

The Chemistry of Chloranil

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THE object of the present paper is to draw attention to the application of chloranil (tetrachloro-*p*-benzoquinone) (I) as an intermediate for dyes and its use in various other industries. It is also an extremely interesting chemical as it undergoes a variety of reactions which are briefly discussed.

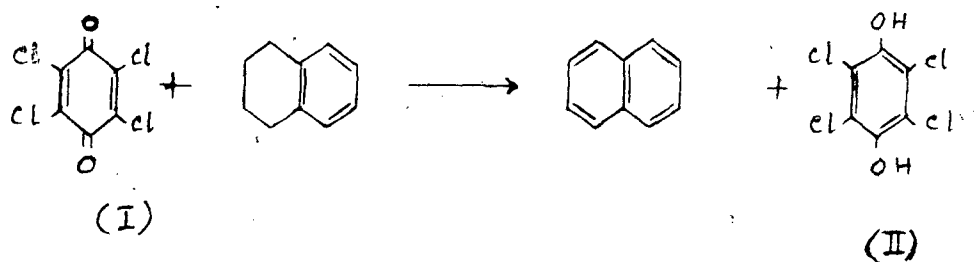
Chloranil (I) is prepared technically from *o*-chlorophenol or aniline by treatment with gaseous chlorine under acidic conditions.^{1, 2} It crystallizes as yellow prisms from benzene and as flakes from toluene or acetic acid melting at 290°. Its dipole moment is 0.86D. It shows three absorption maxima, one in the far ultraviolet, one in the near ultraviolet and the third in the visible region.

The two carbonyl groups that constitute the *p*-quinonoid system in (I) make the chlorine atoms highly labile and reactive. Substituents first replace one pair of *para* chlorine atoms. Under forcing conditions, all the four chlorine atoms are replaceable.

Reaction of (I) with aqueous caustic soda, sodium carbonate or bicarbonate gives the disodium salt of 2:5-dichloro-3:6-dihydroxy-*p*-benzoquinone (chloranilic acid).³ Treatment of (I) with dilute aqueous ammonia gives 2:5-dichloro-3-amino-6-hydroxy-*p*-benzoquinone, whereas concentrated alcoholic ammonia gives

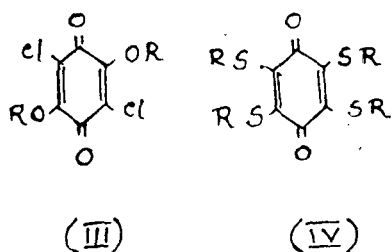
2:5-dichloro-3:6-diamino-*p*-benzoquinone. Reaction of (I) with aqueous sodium nitrite and methanolic potassium cyanide leads to 3:6-dinitro-2:5-dichloro- and 3:6-dicyano-2:5-dichloro-*p*-benzoquinone respectively, whereas manganese dioxide and hydrochloric acid gives hexachlorocyclohexa-1-ene-3:6-dione. Phosphorous trichloride or pentachloride reacts with (I) at 200° giving hexachlorobenzene. Interaction of dilute acidic solution of potassium bisulphite and (I) results in the formation of 2:5-dichlorohydroquinone-3:6-disulphonic acid whereas with concentrated solutions, hydroquinone-tetrasulphonic acid-*monosulphuryl* ester is obtained³.

Chloranil is easily reduced to tetrachlorohydroquinone (II), by sulphurous, hydrochloric, hydrobromic and hydriodic acids.³ Acetyl chloride reacts with (I) to give the diacetyl derivative of (II).³ (I) acts as an oxidising agent when it converts leuco base of Malachite Green to Malachite Green and dimethylaniline to Methyl Violet.³ It is a useful dehydrogenating agent being used for aromatising hydroaromatic compounds.^{4, 5} Dehydrogenation occurs by hydrogen transfer and (I) is converted into (II). Tetralin is thus converted into naphthene, tetrahydrocarbazole to carbazole, phenylcyclohexane to diphenyl, thujone to carvacrol, ethyl benzene to styrene etc.



