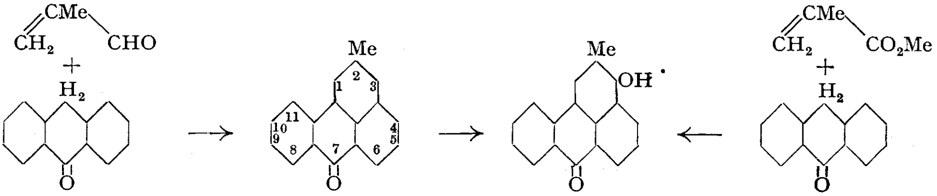
36. *2-Methyl*meso*benzanthrone and Some Derivatives.*

By D. H. Hey, R. J. Nicholls, and C. W. Pritchett.

Various methods for the preparation of α-methylacraldehyde are described and 2-methyl*meso*benzanthrone is prepared from this aldehyde or its acetal and anthrone. 2-Methyl*meso*benzanthrone is converted by standard methods into 16 : 17-dimethyldibenzanthrone and 6 : 15-dimethyl*iso*benzanthrone. 3-Hydroxy-2-methyl-*meso*benzanthrone is formed as a by-product in the conversion of 2-methyl*meso*benzanthrone into 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl and the same compound is also obtained from 2-methyl*meso*benzanthrone by nitration, reduction and the diazo-reaction, as well as from the condensation of anthrone with methyl methacrylate. 16 : 17-Dimethyldibenzanthrone is converted in boiling nitrobenzene solution into a product which, it is suggested, contains a new six-membered ring.

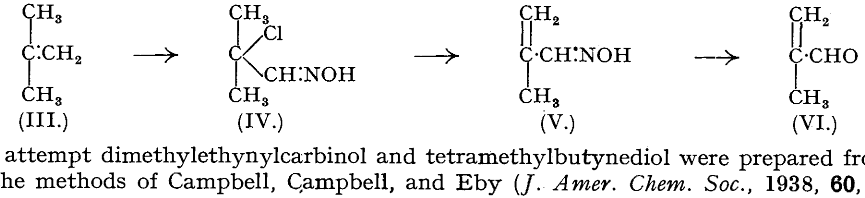
ALKYL*meso*BENZANTHRONES with the substituent group in the benz-ring are prepared by the condensation of an alkyl derivative of glycerol or acraldehyde with anthraquinone or its reduction products, usually in presence of sulphuric acid, following the original method for the preparation of *meso*benzanthrone due to Bally (D.R.-PP. 176,018, 176,019; *Ber.*, 1905, **38**, 194; 1911, **44**, 1656, etc.). Thus the condensation of crotonaldehyde with anthrone yields 1-methyl*meso*benzanthrone * (B.PP. 244,120, 261,400; Baddar and Warren, J., 1939, 944), whereas 3-methyl*meso*benzanthrone is obtained from hydroxymethyleneacetone and anthrone (F.P. 631,995; compare also Liebermann, *Annalen*, 1882, **212**, 96, 120, and Liebermann and Roka, *Ber.*, 1908, **41**, 1423). The comparative difficulty of obtaining suitable β-substituted derivatives of glycerol (cf. Hearne and De Jong, *Ind. Eng. Chem.*, 1941, **33**, 940) has rendered 2-alkyl*meso*benzanthrone less accessible by this route, but under the influence of aluminium chloride alkyl substituents in the 1- and the 3-position in *meso*benzanthrone migrate to the 2-position (U.S.P. 1,713,591; Baddar and Warren, J., 1939, 948). 2-Methyl*meso*benzanthrone (I) prepared in this way has been shown by the latter authors to be identical with the compound prepared by the condensation of β-methylglycerol αγ-diethyl ether with anthraquinone and also with that obtained by the method of Lüttringhaus and Grosskinsky (B.P. 286,602; D.R.-P. 482,839) from the condensation of α-methylacraldehyde (a derivative of β-methylglycerol) or its acetal with anthrone. The latter aldehyde or its acetal was prepared from α-bromo*iso*butaldehyde by the method of Zeisel and Danieck (*Monatsh.*, 1909, **30**, 727), but the possibility of α-methylallyl alcohol becoming readily available, which can be oxidised to α-methylacraldehyde, renders this condensation more attractive. This method, with various modifications, has been mainly used in the present work.



