462. *Aromatic Hydrocarbons. Part LII. Naphtho(2′ : 3′ : 1 : 2)-pyrene, 1 : 2-4 : 5-8 : 9-Tribenzpyrene, and a New Synthesis of 1 : 2-3 : 4-Dibenzanthracene.*

By E. Clar.

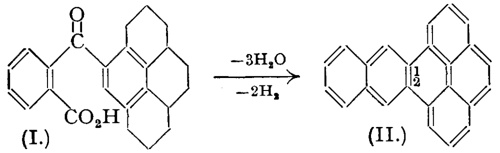
Decahydropyrene was condensed with phthalic anhydride. The keto-acid so formed was fused with sodium chloride and zinc chloride and dehydrogenated with copper powder to naphtho(2′ : 3′-1 : 2)pyrene. In the same way 1 : 2-3 : 4-dibenzanthracene was obtained from *o*-octahydrophenanthroylbenzoic acid.

Octahydroanthracene reacted with two molecules of benzyl chloride and aluminium chloride to form 9 : 10-dibenzyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene, which on dehydrogenation with copper yielded 1 : 2-4 : 5-8 : 9-tribenzpyrene, with 2 : 3-8 : 9-dibenzperylene as a by-product.

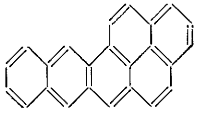
Decahydropyrene reacts in the Friedel–Crafts reaction as an alkylated benzene (Clar, *Chem. Ber.*, 1948, **81**, 520). With phthalic anhydride the *acid* (I) was thus obtained in good yield. When (I) was melted with a mixture of sodium chloride and zinc chloride at 330°, water was easily split off, and the partly hydrogenated hydrocarbon gave, on heating with copper powder, *naphtho*(2′ : 3′-1 : 2)*pyrene* (II). This pale yellow naphthopyrene (II) is strikingly different from the isomeric deep-orange-yellow naphtho(2′ : 3′-3 : 4)pyrene (III) (Cook and Hewett, *J.*, 1933, 403; Clar, *Ber.*, 1936, **69**, 1684). The absorption spectra of the two hydrocarbons are shown in Fig. 1; that of (III) resembles rather that of 1 : 2-6 : 7-dibenzpyrene (Clar, *Ber.*, 1943, **76**, 609).

However, the differences almost disappear in the *addition products* (IV and V) with maleic anhydride. The absorption spectra of these two compounds, shown in Fig. 2, are typical pyrene spectra and differ not more than those of isomeric alkyl derivatives.

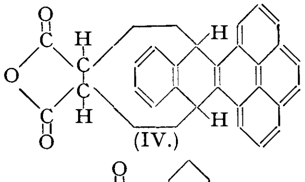
The new method of ring closure of *o*-polyhydroaroylbenzoic acids with sodium chloride and zinc chloride can be successfully applied to other cases, *e.g.*, to *o*-octahydro-9-phenanthroylbenzoic acid (VI). This acid is easily obtained from phthalic anhydride, octahydrophenanthrene, and aluminium chloride (Barnett and Lawrence, *J.*, 1935, 1104). Dehydration by melting with sodium chloride and zinc chloride gave a mixture of 1 : 2-3 : 4-dibenzanthracene (VIII) and its 9 : 10-dihydro-derivative (VII), which could be separated by means of the dissociable maleic anhydride addition product of (VIII). Dehydrogenation of the crude mixture of (VII) and (VIII) with copper powder gave (VIII).



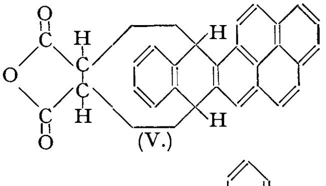
(I.) (II.)



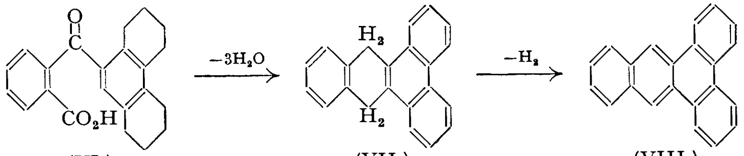
(III.)



