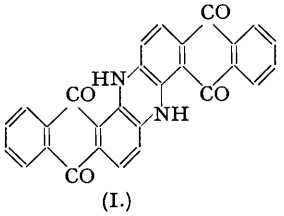
470. *Chemistry of Indanthrone. Part I. The Mode of Formation of Indanthrone from 2-Aminoanthraquinone and Potassium Hydroxide.*

By WILLIAM BRADLEY and EDWARD LEETE.

Since 1901, when Bohn discovered indanthrone (I), several theories have been advanced to account for its formation by alkali fusion of 2-aminoanthraquinone. It has been generally held that the reaction of 2-aminoanthraquinone and intermediates derived from it depends on their ability to assume quinonoid forms. This view is shown to be untenable. It is considered that 2-aminoanthraquinone yields the 2-anthraquinonylamine anion, which then replaces hydrogen in another molecule of 2-aminoanthraquinone forming 2-amino-1 : 2′-dianthraquinonylamine (VI). The cyclisation of (VI) to (I) occurs with great ease. Similarly, the *N*-methyl derivatives of (VI) readily yield the corresponding *N*-methyl derivatives of (I); these are also prepared directly from (I) by methylation. The alkali-salt forming properties of 2-aminoanthraquinone and its derivatives are described, as well as experiments on the replacement of nuclear hydrogen in 2-aminoanthraquinone and its *N*-derivatives by hydroxyl and anilino-groups. The physical and chemical properties of numerous derivatives of anthraquinone are recorded, including those of the methyl derivatives of indanthrone.

History.—In 1901, an attempt to extend the Heumann synthesis of indigo led Bohn to the discovery of indanthrone (G.P. 129,845). He obtained it, together with alizarin, flavanthrone, and other products, by heating 2-aminoanthraquinone with potassium hydroxide. Bohn ascertained the composition of the new colouring matter and assigned to it the structure (I) which was later found to be correct (Scholl, *Ber.*, 1903, **36**, 3410). Bohn considered that, just as 2-hydroxyanthraquinone afforded alizarin when it was fused with potassium hydroxide, so 2-aminoanthraquinone should yield 2-amino-1-hydroxyanthraquinone (II), and finally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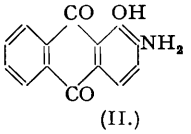
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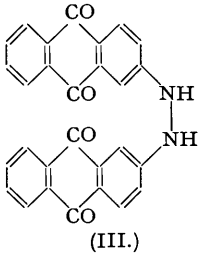
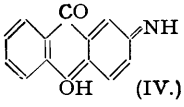

(III.)

indanthrone by dehydration. Scholl, Berblinger, and Mansfield (*ibid.*, 1907, **40**, 320) were unable to confirm Bohn's views of the mechanism of the reaction, and Scholl and Eberl (*Monatsh.*, 1911, **32**, 1035) showed further that 2-hydroxylaminoanthraquinone was not an intermediate in the formation of indanthrone. Scholl and Eberl (*loc. cit.*) believed that *s*-di-2-anthraquinonylhydrazine (III) might be a precursor of indanthrone, but Kopetschni (*Chem. Zentr.*, 1924, II, 2506) showed that indanthrone was formed from (III) only by the agency of strong acids. Scholl and Eberl (*loc. cit.*) suggested further that the enolic form of 2-aminoanthraquinone (IV), if formed, should combine with 2-aminoanthraquinone to yield the adduct (V), from which indanthrone itself should result by repetition of the processes of enolisation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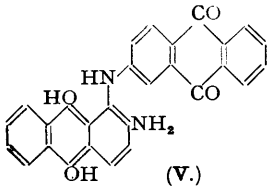
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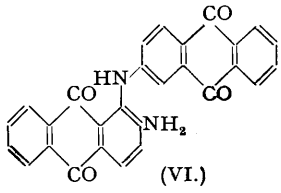
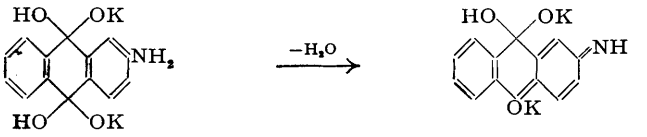
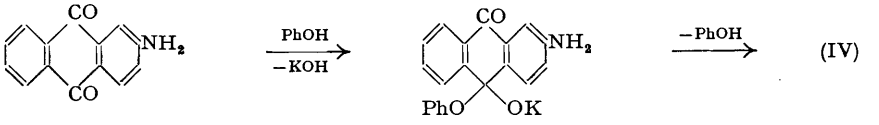

(VI.)

addition, and finally oxidation. The imine-addition hypothesis was adopted by Barnett ("Anthracene and Anthraquinone," London, 1921, p. 344), who regarded 2-amino-1 : 2′-di-

anthraquinonylamine (VI) as the most probable intermediate in the formation of indanthrone. Maki (*J. Soc. Chem. Ind. Japan, Suppl.*, 1929, **32**, 303) adopted the same hypothesis. He observed that 2-aminoanthraquinone, when added to molten potassium hydroxide, yielded a violet melt from which 2-aminoanthraquinone could be regenerated unchanged by addition of water; this was interpreted as an addition of potassium hydroxide followed by loss of water, the changes being reversible :

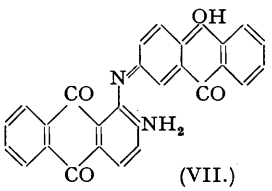


Maki further observed (*ibid.*, 1934, **37**, 748) that the yield of indanthrone was increased by adding phenol to the melt; this was ascribed to a catalytic action of phenol :



Tanaka (*J. Chem. Soc. Japan*, 1935, **56**, 192) also held that indanthrone formation depended on the occurrence of imine salts. Two other points of view have been advanced by Schwenk (*Chem.-Ztg.*, 1928, **52**, 45) who favoured a quinonoid-ion-radical hypothesis, and by Bradley and Robinson (*J.*, 1932, 1254), who considered the formation of indanthrone to be an instance of aromatic substitution, the anion of 2-aminoanthraquinone replacing nuclear hydrogen in a second molecule of the amine.

The Imine-addition Hypothesis.—In the present experiments 2-amino-1 : 2′-dianthraquinonylamine (VI) has been prepared and shown to yield indanthrone (I) under a wide variety of conditions involving the use of acid, neutral, and alkaline media. There can be no doubt that if (VI) is produced as a result of the action of alkalis on 2-aminoanthraquinone, then its cyclisation to indanthrone will follow. Experiments in support of this conclusion are described in Part III. Whether the cyclisation of (VI) to indanthrone requires enolisation of (VI) as an essential step, giving (VII) at an intermediate stage, has been answered by experiments with the *N*-methyl derivative (VIII), which is incapable of affording an analogous enolic form.



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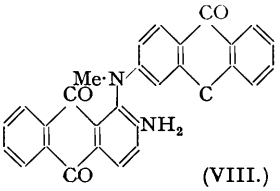

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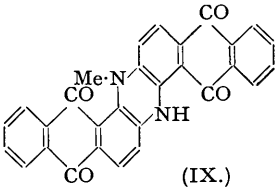
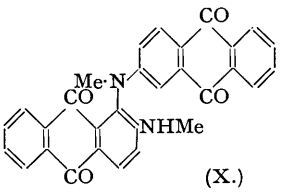
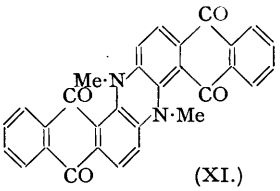


(IX.)

Heating (VIII) with a suspension of potassium hydroxide in pyridine sufficed to convert it into *N*-methylindanthrone (IX), identical with the monomethyl derivative prepared by the direct methylation of indanthrone. In other experiments the dimethyl derivative (X) was prepared and shown to be easily cyclised to *NN*-dimethylindanthrone (XI) identical with the dimethyl derivative prepared from indanthrone directly or by methylating the monomethyl derivative (IX).



(X.)

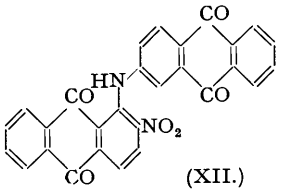


(XI.)

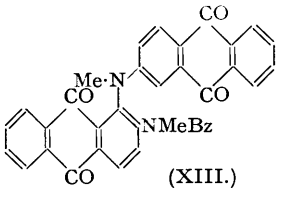
These results indicate that enolisation of the anthraquinone nucleus is not an essential step in the process leading to the linking of the nitrogen of amino- or methylamino-groups with the

nucleus. Further, if, as would be expected, the same considerations apply to the union of two molecules of 2-aminoanthraquinone to give (VI), it must be concluded that enolisation of 2-aminoanthraquinone forming (IV) is not an essential initial step in the process.

The 2-amino-1 : 2′-dianthraquinonylamine employed in these experiments was prepared by condensing 1-chloro-2-nitroanthraquinone with 2-aminoanthraquinone to form (XII), and reducing the product. 1-Chloro-2-nitroanthraquinone is highly reactive; heating it for only a few moments with diethylamine yields 1-diethylamino-2-nitroanthraquinone. Similarly, attempts to improve the preparation of (XII) by addition of potassium acetate led to 1-hydroxy-2-nitroanthraquinone as the main product, the 2-aminoanthraquinone present as a reactant being recovered unchanged.



(XII.)



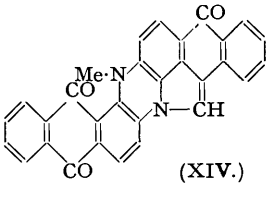
(XIII.)

1-Chloro-2-nitroanthraquinone was first prepared by Kopetschni (G.P. 363,930) by oxidising 2-amino-1-chloroanthraquinone with persulphuric acid. We used Kopetschni's method with success, but the preparation was inconvenient because of the simultaneous formation of by-products. Better results were obtained by applying Hodgson, Mahadevan, and Ward's method (*J.*, 1947, 1392) for the replacement of amino- by nitro-groups to 2-amino-1-chloroanthraquinone.

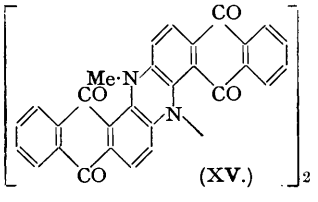
Methylation of 2-nitro-1 : 2′-dianthraquinonylamine gave the *N*-methyl derivative, and this, on reduction, gave 2-amino-1 : 2′-dianthraquinonyl-*N*-methylamine (VIII). The *N*-benzoyl derivative of (VIII) was methylated to give (XIII), and subsequent hydrolysis afforded (X).

2-Nitro-1 : 2′-dianthraquinonylamine formed a deep red addition complex with 0·5 mol. of chlorobenzene. It also combined with toluene, but not with benzene. The addition compounds had considerable stability towards heat; they were readily dissociated by mixing them with ether or ethyl acetate.

Methylation of Indanthrone.—Indanthrone was converted into a mixture of *N*-mono- and *NN*-di-methylindanthrone by heating it in trichlorobenzene with methyl toluene-*p*-sulphonate and dry potassium carbonate. The methyl derivatives were more soluble than indanthrone which remained undissolved in the form of a green alkali derivative. The character of the insoluble product was shown by adding a drop of acetic acid to its suspension in *o*-dichlorobenzene, the liberated indanthrone dispersing in the medium with a blue colour. Water also hydrolysed the green alkali derivative, yielding indanthrone. The trichlorobenzene solution containing the methyl derivatives gave coppery-blue needles of *NN*-dimethylindanthrone (XI); the mother-liquor was chromatographed on alumina; the two main zones were blue, the upper one consisting of (XI), and the lower zone containing a colouring matter (B) which resembled *N*-methylindanthrone (IX) in composition.



(XIV.)



(XV.)

Product B resembled indanthrone and its *N*-methyl and *NN*′-dimethyl derivatives in colour, absorption spectrum in sulphuric acid (see Fig. 1), and in the absorption spectrum in alkaline solution of the brown reduction product obtained by heating it with alkaline dithionite (hydrosulphite) (see Fig. 2). All four colouring matters behaved similarly on quantitative hydrogenation, but B differed from indanthrone and *N*-methylindanthrone in showing no reaction with nitric acid in sulphuric acid, or with potassium hydroxide in pyridine. B differed markedly from *NN*′-dimethylindanthrone in the character of its absorption in pyridine (Fig. 3). It could not be prepared by heating dimethylindanthrone with potassium carbonate in trichlorobenzene. The properties of B are those expected of (XIV), but the mode of derivation of such a compound in the methylation of indanthrone is obscure. The hydrazine structure (XV), which

would result from monomethylindanthrone by dehydrogenation, is excluded since B cannot be converted into indanthrone by demethylation.

Alkali-salt Formation in Derivatives of 2-Aminoanthraquinone.—It has been shown by one of us (*J. Soc. Dyers Col.*, 1942, **58**, 2) that the occurrence of acid characters in derivatives of anthraquinone and many related compounds can be readily demonstrated by adding a drop of a concentrated methanolic potassium hydroxide to a solution of the derivative in dry pyridine. In most instances a marked change is observed in the colour of the solution, and the change is reversed on addition of water or alcohol immediately when the derivative is a very weak acid, less readily when it is stronger. In the present experiments the colour change was dependent on the occurrence of NH– groups attached to an aromatic nucleus and generally, but not invariably, situated either *ortho* or *para* to a carbonyl group.

The pyridine–alkali colour test provided a most useful guide to the progress of reactions involving the conversion of secondary amines into amides and tertiary amines, and to the

FIG. 1. FIG. 2. FIG. 3.

