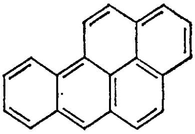
858. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part IX.* The Pyrolysis of Toluene, Ethylbenzene, Propylbenzene, and Butylbenzene.*

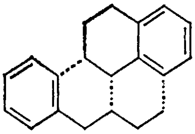
By G. M. Badger and T. M. Spotswood.

Pyrolyses of toluene, ethylbenzene, propylbenzene, and butylbenzene have given the compounds listed in the Table. The yields of higher polycyclic hydrocarbons varied with the nature of the aliphatic side chain, and mechanisms of formation based on scission of molecules to radical intermediates and re-synthesis are proposed. The highest yields of the carcinogenic hydrocarbons 3,4-benzopyrene and 3,4-benzofluoranthene were obtained from butylbenzene.

As a working hypothesis it was suggested [1] that the formation of the carcinogenic hydrocarbon 3,4-benzopyrene (I) at high temperatures may involve two C_6–C_4 units (II). Tars formed by the pyrolysis of phenylbutadiene [2] and of tetralin [3] have already been investigated, and the pyrolysis of butylbenzene is now reported. In order to provide further data on the modes of formation of polycyclic aromatic hydrocarbons, the tars produced by the pyrolysis of toluene, ethylbenzene, and propylbenzene have also been investigated.

(I)





(II)

The pyrolyses were carried out by passing the hydrocarbon vapour, with nitrogen, through a silica tube filled with porcelain chips at 700°. The resulting tars were formed in 95, 77, 65, and 56% yield severally, and methane and ethylene were identified among the exit gases in each case. The tars were analysed, as previously described,[1-3] by distillation, gas–liquid chromatography, chromatography on alumina, and on partially acetylated cellulose,[4] chromatography on acetylated paper,[4] and spectroscopy. The compounds identified, and the percentage compositions, are given in the Table.

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot} + {\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3} \tag{1}$$

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot}CH_2{\cdot} + {\cdot}CH_2{\cdot}CH_2{\cdot}CH_3} \tag{2}$$

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot}CH_2{\cdot}CH_2{\cdot} + {\cdot}CH_2{\cdot}CH_3} \tag{3}$$

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot} + {\cdot}CH_2{\cdot}CH_2{\cdot}CH_3} \tag{4}$$

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot}CH_2{\cdot} + {\cdot}CH_2{\cdot}CH_3} \tag{5}$$

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot} + {\cdot}CH_2{\cdot}CH_3} \tag{6}$$

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot}CH_2{\cdot} + {\cdot}CH_3} \tag{7}$$

$$\mathrm{Ph{\cdot}CH_3 \longrightarrow Ph{\cdot} + {\cdot}CH_3} \tag{8}$$

$$\mathrm{Ph{\cdot}CH_3 \longrightarrow Ph{\cdot}CH_2{\cdot} + {\cdot}H} \tag{9}$$

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* Part VIII, *J.*, 1960, 2825.

[1] Badger, Buttery, Kimber, Lewis, Moritz, and Napier, *J.*, 1958, 2449.

[2] Badger and Spotswood, *J.*, 1959, 1635.

[3] Badger and Kimber, *J.*, 1960, 266.

[4] Spotswood, *J. Chromatog.*, 1959, **2**, 90; 1960, **3**, 101.

Compounds identified in tars produced by the pyrolysis of toluene, ethylbenzene, propylbenzene, and butylbenzene.

