ANTHRAQUINONE-ACRIDONES

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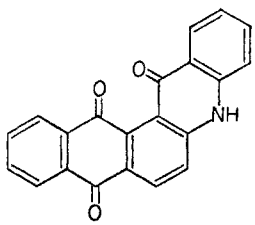
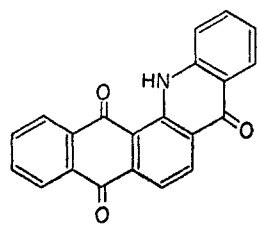
CONTENTS

I. Introduction

The anthraquinone-acridones comprise two isomeric six-membered ring systems containing five fused rings, one junction being angular, and having one nitrogen atom as the hetero element; thus, they are heterocyclic polynuclear quinones.



I
(-1,2- series)



II
(-2,1- series)

The -2,1- series form an important group of anthraquinone derivatives, some of which are of technical value as commercial dyes and were discovered and developed in the large dye laboratories in Germany during the early twentieth century. Exploratory work has been continued and extended along the same or closely related lines, mainly by the staffs of research laboratories of companies engaged in the dye industry.

The statements made in the preceding paragraph may well be illustrated by recounting the history of the discovery of the first anthraquinone vat dye, indanthrone (7, 44a), and its resulting exploitation. Indanthrone contains seven fused six-membered rings, one of which contains two nitrogen atoms, and is discussed at length in a recent book (135). It is one of the most stable dyes known, being unaffected by most reagents that destroy other dyes (67a).

After a quarter of a century of intensive research on the chemistry of indigo and related compounds, it was but a natural extension of the work to include its benzologs. In the case of anthracene, 2-anthraquinonylglycine (3,4-phthaloylphenylglycine) was made and submitted to alkaline fusion. The product was a blue dye, but not an indigoid; the stability and light fastness of the dyeings exceeded the standards set for indigo. After some time, it was found that 2-aminoanthraquinone and not the glycine derivative was the source of the dye (135). The discovery (1901) of indanthrone is attributed to René Bohn (1862–1922), working in the laboratory of the Badische Anilin- und Soda Fabrik (33), but Roland Scholl (Technische Hochschule at Karlsruhe) took the leading part in the elucidation of its structure (127, 130).[1] Impurities, formed as by-products in the syntheses, were alizarin and the yellow dye flavanthrone; the latter resulted

[1] The three great names in early anthraquinone chemistry are Carl Graebe, René Bohn, and Roland Scholl. The collaboration of these investigators was very successful. From it there arose many variations and extensions.

when the operating temperature was too high. When the structure and chemistry of this yellow dye were elucidated by Scholl (128), the logical extension to the analogous fused system without nitrogen was undertaken. This led to the discovery of the pyranthrone series of dyes. The latter may be considered as derivatives of the hydrocarbon pyrene, whereas flavanthrone is derived from a diazapyrene.

Most of the polynuclear aza compounds are dyes or intermediates for dyes and are mentioned only in the numerous patents. Melting points are seldom given, as they are extremely high and have never been determined, but colors, especially of sulfuric acid solutions or of alkaline dithionite "vats," are of more utility. It is impractical to include all the anthraquinone-acridones, "since the number . . . runs into the thousands" (113b). The references given are largely limited to the older ones and to those needed for illustration.

The portions selected for inclusion, therefore, comprise the history, nomenclature, methods of preparation of the various series, emphasis on their chemical behavior, general properties, and less familiar reactions. For instance, among the anthraquinone-acridones the stepwise introduction and removal of halogen is extensive and involved but of considerable interest and technical importance.

Color is one of the physical properties of polynuclear compounds frequently listed as characteristic. Most oxygen-containing derivatives dissolve in concentrated sulfuric acid, forming highly colored solutions. Quinones are reduced by alkaline sodium dithionite to colored "vats," from which vegetable fibers can usually be dyed; subsequent oxidation gives a different color. These three types of behavior could be listed in tables and, where the substances are homogeneous, might be useful. They have not been so included, however, for the following reasons. In most cases the substances are not "pure." Closely related compounds show such slight variations that only absorption spectra are distinctive. Furthermore, each observer describes the colors as he sees them, using words that have a personal significance and might convey an entirely different meaning to another person. It would be most useful, therefore, if agreement could be reached as to precisely what the word describing a given color signifies, and numbers could be assigned to include various ranges and shades. Fortunately, this problem has been recognized and partially solved by inclusion of a Colour Index Hue Indication Chart in Volume 4 of the second edition of the *Colour Index* (44). With the exception of the bright reds (scarlets, magentas, pure reds), the hues shown are reasonably good.

Condensed ring systems have to be built up by cyclizing suitably substituted intermediates having fewer rings. In these intermediates the reactive groups must be in adjacent (ortho) positions; one is usually an amino or a carboxyl group. The most general procedure involves a substituted diphenylamine-*o*-carboxylic acid and is known as the Ullmann reaction.[2] While this reaction has

[2] Fritz Ullmann (1875–1939) was a student of and assistant to Carl Graebe in Geneva for twelve years (1893–1905). In 1905, at the invitation of O. N. Witt, he moved to Berlin as first assistant and docent in the Technologische-chemische Institut der Technischen Hoch-

been discussed in great detail elsewhere (1a), a brief account is appropriate at this point, since frequent reference is made to it throughout the text.

A. ULLMANN REACTION

This reaction consists essentially in the formation of a substituted diphenylamine from a halogen-substituted aromatic compound and an aromatic amine in the presence of a catalytic amount of copper (the metal, its oxide, or a salt) with a halogen acid acceptor and in a high-boiling solvent (nitrobenzene). The effect of copper[3] is extraordinary; for example, 1 g. of copper is sufficient to effect the condensation of 2000 kg. of *o*-chlorobenzoic acid[4] and aniline, to give a 97 per cent yield of diphenylamine-*o*-carboxylic acid (137). To permit cyclization there must be a potential carboxyl group ortho to the amino group. While the free acid is most commonly employed, esters, amides, and nitriles have also been used, as will be shown under the individual compounds. The best evidence indicates that the Ullmann reaction follows a free-radical mechanism (152).

A few factors require mention. A bromine atom on the anthraquinone nucleus is more readily displaced than chlorine (150). With 1,3-dibromoanthraquinone only the bromine in the 1-position reacts (148). Amyl alcohol has been claimed to be superior to nitrobenzene as a solvent (114); cyclohexanol has also been used (78). Of the alternate possibilities, the combination of 1-chloroanthraquinone and anthranilic acid is preferable to that of 1-aminoanthraquinone and *o*-chlorobenzoic acid (147). 1-Nitroanthraquinone can be substituted for the chloro derivative, since the nitro group is as readily replaced.

Since the free acids always undergo a certain amount of decarboxylation at the high temperature used, as well as formation of metal salts, esters are frequently employed (14, 20, 39, 53, 56, 108, 147). The product is likewise an ester, which offers no difficulty in subsequent operations. If an *o*-chlorobenzoic ester is employed, it may be advantageous to condense it with a leuco-1,4-diaminoanthraquinone, only one of the amino groups reacting (53). The addition of

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schule Berlin, soon becoming a professor. Many students took their doctorates with him. He returned to Geneva in 1925.

Ullmann is best known for his introduction of copper catalysts (e.g., Naturkupfer) and their application to what is now known as the Ullmann reaction. This discovery probably led him to specialize in acridine chemistry (possibly encouraged by Graebe), in which field he became an early, prolific investigator. In addition to this work, he adapted the use of copper to the Fittig reaction, introduced dimethyl sulfate and methyl *p*-toluenesulfonate as methylating agents, and called the attention of his friend, Paul Ehrlich, to the diaminoacridinium dyes. He devoted most of his life to the preparation of the *Enzyklopädie der technischen Chemie*, which is to the technician what Beilstein's *Handbuch der organischen Chemie* is to the organic chemist. His experimental work, therefore, gradually diminished after the anthraquinone-acridones were placed on a firm basis (121).

[3] Before the advent of Jena glass, much laboratory apparatus was made of copper. The metal may have had an unrecognized catalytic effect,which would account for the frequently reported inability of later experimentalists to repeat the work described earlier.

[4] For many years *o*-chlorobenzoic acid, a by-product in the formation of *o*-chlorobenzaldehyde, had no application and was accumulated until it formed a small hill (60).

magnesium oxide, calcium carbonate, or the like is said to inhibit decarboxylation.

The structure of the product from an Ullmann reaction is evident from the starting materials. They can be synthesized from starting materials in which the location of substituents is known. This is of particular value when dealing with the identification of substitution products obtained in other ways. When sulfuric acid is used for cyclization, a preliminary treatment with acetic anhydride to form the *N*-acetyl derivative (15, 39, 96) seems to give better results, since there is less tendency for decarboxylation to take place.

B. SCHOLL REACTION

A second method of forming condensed ring systems is by the Scholl reaction (129, 131), which is the intramolecular dehydrogenation of aromatic rings to form a new ring system (107)[5] and is of particular value for converting anthraquinonylamines to carbazoles (52), as described under anthraquinone-2,1-acridone amides (Section II,G,4, page 1018).

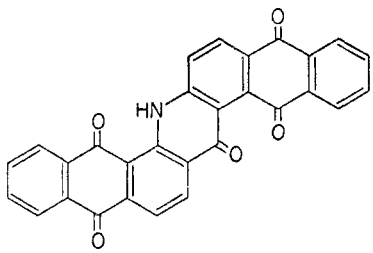
II. ANTHRAQUINONE-2,1-ACRIDONES

A. HISTORY AND NOMENCLATURE

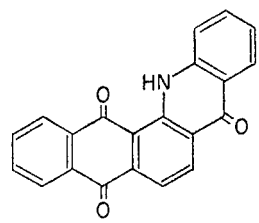
The first representative of the series, which had seven fused rings (Ia), was obtained by an alkaline fusion of 2-methyl-1,2′-dianthraquinonylamine and was revealed in a German patent filed by the Badische Anilin- und Soda Fabrik on October 28, 1906 (8). The first one to be prepared by a synthesis that showed its structure has five fused rings (II) and was disclosed by Ullmann in German patent 221,853, filed on March 3, 1909 (140). It was more completely described in the contemporary chemical journals (139, 149) and was the anthraquinone-acridone from which the name of the series originated. Progress in the field was rapid, judging by the number of patents issued over the following ten years;

[5] Roland Scholl was born in Zurich on September 30, 1865. He attended school there and then studied in Würzburg where his uncle, Johannes Wislicenus, was head of the Chemistry Department; later he worked in Zurich as chemical assistant to Professors Hantzsch and Bamberger, and graduated in Basle in 1890. His thesis dealt with the action of nitrogen tetroxide on oximes; this led to his studies on fulminic acid, which he concluded to be carbonyl oxime, C=NOH. In 1893 he became a lecturer in chemistry, first at the university and then at the Eidgenossische Hochschule in Zurich. In 1896 he became professor of chemistry in Karlsruhe; he moved to Graz in 1906, and finally to Dresden in 1917. A great many publications (about one hundred eighty) describe his research in various fields. After early work on oximes and nitriles, his work on polycyclic compounds began with structural investigations on vat dyes of the indanthrone series, which was enriched by the subsequent discovery of the golden-orange dye pyranthrone. This interest was extended to benzanthrone and the synthesis of the polynuclear hydrocarbons pyrene, perylene, and coronene, which in turn led to dehydrogenation and to desmotropic, mesomeric, and halochromic problems in general. His last years were deeply saddened by nearly complete blindness and the loss of his home and belongings in Dresden in February 1945. He was nearly 80 years old when he died of exhaustion in a refugees' camp on August 22, 1945 (66a, 153).

subsequent work has dealt mainly with polyhalogenated derivatives and very complex structures that are capable of being converted to substances containing the carbazole ring system.

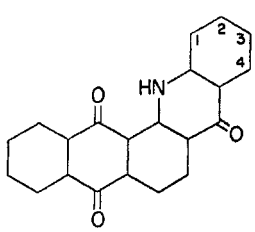


Ia



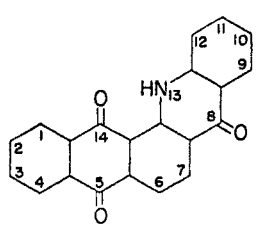
II

As so frequently happens with rapidly developing chemical products, the nomenclature of the intermediates and dyes is very confusing. The dyes were at first regarded as derivatives of acridone. The parent substance (II) has been variously called anthraquinone-2,1-acridone, anthraquinone-2,1-(*N*)-benzacridone, anthraquinone-2,1(*N*)-1′,2′(*N*)-benzacridone (30a), anthraquinonephenacridone (132), phthaloyl-2,1-acridone, phthaloyl-3,4-acridone (30a, 66), 2,3-α-naphthacridine-5,8,13(14)-trione (used by *Chemical Abstracts* until 1936), and naphth[2,3-*c*]acridine-5,8,14-(13*H*)trione, and has been indexed under the last name in *Chemical Abstracts* since 1936. The class may also be considered as naphthoquinone-acridones or anthraquinone-quinolones (1b). According to the "a" system, anthraquinone-2,1-acridone (II) is 13-aza-5,8,14-trioxo-13*H*-dibenzo[*b*,*h*]phenanthrene; since the first-mentioned name is well established, even though inaccurate, it will be retained and used in this section. The familiar orientation (IV) will also be employed in spite of the fact that it makes the numbering awkward. Various methods of representation that have been used are shown in structures III to IX.

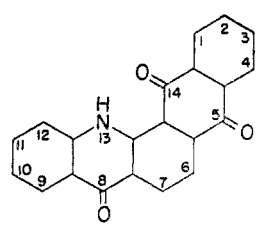


III

(Familiar; used in *Chemical Abstracts* until 1936)

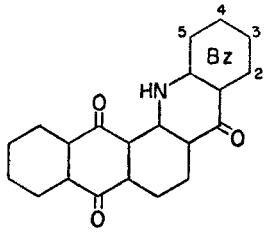


IV (1b, 66, 113b)

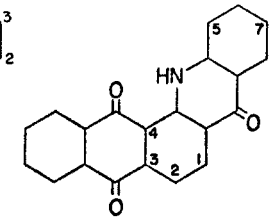


V (122, No. 3296)

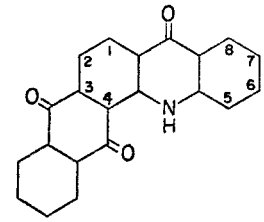
(Currently used by *Chemical Abstracts*)



VI (108)

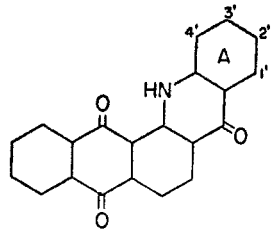


VII



VIII (30a)

Phthaloyl-3,4-acridone



IXa (67)

IXb (115)

IXc (92)

IXd (75)

IXe (40, 88)

B. PREPARATION

In most instances the preparation of anthraquinone-2,1-acridones starts with an arylaminoanthraquinone which, in either the anthraquinone or the aryl ring, has a COOH, COOR, $CONH_2$, CN, or CH_3 group ortho to the amino group. The arylaminoanthraquinones themselves are usually formed by the Ullmann reaction already discussed.

1. Formation from 1-arylaminoanthraquinone-2-carboxylic acids

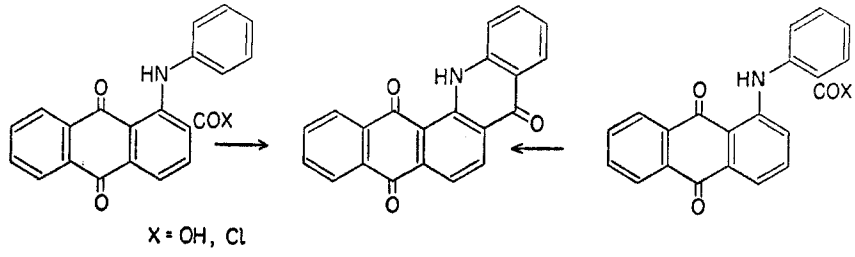
(a) Dehydration

Dehydration to close the acridone ring may be brought about (*a*) by heating in a high-boiling solvent (10, 15) or by the use of such reagents as (*b*) sulfuric acid (49), (*c*) chlorosulfonic acid, (*d*) acetyl chloride, or (*e*) acetic anhydride (145). Concentrated sulfuric acid, at about 100°C., is commonly employed and is satisfactory as long as there is no simultaneous sulfonation (150); 90 per cent sulfuric acid is claimed to give a better yield in some instances. The action of acetyl chloride and acetic anhydride may be very rapid. Some *N*-acetyl derivatives are also cyclized by heating (145–147). Acetyl derivatives are often made prior to dehydration with sulfuric acid (15, 39, 96).