(IV.)

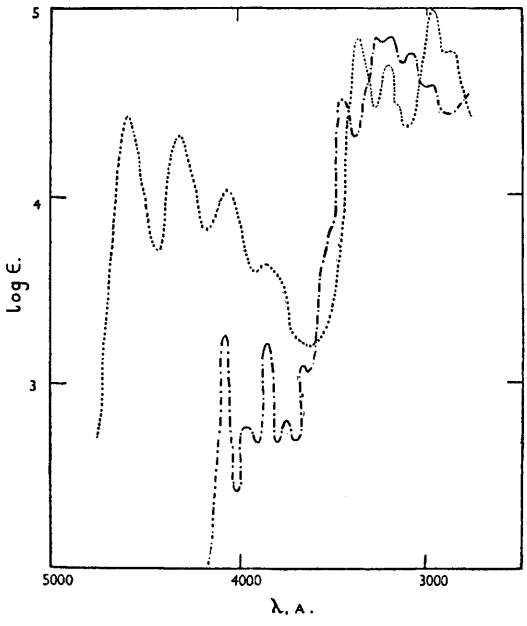


(V.)



(VI.) (VII.) (VIII.)

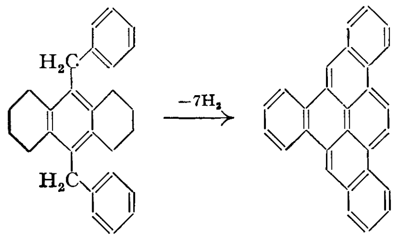
Fig. 1.



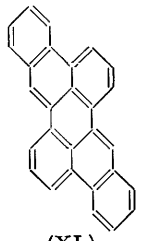
— · — · — · — *Absorption spectrum of naphtho*(2′ : 3′-1 : 2)*pyrene* (*II*) *in benzene. Band maxima in* A. : 4075, 3960, 3860, 3750, 3670; 3450; 3280; 3210; 3090, 2970.

.... *Absorption spectrum of naphtho*(2′ : 3′-3 : 4)*pyrene* (*III*) *in benzene. Band maxima in* A. : 4580, 4310, 4060, 3850; 3350, 3200; 2970, 2860.

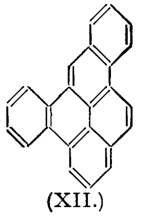
Octahydroanthracene reacted with two molecules of benzyl chloride in presence of a catalytic amount of aluminium chloride to form 9 : 10-dibenzyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene (IX), which with copper powder at 400—420° yielded, by dehydrogenation and simultaneous double ring closure, 1 : 2-4 : 5-8 : 9-tribenzpyrene (X). In some experiments this product was mixed with a small amount of the isomeric 2 : 3-8 : 9-dibenzperylene (XI) (Clar, *Ber.*, 1932, **65**, 846; Schauenstein and Bürgermeister, *Ber.*, 1943, **76**, 208), which was isolated by chromatography and identified by the absorption spectrum.



(IX.) (X.)



(XI.)



(XII.)

FIG. 3.

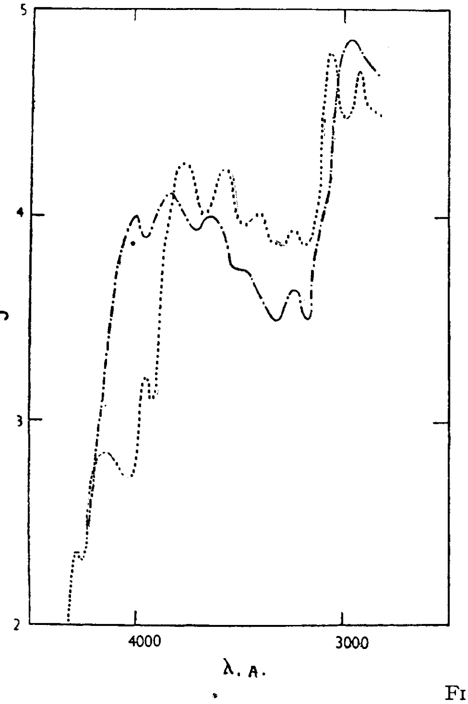


FIG. 2.

