323. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part V.* The Pyrolysis of* 1-*Phenylbuta*-1 : 3-*diene.*

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Pyrolysis of 1-phenylbuta-1 : 3-diene at 700° yields naphthalene, diphenyl, fluoranthene, phenanthrene, triphenylene, 1 : 2-benzanthracene, 9-phenylphenanthrene, 2(?)-phenylphenanthrene, 4(?)-phenylphenanthrene, chrysene, 3 : 4-benzofluoranthene, and 3 : 4-benzopyrene. Mechanisms for their formation are suggested.

The wide occurrence of 3 : 4-benzopyrene and of other carcinogenic hydrocarbons in smoke, soot, tar, and other similar materials has been clearly established. The mode of formation of 3 : 4-benzopyrene at high temperatures is therefore of some importance and a mechanism has been tentatively advanced.[1] It was suggested that this molecule may be built up from relatively simple components, and a detailed analysis of the tar formed by the pyrolysis of styrene has already been reported.[2] As a further contribution, the pyrolysis of 1-phenylbuta-1 : 3-diene has been undertaken.

The pyrolysis was carried out by passing phenylbutadiene vapour, with nitrogen, through a silica tube filled with porcelain chips, at 700°. Much of the material was decomposed to gaseous products, among which only methane and ethylene have been identified with certainty. These compounds, together with hydrogen, seem to be formed in nearly all pyrolyses of hydrocarbons, regardless of their structure, and their presence therefore gives little indication of the mechanism. The tar which was also obtained (in 29% yield) was collected and analysed by chromatography on alumina, gas-liquid partition chromatography, chromatography on acetylated paper,[3] and by spectroscopy. The following compounds were identified in this tar (% by wt. in parentheses): Naphthalene (67·2), diphenyl (5·2), fluoranthene (3·7), phenanthrene (13·3), triphenylene (0·83), 1 : 2-benzanthracene (0·89), 9-phenylphenanthrene (0·13), 4(?)-phenylphenanthrene (0·15), 2(?)-phenylphenanthrene (0·29), chrysene (1·33), 3 : 4-benzofluoranthene (0·78), 3 : 4-benzopyrene (0·12), " compound I " (0·41).

Naphthalene was the only substance identified by Liebermann and Ruber [4] following pyrolysis of phenylbutadiene in a glowing tube. No unchanged material could be detected, a fact of some importance. A C_6–C_4 substance has been postulated [1] as an intermediate in the conversion of acetylene, of butadiene, and of styrene into 3 : 4-benzopyrene. Phenylbutadiene is a typical C_6–C_4 compound, but this was not detected among the products of the pyrolysis of styrene.[2] However, it seems clear from the present work that phenylbutadiene is too readily decomposed, or cyclised, to survive a pyrolysis, and its absence from the products of pyrolyses of acetylene, butadiene, styrene, and similar compounds is not unexpected.

It is generally accepted that the reactions involved in the pyrolysis of hydrocarbons are predominantly radical in nature, and the products formed in pyrolysis of styrene at 710° can be satisfactorily explained on this basis.[2] Radicals have been detected by mass spectrometry in the pyrolysis of a number of aromatic compounds,[5] and the presence of the benzyl radical has been conclusively demonstrated [6] in the photolysis of toluene and ethylbenzene.

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* Part IV, *J.*, 1958, 2458.

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

[2] Badger and Buttery, *J.*, 1958, 2458.

[3] Spotswood, *J. Chromatography*, 1959, **2**, 90.

[4] Liebermann and Ruber, *Ber.*, 1902, **35**, 2696.

[5] Ingold and Lossing, *Canadian J. Chem.*, 1953, **31**, 30; Lossing, Ingold, and Henderson, *J. Chem. Phys.*, 1954, **22**, 621; Farmer, Lossing, Marsden, and McDowell, *J. Chem. Phys.*, 1956, **24**, 52; Steacie, " Atomic and Free Radical Reactions," 2nd edn., Reinhold, New York, 1954.

[6] Porter and Wright, *Trans. Faraday Soc.*, 1955, **51**, 1469.

