ANTHRACENE AND
ANTHRAQUINONE
T. DE BARRY BARNETT

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ANTHRACENE AND ANTHRAQUINONE

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BY

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PREFACE

It is now over forty years since Auerbach published his "Das Anthracen und seine Derivate,"* and during this period, and more particularly during the last fifteen years, enormous advances have been made in our knowledge of the chemistry of the anthracene derivatives. Much of the research which has been carried out has appeared only in the form of patent specifications, and for that reason has escaped the attention which it merits. It seemed, therefore, that a short account of the anthracene derivatives would not be without value, more especially as many of the most valuable fast dyes belong to this class of compound. At the urgent request of several friends the author has therefore arranged his own private notes on the subject in book form, and trusts that the appearance of this volume will lead to greater attention being paid to anthraquinone chemistry in this country than has been the case up to the present. Many of the claims made in the patent literature require elaborating and confirming (or contradicting), and as several anthraquinone derivatives are now manufactured in this country, work of this nature would be suitable for senior students in universities. Such research would be of the utmost value at the present time, when serious attempts are being made to manufacture the very valuable anthraquinonoid dyes in this country.

In the following pages will be found a fairly complete account of the work which has been published up to November, 1920, on the derivatives of anthracene and

* Second German edition, 1880. English translation by Sir William Crookes of first German edition, 1877.

anthraquinone ; but an account of naturally occurring anthracene derivatives, such as chrysarobin, etc., has purposely been omitted, as an up-to-date account of these substances has recently appeared elsewhere.* References have been given liberally, although it is not claimed that those cited form a complete bibliography of the subject. All references given have been read by the author in the original with the exception of a few German patents which have been granted during or since the war, and which at the time of going to press are not available in the Patent Office library. For such patents the author has been compelled to rely on the very inadequate abstracts published in journals such as the *Chemisches Zentralblatt, Chemiker Zeitung,* and *Journal of the Society of Chemical Industry.* The introduction of new systems of notation is not to be encouraged as a rule, but after mature consideration the author decided to make use of his own modification of Pfaff's system. The best excuse he can offer for this is the very considerable saving in the cost of composing which it has effected. In cases where the straight line notation is not suitable, the formulæ have been reproduced by means of blocks.

The author wishes to take this opportunity of expressing his thanks to Mr. J. W. Cook, B.Sc., for much valuable help while the book was passing through the press.

<div align="right">E. DE BARRY BARNETT.</div>

SIR JOHN CASS TECHNICAL INSTITUTE,
  JEWRY STREET, ALDGATE, E.C. 3,
    Jannary, 1921.

* Perkin and Everest, "Natural Organic Colouring Matters."

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ABBREVIATIONS

A.   Annalen der Chemie.
A. ch.   Annales de Chimie et de Physique.
A. P.   United States of America Patent.
Am.   American Chemical Journal.
Am. Soc.   Journal of the American Chemical Society.
B.   Berichte der Deutschen Chemischen Gesellschaft.
Bl.   Bulletin de la Société Chimique de Paris.
C.   Chemisches-Zentralblatt.
C. r.   Comptes rendus de l'Académie des Sciences.
Ch. Z.   Chemiker-Zeitung (Cöthen).
D.R.P.   Patentschrift des Deutschen Reiches.
E.P.   English Patent Specification.
F.P.   French Patent Specification.
F.T.   Zeitschrift f. Farben- u. Textil-Industrie.
F.Z.   Färbe-Zeitung.
G.   Gazetta chimica italiana.
J.   Jahresbericht der Chemie.
J. pr.   Journal für praktische Chemie.
M.   Monatshefte der Chemie.
Mon. Sci.   Moniteur Scientifique.
Pat. Anm.   Patent Anmeldung.
Proc.   Proceedings of the Chemical Society.
R.   Receuil des travaux chimiques des Pays-Bas.
R.G.M.C.   Revue Général des Matières Colorantes.
Soc.   Journal of the Chemical Society.
Z.   Zeitschrift für Chemie.
Z. ang.   Zeitschrift für angewandte Chemie.

FIRMS.

Agfa.   Aktien-Gesellschaft für Anilin Fabrikation, Berlin-Treptow.
B.A.S.F.   Badische Anilin- u. Soda-Fabrik, Ludwigshafen a/Rh.
By.   Farbenfabriken vorm. Friedr. Bayer u. Co. Elberfeld u. Leverkusen.
Cas.   Leopold Cassella u. Co., G.m.b.H. Frankfurt a/M.
G.E.   Chemische Fabrik Griesheim-Elektron, Frankfurt a/M.
K.   Kalle u. Co. Aktien Gesellschaft, Biebrich a/Rh.
M.L.B.   Farbwerke vorm. Meister Lucius u. Brüning, Hochst a/M.
Wed.   Wedekind u. Co. G.m.b.H., Uerdingen.
W.t.M.   Chemische Fabrik vorm. Weiler-ter-Meir, Uerdingen.

ANTHRACENE
AND   ANTHRAQUINONE

CHAPTER I

INTRODUCTION

HISTORICAL SKETCH

ANTHRACENE was first discovered in 1832 by Dumas and Laurent, who obtained it from the higher boiling fractions of coal tar and named it "paranaphthalene," although Laurent, who investigated the substance more closely a few years later, changed the name to anthracene. In 1857 Fritzsche also obtained anthracene from coal tar, and seems to have prepared it in a purer state than Dumas and Laurent; and a few years later, in 1862, Anderson also described its isolation and the preparation from it of several derivatives. In 1866 the first synthesis of anthracene was published, as in this year Limpricht obtained it by heating benzyl chloride with water at 180°, and Berthelot showed that anthracene is obtained by the pyrogenic decomposition of many simpler hydrocarbons.

About this period some doubt was thrown on the belief that anthracene was really a single chemical compound, and Fritzsche regarded it as a mixture of two substances, which he named photene and phosene. That anthracene should be regarded as a mixture is hardly surprising in view of the fact that it is not a particularly easy compound to obtain in a state of purity, and at the period in question very little was known of the constituents of coal tar.

The first structural formula which was proposed for anthracene was due to Graebe and Liebermann, who proposed both the formula now assigned to phenanthrene and also what is now known to be the correct formula. They discussed the merits of both of these, but regarded the phenanthrene formula as being more in accordance with the then known facts. Shortly after, however, the discovery of phenanthrene rendered the second alternative almost certain, final confirmation being obtained by the synthesis of anthracene derivatives from phthalic acid and phenols, and of anthraquinone itself from benzoyl benzoic acid. Further proof of the presence of two benzene rings lies in the fact that whereas nitroanthraquinone on oxidation gives nitrophthalic acid, the corresponding aminoanthraquinone gives phthalic acid itself. The oxidation of anthracene to anthraquinone was first described by Laurent, who named the product " paranaphthalose," or, at a later date, " anthracene." Anderson also prepared anthraquinone and named it " oxanthracene," the modern name, " anthraquinone," being introduced by Graebe and Liebermann.

Up to the year 1868 anthracene was regarded merely as a chemical curiosity, but in that year Graebe and Liebermann made the discovery that alizarin yields anthracene when distilled over zinc dust, and hence that alizarin was to be regarded as a derivative of anthracene.[1] This epoch-making discovery came at an opportune moment, as in 1856 Perkin had started making Mauveïne on a commercial scale, and other synthetic dyes such as Magenta, Nicholson's Blue, Methyl Violet, Saffranine, and Bismarck Brown had rapidly rewarded the labours of those investigating the possibility of obtaining dyewares from coal products. The very great success that had recently attended other researches made with a view to obtaining synthetic dyes, naturally led to hopes that alizarin might also be made by an artificial process, and these expectations were fulfilled

[1] The formula of alizarin had been previously determined by Strecker, who, however, had not published his results in any journal, although he mentioned the matter in his text-book of *inorganic* chemistry, published in 1866.

in a remarkably short space of time, as in the same year synthetic alizarin was prepared in Germany by Graebe and Liebermann, and in the following year the technical process for its manufacture from anthraquinone sulphonic acid was patented independently by Caro, Graebe and Liebermann,[1] and by Perkin.[2]

The successful manufacture of alizarin naturally led to the investigation of other polyhydroxyanthraquinones, and during the following years several of these were described, but although some of them were found to be of value as dyes, their importance from a technical standpoint was relatively small. The investigation of alizarin and its derivatives led to the preparation of its quinoline, Alizarin Blue X, by Prud'homme in 1877, and ten years later Peter Bohn discovered that fresh hydroxyl groups could be introduced into the molecule by direct oxidation. The immediate result of this discovery was the technical manufacture of Alizarin Green X and Alizarin Indigo Blue, but simultaneously, although independently, R. E. Schmidt discovered that the reaction was a very general one in the anthraquinone series, and that by it many hydroxyanthraquinones could be prepared. It is difficult to overestimate the importance of this discovery, as it rendered available compounds which have proved to be of the utmost value as starting-out substances. Among other valuable dyes which were discovered as a direct result of hydroxyanthraquinones being made easily available may be mentioned Alizarin Cyanine Green and Alizarin Saphirol. Both of these discoveries were due to R. E. Schmidt, the former being obtained in 1894 and the latter in 1897. To R. E. Schmidt is also due the credit of the discovery in 1903 that the presence of mercury during the sulphonation of anthraquinone leads almost exclusively to the formation of α-sulphonic acids, but Iljinsky seems to have made the same discovery independently and almost simultaneously.

In a patent applied for in 1894 an insoluble product is

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[1] Patent applied for on June 25, 1869.
[2] Patent applied for on June 26, 1869.

described as being obtained by heating anthrachrysazin with concentrated aqueous ammonia for fifteen hours at 150–200°, and it is claimed that this substance acts as a brownish black vat dye.[1]   This seems to be the first occasion on which the possibility of vat dyeing with anthraquinone derivatives was taken into consideration, and it is truly remarkable that the discovery should have been delayed so long.   At that period, of course, vat dyeing was not a common method of applying a colouring matter, but it was well known that the indophenols could be applied in this way, and in the case of indigo, vat dyeing had been carried out since almost prehistoric times.   The dyestuff described in the patent proved to be of no technical value, and no further interest seems to have been taken in the matter for some seven years.   In 1901, however, Bohn discovered Indanthrene and Flavanthrene, and the great value of these dyestuffs led to an immediate search for other vat dyes containing the anthraquinone ring system.   Success was soon achieved, as Anthraflavene was discovered by Isler in 1905, and Pyranthrene by Scholl in the same year, whereas the next year saw the discovery of Violanthrene by Bally.   Since that time the discovery of new anthraquinonoid vat dyes has been continuous, although during the last two or three years there has been a very remarkable falling off in the number of patents taken out.   This falling off in the patent claims is not, however, confined to the anthraquinone series, but is very noticeable throughout the whole of the chemical industry.   It does not denote any slackening of research, nor does it point to exhaustion of the subject, but is to be attributed to the formation of the " Interessengemeinschaft "   among   the   leading   German firms having removed practically all competition, with the result that the firms interested prefer to preserve their discoveries as trade secrets, and thus avoid furnishing rival concerns in other countries with information.   The depreciated value of the mark rendering protection in foreign countries somewhat costly is also, no doubt, to some extent

[1] M. L. B., D. R. P. 83,068.

responsible for the policy of secrecy. Up to the present the British firms which are now interested in the manufacture of vat dyes have applied for very few patents. This, however, is not at all surprising, as they have naturally been fully engaged in reducing " known " processes to a workable form.

The chief workers on anthraquinone have been Liebermann, R. E. Schmidt, Bally, Bohn, Ullmann, and Scholl. Liebermann worked almost continuously on the subject from 1868 right up to the time of his death in 1916. Ullmann has been responsible for much very useful synthetic work, but in recent years the beautiful work of Scholl must be regarded as taking first place. The names of R. E. Schmidt, Bally, and Bohn are found comparatively little in the literature, as their discoveries are usually patented by the firms with which they are associated. The same remark also applies to Isler, Iljinsky, and others.

DYEING

Any detailed description of either the theory or practice of dyeing would be completely out of place in a volume of this description, but a few very brief notes concerning the more important types of dyestuffs may prove useful to the reader who has not studied tinctorial chemistry.

An *acid dye* is usually a sulphonic acid, and is applied to the fibre from an acid or neutral bath. In the anthraquinone series the most important acid dyes are Alizarin Cyanine Green and Alizarin Irisol, although several others are used. They are almost exclusively used for colouring wool and have little or no affinity for vegetable fibres.

A *basic dye* is a salt of an amine. In the anthraquinone series the basic dyes which have been described are of no importance. Basic dyes are used for dyeing silk and wool, and often give extremely bright shades.

A *mordant dye* is a dye which can only be fixed on the fibre by means of a metallic oxide, usually the oxide of aluminium, chromium, tin, or iron, although nickel and magnesium are also sometimes used. In this case the colour

developed is due to salt formation taking place between the metallic oxide and the dyestuff, although exactly how the salt or " lake " becomes fixed to the fibre is not known. All mordant dyes contain hydroxyl groups and, as will be seen later, the positions occupied by these groups is of great importance. Mordant dyes usually give different shades according to the mordant used, alizarin being a typical dye of this type.

Sometimes when a fibre is dyed with an acid dye, after-treatment with a solution of sodium bichromate or chromium fluoride alters the shade and renders it much faster. The change is brought about by salt formation, so that such dyes can be regarded as mordant dyes in the widest sense. In their case it should be noted that the " mordant " is applied after the dyestuff itself, whereas in the case of the true mordant dyes the mordant is applied first and then the colouring matter. Mordant dyes can be applied to both animal and vegetable fibres.

A *vat dye* is an insoluble coloured substance which, however, is readily reduced to a soluble substance which has affinity for the fibre and which is readily reoxidised on exposure to the air. The soluble reduction product or " vat," may either be colourless, as is the case with indigo, or it may be highly coloured, as is almost always the case where anthraquinone derivatives are concerned. The colour of the " vat," however, has no relation to the colour of the dye itself, as the finished shade is only developed by sub-sequent oxidation by exposing the dyed fibre to the air. All anthraquinone derivatives in which there are two cyclic carbonyl groups in suitable positions, not necessarily form-ing part of the same ring, give easily oxidised reduction products when reduced in alkaline solution. Not all anthra-quinone derivatives, however, are vat dyes, as a vat dye is only obtained when the reduction product has affinity for the fibre.

Vat dyes can be applied either to animal or vegetable fibres, but the use of the anthraquinonoid vat dyes is almost completely confined to cotton dyeing, as the vats are usually

too strongly alkaline to be used for wool. Vat dyeing is almost always carried out with the yarn, as with piece goods penetration is not sufficiently good to allow satisfactory results to be obtained. Vat dyes, however, are largely used in printing, and are often well adapted for obtaining discharge effects, *i.e.* where a white pattern is obtained by dicharging the dye.

Vat dyeing is somewhat expensive, but the shades obtained are usually very fast. Vat dyeing is largely used in the preparation of the best quality shirtings and upholstery materials.

The *commercial names* given to dyes were formerly purely fancy names, and names containing works like anthracene were not given with a view to representing chemical constitution—Anthracene Red, for example, being a disazo dye in no way connected with anthracene. Now, however, a much more sensible system is adopted, as the various manufacturing firms have registered trade names for different types of dyes, the individual dyes being distinguished by a word and initials denoting the shade given. This method of nomenclature has been carried out most systematically in the case of the anthraquinone vat dyes, the following being a list of the chief registered names applying to this class of dye, together with the name of the firm registering.[1]

REGISTERED NAME.	FIRM.
Algol [2]	Bayer & Co.
Caledon	Scottish Dyes, Ltd.
Chloranthrene [3]	British Dyestuffs Corporation, Ltd.
Helindon	Meister Lucius and Brünning.
Hydranthrene	L. B. Holliday & Co., Ltd.
Indanthrene	Badische Anilin u. Soda Fabrik.

[1] Some Cibanon colours (G.C.I.B.) are anthraquinonoid vat dyes containing sulphur.

[2] Also Leucol.

[3] Duranthrene was used by Levinstein, Ltd., before their amalgamation with British Dyes, Ltd.

Colour and Constitution

The relation of colour to constitution will be treated in detail, so far as our present knowledge permits, in connection with the different classes of anthraquinone derivatives, but at this point attention may be drawn to a few generalities which have been found to apply to the simple derivatives in which only one anthraquinone residue is present. The colour referred to is in every case the colour of the finely divided substance, or the colour of its solution in some indifferent solvent, and is not the colour obtained by dye trials. The usual conventional method of considering the shade to " deepen " when it passes successively from yellow to orange, red, violet, blue, and green is employed, the reverse charge being a " lightening " of the shade.

Anthraquinone itself is practically colourless, and the entrance of nitro groups and halogen atoms has but a very slight effect, although bromine atoms deepen the colour rather more than chlorine atoms. The entrance of a hydroxyl group, however, has a very considerable influence, although the auxochromic effect is almost completely destroyed by replacing the hydroxyl hydrogen atom by an alkyl, aryl, or acyl group. As would be expected, the sulphydrate group has a similar but more marked influence than the hydroxyl group.

The influence of a primary amino group is much greater than that of a hydroxyl group, and in this case replacement of one aminohydrogen atom by an alkyl or aryl group increases its auxochromic character, the influence of an aryl group in this direction being considerably greater than that of an alkyl group. On the other hand, replacing one amino hydrogen by an acyl group decreases its auxo-chromic character, although by no means destroying it, and at the same time confers powerful tinctorial properties, so that the acyl amino anthraquinones can be used as vat dyes.

The above facts are well illustrated by the following compounds :—

OH	NH_2	$NHCH_3$	NHPh	$NHCOCH_3$
Yellow.	Brick red.	Bluish red.	Violet red.	Yellow.
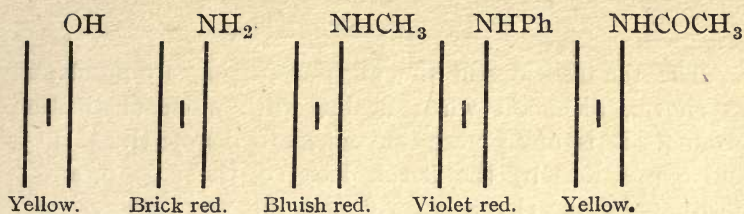
The influence of a group is always much greater when in the α-position than when in the β-position.

When two or more groups are present their effect is more or less additive, but when they are in the *para-* position to one another they seem to reinforce one another, a property which has been made use of to a considerable extent. The following formulæ represent the reinforcing effect of a second substituent in the *para-* position :—

NH_2	NH_2	NHCOPh	NHCOPh
	OH		NHCOPh
Brick red.	Bluish red.	Yellow.	Red.

NH_2	$NHCH_3$	NHPh	NHPh	NHPh CH_3
NH_2	NH_2	NH_2	$NHCH_3$	NHPh CH_3
Violet.	Bluish violet.	Blue.	Greenish blue.	Green.
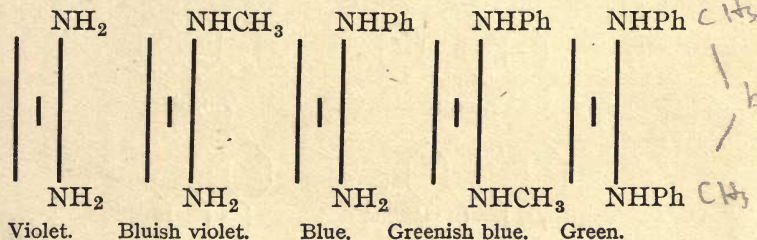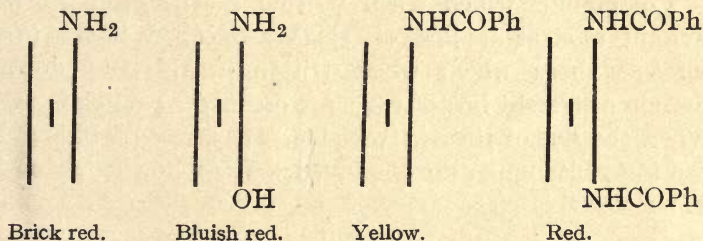
The above rules are very general in their application and render it possible to predict the colour of a simple anthraquinone derivative with considerable accuracy. Where the more complicated compounds are concerned, however, the state of our knowledge at present hardly justifies the drawing of conclusions, although, as will be seen in the sequel, regularities can often be detected.

The ten positions in the anthracene ring are numbered as shown, although when dealing with monosubstitution products it is often more convenient to denote the 1, 4, 5, and 8 positions by the Greek letter α, the 2, 3, 6, and 7 positions by the Greek letter β, and the 9 and 10 positions by the prefix *meso-* or *ms-* :
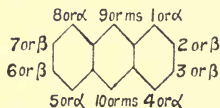

In the case of the more complex condensed derivatives this system is insufficient, and the following notation has been proposed by Scholl.[1]

Compounds which when written in the ordinary way contain a straight line of rings are called linear (*lin.*), whereas those which when written in this way do not contain a straight line of rings are denoted as angular (*ang.*). When the line of rings is twice bent the terms *cis*-bisangular and *trans*-bisangular are employed. The following examples will make this clear :—

Linear.
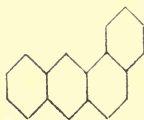
Angular.
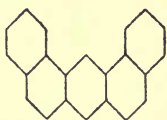
cis-Bisangular.
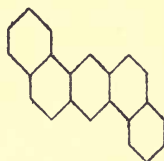
trans-Bisangular.

For greater accuracy condensed systems are regarded as anthracene derivatives and the fused-on rings as substituents. The anthracene ring is numbered as usual, beginning with that α-carbon atom which takes part in the

[1] B. **44**, 1235 ; 1662.

formation of a fused-on (" aufgepropfte ") ring, or is nearest such a ring. The following examples illustrate this system.

1.2-Benzanthracene.   1.9-Benzanthrone.   2.9 Naphthanthrone.
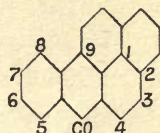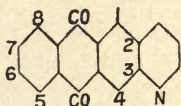
2.3-Pyridinoanthra-
quinone.
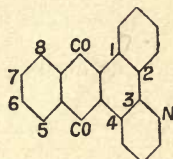
3(N).4-Pyridino-1.2-benzanthra-
quinone.

If two or more independent fused-on rings are present the simplest takes the lowest numbers, isocyclic rings having preference over heterocyclic ones.
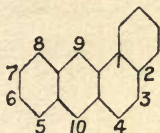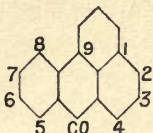
The positions in the fused-on ring are numbered by beginning with the carbon atom nearest the lowest numbered carbon atom of the anthraquinone ring, the rings being specified by the usual prefixes such as Bz., Py, Nt, etc. When the rings are heterocyclic it is often more convenient to denote the positions of substituents by Greek letters.
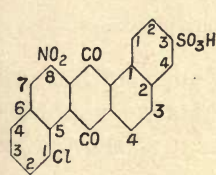
8-Nitro[5.6]Bz.-1-chlor-
1.2.5.6-dibenzanthra-
quinone [1.2] Bz.-3-
sulphonic acid.
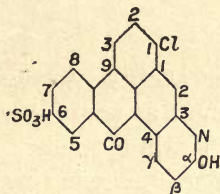
Bz.-1-chlor-Py-α-hydroxy-
3(N)-4-pyridino-1.9-benz-
anthrone - 6 - sulphonic
acid.
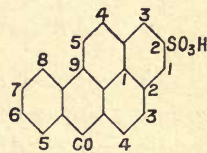
2.9-Naphthanthrone-
Nt-2-sulphonic acid.

If two independent anthraquinone rings are present the above system is applied, but the positions in one anthra-quinone ring and its attached groups are denoted by plain

figures, and the positions in the other anthraquinone ring and its groups by dashed figures :
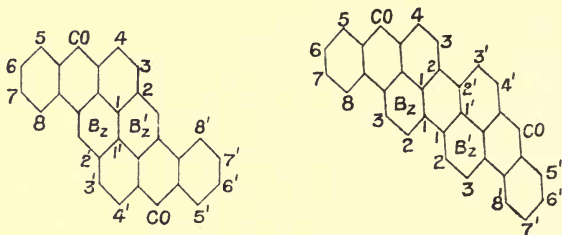
With more highly condensed systems any system of numbering becomes very cumbersome, and it is best to use the formula.

For denoting the position of substituents in simple derivatives of anthracene and anthraquinone the author has for many years employed an adaptation of Pfaff's system. In this anthracene is denoted by three vertical lines of equal length and anthraquinone by two lines of equal length with a shorter line between them :

Anthracene.
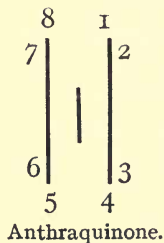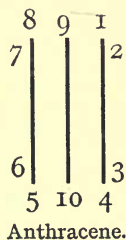
Anthraquinone.

The same system is adopted when dealing with more complex linear bodies, such as naphthacenquinone, naphthacendiquinone, dinaphthanthraquinone, etc., a short line always representing a *para*-quinone ring :

1.4.9.10-Anthradi-
quinone.

2.3-Benzanthraquinone.
lin-Benzanthraquinone

lin-Dibenz-1.4.5.8
anthradiquinone.
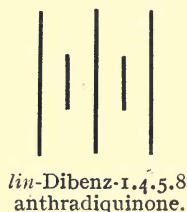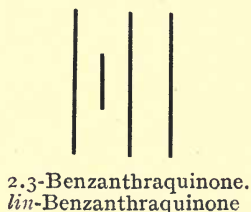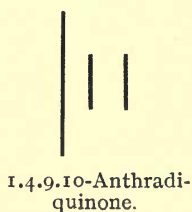
This system has its limitations as it is not well adapted for denoting benzanthrones and other derivatives in which an *ms*-carbon atom forms part of a fused-on ring. It, however, is easily and rapidly written and is perfectly satisfactory in cases where the simpler derivatives of anthracene and anthraquinone are concerned. Its use when making notes will be found a great saving of time.

CHAPTER II

ANTHRACENE AND ITS HOMOLOGUES

ANTHRACENE.—Coal tar is, of course, the only source of anthracene which is of any practical importance, the hydrocarbon being first isolated by Dumas [1] in 1832. Dumas named it " paranaphthalene," and observed that it was oxidised by nitric acid to a yellow crystalline substance. No synthesis of anthracene that is of any practical importance as a method of obtaining the hydrocarbon has yet been devised, but numerous syntheses have been described which have considerable interest from a theoretical standpoint, and the chief of these will be briefly mentioned.

Anthracene has been obtained by several pyrogenic methods, and these throw some light on the probable mechanism of formation of the hydrocarbon during the distillation of coal. Schultz [2] found that anthracene is formed when turpentine vapour is passed through a red-hot tube, and under somewhat similar conditions it was obtained by Letny [3] from Caucasian petroleum, by Liebermann and Burg [4] from lignite tar oil, and by Atterberg [5] from wood tar oil. o-Benzyl toluene also gives it when passed through a red-hot tube,[6] or, in better yield, when passed over lead oxide below a red heat.[7]

Toluene, benzene, or styrene, when mixed with ethylene and passed through a red-hot tube, give anthracene,[8] and in connection with this it is interesting to notice that Kraemer and Spilker [9] have found that methylated benzenes will

[1] A. 5, 10.
[2] B. 7, 113. Cf. Staudinger, B. 46, 2466.
[3] B. 10, 1112; 11, 1210.
[4] B. 11, 723.
[5] B. 11, 1222.
[6] Dorp, A. 169, 216.
[7] Behr and Dorp, B. 6, 754.
[8] Berthelot, A. 142, 254.
[9] B. 23, 3169; 3269.

combine quite readily with styrene in the presence of sulphuric acid to form phenyl aryl propanes, which when passed through a red-hot tube yield anthracene hydrocarbons, the yields being in some cases as high as 63 per cent. It is not impossible that the anthracene derivatives found in coal tar have been formed by very similar reactions.*

Numerous syntheses of anthracene and its homologues by means of aluminium chloride have been recorded. Thus toluene when heated in a sealed tube with anhydrous aluminium chloride gives anthracene, and xylene gives dimethyl anthracene,[1] but in all cases the yields are minute. By condensing an aromatic hydrocarbon in the presence of aluminium chloride with acetylene tetrabromide,[2] ethylidene bromide or chloride,[3] vinyl bromide,[4] perchlorethylene,[5] methylene chloride[6] or chloroform,[7] anthracene hydrocarbons are obtained. In these syntheses it is probable that a *ms*-dihydroanthracene is first formed, which is then oxidised at the expense of part of the halogen compound, or that an *ms*-dichlordihydroanthracene is the first product, this then splitting off two atoms of chlorine. These are not evolved as such, but chlorinate part of the hydrocarbon or react with the carbon bisulphide which is usually used as a dilutant.

Perkin and Hodgkinson[8] and Schramm[9] have shown that benzyl chloride itself gives anthracene under the influence of aluminium chloride, and Limpricht[10] and Zincke[11] have found that benzyl chloride, when heated under pressure with water at 160°, gives a mixture of benzyl alcohol, benzyl ether and ω-chlortolyl phenyl methane, this latter yielding anthracene on distillation.

Jackson and White[12] have applied the method of Wurtz, and by treating *o*-brombenzyl bromide with metallic sodium

* But compare R. Meyer, B. **45**, 1609 ; **46**, 3183, who has obtained anthracene by condensing naphthalene with acetylene.

[1] Anschütz, A. **235**, 157. [2] A. **235**, 157.
[3] A. **235**, 299 ; B. **17**, 165. [4] A. **235**, 323.
[5] Bl. [3] **19**, 554. [6] A. Ch. [6] **11**, 264 ; Bl. **41**, 323.
[7] B. **18**, 348. [8] Soc. **37**, 726.
[9] B. **26**, 1706. [10] A. **139**, 308.
[11] B. **7**, 276. [12] B. **12**, 1965.

obtained a mixture of anthracene and dihydroanthracene. They state that the reaction is very slow when benzene is used as a solvent, but becomes rapid in absolute ethereal solution.   Anthracene in 60 per cent. yield can be obtained by the action of aluminium chloride on benzyl trichloracetate,[1] but in spite of the good yield this method does not seem to have been applied to the study of other anthracene derivatives.

In the distillation of coal tar the anthracene passes over with the fraction which boils between 280–400°. This fraction has a specific gravity of about 1100 and is known as " anthracene oil " or " green oil " on account of its green colour, although after standing in the air for some time the colour usually changes to brown.   The crude oil contains only 5–10 per cent. of anthracene, and on cooling this is deposited together with phenanthrene, carbazol, acridine, and other impurities.   The crude solid thus obtained contains 15–25 per cent. of anthracene, but can be brought up to 40–50 per cent. strength by hot or cold pressing and by washing with solvent naphtha or creosote oil.   It is in this state that it is usually sold, sales always being effected on a percentage basis, and the price at present (1920) being quoted at 9*d*. per unit per cwt., an increase of about 500 per cent. over the pre-war price.   Anthracene in this state is quite suitable for conversion into anthraquinone, as if it is reduced to a state of fine subdivision by distillation with superheated steam and condensation of the vapours with fine jets of water, oxidation with the calculated amount of chromic acid converts the anthracene into anthraquinone without to any great extent affecting the impurities.   The presence of any considerable quantity of methyl anthracene, however, spoils the shade of the alizarin obtained, and the presence of paraffins gives endless trouble by choking the filters.   It is for this latter reason that the crude anthracene obtained by the distillation of mixtures of hard coal with cannel-coal is not popular with dye-makers, and, of course, low-temperature carbonisation also increases the content of paraffins.

[1] Delacre, C. r. **120**, 155 ; Bl. [3] **13**, 302.

Numerous methods have been proposed for purifying crude anthracene. For example, it can be recrystallised from fatty acids such as oleic acid,[1] or it can be washed with acetone,[2] or liquid ammonia,[3] or sulphur dioxide.[4] By far the best method, however, is washing with pyridine or quinoline bases,[5] as this leaves a product containing 90–98 per cent. of anthracene. Graebe [6] obtained anthracene free from carbazol by fusing with caustic potash, the carbazol forming its potassium salt and the anthracene being distilled off. This process has been the subject of several patents [7] but does not seem to have been a commercial success. Wirth [8] attacked the problem in a rather different way, and claims that if crude anthracene is treated with nitrous acid the anthracene is unaffected, whereas the carbazol is converted into a nitroso compound which is soluble in benzene and can therefore be removed by washing with this solvent.

When pure, anthracene is a colourless crystalline solid which melts at 216·5° and boils at 351°. It has an intense violet fluorescence, but this is completely masked by small quantities of impurities. This fluorescence is shown by all anthracene derivatives in which each *meso*-carbon atom is in combination with only one monovalent element or group, and may be due to double symmetrical tautomerism (see p. 19).

Molinari [9] has prepared an ozonide of anthracene but does not seem to have examined its decomposition products.

Schlenk, Appenrodt, and Thal [10] have found that when ethereal suspensions of anthracene are shaken with sodium powder a disodium addition compound is formed. In this

[1] Reney and Erhart, D.R.P. 38,417.

[2] By., D.R.P. 78,861.

[3] Welton, D.R.P. 113,291.

[4] By., D.R.P. 68,474.

[5] Chemische Fabriks-Actiengesellschaft in Hamburg, D.R.P. 42,053. Clark, J. Ind. Eng. Chem. 1919, 204.

[6] A. **202**, 22.

[7] A. G. für Teer- u. Erd-ölindustrie, D.R.P. 111,359; By., D.R.P. 157,123; Agfa, D.R.P. 178,764.

[8] D.R.P. 122,852.

[9] B. **40**, 4160.

[10] B. **47**, 473.

the sodium atoms must be attached to the *ms*-carbon atoms, as treatment with carbon dioxide leads to the formation of the sodium salt of dihydroanthracene dicarboxylic acid :
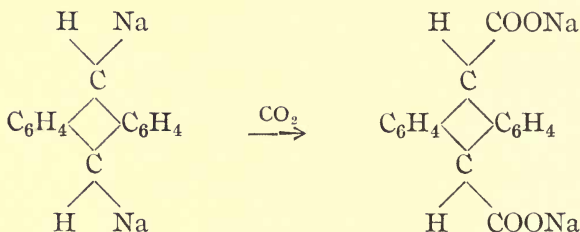
Anthracene forms a well-crystallised picrate with one molecule of picric acid when treated with alcoholic solutions of picric acid.[1]

STRUCTURE.—There is some doubt as to the disposition of the fourth valency of the *meso*-carbon atoms in the anthracene molecule, and the formula of anthracene can be written either as a bridged ring or as a quinonoid compound :

Against the *ortho*-quinonoid formula it may be urged that this would represent a coloured compound, whereas anthracene is colourless.[2]   Our present knowledge of the relationship between molecular structure and the absorption of light, however, is not sufficiently wide to allow much weight to be given to arguments of this nature.   On the other hand, the formation of a disodium addition compound is much more in accordance with the quinonoid structure, as Schlenk, Appenrodt, and Thal [3] have found that in the case of other hydrocarbons the formation of such compounds is closely allied with unsaturation.   Auwers,[4] from a study of the optical anomality of *ms*-amylanthracene and *ms*-amyl-9.10-dihydro-anthracene, also concludes in favour of the

[1] B. **7**, 34 ; A. **139**, 309.
[2] Absorption spectrum.   Baly Soc. **93**, 162.
[3] B. **47**, 473.   [4] B. **53**, 941.

quinonoid structure. The quinonoid structure, however, indicates a type of isomerism among anthracene derivatives which is totally unknown, as a monosubstitution product, for example, should exist in two forms :

$$C_6H_4 \diamondsuit C_6H_3Cl \quad \text{and} \quad C_6H_3Cl \diamondsuit C_6H_4$$
(with CH above and CH below each bridge)

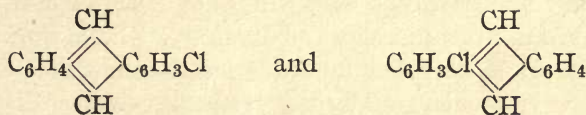The powerful fluorescence of anthracene and of all its derivatives in which the " bridge " remains intact points to double symmetrical tautomerism, so that on the whole the dynamic formula :

$$C_6H_4 \diamondsuit C_6H_4 \rightleftarrows C_6H_4 \vert C_6H_4 \rightleftarrows C_6H_4 \diamondsuit C_6H_4$$
(with CH above and CH below each bridge)
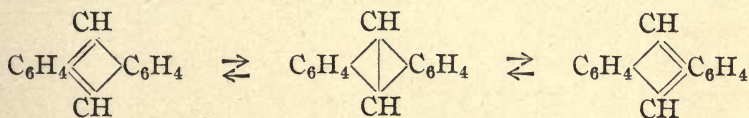
is the best representation. In the following pages the " bridge " formula is used as a matter of convenience ; but its use is without prejudice, and it must be understood that it probably merely represents the middle point of the vibration.

It should be noted that anthracene compounds show a marked capacity for forming addition compounds, *e.g.* with picric acid. This capacity for forming addition compounds apparently lies in the arrangement of the valencies of the central ring, as destruction of the " bridge," *e.g.* by reduction, is accompanied by complete loss of capacity to form a picrate. Destruction of the bridge also leads to the disappearance of fluorescence.

OXIDATION.—The oxidation of anthracene and its derivatives leads usually to anthraquinone or an anthraquinone derivative ; but if one of the benzene rings is weakened by the presence of hydroxyl or amino groups, this ring is usually ruptured. Sulphonic acid groups, halogen atoms, alkyl groups, carboxylic acid groups, etc., do not weaken the ring, so that such derivatives of anthracene on oxidation pass into the corresponding anthraquinone derivative, and

in many cases advantage has been taken of this for determining the position of substituents.

On the other hand, groups attached to the *ms-* carbon atoms are usually eliminated on oxidation, so that *ms-* substituted derivatives of anthracene give anthraquinone on oxidation ; but Simonis and Remmert [1] have shown that 9-10-diphenylanthracene on oxidation does not give anthraquinone, the chief oxidation product being *o*-dibenzoylbenzene :

$$C_6H_4 \Big\langle \!\!\! \overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\displaystyle C}{\underset{\displaystyle C}{}}}} \!\!\! \Big\rangle C_6H_4 \quad \rightarrow \quad C_6H_4 \Big\langle \!\! \overset{\displaystyle COC_6H_5}{\underset{\displaystyle COC_6H_5}{}}$$
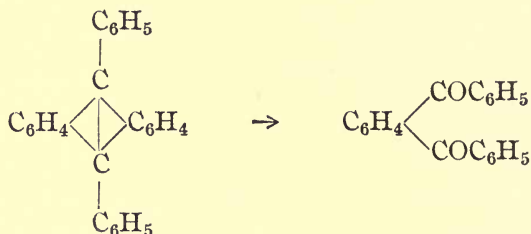
and, curiously enough, 1.2-dimethoxy-9-10-diphenylanthracene on oxidation gives dibenzoyl veratrol :

$$(MeO)_2C_6H_2 \Big\langle \!\!\! \overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\displaystyle C}{\underset{\displaystyle C}{}}}} \!\!\! \Big\rangle C_6H_4 \quad \rightarrow \quad (MeO)_2C_6H_2 \Big\langle \!\! \overset{\displaystyle COC_6H_5}{\underset{\displaystyle COC_6H_5}{}}$$
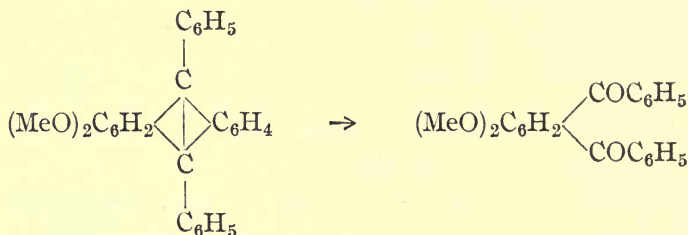
Anthraquinone is a very stable substance and resists the action to oxidising agents to a very marked extent. Hence although it is possible in some cases to rupture the centre ring with the production of an *o*-benzoyl benzoic acid or a phthalic acid, the method is of no importance, as such violent means have to be used that the phthalic acid is usually almost completely destroyed. Of course, if only one of the benzene rings is weakened by the presence of hydroxyl or amino groups, it will be possible to obtain phthalic acid from the substance, and this in many cases gives useful information as to the position of substituents.

[1] B. **48**, 208.

Although anthraquinone is the final stable stage in the oxidation of anthracene, by moderated oxidation it is sometimes possible to isolate lower oxidation products. Thus, Schulze [1] oxidised anthracene with lead dioxide in boiling glacial acetic acid solution and obtained anthraquinol, and Kurt Meyer [2] has shown that under these circumstances the first product formed is acetoxyanthrone, which passes into anthraquinol by hydrolysis and subsequent isomerisation :

$$
\begin{array}{ccccc}
\overset{H \quad OCOCH_3}{\underset{C}{\diagdown\diagup}} & & \overset{H \quad OH}{\underset{C}{\diagdown\diagup}} & & \overset{OH}{\underset{C}{|}} \\
C_6H_4\diamondsuit C_6H_4 & \rightarrow & C_6H_4\diamondsuit C_6H_4 & \rightarrow & C_6H_4\diamondsuit C_6H_4 \\
\underset{O}{\overset{C}{\underset{\|}{}}} & & \underset{O}{\overset{C}{\underset{\|}{}}} & & \underset{OH}{\overset{C}{\underset{|}{}}}
\end{array}
$$
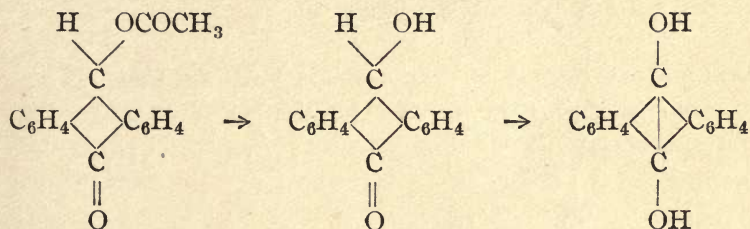
From *ms*-alkyl dihydroanthracenes Liebermann [3] was able to obtain alkylhydroxyanthrones by careful oxidation with chromic acid :

$$
\begin{array}{ccc}
\overset{H \quad R}{\underset{C}{\diagdown\diagup}} & & \overset{HO \quad R}{\underset{C}{\diagdown\diagup}} \\
C_6H_4\diamondsuit C_6H_4 & \rightarrow & C_6H_4\diamondsuit C_6H_4 \\
\underset{CH_2}{} & & \underset{O}{\overset{C}{\underset{\|}{}}}
\end{array}
$$
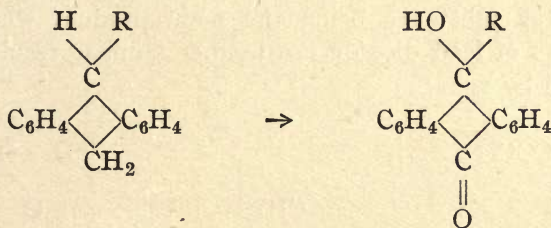
and Baeyer [4] obtained *ms*-phenyl hydroxyanthrone by the careful oxidation of *ms*-phenyl anthracene. In both cases more vigorous oxidation leads to anthraquinone. Liebermann [5] also found that the moderated oxidation of the *ms*-alkyl hydroxydihydroanthracenes led to *ms*-alkyl hydroxyanthrones :
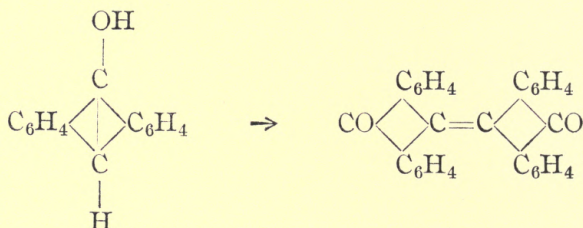
[1] B. **18**, 3036.
[2] A. **379**, 48.
[3] A. **212**, 67; B. **13**, 1596; **15**, 452, 455, 462.
[4] A. **202**, 54.
[5] A. **212**, 101.

$$
\begin{array}{cc}
\text{HO} & \text{R} \\
& \diagdown\diagup \\
& \text{C} \\
\text{C}_6\text{H}_4\diagdown \text{\ }\diagup\text{C}_6\text{H}_4 \\
& \text{CH}_2
\end{array}
\quad\rightarrow\quad
\begin{array}{cc}
\text{HO} & \text{R} \\
& \diagdown\diagup \\
& \text{C} \\
\text{C}_6\text{H}_4\diagdown \text{\ }\diagup\text{C}_6\text{H}_4 \\
& \text{CO}
\end{array}
$$

As will be seen later, the moderated oxidation of the anthranols readily leads to dianthrones :

$$
\begin{array}{c}
\text{OH} \\
| \\
\text{C} \\
\text{C}_6\text{H}_4\diagdown\text{\ }\diagup\text{C}_6\text{H}_4 \\
\text{C} \\
| \\
\text{H}
\end{array}
\quad\rightarrow\quad
\begin{array}{c}
\text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \\
\text{CO}\diagdown\text{\ }\diagup\text{C}=\text{C}\diagdown\text{\ }\diagup\text{CO} \\
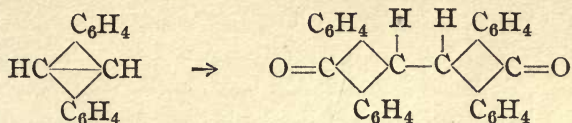\text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4
\end{array}
$$

Kurt Meyer,[1] by oxidising anthracene with one molecule of lead dioxide in boiling glacial acetic acid, obtained a mixture of anthranol acetate and hydroxyanthrone acetate, this latter substance being the main product when two molecules of lead dioxide are used.[2] Similar results were obtained by using

$$
\begin{array}{c}
\text{OCOCH}_3 \\
| \\
\text{C} \\
\text{C}_6\text{H}_4\diagdown\text{\ }\diagup\text{C}_6\text{H}_4 \\
\text{CH}
\end{array}
\ \leftarrow\
\begin{array}{c}
\text{CH} \\
\text{C}_6\text{H}_4\diagdown\text{\ }\diagup\text{C}_6\text{H}_4 \\
\text{CH}
\end{array}
\ \rightarrow\
\begin{array}{c}
\text{H} \quad \text{OCOCH}_3 \\
\diagdown\diagup \\
\text{C} \\
\text{C}_6\text{H}_4\diagdown\text{\ }\diagup\text{C}_6\text{H}_4 \\
\text{C} \\
\| \\
\text{O}
\end{array}
$$
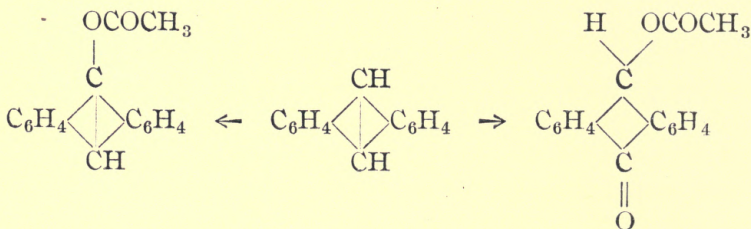
manganese dioxide, ceric acetate, and vanadic acid, all in boiling glacial acetic acid solution. With other solvents, however, the course of the reaction is different, dianthrone often being formed :

[1] A. 397, 73.   [2] Cf. Schulze, B. 18, 3036.

$$\underset{\underset{C_6H_4}{|}}{\overset{\overset{C_6H_4}{|}}{HC\diamondsuit CH}} \rightarrow \underset{\underset{C_6H_4}{|}}{\overset{\overset{C_6H_4\ H\ H\ C_6H_4}{|\ \ \ \ |}}{O=C\diamondsuit C-C\diamondsuit C=O}}\ \underset{C_6H_4}{}$$

The fact that Schulze [1] obtained anthraquinol by oxidising anthracene in glacial acetic acid with lead dioxide is obviously due to the fact that he treated his product with alkali without first examining it, the effect of the alkali being to split off the acetyl group from the acetoxyanthrone and then to enolise the hydroxyanthrone formed (p. 108).
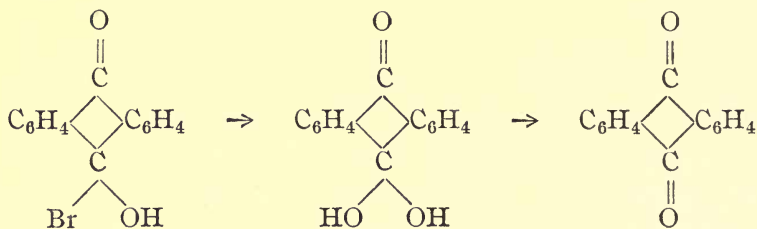
Kurt Meyer [2] has also found that halogens in aqueous solvents below 25° oxidise anthracene very smoothly. In this case oxidation probably takes place by alternate addition and hydrolysis:
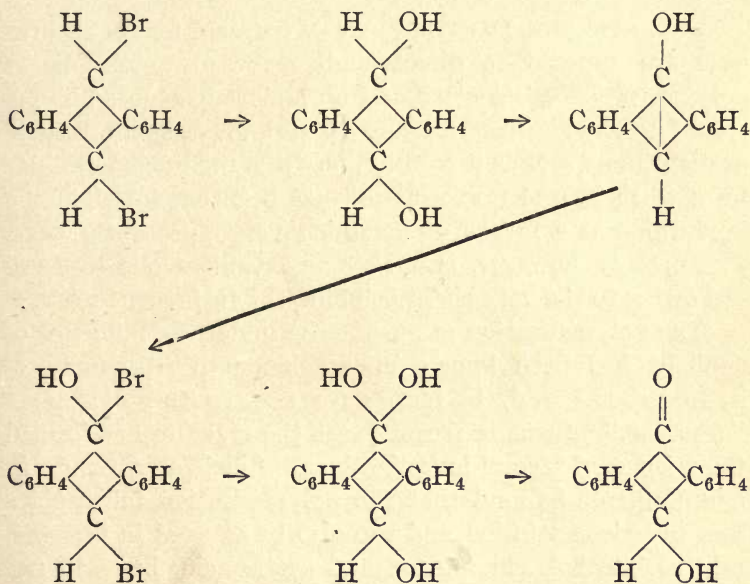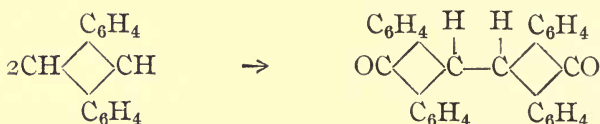

The further action of halogen brings about substitution of the *ms*-hydrogen atom in the hydroxyanthrone, subsequent hydrolysis leading to anthraquinone:

[1] *Loc. cit.*   [2] A. **379**, 73, 166.

$$C_6H_4 \underset{C}{\overset{\overset{\displaystyle O}{\|}}{\diamond}} C_6H_4 \quad \rightarrow \quad C_6H_4 \underset{C}{\overset{\overset{\displaystyle O}{\|}}{\diamond}} C_6H_4 \quad \rightarrow \quad C_6H_4 \underset{C}{\overset{\overset{\displaystyle O}{\|}}{\diamond}} C_6H_4$$
$$\quad\quad Br \quad OH \quad\quad\quad\quad HO \quad OH \quad\quad\quad\quad\quad\quad O$$

The action of nitric acid on anthracene is discussed on p. 50, but Dimroth,[1] by treating anthracene with nitric acid in glacial acetic acid solution, obtained dianthrone :

$$2CH \overset{\textstyle C_6H_4}{\underset{\textstyle C_6H_4}{\diamond}} CH \quad \rightarrow \quad OC \overset{\textstyle C_6H_4}{\underset{\textstyle C_6H_4}{\diamond}} \overset{H}{\underset{\textstyle}{C}} - \overset{H}{\underset{\textstyle}{C}} \overset{\textstyle C_6H_4}{\underset{\textstyle C_6H_4}{\diamond}} CO$$

PARANTHRENE, DIANTHRENE.—When solutions of anthracene are exposed to direct sunlight or ultraviolet light, polymerisation takes place, and an almost insoluble bimolecular [2] polymer is precipitated. This is known as paranthrene or dianthrene, and as it readily reverts to the monomolecular form when heated, its formation has been employed in the laboratory as a means of obtaining very pure anthracene. The process, however, is a very inconvenient one to carry out owing to the very slight solubility of anthracene itself.

The polymerisation of anthracene under the influence of sunlight has been known almost since the discovery of hydrocarbon,[3] and, in fact, gave rise to the old name " photene." In more recent years the reaction has formed the subject of several investigations. Linebarger, Orndorff, and Cameron [4] found that the polymerisation takes place best in xylene solution, and can also be effected in benzene, toluene, alcohol, chloroform, and acetic acid, but will not take place in carbon bisulphide or in ethylene dibromide.

[1] B. **34**, 219.
[2] Elbs, J. pr. [2] **44**, 267.
[3] Fritsche, Z. 1867, 290 ; Ernst Schmidt, J. pr. [2] **9**, 248 ; Graebe and Liebermann, A., Suppl. VII., 264.
[4] Am. **14**, 599.

Weigert [1] and his students, and Byk [2] have examined the reaction from a physico-chemical and thermodynamic point of view, and have found that the amount of change is directly proportional to the light energy absorbed.

The formation of bimolecular polymers by anthracene derivatives has been studied by Fischer and Ziegler [3] and by Weigert and Kummerer.[4] The former investigators showed that α-methyl anthracene is much more rapidly polymerised than either anthracene itself or β-methylanthracene. They also found that 1-4-methylchloranthracene, α-chloranthracene, *ms*-monobromanthracene and α-chlor-*ms*-monobromanthracene all polymerise, whereas dihydroanthracene, dihydromethylanthracene and *ms*-dibromanthracene do not. Weigert and Kummerer studied the action of light on the anthracene monocarboxylic acids and found that all three acids are polymerised, but the α-acid is only polymerised slowly, whereas in the case of the β-acid the action is rapid. The *ms*-acid is also polymerised both in glacial acetic acid solution and in alkaline solution. In the latter case the action of light also causes rapid oxidation by atmospheric oxygen, so that it is necessary to work in evacuated vessels.

The bimolecular polymers are all colourless solids which melt at fairly high temperatures, and either at the melting point or at a slightly higher temperature revert to the monomolecular form. They are not fluorescent, do not form picrates, and on oxidation give the same products as the monomolecular hydrocarbons. In all probability their structure is represented by the formula :
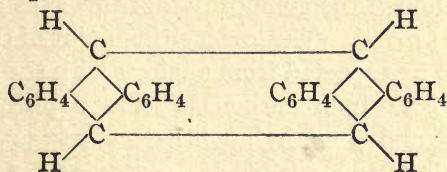
Dianthrene itself melts at 244° and is depolymerised at 272°.

[1] B. **42**, 850 ; 1783 ; *Ann. der Phys.*, **24**, 55, 243 ; Z. f. Elektrochemie, **14**, 591 ; Z. f .physikal. Chemie, **51**, 297 ; **53**, 385 ; **63**, 458.
[2] B. **42**, 1145 ; Z. f. physikal. Chemie, **62**, 454.
[3] J. pr. [2] **86**, 289.   [4] B. **47**, 898.

Homologous Anthracenes

1-METHYLANTHRACENE.—Very little information is available with reference to this substance, although it has been described by two investigators. Birukoff [1] obtained it by condensing phthalic acid with p-cresol and then distilling the resulting 1-methyl-4-hydroxyanthraquinone with zinc dust. He describes it as melting at 199–200° and giving a quinone which melts at 166–167°. O. Fischer [2] repeated Birukoff's work and obtained a hydrocarbon which melted at about 200°, but which on oxidation gave anthraquinone itself, and which he therefore concluded consisted chiefly of anthracene, the methyl group having been split off as methane during the distillation with zinc dust. Fischer also observed that the mother liquor from the recrystallisation of the hydrocarbon contained a substance of very low melting point which on oxidation gave a quinone melting at about 170°, but he did not investigate it further. He, however, prepared 1-methylanthracene by distilling 1-methyl-4-chloranthraquinone, obtained from phthalic acid and p-chlortoluene, with zinc dust and described it as melting at 85–86°, and giving a quinone which melted at 170–171°. At first sight the melting-point seems extremely low, and reminds one of the compounds of uncertain composition which have been obtained by Elbs [3] by the alkaline reduction of methylanthraquinones in which a methyl group is in the α-position to one of the carbonyl groups; but Lavaux [4] has obtained what he describes as 1.8-dimethylanthracene, m.p. 86°, although the composition of this substance cannot be said to be proved. The low melting point of the α-derivative is also to be expected from analogy with the corresponding naphthalene hydrocarbons. Thus naphthalene itself melts at 79° and β-methylnaphthalene at 32·5°, whereas α-methylnaphthalene melts at —20°, and 1.6-dimethylnaphthalene is also liquid at the ordinary temperature. The bimolecular form of α-methyl anthracene melts at 246°.

[1] B. **20**, 2068.   [2] J. pr. [2] **83**, 201.
[3] B. **20**, 1365 ; J. pr. [2] **41**, 12.
[4] C. r. **139**, 976 ; **140**, 44 ; **150**, 1400 ; Bl. [4] **7**, 539.

2-METHYLANTHRACENE.—This is a much more important compound than the isomeric 1-methylanthracene and, as it is much more readily obtained, it has been much more carefully investigated. It seems to be the parent hydrocarbon of many naturally occurring anthracene derivatives, and is obtained from them by distillation with zinc dust. Thus Ciamician [1] obtained it from colophonium, and Liebermann [2] and Jowett and Pother [3] from chrysarobin and emodin. It is present in coal tar and has been isolated from this source by Schulz [4] and Börnstein, [5] and Waschendorff [6] has obtained it from the pitch left from the distillation of commercial aniline oil. Its formation by the pyrogenic decomposition of hydrocarbons seems to be quite common, as Schulz [7] has obtained it by passing turpentine vapour through a red-hot tube, and O. Fischer, [8] Schulz, [9] and Weiler [10] have obtained it by similar means from ditolylmethane and ditolylethane.

Elbs [11] has obtained it by the prolonged boiling of the phenyl xylyl ketone obtained by condensing benzoyl chloride with p-xylene, and Gresley [12] has obtained it by condensing phthalic anhydride with toluene and then distilling the ketonic acid over zinc dust.

A rather interesting synthesis has been carried out by Kraemer and Spilker, [13] who find that methyl benzenes, in this case m-xylene, condense with styrene in the presence of sulphuric acid to form diaryl propanes :

$$C_6H_5CH : CH_2 + C_6H_4(CH_3)_2 \quad \rightarrow \quad C_6H_5C\underset{\underset{\displaystyle CH_3}{|}}{\text{—}}CH_2C_6H_4CH_3$$
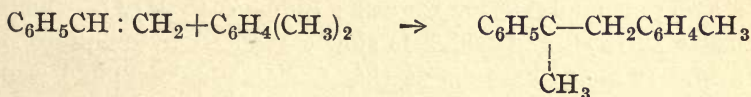
and these when passed through a red-hot tube apparently split off a carbon atom and yield an anthracene derivative.

[1] B. **11**, 269.   [2] A. **183**, 162 ; **212**, 34.   [3] Soc. **81**, 1581.
[4] B. **10**, 1049.   [5] B. **15**, 1821.
[6] B. **10**, 1481.   It must be remembered that this observation was published in 1877.   It is highly improbable that any anthracene derivatives could be obtained from modern commercial aniline oil.
[7] B. **10**, 118.   [8] B. **7**, 1195 ; J. pr. [2] **79**, 555.
[9] B. **10**, 118.   [10] B. **7**, 1185.
[11] J. pr. [2] **35**, 471 ; **41**, 1, 1 ; B. **17**, 2848.
[12] A. **234**, 238.   [13] 12 B. **23**, 3169 ; 3269.

In the case in question a 63 per cent. yield of 2-methyl-anthracene was obtained. This reaction suggests a possible explanation of the presence of methyl anthracene in coal tar.

2-Methylanthracene can, of course, be obtained by the distillation of methylhydroxyanthraquinones over zinc dust,[1] but this method is of theoretical rather than of practical importance. It is most readily obtained by the reduction of the corresponding quinone,[2] and as this is readily obtained from phthalic anhydride and toluene, the hydrocarbon is easily available.

The melting point of 2-methylanthracene given in the literature is very variable, most investigators giving it as 198–204°. Probably the figures given by O. Fischer,[3] viz. 203° (uncor.) and 207° (cor.), are the most reliable. The latter figure is also given by Limpricht and Wiegand,[4] Kraemer and Spilker,[5] and Scholl.[6]

Orndorff and Megraw[7] find that when its solutions are exposed to sunlight 2-methyl anthracene passes into a non-fluorescent bimolecular form which melts at 228–230° with simultaneous reversion to the monomolecular form.

METHANTHRENE.—In addition to α- and β-methyl-anthracene a third isomer has been described by Oudemas,[8] who states that he obtained a hydrocarbon with the formula $C_{15}H_{12}$ by distilling podocarpinic acid with zinc dust. He gives the melting point of the hydrocarbon as 117°, and states that on oxidation it gives a quinone, $C_{15}H_{10}O_2$, which melts at 187°, and which is slowly reduced by sulphurous acid. It seems improbable that Oudemas's compound was an anthracene derivative at all.

DIMETHYL ANTHRACENES.—The chemistry of the dimethyl anthracenes is far more complicated than would seem to be the case at first sight, and in spite of numerous investigations comparatively little really reliable data is

[1] Nietzki, B. **10**, 2013 ; Niementowski, B. **33**, 1633.
[2] Limpricht and Wiegand, A. **311**, 181 ; Scholl, M. **39**, 237.
[3] J. pr. [2] **79**, 555.   [4] A. **311**, 181.
[5] B. **23**, 3169 ; 3269.   [6] M. **39**, 237.
[7] Am. Soc., **22**, 154.   [8] A. **170**, 243 ; J. pr. [2] **9**, 416.

forthcoming. As Lavaux[1] has pointed out, nearly all the reactions which lead to dimethyl derivatives are capable of yielding more than one isomer, and nearly all these reactions have to be carried out under conditions under which there is considerable danger of methyl groups wandering. In addition the isomers have a great tendency to form eutectic mixtures which are extremely difficult to recognise as such, and which can only be separated into their constituents by special means.

Several investigators have described a dimethyl anthracene melting at 225°, and giving on oxidation a quinone melting at 156–160°. Thus Waschendorff and Zincke[2] obtained it from the heavy fractions of commercial aniline oil; Anschütz[3] obtained it by treating toluene with *sym*-tetrabrom-ethane and aluminium chloride, and also by treating toluene with aluminium chloride.[4] Friedel and Crafts[5] obtained it by the action of methylene chloride and aluminium chloride on toluene, and by the action of aluminium chloride on toluene also obtained a dimethyl anthracene. The melting point of this latter substance they give as 231°, but find that it gives a quinone melting at 160°. Elbs and Wittich[6] from toluene, chloroform, and aluminium chloride obtained a dimethyl anthracene melting at 215–216° and giving a quinone melting at 161–162°; but Lavaux has shown that the melting point of their compound was too low owing to the presence of a little monomethyl anthracene.

Lavaux[7] has shown that all these so-called dimethyl anthracenes are really eutectic mixtures, and from them he has isolated two distinct dimethyl anthracenes, one melting at 244·5° and the other melting at 240°. In addition, from the product of Friedel and Crafts reaction he has isolated a third very soluble isomer which melts at 86°. This last he seems to assume to be 1.8-dimethylanthracene, but does not appear to have investigated in detail.

[1] C. r. **146**, 137.   [2] B. **10**, 1481.
[3] A. **235**, 171 ; B. **17**, 2816.   [4] A. **235**, 181.
[5] A. Ch. [6] **11**, 265 ; Bl. **41**, 323.   [6] B. **18**, 348.
[7] C. r. **139**, 976 ; **140**, 44 ; **152**, 1400 ; Bl. [4] **7**, 539.

The compound melting at 244·5° seems to be identical with the dimethyl anthracene obtained by Anschütz and Römig [1] by distilling the condensation product of toluene and ethylidene bromide over zinc dust. On oxidation it gives a quinone melting at 236·5°, and also a methyl anthraquinone carboxylic acid and an anthraquinone dicarboxylic acid. The methyl anthraquinone carboxylic acid was reduced by zinc dust and ammonia to methylanthracene carboxylic acid, and from this it can be concluded that the methyl group is in the β-position, as Elbs [2] has shown that α-methyl anthraquinones do not give the corresponding anthracene derivative by reduction in alkaline solution. Further, Lavaux showed that the methyl anthracene carboxylic acid, by loss of carbon dioxide, gave β-methyl-anthracene.

Lavaux [3] found that his anthraquinone dicarboxylic acid on fusion with caustic potash * gave a mixture of isophthalic acid and terephthalic acid, but no phthalic acid. The only anthraquinone carboxylic acids which could give this are the 2.6- and the 2.7-acids, and Lavaux concluded that his acid was anthraquinone-2.7-dicarboxylic acid, and consequently that the dimethyl anthracene which melted at 244·5° was 2.7-dimethyl anthracene.

Seer [4] by heating *m*-methyl benzoyl chloride with aluminium chloride to 140° obtained a mixture of three dimethyl anthraquinones, of which the main product melted at 235–236°. By the action of *m*-methylbenzoyl chloride on *m*-xylene in the presence of aluminium chloride he obtained a tolyl xylyl ketone which when boiled (b.p. 315–320°) for five days [5] gave a dimethyl anthracene which melted at 243°, and which on oxidation gave a quinone melting at 235–236°. Seer's products are presumably

[1] A. **235**, 317 ; B. **18**, 662.
[2] J. pr. [2] **15**, 121 ; B. **20**, 1365.
[3] C. r. **141**, 354 ; **143**, 687.
* In the anthraquinone series these fusions are often very troublesome to carry out. In the case in question, for example, it was necessary to maintain a temperature of 260° for 300 consecutive hours.
[4] M. **32**, 143.
[5] *Cf*. Elbs, J. pr. [2] **33**, 185.

identical with the products obtained by Lavaux. The fact that the tolyl xylyl ketone gave an anthracene derivative is proof that one methyl group is in the ortho- position to the carbonyl group, and if it is assumed that methyl groups have not wandered there are only two alternatives for the structure of the ketone and the dimethyl anthracene derived from it :
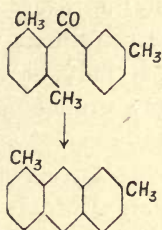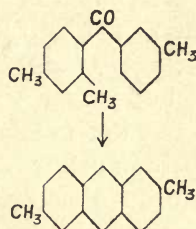
1.7-Dimethylanthracene.   2.6 Dimethylanthracene.

Lavaux, however, has proved conclusively that it is either the 2.6- or the 2.7- compound, and hence Seer concludes that it must be 2.6-dimethyl anthracene.

Lavaux has also investigated the second isomer of his eutectic mixture. This on oxidation gives a methyl anthraquinone carboxylic acid which can be reduced to a methylanthracene carboxylic, this latter by loss of carbon dioxide passing into β-methyl anthracene. By further oxidation an anthraquinone dicarboxylic acid is formed and this by fusion with caustic potash gives a mixture of phthalic, isophthalic, and terephthalic acids, and consequently must be either the 1.6- or the 1.7- dicarboxylic acid. Lavaux considers the former alternative the more probable, and consequently designates the dimethyl anthracene which melts at 240° as 1.6-dimethyl anthracene. The corresponding quinone melts at·169°.

The production of an anthracene derivative by means of methylene chloride is obviously preceded by the production of a dihydroanthracene, subsequent oxidation being brought about at the expense of part of the methylene chloride. In the case of chloroform a dichlordihydroanthracene is the intermediate product, this passing into the

anthracene by loss of two atoms of chlorine. This chlorine is not evolved as such during the reaction but chlorinates part of the toluene or reacts with the carbon disulphide used as a dilutant.

The structure of the dimethyl anthracene described by Dewar and Jones [1] as being obtained by heating toluene with nickel carbonyl and aluminium chloride is very doubtful. They describe it as 2.6-dimethyl anthracene and state that it melts at 215–216° and gives a quinone which melts at 159–160°. Seer [2] suggests that it may be 2.7-dimethyl anthracene, but it seems much more probable that it is a rather impure eutectic mixture.

Other heteronuclear dimethyl anthracenes have also been described. For example, van Dorp [3] by heating xylyl chloride with water to 210° obtained a dimethyl anthracene which melted at 200°, and on oxidation gave a quinone melting at 153°. van Dorp's products were probably complex mixtures, as he states that he made his xylyl chloride from xylene which boiled at 136–139°, and which on oxidation gave a mixture of isophthalic and terephthalic acids, the former " in prepondering amount." The chloride itself he describes as boiling at 190–200° and " consisting chiefly of the desired chloride."

Of the four possible *homonuclear* dimethylanthracenes neither the 1.2- nor the 1.4- isomers have been described, although Gresly [4] and Heller [5] prepared 1.4-dimethyl anthraquinone from *p*-xylene and phthalic acid they do not seem to have reduced it to the anthracene compound.

Elbs and Eurich [6] condensed phthalic anhydride with *o*-xylene and obtained 3-4-dimethylbenzoylbenzoic acid, the position of the methyl groups being proved by F. Meyer,[7] who, by fusion with caustic potash, obtained a mixture of benzoic acid and 2.3-dimethyl-1-benzoic acid. The ketonic acid by loss of water passed into a dimethylanthraquinone

[1] Soc. **85**, 216.   [2] M. **33**, 143.   [3] A. **169**, 207.
[4] A. **240**, 240.   [5] B. **43**, 2892.
[6] B. **20**, 1361 ; J. pr. [2] **41**, 5.   [7] B. **15**, 637.

which melted at 183°.* This might be either 1.2-dimethyl-anthraquinone or 2-3-dimethylanthraquinone; but since toluene yields exclusively β-methylanthraquinone one is justified in assuming that the reaction takes a similar course in the case of o-xylene, the product in this case being 2.3-dimethyl anthraquinone. That this is correct has been proved by the fact that the dicarboxylic acid obtained from it by Elbs by oxidation melts at 340°, whereas the dicarboxylic acid obtained by Scholl [1] by the oxidation of 1.2-benzanthraquinone (naphthanthraquinone) melts at 267–268°. As Scholl's acid must be anthraquinone 1.2-dicarboxylic acid, it follows that Elb's acid must be the 2.3-dicarboxylic acid. Both acids readily yield cyclic anhydrides, which shows that no wandering of the methyl groups can have taken place. Elbs and Eurich reduced the dimethyl-anthraquinone by zinc dust and ammonia and obtained 2.3-dimethylanthracene, m.p. 246°.

Several investigators have prepared 1.3-dimethyl-anthracene, but their descriptions are so conflicting that it is very doubtful if the substance has ever been obtained pure.

Elbs [2] found that benzoyl mesitylene on heating does not pass into a dimethyl anthracene; but Louise,[3] by passing benzyl mesitylene through a red-hot tube obtained two dimethylanthracenes, viz. one which melted at 218–219° and gave a quinone which melted at 170°, and one which melted at 71° and gave a quinone which melted at 157–158°. It is rather difficult to see how two dimethylanthracenes could be produced from benzyl mesitylene unless an impure sample of mesitylene were used, or unless a wandering of the methyl groups takes place either during the passage of the benzyl mesitylene through the red-hot tube, or, more probably, during the preparation of the benzyl compound. Louise's quinone, which melts at 170°, is not identical with Lavaux's 1.6-dimethylanthraquinone (m.p. 169°), as the

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* Limpricht, A. **312**, 99, gives the melting point as 200°, and Heller, B. 43, 2891, as 205–206°.
[1] B. **44**, 2992; D.R.P. 241,624.
[2] J. pr. [2] **35**, 487; **41**, 12.   [3] A. ch. [6] 187.

latter investigator has done a mixed melting point deter-
mination. The very low melting point of the second
isomer would be in agreement with the assumption that it
was the dihydro compound, but Louise's analysis is not in
agreement with this explanation. The low melting point
might, of course, also be explained by the presence of the
methyl group in the α-position (*cf.* α-methylanthracene,
p. 26), and at first sight it would seem possible that the
compound was the unknown 1.4-dimethylanthracene.
This, however, can hardly be the case, as 1.4-dimethylanthra-
quinone [1] melts at 118°. Louise considers that the hydro-
carbon which melts at 71° is really 1.3-dimethylanthracene,
as he has prepared [2] 1.3-dimethylanthraquinone from
benzoyl mesitylenic acid, and finds that it melts at 157–
158°.*

Totally different results have been described by other
investigators. Gresly [3] distilled xyloylbenzoic acid with
zinc dust and obtained what he described as 1.3-dimethyl-
anthracene melting at 202–203°, but did not oxidise it to
the quinone. He obtained the corresponding quinone,
however, by loss of water from the xyloylbenzoic acid, and
gives its melting point as 180°. Birukoff [4] condensed
2.4-dimethyl benzoic acid with gallic acid in the presence of
sulphuric acid and obtained 1.3-dimethyl-6.7.8-trihydroxy-
anthraquinone. This by distillation with zinc dust gave a
dimethylanthracene which melted at 220–226°, and which
on oxidation gave a quinone melting at 112°. Birukoff
obtained his dimethyl benzoic acid from commercial
xylidine, and as the condensation with gallic acid gave a
yield of only two per cent. it is not improbable that the
reaction was taking a different course to that intended.

