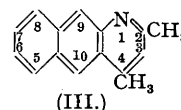
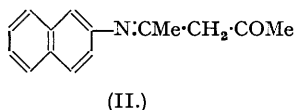
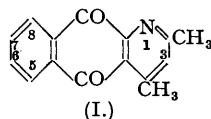


104. The Chemistry of 1-Azanthraquinone. Part III. Chloro-derivatives of 2:4-Dimethyl-1-azanthraquinone.

By G. R. CLEMO and N. LEGG.

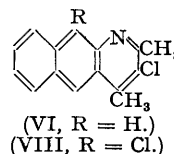
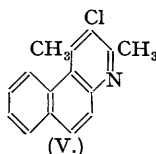
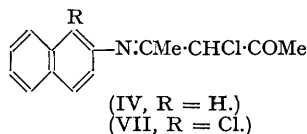
An improved synthesis of 2:4-dimethyl-1-azanthraquinone (I) is described. Attempts to sulphonate (I) to give monosulphonic acids failed. 5-, 6-, and 8-Chloro-2:4-dimethyl-1-azanthraquinones have been synthesised from the hitherto unknown 5-, 6-, and 8-chloro-2-naphthylamines. Attempts to synthesise 3- and 7-chloro-2:4-dimethyl-1-azanthraquinones have failed.

2:4-DIMETHYL-1-AZANTHRAQUINONE (I) was first synthesised by Johnson and Mathews (*J. Amer. Chem. Soc.*, 1944, **66**, 210) by condensing β -naphthylamine with acetylacetone to give 4-(2'-naphthylimino)pentan-2-one (II) and then cyclising this in sulphuric acid to 2:4-dimethyl-1-azanthracene (III) which on oxidation gave (I). It has been found possible to improve the original synthesis so that larger quantities of (I) can be readily prepared.

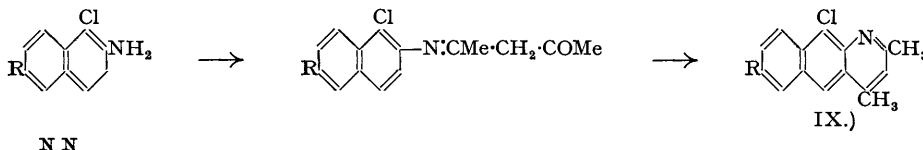


Attempts have been made to sulphonate (I) on the same lines as those used for 1-azanthraquinone (Part II, preceding paper). Concentrated sulphuric acid at 100° and 150°, with and without a mercury catalyst, failed to react, as did also chlorosulphonic acid at 200°. The use of sulphur trioxide at 170°, and 20% oleum, with and without a mercury catalyst, at 100° and 150° caused evolution of sulphur dioxide and formation of oxidation products which were probably polyhydroxysulphonic acids, since they closely resembled polyhydroxyanthraquinonesulphonic acids in their properties. The use of sulphur trioxide (1 or 2 mols.) in chlorosulphonic acid at 100° and 150° also gave rise to oxidation products, although some of the quinone (I) was recovered.

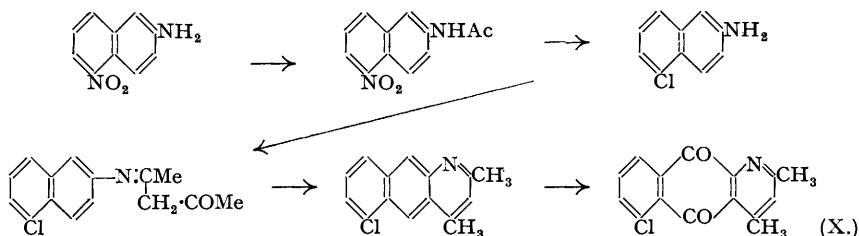
Synthesis of Chloro-2:4-dimethyl-1-azanthraquinones.—3-Chloroacetylacetone (Combes, *Compt. rend.*, 1890, **111**, 273) was heated with β -naphthylamine at 100°, but instead of the expected 3-chloro-4-(2'-naphthylimino)pentan-2-one (IV), acet- β -naphthalide was produced quantitatively. β -Naphthylamine reacted with 3-chloroacetylacetone in neutral aqueous solution to give (IV), which on cyclisation in 90% sulphuric acid gave 3-chloro-2:4-dimethyl-5:6-benzoquinoline (V), instead of 3-chloro-2:4-dimethyl-1-azanthracene (VI). Proof that angular cyclisation had occurred was obtained from a study of the absorption spectra (Fig. 1) (cf. Johnson and Mathews, *loc. cit.*).



