859. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part X.* The Pyrolysis of* 1-*Phenylbuta*-1,3-*diene at* 550°.

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Pyrolysis of 1-phenylbuta-1,3-diene at 550° has given a complex mixture qualitatively similar to that obtained at 700°, but containing some hydrogenated compounds. Some qualitative and quantitative differences are discussed and possible mechanisms of formation are outlined.

THE pyrolysis of 1-phenylbuta-1,3-diene at 700° has already been reported[1] as part of an investigation of the mechanism of formation of the polycyclic aromatic hydrocarbons at high temperatures. Extensive decomposition of the starting material occurred at this temperature but its pyrolysis at 550° is now reported.

The pyrolysis was carried out by passing phenylbutadiene vapour, with nitrogen,

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* Part IX, preceding paper.

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

through a silica tube packed with porcelain chips at 550°. The exit gases were found to contain methane and ethylene, and the tar formed (in 85% yield) was analysed as previously described [1] by distillation, gas chromatography, chromatography on alumina, chromatography on partially acetylated paper,[2] and spectroscopy. The following compounds were identified in the tar (% by wt. in parentheses): 1,2-benzanthracene (0·43), benzene (0·61), 3,4-benzofluoranthene (0·45), 10,11-benzofluoranthene (0·05), 11,12-benzofluoranthene (0·03), 1,2-benzopyrene (trace), 3,4-benzopyrene (0·07), chrysene (0·82), an alkylchrysene (trace), 1,1′-binaphthyl (0·14), 2,2′-binaphthyl (1·72), biphenyl (1·0), fluoranthene (0·22), naphthalene (49·0), perylene (trace), phenanthrene (6·8), 1-phenylbut-2-ene (?) (7·8), 1-phenylphenanthrene (0·33), 2-phenylphenanthrene (1·5), 4-phenylphenanthrene (?) (0·8), 9-phenylphenanthrene (3·36), 2-phenylnaphthalene (0·16), tetralin (18·6), and triphenylene (0·37).

It was suggested previously [1] that at 700° the primary scission of the phenylbutadiene molecule must give phenyl and butadienyl radicals (reaction 1), that the alternative scission to styryl and vinyl radicals (reaction 2) is of minor importance, and that the products of the pyrolysis were accounted for by secondary reactions of the radicals $Ph\cdot$, $Ph\cdot CH{:}CH\cdot CH{:}CH\cdot$, $CH_2{:}CH\cdot CH{:}CH\cdot$, together with naphthalene and the starting material. In the light of further information obtained from other pyrolyses in this series,[3,4,5] it now appears that scission according to reaction (2) may be the main source of several of the components identified.

$$Ph\cdot CH{:}CH\cdot CH{:}CH_2 \longrightarrow Ph\cdot + \cdot CH{:}CH\cdot CH{:}CH_2 \quad \ldots\ldots \quad (1)$$

$$Ph\cdot CH{:}CH\cdot CH{:}CH_2 \longrightarrow Ph\cdot CH{:}CH\cdot + \cdot CH{:}CH_2 \quad \ldots\ldots \quad (2)$$

Radical production by chain scission would be expected to be of smaller importance at 550°; but no unchanged phenylbutadiene could be identified in the products. Dimerisation of phenylbutadiene by a Diels–Alder mechanism has been reported,[6] and should have a high activation energy compared with those of radical-addition reactions; [7] but the products expected from the dimerisation (the phenylphenanthrenes, for example) are obtained in greater yield from the 550° tar. However, if it is assumed that the radical formation from phenylbutadiene can occur by mechanisms other than chain scission, in a similar way to that proposed for the thermal initiation of styrene,[8] for example (reactions 3 and 4), formation of the the phenylphenanthrenes can be regarded as addition of the mesomeric phenylbutadiene radical $Ph\cdot\dot{C}{:}CH\cdot CH{:}CH_2$ as illustrated in (I)—(IV). The configuration of the intermediates indicates the formulation of the reactions as Diels–Alder additions.

