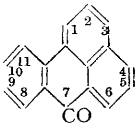
330. *Kationoid Reactivity of Aromatic Compounds. Part VII. The Composition of the Di*meso*benzanthronyl formed by the Action of Alkaline Condensing Agents on* meso*Benzanthrone.*

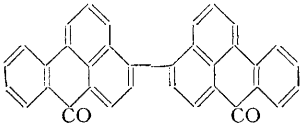
By W. Bradley and G. V. Jadhav.

The action of alcoholic potassium hydroxide or sodium anilide on *meso*benzanthrone yields 4 : 4′-di*meso*benzanthronyl with less than 2·5% of 6 : 6′-*di*meso*benzanthronyl*. The preparation of the latter from 4-hydroxy*meso*benzanthrone is described. Neither 4-methyl- nor 4-*fluoro*-meso*benzanthrone* shows evidence of coupling to a di*meso*benzanthronyl through the 6-position on treatment with alkaline condensing agents. The mode of formation of 4 : 4′-di*meso*benzanthronyl from *meso*benzanthrone is discussed.

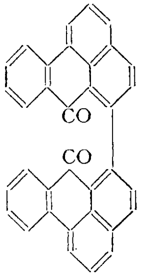
Although *meso*benzanthrone (I) reacts with sodamide–piperidine to form 4-piperidino*meso*benzanthrone (Bradley, *J.*, 1937, **1091**) and with alkyl- or aryl-magnesium iodides to yield 6-alkyl(or aryl)*meso*benzanthrones (Allen and Overbaugh, *J. Amer. Chem. Soc.*, 1935, **57**, 740; Charrier and Ghigi, *Ber.*, 1936, **69**, 2211), yet fused potassium hydroxide in the presence of an oxidant yields both 4- and 6-hydroxy*meso*benzanthrones (Bradley and Jadhav, *J.*, 1937, 1791). Following Badische, B.P. 203,533, Lüttringhaus and Neresheimer (*Annalen*, 1929, **473**, 259) showed that alcoholic potassium hydroxide or sodium anilide transforms *meso*benzanthrone into 4 : 4′-di*meso*benzanthronyl (II) but no reference was made to the possible occurrence of an isomer of (II) in the crude product. The present experiments were carried out to ascertain whether 6 : 6′-*di*meso*benzanthronyl* (III) is also present. 6-Hydroxy*meso*benzanthrone, prepared by the action of aluminium chloride on 1-benzoyl-2-naphthol, was heated with aqueous ammonia to give 6-amino*meso*benzanthrone. From this was obtained 6-chloro-, 6-*bromo*- and 6-*iodo*-meso*benzanthrone* by the Sandmeyer reactions. 6 : 6′-Di*meso*benzanthronyl was prepared by heating 6-chloro*meso*benzanthrone with copper powder. 6 : 6′-Di*meso*benzanthronyl gives a green coloration with acetone in the presence of solid potassium hydroxide. Under the same conditions both *meso*benzanthrone and 4 : 4′-di*meso*benzanthronyl give violet colours, and the difference could have been used to detect the presence of the 6 : 6′- in the 4 : 4′-isomer had not the rate of development of the green colour been retarded and masked by 4 : 4′-di*meso* benzanthronyl. 6 : 6′-Di*meso*benzanthronyl is easily oxidised by means of chromium trioxide and the resulting 1 : 1′-dianthraquinonyl-4 : 4′-dicarboxylic acid gives a green colour with copper and sulphuric acid, doubtless because of the formation of meso*benzodianthrone*-6 : 6′-*dicarboxylic acid* (IV).



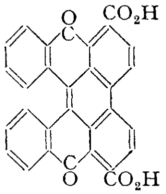
(I.)



(II.)



(III.)

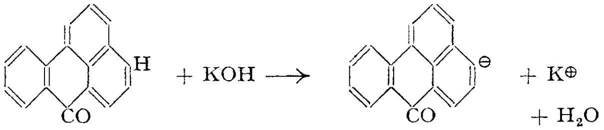


(IV.)

