Chemistry of Indanthrone. Part X.[1] 7,16-Dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine-5,9,14,18-diquinone: A Linear Isomer of Indanthrone

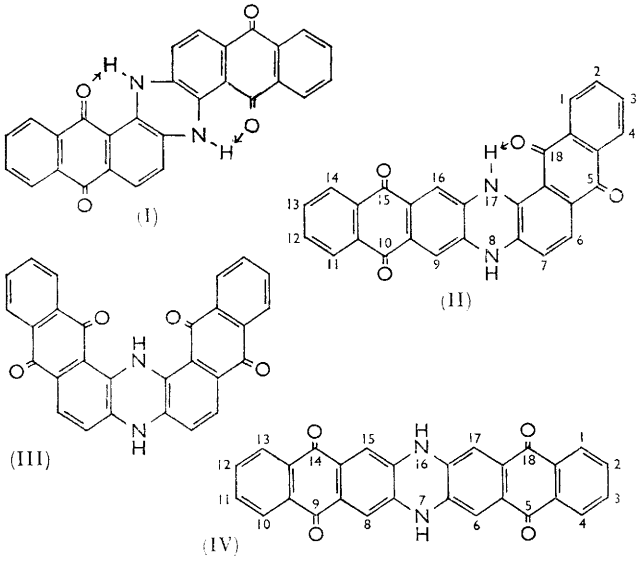
By Malcolm C. Clark

The title compound has been prepared by the self-condensation of 2-amino-3-bromo- or -chloro-anthraquinone under anhydrous conditions, and also by the condensation of 2,3-diaminoanthraquinone with either 2,3-dibromo-anthraquinone or 2,3,9,10-anthradiquinone. The physical properties of the linear isomer are compared with those of indanthrone, and the effect of inter- and intra-molecular hydrogen-bonding in such compounds is discussed. The physical and chemical properties of several 2,3-disubstituted derivatives of anthraquinone are recorded.

In view of the importance of indanthrone (I) and its derivatives as colouring matters, and the interest shown in its structure and chemical properties,[2] comparatively little is known about its isomers. The preparation and properties of the dihydrodinaphthophenazinediquinones (II)[3] and (III)[1] have been described briefly, but virtually nothing was known about the linear isomer (IV).[4]

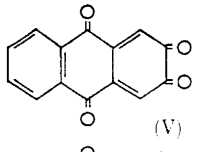
The principal obstacle to a study of the diquinone (IV) has been the lack of a suitable method of preparation. Five methods have been investigated here.

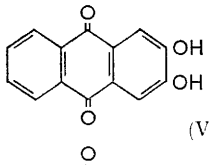
From 2,3,9,10-*Anthradiquinone*.—Schiedt[5] claimed to have prepared compound (IV) by the action of formamide on 2,3,9,10-anthradiquinone (hystazarinquinone) (V), but this was not substantiated in the present work. The preparation of the little-studied hystazarin (VI) and its quinone is of interest. The reaction of

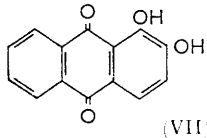


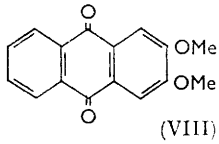
[1] Part IX, W. Bradley, R. F. Maisey, and C. R. Thitchener, *J. Chem. Soc.*, 1954, 272.
[2] G. A. Swann and D. G. I. Felton, "Phenazines," Interscience, New York, 1957, ch. 17.
[3] W. Bradley, E. Leete, and D. S. Stephens, *J. Chem. Soc.*, 1951, 2163.
[4] W. Bradley and M. C. Clark, *Chem. and Ind.*, 1959, 1601.
[5] B. Schiedt, *J. prakt. Chem.*, 1941, **57**, 203.

phthalic anhydride with catechol produced a mixture of (VI) and alizarin (VII) which was difficult to separate.[6-8]

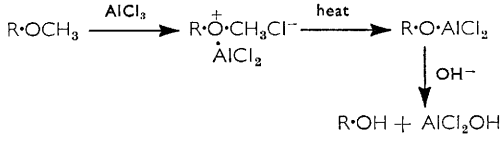

(V)


(VI)


(VII)


(VIII)

Pure hystazarin can be prepared by the demethylation of the dimethyl ether (VIII) with hydrogen bromide,[9] but is more conveniently prepared (92% yield) by the action of aluminium chloride on (VIII) in boiling trichlorobenzene. When nitrobenzene was used as the solvent, a lower yield (27%) of hystazarin was obtained, together with a little monomethyl ether (10%); this was presumably because of the formation of a complex between aluminium chloride and nitrobenzene. The mechanism of this type of dealkylation, according to Pfeiffer and Loewe,[10] is:

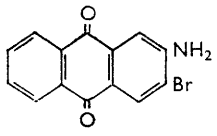


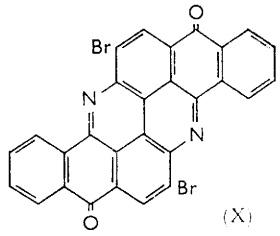
The diquinone (V) was prepared in 10% yield by a modification of Tanaka's method,[8] in which a paste of the pyridine salt [11] of hystazarin in acetic acid is oxidised with lead tetra-acetate.