	Yield (% of tar formed)			
Compound	PhMe	PhEt	$\mathrm{PhPr^n}$	$\mathrm{PhBu^n}$
Acenaphthylene		Trace	Trace	0·37
Anthanthrene		Trace	0·02	0·03
Anthracene	0·009	0·88	0·73	0·93
Alkylanthracene (?)		0·012	Trace	
1,2-Benzanthracene	0·014	0·46	0·62	0·19
Benzene	2·54	34·8	14·6	31·1
3,4-Benzofluoranthene	0·002	0·072	0·198	0·32
10,11-Benzofluoranthene	Trace	0·02	0·076	0·30
11,12-Benzofluoranthene	Trace	0·03	0·085	0·50
1,2-Benzofluorene	0·007	0·42	0·85	0·57
2,3-Benzofluorene	0·017	0·79	1·76	0·96
1,12-Benzoperylene		0·03	0·10	0·52
1,2-Benzopyrene	0·002	0·05	0·19	0·61
3,4-Benzopyrene	0·002	0·065	0·17	0·92
3,4-Benzotetraphene			0·035	0·15
Chrysene	0·03	0·55	0·96	1·82
Alkylchrysene	Trace	0·12	0·14	0·27
1,2:5,6-Dibenzanthracene		0·054	0·16	0·08
3,4:8,9-Dibenzopyrene			0·02	
3,4:9,10-Dibenzopyrene			0·005	
Bibenzyl	1·00	2·20	3·20	0·37
4,4′-Dimethylbiphenyl	0·99			
1,1′-Binaphthyl				0·19
2,2′-Binaphthyl		0·45	0·48	0·76
Biphenyl	0·27	3·11	1·61	2·80
Ethylbenzene		0·76	0·75	0·24
Fluoranthene	Trace	0·34	0·67	1·07
Alkylfluoranthene (?)			Trace	Trace
Fluorene	0·085	0·53	0·40	0·58
Indene		0·41	1·31	1·10
4-Methylbiphenyl			0·31	
1- and 2-Methylnaphthalene		0·01	0·36	0·10
2-Methylstyrene (?)		0·16	0·43	0·28
Naphthalene	0·042	4·54	3·43	21·0
Perylene		0·012	0·015	0·13
Phenanthrene	0·12	14·3	14·0	13·5
Alkylphenanthrene (?)		0·24	0·19	
9-Phenylanthracene		0·017	0·03	
4,5-(*o*-Phenylene)fluoranthene			0·006	0·018
2,3-(*o*-Phenylene)pyrene		0·068	0·13	0·29
2-Phenylnaphthalene		0·47	1·20	0·13
Pyrene	Trace	0·33	0·21	2·0
Alkylpyrene (?)				Trace
Stilbene	0·44	0·15	0·22	0·24
Styrene	0·11 *	9·9	14·7	2·7
Toluene	93·5	21·6	33·0	7·5
Triphenylene			0·06	0·27
p-Xylene	0·05	0·12	0·30	Trace
Resins and losses	0·7	1·9	2·2	4·0

* Mixture of *o*-xylene and styrene.

The C–H bonds in the methyl group of toluene have a dissociation energy of 78 kcal./mole, that for the C–Me group being 89 kcal./mole.[5] The initial decomposition of toluene at high temperatures would therefore be expected to occur predominantly by scission of a C–H bond to give a benzyl radical. For the other alkylbenzenes, scission of a C–C bond is a lower-energy process (dissociation energy 60—80 kcal./mole) than C–H scission (90—100 kcal./mole), and the former would therefore be preferred. Szwarc[6] has suggested that the initial decomposition of ethylbenzene, propylbenzene, and butylbenzene occurs exclusively by scission of a C–C bond to give benzyl radicals, as these are known to be

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[5] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 1954.

[6] Szwarc *et al.*, *J. Chem. Phys.*, 1948, **16**, 128; 1949, **17**, 431; 1952, **20**, 403, 407.

relatively stable. However, the large yield of benzene on pyrolysis of ethyl-, n-propyl-, and butyl-benzene suggests that scission to yield phenyl radicals must also be important. Indeed, scission of the bond linking the side chain to the bulky aromatic nucleus might be expected to be increasingly preferred with increasing chain-length. Scission of other C–C bonds may be less important. However, there may also be a preference for the removal of a two-carbon fragment; this would explain the relative yields of benzene and toluene. It seems likely that equations 1—9 represent the most important reactions for the initial decomposition of the alkylbenzenes studied.

The resulting " primary " radicals must undergo chain-terminating (radical recombination) and chain-propagating reactions or disproportionation. Loss of hydrogen from ethyl and butyl radicals would give ethylene and butadiene respectively. Hydrogen abstraction from the starting material by any radical would also be an important reaction, and with ethyl-, propyl-, and butyl-benzene this would be expected to occur preferentially at an α-carbon atom, *e.g.*:

$$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + {\cdot}R \longrightarrow RH + Ph{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3} \quad . \; . \; . \; . \; . \quad (10)$$

The " secondary " radicals so formed would lose hydrogen, or an alkyl radical, to give styrene and other unsaturated products (*e.g.*, reactions **11**—**13**). Some styrene was found in the present tars, and it may also be noted that hydrogen abstraction reactions (such as 10) probably account for most of the benzene, toluene, and ethylbenzene found.