1-Chloro-2-naphthylamine condensed with 3-chloroacetylacetone at 100° to give 3-chloro-4-(1'-chloro-2'-naphthylimino)pentan-2-one (VII), which on cyclisation gave 3:9-dichloro-2:4-dimethyl-1-azanthracene (VIII). Attempts to oxidise (VIII) to 3-chloro-2:4-dimethyl-1-azanthraquinone by potassium dichromate or chromic anhydride in acetic acid, however, failed, the azanthracene being recovered quantitatively. It was also found that 9-chloro- (IX, R = H) and 9-chloro-6-bromo-2:4-dimethyl-1-azanthracene (IX, R = Br), prepared as shown, could not be oxidised to the corresponding quinones. These results are in striking contrast to the easy oxidation of 9-chloro-azanthracenes to the corresponding quinones (Part II, *loc. cit.*).

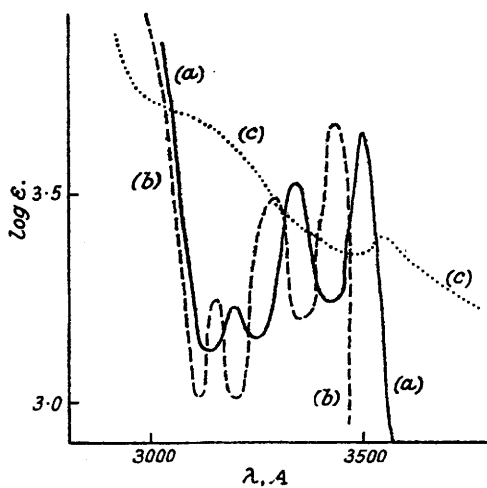


5-Chloro-2:4-dimethyl-1-azantraquinone (X) has been synthesised from 5-nitro-2-naphthylamine (Cohen *et al.*, *J.*, 1934, 656) by the following route:



8-Chloro-2:4-dimethyl-1-azantraquinone was similarly prepared from 8-nitro-2-naphthylamine (Saunders and Hamilton, *J. Amer. Chem. Soc.*, 1932, 54, 638).

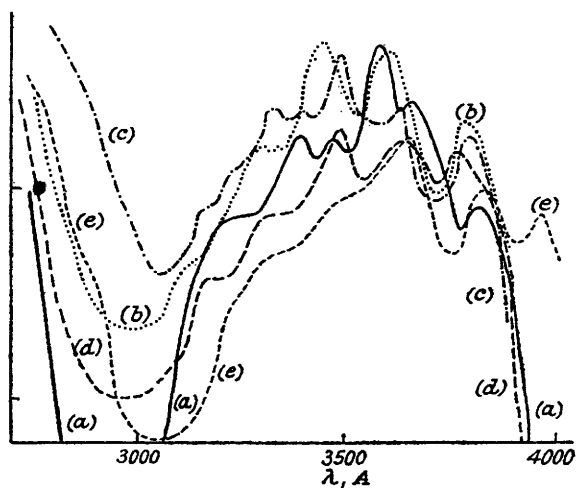
FIG. 1.



Absorption spectra of:

- (a) 2:4-Dimethyl-5:6-benzoquinoline.
- (b) 3-Chloro-2:4-dimethyl-5:6-benzoquinoline.
- (c) 5-Hydroxy-2:4-dimethyl-5:6-benzoquinoline (?).

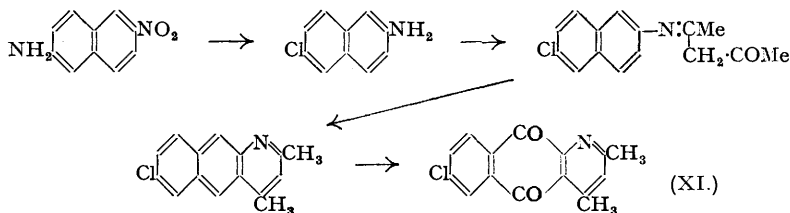
FIG. 2.



