232. *Kationoid Reactivity of Aromatic Compounds. Part VI. The Direct Amination of* meso*Benzanthrone.*

By WILLIAM BRADLEY.

The experiments of Part III (*J.*, 1937, 1091) have been extended to include a study of the direct amination of *meso*benzanthrone. Amination occurs when *meso*benzanthrone is heated in dimethylaniline solution with sodamide and oxygen. The principal products of the reaction are *6-amino*meso*benzanthrone*,* 6-hydroxy*meso*benzanthrone and 6 : 6′-*di*meso*benzanthronylamine*. Indications are obtained of the formation of small amounts of 4-substituted *meso*benzanthrones. The mechanism of these reactions is discussed. The application of the sodamide–oxygen and sodamide–piperidine–oxygen reagents to various types of ketones is described. With the piperidine reagent, anthanthrone yields mainly a *dipiperidino*-derivative.

THE direct replacement of hydrogen attached to an aromatic nucleus by the amino-group has been accomplished in several ways. Graebe (*Ber.*, 1901, **34**, 1178) obtained amines in poor yield by treating aromatic hydrocarbons with hydroxylamine hydrochloride in the presence of anhydrous aluminium chloride. De Turski (D.R.-P. 287,756), using a solution of hydroxylamine and ferrous sulphate in concentrated sulphuric acid, converted anthraquinone, benzophenone, and xanthone into related amino-compounds. Using sodamide at 205—235°, Sachs (*Ber.*, 1906, **39**, 3006) obtained 1 : 5-aminonaphthol from α-naphthol, 5-amino-2-naphthol from β-naphthol, 1 : 5-naphthylenediamine from α-naphthylamine, and 2 : 5-naphthylenediamine from β-naphthylamine. A particularly easy replacement of nuclear hydrogen occurs when certain aromatic nitro-compounds are treated with hydroxylamine in alcoholic alkaline solution (cf. *J.*, 1932, 1254). Angeli (*Gazzetta*, 1901, **31**, 27) prepared 4-nitro-1-naphthylamine from α-nitronaphthalene, and later, Meisenheimer and Patzig (*Ber.*, 1906, **39**, 3534) obtained 2-nitro-1-naphthylamine from β-nitronaphthalene, and a mixture of 2 : 4-dinitroaniline and 4 : 6-dinitro-*m*-phenylenediamine from *m*-dinitrobenzene. Further, heating with sodamide transforms many bases of the pyridine–quinoline series into the corresponding amino-derivatives. Pyridine itself affords both α-amino- and αα′-diamino-pyridine (Tschitschibabin and Seide, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1216; 1920, **50**, 522), *iso*quinoline affords 1-amino*iso*quinoline (Tschitschibabin and Oparina, *ibid.*, p. 543), and quinoline, α-aminoquinoline (Tschitschibabin and Sazepina, *ibid.*, p. 553).

In other instances aromatic amines have been obtained by adding the elements of ammonia to compounds having the character of quinones. For example, indanthroneazine reacts additively with ammonia to form 4-aminoindanthrone (Scholl and Berblinger, *Ber.*, 1903, **36**, 3438).

Attention has recently been directed to the readiness with which *meso*benzanthrone reacts with such reagents as piperidine, potassium hydroxide, and the Grignard reagent to form substitution products, especially in the presence of an oxidant (Bradley, *J.*, 1937, 1091; Bradley and Jadhav, *ibid.*, p. 1791). In each instance the active substituting agent is the anion of a very weak acid, and the characteristic replacement of hydrogen, situated either *ortho* or *para* to the carbonyl group, is fully in accord with modern theoretical views of the course of aromatic substitution (cf., *e.g.*, Robinson, *J. Soc. Dyers and Col.*, Jubilee Issue, 1934, pp. 65, 73; Bradley and Robinson, *J.*, 1932, 1254). These experiments have now been extended to a study of the direct amination of *meso*benzanthrone. As was expected, the reaction occurred when sodamide was used in the presence of oxygen, the composition of the product being determined by the amount of oxygen available. The reaction was strongly exothermic, and useful results could be obtained only when a diluent such as dimethylaniline was added, which was stable to sodamide over the temperature range employed.

When oxygen is passed rapidly through a stirred suspension of sodamide and *meso*benzanthrone (I) in dimethylaniline a reaction commences at 70—80° with evolution of ammonia and rapid rise in temperature. Sodium nitrite is formed in considerable amount and an organic product which consists almost entirely of *6-amino*meso*benzanthrone* (V), 6-hydroxy*meso*benzanthrone (VI), and 6 : 6′-*di*meso*benzanthronylamine* (VIII). No 4-derivative of *meso*benzanthrone could be isolated, but qualitative tests indicated the occurrence of small amounts of 4-amino*meso*benzanthrone (X) and 4-hydroxy*meso*benzanthrone (IX) and the probable presence of 4 : 6′-*di*meso*benzanthronylamine* (XI). There were no indications of the formation either of violanthrone or of polyamino*meso*benzanthrone.

