# 51. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part VI.*[1] *The Pyrolysis of Tetralin.*

By G. M. Badger and R. W. L. Kimber.

Pyrolysis of tetralin at 700° yields benzene, toluene, ethylbenzene, styrene, *o*-xylene, indene, naphthalene, 2-phenylnaphthalene, phenanthrene, anthracene, 1,2′- and 2,2′-binaphthyl, 1,2-benzofluorene, fluoranthene, 3,4-benzophenanthrene, 1,2-benzanthracene, pyrene, chrysene, perylene, 11,12-benzofluoranthene, and 3,4-benzopyrene. Mechanisms for their formation are suggested.

The carcinogenic hydrocarbon 3,4-benzopyrene (I) is very widely distributed in tars and in similar materials which have been produced at high temperatures. As a working hypothesis it has been suggested[2] that this hydrocarbon may be built from simple materials, and tetralin or a similar $C_6$–$C_4$ unit may be an intermediate in its formation. Interaction of two $C_6$–$C_4$ units (to give II), followed by cyclodehydrogenation, could give the 3,4-benzopyrene. 3,4-Benzopyrene is formed when tetralin is treated with aluminium chloride, followed by distillation of the tar,[3] but the mechanism of this process may be unlike those encountered at high temperatures. The pyrolysis of tetralin has now been undertaken.

The pyrolysis was carried out by passing tetralin vapour, with nitrogen, through a silica tube filled with porcelain chips, at 700°.[2] Some gases were produced and methane and ethylene were identified. The semi-solid tar formed (in 72·5% yield) was collected and analysed by distillation, chromatography on alumina, gas–liquid partition chromatography, chromatography on acetylated paper,[4] and by spectroscopy. The following compounds were identified in this tar (% composition w/w in parentheses): Benzene (2·28), toluene (0·86), ethylbenzene (0·34), styrene and *o*-xylene (0·86), indene (3·72), tetralin (1·43), naphthalene (74·4), 1- and 2-methylnaphthalene (?) (0·14), biphenyl (?) (0·02), 2-phenylnaphthalene (0·14), phenanthrene (0·15), anthracene (0·29), 1,2′-binaphthyl (0·58), 2,2′-binaphthyl (1·33), 1,2-benzofluorene (0·04), fluoranthene (0·04), 3,4-benzophenanthrene (0·79), 1,2-benzanthracene (2·6), pyrene (0·008), chrysene (3·43), perylene (0·25), 11,12-benzofluoranthene (0·27), and 3,4-benzopyrene (0·17). It may be noted that (apart from naphthalene and tetralin), no $C_6$–$C_4$ compound could be detected in the tar. The absence of such a compound is not however significant, as it would be expected to

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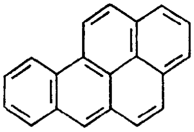
[1] Part V, Badger and Spotswood, *J.*, 1959, 1635.
[2] Badger, Buttery, Kimber, Lewis, Moritz, and Napier, *J.*, 1958, 2449.
[3] Badger and Kimber, *J.*, 1958, 2453.
[4] Spotswood, *J. Chromatography*, 1959, **2**, 90; 1959, in the press.

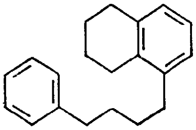
react further; no butylbenzene [5] or 1-phenylbuta-1,3-diene [1] remained unchanged after pyrolysis of these compounds at 700°, for example.

As expected, naphthalene is the major product of this pyrolysis, being formed by dehydrogenation of tetralin. Some binaphthyl was also formed, presumably by a dehydrogenation mechanism involving a dimerisation of either naphthyl radicals or tetralyl radicals (followed in the latter case by further dehydrogenation). Similarly, 11,12-benzofluoranthene (III) is probably formed by cyclodehydrogenation of 1,2′-binaphthyl, and perylene (IV) by the cyclodehydrogenation of 1,1′-binaphthyl.[6]

By analogy with other compounds for which determinations are available, it seems likely that the carbon–carbon single bonds in tetralin all have bond dissociation energies of about 80 kcal./mole.[7] These bonds should therefore undergo ready scission at 700° to give the following radicals: $Ph\cdot$, $Ph\cdot CH_2\cdot$, $Ph\cdot CH_2\cdot CH_2\cdot$, $Ph\cdot CH_2\cdot CH_2\cdot CH_2\cdot$, $Ph\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot$, $Me\cdot C_6H_4\cdot CH_2\cdot$, $Et\cdot C_6H_4\cdot CH_2\cdot$, $Et\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot$, and $Pr^n\cdot C_6H_4\cdot CH_2\cdot$, together with their counterparts in which the odd electron is located at alternative carbon atoms.