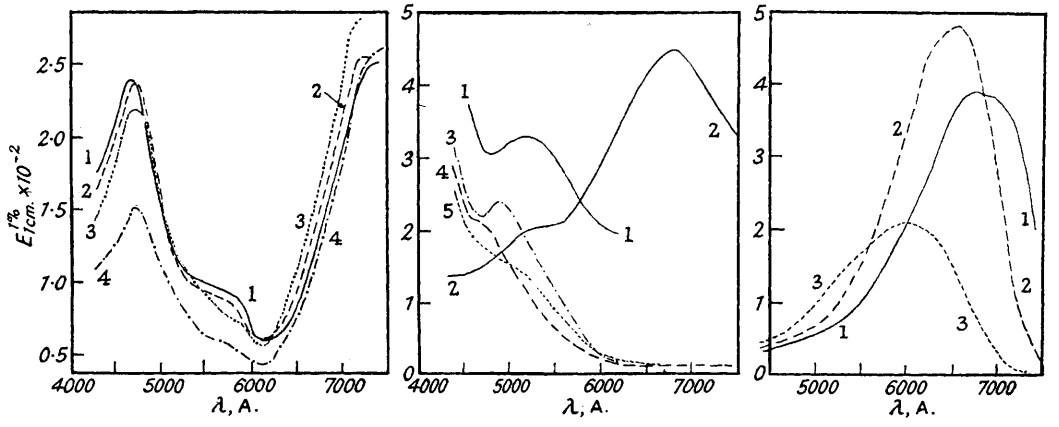


FIG. 1.—*Indanthrone and its* N-*methyl derivatives in concentrated sulphuric acid.*

1, *Indanthrone : Max. at* 4650 Å. (E = 240), *min. at* 6150 Å. (E = 61).
2, N-*Methylindanthrone : Max. at* 4700 Å. (E = 235), *min. at* 6100 Å. (E = 62).
3, NN-*Dimethylindanthrone : Max. at* 4720 Å. (E = 217), *min. at* 6100 Å. (E = 57).
4, *Product B : Max. at* 4750 Å. (E = 150), *min. at* 6100 Å. (E = 44).

FIG. 2.—*Solutions obtained by dissolving indanthrone and its* N-*methyl derivatives in sodium hydroxide containing sodium dithionite.*

1, *Indanthrone, brown solution (tetrahydro-derivative) : Min. at* 4800 Å. (E = 305), *max. at* 5150 Å. (E = 330).
2, *Indanthrone, blue solution (dihydro-derivative) : Max. at* 6800 Å. (E = 450).
3, N-*Methylindanthrone, brown solution : Min. at* 4700 Å. (E = 220), *max. at* 4900 Å. (E = 240).
4, NN-*Dimethylindanthrone.*
5, *Product B.*

FIG. 3.—N-*Methyl derivatives of indanthrone in pyridine.*

1, N-*Methylindanthrone : Max. at* 6700 Å. (E = 390).
2, NN-*Dimethylindanthrone : Max. at* 6550 Å. (E = 480).
3, *Product B : Max. at* 6000 Å. (E = 210).

homogeneity of amines and amides likely to contain analogous –NH– compounds as impurities.

The formation of metallic derivatives of amines and amides has often been described. Fones (*J. Org. Chem.*, 1949, **14**, 1099) prepared the sodium salt of *p*-methoxyacetanilide by means of sodium hydride; Thielepape (*Ber.*, 1935, **68**, 751) obtained the sodium salt of acetanilide by using the free metal. In one instance, *o*-nitroacetanilide, an alkali derivative results when the amide is dissolved in aqueous sodium hydroxide.

There can be little doubt that the colours produced from anthraquinone derivatives by potassium hydroxide in pyridine are due to alkali salts. Their appearance requires the presence of a free –NH– group in the derivative, the use of a strong base, and the almost complete absence of water or hydroxylic solvents from the medium. Potassium hydroxide was more effective than sodium hydroxide; lithium hydroxide showed little tendency to react. One of the

strongest acids encountered was 2-benzamido-1-nitroanthraquinone. Like *o*-nitroacetanilide it dissolved in aqueous sodium hydroxide; it was precipitated unchanged by addition of acid to the red solution. 2-Acetamido-1-nitroanthraquinone behaved similarly. Both acyl derivatives were readily methylated in alkaline solution with formation of the *N*-benzoyl and *N*-acetyl derivatives of 2-methylamino-1-nitroanthraquinone. The colour of the alkali derivatives depends on the medium : it is bluest in pyridine, morpholine, or acetone, less blue in alcohol, and red in water. It does not appear that the basic solvents have any essential part in the formation of the alkali salts, as similar colours are given in acetone (see Fig. 4).

2-Aminoanthraquinone does not form an alkali salt in pyridine, the colour change to green previously reported (*J. Soc. Dyers and Col.*, 1942, **58**, 2) being due to the presence of very small

FIG. 4. FIG. 5. FIG. 6.

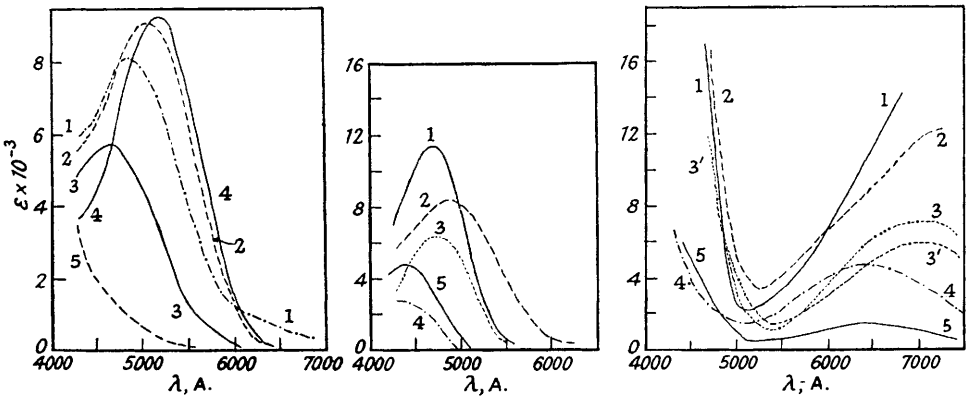


FIG. 4.—*The potassium salt of 2-benzamido-1-nitroanthraquinone in various solvents.*

1, *Morpholine : Max. at* 4850 Å. (ε = 8150).
2, *Acetone : Max. at* 5050 Å. (ε = 9100).
3, *Ethyl alcohol : Max. at* 4700 Å. (ε = 5700).
4, *Pyridine : Max. at* 5200 Å. (ε = 9200).
5, *Water : no max. or min. observed.*

FIG. 5.—*Derivatives of 2-aminoanthraquinone in pyridine.*

1, 2 : 2′-*Dianthraquinonylamine : Max. at* 4700 Å. (ε = 11,400).
2, 1 : 2′-*Dianthraquinonylamine : Max. at* 4850 Å. (ε = 8400).
3, 2-*Anilinoanthraquinone : Max. at* 4750 Å. (ε = 6400).
4, 2-*Amino*-1-*nitroanthraquinone.*
5, 2-*Amino*-1-*chloroanthraquinone : Max. at* 4400 Å. (ε = 4800).

FIG. 6.—*Solutions in pyridine containing excess of methanolic potassium hydroxide.*

1, 2 : 2′-*Dianthraquinonylamine : Min. at* 5100 Å. (ε = 2300).
2, 1 : 2′-*Dianthraquinonylamine : Min. at* 5250 Å. (ε = 3400).
3, 2-*Anilinoanthraquinone : Min. at* 5400 Å. (ε = 1100), *max. at* 7100 Å. (ε = 7200).
3′, 2-*Anilinoanthraquinone* (*with* NaOH *in place of* KOH) : *Min. at* 5400 Å. (ε = 1300), *max. at* 7100 Å. (ε = 6000).
4, 2-*Amino*-1-*nitroanthraquinone : Min. at* 5150 Å. (ε = 1600), *max. at* 6500 Å. (ε = 4700).
5, 2-*Amino*-1-*chloroanthraquinone : Min. at* 5300 Å. (ε = 600), *max. at* 6500 Å. (ε = 1500).

amounts of 2 : 2′-dianthraquinonylamine. 2-Amino-1-nitro-, 2-amino-1-chloro-, and 2-anilinoanthraquinone, and 2 : 2′-, 1 : 2′-, and 1 : 1′-dianthraquinonylamine afford green colours (Figs. 5 and 6). 2-Methylamino-1-nitroanthraquinone gives a pale green colour which is much less intense than that characteristic of the unmethylated nitro-amine. Indanthrone and *N*-methylindanthrone give green colours, *NN*-dimethylindanthrone is unaffected. Acyl derivatives of 2-aminoanthraquinone afford red-violet colours; in all the instances examined, 2-acetamido-, 2-benzamido-, 2-*p*-nitrobenzamido-, and 2-toluene-*p*-sulphonamido-anthraquinone, the wavelength of maximum absorption was in the region 5000—5400 Å. This is also true of 2-benzamidofluorenone. The intensity of the absorption varies with the acyl group; it is highest with the benzoyl and *p*-nitrobenzoyl and less with the acetyl and toluene-*p*-sulphonyl derivatives; the lowest intensity is found in the fluorenone derivatives (Figs. 7 and 8). The presence of carbonyl groups is not essential for the occurrence of acid characters; 2-acetamidoanthracene affords

a colourless solution in pyridine, which becomes yellow on addition of methanolic potassium hydroxide. It is interesting that, unlike 2-anilinoanthraquinone, 1-anilinoanthraquinone exhibits no alkali colour reaction.

Crystalline potassium salts of 2-toluene-*p*-sulphonamidoanthraquinone and its 1-chloro-derivative were readily prepared. Those of 2-benzamido- and 2-*p*-nitrobenzamido-anthraquinone were obtained as amorphous red powders; that of 2-acetamidoanthraquinone prepared in pyridine decomposed when benzene was added. The green sodium salt of 2-anilinoanthraquinone was prepared by the use of sodioanthracene (Schlenk, Appenrodt, Michael, and Thal, *Ber.*, 1914, **47**, 473); it was too unstable for isolation or methylation. The green potassium salt of 1 : 2′-dianthraquinonylamine was easily prepared, but it decomposed rapidly on exposure to air, re-forming the free amine.

2-*Aminoanthraquinone as a Substituting Agent.*—There is no lack of evidence for the ability of amines to replace nuclear hydrogen in aromatic compounds, when nitro-, carbonyl, or similar groups are already present. In each example replacement of hydrogen occurs only when the reactants include a strong base which functions by promoting the ionisation of the amine.

FIG. 7. FIG. 8.

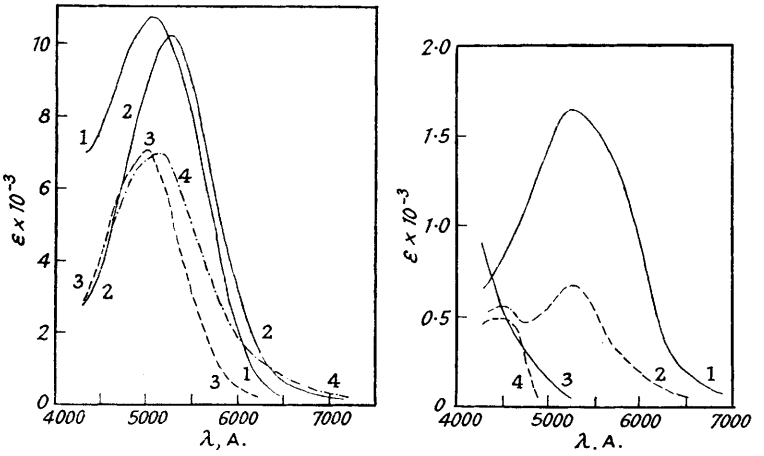


FIG. 7.—*Acylaminoanthraquinones. Solutions in pyridine to which methanolic potassium hydroxide has been added.*

1, 2-p-*Nitrobenzamidoanthraquinone : Max. at* 5060 Å. (ε = 10,800).
2, 2-*Benzamidoanthraquinone : Max. at* 5270 Å. (ε = 10,200).
3, 2-*Toluene*-p-*sulphonamidoanthraquinone : Max. at* 5000 Å. (ε = 7000).
4, 2-*Acetamidoanthraquinone : Max. at* 5150 Å. (ε = 6900).

