

# ANTHRAQUINONE AND ANTHRONE SERIES

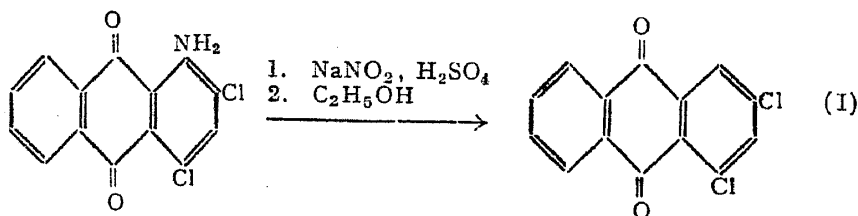
## Part XIV. 1-Amino-3-chloroanthraquinone

By B. S. JOSHI, N. PARKASH AND K. VENKATARAMAN, F.A.Sc.

(Department of Chemical Technology, University of Bombay)

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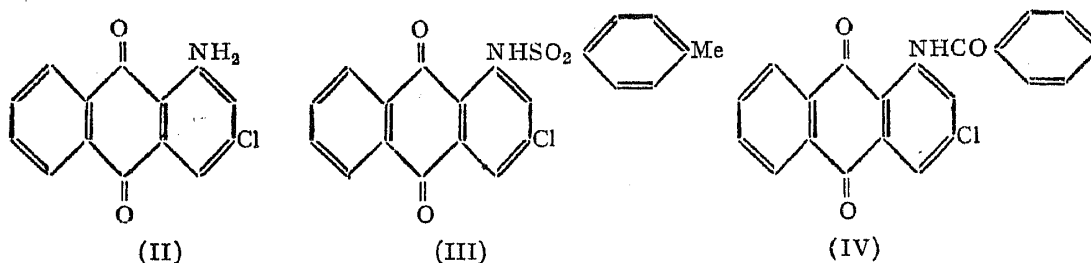
THE methods described in the literature for the preparation of 1:3-dichloroanthraquinone (I) are (i) by the condensation of phthalic anhydride with *m*-dichlorobenzene in presence of aluminium chloride and cyclization of the dichlorobenzoylbenzoic acid with fuming sulphuric acid at 160°<sup>1, 2</sup>; (ii) by deamination of 2-amino-1:3-dichloroanthraquinone<sup>3</sup>; and (iii) by oxidation of 1:3:9:10-tetrachloroanthracene with chromic acid in acetic acid.<sup>4</sup> Since 1-amino-2:4-dichloroanthraquinone<sup>5</sup> is now readily available, its deamination offers a convenient route to 1:3-dichloroanthraquinone; a 95% yield has been obtained by boiling the diazonium sulphate from 1-amino-2:4-dichloroanthraquinone with ethanol in presence of a little copper sulphate.



No reference to 1-amino-3-chloroanthraquinone (II) was available when this work was initiated, but according to a FIAT report<sup>2</sup> it is a valuable base for azoic dyeing, giving very bright shades with excellent fastness properties; combinations of the greatest interest were a scarlet with Naphtol AS-D, a red-brown with Naphtol AS-LT, and a red-yellow with Naphtol I3GH. Citing the FIAT report, Glassman<sup>6</sup> has stated: "In contrast to the pigments obtained by coupling diazotized  $\alpha$ -aminoanthraquinone with naphthols, which are 'muddy' in shade, corresponding ones from 3-bromo- and 3-chloro-1-aminoanthraquinones give reds of a brightness comparable with that of Permanent Reds FRL to F4R. Light fastness is of a very high order, and some of the more outstanding properties are oil fastness and resistance to bleed (overstripe test)."