Absorption spectra of:

- (a) 2:4-Dimethyl-1-azantracene.
- (b) 5-Chloro-2:4-dimethyl-1-azantracene.
- (c) 6-Chloro-2:4-dimethyl-1-azantracene.
- (d) 8-Chloro-2:4-dimethyl-1-azantracene.
- (e) 3:9-Dichloro-2:4-dimethyl-1-azantracene.

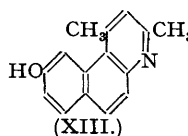
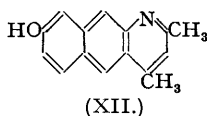
6-Chloro-2:4-dimethyl-1-azantraquinone (XI) has been synthesised from 6-nitro-2-naphthylamine (Saunders and Hamilton, *loc. cit.*) by the following route:



Proof that the pentanones had cyclised linearly to give azantracenes was obtained by a study of the absorption spectra of the azantracenes (Fig. 2).

7-Hydroxy-2-naphthylamine condensed with acetylacetone at 100° to give 4-(7'-hydroxy-2'-naphthylimino)pentan-2-one which was cyclised in 90% sulphuric acid. It has not been possible,

however, to decide whether the *product* has structure (XII) or (XIII) since the absorption spectrum (Fig. 1) does not resemble that of either azanthracenes or 5 : 6-benzoquinolines.



Attempts to replace the hydroxyl group by chlorine by treatment with phosphorus pentachloride, with and without benzene as a solvent, phosphorus oxychloride in tetrachloroethane, a mixture of phosphorus oxychloride and pentachloride, and refluxing the sodium salt with phosphorus oxychloride failed. Attempts to replace the hydroxyl by the amino-group, which could then be converted into the chloro-compound, by treatment with concentrated aqueous ammonia at 240° and a zinc chloride-ammonia complex at 260° also failed.

EXPERIMENTAL.

4-(2'-Naphthylimino)pentan-2-one.— β -Naphthylamine (200 g.) and acetylacetone (240 c.c.) were heated on a water-bath for 4 hours, cooled, and ether (10 c.c.) added. The solid obtained was then pressed on a porous plate; yield 300 g., m. p. 96—99°. Crystallisation from benzene-light petroleum (b. p. 60—80°) gave pale yellow needles, m. p. 98—99°.

2 : 4-Dimethyl-1-azanthracene.—The pentanone (250 g.) was powdered and added to sulphuric acid (850 c.c. of 90%) below 60°, and the yellow solution heated on a water-bath for $\frac{1}{2}$ hour, and poured on ice (3000 g.). The sulphate was collected, stirred into water (3 l.), excess of ammonia added, and the liberated base taken up in benzene. The benzene extract was dried, the solvent removed, and the residue distilled at 1 mm. and then crystallised from benzene, giving pale yellow needles (175 g.), m. p. 92—93°. [Our thanks are due to Dr. MacDonald, Research Department, I.C.I. (Dyestuffs) Ltd., for these experimental details.]

2 : 4-Dimethyl-1-azanthraquinone.—The azanthracene (49 g.), glacial acetic acid (1350 c.c.), water (90 c.c.), and potassium dichromate (70.5 g.) were refluxed for 3 hours, and the solution concentrated in vacuum by removal of 1100 c.c. of solvent. The residue was dissolved in water and basified with sodium hydroxide solution, and the solid collected, washed with water, dried, and extracted with benzene (Soxhlet). The benzene was removed, and the residue crystallised from benzene-light petroleum (b. p. 100—120°) to give 2 : 4-dimethyl-1-azanthraquinone as yellow needles (25 g.), m. p. 214—216° (Johnson and Mathews, *loc. cit.*, give m. p. 215—216°).