The bond-dissociation energies for the carbon–hydrogen bonds in phenylbutadiene have not been determined, but by analogy with other compounds it seems likely that scission should occur preferentially as indicated by reaction (1). Cyclisation of the phenylbutadiene radical would then give naphthalene. The same compound could conceivably arise by direct cyclisation of phenylbutadiene with elimination of a molecule of hydrogen. In any case, naphthalene would be expected as a major product, and this has been found experimentally.

$$\mathrm{Ph{\cdot}CH{:}CH{\cdot}CH{:}CH_2} \longrightarrow \mathrm{Ph{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}} + \mathrm{{\cdot}H} \quad \ldots\ldots\ldots \quad (1)$$

$$\mathrm{Ph{\cdot}CH{:}CH{\cdot}CH{:}CH_2} \longrightarrow \mathrm{Ph{\cdot}} + \mathrm{{\cdot}CH{:}CH{\cdot}CH{:}CH_2} \quad \ldots\ldots\ldots \quad (2)$$

$$\mathrm{Ph{\cdot}CH{:}CH{\cdot}CH{:}CH_2} \longrightarrow \mathrm{Ph{\cdot}CH{:}CH{\cdot}} + \mathrm{{\cdot}CH{:}CH_2} \quad \ldots\ldots\ldots \quad (3)$$

Carbon–carbon single bonds are known to have much smaller dissociation energies than carbon–carbon double bonds,[7] and with phenylbutadiene there are two single bonds in the side chain which could be broken. The bond orders have accordingly been determined by the M.O. method and the values are $\mathrm{Ph}\overset{1{\cdot}437}{\text{—}}\mathrm{CH{=}CH}\overset{1{\cdot}477}{\text{—}}\mathrm{CH{=}CH_2}$. These orders indicate that there may be very little difference in the bond-dissociation energies of the two single bonds in the diene side chain. Nevertheless, the bond between the aromatic nucleus and the side chain does have a lower order, and it may be tentatively concluded that scission of this bond would be preferred, leading to reaction (2). The alternative scission to a styrene radical and an ethylene radical (reaction 3) would also be expected. However, this reaction cannot be of major importance for, if it were, the products of pyrolysis would be similar to those obtained from styrene [2] and this is not the case. For example, no dibenzyl, stilbene, toluene, or styrene could be detected.

The validity of this approach in establishing the nature of the radical fragments formed at high temperatures may be questioned. At the high temperatures involved many of the molecules will be in an excited state and the calculated bond orders may be meaningless. Nevertheless, on this basis, the major initial components of the pyrolysis would be: naphthalene, $\mathrm{Ph{\cdot}}$, $\mathrm{Ph{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}}$, $\mathrm{CH_2{:}CH{\cdot}CH{:}CH{\cdot}}$, and hydrogen, and the other products identified in the resulting tar can all be accounted for by secondary reactions involving these initial products.

Diphenyl could be produced by a chain-propagating reaction involving a phenyl radical and a phenylbutadiene molecule, or by a chain-terminating reaction involving two phenyl radicals. It may be noted that diphenyl is a product of the thermal [8] and photochemical [9] decomposition of tetraphenyl-lead, and it is also formed by the action of sodium on bromobenzene.[10] In all these cases a recombination of phenyl radicals seems probable.

In recent years the reaction of radicals with aromatic hydrocarbons has received some attention. With methyl radicals [11] the logarithms of the rate constants for reactions with different hydrocarbons are linearly related to the minimum localisation energies for the probable positions of attack in these molecules. Similar relationships have been derived for the positions of maximum free valency, for the singlet–triplet excitation energies, and for the polarographic half-wave reduction potentials.[12] Naphthalene, diphenyl, pyrene, and anthracene have already been shown to undergo radical attack at the positions of maximum free valency or lowest atom localisation energy.[13] In the present experiments, therefore, it seems likely that the aromatic hydrocarbons formed will also undergo attack by radicals and that the preferred positions of attack will be those of maximum free valency

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[7] Braude and Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955; Szwarc, *Chem. Revs.*, 1950, **47**, 75.

