THE FORMATION OF AROMATIC HYDROCARBONS AT HIGH TEMPERATURES*

XVIII. THE PYROLYSIS OF n-DECANE

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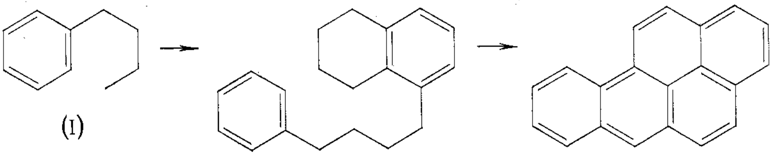
Summary

n-Decane has been pyrolysed at 700°C. Fifty-two compounds have been identified in the resulting tar. Mechanisms of formation are discussed.

I. Introduction

Carcinogenic hydrocarbons are widely distributed in materials such as tar, soot, etc., which have been produced by high temperature processes, and it is important to determine their modes of formation.[1] In Part I of this series[2] it was suggested that the potent carcinogen 3,4-benzopyrene (III) may be formed by free-radical reactions from two C_6–C_4 units (I) via the intermediate (II). Subsequent work has supported this view. Butylbenzene and tetralin may be considered as typical C_6–C_4 units and both compounds, on pyrolysis, have been shown to give tars containing significant amounts of 3,4-benzopyrene.[3,4] Moreover, the pyrolysis of [1-^{14}C]tetralin,[5] and of [δ-^{14}C]butylbenzene,[6] has given tars from which radioactive 3,4-benzopyrene has been isolated; and the 3,4-benzopyrene was found to contain two labelled carbon atoms as expected from the hypothesis.



(I) (II) (III)

Many other compounds have also been pyrolysed and considerable evidence has now accumulated that C_6–C_4 units can be built up, by radical reactions, from smaller units. Thus 3,4-benzopyrene and other polycyclic aromatic hydrocarbons have been formed by the pyrolysis of acetylene, butadiene, styrene, ethylbenzene, and other compounds.[1]

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* Part XVII of this series, *Aust. J. Chem.* **16**: 392.

† Department of Organic Chemistry, University of Adelaide.

[1] Badger, G. M., Kimber, R. W. L., and Spotswood, T. M. (1960).—*Nature* **187**: 663.

[2] Badger, G. M. *et al.* (1958).—*J. Chem. Soc.* **1958**: 2449.

[3] Badger, G. M., and Kimber, R. W. L. (1960).—*J. Chem. Soc.* **1960**: 266.

[4] Badger, G. M., and Spotswood, T. M. (1960).—*J. Chem. Soc.* **1960**: 4420.

[5] Badger, G. M., Kimber, R. W. L., and Novotny, J. (1962).—*Aust. J. Chem.* **16**: 616.

[6] Badger, G. M., and Novotny, J. (1963.)—*Aust. J. Chem.* **16**: 623.

Aust. J. Chem., 1963, **16**, 613–22

However, complex hydrocarbons need not necessarily break down to two-carbon fragments before resynthesis and, as previously pointed out,[2] the C_6–C_4 fragments required for the formation of 3,4-benzopyrene could arise by cyclization of a C_{10} hydrocarbon such as n-decane, or from a higher hydrocarbon (such as dicetyl) by cracking followed by cyclization. 3,4-Benzopyrene is known to be formed by the pyrolysis of dicetyl[7] and of the waxy paraffins found in the tobacco leaf. We now report the results obtained by the pyrolysis of n-decane.