By the Self-condensation of 2-*Amino*-3-*halogenoanthraquinones*.—Since both phenazine [12] and indanthrone [13] have been prepared by the self-condensation of the corresponding *ortho*-aminohalogeno-compound, the possibility of preparing compound (IV) by the self-condensation of 2-amino-3-bromoanthraquinone was investigated. 2-Amino-3-bromoanthraquinone (IX) was prepared [14] by the bromination of 2-aminoanthraquinone, previously purified by acid fractionation.[15,16]

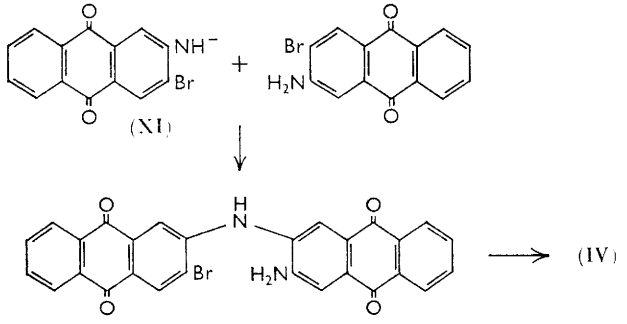
Treatment of compound (IX) with anhydrous sodium acetate and cuprous chloride in refluxing nitrobenzene gave a black insoluble compound, in 3% yield, which did not melt and which dissolved in both sulphuric acid and warm alkaline dithionite forming a brown solution. Analysis of this black residue indicated that two molecules of (IX) had condensed to form compound (IV), $C_{28}H_{14}N_2O_4$. Further evidence supporting the assignment of structure (IV) to this black compound comes from syntheses from other 2,3-disubstituted anthraquinone derivatives (see later), and from its properties.

It is of interest to note that, when Ullmann [17] heated (IX) in nitrobenzene under reflux in the presence of antimony pentachloride, he obtained the reddish-yellow dibromoflavanthrone (X). The yield of compound (IV) was improved to 93% by using anhydrous conditions, *viz.*, fusion of a mixture of (IX) and potassium carbonate at 270–290° (see Experimental section).


(IX)


(X)

The mechanism of this self-condensation probably involves initial formation of the anion (XI) in the alkaline melt, followed by nucleophilic attack of (XI) on an electron-deficient carbon atom in another molecule of (IX); this is likely to be at the 3-position rather than the 1-position on account of the electrophilic nature of the bromine atom. The second condensation then follows rapidly because of the close proximity of the reacting species and the stability of the end-product (IV). The excellent yield obtained in this condensation,


(XI)

(IV)

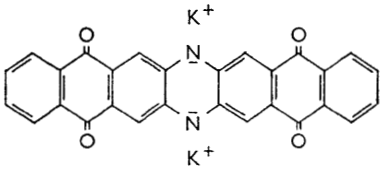
compared with that obtained by Eckert and Steiner [18] for 2,2′-dianthraquinonylamine (*viz.* 2%), obviously derives from the fact that 2-amino-3-bromoanthraquinone has a much greater acidic character than 2-aminoanthraquinone; (IX), unlike 2-aminoanthraquinone, affords a green potassium salt in pyridine (see also Part I [16]).

Support for the ionic nature of this mechanism was given by the detection of the dipotassium salt (XII) during the purification; compound (XII) was slowly hydrolysed to (IV) by aqueous alkali and immediately by dilute acids.

Earlier, Bradley and Leete [16] had isolated the potassium salt of 1-bromo-2-toluene-*p*-sulphonylaminoanthraquinone in a solid form, but present attempts to

[6] A. Baeyer and H. Caro, *Ber.*, 1874, **7**, 968.
[7] C. Liebermann, *Ber.*, 1888, **21**, 2501; C. Liebermann and H. Hohenemser, *ibid.*, 1902, **35**, 1778.
[8] M. Tanaka, *Chemical News*, 1925, **131**, 20.
[9] K. Lagodzinski, *Annalen*, 1905, **342**, 90.
[10] P. Pfeiffer and W. Loewe, *J. prakt. Chem.*, 1936, **147**, 293.
[11] P. Pfeiffer, *Annalen*, 1913, **398**, 191.
[12] H. Hillemann, *Ber.*, 1938, **71**, *B*, 42.
[13] G.P. 193, 121/1907.
[14] W. Junghans, *Annalen*, 1913, **399**, 316.
[15] T. Maki, *J. Soc. Chem. Ind., Japan, Suppl.*, 1933, **36**, 44.
[16] W. Bradley and E. Leete, *J. Chem. Soc.*, 1951, 2129.
[17] F. Ullmann and W. Junghans, *Annalen*, 1913, **399**, 330.
[18] A. Eckert and K. Steiner, *Monatsh.*, 1914, **35**, 1129.