[8] Dull and Simons, *J. Amer. Chem. Soc.*, 1933, **55**, 3898, 4328.

[9] Leighton and Mortensen, *J. Amer. Chem. Soc.*, 1936, **58**, 448.

[10] Horn and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 199; *Z. phys. Chem.*, 1934, *B*, **25**, 151.

[11] Szwarc, *J. Phys. Chem.*, 1957, **61**, 40.

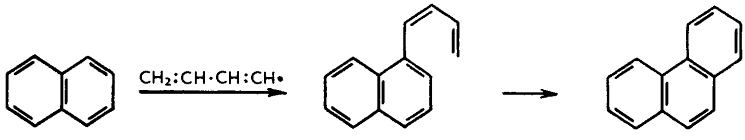
[12] Matsen, *J. Chem. Phys.*, 1956, **24**, 602.

[13] Davies, Hey, and Williams, *J.*, 1958, 1878; Cadogan, Hey, and Williams, *J.*, 1954, 794; Norman, Thompson, and Waters, *J.*, 1958, 175; Beckwith and Waters, *J.*, 1957, 1001.

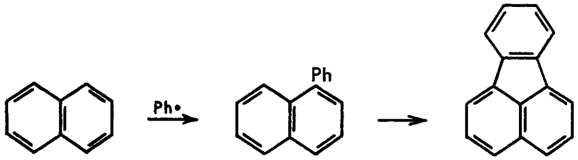
and minimum localisation energy. However, at the high temperature involved a proportion of the molecules may react in an excited state and the positions of substitution may not be as specific as expected from the differences in the localisation energies.

Thus, attack by a butadienyl radical at the 1-position of naphthalene, followed by cyclisation, would give phenanthrene (reaction 4), and this is a major product of the pyrolysis. Similar attack at the 2-position of naphthalene, followed by cyclisation, would also give phenanthrene and perhaps some anthracene. The latter has not been detected, but its absence is not significant in view of its known tendency to undergo further reaction at high temperatures.[14]

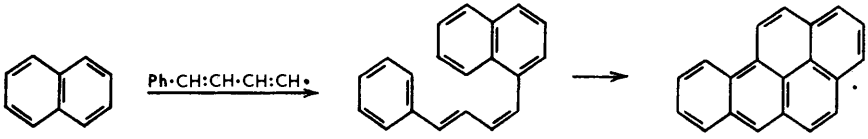
Attack by phenyl radicals on naphthalene would be expected to yield 1-phenylnaphthalene as the major product. This hydrocarbon was not identified in the tar, but it is known to undergo cyclodehydrogenation to fluoranthene,[15] and this substance was present in relatively large amount (reaction 5). A small amount of 2-phenylnaphthalene might also be expected by this process, but was not detected. Its absence is noteworthy,



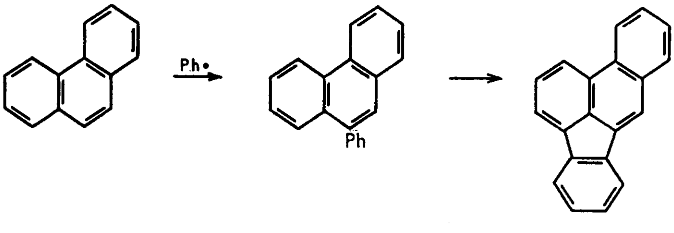
(4)



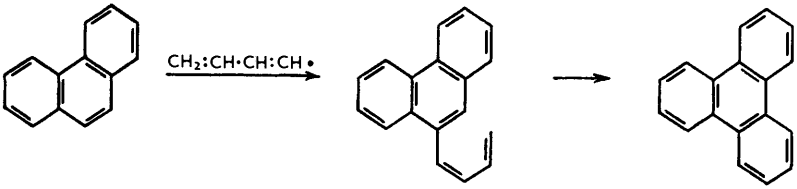
(5)



(6)



(7)



(8)

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[14] Kinney and Debel, *Ind. Eng. Chem.*, 1954, **46**, 548.

