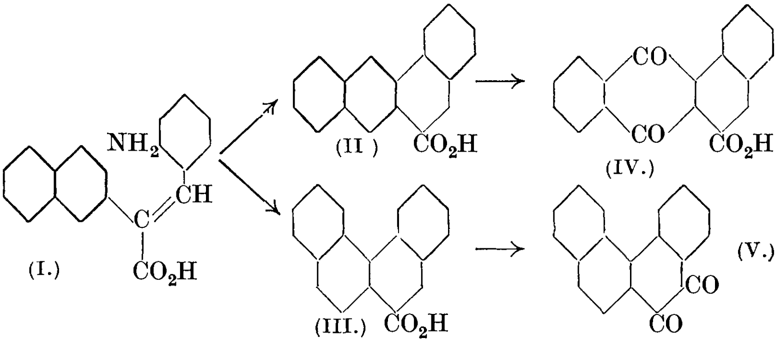
CCCL.—*Polycyclic Aromatic Hydrocarbons. Part VI. 3 : 4-Benzphenanthrene and its Quinone.*

By James Wilfred Cook.

The Pschorr phenanthrene synthesis with α-(2-naphthyl)-*o*-aminocinnamic acid (I) may lead to 1 : 2-*benz*-4-*anthroic acid* (II) or 3 : 4-*benz*-1-*phenanthroic acid* (III). The reaction was first investigated by Weitzenbock and Lieb (*Monatsh.*, 1912, **33**, 564), who isolated a crude acid which, when sublimed in a vacuum, gave an acid, m. p. 243°, and when sublimed at atmospheric pressure gave a hydrocarbon, m. p. 158—160°. The same hydrocarbon was later obtained by Mayer and Oppenheimer (*Ber.*, 1918, **51**, 510), but their acid melted at 218°. These authors all assumed that their hydrocarbon was 3 : 4-benzphenanthrene (Mayer and Oppenheimer prepared its picrate, m. p. 140—141°), since Elbs (*Ber.*, 1886, **19**, 2211) had already described 1 : 2-benzanthracene as melting at 140° and giving a picrate, m. p. 133°. More recently, however, Barnett and Matthews (*Chem. News*, 1925, **130**, 339) and Dziewonski and Ritt (*Bull. Acad. Polonaise, A*, 1927, 186) prepared pure 1 : 2-benzanthracene, m. p. 158—159°, so that the opinion was expressed (Cook, J., 1930, 1090) that the hydrocarbon of Weitzenböck and Lieb was really 1 : 2-benzanthracene. Re-examination of the reaction has shown this to be correct.

By purification of the product of the Pschorr reaction there was obtained the acid, m. p. 218°, which Mayer and Oppenheimer described. This was not benzphenanthroic acid (III) as they supposed, but was a mixture of this compound with benzanthroic acid (II). It was separated into its constituents by fractional crystallisation of the sodium and potassium salts. The former acid (III) had m. p. 240—241° and was evidently the acid which Weitzenbock and Lieb obtained fortuitously. The constitution of the two acids was shown by oxidation with chromic acid, (II) being converted into 1 : 2-*benzanthraquinone*-4-*carboxylic acid* (IV), which passed into 1 : 2-benzanthraquinone when heated, whereas (III) was largely decarboxylated and oxidised to 3 : 4-*benz*-9 : 10-*phenanthraquinone* (V). This *o*-quinone reacted readily with *o*-phenylenediamine to form 1 : 2-*benz*-3 : 4-(1′ : 2′-*naphtha*)*phenazine*.



The crude mixture of acids (II and III) was partly decarboxylated by vacuum sublimation at 230°, but neither the purified mixture nor the pure benzphenanthroic acid could be decarboxylated to any appreciable extent, even by sublimation at 400° at atmospheric pressure. This observation suggested that the decomposition of the crude mixture was due to the catalytic action of an impurity, possibly a trace of copper from the Pschorr reaction, and led successfully to complete elimination of carbon dioxide from the benzphenanthroic acid by heating it in the presence of finely divided copper. The resulting 3 : 4-*benzphenanthrene* was characterised by its *picrate* and by oxidation to the aforementioned *o*-quinone.

