ON THE DERIVATIVES OF ANTHRAHYDROQUINONE DISULPHURIC ACID ESTERS. I. SYNTHESIS OF SOME AZO-COMPOUNDS.

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Bader and Vaucher[1] synthesised leuco-indigo disulphuric acid ester treating indigo white with pyridine salt of chlorosulphonic acid. Its alkali salt is stable and highly soluble in water. In acid solution, however, indigo is easily precipitated by the action of weak oxidising agents such as ferric chloride or sodium nitrite, due to the hydrolysis and oxidation taking place simultaneously. Inasmuch as fabrics may be dyed with indigo without the use of alkali, of the so-called Indigosol dyes belonging to this class, many are actually prepared. Schirmacher, Scharich, and Eishold[2] synthesised the anthrahydroquinone disulphuric acid ester or its derivatives, by mixing anthraquinone or its derivatives with pyridine salt of chlorosulphonic acid, then reducing and esterifying the mixture by means of metallic powder. Moreover the fact that these compounds are soluble in water and easily oxidisable to the original quinone in acid solution has been utilized in many attempts in the field of dye-synthesis[3]. The present author synthesised the same compound and examined the properties.

Sodium salt of anthrahydroquinone disulphuric acid ester was readily prepared as yellow crystals by the method of German patent 473 471. But the isolation of alkali or alkaline earth salts of β-aminoanthrahydroquinone disuphuric acid ester proved unsuccessful owing to the great solubilities of salts. After many experiments, the author succeeded in isolating it in the form of diphenylguanidine salt. The latter is difficultly soluble in water, and may be purified by recrystallisation from alcohol in yellow crystals. On adding alkali, it is converted into the sodium salt, and free diphenylguanidine formed is removed by filtration.

Next, using this compound, the author synthesised some azo-dyes. The diazo-compound is readily prepared by the usual method as the compound is easily soluble in water. By coupling with α- and β-naphthol, dark, violet

(1) *Chimie & Industrie*, **1924**, 449.
(2) D. R. P. 473471.
(3) D. R. P. 461500, 472772, 470809, 476811.
E. P. 333506, 333507, 338891.

powders were obtained which dyed animal fibres in good colour in weak acid baths.

These dyed fabrics were reddish-violet and changed into scarlet by the action of hot ferric chloride solution. Dye from β-naphthol was pure scarlet.

Dye from α-naphthylamine was reddish-orange in alkaline solution and dyed the fibres scarlet. This turned bluish-violet with acid and again violet-red on oxidation. β-Naphthylamine derivative was also orange-red in alkaline solution and dyed the fibre reddish, which turned violet-red by the action of ferric chloride. But its shade did not come out as clear as in the case of α-derivative.

Experimental.

Sodium Salt of Anthrahydroquinone Disulphuric Acid Ester, $C_6H_4(COSO_3Na)_2C_6H_4$. Chlorosulphonic acid (8 g.) was slowly poured into pyridine (50 c.c.) cooled with ice. The mixture was then heated to 30°, anthraquinone (5 g.) was introduced in and the whole was heated to 65°. Copper powder ("Naturkupfer C") was then added in small quantities at a time with constant stirring, the temperature was raised to 70° and maintained for half an hour. After cooling, sodium hydroxide solution (10 g., NaOH) was poured in, pyridine was distilled over with steam, and the solution was filtered while hot. The filtrate was evaporated on the water-bath. On cooling, anthrahydroquinone disulphuric acid ester disodium salt was crystallised out. The yield of the crude product was 10.5 g. After two crystallisations from water, it separated in faintly yellow crystals. The solution showed violet fluorescence and anthraquinone was precipitated on treating the solution with ferric chloride. The solid salt is also unstable and decomposes into anthraquinone when it is kept in a bottle for some days or more rapidly when it is hot. In the above case, reduced iron powder or bronze powder was used as the reducing agent, but the treatment was not found effective.

Diphenylguanidine Salt of β-Aminoanthrahydroquinone Disulphuric Acid Ester, $C_6H_4(COSO_3H\cdot C_{13}H_{13}N_3)_2C_6H_3NH_2$. To well-cooled pyridine (200 c.c.) chlorosulphonic acid (48 c.c.) was added drop by drop with vigorous stirring, keeping the temperature below 5°. The salt thus obtained was warmed to 40°, β-acetaminoanthraquinone (26.5 g.) was introduced to the solution and the mixture was heated to 65°. To this suspended mixture, copper powder ("Naturkupfer C," 30 g.) was added gradually with constant stirring, while the temperature was maintained at 70° for an hour. At first the suspension was dissolved in yellow solution, and in a short time the whole was again crystallised to form a paste. After leaving overnight, the product was heated to 40° with stirring, and sodium hydroxide solution (90 g. NaOH in 300 c.c. of water) was slowly poured in until the product was dissolved. From the solution pyridine was removed by steam distillation and the copper salt was filtered off. The filtrate was cooled, 40 c.c. of hydrochloric acid was added and the brown precipitate was again removed by filtration. The solution was then neutralised with sodium bicarbonate and 400 c.c. of diphenylguanidine hydrochloride [$C_6H_5NH\cdot C(:NH)\cdot NHC_6H_5\cdot HCl$] solution (10%) was poured in, when brown precipitate was deposited. The precipitate was collected, washed with water, and dried. Recrystallised three times from alcohol, lemon-yellow crystals were obtained. The yield was 65.5 g. after one crystallisation, 80% of the theoretical. The salt was dissolved in

hydrochloric acid and treated with ferric chloride while hot. Orange crystalline aminoanthraquinone was deposited (0.4681 g. of the salt gave 0.1294 g. aminoanthraquinone. Found: 27.94. Calculated: 27.64%).