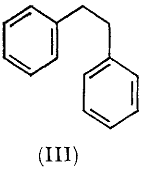
$$\mathrm{Ph{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_3 + {\cdot}H} \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

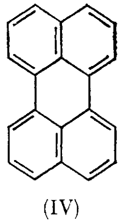
$$\mathrm{Ph{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot}CH{=}CH{\cdot}CH_3 + {\cdot}CH_3} \quad . \; . \; . \; . \; . \; . \; . \quad (12)$$

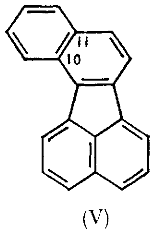
$$\mathrm{Ph{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow Ph{\cdot}CH{=}CH_2 + CH_2{=}CH_2 + {\cdot}H} \quad . \; . \; . \; . \; . \quad (13)$$

The recombination of primary radicals would explain the presence of several of the observed products. Recombination of phenyl radicals, for example, would account for most of the biphenyl; and recombination of benzyl radicals would account for most of the bibenzyl and (by subsequent dehydrogenation) of the stilbene formed. 4,4′-Dimethylbiphenyl could arise from two benzyl radicals by coupling in the *para*-position; and 4-methylbiphenyl could be formed by phenyl-radical attack on a benzyl radical. Fluorene probably arises from phenyl and benzyl radicals *via* diphenylmethane. Independent pyrolysis of the latter hydrocarbon has been shown to yield fluorene.[7] The benzofluorenes found in the tars may be formed from benzyl radicals and naphthalene (or its equivalent).

Some phenanthrene could be formed by cyclisation of bibenzyl or of stilbene; but the small yield of phenanthrene obtained by the pyrolysis of toluene suggests that this cannot be an important reaction with these compounds. It is suggested that most of the phenanthrene found may be formed by addition of a phenyl radical to styrene to give the intermediate (III), followed by cyclisation. Some phenanthrene and anthracene could also arise by reaction of butadiene with a naphthyl or hydronaphthyl radical.


(III)


(IV)



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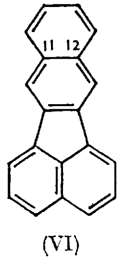

(VI)

Cyclisation of a phenylbutenyl radical or a phenylbutadienyl radical would give naphthalene. The pyrolysis of phenylbutadiene has been shown to yield naphthalene in excellent yield,[2] and it is significant that among the alkylbenzenes now studied the highest

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[7] Meyer and Hofman, *Monatsh.*, 1916, **37**, 681; Graebe, *Ber.*, 1873, **6**, 127.

yield of naphthalene was obtained from butylbenzene. However, the presence of naphthalene in the tars produced by the pyrolysis of toluene, ethylbenzene, and propylbenzene indicates that chain re-synthesis must occur to an appreciable extent, probably by reactions of the type 14—17.

$$\mathrm{Ph\cdot + CH_2{=}CH_2 \longrightarrow Ph\cdot CH_2\cdot CH_2\cdot} \tag{14}$$

$$\mathrm{Ph\cdot CH_2\cdot + CH_2{=}CH_2 \longrightarrow Ph\cdot CH_2\cdot CH_2\cdot CH_2\cdot} \tag{15}$$

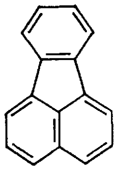
$$\mathrm{Ph\cdot CH_2\cdot CH_2\cdot + CH_2{=}CH_2 \longrightarrow Ph\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot} \tag{16}$$

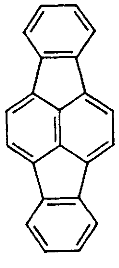
$$\mathrm{Ph\cdot + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow Ph\cdot CH_2\cdot CH{=}CH\cdot CH_2\cdot} \tag{17}$$

