103. *The Chemistry of* 1-*Azanthraquinone. Part II. Sulphonation of* 1-*Azanthraquinone.*

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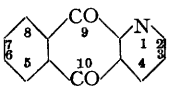
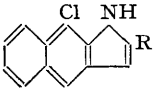
1-Azanthraquinone has been sulphonated to give the 5-, 7-, and 8-monosulphonic acids. These were orientated by conversion into the chloro-1-azanthraquinones. 3-, 5-, and 6-*Chloro*-1-*azanthraquinones* have been synthesised, and the identity of 7- and 8-*chloro*-1-*azanthraquinones* established by degradation. The nitration and the action of methanolic potassium hydroxide solution on some chloro-1-azanthraquinones is described.

1-Azanthraquinone (I) (E.P. 427,485) was sulphonated by 20% oleum at 150°, with and without a mercury catalyst (F.P. 746,689; D.R.-P. 597,833), and in each case a monosulphonic



(I.)



(II, R = H.) (III, R = CO_2Et.)

acid was isolated. These on treatment with potassium chlorate and hydrochloric acid gave isomeric chloro-1-azanthraquinones. It was therefore deduced that the addition of mercury

had an appreciable effect on the sulphonation. Anthraquinone is sulphonated chiefly in the 1-position when a mercury salt is present, whereas 2-sulphonation occurs in its absence (Fierz-David, *Helv. Chim. Acta*, 1927, **10**, 197).

Since the two patents cited gave few details for the sulphonation of 1-azanthraquinone, experiments were carried out to find the best conditions for the process. The methods finally used were sulphonation with: (1) 65% oleum, with a mercury catalyst at 95°; (2) 20% oleum and a mercury catalyst at 150°; (3) 20% oleum at 145°; (4) sulphur trioxide at 170° (Schwenk, *Z. angew. Chem.*, 1931, **44**, 912).

Other methods of sulphonation which were unsuccessfully tried were the use of chlorosulphonic acid at 250° and of pyridine anhydrosulphate (Baumgarten, *Ber.*, 1926, **59**, 1976). Attempts to sulphonate 1-azanthraquinone by passing nitrogen containing sulphur trioxide vapour through a boiling decalin solution led only to the formation of a decalinsulphonic acid (characterised as its *benzyl-ψ-thiouronium* salt).

1-Azanthraquinone was therefore sulphonated by the four methods listed, and the mixed barium salts isolated as usual. The mixture, in each case, was fractionally recrystallised from water and, except in method (3), three isomeric monosulphonates were obtained and characterised as the 5-, 7-, and 8-*isomers*. In addition, a very soluble fraction was obtained in each case, which is probably a mixture of barium hydroxy-1-azanthraquinonesulphonates (referred to as " BaV "). It was pink and readily soluble in water, the colour of the solution being increased by addition of alkali but discharged by acid. It gave no lakes with aluminium or chromium salts, absorbed bromine, and gave only an oily *p*-chlorobenzyl-ψ-thiouronate, facts which indicate a mixture of monohydroxy-1-azanthraquinonesulphonic acids (cf. Houben, " Das Anthracen und die Anthrachinone," 1929, p. 402).

The following table gives the yields of isomers obtained by each method of sulphonation.

Isomer.	Method. 1.	2.	3.	4.	M. p. of chloro-deriv.
8-Sulphonate, %	33·2	31·0	27·1	21·7	217—219°
5-Sulphonate, %	28·7	13·3	nil	13·0	241—242
7-Sulphonate, %	12·8	18·7	9·6	34·8	230—231
" BaV ", %	7·9	13·8	50·1	13·8	—
Loss in working up, %	17·3	23·2	13·2	17·4	—

Owing to the appreciable loss involved in each separation it was not possible to draw any final conclusions as to the effect of the mercury as a catalyst. The yields of " α " isomers (5- +8-sulphonates) was lower when no mercury was present, but the yield of " β "-isomers (7-sulphonate) fell in method 3 in which no mercury was added, although in method 4 it was very much higher than in the catalytic sulphonations.

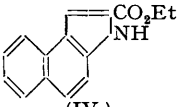
The non-detection of the 6-sulphonic acid was rather surprising, but this might be due to its being formed to such a small extent that it was lost in the working up. Attempts to prepare the 6-sulphonic acid by the action of sodium sulphite solution on 6-bromo-1-azanthraquinone (cf. Schmidt, *Ber.*, 1904, **37**, 66) failed, although the bromine was removed and an acid formed, which gave a *p*-chlorobenzyl-ψ-thiouronate, but the analytical data did not agree with the values required. Attempts to repeat this experiment gave inconsistent results.

