471. *Chemistry of Indanthrone. Part II.** *The Formation of Dianthraquinonyl-*N*-methylamines.*

By William Bradley and Edward Leete.

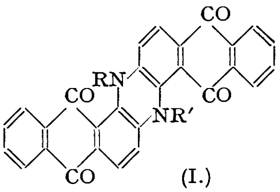
An attempt to prepare *NN*-dimethylindanthrone by the self-condensation of 2-bromo-1-methylaminoanthraquinone yielded *N*-methylindanthrone. It was then found that both 2-bromo-1-methylaminoanthraquinone and *NN*-dimethylindanthrone were readily demethylated when heated in nitrobenzene with copper or its salts and an alkali, formaldehyde being liberated. 1-Chloro-2-methylaminoanthraquinone afforded 2-methylaminoanthraquinone, 2-aminoanthraquinone, and the cuprous derivative (A) of *NN*-di-2-anthraquinonylformamidine (B), dehalogenation, demethylation, and further condensation having occurred. The cuprous derivative (A) was also formed together with *N*-methylindanthrone by heating 1-chloro-2-methylaminoanthraquinone with 2-aminoanthraquinone in the presence of copper or copper salts.

Hydrolysis of (A) afforded (B) and ultimately a mixture of 2-aminoanthraquinone and 2-formamidoanthraquinone. (B) was identical with the product obtained by condensing 2-aminoanthraquinone with ethyl orthoformate. It was transformed into (A) when heated with copper or copper salts. (A) was also prepared by condensing 2-aminoanthraquinone with formaldehyde and heating the resulting bis-2-anthraquinonylaminomethane with nitrobenzene and copper, or a copper salt. The constitution of (A) is considered.

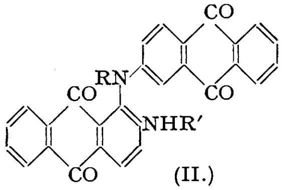
2-Dimethylaminoanthraquinone, when heated in nitrobenzene with an alkali and copper salt, afforded 2-methylaminoanthraquinone. 2-Methylaminoanthraquinone yielded (A) and formaldehyde. 2-*N*-Methylanilinoanthraquinone yielded formaldehyde and a product which gave the reactions of 2-anilinoanthraquinone. 2-Ethylaminoanthraquinone was similarly dealkylated. The condensation of 1-chloroanthraquinone and 2-methylaminoanthraquinone yielded 1 : 2′-dianthraquinonylamine and formaldehyde. 1-Methylaminoanthraquinone gave formaldehyde, 1-aminoanthraquinone, and 1-formamidoanthraquinone. Heated with 2-chloroanthraquinone, 1-methylaminoanthraquinone yielded formaldehyde and a mixture of 1 : 2′-dianthraquinonylamine and its *N*-methyl derivative.

The mechanism of the reactions is discussed.

In Part I * the preparation of the *N*-methyl and *NN*-dimethyl derivatives of indanthrone (I; R = R′ = H) was described. They were obtained by cyclising 2-amino- (II; R = Me, R′ = H) and 2-methylamino-1 : 2′-dianthraquinonyl-*N*-methylamine (II; R = R′ = Me) respectively; both were also prepared by the methylation of indanthrone. They had the



(I.)



(II.)

expected properties, in particular, the dimethyl derivative dissolved in pyridine with a blue colour, which was not affected by the addition of methanolic potassium hydroxide, whilst the monomethyl derivative gave a blue solution which alkali rendered green. In G.P. 158,287 it is claimed that the dimethyl derivative results when 2-bromo-1-methylaminoanthraquinone is heated with sodium acetate and cupric chloride in nitrobenzene; it cannot be the only product of this reaction, however, because the product readily gives a green colour with methanolic potassium hydroxide in pyridine. In the present investigation the procedure

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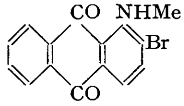
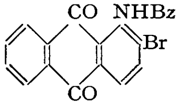
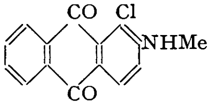
* Part I, preceding paper.

of G.P. 158,287 was repeated with a sample of 2-bromo-1-methylaminoanthraquinone (III) which was entirely free from the 1-amino-quinone. The purity was established by converting a portion into the *N*-benzoyl derivative, which gave a yellow solution in pyridine entirely unaltered by methanolic potassium hydroxide; in similar circumstances 1-benzamido-2-bromoanthraquinone (IV) afforded a deep red solution. The self-condensation of pure (III) yielded a blue colouring matter which again exhibited a green alkali colour reaction; during the condensation under a variety of conditions formaldehyde was liberated. The same result was obtained when copper bronze, cuprous chloride, and cupric acetate were used instead of cupric chloride. With cuprous chloride the yield of colouring matter increased slowly during 5 hours; with cupric acetate it reached a maximum at an earlier stage. The yield of formaldehyde increased throughout the reaction in all cases; in one experiment 61% of the methyl groups were eliminated as formaldehyde. It was then observed that both 2-bromo-1-methylaminoanthraquinone and *NN*-dimethylindanthrone are readily demethylated by heating them with copper salts.

The crude colouring matter obtained by heating 2-bromo-1-methylaminoanthraquinone with cuprous chloride was mainly *N*-monomethylindanthrone; small quantities of indanthrone and, probably, dimethylindanthrone were separated by reduction and chromatography (see Experimental). *N*-Methylindanthrone recovered from the column was identical with the product obtained by cyclising 2-amino-1 : 2′-dianthraquinonyl-*N*-methylamine (Part I) (cf. Fig. 1). The presence of indanthrone was confirmed by means of the reaction with a solution of nitric acid in sulphuric acid which yielded the yellow indanthroneazine.


(III.)


(IV.)

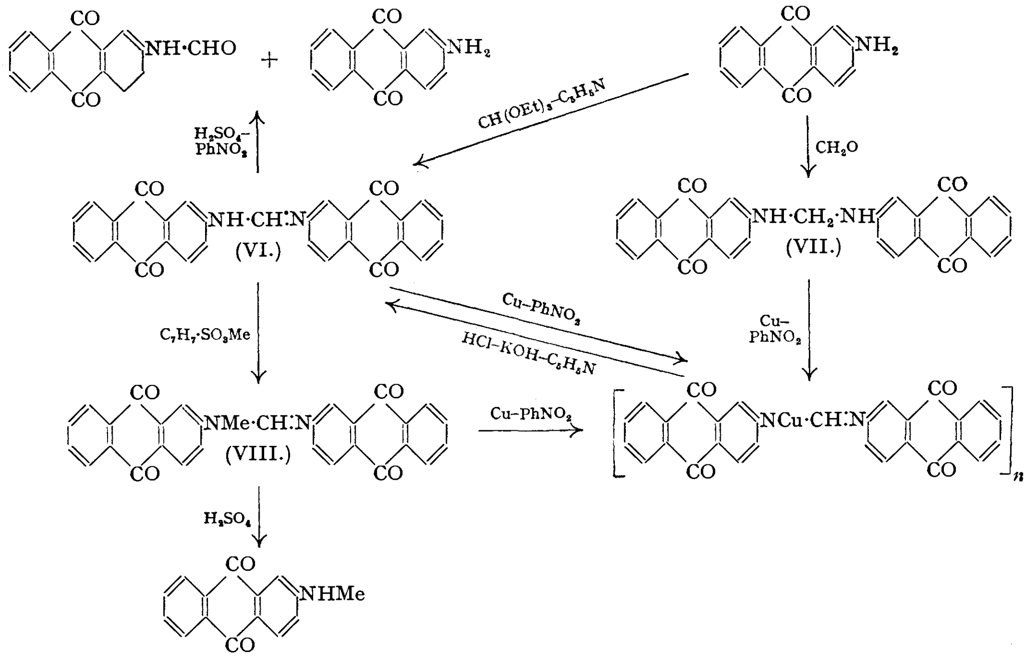

(V.)

