342. *New Derivatives of* meso*Benzanthrone.*

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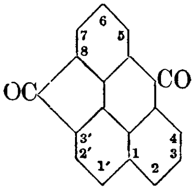
A study has been made of some of the more important reactions of 3′ : 8-keto*meso*benzanthrone and of the closely related *meso*benzanthrone-8-carboxylic acid and -3′-*carboxylic acid*, the last having now been prepared for the first time. All three compounds undergo halogenation and nitration primarily in position 1′; under vigorous treatment with bromine, ketobenzanthrone yields the 1′ : 6-dibromo-derivative.

In the 8- and 3′-carboxylic acids the nuclear hydrogen atoms in the adjacent 3′- and 8-positions are readily oxidised to hydroxyl with subsequent formation of lactones (*e.g.*, with excess of nitric acid, or bromine in nitrobenzene), a change which may be accompanied by substitution in position 1′. Unlike the 8-isomeride, benzanthrone-3′-carboxylic acid is oxidised by chromic acid to form anthraquinone-1-carboxylic acid.

Hydrazoic acid has been employed for the conversion of the 8-carboxylic acid into 8-*amino*meso*benzanthrone*, and of 3′ : 8-ketobenzanthrone into the related *lactam*, probably derived from 8-amino*meso*benzanthrone-3′-carboxylic acid. The latter is apparently identical with the lactam obtained from the 3′ : 8-ketoxime by Beckmann transformation. A different lactam appears to be formed on oxidising the 8-carboxylic acid amide with bromine in nitrobenzene. Dibenzanthrones have been prepared from a number of these derivatives by alkali fusion.

THE preparation of *meso*benzanthrone-8-carboxylic acid and of the 3′ : 8-keto*meso*benzanthrone (I) formed from it by ring closure have been described by Rule and co-workers (J., 1935, 571, 573). Although the ketonic bridge in fluorenone is comparatively stable towards aqueous alkali, the similar structure in keto*meso*benzanthrone slowly undergoes rupture to form the above 8-carboxylic acid, presumably admixed with its 3′-isomeride. Attempts to separate the acidic products of hydrolysis by crystallisation of the acids, their esters or their salts led only to the isolation of extremely small amounts of the known 8-carboxylic acid. Larger quantities of this compound (up to 25%) have now been obtained by esterifying the acid mixture and adsorbing the esters from benzene solution upon aluminium oxide, followed by systematic washing with benzene and fractionation according to the methods of chromatographic analysis (Rule and J. S. Flanders, unpublished). Under no conditions was it found possible to isolate the unknown 3′-carboxylic acid or its ester from such mixtures.

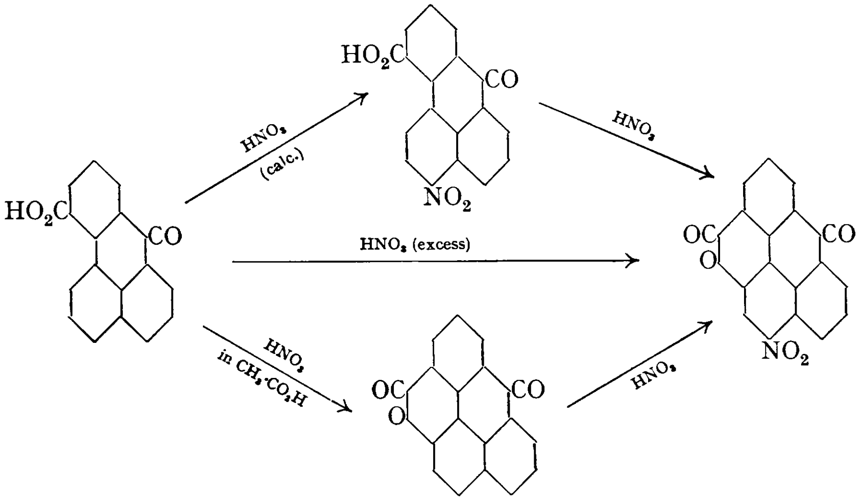


(I.)

meso*Benzanthrone*-3′-*carboxylic acid* has, however, been synthesised in small yield by the Ullmann reaction from methyl 1-bromo-2-naphthoate (new method of preparation), methyl *o*-iodobenzoate and copper-bronze. The main products were diphenic ester and dinaphthyl-ββ′-dicarboxylic ester, but fractional distillation, followed by sulphuric acid treatment, led to the isolation of the pure 3′-carboxylic acid, m. p. 285°, in about 5% yield. Confirmation of the structure of the acid is given by its quantitative conversion into 3′ : 8-keto*meso*benzanthrone on treatment with phosphoric oxide and by its decarboxylation to benzanthrone.