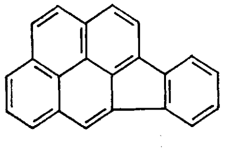
The naphthalene and naphthalene equivalents formed would be expected to undergo further reactions. Binaphthyls are known to be formed by the pyrolysis of tetralin [3] and of naphthalene,[8] and tetralyl or naphthyl radicals are presumably the intermediates which combine to give the observed products. The binaphthyls found in the present series of experiments are probably formed in the same way. The small amounts of perylene (IV), 10,11-benzofluoranthene (V), and 11,12-benzofluoranthene (VI) detected in the tars probably arise by cyclodehydrogenation of binaphthyls. The benzofluoranthenes have been observed after pyrolysis of naphthalene; [8] and perylene is known to be formed by catalytic dehydrogenation of 1,1'-binaphthyl.[9]

The yield of fluoranthene (VII) was found to increase with the length of the alkyl chain. It is probably formed by cyclisation of 1-phenylnaphthalene,[10] or of an intermediate equivalent to this. The 1-phenylnaphthalene could be formed by phenylation of naphthalene, from two styryl radicals, or by some similar process.

The formation of 4,5-(*o*-phenylene)fluoranthene (VIII) can be explained by the phenylation of fluoranthene and subsequent cyclodehydrogenation of the 4-phenylfluoranthene. In the same way, phenylation of pyrene (to give 3-phenylpyrene), followed by cyclodehydrogenation, would give 2,3-(*o*-phenylene)pyrene (IX); and the phenylanthracene observed in some tars may be formed by phenylation of anthracene. In this connection it may be noted that 2,3-(*o*-phenylene)pyrene has been found after pyrolysis of a mixture of pyrene and benzene.[11]


(VII)


(VIII)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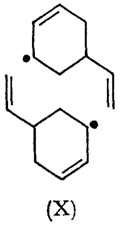
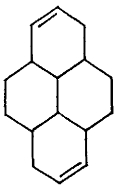
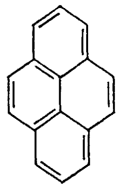

(X)


(XI)


(XII)

The mode of formation of pyrene (XII) presents a problem of particular difficulty. Weizmann *et al.*[12] proposed the union of two styrene molecules, by analogy with the formation of pyrene from *m*-xylene; [13] but the pyrolysis of styrene [14] gave only a small yield of pyrene. Relatively large yields of pyrene have been obtained by pyrolysis of butadiene [15] and of acetylene,[16] and in the present studies butylbenzene was the only alkylbenzene to give a good yield of this hydrocarbon. It seems likely that a four-carbon unit must be the intermediate; two such units would give a molecule or radical related to

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[8] Lang and Buffleb, *Chem. Ber.*, 1957, **90**, 2888.
[9] Orchin and Friedel, *J. Amer. Chem. Soc.*, 1946, **68**, 573.
[10] Orchin and Reggel, *J. Amer. Chem. Soc.*, 1947, **69**, 505.
[11] Lang and Buffleb, *Chem. Ber.*, 1957, **90**, 2894.
[12] Weizmann *et al.*, *Ind. Eng. Chem.*, 1951, **43**, 2312, 2318, 2322, 2325.
[13] Baker, McOmie, and Norman, *J.*, 1951, 1114.
[14] Badger and Buttery, *J.*, 1958, 2458.
[15] Badger and Spotswood, this series, Part XI.
[16] Badger, Lewis, and Napier, *J.*, 1960, 2825.

vinylcyclohexene, and two of these C_6–C_2 units would be expected to react (as in X) to yield a tetracyclic molecule (XI) and finally pyrene (XII).

Only small yields of 3,4-benzopyrene were obtained on pyrolysis of toluene, ethylbenzene, or propylbenzene; but a relatively high yield was obtained from butylbenzene. This is in accord with the view that 3,4-benzopyrene may be formed from two C_6–C_4 units, as in (II).

Other mechanisms may also be of importance, especially in particular cases. Pyrolyses of acetylene,[16] butadiene,[15] and butylbenzene, for example, have been found to give relatively high yields of both pyrene and 3,4-benzopyrene, and in such cases most of the 3,4-benzopyrene and pyrene could be formed from a common intermediate. An intermediate such as (XI), for example, would yield pyrene on dehydrogenation; but reaction with butadiene followed by dehydrogenation would yield 3,4-benzopyrene. This alternative mechanism may account for much of the 3,4-benzopyrene formed in the tars from acetylene, butadiene, and butylbenzene; in the pyrolysis of some other hydrocarbons (*e.g.*, tetralin) the yield of pyrene was small and formation as indicated by (II) may be of major importance.

