548. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part VII.*[1] *The Pyrolysis of Indene.*

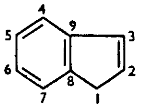
By G. M. Badger and R. W. L. Kimber.

The pyrolysis of indene at 700° yields significant amounts of benzofluorenes, 1,2-benzanthracene, and 3,4-benzophenanthrene in addition to chrysene. Other compounds are formed in smaller amounts.

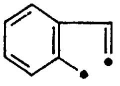
It has long been known that chrysene is formed in good yield when indene is passed through a red-hot tube;[2] but no attempt seems to have been made to identify other compounds formed in this pyrolysis. As indene is a product of the pyrolysis of some other hydrocarbons,[1,3,4] it seemed important to re-examine its behaviour on pyrolysis.

The pyrolysis was carried out by passing indene vapour, with nitrogen, through a silica tube filled with porcelain chips, at 700°. Methane and ethylene were detected in the exit gases, and the tar (obtained in 51·6% yield) was collected and analysed by chromatography on alumina, gas–liquid partition chromatography, chromatography on cellulose acetate and on acetylated paper,[5] and by spectroscopy. The following compounds were identified (% composition w/w in parentheses): methane (—); ethylene (—); benzene (5·4); toluene (0·83); styrene (?) (0·1); unknown *X* (2·3); indene (6·5); naphthalene (4·6); fluorene (0·02); phenanthrene (0·38); anthracene (0·20); 3,4-benzophenanthrene (2·3); unknown *Y* (0·52); pyrene (?) (0·10); fluoranthene (0·27); 1,2-benzofluorene (4·4); 2,3-benzofluorene (4·5); 3,4-benzofluorene (1·0); 1′,2′,3′,4′-tetrahydro-3,4-benzopyrene (?) (0·46); 1,2-benzanthracene (4·6); alkylchrysene (1·1); chrysene (31·7); 3,4-benzofluoranthene (0·008); 10,11-benzofluoranthene (0·01); 11,12-benzofluoranthene (trace); 3,4-benzopyrene (0·002); unidentified high-boiling material (16). Chrysene was thus the major product, but was present in smaller quantity than expected from the literature; and significant quantities of benzofluorenes, 1,2-benzanthracene, and 3,4-benzophenanthrene were also formed.

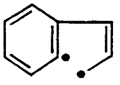
By using the calculated bond orders,[6] it is possible to obtain approximate bond dissociation energies for the carbon–carbon bonds in indene, and hence to predict which bonds are most likely to break to yield radicals. The 2,3- and 3,9-bonds, for example, have bond dissociation energies of about 138 and 108 kcal./mole, respectively; but the 1,2- and 1,8-bonds would seem to have bond dissociation energies of about 90 kcal./mole, and these bonds are therefore more likely to be broken when indene is heated. Ring fission in this manner would give three possible " primary " radicals (II, III, IV), and it is significant that all the major products of the pyrolysis can be explained by suitable reactions involving these " primary " radicals.



(I)



(II)



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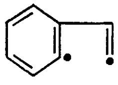

(IV)

The dimerisation of two radicals of type (II) would be expected to give chrysene (as in V, VI) or 1,2-benzanthracene (as in VII). Similarly the dimerisation of two radicals of type (III) could give chrysene (as in VIII, IX); and the combination of one radical of

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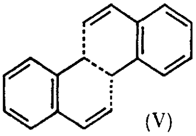
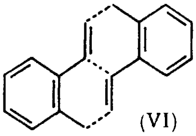
[1] Part VI, Badger and Kimber, *J.*, 1960, 266.
[2] Spilker, *Ber.*, 1893, **26**, 1538.
[3] Badger and Buttery, *J.*, 1958, 2458.
[4] Badger and Spotswood, *J.*, in the press.
[5] Spotswood, *J. Chromatog.*, 1959, **2**, 90; *ibid.*, in the press.
[6] Pullman and Berthier, *Bull. Soc. chim. France*, 1948, **15**, 551.

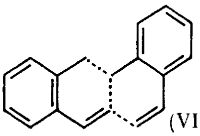
type (II) with one of type (III) would give 1,2-benzanthracene (X, XI) or 3,4-benzophenanthrene (as in XII).

In the same way, the combination of a radical of type (II) with one of type (IV), or of a radical of type (III) with one of type (IV), could yield 1,2-, 2,3-, and 3,4-benzofluorenes; and all these compounds were found in the tar.