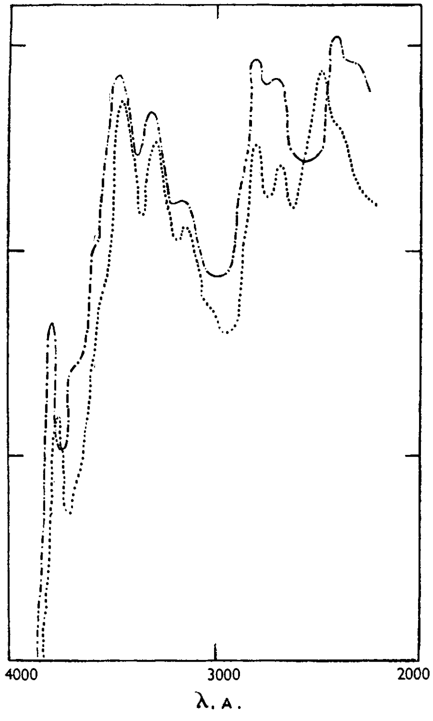


FIG. 2.

— · — · — · — *Absorption spectrum of the disodium salt derived from* (*IV*) *in water. Band maxima in* A. : 3770, 3690; 3470, 3305, 3170; 2805, 2695; 2430, 2360.

.... *Absorption spectrum of the disodium salt derived from* (*V*) *in water. Band maxima in* A. : 3755, 3660; 3440, 3280, 3145; 2805, 2690; 2510, 2400.

FIG. 3.

— · — · — · — *Absorption spectrum of* 1 : 2-4 : 5-8 : 9-*tribenzpyrene* (*X*) *in benzene. Band maxima in* A. : 3990; 3820, 3640, 3470; 3220; 2950.

.... *Absorption spectrum of* 1 : 2-4 : 5-*dibenzpyrene* (*XII*) *in benzene. Band maxima in* A : 4160, 3960; 3780, 3600, 3430, 3275; 3065, 2945.

The absorption spectrum of 1 : 2-4 : 5-8 : 9-tribenzpyrene (X) shows considerable differences from that of pyrene and is related to the structurally similar 1 : 2-4 : 5-dibenzpyrene (XII) (Fig. 3) (Clar, *Ber.*, 1943, **76**, 613).

EXPERIMENTAL.

1-o-*Carboxybenzoyldecahydropyrene* (I).—Powdered aluminium chloride (150 g.) was gradually added to a mixture of decahydropyrene (106 g.) and phthalic anhydride (75 g.) in benzene (200 c.c.). After agitation for 2 hours at room temperature, the mixture was decomposed with dilute hydrochloric acid and ice. The benzene was removed by steam-distillation, and the residue was dissolved in dilute sodium hydroxide solution. The hot filtered solution was acidified with hydrochloric acid. The precipitated acid crystallised immediately when touched with a few drops of ether. Recrystallisation from dilute acetic acid gave colourless prisms, which melted at 176—178° (uncorr.) and dissolved in sulphuric acid to give a yellowish-brown solution (Found : C, 79·6; H, 6·5. $C_{24}H_{24}O_3$ requires C, 80·0; H, 6·7%).