1-Azanthraquinone resembles anthraquinone-1-sulphonic acid in that there is a strongly deactivating group in the 1-position. Further sulphonation of anthraquinone-1-sulphonic acid occurs solely in the other ring (Lauer, *J. pr. Chem.*, 1933, **137**, 176; Fierz-David, *loc. cit.*), and trisulphonic acids cannot be produced owing to the presence of the two deactivating groups (Lauer, *J. pr. Chem.*, 1932, **135**, 361). Since pyridine is sulphonated only in the 3-position under drastic conditions (cf. McElvaine and Goese, *J. Amer. Chem. Soc.*, 1943, **65**, 2333) 1-azanthraquinone was expected to sulphonate only in the benzene ring, and this was found to be the case, since only the 5-, 7-, and 8-sulphonic acids were isolated, and there was no evidence of disulphonation.

The three barium 1-azanthraquinonesulphonates were converted into the corresponding *chloro-1-azanthraquinones* by treatment with potassium chlorate and hydrochloric acid (D.R.-P. 597,833). The identity of these chloro-compounds was then established by synthesis or degradation.

3-Chloroquinoline has been prepared from indole by the action of alcoholic potash and chloroform (Ellinger, *Ber.*, 1906, **39**, 4388). Attempts to prepare 7-chloro-5 : 6-benzindole (II), which on similar treatment was expected to give 3 : 9-dichloro-1-azanthracene, from acetaldehyde 1-chloro-2-naphthylhydrazone by heating with zinc chloride failed, although

Schlieper (*Annalen*, 1886, **236**, 171) was able to convert acetaldehyde β-naphthylhydrazone into 4 : 5-benzindole. Attempts were then made to prepare (III) by Fischer's indole reaction on *ethyl pyruvate* 1-*chloro*-2-*naphthylhydrazone* with a view to obtain (II) by its decarboxylation. The ring closure, however, gave only the " angular " *isomer* (IV).



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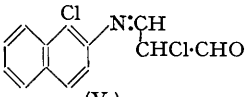

(V.)

Uhle and Jacobs (*J. Org. Chem.*, 1945, **10**, 76) described a new synthesis of 3-substituted quinolines. A substituted malonic dialdehyde is condensed with a primary amine and the product cyclised, angular cyclisation again being favoured. We attempted to prevent this by condensing 1-chloro-2-naphthylamine with chloromalonic dialdehyde to give the Schiff's *base* (V), which on cyclisation and oxidation gave a small yield of 3-*chloro*-1-*azanthraquinone*, m. p. 237—238°. This was different from any of the chloro-compounds obtained from the sulphonates.

5-Chloro-1-azanthraquinone was prepared from 1-chloro-5-amino-2-acetamidonaphthalene (Clemo and Driver, *J.*, 1945, 829) by a route analogous to that used by them for 5-bromo-1-azanthraquinone, and found to be identical with the chloro-1-azanthraquinone, m. p. 241—242°, obtained from one of the barium salts.

1-Chloro-2-acetamidonaphthalene on bromination gives 1-chloro-6-bromo-2-acetamidonaphthalene (Armstrong and Rossiter, *Chem. News*, 1891, **63**, 137) and hence it was expected that chlorination would give 1 : 6-dichloro-2-acetamidonaphthalene. The product obtained, however, was 1 : 4-*dichloro*-2-*acetamidonaphthalene* as proved by hydrolysis to the amine, and conversion of this into the known 1 : 4-dichloro- and 1 : 2 : 4-trichloro-naphthalenes. The *dichloro-amine* was also submitted to the Skraup reaction, and the product oxidised, 1-azanthraquinone being isolated. Similar selective halogenation has been observed in the case of 1-chloro-2-naphthol which on chlorination (Cleve, *Ber.*, 1888, **21**, 891) gives 1 : 4-dichloro-2-naphthol, whereas Armstrong and Rossiter (*Chem. News*, 1889, **59**, 225) found that on bromination 1-chloro-6-bromo-2-naphthol was formed.

