662. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part XIII.* The Pyrolysis of 3-Vinylcyclohexene.*

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Pyrolysis of 3-vinylcyclohexene (a postulated intermediate in the formation of 3,4-benzopyrene at high temperatures) at 700° yields a tar in which 38 compounds have been identified. Mechanisms for the formation of some of these are discussed.

As a working hypothesis it was suggested that the carcinogenic hydrocarbon 3,4-benzopyrene may be formed at high temperatures by a step-wise synthesis from a two-carbon unit.[1] 3-Vinylcyclohexene is a possible intermediate,[2] and it therefore seemed of interest to examine its pyrolysis.

The pyrolysis was carried out by passing vinylcyclohexene 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. The semi-solid tar (obtained in 44·0% yield) was collected and analysed by gas–liquid chromatography, chromatography on alumina, acetylated cellulose, and acetylated paper, and by ultraviolet and fluorescence spectroscopy. The following compounds were identified (% by wt. in parentheses): Benzene (43·67); toluene (16·12); ethylbenzene (0·22); *p*-xylene (1·83); styrene (3·14); indene (0·48); naphthalene (13·16); 1- and 2-methylnaphthalene (3·67); biphenyl (3·44); 4,4′-dimethylbiphenyl (0·06); bibenzyl (0·31); stilbene (0·11); acenaphthylene (1·06); phenanthrene (1·84); fluorene (1·00); anthracene (0·64); pyrene (1·31); fluoranthene (0·34); 2,3-benzofluorene (0·70); 1,2-benzanthracene (0·34); 2,2′-binaphthyl (0·15); 1,2-benzofluorene (0·58); chrysene (0·42); triphenylene (0·11); perylene (0·13); 1,2-benzopyrene (0·31); 1,2:5,6-dibenzanthracene (0·13); 10,11-benzofluoranthene (0·22); 3,4-benzopyrene (0·48); 3,4-benzofluoranthene (0·27); 4,5-(*o*-phenylene)fluoranthene (indeno[1,2,3-*cd*]fluoranthene) (0·18); 11,12-benzofluoranthene (0·38); 1,12-benzoperylene (0·04); anthanthrene (0·15); 2,3-(*o*-phenylene)pyrene (indeno[1,2,3-*mn*]pyrene) (0·38); 3,4:9,10-dibenzopyrene (dibenzo[*a,i*]-pyrene) (0·05); and 3,4-benzotetraphene (0·08).

At the high temperature involved, abstraction of a hydrogen atom from a reactive allylic position in vinylcyclohexene must be an important initial process, giving the radicals (I) and (II). Moreover, carbon–carbon single bonds are known to have bond-dissociation energies of about 80 kcal./mole,[3] and such bonds should therefore undergo ready scission at 700° to give $CH_2{=}CH\cdot$ and the cyclohexenyl radical (III). Several other radicals might be formed by rupture of the ring and/or further scission. In this way the radicals (IV—XV) would all be expected as initial decomposition products of vinylcyclohexene.

These expected scission products show many similarities to the radicals which could be formed by the pyrolysis of buta-1,3-diene, and it is significant that the products obtained by pyrolysis of 3-vinylcyclohexene and buta-1,3-diene show a striking resemblance.[4] The formation of all the major products can be explained by suitable reactions of these radicals.

Benzene could be formed from (III) by dehydrogenation, and from (IX) or (XI) by cyclodehydrogenation. Cyclodehydrogenation of (XII), or reaction of (III) with methyl radicals (followed by dehydrogenation) could account for the large yield of toluene, and a similar mechanism could lead to bibenzyl and (by dehydrogenation) to stilbene and phenanthrene. A much more important route to phenanthrene could be by reaction of (I) and (III), followed by dehydrogenation. *p*-Xylene could be formed by the dimerisation

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* Part XII, preceding paper.

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

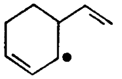
[2] Badger, Kimber, and Spotswood, *Nature*, 1960, **187**, 663.

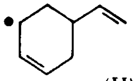
[3] Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954; Braude and Nachod, " Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955.

[4] Badger and Spotswood, *J.*, 1960, 4431.

of two (XIV) radicals, followed by dehydrogenation. Dehydrogenation of vinylcyclohexene itself could account for the observed styrene; but the relatively small yield of this product shows that the scission of carbon–carbon bonds must be a much more important reaction at 700° than dehydrogenation.

