

663. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part XIV.* The Pyrolysis of [α - ^{14}C]Ethylbenzene.*

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Pyrolysis of [α - ^{14}C]ethylbenzene at 700° has given a tar from which several compounds have been isolated and submitted to radiochemical assay. The results indicate that very little randomisation occurs, that the benzene ring system is very stable, that phenanthrene is probably formed by interaction of a $\text{C}_6\text{-C}_2$ unit and a C_6 unit (and not from two $\text{C}_6\text{-C}_1$ units), that anthracene is probably formed by rearrangement from phenanthrene, that 3,4-benzofluoranthene is formed by phenylation of phenanthrene followed by cyclodehydrogenation, and that at least two mechanisms must be involved in the formation of toluene and of pyrene.

PREVIOUS investigations in this series have shown that polycyclic aromatic hydrocarbons (including the carcinogenic 3,4-benzopyrene) are formed by the pyrolysis of simpler hydrocarbons.¹⁻⁸ The compounds pyrolysed have included acetylene,⁴ butadiene,⁶ ethylbenzene,⁵

* Parts XII and XIII, preceding papers.

¹ Badger, Buttery, Kimber, Lewis, Moritz, and Napier, *J.*, 1958, 2449; Badger and Kimber, *J.*, 1958, 2453; Badger and Kimber, *J.*, 1958, 2455; Badger and Buttery, *J.*, 1958, 2458; Spotswood, *J.*, 1960, 4427; Badger, Kimber, and Spotswood, *Nature*, 1960, 187, 663.

² Badger and Spotswood, *J.*, 1959, 1635; Badger and Kimber, *J.*, 1960, 2746.

³ Badger and Kimber, *J.*, 1960, 266.

⁴ Badger, Lewis, and Napier, *J.*, 1960, 2825.

⁵ Badger and Spotswood, *J.*, 1960, 4420.

⁶ Badger and Spotswood, *J.*, 1960, 4431.

⁷ Badger and Novotny, *J.*, part XII.

⁸ Badger and Novotny, *J.*, part XIII.

n-butylbenzene,⁵ and tetralin;³ and mechanisms for the formation of the polycyclic compounds have been advanced. Some theoretically possible mechanisms have been excluded as major routes to some compounds by consideration of the relative yields; but in other cases two or more mechanisms have seemed equally probable. To obtain more precise information we have investigated the use of ¹⁴C-labelled compounds. At the high temperatures involved in pyrolyses it seemed that sufficient randomisation of the active carbon atoms might occur to make this approach useless, and as a preliminary test of the method the pyrolysis of [α -¹⁴C]ethylbenzene, Ph-¹⁴CH₂·CH₃, was undertaken.

[*carbonyl*-¹⁴C]Acetophenone was prepared by a Friedel-Crafts reaction from benzene and sodium [*carboxy*-¹⁴C]acetate, and reduced to [α -¹⁴C]ethylbenzene by catalytic hydrogenation. This labelled ethylbenzene was then pyrolysed under conditions similar to those used for the inactive compound.⁵ Several compounds were isolated from the resulting tar and submitted to radiochemical assay, the activities being expressed as relative molar activities⁹ (which are linearly proportional to the number of labelled carbon atoms per molecule). The following compounds were isolated and analysed in this way (the number of labelled carbon atoms is given in parentheses): benzene (0.024), toluene (0.74), styrene (1.07), naphthalene (2.00), biphenyl (0.045), phenanthrene (1.05), anthracene (1.03), pyrene (2.4, 2.65), chrysene (3.14), and 3,4-benzofluoranthene (0.91). Other compounds known to be formed in this pyrolysis⁵ could not be isolated in sufficient amount or in suitable purity for radiochemical analysis.

It has been generally considered on theoretical grounds, and on practical evidence,^{7,10} that benzene is relatively stable even at 700°, and that the ring system does not break to a significant extent. However, the possibility of ring fission followed by re-formation had not been entirely eliminated. Groll¹¹ suggested that the initial step in pyrolyses involves breakdown to acetylene which then reacts with itself to form other compounds. Weizmann *et al.*¹² regarded butadiene as the precursor of the polycyclic compounds. It is therefore significant that the benzene isolated in the present work was found to be practically inactive; breakdown and resynthesis of the benzene ring must therefore occur only to a very small extent at 700°. This conclusion is supported by the inactivity of the biphenyl isolated, for this product must be formed by a termination reaction between two phenyl radicals, or by a propagation reaction brought about by phenyl-radical attack on ethylbenzene, with elimination of an ethyl radical.