TABLE 1

COMPOSITION OF TAR FOLLOWING PYROLYSIS OF n-DECANE AT 700°C

Fraction	Compound	Percentage in Tar	Method of Identification*
—	Methane	—	i.r.
—	Ethylene	—	i.r., dibromo derivative
—	Propylene	—	i.r., dibromo derivative
—	But-1-ene	—	i.r., dibromo derivative
—	Acetylene	—	i.r.
a	Butane	0·04	r.t.
a	Pentane	0·06	r.t.
a	Hexane	0·06	r.t.
a,b	Cyclohexane	0·29	r.t.
a,b,c	Benzene	43·9	r.t., i.r., u.v.
a,b,c	Toluene	13·8	r.t., i.r., u.v.
c	*p*- and *m*-Xylene	1·95	r.t., i.r.
c	Styrene	6·86	r.t., i.r.
c	α-Methylstyrene	1·25	r.t., i.r.
c,2	Indene	1·48	r.t., i.r., u.v.
c,2,3	Tetralin	1·37	r.t., i.r.
c,2–4	Naphthalene	13·2	r.t., u.v., mixed m.p.
c,2–3	1- and 2-Methylnaphthalene	4·30	r.t., u.v.
2–3	Biphenyl	2·04	r.t., u.v., mixed m.p.
3	Diphenylmethane	0·94	r.t., i.r.
3	Bibenzyl	0·42	r.t.
3–7	Acenaphthylene	1·33	u.v.
5–9	Fluorene	0·73	u.v.
5–7	2-Phenylnaphthalene	0·23	u.v.
5–10	Phenanthrene	1·86	u.v., mixed m.p.
5–10	Anthracene	0·04	u.v.
8–25	Pyrene	0·90	u.v., mixed m.p.
10–26	Fluoranthene	0·53	u.v., mixed m.p.
25–30	2,2′-Binaphthyl	0·17	u.v.
25–35	1,2-Benzanthracene	0·02	u.v.
25–35	Triphenylene	0·05	u.v.
25–35	1,2-Benzofluorene	0·20	u.v.
25–35	3,4-Benzofluorene	0·09	u.v.
25–39	2,3-Benzofluorene	0·29	u.v.
31–39	Chrysene	0·53	u.v., mixed m.p.
36–39	10,11-Benzofluoranthene	0·017	u.v.
36–59	1,2-Benzopyrene	0·122	u.v., mixed m.p.
36–59	3,4-Benzopyrene	0·108	u.v., mixed m.p.

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[7] Lam, J. (1956).—*Acta Path. Microbiol. Scand.* **39**: 198.

TABLE 1 (*Continued*)

Fraction	Compound	Percentage in Tar	Method of Identification*
40–48	Perylene	0·015	u.v.
40–59	3,4-Benzofluoranthene	0·032	u.v., mixed m.p.
40–59	11,12-Benzofluoranthene	0·075	u.v.
49–68	1,12-Benzoperylene	0·039	u.v.
60–86	Benzo[*g,h,i*]fluoranthene	Trace	u.v.
60–86	Picene	0·030	u.v.
60–68	2,3-*o*-(Phenylene)pyrene	0·146	u.v.
69–77	Coronene	0·007	u.v.
69–86	Anthanthrene	Trace	u.v.
78–100	1,2 - 4,5-Dibenzopyrene	0·006	u.v.
87–100	1,2 - 3,4-Dibenzopyrene	Trace	u.v.
87–100	3,4 - 9,10-Dibenzopyrene	Trace	u.v.
	Resins, losses, etc.	0·5	

*i.r., infrared spectroscopy; u.v., ultraviolet spectroscopy; r.t., retention time ratio.

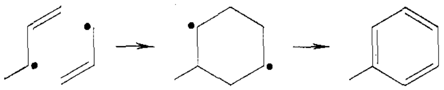
II. RESULTS AND DISCUSSION

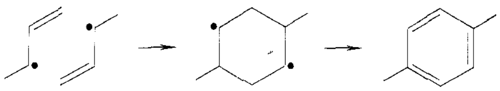
The pyrolysis was carried out by passing the n-decane vapour, with nitrogen, through a silica tube packed with porcelain chips at 700°C. Methane, ethylene, acetylene, propylene, and but-1-ene were detected in the exit gases. The tar (obtained in 13·9% yield) was collected and analysed by distillation, 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 (52 in all) have been collected 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, toluene, styrene, and naphthalene were the *major* constituents of the tar.

By analogy with other compounds for which determinations are available, it seems likely that the carbon–carbon bonds in n-decane all have bond dissociation energies of about 80 kcal/mole, and all these bonds would therefore be expected to break with approximately equal facility. The primary fragments formed at the high temperature would therefore be the methyl, ethyl, propyl, butyl, pentyl, etc. radicals. Abstraction of a hydrogen atom from other molecules would be expected to give the corresponding saturated hydrocarbons; and methane, butane, pentane, and hexane were found among the products.

