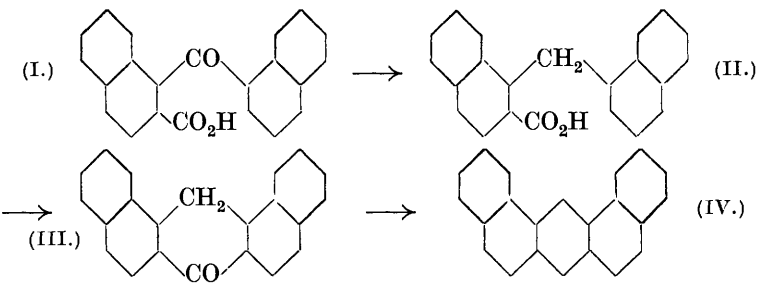
197. *Polycyclic Aromatic Hydrocarbons. Part X.* 1 : 2 : 7 : 8-*Dibenzanthracene.*

By JAMES WILFRED COOK.

THE only one of the five possible dibenzanthracenes still unknown,* namely, the 1 : 2 : 7 : 8-compound (compare Cook, J., 1931, 487), has now been synthesised by two independent methods, and is being utilised in animal experiments for comparison with the cancer-producing 1 : 2 : 5 : 6-isomeride.

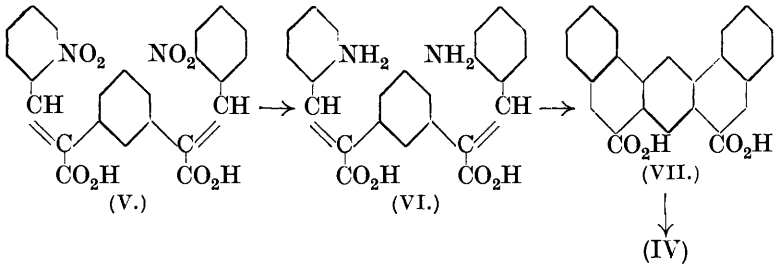
By oxidation with selenious acid at 230—240°, 2-methyl-1 : 1′-dinaphthyl ketone readily passed into 2-*carboxy*-1 : 1′-*dinaphthyl ketone* (I), which could not be directly dehydrated to 1 : 2 : 7 : 8-dibenzanthraquinone (XI), as it underwent a molecular rearrangement, the nature of which is discussed in the sequel. The system was immobilised by reducing the keto-acid (I) to the dinaphthylmethane acid (II), which was not obtained crystalline, and was dehydrated by zinc chloride to 1 : 2 : 7 : 8-dibenz-10-anthrone (III; isolated as the *acetate* of the enol). Subsequent reduction led to 1 : 2 : 7 : 8-*dibenzanthracene* (IV), which was oxidised by chromic acid to 1 : 2 : 7 : 8-*dibenzanthraquinone* (XI) :



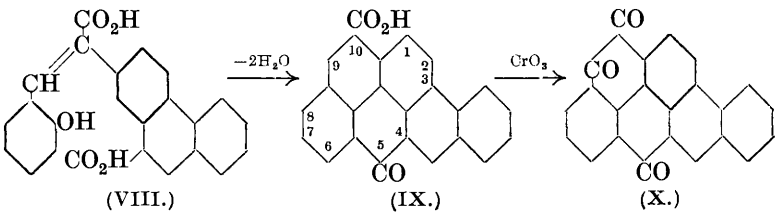
1 : 2 : 7 : 8-Dibenzanthracene was also synthesised by a method analogous to that employed by Weitzenböck and Klinger (*Monatsh.*,

* The deep blue hydrocarbon described as 2 : 3 : 6 : 7-dibenzanthracene-9 : 10-diyl by Clar and John (*Ber.*, 1930, **63**, 2967) is chemically indistinguishable from 2 : 3 : 6 : 7-dibenzanthracene.

1918, **39**, 315) for the 1 : 2 : 5 : 6-compound. For this purpose, *m*-phenylenediacetic acid was condensed with *o*-nitrobenzaldehyde, and the resulting *dinitro-acid* (V) reduced by ferrous hydroxide to the *diamino-acid* (VI). The latter compound, submitted to the Pschorr phenanthrene synthesis, gave, in addition to resinous substances, two main products : the one formed in lesser amount was 1 : 2 : 7 : 8-*dibenzanthracene*-4 : 5-*dicarboxylic acid* (VII). This acid was converted by heat into 1 : 2 : 7 : 8-dibenzanthracene (IV), identical with that obtained from 2-methyl-1 : 1′-dinaphthyl ketone, and the comparison was completed by formation of the *picrate* and by oxidation to the quinone (XI) :

