

### Synthesis of 9 : 18-Diazaisoviolanthrone.

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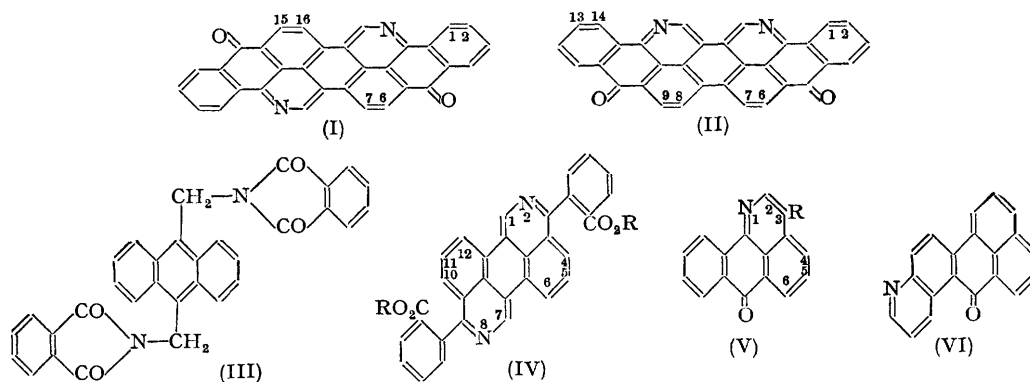
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9 : 18-Diazaisoviolanthrone (I) has been synthesised and its structure confirmed by an alternative synthesis *via* 3-bromo-1-azamesobenzanthrone (V; R = Br). In the alkaline fusion of 1-azamesobenzanthrone (V; R = H), 9 : 18-diazaisoviolanthrone (I) was again obtained and not the expected 15 : 18-diazaviolanthrone (II).

9 : 10-BISPHTHALIMIDOMETHYLANTHRACENE (III) was prepared by treatment of anthracene with *N*-chloromethylphthalimide (Buc, *J. Amer. Chem. Soc.*, 1947, **69**, 254; Sakellarios, *ibid.*, 1948, **70**, 2822) and a trace of zinc chloride in nitrobenzene as in G.P. 442,774 (the product was not characterised in the patent) or alternatively by employing aluminium chloride in carbon disulphide. Degradative oxidation of (III) to anthraquinone established the positions of the side chains.

From the fusion of 9 : 10-bisphthalimidomethylanthracene with a mixture of aluminium chloride and sodium chloride, 3 : 9-diphenyl-2 : 8-diazaperylene-2' : 2''-dicarboxylic acid (IV; R = H) was obtained, as its dihydrochloride dihydrate, and further characterised by conversion into the diethyl ester (IV; R = Et), which was found to be homogeneous by the formation of only one band on chromatography of its nitrobenzene solution on alumina. The above method was based on the conditions used by Ebel for the preparation of 1-phenylisoquinoline-2'-carboxylic acid (G.P. 614,196).

The final cyclisation of (IV; R = H) to 9 : 18-diazaisoviolanthrone was carried out in fuming sulphuric acid at 100° and gave an alkali-soluble product. This, on sublimation at low pressure, gave the dye (I), insoluble in alkali but soluble in hot alkaline sodium dithionite solution, giving a deep blue vat from which cotton was dyed violet. The cyclisation was also brought about by phosphoric oxide in polyphosphoric acid without the formation of an alkali-soluble intermediate.



The dye was shown to be (I) by the identity of its ultra-violet and visible absorption spectra with those of the dye from the potassium hydroxide fusion of 3-bromo-1-azamesobenzanthrone (V; R = Br), obtained by direct bromination of 1-azamesobenzanthrone (G.P. 627,258). The position of the bromine atom has been established by degradative oxidation of the bromo-1-azamesobenzanthrone to anthraquinone-1-carboxylic acid. This showed that the bromine atom was in the pyridine ring, presumably in the expected 3-position because of the absence of bromine in the product from the fusion.

1-Azamesobenzanthrone (V; R = H) on potassium hydroxide fusion at 260—280° also gave 9 : 18-diazaisoviolanthrone (I), no violanthrone isomer (II) being detected. The alkaline fusion of *mesobenzanthrone* at temperatures above 220° gave no *isoviolanthrone* (Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 283), whereas alkaline fusion of

pyridino(3' : 2'-8 : 9)mesobenzanthrone (VI) has been shown by Bradley and Sutcliffe (*J.*, 1952, 2118) to lead to an isoviolanthrone-type structure for cyananthrene. There may be some correlation between the method of cyclisation to isoviolanthrone-type structures and the possession of heterocyclic nitrogen atoms.

Di-1-azamesobenzanthronyl (possibly the 4 : 4'-compound) obtained by the low-temperature alkaline fusion of 1-azamesobenzanthrone (cf. G.P. 627,258) was fused with alkali at a higher temperature and then gave (I).

