*Chemistry of Indanthrone. Part IX.** NN′-*Dihydro*-1 : 2-7 : 8-*diphthaloylphenazine.*

By William Bradley, Roy F. Maisey, and Colin R. Thitchener.

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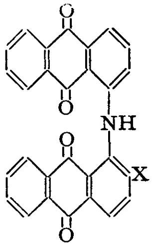
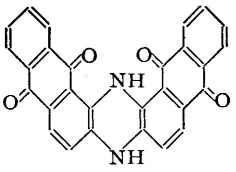
Heating 2-nitro-1 : 1′-dianthraquinonylamine (I; $X = NO_2$) with sodium sulphide or acid stannous chloride affords *NN*′-dihydro-1 : 2-7 : 8-diphthaloylphenazine (II). 2-Amino-1 : 1′-dianthraquinonylamine (I; $X = NH_2$) affords (II) with potassium hydroxide in pyridine–methanol. With sodium hydroxide an intermediate compound is formed. The cyclisation of 2-nitro-1 : 2′-dianthraquinonylamine to *NN*′-dihydro-1 : 2-6 : 7-diphthaloylphenazine (III) is described.

Bradley and Thitchener (*J.*, 1953, 1085) showed that a blue compound resulted when 2-nitro-1 : 1′-dianthraquinonylamine (I; $X = NO_2$) was heated with alcoholic sodium sulphide. This product has now been identified as *NN*′-dihydro-1 : 2-7 : 8-diphthaloylphenazine (III).

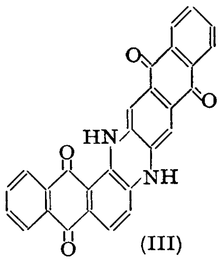
Reduction of 2-nitro-1 : 1′-dianthraquinonylamine with stannous chloride and acetic acid gave 2-amino-1 : 1′-dianthraquinonylamine (I; $X = NH_2$) together with the blue compound previously obtained by Bradley and Thitchener (*loc. cit.*). The amino-compound afforded (II) when heated in pyridine with methanolic potassium hydroxide, a reaction which is analogous to the formation of indanthrone from 2-amino-1 : 2′-dianthraquinonylamine in similar circumstances (Bradley, Leete, and Stephens, *J.*, 1951, 2158). There can be few other instances of so ready a direct substitution of an amino-group into an aromatic nucleus. The constitution of the product rests on the composition, mode of formation, and oxidation to a yellow azine with nitric acid (Bradley and Thitchener, *loc. cit.*). In this last respect (II) resembles indanthrone. Both (II) and *NN*′-dihydro-1 : 2-6 : 7-diphthaloylphenazine (III) are relatively strong acids; for this reason the inertness of indanthrone towards salt-formation with alkalis is most probably due to chelation of both imino-hydrogen atoms with neighbouring carbonyl groups (Robinson, *J. Soc. Dyers Col.*, 1921, **37**, 77).



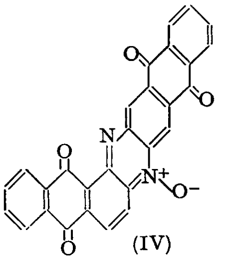
(I)



(II)



(III)



(IV)

In the cyclisation of 2-amino-1 : 2′-dianthraquinonylamine to indanthrone a green intermediate product is formed when sodium hydroxide in pyridine is used as the condensing agent at the room temperature (Bradley, Leete, and Stephens, *loc. cit.*). 2-Amino-1 : 1′-dianthraquinonylamine behaves similarly and the green intermediate is transformed into (II) in hot pyridine.

