

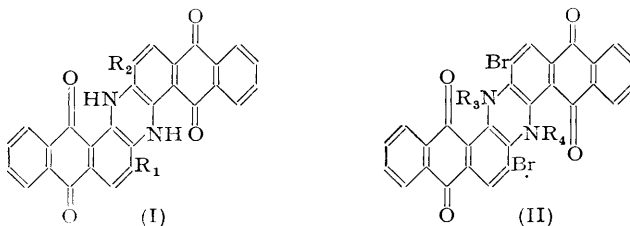
**579.** *Chemistry of Indanthrone. Part VII.\* The Action of Piperidine on 3 : 3'-Dihalogenoindantrones and the N-Methyl Derivatives of 3 : 3'-Dibromoindanthrone.*

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In Part VI \* it was shown that heating 3 : 3'-dihalogeno- and 3 : 3'-dialkylsulphonyl derivatives of indanthrone with piperidine or quinoline caused the replacement of the substituents by hydrogen. Study of the mechanism of the replacement has now indicated that the reaction involves reduction of a quinone nucleus.

IN Part VI \* it was shown that indanthrone (I;  $R_1 = R_2 = H$ ) resulted when 3 : 3'-diethylsulphonylindanthrone (I;  $R_1 = R_2 = SO_2Et$ ) was heated with dry piperidine or quinoline, and in the present investigation an attempt has been made to elucidate the mechanism of the reaction.

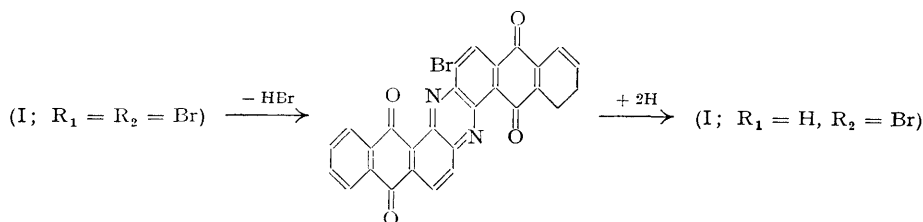
The course of the reaction between amines and 3 : 3'-disubstituted indantrones depends on circumstances. Heating with dry piperidine has no effect on 3 : 3'-dibromoindanthrone (I;  $R_1 = R_2 = Br$ ) (Part VI), but when the reaction is carried out in naphthalene at a higher temperature indanthrone is formed. 3 : 3'-Dichloroindanthrone



(I;  $R_1 = R_2 = Cl$ ) behaves differently; the product in this case is 3-chloro-3'-piperidinoindanthrone (I;  $R_1 = Cl$ ,  $R_2 = NC_5H_{10}$ ). There is no reaction with either of the dihalogenoindantrones when morpholine is used instead of piperidine. The replacement

\* Part VI, *J.*, 1951, 2177.

of chlorine by piperidine is expected, but the replacement of bromine by hydrogen involves reduction. A possible mechanism is reduction of the carbonyl groups followed by the elimination of hydrogen bromide (Part VI). Alternatively, elimination of halogen could occur by the following means :



In order to decide between the alternatives, the reaction of piperidine with the *N*-methyl and *NN'*-dimethyl derivatives of 3 : 3'-dibromoindanthrone has been studied. The *N*-methyl derivative (II;  $R_3 = Me, R_4 = H$ ) afforded *N*-methylindanthrone; the *NN'*-dimethyl compound (II;  $R_3 = R_4 = Me$ ) yielded 3 : 3'-dibromo-*N*-methylindanthrone (II;  $R_3 = Me, R_4 = H$ ) and *NN'*-dimethylindanthrone. The elimination of a methyl group is not unexpected because of the experiments reported below, but the elimination of bromine from 3 : 3'-dibromo-*NN'*-dimethylindanthrone indicates the occurrence of reduction and supports the view of the reaction put forward in Part VI. It could be suggested that the first step in the reaction is the replacement of a halogen substituent by the piperidino-group, and that the product then loses piperidine forming the azine of the dehalogenated compound. This view is unlikely to be correct because 3-chloro-3'-piperidinoindanthrone is not an unstable compound, nor does the proposed mechanism explain the formation of *NN'*-dimethylindanthrone from its 3 : 3'-dibromo-derivative.