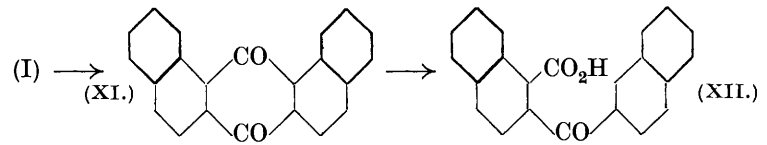


The major product of the Pschorr reaction was not 1 : 2 : 5 : 6-dibenzphenanthrene-4 : 8-dicarboxylic acid, the formation of which might be anticipated in addition to the dibenzanthracene compound. Its composition corresponded to the formula $C_{24}H_{16}O_5$, and it was evidently the *hydroxy-acid* (VIII), formed from the diamino-acid (VI) by ring closure at only one point, the other diazonium group being replaced by hydroxyl. On vacuum sublimation at 330—350°, this hydroxy-acid (VIII) lost two molecules of water to give the very sparingly soluble 1′ : 3′-*naphtha*-3 : 4-*pyren*-5-*one*-10-*carboxylic acid* (IX), which at 420° lost carbon dioxide and passed into 1′ : 3′-*naphtha*-3 : 4-*pyren*-5-*one*. Oxidation of the monocarboxylic acid (IX) by sodium dichromate in acetic acid gave a red quinone-like *compound*, $C_{23}H_{10}O_3$ (X). Furthermore, when the dry sodium salt of the original hydroxy-acid (VIII) was heated with methyl sulphate, it was converted into the *methyl* ester of the naphthapyrenonecarboxylic acid (IX) :

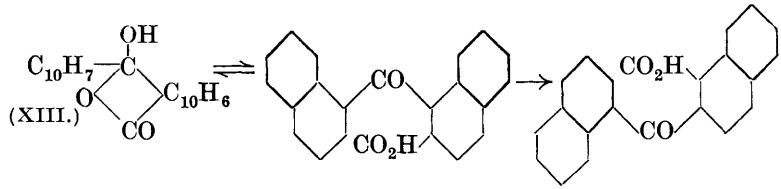


It is very surprising that the new condensed six-ring complex should be formed from the hydroxy-acid (VIII) under such mild conditions, yet there appears to be no alternative explanation of the facts.

As already stated, the dehydration of 2-carboxy-1 : 1′-dinaphthyl ketone (I) was attended by molecular rearrangement, and when the dehydration was effected in nitrobenzene solution, by phosphoric oxide at 150°, 1 : 2 : 5 : 6-dibenzanthraquinone was the sole product. Similar rearrangement accompanied the dehydration of *2-carboxy-1 : 2′-dinaphthyl ketone* (XIV), which under the same conditions gave a mixture of 1 : 2 : 5 : 6-, 1 : 2 : 6 : 7-, and 1 : 2 : 7 : 8-dibenzanthraquinones. The first two quinones might be obtained as normal dehydration products of the keto-acid (XIV), but the 1 : 2 : 7 : 8-compound could only arise as the result of a rearrangement. These intramolecular changes are of exactly the same type as those observed by Hayashi (J., 1927, 2517; 1930, 1513, 1520, 1524) among the halogenohydroxybenzoyltoluic acids, and the examples now cited remove much of the ambiguity which has existed regarding the mechanism of the change. In the cases studied by Hayashi the structures of the quinones were uncertain, and it was suggested by Bennett (*Ann. Reports*, 1929, **26**, 142) that the isomeric change which took place when the halogenohydroxybenzoyltoluic acids were treated with sulphuric acid involved the intermediate formation of anthraquinone derivatives. Such a view is not only intrinsically improbable, but in the cases now under discussion is definitely untenable, for if 2-carboxy-1 : 1′-dinaphthyl ketone (I) were first dehydrated to 1 : 2 : 7 : 8-dibenzanthraquinone (XI), this on hydrolysis could only revert to (I) or give 1-carboxy-2 : 2′-dinaphthyl ketone (XII), which by further dehydration would pass into 1 : 2 : 6 : 7- or 1 : 2 : 7 : 8-dibenzanthraquinone, but not the 1 : 2 : 5 : 6-compound, which was exclusively formed :

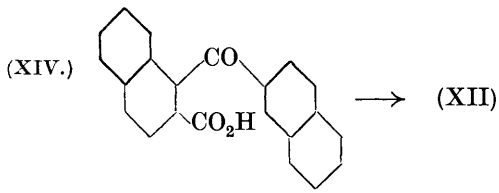


The true explanation of the change is found in one of the two alternatives suggested by Hayashi for the examples which he studied. For, in the case of 2-carboxy-1 : 1′-dinaphthyl ketone (I) it is apparent that the dehydration to 1 : 2 : 5 : 6-dibenzanthraquinone is preceded by αδ-migration of a 1-naphthyl radical (an example of αδ-migration of a phenyl radical is given by Kleinfeller and Eckert, *Ber.*, 1929, **62**, 1598) :