(b) Formation via the acid chloride (5)

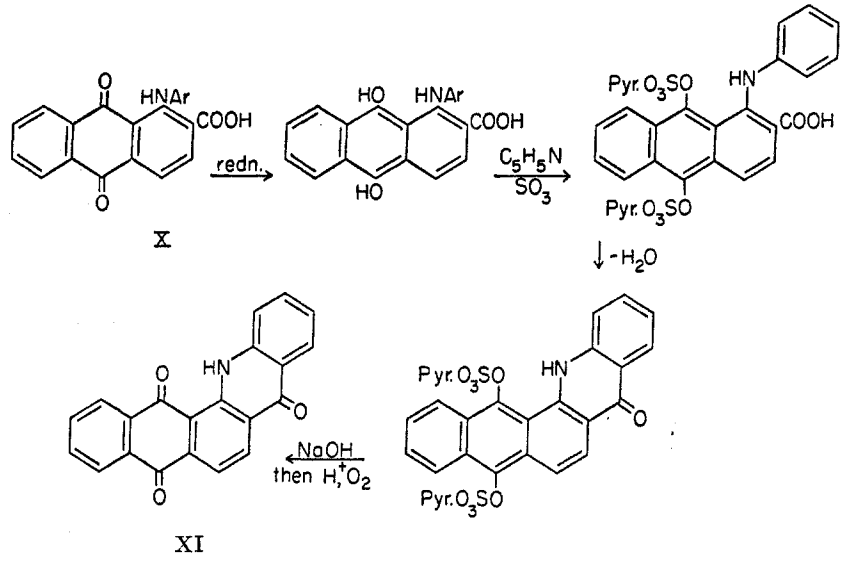
This is probably the best method. While phosphorus pentachloride (9, 17, 147) was often specified in the older patents, it seems likely that thionyl chloride would be currently employed to convert the acid into its chloride. In some instances cyclization is achieved simply by heating as long as hydrogen chloride is

evolved (147), but in others anhydrous aluminum chloride is needed. The acid chloride has also been cyclized by alkaline dithionite (10), but it is probably a complex reaction.



(c) Formation via the ester

Esters possess some advantages over acids in that they are more soluble, and there is less decarboxylation and no formation of metal salts. Methyl, ethyl, and benzyl (39, 40, 108, 133) esters are commonly employed. The esters are, of course,



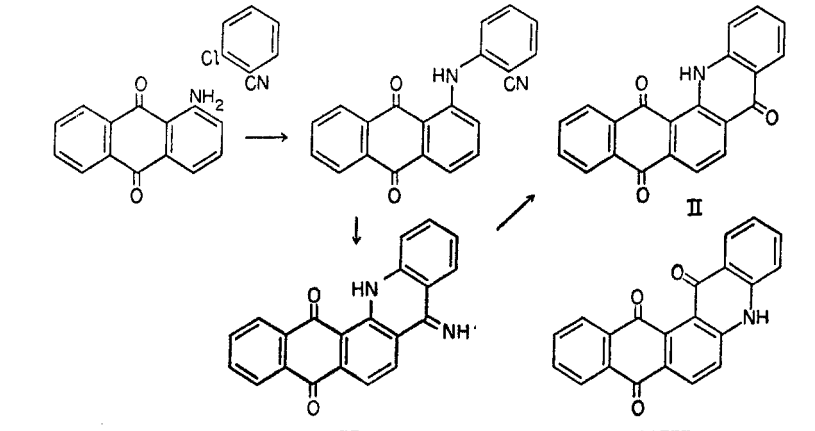
hydrolyzed during the course of succeeding reactions, particularly in the alkaline medium, when zinc dust and ammonia (14) or alkaline dithionite, with exclusion of air, are used (74). In these instances it appears that a leuco-ester is cyclized. This is very obvious when the reduction is carried out so as to obtain a leuco-sulfuric ester.[6] For instance, a 1-arylaminoanthraquinone-2-carboxylic acid (X) in pyridine, using sulfur trioxide, oleum, or methyl chlorosulfonate in the presence of copper, forms a solution containing the cyclized anthrahydroquinone-sulfuric acid ester (XI). If the solution is made alkaline and the pyridine distilled,

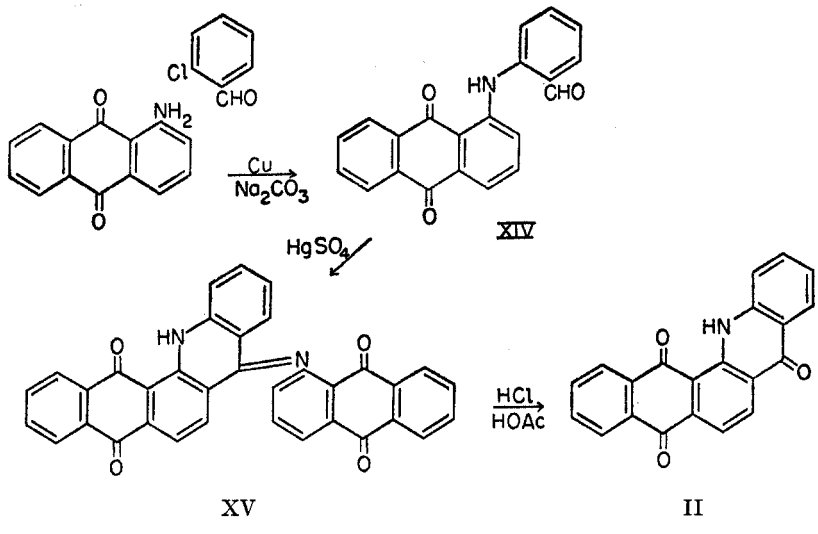
[6] The voluminous literature dealing with the preparation of leuco sulfuric esters is given in the *Colour Index* (44) under No. 59051A.

cotton may be dyed as usual from the vat, or the dye may be precipitated in the usual way by oxidation (146).

2. Schaarschmidt's nitrile method

Schaarschmidt undertook to devise a procedure for the synthesis of polynuclear heterocyclic compounds, using a nitrile and avoiding the isolation of an intermediate amide or acid (125a, 126). His route started with an ortho-substituted nitrile, which was condensed and cyclized in one operation by heating with sulfuric acid. The reaction probably proceeded by way of an imine (XII); this was not isolated, but color changes suggested the likelihood of its formation. As with the Ullmann reaction, the cyano group can be in either the anthraquinone or the amine component. It is advisable to avoid long heating of the sulfuric acid mixture, to minimize sulfonation. Schaarschmidt's procedure is particularly useful for preparing the isomeric anthraquinone-1,2-acridones (XIII) (page 1025) and multi-ring compounds.



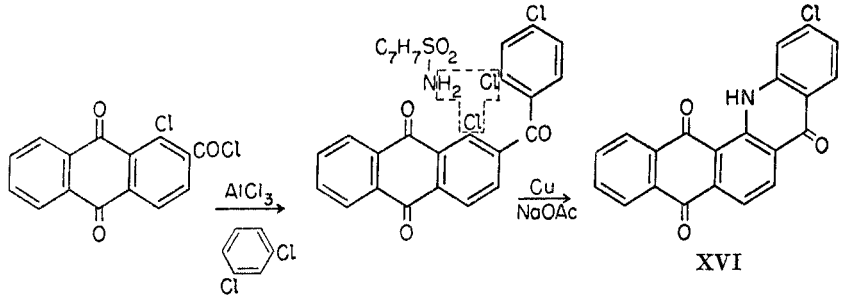


A variation of this synthesis employs an α-aminoanthraquinone and an excess of *o*-chlorobenzaldehyde (106). In this case the intermediate diphenylamine (XIV) can be isolated; upon treatment with a little mercuric sulfate a second mole of the amine reacts to give the arylimide (XV). The latter is formed in one operation if the mercury salt is added to the first reaction mixture. Upon hydrolysis with hydrochloric and acetic acids, the anthraquinone-acridone (II) results. This reaction was discovered (106) in the study of the formation of a blue vat dye of unknown constitution, obtainable from the same components (110, 116).

3. Miscellaneous methods

(a) *p*-Toluenesulfonamide procedure

An interesting procedure (110), which involves the use of *p*-toluenesulfonamide and starts with the 1-chloroanthraquinone-2-carbonyl chloride, is outlined herewith.



XVI

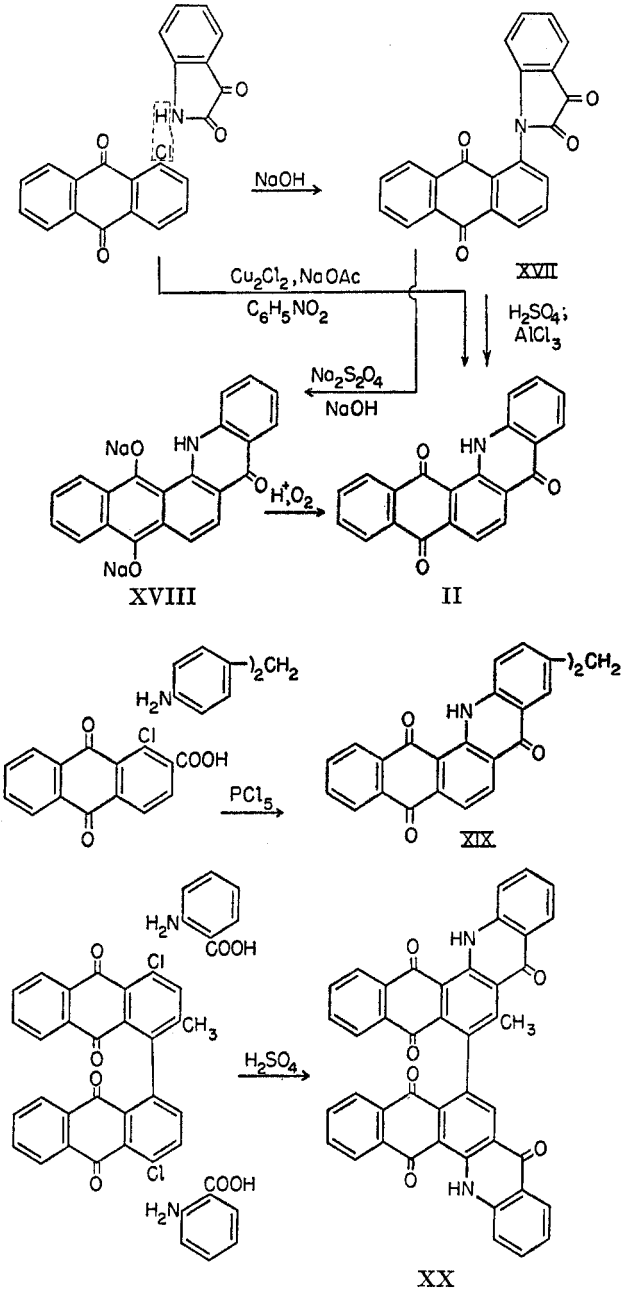
(b) Isatin procedure

The isatin route consists in making an anthraquinonyl-isatin (XVII), which may or may not be isolated (48, 50, 81). For instance, a mixture of 1-chloroanthraquinone, isatin, cuprous chloride, sodium acetate, and hot nitrobenzene (48) gives the familiar anthraquinone-2,1-acridone (II). Under alkaline conditions the isatin intermediate (XVII) can be isolated and subsequently cyclized by sulfuric acid, by anhydrous aluminum chloride in hot nitrobenzene, or by alkaline sodium dithionite. With the latter, the vat (XVIII) of the anthraquinone-acridone is formed and can be used directly for dyeing cotton, or the dye can be isolated after aeration.

(c) Compounds having two anthraquinone-acridone residues

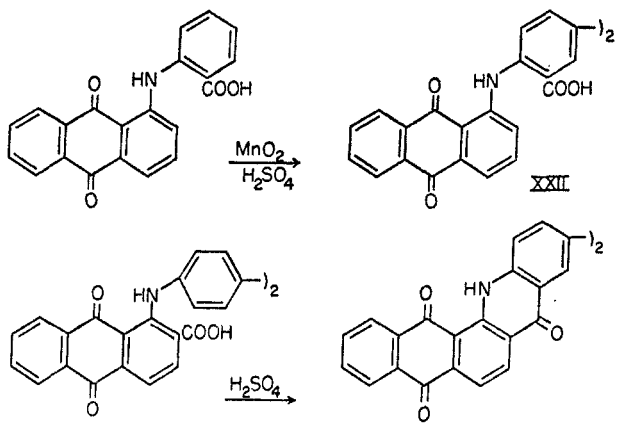
Bis compounds can be made in several ways, most of which are modifications of those already outlined. Thus, by use of an aromatic diamine with 1-chloroanthraquinone-2-carboxylic acid (9) or a 1,1′-dichlorodianthraquinonyl and an anthranilic acid (13), substances having structures XIX and XX result.

When benzidine is condensed with 1-chloro- or 1-nitroanthraquinone-2-car-



boxylic acid and then cyclized (9), a commercial dye, Indanthrene Red Brown R (XXI) (31, 61, 148), is obtained. In actuality, the commercial dye is a mixture of three substances (31, 148). The same product was also obtained from *N,N'*-bis(1-anthraquinonyl)benzidine-*o*-dicarboxylic acid (XXII) by Brass (35, 36),

in his study of the oxidation of anilido-1-naphthoquinones to bis(naphthoquinolyl)benzidines by manganese dioxide in concentrated sulfuric acid. He also made the 12-methyl homolog of XXI.



XXI

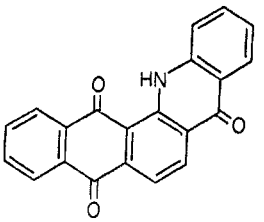
4. Individual compounds

The parent compound (II) of the series has been obtained in many ways: e.g., from 1-anilinoanthraquinone-2-carboxylic acid or the isomeric 1-(2-carboxyanilino)anthraquinone as already mentioned, with various cyclizing agents (9, 10, 14, 49, 125, 139, 149). If sulfuric acid is employed for the cyclization, care must be taken to avoid sulfonation (125). The acridone (II) was also formed by reductive dehalogenation of the 9- or 10-monochloro derivative (90).

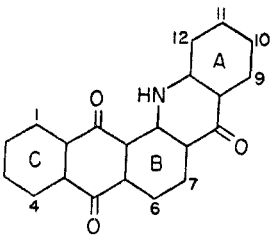
Anthraquinone-2,1-acridone is sparingly soluble in the usual solvents such as nitrobenzene, trichlorobenzene, aniline, pyridine, and the like. It may be recrystallized from aniline, from which it separates as red-violet needles, melting at 380°C. It may be sublimed (35). It dissolves in concentrated sulfuric acid, forming a red solution. It dyes cotton a very fast (to light) violet-red from a blue vat. The fastness to alkali is low.

Anthraquinone-2,1-acridone is very readily halogenated and nitrated, the nitro derivatives are reducible to amines, and the latter can be acylated. Acylamido compounds can also be obtained from certain halogenated derivatives by an Ullmann-type synthesis. A large variety of substitution products are known, of which those containing halogen or amino groups are of considerable technical importance.