Dehydrogenation of ethylbenzene by thermal fission of two C-H bonds would give styrene, and this is supported by the fact that the isolated styrene had one active carbon atom.

However, as previously discussed,⁵ the scission of a C-C bond is a process of lower energy than C-H scission, and ethylbenzene must therefore be expected to break down very readily according to schemes (1) and (2a) to give benzyl, methyl, phenyl, and ethyl radicals. Scission to give a two-carbon unit (*i.e.*, scheme 2a) seems to be preferred in pyrolyses, since ethyl- and butyl-benzene both give larger yields of benzene than toluene, while pyrolysis of propylbenzene gives a larger yield of toluene.⁵ On the other hand, the ethyl radicals could either react as such or undergo further scission (equation 2b) to methyl radicals. Evidence on this point has been provided by an examination of the exit gases: hydrogen, methane, and ethylene (plus ethane) are present in the approximate ratio 4 : 3 : 1. This low proportion of ethylene (plus ethane) suggests that ethyl radicals react more readily than methyl radicals, or that they undergo this further scission to methyl radicals and finally form the more stable compound, methane. The large proportion of hydrogen is expected in view of the predominance of dehydrogenation and cyclo-dehydrogenation at high temperatures. It must be concluded, therefore, that both

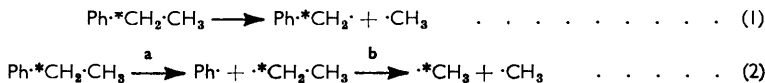
⁹ Birch, Massy-Westropp, Rickards, and Smith, *J.*, 1958, 360.

¹⁰ Egloff, "Reactions of Pure Hydrocarbons," Reinhold Publ. Corp., New York, 1937, p. 498.

¹¹ Groll, *Ind. Eng. Chem.*, 1933, **25**, 784.

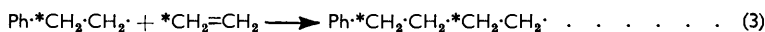
¹² Weizmann *et al.*, *Ind. Eng. Chem.*, 1951, **43**, 2312, 2318, 2322, 2325.

labelled and unlabelled methyl radicals are formed in the pyrolysis, and that the latter predominate.



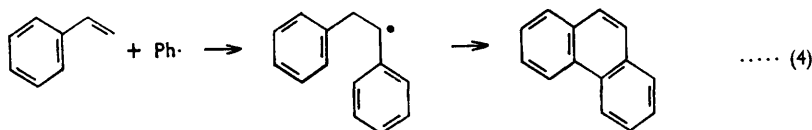
Now if toluene is formed by scission according to scheme (1) and hydrogenation of the benzyl radical, then it should have activity corresponding to one labelled atom. If it is formed by reaction of a methyl radical with a phenyl radical (or benzene) it should have activity corresponding to less than 0.5 labelled atom. Experimentally it was found that the activity corresponded to 0.74 labelled atom, and it seems that both mechanisms operate, the first predominating.

Chain re-synthesis has been postulated⁵ to account for the formation of naphthalene from ethylbenzene. Reaction of a phenethyl radical with ethylene, for example, would be expected to give a phenylbutyl radical (scheme 3) and hence naphthalene; and several variants of this process could also occur. This mechanism would require the resulting naphthalene to have two labelled atoms, and this was found to be the case.



For formation of phenanthrene one possible route would involve a chain termination between two benzyl radicals, and cyclodehydrogenation of the resulting dibenzyl; or the bibenzyl could be formed by chain propagation from toluene and a benzyl radical. This route was earlier considered⁵ to be unimportant in view of the small yield of phenanthrene furnished by pyrolysis of toluene, a conclusion which has been confirmed by the present work. This route should yield phenanthrene with radioactivity corresponding to two labelled carbon atoms; but the phenanthrene obtained contained only one labelled atom. Another possible route, involving reaction between naphthalene and a four-carbon unit (such as a butadienyl radical), must also be excluded as this would yield phenanthrene having approximately four labelled atoms.