Reaction of hydrogen with the radicals $Ph\cdot$, $Ph\cdot CH_2\cdot$, $Ph\cdot CH_2\cdot CH_2\cdot$, and $Me\cdot C_6H_4\cdot CH_2\cdot$ would account for the presence of benzene, toluene, ethylbenzene, and *o*-xylene; styrene would be obtained from $Ph\cdot CH_2\cdot CH_2\cdot$ or ethylbenzene by dehydrogenation. The absence of the corresponding products from the other radicals suggests that these undergo very ready cyclisation or further scission. Indene could be formed by cyclisation of radicals $Ph\cdot CH_2\cdot CH_2\cdot CH_2\cdot$ and $Et\cdot C_6H_4\cdot CH_2\cdot$; it may be noted that the pyrolysis of propylbenzene gives very little indene.[5]


(I)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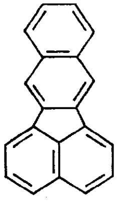
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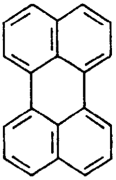
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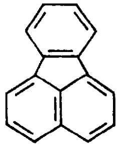
(V)

Biphenyl is evidently formed by the dimerisation of two phenyl radicals. 2-Phenylnaphthalene could be formed by the phenylation of naphthalene, or by the dimerisation of styrene (the pyrolysis of styrene gives 2-phenylnaphthalene in moderate yield [8]). The phenylation of naphthalene would be expected to give 1-phenylnaphthalene as the major product; this compound was not detected in the present tar, but its ultraviolet absorption spectrum is relatively unspecific, and its absence is not conclusive. In any case fluoranthene (V) was detected and this is known to be formed by the cyclodehydrogenation of 1-phenylnaphthalene.[9]

The substitution of naphthalene by benzyl radicals could also occur, and subsequent cyclodehydrogenation would give 1,2-benzofluorene. Similarly phenanthrene could arise by the dimerisation of two benzyl radicals to give bibenzyl, followed by cyclodehydrogenation. Two benzyl radicals could also give anthracene.

The pyrolysis of indene has long been known to give chrysene in good yield,[10] and the chrysene in the present tar could arise mainly from this source. It has recently been found,[11] however, that the pyrolysis of indene also produces significant amounts of 1,2-benzanthracene and 3,4-benzophenanthrene, both of which are present in the tetralin tar. The relative proportions of these compounds in the tetralin tar are not identical with those

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[5] Badger and Spotswood, unpublished.

[6] Hansch, *Chem. Reviews*, 1953, **53**, 353.

[7] Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954; Braude and Nachod, " Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955.

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

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

[10] Spilker, *Ber.*, 1893, **26**, 1538.

[11] Badger and Kimber, unpublished work.

found in the tar produced from indene itself, and it seems likely that chrysene, 1,2-benzanthracene, and 3,4-benzophenanthrene may also be produced by additional processes. The mechanism of the formation of these hydrocarbons from indene will be discussed in a future paper.

Only a very small amount of pyrene could be detected in the tetralin tar, and no convincing mechanism can be advanced for its formation. Weizmann *et al.*[12] suggested that the dimerisation of styrene could give pyrene; but this seems unlikely to be an important reaction as the pyrolysis of styrene gives such a poor yield of this polycyclic compound. Pyrene could conceivably be formed from phenanthrene and a $C_2$ hydrocarbon, and this possibility will be examined.

As suggested earlier in this series,[1,4] 3,4-benzopyrene could arise by interaction of $Ph\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot$ (or a similar radical) with tetralin to give (II), followed by cyclodehydrogenation. Its presence in the tetralin tar adds further weight to this view, but it does not exclude the possibility that 3,4-benzopyrene could also be formed from chrysene and a $C_2$ hydrocarbon or from 1,2-benzanthracene and a $C_2$ hydrocarbon. These possibilities will be explored.

## EXPERIMENTAL

*Tetralin.*—Technical tetralin (B.D.H.) was sulphonated and purified by Schroeter's[13] method to give a product of b. p. 100—101°/125 mm., $n_D^{14}$ 1·5453 (lit. $n_D^{20}$ 1·5451) which was free from naphthalene (tested by gas–liquid chromatography).