(I.) (II.)

The oxidation of α-methylallyl alcohol to α-methylacraldehyde was carried out by means of selenium dioxide in dioxan suspension (B.P. 457,174; D.R.-P. 634,501). Condensations with anthrone were carried out with freshly prepared material, since, unless stabilised by the addition of a trace of quinol, the aldehyde readily polymerises to an opaque solid mass. Consistent yields of 2-methyl*meso*benzanthrone (I) of the order of 50—60% were obtained by this method.

Owing to a temporary shortage of supplies of α-methylallyl alcohol, possible alternative synthetic routes to α-methylacraldehyde were investigated. For instance, the diethyl acetal of α-methylacraldehyde, prepared according to the method of Kinney and Adams (*J. Amer. Chem. Soc.*, 1937, **59**, 897), gave on acid hydrolysis the free aldehyde. For the preparation of 2-methyl*meso*benzanthrone the acetal was used. Further, addition of nitrosyl chloride to *iso*butylene (III) gave α-chloro*iso*butaldoxime (IV), which by removal of hydrogen chloride gave the oxime of α-methylacraldehyde (V), from which the free aldehyde (VI) was best generated by treatment with sodium nitrite in presence of acetic acid (cf. Harries, *Ber.*, 1901, **34**, 1494), but the over-all yield by this method rendered it unsuitable for large-scale preparations.



(III.) (IV.) (V.) (VI.)

In another attempt dimethylethynylcarbinol and tetramethylbutynediol were prepared from acetone and acetylene by the methods of Campbell, Campbell, and Eby (*J. Amer. Chem. Soc.*, 1938, **60**, 2882; see also *Organic Syntheses*, 1940, **20**, 40), Bruson and Kroeger (*J. Amer. Chem. Soc.*, 1940, **62**, 41), and Dupont (*Ann. Chim. Phys.*, 1913, **30**, 490), and both were subjected to partial hydrogenation to give dimethylvinylcarbinol

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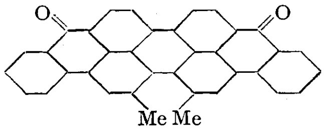
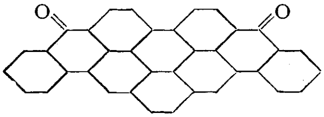
* The method of numbering the *meso*benzanthrone and related systems is that adopted in the "Ring Index" (Patterson and Capell, 1940).

and tetramethylbutenediol respectively (D.R.-P. 288,271; Ott and Schröter, *Ber.*, 1927, **60**, 624). Both the latter carbinol and the diol were subjected to ozonolysis in the normal manner, but the resulting hydroxyaldehyde could not be dehydrated to give α-methylacraldehyde because of the extreme ease with which it underwent polymerisation (cf. Franke, *Monatsh.*, 1900, **21**, 213, 1127; Levene and Walti, *J. Biol. Chem.*, 1931, **94**, 353; Danilov and Venus-Danilova, *J. Gen. Chem.*, *U.S.S.R.*, 1933, **3**, 559).

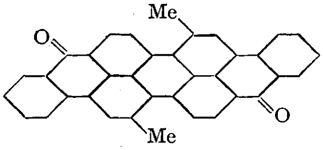
Oxidation of 2-methyl*meso*benzanthrone with chromic acid gave anthraquinone-1-carboxylic acid. Oxidation with manganese dioxide and sulphuric acid gave 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl together with a small quantity of an alkali-soluble product, which was shown to be *3-hydroxy-2-methyl*meso*benzanthrone* (II). Mild fusion of the dimethyldibenzanthronyl with alkali gave 16 : 17-*dimethyldibenzanthrone* (VII) (B.P. 286,602), which was also obtained directly from 2-methyl*meso*benzanthrone by fusion with potassium hydroxide in presence of glucose, or naphthalene and manganese dioxide. 16 : 17-Dimethyldibenzanthrone (VII) gave a deep blue vat, thus resembling dimethoxydibenzanthrone rather than dibenzanthrone itself, and dyeings on cotton were violet-blue but, compared with dibenzanthrone, showed a redder shade which was relatively fast to water-spotting.