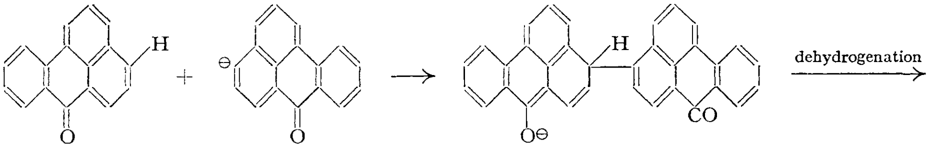
4 : 4′-Di*meso*benzanthronyl, oxidised similarly, affords 2 : 2′-dianthraquinonyl-1 : 1′-dicarboxylic acid. This does not give any green colour when treated with copper and sulphuric acid, a

reaction which is characteristic of 1 : 1′-dianthraquinonyls (Scholl and Mansfield, *Ber.*, 1910, **43**, 1734). In control experiments it was found that mixtures of 4 : 4′- and 6 : 6′-di*meso*benzanthronyls containing at least 2·5% of the latter, when oxidised and the resulting acids treated with copper and sulphuric acid, gave a green coloration. An identical result was obtained when a portion of the 4 : 4′-isomer was replaced by *meso*benzanthrone. The test was negative when applied to the acids obtained by oxidising the crude di*meso*benzanthronyl prepared from *meso*benzanthrone and either alcoholic potassium hydroxide or sodium anilide, an indication that crude di*meso*benzanthronyl does not contain more than 2·5% of the 6 : 6′-isomer.

Mode of Formation of 4 : 4′-*Di*meso*benzanthronyl.*—The conversion of *meso*benzanthrone into 4 : 4′-di*meso*benzanthronyl by means of an alkaline condensing agent suggests that a typical substitution into *meso*benzanthrone is involved, the substituting agent being an anion, and the point of substitution a carbon atom situated *para* to the carbonyl group (cf. Part VI, this vol., p. 1175). The constitution of the product indicates that the anion is derived from *meso*benzanthrone by loss of a proton;



and the formation of 4 : 4′-di*meso*benzanthronyl can be represented as follows :



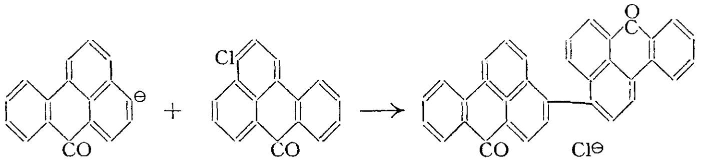
(II)

The dissociation of hydrogen as proton from its attachment to carbon is familiar in such examples as acetylene, indene, fluorene, and hydrogen cyanide, and the process is facilitated by the attachment to carbon of electron-seeking groups (phenylnitromethane, dibenzenesulphonylmethane).

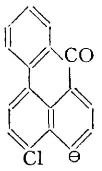
Although the self-coupling of *meso*benzanthrone is the best known example of its type, several other carbonyl compounds yield analogous products when they are heated with alkalis. 1 : 9-Pyrazoleanthrone yields pyrazoleanthrone-yellow, the 1 : 9-pyrazoleanthrone analogue of 4 : 4′-di*meso*benzanthronyl (*Chem.-Ztg.*, Fortschrittsberichte, 1929, p. 56), 5(*N*) : 6-pyridino*meso*benzanthrone yields cyananthrone (Bally, *Ber.*, 1905, **38**, 196), and anthracene-1 : 9-dicarboxyimide yields aceanthrene-green (Kardos, *Ber.*, 1913, **46**, 2086; Houben, "Das Anthracen und die Anthrachinone", p. 771, Leipzig, 1929). It is very probable that these reactions, too, involve the same principle as the formation of 4 : 4′-di*meso*benzanthronyl from *meso*benzanthrone.

The occurrence of an anion derived from *meso*benzanthrone by loss of a proton provides a means of explaining a number of reactions related to the self-condensation of *meso*benzanthrone. Lüttringhaus and Neresheimer found that replacing a hydrogen in the 9-position of *meso*benzanthrone did not inhibit the formation of a 9 : 9′-disubstituted 4 : 4′-di*meso*benzanthronyl, and further that (following Scottish Dyes, B.P. 251,313) the previous linking of two *meso*benzanthrone molecules through the 3-positions did not inhibit the subsequent union through the 4-positions also, to give violanthrone, by the action of alkaline condensing agents.

