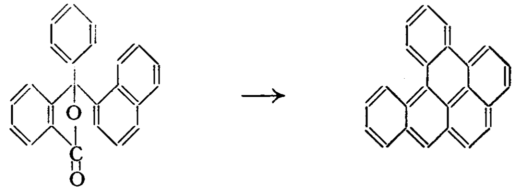
147. *Aromatic Hydrocarbons. Part LIX.* 1 : 2-3 : 4-*Dibenzpyrene.*

By E. Clar and D. G. Stewart.

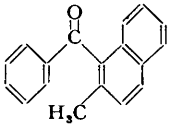
1 : 2-3 : 4-Dibenzpyrene, a strongly carcinogenic hydrocarbon, was synthesised by an unambiguous method, 9-phenyl-1 : 2-benzanthracene being used as an intermediate stage. It was found to be identical with a hydrocarbon obtained by an earlier ambiguous synthesis. An attempt to synthesise oxygen-containing derivatives of 1 : 2-3 : 4-dibenzpyrene is described.

1 : 2-3 : 4-Dibenzpyrene (II), which has been shown to be strongly carcinogenic (Bachmann, Cook, Dansi, de Worms, Hewett, and Robinson, *Proc. Roy. Soc.*, *B*, 1937, **123**, 350; Cook and Kennaway, *Amer. J. Cancer*, 1938, **33**, 53), was obtained directly from α-phenyl-α-1-naphthylphthalide (I) and also indirectly (Clar, *Ber.*, 1930, **63**, 112). However, this synthesis could also yield the isomeric 1 : 2-benzperylene and although considerable support in favour of the

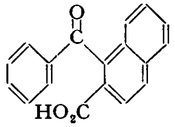
(I.)



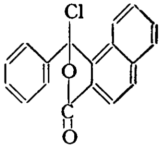
(II.)



(III.)



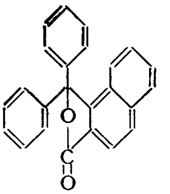
(IV.)



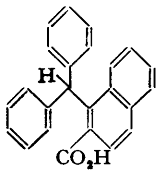
(V.)

dibenzpyrene formula was forthcoming from spectrographical investigations, a direct proof by an unambiguous synthesis was desirable.

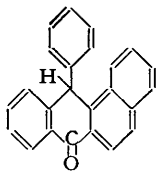
The new synthesis of (II) starts with 1-benzoyl-2-methylnaphthalene (III), which is oxidised to the acid (IV) with aqueous selenious acid under pressure at 250°. The chloro-compound (V) is obtained from (IV) by means of thionyl chloride, and Friedel–Crafts reaction of this with benzene gives the lactone (VI). Unlike the isomeric lactone (I), the former cannot be condensed to dibenzpyrene in a sodium chloride–aluminium chloride melt at 140°, and the starting material is recovered unchanged. The carbonyl group obviously deactivates the naphthalene ring.



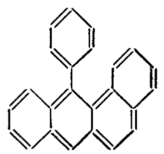
(VI.)



(VII.)



(VIII.)



(IX.)

Reduction of the lactone (VI) with alcoholic potassium hydroxide and zinc dust gives the acid (VII), which after treatment with sulphuric acid at room temperature yields (VIII). Since this compound dissolves in cold aqueous alkali and is oxidisable by molecular oxygen, it must be assumed that it exists in the enol form to a considerable extent. A sodium chloride–aluminium chloride melt of (VIII) at 140° gives poor yields of 1 : 2-3 : 4-dibenzpyrene (II). This *peri*-ring closure can be more easily effected if (VIII) is reduced to 9-phenyl-1 : 2-benzanthracene (IX) with alcoholic potassium hydroxide and zinc dust, and this then treated with aluminium chloride in boiling benzene. The 1 : 2-3 : 4-dibenzpyrene thus obtained and purified by chromatography is identical with the hydrocarbon previously synthesised (Clar,

FIG. 1.

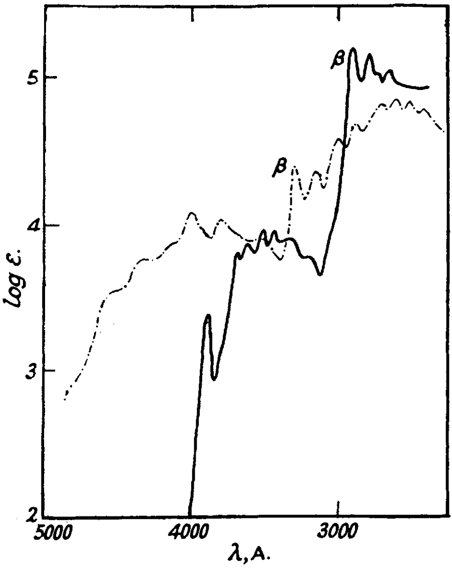


FIG. 2.