prepare the 2-toluene-*p*-sulphonamido-derivative (and its potassium salt) of 2-amino-3-bromoanthraquinone (IX), with the view to preparing (IV) even more easily by self-condensation followed by hydrolysis, were



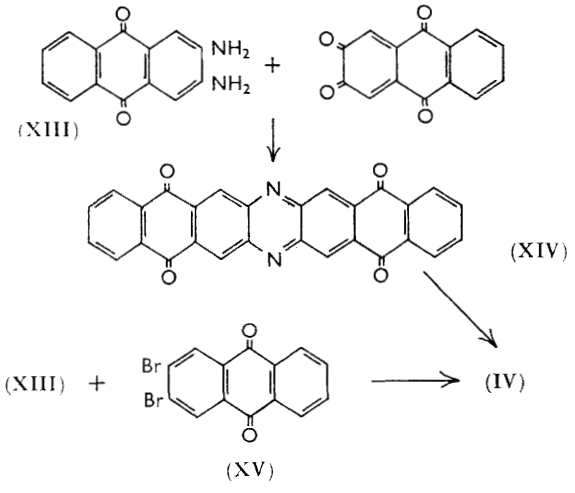
(XII)

unsuccessful, presumably because of the feebly basic nature of (IX).

Compound (IV) was also prepared, although in lower yield (25%), by the analogous self-condensation of 2-amino-3-chloroanthraquinone.

Preparation from 2,3-Diaminoanthraquinone.—2,3-Diaminoanthraquinone (XIII) was prepared by Scholl's method [19] from 2-aminoanthraquinone, but in low yield (18%). Attempts to prepare it more satisfactorily by other routes, *e.g.*, by the action of ethanolic ammonia on either 2-amino-3-chloroanthraquinone, or 2,3-dibromoanthraquinone, or by the initial formation of 2-amino-3-toluene-*p*-sulphonamidoanthraquinone from 2-amino-3-chloroanthraquinone, were unsuccessful.

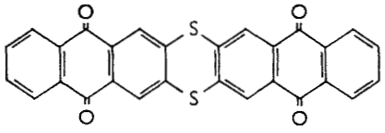
The condensation of 2,3-diaminoanthraquinone with the diquinone (V) in acetic acid afforded a small yield (3%) of a product which was shown, by comparison of absorption spectra and properties, to be identical to compound (IV) derived from the self-condensation of 2-amino-3-bromoanthraquinone. The dinaphthophenazinediquinone (XIV) was probably formed as an intermediate, since it has now been shown later that this is converted into (IV) by prolonged boiling in acetic acid. This method is analogous to the preparation of phenazine by the condensation of *o*-phenylenediamine and *o*-benzoquinone.[20]



(XIII) (XIV) (XIII) + (XV) (IV)

The condensation of 2,3-diaminoanthraquinone with 2,3-dibromoanthraquinone [21] (XV), when effected under anhydrous conditions at 250° in the presence of anhydrous potassium carbonate, afforded compound (IV) in 35% yield.

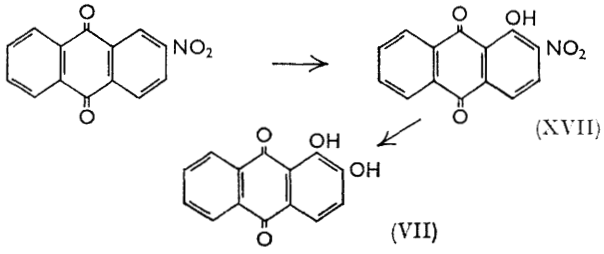
Brass and Heide [22] obtained the sulphur analogue (XVI) of compound (IV) in excellent yield by heating



(XVI)

2,3-dibromoanthraquinone with sodium sulphide, but the corresponding reaction with ammonia did not afford (IV).

Attempted Preparation using the Wohl–Aue Reaction.—Wohl and Aue [23] had found that phenazine was formed by the condensation of nitrobenzene with aniline in the presence of potassium hydroxide, and a mechanism has been suggested.[16] Attempts were made to extend this reaction to the preparation of the dinaphthophenazinediquinone (XIV). However, the attempted condensation of 2-aminoanthraquinone with 2-nitroanthraquinone afforded only the potassium salt of 1-hydroxy-2-nitroanthraquinone (XVII). This afforded alizarin (VII) on alkaline fusion, suggesting that the formation of alizarin by the alkaline fusion of 2-nitroanthraquinone,[16] proceeds by the initial formation of (XVII). The commercial preparation of alizarin by the alkaline fusion



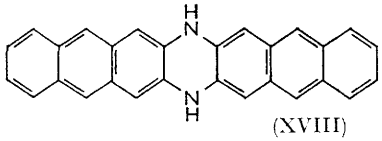
(XVII) (VII)

of anthraquinone-2-sulphonate in the presence of an oxidant [24] thus probably proceeds by a similar mechanism, *i.e.*, the initial formation of 1-hydroxyanthraquinone-2-sulphonate. Bradley, Leete, and Stephens [25] suggested a similar mechanism to explain the formation of alizarin during the preparation of indanthrone by the alkaline fusion of 2-aminoanthraquinone.