The anion of *meso*benzanthrone replaces chlorine attached to the 4- and the 3-position of *meso*benzanthrone more easily than it substitutes into the nucleus. Even at — 5° an equimolecular mixture of *meso*benzanthrone and 3-chloro*meso*benzanthrone forms 3 : 4′-di*meso*benzanthronyl (V) in the presence of sodium anilide. This reaction may be represented as follows :



(V.)

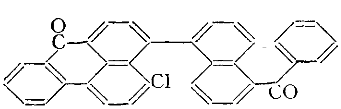


(VI.)

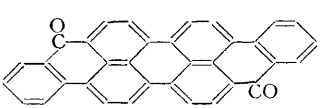
When the halogen compound is 4-chloro*meso*benzanthrone the product is analogously 4 : 4′-di*meso*benzanthronyl. The action of alcoholic potassium hydroxide on 3-chloro*meso*benzanthrone yields *iso*violanthrone (VIII). In this reaction 3-chloro-3′ : 4-di*meso*benzanthonyl (VII) is an intermediate product.

In this reaction it is apparent that 3-chloro*meso*benzanthrone yields the anion (VI) which is able to replace chlorine in another molecule of 3-chloro*meso*benzanthrone giving (VII). Repetition of the processes of proton liberation and halogen replacement then leads to *iso*violanthrone (VIII).

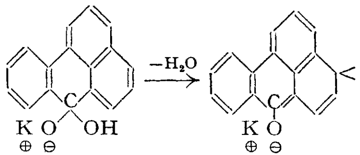
Similarly *meso*benzanthrone reacts with 3-fluoro*meso*benzanthrone in the presence of sodium anilide to form 3 : 4′-di*meso*benzanthronyl (V).



(VII.)



(VIII.)



(IX.) (X.)

In an earlier theory of the formation of 4 : 4′-di*meso*benzanthronyl and violanthrone from *meso*benzanthrone (Schwenk, *Chem.-Ztg.*, 1928, **52**, 62) it was suggested that the action of alkali hydroxides on *meso*benzanthrone was first to form the adduct (IX) which lost water to give the ion-radical (X) and finally 4 : 4′-di*meso*benzanthronyl by polymerisation and oxidation. This view of the course of the reaction is intrinsically improbable, and it does not accommodate the analogous reactions of *meso*benzanthrone with halogenated *meso*benzanthrones in which the halogen is eliminated as an anion.

EXPERIMENTAL.

6-*Hydroxy*meso*benzanthrone.*—An intimate mixture of 1-benzoyl-2-naphthol (10 g.) and anhydrous aluminium chloride (25 g.) was added in small successive portions during 45 minutes to a beaker maintained at 140—150°. The melt was stirred throughout. The cooled product was extracted with boiling concentrated hydrochloric acid, then with water and finally with hot glacial acetic acid. It crystallised from the last (charcoal) in the form of yellow needles, m. p. 177—178°.

6-*Amino*meso*benzanthrone.*—A suspension of 6-hydroxy*meso*benzanthrone (8 g.) in aqueous ammonia (*d* 0·88; 160 c.c.) was heated for six hours at 210—220° (inner temperature) in an oil-jacketed autoclave. On cooling, water was added and the undissolved material collected. Crystallisation from alcohol gave golden-yellow prisms of 6-amino*meso*benzanthrone, m. p. 186—187° (Found : C, 82·9; H, 4·4; N, 5·6. Calc. for $C_{17}H_{11}ON$: C, 83·2; H, 4·5; N, 5·7%) (yield, 6 g.), identical with the amino*meso*benzanthrone obtained by reaction of *meso*benzanthrone with sodamide in the presence of oxygen (Part VI, *loc. cit.*).

6-*Acetamido*meso*benzanthrone*, obtained by boiling 1 g. of 6-amino*meso*benzanthrone with 5 c.c. of acetic anhydride for an hour, crystallised from glacial acetic acid in brownish-yellow needles, m. p. 224—225° (Found : C, 79·5; H, 4·6; N, 5·1. $C_{19}H_{13}O_2N$ requires C, 79·4; H, 4·6; N, 4·9%).

6-*Benzamido*meso*benzanthrone*, prepared from 1 g. of 6-amino*meso*benzanthrone and 2 g. of benzoyl chloride by boiling the reactants for 30 minutes in pyridine solution, crystallised from glacial acetic acid in brownish-yellow needles, m. p. 204—205° (Found : C, 82·5; H, 4·4; N, 4·1. $C_{24}H_{15}O_2N$ requires C, 82·5; H, 4·3; N, 4·0%).