1-Chloro-6-nitro-2-acetamidonaphthalene (Gerhardt and Hamilton, *J. Amer. Chem. Soc.*, 1944, **66**, 479) was reduced to the *amino*-compound, which was converted into 1 : 6-*dichloro*-2-*acetamidonaphthalene*. Hydrolysis, followed by the Skraup reaction and oxidation, gave 6-*chloro*-1-*azanthraquinone*, m. p. 265—266°, not identical with any of the chloroazanthraquinones formed from the sulphonic acids.

Attempts to prepare 7-chloro-2-naphthylamine as an intermediate for 7-chloro-1-azanthraquinone by the action of cuprous chloride in hydrochloric acid on the hydrochloride of the monodiazonium chloride of naphthylene-2 : 7-diamine (Kaufler and Karrer, *Ber.*, 1907, **40**, 3262) have failed.

1-Chloro-8-amino-2-acetamidonaphthalene (Clemo and Driver, *loc. cit.*) was converted into 1 : 8-*dichloro*-2-*naphthylamine* by the usual reactions. This was submitted to the Skraup reaction, and the product oxidised, but instead of the expected 8-chloro-1-azanthraquinone the only product which could be isolated was 6′-*chloro*-5 : 6-*benzoquinoline*.

Of the three chloro-1-azanthraquinones prepared from the sulphonic acids only one, the 5-isomer, had thus been orientated by synthesis. Attempts were made to orientate the other two isomers by oxidation. Johnson and Mathews (*J. Amer. Chem. Soc.*, 1944, **66**, 210) found that 2 : 4-dimethyl-1-azanthraquinone and (unexpectedly in view of the well-known resistance of the pyridine ring to oxidation) 1-azanthraquinone on oxidation with sulphuric acid and potassium permanganate both gave phthalic acid. It was therefore expected that 5-, 6-, 7- and 8-chloro-1-azanthraquinones on similar treatment would give 3-, 4-, 4- and 3-chlorophthalic acids, respectively. Synthesis having settled the orientations of the 5- and 6-chloro-isomers, it was therefore only necessary to apply the oxidation method to the two chloro-1-azanthraquinones of m. p.s 230—231° and 217—219°. These gave 4- and 3-chlorophthalic acids, respectively, thus proving the 7- and 8-positions (cf. table on p. 540).

A number of disubstituted 1-azanthraquinones have been prepared by nitration of some halogenated 1-azanthraquinones. 5-Chloro- and 8-chloro-1-azanthraquinone both gave a *mononitro*-derivative, presumably with the nitro-group in the *p*-position to the chlorine atom since Houben (*loc. cit.*, p. 288) states that α-chloroanthraquinones are nitrated in the *p*-position. 6-Bromo-1-azanthraquinone (E.P. 427,485) on nitration gave two *mononitro*-derivatives, but these disubstituted 1-azanthraquinone compounds have not been orientated.

Attempts to prepare hydroxy-1-azanthraquinones from the 1-azanthraquinonesulphonic acids by treatment with sodium carbonate solution (Iljinsky, *Ber.*, 1903, **36**, 4194), 20% sodium hydroxide solution (Simon, *Ber.*, 1881, **14**, 464), and calcium hydroxide (D.R.-P. 17,626) were unsuccessful. Schmidt (*Ber.*, 1904, **37**, 66), by using a solution of alkali in methanol, converted anthraquinonesulphonic acids into the corresponding hydroxy-compounds. This method when applied to barium 1-azanthraquinone-5-sulphonate gave a small yield of 5-*hydroxy*-1-*azanthraquinone*. A better yield was obtained by using 5-chloro-1-azanthraquinone in place of the sulphonic acid. 8-Chloro-1-azanthraquinone was similarly converted into 8-*hydroxy*-1-*azanthraquinone* which was also obtained by the same method from the nitro-1-azanthraquinone, m. p. 215—218° (Clemo and Driver, *loc. cit.*). This showed it to have the nitro-group in the 8-position, and on oxidation it gave 3-nitrophthalic anhydride. The 5-nitro-1-azanthraquinone which would have given a similar result on oxidation was synthesised by Gerhardt and Hamilton (*loc. cit.*).

6- and 7-Chloro-1-azanthraquinone on similar treatment with methanolic potassium hydroxide gave 6- and 7-*methoxy*-1-*azanthraquinone*.