The most probable route involves the action of a phenyl radical on a C₆-C₂ unit (such as ethylbenzene, styrene, a phenethyl radical or a styryl radical) and cyclodehydration of the product (scheme 4). Such a scheme would give phenanthrene having one labelled atom in agreement with experiment. It may be noted, however, that the present results



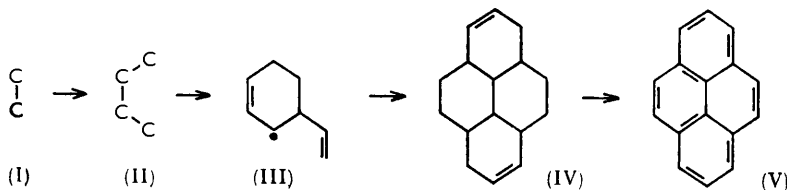
do not preclude the possibility that some phenanthrene may be formed from biphenyl and a two-carbon unit; but consideration of the relative yields of biphenyl and phenanthrene formed by pyrolyses of toluene, ethylbenzene, n-propylbenzene, and n-butylbenzene⁵ indicates that this route cannot be important.

It is also noteworthy that oxidative degradation of the phenanthrene isolated, followed by decarboxylation of the resulting biphenic acid, gave biphenyl having practically no radioactivity. Randomisation must therefore have been practically non-existent.

Anthracene could conceivably be formed from two benzyl radicals, or from naphthalene (or its equivalent) and a four-carbon unit. The former route should give a product having two labelled atoms, and the second a product having approximately four active atoms. As the anthracene isolated had activity corresponding to only one labelled atom neither of these routes can be important, and it seems likely that in this pyrolysis the anthracene is formed by thermal rearrangement of phenanthrene.¹³

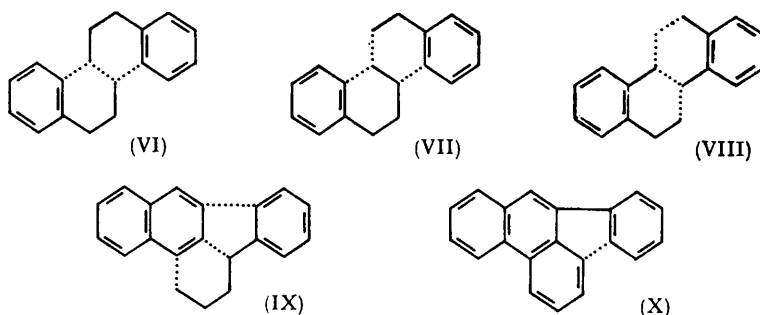
¹³ Orlow, *Ber.*, 1927, **60**, 1950.

The mode of formation of pyrene cannot be determined with certainty by the present work. Various suggestions have been published: possible routes involve dimerisation of styrene (Badger and Buttery¹), 3-vinylcyclohexenyl radicals,^{6,8} or *m*-xylene,¹⁴ or step-wise synthesis from a two-carbon unit.¹¹ The number of labelled carbon atoms found (approx. 2.5) suggests that more than one route may be important. A mechanism involving styrene as an intermediate would give pyrene having two labelled atoms; and one involving *m*-xylene would give pyrene having approximately three labelled atoms (as the *m*-xylene would presumably be formed by attack of methyl radicals on toluene)—the latter route seems very unlikely, for, although the pyrolysis of *m*-xylene is known to give pyrene,¹⁴ *m*-xylene itself has not been identified among the products of the pyrolysis of ethylbenzene or of the other alkylbenzenes studied.⁵



An alternative route to pyrene, involving step-wise synthesis from a two-carbon unit (I \rightarrow V), should give pyrene having eight labelled atoms. The observed activity could then be explained if it is assumed that most is formed from styrene (or its equivalent) and the remainder by the route (I \rightarrow V).

As previously postulated,^{2,3} chrysenes could be formed from two $\text{C}_6\text{-C}_3$ units (as VI), from a $\text{C}_6\text{-C}_4$ and a $\text{C}_6\text{-C}_2$ unit (as VII), and from two $\text{C}_1\text{-C}_6\text{-C}_2$ units (as VIII). Each



of these would give chrysenes having three labelled atoms, in agreement with experiment, providing that chain-lengthening occurs by attack of a methyl radical on a $\text{C}_6\text{-C}_2$ unit (to give the $\text{C}_6\text{-C}_3$ or the $\text{C}_1\text{-C}_6\text{-C}_2$ unit), and not by attack of an ethyl radical on a $\text{C}_6\text{-C}_1$ unit. With these qualifications the original proposals still appear plausible.

