DYES DERIVED FROM CHRYSOQUINONE.

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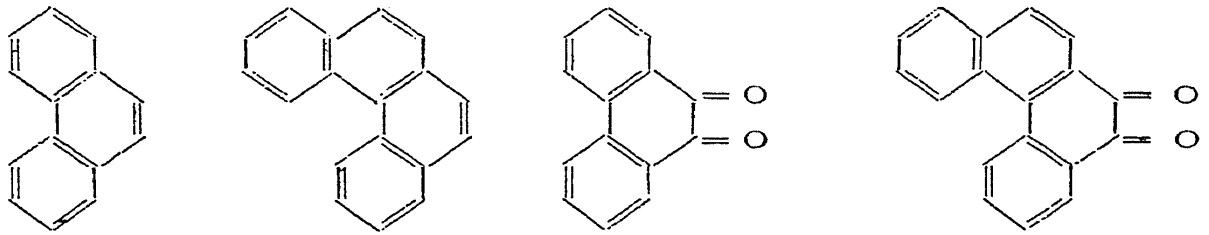
Until before the War, the hydrocarbon phenanthrene which is present in anthracene oil or green oil to the extent of about 30 per cent., and which is so interesting from the theoretical point of view, was almost a waste product and was scarcely manufactured in the pure state. In 1916, Mukherjee and Watson[1] prepared an interesting series of vat and other dyestuffs from phenanthraquinone. The work was continued by Watson and Dutt,[2] Sircar and Dutt[3] and Dutt,[4] and phenanthraquinone was shown to be capable of yielding quite an interesting array of colouring matters of great technical value, and some of these are actually being manufactured.

Chrysene or naphthphenanthrene is another hydrocarbon of coal tar obtained from the higher boiling fractions, which has not found any technical application as yet, and as such, it has still remained of purely theoretical interest. Structurally, the two hydrocarbons phenanthrene (I) and chrysene (II) and their oxidation products, phenanthraquinone (III) and chrysoquinone (IV) are so closely alike, that it is quite natural to expect that chrysene



(I) (II) (III) (IV)

would yield dyestuffs closely analogous to phenanthrene. This was supported by the observations of the present authors that chrysoquinone dyes wool and cotton from an alkaline hydrosulphite vat to beautiful orange shades. The present investigation was therefore undertaken with the object of preparing colouring matters from chrysene *via* chrysoquinone. The attempts were divided into three parts :

A. Attempts to Prepare New Hydroxy Derivatives.

It has been shown by Mukherjee and Watson[1] that the introduction of hydroxy groups into the molecule of phenanthraquinone even by methods of great value in the case of anthraquinone dyestuffs, namely by the action of fuming sulphuric acid and boron trioxide and also by concentrated sulphuric acid and manganese dioxide, was impossible on account of the ease with which the molecule was destroyed by oxidation by these reagents. Similar difficulties were met with in the case of chrysoquinone, and therefore, it was thought advisable to prepare the hydroxy derivatives through nitration, reduction and subsequent diazotisation followed by hydrolysis.

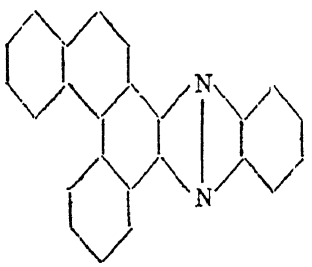
The nitration was successful, but the amines could not be obtained in any yield by reduction, as during the process of reduction with a metal and acid, the amines formed metallic complexes which were quite insoluble in water and consequently could not be satisfactorily decomposed with hydrogen sulphide.

B. Attempts to Prepare Anilino Derivatives of Chrysoquinone.

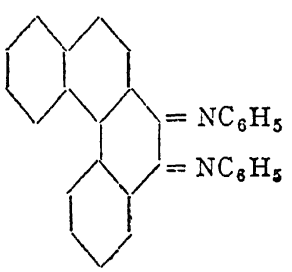
On account of serious difficulties in the methods to produce amino-derivatives from chrysoquinone, the possibilities of dyes in the form of hydroxy-chrysoquinones or acylamino-chrysoquinones were out of question. Consequently the bromination of chrysoquinone with formation of mono- and polybromo derivatives was the only practicable first step towards the production of anilino-chrysoquinones. It was possible to prepare three bromo derivatives of chrysoquinone, two of which were isomeric monobromo derivatives and the third was a pentabromo derivative. From these three bromo derivatives, three anilino derivatives were subsequently obtained, two of which were isomeric monoanilino derivatives and the third was a tetraanilino-monobromo derivative. These have got interesting dyeing properties and dye wool in violet shades.