It has been stated (G.P. 234,294) that heating an equimolecular mixture of 1-amino-2-bromoanthraquinone and 2-bromo-1-methylaminoanthraquinone in nitrobenzene in the presence of cupric chloride and an alkali yields *N*-methylindanthrone. In the present experiments this procedure afforded also some indanthrone, 11% of the methyl groups being lost as formaldehyde after two hours.

1-Chloro-2-methylaminoanthraquinone (V) with copper sulphate and potassium acetate in nitrobenzene yielded both 2-methylamino- and 2-amino-anthraquinone, demethylation and dehalogenation having occurred. In a similar experiment with cuprous chloride all of the chlorine initially present appeared in the product as potassium chloride. There was no formation of indanthrone or a derivative of this in either instance. Maki and Mine (*J. Soc. Chem. Ind. Japan*, 1944, **47**, 522) similarly have been unable to prepare indanthrone by the self-condensation of 2-amino-1-chloroanthraquinone. In the second experiment the product contained a red crystalline compound, later identified as the cuprous derivative of *NN*′-di-2-anthraquinonylformamidine (VI); this contained all the copper present initially. The cuprous derivative of (VI) was also formed when *o*-dichlorobenzene was used in the place of nitrobenzene, and cupric acetate instead of cuprous chloride.

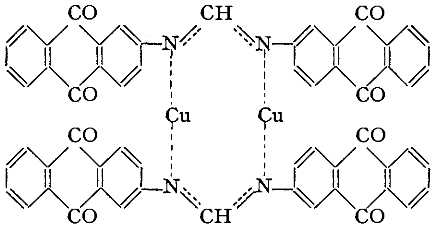
There was no reaction between 1-chloro-2-methylaminoanthraquinone and 2-aminoanthraquinone in the absence of copper salts. When cuprous chloride and potassium acetate were added, *N*-methylindanthrone was formed in small amount, but the main product was again the cuprous derivative of (VI); there was no indication of the presence of 2-methylamino-1 : 2′-dianthraquinonylamine.

The constitution of the copper derivative of *NN*′-di-2-anthraquinonylformamidine (VI) follows from the following considerations. Analysis gives the composition $C_{29}H_{15}O_4N_2Cu$. Heating it with concentrated hydrochloric acid yields cuprous chloride, *NN*′-di-2-anthraquinonylformamidine. and 2-aminoanthraquinone. Heating it with pyridine and methanol containing potassium hydroxide also yielded the formamidine. *NN*′-Di-2-anthraquinonylformamidine, heated with acetic anhydride, yields 2-acetamidoanthraquinone; benzoyl chloride affords 2-benzamidoanthraquinone; hydrolysis with concentrated sulphuric acid gives 2-aminoanthraquinone; heating it with nitrobenzene containing a few drops of sulphuric acid yields 2-formamidoanthraquinone, identical with the product obtained by heating 2-aminoanthraquinone with formic acid. *NN*′-Di-2-anthraquinonylformamidine was synthesised by heating 2-aminoanthraquinone with ethyl orthoformate, following G.P. 248,656, and the cuprous derivative by combining 2-aminoanthraquinone with formaldehyde and oxidising the resulting di-2-anthraquinonylaminomethane (VII) with copper bronze and nitrobenzene. The identities of the various formamidine preparations are confirmed by absorption spectra (Fig. 2).

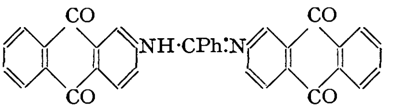


The same copper derivative was formed from (VI) whether copper was employed as copper bronze, cuprous chloride, or cupric acetate. Heating 1 mol. of cupric acetate with 2 mols. of (VI) yielded the same cuprous derivative, one half of the *NN'*-di-2-anthraquinonylformamidine employed remaining unchanged.

The copper derivative showed no tendency to combine with aniline, pyridine, ethylenediamine, or ammonia. It was only very slightly soluble in organic solvents and was hydrolysed by acids only with difficulty.



(IX.)



(X.)

In its stability and colour the copper derivative differed considerably from the cupric derivatives of acetylacetone (Morgan, Drew, and Porter, *Ber.*, 1925, **58**, 333), salicylaldoxime (Cox and Webster, *J.*, 1935, 731) salicylaldehyde (Tyson and Adams, *J. Amer. Chem. Soc.*, 1940, **62**, 1228), and salicylaldimine (Hunter and Marriott, *J.*, 1937, 2000). Copper phthalocyanine (Linstead *et al.*, *J.*, 1934, 1016), whilst more stable, has the typical colour of a cupric derivative. In colour, the red copper *NN'*-di-2-anthraquinonylformamidine derivative approaches more closely the violet-pink cuprous derivative of acetylacetone (Emmert and Gsottschneider, *Ber.*, 1936, **69**, 1319) and the brown cupric derivatives of *o*-hydroxyazobenzene (Hunter, *J.*, 1935, 1598) and 2 : 2'-dihydroxyazobenzene (Pfeiffer, Hesse, Pfitzner, Scholl, and Thielert, *J. pr. Chem.*, 1937, **149**, 235). Its chemical inertness indicates a high degree of covalency between copper and nitrogen (cf. Sherman and Randles, *J.*, 1941, 802; *Chem. Reviews*, 1932, **2**, 153) and a molecular constitution such as (IX) appears probable.

By contrast, the potassium derivative of (VI) was a typical salt soluble in pyridine with a blue colour, stable towards dilution with alcohol but hydrolysed by water. *NN′*-Di-2-anthraquinonylformamidine was readily methylated to an orange monomethyl derivative (VIII), hydrolysed by sulphuric acid to 2-methylaminoanthraquinone. Heating (VIII) in nitrobenzene with copper bronze and potassium carbonate caused demethylation and formation of the cuprous derivative of (VI).

NN′-Di-2-anthraquinonylbenzamidine (X) similarly afforded a crystalline cuprous derivative. This was dark green by reflected, but red by transmitted light (for its absorption see Fig. 2). It was more basic than the formamidine analogue. Its sulphate was comparatively stable to water; correspondingly, the cuprous salt was less stable than that of the formamidine derivative; it was decomposed by heating it with pyridine or acetic acid. The simpler diarylformamidines appear to be basic compounds forming stable hydrochlorides.

FIG. 1.

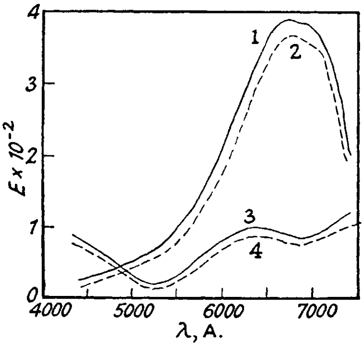


FIG. 2.

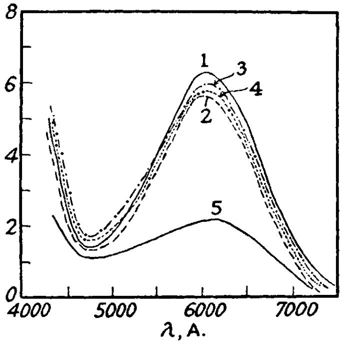


FIG. 3.

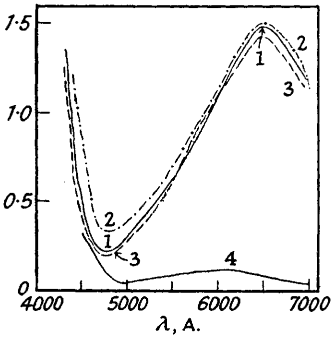


FIG. 1.—N-*Methylindanthrone and its potassium salt in pyridine.*

1, N-*Methylindanthrone obtained by the ring closure of* 2-*amino*-1 : 2′-*dianthraquinonyl*-N-*methylamine : Max. at* 6700 Å. ($E = 390$).
2, *Product obtained by the self-condensation of* 2-*bromo*-1-*methylaminoanthraquinone.*
3, *Potassium salt of the compound recorded in* (1), *formed by addition of methanolic potassium hydroxide to the pyridine solution : Min. at* 5250 Å. ($E = 19$), *max. at* 6350 Å. ($E = 96$), *min. at* 6900 Å. ($E = 84$).
4, *Potassium salt of the compound recorded in* (2).