The formation of 5- and 8-hydroxy and of 6- and 7-methoxy-1-azanthraquinones from the chloro-1-azanthraquinones under identical conditions was also rather surprising, but it was believed that in all cases hydroxylation first took place, followed by subsequent methylation. This, however, took place only in the case of the 6- and 7-isomers, because of chelation in the 5- and 8-isomers between the hydroxyl and carbonyl groups (Sidgwick and Callow, *J.*, 1924, **125**, 527).

Experimental.

Sulphonation of 1-*Azanthraquinone*.—(1) Oleum (65%; 24 c.c.) was added to a finely divided mixture of 1-azanthraquinone (E.P. 427,485) (12 g.) and mercuric sulphate (0·3 g.) and heated at 95—98° for 6 hours. The solution was poured into ice-water (2 l.), and excess of barium carbonate added. The precipitate was filtered off and washed with boiling water (2 l.), and the combined filtrates evaporated to dryness, giving 20·2 g. of a mixture of barium salts. This was added to water (1350 c.c.) heated to 80°. The insoluble *barium* 1-*azanthraquinone*-8-*sulphonate* (6·7 g.) was collected [Found: Ba, 17·5; H_2O, 8·8. $(C_{13}H_6O_5NS)_2Ba,4H_2O$ requires Ba, 17·5; H_2O, 9·15%]. The p-*chlorobenzyl*-ψ-*thiouronium* derivative crystallised from dilute ethanol (1 : 1) in colourless plates, m. p. 265—266° (Found: C, 51·5; H, 3·1. $C_{21}H_{16}O_5N_3ClS_2$ requires C, 51·4; H, 3·3%).

The aqueous filtrate was concentrated to 750 c.c., and on standing a solid (6·3 g.) separated. This was collected and on recrystallisation from water gave *barium* 1-*azanthraquinone*-5-*sulphonate* (4·5 g.) in small, pale yellow needles [Found: Ba, 16·45; H_2O, 14·6. $(C_{13}H_6O_5NS)_2Ba,7H_2O$ requires Ba, 16·45; H_2O, 15·0%]. The p-*chlorobenzyl*-ψ-*thiouronate* crystallised from dilute ethanol in colourless needles, m. p. 227—228° (Found: C, 51·2; H, 3·2%). The aqueous filtrate on further concentration gave another 1·3 g. of the 5-sulphonate. The solution was concentrated further, and the solid (3·3 g.) collected. This crystallised from water to give *barium* 1-*azanthraquinone*-7-*sulphonate* (2·6 g.) as small, pale yellow needles [Found: Ba, 16·1; H_2O, 16·6. $(C_{13}H_6O_5NS)_2Ba,8H_2O$ requires Ba, 16·1; H_2O, 16·7%]. The p-*chlorobenzyl*-ψ-*thiouronate* crystallised from dilute alcohol in colourless plates, m. p. 215—216° (Found: C, 51·5; H, 3·4%).

The original solution on evaporation to dryness gave "BaV" (1·6 g.) as a pale red powder.

(2) Oleum (20%, 24 c.c.) was added to a mixture of 1-azanthraquinone (12 g.) and mercuric sulphate (0·3 g.) and heated at 150—155° for 3½ hours. The product was worked up as before, giving 20·3 g. of a mixture of barium salts. This was separated in the same manner as before to give 6·3, 2·7, and 3·8 g. of the 8-, 5-, and 7-sulphonates, respectively, and 2·6 g. of "BaV."

(3) 1-Azanthraquinone (4 g.) and oleum (20%; 16 c.c.) were heated together at 140—145° for 4 hours. The mixed barium salts (9·6 g.) were isolated as usual, and separated by fractional crystallisation from water, giving 2·6 and 0·95 g. of the 8- and the 7-sulphonate, respectively, and 5·2 g. of "BaV."

(4) 1-Azanthraquinone (3 g.) and sulphur trioxide (4 g.) were heated in a sealed tube to 170° during 2½ hours. The mixed barium salts (4·6 g.) gave on separation 1, 0·6, and 1·6 g. of the 8-, 5-, and 7-sulphonates, respectively, and 0·6 g. of "BaV."

Sulphonation of Decalin.—Nitrogen was passed over the surface of oleum (65%) and then bubbled through boiling decalin for 2 hours. The solid was filtered off, dissolved in water, and the solution filtered. Excess of barium carbonate was added to the filtrate, and the excess solid removed. The filtrate was evaporated, giving a barium salt (3 g.). This was dissolved in boiling water (20 c.c.), and a saturated solution of benzyl-ψ-thiouronium chloride (2 g.) in water added. The precipitate was collected and crystallised from dilute alcohol and then from dioxan, giving the *benzyl*-ψ-*thiouronate* of a decalin-sulphonic acid as colourless needles, m. p. 165—166° (Found: C, 56·0; H, 7·1; N, 7·3. $C_{18}H_{22}O_3N_2S_2$ requires C, 56·2; H, 7·3; N, 7·3%).