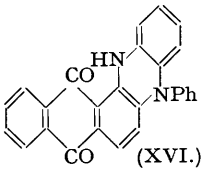
FIG. 8.—*Acylaminofluorenones.*

1, 2-*Benzamidofluorenone in pyridine + methanolic potassium hydroxide : Max. at* 5250 Å. (ε = 1650).
2, 2-*Acetamidofluorenone in pyridine + methanolic potassium hydroxide : Max. at* 5250 Å. (ε = 670).
3, 2-*Benzamidofluorenone in pyridine.*
4, 2-*Acetamidofluorenone in pyridine.*

Whilst carbazole has no action on nitrobenzene, its potassium derivative forms *N*-*p*-nitrophenylcarbazole (G. and M. de Montmollin, *Helv. Chim. Acta*, 1923, **6**, 94); ammonia is without action on *meso*benzanthrone, whilst sodamide forms the 6-amino-derivative (Bradley, *J.*, 1948, 1175). Recently it has been stated (F.I.A.T. Final Report, No. 1313, Vol. III, p. 82) that 2-aminoanthraquinone heated with " caustic " in nitrobenzene yields 2-*p*-nitroanilinoanthraquinone. We have confirmed this result when using potassium hydroxide as condensing agent, and proved the constitution of the product by preparing it from 2-chloroanthraquinone and *p*-nitroaniline. It was not possible to condense 2-aminoanthraquinone with *meso*benzanthrone, but the dimethylaniline used as solvent may have contributed to this by reducing the concentration of the reactants. The successful condensation of 2-aminoanthraquinone with nitrobenzene, however, provides a clear instance of the ability of 2-aminoanthraquinone to function as a substituting agent. In effectiveness it does not approach sodamide or sodamide–piperidine (Bradley, *J.*, 1948, 1175), but it has the same order of activity as the potassium derivative of carbazole. In order to observe the effect of increasing the acid strength of 2-aminoanthraquinone we attempted

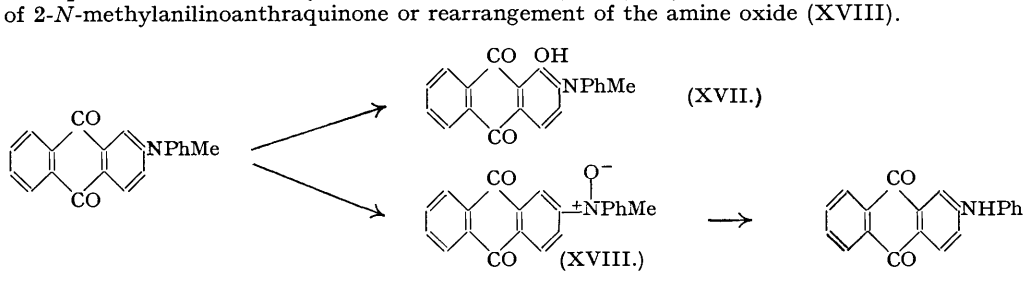
the condensation of 2-amino-1-nitroanthraquinone with nitrobenzene, but without success; this illustrates the rule that only the anions of the weakest acids are able to replace nuclear hydrogen in aromatic nitro- or carbonyl compounds.

Substitution in 2-Aminoanthraquinone and its N-Derivatives.—Tanaka (*J. Chem. Soc. Japan*, 1935, **56**, 192) and Maki (*loc. cit.*) have shown that when 2-aminoanthraquinone is heated with potassium hydroxide in the presence of an oxidant 2-amino-1-hydroxyanthraquinone is formed; under appropriate conditions the yield is 50%. G.P. 360,530 describes the formation of 2-amino-1-anilinoanthraquinone by the action of sodamide–aniline on 2-aminoanthraquinone; 2-anilinoanthraquinone is stated to yield 1 : 2-dianilinoanthraquinone. In G.P. 329,246 it is claimed that 2-anilinoanthraquinone heated with aniline and powdered potassium hydroxide yields 5 : 10-dihydro-5-phenyl-1 : 2-phthaloylphenazine (XVI). These reactions illustrate the ability of 2-aminoanthraquinone and 2-anilinoanthraquinone to undergo substitution at the 1-position by hydroxyl and anilinium ions.



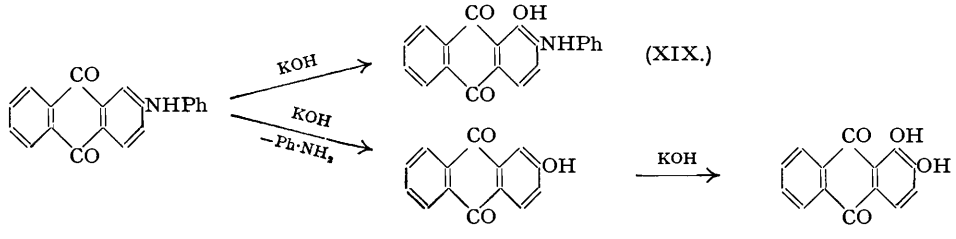
(XVI.)

In the present experiments the alkali fusion of 2-anilino- and 2-*N*-methylanilino-anthraquinone has been studied. Heating the latter with potassium hydroxide and potassium nitrate gave 2-anilinoanthraquinone (3%), unchanged 2-*N*-methylanilinoanthraquinone (more than 50%), and a reddish-brown product, m. p. 200—205°, considered to be 1-hydroxy-2-*N*-methylanilinoanthraquinone (XVII); there was no evidence for the formation of alizarin. The production of 2-anilinoanthraquinone probably occurs by way of the amine oxide (XVIII) and subsequent loss of formaldehyde. The formation of (XVII) may involve the direct hydroxylation of 2-*N*-methylanilinoanthraquinone or rearrangement of the amine oxide (XVIII).



Fusion of 2-anilinoanthraquinone with potassium hydroxide gave alizarin, aniline, and a potassium salt. The last is derived from a violet substance, m. p. 225—226°, which is considered to be 2-anilino-1-hydroxyanthraquinone (XIX) as it gives a boroacetate reaction (Dimroth, *Annalen*, 1926, **446**, 97) and the potassium salt is stable towards fused potassium hydroxide.

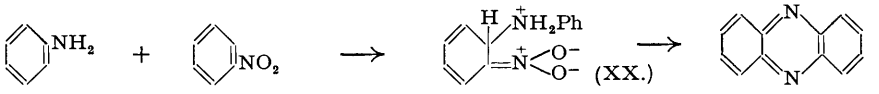
Alkali fusion of 2-anilinoanthraquinone at a higher temperature increased the yield of alizarin, but diminished that of the 2-anilino-1-hydroxyanthraquinone. It appears, therefore, that alizarin results by the hydroxylation of 2-hydroxyanthraquinone, itself produced by hydrolysis of 2-anilinoanthraquinone :



In this example, the formation of (XIX) cannot be ascribed to the intermediate formation of an amine oxide, but hydroxylation of an imino-form of 2-anilinoanthraquinone cannot be excluded. If, however, as is probable, hydroxylation of 2-anilino- and 2-*N*-methylanilino-anthraquinone occurs by the same mechanism, the process in both cases must be the direct replacement of nuclear hydrogen by hydroxyl, as occurs in *meso*benzanthrone (Bradley and Jadhav, *J.*, 1937, 1791).

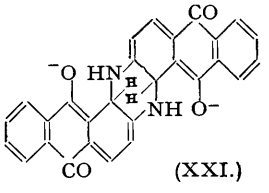
Neither 2-anilinoanthraquinone nor its *N*-methyl derivative yields a derivative of indanthrone on fusion with potassium hydroxide.

The replacement of a hydrogen atom situated *ortho* to a carbonyl group by an amino- or substituted amino-group is a normal reaction, but the problem remains why replacement of hydrogen occurs exclusively at the 1-position in 2-aminoanthraquinone. We consider that the result is determined by the unusual stability of indanthrone, and that, although there are several theoretically possible ways in which 2-aminoanthraquinone may replace a hydrogen atom in a second molecule of the same, the stability factor operates to favour the orientation which leads to indanthrone. Ultimately, the result must be determined by the high resonance energy of the product or some intermediate which precedes it. This high resonance energy may explain many of the unexpected variations in the orientation of substituents which have replaced nuclear hydrogen in aromatic ketones, nitro-compounds, and analogous compounds. For example, whilst sodamide and *meso*benzanthrone yield 6-amino*meso*benzanthrone, the same ketone with sodamide–piperidine yields 4-piperidino*meso*benzanthrone (Bradley, *J.*, 1937, 1091). Nitrobenzene with the potassium derivative of carbazole affords *p*-nitrophenylcarbazole; sodamide–piperidine affords *p*-nitrophenylpiperidine (Bradley and Robinson, *loc. cit.*). On the other hand, potassium hydroxide reacts with nitrobenzene to give mainly *o*-nitrophenol (Wohl, *Ber.*, 1899, **32**, 2486; Wohl and Aue, *ibid.*, 1901, **34**, 2444). It is probable that the condensation of aniline and potassium hydroxide with nitrobenzene to form phenazine,

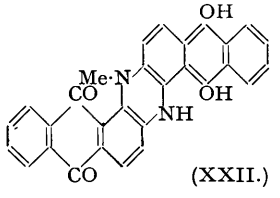


(XX.)

and of 2-naphthylamine with nitrobenzene to form 1 : 2-benzophenazine (Wohl, *Ber.*, 1903, **36**, 4135), are both normal examples of the replacement by amines of nuclear hydrogen situated *ortho* to a nitro-group, the orientation being determined by the attraction between opposite charges in some such intermediate state as (XX). From this point of view the formation of indanthrone may be determined by the ease of formation of (XXI), the hydrogens of the NH groups being shared with the neighbouring oxygens.



(XXI.)



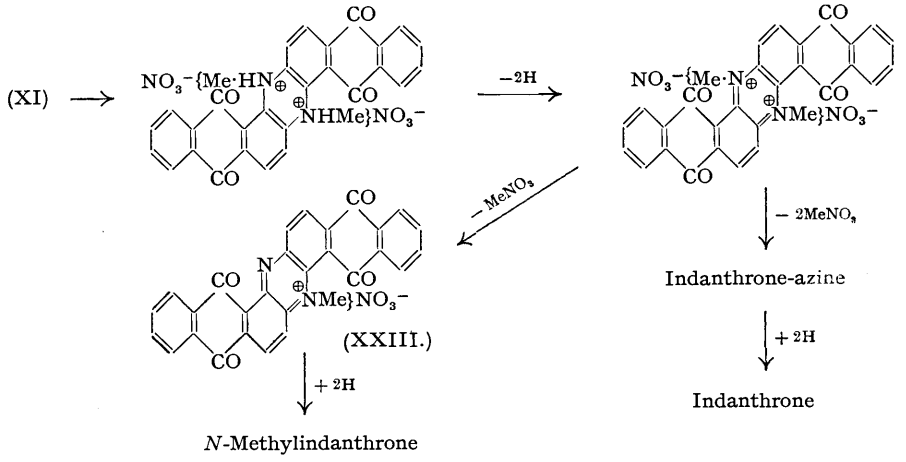
(XXII.)

The methyl derivatives of 2-amino-1 : 2′-dianthraquinonylamine (VI) differed from the parent amine in regard to the conditions in which cyclisation to an indanthrone occurred. Whilst (VI) yielded indanthrone when merely heated alone or suspended in neutral media, or even in boiling acetic acid, as well as by the action of potassium hydroxide in its solution in pyridine, with the methyl derivatives the use of alkaline media was necessary for ring-closure. Both potassium hydroxide and sodium hydroxide were used successfully; lithium hydroxide was not effective. The sequence of colour changes observed on adding potassium hydroxide to a pyridine solution of (VIII) suggests that cyclisation yields dihydro-*N*-methylindanthrone (XXII) at an intermediate stage The initial bright orange colour changes first to green [potassium salt of (VI)], then to brown (XXII), finally to green (potassium salt of *N*-methylindanthrone); addition of water hydrolyses the potassium salt and affords a blue precipitate of *N*-methylindanthrone. The cyclisation of the dimethyl derivative (X) pursues a similar course, except that the ultimate product (*NN*-dimethylindanthrone) is present in the form of a blue solution as it does not yield a potassium salt.

The *N*-benzoyl derivative of (VI) forms a deep reddish-violet potassium derivative with great ease when potassium hydroxide is added to its solution in pyridine. The salt is quite stable to heat in the medium in which it is prepared, but shows no tendency to cyclise to an indanthrone derivative. This provides a further illustration of the rule that an increase in the acid properties of an amine may diminish its effectiveness as a substituting agent for a nucleus with predominantly cationoid reactivity.

Properties of Indanthrone and its N-*Methyl Derivatives.*—Indanthrone and its *N*-methyl and *NN*-dimethyl derivatives are blue dyes which dissolve in concentrated sulphuric acid forming brown solutions. The solubility in organic solvents increases progressively with the degree of methylation, which suggests the occurrence of intermolecular bonding (−NH . . . OC−) in

indanthrone and to a smaller degree in its monomethyl derivative. A similar relation is found between the three isomeric dianthraquinonylamines (less soluble) and their methyl ethers (more soluble). Further, 2 : 2′-dianthraquinonylamine does not sublime, whilst its *N*-methyl ether does so readily. Intermolecular bonding appears to be less prominent in 1 : 1′-dianthraquinonylamine, which not only sublimes readily, but is also more soluble in organic solvents than the 2 : 2′-isomer. Both indanthrone and its *N*-methyl derivative form alkali salts with potassium hydroxide in pyridine; the *NN*-dimethyl derivative does not. The two methyl ethers dissolve in alkaline dithionite forming brown solutions; indanthrone forms two reduction products which yield, respectively, a blue and a brown solution. The behaviour of the three colouring matters on oxidation is characteristic. Nitric acid alone, or in solution in concentrated sulphuric acid, rapidly dehydrogenates indanthrone to indanthrone-azine (Scholl and Berblinger, *Ber.*, 1903, **36**, 3427). *N*-Methylindanthrone is similarly oxidised; a quaternary nitrate (XXIII) separates from the solution in the form of orange crystals. *NN*-Dimethylindanthrone is much more stable : it is not affected by nitric acid in sulphuric acid, but concentrated nitric acid causes demethylation and formation of (XXIII). Reduction of this product by alkaline dithionite, and subsequent aeration of the solution, yield *N*-methylindanthrone. A small quantity of indanthrone-azine is formed also by the action of nitric acid on *NN*-dimethylindanthrone, being recognized by reduction of the oxidation product and chromatography of the reduced form on cellulose; the reduced form of indanthrone has a higher affinity for cellulose than either of its methyl derivatives. The course of the oxidation of *NN*-dimethylindanthrone may be represented by the scheme :



Sodium hypochlorite containing 10% of available chlorine oxidises indanthrone to a green derivative but is without action on *NN*-dimethylindanthrone.