FIG. 2.—*The potassium salts of dianthraquinonylamidines in pyridine.*

1, NN′-*Di*-2-*anthraquinonylformamidine : Min. at* 4800 Å. ($E = 145$), *max. at* 6050 Å. ($E = 630$).
2, *The same product* (*obtained from* 2-*methylaminoanthraquinone*).
3, *The same product* (*obtained from* 2-*dimethylaminoanthraquinone*).
4, *The same product* (*obtained from di*-2-*anthraquinonylaminomethane*).
5, NN′-*Di*-2-*anthraquinonylbenzamidine : Min. at* 4750 Å. ($E = 120$), *max. at* 6150 Å. ($E = 210$).

FIG. 3.—1 : 2′-*Dianthraquinonylamines in concentrated sulphuric acid.*

1, 1 : 2′-*Dianthraquinonylamine : Min. at* 4800 Å. ($E = 23$), *max. at* 6500 Å. ($E = 148$).
2, *Product from the condensation of* 2-*chloroanthraquinone and* 1-*methylaminoanthraquinone.*
3, *Product from the condensation of* 1-*chloroanthraquinone and* 2-*methylaminoanthraquinone.*
4, 1 : 2′-*Dianthraquinonyl*-N-*methylamine : Min. at* 5000 Å. ($E = 5$), *max. at* 6100 Å. ($E = 11$).

Although condensation of aminoanthraquinones with halogenoanthraquinones in the presence of copper salts is a well-established method of preparing the dianthraquinonylamines, the occurrence of dealkylation appears not to have been observed. An investigation of the behaviour of simple alkylaminoanthraquinones towards copper and its salts gave the following results.

2-Methylaminoanthraquinone with potassium acetate and copper bronze in nitrobenzene readily yielded the copper derivative of (VI) and formaldehyde. The amount of the copper derivative increased with the time of heating. It was greatest when the copper catalyst used was cupric acetate, less when it was copper bronze and least, cuprous chloride; this was also the order of efficiency of the three catalysts for the production of formaldehyde from 2-dimethylaminoanthraquinone. The yield of the copper derivative of (VI) was smaller when *o*-dichlorobenzene or naphthalene replaced nitrobenzene as reaction medium; it was nil when the medium was aniline, dimethylaniline, quinoline, or amyl alcohol. The addition of 5% of aniline to nitrobenzene greatly reduced the yield of the copper derivative.

2-Ethylaminoanthraquinone with copper bronze and potassium carbonate in nitrobenzene similarly yielded 2-aminoanthraquinone; 2-*N*-methylanilinoanthraquinone gave formaldehyde and a product which gave the deep green alkali colour reaction of 2-anilinoanthraquinone. 1-Methylaminoanthraquinone yielded formaldehyde, 1-aminoanthraquinone, and also 1-formamidoanthraquinone; in the presence of 2-chloroanthraquinone formaldehyde was again liberated and both 1 : 2′-dianthraquinonylamine and its *N*-methyl derivative were formed. (For the absorptions of products of these and similar reactions see Fig. 3.) Alkali colour reactions indicated the production of *NN*′-di-1-anthraquinonylformamidine in the last reaction; the product decomposed when heated in nitrobenzene or trichlorobenzene, yielding 1-aminoanthraquinone and 1-formamidoanthraquinone. An attempt to prepare *NN*′-di-1-anthraquinonylformamidine by heating 1-aminoanthraquinone with ethyl orthoformate in pyridine was unsuccessful. The formamidine containing *N*-1-anthraquinonyl substituents is evidently less stable than the isomeric compound containing 2-anthraquinonyl groups, a conclusion supported by the fact that, whilst the cuprous derivative of *NN*′-di-2-anthraquinonylformamidine is formed abundantly when 2-methylaminoanthraquinone is heated with nitrobenzene, potassium carbonate, and copper acetate, no corresponding copper derivative is formed when 1-methylaminoanthraquinone is similarly treated. Another instance of ready demethylation was encountered in the formation of *NN*′-di-2-anthraquinonylformamidine by heating its *N*-methyl derivative with copper salts.

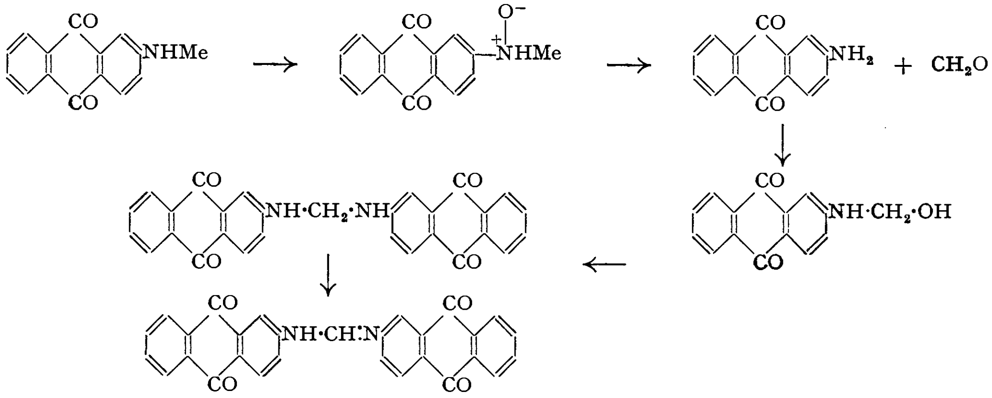
Particularly interesting in the present connection are the properties of *NN*-dimethylindanthrone. It has been shown (Part I) that *NN*-dimethylindanthrone yields *N*-methylindanthrone when it is added to concentrated nitric acid. A similar demethylation occurs when *NN*-dimethylindanthrone is heated in nitrobenzene with potassium carbonate and cupric acetate: formaldehyde is liberated in amount equivalent to 5% of the methyl groups after 5 hours. There is no demethylation when copper bronze is substituted for cupric acetate. An interesting fact, confirmed on several occasions, is that demethylation occurs when *NN*-dimethylindanthrone is heated in *o*-dichlorobenzene, and especially in nitrobenzene, in the presence of alumina. The products are *N*-methylindanthrone and indanthrone, the latter being strongly adsorbed on the alumina. Adsorption must increase the possibility of a reaction, and the greater adsorption of indanthrone must contribute to the result, even if demethylation is not determined by the adsorption factor.

The part played by adsorption in the demethylation process probably gains in importance by the fact that the molecule of indanthrone is planar. In contrast, in the *N*-methyl derivatives, the planes occupied by the component anthraquinone nuclei do not coincide, and the large angle of intersection is bisected by a third plane which carries the methyl groups.

The demethylation of amines in processes involving oxidation has been observed on numerous occasions. Hess, Merck, and Uibrig (*Ber.*, 1915, **48**, 1890) found that aldehydic and ketonic derivatives of 1-methylpyrollidine and 1-methylpiperidine were readily demethylated as a result of intramolecular oxidation–reduction, formaldehyde being liberated. Fischer and Fischer (*Ber.*, 1878, **11**, 1081) obtained formaldehyde on oxidation of malachite-green with manganese dioxide and sulphuric acid. Oxidised with osmium tetroxide and hydrogen peroxide, *p*-dimethylaminoazobenzene yielded both *p*-amino- and *p*-methylamino-azobenzene (Anderson, *Nature*, 1949, **163**, 444). Carter, Moulds, and Riley (*J.*, 1937, 1305) found that dimethylaniline heated with graphitic oxide afforded 4 : 4′-tetramethyldiaminodiphenylmethane; the same product had been obtained by the electrochemical oxidation of dimethylaniline (Fichter and Rothenberger, *Helv. Chim. Acta*, 1922, **5**, 166). A comprehensive survey of the oxidative demethylation of *N*-methyl compounds *in vivo* has been made by Challenger (*Chem. and Ind.*, 1942, **20**, 398).