Whilst the cyclisation of *o*-amino-derivatives of dianthraquinonylamine to dihydrophenazines is now well established, and the occurrence of an analogous reaction of *o*-nitroso-derivatives is probable (Bradley, Leete, and Stephens, *J.*, 1951, 2163), less is known about the direct cyclisation of the corresponding *o*-nitro-derivatives. We have found that 2-nitro-1 : 2′-dianthraquinonylamine can be transformed into (III) by potassium hydroxide in hot dimethylaniline. It appears unlikely that the nitro-group is reduced before cyclisation occurs, but probable that the amine oxide (IV) is generated by dehydration and later decomposed. 2-Amino-1 : 2′-dianthraquinonylamine cannot be an

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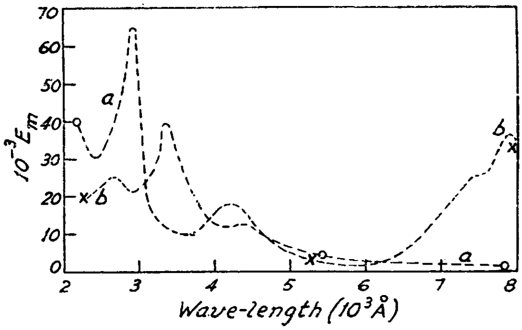
* Part VIII, *J.*, 1953, 924.

intermediate in this reaction, for alkalis convert it into indanthrone, and if a nitroso-compound occurs its reaction with dimethylaniline should follow.

EXPERIMENTAL

Reduction of 2-*Nitro*-1 : 1′-*dianthraquinonylamine*.—The nitro-compound (1 g.) was prepared in a finely divided form by dissolving it in sulphuric acid, adding water, collecting the precipitate, and finally washing with acetic acid. It was then boiled for 10 min. with stannous chloride (2 g.) in glacial acetic acid (20 c.c.). On the addition of water a deep violet precipitate formed. This was collected, dissolved in hot trichlorobenzene, and chromatographed on alumina. Two main zones formed, *viz.*, (A) deep violet and more mobile, and (B) blue and strongly retained. When extracted with pyridine, (A) afforded pale violet needles, m. p. 368° (Found : N, 6·4. $C_{28}H_{16}O_4N_2$ requires N, 6·3%). 2-*Amino*-1 : 1′-*dianthraquinonylamine* afforded a bright yellow solution in concentrated sulphuric acid, and an orange solution in alkaline sodium dithionite.

The blue zone (B), when extracted with pyridine, afforded a solid which showed the same reactions and light absorption in sulphuric acid as the product obtained by reducing the nitro-compound with alcoholic sodium sulphide (Bradley and Thitchener, *loc. cit.*). The blue solution in pyridine gave a green potassium salt on the addition of 30% methanolic potassium hydroxide.



Absorption curves of (*a*)NN′-*dihydro*-1 : 2-7 : 8- *and* (*b*) -1 : 2-6 : 7-*diphthaloylphenazine.*

Cyclisation of 2-*Amino*-1 : 1′-*dianthraquinonylamine. Formation of* (II).—(*a*) On the addition of 30% methyl alcoholic potassium hydroxide to the violet solution of the amino-compound in pyridine and warming, a green, flocculent, potassium salt separated. This was collected and on addition to acetic acid it gave a blue *product* (Found : N, 6·3. $C_{28}H_{14}O_4N_2$ requires N, 6·3%) which showed the same reactions and light absorption in concentrated sulphuric acid as the product from zone (B).

(*b*) On the addition of powdered sodium hydroxide to a solution of the amino-compound in pyridine at the room temperature a green solid was formed during several days. This product was collected; it dissolved in acetic acid with a green colour, changed to blue on the addition of an excess of pyridine. The isolated product showed the same reactions and light absorption in concentrated sulphuric acid as the product from zone (B).

Cyclisation of 2-*Nitro*-1 : 2′-*dianthraquinonylamine*.—The nitro-compound (1 g.; prepared according to G.P. 581,439) was not changed by 5 minutes' heating with dimethylaniline (30 c.c.) at the b. p. On the addition of finely divided potassium hydroxide (10 g.) a dark blue solid was formed rapidly. This was collected after 20 minutes' heating, washed with acetic acid, dissolved in 40 c.c. of concentrated sulphuric acid, and reprecipitated by addition to water. The product (0·7 g.) showed the same reactions and light absorption in concentrated sulphuric acid as *NN*′-dihydro-1 : 2-6 : 7-diphthaloylphenazine prepared by reduction of 2-nitro-1 : 2′-dianthraquinonylamine with alcoholic sodium sulphide.

Absorption curves are annexed.

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THE CLOTHWORKERS' RESEARCH LABORATORY,
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