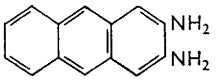
Attempted Preparation via *the Anthracene Analogues.*—Bollert [26] found that when 2-aminoanthracene was treated with refluxing acetic acid, a mixture of 2-acetylaminoanthracene and 2,2′-dianthrylamine was obtained. It was hoped to extend this reaction to the preparation of 7,16-dihydrodinaphtho[2,3-*b*:2′,3′-*i*]phenazine (XVIII) from the hitherto unknown 2,3-diaminoanthracene (XIX), but the latter proved difficultly accessible, since the reduction of 2,3-diaminoanthraquinone with zinc and dilute sodium hydroxide only gave it in 1—2% yield, even starting from the leuco-acid derivative

[19] R. Scholl, *Ber.*, 1904, **37**, 4427.
[20] O. Hinsberg, *Ber.*, 1885, **18**, 1228.
[21] M. Battegay and J. Claudin, *Bull. Soc. chim. France*, 1929, 1021.
[22] K. Brass and K. Heide, *Ber.*, 1924, **57**, 104.
[23] A. Wohl and W. Aue, *Ber.*, 1901, **34**, 2442.
[24] G. P. 186,526/1907.
[25] W. Bradley, E. Leete, and D. S. Stephens, *J. Chem. Soc.*, 1951, 2158.
[26] A. Bollert, *Ber.*, 1883, **16**, 1635.

of 2,3-diaminoanthraquinone. The purification of the diamine (XIX) was effected by alumina chromatography,



(XVIII)



(XIX)

and it was observed that partial oxidation to 2,3-diaminoanthraquinone occurred on the alumina.

Attempts to prepare 2-amino-3-bromoanthracene from 2-amino-3-bromoanthraquinone by reduction with zinc and alkali failed; debromination always preceded anthracene formation, with the resulting formation of 2-aminoanthracene. Other cases of the dehalogenation of anthraquinonoid compounds by metals have been recorded.[27]

The Properties of the Dihydrodinaphthophenazinediquinones.—Indanthrone itself does not melt or sublime below 500°, and is only very sparingly soluble in organic solvents; to explain these properties Bradley and Leete[16] suggested the occurrence of intermolecular bonding. The linear isomer (IV) of indanthrone can even more readily form an intermolecularly bonded structure, and, as expected, is more insoluble and involatile. In contrast, 8,17-dihydrodinaphtho[2,3-*a*:2′,3′-*i*]phenazine-5,10,15,18-diquinone (II) is less capable of such bonding than indanthrone and is consequently the most soluble.

Compounds (I), (II), and (III), are all blue, although the absorption maxima shifts progressively to shorter wavelengths as the degree of internal hydrogen-bonding diminishes in the series (I) : (II) : (III). The linear isomer (IV) is incapable of any resonance due to an intramolecularly bonded structure, has an absorption maximum at even shorter wavelengths than (III), and is no longer blue but reddish-brown (when freshly precipitated).

Similar relationships have been found amongst the three isomeric dianthraquinonylamines,[16] and phthaloylacridones;[28] in each case the linear isomer (which has the greatest degree of intermolecular bonding) has the highest melting point, the lowest solubility in organic solvents, and light absorption at the shortest wavelengths.

All the dihydrodinaphthophenazinediquinones can form potassium salts in pyridine. The potassium salts of isomers (I) and (II) are readily decomposed by water, whereas that of isomer (IV) is moderately stable to water. Clearly, (II) and (III) are weaker acids than (IV), and similarly are more easily dehydrogenated to the related azine.[29]

Many of these compounds are hygroscopic, and one result of this is that the microanalytical figures for the carbon content are often 2—3% below the expected values. Compounds (I) and (IV) adsorb 1—2% and 6·4% of their weight of water, respectively. A similar phenomenon was observed by Pandit[30] who found that, whereas 1,4,5,8-tetra-(α-anthraquinonylamino)anthraquinone was not hygroscopic, its cyclised product [the dyestuff Indanthren Khaki GG (C.I. No. 71050)] adsorbed 7% of water. Clearly, the ability of a compound to adsorb water molecules by means of hydrogen bonding and/or Van der Waals forces is directly related to the substantivity of its leuco-form for cellulose.

