428. *Aromatic Hydrocarbons. Part LI. The Synthesis of Dinaphthopyrenes.**

By E. Clar.

Pyrene was condensed with two molecules of phthalic anhydride, and the two isomeric dicarboxylic acids were separated. Ring-closure gave two phthaloylpyrenes, and thence, by reduction, hydrocarbons which are regarded as dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-8 : 9)-pyrene and dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-9 : 10)pyrene, respectively, by analogy with the corresponding dibenzpyrenes. Oxidation of the hydrocarbons yielded the corresponding dinaphthopyrenequinones.

Pyrene condenses with two molecules of phthalic anhydride in a melt of sodium chloride–aluminium chloride at 150—160° with the formation of a diphthaloylpyrene in small yields (Vollmann, Becker, Corell, and Streeck, *Annalen*, 1937, **531**, 128). It has now been found that two isomeric diphthaloylpyrenes are formed in this condensation, and that they can be obtained pure and in good yield if the reaction is carried out in two stages. Pyrene was condensed with an excess of phthalic anhydride and aluminium chloride in tetrachloroethane at 70—80° and the dicarboxylic acids (I) and (II) were separated by means of the more sparingly soluble sodium salt of the (II). Ring-closure of these acids with boiling benzoyl chloride and a trace of sulphuric acid gave the orange diquinones (III) and (IV). Of these, only (IV) dissolved (with a green colour) in sulphuric acid, (III) being insoluble, and this difference provided another method of separating the two condensation products. Reduction of the diquinones was carried out by means of the zinc-dust melt (Clar, *Ber.*, 1939, **72**, 1645) or, better, with pyridine, zinc dust, and acetic acid (Clar, *Chem. Ber.*, 1948, **81**, 68). Dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-8 : 9)-pyrene (V) is a blue hydrocarbon which reacts easily, like a higher acene, with maleic anhydride in solution. However, the oxidation with selenium dioxide in boiling nitrobenzene did not yield a *p*-quinone, but gave the red dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-8 : 9)pyrene-5 : 10-quinone (VII). The yellow dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-9 : 10)pyrene (VI) reacted considerably more slowly with maleic anhydride than did (V), and by taking advantage of this (V) could be removed from a mixture with (VI). Oxidation of (VI) gave dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-9 : 10)pyrene-5 : 8-quinone (VIII), which is a violet vat dye. These oxidation results show that the two hydrocarbons belong to the pyrene rather than to the acene series.

Fig. 1 shows the absorption spectra of the centro-symmetric (V), 3 : 4-8 : 9-dibenzpyrene, and pyrene. The square root of the wave-length of the first band of the first intense group of bands increases by the same amount ($\sim 9\sqrt{\text{A.}}$) with each increase in the number of rings, as required by the anellation principle (Clar, "Aromatische Kohlenwasserstoffe," Berlin, 1941, p. 20). The shift towards the red amounts to half of this value ($\sim 4{\cdot}5\sqrt{\text{A.}}$) in the plane-symmetric series (VI), 3 : 4-9 : 10-dibenzpyrene, and pyrene. The theoretical implications of this will be discussed elsewhere. Comparison of these absorption spectra shows clearly that the structures assigned to the hydrocarbons are correct. Further evidence is provided by the pyrenequinones : the plane-symmetric quinones are deeper coloured than the centro-symmetric

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quinones; thus the pyrene- and dibenzpyrene-quinones are yellow and red, respectively, the dinaphtho-pyrenequinones (VII) and (VIII) are red and violet, respectively.