3,4-Benzofluoranthene could conceivably be formed either by interaction of two $\text{C}_6\text{-C}_4$ units (as IX), or by cyclodehydrogenation of 9(or 1)-phenylphenanthrene (as X). In pyrolysis of [$\alpha\text{-}^{14}\text{C}$]ethylbenzene the former route should yield 3,4-benzofluoranthene having four labelled atoms (as each $\text{C}_6\text{-C}_4$ unit would have two labelled atoms). The second route should also give 3,4-benzofluoranthene containing four active atoms if the phenylphenanthrene is formed from two $\text{C}_6\text{-C}_4$ units; but if the intermediate is formed by phenylation of phenanthrene then only one labelled atom would be expected. In fact the product showed activity corresponding to one radioactive carbon atom and the latter route therefore seems to be confirmed.

¹⁴ Baker, McOmie, and Norman, *Chem. and Ind.*, 1950, 77.

EXPERIMENTAL

Radioactive Assay.—Specimens were assayed for radioactivity, with an end-window counter, as infinitely thick, solid samples of 1 cm.² cross-sectional area;¹⁵ and counting rates were corrected for background and dead time of the instrument. The counting equipment consisted of an EKCO automatic scaler type N530D, in conjunction with an EKCO probe unit type N558 and an EW3H Geiger tube. The counts per min. were determined by recording five readings each of 5 min. duration for each sample. All assays were usually repeated twice, either with a new sample or with the original sample repacked. In this way errors due to differences in packing, and to losses during dilution, were almost eliminated. The statistical counting error was calculated as standard deviations for each series of counts and was in no case greater than 1.5% (except for the practically inactive products). Van Slyke-Folch oxidations were carried out essentially as described in the literature;¹⁶ however, the apparatus was adapted for oxidation of liquids by using sealed capillaries containing the material to be oxidised. The Van Slyke fluid was contained in a 2-neck 25 ml. flask. The second neck contained the capillary tube which, after evacuation of the system, was fractured on a lip protruding through the joint from the main part of the system, by twisting the flask.

The samples were prepared by the "pellet" technique.¹⁵ It was found that the technique of gently rotating the press before removing it to prevent the pellet getting stuck was often unsatisfactory for some low-melting substances (*e.g.*, styrene dibromide, biphenyl, naphthalene). Quite clean separations were obtained, however, if the planchette was first cooled on a block of solid carbon dioxide for 4–5 sec., and the press warmed by immersion for a similar time in hot water and then dried. Difficulty due to static electrical effects for substances such as anthraquinone, chrysene, and 3,4-benzofluoranthene was overcome by grinding the material with a drop of water in an agate mortar. After pelleting, the sample was dried under an infrared lamp.

[carbonyl-¹⁴C]Acetophenone.—Sodium [carboxy-¹⁴C]acetate (1.0 mc; 20.4 mg.) was scraped from the phial with a spatula into a 3-neck flask. The phial was rinsed with ten 1 ml. portions of benzene, and the washings were poured into the reaction vessel (~98% transfer). Pure inactive anhydrous sodium acetate was added to give total acetate (2.46 g., 0.03 mole). Aluminium chloride (16.5 g., 0.12 mole) and benzene (5 ml.) were added, and the mixture stirred and refluxed for 8 hr., then worked up as in method I for the preparation of [carbonyl-¹⁴C]-acetophenone described by Murray and Williams.¹⁷ Final purification was effected by distillation in a vacuum line, to give [carbonyl-¹⁴C]acetophenone (2.62 g., 85%), n_D^{15} 1.5353 (lit.,¹⁸ n_D^{15} 1.5363)