[15] Orchin and Reggel, *J. Amer. Chem. Soc.*, 1947, **69**, 505.

for it was a major product of the thermal decomposition of styrene,[2] but in the latter case its presence can be explained by a different mechanism.

In the same way the attack of a phenylbutadienyl radical at the 1-position of naphthalene, followed by *cyclo*dehydrogenation of the product, would be expected to give 3 : 4-benzopyrene (reaction 6), which was also identified in the tar. This reaction was postulated in Part I of the present series.[1] Cyclisations of this type are certainly known to occur [16] and cyclodehydrogenation of 1-4′-phenylbutylnaphthalene has been shown to yield 3 : 4-benzopyrene and other products.[17]

Phenanthrene is formed in relatively large amount in the present pyrolysis, so that attack by radicals on this hydrocarbon might also be expected. It seems likely that the 9-position would be the preferred position for attack. However, calculation of the atom localisation energies for the various positions in phenanthrene, by Dewar's simplified method,[18] shows that the differences between these positions are considerably less than that between the 1- and the 2-position of naphthalene.

Attack by phenyl radicals would therefore give 9-phenylphenanthrene and perhaps other phenylphenanthrenes. 9-Phenylphenanthrene has been conclusively identified, as well as 3 : 4-benzofluoranthene which could arise from it by cyclodehydrogenation (reaction 7). Two other phenylphenanthrenes were also detected. These are provisionally regarded as the 2- and the 4-isomer, but their orientation has not been established beyond doubt.

In the same way, substitution of phenanthrene by butadienyl radicals followed by cyclisation of the various products would yield triphenylene (reaction 8), chrysene, 1 : 2-benzanthracene, and 3 : 4-benzophenanthrene. With the exception of 3 : 4-benzophenanthrene (which has a non-planar structure and is doubtless less stable), all these compounds have been identified in the tar.

These mechanisms offer a coherent explanation for the formation of the observed products, but they do not exhaust the possibilities and alternative mechanisms could occur simultaneously with the above.

In a study of the cracking of hydrocarbon oils, Weizmann *et al.*[19] suggested that condensation may be effected by a Diels–Alder addition of a butadiene molecule to aromatic hydrocarbons, followed by dehydrogenation. However, this type of mechanism cannot satisfactorily explain all the present results. On the basis of a Diels–Alder addition, the aromatic bond having the lowest bond localisation energy (or highest bond order) should be involved. The 9 : 10-bond of phenanthrene is known to have pronounced double-bond character, and Diels–Alder addition of butadiene to phenanthrene would be expected to give triphenylene as the major product. In fact, however, this is not formed in large amount. Moreover, it is very difficult to explain the formation of fluoranthene and 3 : 4-benzofluoranthene on Weizmann's theory, as no acenaphthene could be detected.

For the present purpose the mechanism of the formation of 3 : 4-benzopyrene is of paramount importance. If a Diels–Alder addition mechanism is assumed, then butadiene would have to react with pyrene, and both 3 : 4- and 1 : 2-benzopyrene would be expected. It is noteworthy, however, that neither pyrene nor 1 : 2-benzopyrene could be identified in the tar resulting from the pyrolysis of phenylbutadiene.

Authentic specimens of most of the compounds identified in the present tar were available for direct comparison of retention times (in gas–liquid chromatography), of R_F values (in chromatography on acetylated paper), and of spectra. 3 : 4-Benzofluoranthene was, however, synthesised by dehydrohalogenation of 9-(2′-chlorobenzylidene)fluorene with potassium hydroxide in quinoline.

The bond orders in phenylbutadiene have been calculated by the molecular orbital

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[16] Hansch, *Chem. Revs.*, 1953, **53**, 353; Cook and Robinson, *J.*, 1940, 303.

[17] Badger and Kimber, *J.*, 1958, 2455.

[18] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.

[19] Weizmann *et al.*, *Ind. Eng. Chem.*, 1951, **43**, 2312, 2318, 2322, 2325.

method. Previous calculations [20] on this molecule have been confined to the determination of the energy levels of the orbitals. The eigenvalues and the eigenvectors of the secular matrix have now been determined by the usual methods, equal Coulomb and resonance integrals being assumed, and overlap neglected, and the bond orders calculated from the relationship

$$p_{rs} = \sum_j n_j c_{rj} c_{sj}$$

The resonance energy is found to be 2·9323β.