C. Attempts to Prepare Condensation Products of Chrysoquinone with Aromatic Amines.

Chrysoquinone condenses fairly easily with aromatic amines with formation of chrysophenazines (V) and chrysoquinone-anilides (VI) and condensation



(V)



(VI)

products were obtained with the following amines : *o*-phenylene-diamine, *o*-aminophenol, 1 : 2-naphthalenediamine, *o*-anisidine, *o*-toluidine, *m*-toluidine, α-naphthylamine, β-naphthylamine, *o*-phenetidine, *p*-phenetidine, aniline, phenylhydrazine and 2 : 3-diamino-phenazine. The behaviour of all the azines and anilides obtained in this way was normal. All these compounds on examination were found to be good dyestuffs. They dye unmordanted wool from an acid-bath, and also cotton from hydrosulphite vat in various shades ranging from brilliant yellow to dark violet. Their absorption maxima range from 4,400 to 5,900 in Angstrom units.

Experimental.

Preparation of chrysoquinone.—The best oxidising agent for the preparation of chrysoquinone was found to be sodium dichromate in glacial acetic acid. Finely powdered chrysene (5 gm.) was added to a solution of sodium dichromate (22 gm.) in glacial acetic acid (50 c.c.) and the mixture refluxed on a sand-bath for nine hours. An equal volume of hot water was then added and the crystalline precipitate of chrysoquinone filtered off and recrystallised from boiling glacial acetic acid. Orange-red glistening plates, melting at 239° C. Yield, 4·75 gm.

Mononitro-chrysoquinone.—Chrysoquinone (1 gm.) was dissolved in concentrated nitric acid (S.G. 1·4, 10 c.c.) and the solution allowed to stand for 24 hours. The mixture on dilution with water yielded the nitro-derivative as a yellow precipitate, which was crystallised from nitrobenzene in glistening yellow needles, melting at 256–57° C. (Found : N = 4·85 ; $C_{18}H_9O_4N$ requires N = 4·62 per cent.)

Dinitro-chrysoquinone.—Chrysoquinone (1 gm.) was heated with concentrated nitric acid (10 c.c.) on a water-bath under reflux for three hours. On cooling the solution, the dinitro derivative separated out in orange-yellow crystals. The product was recrystallised from nitrobenzene in fine yellow prisms melting at 235° C. Yield, 0·75 gm. (Found : N = 8·81 ; $C_{18}H_8O_6N_2$ requires N = 8·59 per cent.)

Tetranitro-chrysoquinone.—Chrysoquinone (1 gm.) was treated with fuming nitric acid (S.G. 1·51, 10 c.c.) and the resultant solution heated on the water-bath under reflux for eight hours. On cooling the tetranitro derivative separated as an orange microcrystalline powder. The substance is insoluble in all the organic solvents. It can only be recrystallised from fumimg nitric acid in microscopic prisms, melting above 300° C. Yield, 1·21 gm. (Found : N = 12·5 ; $C_{18}H_6O_{10}N_4$ requires N = 12·78 per cent.)

Monobromo-chrysoquinone (*A*)—Chrysoquinone was dissolved in nitrobenzene (1 gm. in 20 c.c.) and the solution treated with bromine (1 c.c.) in

the same solvent (10 c.c.). The mixture was heated on an oil-bath under reflux at 110° C. for two hours. On cooling the monobromo compound crystallised out in yellow glistening leaflets melting at 246° C. (Found : Br = 24·1 ; $C_{18}H_9BrO_2$ requires Br = 23·7 per cent.)

Monobromo-chrysoquinone (*B*).—This substance was prepared in the same manner as the above-mentioned compound with the exception that glacial acetic acid was used as the solvent instead of nitrobenzene. The substance crystallised from glacial acetic acid in glistening yellow needles melting at 218° C. (Found : Br = 24·08 ; $C_{18}H_9BrO_2$ requires Br = 23·7 per cent.)