[α -¹⁴C]Ethylbenzene.—[carbonyl-¹⁴C]Acetophenone (2.17 g.), "AnalaR" acetic acid (6 ml.), 70% perchloric acid (5 drops), and 5% palladium-charcoal (2 g.) were hydrogenated for 72 hr. at 50 lb./in.² in a Cook and Son's low-pressure hydrogenator adapted for semimicro-work. The reaction mixture was filtered through a sintered-glass funnel, and the catalyst washed with ethanol (5 ml.). The filtrate was neutralised with sodium hydroxide solution and extracted with ether (2 × 10 ml.); the extract was washed with water, dried, and evaporated, and the residue diluted to 100 ml. with inactive ethylbenzene and then distilled, giving [α -¹⁴C]ethylbenzene, b. p. 133–134°, n_D^{14} 1.4983 (lit.,¹⁹ $n_D^{14.5}$ 1.4983). Van Slyke-Folch oxidation gave barium carbonate which was collected for radioactive assay (Found: relative molar activity × 10⁻², 20.8 ± 0.19).

Degradation of [α -¹⁴C]Ethylbenzene.—[α -¹⁴C]Ethylbenzene (0.05 ml.) was diluted to 0.5 ml. with inactive material and degraded by side-chain bromination, followed by hydrolysis and permanganate oxidation to benzoic acid.²⁰ Recrystallisation from water gave [carboxy-¹⁴C]-benzoic acid, m. p. 120.5–122° (Found: relative molar activity × 10⁻², 21.8 ± 0.70; 1°C requires 20.8).

Pyrolysis of [α -¹⁴C]Ethylbenzene.—[α -¹⁴C]Ethylbenzene (40 g.) was pyrolysed under similar

¹⁵ Popjak, *Biochem. J.*, 1950, **46**, 560.

¹⁶ Calvin, Heidelberger, Reid, Talbert, and Yankwich, "Isotopic Carbon," Wiley, New York, 1949, p. 92.

¹⁷ Murray and Williams, "Organic Synthesis with Isotopes," Part I, Interscience Publ. Inc., New York, p. 662.

¹⁸ Timmermans and Hennaut-Roland, *J. Chim. phys.*, 1935, **32**, 525.

¹⁹ "Handbook of Physics and Chemistry," Chemical Rubber Publ. Co., Cleveland, Ohio, 1958, 834.

²⁰ Roberts, Ropp, and Neville, *J. Amer. Chem. Soc.*, 1955, **77**, 1764.

conditions to those described for the inactive compound.⁵ It was vaporised (8 drops/min.) and passed with nitrogen (1 ml./sec.) through the pyrolysis tube maintained at 700°. The resulting tar (19.5 g.) together with the chloroform washings from the pyrolysis tube was distilled, to give fractions (a) b. p. 80—140° (12.0 g.), (b) b. p. 80—120°/20 mm. (2.5 g.), and (c) a residue (4.25 g.).

Analysis.—Gas-liquid chromatography, chromatography on activated alumina and on columns of partially acetylated cellulose, and recrystallisation were used to separate and purify the compounds which were identified by m. p.s and ultraviolet and fluorescence spectra. Radioactive assay could only be carried out on compounds obtained pure in quantity such that dilution did not appreciably affect the accuracy of the determinations (usually not less than 5—10 mg. were required).

Exit Gases.—The infrared spectrum of a sample of the exit gases showed the presence of methane and ethylene. Further samples were analysed by gas-liquid chromatography in a Perkin-Elmer vapour fractometer. Comparison of retention times with those of standard samples of methane and ethylene gave the following analysis: methane ~18.3%, ethylene $4.8 \pm 0.4\%$, ethane (?) $2 \pm 0.4\%$, nitrogen ~50%, and (by difference) hydrogen ~24.9%. Hydrogen was used as the carrier gas. Therefore the gases formed in the pyrolysis were methane 36.6%, ethane (?) 4%, ethylene 9.6%, and hydrogen 49.8%. The ethane was provisionally identified by comparison with recorded retention times.

Fractions (a) and (b).—Fraction (a) was shown by gas-liquid chromatography in a Griffin and George vapour-phase chromatographic apparatus (mark II) to contain benzene, toluene, and styrene. Fraction (b) was found to contain mainly naphthalene and biphenyl. These compounds were separated and purified as described below.