6-*Chloro*meso*benzanthrone.*—A solution of 6-amino*meso*benzanthrone (15 g.) in concentrated sulphuric acid (55 c.c.) was added gradually to a stirred solution of sodium nitrite (6 g.) in concentrated sulphuric acid (40 c.c.), the temperature being kept below 10°. Stirring was continued for an hour after the addition of the 6-amino*meso*benzanthrone was complete and then the product was poured over crushed ice. A brick-red solid separated. This was collected and washed with water. It was much more soluble in water than in dilute sulphuric acid. The red solid, made into a paste with 75 c.c. of concentrated hydrochloric acid, was added to a well-stirred solution prepared by dissolving 15 g. of cuprous chloride in 225 c.c. of 12% hydrochloric acid. Stirring was continued at room temperature until evolution of nitrogen ceased. The yellow undissolved solid was collected, washed, and crystallised from hot glacial acetic acid. Recrystallisation from alcohol gave yellow granules, m. p. 146—147° (Found : C, 77·1; H, 3·6; Cl, 13·3. Calc. for $C_{17}H_9OCl$: C, 77·1; H, 3·4; Cl, 13·4%). A product, m. p. 152°, considered to be 6-chloro*meso*benzanthrone was described by I.G. in B.P. 301,197 (1927).

The product (2 g.) obtained by the present preparation was oxidised by adding gradually a solution of 4·5 g. of chromium trioxide in 10 c.c. of 50% acetic acid. Carbon dioxide was evolved freely, and when the reaction was complete, water was added and the separated solid collected. After being washed, dissolved in dilute aqueous ammonia, and reprecipitated by addition of acid, it was crystallised from glacial acetic acid. The product, 4-chloroanthraquinone-1-carboxylic acid, melted at 229—230° (Found : C, 62·5; H, 2·5; Cl, 12·1. Calc. for $C_{15}H_7O_4Cl$: C, 62·8; H, 2·5; Cl, 12·4%). [Ullmann, D.R.-P. 243,788, Frdl., **10**, 598 (1909), records m. p. 229°; Heller and Shülke, *Ber.*, 1908, **41**, 3636, give m. p. 228—229°; Ullmann and Miriajeff, *Annalen*, 1912, **388**, 217, m. p. 229°; Stanley and Adams, *J. Amer. Chem. Soc.*, 1931, **53**, 2364, m. p. 220—224°; Heilbron, Heslop, and Irving, *J.*, 1936, 781, m. p. 231—232°.]

6-*Bromo*meso*benzanthrone.*—A solution of 6-amino*meso*benzanthrone (2·5 g.) in concentrated sulphuric acid (15 c.c.) was added at 5—10° to a solution of sodium nitrite (1 g.) in concentrated sulphuric acid (18 c.c.). The mixture was stirred for an hour and then poured on crushed ice. The precipitated diazonium sulphate was collected, washed with a small volume of water, then made into a paste with water and added to a solution of cuprous bromide which had been prepared as follows: Copper powder (1 g.) and sodium bromide (8 g.) were added to a solution of copper sulphate (5 g.) in water (40 c.c.), and the suspension boiled until the solution was colourless. The suspension of the diazonium sulphate in the cuprous bromide solution was stirred at the room temperature until evolution of nitrogen ceased. The almost black solid product was collected, washed with water, dried, and then extracted by means of glacial acetic acid. The filtered extracts were combined, concentrated, and finally mixed with water. The *bromo*-compound separated as a yellow solid which crystallised from alcohol in needles, m. p. 144—145° (Found: C, 66·1; H, 2·9; Br, 25·6. $C_{17}H_9OBr$ requires C, 66·0; H, 2·9; Br, 25·9%).

4-*Bromoanthraquinone*-1-*carboxylic Acid*.—A solution of chromium trioxide (3 g.) in 50% acetic acid (8 c.c.) was added slowly to a hot solution of 6-bromo*meso*benzanthrone (1·5 g.) in glacial acetic acid (15 c.c.). Carbon dioxide was evolved and after the vigorous reaction had moderated the solution was boiled for three hours and then added to water. The solid which separated was collected, washed with water, and extracted by means of hot dilute ammonia. The filtered, reddish-yellow ammoniacal solution gave a yellowish solid when acidified, and this, after several recrystallisations from glacial acetic acid, had m. p. 250—251° (Found: C, 54·8; H, 2·3; Br, 24·4. $C_{15}H_7O_4Br$ requires C, 54·4; H, 2·1; Br, 24·1%).