A number of analogous demethylations have been observed in the phenazine series. McIlwain (*J.*, 1937, 1704) found that *N*-methylphenazinium hydroxide decomposed in aqueous solution yielding phenazine, and Clemo and McIlwain (*J.*, 1935, 738) have shown that *NN*-dimethyldihydrophenazine yields phenazine, when its solution is exposed to air. Similarly, oxidation of pyocyanine yields formic acid and 1-hydroxyphenazine (Wrede and Strack, *Ber.*, 1929, **62**, 2054).

The preparation of several intermediates of general interest was investigated during the work. 2-Nitroanthraquinone was best prepared from 2-aminoanthraquinone by the diazonium reaction; on fusion with potassium hydroxide it yielded alizarin. 2-Anilinoanthraquinone was obtained by prolonged heating of aniline with 2-chloroanthraquinone. The use of 2-iodoanthraquinone did not afford a better yield; the method of G.P. 288,464, involving the heating of anthraquinone-2-sulphonic acid with aniline and potassium hydroxide in a current of air, was less satisfactory than the method finally employed. In an attempt to hasten the reaction between 2-chloroanthraquinone and aniline, a solution of sodium anilide in aniline was used. The main product was a blue compound, m. p. 236—237°, having the same composition as a product, m. p. 233°, obtained, according to G.P. 329,246, when 2-anilinoanthraquinone was heated with aniline and powdered potassium hydroxide. The structure assigned to the product of m. p. 233° is 5 : 10-dihydro-5-phenyl-1 : 2-phthaloylphenazine (XVI). The compound of

m. p. 236—237° dissolves in pyridine with a blue colour, unchanged by addition of methanolic potassium hydroxide; in this it resembles 1-anilinoanthraquinone but differs from 2-anilinoanthraquinone. It is probably correctly represented by (XVI).

2 : 2′-Dianthraquinonylamine was obtained only in poor yield by existing methods (Eckert and Steiner, *Monatsh.*, 1914, **35**, 1133; G.P. 162,824) Ultimately it was prepared satisfactorily from 2-aminoanthracene, by way of di-2-anthrylamine (Bollert, *Ber.*, 1883, **16**, 1635), forming its *N*-benzoyl derivative, and *NN*-di-2-anthraquinonylbenzamide.

In an attempt to prepare 2-anilino-1-hydroxyanthraquinone, 2-chloro-1-nitroanthraquinone was heated with aniline; the product was 1-anilino-2-chloroanthraquinone. According to Schmidt (*Bull. Soc. Ind. Mulhouse*, 1914, **84**, 409) an analogous replacement of an α-nitro-group occurs when 1-nitroanthraquinone is heated with aniline.

Difficulty was at first encountered in methylating 1 : 2′-dianthraquinonylamine; the successful methyl toluene-*p*-sulphonate–trichlorobenzene–potassium carbonate procedure (p. 2140) was also successful with 2 : 2′-dianthraquinonylamine, indanthrone, *N*-methylindanthrone, 2-nitro-1 : 2′-dianthraquinonylamine, 2-anilino- and 2-benzamido-anthraquinone, and 2-benzamido-1 : 2′-dianthraquinonyl-*N*-methylamine. In some instances the medium employed was *o*-dichlorobenzene. The potassium salt of 2-toluene-*p*-sulphonamidoanthraquinone was readily alkylated to form the methyl, ethyl, and *n*-butyl derivatives, from which were prepared 2-methylamino- and 2-ethylamino-anthraquinone. Similarly 1-chloro-2-toluene-*p*-sulphonamidoanthraquinone afforded the methyl derivative, from which 1-chloro-2-methylaminoanthraquinone was prepared and its *N*-acetyl and *N*-benzoyl derivatives.

Experimental.

1 : 2′-*Dianthraquinonylamine.*—This was prepared from 1-chloroanthraquinone and 2-aminoanthraquinone by Eckert and Steiner's method (*loc. cit.*). It sublimed with difficulty at 1 mm. from a bath at 330°; it crystallised from nitrobenzene in reddish-brown needles, m. p. 387—388°. Its orange solution in acetic anhydride became violet when warmed with boric acid.

The 2-aminoanthraquinone employed throughout this investigation was purified by crystallisation of the sulphate from sulphuric acid as recommended by Maki (*J. Soc. Chem. Ind. Japan, Suppl.*, 1933, **36**, 44). The free base was regenerated by hydrolysis, then collected, dried, dissolved in benzene, and chromatographed on alumina. A single orange zone resulted; this was eluted, and the recovered 2-aminoanthraquinone crystallised from acetic acid as orange needles, m. p. 306—307°.

N-*Benzoyl*-1 : 2′-*dianthraquinonylamine.*—1 : 2′-Dianthraquinonylamine (0·5 g.) was heated under reflux during 4 hours with benzoyl chloride (25 c.c.). The solution, initially red, became yellow-brown. The solution was cooled, then added to ethyl alcohol (100 c.c.); the N-*benzoyl* derivative slowly separated, and crystallised from acetic acid as yellow prisms (0·4 g.), m. p. 272—273° (Found : N, 2·7. $C_{35}H_{19}O_5N$ requires N, 2·6%). The benzoyl derivative was very readily hydrolysed. Its yellow solution in pyridine remained unaltered for a moment after addition of methanolic potassium hydroxide, but a pale green colour quickly appeared and finally the deep green characteristic of 1 : 2′-dianthraquinonylamine. It dissolved in concentrated sulphuric acid with a yellow colour, which changed to greenish-blue on storage; the addition of water then precipitated 1 : 2′-dianthraquinonylamine. Hydrolysis also occurred readily during the preparation of the benzoyl derivative if the hot solution in benzoyl chloride was added to water.

1 : 2′-*Dianthraquinonyl*-N-*methylamine.*—1 : 2′-Dianthraquinonylamine (2·1 g.), methyl toluene-*p*-sulphonate (2·5 g.), and dry potassium carbonate (1·0 g.) were heated under reflux in trichlorobenzene (40 c.c.) during 5 hours. The hot solution was filtered, and the residue washed with more of the hot solvent. Filtrate and washings were concentrated to 15 c.c. and then mixed with light petroleum. A red *amine* separated (1·5 g.), which recrystallised from acetic acid as red needles (1·3 g.), m. p. 284—285° (Found : N, 3·1. $C_{29}H_{17}O_4N$ requires N, 3·2%). 1 : 2′-Dianthraquinonyl-*N*-methylamine dissolved in pyridine with an orange colour, unaffected by addition of methanolic potassium hydroxide. It dissolved in sulphuric acid with a pale green colour; when warmed, the solution became reddish-violet. The base was not affected by an hour's boiling with benzoyl chloride containing a small proportion of concentrated sulphuric acid. It was more soluble in organic solvents than was 1 : 1′-dianthraquinonyl-*N*-methylamine.

2 : 2′-*Dianthraquinonylamine.*—(*a*) The following procedure is an improvement on that of Eckert and Steiner (*loc. cit.*). An intimate mixture of 2-aminoanthraquinone (4·4 g.), 2-chloroanthraquinone (4·8 g.), and anhydrous potassium carbonate (2·0 g.) was made into a paste with nitrobenzene (10 c.c.) and heated at 270—290° for 6 hours. The black product was washed by alcohol, the residue (6·5 g.) was dissolved in nitrobenzene (300 c.c.), and the solution treated with charcoal and then filtered. Copper-coloured plates of 2 : 2′-dianthraquinonylamine separated (0·2 g.). These decomposed without melting at about 500° (Found : N, 3·6. Calc. for $C_{28}H_{15}O_4N$: N, 3·3%).

(*b*) 2 : 2′-Dianthrylamine was prepared from 2-aminoanthracene by Bollert's method (*Ber.*, 1883, **16**, 1635). A suspension containing 2 : 2′-dianthrylamine (12·4 g.) and benzoyl chloride (50 c.c.) in pyridine (100 c.c.) was heated under reflux for 2 hours. The resulting pale brownish-yellow solution was added to alcohol (150 c.c.); the *benzoyl* derivative separated in pale yellow needles (13·5 g.), m. p. 248—249° (Found : N, 3·3. $C_{35}H_{23}ON$ requires N, 3·0%). It dissolves in concentrated sulphuric acid with a reddish-brown colour; water changes the colour to yellow.

Powdered chromium trioxide (25 g.) was added in small successive amounts to a solution containing dianthrylbenzamide (13·5 g.) in boiling acetic acid (1 l.). The addition complete, boiling was continued for 10 minutes, and then the solution was added to water (3 l.). The yellow precipitate was collected, washed with water, dried (yield, 13·7 g.), and recrystallised from acetic acid. Small yellow prisms separated, of m. p. 267—268° (Found: C, 78·4; H, 3·7; N, 2·7. $C_{35}H_{19}O_5N$ requires C, 78·8; H, 3·6; N, 2·6%). Yield, 10·2 g. NN-2 : 2′-*Dianthraquinonylbenzamide* affords a pale yellow solution in pyridine; addition of methanolic potassium hydroxide causes hydrolysis almost immediately, a deep green solution being formed.

A solution containing *NN*-2 : 2′-dianthraquinonylbenzamide (8·0 g.) in concentrated sulphuric acid was heated for an hour at 100°; the yellow-orange solution became deep blue. The solution was then cooled and added to water, and the bulky red precipitate collected and washed until neutral. The yield of 2 : 2′-*dianthraquinonylamine* was 6·5 g. A portion recrystallised from 1200 parts of boiling nitrobenzene afforded small, orange-red prisms having a coppery lustre and decomposing about 500° (Found: C, 78·4; H, 3·6; N, 3·3. $C_{28}H_{15}O_4N$ requires C, 78·3; H, 3·5; N, 3·3%). It forms an orange solution in pyridine, becoming deep green on the addition of methanolic potassium hydroxide.

(*c*) The same 2 : 2′-dianthraquinonylamine was also isolated from technical 2-aminoanthraquinone by the following means. 2-Aminoanthraquinone (200 g.) was heated during 5 minutes with a boiling mixture of acetic anhydride (350 c.c.) and acetic acid (200 c.c.). On cooling, the solid was collected and heated with acetic acid (5 l.). The hot extract was separated and the residue washed with boiling acetic acid. The dark brown residue (0·4 g.) was again extracted by means of acetic acid, and then crystallised from boiling nitrobenzene. On cooling, reddish-brown prisms of 2 : 2′-dianthraquinonylamine separated (Found: N, 3·6%).

2 : 2′-*Dianthraquinonyl*-N-*methylamine*.—2 : 2′-Dianthraquinonylamine (1·05 g.), methyl toluene-*p*-sulphonate (4·0 g.), and dry potassium carbonate (1·0 g.) were added to trichlorobenzene (100 c.c.). The suspension was heated under reflux for 8 hours and then filtered. The orange filtrate was concentrated to small bulk; orange prisms (0·3 g.), m. p. 330°, separated on cooling. The product was sublimed at 320° (bath)/0·5 mm. An orange sublimate formed, and this was recrystallised from nitrobenzene. Small orange prisms were obtained, having m. p. 332—333° (Found: C, 78·2; H, 3·7; H, 3·3. $C_{29}H_{17}O_4N$ requires C, 78·5; H, 3·8; N, 3·2%). 2 : 2′-*Dianthraquinonyl*-N-*methylamine* dissolves in pyridine with an orange colour, unchanged on addition of methanolic potassium hydroxide.

1-*Chloro*-2-*nitroanthraquinone*.—2-Amino-1-chloroanthraquinone (30 g.; prepared by the method of Ullmann and Junghans, *Annalen*, 1913, **399**, 320) was dissolved in concentrated sulphuric acid (150 c.c.). The solution was cooled to 0°, and powdered sodium nitrite (10·2 g.) was added, with stirring, during 10 minutes. Stirring was continued for an hour, and then the solution was added to ice. The yellow precipitate was collected, washed with ice-water until the washings were only faintly acid to Congo-red, and then added to a suspension of copper sulphite in sodium nitrite; this was prepared by mixing aqueous solutions of copper sulphate (80 g.) and sodium sulphite (100 g.), collecting the brown precipitate, washing it free from sodium sulphite, and finally suspending it in water containing sodium nitrite (200 g.). Frothing occurred; this was controlled by addition of ether. After 2 hours' stirring, the product was collected and stirred with dilute hydrochloric acid. The brownish-yellow residue (34 g.; m. p. 220—240°) was extracted with *o*-dichlorobenzene (60 c.c.), and the extract treated with charcoal and filtered. On cooling, crude 1-chloro-2-nitroanthraquinone separated (yield 12 g.; m. p. 250—257°). Two recrystallisations from acetic acid gave yellow needles, m. p. 262—263° (Found: C, 58·7; H, 2·0; N, 4·7; Cl, 12·0. Calc. for $C_{14}H_6O_4NCl$: C, 58·5; H, 2·1; N, 4·9; Cl, 12·4%). Kopetschni (G.P. 363,930) records m. p. 257—258° for the quinone prepared by oxidising 2-amino-1-chloroanthraquinone

1-*Diethylamino*-2-*nitroanthraquinone*.—1-Chloro-2-nitroanthraquinone (0·5 g.) was heated under reflux during 30 minutes with diethylamine (25 c.c.), in the presence of potassium acetate (0·5 g.). The colour of the solution changed from yellow to deep violet-red. Water was added, and the violet *quinone* precipitated (0·55 g.) crystallised several times from acetic acid. Reddish-violet needles, m. p. 145—146°, were obtained (Found: C, 66·5; H, 4·6; N, 8·2. $C_{18}H_{16}O_4N_2$ requires C, 66·7; H, 4·9; N, 8·6%).