Kraemer and Spilker [5] condensed styrene with un-
symmetrical trimethyl benzene (pseudocumene ?), and by

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[1] Gresly, A. **234**, 240.
[2] A. ch. [6] **6**, 233.
* Elbs, J. pr. [2] **33**, 319, obtained 1.3-dimethylanthraquinone from
m-xylene and phthalic anhydride, and gives the m.p. as 162°. B. A. S. F.
in D.R.P. 200,335 refer to 1.3-dimethylanthraquinone, m.p. 159–163°.
[3] A. **234**, 240.
[4] B. **20**, 870.   [5] B. **23**, 3169 ; 3269.

passing the product through a red-hot tube obtained a dimethylanthracene. This, unfortunately, cannot be compared with the dimethylanthracenes described by other investigators, as, owing to a misprint, Kraemer and Spilker give the melting point of their product as 298 uncor. = 235° cor.

TRIMETHYLANTHRACENES.—Excluding *ms* - compounds there are sixteen possible trimethylanthracenes. Of these very few have been prepared, and in view of the very contradictory results obtained in the case of the dimethyl compounds the structures allotted to the trimethyl compounds can only be accepted with some reserve pending further investigation. As the trimethylanthracenes are of very little interest they will be treated very briefly.

Gresly [1] by distilling 2.4.5-trimethylbenzoyl benzoic acid with zinc dust obtained 1.2.4-trimethylanthracene, m.p. 243°, the quinone melting at 161°; and Elbs [2] has repeated this work with almost exactly similar results, his melting points being 244° and 162°. The same compounds have also been obtained by Wende [3] by condensing durylic acid with gallic acid by means of sulphuric acid and then distilling the trimethyltrihydroxy anthraquinone with zinc dust. By this means he obtained 1.2.4-trimethylanthracene and from it the quinone by oxidation. He gives the melting points as 236° and 157–160°.

Elbs [4] has obtained 1.3.6- and 1.4.7-trimethylanthracenes by heating 2.4.2'.4'- and 2.5.2'.5'-tetramethylbenzophenone. He finds that they melt at 222° and 227°, the corresponding quinones melting at 190° and 184°.

In the case of the trimethylanthracenes it is noticeable that methyl groups in the α-position do not seem to cause any fall in the melting point. This phenomenon cannot at present be compared with the behaviour of the corresponding naphthalene derivatives, as very few trimethylnaphthalenes have been described, but 1.4-dimethylnaphthalene is a liquid and melts at −18°.

TETRAMETHYLANTHRACENES.—Friedel and Crafts [5] by

[1] A. **234**, 238.   [2] J. pr. [2] **41**, 121.   [3] B. **20**, 867.
[4] J. pr. [2] **35**, 482 ; **41**, 141 ; B. **19**, 408.   [5] A. ch. [6] **11**, 267.

treating *m*-xylene with methylene chloride and aluminium chloride obtained a tetramethylanthracene which melted at 162–163°, and which on oxidation gave a quinone which melted at 204–206°. From pseudocumene and methylene chloride they obtained the same substance and also a tetramethylanthracene melting at 290°, and a hexamethyl-anthracene melting at 220°. Friedel and Craft's first compound (m.p. 162–163°) is probably identical with the 1.3.5.7-tetramethylanthracene obtained by Seer [1] by the action of aluminium chloride on the chloride of mesitylenic acid :
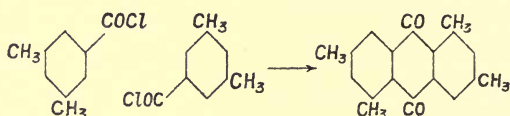
and subsequent reduction by distillation with zinc dust. Seer also obtained the same tetramethyl compound directly from xylyl mesityl ketone by the action of heat. He agrees with Friedel and Crafts as regards the melting point of the hydrocarbon (163–164°), but gives the melting point of the quinone as 235°.

Anschütz,[2] by heating *m*-xylene with acetylene tetra-bromide and aluminium chloride, or by heating xylene in a sealed tube with aluminium chloride, obtained a tetramethyl compound which melted rather indefinitely at 280°, and gave a quinone melting at 228–230°. Dewar and Jones [3] by heating *m*-xylene with nickel carbonyl obtained a tetramethyl anthracene which melted at 280°, and gave a quinone melting at 228–230°. This they conclude is 1.3.5.7-tetramethylanthracene, on the ground that the action of nickel carbonyl in the cold leads to 2.4-dimethyl-benzaldehyde. On their own showing, however, it is very improbable that the aldehyde is formed as an intermediate product when anthracene compounds are produced, as although benzene and nickel carbonyl gives anthracene, they were unable to obtain anthracene from benzaldehyde.

Seer [4] has repeated the work of Friedel and Crafts, and

[1] M. **33**, 33.   [2] A. **235**, 173.   [3] Soc. **85**, 216.   [4] M. **33**, 33.

by a slight variation in the experimental conditions has obtained a very small quantity of a tetramethylanthracene which melted at 281°. He concludes that the product obtained by Friedel and Crafts consisted mainly of 1.3.5.7-tetramethylanthracene (m.p. 162–163°) with a little 1.3.6.8-tetramethylanthracene (m.p. 281°). The products obtained by Dewar and Jones and by Anschütz are probably also 1.3.6.8-tetramethylanthracene.

OTHER ANTHRACENE HOMOLOGUES.—There seem to be no records of attempts to prepare homologous anthracenes by the Friedel and Crafts' reaction, but Lippmann, Pollok, and Fritsch,[1] by the prolonged boiling of anthracene with benzyl chloride in carbon bisulphide solution in the presence of zinc dust, claim to have obtained mono- and di-benzyl anthracenes. The former of these was also obtained by Bach[2] by benzylating anthraquinol. The monobenzyl compound melts at 119° and the dibenzyl compound at 239–240°. Both on oxidation give anthraquinone, so that the benzyl groups must be attached to the *ms*-carbon atoms. The dibenzyl compound gives a monobrom substitution product, which when treated with basic substances such as potassium acetate, potassium carbonate, pyridine, or quinoline, loses hydrobromic acid and passes into two new compounds. These Lippmann regards as dibenzalanthracene and *bis*-dibenzalanthracene and assigns them the formulæ :

$$C_6H_4 \Big< \begin{matrix} C\text{------}CHC_6H_5 \\ \\ C\text{------}CHC_6H_5 \end{matrix} \Big| \qquad \text{and} \qquad C_6H_4 \Big< \begin{matrix} C\text{---}CHC_6H_5\text{---}CHC_6H_5\text{---}C \\ \\ C\text{---}CHC_6H_5\text{---}CHC_6H_5\text{---}C \end{matrix} \Big> C_6H_4$$

Dibenzalanthracene,
m.p. 236°.

bis-Dibenzalanthracene,
m.p. 184°.
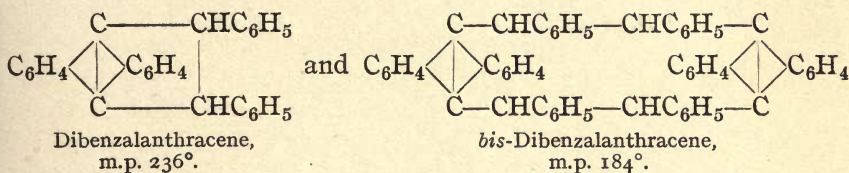
It is surprising that the bimolecular compound should melt at such a much lower temperature than the mono-molecular form, and in any case the formulæ can only be accepted with some reserve pending further confirmation.

Other *ms*-homologues of anthracene have also been described, but they are invariably obtained by indirect

[1] M. **23**, 672 ; **25**, 793.   [2] B. **23**, 1570.

methods. Thus, Jüngermann [1] obtained *ms*-diamyl anthra-
cene by reducing the product obtained by the action of
amyl-magnesium bromide on amylhydroxy anthrone :

$$
C_6H_4 \underset{\underset{\substack{\diagdown \\ HO \quad C_5H_{11}}}{C}}{\overset{CO}{\diagup}} C_6H_4 \rightarrow
C_6H_4 \underset{\underset{\substack{\diagdown \\ HO \quad C_5H_{11}}}{C}}{\overset{\overset{\substack{HO \quad C_5H_{11} \\ \diagdown \diagup}}{C}}{}} C_6H_4 \rightarrow
C_6H_4 \underset{\underset{\substack{| \\ C_5H_{11}}}{C}}{\overset{\overset{\substack{C_5H_{11} \\ |}}{C}}{}} C_6H_4
$$
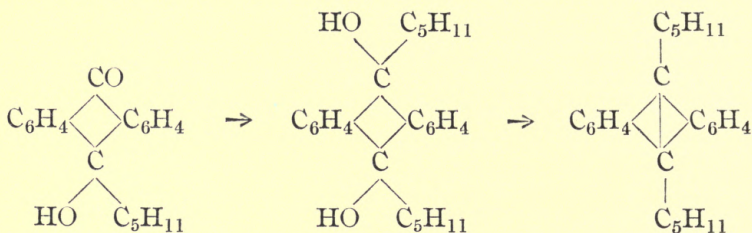
It melts at 132–137°. Other homologous anthracenes have
been obtained by similar methods, and will be referred to
elsewhere. *ms*-Diphenylanthracene has been obtained by
Simonis and Remmert [2] by treating *o*-brombenzyltriphenyl
carbinol with concentrated sulphuric acid :

$$
C_6H_4 \underset{\underset{\substack{| \\ Ph}}{C} \diagdown OH}{\overset{\overset{\substack{H \\ |}}{C} \diagup Br}{\diagup}} C_6H_5 \rightarrow
C_6H_4 \underset{\underset{\substack{| \\ Ph}}{C}}{\overset{\overset{\substack{Ph \\ |}}{C}}{}} C_6H_4
$$
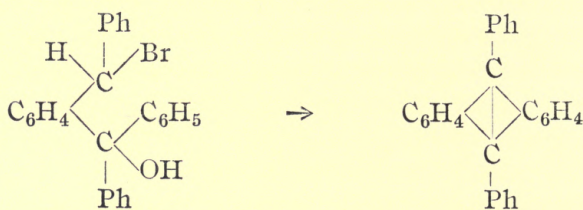
and by a similar reaction the same investigators have pre-
pared 1.2-dimethoxy-*ms*-diphenylanthracene.

[1] B. **38**, 2868.   [2] B. **48**, 208.

CHAPTER III

SIMPLE DERIVATIVES OF ANTHRA-
CENE

HYDROANTHRACENES

A CONSIDERABLE number of hydroanthracenes have been described, although none of them are of any particular interest. They are almost invariably obtained by the reduction of the anthracenes, although some of the lower members can be conveniently obtained by the partial dehydrogenation of the higher members, a method chiefly developed by Godchot.[1]

The reduction of anthracene and its derivatives can be effected by various reducing agents. Liebermann[2] and his co-workers made extensive use of hydriodic acid and red phosphorus, and by varying the concentration of the acid and the temperature and time of heating were able to obtain di-, tetra- and hexahydroanthracenes. More recently O. Fischer and Ziegler[3] have found that 1-methyl-4-chloranthracene can be reduced to a dihydro compound by simply passing a stream of hydriodic acid gas through its boiling solution in glacial acetic acid. The ease with which this reduction takes place is probably exceptional, as O. Fischer and Reinkober[4] have found that β-methyl-anthracene is quite unaffected by treatment in this way. Sodium amalgam[5] in conjunction with ethyl or amyl alcohol has been used by several investigators, and, like

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[1] A. ch. [8] **12**, 468 ; Bl. [4] **1**, 701 ; C. r. **139**, 605 ; **141**, 1029 ; **142**, 1202.

[2] A. Suppl. VII., 257 ; **212**, 5 ; B. **1**, 187 ; **9**, 1202.

[3] J. pr. [2] **86**, 289.

[4] J. pr. [2] **92**, 51.

[5] Bamberger and Lodter, B. **20**, 3076 ; Padova, C. r. **148**, 290 ; Wieland, B. **45**, 492.

hydriodic acid, seems to produce hydroanthracenes in which the *ms*-carbon atoms are affected, as the reduction products are non-fluorescent, do not form picrates, and, so far as any information is available, do not polymerise to bimolecular compounds when their solutions are exposed to direct sunlight.

Catalytic reduction of anthracene by hydrogen in the presence of finely divided nickel at 200–250° has been studied by Godchot [1] and by Ipatjew, Jacowlew and Rakitin,[2] and often leads to products which differ from those obtained by hydriodic acid or by sodium amalgam. Thus the tetra-hydroanthracene obtained by means of hydriodic acid melts at 101–103°, is not fluorescent, and gives no picrate, whereas that obtained by reduction by hydrogenation in the presence of nickel melts at 89°, shows a blue fluorescence, and gives a picrate.

The hydroanthracenes as a rule are colourless solids which melt below 100°, and which are more or less fully dehydrogenated by passing through a red-hot tube. They reduce sulphuric acid to sulphur dioxide, although Godchot [3] states that octahydroanthracene gives a sulphonic acid in which sulphonic acid group is attached to one of the *ms*-carbon atoms.

Of the individual members, only one dihydroanthracene, $C_{14}H_{12}$, is known. This melts at 108·5°, and is dehydrogenated when shaken in benzene solution with finely divided palladium.[4]   Two tetrahydroanthracenes, $C_{14}H_{14}$, are known, which melt at 101–103° and at 89°. The former is obtained by means of hydriodic acid, and the latter by catalytic reduction. As the latter is fluorescent and gives a picrate the *ms*-carbon atoms are probably intact. Two hexahydro compounds, $C_{14}H_{16}$, have been described. One is obtained by reduction with hydriodic acid and melts at 63°, and boils at 290°. The other is obtained by loss of water from octahydroanthranol [5] and melts at 66·5°, and

[1] A. ch. [8] **12**, 468 ; Bl. [4] **1**, 701 ; C. r. **139**, 605 ; **141**, 1029 ; **142**, 1202.
[2] B. **40**, 1289 ; **41**, 997.   [3] Bl. [4] **1**, 701.   [4] Wieland, B. **45** 492.
[5] Godchot, C. r. **142**, 1203 ; A. Ch. [8] **12**, 468.

boils at 303–306°. The method of formation renders it almost certain that the *ms*-carbon atoms are intact, and this is supported by the blue fluorescence of the compound. An octahydroanthracene, $C_{14}H_{18}$, has been prepared by catalytic reduction. It melts at 71°, gives a picrate, and shows a green fluorescence. Hence, in all probability the *ms*-carbon atoms are intact, although Godchot [1] brings forward some arguments to the contrary, *e.g.* it gives hexahydroanthrone on oxidation with chromic acid. Dekahydroanthracene, $C_{14}H_{20}$, melts at 73°; dodekahydroanthracene, $C_{14}H_{22}$, boils at 140–150° at 15 mm.; and perhydroanthracene, $C_{14}H_{24}$, melts at 88° and boils at 270°. None of them form picrates, and none of them are fluorescent.

HALOGEN COMPOUNDS

The action of chlorine and bromine on anthracene has been studied by many investigators, but often with contradictory results. The reactions which take place are somewhat complicated, as their course is very largely dependent on the solvent used and on the temperature at which the experiment is carried out, but as a rule the first compound formed is an addition compound which readily splits out halogen acid to give halogen anthracenes, in which one or both of the *meso-* hydrogen atoms have been substituted. The resulting halogen anthracenes then again form addition compounds with more halogen atoms, and these again lose halogen acid, substitution now taking place in the benzene rings. The case is complicated by the fact that in addition to place isomerism the addition compounds also exhibit geometrical isomerism of the *cis-trans* type.

Diel [2] by passing chlorine gas over anthracene, first at the ordinary temperature and then at 230°, obtained a dichloranthracene tetrachloride, $C_{14}H_8Cl_2.Cl_4$. This melted with decomposition at 141–145°, and when treated with alcoholic caustic soda passed into a tetrachlor anthracene, m.p. 220°. By treating anthracene at 200° with chlorine

[1] Bl. [4] **1**, 121.　　　　　　[2] B. **11**, 173.

in the presence of antimony pentachloride, he obtained hexa-, hepta-, and octa-chlor anthracene, the former passing into tetrachloranthraquinone on oxidation. The passage of a hexachlor anthracene into a tetrachloranthraquinone shows that two of the chlorine atoms are attached to the *ms*-carbon atoms, and, as the tetrachloranthraquinone is quite different from that synthesised from tetrachlor phthalic acid, the remaining four chlorine atoms must be heteronuclear. Their exact positions have not been determined, but Diel's hexachloranthracene was probably a mixture, as he gives the melting point as 320–330°. Meyer and Zahn [1] have shown that *ms*-dichloranthracene tetrachloride when heated decomposes into 2.3.9.10-tetrachloranthracene, so that the chief constituent of Diel's hexachlor compound was probably 2.3.6.7.9.10-hexachloranthracene.

Diel also studied the action of bromine on anthracene and found that when heated to 120° in the presence of a trace of iodine a hexabromanthracene was formed, whereas at 200° he obtained a mixture of heptabrom- and octabrom-anthracene. The hexabrom- and the heptabrom- compounds on oxidation gave respectively tetra- and penta-brom-anthraquinone. Anderson [2] also studied the action of bromine vapour on anthracene, and working at the ordinary temperature he obtained what he thought was an addition product (anthracene hexabromide, $C_{14}H_{10}Br_6$); but Graebe and Liebermann [3] have proved it to be dibromanthracene tetrabromide. When heated alone it gives tribromanthra-cene, and when treated with alcoholic potash tetrabrom-anthracene. Hammerschlag [4] found that the final product of the action of bromine vapour on anthracene at the ordinary temperature was tetrabromanthracene tetrabromide. This on heating alone to 180° lost one molecule of hydrobromic acid and two atoms of bromine, and yielded a penta-bromanthracene giving a tribromanthraquinone on oxidation. On treatment with alcoholic caustic soda, on the other hand, it lost two molecules of hydrobromic acid and

[1] Page 44.   [2] A. **122**, 304.
[3] A. Suppl. VII, 304.   [4] B. **10**, 1212.

passed into hexabromanthracene, from which tetrabrom-anthraquinone was obtained by oxidation.

Very similar reactions take place when *ms*-dichloranthracene is treated with bromine vapour,[1] addition and substitution products being formed, which when heated alone lose both bromine and hydrobromic acid, whereas only hydrobromic acid is lost by treatment with alcoholic caustic alkali.

More definite information as to the positions of the bromine atoms has been obtained by Kauffler and Imhoff.[2] They treated *ms*-dibromanthracene with bromine vapour and obtained a dibromanthracene tetrabromide. From this they obtained a tribromanthracene, m.p. 171°, which on oxidation gave 2-bromanthraquinone, and a tetrabrom-anthracene, m.p. 298–300°, which on oxidation gave a dibromanthraquinone (m.p. 289–290°), which was identical with the 2.6-dibromanthraquinone obtained from the corresponding diaminoanthraquinone by the diazo reaction.

When anthracene is treated with chlorine or bromine in carbon bisulphide solution [3] the first action is the formation of a very unstable addition compound, anthracene dihalide, which then splits off halogen acid and yields *ms*-halogen anthracene, the second *ms*-hydrogen atom being replaced in the same way.[4] The action of chlorine on anthracene in chloroform and benzene solution was first studied by Schwazer,[5] who obtained first *ms*-dichloranthracene, which by the further action of chlorine passed into dichloranthracene dichloride. This on heating did not split off free halogen, but at 170° lost one molecule of hydrochloric acid and gave trichloranthracene. More recently Meister Lucius and Brüning [6] have re-examined the action of chlorine on anthracene in chloroform and in benzene solution. They state that Schwazer's dichloranthracene dichloride is really

[1] Schwazer, B. **10**, 376; Hammerschlag, B. **19**, 1106.
[2] B. **37**, 4708.
[3] Perkin, Bl. [1] **27**, 464; Chem. News, **34**, 145; Graebe and Liebermann, A. Suppl. VII. 257; B. **1**, 186; Anderson, A. **122**, 306; O. Fischer. and Ziegler, J. pr. [2] **86**, 291.
[4] Meyer and Zahn, A. **396**, 166.
[5] B. **10**, 376. Cf. Radulescu, C. 1908 (2), 1032.
[6] D.R.P. 283,106.

a mixture of anthraquinone tetrachloride (m.p. 180°) and dichloranthracene dichloride (m.p. 139–140°) :
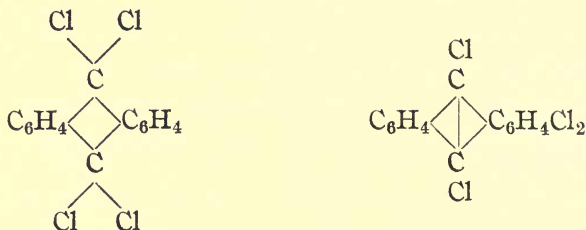
They find that low temperatures and the use of chloroform as a solvent favours the formation of the former; whereas higher temperatures, certain carriers, such as phosphorus pentachloride, and the use of benzene as a solvent, favour the formation of the latter. By chlorinating anthracene or *ms*-dichloranthracene in chloroform suspension at 2°, or in tetrachlorethane at —10° to —15°, they obtain pure anthraquinone tetrachloride, whereas almost pure dichloranthracene dichloride is obtained by chlorinating in benzene at 60°. In a later patent [1] they claim that chlorination in chloroform in the presence of iodine or in sulphuryl chloride leads to dichloranthracene hexachloride and dichloranthracene octachloride.

Hammerschlag,[2] by treating anthracene in benzene solution with chlorine, obtained a dichloranthracene tetrachloride which yielded a tetrachloranthracene when treated with alcoholic potash. This latter on oxidation gave a dichloranthraquinone which melted at 205°.

Meyer and Zahn [3] have repeated Hammerschlag's work, and state that Hammerschlag's tetrachloride was impure. They were unable to obtain any isomeric forms of dichloranthracene tetrachloride, and state that their product is identical with that obtained by Liebermann and Lindenbaum [4] by treating " nitrosoanthrone " with phosphorus pentachloride. On heating it does not split off free halogen like the corresponding bromo- compound (see below), but parts with two molecules of hydrochloric acid, and forms

[1] D.R.P. 284,790.   [2] B. **19**, 1106.   [3] A. **396**, 166.   [4] B. **13**, 1588.

tetrachloranthracene. An isomeric tetrachloranthracene is also formed by treatment with alcoholic caustic potash. The tetrachloranthracene formed by the action of heat must be 2.3.9.10-tetrachloranthracene, as on oxidation it yields 2.3-dichloranthraquinone, the structure of which is known by its synthesis from 3.4-dichlorphthalic acid.[1] The isomeric tetrachloranthracene obtained by the action of alcoholic caustic potash must be 1.3.9.10-tetrachloranthracene, as on oxidation it gives a dichloranthraquinone which is not identical with 1.2-dichloranthraquinone obtained from 3.4-dichlorphthalic acid, nor with 1.4-dichloranthraquinone obtained from 3.6-dichlorphthalic acid.[2]
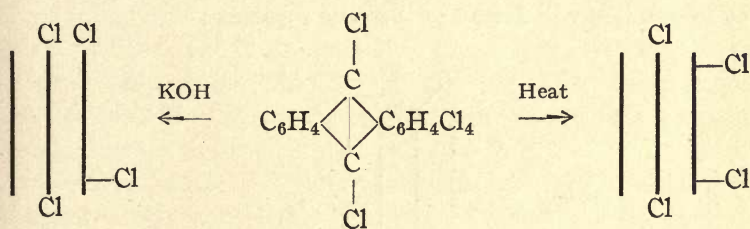
By heating anthracene or *ms*-dibromanthracene in chloroform solution with bromine, Meyer and Zahn [3] obtained a dibromanthracene tetrabromide. This when heated and when treated with alcoholic caustic potash gives the same tribrom- and tetrabrom-anthracene as Graebe and Liebermann [4] obtained from their tetrabromide, but Meyer and Zahn's bromide (α-compound) differs widely in its physical properties from Graebe and Liebermann's product (β-compound). Thus Meyer and Zahn's tetrabromide melts at 134°, whereas Graebe and Liebermann's product melts at 182°. The substances differ also in their crystalline form and solubility. The most marked difference, however, is in their behaviour towards light, for whereas Graebe and Liebermann's compound is unaffected, Meyer and Zahn's compound loses four atoms of bromine and passes into *ms*-dibromanthracene. The reaction, however, takes place only in benzene solution or, very slowly, in chloroform solution.

[1] Ullmann, A. **381**, 27. [2] Ullmann, A., **381**, 13, 26.
[3] A. **396**, 166. [4] A. Suppl. VII., 304.

Meyer and Zahn have also obtained a dichloranthracene tetrabromide which is sensitive to light and which is isomeric with the compound obtained by Schwazer [1] and by Hammerschlag.[2] The isomerism is probably geometrical, Meyer and Zahn's compounds being the *cis*- form and Graebe and Liebermann's, Schwazer's and Hammerschlag's being *trans*- forms. This is in agreement with the great ease with which α- compounds lose bromine, and also with the general rule that the *trans*- isomer has the higher melting point.[3]

In connection with the above it is interesting to notice that Radulescu,[4] by heating anthraquinone with a large excess of phosphorus pentachloride, has obtained a hexachlor compound to which he ascribes the formula :
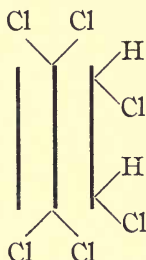
He states that it exists in two stereoisomeric forms, one melting with decomposition at 185°, and one melting with decomposition at 149°. Both on heating give the same trichloranthracene.

Kurt Meyer and Zahn [5] have also studied the chlorination of anthracene in other solvents. They find that in water or dilute acetic acid the action of chlorine at temperatures below 25° is chiefly an oxidising action, hydroxyanthrone (anthraquinol) and anthraquinone being formed, whereas at higher temperatures *ms*-dichloranthracene is produced. In alcoholic solution the action is very similar, alkoxyanthrone and anthraquinone being produced in dilute solutions, whereas from concentrated solutions *ms*-

[1] B. **10**, 376.   [2] B. **19**, 1106.
[3] Stewart, " Stereochemistry " (1919), p. 107.
[4] Bull. Soc. Stii. Bucuresci, **17**, 29 ; C. 1908 (2), 1032.
[5] A. **396**, 166.

dichloranthracene can be obtained. Ether has much the same effect as carbon bisulphide, anthracene dichloride and mono- and di-chloranthracene being produced. When glacial acetic acid is used as a solvent they find that the chief products are anthraquinone and dichloranthracene tetrachloride.

Liebermann [1] and Schilling [2] have prepared numerous chloranthracenes by reducing the corresponding chloranthraquinones with zinc dust and ammonia.[3] They find that, as in the case of the chloranthraquinones the α-chloranthracenes melt at considerably lower temperatures than the corresponding β- compounds.

Liebermann finds that the α-chloranthracenes readily give addition products with chlorine, whereas the β- compounds only give them with difficulty, as the chlorine atom in the β-position seems to facilitate the substitution of the *ms*-hydrogen atoms. The ease with which α-chlor- compounds form addition products is borne out by O. Fischer and Ziegler,[4] who obtained a dibromide from 1-chlor-4-methyl anthracene by treating it with bromine in carbon bisulphide solution :
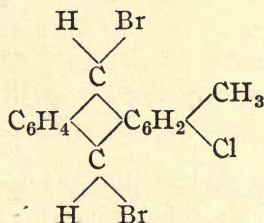
According to a patent [5] by Meister, Lucius, and Brüning, although the *ms*-dichloranthracene polyhalides lose halogen acid when treated with alcoholic caustic potash, they do not do so when treated with aqueous alkali unless benzyl sulphanilic acid is present. By means of this reagent they obtain pentachlor- and hexachloranthracene, and suggest their use as yellow pigments.

[1] B. **47**, 1011.   [2] B. **46**, 1066.
[3] Cf. Fischer and Ziegler, J. pr. [2] **86**, 291.
[4] J. pr. [2] **86**, 291.   [5] D.R.P. 282,818.

The chlorination of anthracene and of 9.10-dichloranthracene by the action of sulphuryl chloride in the presence of an inert solvent, *e.g.* nitrobenzene at 100°, has been investigated and it is claimed [1] that in both cases the product is 2.9.10-trichloranthracene.

Very little work has been done on the halogenation of the homologous anthracenes, but O. Fischer and Reinkober [2] have studied the action of bromine and chlorine on β-methylanthracene. With bromine they claim to have obtained a pentabrom substitution product, but with chlorine they obtained impure substances which seemed to be mixtures of compounds containing five, six, nine, and ten chlorine atoms.

Lippmann and Pollok [3] endeavoured to chlorinate anthracene by treating it with sulphur chloride in petroleum ether solution. They claim that prolonged action leads to *ms*-dichloranthracene, but that an intermediate compound, $C_{14}H_9S_2Cl$, is first formed. This, they state, on oxidation yields anthraquinone and on reduction takes up two atoms of hydrogen. To the addition compound and its reduction product they assign the formulae :

$$Cl—S : S \qquad\qquad Cl—SH—SH$$
$$|\qquad\qquad\qquad\qquad |$$
$$C \qquad\qquad\qquad\qquad C$$
$$C_6H_4\!\!\left\langle\;\;\right\rangle\!\!C_6H_4 \quad\overset{H}{\rightarrow}\quad C_6H_4\!\!\left\langle\;\;\right\rangle\!\!C_6H_4$$
$$CH \qquad\qquad\qquad\qquad CH$$
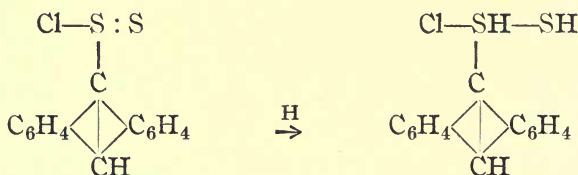
but as they state themselves that the addition compound is unaffected by boiling alcoholic potash, these formulæ can hardly be accepted pending some independent confirmation.

In addition to methods depending on the direct chlorination of anthracene, chloroanthracenes can be obtained by other methods. Graebe and Liebermann [4] heated anthracene to 200° with a mixture of phosphorus pentachloride and oxychloride and obtained what appeared to be a mixture of trichlor- and tetrachloranthracene. More recently this reaction has been examined by Radulescu,[5] who finds that

[1] M.L.B., D.R.P. 292,356.   [2] J. pr. [2] **92**, 49.
[3] B. **34**, 2768.   [4] A. **160**, 126.
[5] Bull. Soc. Stii. Bucuresci, **17**, 29. C. 1908 (2), 1032.

the first product is anthraquinone tetrachloride (red needles, m.p. 139°, with decomposition), and that this on heating then passes into dichloranthracene dichloride and trichloranthracene :

$$
\begin{array}{ccc}
\overset{Cl\quad Cl}{\underset{C}{\diagdown\diagup}} & \overset{Cl}{\underset{C}{|}} & \overset{Cl}{\underset{C}{|}} \\
C_6H_4\diagup\hspace{-6pt}\diagdown C_6H_4 \;\rightarrow\; C_6H_4\diagup\hspace{-6pt}|\hspace{-6pt}\diagdown C_6H_4Cl_2 & & C_6H_4\diagup\hspace{-6pt}|\hspace{-6pt}\diagdown C_6H_3Cl \\
\underset{Cl\quad Cl}{\overset{C}{\diagup\diagdown}} & \underset{Cl}{\overset{C}{|}} & \underset{Cl}{\overset{C}{|}}
\end{array}
$$
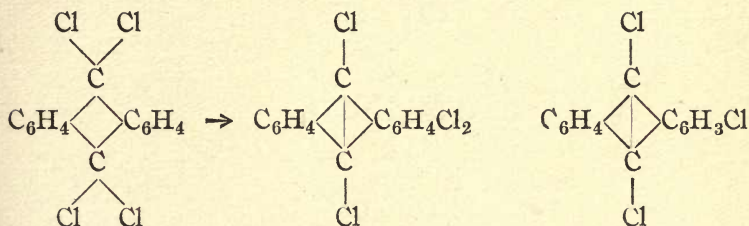
As stated on p. 46, he finds that the use of larger quantities of phosphorus pentachloride leads to the formation of two stereoisomeric hexachlor compounds.

As already stated (p. 47), Liebermann, Schilling, and O. Fischer and Ziegler have prepared chloroanthracenes by reducing the corresponding chloroanthraquinones with zinc dust and ammonia. Kircher [1] endeavoured to obtain 1.2.3.4-tetrachloranthracene in the same way from tetrachloranthraquinone, but during reduction two chlorine atoms were lost, so that the product was a dichloranthracene. This, Kircher states, gave a dichloranthraquinone on oxidation which gave alizarin on fusing with caustic potash. From this he concluded that his reduction product was 1.2-dichloranthracene; but Ullmann and Billig [2] have since proved it to be 2.3-dichloranthracene, as its oxidation product is identical with the dichloranthraquinone obtained from 4.5-dichlorphthalic acid. Although Kircher was unable to obtain tetrachloranthracene by the reduction of tetrachloranthraquinone, he succeeded in obtaining it by heating tetrachlor-*o*-benzoyl benzoic acid with hydriodic acid to 220°.

Very little is known of the chloranthracene sulphonic acids, but *ms*-dichloranthracene-β-sulphonic acid is said to be obtained by sulphonating *ms*-dichloranthracene with chlorsulphonic acid, preferably in the presence of some neutral solvent such as chloroform,[3] or with oleum.[4]

[1] A. **238**, 346. [2] A. **381**, 26.
[3] B.A.S.F., D.R.P. 260,562. [4] M.L.B., D.R.P. 292,590.

It has recently been found that 9.10-dichloranthracene, when treated in the cold with nitric acid and an inert solvent, forms an addition compound with one molecule of the acid.[1] This addition compound apparently has the formula :

$$
\begin{array}{ccc}
HO & & Cl \\
 & \diagdown \diagup & \\
 & C & \\
C_6H_4 & \diagup \diagdown & C_6H_4 \\
 & C & \\
 & \diagup \diagdown & \\
NO_2 & & Cl
\end{array}
$$
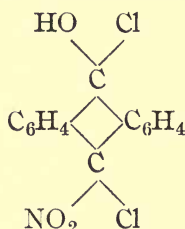
and on heating to 90-95° is decomposed into anthraquinone. The formation of such addition compounds seems to be common to nearly all derivatives of 9.10-dichloranthracene.

ACTION OF NITRIC ACID ON ANTHRACENE

The action of nitrous and nitric acids on anthracene was first studied by Liebermann and his co-workers [2] and by A. G. Perkin,[3] and also at a later date by Dimroth [4] and others. The somewhat complicated reactions which take place have more recently been fully investigated by Meisenheimer,[5] who has established the constitution of the various products formed, and also the mechanism of the reactions which lead to them. He has to a large extent confirmed the experimental results obtained by Liebermann and A. G. Perkin, but has shown that their interpretations of the reactions involved were usually quite erroneous.

Although the exhaustive action of nitrous or nitric acid on anthracene leads, as would be expected, to anthraquinone, the moderated action leads to several interesting compounds, including a mono- and a dinitro- compound in which the nitro groups are attached to the *ms*- carbon atoms.   Nitro derivatives of anthracene in which the nitro groups are attached to benzene nuclei are as yet unknown.

[1] M.L.B., D.R.P. 296,019.   [2] B. **13**, 1584 ; **14**, 467.
[3] Soc. **59**, 644 ; **61**, 866.
[4] B. **20**, 974 ; **33**, 3548 ; **34**, 221.   D.R.P. 127,399.
[5] A. **323**, 205 ; **330**, 133.

If anthracene is suspended in acetic acid and then treated with exactly one molecule of nitric acid, the first action is one of addition, 9-hydroxy-10-nitro-9.10-dihydro-anthracene being obtained (dihydro-nitro-anthranol) :

$$
\begin{array}{c}
\text{H} \quad \text{OH} \\
\diagdown \diagup \\
\text{C} \\
\text{C}_6\text{H}_4 \diagdown \quad \diagup \text{C}_6\text{H}_4 \\
\text{C} \\
\diagup \diagdown \\
\text{H} \quad \text{NO}_2
\end{array}
$$
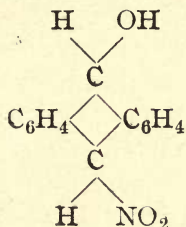
Liebermann and Lindemann [1] described this compound as being obtained by the action of nitrous oxides of anthracene, and named it " salpetersaüreanthracen ; " but Meisenheimer failed to obtain it, and pointed out the probable cause of the error on the part of Liebermann (see p. 52). The hydroxyl group in this compound is excessively reactive, so that in the presence of acetic acid it is at once acetylated, the acetyl derivative being formed :

$$
\begin{array}{c}
\text{H} \quad \text{OCOCH}_3 \\
\diagdown \diagup \\
\text{C} \\
\text{C}_6\text{H}_4 \diagdown \quad \diagup \text{C}_6\text{H}_4 \\
\text{C} \\
\diagup \diagdown \\
\text{H} \quad \text{NO}_2
\end{array}
$$
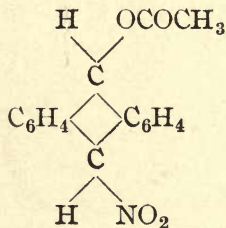
If this compound is treated with hydrochloric acid the corresponding chloride is obtained, whereas with nitrous acid it yields the nitrite, a somewhat unstable substance which, like the other esters, yields the methoxy compound very readily when treated with methyl alcohol.

$$
\begin{array}{ccc}
\begin{array}{c}
\text{H} \quad \text{ONO} \\
\diagdown \diagup \\
\text{C} \\
\text{C}_6\text{H}_4 \diagdown \quad \diagup \text{C}_6\text{H}_4 \\
\text{C} \\
\diagup \diagdown \\
\text{H} \quad \text{NO}_2
\end{array}
& \rightarrow &
\begin{array}{c}
\text{H} \quad \text{OCH}_3 \\
\diagdown \diagup \\
\text{C} \\
\text{C}_6\text{H}_4 \diagdown \quad \diagup \text{C}_6\text{H}_4 \\
\text{C} \\
\diagup \diagdown \\
\text{H} \quad \text{NO}_2
\end{array}
\end{array}
$$
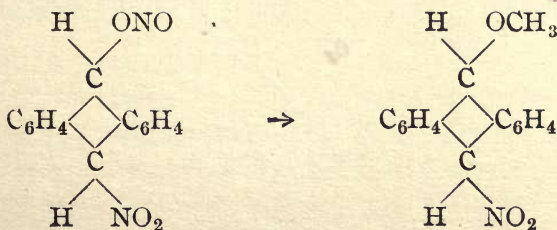
[1] B. **13**, 1584.

It was probably this nitrite that Liebermann and Lindemann obtained, as it corresponds very closely in its properties with their " salpetersaüreanthracen," although differing considerably in composition. Liebermann, however, states in his paper that the sample analysed was recrystallised from benzene, and Meisenheimer has pointed out that under these conditions the nitrite is decomposed into nitroanthrone, which differs but slightly in composition from the substance analysed.   The formation of the nitrite was no doubt due to Liebermann having generated his oxides of nitrogen from arsenious acid and nitric acid $(D=1\cdot33)$, as under these conditions it is very difficult to prevent nitric acid being carried over.   If this were the case the nitric acid would cause the formation of Meisenheimer's acetate, which would then be precipitated as the nitrite by the nitrous acid.

The formation of dihydronitroanthranol as the primary product of the action of nitric acid on anthracene is confirmed by the study of the action of nitric acid on ethyl dihydroanthracene, and Meisenheimer has shown that in this case the first action of the nitric acid is to oxidise the dihydrocompound to *ms*-ethyl anthracene :

$$\begin{array}{ccc}
\text{H}\quad\text{C}_2\text{H}_5 & & \text{C}_2\text{H}_5 \\
\diagdown\diagup & & | \\
\text{C} & & \text{C} \\
\text{C}_6\text{H}_4\diagdown\diagup\text{C}_6\text{H}_4 & \rightarrow & \text{C}_6\text{H}_4\diagdown\diagup\text{C}_6\text{H}_4 \\
\text{C} & & \text{C} \\
\diagup\diagdown & & | \\
\text{H}\quad\text{H} & & \text{H}
\end{array}$$
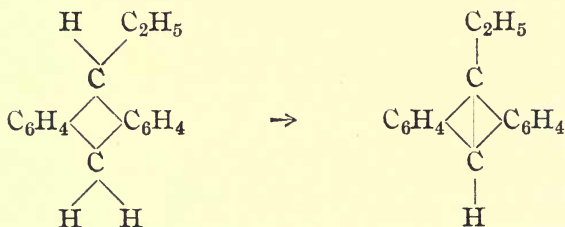
This then adds on nitric acid to form *ms*-ethyl-nitroanthranol, but the influence of the ethyl group has been to render the hydroxyl group much less reactive, so that the free hydroxy- compound is stable and can be isolated.

$$\begin{array}{c}
\text{HO}\quad\text{C}_2\text{H}_5 \\
\diagdown\diagup \\
\text{C} \\
\text{C}_6\text{H}_4\diagdown\diagup\text{C}_6\text{H}_4 \\
\text{C} \\
\diagup\diagdown \\
\text{H}\quad\text{NO}_2
\end{array}$$
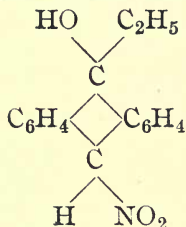
If nitric acid is added to nitroanthranol acetate the nitrate is not obtained, as the action of an excess of nitric acid causes a different reaction to take place ; but Meisenheimer was able to prepare the nitrate by nitrating anthracene in chloroform solution. If any attempts are made to hydrolyse these esters, loss of water takes place at once with the formation of *ms*-nitroanthracene :

$$
\begin{array}{ccc}
\begin{array}{c}
\text{H} \quad \text{OH} \\
\diagdown / \\
\text{C} \\
\text{C}_6\text{H}_4 \diamond \text{C}_6\text{H}_4 \\
\text{C} \\
/ \diagdown \\
\text{H} \quad \text{NO}_2
\end{array}
& \rightarrow &
\begin{array}{c}
\text{H} \\
| \\
\text{C} \\
\text{C}_6\text{H}_4 \diamond \text{C}_6\text{H}_4 \\
\text{C} \\
| \\
\text{NO}_2
\end{array}
\end{array}
$$
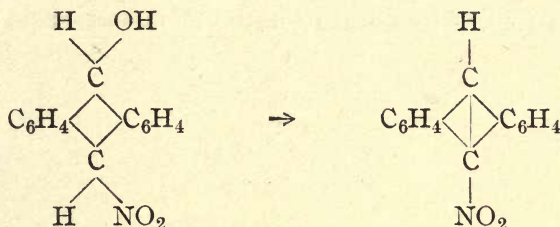
a perfectly stable substance which melts at 145–146°, and which distils *in vacuo* at over 300° without decomposition. On reduction it gives the corresponding amino compound.[1] The nitro- compound can also be obtained directly by the nitration of anthracene in acetic acid solution in the presence of acetic anhydride, but it is more easily obtained by the hydrolysis of the acetate.

Perkin [2] nitrated anthracene in the presence of methyl alcohol, and obtained a compound which he named anthracene methyl nitrate. Other alcohols, such as ethyl alcohol, propyl alcohol, and *iso*-butyl alcohol, gave similar products, and these are undoubtedly formed by the action of the alcohol on the nitroanthranol nitrate or nitrite first formed :

$$
\begin{array}{ccc}
\begin{array}{c}
\text{H} \quad \text{ONO} \\
\diagdown / \\
\text{C} \\
\text{C}_6\text{H}_4 \diamond \text{C}_6\text{H}_4 \\
\text{C} \\
/ \diagdown \\
\text{H} \quad \text{NO}_2
\end{array}
& \rightarrow &
\begin{array}{c}
\text{H} \quad \text{OCH}_3 \\
\diagdown / \\
\text{C} \\
\text{C}_6\text{H}_4 \diamond \text{C}_6\text{H}_4 \\
\text{C} \\
/ \diagdown \\
\text{H} \quad \text{NO}_2
\end{array}
\end{array}
$$
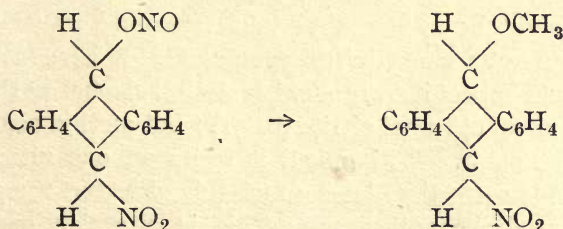
They are very readily hydrolysed by alkali and simultaneously lose water, the product being *ms*-nitroanthracene.

If anthracene in glacial acetic acid is treated with 2½

---

[1] D.R.P. 127,399. [2] Soc. **59**, 648 ; **61**, 866.

molecules of nitric acid instead of with one molecule, the reaction takes a somewhat different course and two unstable substances are formed. One of these is soluble in hot alkali, and Meisenheimer has identified it as nitroanthrone; a compound first obtained by Perkin [1] by the action of nitric acid on anthracene in the presence of *iso*-butyl alcohol under certain conditions, and more lately and in good yield by Kurt Meyer [2] by nitrating anthrone in acetic acid :

$$
\begin{array}{c}
O \\
\parallel \\
C \\
C_6H_4 \diamondsuit C_6H_4 \\
C \\
H \quad NO_2
\end{array}
$$
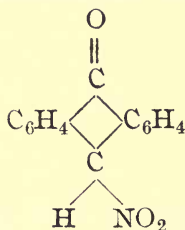
The other substance is insoluble in alkali, but is left behind as a decomposition product. Meisenheimer obtained it in the pure state by fractional precipitation from chloroform by the addition of petroleum ether, and identified it as trinitro-dihydroanthracene :

$$
\begin{array}{c}
H \quad NO_2 \\
C \\
C_6H_4 \diamondsuit C_6H_4 \\
C \\
NO_2 \quad NO_2
\end{array}
$$
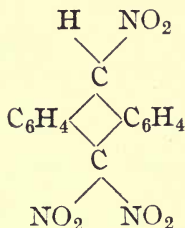
It might be argued that this compound was a nitrous ester and not a true trinitro- compound. If it were an ester one would expect it to react with methyl alcohol in the same way as nitroanthranol nitrite (p. 51) ; but methyl alcohol has no effect on it. With alkali it splits off one nitro group and at the same time loses a molecule of water, the product being *ms*-dinitroanthracene. This is a stable compound melting at 294°, which has also been obtained by Perkin,[3] together with the mononitro compound, by nitrating anthracene in nitrobenzene solution. He did not recognise it,

[1] Soc. **61**, 868.   [2] A. **396**, 150.   [3] Soc. **59**, 637.

however, as dinitroanthracene, and appears to have satisfied himself with identifying it as being identical with the " nitrosonitroanthracene " previously obtained by Liebermann and Landshoff.[1]

The composition of the above trinitro- compound receives support from the investigation of the action of nitric acid on ethyl-dihydroanthracene carried out by Meisenheimer. As stated previously, the first product formed is ethyl nitroanthranol :

$$
\begin{array}{c}
\text{HO} \quad \text{C}_2\text{H}_5 \\
\diagdown \diagup \\
\text{C} \\
\text{C}_6\text{H}_4 \diamondsuit \text{C}_6\text{H}_4 \\
\text{C} \\
\diagup \diagdown \\
\text{H} \quad \text{NO}_2
\end{array}
$$
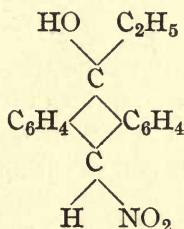
This forms stable alkali salts from which it is reprecipitated as such by acetic acid, although mineral acids cause an immediate loss of water and formation of ethyl nitroanthracene :

$$
\begin{array}{c}
\text{C}_2\text{H}_5 \\
| \\
\text{C} \\
\text{C}_6\text{H}_4 \diamondsuit \text{C}_6\text{H}_4 \\
\text{C} \\
| \\
\text{NO}_2
\end{array}
$$
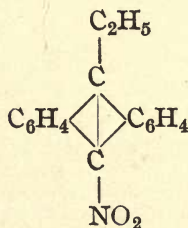
a stable compound melting at 135°.

The further action of nitric acid on ethyl anthracene takes two directions. In the first, oxidation takes place with the production of ethyl nitroanthrone :

$$
\begin{array}{c}
\text{O} \\
\| \\
\text{C} \\
\text{C}_6\text{H}_4 \diamondsuit \text{C}_6\text{H}_4 \\
\text{C} \\
\diagup \diagdown \\
\text{C}_2\text{H}_5 \quad \text{NO}_2
\end{array}
$$
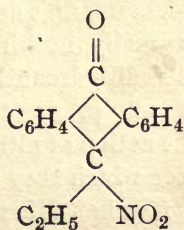
[1] B. **14**, 470.

while in the second place the nitrous acid thus generated combines with the ethyl nitroanthracene formed simultaneously to produce trinitrodihydroethylanthracene :

$$
\begin{array}{c}
C_2H_5 \quad NO_2 \\
\diagdown \diagup \\
C \\
C_6H_4 \diagdown \diagup C_6H_4 \\
C \\
\diagup \diagdown \\
NO_2 \quad NO_2
\end{array}
$$
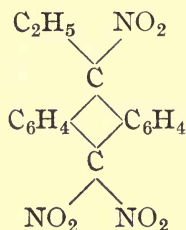
This corresponds exactly to the trinitro compound obtained from anthracene.   It cannot be a nitrous ester as it is stable towards alkali, and can in fact be warmed with 30 per cent. methyl alcoholic caustic potash without undergoing decomposition.

Liebermann and Landshoff [1] nitrated dihydroanthracene and obtained a substance which they named hydroanthracene nitrite, and to which they ascribed the formula :

$$
\begin{array}{ccc}
\begin{array}{c}
H \quad H \\
\diagdown \diagup \\
C \\
C_6H_4 \diagdown \diagup C_6H_4 \\
C \\
\diagup \diagdown \\
ONO \quad ONO
\end{array}
& \text{or} &
\begin{array}{c}
H \quad H \\
\diagdown \diagup \\
C \\
C_6H_4 \diagdown \diagup C_6H_4 \\
C \\
\diagup \diagdown \\
ONO \quad NO_2
\end{array}
\end{array}
$$
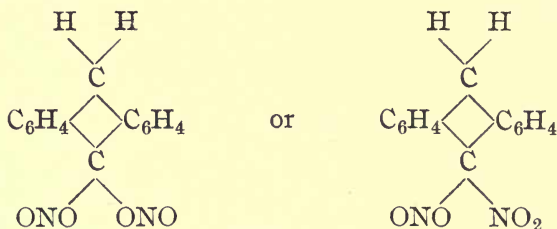
It seemed very improbable that dihydroanthracene would react differently towards nitric acid than anthracene itself, especially as ethyl dihydroanthracene reacts in the same way as anthracene, and Meisenheimer therefore re-examined the point and found that Liebermann's and Landshoff's " hydroanthracene nitrite " is really nothing but a mixture of nitroanthrone and trinitrodihydroanthracene.

It was mentioned on p. 51 that Liebermann and Lindemann [2] studied the action of nitrous acid on anthracene and obtained a substance which they named " salpetersäure-anthracen."   Under somewhat different conditions and by

[1] B. **14**, 467.   [2] B. **13**, 1585 ; **14**, 484 ; **33**, 3547.

using nitrous oxides carefully freed from nitric acid, they obtained a different compound, which they named " untersalpetersäureanthracen." This has also been re-investigated by Meisenheimer, who confirms Liebermann and Lindemann's results, but finds the compound is most readily obtained if the nitrogen dioxide is generated by heating lead nitrate. He considers that the compound is *sym*-dinitro-dihydroanthracene, and that it is formed by the addition of two (single) molecules of nitrogen dioxide :

$$
\begin{array}{c}
H \quad NO_2 \\
\diagdown \diagup \\
C \\
C_6H_4 \diagup \diagdown C_6H_4 \\
C \\
\diagup \diagdown \\
H \quad NO_2
\end{array}
$$
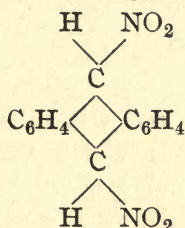
With reference to this it should be noted that a similar reaction takes place between stilbene and nitrogen dioxide : [1]

$$
C_6H_5CH=CHC_6H_5 \quad \rightarrow \quad
\begin{array}{cc}
H & H \\
| & | \\
C_6H_5C\!\!-\!\!-\!\!-\!\!CC_6H_5 \\
| & | \\
NO_2 & NO_2
\end{array}
$$
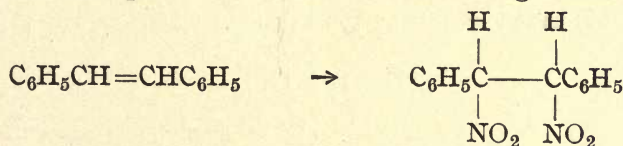
The action of alkali on the various nitration products of anthracene is very interesting.

As stated on p. 53, the esters and ethers of nitroanthranol when treated with alkali pass into *ms*-nitroanthracene. This, by the further action of alkali, passes into anthraquinone-monoxime,[2] a compound which was obtained by Perkin by this method, but which, curiously enough, he did not identify, although he prepared an acetyl derivative : [3]

$$
\begin{array}{ccccc}
H & & OH & & O \\
| & & | & & \| \\
C & & C & & C \\
C_6H_4\diagup\diagdown C_6H_4 & \rightarrow & C_6H_4\diagup\diagdown C_6H_4 & \text{or} & C_6H_4\diagup\diagdown C_6H_4 \\
C & & C & & C \\
| & & | & & \| \\
NO_2 & & NO & & NOH
\end{array}
$$
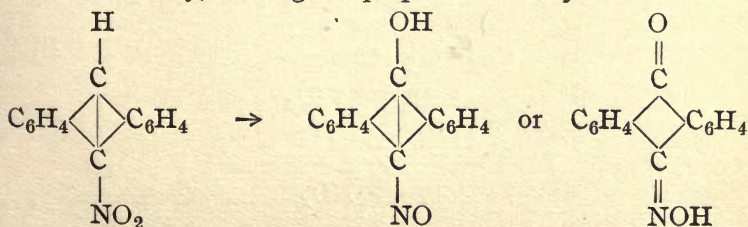
[1] B. **34**, 3540.   [2] A. **323**, 232.   [3] Soc. **59**, 644 ; B. **16**, 2179.

The change is obviously due to the wandering of an oxygen atom, and although it seems curious at first sight, it is by no means unique. Thus 1-nitro-naphthalene-3.8-disulphonic acid when boiled with aqueous caustic soda passes into 1.4-nitrosonaphthol-3.8-disulphonic acid : [1]

and dinitro-, trinitro-, and tetranitronaphthalene also give nitronitroso- compounds under the influence of alkali.[2] sym-Trinitrobenzene and sym-trinitrotoluene behave in a somewhat similar manner.

Meisenheimer [3] has made a very careful study of the action of potassium methoxide on ms-nitroanthracene. He finds that the first action is one of addition, the product being :

By the action of potassium hypobromite on this compound he obtained :

[1] B. 28, 1535.   [2] B. 32, 2876, 3528 ; D.R.P. 127,295.   [3] A. 323, 205.

which by loss of hydrobromic acid gave methoxynitro-anthracene. By treating this with potassium methoxide and then with sodium hypobromite he got :

$$CH_3O \quad OCH_3$$

$$C_6H_4 \diamondsuit C_6H_4 \qquad \text{and} \qquad C_6H_4 \diamondsuit C_6H_4$$
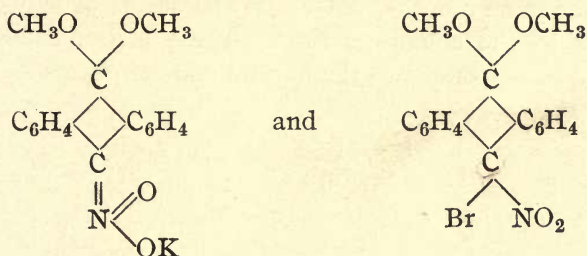
This last compound he oxidised to dimethoxyanthrone. On treating it with mineral acids, however, it was instantaneously hydrolysed to anthraquinone oxime.

Trinitrodihydroanthracene under the influence of alkali loses a nitro group and passes quantitatively into dinitro-anthracene :

$$C_6H_4 \diamondsuit C_6H_4 \quad \rightarrow \quad \left[C_6H_4 \diamondsuit C_6H_4 \right] \quad \rightarrow \quad C_6H_4 \diamondsuit C_6H_4$$
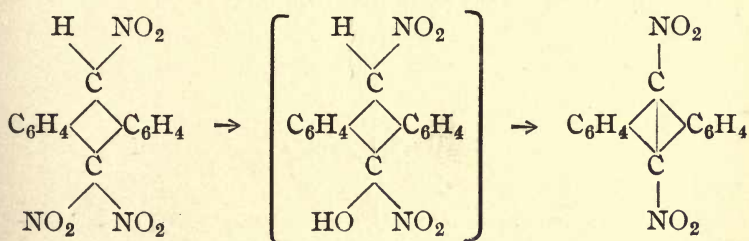
and dinitrodihydroanthracene by a very similar reaction gives mononitroanthracene :

$$C_6H_4 \diamondsuit C_6H_4 \quad \rightarrow \quad \left[C_6H_4 \diamondsuit C_6H_4 \right] \quad \rightarrow \quad C_6H_4 \diamondsuit C_6H_4$$
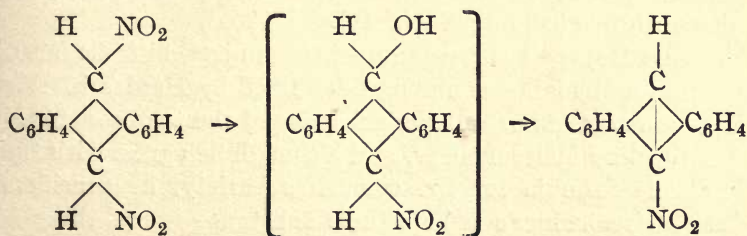
Nitroanthrone dissolves in alkali to form a coloured solution from which it is reprecipitated by acetic acid in

the original colourless form. If, however, a mineral acid is used to liberate it from its salts it can be obtained in a less stable red form. This can be preserved in a vacuum in the dark for some months, but under the action of light slowly reverts to the colourless form. These Meisenheimer considered corresponded to the normal and *aci-* forms :

$$\begin{array}{ccc}
& \text{O} & \\
& \| & \\
& \text{C} & \\
\text{C}_6\text{H}_4 & \diamond & \text{C}_6\text{H}_4 \\
& \text{C} & \\
\text{H} & & \text{NO}_2 \\
\end{array}
\qquad
\begin{array}{ccc}
& \text{O} & \\
& \| & \\
& \text{C} & \\
\text{C}_6\text{H}_4 & \diamond & \text{C}_6\text{H}_4 \\
& \text{C} & \\
& \| \; /\text{O} & \\
\text{N} & \diagdown & \\
& & \text{OH} \\
\end{array}$$
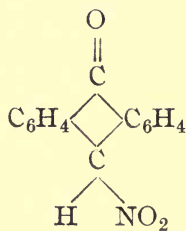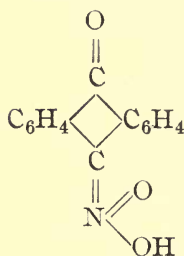
Colourless.   Red.

and Hantzsch[1] claims to have isolated a third, yellow, variety which is very unstable and rapidly passes into the red form. He ascribes to it the formula :

$$\begin{array}{c}
\text{OH} \\
| \\
\text{C} \\
\text{C}_6\text{H}_4 \diamond \text{C}_6\text{H}_4 \\
\text{C} \\
| \\
\text{NO}_2 \\
\end{array}$$
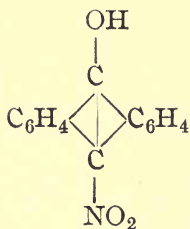
This compound was described by Perkin,[2] but Meisenheimer[3] has shown that Perkin's substance was really pure nitroanthrone (colourless variety).

Kurt Meyer[4] has re-examined the subject, but has failed to obtain the labile compound described by Hantzsch. He has, however, confirmed the existence of the two isomerides described by Meisenheimer, and although he agrees with the anthrone formula for the colourless variety, he considers that Meisenheimer's red unstable substance is not the *aci-* (nitrolic) form, but is nitroanthranol :

[1] B. **42**, 1216.   [2] Soc. **61**, 868.
[3] A. **330**, 153.   [4] A. **396**, 137.

$$
\begin{array}{cc}
\overset{\displaystyle O}{\underset{\displaystyle C}{\|}} & \overset{\displaystyle OH}{\underset{\displaystyle C}{|}} \\
C_6H_4\diamondsuit C_6H_4 & C_6H_4\diamondsuit C_6H_4 \\
C & C \\
H \quad NO_2 & NO_2 \\
\text{Colourless.} & \text{Red.}
\end{array}
$$
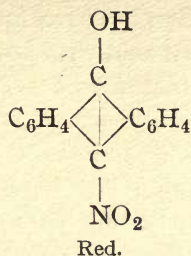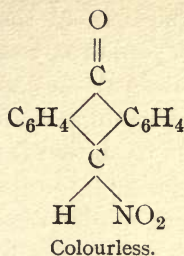
The latter compound should give an acetyl derivative, and although Meisenheimer failed to obtain one, Meyer has been able to do so by treating it with acetyl chloride in pyridine solution. He has also obtained a benzoyl derivative by the same means.

It might be argued that the latter anthranol formula represents a fluorescent compound, whereas nitroanthranol shows no fluorescence. The nitro- group, however, has a great influence in hindering fluorescence, so that this objection does not hold good, and it is fairly certain that Meyer's interpretation of the isomerism is the correct one.

The question of anthrone-anthranol isomerism will be found more fully discussed on p. 119.

SULPHONIC ACIDS

The anthracene sulphonic acids can be obtained either by sulphonating anthracene or by the reduction of the corresponding anthraquinone sulphonic acid.

As regards the sulphonation of anthracene, the literature is very confusing, and even now it is not at all clear exactly what takes place. Linke,[1] by sulphonating anthracene claimed to have obtained two different monosulphonic acids, each of which gave a different hydroxyanthracene when fused with caustic potash. Liebermann,[2] however, repeated Linke's work and failed to obtain any monosulphonic acid the conditions specified by Linke always leading to disulphonic acids. Graebe and Liebermann,[2] and Liebermann and Rath,[3] however, obtained a monosulphonic acid by

[1] J. pr. [2] **11**, 227.   [2] A. **212**, 43 ; B. **11**, 1613.   [3] B. **8**, 246.

sulphonation. These latter observers distilled the sodium salt of their acid with potassium ferrocyanide and saponified the resulting nitrile. They thus obtained an anthracene carboxylic acid which gave a soluble barium salt and which melted rather indefinitely at 260°. On oxidation it gave the corresponding anthraquinone carboxylic acid, m.p. 282–284°. There can be but little doubt that the sulphonic acid they obtained was anthracene-1-sulphonic acid. They give no details of the sulphonation process except to state that it was carried out at as low a temperature as possible.

On the other hand, the Société Anonyme des Matières Colorantes [1] sulphonate anthracene at a temperature of 120–135°, with an acid of 67 per cent. strength (53° Bé.), and obtain yields of 60 per cent. of anthracene-1-sulphonic acid. They state that the same product is formed when the sulphonation is carried out at 140–150° with sodium bisulphate or nitre-cake instead of with sulphuric acid.[2] They also state that a certain quantity of three different disulphonic acids is formed at the same time, and that one of these, by heating with hydrochloric acid under pressure, is hydrolysed and converted into anthracene or anthracene monosulphonic acid. None of these acids seem to have been investigated, but the one that is hydrolysed is probably an α-sulphonic acid, as sulphonic acid groups in the α- position are much more readily removed than those in the β- position. More recently Bayer and Co.[3] have described the sulphonation of anthracene by chlorsulphonic acid in glacial acetic solution at 95°, and claim to obtain a yield of 50 per cent. of anthracene-1-sulphonic acid and 30 per cent. of anthracene-2-sulphonic acid. Heffter [4] has carried out some investigations with the monosulphonic acid made by the French process and has prepared the sulphochloride. This is remarkably stable for a sulphochloride and can be boiled with water for a few minutes without it undergoing decomposition. In order to convert it into the sulphamide he apparently found it necessary to heat it in a sealed tube for

[1] D.R.P. 72,226 ; 73,961 ; 76,280.   [2] D.R.P. 77,311.
[3] D.R.P. 251,695.   [4] B. 28, 2258.

four hours at 150° with alcoholic ammonia. By reduction with zinc and ammonia or with sodium sulphite he obtained the sulphinic acid.

Liebermann [1] by sulphonating anthracene obtained two disulphonic acids which he separated by taking advantage of the different solubilities of their lead and sodium salts. These on fusion with caustic alkali gave two different hydroxyanthracenes, the acetyl derivatives of which Liebermann oxidised and then hydrolysed, and thus obtained anthrarufin and chrysazin. He therefore concluded that the two sulphonic acids were the 1.5 and the 1.8 isomers, and states that a high temperature during sulphonation favours the formation of the former.[2] This deduction, however, is hardly justified, as caustic fusion is notoriously unreliable as a method of determining constitution, and at high temperatures hydroxyl groups have a great tendency to wander to the α- position. It is true that Lampe [3] has obtained the two disulphonic acids by the reduction of the corresponding anthraquinone sulphonic acids, and states that they are the same as those obtained by Liebermann; but the description he gives of the acids is not full enough to justify this statement, and it must therefore be accepted with some reserve until further information is forthcoming.

It seems reasonably certain that under some conditions anthracene is sulphonated in the α- position, while it is equally certain that under other conditions it is the β-position that is attacked. In the naphthalene series exactly the same phenomenon is encountered, as when sulphonated below 80° the α-sulphonic acid is almost the sole product, whereas above 80° the β- isomer predominates, and on heating with sulphuric acid the α- acid is converted into the β- acid by the wandering of the sulphonic acid group. This wandering must be regarded as hydrolysis and subsequent sulphonation, and the conditions specified in the patented process for the manufacture of anthracene-1-sulphonic acid would favour hydrolysis. It is, of course, quite possible that sulphonation first takes place at the *ms-* carbon atoms, but

[1] A. **212**, 43 ; B. **11**, 1613.   [2] B. **12**, 182.   [3] B. **42**, 1413.

no anthracene *ms*-sulphonic acids seem to have been described.

The reduction of the anthraquinone sulphonic acids can be carried out with hydriodic acid and phosphorus,[1] or with zinc and ammonia.[2] Reduction must, however, not be more vigorous than is necessary, as otherwise the sulphonic acid group may be split off. This is particularly likely to happen in the case of the α-sulphonic acid. Liebermann and Hörmann,[3] by reducing anthraquinone sulphonic acid, obtained an anthracene sulphonic acid which on fusion with caustic potash gave an hydroxyl compound the acetyl derivative of which melted at 139°, *i.e.* was probably 1-acetoxyanthracene. It is improbable that Liebermann and Hörmann were using anthraquinone-1-sulphonic acid, as it is only in recent years that this has been available, and it must therefore be concluded that the production of 1-hydroxyanthracene was due to a wandering of the hydroxyl group during the alkali fusion. This receives confirmation from the fact that Liebermann and Bischoff[4] reduced commercial anthraquinone sulphonic acid with hydriodic acid and then distilled the sodium salt of the resulting anthracene sulphonic acid with potassium ferrocyanide. On hydrolysing the resulting nitrile they obtained an acid which melted rather indefinitely at over 280° and which gave an insoluble barium salt and was undoubtedly anthracene-2-carboxylic acid. It was accompanied by a small quantity of an isomeric acid which gave a soluble barium salt and which Liebermann[5] has since recognised as anthracene-α-carboxylic acid, and which, as he has proved, was derived from the small amount of anthraquinone-α-sulphonic acid always present in commercial samples of the β- acid.

HYDROXYANTHRACENES

Hydroxyanthracenes, in which the hydroxyl groups are attached to the *ms*-carbon atoms, the anthranols and anthra-

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[1] A. **212**, 43 ; B. **12**, 589.   [2] B. **13**, 47.
[3] B. **15**, 1807 ; **37**, 70 ; **38**, 2863.   D.R.P. 21,178 (Agfa).
[4] B. **13**, 47.   [5] B. **37**, 646.

quinols, differ very considerably in their properties from those in which the hydroxyl groups are attached to the benzene rings. These *ms*-compounds are almost invariably obtained by the reduction of the corresponding anthraquinone, and will be described in Chapter IV.

The hydroxyanthracenes, in which the hydroxyl groups are situated in the benzene rings, are known as anthrols to distinguish them from the anthranols, in which the hydroxyl group is attached to one of the *ms*-carbon atoms. They can be obtained by the reduction of the corresponding hydroxyanthraquinones, *e.g.* with zinc dust and ammonia ; but simultaneous loss of one or more of the nuclear hydroxyl groups is very apt to take place, so that the anthrol obtained often contains fewer hydroxyl groups than the anthraquinone derivative from which it was made.[1]   A much more generally useful method, however, is the fusion of the corresponding anthracene sulphonic acids with caustic potash, although, as the sulphonic acid groups are very firmly held, a rather high temperature is necessary. This method has been largely developed by Liebermann and his students,[2] and has been applied not only to the sulphonic acids obtained by sulphonating anthracene, but also to the anthracene sulphonic acids which are readily obtained by the reduction of the corresponding anthraquinone sulphonic acids. A third method which is sometimes useful, although limited in its application, consists in the reduction of derivatives of 1.2-anthraquinone or 1.4-anthraquinone. Both these substances are true quinones, and their reduction apparently can be readily effected without danger of simultaneous loss of hydroxyl groups. So far, however, the method has been very little applied.[3]

As would be expected, the anthrols resemble the phenols

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[1] Cf. pp. 264–266 ; Lagodzinski, A. **342**, 104 ; B. **28**, 1533.

[2] Liebermann, B. **11**, 1610.   Liebermann and Boeck, B. **12**, 185, 1613.   Liebermann and Hörmann, B. **12**, 589.   Schüler, B. **15**, 1807. R. E. Schmidt, B. **37**, 70.   Dienel, B. **38**, 2863.   Lampe, B. **42**, 1414. Liebermann, A. **212**, 43.   Linke, J. pr. [2] **11**, 227.   Agfa, D.R.P. 21,178.

[3] Lagodzinski, B. **39**, 1717 ; A. **342**, 59.   Dienel, B. **39**, 930.   Haslinger, B. **39**, 3537.   Pisovschi, B. **41**, 1436.

very closely in their deportment.   Thus they are soluble in caustic alkali, give nitroso compounds [1] with nitrous acid, and in alkaline solution couple with diazo- solutions to produce hydroxy azo compounds.[2]   The corresponding alkyl ethers are very readily prepared, it being sufficient to saturate the warm alcoholic solution with hydrochloric acid gas.[3]   By this procedure the alkylated anthrol is usually obtained in almost quantitative yield, whereas the phenols of the benzene series are almost unaffected.   The naphthols can be alkylated by saturating their alcoholic solutions with hydrogen chloride, but the reaction takes place with some difficulty and the yields are poor.