The reaction of the styryl radical (IV) with hydrogen would account for the small amount of styrene obtained; and secondary fission of this radical, or of styrene itself, would account for the benzene and ethylene observed. (The pyrolysis of styrene is known to yield benzene in 6·4% yield.[3]) The toluene present in the indene tar could be formed by secondary fission of the radical (II), followed by reaction with hydrogen. Reaction between a benzyl radical and benzene, followed by cyclodehydrogenation, would explain the presence of fluorene; and reaction between two benzyl radicals could lead eventually to phenanthrene or anthracene.[1,7]


(V)


(VI)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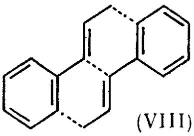
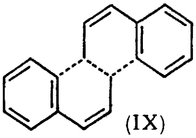
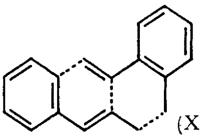
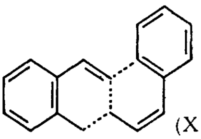
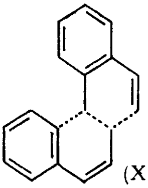

(VIII)


(IX)


(X)


(XI)


(XII)

The presence of naphthalene in this tar can only be explained on the basis of a chain-lengthening process. The most likely mechanism would seem to be the attack of ethylene on the styryl radical (IV) to give a C_6–C_4 hydrocarbon (such as phenylbutadiene) which would yield naphthalene on cyclisation with loss of hydrogen.[8]

Only a very small amount of 3,4-benzopyrene was found in the indene tar. It can be reasonably concluded from this that 3,4-benzopyrene is not formed in significant quantities from chrysene and a C_2 hydrocarbon (such as ethylene), or from 1,2-benzanthracene and a C_2 hydrocarbon. Ethylene, chrysene, and 1,2-benzanthracene were all formed in considerable quantity, and would be expected to give a relatively large amount of 3,4-benzopyrene if this hydrocarbon could be formed to any significant extent by either of these mechanisms. It seems more likely, therefore, that the 3,4-benzopyrene must be formed from two C_6–C_4 units as previously postulated,[9] or from pyrene by attack with a C_4 unit (such as a butadienyl radical).

EXPERIMENTAL

Pyrolysis of Indene.—Purified indene (93 g., n_D^{14} 1·5676; no impurities could be detected by gas–liquid chromatography) was pyrolysed at 700° by the method used for tetralin.[1] The resulting tar (44 g.) was collected, and more (1 g.) was obtained by washing the tube with boiling chloroform and evaporating the solvent. A final trap cooled in solid carbon dioxide–ethanol collected a further 3·0 g. (fraction *a*). Distillation of the tar gave the following fractions: (*b*) b. p. 90°/25 mm. (3 g.); (*c*) b. p. 95—105°/30 mm. (4 g.); and (*d*) a residue.

Analysis.—Fractions (*a*), (*b*), and (*c*) were analysed by gas–liquid chromatography as previously described.[1] Fraction (*a*) contained benzene (2·6 g.) and toluene (0·4 g.), fraction (*b*) contained unknown *X* (0·6 g.), indene (2·3 g.), and naphthalene (0·1 g.); and fraction (*c*)

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[7] Porter and Wright, *Trans. Faraday Soc.*, 1955, **51**, 1469.
[8] Badger and Spotswood, *J.*, 1959, 1635.
[9] Badger, Buttery, Kimber, Lewis, Moritz, and Napier, *J.*, 1958, **2449**.

also contained unknown *X* (0·52 g.), indene (0·81 g.), and naphthalene (2·6 g.). Fractions (*b*) and (*c*) also contained trace amounts of a material with a retention time corresponding to styrene.

Fraction (*d*) was extracted (Soxhlet) with benzene–hexane (1 : 4) and gave a sparingly soluble residue (0·5 g.) (fraction *e*). The extract was evaporated and then chromatographed in hexane on alumina (70 × 5 cm.). Development with hexane gave fractions 1—14; with benzene–hexane (1 : 2), fractions 15—27; and with benzene, fractions 28—51. Final extraction with ether gave fraction (*f*) (10·5 g.) and a black tar (2 g.) which was added to fraction *e*. The following fractions, which showed similar ultraviolet absorption spectra, were re-combined: fractions 1—5 (0·1 g.); fractions 6—11 (0·11 g.); fractions 12—14 (0·164 g.); fractions 15—18 (1·22 g.); fractions 19—21 (3·0 g.), and fractions 22—30 (11·08 g.).