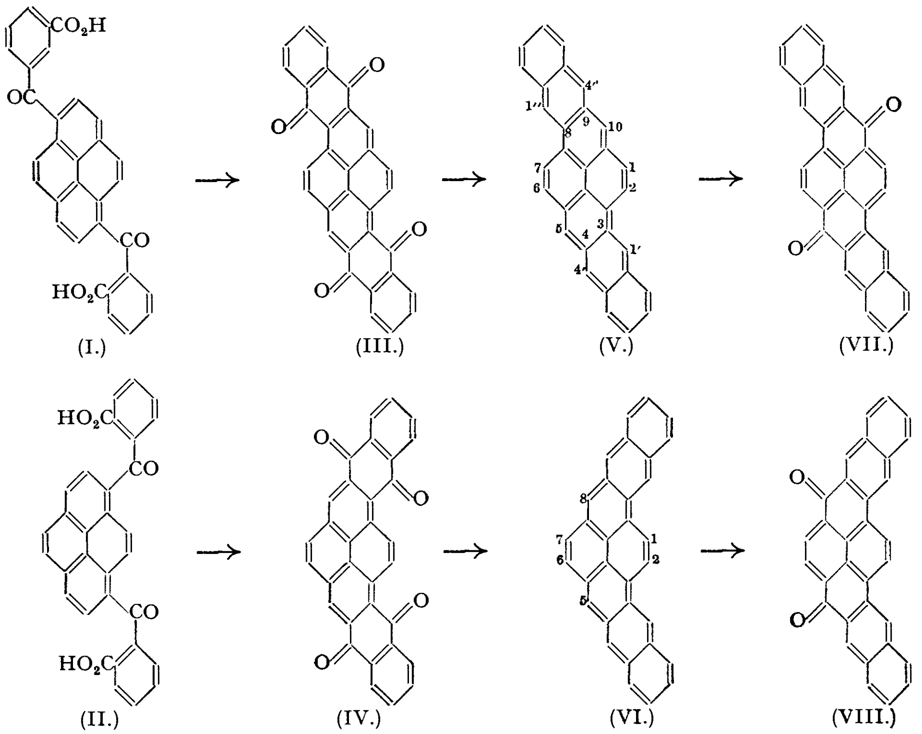
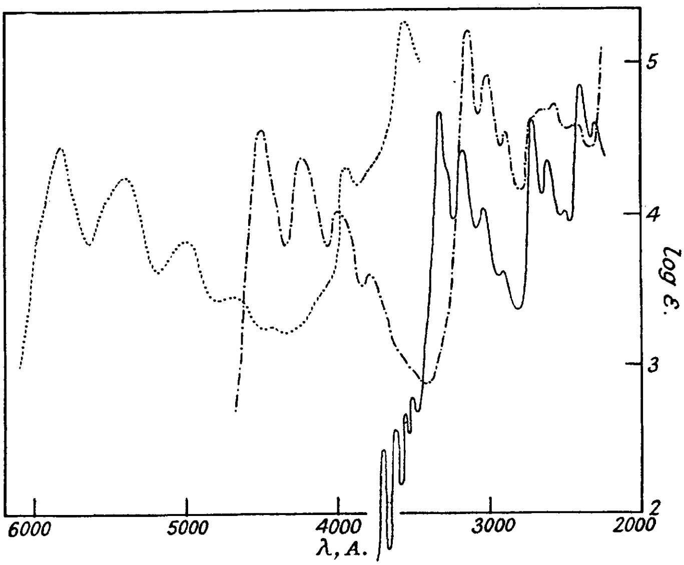


Fig. 1.

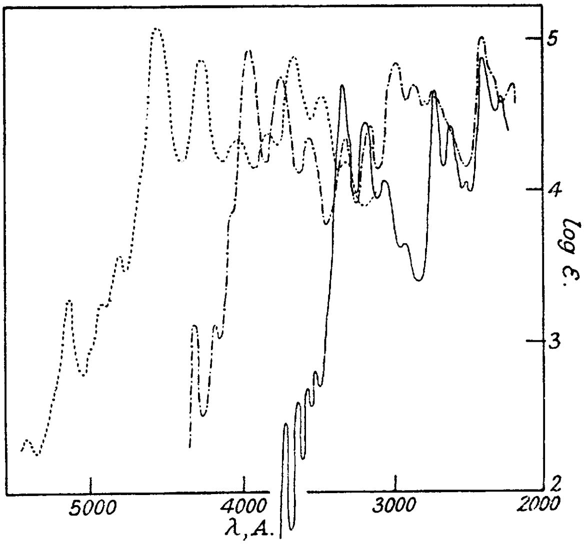


. . . . . . *Absorption spectrum of dinaphtho*(2′ : 3′-3 : 4)(2″ : 3″-8 : 9)*pyrene* (*V*) *in* 1-*methylnaphthalene. Band maxima* (*in* A.) : 5820, 5390, 4990, 4660, 4400; 3930; 3530.