*N-Methyl Derivatives of 3 : 3'-Dibromoindanthrone.*—The methylation of 3 : 3'-dibromoindanthrone by methyl toluene-*p*-sulphonate and potassium carbonate in tetrachlorobenzene yields the *N*-methyl derivative (II;  $R_3 = Me, R_4 = H$ ) or the *NN'*-dimethyl derivative (II;  $R_3 = R_4 = Me$ ) according to the reaction conditions. At the same time there is formed a trimethyl derivative the structure of which is not yet established. The constitution of the *NN'*-dimethyl derivative has been confirmed by its synthesis from 1 : 3-dibromo-2-methylaminoanthraquinone, sodium acetate, and copper acetate in *o*-dichlorobenzene.

The *NN'*-dimethyl derivative is relatively unstable; on exposure to light a solution in  $\alpha$ -chloronaphthalene gives the *N*-methyl derivative. The *N*-methyl compound also results when the *NN'*-dimethyl derivative is heated with concentrated sulphuric acid at 100° for 30 minutes. These two reactions establish the constitution of the *N*-methyl derivative. The *NN'*-dimethyl compound shows the property of thermochromism in organic solvents : solutions are blue when cold but become red-violet when heated. There are also unexpected features in the absorption spectra of this compound.

In concentrated sulphuric acid indanthrone and its *N*-methyl, *NN'*-dimethyl, and 3 : 3'-dibromo-derivatives show almost identical spectra. In the same solvent the *N*-methyl and *NN'*-dimethyl derivatives of 3 : 3'-dibromoindanthrone resemble one another but differ from indanthrone. With respect to indanthrone their absorption occurs at shorter wave-lengths and the intensity is smaller, particularly in the case of the *NN'*-dimethyl compound (see Table). In  $\alpha$ -chloronaphthalene or chlorobenzene the main

Compound	$m\mu$	Absorption max. in conc. sulphuric acid					
		$\epsilon \times 10^{-4}$	$m\mu$	$\epsilon \times 10^{-4}$	$m\mu$	$\epsilon \times 10^{-4}$	$m\mu$
Indanthrone .....	470	1.25	570 **	0.41	>720	>1.19	
<i>Indanthrone derivative.</i>							
* <i>N</i> -Methyl .....	470	1.07	570 **	0.41	720	1.15	
* <i>NN'</i> -Dimethyl .....	472	1.02	580 **	0.33	>720	>1.26	
3 : 3'-Dibromo .....	470	1.32	580	0.42	>730	>1.92	
3 : 3'-Dibromo- <i>N</i> -methyl .....	<440	>1.69			575	1.23	
3 : 3'-Dibromo- <i>NN'</i> -dimethyl ...	<460	>0.54			575	0.31	

\* Part I (*J.*, 1951, 2129).

\*\* Inflexion.

absorption maxima of all the following 3 : 3'-disubstituted indantrones, diethylsulphonyl-, dibutylsulphonyl-, dichloro-, dibromo-, and di-*tert.*-butyl-, occur in the range 705—725  $m\mu$  (*J.*, 1951, 2177, 2179). In *o*-dichlorobenzene the main absorption maxima of *N*-methyl- and *NN'*-dimethyl-indantrones occur at 665 and 655  $m\mu$ , whereas in  $\alpha$ -chloronaphthalene the maximum absorption of the 3 : 3'-dibromo-derivatives of these two compounds has been displaced to 610  $m\mu$  ( $\epsilon = 1.50 \times 10^4$ ) and 580  $m\mu$  ( $\epsilon = 1.21 \times 10^4$ ). The unusual features of the absorption spectra of the *N*-methyl and the *NN'*-dimethyl derivative of 3 : 3'-dibromoindanthrone are typical of non-planar compounds (cf. Braude *et al.*, *J.*, 1949, 1890; Jeffreys and Knott, *J.*, 1951, 1028; Kiprianov and Ushenko, *Bull. Acad. Sci. U.R.S.S., Classe Sci. chim.*, 1950, 492). Similar compounds are likewise non-planar (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838; Brown, Widiger, and Letang, *ibid.*, 1939, **61**, 2597; von Braun, *Ber.*, 1916, **49**, 1101).

