225. *The Occurrence of Direct Hydroxylation and Self-condensation in the Action of Potassium Hydroxide on Three Isomeric Benzo-derivatives of* meso*Benzanthrone.*

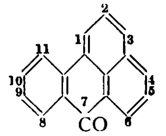
By William Bradley and F. K. Sutcliffe.

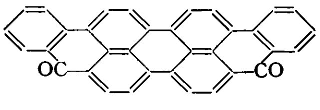
Three isomeric benzo-derivatives of *meso*benzanthrone have been prepared and their reactions with potassium hydroxide investigated. The 5 : 6-benzo-compound is characterised by the ease with which it affords a monohydroxy-derivative; at higher temperatures condensation to a derivative of violanthrone occurs. The 10 : 11-benzo-derivative undergoes self-condensation even at low temperatures, a derivative of *iso*violanthrone resulting. The 8 : 9-benzo-compound is the least reactive of the isomers; at high temperatures self-condensation to a derivative of violanthrone takes place, and a small proportion of hydroxylation occurs at the same time.

The relation between the hydroxylation and the self-condensation reactions is discussed.

*meso*Benzanthrone (I), heated with potassium hydroxide at 230—240°, affords a mixture of violanthrone (II) and *iso*violanthrone (III) (Bally, *Ber.*, 1905, **38**, 195; Scholl and Seer, *Annalen*, 1912, **394**, 126; Zincke, Linner, and Wolfbauer, *Ber.*, 1925, **58**, 323; Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 259), and many simple derivatives of *meso*benzanthrone exhibit a similar ability for self-condensation to colouring matters having the properties of quinones. Chloro*meso*benzanthrones (G.P. 188 193, 436 533), methyl*meso*benzanthrones (G.P. 188 193), and alkoxy*meso*benzanthrones (G.P. 413 738, 436 887, 442 511) all possess this property. The reaction depends on the presence in *meso*benzanthrone of a carbonyl group and a nucleus which readily transmits its chemical effects (Bradley and Jadhav, *J.*, 1948, 1622, 1746). 6-Hydroxy*meso*benzanthrone (IV) is stable towards fused alkalis (Bradley and Jadhav, *J.*, 1937, 1791), and this accords with the lower reactivity of the carbonyl group which results from conjugation with the hydroxyl substituent (Bradley and Sutcliffe, *J.*, 1951, 2118).

(I)





(II)

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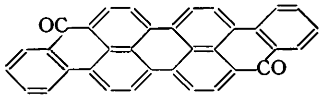

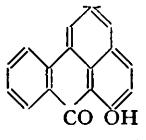

(IV)

In the present communication three ring-homologues of *meso*benzanthrone have been examined with the object of observing their ability to yield quinones of the violanthrone–*iso*violanthrone type. At the same time the compounds have been studied for their ability to undergo direct hydroxylation with alkalis as reported for *meso*benzanthrone by Perkin and Spencer (*J.*, 1922, **121**, 479) and by Bradley and Jadhav (*J.*, 1937, 1791).

The condensation of 1 : 2-benzanthraquinone with glycerol and sulphuric acid to form " benznaphthanthrone " was first described in G.P. 181 176. The constitution of the product was not then known. Scholl and Seer (*Annalen*, 1912, **394**, 111) prepared 8 : 9-benzo*meso*benzanthrone * (V) by the ring-closure of di-1-naphthyl ketone, and Cook (*J.*, 1939, 268) showed it to be identical with " benznaphthanthrone." In the present work the condensation of 1 : 2-benzanthraquinone with glycerol yielded two products separable by crystallisation. One was the expected 8 : 9-benzo*meso*benzanthrone, the other was a

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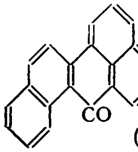
* This type of nomenclature is used for convenience in denoting the relations of isomers; Ring Index names are added in the Experimental section.

red isomeric ketone. This was considered to be 5 : 6-benzo*meso*benzanthrone (VI) for the reason that it differed from (V) and also from 10 : 11-benzo*meso*benzanthrone (VII). The 10 : 11-isomer was prepared by decarboxylating its 4′-carboxylic acid which results by partial cyclisation of 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid (Rule and Smith, *J.*, 1937, 1096).