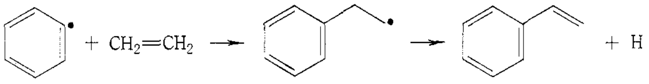
The formation of ethylene, propylene, and of but-1-ene, from ethyl, propyl, and butyl radicals would also be low energy processes. All these unsaturated hydrocarbons were identified in the exit gases, and it seems likely that they are major products of the pyrolysis. The longer-chain primary radicals would be expected to decompose into ethylene and a radical containing two carbons less than the primary radical; in this way the concentration of ethylene would be increased and the concentration of long-chain radicals decreased. Long-chain olefins could not be detected among the products.

Benzene is known to be formed by the pyrolysis of ethylene, or of acetylene,[8] and some of the benzene formed in the present pyrolysis could be formed in this way. Some could also be formed from hexyl radicals via cyclohexane, and it may be noted that a little cyclohexane was found in the tar. Benzene could also be formed from two propyl radicals; or from ethylene and a C_4 radical. It is impossible to determine the most important process in this particular pyrolysis, and all the above mechanisms probably contribute to the high yield of benzene. The relatively high yield of toluene suggests that this compound may be formed from a butene radical and propene or a propene radical (eqn. (1)); and *p*-xylene probably arises from two butene radicals (eqn. (2)). Nevertheless some toluene (and some xylene) is probably formed by methylation of benzene with the methyl radicals formed as primary radicals from the n-decane.


(1)


(2)

The high yield of styrene is remarkable, and again several reasonable mechanisms for its formation can be suggested. In view of the very high yield of benzene, however, it seems not unlikely that the styrene is largely formed from phenyl radicals and ethylene (eqn. (3)); and a similar mechanism involving phenyl radicals and propylene would account for the presence of the indene in the tar (eqn. (4)). In the same way, α-methylstyrene could be formed from benzyl radicals and propylene.



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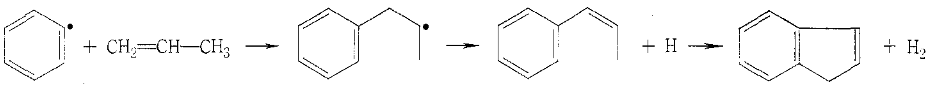

(4)

The pyrolysis of benzene is known to give a high yield of biphenyl, together with some triphenylene.[9] The high yield of benzene in the present pyrolysis therefore suggests that the biphenyl is formed by the phenylation of benzene, or from two phenyl radicals. Further phenylation would be expected to give some *o*-terphenyl, and hence triphenylene by cyclodehydrogenation.[9, 10]

It seems likely that phenyl radicals are also implicated in the formation of fluorene. Interaction with benzyl radicals, for example, would give diphenylmethane (also found in the tar), and cyclodehydrogenation would give fluorene.

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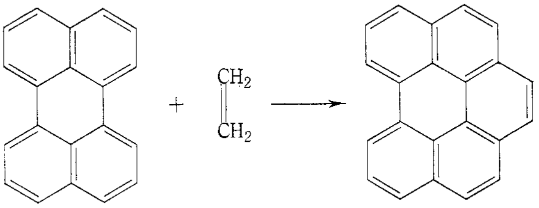
[8] Badger, G. M., Lewis, G. E., and Napier, I. M. (1960).—*J. Chem. Soc.* **1960**: 2825.

[9] Badger, G. M., and Novotny, J. (1961).—*J. Chem. Soc.* **1961**: 3400.

[10] Copeland, P. G., Dean, R. E., and McNeil, D. (1960).—*J. Chem. Soc.* **1960**: 1687.