Thermochromism due to the formation of diradicals has been reported in the case of dianthronyl (Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419; Theilacker, Kortüm, and Friedheim, *Chem. Ber.*, 1950, **83**, 508), and thermochromism due to zwitterion formation has been discussed for 2-*spiro*bis-2-[naphtho(1' : 2'-5 : 6)pyran] by Schönberg, Mustafa, and Askar (*J. Amer. Chem. Soc.*, 1951, **73**, 2876), Koelsch (*J. Org. Chem.*, 1951, **16**, 1362), and Knott (*J.*, 1951, 3038), but neither of these phenomena would provide a satisfactory explanation of the thermochromism of 3 : 3'-dibromo-*NN'*-dimethylindanthrone. Thus with indanthrone derivatives the wave-length of maximum absorption is not greatly influenced by the dielectric constant of the medium. *NN'*-Dimethylindanthrone exhibits an absorption maximum at 645  $m\mu$  ( $\epsilon = 2.00 \times 10^4$ ) in toluene (dielectric constant = 2.4), and at 655  $m\mu$  ( $\epsilon = 2.51 \times 10^4$ ) in nitrobenzene (dielectric constant = 36).

It remains a possibility that the thermochromism of 3 : 3'-dibromo-*NN'*-dimethylindanthrone is the result of interchange between *cis*- and *trans*-forms.

The two procedures for methylating 3 : 3'-dibromoindanthrone described in the experimental portion afford, respectively, (a) the *NN'*-dimethyl derivative (26%) and a trimethyl derivative (18%), and (b) the *N*-methyl derivative (6%) and the same trimethyl derivative (7.5%). The formation of the trimethyl derivative does not involve methylation of either nitrogen or carbon, because the compound readily yields 3 : 3'-dibromoindanthrone when it is heated with sulphuric acid; under the same conditions 3 : 3'-dibromo-*N*-methylindanthrone is recovered unchanged. In the presence of Raney nickel the trimethyl derivative absorbs only 0.41 mol. of hydrogen. Under the same conditions 3 : 3'-dibromo-*NN'*-dimethylindanthrone takes up 1.72 mols. of hydrogen. The trimethyl compound appears to be an *O*-derivative, but further work is needed to establish its constitution.

In preparing 1 : 3-dibromo-2-methylaminoanthraquinone a number of practical difficulties were encountered. Bromine (1.1 mols.) in acetic acid reacted with 2-methylaminoanthraquinone to form 3-bromo-2-methylaminoanthraquinone in 40% yield. Increasing the proportion of bromine to 2.5 mols. gave a similar result, 29% of the methylaminoanthraquinone being recovered. *N*-Bromosuccinimide (2 mols.) in benzene gave 1-bromo-2-methylaminoanthraquinone (54%) together with a small amount of the 3-bromo-compound. In one experiment 1 : 3-dibromo-2-methylaminoanthraquinone (21%) and the 1-bromo-compound (26%) were obtained. The 1 : 3-dibromo-derivative did not result when the 1-bromo-compound was treated with bromine in acetic acid or when the 3-bromo-compound was treated with *N*-bromosuccinimide. Bromine (2 mols.) in nitrobenzene gave a mixture of the 1- and the 3-bromo-derivative, the proportions varying with the temperature of the reaction. In attempting to methylate 2-amino-1 : 3-dibromoanthraquinone we found that the use of methyl toluene-*p*-sulphonate and potassium carbonate in *o*-dichlorobenzene (yield 31%) or polychlorobenzenes (b. p. *ca.* 230°) (yield 19%) was successful. The product was 1 : 3-dibromo-2-methylaminoanthraquinone identical with the compound referred to above.

