390. *The Sulphonation of* meso*Benzanthrone and Some of its Derivatives.*

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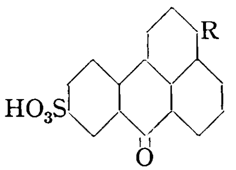
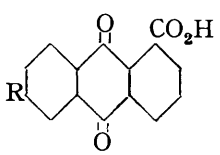
The main product of the monosulphonation of *meso*benzanthrone has been shown to be *meso*benzanthrone-6-sulphonic acid by oxidation of its sodium salt to 6-*sulphoanthraquinone*-1-*carboxylic acid*, which can be converted into 6-chloroanthraquinone-1-carboxylic acid. *meso*Benzanthrone-1'-sulphonic acid is probably also formed in small amount. The sulphonation of 1'-chloro-, 1'-bromo-, and 1'-nitro-*meso*benzanthrones results in the formation in each case of the 6-sulphonic acid, and 6 : 7-dichloro*meso*benzanthrone yields probably the 1'-acid. From the *sodium* salt of the last a new trichloro*meso*benzanthrone has been prepared, which is formed also by the direct chlorination of 6 : 7-dichloro*meso*benzanthrone, and it is considered to be 1' : 6 : 7-*trichloro*meso*benzanthrone*. Both the dichloro-compound and the sodium salt of the dichloro-sulphonic acid yield on oxidation 6 : 7-*dichloroanthraquinone*-1-*carboxylic acid*. 1' : 6-Dibromo*meso*benzanthrone (Rule and Smith, J., 1937, 1098) can be prepared from the *sodium* salt of 1'-bromo*meso*benzanthrone-6-sulphonic acid. It yields on oxidation with chromic acid 6-*bromoanthraquinone*-1-*carboxylic acid*.

Owing to their importance as dye intermediates the chemistry of *meso*benzanthrone and its derivatives has been extensively investigated, but little attention has apparently been directed to the sulphonic acids. Lauer and Irie (*J. pr. Chem.*, 1936, **145**, 281) prepared

(I.)





(II.)

from *meso*benzanthrone a sodium salt which they considered to be sodium *meso*benzanthrone-6-sulphonate (as I, R = H), since it gave on treatment with potassium chlorate and hydrochloric acid a mixture of 6-chloro- and 1′ : 6-dichloro-*meso*benzanthrones. A disulphonic acid obtained by the sulphonation of dibenzanthrone has also been described (Soc. Chem. Ind. Basle, B.P. 279,479).

It seemed to us desirable to obtain a more rigid proof of the structure of Lauer and Irie's acid, since chlorination, bromination, and nitration of *meso*benzanthrone result mainly in the formation of 1′-mono-substitution products. In the *meso*benzanthrone series it is not possible to apply the usual methods for the orientation of sulpho-groups, since replacement with the hydroxy-group by alkali fusion leads to the formation of dihydroxydibenzanthrones (or dihydroxy*iso*dibenzanthrones) and replacement with halogen by heating the sulphonyl halides, a method which has proved so valuable in the orientation of the naphthalenesulphonic acids, if at all possible, gives extremely poor yields.

We have, however, been able to provide a rigid proof that Lauer and Irie's acid has the structure which they assigned to it. On oxidation of the sodium salt with chromic acid it yields 6-*sulphoanthraquinone*-1-*carboxylic acid* (II, R = SO_3H), m. p. 271—274°, the structure of which is proved by the replacement of the sulpho-group by chlorine to give 6-chloroanthraquinone-1-carboxylic acid (II, R = Cl), m. p. 305—306°, methyl ester, m. p. 190—191° (Cahn, Jones, and Simonsen, J., 1933, 444). By the action of ammonia on the sulphonic acid, 6-*aminoanthraquinone*-1-*carboxylic acid* (II, R = NH_2), m. p. 247—249°, is obtained in poor yield together with a substance, m. p. 295—297°, yielding an acetyl derivative, m. p. 257—258°. Although the analytical data are unsatisfactory, there can be little doubt that these substances consist essentially of 2-aminoanthraquinone and its acetyl derivative contaminated with a little of the amide of the amino-acid.

