501. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part IV.* The Pyrolysis of Styrene.*

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Pyrolysis of styrene at 710° gives a complex mixture of products.

Pyrolysis of butadiene [1] yields relatively large quantities of styrene and ethylbenzene, and the further pyrolysis of these products is of interest. Berthelot [2] found that styrene gave acetylene and benzene when passed through a porcelain tube at bright-red heat, but the temperature seems to be critical. A 99% recovery of styrene has been reported [3] following heating at 550°, and 95·3% after heating [4] at 625°. At higher temperatures there is much more " decomposition," but little attempt has been made to examine the products. The pyrolysis of styrene has now been investigated to determine whether it can act as an intermediate in the formation of polycyclic aromatic hydrocarbons, such as 3 : 4-benzopyrene, at high temperatures.

Styrene vapour, with nitrogen, was passed through a silica tube, filled with porcelain chips, at 710°. The resulting tar was analysed by distillation, spectra, and gas-liquid partition chromatography. In this way all the major products having boiling points below that of pyrene, and formed in more than 0·2% yield, have been identified:

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* Part III, preceding paper.

[1] Weizmann *et al.*, *Ind. Eng. Chem.*, 1951, **43**, 2312, 2318.

[2] Berthelot, " Les Carbures d'Hydrogène," Gauthier-Villars, Paris, 1901.

[3] Mackinnon and Ritchie, *J.*, 1957, 2564.

[4] Balandin, Marukyan, and Tolstopyatove, *Zhur. priklad. Khim.*, 1946, **19**, 1079; Balandin and Tolstopyatova, *Zhur. obshchei Khim.*, 1947, **17**, 2182.

Methane (—), ethylene (—), benzene (6·4), toluene (3·3), ethylbenzene (1·6), indene (0·4), naphthalene (6·1), methylnaphthalenes(?) (0·2), diphenyl (1·6), dibenzyl (0·9), fluorene (1·3), stilbene (1·3), phenanthrene (11·1), anthracene (0·3), 2-phenylnaphthalene (2·5), a pyrene-containing fraction, b. p. 220—250°/21 mm. (1·9), a chrysene-containing fraction, b. p. 250—265°/21 mm. (3·3), and a C_{20}-fraction, b. p. 265—315°/21 mm. (4·6), which contained 3 : 4-benzopyrene (*ca.* 0·02) (values in parentheses are percentage yields, by weight).

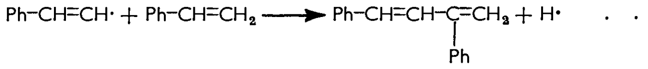
Contrary to the findings by Berthelot, no acetylene could be detected. Addition of aniline and phenol is known to inhibit the " decomposition " of styrene,[4] and there can be little doubt that the high-temperature reactions leading to the formation of these products are predominantly radical. It is therefore important to determine which bonds are most likely to break to yield radicals.

From consideration of bond-dissociation energies [5] for various types of carbon–hydrogen and carbon–carbon bonds, it seems likely that the carbon–hydrogen bonds in styrene all have bond-dissociation energies of the order of 100 kcals. If account is taken of their bond orders,[6] approximate values for the bond-dissociation energies for the carbon–carbon bonds can also be obtained. Thus the carbon–carbon double bond probably has a bond-dissociation energy of *ca.* 140 kcals., and the carbon–carbon single bond linking the ethylenic group to the benzene ring, a bond dissociation energy of *ca.* 110 kcals. There is thus little difference in the energy required to break any C–H bond and the carbon–carbon single bond; but a much greater energy is required to break the carbon–carbon double bond (or the aromatic ring). This leads to the conclusion that the most important radicals may be $\mathrm{Ph\cdot}$, $\mathrm{\cdot CH{=}CH_2}$, $\mathrm{Ph{-}CH{=}CH\cdot}$, $\mathrm{Ph{-}\underset{\bullet}{C}{=}CH_2}$, and $\mathrm{\cdot C_6H_4{-}CH{=}CH_2}$.