A few methylated anthraquinone-acridones are known. The 6-methyl (14), 10-methyl (86, 90), 11-methyl (87), and 10,12-dimethyl (86) derivatives have been obtained by the usual types of synthesis and from starting materials that determine the location of the methyl groups. These methylated compounds are more soluble in solvents and give slightly bluer shades on cotton than the parent substance (14).



II



XXIII

C. HALOGENATION

1. General

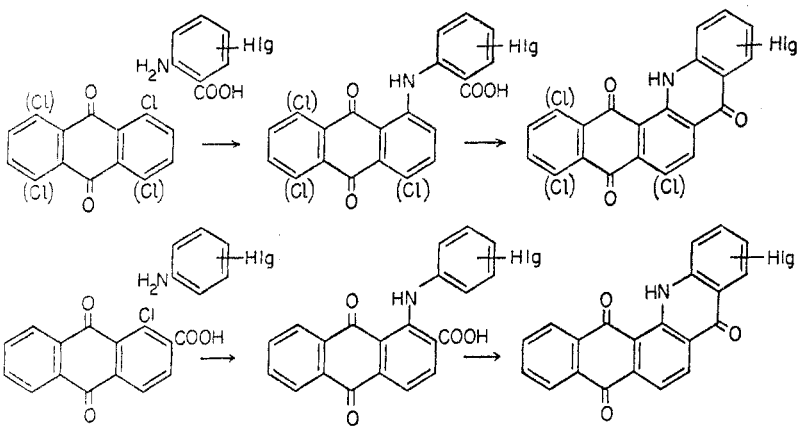
The chlorinated anthraquinone-2,1-acridones have been very extensively disclosed in the patent literature. There are a few brominated products, particularly mixed bromochloro derivatives, but none containing iodine. Those with fluorine are of only one type and have a trifluoromethyl group.

Chlorination was resorted to in an attempt to increase the fastness properties, but since the shade produced was not only brighter but of a more desirable hue (e.g., Turkey red), a systematic investigation was subsequently put into effect. The position taken by an entering group is not known until determined by synthesis from known substances. Halogenation makes the substances more soluble and lowers their melting points.

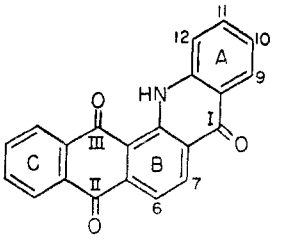
In an early publication, Ullmann (149) described a bromination that gave a monobromo derivative, without locating the entering atom, other than to say that it was in the benzene ring, A. It is now known that the substituent is in position 10 (30b). As would be expected, mixtures result upon chlorination, even when calculated amounts of the chlorinating agent are employed, though one predominates. Thus, a trichloro derivative is reported (114) to be a mixture of 78 per cent of the trichloro and 22 per cent of the dichloro derivatives. In the absence of catalysts the first halogen atom enters ring A, whereas in their presence the first atom is said to take the 6-position (108). Dyes of the latter group are, in general, more bluish. The maximum number of chlorine atoms that enter the acridone is six; the reaction can be pushed still further, so that the product contains eight atoms of chlorine, but the substance is now an acridine (76), the carbonyl group I (see formula on page 996) having been replaced by two chlorine atoms.

The usual chlorinating agents are sulfuryl chloride and chlorine; the catalysts are iodine, sulfur, ferric chloride, and the like (40, 84, 85, 99). The common solvents are sulfuric and chlorosulfonic acids, nitrobenzene, and trichlorobenzene, and temperatures may be as high as 180°C. In some instances (99) the location of the chlorine atoms in the product appears to be related to the catalyst or procedure employed. In order to have a clear picture of the situation, it is important to have reference compounds in which the location of the halogen atoms is known. Hence all the isomers believed possible have been synthesized by routes that de-

termine the positions of these elements. There are two paths of synthesis that serve to locate those in ring A (positions 9, 10, 11, 12). In one, 1-chloroanthraquinone undergoes an Ullmann reaction with a haloanthranilic acid; in the other a substituted aniline is condensed with 1-chloroanthraquinone-2-carboxylic acid. Cyclization, in a second step, completes the synthesis. The reactions are unambiguous except in the case of 3-chloro- and 3,4-dichloroanilines. The former can give 9- and 11-chloro isomers; both are produced and the mixture has been separated. The pure 11-chloro isomer has been obtained by the use of 2-amino-4-chlorobenzoic acid. When 1,4-dichloroanthraquinone is used with one equivalent of anthranilic acid, the product will contain a chlorine atom in the 6-position. Similarly, 1,5,8-dichloroanthraquinones can give rise to compounds substituted in ring C (positions 1–4).



A very useful tool for locating halogen in some of the polyhalo compounds is stepwise reduction (22, 87, 103), which removes one at a time. This dehalogenation is clean-cut, being essentially quantitative. The reaction has been known for a long time, for vatting (the use of alkaline sodium dithionite) often removed a halogen atom from the 7- or 6-position; the action is probably due to the alkali rather than to the reducing agent. The general procedure involves the use of a reducing agent in the presence of certain metals or their salts at an elevated temperature and in a solvent (pyridine, quinoline, pyridine bases). Hydrazine is one of the preferred reducing agents; others are hydroquinone, dioxindole, hydrazobenzene, glyoxal, guanidine, formamide, formic acid, and the like. The metals are usually copper, nickel, and silver, and are used in stoichiometric amounts. Catalytic reduction procedures (80) are of less utility. The first halogen to be removed (after the one at 7) is the one in ring A, in position 9, ortho to the acridone carbonyl group, I; the second comes from the 6-position, ortho to the quinone carbonyl, II. The subsequent order in ring A is 11, 10, 12. Treatment of the pentachloro compound with diethylaniline preferentially removes the halogen from the 6-position (40).



Much of this halogenation and dehalogenation work was done before the development of modern theories of reactivity. Taking the latter into account, the results are those that would have been expected. Since the imino group is strongly electron-donating, it will activate rings A and B, and since it is ortho-para directing, the entering chlorine would be expected to take position 10 first, and then 6, and 12. Under more drastic conditions, the remaining positions 9, 11, and and 7 can be filled. As C is part of an anthraquinone ring, it will not be subject to chlorination; any chloro substitution products here will have to be obtained by synthesis from chlorine-containing intermediates.

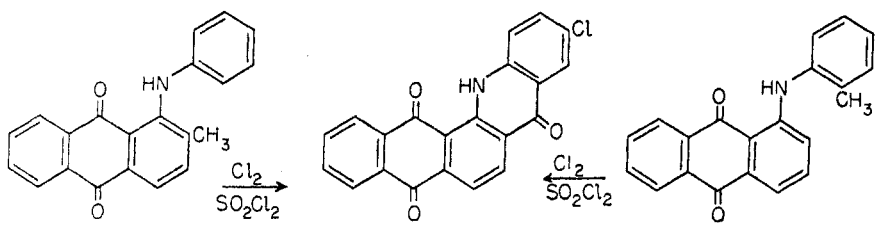
The situation is similar regarding removal of halogen atoms by reducing agents. The 7-position is active for nucleophilic displacement reactions because of the electron-attracting effect of the two carbonyl groups I and III, which is transmitted along the two conjugated systems. The 9-position is similarly active, although to a lesser degree, because of carbonyl group I, and the 6-position last (of the three), because of the inductive effect of carbonyl group III. The 11-halogen should go next, since it is vinylogously related to carbonyl group I. Further predictions are on a less firm basis. A halogen at position 10 might be removed before the one at 12, provided there is some involvement of the latter with the imino group. Any halogens removed from ring C could be predicted on the same basis, but none have been tested in the same way.

What are the facts? It is known that when anthraquinone-2,1-acridone is halogenated in the absence of catalysts the first halogen enters at position 10; with catalysts, position 6 (these are para to the imino group). Subsequent halogenation is not clean-cut. The next stopping point is with the 6,10,12-trichloro derivative; after this the pentachloro and completely substituted hexachloro compounds can be made and are readily isolable. A complicating factor appears at this point; since the 7-chloro atom is readily removed by basic reagents which are used in the purification of the reaction products, the pentachloro derivatives may well be a result of dechlorination of the hexachloro compound. Agreement with the predictions may be said to be fair. However, the removal of chlorine by the reducing agents is most instructive and convincing. If one can assume that the removal of chlorine atoms is roughly the reverse of their introduction, agreement with prediction is excellent. The first to go is, of course, the one in position 7, followed by the chlorine atoms in positions 9, 6, 11, 10, and 12 in this order.

2. Chlorination

(a) Monochloro derivatives

1-Chloroanthraquinone-2,1-acridone has been used (82), but its source was not revealed. 4-Chloroanthraquinone-2,1-acridone has been prepared by the isatin procedure (48) from 1,5-dichloroanthraquinone and one equivalent of isatin. Other isomers with a chlorine atom in ring C must have been made, because their use is specified in a patent supplement (70). 6-Chloroanthraquinone-2,1-acridone [2-chloro-3,4-phthaloylacridone (30)] was made by condensing 1,4-dichloroanthraquinone with one equivalent of anthranilic acid and cyclizing the product using the acid chloride procedure (144). It melts at 267°C. (corr.) and is soluble in aniline and pyridine (1:10). 9-Chloroanthraquinone-2,1-acridone is obtained, mixed with the 11-chloro isomer, when *m*-chloroaniline is condensed with 1-chloroanthraquinone-2-carboxylic acid, and the product cyclized (90). The mixture can be separated by fractional crystallization (83). 10-Chloroanthraquinone-2,1-acridone [7-chloro-3,4-phthaloylacridone (30) (XXIV)] has been obtained in several ways. The route from *p*-chloroaniline and 1-chloroanthraquinone-2-carboxylic acid establishes the position of the chlorine atom (9, 15, 49, 85). The 10-chloro isomer has also been obtained by a reaction of somewhat limited utility. 1-Anilino-2-methyl- or 1-*o*-toluidinoanthraquinones are chlorinated in a solvent at an elevated temperature (160–170°C.) for several hours (24, 26, 27). One of the products is identical with that obtained from 1-(4-chloroanilino)anthraquinone-2-carboxylic acid (15). A modification of this procedure (74) gives polychloro derivatives.

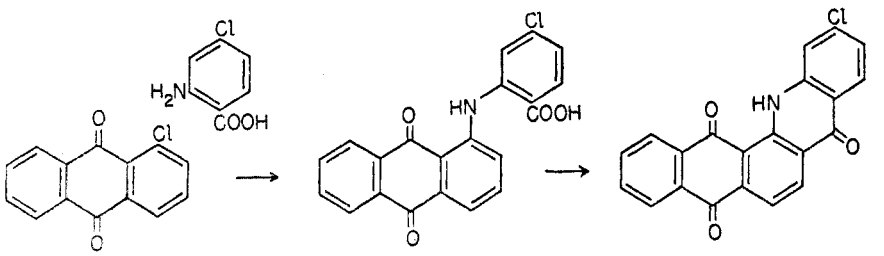


XXIV

The 10-chloro isomer has also been prepared by reduction of the 6,10- and 9,10-dichloro derivatives (87). 11-Chloroanthraquinone-2,1-acridone, 6-chloro-3,4-phthaloylacridone, 11-chloronaphth[2,3-*c*]acridine-5,8,14(13*H*)trione, Indanthrene Violet RRK[7] (*cf.* dye of same name, below), C.I. No. 67800 (44) (XVI), is a vat dye, probably of little current interest, and was discovered by A. Lüttringhaus about 1911. It is prepared by the usual methods: (*a*) by condensation of 1-chloroanthraquinone with 2-amino-4-chlorobenzoic acid (41, 55),

[7] Two errors under C.I. No. 67800 should be mentioned. (*1*) The chlorination of phthaloylacridone gives the trichloro derivative (which is Indanthrene Violet RRK) without stopping at an earlier stage (86); (*2*) German patent 229,394 (Frdl. **10**, 601) is for the preparation of 1-nitroanthraquinone-2-carboxylic acid.

a method which shows its structure; (*b*) by the sulfonamide process, from the product of the interaction of 1-chloroanthraquinone with 2,4-dichlorobenzoyl chloride (25); (*c*) by dehalogenation of the 9,11-dichloroanthraquinone-acridone (87). It is also formed from *m*-chloroaniline, as mentioned under the 9-chloro isomer (83).



XVI

12-Chloroanthraquinone-2,1-acridone has been prepared from *o*-chloroaniline (83, 85), thus locating the position of the halogen. 12-Chloro-10-methylanthraquinone-acridone is also known (87).

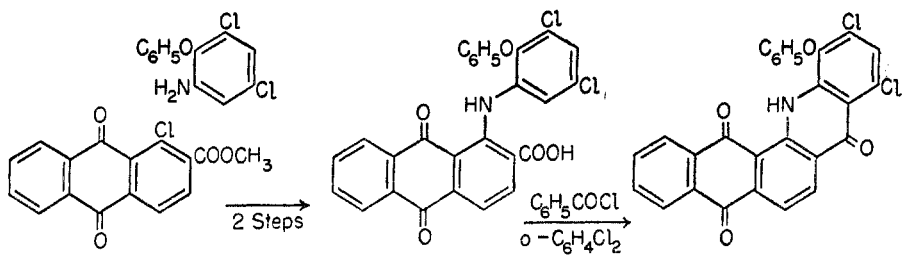
(b) Dichloro derivatives

Of the large number theoretically possible, those substances having both chlorine atoms in the top ring (A) have been the most investigated. Six of these are possible, and all are known: 9,10, 9,11, 9,12, 10,11, 10,12, and 11,12. In order to obtain the homogeneous individual substances, syntheses of the usual type from dichloroanilines or dichloroanthranilic acids are required. Thus, the use of 2,3-dichloroaniline will give the 11,12-dichloro isomer (83, 108), 2,4-dichloroaniline gives the 10,12-dichloro isomer (75, 84), 2,5-dichloroaniline yields the 9,12-dichloro isomer (83, 108), and 3,5-dichloroaniline gives the 9,11-dichloro isomer (39, 40, 85). The use of 3,4-dichloroaniline is ambiguous, since it could give both the 9,10- and the 10,11-dichloro isomers (87); the 9,10-dichloro isomer is said to be the product (85). The 10,11-dichloro isomer is obtained by the dehalogenation of 6,10,11-trichloroanthraquinone-acridone (87). The 10,12-dichloro isomer (XXVII) has been prepared using 3,5-dichloroanthranilic acid (84) and by dehalogenation of the 6,10,12-trichloro compound (22, 84, 87). The 6,10-dichloro isomer has been obtained by dehalogenation of the 6,9,10-trichloro compound (87). It was, at one time, thought that the dye Indanthrene Violet RRK was the 10,11-dichloro isomer (132). The dye Indanthrene Red KK New, C.I. No. 67805 (44), is the 10,12-dichloro isomer.

Chlorination of the parent substance (II) with two equivalents of a chlorinating agent leads to mixtures; one of the chlorine atoms is most certainly in position 6. Different mixtures result when *x*,*x*,*x*-trichloro derivatives (86) are dehalogenated (22). The mixtures are separated and "purified" by treating with oxidizing agents, such as sodium hypochlorite, or by making "oxonium salts (18, 83)."

x,x-Dichloro-10-methyl (86, 87) and x,x-dichloro-10,12-dimethyl (86) homologs have been recorded in the patent literature; they were prepared by the action of chlorine (sulfur catalyst) upon a chlorosulfonic acid solution of the corresponding base at 20–25°C. for 6 hr.

Indanthrene Brilliant Rose (61) (or Pink (104)) BL, C.I. Vat Red 3, C.I. No. 67810 (44), is 9,11-dichloro-12-phenoxyanthraquinone-2,1-acridone (XXV). It is synthesized from methyl 1-chloroanthraquinone-2-carboxylate and 3,5-dichloro-2-phenoxyaniline by the usual Ullmann reaction, the ester being hydrolyzed in a separate step. Ring closure is brought about by benzoyl chloride in *o*-dichlorobenzene (104).