Whilst, therefore, *meso*benzanthrone-6-sulphonic acid forms the main product of the sulphonation of *meso*benzanthrone, it is accompanied by a little of the 1′-sulphonic acid, since, if the crude acid is treated with phosphorus pentachloride and the resulting sulphonyl chloride is heated with xylene, a small quantity of 1′-chloro*meso*benzanthrone can be isolated from the resinous product. It is in our opinion improbable that the 1′-acid can be the primary product of the sulphonation, rearranging at the high temperature of the reaction to the 6-sulphonic acid, since we have found that, if the sulphonation of *meso*benzanthrone is carried out at room temperature in the presence of a mercury catalyst, the 6-sulphonic acid is still the main product. Under more vigorous conditions, *meso*benzanthrone yields a disulphonic acid, isolated as its *sodium* salt. This has not been oriented, but we consider that it is most probably the 1′ : 6-disulphonic acid (I, R = SO_3H).

We have investigated also the sulphonation of 1′-chloro-, 1′-bromo-, 1′-nitro-, and 6 : 7-dichloro-*meso*benzanthrones. As would be anticipated, sulphonation of the 1′-substituted *meso*benzanthrones occurs in the 6-position, as was proved by the oxidation of the pure sodium salts of the individual sulphonic acids to 6-sulphoanthraquinone-1-carboxylic acid. 1′ : 6-Dibromo*meso*benzanthrone, m. p. 256—257°, was prepared by heating 1′-bromo*meso*benzanthrone-6-sulphonyl bromide with xylene. On oxidation with chromic acid, it yielded 6-*bromoanthraquinone*-1-*carboxylic acid* (II, R = Br), m. p. 298—299°, *methyl* ester, m. p. 198—199°. From 1′-chloro*meso*benzanthrone a disulphonic acid was prepared which, although not directly oriented, is probably from analogy the 1′-chloro-*meso*benzanthrone-6 : 8-disulphonic acid.

Sulphonation of 6 : 7-dichloro*meso*benzanthrone yields a sulphonic acid which gives on oxidation 6 : 7-*dichloroanthraquinone*-1-*carboxylic acid*, m. p. 275—276°, *methyl* ester, m. p. 197—198°. This acid can be prepared also by the oxidation of 6 : 7-dichloro*meso*benzanthrone and it follows, therefore, that the sulpho-group must be in the *Bz* nucleus, probably in the 1′-position. By heating the sulphonyl chloride with xylene, a trichloro-*meso*benzanthrone was obtained, which could be readily prepared by the direct chlorination of 6 : 7-dichloro*meso*benzanthrone. Since it has been shown previously (Cahn, Jones, and Simonsen, *loc. cit.*) that 6- and 7-chloro*meso*benzanthrone yield on chlorination 1′ : 6- and 1′ : 7-dichloro*meso*benzanthrone respectively, there can be little doubt that the new trichloro-compound, m. p. 349—350°, is 1′ : 6 : 7-*trichloro*meso*benzanthrone*, although a rigid proof is not yet available.

EXPERIMENTAL.

meso*Benzanthrone*-6-*sulphonic Acid*.—A mixture of *meso*benzanthrone (50 g.) and fuming sulphuric acid (SO_3 5%; *d* 1·847; 500 g.) was heated in an oil-bath at 145—150° for 2 hours, cooled, and poured into ice-water (1500 g.). Unchanged *meso*benzanthrone was removed, and sodium carbonate (1500 g.) added with stirring at 95°. The liquid was made up to 10 l. by the addition of saturated salt solution, boiled, and allowed to cool. The crystalline sodium salt of the sulphonic acid (103 g.), which separated, was collected, washed with salt solution, and purified by three crystallisations from hot water, from which it separated as a greenish-yellow crystalline powder, which was dried at 100° for analysis (Found: S, 8·8; Na, 6·3. Calc. for $C_{17}H_9O_4SNa,2H_2O$: S, 8·7; Na, 6·3%). The sulphonic acid, isolated by decomposition of the barium salt with sulphuric acid, was a brown amorphous solid.