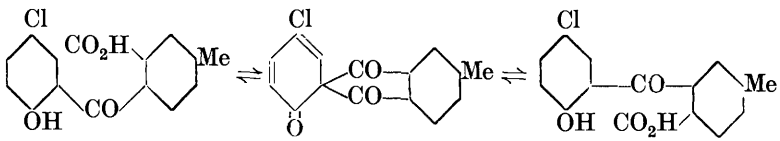


Such a migration is closely allied to the pinacol–pinacolin and Wagner transformations, and from this standpoint the hydroxy-lactone structure (XIII) for the keto-acid (for which evidence is adduced) corresponds to the ethylene oxide structure which may sometimes occur as an intermediary in the pinacol–pinacolin transformation. In fact, it seems probable that the tautomerism, keto-acid $\rightleftharpoons$ hydroxy-lactone, is one of the factors which determine the migration.

In an analogous manner, 2-carboxy-1 : 2′-dinaphthyl ketone (XIV) must be regarded as undergoing migration of a 2-naphthyl radical to give 1-carboxy-2 : 2′-dinaphthyl ketone (XII), the precursor of the 1 : 2 : 7 : 8-dibenzanthraquinone which was formed, together with the 1 : 2 : 5 : 6- and 1 : 2 : 6 : 7-compounds :



In the compounds in which migration occurred, which were studied by Hayashi, a hydroxyl group was attached to the migrating aryl radical, so that an alternative explanation was suggested involving the intermediate formation of a spirocyclic hemiquinonoid compound, in accordance with the scheme :



Since there is no phenolic group present in the naphthoyl-naphthoic acids (I and XIV) which undergo the same type of change, such a mechanism is definitely disproved. In Hayashi's papers no preference was shown towards either of the possible alternative mechanisms, and in reporting his results Bennett and Chapman (*Ann. Reports*, 1930, **27**, 124) were quite unjustified in asserting that the " quinonoid " mechanism was established, while making no mention of the alternative, which is now shown to be correct.

A study of their reduction products confirmed the structures assigned to the two naphthoylnaphthoic acids, and showed that they were not products of rearrangement formed by heating with selenious acid during the oxidation of the methyldinaphthyl ketones. For, while the acid (I) produced by oxidation of 2-methyl-1 : 1′-dinaphthyl ketone was converted into 1 : 2 : 7 : 8-dibenzanthracene in the manner already described, its isomeride (XIV) produced by oxidation of 2-methyl-1 : 2′-dinaphthyl ketone gave, under similar conditions, 1 : 2 : 5 : 6- and probably 1 : 2 : 6 : 7-dibenzanthracene, but not the 1 : 2 : 7 : 8-compound.

The naphthyl migrations shown by the naphthoylnaphthoic acids are reminiscent of the hydroxynaphthyl migrations which Warren and Smiles (J., 1930, 956; 1931, 914, 2207) have established in the cases of 2-naphthol-1-sulphide and 2-naphthol-1-sulphone.

EXPERIMENTAL.

Naphthoylnaphthoic Acids.

2-*Carboxy*-1 : 1′-*dinaphthyl Ketone* (I).—Attempts to oxidise 2-methyl-1 : 1′-dinaphthyl ketone (Clar, *Ber.*, 1929, **62**, 355) by alkaline permanganate, or indirectly through the bromomethyl compounds, were fruitless. The oxidation was successfully accomplished, however, by dry selenious acid in boiling nitrobenzene, better results being obtained by heating under pressure with aqueous selenious acid : *

A mixture of 2-methyl-1 : 1′-dinaphthyl ketone (12 g.), selenious acid (20 g.) and water (20 g.) was heated at 230—240° for 4 hours. The solid reaction product was washed with water, extracted with boiling dilute sodium carbonate solution, and the solution, filtered from selenium and unchanged ketone (3 g.), acidified. The precipitated acid was recrystallised from acetic acid and then formed a slightly brownish, crystalline powder (8·5 g.), m. p. 238—239°. For purification, the acid (7·5 g.) was converted into the *acetoxylactone* (derived from XIII) by heating at 100° for 2 hours with acetic anhydride (10 c.c.) in pyridine (35 c.c.). The product crystallised from alcohol (animal charcoal) as a colourless crystalline powder, m. p. 196° (Found : C, 77·9; H, 4·5. $C_{24}H_{16}O_4$ requires C, 78·2; H, 4·4%). This acetoxy-lactone was hydrolysed by alco-

* This selenious acid method of oxidation had formerly been used by the I.G. Farbenind. A.-G. (D.R.-P. 347,743) for the oxidation of side chains in other polycyclic aromatic compounds, and I am indebted to Dr. E. H. Rodd for directing my attention to this specification. The method is not of general application, however, as it was not found possible to oxidise 2-methyl-1-naphthoic acid to naphthalene-1 : 2-dicarboxylic acid, or 6-methyl-1 : 2-benzanthraquinone to the corresponding carboxylic acid, by heating under pressure with aqueous selenious acid.

holic potassium hydroxide, and the resulting *2-carboxy-1 : 1′-dinaphthyl ketone* (I) recrystallised from acetic acid, forming colourless plates, m. p. 241—242° (Found : C, 80·6; H, 4·4. $C_{22}H_{14}O_3$ requires C, 81·0; H, 4·3%). The green solution of this acid in concentrated sulphuric acid became deep blue on gentle warming.