In general properties it strongly resembles the isomeric 8-carboxylic acid, but whereas oxidation with chromic acid converts the latter into the lactone of 3′-hydroxy*meso*benzanthrone-8-carboxylic acid (Grieve and Rule, J., 1937, 535), the former yields anthraquinone-1-carboxylic acid. There is strong evidence for believing that the lactone of the 8-hydroxy-3′-carboxylic acid is produced in the form of a nitro-derivative when the parent 3′-carboxylic acid is boiled with excess of nitric acid, since the yellow compound only dissolves slowly in boiling alkali, yielding a blue solution. The new acid was brominated under prolonged treatment to give 1′-*bromo*meso*benzanthrone*-3′-*carboxylic acid*. Hence, in comparison with *meso*benzanthrone itself, the introduction of the carboxyl group in position 3′ does not affect the primary point of attack, although the ease of substitution is greatly diminished.

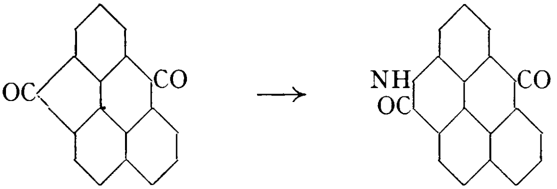
*meso*Benzanthrone-8-carboxylic acid was also found to undergo halogenation somewhat slowly, to form 1′-*chloro*meso*benzanthrone*-8-*carboxylic acid* and the related 1′-bromo-acid, the structure of the former being established by decarboxylation to the known 1′-chlorobenzanthrone. A characteristic property of benzanthrone-8-carboxylic acid is its tendency to undergo oxidation in position 3′ to yield the lactone of the 3′-hydroxy-acid. Thus when it was boiled with a solution of bromine in nitrobenzene, only oxidation occurred and the bromine-free lactone was isolated in high yield, no change being observed with nitrobenzene alone. A similar tendency is found in the reactions of the acid towards nitric acid. With the calculated amount of nitric acid in cold sulphuric acid, the product is 1′-nitro*meso*benzanthrone-8-carboxylic acid, but with excess of boiling nitric acid oxidation also occurs to form the *lactone* of *1′-nitro-3′-hydroxy*meso*benzanthrone-8-carboxylic acid* (soluble in alkali to a purple solution). On the other hand, if excess of nitric acid in boiling acetic acid is employed, oxidation alone takes place to give the un-nitrated lactone. These reactions are summarised in the scheme :



A change of a different kind is the conversion of the 8-carboxylic acid into *8-amino-*meso*benzanthrone* by direct replacement of the carboxyl by an amino-group, which is readily effected by use of hydrazoic acid. The red amino-compound is a very weak base, and does not form salts with aqueous acids. It could be diazotised and coupled with β-naphthol to give an azo-dye, and on fusion with sodium hydroxide yielded a blue-black vat dye of dibenzanthrone type.

3′ : 8-Keto*meso*benzanthrone underwent chlorination and bromination in acid aqueous suspension somewhat more readily than the above carboxylic acids, the halogen attacking position 1′ to form *1′-chloro-3′ : 8-keto*meso*benzanthrone* or the corresponding bromo-compound. Longer treatment under these conditions with chlorine led to the production of a mixture of isomeric dichloro-derivatives, but use of liquid bromine gave rise to the pure 1′ : 6-dibromo-compound in good yield. Interaction between the keto-compound and nitric acid at low temperatures resulted in the formation of 1′-nitroketobenzanthrone. Under more vigorous treatment, nitration was accompanied by rupture of the ketonic ring and oxidation to nitrated lactones of the isomeric hydroxy-acids. It has been found that keto*meso*benzanthrone forms a stable *molecular compound*, m. p. 322°, with nitrobenzene.

Following the successful use of hydrazoic acid for converting the 8-carboxylic acid into the corresponding amine, this reagent was employed in the presence of sulphuric acid for effecting the transformation of ketobenzanthrone into the related *anthridone* or lactam (cf. Walls, J., 1935, 1405). The compound (possibly of structure II; see below) was obtained as an extremely sparingly soluble, yellow powder having no melting point below 360°. It was formed in high yield, but the actual arrangement of the CO and NH groups in the expanded ring could not be established with certainty. Apparently the same product was formed when meso*benzanthrone-3′ : 8-ketoxime* was submitted to the Beckmann change using phosphorus pentachloride in anisole. In view of the suggestion made by Schmidt (*Ber.*, 1924, **57**, 704) and by Walls that the ketone–anthridone conversion brought about by means of hydrazoic acid is akin to a Beckmann change it may be noted that the above oxime could not be made to undergo the rearrangement with sulphuric acid as agent, indicating that some mechanism other than the Beckmann change is in operation (see also Spielman and Austin, *J. Amer. Chem. Soc.*, 1937, **59**, 2658). Fusion of the oxime with zinc chloride at 280°, a procedure employed by Pictet and Gonset (*Chem. Zentr.*, 1897, I, 413) and by Moore and Huntress (*J. Amer. Chem. Soc.*, 1927, **49**, 2618) for the conversion of fluorenoneoxime into phenanthridone, led in the present case to hydrolysis of the oxime.



(II.)