EXPERIMENTAL

Materials for Pyrolysis.—Toluene and ethylbenzene were pure laboratory reagents, further purified by fractional distillation. Propylbenzene and butylbenzene were prepared by reduction of propiophenone and butyrophenone respectively by the Huang-Minlon modification of the Wolff–Kishner method; the ketones were prepared from benzene by the Friedel–Crafts method. Purification was effected by fractional distillation. In each case the purity of the hydrocarbon was confirmed by gas–liquid chromatography.

Pyrolysis of Toluene.—Toluene (100 g.) was vaporised at 7 g./hr. by dropping the liquid directly into the pyrolysis tube (40″ × 0·75″ internal diameter),[1,2] and the vapour was carried through the tube which was kept at 700°. The resulting tar (94·5 g.) was distilled to give the following fractions: A, b. p. 80—110° (9 g.); B, b. p. 110—140° (68 g.); C, b. p. 40—60°/35 mm. (9·8 g.); C, b. p. 60—120°/35 mm. (6·6 g.); and E, a residue (1·1 g.). The lighter fractions were separated and identified by gas–liquid chromatography. The residue was chromatographed on alumina; the early fractions from this were then submitted to gas–liquid chromatography, and the later fractions were examined by chromatography on acetylated paper.[4] The exit gases were examined by infrared spectroscopy. The Table summarises the compounds identified.

Pyrolysis of Ethylbenzene.—Ethylbenzene (100 g.) was pyrolysed by the method used for toluene. The resulting tar (77·5 g.) was distilled to give the following fractions: A, b. p. 80—120° (35·3) g.; B, b. p. 40—60°/40 mm. (11 g.); C, b. p. 60—100°/35 mm. (2·2 g.); D, b. p. 100—120°/35 mm. (4 g.); and E, a residue (25 g.). The fractions were analysed as previously described, and the compounds identified are listed in the Table.

Pyrolysis of Propylbenzene.—Propylbenzene (100 g.) was pyrolysed by the method used for toluene. The resulting brown liquid tar (65·5 g.) was distilled to give the following fractions: A, b. p. 80—120° (23·8 g.); B, b. p. 40—70°/35 mm. (16·7 g.); C, b. p. 70—130°/35 mm. (5 g.); and D, a residue (20 g.). The fractions were analysed as previously described, and the compounds identified are listed in the Table.

Pyrolysis of Butylbenzene.—Butylbenzene (80 g.) was pyrolysed as usual and gave a dark brown liquid tar (46 g.). Distillation gave the following fractions: A, b. p. 60—80° (4 g.); B, b. p. 80—110° (14 g.); C, b. p. 80—120°/35 mm. (5 g.); D, b. p. 120—135°/35 mm. (7 g.); and E, a residue (16 g.). Analysis by the methods previously described gave the results summarised in the Table.

Analysis.—In all four pyrolyses the infrared spectrum of the exit gases showed the presence of methane and ethylene together with traces of other hydrocarbons. The liquid and solid fractions were examined by gas–liquid chromatography, chromatography on alumina, chromatography on partially acetylated cellulose powder and by chromatography on acetylated paper, as previously described.

Details of Identification.—The identifications were carried out on the products of all four tars; the following details are typical and (except for the compounds marked *) refer to the butylbenzene pyrolysis. Unless otherwise stated, spectra agreed with those of authentic specimens.

Benzene. Isolated by gas–liquid chromatography, it had infrared maxima (liquid film) at 2·38, 2·46, 3·23, 3·29, 4·21, 4·30, 4·39, 4·53, 5·11, 5·70, 5·98, 6·31, 6·54, 6·75, 7·17, 8·50, and 9·65 μ.

Toluene. Its infrared spectrum (liquid film) showed maxima at 2·41, 2·72, 3·28, 3·39, 3·41, 3·63, 3·84, 5·10, 5·34, 5·50, 5·74, 6·22, 6·35, 6·57, 6·70, 6·83, 7·25, 7·61, 8·00, 8·26, 8·50, 8·62, 9·02, 9·23, 9·60, 9·70, 11·20, 11·85, 12·78, 13·75, and 14·42 μ.

Styrene. Its 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.