Such radicals could undergo a variety of reactions, both chain-propagating and chain-terminating. Reaction 1 would explain the formation of stilbene. If it is assumed that cyclisation to an aromatic system would readily follow, then reactions (1—4) would offer satisfactory schemes for the observed relatively high yields of phenanthrene, naphthalene, and 2-phenylnaphthalene. It may here be noted that phenanthrene is formed when stilbene is passed through a red-hot tube,[7] and naphthalene is formed by the pyrolysis of phenylbutadiene [8] and other similar hydrocarbons. The known interconversion of phenanthrene and anthracene [9] at high temperature could account for the small yield of anthracene.

$$\mathrm{Ph{-}CH{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH{-}Ph + CH_2{=}CH\cdot} \quad . \ . \ . \ . \ . \ . \quad (1)$$

$$\mathrm{Ph{-}CH{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH{-}CH{=}CH_2 + Ph\cdot} \quad . \ . \ . \ . \ . \ . \quad (2)$$



$$\mathrm{Ph{-}CH{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH{-}\underset{\displaystyle |\atop \displaystyle Ph}{C}{=}CH_2 + H\cdot} \quad . \ . \ . \ . \ . \ . \quad (3)$$

$$\mathrm{Ph{-}CH{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH{-}C_6H_4\cdot + CH_2{=}CH_2} \quad . \ . \ . \ . \quad (4)$$

The propagation of this radical chain could result by reactions such as (5—7). The large yield of benzene and the predominance of ethylene among the gaseous products would indicate the importance of such collisions.

$$\mathrm{Ph\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH\cdot + PhH} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

$$\mathrm{CH_2{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH\cdot + CH_2{=}CH_2} \quad . \ . \ . \ . \ . \ . \ . \quad (6)$$

$$\mathrm{H\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH\cdot + H_2} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

Diphenyl could be formed by a chain-terminating reaction involving two phenyl radicals, or more probably, by a chain propagating reaction of a phenyl radical with a styrene molecule.

[5] Braude and Nachod, " Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955; Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954.

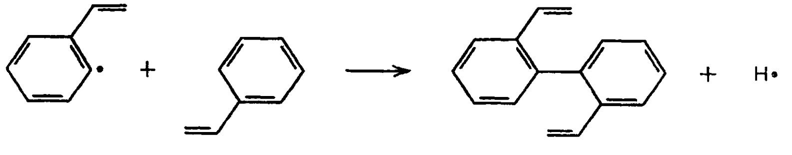
[6] Buu-Hoï, Coulson, Daudel, Daudel, Martin, Pullman, and Pullman, *Rev. Sci.*, 1947, **85**, 1041.

[7] Graebe, *Ber.*, 1873, **6**, 125; see also Zelinsky and Titz, *Ber.*, 1929, **62**, 2869.

[8] Liebermann and Riiber, *Ber.*, 1902, **35**, 2697.

[9] Orlow, *Ber.*, 1927, **60**, 1950.

Toluene is the only methylated hydrocarbon of which more than a trace is formed and this is probably formed in a secondary reaction. Thus reduction of stilbene would give dibenzyl, the central bond of which has a very small bond-dissociation energy.[10] Fission would give two benzyl radicals, and toluene could then be formed by chain termination or propagation. Similarly fluorene could result by reaction of a benzyl radical with a phenyl radical (to give diphenylmethane), followed by cyclodehydrogenation. Pyrolysis of diphenylmethane yields fluorene.[11] The benzyl radical may also be involved in the formation of indene. Thus reaction of ethylene, or a vinyl radical, with a benzyl radical, followed by cyclohydrogenation would give this hydrocarbon.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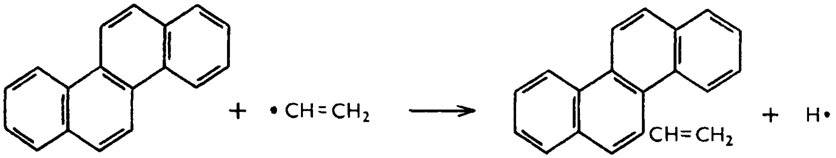
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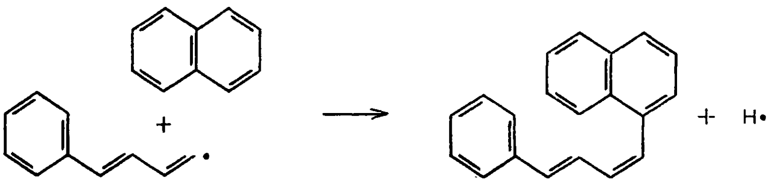
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Chrysene is obtained in good yield by the pyrolysis of indene,[12] and the chrysene detected is probably formed in this way.