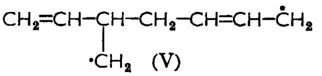
The small amount of indene obtained could be formed by reaction of (III) with (XIII), followed by dehydrogenation; and naphthalene could be similarly formed from (III) and (VII), (VIII), or (XIV). Biphenyl could be obtained from two cyclohexenyl radicals (III), followed by dehydrogenation; and 4,4′-dimethylbiphenyl could be formed by dimerisation of two benzyl radicals. The relatively small yield of fluoranthene is somewhat surprising as it would be thought that this compound could arise by the dimerisation of two radicals of type (I).

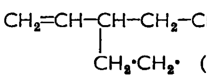

(I)


(II)


(III)

$CH_2{=}CH{-}\dot{C}H{-}CH_2{-}CH_2{-}CH{=}CH{-}\dot{C}H_2$
(IV)


$CH_2{=}CH{-}\underset{\cdot CH_2}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH{-}\dot{C}H_2$
(V)


$CH_2{=}CH{-}\underset{CH_2\cdot CH_2\cdot}{\underset{|}{CH}}{-}CH_2{-}CH{=}\dot{C}H$
(VI)

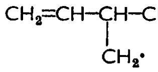
$CH_2{=}CH{-}\dot{C}H{-}\dot{C}H_2$
(VII)

$\dot{C}H_2{-}CH{=}CH{-}\dot{C}H_2$
(VIII)

$\dot{C}H_2{-}\dot{C}H{-}CH_2{-}CH{=}CH{-}\dot{C}H_2$
(IX)

$\dot{C}H_2{-}\dot{C}H_2$
(X)

$CH_2{=}CH{-}\dot{C}H{-}CH_2{-}CH{=}\dot{C}H$
(XI)

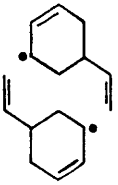

$CH_2{=}CH{-}\underset{CH_2\cdot}{\underset{|}{CH}}{-}CH_2{-}CH{=}\dot{C}H$
(XII)

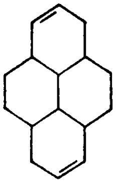
$\dot{C}H{=}CH{-}\dot{C}H_2$
(XIII)

$CH_2{=}CH{-}CH_2{-}\dot{C}H_2$
(XIV)

$\dot{C}H_2{-}\dot{C}H{-}CH_2{-}CH{=}\dot{C}H$
(XV)

The pyrolysis of naphthalene has been shown to yield the three isomeric binaphthyls, together with perylene, 10,11-benzofluoranthene, and 11,12-benzofluoranthene.[5] In the present work these products are almost certainly formed from naphthalene-type intermediates by similar dehydrogenations. In the same way the two *o*-phenylenepyrenes identified among the products must be formed by the cyclodehydrogenation of phenylpyrenes.[6]


(II)


(XVI)

As expected, both 1,2-benzopyrene and 3,4-benzopyrene were found among the products (0·31 and 0·48% respectively), while pyrene was present to the extent of 1·31%. This agrees with the earlier conclusion [2] that tars embodying high yields of pyrene (for example, those formed by pyrolysis of acetylene, butadiene, or n-butylbenzene) also contain relatively large amounts of 3,4-benzopyrene. A tentative conclusion would be that dimerisation of two vinylcyclohexene radicals (II) would give a hydropyrene (XVI). This could suffer dehydrogenation to pyrene, or reaction with a four-carbon unit, followed by dehydrogenation, to give 3,4-benzopyrene.

EXPERIMENTAL

3-*Vinylcyclohexene*.—This was prepared by the thermal dimerisation of buta-1,3-diene as described by Ziegler and Wilms.[7] It had b. p. 131—132°, n_D^{14} 1·4672, n_D^{17} 1·4660 (lit.,[8] n_D^{20} 1·4653), and no impurities could be detected by gas–liquid chromatography.

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[5] Lang, Buffleb, and Kalowy, *Chem. Ber.*, 1957, **90**, 2888, 2894; 1958, **91**, 2686; 1960, **93**, 303.
[6] Badger and Spotswood, *J.*, 1960, 4420.
[7] Ziegler and Wilms, *Annalen*, 1950, **567**, 28; 1954, **589**, 148.
[8] Reed, *J.*, 1951, 685.

Pyrolysis.—3-Vinylcyclohexene (50 g.) was vaporised at 7 g./hr. in a flash evaporator (maintained at 360°), and carried with a stream of 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.[1] The resulting dark brown fluid tar (22 g.), and samples of the exit gases, were collected.

