860. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part XI.* The Pyrolysis of Buta-1,3-diene and of Buta-1,3-diene with Pyrene.*

By G. M. Badger and T. M. Spotswood.

The tar produced by the pyrolysis of buta-1,3-diene has been found to contain 1,2- (0·31%) and 3,4-benzopyrene (0·34%), and numerous other polycyclic compounds have also been identified. The tar produced by the pyrolysis of a mixture of butadiene and pyrene contained similar amounts of the two benzopyrenes. Mechanisms for the formation of the polycyclic hydrocarbons are discussed in the light of this observation.

During investigations into the formation of 3,4-benzopyrene and other carcinogenic hydrocarbons by high-temperature pyrolysis, tars obtained by pyrolysis of styrene,[1] 1-phenylbuta-1,3-diene,[2,3] tetralin,[4] indene,[5] toluene,[6] ethylbenzene,[6] propylbenzene,[6] butylbenzene,[6] and acetylene [7] have been shown to contain a range of hydrocarbons of qualitatively similar composition. The yields of the higher polycyclic hydrocarbons increased with the length of the side-chain, and it has been proposed [6] that buta-1,3-diene may be the important intermediate in their formation. Many types of hydrocarbon yield buta-1,3-diene on pyrolysis,[8] and Weizmann *et al.*[9] have identified it in the products of thermal cracking of petroleum fractions. As a further contribution, the pyrolysis of buta-1,3-diene [10] is now reported; the tar obtained by pyrolysis of a mixture of buta-1,3-diene and pyrene has also been examined to test the adequacy of a hypothesis proposed by Weizmann *et al.*[9] in which the polycyclic hydrocarbons were assumed to be synthesised by successive Diels–Alder additions of buta-1,3-diene to simpler hydrocarbons.

The pyrolysis of buta-1,3-diene was carried out by passing butadiene vapour, with nitrogen, through a silica tube packed with porcelain chips and maintained at 700°. The tar formed (in 52% yield) was analysed by distillation, gas–liquid chromatography, chromatography on alumina and silica gel, chromatography on columns of partially acetylated cellulose,[12] chromatography on partially acetylated paper,[11] and by spectroscopy.

The following compounds were identified (% by wt. in parentheses): methane (—); ethylene (—); acenaphthylene (1·44); anthanthrene (0·1); anthracene (0·65); 1,2-benzanthracene (0·31); benzene (41); 3,4-benzofluoranthene (0·05); 10,11-benzofluoranthene (0·06); 11,12-benzofluoranthene (0·26); 1,2-benzofluorene (0·46); 2,3-benzofluorene (0·76); 1,12-benzoperylene (0·34); 1,2-benzopyrene (0·31); 3,4-benzopyrene (0·34); 3,4-benzotetraphene (0·04); chrysene (0·39); an alkylchrysene (0·10); 1,2:5,6-dibenzanthracene (0·07); bibenzyl (0·20); 2,2′-binaphthyl (0·40); biphenyl (2·09); ethylbenzene (0·12); fluoranthene (0·54); fluorene (1·67); indene (1·44); 4-methylbiphenyl (0·4); 1- and 2-methylnaphthalene (1·24); naphthalene (14·0); perylene (0·1); phenanthrene (4·2); 9-phenylanthracene (trace); 4,5-(*o*-phenylene)fluoranthene (0·008); 2,3-(*o*-phenylene)pyrene (0·19); 2-phenylnaphthalene (0·32); pyrene (1·0); stilbene (0·2);

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* Part X, preceding paper.