Pyrene may be formed in a manner similar to that suggested by Weizmann *et al.*,[1] *i.e.*, eqn. (8), followed by cyclodehydrogenation. An analogous synthesis [13] by catalytic cyclodehydrogenation of di-*m*-xylylene is of interest. However, the small yield of pyrene indicates that this cannot be an important reaction.

3 : 4-Benzopyrene was a product of the pyrolysis of styrene but only in small amount, and no decision can be made regarding its method of formation. Two reactions seem probable. The first would involve the attack of a vinyl radical on chrysene [eqn. (9)] followed by cyclodehydrogenation; there are four positions at which the vinyl radical could possibly attack chrysene and lead to 3 : 4-benzopyrene. The second mechanism would involve the reaction of a phenylbutadiene radical with naphthalene [eqn. (10)], and cyclodehydrogenation of the product. Phenylbutadiene was not identified, but this could well be due to its reactivity and instability at the reaction temperature. Its conversion into naphthalene has been established; moreover, an unidentified product (0·2% yield) had a retention time close to that of *n*-butylbenzene, and this is the expected product from the reduction of phenylbutadiene.

EXPERIMENTAL

Styrene.—Styrene (Reichhold Chemicals Inc.) was distilled through a 15-cm. Vigreux column, and had b. p. 81°/90 mm., n_D^{25} 1·5440 (lit. n_D^{23} 1·5440). Gas–liquid partition chromatography did not detect ethylbenzene.

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[10] Horrex and Miles, *Discuss. Faraday Soc.*, 1951, **10**, 187.

[11] Graebe, *Ber.*, 1873, **6**, 127; *Annalen*, 1874, **174**, 185.

[12] Spilken, *Ber.*, 1893, **26**, 1538.

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

Pyrolysis of Styrene at 710°.—Styrene (100 g.) was vaporised by adding it dropwise (1 drop/8 sec.; 10 g./hr.) to a Pyrex tube immersed in a lead bath at 340°, and carried in a stream of nitrogen (30 c.c./min.) into the furnace at 710°. The vapours leaving the furnace were passed through an air-condenser and an efficient vertical water-condenser, and finally through a trap of solid carbon dioxide. The average yield of liquid was 84 g., and more (1 g.) was obtained by washing the pyrolysis tube with benzene, followed by evaporation of the benzene. The gaseous products gave no precipitate with ammoniacal cuprous bromide but decolorised aqueous permanganate. Samples of gaseous product were examined in the infrared spectrometer.

Gas–liquid chromatographic analysis.

		Conditions *					Retention time	
Fraction	B. p.°/mm.	*A*	*B*	*C*	*D*	Product	min.	sec.
I	40—70/110	113°	0·7	—	atmos.	benzene	2	50
						toluene	6	30
						ethylbenzene	12	—
						styrene	16	—
II	65—92/30	175°	0·7	—	atmos.	styrene	3	30
						indene	9	20
						naphthalene	23	10
III	92—134/24	169	—	220	18	naphthalene	6	50
						diphenyl	17	40
IV	134—185/21	220	—	230	18	naphthalene	2	30
						diphenyl	5	20
						dibenzyl	9	10
						fluorene	16	10
						stilbene	24	10
V	185—220/21	265	—	200	18	fluorene	6	20
						phenanthrene	14	40
						pyrene	52	30
						chrysene	*ca.* 2 hr.	

* *A*, temperature. *B*, flow rate, c.c./sec. *C*, initial pressure. *D*, outlet pressure.

Details of Chromatographic Analysis.—The tar was fractionally distilled at reduced pressure in a 30 cm. electrically heated, jacketed, unpacked column. Some fractions were examined separately, but for the major chromatographic analysis several were combined to form five main fractions. Each main fraction was then submitted to gas–liquid chromatography as specified in the Table, which also gives the retention times for the major components of each fraction.

The compositions were determined by comparison of areas under the peaks in the chromatographic curves. The method of multiplying peak height by peak width at half-peak height was used. Each component was checked by using known mixtures and tests over a wide range of composition showed most determinations to be within 7% of the true value, with a maximum error of 11%. Anthracene has the same retention time as phenanthrene and its proportion was determined by ultraviolet spectroscopy. The results are summarised in the Introduction.