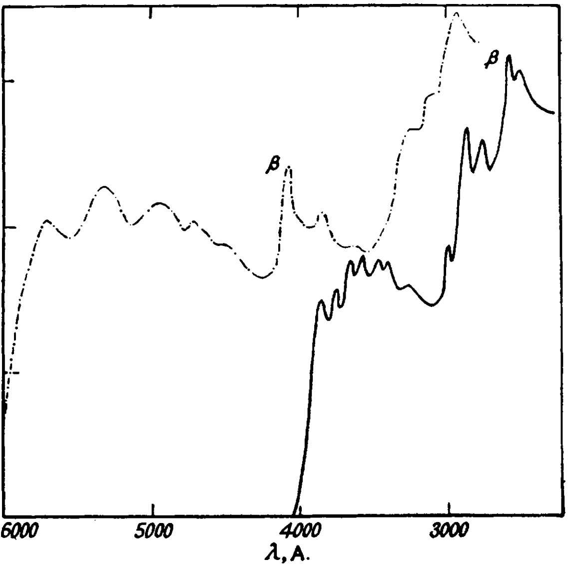


FIG. 1. — · — · — *Absorption spectrum of* 1 : 2-3 : *4-dibenzpyrene in alcohol. Band maxima in* A. : 4540, 4260, 4120, 4010, 3790, 3590: β; 3305, 3150, 3010, 2890, 2710, 2610, 2530, 2400.

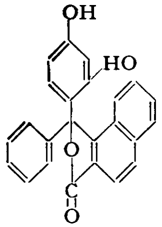
———— *Absorption spectrum of* 9-*phenyl*-1 : 2-*benzanthracene in alcohol. Band maxima in* A. : 3890, 3680, 3620, 3520, 3450, 3350, 3200 : β; 2900, 2795, 2690.

FIG. 2. — · — · — *Absorption spectrum of the red hydrocarbon in benzene. Band maxima in* A. : 5710, 5330, 4940, 4630 : β; 4080, 3850, 3630; 3230, 3090; 2925.

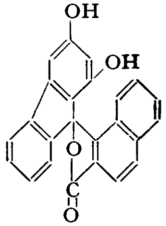
———— *Absorption spectrum of octa- or deca-hydro*-1 : 2-3 : 4-*dibenzpyrene in alcohol. Band maxima in* A. : 3865, 3760, 3660; 3580, 3480, 3410, 3260; 3000; 2875, 2775 : β; 2595, 2520.

loc. cit.). Its absorption spectrum (Fig. 1) shows the expected striking difference from that of the formally similar 9-phenyl-1 : 2-benzanthracene (IX).

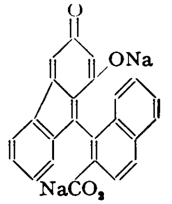
The chromatographic purification of the crude dibenzpyrene also gives two other hydrocarbons in small yield, one of which is deep red, the other colourless. Their absorption spectra are reproduced in Fig. 2. The β-band at 2595 A. of the colourless hydrocarbon, which is readily volatile in a vacuum, requires a conjugated system of at least 14 π-electrons as in phenanthrene or anthracene, according to the anellation principle. The analytical figures indicate an octahydro- or decahydro-1 : 2-3 : 4-dibenzpyrene, and it is obvious that this hydrocarbon acts as a hydrogen acceptor during the condensation.



(X.)



(XI.)



(XII.)

To obtain an oxygen-containing dibenzpyrene, (V) was condensed with resorcinol in boiling glacial acetic acid. The melt of the product (X) with sodium chloride–aluminium chloride at 140°, due to an incomplete ring closure, yields a compound which according to the analytical data, and taking into account the resistance of the naphthalene complex to *peri*-condensation, probably has the structure (XI). It gives a pale-yellow solution in hot sodium carbonate solution and a deep red-brown one in cold sodium hydroxide solution. In the latter case the quinoid salt (XII) is obviously formed.

EXPERIMENTAL.

(All m. p.s are uncorrected and taken in evacuated capillaries.)

1-*Benzoyl*-2-*methylnaphthalene* (III).—This ketone was prepared from 2-methylnaphthalene (75 g.) and benzoyl chloride (75 g.) in benzene (75 g.), with aluminium chloride (75 g.). After the usual decomposition the oil was distilled in a vacuum and gave a 85% yield of crystalline material.