In the hope of obtaining some evidence bearing upon the structure of the above anthridone, an attempt was made to effect the cyclisation of the CO·NH$_2$ group in the *amide* of meso*benzanthrone*-8-*carboxylic acid* by the use of sodium hypobromite. The compound remained unaffected by the treatment, but after it had been heated with bromine in nitrobenzene the cooled liquid deposited yellow-green needles, which in respect of their analytical data, high melting point (> 360°), extreme insolubility and stability to alkali are concluded to consist of the anthridone in question. As has already been mentioned above, treatment with bromine in nitrobenzene converts the free acid into the lactone of the 3′-hydroxy-acid; and by analogy the acid amide may be expected to yield the lactam. The product obtained from ketobenzanthrone or its oxime, however, differed slightly in appearance and colour reactions from that prepared from the amide. Since the latter, if it is of the lactam type, must be that of a 3′-amino-8-carboxylic acid, the former is provisionally assigned the isomeric 8-amino-3′-carboxylic structure. On fusing the lactam obtained from ketobenzanthrone with sodium hydroxide at 280°, a very sparingly soluble blue-black vat dye was obtained, which dyed cotton a fast purple-grey colour.

During preliminary work in the preparation of *meso*benzanthrone-3′-carboxylic acid a portion of the resulting fluorenonecarboxylic acid (see below) was nitrated in the belief that it was a benzanthrone derivative, and in an attempt to orient the product 3-*nitro*-meso*benzanthrone*-8-*carboxylic acid* was synthesised from methyl 8-bromo-3-nitro-1-naphthoate and methyl *o*-iodobenzoate in the presence of copper-bronze. This acid was further cyclised to 3-*nitro*-3′ : 8-*keto*meso*benzanthrone* and decarboxylated to 3-*nitro*meso*benzanthrone*.

EXPERIMENTAL.

meso*Benzanthrone*-3′-*carboxylic Acid*.—1-Bromo-2-naphthylamine hydrochloride (50 g., prepared according to Franzen and Eidis, *J. pr. Chem.*, 1913, **88**, 755) was finely powdered, suspended in a mixture of water (150 c.c.) and concentrated hydrochloric acid (50 c.c.), and treated with a slight excess of sodium nitrite solution (20 g. in 25 c.c. of water) at 0—5°. The clear diazo-solution was added in portions with vigorous stirring to a cuprous cyanide solution, obtained by mixing solutions of sodium cyanide (120 g. in 300 c.c. of water) and of copper sulphate (100 g. of $CuSO_4,5H_2O$ in 400 c.c. of water) and filtration from a trace of sediment. A brown precipitate formed, which after 3 hours' further heating and stirring changed into brown oily drops of nitrile. After standing overnight, the solidified nitrile was removed and heated under reflux for 24 hours with a mixture of acetic acid (400 c.c.), sulphuric acid (200 c.c.), and water (100 c.c.). On pouring into 2 l. of water, crude 1-bromo-2-naphthoic acid separated; it was digested with aqueous alkali at 50° for a few minutes, and the filtered solution acidified. The yield of light brown acid, m. p. 187—189°, was 21 g. (43%). A portion crystallised from benzene gave colourless needles, m. p. 191° (Mayer and Sieglitz, *Ber.*, 1922, **55**, 1859, record m. p. 186° for the acid prepared by oxidising the corresponding aldehyde).

The crude acid (15 g.) from hydrolysis of the nitrile was esterified by use of thionyl chloride and methyl alcohol, giving *methyl* 1-*bromo*-2-*naphthoate* (14 g., 90%), m. p. 58—59°. Another crystallisation from light petroleum afforded colourless plates, m. p. 60° (Found: Br, 30·0. $C_{12}H_9O_2Br$ requires Br, 30·2%).

Attempts to couple methyl 1-bromo-2-naphthoate (25 g.) with methyl *o*-iodobenzoate (50 g.) in presence of copper-bronze (30 g.) at 175—180° gave a mixture from which no solid esters could be isolated. Heating this with sulphuric acid, followed by dilution with water, gave a mixture of solids from which only diphenic acid, anthanthrone and fluorenone-4-carboxylic acid could be obtained, although the occurrence of a small proportion of *meso*benzanthrone-3′-carboxylic acid was indicated by the isolation by chemical changes of small amounts of *meso*benzanthrone and of keto*meso*benzanthrone from the crude fluorenone-4-carboxylic acid. The bulk of the latter acid could be precipitated by means of dinitrophenylhydrazine, but this reaction was not quantitative and no specimen of benzanthrone-3′-carboxylic acid could be prepared in this manner.

