499. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part II.* An Examination of "Schroeter Tar."*

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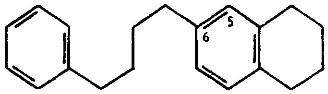
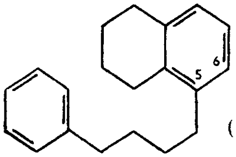
3 : 4-Benzopyrene has been isolated from "Schroeter tar," formed by the action of aluminium chloride on tetralin.

When tetralin is treated with aluminium chloride a complex mixture ("Schroeter tar") is obtained,[1] which is carcinogenic after being heated.[2] The fluorescence spectrum of this mixture is similar to that given by other carcinogenic tars,[3] and the presence of 3 : 4-benzopyrene has long been presumed. Schroeter[1] showed that the mixture contained 6-4′-phenylbutyltetralin (I), and Cook and Hewett[4] suggested that it may also contain 5-4′-phenylbutyltetralin (II). This could give 3 : 4-benzopyrene by cyclodehydrogenation; it is a very likely intermediate, and may be difficult to detect owing to its rapid conversion.

"Schroeter tar" has now been distilled; several fractions gave diffuse fluorescence spectra corresponding to 3 : 4-benzopyrene. By chromatography on alumina, 3 : 4-benzopyrene has been isolated and characterised. A fraction, b. p. 205—240°/0·5 mm., which approximately corresponds to that which Kennaway[2] found to be strongly carcinogenic, contains as much as 4% of 3 : 4-benzopyrene. No 1 : 2-benzopyrene could be detected, but there was some evidence for the presence of perylene. Another hydrocarbon was isolated from the fraction of highest boiling point, but has not been identified.

(I)





(II)

5-4′-Phenylbutyltetralin (II) could not be detected, although the 6-isomer and 2 : 6′-ditetralyl were isolated in agreement with Schroeter.[1] Oxidation of the appropriate fraction with potassium permanganate[1] and esterification of the resulting acid with diazomethane gave trimethyl benzene-1 : 2 : 4-tricarboxylate but none of the 1 : 2 : 3-isomer [which would be formed by oxidation of (II)].

These experiments did not eliminate the possibility that 5-4′-phenylbutyltetralin (II) might be present in small amounts; but if so it should be cyclodehydrogenated to 3 : 4-benzopyrene when heated further. The fraction, b. p. 230—240°/15 mm., from which virtually all the 3 : 4-benzopyrene had been removed was accordingly pyrolysed at 360° and at 600°. Only a trace of 3 : 4-benzopyrene could be detected after heating at the lower temperature. Heating at 600° resulted in considerable decomposition and gave a complex tar in which naphthalene, 2-methylnaphthalene, and 2-ethylnaphthalene were positively identified. Peaks corresponding to toluene, ethylbenzene, styrene, and other simple products were observed in the gas-phase chromatogram. A hydrocarbon having a phenanthrene-type spectrum was isolated and 2 : 2′-dinaphthyl was also formed in reasonable quantity. Traces only of perylene and 3 : 4-benzopyrene were detected.

Experimental

"Schroeter Tar."—A mixture of tetralin (2·5 kg.) and aluminium chloride (50 g.) was stirred for 10 hr. at 50—70°, then poured on ice. The product was collected and distilled. After removal of the lower-boiling fraction (containing benzene, tetralin, octahydroanthracene, and octahydrophenanthrene[1]), three fractions were collected: (i) b. p. 230—240°/15 mm. (280 g.);

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* Part I, preceding paper.

[1] Schroeter, *Ber.*, 1924, **57**, 1990.

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

[3] Hieger, *ibid.*, p. 505.

[4] Cook and Hewett, *J.*, 1933, 398.

(ii) b. p. 205—240°/0·5 mm. (75 g.); and (iii) b. p. 245—300°/1 mm. (71 g.). All fractions having b. p. greater than 120°/15 mm. showed fluorescence bands corresponding to 3 : 4-benzopyrene.

Analysis of Fraction (*i*).—The crude fraction (63 g.) was chromatographed in hexane on alumina. The main bulk was eluted with hexane (1 l.), but further elution with benzene–hexane (1 : 2) gave 8 fractions (of 70 c.c.) showing strong 3 : 4-benzopyrene fluorescence spectra. Evaporation of the solvent and recrystallisation of the solid (60 mg.) from ethanol gave 3 : 4-benzopyrene, m. p. and mixed m. p. 174—176° (lit. 176—177°); $\lambda_{max.}$ (log ε) (in ethanol) 226 (4·40), 255 (4·58), 265 (4·65), 274 (4·44), 284 (4·62), 296 (4·73), 331 (3·65), 347 (4·04), 364 (4·30), 384 (4·37), 404 (3·50) in good agreement with the literature.[5] The spectrum also showed a maximum at 434 mμ (2·78) presumably due to contamination (<1%) with perylene (lit.,[6] 434 mμ).