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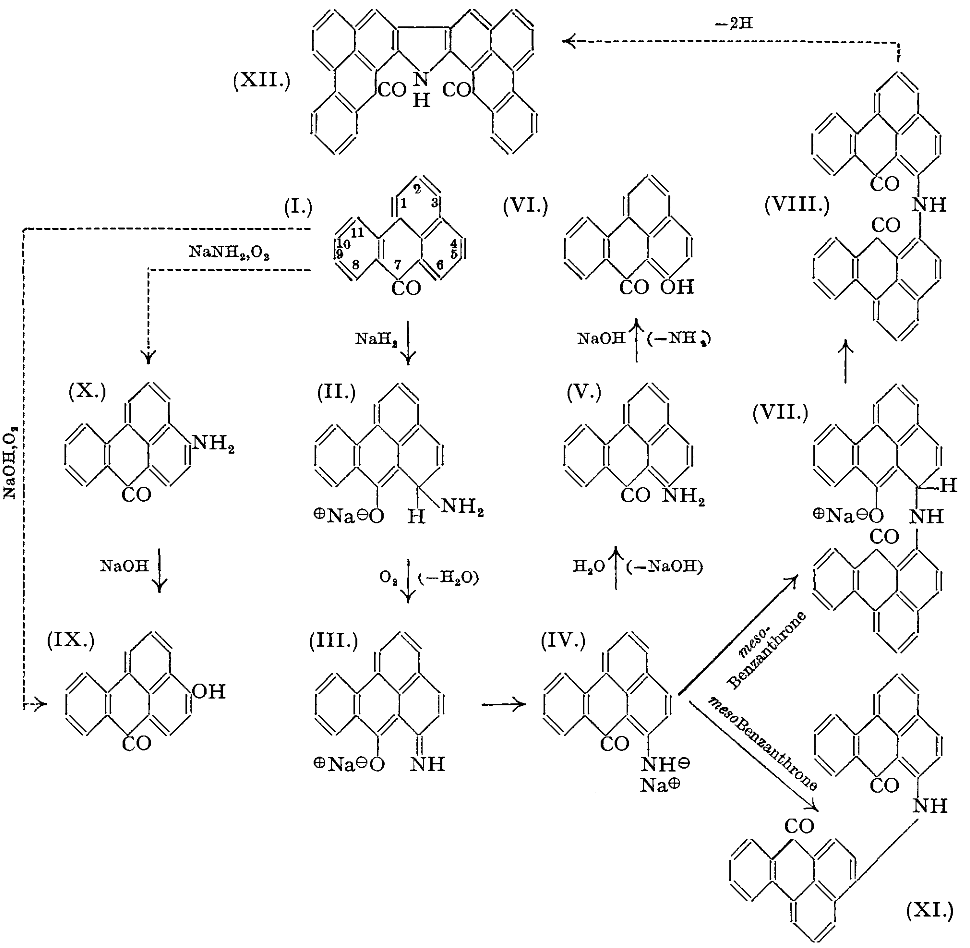
* The numbering of the benzanthrene ring system now used is that shown in (I); that in earlier papers cited was based on anthracene.—Editor.

The constitution of 6-amino*meso*benzanthrone follows from its very easy conversion into 6-hydroxy*meso*benzanthrone (Bradley and Jadhav, *loc. cit.*) when it is heated with amyl-alcoholic potassium hydroxide. Further, it may be synthesised by the action of ammonia on 6-hydroxy-*meso*benzanthrone (Bradley and Jadhav, unpublished experiment). 6-Amino*meso*benzanthrone is very probably identical with the amino*meso*benzanthrone having the same m. p. (185°) which was obtained by Pieroni (*Ann. Chim. appl.*, 1931, **21**, 155) by the action of sodamide on *meso*benzanthrone in toluene. The constitution of the product regarded as 6 : 6′-di*meso*-benzanthronylamine was indicated by the formation of both 6-amino- and 6-hydroxy-*meso*-benzanthrone when it was hydrolysed by means of alcoholic potassium hydroxide. It was synthesised by condensing 6-amino- with 6-chloro-*meso*benzanthrone. The purification of the di*meso*benzanthronylamine prepared directly from *meso*benzanthrone and sodamide was rendered difficult because of the presence of another product having a similar range of solubilities. The composition of the partly purified product was that of a homogeneous di*meso*benzanthronylamine, which suggests that the second product is either an isomeride of the 6 : 6′-derivative of the *carbazole* (XII) formed from 6 : 6′-di*meso*benzanthronylamine by dehydrogenation. Carbazole formation is commonly observed when anthrimides are heated with alkalis (cf. D.R.-PP. 262,788, 267,522; Friedlander, "Fortschritte in der Teerfarbenfabrikation", Vol. II, pp. 618, 620), and it is possible that a portion of the crude product is of this type. An isomeride of 6 : 6′-di*meso*benzanthronylamine is present since the crude di*meso*benzanthronylamine is hydrolysed by heating with alcoholic potassium hydroxide to a mixture of amines and phenols. The amines show the characteristic property of 4-amino*meso*benzanthrone of dissolving in alcohol to form a yellow solution with a green fluorescence; 6-amino*meso*benzanthrone gives a yellow non-fluorescent solution. The phenols dissolve in dilute sodium hydroxide with a brownish-yellow colour and an intense green fluorescence which is characteristic of 4-hydroxy*meso*benzanthrone; 6-hydroxy*meso*benzanthrone forms a yellow, non-fluorescent solution. These are the scission products to be expected of either 4 : 6′- or 4 : 4′-di*meso*benzanthronylamine. Actually the former isomeride is the more likely possibility because the di*meso*benzanthronylamines are formed by the interaction of *meso*benzanthrone with the anion of 6-amino*meso*benzanthrone (see below), a process which can yield only a mixture of the 6 : 6′- and 4 : 6′-forms.