The large yield of naphthalene in this pyrolysis is noteworthy, but not unexpected from a C_{10} hydrocarbon. No doubt tetralin is an intermediate for much of the naphthalene formed, and some tetralin was also found in the tar. As mentioned above, carbon–carbon fission of the n-decane would be expected to give methyl and other radicals, and the methylnaphthalenes found in the tar could be formed by methylation of the naphthalene. In the same way the phenylation of naphthalene would be expected to give 2-phenylnaphthalene (0·23% yield) and 1-phenylnaphthalene, which would undergo cyclodehydrogenation to fluoranthene (0·53% yield). 2,2′-Binaphthyl, perylene, 10,11-benzofluoranthene, and 11,12-benzofluoranthene (all of which were identified in the tar) would be expected to arise from naphthalene and a naphthyl radical, followed by cyclodehydrogenation, as previously explained.[5, 11]

The presence of 1,12-benzoperylene and of a very small amount of coronene in the tar is of interest, expecially as the latter hydrocarbon has not previously been identified in a tar produced at a temperature as low as 700°C (but there is some evidence to suggest that it is formed in reasonable yield in pyrolyses at much higher temperatures). It is tentatively suggested that 1,12-benzoperylene is formed from a 1,1′-binaphthyl or a perylene radical and a C_2 unit, such as ethylene (eqn. (5)); and that coronene is similarly formed from perylene or a perylene radical and two C_2 units (eqn. (6)).



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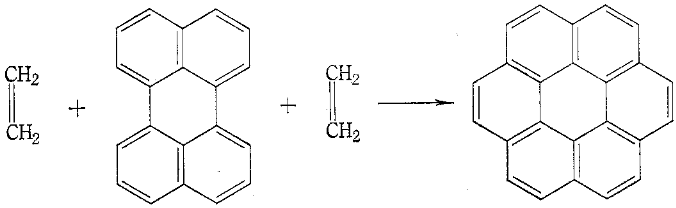
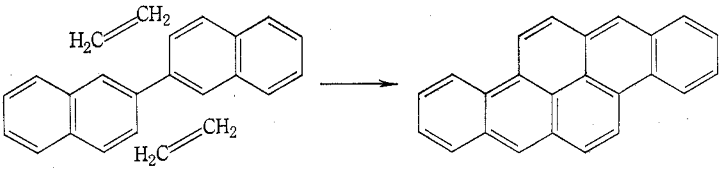


(6)

Anthanthrene could be formed in a similar fashion from 2,2′-binaphthyl and ethylene (eqn. (7)). All these processes (eqns. (5), (6), and (7)) would be expected to involve high energies, and this is consistent with the finding that these hydrocarbons require relatively high temperatures for their formation.



(7)

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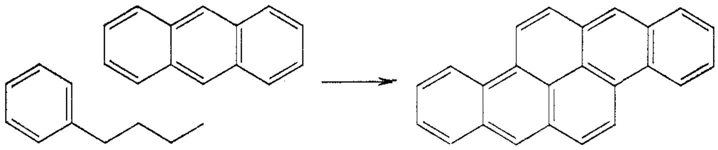
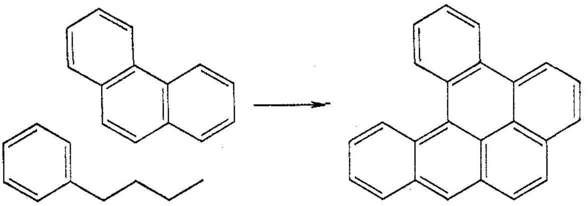
[11] Copeland, P. G., Dean, R. E., and McNeil, D (1960).—*J. Chem. Soc.* **1960**: 1689.

The probable mode of formation of 3,4-benzopyrene, from two C_6–C_4 units, has been mentioned in the introduction. 3,4-8,9-Dibenzopyrene could be formed by interaction of a C_6–C_4 unit with anthracene (found in small amount in the tar) followed by a cyclodehydrogenation (eqn. (8)). 1,2-3,4-Dibenzopyrene could be formed from phenanthrene and a C_6–C_4 unit (eqn. (9)); and 3,4-9,10-dibenzopyrene could arise from the same intermediates (eqn. (10)).