Fractions 1—5 contained naphthalene. Fractions 6—11 contained oily material which could not be identified. Chromatography of fractions 12—14 on cellulose acetate showed the presence of phenanthrene, anthracene, and fluorene. In the same way, phenanthrene, anthracene, 3,4-benzophenanthrene, pyrene (?), and fluoranthene were identified from fractions 15—18, and 1,2-, 2,3-, and 3,4-benzofluorenes, 1′,2′,3′,4′-tetrahydro-3,4-benzopyrene (?), 3,4-benzophenanthrene, and 1,2-benzanthracene from fractions 19—21. Three recrystallisations of fractions 22—30 from benzene gave chrysene, while the mother-liquors, by chromatography on cellulose acetate, were found to contain (in order of elution from the column), 2,3- and 1,2-benzofluorenes, 1,2-benzanthracene, an alkylchrysene, 10,11- and 11,12-benzofluoranthenes, chrysene, 3,4-benzofluoranthene, and 3,4-benzopyrene.

Fraction *f* was recrystallised from benzene and gave almost pure chrysene (3 g.). The combined mother-liquors were chromatographed in benzene on alumina. Elution with benzene–hexane, and re-chromatography of the eluate on cellulose acetate showed the presence of 1,2- and 2,3-benzofluorenes, 1,2-benzanthracene, and chrysene.

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 in the 7·8—8·5 μ region [10] (maxima at 7·62, 7·73, 7·77, 7·81, 7·86, 7·90, 8·00, 8·05, 8·10, 8·17, 8·24, and 8·30 μ), and ethylene in the 10—11 μ region (maxima at 10·00, 10·11, 10·21, 10·31, 10·52, 10·75, 10·84, 10·94, 11·00, 11·09, 11·17, and 11·24 μ).

Benzene. This was identified by its retention time and by its infrared spectrum [10] (examined as vapour) which showed maxima at 2·40, 3·23, 5·06, 5·48, 6·65, 6·71, 7·18, 9·51, 9·63, 9·74, 12·82, 14·55, and 14·90 μ.

Toluene. This was identified by its retention time and infrared spectrum [10] (liquid film) which showed maxima at 2·16, 2·31, 2·34, 2·47, 2·61, 2·74, 3·29, 3·31, 3·43, 3·48, 3·67, 3·90, 4·17, 4·46, 4·64, 5·03, 5·11, 5·14, 5·34, 5·39, 5·50, 5·55, 5·76, 6·85, and 7·29 μ.

Styrene (?). A very small peak in the gas–liquid chromatograms of fractions (*b*) and (*c*) had a retention time identical with that obtained with authentic styrene.

Indene. This was identified in fractions (*b*) and (*c*) by its retention time. Its infrared spectrum was identical with that of an authentic specimen.

Naphthalene. This was isolated from fractions (*b*), (*c*), and (*d*), and had m. p. and mixed m. p. 79·5—80°.

Phenanthrene. This was isolated from fraction (*d*) and had m. p. 99—100°, not depressed by admixture with an authentic specimen. Its identity was confirmed by its ultraviolet absorption spectrum [11] which had maxima at 221, 245 (infl.), 252, 276, 283, 295, 316, 324, 332, 339, and 346 mμ.

Fluorene (?). Some of the early fractions following the chromatography of the phenanthrene fractions on cellulose acetate showed maxima at 262 (infl.), 274 (infl.), 290, 294 (infl.), and 301 mμ, suggesting the presence of fluorene.[12]

Anthracene. The next fraction from the column, although contaminated with phenanthrene, showed maxima at 252, 340, 353 (infl.), 358, 372 (infl.), and 377 mμ, indicative of anthracene.[11] This was confirmed by its fluorescence spectrum, which showed bands at 403, 429, and 455 mμ, in good agreement with the literature values.[13]

Fluoranthene. Isolated by chromatography of fractions 15—18 on cellulose acetate, this

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

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

[12] Mayneord and Roe, *Proc. Roy. Soc.*, 1937, *A*, **158**, 634.

[13] Millar and Baumann, *Cancer Res.*, **1943**, **3**, 217.

was identified by its ultraviolet absorption spectrum,[11] with maxima at 230 (infl.), 236, 252, 262, 272, 276, 282, 287, 310, 321, 340, and 359 mμ. This was confirmed by its fluorescence spectrum with bands at 430—450, 465, 513, and 573 mμ.