The sulphonic acid could be prepared also by allowing fuming sulphuric acid (18%) to act on *meso*benzanthrone for 11 days at room temperature in the presence of a mercury catalyst.

On admixture of the sodium or potassium salt of the sulphonic acid (10 g.) with phosphorus pentachloride (10 g.) a vigorous reaction ensued, which was completed by heating on the water-bath for 6 hours. After the addition of ice-water, the reddish-brown solid was collected, dried, powdered, and heated under xylene at 140—145° for 3 hours, the xylene removed in steam, and the residue (8·4 g.) extracted with hot acetic acid (charcoal). On cooling, an orange-red crystalline solid, m. p. 265—272°, softening at 259°, was obtained in small yield, but a homogeneous chloro*meso*benzanthrone could not be isolated.

6-*Sulphoanthraquinone*-1-*carboxylic Acid*.—To a boiling solution of chromic acid (26 g.) in aqueous acetic acid (50%; 90 c.c.), a solution of *meso*benzanthrone-6-sulphonic acid (7·5 g.) in acetic acid (90 c.c.) was added during 3 hours. After saturation with sulphur dioxide to remove the excess of chromic acid, the solution was diluted with water, and the excess of sulphur dioxide and acetic acid removed by evaporation. After the addition of an excess of aqueous ammonia to precipitate the chromium salts, the filtered solution was concentrated, the *ammonium* salt of the acid (2·75 g.) separating from the cooled solution in fine yellow needles. It was recrystallised from aqueous alcohol (30%) (Found: C, 49·4; H, 4·2; N, 7·6; S, 8·7. $C_{15}H_{14}O_7N_2S$ requires C, 49·2; H, 3·8; N, 7·7; S, 8·7%). Addition of a barium chloride solution to an aqueous solution of the ammonium salt precipitated the sparingly soluble *barium* salt as a white powder, which was dried at 100° for analysis (Found: Ba, 28·4. $C_{15}H_6O_7SBa,H_2O$ requires Ba, 28·3%). It was decomposed with the calculated quantity of N/20-sulphuric acid, 6-*sulphoanthraquinone*-1-*carboxylic acid* remaining as a yellow powder, m. p. 255—262°, on evaporation of the aqueous solution. The acid, which was readily soluble in water, alcohol and acetic acid, crystallised from hydrochloric acid in fine yellow needles, m. p. 271—274°, decomposing above 275° (Found: C, 50·3; H, 3·4; S, 8·7. $C_{15}H_8O_7S,1·5H_2O$ requires C, 50·1; H, 3·0; S, 8·9%).

6-*Chloroanthraquinone*-1-*carboxylic Acid*.—To a mixture of the preceding ammonium salt (5 g.), water (100 c.c.), and concentrated hydrochloric acid (15 c.c.) at 95°, a solution of potassium chlorate (5 g.) in water (50 c.c.) was added during ½ hour (mechanical stirring). The solid was collected after 1½ hours' heating, boiled with water (50 c.c.) to remove inorganic matter, and dried. The chloro-acid (3·4 g., m. p. 294—295°) crystallised from acetic acid in faintly yellow needles, m. p. 305—306°. The methyl ester, prepared from the acid chloride, crystallised from methyl alcohol in flat straw-coloured needles, m. p. 190—191° (Found: Cl, 11·9. Calc. for $C_{16}H_9O_4Cl$: Cl, 11·8%).