#### EXPERIMENTAL

9 : 10-Bisphthalimidomethylanthracene (III).—(a) *N*-Chloromethylphthalimide (8 g.), anthracene (3.8 g.), freshly sublimed aluminium chloride (5 g.), and carbon disulphide (50 c.c.) were refluxed until no further hydrogen chloride was evolved (about 8 hr.), stirring being continued as long as possible. The carbon disulphide was then distilled off, and ice (*ca.* 100 g.) and concentrated hydrochloric acid (20 c.c.) were added. After decomposition the mixture was filtered and the precipitate washed with water. The 9 : 10-bisphthalimidomethylanthracene crystallised from *m*-cresol as yellow needles (1.15 g.), m. p. > 360° (Found : C, 77.1; H, 4.0; N, 6.0.  $C_{32}H_{20}O_4N_2$  requires C, 77.4; H, 4.1; N, 5.6%).

(b) (cf. G.P. 442,774) *N*-Chloromethylphthalimide (24 g.), anthracene (11.4 g.), and fused zinc chloride (1.3 g.) were heated at 100° in redistilled nitrobenzene (75 c.c.) with stirring for 8 hr. The mixture was cooled and filtered and the solid washed thoroughly with benzene. The crude yellow product (10.9 g.) was satisfactory for the next stage of the synthesis and crystallised from *m*-cresol in yellow needles identical with the above (Found : C, 77.2; H, 4.0%).

Oxidation of 9 : 10-Bisphthalimidomethylanthracene (III).—A suspension of 9 : 10-bisphthalimidomethylanthracene (1 g.) in acetic acid (20 c.c.) was refluxed during the addition of chromium trioxide (6 g.) in water (6 c.c.) and for a further 6 hr. Water was added and, after standing, the solid (0.40 g.) was filtered off, washed, dried, and crystallised from acetic acid. The anthraquinone obtained had m. p. 285° and was not depressed on admixture with an authentic specimen.

3 : 9-Diphenyl-2 : 8-diazaperylene-2' : 2''-dicarboxylic Acid (IV; R = H).—Freshly sublimed aluminium chloride (43 g.) and sodium chloride (8.6 g.) were heated at 130–140° and 9 : 10-bisphthalimidomethylanthracene (8.6 g.) added with stirring. The temperature was maintained for 8 hr. and the cooled mass, after decomposition by the addition of ice, was extracted with hot hydrochloric acid (10%; 4 × 100 c.c.). 3 : 9-Diphenyl-2 : 8-diazaperylene-2' : 2''-dicarboxylic acid dihydrochloride dihydrate (2.48 g.) separated as orange needles, which were dried at room temperature under vacuum (Found : C, 63.9; H, 4.5.  $C_{32}H_{18}O_4N_2 \cdot 2HCl \cdot 2H_2O$  requires C, 63.7; H, 4.0%). Analyses showed that drying at higher temperatures led to products of indefinite composition with loss of water and hydrogen chloride.

The mother-liquors of the product were heated to the b. p., aqueous ammonia was added to precipitate the aluminium hydroxide, the whole was filtered, the residue was extracted with boiling water containing a little aqueous ammonia and filtered, and the filtrates were evaporated to *ca.* 100 c.c., to give the free base (0.05 g.), m. p. > 360°.

The above dihydrochloride dihydrate was dried on the water-bath, and the product (1.0 g.) was refluxed for 1 hr. with thionyl chloride (10 c.c.). The excess of thionyl chloride was removed under vacuum, and the product refluxed for 2 hr. with ethanol (20 c.c.). Ethanol was removed and the solid extracted twice with hot sodium carbonate solution, filtered, washed, and dried, to give diethyl 3 : 9-diphenyl-2 : 8-diazaperylene-2' : 2''-dicarboxylate (0.94 g.), which crystallised from nitrobenzene in yellow needles, m. p. 276° (Found : C, 78.5; H, 4.9; N, 4.9.  $C_{28}H_{26}O_4N_2$  requires C, 78.5; H, 4.8; N, 5.1%).

3-Bromo-1-azamesobenzanthrone (cf. G.P. 627,258).—1-Azamesobenzanthrone (2.2 g.), nitrobenzene (65 c.c.), bromine (3.5 c.c.), and iodine (0.02 g.) were refluxed for 5 hr. On cooling, crystals of 3-bromo-1-azamesobenzanthrone (2.7 g., 91%) separated. These were filtered off, washed with benzene, dried, and recrystallised from nitrobenzene as yellow needles, m. p. 256° (Found : C, 62.0; H, 2.7; Br, 26.2. Calc. for  $C_{18}H_8ONBr$  : C, 62.0; H, 2.6; Br, 25.8%).

Oxidation of 3-Bromo-1-azamesobenzanthrone.—3-Bromo-1-azamesobenzanthrone (1.0 g.), chromium trioxide (1.62 g.), and glacial acetic acid (40 c.c.) were refluxed for 6 hr. On cooling, unchanged 3-bromo-1-azamesobenzanthrone (0.03 g.) separated and was filtered off. The filtrate was diluted with water (100 c.c.) and evaporated to 20 c.c. twice, and acidified with hydrochloric acid, and the precipitated acid was filtered off and purified by acidification of its

soluble ammonium salt. The acid was converted through its acid chloride into ethyl anthraquinone-1-carboxylate, m. p. 167°, admixture with an authentic specimen giving no depression.