The crude mixed esters from another Ullmann reaction were therefore fractionated under 12 mm. pressure through a column. At 195—200° the bulk of the diphenic ester distilled (m. p. 73—74°), most of the product which gives rise to fluorenonecarboxylic acid thus being removed. The second fraction, b. p. 225—240°, was a yellow viscid liquid, which after treatment with sulphuric acid and dilution with water gave a brown solid. The latter was digested with alkali, and the filtered solution acidified. The crude acid (4·5 g.), m. p. 234—239°, obtained still contained a considerable proportion of fluorenonecarboxylic acid. It was boiled with chlorobenzene (150 c.c.) for 10 mins., the filtrate depositing on cooling fluorenonecarboxylic acid; the light brown undissolved portion (1·02 g.) melted at 272—273°, and on crystallisation from nitrobenzene afforded 0·85 g. (3%) of meso*benzanthrone*-3′-*carboxylic acid*, m. p. 283—284°, raised to 285° by further crystallisation (Found: C, 78·8; H, 3·8. $C_{19}H_{10}O_3$ requires C, 78·8; H, 3·7%). The acid dissolves readily in alkalis, forming deep yellow solutions, with bright green fluorescence. In concentrated sulphuric acid the solution is red with green fluorescence.

Owing to the difficulty of obtaining this acid, only the following brief examination of its reactions was undertaken. (a) When 0·1 g. in phthalic anhydride (5 g.) was maintained for 2 hours at 200° with addition of phosphoric oxide (0·2 g.), keto*meso*benzanthrone (0·084 g.; 90%) was obtained, m. p. and mixed m. p. 327—328°. (b) Decarboxylation of the crude acid with quinoline and copper-bronze led to the isolation of *meso*benzanthrone, m. p. and mixed m. p. 171—172°. (c) The acid (0·1 g.) was dissolved in sulphuric acid (3 c.c.), and water (10 c.c.) added. The resulting fine suspension was treated in portions with chromic acid and boiled under reflux for 6 hours. Dilution with water threw down a brown precipitate (0·055 g.; 64%), m. p. 287—290°, which on crystallisation from alcohol afforded fine colourless needles, m. p. 293—294°, not depressed by admixture with anthraquinone-1-carboxylic acid. (d) A suspension prepared from the acid (0·3 g.), sulphuric acid (3 c.c.), and water (25 c.c.) was treated with bromine (1·5 g.) and maintained at the b. p. for 6 hours. The excess of bromine was distilled off, and the orange solid separated. Yield, 0·37 g. (96%), m. p. 305—308°. Two crystallisations from nitrobenzene afforded fine yellow needles of pure 1′-*bromo*-meso*benzanthrone*-3′-*carboxylic acid*, m. p. 319—320°; yield, 0·2 g. (51%) (Found: Br, 22·5. $C_{18}H_9O_3Br$ requires Br, 22·6%). The acid dissolves in alkalis to form yellow solutions with vivid green fluorescence; in concentrated sulphuric acid it gives a purple solution with greenish fluorescence. The position of the bromine atom was established by treating the compound with phosphoric oxide and phthalic anhydride at 200°; an almost quantitative yield was then obtained of 1′-bromo-3′ : 8-keto*meso*benzanthrone, m. p. 323—325° (confirmed by mixed m. p. and its colour reaction in sulphuric acid; see below). (e) *meso*Benzanthrone-3′-carboxylic acid (0·1 g.) was dissolved in concentrated nitric acid (2 c.c.) and heated to the b. p. for 15 mins. Water was added, and the precipitated solid recrystallised thrice from acetic acid, giving fine yellow needles, m. p. 256—257°. These contained nitrogen and dissolved *slowly* in alkali to form a pure blue non-fluorescent solution, suggesting that the product was probably a nitrated *lactone* of 8-hydroxy*meso*benzanthrone-3′-carboxylic acid (Found: C, 67·3; H, 2·4; N, 4·7. $C_{18}H_7O_5N$ requires C, 68·1; H, 2·2; N, 4·4%). Owing to lack of material no further examination was made.

meso*Benzanthrone*-8-*carboxylic Acid*.—The acid was prepared according to the method of Rule and co-workers (J., 1935, 571, 573) and the following reactions were carried out.

Chlorination. The acid (0·5 g.) was dissolved in sulphuric acid (5 c.c.), and water (25 c.c.) added. A slow stream of chlorine was passed into the boiling fine suspension for 4 hours. The resulting yellow solid crystallised from nitrobenzene in stout yellow needles of 1′-*chloro*-meso*benzanthrone*-8-*carboxylic acid* (0·42 g., 74%), m. p. 317—318° (Found: Cl, 11·3. $C_{18}H_9O_3Cl$ requires Cl, 11·5%). The acid dissolves in alkalis to yellow solutions with vivid green fluorescence; in sulphuric acid the solution is bright red with green fluorescence.

Decarboxylation by copper and quinoline afforded, after recrystallisation from chlorobenzene, light brown needles of 1′-chloro*meso*benzanthrone (56% yield), m. p. and mixed m. p. 184°. The chlorine atom in the acid therefore occupies the 1′-position.

Bromination. This could not be effected under the conditions recommended for benzanthrone itself in D.R.-P. 193,959 (*Chem. Zentr.*, 1908, I, 1112), namely, by boiling an aqueous suspension with bromine for 1 hour, but when a suspension in dilute sulphuric acid was treated with excess of bromine and maintained at the b. p. for 5 hours, the product after crystallisation from nitrobenzene gave yellow needles of 1′-bromo*meso*benzanthrone-8-carboxylic acid in 70% yield; m. p. 315—316° (sintering at 305°), alone or admixed with the synthetic 1′-bromo-acid of Rule and Smith (J., 1937, 1101).