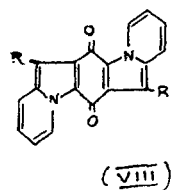
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Sodio-derivatives of aliphatic alcohols react with (I) to give generally 2:5-dichloro-3:6-dialkoxy-*p*-benzoquinones (III)³. However, in the case of methanol and ethanol, 2:6-dichloro-3:5-dialkoxy derivatives have been isolated in addition to (III) by K  hrmann.⁶ Chloranil reacts with potassium phenate in aqueous medium to give 2:5-dichloro-3:6-diphenoxy-*p*-benzoquinone (III, $R=Ph$).⁷ With excess of potassium phenate, tetraphenoxo-*p*-benzoquinone results. (III, $R=Ph$) is a very interesting intermediate, for in its reactions with pyridine, alkali, and sodio-derivatives of compounds containing a reactive methylene group, it gives the same reaction products as those obtained from (I). The phenoxy groups are thus preferentially replaced leaving the chlorine atoms unaffected. Since chloranil also gives the same reaction products as (III, $R=Ph$), the substituent groups in the above reactions with (I) are attached to the 2:5-positions in the quinone nucleus. Aliphatic and aromatic thiols react with (I) to give tetrakisalkyl- or tetrakisaryl-*p*-benzoquinones (IV)^{8,9}.

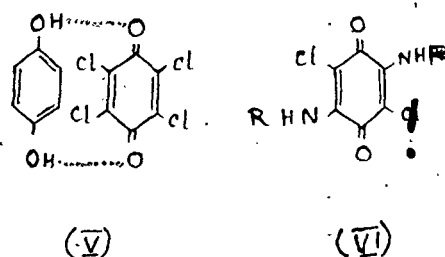


R = Alkyl or aryl group

Chloranil forms addition compounds with a large number of organic compounds like phenylhydrazone, diphenylamine, pyrrole, indole, carbazole, etc. With hydroquinone, it forms a quinhydrone (V). Addition compounds from



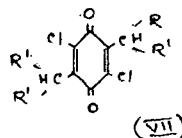
naphthalene, acenaphthene, durene etc. have also been described.³



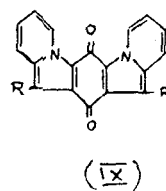
R = Alkyl or aryl group

Aliphatic and aromatic primary amines react with (I) to give 2:5-dialkylamino or diarylamino-3:6-dichloro-*p*-benzoquinone (VI).³ The reaction between (I) and amines is of great technical importance in the synthesis of oxazine and thiazine dyes. The utilisation of (I) as a dye intermediate will be discussed later.

Chloranil reacts with sodio derivatives of compounds containing a reactive methylene group such as, ethyl acetoacetate, diethyl malonate, acetylacetone etc. to give compounds of the type (VII).¹⁰ However, when the condensation between (I) and compounds containing a reactive methylene group is carried out in pyridine, 5:11-substituted benzo-(1:2-b, 4:5-b')-dipyrrocoline-6:12-quinone (VIII) and 5:7-substituted benzo-(1:2-b, 5:4-b')-dipyrrocoline-6:12-quinone (IX) are formed which are useful as vat dyes.¹⁰

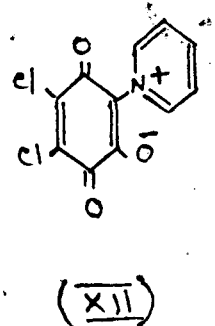
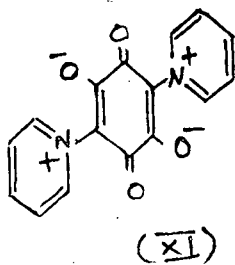
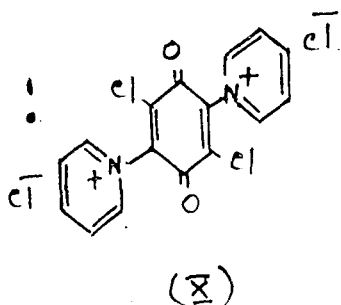


R = COOEt, COCH₃, COPh etc.
 R' = COOEt, COCH₃, COPh etc.