(8)



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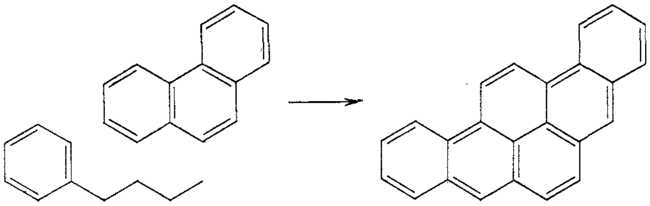
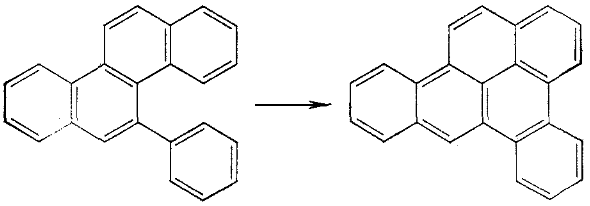


(10)

The most reasonable mechanism for the formation of 1,2-4,5-dibenzopyrene would seem to be by phenylation of chrysene, followed by cyclodehydrogenation (eqn. (11)):



(11)

III. Experimental

(a) General

n-Decane.—B.D.H. reagent was purified by fractional distillation from sodium. The fraction b.p. 173–174°C, n_D^{18} 1·41279 (lit. n_D^{20} 1·41203, n_D^{25} 1·40967;[12] n_D^{20} 1·41189, n_D^{25} 1·40967[13]) contained no impurities which could be detected by gas-liquid chromatography.

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[12] Shepard, A. F., Henne, A. L., and Midgley, T. (1931).—*J. Amer. Chem. Soc.* **53**: 1948.

[13] Forziati, A. F. *et al.* (1946).—*J. Res. Nat. Bur. Stand.* **36**: 129. (*Chem. Abstr.* **40**: 4341.)

Pyrolysis of n-Decane.—n-Decane (100 g) was vaporized at 7 g/hr and passed with nitrogen (1 ml/sec) through a silica tube (36 × 1 in.) which was maintained at 700°C in an electrically heated furnace.[2] Samples of the exit gases were collected, and a dark brown tar (13·9 g) was obtained.

Analysis.—The tar was distilled to give fractions; (*a*) b.p. 40–80°C/760 mm (2·2 g); (*b*) b.p. 80–100°C/760 mm (3·1 g); (*c*) b.p. 40–100°C/30 mm (4·7 g); and (*d*) a residue (3·9 g).

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

A quarter of the residue (*d*) was chromatographed on a column (25 × 3 cm) of Spence alumina (200 g) by dissolving the whole residue in chloroform, adding alumina (45 g), evaporating the solvent on the water-bath, and adding a quarter of the adsorbed residue to the column in the usual way. The dark brown layer of alumina containing the residue was covered with a thin layer of alumina (30 g). Elution gave the following fractions (each of 100 ml): with hexane, fractions 1–24; with hexane–benzene (1 : 12 v/v), fractions 25–48; with hexane–benzene (2 : 11 v/v), fractions 49–57; with hexane–benzene (3 : 10 v/v), fractions 58–72; with hexane–benzene (4 : 9 v/v) fractions 73–84; with hexane–benzene (5 : 8 v/v), fractions 85–90; with benzene, fractions 91–94 (250 ml each); with chloroform, fractions 95–97; with ethanol, fractions 98–99; and with diethyl ether, fraction 100. On the basis of their ultraviolet spectra these fractions were recombined to give 16 main fractions.

Fractions 1–3 were further examined by gas-liquid chromatography, and the remainder by chromatography on columns of partially acetylated cellulose and on partially acetylated paper.[14, 15]

Absorption Spectra.—These were determined in 95% ethanol using an Optica CF_4 recording spectrophotometer.

(*b*) *Details of Identification*

Methane.—Samples of the exit gases were collected in a gas cell for infrared analysis. Methane was identified from the characteristic band system in the 7·3–8·5 μ region (maxima at 7·36, 7·43, 7·52, 7·62, 7·66, 7·70, 7·78, 7·82, 7·88, 7·90, 7·94, 7·97, 8·05, 8·10, 8·17, and 8·22 μ).