When heated in chlorobenzene with sodium acetate and a small proportion of copper acetate, 1-bromo-2-methylaminoanthraquinone gave *NN'*-dimethylindanthrone (5%) together with 2-methylaminoanthraquinone and flavanthrone. *NN'*-Dimethylindanthrone

was prepared similarly from 2-bromo-1-methylaminoanthraquinone; the result is interesting because when nitrobenzene is employed as the solvent *NN'*-dimethylindanthrone is not obtained (Part II, *J.*, 1951, 2148). Further, the formation of flavanthrone in a condensation of this kind is unusual, the most nearly related instance being the formation of 3 : 3'-di-*tert.*-butylflavanthrone in the self-condensation of 2-amino-1-bromo-3-*tert.*-butylanthraquinone (Part V, *J.*, 1951, 2176; cf. also D.R.-P. 172,733). 2-Amino-1-chloroanthraquinone has been stated to yield flavanthrone (Kopetschni and Wiesler, *Sitzungsber. Akad. Wiss. Wien*, 1922, **131**, II, B, 41), but the result has been disputed (Maki and Mine, *J. Soc. Chem. Ind. Japan*, 1944, **47**, 522B).

Under similar conditions 1 : 3-dibromo-2-methylaminoanthraquinone gave 1 : 3-dibromo-*NN'*-dimethylindanthrone (39%), identical with the compound already described.

#### EXPERIMENTAL

M. p.s below 360° are corrected.

*Action of Piperidine on 3 : 3'-Dibromoindanthrone.*—3 : 3'-Dibromoindanthrone (Found : Br, 26.7. Calc. for  $C_{28}H_{12}O_4N_2Br_2$  : Br, 26.7%) (0.1 g.) was refluxed for 24 hours with piperidine (5 c.c.) and naphthalene (20 g.). The resulting suspension was cooled, mixed with benzene, and then filtered. The residue, after being washed with hot benzene, consisted of red-violet crystals (60 mg.) (Found : N, 5.9; Br, 2.3%) having a coppery lustre. The main portion of the product was indanthrone.

Under similar conditions 3 : 3'-dibromoindanthrone was recovered unaltered after being heated with a mixture of morpholine and naphthalene. The bromo-compound was much less soluble in this reagent.

*Action of Piperidine on 3 : 3'-Dichloroindanthrone.*—Under the conditions used with the dibromo-analogue 3 : 3'-dichloroindanthrone (Found : Cl, 14.1. Calc. for  $C_{28}H_{12}O_4N_2Cl_2$  : Cl, 13.9%) (0.1 g.) afforded lustrous violet-blue needles (0.09 g.) (Found : N, 7.2; Cl, 6.1.  $C_{33}H_{22}O_4N_3Cl$  requires N, 7.5; Cl, 6.3%). 3-Chloro-3'-piperidinoindanthrone was only slightly soluble in pyridine; it dissolved with a blue colour in alkaline sodium dithionite (hydrosulphite).

Under the same conditions, 83% of the dichloro-compound was recovered when a mixture of morpholine and naphthalene was used.

3 : 3'-Dibromo-*NN'*-dimethylindanthrone.—(a) Finely divided 3 : 3'-dibromoindanthrone (0.5 g.) was heated in an open flask with anhydrous potassium carbonate (2.3 g.) and mixed polychlorobenzenes (50 c.c.; b. p. 230—250°) until moisture had been expelled. A solution of methyl toluene-*p*-sulphonate (3.1 g.) in polychlorobenzene (50 c.c.) was then added gradually during 30 minutes to the boiling suspension. Thirty minutes after the addition was complete, the boiling solution was filtered and the filtrate concentrated to small volume. Chromatography on alumina, with chlorobenzene to develop the bands, gave two main zones. The more mobile was dark blue, the less mobile red-violet. The column was cut and the two colouring matters were eluted with hot chlorobenzene. The extracts were concentrated, then cooled and mixed with acetone.