EXPERIMENTAL

Hystazarin.—(*a*) Hystazarin dimethyl ether[9] (2 g.) and anhydrous aluminium chloride (8 g.) were heated under reflux in nitrobenzene for 5 hr. by which time the evolution of halide fumes had slackened considerably. Sodium hydroxide solution was then added to the cooled suspension, and the nitrobenzene removed by steam-distillation. The deep greenish-blue mixture was then filtered, and the filtrate acidified, giving crude hystazarin (0·5 g.). When the distillation residue was further extracted with aqueous alkali, a yellowish-green product (0·2 g.), m. p. 225—230°, was obtained on acidification of the extract. Recrystallisation from acetic acid afforded a greenish-yellow compound, m. p. 228—232°, which was shown to be hystazarin monomethyl ether (lit.,[9] m. p. 236°) by its colour reactions and properties.

(*b*) Hystazarin dimethyl ether (30 g.) and anhydrous aluminium chloride (90 g.) were heated under reflux in trichlorobenzene (1·5 l.) for 5—6 hr., and the mixture was filtered hot. The residue was extracted several times with dilute sodium hydroxide, the deep-blue extracts were acidified, and the resulting precipitate of hystazarin was collected (24·8 g., 92%). Hystazarin sublimed *in vacuo* to give orange-yellow needles, which melted slowly with decomposition above 340° (Found: C, 69·6; H, 3·1. Calc. for $C_{14}H_8O_4$: C, 70·0; H, 3·3%). Hystazarin dissolved readily in pyridine giving a yellow solution, which turned bluish-green on the addition of methanolic potassium hydroxide. It afforded a diacetate, light brown needles from acetic acid, m. p. 212° (lit.,[31] 205—207°).

2,3,9,10-*Anthradiquinone.*—The pyridine salt[11] of hystazarin (3 g.) was pasted up with the minimum amount of glacial acetic acid, and lead tetra-acetate (6 g.) added slowly with vigorous stirring; the mixture became hot and its colour changed to brownish-red. The mixture was stirred for 15 min., then heated with acetic acid (25 ml.) and poured into water (175 ml.). The resulting precipitate consisted of hystazarin and the required diquinone, whilst the lead salts remained mainly in solution. The precipitate was extracted with boiling acetic acid, and the red extract, on cooling, afforded the crude diquinone (0·8 g.), which was purified either by removing the hystazarin by extraction with cold pyridine, or by chromatography in nitrobenzene on alumina when two bands were observed: (i) a mobile red band which contained the diquinone (5—10%), (ii) a strongly adsorbed violet-orange band containing hystazarin. The diquinone crystallised from quinoline as red needles or leaflets having a metallic lustre which sublimed slightly at 415° and decomposed at *ca.* 480° (Found: C, 70·65; H, 3·0. Calc. for $C_{14}H_6O_4$: C, 70·6; H, 2·5%). The yield was not improved by effecting the oxidation in complete solution in acetic acid.

Attempted Reaction of Hystazarin with Formamide.—

[27] E. Kopetschni and H. Wiesler, *Monatsh.*, 1922, **43**, 92; F. Ullmann and W. Minajeff, *Ber.*, 1912, **45**, 687.
[28] W. Bradley and H. Kaiwar, *J. Chem. Soc.*, 1960, 2859.
[29] W. Bradley and M. C. Clark, *Chem. and Ind.*, 1961, 589.
[30] P. N. Pandit, Ph.D. Thesis, Leeds University, 1957.
[31] O. Dimroth, *Annalen*, 1926, **446**, 110.

Hystazarin (3 g.) was heated wth formamide (50 ml.) at 130° for 3 hr., and the deep red mixture then filtered. The residue was extracted successively with acetic acid, hydrochloric acid, and acetone; the final residue (1 g.) was shown to be hystazarin by its colour reactions and formation of the diacetyl derivative, m. p. 205—207°. The original mother-liquor was heated with further formamide (10 ml.) at 130° for 4 hr., and then cooled and filtered; the resulting residue was again shown to be hystazarin.

The above experiment was repeated in the presence of a molar equivalent of sodium anthraquinone-2-sulphonate, and again only the starting products were recovered.

Attempted Reaction of the Diquinone (V) *with Formamide.*—The diquinone (0·2 g.) was heated with formamide (15 ml.) at 130° for 12 hr. The deep red mixture was filtered, and the residue extracted with boiling nitrobenzene and washed with alcohol. The residue crystallised from quinoline as red leaflets having a bronze lustre (0·05 g.) and was shown to be starting material. The original formamide mother-liquor was left for several days when an almost black precipitate (0·07 g.) of more starting material separated.