Ethylene.—This was identified from the characteristic band system in the 9·0–11·5 μ region (maxima at 9·91, 10·01, 10·11, 10·21, 10·31, 10·40, 10·51, 10·75, 10·83, 10·92, 11·02, 11·07, 11·16, and 11·25 μ). Its presence was confirmed by the isolation of 1,2-dibromoethane following gas-liquid chromatography of the bromo derivatives obtained by passing the exit gases through bromine water. The infrared spectrum of 1,2-dibromoethane was identical with that of an authentic specimen.

Propylene.—This was identified in the exit gases from its infrared spectrum in the 6·0–6·5 μ region. Its presence was confirmed by the isolation of 1,2-dibromopropane by gas-liquid chromatography of the mixture of bromo derivatives obtained by passing the exit gases through bromine water. The infrared spectrum of the 1,2-dibromopropane was identical with the published curve.[16]

But-1-ene.—Isolated as 1,2-dibromobutane following gas-liquid chromatography of the mixture of bromo derivatives obtained by passing the exit gases through bromine water. The infrared spectrum of the 1,2-dibromobutane was identical with that of an authentic specimen.

Acetylene.—This was identified in the exit gases from the characteristic band system in the 12·5–14·5 μ region.

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[14] Spotswood, T. M. (1959).—*J. Chromatogr.* **2**: 90.

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

[16] Eckstein, B. H., Scheraga, H. A., and Van Artsdalen, E. R. (1954).—*J. Chem. Phys.* **22**: 28.

Butane.—Identified in fraction (*a*) by comparison of the retention time ratio with that of an authentic specimen.

Pentane.—Identified in fraction (*a*) by comparison of the retention time ratio with that of an authentic specimen.

Hexane.—Identified in fraction (*a*) by comparison of the retention time ratio with that of an authentic specimen.

Cyclohexane.—Identified in fraction (*a*) and (*b*) by comparison of the retention time ratio with that of an authentic specimen.

Benzene.—Isolated from fractions (*a*), (*b*), and (*c*) by gas-liquid chromatography. Its infrared spectrum (liquid film) showed maxima at 3·25, 3·31, 4·31, 4·53, 5·10, 5·51, 5·70, 6·00, 6·31, 6·54, 6·76, 7·20, 8·52, and 9·67 μ.

Toluene.—Isolated from fractions (*a*), (*b*), and (*c*) by gas-liquid chromatography. It had infrared maxima (liquid film) at 3·29, 3·42, 3·48, 3·64, 5·14, 5·38, 5·55, 5·74, 6·22, 6·56, 6·69, 6·84, 7·26, 9·25, 9·70, 13·73, and 14·42 μ.

p- *and* m-*Xylenes.*—Isolated from fraction (*c*) by gas-liquid chromatography. Its infrared spectrum (liquid film) showed maxima at 3·30, 3·42, 3·48, 3·64, 5·20, 5·32, 5·42, 5·63, 5·78, 6·24, 6·62, 6·73, 6·91, 7·30, 8·60, 8·92, 9·06, 9·58, 11·02, 11·31, 12·53, 12·98, 13·44, and 14·46 μ.

Styrene.—Isolated from fraction (*c*) by gas-liquid chromatography. Its infrared spectrum (liquid film) showed maxima at 3·20, 3·25, 5·10, 5·30, 5·50, 5·70, 5·90, 6·11, 6·22, 6·31, 6·52, 6·70, 6·90, 7·08, 7·50, 7·60, 7·73, 8·32, 8·50, 8·68, 9·06, 9·26, 9·78, 10·10, 11·00, 11·91, 12·90 and 14·40 μ.

α-Methylstyrene.—Isolated from fraction (*c*) by gas-liquid chromatography. Its infrared spectrum (liquid film) showed maxima at 3·22, 3·32, 4·35, 5·16, 5·36, 5·60, 5·86, 5·96, 6·14, 6·28, 6·40, 6·73, 6·98, 7·34, 7·42, 7·76, 7·96, 8·60, 9·40, 9·80, 10·02, 10·54, 11·26, 12·83, and 13·16 μ.