N-*Methyl*-2-*nitro*-1 : 2′-*dianthraquinonylamine*.—2-Nitro-1 : 2′-dianthraquinonylamine was prepared by condensing 1-chloro-2-nitroanthraquinone (10·4 g.) with 2-aminoanthraquinone (8·0 g.) by heating in trichlorobenzene during 4 hours. The deep red solution, on cooling, gave red needles, m. p. 294—295° (14·4 g.). Recrystallisation from *o*-dichlorobenzene afforded pure 2-nitro-1 : 2′-dianthraquinonylamine, m. p. 296—297° (12·2 g.). This gave a reddish-blue solution in concentrated sulphuric acid. It dissolved in pyridine with an orange-red colour which became deep green on addition of methanolic potassium hydroxide. Unlike the green colour obtained with most secondary bases of the series, that produced from 2-nitro-1 : 2′-dianthraquinonylamine is comparatively stable; it is not affected by the addition of considerable proportions of alcohol.

An attempt to prepare 2-nitro-1 : 2′-dianthraquinonylamine by heating a mixture of 1-chloro-2-nitroanthraquinone (2·9 g.), 2-aminoanthraquinone (2·25 g.), and potassium acetate (3 g.) in nitrobenzene (30 c.c.) for 3 hours gave a violet-brown product (1·8 g.), which was almost insoluble in boiling nitrobenzene. It was sparingly soluble in hot water forming a red solution, from which a yellow solid was precipitated by acid. The yellow product, crystallised several times from acetic acid, afforded glistening pale yellow plates of 1-*hydroxy*-2-*nitroanthraquinone*, m. p. 197—198° (Found: C, 62·4; H, 2·5; N, 4·8. $C_{14}H_7O_5N$ requires C, 62·4; H, 2·6; N, 5·2%).

1-Hydroxy-2-nitroanthraquinone was also formed when 1-chloro-2-nitroanthraquinone and 2-aminoanthraquinone were heated together in nitrobenzene solution, with the addition of copper and sodium acetate.

2-Nitro-1 : 2′-dianthraquinonylamine (10·0 g.), methyl toluene-*p*-sulphonate (10·0 g.), and dry potassium carbonate (8·0 g.) were heated together in *o*-dichlorobenzene (40 c.c.) for 8 hours. The

suspension was filtered, the residue washed by means of hot *o*-dichlorobenzene, and the washings and filtrate were combined and concentrated to small volume. On addition of ether, an orange-brown precipitate (8·2 g.; m. p. 160° with previous softening) was obtained. It was taken up in chlorobenzene and chromatographed on alumina; a dark brown, strongly adsorbed zone formed, and a main orange-red zone. Elution of the main zone by ethyl acetate and evaporation of the solvent gave orange prisms (6·1 g.), m. p. 264—265° (Found: C, 71·4; H, 3·2; N, 5·6. $C_{29}H_{16}O_6N_2$ requires C, 71·3; H, 3·3; N, 5·7%). N-*Methyl*-2-*nitro*-1 : 2′-*dianthraquinonylamine* forms an orange solution in pyridine which remains unaltered by the addition of methanolic potassium hydroxide. The solution in concentrated sulphuric acid is deep blue; addition of water precipitates a red material, which becomes orange on further dilution. Crystallisation from chlorobenzene yields dark red prisms of the *molecular compound*, $(C_{29}H_{16}O_6N_2)_2,C_6H_5Cl$, m. p. 169—170° (Found: N, 5·6; Cl, 3·6. $C_{64}H_{37}O_{12}N_4Cl$ requires N, 5·2; Cl, 3·3%). Solvents such as ether or ethyl acetate decompose the adduct, *N*-methyl-2-nitro-1 : 2′-dianthraquinonylamine, m. p. 264°, being regenerated. The nitro-amine crystallises unchanged from benzene, but dark red crystals, m. p. 160—180°, separate from its solution in *o*-dichlorobenzene. A dark red product, indistinctly crystalline, m. p. 152—168°, separates from its solution in toluene.

2-*Amino*-1 : 2′-*dianthraquinonyl*-N-*methylamine*.—(*a*) *N*-Methyl-2-nitro-1 : 2′-dianthraquinonylamine (2·0 g.) was added to a boiling solution containing stannous chloride (4·0 g.) in acetic acid (40 c.c.). After 10 minutes, the solution was cooled and mixed with water; a reddish-brown precipitate (2·0 g.), m. p. 210°, formed. This was dissolved in chlorobenzene and chromatographed on alumina. A number of brown, yellow, and red zones formed. The main zone was red, and this was eluted by ethyl acetate. Evaporation of the eluate gave the tertiary *amine* as bright red needles (0·45 g.), m. p. 306° (Found: C, 75·3; H, 3·9; N, 6·4. $C_{29}H_{18}O_4N_2$ requires C, 76·0; H, 3·9; N, 6·1%).

(*b*) *N*-Methyl-2-nitro-1 : 2′-dianthraquinonylamine (4·0 g.) was prepared in a finely divided state by dissolution in sulphuric acid (40 c.c.) and addition to water. The orange-yellow precipitate was collected, washed neutral, then added to a solution containing hydrated sodium sulphide (5·5 g.) and potassium hydroxide (5·5 g.) in water (160 c.c.). The suspension was stirred for 1 hour at 95°, then filtered, and the reddish-brown residue washed free from alkali and dried (3·0 g.; m. p. 280—290°). It was dissolved in chlorobenzene and chromatographed on alumina. The main red zone, eluted by ethyl acetate, yielded 1·4 g. of 2-amino-1 : 2′-dianthraquinonyl-*N*-methylamine as red needles, m. p. 306°. A reddish-orange zone of the column contained the unreduced nitro-compound in the form of its adduct with chlorobenzene. At the top of the column was a blue zone; this was eluted by quinoline. The blue substance dissolved in concentrated sulphuric acid with a brown colour. It dissolved in alkaline dithionite ($Na_2S_2O_4$) forming a brown solution, from which cotton was dyed; aeration gave the blue of the original colouring matter. (Cf. Part IV.)

2-*Benzamido*-1 : 2′-*dianthraquinonyl*-N-*methylamine*.—A solution containing 2-amino-1 : 2′-dianthraquinonyl-*N*-methylamine (1·2 g.) and a drop of concentrated sulphuric acid in benzoyl chloride (10 c.c.) was heated for 5 minutes under reflux, then cooled, and mixed with alcohol (30 c.c.). Orange-yellow crystals separated; these were collected and washed with alcohol (1·33 g.; m. p. 314°). Crystallisation from acetic acid, in which it was sparingly soluble, gave orange-yellow needles, m. p. 314—315° (Found: C, 76·7; H, 3·7; N, 4·9. $C_{36}H_{22}O_5N_2$ requires C, 76·9; H, 3·9; N, 5·0%). The *benzoyl* derivative dissolved in pyridine with an orange-yellow colour, becoming deep violet on addition of methanolic potassium hydroxide. The violet colour was stable towards a small proportion of water; more water reversed the colour change to yellow. The benzoyl derivative dissolved in concentrated sulphuric acid with a bright blue colour, which slowly became violet owing to hydrolysis of the benzoyl groups.

2-Amino-1 : 2′-dianthraquinonyl-*N*-methylamine was recovered unchanged after being heated for 5 hours with a solution of toluene-*p*-sulphonyl chloride in pyridine.

N-*Methyl*-2-N-*methylbenzamido*-1 : 2′-*dianthraquinonylamine*.—Methyl toluene-*p*-sulphonate (1·0 g.), 2-benzamido-1 : 2′-dianthraquinonyl-*N*-methylamine (1·0 g.), and dry potassium carbonate (0·6 g.) were heated under reflux in *o*-dichlorobenzene (20 c.c.) for 3 hours. The hot solution was filtered, and the filtrate mixed with benzene, then chromatographed on alumina. The main fraction formed an orange zone; this was eluted by acetone, and the eluate was concentrated and mixed with ether. The NN′-*dimethyl* derivative separated as orange prisms (0·2 g.), m. p. 195—196° (Found: C, 76·5; H, 4·5; N, 4·8. $C_{37}H_{24}O_5N_2$ requires C, 77·1; H, 4·2; N, 4·9%). It dissolved in pyridine with a yellow colour, unchanged by methanolic potassium hydroxide; in concentrated sulphuric acid the colour was deep blue.

N-*Methyl*-2-N-*methylamino*-1 : 2′-*dianthraquinonylamine*.—A solution containing the benzoyl derivative (0·1 g.) in concentrated sulphuric acid (2 c.c.) was heated at 100°; the colour changed from blue to violet. The solution was cooled, then added to water. An orange precipitate of the free *amine* formed (0·06 g.), having m. p. 338—340° (Found: N, 5·6. $C_{30}H_{20}O_4N_2$ requires N, 5·9%).

An attempt to prepare this derivative by methylating 2-amino-1 : 2′-dianthraquinonyl-*N*-methylamine by methyl toluene-*p*-sulphonate was unsuccessful.

NN-*Dimethylindanthrone*.—Indanthrone (Found: N, 6·3. Calc. for $C_{28}H_{14}O_4N_2$: N, 6·3%) was prepared by crystallising the sulphate from sulphuric acid and hydrolysing this with water. It was very sparingly soluble in boiling pyridine, forming a pale blue solution.

A suspension containing indanthrone (5 g.), methyl toluene-*p*-sulphonate (20 g.), and dry potassium carbonate (15 g.) in trichlorobenzene (200 c.c.) was heated under reflux during 48 hours. The suspension was filtered hot, and the green residue washed with hot trichlorobenzene. The filtrate and washings were combined and then evaporated to 40 c.c.; on cooling, violet-blue prisms having a coppery lustre separated (1·64 g.) (product A). The blue mother-liquor was mixed with benzene (300 c.c.), and then chromatographed on alumina. Development with benzene yielded the following zones in order of increasing mobility: black, pink, blue, violet, blue I, green, blue II, pale brown; a solution having a green fluorescence passed through the column.

The blue I zone was unaffected by acetone or other solvents of low b. p. Hot quinoline at 150°

eluted the blue colouring matter; it separated from the eluate during 48 hours as violet-blue crystals having a coppery lustre (0·05 g.). Its absorption spectrum in pyridine was identical with that of product A. Analysis showed it to consist of NN-*dimethylindanthrone* (Found: C, 76·2; H, 3·8; N, 5·9; NCH_3, 10·6, 11·0. $C_{30}H_{18}O_4N_2$ requires C, 76·6; H, 3·8; N, 6·0; NCH_3, 12·3%). *NN*-Dimethylindanthrone was readily soluble in pyridine with a deep blue colour. Unlike indanthrone it crystallised unaltered from solution after 0·5 g. had been heated for 200 hours under reflux with dry potassium carbonate (0·5 g.) in trichlorobenzene (10 c.c.); it was unaffected by dilute nitric acid. The solubility of *NN*-dimethylindanthrone in *o*-dichlorobenzene at 20° was 0·018 g./100 c.c.

The zone blue II was the most prominent. The colouring matter (product B) was readily eluted by acetone; the eluate on evaporation yielded bluish-violet prisms having a coppery lustre (0·19 g.) (Found: C, 77·5; H, 3·9; N, 5·6; NCH_3, 3·6; 4·2%). This product (0·1 g.) afforded a violet-blue solution in trichlorobenzene (3 c.c.), which remained unaltered on being heated with dry potassium carbonate (0·1 g.) for 150 hours. It was unaffected by dilute nitric acid.

Under other conditions the methylation of indanthrone was less satisfactory. Indanthrone (1 g.), methyl toluene-*p*-sulphonate (2 g.), and dry potassium carbonate (1·4 g.), heated under reflux for 6 hours with trichlorobenzene (100 c.c.), afforded an undissolved portion, consisting mainly of indanthrone, and a solution from which 0·2 g. of blue needles separated on filtration and cooling. This product dissolved in pyridine with a blue colour, becoming green on the addition of methanolic potassium hydroxide. The evaporated mother-liquor afforded 0·03 g. of violet-blue crystals; these dissolved in pyridine with a blue colour, rendered only slightly greener by methanolic potassium hydroxide.

Oxidation of NN-*Dimethylindanthrone.*—(*a*) *NN*-Dimethylindanthrone (0·3 g.) dissolved in concentrated sulphuric acid (6 c.c.), forming a brown solution. This was cooled to 0°, and powdered potassium nitate (0·3 g.) added; there was an immediate change in colour to bright blood-red. The mixture was stirred for 3 hours at 0°, then added to water; a blue precipitate formed. (In similar circumstances indanthrone affords a yellow oxidation product.) The suspension was made alkaline, sodium dithionite (1·0 g.) was added, and the mixture warmed to 50°. A brown solution resulted; this was filtered and the filtrate oxidised by a current of air. The precipitated blue material was easily soluble in pyridine; the colour remained unaltered when methanolic potassium hydroxide was added.

(*b*) Finely powdered *NN*-dimethylindanthrone (0·5 g.) was added at 0°, and with stirring, to nitric acid (*d* 1·4; 5·0 c.c.). After 5 minutes, fine orange-red needles separated from the yellow-brown solution. These were collected after an hour and washed by means of acetic acid; the colour changed to orange-brown. The product was insoluble in ether, alcohol, ethyl acetate, and benzene; ammonia changed it to a bluish-black material immediately. The product, dried *in vacuo* over sodium hydroxide, afforded an amorphous brownish-yellow powder (0·40 g.) (Found: C, 60·5; H, 3·1; N, 7·6, 7·9%). Heating it to 100°, or keeping it for a long period at the room temperature, caused it to become green; its yellow solution in acetic acid became green on boiling. Warming with sodium hydroxide and sodium dithionite solution reduced it, an orange solution resulting. Chromatographed on cellulose the solution afforded a thin, strongly absorbed blue zone; the remainder was removed from the column by elution with alkaline dithionite. The orange eluate, exposed to air, afforded a blue precipitate having the properties of *N*-methylindanthrone. Treatment with methyl toluene-*p*-sulphonate and potassium carbonate in trichlorobenzene reconverted it into *NN*-dimethylindanthrone.