Attempted Synthesis of 3-Chloro-2 : 4-dimethyl-1-azanthraquinone.—(a) 3-Chloro-4-(2'-naphthylimino)pentan-2-one. (1) β -Naphthylamine (0.7 g.) and 3-chloroacetylacetone (0.86 g.) were heated on a water-bath for 3 hours, and the solid collected and crystallised from benzene-light petroleum (b. p. 60—80°) to give colourless plates (0.7 g.) of acet- β -naphthalide, m. p. and mixed m. p. 132—134°. (2) β -Naphthylamine (2 g.), concentrated hydrochloric acid (4 c.c.), and water (80 c.c.) were warmed to 60°, and a suspension of 3-chloroacetylacetone (2 g.) in *N*/5-sodium hydroxide solution (74 c.c.) added with stirring. After 3 hours the solid was collected, washed with water and dried. The 3-chloro-4-(2'-naphthylimino)pentan-2-one crystallised from light petroleum (b. p. 60—80°) in colourless needles (2.8 g.), m. p. 96—97° (Found : C, 69.5; H, 5.4. $C_{15}H_{14}ONCl$ requires C, 69.3; H, 5.4%).

(b) 3-Chloro-2 : 4-dimethyl-5 : 6-benzoquinoline (V). The above compound (2.8 g.) and sulphuric acid (14 c.c. of 90%) were heated on a water-bath for $\frac{1}{2}$ hour, the solution poured into water, basified, and the solid collected and crystallised from light petroleum (b. p. 60—80°) to give colourless needles (1.8 g.), m. p. 143—144° (Found : C, 74.3; H, 4.8. $C_{15}H_{12}NCl$ requires C, 74.5; H, 5.0%). Ultra-violet absorption spectrum (0.000249M-solution in hexane) : Maxima at 3200 Å. (ϵ 1660), 3350 Å. (ϵ 3390), and 3510 Å. (ϵ 4470).

(c) 3-Chloro-4-(1'-chloro-2'-naphthylimino)pentan-2-one. 1-Chloro-2-naphthylamine (8.4 g.) and 3-chloroacetylacetone (6.3 g.) were heated on a water-bath for 2 hours, and the water and excess of ketone distilled off under reduced pressure. The black residue was stirred with benzene (10 c.c.), and the yellow solid which was filtered off (4.5 g.) was crystallised from benzene-light petroleum (b. p. 60—80°), affording colourless needles, m. p. 137—138° (Found : C, 61.6; H, 4.5; N, 5.0. $C_{15}H_{13}ONCl_2$ requires C, 61.2; H, 4.3; N, 4.8%).

(d) 3 : 9-Dichloro-2 : 4-dimethyl-1-azanthracene (VIII). The pentanone (3.5 g.) and sulphuric acid (18 c.c. of 90%) were heated on a water-bath for $\frac{1}{2}$ hour, the solution poured on ice and basified, and the solid collected. Crystallisation from benzene gave colourless needles (3 g., m. p. 224—225°) (Found : C, 65.1; H, 4.1; N, 5.1. $C_{15}H_{11}NCl_2$ requires C, 65.2; H, 4.0; N, 5.0%). Ultra-violet absorption spectrum (0.000261M-solution in absolute alcohol) : Maxima at 3350 Å. (inflexion) (ϵ 2290), 3500 Å. (ϵ 3160), 3650 Å. (ϵ 4470), 3770 Å. (ϵ 3800), and 3970 Å. (ϵ 2880).

4-(1'-Chloro-2'-naphthylimino)pentan-2-one. 1-Chloro-2-naphthylamine (5 g.) and acetylacetone (4 c.c.) were heated on a water-bath for 4 hours, cooled, and ether (1 c.c.) added; the oil then solidified. Crystallisation from benzene-light petroleum (b. p. 60—80°) gave colourless needles (3.1 g., m. p. 87—88°) (Found : C, 69.5; H, 5.4. $C_{15}H_{14}ONCl$ requires C, 69.3; H, 5.4%).