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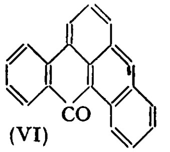

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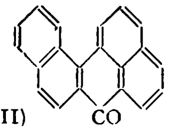
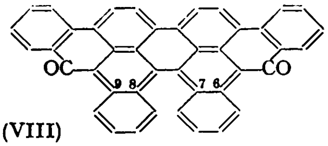


(VII)

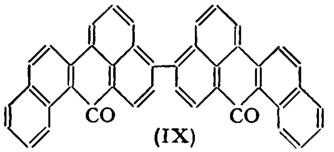
Heating with alcoholic potassium hydroxide at 110° transforms 5 : 6-benzo*meso*benzanthrone (VI) into a monohydroxy-derivative, an instance of unusually ready direct hydroxylation, which recalls the somewhat similar conversion of aceanthrenequinone into 1 : 9-oxalylanthr-10-one, amongst other products, by hot aqueous potassium hydroxide (Liebermann and Kardos, *Ber.*, 1914, **47**, 1203). The new product is considered to be the 4-hydroxy-derivative of (VI) since direct hydroxylation of *meso*benzanthrone yields a mixture of 4- and 6-hydroxy*meso*benzanthrones (Bradley and Jadhav, *J.*, 1937, 1791). Like 4-hydroxy*meso*benzanthrone, to which it is structurally analogous, 4-hydroxy-5 : 6-benzo*meso*benzanthrone affords a coloured and strongly fluorescent solution in aqueous alkali hydroxides.

The greater ease of hydroxylation of 5 : 6-benzo*meso*benzanthrone than of *meso*benzanthrone accords with the known greater reactivity of the *meso*-ring of anthracene than of with the nucleus of naphthalene.

Fused with potassium hydroxide at 220—230°, 5 : 6-benzo*meso*benzanthrone yields the 4-hydroxy-derivative and a green, neutral diketone, which dissolves in alkaline dithionite (hydrosulphite) forming a purple solution. The absorption spectrum of a solution of the diketone in concentrated sulphuric acid shows the same general features as that of violanthrone in the same solvent and differs entirely from that of *iso*violanthrone. For this reason, as well as by analogy with *meso*benzanthrone, which yields violanthrone with alkalis at 220—230°, the green diketone is considered to be 6 : 7-8 : 9-dibenzoviolanthrone (VIII).

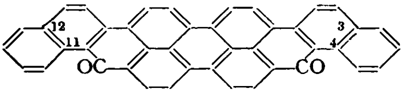


(VIII)



(IX)

The isomeric 8 : 9-benzo*meso*benzanthrone (V) behaves quite differently. There is little or no reaction at 110° with alcoholic potassium hydroxide. No hydroxylation occurs nor is there formed any di-(8 : 9-benzo*meso*benzanthron-4-yl) (IX), analogous in structure to the di*meso*benzanthron-4-yl which results easily from *meso*benzanthrone under similar conditions (Lüttringhaus and Neresheimer, *loc. cit.*). In G.P. 181 176 and 185 223 the formation of a blue diketone by the alkali fusion of " benznaphthanthrone " at 220—230° is described. 8 : 9-Benzo*meso*benzanthrone would be expected to show the same behaviour as *meso*benzanthrone, and for this reason the blue diketone should be 3 : 4-11 : 12-dibenzoviolanthrone (X). On alkali fusion of 8 : 9-benzo*meso*benzanthrone at 220° reaction



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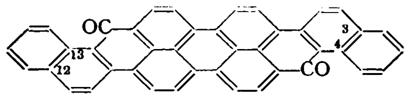
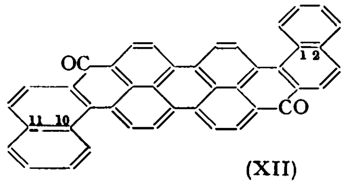


(XI)

occurred with particular ease, giving a blue colouring matter and a very small amount of a phenol which, like 4-hydroxy*meso*benzanthrone, dissolved in alkali hydroxides with a reddish-brown colour and a green fluorescence. The blue colouring matter, after purification, gave a blue solution in concentrated sulphuric acid. This showed the light absorption characteristic of violanthrone, but there was a slight increase in the red absorption similar to that found with *iso*violanthrone but not with violanthrone, which suggested the presence of a small proportion of 3 : 4-12 : 13-dibenzo*iso*violanthrone (XI).