XXV

(c) Trichloro derivatives

Only eleven of the possible trichloro derivatives have been revealed in the literature, and most of these have the halogen in ring A. The 6,10,11- (87), 6,10,12- (87), and 10,11,12-trichloro (103) isomers were obtained by reducing one chlorine atom from the 6,9,10,11-, 6,9,10,12-, 6,10,11,12-, and 9,10,11,12-tetrachloro derivatives, respectively. The 9,10,11-, 9,10,12-, 9,11,12-, and 10,11,12-trichloro isomers were synthesized unambiguously from 3,4,5-trichloroaniline (83, 86), 2,4,5-trichloroaniline (83), 2,3,5-trichloroaniline (83, 85, 108), and 2,3,4-trichloroaniline (77), and 1-chloroanthraquinone-2-carboxylic acid; the 7,10,12-trichloro isomer was obtained from 2,4-dichloroaniline and 1,3-dichloroanthraquinone-2-carboxylic acid. These syntheses confirmed the location of the chlorine atoms.

The 6,10,12-, x,9,11-, x,9,12-, x,10,12-, 10,11,12-, and x,x,12-trichloro compounds were obtained by chlorination of monochloro and dichloro compounds (85, 89, 108). The x,10,12-trichloro compound is an isomer of the 6,10,12-trichloro compound. Since the amount of chlorination of the lower halologs is often regulated by noting the color change (formation of more rosy red (99)), it is not surprising that mixtures result. In one patent (99) it is specified that at least *one* position ortho or para to the imino group must be free, so it appears very likely that the entering chlorine appears at that point; thus, in the x,9,12-trichloro isomer, the x is probably 6.

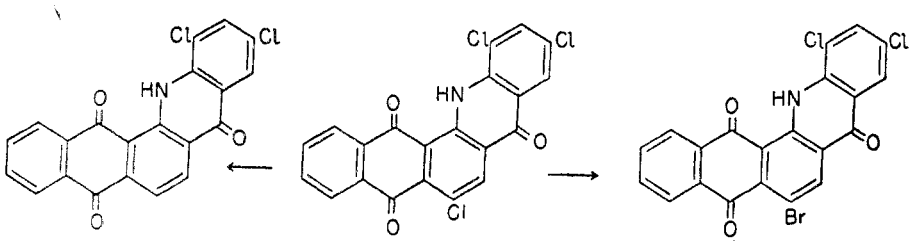
The only technically important isomer is 6,10,12-trichloroanthraquinone-2,1-acridone (XXVI). This substance is the main component of the commercial dye

C.I. No. 67895, C.I. Vat Violet 14 (44), Indanthrene Violet RRK, Caledon Red Violet 2 RN (61), which was discovered by Bally in 1910, and which has been the subject of many patents. Probably this confusion can largely be attributed to the difficulty of determining the identity of the mixtures of products formed by the slightly varied methods of chlorination followed by the competing companies (21, 22, 67, 75, 86, 100, 114). The usual procedure is to chlorinate anthraquinone-acridone (II) with sulfuryl chloride in nitrobenzene until three chlorine atoms have been taken up; the product always contains some of the dichloro derivatives (114). The use of chlorine itself gives a more complex mixture. The same dye is also formed when 1-anilinoanthraquinone-2-carboxylic acid is chlorinated and simultaneously cyclized in concentrated sulfuric acid.

When the trichloro compound of German patent 258,561 (21), which certainly has the halogen atoms in the 6,10,12-positions, is treated with phosphorus pentachloride, to replace the acridone carbonyl oxygen with two chlorine atoms, and then chlorinated, hydrogen chloride eliminated from this product by phenol, and the chloroacridine worked up in the usual way with sulfuric acid, the resulting acridone dyes cotton a pure red, in contrast to the red-violet of the 6,10,12-trichloro derivative. The number of chlorine atoms in the substance is not given (101). Finally, the trichloro compound is formed by dechlorinating the tetrachloroanthraquinone-acridone formed by the action of chlorine on the base (II) (103).

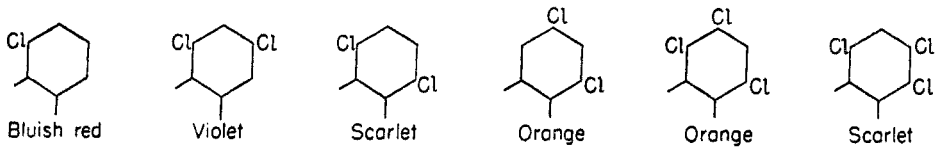
The location of the chlorine atoms in the dye remained in doubt for a long time and is incorrectly shown in much of the literature (61, 114). It was even suggested by Schultz (132) that the product from 3,4-dichloroaniline was a possibility. The structure now accepted as correct appears in a patent (100), in F.I.A.T. (59), and in the *Colour Index* (44).

The 6,10,12-trichloro compound can be further chlorinated (103), as would be expected. Quite remarkably, the chlorine atom in position 6 can be removed by reduction, with consequent formation of 10,12-dichloroanthraquinone-2,1-acridone (XXVI) (100, 103). An unusual reaction is the previously mentioned replacement of the 6-chlorine atom by bromine (100).



XXVII XXVI XXVIII

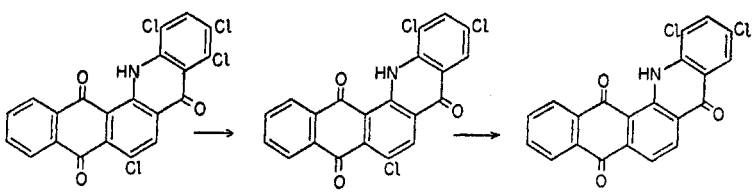
The position of the chlorine atoms in ring A of the halo derivative has a marked effect on the hue (136b). The introduction of chlorine in position 9 produces a strong hypsochromic effect, converting violets to orange. A chlorine in position 6 has a much smaller effect.



(d) Tetrachloro derivatives

Thirteen of these have been mentioned in the patent literature, but it is possible that there are actually fewer, because the position of some of the halogens in four is not clear from the preparative methods. A few have been obtained by the standard syntheses that determine the location; e.g., the 6,9,10,11-tetrachloro isomer (83) from 3,4,5-trichloroaniline, the 6,10,11,12-tetrachloro isomer (41, 77) from 2,3,4-trichloroaniline, the 9,10,11,12-tetrachloro isomer (39, 40, 75) from tetrachloroaniline—the first two with 1,4-dichloroanthraquinone-2-carboxylic acid, and the third with 1-chloroanthraquinone-2-carboxylic acid. The 7,9,10,11- and 7,9,10,12-tetrachloro isomers were made using the appropriate trichloroaniline and 1,3-dichloroanthraquinone-2-carboxylic acid (96). The 1,6,9,11-, 3,6,9,11-, and 4,6,9,11-tetrachloro isomers were prepared by chlorination of the corresponding 1-, 4-, and 6-chloroanthraquinone-acridones, a process which locates those chlorine atoms (82); the other three are placed by analogy with the chlorination product of the unsubstituted base (II). The $x,x,9,12$- (108), 6,10,11,12- (41, 77), $x,6,10,12$- (85, 99, 103), $x,9,10,11$- (99), and $x,10,11,12$-tetrachloro (99) isomers have been obtained by chlorination of the corresponding chloro derivatives. A 4,6,9,12-tetrachloro isomer is said to be made by the chlorination of the 9,12-dichloro derivative, using sulfur monochloride and sulfuryl chloride, catalyzed by iodine (151). The introduction of chlorine in the 4-position is exceptional. This is probably an error, since in a patent (108) on polychlorinated products with the halogen in ring A, a similar reaction is said to give the $x,x,9,12$-tetrachloro isomer. Attention should be called to the difference in color between the 6,10,11,12-tetrachloro (red) and 9,10,11,12-tetrachloro (orange) isomers; this is an additional example of the powerful hypsochromic effect of a halogen in the 9-position.

Reducing agents, e.g., hydrazine (87), remove the 9-halogen atom first, from the 6,9,10,12- and 9,10,11,12-tetrachloro compounds. Since reduction goes stepwise, the 6,9,10,12-tetrachloro compound (XXIX) gives first the 6,10,12-trichloro (XXVI) and then the 10,12-dichloro (XXVII) derivatives.

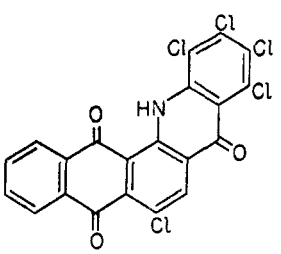


XXIX XXVI XXVII

(e) Pentachloro derivatives

Only two of these are well known, the 6,9,10,11,12- and the 7,9,10,11,12-pentachloro isomers (XXX and XXXI). While both are commonly obtained in admixture by the chlorination of lower homologs (40, 42, 75, 84, 85, 96, 99), both have been unambiguously synthesized from 2,3,4,5-tetrachloroaniline and 1,4- and 1,3-dichloroanthraquinone-2-carboxylic acids (39, 40, 75, 96). Dyes with a 7-chloro substituent are more intensely colored and brilliant than those with a 6-chloro substituent (96).

In subsequent patents (38, 42) the chlorination of methyl derivatives of anthraquinones to give polychloro anthraquinone-acridones was described. The procedure is reminiscent of the one followed by the discoverers (8) of the first representative (a benzolog) of the series. It consists in a high-temperature (170–180°C.) chlorination of a 1-anilino-2-methylanthraquinone in a solvent such as trichlorobenzene, until the product contains about five atoms of chlorine. The pentachloro derivative has the chlorine atoms in positions 6, 9, 10, 11, and 12 (39). A chlorine atom in the 6-position is readily replaced by hydrogen on boiling with diethylaniline (40, 42).



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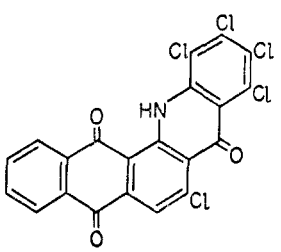


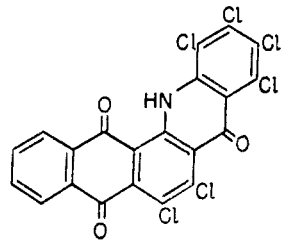
XXXI

The commercial dye Indanthrene Brilliant Rose (Pink) BBL, C.I. Vat Red 39 (44), C.I. No. 67900, is a mixture of both pentachloro isomers, the 6,9,10,11,12-isomer predominating (61, 151). It is prepared by chlorination of the base (II) to a halogen content of at least five chlorine atoms (76, 86). Any excess amount is removed by hydrolysis during the working up of the reaction mixture (see following paragraphs). Of theoretical interest is the easy preferential replacement of the 6-chlorine atom by bromine, by the procedure previously mentioned (100), giving 6-bromopentachloroanthraquinone-acridone.

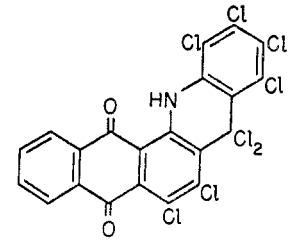
(f) Hexachloro derivatives

6,7,9,10,11,12-Hexachloroanthraquinone-acridone (XXXII) is formed by exhaustive chlorination of the base (II) or lower halologs (42). Alternatively, it can be obtained by exhaustively chlorinating 1-anilino-2-methylanthraquinone in trichlorobenzene at 160–170°C. as long as hydrogen chloride is evolved. A keto-chloride, which is really the octachloroacridine (42, 76) (XXXIII), is first

formed; two chlorine atoms are removed by hydrolysis, using concentrated sulfuric acid.



XXXII

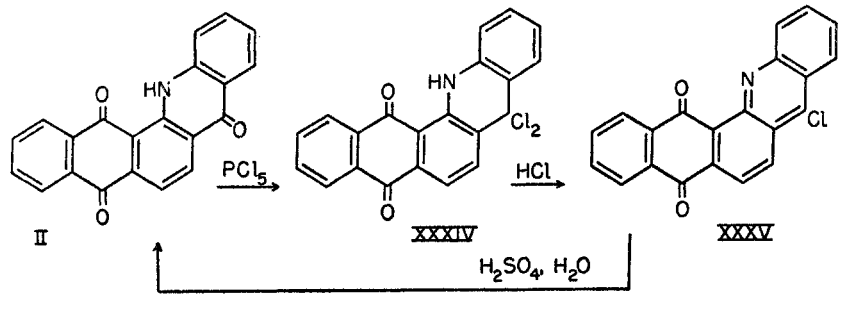


XXXIII

The dye Indanthrene Pink B (61), C.I. No. 67905 (44), is the hexachloro derivative. The 7-chlorine atom (the only one under the influence of two carbonyl groups) was easily removed by vatting, which would result in the fabric's actually being dyed by the pentachloro compound already mentioned; hence the dye is probably obsolete (151). Likewise, one of the chlorine atoms is readily displaced by bromine (100), as was just pointed out with the pentachloro halolog. This is a bluer dye than the hexachloro compound.

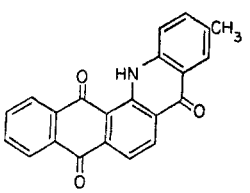
(g) Chloroacrid*i*nes

It has been noted that polychlorinated products have been mentioned in several places (38, 42, 76, 101). For instance, if the anthraquinone-acridone is treated with phosphorus pentachloride before chlorination, the products are different from those obtained in the usual way. Obviously, a keto-chloride (XXXIV) is the primary product. This substance is an acrid*a*ne (dihydroacridine) and therefore easily loses hydrogen chloride to very mild reagents (phenol) (38, 101) or on being heated; the product is 8-chloroanthraquinone-2,1-acrid*i*ne (XXXV) (37, 70, 116). Upon solution in concentrated sulfuric acid and dilution, the 8-chlorine atom is replaced by OH, so that the acridone is regenerated (37, 76, 101). 8-Chloroanthraquinone-2,1-acrid*a*ne, formed by the action of zinc chloride, hydrogen chloride, and acetic acid in a sealed tube, has also been described (116).

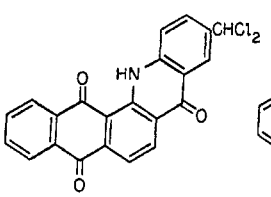


(h) Side-chain chlorination

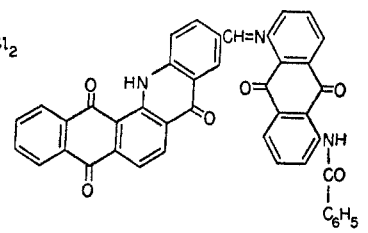
When chlorination of 10(or 11)-methylanthraquinone-acridone (XXXVI) is carried out at a high temperature, two chlorine atoms enter the side chain, resulting in the formation of a dichloromethyl derivative (XXXVII) (45). Chlorine may enter the same ring simultaneously. The dichloromethyl derivatives are condensed with primary amines to give orange to red azomethine dyes (XXXVIII).



XXXVI



XXXVII



XXXVIII

3. Bromo derivatives

Relatively few brominated anthraquinone-acridones have been described in the literature. Since the action of bromine is more sluggish than that of chlorine, the second atom is picked up more slowly than the first (2), and the maximum number recorded is three. Bromination is carried out in nitrobenzene (2, 103, 142, 149) or sulfuric and chlorosulfonic acids for varying times and at several temperatures. The first bromine enters at position 10 (30c, 149). The next one goes in at 6 or 10, by analogy with the behavior of chlorine, while the third takes the remaining possibility. The reaction may not be clean, because it has been noted that bromination of 1-anilinoanthraquinone-2-carboxylic acid with simultaneous ring closure (21, 90) gives a tribromo derivative with better dyeing characteristics than the one that results from the already cyclized product (II) (2, 103). Since the tribromo compound, upon reduction with hydrazine, gives the 10,12-dibromo compound (100), the location of two of the bromine atoms is fixed; in the patent the compound is definitely called 6,10,12-tribromoanthraquinone-acridone. The 10-bromo isomer has also been made by brominating the anthraquinonylanthranilic acid before cyclizing (6).