The following anthrols have been described :—

Position of OH.	Name.	M.p.	Acetyl derivative, m.p.	Methyl ether, m.p.	Ethyl ether, m.p.
1	—	152° decomp.	128–130° decomp.	70°	69°
2	—	Decomp. at 200°	198°	175–178°	145–146°
1.2	—	131° decomp.	145°	—	—
1.4	—	—	169°	—	—
1.5	Rufol	265° decomp.	196–198°	224°	179°
1.8	Chrysol	225° decomp.	184°	198°	139°
2.3	—	Decomp. 180°	155–160°	204°	—
? ?	Flavol	260–270°	254–255°	—	229°

Flavol was described by Schüler,[4] who reduced commercial anthraquinone disulphonic acid to anthracene disulphonic acid and then fused this with caustic potash.   It is probably either 2.6-dihydroxy anthracene or 2.7-dihydroxy anthracene, or it may be a mixture of the two.

Of the anthracene *mercaptans* very little is known, but Heffter,[5] by reducing anthracene-β-sulphinic acid with zinc and hydrochloric acid, obtained anthracene-β-mercaptan. Kehrmann and Sava,[6] by treating its lead salt with dimethyl sulphate, obtained dimethyl-β-anthraquinonyl sulphonium salts.

[1] Dienel, B. **39**, 930.   Lagodzinski, A. **342**, 59.
[2] Lagodzinski, B. **39**, 1717.   Agfa, D.R.P. 21,178.
[3] Liebermann and Hagen, B. **15**, 1427 ; B. **21**, 2057.   Dienel, B. **38**, 2863.   Lampe, B. **42**, 1413.
[4] B. **15**, 1807.   [5] B. **28**, 2263.   [6] B. **45**, 2898.

AMINOANTHRACENES

Methods involving the reduction of nitro groups are not, as a rule, available for the preparation of anthramines, as anthracene is only nitrated with difficulty, and the *ms*-nitroanthracenes are the only known nitro compounds. The anthramines, however, are fairly easily prepared by other methods.

ms-Anthramine (*ms*-aminoanthracene) was first prepared by Goldmann [1] by heating anthranol with concentrated aqueous ammonia at 200°, and later was prepared by Meisenheimer [2] and Dimroth [3] by the reduction of *ms*-nitroanthracene with tin and hydrochloric acid, or with zinc dust and ammonium chloride. It is a rather unstable substance, which melts indefinitely at about 115°. When treated with acetic anhydride at the ordinary temperature it gives a stable monoacetyl derivative (m.p. 273–274°), whereas when treated with boiling acetic anhydride it readily gives a diacetyl derivative (m.p. 159°). N-Arylanthramines have been prepared by Padova [4] by heating anthranol with excess of primary aromatic amines, such as aniline and α- and β- naphthylamine.

The B*z*-anthramines are best obtained from the anthrols by heating with aqueous ammonia,[5] calcium chloride ammonia,[6] or acetamide,[7] but *o*- and *p*-amino anthrols and *o*- and *p*-diamino anthracenes are more readily obtained by the reduction of the corresponding nitrosoanthrol,[8] or the hydroxy or amino azo- compound.[9]

Anthramines can also sometimes be obtained by reducing the corresponding aminoanthraquinone, *e.g.* Römer [10] obtained β-anthramine by heating β-aminoanthraquinone with hydriodic acid and phosphorus ; but the method is not

[1] B. **23**, 2522 ; A. **330**, 165 ; By. D.R.P. 127,399.
[2] B. **33**, 3548.
[3] B. **34**, 220.
[4] C. r. **149**, 217.
[5] Liebermann and Bollert, B. **15**, 816.
[6] Pisovschi, B. **41**, 1434. Liebermann, *loc. cit.* (footnote).
[7] Liebermann and Bollert, B. **15**, 226 ; A. **212**, 56. Dienel, B. **38**, 2863. Liebermann, B. **41**, 1434 (footnote).
[8] Dienel, B. **38**, 930. Lagodzinski, A. **342**, 73.
[9] Pisovschi, B. **41**, 1434. Lagodzinski, B. **39**, 1717. A. **342**, 75.
[10] B. **15**, 223.

a satisfactory one, and Graebe and Blumenfeld [1] failed to reduce a-aminoanthraquinone to a-anthramine.

The anthramines are very weak bases, and consequently are scarcely soluble in hydrochloric acid, although salts can be precipitated by adding an acid to the ethereal solution of the anthramine. These salts, however, are at once hydrolysed by water. [2] They give monoacetyl derivatives on prolonged boiling with acetic anhydride, and in this way the Bz-anthramines differ from ms-anthramine, this latter, as stated on p. 67, readily yielding a diacetyl derivative.

The primary anthramines pass with great ease into the dianthramines, boiling for a short time with glacial acetic acid being sufficient to bring about the change; but in the case of a-anthramine the reaction is considerably slower than with β-anthramine. [3] The primary anthramines react very readily with methyl iodide and pass directly into quaternary ammonium salts, $C_{14}H_9N(CH_3)_3I$, from which the quaternary base can be liberated by means of silver oxide. This when boiled with water, or, more readily, when heated with water to $120-130°$, loses methyl alcohol, and passes into the dimethylanthramine. [4]

The anthramines do not seem to be readily diazotised, although Pisovschi [5] states that he obtained aminoazo anthracene by treating a-anthramine with amyl nitrite in alcoholic solution. Bollert, [6] on the other hand, states that β-anthramine when treated in alcoholic solution either with nitrous acid or amyl nitrite yields $(C_{14}H_9NH)_2NO$. In Bollert's compound, however, it is not improbable that one of the ms-hydrogen atoms had been affected.

The following simple anthramines have been described :—

Position of NH_2.	M.p.	Acetyl derivative, m.p.
1	119°	198°
2	236–237°	240°
1.4	—	322°
ms.	About 115°	{ Monoacetyl, 273–274° { Diacetyl, 115°

[1] B. **30**, 1118.   [2] Liebermann and Bollert, B. **15**, 226; A. **212**, 56.
[3] Bollert, B. **16**, 1634.   Dienel, B. **38**, 2863.   [4] Bollert, B. **16**, 1634.
[5] B. **41**, 1434.   [6] B. **16**, 1634.

NITRILES AND CARBOXYLIC ACIDS

The *ms*-nitrile of anthracene has not been described, but several nuclear nitriles have been prepared. They are usually best obtained by distilling the potassium salts of the corresponding sulphonic acids with potassium cyanide.[1] They are of no particular interest, and, like the naphtho-nitriles, are very difficult to hydrolyse.

Anthracene-*ms*-carboxylic acid (anthroic acid) was first obtained by Graebe and Liebermann [2] by heating anthracene under pressure with carbonyl chloride at 180°, and at a later date Behla [3] and Liebermann and Zsuffa [4] showed that if the temperature is raised simultaneous chlorination takes place, the product being *ms*-chloranthroic acid. The yields of anthroic acid obtained by this method are very poor, but more recently Liebermann and Zsuffa [5] have obtained it in eighty per cent. yield by heating anthracene with oxalyl chloride to 160–170°. If oxalyl chloride is used in conjunction with aluminium chloride the yield of anthroic acid falls to about thirty per cent., but aceanthrene quinone is simultaneously formed in sixty per cent. yield :
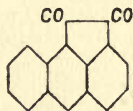
and this, on careful oxidation in neutral or alkaline solution, gives anthracene-1.9-dicarboxylic acid.[6] The behaviour of anthracene homologues and halogen substitution products towards oxalyl chloride is very similar.[7]

The anthroic acids are somewhat unstable, and lose carbon dioxide readily when heated, loss of carbon dioxide commencing at 150° in the case of anthroic acid itself. On oxidation the *ms*- carboxyl group is lost, anthroic acid itself being quantitatively converted into anthraquinone. As

[1] Liebermann and Rath, B. **8**, 246. Liebermann and Bischoff, B. **13**, 47. Liebermann and Pleus, B. **37**, 646. Dienel, B. **39**, 932.

[2] A. **160**, 137; B. **2**, 678.   [3] B. **18**, 3169; **20**, 704.

[4] B. **44**, 202.   [5] B. **44**, 202.

[6] B.A.S.F., D.R.P. 280,092.   [7] B. **45**, 1213.

would be expected from stereochemical considerations, the anthroic acids are only esterified with the utmost difficulty, prolonged heating of the silver salt with the alkyl iodide under pressure usually being necessary.

The nuclear carboxylic acids cannot be obtained directly by the oxidation of the methyl anthracenes, as simultaneous oxidation of the *ms*-carbon atoms always takes place, the product invariably being an anthraquinone carboxylic acid. These, however, are readily reduced to the anthracene derivative, *e.g.* by zinc dust and ammonia, and the reduction of the anthraquinone carboxylic acids forms the easiest means of obtaining the anthracene carboxylic acids.[1] The acids can also be obtained by the hydrolysis of the nitriles, and this method has been applied in several instances by Liebermann and his students.

The following nuclear carboxylic acids have been described :—

Position of COOH.	M.p. of acid.
1	245°
2	—
1.3	Above 330°
1.4	320° approx.
2.3	345°
1.2.4	—

ALDEHYDES AND KETONES

No aldehydes of the anthracene series have been described, and very little is known of the ketones. Perrier[2] condensed anthracene with benzoyl chloride in the presence of aluminium chloride, and obtained three compounds, having melting points of 75°, 143°, and 203°. Lippmann and Fleisser,[3] and Lippmann and Keppich[4] also obtained three compounds, viz. a monobenzoyl derivative melting at 148°, a dibenzoyl

[1] Elbs, B. **20**, 1363; J. pr. [2] **41**, 6, 121. Graebe and Blumenfeld, B. **30**, 1118. Lavaux, C. r. **143**, 687.
[2] B. **33**, 816.   [3] B. **32**, 2249.   [4] B. **33**, 3086.

derivative melting at 158°, and a tribenzoyl derivative melting over 300°. All three compounds gave anthraquinone on oxidation, and hence it would appear that in all of them the benzoyl groups are attached to the *ms*-carbon atoms. It is somewhat difficult, however, to account for three benzoyl groups. In a later paper Lippmann and Pollok [1] claim that better yields of the monobenzoyl compound, anthraphenone, are obtained by warming anthracene with benzoyl chloride and zinc dust in carbon bisulphide solution for 480 consecutive hours.

[1] B. **34**, 2766.

CHAPTER IV

THE ANTHRAQUINONES AND DIANTHRAQUINONYLS

THEORETICALLY six monoquinones might be derived from anthracene, viz. four homonuclear quinones :

1.2-Anthra quinone.	1.4-Anthra- quinone.	2.3-Anthra- quinone.	9.10-Anthra- quinone.
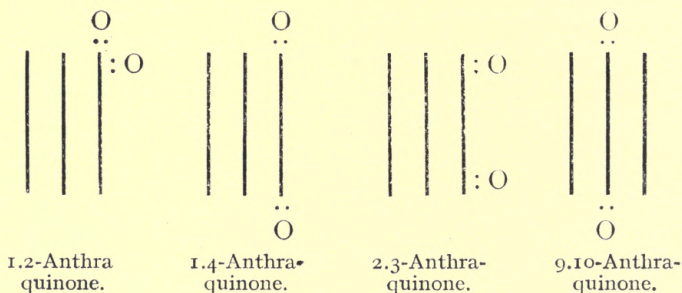
and two heteronuclear quinones :

1.5-Anthraquinone.   2.6-Anthraquinone.
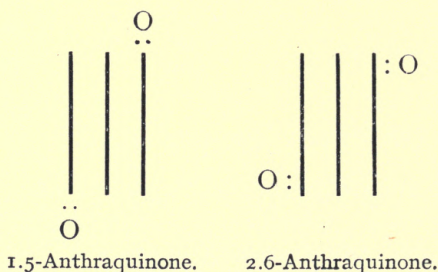
Of these 9.10-anthraquinone is by far the most important and is what is ordinarily understood by the term "anthra-quinone." Of the other isomers 1.2-anthraquinone and 1.4-anthraquinone have both been prepared, but 2-3 anthra-quinone is unknown, and the same applies to the heteronuclear quinones.

In addition to the monoquinones there is a possibility of the existence of numerous diquinones, some of which are known, and a triquinone has also been described.

1.2-ANTHRAQUINONE

This was obtained by Dienel[1] and Lagodzinski[2] by oxidising 2-amino-1-anthrol with ferric chloride and hydrochloric acid. It crystallises from water in red needles, which melt with decomposition at 185–190°. It is not volatile with steam, and on reduction with zinc dust and acetic anhydride passes into 1.2-diacetoxyanthracene. Like all α-diketonic compounds it condenses with o-phenylene diamine to form an azine. Lagodzinski[3] endeavoured to obtain 2.3-anthraquinone by oxidising 2·3-dihydroxyanthracene, but without success.

1.4-ANTHRAQUINONE

This was first described almost simultaneously by Dienel[4] and Lagodzinski,[5] both of whom obtained it by oxidising 4-amino-1-anthrol with ferric chloride, and shortly after Pisovschi[6] obtained it by oxidising 1.4-diamino anthracene. It forms yellow needles which, according to Dienel, melt at 206°, whereas Pisovschi states that the compound darkens at 210° and melts with decomposition at 218°. Like all true p-quinones it is very volatile. It is converted into quinizarin by reduction with zinc dust and acetic anhydride, and subsequent oxidation and hydrolysis.[7]

9.10-ANTHRAQUINONE

Synthetic methods for building up the anthraquinone ring are discussed in Chapter VI., and although the synthesis from phthalic acid is useful in the laboratory, the only method of any technical importance is the oxidation of anthracene.

In the laboratory the oxidation is best brought about by

[1] B. **39**, 930.　　　　　　[2] B. **27**, 1438; **28**, 1422; A. **342**, 59.
[3] B. **28**, 1533.　　　　　　[4] B. **39**, 931.　　　　[5] B. **39**, 1717.
[6] B. **41**, 1436.　　　[7] Dienel, B. **39**, 931.　Haslinger, B. **39**, 3537.

an excess of chromic acid in boiling glacial acetic acid solution,[1] but on the manufacturing scale the cost of the acetic acid is prohibitive, and in addition sufficient chromic acid must be used not only to oxidise the anthracene but also to oxidise the impurities present. The acetic acid method, however, gives quantitative results, and is universally used for the estimation of anthracene in commercial samples of the hydrocarbon.

Anthracene can be oxidised by aqueous solutions of chromic acid (bichromate and sulphuric acid) provided it is first reduced to a state of fine subdivision, and this method has the advantage that the anthracene is attacked more readily than the impurities, so that it is only necessary to use the calculated amount of chromic acid. In order to reduce the anthracene to the desired physical condition it is sublimed in a current of superheated steam and the vapour condensed by fine jets of water. The paste thus obtained is oxidised with sodium bichromate and sulphuric acid, and the chromic acid regenerated from the liquors electrically.[2] The crude anthraquinone, the purity of which depends, of course, on the grade of anthracene used, is filtered off, washed, dried, and then dissolved in concentrated sulphuric acid at 130°. This treatment does not affect the anthraquinone, but sulphonation of most of the impurities takes place, and at the same time the acridine is converted into the soluble sulphate. The acid solution, without cooling, is run into *boiling* water, when the anthraquinone is precipitated, and the sulphonated impurities and the acridine sulphate dissolve. It is necessary to run the hot acid solution into boiling water, as otherwise the anthraquinone separates as a fine sludge, which is very difficult to filter. After washing the anthraquinone is quite pure enough for all ordinary purposes, but can be further purified by sublimation or by recrystallisation, *e.g.* from tetrachlorethane, aniline, nitrobenzene or nitrotoluene.[3]

[1] Kopp, Monit. Sci. [3] **8,** 1159.   Graebe and Liebermann, *ibid.* [3] **9,** 421.
[2] By. D.R.P. 252,759. This patent describes a continuous electrical recovery process.   [3] Sadler & Co., D.R.P. 137,495.

Further purification can be effected if desired by reducing the anthraquinone to the alkali soluble anthraquinol, filtering off impurities and then oxidising the clear alkaline solution with atmospheric oxygen. On a technical scale it is stated that the reduction can be effected with finely divided iron and alkali.[1]

In addition to the chromic acid method, several other processes have been described for oxidising anthracene to anthraquinone. Thus, Hofmann, Ehrhart, and Schneider [2] have described the oxidation with potassium chlorate in the presence of a trace of an osmium salt, and Hofmann, Quoos, and Schneider [3] have described the oxidation by sodium nitrate or chlorate in the presence of a large excess of molten crystallised magnesium chloride. They state that the reaction starts at 125°, and is almost quantitative at 300°, whereas without the magnesium chloride no anthraquinone at all is formed, even at 330°. Hofmann and Ritter [4] have described the oxidation at the ordinary temperature by the use of aqueous sodium hypochlorite in the presence of a trace of an osmium salt, and Hofmann and Schumpelt [5] have described the oxidation by potassium chlorate in *formic* acid solution.

The electrolytic oxidation of anthracene has been described, and quantitative yields with a current efficiency of almost 100 per cent., have been claimed by carrying out the oxidation in 20 per cent. sulphuric acid suspension in the presence of a little ceric sulphate as a catalyst.[6]

Several patents have been granted for the use of nitric acid and oxides of nitrogen under various conditions. The action of nitric acid in the presence of a solvent such as nitrobenzene, with or without the use of mercury as a catalyst, has been investigated by the Chemische Fabrik Griesheim-Elektron, and good results claimed.[7]   Probably *ms*-nitro-

[1] Lewis and Gibbs, A.P. 1,293,610 (1918).
[2] B. **45**, 3334 ; **46**, 1669.
[3] B. **47**, 1991.   Hofmann, D.R.P. 277,733.
[4] B. **47**, 2238.
[5] B. **48**, 821.
[6] E.P. 19,178^{02}.
[7] D.R.P. 283,213 ; 284,083–4 ; 284,179.   Cf. A.P. 1,119,546.

compounds are first formed and then pass into anthraquinone.

The use of oxides of nitrogen has been described in several patents, and is of considerable interest in view of the ready production of these by the catalytic oxidation of ammonia. The Badische Anilin u. Soda Fabrik claim the use of nitrogen dioxide in the presence of a suitable solvent such as nitrobenzene,[1] and the Aktien Gesellschaft Grünau, Landshoff u. Meyer,[2] claim oxidation by nitrogen dioxide at a temperature of 100–200°, preferably at 200°, and state that an improved quality of anthraquinone is obtained if the anthracene is mixed with zinc dust or other substance which will destroy nitric acid.[3]

In addition to the experiments of Hofmann and his students referred to on p. 75, Meister, Lucius, and Brünning have developed the use of chlorates, and in two patents [4] claim the use of the chlorates of iron, nickel, cobalt, manganese, and chromium.

Attempts have been made to carry out the oxidation with oxygen, and it has been stated that anthracene can be oxidised in aqueous suspension at 170° with oxygen under pressure if a suitable catalyst is used.[5]   The best catalyst is said to be cupric oxide, but nickel, cobalt, iron and lead compounds are also effective. The oxidation in the vapour phase has also been described, the Barrett Co. (New York) [6] claiming oxidation by air or oxygen by passing anthracene vapour over a vanadium catalyst at 300–500°.

The use of ozone has also been claimed.[7]

Anthraquinone is a yellow crystalline solid which melts at 280°.[8] It can be sublimed fairly easily, but is not nearly as volatile as most p-quinones, and in this respect differs

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[1] D.R.P. 268,049.

[2] D.R.P. 234,289 ; 254,710.

[3] M.L.B., D.R.P. 256,623 (taken over from Akt. Ges. Grünau, Landshoff u. Meyer).

[4] D.R.P. 273,318–9.

[5] M.L.B., D.R.P. 292,681.

[6] E.P. 134,522[18].

[7] Heinemann, E.P. 5514[15].

[8] Phillipi, M. **33**, 373. Kempf, J. pr. [2] **78**, 257. The melting point usually given in the literature, viz. 278°, is too low.

sharply from the isomeric 1.4-anthraquinone. It is a very stable substance and is only attacked by oxidising agents with great difficulty, and then yields phthalic acid. Its behaviour towards reducing agents is discussed in detail elsewhere, but attention may here be drawn to the fact that the formation of a deep red solution by reduction in the presence of alkali (zinc dust and ammonia or caustic soda, or sodium hydrosulphite and caustic soda) serves as a convenient test for anthraquinone, and as the "vat" is very easily oxidised by air or weak oxidising agents, such as hydrogen peroxide, reduction and subsequent oxidation is often a convenient method of getting rid of impurities.

Anthraquinone hardly behaves like a true quinone, nor does it behave like a true ketone. It forms no phenyl hydrazone, and only reacts with hydroxylamine to form a monoxime. Even this monoxime is only formed with great difficulty,[1] and it is only obtained directly by heating anthraquinone with alcoholic solutions of hydroxylamine hydrochloride in sealed tubes at 180°. Indirectly, however, both the monoxime [2] and the monophenyl hydrazone [3] can be obtained fairly easily by treating dibromanthrone with hydroxylamine or phenyl hydrazine. The monoxime melts at 224°. The phenyl hydrazone is identical with the azo-dye obtained by coupling benzene diazonium salts with anthranol in alkaline solution.

Although the anthraquinone itself only undergoes oxime formation with the greatest difficulty, this is not the case when chlorine atoms are present in the α- position, and Freund and Achenbach [4] have found that 1-chloranthraquinone gives a monoxime quite easily, and that 1.5-dichloranthraquinone readily forms both monoximes and dioximes. The monoximes of 1-chloranthraquinone and of 1.5-dichloranthraquinone both exist in two isomeric forms, of which one gives an isoxazole, whereas the other does not, and the dioxime also exists in two forms. The isomerism is

[1] Goldschmidt, B. **16**, 2179. Cf. Schunck and Marchlewski, B. **27**, 2125.
[2] Kurt Meyer, A. **396**, 165.
[3] Kaufler and Suchanek, B. **40**, 518.
[4] B. **43**, 3251.

probably geometrical, although in the case of the oxime of 1-chloranthraquinone positional isomerism is not impossible :

Gives no isoxazole.   Gives isoxazole.
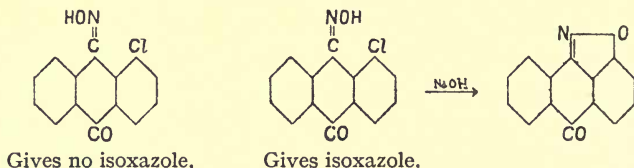
The formation of isoxazoles by one isomer and not by the other is in agreement with Victor Meyer's observation [1] that one of the oximes of *o*-chlorbenzophenone will give an isoxazole whereas the other will not.

Freund and Achenbach have also studied oxime formation with other α- derivatives of anthraquinone. They find that erythrohydroxy anthraquinone will give no oxime, whereas its alkyl and aryl ethers give monoximes with difficulty, and anthrarufin dimethyl ether will give a monoxime. No oxime could be obtained from 1.5-diamino anthraquinone or from 1-chlor-5-amino anthraquinone.

Although the carbonyl oxygen atoms in anthraquinone are not very reactive, they readily enter into the formation of new rings and, as will be seen in the sequel, some of these ring compounds have proved to be very valuable dyestuffs. Staudinger [2] has found that anthraquinone will react with diphenyl ketene, but only with difficulty, and analysis and molecular weight determinations point to the formula :
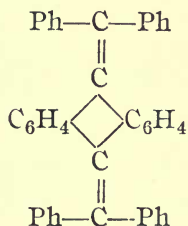
for the product. The substance obtained, however, forms colourless needles which melt at 302-303°, and in view of the lack of colour Staudinger is doubtful of the quinonoid formula.

[1] B. **25**, 1498 ; 3293.   [2] B. **41**, 1362.

Gosch [1] has found that anthraquinone condenses with aldehyde ammonia if heated with it for six hours at 220°. The product melts at 281°, and he ascribes to it the formula :

$$
\begin{array}{c}
\text{H—C—CHO} \\
\parallel \\
\text{C} \\
\text{C}_6\text{H}_4 \diamondsuit \text{C}_6\text{H}_4 \\
\text{C} \\
\parallel \\
\text{H—C—CHO}
\end{array}
$$
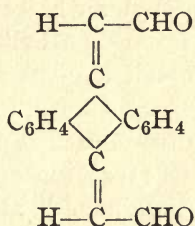
Bayer & Co.[2] state that if anthraquinone is boiled with primary aromatic amines and a condensing agent such as boric acid, products are obtained in which both the carbonyl oxygen atoms have been replaced by ArN: groups. They state that the reaction is facilitated by the presence of reducing agents, such as stannous chloride, but do not describe the resulting compounds in detail. Very similar products seem to be obtained from anthraquinone-β-sulphonic acid,[3] but as these are practically insoluble in dilute caustic soda, it would seem that the sulphonic acid group had also reacted. This is supported by the analytical figures given for the condensation product with *p*-toluidine. These point to the presence of three toluido groups, and are in approximate agreement with the formula $C_{35}H_{33}O_2N_3S$.

· Anthraquinone, when fused with caustic potash, yields benzoic acid,[4] and caustic fusion has been applied in some cases for determining the constitution of anthraquinone derivatives. Owing to the stability of the anthraquinone ring, however, the method is rather tedious to carry out, and in the case of dimethyl anthraquinone Lavaux found it necessary to heat to 260° for three hundred consecutive hours.

HOMOLOGOUS ANTHRAQUINONES

The alkyl anthraquinones are of no great importance, and have not been studied in detail. Most of the *methyl*

[1] Soc. **111**, 610.　　[2] D.R.P. 148,079.　　[3] By. D.R.P. 136,872 ; 147,277.
[4] Graebe and Liebermann, A. **160**, 129.

anthraquinones have been already mentioned in connection with the methyl anthracenes. The most important is β-methyl anthraquinone, and this can be obtained by the oxidation of the β-methyl anthracene obtained from coal tar, or from toluene by the phthalic acid method. When treated with caustic alkali it gives anthraflavone. *β-Ethyl* anthraquinone and *β-propyl* anthraquinone were prepared by Scholl [1] from ethyl benzene, and propyl benzene, but are of no great interest. Of greater interest are the benzanthraquinones (naphthanthraquinones), and these are treated in a separate chapter.

REDUCTION PRODUCTS.—Unlike true quinones, 9.10-anthraquinone and its derivatives are not reduced by sulphurous acid or the sulphites.[2] They are, however, readily reduced by other reducing agents, such as hydriodic acid, stannous chloride or tin and hydrochloric acid, zinc dust and caustic soda or ammonia, sodium hydrosulphite, etc., and a considerable variety of products can be obtained according to the conditions under which the reduction is carried out. In studying the reduction of anthraquinone derivatives it must be borne in mind that the partial reduction of the cyclic carbonyl groups often has a great influence on the stability of groups attached to the nucleus, so that such groups are frequently split off.[3]

Rosentiel [4] seems to have been the first to make use of hydriodic acid and phosphorus, but Liebermann [5] and his students made a much more thorough examination of the reaction. They found that when the reduction is carried out in open vessels the product formed depends on the concentration of the acid, on the temperature used, and on the time of heating, but that as a rule reduction cannot be taken beyond the dihydro-anthracene stage. By working

---

[1] M. **32**, 687.

[2] In the abstracts published by the Chemical Society statements will sometimes be found, *e.g.* Soc. **94** (i), 786, that anthraquinone derivatives are reduced by sodium hydrogen sulphite. Reference to the original or to the Zentralblatt, however, will show that in these cases the abstractor has wrongly translated " hydrosulfit " as " hydrogen sulphite."

[3] For example see pp. 179, 265.

[4] C. r. **79**, 764.

[5] A. **212**, 5.   B. **9**, 1202; **10**, 607; **11**, 1610; etc.

in sealed tubes, however, they were able to obtain more highly hydrogenated substances.[1] By carrying out the reduction with a more dilute acid, less fully reduced products are obtained, and it is possible to isolate the anthraquinol, anthrone and hydroxydihydroanthracene compounds : [2]

| Anthraquinol. | Anthrone. | Hydroxydihydro-anthracene. |
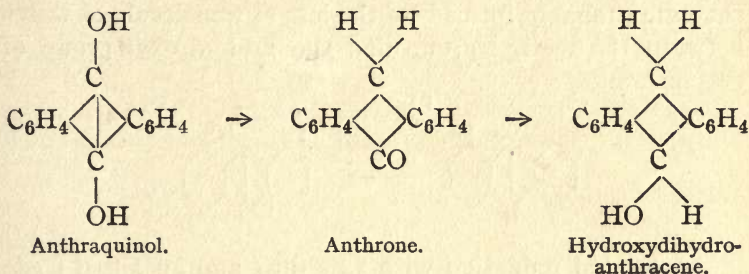
Compounds of this last type are somewhat unstable, and very readily lose a molecule of water.

Liebermann [3] has more recently studied the mechanism of the reduction of anthraquinone compounds with hydriodic acid, and has isolated several addition compounds containing iodine and hydriodic acid.

Much more interesting results have been obtained with other reducing agents. Thus Liebermann,[4] by reducing anthraquinone with tin and hydrochloric acid, obtained anthrone in good yield; and more recently Kurt Meyer [5] has improved the method by using tin and hydrochloric acid in boiling glacial acetic acid. Zinc dust and ammonia or caustic soda has been employed by a very large number of investigators,[6] and if the reaction is carried sufficiently far, almost invariably leads to the anthracene derivative, this being one of the most convenient methods of preparing anthracene derivatives from the corresponding anthraquinone compounds, as there is no danger of the production of more highly hydrogenated derivatives. It is not applicable,

[1] See Chapter III.
[2] Liebermann and Pleus, B. **35**, 2923.
[3] B. **37**, 3341; **38**, 1784.
[4] B. **20**, 1854.
[5] A. **397**, 55.
[6] *E.g.* Elbs, J. pr. [2] **41**, 6, 121; B. **20**, 1365. Lampe, B. **42**, 1414, etc. R. E. Schmidt, B. **37**, 70.

however, to anthraquinone derivatives in which there is a methyl group in the α- position, as Elbs [1] has found that these on alkaline reduction pass into hydrocarbons in which one of the *ms*- carbon atoms seem to be affected. These are monomolecular and form picrates, and Elbs considers that they are probably formed by the loss of a molecule of water between the methyl group and the *ms*-hydroxyl group of the anthranol, *c.g.*
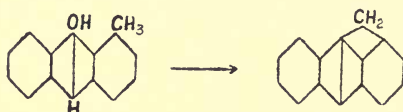
Moderated reduction with zinc dust and an alkali leads first to the anthraquinol,[2] and Perger [3] has found that further reduction leads to the *ms*-hydroxydihydroanthracene, which by loss of water passes into the anthracene. The course of the reduction is, therefore, very similar to that pursued in the case of hydriodic acid.

Schulze [4] has repeated Perger's work, and finds that in addition to hydroxydihydroanthracene, anthrapinacone is also formed :
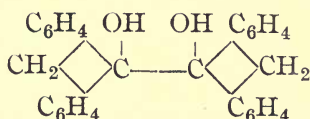
which by loss of water passes into dianthryl :
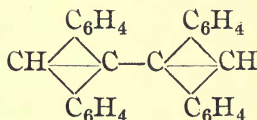
This Liebermann and Gimbel [5] managed to obtain direct from anthraquinone by reduction with tin and hydrochloric acid ; and more recently Eckert and Hofmann [6] have repeated Liebermann's work and find that much better yields are

[1] J. pr. [2] **41**, 6, 121 ; B. **20**, 1365.
[2] Graebe and Liebermann, A. **160**, 126.   Liebermann, A. **212**, 65. Römer and Schwazer, B. **15**, 1040.
[3] J. pr. [2] **23**, 127.   [4] B. **18**, 3034.   [5] B. **20**, 1854.   [6] M. **36**, 497.

obtained if the reduction is carried out in the presence of a trace of a platinum salt.

Hans Meyer,[1] by reducing anthraquinone with zinc and caustic soda under pressure at a high temperature, has obtained dianthrol, which by prolonged heating with hydrochloric acid passes into the ketonic isomer, dianthrone. caustic alkali causing the reverse change :

Dianthrol.   Dianthrone.
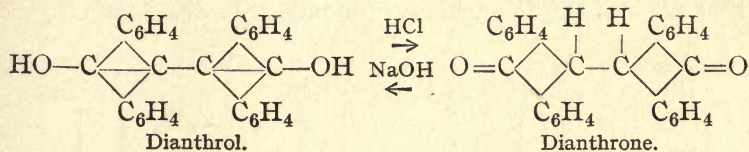
This latter on reduction in glacial acetic acid with tin and hydrochloric acid gives tetrahydrodianthrol, which passes into dianthryl very readily by loss of water : [2]
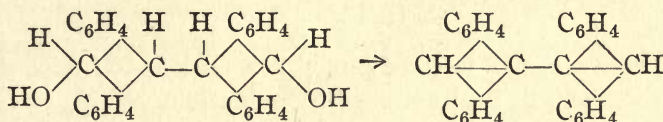
From a commercial point of view alkaline sodium hydrosulphite ($Na_2S_2O_4$) is the most important reducing agent for anthraquinone derivatives, as it readily converts them into the soluble vats, these being readily oxidised to the original substance on exposure to the air. The reaction has been examined by Grandmougin,[3] who has found that the reduction product is the anthraquinol :
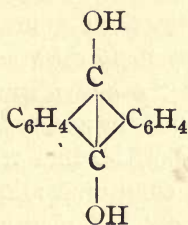
As will be seen later, the anthraquinone vat dyes often

[1] B. **42**, 143. M. **30**, 165.
[2] M. **36**, 497.
[3] J. pr. [2] **76**, 138; R.G.M.C. **12**, 44.

contain two or more anthraquinone groups, either or both of which may become reduced in the vat.

The alkaline reduction of anthraquinone derivatives is sometimes hindered by the presence of substituents in the α-position. The abnormal behaviour of anthraquinone derivatives in which there is a methyl group in the α-position has already been mentioned, and Seer[1] has shown that none of the following compounds will give " vats " :
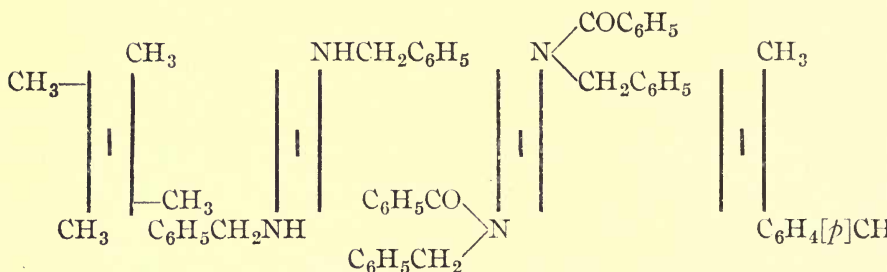
In the case of this last compound it is curious to notice that the dicarboxylic acid obtained by oxidation :
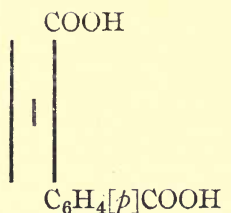
can be reduced in alkaline solution.

The use of amalgamated zinc and hydrochloric acid has been advocated by Clemmensen,[2] who claims that by this means both anthraquinone and alizarin can be reduced to dihydro- and hexahydro-anthracene.

The results obtained with other reducing agents will be found discussed in the chapter dealing with the anthrones and dianthryl derivatives ; but mention may be made here of the fact that all hydroxyanthraquinones when distilled with zinc dust yield anthracene, a reaction which has

[1] M. **31**, 379; **33**, 33, 546; **34**, 579.
[2] B. **47**, 684. *Cf.* By., D.R.P. 296,091 ; 301,452 ; 305,886.

proved of the utmost value in the study of naturally occurring anthraquinone compounds.

ACTION OF GRIGNARD'S SOLUTION.—Anthraquinone reacts with either one or two molecules of magnesium alkyl halides, the products being alkyl hydroxy anthrone and dialkyl-dihydroxydihydroanthracene :

$$
\begin{array}{cc}
R \quad OH & R \quad OH \\
\diagdown\diagup & \diagdown\diagup \\
C & C \\
C_6H_4 \diamond C_6H_4 & C_6H_4 \diamond C_6H_4 \\
CO & C \\
& \diagup\diagdown \\
& R \quad OH
\end{array}
$$
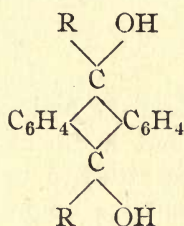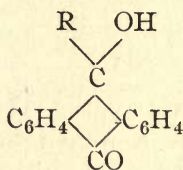
With magnesium aryl halides the reaction is similar, anthraquinone, for example, reacting with two molecules of phenyl magnesium bromide to form : [1]

$$
\begin{array}{c}
HO \quad Ph \\
\diagdown\diagup \\
C \\
C_6H_4 \diamond C_6H_4 \\
C \\
\diagup\diagdown \\
HO \quad Ph
\end{array}
$$
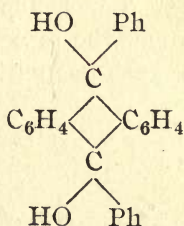
In these compounds in which an aryl and a hydroxyl group are attached to each *ms*-carbon atom, the hydroxyl groups are very reactive and are readily replaced by chlorine by treatment with alcoholic hydrochloric acid,[2] and can be methylated by methyl alcohol and hydrochloric acid. The dichloro compounds thus formed are not very stable, and on treatment with potassium iodide readily split off their chlorine and pass into *sym*-diaryl anthracenes. By starting with a diaryl anthrone and treating this with an aryl magnesium bromide, a compound containing three aryl groups

[1] C. r. **138**, 327, 1251 ; **139**, 9; **150**, 1290; Bl. [3] **33**, 1104. Clarke, B **41**, 935. Am. Soc. **33**, 1966.
[2] *Loc. cit.*

and a hydroxyl group attached to the two *ms*-carbons is obtained,[1] *e.g.*

$$
\begin{array}{c}
\text{Ph} \quad \text{Ph} \\
\diagdown\diagup \\
\text{C} \\
\text{C}_6\text{H}_4\diagdown\,\,\diagup\text{C}_6\text{H}_4 \\
\text{C} \\
\diagup\diagdown \\
\text{Ph} \quad \text{OH}
\end{array}
$$
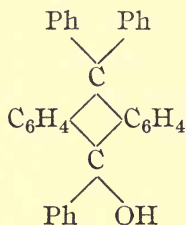
In these the hydroxyl group is very easily etherified by alcohol and hydrochloric acid, but a fourth aryl group cannot be attached to the *ms*-carbon atom unless this aryl group contains an amino group or a phenolic hydroxyl group [2] (see p. 89).

By treating anthraquinone with a molecule of magnesium benzyl chloride, Haller and Padova [3] obtained benzyl hydroxy anthrone, which under the influence of hydrochloric acid readily lost a molecule of water and passed into benzylidene anthrone, the same compound being also obtained by condensing anthrone with benzaldehyde :

$$
\begin{array}{ccccc}
\text{HO} \quad \text{CH}_2\text{C}_6\text{H}_5 & & \text{CHC}_6\text{H}_5 & & \text{CH}_2 \\
\diagdown\diagup & & \text{C} & & \text{C} \\
\text{C} & & & & \\
\text{C}_6\text{H}_4\diagdown\diagup\text{C}_6\text{H}_4 & \xrightarrow{-\text{H}_2\text{O}} & \text{C}_6\text{H}_4\diagdown\diagup\text{C}_6\text{H}_4 & \xleftarrow{\text{C}_6\text{H}_5\text{CHO}} & \text{C}_6\text{H}_4\diagdown\diagup\text{C}_6\text{H}_4 \\
\text{CO} & & \text{C} & & \text{CO} \\
& & \text{O} & &
\end{array}
$$
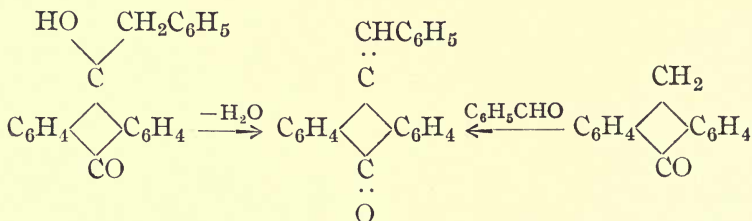
Benzylidene anthrone was also obtained by Levi [4] and by Bach [5] by benzylating alkaline solutions of anthraquinol with benzyl bromide and subsequently treating the benzyl hydroxy anthrone with concentrated sulphuric acid, and their description of the substance is in close agreement with that given by Haller and Padova. Tschilikin,[6] however, has recently prepared the substance by treating anthraquinol with dimethylphenylbenzyl ammonium chloride (leuco-

[1] C. r. **139**, 9. [2] C. r. **140**, 283, 343. [3] C. r. **141**, 857.
[4] B. **18**, 2152. [5] B. **23**, 1567. [6] B. **47**, 1055.

trope D) and gives the melting point as 117° in place of the 126–127° found by Levi, Bach and Haller, and Padova. Tschilikin obtained benzylhydroxy anthrone simultaneously.

By treating anthraquinone with two molecules of magnesium methyl iodide, Guyot and Stähling [1] obtained a dimethyl dihydroxy derivative which, like its phenyl analogue, is very readily methylated by alcohol and hydrochloric acid. Both the hydroxy compound and its methyl ether are decomposed by heat :

$$
\begin{array}{ccc}
CH_3 \quad OH & & CH_3 \quad OCH_3 \\
\diagdown \diagup & & \diagdown \diagup \\
C & & C \\
C_6H_4 \diamond C_6H_4 & \rightarrow & C_6H_4 \diamond C_6H_4 \\
C & & C \\
\diagup \diagdown & & \diagup \diagdown \\
CH_3 \quad OH & & CH_3 \quad OCH_3 \\
\downarrow & & \downarrow
\end{array}
$$

$$
\begin{array}{ccc}
CH_2 & & CH_2 \\
\ddot{C} & & \ddot{C} \\
C_6H_4 \diamond C_6H_4 & & C_6H_4 \diamond C_6H_4 \\
C & & C \\
\diagup \diagdown & & \diagup \diagdown \\
CH_3 \quad OH & & CH_3 \quad OCH_3
\end{array}
$$
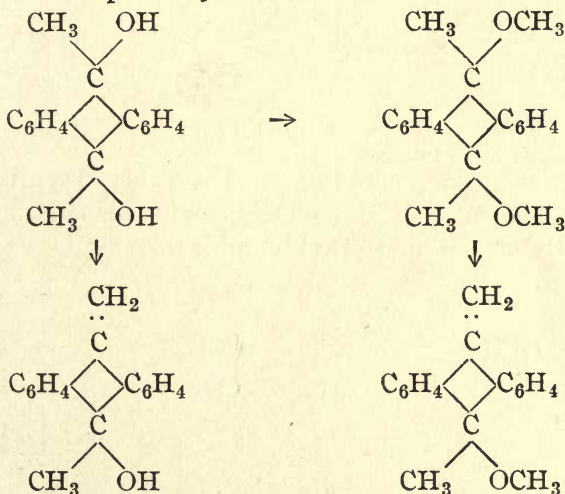
the reaction being exactly similar to that undergone by the benzyl derivative described on the previous page.

Similar compounds were obtained by treating phenyl methoxy anthrone with an alkyl magnesium iodide and then boiling the resulting substance with glacial acetic acid :

$$
\begin{array}{ccc}
C_6H_5 \quad OCH_3 & & C_6H_5 \quad OCH_3 \\
\diagdown \diagup & & \diagdown \diagup \\
C & & C \\
C_6H_4 \diamond C_6H_4 & \rightarrow & C_6H_4 \diamond C_6H_4 \\
C & & C \\
\diagup \diagdown & & \\
CH_3 \quad OH & & \ddot{C}H_2
\end{array}
$$
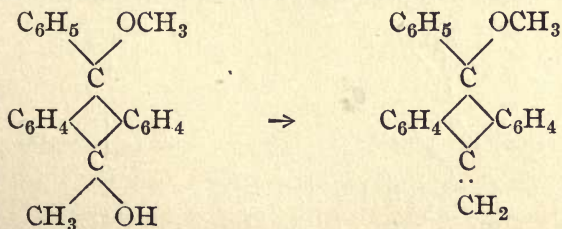
[1] Bl. [3] **33**, 1144. Cf. Clarke, B. **41**, 935; Am. Soc. **33**, 1966 (corresponding ethyl compounds).

Haller and Guyot [1] have studied the action of Grignard's solutions on other anthrones. Starting with diphenylanthrone they treated this with magnesium phenyl bromide, and obtained a triphenyl hydroxy dihydroanthracene, which on reduction with zinc and acetic acid gave triphenyl dihydroanthracene :

$$
\begin{array}{ccc}
\underset{\displaystyle C_6H_4\!\!\diagdown\underset{CO}{\diagup}\!\!C_6H_4}{\overset{\overset{\displaystyle Ph\quad Ph}{\diagdown\diagup}}{\overset{\displaystyle C}{|}}}
&\rightarrow&
\underset{\displaystyle C_6H_4\!\!\diagdown\!\!C_6H_4}{\overset{\displaystyle C}{\underset{\overset{\displaystyle C}{\diagdown}}{}}}
\end{array}
$$
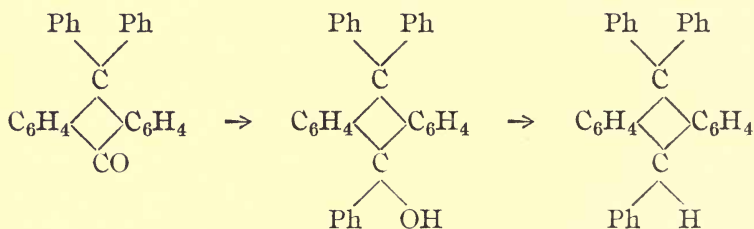
This latter compound they were also able to synthesise by treating the methyl ester of triphenylmethane-*o*-carboxylic acid with magnesium phenyl bromide :
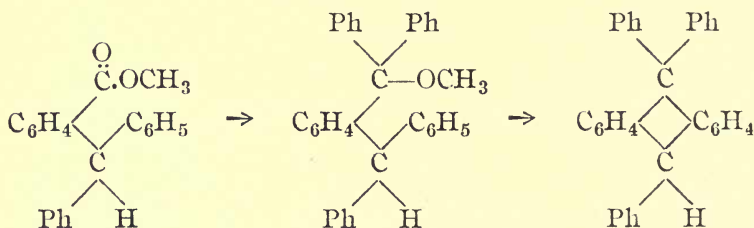
This latter synthesis closely resembles the synthesis of *ms*-diphenylanthracene by Simonis and Remmert.[2] These investigators found that *o*-brombenzyl triphenyl carbinol loses hydrobromic acid very readily when treated with sulphuric acid and passes into *ms*-diphenylanthracene :
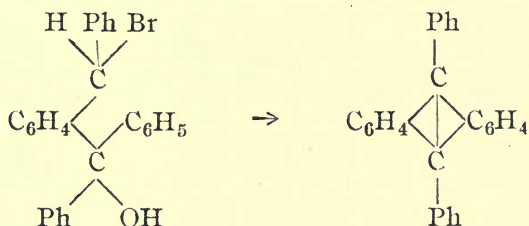
[1] C. r. **139**, 9.   [2] B. **48**, 208.   *Cf.* C. r. **138**, 1252 ; **140**, 1461.

and 1.2-dimethoxy-*ms*-diphenylanthracene can be obtained in a very similar manner :

$$\underset{\underset{\text{Ph}}{\overset{\text{HO Ph H}}{\underset{|}{\overset{\backslash|/}{\text{C}}}}}{(CH_3O)_2C_6H_2} \diagdown \overset{C_6H_5}{\underset{\overset{|}{\text{C}}}{}} \quad \to \quad (CH_3O)_2C_6H_2 \diagdown \overset{\overset{\text{Ph}}{\underset{|}{\text{C}}}}{\underset{\underset{\text{Ph}}{\overset{|}{\text{C}}}}{}} \diagdown C_6H_4$$
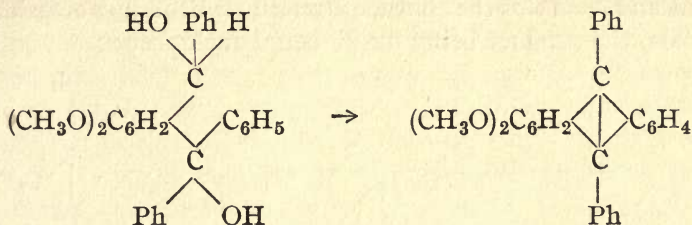
As stated on p. 86, the hydroxyl group in triphenyl hydroxy dihydroanthracene cannot be replaced by an aryl group, but these compounds react readily with compounds of the type ArX when Ar is an aryl group and X an hydroxyl or primary, secondary or tertiary amino- group. The condensation is brought about by boiling in glacial acetic acid solution,[1] and leads to compounds of the type :

$$\underset{\underset{\text{Ph} \quad ArN(CH_3)_2}{\overset{|}{\text{C}}}}{\overset{\overset{\text{Ph} \quad Ph}{\backslash/}}{\underset{\overset{|}{\text{C}}}{C_6H_4 \diagdown \diagup C_6H_4}}}$$
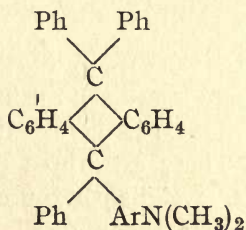
· The diphenyl dihydroxy dihydroanthracene which is obtained by the action of magnesium phenyl bromide on anthraquinone will also condense with tertiary amines. The products are compounds of the type :

$$\underset{\underset{\text{Ph} \quad C_6H_4NMe_2}{\overset{|}{\text{C}}}}{\overset{\overset{\text{Ph} \quad C_6H_1NMe_2}{\backslash/}}{\underset{\overset{|}{\text{C}}}{C_6H_4 \diagdown \diagup C_6H_4}}}$$
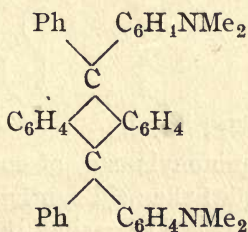
and exhibit geometrical isomerism.[2]

---

[1] Haller and Guyot, C. r. **140**, 283. [2] C. r. **140**, 283, 343.

The dihydroxy compound can also be converted into the dichlor- compound by means of alcoholic hydrochloric acid, and from this the chlorine is readily split off by potassium iodide, the product being *ms*-diphenyl anthracene :
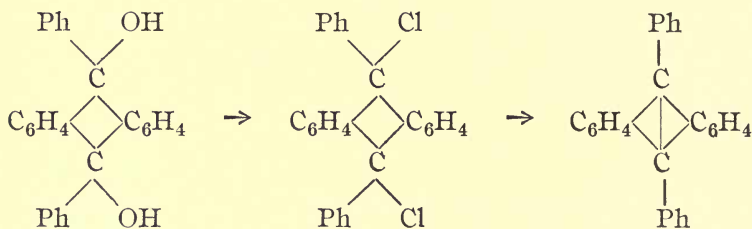
From this it will be seen that the use of Grignard's solution forms a convenient means of synthesising both complex and simple derivatives of anthracene in which the *meso*-carbon atoms are involved. A considerable number of such compounds have been prepared by Haller and his co-workers, for details of which reference must be made to the literature.[1]

THE DIANTHRAQUINONYLS

The dianthraquinonyls are the anthraquinone analogues of diphenyl and are not to be confused with the dianthraquinones (p. 116). There are three possible isomeric dianthraquinonyls, viz. 1.1'-dianthraquinonyl, 2.2'-dianthraquinonyl, and 1.2'-dianthraquinonyl, but neither this last-named substance nor any of its derivatives have been described :
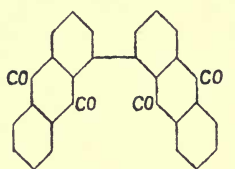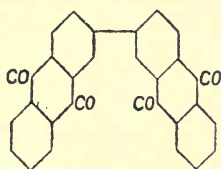
1.1'-Dianthraquinonyl.   2.2'-Dianthraquinonyl.

The dianthraquinonyls can, of course, be built up from diphenyl by the phthalic acid synthesis, and this method is discussed on p. 135. The results, however, are not satisfactory, and the dianthraquinonyls are much more readily

[1] Bl. [3] **25**, 315; Bull. Soc. ind. Mulhaus, **72**, 268.

obtained by reactions which lead to the union of two anthraquinone residues. In some cases the union of two anthraquinone molecules can be effected by oxidation, and this is particularly the case when hydroxyl groups are present in the molecule. Thus erythrohydroxy anthraquinone on fusion with caustic potash gives 1.1'-dihydroxy-2.2'-dianthraquinonyl,[1] the structure being proved by its giving a furfurane derivative by loss of water, and by its giving 2.2'-dianthryl on distillation with zinc dust.[2] In the case of quinizarin, dianthraquinonyl formation takes place more readily, heating with aqueous sodium carbonate at 120°, sufficing to produce a tetrahydroxy dianthraquinonyl.[3] This also gives 2.2'-dianthryl on distillation with zinc dust, and as it passes into a furfurane derivative by loss of water it must be 1.4.1'.4'-tetrahydroxy-2.2'-dianthraquinonyl.[4] The oxidation of hydroxyanthraquinones by hypochlorites usually leads either to halogenation or to complete rupture of the ring system, but Scholl [5] has found that alizarin can be oxidised to 1.2.1'.2'-tetrahydroxy-3.3'-dianthraquinonyl by treatment under suitable conditions with potassium hypochlorite and caustic potash. The proof of the structure of the product rests on its conversion into a furfurane derivative by loss of water, and into 2.2'-dianthryl by distillation with zinc dust.

Dianthraquinonyls can be obtained from the anthraquinone diazonium salts by treatment with copper powder or with cuprous salts. Thus diazonium sulphates when warmed with cuprous chloride or bromide in aqueous solution or suspension pass very readily into the dianthraquinonyl, provided that no very considerable quantity of halogen acid is present,[6] and diazonium sulphates can also be converted into the dianthraquinonyl by treating them with copper in the presence of acetic anhydride.[7]

[1] By., D.R.P. 167,461.
[2] Scholl, B. **52**, 2254.
[3] By., D.R.P. 146,223.
[4] Scholl, B. **52**, 2254.
[5] B. **52**, 1829; D.R.P. 274,784.   [6] B.A.S.F., D.R.P. 215,006.
[7] Scholl, B. **40**, 1696.   B.A.S.F., D.R.P. 184,495.   Cf. Knœvenagel, B. **28**, 2049

Although all the above methods of preparing dianthra-quinonyls have proved useful, the most general method consists in heating a halogen anthraquinone with copper powder, either alone or in the presence of some indifferent solvent such as nitrobenzene or naphthalene.[1] Both α- and β- halogen compounds can be used, and although, as would be expected, the reaction takes place most rapidly in the case of the iodo- compounds, both chlor and brom compounds can be used, and in many cases give yields amounting to 70-80 per cent. of the theoretical. If the halogen atom is in the α- position and there is also an amino group in the *ortho*- position to it, dianthraquinonyl formation is accompanied by the production of a flavanthrone, and in order to avoid this the amino group must be protected by the use of the benzylidene derivative.[2]

The dianthraquinonyls themselves are of no great importance, their chief interest lying in their relation to the helianthrones (p. 333) and flavanthrones (p. 301). They are readily nitrated, but the nitration products have not been studied in detail.[3] Methyl groups when present can be oxidised to carboxyl groups.[4]

The Anthradiquinones

Polyhydroxy anthraquinones in which two hydroxyl groups are in the *para*- positions to one another, *e.g.* quinizarin, readily yield anthradiquinones when oxidised. The oxidation can be brought about in concentrated sulphuric acid solution by means of various oxidising agents such as manganese dioxide, arsenic acid, lead dioxide, etc., but under these conditions simultaneous hydroxylation by oxidation is very apt to occur.[5] Lesser,[6] and Dimroth and

[1] Scholl, B. **40**, 1696; **43**, 355, 1738; **44**, 1086; **51**, 452; M. **32**, 687. Seer, M. **34**, 631. Benesh, M. **32**, 447. Eckert and Tomaschek, M. **39**, 843. Ullmann, B. **45**, 689; **49**, 740, 2161; A. **399**, 332; D.R.P. 248,999. B.A.S.F., D.R.P. 180,157; 241,472.
[2] Scholl, B. **51**, 452. Ullmann, A. **399**, 332. D.R.P. 248,999.
[3] Scholl, B. **43**, 355, 1738.
[4] Scholl, B. **40**, 1696.
[5] By., D.R.P. 66,153; 68,113; 68,114; 68,123; 69,842
[6] B. **47**, 2526.

Schultze[1] obtained 1.4.9.10-anthradiquinone by oxidising quinizarin with lead dioxide, the former investigator using benzene as a solvent, whereas the latter worked with glacial acetic acid solutions. It is a not very stable substance which melts at 211–213° when rapidly heated, the bath being preheated to 205°. When its aqueous suspensions are heated it undergoes decomposition with simultaneous oxidation and reduction, part being reduced to quinizarin at the expense of another part, which becomes oxidised to phthalic acid.

All the anthradiquinones are true quinones and, like 1.4-anthraquinone, show the usual quinone reactions. Thus, 1.4.9.10-anthradiquinone is rapidly reduced to quinizarin by sulphurous acid, it adds on a molecule of hydrochloric acid to form 3-chlorquinizarin, and when warmed with concentrated sulphuric acid takes up a molecule of water and passes into purpurin. This last reaction is a somewhat important one, for, as will be seen later, the formation of many polyhydroxyanthraquinones is probably due to the addition of the elements of water to a diquinone.

When *p*-diaminoanthraquinone or *p*-hydroxyamino-anthraquinone is treated with sodium chlorate and hydrochloric acid 2.3-dichlor-1.4.9.10-anthradiquinone is obtained, simultaneous chlorination and oxidation taking place, and diaminoanthrarufin under similar treatment yields tetra-chlor-1.4.5.8.9.10-anthratriquinone.[2]

The anthradiquinones when treated with phenols yield violet or blue mordant dyes, which are probably similar in nature to phenoquinone. Up to the present 1.2.9.10-anthradiquinone has not been isolated, but Dimroth and Schultze have obtained a straw-yellow solution by oxidising alizarin suspended in a mixture of equal volumes of glacial acetic acid and ether with lead dioxide. This solution exhibits all the properties of a true quinone, viz. it liberates iodine from potassium iodide, is at once reduced to alizarin by sulphurous acid, and gives chloralizarin when treated with hydrochloric acid. It undoubtedly consists of a solution

of 1.2.9.10-anthradiquinone, but the quinone is so unstable that it was found impossible to isolate it.

ANTHRAFLAVONES

If β-methyl anthraquinone is fused with caustic potash, or better if it is heated with alcoholic caustic potash, a yellow vat dye is obtained.[1]   This has come into fairly general use under the name Anthraflavone G, and was originally believed to have the structure :
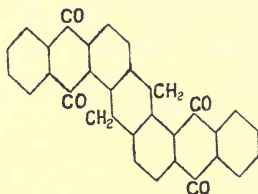
although Scholl [2] showed that neither β-ethylanthraquinone nor β-propylanthraquinone gave any trace of an anthra-flavone compound when treated with caustic potash.   A compound of the structure shown above would pass on oxidation into a new complex containing a third quinonoid group, whereas Ullmann and Klingenberg [3] found that the oxidation product consisted only of anthraquinone-β-car-boxylic acid.   Further, they pointed out that anthraflavone adds on a molecule of bromine without any evolution of hydrobromic acid, and that the dibromo- product thus obtained is quantitatively changed back to anthraflavone by treatment with diethylaniline.   These facts all point to anthraflavone being really dianthraquinonyl ethylene, and this is in agreement with the observation of Ullmann and Klingenberg,[4] that anthraflavone is obtained when ω-dibrom-β-methyl anthraquinone is heated with dimethyl-aniline, or better with diethylaniline.

The stilbene structure has been fully confirmed by the work of other investigators.   Thus, Hepp, Uhlenhuth and

---

[1] B.A.S.F., D.R.P. 179,893 ; 199,756.   Bohn, B. **43**, 1001.
[2] M. **32**, 690.   [3] B. **46**, 712.   [4] *Loc. cit.*

Römer [1] obtained anthraflavone by heating ω-dibrommethyl anthraquinone with sodium iodide in acetone solution, or by treating it with copper powder; [2] and Ullmann [3] has employed this method for preparing dichloranthraflavone from 2-chlor-3-dibrommethyl anthraquinone.

Scholl [4] condensed phthalic acid with β-methyl naphthalene, and from the 3-methyl-1.2-benzanthraquinone thus obtained he got an anthraflavone which no doubt had the structure
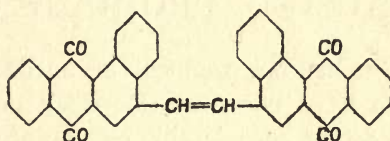
although Scholl gave it cyclic formula in conformity with the then belief that anthraflavone contained a seventh ring. Scholl's product was a vat dye, and gave reddish shades of yellow. A vat dye which gives orange shades is said to be obtained by adding bromine to a boiling solution of 1-chlor-4-methyl anthraquinone in nitrobenzene. [5] The constitution of the dye is unknown, but it may be a stilbene derivative.

[1] B. **46**, 709.   M.L.B., D.R.P. 260,662 ; 267,546.
[2] *Cf.* Eckert, M. **35**, 300.   [3] B. **47**, 560.
[4] M. **32**, 997.   [4] M.L.B., D.R.P. 259,881.

ANTHRONE, ANTHRANOL, AND ALLIED PRODUCTS

THESE are all reduction products of anthraquinone and several of them have been mentioned already. Many of them, however, are of considerable importance, and as they exhibit extremely interesting dynamic isomerism they will be discussed in some detail.

ANTHRONE AND ANTHRANOL

Anthrone itself was first obtained by Liebermann [1] by the moderated reduction of anthraquinone with hydriodic acid or with tin and hydrochloric acid in glacial acetic acid solution. More recently the experimental details of this latter method have been improved by Kurt Meyer,[2] but as a rule the reduction is best carried out by means of copper or aluminium bronze [3] and concentrated sulphuric acid at 30–40°. This last process has been investigated by Eckert and Pollak,[4] who find that the first product formed is the anthraquinol (hydroxyanthrone ?), the anthrone then being formed by further reduction.

Baeyer [5] obtained *ms*-phenyl anthrone by heating triphenylmethane-*o*-carboxylic acid with dehydrating agents :

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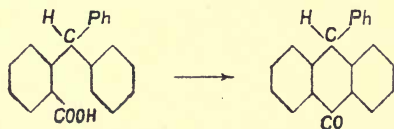
[1] A. **212**, 5 ; B. **20**, 1854.   [2] A. **397**, 55.
[3] B.A.S.F., D.R.P. 190,656 ; By., D.R.P. 201,542.
[4] M. **38**, 11 ; **39**, 839.   [5] A. **202**, 54.

and Bistrzycki and Ulffers [1] have prepared hydroxy-anthrone and one or two other anthrone derivatives by this method, although the reaction is often complicated by phthalide formation.

A somewhat similar synthesis of more complex anthrone derivatives has been worked out by Haller and Guyot.[2] They condensed 4′-dimethylaminobenzophenone-1-carboxylic acid with dimethylaniline by boiling in acetic anhydride :
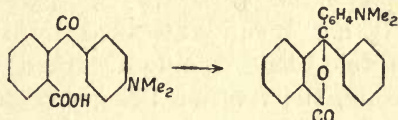
The phthalide thus formed they reduced to the corresponding triphenylmethane carboxylic acid, which, on boiling with phosphorus oxychloride in dimethylaniline solution, lost a molecule of water and passed into an anthrone derivative :
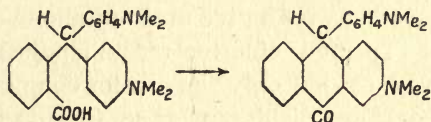
The same investigators [3] obtained *ms*-diphenylanthrone by condensing phthalyl tetrachloride with benzene in the presence of aluminium chloride :
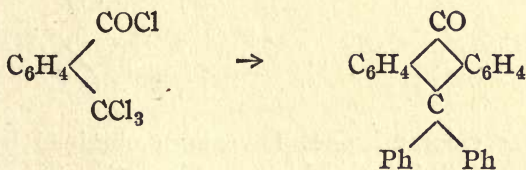
and also by condensing dichloranthrone or phenylchlor-anthrone with benzene
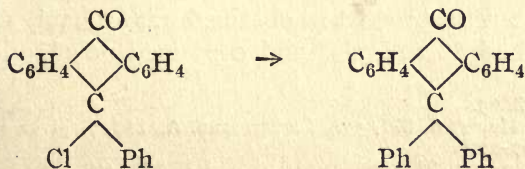
[1] B. **31**, 2799.   [2] Bl. [3] **25**, 315.   [3] C. r. **121**, 102.

Baeyer [1] had previously obtained the same compound by heating phenyl hydroxyanthrone with benzene and sulphuric acid although he did not describe it in detail.

Anthrone itself is a colourless crystalline compound which does not exhibit fluorescence, and which melts at 154°.[2] It is insoluble in cold alkali, but dissolves on heating owing to its conversion into the enolic form (anthranol), and when boiled with acetic anhydride it forms the acetyl derivative of this latter compound.

Anthrone is not readily attacked by mild oxidising agents in the cold, and is only attacked comparatively slowly on heating, the reaction being most rapid in those solvents which favour enolisation. Goldmann [3] has studied the action of chlorine and bromine on anthrone. He finds that bromine gives first a monobrom compound (m.p. 148–151° decomp.), and then a dibrom compound (m.p. 157°). In both of these the halogen atoms must be united to a *meso*-carbon atom, as both give anthraquinone on oxidation. As was to be expected, chlorine reacts similarly, but much more vigorously, so that only the dichlor compound could be isolated. The same dichloranthrone (m.p. 132–134)° had previously been obtained by Thörner and Zincke [4] by treating *o*-methylbenzophenone with chlorine :

$$C_6H_4\diagup{\overset{\displaystyle CO}{\underset{\displaystyle CH_3}{}}}\diagdown C_6H_5 \quad \rightarrow \quad C_6H_4\diagup{\overset{\displaystyle CO}{\underset{\displaystyle CCl_2}{}}}\diagdown C_6H_4$$

Nuclear chloranthrones have been obtained by Eckert and Tomaschek [5] by reducing chloranthraquinones with copper powder and concentrated sulphuric acid. Padova [6] has found that anthrone reacts with phosphorus pentachloride, but the product he obtained was probably dianthryl, as it melted at 298–300° and contained no chlorine. The

[1] A. **202**, 65.
[2] Kurt Meyer, A. **397**, 55. Liebermann, A. **212**, 7, gives the melting point as 167–170°.
[3] B. **20**, 2436; **21**, 1176.   [4] B. **10**, 1478.
[5] M. **39**, 839.   [6] C. r. **149**, 217.

alkyl chloranthrones are obtained by the action of phosphorus pentachloride on the products obtained by alkylating hydroxyanthranol (anthraquinol),[1] and Liebermann and his students [2] have more recently found that the use of phosphorus pentachloride is superfluous, as the reaction is easily brought about by cold hydrochloric or hydrobromic acid. The halogen atoms in the halogen anthrones are extremely reactive, so that monobromanthrone is converted into hydroxyanthrone by aqueous solvents,[3] and into methoxyanthrone by methyl alcohol.[4] Ammonia does not convert it into an amino compound, but into bromdianthrone, but arylamino anthrones are obtained by treatment with primary aromatic amines.[5] Copper powder converts it into dianthrone.[6]

Anthrone reacts normally with nitroso dimethyl aniline,[7] and Padova [8] has found that with benzaldehyde it gives phenylmethylene anthrone, and with benzophenone chloride [9] it yields diphenylmethylene anthrone :
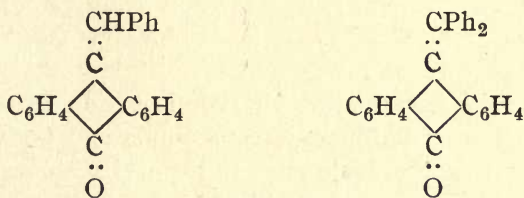
It does not, however, react with aniline, dimethylaniline or with benzophenone itself. With benzo-trichloride, however, it gives phenyldichlormethyl anthrone,[9] which when heated with pyridine splits off a molecule of hydrochloric acid and passes into phenylchlormethylene anthrone :

---

[1] A. **212**, 67.   B. **13**, 1596 ; **15**, 452, 455, 462.   C. r. **121**, 102.
[2] B. **37**, 3337.
[3] A. **379**, 45.
[4] A. **323**, 236 ; **379**, 45.   *Cf.* also B. **38**, 2868.
[5] A. **396**, 133, 145.
[6] A. **396**, 143.
[7] B. **40**, 525.   *Cf.* B. **32**, 2341 ; **33**, 959 ; **34**, 118, 3047.
[8] C. r. **141**, 857.   *Cf.* Weitz, A. **418**, 29.
[9] C. r. **143**, 121.   In the abstract of this paper published by the Chemical Society (Soc. **90**, (i) 741), " chlorure de benzophénone " is mistranslated as " chlorobenzophenone."

$$
\underset{\text{O}}{\overset{\overset{\displaystyle\text{H}\quad\text{CCl}_2\text{Ph}}{\diagdown\diagup}}{\underset{\displaystyle\text{C}}{\text{C}_6\text{H}_4\diamondsuit\text{C}_6\text{H}_4}}}
\quad\rightarrow\quad
\underset{\text{O}}{\overset{\overset{\displaystyle\text{ClCPh}}{\text{C}}}{\underset{\displaystyle\text{C}}{\text{C}_6\text{H}_4\diamondsuit\text{C}_6\text{H}_4}}}
$$
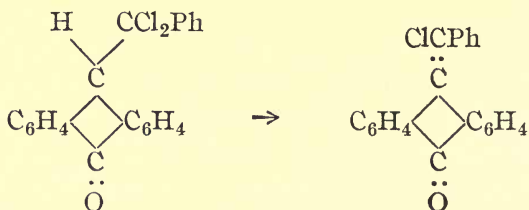
Padova [1] also found that anthrone reacts with chloroform in alcoholic solutions of caustic potash to form a compound :

$$
\text{O}=\text{C}\underset{\text{C}_6\text{H}_4}{\overset{\text{C}_6\text{H}_4}{\diamondsuit}}\text{C}=\text{CH}-\text{C}\underset{\text{C}_6\text{H}_4}{\overset{\text{C}_6\text{H}_4}{\diamondsuit}}\text{C}-\text{OH}
$$
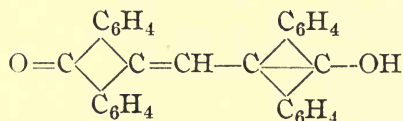
and Friedländer [2] and Kalle & Co.[3] have obtained vat dyes by condensing it with isatine dichloride and dibromoxythionaphthene :

$$
\text{CO}\underset{\text{C}_6\text{H}_4}{\overset{\text{C}_6\text{H}_4}{\diamondsuit}}\text{C}=\text{C}\underset{\text{CO}}{\overset{\text{NH}}{\diamondsuit}}\text{C}_6\text{H}_4
\qquad
\text{CO}\underset{\text{C}_6\text{H}_4}{\overset{\text{C}_6\text{H}_4}{\diamondsuit}}\text{C}=\text{C}\underset{\text{CO}}{\overset{\text{S}}{\diamondsuit}}\text{C}_6\text{H}_4
$$
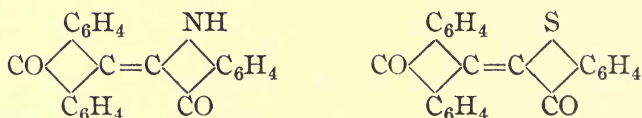
Meerwein [4] has studied the condensation of anthrone with unsaturated β-diketonic compounds and finds that in the case of benzal malonic ester and benzal aceto acetic ester addition takes place very readily :

$$
\underset{\underset{\text{CO}}{\displaystyle\text{C}_6\text{H}_4\diamondsuit\text{C}_6\text{H}_4}}{\overset{\displaystyle\text{C}_6\text{H}_5\text{CHCH(COOEt)}_2}{\underset{|}{\text{CH}}}}
\qquad
\underset{\underset{\text{CO}}{\displaystyle\text{C}_6\text{H}_4\diamondsuit\text{C}_6\text{H}_4}}{\overset{\displaystyle\text{C}_6\text{H}_5\text{CHCH}\diagup\overset{\text{COCH}_3}{\diagdown\text{COOEt}}}{\underset{|}{\text{CH}}}}
$$
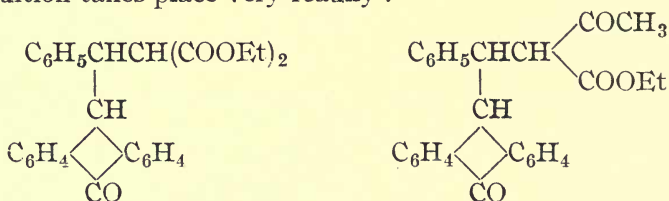
Attempts to hydrolyse such compounds usually lead to the formation of anthrone, but in the case of the addition compound with benzalmalonic ester the hydrolysis could be effected by means of sulphuric acid in glacial acetic acid solution and lead to :

[1] C. r. **140**, 290.   [2] B. **42**, 1060.
[3] D.R.P. **193,272**.   [4] J. pr. [2] **97**, 284.

$$C_6H_5CHCH_2COOH$$
$$|$$
$$CH$$

$$C_6H_4 \diamondsuit C_6H_4$$

$$CO$$
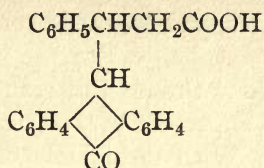
Meerwein also found that anthrone forms an addition compound with benzalacetophenone.