Indene.—Isolated from fractions (*c*) and (2) by gas-liquid chromatography. Its infrared spectrum (liquid film) showed maxima at 3·25, 3·46, 3·60, 6·24, 6·50, 6·92, 7·24, 7·40, 7·58, 7·68, 7·82, 8·20, 8·34, 8·62, 8·94, 9·40, 9·84, 10·56, 10·92, 11·60, 12·06, 13·02, 13·70, 13·92, and 14·42 μ.

Tetralin.—Isolated from fractions (*c*), (2), and (3) by gas-liquid chromatography. Its infrared spectrum (liquid film) showed maxima at 3·31, 3·42, 3·53, 3·69, 5·20, 5·42, 5·62, 5·85, 6·26, 6·40, 6·72, 6·90, 7·30, 8·31, 8·54, 9·08, 9·28, 9·62, 9·74, 11·14, 11·57, 13·60, and 14·32 μ.

Naphthalene.—Isolated from fractions (*c*) and (2–4) by gas-liquid chromatography and by chromatography on acetylated cellulose. Its ultraviolet absorption spectrum in 95% ethanol showed maxima at 248, 257, 266, 275, 285, and 311 mμ; and it had m.p. and mixed m.p.78–80°C.

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

Biphenyl.—Isolated from fractions (2) and (3) by gas-liquid chromatography, its ultraviolet spectrum showed a maximum at 248 mμ. It had m.p. and mixed m.p. 69–70°C.

Diphenylmethane.—Isolated from fraction (3) by gas-liquid chromatography. Its infrared spectrum (liquid film) showed maxima at 3·39, 3·40, 3·46, 3·52, 5·18, 5·58, 6·00, 6·08, 6·24, 6·34, 6·72, 6·92, 7·28, 7·42, 7·62, 7·86, 8·34, 8·50, 8·70, 9·08, 9·30, 9·70, 9·98, 10·62, 10·88, 11·18, 11·84, 12·32, 12·82, 13·50, and 14·30 μ.

Bibenzyl.—Identified in fraction (3) by comparison of its retention time ratio with that of an authentic specimen.

Acenaphthylene.—Isolated from fractions (3–7) by chromatography on partially acetylated cellulose. Its 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 (5–9) by chromatography on partially acetylated cellulose, its ultraviolet spectrum showed maxima at 260, 290, and 301 mμ in agreement with an authentic specimen.

2-Phenylnaphthalene.—Identified in fractions (5–7) by chromatography on partially acetylated cellulose, its ultraviolet spectrum showed maxima at 250 and 296 mμ.

Phenanthrene.—Isolated from fractions (5–10) by chromatography on partially acetylated cellulose; 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; and it had m.p. and mixed m.p. 96–98°C.

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

Pyrene.—Isolated from fractions (8–25) by chromatography on 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. 145–147°C.

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

2,2′-Binaphthyl.—Identified in fractions (25–30) by chromatography on partially acetylated cellulose; its ultraviolet spectrum showed maxima at 255 and 309 mμ in agreement with an authentic specimen.

1,2-Benzanthracene.—Identified in fractions (25–35) by chromatography on partially acetylated cellulose, its ultraviolet spectrum had maxima at 227, 256, 268, 278, 289, 300, 315, 326, 341, 358, 365, 374, and 384 mμ in agreement with an authentic specimen.

Triphenylene.—Identified in fractions (25–35) by chromatography on partially acetylated cellulose, its ultraviolet spectrum showed maxima at 250, 257, 275, 286, 316, 330, and 341 mμ in agreement with an authentic specimen.

1,2-Benzofluorene.—Identified in fractions (25–35) after chromatography on partially acetylated cellulose, its ultraviolet spectrum showed maxima at 229, 238, 253, 257, 262, 274, 286, 294, 303, 316, and 340 mμ in agreement with an authentic specimen.

3,4-Benzofluorene.—Identified in fractions (25–35) after chromatography on partially acetylated cellulose; its ultraviolet spectrum showed maxima at 230, 251, 262, 302, 311, 321, 329, and 337 mμ in agreement with an authentic specimen.

2,3-Benzofluorene.—Identified in fractions (25–39) after chromatography on partially acetylated cellulose; its ultraviolet spectrum showed maxima at 255, 264, 273, 285, 304, 317, 325, 333, and 340 mμ.