Ethylbenzene and p-*xylene.* These two compounds were identified by comparison or retention times with those of authentic specimens. Insufficient separation was obtained between the two peaks to permit clean fractionation; but the infrared spectrum of the mixture was consistent with the identification made.

Indene. Its infrared spectrum (in CCl_4) showed maxima at 3·21, 3·39, 3·51, 5·10, 5·18, 5·23, 5·32, 5·40, 5·52, 5·80, 5·98, 6·18, 6·82, 7·14, 7·31, 7·49, 7·60, 7·84, 7·88, 8·17, 8·30, 8·56, 8·62, 8·90, 9·42, 9·81, 10·54, 10·90, and 11·60 μ.

Naphthalene. This has m. p. and mixed m. p. 79—80°. Its ultraviolet absorption spectrum showed maxima at 248, 257, 266, 275, 285, and 311 mμ.

1- *and* 2-*Methylnaphthalenes.* These compounds were identified by comparison of their retention times with those of authentic specimens. The compounds were insufficiently resolved to allow them to be collected separately, and no further identification was attempted.

Biphenyl. Its infrared spectrum (in CCl_4) showed maxima at 2·46, 3·27, 3·32, 3·40, 3·46, 5·08, 5·12, 5·26, 5·31, 5·35, 5·46, 5·56, 5·65, 5·75, 5·98, 6·04, 6·76, 6·88, 7·00, 7·26, 7·74, 7·97, 8·16, 8·48, 8·52, 9·27, 9·60, 9·70, 9·90, 10·10, 10·40, 10·88, and 11·3 μ.

4,4′-*Dimethylbiphenyl.** Separated following chromatography of the toluene tar this compound gave an infrared spectrum with maxima at 3·20, 3·32, 5·10, 5·20, 5·30, 5·50, 5·90, 6·20, 6·70, 6·88, 7·10, 7·20, 7·60, 7·68, 7·76, 7·90, 8·02, 8·40, 8·54, 8·70, 9·00, 9·12, 9·30, 9·60, 9·70, 9·80, 9·94, 10·40, 11·12, 11·35, 11·60, and 12·20 μ (in CCl_4). The recorded spectrum [17] is not sufficiently clear to enable the identity of this compound to be established with certainty.

Alkylfluoranthene(?).* An eluate from paper chromatograms showed maxima at 238, 247, 255, 263, 274, 290, 311, 325, 346, and 360 mμ. The general shape of the spectrum corresponded closely to that of fluoranthene, and further identification was not attempted.

4-*Methylbiphenyl.** Isolated by gas–liquid chromatography, it gave infrared maxima at 3·22, 3·31, 5·07, 5·24, 5·28, 5·31, 5·48, 5·60, 5·70, 6·20, 6·70, 6·84, 6·92, 7·20, 7·50, 7·84, 8·46, 9·32, 9·55, 9·70, 9·90, 10·1, 10·9, 11·1, 11·3, and 11·7 μ (in CCl_4 soln.), in substantial agreement with the recorded spectrum.

2-*Methylstyrene*(?).* Isolated by gas–liquid chromatography, it gave infrared maxima at 3·28, 3·38, 3·42, 3·62, 5·10, 5·20, 5·30, 5·42, 5·83, 6·10, 6·30, 6·40, 6·60, 6·70, 6·90, 7·00, 7·10, 7·20, 7·55, 7·80, 8·30, 8·44, 8·57, 8·60, 8·92, 9·10, 9·70, 9·80, 10·1, and 11·0 μ (in CCl_4). The general appearance of the spectrum corresponded to that of an alkylstyrene but differed from the spectra of α- and β-methylstyrene.

Acenaphthylene. Isolated by gas–liquid chromatography it gave ultraviolet maxima at 265, 308, 324, 333, and 340 mμ.

Bibenzyl. Its infrared spectrum (in CCl_4) showed maxima at 2·40, 3·24, 3·35, 3·45, 5·11, 5·29, 5·53, 5·65, 5·92, 6·74, 6·90, 7·24, 7·50, 8·52, 9·30, 9·75, 10·84, and 11·3 μ. Bands at 7·00 and 7·04, and reinforcement of the band at 3·24 μ (traces of biphenyl) were also observed.