The formation of benzanthrones from anthrones is an extremely important reaction, and is treated in detail in Chapter XVI.

Kurt Meyer [1] has found that dibromanthrone reacts easily with hydroxylamine and yields anthraquinone monoxime; and Haller and Guyot [2] have shown that dichloranthrone condenses with dimethylaniline in the presence of anhydrous aluminium chloride to form a compound

$$Me_2NC_6H_4 \qquad C_6H_4NMe_2$$

$$C$$

$$C_6H_4 \diamondsuit C_6H_4$$

$$CO$$
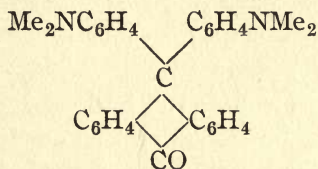
Liebermann and Mamlock [3] found that bromanthrone reacts very readily with resorcinol by simply boiling in benzene solution, no condensing agent being required. Under these conditions one would rather expect the hydroxyl groups of the resorcinol to react with the production of a phenolic ether; but as the product gives a triacetyl compound it must be regarded as a triphenyl methane derivative :

$$H \qquad C_6H_3(OH)_2 \qquad\qquad C_6H_3(OH)_2$$

$$C \qquad\qquad\qquad C$$

$$C_6H_4 \diamondsuit C_6H_4 \quad . \text{ or } \quad C_6H_4 \diamondsuit C_6H_4$$

$$C \qquad\qquad\qquad C$$

$$\| \qquad\qquad\qquad |$$

$$O \qquad\qquad\qquad OH$$
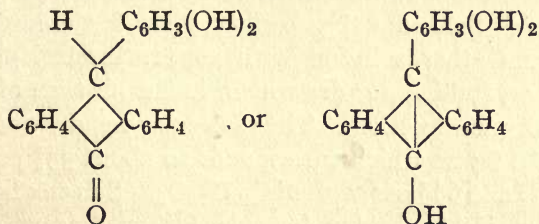
As the compound apparently is not fluorescent the first formula is the more probable. The triacetyl derivative,

[1] A. **396**, 152.   [2] C. r. **136**, 535.   [3] B. **38**, 1796.

which must correspond to the second formula, is strongly fluorescent.

In phenylchloranthrone the reactivity of halogen atom is, as would be expected, greater than it is in the case of brom-anthrone. With resorcinol condensation takes place in exactly the same way as with bromanthrone, but in the case of the simpler phenols, such as phenol and cresol, the reaction is different, the hydroxyl group reacting with the halogen atom and at the same time condensation taking place with the carbonyl group ; products of the structure :

$$\begin{array}{c} \text{Ph} \qquad \text{OR} \\ \diagdown \diagup \\ \text{C} \\ \text{C}_6\text{H}_4 \diagdown \diagup \text{C}_6\text{H}_4 \\ \text{C} \\ \diagup \diagdown \\ \text{RO} \qquad \text{OH} \end{array}$$
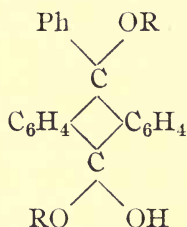
being obtained.[1]

In the case of alcohols the hydroxyl group reacts with the halogen atom, but simultaneous condensation with the carbonyl group does not take place, so that the products are alkoxyanthrones.

The structure of phenylchloranthrone is very similar to that of triphenylmethyl chloride, a compound which it resembles in many of its reactions. It is therefore not impossible that when treated with metals it might form a compound similar to triphenyl methyl. Liebermann[2] and his co-workers have found evidence that this is actually the case, and Schlenk,[3] by boiling phenyl chloranthrone in petroleum ether solution with copper bronze, obtained a yellow crystalline powder which, in the absence of air, gave a red solution in ether. The molecular weight was found to be 400, a figure which corresponds to about $33\frac{1}{3}$ per cent. of $C_{20}H_{13}O$ and $66\frac{2}{3}$ per cent. of $C_{40}H_{26}O_2$. Schlenk has pointed out that if the bridge formula for anthracene is correct *ms*-diphenyl anthracene is really a derivative of the unknown hexaphenylethane :

[1] B. **38**, 1800.   [2] B. **37**, 3337 ; **38**, 1799.   [3] A. **394**, 3340.

$$C_6H_5—C \diamondsuit C—C_6H_5$$

with C_6H_4 above and C_6H_4 below the central structure.

Diphenylanthracene.

$$C_6H_5—C \diamondsuit C—C_6H_5$$

with C_6H_5 C_6H_5 above and C_6H_5 C_6H_5 below.
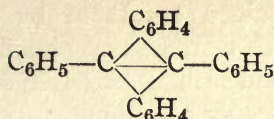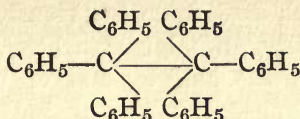
Hexaphenyl ethane.

and consequently might readily form a compound containing two trivalent carbon atoms. He was unable, however, to bring about this change.

ms-Nitroanthrone is formed when anthracene is treated with nitric acid under certain conditions,[1] and also when anthrone is nitrated in glacial acetic acid solution.[2] On reduction it loses ammonia, anthrone and anthraquinol being formed respectively when the reduction is carried out in acid and alkaline solution.[3] The corresponding *ms*-amino anthrone has never been obtained pure, but by reducing phenyl-azo-anthranol Kurt Meyer[4] obtained an impure substance which lost ammonia very readily and formed anthraquinol. This was probably amino anthrone, but owing to its instability it could not be purified sufficiently for analysis.

The chlorine atoms in dichloranthrone are capable of reacting with nuclear hydrogen atoms under the influence of aluminium chloride, and by this means Haller and Guyot[5] have prepared tetramethyl and tetraethyl diaminodiphenyl anthrone from dichloranthrone (anthraquinone dichloride) and dimethyl and diethyl aniline :

$$C_6H_4 \diamondsuit C_6H_4 + 2C_6H_5NMe_2 \rightarrow C_6H_4 \diamondsuit C_6H_4$$

left structure with Cl Cl on C above and CO below; right structure with $Me_2NC_6H_4$ $C_6H_4NMe_2$ on C above and CO below.
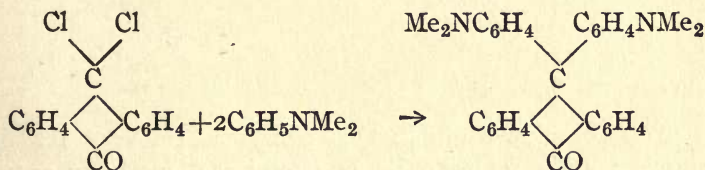
In the case of aryl chlor anthranones the reactivity of the chlorine atom is very much greater, and by condensing phenyl chloranthrone with benzene in the presence of aluminium chloride diphenyl anthrone is produced, a compound

[1] Perkin, Soc. **59**, 648 ; **61**, 866.   [2] Kurt Meyer, A. **396**, 150.
[3] A. **396**, 133.   [4] *Loc. cit.*   [5] C. r. **136**, 535.

which had been previously obtained by them by condensing phthalyl tetrachloride with benzene and aluminium chloride,[1] and by Baeyer by condensing phenyl hydroxy anthranol with benzene in the presence of sulphuric acid : [2]

$$C_6H_4\!\!<^{CCl_2}_{CCl_2}\!\!>O + C_6H_6 \;\rightarrow\; C_6H_4\!\!<^{\overset{Ph\;\;\;Ph}{\diagdown C\diagup}}_{CO}\!\!>C_6H_4 \;\leftarrow\; C_6H_6 + C_6H_4\!\!<^{\overset{Cl\;\;\;Ph}{\diagdown C\diagup}}_{CO}\!\!>C_6H_4$$

$$\uparrow$$

$$C_6H_6 + C_6H_4\!\!<^{\overset{Ph\;\;\;OH}{\diagdown C\diagup}}_{CO}\!\!>C_6H_4$$
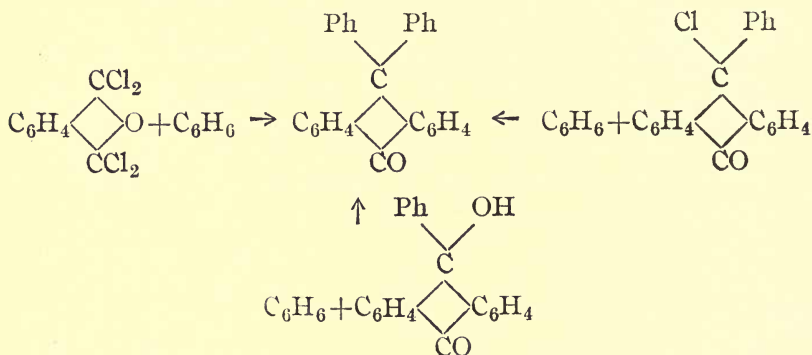
Starting with this substance several interesting syntheses have been carried out.

Liebermann and Lindenbaum * found that it was very readily reduced by zinc and acetic acid to the corresponding hydrocarbon, and that by treating this latter with bromine one, and only one, of the hydrogen atoms attached to the *ms*-carbon atom could be replaced :

$$C_6H_4\!\!<^{\overset{Ph\;\;\;Ph}{\diagdown C\diagup}}_{\underset{H\;\;\;H}{\diagup C\diagdown}}\!\!>C_6H_4 \;\rightarrow\; C_6H_4\!\!<^{\overset{Ph\;\;\;Ph}{\diagdown C\diagup}}_{\underset{H\;\;\;Br}{\diagup C\diagdown}}\!\!>C_6H_4$$
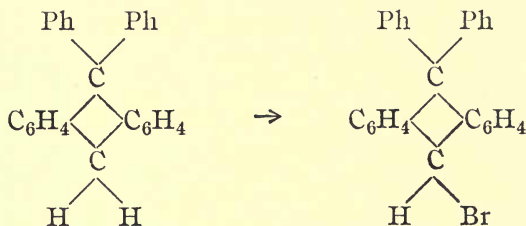
The bromine atom in this compound is very reactive and is readily replaced by hydroxyl and methoxy groups by treatment with water or alcohol. The most interesting reaction undergone by the compound is its behaviour when

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[1] C. r. **121**, 102.

[2] A. **202**, 65.   B. **38**, 1799.

* Liebermann and Lindenbaum give it the formula $C_{52}H_{36}$ and show two extra hydrogen atoms. Such a compound would only be formed by loss of bromine and not by loss of hydrobromic acid, and the above formula is the more probable.

heated, as it melts at 214–216° with evolution of hydro-bromic acid and almost immediately solidifies, the same change being brought about by heating with neutral solvents of high boiling point, such as naphthalene. The resulting compound contains no bromine, and undoubtedly has the structure :
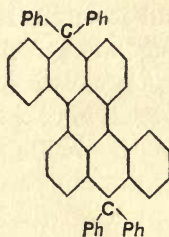
It is an extraordinarily stable substance which forms slightly yellow crystals which are practically insoluble in all media and which do not melt at 360°. It is hardly attacked by boiling concentrated sulphuric acid.

Anthranol and its derivatives are to be regarded as enolic tautomers of the corresponding anthrones (p. 118). They are much more sensitive to oxidation than to corre-sponding anthrones, and are usually attacked by atmo-spheric oxygen. Anthranol itself on moderated oxidation passes into dianthrone, but the arylamino-anthranols pass into the corresponding anil : [1]
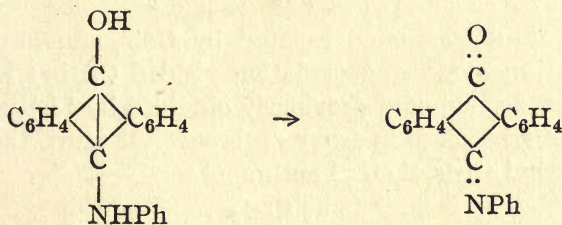
Goldmann [2] has studied the behaviour of anthranol when heated in alkaline solution with ethyl iodide and has isolated three products. The first of these is anthranol ethyl ether (*ms*-ethoxy anthracene). It reacts violently with bromine, but at −20° forms an unstable addition

[1] A. **396**, 147.   [2] B. **21**, 1178, 2505.

compound which evolves hydrobromine acid at 0°, and passes into a more stable dibrom compound. This on oxidation yields, first, the monoethyl ether of Bz.-bromanthraquinol and then bromanthraquinone, and hence must contain one bromine atom attached to the *ms*-carbon atom and one attached to one of the benzene rings.

The second compound isolated by Goldmann is a very stable substance melting at 136°. It is unaffected by bromine, boiling aqueous caustic potash and alcoholic hydrochloric acid at 180°. It is very stable to both oxidising and reducing agents, but by boiling with chromic acid in glacial acetic acid solution it can be oxidised with difficulty to anthraquinone. When heated with hydriodic acid and phosphorus in a sealed tube it is reduced to *unsym*-diethyl dihydroanthracene, and must, therefore, be diethylanthrone :

$$\begin{array}{ccc}
\text{Et} \quad \text{Et} & & \text{Et} \quad \text{Et} \\
\diagdown \diagup & & \diagdown \diagup \\
\text{C} & & \text{C} \\
\text{C}_6\text{H}_4 \diagdown \diagup \text{C}_6\text{H}_4 & \rightarrow & \text{C}_6\text{H}_4 \diagdown \diagup \text{C}_6\text{H}_4 \\
\text{CO} & & \text{CH}_2
\end{array}$$

It is interesting to observe the difficulty with which this reduction is effected in view of the fact that the corresponding diaryl compounds, *e.g.* diphenylanthrone, are very readily reduced to the *unsym*-diaryldihydroanthracenes by boiling with zinc and glacial acetic acid.[1]

The third compound isolated by Goldmann melted at 77°, and on moderated oxidation yielded C-ethyl hydroxy anthrone, a compound previously obtained by Liebermann [2] by the ethylation of hydroxy anthrone. It must, therefore, be the ethyl ether of ethyl anthranol :

$$\begin{array}{c}
\text{C}_2\text{H}_5 \\
| \\
\text{C} \\
\text{C}_6\text{H}_4 \diagdown \diagup \text{C}_6\text{H}_4 \\
\text{C} \\
| \\
\text{OC}_2\text{H}_5
\end{array}$$
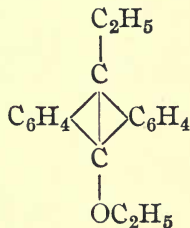
[1] B. **38**, 1799.   [2] A. **212**, 70.

Hallgarten [1] has carried out similar experiments with methyl iodide, *iso*-amylbromide and benzyl chloride, but has only been able to obtain the dialkylanthrones. These, like the diethyl compound, can only be reduced with difficulty.

Kurt Meyer [2] and his co-workers have carried out some very interesting experiments on the action of diazonium salts on the anthranol ethers. They find that, contrary to the belief usually held, diazonium salts often couple quite readily with phenolic ethers and even with unsaturated aliphatic hydrocarbons. The coupling is greatly facilitated by the presence of negative substituents such as nitro groups and halogen atoms, when in the ortho or para position to the diazo group, but is hindered by negative groups in the phenolic ether. Positive groups, especially alkoxy groups, in the phenolic ether greatly facilitate the coupling when in the meta position. In the case of the phenolic ethers derived from phenols and naphthols, dealkylation does *not* take place, the product being an alkoxyazo compound. When anthranol methyl ether is used, however, dealkylation does take place. Meyer suggests that the first stage of the reaction consists in the formation of an addition compound, which then passes into the azo compound either by loss of water, or, in the case of anthranol methyl ether, by the loss of a molecule of methyl alcohol :

$$\begin{array}{ccc}
\text{MeO} \quad \text{OH} & & \text{O} \\
\diagdown \diagup & & \vdots \\
\text{C} & & \text{C} \\
\text{C}_6\text{H}_4 \diamondsuit \text{C}_6\text{H}_4 & \rightarrow & \text{C}_6\text{H}_4 \diamondsuit \text{C}_6\text{H}_4 \\
\text{C} & & \text{C} \\
\diagup \diagdown & & \vdots \\
\text{H} \quad \text{N:NAr} & & \text{N.NHAr}
\end{array}$$
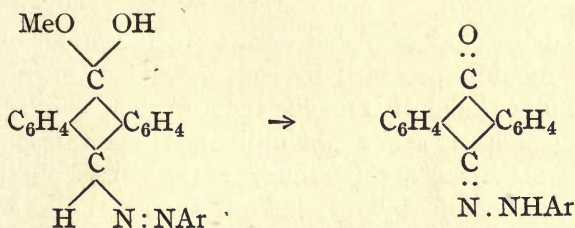
Methylanthranol methyl ether also couples with dizaonium salts, and it is probable that the mechanism of the reaction is somewhat similar :

[1] B. **21**, 2508.
[2] B. **47**, 1741. *Cf.* A. **898**, 74 ; B. **52**, 1468.

$$
\begin{array}{ccc}
\underset{\underset{\text{C}}{|}}{\text{OCH}_3} & \text{CH}_3\text{O} \quad \text{OH} & \overset{\text{O}}{\underset{\text{C}}{\overset{\cdot\cdot}{}}} \\
\text{C}_6\text{H}_4 \langle \rangle \text{C}_6\text{H}_4 \;\rightarrow\; & \text{C}_6\text{H}_4 \langle \rangle \text{C}_6\text{H}_4 \;\rightarrow\; & \text{C}_6\text{H}_4 \langle \rangle \text{C}_6\text{H}_4 \\
\underset{\text{CH}_3}{\overset{\text{C}}{|}} & \text{CH}_3 \quad \text{N:NAr} & \text{CH}_3 \quad \text{N:NAr}
\end{array}
$$
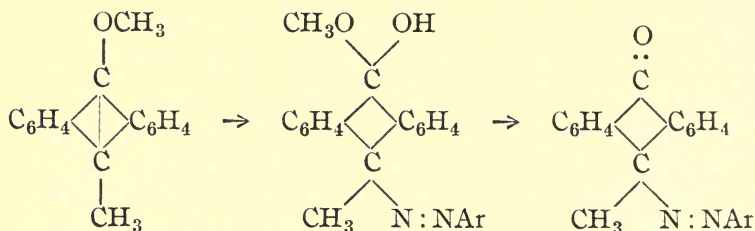
HYDROXYANTHRONE AND ANTHRAQUINOL

Hydroxyanthrone is to be considered as the tautomeric (ketonic) form of anthraquinol, although in this case the transformation of one isomer into the other is very slow, so that solutions only attain equilibrium after prolonged boiling (p. 121). Kurt Meyer [1] obtained hydroxyanthrone by treating bromanthrone with water, and found it to be a colourless, non-fluorescent crystalline substance which melted at 167°. He obtained the acetate by treating bromanthrone with anhydrous potassium acetate and boiling glacial acetic acid, and also by oxidising anthracene in boiling glacial acetic acid solution with two and a half molecules of lead dioxide,[2] or by treating it in aqueous suspension with chlorine or bromine below 25°. It is enolised by hydrochloric acid and by sodium acetate, and also dissolves in hot alkali owing to its conversion into the enolic form. The ketonic form is quite stable in the air, and is only attacked by mild oxidising agents when heated, oxidation being probably preceded by conversion into anthraquinol. On the other hand, it is readily reduced to anthranol by zinc and glacial acetic acid at the ordinary temperature.

The methyl ether (methoxy anthrone) is obtained by the action of methyl alcohol on bromanthrone [3] and is enolised by caustic soda.

Liebermann [4] endeavoured to prepare alkoxy anthranols by heating alkaline solutions of anthraquinol with alkyl halides, but instead he obtained stable compounds which

[1] A. **379**, 63.   [2] A. **397**, 76.   [3] A. **323**, 236.
[4] A. **212**, 67.   B. **13**, 1596; **15**, 452, 455, 462.

must be regarded as C-alkyl hydroxy anthrones for the following reasons :—

(1) On reduction with hydriodic acid and phosphorus they are converted quantitatively into *ms*-alkyl dihydro anthracenes, which on oxidation with chromic acid first pass back into the original alkylhydroxy anthrone and then into anthraquinone. The composition of the alkyl dihydro-anthracenes is almost identical with that of the various hydroanthracenes, as will be seen from the following table, so that elementary analysis is not sufficient to establish definitely that the products still contain the alkyl group :—

	Ethyl dihydro anthracene.	Butyl dihydro anthracene.	Amyl dihydro anthracene.	Tetra hydro anthracene.	Hexa hydro anthracene.
Carbon	92·3	91·5	91·2	92·3	91·3
Hydrogen	7·7	8·5	8·8	7·7	8·7

Liebermann, however, carried out quantitative oxidations by chromic acid, and by weighing the amount of anthraquinone formed, established beyond doubt that the substances were not hydroanthracenes.

(2) On treatment with phosphorus pentachloride (one molecule) a vigorous reaction takes place and the hydroxyl group is replaced by a chlorine atom. A similar replacement is also brought about very readily by cold hydrochloric or hydrobromic acid.[1]

(3) Although the hydroxyl group cannot be acetylated in the ordinary way, Liebermann found that by treating the chloride with anhydrous sodium acetate he was able to obtain an acetyl compound, although he failed to obtain it in a state of purity. This difficulty of acetylation is in harmony with the fact that the C-phenyl hydroxy anthranol obtained by Baeyer [2] by oxidising *ms*-phenyl anthracene does not give an acetyl derivative.

(4) When reduced by zinc dust and ammonia, alkyl dihydroanthranols are formed which very readily split off water and pass into *ms*-alkyl anthracenes :

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[1] B. **37**, 3337.   [2] A. **202**, 54.

$$\text{HO} \quad \text{R} \qquad\qquad \text{HO} \quad \text{R} \qquad\qquad\qquad \text{R}$$

$$C_6H_4 \underset{\overset{C}{\underset{\ddot{O}}{}}}{\overset{C}{\diamondsuit}} C_6H_4 \quad \overset{H}{\rightarrow} \quad C_6H_4 \underset{\overset{C}{\underset{H\;\;H}{}}}{\overset{C}{\diamondsuit}} C_6H_4 \quad \overset{-H_2O}{\longrightarrow} \quad C_6H_4 \underset{\overset{C}{\underset{H}{}}}{\overset{C}{\diamondsuit}} C_6H_4$$
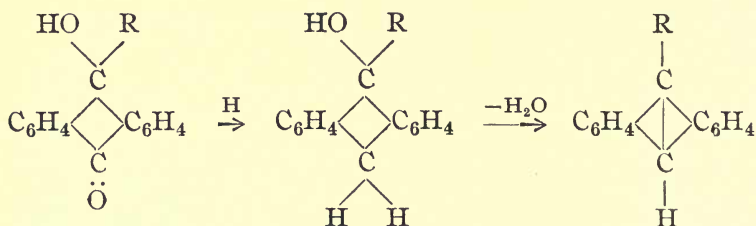
The reaction here is exactly analogous to the reduction of
anthraquinone to anthracene carried out by Perger.[1]   It
has received confirmation by Liebermann,[2] who alkylated
Perger's hydroxy dihydro anthracene and obtained sub-
stances which readily passed into *ms*-alkyl anthracenes by
loss of water, and which on moderated oxidation yielded
alkyl hydroxy anthrones :
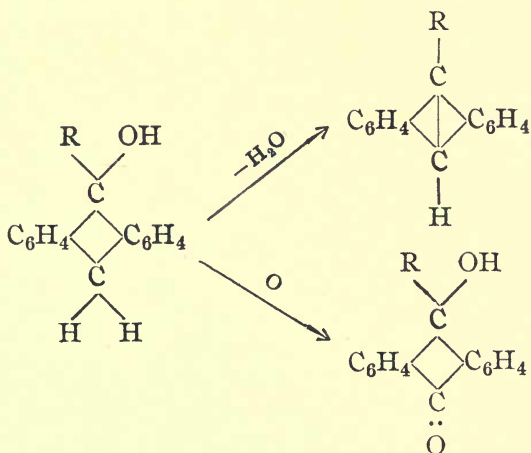
The above reactions were all obtained with the ethyl,
propyl, *iso*-butyl and *iso*-amyl compounds, but when
alkaline solutions of hydroxy anthranol were heated with
methyl iodide the reaction took a different course and a
methyl compound was obtained which formed methyl
iodide when heated with hydriodic acid, and which did not
react with phosphorus pentachloride. Its melting point
(187°) was also higher than the melting points of its homo-

[1] J. pr. [2] **23**, 137.   [2] A. **212**, 67. B. **13**, 1596; **15**, 452, 455, 462

logues.   Obviously this is an O-methyl compound (methoxy anthrone) :

$$\begin{array}{c} \text{H} \quad \text{OMe} \\ \diagdown\diagup \\ \text{C} \\ C_6H_4 \diamond C_6H_4 \\ \text{CO} \end{array}$$
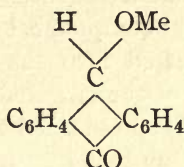
On one occasion, however, Liebermann [1] obtained an isomeric substance which melted at 98°, and which behaved like a C-methyl compound, but he was unable to repeat his experiment.

It will be noticed that methoxy anthrone can be considered as tautomeric with anthraquinol monomethyl ether :

$$\begin{array}{c} \text{H} \quad \text{OMe} \\ \diagdown\diagup \\ \text{C} \\ C_6H_4 \diamond C_6H_4 \\ \text{CO} \end{array} \qquad\qquad \begin{array}{c} \text{OMe} \\ | \\ \text{C} \\ C_6H_4 \diamond C_6H_4 \\ \text{C} \\ | \\ \text{OH} \end{array}$$
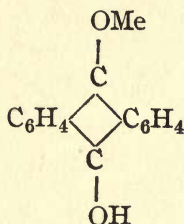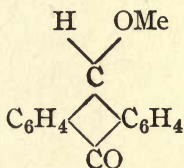
and this tautomerism is discussed on p. 121.

Kurt Meyer [2] has investigated the methylation and ethylation of anthraquinol by means of methyl and ethyl sulphate.   With methyl sulphate he obtained a monomethyl ether (m.p. 164°), and a dimethyl ether (m.p. 202°), and with ethyl sulphate a mono- and a di-ethyl ether and also Liebermann's C-ethyl hydroxy anthrone.

The formation of C-alkyl compounds by the alkylation of hydroxy anthranol is very similar to the formation of C-alkyl compounds from sodio-acetoacetic ester.   In this latter case Saar has proposed that the transition from the enolic to the ketonic state and vice versa is so rapid that as soon as a molecule of one form enters into a reaction the equilibrium is restored by the rearrangement of a molecule of the other form.   In the case of the hydroxy anthranols this theory is not applicable, as Kurt Meyer has shown that

[1] B. **21**, 1175.   [2] A. **379**, 47.

the transition from the anthrone to the anthranol form and vice versa is slow.   Claissen's theory that in the case of acetoacetic ester O-alkyl compound is first formed, and that this is at once rearranged into the C-alkyl compound, is hardly tenable in view of the fact that O-alkyl compounds of acetoacetic ester have been obtained and have been found to be stable substances, and the same objection of course applies to the monoalkyl ethers of anthraquinol.   In the case of acetoacetic ester Michael has proposed that alkylation is preceded by addition, and in the case of the alkylation of anthraquinol this theory also furnishes the best explanation of the formation of C-alkyl compounds :
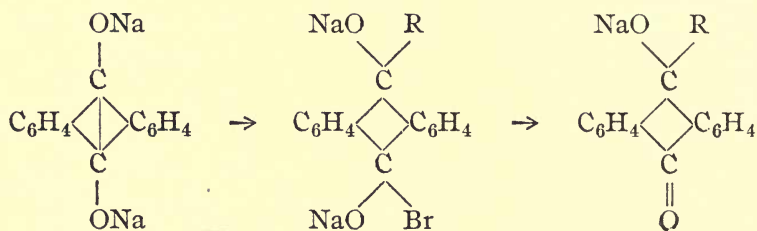
The production of the O-methyl compound is to be ascribed to the predominance of the " normal " reaction in this case :
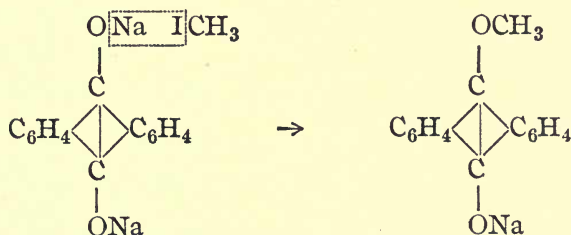
The alkyl and aryl hydroxy anthrones can also be obtained by the action of Grignard's solutions on anthraquinone, and this method of formation is discussed on p. 85.

The hydroxyl group of the aryl hydroxy anthrones is very reactive and, as is pointed out elsewhere (p. 85), is readily replaced by chlorine or bromine by treatment with halogen acid.   The carbonyl group is also reactive and

Haller and Guyot [1] have found that in some cases heating with concentrated sulphuric acid and an aromatic hydrocarbon such as benzene or toluene is sufficient to cause condensation to take place :

$$Me_2NC_6H_4 \quad OH \qquad\qquad Me_2NC_6H_4 \quad OH$$
$$\diagdown \diagup \qquad\qquad\qquad \diagdown \diagup$$
$$C \qquad\qquad\qquad\qquad C$$
$$C_6H_4 \diamondsuit C_6H_4 \quad \rightarrow \quad C_6H_4 \diamondsuit C_6H_4$$
$$CO \qquad\qquad\qquad\qquad C$$
$$\qquad\qquad\qquad\qquad\qquad Ph \quad OH$$
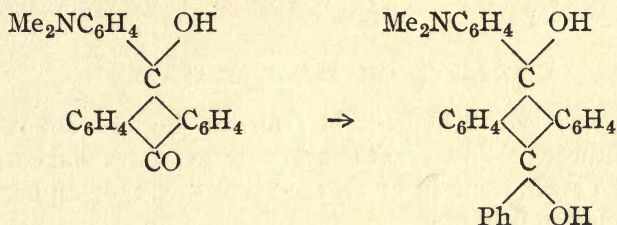
The anthraquinols are the enolic forms of the hydroxy anthrones and are of great importance, as they are readily soluble in dilute alkali and the alkaline solutions are very rapidly oxidised by the air or by weak solutions of hydrogen peroxide with the formation of the corresponding anthraquinone. The insoluble vat dyes are always applied to the fibre in the form of their anthraquinol derivative (" vat " or " leuco- compound "), the insoluble dyestuff being subsequently precipitated on the fibre by exposure to the air or by after-treatment with a mild oxidising agent.

Anthraquinol itself was first prepared by Graebe and Liebermann [2] by the reduction of anthraquinone with zinc dust and caustic soda, and more recently Grandmougin [3] has shown that the reduction is better effected with sodium hydrosulphite in alkaline solution, the reducing agent always used in vat dyeing. Owing to the ease with which the anthraquinols are oxidised by the air their isolation is a matter of some difficulty, and for this reason Liebermann [4] introduced the method of carrying out the reduction with zinc dust in boiling glacial acetic acid solution in the presence of anhydrous sodium acetate. Under these conditions the anthraquinol is acetylated as soon as formed, and as the acetyl derivatives are quite stable they can easily be purified. They can be hydrolysed by alkali, but owing to the sensitiveness of the free hydroxy compounds it is necessary to work

[1] C. r. **137**, 606.
[3] J. pr. [2] **76**, 138; B. **39**, 3963.
[2] A. **160**, 126.
[4] B. **21**, 436, 1172.

in an inert atmosphere if pure products are to be obtained. The behaviour of the anthraquinols when alkylated with alkyl halides and with dimethyl and diethyl sulphate has already been described (p. 111).

DIANTHRYL AND ITS DERIVATIVES

Dianthryl is the hydrocarbon formed by the union of two anthracene residues by their *ms*-carbon atoms, and corresponds to anthracene in much the same way that diphenyl corresponds to benzene :
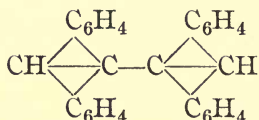
Theoretically five other dianthryls are possible which may be represented as $A[9][1]A$, $A[9][2]A$, $A[1][1]A$, $A[1][2]A$ and $A[2][2]A$, where A indicates an anthry ($C_{14}H_9$) group, and the numbers indicate the carbon atoms at which junction is effected. These compounds do not seem to have been described as yet, although some of the corresponding quinones of the three last are well known. Dianthryl was first obtained by Schulze [1] by the action of dehydrating agents on anthrapinacone :
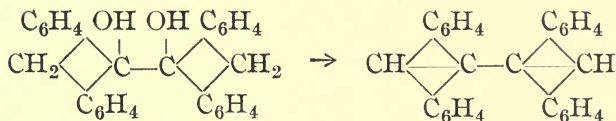
and Liebermann and Gimbel [2] soon afterwards found that it could be obtained direct from anthraquinone by reduction with tin and hydrochloric acid in glacial acetic acid solution. More recently Eckert and Hofmann [3] have improved the experimental details by carrying out the reduction with tin and hydrochloric acid in glacial acetic acid solution in the presence of a trace of a platinum salt, and claim to have obtained excellent yields.

[1] B. **18**, 3035.   [2] B. **20**, 1854.   [3] M. **36**, 497.

Dianthryl is a colourless fluorescent compound which melts at 300°. When nitrated in acetic acid solution it gives a dinitro compound,[1] and as this on oxidation gives anthraquinone, the nitro groups must be attached to the *ms*-carbon atoms. The dinitro compound is quite stable, and melts at 337° decomp. On reduction the dinitro compound gives the corresponding diamino- compound (m.p. 307–309° decomp.), which by gentle oxidation passes into the di-imide, the tautomerism of which is discussed on p. 124.

Dianthranol corresponds to dianthryl in the same way that anthranol corresponds to anthracene :

$$HOC\underset{C_6H_4}{\overset{C_6H_4}{\diamondsuit}}C\text{---}C\underset{C_6H_4}{\overset{C_6H_4}{\diamondsuit}}COH$$
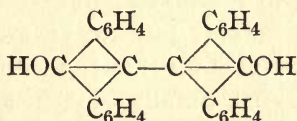
It was first prepared by Hans Meyer[2] by the reduction of anthraquinone with zinc and caustic soda under pressure at a high temperature, and more recently Eckert and Hofmann[3] have obtained it by the alkaline hydrolysis of the diacetate obtained by oxidising dianthryl with lead dioxide in glacial acetic acid solution :

$$CH\underset{C_6H_4}{\overset{C_6H_4}{\diamondsuit}}C\text{---}C\underset{C_6H_4}{\overset{C_6H_4}{\diamondsuit}}CH \overset{O}{\rightarrow} CH_3CO.OC\underset{C_6H_4}{\overset{C_6H_4}{\diamondsuit}}C\text{---}C\underset{C_6H_4}{\overset{C_6H_4}{\diamondsuit}}CO.COCH_3$$

$$\downarrow$$

$$HOC\underset{C_6H_4}{\overset{C_6H_4}{\diamondsuit}}C\text{---}C\underset{C_6H_4}{\overset{C_6H_4}{\diamondsuit}}COH$$
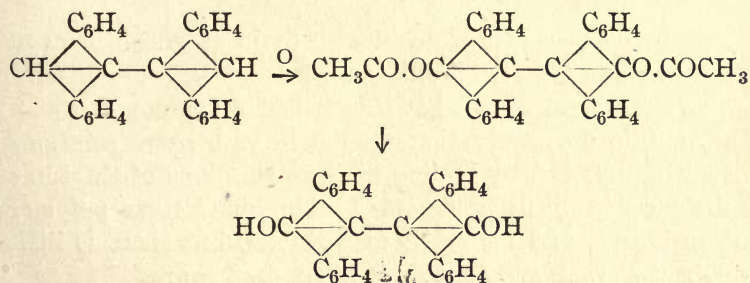
It melts rather indefinitely at 230°, its diacetyl compound melting at 273° and its dimethyl ether at 245°. It is easily oxidised to anthraquinone by chromic acid, but mild oxidising agents, such as ferric chloride, alkaline potassium permanganate or iodine in potassium iodide convert it into dianthraquinone :[4]

---

[1] B. **20,** 2433.　　[2] B. **42,** 143 ; M. **30,** 165 ; Kinzlberger & Co., D.R.P. 223,210.
　　　　[3] M. **36,** 497.　　　　　　　　[4] B. **42,** 143.

$$O : C \underset{C_6H_4}{\overset{C_6H_4}{\diamond}} C = C \underset{C_6H_4}{\overset{C_6H_4}{\diamond}} C : O$$
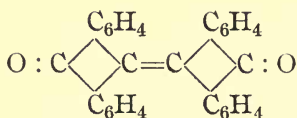
It has been stated that *meso*-ethers of hydroxylated dianthranols are formed when mandelic acid is heated with pyrocatechol or hydroquinone at 200–300°, although in the case of resorcinol the product is dihydroxydiphenyl methane carboxylic acid.[1] The course of the reaction is not clear, and the results claimed cannot be unreservedly accepted without further confirmation.

Dianthrone is the tautomeric form of dianthranol, just as anthrone is the ketonic form of anthranol, and the two isomers are interconvertible by the action of acids and alkalis (see p. 124). It is obtained by the action of copper on bromanthrone,[2] and Dimroth[3] has obtained it in quantitative yield by the action of ferric chloride on anthranol, and in smaller yield by the action of nitric acid on anthracene :

$$2 O : C \underset{C_6H_4}{\overset{C_6H_4}{\diamond}} C \overset{H}{\underset{Br}{\diamond}} \rightarrow O : C \underset{C_6H_4}{\overset{C_6H_4}{\diamond}} C - C \underset{C_6H_4}{\overset{C_6H_4}{\diamond}} C : O$$
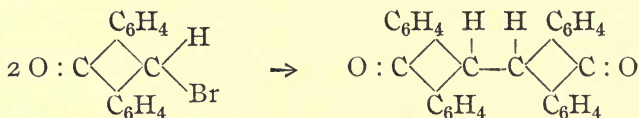
Padova[4] has also claimed that it is obtained in good yield when dianthranol is oxidised with phenanthraquinone.

Orndorff and Bliss[5] have described a compound which they obtained by the action of sunlight on benzene solutions of anthranol, and by boiling benzene solutions of the same substance. This they regarded as a bimolecular polymer of anthranol, and named it dianthranol, but there is little doubt that their substance was really dianthrone.

Dianthrone melts rather indefinitely at 245–255°, and is insoluble in cold alkali.

Dianthraquinone is readily obtained by the oxidation of dianthranol, Eckert and Hofmann[6] finding that it is produced by the sulphuric acid hydrolysis of dianthranol

[1] H. von Liebig, J. pr. [2] **78**, 95.   [2] A. **379**, 44.
[3] B. **34**, 219.   *Cf.* Scholl, B. **44**, 1075.   [4] C. r. **149**, 217.
[5] Am. **18**, 453.   [6] M. **36**, 497.

diacetate, although more readily obtained by oxidising dianthranol in alkaline solution with potassium persulphate or hydrogen peroxide,[1] or, according to Kinzlberger & Co., by potassium permanganate : [2]

$$
HOC \underset{C_6H_4}{\overset{C_6H_4}{<>}} C - C \underset{C_6H_4}{\overset{C_6H_4}{<>}} COH \;\rightarrow\; O:C \underset{C_6H_4}{\overset{C_6H_4}{<>}} C = C \underset{C_6H_4}{\overset{C_6H_4}{<>}} C:O
$$
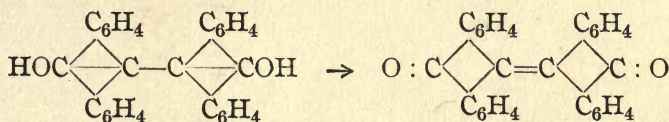
Padova [3] has stated that it is also obtained when dianthranol is oxidised by amyl nitrite in pyridine solution ; but according to Meyer, Bondy and Eckert [4] the substance obtained by Padova was really only a mixture of anthraquinone and unchanged dianthranol. Eckert and Tomaschek [5] have studied the chlordianthraquinones. These they obtained by oxidising the chlordianthranols with potassium persulphate, and found that they are oxidised by atmospheric oxygen under the influence of light to more highly condensed compounds, e.g.—

Kurt Meyer [6] endeavoured to prepare aminoanthrone by the action of ammonia on bromanthrone, but always obtained brom-dianthrone, which by treatment with copper powder or when heated alone lost hydrobromic acid and passed into dianthraquinone :

$$
O:C \underset{C_6H_4}{\overset{C_6H_4\;Br}{<>}} C - C \underset{C_6H_4}{\overset{H\;C_6H_4}{<>}} C:O \;\rightarrow\; O:C \underset{C_6H_4}{\overset{C_6H_4}{<>}} C:C \underset{C_6H_4}{\overset{C_6H_4}{<>}} C:O
$$
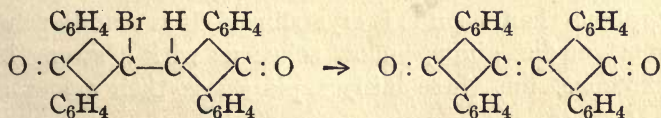
[1] M. **33**, 1447. [2] D.R.P. **223,210**.
[3] C. r. **148**, 290. [4] M. **33**, 1447.
[5] M. **39**, 839. [6] A. **396**, 133.

TAUTOMERISM

Kurt Meyer [1] has studied the question as to what extent anthranol and anthrone compounds can be considered to be tautomeric :

Anthranol.   Anthrone.
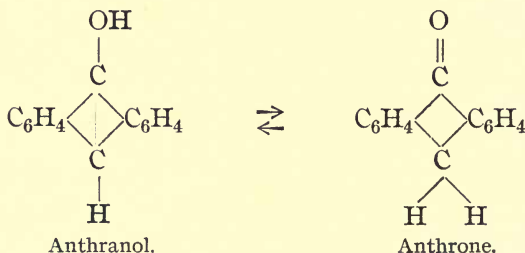
He points out that the formation of soluble alkali salts with hot caustic alkali and the formation of acetyl derivatives point to the enolic formula, whereas the insolubility in cold alkali points to the ketonic formula.   Also Padova [2] has prepared condensation products with aldehydes and ketones (see p. 99), and Kaufler and Suchannek [3] have found that anthranol will not react with phenyl isocyanate. These facts point to the ketonic (anthrone) formula, as does also the absence of, or very slight, fluorescence shown by the compounds.

Kurt Meyer found that if an alkaline solution of Liebermann's anthranol is acidified below —5° with dilute sulphuric acid an isomeric substance separates out, which crystallises in yellow needles which melt at 120° when suddenly heated, whereas the original substance is colourless and melts at 154°.* The new substance has a very strong fluorescence and is easily soluble in cold aqueous alkali. On keeping it slowly changes back to the original substance, the change being much more rapid when the substance is amorphous than when it is crystalline.   It is readily soluble in most media, giving yellow solutions with a strong blue fluorescence, but these fairly rapidly lose their colour and

[1] A. **379**, 37.
[2] C. r. **141**, 857 ; **143**, 121.
[3] B. **40**, 518.
* Liebermann (A. **212**, 7) gives the melting point as 167–170°.

fluorescence, especially when boiled, and the colourless solutions on cooling deposit the original colourless substance.

Kurt Meyer therefore concludes that the colourless form (m.p. 154°) is anthrone, and the yellow fluorescent form anthranol :

$$C_6H_4 \underset{CH_2}{\overset{CO}{\diamond}} C_6H_4 \qquad\qquad C_6H_4 \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{\diamond}} C_6H_4$$
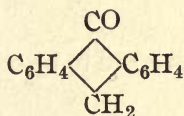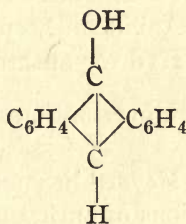
Anthrone.   Anthranol.

In the solid state each of these can exist, but in solution a state of equilibrium is reached, the change from enolic to ketonic form being accelerated by the presence of a trace of hydrochloric acid. At the equilibrium point the ketonic state is always predominant in the case of the unsubstituted substances, but depends to some extent on the solvent. It seems that glacial acetic acid favours the enolic form more than other solvents, whereas chloroform and acetone are especially active in favouring the ketonic form.

The enolic but not the ketonic form is readily oxidised by bromine to the non-fluorescent dianthrone, and as the velocity of the change from ketone to enole is low, it is possible to estimate the amount of enole present by titration with bromine solution. This Kurt Meyer [1] has done by using the disappearance of fluorescence to determine the end point, as this is very easily seen when the solution is strongly illuminated by an iron-arc. He compared various derivatives and determined the per cent. of enole present at the equilibrium point in ·1 per cent. alcoholic solution at the ordinary temperature.

Equilibrium is also set up on fusion, and if anthrone is

[1] A. **396**, 140.

melted and then suddenly cooled it is found to be partially soluble in cold alkali.

Compound.				Per cent enole.
Anthrone	..	..	..	11
Nitroanthrone	..	..	..	3
Phenylanthrone	..	..	..	30
Anilidoanthrone	..	..	..	80
Hydroxyanthrone	..	..	..	96

In pyridine solution all the above seemed to be completely enolised.

Kurt Meyer [1] has noted the following differences between the reactions of anthranol and anthrone :—

(1) Anthranol is readily attacked by mild oxidising agents such as ferric chloride, bromine, amyl nitrite, etc., whereas anthrone is not attacked in the cold and only with difficulty on heating. As anthrone is most readily oxidised in those solvents which favour the change to the enolic form, it is probable that oxidation only takes place subsequent to enolisation. It is noticeable that the oxidation product is always the ketonic dianthrone and never the enolic dianthranol, this being the case even when the oxidation is carried out with potassium ferricyanide in alkaline solution.

(2) Anthranol couples with diazonium solutions to yield azo- dyes, whereas the anthrone does not. Kurt Meyer [2] has examined these with a view to determining whether they are enolic or ketonic, but has been unable to come to any definite conclusion. He obtained the same product by coupling phenyl diazonium chloride with anthranol as he obtained by condensing dibromanthrone with ·phenyl hydrazine. He obtained two isomeric benzoyl derivatives, however, one of which must be ketonic, as he obtained it by condensing dibromanthrone with benzoyl phenyl hydrazine. The other isomer he obtained by coupling diazotised aniline with anthranol, and then benzoylating the azo dye. This latter must be enolic, and by comparing the properties of the two benzoyl derivatives Meyer formed the opinion that the

[1] A. **379**, 37.   [2] A. **396**, 152.

parent azo- dye was probably enolic. Kauffler and Such-annek,[1] and more recently Charrier,[2] on the other hand, prefer the ketonic (hydrazone) formula.[3]

(3) Anthranol condenses with nitroso dimethyl aniline to form an anil, whereas anthrone does not.[4]

Kurt Meyer [5] has also examined the isomerism of anthra-quinol :

$$
\begin{array}{ccc}
\underset{\substack{|\\ C \\ C_6H_4 \diamondsuit C_6H_4 \\ C \\ |}}{OH} & \rightleftarrows & \underset{\substack{\ddot{C} \\ C_6H_4 \diamond C_6H_4 \\ C}}{O} \\
OH & & H \quad OH
\end{array}
$$

| Anthraquinol. | Hydroxyanthrone. |
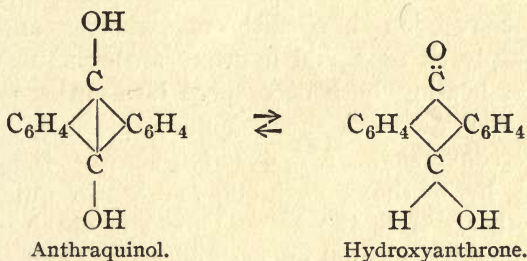
which is obviously enolic, as it is soluble in cold aqueous alkali, is fluorescent and is very readily oxidised. If its alkaline solutions are acidified at a low temperature it is not precipitated in the ketonic form, nor is it ketonised by boiling with alcoholic hydrochloric acid. Meyer was unable to convert it into hydroxyanthrone, but succeeded in preparing this latter substance by treating bromanthrone with water :

$$
\underset{\substack{C \\ C_6H_4 \diamondsuit C_6H_4 \\ CO}}{H \quad Br} \rightarrow \underset{\substack{C \\ C_6H_4 \diamondsuit C_6H_4 \\ CO}}{H \quad OH}
$$
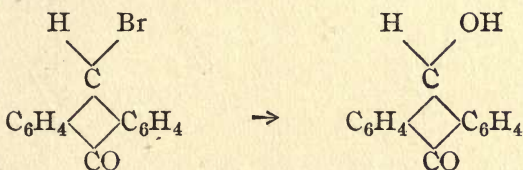
He found it to be colourless, non-fluorescent and stable to atmospheric oxygen. Unlike anthraquinol it is only attacked by bromine on heating, and even then the reaction is slow, and it is readily reduced by zinc and acetic acid to anthranol, whereas anthraquinol is not. It is insoluble in cold alkali, but is enolised to anthraquinol by boiling alcoholic alkali. The interconversion of the isomers in this case is much

[1] B. **40,** 518.   [2] G. **45,** 502.
[3] For absorption spectrum see Sircar, Soc. **109,** 762.
[4] B. **40,** 525.   [5] A. **379,** 44.

more difficult than in the case of anthrone and anthranol, so that solutions do not reach the equilibrium point until after being submitted to prolonged boiling, unless a catalyst such as hydrochloric acid or sodium acetate is present. This difficulty of interconversion renders the behaviour of the substances when heated different. Thus anthranol when heated slowly shows no sharp melting point owing to its gradual conversion into anthrone, whereas anthraquinol melts sharply at 180°, and hydroxy anthrone at 167°, and on further heating both decompose into anthrone, anthraquinone and water, without apparently first undergoing any interconversion. An exactly similar isomerism is exhibited by methoxy anthrone and anthraquinol monomethyl ether. Here the ketonic form is obtained by the action of methyl alcohol on bromanthrone,[1] and is enolised by warm dilute alkali, the enolic form being obtained direct by the action of methyl iodide or dimethyl sulphate on anthraquinol.[2] This on oxidation gives dimethoxydianthrone, which cannot form an enolic isomer as it has no labile hydrogen atom :

---
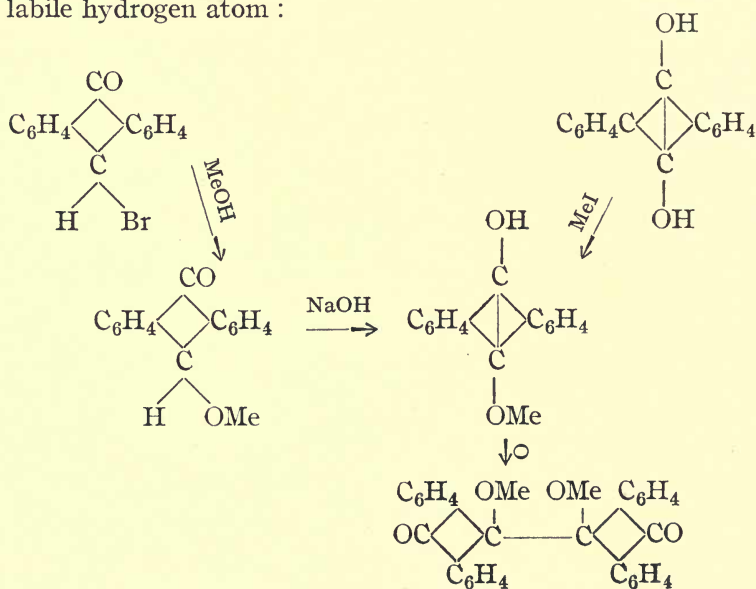
[1] A. **323**, 236.   [2] A. **376**, 47.

Baeyer[1] obtained phenyl anthrone by heating tri-phenyl methane-*o*-carboxylic acid with sulphuric acid.

$$
\begin{array}{cc}
\text{Ph} \quad \text{H} & \text{Ph} \quad \text{H} \\
\diagdown \diagup & \diagdown \diagup \\
\text{C} & \text{C} \\
C_6H_4 \diagup \diagdown C_6H_5 & C_6H_4 \diamond C_6H_4 \\
\text{COOH} & \text{CO}
\end{array}
$$
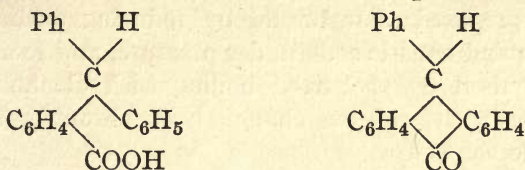
This is obviously ketonic, as it is not fluorescent, is in-soluble in cold alkali, and is not oxidised by cold alcoholic bromine.[2] It dissolves in hot alkali, and if the solution is cooled to $-5°$ and acidified with dilute sulphuric acid, the enolic form separates out. This is strongly fluorescent, soluble in cold alkali, and is readily oxidised by bromine, or by air when in alkaline solution. It is much less stable than anthranol itself, and on keeping rapidly reverts to the ketonic form.

Kurt Meyer[3] endeavoured to prepare amino anthrone, but was unable to obtain it in a pure state. However, he was able to prepare arylamino anthrones by treating brom-anthrone with primary aromatic amines and found that they exhibit the same keto-enole tautomerism. As was to be expected, the ketonic form is non-fluorescent, and is not sensitive to bromine, whereas the enolic form, obtained from the ketonic form by boiling with a catalyst, such as hydro-chloric acid or sodium acetate, is fluorescent and sensitive to bromine. In most solvents the enolic form predominates, but in glacial acetic acid it is the ketonic form which is predominant. On oxidation the enolic form yields the anil, and it is curious to note that whereas the monoanil is deep red, the dianil is only yellow :

$$
\begin{array}{cc}
\text{O} & \text{NPh} \\
\text{C} & \text{C} \\
C_6H_4 \diamond C_6H_4 & C_6H_4 \diamond C_6H_4 \\
\text{C} & \text{C} \\
\text{NPh} & \text{NPh} \\
\text{Deep red.} & \text{Yellow.}
\end{array}
$$
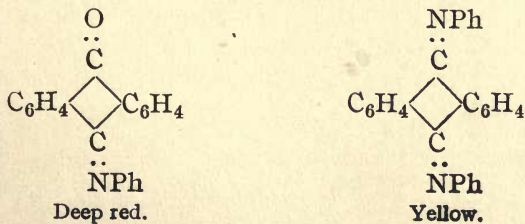
[1] A. 202, 54.   [2] A. 396, 133.   [3] *Loc. cit.*

Dianthranol and dianthrone exhibit the same form of isomerism as anthranol and anthranone. Thus, Hans Meyer [1] prepared dianthranol by reducing anthraquinone with zinc and caustic soda under pressure, and found that it was ketonised by prolonged boiling with alcoholic hydrochloric acid, the reverse change being brought about by caustic potash :

$$\underset{C_6H_4}{\overset{C_6H_4}{HOC}} C\text{—}C \underset{C_6H_4}{\overset{C_6H_4}{COH}} \quad \overset{HCl}{\underset{KOH}{\rightleftharpoons}} \quad O:C \underset{C_6H_4}{\overset{C_6H_4}{\underset{}{}}} \overset{H}{C}\text{—}\overset{H}{C} \underset{C_6H_4}{\overset{C_6H_4}{\underset{}{}}} C:O$$
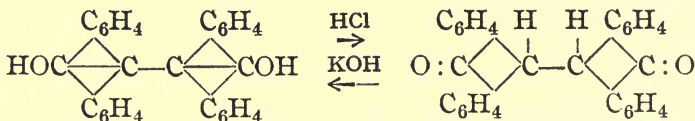
and Kurt Meyer [2] has found that *ms*-anthramine when oxidised by amyl nitrite,[3] or by other oxidising agents such as bromine, gives an imide (m.p. 205°), which is partially isomerised on melting or when boiled with sodium acetate or aqueous caustic potash, and is completely isomerised by alcoholic potash :

$$HN:C \underset{C_6H_4}{\overset{C_6H_4}{\underset{}{}}} \overset{H}{C}\text{—}\overset{H}{C} \underset{C_6H_4}{\overset{C_6H_4}{\underset{}{}}} C:NH \quad \rightarrow \quad H_2N.C \underset{C_6H_4}{\overset{C_6H_4}{\underset{}{}}} C\text{—}C \underset{C_6H_4}{\overset{C_6H_4}{\underset{}{}}} C.NH_2$$
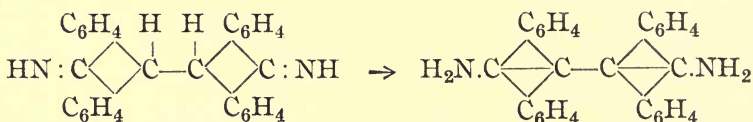
This latter compound melts rather indefinitely at 324–334°, and was obtained by Gimbel [3] by nitrating and reducing dianthryl. So far the reverse change has not been brought about.

[1] B. **42**, 143. [2] B. **46**, 29. [3] B. **20**, 2433.

CHAPTER VI

ANTHRAQUINONE RING SYNTHESES

THE synthetic methods which have been employed for the production of anthracene derivatives, and the oxidation of these to the corresponding anthraquinones, are described elsewhere,[1] and in this chapter only those methods will be treated by which an anthraquinone is formed without the previous production of an anthracene derivative. Some of the methods to be described have proved to be of the greatest assistance in the study of the more complex anthraquinone vat dyes; but special methods of building up these complexes will only be mentioned very shortly, as they are more conveniently treated in detail when dealing with the special classes of compounds involved.

I. FROM AROMATIC MONOCARBOXYLIC ACIDS

When aromatic monocarboxylic acids are heated with dehydrating agents, such as phosphorus pentoxide or anhydrous zinc chloride, loss of two molecules of water between two molecules of the acid often takes place with the production of an anthraquinone derivative :
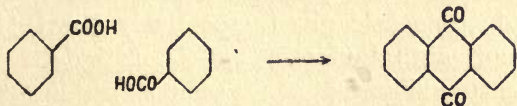
The production of anthraquinone itself by this method was achieved by Behr and van Dorp [2] by heating benzoic acid with phosphorus pentoxide, but the yields are exceedingly

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[1] Chapter II. [2] B. **7**, 16, 578.

poor. The reaction takes place much more readily if a hydroxy benzoic acid is used in place of benzoic acid, and in some cases quite satisfactory yields are obtained by heating the hydroxy acid with concentrated sulphuric acid. Thus Schunck and Römer[1] found that when *m*-hydroxy-benzoic acid is heated with concentrated sulphuric acid a mixture of various dihydroxy anthraquinones is formed in 42 per cent. yield. Of the isomers formed anthraflavic acid is the most plentiful (82 per cent.), the remainder consisting chiefly of anthrarufin and a little 1.7-dihydroxy anthraquinone. They contradict Rosentiel's statement[2] that *iso*-anthraflavic acid is also formed. Other hydroxy benzoic acids behave in a similar way to *m*-hydroxy benzoic acid, *e.g.* 2-methyl-3-hydroxy-1-benzoic acid gives 1.5-dimethyl anthraflavic acid,[3] and gallic acid gives rufigallol.[4]

The above method can be extended by heating a molecular mixture of two different aromatic monocarboxylic acids with a dehydrating agent, although, as would be expected, this procedure often results in a complex mixture of various anthraquinone derivatives. As examples of this method may be mentioned the production of dimethyl anthragallol by Birukoff,[5] by heating a mixture of benzoic acid and gallic acid with concentrated sulphuric acid, of trimethyl anthragallol by Wende[6] from durylic acid and gallic acid, and of anthragallol itself from benzoic acid and gallic acid.[7] The yields, however, are very poor ; Birukoff, for example, obtaining only a yield of two per cent. When, however, gallic acid is condensed with a hydroxy benzoic acid better results are obtained, *e.g.* gallic acid when condensed with 2-methyl-3-hydroxy-1-benzoic acid and with 2-methyl-5-hydroxy-1-benzoic acid gives respectively 5-methyl-1.2.3.6-tetrahydroxy anthraquinone and 5-methyl-1.2.3.8-tetra-hydroxy anthraquinone.[8]

There would seem to be some possibility that the above

[1] B. **10**, 1225 ; **11**, 969, 1225.   [2] B. **10**, 1033.   [3] K., D.R.P. 87,620.
[4] Robiquet, A. **19**, 204 (1836).   Schiff, A. **163**, 218.
[5] B. **20**, 870.   [6] B. **20**, 867.
[7] Seuberlich, B. **10**, 38.   Auerbach, Ztg. 1882, 910.
[8] K., D.R.P. 87,620.

method of forming the anthraquinone ring could be carried out by a catalytic method, *e.g.* by passing the vapour of the aromatic monocarboxylic acid over a suitable catalyst, such as precipitated silica or aluminium or calcium phosphate, although no such method has been recorded.

II. FROM PHTHALIC ACID BY THE DIRECT METHOD

It is usually best to build up anthraquinone derivatives from phthalic acid in two steps, by first forming the phthaloyl derivative (*o*-benzoyl benzoic acid), and then subsequently closing the anthraquinone ring by treatment with a dehydrating agent. This method is treated in detail in the next section under the heading " Phthalic Acid Synthesis," and in the present section only those methods will be mentioned by which an anthraquinone derivative can be obtained from phthalic acid in one step. The method is confined to the production of hydroxyanthraquinones.

In some cases phthalic acid will condense with a phenol to form a hydroxy anthraquinone simply under the influence of heat, no dehydrating agent or catalyst being used. Thus, Baeyer and Drewson [1] obtained 4-methylerythrohydroxy anthraquinone by heating phthalic anhydride with *p*-cresol for two days at 160–200°, and more recently Ullmann [2] has found that when phthalic anhydride is heated with *p*-chlorphenol a mixture of 4-chlorerythrohydroxy anthraquinone and of *o*-hydroxychlorbenzoyl benzoic acid is obtained. As a rule, however, the condensation only takes place in the presence of a condensing agent such as sulphuric acid, although, as will be seen, boric acid or aluminium chloride are often effective.

When sulphuric acid is used as a condensing agent phthaleïn formation takes place simultaneously, so that the yields obtained are often extremely poor. Baeyer and Caro, and Liebermann and his students have studied the condensation of phthalic anhydride with various phenols in the presence of concentrated sulphuric acid, and have

[1] A. **212,** 345.   [2] D.R.P. 282,493.

obtained various hydroxy anthraquinones, such as erythro-hydroxyanthraquinone mixed with a little β-hydroxyanthra-quinone from phenol itself,[1] alizarin and hystazarin from pyrocatechol,[2] and quinizarin from hydroquinone.[3] The yields, however, never exceeded 5 per cent. of the theoretically possible, and Birukoff [4] states that the condensation of phthalic anhydride with *p*-cresol gives a yield of only 1¼ per cent. of 4-methylerythrohydroxyanthraquinone. It should be noted that during the condensation of phthalic anhydride with *p*-chlorphenol simultaneous replacement of the chlorine atom by hydroxyl takes place, the product being quinizarin. In this case the yield obtained is nearly 10 per cent. of that theoretically possible, and prior to the discovery of the direct oxidation of anthraquinone to quinizarin this was the best method of preparing the substance.[5]

The condensation of phthalic anhydride with phenols under the influence of concentrated sulphuric acid has been extended to the preparation of 3-methyl quinizarin from phthalic anhydride and methylhydroquinone by Nietzki,[6] and to the preparation of various heteronuclear methyl-dihydroxy anthraquinones from 5-methyl phthalic acid and pyrocatechol and hydroquinone by Niementowski,[7] but the yields are unsatisfactory.

By using chlorphthalic acid in place of phthalic acid, heteronuclear chlorhydroxy anthraquinones can be obtained, and it has been claimed [8] that hydroquinone condenses readily under the influence of concentrated sulphuric acid with chlorinated phthalic acids, in which not more than one chlorine atom is in the *ortho-* position to a hydroxyl group. The reaction is described as taking place readily with 3-chlorphthalic acid, and particularly readily in the case of 4.5-dichlorphthalic acid, but as failing completely in the case of 3.6-dichlorphthalic acid and tetrachlorphthalic acid.

[1] Baeyer and Caro, B. **7**, 972 ; **8**, 152.
[2] Baeyer and Caro, B. **7**, 972 ; **8**, 152.   Schoeller, B. **21**, 2503.
[3] Grimm, B. **6**, 972 ; Baeyer and Caro, B. **7**, 972.
[4] B. **20**, 2068.
[5] Liebermann, B. **10**, 608 ; A. **212**, 10.
[6] B. **10**, 2011.   [7] B. **33**, 1631.
[8] M.L.B., D.R.P. 172,105.

Crossley [1] has investigated the condensation of 4-amino-phthalic acid with hydroquinone in the presence of sulphuric acid at 170–190°, and finds that the main product is 1.4.6-trihydroxyanthraquinone, although some 6-aminoquinizarin is also formed. Here apparently the amino group is replaced by hydroxyl, but the results must be accepted with some reserve, as Crossley states that his 1.4.6-trihydroxy compound did not melt at 300°, whereas Dimroth and Fick [2] give its melting point as 256°.

In some cases the yield of hydroxyanthraquinone is greatly improved by carrying out the condensation with concentrated sulphuric acid in the presence of boric acid, and by this means it has been claimed [3] that quinizarin can be obtained in 75 per cent. yield from phthalic anhydride and either hydroquinone or *p*-chlorphenol. In this case the improved yield is no doubt due to the formation of a boric ester hindering phthaleïn formation, but there is no information available to say whether boric acid has a similar beneficial influence on the condensation of phthalic anhydride with other phenols.

Boric acid alone at about 210° can also bring about the condensation between a phthalic acid and a phenol. Thus, Dimroth and Fick [4] obtained 1.2.4.6-tetrahydroxyanthraquinone by heating 4-hydroxyphthalic acid with hydroxyquinol triacetate and boric acid in benzoic acid solution. In the same way they obtained 1.4.6-trihydroxybenzoic acid from hydroxyphthalic acid and quinol, and 1-methyl-3.5.8-trihydroxyanthraquinone from coccinic acid and quinol diacetate.

As will be seen later, anhydrous aluminium chloride is almost invariably used in the synthesis of anthraquinone derivatives by the indirect method. In some cases, however, it leads to the anthraquinone compound in one step, and it has recently been found that hydroxyanthraquinones can be obtained by heating phthalic anhydride with phenols, naphthols, anthrols or hydroxyanthranols at 180–250° in

[1] Am. Soc. **40**, 404.
[3] By., D.R.P. 255,031
[2] A. **411**, 330.
[4] A. **411**, 325.

the presence of anhydrous aluminium chloride.[1] The reaction is best carried out by using a great excess of phthalic anhydride as a solvent. By this means hystazarin is obtained from pyrocatechol, no alizarin being formed.

III. Phthalic Acid Synthesis

This extremely important method of building up anthraquinone derivatives consists in first forming a phthaloyl derivative (*o*-benzoyl benzoic acid) by condensing phthalic anhydride with an aromatic compound, usually in the presence of anhydrous aluminium chloride, and then closing the anthraquinone ring by treatment with a dehydrating agent, such as concentrated sulphuric acid :

$$C_6H_4\begin{matrix} CO \\ \diagup \quad \diagdown \\ CO \end{matrix}O + C_6H_6 \ \rightarrow \ C_6H_4\begin{matrix} CO \\ \diagup \quad \diagdown \\ COOH \end{matrix}C_6H_5 \ \rightarrow \ C_6H_4\begin{matrix} CO \\ \diagup \quad \diagdown \\ CO \end{matrix}C_6H_4$$
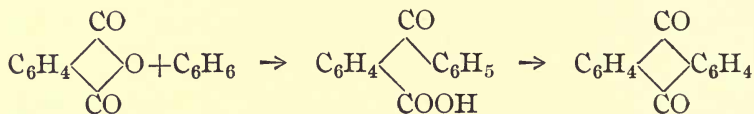
As the method is of very general application, and as the yields are often almost theoretical, it has met with very extended use, and many investigations have been carried out with a view to determining the optimum conditions.

The first step of the process, viz. the formation of the ketonic acid, is brought about by anhydrous aluminium chloride, and usually starts at or about the ordinary temperature, although as a rule is only completed by heating on the water bath for 6–12 hours, viz. until the evolution of hydrochloric acid gas ceases. In carrying out the reaction it is absolutely essential to use a whole (double) molecule of aluminium chloride, as although the action of the chloride is catalytic, it combines with the ketonic acid to form an addition compound, and is thus rendered inoperative.[2] Hence, if less than a molecular proportion is used the yields obtained are proportionally small. As a rule, the best solvents to use during the condensation are carbon bisulphide or light petroleum, but in some cases the use of a different solvent gives more satisfactory results. These will be discussed when dealing with the various classes of substance which have been

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[1] By., D.R.P. 298,345.　　[2] Heller and Schulke, B. **41**, 3627.

found to undergo the condensation. As a rule, the best procedure is to add 1 part of powdered aluminium chloride to 1½-2 parts of solvent, and then to add all at once an equimolecular mixture of finely powdered phthalic anhydride with the substance with which it is to be condensed. The reaction sets in either at the ordinary temperature or on gently warming and is completed by boiling under a reflux condenser until no more hydrochloric acid is evolved. Water is then added to destroy the aluminium chloride, and the solvent removed by distillation with steam. It is not generally necessary to purify the ketonic acid before converting it into the anthraquinone derivative, but if desired to do so it will often be found that the most satisfactory results are obtained by crystallising the ammonium salt.

In carrying out the above condensation it must be remembered that the aluminium chloride may bring about side reactions. Thus, if alkoxy groups are present in the molecule, partial or complete dealkylation will almost certainly be brought about, and if methyl groups are present intramolecular or intermolecular wandering of these may take place. The same remark also applies to some extent to halogen atoms, so that conclusions as to the orientation of groups in the finished product can only be drawn with great caution and, as far as possible, should be confirmed by independent methods. As the ketonic acids are stable substances it is often possible to introduce new groups into the molecule before closing the anthraquinone ring.

For closing the anthraquinone ring concentrated sulphuric acid (six to ten parts) is usually employed, but the ease with which water is lost varies very much with the individual compounds. Thus, naphthoyl benzoic acid loses water at 45–50°, whereas benzoyl benzoic acid requires a temperature of about 120°, and in other cases the reaction only takes place at temperatures of 150° or above. When this is the case sulphonation frequently takes place simultaneously. If the ketonic acid becomes sulphonated it is usually impossible to close the ring at all, whereas if ring formation precedes sulphonation the finished product is a sulphonic acid.