All the other hydrocarbons composed of four condensed benzene rings are well-characterised compounds, and this final member of the group, in common with the others, is now being utilised in animal experiments, in the search for cancer-producing hydrocarbons of known chemical structure. In its low melting point (68°) and ready solubility 3 : 4-benzphenanthrene is in striking contrast to some of the other members of this group (naphthacene, m. p. 331°, and chrysene, m. p. 254°).

EXPERIMENTAL.

(Analyses marked with an asterisk are microanalyses by Dr. A. Schoeller.)

α-(2-Naphthyl)-*o*-aminocinnamic acid (I) was conveniently purified through its somewhat sparingly soluble potassium salt and was then recrystallised from aqueous alcohol. The purified amino-acid (40 g.) was diazotised and shaken with copper powder as described by Mayer and Oppenheimer (*loc. cit.*). After 30 hours the solution no longer gave a diazo-reaction, and the solid was collected, dried in a vacuum desiccator, and extracted with boiling benzene. The concentrated benzene extract deposited crystals (14 g.), red resinous by-products mostly remaining in the liquor. The solid was sublimed at 230—260°/4 mm., and the sublimate extracted with warm dilute aqueous ammonia. The insoluble residue (1·8 g.) was crystallised from alcohol and yielded 1 : 2-benzanthracene (0·4 g.), which, after recrystallisation from alcohol, formed colourless plates, m. p. 159—160°, alone or mixed with an authentic sample prepared by the method of Barnett and Matthews (*loc. cit.*). Oxidation with sodium dichromate in boiling acetic acid yielded pure 1 : 2-benzanthraquinone. The alcoholic liquors from the benzanthracene yielded no pure substance.

The precipitate obtained by acidifying the ammoniacal extract crystallised from acetic acid as a yellow powder, m. p. 218—220°, the m. p. being unaltered by further crystallisation (yield, 9 g.). The substance was dissolved in warm dilute sodium hydroxide solution. The crystals which separated on cooling were recrystallised from water until they formed colourless leaflets, a sample of which gave an acid melting sharply at 240°. This required two or more recrystallisations, depending on the concentration of the solution and the time of standing. 3 : 4-*Benz*-1-*phenanthroic acid* (III), precipitated from a solution of the sodium salt, and crystallised from acetic acid, formed very pale yellow, silky needles, m. p. 240—241°, unchanged by further crystallisation from methyl alcohol (Found : C, 83·7; H, 4·7. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%). Solutions of this acid had a violet fluorescence. The combined liquors from the crystallisation of the sodium salt were acidified, the precipitate was recrystallised from alcohol and then dissolved in dilute potassium hydroxide solution. The resulting potassium salt was twice recrystallised from a little hot water. The almost colourless, silky needles were decomposed with hydrochloric acid; the resulting 1 : 2-*benz*-4-*anthroic acid* (II) crystallised from acetic acid as yellow needles, m. p. 281—282° (*Found : C, 83·6; H, 4·6. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%). From 40 g. of α-(2-naphthyl)-*o*-aminocinnamic acid, prepared from 600 g. of 2-methylnaphthalene, there were obtained 2·25 g. of benzphenanthroic acid and 0·2 g. of benzanthroic acid.

1 : 2-*Benzanthraquinone*-4-*carboxylic Acid* (IV).—1 : 2-Benz-4-anthroic acid (1 part) was oxidised by boiling its solution in glacial acetic acid with sodium dichromate (2 parts) for ¾ hour. The product, which was completely soluble in hot dilute sodium carbonate solution, crystallised from alcohol in yellow-ochre needles, m. p. 292—293° (decomp.) (Found : C, 75·2; H, 3·5. $C_{19}H_{10}O_4$ requires C, 75·5; H, 3·3%). When 1 : 2-*benzanthraquinone*-4-*carboxylic acid* was sublimed at 360—380° in an atmosphere of carbon dioxide, it was largely decarboxylated. The sublimate, after treatment with ammonia to remove unchanged acid, was recrystallised from alcohol and shown to consist of 1 : 2-benzanthraquinone by direct comparison with an authentic sample.