Fluorene. Isolated by gas–liquid chromatography it showed ultraviolet absorption maxima at 261, 290, and 301 mμ.

2-*Phenylnaphthalene.* A sample from the gas–liquid chromatogram showed absorption maxima at 250 and 295 mμ. The identification was confirmed by comparison with an authentic specimen on acetylated paper.

Stilbene. This was identified by comparison of its retention time with that of an authentic specimen. A sample isolated from an extract from paper chromatograms by microsublimation had m. p. and mixed m. p. 119—124°.

Phenanthrene. Isolated after chromatography on a column of partially acetylated cellulose, this had absorption maxima at 243, 252, 274, 281, and 294 mμ. It had m. p. and mixed m. p. 98—100°.

Anthracene. This was identified by chromatography on a column of partially acetylated

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[17] Cannon and Sutherland, *Spectrochim. Acta*, 1951, **4**, 373.

cellulose followed by paper chromatography. It could not be obtained free from traces of phenanthrene, but showed the characteristic long-wavelength bands at 340, 357, and 376 mμ. Subsequent analysis on a 90 cm. column of partially acetylated cellulose (34—36% acetyl) gave almost pure anthracene, showing maxima at 252, 308, 323, 339, 356, and 376 mμ.

Alkylanthracene (?).* An extract from paper chromatograms (ethylbenzene pyrolysis) showed absorption maxima at 255, 342, 360, 380 mμ, consistent with those of an anthracene derivative.

Alkylphenanthrene (?).* Very small amounts of a compound related to phenanthrene were found in fractions obtained by chromatography on a column of partially acetylated cellulose (ethylbenzene and propylbenzene pyrolyses). An extract from paper chromatograms showed maxima at 244, 254, 276, 283, and 297 mμ, but further identification was not possible.

9-*Phenylanthracene*.* An extract from paper chromatograms showed maxima at 258, 346, 366, and 385 mμ; but the spectrum in the 220—280 mμ region was complicated by the presence of impurities. The identification was confirmed by the fluorescence spectrum which was identical with that of an authentic specimen.

Pyrene. An extract from the paper chromatogram showed maxima at 231, 242, 252, 262, 272, 305, 318, and 335 mμ. Traces of phenanthrene were difficult to remove from this compound but chromatography on a 90 cm. column of partially acetylated cellulose (34% acetyl) gave a relatively pure compound showing no extraneous absorption in the 220—360 mμ region.

Fluoranthene. A sample isolated by chromatography on a column of partially acetylated cellulose was purified by microsublimation and had m. p. and mixed m. p. 106—108°, $\lambda_{\max.}$ 237, 245, 253, 262, 272, 288, 309, 324, 343, and 359 mμ.

1,1′-*Binaphthyl.* An extract from paper chromatograms showed maxima at 221, 284, and 295 mμ.

2,2′-*Binaphthyl.* An extract from paper chromatograms was purified by microsublimation and had m. p. 178—182° (lit., 188°), $\lambda_{\max.}$ 254 and 308 mμ.

Triphenylene. An extract from paper chromatograms showed absorption maxima at 250, 257, 274, 286, 316, 331, and 340 mμ.

1,2-*Benzofluorene.* An extract from paper chromatograms showed absorption maxima at 253, 262, 293, 302, 316, 328, and 342 mμ (cf. ref. 18).

2,3-*Benzofluorene.* An extract from paper chromatograms showed absorption maxima at 255, 263, 272, 284, 303, 318, 334, and 340 mμ.

1,2-*Benzanthracene.* Isolated by chromatography on a column of partially acetylated cellulose this compound had m. p. and mixed m. p. 156—158°, $\lambda_{\max.}$ 227, 254, 267, 278, 289, 300, 315, 326, 341, and 358 mμ.

Chrysene. Isolated by chromatography on a column of partially acetylated cellulose this was recrystallised and had m. p. and mixed m. p. 253—255°, $\lambda_{\max.}$ 242, 258, 268, 283, 294, 306, 320, 344, 350, and 361 mμ.

Alkylchrysene. An extract from paper chromatograms had an ultraviolet absorption spectrum similar in appearance to that of chrysene, but with maxima at 243, 260, 271, 296, 307, 322, 352, and 363 mμ.