When trouble is experienced through sulphonation taking place it will often be found advantageous to use oleum containing from 10 to 30 per cent. of free anhydride in place of concentrated sulphuric acid, as if this is done it is usually possible to work at a much lower temperature, and by selecting suitable conditions it will often be found possible to close the ring without appreciable sulphonation taking place.[1] In any case the addition of boric acid is frequently advantageous, and the same remark applies when ordinary concentrated sulphuric acid is being used.

In addition to the danger of sulphonation taking place, the use of sulphuric acid has the drawback that it often demethylates methoxy groups when these are present, even when they have escaped the hydrolytic action of the aluminium chloride, and also in some cases brings about simultaneous oxidation. Thus, Gresly [2] condensed phthalic anhydride with pseudo-cumene and obtained a trimethyl benzoyl benzoic acid which, when heated with oleum, gave dimethyl-anthraquinone carboxylic acid and not the trimethylanthraquinone as expected.

In order to avoid such side reactions phosphorus pentoxide can be used in place of sulphuric acid,[3] and Elbs [4] has used phosphorus pentoxide in conjunction with sulphuric acid. In this latter case it is difficult to see what advantage phosphorus pentoxide and sulphuric acid can have over oleum, unless phosphoric acid has a beneficial action resembling that of boric acid.

Another method of closing the ring which has often proved of value in obstinate cases consists in reducing the ketonic group and thus obtaining the diphenyl methane derivative. The ring can then often be closed by means of sulphuric acid or oleum, zinc chloride or sodamide, and the

[1] Bentley, Gardner and Weizmann, Soc. **91**, 1630. Bentley and Weizmann, Soc. **93**, 435. Harrop, Norris and Weizmann, Soc. **95**, 1212. Walsch and Weizmann, Soc. **97**, 687. Bentley and Weizmann, Soc. **105**, 2748. Heller and Schülke, B. **41**, 3627. Mettler, B. **45**, 800. Gresly, A. **234**, 241.

[2] A. **234**, 238. *Cf.* also Ullmann, A. **388**, 217.

[3] Behr and van Dorp, B. **7**, 578. Bentley and Weizmann, Soc. **93**, 435. M.L.B., D.R.P. 194,328.

[4] J. pr. [2] **41**, 122.

resulting anthrone then oxidised to the anthraquinone. This method has often proved useful in the synthesis of the more complex anthraquinone derivatives, and is also often of service when it is desired to introduce a new group before closing the ring.[1]

HOMOLOGOUS ANTHRAQUINONES.—The phthalic acid synthesis originated in an observation by Friedel and Crafts,[2] that small quantities of anthraquinone were present in the products formed by the action of anhydrous aluminium chloride on phthalic anhydride in benzene solution, and at a later date [3] they extended their investigations to the products formed from toluene and xylene, and at the same time pointed out that acetic anhydride behaves in much the same way as phthalic anhydride, acetic anhydride and benzene giving acetophenone when treated with aluminium chloride. Previous to this Bürcker [4] had shown that succinic anhydride will condense with benzene in the presence of aluminium chloride to give β-benzoyl propionic acid.

The preparation of anthraquinone [5] itself from benzene and phthalic anhydride has been investigated in great detail, as at one time it was proposed to manufacture anthraquinone by this process, although the scheme was abandoned on account of the cost of the aluminium chloride.[6] The yields, however, are excellent, about 97 per cent. of the theoretically possible, and there is no difficulty in closing the anthraquinone ring by heating the benzoyl benzoic acid with ordinary concentrated sulphuric acid at 125–150°. If oleum is used instead of concentrated sulphuric acid, simultaneous sulphonation takes place with production of anthraquinone-β-sulphonic acid.[7] The condensation of the phthalic

[1] Gresly, A. **235**, 238. Bistrzycki and Schepper, B. **31**, 2793. Scholl, B. **44**, 1075. M. **32**, 687. Limpricht, A. **309**, 121. Weitz, A. **418**, 29. Seer, M. **33**, 540.
[2] Bl. **41**, 323.
[3] A. ch. [6] **14**, 446.
[4] A. ch. [5] **26**, 435.
[5] Friedel and Crafts, A. ch. [6] **14**, 446. Pechmann, B. **13**, 1612. Haller and Guyot, C. r. **119**, 139. Gresly, A. **234**, 238. Graebe and Ullmann, A. **291**, 9. Elbs, J. pr. [2] **41**, 1. Heller, Z. ang. **19**, 669. Heller and Schülke, B. **41**, 3627. Rubidge and Qua. Am. Soc. **36**, 732.
[6] Heller, Z. ang. **19**, 669.
[7] Liebermann, B. **7**, 805.

anhydride with benzene is most conveniently effected by using a large excess of the hydrocarbon as a solvent, and the same is true when methyl anthraquinones are being prepared from toluene or the xylenes.

From toluene [1] the main product obtained is β-methyl-anthraquinone, from *o*-xylene [2] 2.3-dimethylanthraquinone, from *m*-xylene [3] 1.3-dimethylanthraquinone and from *p*-xylene [4] 1.4-dimethylanthraquinone. Pseudo-cumene gives 1.2.3-trimethylanthraquinone,[5] although, as has already been pointed out, the final closing of the ring by means of sulphuric acid is apt to be accompanied by simultaneous oxidation of one methyl group to carboxyl. Scholl [6] has prepared ethyl, propyl and *iso*-propyl anthraquinone from phthalic anhydride and ethyl, propyl, and *iso*-propyl benzene. Condensation between phthalic anhydride and naphthalene [7] takes place with great ease, and the resulting naphthoyl benzoic acid loses water very readily when warmed to 45–50° with concentrated sulphuric acid, the product being 1.2-benzanthraquinone. This compound and its derivatives are treated in greater detail in Chapter VII., but here it may be pointed out that so easily does naphthalene condense with phthalic anhydride that the reaction may be carried out in benzene, toluene or xylene solution without the solvent being attacked, provided no excess of phthalic anhydride is used. Benzene, in fact, is the best solvent to employ.

Anthracene [8] also condenses readily with phthalic anhydride, and here again benzene is the best solvent provided an excess of phthalic anhydride is avoided.

[1] Friedel and Crafts, A. ch. [6] **14**, 446. Limpricht, A. **299**, 300. Limpricht and Wiegand, A. **311**, 181. Heller and Schülke, B. **41**, 3627. Elbs, J. pr. [2] **41**, 4.

[2] F. Meyer, B. **15**, 636. Limpricht, A. **312**, 99. Elbs, J. pr. [2] **41**, 6; B. **20**, 1361. Heller, B. **43**, 2891.

[3] F. Meyer, B. **15**, 637. Gresly, A. **234**, 238. Elbs, J. pr. [2] **41**, 13; B. **20**, 1364. Scholl, B. **43**, 353.

[4] Gresly, A. **234**, 238. Elbs, J. pr. [2] **41**, 27. Heller, B. **43**, 2892.

[5] Gresly, A. **234**, 238. Elbs, J. pr. [2] **41**, 122.

[6] M. **32**, 687.

[7] Elbs, B. **19**, 2209. Gabriel and Colman, B. **33**, 448. Heller and Schülke, B. **41**, 3627. Heller, D.R.P. 193,961.

[8] Heller and Schülke, B. **41**, 3627; **45**, 669. Heller, D.R.P. 193,961. *Cf* also Schaarschmidt, B. **49**, 381.

Treatment of the product with dehydrating agents, however, does not lead to an anthraquinone, but to rupture of the molecule with formation of anthracene and phthalic acid, so that the phthaloyl group is probably attached to the *ms*-carbon.

Phthalic anhydride will also condense with phenanthrene,[1] and the phenanthroyl benzoic acid, when treated with phosphorus pentoxide, gives an anthraquinone derivative which is probably 1.2.3.4-dibenzanthraquinone and has the structure

$$\begin{matrix} C_6H_4-C-CO \\ | \quad\quad || \quad\quad >C_6H_4, \\ C_6H_4-C-CO \end{matrix}$$ although this has never been proved.

Elbs[2] and Kaiser[3] were only able to condense one molecule of phthalic anhydride with one molecule of diphenyl, thus obtaining phenylbenzoyl benzoic acid which they could not transform into an anthraquinone derivative. Scholl[4] at a later date reinvestigated the subject and succeeded in closing the ring by heating phenyl benzoyl benzoic acid alone at 340°, or with aluminium or zinc chloride at 150°. In both cases, however, the yields were very poor. Benzoyl benzoic acid itself is readily and quantitatively reduced to the diphenyl methane derivative by ammonia and zinc dust in the presence of copper sulphate, but in the case of phenyl benzoyl benzoic acid the yield by this method was only 15 per cent. By using a mixture of caustic soda, ammonia, ammoniacal copper sulphate and zinc dust, however, Scholl obtained an almost quantitative yield of the phenyl diphenyl methane carboxylic acid, although the reaction was slow and required 144 hours. From this compound he was unable to split out water by means of sulphuric acid, owing to sulphonation taking place, but by heating with zinc chloride or sodamide at 190° he obtained phenyl anthrone, from which β-phenylanthraquinone was obtained by oxidation. Scholl[5] also succeeded in condensing one molecule of diphenyl with two molecules of phthalic anhydride, and from the product he obtained 2.2'-dianthraquinonyl.

[1] M.L.B., D.R.P. 194,328. [2] J. pr. [2] 41, 145.
[3] A. 257, 95. [4] B. 44, 1075. [5] B. 44, 1086.

Scholl found that *o*-ditolyl[1] will also condense with two molecules of phthalic anhydride, but a dimethyl dianthraquinonyl can only be obtained from the product with the utmost difficulty. As it gives no pyranthrone it must be 3.3'-dimethyl-2.2'-dianthraquinonyl. *p*-Ditolyl, on the contrary, will only condense with one molecule of phthalic anhydride, and the product tends to pass into a phthalide, rather than into an anthraquinone.[2] By reduction, dehydration, and subsequent oxidation, however, 1-methyl-4-*p*-tolyl anthraquinone can be obtained.[3]

as-Dixylyl (2.4.2'.4'-tetramethyl diphenyl) condenses with two molecules of phthalic anhydride to produce a mixture of phthaloylic acids. From these 2.4.2'.4'-tetramethyl-1-1'-dianthraquinonyl[4] can be obtained by treatment with concentrated sulphuric acid at 100°.

HALOGENATED ANTHRAQUINONES.—Homonuclear halogen anthraquinones can be formed by the phthalic acid synthesis either by condensing phthalic acid with an aromatic halogen compound, or by condensing a halogenated phthalic acid with an aromatic hydrocarbon. Heteronuclear halogen anthraquinones are, of course, obtained when a halogenated phthalic acid is condensed with an aromatic halogen compound. Halogen compounds are also sometimes obtained by halogenating the benzoyl benzoic acid and then closing the ring. By this last method Mettler[5] obtained a dichlordihydroxy anthraquinone by chlorinating the dihydroxy benzoyl benzoic acid obtained by the oxidation of fluoresceïne, and then closing the ring, and 1-amino-4-chloranthraquinone has been obtained by preparing 3-acetyl amino benzophenone-3'-carboxylic acid and then treating with dehydrating agents.[6] The method, however, has been very little developed.

The formation of homonuclear halogen anthraquinones from phthalic anhydride and aromatic halogen compounds has been fairly fully investigated. Chlorobenzene[7] and

[1] B. **44**, 1091.   [2] Scholl, B. **44**, 1091.
[3] Seer, M. **33**, 540.   [4] Scholl, B. **43**, 512.
[5] B. **35**, 800.   [6] Agfa, D.R.P. 254,091.
[7] M.L.B., D.R.P. 75,288.

bromobenzene [1] lead to the corresponding β-halogen anthraquinones, and *p*-chlortoluene leads, of course, to 1-methyl-4-chloranthraquinone.[2] From *o*-chlortoluene Heller and Schülke [3] obtained a methylchloranthraquinone which on oxidation and subsequent loss of carbon dioxide passed into β-chloranthraquinone, thus showing that the product was either 1-methyl-2-chlor-anthraquinone or 3-methyl-2-chloranthraquinone. Ullmann [4] proved the latter of these to be correct by oxidising it to the corresponding carboxylic acid and then condensing with aniline. The resulting anilidoanthraquinone carboxylic acid by loss of water passed into an acridone which was neither anthraquinone-1.2-acridone nor anthraquinone-2.1-acridone, and hence must have been anthraquinone-2.3-acridone.

The condensation of phthalic anhydride with *o*-, *m*-, and *p*-brom toluene has been studied by Heller,[5] who finds that in each case a mixture of methylbrombenzoylbenzoic acids is formed, but that from each of these mixtures the same methyl brombenzoyl benzoic acid can be isolated and that this by loss of water passes into 2.3-methylbromanthraquinone. From this it is clear that in the case of *m*- and *p*-bromtoluene the aluminium chloride has caused either the methyl group or the bromine atom to wander, and as the same phenomenon is not observed in the cases of the corresponding chlortoluenes, it is probable that it is the bromine atom that has changed its position. The wandering of bromine atoms under the influence of aluminium chloride has, of course, long been known; Roux,[6] for example, having shown that aluminium chloride is capable of converting a-bromnaphthalene into β-bromnaphthalene.

The condensation of 3.6-dichlorphthalic acid and 2.4-dichlorphthalic acid with aromatic hydrocarbons has been studied by several investigators,[7] without any results of

[1] Ullmann, A. **380**, 337.
[2] Heller and Schülke, B. **41**, 3627.   Heller, B. **45**, 792.
[3] Heller and Schülke, B. **41**, 3627.   Heller, B. **45**, 792.
[4] B. **47**, 553.
[5] B. **47**, 792.   [6] A. ch. [6] **12**, 334.
[7] Harrop, Norris and Weizmann, Soc. **95**, 1212.   Ullmann and Biliig, A. **381**, 1.   Le Royer, A. **238**, 356.   Rée, A. **234**, 239.

particular interest being recorded, although it is worth noting that the ketonic acid obtained from 3.6-dichlorphthalic acid and *m*-xylene only passes into the anthraquinone with the utmost difficulty, and yields of over 5 per cent. could not be obtained.[1] Tetrachlorphthalic acid has also been employed for preparing homonuclear tetrachloranthraquinone.[2]

A large number of heteronuclear chloranthraquinones have been obtained by Hofmann [3] by condensing various chlorphthalic acids with aromatic halogen compounds, but they are of no particular interest.

HYDROXYANTHRAQUINONES.—Phthalic acid as a rule will not condense with free phenols under the influence of aluminium chloride to produce a hydroxybenzoyl benzoic acid, as a phthaleïn is usually the sole product, although recently Ullmann and Schmidt [4] have found that in many cases a good yield of the hydroxybenzoyl benzoic acid can be obtained if the condensation is carried out in tetrachlorethane solution. It is too early to say if this method is a general one and is applicable to all phenols, but from the results already published its value is obvious. When phthalic acid itself is used the carbonyl group prefers the *ortho*- position with reference to the hydroxyl group, although small amounts of other isomers are formed simultaneously, and when tetrachlorphthalic acid is employed it is exclusively the *ortho*- position which is taken. It is interesting to notice that the condensation of phthalic anhydride with *p*-chlorphenol under the influence of aluminium chloride leads to a mixture of *p*-chlorhydroxybenzoyl benzoic acid and 1.4-hydroxychloranthraquinone, the conversion of the former into the latter being completed by warming with concentrated sulphuric acid,[5] whereas as already stated the direct condensation of phthalic anhydride with *p*-chlorphenol by sulphuric acid leads only to quinizarin.[6]

[1] Harrop, Norris and Weizmann, Soc. **95**, 1212.

[2] Kircher, A. **238**, 344.　　　　　　　　[3] M. **36**, 805.

[4] Ullmann and W. Schmidt, B. **52**, 2098. Ullmann and Conzetti, B. **53**, 830. Ullmann, D.R.P. 292,066.

[5] Ullmann, D.R.P. 282,493.

[6] Liebermann, A. **212**, 10; B. **10**, 608. By., D.R.P. **255,031**. See also pp. 128, 129.

The condensation of phthalic anhydride with phenols can often be brought about with satisfactory results by first methylating the hydroxyl groups, as this hinders phthaleïn formation. During the condensation, however, the aluminium chloride usually causes partial or complete demethylation, and methoxy groups which escape hydrolysis by the aluminium chloride are usually demethylated during the closing of the anthraquinone ring. This method was used by Lagodzinski,[1] who obtained quinizarin from quinol dimethyl ether, and hystazarin from veratrol, but Nourrison [2] had previously shown that β-hydroxyanthraquinone could be obtained from anisol. It has also been used to a considerable extent by Weizmann [3] and his students, who have obtained various hydroxyanthraquinone derivatives by condensing phthalic acid or a methoxy phthalic acid, such as hemipinic acid with aromatic hydrocarbons or phenolic ethers.

The preparation of hydroxyanthraquinones from phenols can also be effected without protecting the hydroxyl groups if boric acid is used in place of aluminium chloride. This method was first introduced by Deichler and Weizmann,[4] who obtained hydroxynaphthoyl benzoic acid by heating α-naphthol with phthalic anhydride and boric acid at 190°, and has been extended by Weizmann and his students,[5] who have prepared numerous hydroxyanthraquinone derivatives from phthalic acid or hydroxy phthalic acid and various phenols such as the cresols. Frey [6] has used the method for condensing various dichlorphthalic acids with hydroquinone, Hövermann [7] has condensed tetrachlorphthalic acid with hydroquinone, and Dimroth and Fick [8] have condensed phthalic acid, 4-hydroxyphthalic

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[1] B. **28**, 117 ; A. **342**, 90.

[2] B. **19**, 2105.

[3] Bentley, Gardner and Weizmann, Soc. **91**, 1630.   Bentley and Weizmann, Soc. **93**, 435.   Walsch and Weizmann, Soc. **97**, 687.   Bradbury and Weizmann, Soc. **105**, 2748.   *Cf.* also Bistrzycki and Schepper, B. **31**, 2793.

[4] Deichler and Weizmann, B. **36**, 547.

[5] Bentley, Gardner and Weizmann, Soc. **91**, 1630.

[6] B. **45**, 1358.

[7] B. **47**, 1210.   [8] A. **411**, 315

acid and coccinic acid (6-methyl-4-hydroxyphthalic acid) with hydroquinone and hydroxyhydroquinone. In the case of hydroxyhydroquinone they find it best to use the triacetyl derivative, and find that the reaction takes place most easily when benzoic acid is used as a solvent. Even by the use of boric acid as a condensing agent phthaleïn formation cannot be altogether avoided, a phthaleïn, for example, being the sole product formed when 4-hydroxy phthalic acid is condensed with *o*-cresol.

Schaarschmidt [1] condensed phthalic acid with α-anthrol by the use of boric acid, but was unable to close the ring.

MISCELLANEOUS SUBSTANCES.—*Carboxylic acids* can sometimes be obtained by the phthalic acid synthesis, although the method has not been developed to any extent. The preparation of dimethyl anthraquinone carboxylic acid by Gresly [2] has already been mentioned, and the preparation of anthraquinone-β-carboxylic acid by oxidising toluyl benzoic acid and then closing the ring has been the subject of a patent.[3] It is claimed that oxidising the methyl group before closing the ring leads to a much purer product. Graebe and Blumenfeld,[4] and Graebe and Leonhardt,[5] obtained anthraquinone α-carboxylic acid from hemimellitic acid and benzene in the usual way, but in some cases the presence of the carboxyl group seems to hinder the closing of the ring. Thus, Heller and Schülke [6] condensed phthalic acid with *p*-chlortoluene and then oxidised the methyl group to carboxyl, but were unable to close the ring although before oxidation the ring closed quite easily, and they experienced no difficulty in oxidising 1-methyl-4-chloranthraquinone to the corresponding carboxylic acid.

One or two *tertiary amino anthraquinones* have been obtained by the phthalic acid synthesis, as Haller and Guyot [7] have found that phthalic anhydride will condense with tertiary aromatic amines which have a free *para-*

[1] B. **49**, 381.   [2] See p. 132.
[3] M.L.B., D.R.P. 80,407.   [4] B. **30**, 1116.
[5] A. **290**, 231.   [6] B. **41**, 3627.
[7] Bl. [3] **25**, 166; C. r. **119**, 139. *Cf.* Société anonyme des Matières Colorantes, D.R.P. 108,837; 112,913; 112,297; 114,197-8. Also Weitz, A. **418**, 29.

position such as dimethyl aniline, diethyl aniline and ethyl benzyl aniline, and Scholl and Neovious [1] have condensed two molecules of phthalic anhydride with one molecule of carbazol.

Thianthrene and *thiodiphenylamine* will also condense with either one or two molecules of phthalic anhydride, and the rings can be closed by means of zinc chloride or concentrated sulphuric acid.[2]

One or two variations of the usual phthalic acid synthesis have been described although they have not led to any important results. Thus, Louise [3] condensed benzoyl chloride with mesitylene and then oxidised one of the methyl groups of the resulting trimethyl benzophenone to carboxyl. The monocarboxylic acid thus obtained when treated with dehydrating agents passed into 1.3-dimethylanthraquinone.

Limpricht [4] endeavoured to carry out a somewhat similar synthesis. He condensed phthalic acid with *o*-xylene and then oxidised both methyl groups to carboxyl. He then condensed the resulting benzophenone tricarboxylic acid with toluene, but subsequent treatment with a dehydrating agent failed to give a diquinone. Methods of this nature would seem capable of further development and should lead to interesting results.

[1] B. **44**, 1249. [2] Scholl and Seer, B. **44**, 1233.
[3] A. ch. [6] **6**, 233. [4] A. **312**, 99.

THE BENZANTHRAQUINONES

THERE are two possible anthraquinones in which one of the benzene rings has been replaced by a naphthalene ring, viz.—
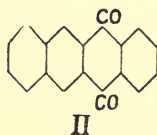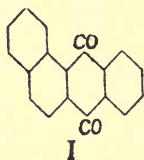
and both are known. In the literature they are usually designated respectively as naphthanthraquinone and naphthacenquinone; but this nomenclature is open to many objections, and it is much better to adopt Scholl's system and denote them as 1.2-benzanthraquinone or *ang.*-benzanthraquinone (I) and 2.3-benzanthraquinone or *lin.*-benzanthraquinone (II).

Compounds containing five rings have also been prepared, and of course the isomerism in this case becomes more complicated. Most of the derivatives described up to the present, however, are *linear*, the parent quinone (III) being named dinaphthanthraquinone, although here again it is preferable to adopt Scholl's system of nomenclature and designate it as *lin.*-dibenzanthraquinone or 2.3.6.7-dibenzanthraquinone—
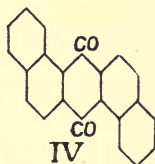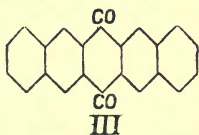
Compounds of this nature are, of course, capable of forming numerous mono-, di-, and tri-quinones, and several such derivatives have been isolated.

trans-bisang.-Dibenzanthraquinone or 1.2.5.6-dibenzanthraquinone (IV) has also been synthesised, but its derivatives have not been studied.

I. *ang.*-BENZANTHRAQUINONE (NAPHTHANTHRAQUINONE)

ang.-Benzanthraquinone is extremely easily obtained from naphthalene by the phthalic acid synthesis,[1] either by using carbon disulphide as a solvent,[2] or, preferably, by carrying out the reaction in benzene or toluene solution, as the phthalic anhydride condenses with the naphthalene so readily that the solvent remains unaffected provided no excess of phthalic anhydride is used.[3] The structure of the quinone was proved by Scholl,[4] who showed that oxidation with potassium chlorate, nitric acid, chromic acid or potassium permanganate and sulphuric acid led to anthraquinone-1.2-dicarboxylic acid, yields of 75 per cent. being obtainable when the oxidation is carried out with permanganate.

ang.-Benzanthraquinone is a powerful vat dye (Sirius Yellow G) and has considerable affinity for vegetable fibres although used chiefly as a pigment. On reduction by distillation with zinc dust [5] or by boiling with zinc dust and ammonia [6] it yields the parent hydrocarbon (*ang.*-benzanthracene), which reverts to the quinone when oxidised.

Very few homologues of *ang.*-benzanthraquinone have been described. From α-methylnaphthalene Scholl [7] obtained a monomethyl compound which was probably 3-methyl-1.2-benzanthraquinone. β-Methyl naphthalene also readily condensed with phthalic anhydride, but the resulting methylnaphthoyl benzoic acid would not pass into a quinone,

so that in this case it is probable that the carbonyl group had become attached to the α-carbon atom which was next to the methyl group.

From α-chlornaphthalene and phthalic anhydride Heller [1] obtained 3-chlor-1.2-benzanthraquinone, but β-chlornaphthalene led to a chlor-2.3-benzanthraquinone. Graebe and Peter [2] condensed 3.6-dichlorphthalic acid with naphthalene, but the closing of the anthraquinone ring was accompanied by sulphonation, so that dichlor-1.2-benzanthraquinone sulphonic acid was obtained. As naphthanthraquinone itself is not sulphonated under similar conditions it is probable that the sulphonic acid group enters the benzene and not the naphthalene ring.

The hydroxy *ang.*-benzanthraquinones have been very little investigated. Scholl [3] condensed phthalic anhydride with 1-methyl-2-methoxy naphthalene and then, after reducing the ketonic acid, closed the ring and finally oxidised to the quinone. As the quinone when oxidised gave anthraquinone-1.2-dicarboxylic acid, the methoxy and methyl groups must be in the benzene ring, and the quinone probably has the structure I.
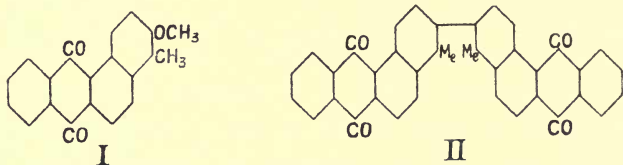
By demethylating the free hydroxy compound could be obtained, but it was found impossible to replace the hydroxyl group by an amino group. If, however, the methyl methoxy naphthoyl benzoic acid was demethylated there was no difficulty in replacing the hydroxyl group by an amino group, and the anthraquinone ring could then be closed by the action of dilute oleum. By this means Scholl was able to obtain an amino methyl benzanthraquinone in which the amino group could be replaced by chlorine or iodine in the

[1] B. **45**, 669. *Cf.* G.C.I.B., D.R.P. 230,455.   [2] A. **340**, 265.
[3] M. **33**, 507.

usual way. The iodo compound when heated with copper powder gave a dimethyl di-benzanthraquinonyl (II), and the fact that this gave no pyranthrone dye when fused with caustic potash supports Scholl's views as to the position of the methyl groups.

When *ang.*-benzanthraquinone is nitrated [1] two mono-nitro compounds (IV and V) are formed :
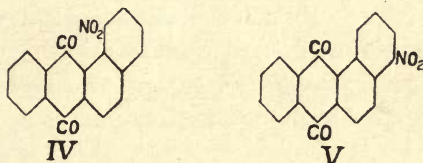
The structure assigned to these is based on their behaviour when reduced, as one of them (IV) gives a pyrrol derivative whereas the other (V) gives an amino compound. As this amino compound gives no vat dye either when fused with caustic potash or when heated with antimony pentachloride, it is extremely improbable that the amino group is in the anthraquinone ring, and as the nitro group invariably enters the naphthalene ring in the α-position formula V is reasonably certain.

II. *lin.*-BENZANTHRAQUINONE (NAPHTHACENEQUINONE)

When phthalic anhydride is condensed with succinic acid by heating with sodium or potassium acetate, a substance is formed which is now known to be ethine diphthalide (I) although it was originally regarded as bisdiketohydrindene [2]—

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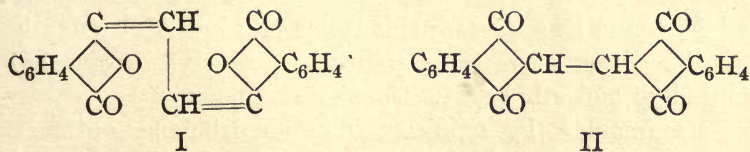
[1] Scholl, B. **44**. 2370.

[2] Gabriel and Michael, B. **10**, 1559. Gabriel, B. **17**, 2531. Gabriel and Leupold, B. **31**, 1159. Roser, B. **17**, 2619. *Cf.* also B. **10**, 391, 2199 ; **11**, 1007.

Nathanson,[1] and Gabriel and Leupold [2] have shown that this substance undergoes a remarkable rearrangement when treated with sodium methylate, both the lactone rings being opened and loss of two molecules of water subsequently taking place between the carboxyl groups and the hydrogen atoms of the aliphatic chain, with the formation of bisdiketo hydrindene (II) and *iso*-ethine diphthalide, the ketonic form of this latter substance being identical with dihydro *lin.*-benzanthradiquinone :

iso-Ethinediphthalide or dihydro-*lin.*-Benzanthradiquinone.
Enolic form.   Ketonic form.

Dihydro-*lin.*-benzanthradiquinone is, of course, also the ketonic form of dihydroxy-*lin.*-benzanthraquinone.

The above rearrangement is fairly general and is shown also by the condensation product obtained by heating phthalic anhydride with acetic acid and sodium or potassium acetate, although in this case the formation of only one compound is possible, viz. diketohydrindene :
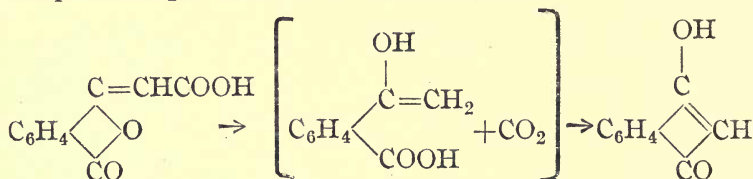
Diketohydrindene.
Enolic form.

As would be expected, this compound is formed directly by the action of metallic sodium on a mixture of ethyl phthalate and ethyl acetate.[3]

Kaufmann [4] by oxidising diketohydrindene obtained two products, one of which he regarded as bisdiketohydrindene, although it differs completely from Nathanson's

[1] B. **26**, 2582.   [2] B. **31**, 1160.
[3] Wislicenus, B. **20**, 593 ; A. **246**, 347 ; **252**, 72.   [4] B. **30**, 382.

product, and the other of which he named indenigo and ascribed to it the formula :

$$C_6H_4 \diagdown \begin{array}{c} CO \\ \\ CO \end{array} \diagup C=C \diagdown \begin{array}{c} CO \\ \\ CO \end{array} \diagup C_6H_4$$
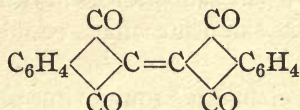
although Gabriel and Leupold [1] have since shown that indenigo is almost certainly identical with their *iso*-ethine diphthalide.

The reduction of *iso*-ethine diphthalide was also effected by Gabriel and Leupold,[2] who thereby obtained two hydrocarbons, viz. $C_{18}H_{12}$, which they named naphthacene (*lin.*-benzanthracene), and its dihydro compound $C_{18}H_{14}$ (dihydronaphthacene or dihydro-*lin.*-benzanthracene). Both on oxidation give *lin.*-benzanthraquinone (naphthacenquinone). This latter substance forms yellow needles which melt at 294°, and when fused with caustic potash is decomposed into benzoic acid and β-naphthoic acid.

Nothing is known of the homologues of *lin.*-benzanthraquinones, and in fact, up to the present the hydroxyl derivatives are the only ones which have been studied in any detail. By treating *iso*-ethine diphthalide with phosphorus pentachloride Gabriel and Leupold obtained 1.4-dichlor-2.3-benzanthraquinone. In this the chlorine atoms are fairly reactive, so that boiling for ten minutes with aniline sufficed to convert it into the dianilido compound.

The *hydroxy derivatives* have been studied chiefly by Weizmann and his students, although Liebermann and Voswinckel,[3] by heating 1-methyl-3-hydroxybenzene-4.5.6-tricarboxylic acid to 200° with succinic acid and potassium acetate, obtained a substituted ethine diphthalide which by treatment with sodium methylate gave a dimethyltetrahydroxy-*lin.*-benzanthraquinone :
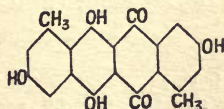
[1] B. **31**, 1272.   [2] *Cf.* also Deichler and Weizmann, B. **36**, 547.
[3] B. **37**, 3344.

This very closely resembled the substance obtained by heating carminic acid to 200° in the air, although owing to the insolubility of the substance in all solvents except caustic alkali the identification could not be made complete.

Deichler and Weizmann [1] found that phthalic acid would condense with α-naphthol when heated in the presence of boric acid, and the resulting 1-hydroxy-2-*o*-naphthoyl benzoic acid when heated with concentrated sulphuric acid passed into 1-hydroxy-2.3-benzanthraquinone, and the synthesis of hydroxy *lin.*-benzanthraquinones by this method is fairly general. Thus Deichler and Weizmann [2] condensed phthalic acid with 1-naphthol-4-, 5-, and 8-sulphonic acids, and Bentley, Friedl, Thomas, and Weizmann [3] extended the method to 1.5-dihydroxy naphthalene. In this latter case two molecules of phthalic acid condensed with one molecule of the naphthol; but subsequent treatment with sulphuric acid led to the closing of only one ring, as the second phthaloyl group split off and was replaced by a hydroxyl group, the final product obtained being 4-hydroxy-Bz.-1.2-dihydroxy-2.3-benzanthraquinone.

Hydroxy derivatives have also been obtained by condensing 4-hydroxy phthalic acid,[4] 3-methoxy phthalic acid,[5] and hemipinic acid [6] with naphthols, and nitro-hydroxy compounds have been obtained from nitrophthalic acid,[7] and chlorhydroxy compounds from 3.6-dichlorphthalic acid and tetrachlorphthalic acid.[8] In some cases the closing of the anthraquinone ring can only be effected by very drastic treatment, such as heating to 130° with oleum containing 70 per cent. of free anhydride, and under these conditions sulphonation and hydroxylation often take place simultaneously. To some extent this can be avoided by dissolving the naphthoyl benzoic acid in concentrated sulphuric acid and boric acid, and then adding oleum slowly.

[1] B. **36**, 547.   [2] D.R.P. 134,985.   [3] Soc. **89**, 115 ; **91**, 1588.
[4] Orchardson and Weizmann, Soc. **89**, 115.   [5] *Ibid.*
[6] Bentley, Friedl, and Weizmann, Soc. **91**, 1588.   [7] *Ibid.*
[8] Harrop, Norris, and Weizmann, Soc. **95**, 279.

Hydroxyl groups can also be inserted into the molecule by direct oxidation with oleum and boric acid, nitrosyl sulphuric acid, or by fusion with caustic potash and potassium chlorate, and by this means 1.4-dihydroxy-2.3-benzanthraquinone (*iso*-ethinediphthalide) has been obtained from 1-hydroxy-2.3-benzanthraquinone.[1]

When sulphonic acid groups are present in the molecule they can be replaced by hydroxyl groups by fusion with caustic alkali, although this method has been very little applied.[2] Weizmann[3] records one case in which an amino group is replaced by hydroxyl by fusion with caustic alkali, but as a rule he appears to find it best to carry out the replacement by means of the diazo- reaction.[4]

Halogen atoms when present in a hydroxynaphthoyl benzoic acid are often replaced by hydroxyl groups when the ring is closed, and Weizmann has obtained several hydroxy 1.2-benzanthraquinones by brominating the hydroxynaphthoyl benzoic acid and then closing the ring.[5] Under suitable conditions it is usually possible to obtain a certain amount of the bromohydroxy quinone at the same time, and chlorine atoms seem to be much more firmly bound than bromine atoms, as 1-hydroxy-4-chlor-naphthoyl-(2)-*o*-benzoic acid, obtained by treating the hydroxynaphthoyl benzoic acid with sulphuryl chloride, gives 1.4-hydroxychlor-2.3-benzanthraquinone.[6]

As regards the relationship between the colour of the hydroxy compounds and the position of the hydroxyl groups, Weizmann[7] considers that hydroxyl groups in the naphthalene ring tend to deepen the colour, whereas when in the benzene ring the tendency is rather to lessen it. Baly and Tuck[8] have examined the absorption spectra of some of

[1] Deichler and Weizmann, B. **36**, 719. D.R.P. 138,324–5.
[2] Deichler and Weizmann, B. **36**, 719. Bentley, Friedl, Thomas, and Weizmann, Soc. **91**, 411.
[3] Soc. **91**, 411.
[4] Deichler and Weizmann, B. **36**, 2326.
[5] Orchardson and Weizmann, Soc. **89**, 115. Bentley, Friedl, Thomas, and Weizmann, Soc. **91**, 411. Harrop, Norris, and Weizmann, Soc. **95**, 279.
[6] Geigy, D.R.P. 226,230.
[7] Soc. **91**, 411.
[8] Soc. **91**, 426.

the hydroxy compounds, but as very few of the large number of possible compounds have been described, the data available are insufficient to justify any generalisation.

Very few *halogen derivatives* other than hydroxy halogen compounds have been described, but Orchardson and Weizmann,[1] by treating hydroxynaphthoyl benzoic acid with phosphorus pentachloride, obtained the corresponding chloro acid, from which 1-chlor-2.3-benzanthraquinone was obtained. At the same time they obtained a bright red compound which they regarded as an isomeric chlorobenzanthraquinone although their analytical figures hardly support this assumption (found, Cl=11·2 ; calculated, Cl=12·1). By brominating their chlornaphthoyl benzoic acid Orchardson and Weizmann obtained a bromo compound from which they obtained 1-chlor-3-brom-2.3-benzanthraquinone, but could not obtain it in a pure condition owing to the tendency to split off hydrobromic acid.

Heller,[2] by condensing phthalic acid with β-chlornaphthalene, obtained a chlornaphthoyl benzoic acid from which a quinone was obtained by loss of water. This he originally believed to be 4-chlor-1.2-benzanthraquinone, but at a later date found that on oxidation it gave anthraquinone-2.3-dicarboxylic acid, and hence must be Bz.-2-chlor-2.3-benzanthraquinone.[3] The preparation of the 1.4-dichlor compound by the action of phosphorus pentachloride on *iso*-ethinediphthalide has already been mentioned.[4]

A *mononitro compound* was obtained by Gabriel and Leupold [5] by nitrating *lin.*-benzanthraquinone, but they did not determine the position of the nitro group. Deichler and Weizmann,[6] by nitrating 1-hydroxy-2.3-benzanthraquinone, obtained 1-hydroxy-4-nitro-2.3-benzanthraquinone, from which by reduction and diazotisation the dihydroxy compound (*iso*-ethinediphthalide) was obtained, thus determining the position of the nitro group. Further

[1] Soc. **89**, 115. *Cf.* Pickles and Weizmann, Proc. **20**, 220.
[2] B. **45**, 669.   [3] B. **46**, 1497.   [4] Page 147.
[5] B. **31**, 1272.   [6] B. **36**, 2326.

nitration led to a dinitro compound. The analytical values found for both the mono- and the dinitro compounds are in very poor agreement with the calculated values, so that pending further investigation it cannot be assumed that either compound was obtained in a state of purity.

By nitrating methoxy naphthoyl benzoic acid Orchardson and Weizmann [1] obtained a nitro compound but were unable to convert it into the quinone, as sulphuric acid caused decomposition.

Hydroxy *amino derivatives* have been obtained by Deichler and Weizmann,[2] and by Bentley, Friedl and Weizmann [3] by the reduction of the nitrohydroxy compounds, although here again the analytical figures given leave the purity of some of the substances described open to doubt. Amino groups have also been introduced into the molecule by coupling the hydroxy compounds with benzene diazonium chloride and then reducing the azo dye formed.[4] Negative groups or atoms when present in the molecule are usually fairly readily replaced by arylamino groups by boiling with primary aromatic amines,[5] although in those chloro- compounds obtained from chlorinated phthalic acid the data available point to its only being those chlorine atoms which are in the α-position which react in this way.

Amino groups can also be introduced into the molecule before closing the anthraquinone ring, either by nitration and reduction, or by forming an azo- dye and then reducing this. In the case of 4-amino-1-hydroxy-naphthoyl (2)-benzoic acid the formation of the quinone takes place with very great ease, it being sufficient to boil with nitrobenzene,[6] and the same amino-hydroxy quinone is formed

[1] Soc. **89**, 115.
[2] B. **34**, 2326.
[3] Soc. **91**, 1588.
[4] Harrop, Norris, and Weizmann. Soc. **95**, 279.
[5] Gabriel and Leupold, B. **31**, 1272. Orchardson and Weizmann, Soc. **89**, 115. Bentley, Thomas, Friedl, and Weizmann, Soc. **91**, 411. Harrop, Norris, and Weizmann, Soc. **95**, 279.
[6] Bentley, Friedl, Thomas, and Weizmann, Soc. **91**, 411.

directly when the corresponding hydroxy nitronaphthoyl benzoic acid is reduced with zinc and acetic acid.[1]

The only amino-*lin.*-benzanthraquinone which contains no other substituents to have been described up to the present seems to be 1-amino-2.3-benzanthraquinone,[2] which was obtained by heating the corresponding hydroxy compound with aqueous ammonia at 200°.

III. *lin.*-BENZANTHRADIQUINONE (NAPHTHACENDIQUINONE)

Of the numerous *lin.*-benzanthradiquinones which are theoretically possible, only one, viz. 2.3-benz-1.4.9.10-anthradiquinone, has been described up to the present. This was obtained by Gabriel and Leupold [3] by oxidising 1.4-dihydroxy-2.3-benzanthraquinone (*iso*-ethinediphthalide) with nitric acid, and Deichler and Weizmann [4] have shown that the reverse change can be brought about by mild reducing agents such as ammonium sulphide or ferrous salts.

The reactions of the diquinone have not been studied in any great detail, but from the investigations which have appeared it would seem that one of the quinone rings is somewhat easily ruptured. Voswinckel [5] has studied the action of the halogens on the diquinone and has found that treatment with chlorine leads to the addition of two chlorine atoms with the formation of a dichloride (I), which when warmed with caustic soda undergoes rupture of one ring with the formation of a ketonic acid (III), although at the same time a small quantity of *iso*-ethinediphthalide (IV) is formed. Probably the first action of the alkali is to bring about the formation of a ketone hydrate [6] (II), subsequent loss of two molecules of hypochlorous acid then taking place.

[1] Orchardson and Weizmann, Soc. **89**, 115.
[2] Bentley, Friedl, Thomas, and Weizmann, Soc. **91**, 411.
[3] B. **31**, 1272.
[4] B. **36**, 719.
[5] B. **38**, 4015.
[6] *Cf.* Zincke, B. **20**, 3229.
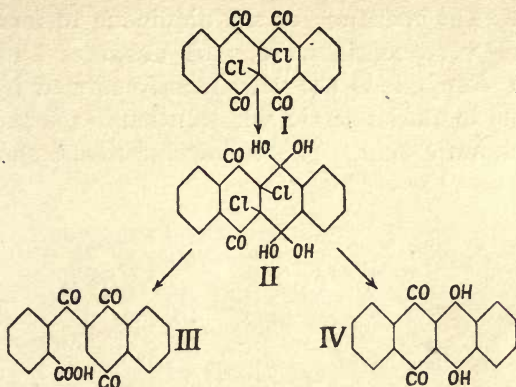
With bromine a somewhat similar reaction takes place, but in this case the dibromide cannot be isolated although Voswinckel obtained a monobromketone monohydrate :
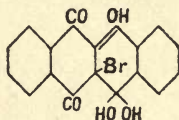
This is very readily decomposed with rupture of the quinone ring, and apparently gives the same ketonic acid as is obtained from the dichloride. On this point, however, Voswinckel could not be absolutely certain, as the melting points of the acids from the two sources differed somewhat, that from the bromo- compound melting at 199°, whereas that from the dichloride melted at 185°.

The bromo-compound is much more reactive than the dichloride, and when treated with aqueous sodium acetate is readily converted into *iso*-ethinediphthalide. As obtained by this means, however, the substance is almost black, and its appearance is not appreciably altered by several re-crystallizations from nitrobenzene or ethyl benzoate, whereas a single recrystallisation from pyridine suffices to convert it into the usual red needles. The black substance may possibly represent one of the numerous possible tautomeric forms, but Voswinckel [1] inclines to regard it as quinhydrone

[1] B. **42**, 465.

in nature. The tendency of the diquinone to form ketone hydrates is very considerable, and Voswinckel has found that such compounds are very readily formed by boiling with phenol in glacial acetic acid solution in the presence of a little sulphuric acid. The following scheme shows their chief reactions [1] :—
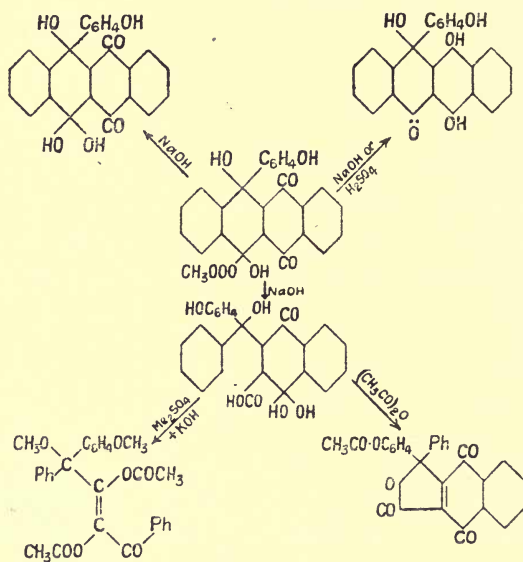
By the action of bleaching powder on the diquinone Voswinckel obtained an internal cyclic oxide which, when treated with caustic soda, gave the same ketonic acid that he obtained from the dichloride (formula III, p. 153). The acid when prepared in this way melted at 199°.

IV. *trans-bisang.*-DIBENZANTHRAQUINONE (DINAPHTH-ANTHRAQUINONE)

trans - bisang.-Dibenzanthraquinone (1.2.5.6. - dibenz-anthraquinone) has been synthesised by Weitzenböck and Klinger [2] as shown by the following scheme :—

[1] Voswinckel, B. **42**, 458, 4648.
[2] Weitzenböck and Klinger, M. **39**, 315.

3·4·5·6–Dibenzphenanthrene.

1·2·5·6–Dibenzanthracene   1·2·5·6–Dibenzanthraquinone
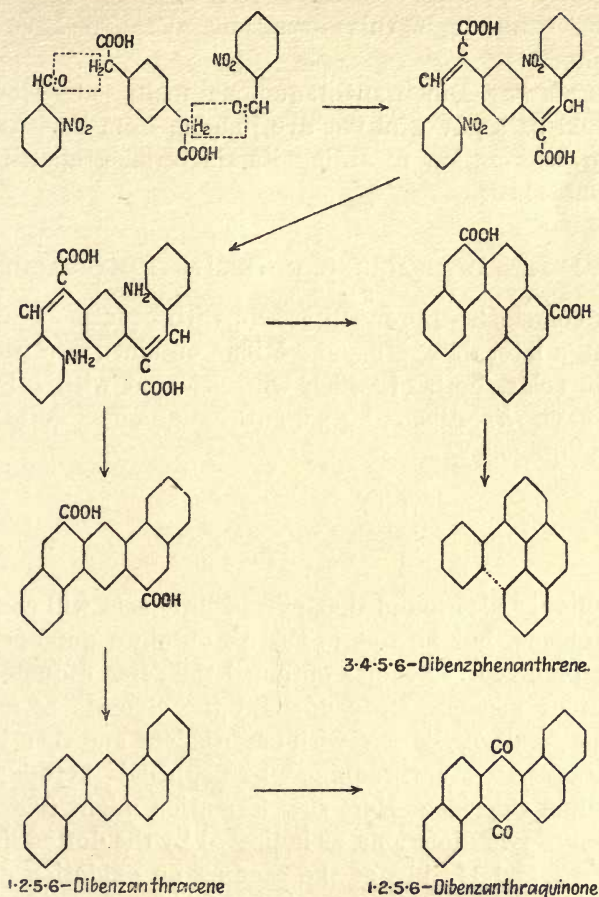
The closing of the rings in the diamino compound was effected by Pschorr's method,[1] viz. by treating the diazonium salt with copper powder. Two alternative reactions were possible and both took place, both an anthracene and a phenanthrene being formed. It should be observed that in the dibenzphenanthrene obtained there are two carbon atoms in the *peri-* position to one another, so that when heated with aluminium chloride a highly condensed hydrocarbon, indicated by the dotted line, should be

[1] Pschorr, B. **29**, 496.

obtained,[1] although this does not seem to have been attempted.

trans-bisang.-Dibenzanthraquinone melts at 248–249°. It should be a powerful vat dye judging from its structure, but no information regarding its tinctorial properties has been published.

V. *lin.*-DIBENZANTHRAQUINONE (DINAPHTHANTHRAQUINONE)

By condensing pyromellitic acid with benzene, Philippi [2] and, at a later date, Mills and Mills [3] obtained two isomeric ketonic acids, both of which when treated with sulphuric acid gave *lin.*-dibenz-1.4.5.8-anthradiquinone (dinaphth-anthradiquinone) :
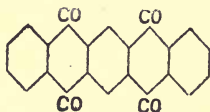
Philippi [4] also found that pyromellitic acid will condense with toluene, but he was unable to obtain a quinone from the ketonic acid. Scholl [5] obtained the same diquinone by a different means. He condensed the chloride of anthra-quinone-β-carboxylic acid with naphthalene and then heated the resulting 2-anthraquinonyl-1-naphthyl ketone with aluminium chloride. Here ring formation might take place in either of two directions, as indicated by the dotted lines in formulæ I and II ; but as the product on oxidation gave a diquinone monocarboxylic acid, which by loss of carbon dioxide passed into Philippi's diquinone, the reaction indicated by I must be that which actually takes place.
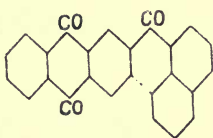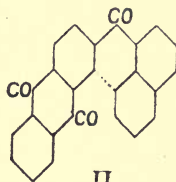
I   II

[1] See pp. 324, 328.   Scholl, A. **394**, 111 ; B. **44**, 1656.   [2] M. **32**, 624.
[3] Soc. **101**, 2194.   [4] M. **34**, 705.   [5] A. **394**, 159.

It will be observed that the substance represented by I can be regarded as a benzanthrone, and for a matter of fact Scholl found that when fused with caustic potash it gave a bluish-black vat dye which is probably a highly complex violanthrone.

A substance which is probably a dihydroxy derivative of the above diquinone is said to be obtained by condensing phthalic anhydride with *leuco*-quinizarin and then oxidising the product,[1] and compounds of similar structure are claimed as being obtained by using hydroxyanthracenes or other *leuco*-hydroxyanthraquinones in place of *leuco*-quinizarin.

By reducing their diquinone Mills and Mills[2] obtained a hydrocarbon and an anthrone, the latter on oxidation giving a monoquinone, viz. *lin.*-dibenzanthraquinone :
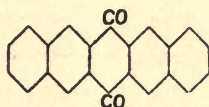
Philippi,[3] however, has criticised Mills and Mills' work, and has concluded that some of their reduction products were impure. Russig[4] when studying the action of carbon dioxide under pressure on naphthoquinol obtained, in addition to 1.4-dihydroxynaphthalene-2-carboxylic acid, a yellow substance which was probably a 1.4.5.8-tetrahydroxy-*lin.*-dibenzanthraquinone (III) and a green substance which he regarded as 5.8-dihydroxy-*lin.*-dibenz-1.4.9.10-anthradiquinone (IV) :
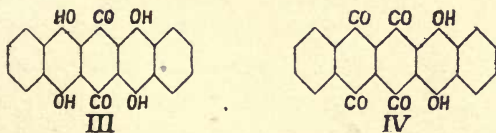
By treating 1.4-dihydroxynaphthalene-2-carboxylic acid with sulphuric acid he obtained the triquinone, *lin.*-dibenz-1.4.5.8.9.10-anthratriquinone (V). By distilling his dihydroxy

[1] By., D.R.P. 298,345.   [2] Soc. **101**, 2194.   [3] M. **35**, 380.
J. pr. [2] **62**, 44. *Cf.* Hartenstein, Dissertation, Jena, 1892.

diquinone with zinc dust he obtained what appeared to be the parent hydrocarbon, *lin.*-dibenzanthracene (VI).

V   VI
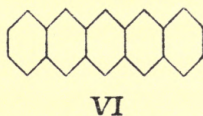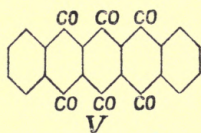
The complicated conjugation of carbonyl groups with double bonds which appears to exist in the triquinone renders it an interesting substance.

CHAPTER VIII

ALDEHYDES, KETONES, AND CARBOXYLIC ACIDS

I. ALDEHYDES

COMPARATIVELY little is known of the aldehydes of the anthraquinone series, as they are somewhat troublesome to prepare, although several members have been described.

The direct oxidation of methyl groups to the aldehydic group can be effected by means of manganese dioxide and sulphuric acid,[1] although, as in the aromatic series, there is considerable difficulty in preventing the oxidation going too far. Ullmann and Klingenberg[2] have endeavoured to avoid this by carrying out the oxidation by Thiele and Winter's method, i.e. by oxidising with chromic acid in glacial acetic acid solution in the presence of acetic anhydride and concentrated sulphuric acid, and subsequently hydrolysing the resulting acetate, and by this means have prepared anthraquinone-β-aldehyde from β-methylanthraquinone. The method, however, is very troublesome owing to the very slight solubility of methylanthraquinone.

The ω-dihalogen methyl anthraquinones do not give the aldehyde on hydrolysis with alkali, but do so readily when heated with concentrated sulphuric acid to 130°, with or without the addition of boric acid, and this forms the most convenient method of preparing the aldehydes.[3] It has also been applied to the preparation 1.1'-dianthraquinonyl-2.2'-dialdehyde from 2.2'-dichlormethyl-1.1'-dianthraquinonyl.[4]

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[1] Agfa, D.R.P. 267,081. [2] B. 46, 712.
[3] Ullmann, B. 47, 559; 49, 744. B.A.S.F., D.R.P. 174,984.
[6] B.A.S.F., D.R.P. 241,472.

Amongst other methods of preparing aldehydes may be mentioned the preparation of 1-nitroanthraquinone-6-aldehyde by Eckert [1] by the action of nitric acid on β-anthraquinonyl-β-acrylic acid, and of 1-aminoanthraquinone-2-aldehyde by Kalischer [2] by treating with acids the condensation products obtained by heating 1-amino-2-methylanthraquinone with aromatic nitro compounds and alkalis, with or without the addition of primary aromatic amines.

The anthraquinonyl aldehydes form oximes, semicarbazones, phenylhydrazones and azines (two molecules of aldehyde with one molecule of hydrazine) in the usual way,[3] and with dimethyl aniline green dyes of similar structure to malachite green are obtained. These are somewhat yellower in shade than malachite green, are difficultly soluble, and are not at all fast.

II. KETONES

Extremely little is known of the anthraquinone ketones, and it seems that the only substances described so far are anthraquinonyl aryl ketones. These are prepared by the action of the chlorides of the anthraquinone carboxylic acids on aromatic compounds such as hydrocarbons, chlorohydrocarbons, etc., in the presence of aluminium chloride.[4] The chlorides of both anthraquinone-α-carboxylic acid and anthraquinone-β-carboxylic acid react, but the latter reacts most readily. Ullmann [5] condensed the chloride of 2-chloranthraquinone-3-carboxylic acid with benzene and then converted the resulting chloranthraquinonyl phenyl ketone into the corresponding aminoketone by his sulphonamide process.[6] From this by diazotising and then treating the diazonium salt with copper powder he was able to close the fluorenone ring :

[1] M. **35**, 290.
[2] A.P. 1,285,726–7 (1918).
[3] Ullmann and Klingenberg, B .**46**, 712.   B.A.S.F., D.R.P. 240,520 ; 241,786.
[4] Ullmann, B. **47**, 566.   Schaarschmidt, B. **48**, 831.
[5] B. **47**, 566.
[6] See p. 197.
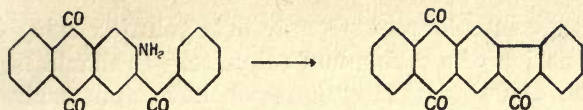
The product was found to be a yellow vat dye, but the tinctorial properties were very feeble.

Schaarschmidt [1] finds that the ketones derived from anthraquinone-α-carboxylic acid react quite differently from those derived from anthraquinone-β-carboxylic acid when reduced in acid solution, *e.g.* with concentrated sulphuric acid and aluminium bronze. The latter compounds behave quite normally and are converted into the colourless anthrones, whereas the former give highly coloured products. These are green when dissolved in sulphuric acid of over 50 per cent. strength, but become violet when the solution is diluted. They are insoluble in alkali, but behave like other anthraquinone compounds towards alkaline reducing agents.

Schaarschmidt regards the violet compound as the pinacone and the green compound as its cyclic anhydride :

Violet compound. Green compound.
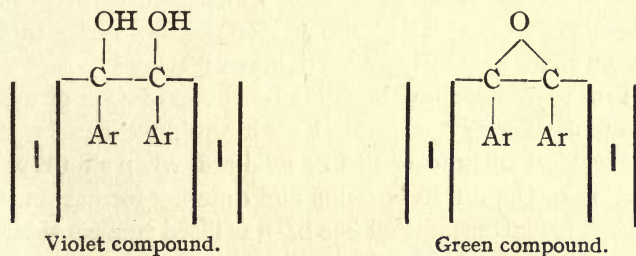
but this theory seems somewhat improbable, as it provides no explanation of the failure of the β-ketones to form similar compounds. It is much more probable that condensation has taken place between the ketonic carbonyl group and the reduced cyclic carbonyl group, with the production of some such structure as
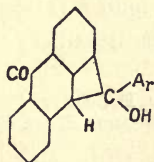
[1] B. **48**, 972 ; 1226: 49, 386.

the change in colour in strongly acid solution being due to the formation of a carbonium sulphate. It should be noted that the α-methylanthraquinones behave abnormally when reduced in alkaline solution.

III. CARBOXYLIC ACIDS

In a few cases anthraquinone carboxylic acids have been built up by the phthalic acid synthesis, *e.g.* from hemimellitic acid,[1] but as a rule it is much better to introduce the carboxyl groups into the molecule after the formation of the anthracene or anthraquinone ring. In the case of the α-carboxylic acids this can be done by treating anthracene with oxalyl chloride and aluminium chloride and then oxidising the resulting anthracene carboxylic acid or aceanthrenequinone,[2] but the method is of no great importance.

As a rule the anthraquinone carboxylic acids are obtained either by the hydrolysis of the nitriles or by the oxidation of the methyl anthraquinones. The hydrolysis of the nitriles takes a perfectly normal course, and the method has been made use of by several investigators.[3]

In preparing carboxylic acids by the oxidation of methyl compounds, either the methyl anthraquinone can be used, or the methyl anthracene can be oxidised, when simultaneous oxidation of the methyl groups and quinone formation takes place. This latter method has been utilised to a considerable extent as a means of identifying the homologous anthracenes, and references will be found in Chapter II.

The oxidation of methyl anthraquinones to the corresponding carboxylic acids can be effected by boiling with chromic acid in glacial acetic acid solution; but as a rule the best results are obtained by heating to 200–230° in a sealed tube with dilute nitric acid [4] (D=1100), although in some cases it is preferable to use other means. Thus 1-nitro-2-

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[1] See p. 140.
[2] See p. 69. Also Butescu, B. **46**, 212.
[3] Dienel, B. **39**, 932. Ullmann, B. **49**, 735, 746; A. **388**, 205; D.R.P. 243,788.
[4] Elbs, J. pr [2] **41**, 6, 121. Heller and Schülke, B. **41**, 3627. O. Fischer and Ziegler, J. pr. [2] **86**, 293.

methyl anthraquinone is only oxidised with difficulty, and when heated under pressure with nitric acid the yield of carboxylic acid does not exceed 30 per cent. In this case the oxidisation is best brought about by boiling with nitric acid (D=1383) and slowly adding chromic acid.[1]

a-Methylanthraquinone and its derivatives are usually rather stable towards oxidation,[2] and although the carboxylic acid can usually be obtained by heating under pressure with dilute nitric acid, it has been claimed that treatment with chlorine in nitrobenzene solution at 160° gives the most satisfactory results.[3] In other cases it is claimed that oxidation can best be effected by the use of oxides of nitrogen,[4] preferably in conjunction with some indifferent solvent.

The ease with which oleum, nitrosyl sulphuric acid and manganese dioxide bring about hydroxylation would point to these reagents as being unsuited for the purpose of oxidising methyl groups to carboxyl groups. This, however, is not altogether the case, as Ullmann [5] has found that 1-methyl-4-chloranthraquinone is oxidised to the carboxylic acid when heated with concentrated sulphuric acid or oleum to 120°. In the case of 2-methyl quinizarin the corresponding carboxylic acid, quinizarin-2-carboxylic acid, can be obtained by oxidation with nitrosyl sulphuric acid in the presence of boric acid.[6]

Instead of oxidising a methylanthraquinone directly to the carboxylic acid it is, of course, possible to convert it first into the aldehyde and then to oxidise this. As a rule this method has but little advantage over those depending on direct oxidation, but in some cases Ullmann [7] has found it useful, particularly when dealing with large quantities. It seems probable that in many cases the benzanthrone derivative is a suitable source of anthraquinone-a-carboxylic

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[1] B.A.S.F., D.R.P., 229,394. Terres, B. **46**, 1638.
[2] Birukoff, B. **20**, 2068.
[3] B.A.S.F., D.R.P. 259,365.
[4] B.A.S.F., D.R.P. 250,742.
[5] A. **388**, 217. *Cf.* O. Fischer and Sapper, J. pr. [2], **83**, 207. Gresly, A. **234**, 238.
[6] Ullmann, B. **52**, 511, 2111 ; By., D.R.P. 273,341.
[7] B. **47**, 561 ; **49**, 735, 746.

acids, as Perkin [1] has found recently that anthraquinone-1-carboxylic acid itself can be obtained in 85 per cent. yield by oxidising benzanthrone with chromic acid in acetic acid solution.

A few carboxylic acids have been described in which the carboxyl group is situated in the side chain, and is not directly attached to the nucleus. Thus β-(2)-anthraquinonyl acrylic acid can be obtained from β-dichlormethyl anthraquinone [2] or anthraquinone-β-aldehyde [3] by heating with sodium acetate and acetic anhydride.

The individual anthraquinone carboxylic acids are of no particular interest, and for a description of them the reader is referred to the original literature.[4] It should be noted, however, that they all lose carbon dioxide rather easily, so that samples which have been purified by sublimation frequently show a low melting point.[5] One of the most readily accessible acids is anthraquinone-1.2-dicarboxylic acid, which is very easily obtained by oxidising 1.2-benzanthraquinone.[6] Like the isomeric anthraquinone 2.3-dicarboxylic acid, it readily gives a cyclic anhydride. From this latter acid Willgerodt and Maffelzzoli [7] endeavoured to prepare the anthraquinone analogue of indigo, but failed, as they could not get the glycine. By fusing the acid with zinc chloride and resorcinol they obtained anthraquinone fluoresceïne, which, however, was only feebly fluorescent.

The *halogen carboxylic acids* can be obtained from a halogenated nitrile by hydrolysis, or from a halogenated methylanthraquinone by oxidation. Dichloranthraquinone

[1] Soc. **117**, 706.

[2] By., D.R.P. 282,265.

[3] Eckert, M. **35**, 290.

[4] In addition to those already given, the following are the more important references: Limpricht and Wiegand, A. **311**, 180. Weiler, B. **7**, 1185. O. Fischer, B. **7**, 1195. Liebermann and Rath, B. **8**, 248. Schültz, B. **10**, 118, 1049. Nietzki, B. **10**, 2013. Wachendorff and Zincke, B. **10**, 1481. Ciamician, B. **11**, 269. Hammerschlag, B. **11**, 82. Börnstein, B. **15**, 1821. Liebermann and Glock, B. **17**, 888. Elbs, B. **17**, 2848; **20**, 1361. Heller, B. **43**, 2891. Elbs, J. pr. [2] **35**, 471. O. Fischer, J. pr. [2] **79**, 561. Fischer and Reinkober, J. pr. [2] **92**, 53. Seer, M. **32**, 163. Eckert, M. **35**, 299. Lavaux, C. r. **143**, 687.

[5] Limpricht and Wiegand, A. **311**, 180.

[6] Scholl, B. **44**, 2992. D.R.P. 241,624; 243,077.

[7] J. pr. [2] **82**, 205.

carboxylic acids [1] can also be obtained by chlorinating the anthraquinone carboxylic acids themselves in concentrated sulphuric acid solution at 125°.

Nitrocarboxylic acids can be obtained from nitro nitriles or nitromethylanthraquinones by the usual methods, and Eckert [2] obtained 6-nitroanthraquinone-1-carboxylic acid by treating β(2)-anthraquinonylacrylic acid with nitric acid, and then oxidising the resulting nitro aldehyde.

Liebermann and Glock [3] nitrated anthraquinone-β-carboxylic acid and obtained a nitro acid, but did not determine the position of the nitro group. Ullmann [4] nitrated anthraquinone-α-carboxylic acid and obtained 5-nitroanthraquinone-1-carboxylic acid, the structure being proved by its preparation from 1.5-dinitroanthraquinone through the nitro amino compound and nitro nitrile.

Acid chlorides and *acid amides* are obtained by the usual means,[5] *e.g.* by phosphorus pentachloride and ammonia. They are much more stable than the corresponding compounds of the benzene series. Thus Liebermann and Glock found that the chloride of anthraquinone-β-carboxylic acid, after remaining in contact with water at the ordinary temperature for 120 hours, was only hydrolysed to the extent of $7\frac{1}{2}$ per cent. The corresponding amide they found was not hydrolysed by cold concentrated sulphuric acid or by boiling dilute alkali, although it was hydrolysed by hot concentrated alkali.

The *anthraquinone nitriles* can be obtained from the anthraquinone sulphonates by heating with potassium cyanide or, in some cases, from the chloranthraquinones by heating with cuprous cyanide and an indifferent solvent.[6] They can also be obtained from the anthracene sulphonates by distilling these with potassium cyanide and then oxidising the resulting anthracene nitrile. According to Ullmann,[7]

[1] By., D.R.P. 255,121.   [2] M. 35, 290.
[3] B. 17, 891.   [4] A. 388, 207.
[5] Liebermann and Glock, B. 17, 888. Graebe and Blumenfeld, B. 30, 1116. Wilgerodt and Maffelzzoli, J. pr. [2] 86, 205. Seer, M. 32, 163. Eckert, M. 35, 290.
[6] M.L.B., D.R.P. 271,790; 275,517.
[7] A. 388, 204. *Cf.* Dienel, B. 39, 932.

however, the product obtained from anthracene-α-sulphonic by this method consists chiefly of anthraquinone itself.

The usual method of preparing the nitriles, however, is by treating the diazonium salts with potassium cupro-cyanide, although the yields obtained are often very poor, *e.g.* Ullmann [1] obtained a yield of only 16 per cent. from 2-amino-1-chloranthraquinone. In some cases the poor yield obtained is due to the reducing action of the cupro-cyanide, and Terres [2] has found that the diazonium salt from 2-methyl-1-amino anthraquinone when treated with potassium cuprocyanide gives β-methylanthraquinone.

A considerable number of nitriles have been prepared by Schaarschmidt,[3] who finds that their tinctorial properties are very feeble, although this can be remedied to some extent by halogenating.

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[1] B. **49**, 735, 746.   *Cf.* also A. **388**, 203.
[2] B. **46**, 1646.   [3] A. **405**, 95.

CHAPTER IX

THE NITRO, NITROSO, AND HALOGEN ANTHRAQUINONES

I. THE NITRO COMPOUNDS

WHEN anthraquinone is nitrated the α-position is first attacked exclusively, no β-nitroanthraquinone being formed. The preparation of α-nitroanthraquinone has been described by several investigators,[1] the most recent descriptions being those by Ullmann[2] and Lauth.[3] Both of these last carry out the nitration by the addition of nitric acid to anthraquinone dissolved in concentrated sulphuric acid, the former specifying a temperature of about 50°. Ullmann states that the crude product contains about 8 per cent. of dinitro compounds, all of which, with the exception of the 1.8-dinitro compound, can be got rid of by recrystallisation from toluene. In order to remove the 1.8-dinitroanthraquinone he suggests distillation *in vacuo*,[4] and gives the boiling point as 270–271° at 7 mm. Lauth does not state the amount of dinitro compounds formed under the conditions he uses, but as his crude product melted at 218° instead of at 220° the quantity must have been very small. This is in accordance with the author's experience, who has prepared several pounds of nitroanthraquinone in the laboratory by adding potassium nitrate in 5 per cent. excess to anthraquinone dissolved in concentrated sulphuric acid, the whole being allowed to stand at the ordinary temperature for 48 hours.

The further nitration of anthraquinone leads to a mixture

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[1] Böttger and Petersen, A. **166**, 147. Römer, B. **15**, 1786. Graebe and Blumenfeld, B. **30**, 1118.
[2] A. **388**, 203. [3] C. r. **137**, 662. [4] D.R.P. 281,490.

of dinitro compounds.[1]   According to a patent specification [2] this contains 60 per cent. of 1.5- and 1.8-dinitroanthraquinone, the remainder being chiefly 1.6-dinitroanthraquinone with small quantities of 1.7-dinitroanthraquinone and very small quantities of 2.6- and 2.7-dinitroanthraquinone.   Eckert,[3] who gives full details of the nitration, separated the isomers by fractional crystallisation from glacial acetic acid and arrived at a different result.   He found 75 per cent. of the 1.5-dinitro compound, 10 per cent. of the 1.6-dinitro compound, and 5 per cent. each of the 1.7- and 1.8- isomers.   Holdermann [4] nitrated anthraquinone in the presence of mercury, but failed to detect any directing influence.

β-Nitroanthraquinone cannot be obtained by the nitration of anthraquinone, but has been prepared by Kauffler [5] by heating anthraquinone-β-diazonium nitrate with copper nitrite,[6] and by Scholl [7] by nitrating β-aminoanthraquinone and then removing the amino group from the resulting 2-amino-3-nitroanthraquinone by the diazo- reaction.   It is much less reactive than α-nitroanthraquinone and does not react with primary aromatic amines, although it is readily converted into β-methoxyanthraquinone by potassium methoxide.

The nitration of α-methylanthraquinone has been carried out by O. Fischer and Ziegler.[8]   They obtained a mononitro compound but did not determine the position of the nitro group.

The dinitration of β-methyl anthraquinone has been effected by Schaarschmidt,[9] who found that the product contained 65 per cent. of 2-methyl-1.5-dinitroanthraquinone and 30 per cent. of 2-methyl-1.8-dinitroanthraquinone.

By the nitration of 1.3-dimethylanthraquinone Scholl [10]

[1] Fritsche, J. pr. [1] **106**, 287. Böttger and Petersen, A. **160**, 185; B. **6**, 16.   Graebe and Liebermann, B. **3**, 905. Römer, B. **16**, 363.
[2] M.L.B., D.R.P. 167,699.
[3] M. **35**, 297.
[4] B. **39**, 1256.
[5] B. **37**, 63.
[6] *Cf.* Sandmeyer, B. **20**, 1495; **23**, 1630. Hantzsch and Blagden, B. **33**, 1544.
[7] Scholl, M. **32**, 1037. Scholl and Eberle, B. **37**, 4434.
[8] J. pr [2] **86**, 292.   [9] B. **45**, 3452.   [10] B. **43**, 353.

obtained 1.3-dimethyl-4-nitroanthraquinone and 1.3-dimethyl-2.4-dinitroanthraquinone, and from 2.6-dimethyl-anthraquinone Seer [1] obtained 2.6-dimethyl-1.5-dinitro-anthraquinone. By nitrating 1.3.5.7-tetramethylanthra-quinone Seer [2] obtained a mixture of the 4.8-dinitro compound and the tetranitro compound.

The reduction of the nitro compounds to amino compounds is discussed in the chapter dealing with these latter substances, the reduction being particularly easily effected by boiling with aqueous sodium sulphide solution. The change of dinitroanthraquinone into polyhydroxyanthra-quinones when heated with concentrated sulphuric acid or oleum, with or without the addition of sulphur, will be found described on p. 242.