6-*Aminoanthraquinone*-1-*carboxylic Acid*.—A mixture of the ammonium salt of the sulphonic acid (1·5 g.), freshly precipitated manganese dioxide * (0·8 g.) made into a paste with water (4·5 c.c.), and aqueous ammonia (25%; 10 g.) was heated in a sealed tube for 25 hours at 200°, diluted with water, and boiled, and the separated manganese dioxide extracted with hot water. The combined filtrates were evaporated to dryness, the residue dissolved in the minimum amount of water, and the solution made faintly acid with dilute hydrochloric acid. The precipitated reddish-brown solid was collected, and after four crystallisations from very dilute acetic acid, 6-*aminoanthraquinone*-1-*carboxylic acid* was obtained in brown needles, m. p. 247—249°, sintering at 245° (Found: C, 67·3; H, 3·6. $C_{15}H_9O_4N$ requires C, 67·4; H, 3·4%).

* The manganese dioxide was found to be most active if prepared in the following manner. A dilute solution of potassium permanganate was added gradually with stirring to a dilute solution of sulphuric acid containing more than sufficient ethyl alcohol to decolorise all the permanganate. The manganese dioxide was repeatedly washed by decantation with warm water until free from mineral acid. The thick paste. after draining on a funnel, was used as soon as possible.

The manganese dioxide which had been filtered off contained crystalline material. It was extracted with acetone (Soxhlet), evaporation of the acetone leaving a deep red residue. This was sublimed in a low vacuum; the sublimate crystallised from nitrobenzene in dark reddish-brown needles, m. p. 295—297° (Found: C, 74·5; H, 4·0. Calc. for $C_{14}H_9O_2N$: C, 75·3; H, 4·0%). The acetyl derivative crystallised from acetic acid in bright yellow needles, m. p. 257—258° (Found: C, 71·1; H, 4·2. Calc. for $C_{16}H_{11}O_3N$: C, 72·4; H, 4·1%). The structures of these two substances are discussed on p. 2048.

Action of Phosphorus Pentachloride on meso*Benzanthronesulphonic Acid.* 1′-*Chloro*meso*benzanthrone.*—A mixture of crude *meso*benzanthronesulphonic acid (5·3 g.) and phosphorus pentachloride (7 g.) was heated on the water-bath for 3 hours. After the addition of ice-water to the cooled mixture, the solid was collected, dried, and extracted with hot benzene, leaving an insoluble residue (1 g.). Evaporation of the benzene gave the sulphonyl chloride as a dark powder (3·1 g.). The chloride (1·1 g.) was digested with xylene for 1 hour, the xylene removed in steam, and the residue sublimed in a low vacuum; the sublimate formed yellow needles, m. p. 160—170°, raised by repeated crystallisation from acetic acid to 181—182°, both alone and in admixture with 1′-chloro*meso*benzanthrone.

Action of Potassium Chlorate on Sodium meso*Benzanthronesulphonate.*—To a mixture of the sodium salt (25 g.), water (500 c.c.), and concentrated hydrochloric acid (50 c.c.) at 95°, a solution of potassium chlorate (25 g.) in water (400 c.c.) was slowly added (mechanical stirring). After an hour's heating, the solid (1·2 g.) was collected from the hot solution and after recrystallisation from acetic acid and chlorobenzene gave 1′ : 6-dichloro*meso*benzanthrone, m. p. 267—268°, both alone and in admixture with an authentic specimen (Found: Cl, 23·5. Calc. for $C_{17}H_8OCl_2$: Cl, 23·7%). From the acetic acid and chlorobenzene mother-liquors a small quantity of a second chloro*meso*benzanthrone, m. p. 184°, was isolated; this was probably 6-chloro*meso*benzanthrone.