While the production of formaldehyde or compounds derived from it is a well-established occurrence in the oxidation of methylated amines, the mode of its formation is less certain. Dehydrogenation of $>CH\cdot NH-$ to $>C{:}N-$, which occurs in the oxidation of α-amino- to α-keto-acids, could also explain the oxidation of tertiary amines in acid solution ($CH_3\cdot NR_2 \xrightarrow{H^+} CH_3\cdot NHR_2^+ \xrightarrow{-2H} CH_2{:}NR_2^+$). Experiment shows, however, that the demethylation of methylaminoanthraquinones and dianthraquinonyl-*N*-methylamines by copper salts is favoured by the presence of alkalis. An alternative view is that the liberation of formaldehyde is preceded by hydroxylation of the methyl group. This hypothesis has been adopted by Kruger and Oberlies (*Ber.*, 1941, **74**, 663) to account for the oxidation of dimethylaniline, and also by

Clarkson, Holden, and Malkin (*J.*, 1950, 1561) who showed that the oxidation of 2 : 4-dinitro-*NN*-dimethylaniline yielded formaldehyde, formic acid, and 2 : 4-dinitro-*N*-methylaniline. The production of a hydroxymethylamine at some stage in the total oxidation of 2-methylaminoanthraquinone appears to be necessary because the cuprous salt of *NN'*-di-2-anthraquinonylformamidine is a major product of the reaction and its formation is difficult to explain except by the interaction of 2-hydroxymethylaminoanthraquinone with 2-aminoanthraquinone followed by oxidation. It was shown that the yield of the cuprous derivative could be doubled by adding an equimolar amount of 2-aminoanthraquinone to the 2-methylaminoanthraquinone employed, and also that heating a mixture of 2-formamidoanthraquinone and 2-aminoanthraquinone did not yield *NN'*-di-2-anthraquinonylformamidine. All the results can be explained equally well, however, by the initial formation of an amine oxide, which decomposes to yield formaldehyde and 2-aminoanthraquinone.



The de-ethylation of 2-ethylaminoanthraquinone did not yield a formamidine derivative, nor did the reaction occur so readily as the demethylations. This accords with the greater stability of 5-ethylphenazinium ethyl sulphate in comparison with the *N*-methyl analogue (McIlwain, *J.*, 1937, 1705). The same relationship has been observed biologically in derivatives of glycine (Abbot and Lewis, *J. Biol. Chem.*, 1941, **137**, 535).

EXPERIMENTAL.

Condensation of 1-Chloroanthraquinone and 2-Methylaminoanthraquinone.—1-Chloroanthraquinone (4·8 g.), 2-methylaminoanthraquinone (4·7 g.), dry potassium acetate (3·0 g.), and copper bronze (0·4 g.) were heated under reflux with nitrobenzene (40 c.c.) for 18 hours. The solution was filtered hot, and the residue (2·6 g.) washed with alcohol and then water. Reddish-brown prisms (0·55 g.), which crystallised from the nitrobenzene filtrate, did not melt below 300° (Found : C, 77·9; H, 3·5; N, 3·3. Calc. for $C_{28}H_{15}O_4N$: C, 78·3; H, 3·5; N, 3·3%); they were identified as 1 : 2'-dianthraquinonylamine by the green colour and absorption spectrum of a solution in concentrated sulphuric acid (Fig. 2), and by the green colour developed when methanolic potassium hydroxide was added to an orange solution of the product in pyridine. The residue (2·6 g.) was extracted by acetic acid or concentrated aqueous ammonia and ammonium chloride until copper no longer dissolved; the residual *copper* derivative (2·3 g.) consisted of hair-like red needles (A) (Found : C, 67·4; H, 3·0; N, 5·5; Cu, 12·7, 12·3, 11·8. $C_{29}H_{15}O_4N_2Cu$ requires C, 67·1; H, 2·9; N, 5·4; Cu, 12·3%).

Further experiments showed that (A) was derived from 2-methylaminoanthraquinone.

Conversion of 2-Methylaminoanthraquinone into the Cuprous Derivative (A) *of* NN'*-Di-2-anthraquinonylformamidine.*—The variation in the yield of (A) from 2-methylaminoanthraquinone with the experimental conditions is shown in the following Tables. For work reported in the second Table the time of heating was 24 hours and the added alkali potassium carbonate.

2-Methylamine-anthraquinone (g.).	Alkali (g.).	Copper bronze (g.).	Nitro-benzene (c.c.).	Time (hrs.).	Yield of A (g.).
10	6 (KOAc)	0·8	80	16	2·7
5	absent	absent	40	16	0
5	absent	0·4	40	16	0
0	3 (KOAc)	0·4	40	16	0
10	6 (KOAc)	2·0	80	5	6·4
5	3 (K_2CO_3)	1·0	40	5	2·0

Solvent.	Copper or copper derivative.	Yield (%) of A, calc. on 2-methylaminoanthraquinone.
Nitrobenzene	Copper bronze	75 *
	Cuprous chloride	16
	Cupric acetate	84
o-Dichlorobenzene	Copper bronze	0
	Cuprous chloride	2
	Cupric acetate	17
Naphthalene	Copper bronze	0
	Cupric acetate	10

* In a parallel experiment, in which an equimolecular amount of 2-aminoanthraquinone was added to the reactants, the yield of A was increased to 134%.

The compound A was not formed when the solvent was aniline, dimethylaniline, quinoline, or amyl alcohol, whether copper bronze or cupric acetate was used. In the nitrobenzene–copper bronze experiment the yield was reduced to 8% when 5% of aniline was added to the reactants. In the nitrobenzene–cuprous chloride experiment, aniline was found in the product.

Product A was insoluble in the available organic solvents; it was recovered unaltered after being heated with acetic anhydride. It gave a blue solution in pyridine containing a few drops of methanolic potassium hydroxide. Identical copper derivatives were formed when the copper bronze was replaced by cuprous chloride (Found : Cu, 12·2%) and cupric acetate (Found : Cu, 13·0%).

Hydrolysis. (*a*) Product A (1·0 g.) was heated with concentrated hydrochloric acid (100 c.c.) at the b. p.; after 30 minutes the solution had become yellow and a grey precipitate had separated. The suspension was filtered hot and the residue washed with water and then dilute aqueous ammonia. During the ammonia washing it became brown; the dried residue was an orange-brown powder (0·7 g.). Crystallisation from nitrobenzene gave NN'-*di-2-anthraquinonylformamidine* as small orange needles (B), m. p. 385—390° (Found : C, 76·0; H, 3·3; N, 6·3. $C_{29}H_{16}O_4N_2$ requires C, 76·3; H, 3·5; N, 6·1%).

The hydrochloric acid filtrate contained a soluble copper salt. Addition of ammonia gave an orange-brown precipitate (0·15 g.) of crude 2-aminoanthraquinone, m. p. 270°. Acetylation gave yellow prisms, m. p. 266—267°, not depressed on admixture with authentic 2-acetamidoanthraquinone.

(*b*) Product A (1·0 g.) was heated under reflux with pyridine (50 c.c.) and methanolic potassium hydroxide (3 c.c. of 30%). After 10 minutes' boiling the blue solution was filtered and the filtrate added to methyl alcohol (300 c.c.). The orange-brown precipitate (0·6 g.) which formed was filtered off and crystallised from nitrobenzene as orange needles, m. p. 380—390° (decomp.) (Found : C, 75·8; H, 3·4; N, 6·1%). Compound B dissolved in concentrated sulphuric acid with an orange-brown colour; on addition of water the solution became colourless. It dissolved in pyridine with a yellow colour; a deep blue colour developed on addition of methanolic potassium hydroxide, and this became violet and finally yellow on addition of methyl alcohol.

Conversion of B *into* A.—The copper derivative was formed when B was heated with copper or one of its salts under a variety of conditions as shown in the annexed Table. The copper derivative obtained by heating B with cupric acetate in nitrobenzene was analysed (Found : C, 66·6; H, 2·8; N, 5·7; Cu, 12·5%).