*Di-1-azamesobenzanthronyl* (possibly the 4 : 4'-isomer) (cf. G.P. 627,258).—1-Azamesobenzanthrone (1.0 g.), ethanol (15 c.c.), and finely ground potassium hydroxide (10 g.) were heated at 110—120° in a nickel crucible with occasional stirring. The mixture rapidly became dark green, and after 1 hr. was diluted with water (50 c.c.), and excess of hydrogen peroxide solution (20-vol.) gradually added to oxidise any reduced material. After filtration and drying, the product was extracted for 6 hr. in a Soxhlet extractor with ethanol to remove unchanged 1-azamesobenzanthrone. The residue (0.75 g.) was twice sublimed at 400°/10<sup>-3</sup> mm. *Di-1-azamesobenzanthronyl* was obtained as an orange-brown product, m. p. >360°, which was slightly soluble on boiling with sodium dithionite and dilute sodium hydroxide solution (Found : C, 83.6; H, 3.2. Calc. for C<sub>32</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub> : C, 83.5; H, 3.5%).

9 : 18-*Diazaisoviolanthrone* (I).—(a) Dried 3 : 9-diphenyl-2 : 8-diazaperylene-2' : 2''-dicarboxylic acid hydrochloride (0.72 g.) and fuming sulphuric acid (23% of SO<sub>3</sub>; 10 c.c.) were heated at 100° for 2½ hr. The mixture was poured on ice (75 g.), and the precipitate filtered off and washed with water. The dry product (0.51 g.), which was soluble in sodium hydroxide solution, was sublimed at 450°/10<sup>-3</sup> mm. with considerable charring. 9 : 18-*Diazaisoviolanthrone* (0.18 g.) was obtained as fine purple needles, with a strong green reflex, and was insoluble in sodium hydroxide solution. It dissolved in hot dilute sodium hydroxide solution containing sodium dithionite, giving an intense blue vat which was filtered; the dye was reprecipitated from the filtrate by the passage of air or by the gradual addition of hydrogen peroxide solution (20-vol.). The product after being filtered, washed, and dried was resublimed as before (Found : C, 83.2; H, 3.4; N, 6.2. C<sub>32</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub> requires C, 83.8; H, 3.1; N, 6.1%). A portion of the dye was converted into its vat and chromatographed, on a 40-cm. alumina column jacketed with carbon tetrachloride vapour; sodium hydroxide solution (2%) containing a little sodium dithionite was used as eluent. Only one band was observed. The ultra-violet and visible absorption spectra of the dye were determined in concentrated sulphuric acid, the dye being insoluble in all the usual organic solvents [light absorption : Max., 2500 (ε 3.95 × 10<sup>4</sup>), 2930 (ε 3.52 × 10<sup>4</sup>) and 6630 Å (ε 4.97 × 10<sup>4</sup>); Min., 2790 Å (ε 3.18 × 10<sup>4</sup>)]. The determinations were made by means of a Unicam S.P. 500 quartz spectrophotometer (kindly lent by the Wool Textile Research Council).

(b) The above dihydrochloride dihydrate (0.2 g.), phosphoric oxide (1.0 g.), and phosphoric acid (10 g., previously heated at 250° for 3 hr.) were heated with stirring for 3 hr. at 250—260°. The product was cooled and made alkaline with sodium hydroxide, sodium dithionite added, and the solution boiled and filtered. The hot filtrate was oxidised with hydrogen peroxide, and filtered after settling. The dye (0.08 g.) was purified as above and identified by its spectrum, this method also being used in the following three experiments.

(c) 1-Azamesobenzanthrone (0.5 g.), finely ground potassium hydroxide (4.5 g.), and anhydrous potassium acetate (0.5 g.) were heated at 240—250° for 1 hr. with stirring in a nickel crucible set in an iron block. The mixture was cooled, then diluted with water (50 c.c.), and hydrogen peroxide solution was gradually added. The precipitated dye was filtered off and the dry residue (0.48 g.) was extracted for 6 hr. in a Soxhlet extractor with ethanol to remove unchanged starting material. The dye (0.30 g.) was further purified as above (Found : C, 84.1; H, 3.2%) and, as before, only one band was obtained on the column.

(d) 3-Bromo-1-azamesobenzanthrone (0.45 g.), finely ground potassium hydroxide (4.5 g.), and anhydrous potassium acetate (0.5 g.) were heated at 260—270° for 1 hr. The dye (0.25 g.) was isolated as described above and chromatography failed to reveal the presence of more than one compound.

(e) 4 : 4'-*Di-1-azamesobenzanthronyl* (0.2 g.), finely ground potassium hydroxide (4.5 g.), and anhydrous potassium acetate (0.5 g.) were heated at 260—280° for 1 hr. to give the dye (0.11 g.) as above.

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