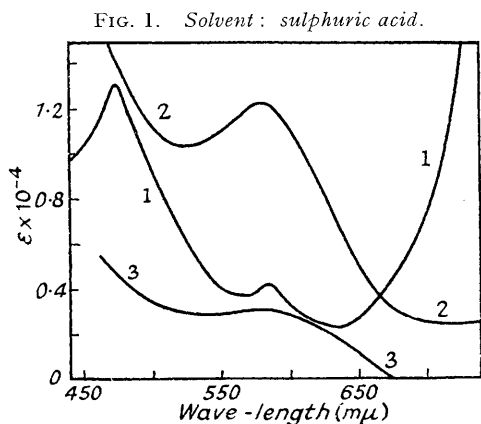
(i) The dark blue band gave lustrous crystals of 3 : 3'-dibromo-*NN'*-dimethylindanthrone (Found : C, 57.6; H, 2.5; N, 4.5; Br, 25.7; NMe, 9.7.  $C_{30}H_{16}O_4N_2Br_2$  requires C, 57.3; H, 2.5; N, 4.5; Br, 25.5; NMe, 9.2%) (Found, under the conditions of methoxyl determination : NMe, 4.6%). The compound (yield, 0.138 g.) had m. p. 376° (decomp.). It was paramagnetic. There was no colour change when methyl-alcoholic potassium hydroxide was added to its blue solution in cold pyridine; in the same test 3 : 3'-dibromoindanthrone changed from blue to green. The solution in concentrated sulphuric acid was yellow-brown, becoming yellow on the addition of a small volume of water; a violet-blue precipitate formed on further dilution. Addition of nitric acid to the solution in sulphuric acid gave a deep red-brown colour. The compound dissolved in alkaline sodium dithionite, forming an orange solution. It was only very sparingly soluble in acetone or ligroin. The blue solution in organic solvents became red-violet when heated; the colour change was reversed on cooling. Hydrogenation in  $\alpha$ -chloronaphthalene acetic-acid in the presence of Raney nickel caused the absorption of 1.72 mols. of hydrogen.

(ii) The red-violet band afforded minute, violet needles (0.097 g.) of a trimethyl derivative of 3 : 3'-dibromoindanthrone (A) (see below).

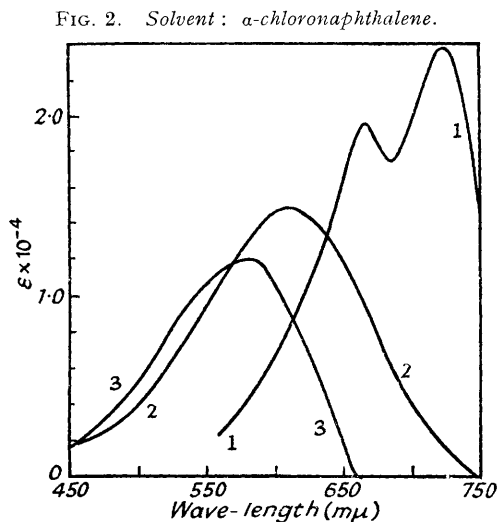
(b) 1 : 3-Dibromo-2-methylaminoanthraquinone (0.1 g.) was heated under reflux for 5.5 hours in *o*-dichlorobenzene (7 c.c.) containing finely powdered anhydrous sodium acetate

(0.1 g.) and a very small quantity of cupric acetate. The suspension changed in colour from red to blue. It was filtered hot, and the filtrate was cooled and chromatographed on alumina. Several zones formed and from these were isolated (i) unchanged 1 : 3-dibromo-2-methylamino-anthraquinone (0.028 g., 28%), (ii) 3 : 3'-dibromo-*NN'*-dimethylindanthrone (0.031 g., 39%), and (iii) unidentified product (0.018 g.). Fraction (ii) was identified by its absorption spectrum and colour reactions. When the heating was carried out for 24 hours the yields were (ii) 42% and 2-bromo-3-methylaminoanthraquinone 17%. Phenolic compounds were formed under both conditions, the amount increasing with duration of heating; there was no flavanthrone.

*Action of Piperidine on 3 : 3'-Dibromo-*NN'*-dimethylindanthrone.*—The dimethyl compound (0.039 g.) was refluxed in piperidine (10 c.c.) for 4 hours. The resulting solution was cooled and then mixed with acetone. The minute, lustrous crystals (0.011 g.) which separated were chromatographed on alumina; several green and blue zones were formed. The colouring matter was extracted from the main blue zone by chlorobenzene containing a small volume of pyridine. The extract was concentrated, and then mixed with ligroin. Blue needles (0.004 g.) having a



- 1, 3 : 3'-Dibromoindanthrone: maxima:  $\lambda > 730$ ,  $\epsilon > 19,200$ ;  $\lambda 580$ ,  $\epsilon 4200$ ;  $\lambda 470$ ,  $\epsilon 13,200$ .  
 2, 3 : 3'-Dibromo-*N*-methylindanthrone: maxima:  $\lambda 575$ ,  $\epsilon 12,300$ ;  $\lambda < 440$ ,  $\epsilon > 16,900$ .  
 3, 3 : 3'-Dibromo-*NN'*-dimethylindanthrone: maxima:  $\lambda 575$ ,  $\epsilon 3100$ ;  $\lambda < 460$ ,  $\epsilon > 5400$ .