(VII.)



(VIII.)



(IX.)

The purification of 16 : 17-dimethyldibenzanthrone (VII) was effected by extraction with boiling *o*-dichlorobenzene, but when boiling nitrobenzene was used as solvent an entirely different product resulted which, while still giving a blue vat, dyed cotton in rather weak dull red shades. This new product did not contain nitrogen and it was found that its formation from the dimethyldibenzanthrone was favoured by the presence of barium oxide. It is tentatively suggested that the rôle of the nitrobenzene in this instance is that of an oxidising agent, the two methyl groups having lost hydrogen with resultant ring closure to give the compound (VIII). This is the more likely since it is already known that 2 : 2′-dimethyl*meso*benzdianthrone is converted into *allomeso*naphthadianthrone under the influence of alkali (B.P. 303,184; D.R.-P. 456,583) : in the present instance traces of alkali may be present from the original fusion.

*3-Chloro-2-methyl*meso*benzanthrone* was prepared from 2-methyl*meso*benzanthrone and dichloramine-T in acetic acid solution, and when heated in presence of selenium, calcium hydroxide and copper bronze it gave 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl selenide. Fusion of the latter with alkali gave 6 : 15-*dimethyl*iso*dibenzanthrone* (IX), which gave violet-blue dyeings on cotton from a bright blue vat. The same compound was also prepared by the direct alkaline fusion of 3-chloro-2-methyl*meso*benzanthrone.

In the oxidation of *meso*benzanthrone to dibenzanthronyl some 2-hydroxy*meso*benzanthrone is formed as a by-product (Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 272), whereas, as recorded above, in the similar oxidation of 2-methyl*meso*benzanthrone (I), the alkali-soluble by-product proved to be 3-hydroxy-2-methyl*meso*benzanthrone (II). The constitution of the latter was proved by the identity of its *methyl* ether with (*a*) the product obtained from 2-methyl*meso*benzanthrone by nitration, reduction, conversion of the *3-amino-2-methyl*meso*benzanthrone* by means of the diazo-reaction into the corresponding hydroxy-compound, and subsequent methylation, and also with (*b*) the product obtained from the condensation of methyl methacrylate with anthrone in presence of sulphuric acid, followed by methylation. The latter condensation would be expected to yield 3-hydroxy-2-methyl*meso*benzanthrone in the same way as acrylic acid and anthrone yield 3-hydroxy*meso*benzanthrone (D.R.-P. 552,269). Like 3-methoxy*meso*benzanthrone, 3-methoxy-2-methyl*meso*benzanthrone dyes cellulose acetate rayon in bright orange shades. Oxidation of *3-nitro-2-methyl*meso*benzanthrone* with chromic acid gave anthraquinone-1-carboxylic acid, thus confirming the entry of the nitro-group into the benz-ring during the nitration of 2-methyl*meso*benzanthrone. Direct bromination of 2-methyl*meso*benzanthrone gave *3-bromo-2-methyl*meso*benzanthrone*, identical with the product obtained from 3-amino-2-methyl*meso*benzanthrone by means of the diazo-reaction.

EXPERIMENTAL.