6 : 6′-*Dimethoxydibenzanthrone.*—To a mixture of sodium hydroxide (6 g.) and potassium hydroxide (6 g.) at 220—230°, finely powdered sodium *meso*benzanthronesulphonate (14 g.) was gradually added, and the fusion continued for 1 hour. The product was dissolved in hot water (400 c.c.), and the solution acidified, yielding a black solid (4·4 g.). The crude dihydroxydibenzanthrone (1 g.) in *o*-dichlorobenzene (100 g.) was refluxed with methyl sulphate (12·7 g.) and anhydrous sodium carbonate (14 g.) for 6 hours. After the addition of aqueous ammonia (25%; 30 c.c.) the solvent was removed in steam, the residue made strongly alkaline with 2N-sodium hydroxide (5 c.c.), and the solid (0·85 g.) collected. This was refluxed with nitrobenzene (200 g.), the dark green solution, which showed a deep red fluorescence, was filtered and concentrated to 30 c.c., and the solid which separated on cooling was collected. The *dimethoxydibenzanthrone* was recrystallised from aniline, in which it formed a greenish-blue solution and from which it separated as a black crystalline powder (Found: C, 83·2; H, 3·6. $C_{34}H_{16}O_4$ requires C, 83·6; H, 3·3%).

meso*Benzanthrone*-6 : ?-*disulphonic Acid.*—A mixture of *meso*benzanthrone (5 g.) and fuming sulphuric acid (10% SO_3; 50 g.) was heated in an oil-bath at 165—170° for 2 hours, and the cooled solution poured into ice-water (500 g.). White lead (115 g.) was added with stirring to the hot solution, the lead sulphate removed, and, after concentration, the filtrate was poured into a well-stirred saturated salt solution (500 c.c.). The *sodium* salt, which separated, was collected, washed with saturated salt solution, and, after one crystallisation from water and from dilute alcohol, obtained as a greenish-yellow crystalline powder. It was dried at 100° for analysis (Found: S, 14·5; Na, 10·7. $C_{17}H_8O_7S_2Na_2$ requires S, 14·8; Na, 10·6%).

When this sodium salt was heated with phosphorus pentachloride, and the product decomposed by digestion with xylene, a substance was obtained which crystallised from acetic acid (charcoal) in fine colourless needles, m. p. 247—248° (Found: Cl, 33·9%). This substance was not identified.

1′-*Chloro*meso*benzanthrone*-6-*sulphonic Acid.*—A mixture of 1′-chloro*meso*benzanthrone (20 g.) and fuming sulphuric acid (SO_3 5%; *d* 1·847; 200 g.) was heated in an oil-bath at 165—170° for 2 hours, and the cooled mixture poured into a saturated salt solution (2 l.). The *sodium* salt, which separated, was crystallised from aqueous alcohol (15%) and from dilute alcohol (50%) and obtained as a yellow crystalline powder. For analysis it was dried at 100° (Found: Cl, 9·4; S, 8·7; Na, 6·6. $C_{17}H_8O_4ClSNa$ requires Cl, 9·7; S, 8·7; Na, 6·3%). The free acid, isolated through the barium salt, was a brownish-yellow solid which could not be crystallised. Oxidation of the sodium salt with chromic acid gave 6-sulphoanthraquinone-1-carboxylic acid, which was isolated through its sparingly soluble barium salt as described above.

It had m. p. 271—274° both alone and in admixture, and its identity was confirmed by its conversion into methyl 6-chloroanthraquinone-1-carboxylate, m. p. 189—190°.

1′-*Chloro*meso*benzanthrone*-6 : ?-*disulphonic Acid.*—A mixture of 1′-chloro*meso*benzanthrone (10 g.) and fuming sulphuric acid (SO_3 10% ; *d* 1·888 ; 250 g.) was heated in an oil-bath at 145—150° for 2 hours. The cooled mixture was poured into a saturated salt solution (2·5 l.) and the precipitated *sodium* salt (115 g.), which contained much sodium chloride, was crystallised from water and from aqueous alcohol (35%), being obtained as a yellow crystalline powder. It was dried at 100° for analysis (Found : Cl, 7·8; S, 13·0. $C_{17}H_7O_7ClS_2Na_2$ requires Cl, 7·6; S, 13·7%). The free sulphonic acid could not be crystallised. The *acid chloride*, prepared by the action of phosphorus pentachloride on the acid, crystallised from xylene–chloroform in fine yellow needles, m. p. 230—255°. Analysis showed it to be somewhat impure (Found : Cl, 21·9. $C_{17}H_7O_5Cl_3S_2$ requires Cl, 23·1%).