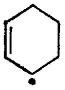
[1] Badger and Buttery, *J.*, 1958, 2458.
[2] Badger and Spotswood, *J.*, 1959, 1635.
[3] Badger and Spotswood, preceding paper.
[4] Badger and Kimber, *J.*, 1960, 266.
[5] Badger and Kimber, *J.*, 1960, 2746.
[6] Badger and Spotswood, *J.*, 1960, 2825.
[7] Badger, Lewis, and Napier, *J.*, .
[8] Egloff and Hulla, *Chem. Rev.*, 1944, **35**, 279.
[9] Weizmann *et al.*, *Ind. Eng. Chem.*, 1951, **43**, 2312, 2318, 2322, 2325.
[10] Cf. Murphy and Duggan, *J. Amer. Chem. Soc.*, 1949, **71**, 3347.
[11] Spotswood, *J. Chromatog.*, 1959, **2**, 90.
[12] Spotswood, *J. Chromatog.*, 1960, **3**, 101.

styrene (5·0); toluene (15·6); triphenylene (0·18); *p*-xylene (1·0) and traces of alkylphenanthrenes, -anthracenes, -fluoranthenes, and -pyrenes which could not be fully identified.

The pyrolysis of a mixture of butadiene and pyrene was carried out by introducing a weighed amount of pyrene into the pyrolysis tube in such a position that the temperature in its immediate vicinity was 300—350°; butadiene vapour was passed into the tube as before, and the mixed vapours, with nitrogen, were carried through the hot portion of the silica pyrolysis tube packed with porcelain chips and maintained at 700°. The tar formed (in 55% yield) was analysed in the usual way, but the gravimetric determinations were confined to 1,2-benzopyrene and 3,4-benzopyrene, which were obtained in 0·41 and 0·38% yield (based on tar formed) respectively. Qualitative examination of the remainder of the tar established the presence of most of the compounds obtained in the tar formed from buta-1,3-diene alone.

The nature of the initiation process in the thermal polymerisation of butadiene is unknown; mechanisms have been proposed for the reaction initiated by excited mercury atoms,[13] but the results cannot be applied to the present pyrolyses since the whole of the excitation energy of the mercury atom (112 kcal./g.-atom) is available for transfer, and this is sufficient to break most carbon–carbon and carbon–hydrogen bonds.

Under the present reaction conditions, free-radical formation would be expected and the presence of large amounts of methane in the exit gases indicates the presence of methyl radicals in the reaction system. Hydrogen abstraction from buta-1,3-diene would then lead to the radicals $\cdot CH{:}CH{\cdot}CH{:}CH_2$ and $CH_2{:}\dot{C}{\cdot}CH{:}CH_2$, and these must be major components of the reaction system. Reaction of buta-1,3-diene with ethylene yields cyclohexene,[14] and dimerisation of buta-1,3-diene produces 3-vinylcyclohexene;[14] these compounds and the radicals derived from them by hydrogen abstraction from the reactive allylic positions (I—III) must also be important components. The observed products can be reasonably explained on the basis of radicals and compounds derived from these intermediates.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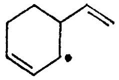
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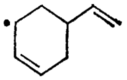

(III)

The products obtained from the pyrolysis of buta-1,3-diene show a remarkable similarity to those obtained by pyrolysis of butylbenzene,[6] and it is thought that similar mechanisms may apply to both reactions, the observed variations in yields being a function of the differing state of hydrogenation of the important intermediates. Phenyl radicals and benzyl radicals must be produced in the primary decomposition of the butylbenzene molecule, but in the pyrolysis of buta-1,3-diene they must, of course, be produced in secondary reactions. In the present case, the cyclohexenyl radical (I) is the intermediate corresponding to the phenyl radical.

Benzene and styrene would be readily obtained from cyclohexene and 3-vinylcyclohexene by dehydrogenation, and reaction of the radical (I) with methyl radicals could account for the toluene obtained. The relatively high yield of *p*-xylene obtained could arise by reaction of the radical $CH_2{:}\dot{C}{\cdot}CH{:}CH_2$ with buta-1,3-diene (IV), with subsequent hydrogenation; biphenyl from reaction of two cyclohexenyl radicals followed by dehydrogenation; and bibenzyl by reaction of two benzyl radicals.