The amines encountered in the amination of *meso*benzanthrone show interesting differences in behaviour when a drop of methyl-alcoholic potassium hydroxide is added to their solutions in dry pyridine (Bradley, *J. Soc. Dyers Col.*, 1942, **58**, 2). 4-Amino*meso*benzanthrone, like β-aminoanthraquinone, readily forms an alkali derivative whose solution in pyridine is orange. 6-Amino*meso*benzanthrone resembles α-aminoanthraquinone in that the colour of its pyridine solution remains unaltered on adding the alkali. The acetyl derivatives of both the amino*meso*benzanthrones form potassium salts quite readily. Both 6 : 6′- and 4 : 6′-di*meso*-benzanthronylamine form deep bluish-green potassium salts which resemble the analogous derivatives of 1 : 1′- and 1 : 2′-dianthraquinonylamine (Bradley, *loc. cit.*).

Steps in the Substitution Process.—When oxygen is present in sufficient excess the first step in the reaction between sodamide and *meso*benzanthrone probably involves the attack of amide ions on free *meso*benzanthrone at a carbon atom situated in the *ortho*-position relative to the carbonyl group, an orientation which corresponds with that of the basic group in the products formed by adding ammonia or primary or secondary amines to αβ-unsaturated ketones. A complex ion (II) is formed which then by further change yields 6-amino*meso*benzanthrone (V). There appear to be two possible courses of the second stage in the formation of this compound; (*a*) the complex anion is oxidised directly to 6-amino*meso*benzanthrone and a hydroxyl ion, or (*b*) the complex anion is first dehydrogenated by oxygen to the anion of 6-amino*meso*benzanthrone (III, IV) which subsequently reacts with water to form a hydroxyl ion and the free base. A decision in favour of the second hypothesis is indicated by the following considerations. In the first place, sodamide and oxygen react by an independent process to form sodium nitrite (cf. Bergstrom and Fernelius, *Chem. Reviews*, 1933, **12**, 43) which, in fact, is always encountered amongst the products of the reaction. Increase in the rate of passing oxygen should decrease the proportion of sodamide which is available for the substitution process. Secondly, increase in the oxygen rate reduces the yields of both 6-amino- and 6-hydroxy-*meso*benzanthrone (VI) but notably increases the yield of 6 : 6′-di*meso*benzanthronylamine. Since the last must be generated by the interaction of the anion of 6-amino*meso*benzanthrone with *meso*benzanthrone by a process analogous to that which yields the complex ion (II), it follows that the anion of 6-amino*meso*benzanthrone is not formed in the substitution process by the interaction of 6-amino*meso*benzanthrone with sodamide but results directly from the complex anion (II) by dehydrogenation. A notable feature of the direct amination of *meso*benzanthrone is the marked preponderance of substitution *ortho* to the carbonyl group. Piperidination on the contrary yields almost exclusively, if not entirely, the *para*-derivative (Bradley, *J.*, 1937, 1091). The circumstances which control the type of substitution are doubtless complex, and it is easy to demonstrate that several possible contributory factors are in themselves insufficient. One of these is the composition of the attacking anion; whilst *meso*benzanthrone is hydroxylated principally *para* to the carbonyl group, nitrobenzene yields mainly *ortho*-nitrophenol (Bradley and Jadhav, *loc. cit.*). Another is the co-ordinating power of the anion; the order is alkyl > NC_5H_{10} > NH_2 > OH, yet sodamide and the Grignard reagent (Charrier and Ghigi, *Gazzetta*, 1932, **62**, 928; Allen and Overbaugh, *J. Amer. Chem. Soc.*, 1935, **57**, 740) yield *ortho*-derivatives while sodiopiperidine and potassium hydroxide form *para*. Steric factors are frequently involved, but in the present instance the bulky anion of 6-amino*meso*benzanthrone reacts in the same sense as the amide ion and unlike the piperidine ion whose size is intermediate. The decisive factor which regulates the type of substitution is most probably the character of the complex anion formed at the first stage of the substitution process. Energy considerations will favour the formation of one particular form of the anion. Further, one form will be more easily dehydrogenated to a stable aromatic configuration than any other. The first of these factors is the more significant. A general consideration of the results of hydrogen replacement by anions in typical aromatic compounds activated by C=O, C=N or NO_2 groups shows that hydroaromatic products are only rarely encountered. The rate-determining step which fixes the type of substitution whether *ortho* or *para* is thus the first, since the dehydrogenation of the complex anion initially formed is always an easier process. This view is also in agreement with



