570. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part VIII.* The Pyrolysis of Acetylene.*

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The pyrolysis of acetylene at 700° yields a number of polycyclic aromatic hydrocarbons (including 3,4-benzopyrene) in addition to benzene and simple benzene derivatives.

In 1866 Berthelot [1] found that when acetylene is strongly heated it forms a tar which contains benzene and other aromatic hydrocarbons. This thermal polymerisation has been further studied by Zelinsky [2] and others; [3] and in 1925, Kennaway [4] found that the tar produced by the pyrolysis of acetylene at 700° has considerable cancer-producing power. The tar gave [5] a fluorescence spectrum similar to that given by 3,4-benzopyrene, and the presence of this hydrocarbon has been generally assumed. The pyrolysis of acetylene has now been re-investigated.

The purified gas was passed through an unpacked silica tube having a temperature gradient such that only the last few inches were kept at 700°. The reaction is strongly exothermic, and considerable trouble was caused by blockage of the tube by carbon deposits. The resulting tar was analysed by distillation, gas-liquid partition chromatography, chromatography on acetylated paper, and spectroscopy, and contained the following (% composition w/w in parentheses): Benzene (28), toluene (3), *o*-xylene (trace), styrene (trace), indene (trace), naphthalene (12), biphenyl (2·7), fluorene (4·5), phenanthrene (13), fluoranthene (3·7), chrysene (0·5), 1,2-benzanthracene (0·4), pyrene (6·5), perylene (trace), 1,12-benzoperylene (trace), 3,4-benzofluoranthene (trace), 11,12-benzofluoranthene (trace), 3,4-benzopyrene (2), 2,3-*o*-phenylenepyrene (2·7); and intractable "polymeric" material (20).

A substantially similar tar was obtained after pyrolysis at 530° (last portion only of furnace). Ethylbenzene (0·8%) and *m*- or *p*-xylene (1·7%) were also detected in this tar, and indene (2·8%), naphthalene (20·2%), and pyrene (21%) were present in higher concenconcentration; but biphenyl, fluorene, 3,4-benzofluoranthene, 11,12-benzofluoranthene, and 2,3-*o*-phenylenepyrene were not detected in the tar formed at 530°.

As expected [1] benzene is the major product of this pyrolysis; but it is significant that biphenyl was detected only in the 700° tar. It seems that the dehydrogenation of benzene to biphenyl takes place only above 530°.[cf. 6] Similarly, the highly condensed products fluorene, fluoranthene, 3,4-benzofluoranthene, 11,12-benzofluoranthene, and 2,3-*o*-phenylenepyrene were identified only in the 700° tar. Here again it seems likely that these products must be formed (presumably from diphenylmethane, 1-phenylnaphthalene, 9-phenylphenanthrene, 1,2′-binaphthyl, and 3-phenylpyrene) by cyclodehydrogenation at high temperatures.[7] The amounts of indene and of naphthalene were smaller in the 700° tar than in that formed at 530°, and it can be assumed that these compounds undergo further transformations at the higher temperature. This has been confirmed by independent pyrolyses of indene and of naphthalene.[8,9] Surprisingly, more pyrene was present in the 530° tar than in that formed at 700°; but at the higher temperature some pyrene must be used to form 2,3-*o*-phenylenepyrene.[10]

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* Part VII, *J.*, 1960, 2746.

[1] Berthelot, *Ann. Chim.*, 1866, **9**, 445.

[2] Zelinsky, *Compt. rend.*, 1923, **177**, 882; *Ber.*, 1924, **57**, 264.

[3] Kuri, *Bull. Chem. Soc. Japan*, 1953, **26**, 280; Pascal and Coupard, *Compt. rend.*, 1942, **214**, 757; Sabatier and Senderens, *Compt. rend.*, 1900, **130**, 250; Minkoff, *Canad. J. Chem.*, 1958, **36**, 131.

[4] Kennaway, *Brit. Med. J.*, 1925, ii, 1.

[5] Kennaway, *Biochem. J.*, 1930, **24**, 497.

[6] Brooks, *Ind. Eng. Chem.*, 1926, **18**, 518; Bachmann and Clarke, *J. Amer. Chem. Soc.*, 1927, **49**, 2089.

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

[8] Badger and Kimber, *J.*, in the press.

[9] Lang, Buffleb, and Kalowy, *Chem. Ber.*, 1957, **90**, 2888.

[10] Lang and Buffleb, *Chem. Ber.*, 1957, **90**, 2894.