6-*Iodo*meso*benzanthrone*.—The diazonium sulphate from 5 g. of 6-amino*meso*benzanthrone was made into a paste with water and stirred with a solution of 30 g. of sodium iodide in 200 c.c. of water. Nitrogen was evolved. The black *iodo*-compound, washed, dried, and crystallised several times from methanol, afforded small yellow needles that sintered at 125° and melted completely at 133° (Found: C, 57·3; H, 2·6; I, 35·3. $C_{17}H_9OI$ requires C, 57·3; H, 2·5; I, 35·7%).

6-N-*Methylanilino*meso*benzanthrone*, prepared by heating 6-chloro*meso*benzanthrone with an excess of monomethylaniline at the boiling point for four hours, crystallised from alcohol in yellow needles, m. p. 155—156° (Found: C, 86·1; H, 4·8; N, 4·6. $C_{24}H_{17}ON$ requires C, 86·0; H, 5·1; N, 4·2%).

6 : 6′-*Di*meso*benzanthronyl*.—A solution of 6-chloro*meso*benzanthrone (10 g.) in nitrobenzene (70 c.c.) was heated under reflux with copper dust (10 g.). The reaction proceeded smoothly for two hours but at this stage the separating solid caused bumping. After two hours longer an additional quantity of nitrobenzene (20 c.c.) was added, the suspension filtered, and the residue extracted with more nitrobenzene. On cooling, a yellow solid separated from the nitrobenzene solutions. It was insoluble in the common organic solvents. It did not melt below 355°. It was purified by extracting it with a large volume of acetone and then repeatedly crystallising the insoluble part from nitrobenzene. In this way it was obtained in the form of silky yellow needles, m. p. > 360° (Found: C, 88·3; H, 4·4. $C_{34}H_{18}O_2$ requires C, 89·1; H, 4·0%). 6 : 6′-*Di*meso*benzanthronyl* dissolved in concentrated sulphuric acid with a red colour. It was unaffected by stirring with aluminium powder and concentrated sulphuric acid at 30—40°, by warming with sodium amalgam and pyridine containing a small proportion of water, or by heating with amalgamated zinc and concentrated hydrochloric acid.

Reaction of 6 : 6′-*Di*meso*benzanthronyl with Sodium and Amyl Alcohol*.—Sodium (6 g.) was added to a boiling suspension of 6 : 6′-di*meso*benzanthronyl (2 g.) in amyl alcohol (60 c.c.). The colour changed from yellow to green. Soon after all of the metal had reacted, the colour began to change to reddish-brown. At this stage the product was cooled, mixed with water, and acidified with hydrochloric acid. The amyl alcohol was removed by steam-distillation, leaving a brown oil which solidified. The solid was collected, washed, and dried. It was soluble in alcohol, ether, benzene, or chloroform, but it could not be crystallised. It was precipitated from benzene solution on adding light petroleum, and several repetitions of this process gave a solid which melted in the range 205—220° (Found: C, 83·5; H, 6·0. $C_{44}H_{42}O_4$ requires C, 83·2; H, 6·7%).

Reaction of 6 : 6′-*Di*meso*benzanthronyl with Compounds containing Reactive Methylene Groups*.—A 0·1% solution of 6 : 6′-di*meso*benzanthronyl in pyridine (5 c.c.) with acetone (1 g.) and 1 g. of solid potassium hydroxide in the form of pellets changed in colour from yellow to green in the course of a few minutes. After two hours the solution acquired a violet tinge. No colour change was observed when the following compounds were used in the place of acetone; methyl ethyl ketone, diethyl ketone, acetophenone, propiophenone, butyrophenone, *cyclo*hexanone, diethyl malonate, ethyl acetoacetate, acetonitrile, propionitrile, benzyl cyanide, ethyl cyanoacetate. *meso*Benzanthrone gave a reddish colour becoming violet with acetone, and greenish, slowly fading, with acetophenone. 4 : 4′-Di*meso*benzanthronyl gave a green colour with acetophenone and a reddish colour changing to violet with acetone. The green colour produced by the interaction of 6 : 6′-di*meso*benzanthronyl and acetone does not appear so quickly if a small proportion of 4 : 4′-di*meso*benzanthronyl is present, and the green colour is soon masked by the violet colour due to the 4 : 4′-isomer.