Amount of B (g.).	Solvent.	Vol. (c.c.).	Copper or copper derivative.	Yield (g.).	Time (hrs.).	Conversion.
0·5	$PhNO_2$	30	Cu bronze	0·2	0·5	Complete
0·2	,,	20	Absent	—	2·0	None
0·5	,,	20	Cu powder	0·2	2·0	Complete, slow
0·2	,,	20	$CuAc_2$	0·5	0·5	Complete, 10 mins.
0·5	,,	50	CuCl	0·2	2·0	Incomplete
0·05	*o*-$C_6H_4Cl_2$	5	Cu bronze	0·25	24·0	Incomplete
0·05	,,	5	CuCl	0·2	24·0	Incomplete
0·02	,,	5	$CuAc_2$	0·02	4·0	Complete, rapid
0·5	C_5H_5N	100	CuCl–KOAc	0·3, 0·05	2·0	Amorphous product
0·1	,,	100	$CuAc_2$	0·2	1·0	—

Reactions of (B).—(a) *Acetylation.* A suspension of B (1·0 g.) in acetic anhydride (50 c.c.) was heated under reflux for 30 minutes. The solution was filtered from undissolved material (0·05 g.) and then mixed with an equal volume of water; a brown solid (0·5 g.), m. p. 255—260°, separated and, recrystallised from acetic acid, afforded yellow prisms, m. p. 266—267°, not depressed on admixture with authentic 2-acetamidoanthraquinone.

(b) *Benzoylation.* A suspension of B (1·0 g.) in benzoyl chloride (50 c.c.) was heated under reflux for 30 minutes. A clear, dark yellow solution resulted, and from this crystals, m. p. 210—235° (0·1 g.), separated on cooling. Addition of alcohol to the mother-liquor gave crystals, m. p. 230° (0·2 g.), and these separated from nitrobenzene in yellow needles, m. p. 233—234°, not depressed on admixture with 2-benzamidoanthraquinone.

(c) *Hydrolysis.* (i) A solution containing B (1·0 g.) in concentrated sulphuric acid (200 c.c.) was prepared at room temperature, and then kept for 4 days. It was then added to water; a yellow precipitate (0·8 g.; m. p. 284—300°) formed. This was dissolved in benzene and chromatographed on alumina. Two zones formed. The less strongly adsorbed, orange zone was eluted by means of acetone, yielding 2-aminoanthraquinone, further characterised by the acetyl and benzoyl derivatives. (ii) To B (0·5 g.)

in boiling nitrobenzene (300 c.c.) a few drops of concentrated sulphuric acid in nitrobenzene were added, the heating was continued for 5 minutes, and the whole then concentrated to half-volume by distillation. Brownish-yellow crystals, m. p. 285—290°, which separated, recrystallised from *o*-dichlorobenzene as star-shaped clusters of pale yellow, fine needles, m. p. 291—292° (Found: C, 71·8; H, 3·7; N, 5·7. $C_{15}H_9O_3N$ requires C, 71·7; H, 3·6; N, 5·6%). This product was identical with *2-formamidoanthraquinone* prepared in the following way. 2-Aminoanthraquinone (5·0 g.) and 98% formic acid (15 c.c.) were heated for 5 hours at 170°. The product (5·25 g.), crystallised twice from nitrobenzene, yielded 4·1 g. of 2-formamidoanthraquinone, m. p. 291—292° (Found: C, 71·7; H, 3·7; N, 5·3%).

(d) *Reduction.* To sodium hydroxide (1 g.) and sodium dithionite (0·3 g.) in water (50 c.c.) was added 0·3 g. of (B). On being warmed to 70°, B dissolved with a deep brownish-red colour; the solution was boiled for 10 minutes, then filtered hot. The filtrate, aerated, gave 0·2 g. of orange material, m. p. 270—280°. This was sublimed at 280°/0·1 mm. and the sublimate (m. p. 290—300°) acetylated. The product had m. p. 266°, not depressed on admixture with 2-acetamidoanthraquinone.

Bis-2-anthraquinonylaminomethane.—2-Aminoanthraquinone (5·0 g.) was made into a paste with 40% formaldehyde (25 c.c.), then heated at 100° for 12 hours. The product (4·5 g.; m. p. 304°) was collected, washed with water, and extracted by acetic acid. A sparingly soluble orange residue (1·6 g.) was crystallised from 600 c.c. of nitrobenzene (charcoal), yielding 0·8 g. of *bis-2-anthraquinonylaminomethane* as orange, short, prismatic needles, m. p. 332—334° (decomp.) (Found: C, 75·6; H, 4·2; N, 6·3. $C_{29}H_{18}O_4N_2$ requires C, 76·0; H, 3·9; N, 6·1%). This was probably the main constituent of the substance, m. p. 325—335° (not analysed), obtained according to G.P. 287,907 by condensing formaldehyde with 2-aminoanthraquinone in the presence of mineral acids. The product, m. p. 332—334°, was not affected by boiling concentrated hydrochloric acid or acetic anhydride, nor was formaldehyde produced when the product was heated with sulphuric acid in a current of air. It was unaffected by long exposure to light.

Under other conditions the condensation took a different course (cf. U.S.P. 2,091,235).

A solution containing 2-aminoanthraquinone (5 g.) in concentrated sulphuric acid (100 c.c.) was cooled to 0° and then added at 0° to a stirred solution containing paraformaldehyde (6 g.) in concentrated sulphuric acid (100 c.c.). After 2 hours at 0°, and then at the room temperature for 12 hours, the solution was added to water. The red precipitate was collected, washed with dilute aqueous ammonia, and the dried, insoluble portion (6·6 g.) crystallised from nitrobenzene. The red needles (4·5 g.; m. p. 220—230°) so obtained were chromatographed on alumina from a solution in benzene (0·5 g. in 300 c.c.). Two main zones resulted. The upper zone yielded 0·03 g. of orange needles, m. p. 306°, which with hot acetic anhydride gave 2-acetamidoanthraquinone, m. p. 265—266°. The lower red zone, eluted by methanol, afforded 0·25 g. of reddish-orange needles, m. p. 232°, alone or mixed with 2-methylaminoanthraquinone.

NN′-*Di-2-anthraquinonylformamidine.*—(*a*) The compound, m. p. 332—334° (0·8 g.), was heated under reflux with copper bronze (0·4 g.) and potassium carbonate (0·4 g.) in nitrobenzene (40 c.c.) for an hour. Red needles (1·1 g.) which separated were filtered off and heated under reflux with concentrated hydrochloric acid (100 c.c.). The undissolved material crystallised from nitrobenzene in orange-yellow needles (Found: C, 75·8; H, 3·8; N, 6·4. Calc. for $C_{29}H_{16}O_4N_2$: C, 76·3; H, 3·5; N, 6·1%). This product was identical with (B), prepared as above. In pyridine it formed a solution which became blue on addition of methanolic potassium hydroxide. The absorption spectrum of the blue solution was identical with that of B (Fig. 2).

(*b*) The same compound B was also prepared by condensing 2-aminoanthraquinone with ethyl orthoformate, essentially by the method of G.P. 248,656. It crystallised from nitrobenzene in fine orange needles, m. p. 385—390° (decomp.) (Found: C, 76·2; H, 3·4; N, 6·4%), and gave in pyridine a yellow colour which became deep blue on addition of methanolic potassium hydroxide. Its solubility in hot nitrobenzene was approx. 0·16%.

Copper derivative. Heated in nitrobenzene with copper acetate the dianthraquinonylformamidine yielded a cuprous derivative, in the form of red, hair-like needles, identical with (A) (below).

(*c*) Heating 2-aminoanthraquinone (2·0 g.), paraformaldehyde (0·5 g.), potassium carbonate (1·0 g.), and copper bronze (0·5 g.) in nitrobenzene (40 c.c.) gave red needles (A) in 10 minutes. After 1·5 hours, the suspension was filtered while hot, and the residue (2·4 g.) extracted by acetic acid. The yield of residual cuprous derivative was 2·0 g. (86% calc. on the 2-aminoanthraquinone used). When potassium carbonate was omitted the reaction progressed more slowly; after 6 hours the yield of cuprous derivative was only 11%.