Dehydration. (i) By heating a solution of the above acid (I) in concentrated sulphuric acid at 85—90° for 1¼ hours, a small yield of a mixture of quinones (m. p. 190—210°) was obtained. The greater part of the material was sulphonated; at lower temperatures ring closure was not effected.

(ii) The acid (2·5 g.) was added to a mixture of anhydrous aluminium chloride (25 g.) and sodium chloride (5 g.) at 130°, and the melt stirred for an hour at this temperature. After decomposition with water, the insoluble residue was sublimed in a vacuum. The mixture of quinones (m. p. 180—215°) gave pure 1 : 2 : 5 : 6-dibenzanthraquinone after three recrystallisations from benzene. No pure substance was isolated from the liquors.

(iii) Phosphoric oxide (2 g.) was added to a solution of the keto-acid (I) (1 g.) in nitrobenzene (20 c.c.), at 150°. After being stirred for ¾ hour at this temperature, the whole was cooled, decomposed with water, and the nitrobenzene removed in steam. The residue was free from unchanged acid; a trace of colouring matter was removed by boiling with acetic acid containing sodium dichromate, and the product crystallised from benzene; it then gave pure 1 : 2 : 5 : 6-dibenzanthraquinone, m. p. 248—250°, in good yield. The quinone was identified by comparison with a sample prepared by the method of Clar (*Ber.*, 1929, **62**, 357).

2-Carboxy-1 : 2′-dinaphthyl Ketone (XIV).—(i) *Formation.* 2-Methyl-1 : 2′-dinaphthyl ketone (Clar, *loc. cit.*) was oxidised with selenious acid in the same way as the isomeride. The acid was extracted from the reaction product with dilute sodium carbonate solution, the crude acid dissolved in glacial acetic acid, and the solution diluted with a little water. A small amount of dark brown solid separated. Addition of more water to the filtered solution gave an almost white precipitate of the keto-acid (14 g. from 24 g. of ketone), which was converted into the *acetoxy-lactone* by pyridine–acetic anhydride at 100°. This acetoxy-lactone was crystallised from alcohol (animal charcoal) and benzene–alcohol and then formed small colourless crystals, m. p. 185—186° after slight sintering (Found : C, 78·2; H, 4·5. $C_{24}H_{16}O_4$ requires C, 78·2; H, 4·4%). Hydrolysis with alcoholic potassium hydroxide gave *2-carboxy-1 : 2′-dinaphthyl ketone* (XIV), which had poor power of crystallisation, and was sufficiently pure for ordinary purposes when precipitated from a solution of its potassium salt. The acid separated

from its hot solution in xylene as a gelatinous solid, which dried to a colourless amorphous powder, m. p. 258—259° after slight sintering (Found: C, 80·6; H, 4·5. $C_{22}H_{14}O_3$ requires C, 81·0; H, 4·3%).

(ii) *Dehydration.* The aforesaid keto-acid (XIV) (2 g.) was dehydrated with phosphoric oxide in nitrobenzene at 150°, exactly as described for the isomeride. The resulting mixture of quinones (1 g.) could not be separated by recrystallisation, and was reduced to the corresponding mixture of hydrocarbons. For this purpose, reduction was first carried out with aluminium powder and sulphuric acid, as described for 1 : 2 : 5 : 6-dibenzanthraquinone (Cook, J., 1931, 3278), and the resulting mixture of dibenzanthrones boiled with *N*-sodium hydroxide and zinc dust for 3 hours. The excess of zinc was removed by hydrochloric acid, and the hydrocarbon mixture extracted with alkaline hydrosulphite to remove a trace of quinone. A solution of the residual solid (0·25 g.) in xylene (20 c.c.) was boiled with maleic anhydride (0·2 g.) for ¾ hour,* and the xylene removed in steam, in presence of dilute sodium hydroxide solution. By this treatment 2′ : 3′-naphtha-2 : 3-phenanthrene (the reduction product of 1 : 2 : 6 : 7-dibenzanthraquinone) was converted into the water-soluble sodium salt of its maleic anhydride additive compound. The aqueous solution was acidified, and the precipitate dried and sublimed in a vacuum at 300°. The sublimate was extracted with alcohol, and the residue recrystallised from xylene, forming golden-orange leaflets, m. p. 262—263°, alone or mixed with authentic 2′ : 3′-naphtha-2 : 3-phenanthrene (Cook, J., 1931, 505). The hydrocarbons not attacked by maleic anhydride were recrystallised from acetic acid and then benzene, whereby pure 1 : 2 : 5 : 6-dibenzanthracene was obtained. The acetic acid liquors gave a product which was purified through the picrate and then recrystallised from acetic acid. The resulting long, colourless, slender needles had m. p. 182—186°, and were shown by direct comparison to be almost pure 1 : 2 : 7 : 8-dibenzanthracene (below).