α-Methylacraldehyde.—(*a*) *From methylallyl alcohol* (cf. B.P. 457,174; D.R.-P. 634,501). To a suspension of selenium dioxide (35 g.) in dioxan (80 g.) stirred at 95—100°, α-methylallyl alcohol (45·5 g.) was added dropwise during 2 hours. The α-methylacraldehyde was allowed to distil through a Lapworth column at the same rate as the alcohol was added, the temperature at the head of the column never exceeding 90°. A further quantity of selenium dioxide (5 g.) was introduced after the alcohol had been added. The crude distillate, which contained a high proportion of dioxan, was fractionally distilled and collected between 65° and 85° (25 g.). The b. p. recorded in B.P. 457,174 and D.R.-P. 634,501 is 68—69°, and B.P. 286,602 and D.R.-P. 482,839 record the b. p. as "about 90°" : Shriner and Sharp (*J. Amer. Chem. Soc.*, 1940, **62**, 2245) record b. p. 73·5° and Hearne, Tamele, and Converse (*Ind. Eng. Chem.*, 1941, **33**, 805), b. p. 68·4°. This product was sufficiently pure for use in the preparation of 2-methyl*meso*benzanthrone. Further purification resulted in considerable loss of material. The 2 : 4-dinitrophenylhydrazone, prepared in the usual manner, crystallised from ethyl acetate in small red needles, m. p. 202° (decomp.), and the semicarbazone separated from methyl alcohol in needles, m. p. 194°. Shriner and Sharp (*loc. cit.*) record m. p. 206—206·5° and 197·5—198° for these two derivatives. Attempts to use other solvents (phenetole, anisole, ethyl phthalate and diamyl ether) in the oxidation in place of dioxan gave reduced yields of aldehyde.

(*b*) *From α-bromo*iso*butaldehyde diethylacetal.* The acetal of α-bromo*iso*butaldehyde was prepared and converted into α-methylacraldehyde diethyl acetal by the method of Kinney and Adams (*loc. cit.*). Hydrolysis with boiling 10% sulphuric acid liberated the free aldehyde, which was identified by m. p. and mixed m. p. of its 2 : 4-dinitrophenylhydrazone.

(*c*) *From* iso*butylene. iso*Butylene, prepared by dropping *tert.*-butyl alcohol (100 g.) on to anhydrous oxalic acid (80 g.) at 80° to 90° during 2½ hours and dried (calcium chloride), was passed into a solution of nitrosyl chloride (100 g.) in dry ether (700 c.c.) maintained at −20° to −15°. After standing over-night at −5° to 0°, the α-chloro*iso*butaldoxime (IV) separated in white needles and a further crop was obtained by partial evaporation of the green ethereal filtrate in a current of dry air (total yield 33 g., m. p. 103—104°; cf. Tilden and Sudborough, J., 1893, **63**, 479; Ipatieff and Ssolonina, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 496). Further concentration of the mother-liquor gave only a deep blue oil (65 g.) with a camphor-like odour. A solution of the oxime (20 g.) in ethyl alcohol (150 c.c.) was refluxed for ½ hour with fused potassium acetate (40 g.) and, after filtration from potassium chloride and excess of acetate, the solution was diluted with water and extracted with ether. Distillation of the dried ethereal extract gave a brown oily residue, which yielded *α-methylacraldoxime* (V) as a colourless oil (12 g.), b. p. 65°/14 mm. (Found : N, 16·2. C_4H_7ON requires N, 16·5%). A solution of sodium nitrite (6 g.) in water (22 c.c.) was added dropwise with stirring to a solution of the oxime (5 g.) in glacial acetic acid (25 c.c.) maintained at 60—70°. Stirring was then continued for 15 minutes at the same temperature. Treatment of a portion of the resulting solution with a solution of 2 : 4-dinitrophenylhydrazine in hydrochloric acid gave α-methylacraldehyde 2 : 4-dinitrophenylhydrazone as an orange-red precipitate, which after purification had m. p. 198—199°, undepressed on admixture with an authentic specimen prepared from α-methylallyl alcohol as described above.