10 : 11-Benzo*meso*benzanthrone differs from both 5 : 6- and 8 : 9-benzo*meso*benzanthrones in its reaction with alkalis. Already at 110° it is transformed by alcoholic potassium hydroxide into a blue quinonoid diketone. A solution of the product in concentrated sulphuric acid shows a typical *iso*violanthrone absorption. For this reason it is considered to be 1 : 2-10 : 11-dibenz*iso*violanthrone (XII).

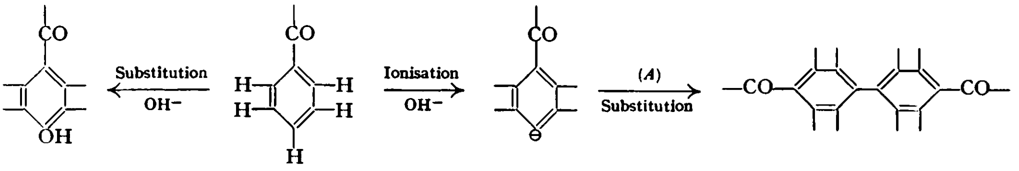


(XII)

The *trans*-union of 10 : 11-benzo*meso*benzanthrone at 110° harmonises with the known behaviour of *meso*benzanthrone, which yields violanthrone (*cis*) and *iso*violanthrone (*trans*) on alkali fusion, the proportion of *iso*violanthrone increasing the lower the reaction temperature (Lüttringhaus and Neresheimer, *loc. cit.*).

The action of alcoholic potassium hydroxide at 110° in causing the hydroxylation of 5 : 6-benzo*meso*benzanthrone and the self-coupling of 10 : 11-benzo*meso*benzanthrone affords a further illustration of the close connection between nuclear substitution by anions and the self-coupling reaction to which brief reference has already been made (Bradley and Jadhav, *J.*, 1948, 1623).

In general terms, an aromatic carbonyl compound (*A*) having the appropriate degree of nuclear reactivity may undergo either direct hydroxylation or ionisation in the presence of strong alkalis. The anion, if formed, may simulate the hydroxyl ion in forming a covalent link with carbon situated *ortho* or *para* to the carbonyl group.



(*A*)

The factors which determine the occurrence of the two reactions remain to be more fully investigated, but several points appear clear. Ketones which ionise with difficulty even in the presence of concentrated alkalis can undergo only hydroxylation. With the development of acid character the coupling reaction may occur. Finally, if the ketone is potentially a relatively strong acid, the derived anion may form a covalent link less readily and hydroxylation may become again the only important reaction. Self-condensation should occur more readily in the absence of competing hydroxyl ions. The formation of dipyridyls when pyridine is heated with sodium (Wibaut and Dingemanse, *Rec. Trav. chim.*, 1923, **42**, 240) may be a reaction of this kind, the essential intermediate being the pyridyl anion, and Brown and Hammick (*J.*, 1949, 173) have shown that the decarboxylation of quinaldic acid in quinoline yields 2 : 2′-diquinolyl, a reaction which they attribute to the intermediate formation of the 2-quinolyl anion and its subsequent union with quinoline.

EXPERIMENTAL

5 : 6- (VI) *and* 8 : 9-*Benzo*meso*benzanthrone* (V) (13-*Ketodibenzo*[b,mn]*phenanthrene and* 7-*Ketobenzo*[hi]*chrysene respectively*).—The crude product obtained by condensing 1 : 2-benzanthraquinone (50 g.), glycerol (50 g.), and aniline (70 g.) by the method of G.P. 181 176 was a black resin. It was extracted by means of acetone (500 c.c.). The extract was filtered hot. The orange-brown residue (18·5 g.; m. p. 137—142°), crystallised first from toluene and then from pyridine, gave two products. The less soluble 5 : 6-*benzo*meso*benzanthrone* (3·6 g.) was

obtained as long, red needles, m. p. 199·5—200·5° (Found : C, 90·0; H, 4·5. $C_{21}H_{12}O$ requires C, 90·0; H, 4·3%). The more soluble 8 : 9-benzo*meso*benzanthrone (3·25 g.) separated as short, yellow needles, m. p. 188—189° (Found : C, 89·5; H, 4·5%), and did not depress the m. p. of 8 : 9-benzo*meso*benzanthrone prepared from 1 : 1′-dinaphthyl ketone by Scholl and Seer's method (*loc. cit.*, p. 111). Whilst 8 : 9-benzo*meso*benzanthrone dissolves in concentrated sulphuric acid with a deep orange colour, 5 : 6-benzo*meso*benzanthrone affords a red solution with a slight bluish tinge. The former exhibits maxima at 5430 (E = 2·64) and 5820 Å (E = 4·14), the latter a maximum at 4950 Å (E = 3·34) (E = extinction coefficient for 0·002% solutions in " AnalaR " sulphuric acid contained in a cell of 2-cm. thickness).