Orientation of the Barium 1-*Azanthraquinonesulphonates by Conversion into Chloro*-1-*azanthraquinones*.—5-*Chloro*-1-*azanthraquinone*. To a hot solution of barium 1-azanthraquinone-5-sulphonate (0·4 g.) in water (20 c.c.) and concentrated hydrochloric acid (8 c.c.) was added, during 2 hours, a hot solution of potassium chlorate (2 g.) in water (40 c.c.). After refluxing for a further 2 hours, the solution was cooled and basified. The solid was collected and extracted with chloroform. The solvent was distilled off and the residue crystallised from acetic acid, giving yellow needles of 5-*chloro*-1-*azanthraquinone* (0·1 g.), m. p. 240—241°, not depressed by admixture with an authentic specimen (see later).

7-*Chloro*-1-*azanthraquinone*, similarly prepared from the 7-sulphonate (0·5 g.), crystallised from acetic acid in yellow needles (0·08 g.; m. p. 230—231°) (Found: C, 64·0; H, 2·3. $C_{13}H_6O_2NCl$ requires C,

64·1; H, 2·5%). Oxidation by the method of Johnson and Mathews (*loc. cit.*) gave 4-chlorophthalic anhydride, and since 6-chloro-1-azanthraquinone has been synthesised (see later) this must be the 7-isomer.

8-*Chloro*-1-*azanthraquinone*, similarly prepared from the 8-sulphonate (1 g.), crystallised in pale yellow needles (0·1 g.; m. p. 217—219°) from acetic acid (Found: C, 64·2; H, 2·6%). Oxidation by Johnson and Mathews's method gave 3-chlorophthalic anhydride, thus providing the identity of 8-chloro-1-azanthraquinone.

3-*Chloro*-1-*azanthraquinone*.—(a) 1-*Chloro*-2-*naphthylhydrazine*. A solution of diazotised 1-chloro-2-naphthylamine (20 g.) (Cleve, *Ber.*, 1887, **20**, 1990) was run into one of stannous chloride (50 g.) in hydrochloric acid (100 c.c.). After 1 hour the hydrazine hydrochloride was collected and basified. The precipitated 1-*chloro*-2-*naphthylhydrazine* was filtered off, washed, dried, and crystallised from dilute alcohol, forming glistening white leaflets which rapidly darkened (15 g.; m. p. 110—111°) (Found: C, 62·7; H, 4·4. $C_{10}H_9N_2Cl$ requires C, 62·5; H, 4·7%).

Pyruvic acid 1-*chloro*-2-*naphthylhydrazone*. To a solution of the hydrazine (15 g.) in acetic acid (60 c.c.) and water (35 c.c.) pyruvic acid (9 g.) and water (42 c.c.) were added. The precipitated *hydrazone* (18·5 g.) was collected, and crystallised from dilute alcohol in pale yellow needles, m. p. 188 189° (decomp.) (Found: C, 59·5; H, 4·3. $C_{13}H_{11}O_2N_2Cl$ requires C, 59·4; H, 4·2%).

Ethyl pyruvate 1-*chloro*-2-*naphthylhydrazone* was prepared by refluxing the acid hydrazone (15 g.) with absolute alcohol (150 c.c.) and concentrated sulphuric acid (15 c.c.) for 2 hours. The solution was poured into water, and the solid collected. Crystallisation from alcohol gave pale yellow needles (15 g.; m. p. 92—93°) (Found: C, 60·3; H, 5·1. $C_{15}H_{15}O_2N_2Cl$ requires C, 60·2; H, 5·4%).

2-*Carbethoxy*-4 : 5-*benzindole*. The above hydrazone (2 g.) was heated with glacial acetic acid (10 c.c.) and concentrated sulphuric acid (0·7 c.c.) on a water-bath for 1 hour. Addition of water precipitated a solid, which was collected and crystallised successively from benzene–light petroleum (b. p. 60—80°) and methanol to give 2-*carbethoxy*-4 : 5-*benzindole* (2 g.), m. p. 161—162° (Found: C, 75·3; H, 5·6. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4%).