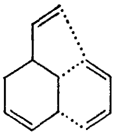
Reaction of the radical (III) with butadiene would yield acenaphthylene on dehydrogenation (V). It is notable that, of the other compounds pyrolysed in the present investigations, only butylbenzene[6] gave measurable yields of this compound. Naphthalene could

[13] Collin and Lossing, *Canad. J. Chem.*, 1957, **35**, 778.

[14] Rowley and Steiner, *Discuss. Faraday Soc.*, 1951, **10**, 198.

be formed by the sequence of reactions (VI ⟶ IX); the yields were of the same order as from butylbenzene,[6] for which similar mechanisms involving a phenyl radical have been proposed.


(IV)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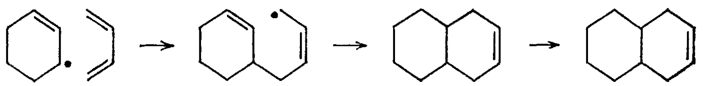
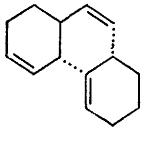

(VI) (VII) (VIII) (IX)

Condensation of a cyclohexenyl radical with styrene or 3-vinylcyclohexene would yield phenanthrene (X), and the small yield of this compound may be ascribed to the degree of hydrogenation of the intermediates.

The intermediate radical (VIII), and the octahydronaphthalene (IX), by dimerisation and radical addition, could yield 10,11-benzofluoranthene, 11,12-benzofluoranthene, and perylene (XI—XIII). 1,1′-Binaphthyl could conceivably be formed by similar processes, but it was not observed. However, its absence is not considered significant in view of the difficulty of identifying small amounts of this compound in the complex reaction mixture. 2,2′-Binaphthyl is known to be formed in moderate yield on pyrolysis of naphthalene,[15] and it is probable that similar mechanisms apply in the present pyrolysis. Similar condensations of 1,1′-binaphthyl to perylene[16] and of 1,2′-binaphthyl to 10,11- and 11,12-benzofluoranthenes[17] have been reported as a result of catalytic cyclodehydrogenations.

The formation of pyrene has already been discussed in connection with the pyrolysis of the alkylbenzenes,[6] and a mechanism involving dimerisation of the radical (III), or reaction of the radical with styrene, was proposed by analogy with the formation of pyrene from *m*-xylylene.[18] A similar mechanism is suggested for the present pyrolysis (XIV ⟶ XVI).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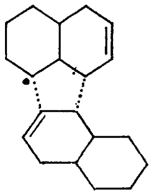
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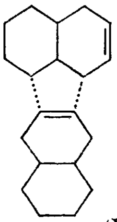
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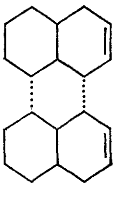
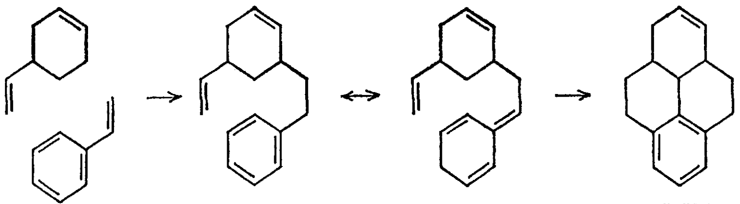
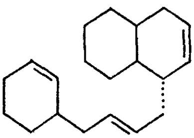

(XIII)

The formation of 3,4-benzopyrene and 1,2-benzopyrene in the present pyrolysis is thought to proceed mainly by addition of butadiene to the hydrogenation intermediate (XV), or to the radicals derived from it. The relative yields of these two compounds would then depend on the stage at which dehydrogenation to an aromatic structure occurs.


(XIV) (XV) (XVI)


(XVII)

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

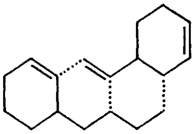
[16] Orchin and Friedel, *J. Amer. Chem. Soc.*, 1946, **68**, 573.

