

661. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part XII.* The Pyrolysis of Benzene.*

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Pyrolysis of benzene at 700° has been shown to yield biphenyl as the major product, with significant amounts of *p*-terphenyl, *m*-terphenyl, and triphenylene. Fluorene, phenanthrene, anthracene, *o*-terphenyl (?), fluoranthene, chrysene, and 3,4-benzofluoranthene were also detected, and methane and ethylene were identified in the exit gases.

TARS produced by the pyrolysis of acetylene,¹ butadiene,² alkylbenzenes,³ 1-phenylbuta-1,3-diene,⁴ styrene,⁵ indene,⁶ and tetralin⁷ have all been shown to contain significant quantities of benzene. It therefore seemed to be important to determine to what extent this hydrocarbon undergoes pyrolytic conversion into polycyclic compounds. Previous

* Part XI, *J.*, 1960, 4431.

¹ Badger, Lewis, and Napier, *J.*, 1960, 2825.

² Badger and Spotswood, *J.*, 1960, 4431.

³ Badger and Spotswood, *J.*, 1960, 4420.

⁴ Badger and Spotswood, *J.*, 1959, 1635.

⁵ Badger and Buttery, *J.*, 1958, 2458.

⁶ Badger and Kimber, *J.*, 1960, 2746.

⁷ Badger and Kimber, *J.*, 1960, 266.

investigations⁸ have shown that benzene is readily dehydrogenated to biphenyl; and other hydrocarbons including *m*- and *p*-terphenyl and triphenylene have been identified.⁹ As more efficient methods of separation and of identification of polycyclic compounds are now available, the pyrolysis of benzene has been re-examined.

The pyrolysis was carried out by passing the hydrocarbon vapour, with nitrogen, through a silica tube filled with porcelain chips at 700°. Methane and ethylene were detected in the exit gases. The liquid tar formed (in 78.2% yield) was collected and analysed by gas-liquid chromatography, chromatography on alumina, on acetylated cellulose, and on acetylated paper, and by spectroscopy. The following compounds were identified in this tar (% composition w/w in parentheses): benzene (75.91), biphenyl (20.84), fluorene (0.08), phenanthrene (0.10), anthracene (0.13), *p*-terphenyl (1.02), *m*-terphenyl (0.37), fluoranthene (0.06), *o*-terphenyl (? trace), triphenylene (0.67), chrysene (0.13), and 3,4-benzofluoranthene (0.05).

Biphenyl is thus the major product and indeed it may be conveniently prepared by this method. The only other substance formed in relatively large amounts were *p*-terphenyl, *m*-terphenyl and triphenylene, all of which must be formed by further phenylation (and cyclodehydrogenation) of biphenyl. A very small amount of a compound believed to be *o*-terphenyl was detected; but the quantity was insufficient for positive identification.¹⁰ It seems likely that the *o*-terphenyl formed by further phenylation of biphenyl is rapidly converted into triphenylene.

The remaining hydrocarbons identified in the tar were present in very small amounts, totalling only 0.5% of the tar. Some fission of the benzene ring does occur, as shown by the identification of methane and ethylene in the exit gases, and plausible schemes for the formation of the compounds found can be suggested. Thus fluorene and phenanthrene could be formed from biphenyl by reaction with a one-carbon unit and a two-carbon unit respectively. Fluoranthene could be formed from biphenyl and a four-carbon unit (followed by cyclodehydrogenation); and 3,4-benzofluoranthene could be formed by phenylation of phenanthrene (followed by cyclodehydrogenation).

EXPERIMENTAL

Benzene.—Benzene was purified by shaking it with concentrated sulphuric acid, water, dilute sodium hydroxide, and water. After drying over sodium, the benzene was distilled. No impurity could be detected by gas-liquid chromatography.

Pyrolysis.—Benzene (100 g.) was vaporised at 10 g./hr. and passed with nitrogen ($\frac{1}{2}$ c.c./sec.) through a silica tube (36 in. \times 1 in.) packed with porcelain chips ($\frac{3}{8}$ — $\frac{1}{4}$ in.) which was maintained at 700° in an electrically heated furnace.¹² The resulting yellow tar (78.2 g.) was collected. The gaseous products decolorised bromine water and neutral and alkaline permanganate.

Analysis.—The tar was distilled to give the fractions (a) b. p. 80—100°/760 mm. (58.2 g.), (b) b. p. 100—140°/760 mm. (1.2 g.), and (c) a residue (18.8 g.). Fractions (a) and (b) were examined by gas-liquid chromatography over Apiezon L supported on Celite (40—80 mesh; 1:4 w/w) as stationary phase, and nitrogen as carrier gas. No products other than benzene could be detected. The residue (c) was chromatographed on alumina (4 g. at a time), and sixteen fractions were collected. The first was examined by gas-liquid chromatography, and the remainder by chromatography on columns of partially acetylated cellulose, and on partially acetylated paper.¹³ The following compounds were identified in the fractions enumerated:

⁸ E.g., Berthelot, *Bull. Soc. chim. France*, 1866, **6**, 272; *Ann. Chim. Phys.*, 1866, **9**, 451; *Z. Chem.*, 1866, 707; Schultz, *Annalen*, 1874, **174**, 201; Smith and Lewcock, *J.*, 1912, **101**, 1453.