(b) *Chloromalonic dialdehyde*. 1 : 2 : 3 : 3-Tetrachloropropyl-1-ene (Heilbron, Heslop, and Irving, *J.*, 1936, 781) (15 g.) and concentrated sulphuric acid (50 c.c.) were stirred together for 6 hours at 45°. Ice (200 g.) was added, and the solution extracted twice with chloroform (50 c.c.). The chloromalonic dialdehyde was extracted with ether, and the ether distilled off, leaving the aldehyde (6 g.), m. p. 142—144° (lit. m. p. 144—145°).

2′-*Chloro*-2′-*formylethylidene*-1-*chloro*-2-*naphthylamine*. Chloromalonic dialdehyde (2 g.), dissolved in N/5-sodium hydroxide solution (500 c.c.), was added with stirring to a hot suspension of 1-chloro-2-naphthylamine (3 g.) in hydrochloric acid (100 c.c., 2%). When cold, the solid was collected and crystallised from alcohol to give nearly colourless needles (4·3 g.; m. p. 227—228°) (Found: C, 58·7; H, 3·3. $C_{13}H_9ONCl_2$ requires C, 58·6; H, 3·4%).

(c) 3-*Chloro*-1-*azanthraquinone*. The above Schiff's *base* (3·5 g.) and powdered fused zinc chloride (3·5 g.) were well mixed and heated at 290—300° until molten. When cold, the solid was powdered and extracted with hot hydrochloric acid (1 : 1). The acid extract was basified, and the oil separated. It was dissolved in acetic acid (15 c.c.), heated on the water-bath with chromic anhydride (2 g.) for 1 hour, and poured into saturated brine (25 c.c.). The solution was extracted with benzene, the benzene extracts washed with sodium hydroxide solution and water, and finally dried. Removal of the benzene gave 3-*chloro*-1-*azanthraquinone* which crystallised from benzene–light petroleum (b. p. 60—80°) in pale yellow needles (50 mg.; m. p. 237—238°) (Found: C, 64·2; H, 2·6; N, 5·8. $C_{13}H_6O_2NCl$ requires C, 64·1; H, 2·5; N, 5·75%).

5-*Chloro*-1-*azanthraquinone*.—(a) 1 : 5-*Dichloro*-2-*acetamidonaphthalene*. 1-Chloro-5-amino-2-acetamidonaphthalene (Clemo and Driver, *loc. cit.*) (10·7 g.) in glacial acetic acid (65 c.c.) was added below 25° to a stirred solution of sodium nitrite (3·7 g.) in concentrated sulphuric acid (37 c.c.). The diazo-solution was run into a solution of cuprous chloride (40 g.) in concentrated hydrochloric acid (250 c.c.). After nitrogen evolution had ceased, water (500 c.c.) was added, and the solid collected. It crystallised from alcohol in white needles (8 g.; m. p. 180—181°) (Found: C, 56·5; H, 3·5. $C_{12}H_9ONCl_2$ requires C, 56·7; H, 3·5%).

(b) 1 : 5-*Dichloro*-2-*naphthylamine*. The *acetyl* compound (7·0 g.) was refluxed with alcohol (70 c.c.) and concentrated hydrochloric acid (35 c.c.) for 1 hour, water (300 c.c.) added, and the solution basified. The *amine* was collected, and crystallised from alcohol giving colourless needles (5 g.; m. p. 124—125°) (Found: C, 56·8; H, 3·4. $C_{10}H_7NCl_2$ requires C, 56·6; H, 3·3%).

(c) 5-*Chloro*-1-*azanthraquinone*. The amine (5 g.) and sulphuric acid (50 c.c.; 66%) were heated under reflux, and glycerol (5 g.) and sodium *m*-nitrobenzenesulphonate (7·5 g.) added during ½ hour, refluxing being continued for a further 5 hours. Water was added, the solution basified, and the black solid collected, washed, dried, and extracted with acetone. Removal of the acetone left a yellow solid which was oxidised by dissolving it in acetic acid (50 c.c.), adding chromic anhydride (6 g.), and heating the mixture on a water-bath for 1 hour. Water was added, and the solid collected, washed, dried, and extracted with boiling chlorobenzene. Removal of the solvent left yellow needles (1·5 g.; m. p. 240—241°, raised to 243—244° by crystallisation from acetic acid) (Found: C, 63·9; H, 2·8%).