EXPERIMENTAL

Pyrolysis of 1-*Phenylbuta*-1 : 3-*diene at* 700°.—1-Phenylbuta-1 : 3-diene [21] (n_D^{20} 1·6070; 70 g.) was vaporised at 7 g./hr. in a flash-evaporator (kept at 400°) and carried with a stream of nitrogen (1 c.c./sec.) through a silica tube (40″ × $\frac{3}{4}$″ internal diam.) packed with porcelain chips ($\frac{1}{4}$″—$\frac{1}{2}$″), kept at 700°.[1] The product was a semi-solid mass (18 g.), but carbon (3 g.) was deposited in the tube and there was a non-volatile residue (3 g.) in the evaporator. The remainder of the material appeared in the exit gases, which burnt with a luminous flame.

The product gave no distillate when heated at 120°/18 mm. and was therefore chromatographed in hexane on a column (50 × 5 cm.) of type H activated alumina. Elution was with hexane followed by hexane–benzene mixtures containing increasing amounts of benzene. The 120 fractions collected were evaporated, and the residues chromatographed on acetylated paper, by the ascent method, ethanol–toluene–water (17 : 4 : 1, v/v) being used as developing solvent.[3] The positions of fluorescent compounds were determined by viewing the papers under ultraviolet light. After these spots had been marked, the papers were sprayed with 2% tetrachlorophthalic anhydride in acetone-chlorobenzene (10 : 1; v/v) and again examined under ultraviolet light. Under these conditions all the non-fluorescent compounds tested (with the exception of naphthalene and its simple derivatives) gave bright yellow or orange spots. Some weakly-fluorescent compounds also gave yellow spots, and a number of the more strongly fluorescent compounds (*e.g.*, pyrene and perylene) gave orange spots after prolonged heating of the sprayed paper. With these paper chromatograms as a guide the various fractions were then re-combined to give seven major fractions each of which was separately analysed.

Analysis of Exit Gases.—The infrared spectrum of the exit gases showed the presence of several hydrocarbons. Methane was positively identified from the characteristic band system around 1300 cm.$^{-1}$, and ethylene from that around 950 cm.$^{-1}$.

Analysis by Gas–Liquid Chromatography.—Fraction 1 was analysed in a Griffin and George vapour-phase chromatographic apparatus. The column was packed with Apiezon L supported on Celite (40—80 mesh, B.S.S.; 1 : 4, w/w), and kept at 180°. Nitrogen (1 l./hr.; inlet pressure, 41 cm.; outlet pressure, 0·5 cm.) was used as carrier gas. Peaks corresponding to naphthalene (retention time, 6·4 min.) and diphenyl (retention time, 14·2 min.) were obtained in agreement with the times for authentic specimens. The diphenyl was collected and identified by infrared spectroscopy (see below), and the percentage composition of the fraction was determined by calculating the ratio of the areas under the peaks.

Analysis by Chromatography on Acetylated Paper.—Fractions 2—7 were analysed by chromatography on acetylated paper by the technique already described.[3] The papers were developed with methanol–ether–water (4 : 4 : 1, v/v) by the ascent method. Fluorescent compounds were located by observation under ultraviolet light, and non-fluorescent compounds by spraying a strip cut from the chromatogram with tetrachlorophthalic anhydride (see above). Spots were then cut out and extracted with ether in a small Soxhlet apparatus, the extracts evaporated, and the residues dissolved in 95% ethanol for ultraviolet spectrographic examination. To obtain sufficiently intense spectra, several chromatograms were combined, and the concentration of the ethanolic solution adjusted to give suitable optical density readings. In some cases, in order to obtain good separations, it was necessary to develop the papers by the descent method, and to allow the solvent-front to over-run the end of the paper. In cases of particular difficulty (*e.g.*, the separation of 3 : 4-benzopyrene and 3 : 4-benzofluoranthene), the spots were cut out, and the extracts rechromatographed on acetylated paper, the descent method being used with extended development time.