1 : 1′-*Dianthraquinonyl*-4 : 4′-*dicarboxylic Acid*.—To a warm suspension of 6 : 6′-di*meso*benzanthonyl (1 g.) in glacial acetic acid (20 c.c.) was added gradually to a solution of chromium trioxide (2·5 g.) in 50% acetic acid (5 c.c.). Carbon dioxide was liberated vigorously, and when the initial reaction had ceased the product was boiled for five hours, then mixed with water and again heated to boiling. The solid which separated was collected, washed, and extracted by means of hot dilute sodium hydroxide solution The filtered alkaline solution gave a yellow precipitate when acidified. The precipitated acid was almost insoluble in the common solvents. After drying it dissolved sparingly in pyridine and from the solution the *monopyridinium* salt crystallised in cream-coloured needles, m. p. above 360° (Found: C, 72·0; H, 3·5; N, 2·5. $C_{35}H_{19}O_8N$ requires C, 72·3; H, 3·3; N, 2·4%). 1 : 1′-Dianthraquinonyl-4 : 4′-dicarboxylic acid was obtained by boiling this salt with dilute hydrochloric acid. It did not melt below 360° (Found: C, 71·9; H, 3·2. Calc. for $C_{30}H_{14}O_8$: C, 71·7; H, 2·8%).

meso*Benzodianthrone*-6 : 6′-*dicarboxylic Acid*.—Finely divided copper powder (1 g.) was stirred with a solution of 1 : 1′-dianthraquinonyl-4 : 4′-dicarboxylic acid (1 g.) in concentrated sulphuric acid (30 c.c.) at 50—60°. The mixture turned green, and after 20—25 minutes it was poured over crushed ice. A yellow solid separated. The suspension was heated to boiling, then filtered, and the washed residue extracted by means of dilute sodium hydroxide solution. The filtered extract gave a brown gelatinous precipitate when acidified. The suspension was boiled, and the precipitate collected, washed, and dried.

It crystallised from nitrobenzene in small brown needles, m. p. 325° (Found: C, 76·4; H, 3·1. $C_{30}H_{14}O_6$ requires C, 76·6; H, 3·0%). meso*Benzodianthrone*-6 : 6′-*dicarboxylic acid* dissolved with a green colour in alkaline hyposulphite (dithionite). When the solution was boiled it became yellowish-brown even in the presence of an excess of alkaline hyposulphite.

Detection of 6 : 6′-*D*i*meso*b*enzanthronyl in Mixtures with* meso*Benzanthrone and* 4 : 4′-*D*i*meso*-*benzanthronyl*.—The acid product obtained by oxidising *meso*benzanthrone, 4 : 4′-di*meso*benzanthronyl, or mixtures of these with chromium trioxide dissolved in concentrated sulphuric acid with a yellow colour which did not change in the presence of copper powder. The following mixture, *viz.*, *meso*-benzanthrone (40%), 4 : 4′-di*meso*benzanthronyl (50%), and 6 : 6′-di*meso*benzanthronyl (10%) yielded a mixture of acids which gave a green solution in concentrated sulphuric acid containing copper powder; so also did the mixtures in which the proportion of 6 : 6′-di*meso*benzanthronyl was not less than 2·5%.

Composition of the Crude Di*meso*b*enzanthronyl obtained by the Action of Basic Condensing Agents on* meso*Benzanthrone*.—The crude di*meso*benzanthronyl (1 g.) obtained from *meso*benzanthrone by the action of alcoholic potassium hydroxide (Lüttringhaus and Neresheimer, *loc. cit.*) was suspended in 20 c.c. of warm glacial acetic acid and treated gradually with chromium trioxide (2·5 g.) dissolved in 5 c.c. of 50% acetic acid. When the initial rapid evolution of carbon dioxide had ceased the solution was boiled for five hours. The acid products were isolated, dissolved in concentrated sulphuric acid, and stirred with copper powder. There was no change in the initial colour of the solution, indicating that the original crude di*meso*benzanthronyl contained less than 2·5% of 6 : 6′-di*meso*benzanthronyl.