3,4-*Benzofluoranthene.* Isolated by chromatography on a column of partially acetylated cellulose this had m. p. and mixed m. p. 162—165°, $\lambda_{\max.}$ 238, 256, 266, 276, 289, 293, 301, 320, 338, 350, and 369 mμ.

10,11-*Benzofluoranthene.* An extract from paper chromatograms showed maxima at 226, 242, 282, 292, 308, 318, 332, 344, 365, 376, and 383 mμ (cf. ref. 19).

11,12-*Benzofluoranthene.* Identified after chromatography on a column of partially acetylated cellulose, this showed absorption maxima at 240, 269, 283, 297, 308, 361, 383, and 401 mμ. The fluorescence spectrum of an extract from paper chromatograms was identical with that of an authentic specimen and showed maxima at 409, 432, 467, and 500 mμ.

1,2-*Benzopyrene.* An extract of paper chromatograms showed maxima at 237, 257, 267, 278, 289, 304, 317, 332, and 366 mμ (cf. ref. 19), but the compound could not be obtained free from traces of perylene (maxima at 405 and 434 mμ).

3,4-*Benzopyrene.* Isolated by chromatography on a column of partially acetylated

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[18] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951.

[19] Clar, "Aromatische Kohlenwasserstoffe," Springer, Berlin, 2nd edn., 1952.

cellulose, followed by recrystallisation and microsublimation, this had m. p. and mixed m. p. 173—175°, $\lambda_{max.}$ 254, 264, 273, 279, 284, 296, 347, 364, 384, and 404 mμ.

Perylene. An extract from paper chromatograms showed the typical long-wavelength absorption spectrum for perylene with maxima at 366, 386, 405, and 434 mμ; but the complete spectrum could not be obtained. The fluorescence spectrum of an extract purified by repeated paper chromatography showed bands at 445, 475, and 502 mμ in agreement with those of an authentic specimen.

1,12-*Benzoperylene.* An extract obtained by chromatography on alumina was purified through the picrate, and the recovered material was chromatographed on acetylated paper. An extract showed maxima (in C_6H_6) at 292, 304, 332, 348, 368, and 389 mμ.

1,2:5,6-*Dibenzanthracene.* An extract from paper chromatograms showed maxima at 230, 276, 287, 297, 320, 334, and 347 mμ.

3,4:8,9-*Dibenzopyrene.** This was isolated (propylbenzene pyrolysis) by chromatography on a column of partially acetylated cellulose, and had m. p. 298—304° (lit., 308°). Its ultraviolet absorption spectrum showed maxima at 242, 256, 264 (in EtOH), or 291, 301, 314, 379, 401, 424, and 452 mμ (in C_6H_6) (cf. ref. 19).

3,4:9,10-*Dibenzopyrene.** An extract from paper chromatograms (propylbenzene pyrolysis) showed absorption maxima at 221, 243, 272, 283, 294, 314, 330, 352, 372, and 393 mμ.

2,3-(o-*Phenylene*)*pyrene.* Isolated by chromatography on partially acetylated cellulose, this had m. p. 157—159° (lit., 163—164°). Its ultraviolet absorption showed maxima at 246, 251, 269, 274, 292, 304, 316, 360, 376, 385, and 406 mμ (cf. ref. 11). On acetylated paper it had R_F 1·6 relative to 3,4-benzopyrene and appeared as a bright yellow fluorescent spot under ultraviolet light.

3,4-*Benzotetraphene.* An extract from paper chromatograms showed maxima (in C_6H_6) at 291, 307, 332, 350, 367, and 392 mμ. It appeared as a blue-violet fluorescent spot on paper chromatograms under ultraviolet light, and had R_F 1·8 relative to 3,4-benzopyrene.

4,5-(o-*Phenylene*)*fluoranthene.* Isolated after chromatography ona cetylated cellulose, this had m. p. 257—259° (lit., 261—262°) and its ultraviolet absorption spectrum had maxima at 253, 263, 271, 276, 282, 287, 293, 316, 367, 380, 387, 401, and 410 mμ (cf. ref. 19).

Anthanthrene. This was identified by its characteristic absorption bands in the long-wavelength region at 401, 407, 421, and 431 mμ.

Ultraviolet Spectra.—Unless otherwise specified all ultraviolet spectra were determined for 95% EtOH solution with an Optica CF_4 recording spectrophotometer.

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