The sodium salt was obtained as a solution by treating the diphenylguanidine salt with sodium hydroxide and filtering it. The solution was brownish-yellow with strong, green fluorescence.

Sodium Salt of Leuco-β-anthraquinone-azo-α-naphthol Disulphuric Acid Ester, $C_6H_4(COSO_3Na)_2C_6H_3N{:}NC_{10}H_6OH(4)$. Aminoanthrahydroquinone sulphuric acid ester diphenylguanidine salt (8.1 g., 1/100 mol) was changed into sodium salt by treating with caustic soda solution (3 g. NaOH in 30 c.c. of water), filtering, and washing with water. The yellow solution (80 c.c.) was then cooled to 0°, 10 c.c. of hydrochloric acid was added and diazotised by dropping sodium nitrite solution (0.69 g. in 7 c.c. of water). The diazo-compound was not easily soluble in water and formed carmine-red precipitate. α-Naphthol (1.45 g., 1/100 mol) with sodium hydroxide (4 g.) was dissolved in 80 c.c. of water, and to this cold solution the above diazo-solution was poured in as a thin stream with constant stirring. A violet solution obtained was stirred for two hours more and heated to 80° for an hour. This was filtered and salted out with sodium chloride and sodium bicarbonate. The dark-violet, amorphous powder was collected, washed with salt solution, and dried. It gave a deep-reddish-violet solution and dyed the animal fibre violet-red in a weak acid-bath. This colour of the dyed fabrics may be changed red by oxidation with hot ferric chloride and hydrochloric acid, but the colour shade of this changed dye is not so fine as that of the β-isomer.

Sodium Salt of Leuco-β-anthraquinone-azo-β-naphthol Disulphuric Acid Ester, $C_6H_4(COSO_3Na)_2C_6H_3N{:}NC_{10}H_6OH(2)$. Diazotisation and coupling were carried out similarly to the above case. On salting out the dye with sodium chloride, violet precipitate was formed. This was collected, washed with salt solution, and dried. It was very soluble in water and produced a violet-red solution. Silk was dyed violet-red from its weak acid-bath, the colour was changed into bright-scarlet when oxidised with ferric chloride solution. The solution also gives a scarlet precipitate by the action of ferric chloride. The latter was recrystallised from tetraline, from which it separated in scarlet needles, m.p. 262°. The product thus obtained is β-anthraquinone-azo-β-naphthol. Kaufler[4] and Maki[5] synthesised the same substance from β-diazoanthraquinone and β-naphthol, and gave m.p. 262°.

Sodium Salt of Leuco-β-anthraquinone-azo-α-naphthylamine Disulphuric Acid Ester, $C_6H_4(COSO_3Na)_2C_6H_3N{:}NC_{10}H_6NH_2(4)$. Diphenylguanidine salt (8.1 g., 1/100 mol) was treated with sodium hydroxide solution and the solution of sodium salt (80 c.c.) was acidified with 10 c.c. of hydrochloric acid. This was cooled well and diazotised with sodium nitrite solution until the reaction was complete when tested with potassium-iodide-starch-paper. α-Naphthylamine (1.43 g., 1/100 mol) was dissolved in hot solution of hydrochloric acid (3 c.c. in 80 c.c. of water) and cooled rapidly. To this suspension of hydrochloride, the above diazo-solution was poured in and the sodium acetate solution (20 g. in 30 c.c. of water) was added gradually with vigorous mixing. The stirring was continued for 3 hours and the mixture became brownish. On standing overnight, it was heated to 80° for an hour and made alkaline with sodium hydroxide solution. From the filtered solution, a brownish-red precipitate was produced by salting out with sodium

(4) *Chem. Zentr.*, **1904**, I, 289.
(5) *J. Soc. Chem. Ind., Japan*, **32** (1929), 348 B.

chloride. This was collected and washed with sodium chloride solution. This substance is brownish-red in aqueous solution but in acid solution the colour changed to violet, and dyed the animal fibre deep-violet in weak acid-bath. It was changed reddish-violet by the action of oxidising agent.

Potassium Salt of Leuco-β-anthraquinone-azo-β-naphthylamine Disulphuric Acid Ester, $C_6H_4(COSO_3K)_2C_6H_3N{:}NC_{10}H_6NH_2(2)$. This dye was synthesised similarly to the above case. As its sodium salt was very viscid, the coupled solution was made alkaline with potassium hydroxide when a deep-scarlet solution was obtained. It was filtered and salted out with potassium chloride as brownish-red powder, which was collected and washed with a solution of the same salt. It dyes the fibre orange-red and turns violet-red by oxidation. Its shade is somewhat not clear.

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