The nitro groups in the nitroanthraquinones, especially when in the α-positions, are decidedly more reactive than is usually the case with aromatic nitro compounds. Thus they are often readily replaced by arylamino groups when boiled with primary aromatic amines such as aniline,[3] and are very easily replaced by methoxy groups by treatment with alcoholic solutions of potassium methoxide.[4]

II. The Nitroso Compounds

Scarcely anything is known of the nitrosoanthraquinones. Walker [5] found that 1-nitroanthraquinone-2-sulphonic acid, when reduced with glucose in alkaline solution, gave the corresponding hydroxylamine derivative, which on oxidation passed into 1-nitrosoanthraquinone-2-sulphonic acid. From this the hydroxylamine derivative could be regenerated by reduction with glucose. As stated elsewhere,[6] 1.5-dinitro-anthraquinone when heated to 50° with oleum containing 30 per cent. of free anhydride passes into 1-nitro-5-nitroso-8-hydroxyanthraquinone, reduction of this leading to the corresponding diamino compound.

[1] M. **32**, 158. [2] M. **33**, 33. [3] See p. 198. [4] See p. 287.
[5] B. **35**, 666. [6] See p. 244. By., D.R.P. 104,282.

III. The Halogen Compounds

DIRECT HALOGENATION.—Anthraquinone itself is only attacked by halogens with the greatest difficulty, although Diehl,[1] by the action of bromine in the presence of iodine, obtained di-, tri-, tetra-, and penta-brom compounds. The attack takes place somewhat more readily when concentrated sulphuric acid or oleum is used as a solvent, and it is claimed that under these conditions anthraquinone can be chlorinated in steps.[2] The reaction is carried out at a temperature of 60–130° and is facilitated by the use of iodine as a catalyst. The entering halogen atom seems to prefer the α-positions, as it is stated that α-chloranthraquinone is converted into 1.4.5.8-tetrachloranthraquinone, whereas 2.6- and 2.7-dichloranthraquinone yield hexachlor compounds.

According to another patent specification [3] anthraquinone can be brominated at 50–60° when dissolved in oleum containing 80 per cent. of free anhydride, and then leads to a tetrabromanthraquinone (m.p. 295°) and a heptabromanthraquinone (m.p. over 350°); but Eckert and Steiner [4] have repeated the work and have stated that the tetrabromo compound is not formed.

The chlorination of anthraquinone can also be effected by means of antimony pentachloride, and by this means Diehl [5] obtained di-, tri-, tetra-, and penta-chlor compounds although he did not determine the positions occupied by the chlorine atoms. There can be no doubt, however, that Diehl's tetra-chlor compound was 1.4.5.8-tetrachloranthraquinone. More recently Eckert and Steiner [6] have re-investigated the action of antimony pentachloride on anthraquinone. By heating the two substances together in the presence of a trace of iodine they were able to obtain a heptachlor compound, but all attempts to obtain an octachlor compound failed, as further chlorination led to the rupture of the anthraquinone ring and formation of perchlor-

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[1] B. **11**, 179.   [2] By., D.R.P. 228,901.
[3] By., D.R.P. 107,721.   [4] M. **36**, 269.
[5] B. **11**, 179.   [6] M. **35**, 175; **36**, 269. B. **47**, 2628.

benzoyl benzoic acid and tetrachlorphthalic acid. The heptachlor compound melted at 380°, and in view of the fact that halogens first attack the α-positions, it would seem probable that the unchlorinated position was a β-position, *i.e.* that the compound was 1.2.3.4.5.6.8-heptachloranthraquinone. Eckert and Steiner, however, prepared this compound from tetrachlorphthalic acid and 1.2.4-trichlorbenzene and found that it melted at 302°, although by heating with phosphorus pentachloride it was converted into the isomeric compound melting at 380°. By heating 1.2.3.4-tetrachloranthraquinone with antimony pentachloride a mixture of the two heptachlor compounds was formed. From the above facts it would seem that the chlorination of anthraquinone leads first to 1.2.3.4.5.6.8-heptachloranthraquinone (m.p. 302°), which then passes into 1.2.3.4.5.6.7-heptachloranthraquinone (m.p. 380°) by the wandering of a chlorine atom. Reactions of this type are not new, as it has long been known that α-bromnaphthalene passes into β-bromnaphthalene under the influence of aluminium chloride.

When methyl anthraquinones are halogenated the halogen atom can enter either the nucleus or the side chain, which reaction takes place depending on the conditions of the experiment, although owing to the paucity of the data available it is impossible to draw any very definite conclusions as to the conditions which favour each type of reaction. Ullmann[1] finds that when β-methyl anthraquinone is heated on the water bath with sulphuryl chloride in nitrobenzene solution, 2-methyl-1-chloranthraquinone is formed in 80 per cent. yield. On the other hand, sulphuryl chloride at 175° appears to convert β-methylanthraquinone into β-dichlormethylanthraquinone.[2]

β-Methylanthraquinone when chlorinated in nitrobenzene solution at 100° with molecular chlorine yields nuclear methylchloranthraquinones,[3] whereas with chlorine at 175° halogenation seems to take place in the side chain.[4] The action of bromine at 160–175°, with or without a solvent

[1] B. **49**, 737. Agfa, D.R.P. 269,249.   [2] B.A.S.F., D.R.P. 216,715.
[3] Agfa, D.R.P. 293,156.   [4] B.A.S.F., D.R.P. 216,715.

such as nitrobenzene, seems to be very similar, Ullmann and Klingenberg,[1] and Hepp, Uhlenhuth, and Römer [2] obtaining β-dibrommethylanthraquinone, and Eckert [3] obtaining β-tribrommethyl anthraquinone, although unable to obtain the β-monobrommethyl anthraquinone described in the patent literature.[4] Among other similar results may be mentioned the preparation of ω-dibrom compounds from 2-methyl-1-chloranthraquinone and from 2-methyl-3-chloranthraquinone by Ullmann,[5] by the action of bromine at 160–170° in nitrobenzene solution. These brominations can be carried out in open vessels and the yields are often excellent.

The presence of an amino group in the anthraquinone nucleus greatly facilitates the entrance of halogen atoms, and use has been made of this in the preparation of nuclear halogen anthraquinones. Thus Ullmann [6] was able to prepare 1.3-dibromanthraquinone by brominating β-aminoanthraquinone and then removing the amino group from the resulting 2-amino-1.3-dibromanthraquinone in the usual way by diazotising and reducing.[6]

RETROGRESSIVE SUBSTITUTION.—Halogen atoms when in the α-position are fairly easily removed by reduction, whereas those in the β-position are much more firmly bound. Retrogressive substitution, therefore, sometimes forms a convenient method of preparing the lower halogenated compounds and also furnishes some indication of the positions occupied by the halogen atoms. Kircher [7] reduced 1.2.3.4-tetrachloranthraquinone with zinc dust and ammonia and obtained a dichloranthracene (m.p. 255°), which on oxidation gave a dichloranthraquinone (m.p. 261°), which he believes to be 1.2-dichloranthraquinone, but which Ullmann [8] has since shown to be 2.3-dichloranthraquinone. More recently Ullmann [9] has found that chlorine atoms when in the α-position, but not when in the β-position, can be removed by heating the compound, e.g. in nitrobenzene solution, with potassium acetate and a trace of copper powder. Thus,

[1] B. 46, 712. [2] B. 46, 709. [3] M. 35, 299.
[4] B.A.S.F., D.R.P. 216,715. [5] B. 47, 558; 49, 737. [6] B. 49, 2157.
[7] A. 238, 344. [8] A. 381, 26. [9] B. 45, 687.

although β-chloranthraquinone is unaffected, α-chloranthraquinone is reduced to anthraquinone itself, and 1-methyl-4-chloranthraquinone to α-methylanthraquinone. In the case of 1.2.3.4-tetrachloranthraquinone only two chlorine atoms are removed, the product being 2.3-dichloranthraquinone.

REPLACEMENT OF GROUP.—*Amino groups* are usually quite readily replaced by halogen atoms by first preparing the diazonium salt and then treating this with cuprous halide in the usual way.[1] In some cases, however, there is a tendency for the cuprous halide to form a dianthraquinonyl derivative.[2]

Hydroxyl groups can be replaced by chlorine atoms by treatment with phosphorus trichloride, phosphorus pentachloride or phosphorus oxychloride.[3] The cyclic carbonyl groups are unaffected.

Nitro- groups either in the α-position or in the β-position can be replaced by chlorine atoms by dissolving the nitro compound in some suitable solvent such as trichlorbenzene, and then treating it at 160° with chlorine.[4] Methyl groups if present are simultaneously chlorinated, but in the case of nitroanthraquinone sulphonic acids, the sulphonic acid groups are replaced before the nitro groups.

Sulphonic acid groups, either in the α-position or in the β-position, are very readily replaced by chlorine or bromine atoms, and in many cases this reaction forms the most convenient means of preparing halogen anthraquinones. The reaction can be brought about by heating to 170° with thionyl chloride,[5] nitro groups if present remaining unaffected; but it is much more convenient to treat a boiling aqueous solution of the sulphonic acid with molecular or nascent chlorine or bromine.[6] The nascent chlorine can

[1] Kauffler, B. **36**, 60. Scholl, B. **40**, 1696; **43**, 354. Laube, B. **40**, 3566. By., D.R.P. 131,538.

[2] B.A.S.F., D.R.P. 215,006.

[3] Ullmann and Conzetti, B. **53**, 832. Afga, D.R.P. 290,879.

[4] B.A.S.F., D.R.P. 128,845, 252,578, 254,450.

[5] M.L.B., D.R.P. 267,544, 271,681, 284,976.

[6] Ullmann, A. **381**, 2. Wölbling, B. **36**, 3941. Heller, B. **46**, 2703, By., D.R.P. 205,195, 205,913, 214,150. M.L.B., D.R.P. 77,179, 78,642, 97,287.

be generated by allowing sodium hypochlorite solution, or sodium chlorate solution, to run slowly into a boiling solution of the sulphonic acid in dilute hydrochloric acid, and the author has found that the use of sodium chlorate gives particularly good results. The reaction proceeds quite readily and the chloro compound usually separates out in the crystalline condition, but it is advisable to use rather dilute solutions. There is no necessity to isolate the sulphonic acids, it being sufficient to pour the crude sulphonation melt into water and then treat the resulting solution with molecular or nascent chlorine or bromine. In the case of polysulphonic acids either one or more sulphonic acid groups can be replaced by halogen, and if nitro groups are present these remain unaffected. Sulphonic acids when treated with halogens in concentrated sulphuric acid are halogenated without the sulphonic acid group being affected, so that by halogenating an anthraquinone sulphonic acid in concentrated sulphuric acid solution and then running the melt into water and again treating with halogen, a very large number of halogen anthraquinones can be obtained with very little trouble.[1]   Another very fruitful method is to sulphonate, with or without the addition of mercury, a halogen anthraquinone and then to dilute the melt and treat it with a halogen.[2]

If an anthracene sulphonic acid is treated with sodium chlorate in boiling dilute hydrochloric acid solution, simultaneous replacement of the sulphonic acid group and oxidation take place, the product being a chlorinated anthraquinone.[3]

PROPERTIES.—Halogen atoms when situated in a side chain seem to be rather less reactive than would be expected, and as a rule the ω-dihalogenmethyl anthraquinones are unaffected by dilute alkali and can only be converted into the corresponding aldehyde by heating to 130° with concentrated sulphuric acid.[4]   Eckert,[5] however, states that β-tribrommethyl anthraquinone gives the carboxylic acid

[1] B.A.S.F., D.R.P. 214,714, 216,071.
[2] Hepp, Uhlenhuth, and Römer, B. **46**, 709.   Schilling, B. **46**, 1066.
[3] B.A.S.F., D.R.P. 228,876.
[4] See p. 159.   [5] M. **35**, 299.

when heated to 180° with milk of lime. In some ways the ω-dibrommethyl compounds, however, are very reactive, and β-dibrommethylanthraquinone when heated to 240–250° evolves torrents of hydrobromic acid and passes into dianthraquinonyldibromethylene, $C_{14}H_7O_2CBr : CBrC_{14}H_7O_2$, from which dianthraquinonyl acetylene can be obtained by the action of diethylaniline or sodium phenolate.[1]

Halogen atoms when directly attached to the nucleus are somewhat less firmly bound than is usually the case with aromatic halogen compounds. When in the α-position they are decidedly more reactive than when in the β-position.

Halogen atoms in the α-position direct the entering nitro group to the *p*-position, so that α-chloranthraquinone gives 1-chlor-4-nitroanthraquinone, and 1.5- and 1.8-dichloranthraquinones give corresponding compounds.[2] From 1.4-dichloranthraquinone Walsch and Weizmann[3] obtained a mononitro compound (m.p. 238°), but did not determine the position of the nitro group. From 1.4-dichlor-5.8-dimethyl anthraquinone Harrop, Norris, and Weizmann[4] obtained a dinitro compound, but offer no information as to the position of the nitro group. Heller[5] by nitrating 3-chloralizarin obtained a mononitro compound which must be 3-chlor-4-nitroalizarin, as it gives phthalic acid when oxidised.

[1] Ullmann and Klingenberg, B. **46**, 712.
[2] Eckert and Steiner, M. **35**, 1138.   By., D.R.P. 137,782, 249,721.
[3] Soc. **97**, 687.   [4] Soc. **95**, 1318.   [5] B. **46**, 2703.

THE SULPHONIC ACIDS, MERCAPTANS, AND SULPHIDES

I. THE SULPHONIC ACIDS

ANTHRAQUINONE is not very easily sulphonated, but treatment with oleum leads first to the β-monosulphonic acid and then to a mixture of disulphonic acids in which the 2.6- and the 2.7-disulphonic acids predominate.[1] If it is desired to prepare anthraquinone monosulphonic acid reasonably free from disulphonic acid it is absolutely essential to interrupt the reaction while some 20 per cent. of the anthraquinone is still unchanged, as if the process is carried on until the whole of the anthraquinone has been attacked the product will be found to contain considerable quantities of disulphonic acid. In any case the sulphonation of anthraquinone is always accompanied by a certain amount of simultaneous hydroxylation, and consequently a deep purple colour is developed when a portion of the melt is made alkaline. Under suitable conditions, however, the loss by hydroxylation is only slight.

Both the β-sulphonic acid and the two disulphonic acids are manufactured on the technical scale and are used in the manufacture of alizarin dyes. The monosulphonic acid is isolated by diluting the sulphonation melt, filtering off the unchanged anthraquinone and then saturating the solution with sodium chloride. Under these conditions the sodium

[1] Perkin, A. **158**, 323. Graebe and Liebermann, A. **160**, 130. Caro, Graebe, and Liebermann, B. **3**, 359. Liebermann and Bollert, A. **212**, 56; B. **15**, 229. Schunck and Römer, B. **9**, 679. Liebermann and Dehnst, B. **12**, 1288. Perger, B. **12**, 1566. Römer, B. **15**, 224. Crossley, Am. Soc. **37**, 2178.

salt of the monosulphonic acid separates out in silvery scales, the silvery appearance having given rise to the technical name "silver salt." The disulphonic acids are more soluble, and to isolate them it is best to neutralise the solution and then remove the sodium sulphate by fractional crystallisation.

It should be noticed that when anthraquinone is sulphonated without the use of a catalyst only two sulphonic acid groups can be introduced into the molecule, and that the products formed are almost exclusively β-sulphonic acids although very small quantities of α-sulphonic acids are also formed.[1]

If the sulphonation of anthraquinone is carried out in the presence of a small quantity of mercuric sulphate a totally different result is obtained, the sulphonic acid groups under these circumstances exclusively entering the α-positions.[2] The first product formed is anthraquinone-α-sulphonic acid, further sulphonation leading to a mixture of the 1.5- and 1.8-disulphonic acids. All these are easily salted out as their potassium salts by adding potassium chloride to their solutions in dilute sulphuric acid. The two disulphonic acids are readily separated by taking advantage of the fact that the 1.5-disulphonic acid is insoluble in concentrated sulphuric acid, whereas the 1.8-disulphonic acid is soluble. If, therefore, the sulphonation melt is diluted with concentrated sulphuric acid the former acid crystallises out and can be filtered off and washed with concentrated sulphuric acid and finally dissolved in water and salted out by the addition of potassium chloride. The concentrated sulphuric acid mother liquors contain the 1.8-disulphonic acid, and when they are diluted and treated with potassium chloride the potassium salt of this acid separates.

By sulphonating anthraquinone itself in the presence of mercury only two sulphonic acid groups can be introduced into the molecule, but trisulphonic acids, presumably the 1.3.6- and the 1.3.7-trisulphonic acids, can be obtained

[1] Dünschmann, B. **37**, 331. Liebermann and Pleus, B. **37**, 646.
[2] Iljinsky, B. **36**, 4194. R. E. Schmidt, B. **37**, 66. By., D.R.P. 149,801.

either by sulphonating an α-sulphonic acid without the addition of mercury, or by sulphonating a β-sulphonic acid in the presence of mercury.[1]

By sulphonating anthraquinone itself in the presence of mercuric sulphate which is only coarsely powdered, it has been claimed that anthraquinone-1.6- and 1.7-disulphonic acids can be obtained in one operation.[2]

The directing influence of mercury is not confined to anthraquinone itself, but also extends to anthraquinone derivations, and Ullmann [3] has found that when halogen anthraquinones are sulphonated in the presence of mercury the sulphonic acid group enters the α- position.

It has been claimed that the sulphonation of anthraquinone is facilitated by the catalytic action of vanadium, but experiments which have been made by the author fail to support this claim.[4]

Although direct sulphonation is by far the most important method of preparing anthraquinone sulphonic acids, sulphonic acid groups can also sometimes be introduced into the molecule by other means. Thus halogen atoms are sometimes replaced by sulphonic acid groups by treatment with sulphuric acid,[5] although the reaction is by no means a general one, and many halogen compounds can be sulphonated in a normal manner.[6] In the case of 1-amino-4-arylamino-2-halogen anthraquinones the halogen atom can be replaced by the sulphonic acid group by heating with aqueous sodium sulphite solution.[7]

Boiling with aqueous sodium sulphite solution in many cases leads to the production of sulphonic acids by replacement of the nitro group, 1-nitroanthraquinone, 1.5- and 1.8-dinitroanthraquinone and some hydroxynitroanthraquinones reacting in this way.[8] In the case of 1.4-dihydroxy-

[1] Wed., D.R.P. 170,329 ; 202,398.

[2] Wed., D.R.P. 202,398.

[3] D.R.P. 223,642.

[4] Thümmler, D.R.P. 214,156.

[5] Perkin, A. **158**, 319. Graebe and Liebermann, A. **160**, 137.

[6] *E.g.* Walsh and Weizmann, Soc. **97**, 688. By., D.R.P. **217,552.** Ullmann, D.R.P. 223,642.

[7] By., D.R.P. 288,878.

[8] R. E. Schmidt, B. **36**, 39. By., D.R.P. 164,292, 167,169.

anthraquinones, 1.4-aminohydroxyanthraquinones and 1.4-diaminoanthraquinones, treatment with aqueous sodium sulphite solution will bring about sulphonation without replacement.[1] Here the reaction is no doubt due to the formation of a true quinonoid compound, *p*-quinone, quinone-imide or quinone di-imide, and then addition to this of sodium bisulphite. This view of the reaction is supported by the fact that sulphonation takes place most readily in the presence of an oxidising agent such as manganese dioxide. In the absence of an oxidising agent the formation of the quinonoid compound is no doubt brought about at the expense of part of the oxygen of the cyclic carbonyl groups.

The anthraquinone sulphonic acids are usually fairly easily desulphonated by hydrolysis, although the ease with which the sulphonic acid group is split off varies to a great extent in different individual substances. As a rule, the hydrolysis can be effected by heating to 170–190° with sulphuric acid of 80 per cent. strength,[2] but sulphonic acid groups in the α-position are somewhat less firmly held than similar groups in the β-position and are usually readily split off by treatment with sulphuric acid of 50–80 per cent. strength.[3] The addition of boric acid sometimes has a favourable effect, and in many cases the addition of a reducing agent such as a phenol, amine, sugar, metal, or stannous chloride greatly assists the reaction. The effect of the reducing agent is largely catalytic, as only relatively small amounts are required.[4] The presence of other groups in the molecule also renders hydrolysis more easy, a notable example being that of 1.3.5.7-tetrahydroxy-4.8-dinitro-anthraquinone-2.6-disulphonic acid, which is desulphonated when boiled with sulphuric acid of 20 per cent. strength.[5] It should be remembered that during hydrolysis bromine atoms if present are apt to wander.[6]

[1] By., D.R.P. 287,867 ; 288,474 ; 289,112.
[2] By., D.R.P. 56,951 ; 172,688. Wed., D.R.P. 210,863.
[3] By., D.R.P. 160,104.
[4] By., D.R.P. 190,476.
[5] M.L.B., D.R.P. 71,964 ; 77,720.
[6] B.A.S.F., D.R.P. 263,395 ; 265,727 ; 266,563. M.L.B., D.R.P. 253,683. G.E., D.R.P. 277,393.

Desulphonation of sulphonic acids can also sometimes be brought about by reduction. Thus hexahydroxy anthraquinone is obtained when its disulphonic acid is reduced in acid solution by zinc, iron, or aluminium, the sulphonic acid group being split off in the form of sulphuretted hydrogen.[1]

The anthraquinone sulphonic acids are converted into the sulphochlorides by treatment with phosphorus pentachloride and phosphorus oxychloride,[2] sulphochlorides also being obtained in many cases by the action of chlorsulphonic acid on the anthraquinone sulphonic acids.[3]

These sulphochlorides behave like other sulphochlorides. On reduction with sodium sulphide they give the corresponding sulphinic acids.[4]

The nitration of anthraquinone-α-sulphonic acid leads to a mixture of 1.5- and 1.8-nitroanthraquinone sulphonic acids, the isomers being very easily separated owing to the insolubility of the former in the nitrating acid.[5] The nitration of anthraquinone-β-sulphonic also leads to two isomeric mononitro compounds, one of which, according to Claus[6] and Lifschütz,[7] can be converted into alizarin. R. E. Schmidt,[8] however, has found that the two nitro compounds formed are really 1-nitroanthraquinone-6-sulphonic acid and 1-nitroanthraquinone-7-sulphonic acid, and Frobenius and Hepp[9] have severely criticised Claus' work and have shown that what Claus described as erythrohydroxyanthraquinone sulphonic acid is really the diazo sulphonic acid, Claus having overlooked the presence of nitrogen.

II. The Sulphinic Acids

The anthraquinone sulphinic acids are of no particular interest and can be obtained either by reducing the sulphochlorides with sodium sulphide,[10] or by the oxidation of the sulphenic acids (sulphoxylic acids). They behave very much like other aromatic sulphinic acids. Thus anthra-

[1] By., D.R.P. 103,898.   [2] Ullmann, B. **52**, 545.   [3] M.L.B., D.R.P. 266,521.
[4] M.L.B., D.R.P. 263,340.   *Cf.* M.L.B., D.R.P. 224,019.
[5] R. E. Schmidt, B. **37**, 71.   [6] B. **15**, 1521.
[7] B. **17**, 899.   [8] B. **37**, 69.   [9] B. **40**, 1048.
[10] M.L.B., D.R.P. 263,340.   *Cf.* M.L.B., D.R.P. 224,019.

quinone-β-sulphinic acid very readily condenses with tetramethyldiaminobenzhydrol (Mischler's hydrol) to form an ester,[1] $C_{14}H_7O_2.SOOCH(C_6H_4NMe_2)_2$, and also readily adds on to quinonoid compounds,[2] *e.g.* with benzoquinone it gives $C_{14}H_7O_2.SO_2.C_6H_3(OH)_2$.

III. The Sulphenic (Sulphoxylic) Acids

When an anthraquinone mercaptan or disulphide is treated with chlorine or bromine in chloroform solution an anthraquinone sulphur halide, $C_{14}H_7O_2.SHlg$, is often obtained, although the reaction is by no means a general one and several exceptions are known.[3] The bromides are also often obtained by reducing the sulphinic acids in glacial acetic acid solution by means of hydrobromic acid.[4]

The sulphur halides of the anthraquinone series usually show reactions very similar to those of other aromatic sulphur halides,[5] although they are much more stable than is usually the case with compounds of this class. Thus anthraquinone-β-sulphur chloride reacts with acetone to form an acetyl compound, and with water to give the anhydride of the sulphenic acid $(C_{14}H_7O_2S)_2O$. With alcohol it gives a mixture of disulphide, disulphoxide, and sulphinic acid.[6]

Anthraquinone-α-sulphur chloride is not nearly so reactive as the β-compound and will not react with acetone, phenyl benzyl ketone, acetophenone, or acetoacetic ester, although it behaves normally towards ammonia with the production of a sulphamide which under the influence of mineral acids readily passes into a thiazole :
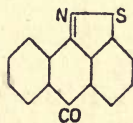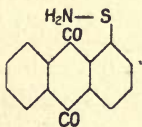
[1] Hinsberg, B. **50**, 472.   [2] Hinsberg, B. **50**, 953.
[3] Friess, B. **45**, 2965.   Friess and Schürmann, B. **52**, 2182.
[4] Friess and Schürmann, B. **47**, 1192.   M.L.B., D.R.P. 277,439.
[5] *Cf.* Zincke, A. **391**, 55 ; **400**, 1 ; **416**, 86.
[6] Friess, B. **47**, 2965.   Friess and Schürmann, B. **52**, 2170.

The α-sulphur chloride is quite stable towards water and only reacts with alcohol after prolonged boiling, and then gives the ester of the sulphenic acid, from which the free acid can be obtained by hydrolysis although it cannot be obtained from the chloride directly by the action of water. The alkali salts of the acid when treated with dimethyl sulphate give the methyl ester of the acid, but the free acid itself gives methyl anthraquinonyl sulphoxide, so that salt formation is probably accompanied by a change in structure :[1]

$$C_{14}H_7O_2.S{<}^{O}_{H} \qquad \rightleftarrows \qquad C_{14}H_7O_2.S{-}OH$$

Normal form.   Pseudo form.

Alkaline solutions of the acid are readily oxidised by the air with the production of the sulphinic acid. When the acid itself is boiled in glacial acetic acid solution simultaneous oxidation and reduction takes place with the production of a mixture of sulphinic acid and disulphide.

As stated above anthraquinone-α-sulphur chloride will not react with acetoacetic ester. It will react, however, with sodioacetoacetic ester, the product on hydrolysis giving an acetyl thiopheneanthrone :
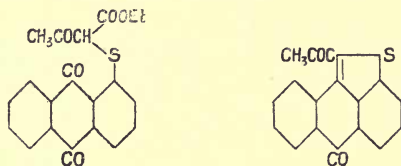
IV. The Mercaptans

The anthraquinone diazonium salts do not give the mercaptan when treated with potassium sulphydrate, although, as will be seen later, they readily give mixed sulphides when treated with aromatic alkali mercaptides. The mercaptans can, however, be prepared from the diazonium salts by indirect methods. The diazonium salts react

[1] Friess, B. **45**, 2965.   Friess and Schürmann, B. **52**, 2170.

only very slowly with copper thiocyanate, but react readily
with potassium thiocyanate, and this is especially true when
the diazonium group occupies an α-position. The resulting
thiocyanate cannot be hydrolysed by acids but can be
hydrolysed by alcoholic caustic potash, and then yields the
mercaptan.[1] A second method of obtaining the mercaptan
is to treat the diazonium salt with potassium xanthate and
then to hydrolyse the resulting anthraquinone xanthate by
boiling with aqueous alcoholic alkali.[2] Another alternative
method is to treat the diazonium salt with thiourea, no
catalyst being necessary, and then to hydrolyse the carbamyl
derivative thus formed.[3] In this case, however, there is
some tendency when dealing with α-derivatives of a side
reaction taking place with the formation of a heterocyclic
compound in which one of the cyclic carbonyl groups is
involved :
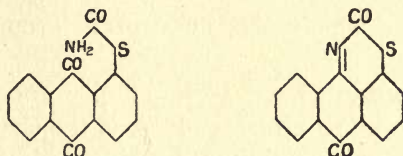
Both α-chloranthraquinone and β-chloranthraquinone
give the corresponding mercaptan when heated with alkali
sulphide, sulphydrate, or polysulphide,[4] and anthraquinone-
1-mercaptan and anthraquinone-1.5-dimercaptan can be
obtained in the same way from anthraquinone-1-sulphonic
acid and from anthraquinone-1.5-disulphonic acid.[5] Mer-
captans can also be obtained by reducing the corresponding
sulphochlorides[6] or disulphides,[7] and in the case of α-
hydroxyanthraquinones and β-hydroxyanthraquinones a
mercaptan group can be directly inserted into the molecule
in the *ortho*- position by fusing with sodium sulphide at 150°.

[1] Gattermann, A. **393**, 113. By., D.R.P. 206,054 ; 208,640.
[2] M.L.B., D.R.P. 241,985.
[3] M.L.B., D.R.P. 239,762.
[4] By., D.R.P. 204,772 ; 206,536.
[5] By., D.R.P. 212,857.
[6] M.L.B., D.R.P. 292,457. By., D.R.P. 281,102.
[7] Gattermann, A. **393**, 113. Ullmann, B. **49**, 739. Friess and Schür-
mann, B. **52**, 2176, 2186.

When two hydroxyl or amino groups are present in α-positions, if these two groups are attached to different benzene nuclei, two mercaptan groups can be inserted; but if the amino or hydroxyl groups are attached to the same nucleus, *e.g.* as in quinizarin, only one mercaptan group enters the molecule.[1] Finally, anthraquinone mercaptans have been obtained by inserting the mercaptan group into the benzoyl benzoic acid and then closing the anthraquinone ring.[2]

The anthraquinone mercaptans are rather troublesome substances to handle as they are very readily oxidised to the corresponding disulphide, in the absence of an external oxidising agent the oxidation often being brought about at the expense of the cyclic carbonyl groups. Those mercaptans in which the mercaptan group is in the α-position are much more easily oxidised than those compounds in which the mercaptan group occupies a β-position.

The mercaptans have great affinity for the fibre but are scarcely to be regarded as dyes, as the shade obtained is that of the corresponding disulphide owing to oxidation taking place in the dye bath. Thus, if a dyeing is carried out with anthraquinone-α-mercaptan at a temperature of over 50° the shade obtained is fast, but is that of the disulphide owing to oxidation taking place. Even if the dyeing is carried out in an atmosphere of carbon dioxide the disulphide is formed owing to intermolecular oxidation and reduction. If the dyeing is carried out at a temperature below 50° the shade obtained is that due to the mercaptan but is very loose to soap. Owing to their greater stability it is somewhat easier to apply the β-mercaptans to the fibre, but the shades obtained are very poor. The benzoyl derivative of anthraquinone-α-mercaptan has been prepared [3] but was found to have no tinctorial properties.

The mercaptans are, as would be expected, much more highly coloured than the corresponding oxygen compounds,

[1] G.E., D.R.P. 290,084.　　　　[2] B.A.S.F., D.R.P. 247,412.
[3] Seer and Weitzenböck, M. **31**, 371.

and this is particularly true of the alkali salts. This will be clearly seen by comparing the following substances, the colours given being in all cases those of the solutions in caustic soda :—

Red.   Violet.   Yellowish-Red.   Bluish-Red.

Violet.   Blue.   Green.

Yellowish-Red.   Violet.

V. The Selenophenols

Selenophenols of the anthraquinone series have been obtained by treating anthraquinone diazonium salts with potassium selenocyanide and then hydrolysing the seleno-cyanide,[1] and also from negatively substituted anthra-quinones, such as α-chloranthraquinone and β-chloranthra-quinone, by heating with alkali selenides.[2] They are of no particular interest.

[1] By., D.R.P. 264,940.   [2] By., D.R.P. 264,941.

VI. The Sulphides

Sulphides of the anthraquinone series can be obtained by condensing anthraquinone mercaptans with alkyl, aryl, or anthraquinonyl halides,[1] but when an anthraquinone-α-mercaptan is condensed with an alykl halide there is often a great tendency for loss of water to take place with formation of a thiophene anthrone.[2] When preparing dianthraquinonyl sulphides it is often unnecessary to isolate the mercaptan, dianthraquinonyl sulphides, for example, being obtained in one operation when either α- or β-chloranthraquinone is boiled with potassium xanthate in some suitable solvent such as amyl alcohol or nitrobenzene.[3] The dianthraquinonyl sulphides are also obtained from the mercaptans when these latter are heated to about 320°, either alone or with some substance such as an alkali or a metal which is capable of combining with sulphuretted hydrogen.[4]

The sulphur chlorides of the anthraquinone series also condense quite readily with aromatic substances such as benzene under the influence of aluminium chloride, and in the case of dimethyl aniline and phenols, especially resorcinol and β-naphthol, the sulphide is formed without the use of any condensing agent.[5] Very similar to this is the formation of sulphides [6] by condensing anthraquinone mercaptans with aromatic compounds such as benzene, toluene, naphthalene, phenol, etc., by treatment with concentrated sulphuric acid at about 30°. Here no doubt the sulphuric acid first oxidises the mercaptan to the sulphenic acid, sulphide formation then taking place by loss of water.[7] All the above methods involve the preparation of anthraquinone mercaptans, but sulphides can also be obtained from anthraquinone compounds containing negative substituents,

[1] Gattermann, A. **393**, 113. Friess and Schürmann, B. **52**, 2194. By., D.R.P. 213,960 ; 272,300 ; 274,357. M.L.B., D.R.P. 249,225 ; 253,507.
[2] See p. 370.
[3] Ullmann and Goldberg, D.R.P. 255,591. By., D.R.P. 272,298.
[4] By., D.R.P. 254,561.
[5] Friess and Schürmann, B. **52**, 2179, 2194. M.L.B., D.R.P. 277,439.
[6] M.L.B., D.R.P. 262,477.
[7] *Cf.* Davis and Smiles, Soc. **97**, 1220, Prescott, Hutchison, and Smiles, Soc. **99**, 640.

such as sulphonic acid groups,[1] nitro groups,[2] or halogen atoms,[3] by condensing them with an alkali salt of an aromatic mercaptan.

The sulphides are usually yellow vat dyes, although of no technical importance. The presence of a hydroxyl or an amino group in the *para*- position to the sulphur atom changes the shade to violet or blue.

VII. The Disulphides

The anthraquinone disulphides are easily obtained from the halogen anthraquinones by the action of alkali disulphides,[4] and as already stated are very readily produced by the oxidation of the mercaptans either by atmospheric oxygen or by potassium ferricyanide.[5] Ullmann[6] has found that α-chloranthraquinone will condense with thiolbenzoic acid, and that the product on hydrolysis yields a disulphide. Here probably the mercaptan combines with the thiolbenzoic acid to form *S*-benzoylanthraquinone-1-mercaptan, hydrolysis of this leading to the mercaptan, which under the experimental condition undergoes intramolecular oxidation with the formation of a disulphide :

β-Chloranthraquinone does not condense with thiolbenzoic acid, but from β-bromanthraquinone 2.2'-dianthraquinonyl disulphide can be obtained.

The sulphonic acids of the disulphides have very great

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[1] Decker and Würsch, A. **348**, 238. By., D.R.P. 224,589.

[2] By., D.R.P. 116,951 ; 224,589.

[3] Harrop, Norris, and Weizmann, Soc. **95**, 1316. Schaarschmidt, A. **409**, 59. B.A.S.F., D.R.P. 250,273 ; 251,115 ; 251,709. By., D.R.P. 224,589.

[4] Friess, B. **45**, 2967 ; **52**, 2176, 2186. Ullmann, B. **49**, 739. By., D.R.P. 204,772 ; 206,536.

[5] Gattermann, A. **393**, 113.   [6] A. **399**, 352.

affinity for animal fibre, the dyestuff being taken up quantitatively and the dyebath left completely colourless.

A large number of sulphur containing dyes have been described as being obtained by heating anthraquinone derivatives with sulphur chloride or sodium sulphide and/or sulphur.[1] The constitution of these compounds is quite unknown, but they are probably sulphides, disulphides, or mercaptans. In a number of cases it is claimed that a brighter shade and improved fastness is obtained by treating the dye with a mild oxidising agent such as a hypochlorite,[2] and this improvement in the tinctorial properties is probably due to the oxidation of a mercaptan to a disulphide.

Yellow and brown vat dyes have also been claimed as being obtained when anthraquinone diazonium salts are treated with sulphur chloride [3] or with a thioarsenate, thiostannate, or thioantimonate ; [4] nothing whatsoever is known of the constitution of these bodies. The same remark also applies to the dyes obtained by treating anthraquinone derivatives with sodium thiosulphate.[5]

VIII. The Diselenides

The diselenides are of very little interest, but have been obtained by the action of alkali diselenides on α-chloranthraquinone and on β-chloranthraquinone.[6]

IX. The Thianthrenes

From thianthrene itself by the phthalic acid synthesis Scholl [7] obtained a compound which was probably *lin.*-

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[1] The following are the chief patents relating to this class of compound : Agfa, D.R.P. 240,792 ; 246,867. B.A.S.F., D.R.P. 91,508 ; 186,990 ; 242,621. By., D.R.P. 172,575 ; 175,629 ; 176,641 ; 176,955 ; 178,840 ; 179,608 ; 179,671 ; 180,016 ; 226,879 ; 226,957. Cassella, D.R.P. 242,029 ; 247,416. G.C.I.B., D.R.P. 204,958 ; 205,212 ; 205,217–8 ; 208,559; 209,231 ; 209,232–3 ; 209,351; 211,967; 213,506; 223,176; 243,751 ; 254,098 ; 261,557 ; 265,194. M.L.B., D.R.P. 251,234–5 ; 311,906. Wed., D.R.P. 237,946; 293,970 ; 311,906.

[2] *E.g.* G.C.I.B., D.R.P. 209,231–2–3 ; 211,967 ; 213,506 ; 265,194.
[3] Agfa, D.R P. 229,465.   [4] Agfa, D.R.P. 229,110.
[5] Wed., D.R.P. 296,207 ; 297,079 ; 297,080 ; 297,567 ; 298,182-·3 ; 299,510.
[6] By., D.R.P. 264,941.   [7] B. **44**, 1233.

diphthaloylthianthrene (I.), whereas from methylthianthrene he obtained what was most probably *trans. bisang.*-4.4'-dimethyldiphthaloylthianthrene (II.) :
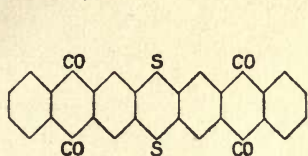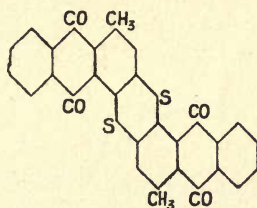
I   II

trans. bisang-Diphthaloylthianthrene itself can be obtained by condensing 1.2-dichloranthraquinone with anthraquinone-1.2-dimercaptan.[1]

All three of these substances are red in colour, but only the two *trans. bisang.* compounds are capable of being used as dyes, as the *lin.*-compound has no tinctorial properties.

[1] B.A.S.F., D.R.P. 248,171.

THE AMINOANTHRAQUINONES AND DIANTHRAQUINONYLAMINES

THE aminoanthraquinones are of great importance, as they form the starting-out point in the synthesis of a very large number of important anthraquinone derivatives. The simple primary aminoanthraquinones as a rule have no tinctorial properties, although some of the amino-hydroxy compounds are valuable dyes, e.g. Alizarin Saphirol.[1] The sulphonated aryl aminoanthraquinones are used as acid wool dyes to a considerable extent, the best known being Alizarin Cyanine Green [2] :

$$NHC_6H_3\!\!<\!\!{}^{CH_3}_{SO_3H}$$

$${}^{CH_3}_{SO_3H}\!\!>\!\!C_6H_3NH$$
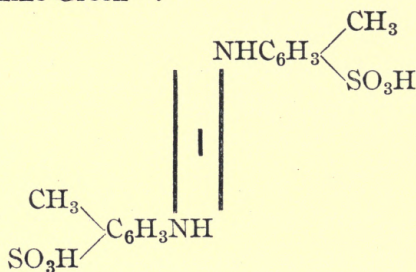
This dyes in yellowish-green shades which become faster when after-chromed.

The dianthraquinonylamines are vat dyes, but as a rule the tinctorial properties are feeble unless three anthra-quinonyl groups are present, these dianthraquinonylamino anthraquinones acting as a rule as vat dyes giving bordeaux shades, e.g. Indanthrene Bordeaux B :

[1] Solway Blue (Scottish Dyes, Ltd.).
[2] Kymric Green (Scottish Dyes, Ltd.).
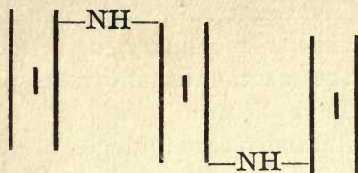
Although neither the primary aminoanthraquinones nor their acetyl derivatives have any tinctorial properties, the acylamino anthraquinones, in which the acyl group is derived from a dibasic fatty acid, or from a mono- or di-basic aromatic acid, are powerful vat dyes, and by selecting a suitable aminoanthraquinone all shades from yellow to blue and violet can be obtained. Two of the simplest dyes of this class which have found technical application are Algol Yellow W.G (a-benzoyl aminoanthraquinone) and Algol Yellow 3G (a-succinyl aminoanthraquinone) :
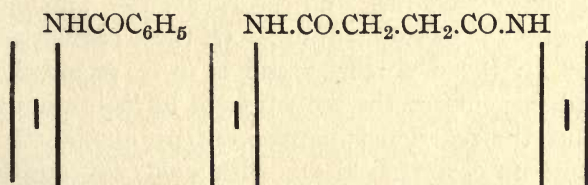
Algol Yellow W.G.

Algol Yellow 3G.

The anthraquinonyl ureas also belong to this class and are vat dyes.

The two chief methods which are utilised for introducing the amino group into the anthraquinone molecule are the reduction of nitro groups, and the replacement of negative atoms or groups such as halogen atoms or nitro, hydroxyl, or sulphonic acid groups. In addition amino and hydroxyl groups can often be introduced simultaneously by reducing the nitro compound to the hydroxylamine derivative and then treating this with an acid in order to cause the hydroxyl group to wander to the *para-* position. This last type of reaction will be discussed in the section dealing with the aminohydroxy anthraquinones.

The reduction of the nitro group leads, of course, only to primary amino compounds; but the second method, viz.

the replacement of negative groups, can be used for the production of primary, secondary, or tertiary amino compounds, and as the reaction usually takes place very easily it has been widely applied.

The primary aminoanthraquinones are extremely weak bases, but the basicity increases with the entrance of alkyl groups, the alkylaminoanthraquinones being more strongly basic than the primary compounds, and the dialkylamino anthraquinones being sufficiently basic to form salts which are not hydrolysed.

REDUCTION OF NITRO GROUPS

Although nitro groups when attached to the anthraquinone nucleus can be reduced by tin and hydrochloric or acetic acid,[1] it is much better to carry out the reduction in alkaline solution by means of sodium stannite,[2] glucose and caustic soda,[3] zinc dust and caustic soda or ammonia,[4] or sodium sulphide or sulphydrate.[5] Of these sodium sulphide gives by far the best results, and is to be regarded as the standard reagent for the reduction of nitroanthraquinones. As a rule, the reaction is carried out by making the nitro compound into a thin paste with cold aqueous sodium sulphide solution and then pouring this into boiling water and boiling the whole for a few minutes. The action of the cold sodium sulphide on the nitro compound usually produces a highly coloured solution owing to reduction to the hydroxylamine derivative, reduction to the amino compound only taking place on the application of heat. As a rule, the yield of amino compound obtained by the above method is almost quantitative, but in some cases the production of substances containing sulphur has been recorded. Thus

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[1] Böttger and Petersen, A. **160**, 149. Walsh and Weizmann, Soc. **97**, 687. Lifschütz, B. **17**, 899.

[2] Böttger and Petersen, A. **160**, 149. Römer, B. **15**, 1790 ; **16**, 366.

[3] Wacker, B. **34**, 3922.

[4] Claus, B. **15**, 1517. Przibram, D.R.P. 6,526.

[5] Böttger and Petersen, A. **160**, 149 ; **166**, 149. Ullmann, A. **388**, 203. Schaarschmidt, A. **407**, 184. Claus, B. **15**, 1517. R. E. Schmidt, B. **37**, 171. Scholl and Kacer, B. **37**, 4531. Noelting and Wortmann, B. **39**, 637. Scholl, B. **40**, 1696 ; **43**, 354. Schaarschmidt and Stahlschmidt, B. **45**, 3454. Seer, M. **32**, 160. Eckert, M. **35**, 298. By., D.R.P. 100,138 ; 119,228. Lauth, C. r. **137**, 662.

Terres [1] states that when 1-nitro-2-aminoanthraquinone is reduced with sodium sulphide side reactions take place with the production of compounds containing sulphur, but that this is not the case if ammonium sulphide is used in place of the sodium salt.[2] Schaarschmidt,[3] on the other hand, reduced both 2-nitro-3-aminoanthraquinone and 1-nitro-2-aminoanthraquinone with sodium sulphide and does not seem to have noticed any marked tendency to produce sulphur compounds. In the case of the former substance he states that the yield of the diamino compound was almost theoretical, but that in the preparation of 1.2-diaminoanthraquinone the yield was not quite so good. He gives the melting point as 301° as compared with 297–298° found by Terres.

Although the use of sodium sulphide may in some cases lead to an impure amino compound, the results as a rule are excellent, the preparation of α-aminoanthraquinone from α-nitroanthraquinone being particularly easy.[4] In this case there is no need to purify the nitroanthraquinone before reduction, as the author has found that reduction of a crude nitro compound melting fifteen or twenty degrees below the correct temperature will give an amino compound, which without recrystallising will melt within three degrees of the correct melting point.

In some cases the reduction of nitroanthraquinone sulphonic acids is accompanied by simultaneous loss of the sulphonic acid group, although this can usually be avoided by carrying out the reduction under carefully controlled conditions. Claus [5] for example, finds that 1-nitro-anthraquinone-2-sulphonic acid is best reduced to the amino acid by means of sodium amalgam.

The *partial reduction* of dinitroanthraquinones can in some cases be effected by heating under pressure with sodium sulphite,[6] although there is considerable danger

[1] B. **46**, 1641. *Cf.* Schaarschmidt, A. **407**, 84. M.L.B., D.R.P. 72,552 ; 73,684 ; 77,720 ; 81,741 ; 145,237.
[2] *Cf.* Römer, B. **15**, 1790.   [3] A. **407**, 184.
[4] Lauth, C.r. **137**, 662.   Ullmann, A. **388**, 203.
[5] B. **15**, 1517.   [6] M.L.B., D.R.P. 78,772.

that the reaction will take a different course, the nitro groups being replaced by sulphonic acid groups.[1] In the case of 1.5-dinitroanthraquinone and 1.8-dinitroanthraquinone reduction of one nitro group is easily and quantitatively brought about by heating with secondary or tertiary aromatic amines, especially dimethyl aniline.[2] This is a rather remarkable reaction and merits greater attention than it seems to have received.

The *simultaneous reduction and sulphonation* of nitroanthraquinones is sometimes brought about by the use of sodium bisulphite. This is particularly the case with dinitrodiaminoanthraquinone,[3] dinitroanthrarufin, and dinitroanthrachrysazin,[4] although not confined to these substances.[5] The simultaneous reduction and sulphonation of nitro compounds by the action of sulphites is, of course, a well-known reaction in the aromatic series, one of the best known examples being the formation of *m*-nitraniline sulphonic acid from *m*-dinitrobenzene.[6]

The *simultaneous reduction* and *bromination* of nitroanthraquinones can be effected by heating under pressure with hydrobromic acid with or without the addition of bromine.[7]

Instead of preparing aminoanthraquinones by nitrating and then reducing an anthraquinone compound, a benzoyl benzoic acid can be nitrated and reduced,[8] and the aminobenzoyl benzoic acid then converted into the aminoanthraquinone by closing the anthraquinone ring in the usual way, viz. by heating with sulphuric acid.[9] In many cases the aminobenzoyl benzoic acid can be readily purified by converting it into its well-crystallised and sparingly soluble lactam.[10]

When crude dinitroanthraquinone, obtained by the nitration of anthraquinone, is reduced with sodium sulphide a mixture of diaminoanthraquinones is obtained. This has been examined by Noelting and Wortmann,[11] who found that

[1] By., D.R.P. 164,292; 167,169.   [2] By., D.R.P. 147,851.
[3] M.L.B., D.R.P. 126,804.   [4] By., D.R.P. 103,395; 152,013.
[5] See p. 283.   [6] Nietzki, B. **29**, 2448.   D.R.P. 86,097.
[7] B.A.S.F., D.R.P. 128,845.   [8] Agfa, D.R.P. 248,838.
[9] Agfa, D.R.P. 260,899.   See also p. 140.   [10] Agfa, D.R.P. 258,343.
[11] B. **39**, 637.

if the crude bases are recrystallised from aqueous sulphuric acid (1 : 1 by volume) the difficultly soluble sulphate of 1.5-diaminoanthraquinone separated. The free bases could then be precipitated from the mother liquor and boiled in equal volumes of glacial acetic acid and acetic anhydride. On cooling the acetyl derivative of 1.8-diaminoanthraquinone separated. Fritzsche [1] obtained a dinitroanthraquinone by boiling anthracene with dilute nitric acid, and this on reduction gives a diaminoanthraquinone, which Noelting and Wortmann [2] have identified as 2.7-diaminoanthraquinone, as they find that it gives isoanthraflavic acid when diazotised and boiled with water.

Scholl has found that 1-nitro-2-methylanthraquinone is reduced to 1-amino-2-methylanthraquinone when boiled with methyl alcoholic caustic potash of 30 per cent. strength. In relation to this he discusses the mechanism of the change of *o*-nitrotoluene to anthranilic acid when heated with aqueous or alcoholic alkali, or even with water at 500–1000° C., and concludes that the first step is the formation of the quinonoid *o*-methylene nitrolic acid, which then passes into the nitrosobenzyl alcohol by the wandering of the hydroxyl group ; but for details the reader is referred to the original literature.[3]

REPLACEMENT OF NEGATIVE GROUPS

Negative atoms and groups, especially when in the *α*-position, are very readily replaced by primary amino groups by heating with ammonia, and if a primary or secondary amine is used in place of ammonia, secondary and tertiary amino compounds can be obtained. Piperidine behaves like a secondary amine and leads to N-anthraquinonyl piperidines.

Owing to the importance of the reaction the number of patents which have been taken out is extremely large, and

[1] Z. 1869, 114. *Cf*. E. Schmidt, J. pr. [2] **9**, 266.
[2] B. **39**, 637.
[3] Scholl, M. **34**, 1011.

only the more important of these will receive individual notice in the text.[1]

The dianthraquinonylamines will receive separate treatment, as they are somewhat less readily obtained than the other amino and alkyl- and aryl-aminoanthraquinones, although of considerable importance as vat dyes.

In addition to their preparation directly from negatively substituted anthraquinones, the secondary and tertiary compounds can, of course, also be obtained by the alkylation and arylation of the primary compounds, and reactions of this nature will be discussed after the description of the direct method.

REPLACEMENT OF HALOGEN ATOMS.—Halogen atoms are usually fairly easily replaced by amino groups when the halogen compound is heated with aqueous ammonia,[2] the reaction in many cases being facilitated by the use of metallic copper as a catalyst.[3] In preparing 1-aminoanthraquinone-2-carboxylic acid from the corresponding chloro acid, Ullmann[4] found that the best results were obtained by using an ester instead of the free acid, and according to the Badische Anilin u. Soda Fabrik,[5] esters with aromatic alcohols such as benzyl alcohol are the most suitable.

Halogen anthraquinones will not usually react with secondary aromatic amines, but will react with primary aromatic amines and with primary and secondary aliphatic amines, including piperidine, and here again the reaction is facilitated by the use of a copper catalyst.[6] The ease with

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[1] In addition to those mentioned in the sequel, the following are the more important patents and for the most part deal with alkyl and arylamino anthraquinone sulphonic acids. Agfa, D.R.P. 261,885. B.A.S.F., D.R.P. 106,227; 108,274; 108,873; 111,866; 113,011; 113,934; 121,155; 206,645. By., D.R.P. 101,805–6; 103,396; 107,730; 116,867; 125,578; 125,666; 126,542; 127,458–9; 127,532; 137,078; 142,052; 145,239; 148,767; 151,511; 159,129; 163,646; 165,140; 166,433; 216,773; 263,424. M.L.B., D.R.P. 99,078; 108,420; 144,111; 149,780; 158,257; 183,395; 185,546; 191,731; 209,321; 265,725; 268,454; 269,749; 272,614; 282,672; 286,092.

[2] Frey, B. **45**, 1360. Ullmann, B. **47**, 561. Schaarschmidt, A. **405**, 95. M.L.B., D.R.P. 231,091. By., D.R.P. 295,624.

[3] Ullmann, B. **49**, 747. By., D.R.P. 195,139; 295,624.

[4] B. **49**, 747. *Cf.* B. **47**, 561. [5] D.R.P. 247,411; 256,344.

[6] Ullmann, B. **52**, 2109. B.A.S.F., D.R.P. 247,411. Agfa, D.R.P. 280,646; 288,665. By., D.R.P. 195,139; 295,624. M.L.B., D.R.P. 270,790.

which the reaction takes place depends also on what other groups are present in the molecule. Thus Schaarschmidt [1] finds that the bromine atom in 1-nitrilo-2-bromanthraquinone is very reactive and is very easily replaced by an amino or alkyl or arylamino group. With ammonia, however, the condensation is accompanied by the hydrolysis of the nitrile group, the product being the amide of 2-aminoanthraquinone-1-carboxylic acid. With methylamine the tendency to hydrolyse the nitrile group was not so great, and fair yields of the N-methylamino nitrile could be obtained. The bromine atoms in 4.8-dibromanthrarufin-2.6-disulphonic acid are also extremely reactive and are readily replaced by amino groups by heating to 30–40° with aqueous ammonia of 20 per cent. strength in the presence of copper.

In some cases the use of boric acid has been recommended as facilitating the replacement of halogen atoms by arylamino groups, and Harrop, Norris, and Weizmann [2] have applied this method to various derivatives of 1.4-dichloranthraquinone.

In the great majority of cases alkylamines will only react with chloroanthraquinones when heated with them under pressure,[3] and in order to prepare alkylamino anthraquinones from chloroanthraquinones without the necessity of using an autoclave Ullmann [4] introduced what is usually known as the sulphonamide process. This elegant method is based on the fact that sulphonamides will condense with chloroanthraquinone at the ordinary pressure, and that the sulphonic acid group is then readily split off by hydrolysis. The sulphonamide generally employed is that of the easily accessible *p*-toluene sulphonic acid. If *p*-toluene sulphonamide itself is used the condensation product with a chloroanthraquinone on hydrolysis gives a primary aminoanthraquinone. If, however, *p*-toluene sulphochloride is first condensed with a primary amine, a N-alkyl sulphonamide is

[1] A. **405**, 95.
[2] Soc. **95**, 1313.
[3] By., D.R.P. 136,777–8.
[4] A. **380**, 317 ; **381**, 17. B. **49**, 741, 2158 ; **52**, 2112 ; **53**, 834. D.R.P. 224,982 ; 227,324. *Cf.* B.A.S.F., D.R.P. 293,100.

obtained, and this can then be condensed with a chloro-anthraquinone to a product which on hydrolysis gives an N-alkylaminoanthraquinone :
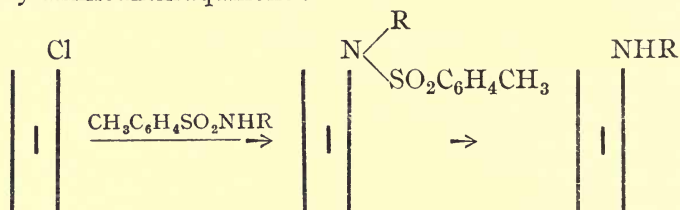
An exactly similar reaction takes place with N-aryl sulphonamides, the final product in this case being, of course, an N-aryl aminoanthraquinone. The sulphonamide process has proved to be of the utmost use in the study of the secondary aminoanthraquinones, and Schaarschmidt[1] attempted to apply it to the preparation of 1-nitrilo-2-aminoanthraquinone. In this case, however, it was not successful, as the hydrolysis of the anthraquinonyl sulphonamide was always accompanied by the hydrolysis of the nitrile group.

The replacement of halogen atoms by heating halogen anthraquinones with amines has been applied to the manufacture of one or two dyestuffs. Thus Alizarin Pure Blue B is obtained from 2.4-dibrom-1-aminoanthraquinone by heating it with *p*-toluidine and then sulphonating the product, and Anthraquinone Blue SR Extra is obtained by heating tetrabromdiaminoanthraquinone with aniline and then sulphonating[2]

REPLACEMENT OF NITRO GROUPS.—Nitro groups can be replaced by amino groups by heating the nitro compound with ammonia,[3] or with primary[4] or secondary aliphatic amines,[5] or primary aromatic amines.[6] An amino compound is not formed, however, when a nitroanthraquinone is heated with a secondary aromatic amine. The reaction in the case of 1-nitroanthraquinone-2-carboxylic acid is particularly

[1] A. **405**, 95.
[2] B.A.S.F., D.R.P. 121,684.
[3] Przibram, D.R.P. 6,526.
[4] By., D.R.P. 139,581 ; 144,634.
[5] By., D.R.P. 136,777–8. *Cf.* D.R.P. 151,512–3.
[6] Heller, B. **46**, 2702. By., D.R.P. 125,578 ; 126,803 ; 148,767. M.L.B., D.R.P. 150,332.

easy and can be brought about simply by boiling this substance in aqueous solution with the amine.[1]

It is very doubtful if a nitro group in the β-position is sufficiently reactive to be replaced by an amino or an alkyl or arylamino group. All the examples of the replacement of the nitro group by heating with a base seem to be confined to compounds in which the nitro group occupies an α-position,[2] and Kauffler [3] states that β-nitroanthraquinone is unaffected by boiling with aniline or toluidine, although similar treatment of α-nitroanthraquinone leads to the production of phenyl and tolyl aminoanthraquinone. In this connection it is notable that the nitro group of β-nitroanthraquinone is very readily replaced by the methoxy group by boiling with methyl alcoholic caustic potash.

The most important application of replacement of nitro groups by arylamino groups is the preparation of Anthraquinone Violet, which is obtained by heating 1.5-dinitroanthraquinone with p-toluidine and then sulphonating the product.[4] It is used as an acid dye for wool and silk, and gives fast shades of violet. The fastness of the dye is increased by chroming, although the shades are scarcely altered. The difference in colour between Anthraquinone Violet and the isomeric 1.4-compound (Alizarin Cyanine Green, p. 203) should be noted.

Anthraquinone Violet.　　　Erweco Acid Alizarin Blue R.
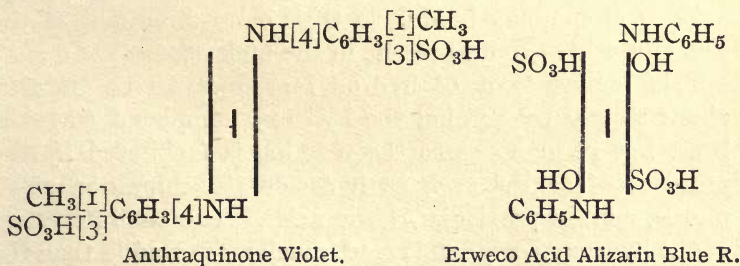
Erweco Acid Alizarin Blue R is obtained by heating dinitroanthraflavic acid disulphonic acid with aniline.[5] It

[1] B.A.S.F., D.R.P. 247,411.
[2] *Cf.* Wed., D.R.P. 235,776; 244,372; 245,014; 247,245.
[3] B. **36**, 65.　　　　　　　[4] B.A.S.F., D.R.P. 108,274.
[5] Wed., D.R.P. 235,776.

dyes wool from an acid bath in violet-red tones which change to deep blue on chroming. The shades are very fast.

REPLACEMENT OF HYDROXYL GROUPS.—The replacement of hydroxyl groups by amino groups by heating hydroxyl-anthraquinones with ammonia or primary or secondary aliphatic amines or primary aromatic amines is a reaction of very considerable importance in view of the ease with which hydroxyl groups can be introduced into the anthraquinone molecule by direct oxidation. The replacement of a hydroxyl group by an amino group appears to take place with rather greater difficulty than does the replacement of a nitro group or a halogen atom. Thus Heller [1] was able to replace the nitro group in 3-chlor-4-nitroalizarin without affecting the hydroxyl groups or the halogen atoms, and Ullmann [2] found that when 1-chlor-2-methyl-4-hydroxy anthraquinone was heated with p-toluidine and copper only the chlorine atom was affected. The production of 2-phenylamino-quinizarin from 2-bromquinizarin and aniline,[3] and the conversion of 4-nitroalizarin monoalkyl ethers into the 4-arylamino compounds [4] also supports this view, and other instances could be cited. The data available, however, do not justify any definite conclusions being drawn, and in the above cases the increased reactivity of the nitro groups or halogen atoms may be due to their orientation and to the effect of other groups present in the molecule.

The replacement of hydroxyl groups can be brought about simply by heating the hydroxy compound with the base, but in many cases the reaction is facilitated by the presence of acids,[5] such as hydrochloric, sulphuric, phosphoric, and, in particular, boric acids. The sulphite esters of the hydroxy compounds react much more readily than the hydroxy compounds themselves, and it is claimed that amino compounds can be obtained from sulphite esters by the action of ammonia at the ordinary temperature.[6]

Replacement of hydroxyl by amino groups is also

[1] B. **46**, 2702.   [2] B. **52**, 2109.
[3] By., D.R.P. 114,199.   [4] M.L.B., D.R.P. 150,322.
[5] By., D.R.P. 86,150.   [6] By., D.R.P. 61,919; 65,650; 66,917.

greatly facilitated by first reducing the hydroxyl anthra-
quinone to its *leuco-* compound, and then treating this with
ammonia or an amine, the product being finally converted
into the aminoanthraquinone by oxidation.[1] The increase
in reactivity of nuclear hydroxyl groups which takes place
on the reduction of one or both of the cyclic carbonyl groups
is remarkable, condensation with ammonia and aliphatic
amines often taking place at or about the ordinary tempera-
ture, and condensation with primary aromatic amines being
rapidly effected at or below 100°.

In some cases it is not necessary to reduce the whole of
the hydroxy compound in order to take advantage of the
increased reactivity of the reduction product. Thus it has
been claimed [2] that if a mixture of quinizarin and *leuco-*
quinizarin is heated with *p*-toluidine, the *leuco*-quinizarin
reacts with the toluidine to produce *leuco*-ditolylamino
anthraquinone, which then reduces an equivalent amount of
quinizarin to *leuco*-quinizarin, being itself thereby oxidised
to 1.4-ditolylamino anthraquinone. The *leuco*-quinizarin
thus produced then reacts with *p*-toluidine and the process
is repeated until the whole of the quinizarin has been
converted into ditolylamino anthraquinone. It will be
seen that the action of the *leuco*-quinizarin is purely
catalytic.

When the *leuco*-hydroxyanthraquinones are heated with
ammonia or an amine the hydroxyl groups attached to the
ms-carbon atoms remain unaffected, although under more
drastic conditions it is probable that they would be involved in
the reaction, as it has been found that such compounds can be
obtained from the reduction products of anthraquinone and
anthraquinone sulphonic acid by heating with *p*-toluidine.[3]
Even without reduction there is danger of the cyclic carbonyl
groups becoming involved if too drastic conditions are
employed. Thus von Perger,[4] by heating alizarin with

[1] Schrobsdorf, B. **35**, 2930. By., D.R.P. 91,149. M.L.B., D.R.P.
205,096 ; 205,149 ; 205,551.
[2] By., D.R.P. 91,150.
[3] By., D.R.P. 136,872 ; 147,277 ; 148,079.
[4] J. pr. [2] **18**, 133.

aqueous ammonia, obtained a substance which he considered to be 1.2-diaminoanthraquinone, and Liebermann and Troschke [1] by the same method obtain a substance which they considered to be an ammonium salt of an imide of alizarin. More recently Scholl and Parthey [2] have shown that the substances obtained by von Perger and by Liebermann and Troschke are really identical. They state that it is not 1.2-diaminoanthraquinone, and as it is soluble in alkali it apparently contains a hydroxyl group. As on hydrolysis it loses a molecule of ammonia and passes into 1-hydroxy-2-aminoanthraquinone Scholl and Parthey consider that it must be :
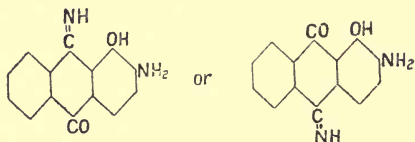
Prudhomme,[3] by the action of ammonia on *leuco*-alizarin, claims to have isolated both of these isomers, and states that he has obtained similar compounds from anthrapurpurin. In the case of hydroxyanthraquinones in which two or more hydroxyl groups are present, it is often possible to replace only one group by heating with an amine.[4] The remaining hydroxyl groups can then be replaced by treatment with a different base if desired, and by this means a great variety of amino compounds can be prepared.[5]

Alkoxy groups and aryloxy groups can also be replaced by amino groups by heating with primary or secondary amines, and in many cases the reaction takes place more readily than when the free hydroxyl compound is used.[6]

The replacement of hydroxyl groups by amino or alkyl or arylamino groups has been used for the preparation of a number of dyestuffs of which the following are the more important.

[1] A. **183**, 209.
[2] B. **39**, 1201.
[3] Bl [3] **35**, 71.
[4] Schrobsdorf, B. **35**, 2930.
[5] By., D.R.P. 86,539.
[6] By., D.R.P. 165,728 ; 205,881.   M.L.B., D.R.P. 201,905.

Alizarin Irisol D.[1]—This is obtained by heating quinizarin with one molecule of *p*-toluidine and then sulphonating the product.[2] It dyes silk and wool from an acid bath in bluish-violet shades which are fast to light, and which become greenish-blue when after-chromed. Alizarin Direct Violet R and Alizarin Cyanol Violet R are very similar and differ only from Alizarin Irisol D in the position of the sulphonic acid group. They are obtained by condensing *leuco*-quinizarin with *p*-toluidine-2-sulphonic acid.

$$NH[4]C_6H_3{[1]CH_3 \atop [3]SO_3H}$$

$$NH[4]C_6H_3{[1]CH_3 \atop [2]SO_3H}$$

OH

OH
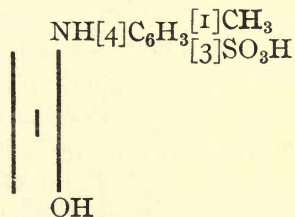
Alizarin Irisol D.
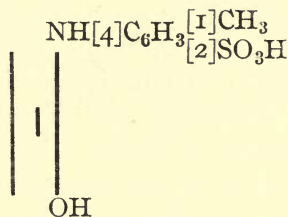
Alizarin Direct Violet R.
Alizarin Cyanol Violet R.

By replacing both the hydroxyl groups in quinizarin several important dyestuffs have been obtained. By far the most important of these is Alizarin Cyanine Green or Quinizarin Green,[3] which is obtained by heating quinizarin[4] or much better *leuco*-quinizarin[5] with *p*-toluidine and then sulphonating the product,[6] but 1.4-dichloranthraquinone or 1-chlor-4-nitroanthraquinone can be used in place of quinizarin.[7] The product dyes wool green from an acid bath, the shades being very fast and becoming even more so by chroming.

Alizarin Direct Green G and Alizarin Brilliant Green G are isomeric with Alizarin Cyanine Green and are obtained by condensing *leuco*-quinizarin with *p*-toluidine-2-sulphonic acid : [8]

[1] Solway Purple (Scottish Dyes, Ltd.).
[2] By., D.R.P. 86,150 ; 91,149.
[3] Kymric Green (Scottish Dyes, Ltd.).
[4] By., D.R.P. 86,150 ; 86,539.
[5] By., D.R.P. 91,149 ; 91,150 ; 91,152 ; 92,591 ; 93,223 ; 94,396.
[6] By., D.R.P. 84, 509 ; 89,862 ; 93,310.
[7] By., D.R.P. 125,698 ; 126,803.
[8] B.A.S.F., D.R.P. 128,753 ; 137,566 ; 148,306 ; 151,018 ; 151,384 ; 155,572. *Cf.* M.L.B., D.R.P. 172,464 ; 181,879 ; 201,905.

$NH[4]C_6H_3[_3^{[1]CH_3}]SO_3H$

$NH[4]C_6H_3[_3^{[1]CH_3}]SO_3H$
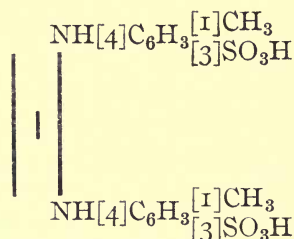
Alizarin Cyanine Green.
Quinizarin Green.

$NH[4]C_6H_3[_2^{[1]CH_3}]SO_3H$

$NH[4]C_6H_3[_2^{[1]CH_3}]SO_3H$
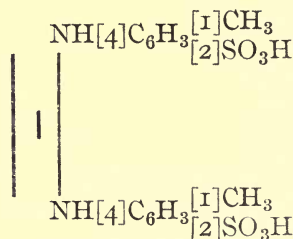
Alizarin Direct Green G.
Alizarin Brilliant Green G.

Isomeric green dyes in which the sulphonic acid groups are in the anthraquinone nucleus are obtained by condensing *leuco*-quinizarin sulphonic acid with *p*-toluidine.[1]   They are said to give purer shades of green than either of the above but do not seem to have come into technical use.   In this connection it is interesting to notice that it has been claimed that 1.4-ditoluido-8-hydroxyanthraquinone is sulphonated in the anthraquinone nucleus when the sulphonation is carried out in the presence of boric acid.[2]   If this is the case it is no doubt due to the directing influence of the hydroxyl group, or rather of its boric ester.

As stated on p. 202, the two hydroxyl groups in quinizarin and other polyhydroxy anthraquinones can be replaced by different aryl or alkylamino groups.   This has been done in the case of Alizarin Astrol, in which one hydroxyl group has been replaced by a methylamino group and the other by a tolylamino group, the sulphonated product being a greenish-blue wool dye.   It is interesting to notice the transition in colour from Alizarin Pure Blue through Alizarin Astrol to Alizarin Cyanine Green :

$NHC_6H_3\!<^{CH_3}_{SO_3H}$

Br
NH_2

Alizarin Pure Blue.

$NHC_6H_3\!<^{CH_3}_{SO_3H}$

$NHCH_3$

Alizarin Astrol.

$NHC_6H_3\!<^{CH_3}_{SO_3H}$

$NHC_6H_3\!<^{CH_3}_{SO_3H}$
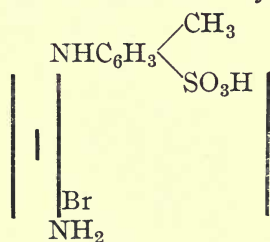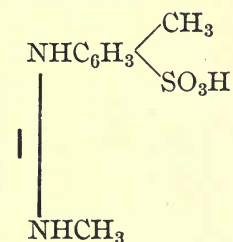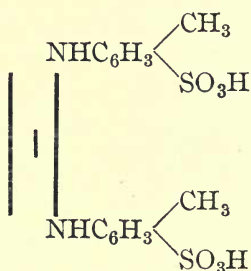
Alizarin Cyanine Green.

[1] By., D.R.P. 95,625 ; 101,919.   [2] By., D.R.P. 170,113.