1-*Benzoyl*-2-*naphthoic Acid* (IV).—1-Benzoyl-2-methylnaphthalene (10 g.), selenium dioxide (17·5 g.) and water (10 g.) were heated for 10 hours at 250° in a sealed glass-tube. The brown solid obtained was washed with water and dissolved in boiling dilute sodium hydroxide solution. After being boiled with charcoal the hot solution was filtered and, on cooling, the sodium salt of the acid crystallised in plates, which were redissolved in hot water and acidified with hydrochloric acid. The *acid* thus obtained was recrystallised from xylene and yielded colourless needles, m. p. 220—221° (Found : C, 78·5; H, 4·5. $C_{18}H_{12}O_3$ requires C, 78·2; H, 4·4%). Another portion of acid was obtained from the alkaline mother-liquors, bringing the total yield up to 76%. The acid dissolved readily in concentrated sulphuric acid to give a dark-green solution.

1-(α-*Hydroxydiphenylmethyl*)-2-*naphthoic Acid Lactone* (VI).—The chloride (V) (24 g.), obtained by boiling the acid with thionyl chloride (100 g.) and removing the excess of the latter in a vacuum, was dissolved in benzene (200 g.). Aluminium chloride (30 g.) was added with ice-cooling, and next morning the temperature was raised to 50° for a few minutes. The usual decomposition yielded a light-brown benzene layer, from which colourless needles (11 g.) separated on cooling. Recrystallisation from acetic acid gave crystals (11 g.), m. p. 236—237° (Found : C, 85·0; H, 4·9. $C_{24}H_{16}O_2$ requires C, 85·7; H, 4·8%). Another portion (10 g.) was obtained by concentration of the benzene mother-liquors, the total yield being 77%. The *lactone* dissolved in concentrated sulphuric acid to a yellowish-green solution.

1-*Diphenylmethyl*-2-*naphthoic Acid* (VII).—The lactone (7·5 g.) was dissolved by boiling it with 20% alcoholic potassium hydroxide (150 c.c.) for 2 hours. Zinc dust (30 g.), activated with copper, was added in 5-g. portions during 2½ hours, and the mixture refluxed for a further 3 hours. The hot solution was filtered and the excess of zinc dust extracted with boiling dilute sodium hydroxide. The combined filtrates were diluted with water and acidified with hydrochloric acid. The *acid* yielded colourless crystals (7 g.), m. p. 227—228°, after recrystallisation from xylene (Found : C, 84·7; H, 5·6. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·4%).

9-*Phenyl*-1 : 2-*benzanthrone* (VIII).—The acid (VII) (6 g.) was powdered and dissolved in concentrated sulphuric acid (250 c.c.) at 10°. The solution was yellow-orange at first but after a few minutes it darkened to a deep orange-brown. The temperature was not allowed to rise above 18°. After precipitation with iced water, the solid was filtered off and treated with boiling dilute ammonia solution. The greyish-white residue was recrystallised from acetic acid and gave colourless crystals (5 g.), m. p. 185—187°, of the *benzanthrone*, which on exposure to air and light became tinged violet . The analytical figures are therefore not quite satisfactory (Found : C, 88·3; H, 5·1. $C_{24}H_{16}O$ requires C, 90·0; H, 5·0%).

9-*Phenyl*-1 : 2-*benzanthracene* (IX).—9-Phenyl-1 : 2-benzanthrone (2·5 g.) was added to a boiling suspension of zinc dust (10 g.), activated with copper, in 20% alcoholic potassium hydroxide (100 c.c.) and the mixture heated for 8 hours on a water-bath. The solution lost its initial deep-yellow colour. The excess of zinc dust was filtered off whilst hot, and thoroughly washed with boiling alcohol. The combined filtrates were concentrated to 75 c.c.; on cooling, light-brownish needles crystallised. A second crop was obtained after dilution of the mother-liquors with water. Recrystallisation from alcohol yielded colourless silky needles (2·2 g.), m. p. 154—155° (Found : C, 94·8; H, 5·4. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%). The *compound* dissolved in concentrated sulphuric acid to a deep cherry-red solution which became light-brown on being kept. The solution in benzene showed a blue fluorescence.

1 : 2-3 : 4-*Dibenzpyrene from* 9-*Phenyl*-1 : 2-*benzanthrone*.—9-Phenyl-1 : 2-benzanthrone (VIII) (1 g.) was added to a melt of sodium chloride (1·2 g.)–aluminium chloride (6 g.) at 140°, and this temperature maintained for 1 hour. The dark-brown melt was poured into dilute hydrochloric acid, and the solid washed thoroughly with hot water. The dry substance was dissolved in anhydrous benzene (50 c.c.) and chromatographed on activated alumina (60 g.; 50 cm. high column). The first eluate with benzene yielded a very small quantity of crystals melting unsharply at 152—155°. The main fraction, a bright yellowish-green solution with a brilliant green fluorescence, gave, after concentration to small volume and addition of acetic acid, a small quantity of yellow needles, m. p. 221—225°. The mixed m. p. with a previous sample of 1 : 2-3 : 4-dibenzpyrene (m. p. 226—227°) was 223—226°. The needles, like the previous sample, gave a violet-red solution in concentrated sulphuric acid, which changed to green on being kept.