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[20] Syrkin and Diatkina, *Acta Physicochem. U.R.S.S.*, 1946, **21**, 641 (*Chem. Abs.*, 1947, **41**, 1648); Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 4077.

[21] Grummitt and Becker, *Org. Synth.*, 1950, **30**, 75.

The percentage composition of each fraction was determined by calculating the weight present in each extract from the observed optical density at several wavelengths, and comparing them with the recorded extinction coefficients. Although the effect of background absorption is appreciable, the relative amounts of the components in a mixture could thus be determined with reasonable precision.

The results of the analysis of 12·5 g. of tar are summarised as follows: fraction 2 (1·5 g.), phenanthrene and fluoranthene; fraction 3 (0·5 g.), fluoranthene, phenanthrene, and triphenylene; fraction 4 (0·2 g.), triphenylene, fluoranthene, 1 : 2-benzanthracene, and 9-phenylphenanthrene; fraction 5 (0·24 g.), chrysene, 4(?)-phenylphenanthrene, 1 : 2-benzanthracene, 3 : 4-benzopyrene, 3 : 4-benzofluoranthene, and " compound I "; fraction 6 (0·18 g.), 3 : 4-benzofluoranthene, 1 : 2-benzanthracene, 3 : 4-benzopyrene, 2(?)-phenylphenanthrene, and " compound I "; and fraction 7 (0·1 g.), not identified.

Details of Identification.—Naphthalene. This was isolated from fraction 1 by repeated sublimation. It had m. p. 80°, not depressed by admixture with an authentic specimen.

Diphenyl. This was isolated after gas–liquid chromatography of fraction 1. After recrystallisation from ethanol it had m. p. and mixed m. p. 68—70°; $\nu_{\max.}$ (in Nujol mull) 5·10, 5·25, 5·41, 5·50, 5·68, 5·82, 6·00, 6·12, 6·58, 7·21, 7·40, 7·60, 7·82, 8·42, 8·50, 8·61, 8·95, 9·12, 9·28, 9·58, 9·90, 11·08, 11·90, 12·80, 13·7, and 14·8 μ. An authentic specimen showed the same maxima, but the 12·80 μ maximum was less pronounced.

Fluoranthene. This was identified by comparison of its behaviour on acetylated paper with an authentic specimen. An extract prepared from paper chromatograms showed $\lambda_{\max.}$ 236, 245, 262, 276, 287, 323, 342, and 360 mμ characteristic of fluoranthene,[22] and $\lambda_{\max.}$ 257, 273, and 302 mμ due to traces of triphenylene.

Phenanthrene. Extracts of spots obtained in paper chromatograms showed $\lambda_{\max.}$ 242, 251, 274, 280, 293, 318, 330, 336, and 346 mμ, in good agreement with recorded values for phenanthrene.[22] Repeated recrystallisation of fraction 3 from ethanol and chromatography of the product on alumina gave crystalline material, m. p. and mixed m. p. 99—101°.

Triphenylene. This was identified by comparison with an authentic specimen on acetylated paper. An extract showed $\lambda_{\max.}$ 250, 257, 274, 286, 302, 316, 332, and 340 mμ, in good agreement with values in the literature.[22]

1 : 2-*Benzanthracene.* This was identified by comparison with an authentic specimen on acetylated paper. An extract showed $\lambda_{\max.}$ 227, 254, 267, 277, 288, 300, 315, 326, 341, and 358 mμ, in good agreement with recorded values.[22]

9-*Phenylphenanthrene.* This was identified by comparison with an authentic specimen on acetylated paper. An extract showed $\lambda_{\max.}$ 236 and 253 mμ with a point of inflexion at 296 mμ, in good agreement with the literature.[22]

4(?)-*Phenylphenanthrene.* An extract from a paper chromatogram showed $\lambda_{\max.}$ 229, 237, 254, 270, 290, and 335 mμ. These values are in good agreement with those obtained from the curve given by Campbell [23] for this compound, and the shapes of the two curves were similar.