Pentabromo-chrysoquinone.—Chrysoquinone (1 gm.) was heated with a large excess of bromine (5 c.c.) in a sealed tube under pressure at 100° C. for six hours. The product was crystallised from nitrobenzene in glistening orange-yellow leaflets melting above 300° C. (Found : Br = 64·8 ; $C_{18}H_5Br_5O_2$ requires Br = 64·3 per cent.)

Monoanilino-chrysoquinone (*A*).—This was obtained from monobromo-chrysoquinone (A) by treatment with aniline in presence of copper-bronze according to the well-known method of Ullmann. The anilino compound was crystallised from a mixture of nitrobenzene (1 part) and glacial acetic acid in dark brown microscopic needles melting at 210–12° C. (Found : N = 4·17 ; $C_{24}H_{15}O_2N$ requires N = 4·01 per cent.)

Monoanilino-chrysoquinone (*B*).—This was prepared from monobromo-chrysoquinone (B) in the same way as the above-mentioned compound. It could not be crystallised, but was purified from alcohol. The substance is a dark green powder melting at 153–55° C. (Found : N = 4·47 ; $C_{18}H_{15}O_2N$ requires N = 4·01 per cent.)

Tetranilino-bromo-chrysoquinone.—This was obtained from pentabromo-chrysoquinone by Ullmann's reaction with aniline in the usual manner. It could not be crystallised, but was purified by solution in nitrobenzene and precipitation with alcohol. It is a dark brown powder melting at 291–93° C. (Found : N = 47 ; $C_{42}H_{29}O_2N_4Br$ requires N = 7·98 per cent.)

Chrysophenazine.—This was obtained by condensation of chrysoquinone with *o*-phenylene diamine in molecular proportions in boiling glacial acetic acid solution. It crystallised from nitrobenzene in glistening yellow needles melting at 207–08° C. and from glacial acetic acid in bright yellow prisms melting at 199° C. (Found : N = 8·08 ; $C_{24}H_{14}N_2$ requires N = 8·48 per cent.)

Chryso-1 : 2-*naphthazine.*—This was obtained in a similar way to the above, by using 1 : 2-naphthalene-diamine in place of *o*-phenylenediamine.

It crystallised from boiling toluene in bright yellow needles with a silky lustre. M.P. 238° C. (Found : N = 7·23 ; $C_{28}H_{16}N_2$ requires N = 7·36 per cent.)

Chrysophenoxozine.—This was obtained by condensation of chrysoquinone (1 mol.) with *o*-aminophenol (2 mols.) in hot glacial acetic acid solution. The dark brown precipitate obtained by pouring the reaction product into water was crystallised from alcohol in brown microscopic needles melting at 236° C. (Found : N = 6·5 ; $C_{30}H_{20}O_2N_2$ requires N = 6·8 per cent.)

Chrysoquinone-di-anilide.—This was obtained by the condensation of chrysoquinone with excess of aniline in glacial acetic acid solution. The reaction product was poured into dilute hydrochloric acid and the precipitated compound crystallised from a mixture of equal parts of nitrobenzene and alcohol in dark brown microscopic needles melting at 228–29° C. (Found : N = 6·42 ; $C_{30}H_{20}N_2$ requires N = 6·86 per cent.)

*Chrysoquinone-di-*o*-toluidide.*—This was obtained from chrysoquinone and *o*-toluidine in a similar way to the above. Brown needles melting above 300° C. (Found : N = 6·6 ; $C_{32}H_{24}N_2$ requires N = 6·4 per cent.)

*Chrysoquinone-di-*m*-toluidide.*—Obtained from chrysoquinone and *m*-toluidine as above. Brown needles melting at 163–65° C. (Found : N = 6·24 ; $C_{32}H_{24}N_2$ requires N = 6·4 per cent.)

*Chrysoquinone-di-*o*-anisidide.*—This was obtained by condensing chrysoquinone with excess of *o*-anisidine in boiling glacial acetic acid solution. After refluxing for three hours, the product was poured into dilute hydrochloric acid, and the precipitate crystallised from a mixture of equal parts of nitrobenzene and glacial acetic acid in dark brown needles. M.P. 160–63° C. (Found : N = 5·92 ; $C_{32}H_{24}N_2O_2$ requires N = 5·65 per cent.)