1 : 2-3 : 4-*Dibenzpyrene from* 9-*Phenyl*-1 : 2-*benzanthracene*.—9-Phenyl-1 : 2-benzanthracene (IX) (0·75 g.) and powdered aluminium chloride (5 g.) were heated in benzene (75 c.c.) on a water-bath. Almost at once a deep-violet colour developed which quickly changed to dark brown and then to a deep red. After decomposition with dilute hydrochloric acid, the benzene layer was washed and dried ($CaCl_2$). The result of the chromatographic separation was found to depend on the period of condensation.

A condensation product in benzene which was obtained by 3-hours heating with aluminium chloride was adsorbed on alumina and developed with light petroleum (40—60°)-benzene. The first eluate (*A*) was colourless with a violet-blue fluorescence, the second (*B*) was yellow with a green fluorescence, and a brown band remained on the column. If the condensation was carried out for 5—10 minutes only, a deep-red eluate (*C*) was obtained following the yellow fraction (*B*). In addition a small green zone developed below the brown band but these were not investigated.

In every case 1 : 2-3 : 4-dibenzpyrene was obtained from the yellow solution (*B*) by concentration and recrystallisation from a small quantity of benzene. It melted at 224—226° and had a melting point of 224—226° when mixed with a previous sample of dibenzpyrene. The dibenzpyrene prepared by this new method was identical with that obtained from earlier syntheses in its fluorescence in solution and in the solid state, in the colour of its solution in sulphuric acid, and in its absorption spectrum.

Octahydro- or Decahydro-1 : 2-3 : 4-*dibenzpyrene*.—Fraction (*A*) was concentrated to a small volume and colourless crystals were obtained, which, after recrystallisation from alcohol, melted at 231—232°. They sublimed readily in a vacuum and dissolved in concentrated sulphuric acid to give a yellow solution, which, on being kept, changed to green (Found: C, 92·4, 92·8; H, 7·6, 7·5. $C_{24}H_{22}$ requires C, 92·8; H, 7·1. $C_{24}H_{24}$ requires C, 92·3; H, 7·7%).

The red condensation product was obtained by concentration of the red fraction (*C*) and recrystallisation from benzene. The deep-red needles (m. p. 213—214°) which fluoresced orange in benzene gave a red-brown solution in concentrated sulphuric acid which changed to violet on being kept. The absorption spectrum is shown in Fig. 2. The amount of hydrocarbon obtained was not sufficient to permit establishment of the exact composition.

1-(α-*Hydroxy*-2 : 4-*dihydroxydiphenylmethyl*)-2-*naphthoic Acid Lactone* (X).—1-(α-Chloro-α-hydroxybenzyl)-2-naphthoic acid lactone (V) (5 g.) and resorcinol (5 g.) were dissolved in glacial acetic acid (50 c.c.) and heated to boiling. Hydrogen chloride was evolved copiously, and the dark-brown solution became paler. A heavy deposit of crystals was obtained and more was isolated from the mother liquors by steam-distillation. Recrystallisation from acetic acid yielded colourless crystals (5 g.) which gave an orange-red melt at 289—290° and dissolved in concentrated sulphuric acid to a deep-red solution which rapidly became pale yellow (Found : C, 78·3; H, 4·5. $C_{24}H_{16}O_4$ requires C, 78·3; H, 4·4%).

1-(1 : 3 : 9-*Trihydroxy*-9-*fluorenyl*)-2-*naphthoic Acid Lactone* (XI).—Sodium chloride (4 g.) and powdered aluminium chloride (17 g.) were fused at 140°, and (X) (2 g.) was added. After 1 hour the melt was decomposed with dilute hydrochloric acid, and the dark-brown precipitate was filtered off and washed with hot water. After repeated crystallisation from dilute acetic acid (charcoal) and xylene–acetic acid, light brownish-yellow plates, m. p. 322—324°, were obtained (Found : C, 78·7; H, 4·1. $C_{24}H_{14}O_4$ requires C, 78·7; H, 3·9%). These gave a yellow solution in concentrated sulphuric acid which became pale violet and then colourless on being kept. The lactone dissolved in boiling sodium carbonate to a pale yellow solution, and in cold sodium hydroxide to a deep red-brown one.

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