2(?)-*Phenylphenanthrene.* An extract from a paper chromatogram showed $\lambda_{\max.}$ 258, 265, 292, 302, and 340 mμ. With the exception of the 340 mμ peak, these values are in good agreement with those recorded for 2-phenylphenanthrene; [22] but as this peak was retained even after further chromatography on acetylated paper its identification is in some doubt. 3-Phenylphenanthrene has not been described and its absorption spectrum may be similar to that of 2-phenylphenanthrene.

Chrysene. This was identified by comparison with an authentic specimen on acetylated paper. An extract showed $\lambda_{\max.}$ 242, 258, 268, 283, 294, 306, 320, 344, 350, and 361 mμ, together with a point of inflexion at 333 mμ, in good agreement with recorded values.[22] Chromatography of fraction 5 on alumina, followed by repeated recrystallisation of the product from ethanol, gave chrysene, m. p. and mixed m. p. 253—254°.

3 : 4-*Benzofluoranthene.* This was identified by comparison with an authentic specimen on acetylated paper. An extract showed $\lambda_{\max.}$ 238, 256, 266, 276, 290, 301, 320, 338, 350, and 369 mμ in good agreement with the recorded values [22] with the exception of the peak at 290 mμ which should show a double peak at 289 and 293 mμ.

3 : 4-*Benzopyrene.* Initial identification of this compound was made by comparison of the

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[22] Clar, " Aromatische Kohlenwasserstoffe," 2nd edn., Springer-Verlag, Berlin, 1952; Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951.

[23] Campbell, *J.*, 1954, 3659.

fluorescence spectrum [1] of an extract from a paper chromatogram with that of an authentic specimen: the spectra were identical. The extract was twice rechromatographed on acetylated paper and an extract in 95% ethanol showed $\lambda_{\max.}$ 254, 264, 273, 279, 284, 296, 347, 364, 384, and 404 mμ in good agreement with recorded values.[22] The identity of the compound was further confirmed by direct comparison with an authentic specimen on acetylated paper: 3 : 4-benzopyrene shows a highly characteristic intense violet fluorescent spot under ultraviolet light.

"*Compound* I." This compound showed a light blue fluorescence in solution and a yellow-green fluorescent spot on acetylated paper. An extract from a paper chromatogram showed $\lambda_{\max.}$ 258, 262, 274, 288, 316, 331, 360, and 366 mμ with points of inflexion at 300, 340, and 350 mμ. This spectrum suggests a phenanthrene derivative, but the substance has not been positively identified.

Synthesis of 3 : 4-*Benzofluoranthene.*—The following procedure is adapted from that in the patent literature.[24] Fluorene (16 g.) was added to a solution of sodium ethoxide [from sodium (4 g.)] in ethanol (250 c.c.), and the mixture heated to 75°. *o*-Chlorobenzaldehyde (14 g.) in ethanol (100 c.c.) was added dropwise with shaking, and the mixture refluxed for 30 min. Ethanol (300 c.c.) was then removed under reduced pressure, and the residue poured into water (400 c.c.). The benzene (200 c.c.) extract was washed with water, dried ($MgSO_4$), and evaporated. Chromatography on alumina, and elution with hexane, gave a yellow oil, b. p. 180°/0·7 mm. Recrystallisation from methanol gave 9-(*o*-chlorobenzylidene)fluorene (9·2 g., 30%), m. p. 69—70°.

A mixture of this product (1 g.), potassium hydroxide (3 g.), and quinoline (10 c.c.) was refluxed for 90 min., cooled, and poured into concentrated hydrochloric acid (150 c.c.). The benzene (100 c.c.) extract was washed with water, dilute aqueous sodium carbonate, and water, then dried and evaporated. Chromatography on alumina and elution with hexane gave unchanged material (0·5 g.); further elution with benzene–hexane (1 : 2) gave 3 : 4-benzofluoranthene. After recrystallisation from ethanol it formed needles, m. p. 167° (210 mg.; 24%). Its benzene solution was strongly fluorescent and its ultraviolet absorption was identical with that recorded.[22]

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[24] B.P. 459,108; *Chem. Abs.*, 1937, **31**, 4136.