Examination of Residue.—The residue (c) was chromatographed in a minimum amount of benzene-hexane (1 : 2) on alumina (Spence). Elution gave the following fractions (200 ml. each): with hexane, fractions 1—19; with benzene-hexane (1 : 10), fractions 20—47; with benzene-hexane (1 : 4), fractions 48—56; with benzene-hexane (1 : 2), fractions 57—63; with benzene-hexane (1 : 1), fractions 64—71, and with benzene-hexane (2 : 1), fractions 72—76. On the basis of their fluorescence and ultraviolet spectra, these fractions were recombined to give twelve main fractions. By the techniques described below for the individual compounds the following pure substances (or their derivatives) were isolated from seven of these fractions: fractions 1—10, naphthalene and biphenyl; fractions 11—22, phenanthrene; fractions 23—26, anthracene and pyrene; fractions 27—30, pyrene; fractions 51—55, chrysene; fractions 56—65 and 66—69, 3,4-benzofluoranthene.

Isolations.—*Benzene.* Fraction (a) was fractionated through a 10 cm. Vigreux column. Gas-liquid chromatography showed that the distillate contained 4—6% of toluene. Re-fractionation (twice) gave benzene, $n_D^{16.5} 1.5033$ (lit.,²¹ $n_D^{16} 1.5038$). A sample (12 mg.) was oxidised by the Van Slyke-Folch technique and the resulting barium carbonate collected for radioactive assay (Found: relative molar activity $\times 10^{-2}$, 0.5 ± 0.08).

Toluene. A portion of the combined residues from the fractionation of fraction (a) was chromatographed in the gas-liquid chromatograph, and the toluene fraction collected.²² Further gas-liquid chromatography of a sample of this toluene showed it contained <2% of impurities. Van Slyke-Folch oxidation gave barium carbonate which was washed and collected for radioactive assay (Found: relative molar activity $\times 10^{-2}$, 15.5 ± 0.14 ; 1°C requires 20.8).

Styrene. The combined residues from fraction (a), after the toluene had been removed, was shown by gas-liquid chromatography to contain approx. 20% of styrene. The portion not used for the toluene analysis was treated dropwise with bromine until a red colour persisted. On cooling, the dibromide separated. Recrystallisation from 80% ethanol (with charcoal) gave styrene dibromide (6 mg.), m. p. 66—68°. Dilution with inactive dibromide (24 mg.) gave sufficient material for radiochemical assay (Found: relative molar activity $\times 10^{-2}$, 22.4 ± 0.26 ; 1°C requires 20.8).

Naphthalene. Fraction (b) was redistilled slowly on a water-bath under water-pump vacuum. Recrystallisation of the solid distillate gave naphthalene, m. p. 79—80° (Found: relative molar activity $\times 10^{-2}$, 41.5 ± 0.01 ; 2°C requires 41.6).

Biphenyl. The residue left after the distillation of fraction (b) was chromatographed on alumina. Elution with hexane gave twenty-four fractions. The ultraviolet spectrum of

²¹ Landolt and Jahn, *Z. phys. Chem.*, 1892, **10**, 303.

²² Napier and Rodda, *Chem. and Ind.*, 1958, 1319.

fractions 12—18 showed the presence of biphenyl. Recrystallisation of the combined fractions from ethanol gave biphenyl, m. p. and mixed m. p. 56—57° (Found: relative molar activity $\times 10^{-2}$, 0.94 ± 0.11).

Phenanthrene. The crude phenanthrene from fractions 11—22 of the original chromatogram was recrystallised from ethanol and then rechromatographed on alumina. Further chromatography on partially acetylated cellulose, followed by fractional sublimation, gave phenanthrene, m. p. 96—98°. The fluorescence spectrum of this material suggested that the small amount of impurity may have been 9,10-dihydrophenanthrene. Formation of the picrate, and recrystallisation, followed by chromatography on alumina to decompose the complex, gave phenanthrene, m. p. 98—99° (Found: relative molar activity $\times 10^{-2}$, 22.0 ± 0.21 , 1°C requires 20.8).

Anthracene. The ultraviolet and fluorescence spectra of fractions 23—26 showed the presence of a considerable proportion of anthracene together with some phenanthrene and pyrene. Oxidation was carried out in boiling ethanol (10 ml.) with nitric acid (0.2 g.) for 1½ hr. The orange-yellow product was recrystallised from benzene-ethanol (1 : 2). Sublimation under a high vacuum removed traces of the orange phenanthraquinone, leaving a residue of pale yellow 9,10-anthraquinone (5 mg.), m. p. 282—285° (Leitz hot-stage microscope). The sample was diluted with inactive 9,10-anthraquinone (20 mg.) for radiochemical analysis (Found: relative molar activity $\times 10^{-2}$, 21.4 ± 0.21 ; 1°C requires 20.8).