(iii) *Reduction.* A solution of 2-carboxy-1 : 2′-dinaphthyl ketone (XIV) (5 g.) in *N*-potassium hydroxide (250 c.c.) was heated for 24 hours with zinc dust (25 g.). The filtered solution was acidified, the precipitate dissolved in sodium carbonate solution, filtered, and the acid reprecipitated; it was recrystallised from acetic acid and then from benzene (Found: C, 84·3; H, 5·2. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·2%). 1 : 2′-*Dinaphthylmethane-2-carboxylic acid* formed a colourless microcrystalline powder, m. p. 193—195°.

* This method of separation depends on the fact that 2′ : 3′-naphtha-2 : 3-phenanthrene, like 2 : 3-benzanthracene, reacts additively with maleic anhydride very rapidly, whereas the *angular* dibenzanthracenes react with great reluctance (compare Clar, *Ber.*, 1931, **64**, 2195; Cook, J., 1931, 3274).

An intimate mixture of this acid (1 g.) and anhydrous zinc chloride (3 g.) was heated at 180—185° for ½ hour, cooled, powdered, and extracted with water. The mixture of anthrone-like substances was reduced for 2 hours by zinc dust and boiling 2*N*-sodium hydroxide, and the yellow hydrocarbon mixture (0·5 g.), freed from zinc, was treated with maleic anhydride in xylene in the manner already described. A small amount of orange-yellow 2′ : 3′-naphtha-2 : 3-phenanthrene was thus removed, but was not isolated in the pure state. The main product was 1 : 2 : 5 : 6-dibenzanthracene, and there was no evidence of the presence of 1 : 2 : 7 : 8-dibenzanthracene. This confirms the structure assigned to the keto-acid (XIV).

Synthesis of 1 : 2 : 7 : 8-*Dibenzanthracene.*

Method I.—A solution of 2-carboxy-1 : 1′-dinaphthyl ketone (I) (10 g.) in *N*-potassium hydroxide (500 c.c.) was boiled with zinc dust (25 g.) for 24 hours. The crude dinaphthylmethanecarboxylic acid (II) (8·8 g.) contained resinous impurities which prevented its crystallisation. It was therefore intimately mixed with anhydrous zinc chloride (27 g.) and heated at 180—185° for ½ hour. After cooling, the melt was powdered, extracted with water, and warmed with 0·1*N*-sodium carbonate to remove a trace of unaltered acid. The crude dibenzanthrone (III) was dried in a vacuum desiccator (8·1 g.).

1 : 2 : 7 : 8-*Dibenzanthranyl* 10-*acetate.* A solution of this crude dibenzanthrone (1 g.) in pyridine (5 c.c.) and acetic anhydride (1·5 c.c.) was heated on the water-bath for an hour, treated with water, and the resinous mass extracted with boiling alcohol. The insoluble residue was twice recrystallised from benzene; it then formed colourless microscopic needles, m. p. 255—256° (slight decomp.) (* Found : C, 86·0; H, 5·0; *M*, cryoscopic in camphor, 339, 334. $C_{24}H_{16}O_2$ requires C, 85·7; H, 4·8%; *M*, 336).

This *acetate* gave a colourless solution with a violet fluorescence in benzene, and a yellow solution with a green fluorescence in alcoholic potassium hydroxide.

1 : 2 : 7 : 8-*Dibenzanthracene* (IV). Crude 1 : 2 : 7 : 8-dibenz-10-anthrone (III) (8 g.) was reduced by zinc dust (15 g.) and boiling *N*-sodium hydroxide (500 c.c.) for 3 hours. The solid was collected, and extracted with hydrochloric acid to remove as much excess zinc as possible. The undissolved resin was dissolved in acetic acid, and the filtered solution treated with picric acid (10 g.). The brick-red picrate (2·5 g.) was collected, decomposed with ammonia, and the crude hydrocarbon sublimed in a vacuum; the sublimate was dissolved in benzene and treated with an equal weight of picric acid. After recrystallisation from benzene, 1 : 2 : 7 : 8-*dibenzanthracene picrate* formed long crimson needles, m. p. 210° (*Found : N, 8·3.