Details of Identification.—*Methane and ethylene.* Gaseous products from the furnace were passed into an 11-cm. gas cell for infrared analysis. Methane was identified by its characteristic spectrum [14a] in the 7·5—8·5 μ region (maxima at 7·65, 7·7, 7·75, 7·78, 7·82, 7·86, 7·92, 7·95, 8·00, 8·03, 8·05, 8·13, 8·18, and 8·26). Ethylene was identified by its characteristic spectrum [14b] in the 9·0—11·5 μ region (maxima at 9·93, 10·02, 10·13, 10·22, 10·3, 10·53, 10·63, 10·76, 10·84, 10·93, 11·01, 11·07, 11·16, and 11·25 μ). There were also other bands characteristic of ethylene in other regions. The furnace gases decolorised neutral permanganate.

Benzene. A fraction, b. p. 80—84°, was examined in the infrared region; maxima at 2·14, 2·44, 2·72, 3·25, 3·76, 3·84, 4·18, 4·27, 4·48, 5·08, 5·5, 5·7, 5·82, 5·97, 6·23, 6·55, 6·8, 7·19, 8·02, 8·5, 9·5, and 9·7 μ were characteristic of benzene; [14c] some peaks characteristic of toluene were also identified.

Toluene. The fraction, b. p. 90—100°, gave maxima at 2·15, 2·44, 2·72, 3·26, 3·4, 3·45, 3·65,

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[14] American Petroleum Institute Research Project 44, Infrared Spectral Data (*a*) No. 528; (*b*) No. 18; (*c*) No. 307; (*d*) No. 308; (*e*) No. 170.

3·85, 4·28, 4·5, 5·10, 5·36, 5·5, 5·76, 6·25, 6·35, 6·57, 6·8, 7·25, 7·5, 7·61, 8·03, 8·30, 8·50, 9·05, 9·28, 9·7, 10·1, 11·0, and 11·85 μ characteristic of toluene; [14d] some peaks characteristic of benzene were also noted.

Ethylbenzene. This was identified only by the ratio of its retention time to that of benzene (4·5). *m*- and *p*-Xylene under the same conditions gave corresponding ratios of 5·1 and *o*-xylene had a higher ratio.

Styrene. Isolated from fraction (I) this had n_{D}^{15} 1·5490 (lit. $n_{\mathrm{D}}^{16\cdot6}$ 1·5485) and gave maxima at 2·4, 3·2, 3·22, 5·04, 5·28, 5·44, 5·68, 5·89, 6·1, 6·21, 6·31, 6·5, 6·68, 6·85, 7·04, 7·45, 7·55, 7·72, 8·3, 8·45, 8·65, 9·0, 9·2, 9·28, 10·08, 11·0, 11·9, 12·9, and 14·35 μ, in agreement with the literature.[14e] The isomeric xylenes have retention times similar to that of styrene. However, the absence of the strong maxima at 11·5, 12·5, and 13·5 μ in the infrared spectrum indicates the absence of *m*-, *p*-, and *o*-xylene, respectively.

Indene. This was isolated from fraction (II). In carbon tetrachloride it showed maxima at 3·19, 3·26, 3·32, 3·39, 3·47, 3·63, 5·15, 5·22, 5·3, 5·35, 5·39, 5·48, 5·57, 5·77, 5·86, 5·92, 6·04, 6·22, 6·87, 7·2, 7·48, 7·8, 8·05, and 8·35 μ, in agreement with those obtained on an authentic specimen.

Naphthalene. Isolated from fraction (II), this had m. p. and mixed m. p. 79—80°.

Methylnaphthalenes. Gas–liquid chromatography of the fraction, b. p. 98—134°/24 mm., under the conditions used for fraction (III) showed a minor broad band with ratio of retention time of 2·0 compared to that of naphthalene. An authentic mixture of 1- and 2-methylnaphthalene gave the same ratio.

Diphenyl. This was isolated from fraction (III). In carbon tetrachloride it showed maxima at 2·46, 3·27, 3·30, 3·42, 3·48, 5·10, 5·14, 5·26, 5·31, 5·35, 5·49, 5·55, 5·49, 5·55, 5·68, 5·74, 5·95, 6·04, 6·78, 6·88, 6·99, 7·26, 7·74, 7·97, and 8·16 μ, in agreement with those shown by an authentic specimen.