- 1, 3 : 3'-Dibromoindanthrone: maxima:  $\lambda 722$ ,  $\epsilon 23,800$ ;  $\lambda 665$ ,  $\epsilon 19,700$ .  
 2, 3 : 3'-Dibromo-*N*-methylindanthrone: maximum:  $\lambda 610$ ,  $\epsilon 15,000$ .  
 3, 3 : 3'-Dibromo-*NN'*-dimethylindanthrone: maximum:  $\lambda 580$ ,  $\epsilon 12,100$ .

coppery lustre separated. These did not contain halogen; they were identified as *NN'*-dimethylindanthrone by their absorption spectrum in *o*-dichlorobenzene, by the colour of their solution in pyridine, concentrated sulphuric acid, and alkaline sodium dithionite, and by the absence of a colour change on the addition of methyl-alcoholic potassium hydroxide to the blue solution in pyridine.

When the reaction was carried out for 2 hours, chromatography showed the presence of 3 : 3'-dibromo-*N*-methylindanthrone (see below).

*3 : 3'-Dibromo-*N*-methylindanthrone.*—(a) Finely divided 3 : 3'-dibromoindanthrone (0.5 g.) was methylated under the conditions used for the dimethyl derivative except that four times the volume of polychlorobenzenes was employed, the methylating agent was added in one portion and the duration of heating was 2 hours. The resulting suspension was filtered hot from inorganic material and unchanged dibromoindanthrone, and the violet-blue filtrate was evaporated to a small volume and then chromatographed on alumina. Development with chlorobenzene gave two main zones. (i) The more mobile band was blue; the colouring matter was extracted with chlorobenzene, and the extract concentrated and then cooled. Blue crystals (0.029 g.) having a coppery lustre separated. These consisted of the *monomethyl* derivative, m. p. 356° (decomp.) (Found: C, 57.3; H, 2.4; N, 4.3; Br, 25.7; NMe, 4.7.  $C_{29}H_{14}O_4N_2Br_2$  requires C, 56.7; H, 2.3; N, 4.6; Br, 26.1; NMe, 4.8%). It dissolved somewhat easily in organic solvents with a blue colour; the solution in acetic anhydride became violet when heated, but the blue colour

returned on cooling. The solution in pyridine remained blue after the addition of methyl-alcoholic potassium hydroxide. It dissolved in alkaline sodium dithionite with a red-brown colour, and in concentrated sulphuric acid forming a brown solution; this became yellow on the addition of water and a blue precipitate separated on further dilution. (ii) The less mobile band was red-violet. The colouring matter, a *trimethyl* derivative of 3 : 3'-dibromoindanthrone, was obtained, on elution, in the form of minute, violet needles, which charred above 300° (Found : C, 58.1; H, 2.6; N, 4.7; Br, 24.15; NMe, 13.6.  $C_{31}H_{18}O_4N_2Br_2$  requires C, 57.9; H, 2.8; N, 4.4; Br, 24.9; NMe, 13.6%). It was identical with the product (A) obtained in the preparation of 3 : 3'-dibromo-*NN'*-dimethylindanthrone.

3 : 3'-Dibromotrimethylindanthrone dissolved in concentrated sulphuric acid with an olive colour; a red-violet precipitate formed on addition of the solution to water. When the temperature was allowed to rise during the dilution the precipitate was blue. The red-violet solution in pyridine became browner on the addition of methyl-alcoholic potassium hydroxide. The compound dissolved in alkaline sodium dithionite with a green colour. Hydrogenation in  $\alpha$ -chloronaphthalene-acetic acid in the presence of Raney nickel caused the absorption of 0.41 mol. of hydrogen. The reduced compound was green; when kept for a long time in an atmosphere of hydrogen it became brown. Heated at 100° for 30 minutes with sulphuric acid, the compound yielded 3 : 3'-dibromoindanthrone.