⁹ Bachmann and Clarke, *J. Amer. Chem. Soc.*, 1927, **49**, 2089.

¹⁰ Cf. Kaplan and Petrov, *Zhur. priklad. Khim.*, 1960, **33**, 1226; Andrianov, Kvitner, and Titova (*J. Chem. Ind. U.S.S.R.*, 1937, **4**, 161) also isolated a substance provisionally regarded as *o*-terphenyl but the physical constants now known preclude this identification.

¹¹ Copeland, Dean, and McNeil, *J.*, 1960, 1687.

¹² Badger, Buttery, Kimber, Lewis, Moritz, and Napier, *J.*, 1958, 2449.

¹³ Spotswood, *J. Chromatog.*, 1959, **2**, 90; 1960, **3**, 101.

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(1) biphenyl; (2) fluorene, phenanthrene, anthracene, *p*-terphenyl; (3) *p*-terphenyl, *m*-terphenyl, fluoranthene; (4) fluoranthene, *o*-terphenyl (?), triphenylene, (5) triphenylene, chrysene; (6) chrysene; (7—8) chrysene, 3,4-benzofluoranthene; (9—16) not identified.

Identifications.—Samples of the exit gases were collected in a gas cell for infrared analysis. Methane was identified by its spectrum in the 7.3—8.5 μ region (max. at 7.36, 7.42, 7.66, 7.73, 7.79, 7.81, 7.85, 7.90, 7.94, 7.98, 8.05, 8.11, 8.17, and 8.22 μ), and ethylene by its spectrum in the 9.0—11.5 μ region (max. at 9.91, 10.01, 10.11, 10.21, 10.31, 10.40, 10.51, 10.75, 10.83, 10.92, 11.01, 11.07, 11.16, and 11.25 μ).¹⁴

Compounds identified were as follows; spectral maxima agreed with those of authentic specimens or with the literature.

Benzene, isolated from fractions (a) and (b) by gas-liquid chromatography. The b. p. and retention time were identical with those of an authentic specimen.

Biphenyl, isolated from fraction (1) by recrystallisation from ethanol; λ_{\max} , 248 m μ ; m. p. and mixed m. p. 70° (cf. ref. 9).

Fluorene, identified in fraction (2) after chromatography on partially acetylated cellulose; λ_{\max} , 261, 290, and 301 m μ .

Phenanthrene, isolated from fraction (2) by chromatography on partially acetylated cellulose; λ_{\max} , 243, 251, 275, 281, and 294 m μ ; fluorescence max. 348, 362, and 382 m μ .

Anthracene, identified in fraction (2) by chromatography on partially acetylated cellulose; λ_{\max} , 252, 308, 323, 339, 355, and 376 m μ ; fluorescence max. 380, 403, 427, and 450 m μ (cf. ref. 15).

p-Terphenyl, identified in fractions (2) and (3) by chromatography on partially acetylated cellulose; λ_{\max} , 280 m μ ; fluorescence max. 342 m μ ; m. p. and mixed m. p. 213—214° (cf. ref. 9).

m-Terphenyl, isolated from fraction (3); m. p. 85—86° (lit.,⁹ 87°); λ_{\max} , 250 m μ (cf. ref. 16); fluorescence band at 317 m μ .

Fluoranthene, identified in fractions (3) and (4); λ_{\max} , 237, 245, 253, 262, 271, 288, 309, 324, 343, and 359 m μ ; fluorescence max. 446 and 465 m μ .

o-Terphenyl (?), isolated from fraction (3) by chromatography on partially acetylated cellulose; λ_{\max} , 233 m μ (cf. ref. 17).

Triphenylene, isolated from fractions (4) and (5); λ_{\max} , 250, 257, 274, 286, 316, 331, and 340 m μ ; fluorescence max. 352, 360, and 368 m μ ; m. p. and mixed m. p. 195—197° (lit.,⁹ 199°).

Chrysene, isolated from fractions (5—8); λ_{\max} , 242, 259, 267, 283, 294, 306, 320, 344, 350, and 361 m μ ; fluorescence max, 360, 381, 401, and 425 m μ .

3,4-Benzofluoranthene, isolated from fractions (7—8); λ_{\max} , 238, 256, 266, 276, 289, 293, 301, 320, 338, 350, and 369 m μ ; fluorescence max. 443 and 462 m μ .

Ultraviolet Spectra.—These were examined in 95% ethanol by using a Optica CF₄ recording spectrophotometer.

Fluorescence Spectra.—These were examined in 95% ethanol in a Farrand recording spectrofluorometer.

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¹⁴ American Petroleum Institute Research Project 44, I.R. Spectral Data.

¹⁵ Sawicki, Hauser, and Stanley, *Internat. J. Air Poll.*, 1960, **2**, 253.

¹⁶ Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951; Clar, "Aromatische Kohlenwasserstoffe," Springer, Berlin, 1952.

¹⁷ Mueller and Pickens, *J. Amer. Chem. Soc.*, 1950, **72**, 3626.