Analysis.—The tar was distilled to give fractions (*a*) b. p. 80—100°/760 mm. (11·1 g.), (*b*) b. p. 100—140°/760 mm. (2·3 g.), (*c*) b. p. 40—90°/30 mm. (1·08 g.), (*d*) b. p. 90—130°/30 mm. (3·2 g.), and (*e*) a residue (4·4 g.). Fractions (*a*—*d*) were examined by gas–liquid chromatography (as in the preceding paper). Peaks corresponding to benzene, toluene, ethylbenzene, *p*-xylene, styrene, and indene, naphthalene, 1- and 2-methylnaphthalene, and biphenyl were observed. The residue (*e*) was chromatographed on a column of Spence alumina and seventeen fractions were collected. Fractions 1—3 were further examined by gas–liquid chromatography, and the remainder by chromatography on columns of partially acetylated cellulose and partially acetylated paper.[9] The following compounds were identified in the fractions enumerated: (1) naphthalene, 1- and 2-methylnaphthalene; (2) naphthalene, 1- and 2-methylnaphthalene, biphenyl, 4,4′-dimethylbiphenyl, bibenzyl; (3) biphenyl, stilbene; (4) acenaphthylene, phenanthrene; (5) acenaphthylene, phenanthrene, fluorene; (6) phenanthrene, anthracene, pyrene; (7) phenanthrene, pyrene, fluoranthene; (8) 2,3-benzofluorene, fluoranthene, 1,2-benzanthracene, 2,2′-binaphthyl; (9) 2,3-benzofluorene, 1,2-benzofluorene, 1,2-benzanthracene; (10) 2,3-benzofluorene, 1,2-benzofluorene, 1,2-benzanthracene, chrysene; (11) 2,3-benzofluorene, 1,2-benzofluorene, triphenylene, perylene, 1,2-benzopyrene, 1,2:5,6-dibenzanthracene, chrysene; (12) perylene, 1,2-benzopyrene, 1,2:5,6-dibenzanthracene, chrysene, 10,11-benzofluoranthene, 3,4-benzopyrene; (13) chrysene, 10,11-benzofluoranthene, 3,4-benzofluoranthene, 4,5-(*o*-phenylene)fluoranthene, 3,4-benzopyrene; (14) 11,12-benzofluoranthene, 10,11-benzofluoranthene, 3,4-benzofluoranthene, 4,5-(*o*-phenylene)fluoranthene, 3,4-benzopyrene; (15) 1,12-benzoperylene, anthanthrene, 2,3-(*o*-phenylene)pyrene, 3,4-benzopyrene; (16—17) 3,4:9,10-dibenzopyrene, anthanthrene, 3,4-benzotetraphene, 2,3-(*o*-phenylene)pyrene.

Identifications.—The gaseous products were collected and examined by infrared spectroscopy. Methane was identified by its spectrum in the 7·3—8·5 μ region (max. at 7·41, 7·48, 7·67, 7·78, 7·81, 7·86, 7·93, 8·04, 8·10, 8·16, and 8·21 μ), and ethylene by its spectrum in the 10·0—11·5 μ region (max. at 10·01, 10·11, 10·21, 10·30, 10·40, 10·50, 10·60, 10·73, 10·82, 10·90, 10·99, 11·06, 11·13, and 11·24 μ).[10]

The following were also identified; spectral data were in agreement with those of authentic specimens or with the literature.

Benzene, isolated from fractions (*a*) and (*b*) by gas–liquid chromatography; $\nu_{\text{max.}}$ (liquid film) 3·19, 3·80, 4·21, 4·41, 5·00, 5·41, 5·60, 5·89, 6·51, 6·76, 7·13, 8·50, and 9·16 μ.

Toluene, isolated from fractions (*a*) and (*b*); $\nu_{\text{max.}}$ (liquid film) 3·29, 3·42, 3·48, 3·64, 5·14, 5·38, 5·55, 5·76, 6·24, 6·56, 6·69, 6·84, 7·26, 9·25, 9·70, 13·73, and 14·42 μ.

Ethylbenzene, identified in fractions (*b*) and (*c*) by comparison of retention time ratio with that of an authentic specimen.

p-Xylene, isolated from fractions (*b*) and (*c*) by gas–liquid chromatography; $\nu_{\text{max.}}$ (liquid film) 3·30, 3·42, 3·48, 3·65, 5·45, 5·58, 6·14, 6·58, 6·87 7·25, 8·20, 8·92, 9·06, 9·58, 9·78, 10·04, and 12·59 μ.