No homogeneous material could be obtained from the acetone extract. Evaporation gave a brown solid, m. p. 120—180°, and this, repeatedly crystallised from glacial acetic acid, afforded material, m. p. 145—146°, unaltered by further crystallisation from the same solvent. A solution in benzene, passed through a column of alumina, afforded a small, dark, strongly adsorbed band containing impurities, but the main constituents formed a single, uniform, orange band.

10 : 11-*Benzo*meso*benzanthrone* (VII) (7-*Ketodibenz*[a,kl]*anthracene*).—10 : 11-*meso*Benzanthrone-4′-carboxylic acid (20 g. ; m. p. 280°) (Rule and Smith, *J.*, 1937, 1096) was heated under reflux during 7 hours with quinoline (50 c.c.) and copper bronze (1 g.). The cooled suspension was filtered and the dark filtrate added to alcohol (400 c.c.). After 2 days the small precipitate was collected and the mother-liquor was added to an excess of dilute hydrochloric acid ; a second precipitate formed. The combined precipitates were extracted with successive small volumes of 5% aqueous sodium carbonate (800 c.c. in all) until nothing more dissolved. The alkali extracts, united and acidified, yielded 9·5 g. of unchanged starting material, m. p. 278—280°. The alkali-insoluble material was extracted by means of glacial acetic acid. The extract was treated with charcoal, filtered, and concentrated ; crystals, m. p. 178—179°, slowly separated. Recrystallisation from glacial acetic acid gave the 10 : 11-*benzo*-derivative as brownish yellow needles, m. p. 181—182° (Found : C, 89·5; H, 4·3%). The solution in concentrated sulphuric acid was brownish-red, and at lower concentrations of the solute orange-yellow.

4-*Hydroxy*-5 : 6-*benzo*meso*benzanthrone* (8-*Hydroxy*-13-*ketodibenzo*[b,mn]*phenanthrene*).—To a solution containing potassium hydroxide (10 g.) and potassium acetate (1 g.) in ethanol (20 c.c.) was added 5 : 6-benzo*meso*benzanthrone (2 g.). The mixture was heated under reflux with stirring, the internal temperature being 110°. The reactants thickened, owing to the formation of a bulky solid, and became dark reddish-brown. After 1 hour, the product was cooled, and mixed with water (200 c.c.), and the resulting suspension heated and aërated on the water-bath. The insoluble material (1·5 g. ; mainly unchanged 5 : 6-benzo*meso*benzanthrone) was collected and washed with hot dilute sodium hydroxide solution and then with water. The combined alkaline solutions were pink, with a yellow fluorescence. Acidification afforded a precipitate ; this was collected, washed thoroughly with water, and dried. The product (0·4 g), heated for a few minutes with boiling acetic anhydride (25 c.c.) containing a few drops of pyridine, yielded 0·4 g. of fine, pale yellow needles, m. p. 280—281° (decomp.). This derivative was insoluble in cold aqueous sodium hydroxide, but when 0·3 g. was heated with a solution of sodium hydroxide (1·5 g.) in 50% aqueous alcohol (50 c.c.) it dissolved readily to form a pink solution with a yellow fluorescence. Acidification gave 4-*hydroxy*-5 : 6-*benzo*meso*benzanthrone* (0·2 g.) as orange-yellow needles, m. p. 324—326° (decomp.), unchanged by further crystallisation from nitrobenzene (Found : C, 84·4; H, 4·2. $C_{21}H_{12}O_2$ requires C, 85·1; H, 4·1%). It dissolved in concentrated sulphuric acid with a pink colour and a yellow-green fluorescence (maximum light absorption at 5400 Å; E = >5·0).