2-*Methyl*meso*benzanthrone* (I) (D.R.-P. 482,839).—(*a*) Sulphuric acid (30 g., *d* 1·53) was added to a solution of anthrone (9·7 g., prepared as described in *Organic Syntheses*, Collective Vol. I, p. 52) in glacial acetic acid (97 g.) and to the resulting solution heated at 80°, α-methylacraldehyde (12 g.), diluted with an equal volume of dioxan, was added during 20 minutes with stirring. The reaction mixture was poured slowly into water (1500 c.c.) with stirring. The tarry greenish precipitate was collected, washed with water, and dried. Purification was effected either by trituration with a small volume of acetone, which removed most of the green impurity, followed by several crystallisations from alcohol–acetone, by distillation with superheated steam at 200°, followed by crystallisation from alcohol, or by chromatographic adsorption on alumina from benzene solution (1 kg. of " Birlec " alumina per 20 g. of crude product) and subsequent elution with the same solvent and evaporation. 2-Methyl*meso*benzanthrone was obtained in yellow needles, m. p. 164° (Found : C, 88·3; H, 4·8. Calc. for $C_{18}H_{12}O$: C, 88·5; H, 4·9%). Purification by chromatographic adsorption gave yields of 50—60% calculated on the anthrone used, the alternative methods affording rather smaller yields.

(*b*) α-Methylacraldehyde diethylacetal (12 g.) was added dropwise during 30 minutes with vigorous stirring to a solution of anthrone (9·7 g.) in sulphuric acid (170 g., *d* 1·706) at 60°. The crude yellow solid (10 g.), which separated on pouring into ice-water, was collected, washed, dried, and purified as described above.

Oxidation of 2-*Methyl*meso*benzanthrone.*—A solution of chromic anhydride (5 g.) in 50% acetic acid (25 c.c.) was added during 20 minutes to a hot solution of 2-methyl*meso*benzanthrone (1 g.) in glacial acetic acid (20 c.c.). After heating on the steam-bath for 2 hours, water was added, and the precipitated solid collected, taken up in aqueous ammonia and filtered. Acidification of the filtrate deposited anthraquinone-1-carboxylic acid, which separated from acetic acid in faintly yellow plates, m. p. 285° (decomp.) both alone and on admixture with an authentic specimen prepared from *meso*benzanthrone by the method of Perkin (J., 1920, **117**, 706).

16 : 17-*Dimethyldibenzanthrone* (VII).—(a) Via 2 : 2′-*dimethyl*-3 : 3′-*dibenzanthronyl* (cf. B.P. 286,602 and 430,914). Manganese dioxide (6 g.) was added during 7 hours to a stirred solution of 2-methyl*meso*benzanthrone (10 g.) in 80% sulphuric acid (240 g.) at 0—5°. Stirring was continued for 20 hours, water (16 c.c.) then added, and the mixture poured slowly with stirring into more water (1200 c.c.). Sodium bisulphite was added (6 g.) and the whole boiled, filtered, washed free from acid, and treated with boiling dilute sodium hydroxide solution. After filtration and washing alkali-free, the residue was dried and washed several times with hot toluene to remove unchanged 2-methyl*meso*benzanthrone. Crude 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl (6 g.) was obtained as a greenish powder in 78% yield, which on crystallisation from *o*-dichlorobenzene gave small yellowish needles, m. p. >360°. The purple-blue alkaline washings gave crude 3-hydroxy-2-methyl*meso*benzanthrone (0·4 g.) on acidification (see below). The dimethyldibenzanthronyl (5 g.) was added during 30 minutes to a melt of potassium hydroxide (50 g.) and ethyl alcohol (45 g.) heated at 120—130°. This temperature was maintained for a further 20 minutes with stirring. The deep blue melt was drowned in water and aerated to complete the precipitation of the dye, which was collected, washed with water until free from alkali, and dried. The product (4·7 g.) was further purified by extraction with boiling *o*-dichlorobenzene. 16 : 17-*Dimethyldibenzanthrone* was obtained in minute violet-black crystals (Found : C, 88·8; H, 4·3. $C_{36}H_{20}O_2$ requires C, 89·2; H, 4·1%). With concentrated sulphuric acid it gave a violet coloration.