$C_{22}H_{14},C_6H_3O_7N_3$ requires N, 8·3%). Excess of picric acid gave a picrate of a lighter colour and different crystalline form, possibly a dipicrate, which was converted into this monopicrate by repeated crystallisation from benzene.

A benzene solution of the 1 : 2 : 7 : 8-dibenzanthracene picrate was shaken with dilute sodium carbonate solution, the benzene removed on the water-bath, and the residue recrystallised from acetic acid (*Found : C, 94·7; H, 5·1. $C_{22}H_{14}$ requires C, 94·9; H, 5·1%). 1 : 2 : 7 : 8-*Dibenzanthracene* formed long, colourless, silky needles, m. p. 196°, and gave no colour with concentrated sulphuric acid. Oxidation with sodium dichromate in acetic acid gave a substance identical with the 1 : 2 : 7 : 8-dibenzanthraquinone prepared as described under Method II.

Method II.—m-*Phenylenediacetic acid* A suspension of *m*-xylylene dicyanide (30 g.) in concentrated sulphuric acid (100 c.c.) and water (200 c.c.) was boiled under reflux for 2 hours. The solid which separated on cooling was recrystallised from hot water and gave pure *m*-phenylenediacetic acid, m. p. 171—172°. A solution of the acid (156 g.) in hot methyl alcohol (500 c.c.) was treated with a solution of potassium hydroxide (90 g.) in methyl alcohol (200 c.c.). The dipotassium salt crystallised on cooling, and a further quantity was obtained from the liquors by concentration. In this way, 335 g. of *m*-xylylene dicyanide were converted into 373 g. of *m*-phenylenediacetic acid, which gave 457 g. of the dipotassium salt.

Di-α-o-nitrobenzylidene-m-phenylenediacetic acid (V). Dry potassium *m*-phenylenediacetate (54 g.) was heated under reflux at 130—140° for 7 hours with *o*-nitrobenzaldehyde (70 g.) and acetic anhydride (400 c.c.). The hot liquid was poured into a large volume of water and kept over-night; the aqueous liquid was then decanted, and the residual resin dissolved in hot dilute sodium carbonate solution. The filtered solution was acidified with hydrochloric acid, and the precipitate collected, washed, and dried in a vacuum desiccator. The light brown powder was extracted with boiling benzene, which removed resinous material, and recrystallised from methyl alcohol (animal charcoal), glacial acetic acid, and finally methyl alcohol (Found : C, 62·7; H, 3·9; N, 6·1. $C_{24}H_{16}O_8N_2$ requires C, 62·6; H, 3·5; N, 6·1%). This *dinitro-acid* (V) formed small colourless leaflets, m. p. 239—240°, unchanged by further crystallisation of the sparingly soluble ammonium salt.

The *diethyl* ester was formed when a suspension of the dinitro-acid (5 g.) in alcoholic hydrogen chloride (50 c.c.) was boiled for 3 hours. It separated from methyl alcohol in large colourless crystals, m. p. 106—107° (Found : C, 64·9; H, 5·0. $C_{28}H_{24}O_8N_2$ requires C, 65·1; H, 4·7%).

Di-α-o-aminobenzylidene-m-phenylenediacetic acid (VI). The dinitro-acid (V) was readily reduced by ferrous hydroxide or by aqueous sodium sulphide, but in spite of many attempts under various conditions, no product of definite m. p. could be isolated. This was probably due to the production of mixtures of stereoisomerides, as sodium nitrite titrations indicated that the products consisted essentially of the diamino-compound. Moreover, the analytical samples of diamino-acid showed a deficiency in carbon; this indicated retention of solvent, for the discrepancy was removed when the dihydrochloride was prepared. The following experiments are typical:

(i) A boiling solution of the dinitro-acid (V) (5 g.) in water (60 c.c.) and concentrated aqueous ammonia (5 c.c.) was added slowly to a boiling suspension prepared by the addition of concentrated aqueous ammonia (200 c.c.) to a solution of ferrous sulphate (65 g.) in water (600 c.c.). After boiling for ½ hour, the suspension was filtered, and the filtrate heated to boiling in an open vessel for some time, whereby a small amount of hydrated iron oxides was precipitated. The iron oxide sludge was extracted several times with boiling dilute aqueous ammonia, and the combined filtrates were cooled and acidified with dilute acetic acid. The yellow precipitate was collected and purified by crystallisation of the sparingly soluble dihydrochloride. This was then dissolved in aqueous ammonia, and the diamino-acid reprecipitated by dilute acetic acid and dried in a vacuum desiccator. The dry diamino-acid was dissolved in methyl alcohol, and the solution concentrated (in other reductions, effected by heating for a longer period with a smaller excess of ferrous hydroxide or with sodium sulphide, canary-yellow plates separated at this stage; these melted indefinitely at about 80° and had substantially the same elementary composition as the product now to be described). The cold clear solution was diluted somewhat with water. Crystallisation slowly set in, and the product was recrystallised from dilute alcohol. The *diamino-acid* (VI) formed a yellowish crystalline powder, and either melted and gave off gas at 150°, or sintered at about 146°, but was not completely molten at 200°, the behaviour depending upon the rate of heating (Found: C, 70·1; H, 5·7. $C_{24}H_{20}O_4N_2,C_2H_6O$ requires C, 69·9; H, 5·9%).