6 : 7-8 : 9-*Dibenzoviolanthrone*.—5 : 6-Benzo*meso*benzanthrone (2 g.) was added to a melt of potassium hydroxide (10 g.) and potassium acetate (1 g.) at 220—230°. The mixture rapidly became greenish-black. After 1 hour it was cooled and extracted with water (200 c.c.), and the resulting suspension was heated on the steam-bath and aërated ; finally it was filtered. The alkaline extract, acidified, yielded 0·2 g. of a light brown product which crystallised from nitrobenzene in needles, m. p. 318—320°, not depressed on admixture with 4-hydroxy-5 : 6-benzo*meso*benzanthrone, m. p. 324—326°. The alkali-insoluble material (1·7 g.) was stirred for 3 hours with a cold solution of sodium dithionite (4 g.) and sodium hydroxide (5 g.) in water (200 c.c.). A purple solution resulted and this was filtered from a residue of impure 5 : 6-benzo*meso*benzanthrone. The filtrate, aërated, afforded a greenish-black precipitate (1·3 g.) ; this was collected, washed, and dried. A portion of the product dissolved in trichlorobenzene was passed through an alumina column. The solute was strongly adsorbed but development with a large volume of trichlorobenzene afforded two adjacent bands ; the more strongly

adsorbed was blue-black, the more mobile red. The bands were separated and the colouring matters eluted by means of cresol at 100°. The red band afforded a small amount of 5 : 6-benzo*meso*benzanthrone. The blue-black band afforded a solution which when concentrated and then mixed with toluene yielded 6 : 7-8 : 9-*dibenzoviolanthrone* as a greenish-black powder (Found : C, 90·5; H, 4·1. $C_{42}H_{20}O_2$ requires C, 90·7; H, 3·6%). It dissolved in concentrated sulphuric acid forming a reddish-brown solution (maximum light absorption at 5250 Å; $E = 0{\cdot}98$). It afforded a purple solution in alkaline dithionite.

Action of Alkalis on 8 : 9-*Benzo*meso*benzanthrone and* 10 : 11-*Benzo*meso*benzanthrone.*—8 : 9-Benzo*meso*benzanthrone (1·0 g.), heated under reflux with a solution of potassium hydroxide (5 g.) and potassium acetate (0·5 g.) in ethanol (10 c.c.) at 110° (inner temp.), afforded mainly unchanged material, soluble in benzene, together with 0·05 g. of a violet-black, benzene-insoluble product which dissolved with a deep blue colour in alkaline dithionite containing pyridine. There was no evidence of hydroxylation.

Stirred at 220—230° for 15 minutes, 8 : 9-benzo*meso*benzanthrone (3 g.), potassium hydroxide (15 g.), and potassium acetate (1·5 g.) afforded a dark product most of which separated from the melt. This product consisted of a small quantity of a phenol, soluble in alkalis with a reddish-brown colour and a green fluorescence, and alkali-insoluble material (3 g.). The latter, extracted with boiling 1 : 2 : 4-trichlorobenzene (100 c.c.), afforded a residue (1·5 g.). All but 0·3 g. of this dissolved in hot cresol (200 c.c.), and 0·5 g. separated on cooling. Recrystallisation from quinoline yielded bluish-black 3 : 4-11 : 12-*dibenzoviolanthrone* (?), m. p. > 360° (Found : C, 89·0, 88·8; H, 3·7, 3·9. $C_{42}H_{20}O_2$ requires C, 90·7; H, 3·6%) which dissolved in concentrated sulphuric acid with a blue colour (light absorption maximum at *ca.* 4800 Å; $E = 1{\cdot}1$). It dissolved with a blue-green colour in alkaline dithionite containing pyridine.

10 : 11-Benzo*meso*benzanthrone (0·5 g.) was stirred under reflux with potassium hydroxide (2·5 g.), potassium acetate (0·25 g.), and 95% alcohol (5 c.c.) at 110° (inner temp.) for 2·5 hours. The product was added to water, and the insoluble solid (0·5 g.) collected. This was dried and extracted by boiling trichlorobenzene, and the residue was taken up in hot cresol. Addition of alcohol to the cresol solution precipitated 0·21 g. of a bluish-black 1 : 2-10 : 11-*dibenz*iso*violanthrone* (?) which dissolved in concentrated sulphuric acid with a green colour [light absorption maxima at 6540 ($E = 3{\cdot}1$) and 7250 Å ($E = 1{\cdot}8$)], m. p. > 360° (Found : C, 87·4, 87·1; H, 4·9, 3·1. $C_{42}H_{20}O_2$ requires C, 90·7; H, 3·6%). It dissolved with a blue colour and a red fluorescence in sodium hydroxide solution containing sodium dithionite.

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CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

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