$$2Ph\cdot CH{:}CH\cdot CH{:}CH_2 \longrightarrow Ph\cdot\dot{C}{:}CH\cdot CH{:}CH_2 + Ph\cdot\dot{C}H\cdot CH{:}CH\cdot CH_3 \quad \ldots \quad (3)$$

$$2Ph\cdot CH{:}CH\cdot CH{:}CH_2 \longrightarrow Ph\cdot CH{:}CH\cdot\dot{C}{:}CH_2 + Ph\cdot CH{:}CH\cdot\dot{C}H\cdot CH_3 \quad \ldots \quad (4)$$

The products in the 550° tar are similar to those obtained at 700°, but unlike those obtained by pyrolysis of aromatic compounds with a saturated side chain.[3] Although appreciable yields of biphenyl are obtained, probably by dimerisation of phenyl radicals, there is little benzene formed by abstraction of hydrogen. The low activation energy required for radical addition to phenylbutadiene apparently leads exclusively to this type of reaction; addition of a phenyl radical followed by cyclisation would account for the

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

[3] Badger and Spotswood, preceding paper.

[4] Badger and Kimber, *J.*, 1960, 266, 2746.

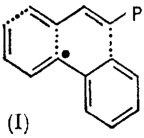
[5] Badger, Lewis, and Napier, *J.*, 1960, 2825.

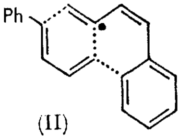
[6] Alder, Haydn, and Vogt, *Chem. Ber.*, 1953, **86**, 1302.

[7] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955.

[8] Walling, " Free Radicals in Solution," Wiley, New York, 1957.

relatively high yields of fluoranthene obtained on pyrolysis at 700°. Similarly styrene[9] gives relatively small yields of benzene on pyrolysis.


(I)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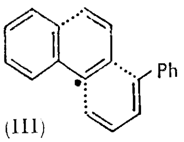
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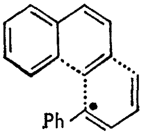
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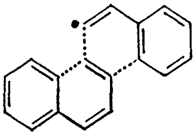
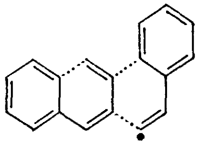

(V)


(VI)

Hydrogenated products (tetralin and 1-phenylbut-2-ene) were obtained at 550°, but not at 700°, and must arise from hydrogenation of the intermediate dihydronaphthalene obtained in the ring closure of phenylbutadiene, and from phenylbutadiene, respectively. The formation of triphenylene, 1,2-benzanthracene, and chrysene was previously explained by assuming attack of a butadienyl radical on phenanthrene; but results obtained by Lang and Buffleb[10] for a mixed pyrolysis of pyrene and benzene suggest that the extent of radical attack on phenanthrene would not be sufficient to account for the yields obtained, and formation by the addition of a styryl radical to phenylbutadiene is now proposed as an additional mechanism (V and VI).

The formation of 3,4-benzofluoranthene has already been discussed, and similar mechanisms apply to the present pyrolysis. The mode of formation of this compound is of particular interest since it has recently been reported[11] to have strong carcinogenic activity.

Traces of 10,11-benzofluoranthene, 11,12-benzofluoranthene, and perylene were identified, and re-examination of the 700° tar has established their presence in this tar also. These compounds probably arise by cyclisation of intermediates related to 1,1'-binaphthyl and 1,2'-binaphthyl in ways which have already been discussed,[3] and the 2,2'-binaphthyl identified in the 550° tar (and in the 700° tar on re-examination) could arise by dimerisation of naphthalene or its precursors.

A compound previously described as " Compound I " obtained in the 700° tar has been identified, by improved fractionation methods, as a mixture of triphenylene with a small amount of 1,2-benzopyrene.

EXPERIMENTAL

Pyrolysis.—The method of pyrolysis has previously been described.[1] Phenylbutadiene (33 g.) gave a semi-solid tar (28 g.), a non-volatile residue (1 g.) remained in the flash evaporator, and carbon (1·4 g.) was deposited in the reaction tube. The exit gases were shown to contain methane and ethylene by infrared spectroscopy, and the tar was analysed by distillation, chromatography on alumina, gas–liquid chromatography, and chromatography on partially acetylated paper[2] in ways already described.

The analytical methods used have been described in detail for other pyrolyses[1,3,4,5] and details of identification are given only for compounds not previously identified in the products obtained by pyrolysis of 1-phenylbuta-1,3-diene at 700°.