general theoretical requirements, the effect of the initial anion-attack being to modify the stable aromatic nucleus to a hydroaromatic form which is unlikely to possess the same high resonance energy, while dehydrogenation of the complex anion reconstitutes the aromatic form.

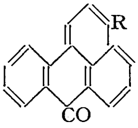
A point of interest is the high yield of 6-hydroxy*meso*benzanthrone obtained by the action of sodamide on *meso*benzanthrone. This phenol arises by the hydrolysis of 6-amino*meso*benzanthrone, a reaction which occurs with great ease in alkaline solution. An alternative route is by the direct hydroxylation of *meso*benzanthrone; but no more than a trace should have been formed by this means, which always yields a much higher proportion of the 4-derivative (Bradley and Jadhav, *loc. cit.*).

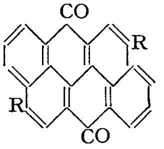
The Application of Sodamide and Sodamide–Piperidine to Ketones other than meso-*Benzanthrone.*—Attempts to bring about the direct amidation or piperidination of aromatic ketones of various types have shown that few are so easily substituted as *meso*benzanthrone. The sodamide–piperidine reagent has been used more frequently because it is generally more effective and safer than sodamide when oxygen is employed as hydrogen-acceptor.

Amination. Under conditions which easily transformed *meso*benzanthrone into 6-amino-*meso*benzanthrone, pyranthrone remained completely unchanged, nor could a basic derivative of violanthrone be obtained. *trans*-Dibenzpyrenequinone showed no tendency to react below 140°, at which temperature a violent explosion occurred. An explosion occurred with anthanthrone at a slightly lower temperature.

Piperidination. Although *meso*benzanthrone readily formed 4-piperidino*meso*benzanthrone when oxygen was passed through its suspension in piperidine containing sodamide, yet 1 : 3 : 5-tribenzoylbenzene, phenyl α-naphthyl ketone, fluorenone, 1 : 2-benzanthraquinone and *peri*naphthalimide failed to yield basic derivatives under the same conditions. Both 3-nitro-(XIII; R = NO_2) and 3-benzoyl-*meso*benzanthrone (XIII; R = COPh) on the other hand reacted slowly even in the cold. An interesting case was encountered in 4-methyl*meso*benzanthrone, which reacted slowly to form a basic derivative in very small yield. Apparently the piperidide ion is almost incapable of replacing the *ortho*-hydrogen of *meso*benzanthrone even when the *para*-position is occupied by a methyl group. Piperidine and sodamide reacted readily with anthanthrone (XIV; R = H), forming a deep violet basic derivative which appeared to be mainly a *dipiperidino-anthanthrone* [probably (XIV, R = NC_5H_{10})] with a smaller proportion of a mono-derivative. These products were not investigated in detail but their character as substituted anthanthrones is clear since they are soluble in acids, insoluble in aqueous sodium hydroxide, but soluble with a violet colour in the same alkali containing sodium hyposulphite (dithionite).

(XIII.)





(XIV.)

Experimental.

The Reaction between Sodamide and meso*Benzanthrone in the Presence of Oxygen.*—A rapid current of oxygen was passed through a stirred suspension of sodamide (16 g.) and *meso*benzanthrone (50 g.) in dry dimethylaniline (200 c.c.), access of moisture being prevented. The mixture was heated in an oil-bath. An exothermic reaction commenced at 70° with evolution of ammonia, and the colour of the suspension changed from brown, through green to black. The inner temperature was kept at 130—140° for an hour, and then the product was cooled and stirred with water.

Larger amounts of *meso*benzanthrone could be treated if, when the first exothermic reaction was almost complete, the temperature was reduced to 90°, and further quantities of sodamide (16 g.), *meso*benzanthrone (50 g.), and dimethylaniline (100 c.c.) were added, the stirring being continued until the second exothermic change was complete. Further additions could be made in the same manner. At least 200 g. of *meso*benzanthrone could be treated without loss of yield or purity. When a large amount of *meso*benzanthrone was treated in a single operation, a violent, uncontrollable reaction ensued.