9-Chloro-2 : 4-dimethyl-1-azanthracene (IX, R = H). The pentanone (2.5 g.) was added, with stirring, to concentrated sulphuric acid (10 c.c.) at 0—2°, the yellow solution heated to 60° for 2 minutes, poured on ice, basified, and extracted with ether. Removal of the ether gave a solid which crystallised from benzene-light petroleum (b. p. 100—120°) in colourless needles (1.2 g., m. p. 166—167°) (Found : C, 74.6; H, 5.1. $C_{15}H_{12}NCl$ requires C, 74.5; H, 5.0%).

4-(1'-Chloro-6'-bromo-2'-naphthylimino)pentan-2-one, from 1-chloro-6-bromo-2-naphthylamine (5 g.) and acetylacetone (4 c.c.), crystallised from light petroleum (b. p. 100—120°) in white needles (3.0 g., m. p. 133—134°) (Found: C, 53.0; H, 3.8. $C_{15}H_{13}ONClBr$ requires C, 53.2; H, 3.8%).

9-Chloro-6-bromo-2 : 4-dimethyl-1-azanthracene (IX, R = Br) was prepared by cyclising the pentanone (3 g.) with sulphuric acid (15 c.c. of 90%). It crystallised from ethanol as colourless needles, (2.1 g., m. p. 166—168°) (Found: C, 56.0; H, 3.4. $C_{15}H_{11}NClBr$ requires C, 56.1; H, 3.4%).

5-Chloro-2 : 4-dimethyl-1-azanthraquinone (X).—(a) 5-Amino-2-acetamidonaphthalene. Iron filings (100 g.), alcohol (170 c.c.), and concentrated hydrochloric acid (37 c.c.) were stirred for $\frac{1}{2}$ hour and refluxed for 10 minutes, the liquid decanted, and the iron washed twice with water. A solution of 5-nitro-2-acetnaphthalide (15.2 g.) in alcohol (400 c.c.) was added to the etched iron and stirred under reflux for 4 hours. The mixture was filtered, the residue washed with boiling alcohol (100 c.c.), and the combined filtrates concentrated, 5-amino-2-acetnaphthalide (11.4 g., m. p. 132—134°) being obtained. Crystallisation from dilute ethanol gave colourless needles, m. p. 136—137° (Found: C, 72.2; H, 5.9. $C_{12}H_{10}ON_2$ requires C, 72.0; H, 6.0%).

(b) 5-Chloro-2-acetnaphthalide. The amino-compound (10 g.) in glacial acetic acid (100 c.c.) was added to a solution of sodium nitrite (5.0 g.) in concentrated sulphuric acid (50 c.c.), the temperature being kept below 20°. After $\frac{1}{2}$ hour the solution was added to cuprous chloride (30 g.) in concentrated hydrochloric acid (200 c.c.). After 20 hours, water (700 c.c.) was added, and the solid collected and crystallised from ethanol to give light brown needles (8.5 g., m. p. 147—148°) (Found: C, 65.6; H, 4.6. $C_{12}H_{10}ONCl$ requires C, 65.5; H, 4.55%).

(c) 5-Chloro-2-naphthylamine. The acetyl derivative (8 g.), alcohol (100 c.c.), and concentrated hydrochloric acid (50 c.c.) were refluxed for 1 hour, the solution poured into water and basified, the oil extracted with benzene, and the benzene extract dried. The benzene was removed, and the residue distilled at 1 mm. to give a pale yellow oil (6 g.) which rapidly solidified. Crystallisation from light petroleum (b. p. 40—60°) gave colourless needles, m. p. 35—36° (Found: C, 67.9; H, 4.3. $C_{10}H_8NCl$ requires C, 67.6; H, 4.5%).

(d) 4-(5'-Chloro-2'-naphthylimino)pentan-2-one was prepared from 5-chloro-2-naphthylamine (3.5 g.) and acetylacetone (4.5 c.c.). It crystallised from light petroleum (b. p. 60—80°) in pale yellow needles (3.5 g., m. p. 68—69°) (Found: C, 69.5; H, 5.25. $C_{15}H_{14}ONCl$ requires C, 69.3; H, 5.4%).