(b) *From 2-methyl*meso*benzanthrone* (cf. D.R.-P. 467,697). A mixture of 2-methyl*meso*benzanthrone (10 g.) and glucose (12·5 g.) was added to molten potassium hydroxide (50 g.) at 230—240°, and the whole well stirred. When effervescence had subsided, the melt was poured into water, and the product (6 g.) isolated by aeration, filtration, washing and drying as above. In a second method (cf. B.P. 430,665) fused potassium acetate (2·5 g.) was added to methyl alcohol (2·5 g.) and stirred until substantially dissolved, potassium hydroxide (15 g.) then added, and the whole heated to 125—130°. Molten naphthalene (25 g.) was then added, followed by 2-methyl*meso*benzanthrone (5 g.). The temperature was raised to 140° during 30 minutes and then manganese dioxide (5 g.) was stirred in during 5—10 minutes. Heating was continued up to 215°, and the melt stirred until almost solid owing to volatilisation of naphthalene. After cooling to 80—90°, water was added, and the naphthalene removed with steam. The residual solid was collected, and the excess of manganese dioxide removed by boiling with water (150 c.c.) containing sulphuric acid (15 g.) and sodium bisulphite (3·5 g.). After filtration, washing, drying and extraction with *o*-dichlorobenzene 16 : 17-dimethyldibenzanthrone (4 g.) was obtained as a violet-black powder identical with that described above.

Oxidation of 16 : 17-*Dimethyldibenzanthrone.*—Crude 16 : 17-dimethyldibenzanthrone (5 g.), contained in an extraction thimble held in a copper gauze bucket suspended in the vapour of the solvent from the lower end of the reflux air-condenser, was extracted with boiling nitrobenzene (40 c.c.) for 8 hours. When cold, the precipitated solid was collected and washed with acetone. The dried product (3 g.), obtained as a dark brown powder with a reddish tinge, dyed cotton with a weak dull red shade from a blue vat. A similar product was obtained on refluxing for 2 hours the crude dimethyldibenzanthrone (9·5 g.) with nitrobenzene (200 c.c.) in presence of barium oxide (2 g.). In this case a portion of the product was filtered off on cooling, and the remainder separated when the filtrate was added to an equal volume of ethyl alcohol. The combined products were digested with dilute hydrochloric acid at 60°, filtered, washed with water, and dried (6 g.).

3-*Chloro*-2-*methyl*meso*benzanthrone* (cf. Cahn, Jones, and Simonsen, J., 1933, **444**).—Concentrated hydrochloric acid (0·5 c.c.) was added to a solution of 2-methyl*meso*benzanthrone (5 g.) in warm glacial acetic acid (100 c.c.), followed by the addition of dichloroamine-T (2·5 g.) in small portions with agitation. Fine yellow needles began to separate almost immediately. The mixture was then heated on the steam-bath for 15 hours, after which water (100 c.c.) was added.

When cold, the precipitated product was collected and crystallisation from glacial acetic acid gave 3-*chloro*-2-*methyl*meso*benzanthrone* (4 g.) in golden-yellow needles, m. p. 227—228° (Found : C, 77·4; H, 3·9. $C_{18}H_{11}OCl$ requires C, 77·5; H, 4·0%).

6 : 15-*Dimethyl*iso*dibenzanthrone* (IX).—(a) *From* 3-*chloro*-2-*methyl*meso*benzanthrone* (cf. D.R.-PP. 194,252, 467,697). 3-Chloro-2-methyl*meso*benzanthrone (1·5 g.) was stirred into a melt of potassium hydroxide (6·5 g.) and ethyl alcohol (7·5 c.c.) at 140° and the temperature was gradually raised and maintained at 150—155° for ½ hour. The deep blue melt was poured into water (200 c.c.) and after aeration the precipitated dye was collected, washed free from alkali with water, and dried. 6 : 15-*Dimethyl*iso*dibenzanthrone* was obtained in almost quantitative yield as a dark violet powder (Found : C, 88·7; H, 4·3. $C_{36}H_{20}O_2$ requires C, 89·2; H, 4·1%).