Pyrene. The mother-liquor from which the crude anthraquinone crystallised was combined with fractions 27—30. (Ultraviolet spectroscopy showed the presence of pyrene in both fractions.) The residue after removal of the solvent was taken up in a few ml. of nitrobenzene, brominated by the addition of a few drops of bromine, and boiled for 2—3 min. The bromo-compound which crystallised on cooling was recrystallised three times from nitrobenzene (the first with a small amount of charcoal) to give 3,5,8,10-tetrabromopyrene (17 mg.), m. p. and mixed m. p. 400—402°. The sample was diluted with an equal amount of inactive material for radiochemical assay (Found: relative molar activity $\times 10^{-2}$, 50.0 ± 0.27 ; 2.5°C requires 52.0). A second run gave tetrabromopyrene (28 mg.) which was assayed undiluted (Found: relative molar activity $\times 10^{-2}$, 55.2 ± 0.10).

Chrysene. After removal of the solvent from fractions 51—55 the pale yellow residue was recrystallised twice from ethanol, to give chrysene, m. p. 250—251°. This was diluted with twice its weight of inactive chrysene for radiochemical assay (Found: relative molar activity $\times 10^{-2}$, 65.3 ± 0.08 ; 3°C requires 62.4).

3,4-Benzofluoranthene. Fractions 55—56 and 66—69 were (each set) chromatographed on columns of partially acetylated cellulose. The fractions were examined by ultraviolet spectroscopy, and those fractions containing almost pure 3,4-benzofluoranthene combined and recrystallised from ethanol. Further recrystallisation gave 3,4-benzofluoranthene (9 mg.), m. p. 164—165°. This was diluted with inactive 3,4-benzofluoranthene (18 mg.) for radiochemical analysis (Found: relative molar activity $\times 10^{-2}$, 19.0 ± 0.13 ; 1°C requires 20.8).

Other products. Attempted purification of 1,2-benzanthracene (from fractions 49—55) and 3,4-benzopyrene (from fractions 56—65 and 66—69) gave products neither sufficiently pure nor in sufficient quantity for radiochemical analysis.

*Degradation of Phenanthrene.—Oxidation.*²³ To phenanthrene (0.75 g.), isolated from the pyrolysis, were added glacial acetic acid (6.6 g.) and 50% hydrogen peroxide (2.1 g.). The bath-temperature was raised to 110°, whereupon the reaction commenced. After 45 min., the mixture was refluxed for 15 min. The warm solution was poured into an equal volume of water and basified with 25% sodium hydroxide solution (which was added with stirring and warming). After cooling, a small amount of resin was removed. The mixture was warmed (charcoal), filtered, and acidified with hydrochloric acid. Extraction with ether for 6 hr. in a continuous extractor, removal of the solvent, and recrystallisation of the product from water gave 2,2'-biphenic acid, m. p. 225—227°.

Decarboxylation. A mixture of 2,2'-biphenic acid (0.16 g.), copper bronze (0.08 g.), and pure quinoline (7 ml.) was refluxed for 2 hr. The carbon dioxide evolved was led from the top of the condenser and bubbled through a 4% solution of barium hydroxide in a 2-neck flask protected by a potassium hydroxide tube. The whole apparatus was initially swept with dry carbon dioxide-free nitrogen. The barium carbonate was collected for radiochemical assay (Found: relative molar activity $\times 10^{-2}$, 22.3 ± 0.12 ; 1°C requires 20.8). The products

²³ O'Connor and Moriconi, *Ind. Eng. Chem.*, 1953, **45**, 277.

were treated with ether (50 ml.) and the filtered solution was extracted with concentrated hydrochloric acid. The aqueous layer was extracted with further portions of ether (2×25 ml.), and the combined extracts were washed with 10% hydrochloric acid, 10% sodium hydroxide solution, and water. After drying (CaCl_2), the solvent was removed and the residue recrystallised from ethanol-water, to give biphenyl, m. p. 69—70°. The sample was diluted with an equal amount of inactive biphenyl and submitted to radiochemical assay [Found: relative molar activity $\times 10^{-2}$, 1.36 ± 0.02].

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