed by admixture with an authentic specimen. The ultraviolet spectrum showed maxima at 236, 253, 263, 273, 278, 282, 288, 309, 323, 342, and 360 mμ in agreement with an authentic specimen.

Perylene

Identified following chromatography on a column of acetylated cellulose followed by thin-layer chromatography. The absorption spectrum showed maxima at 245, 253, 263, 367, 386, 407, and 435 mμ in agreement with an authentic specimen.

1,2-Benzopyrene

Identified following chromatography on a column of acetylated cellulose followed by thin-layer chromatography on acetylated cellulose. An extract showed maxima at 238, 258, 268, 278, 289, 305, 317, and 333 mμ in agreement with an authentic specimen.

3,4-Benzopyrene

Isolated following chromatography on acetylated cellulose, the 3,4-benzopyrene had m.p. 174–176°, not depressed by admixture with an authentic specimen. The ultraviolet spectrum showed maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385, and 404 mμ, and the fluorescence spectrum maxima at 397, 422, 448, and 478 mμ in agreement with those given by an authentic specimen.

10,11-Benzofluoranthene

Identified by ultraviolet spectroscopy following chromatography on acetylated cellulose: $\lambda_{\max.}$ 241, 282, 293, 309, 318, 333, 345, 365, 376, and 383 mμ in agreement with an authentic specimen.

3,4-Benzofluoranthene

Identified by chromatography on a column of acetylated cellulose followed by thin-layer chromatography. An extract showed maxima at 238, 247, 269, 283, 297, 309, 361, 380, and 402 mμ in agreement with an authentic specimen.

11,12-Benzofluoranthene

Identified by ultraviolet spectroscopy following chromatography on acetylated cellulose: $\lambda_{\max.}$ 238, 269, 283, 297, 309, 361, 380, and 402 mμ in agreement with an authentic specimen.

Anthanthrene

Isolated by chromatography on a column of acetylated cellulose followed by thin-layer chromatography. An extract showed maxima at 233, 256, 259, 295, 308, 365, 382, 401, 407, 421, and 431 mμ in agreement with an authentic specimen.

2,3-(o-*Phenylene)pyrene*

Isolated following chromatography on acetylated cellulose, this had m.p. 158–159° (lit.[11] 163°). The ultraviolet absorption spectrum showed maxima at 251, 261, 275, 292, 304, 315, 360, 376, 385, and 407 mμ in good agreement with Badger and Spotswood.[12] Long wavelength bands reported at 422 and 431 mμ for this compound[13] are due to anthanthrene impurity.

[11] Aitken, M., and Reid, D. H., *J. Chem. Soc.*, 1956, 3487.

[12] Badger, G. M., and Spotswood, T. M., *J. Chem. Soc.*, 1960, 4420.

[13] Badger, G. M., and Novotny, J., *J. Chem. Soc.*, 1961, 3403.

3,4 : 9,10-Dibenzopyrene

This was identified after repeated chromatography on columns of acetylated cellulose. The ultraviolet absorption spectrum showed maxima at 234, 242, 273, 283, 296, 315, 331, 353, 373, and 393 mμ, and its fluorescence spectrum maxima at 428, 456, 489, and 520 mμ in agreement with an authentic specimen.

3,4 : 8,9-Dibenzopyrene

Isolated following chromatography on partially acetylated cellulose, this had m.p. 303–305° (lit.[14] 308°). Its ultraviolet absorption spectrum showed maxima at 291, 301, 314, 379, 401, 424, and 452 mμ in agreement with recorded values.[14] The fluorescence spectrum showed maxima at 449, 475, and 512 mμ in agreement with the literature.[15]

Coronene

Isolated following chromatography on acetylated cellulose, this had m.p. 436–438°, not depressed by admixture with an authentic specimen. Its ultraviolet spectrum showed maxima at 293, 305, 317, 320, 325, 336, 341, 348, 355, 369, 378, 381, 388, 397, 402, 410, 419, and 427 mμ in agreement with an authentic specimen.

9,9′-Bianthryl

Isolated following chromatography on acetylated cellulose, this had m.p. 310–312°, not depressed by admixture with an authentic specimen. The ultraviolet spectrum (95% ethanol) showed maxima at 253·5, 316, 333, 349·5, 369·5, and 388·5 mμ in agreement with an authentic sample; in benzene it showed maxima at 252, 317, 334, 350, 370, and 393 mμ in agreement with the literature.[16] An authentic specimen was prepared by the method of Bell and Waring.[17]

2,2′-Bianthryl

Isolated following chromatography on acetylated cellulose, this had m.p. 367–369° (lit.[18] 369–371°). The ultraviolet spectrum (benzene) showed maxima at 284, 304, 317, 355, 388, and 402 mμ in agreement with the literature.[18]

1,1′-Bianthryl

Isolated following chromatography on acetylated cellulose, this had m.p. 319–320° (lit.[17] 321–322°). The ultraviolet spectrum (ethanol) showed maxima at 254, 316, 329·5, 345, 365, and 383 mμ in agreement with an authentic specimen prepared by the decarboxylation of 1,1′-bianthryl-2,2′-dicarboxylic acid.

1,2 : 11,12-Dibenzoperylene

Identified following chromatography on acetylated cellulose; the ultraviolet spectrum (benzene) showed maxima at 300, 313, 353, 371, 446, 478, 516, and 558 mμ in agreement with recorded values.[14]

Bisanthrene

Identified following chromatography on acetylated cellulose; the spectrum in the visible region showed maxima at 399, 424, 555, 602, and 662 mμ in agreement with the literature.[19]

[14] Clar, E., "Aromatische Kohlenwasserstoffe." 2nd Ed. (Springer-Verlag: Berlin 1952.)

[15] Lyons, M. J., and Johnston, H., *Brit. J. Cancer*, 1957, **11**, 544.

[16] Clar, E., *Ber. dt. chem. Ges.*, 1932, **65**, 503.

[17] Bell, F., and Waring, D. H., *J. Chem. Soc.*, 1949, 267.

[18] Lang, K. F., and Buffleb, H., *Chem. Ber.*, 1961, **94**, 1075.

[19] Clar, E., *Chem. Ber.*, 1949, **82**, 55.

2,3-Benzonaphtho[2′,3′-11,12]fluoranthene

Isolated following chromatography on acetylated cellulose, this had m.p. 319–320°, not depressed by admixture with an authentic specimen. The ultraviolet spectrum showed maxima at 284, 298, 357, 380, 416, 441, 472, and 505 mμ in agreement with an authentic specimen.

Benzonaphthofluoranthenes (IX) and (XIV)

(i) The first isomer isolated following chromatography on partially acetylated cellulose had m.p. 240–241°, not depressed by admixture with a specimen of benzonaphthofluoranthene kindly presented by Dr. K. Lang. The absorption spectrum showed maxima at 320, 349, 375, 414, 438, 465, 535, and 570 mμ in agreement with Dr. Lang's specimen.

(ii) The second isomer eluted from the column of acetylated cellulose had m.p. 227–228° in agreement with that recorded for the isomeric benzonaphthofluoranthene.[16] The ultraviolet spectrum showed maxima at 298, 380, 388, 396, 420, 445, 474, 525, and 560 mμ in agreement with the literature.[16]

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