Dibenzyl. In carbon tetrachloride this showed maxima at 2·4, 3·25, 3·37, 3·45, 5·1, 5·29, 5·5, 5·65, 5·9, 6·75, 6·90, 6·99, 7·08, 7·21, 7·5, 7·62, 8·5, 9·34, 9·75, 10·85, and 11·3 μ. Authentic dibenzyl showed maxima at all these wavelengths except 6·99, 7·08, and 7·62 μ. The shapes of the spectra were very similar, but the fraction isolated showed reinforcement of some bands. Diphenyl is a probable impurity.

Fluorene. The fluorene sample had ultraviolet spectra maxima at 300, 290, and 260 mμ. Clar [15] gives maxima at 300·5, 289, and 261 mμ.

Stilbene. This was isolated from fraction (IV) by chromatography at 265° (as for fraction V), (retention time 8 min. 50 sec.), and had m. p. and mixed m. p. 124·5—125°; $\lambda_{\text{max.}}$ at 220, 295, and (infl.) 307 mμ (literature [16] max. at 295 infl. at 307 mμ).

Anthracene and phenanthrene. A mixture was isolated (retention time 14 min. 40 sec.) from the fraction, b. p. 192—198°/21 mm., by chromatography at 265° under vacuum. Its ultraviolet absorption spectrum in 95% ethanol showed maxima at 252·5, 275, and 292·5 mμ (characteristic of phenanthrene) and at 340, 357·5, and 375 mμ, with inflexions at 310, 325, and at 371 mμ (characteristic of anthracene). The proportion of anthracene was estimated from the intensity of the band at 375 mμ. Recrystallisation gave substantially pure phenanthrene, m. p. and mixture m. p. 96—100°.

2-*Phenylnaphthalene.* This was isolated (retention time 24 min. 54 sec.) from the fraction, b. p. 192—198°/21 mm., by chromatography at 265° under vacuum. It had m. p. 99·5—101°, undepressed by admixture with an authentic specimen.

Pyrene. The crude fraction, b. p. 215—220°/21 mm., showed $\lambda_{\text{max.}}$ at 375, 357·5, 335, 319, 292·5, 272·5, 255, and 242·5 mμ. Peaks at 335, 319, 272·5, and 242·5 mμ are characteristic of pyrene.

The crude fraction was treated with picric acid in ethanol; the complex after recrystallisation had m. p. and mixed m. p. 215—218°. Tetrabromopyrene, prepared from the crude fraction in nitrobenzene, had m. p. and mixed m. p. 400—402°.

Chrysene. Part of the fraction, b. p. 250—264°/21 mm. (0·393 g.), was recrystallised from glacial acetic acid, yielding substantially pure chrysene (0·03 g.); $\lambda_{\text{max.}}$ 360, 340, 317·5, 305, 295, 285, 267·5, 257·5, 240, and 220 mμ. Except for that at 340 mμ, these maxima are characteristic of chrysene.[15]

3 : 4-*Benzopyrene.* The fraction, b. p. 300—310°/21 mm. (4 g.), was dissolved in benzene (50 c.c.) and shaken with concentrated sulphuric acid (50, 40, then 30 c.c.) at 5°. The sulphuric

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[15] Clar, "Aromatische Kohlenwasserstoffe," 2nd Edn., Springer, Berlin, 1952.

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

acid solution was poured on ice (150 g.), and water (150 c.c.) added.[17] The mixture was then extracted with benzene, and the solution washed, dried, and concentrated to 20 c.c. Hexane (20 c.c.) was then added and the solution chromatographed on alumina, hexane–benzene (2 : 1) being used as eluant. Those fractions showing fluorescence in the region characteristic for 3 : 4-benzopyrene were combined and evaporated. The resulting solid (0·19 g.) was crude 3 : 4-benzopyrene; it showed characteristic fluorescence bands at 404, 433, and 456 mμ (in light petroleum), and ultraviolet absorption maxima at 404, 385, 365, 345, 319, 295, 285, 267·5, 257·5, and 225 mμ (in 95% ethanol). With the exception of the bands at 319, 267·5, and 257·5 mμ (chrysene?), these are characteristic of 3 : 4-benzopyrene.[16]

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[17] Berenblum, *Nature*, 1945, **156**, 601.