[17] Orchin and Reggel, *J. Amer. Chem. Soc.*, 1947, **69**, 505.

[18] Baker, McOmie, and Norman, *J.*, 1951, 1114.

Mechanisms (XVII) involving the reaction of two C_6—C_4 units previously postulated [6,9] may also be of importance and contribute to the formation of 3,4-benzopyrene.

Chrysene and 1,2-benzanthracene could be formed by reaction of the C_6–C_4 radical involved in the formation of naphthalene with either styrene or vinylcyclohexene (XVIII, XIX), and similar mechanisms are thought to apply in the pyrolysis of the alkylbenzenes.



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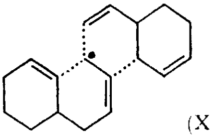

(XIX)

The formation of the other compounds identified has already been discussed in relation to other pyrolyses: [1-7] fluoranthene could be formed by dimerisation of 3-vinylcyclohexene to give 1-phenylnaphthalene followed by cyclisation, a process known to occur under catalytic conditions; [17] fluorene by ring closure of diphenylmethane; 4,5-(*o*-phenylene)fluoranthene by phenylation of fluoranthene or its precursors, followed by cyclisation; and 2,3-(*o*-phenylene)pyrene by phenylation of pyrene (to give 3-phenylpyrene) followed by cyclisation. Suitable mechanisms for the other C_{22} hydrocarbons identified (1,12-benzoperylene, 1,2:5,6-dibenzanthracene, 3,4-benzotetraphene, and anthanthrene) cannot yet be proposed.

It has sometimes been suggested [9] that the higher polycyclic hydrocarbons could be formed by successive Diels–Alder additions of butadiene to simpler hydrocarbons; but the results obtained from a mixed pyrolysis of buta-1,3-diene and pyrene suggest that this reaction is not an important synthetic route for the benzopyrenes. The small increase in yield observed was barely significant, and a much higher conversion would be required to account for the formation of 1,2- and 3,4-benzopyrene in the present series of pyrolyses.

EXPERIMENTAL

Pyrolysis of Buta-1,3-*diene*.—Buta-1,3-diene was transferred to a small pressure vessel which was connected to the pyrolysis apparatus already described.[19] Butadiene vapour (7—9 g./hr.), with nitrogen (1 ml./sec.), was passed through a silica tube (36 in. × 1 in.) packed with porcelain chips, maintained at 700°. A liquid tar (25 g.) was obtained from 49 g. of butadiene, and carbon (*ca.* 1 g.) was deposited in the pyrolysis tube. The tar was distilled to give the following fractions: (*a*) b. p. 80—100°/760 mm. (11·8 g.); (*b*) b. p. 0—40°/30 mm. (3·0 g.); (*c*) b. p. 40—60°/30 mm. (1 g.); (*d*) b. p. 60—100°/30 mm. (4 g.); and (*e*) a residue (5·2 g.).

Analysis by Gas–Liquid Chromatography.—Low-boiling fractions were analysed by gas–liquid chromatography in a Griffin and George vapour-phase chromatographic apparatus (Mark II) modified for collection of samples.[20] The column packings used were Apiezon or Silicone 30 *L* supported on Celite (40—80 mesh, B.S.S.; 1 : 4 w/w). The compounds were collected and whenever possible were identified by infrared spectroscopy. The percentage composition of the fractions was determined from the areas under the peaks.

Analysis of Fractions (a), (b), (c), *and* (d).—Analysis by gas–liquid chromatography showed the presence of benzene, toluene, ethylbenzene, *p*-xylene, styrene, naphthalene, indene, and a compound tentatively identified as 2-methylstyrene.