—·—·— *Absorption spectrum of* 3 : 4-8 : 9-*dibenzpyrene. Band maxima* (*in* A.) : 4510, 4240, 4010, 3790; 3135; 3010, 2900 *in benzene*, 2640, 2560, 2420 *in alcohol.*

——— *Absorption spectrum of pyrene in alcohol. Band maxima* (*in* A.) : 3715, 3620, 3560, 3515; 3335, 3180, 3050, 2920; 2720, 2615, 2510; 2410; 2305.

FIG. 2.



. . . . . . *Absorption spectrum of dinaphtho*(2′ : 3′-3 : 4)(2″ : 3″-9 : 10)*pyrene* (*VI*) *in trichlorobenzene. Band maxima* (*in* A.) : 5450; 5150, 5940, 4820; 4560, 4270, 4030; 3820; 3655, 3490, 3310.

— · — · — *Absorption spectrum of* 3 : 4-9 : 10-*dibenzpyrene. Band maxima* (*in* A.) : 4330, 4190, 4080; 3970, 3750, 3565; 3320, 3170, 2970, 2850 *in benzene*, 2720; 2420, 2220 *in alcohol*

———— *Absorption spectrum of pyrene as in Fig.* 1.

EXPERIMENTAL.

3 : 10-*Di*-(o-*carboxybenzoyl*)*pyrene* (II).—Pyrene (40 g.) and phthalic anhydride (70 g.) were melted together, and tetrachloroethane (130 c.c.) was poured into the hot liquid. Powdered aluminium chloride (130 g.) was gradually added at 50°, and the mixture was heated for one hour at 70°. After decomposition with dilute hydrochloric acid in the usual way, the tetrachloroethane was removed by steam-distillation, and the residue washed with water and dissolved in dilute sodium hydroxide solution. The hot solution was made just acid with acetic acid in order to separate impurities. The dicarboxylic acid (90 g.) was then precipitated with hydrochloric acid, powdered, and treated with 200 c.c. of boiling acetic acid. After the mixture had cooled, the crystals (40 g.) were collected and washed with ether. Repeated recrystallisation from dilute aqueous sodium hydroxide gave yellow needles (11 g.) of the sodium salt of 3 : 10-*di*-(o-*carboxy*)*benzoylpyrene* (II). The free acid obtained from it by acidification crystallised from 1-methylnaphthalene in yellow needles, m. p. 325° (decomp.), which dissolved in sulphuric acid to give a red solution which afterwards turned blue (Found : C, 77·6; H, 3·9. $C_{32}H_{18}O_6$ requires C, 77·1; H, 3·6%). 3 : 8-*Di*-(o-*carboxybenzoyl*)*pyrene* (I) was obtained by acidification of the alkaline mother-liquors from the recrystallisation of the salt of (II). Recrystallisation from nitrobenzene yielded pale yellow crystals, m. p. 305—310° (decomp.), which dissolved in sulphuric acid giving a violet solution which turned green on heating (Found : C, 76·0; H, 3·8. $C_{32}H_{18}O_6$ requires C, 77·1; H, 3·6%). This purification does not ensure that the product is free from its isomer, which sometimes can be traced in the subsequent condensation.

3 : 4-8 : 9-*Diphthaloylpyrene* (III).—The acid (I) (5 g.), benzoyl chloride (15 g.), and two drops of concentrated sulphuric acid in nitrobenzene (150 c.c.) were boiled for ½ hour. A thick mass of orange needles which was precipitated from the hot liquid was filtered off at 100° and washed with nitrobenzene and ether (yield, 4·3 g.). Recrystallisation from nitrobenzene gave orange needles, which sintered at 450° (evacuated capillary; uncorr.) and charred, without melting, at higher temperatures (Found : C, 83·0; H, 3·3. $C_{32}H_{14}O_4$ requires C, 83·1; H, 3·1%). The pure *diquinone* is not soluble in cold concentrated sulphuric acid. Occasionally green solution indicates the presence of the isomeric diquinone which can be removed by filtering through a porous filter-plate. 3 : 4-9 : 10-*Diphthaloylpyrene* (IV), prepared in the same way from 3 : 10-di-(*o*-carboxybenzoyl)pyrene (II), formed orange needles, m. p. 450—455° (evacuated capillary; uncorr.), which dissolve in concentrated sulphuric acid with a pure green colour (Found : C, 83·2; H, 3·6%). Both diquinones gave a brownish-red vat in alkaline sodium hydrosulphite (dithionite).