*Chrysoquinone-di-*o*-phenetidide.*—Chrysoquinone (2 gm.) was directly condensed with *o*-phenetidine (5 gm.) by heating under reflux for three hours. The product was poured into dilute hydrochloric acid and the precipitated compound crystallised from alcohol. M.P. 188–90° C. (Found : N = 5·44 ; $C_{34}H_{28}O_2N_2$ requires N = 5·6 per cent.)

*Chrysoquinone-di-*p*-phenetidide.*—This was obtained from chrysoquinone and *p*-phenetidide in the same way as above. M.P. 205–07° C. (Found : N = 5·56 ; $C_{34}H_{28}O_2N_2$ requires N = 5·6 per cent.)

Chrysoquinone-di-α-naphthylimide.—This was obtained from chrysoquinone and α-naphthylamine by condensation in hot glacial acetic acid solution, in the usual manner. The product crystallised from a mixture of equal volumes of nitrobenzene and glacial acetic acid in dark brown

needles melting at 198–200° C. (Found: N = 5·32; $C_{38}H_{24}N_2$ requires N = 5·47 per cent.)

Chrysoquinone-di-β-naphthylimide.—This was obtained from chrysoquinone and β-naphthylamine in the same way as the above. M.P. 203° C. (Found: N = 5·83; $C_{38}H_{24}N_2$ requires N = 5·47 per cent.)

Properties of the Chrysoquinone Dyestuffs.

Name of the compound (c.q. = chrysoquinone)	Shade of dyeing on wool from acid-bath	Shade of dyeing on cotton from hydrosulphite vat	Absorption maxima in wave-lengths
Chrysoquinone	Light yellow	Orange yellow	4400
Mononitro-c.q.	..	Light orange	4400
Dinitro-c.q.	..	Light brown	4560
Tetranitro-c.q.	..	Light brown	Insoluble
Monobromo-c.q. (A)	..	Light yellow	4350
Monobromo-c.q. (B)	..	Light yellow	4400
Monoanilino-c.q. (A)	Dark neutral grey	Dark grey	5850
Monoanilino-c.q. (B)	Dark reddish-violet	Brownish-violet	5900
Tetranilinobromo-c.q.	..	Bottle green	Insoluble
Chrysophenazine	Greenish-yellow	Greenish-yellow	4350
Chrysonaphthazine	Greenish-yellow	Greenish-yellow	4350
Chrysophenoxazine	Orange-yellow	Orange-yellow	4350
C.q.-dianilide	Medium yellow	..	4850
C.q.-di-*o*-toluidide	Medium yellow (broken tones)	..	4970
C.q.-di-*m*-toluidide	Dark neutral-grey	..	4900
C.q.-di-anisidide	Medium grey	..	5870
C.q.-di-*o*-phenetidide	Dark neutral-grey	..	5900
C.q.-di-*p*-phenetidide	Greyish-yellow	..	Insoluble
Chryso-2 : 3-diamido-phenazineazine	Dark reddish-violet	..	5050
C.q.-di-α-naphthylimide	Dark violet-red	..	5270
C.q.-di-β-naphthylimide	Light violet	..	5100
C.q.-di-phenylhydrazone	Dark brown	..	5150

Chrysoquinone-diphenylhydrazone.—This was obtained from chrysoquinone and excess of phenylhydrazine in glacial acetic acid solution, in the usual manner. It crystallised from a mixture of equal parts of nitrobenzene and glacial acetic acid in dark brown microscopic needles melting at 228–29° C. (Found : N = 12·65 ; $C_{30}H_{22}N_4$ requires N = 12·78 per cent.)

Chryso-2 : 3-*diamidophenazineazine.*—This was obtained from chrysoquinone and 2 : 3-diamidophenazine by condensation in glacial acetic acid solution. The substance was crystallised from nitrobenzene in almost black needles melting above 300° C. (Found : N = 12·8 ; $C_{30}H_{16}N_4$ requires N = 12·9 per cent.)

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4. Dutt, *ibid.*, 1922, **121**, 1951.