*Pyrolysis of Tetralin.*—Purified tetralin (100 g.) was vaporised (6 drops/min.) and passed with nitrogen (1 c.c./sec.) through a silica tube (36 in. × 1 in.) packed with porcelain chips (3/8—1/4 in.) which was maintained at 700° in an electrically heated furnace.[2] The resulting semi-solid tar (70 g.) was collected and a further quantity (0·5 g.) was obtained by washing the tube with chloroform followed by evaporation of the solvent. A final trap, cooled in solid carbon dioxide–ethanol, collected a further 2·0 g. of low-boiling material (fraction *a*). The exit gases decolorised bromine water and both neutral and alkaline permanganate, and samples were collected for examination by infrared spectroscopy. Distillation of the tar gave the following fractions: (*b*) b. p. 40—80°/14 mm. (0·8 g.); (*c*) b. p. 90—95°/14 mm. (56 g.); and (*d*) a residue (9 g.).

*Analysis by Gas–Liquid Chromatography.*—Low-boiling fractions were examined by gas–liquid chromatography, with use of a Griffin and George vapour-phase chromatographic apparatus (Mark II) modified to collect samples.[14] The column was packed with Apiezon L supported on Celite (40—80 mesh, B.S.S.; 1 : 4 w/w). The compounds were collected and identified by infrared spectroscopy, and the percentage compositions were determined from the areas under the peaks.

*Analysis by Chromatography on Acetylated Paper.*—Fractions of higher molecular weight were chromatographed by descent on acetylated paper[3] with ethanol–toluene–water (17 : 4 : 1). Fractions of similar composition (as judged by the spots under ultraviolet light) were combined and rechromatographed with larger amounts of material and development with either methanol–ether–water (4 : 4 : 1) or ethanol–toluene–water (17 : 4 : 1). After thorough drying of the paper the fluorescent spots were cut out and each was extracted with 95% ethanol. The positions of non-fluorescent spots were found by contact printing through the paper on Ilford Reflex Document Paper No. 50, an ultraviolet light source emitting 90% of the 2537 Å Hg line being used, and then these spots were likewise cut out and extracted. The ultraviolet spectra of the resulting solution were then determined with an Optica $CF_4$ Recording Spectrophotometer.

*Examination of Fractions* (*a*), (*b*), *and* (*c*).—These were analysed by gas–liquid chromatography. Fraction (*a*) contained benzene (1·6 g.) and toluene (0·4 g.). Fraction (*b*) contained toluene, ethylbenzene, styrene, *o*-xylene, and indene; and fraction (*c*) indene, tetralin, and naphthalene.

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[12] Weizmann *et al.*, *Ind. Eng. Chem.*, 1951, **43**, 2312, 2318.
[13] Schroeter, *Annalen*, 1921, **426**, 1.
[14] Napier and Rodda, *Chem. and Ind.*, 1958, 1319.

*Examination of Residue.*—The residue (fraction *d*) was washed with cold benzene, and the pale yellow crystalline material remaining (2 g.) was almost pure chrysene (see below).

The benzene solution was evaporated, and the residue (7 g.) dissolved in the minimum amount of benzene–hexane (1 : 1) and chromatographed on alumina. Elution gave the following fractions (70 c.c. each): with hexane, fractions 1—16; with benzene–hexane (1 : 4), fractions 17—23; with benzene–hexane (1 : 2), fractions 24—31; with benzene–hexane (1 : 1), fractions 32—37; with benzene–hexane (2 : 1), fractions 38—41; with benzene, fractions 42—45, and with benzene–chloroform (1 : 1), fractions 46—49. Fractions 1—21, which were oils, were combined and distilled to give: (*e*) b. p. 95—210°/19 mm. (0·5 g.); (*f*) b. p. 155—160°/0·3 mm. (0·2 g.); and (*g*) a residue (1·2 g.). Gas–liquid chromatography of fraction (*e*) showed the presence of naphthalene, 1- and 2-methylnaphthalene, biphenyl (?), and unknown material. Paper chromatography of fraction (*f*) showed the presence of anthracene, phenanthrene, fluoranthene, pyrene, and 2-phenylnaphthalene. Fraction (*g*) was chromatographed on alumina, and elution with light petroleum, hexane, and benzene–hexane (1 : 4) gave 20 fractions (each 70 c.c.), each of which was examined by paper chromatography. In this way 1,2′- and 2,2′-binaphthyl, 2-phenylnaphthalene, 1,2-benzofluorene, 1,2-benzanthracene, and 3,4-benzophenanthrene were identified.

Fractions 22—49 were likewise examined by paper chromatography and contained perylene, chrysene, 11,12-benzofluoranthene, and 3,4-benzopyrene.