When *meso*benzanthrone-8-carboxylic acid was heated with bromine in boiling nitrobenzene for 3 hours, a high yield (60%) of the lactone of 3′-hydroxy*meso*benzanthrone-8-carboxylic acid was isolated. With boiling nitrobenzene alone the starting material was recovered unchanged.

Nitration. A solution of *meso*benzanthrone-8-carboxylic acid (1·5 g.) and concentrated sulphuric acid (30 c.c.) was cooled to 0°, and a cooled solution of nitric acid (*d* 1·42; 0·42 c.c.) in concentrated sulphuric acid (5 c.c.) added with stirring. The colour gradually changed from red to orange and after 15 mins. the solution was poured into water (200 c.c.) and made alkaline with sodium hydroxide. The purple colour was then just discharged from the alkaline solution by careful acidification, and the precipitated nitro-lactone filtered off, leaving an orange non-fluorescent solution. Acidification of the latter precipitated yellow 1′-nitro*meso*benzanthrone-8-carboxylic acid (1·30 g.), m. p. 292—295° (decomp.), raised to m. p. 310° (yield, 50%) after two crystallisations from nitrobenzene. It was identified by mixed m. p. and colour reactions with the synthetic product of Rule and Smith (*loc. cit.*, p. 1102).

A larger proportion of nitric acid than the above, or a higher temperature, increases the yield of nitro-lactone. Thus 0·5 g. of the 8-carboxylic acid and 10 c.c. of concentrated nitric acid, after boiling for 15 minutes, gave a product which, twice recrystallised from acetic acid, afforded yellow needles (0·36 g.; 62%), m. p. 317—318° (decomp.), of the *lactone* of 1′-*nitro*-3′-*hydroxy*meso*benzanthrone*-8-*carboxylic acid* (Found: N, 4·4. $C_{18}H_7O_5N$ requires N, 4·4%). The same compound was obtained (a) by nitrating the lactone of the 3′-hydroxy-acid under the above conditions and (b) by oxidising 1′-nitro*meso*benzanthrone-8-carboxylic acid with chromic acid (60% yield). The nitro-lactone dissolves in aqueous alkali on boiling, forming a purple non-fluorescent solution; in concentrated sulphuric acid the solution is orange and non-fluorescent. An attempt to nitrate *meso*benzanthrone-8-carboxylic acid with excess of concentrated nitric acid in boiling acetic acid solution led only to the isolation of the un-nitrated lactone of 3′-hydroxy*meso*benzanthrone-8-carboxylic acid in 46% yield.

Conversion into 8-*amino*meso*benzanthrone.* Benzanthrone-8-carboxylic acid (4 g.), in sulphuric acid (25 c.c.) with addition of chloroform (100 c.c.), was treated at 45—50° with sodium azide (4·4 g.), added in portions with stirring during 2 hours. The reddish precipitate obtained when the mixture was poured into water was boiled out with aqueous sodium hydroxide to remove a little unchanged acid and the remaining solid was filtered off. Yield, 3·04 g.; m. p. 207—211°. Crystallisation from alcohol gave dark red needles of 8-*amino*meso*benzanthrone*, m. p. 215—217° (Found: C, 82·9; H, 4·5; N, 5·8. $C_{17}H_{11}ON$ requires C, 83·3; H, 4·5; N, 5·7%). The amine dissolves sparingly in boiling alcohol, and less readily in benzene and ethyl acetate. In sulphuric acid the solution is blood-red with yellowish fluorescence. It is not appreciably soluble in dilute mineral acids, although the colour of the solid changes from red to orange-yellow owing to surface salt formation. When the amine is diazotised in acetic acid by use of sodium nitrite in concentrated sulphuric acid, and added to an alkaline solution of β-naphthol, a red azo-dye is precipitated.

With formic acid at the b. p. (20 mins.) the amine afforded 8-*formamido*meso*benzanthrone*, which separated from alcohol in golden-yellow needles, m. p. 268—271°, insoluble in alkalis and yielding in sulphuric acid a blood-red solution without fluoresence (Found: C, 78·6; H, 4·4; N, 5·2. $C_{18}H_{11}O_2N$ requires C, 79·1; H, 4·2; N, 5·1%). Short treatment with acetic anhydride converted the amine into 8-*acetamido*meso*benzanthrone*, which crystallised from alcohol in yellow needles, m. p. 278—279°, sparingly soluble in alcohol, acetic acid, and benzene (Found: N, 4·6. $C_{19}H_{13}O_2N$ requires N, 4·9%).