3 : 4-*Benz*-9 : 10-*phenanthraquinone* (V).—3 : 4-Benz-1-phenanthroic acid (0·25 g.) was oxidised by boiling its solution in glacial acetic acid with sodium dichromate (0·5 g.) for ¾ hour. The product was extracted with very dilute sodium carbonate solution. Very little passed into solution, and the residue was dried and recrystallised from *cyclo*hexane (*Found : C, 83·5; H, 4·0. $C_{18}H_{10}O_2$ requires C, 83·7; H, 3·9%). 3 : 4-*Benz*-9 : 10-*phenanthraquinone* formed ruby-red needles, m. p. 187—188°, and was completely soluble in sodium bisulphite solution containing a little alcohol. The red quinone was reprecipitated when the clear yellow solution was boiled with mineral acid.

The same quinone was formed by oxidation of 3 : 4-benzphenanthrene (see below) with sodium dichromate in acetic acid.

1 : 2-*Benz*-3 : 4-(1′ : 2′-*naphtha*)*phenazine*.—A solution of 3 : 4-

benzphenanthraquinone (V; 0·07 g.) in glacial acetic acid (10 c.c.) was boiled for a few minutes with *o*-phenylenediamine (0·07 g.). On cooling, the *phenazine* separated as canary-yellow needles which, after recrystallisation from acetic acid, had m. p. 189—190° (*Found: N, 8·2. $C_{24}H_{14}N_2$ requires N, 8·5%).

3 : 4-*Benzphenanthrene.*—3 : 4-Benz-1-phenanthroic acid (III; 1 g.) was intimately mixed with copper powder (0·2 g.) prepared by the method of Gattermann, and the mixture heated at 400° in an atmosphere of carbon dioxide. Oily drops collected in the upper part of the sublimation tube. These became solid when well cooled and the product, which was completely insoluble in aqueous ammonia, was dissolved in a little hot alcohol. The cooled solution deposited a very small amount of a substance which crystallised in slender yellow needles, m. p. 230—231°. This gave no benzphenanthraquinone on oxidation and was not further examined. The alcoholic filtrate was treated with an alcoholic solution of picric acid (1 g.). The *picrate* which separated (0·9 g.) was recrystallised from alcohol and formed long vermilion needles, m. p. 126—127° (Found: C, 63·1; H, 4·1. $C_{18}H_{12},C_6H_3O_7N_3$ requires C, 63·0; H, 3·3%).

A benzene solution of this picrate was decomposed by shaking with dilute aqueous ammonia, the benzene removed on the water-bath, and the residual oil dissolved in a little alcohol. The cold solution slowly deposited 3 : 4-*benzphenanthrene* as colourless needles, m. p. 68° (Found: C, 94·4; H, 5·6. $C_{18}H_{12}$ requires C, 94·7; H, 5·3%). This hydrocarbon, unlike 1 : 2-benzanthracene, gave no colour with concentrated sulphuric acid.

1 : 2-*Benzanthracene Picrate.*—1 : 2-Benzanthracene (5 g.) was treated with picric acid (12·5 g.) in alcoholic solution, and the picrate twice recrystallised from benzene. It formed dark red needles, m. p. 141·5—142·5° (compare Mayer and Oppenheimer, *loc. cit.*), and contained one molecule of picric acid and not two molecules, as stated by Elbs (*loc. cit.*) (Found: C, 63·2; H, 3·9. Calc. for $C_{18}H_{12},C_6H_3O_7N_3$: C, 63·0; H, 3·3%).

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