NN′-*Di-2-anthraquinonyl-*N*-methylformamidine.*—*NN′*-Di-2-anthraquinonylformamidine (1·0 g), methyl toluene-*p*-sulphonate (1·0 g.), and potassium carbonate (0·75 g.) were heated under reflux in trichlorobenzene (80 c.c.) for 5 hours; the formamidine derivative dissolved in 2 hours. On cooling, the filtered solution gave orange needles of the *methyl* derivative (0·65 g.), m. p. 316—317° (Found: C, 76·1; H, 3·6; N, 6·1. $C_{30}H_{18}O_4N_2$ requires C, 76·6; H, 3·8; N, 6·0%). It dissolved in pyridine with a yellow colour, unchanged by methyl alcoholic potassium hydroxide.

An identical compound, m. p. 316—317°, not depressed when mixed with the above *N*-methyl derivative, was obtained by treating (B) with methyl toluene-*p*-sulphonate and potassium carbonate under the conditions above described.

Heating the copper derivative (A) (3·0 g.) with methyl iodide (10 c.c.) at 150—160° for 10 hours gave only the copper-free *NN′*-di-2-anthraquinonylformamidine, m. p. >360°, characterised by the blue colour given on addition of methyl alcoholic potassium hydroxide to its solution in pyridine.

Hydrolysis. The above methyl derivative (0·1 g.) was heated in concentrated sulphuric acid (10 c.c.) to 100°, and allowed to cool. After being kept overnight the brown solution was added to water. A white precipitate formed, and this became orange when the acid was neutralised by ammonia.

The dried product (0·09 g.), m. p. 215—259°, was dissolved in benzene and chromatographed on alumina; two zones resulted. The upper zone, eluted with acetone, afforded orange needles, m. p. 290—300°. The lower, reddish-violet zone, eluted with acetone, yielded red, prismatic needles, m. p. 230°, alone or mixed with 2-methylaminoanthraquinone.

Demethylation of 2-Methylaminoanthraquinone.—(*a*) 2-Methylaminoanthraquinone (10·0 g.), dry potassium carbonate (6·0 g.), copper bronze (2·0 g.), and nitrobenzene (80 c.c.) were heated under reflux in a current of air which had been passed through an aqueous solution of 2 : 4-dinitrophenylhydrazine hydrochloride and then dried by calcium chloride. The volatile products of the reaction were passed through a vertical condenser, then through a trap, and finally through a solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. Yellow needles of formaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 165—166°, separated. After 5 hours the mitrobenzene suspension was distilled in steam. The residue (5·2 g.), m. p. 228°, was chromatographed in benzene on alumina. Two bands formed, an upper zone of strongly adsorbed black material, and a lower zone, which afforded red needles of 2-methylaminoanthraquinone. In this experiment the yield of (A) was 4·0 g.

(*b*) In a similar experiment in which 3·4 g. of cuprous chloride were used instead of copper bronze and the reaction time was 24 hours, the yield of (A) was 1·76 g. From the mother-liquor 2-methylaminoanthraquinone (4·0 g.) separated. After removal of this derivative, the nitrobenzene solution was washed with 10% hydrochloric acid. The acid extract was cooled to 0°, sodium nitrite (0·5 g.) was added, and the yellow solution added to one of β-naphthol (1 g.) in aqueous sodium hydroxide. The reddish-brown precipitate was collected, washed with aqueous sodium hydroxide, dried, and chromatographed in toluene on alumina. The main orange zone, eluted by methyl alcohol, afforded 1-phenylazo-2-naphthol, m. p. 130°, not depressed on admixture with an authentic sample.

Demethylation of 2-Dimethylaminoanthraquinone.—2-Dimethylaminoanthraquinone (2·5 g.), potassium carbonate (1·5 g.), and copper bronze (0·5 g.) were heated under reflux in nitrobenzene (20 c.c.) for 24 hours. The yield of (A) was 0·39 g. The nitrobenzene solution was distilled in steam, leaving a dark brown residue (2·2 g.). A portion (0·5 g.) of this was chromatographed in benzene (200 c.c.) on alumina; three zones formed. The most strongly adsorbed was black. Two red zones were eluted by acetone; the more strongly adsorbed of these yielded 0·05 g. of 2-methylaminoanthraquinone, m. p. 231°, not depressed on admixture with the authentic compound. The other yielded 0·35 g. of unchanged 2-dimethylaminoanthraquinone, m. p. 186°.

The 2-dimethylaminoanthraquinone used in this experiment was chromatographed before use and shown to be free from 2-methylaminoanthraquinone. The use of 0·85 g. of cuprous chloride instead of the copper bronze led to the formation of 0·31 g. of (A); when 1·5 g. of cupric acetate were used, the yield of (A) was 0·49 g.

Dealkylation of 2-Ethylaminoanthraquinone.—2-Ethylaminoanthraquinone (2·0 g.), potassium carbonate (1·5 g.), copper bronze (0·5 g.), and nitrobenzene (25 c.c.) were heated under reflux for 24 hours. When the mixture was then set aside, a dark product separated from the medium; this was collected and chromatographed in benzene on alumina. The main zone, extracted with ethyl alcohol, afforded 0·15 g. of unchanged 2-ethylaminoanthraquinone. A more strongly adsorbed orange zone gave, with acetone, 0·02 g. of needles, m. p. 302°. This product, acetylated, yielded 2-acetamidoanthraquinone, m. p. 266—267°, not depressed on admixture with an authentic sample.

Demethylation of NN′-*Di*-2-*anthraquinonyl*-N-*methylformamidine.*—A solution of the above formamidine (0·05 g.) in nitrobenzene (5 c.c.) was heated under reflux for 3 hours with potassium carbonate (0·10 g.) and copper bronze (0·05 g.). The hot solution was filtered; the residue contained the characteristic red needles of (A), the identity of which was further confirmed by the deep blue colour obtained on heating to boiling a suspension of the product in pyridine containing methanolic potassium hydroxide. In a similar experiment in which the potassium carbonate was omitted the original formamidine (0·04 g.) was recovered unchanged; there was no indication of the occurrence of demethylation.

NN′-*Di*-2-*anthraquinonylbenzamidine.*—This was prepared by the method of G.P. 248,656. Crystallised from *o*-dichlorobenzene it formed fine yellow prismatic needles, m. p. 327° (Found : C, 78·4; H, 3·9; N, 4·8. Calc. for $C_{35}H_{20}O_4N_2$: C, 78·9; H, 3·8; N, 5·3%). *NN*′-Di-2-anthraquinonylbenzamidine dissolved in concentrated sulphuric acid with a reddish-brown colour; on addition of water, the buff-coloured sulphate separated; on the further addition of aqueous ammonia the yellow free base was regenerated. It dissolved in hot pyridine with a yellow colour, changed by methyl alcoholic potassium hydroxide to a greenish-blue; addition of alcohol caused a change to violet and ultimately to yellow.

Hydrolysis. A solution containing the benzamidine (1·0 g.) dissolved in concentrated sulphuric acid (10 c.c.) was heated for a few minutes to 200°, then cooled, and added to water. The orange precipitate was collected and washed with dilute aqueous ammonia. Evaporation of the washings and acidification gave 0·01 g. of benzoic acid, m. p. 120°. The insoluble residue (0·8 g.) was heated under reflux with acetic anhydride. The yellow product which separated recrystallised from acetic acid as yellow prisms, m. p. 264—265° alone or mixed with 2-acetamidoanthraquinone.

Copper derivative. A solution of the benzamidine (0·5 g.) in nitrobenzene (20 c.c.) was heated under reflux for 6 hours with copper bronze (0·25 g.). The residue obtained on filtering the hot suspension was stirred for 24 hours with a mixture of concentrated aqueous ammonia and ammonium chloride. The residue was then free from copper bronze; it was collected (0·11 g.) and obtained in the form of dark, olive-green, prismatic needles, which appeared red by transmitted light (Found : C, 70·2; H,3·3; N, 4·6; Cu, 10·9. $C_{35}H_{19}O_4N_2Cu$ requires C, 70·7; H, 3·2; N, 4·7; Cu, 10·7%). When finely divided the *copper* derivative appeared reddish-brown. It decomposed on being heated with either pyridine, or acetic acid, the free benzamidine passing into solution.