Pyrene (?). Several fractions obtained by the chromatography of fractions 15—18 on cellulose acetate had absorption maxima at 319 and 335 mμ, suggesting the presence of pyrene.[11] The fluorescence spectrum although diffuse had the same bands as an authentic specimen.

3,4-*Benzophenanthrene*. This was isolated from fractions 15—18 and 19—21 and had m. p. 66—67·5° not depressed by admixture with an authentic specimen. Its ultraviolet absorption spectrum had maxima at 217, 227 (infl.), 229, 244, (infl.), 254 (infl.), 263 (infl.), 272, 282, 303, 316, 327, 354, and 372 mμ in good agreement with the literature values.[11]

1,2-*Benzofluorene*. Some of the early fractions from the chromatography of fractions 19—21, 22—30, and of fraction (*f*) on cellulose acetate, showed ultraviolet absorption maxima at 245, 254, 258, 263, 288, 294, 302, 315, 328, and 342 mμ, indicative of 1,2-benzofluorene.[12]

2,3-*Benzofluorene*. This was identified [14] from the same fractions by maxima at 216, 255, 264, 274 (infl.), 285, 292 (infl.), 304, 313 (infl.), 317, 325, 333, and 340 mμ. One specimen had m. p. 205—206° alone and 207—208° when admixed with an authentic specimen, m. p. 208—209°.

3,4-*Benzofluorene*. Some fractions containing the above benzofluorenes also had absorption maxima at 230, 329, and 336 mμ, suggesting the presence of 3,4-benzofluorene.[14]

1,2-*Benzanthracene*. This was found in various fractions and was identified by its m. p., ultraviolet and fluorescence spectra, and by its R_F value on acetylated paper. One specimen, isolated by micro-sublimation from an acetylated paper " spot " on to a microscope cover-slip, had m. p. and mixed m. p. 158—159° (Leitz hot-stage microscope). Its light absorption showed maxima at 222, 238, 254 (infl.), 257, 268, 278, 288, 301, 314, 325, 340, 359, 374, and 384 mμ.[11]

Alkylchrysene. This was observed in fractions 22—30; its ultraviolet absorption spectrum had maxima at 260, 270, 282, 291, 296, 308, and 320 mμ, suggesting an alkylchrysene.[14]

Chrysene. This was isolated and had m. p. 251—252°, not depressed by admixture with an authentic specimen. Its light absorption showed maxima at 220, 241, 258, 268, 283, 296, 307, 320, 343, and 361 mμ.[11]

10,11-*Benzofluoranthene*. This was isolated following chromatography on cellulose acetate. Its ultraviolet absorption spectrum had maxima at 292, 306, 317, 333, 364, 375, and 382 mμ, in substantial agreement with the literature values.[11]

11,12-*Benzofluoranthene*. One of the first fractions containing 10,11-benzofluoranthene also showed maxima at 378 and 401 mμ, indicative of 11,12-benzofluoranthene.[11] This was confirmed by its distinctive fluorescence spectrum, with bands at 409, 432, 467, and 500 mμ, identical with those of an authentic specimen.

1′,2′,3′,4′-*Tetrahydro*-3,4-*benzopyrene* (?). One fraction obtained during the separation of the benzofluorenes could not be obtained in a pure state. It had maxima at 245, 266, 279, 303, 316, 330, 345, 358, 364 (infl.), 370, and 377 mμ, suggesting the presence of a substituted pyrene such as 1′,2′,3′,4′-tetrahydro-3,4-benzopyrene.[15]

3,4-*Benzofluoranthene*. This was identified by comparison with an authentic specimen on acetylated paper. An extract showed absorption maxima at 239, 256, 276, 281 (infl.), 289, 292, 302, 338, 350, and 369 mμ,[11] and its fluorescence spectrum was identical with that of an authentic specimen.

3,4-*Benzopyrene*. This was identified by comparison with an authentic specimen on acetylated paper. An extract showed absorption maxima at 226, 256, 265, 273, 284, 297, 331, 364, 381, 384, and 405 mμ, in good agreement with the literature values; [16] and its identity was confirmed by its fluorescence spectrum, with bands at 404, 409, 417, 427, 456, and 485 mμ.[17]

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

[15] Kon and Roe, *J.*, 1945, 143.

[16] Clar, *Ber.*, 1936, **69**, 1671.

[17] Weigert and Mottram, *Nature*, 1940, **145**, 895.