Styrene, isolated from fractions (*b*) and (*c*) by gas–liquid chromatography; $\nu_{\text{max.}}$ (liquid film) 3·20, 5·10, 5·30, 5·50, 5·70, 5·90, 6·11, 6·22, 6·32, 6·70, 6·90, 7·08, 7·50, 7·60, 7·73, 8·32, 9·26, 9·78, 10·10, 11·00, 11·90, 12·90, and 14·40 μ.

Indene, identified in fraction (*c*) by gas–liquid chromatography by comparison of retention time ratio with that of an authentic specimen.

Naphthalene, isolated from fractions (*d*), 1, and 2 by gas–liquid chromatography; $\lambda_{\text{max.}}$ 248, 257, 266, 275, 285, and 311 mμ, m. p. and mixed m. p. 78—80°; fluorescence max. 330 mμ.

1- and 2-Methylnaphthalene, identified in fractions (*d*), 1, and 2, by gas–liquid chromatography by comparison of their retention time ratios with those of authentic specimens; attempts to separate the isomers were unsuccessful, but the predominance of the 2-isomer may be inferred from the shape of the curve.

Biphenyl, isolated from fractions (*d*), 1, 2, and 3 by gas–liquid chromatography; m. p. and mixed m. p. 69—70°; $\lambda_{\text{max.}}$ 250 mμ.

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

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

4,4′-Dimethylbiphenyl, identified in fraction 2 by gas–liquid chromatography and comparison of its retention time ratio with that of an authentic specimen.

Bibenzyl, identified in fraction 2 on gas–liquid chromatography and comparison of its retention time ratio with that of an authentic specimen.

Stilbene, isolated from fraction 3 by gas–liquid chromatography; m. p. and mixed m. p. 120—122°.

Acenaphthylene, isolated from fractions 4 and 5 by chromatography on partially acetylated cellulose; $\lambda_{max.}$ 229, 258, 266, 276, 309, 323, 334, and 340 mμ.

Phenanthrene, isolated from fractions 4—7 by chromatography on partially acetylated cellulose; m. p. and mixed m. p. 96—98°; $\lambda_{max.}$ 243, 252, 275, 282, 294, 310, 317, 324, 331, 339, and 346 mμ; fluorescence max, 350, 363, and 383 mμ.

Fluorene, isolated from fraction 5 by chromatography on partially acetylated cellulose; $\lambda_{max.}$ 260, 290, and 301 mμ; fluorescence max. 320 mμ.

Anthracene, isolated from fraction 6 by chromatography on partially acetylated cellulose; $\lambda_{max.}$ 246, 253, 308, 323, 339, 357, and 377 mμ; fluorescence max. 380, 403, 430, and 460 mμ.

Pyrene, isolated from fractions 6 and 7 by chromatography of partially acetylated cellulose; $\lambda_{max.}$ 231, 241, 253, 263, 274, 306, 319, 335, 351, 358, 364, and 373 mμ; fluorescence max. 385 and 395 mμ; m. p. and mixed m. p. 146—147°.

Fluoranthene, isolated from fractions 7 and 8 by chromatography on partially acetylated cellulose; m. p. and mixed m. p. 105—107°; $\lambda_{max.}$ 236, 253, 263, 273, 278, 282, 288, 309, 323, 342, and 360 mμ; fluorescence max. 446 and 466 mμ.

2,3-Benzofluorene, identified in fractions 8—11 by chromatography on partially acetylated cellulose, followed by chromatography on partially acetylated paper; $\lambda_{max.}$ 255, 264, 273, 285, 304, 317, 325, 333, and 340 mμ; fluorescence max. 342 and 358 mμ.

1,2-Benzanthracene, isolated from fractions 8—10 by chromatography on partially acetylated cellulose; $\lambda_{max.}$ 222, 227, 256, 268, 278, 289, 300, 315, 326, 341, 358, 365, 374, and 384 mμ; fluorescence max. 377, 396, 418, and 445 mμ.

2,2′-Binaphthyl, isolated from fraction 8 by chromatography on partially acetylated cellulose, followed by chromatography on acetylated paper; $\lambda_{max.}$ 255 and 309 mμ; fluorescence max. 352 and 365 mμ.

1,2-Benzofluorene, isolated from fractions 9—11 by chromatography on a column of acetylated cellulose and then on acetylated paper; $\lambda_{max.}$ 254, 263, 294, 304, 317, 330, and 343 mμ; fluorescence max, 342 and 350 mμ (cf. ref. 11).

Chrysene, isolated from fractions 10—13 by chromatography on acetylated cellulose; $\lambda_{max.}$ 242, 259, 267, 283, 294, 306, 320, 344, 351, and 363 mμ; fluorescence max. 359, 374, 395, and 419 mμ; m. p. and mixed m. p. 253—255°.