Demethylation of 2-N-*Methylanilinoanthraquinone.*—2-*N*-Methylanilinoanthraquinone (1·0 g.), potassium carbonate (0·5 g.), cupric acetate (0·5 g.), and nitrobenzene (40 c.c.) were heated under reflux in a slow stream of air. The volatile products were passed through a solution of dimedone; formaldehyde was detected after an hour. After 10 hours, the suspension containing the dimedone precipitate was set aside for 12 hours and then filtered. The yield of condensation product was 0·023 g., equivalent to the demethylation of 2·5% of the 2-*N*-methylanilinoanthraquinone.

The nitrobenzene solution was distilled in steam; a residue (1·1 g) was chromatographed in benzene on alumina. A continuous orange zone formed. This was cut into three equal portions and from each of these the adsorbed colouring matter was eluted by acetone. That from the most strongly adsorbed section (0·1 g.; m. p. 170—215°) dissolved in pyridine with an orange colour, changed to deep green by methanolic potassium hydroxide. The two remaining sections yielded unchanged 2-*N*-methylanilinoanthraquinone, m. p. 163° (0·65 g.).

1 : 2′-Dianthraquinonyl-*N*-methylamine was recovered unaltered (0·45 g.; m. p. 285°) when 0·5 g. was heated for 30 hours with copper bronze (1·0 g.) and potassium carbonate (1·0 g.) in nitrobenzene (50 c.c.). Neither formaldehyde nor formate could be detected, and the absence of 1 : 2′-dianthraquinonylamine was shown by the negative response of the product in the pyridine–methanolic potassium hydroxide test. A similar result was obtained when cupric acetate was used instead of copper bronze.

Demethylation of 1-*Methylaminoanthraquinone*.—(*a*) A suspension containing 1-methylaminoanthraquinone (2·5 g.), cupric acetate (1·5 g.) and potassium carbonate (1·5 g.) in nitrobenzene (20 c.c.) was heated under reflux for 24 hours, then filtered hot. The residue gave a negative response in the pyridine–methanolic potassium hydroxide test. The filtrate was distilled in steam; the residue was chromatographed in benzene on alumina. In addition to a lower violet zone from which 1-methylaminoanthraquinone, m. p. 170°, was recovered, there was a more strongly adsorbed red zone which yielded 1-aminoanthraquinone, m. p. 252°, on extraction with acetone. There was no indication of the presence of 1-formamidoanthraquinone.

(*b*) 1-Methylaminoanthraquinone (5·0 g.), potassium carbonate (5·0 g.), and copper bronze (2·0 g.) were heated under reflux in nitrobenzene (50 c.c.) in a current of dry air for 8 hours. Formaldehyde was liberated almost immediately; it was collected in dimedone solution and in this way yielded 0·29 g. of the condensation product, equivalent to the demethylation of 5% of the 1-methylaminoanthraquinone employed. The nitrobenzene solution was filtered hot; there was a residue (3·1 g.) consisting mainly of copper bronze. The filtrate deposited a brown solid [C; 0·8 g.; m. p. 284° (decomp.)] on storage. Product C formed in pyridine a yellow solution which became green on addition of methanolic potassium hydroxide, and violet on the further addition of alcohol. It formed a brown solution in concentrated sulphuric; this became colourless on addition of water, and an orange-red precipitate formed on further dilution. There was no indication of the formation of a copper derivative when C was heated with cupric acetate in nitrobenzene. Crystallisation from nitrobenzene and then from acetic acid gave an orange-red product, m. p. 180—186°. Dissolved in toluene and chromatographed on alumina, the product yielded a main orange-yellow zone. The lowest third extracted by means of acetone yielded fine red needles, m. p. 252·5°, not depressed by 1-aminoanthraquinone. The top third yielded orange needles, m. p. 206—220°; these were dissolved in benzene and again chromatographed on alumina. A continuous zone resulted; the lower half yielded a further quantity of 1-aminoanthraquinone. The upper half yielded orange needles, m. p. 223—224°, not depressed on admixture with 1-formamidoanthraquinone. This product dissolved in pyridine with a yellow colour, changed to reddish-orange by methanolic potassium hydroxide.

1-Aminoanthraquinone and 1-formamidoanthraquinone were also obtained when trichlorobenzene was substituted for nitrobenzene in the recrystallisation of C.

1-*Formamidoanthraquinone*.—1-Aminoanthraquinone (5 g.) was made into a paste with 98% formic acid (15 c.c.) and heated at 170—180° for 6 hours. The *formyl* derivative (5·2 g.; m. p. 215°) crystallised from acetic acid as orange meedles, m. p. 222—223° (Found: C, 71·4; H, 3·7; N, 5·5. $C_{15}H_9O_3N$ requires C, 71·7; H, 3·6; N, 5·6%). Its yellow solution in pyridine becomes red when methyl-alcoholic potassium hydroxide is added.

There was no reaction when 1-aminoanthraquinone (2 mols.) was heated with ethyl orthoformate (1 mol.) in nitrobenzene. 1 Aminoanthraquinone (5 g.) with ethyl orthoformate (11 c.c.) in nitrobenzene (50 c.c.) at 140° (4 hours) yielded a product (3·1 g.) which crystallised from acetic acid in orange needles, m. p. 177—178°. Warmed with concentrated sulphuric acid at 100° for an hour, this compound yielded 1-aminoanthraquinone, m. p. 252°.

Condensation of 1-*Methylaminoanthraquinone and* 2-*Chloroanthraquinone*.—1-Methylaminoanthraquinone (4·7 g.), 2-chloroanthraquinone (4·8 g.), potassium acetate (5·0 g.), and cuprous chloride (0·5 g.) were heated under reflux in nitrobenzene (50 c.c.) for 40 hours, whilst a current of air was passed through the mixture and thence through a solution of dimedone. The formaldehyde–dimedone condensation product was observed after 16 hours; the final yield was 0·029 g. The nitrobenzene solution was filtered hot; on cooling, red prisms of 1 : 2′-dianthraquinonylamine (2·5 g.) separated. This product was characterised by its absorption spectrum in concentrated sulphuric acid (Fig. 3), the green colour obtained on addition of methanolic potassium hydroxide to its solution in pyridine, and by the *N*-benzoyl derivative, m. p. 272—273°, not depressed when mixed with authentic *N*-benzoyl-1 : 2′-dianthraquinonylamine. When kept for several days the nitrobenzene mother-liquor yielded 1·9 g. of red crystals, m. p. 265—275°. Recrystallisation from nitrobenzene gave a product, m. p. 280—281°, not depressed by an authentic sample of 1 : 2′-dianthraquinonyl-*N*-methylamine, m. p. 283—284°. The product dissolved in pyridine with an orange colour, unchanged by methanolic potassium hydroxide.

Condensation of 1-*Chloro*-2-*methylaminoanthraquinone with* 2-*Aminoanthraquinone*.—1 Chloro-2-methylaminoanthraquinone (2·7 g.), 2-aminoanthraquinone (2·25 g.), potassium acetate (1·5 g.), and cuprous chloride (0·2 g.) were heated under reflux in nitrobenzene (20 c.c.). After 3 hours the solution was greenish-blue. It was filtered whilst hot and the residue was washed with water. The residue consisted of reddish-brown crystals (0·8 g.) (Found : N, 5·1; Cu, 11·8. Calc. for $C_{29}H_{15}O_4N_2Cu$: N, 5·1; Cu, 12·2%) of the cuprous derivative of *NN'*-di-2-anthraquinonylformamidine. It was entirely free from chlorine. The filtrate yielded on cooling a black, indefinitely crystalline product, m. p. 237° (1·7 g.). This was chromatographed in chlorobenzene on alumina; three main zones resulted. The most strongly adsorbed, blue zone, eluted by *o*-dichlorobenzene, gave well-defined blue needles (0·02 g.) which crystallised well from quinoline and showed the characteristic properties of *N*-methylindanthrone. Its solubility in *o*-dichlorobenzene at 20° was 0·0015 g./100 c.c. Under identical conditions the solubility of a specimen of methylindanthrone prepared by the cyclisation of 2-amino-1 : 2'-dianthraquinonyl-*N*-methylamine was 0·00076 g. The total solubility of a mixture of the two specimens was 0·0013 g.