The presence of 3,4-benzopyrene (2% in both tars) has been confirmed by the present work, and the quantity present would be sufficient to account for the carcinogenic properties reported by Kennaway.[4] In addition, the tar contains[5] other carcinogens, notably 3,4-benzofluoranthene.

The mechanism of the formation of 3,4-benzopyrene cannot be deduced from the present work. Nevertheless, its formation by the pyrolysis of acetylene is not inconsistent with the working hypothesis advanced in Part I of this series.[11] According to this view, acetylene could be converted into C_6—C_4 units (*e.g.*, phenylbutadiene, naphthalene, tetralin, etc.); and two such units could undergo cyclodehydrogenation to give 3,4-benzopyrene, and other compounds such as perylene and 11,12-benzofluoranthene.

EXPERIMENTAL

Furnace.—Preliminary experiments using the furnace previously described[11] were unsatisfactory, the tube being very rapidly choked with carbon. More satisfactory results were obtained with a furnace designed to reduce the contact time at the maximum temperature. The furnace consisted of a silica tube (30 in.; 1¼ in. outside diam.) wound for 4 in., 12 in., and 6 in. of its length with three separately controlled heating elements (nichrome wire). During the pyrolysis heating was arranged so that the temperature rose gradually along the length of the furnace, the final 6 in. being at 700°. This tube was mounted along the centre of a 6½ in. diam. asbestolite cylinder, filled with "vermiculite." The acetylene was passed through a second tube (4 ft.; 0·8 in. int. diam.) which just fitted into the heated tube, and this in turn contained a concentrically placed silica tube (¼ in. outside diam.), open at both ends, to take a beaded chromel–alumel thermocouple. The whole furnace was inclined at 60° to facilitate collection of the tar.

Pyrolysis of Acetylene.—Acetylene was generated from calcium carbide, washed with copper sulphate (150 g./l.) in 5N-sulphuric acid, with 5N-hydrochloric acid saturated with mercuric chloride, and with 4N-sodium hydroxide and collected in two sets of aspirators so connected that when acetylene was being used from one set, the other could be refilled. The gas was then passed through concentrated sulphuric acid and over fused calcium chloride before being led into the furnace. With a flow-rate of 6 l./hr., 400 l. acetylene gave 43·8 g. of tar, and a further 0·5 g. was obtained from a final trap cooled with solid carbon dioxide. Distillation of the tar gave the following fractions: (i) b. p. 80°/760 mm. (12·5 g.); (ii) b. p. 18—100°/20 mm. (5·3 g.); (iii) b. p. 100—170°/20 mm. (3·3 g.); (iv) b. p. 170—230°/20 mm. (5·5 g.); (v) 230—245°/20 mm. (2·4 g.); (vi) b. p. 245—280°/20 mm. (2·3 g.); (vii) residue (10 g.); and (viii) collected from the distillation trap (0·5 g.). Fractions (i) and (viii) were analysed by gas-liquid chromatography, the fractions being collected and identified by infrared spectroscopy. The remaining fractions were analysed by chromatography on acetylated paper, methods already described being used.[7,12] The spots were cut out and the extracts examined by spectroscopy.

Details of Identification.—*Benzene.* This was identified by its retention time and by its infrared spectrum[13] which showed (CCl_4 solution) maxima at 2·40, 3·20, 3·25, 5·06, 5·48, 6·55, 6·77, 7·17, 8·50, and 9·65 μ.

Toluene.—This was identified by its retention time ratio and by its infrared spectrum (CCl_4 solution)[13] which showed maxima at 2·40, 3·24, 3·35, 3·41, 3·60, 5·11, 5·33, 5·50, 5·73, 6·21, 6·70, 6·85, 7·23, 8·49, 9·03, 9·25, 9·61, 9·71, and 11·20 μ.

Ethylbenzene. This was identified by its retention time ratio and by its infrared spectrum (CCl_4 solution)[13] which showed maxima at 3·24, 3·30, 3·35, 3·40, 6·20, 6·67, 6·85, 7·23, 9·63, 9·70, and 11·07 μ.