Analysis of Residue.—The residue (fraction *e*) was chromatographed on a column of activated alumina (500 g.). Elution with hexane, followed by hexane containing increasing amounts of benzene, and finally with benzene containing 5% of ethanol gave a number of fractions which were recombined on the basis of a preliminary examination by chromatography on partially acetylated paper to give thirteen major fractions. Fraction 13 was then rechromatographed on deactivated alumina (equilibrated over 60% sulphuric acid) to give a further four fractions, and fraction 16 was rechromatographed on a column of silica gel, deactivated by the addition of 12% of water.

The first six fractions were examined by gas–liquid chromatography and the remainder were examined separately by chromatography on a column of partially acetylated cellulose

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

[20] Napier and Rodda, *Chem. and Ind.*, 1958, 1319.

with benzene–ethanol–water (4 : 17 : 1) as developing solvent in the manner previously described.[11,12] Each fraction was examined by ultraviolet spectroscopy, and when necessary further fractionation was obtained by chromatography on partially acetylated paper. The fractions containing phenanthrene and pyrene were examined by chromatography on a 90 cm. column of partially acetylated cellulose.

The compounds identified in the individual fractions are summarised below. Fractions 1 and 2 contained naphthalene and biphenyl; fractions 3—5 contained biphenyl, bibenzyl, acenaphthylene, fluorene, and 2-phenylnaphthalene; fraction 6 contained acenaphthylene, fluorene, phenanthrene, and 2-phenylnaphthalene; fractions 7—9 contained fluorene, phenanthrene, anthracene, pyrene, fluoranthene, and 1,2-benzanthracene; fraction 10 contained 1,2-benzofluorene, 2,3-benzofluorene, triphenylene, pyrene, 1,2-benzanthracene, chrysene, an alkylchrysene, and 3,4-benzopyrene; fraction 11 contained 2,3-benzofluorene, triphenylene, 1,2-benzofluorene, 1,2-benzopyrene, perylene, chrysene, an alkylchrysene, 10,11-benzofluoranthene, 3,4-benzofluoranthene, and 3,4-benzopyrene; fraction 12 contained 1,2-benzopyrene, 3,4-benzopyrene, perylene, 1,12-benzoperylene, 11,12-benzofluoranthene, an alkylchrysene, 3,4-benzofluoranthene, and 4,5-(*o*-phenylene)fluoranthene; fraction 13 contained 2,3-benzofluorene, 1,2-benzopyrene, an alkylchrysene, 11,12-benzofluoranthene, 3,4-benzofluoranthene, 3,4-benzopyrene, and 1,2:5,6-dibenzanthracene; fraction 14 contained 1,12-benzoperylene, 11,12-benzofluoranthene, 2,3-(*o*-phenylene)pyrene, anthanthrene, and 3,4-benzopyrene; and fractions 15 and 16 contained 1,12-benzoperylene, 2,3-(*o*-phenylene)pyrene, anthanthrene, and 3,4-benzotetraphen.

Details of Identification.—Spectra quoted for identifications agreed with those of authentic specimens unless otherwise stated.

Benzene. Isolated by gas–liquid chromatography, it had infrared maxima at 2·38, 2·46, 3·18, 3·21, 3·78, 4·22, 4·41, 5·02, 5·41, 5·62, 5·90, 6·52, 6·75, 7·13, 8·48, and 9·62 μ (liquid film).

Toluene. Isolated by gas–liquid chromatography, it had infrared maxima at 2·40, 3·22, 3·34, 3·40, 3·60, 5·09, 5·31, 5·49, 5·72, 6·20, 6·32, 6·52, 6·67, 6·80, 7·22, 8·00, 8·24, 8·48, 8·64, 9·00, 9·21, 9·58, 9·70, 11·17, 11·90, 12·74, 13·74, and 14·40 μ (liquid film).