Triphenylene, isolated from fraction 11 by chromatography on partially acetylated cellulose; $\lambda_{max.}$ 250, 257, 275, 286, 316, 330, and 341 mμ; fluorescence max. 352, 361, and 369 mμ.

Perylene, isolated from fractions 11 and 12 by chromatography on acetylated cellulose followed by chromatography on acetylated paper; $\lambda_{max.}$ 245, 253, 263, 367, 386, 407, and 435 mμ; fluorescence max. 436, 460, and 493 mμ.

1,2-Benzopyrene, isolated from fractions 11 and 12 by chromatography on acetylated cellulose followed by chromatography on acetylated paper; $\lambda_{max.}$ 238, 258, 268, 278, 289, 305, 317, 333, and 366 mμ in substantial agreement with the literature;[12] fluorescence max. 385 and 405 mμ (cf. ref. 11).

1,2:5,6-Dibenzanthracene, isolated from fractions 11 and 12 by chromatography on acetylated cellulose; $\lambda_{max.}$ 231, 288, 298, 319, 335, 348, 374, and 383 mμ; fluorescence max. 377, 388, and 400 mμ.

10,11-Benzofluoranthene, isolated from fractions 12—14 by chromatography on acetylated cellulose; $\lambda_{max.}$ 241, 282, 293, 309, 318, 333, 345, 365, 376, and 383 mμ; peaks at 258 and 267 mμ, probably due to chrysene, were also observed. The fluorescence spectrum showed maxima at 480 and 508 mμ.

3,4-Benzopyrene, isolated from fractions 12—15 by chromatography on partially acetylated cellulose; $\lambda_{max.}$ 255, 266, 273, 284, 297, 332, 347, 365, 379, 385, and 404 mμ; fluorescence max. 397, 422, 448, and 478 mμ.

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[11] Sawicki, Hauser, and Stanley, *Internat. J. Air Poll.*, 1960, **2**, 253.

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

3,4-Benzofluoranthene, isolated from fraction, 14 by chromatography on acetylated cellulose, had m. p. and mixed m. p. 160—164°; $\lambda_{max.}$ 239, 256, 266, 276, 290, 294, 301, 320, 339, 351, and 369 mμ; fluorescence max. 398, 426, and 445 mμ.

4,5-(*o*-Phenylene)fluoranthene, identified in fractions 13 and 14 by chromatography on acetylated cellulose followed by chromatography on acetylated paper; $\lambda_{max.}$ 253, 262, 272, 368, 380, 387, 402, and 411 mμ (cf. ref. 6).

11,12-Benzofluoranthene, identified in fraction 14 after chromatography on acetylated cellulose; $\lambda_{max.}$ 238, 247, 269, 283, 297, 309, 361, 380, and 402 mμ; fluorescence max. 400, 427, and 455 mμ (cf. ref. 6).

1,12-Benzoperylene, isolated from fraction 15 by chromatography on acetylated cellulose; $\lambda_{max.}$ 268, 276, 289, 300, 315, 325, 330, 345, 363, and 383 mμ; fluorescence max. 390, 402, 414, 426, and 436 mμ.

Anthanthrene, isolated from fractions 15—17 by chromatography on acetylated cellulose followed by chromatography on acetylated paper; $\lambda_{max.}$ 233, 256, 259, 295, 308, 365, 382, 402, 407, 422, and 431 mμ; fluorescence max. 428, 454, and 484 mμ.

2,3-(*o*-Phenylene)pyrene, isolated from fractions 15—17 by chromatography on acetylated cellulose followed by chromatography on acetylated paper; $\lambda_{max.}$ 251, 269, 277, 292, 304, 315, 360, 376, 385, 402, 408, 422, and 431 mμ (cf. refs. 5, 6); fluorescence max. 476 and 504 mμ.

3,4:9,10-Dibenzopyrene, isolated from fractions 16—17 by chromatography on acetylated cellulose followed by chromatography on acetylated paper; $\lambda_{max.}$ 234, 242, 273, 283, 296, 315, 331, 353, 373, and 393 mμ; fluorescence max. 428, 456, 489, and 520 mμ.

3,4-Benzotetraphene, isolated from fractions 16—17 by chromatography on acetylated cellulose followed by chromatography on acetylated paper; $\lambda_{max.}$ 248, 277, 287, 304, 318, 332, 345, 363, 382, and 390 mμ; fluorescence max. 392, 414, and 440 mμ.

Spectra.—See preceding paper.

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