The base (II) has been prepared from (I) by a known method; condensation with *p*-toluenesulphonamide gave a quantitative yield of 3-chloro-1-

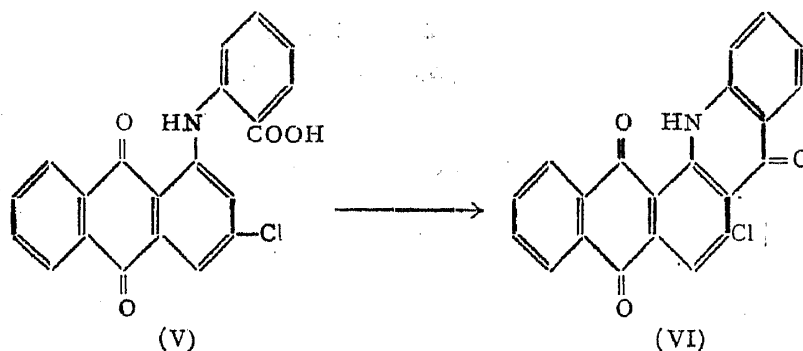
*p*-toluenesulphonamidoanthraquinone (III), hydrolysis of which with concentrated sulphuric acid gave (II), also in excellent yield. In combination



with Naphtol AS, AS-LT and AS-D diazotized (II) produced bright red, red-brown and scarlet shades on cotton with light fastness 7-8, chlorine fastness 3-4, and soda boil fastness 2-3. For comparison diazotized 1-amino-4-chloroanthraquinone and 1-amino-2:4-dichloroanthraquinone were used for developing cotton yarn impregnated with Naphtol AS, when corinth and dull brown shades with light fastness 3-4, chlorine fastness 2-3 and soda boil fastness 1-2 were obtained.

1-Amino-3-chloroanthraquinone (II) was characterized by its N-acetyl and N-benzoyl (IV) derivatives. The latter (IV) dyed a brighter and deeper yellow than  $\alpha$ -benzamidoanthraquinone. The chlorine atom in the 3-position also improved the light and soda boil fastness properties. The terephthaloyl and isophthaloyl derivatives of (II) were also prepared; these were found to give bright greenish yellow shades with improved chlorine and soda boil fastness when compared with Paradone Yellow 5GK and Indanthrene Yellow 5GK, the analogues from  $\alpha$ -aminoanthraquinone. The light fastness, however, was inferior.

1-Anilino-3-chloroanthraquinone and its 2'-carboxy derivative (V) were prepared by condensing 1:3-dichloroanthraquinone (I) with aniline and anthranilic acid respectively. The anthranilic acid derivative (V) was cyclized to 7-chloroanthraquinoneacridone (VI) by means of phosphorus pentachloride in nitrobenzene. The acridone (VI) dyed a red-violet shade from a deep violet vat. It is of interest to note that (VI), which does not



have an amino group in the 6-position adjacent to the chlorine atom, was not dehalogenated by treatment with alkaline hydrosulphite at 30° for one hour.<sup>7</sup>

The chlorine atom in 1-amino-3-chloroanthraquinone (II) failed to react with *p*-toluenesulphonamide or anthranilic acid, but the *N*-benzoyl derivative condensed readily with *p*-toluenesulphonamide to give 1-benzamido-3-*p*-toluenesulphonamidoanthraquinone, which was hydrolysed with sulphuric acid to 1:3-diaminoanthraquinone.

#### EXPERIMENTAL

##### 1:3-Dichloroanthraquinone (I)

A solution of 1-amino-2:4-dichloroanthraquinone (45 g.) in glacial acetic acid (450 c.c.) was cooled to 20° and poured into an ice-cold solution of sodium nitrite (45 g.) in conc. sulphuric acid (360 c.c.). After 30 minutes the mixture was diluted to 2 l. with ice-water, treated with 95% alcohol (1250 c.c.) and copper sulphate (10 g.), and refluxed for 3 hours. Dilution with water gave a product (40 g.) which was collected, and treated with chromic acid (5 g.) in boiling acetic acid (200 c.c.) for a few minutes. On filtering the hot solution and cooling, yellow needles of 1:3-dichloroanthraquinone, m.p. 208°, separated (Found: C, 60.3; H, 2.3; Cl, 25.8. Calc. for  $C_{14}H_6Cl_2O_2$ : C, 60.6; H, 2.4; Cl, 25.6%).