Fusion of the amine (0·5 g.) with potassium hydroxide (4 g.) at 220° for 30 mins. gave a bluish melt, which was boiled out with water and filtered. The alkali-insoluble material (0·43 g.) consisted of a blue-black powder, with no m. p. below 360°. It was extracted with hot alcohol to remove any unchanged starting material and then dissolved in boiling nitrobenzene, subsequent addition of light petroleum throwing down 0·12 g. of a dark blue-black micro-crystalline product, presumably of *diaminodibenzanthrone* (Found: N, 6·0. $C_{34}H_{18}O_2N_2$ requires N, 5·8%). It was extremely sparingly soluble in aqueous alkaline hyposulphite; the faintly green vat (blue fluorescence) dyed cotton a fast pale grey-green colour. In sulphuric acid the diamino-compound dissolved to a brown solution with green fluorescence.

meso*Benzanthrone*-8-*carboxyamide* was prepared by interaction of the acid chloride with concentrated aqueous ammonia. It separated from nitrobenzene in yellow needles, soluble in sulphuric acid to form a blood-red solution with yellowish fluorescence (Found : C, 78·2; H, 4·2; N, 5·2. $C_{18}H_{11}O_2N$ requires C, 79·1; H, 4·0; N, 5·1%). In the melting point tube the amide sinters at 300—310°, softens at 320°, and melts at 325—327°. Fusion is followed by resolidification at 327—330° with no further change up to 360°. On occasion a little gas evolution was noted about 325° and 330°. The product so obtained is a mixture which no longer dissolves in sulphuric acid with red coloration, but gives a brown colour with vivid green fluorescence. The amide could only be hydrolysed effectively by use of nitrous acid, yielding the free acid together with about 25% of the lactone of the 3′-hydroxy-acid.

Ring closure of the amide to the related lactam was attempted in three ways : (a) The amide (1 g.) was dissolved in sulphuric acid (10 c.c.), and an equal volume of water added. The mixture was treated with chromic acid (1·4 g.) and kept at the b. p. for 2 hours. The dried precipitate melted at 351—354° (0·78 g.), raised after crystallisation from acetic acid to 356—357° (0·46 g.) alone or admixed with the lactone of the 3′-hydroxy-acid. It was slowly but almost completely soluble in warm alkali to a purple fluorescent solution. No other product could be isolated. (b) The amide (0·5 g.) freshly pasted from sulphuric acid, was boiled for 8 hours with N-sodium hydroxide (10 c.c.) to which bromine (0·1 c.c.) had been added. The amide was recovered unchanged. (c) The amide (0·5 g.) freshly pasted and dried, was boiled for 3 hours with bromine (0·1 c.c.) in nitrobenzene (50 c.c.). Yellow needles were deposited (0·26 g.) having no m. p. below 360° : they were insoluble in alkali and dissolved in sulphuric acid to a yellow solution with green fluorescence (the original amide gives a deep red solution). The compound was very sparingly soluble in organic solvents (*e.g.*, 0·25 g. dissolved in 160 c.c. of boiling nitrobenzene) and contained nitrogen but no halogen. Analysis of the product twice recrystallised from nitrobenzene gave figures, especially the critical hydrogen values, in agreement with the *lactam* of 3′-*amino*meso*benzanthrone*-8-*carboxylic acid* (Found * : C, 78·8; H, 3·3; N, 5·3. $C_{18}H_9O_2N$ requires C, 79·7; H, 3·3; N, 5·2%). Under the above treatment the free acid yields the corresponding lactone of the hydroxy-acid.

3′ : 8-*Keto*meso*benzanthrone*.—*Chlorination*. The ketone (0·5 g., prepared according to Bigelow and Rule, J., 1935, 573) was dissolved in warm sulphuric acid (5 c.c.), and a fine suspension formed by addition of water (25 c.c.). This was treated at the b. p. for 3 hours with a slow stream of chlorine. Filtration, followed by two crystallisations from acetic acid or chlorobenzene, gave red needles of 1′-*chloro*-3′ : 8-*keto*meso*benzanthrone*, m. p. 335—336° (sintering at 245°). Yield, 0·36 g. (67%) (Found : Cl, 12·2. $C_{18}H_7O_2Cl$ requires Cl, 12·3%). This product was identical with that obtained by cyclising the 1′-chloro*meso*benzanthrone-8-carboxylic acid described above, the position of the chlorine atom thus being established. It dissolved in sulphuric acid to a reddish-purple solution. Sintering at a temperature considerably below the m. p. appears to be a characteristic of compounds of this type (cf. Rule and Smith, *loc. cit.*).

The same substance was also obtained by passing a slow stream of chlorine into an acetic acid solution of the keto-compound (0·5 g. in 25 c.c.) at 100°. An orange precipitate appeared after 5 mins., and chlorination was stopped after 10 mins. When chlorine was passed in for 1 hour, the solid assumed a redder tint (yield, 0·48 g.) and melted over the range 334—339°, not appreciably altered by repeated crystallisation from nitrobenzene nor depressed by admixture with the 1′-chloro-compound. This product appeared to be a mixture of isomeric *dichloro*-3′ : 8-*keto*meso*benzanthrones*. It was only slightly soluble in acetic acid, but dissolved in sulphuric acid to give a purple solution, changing to blue on further dilution with the solvent (Found : Cl, 21·3. $C_{18}H_6O_2Cl_2$ requires Cl, 21·8%).