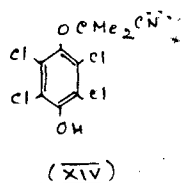
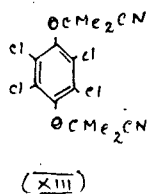
Interaction of chloranil and excess of pyridine gives a pyridinium complex (X) which on treatment with water yields the

water-soluble betaine (XI). With equimolar quantities of (I) and pyridine the *mono*-betaine (XII) is obtained.¹¹



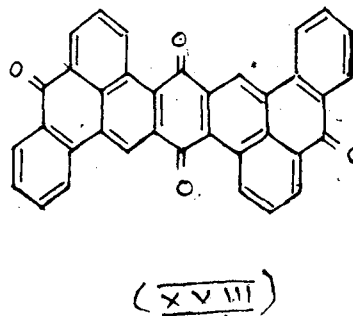
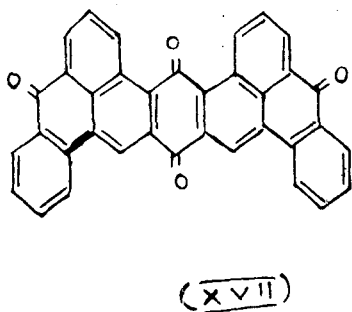
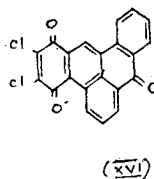
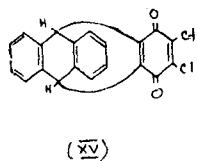
Chloranil reacts with *α,α*-azo-isobutyronitrile in chlorobenzene at 100° to give a mixture of (XIII) and (XIV). The

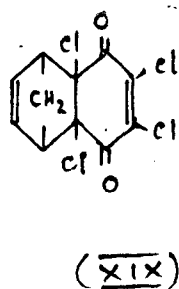
formation of the above is explained on the basis of the formation of dimethyl cyanomethyl radical.¹²



Being a *p*-benzoquinone derivative, (I) takes part in Diels-Alder reaction. With anthracene, it gives (XV) and with 10-

methylene-9-anthranol, (XVI), (XVII) and (XVIII) are formed.¹³





Cyclopentadiene reacts with (I) to give (XIX). The synthesis of 2:3dichloro-1-4-naphthoquinone from (I) and butadiene has recently been investigated by Gaertner.¹⁴

The utilisation of (I) as a polymerisation inhibitor has been recently investigated. (I) can be used with advantage for the polymerisation of methyl acrylate, vinyl chloride, isoprene etc. With styrene (I) forms a copolymer in presence of benzoyl peroxide. The use of chloranil for cold mastication of rubber has recently been suggested. The tensile strength of plasticised cellulose ethers can be greatly increased by admixture with chloranil. During the polymerisation of butadiene, the addition of (I) gives soft rubber. Thus in the synthetic rubber and plastic industry chloranil is being increasingly used.

Chloranil is also used as an agricultural insecticide and antimildew agent in the United States, where it is marketed as "Spergon".

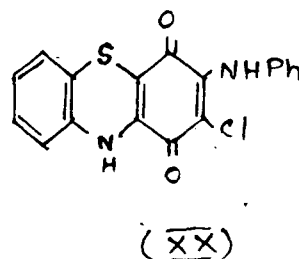
Dyes derived from chloranil:—

As already mentioned, chloranil, is an important intermediate for the manufacture of oxazine and thiazine dyes^{15, 16}. A few vat dyes are also known from chloranil.