The water and dimethylaniline solutions were filtered from undissolved material, and this was extracted alternately with benzene and water. The residue (10·5 g.) was a friable, reddish-brown powder, (A).

The benzene and dimethylaniline solutions were combined, and were then washed with water. The washings were added to the aqueous solutions already obtained. The united aqueous solutions were brown and showed a green fluorescence. Nitrites were present in considerable amount; when the solution was acidified, brown nitrous fumes were evolved. Acidification in the presence of urea (50 g.) gave an ochre-yellow solid (2·5 g., m. p. 138—142°), from which 1·5 g. of crude 6-hydroxy*meso*benzanthrone were extracted by treatment with benzene. The residue was a dark brown powder, m. p. 180—220°. It could not be obtained in a homogeneous condition by either crystallisation or sublimation.

4-Hydroxy*meso*benzanthrone was present (fluorescence); a portion of the material was soluble in cold sodium hydrogen carbonate solution, a circumstance suggesting the presence of carboxylic acids.

The combined benzene and dimethylaniline solutions were evaporated on the water-bath, and concentrated hydrochloric acid was added to the residual oil. A deep orange solution was obtained. The undissolved material was further treated with hot concentrated hydrochloric acid until nothing more dissolved. The united acid solutions, filtered through glass-wool, cooled, and then added to water, gave an abundant canary-yellow precipitate (19·2 g., m. p. 165—168°). Recrystallisation from alcohol gave golden-yellow prisms, m. p. 186°, consisting of 6-*amino*meso*benzanthrone* (Found: C, 83·5; H, 4·3; N, 5·5. $C_{17}H_{11}ON$ requires C, 83·2; H, 4·5; N, 5·7%). Whilst the pure base dissolved in alcohol to a yellow non-fluorescent solution, the crude base exhibited a green fluorescence, a circumstance indicating the probable presence of 4-amino*meso*benzanthrone. The amount of the latter, if present, was no doubt quite small, since none could be isolated by fractional crystallisation or adsorption of the crude base. A further indication of its presence was given when 1 g. of the oily material, which resulted when the final mother-liquors were evaporated completely, was fused at 200—240° for 30 minutes with 10 g. of potassium hydroxide and 1 c.c. of water. The product was partly soluble in water with a brown colour and a green fluorescence (hydrolysis to 4-hydroxy*meso*benzanthrone?). Determinations of the nitrogen content of the crude base (Found: N, 5·3, 5·3, 5·5%) excluded the presence of polyamino*meso*benzanthrones, and fractional extraction of the crude base by means of 10% hydrochloric acid, in which 6-amino*meso*benzanthrone dissolved hot to a lemon-yellow solution but separated almost completely on cooling, disclosed no constituent more strongly basic than 6-amino*meso*benzanthrone itself.

6-Aminomesobenzanthrone dissolves in concentrated sulphuric acid with a bright cherry-red colour, which is easily distinguished from the orange of 4-amino*meso*benzanthrone in the same solvent.

Hydrolysis of 6-*amino*meso*benzanthrone to* 6-*hydroxy*meso*benzanthrone.* 1 G. of the base was boiled with a suspension of potassium hydroxide (7 g.) in amyl alcohol (30 c.c.). A copious crystalline yellow precipitate separated quickly. After 1 hour, this was collected, washed with alcohol and then with water, and finally extracted by means of hot concentrated hydrochloric acid, giving a residue (0·4 g.), whose m. p. (176°) was not depressed by pure 6-hydroxy*meso*benzanthrone (m. p. 178°), obtained by heating 1-benzoyl-2-naphthol with aluminium chloride (Bradley and Jadhav, *loc. cit.*). The evaporated amyl-alcoholic mother-liquor gave 0·35 g. of similar material, m. p. 171°.

6-*Acetamido*meso*benzanthrone.* This *derivative* separated when the base (1 g.) was boiled for an hour with 20 c.c. of acetic anhydride. It crystallised from glacial acetic acid in slender yellow prisms, m. p. 223° (Found: N, 4·9. $C_{20}H_{15}O_2N$ requires N, 4·9%). It gave an orange solution in concentrated sulphuric acid with a yellow fluorescence.