Reduction of the Diquinones.—(a) *By the zinc dust melt.* The diquinone (5 g.) and zinc dust (10 g.) were finely powdered together, and sodium chloride (7 g.) and moist zinc chloride (25 g.) were added. The mixture was melted, stirred, and heated to 300° within about 15 minutes. The cold melt was dissolved in hydrochloric acid. The excess of zinc dust was thus removed, and the carefully washed residue was sublimed at 1 mm. in a current of carbon dioxide. The sublimate was recrystallised from 1-methylnaphthalene.

(b) *By zinc dust, pyridine, and acetic acid.* Acetic acid (80%; 50 c.c.) was added drop by drop to a boiling suspension of diquinone (5 g.), zinc dust (13 g.), and pyridine (120 c.c.) during 5 hours. The solution, which was at first red, became gradually pale-orange and was decanted from the zinc dust and poured into water. Sublimation of the washed precipitate or recrystallisation from 1-methylnaphthalene yielded the hydrocarbon.

Dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-8 : 9)*pyrene* (V) formed beautiful blue leaflets, m. p. 460° (evacuated capillary; uncorr.), which gave a brownish-yellow solution in concentrated sulphuric acid (Found : C, 95·6; H, 4·9. $C_{32}H_{18}$ requires C, 95·5; H, 4·5%). Its solutions in xylene or 1-methylnaphthalene show a strong orange fluorescence.

Dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-9 : 10)*pyrene* (VI) formed yellow leaflets, m. p. 420° (evacuated capillary; uncorr.), which dissolved in concentrated sulphuric acid to give a brown solution, which afterwards turned green and then blue (Found: C, 95·4; H, 4·7%). The solution in xylene showed a strong green fluorescence.

Mixtures of the hydrocarbons (V) and (VI) can be separated by adding small portions of maleic anhydride to the boiling solution in nitrobenzene or 1-methylnaphthalene until the visible spectrum of (V) has almost disappeared; (VI) then crystallises unchanged. Since the blue (V) is considerably less soluble than (VI), it can be obtained from the mixture with (VI) by simple fractional crystallisation.

Oxidation of the Hydrocarbons.—The hydrocarbon (1·5 g.) and selenium dioxide in nitrobenzene (150 c.c.) was boiled for ½ hour. After the mixture had cooled, the precipitate was filtered off, washed with nitrobenzene, ether, water, and alcohol, and sublimed at 1 mm. in a current of carbon dioxide. The selenium sublimed first and could be easily separated from the quinone.

Dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-8 : 9)*pyrene*-5 : 10-*quinone* (VII) sublimed in dark-reddish-brown, silky needles, m. p. 479° (decomp.) (evacuated capillary; uncorr.) (Found : C, 88·7; H, 3·7. $C_{32}H_{16}O_2$ requires C, 88·8; H, 3·7%). The solution in concentrated sulphuric acid was pure green, and gave a red precipitate when poured into water. The vat in alkaline hydrosulphite is brownish-olive-red in a thin layer and yields the deep red quinone on oxidation with air.

Dinaphtho(2′ : 3′-3 : 4)(2″ : 3″-9 : 10)*pyrene*-5 : 8-*quinone* (VIII) sublimed in dark violet needles, m. p. 460° (decomp.) (evacuated capillary; uncorr.), which gave a brown solution in concentrated sulphuric acid (Found : C, 88·8; H, 4·1%). A violet vat is formed with alkaline sodium hydrosulphite, from which the violet quinone is precipitated by air.

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