Some of the 2:5-diarylamino-3:6-dichloro-*p*-benzoquinones (VI) obtained

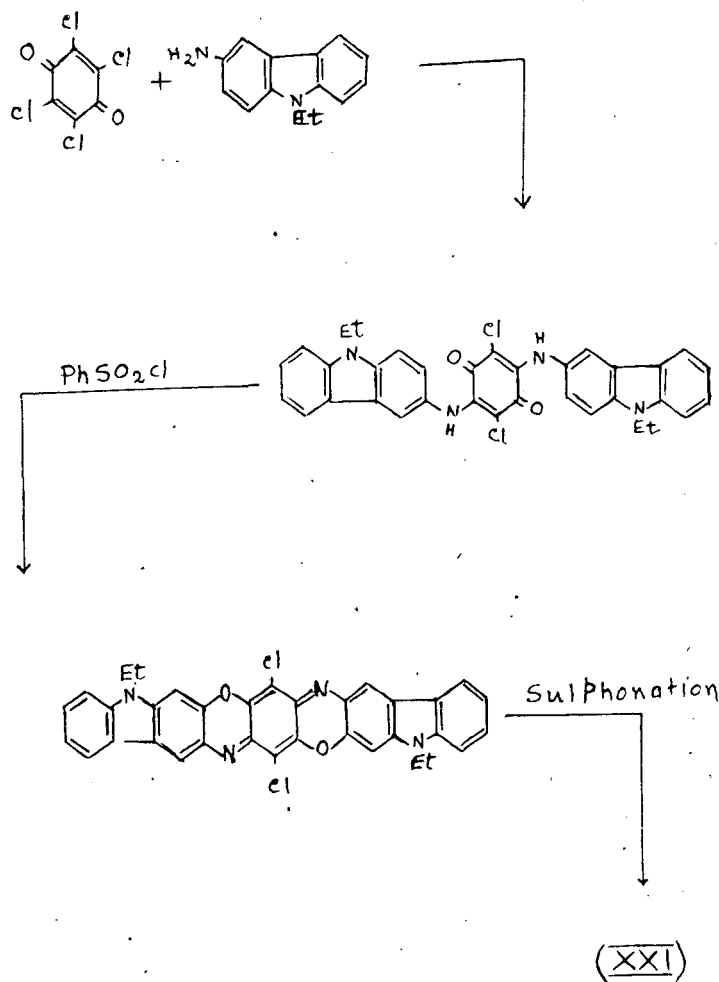
from (I) and arylamines are mordant dyes for wool. The arylamines used contain carboxylic and hydroxyl groups as in *p*-aminosalicylic acid, *o*-aminosalicylic acid, 4-amino-2-naphthol-3-carboxylic acid etc. Mordant dyes for wool are obtained by treating (I) with sodium sulphide, sodium thiosulphate or potassium thiocyanate and condensing the resulting product with 4-aminodiethylaniline-thio-sulphonic acid.

Helindone Brown CV (XX), a vat dye for wool with exceptional fastness for light and milling, is obtained by treating (VI, R=Ph) with sodium hydrogen sulphide followed by oxidation. Heating (I), aniline, sulphur and water at 165°, Helindone Khaki CR is obtained.

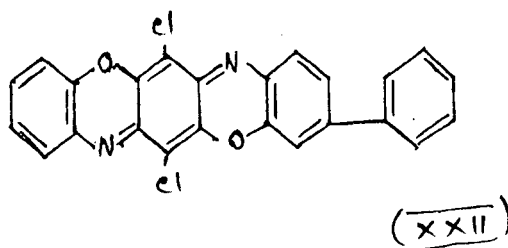


Oxazine dyestuffs constitute the most important class of dyes from (I). Sirius Supra and Sirius Light colours include a few dyes derived from chloranil. These possess excellent light fastness. Sirius Supra Blue FFRL (XXI) is prepared from (I) and 3-amino-N-ethylcarbazole as shown below.

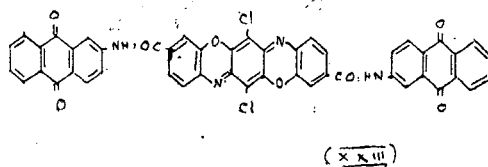
Sirius Light Blue F3RL is obtained from (I) and 3-amino-carbazole. Other important dyes in this group are Sirius Light Blue F3GL (from chloranil and 1-aminopyrene), Sirius Light Violet FFR (from chloranil and aminofluorene), Sirius Light Blue FF2GL (from chloranil and 4-aminodiphenylamine-2-sulphonic acid) and Sirius Light Blue FFB (from chloranil and 4-chloro-4'-aminodiphenylamine-2'-sulphonic acid).



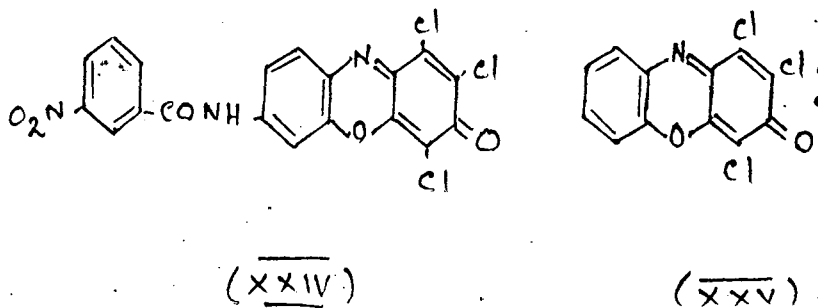
Unsymmetrical dioxazine dyes of the type (XXII) are also known.