The Neutral Fraction of the Amination Product.—(a) 6-*Hydroxy*meso*benzanthrone.* The brownish-yellow substance (23 g.), which remained when the evaporated benzene–dimethylaniline solution had been treated with hydrochloric acid, contained neither 4 : 4′-di*meso*benzanthronyl nor violanthrone. When it was treated with benzene, all but a very small amount dissolved readily, and the concentrated solution gave 20·5 g. of crude 6-hydroxy*meso*benzanthrone (m. p. 150—152°), together with 2 g. of dark substance, m. p. 80—90°. Recrystallisation from glacial acetic acid gave pure 6-hydroxy*meso*benzanthrone, m. p. 176—178°. The mother-liquors contained *meso*benzanthrone, indicated by formation of violanthrone when 0·5 g. of the recovered solute was fused for 15 minutes at 240° with 10 g. of potassium hydroxide and 1 c.c. of water. It was possible to estimate the amount of 6-hydroxy*meso*benzanthrone in the neutral fraction by taking advantage of its ready formation of a boroacetate (cf. *J.*, 1937, 1791), and of the sparing solubility of this derivative in acetic anhydride. When 10 g. of pure 6-hydroxy*meso*benzanthrone dissolved in 60 c.c. of acetic anhydride were boiled for an hour with a solution of boroacetic anhydride, prepared from boric acid (20 g.) and acetic anhydride (100 c.c.), 14·6 g. of the boroacetate, m. p. 262—264° (decomp.) (*i.e.*, 96% of the theoretical yield), separated from the partly evaporated solution on cooling and standing. Treated similarly, 10 g. of the benzene-soluble fraction of the neutral product gave 9·2 g. of the boroacetate (m. p. 262—264°, decomp.). The amount of 6-hydroxy*meso*benzanthrone present in the whole of the reaction product was therefore 13—14 g.

(b) 6 : 6′-*Di*meso*benzanthronylamine.* The reddish-brown product (A) was extracted successively with 10% sodium hydroxide solution and with hot concentrated hydrochloric acid. The undissolved portion (10 g., m. p. 310—340°. Found: N, 2·9. Calc. for $C_{34}H_{17}O_2N$: N, 3·0%) was treated with boiling glacial acetic acid, which dissolved only traces of the substance, and then crystallised from nitrobenzene. A product, m. p. 360—365°, was readily obtained, but further purification was difficult. Ultimately, brownish-red prisms, m. p. 380—382° (Found: N, 3·4, 3·2. $C_{34}H_{17}O_2N$ requires N, 3·0%), separated, which were identical with the 6 : 6′-*di*meso*benzanthronylamine* prepared by heating together 6-amino- and 6-chloro-*meso*benzanthrone.

A solution of 6-chloro*meso*benzanthrone (9 g.) and 6-amino*meso*benzanthrone (8·5 g.) in nitrobenzene (30 c.c.) was boiled for 4 hours. Even in the absence of any condensing agent the initial yellow colour of the solution changed rapidly through orange to deep red. Thin, reddish-bronze prisms separated on cooling, and these, recrystallised from nitrobenzene, gave a pure product, m. p. 382° (Found: N, 3·3. $C_{34}H_{17}O_2N$ requires N, 3·0%). 6 : 6′-Di*meso*benzanthronylamine gives a reddish streak with a violet tinge when rubbed on porcelain. Solutions in concentrated sulphuric acid are blue in thin and reddish-violet in thick layers; they show a faint reddish fluorescence. It is slightly soluble in hot acetic anhydride to a brownish-yellow solution with a pink tinge, which becomes deep reddish-orange, violet in thin layers, when boroacetic anhydride is added. It dissolves sparingly in hot propyl alcohol, giving a rose-yellow solution which becomes bluish-grey with propyl-alcoholic potassium hydroxide, and pale green on the further addition of pyridine. It is rather more soluble in hot amyl alcohol. The yellow solution becomes deep emerald-green with hot amyl-alcoholic potassium hydroxide, but the original colour is restored on cooling or even on dilution with hot amyl alcohol. The brownish-yellow solution in dry pyridine shows no immediate change when solid potassium hydroxide is added, but on warming, a deep brownish-green colour develops and a green precipitate forms on standing. A deep emerald-green colour is also obtained when methyl-alcoholic potassium hydroxide is added to a solution in pyridine; sodium causes a similar change of colour and ultimately a green precipitate.

4-*Iodo*meso*benzanthrone.* 4-Amino*meso*benzanthrone was diazotised by dissolving 12·5 g. in 50 c.c. of cold, concentrated sulphuric acid and adding the solution as a thin stream to a stirred solution of sodium nitrite (4 g.) in concentrated sulphuric acid (25 c.c.), the temperature being kept below 10°. After 30 mins.' standing, the solution was added to ice-water and the slight excess of nitrous acid decomposed by adding urea. The precipitated diazonium salt was collected, suspended in water (250 c.c.) and stirred with a solution of potassium iodide (25 g.) in water (75 c.c.). Crude 4-*iodo*meso*benzanthrone* was precipitated as a granular powder, m. p. 158—160° with slight previous softening. Crystallisation from alcohol raised the m. p. to 164—165° (Found: C, 57·6; H, 2·6. $C_{17}H_9OI$ requires C, 57·3; H, 2·6%).