Styrene. Isolated by gas–liquid chromatography, it had infrared maxima at 2·40, 3·24, 3·30, 5·09, 5·29, 5·42, 5·69, 5·90, 6·10, 6·20, 6·32, 6·50, 6·68, 6·89, 7·02, 7·46, 7·56, 7·74, 8·30, 8·46, 8·65, 8·92, 9·02, 9·21, 9·80, 10·07, 11·00, 11·90, 12·90, and 14·40 μ (liquid film), together with peaks at 6·80, 9·50, and 13·42 μ, probably due to traces of *o*-xylene.

Ethylbenzene and p-*xylene.* These were identified by comparison of retention time ratios in gas–liquid chromatography with those of authentic specimens. Although the amount of ethylbenzene appeared to be small, the peak corresponding to *p*-xylene did not give a pure infrared spectrum of this compound. The interpretation of the spectrum was difficult but the maxima agreed with a mixture of *m*- and *p*-xylene.

Indene. Isolated by gas–liquid chromatography, this had infrared maxima at 3·21, 3·38, 3·51, 5·10, 5·18, 5·22, 5·32, 5·40, 5·52, 5·80, 5·98, 6·18, 6·82, 7·14, 7·31, 7·49, 7·60, 7·74, 7·88, 8·17, 8·30, 8·56, 8·90, 9·42, 9·81, 10·54, 10·90, and 11·60 μ (in CCl_4).

Naphthalene. Isolated by gas–liquid chromatography, it had maxima at 248, 257, 266, 275, 285, and 311 mμ.

Biphenyl. Isolated by gas–liquid chromatography, it had infrared maxima at 2·46, 3·26, 3·30, 3·41, 3·45, 5·05, 5·14, 5·24, 5·30, 5·34, 5·45, 5·58, 5·62, 5·75, 6·00, 6·02, 6·76, 6·88, 7·00, 7·23, 7·72, 7·98, 8·50, 8·53, 9·23, 9·60, 9·71, 9·90, 10·10, 10·40, 10·90, and 11·3 μ (in CCl_4).

1- *and* 2-*Methylnaphthalene.* These were identified by comparison of retention time ratios with those of authentic specimens in gas–liquid chromatography. Further identification was not attempted in view of previous experience in the detection of these compounds.

Bibenzyl. It was identified by comparison of retention time ratios with that of an authentic specimen in gas–liquid chromatography. The small amount did not allow further identification.

Fluorene. This was identified by comparison of retention time ratios in gas–liquid chromatography with that of an authentic specimen. Confirmation was by chromatography on a 90 cm. column of partially acetylated cellulose: an eluate showed maxima at 261, 290, and 301 mμ.

Acenaphthylene. Its presence was identified by comparison of retention time ratios in gas–liquid chromatography with those of an authentic specimen, and confirmed by chromatography on a column of partially acetylated cellulose (90 cm.). An eluate showed maxima at 265, 308, 324, 333, and 340 mμ.

2-*Phenylnaphthalene.* It was identified by comparison of retention time ratios with those of an authentic specimen in gas–liquid chromatography. A smaller amount of an over-lapping peak made isolation of this compound impossible and chromatography of fraction 6 on a column of partially acetylated cellulose was inconclusive. While the spectrum obtained showed peaks at 250 and 295 mμ, in agreement with an authentic specimen, the general shape of the spectrum was not identical with that of the pure compound.

Phenanthrene. Isolated by chromatography on a 90 cm. column of partially acetylated cellulose, this had maxima at 243, 252, 274, 281, and 294 mμ.

Anthracene. Isolated by chromatography on a 90 cm. column of partially acetylated cellulose, it had maxima at 252, 308, 323, 339, and 376 mμ.

Pyrene. Isolated by chromatography on a 90 cm. column of partially acetylated cellulose, a sample showed maxima at 231, 242, 252, 262, 272, 305, 318, 335, and 372 mμ.

Fluoranthene. Isolated by chromatography on a 90 cm. column of partially acetylated cellulose, a sample showed maxima at 237, 245, 253, 262, 272, 288, 309, 324, 343, and 359 mμ.