A French patent¹⁷ describes the synthesis of dyes of the type (XXIII) by condensing (I) with arylamine carboxylic acids and cyclising the resulting product to the dioxazine followed by condensation with aminoanthraquinones.



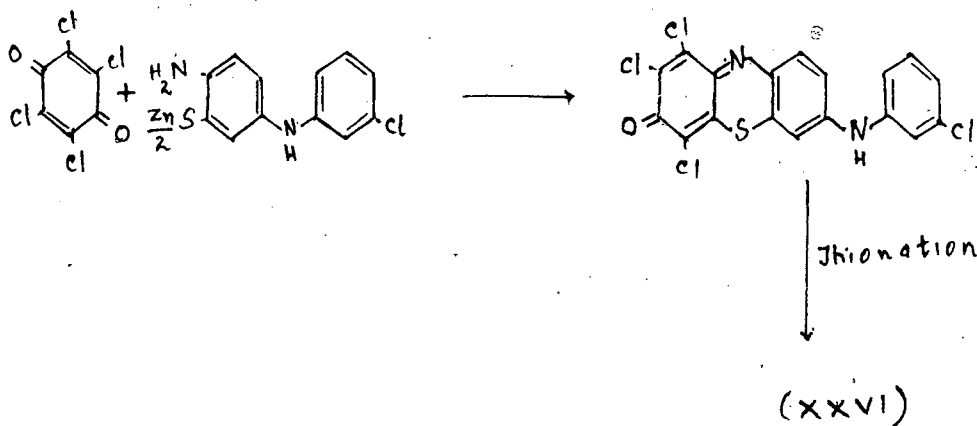
- Synthesis of sulphur dyes from (I) has also been described. Immedial Bordeaux
 • 3BL is prepared by the thionation of the



Thionation of (XXV) gives Immedial New Blue 5R.

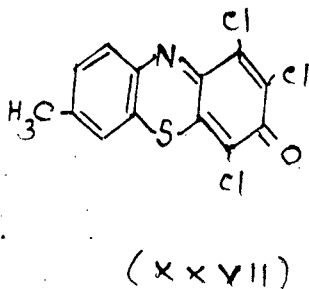
Several thiazine dyes are also prepared

from (I). Indanthrene Printing Blue 3R (XXVI), the most important vat printing colour in this series is prepared as shown below.



2-Mercapto-*p*-toluidine and (I) react together to give the thiazine (XXVII), which on thionation gives Immedial Red Brown CL3R. Similarly from the

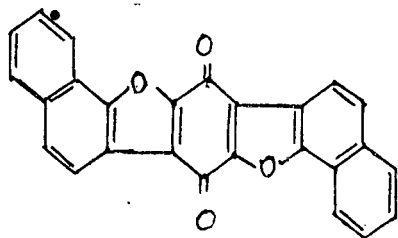
thiazine obtained from (I) and 2-mercapto-*p*-phenitidine, is obtained Immedial Red Brown CL4B.



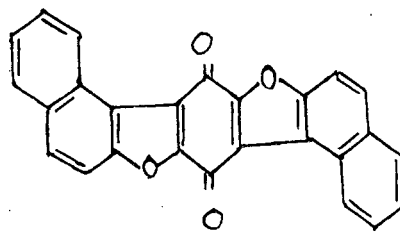
Chloranil has been employed in the elucidation of the constitution of Hydron Blue, an important sulphurised vat dye obtained from carbazole indophelol¹⁸.

Recently, the synthesis of vat dyes by

the condensation of chloranil with α - and β -naphthols and their derivatives has been undertaken. Condensation of (I) with α -naphthol and β -naphthol gives (XXVIII) and (XXIX) respectively.¹⁹



(XXVIII)



(XXIX)

The synthesis of substituted benzodipyrrocolinequinones from (I), compounds containing a reactive methylene group and pyridine has already been referred to earlier.¹⁰ Some of these dye attractive shades on cotton as vat dyes.

References :

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