2-*Bromo*-1-*methylaminoanthraquinone*.—This *quinone* was prepared by the method of G.P. 288,825. The crude dark violet-red product, m. p. 140—150°, was crystallised several times from acetic acid and obtained in the form of red, prismatic needles, m. p. 170—171° (Found : C, 57·4; H, 3·3; N, 4·5; Br, 25·2. $C_{15}H_{10}O_2NBr$ requires C, 57·0; H, 3·2; N, 4·4; Br, 25·3%).

2-*Bromo*-1-N-*methylbenzamidoanthraquinone*.—A mixture of 2-bromo-1-methylaminoanthraquinone (1·0 g.), benzoyl chloride (3 c.c.), pyridine (5 c.c.), and a drop of concentrated sulphuric acid was heated to boiling. The solution became yellow after 5 minutes. It was added to alcohol and the precipitate (0·85 g.; m. p. 172—173°) collected. Recrystallisation from acetic acid gave yellow plates of 2-*bromo*-1-N-*methylbenzamidoanthraquinone* (0·62 g.), m. p. 176—177° (Found : N, 3·6. $C_{22}H_{14}O_3NBr$ requires N, 3·8%).

Self-condensation of 2-*Bromo*-1-*methylaminoanthraquinone*.—In the experiments recorded in the annexed Table 2-bromo-1-methylaminoanthraquinone (R) was heated under reflux with copper bronze (Cu), cuprous chloride, or cupric acetate and either sodium acetate or potassium acetate in nitrobenzene. A slow current of dry air was drawn through the reactants and any formaldehyde produced was absorbed in a 0·2% dimedone solution. At the end of the experiment the nitrobenzene suspension was cooled and then filtered. The residue was washed with alcohol, then with distilled water, and extracted by ammonia and ammonium chloride to remove copper and its salts. The undissolved residue was blue and consisted mainly of *N*-methylindanthrone. The distilled aqueous extract was acidified with nitric acid, and bromide ion precipitated as silver bromide; when cuprous chloride was used as condensing agent it was assumed that the all the halogen would appear in the silver precipitate as silver chloride.

	Reactants.					Products and yields (%).		
Exp. no.	R (g.).	Cu or Cu salt (g.).	NaOAc/KOAc (g.).	$PhNO_2$ (c.c.).	Time (hrs.).	Blue product.	CH_2O.	AgBr.
1	5	CuCl (0·25)	KOAc (3·0)	50	1	20	0	36
2	,,	,,	,,	60	5	46	11	83
3	1	Cu (0·1)	NaOAc (0·5)	20	2	12	30	trace
4	2	$Cu(OAc)_2$ (0·2)	NaOAc (1·0)	40	1	7	24	2
5	,,	,,	,,	,,	2	6	48	trace
6	,,	,,	,,	,,	4	6	61	,,
7	*	CuCl (0·2)	KOAc (2·4)	50	2	64	11	64

* The reactants were 1-amino-2-bromo- (1·8 g.) and 2-bromo-1-methylamino-anthraquinone (1·9 g.).

The nitrobenzene mother-liquor of experiment 5 was distilled in steam, and the dark reddish-brown residue was chromatographed in benzene on alumina. Elution with benzene gave first red-violet needles of 2-bromo-1-methylaminoanthraquinone, and then fine orange needles of 1-amino-2-bromoanthraquinone, m. p. 177—178°, not depressed on admixture with an authentic sample.

The colouring matter obtained in experiment 1 approximated in composition and properties to *N*-methylindanthrone. It crystallised from quinoline in short, violet needles (Found : C, 76·0; H, 3·5; N, 5·8; NCH_3, 6·3. Calc. for $C_{29}H_{16}O_4N_2$: C, 76·3; H, 3·5; N, 6·1; NCH_3, 6·4%). It dissolved in concentrated sulphuric acid with a brown colour and with the same colour in alkaline dithionite.

(*a*) A solution containing 0·5 g. of the product in concentrated sulphuric acid (4 c.c.) was cooled to 0°, a suspension of sodium nitrate (0·4 g.) in concentrated sulphuric acid (2 c.c.) was added, and the mixture stirred for an hour. Glacial acetic acid (20 c.c.) was then added, the product kept for 16 hours, and then the brown precipitate was collected. After being washed with sodium carbonate solution it was dissolved in alkaline dithionite. Aeration of the filtered blue solution gave indanthrone. The product crystallised from quinoline in the violet-blue curved needles characteristic of indanthrone.

(*b*) The blue product (0·05 g.) was dissolved in hot *o*-dichlorobenzene (100 c.c.) and poured on a column of alumina, previously heated for several hours at 140—150°. Development with a 20% solution of quinoline in *o*-dichlorobenzene at 140—150° gave a lower band of *N*-methylindanthrone, and a strongly adsorbed band of indanthrone.

(*c*) The blue product was recovered unaltered after being heated under reflux with quinoline or *o*-dichlorobenzene for 150 hours. Refluxing for only 5 hours in *o*-dichlorobenzene containing alumina served to convert the *N*-methylindanthrone into indanthrone. The colouring matter became adsorbed on the alumina.

(*d*) A column of cellulose was prepared from a suspension of cellulose pulp (Whatman No. 1 filter paper) in a large volume of water. The column was washed with a solution containing sodium hydroxide (1%) and sodium dithionite (0·5%) in boiled-out distilled water. A solution prepared from the blue product and alkaline dithionite was then poured on the column. Two zones developed and were eluted by alkaline dithionite. The more mobile orange-brown band yielded a clear solution having the same colour, from which *N*-methylindanthrone separated on exposure to air. The identity of the product was confirmed by means of its absorption spectrum in pyridine, and by the green colour which resulted when methanolic potassium hydroxide was added to the pyridine solution (Fig. 1). The less mobile zone was blue; it consisted of indanthrone.

The product of experiment 7 was similarly shown to consist of indanthrone and *N*-methylindanthrone by differential absorption of the reduced forms on cellulose.

A synthetic mixture of indanthrone (0·05 g.) and *N*-methylindanthrone (0·05 g.; prepared from 2-amino-1 : 2′-dianthraquinonyl-*N*-methylamine) was similarly shown to be separable on a column of cellulose.

Self-condensation of 1-*Chloro*-2-*methylaminoanthraquinone*.—(*a*) A solution containing 1-chloro-2-methylaminoanthraquinone (2·0 g.) in nitrobenzene (20 c.c.) was heated under reflux with copper sulphate (0·05 g.) and potassium acetate (1·25 g.) for 24 hours. The solution was filtered hot from a negligible residue. The brown filtrate was distilled in steam; a residue (1·9 g.; m. p. 170—180°) remained. A portion of this product was heated with acetic anhydride; it gave yellow crystals, m. p. 258°, which, recrystallised from acetic acid, formed needles, m. p. 265°, alone or mixed with 2-acetamidoanthraquinone. The remainder of the product was chromatographed in benzene on alumina. The main zone was orange-red; extracted with acetone it yielded reddish-brown needles of 2-methylaminoanthraquinone, m. p. 232—233°. Acetylation gave 2-*N*-methylacetamidoanthraquinone, m. p. 156°.

(*b*) When in (*a*) the condensing agent employed was sodium acetate (3 g.) and cupric chloride (0·25 g.) in nitrobenzene (50 c.c.), the cuprous derivative of *NN*′-di-2-anthraquinonylformamidine (0·9 g.) was obtained. The total ionised chloride yielded 3·02 g. of silver chloride, indicating that complete dehalogenation of the 1-chloro-2-methylaminoanthraquinone had occurred.

The same cuprous derivative was also obtained when the condensing agents were sodium acetate and cupric acetate and the medium *o*-dichlorobenzene.

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CLOTHWORKERS RESEARCH LABORATORY,
UNIVERSITY OF LEEDS.

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