(e) 5-Chloro-2 : 4-dimethyl-1-azanthracene. The pentanone (3.4 g.) was cyclised in sulphuric acid (17 c.c. of 90%). The azanthracene crystallised from light petroleum (b. p. 60—80°) in white needles (2.6 g., m. p. 145—146°) (Found: C, 74.5; H, 4.85. $C_{15}H_{12}NCl$ requires C, 74.4; H, 5.0%). Ultra-violet absorption spectrum (0.000318M-solution in hexane): maxima at 3150 Å. (inflexion) (ϵ 2240), 3300 Å. (ϵ 4070), 3340 Å. (ϵ 4070), 3450 Å. (ϵ 7240), 3610 Å. (ϵ 7080), and 3800 Å. (ϵ 4786).

(f) 5-Chloro-2 : 4-dimethyl-1-azanthraquinone. Chromic anhydride (0.5 g.) was added to a solution of the azanthracene (0.5 g.) in glacial acetic acid (15 c.c.), and the mixture heated for 1½ hours on a water-bath, poured into saturated brine (25 c.c.), and extracted with benzene. The benzene extracts were washed with sodium hydroxide solution and water and dried. The benzene was removed, and the residue crystallised from benzene-light petroleum (b. p. 60—80°) to give bright yellow plates (25 mg., m. p. 210—211°) (Found: C, 66.4; H, 3.7. $C_{15}H_{10}O_2NCl$ requires C, 66.2; H, 3.7%).

Synthesis of 6-Chloro-2 : 4-dimethyl-1-azanthraquinone.—(a) 6-Chloro-2-nitronaphthalene. A suspension of 6-nitro-2-naphthylamine (20 g.) in glacial acetic acid (200 c.c.) was added, with stirring, to a solution of sodium nitrite (10 g.) in concentrated sulphuric acid (100 c.c.), the temperature being kept below 20°. After $\frac{1}{2}$ hour the diazo-solution was added to cuprous chloride (50 g.) dissolved in concentrated hydrochloric acid (400 c.c.). After 25 hours water (1000 c.c.) was added, and the solid collected and crystallised from ethanol to give pale yellow needles (19.1 g., m. p. 181—182°) (Found: C, 57.8; H, 2.9. $C_{10}H_6O_2NCl$ requires C, 57.8; H, 2.9%).

(b) 6-Chloro-2-naphthylamine. The nitro-compound (18 g.) in alcohol (500 c.c.) was reduced by etched iron (from iron filings, 120 g.). After removal of the iron residues, the alcohol was distilled from a water-bath, and the residue crystallised twice from light petroleum (b. p. 60—80°) to give colourless needles (14.5 g., m. p. 120—121°) (Found: C, 67.8; H, 4.3. $C_{10}H_8NCl$ requires C, 67.6; H, 4.5%). The acetyl derivative, from the amine and acetic anhydride, crystallised from ethanol in white needles, m. p. 184—185° (Found: C, 65.3; H, 4.6. $C_{12}H_{10}ONCl$ requires C, 65.5; H, 4.55%).

(c) 4-(6'-Chloro-2'-naphthylimino)pentan-2-one was prepared in the same manner as the 5-isomer from 6-chloro-2-naphthylamine (8 g.). It crystallised from light petroleum (b. p. 60—80°) in colourless needles (10.5 g., m. p. 110—111°) (Found: C, 69.6; H, 5.3. $C_{15}H_{14}ONCl$ requires C, 69.3; H, 5.4%).

(d) 6-Chloro-2 : 4-dimethyl-1-azanthracene. The pentanone (9 g.) was cyclised as before. Crystallisation from light petroleum (b. p. 60—80°) gave colourless needles (7.2 g., m. p. 130—131°) (Found: C, 74.6; H, 4.95. $C_{15}H_{12}NCl$ requires C, 74.4; H, 5.0%). Ultra-violet absorption spectrum (0.000248M-solution in hexane): Maxima at 3170 Å. (inflexion) (ϵ 2880), 3320 Å. (ϵ 5010), 3400 Å. (ϵ 5010), 3490 Å. (ϵ 6760), 3630 Å. (ϵ 5500), and 3780 Å. (ϵ 4270).