*Details of Identification.*—*Methane and ethylene.* Samples of the exit gases were collected in a gas cell for infrared analysis. Methane was identified by its spectrum [15] in the 7·5—8·5 μ region (maxima at 7·61, 7·73, 7·77, 7·81, 7·85, 7·90, 7·94, 7·98, 8·05, 8·11, 8·17, 8·22, and 8·31 μ), and ethylene by its spectrum [15] in the 9·0—11·5 μ region (maxima at 9·33, 9·44, 9·53, 9·63, 9·72, 9·79, 9·83, 9·91, 10·01, 10·11, 10·20, 10·30, 10·51, 10·75, 10·83, 10·92, 11·00, 11·07, 11·16, 11·24, and 11·35 μ).

*Benzene.* Separation of fraction (*a*) by gas–liquid chromatography gave benzene showing the following infrared maxima [15] (examined as vapour): 2·40, 3·23, 5·05, 5·47, 6·65, 6·71, 7·18, 9·51, 9·62, 9·75, 12·82, 14·55, and 14·90 μ.

*Toluene.* This was identified by its infrared spectrum [15] which showed ($CCl_4$ solution) maxima at 2·16, 2·31, 2·35, 2·47, 2·60, 2·74, 3·29, 3·31, 3·42, 3·48, 3·67, 3·90, 4·17, 4·45, 4·64, 5·04, 5·11, 5·14, 5·34, 5·38, 5·50, 5·55, 5·76, 6·85, and 7·29 μ.

*Ethylbenzene.* This was identified by its infrared spectrum [15] which showed ($CCl_4$ solution) maxima at 2·30, 2·70, 3·25, 3·32, 3·35, 3·41, 3·60, 3·78, 4·10, 4·30, 5·10, 5·31, 5·50, 5·71, 6·08, 6·85, 7·22, 7·48, 8·46, 8·62, 9·01, 9·20, 9·40, 9·70, and 11·03 μ.

*Styrene and* o-*xylene.* The material obtained by gas–liquid chromatography of fraction (*b*) was a mixture of styrene and *o*-xylene. Styrene was identified [15] by its infrared maxima ($CCl_4$ solution) at 2·12, 2·25, 2·41, 2·70, 3·26, 3·30, 3·61, 5·10, 5·29, 5·45, 5·70, 5·89, 6·10, 6·70, 6·88, 7·05, 7·20, 7·47, 7·57, 7·75, 8·30, 8·46, 8·65, 9·05, 9·25, and 11·00 μ, in substantial agreement with the literature, and *o*-xylene by maxima at 3·40 (infl.), 4·08, 4·27, 8·91, and 9·50 μ. The mixture also decolorised bromine-water.

*Indene.* A specimen isolated by gas–liquid chromatography of fractions (*b*) and (*c*) showed infrared maxima ($CCl_4$ solution) at 2·15, 2·32, 2·39, 2·52, 3·00, 3·26, 3·42, 3·58, 3·71, 3·82, 4·07, 4·86, 5·12, 5·20, 5·27, 5·36, 5·44, 5·54, 7·74, 5·90, 6·00, 6·86, 7·17, 7·35, 7·49, 7·61, 7·77, 8·57, 8·66, 8·90, 9·38, 10·59, 10·81, and 10·93 μ. An authentic specimen showed the same maxima.

*Tetralin.* This was identified by its retention-time ratio in the gas–liquid chromatography of fraction (*c*). The specimen collected had an infrared spectrum identical with that of authentic tetralin.

*Naphthalene.* Isolated from fractions (*c*) and (*e*) this had m. p. and mixed m. p. 79—80°.

*Methylnaphthalenes.* Gas–liquid chromatography of fraction (*e*) gave a peak with shoulder similar to that given by an authentic mixture of 1- and 2-methylnaphthalene and with the same retention times.

*Biphenyl* (?). A small peak obtained in the gas–liquid chromatogram of fraction (*e*) had the same retention time ratio as biphenyl.

2-*Phenylnaphthalene.* An extract from the paper chromatogram showed $\lambda_{max.}$ 250 and 287 mμ (lit.,[16] $\lambda_{max.}$ 251, 288 mμ).

*Anthracene.* Fraction (*f*) was recrystallised from light petroleum and sublimed *in vacuo.*

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[15] American Petroleum Institute Research Project 44, Infrared Spectral Data.

[16] Elsevier's Encyclopedia of Organic Chemistry, Series III, 12*B*, 208.