Details of Identification.—*Benzene*. Isolated by gas–liquid chromatography, it showed

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[9] Badger and Buttery, *J.*, 1958, 2458.
[10] Lang and Buffleb, *Chem. Ber.*, 1957, **90**, 2894.
[11] Kotin and Falk, *Cancer*, 1959, **12**, 147.

infrared maxima at 2·38, 2·46, 3·23, 3·29, 4·21, 4·30, 4·39, 4·53, 5·11, 5·51, 5·70, 5·98, 6·31, 6·54, 6·75, 7·17, 8·50, and 9·65 μ (liquid film) in agreement with an authentic specimen.

Tetralin. Isolated by gas–liquid chromatography, it showed infrared maxima at 3·31, 3·41, 3·47, 3·51, 3·54, 3·74, 4·44, 5·17, 5·24, 5·48, 5·55, 5·80, 5·95, 6·26, 6·35, 6·71, 6·90, 6·98, 7·41 7·49, 7·80, 8·05, 8·12, 8·36, 8·54, 8·66, 9·00, 9·36, 9·65, 9·96, 10·15, 10·58, 11·14, 11·57, 12·25, 12·44, 13·48, and 14·29 μ (liquid film) in agreement with an authentic specimen. In addition bands at 7·80, 9·90, 10·6, and 12·8 μ, characteristic of naphthalene, were observed.

1-*Phenylbut*-2-*ene* (?). Isolated by gas–liquid chromatography, it had infrared maxima at 3·30, 3·40, 3·50, 3·90, 4·12, 4·40, 4·83, 5·12, 5·32, 5·56, 5·72, 5·96, 6·04, 7·28, 7·41, 7·51, 7·61, 7·80, 7·89, 8·08, 8·28, 8·48, 8·65, 8·88, 9·08, 9·32, 9·80, 9·89, 10·40, 11·02, 11·90, 12·0, 12·80, 13·09, 13·52, 14·09, and 14·50 μ (in CCl_4). The recorded spectrum [12] is not sufficiently clear to enable the identification to be made with complete certainty.

1,1′-*Binaphthyl.* An extract from paper chromatograms showed maxima at 221, 282, and 295 mμ, in agreement with an authentic specimen, and a sample prepared by microsublimation had m. p. 137—141° (authentic 144—145°).

2,2′-*Binaphthyl.* An extract from paper chromatograms showed maxima at 254 and 308 mμ, in agreement with an authentic specimen. A sample prepared by microsublimation had m. p. 180—184° (authentic 188°).

2-*Phenylnaphthalene.* Identified by comparison of retention ratios in gas–liquid chromatography with those of an authentic specimen, and confirmed by paper chromatography. An extract from paper chromatograms showed maxima at 250—251 and 295 mμ.

Phenylphenanthrenes. The identification of 9-, 2-, and 4-phenylphenanthrene has already been described. Confirmation was obtained by comparison with authentic specimens on acetylated paper. 1-Phenylphenanthrene was identified in the same way; an extract from paper chromatograms showed maxima at 246, 257, 290, and 300 mμ, in agreement with an authentic specimen.

Perylene. This was identified in fractions containing 1,2-benzanthracene. An extract of the spot on paper chromatograms corresponding to 1,2-benzanthracene showed the typical long-wavelength spectrum of perylene with maxima at 386, 405, and 434 mμ, and the fluorescence spectrum showed strong bands at 445, 475, and 502 mμ in agreement with an authentic specimen.

10,11-*Benzofluoranthene.* An extract from the high R_F section of the spot corresponding to chrysene obtained in paper chromatograms was rechromatographed with extended development time and an extract showed maxima at 292, 308, 318, 332, 344, 365, and 383 mμ, characteristic of 10,11-benzofluoranthene, and peaks at 242, 258, and 268 mμ, characteristic of chrysene. The latter set of peaks was removed by the addition of small amounts of chrysene to the reference cell.

11,12-*Benzofluoranthene.* An extract from paper chromatograms showed maxima at 240, 269, 283, 297, 308, 361, 383, and 401 mμ in agreement with an authentic specimen.

1,2-*Benzopyrene.* An extract from paper chromatograms showed maxima at 237, 257, 269, 288, 303, 316, and 331 mμ in agreement with recorded values.[13]

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[12] Proell, *J. Org. Chem.*, 1951, **16**, 178.

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