The *dihydrochloride* separated from a solution of the diamino-acid (VI) in dilute hydrochloric acid as an almost colourless, crystalline powder, which was dried in a vacuum desiccator over sulphuric acid and potassium hydroxide. It melted at 240° (with intumescence) after sintering (Found: C, 60·7; H, 5·8. $C_{24}H_{20}O_4N_2,2HCl$ requires C, 60·9; H, 4·7%).

(ii) The dinitro-acid (V) (20 g.) was reduced by a ferrous hydroxide suspension prepared from ferrous sulphate (250 g.), water (1250 c.c.), and concentrated aqueous ammonia (150 c.c.), exactly as described under (i) except that the whole was heated on the water-bath for 5 hours. The crude diamino-acid (15 g.) was purified through the dihydrochloride, and the reprecipitated diamino-acid (13 g.) used for the Pschorr reaction.

*Pschorr reaction with di-α-o-aminobenzylidene-*m*-phenylenediacetic acid.* An ice-cold aqueous solution prepared from the diamino-acid (8·3 g.), potassium carbonate (3 g.), and sodium nitrite (2·84 g., *i.e.*, the requisite amount for complete tetrazotisation, determined by titration) was added, slowly with agitation, to ice-cold 5*N*-sulphuric acid (150 c.c.). To the clear yellow solution was added precipitated copper powder (15 g.), and the suspension shaken at room temperature for 15 hours; a filtered sample then gave no colour with alkaline β-naphthol. The product was collected, washed with water, and extracted with hot dilute sodium carbonate solution. The copper powder was removed by filtration (which proceeded extremely slowly) and the filtrate acidified, heated to boiling, and the precipitate collected and dried at 100° (6·75 g.). This was extracted with boiling methyl alcohol (300 c.c.), and the insoluble residue washed with a little boiling glacial acetic acid, then with alcohol, and dried (0·95 g.). This product was the crude 1 : 2 : 7 : 8-dibenzanthracene-4 : 5-dicarboxylic acid (VII). The methyl-alcoholic extract was concentrated to about 20 c.c., and the solution cooled. The light brown crystalline powder (2·3 g.) which separated was shown to be the hydroxy-acid, $C_{24}H_{16}O_5$ (VIII). The methyl-alcoholic liquors contained dark brown resinous substances from which no pure compound could be isolated.

1 : 2 : 7 : 8-*Dibenzanthracene*-4 : 5-*dicarboxylic acid* (VII). A solution of the crude acid (0·5 g.) in very dilute sodium hydroxide was boiled for ½ hour with animal charcoal, and the filtered solution evaporated to small bulk. The sodium salt, which crystallised on cooling, was recrystallised from hot water and then formed colourless pearly leaflets, which were dissolved in boiling water and the solution acidified. The gelatinous precipitate was collected, washed, and dried (0·12 g.), and recrystallised from boiling nitrobenzene (150 c.c.). The *dicarboxylic acid* (VII) formed pale yellow, hair-like, microscopic needles, m. p. above 365° (*Found : C, 78·2; H, 3·7. $C_{24}H_{14}O_4$ requires C, 78·7; H, 3·85%). Oxidation of this acid with sodium dichromate in acetic acid led to a product which gave a bright red vat with zinc dust and sodium hydroxide solution.

1 : 2 : 7 : 8-*Dibenzanthracene* (IV). The crude dicarboxylic acid (VII) (0·5 g.) was sublimed at 340—350°/3—4 mm., and the sublim-

ate (0·2 g.) extracted with benzene (there remained undissolved 0·05 g. of material which was mostly soluble in dilute aqueous ammonia). The benzene extract was treated with picric acid (0·15 g.), and the resulting picrate recrystallised from benzene. It formed long crimson needles, m. p. 209—210°, alone or mixed with a sample of 1 : 2 : 7 : 8-dibenzanthracene picrate prepared as described under Method I. The hydrocarbon regenerated from the picrate was identical with the 1 : 2 : 7 : 8-dibenzanthracene formed by the first method. When the pure acid was employed, it was largely charred at the higher temperature (400—420°) required for decarboxylation.