Cyclisation of N-*Methyl*-2-N-*methylamino*-1 : 2′-*dianthraquinonylamine. Formation of* NN′-*Dimethylindanthrone.*—*N*-Methyl-2-*N*-methylamino-1 : 2′-dianthraquinonylamine was recovered unchanged after being heated with acetic acid or pyridine. The amine was readily cyclised, however, by hot methanolic potassium hydroxide. The amine (0·03 g.) was dissolved in pyridine (30 c.c.) and a solution of potassium hydroxide in methanol (0·5 c.c. of 30%) was added; there was no change in the orange colour of the solution. Heating to boiling changed the colour to olive brown and then, on shaking, to bright reddish-brown. As the shaking was continued at the b. p., the colour changed to bright green, and finally to greenish blue. The product was exposed to air for 12 hours, then mixed with methanol. The blue precipitate was collected, then washed in turn with methanol and water. The methanolic filtrate was colourless, an indication that the amine reactant was no longer present. The blue residue (0·03 g.) dissolved readily in *o*-dichlorobenzene. At 20° its solubility was 0·017 g./100 c.c. The total solubility of a mixture of the product with *NN′*-dimethylindanthrone (prepared by the direct methylation of indanthrone) was 0·018 g./100 c.c. The product was not completely homogeneous, because its blue solution in pyridine was rendered green by methanolic potassium hydroxide. A solution in *o*-dichlorobenzene chromatographed on alumina afforded two blue zones. An attempt to extract the adsorbed colouring matters by boiling *o*-dichlorobenzene resulted in the isolation of indanthrone. (Cf. Part II.)

Cyclisation of 2-*Amino*-1 : 2′-*dianthraquinonyl*-N-*methylamine. Formation of* N-*Methylindanthrone.*—(*a*) The amino-compound was recovered unaltered after 8 hours' heating with acetic acid, 16 hours' with pyridine, 12 hours' with anthracene or for 6 hours' with nitrobenzene, all at the b. p. Heating 0·1 g. of the amine with acetic anhydride (10 c.c.) for 4 hours afforded an orange product (0·1 g.), m. p. 190—200°, doubtless the *N*-acetyl derivative, which dissolved in pyridine with a yellow colour, becoming reddish-violet on addition of methanolic potassium hydroxide.

(*b*) Powdered sodium hydroxide (0·2 g.) was added to a solution of the amine (0·2 g.) in pyridine (5 c.c.). The suspension was kept at the room temperature for 10 days with occasional shaking and stirring. There was no immediate change in colour on addition of the alkali but, after 24 hours, the surface of the suspension had become green. After 10 days the whole suspension had become green; at the surface there were areas containing blue colouring matter. Methanol was added and the blue product (0·15 g.) collected. The filtrate was pale orange, an indication of the presence of unchanged amine.

(*c*) In a similar experiment in which 0·2 g. of potassium hydroxide was used, the yield of the blue colouring matter was 0·17 g.

The two blue products were combined and crystallised from quinoline; violet needles of N-*methylindanthrone* (0·17 g.) separated (Found : C, 76·4; H, 3·3; N, 5·8; NCH_3, 6·5. $C_{29}H_{16}O_4N_2$ requires C, 76·3; H, 3·5; N, 6·1; NCH_3, 6·4%). *N*-Methylindanthrone was easily soluble in hot pyridine with a deep blue colour; on addition of methanolic potassium hydroxide the colour changed immediately to green; the further addition of water or alcohol restored the original blue colour and precipitated the original blue colouring matter. *N*-Methylindanthrone dissolved in concentrated sulphuric acid with a brown colour; a blue precipitate formed immediately on addition of water. Its solubility in *o*-dichlorobenzene at 20° was 0·00076 g./100 c.c.

Oxidation of N-*Methylindanthrone*.—*N*-Methylindanthrone (0·05 g.) was stirred at 0° with nitric acid (*d* 1·4; 0·5 c.c.). It dissolved with a bright orange colour; after a short time orange needles separated (0·02 g.), identical with those obtained by the action of cold, concentrated nitric acid on *NN*-dimethylindanthrone. The product dissolved in alkaline dithionite forming a brown solution; on exposure to air the solution re-formed *N*-methylindanthrone.

Methylation.—*N*-Methylindanthrone (20 mg.), methyl toluene-*p*-sulphonate (40 mg.) and dry potassium carbonate (20 mg.) were heated under reflux during 8 hours with *o*-dichlorobenzene (3 c.c.). The suspension was filtered while hot, cooled, mixed with benzene, and chromatographed on alumina; a single, uniform, blue zone resulted. The colouring matter was eluted by means of quinoline and the eluate evaporated to a small volume. The characteristic coppery-blue crystals of *NN*-dimethylindanthrone (12 mg.) separated. The product dissolved in pyridine with a blue colour which remained unaltered on adding methanolic potassium hydroxide. Its absorption spectrum in pyridine was identical with that of *NN*-dimethylindanthrone prepared by methylation of indanthrone. The solubility in *o*-dichlorobenzene was 0·029 g./100 c.c. at 20°. The solubility of a mixture of the product with *NN*-dimethylindanthrone, prepared by the methylation of indanthrone, was 0·026 g./100 c.c.

2-Amino-1 : 2′-dianthraquinonylmethylamine (0·2 g.) was recovered unaltered when its solution in pyridine (5 c.c.) was shaken at intervals during 10 days with lithium hydroxide (0·2 g.), and methyl alcohol was subsequently added. A slight green colour developed after 3 days.

2-N-*Methylacetamidoanthraquinone*.—2-Methylaminoanthraquinone (1·0 g.) was heated under reflux for an hour with acetic acid (10 c.c.) containing acetic anhydride (10 c.c.). The orange precipitate, obtained on adding the mixture to water, crystallised from alcohol (charcoal) in pale yellow needles (0·6 g.), m. p. 159—160° (Found : C, 72·8; H, 4·7; N, 5·2. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7; N, 5·0%). The pale yellow solution of the *acetyl* derivative in pyridine remained unchanged in colour on addition of methanolic potassium hydroxide.

Potassium Salt of 2-*Benzamidoanthraquinone*.—A solution containing potassium hydroxide (0·2 g.) in methyl alcohol (0·6 c.c.) was added to one containing 2-benzamidoanthraquinone (0·5 g.) in pyridine (10 c.c.). The deep red-violet solution was added to benzene (500 c.c.); a flocculent precipitate separated. This was filtered off; the filtrate was yellow, owing to the presence of excess of the benzoyl derivative. The residue, after drying *in vacuo*, consisted of bluish-red flakes (0·45 g.) (Found : N, 3·8; K, 10·8. $C_{21}H_{12}O_3NK$ requires N, 3·8; K, 10·7%). The *potassium* salt dissolved in pyridine with a reddish-violet colour, becoming orange and then yellow on addition of methanol. It darkened at 160° and melted at 246—250°. Apparently, fusion occurred without decomposition, because the fused salt dissolved in pyridine with a violet colour rendered yellow on adding water. On exposure to air the colour of the salt became yellow; at the same time potassium carbonate was formed.

An attempt to methylate the potassium salt (3·0 g.) by methyl iodide (10 c.c.) at 120—130° for 24 hours gave only 2-benzamidoanthraquinone.

2-N-*Methylbenzamidoanthraquinone*.—(*a*) 2-Methylaminoanthraquinone (1·0 g.) was heated with benzoyl chloride (2 c.c.) in pyridine (20 c.c.) for 30 minutes. The *benzoyl* derivative crystallised from aqueous acetic acid in bright orange-yellow needles (0·45 g.), m. p. 171—172° (Found : C, 77·4; H, 4·2; N, 4·2. $C_{22}H_{15}O_3N$ requires C, 77·3; H, 4·4; N, 4·1%). There was no change in colour on addition of methanolic potassium hydroxide to its yellow solution in pyridine.

(*b*) 2-Benzamidoanthraquinone (1·0 g.), methyl toluene-*p*-sulphonate (1·0 g.), and dry potassium carbonate (0·6 g.) were heated together in *o*-dichlorobenzene (20 c.c.) for 5 hours. The suspension was filtered, and the filtrate evaporated to a small volume, and then mixed with ether; pale yellow crystals (0·47 g.), m. p. 165—168°, separated. This product was dissolved in benzene and chromatographed on alumina. Two zones formed; the more strongly adsorbed was 2-benzamidoanthraquinone. The yellow, less strongly adsorbed, zone was eluted with acetone and the eluate evaporated. Orange-yellow crystals, m. p. 172—173°, were obtained, the m. p. of which was not depressed by admixture with authentic 2-*N*-methylbenzamidoanthraquinone. The methylated product dissolved in pyridine with a yellow colour, which was not affected by methyl alcoholic potassium hydroxide.

2-p-*Nitrobenzamidoanthraquinone*.—2-Aminoanthraquinone (2·0 g.) was heated under reflux for 30 minutes with pyridine (10 c.c.) containing *p*-nitrobenzoyl chloride (4 g.). The colour of the solution changed from orange to yellow; on addition of alcohol the p-*nitrobenzoyl* derivative (2·5 g.) crystallised. It separated from nitrobenzene in bunches of pale yellow needles (1·7 g.), m. p. 303—304° (Found : C, 67·6; H, 3·1; N, 7·2. $C_{21}H_{12}O_5N_2$ requires C, 67·7; H, 3·2; N, 7·5%). 2-*p*-Nitrobenzamidoanthraquinone dissolved in pyridine with a pale yellow colour which became deep red-violet on addition of methyl alcoholic potassium hydroxide and pale orange on the further addition of methyl alcohol.

Potassium salt. This *derivative* was obtained as a red powder (Found : N, 6·4; K, 9·5. $C_{21}H_{11}O_5N_2K$ requires N, 6·8; K, 9·5%) by treating potassium hydroxide with 2-*p*-nitrobenzamidoanthraquinone by the method adopted for the analogous derivative of 2-benzamidoanthraquinone. It dissolved in pyridine with a red colour; it was more stable towards hydrolysis than the un-nitrated salt.

2-N-*Methyl*-p-*nitrobenzamidoanthraquinone*.—Prepared similarly by heating 2-methylaminoanthraquinone (1·0 g.) with *p*-nitrobenzoyl chloride (2·0 g.) in pyridine (20 c.c.) for an hour, this *amide*

crystallised from acetic acid in pale yellow needles (0·55 g.), m. p. 233° (Found : C, 68·0; H, 4·1; N, 7·3. $C_{22}H_{14}O_5N_2$ requires C, 68·4; H, 3·6; N, 7·3%). Its pale yellow solution in pyridine remained unaltered in colour on addition of methanolic potassium hydroxide.

2-N-*Methylacetamido*-1-*nitroanthraquinone*.—2-Acetamido-1-nitroanthraquinone (10 g.; Ullmann and Medenwald, *Ber.*, 1913, **46**, 1798) was added to 500 c.c. of 5% sodium hydroxide solution and warmed to 60—70°. The orange solution was filtered, leaving a residue of 2-amino-1-nitroanthraquinone, m. p. 306°. The red filtrate was stirred for 30 minutes with methyl sulphate (20 c.c.); an orange precipitate formed (6·8 g.), having m. p. 247°. Several recrystallisations from acetic acid afforded glistening pale yellow plates (3·3 g.), m. p. 260—261° (Found : C, 62·6; H, 3·6; N, 8·2. $C_{17}H_{12}O_5N_2$ requires C, 62·9; H, 3·7; N, 8·6%). The *methyl* derivative dissolved in pyridine with a pale yellow colour which remained unchanged on adding methanolic potassium hydroxide

2-*Methylamino*-1-*nitroanthraquinone*.—A solution containing 1·0 g. of 2-*N*-methylacetamido-1-nitroanthraquinone in 10 c.c. of concentrated sulphuric acid was heated at 100° for 1 hour and then added to water; an orange precipitate (0·65 g.; m. p. 218—230°) formed. Crystallisation from alcohol afforded orange needles of 2-*methylamino*-1-*nitroanthraquinone* (0·2 g.), m. p. 246° (Found : C, 63·7; H, 3·5; N, 9·9. $C_{15}H_{10}O_4N_2$ requires C, 63·8; H, 3·6; N, 9·9%). It dissolved in pyridine forming an orange solution which became pale green on addition of methanolic potassium hydroxide. The intensity of the green colour was much less than that characteristic of 2-amino-1-nitroanthraquinone.

2-*Benzamido*-1-*nitroanthraquinone*.—Concentrated sulphuric acid (2—3 drops) was added at 100° to a solution containing 2-amino-1-nitroanthraquinone (3·0 g.) in benzoyl chloride (20 c.c.). The solution was agitated for an hour and then mixed with alcohol. The *benzoyl* derivative separated (4·7 g.; m. p. 235—240°). Crystallisation from acetic acid (charcoal) afforded long, pale yellow needles (3·4 g.), m. p. 246—247° (Found : C, 67·8; H, 3·1; N, 7·6. $C_{21}H_{12}O_5N_2$ requires C, 67·7; H, 3·2; N, 7·5%).