Chrysene.—Isolated from fractions (31–39) by chromatography on partially acetylated cellulose; its ultraviolet spectrum showed maxima at 242, 259, 267, 283, 294, 306, 320, 344, 351, and 363 mμ in agreement with an authentic specimen; and it had m.p. and mixed m.p. 253–254°C.

10,11-Benzofluoranthene.—Identified in fractions (36–39) after chromatography on partially 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.

1,2-Benzopyrene.—Isolated from fractions (36–59) by chromatography on partially acetylated cellulose; its 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. 173–175°C.

3,4-Benzopyrene.—Isolated from fractions (36–59) by chromatography on partially acetylated cellulose; its ultraviolet spectrum showed maxima at 255, 266, 273, 284, 297, 332, 347, 365, 379, 385, and 404 mμ in agreement with an authentic specimen; and it had m.p. and mixed m.p. 174–176°C.

Perylene.—Identified in fractions (40–48) after chromatography on partially acetylated cellulose; its ultraviolet spectrum showed maxima at 245, 253, 263, 367, 386, 407, and 435 mμ in agreement with an authentic specimen.

3,4-Benzofluoranthene.—Isolated from fractions (40–59) by chromatography on partially acetylated cellulose; its absorption spectrum showed maxima at 239, 256, 266, 276, 290, 294, 301, 320, 339, 351, and 369 mμ in agreement with an authentic specimen; and it had m.p. and mixed m.p. 160–163°C.

11,12-Benzofluoranthene.—Identified in fractions (40–59) after chromatography on partially acetylated cellulose; its ultraviolet spectrum showed maxima at 238, 247, 269, 283, 297, 309, 361, 380, and 402 mμ in agreement with an authentic specimen.

1,12-Benzoperylene (≡ *benzo*[g,h,i]*perylene*).—Identified in fractions (49–68) by chromatography on partially acetylated cellulose; its absorption spectrum showed maxima at 268, 276, 289, 300, 315, 325, 330, 345, 363, and 383 mμ in agreement with an authentic specimen.

7,10-Benzofluoranthene (≡ *benzo*[g,h,i]*fluoranthene*).—Identified in fractions (60–68) after chromatography on partially acetylated cellulose; its absorption spectrum showed maxima at 233, 245, 251, 260, 282, 291, 331, 348, 378, 398, and 420 mμ in agreement with an authentic specimen.

Picene.—Identified in fractions (60–86) after chromatography on partially acetylated cellulose; its absorption spectrum showed maxima at 232, 256, 274, 284, 301, 312, and 326 mμ in agreement with an authentic specimen.

2,3-(o-*Phenylene*)*pyrene.*—Identified in fractions (60–68) by chromatography on partially acetylated cellulose; its absorption spectrum showed maxima at 259, 269, 277, 292, 304, 315, 360, 376, 385, 402, 422, and 431 mμ in agreement with an authentic specimen.

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

Anthanthrene.—Identified in fractions (69–86) by chromatography on partially acetylated cellulose; its 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 (≡ *dibenzo*[a,e]*pyrene*).—Identified in fractions (78–100) after chromatography on partially acetylated cellulose; its absorption spectrum showed maxima at 241, 247, 251, 271, 291, 303, 324, 339, 354, 370, and 372 mμ in agreement with an authentic specimen.

1,2-3,4-Dibenzopyrene (≡ *dibenzo*[b,e]*pyrene*).—Identified in fractions (87–100) after chromatography on partially acetylated cellulose, followed by chromatography on partially acetylated paper; its absorption spectrum showed maxima at 262, 269, 290, 303, 315, 331, 355, 363, 372, and 402 mμ in agreement with an authentic specimen.

3,4-9,10-Dibenzopyrene (≡ *dibenzo*[a,i]*pyrene*).—Identified in fractions (87–100) after chromatography on partially acetylated cellulose, followed by chromatography on partially acetylated paper; its absorption spectrum showed maxima at 232, 242, 273, 283, 296, 315, 331, 353, 373, and 393 mμ.

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