2,2′-*Binaphthyl.* Isolated by chromatography on a 90 cm. column of partially acetylated cellulose, a sample showed maxima at 255 and 308 mμ.

Triphenylene. This was identified by chromatography on a column of partially acetylated cellulose followed by paper chromatography. An extract showed maxima at 250, 257, 274, 286, 316, 331, and 350 mμ.

1,2-*Benzofluorene.* It was identified by chromatography on a column of partially acetylated cellulose followed by paper chromatography. An extract showed maxima at 253, 263, 293, 302, 316, 328, and 342 mμ (cf. ref. 21).

2,3-*Benzofluorene.* It was identified by chromatography on a column of partially acetylated cellulose followed by paper chromatography. An extract showed maxima at 255, 263, 272, 284, 303, 318, 334, and 340 mμ.

1,2-*Benzanthracene.* Isolated by chromatography on a column of partially acetylated cellulose, a sample showed maxima at 227, 254, 267, 278, 289, 300, 315, 326, 341, and 359 mμ.

Chrysene. Isolated by chromatography on a column of partially acetylated cellulose, a sample showed maxima at 242, 259, 267, 283, 294, 306, 320, 344, 350, and 361 mμ.

Alkylchrysene. Identified by chromatography on a column of partially acetylated cellulose, a sample showed maxima at 243, 260, 271, 284, 296, 307, 322, 352, and 363 mμ, in agreement with values obtained for a similar type of compound in other pyrolyses. Traces of a second alkylchrysene having an appreciably higher R_F than that usually obtained and showing maxima at 260, 270, 284, 295, 318, and 322 mμ were observed, but insufficient material was available for identification.

3,4-*Benzofluoranthene.* Identified by chromatography on a column of partially acetylated cellulose, a sample showed maxima at 238, 266, 276, 289, 293, 301, 320, 338, 350, and 369 mμ.

10,11-*Benzofluoranthene.* It was identified by chromatography on a column of partially acetylated cellulose, followed by paper chromatography. An extract showed maxima at 226, 242, 282, 292, 308, 318, 332, 344, 365, 376, and 383 mμ (cf. ref. 22), together with the maxima at 258 and 267 mμ probably due to traces of chrysene.

11,12-*Benzofluoranthene.* Isolated by chromatography on a column of partially acetylated cellulose, a sample showed maxima at 240, 269, 283, 297, 308, 361, 383, and 401 mμ.

Perylene. This was identified by chromatography on a column of partially acetylated cellulose. The fraction containing 1,2-benzopyrene also showed the typical long-wavelength spectrum of perylene, with maxima at 366, 386, 405, and 434 mμ. The fluorescence spectrum was identical with that of an authentic specimen.

1,2-*Benzopyrene.* Identified by chromatography on a column of partially acetylated cellulose, a sample showed maxima at 237, 257, 267, 278, 289, 304, 317, 332, and 366 mμ (cf. ref. 21), together with minor peaks corresponding to perylene at 405 and 434 mμ.

3,4-*Benzopyrene.* Isolated by chromatography on a column of partially acetylated cellulose, a sample showed maxima at 254, 264, 273, 279, 284, 296, 347, 364, 384, and 404 mμ. A purified sample had m. p. and mixed m. p. 171—175°.

1,12-*Benzoperylene.* It was identified by chromatography on a column of partially acetylated cellulose and purified through the picrate and by paper chromatography. An extract showed maxima at 278, 289, 300, 330, 345, 363, and 383 mμ.

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[21] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951.

2,3-(o-*Phenylene*)*pyrene.* Identified by chromatography on a column of partially acetylated cellulose, a sample showed maxima at 246, 251, 269, 274, 292, 304, 316, 360, 376, 385, and 406 mμ (cf. ref. 15).