(b) Via 2 : 2′-*dimethyl*-3 : 3′-*dibenzanthronyl selenide* (cf. B.PP. 367,462, 435,321). 3-Chloro-2-methyl*meso*benzanthrone (1·5 g.), selenium powder (0·5 g.), calcium hydroxide (0·5 g.), copper bronze (0·5 g.), and ethyl alcohol (25 c.c.) were heated for 60 hours at 200° in a sealed tube. When cold, the product was washed out with alcohol into water (200 c.c.). Hydrochloric acid (0·5 c.c.) was added and, after boiling, the product was collected, washed with water, and dried in an air-oven. Subsequent extraction with boiling nitrobenzene gave 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl selenide (1 g.) as a yellow-brown powder, m. p. 310—315°. The selenide (1·5 g.) was stirred into a melt of potassium hydroxide (4·7 g.) and ethyl alcohol (4 c.c.) at 120° during 15 minutes. The temperature was raised to 130° and after 1½ hours the product was poured into water (40 c.c.). Aqueous sodium bisulphite (1·5 c.c. of 45% solution) was added and, after boiling, the precipitated dye was collected, washed free from alkali, and dried. It was identical in properties with that obtained by method (a).

3-*Nitro*-2-*methyl*meso*benzanthrone* (cf. Lüttringhaus and Neresheimer, *loc. cit.*, p. 285).—Nitric acid (88%; 3 c.c.) was added dropwise to a suspension of finely divided 2-methyl*meso*benzanthrone (5 g.) in nitrobenzene (40 c.c.) at room temperature. A brownish-red solution resulted and the temperature rose spontaneously to 40°. Stirring was continued for 2½ hours at 40—50°, during which time a mass of fine yellow needles separated. When cold, ethyl alcohol (40 c.c.) was added, and the precipitated solid collected, washed with alcohol, and dried (5 g., m. p. 215—217°). Recrystallisation from benzene or glacial acetic acid gave 3-*nitro*-2-*methyl*meso*benzanthrone* (3·6 g.) in orange-yellow needles, m. p. 218—219° (Found : C, 75·0; H, 3·9. $C_{18}H_{11}O_3N$ requires C, 74·8; H, 3·8%). Oxidation of the nitro-compound with chromic acid, as described above for the oxidation of 2-methyl*meso*benzanthrone, gave anthraquinone-1-carboxylic acid, m. p. and mixed m. p. with an authentic specimen 285°.

3-*Amino*-2-*methyl*meso*benzanthrone*.—Finely divided 3-nitro-2-methyl*meso*benzanthrone (3 g.) in suspension in aqueous sodium sulphide (30 c.c.; 15% solution) was stirred for ½ hour at room temperature, and the temperature then raised slowly to boiling. After boiling for 1 hour, the red solid was collected and washed well with water (2·7 g.; m. p. 225—231°). Crystallisation from dilute pyridine gave 3-*amino*-2-*methyl*meso*benzanthrone* (2·2 g.) in bright red needles, m. p. 232° (Found : C, 83·3; H, 5·2. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·0%).

3-*Bromo*-2-*methyl*meso*benzanthrone*.—(a) *From* 2-*methyl*meso*benzanthrone*. A 25% solution of bromine in glacial acetic acid (16 g.) was added dropwise with stirring to a solution of 2-methyl*meso*benzanthrone (5 g.) in glacial acetic acid (80 g.) at 80°. The mixture became pasty, rendering stirring difficult, and the temperature was then raised and maintained at 90—100° until evolution of hydrogen bromide ceased. Water (20 c.c.) was added, and the precipitated solid collected, washed, and dried (4·5 g., m. p. 216—222°). Purification by high-vacuum sublimation or chromatographic adsorption on alumina from benzene solution gave 3-*bromo*-2-*methyl*meso*benzanthrone*, which formed orange-yellow needles, m. p. 225°, from glacial acetic acid (Found : C, 66·7; H, 3·5. $C_{18}H_{11}OBr$ requires C, 66·9; H, 3·4%).