(b) 3 : 3'-Dibromo-*NN'*-dimethylindanthrone (0.050 g.) and concentrated sulphuric acid (3 c.c.), heated on a steam-bath for 30 minutes, gave a solution which, added to water, yielded 0.046 g. (94%) of 3 : 3'-dibromo-*N*-methylindanthrone.

*Action of Piperidine on 3 : 3'-Dibromo-N-methylindanthrone.*—The dibromo-compound (0.044 g.) was refluxed in piperidine (10 c.c.) for 7 hours. The solution was cooled and then filtered. The halogen-free residue (0.005 g.) (Found : N, 6.5. Calc. for  $C_{29}H_{16}O_4N_2$  : N, 6.1%) was a violet, microcrystalline powder which showed almost the same absorption maximum (660  $m\mu$ ) in *o*-dichlorobenzene as *N*-methylindanthrone (absorption maximum 665  $m\mu$ ). The colour reactions in pyridine, pyridine with methyl-alcoholic potassium hydroxide, alkaline sodium dithionite, and concentrated sulphuric acid were identical with those of *N*-methylindanthrone.

*1-Bromo-2-methylaminoanthraquinone.*—*N*-Bromosuccinimide (0.6 g.) was heated for 3 hours with a refluxing solution of 2-methylaminoanthraquinone (0.4 g.) in benzene (200 c.c.). The resulting suspension was filtered hot, and the filtrate was concentrated and then chromatographed on alumina. The most mobile band was faint pink; it contained 3-bromo-2-methylaminoanthraquinone. The main zone was orange-red. Extraction with acetone gave 1-bromo-2-methylaminoanthraquinone (0.29 g.), and this crystallised from acetic acid in yellowish-orange needles, m. p. 198—199° (decomp.) (Found : C, 57.5; H, 3.3; N, 4.8; Br, 25.6.  $C_{15}H_{10}O_2NBr$  requires C, 57.0; H, 3.2; N, 4.4; Br, 25.3%). It dissolved in concentrated sulphuric acid with a greenish-yellow colour and in alkaline sodium dithionite forming a red solution. The orange solution in pyridine became yellow-green on the addition of a drop of methyl-alcoholic potassium hydroxide. In one preparation the main orange-red band was preceded by a yellow band from which were isolated yellow needles of 1 : 3-dibromo-2-methylaminoanthraquinone (21%), m. p. 189—190° (Found : C, 45.5; H, 2.3; N, 3.7; Br, 40.65.  $C_{15}H_9O_2NBr_2$  requires C, 45.6; H, 2.3; N, 3.5; Br, 40.5%). These showed the same reactions with concentrated sulphuric acid and sodium dithionite as the 1-bromo-compound. The solution in pyridine was yellow, changed to green by the addition of methyl-alcoholic potassium hydroxide.

*3-Bromo-2-methylaminoanthraquinone.*—Bromine (1 c.c.) was dissolved in acetic acid (100 c.c.). A portion of the solution (12.7 c.c.) was added to 2-methylaminoanthraquinone (0.5 g.) in hot acetic acid (70 c.c.). After 2 hours at 100° the solution was diluted and cooled. 3-Bromo-2-methylaminoanthraquinone (0.27 g.; 40%) separated. Repeated crystallisation from acetic acid gave orange needles, m. p. 241° (Found : C, 56.6; H, 3.1; N, 4.25; Br, 25.7.  $C_{15}H_{10}O_2NBr$  requires C, 57.0; H, 3.2; N, 4.4; Br, 25.3%). The compound resembled the 1-bromo-isomer in its reactions with concentrated sulphuric acid and alkaline sodium dithionite. The orange solution in pyridine became yellow green on the addition of methyl-alcoholic potassium hydroxide.

In the early stages of the bromination pink crystals, m. p. 200—213° (decomp.), frequently separated. In contact with alcohol they readily formed 3-bromo-2-methylaminoanthraquinone.