##### 3-Chloro-1-*p*-toluenesulphonamidoanthraquinone (III)

A mixture of 1:3-dichloroanthraquinone (2 g.), *p*-toluenesulphonamide (1.8 g.), anhydrous sodium acetate (0.9 g.), copper acetate (0.1 g.) and amyl alcohol (25 c.c.) was refluxed for 15 hours. The product crystallized from glacial acetic acid in orange-red plates, m.p. 215° (Found: Cl, 8.5; N, 3.4.  $C_{21}H_{14}ClNO_4S$  requires Cl, 8.6; N, 3.4%).

##### 1-Amino-3-chloroanthraquinone (II)

3-Chloro-1-*p*-toluenesulphonamidoanthraquinone (0.5 g.) and conc. sulphuric acid (10 c.c.) were heated on a water-bath for 1 hour and poured into water. The product crystallized from acetic acid in red needles, m.p. 230° (Found: Cl, 13.6; N, 5.8.  $C_{14}H_8ClNO_2$  requires Cl, 13.8; N, 5.5%).

##### 1-Acetamido-3-chloroanthraquinone

1-Amino-3-chloroanthraquinone (0.5 g.) was boiled with acetic anhydride (1.8 c.c.) and sodium acetate (0.3 g.) for 3 hours. The yellow precipitate obtained on adding the solution to ice crystallized from alcohol in yellow plates, m.p. 216° (Found: N, 5.1.  $C_{16}H_{10}ClNO_3$  requires N, 4.7%).

**1-Benzamido-3-chloroanthraquinone (IV)**

1-Amino-3-chloroanthraquinone (1.2 g.), benzoyl chloride (2 c.c.) and *o*-dichlorobenzene (10 c.c.) were heated at 190° for 2 hours, the solution cooled, and the precipitate collected. On recrystallization from *o*-dichlorobenzene yellow plates, m.p. 255°, were obtained (Found: Cl, 9.5; N, 3.9.  $C_{21}H_{12}ClNO_3$  requires Cl, 9.8; N, 3.9%). The substance gives a red vat and dyes cotton a redder and deeper shade than  $\alpha$ -benzamidoanthraquinone. The fastness properties are light 7, chlorine 4 and soda boil 4.

**1-Benzamido-3-*p*-toluenesulphonamidoanthraquinone**

A mixture of 1-benzamido-3-chloroanthraquinone (1.8 g.), *p*-toluenesulphonamide (1.0 g.), anhydrous potassium carbonate (0.5 g.), copper powder (0.1 g.) and nitrobenzene (100 c.c.) was refluxed for 6 hours. Nitrobenzene was removed by steam distillation, and the product filtered, washed and dried (2.1 g.). Crystallization from acetic acid gave yellow needles, m.p. 287–88° (Found: N, 5.7; S, 6.3.  $C_{28}H_{20}O_5N_2S$  requires N, 5.7; S, 6.5%). The sulphonamide (0.5 g.) and concentrated sulphuric acid (15 c.c.) were heated on a water-bath for 8 hours, diluted with water and filtered. The red-brown product crystallized from *o*-dichlorobenzene in red rhomboidal plates, m.p. 290° (m.p. of 1:3-diaminoanthraquinone, 290°).<sup>8</sup>

***Terephthalic acid derivative of 1-amino-3-chloroanthraquinone***

Terephthalic acid (0.2 g.) was heated with thionyl chloride (5 c.c.) for 6 hours, excess thionyl chloride distilled off, and the residual acid chloride dried under vacuum on a water-bath for 2 hours. *o*-Dichlorobenzene (50 c.c.) and 1-amino-3-chloroanthraquinone (0.7 g.) were added and the solution refluxed for 2 hours, when yellow needles separated. After cooling, the product was collected (0.67 g.) and crystallized from nitrobenzene, when golden yellow needles, m.p. > 360°, were obtained (Found: N, 4.5.  $C_{38}H_{20}Cl_2N_2O_6$  requires N, 4.4%). The substance dyes cotton a yellow shade from a violet vat (fastness to light 3, chlorine 4-5, and soda boil 4).