Self-condensation of 2-Amino-3-bromoanthraquinone.—(*a*) A mixture of 2-amino-3-bromoanthraquinone [14] (10 g.), anhydrous sodium acetate (5 g.), and cuprous chloride (0·5 g.) was heated under reflux in nitrobenzene (170 ml.) for 46 hr., and then filtered hot. The filtrate, on cooling, gave yellowish-brown needles (5·5 g.), m. p. 297—298°, undepressed on admixture with an authentic sample of 2-amino-3-bromoanthraquinone. The residue was extracted with boiling nitrobenzene and washed successively with methanol, ammonia solution (until the washings were no longer blue because of the presence of copper salts), hot water, and finally methanol. The black residue of *7,16-dihydrodinaphtho*[2,3-b:2′,3′-i]*phenazine-5,9,14,18-diquinone* (IV) (0·23 g.), which did not melt, gave a reddish-brown solution with hot alkaline dithionite from which a brown solid slowly separated on standing (Found, for black compound: Br, 0·0; N, 6·05. $C_{28}H_{14}N_2O_4$ requires Br, 0·0; N, 6·3%).

When the above experiment was repeated using only the minimum amount (70 ml.) of nitrobenzene required to dissolve the 2-amino-3-bromoanthraquinone, the yield of the black compound was 0·33 g.

(*b*) A preliminary experiment showed that the self-condensation of 2-amino-3-bromoanthraquinone under anhydrous conditions afforded the diquinone (IV) in 37% yield. Numerous experiments were carried out to determine the optimum conditions for the fusion; the results are summarised in the Table. The following method was the one subsequently employed.

Optimum conditions for the preparation of compound (IV)

2-Amino-3-bromoanthraquinone (g.)	Anhydrous K_2CO_3 (g.)	Temp.	Time (hr.)	Yield of (IV) (g.) *
5	2·5	250—270°	3	1·5
5	2·5	250—270	6	2·5
5	2·5	270—290	5	2·6
5	2·5	270—290	7	3·1
5	2·5	290—310	5	2·9
5	2·5	290—310	7	2·8
5	2·5	270—290	9	3·1
5	2·0	270—290	7	2·3
5	3·0	270—290	7	2·1
5	2·5	270—290	20	3·55

* Theoretical yield, 3·66 g.

An intimate mixture of 2-amino-3-bromoanthraquinone (100 g.) and anhydrous potassium carbonate (50 g.) was fused at 270—290° for 7 hr.; the mixture liquefied at first but then slowly solidified. The cooled product was powdered, and then extracted successively with nitrobenzene, water, and acetone at their boiling points. The residual black product was dried at 100° (68 g., 93%).

It was observed that the aqueous extract was always brownish-orange with a slight greenish reflex. A reddish-brown solid slowly separated from this extract after several days; the formation of this solid was immediate if the extract was acidified. This reddish-brown solid (0·1 g.) dried black, and was shown to be compound (IV) by a comparison of its properties and by its absorption spectrum in concentrated sulphuric acid.

The following method was found to be the best for the purification of the crude diquinone. The crude product (68 g.) obtained from the fusion was dissolved in concentrated sulphuric acid (272 ml.) at 60°, the mixture filtered, and water (82 ml.) added carefully to the well-stirred deep-brown filtrate. After being allowed to cool overnight, the mixture was filtered and the precipitate washed with cold 80% sulphuric acid and sucked dry. The precipitate was suspended into water, and the suspension neutralised with sodium carbonate before filtration; the residue was washed with water until neutral, and then with acetone, before being sucked dry. The product was then extracted with boiling pyridine for one hour without prior drying (to avoid aggregation); the residue was washed successively with hot water and acetone until the washings were clear, and finally dried at 100° (26 g., 35·5%).

The so-purified 7,16-dihydrodinaphtho[2,3-*b*; 2′,3′-*i*]phenazine-5,9,14,18-diquinone (0·3 g.) was warmed with sodium hydroxide (5 ml. of 20%), sodium dithionite (1 g.), and water (20 ml.), and the resulting reddish-brown solution chromatographed on a column of cellulose powder; the eluent used was 2% aqueous sodium hydroxide containing 1% sodium dithionite. Only a single, dark brown, strongly adsorbed band was obtained which could neither be eluted, nor after drying, extracted with pyridine. The pure product (Found: C, 73·6; H, 3·2; N, 6·2. Calc. for $C_{28}H_{14}N_2O_4$: C, 76·0; H, 3·2; N, 6·3%) was hygroscopic and gained 6·4% of its weight of water. It had $\lambda_{max.}$ 257, 295, 350 mμ, $\lambda_{min.}$ 230, 800 mμ.