(e) 6-Chloro-2 : 4-dimethyl-1-azanthraquinone. The azanthracene (1 g.) was oxidised in the same manner as the 5-isomer. The quinone crystallised from benzene-light petroleum (b. p. 60—80°) in pale yellow needles (30 mg., m. p. 201—202°) (Found: C, 66.3; H, 3.7. $C_{15}H_{10}O_2NCl$ requires C, 66.2; H, 3.7%).

Attempted Synthesis of 7-Chloro-2 : 4-dimethyl-1-azanthraquinone.—4-(7'-Hydroxy-2'-naphthylimino)pentan-2-one. 7-Hydroxy-2-naphthylamine (4.7 g.) was condensed with acetylacetone (7.0 c.c.) as usual, and the product crystallised from benzene to give white needles (6.6 g., m. p. 150—151°) (Found: C, 74.9; H, 6.3. $C_{11}H_{15}O_2N$ requires C, 74.7; H, 6.2%).

5'-Hydroxy-2 : 4-dimethyl-5 : 6-benzoquinoline (?). The pentanone (6 g.) was cyclised in 90% sulphuric acid, and the solution run into water and basified with sodium carbonate. The solid was collected, and crystallised from benzene in orange needles (4.6 g., m. p. 268—270°) (Found: C, 80.8; H, 5.8. $C_{15}H_{13}ON$ requires C, 80.7; H, 5.8%). Ultra-violet absorption spectrum (0.000202M-solution in chloroform): Maxima at 3030 Å. (inflexion) (ϵ 5250) and 3560 Å. (ϵ 2570).

Synthesis of 8-Chloro-2 : 4-dimethyl-1-azanthraquinone.—(a) 8-Amino-2-acetnaphthalide was

obtained by reducing 8-nitro-2-acetnaphthalide (14.5 g.) in alcohol (400 c.c.) with etched iron, from iron filings (100 g.). It crystallised from benzene in colourless needles (10.5 g., m. p. 148—149°) (Found: C, 72.1; H, 6.1. $C_{13}H_{13}ON_2$ requires C, 72.0; H, 6.0%).

(b) 8-Chloro-2-acetnaphthalide was obtained from the amino-compound (10 g.) in the same manner as the 5-isomer. Crystallisation from dilute ethanol gave white microcrystals (8.5 g., m. p. 157—158°) (Found: C, 65.3; H, 4.3. $C_{12}H_{10}ONCl$ requires C, 65.5; H, 4.45%).

(c) On hydrolysis, the acetyl compound gave 8-chloro-2-naphthylamine (5 g.) as colourless needles from light petroleum (b. p. 60—80°); m. p. 69—70° (Found: C, 67.8; H, 4.4. $C_{10}H_8NCl$ requires C, 67.6; H, 4.5%).

(d) 4-(8'-Chloro-2'-naphthylimino)pentan-2-one. 8-Chloro-2-naphthylamine (3 g.) was condensed with acetylacetone, and the product crystallised from light petroleum (b. p. 60—80°) to give pale yellow needles (3.4 g., m. p. 72—73°) (Found: C, 69.2; H, 5.3. $C_{15}H_{14}ONCl$ requires C, 69.3; H, 5.4%).

(e) 8-Chloro-2:4-dimethyl-1-azanthracene. The pentanone (3 g.) was cyclised as usual and the resulting product crystallised from benzene-light petroleum (b. p. 60—80°) to give colourless needles (2.1 g., m. p. 153°) (Found: C, 74.7; H, 4.7. $C_{15}H_{12}NCl$ requires C, 74.5; H, 4.9%). Ultra-violet absorption spectrum (0.000263M-solution in hexane): Maxima at 3200 Å. (inflexion) (ϵ 1950), 3340 Å. (inflexion) (ϵ 2750), 3480 Å. (ϵ 3550), 3650 Å. (ϵ 3470), and 3830 Å. (ϵ 3310).

(f) 8-Chloro-2:4-dimethyl-1-azanthraquinone. The azanthracene (0.5 g.) was oxidised in the same manner as the 5-isomer. The quinone crystallised from benzene-light petroleum (b. p. 60—80°) in yellow needles (20 mg., m. p. 228—229°) (Found: C, 66.1; H, 3.55. $C_{15}H_{10}O_2NCl$ requires C, 66.2; H, 3.7%).

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