***Isophthalic acid derivative of 1-amino-3-chloroanthraquinone***

The chloride was prepared as above from isophthalic acid (0.5 g.) and heated with 1-amino-3-chloroanthraquinone (1.55 g.) and *o*-dichlorobenzene (50 c.c.) at the boil for 4 hours when a yellow product separated. On cooling, the dye was collected (1.5 g.) and crystallized from nitrobenzene. The yellow needles did not melt below 360° (Found: N, 4.3.  $C_{38}H_{20}Cl_2N_2O_6$  requires N, 4.4%). The product dyes cotton a yellow shade from a violet vat (fastness to light 3, chlorine 4-5, soda boil 4).

Cotton dyed with the terephthalic and isophthalic acid derivatives of 1-amino-3-chloroanthraquinone was tendered by the action of light to a greater extent than cotton dyed with the aminoanthraquinone analogues. After exposure in a fadeometer for 48 hours, cotton dyed with the 1-amino-3-chloroanthraquinone derivatives gave cuprammonium fluidity values of 37.71 and 35.72 in comparison with the values of 31.83 for Paradone Yellow 5GK, 32.72 for Indanthrene Yellow 5GK, and 9.61 for the undyed cotton.

#### *1-Anilino-3-chloroanthraquinone*

1 : 3-Dichloroanthraquinone (2 g.), aniline (10 c.c.), anhydrous potassium acetate (0.6 g.) and a little copper acetate were refluxed for 1 hour and cooled. The mixture was poured into dilute hydrochloric acid and filtered. The precipitate (2.2 g.) crystallized from glacial acetic acid in long red-brown needles having a violet reflex. After two further crystallizations from the same solvent the m.p. was 166–67° (Found Cl, 10.9; N, 4.6.  $C_{20}H_{22}ClNO_2$  requires Cl, 10.6; N, 4.2%). With concentrated sulphuric acid, a blue solution is obtained, which changes to violet on dilution and on further dilution gives a red-brown precipitate.

#### *1-Anthranilino-3-chloroanthraquinone (V)*

1 : 3-Dichloroanthraquinone (2.8 g.), anthranilic acid (2.1 g.), anhydrous potassium acetate (2.0 g.), copper bronze (50 mg.), copper acetate (50 mg.) and amyl alcohol (25 c.c.) were refluxed under stirring in an oil-bath at 155° for 3 hours. The mixture was filtered and the violet residue separated and boiled with hydrochloric acid. The product (3 g.) crystallized from toluene in brick-red needles, m.p. 272° (Found: Cl, 9.3; N, 3.7.  $C_{21}H_{12}ClNO_4$  requires Cl, 9.5; N, 3.7%). The substance gives a yellow-brown solution in sulphuric acid and a red precipitate on dilution. With sodium hydroxide it gives a violet salt.

#### *7-Chloroanthraquinoneacridone (VI)*

1-Anthranilino-3-chloroanthraquinone (2 g.) was heated with toluene (20 c.c.) and phosphorus pentachloride (1.5 g.) for 30 minutes. The solution was cooled, the red product collected, washed with hexane, and a solution in nitrobenzene (12 c.c.) boiled till evolution of hydrochloric acid ceased. The product (1.7 g.) crystallized from *o*-dichlorobenzene in violet-red needles, m.p. 300° (Found: N, 3.8.  $C_{21}H_{10}ClNO_3$  requires N, 3.9%). The acridone gives with sulphuric acid a yellow-orange solution and a red-violet precipitate on dilution. It dyes cotton a violet shade from a deep violet vat.

### SUMMARY

1:3-Dichloroanthraquinone has been prepared by the deamination of 1-amino-2:4-dichloroanthraquinone. The dichloroanthraquinone is useful for the preparation of 1-amino-3-chloroanthraquinone.

### ACKNOWLEDGMENT

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