2-N-*Methylbenzamido*-1-*nitroanthraquinone*.—2-Benzamido-1-nitroanthraquinone (2·0 g.) was added to 5% sodium hydroxide solution (200 c.c.) and warmed to 80°. The deep-red solution was filtered, and the filtrate stirred for 2 hours with methyl sulphate (12 c.c.). The orange-yellow precipitate was collected and extracted by dilute sodium hydroxide solution until the extract was colourless; finally it was washed by means of water and dried. The *methylamide* (1·1 g.; m. p. 228—230°) crystallised from acetic acid in fine, pale yellow needles (0·6 g.), m. p. 231—232° (Found : C, 68·8; H, 3·4; N, 7·0. $C_{22}H_{14}O_5N_2$ requires C, 68·4; H, 3·6; N, 7·3%). This product dissolved in pyridine with a very pale yellow colour; there was no change on addition of methanolic potassium hydroxide. Hydrolysis with concentrated sulphuric acid gave orange needles of 2-methylamino-1-nitroanthraquinone, m. p. 246—247°, not depressed when mixed with an authentic specimen.

2-*Dimethylaminoanthraquinone*.—2-Chloroanthraquinone (4·0 g.), potassium acetate (4·0 g.), copper bronze (0·1 g.), cupric acetate (0·1 g.), and aqueous dimethylamine (24 c.c. of 33%) were heated for 2 hours at 200°. The red product crystallised from glacial acetic acid in fine, orange-red needles (3·5 g.), m. p. 185—186° (Found : C, 76·5; H, 5·3; N, 5·6. Calc. for $C_{16}H_{13}O_2N$: C, 76·5; H, 5·2; N, 5·6%). Haller and Cryot (*Bull. Soc. chim.*, 1901, **25**, 206) obtained this compound by cyclising *o*-4-dimethylaminobenzylbenzoic acid and oxidising the product; they recorded m. p. 181°. The yellow solution of 2-dimethylaminoanthraquinone in pyridine was unaltered on addition of methanolic potassium hydroxide.

2-*Anilinoanthraquinone*.—This was obtained as golden-orange plates, m. p. 238—239°, by treating 2-chloroanthraquinone with aniline in the presence of copper bronze, cupric acetate, and potassium acetate (G.P. 288,464 records m. p. 234—236°).

The following experiment was carried out with the object of finding a more convenient preparation of 2-anilinoanthraquinone. Sodamide (4·0 g.) and aniline (50 c.c.) were heated to 150°, the liberated ammonia being removed under reduced pressure. A solution containing 2-chloroanthraquinone (5 g.) in aniline (50 c.c.) was then added; the mixture became greenish. It was heated under reflux at 150°, under reduced pressure, for 30 minutes, then cooled, and carefully mixed with water. Aniline was removed by distillation in steam, the green residue (5 g.) dissolved in benzene, and the solution chromatographed on alumina. A yellow zone was weakly adsorbed and easily eluted from the column by benzene; it consisted of 2-chloroanthraquinone. The main zone was blue; elution with acetone and evaporation of the extract afforded a residue which crystallised from acetic acid in blue needles having a coppery lustre (0·45 g.), m. p. 236—237° (Found : C, 79·8; H, 4·3; N, 6·7; Cl, 0·1. Calc. for $C_{26}H_{16}O_2N_2$: C, 80·4; H, 4·1; N, 7·2%). The product dissolved in pyridine with a reddish-blue colour which was little affected by adding methanolic potassium hydroxide. Its solution in concentrated sulphuric was greenish-yellow, becoming green on adding water; subsequently a blue precipitate formed. It dissolved in alkaline dithionite, forming a reddish-brown solution.

Sodium salt. A solution of sodioanthracene in ether was prepared by shaking a suspension of anthracene (3 g.) and powdered sodium (4 g.) in dry ether (250 c.c.). The blue solution was filtered into one of 2-anilinoanthraquinone (0·3 g.) in dry ether; a green precipitate formed. The green product was filtered off, and then brought into contact with methyl iodide. (All these operations were carried out in nitrogen free from oxygen.) The methylation product did not appear to contain 2-*N*-methylanilinoanthraquinone. In another experiment the green sodio-derivative was exposed to air; it became brown, the decomposed product dissolving in pyridine with an orange colour and then affording a green solution on the addition of methanolic potassium hydroxide.

2-*Acetanilidoanthraquinone*.—2-Anilinoanthraquinone (0·5 g.) potassium acetate (2·0 g.) and acetyl chloride (20 c.c.) were heated under reflux for 3 hours; the colour of the solution changed from orange to yellow. The product was mixed with methyl alcohol, and potassium acetate was added until the suspension was neutral to Congo-red. The filtered solution was evaporated almost to dryness, then mixed with water, and the sticky precipitate crystallised from methyl alcohol (charcoal). The product (0·1 g.) was obtained as pale yellow needles, m. p. 131° (Found : N, 4·1. $C_{22}H_{15}O_3N$ requires N, 4·1%)

It dissolved in pyridine with a yellow colour; methanolic potassium hydroxide changed the colour to green almost immediately as a result of hydrolysis.

2-*Benzanilidoanthraquinone*.—2-Anilinoanthraquinone (0·5 g.), benzoyl chloride (5 c.c.), and pyridine (3 c.c.) were heated together under reflux for an hour. Alcohol was added; the *benzoyl* derivative (0·2 g.; m. p. 155—156°) separated very slowly. Recrystallisation from alcohol gave silvery grey needles, m. p. 159—160° (Found : C, 79·9; H, 4·3; N, 3·4. $C_{27}H_{17}O_3N$ requires C, 80·3; H, 4·2; N, 3·5%). The yellow solution in pyridine showed no immediate change on addition of methanolic potassium hydroxide, but a deep-green colour gradually developed, and addition of water then precipitated 2-anilinoanthraquinone, m. p. 235—236°. The benzoyl derivative dissolved in concentrated sulphuric acid with an orange-red colour; warming brought about a blue colour as a result of hydrolysis to 2-anilinoanthraquinone.

2-N-*Methylanilinoanthraquinone*.—2-Anilinoanthraquinone (10 g.), methyl toluene-*p*-sulphonate (12·5 g.), and dry potassium carbonate (6·7 g.) were heated under reflux for 5 hours in *o*-dichlorobenzene (80 c.c.). The suspension was filtered hot, the residue washed by *o*-dichlorobenzene, and the combined washings and filtrate were evaporated to 30 c.c. and then mixed with ligroin. An orange product separated (8·6 g.; m. p. 160°). Crystallisation from alcohol gave the tertiary *amine* as orange needles (7·5 g.), m. p. 163—164° (Found : C, 80·3; H, 4·5; N, 4·5. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8; N, 4·5%). The orange solution in pyridine was unaffected by methanolic potassium hydroxide.

Potassium salt of 2-*Toluene*-p-*sulphonamidoanthraquinone*.—2-Toluene-*p*-sulphonamidoanthraquinone (38 g.) was dissolved in a hot solution containing potassium hydroxide (10 g.) in water (500 c.c.). The red solution was filtered; on cooling, the *potassium* salt separated (35 g.). It crystallised from 95% alcohol in bluish-red rhombs (Found : C, 60·2; H, 3·7; N, 3·3; S, 7·3; K, 10·0. $C_{21}H_{14}O_4NSK$ requires C, 60·6; H, 3·4; N, 3·4; S, 7·7; K, 9·4%).

Heating the potassium salt (9·0 g.) with ethyl iodide (10 c.c.) at 110° for 24 hours gave 7 g. of an alkali-insoluble product, m. p. 139°. Crystallisation from alcohol gave pale yellow needles of N-*ethyltoluene*-p-*sulphonamidoanthraquinone*, m. p. 139—140° (5·4 g.) (Found : C, 68·0; H, 4·6; N, 3·7; S, 8·2. $C_{23}H_{19}O_4NS$ requires C, 68·1; H, 4·7; N, 3·5; S, 7·9%). Warming the *N*-ethyl derivative (6 g.) with concentrated sulphuric acid (50 c.c.) at 100° for 30 minutes and adding the resulting solution to water gave 3·9 g. of an orange precipitate, m. p. 198—199°. Crystallisation from acetic acid gave orange needles of 2-ethylaminoanthraquinone (3·5 g.), m. p. 198—199° (Found : C, 76·4; H, 5·3; N, 5·9. Calc. for $C_{16}H_{13}O_2N$: C, 76·5; H, 5·2; N, 5·6%). This derivative dissolved in pyridine with a yellow colour, unchanged by methanolic potassium hydroxide. Marcinków and Plażek (*Rocz. Chem.*, 1936, **16**, 395) claim to have prepared this compound by the action of ethylamine on 2-chloroanthraquinone, but do not record the m. p.

The potassium salt (5 g.) did not appear to react with *n*-butyl bromide at 110° during 48 hours. Heated further at 150° for 24 hours, and then extracted by means of aqueous sodium hydroxide, it gave an alkali-insoluble product (4·9 g.; m. p. 144—146°). This crystallised from acetic acid in stout yellow prisms of 2-N-n-*butyltoluene*-p-*sulphonamidoanthraquinone* (2·3 g.), m. p. 147° (Found : C, 69·0; H, 5·3; N, 3·2; S, 7·0. $C_{25}H_{23}O_4NS$ requires C, 69·3; H, 5·3; N, 3·2; S, 7·4%). There was no change in the yellow colour of a solution of this derivative in pyridine on addition of methanolic potassium hydroxide.

1-*Chloro*-2-*toluene*-p-*sulphonamidoanthraquinone*.—A solution containing 2-amino-1-chloroanthraquinone (100 g.) and toluene-*p*-sulphonyl chloride (80 g.) in pyridine (500 c.c.) was heated under reflux for 4 hours. One-half of the pyridine was then distilled off, and alcohol was added to the residue. The yellow product which separated was collected, washed with alcohol (yield, 131 g.; m. p. 205°), and recrystallised from acetic acid. Fine yellow needles separated, having m. p. 208—209° (Found : C, 61·2; H, 3·5; N, 3·4; Cl, 9·0; S, 7·9. Calc. for $C_{21}H_{14}O_4NClS$: C, 61·2; H, 3·4; N, 3·5; Cl, 8·6; S, 7·8%). The compound has been prepared (G.P. 376,471) by heating 2-toluene-*p*-sulphonamidoanthraquinone with sulphuryl chloride and borax.

The *potassium* derivative was obtained by adding 8·2 g. of the amide to a warm solution of potassium hydroxide (1·7 g.) in water (100 c.c.). A red tarry product was formed, but this became granular as the temperature was raised to the b. p. Having been filtered off, washed and dried, the product (7·5 g.) was crystallised from ethyl alcohol, in which it was sparingly soluble. It formed reddish-orange prisms, m. p. above 300° (Found, in material dried *in vacuo* : C, 56·0; H, 3·0; N, 3·1; Cl, 8·3; S, 6·9; K, 9·4. $C_{21}H_{13}O_4NClSK$ requires C, 56·0; H, 2·9; N, 3·1; Cl, 7·9; S, 7·1; K, 8·7%).

1-*Chloro*-2-N-*methyltoluene*-p-*sulphonamidoanthraquinone*.—This *derivative* resulted when the potassium salt (15 g.) was heated at 100—110° for 24 hours with methyl iodide (15 c.c.). The product was extracted with hot sodium hydroxide solution, and the insoluble portion (13·7 g.) dried and recrystallised from acetic acid. It formed yellow needles (11·2 g.), m. p. 209° (Found : C, 61·8; H, 3·9; N, 3·3; Cl, 8·8; S, 7·8. $C_{22}H_{16}O_4NClS$ requires C, 62·0; H, 3·8; N, 3·3; S, 7·5; Cl, 8·3%).

1-*Chloro*-2-*methylaminoanthraquinone*.—The toluene-*p*-sulphonyl derivative (10 g.) was heated at 95° for an hour with concentrated sulphuric acid (50 c.c.), and the resulting solution added to water. The precipitate, collected, washed, dried, and crystallised from acetic acid, gave 6·3 g. of orange needles, m. p. 240° (Found : C, 66·4; H, 3·5; N, 4·8; Cl, 12·9. $C_{15}H_{10}NCl$ requires C, 66·5; H, 3·7; N, 5·2; Cl, 13·1%). This *quinone* dissolved in pyridine with an orange colour; methanolic potassium hydroxide caused a faint, but distinct, green coloration. It was shown that this could not be due to small amounts of 2-amino-1-chloroanthraquinone.

1-*Chloro*-2-N-*methylacetamidoanthraquinone*.—A suspension containing 1-chloro-2-methylaminoanthraquinone (0·5 g.) and potassium acetate (1 g.) in acetyl chloride (10 c.c.) was heated under reflux until a pale yellow solution resulted. The *acetyl* derivative, precipitated by addition of the mixture to water and recrystallised from alcohol, gave pale yellow needles (0·2 g.), m. p. 204—205° (Found : N, 4·7; Cl, 11·7. $C_{17}H_{12}O_3NCl$ requires N, 4·5; Cl, 11·3%). It dissolved in pyridine with a yellow colour, unaltered by methanolic potassium hydroxide.

1-*Chloro*-2-*ditoluene*-p-*sulphonylaminoanthraquinone*.—2-Amino-1-chloroanthraquinone (7 g.), toluene-*p*-sulphonyl chloride (7 g.), and pyridine (40 c.c.) were heated under reflux for 4 hours. The resulting solution was mixed with alcohol, and the pale yellow product (11·5 g.), m. p. 250—260°, was extracted with a solution containing potassium hydroxide (4 g.) in alcohol–water (100 : 200 c.c.). The residual 2-*disulphonylamino-quinone* (7 g.) crystallised from nitrobenzene in pale yellow needles (5·9 g.), m. p., 297—298° (Found : C, 59·8; H, 3·8; N, 2·7; Cl, 6·5; S, 11·5. $C_{28}H_{20}O_6NClS_2$ requires C, 59·4; H, 3·5; N, 2·5; Cl, 6·3; S, 11·3%). It was sparingly soluble in acetic acid. The yellow colour of its solution in pyridine remained unaffected by methyl alcoholic potassium hydroxide.