4-*Methylamino*meso*benzanthrone.*—A suspension of 4-iodo*meso*benzanthrone (0·9 g.) in 15 c.c. of 33% (w/v) aqueous methylamine was heated at 200° during 6 hours. The product consisted of a pale yellow solution containing a small quantity of 4-hydroxy*meso*benzanthrone and dark, brownish-red crystals which exhibited a marked green lustre. These were extracted with alcohol, giving a yellow solution and a small granular residue, m. p. 270—320°. The solution yielded slender, golden-yellow prisms, m. p. 223—224° (Found: N, 5·2. $C_{18}H_{13}ON$ requires N, 5·4%), of 4-*methylamino*meso*benzanthrone*, showing a bluish-green fluorescence in alcohol.

4 : 6′-*Di*meso*benzanthronylamine.*—4-Iodo*meso*benzanthrone (2·6 g.) and 6-amino*meso*benzanthrone (1·8 g.) were heated together in boiling nitrobenzene (15 c.c.) with the addition of a trace of copper powder. (There was no reaction in the absence of copper.) The colour of the solution quickly changed from yellow to red, and after 10 hours it was filtered, cooled, and then diluted with alcohol. The crystalline precipitate was collected, and exhaustively extracted with hot alcohol. The residue was crystallised first from glacial acetic acid and then from pyridine, giving orange-red prisms with a bronze lustre, m. p. 395° (Found: N, 3·0. $C_{34}H_{17}O_2N$ requires N, 3·0%). 4 : 6′-*Di*meso*benzanthronylamine* gives an orange streak with a greenish-yellow lustre when rubbed on porcelain. Its solution in concentrated sulphuric acid is reddish-violet in thick, and blue in thin layers. It dissolves in acetic anhydride with a golden-yellow colour which remains quite unaltered when boroacetic anhydride is added. A solution in hot amyl alcohol is yellow without pink tinge, and a weak olive-green colour develops when amyl-alcoholic potassium hydroxide is added. It is very sparingly soluble in hot propyl alcohol to a yellow solution, which shows no change of colour when hot propyl-alcoholic potassium hydroxide is added, or any on the further addition of pyridine. A yellow solution in dry pyridine, however, gives an immediate deep blue-green coloration with a drop of methyl-alcoholic potassium hydroxide.

Action of Potassium Hydroxide on Various Products.—(1) 6 : 6′-*Di*meso*benzanthronylamine.* (*a*) 1 G. of the amine was boiled for 2 hours with a solution of potassium hydroxide (5 g.) in 20 c.c. of amyl alcohol. The maroon suspension rapidly became bluish-green and finally yellowish-green with evolution of ammonia. Water was then added, and the amyl alcohol removed in steam. The suspension so obtained was kept for 12 hours, and then filtered. The acidified filtrate afforded a flocculent yellow precipitate (0·1 g., m. p. 165—168°) which gave pure 6-hydroxy*meso*benzanthrone when crystallised from benzene. The alkali-insoluble portion was taken up in benzene, and recovered from the dried solution by evaporating the solvent. The black tarry residue, taken up in 10 c.c. of acetic anhydride and then boiled for an hour with boroacetic anhydride (from 3 g. of boric acid and 15 c.c. of acetic anhydride), gave 0·3 g. of the boroacetate of 6-hydroxy*meso*benzanthrone, m. p. 225—227°.

(*b*) A solution of potassium hydroxide (10 g.) in ethyl alcohol (40 c.c.) was added to a suspension of 6 : 6′-di*meso*benzanthronylamine (1·6 g.) in pyridine (15 c.c.), and the mixture boiled for 30 hours. A green solution formed slowly, and this finally became almost yellow. It was then added to water and rendered acid to Congo-red. A yellow precipitate formed (1·35 g., m. p. 138—148°). It was extracted by means of hot concentrated hydrochloric acid, affording a yellow solution from which 0·4 g. of 6-amino*meso*benzanthrone, m. p. 165—168°, separated when water was added. The acid-insoluble portion of the product (1·1 g., m. p. 156—160°) was nearly pure 6-hydroxy*meso*benzanthrone.

(*c*) Finely powdered 6 : 6′-di*meso*benzanthronylamine (1 g.) was stirred into a melt of potassium hydroxide (50 g.) and water (5 g.) at 200°, and then the temperature was slowly raised to 280° during 1 hour. The product was a deep violet paste. It dissolved partly in water to a violet solution from which a brownish-violet solid separated on exposure to air. The supernatant liquid was yellowish-brown and non-fluorescent; only a trace of material separated when it was acidified. The brownish-violet product, although quite insoluble in water and alkalis, dissolved readily in alkaline sodium hyposulphite (dithionite) solution with a permangate-red colour. In pyridine, xylene, or glacial acetic acid it dissolved sparingly with a brownish-yellow colour, and in concentrated sulphuric acid to a violet solution; in no instance was a fluorescence observed.