Styrene and o-*xylene.* Material collected from the gas–liquid chromatogram was a mixture of styrene and *o*-xylene. Its infrared spectrum (CCl_4 solution) showed maxima at 2·4, 3·20—3·31, 5·07, 5·28, 5·43, 6·08, 6·20, 6·31, 6·67, 6·87, 7·03, 7·73, 8·32, 9·23, 9·80, 10·10, and 11·0 μ corresponding to styrene,[13] and at 6·80, 7·20, 8·92, and 9·50 μ corresponding to *o*-xylene.[13]

Indene. This was identified by its retention time ratio and by its infrared spectrum which showed maxima at 3·32, 3·47, 3·62, 5·15, 5·23, 5·30, 5·40, 5·49, 5·57, 5·95, 6·05, 6·22, 6·90, 7·20, 7·50, 7·80, and 8·05 μ, in substantial agreement with those obtained from an authentic specimen.

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[11] Badger *et al.*, *J.*, 1958, 2449.

[12] Spotswood, *J. Chromatography*, 1959, **2**, 90; 1960, in the press.

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

m- *or* p-*Xylene.* Identified only by comparison of its retention time with authentic specimens.

Naphthalene. This was identified by its ultraviolet absorption spectrum which showed $\lambda_{max.}$ at 220, 257, 267, 276, 283, and 287 mμ, and by its infrared spectrum which was identical with that of an authentic specimen. In one run a fraction, b. p. 100—110°/18 mm., was recrystallised from methanol and gave plates, m. p. and mixed m. p. 80°.

Biphenyl. This was identified by its infrared spectrum, which was identical with that of an authentic specimen.

Fluorene. An extract from a paper chromatogram showed $\lambda_{max.}$ at 221, 260, 274, 289, 294, and 301 mμ in substantial agreement with the literature values.[14] In one run a fraction, b. p. 170°/18 mm., was recrystallised from hexane and gave plates, m. p. 116° alone or admixed with authentic fluorene.

Phenanthrene. An extract from a paper chromatogram showed $\lambda_{max.}$ at 220, 245, 250, 273, 282, 286, and 292·5 mμ in substantial agreement with the literature values.[14]

Fluoranthene. This was identified by its absorption spectrum which showed maxima at 236, 261, 275, 287, 307·5, 321·5, 340, and 360 mμ (in agreement with the literature values [14]), and confirmed by its fluorescence spectrum which was identical with that of an authentic specimen.

Chrysene. An extract from a paper chromatogram showed $\lambda_{max.}$ at 241, 258, 267, 284, 293, 304·5, 317, 340, and 361 mμ (agreeing with the literature values [14]). In one run a fraction, b. p. 271°/18 mm., was chromatographed on alumina, and the product recrystallised from hexane, giving plates, m. p. and mixed m. p. 148°.

1,2-*Benzanthracene.* This was identified by its absorption spectrum which showed maxima at 257·5, 267·5, 277·5, 288, 300, 326, 340, and 359 mμ (literature values [14]). It was confirmed by its fluorescence spectrum which was identical with that of an authentic specimen.

Pyrene. An extract from a paper chromatogram showed $\lambda_{max.}$ at 234, 240, 259, 273, 290, 305, 318, and 335 mμ (literature values [14]). In one run a fraction, b. p. 238°/18 mm., was chromatographed on alumina, and crystallised from hexane, giving plates, m. p. and mixed m. p. 149°. Its trinitrobenzene complex had m. p. and mixed m. p. 244°.

Perylene. This was identified by its absorption spectrum which showed maxima at 244, 251, 385, 407, and 434 mμ (literature values [14]) and by its fluorescence spectrum which was identical with that of an authentic specimen.

1,12-*Benzoperylene.* This was also identified by its absorption spectrum which showed $\lambda_{max.}$ 290, 300, 330, 344, 364, and 380 mμ (literature values [14]), and by its fluorescence spectrum which was identical with that of an authentic specimen.

3,4-*Benzofluoranthene.* An extract from a paper chromatogram showed $\lambda_{max.}$ 222, 239, 256, 276, 291, 301, and 350 mμ (literature values [14]), and its fluorescence spectrum was found to be identical with that of an authentic specimen.

11,12-*Benzofluoranthene.* Its absorption spectrum showed maxima at 236, 296, 308, 335, 360, 379, and 400 mμ (literature values [14]), and its identity was also confirmed by its fluorescence spectrum.

3,4-*Benzopyrene.* An extract of a paper chromatogram showed maxima at 226, 255, 263, 284, 296, 328, 346, 365, 385, and 404 mμ in good agreement with the literature values.[14] It was also identified by its fluorescence spectrum which was identical with that given by an authentic specimen.

2,3-o-*Phenylenepyrene.* An extract of a paper chromatogram showed maxima at 250, 270, 303, 315, 360, 380, 407, 420, and 430 mμ, in substantial agreement with the recorded values for this hydrocarbon.[10]

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