Its light absorption showed $\lambda_{max.}$ 252, 323, 339, 357, and 375 mμ with inflexions at 246, 352, and 371 mμ indicative of anthracene.[17]

*Phenanthrene.* After separation of the anthracene the mother liquors were chromatographed on acetylated paper. An extract of a spot with $R_F$ corresponding to phenanthrene had $\lambda_{max.}$ 246 (infl.), 251, 274, 282, and 293 mμ.[17]

*Fluoranthene and pyrene.* An extract of a further spot on the paper chromatogram showed maxima at 233 (infl.), 236, 253 (infl.), 262, 272, 277, 282, 288, 309, 323, 342, and 360 mμ indicative of fluoranthene,[17] and at 242, 319, and 335 mμ suggesting the presence of pyrene.[17] The latter was confirmed by its fluorescence spectrum, which was identical with that given by an authentic specimen.

1,2′-*Binaphthyl.* Paper chromatography of the solutions resulting from the chromatography of fraction (*g*) on alumina gave several spots of high $R_F$ values which showed violet-blue fluorescence. An extract of one such spot showed $\lambda_{max.}$ 219 and 283 mμ, with inflexions at 225 and 273 mμ in agreement with the literature [18] for 1,2′-binaphthyl.

2,2′-*Binaphthyl.* This was isolated by chromatography of fraction (*g*) on alumina. After recrystallisation from benzene–hexane (1 : 4) it formed colourless plates, m. p. 184—185° alone, and 184—186° when mixed with an authentic specimen. Its infrared and ultraviolet spectra were identical with those of authentic specimens.

3,4-*Benzophenanthrene.* Fraction (*g*) was chromatographed on alumina and the eluates which gave a spot on acetylated paper corresponding to benzophenanthrene were combined and evaporated. Micro-distillation gave an oil, b. p. 150—155°/0·05 mm., which was converted into the picrate. After three recrystallisations it formed orange-red plates, m. p. 118—121°. After decomposition with dilute ammonium hydroxide, and extraction with ether, the product was re-chromatographed on paper. An extract of the violet-blue spot showed $\lambda_{max.}$ 218, 230, 272, 282, 304 (infl.), 315, and 326 (infl.) indicative of 3,4-benzophenanthrene.[17]

1,2-*Benzanthracene.* This was identified by comparison with an authentic specimen on acetylated paper. An extract showed $\lambda_{max.}$ 222, 228, 254, 258, 263, 278, 288, 300, 314, 325, 340, 359, 373, and 384 mμ, and its fluorescence spectrum showed bands at 408, 435, and 464 mμ; both spectra are in substantial agreement with the literature.[16]

1,2-*Benzofluorene.* This was identified by chromatography of fraction (*g*) on acetylated paper. An extract showed $\lambda_{max.}$ 230, 245 (infl.), 254, 262, 282, 294, 303, 313, 328 (infl.), and 340 mμ in agreement with the literature.[18]

*Chrysene.* The sparingly-soluble material from fraction (*d*) was recrystallised from benzene. The resulting chrysene had m. p. 251—252° not depressed by admixture with an authentic specimen (Found: C, 94·9; H, 5·3. Calc. for $C_{18}H_{12}$: C, 94·7; H, 5·3%). Its light absorption (in 95% ethanol) showed the following $\lambda_{max.}$ (log ε in parentheses): 220 (4·45), 241 (4·25), 259 (4·80), 268 (5·10), 283 (4·10), 295 (4·07), 307 (4·11), 320 (4·10), 343 (2·80), and 361 mμ (2·80).

*Perylene.* This was identified by comparison with an authentic specimen on acetylated paper. An extract showed $\lambda_{max.}$ 245, 252, 386, 408, 426 (infl.), and 435 mμ in the ultraviolet, and its fluorescence spectrum showed bands at 445, 475, and 502 mμ; both spectra are in substantial agreement with the literature.[16]

11,12-*Benzofluoranthene.* This compound had a slightly higher $R_F$ than 3,4-benzopyrene on acetylated paper. An extract showed $\lambda_{max.}$ 220, 236, 246 (infl.), 268, 283, 296, 308, 360, 378, and 401 mμ, in good agreement with the literature.[17]

3,4-*Benzopyrene.* This was identified by comparison with an authentic specimen on acetylated paper. An extract showed $\lambda_{max.}$ 226, 255, 266, 274, 284, 296, 330, 364, 384, and 404 mμ in good agreement with the literature.[19] The identification was confirmed by its fluorescence spectrum,[2] with bands at 398, 404, 409, 417, 427, 456, and 485 mμ.

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[17] Clar, " Aromatische Kohlenwasserstoffe," 2nd edn., Springer, Berlin, 1952.
[18] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951.
[19] Clar, *Ber.*, 1936, **69**, 1671.