1 : 2 : 7 : 8-*Dibenzanthraquinone* (XI).—The hydrocarbon (0·1 g.) was oxidised by sodium dichromate (0·2 g.) in boiling glacial acetic acid (10 c.c.) for ¾ hour. The compound which crystallised on cooling was recrystallised from benzene; it then melted at 224—225° after sintering. For purification, the substance was boiled with zinc dust and dilute sodium hydroxide solution, and the bright red filtered solution oxidised by atmospheric oxygen. The precipitate was collected, sublimed at 200—230°/4 mm., and the sublimate recrystallised from glacial acetic acid (*Found : C, 85·7; H, 4·0. $C_{22}H_{12}O_2$ requires C, 85·7; H, 3·9%). 1 : 2 : 7 : 8-*Dibenzanthraquinone* (XI) formed deep orange, silky needles, m. p. 225—226°.

Derivatives of 1′ : 3′-*Naphtha*-3 : 4-*pyrene.*

α-o-*Hydroxybenzylidene*-10-*carboxy*-2-*phenanthrylacetic Acid* (VIII).—The crude hydroxy-acid, formed as a product of the Pschorr reaction (p. 1482), was recrystallised twice from acetic acid; it then formed a cream-coloured crystalline powder, m. p. 326—327°, free from nitrogen (Found : C, 75·3; H, 4·2. $C_{24}H_{16}O_5$ requires C, 75·0; H, 4·2%).

When a warm alkaline solution of this hydroxy-acid was shaken with methyl sulphate, some methylation occurred, but the reaction was incomplete and the product contained unchanged hydroxy-acid.

1′ : 3′-*Naphtha*-3 : 4-*pyren*-5-*one*-10-*carboxylic Acid* (IX).—The aforesaid hydroxy-acid (VIII) (0·3 g.) was sublimed at 330—350°/3—4 mm. The yellow sublimate was washed with boiling xylene and recrystallised from nitrobenzene (*Found : C, 82·3; H, 3·5. $C_{24}H_{12}O_3$ requires C, 82·7; H, 3·5%). This *carboxylic acid* formed very sparingly soluble, canary-yellow, microscopic needles, giving a yellow solution in boiling, very dilute sodium carbonate solution and a red solution in concentrated sulphuric acid. The m. p. varied from 360° to 380°, depending upon the rate of heating.

Methyl 1′ : 3′-*Naphtha*-3 : 4-*pyren*-5-*one*-10-*carboxylate.*—A solution of the hydroxy-acid (VIII) (0·55 g.) in *N*-sodium hydroxide

(5 c.c.) was evaporated to dryness on the water-bath. The powdered residue was suspended in methyl sulphate (3 c.c.), heated (oil-bath at 120—140°) for ½ hour, and cooled, alcohol added, and the yellow solid collected, washed with alcohol, and extracted with boiling water. The insoluble residue (0·48 g.) was recrystallised three times from nitrobenzene and washed with boiling benzene; it then formed canary-yellow microscopic needles, m. p. 253—254° (*Found: C, 82·5; H, 4·0; *M*, cryoscopic in camphor, 417, 400. $C_{25}H_{14}O_3$ requires C, 82·85; H, 3·9%; *M*, 362).

This *methyl* ester was hydrolysed by boiling for an hour with alcohol (50 c.c.) and potassium hydroxide (2 g.). A large volume of water was added, and the alcohol removed by distillation. Acidification of the clear orange-yellow boiling solution gave a gelatinous precipitate, which was recrystallised from nitrobenzene and shown by direct comparison to be identical with the naphthapyrenonecarboxylic acid (IX) formed by pyrolysis of the hydroxy-acid.

1′:3′-*Naphtha*-3:4-*pyrene*-5:9:10-*trione* (X).—A suspension of the yellow monocarboxylic acid (IX) (0·05 g.) in acetic acid (20 c.c.) was boiled for 12 hours, sodium dichromate (0·4 g. in all) being added in portions during the first 6 hours. The yellow solid in suspension was gradually replaced by rosettes of bright red needles, which were recrystallised from nitrobenzene. The *trione*, m. p. above 365°, was not obtained quite pure, on account of the insoluble nature of these compounds, but the analytical figures clearly showed that oxidation to the quinone was accompanied by decarboxylation (*Found: C, 81·7; H, 3·1. $C_{23}H_{10}O_3$ requires C, 82·6; H, 3·0%).

1′:3′-*Naphtha*-3:4-*pyren*-5-*one*.—The hydroxy-acid (VIII) (0·1 g.) was heated in a metal-bath at 420° for 10 minutes, by which time gas evolution had ceased. The residue was sublimed at 300—320°/3 mm., and the sublimate recrystallised from xylene. The *naphthapyrenone* formed soft canary-yellow needles, m. p. 268—269°, and gave a pale green solution, with a strong red fluorescence, in concentrated sulphuric acid (*Found: C, 90·8; H, 4·0. $C_{23}H_{12}O$ requires C, 90·8; H, 4·0%).

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