2-*Benzamido*-1-*chloroanthraquinone*.—2-Amino-1-chloroanthraquinone (5 g.), benzoyl chloride (10 c.c.), and pyridine (20 c.c.) were heated under reflux for 10 minutes, then cooled, and mixed with alcohol. The *benzamido*-derivative which separated (4·3 g.) was crystallised twice from acetic acid; it formed fine pale yellow needles (3·1 g.), m. p. 219—220° (Found : C, 70·0; H, 3·6; N, 4·2; Cl, 10·0. $C_{21}H_{12}O_3NCl$ requires C, 69·8; H, 3·3; N, 3·9; Cl, 9·9%).

2-*Chloro*-1-*nitroanthraquinone*.—Nitric acid (*d* 1·35; 55 c.c.) was added with stirring to a solution containing 2-chloroanthraquinone (25 g.) in concentrated sulphuric acid (135 c.c.), the temperature being kept below 10°. Yellow crystals separated; after 5 hours these were collected and washed by means of water. The *nitro-quinone* (15 g.; m. p. 190—210°), crystallised from *o*-dichlorobenzene and then from acetic acid, had m. p. 280—281° (Found : N, 4·6; Cl, 12·9. $C_{14}H_6O_4NCl$ requires N, 4·9; Cl, 12·4%). The yield of pure material was 3·5 g.

1-*Anilino*-2-*chloroanthraquinone*.—2-Chloro-1-nitroanthraquinone (1·0 g.), potassium acetate (1·0 g.), copper bronze (0·02 g.), cupric acetate (0·02 g.), and aniline (20 c.c.) were heated under reflux for 6 hours. The product was distilled in steam, the violet residue (1·25 g.) dissolved in benzene, and the solution chromatographed on alumina. A weakly adsorbed violet zone resulted; this was eluted by benzene and recovered (0·52 g.; m. p. 196—197°). Crystallisation from acetic acid gave the *base* as violet needles, m. p. 204—205° (Found : C, 71·2; H, 3·8; N, 4·4; Cl, 10·6. $C_{20}H_{12}O_2NCl$ requires C, 71·6; H, 3·6; N, 4·2; Cl, 10·6%). Like 1-anilinoanthraquinone the product dissolved in pyridine with a violet colour which was unaltered by methyl alcoholic potassium hydroxide.

2-*Nitroanthraquinone*.—An ice-cold solution containing 2-aminoanthraquinone (10 g.) in concentrated sulphuric acid (70 c.c.) was added during an hour to a stirred solution containing ammonium persulphate (50 g.) in water (200 c.c.), at $<5°$. The addition being complete, stirring was continued at 5° for an hour, then at 90° for 2 hours; the colour of the suspension changed from orange to dull yellow. The solid was collected, washed acid-free, and dried (9·3 g.; m. p. 157—166°). Extraction with acetic acid (100 c.c.) gave a solution from which orange-brown crystals (5 g.; m. p. 176—177°) separated. Repeated crystallisation from acetic acid afforded 1·3 g. of bright yellow plates of 2-nitroanthraquinone, m. p. 183—184° (Found : C, 66·2; H, 2·7; N, 5·6. Calc. for $C_{14}H_7O_4N$: C, 66·4; H, 2·8; N, 5·5%). The material (0·5 g.; m. p. 330—335°) insoluble in acetic acid separated in indistinct crystals, m. p. 335—340° (decomp.) (Found : C, 73·3; H, 3·0; N, 6·1. Calc. for $C_{28}H_{14}O_5N_2$: C, 73·4; H, 3·1; N, 6·1%). This product (2 : 2′-azoxyanthraquinone) dissolved in concentrated sulphuric acid with an orange-brown colour; a pale yellow precipitate formed on addition of water. Warming with acetone and methanolic potassium hydroxide gave a dull blue colour (cf. Scholl and Eberl, *Monatsh.*, 1911, **32**, 1035).

Fusion of 2-Nitroanthraquinone with Potassium Hydroxide. Formation of Alizarin.—2-Nitroanthraquinone (1·0 g.) and potassium hydroxide (10 g.) were powdered together, water (4 c.c.) was added, and the mixture heated. At 120° the mixture became fluid and deep green, at 160—180° it became violet. The product was cooled and added to water, and air was passed through the resulting solution. The violet solution was filtered (there was only a trace of a residue), and the filtrate acidified. The orange-brown precipitate (0·6 g.; m. p. 270—280°), crystallised from acetic acid in orange-brown needles, m. p. 289—290°, not depressed on admixture with alizarin.

Fusion of 2-Anilinoanthraquinone with Potassium Hydroxide.—(a) *At* 180°, *in the presence of oxidants*. A finely powdered mixture of 2-anilinoanthraquinone (10 g.), anhydrous potassium acetate (5·0 g.), and potassium nitrate (1·2 g.) was added during 10 minutes to a melt containing potassium hydroxide (30 g.) and water (4 c.c.) at 180°. An even temperature was secured by carrying out the fusion in a nickel crucible immersed in a fusible-metal bath. The first portions of 2-anilinoanthraquinone dissolved with a green colour, which quickly changed to blue. The smell of aniline was noticed. The addition being complete, the melt was stirred at 180—190° for 30 minutes, during which it acquired a coppery lustre; considerable frothing occurred. The melt was added to water containing ice, a solution containing concentrated sulphuric acid (8 c.c.) in water was added, and the still alkaline solution was heated to 100° and then aerated for 2 hours. Filtration afforded a violet residue (A); this was washed by water. The filtrate from (A) was acidified and the resulting brownish-yellow gelatinous precipitate was collected and dried (3·8 g.; m. p. 282—283°). Recrystallisation from acetic acid gave brownish-yellow needles, m. p. 287—288°, not depressed by mixing them with alizarin, m. p. 289°. Acetylation afforded 2-acetylalizarin, m. p. 203°. Methylation by potassium hydroxide and methyl sulphate gave alizarin 2-methyl ether, m. p. 228—229°.

The violet product (A) (5·9 g.; m. p. $>300°$) dissolved in concentrated sulphuric acid with an olive green colour; warming changed the colour to blue; a reddish-violet precipitate formed on addition of the solution to water. The material (A) was sparingly soluble in 1% aqueous potassium hydroxide; ultimately a solution was obtained which, acidified, yielded a violet product (1·1 g.), probably 2-*anilino*-1-*hydroxyanthraquinone*. This dissolved in glacial acetic acid forming a red solution, from which it separated in violet prisms, m. p. 225—226° (Found : C, 75·6; H, 4·3; N, 4·3. $C_{20}H_{13}O_3N$ requires C, 77·1; H, 4·0; N, 4·3%). It dissolved in hot aqueous potassium hydroxide; on cooling, a violet potassium salt separated, identical with the main constituent of the residue (A). It dissolved in pyridine with a red colour; addition of methanolic potassium hydroxide changed the colour to blue; a violet solution resulted when water was added. Heating with a mixture of boric anhydride and acetic anhydride changed

the colour to greenish-blue; addition of chloroform yielded a green solution, but further addition changed the colour to violet-brown.

There was no evidence of unchanged 2-anilinoanthraquinone amongst the products.

(b) *At* 200—210°, *in the presence of oxidants.* Experiment (*a*) was repeated at 200—210°; the period of fusion was 40 minutes. The products were crude alizarin (6·0 g.) and the violet product A (3·5 g.). From the latter was prepared the violet derivative, m. p. 223—224° (2·2 g.).

(c) *At* 180—200°, *in the presence of phenol.* 2-Anilinoanthraquinone (10 g.) was added to 180° to a melt consisting of potassium hydroxide (34 g.), water (6 g.), and phenol (6 g.). The mass was stirred for 45 minutes, during which the temperature was allowed to rise to 200°; there was little tendency to froth. The product was added to water and aerated for several hours. The resulting suspension was filtered; the violet filtrate on acidification gave alizarin (4·5 g.) as a bright orange-yellow precipitate; it crystallised from acetic acid in brownish needles, m. p. 289°, alone or when mixed with an authentic sample. The residue remaining after separation of the violet filtrate was red; most of it (4·2 g.) was soluble in hot benzene and separated on cooling as orange-brown crystals (3·0 g.) of 2-anilinoanthraquinone, m. p. 233—235°. A portion of the residue (0·7 g.) did not dissolve in benzene; this crystallised from acetic acid in violet-blue prisms, m. p. 222° (0·2 g.), identical with the product of m. p. 225—226° obtained by the alkali fusion of 2-anilinoanthraquinone in the presence of an oxidant.

Potassium hydroxide fusion of product, m. p. 225—226°. The product, m. p. 225—226° (0·5 g.), was added at 200° to a melt of potassium hydroxide (5 g.) and water (1 c.c.), and the mixture was stirred for 15 minutes; there was little evidence of reaction. Finally, the temperature was raised to 240—250°, and then the melt was added to water. The violet solution was filtered from the undissolved material (0·35 g.); the residue separated from acetic acid in violet crystals, m. p. 224—225°, identical with the starting material. The violet filtrate, acidified, yielded 0·1 g. of a reddish-violet precipitate, m. p. 204—220°.

Fusion of 2-N-*Methylanilinoanthraquinone with Potassium Hydroxide.*—A finely powdered mixture of 2-*N*-methylanilinoanthraquinone (5·0 g.), potassium nitrate (0·6 g.), and potassium acetate (2·5 g.) was added during 10 minutes to a melt of potassium hydroxide (15 g.) and water (2 c.c.). There was no apparent reaction. After 30 minutes' stirring, the melt was added to water, and the suspension heated to boiling, aerated, and filtered. The pale violet filtrate gave on acidification a red-violet precipitate, m. p. 130—150°. The residue (4·5 g.), m. p. 145°, was extracted by benzene until nothing more dissolved; a residue (0·5 g.) remained.

The residue was a potassium salt; it reacted with acetic acid and the product, 2-N-*methylanilinoanthraquinone*, crystallised from the solvent in red-brown needles (0·2 g.), m. p. 200—205° (Found: C, 75·9; H, 4·8; N, 3·8. $C_{21}H_{15}O_3N$ requires C, 77·4; H, 4·4; N, 4·1%). This compound dissolved in pyridine with a red colour; addition of methanolic potassium hydroxide changed the colour to violet-blue, and this was stable on further addition of water.

The benzene solution, chromatographed on alumina, afforded three main zones. Most strongly adsorbed was a blue substance. This could not be eluted by means of acetone; it dissolved in concentrated sulphuric acid, forming a deep green solution from which a violet precipitate separated on addition of water. The violet product (0·05 g.) had m. p. 200°; it was identical with the substance, m. p. 200—205°, obtained by treating the benzene-insoluble residue with acetic acid.

The second zone was eluted by means of acetone; on evaporation the eluate afforded orange-brown needles (0·15 g.), m. p. 235°, not depressed by mixing it with authentic 2-anilinoanthraquinone. The product also showed the reactions of 2-anilinoanthraquinone including the development of a deep green colour on addition of methanolic potassium hydroxide to its orange solution in pyridine. (The 2-*N*-methylanilinoanthraquinone employed in this experiment was free from 2-anilinoanthraquinone.)

The least strongly adsorbed zone was red. Elution with benzene and evaporation of the eluate afforded 3·02 g. of fine red needles, m. p. 157—161°; after recrystallisation from alcohol the m. p. was 163°, not depressed by mixing the product with 2-*N*-methylanilinoanthraquinone.

Condensation of 2-*Aminoanthraquinone with Nitrobenzene.*—The preparation was carried out as outlined in F.I.A.T. Final Report 1313, Vol. III, p. 82. The *product* was obtained by crystallisation from nitrobenzene as yellow needles having a coppery lustre, m. p. 356—357° (Found: C, 70·1; H, 3·8; N, 7·9. $C_{20}H_{12}O_4N_2$ requires C, 69·8; H, 3·5; N, 8·1%). It dissolved in pyridine with an orange colour changed to deep violet by a drop of methanolic potassium hydroxide, and green, finally orange, by further addition of methanol. It dissolved in concentrated sulphuric acid with a deep blue colour.

2-p-*Nitroanilinoanthraquinone.*—2-Chloroanthraquinone (9·6 g.), *p*-nitroaniline (7·2 g.), potassium carbonate (5·5 g.), cupric acetate (0·5 g.) and copper bronze (0·2 g.) were heated under reflux in nitrobenzene (100 c.c.) for 3 hours. The resulting suspension was filtered hot; on cooling the filtrate afforded pale brown crystals (6·7 g.; m. p. *ca.* 208°). The crystals were extracted by acetic acid; a brown residue remained, having m. p. >300°. Crystallised from nitrobenzene (charcoal), the residue afforded microscopic yellow needles having a coppery lustre (1·1 g.), m. p. 357°, not depressed by mixing it with the product obtained by condensing 2-aminoanthraquinone with nitrobenzene. The colour reactions of the two products were identical.

The authors thank the University of Leeds for the award of a Clothworkers Research Scholarship, and the Trustees of Messrs. Courtaulds' Scientific and Educational Trust Fund for the award of a grant to one of them (E. L.). They also thank Imperial Chemical Industries Limited for gifts of intermediates and grants to meet the cost of microanalyses.

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[*Received, February 27th,* 1951.]