6 : 7-*Dichloro*meso*benzanthrone*-1′-*sulphonic Acid.*—A mixture of 6 : 7-dichloro*meso*benzanthrone (10 g.) and fuming sulphuric acid (SO_3 5% ; *d* 1·847 ; 100 g.) was heated in an oil-bath at 165—170° for 2 hours, and the cooled mixture poured into saturated salt solution (2 l.). The *sodium* salt was collected, washed with brine, and crystallised from aqueous alcohol, separating as a greenish-yellow crystalline powder (Found : Cl, 17·4; S, 7·7; Na, 5·8. $C_{17}H_7O_4Cl_2SNa$ requires Cl, 17·7; S, 8·0; Na, 5·7%).

1′ : 6 : 7-*Trichloro*meso*benzanthrone.*—(i) An intimate mixture of sodium 6 : 7-dichloro*meso*benzanthrone-1′-sulphonate (5 g.) and phosphorus pentachloride (5 g.) was heated on the water-bath for 3 hours. The mixture was extracted with hot xylene, and the filtered xylene solution boiled for 3 hours. After removal of the xylene in steam the dried residue (3·3 g.) was sublimed in a low vacuum, yielding a crystalline sublimate (0·6 g.), m. p. 295—300°. After repeated crystallisation from chlorobenzene, the *trichloro*-compound was obtained in fine yellow needles, m. p. 344—345°, raised to 349—350° on admixture with a specimen of the trichloride prepared as described below (Found : Cl, 32·1. $C_{17}H_7OCl_3$ requires Cl, 32·0%).

(ii) Chlorine was passed for 2 hours through a solution of 6 : 7-dichloro*meso*benzanthrone (0·7 g.) in acetic acid (250 c.c.) heated on the water-bath, and the heating continued for 6 hours. The trichloro-compound, which had separated, crystallised from chlorobenzene in yellow needles, m. p. 349—350° (Found : Cl, 32·1%).

6 : 7-*Dichloroanthraquinone*-1-*carboxylic Acid.*—(i) To a boiling solution of 6 : 7-dichloro*meso*benzanthrone (3 g.) in acetic acid (100 c.c.), a solution of chromic acid (15 g.) in acetic acid (50% ; 30 c.c.) was slowly added. After dilution with water the mixture was kept for 2 days, the precipitated solid collected, dissolved in hot aqueous ammonia, and filtered from chromium hydroxide, and the filtrate acidified. 6 : 7-*Dichloroanthraquinone*-1-*carboxylic acid* (0·85 g.) crystallised from acetic acid in pale yellow needles, m. p. 275—276° (Found : Cl, 21·7. $C_{15}H_6O_4Cl_2$ requires Cl, 22·2%). The *methyl* ester, prepared from the acid chloride, crystallised from methyl alcohol in pale yellow needles, m. p. 197—198° (Found : Cl, 21·1. $C_{16}H_8O_4Cl_2$ requires Cl, 21·2%).

(ii) To a boiling solution of sodium 6 : 7-dichloro*meso*benzanthrone-1′-sulphonate (2 g.) in acetic acid (15 c.c.), a solution of chromic acid (4 g.) in aqueous acetic acid (50% ; 15 c.c.) was gradually added. Water (200 c.c.) was added, the mixture kept for 2 days, and the precipitated acid (0·22 g.) purified as described above. It had m. p. 275—276° both alone and in admixture. The methyl ester had m. p. 197—198°.

1′-*Bromo*meso*benzanthrone*-6-*sulphonic Acid.*—A mixture of 1′-bromo*meso*benzanthrone (4 g.) and fuming sulphuric acid (SO_3 5% ; *d* 1·847; 40 g.) was heated in an oil-bath at 125—130° for 2 hours. The cooled solution was poured into ice-water (200 g.), white lead (85 g.) added with stirring to the hot mixture, and the precipitated lead sulphate removed. The *sodium* salt was precipitated as usual, and was obtained as a green crystalline powder after recrystallisation from water and aqueous alcohol. It was dried at 100° for analysis (Found : Br, 19·4; Na, 5·9. $C_{17}H_8O_4BrSNa$ requires Br, 19·5; Na, 5·6%). On oxidation with chromic acid it gave 6-sulphoanthraquinone-1-carboxylic acid, m. p. 271—274°, both alone and in admixture, the identity being confirmed by its conversion into methyl 6-chloroanthraquinone-1-carboxylate, m. p. 190—191°.