6-*Chloro*-1-*azanthraquinone*.—(a) *Chlorination of* 1-*chloro*-2-*acetamidonaphthalene*. Chlorine, prepared from potassium permanganate (20 g.) and hydrochloric acid, was bubbled slowly during 3 hours through a boiling solution of 1-chloro-2-acetamidonaphthalene (20 g.) in glacial acetic acid (200 c.c.). On cooling, 1 : 4-*dichloro*-2-*acetamidonaphthalene* crystallised. Recrystallisation from alcohol gave white leaflets (6·3 g.; m. p. 212—213°) (Found: C, 56·5; H, 3·4; Cl, 27·8. $C_{12}H_9ONCl_2$ requires C, 56·7; H, 3·5; Cl, 28·0%). Unchanged material (12·5 g.) was recovered from the acetic acid mother-liquor.

1 : 4-*Dichloro*-2-*naphthylamine*, prepared by hydrolysis of the acetyl derivative with hydrochloric acid and alcohol, crystallised from methanol in white needles, m. p. 92—93° (Found: C, 56·8; H, 3·3; Cl, 33·3. $C_{10}H_7NCl_2$ requires C, 56·6; H, 3·3; Cl, 33·5%). That chlorination had occurred in the 4-position was established by converting the amine into the known 1 : 4-dichloro- and 1 : 2 : 4-trichloro-

naphthalenes. A Skraup reaction on the amine, using the same method as for the 5-isomer, gave 1-azanthraquinone after oxidation.

(b) *1-Chloro-6-amino-2-acetamidonaphthalene.* Iron filings (40 g.) were etched by vigorous stirring for ½ hour with alcohol (66 c.c.) and concentrated hydrochloric acid (14 c.c.) and refluxing for 15 mins. The alcohol was decanted, and the etched iron washed twice with water. 1-Chloro-6-nitro-2-acetamidonaphthalene (Gerhardt and Hamilton, *loc. cit.*) (8 g.) in alcohol (400 c.c.) was added, the mixture refluxed with stirring for 5 hours, filtered, and the alcohol evaporated. The residue crystallised from dilute acetic acid in white needles (6 g.; m. p. 159—160°) (Found: C, 61·6; H, 4·5. $C_{12}H_{11}ON_2Cl$ requires C, 61·4; H, 4·7%).

1 : 6-*Dichloro-2-acetamidonaphthalene* was prepared from the above amine (6·3 g.) in the same manner as the 1 : 5-isomer. It crystallised from alcohol in white needles (5·3 g.; m. p. 219—220°) (Found: C, 56·9; H, 3·7%).

1 : 6-*Dichloro-2-naphthylamine* was prepared by hydrolysis of the acetyl compound and crystallised from alcohol, m. p. 100—101° (Found: C, 56·6; H, 3·5%).

6-*Chloro-1-azanthraquinone* was prepared from 1 : 6-dichloro-2-naphthylamine (5 g.) in the same manner as the 5-isomer, and crystallised as pale yellow needles (1 g.; m. p. 265—266°) from acetic acid (Found: C, 64·3; H, 2·6%).

Attempted Synthesis of 8-Chloro-1-azanthraquinone.—1 : 8-*Dichloro-2-acetamidonaphthalene* was prepared from 1-chloro-8-amino-2-acetamidonaphthalene (Clemo and Driver, *loc. cit.*) (8·5 g.) in the same manner as the 1 : 5- and the 1 : 6-isomer. Crystallisation from alcohol gave white needles (4·9 g., m. p. 146—147°) (Found: C, 56·6; H, 3·7%).

1 : 8-*Dichloro-2-naphthylamine,* obtained by hydrolysis of the acetyl compound, crystallised from methanol in colourless needles, m. p. 71—72° (Found: C, 56·7; H, 3·5%). This amine (2·5 g.) was submitted to the Skraup reaction under the above conditions but gave only 6′-*chloro-5* : 6-*benzoquinoline* (0·5 g.), crystallising from light petroleum (b. p. 60—80°) in colourless needles, m. p. 89—90° (Found: C, 73·0; H, 3·6; N, 6·4. $C_{13}H_8NCl$ requires C, 72·9; H, 3·7; N, 6·5%).