Bromination of 2-methylaminoanthraquinone in nitrobenzene yielded a mixture of the 1- and the 3-bromo-derivative. To a solution of 2-methylaminoanthraquinone (0.2 g.) in nitrobenzene (20 c.c.) were added 11.6 c.c. of a solution prepared from bromine (1 c.c.) and

nitrobenzene (100 c.c.). After 2 hours at 100° the solvent was distilled in steam and the residual orange powder (0.3 g.; m. p. 175—185°) was chromatographed on alumina from benzene. Two orange bands formed. From the more mobile was obtained 3-bromo-2-methylaminoanthraquinone (0.12 g., 45%), and from the other 1-bromo-2-methylaminoanthraquinone (0.073 g., 27%). Bromination at 140—150° for 4 hours gave 23% of the 3-bromo- and 8% of the 1-bromo-derivative.

When 2.7 c.c. of a solution of bromine (1 c.c.) in acetic acid (100 c.c.) were added to 1-bromo-2-methylaminoanthraquinone (0.1 g.) in acetic acid (20 c.c.) and heated at 100° for 2.5 hours the product was a mixture. Chromatography on alumina gave several zones; the only compound identified was 2-methylaminoanthraquinone (13%).

The starting material was recovered in 40% yield when 3-bromo-2-methylaminoanthraquinone (0.2 g.) was heated under reflux with *N*-bromosuccinimide (0.12 g.) in benzene (50 c.c.).

**1 : 3-Dibromo-2-methylaminoanthraquinone.**—A suspension of potassium carbonate (2 g.) in a solution of 2-amino-1 : 3-dibromoanthraquinone (1.4 g.) in mixed polychlorobenzenes (100 c.c.; b. p. ca. 230°) was heated to boiling to expel moisture, and then methyl toluene-*p*-sulphonate (2 g.) was added and the refluxing continued for 2 hours. The product was filtered hot, and the filtrate was concentrated to small volume and then chromatographed on alumina. Development with benzene gave several bands. The most mobile, orange band eluted with acetone afforded 1 : 3-dibromo-2-methylaminoanthraquinone (0.27 g., 19%), identical with one of the products obtained by heating 2-methylaminoanthraquinone with *N*-bromosuccinimide. A similar preparation carried out in *o*-dichlorobenzene gave the dibromo-compound in 31% yield, but when chlorobenzene was used 87% of the starting material was recovered unchanged.

There was no indication of methylation having occurred when 2-amino-1 : 3-dibromoanthraquinone was treated as follows: (*a*) stirred with 20% oleum and 40% formaldehyde at 0° or 100° (cf. U.S.P. 2,091,235); (*b*) treated with paraformaldehyde and sulphuric acid at 0° or 100°; or (*c*) heated with methyl sulphate and sulphuric acid for 2 hours at 100°. There was no indication of acylation when 2-amino-1 : 3-dibromoanthraquinone was refluxed for 30 minutes with toluene-*p*-sulphonyl chloride and pyridine.

**Self-condensation of 2-Bromo-1-methylaminoanthraquinone.**—2-Bromo-1-methylaminoanthraquinone (0.1 g.), finely powdered anhydrous sodium acetate (0.1 g.), and a very small proportion of cupric acetate were heated under reflux for 24 hours in *o*-dichlorobenzene (7 c.c.). The solution changed in colour from red to violet-blue. It was filtered hot and the filtrate chromatographed on alumina. Development with *o*-dichlorobenzene gave several zones. Amongst the less mobile was a blue band and from this the colouring matter was eluted by means of quinoline at 150°. The eluate, concentrated and then mixed with acetone, gave *NN'*-dimethylindanthrone in very small amount, identified by its colour reactions and absorption spectrum in *o*-dichlorobenzene.

**Self-condensation of 1-Bromo-2-methylaminoanthraquinone.**—Under the same conditions 1-bromo-2-methylaminoanthraquinone gave 0.004 g. of *NN'*-dimethylindanthrone. In addition a more mobile, red band on the alumina column was found to contain 2-methylaminoanthraquinone. Further flavanthrone was found in the residue obtained at the first filtration stage.

Under the same conditions 3-bromo-2-methylaminoanthraquinone gave a complex product containing 46% of unchanged initial material.

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