Analysis of Fraction (*ii*).—The crude fraction (55 g.) was chromatographed as for fraction (i). Elution with benzene–hexane gave 8 fractions (of 175 c.c.), but most of the 3 : 4-benzopyrene was present in fractions 2—5.

Evaporation of the solvent gave crude 3 : 4-benzopyrene (2·1 g.). After recrystallisation this had m. p. and mixed m. p. 174—175° (Found: C, 95·0; H, 5·0. Calc. for $C_{20}H_{12}$: C, 95·2; H, 4·8%). The trinitrobenzene complex had m. p. 223—224° [lit., 226—227° (corr.)] (Found: C, 67·15; H, 3·2. Calc. for $C_{26}H_{15}O_6N_3$: C, 67·1; H, 3·2%). Absorption spectroscopy showed perylene to be present (<1%).

Analysis of Fraction (*iii*).—This fraction (71 g.) was chromatographed as above. The fractions eluted with benzene–hexane were combined (1·5 l.) and evaporated. The residue, in benzene, was then extracted with cold concentrated sulphuric acid, the acid solution poured on ice, the mixture extracted with benzene, and the benzene solution washed and dried. Further chromatography and elution with benzene–hexane gave an orange residue (20 mg.) which formed orange-brown prisms, m. p. 255—257°; $\lambda_{max.}$ 220, 246, 255, 269, 297, 310, 323, 354, 374, 396, 422, 448, and 456 (infl.) mμ.

Pyrolysis at 360°.—Fraction (i) (2 g.) from which the 3 : 4-benzopyrene had been removed by chromatography was refluxed for 1 hr. Chromatography of the product on alumina yielded traces (*ca.* 0·5 mg.) of 3 : 4-benzopyrene and perylene as estimated from the ultraviolet spectra.

Pyrolysis at 600°.—Fraction (i) (20 g.) from which the benzopyrene had been removed was vapourised at the rate of 1 drop/15 sec. and passed with nitrogen (1 c.c./sec.) through a silica tube (36 in. × 1 in.) packed with porcelain chips (3/8 in.—1/4 in.) heated to 600°. Distillation of the resulting tar gave fractions: F1, b. p. 80° (0·25 g.); F2, b. p. 80—120° (0·5 g.); F3, b. p. 80—110°/21 mm. (3 g.); F4, b. p. 110—120°/21 mm. (2·5 g.); F5, b. p. 120—140°/21 mm. (0·5 g.); F6, b. p. 100—150°/1·2 mm. (3 g.); F7, b. p. 150—180°/1·2 mm. (2 g.); F8, b. p. 180—220°/1·2 mm. (1 g.); and the residue (2 g.).

Gas-phase chromatography of fractions F1—3 gave peaks with retention times corresponding to toluene, ethylbenzene, styrene, three unknown substances, naphthalene, and 2-methylnaphthalene. Naphthalene was collected from the chromatogram and identified by m. p. and mixed m. p. 2-Methylnaphthalene was collected; its infrared spectrum showed maxima at 5·18, 5·38, 5·53, 5·66, 6·08, 6·23, 6·98, 7·12, 7·28, 7·36, 7·55, 7·89, 8·10, 8·32, 8·53, 8·67, 8·76, 8·89, 9·64, 10·44, and 14·34 μ in substantial agreement with the literature.[7] It also showed maxima at 5·90, 6·85, 7·22, 7·42, and 9·28 μ probably indicative of 1-methylnaphthalene.

Fractions F4—5 showed the presence of naphthalene, 1-methylnaphthalene, and 2-ethylnaphthalene. The latter was collected, and showed maxima in the infrared region at 5·20, 5·42, 5·61, 5·85, 6·10, 6·23, 7·88, 8·30, 8·55, 8·67, 8·76, 8·89, 9·37 (infl.), 9·47, 9·81 10·28 (infl.), 10·39, 10·56, 11·26, 11·73, 12·24, 12·79, and 13·11 μ in agreement with the literature.[7] In the region 6·5—8 μ the maxima corresponded with those of 1-ethylnaphthalene.

Fraction F6 was chromatographed on alumina. Evaporation of the solvent and recrystallisation of the product (2 g.) from ethanol gave a hydrocarbon as prisms, m. p. 150—157°. Its ultraviolet absorption ($\lambda_{max.}$ 250, 252, 276, 288, 300, 323, 340, and 358 mμ) suggested a phenanthrene derivative, but it was not identified.

Chromatography of the residue on alumina gave 2 : 2′-dinaphthyl (1·0 g.), m. p. and mixed m. p. 182—183°; $\lambda_{max.}$ (log ε) 231 (4·12), 2·54 (4·94), and 304 (4·25) (Found: C, 94·5; H, 5·5. Calc. for $C_{20}H_{14}$: C, 94·4; H, 5·6%). Traces of 3 : 4-benzopyrene and perylene were also detected.

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

[6] Clar, *Spectrochim. Acta*, 1950, **4**, 119.

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