(2) 4 : 6′-*Di*meso*benzanthronylamine.* 0·1 G. of 4 : 6′-di*meso*benzanthronylamine was added to a boiling solution of potassium hydroxide (5 g.) in propyl alcohol (20 c.c.). Within a few minutes a portion of the amine had dissolved to a bluish-green solution which changed to a yellow with a green fluorescence. The products of the reaction could not be isolated in a state of purity. When water was added and the propyl alcohol was distilled off, the resulting aqueous solution was brownish-yellow with an intense green fluorescence (4-hydroxy*meso*benzanthrone ?).

(3) *The neutral amination product, m. p.* 310—340°. A suspension of 3 g. of this product in 30 c.c. of pyridine was boiled for 16 hours with a solution of potassium hydroxide (40 g.) in ethyl alcohol (80 c.c.). A bluish-green solution formed and this changed to brownish-yellow. Ammonia was evolved. Water was added, giving a brownish-yellow alkaline solution with an intense green fluorescence, and an insoluble product. A yellow precipitate formed when the aqueous solution was acidified (4-hydroxy*meso*benzanthrone ?), but the quantity obtained was too small to allow of purification. The insoluble product was partly soluble in hot concentrated hydrochloric acid to a yellow solution from which a brownish-yellow basic substance (0·3 g., m. p. 155—160°) separated when water was added. It appeared to be essentially a mixture of 4- and 6-amino*meso*benzanthrones (Found: N, 4·9, 5·0. Calc. for $C_{17}H_{11}ON$: N, 5·7%). It dissolved in alcohol to a yellow solution with an intense green fluorescence (4-amino*meso*benzanthrone), and in acetic anhydride with a yellow colour becoming brown and developing an intense green fluorescence when boroacetic anhydride was added (6-amino*meso*benzanthrone). When it was

boiled for an hour with acetic anhydride (10 c.c.), and the solution cooled, a bronzy mass, m. p. 208—215°, separated. Recrystallisation from glacial acetic acid gave pure 6-acetamido*meso*benzanthrone.

The neutral fraction of the reaction product was partly soluble in benzene; an oily solid remained when the solution was evaporated. Treatment with glacial acetic acid gave pure 6-hydroxy*meso*benzanthrone. The benzene-insoluble product was insoluble also in hot glacial acetic acid. It was a dark brown powder, m. p. above 400° (Found : N, 2·4%), which dissolved in concentrated sulphuric acid with a brown colour, and in acetic anhydride to a brownish-yellow solution unchanged on addition of boroacetic anhydride.

*Absorption Spectra of the Di*meso*benzanthronylamines.*—Both the 4 : 6′- and the 6 : 6′-derivative are very sparingly soluble in cold solvents. For the measurements, a 0·01% solution of the former and 0·01% and 0·05% solutions of the latter in pyridine were used. The 4 : 6′-derivative exhibited a broad absorption band extending from the violet to about 5600—5700 A., beyond which the absorption was very small and without characteristic features. The 6 : 6′-isomer showed a similar band which passed through a minimum at about 5800 A. There was a rounded maximum at 6175 A., beyond which the absorption decreased.

Action of Sodamide and Piperidine on Anthanthrone.—A suspension of finely powdered anthanthrone (5 g.) and sodamide (2·5 g.) in piperidine (40 c.c.) was agitated by means of a current of oxygen while being heated under reflux in an oil-bath. The mixture which was initially orange changed to brownish-red. The inner temperature was raised from 100° to 130° during 2 hours and then the semi-solid product was cooled and mixed with ice and water. Concentrated hydrochloric acid was added, and the red solution was separated from the undissolved material, which was again extracted with hot 20% hydrochloric acid. Ultimately 3·4 g. of residue remained; this was mainly unchanged anthanthrone. Addition of ammonia to the filtered acid extracts gave 1·7 g. of deep violet basic product. This was taken up in hydrochloric acid and fractionally reprecipitated by adding sodium acetate. No significant difference in composition could be detected between the first and the final fraction [Found (respectively) : N, 5·2, 5·4. $C_{32}H_{28}O_2N_2$ (*dipiperidinoanthanthrone*) requires N, 5·9%. $C_{27}H_{19}O_2N$ (*monopiperidinoanthanthrone*) requires N, 3·6%). The two fractions behaved identically towards solvents and chemical reagents. They were sparingly soluble in alcohol but more easily in pyridine, forming violet solutions. They were insoluble in dilute sodium hydroxide but dissolved with a violet colour when sodium hyposulphite (dithionite) was added. The sodium salt of the reduction product was in each case sparingly soluble in aqueous sodium hydroxide of greater than 1% concentration.

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