Naphtho(2′ : 3′-1 : 2)*pyrene* (II).—The acid (I) (95 g.) was mixed with sodium chloride (10 g.) and zinc chloride (50 g.) and heated to 330°. The green colour of the melt disappeared during a vigorous evolution of steam, and two layers were formed. The upper layer was dissolved in hot xylene and filtered, and the xylene evaporated. Copper powder (8 g.) was added and the molten hydrocarbon was heated at 400—410° for 2 hours. Hydrogen was evolved. The powdered residue of *naphthopyrene* was sublimed in a vacuum at 300° and then recrystallised from xylene, yielding long pale yellow needles, m. p. 259—260° (evacuated capillary; uncorr.) (Found : C, 95·2, 95·3; H, 4·6, 4·7. $C_{24}H_{14}$ requires C, 95·3; H, 4·7%), which gave a reddish-brown solution in concentrated sulphuric acid. The solution in organic solvents showed a strong blue fluorescence. A *picrate*, forming long red needles, m. p. 212—213° (decomp.; evacuated capillary; uncorr.) (Found : N, 8·4. $C_{30}H_{17}O_7N_3$ requires N, 7·9%), was obtained by use of an excess of picric acid in hot benzene.

1′ : 4′-endo*Ethylenenaphtho*(2′ : 3′-1 : 2)*pyrene-αβ-dicarboxylic Anhydride* (IV).—The naphthopyrene (II) (1 g.), maleic anhydride (1 g.), and xylene (20 c.c.) were boiled for 1 hour. Dilute sodium hydroxide was added and the xylene removed with steam. The filtered hot solution was acidified with hydrochloric acid. The precipitated *anhydride*, when recrystallised from acetic anhydride, formed colourless needles, m. p. 238—245° (decomp.; evacuated capillary; uncorr.), which gave a yellowish-green solution in concentrated sulphuric acid, which later became bluish-green (Found : C, 84·1; H, 3·8. $C_{28}H_{16}O_3$ requires C, 84·0; H, 4·0%).

1 : 2-3 : 4-*Dibenzanthracene* (VIII).—*o*-Octahydro-9-phenanthroylbenzoic acid (VI) was fused with sodium chloride and zinc chloride as described for preparation of (I) and distilled directly from the melt in a vacuum. The distillate consisted of 1 : 2-3 : 4-dibenzanthracene (VIII) and its dihydro-derivative (VII), which can be separated through the addition product of (VIII) with maleic anhydride (Clar and Lombardi, *Ber.*, 1932, **65**, 1418). If only 1 : 2-3 : 4-dibenzanthracene is desired, the crude dehydration product is dehydrogenated as described above. 1 : 2-3 : 4-Dibenzanthracene formed long colourless needles, m. p. 205°(uncorr.), identical, by direct comparison, with an authentic sample (Clar, *Ber.*, 1929, **62**, 350, 1574).

9 : 10-*Dibenzyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene* (IX).—Benzyl chloride (126 g.) was added dropwise to an agitated mixture of octahydroanthracene (90 g.) and powdered aluminium chloride (5 g.) in tetrachloroethane (100 c.c.). Colourless crystals separated, and hydrochloric acid was evolved. After decomposition with dilute hydrochloric acid the solvent was removed with steam. The residue was dissolved in hot xylene. The *product* crystallised in colourless needles (39 g.), m. p. 189—190° (Found : C, 92·0; H, 8·2. $C_{28}H_{30}$ requires C, 91·8; H, 8·2%), from the solution on cooling. It gave a brown solution in hot concentrated sulphuric acid. The mother-liquor still contained much of the hydrocarbon, part of which could be obtained by concentration.

1 : 2-4 : 5-8 : 9-*Tribenzpyrene* (X).—Dibenzyloctahydroanthracene (IX) was heated with 15% of copper powder for 4 hours at 400—420°. Hydrogen was evolved and some oil, formed by cracking, distilled. The residual *tribenzpyrene* gave, after sublimation in a vacuum and repeated recrystallisation from xylene, pale yellow leaflets, m. p. 297° (evacuated capillary; uncorr.), which gave an olive-green solution in warm concentrated sulphuric acid (Found: C, 95·5; H, 4·9. $C_{28}H_{16}$ requires C, 95·4; H, 4·6%). The fluorescence of the solution in xylene was blue.

In some cases the hydrocarbon contained a small quantity of 2 : 3-8 : 9-dibenzperylene which was identified by its absorption bands at 4340 and 4080 A. in benzene. It could be removed by chromatographic adsorption of the solution in benzene on an alumina column.

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