The *diquinone* (IV) did not melt or sublime below 500°, and was insoluble in most organic solvents. It was very sparingly soluble in boiling pyridine (100 ml. dissolved 0·00072 g.) giving a pale orange-brown solution, which turned olive-brown on the addition of methanolic potash, stable to the addition of a little water but slowly decomposed by an excess forming an orange-brown solution, from which the reddish-brown form of (IV) slowly separated. It gave a reddish-brown solution with hot alkaline dithionite, from which the brown tetrasodium salt of the leuco-form was precipitated on the addition of sodium hydroxide solution. Aeration of an aqueous suspension of this tetrasodium salt regenerated (IV). Unlike indanthrone,[32] it was not found practical to purify (IV) in this way. Compound (IV) was partially soluble in a solution of aluminium chloride in nitrobenzene [33] forming a brown solution, from which it was regenerated by the addition of excess of pyridine.

[32] G.P. 129,848/1902.
[33] W. Bradley and P. N. Pandit, *Chem. and Ind.*, 1957, 955.

Attempted Preparation of 3-*Bromo*-2-*toluene*-*p*-*sulphonamidoanthraquinone*.—2-Amino-3-bromoanthraquinone (4 g.) and toluene-*p*-sulphonylchloride (3·2 g.) were heated under reflux in pyridine (20 ml.) for 4 hr. One-half of the pyridine was then distilled off, and the residue, on cooling, afforded golden yellow needles (3 g.), m. p. 319°, undepressed on admixture with an authentic sample of 2-amino-3-bromoanthraquinone.

Self-Condensation of 2-*Amino*-3-*chloroanthraquinone*.—An intimate mixture of 2-amino-3-chloroanthraquinone [34] (10 g.) and anhydrous potassium carbonate (5 g.) was fused at 270—290° for 7 hr. After cooling, the fusion product was extracted successively with nitrobenzene, water and acetone at their boiling points, and the black residue of compound (IV) dried (3·5 g.).

Attempted Preparation of 2,3-*Diaminoanthraquinone from* 2-*Amino*-3-*chloroanthraquinone*. — (*a*) 2-Amino-3-chloroanthraquinone (4 g.), cupric acetate (0·5 g.), ethanol (25 ml.), and ammonia (25 ml.; *d* 0·88) were heated at 130° in a sealed tube for 44 hr. After cooling, the tube was opened and the contents were taken up in chlorobenzene and chromatographed on alumina; only a single yellow band containing 2-amino-3-chloroanthraquinone was obtained.

(*b*) 2-Amino-3-chloroanthraquinone (5 g.) and toluene-*p*-sulphonamide (3·65 g.) were heated under reflux in pyridine (150 ml.) for 24 hr. in the presence of a trace of copper powder. The solution, on cooling, gave golden yellow silky needles, m. p. 311—312°, undepressed on admixture with an authentic sample of 2-amino-3-chloroanthraquinone.

The same result was obtained when using trichlorobenzene (250 ml.) as the solvent.

Condensations using 2,3-*Diaminoanthraquinone*.—(*a*) 2,3-Diaminoanthraquinone (0·05 g.) [19] and orthophosphoric acid (10 ml.; previously heated above 220°) were heated together at 250° for 4 hr., then cooled and diluted with ethanol (30 ml.). The resulting precipitate was found to be 2,3-diaminoanthraquinone.

(*b*) A solution of 2,3,9,10-anthradiquinone (3·2 g.) in acetic acid (480 ml.) was added to a solution of 2,3-diaminoanthraquinone (3·3 g.) in acetic acid (750 ml.), and the mixture heated under reflux for 5 hr. and filtered hot. The black residue was extracted with boiling nitrobenzene, washed with ethanol, and dried to give compound (IV) (0·17 g.).

Condensation of 2,3-*Diaminoanthraquinone with* 2,3-*Dibromoanthraquinone*.—(*a*) A mixture of 2,3-diaminoanthraquinone (1·25 g.) and 2,3-dibromoanthraquinone [21] (2 g.) was heated under reflux in pyridine (40 ml.) for 17 hr., but no condensation product was detected.

(*b*) An intimate mixture of 2,3-diaminoanthraquinone (0·62 g.), 2,3-dibromoanthraquinone (1 g.), and anhydrous potassium carbonate (0·5 g.) was fused at 250° for 6 hr. The cooled fusion product was powdered, and extracted successively with nitrobenzene, water, and ethanol at their boiling points, leaving a black residue of compound (IV) (0·42 g.).

Attempted Reaction of 2-*Nitroanthraquinone with* 2-*Aminoanthraquinone in the Presence of Potassium Hydroxide*.—A mixture of 2-aminoanthraquinone (4 g.), 2-nitroanthraquinone [16,19] (3·8 g.), and finely powdered dry potassium hydroxide (4 g.) was heated under reflux in toluene (80 ml.) with vigorous stirring for 7 hr. and then drowned into water and filtered. The residue was extracted with boiling nitrobenzene, washed with ethanol, and dried (0·4 g.). The dark reddish-brown residue did not melt, decomposed slowly above 300°, and left a white ash on heating on a platinum foil. It was slightly soluble in hot water giving a red alkaline solution from which a yellow precipitate was obtained on acidification. It gave a yellow solution with acetic acid, and repeated recrystallisation (charcoal) from this solvent afforded pale yellow plates of 1-hydroxy-2-nitroanthraquinone, m. p. 194—196° (lit.,[16] 197—198°) (Found: C, 62·7; H, 2·9; N, 4·8. Calc. for $C_{14}H_7NO_5$: C, 62·45; H, 2·6; N, 5·2%). The reddish-brown residue was therefore the potassium salt of 1-hydroxy-2-nitroanthraquinone.