Of the various other dyes which have been obtained by heating hydroxyanthraquinones with bases only two call for special notice. Alizarin Viridine is 5.6-dihydroxy-quinizarin green and is obtained by heating Alizarin Bordeaux with p-toluidine and then sulphonating the product. It is a mordant dye and is used for producing green shades on chrome mordanted cotton. Alizarin Blue-Black [1] is obtained by heating purpurin with aniline and then sulphonating the product. As it is also obtained by sulphonating the condensation product of 2-bromquinizarin and aniline it must have the formula [2] :

$$NHC_6H_4SO_3H$$
$$-NHC_6H_4SO_3H \qquad\qquad OH$$
$$\qquad\qquad\qquad NHC_6H_4SO_3H$$

or

$$OH \qquad\qquad\qquad NHC_6H_4SO_3H$$
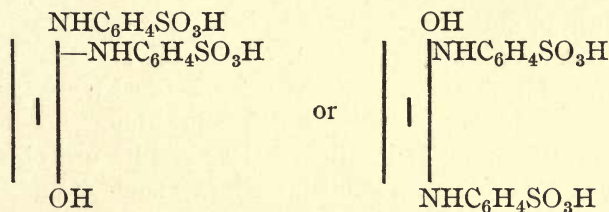
and cannot be a sulphonation product of 2-hydroxy-1.4-diphenylaminoanthraquinone as originally thought.

REPLACEMENT OF SULPHONIC ACID GROUPS.—The replacement of sulphonic acid groups by amino groups is of very considerable importance, as a very large number of sulphonic acids can be readily obtained by sulphonating with or without the addition of a mercury catalyst (p. 176). As sulphonic acid groups enter the anthraquinone nucleus in the β-position when the sulphonation is carried out in the absence of mercury, the replacement of the sulphonic acid group renders β-amino compounds easily accessible, although they are often troublesome to obtain by other methods. Thus β-aminoanthraquinone, the mother substance of many of the valuable Indanthrene colours, is easily obtained from sodium anthraquinone-β-sulphonate (the " silver salt " of commerce) by heating with aqueous ammonia, although it is expensive and troublesome to produce by other methods. The conversion of the sulphonic acids into the amine is also the best method of characterising the sulphonic acids, the

[1] Solway Blue-Black (Scottish Dyes, Ltd.). [2] By., D.R.P. 114,199.

methylamino compounds, obtained by the use of methyl-amine, being specially suitable for this purpose.

The sulphonic acid group can be replaced by the primary amino group by heating the sodium salt with sodamide,[1] but it is much simpler and better to use aqueous ammonia ; [2] and primary and secondary alkylamines and primary arylamines react in the same way. It is usual to employ aqueous solutions, and to obtain a sufficiently high tempera-ture it is necessary to work under increased pressure.

In all these reactions sodium sulphite is formed, and at the high temperatures used (about 180–220°) this attacks the anthraquinone nucleus unless it is destroyed or rendered inactive as rapidly as formed. This can be done by the addition of barium chloride,[4] as this reacts with the sulphite to form the barium sulphite, which being almost insoluble is more or less harmless. Much better results are obtained, however, by adding an oxidising agent,[5] such as manganese dioxide (preferably in the form of Weldon mud), which is capable of oxidising the sulphite to sulphate. Attempts have also been made to utilise the reducing power of the sulphite. Thus it has been stated [6] that satisfactory yields of β-aminoanthraquinone are obtained by heating sodium anthraquinone β-sulphonate with aqueous ammonia and nitrobenzene. In this case the nitrobenzene acts as an oxidising agent and is thereby reduced to aniline, so that the manufacture of aniline and of β-aminoanthraquinone is combined in one process. As the aminoanthraquinones are not volatile with steam there is no difficulty in separating the β-aminoanthraquinone from the aniline and unchanged nitrobenzene.

HOFMANN'S REACTION.—Aminoanthraquinones can be prepared from the amides of the anthraquinone carboxylic acids by Hofmann's method (treatment with hypochlorite or hypobromite), but the method has not been extensively used

[1] Sachs, B. **39**, 3019.
[2] R. E. Schmidt, B. **37**, 70.
[3] By., D.R.P. **135,634** ; **142,154** ; **175,024** ; **181,722**. B.A.S.F., D.R.P. 288,464. *Cf.* D.R.P. 77,721 ; 90,720.
[4] M.L.B., D.R.P. 267,212. *Cf.* Geigy, E.P. 127,223[19].
[5] B.A.S.F., D.R.P. 256,515. [6] G.C.I.B., A.P. 1,255,719.

as the amides are not particularly accessible and the amino-
anthraquinones are usually more easily obtained by other
methods. Hofmann's method, however, has been employed
by Eckert [1] and by Willgerodt and Maffelzzoli,[2] who prepared
2-aminoanthraquinone-3-carboxylic acid from the amide of
anthraquinone-2.3-dicarboxylic acid. Other investigators
have also made use of the method [3] although to no consider-
able extent.

ALKYLATION AND ARYLATION.

So far the methods which have been discussed have been
those by which an amino group is introduced into the
anthraquinone molecule. The primary amino anthra-
quinones can, however, be converted into secondary and
tertiary compounds by the usual methods of alkylation
and arylation, and attention will now be directed to some
of the more interesting results which have been obtained.
The description of compounds in which two anthraquinone
residues are attached to the same nitrogen atom (the di-
anthraquinonylamines) will, however, be reserved for a
separate section (p. 231) as they merit special treatment.

The *alkylation* of the aminoanthraquinones can be
brought about in the usual way by means of alkyl halides,
but in some cases abnormal results are obtained. Eckert,[4]
for example, endeavoured to prepare the glycine of 2-amino-
anthraquinone-3-carboxylic acid by treating it with chlor-
acetic ester, but instead of the glycine the chloracetyl
compound $C_{16}H_6O_2(COOH)(NHCOCH_2Cl)$ was obtained.
Seer and Weitzenböck [5] succeeded in preparing glycines
from monamino and 1.5-diamino anthraquinone and found
that the diglycine of the latter compound had tinctorial
properties and was capable of dyeing wool in red shades.
They also prepared some benzyl derivatives and found
that 1.5- and 1.8-dibenzylaminoanthraquinone could not be
reduced in alkaline solution.

[1] M. **35**, 290.　　　　　　　[2] J. pr. [2] **82**, 205.
[3] Scholl, B. **40**, 1691. Schaarschmidt, B. **50**, 294 ; **51**, 1074. Terres,
B. **46**, 1640. Graebe and Blumenfeld, B. **30**, 1116.
[4] M. **35**, 290.　　　　　　　[5] M. **31** 379.

Methylation with dimethyl sulphate sometimes leads to abnormal results as 1-amino-4-arylamino anthraquinones are simultaneously sulphonated,[1] the product being a 1-methylamino-4-arylaminoanthraquinone sulphonic acid, although it is doubtful whether the sulphonic acid group is attached to the anthraquinone nucleus or to the aryl group. The sulphonation can hardly be a side reaction due to liberation of sulphuric acid from the dimethylsulphate, as it takes place even in the presence of excess of sodium carbonate. Other amino anthraquinones are conveniently methylated by heating to 180–200° with methyl alcohol or dimethyl sulphate in the presence of concentrated sulphuric acid or oleum, this procedure rendering possible the use of open vessels.[2]

Alkylene oxides will combine with primary aminoanthraquinones, α-aminoanthraquinone and ethylene oxide [3] giving $C_{14}H_7O_2NHCH_2CH_2OH$, and epichlorhydrin [4] giving a compound which contains chlorine and probably has the formula $C_{14}H_7O_2NHCH_2CHOHCH_2Cl$. On sulphonation this yields a yellow acid dye.[5]

Glyoxylic acid combines with α- and β-aminoanthraquinol to form the glycine of α- and β-aminoanthraquinone.[6] Here probably the azomethine compound of anthraquinol is first formed, the azomethine group then being reduced at the expense of the quinol group :

$$
\begin{array}{c}
\text{OH} \\
| \\
\text{C} \\
\text{C}_6\text{H}_4\!\!<\!\!\bigcirc\!\!>\!\!\text{C}_6\text{H}_3\text{N}:\text{CHCOOH} \rightarrow \\
\text{C} \\
| \\
\text{OH}
\end{array}
\qquad
\begin{array}{c}
\text{CO} \\
\text{C}_6\text{H}_4\!\!<\!\!\bigcirc\!\!>\!\!\text{C}_6\text{H}_3\text{NHCH}_2\text{COOH} \\
\text{CO}
\end{array}
$$
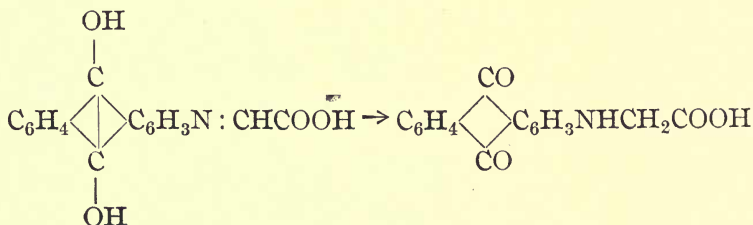
In some cases primary aminoanthraquinones can be converted into secondary and tertiary compounds by diazotising and then treating the diazonium salts with a

[1] M.L.B., D.R.P. 174,131. [2] By., D.R.P. 288,825.
[3] By., D.R.P. 235,312. [4] By., D.R.P. 218,571.
[5] By., D.R.P. 220,627. [6] M.L.B., D.R.P. 232,127.

primary or secondary amine, and this process has been investigated by Wacker.[1] He found that 1-aminoanthra-quinone-2-sulphonic acid when diazotized gave an internal anhydride which reverted to the original amino compound when treated with ammonium carbonate, but which gave the methylamino and diethylamino sulphonic acid when treated with methylamine carbonate or diethylamine :
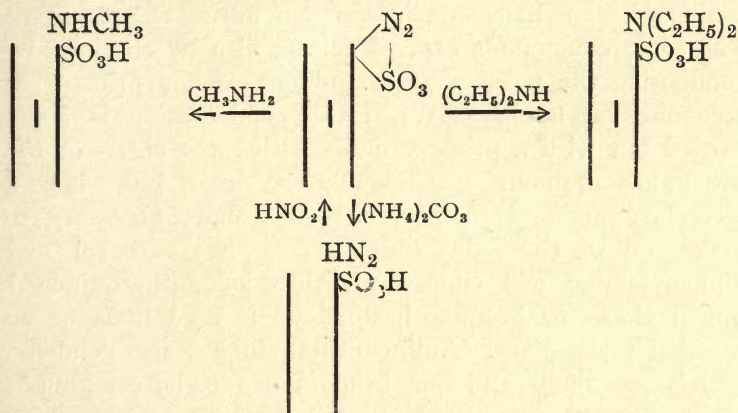
When treated with aniline, however, the diazo anhydride gave first the diazoamino compound, which under the influence of acids broke down into the original amino-sulphonic acid, phenol and nitrogen.

The above reactions are by no means general, as 1.5- and 1.8-diaminoanthraquinone when tetrazotized gave with ammonia a mixture of the original diamino compound and an aminohydroxy compound, with methylamine the original diamino compound only, and with diethylamine only the dihydroxy compound, whereas the diazonium salt of 1-amino-4-hydroxyanthraquinone when treated with methylamine gave quinizarin.

Primary aminoanthraquinones combine with aldehydes and compounds of the type $C_{14}H_7O_2NHCH_2[1]C_6H_4[4]NR_2$ are obtained by condensing α-aminoanthraquinone with formaldehyde and tertiary aromatic amines such as di-methyl aniline.[2] Kauffler[3] has studied the benzylidene

[1] B. **34**, 2593, 3922. [2] M.L.B., D.R.P. 236,769. [3] F.T. **2**, 471.

aminoanthraquinones but without obtaining results of any particular interest.

The *arylation* of the aminoanthraquinones can be carried out in the usual way by heating the amino compound with the aryl halide in the presence of a copper catalyst such as copper powder, copper acetate or cuprous chloride, and a substance such as sodium acetate which is capable of combining with the halogen acid split out during the reaction.[1] The same compounds can, of course, also be obtained by condensing the halogen anthraquinone with a primary or secondary arylamine.[2] When the condensation is being carried out with a primary amine either the chlor- or the brom-anthraquinone can usually be used, but when a secondary amine is employed it is usually necessary to make use of the iodo- compound. Thus carbazol and diphenylamine will condense with α-iodoanthraquinone,[3] but if chlor- or brom-anthraquinone is used little or no reaction takes place. Aminoanthraquinones also condense with benzoquinone and α-naphthoquinone to give compounds of the type $(HO)_2[1.4]C_6H_3[2]NHC_{14}H_6O_2NH_2$, from which vat dyes giving fast shades of bordeaux can be obtained by condensation with halogen anthraquinones so as to form a dianthraquinonylamine derivative.[4]

Tinctorial Properties.

Although the primary aminoanthraquinones are highly coloured substances, they have little or no affinity and consequently are useless as dyestuffs. To a certain extent the same is true of the secondary and tertiary compounds, but in some cases these show very considerable affinity, and as has already been shown (p. 203), valuable acid dyes are formed by sulphonating the secondary 1.4-diaminoanthraquinones.

[1] Laube, B. **40**, 3564. By., D.R.P. 175,069. B.A.S.F., D.R.P. 280,881. For further references see p. 211.

[2] Laube and König, B. **41**, 3874. Agfa, D.R.P. 243,489. M.L.B., D.R.P. 255,821.

[3] Laube, B. **40**, 3564.   [4] Cas., D.R.P. 267,414–5–6 ; 269,801.

When the nitrogen atoms of two molecules of an amino-anthraquinone are joined by a carbon chain so as to produce a compound of the type $C_{14}H_7O_2NH—X—NHC_{14}H_7O_2$, tinctorial properties are often developed and some of the products thus formed are said to act as very fast vat dyes, although they do not seem to have been placed on the market. One of the simplest of these is *sym*-dianthraquinonyl-ethylenediamine, which Ullmann and Medenwald [1] prepared from β-aminoanthraquinone and ethylene dibromide by the sulphonamide process. When used as a vat dye it gives orange shades, but the affinity is very poor. Curiously enough, the corresponding compound derived from α-amino-anthraquinone does not seem to have been described, although it should be of considerable interest, as it would no doubt readily pass into a complex heterocyclic compound.

In the above type of compound much greater affinity is obtained when X represents an aryl residue, and at the same time the colour is shifted towards the violet end of the spectrum. Such compounds can be obtained by condensing two molecules of a halogen anthraquinone with one molecule of an aromatic diamine such as *p*-phenylene diamine, benzidine,[2] etc., or by condensing two molecules of an amino-anthraquinone with one molecule of an aromatic dihalogen compound such as *p*-dichlorbenzene [3] (violet shades), p_2-dichlorbenzil [4] (red shades), p_2-dichlordiphenylmethane [5] (bordeaux shades), dichlorphenanthraquinone [6] (red shades), dichlorbenzophenone " [7] (red shades), or p_2-dichlordiphenyl [8] (violet shades). The condensation product from amino-anthraquinone and p_2-dichlordiphenyl can also be obtained from chloranthraquinone and benzidine, and Brass [9] has obtained it and similar compounds by oxidising diaryl-aminoanthraquinones with manganese dioxide and sulphuric acid.

Vat dyes have also been obtained [10] by condensing

[1] B. **46**, 1798. [2] Agfa, D.R.P. 243,489.
[3] By., D.R.P. 215,294. [4] B.A.S.F., D.R.P. 222,205; 230,400.
[5] B.A.S.F., D.R.P. 230,411. [6] B.A.S.F., D.R.P. 222,206; 230,400.
[7] B.A.S.F., D.R.P. 220,579; 230,399. [8] By., D.R.P. 230,409.
[9] B. **46**, 2907. W.T.M., D.R.P. 251,845. [10] By., D.R.P. 248,655

two molecules of a primary aminoanthraquinone with one molecule of a compound of the general formula ClAr—X—ArCl, where Ar represents an aryl residue and X is O, S, or NH, and may or may not form part of a ring, *e.g.* a carbazol ring.

Of somewhat different structure are the vat dyes which are obtained by condensing two molecules of an aminoanthraquinone with one molecule of a *sym*-dihalogen diaryl urea,[1] or with compounds of the type [2] $HlgRNHCO(CH_2)_n$-$CONHRHlg$, where n is 0, 1, 2, 3, etc. Somewhat similar dyes are obtained by condensing dihalogen sulphones with aminoanthraquinones.[3]

The shades produced by the diarylaminoanthraquinones depend to a considerable extent on the position of the arylamino groups. As already shown (p. 203) the 1-4-diarylaminoanthraquinones give rise to green dyes, *e.g.* Alizarin Cyanine Green. When the arylamino groups are in the 1.5 positions, the shades are usually violet, *e.g.* Anthraquinone Violet (p. 199), whereas when in the 1.8- positions they are red.

Acylaminoanthraquinones

Converting an aminoanthraquinone into an acylamino compound is always accompanied by a marked increase in tinctorial properties, powerful vat dyes being obtained when the acyl group is derived from an aromatic acid like benzoic acid, or from a dibasic fatty acid such as malonic or succinic acid. The acyl groups derived from the monobasic fatty acids, such as formic and acetic acid, also confer tinctorial properties, although to a much lesser degree, the affinity of the resulting acyl aminoanthraquinones being too slight for them to be of any value as technical dyes. Although the acyl aminoanthraquinones derived from monobasic aromatic carboxylic acids have great affinity, this is not the case with the derivatives of aromatic sulphonic acids,

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[1] M.L.B., D.R.P. 241,837.   [2] M.L.B., D.R.P. 241,838.
[3] By., D.R.P. 234,518.

the N-anthraquinonyl sulphonamides as a rule having no tinctorial properties.[1]

The acylaminoanthraquinones are very readily obtained from the amino compound by heating it with the acid chloride [2] or with the free acid [3] in some inert solvent of high boiling point such as nitrobenzene or naphthalene. The acid chloride, of course, reacts most readily, sodium acetate being added in order to neutralise the hydrochloric acid liberated. When preparing acetyl derivatives it is often advantageous to dissolve the amino compound in concentrated sulphuric acid or oleum containing 10–25 per cent. of sulphur trioxide and then to add acetic anhydride, glacial acetic acid or anhydrous sodium acetate. By this means both primary and secondary compounds, including dianthraquinonyl-amines, can be acetylated, although in some cases acetylation only takes place with difficulty when less drastic methods are employed.[4]

In some cases an ester or an amide of the acid can be used for inserting the acyl group,[5] but in other cases the reaction takes a different course.[6] Thus the aminoanthraquinones, when heated with alkaline alcoholic solutions of ethyl oxalate, do not give the oxalyl derivatives, but yield yellow or red vat dyes which probably have the constitution A—N=C—C=N—A, where A is an anthraquinone residue.

$$\underset{\displaystyle OEt}{\overset{\displaystyle |}{}} \quad \underset{\displaystyle OEt}{\overset{\displaystyle |}{}}$$
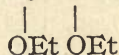
Acylaminoanthraquinones can also be obtained by condensing a halogen anthraquinone with an acid amide,[7] although this method has not been employed to any great extent. The condensation is carried out in the presence of a copper catalyst, sodium acetate being added to neutralise the hydrochloric acid liberated.

As stated on p. 212, the acylaminoanthraquinones

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[1] Seer and Weitzenböck, M. **31**, 371.

[2] By., D.R.P. 223,069 ; 225,232 ; 227,104 ; 227,398 ; 248,289.

[3] By., D.R.P. 210,019 ; 212,436 ; 216,980 ; 223,069 ; 223,510 ; 224,808 ; 226,940.

[4] B.A.S.F., D.R.P. 211,958.

[5] By., D.R.P. 210,019 ; 212,436 ; 216,980.

[6] By., D.R.P. 270,579.   [7] By., 216,772.

derived from the monobasic fatty acids are of but minor interest owing to their feeble tinctorial properties. Greater affinity is obtained by condensing one molecule of chloracetyl chloride with two molecules of aminoanthraquinone, the resulting N-anthraquinonylglycylaminoanthraquinones being brown or bordeaux dyes.[1] The shades, however, are rather weak, and not particularly fast to light, so that the substances have but little technical interest.

Of the acylaminoanthraquinones derived from dibasic fatty acids, compounds derived from oxalic, malonic, succinic, adipic, maleic, malic, tartaric, and camphoric acids have been described.[2] These are all vat dyes, and are fairly readily obtained by boiling an aminoanthraquinone with the acid in nitrobenzene solution, with or without the addition of a condensing agent such as phosphorus pentachloride, zinc chloride, boric acid, etc. The reaction takes place in two steps, and if desired one molecule of the acid can be made to condense with two different aminoanthraquinones.[3] The only technical dyestuff derived from a dibasic fatty acid appears to be Algol Yellow 3G (succinyl-α-aminoanthraquinone), although it is probable that Algol Brilliant Violet R is succinyl diaminoanthrarufin.

Of the aromatic acids which have been used for preparing acylaminoanthraquinones, benzoic, phthalic, terephthalic, salicylic and cinnamic have all been used,[4] and yellow and orange vat dyes have also been obtained by condensing the chloride of anthraquinone carboxylic acid with diamines such as benzidine,[5] and also with aminoanthraquinone.[6] They are, however, of no technical importance. Only the benzoyl derivatives have met with any wide technical application, and these are almost invariably prepared by means of the readily accessible benzoyl chloride. α-Salicylaminoanthraquinone has, however, been used to a

[1] B.A.S.F., D.R.P. 248,997.
[2] By., D.R.P. 210,019; 212,436; 216,980; 223,069; 226,940. For ureas, thioureas, urea chlorides and urethanes, see p. 219.
[3] By., D.R P. 223,510; 224,808.
[4] For references see p. 213.
[5] B.A.S.F., D.R.P. 215,182; 236,442.
[6] Seer and Weitzenböck, M. 31, 371.

certain extent as a pigment colour under the name Helio Fast Yellow.

Of the technical dyes which are benzoylaminoanthra-quinones the following are the most important :—

NHCOC$_6$H$_5$ NHCOC$_6$H$_5$ NHCOC$_6$H$_5$

OH   OCH$_3$
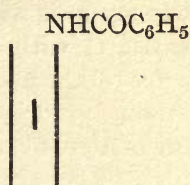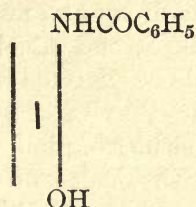
Algol Yellow WG.   Algol Pink R.   Algol Scarlet G.

NHCOC$_6$H$_5$ NHCOC$_6$H$_5$

NHCOC$_6$H$_5$ C$_6$H$_5$CONH
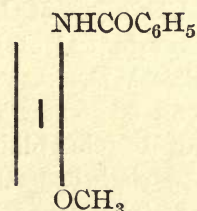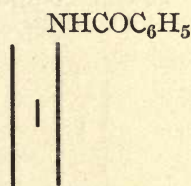
Algol Red 5G.[1]   Algol Yellow R.

HO   NHCOC$_6$H$_5$ HO   NHCOC$_6$H$_5$

C$_6$H$_5$CONH   C$_6$H$_5$CONH   OH
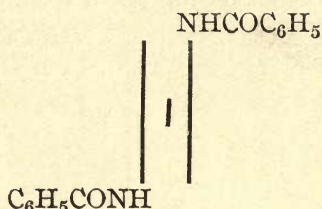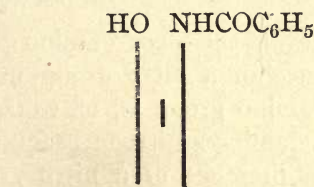
Algol Red FF.   Algol Brilliant Violet 2B.

HO   NHCOC$_6$H$_5$

HO   OH
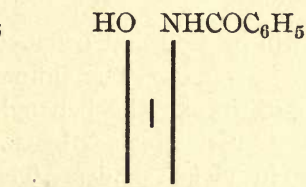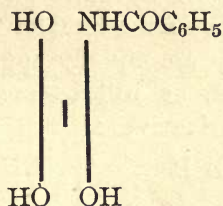
Algol Violet B.

The position and nature of substituent groups has a considerable effect on the colour of the benzoylaminoanthra-quinones. Thus when there is a benzoylamino group at 1 :

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[1] Caledon Red 5G (Scottish Dyes Ltd.).

(*a*) Substituents at 2 have comparatively little effect.

(*b*) Substituents at 4, other than halogen atoms, have a great effect and shift the shade towards the violet end of the spectrum.

The effect of the hydroxy and methoxy group is seen by comparing Algol Pink R and Algol Scarlet G with Algol Yellow WG. As would be expected, the effect of the hydroxy group is greater than that of the methoxy group, Algol Pink R giving bluish shades of pink, whereas Algol Scarlet G gives slightly yellowish shades of scarlet. The effect of an amino group is very pronounced, as will be seen by comparing the shades obtained from the following compounds :

$NHCOC_6H_5$	$NHCOC_6H_5$	$NHCOC_6H_5$
NH_2	$NHCH_3$	$NHCOC_6H_5$
Corinth.	Blue.	Yellowish-red.

It will be seen that benzoylating the second amino group lessens its effect. The influence of a nitro group in the *para*- position to the benzoylamino group is, as would be expected, very great, 1-benzoylamino-4-nitroanthraquinone dyeing in violet shades. The presence of a nitro group, however, is objectionable in a vat dye owing to its liability to become reduced in the dyebath.

Although the above remarks refer to the benzoyl amino-anthraquinones, they are equally applicable to other acyl-aminoanthraquinones, as will be seen by comparing the following succinyl derivatives :

$NHCOCH_2CH_2CONH$	$NHCOCH_2CH_2CONH$
	OH HO
Yellow.	Scarlet.

NHCOCH₂CH₂CONH   NHCOCH₂CH₂CONH

OCH₃   CH₃O   NO₂   NO₂

Orange.   Violet-red.

(c) Substituents at 5 have, as a rule, comparatively little effect on the colour, amino groups producing red shades.

The effect of the nitro group is extraordinarily small and merely changes the colour from yellow to orange or red. The very slight influence of groups at 5 will be clearly seen by comparing the shades produced by the following compounds with those obtained from the isomers mentioned above :

NHCOC₆H₅   NHCOC₆H₅   NHCOC₆H₅

CH₃NH   HO   NO₂

Red.   Yellow.   Orange-red.

NHCOCH₂CH₂CONH   NHCOCH₂CH₂CONH

NH₂   NH₂ NO₂   NO₂

Orange.   Red.
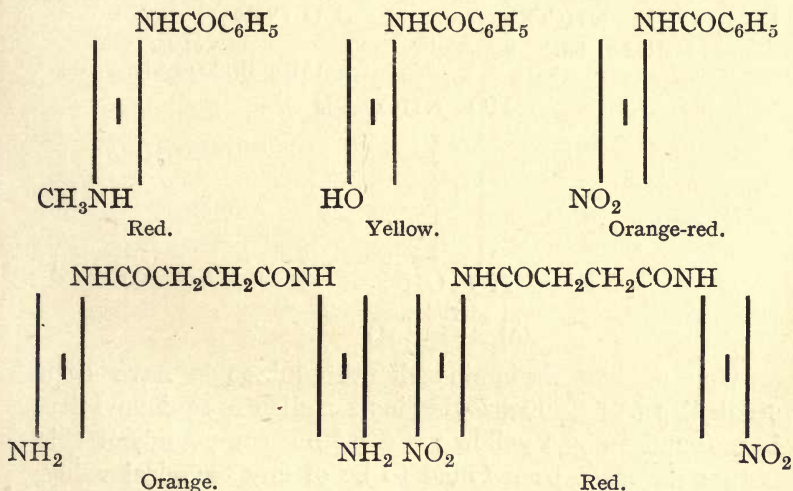
(c) But little information is available as regards the influence of substituents at 8, but the effect is probably decidedly less than that of substituents at 4, as the succinyl derivative of 1.8-diaminoanthraquinone dyes only in yellow shades.

(d) When several substituents are present the case becomes somewhat complicated, as they often modify or

reinforce one another. In connection with this it will be sufficient to give five examples :

NHCOC$_6$H$_5$
NHCOC$_6$H$_5$
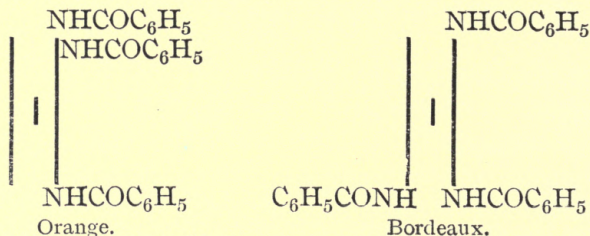
NHCOC$_6$H$_5$
Orange.
(Algol Brilliant Orange FR.)

NHCOC$_6$H$_5$

C$_6$H$_5$CONH   NHCOC$_6$H$_5$
Bordeaux.

C$_6$H$_5$CONH   NHCOC$_6$H$_5$

C$_6$H$_5$CONH   NHCOC$_6$H$_5$
Red-violet.

HO   NHCOC$_6$H$_5$

C$_6$H$_5$CONH   OH
Blue-violet.
(Algol Brilliant Violet 2B.)

HO   NHCOC$_6$H$_5$
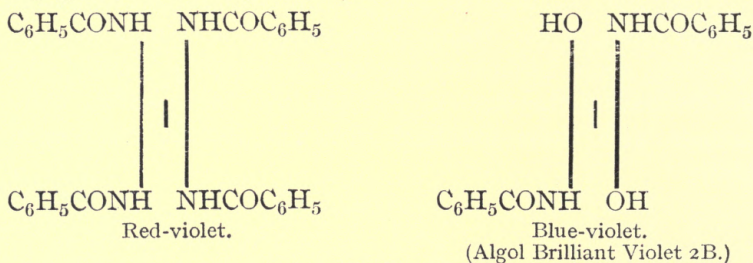
HO   OH
Red-violet.
(Algol Violet B.)
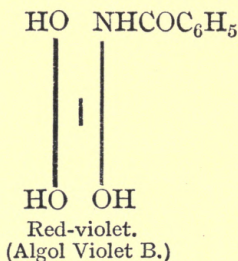
One or two acylamino dianthraquinonyls have been studied, e.g. 4.4'-dibenzoylamino-1.1'-dianthraquinonyl has been found to be a yellow vat dye,[1] but compounds of this nature have not been found to be of any technical value. It should be noted that the shades obtained from amino-benzoylaminoanthraquinones are usually rather loose to acids and chlorine, although this can be remedied to a large extent by acetylating the amino group.[2]

The presence of a sulphonic acid group attached to the anthraquinone nucleus has the effect of reducing the colour slightly. The products, however, are readily soluble in

[1] By., D.R.P., 227,104.   [2] M.L.B., D.R.P. 240,079.

water and are not hydrolysed by boiling dilute acids, and can, therefore, be used as acid wool dyes.[1]

UREAS AND THIOUREAS

A considerable amount of work has been carried out in the study of the carbonic acid derivatives of the aminoanthraquinones, but the whole of the work published so far has been in the form of patent specifications, and consequently the information available at present is far from complete.

Ureas are formed by the action of carbonyl chloride on the aminoanthraquinones at about 170° in solution or suspension in some indifferent solvent such as nitrobenzene.[2] In the case of β-aminoanthraquinone the reaction takes place without the use of any condensing agent, but a urea can only be obtained from α-aminoanthraquinone in the presence of anhydrous sodium acetate or other substance capable of neutralising the hydrochloric acid set free. The urea is not the only product obtained by the action of phosgene on aminoanthraquinones, as at the ordinary temperature a mixture of the urea chloride and the hydrochloride of the base is formed.[3] This latter substance by the prolonged action of excess of phosgene passes into the urea chloride, although the change is more rapid if the calculated amount of phosgene is allowed to react with it at 40–120°. Anthraquinone *iso*-cyanates do not seem to be formed directly by the action of phosgene on the amino compounds, although they are obtained in good yield by heating the urea chloride in nitrobenzene solution.[4]

Instead of treating the aminoanthraquinone with phosgene the urea can be prepared by means of chlorcarbonic ester, β-aminoanthraquinone, for example, giving the urea when boiled in naphthalene solution with ethylchlorcarbonate,[5] although under less drastic conditions the urethane is produced.[6] The urea is also formed when

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[1] By., D.R.P. 223,069.
[2] M.L.B., D.R.P. 232,739.
[3] M.L.B., D.R.P. 238,550 ; 241,822.
[4] M.L.B., D.R.P. 224,490.
[5] M.L.B., D.R.P. 242,292.
[6] By., D.R.P. 167,410 ; 171,588.

β-aminoanthraquinone is heated to 70° with urea in nitro-benzene solution.[1]

Mixed ureas containing either two different anthra-quinone residues, or one anthraquinone residue and one aromatic residue, can be obtained by condensing the anthra-quinone urea chloride or the urethane [2] with a molecule of an aminoanthraquinone or an alkylamine or arylamine. By using ammonia a monoanthraquinonyl urea is obtained.[3] The procedure can, of course, be inverted and the urethane condensed with β-aminoanthraquinone. In this case ure-thane itself gives dianthraquinonyl urea,[4] whereas mixed aryl anthraquinonyl ureas are obtained from aryl urethanes.[5] Mixed ureas can also be obtained by condensing an amino-anthraquinone with an aryl *iso*-cyanate,[6] or by condensing an anthraquinone-*iso*-cyanate with a primary or secondary aliphatic amine or a primary aromatic amine.[7] Finally, it may be pointed out that an aminobenzoyl benzoic acid can be converted into a urea derivative by any of the usual means, *e.g.* by treatment with phosgene, and the anthra-quinone ring then closed by treatment with a dehydrating agent, such as concentrated sulphuric acid at 90°. As a rule, the closing of the ring takes place very easily and to avoid hydrolysis should be brought about at as low a tempe-rature as possible.[8]

Sulphonated anthraquinonyl ureas can be obtained by converting an anthraquinone sulphonic acid into its urea derivative,[9] or by sulphonating the anthraquinonyl urea,[10] but are of but little interest. The ureas can also be halo-genated.[11]

Very few of the anthraquinonyl ureas have been found to be of sufficient value to justify their use as commercial dyes, but 2.2′-dianthraquinonyl urea has been placed on the market as Helindon Yellow 3GN, and a more complex

[1] M.L.B., D.R.P. 238,551 ; 238,553.   *Cf.* Sonn, B. **47**, 2437.
[2] M.L.B., D.R.P. 236,375 ; 236,978–9 ; 236,980 ; 236,983–4 ; 238,550.
[3] M.L.B., D.R.P. 236,978.   [4] M.L.B., D.R.P. 238,552.
[5] M.L.B., D.R.P. 236,981.   [6] M.L.B., D.R.P. 229,111.
[7] M.L.B., D.R.P. 231,853.   [8] Agfa, D.R.P. 281,010.
[9] M.L.B., D.R.P. 236,984.   [10] M.L.B., D.R.P. 229,408.
                    [11] M.L.B., D.R.P. 240,192.

dye, Helindon Brown 2GN, is obtained by condensing two molecules of anthraquinone-β-urea chloride with various diaminoanthraquinones :

$$|-NHCONH-| \qquad |-NHCONHC_{14}H_6O_2NHCONH-|$$

Helindon Yellow 3GN.   Helindon Brown 3GN.

The urea chlorides condense readily with phenols and naphthols when boiled with these in some indifferent solvent such as xylene.[1] The products are yellow vat dyes, but are of no particular interest. They have the structure $C_{14}H_7O_2NHC—OAr.$

$$\overset{\|}{O}$$

Of greater interest are the yellow vat dyes which are obtained when the urea chloride is treated with a tertiary base such as dimethyl aniline or pyridine.[2] The reaction takes place at the ordinary temperature with the evolution of heat, but the constitution of the products obtained is not known. They are yellow, but become red or violet in the presence of strong alkali, the colour being discharged, however, on dilution. The urea chlorides also undergo a little-understood condensation when boiled with sodium acetate or sodium carbonate and some indifferent solvent, such as nitrobenzene.[3] The products are vat dyes, Helindon Orange GRN being obtained from anthraquinone-β-urea chloride by this reaction. The same products are obtained from the *iso*-cyanates and from the dianthraquinonyl ureas themselves.[4]

The *thioureas* of the anthraquinone series have been much less studied than the ureas, and the information in the patent literature is often contradictory. Thus, the Höchst colour works state that the thiourea is formed when an aminoanthraquinone is treated with thiocarbonyl chloride,[5]

[1] M.L.B., D.R.P. 242,291.   [2] M.L.B., D.R.P. 236,982.
[3] M.L.B., D.R.P. 232,135.   [4] *Loc. cit.*   [5] M.L.B., D.R.P. 232,791–2.

whereas the Badische Anilin u. Soda Fabrik state that the action of thiocarbonyl chloride on β-aminoanthraquinone gives a substance which is useless as a vat dye and is certainly not the thiourea.[1] According to their patent the product consists of at least two substances, and can be separated into two parts by the action of alkali, the portion which is insoluble in alkali being converted into a fast orange-yellow vat dye when heated alone or with an indifferent solvent. It is probable that the action of thiocarbonyl chloride on aminoanthraquinone leads to a mixture of the thiourea and thiourea chloride, and this view receives some confirmation from the fact that Bayer & Co. claim the production of orange-yellow vat dyes by the prolonged heating of β-amino-anthraquinone with excess of thiocarbonyl chloride.[2]

The anthraquinonyl thioureas can also be obtained by heating the aminoanthraquinones with carbon bisulphide, best by using pyridine as a solvent,[3] or with sodium xanthate,[4] and in addition also seem to be formed when aminoanthra-quinones are heated with perchlormethyl mercaptan in an indifferent solvent, such as nitrobenzene, with or without the addition of copper or copper salts and basic substances.[5] They can also be built up from the thioureas of the amino-benzoyl benzoic acids by closing the anthraquinone ring by means of sulphuric acid.[6]

As in the case of the formation of anthraquinonyl ureas by this method the ring closes very easily, and as the thioureas are not very readily hydrolysed a higher tempera-ture can be used than is permissible in the case of the ureas themselves.

Mixed alkyl and aryl anthraquinonyl thioureas can be obtained by condensing the anthraquinonyl *iso*-thiocyanates with primary or secondary aliphatic amines or primary aromatic amines.[7] The reaction is facilitated and a much purer product obtained if a condensing agent such as aluminium chloride is used.[8]

[1] B.A.S.F., D.R.P. 246,086. [2] By., D.R.P. 256,900.
[3] By., D.R.P. 271,475. [4] G.E., D.R.P. 291,984.
[5] B.A.S.F., D.R.P. 234,922. [6] Agfa, D.R.P. 282,920.
[7] M.L.B., D.R.P. 229,111. [8] M.L.B., D.R.P. 254,744.

If an anthraquinone aldehyde or an ω-dibrommethyl anthraquinone is heated to $120-130°$ with thiourea in a suitable solvent such as pyridine or quinoline, a compound which contains both the thiourea and the azo-methine group is obtained.[1] These are red vat dyes, the corresponding oxygen compounds, obtained in the same way from urea, being yellow :

$$C_{14}H_7O_2.C:N.C.N:C.C_{14}H_7O_2 \quad C_{14}H_7O_2.C:N.C.N:C.C_{14}H_7O_2$$
$$\overset{\|}{S} \qquad\qquad\qquad \overset{\|}{O}$$
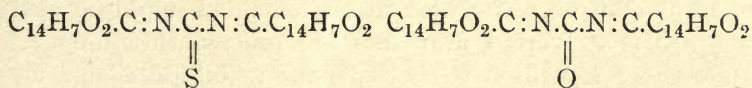
Addendum

At this point brief mention may conveniently be made of compounds which appear to be derived from the amidines of the aromatic acids. These can be obtained by condensing one molecule of benzotrichloride with two molecules β-aminoanthraquinone :

$$C_6H_5CCl_3 + 2C_{14}H_7O_2NH_2 \rightarrow C_6H_5C\Big\langle\begin{matrix}NC_{14}H_7O_2\\NHC_{14}H_7O_2\end{matrix}$$
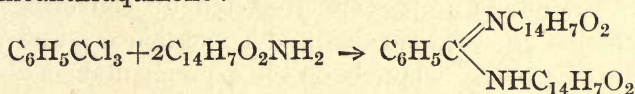
or by condensing β-aminoanthraquinone simultaneously with carbon tetrachloride or other derivative of carbonic acid, such as chlorcarbonic ester, and an aromatic hydrocarbon such as naphthalene, diphenyl, etc., the condensation taking place in the presence of copper.[2] The reaction is an interesting one and is worthy of further investigation.

Nitration

The nitration of the aminoanthraquinones is complicated by the fact that the position taken by the entering nitro group is influenced not only by the position of the amino group, but is also dependent to a considerable extent on the means, if any, which have been taken to protect this group, and further complications arise from the fact that in the anthraquinone series there is a considerable tendency towards the formation of nitramines. These latter, however,

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[1] B.A.S.F., D.R.P. 241,805.   [2] B.A.S.F., D.R.P. 246,477 ; 248,656.

are only formed in nitration reactions after all the easily available ring positions have been occupied by nitro groups. They are briefly discussed on p. 226.

Primary aminoanthraquinones are much more stable than the majority of primary aromatic amines, and can often be nitrated without previously protecting the amino group. Thus, β-aminoanthraquinone when treated with the calculated amount of nitric acid in concentrated sulphuric acid at —5° is converted into 2-amino-3-nitroanthraquinone.[1] Here the *o-β* position is the only one readily available for nitration, and the further action of nitric acid leads to the formation of a nitramine.[2] When the amino group is in the *α-* position, however, both the *ortho-* and *para-* positions are readily nitrated. Thus, 1.5-diaminoanthraquinone gives a tetranitro compound, the further nitration of this leading to nitramine formation.[3]

If the amino groups are protected by conversion into acyl amino groups, then the products obtained on nitration seem to depend very largely on the experimental conditions. By nitrating 1-acetylaminoanthraquinone, and 1.5 and 1.8-diacetylamino anthraquinone, Eckert and Steiner [4] obtained nitro compounds in which the nitro groups were in the *para-* position to the amino groups, but the nitration of 1-acyl-alkylamino anthraquinones leads to a heteronuclear nitro compounds, the nitration product, after hydrolysis, being 5-nitro-1-alkylamino anthraquinone.[5] The nitration of the unacylated α-monalkyl aminoanthraquinones and of the α-dialkylamino anthraquinones, however, leads to homonuclear nitro compounds, the nitro group taking the *para-* position.[6] The nitration of 2-acetylaminoanthraquinone leads to 2-amino-1-nitroanthraquinone.[7]

The products obtained by the nitration of 1.4-diacyl-aminoanthraquinone depend very largely on experimental

[1] M. **32**, 1037. G.E., D.R.P. 290,814.
[2] Scholl and Eberle, B. **37**, 4434. M. **32**, 1037.
[3] B.A.S.F., D.R.P. 146,848.
[4] M. **35**, 1137. *Cf.* M.L.B., D.R.P. 158,076. Noelting and Wortmann, B. **39**, 643.
[5] M.L.B., D.R.P. 292,395.
[6] By., D.R.P. 156,759.   [7] Ullmann and Medenwald, B. **46**, 1798.

conditions, the action of mixtures of nitric and sulphuric acids leading to the heteronuclear nitration with the production of both 1.4-diacylamino-5- and 8-nitroanthraquinone,[1] whereas the action of nitric acid and an indifferent solvent such as nitrobenzene leads to homonuclear nitration, the product being 1.4-diacylamino-2-nitroanthraquinone.[2] If 1.4-diaminoanthraquinone is heated to 50–60° with oleum containing 45 per cent. of free sulphur trioxide a sulphonamide, $C_{14}H_6O_2(N:SO_2)_2$, is formed. This is a perfectly stable compound which is insoluble in water, and its formation provides a convenient means of protecting the amino groups. On nitration and subsequent hydrolysis it yields 1.4-diamino-5-nitroanthraquinone.

Amino groups can also be protected during nitration by converting the aminoanthraquinone into the urethane, either by treatment with chlorcarbonic ester or by the action of carbonyl chloride followed by treatment of the resulting urea chloride [3] with alcohol. When nitrated the urethane of α-aminoanthraquinone gives a mixture 1-amino-2-nitroanthraquinone and 1-amino-4-nitroanthraquinone, further nitration of both isomers leading to 1-amino-2.4-dinitroanthraquinone. The diurethanes of both 1.5- and 1.8-diaminoanthraquinone behave in the same way, the nitro groups taking the *ortho-* and *para-* positions to the amino groups. The urethane of β-aminoanthraquinone when nitrated gives first a mixture of 2-amino-1-nitroanthraquinone and 2-amino-3-nitroanthraquinone. Both of these on further nitration yield the same dinitroamino compound which must, therefore, be 1.3-dinitro-2-aminoanthraquinone.[4] From this it is clear that the behaviour of the urethanes on nitration differs from that of other acylamino compounds. The diurethanes of the heteronuclear ββ-diaminoanthraquinones behave in the same way. Ullmann and Medenwald [5] have also studied the nitration of the urethane of 2-aminoanthraquinone and find that the

[1] By., D.R.P. 268,984.
[2] By., D.R.P. 267,445. *Cf.* M.L.B., D.R.P. 254,185.
[3] See p. 219.
[4] By., D.R.P. 167,410; 171,588.   [5] B. **46**, 1798.

chief product is 2-amino-1-nitroanthraquinone, but that about 20 per cent. of 2-amino-3-nitroanthraquinone is also formed. As the separation of the isomers is easy the nitration of the urethane provides a ready means of obtaining this latter substance.

Amongst other methods which have been proposed for protecting amino groups during nitration may be mentioned the formation of the azomethine compound, obtained by warming the amino compound with formaldehyde or trioxymethylene and concentrated sulphuric acid, and the conversion of the aminoanthraquinone into the oxaminic acid by heating to 150° with oxalic acid. The nitration of α-methyleneaminoanthraquinone yields a mixture of the *ortho* and *para* nitro compound.[1] The oxaminic acids are said to be particularly suited for nitration purposes as they are readily obtained, and although the free acids are almost insoluble their salts are often readily soluble and well crystallised. On nitration the nitro group enters the *para-* position to the amino group.[2]

THE NITRAMINES.—When a primary or secondary aminoanthraquinone is nitrated, the nitro groups first enter the easily attacked ring positions, but when these positions are all occupied the nitro group enters the amino group.[3] Thus, if β-aminoanthraquinone is nitrated first 2-amino-3-nitroanthraquinone is formed.[4] In this there is no readily nitrated ring position vacant, so that the further action of nitric acid leads to 2-nitramino-3-nitroanthraquinone. In the case of α-aminoanthraquinone there are two easily nitrated ring positions available so that first 1-amino-2.4-dinitroanthraquinone is formed, and then 1-nitramino-2.4-dinitroanthraquinone. The behaviour of 1.5-diaminoanthraquinone is exactly similar, first diaminotetranitroanthraquinone being formed and then the dinitramine. In 1.5-diamino-2.4.6.8-tetrabromanthraquinone, on the other hand,

[1] B.A.S.F., D.R.P. 279,866.
[2] M.L.B., D.R.P. 158,076.
[3] B.A.S.F., D.R.P. 111,866; 121,155; 146,848.
[4] Scholl and Eberle, B. 37, 4434. M. 32, 1037. Ullmann and Medenwald, B. 46, 1798.

no readily nitrated ring position is available so that nitration leads at once to the dinitramine.

The sodium salts of the nitramines can be obtained by the action of sodium hypochlorite on the anthraquinone diazonium sulphates, and the free nitramines can be liberated from these salts by the action of weak acids such as carbonic or acetic acid.[1] This reaction, however, seems to be confined to the anthraquinone-α-diazonium sulphates, as in another patent[2] it is stated that under similar conditions the β-diazonium sulphates give only unstable substances which smell of and contain chlorine. The anthraquinone β-nitramines can be obtained, however, by oxidising the *iso*-diazotates with hypochlorites.[3]

The nitramines are rather unstable compounds which are more or less explosive but can, as a rule, be nitrated,[4] *e.g.* by the action of fuming nitric acid at 0°. Owing to their instability they act as nitrating agents towards easily nitratable substances,[5] such as phenol, benzene, etc., and frequently undergo self-nitration when treated with concentrated sulphuric acid.[6] During this self-nitration the nitro group takes the *ortho-* position to the amino group, 1-nitraminoanthraquinone passing into 1-amino-2-nitroanthraquinone, whereas when the nitramine is treated with nitric acid the entering nitro group takes the *para-* position, 1-nitraminoanthraquinone forming 1-nitramino-4-nitroanthraquinone.[7]

The nitramines on reduction lose the nitro group and pass into the primary amine, whereas when heated with water slightly soluble substances of unknown composition are formed which dye mordanted or unmordanted wool brown.[8]

HALOGENATION

A considerable amount of work has been recorded dealing with the behaviour of the aminoanthraquinones when

[1] M.L.B., D.R.P. 156,803.
[2] G.E., D.R.P. 262,076.
[3] G.E., D.R.P. 259,432.
[4] M.L.B., D.R.P. 156,803.
[5] B.A.S.F., D.R.P. 148,109.
[6] G.E., D.R.P. 259,432.
[7] G.E., D.R.P. 156,803.
[8] By., D.R.P. 220,032.

halogenated under various conditions, the subject being complicated by the great ease with which halogen atoms under certain conditions wander from one position to another. It should also be noted that aminoanthraquinones, at all events the α-amino compounds, can under certain conditions form N-halogen derivatives quite readily.[1] Thus α-aminoanthraquinone when brominated under suitable conditions yields N-brom-α-aminoanthraquinone, $C_{14}H_7O_2NHBr$, and 1.5-diaminoanthraquinone' gives an octachlor compound in which some of the chlorine atoms are attached to the nitrogen atoms.[2] Scholl and Berblinger[3] have also found that the bromination of 1.5-diaminoanthraquinone by molecular bromine without a solvent leads to a product which loses the whole of its bromine when kept in a vacuum. This may be merely a solid solution, although Scholl and Berblinger incline to the belief that it is a perbromide, although they were unable to obtain it in a pure state. Against the belief that the substance in question was a perbromide it must be pointed out that tertiary α-dialkylaminoanthraquinones when treated with bromine are brominated in the *para*- position to the amino group, and at the same time add on two atoms of bromine to form a perbromide.[4] These perbromides are well crystallised substances and are stable towards water, although they readily lose bromine when treated with bases. The substance obtained by Scholl and Berblinger, on the other hand, was decomposed by water with the production of tetrabromaminoanthraquinone.

N-Chlor- compounds can also sometimes be obtained by the action of hypochlorous acid, 1-acetylaminoanthraquinone giving by this means N-chlor-1-acetaminoanthraquinone. In all these compounds the halogen is very easily removed by reduction.

The majority of investigators who have studied the halogenation of the aminoanthraquinones have used molecular chlorine, although it has been claimed[5] that aminoanthraquinones are very smoothly chlorinated by sulphuryl

[1] By., D.R.P. 104,901 ; 115,048 ; 126,392–3.
[2] B.A.S.F., D.R.P. 125,094.   [3] B. **37**, 4180.
[4] By., D.R.P. 146,691.   [5] B.A.S.F., D.R.P. 158,951.

chloride, either at the ordinary temperature or on the water bath.

When α-*aminoanthraquinone* is brominated in glacial acetic acid solution the first bromine atoms enter the *ortho*-position,[1] further bromination (or chlorination) leading to 1-amino-2.4-dihalogenanthraquinone.[2] The alkyl and acyl α-aminoanthraquinones, however, differ from the primary compound as the *para*- position is first attacked,[3] this difference in behaviour probably being due to the primary compound first forming an N-halogen derivative, the halogen atom then wandering to the *ortho*- position.[4] The exhaustive chlorination of α-aminoanthraquinone has recently been studied by Friess and Auffenberg,[5] who find that the amino group is split out and then the anthraquinone ring opened, the products being 2.3.4.5.6-pentachlorbenzophenone and finally phthalic acid and pentachlorphenol.

The behaviour of 1.5-diaminoanthraquinone when brominated is analogous to that of α-aminoanthraquinone, the 2.4.6.8-tetrabrom derivative being formed.[6] On chlorination an octachlor compound is formed as mentioned on p. 228, and also a hexachlordihydroxyanthraquinone and octachlor-anthraquinone.[7] It is curious to notice that both dibrom- and tetrabrom-1-5-diaminoanthraquinone give tetra-acetyl derivatives, although the unbrominated product will give only a diacetyl compound.[8]

Probably owing to the instability of the N-halogen compounds the presence of a primary amino group in the β- position greatly facilitates the entrance of halogen atoms into the anthraquinone ring. The halogenation of β-amino-anthraquinone has been studied in some detail by several investigators, and it has been found that its reactivity is so great that it is almost impossible to obtain a monohalogen

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[1] By., D.R.P. 160,169.
[2] Ullmann, B. **49**, 2165. B.A.S.F., D.R.P. 199,758.
[3] By., D.R.P. 164,791.
[4] Compare the behaviour of the nitramines (p. 227).
[5] B. **53**, 23.
[6] Scholl and Berblinger, B. **37**, 4180. B.A.S.F., D.R.P. 137,783.
[7] B.A.S.F., D.R.P. 125,094 ; 137,074.
[8] Scholl and Berblinger, B. **37**, 4180. Römer, B. **16**, 366.

compound, the result of using only the calculated amount of the halogen being usually to produce a mixture of 2-amino-1.3-dihalogenanthraquinone and unchanged 2-aminoanthraquinone.[1] If, however, 2-aminoanthraquinone is treated with bromine dissolved in an organic solvent, such as glacial acetic acid or nitrobenzene, it is possible, under carefully controlled conditions, to obtain 2-amino-3-bromanthraquinone, the position of the bromine atom being proved by the fact that the substance gives 2-bromanthraquinone when the amino group is eliminated by the diazo reaction.[2] As stated above, the usual product obtained by brominating 2-aminoanthraquinone is 2-amino-1.3-dibromanthraquinone. In this compound the bromine atom in the α-position exhibits remarkable reactivity, and is readily split off when boiled with compounds like acetic acid or aniline, these substances being brominated in the process and the aminodibromanthraquinone being simultaneously degraded to 2-amino-3-bromanthraquinone. The same reaction takes place when the aminodibrom compound is heated with 2-aminoanthraquinone, one molecule of 2-amino-1.3-dibromanthraquinone reacting with one molecule of 2-aminoanthraquinone to produce two molecules of 2-amino-3-bromanthraquinone, a reaction which has been made use of in the preparation of the last-named substance.[3]

The acetyl derivative of 2-aminoanthraquinone is much less readily halogenated than the primary compound itself, and by chlorinating 2-acetaminoanthraquinone a monochlor compound can be obtained.[4] In this, however, the halogen atom is in the α-position, as Junghaus has found that it gives 1.2-diaminoanthraquinone when the chlorine atom is replaced by an amino group by the sulphonamide process.[5] It is interesting to observe that whereas a primary amino group in the β- position directs the entering halogen atom first to the contiguous β- position, the acetylamino group directs the halogen to the contiguous α- position, although

[1] Scholl, B. **40**, 1701. Junghaus, A. **399**, 316. D.R.P. 273,809. M.L.B., D.R.P. 253,683.
[2] Junghaus, *loc. cit.*   [3] B.A.S.F., D.R.P. 261,270–1.
[4] B.A.S.F., D.R.P. 199,758.   [5] A. **399**, 316.

the ß-halogen compound must be regarded as the more stable, as the halogen atom in all homonuclear halogen derivatives of both α- and ß- aminoanthraquinone wanders to the ß- position which is contiguous to the amino group if this position is unoccupied.[1] This wandering of the halogen atom is brought about by heating the substance alone or with sulphuric or phosphoric acids. If the ß- position contiguous to the amino group is occupied by a sulphonic acid group this latter is split off by heating with acids, and as a rule a simultaneous wandering of the halogen atom takes place, 2-amino-1-bromanthraquinone-3-sulphonic acid, for example, passing into 2-amino-3-bromanthraquinone when boiled with sulphuric acid of 80 per cent. strength.[2] This wandering of the halogen atom can often be avoided by carrying out the hydrolysis of the sulphonic acid at as low a temperature as possible, by avoiding prolonged heating or by carrying out the hydrolysis by means of concentrated sulphuric acid, monohydrate or dilute oleum, preferably in the presence of mercury.[3]

When an *aminoanthraquinone sulphonic acid* is halogenated the halogen can enter the molecule either by the replacement of hydrogen or by the replacement of the sulphonic acid groups. Which reaction takes place depends very largely on the position of the groups present, and on the experimental conditions under which the halogenation is carried out, but for further information the reader is referred to the original literature.[4]

THE DIANTHRAQUINONYLAMINES

Although dianthraquinonylamines can be obtained by heating α-aminoanthraquinone or ß-aminoanthraquinone with α-nitroanthraquinone[5] or with an anthraquinone-α- or -ß-sulphonic acid,[6] preferably in the presence of sodium

[1] By., D.R.P. 275,299.
[2] M.L.B., D.R.P. 253,683. B.A.S.F., D.R.P. 263,395.
[3] B.A.S.F., D.R.P. 265,727 ; 266,563.
[4] Ullmann and Medenwald, B. **46**, 1798. B.A.S.F., D.R.P. 113,292 ; 114,840 ; 128,196 ; 138,134 ; 138,166.
[5] M.L.B., D.R.P. 201, 327.   [6] M.L.B., D.R.P. 216,083.

carbonate, the reaction only takes place with some difficulty, so that they are always made by condensing a primary aminoanthraquinone with a halogen anthraquinone. The condensation is usually brought about by heating the amine and the halogen compound together in some indifferent solvent of high boiling point, such as naphthalene or nitrobenzene, copper powder or cuprous chloride being used as a catalyst, and anhydrous sodium carbonate or acetate being added to neutralise the halogen acid liberated.[1] By condensing two molecules of a halogen anthraquinone with one molecule of a diaminoanthraquinone, or, *mutatis mutandis*, by condensing two molecules of an aminoanthraquinone with one molecule of a dihalogen anthraquinone, dianthraquinonylaminoanthraquinones * are obtained, several of which have found application as vat dyes. $\beta\beta$-Dianthraquinonylamines can also be obtained by condensing anthraquinone-β-diazonium salts with ammonia and then heating the resulting product with a solvent of high boiling point, with or without a condensing agent.[2]

The ease with which dianthraquinonylamines are formed depends on the orientation of the amino group and of the halogen atom in the reacting substances. If both are in the $\alpha \cdot$ position the reaction takes place easily, *e.g.* α-chloranthraquinone reacts readily with α-aminoanthraquinone to form 1.1'-dianthraquinonylamine.

If one group is in the β- position the reaction takes place with rather greater difficulty, and in this case it is best to condense the β-halogen compound with the α-amine.[3] Thus, β-chloranthraquinone and α-aminoanthraquinone yield 1.2' dianthraquinonylamine rather more readily than do α-chloranthraquinone and β-aminoanthraquinone. When both

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[1] Seer, M. **32**, 162. Eckert, M. **35**, 762. Eckert and Steiner, M. **35**, 1129. Ullmann, B. **47**, 564; **49**, 2162. Frey, B. **49**, 1363. B.A.S.F., D.R.P. 184,905; 197,554; 206,717; 212,470; 216,280; 217,395–6; 218,161; 279,867; *cf.* also 176,956. By., D.R.P. 162,824; 174,699; 194,253; 208,162; 216,668; 220,581; 230,052; 240,276. M.L.B., D.R.P. 257,811.

* In the literature these are frequently described as trianthraquinonylamines, a nomenclature which would suggest that three anthraquinonyl groups are attached to the same nitrogen atom (*cf.* triphenylamine).

[2] M.L.B., D.R.P. 308,666.   [3] By., D.R.P. 174,699.

the halogen atom and the amino group are in the β- position, *e.g.* β-chloranthraquinone and β-aminoanthraquinone, the reaction only takes place with great difficulty,[1] and under these circumstances it is advisable to use the iodo compound.

Hydroxydianthraquinonylamines can be obtained by condensing an aminohydroxyanthraquinone with a halogen anthraquinone, or a hydroxy halogen anthraquinone with an amino anthraquinone, but hydroxyl groups can also be introduced into the dianthraquinonylamine molecule by the usual methods, *e.g.* by direct oxidation with nitrosyl sulphuric acid in the presence of boric acid,[2] or by the replacement of halogen atoms or nitro groups by heating with alcoholic caustic potash.[3]

On nitration 1.1'-dianthraquinonylamine gives a dinitro compound in which the nitro groups must be in the *para*-positions to the imino group, as the same compound is obtained by condensing 1-chlor-4-nitroanthraquinone with 1-amino-4-nitroanthraquinone. Further nitration leads to a tetranitro, and possibly also to a pentanitro, compound.[4]

The nitration of 1.2'-dianthraquinonylamine gives first 4.1'-dinitro-1.2'-dianthraquinonylamine [5] and then 2.4.1'-trinitro-1.2'-dianthraquinonylamine.[6]

Reduction of 4.4'-dinitro-1.1'-dianthraquinonylamine with sodium sulphide gives the corresponding diamino compound,[7] but reduction with boiling sodium stannite leads to replacement of the nitro groups by hydroxyl groups, the product being 4.4'-dihydroxy-1.1'-dianthraquinonylamine.[8] The tetranitro compound on reduction with alkaline stannite also loses two nitro groups and forms 2.2'-diamino-4.4'-dihydroxy-1.1'-dianthraquinonylamine.[9] Reduction with sodium sulphide, however, appears to lead first to the

[1] Eckert and Steiner, M. **35**, 1129.

[2] M.L.B., D.R.P. 249,938. *See also* p. 251 *et seq.*

[3] By., D.R.P. 232,262. *Cf.* Eckert and Steiner, M. **35**, 1129.

[4] Eckert and Steiner, *loc. cit.* By., D.R.P. 213,501. M.L.B., D.R.P. 254,186.

[5] Eckert and Steiner, *loc. cit.* B.A.S.F., D.R.P. 186,465.

[6] Eckert and Steiner, *loc. cit.* By., D.R.P. 178,129.

[7] M.L.B., D.R.P. 255,822.

[8] Eckert and Steiner, M. **35**, 1129. *Cf.* By., D.R.P. 178,129.

[9] Eckert and Steiner, *loc. cit.*

tetramino compound, which at once loses a molecule of ammonia and passes into diaminoindanthrone : [1]
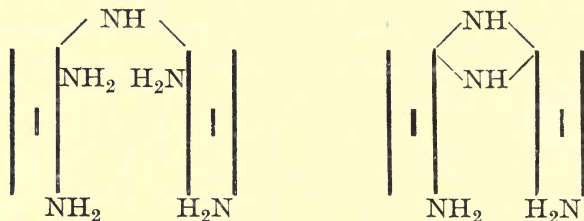
The reduction of 4.1'-dinitro-1.2'-dianthraquinonylamine by sodium stannite also leads to the replacement of the nitro groups by hydroxyl groups (4.1'-dihydroxy-1.2'-dianthra-quinonylamine), although the diamino compound is obtained when the reduction is carried out in acid solution.[2]   As would be expected, the trinitro compound on alkaline reduction yields 2-amino-4.1'-dihydroxy-1.2'-dianthraquinonyl-amine, it being only nitro groups in the α- positions which are replaced.[3]

Although the aminodianthraquinonylamines can be obtained in some cases by the reduction of the nitro compounds it is usually best to obtain them by condensing halogen anthraquinones with polyaminoanthraquinones, one or more amino groups being protected during the reaction by previous acylation.[4]

The dianthraquinonylamines when treated with condensing agents such as caustic alkali,[5] aluminium chloride,[6] or zinc chloride,[7] give rather indefinite products, many of which have tinctorial properties.   The constitution of these products is unknown although some at least of them seem to be carbazol derivatives.[8]   For further information the reader is referred to the original literature.

The tinctorial properties of the simple dianthraquinonyl-amines are, as a rule, somewhat feeble, although 1.2'-dianthraquinonylamine has been placed on the market under

[1] Eckert and Steiner, *loc. cit.*
[2] *Ibid.*   [3] *Ibid.*   [4] By., D.R.P. 220,581.
[5] M.L.B., D.R.P. 208,969 ; 251,021.   By., D.R.P. 230,407.
[6] M.L.B., D.R.P. 240,080 ; 262,788.
[7] M.L.B., D.R.P. 251,350.   [8] M.L.B., D.R.P. 267,522 ; 267,833.

the name Algol Orange R, and Algol Red B is also a dianthra-quinonylamine although containing also a pyridone ring.[1] The introduction of a benzoylamino group, however, confers tinctorial properties,[2] although the unbenzoylated amino-dianthraquinonylamines have little or no affinity, so that in this respect there is a close analogy between the aminodi-anthraquinonylamines and the aminoanthraquinones. The anthraquinonylaminodianthraquinonylamines are usually powerful dyes and, when other substituents are absent, produce red or bordeaux shades. Several dyes of this class have been placed on the market, of which the two following are typical :
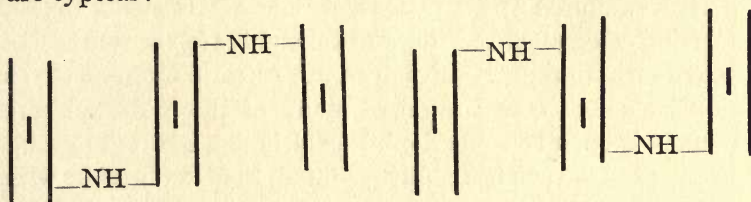
Indanthrene Bordeaux B.   Indanthrene Red G.

Indanthrene Bordeaux R Extra is a dichlor compound somewhat similar to the above, and is derived from 1-amino-6-chloranthraquinone (2 molecules) and 2.7-dichloranthra-quinone (one molecule). It would be interesting to trace the relation between the colour and the constitution of the dianthraquinonylamines and the anthraquinonylamino-dianthraquinonylamines, but the data available at present are insufficient to render possible any generalisation.

The introduction of amino, hydroxy or alkoxy groups into the molecule often has a considerable effect on the shade of the resulting dye, and in many cases shifts the colour right into the violet end of the spectrum. A fair number of derivatives of this nature have been described,[3] but the subject is a very complicated one and no inferences of the relationship between colour and constitution can be drawn profitably from the facts so far available.

[1] By., D.R.P. 194,253.   [2] By., D.R.P. 220,581 ; 238,488.
[3] B.A.S.F., D.R.P. 206,717 ; 212,470 ; 216,280.   By., D.R.P. 208,162 ; 216, 668.

THE HYDROXY- AND AMINOHYDROXY-
ANTHRAQUINONES AND ETHERS

I. THE HYDROXY COMPOUNDS

THE hydroxyanthraquinones constitute a very important class
of substances, partly on account of the valuable tinctorial pro-
perties exhibited by many of them, and partly owing to their
forming convenient starting-out substances in the synthesis of
other anthraquinone derivatives, *e.g.* Alizarin Cyanine Green.

The actual constitution of many of the hydroxyl com-
pounds is open to some doubt, as although hydroxyl groups
in any position can be readily acylated, hydroxyl groups when
in the *ortho-* position to a carbonyl group cannot be alkylated,
or can only be alkylated with the utmost difficulty, by
the usual means, *e.g.* by treatment with dimethyl sulphate
or methyl iodide and caustic potash. Hydroxyl groups in
the *β-* position, however, behave in a perfectly normal
manner towards alkylating agents. The abnormal behaviour
of hydroxyl groups in the *α-* position is obviously due in
some way to the influence of the carbonyl group, as the
difficulty of alkylation disappears when the anthraquinone
compound is reduced to the corresponding anthrone, and
the corresponding hydroxyanthracenes, the *α*-anthrols, can
be alkylated without any trouble. It has been suggested
that the *α*-hydroxyanthraquinones really have the tautomeric
o-quinonoid structure :

and this would explain the difficulty in alkylation.

Although, as stated above, hydroxyl groups both in the

α- and β- position can be acylated with ease, groups in the β- position are more easily attacked than those in the α- position, so that by moderating the conditions of experiment it is often possible to acylate groups in the β- position without affecting those in the α- position.   In the case of acetyl derivatives Dimroth, Friedemann and Kämmerer [1] have found that this is most readily effected by dissolving the hydroxy compound in pyridine and then, without heating, adding the calculated amount of acetic anhydride necessary to acetylate the β-hydroxyl groups. Only the calculated amount of acetic anhydride must be used, as otherwise all the hydroxyl groups will be attacked, although those in the α-position react only slowly with acetic anhydride in cold pyridine solution.

In addition to methods based on the replacement of other groups such as amino groups, sulphonic acid groups, nitro groups, etc., the hydroxyl group can be inserted into the anthraquinone molecule with great ease by direct oxidation, and it is possible by this means to obtain a very large number of different hydroxy compounds according to the conditions employed.   As has been already stated, hydroxyanthraquinones can often be built up from phenolic ethers by the phthalic acid synthesis, and in many cases the reduction of the higher hydroxylated anthraquinones leads to the loss of hydroxyl groups.   The oxidation of the hydroxy anthracenes, or rather of their acetyl derivatives or methyl ethers, also leads to hydroxyanthraquinones, although the method is of little importance except as a means of identifying the anthrols.[2]

A great many of the hydroxyanthraquinones have received special names, and for ease of reference these have been tabulated together with the melting point of the hydroxy compound and its acetyl derivative.   The preparation of the acetyl derivatives is usually very easily effected by boiling the hydroxy compound with acetic anhydride and anhydrous sodium acetate, and they often provide a ready means of characterising the hydroxy compound.

[1] B. **53**, 481.
[2] Liebermann and Boeck, B. **11**, 1616 ; **12**, 185.   Liebermann and Hörmann, B. **12**, 259.   Dienel, B. **38**, 2862.

HYDROXYANTHRAQUINONES.

Position of Hydroxyl.	Usual name.	M.p.	Acetyl derivative m.p.
1-	Erythrohydroxyanthraquinone	190°	176–179°
2-	—	302°	159°
1.2-	Alizarin	289–290°	184°
1.3-	{ Purpuroxanthin. Xantho-purpurin }	262–263°	184°
1.4-	Quinizarin	194°	200°
1.5-	Anthrarufin	280°	244–245°
1.6-	— [1]	276°	205–206°
1.7-	—	291–293°	199°
1.8-	Chrysazin	191°	227–232°
2.3-	Hystazarin	{ Decomp. above 260° }	206–207°
2.6-	Anthraflavic acid	Above 330°	228°
2.7-	*iso*-Anthraflavic acid	Above 330°	About 195°
1.2.3-	{ Anthragallol, Anthragallic acid }	310°	181–182°
1.2.4-	Purpurin	256°	192–193°
1.2.5-	Hydroxyanthrarufin [2]	278°	228°
1.2.6-	Flavopurpurin	Above 330°	195–196°
1.2.7-	Anthrapurpurin. *iso*-Purpurin	369°	224°
1.2.8-	Hydroxychrysazin [2]	239–240°	219°
1.4.5-	— [3]	—	—
1.4.6-	— [4]	256°	—
1.4.8-	— [5]	—	—
1.2.3.4-	—	—	205°
1.2.4.6-	Hydroxyflavopurpurin	202°	—
1.2.4.7-	Hydroxyanthrapurpurin	—	214°
1.2.4.8-	—	—	—
1.2.5.6-	—	—	—
1.2.5.8-	Rufiopin [6]	—	—
1.2.7.8-	Quinalizarin. Alizarin Bordeaux	Above 275°	201°
1.3.5.7-	— [7]	—	—
1.4.5.8-	Anthrachrysazin	Above 360°	253°
	—	246°	{ Decomp. about 250° }
1.?.?.8-	— [8]	217°	195°
1.?.?.8-	— [9]	292°	238–240°
1.2.4.?-	Hydroxypurpurin [10]	Above 290°	Above 240°

[1] Frobenius and Hepp, B. **40**, 1048.   Wed., D.R.P. 202,398.

[2] Wed., D.R.P. 205,965 ; 210,863.

[3] By., D.R.P. 161,026 ; 163,041.

[4] Dimroth and Fick, A. **411**, 315.   Crossley, Am. Soc. **40**, 404, states that the substance does not melt below 300°.

[5] R. E. Schmidt, Bull. Soc. Ind. Mull. **84**, 409.

[6] Liebermann and Chojnacki, A. **162**, 323 (from hemipinic or opianic acid and conc. H_2SO_4).   By., D.R.P. 103,988 (from anthrarufin).

[7] By., D.R.P. 103,988.   See also note 9.

[8] Schrobsdorf, B. **36**, 2936.

[9] Wölbling, B. **36**, 2941.   Probably identical with 1.2.7.8-tetrahydroxy-anthraquinone.