The 7-monobromo (148) (1-bromo-3,4-phthaloylacridone) (30), the 11-monobromo (55), and the 10,12-dibromo (14) derivatives have been obtained by syntheses from starting materials in which the location of the bromine was known.

4. Mixed chloro-bromo derivatives

Considerable experimental work would be required to establish the location of all the halogen atoms in the known mixed polyhalo compounds; such a problem is probably only of academic interest. The substances containing both chlorine and bromine are obtained by brominating chloro compounds (39, 85, 87, 89, 90,

100, 108, 109), by chlorinating bromo compounds in the presence of a catalyst (iodine, sulfur) (85), by replacing chlorine by bromine (100), and by dehalogenating more highly halogenated compounds (87, 103). In most instances the location of the halogen already present is known, but that of the entering halogen has to be assumed by analogy. The location of all the halogens is known with certainty in one instance (11-chloro-10,12-dibromoanthraquinone-2,1-acridone) in which 3-chloro-2,4-dibromoanthranilic acid was used (14). If bromination resembles chlorination, the bromine atoms will be expected to enter the same positions (ortho and para to the imino group). However, when a catalyst is used during chlorinations (84, 99), the product is said to be different from the one obtained otherwise.

In the few instances (100) in which a 6-chlorine atom is replaced by bromine, the location of the latter is established. This little-known reaction consists in treatment of the substance with hydrobromic acid in the presence of a copper catalyst. Copper salts, potassium bromide, and phosphoric acid are the reagents. Oxidizing agents must be excluded; otherwise the halogen is replaced by hydrogen. The replaceable halogen must be activated by other halogens, or by acidic, oxo, or quinone groups.

In dehalogenation it is known that the *first* halogen to be removed is the one ortho to the acridone carbonyl, and the second one is ortho to the anthraquinone carbonyl. Furthermore, the reaction proceeds stepwise but is essentially quantitative at each step.

D. NITRO COMPOUNDS

Very few nitro compounds have been noted in the literature. In some instances they are intermediates for the preparation of amines, but most amino derivatives are preferably obtained by an Ullmann synthesis by way of a halogen compound. Nitrohalo compounds are described in the patents as being formed by nitration of a chloro compound (94, 95) or by chlorination of a nitro compound (84).

10-Nitroanthraquinone-2,1-acridone was first described by Ullmann and was obtained by nitration of the parent base (II) (4, 30c, 149). 10-Nitro-12-chloroanthraquinone-2,1-acridone is formed by the hydrazine dehalogenation (87) of 6,12-dichloro-10-nitroanthraquinone-2,1-acridone, the latter being obtained by chlorination of the 10-nitro derivative, using sulfuryl chloride in the usual way.

In German patent 254,096 (19) the nitration of a monobromo compound is mentioned; since the latter was formed by the bromination of anthraquinone-2,1-acridone, it must be the 10-bromo derivative. Similarly, a chloro compound is nitrated, but in this case it was formed by the use of sulfuryl chloride, which could introduce more than one chlorine atom. In both instances it is specified that the halogen must be in the benzene ring (ring A), which suggests that in the latter product one chlorine atom is in the 10-position. At the end of this patent the U. S. patent equivalent is given as 1,052,507; the latter is Neresheimer's pat-

ent (119) on 6-amino-10,12-dichloroanthraquinone-2,1-acridone (Indanthrene Turquoise Blue 3GK) (105). One method for its preparation is by reduction of the 6-nitro-10,12-dichloro compound; that is, the sulfuryl chloride treatment *did* give a dichloro compound.

A most unusual nitration involves treatment of a mixture of *m*-dinitrobenzene and 10,12-dichloroanthraquinone-2,1-acridone in trichlorobenzene at 140–150°C. with chlorine; a nitro group is introduced (91). Since the resulting compound is bluish-red, it suggests that entry has been into the 6-position.

A very curious observation is recorded concerning the action of chlorine on 6-nitro-10,12-dichloroanthraquinone-2,1-acridone (84). The latter is said to be a greenish-blue dye, whereas the chlorinated product is a red-violet dye. In the absence of further data it would appear that the nitro group must have been replaced by chlorine, for the 6,10,12-trichloro compound is known to be red-violet.

1. Halonitro derivatives

The halonitroanthraquinone-2,1-acridones mentioned in patents are collected in table 1.

TABLE 1

Substituted nitroanthraquinone-2,1-acridones

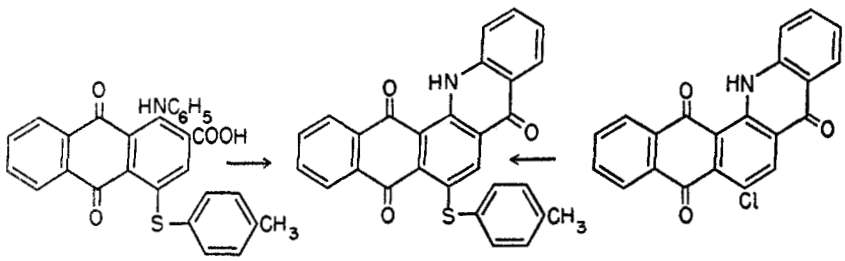
Substituents and Location					Method*	References
6	9	10	11	12		
		NO_2			a	(4, 30, 149)
NO_2		Cl			a	(95)
		NO_2		Cl	c	(87)
NO_2		Br			a	(19)
Cl		NO_2		Cl	b	(87)
NO_2		Cl		Cl	a, b, c	(19, 84, 87, 91, 94, 95)
NO_2	Cl	Cl	Cl		a	(95)
NO_2	Cl	Cl		Cl	a	(22, 87, 94)
NO_2	Br	Cl		Cl	a	(95)
NO_2	Cl	Cl	Cl	Cl	a	(95)

* a, by nitration; b, by chlorination; c, by dehalogenation.

E. ETHERS

10-Methoxy- and 11-methoxyanthraquinone-2,1-acridones can be obtained by the usual ring-closure procedures (147). A phenoxy derivative, Indanthrene Brilliant Rose BL, has already been described (61, 104) in Section II,C,2,(b).

A thioether, 6-cresylthioanthraquinone-2,1-acridone (XXXIX), has been obtained in two ways—by cyclizing the substituted anthraquinone-2-carboxylic acid, using phosphorus pentachloride, and by treatment of 6-chloroanthraquinone-2,1-acridone with potassium hydroxide and *p*-thiocresol (17). It forms blue-violet crystals, dissolves in concentrated sulfuric acid with production of a greenish-blue color that soon changes to red-violet, and dyes cotton blue from a violet vat.



XXXIX

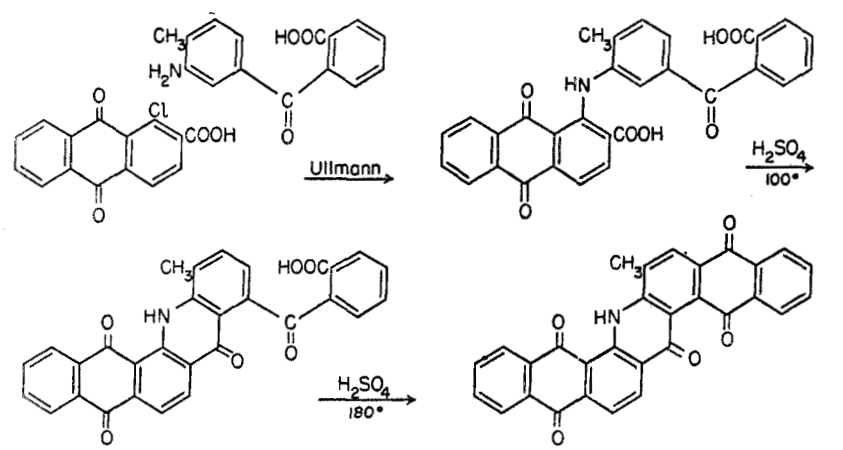
9,10-Dimethoxy- and 11,12-dimethoxyanthraquinone-2,1-acridones are made by the usual Ullmann type of synthesis, but substituting 1-aminoanthraquinone for the 1-chloro derivative (32).

F. ACIDIC DERIVATIVES

1. Acids

Almost no anthraquinone-acridones having free carboxy or ester groups have been described, although some are mentioned as being intermediates for the preparation of more complex substances. The latter are amides, formed by the action of the acid chlorides on polynuclear amines.

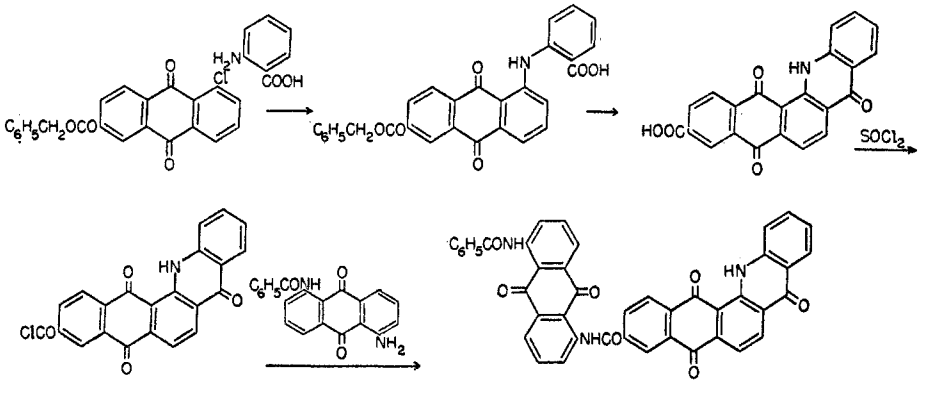
9-(*o*-Carboxybenzoyl)-12-methylanthraquinone-2,1-acridone (XL) (11, 23) is an intermediate on the way to the preparation of 16-methyl-15-azadinaphth-[2,3-*a*,2′,3′-*h*]anthra-5,18,9,14-diquinone (XLI). It is obtainable by the usual cyclization procedure, using sulfuric acid at 100°C., from the condensation product of 3-amino-2′-carboxy-4-methylbenzophenone and 1-chloroanthraquinone-2-carboxylic acid. The subsequent formation of an anthraquinone ring takes place if the mixture is heated at 180°C. The acid is soluble in alkali, as expected.



XL XLI

2. Acid chlorides

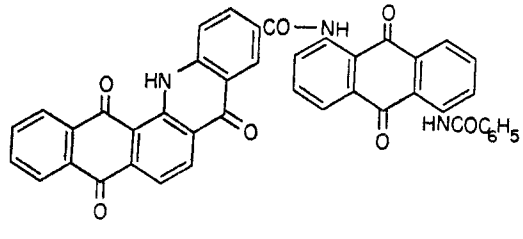
3-Chlorocarbonylanthraquinone-2,1-acridone (XLII) can be obtained, stepwise, from 1-chloroanthraquinone-6-carboxylic acid (79). The benzyl ester of the latter is condensed with anthranilic acid, the product cyclized by sulfuric acid, and the resulting 3-carboxyanthraquinone-2,1-acridone treated with thionyl chloride. The acid melts at 285°C. The acid chloride has been condensed with several aminoanthraquinones (79).



XLII XLIII

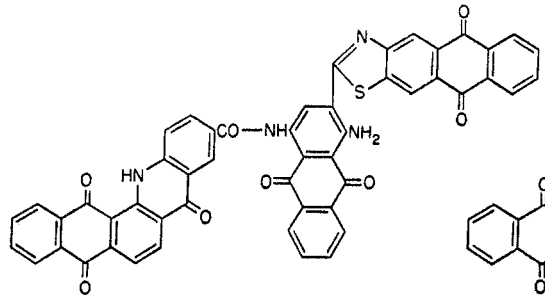
10-Carboxyanthraquinone-2,1-acridone is prepared by the usual Ullmann synthesis, followed by cyclization (79). None of its properties are given, but many amides have been made from it as outlined. 10-(4-Chlorocarbonylphenyl)anthraquinone-2,1-acridone (XLV) has likewise been condensed with many polynuclear amines.

Some of the amides (see Section II,G) derived from carboxyanthraquinone-acridones and polynuclear amines are valuable dyes; considerable recent research has been concentrated in this field. One example is Indanthrene Orange RR (61, 79), C.I. Vat Orange 13 (44), C.I. No. 67820, *N*-5-(benzamido-1-anthraquinonyl)-10-carbamylanthraquinone-2,1-acridone, and is shown in structure XLIV; it is isomeric with XLIII, used in illustrating an application of the 3-chlorocarbonyl derivative (XLII).

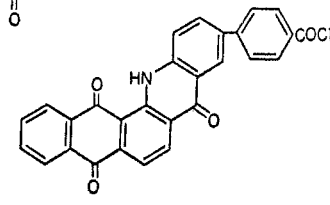


XLIV

More complex amides, such as XLVI, are of the same type and dye vegetable fibers gray tones which are very fast to light (59b). The nonhalogenated form is equally good. The amides from the acid chloride (XLV) and the same polynu-



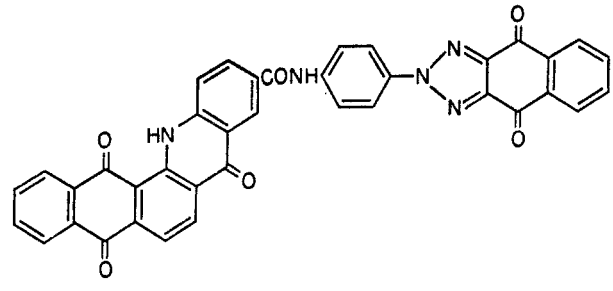
XLVI



XLV

clear amines gave brown dyes which had poor affinity for cotton but were of good light fastness (59c).

A new vat orange, too expensive to be a commercial product but superior in fastness, is shown in XLVIa (59c).



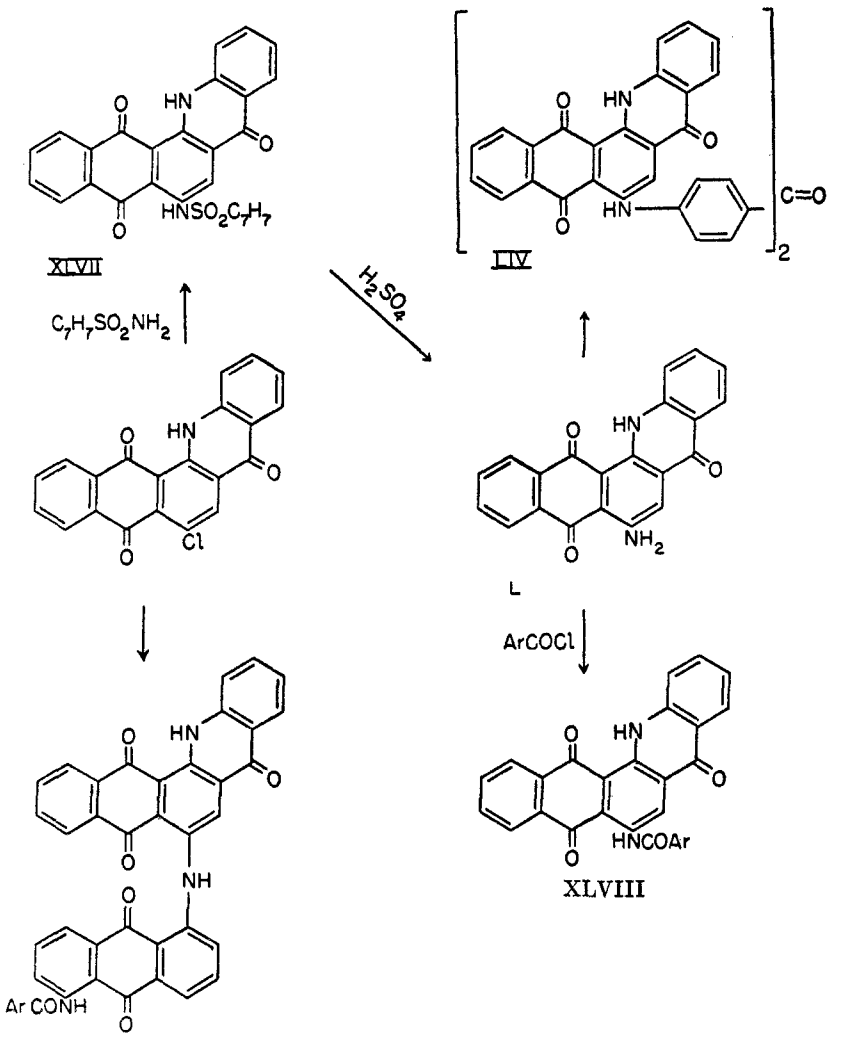
XLVIa

G. AMINOANTHRAQUINONE-2,1-ACRIDONES

The amino derivatives are, perhaps, the anthraquinone-acridones of most recent interest, because of the ease with which they can be "carbazoled" (dehydrogenated, to form a carbazole ring system) to brown and gray light-fast dyes. The reaction will be described at the end of this section. Introduction of the amino group into the anthraquinone-acridone results in a marked bathochromic shift of absorption, so that the dyes with a less complex structure are blue; some of these are commercial products.