4,5-(o-*Phenylene*)*fluoranthene.* Isolated by chromatography on a column of partially acetylated cellulose, a sample showed maxima at 253, 263, 271, 282, 287, 293, 316, 367, 380, 387, 401, and 410 mμ (cf. ref. 22).

Anthanthene. This was a contaminant in some samples of 2,3-(*o*-phenylene)pyrene. Chromatography of the fractions on a 50 cm. column of partially acetylated cellulose (34—36% Ac) gave anthanthrene showing maxima at 240, 257, 294, 307, 381, 401, 407, 421, and 431 mμ.

3,4-*Benzotetraphene.* It was identified by chromatography on acetylated paper. An extract showed maxima at 287, 304, 330, 346, 363, and 389 mμ.

1,2:5,6-*Dibenzanthracene.* This was identified by chromatography on acetylated paper. An extract showed maxima at 230, 276, 287, 297, 320, 334, and 347 mμ.

Alkyl-substituted Compounds.—Traces of alkyl-anthracenes, -phenanthrenes, -fluoranthenes, and -pyrenes were tentatively identified in fractions obtained in the analysis of fractions 8 and 9 on a column of partially acetylated cellulose. Insufficient material was available for further identification. In general, the spectra showed the same pattern as the parent compounds with small bathochromic shifts in the positions of the maxima, and different R_F values.

9-*Phenylanthracene.* An extract from paper chromatograms showed maxima at 258, 346, 366, and 385 mμ.

Stilbene. Identified by comparison of retention time ratios in gas–liquid chromatography (Silicone 30 as stationary phase) with those of an authentic specimen.

2-*Methylstyrene* (?). A fraction by gas–liquid chromatography had infrared maxima at 3·28, 3·38, 3·42, 3·60, 5·10, 5·20, 5·30, 5·44, 5·80, 6·10, 6·30, 6·41, 6·60, 6·70, 6·90, 7·02, 7·10, 7·22, 7·54, 7·80, 8·30, 8·46, 8·56, 8·92, 9·10, 9·70, 9·80, 10·1, 11·0 μ. This compound has not been definitely identified, but the general pattern of the spectrum is similar to that of styrene but does not correspond to that of α- or β-methylstyrene.

4-*Methylbiphenyl.* This was isolated by gas–liquid chromatography; the infrared spectrum showed maxima at 3·22, 3·32, 5·08, 5·20, 5·26, 5·30, 5·50, 5·61, 5·70, 6·21, 6·72, 6·84, 6·93, 7·20, 7·50, 7·88, 8·46, 9·30, 9·57, 9·70, 9·90, 10·1, 10·9, 11·1, 11·3, and 11·7 μ (in CCl_4). The recorded spectrum [23] is difficult to assess accurately, but is in substantial agreement with the above values.

Pyrolysis of a Mixture of Buta-1,3-*diene and Pyrene.*—The same experimental conditions were used as for the pyrolysis of butadiene. Pyrene (Light's; 99% purity) was introduced into the reaction tube in a small porcelain boat, so placed in the furnace that the temperature in the immediate vicinity of the boat was 300—350°. Butadiene (56 g.) was admitted at 9 g./hr. and the amount of pyrene used (4·2 g.) was determined by weighing the contents of the boat after pyrolysis. A dark-brown tar (30 g.) was obtained, and carbon (*ca.* 1 g.) was deposited in the reaction tube. The exit gases were shown to contain methane and ethylene by infrared spectroscopy.

Analysis of Tar.—The method of analysis was that described above. After chromatography on activated alumina, fractions containing 3,4-benzopyrene were rechromatographed to obtain better fractionation, and the subfractions were chromatographed on a column of partially acetylated cellulose. The composition of the fractions was determined by direct weighing and the compounds identified by ultraviolet spectroscopy in the usual way.

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[22] Clar, " Aromatische Kohlenwasserstoffe," Springer, Berlin, 2nd edn., 1952.

[23] Cannon and Sutherland, *Spectrochim. Acta,* 1951, **4**, 373.