Nitration of Some Halogeno-1-azanthraquinones.—6-Bromoazanthraquinone (E.P. 427,485) (3 g.) was heated for 1 hour on the water-bath with a mixture of concentrated sulphuric acid (60 c.c.) and concentrated nitric acid (6 c.c.), the solution poured on ice and basified, and the solid collected. Fractional crystallisation from acetic acid gave 6-*bromo*-x-*nitro*-1-*azanthraquinone* (2 g.) as yellow needles, m. p. 292—293° (Found: C, 47·0; H, 1·6. $C_{13}H_5O_4N_2Br$ requires C, 46·8; H, 1·5%), and 6-*bromo*-y-*nitro*-1-*azanthraquinone* (0·3 g.) as yellow needles, m. p. 255—256° (Found: C, 46·5; H, 1·75%).

5-Chloro-1-azanthraquinone (0·2 g.) when nitrated as above gave 5-*chloro*-8(?)-*nitro*-1-*azanthraquinone* (0·15 g.) as bright yellow needles (from dilute acetic acid), m. p. 257—258° (Found: C, 54·0; H, 1·9. $C_{13}H_5O_4N_2Cl$ requires C, 54·0; H, 1·7%). 6-Chloro-1-azanthraquinone (0·2 g.) on similar treatment gave 6-*chloro*-x-*nitro*-1-*azanthraquinone* (0·1 g.) as pale yellow needles, m. p. 283—284°, from dilute acetic acid (Found: C, 54·2; H, 2·0%). 8-Chloro-1-azanthraquinone (0·1 g.) on nitration gave 8-*chloro*-5(?)-*nitro*-1-*azanthraquinone* (0·08 g.) as orange needles, m. p. 222—223°, from dilute acetic acid (Found: C, 54·1; H, 1·8%).

All the above nitro-compounds slowly darkened on exposure to light.

5-*Hydroxy*-1-*azanthraquinone.*—(*a*) 5-Chloro-1-azanthraquinone (0·3 g.) and a solution of potassium hydroxide in methanol (15 c.c.; 2%) were heated together in a sealed tube for 18 hours at 100°. Water was added, the methanol removed, the residual solution just acidified with acetic acid, and the *hydroxyazanthraquinone* extracted with chloroform. Removal of the solvent left a yellow solid (0·25 g.) which, after crystallisation from water and sublimation at 1 mm., was obtained as bright yellow needles, m. p. 214—215° (Found: C, 69·1; H, 3·2. $C_{13}H_7O_3N$ requires C, 69·3; H, 3·1%).

(*b*) Barium 1-azanthraquinone-5-sulphonate (0·3 g.) on similar treatment gave 5-hydroxy-1-azanthraquinone (30 mg.).

8-*Hydroxy*-1-*azanthraquinone.*—(*a*) 8-Chloro-1-azanthraquinone (0·3 g.) when similarly treated gave 8-*hydroxy*-1-*azanthraquinone* (0·23 g.) which, after crystallisation from water and sublimation at 1 mm., was obtained as bright yellow needles, m. p. 199—200° (Found: C, 69·5; H, 3·3%).

(*b*) The nitro-azanthraquinone (m. p. 215—218°) (Clemo and Driver, *loc. cit.*) (0·3 g.) when similarly treated gave 8-hydroxy-1-azanthraquinone (0·2 g.), m. p. and mixed m. p. 197—199°. The nitro-group is therefore in the 8-position, and this was confirmed by oxidation with acid permanganate (Johnson and Mathews, *loc. cit.*), 3-nitrophthalic anhydride being obtained.

6-*Methoxy*-1-*azanthraquinone.*—6-Bromo-1-azanthraquinone (1 g.) and methanolic potassium hydroxide solution (50 c.c.; 2%) were heated for 18 hours at 100° in a sealed tube. The methanol was removed, water added, and the solid (0·7 g.) collected. This was again heated with the potassium hydroxide solution (35 c.c.) as before, and the solid isolated and crystallised from acetic acid, to give 6-*methoxy*-1-*azanthraquinone* (0·5 g.) as yellow needles, m. p. 259—261° (Found: C, 70·3; H, 3·8. $C_{14}H_9O_3N$ requires C, 70·3; H, 3·8%).

7-*Methoxy*-1-*azanthraquinone,* similarly prepared from 7-chloro-1-azanthraquinone (0·2 g.), crystallised from acetic acid in pale yellow needles (0·1 g.), m. p. 205—207° (Found: C, 70·1; H, 3·6%).

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