The amino group is formed in several ways, the principal ones being: (*a*) by reduction of a nitroanthraquinone-acridone; (*b*) by hydrolysis of the *p*-toluenesulfonamido derivative (XLVII) which results from an Ullmann condensation between *p*-toluenesulfonamide and a chloroanthraquinone-acridone; (*c*) by cyclization of an anthraquinonyliminoanthranilic acid; (*d*) by the direct syn-

thesis, previously outlined, from a leuco-diaminoanthraquinone; (*e*) by the isatin procedure. A secondary amine (XLIX) is essential for carbazoling; this type of compound is formed by the action of a primary amine on a chloro compound.

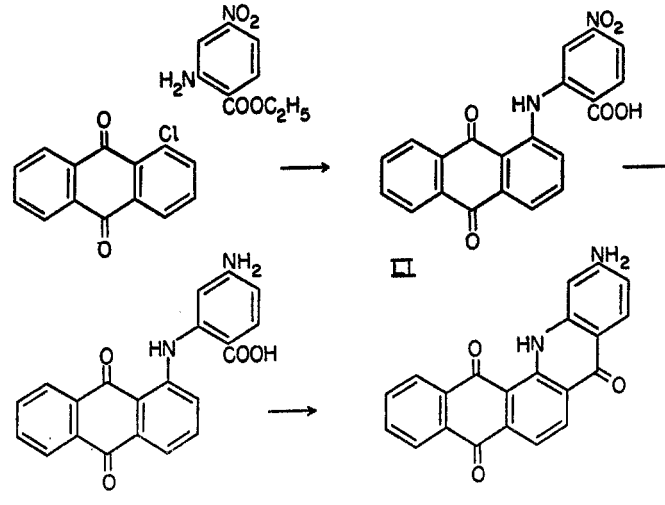


Acylamido groups are often present in dyes (XLVIII, XLIX) and are introduced by acylation of an aminoanthraquinone-acridone or by an Ullmann synthesis using an acylamide. 1(and 4)-Aminoanthraquinone-2,1-acridones are mentioned in a patent (63) in which their condensation products with cyanuric chloride are described. There were no details, other than to state that diaminoanthraquinones were the starting compounds.

6-Aminoanthraquinone-2,1-acridone, 2-amino-3,4-phthaloylacridone (L), has been prepared by the sulfonamide procedure (144) by dehalogenation of the 6-amino-7-chloro derivative (111), by cyclization of 4-aminoanthraquinone-1-anthranilic acid (51, 105) (using fluorosulfonic acid) (68), and through the interaction of leuco-1,4-diaminoanthraquinone and ethyl *o*-chlorobenzoate as already outlined (53, 74); the ring closure was brought about in chlorosulfonic acid solution by warming for only 5 min. at 30–40°C. (53). It is somewhat soluble in aniline, pyridine, and nitrobenzene; it crystallizes from the latter in blue needles, melting "above 410°." It dyes cotton blue (after oxidation) from a violet vat. This amine has been acylated by a great variety of acid chorides, as indicated under amides.

10-Aminoanthraquinone-2,1-acridone can be obtained by the ring-closure procedure (147) and by a sodium sulfide reduction of the corresponding nitro compound at 90–100°C. (4). It melts with decomposition at 340°C. The vat is gray-green; the color on cotton is violet and is turned brown by bleaching powder.

11-Aminoanthraquinone-2,1-acridone (LIII) was obtained by starting with ethyl *m*-nitroanthranilate (147). Since the nitro acid (LI) cannot be cyclized, it is first reduced to the amine (LII) in which the ring is closed readily.



LII LIII

This amine is somewhat soluble in aniline and nitrobenzene; it crystallizes from the latter in blue-violet plates, which melt "toward 340°." The sulfuric acid solution is green. Cotton is dyed a weak violet from a red-violet vat. 6-Methylaminoanthraquinone-2,1-acridone is formed by the isatin procedure, from 4-bromo-1-methylaminoanthraquinone (48). Cotton is colored a greenish-blue from a brown vat.

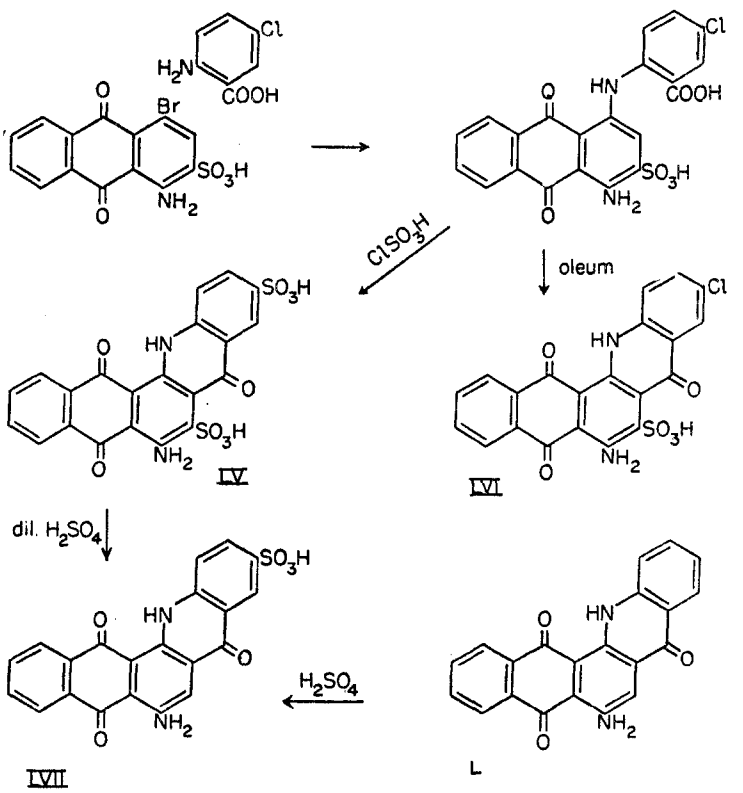
The 6-anilino (51), 6-*p*-bromanilino (51), 6-*p*-toluidino (48), 6-(1-naphthylamino) (51), 6-(2-naphthylamino) (51), 6-(1-anthraquinonylamino) (51, 54, 144,

148), and 6-(2-anthraquinonylamino) (51, 139) derivatives can be obtained by following the Ullmann procedure, as can both 10-anthraquinonyl-2,1-amines (3). The 10-anthraquinonyl isomer has also been obtained by brominating the 1-anthraquinonylanthranilic acid before ring closure, and then proceeding in the usual way. This reaction serves to locate the bromine atom, since the same dye results by both procedures (6). The 1-anthraquinonyl derivative is extraordinarily insoluble in all solvents, including hot quinoline and diphenylamine (144).

If ethyl 4-aminobenzoate (also with halogen in the nucleus) is condensed with 6-chloroanthraquinone-2,1-acridone and the ester hydrolyzed, the resulting acid can be converted to the acid chloride, 6-(4-chlorocarbonylanilino)anthraquinone-2,1-acridone, and the latter used to make a great variety of amides (112). Bis compounds of several types are readily obtainable by the Ullmann reaction. The amines can be condensed at one or both ends with, for instance, 4,4′-dibromobenzophenone (LIV), dibromofluorenone, and dibromoterphenyl (92, 93).

1. Sulfonated aminoanthraquinone-2,1-acridones

Several of these have been described (28, 29), all bearing an amino group. They were prepared as acid dyes for wool. The synthesis of LVI starts with



1-amino-4-bromoanthraquinone-2-sulfonic acid ("bromamine acid"), which is condensed in the usual way with potassium 4-chloroanthranilate. The intermediate is very easily cyclized by the use of 23 per cent oleum at 20–25°C. for 3–4 hr. If chlorosulfonic acid is used for ring closure, the 10-chlorine atom is replaced by —SO_3H, giving the disulfonic acid (LV). The 10-sulfonic acid is also a "rearrangement product" of the 7-isomer (29). The sulfo group in position 7 is very easily removed, e.g., by dilute sulfuric acid, to give the 10-sulfonic acid (LVII). The latter also results when the amino derivative (L) is sulfonated (29). Wool is dyed from an acid bath—green from LVI, bluish-green from LV, but a pure blue from LVII. The hypsochromic effect of the group at position 7 is evident.

2. Aminohalo compounds

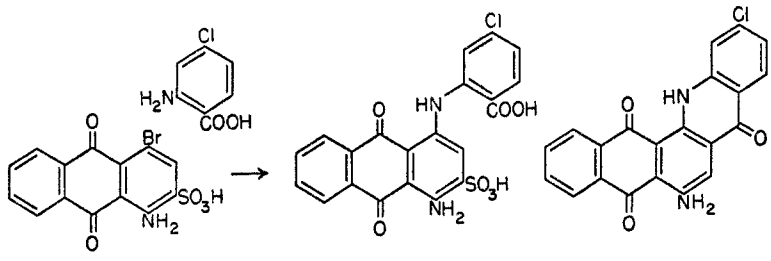
As was the case with the halogenated anthraquinone-acridones, in those having an amino group the location of the halogen atoms is usually uncertain. In some instances interpretation of the known facts renders it possible to assign them tentatively a certain position.

A halogen atom in the 7-position is easily removed by mild reducing agents, with a subsequent oxidation of the vat formed (111). Reagents specified are ferrous sulfate and ammonium hydroxide, stannous chloride and hydrochloric acid, sodium dithionite, hydrogen in the presence of a nickel catalyst, and diethylaniline. It is difficult to regard the latter as a reducing agent; possibly hydrogen chloride is removed from some intermediate. The mild oxidizing agent used is "Ludigol" (sodium *m*-nitrobenzenesulfonate).

6-Amino-7-bromoanthraquinone-2,1-acridone, 1-bromo-2-amino-3,4-phthaloylacridone, is obtained by the usual ring closure of the Ullmann condensation product of 1-amino-2,4-dibromoanthraquinone and anthranilic acid (57, 148). It is a blue-gray powder which may be recrystallized from 1-chloronaphthalene, decomposes at 260–270°C., and loses hydrogen bromide on heating (51). The analytically pure material, recrystallized from nitrobenzene, melts above 400°C. It forms a violet-brown vat; the color on cotton is blue. The 7-bromo atom is replaced by hydrogen during the vatting. The corresponding chlorine compound is similar (57, 105, 111).

6-Amino-*x*-bromo- and 6-amino-*x*-chloroanthraquinone-2,1-acridones (where the *x* is probably 10) are made by reducing the corresponding nitro compounds by means of sodium dithionite (19).

6-Amino-11-chloroanthraquinone-2,1-acridone (LVIII), Indanthrene Turquoise BK (GK) (61, 105), C.I. Vat Blue 32 (44), C.I. No 6.7910, was discovered by R. Berliner and was synthesized from starting materials in which the location of the substituents was known. In this instance the Ullmann reaction involved the use of 1-amino-4-bromoanthraquinone-2-sulfonic acid ("bromamine acid"), 4-chloro-2-aminobenzoic (*m*-chloroanthranilic) acid, a copper catalyst (59c), and sodium salts (59c, 78). The 7-sulfo group is removed by alkaline sodium dithionite at 60°C.; this is parallel to the loss of a 7-halogen atom, as previously discussed.



LVIII

The isomeric 6-amino-10-chloroanthraquinone-2,1-acridone is greener; absorption spectra have been recorded for these and related compounds (105). 6-Amino-10-chloro (and 10-bromo)-7-sulfoanthraquinone-2,1-acridones (7-chloro-2-amino-3,4-phthaloylacridone-1-sulfonic acid) have been described (29). 9-Amino-12-chloroanthraquinone-2,1-acridone can be obtained by the *p*-toluenesulfonamide procedure (141).

10-Amino-12-chloroanthraquinone-2,1-acridone has been obtained by the selective reduction with hydrazine of the 10-amino-6,12-dichloro compound. It may be noted that when the amino group is in the 6-position, the dyes are blue to gray, whereas the isomers like this dye cotton violet to orange (87).

6-Amino-7-bromo-11-chloroanthraquinone-2,1-acridone crystallizes from nitrobenzene in blue needles (78). It dissolves to an orange solution in concentrated sulfuric acid and forms a brown vat; the color on cotton is blue. Since the 7-bromine atom is probably lost during vatting, the dyed cotton should be the same as a sample dyed with Indanthrene Turquoise BK.

6-Amino-7,10-dichloroanthraquinone-2,1-acridone (78, 105), Indanthrene Blue GK (62, 132), is of no value, since the 7-chlorine atom is lost during vatting (151). Examples are given in the same patent (78) for 6-amino-7-bromo-10-chloro-, 6-amino-7,11-dichloro- (105), and 6-amino-7,10,12-trichloroanthraquinone-acridones. The latter can be synthesized by the standard procedure from 1-amino-2,4-dichloroanthraquinone and 5-chloroanthranilic acid (105).

6-Amino-10,11-dichloroanthraquinone-2,1-acridone results from the reduction with hydrazine of 6-nitro-9,10,11-trichloroanthraquinone-2,1-acridone, the nitro group being reduced and the 9-chlorine atom selectively removed simultaneously.

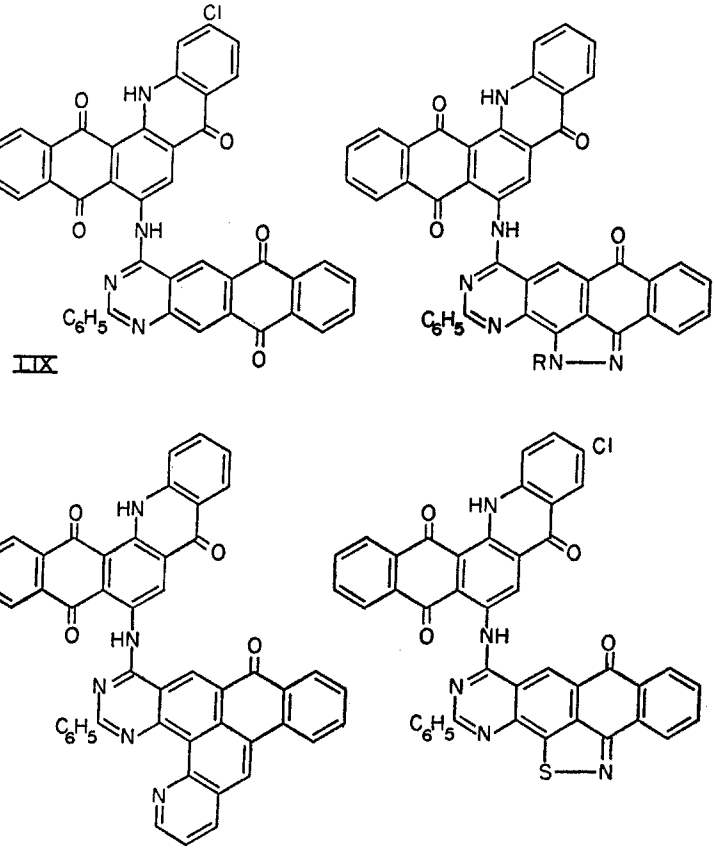
6-Amino-10,12-dichloroanthraquinone-2,1-acridone, Indanthrene Turquoise Blue 3 GK (105), C.I. Vat Blue 33 (44), C.I. No. 67915, was discovered by Neresheimer in 1912 (119). It can be made in several ways: (*a*) from 6,10,12-trichloroanthraquinone-2,1-acridone, which is treated with *p*-toluenesulfonamide and the product is then hydrolyzed (143); (*b*) from "bromamine acid" and a mixture of chlorinated anthranilic acids, the sulfonic acid group being hydrolyzed off simultaneously (28, 78); (*c*) by nitration of 10,12-dichloroanthraquinone-2,1-acridone, followed by reduction (105). Since, in the examples of German patent 531,013 (78), 1-amino-2,4-dibromo- and 1-amino-2,4-dichloroanthraquinones are used with 4-chloro- and 3,5-dichloroanthranilic acids (operating in cyclohexanol and cyclizing by sulfuric acid), it seems likely that

the commercial dye is a mixture. The pure 6-amino-10,12-dichloroanthraquinone-2,1-acridone has been synthesized from pure starting materials (105); its absorption spectrum was also recorded.