Bromination. This could not be effected in boiling acetic acid or in nitrobenzene solution. The keto-compound (1 g.), in fine suspension in dilute sulphuric acid, was treated with excess of bromine (1 g.), and the mixture maintained at the b. p. for 4 hours. Recrystallisation from acetic acid afforded bright red needles of 1′-bromo-3′ : 8-keto*meso*benzanthrone, m. p. 326—327° (sintering at 200°) alone or mixed with the synthetic product of Rule and Smith (*loc. cit.*). The yield was almost quantitative.

3′ : 8-Keto*meso*benzanthrone (0·5 g.) was boiled at 50—60° for 2 hours with excess of bromine. The recovered solid after five crystallisations from nitrobenzene gave small, deep red crystals

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* Difficulty has often been encountered in obtaining good carbon analyses for benzanthrone derivatives, although hydrogen and nitrogen are readily determined with accuracy. The tendency is for carbon to be found low.

(0·40 g., 48%) of pure 1′ : 6-dibromo-3′ : 8-keto*meso*benzanthrone, m. p. 298—299° alone or admixed with the synthetic compound (Rule and Smith, *loc. cit.*).

Nitration. A solution of keto*meso*benzanthrone (0·5 g.) in sulphuric acid (15 c.c.) was cooled, and 0·14 c.c. (1 mol.) of concentrated nitric acid (*d* 1·42) added with stirring. The purple solution rapidly changed to deep orange and after 15 mins. was poured into water (100 c.c.). The resulting solid, after three crystallisations from nitrobenzene, gave greenish-yellow needles of pure 1′-nitro-3′ : 8-keto*meso*benzanthrone (0·16 g., 27%), m. p. 284—285° alone or admixed with a synthetic specimen.

When nitrated with excess of boiling nitric acid, the original keto-compound afforded an inseparable mixture, which dissolved in alkali only on boiling, to form a purple solution without fluorescence. This possibly consisted of a mixture of nitro-derivatives of the lactones of 3′-hydroxy-8-carboxy- and of 8-hydroxy-3′-carboxy-*meso*benzanthrones.

An attempt to effect the nitration of keto*meso*benzanthrone in acetic acid, under conditions under which *meso*benzanthrone yields the 2′-nitro-derivative, left the compound unchanged even after prolonged treatment.

Oxime formation. A boiling suspension of keto*meso*benzanthrone (3 g.) in alcohol (500 c.c.) was treated with hydroxylamine hydrochloride (1·62 g.) and 2N-sodium hydroxide (30 c.c.) was then run in slowly. Most of the ketone passed into solution, the colour of which changed from orange to deep red. After filtration of unchanged ketone (0·8 g.), the clear liquid was acidified, and the precipitate collected (2·5 g., m. p. 307—313°). Purification was best effected from boiling decalin or xylene (100 c.c./0·2 g.), subsequent addition of light petroleum yielding orange microcrystalline needles of meso*benzanthrone*-3′ : 8-*ketoxime*, m. p. 314°, unchanged by sublimation under reduced pressure (Found : C, 78·8; H, 3·5; N, 4·7. $C_{18}H_9O_2N$ requires C, 79·7; H, 3·3; N, 5·1%). The oxime is soluble in boiling alkali to form a deep pink solution with orange fluorescence. In sulphuric acid the colour is purple, as for the parent ketone. Attempts to crystallise the crude oxime from boiling nitrobenzene, particularly with addition of animal charcoal, led to partial hydrolysis and the isolation of orange brown needles of a *compound* containing equimolecular proportions of keto*meso*benzanthrone and nitrobenzene, m. p. 322°, depressed to 299—311° by admixture with the oxime but only slightly affected by admixture with keto*meso*benzanthrone (Found : C, 76·1; H, 3·5; N, 3·9. $C_{18}H_8O_2,C_6H_5O_2N$ requires C, 76·0; H, 3·4; N, 3·7%). Nitrobenzene was eliminated quantitatively from this compound on heating for 2 hours at 220°. Unsuccessful attempts were made to prepare an isomeric oxime.