1′ : 6-*Dibromo*meso*benzanthrone.*—(i) Sodium 1′-bromo*meso*benzanthrone-6-sulphonate (15 g.) and phosphorus pentabromide (30 g.) were intimately mixed, and heated on the water-bath for 7 hours. After the addition of ice-water, the sulphonyl bromide (14·6 g.) was collected, dried, and heated under xylene at 155—160° for 5 hours. The xylene was removed in steam, and the dried residue (9·4 g.) sublimed in a low vacuum at 350—400°. The orange-yellow sublimate, m. p. 245—253°, was recrystallised from nitrobenzene, and the dibromo-compound obtained in yellow needles, m. p. 255—256°, both alone and in admixture with that prepared as described below (Rule and Smith, *loc. cit.*, give m. p. 255—256°).

(ii) To a well-stirred suspension of 1′-bromo*meso*benzanthrone (5 g.) in water (100 c.c.) at 40°, bromine (3 g.) was added during 1 hour, the mixture being then heated on the water-bath for 12 hours. The precipitated brownish-yellow solid (5·7 g.) crystallised from nitrobenzene in fine yellow needles, m. p. 256—257° (Found : Br, 41·0. Calc. for $C_{17}H_8OBr_2$: Br, 41·2%).

6-*Bromoanthraquinone*-1-*carboxylic Acid*.—To a boiling solution of 1′ : 6-dibromo*meso*benzanthrone (3 g.) in acetic acid (30 c.c.), a solution of chromic acid (9 g.) in aqueous acetic acid (50%; 30 c.c.) was gradually added. After dilution with water, the mixture was kept for 2 days, and the precipitated yellow solid (1·2 g.) collected; a further quantity (0·5 g.) was obtained from the filtrate after acidification with sulphuric acid and concentration. The crude acid was dissolved in aqueous ammonia, and the solution filtered from a little chromium hydroxide and acidified; the precipitated 6-*bromoanthraquinone*-1-*carboxylic acid* crystallised from acetic acid in fine pale yellow needles, m. p. 298—299° (Found : Br, 24·5. $C_{15}H_7O_4Br$ requires Br, 24·2%). The *methyl* ester, prepared from the acid chloride, crystallised from methyl alcohol in long yellow needles, m. p. 198—199° (Found : Br, 22·9. $C_{16}H_9O_4Br$ requires Br, 23·2%).

1′-*Nitro*meso*benzanthrone*-6-*sulphonic Acid*.—A mixture of 1′-nitro*meso*benzanthrone (4 g.) and fuming sulphuric acid (SO_3 5%; *d* 1·847; 40 g.) was heated in an oil-bath at 125—130° for 2 hours. The cooled mixture was poured into ice-water (100 g.), white lead (85 g.) added to the well-stirred hot mixture, the lead sulphate removed, and the concentrated filtrate added to a saturated salt solution (500 c.c.). The dark brown *sodium* salt, which separated, was re-crystallised from water and finally from aqueous alcohol, being obtained as a brown crystalline powder, which was dried at 100° for analysis (Found : S, 8·7; Na, 5·9. $C_{17}H_8O_6NSNa$ requires S, 8·5; Na, 6·1%). The salt dissolved in water to give a brownish-red solution, which became greenish-blue on dilution. On oxidation with chromic acid in the usual manner, 6-sulphoanthraquinone-1-carboxylic acid, m. p. 271—274°, was obtained, the identity of which was confirmed by its conversion into methyl 6-chloroanthraquinone-1-carboxylate, m. p. 189—190°.

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