6-Amino-7,10,12-trichloroanthraquinone-2,1-acridone is synthesized in the usual way, thus locating the halogen atoms (78). The 6-amino-9,10,11-trichloro isomer is mentioned once (87).

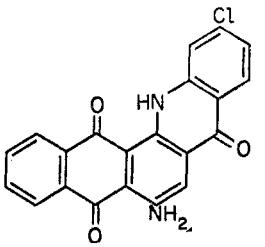
Several 6-aminoanthraquinone-2,1-acridones bearing varied substituents are mentioned in a patent (111). The groups and positions on the ring are 1-amino, 1-methoxy, 9,10-dichloro, 10-methanesulfonyl, and 2-*N*,*N*-dimethylsulfonamido.

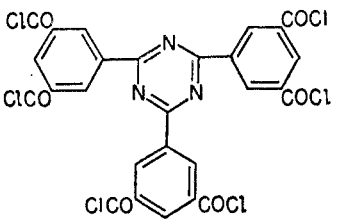
A complex dye, Indanthrene Green 4G (LIX) (31b, 61), is of interest since it has no bluish tint, in contrast to other green anthraquinone-acridones. It is prepared from 6-amino-11-chloroanthraquinone-2,1-acridone and 4-chloro-2-phenyl-6,7-phthaloylquinazoline in naphthalene at 210–180°C. for 6 hr., using *p*-toluenesulfonic acid as a catalyst. Other new green vat dyes with complicated polynuclear systems attached similarly have also been made. The examples shown herewith serve to illustrate the exceeding complexity of possible dye molecules.



LIX

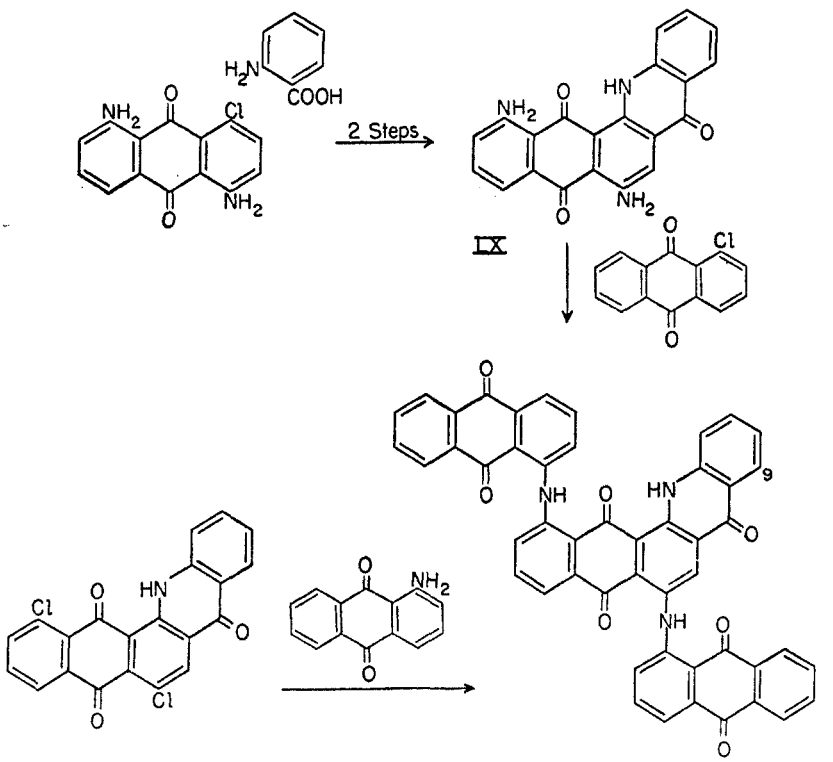
When 6-amino-11-chloroanthraquinone-2,1-acridone was condensed with the triazine hexachloride, the product was a mediocre blue dye (103c).





3. Diaminoanthraquinone-acridones

Several diamino-2,1-anthraquinone-acridones, without any description, have been made as intermediates for conversion to bisanthraquinonylamines (dianthrimides) and carbazoles (82). 1,6-Diaminoanthraquinone-2,1-acridone (LX) is obtained from 1-chloro-4,8-diaminoanthraquinone and anthranilic acid. When this is treated with two moles of 1-chloroanthraquinone, it gives a bisanthraquinonylanthraquinone-acridone (LXI). The latter type can also be obtained from dichloroanthraquinone-acridone and aminoanthraquinones.

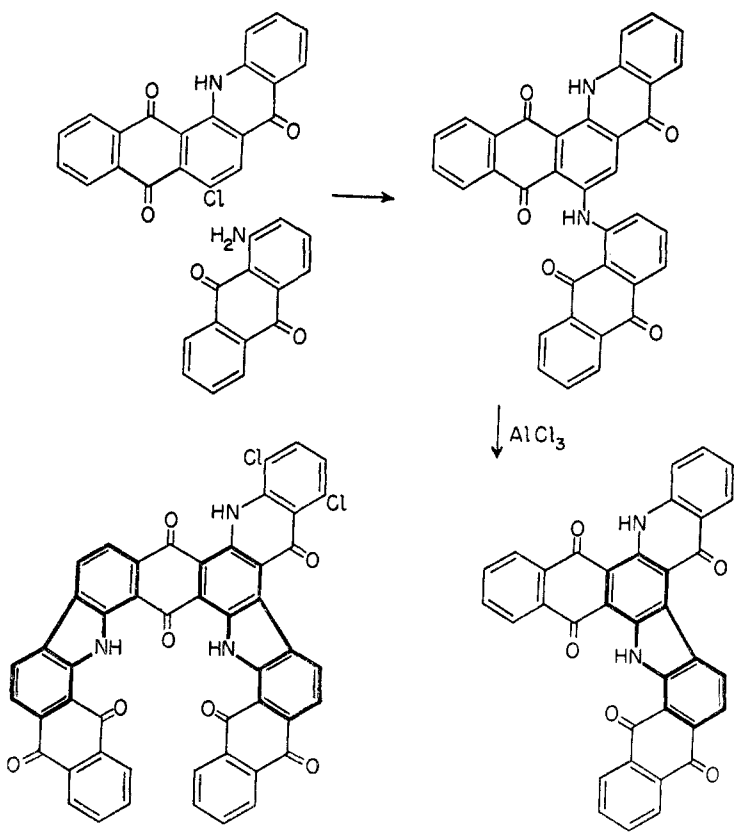


LXI

In this way 1,6-, 3,6-, and 4,6-bisanthraquinonylanthraquinone-2,1-acridones have been made, using 1,6,9,11-, 3,6,9,11-, and 4,6,9,11-tetrachloroanthraquinone-2,1-acridones, respectively (82). Only the halogen in the anthraquinone residue reacts.

4. Carbazoles

When dianthraquinonylamines are submitted to the action of dehydrogenating reagents (oleum, anhydrous aluminum chloride), a bond is formed, closing a five-membered ring between the rings bearing the imino group. In this way, complex anthraquinone-acridone-carbazoles (46, 61, 117) result; a simple one is shown in formula LXII. The carbazole ring is outlined in the structure. Indanthrene Khaki GR is the dichloroanthraquinone-acridone-biscarbazole (LXIII) formed by carbazoling a bisanthraquinonylaminoanthraquinone-acridone of the type of LXI.

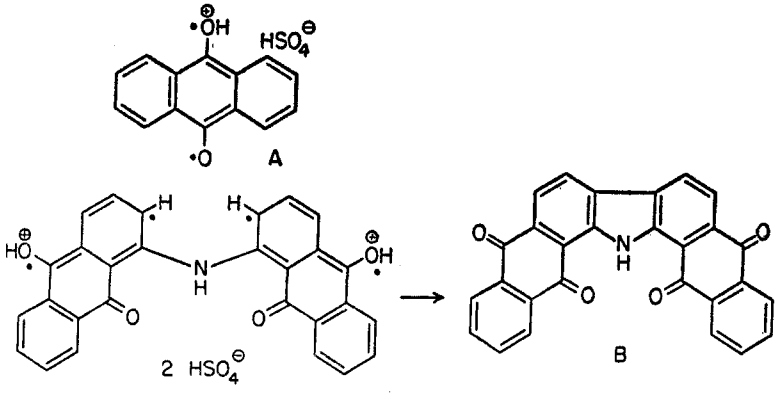


LXIII LXII

The conversion of a dianthraquinonylamine to a carbazole results in an increase in affinity of the dye for cotton, probably on account of the planar configuration of the carbazole nucleus. If an α-anthraquinonylamino substituent is introduced

into a carbazole, the affinity is reduced, but if this is carbazoled, the affinity is regained or improved.

The cyclization requires the use of strong acids (sulfuric or chlorosulfonic) or a Lewis acid (anhydrous aluminum or titanium chloride). The mechanism of this cyclization, for many years an uncertainty, has only recently been explained (34). It is now believed to be a self-union of diradicals, formed under the acidic conditions. Nuclear magnetic resonance studies have shown that a solution of anthraquinone in concentrated sulfuric acid contains the diradical A; it is assumed that this is a stronger base than the quinone from which it is derived. In a diradical of this sort, electrons are available on the carbon atom which is para to the carbonyl group. In dianthraquinonylamines both para carbon atoms, which are at the same time ortho to the imino group, would show diradical character; their union, forming a bond, results in a carbazole (B).



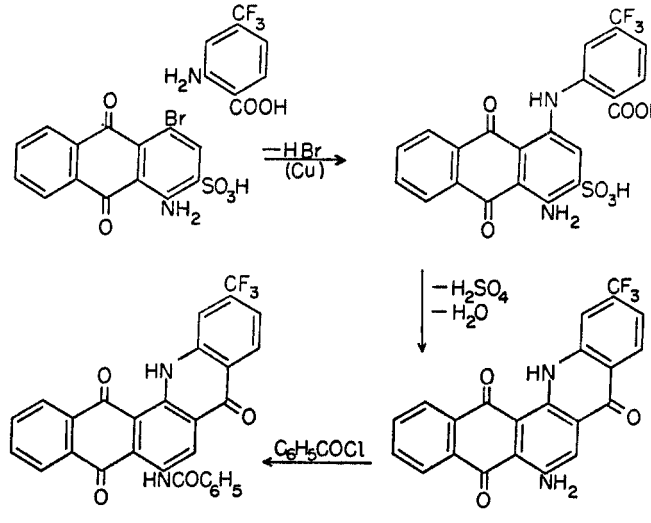
H. AMIDES

Amides are obtainable by acylation of the aminoanthraquinone-acridones, or by an Ullmann reaction between a chloroanthraquinone-acridone and an amide. *p*-Toluenesulfonamido derivatives have already been mentioned (Section VI), since they are intermediates in one procedure for making amines. The amidoanthraquinone-acridones are vat dyes in their own right, but are very often intermediates for carbazoling. Only a few examples will be given, but there is a considerable variety mentioned in the patents. 10-Acetamido- and 10-benzamidoanthraquinone-2,1-acridones are prepared by acylation of the 10-amine (4); the latter is also formed by the action of benzamide on the 10-bromo derivative (5). Cotton is dyed a very fast, pure blue by the latter. 6-Benzamidoanthraquinone-2,1-acridone is the parent of a series made by aroylation; benzoyl, methyl-, nitro-, chloro-, dichloro-, methoxy-, and ethoxybenzoyl chlorides, oxalyl, isophthaloyl, and terephthaloyl chlorides have been used (95).[8] The 10-methyl derivative has been made by the isatin procedure (50). 6-Benzamidoanthraquinone-2,1-acridone gives a reddish-blue color to cotton (51); a chlorine atom

[8] These are only simple aroyl chlorides. A complete list of the many chlorides with more complex systems has had to be omitted; they will be found in the patent literature.

in the 11-position makes it less red (151). The presence of halogens in the 9,12-positions leads to blue and bluish-gray dyes (95, 101). Perhaps the most interesting are the trifluoromethyl derivatives, of which a series with different aroyl groups has been made (31d). The benzoyl was the best of these. Cinnamoylamido compounds have also been patented (118, 134).

6-Benzamido-11-trifluoromethylanthraquinone-2,1-acridone, 6-benzamido-11-trifluoromethyl-3,4-phthaloyl-acridone (31c, 58), Indanthrene Printing Blue FG (31d), C.I. Vat Blue 21 (44), C.I. No. 67920 (LXIV), is a chlorine-fast dye, the discovery of which is credited to Schlichenmaier and Berlin in 1937. The preparative procedure starts with 4-trifluoromethylanthranilic acid (3-amino-4-carboxybenzotrifluoride) and "bromamine acid," which undergo an Ullmann condensation to "sulfacridylic acid" [1-amino-4-(2-carboxy-5-trifluoromethylanilino)anthraquinone-2-sulfonic acid], which is isolated as the potassium salt. This is cyclized, in the *absence of iron*, by sulfuric acid monohydrate; the 6-amino-11-trifluoromethylanthraquinone-2,1-acridone (LXV) melts at 345°C. The benzoylation is done in dry chlorobenzene, heating being continued as long as hydrogen chloride is given off. The dye melts at 365°C.

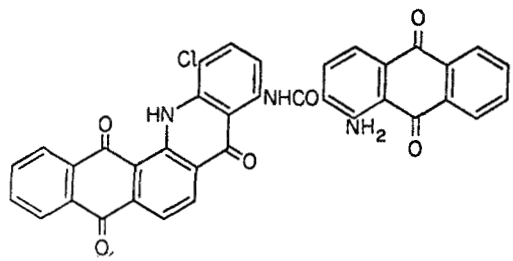


LXIV LXV

9-*N*-(1-Amino-2-anthaquinoyl)carbamyl-12-chloroanthraquinone-2,1-acridone (LXVI), Indanthrene Bordeaux BB, C.I. No. 67815 (44), is obtained by condensing 2,5-dichloroaniline with 1-nitroanthraquinone-2-carboxylic acid, cyclizing, replacing the chlorine at position 9 by an amino group, and acylating with 1-aminoanthraquinone-2-carboxy chloride.

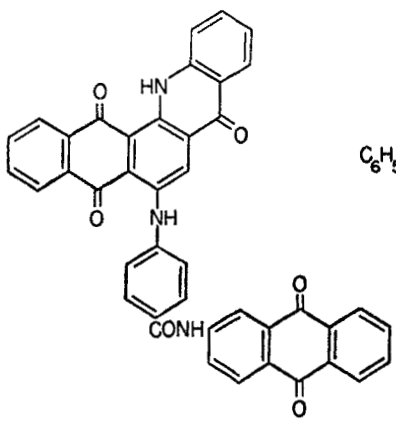
Analogously prepared amides are known in which the group is at other positions than 6 (72, 82, 102, 115). 1,4-Dibenzamidoanthraquinone-2,1-acridone is made from 1-amino-5,8-dibenzamidoanthraquinone and ethyl *o*-chlorobenzo-

ate, cyclizing by the dithionite procedure, or from 1-chloro-5,8-dibenzamidoanthraquinone and anthranilic acid, cyclizing by sulfuric acid. The latter procedure is of interest because one of the benzoyl groups is lost during the cyclizing, so that the substance has to be rebenzoylated (98).