Keto*meso*benzanthrone was converted by two methods into a related anthridone : (a) The oxime (0·5 g.) was dissolved in anisole (150 c.c.) and treated for 5 hours at 75° with phosphorus pentachloride (0·5 g.). Removal of anisole in steam left a yellow solid, which was boiled out with alkali (only a trace removed) and purified from nitrobenzene, yielding 0·12 g. of a yellow microcrystalline powder having no m. p. below 360°. The product is assumed to be the *lactam* either of 8-*amino*meso*benzanthrone*-3′-*carboxylic acid*, or of the isomeric 3′ : 8-derivative (Found : N, 5·0. $C_{18}H_9O_2N$ requires N, 5·2%). Attempts to effect the change by use of benzenesulphonyl chloride or sulphuric acid or by fusion with zinc chloride (cf. Moore and Huntress, *J. Amer. Chem. Soc.*, 1927, **49**, 2618) were unsuccessful. (b) Apparently the same compound was formed in much greater yield by the method of Walls (J., 1935, 1405) for the conversion of fluorenones into phenanthridones. A solution of 3′ : 8-keto*meso*benzanthrone (0·5 g.) in sulphuric acid (5 c.c.) was cooled in ice, and solution of sodium azide (0·5 g.) added drop by drop with stirring. A vigorous evolution of nitrogen occurred and after 30 mins. the mixture was poured into water and the precipitated light brown solid (0·53 g.) filtered off. After a trace of alkali-soluble material had been extracted with boiling acetic acid, the yellow undissolved residue was crystallised from nitrobenzene. Yield, 0·38 g., with no m. p. below 360° (Found : C, 79·0; H, 3·4; N, 5·4. $C_{18}H_9O_2N$ requires C, 79·7; H, 3·3; N, 5·2%). This compound gave the same colour reactions as that prepared from the oxime. It dissolves in sulphuric acid to form a red solution with orange fluorescence. With aqueous alkali the yellow colour changes to red and a trace of solid passes into solution on boiling (orange to pink colour with pink fluorescence); the yellow colour is restored by washing the red salt (?) with water or by treatment with acid. Benzanthrone itself remains unaffected by treatment with hydrazoic acid under the above conditions.

On fusion with potassium hydroxide for 1 hour at 280° the anthridone (from *b*) afforded a blue-black powder. This was extracted in succession with boiling nitrobenzene and alcohol, and finally with alkali solution, the last of which removed a small amount of an acidic blue-black product probably of phenolic type (cf. Maki, *J. Soc. Chem. Ind., Japan*, 1932, **35**, 579B).

The remaining solid was assumed to be the crude dilactam of dibenzanthrone type. It was difficult to purify and to analyse (Found: N, 3·35. $C_{36}H_{14}O_4N_2$ requires N, 5·2%). It dissolves in sulphuric acid to a greenish-blue solution and very sparingly in boiling nitrobenzene to a green solution without fluorescence. In hot alkaline hyposulphite it dissolves very sparingly to form a bluish-green vat, which dyes cotton a fast soft purple-grey colour.

Synthesis of 3-*Nitro*meso*benzanthrone*.—Methyl 8-bromo-3-nitro-1-naphthoate (20 g.) and methyl *o*-iodobenzoate (40 g.) were heated with stirring at 160°, and copper-bronze (25 g.) added in portions during 1 hour. After a further 3 hours' heating at 180°, the melt was cooled and extracted with acetone (200 c.c.). On removal of the solvent and addition of ether (25 c.c.) a light brown, crystalline precipitate slowly formed, which separated from alcohol in yellow needles, m. p. 141—142° (9·4 g., 40%). The pure *methyl* 3-*nitro*-8-(o-*carbomethoxyphenyl*)-1-*naphthoate* melts at 143° (Found: C, 65·6; H, 4·0; N, 3·7. $C_{20}H_{15}O_6N$ requires C, 65·8; H, 4·1; N, 3·8%). A preliminary attempt to cyclise this ester to the benzanthrone by heating for 1 hour at 100° with sulphuric acid gave a high-melting solid which was insoluble in the usual solvents. On prolonged boiling with dilute alkali solution it was converted into 3-*nitro*-meso*benzanthrone*-8-*carboxylic acid*, and thus appears to be the anhydride of this acid. The free acid was formed in better yield when the ester (2 g.) was treated with sulphuric acid for 30 mins. at 80°. Yield, 1·72 g. (98%); m. p. 298—301° (decomp.). Recrystallisation from nitrobenzene afforded yellow needles of the pure nitro-acid, m. p. 309° (decomp.) (Found: N, 4·0. $C_{18}H_9O_5N$ requires N, 4·4%). The compound dissolves in alkalis to give yellow non-fluorescent solutions and in sulphuric acid to form a blood-red solution also without fluorescence. Admixed with the 1′-nitro-isomeride (m. p. 310° decomp.) the m. p. is depressed to 288—291°.

By use of boiling quinoline and copper-bronze the acid was decarboxylated to 3-*nitro*meso*benzanthrone*, which formed fine brown needles, m. p. 287°, from acetic acid; yield, 40% (Found: C, 73·8; H, 3·2; N, 5·3. $C_{17}H_9O_3N$ requires C, 74·2; H, 3·3; N, 5·1%). It is soluble in sulphuric acid to a red non-fluorescent solution and is not appreciably attacked by alkaline hyposulphite. Treatment with phosphoric oxide in phthalic anhydride converted the free acid largely into the same insoluble high-melting compound (assumed to be the anhydride) as was encountered in the cyclisation of the phenyl-naphthyl derivative into the benzanthrone by use of sulphuric acid. This reduced the yield of 3-*nitro*-3′ : 8-*keto*meso*benzanthrone* to 13%. The compound crystallised from nitrobenzene in fine orange needles, m. p. 319—320° (Found: N, 4·3. $C_{18}H_7O_4N$ requires N, 4·6%).

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