(b) *From* 3-*amino*-2-*methyl*meso*benzanthrone*. A solution of the base (1 g.) in concentrated sulphuric acid (10 c.c.) was diazotised with sodium nitrite (0·3 g.). After ½ hour the solid diazonium sulphate, obtained as a yellowish-brown precipitate when the solution was poured on ice, was added to a solution of cuprous bromide (2 g.) in hydrobromic acid (10 c.c.; *d* 1·45) stirred at room temperature. When evolution of nitrogen had ceased, the mixture was heated on the steam-bath. Dilution with water precipitated the product as a brown solid (1·1 g.). Crystallisation from glacial acetic acid gave 3-bromo-2-methyl*meso*benzanthrone in yellow needles, m. p. 225°, identical with the product prepared by method (a).

3-*Hydroxy*-2-*methyl*meso*benzanthrone* (II).—(a) *From the oxidation of* 2-*methyl*meso*benzanthrone*. The purple-blue alkaline washings obtained in the preparation of 2 : 2′-dimethyl-3 : 3′-dibenzanthronyl described above were acidified with hydrochloric acid, and the resulting orange-brown precipitate collected, washed with water, and dried. Purification was effected by chromatographic adsorption on alumina from benzene containing 10% of ethyl alcohol. The bright purple band was eluted with the same solvent and concentration of the elutriate deposited 3-*hydroxy*-2-*methyl*meso*benzanthrone* in small brick-red needles, m. p. 206—208° (decomp.) (Found : C, 83·0; H, 4·7. $C_{18}H_{12}O_2$ requires C, 83·1; H, 4·6%).

(b) *From methyl methacrylate and anthrone*. Methyl methacrylate (20 g.) was added slowly during ½ hour to a well-stirred solution of anthrone (40 g.) in concentrated sulphuric acid (200 g.) at 70°. After being stirred for 2½ hours at this temperature, the dark-red solution (blue fluorescence) was cooled and poured on ice. The precipitated solid was extracted with aqueous sodium hydroxide, and the filtered dark green solution aerated until the colour had become purple-blue. Acidification with hydrochloric acid deposited an orange-brown precipitate, which was collected, washed, and dried at 50°. Chromatographic adsorption on alumina (1 kg.) was carried out as described above, and the purple band separated mechanically. Elutriation as before gave 3-hydroxy-2-methyl*meso*benzanthrone (3 g.) in small red needles.

(c) *From* 3-*amino*-2-*methyl*meso*benzanthrone*. A solution of 3-amino-2-methyl*meso*benzanthrone (1 g.) in 50% sulphuric acid (20 c.c.) was diazotised with sodium nitrite (0·4 g.). After standing for ½ hour at room temperature, the mixture was diluted with an equal volume of water and heated on the steam-bath. When evolution of nitrogen had ceased, the suspended solid was collected (pump), and dissolved in aqueous sodium hydroxide (purple-blue solution); from the filtered solution, the hydroxy-compound (1 g.) was precipitated with hydrochloric acid.

3-*Methoxy*-2-*methyl*meso*benzanthrone*.—Solutions of 3-hydroxy-2-methyl*meso*benzanthrone (2 g.), prepared by methods (a), (b) and (c) above, in acetone (100 c.c.) were refluxed for 10 hours with methyl iodide (1·2 g.) and anhydrous potassium carbonate (0·6 g.). The solvent was removed by distillation, and the residue boiled with water. The brownish-yellow solid was collected, dissolved in benzene, and purified either chromatographically by adsorption on alumina or by vacuum sublimation. Subsequent crystallisation from benzene–light petroleum (b. p. 40—60°) or dilute methyl alcohol gave in all three cases 3-*methoxy*-2-*methyl*meso*benzanthrone* (2 g.) in lemon-yellow needles, m. p. 142° (Found : C, 83·0; H, 5·4. $C_{19}H_{14}O_2$ requires C, 83·2; H, 5·1%).

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