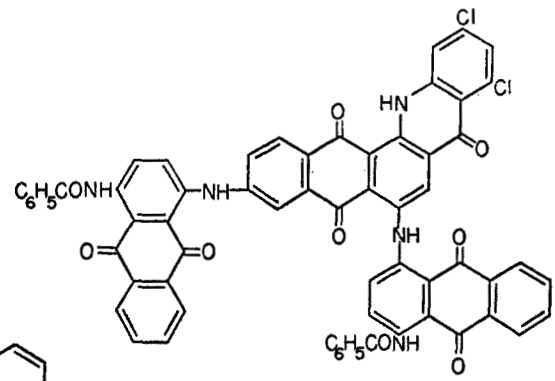


LXVI

A slight variant is shown in compound LXVII, which is prepared by an Ullmann condensation between 6-aminoanthraquinone-2,1-acridone and 2-(4-bromobenzamidoanthraquinone). This is a clear, bright green dye (151). Related bisamides (LXVIII) are gray dyes (72, 115).



LXVII

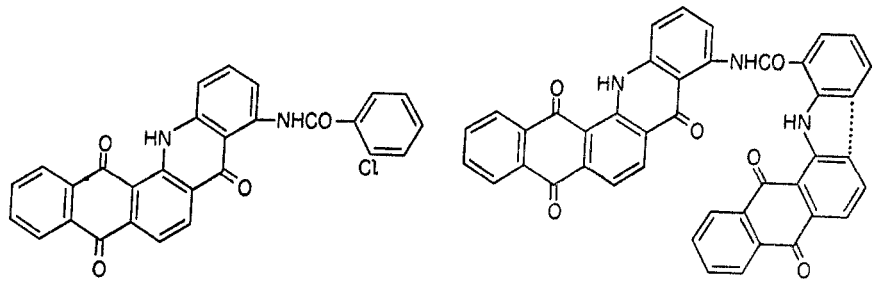


LXVIII

6-*p*-Toluenesulfonamidoanthraquinone-2,1-acridone (XLVII) is difficultly soluble in pyridine, aniline, and nitrobenzene. It dissolves in acetic acid (1:3000), from which it separates in needles melting at 295°C. (144). 12-Chloro-9-*p*-toluenesulfonamidoanthraquinone-2,1-acridone has been made (141).

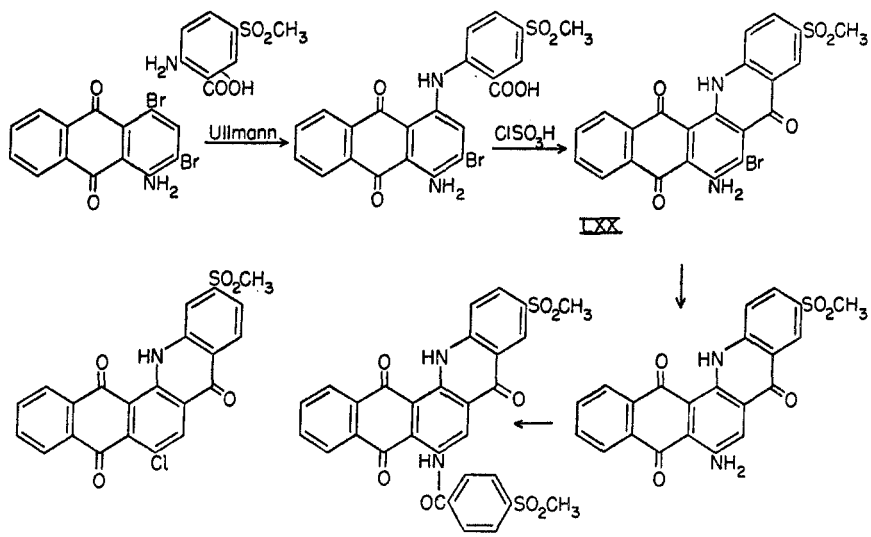
Indanthrene Brown 3GT is an anthraquinone-acridone-carbazole, prepared by condensing Indanthrene Red Violet RRK [6,10,12-trichloroanthraquinone-2,1-acridone (XXVI)] with one mole of 1-amino-5-benzamidoanthraquinone and carbazoling (31e, 69, 73). Indanthrene Browns NGR and IVGR are the biscarbazoles from bis(benzamidoanthraquinone-acridones) (71, 72). An inter-

esting amide type, an intermediate for carbazoles, is shown in structure LXIX (115).



LXIX

Methanesulfonyl derivatives are varied and numerous (65, 66).



LXXIII LXXII LXXI

I. HYDROXYANTHRAQUINONE-ACRIDONES

Very few of these compounds have been recorded, because the presence of the hydroxyl group increases the solubility in alkali, so that dyed fabrics fade on washing. Consequently, it is disquieting to note that a substance, melting at 321°C. and *insoluble* in alkali, is said to be 6-hydroxyanthraquinone-2,1-acridone (146). The unusually low melting point is also noteworthy.

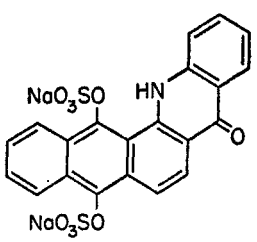
7-Chloro-6-hydroxyanthraquinone-2,1-acridone is prepared from 2,4-dichloro-1-hydroxyanthraquinone and anthranilic acid in the usual way (141). Upon treatment with 1-aminoanthraquinone the halogen is replaced, giving 7-(1-anthraquinonylimino)-6-chloroanthraquinone-2,1-acridone (141).

J. SOLUBILIZED ANTHRAQUINONE-ACRIDONES

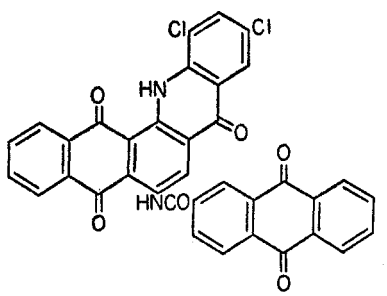
1. Anthrasols

The anthraquinone-acridones form the usual "vats" on reduction with alkaline dithionite solution; these are sodium salts of anthrahydroquinone-2,1-acridone. In a few instances, already cited (14), the vats are formed during the synthetic procedure and are used directly.

Stabilized esters, Anthrasols, of types XI and LXXIV (*cf.* Section II,B,3), can be prepared in the usual manner (44, 122), which consists in treatment of the dye in pyridine with a metal (copper, zinc, iron) and a source of sulfur trioxide (pyridine–sulfur trioxide complex, chlorosulfonic acid, or methyl chlorosulfonate); this is followed by making alkaline, filtering, and removing the pyridine by steam distillation. Alternatively, the leuco dye may be treated with chlorosulfonic acid and worked up as before. Difficultly soluble vat dyes are claimed to form esters more readily if diethylcyclohexylamine and an inert solvent are employed, with the metal and chlorosulfonic acid (47). The solubilized form of 6-(1-aminoanthraquinoylamido)-10,12-dichloroanthraquinone-2,1-acridone (LXXV) is "one of the best of the new anthrasol grays developed (59d)."



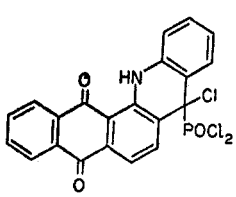
LXXIV



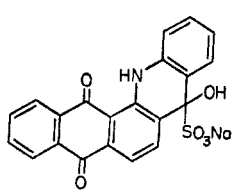
LXXV

2. Hydroxysulfonates

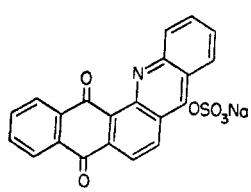
A characteristic reaction that is applicable only to acridones consists in reducing the dye to its vat and treating the mixture with phosphoryl chloride, water, and a dispersing agent (e.g., Nekal BX). The water-soluble reaction product, a dihydroacridine, believed to be LXXVI, is salted out of the solution with sodium sulfate.



LXXVI



LXXVII



LXXVIII

Upon reaction with sodium bisulfite, a hydroxysulfonate (LXXVII) is formed; it can also be salted out. The acridone is regenerated from this new class of substance by a mild alkali (sodium carbonate). The one shown is not soluble enough to have technical value, but those from bisacridones appear to be potentially important (59e). A similar salt is said to have been obtained by heating 1-(2-formylanilino)anthraquinone with sulfuric acid (d. = 1.31) at 110–115°C. (116).

3. "Oxonium salts"

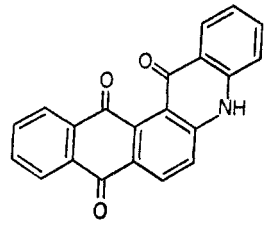
When the acridones are dissolved in concentrated sulfuric acid, "oxonium salts" are formed. These are probably sulfates (esters, LXXVIII) of the tautomeric acridol structure. The alternative possibility, that these are quaternary nitrogen salts, has been neither excluded nor established. They sometimes separate upon dilution and are useful for purification (18, 83).

There appear to be no thiono- or selenoanthraquinone-2,1-acridones. They should be preparable by the standard procedure employed with acridone (64), which proceeds by way of the chloroacridinium dichlorophosphate (LXXVI).

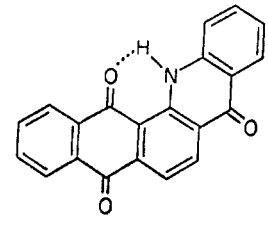
K. PHYSICAL PROPERTIES OF ANTHRAQUINONE-2,1-ACRIDONES

The anthraquinone-2,1-acridones are all highly colored, high-melting solids. They often separate from reaction mixtures in analytically pure form. This is fortunate, because they are so very slightly soluble in most reagents. At the time much of the experimental work was done, the available useful solvents were pyridine bases, quinoline, nitrobenzene, aniline, dialkylanilines, and, later, trichlorobenzene. In these, 1 g. of substance might be recrystallized from 1 liter of solvent. Of the more recently available solvents, pyrrolidone, dimethyl sulfoxide, benzonitrile, and nonylphenol appear to be about equal to the older ones in dissolving power. Dimethylformamide is satisfactory in some cases but causes unexplained changes in others. On a small scale, these sparingly soluble compounds can be recrystallized by placing them in the thimble of a hot Soxhlet extractor (123).

The solubility, of course, depends upon the substance. Roughly speaking, melting points are lowered and solubility increased by introduction of halogens and alkyl substituents, while solubility is decreased by more complexity, especially by the addition of fused benzene rings.



XIII



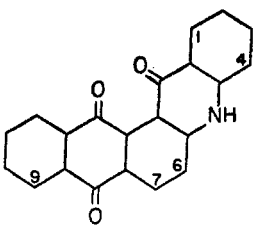
LXXIX

Many anthraquinone-2,1-acridones are vat dyes. For their properties and uses specialized texts must be consulted (44, 113, 136, 151). The simpler members do not impart deep shades to the fiber (136) and, in many instances, are not tightly held (i.e., "fast") (125b). Even if not fast when dyed from a vat, many can be applied by printing. The dyes are found in all colors except yellow. The isomeric anthraquinone-1,2-acridones (XIII) are yellow (150), but are not useful as dyes. The reason for the difference may be, in part, at least, attributed to the possibility of forming a chelate ring (LXXIX) in the -2,1- series.

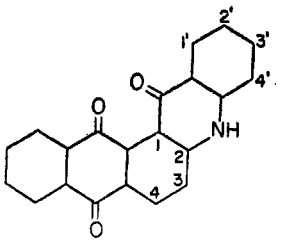
III. Anthraquinone-1,2-acridones

This series is isomeric with the industrially very important anthraquinone-2,1-acridones, and was discovered by Ullmann (139) at the same time. Since the dyes (yellow or orange) are sensitive to alkali and are not fast on cotton, there has been very little interest in the group.

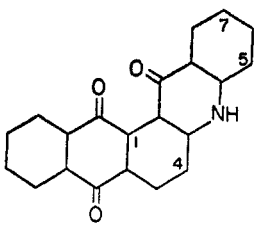
The nomenclature and numbering used in this series is not as confusing as with the isomeric -2,1-acridones. The parent compound (XIII) has been variously named as anthraquinone-1,2-acridone (30c, 67b, 139, 140, 150), 1,2-phthaloylacridone (30c), 2,3,γ-naphthacridine-8,13,14(5)-trione (43), and anthraquinone-1,2(*N*);1′,2′(*N*)-benzacridone (30c). By the "a" system it is 5-aza-5*H*-dibenzo[*b*,*h*]phenanthrene-8,13,14-trione. The numberings that have been employed are shown herewith.



XIII: R.I. No. 3295
(used in this paper)



(Houben)

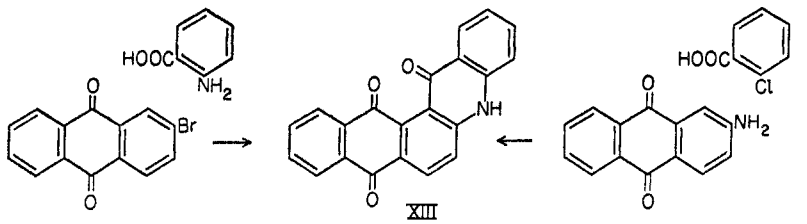


1,2-Phthaloylacridone

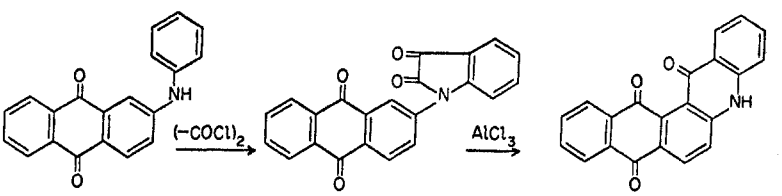
The same general methods of preparation (139, 140, 150, 151) used with the isomeric -2,1-acridones are applicable, except that the anthraquinones have a reactive bromine atom or amino group in the 2-position. The use of intermediates having substituents in known positions serves to locate them in the products. The same condensing and cyclizing agents are employed. Schaarschmidt's nitrile (125b) and the isatin (50) procedures are also applicable.

Anthraquinone-1,2-acridone is a sparingly soluble (0.8 per cent in boiling pyridine or nitrobenzene), orange-red substance which dissolves in alcoholic sodium hydroxide solution with a violet color. 9-Amino, 9-chloro, 9-hydroxy, and 10-hydroxy derivatives are mentioned in a patent (12). A 6-amino derivative is said to condense with cyanuric chloride (97).

2-Chloroanthraquinone-1,2-acridone, 7-chloro-1,2-phthaloylacridone, 5′-chloroanthraquinonyl-1,2(*N*);1′,2′(*N*)-benzeneacridone (LXXX), separates from



XIII

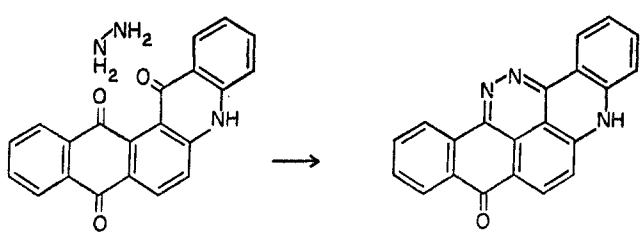


LXXX

XIII

nitrobenzene as an orange-brown crystalline powder, which dyes cotton a deep orange-yellow (125b). The 10-chloro isomer is mentioned in a patent (12).

Anthraquinone-1,2-acridone is a 1,4-diketone, as is readily evident from its reaction with hydrazine. Two molecules of water are eliminated and the triaza compound, anthraquinone-1,2-acridoneazine (LXXXI), results (16, 150).



LXXXI

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IV. References[9]

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