A similar result was obtained using the crude di*meso*benzanthronyl prepared by the use of sodium anilide [I.G., D.R.-P. 407,838; Frdl., **14**, 892 (1922)].

Experiments with 4-*Substituted* meso*Benzanthrones*.—(1) 4-*Methyl*meso*benzanthrone*. Potassium hydroxide was dissolved in absolute alcohol and then the solution was evaporated until 15 g. of alcohol remained. The residual paste was stirred with 4-methyl*meso*benzanthrone (3 g.) at 100—105° for six hours, sufficient alcohol being added from time to time to keep the mass pasty. The product was isolated by adding water, heating to boiling, and filtering. The washed residue was dried, and 1 g. of it was mixed with glacial acetic acid (20 c.c.) and oxidised by means of chromium trioxide (3 g.) and 50% acetic acid (6 c.c.) at the boiling point for 5 hours. The acidic products were isolated and tested by means of concentrated sulphuric acid and copper. There was no development of a green colour.

(2) 4-*Fluoro*meso*benzanthrone*. The diazonium sulphate, prepared from 4-amino*meso*benzanthrone by dissolving 5 g. of the base in 20 c.c. of concentrated sulphuric acid and stirring with a solution of sodium nitrite (2 g.) in concentrated sulphuric acid (20 c.c.), was precipitated by adding it to water, collected, washed with a small volume of water, and then dissolved in the minimum volume of water. The solution was added to one of boric acid (5 g.) in 40% hydrofluoric acid (20 g.). The diazonium fluoborate separated in the form of an orange precipitate. After being stirred for 2 hours the precipitate was collected and washed. The first washings were almost colourless, later red, and finally almost colourless. The remaining solid was washed with alcohol then with ether and lastly dried in a vacuum. The product was heated slowly to 140—150° until evolution of gas ceased. The resulting black mass was extracted by means of boiling acetic acid. The extracts deposited coloured material on cooling, and this was removed by filtration. The clear filtrate, added to water, gave a yellow precipitate. The precipitate was collected, washed, dried, and sublimed under reduced pressure. Yellow needles, m. p. 186—187°, were obtained (Found: C, 82·2; H, 3·7. $C_{17}H_9OF$ requires C, 82·2; H, 3·7%).

To a paste prepared by dissolving 10 g. of potassium hydroxide in absolute alcohol and evaporating until 5 g. of the solvent remained, was added 1 g. of the above 4-*fluoro*meso*benzanthrone*. The mixture was stirred at 105—110° for 7 hours, small successive amounts of alcohol being added to keep the paste fluid. Water was then added, and the resulting suspension boiled and filtered (for residue, see below). The deep yellow filtrate showed a green fluorescence. Acidified with hydrochloric acid, it afforded a yellow gelatinous precipitate which, when collected, washed, and dried, had m. p. 300—304° (yield, 0·7 g.). It was identified as 4-hydroxy*meso*benxanthrone by treatment with acetic anhydride and sodium acetate to give 4-acetoxy*meso*benzanthrone, m. p. 195—198°, not depressed when mixed with an authentic sample.

The alkali-insoluble portion of the product of the above reaction was oxidised by suspending 0·3 g. in 7 c.c. of glacial acetic acid and adding 5 c.c. of a solution prepared by dissolving 1 g. of chromium trioxide in 8 c.c. of 50% acetic acid. The mixture was boiled for four hours, then added to water, the suspension boiled, and the solid collected and extracted by means of dilute sodium hydroxide solution. The filtered alkaline solution gave a reddish precipitate when acidified. This was collected, redissolved in dilute alkali, and recovered by acidifying the filtered solution. When the acid product was dissolved in concentrated sulphuric acid and copper powder added there was no development of a green colour.

The experiments described in the present paper were carried out in the Department of Applied Chemistry, College of Technology, Manchester. The authors are indebted to Prof. J. Kenner, F.R.S., for providing facilities for the work, and thank the University of Bombay for the award of a Sir Mangaldas Nathubai Scholarship, and I.C.I. (Dyestuffs) Ltd. for a grant and gifts of intermediates.

HIGHGATE, LONDON.
ISMAIL YUSUF COLLEGE, BOMBAY.

[*Received, November* 24*th*, 1947