The deep red mother-liquor, on acidification, afforded 1-hydroxy-2-nitroanthraquinone (0·4 g.), m. p. and mixed m. p. 195—196° (from acetic acid). It gave an orange solution in sulphuric acid and an orange solution in pyridine which turned cherry-red on the addition of methanolic potassium hydroxide.

Fusion of 1-*Hydroxy*-2-*nitroanthraquinone with Potassium Hydroxide*.—1-Hydroxy-2-nitroanthraquinone (1 g.) was added to a melt of potassium hydroxide (10 g.) at 120°, and the mixture heated at 150—170° for 30 min., and then drowned into water. The deep violet solution, on acidification, gave a brownish-orange precipitate (0·6 g.), m. p. 270—280°, which on purification by sublimation gave orange needles, m. p. 287—288°, not depressed on admixture with alizarin.

2,3-*Diaminoanthracene*.—(*a*) 2,3-Diaminoanthraquinone (2·4 g.) was heated under reflux with fresh zinc dust (4 g.) in 5% aqueous sodium hydroxide (100 ml.) for 15 hr.; at first a red solution was obtained, from which a yellowish-brown solid slowly separated. The suspension was filtered hot and the residue washed with hot water. The red filtrate, on aeration, afforded 2,3-diaminoanthraquinone (2 g.). The residue was extracted with boiling toluene and the yellow extract (which had a green fluorescence) chromatographed on alumina. Three zones were obtained: (i) a strongly adsorbed brown band which could not be eluted and which probably contained a hydroxy-compound; (ii) a violet band containing 2,3-diaminoanthraquinone (this must have arisen by oxidation of the anthracene derivative on the column since the original extract was a clear yellow solution and not red); (iii) the most mobile yellow band which, on elution with toluene and evaporation of the solvent, gave greenish-olive leaflets (0·03 g.) of 2,3-*diaminoanthracene*, which did not melt but decomposed slowly above 200° (Found: C, 80·9; H, 5·6. $C_{14}H_{12}N_2$ requires C, 80·8; H, 5·8%). It dissolved in sulphuric acid giving a pale greenish-yellow solution, and in pyridine giving a yellow solution which was unchanged on the addition of methanolic potassium hydroxide.

(*b*) The leuco-derivative (5 g.) of 2,3-diaminoanthraquinone, prepared by acidification of the red solution of the disodium salt of the leuco-compound, was heated under reflux with fresh zinc dust (10 g.) in 5% aqueous sodium hydroxide (200 ml.) for 15 hr., and the reaction mixture worked up as before. Again only a 1—2% yield of 2,3-diaminoanthracene was obtained.

Attempted Preparation of 2-*Amino*-3-*bromoanthracene*.—(*a*) 2-Amino-3-bromoanthraquinone (20 g.) was heated under reflux with fresh zinc dust (40 g.) in 5% aqueous sodium hydroxide (800 ml.) for 16 hr. The mixture was filtered hot, and the yellow residue washed with water. The red filtrate, on aeration, afforded 2-amino-3-bromo-

[34] B.I.O.S. Final Report No. 987, p. 11.

anthraquinone (2 g.). The residue was extracted with boiling toluene, and the extract (yellow having a greenish-blue fluorescence) on cooling gave greenish-yellow leaflets (9·5 g., 75%). Recrystallisation from toluene gave shining yellow plates, m. p. 248°, not depressed on admixture with 2-aminoanthracene (lit.,[35] m. p. 238°).

This experiment was repeated but for a shorter refluxing time (3 hr.); again 2-aminoanthracene was isolated (56%).

(*b*) 2-Amino-3-bromoanthraquinone (2·5 g.) was heated under reflux with fresh zinc dust (4 g.) and 20% ammonia solution (50 ml.). A deep red solution was first formed, which became colourless after 2 hr. The mixture was filtered hot and the residue extracted with boiling toluene; the yellow extract, on cooling, gave yellow needles (A) (2 g.), m. p. 195°. (A) on drying at 80° slowly turned orange and now had m. p. 180—185°; (A) gave a yellow solution (having a green fluorescence) in cold acetic acid which turned orange on warming. The substance obtained by drying (A) at 80° gave an acetyl derivative, m. p. 259—260° (from ethanol), undepressed on admixture with 2-acetylaminoanthraquinone. (A) was thus probably 2-aminoanthr-10-one.

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[35] H. Roemer, *Ber.*, 1882, **15**, 223.