[10] Diehl, B. **11**, 185.   Gattermann, J. pr. [2] **43**, 251.

HYDROXYANTHRAQUINONES—*continued.*

Position of Hydroxyl.	Usual name.	M.p.	Acetyl derivative m.p.
1.2.3.5 or 7-	α-Hydroxyanthragallol [1]	Above 350°	207–209°
1.2.3.5 or 7-	β-Hydroxyanthragallol [1]	Above 380°	189°
1.2.3.5.7-	Dihydroxyanthragallol	Above 360°	229°
1.2.3.6.7-	— [2]	—	—
1.2.4.5.8-	Alizarin Cyanine R	—	—
1.2.5.?.8-	— [3]	—	—
1.2.3.5.6.7-	Rufigallic acid	—	282–283°
1.2.4.5.6.8-	Anthracene Blue WR	—	—
1.2.4.5.7.8-	— [4]	—	—
1.2.3.4.5.6.7.8-	— [5]	—	{ Decomp. at 330°

REPLACEMENT OF GROUPS

REPLACEMENT OF SULPHONIC ACID GROUPS.—The conversion of an anthraquinone sulphonic acid into a hydroxyanthraquinone by fusion with caustic alkali is complicated by the fact that during the alkali melt simultaneous oxidation takes place, so that the product usually contains more hydroxyl groups than there were sulphonic acid groups in the original acid, anthraquinone-2-sulphonic acid when fused with caustic soda giving alizarin, purpurin, and other polyhydroxyanthraquinones. Here it will be seen that replacement of the sulphonic acid group is accompanied by hydroxylation by oxidation, and this type of reaction is discussed in greater detail on p. 252.

By moderating the conditions under which the caustic melt is carried out, it is often possible to replace sulphonic acid groups in the β- position without simultaneous oxidation taking place, although the yields are usually poor. Thus, Graebe and Liebermann [6] found β-hydroxyanthraquinone in crude alizarin, and Liebermann and Simon [7] were able to obtain the same substance from anthraquinone-β-sulphonic

[1] From gallic acid and *m*-hydroxybenzoic acid. Noah, A. **241**, 270.
[2] Bentley and Weizmann, Soc. **93**, 438. (Tetramethyl ether.)
[3] R. E. Schmidt, J. pr. [2] 43, 242. Gattermann, *ibid.* 250.
[4] By., D.R.P. 103,988.   [5] Georgievics, M. **32**, 347.
[6] A. **160**, 143.   [7] B. **14**, 464 ; A. **212**, 25, 53.

acid by fusion with caustic alkali.   The anthraflavic acid and *iso*-anthraflavic acid which Römer and Schunck [1] found in commercial alizarin no doubt originated in the anthraquinone disulphonic acids present in the crude monosulphonate from which the alizarin was made, and a few years later Römer and Schwazer [2] succeeded in making *iso*-anthraflavic acid from anthraquinone-2.7-disulphonic acid.   Since then many other cases have been discovered in which replacement of sulphonic acid groups takes place in the alkali melt without simultaneous oxidation,[3] but as a rule it is difficult to avoid oxidation taking place unless one of the modified methods described below is employed.   It should be noted that the above remarks apply chiefly to anthraquinone sulphonic acids in which the sulphonic acid group is in the β-position.   When the sulphonic acid group is in the α- position fusion with caustic alkali usually leads to rupture of the benzene ring, so that in these cases it is essential to use special methods in order to obtain a hydroxyanthraquinone.

Sulphonic acid groups in the α- position are somewhat more reactive than similar groups in the β- position, and are usually replaced by hydroxyl groups when the compound is heated to about 200° with aqueous sodium carbonate, anthraquinone-1-sulphonic acid, for example, giving erythro-hydroxyanthraquinone when treated in this way.[4]   They can also often be replaced by the use of caustic alkali, for although fused caustic alkali or highly concentrated solutions almost always cause rupture of the ring when there is a sulphonic acid group in the α- position, this is not the case when more dilute solutions are used at a comparatively low temperature,[5] and anthraquinone-α-sulphonic acids are often fairly readily converted into α-hydroxyanthraquinones when heated with ten per cent. caustic soda solution at about 150°.

Sulphonic acid groups in any position in the anthra-

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[1] B. **8**, 1628 ; **9**, 379.   [2] B. **15**, 1040.
[3] Wölbling, B. **36**, 3941.   By., 103,686 ; 103,988 ; 178,631.   *Cf.* also Lifschütz, B. **17**, 901.   Frobenius and Hepp, B. **40**, 1048.
[4] By., D.R.P. 197,649.   M.L.B., D.R.P. 149,781.
[5] By., D.R.P. 172,642.

quinone molecule can be replaced by hydroxyl groups by the use of aqueous solutions of calcium or barium hydroxide at temperatures of 150–180°. This method has the great advantage that in the case of anthraquinone-α-sulphonic acids rupture of the ring does not take place, and that in the case of anthraquinone-β-sulphonic acids replacement of the sulphonic acid group by hydroxyl can be effected without simultaneous oxidation taking place.[1] In many cases the sulphonic acid groups in aminoanthraquinone sulphonic acids can be replaced by hydroxyl groups by this means without affecting the amino group, *e.g.* 1-amino-anthraquinone 5- and -8- sulphonic acids give respectively 1-amino-5- and -8- hydroxy anthraquinone.[2] As the sodium or potassium salt of the sulphonic acid is almost invariably used, hydroxylation by means of alkali earth hydroxide leads to the liberation of sodium or potassium sulphite :

$$2C_{14}H_7O_2SO_3Na + Ca(OH)_2 = 2C_{14}H_7O_2.OH + CaSO_3 + Na_2SO_3$$
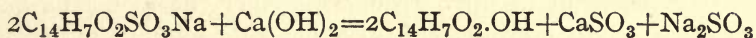
and it is advisable to destroy this or to render it harmless as rapidly as formed by carrying out the reaction in the presence of an oxidising agent such as a chlorate or nitrate, or in the presence of calcium or barium chloride.[3]

The alkali earth hydroxide method has been used to a considerable extent, and in the case of anthraquinone disulphonic acids it has been found possible to replace one group at a time,[4] *e.g.* in the cases of anthraquinone-2.6- and -2.7-disulphonic acids. From alizarin-5-sulphonic acid, hydroxyanthrarufin has been obtained, alizarin-8-sulphonic acid giving hydroxychrysazin.[5] Sulphonic acid groups can also be replaced by heating the sulphonic acid with methyl alcoholic caustic potash, but in this case a methoxy and not a hydroxy group is inserted. This type of reaction is treated in greater detail on p. 287, in connection with the ethers.

REPLACEMENT OF NITRO- GROUPS.—Nitro groups can, of

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[1] R. E. Schmidt, B. **37**, 69. By., D.R.P. 172,642 ; 197,607. M.L.B., D.R.P. 106,505 ; 145,188.

[2] M.L.B., D.R.P. 148,875.

[3] Wed., D.R.P. 195,874.

[4] M.L.B., D.R.P. 106,505.

[5] Wed., 170,329 ; 202,398 ; 210,863. *Cf.* Frobenius and Hepp, B. **40**, 1048.

course, be replaced by hydroxyl groups indirectly by first reducing the nitro compound to the amino compound and then treating this by any of the methods discussed on p. 249. The direct replacement of nitro groups can, however, often be effected. If the nitro groups are in α- positions heating with aqueous alkali or alkali earth hydroxide sometimes leads to their replacement by hydroxyl groups, *e.g.* 1.5- and 1.8-dinitroanthraquinone give respectively anthrarufin and chrysazin, but the yields are usually very poor.[1] Alcoholic alkali reacts more readily, but unless water is carefully excluded simultaneous reduction is apt to take place and impure products are obtained.[2] When absolute alcoholic alkali is employed it is the alkyl ether of the hydroxy compound which is formed, the free hydroxy compound being liberated by subsequent hydrolysis.[2] The method, however, often gives excellent results and is applicable to the replacement of nitro groups in either the α- or the β- position.[3] Nitro groups can also be replaced by hydroxyl groups with great ease by heating the nitro compound in open or closed vessels with crude pyridine or quinoline, α-nitroanthraquinone giving erythrohydroxyanthraquinone and 1.5- and 1.8-dinitroanthraquinone giving respectively anthrarufin and chrysazin.[4] The reaction is an interesting one and deserves further investigation. The patent does not state if the method is also applicable to the replacement of nitro groups when in the β- position, but in all the examples given the nitro groups occupy α- positions.

Much more important than the above is the replacement of nitro groups by hydroxyl groups by heating with concentrated sulphuric acid or oleum. The reactions which take place are extremely complicated and are rendered more so by the fact that the nitrous acid liberated may react with the hydroxyanthraquinone, either reducing hydroxyl groups present,[5] or inserting more hydroxyl groups into the molecule by oxidation. Sulphonation, of course, also often takes

[1] By., D.R.P. 158,891. M.L.B., D.R.P. 75,054.
[2] Kaufler, B. **37**, 63. Eckert, M. **35**, 290. M.L.B., D.R.P. 73,860 ; 75,054 ; 77,818 ; 167,699.
[3] See p. 287.   [4] By., D.R.P. 145, 238.   [5] Nienhaus, B. **8**, 778.

place, and insoluble products are then only obtained by subsequently boiling the hydroxyanthraquinone sulphonic acids with dilute sulphuric acid, although in many cases the sulphonic acid groups can be split off by heating with hydrochloric or phosphoric acid or even alone with water.[1]

Work on the replacement of nitro groups has chiefly been published in patent specifications, and in many cases the nature of the product is not stated and no information is given as to whether it is nitrogenous or not. Also many specifications describe the reaction as being carried out by heating " nitroanthraquinones or partially reduced nitro-anthraquinones with concentrated sulphuric acid or oleum, with or without the addition of a reducing agent such as sulphur." As the mechanism of the reaction seems to depend very largely on whether a nitroanthraquinone or a partially reduced compound is used, and on whether a reducing agent such as sulphur is or is not added to the melt, it is difficult to co-ordinate the various claims.

It appears that the nitro group is particularly easily replaced when it is in the *para-* position to a hydroxyl group, and under these circumstances the reaction is best carried out by heating with concentrated sulphuric acid in the presence of boric acid.[2] The action of the boric acid in this case seems to be specific and not to be limited to protecting hydroxyl groups, as dinitroanthrarufin is stable towards concentrated sulphuric acid at 100° in the absence of boric acid, but in the presence of boric acid one nitro group is replaced by a hydroxyl group at this temperature, and at higher temperatures both are replaced. Dinitro-anthrarufin disulphonic acid exhibits the same behaviour, as it is unaffected when heated for four hours at 150° with concentrated sulphuric acid in the absence of boric acid, but in the presence of boric acid one nitro group is easily replaced at 80–90°, and both are replaced at 120°.

The action of concentrated sulphuric acid on nitroanthra-quinones was first studied by Graebe and Liebermann,[3]

[1] B.A.S.F., D.R.P. 76,941.   [2] By., D.R.P. 125,579.
[3] B. 3, 905 ; 4, 231.

Böttger and Petersen,[1] and Liebermann and Hagen.[2]   These last treated the product with nitrous acid and obtained erythrohydroxyanthraquinone   and   a   dihydroxyanthraquinone which they regarded as xanthopurpurin.   Their analyses agreed with the figures required by the formula $C_{28}H_{18}O_7N_2$, and they concluded that the substance in question was probably an amide of erythrohydroxyanthraquinone and xanthopurpurin.

Claus [3] examined the action of concentrated sulphuric acid on nitroanthraquinone sulphonic acid and obtained two products to which he gave the formulæ :

$$C_{14}H_5O_2 \begin{cases} OSO_3H \\ OH \\ NO_2 \end{cases} \quad \text{and} \quad \left[C_{14}H_4O_2 \begin{cases} SO_3H \\ OH \\ NO_2 \end{cases} \right]_2 O$$
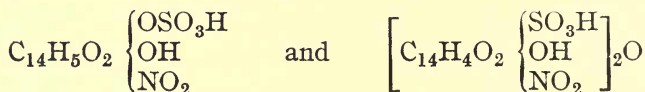
but he was unable to obtain them in a state of purity ; and Lifschütz,[4] on repeating Claus' experiments, was unable to obtain either.

Lifschütz [5] studied the action on concentrated sulphuric acid on 1.5-dinitroanthraquinone and isolated four substances. All these when diazotised and reduced gave dihydroxyanthraquinones, such as anthrarufin, and Lifschütz regarded them as anhydrides (ethers) of aminohydroxyanthraquinones, *e.g.* $[C_{14}H_4O_2(OH)(NH_2)_2]_2O$. His analyses, however, do not agree sufficiently well either among themselves or with the figures calculated for the proposed formulæ to allow these results to be accepted without further confirmation.

More definitive information concerning the action of sulphuric acid on dinitroanthraquinone is to be found in two patents.[6]   In these it is stated that when 1.5-dinitroanthraquinone is treated with oleum containing 30 per cent. of free anhydride at 50° a molecular rearrangement takes place and 1-hydroxy-4-nitroso-8-nitroanthraquinone is formed, 1.8-dinitroanthraquinone and also, apparently, 1.8-dinitronaphthalene reacting in the same way. These *p*-nitrosophenols are, of course, tautomeric with the quinone mon-

[1] A. **160**, 155 ; **166**, 152.   B. **4**, 229, 301.   [2] B. **15**, 1801.
[3] B. **15**, 1521.   [4] B. **17**, 902.   [5] B. **17**, 891.
            [6] By., D.R.P. 104,282 ; 105,567.

oximes so that hydroxylation can take place by the addition of the elements of water, subsequent loss of water leading to the formation of a quinoneimide :
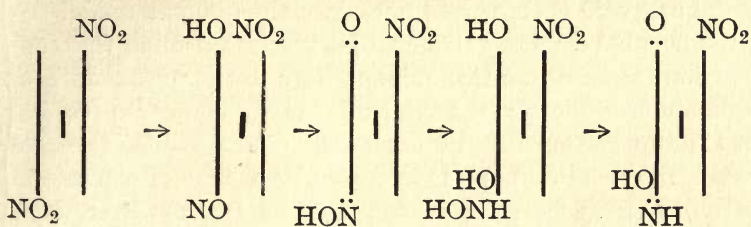
Presumably the other nitro group reacts in exactly the same way, so that the final product is a bisquinoneimide, or its sulphonic acid :
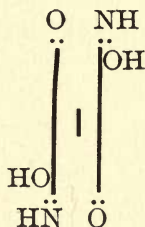
In support of this view of the reaction the patentees point out that although the final product of the action of oleum on 1.5-dinitroanthraquinone is 1.2.4.5.6.8-hexahydroxy anthraquinone disulphonic acid, the absorption spectrum of the finished melt is quite different from the absorption spectrum of a solution of hexahydroxyanthraquinone sulphonic acid in concentrated sulphuric acid. Also the solution at first obtained by running the melt into water is bluish-violet in colour although it changes almost at once to red. Finally, they claim that by running the melt into a saturated solution of sodium chloride or potassium chloride at −10° the disulphonic acid of the bisquinoneimide can be isolated.

The quinoneimide is unstable towards water and is very readily hydrolysed with loss of ammonia and production of the hexahydroxyanthraquinone, but if the solution in concentrated sulphuric acid or oleum is run direct into a reducing

solution (*e.g.* sulphurous acid) reduction takes place, and diaminoanthrachrysazin disulphonic acid is obtained,[1] which by oxidation with oleum or manganese dioxide and sulphuric acid is converted back into the quinone imide.

The above facts render it fairly certain that the conversion of dinitroanthraquinone into hexahydroxyanthraquinone by concentrated sulphuric acid or oleum is preceded by the formation of a quinoneimide. This is also the case when the reaction is brought about by means of oleum and a reducing agent such as sulphur.[2] Here, however, it is probable that the formation of the quinoneimide is not due so much to the preliminary formation of a *p*-nitrosophenol as to partial reduction of the nitro groups to hydroxylamine groups, and then immediate rearrangement of these hydroxylamine compounds to *p*-hydroxyamines : [3]
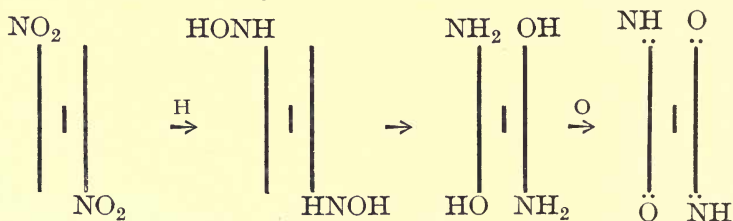
The rearrangement of hydroxylamine derivatives into *p*-aminophenols under the influence of acids is, of course, a well-known reaction which is common to the aromatic series. That the anthraquinonyl hydroxylamines react normally in this respect has been shown by several investigators.[4]

From the above it will be seen that the final product of the action of sulphuric acid or oleum, with or without the addition of sulphur, on 1.5-dinitroanthraquinone is 1.2.4.5.6.8-hexahydroxyanthraquinone disulphonic acid, a water-soluble product used to some extent as a mordant dye under various trade names such as Acid Alizarin Blue BB, Alizarin Cyanine WRS, BBS, 3RS and Anthracene Blue SWX.

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[1] By., D.R.P. 115,002.
[2] B.A.S.F., D.R.P. 76,262 ; 87,729 ; 88,083 ; 89,144 ; 92,800 ; 92,998 ; 109,613 ; 121,315. By., D.R.P. 96,197 ; 105,567 ; 108,362 ; 113,724 ; 116,746 ; 119,229.
[3] R. E. Schmidt and Gattermann, B. **29**, 2934. By., D.R.P. 81,694.
[4] R. E. Schmidt and Gattermann, B. **29**, 2934. By., D.R.P. 119,229.

Hydrolysis, *e.g.* by heating with concentrated sulphuric acid, has the effect of removing the sulphonic groups and rendering the product insoluble (Anthracene Blue WR, WG, WB). The commercial dyes as a rule consist of mixtures of isomeric hexahydroxy and pentahydroxy compounds.

The production of polyhydroxyanthraquinones by the action of sulphuric acid or oleum, with or without the addition of sulphur, on nitro compounds has been extended to substances such as nitromethylanthraquinone, dinitroanthrarufin, tetranitrochrysazin, nitroalizarin, nitroflavopurpurin, nitroanthrapurpurin, etc., but without results of any particular interest.[1]

REPLACEMENT OF HALOGEN ATOMS.—Halogen atoms when attached to the anthraquinone nucleus are not easily replaced by hydroxyl groups by the action of alkali, although the first synthesis of alizarin was effected by Graebe and Liebermann by fusing dibromanthraquinone with caustic potash.[2] Alcoholic alkali is much more effective than aqueous solutions and will attack halogen atoms when these are situated in α- positions, but as a rule the ether and not the free hydroxyl compound is obtained,[3] although, of course, the alkyl group can be removed by subsequent hydrolysis, and according to O. Fischer and Sapper [4] this is generally the most satisfactory method of replacing halogen atoms by hydroxyl groups. In some cases, however, alcoholic alkali can be employed for replacing halogen atoms directly by hydroxyl groups, and Decker and Laube [5] have found that when 1-chlor-2-methoxyanthraquinone is heated with methyl alcoholic caustic potash a mixture of alizarin dimethyl ether and alizarin β-monomethyl ether is obtained. The use of solutions of caustic potash in ethyl alcohol gave very similar results, viz. a mixture of alizarin methyl ethyl ether and alizarin β-monomethyl ether. Schrobsdorf [6] has obtained a tetrahydroxy compound from dibromchrysazin by fusing it with caustic potash, and this tetrahydroxy

[1] By., D.R.P. 101,486 ; 119,229.
[2] B. **2**, 14, 332, 505. Mon. Sci. 1869, 384.
[3] See p. 287. [4] J. pr. [2] **83**, 206.
[5] B. **39**, 112. [6] B. **36**, 2936.

compound is not identical with that obtained by Wölbling [1] from chrysazin disulphonic acid, as it melts at 217° and its acetyl derivative at 195°, whereas Wölbling's product melts at 292° and gives a tetraacetyl derivative melting at 238–240°.

Halogen atoms can also sometimes be readily replaced by hydroxyl groups by heating to 150–160° with concentrated sulphuric acid and boric acid, and in this way Ullmann and Conzetti [2] prepared quinizarin from 1-hydroxy-4-chloranthraquinone. Only halogen atoms which occupy a- positions are affected, so that 1-hydroxy-2.4-dichloranthraquinone gives 2-chlorquinizarin.

Although halogen atoms are only replaced by hydroxyl groups with difficulty under the influence of caustic alkali, it seems that in some cases solutions of the alkali earth hydroxides in the presence of a copper catalyst are effective, as Hövermann [3] obtained a dichlortetrahydroxy compound (probably 2.3-dichlor-1.4.5.8-tetrahydroxyanthraquinone) by heating tetrachlorquinizarin with lime-water and a trace of copper under pressure. It is probable in this case that the replacement was chiefly due to the catalytic action of the copper, as Frey [4] had previously obtained 1.4.5.8-tetrahydroxyanthraquinone by heating 4.8-dichlorquinizarin with water and a trace of copper at 250°.

Halogen atoms when in the a- position can sometimes be replaced by hydroxyl groups by heating with concentrated sulphuric acid or oleum, with or without the addition of boric acid. By this means quinizarin is readily obtained from 1.4-dichloranthraquinone or 1-hydroxy-4-chlor anthraquinone,[5] and Ullmann [6] has found that 2-methyl-1-hydroxy-4-chloranthraquinone passes into 2-methyl quinizarin when heated to 150–160° with concentrated sulphuric acid and boric acid. Fuming nitric acid, with or without the addition of boric acid, can also in some cases cause the replacement of halogen atoms by hydroxyl groups, O. Fischer and Rebsamen [7] having found that 1-methyl-4-chloranthraquinone is

[1] B. **36**, 2941.   [2] B. **53**, 833.   Cf. By., D.R.P. 203,083.
[3] B. **47**, 1210.   [4] B. **45**, 1361.   [5] By., D.R.P. 203,083.
                [6] B. **52**, 2110.   [7] B. **47**, 461.

converted into 1-methyl-4-hydroxynitroanthraquinone under the influence of nitric acid and boric acid, whereas without boric acid a methyl dihydroxynitroanthraquinone was obtained. The exact positions of the groups in these two compounds is uncertain, but they must all be attached to the same benzene ring, as both give phthalic acid when oxidised. The behaviour of the nitro compound, however, is peculiar, as it is slowly decomposed by alkali at the ordinary temperature and rapidly on heating, and decomposes with the evolution of nitrous fumes when boiled with acetic anhydride and sodium acetate. It is not unlikely that the nitro group is situated in the side chain.

In the case of the phthalic acid synthesis, when halogen atoms are present in the benzoyl benzoic acid there is a possibility of their being replaced by hydroxyl groups during the closing of the anthraquinone ring, *e.g.* dichlordihydroxy-benzoyl-benzoic acid when heated with oleum and boric acid gives chlorpurpurin.[1]

REPLACEMENT OF AMINO GROUPS.—Amino groups can be replaced by hydroxyl groups in the usual way by diazo-tising and then boiling the diazonium sulphates with water or dilute sulphuric acid,[2] but as a rule it is best to diazotise the amine in concentrated sulphuric acid solution, and then to heat to 90–100° without first diluting.[3] A large number of hydroxyanthraquinones have been obtained by this method, which has proved of considerable value as a means of determining the position of amino groups.

Amino groups can in some cases be replaced by hydroxyl groups by boiling with caustic alkali,[4] but the reaction takes place much more readily if the cyclic carbonyl groups are first partly reduced, the amino compounds in this way resembling other substituted anthraquinones. Advantage has been taken of this to combine the preparation of the amino compound and the replacement of the amino group in one

[1] Mettler, B. **45**, 801.
[2] Böttger and Petersen, A. **166**, 151.   Römer, B. **15**, 1793 ; **16**, 369 ; Lifschütz, B. **17**, 900.
[3] Eckert, M. **35**, 290.   Ullmann and Conzetti, B. **53**, 828. M.L.B., D.R.P. 97,688.   B.A.S.F., D.R.P. 108,459.
[4] M.L.B., D.R.P. 75,490 ; 81,742 ; 104,367.

operation, this result being achieved by reducing the corresponding nitro compound in boiling alkaline solution.[1] The majority of the cases recorded in which the above reaction has been applied refer to compounds in which the nitro (or amino) group occupies an α- position, but it appears also to be applicable to β-nitro (or amino) compounds, as Simon [2] has found that 2-hydroxy-1.3-dinitroanthraquinone gives anthragallol when reduced in boiling alkaline solution. Amino groups can also often be replaced by hydroxyl groups by reduction in acid solution, a good example of this type of reaction being the production of quinizarin by the reduction of 1.4-aminohydroxyanthraquinone, 1.4-hydroxynitroanthraquinone or 1.4-diamino anthraquinone by stannous chloride and hydrochloric acid.[3]

It must be borne in mind, however, that the reduction of the cyclic carbonyl group also loosens other groups attached to the anthraquinone ring and these may be simultaneously split off. Thus, in the above reactions 1.4-aminoalkoxyanthraquinone and 1.4-alkoxynitroanthraquinone are dealkylated on reduction and yield quinizarin and not quinizarin monoalkyl ether. Alkoxy groups if present at 2 or 3 are also dealkylated, and halogen atoms or nitro, amino or sulphonic acid groups if present in these positions, are replaced by hydrogen.[4] The production of hydroxyanthraquinones by the reduction of nitroanthraquinones in concentrated sulphuric acid or oleum is usually accompanied by simultaneous hydroxylation, the reaction being due to the production of hydroxylamine compounds and quinoneimides, and this reaction is discussed at greater length elsewhere.[5]

Exhaustive chlorination of primary aminoanthraquinones in glacial acetic acid, chloroform, or other suitable solvent sometimes leads to the replacement of the amino group by hydroxyl, but in these cases replacement of amino by halogen also takes place, *e.g.* 1.5- and 1.8-diamino anthraquinone

[1] M.L.B., D.R.P. 75,490.   [2] D.R.P. 119,755.
[3] M.L.B., D.R.P. 148,792 ; 207,668.   [4] M.L.B., D.R.P. 183,332.
[5] See p. 244.

give a mixture of hexachloranthrarufin, hexachlorchrysazin, and octachloranthraquinone.[1] In some cases the action of the halogen depends on the solvent used. Thus, 3-amino-alizarin when treated with bromine in a mixture of glacial acetic acid and concentrated sulphuric acid is brominated, 3-amino-4-bromalizarin being formed ; but if treated with bromine in aqueous solution the amino group is replaced by hydroxyl, the product being anthragallol ; and other β-amino-hydroxyanthraquinones behave in the same way.[2]

DIRECT OXIDATION

Anthraquinone differs from other aromatic compounds in the great ease with which hydroxyl groups can be inserted into the molecule by direct oxidation, and use has been made of this reaction very widely both in the laboratory and on the large scale. In spite of the large amount of work which has been recorded on the preparation of hydroxyanthra-quinones by direct oxidation, investigators seem to have paid little or no attention to the mechanism of the reaction, a fact which may be due to the very great majority of the work having only been published in the form of patent specifications. Consequently there is little or no data on which any theory of the actual mechanism of the change can be based, and, indeed, it is probable that the actual mechanism depends in some degree on the oxidising agent used.[3]

If the peroxide formula is adopted as representing one of the phases in the vibration of the anthraquinone molecule, then when the molecule is in this state one of the benzene rings will have an *ortho-* quinonoid structure. All quinonoid bodies show enhanced reactivity, and in this case addition of the elements of water would lead to a body which, by tauto-meric change, would pass into a hydroxyanthraquinol. The anthraquinols are well-known compounds and are extremely readily oxidised to the corresponding anthra-quinone, in this case the hydroxyanthraquinone. On this

[1] B.A.S.F., D.R.P. 125,094 ; 137,074.
[2] By., D.R.P. 126,015. B.A.S.F., D.R.F. 126,603.
[3] *Cf.* Bucherer, " Lehrbuch der Farbenchemie " (1914), pp. 327–328.

basis the formation of a hydroxy anthraquinone would take place in successive stages thus :
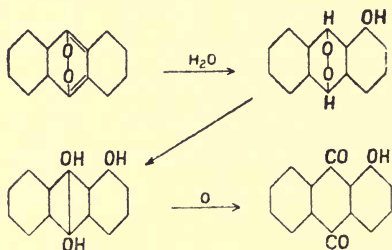
Further hydroxylation might then take place in exactly the same way, or through the production of a compound of quinonoid structure by the wandering of the hydroxyl hydrogen atom :
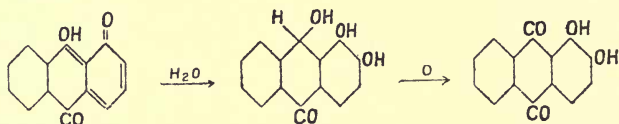
It should be noted that when hydroxylation is brought about without the use of an oxidising agent, *e.g.* when anthraquinone-β-sulphonic acid is fused with caustic soda without the addition of a nitrate or chlorate, the hydroxyl compound is obtained as its reduction product.

Hydroxyl groups can be introduced into the anthraquinone molecule by direct oxidation in either alkaline or acid solution, the most interesting results being obtained by the latter means, although oxidation in alkaline solution is of great technical importance, as it is by this means that alizarin is manufactured.

ALKALINE SOLUTION.—As stated on p. 239, when an anthraquinone-β-sulphonic acid is fused with caustic alkali, not only are the sulphonic acid groups replaced by hydroxyl groups, but at the same time oxidation takes place and further hydroxyl groups enter the molecule. If no oxidising agent is present in the melt the hydroxy compound is obtained in the form of its reduction product, this being due either to the reaction having taken the course outlined

above, or to the oxidation of one molecule having taken place at the expense of the ketonic oxygen atoms of another molecule, or to a combination of these causes. In order to obtain a more satisfactory yield of the hydroxyanthraquinone it is usual to carry out the alkali melt in the presence of an oxidising agent such as air or an alkali nitrate or chlorate, chlorates usually giving the most satisfactory results. The reaction obviously takes place in at least two steps, viz. replacement of the sulphonic acid groups followed by further hydroxylation, as further hydroxyl groups can be introduced into the hydroxyanthraquinones themselves by fusion with caustic alkali and an oxidising agent. Thus, Schunck and Römer[1] obtained flavopurpurin and anthrapurpurin by fusing anthraflavic acid and *iso*-anthraflavic acid with caustic potash, and more recently several patents have been granted for improved methods of carrying out these reactions.[2] Anthrarufin and chrysazin are also readily converted into trihydroxy compounds (hydroxyanthrarufin and hydroxychrysazin) by heating with caustic alkali[3] and alkali nitrate, and many other examples of this type of reaction are known.

The most important product obtained by the fusion of an anthraquinone sulphonic acid with caustic alkali is, of course, alizarin, this dyestuff being obtained almost universally by fusing the sodium salt of anthraquinone-β-sulphonic acid with caustic soda and sodium chlorate.[4] As a rule the alkali melt is carried out with caustic soda solution of 30 to 40 per cent. strength, the heating being effected in an autoclave.[5] The alizarin obtained by this method is not pure and contains also higher hydroxylated anthraquinones such as flavopurpurin and anthrapurpurin, derived from the disulphonic acid present as an impurity in the technical

[1] B. **9**, 678.

[2] Wed., D.R.P. 194,955. By., D.R.P. 205,097 ; 223,103.

[3] M.L.B., D.R.P. 195,028 ; 196,980.

[4] For references to the literature dealing with the earlier history of alizarin, see Schultz, " Chemie des Steinkohlenteers," vol. ii. pp. 250–262, and Auerbach, "Das Anthracen."

[5] For technical details see Ullmann, " Enzyklopädie der technischen Chemie."

monosulphonic acid, and purpurin, derived from alizarin by oxidation. The presence of the flavopurpurin and anthrapurpurin causes the alizarin to dye in rather yellowish shades, and various mixtures of alizarin with flavopurpurin and anthrapurpurin are sold as Alizarin RA, RR, etc., the letters referring to the shades obtained from the different brands.[1]

Another method[2] of carrying out the manufacture of alizarin is to mix intimately six parts of finely powdered caustic potash with six parts of sodium anthraquinone-β-sulphonate and one part of alcohol. The mixing must be very intimate and must be carried out with the total exclusion of air. When the mixture is exposed to the air in thin layers it immediately warms up and alizarin is formed. This method of carrying out an " alkali melt " is not confined to the preparation of alizarin but seems to be fairly general, e.g. indanthrone can be made from β-aminoanthraquinone, and pyranthrone can be obtained from 2.2′-dimethyl-1.1′-dianthraquinonyl by a similar procedure. The method is a rapid one and is well adapted for continuous working.

As stated above, anthraquinone-2.6- and -2.7-disulphonic acids when fused with caustic alkali yield flavopurpurin (Alizarin RG, GI, SDG, etc.) and anthrapurpurin (Alizarin SX, GD, RX, etc.), but if the fusion is carried out in the presence of air under suitable conditions it is possible to replace only one sulphonic acid group, the products being alizarin - 6 - sulphonic acid and alizarin-7-sulphonic acid.[3]

The insertion of hydroxyl groups into the anthraquinone molecule by alkaline media is not confined to the hydroxy-anthraquinones, as anthraquinone itself can be hydroxylated under suitable conditions by fusion with caustic soda and a chlorate. The product in this case is alizarin of exceptional purity and free from anthrapurpurin and flavopurpurin. Such alizarine dyes in slightly bluish shades of red (Alizarin No. 1, Alizarin V, Alizarin mit Blaustich), and the process

[1] Schultz, " Farbstofftabellen."   [2] B.A.S.F., D.R.P. 287,270.
[3] By., D.R.P. 50,164 ; 50,708.

seems well adapted to its manufacture.[1] The alkaline oxidation of anthraquinone under other conditions can lead to various hydroxyanthraquinones, and it is claimed that when the oxidation is brought about by heating to 200° for 3–4 days with caustic soda of 30 per cent. strength together with a sulphite, or compound capable of yielding a sulphite, and an oxidising agent such as potassium nitrate, the product is β-hydroxyanthraquinone, alizarin, anthrapurpurin, flavopurpurin or anthraflavic acid or a mixture of these.[2]

In connection with the preparation of hydroxyanthraquinones by the alakli melt method it is interesting to notice that if lime, strontia, baryta, or magnesia is added to the alkali melt before heating, the hydroxyanthraquinone is left as an insoluble lake which can be filtered off, and it is claimed that this procedure greatly facilitates the recovery of the excess of alkali.[3]

ACID SOLUTION.—The preparation of hydroxyanthraquinones by the direct oxidation in acid solution of anthraquinone or lower hydroxylated derivatives is a reaction of the greatest importance and has been very widely applied. Here again, however, nearly all the work published has only been recorded in the form of patent specifications, with the usual result that the information available is insufficient to permit any general rules to be detected. Also the directions given in the specifications are often unsuitable for laboratory experiments, and in the majority of cases any statements as regards yield are conspicuous by their absence. The writer, however, has prepared several hydroxyanthraquinones by direct oxidation in acid solution and has found that the yields obtained are usually quite satisfactory.

Oxidation in acid solution is always brought about in concentrated sulphuric acid, and may be effected with concentrated sulphuric acid or monohydrate alone, with oleum, with nitrosyl sulphuric acid or with sulphuric acid and an oxidising agent such as nitric acid, manganese

[1] B.A.S.F., D.R.P. 186,526.
[2] By., D.R.P. 241,806 ; 245,987 ; 249,368 ; 251,236.
[3] M.L.B., D.R.P. 17,627.

dioxide, arsenic acid, ammonium persulphate, etc. The introduction of hydroxyl groups, of course, weakens the benzene ring, and to prevent further oxidation with rupture of the ring taking place it is usually necessary to carry out the oxidation under such conditions that the hydroxyl group becomes protected. This is best done by carrying out the oxidation in the presence of excess of boric acid, as under these conditions a boric ester is formed which is much more stable towards oxidising agents than the free hydroxy compounds. These boric esters, however, are easily hydrolysed by dilute acids, so that when the oxidation is complete it is only necessary to dilute the solution and then boil for a few minutes in order to liberate the free hydroxy compound.

CONCENTRATED SULPHURIC ACID OR OLEUM.—Oleum of high concentration, viz. an acid containing about 80 per cent. of free anhydride, readily hydroxylates anthraquinone and its derivatives, the reaction usually being carried out at 35°–40°, and never at a temperature exceeding 100°. With oleum of lower strength a higher temperature is necessary and, of course, the same is true if the oxidation is brought about by means of ordinary concentrated sulphuric acid or sulphuric acid monohydrate,* in these cases temperatures of 260–280° usually being the most suitable.

When sulphuric acid acts as an oxidising agent it is, of course, reduced to sulphurous acid and this combines with the hydroxy compound produced to form a sulphite ester, this ester formation to some extent protecting the hydroxylated anthraquinone from destruction by further oxidation. Much more satisfactory results are obtained, however, by carrying out the oxidation in the presence of boric acid so that the boric ester is formed, and the same method is used when the oxidation is carried out with sulphuric acid and an oxidising agent. In any case when oxidation is complete the melt must be diluted and then boiled in order to hydrolyse

* The term "monohydrate" denotes an acid containing 100 per cent. of H_2SO_4, i.e. the monohydrate of sulphur trioxide. This explanation appears necessary as in the abstracts published by the Chemical Society, e.g. Soc. **100**, 548, it is sometimes quite wrongly taken to mean $H_2SO_4.H_2O$.

the ester present. When the boric acid method is employed it is usual to add one part of crystallised boric acid to twenty parts of concentrated sulphuric acid, monohydrate, or oleum, and then to add the anthraquinone compound (one part) which it is desired to oxidise. The temperature is then maintained at a suitable point until examination of a sample shows that oxidation has gone as far as desired, when the whole is cooled, diluted with water, boiled to hydrolyse the ester, and the hydroxy compound then filtered off.

The addition of boric acid also slows down the reaction and, if sufficient is added, may even in some cases inhibit it altogether. This retarding action of boric acid is often very useful in preventing the reaction going too far. Thus the oxidation of alizarin with oleum of high concentration leads to quinalizarin in the absence of boric acid, but with the addition of a suitable amount of boric acid the reaction is so retarded that an almost quantitative yield of hydroxy-anthrarufin can be obtained. In the same way the addition of boric acid renders it possible to oxidise chrysazin to 1.4.8-trihydroxyanthraquinone.

It is impossible to detect with certainty any regularities in the positions taken by entering hydroxyl groups, but it seems to be a fairly general rule that the α-position is preferred, and that the β-position is never taken unless there is a hydroxyl group in the contiguous α- position. Even when there is such a group present the entering hydroxyl group often prefers the α- position. The ease with which hydroxylation takes place varies very much with the different compounds used as starting-out substances. Thus oleum of high concentration rapidly converts erythrohydroxy-anthraquinone into anthrarufin, but the conversion of anthrarufin or quinizarin into 1.2.4.5.6.8-hexahydroxy-anthraquinone only takes place extremely slowly. On the other hand, this hexahydroxy compound is rapidly and quantitatively formed from chrysazin, and from anthra-chrysazin its formation is almost instantaneous.

Oxidation by means of sulphuric acid is a catalytic

reaction and does not take place if chemically pure acids are used. When ordinary commercial acids are employed the small quantities of selenium present act as the catalyst :

$$SeO_2 = Se + O_2$$
$$Se + 2SO_3 = SeO_2 + 2SO_2$$
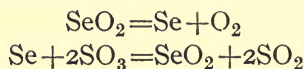
Oxidation by means of sulphuric acid is also facilitated by the presence of mercury compounds,[1] and bromine is stated to facilitate attack by oleum, although this can hardly be regarded as a catalytic effect as bromination and hydroxylation take place simultaneously.[2] Hydroxylation by oxidation with sulphuric acid or oleum often leads to the production of polyhydroxyanthraquinone sulphonic acids, but in many cases the sulphonic acid groups are readily removed by hydrolysis by heating the product with sulphuric acid of about 70 per cent. strength.[3]

Hydroxylation by means of sulphuric acid or oleum often leads to the simultaneous replacement of other groups such as halogen atoms [4] and amino and nitro groups [5] when these are present in the molecule, and it is possible to obtain hydroxyanthraquinones from halogen derivatives of anthracene in which both *ms*-hydrogen atoms have been replaced by halogen atoms.[6] The behaviour of the nitroanthraquinones towards oleum is particularly interesting but has already been discussed.[7] Amino groups in aminoanthraquinones, although often replaced by hydroxyl groups under the influence of oleum, by no means always behave in this way, both α-amino and α-alkylaminoanthraquinones being often converted into *para*-hydroxyaminoanthraquinones by treatment with 80 per cent. oleum at 30–40°, or with 20 per cent. oleum, monohydrate or concentrated sulphuric acid [8] in the presence of boric acid at 200°.

[1] Georgievics, M. **32**, 347. By., D.R.P. 162,035 ; 172,688.
[2] By., D.R.P. 97,674 ; 99,314.
[3] By., D.R.P. 172,688. *Cf.* M.L.B., D.R.P. 71,964.
[4] By., D.R.P. 81,962 ; 83,055.
[5] M.L.B., D.R.P. 75,490. By., D.R.P. 79,768 ; 81,244 ; 83,055 ; 83,085.
[6] By., D.R.P. 68,775 ; 69,835.
[7] Page 242.
[8] By., D.R.P. 154,353 ; 155,440.

Sulphonic acid groups when present in the molecule have a tendency to protect the benzene ring to which they are attached, and when there is only one sulphonic group present the hydroxyl groups enter the other ring. Thus anthraquinone-α-sulphonic acid when treated with oleum gives alizarin-5-sulphonic acid [1] and purpurin-8-sulphonic acid,[2] the use of boric acid and mercury apparently not influencing the positions taken by the hydroxyl groups. The influence of sulphonic acid groups in the β- position is uncertain.

The data available as regards the product obtained when fresh hydroxyl groups are introduced into a molecule in which such groups are already present are confusing and insufficient to allow any reliable deductions to be made. Many of the hydroxyl compounds described in the patent literature are not characterised, and probably a large proportion of them are mixtures of isomers. It appears, however, that when two hydroxyl groups are present in the *para-* position to one another, the tendency of the entering hydroxyl group is to attach itself to the same ring, *e.g.* quinizarin gives purpurin,[3] and quinizarin-8-sulphonic acid gives purpurin-3.8-disulphonic acid.[4] This is the behaviour that would be expected on the assumption that direct hydroxylation is primarily the addition of the elements of water to a compound with a quinonoid structure, as quinizarin is fairly easily oxidised to anthradiquinone, a compound which is a true quinone in its chemical reactions. Gattermann,[5] however, finds that quinizarin when oxidised with oleum under certain conditions gives quinalizarin.

Anthraquinone itself when oxidised with oleum containing about 80 per cent. of free anhydride and boric acid gives anthrarufin,[6] whereas with more dilute oleum or with ordinary concentrated sulphuric acid it is first rapidly converted into quinizarin and then more slowly into

[1] By., D.R.P. 172,688.   M.L.B., D.R.P. 158,413.
[2] R. E. Schmidt, B. **37**, 71.   By., D.R.P. 155,045.
[3] By., D.R.P. 81,481.   [4] By., D.R.P. 172,688.
[5] J. pr. [2] **43**, 246.   [6] By., D.R.P. 101,220.

purpurin.[1] Oleum of high concentration also seems capable of oxidising anthraquinone to a hexahydroxy compound,[2] probably Anthracene Blue WR.

Erythrohydroxyanthraquinone on oxidation with oleum of high concentration gives anthrarufin,[3] but the effect of more dilute acids does not seem to have been studied, and there appears to be no record of the hydroxylation of β-hydroxyanthraquinone by acids.

Alizarin when oxidised by oleum of high concentration gives quinalizarin [4] (Alizarin Bordeaux B, Alizarin Cyanine 3R) and hydroxyanthrarufin,[5] chrysazin gives 1.4.5-trihydroxyanthraquinone,[6] and anthragallol when oxidised with dilute oleum or concentrated sulphuric acid in the presence of boric acid gives 1.2.3.4-tetrahydroxyanthraquinone.[7]

Oxidation with monohydrate in the presence of mercuric sulphate and boric acid has resulted in the preparation of octahydroxyanthraquinone, Georgievics [8] having prepared this substance from rufigallic acid by this method.

Polyhydroxyanthraquinones have also been obtained by the action of oleum or sulphuric acid upon purpurin,[9] anthrapurpurin,[10] flavopurpurin,[11] hydroxyanthrarufin,[12] hydroxychrysazin,[13] rufigallic acid,[14] and many other similar compounds.[15]

NITROSYL SULPHURIC ACID.—Nitrosyl sulphuric acid is a valuable reagent for inserting hydroxyl groups into the anthraquinone molecule and can be used either as chamber crystals or, more conveniently, simply as the solution obtained by slowly adding solid sodium nitrite to about 15 parts of cold concentrated sulphuric acid. Oxidation is usually carried out at a temperature of 180–230°, and

[1] By., D.R.P. 81,960.
[2] By., D.R.P. 65,182.
[3] By., D.R.P. 97,674.
[4] By., D.R.P. 60,855.
[5] By., D.R.P. 156,960.
[6] By., D.R.P. 161,026.
[7] By., D.R.P. 86,968. *Cf.* By., D.R.P. 60,855.
[8] M. **32**, 347.
[9] By., D.R.P. 60,855.
[10] By., D.R.P. 60,855 ; 67,061.
[11] By., D.R.P. 60,855 ; 67,061.
[12] By., D.R.P. 67,063.
[13] By., D.R.P. 67,063.
[14] By., D.R.P. 62, 531.
[15] By., D.R.P. 63,693 ; 64,418 ; 65,375 ; 65,453 ; 69,013 ; 81,481 ; 81,959 ; 172,688.

boric, arsenic, or phosphoric acid [1] is added to protect the hydroxyl compound as formed by converting it into an ester. Boric acid is certainly the most efficient of these, and is usually added in the proportion of one part of crystallised acid to one part of substance to be oxidised, but it is probable that in many cases better results would be obtained by using different proportions. Thus Dimroth and Fick [2] found that the oxidation of flavopurpurin and anthrapurpurin to the tetrahydroxy compounds by means of nitrosyl sulphuric acid was best effected when only one-tenth of the above proportion of boric acid was used, as if larger quantities were employed it was necessary to carry out the oxidation at a higher temperature and the yields obtained were much poorer.

Hydroxylation with nitrosyl sulphuric acid is a catalytic reaction and depends on the presence of mercury. If the nitrosyl sulphuric acid is made from *pure* sulphuric acid no hydroxylation takes place, but as a rule commercial sulphuric acid which has been made from pyrites contains sufficient mercury. In most cases, however, the addition of a mercury salt is advantageous,[3] and the study of the reaction under these conditions has thrown some light on its mechanism. Thus it has been found that the action of nitrosyl sulphuric acid at 120° in the presence of boric acid and mercuric sulphate converts anthraquinone into 1-hydroxyanthraquinone-4-diazonium sulphate,[4] this being converted into quinizarin when heated with concentrated sulphuric acid at 170°–180°. This direct insertion of the diazonium group is rather remarkable, and the reaction is one which merits further investigation.

Other groups when present in the molecule are often affected during the process of hydroxylation, β-methyl-anthraquinone, for example, being converted into quinizarin carboxylic acid,[5] and 1.5-dinitroanthraquinone yielding 5-nitroquinizarin.[6]

[1] B.A.S.F., D.R.P. 153,129 ; 154,337. [2] A. **411**, 326.
[3] B.A.S.F., D.R.P. 153,129 ; 154,337. [4] By., D.R.P. 161,954.
[5] By., D.R.P. 84,505. [6] By., D.R.P. 90,041.

Oxidation with nitrosyl sulphuric acid seems specially adapted to the preparation of hydroxyanthraquinones in which two hydroxyl groups are in the *para-* position to one another, and it appears that a hydroxyl group does not enter a β- position unless both α- positions in that ring are already occupied by hydroxyl. Too great reliance, however, must not be placed on this rule, as the data available are insufficient to establish it beyond doubt.

Anthraquinone on oxidation with nitrosyl sulphuric acid gives quinizarin,[1] reference having already been made to the production of 1-hydroxyanthraquinone-4-diazonium sulphate as an intermediate product. The production of quinizarin by this method takes place very readily, and as the yields obtained are quite satisfactory it forms the easiest means of obtaining quinizarin in the laboratory.

Erythrohydroxyanthraquinone also gives quinizarin[2] and, curiously enough, so does β-hydroxyanthraquinone.[3] In this latter case it is probable that the nitrous acid first reduces the hydroxyl group and then oxidises the resulting anthraquinone, and this behaviour explains why hydroxyl groups so rarely take the β-position.

Quinizarin on oxidation gives purpurin,[4] although in poor yield, and this is one of the very few cases in which a hydroxyl group enters the β-position.

Chrysazin gives 1.4.5-trihydroxyanthraquinone very readily and in a state of purity, as, curiously enough, no 1.4.5.8-tetrahydroxyanthraquinone is formed.[5]

Flavopurpurin on oxidation yields hydroxyflavopurpurin (1.2.4.6.), and anthrapurpurin yields hydroxyanthrapurpurin (1.2.4.7), the position of the hydroxyl groups being proved by the fact that both hydroxyflavopurpurin and hydroxy-anthrapurpurin on reduction and subsequent oxidation of the *leuco-* compound give 1.4.6-trihydroxyanthraquinone, the orientation of the hydroxyl groups in this compound

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[1] By., D.R.P. 81,245 ; 161,954. B.A.S.F., D.R.P. 154,337.
[2] By., D.R.P. 162,792.
[3] By., D.R.P. 86,630.
[4] By., D.R.P. 86,630. B.A.S.F., D.R.P. 153,129.
[5] By., D.R.P. 163,041.

being known by its formation from 4-hydroxyphthalic acid and hydroquinone.[1]

Anthraquinone-β-sulphonic acid when heated with nitrosyl sulphuric acid gives a purpurin sulphonic acid which is different from that obtained by the sulphonation of purpurin, as the sulphonic acid group is not removed by hydrolysis when the acid is heated with hydrochloric acid.[2]

VARIOUS OXIDISING AGENTS.—Hydroxyl groups have been introduced into the anthraquinone nucleus by the use of numerous oxidising agents in conjunction with concentrated sulphuric acid, and in all of these cases it has been found that boric acid exerts a very beneficial influence by protecting the hydroxy compounds formed from further attack.[3]

Nitric acid in the presence of concentrated sulphuric acid can act on hydroxyanthraquinones either as a nitrating agent or as an oxidising agent or as both. Thus alizarin sulphonic acid when dissolved in concentrated sulphuric acid at 10° and then treated with nitric acid gives purpurin sulphonic acid,[4] alizarin itself when nitrated giving a mixture of nitroalizarin, purpurin, and nitropurpurin.[5] Flavopurpurin and anthrapurpurin are also oxidised by nitric acid when dissolved in concentrated sulphuric acid and give tetranitro compounds.[6] The action of nitric acid on the polyhydroxyanthraquinones is often complicated by the formation of diquinones,[7] although to some extent this can be avoided by the protecting influence of boric acid. Highly hydroxylated derivatives often undergo complete decomposition, rufigallic acid giving only oxalic acid,[8] and amino groups when present are often replaced by nitro groups.[9]

The action of nitric and sulphuric acids at a high temperature on anthraquinone derivatives is in many cases similar to the action of sulphuric acid on the nitroanthraquinones,

[1] Dimroth and Fick, A. **411**, 326.   [2] B.A.S.F., D.R.P. 154,337.
[3] By., D.R.P. 102,638.   [4] M.L.B., D.R.P. 84,774.
[5] M.L.B., D.R.P. 150,322.   [6] M.L.B., D.R.P. 84,774.
[7] By., D.R.P. 70,782.   [8] Klobukowski, B. **8**, 931 ; **9**, 1256.
[9] M.L.B., D.R.P. 104,244 ; 107,238 ; 111,919.

a somewhat important reaction which is treated in greater detail elsewhere.[1]

Manganese dioxide in the presence of concentrated sulphuric acid oxidises hydroxyanthraquinones to higher hydroxylated compounds, the product usually being obtained in the form of an anthradiquinone, which can be reduced to the corresponding hydroxyanthraquinone by sulphur dioxide.[2]   The most important application of this reaction is the oxidation of quinalizarin to 1.2.4.5.8-pentahydroxy-anthraquinone (Alizarin Cyanine R, 2R, RA Extra, etc.), the diquinone at first obtained being subsequently reduced.[3] The pentahydroxy compound is a powerful mordant dye giving violet shades on alumina and blue shades on chrome.

Anthragallol is readily oxidised to 1.2.3.4-tetrahydroxy-anthraquinone by manganese dioxide and sulphuric acid in the presence of boric acid at or about the ordinary tempera-ture.   The presence of boric acid is absolutely essential, as otherwise the anthragallol is completely destroyed.[4]

Alizarin-3-carboxylic acid is also oxidised by manganese dioxide and sulphuric acid at or about the ordinary tempera-ture and passes into purpurin-3-carboxylic acid, a substance which has proved to be identical with the " *pseudo*-purpurin " present in madder.[5]

In addition to the oxidising agents mentioned above hydroxyl groups can be introduced into the anthraquinone ring by means of lead dioxide, bleaching powder, arsenic acid, ferric salts, chromates, persulphates, and perchlorates,[6] but for further details the reader is referred to the original literature.   Electrolytic oxidation has also been described.[7]

REDUCTION OF POLYHYDROXY COMPOUNDS

Hydroxyanthraquinones can sometimes be obtained from the higher hydroxylated compounds by removing one

[1] See pp. 242–247.   [2] By., D.R.P. 66,153 ; 68,113 ; 68,114.
[3] By., D.R.P. 62,018.   [4] By., D.R.P. 102,638.
[5] By., D.R.P. 260,765 ; 272,301.
[6] By., D.R.P. 62,018 ; 62,504–5–6 ; 66,153 ; 68,123 ; 68,113 ; 68,114 ; 69,842 ; 69,933–4 ; 73,942 ; 102,638 ; 104,244 ; 107,238 ; 111,919.
[7] By., D.R.P. 74,353.

or more hydroxyl groups by reduction, although the method is not one of great importance. The cyclic carbonyl groups are, of course, simultaneously reduced, but if the reduction is carried out under suitable conditions it is usually possible to avoid their reduction being carried beyond the quinol stage, so that the product is readily converted into the anthraquinone derivative by air oxidation.

Exhaustive reduction of hydroxyanthraquinones by means of hydriodic acid and red phosphorus leads to hydrogenated anthracenes,[1] but under less drastic conditions it is often possible to split off one hydroxyl group without reducing the carbonyl groups beyond the anthraquinol stage. Thus Liebermann[2] and Pleus[3] by reducing quinizarin obtained 1-hydroxy-anthraquinol from which erythrohydroxyanthraquinone was obtained by mild oxidation. Hydriodic acid, however, is not a particularly suitable reducing agent for removing hydroxyl groups while avoiding complete reduction of the cyclic carbonyl groups.

The reduction of purpurin with alkaline stannite solution leads to xanthopurpurin,[4] and the same substance is said to be obtained in quantitative yield when the reduction is carried out by sodium hydrosulphite and ammonia.[5] In acid solution it seems, however, that a different hydroxyl group is split off, the product being quinizarin. According to one patent[6] the reduction of purpurin with zinc and glacial acetic acid leads to two products which are designated as *leuco*-quinizarin I and *leuco*-quinizarin II. Of these the analytical figures and the melting point (150°) quoted in the specification for *leuco*-quinizarin II agree closely with those of 1.4-dihydroxyanthraquinol.[7] The analytical figures quoted for *leuco*-quinizarin I, however, agree with those required for a trihydroxyanthraquinol,* so that the so-called "*leuco*-quinizarin I" would appear to be nothing but

[1] Liebermann, A. **212**, 26.   [2] A. **212**, 14. B. **10**, 607 ; **11**, 1610.
[3] B. **35**, 2923.   [4] Plath, B. **9**, 1204.
[5] M.L.B., D.R.P. 212,697.   [6] By., D.R.P. 89,027.
[7] Liebermann, A. **212**, 14. B. **10**, 608. Grandmougin, J. pr. [2] **76**, 138.
  * Found C=65·11, 65·08 ; H=3·95, 3·90. Calculated for $C_{14}H_{10}O_5$, C=65·12 ; H=3·88.

leuco-purpurin, the reduction not having been taken far enough to remove the hydroxyl group. In spite of this, however, the specification states emphatically in two places that "*leuco*-quinizarin I" is more readily oxidised to quinizarin than is *leuco*-quinizarin II. This is rather difficult to understand if the analytical figures given were really obtained experimentally.* In a later patent [1] the same firm claims that the best yields of *leuco*-quinizarin are obtained by reducing purpurin with aluminium bronze and concentrated sulphuric acid in the presence of boric acid. Elimination of hydroxyl groups can also be brought about by reducing other polyhydroxyanthraquinones with zinc and glacial acetic acid, Dimroth and Fick,[2] for example, obtaining 1.4.6-trihydroxyanthraquinone from both hydroxyflavopurpurin and hydroxyanthrapurpurin by this method.

In some cases nitrous acid appears capable of removing hydroxyl groups from hydroxyanthraquinones, Nienhaus [3] having reduced both alizarin and purpurin by treating them with nitrous acid in concentrated sulphuric acid solution. The reaction is, however, not one that is likely to find any extensive use owing to the tendency of nitrosyl sulphuric acid to introduce fresh hydroxyl groups.[4]

Hydroxyl groups can in some cases be removed by an indirect method. Thus Schrobsdorf,[5] by heating chrysazin with ammonia, replaced one hydroxyl group by an amino group, and by then diazotising and reducing the 1.8-aminohydroxyanthraquinone obtained erythrohydroxyanthraquinone.

Miscellaneous Methods

The hydroxyanthracenes can be converted into the corresponding hydroxyanthraquinones by first protecting the hydroxyl groups by acetylation and then oxidising. In this way erythrohydroxyanthraquinone,[6] β-hydroxyanthraquinone,[7] chrysazin,[8] and other hydroxyanthraquinones

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* For explanation of this reaction *see* "Addenda."
[1] By., D.R.P. 246,079.   [2] A. **411**, 330.
[3] B. **8**, 778.   [4] See p. 260.
[5] B. **35**, 2930.   [6] Dienel, B. **38**, 2862.
[7] Liebermann and Hörmann, B. **12**, 259.
[8] Liebermann and Boeck, B. **11**, 1616; **12**, 185.

have been obtained, but the method is chiefly valuable for determining the positions of the hydroxyl groups in the hydroxyanthracenes. The *ms*-nitro derivatives of anthracene, such as dihydrotrinitroanthracene and Meisenheimer's nitroanthrone,[1] pass into alizarin when heated with alkali to temperatures exceeding 100°. The yield is said to be improved by adding lime, sodium nitrate, and sodium sulphite to the melt.[2]

PROPERTIES AND REACTIONS

The hydroxyanthraquinones show the ordinary reactions of the phenols and dissolve in caustic alkali to form highly coloured solutions. Hydroxyl groups when in the α-position are influenced by the cyclic carbonyl groups and are then only alkylated with the utmost difficulty, and are rather more difficult to acetylate than when in the β-position. Whether the influence of the carbonyl group upon a hydroxyl group in the *ortho*- position to it is due to the formation of a quinonoid compound or whether it is due to other causes cannot be decided with certainty from the data available at present.

The absorption spectra[3] of erythrohydroxyanthraquinone and anthrarufin in alkaline solution are almost identical, each showing one and only one broad band with its head at 500μμ. In concentrated sulphuric acid solution erythrohydroxyanthraquinone shows a broad band with its head at 475μμ and also two narrow bands with their heads at 305μμ and 260μμ, and closely resembles that of anthraquinone in sulphuric acid solution. Anthrarufin, on the other hand, when in concentrated sulphuric acid solution has an absorption spectrum almost identical with that of quinizarin although the bands are slightly nearer the red end of the spectrum, whereas although the sodium salts of anthrarufin and quinizarin have absorption spectra which are somewhat

[1] See p. 54.   [2] G.E., D.R.P. 292,247.
[3] R. Meyer and O. Fischer, B. **46**, 85. Meek and Watson, Soc. **109**, 557.

similar, the addition of excess of alkali affects that of quini-zarin to a considerable extent.

The absorption spectrum of β-hydroxyanthraquinone in alkaline solution differs from that of erythrohydroxyanthraquinone by showing two narrow bands with heads at $305\mu\mu$ and $235\mu\mu$, whereas in concentrated sulphuric acid solution it shows very shallow bands at $410\mu\mu$ and $325\mu\mu$, and a slightly deeper band at $290\mu\mu$, these in addition to the broad band with its head at $500\mu\mu$.

The spectrum of the sodium salt of alizarin in the absence of excess of alkali resembles that of β-hydroxyanthraquinone, whereas when excess of alkali is present the absorption spectrum is very similar to that of purpurin, although the bands in the visible region are nearer the red end of the spectrum. The spectra of anthraflavic acid and *iso*-anthraflavic acid in alkaline solution are, as would be expected, somewhat similar, although the bands differ in breadth and persistence. They both show absorption in the ultraviolet, and so far as alkaline solutions are concerned this type of absorption seems to be confined to hydroxyanthraquinones in which there is at least one hydroxyl group in the β- position. In concentrated sulphuric acid solution, however, ultraviolet absorption seems to be exhibited by all hydroxyanthraquinones including anthraquinone itself.[1]

A comparison of the absorption spectra of the hydroxyanthraquinones and their ethers would be interesting and might throw light on the constitution of the α-hydroxy compounds, but at present data are not available.

The presence of hydroxyl groups in the anthraquinone nucleus weakens the ring to which they are attached, although not to the same extent as is usually the case in the aromatic series. The weakening influence is especially marked when two groups are present in the *p*- positions to one another, this being no doubt due to the ease with which compounds pass into anthradiquinones on oxidation. Thus

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[1] R. Meyer and O. Fischer, B. **46**, 90. *Cf.* Baly and Stewart, Soc. **89**, 511.

both purpurin and quinizarin are readily oxidised to phthalic acid by the action of atmospheric oxygen on their alkaline solutions, whereas alizarin is not destroyed under similar conditions.[1]

The further hydroxylation of hydroxyanthraquinones by direct oxidation has already been discussed,[2] and so also has the formation of anthradiquinones,[3] and but little information is available as to what products are obtained under different conditions.

Scholl[4] has found that when alizarin is oxidised in alkaline solution with a hypochlorite 1.1'.2.2'-tetrahydroxy-3.3'-dianthraquinonyl is formed, and that the same product is also formed to some extent when alizarin is fused with caustic soda under suitable conditions. Oxidation with ferricyanide in alkaline solution, on the other hand, leads to rupture of the benzene ring, the product obtained at the ordinary temperature being 2-hydroxy-(1.4)-naphthoquinonyl-3-acrylic acid.[5]

Naphthoquinonyl derivatives have also been obtained by Dimroth and Schulze[6] by the degradation of carminic acid and other naturally occurring hydroxyanthraquinone derivatives, and Bamberger and Praetorius[7] have obtained 3-hydroxy-(1.4)-naphthoquinonyl-2-acetic acid by the auto-oxidation of anthragallol in alkaline solution. They explain the degradation as follows, anthragallol being assumed to be *p*-quinonoid when in alkaline solution :
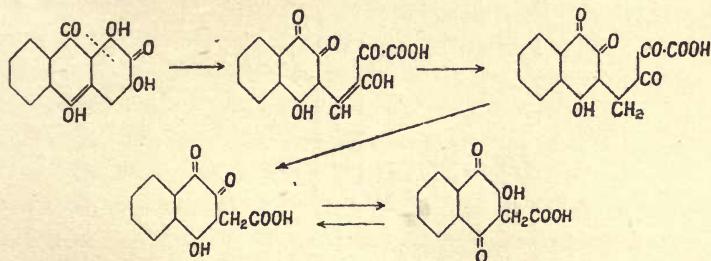
The same investigators have also found that the oxidation

[1] Dralle, B. **17**, 376.   [2] Pp. 251–264.   [3] Pp. 92–94.
[4] B. **52**, 1829 ; 2254.   *Cf.* By., D.R.P. 146,223 ; 167,461.
[5] Scholl, B. **51**, 1419.   [6] A. **411**, 339.   [7] M. **23**, 688.

of purpurin in alkaline solution by hydrogen peroxide in the presence of a cobalt catalyst leads to 2-hydroxy-3-acetyl-1.4-naphthoquinone, a change which they explain by a similar series of reactions to those just given.

Wolffenstein and Paar [1] have studied the action of boiling nitric acid on anthraflavic acid, 1.7-dihydroxy-anthraquinone and anthrarufin. The first action of the nitric acid is to nitrate the hydroxyanthraquinone, but further action leads to the rupture of the central ring and formation of 3.5-dihydroxy-2.4.6-trinitrobenzoic acid.

The hydroxyanthraquinones in many cases combine with formaldehyde to yield hydroxyanthraquinonyl carbinols, and in this way resemble the ordinary phenols. Thus anthrachrysazin [2] combines very readily with formaldehyde to form a dicarbinol (I), which in turn will combine with tertiary aromatic amines,[3] such as dimethyl aniline, to produce compounds such as II, or with ammonia or with a primary or secondary aliphatic amine [4] or a primary aromatic amine [5] to produce such compounds as III :

$$\begin{array}{cc}
\text{OH} & \text{OH} \\
\text{HO} \quad \text{CH}_2\text{OH} & \text{HO} \quad \text{CH}_2\text{C}_6\text{H}_4\text{NR}_2 \\
\\
\text{HOCH}_2 \quad \text{OH} & \text{R}_2\text{NC}_6\text{H}_4\text{CH}_2 \quad \text{OH} \\
\text{HO} & \text{HO} \\
\text{I.} & \text{II.}
\end{array}$$

$$\begin{array}{c}
\text{OH} \\
\text{HO} \quad \text{CH}_2\text{NHAr} \\
\\
\text{ArNHCH}_2 \quad \text{OH} \\
\text{HO} \\
\text{III.}
\end{array}$$
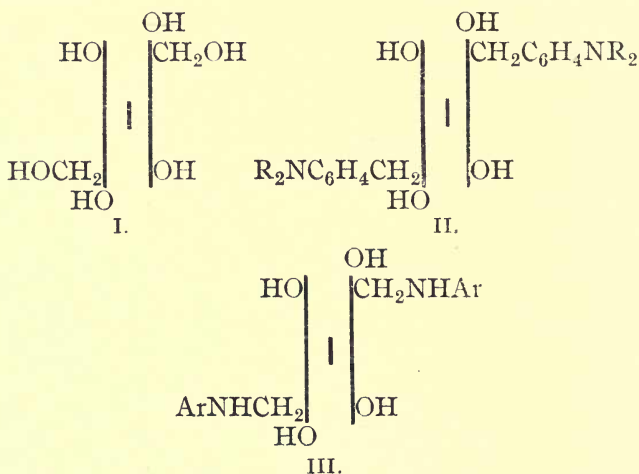
Attention has already been drawn to the acetylation of hydroxyanthraquinones by means of acetic anhydride and

[1] B. **46**, 586.   [2] B.A.S.F., D.R.P. 192,484.   M.L.B., D.R.P. 184,768.
[3] M.L.B., D.R.P. 184,807; 188,597.   [4] M.L.B., D.R.P. 188,189.
[5] M.L.B., D.R.P. 184,808 ; 188,596.

pyridine,[1] but it may here be remarked that benzoylation can often be effected by heating at atmospheric pressure with 10–15 parts of benzoic acid with or without the addition of concentrated sulphuric acid, thus avoiding the use of benzoyl chloride.[2] It is claimed that β-hydroxyanthraquinone, anthraflavic acid, flavopurpurin and anthrapurpurin are especially easily benzoylated by this method.

The reduction of the hydroxyanthraquinones to the corresponding anthranols can be brought about in the usual way, although, as pointed out on p. 264, there is always a danger of partial dehydroxylation taking place simultaneously. Reduction can also be effected by means of zinc dust and acid,[3] and some of the hydroxyanthranols have been recommended as valuable remedies for psoriasis and other skin diseases.

TINCTORIAL PROPERTIES

The absorption spectra of the hydroxyanthraquinones in alkaline and in concentrated sulphuric acid has been already discussed, and it need only be added that Meek and Watson [4] have measured the coefficient of absorption of light of various wave-lengths when reflected from fabric dyed with several of the more important hydroxyanthraquinones on various mordants. Georgievics [5] has discussed the position of hydroxyl groups in relation to the shade of the dye and has come to the general conclusion that hydroxyl groups in the α- position tend to produce red or blue shades, whereas hydroxyl groups in β- positions favour the production of yellows and browns, although too much reliance must not be placed on these conclusions, as one group may mask the effect of another. These conclusions have been criticised by Meek and Watson,[6] who consider that they have sufficient evidence to support the following conclusions :—

(*a*) Two homonuclear hydroxyl groups in the *ortho-* or

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[1] Page 237.   [2] Wed., D.R.P. 297,261.
[3] By., D.R.P. 296,091 ; 301,452 ; 305,886.   [4] Soc. **109**, 545.
[5] M. **32**, 329.   [6] Soc. **109**, 545.

para- positions to one another are necessary in order to deepen the colour, *i.e.* to produce reds, violets, or blues.

(*b*) If both rings contain such pairs of hydroxyl groups, each pair reinforces the effect of the other.

(*c*) Three hydroxyl groups at 1, 2, and 4 produce a greater effect than a pair in the *ortho-* or *para-* positions to one another.

(*d*) Three hydroxyl groups at 1, 2, and 3 produce a brown.

The connection between the position of the hydroxyl groups and the capacity of a hydroxyanthraquinone to form a lake is quite obscure, and is likely to remain so until some satisfactory definition as to the meaning of " mordant dye " is evolved. The old rule (Rule of Kostanecki and Liebermann) that two hydroxyl groups in the " alizarin position," *i.e.* at 1 and 2, are necessary in order to produce a mordant dye is certainly not a law of nature, although for a matter of fact all the hydroxyanthraquinones which have proved to be of commercial value have such hydroxyl groups. Alizarin itself is a powerful mordant dye, but quinizarin, hystazarin and xanthopurpurin all have marked tinctorial properties, and the other dihydroxyanthraquinones, and even the monohydroxy compounds, have slight capacity for forming lakes.[1]

Increase in the number of hydroxyl groups does not necessarily increase tinctorial properties, as although quinizarin is a comparatively powerful mordant dye, 1.4.5.8-tetrahydroxyanthraquinone has no capacity for forming lakes [2] except, curiously enough, on a beryllium mordant,[3] and octahydroxyanthraquinone has very feeble tinctorial properties. The presence of other groups or atoms in the molecule also affects the capacity for forming lakes, as although rufigallol itself is a very feeble mordant dye its affinity is very greatly enhanced by halogenating.[4]

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[1] Georgievics, F.T. **1**, 623.   [2] Georgievics, F.T. **4**, 185.
[3] Georgievics; Grandmougin, " Lehrbuch der Farbenchemie," fourth edition, p. 257.
[4] By., D.R.P. 114,263. *Cf.* also L. B. Holliday & Co., Ltd., and H. D. Law, E.P. 126,528[18].

The constitution of the lakes formed by the hydroxy-anthraquinones and, for example, the exact function of the lime and Turkey red oil used in alizarin dyeing, has never been properly cleared up, although there is no doubt that the usual alumina lake is a complex aluminium calcium salt.[1]

For further information as to theories of lake formation the reader is referred to the original literature,[2] a good review of the subject having been recently published by Scholl and Zinke.[3]

HALOGENATION

A considerable amount of work on the halogenation of the hydroxyanthraquinones has been recorded, but as in a great many cases the positions of the halogen atoms in the product have not been determined, it is difficult to detect with certainty any rules relating to the directing influence exerted by the hydroxyl groups, although from the data available one or two conclusions can be drawn.

When hydroxyl groups are present only in α- positions the entering halogen atom is first directed to the *para*-position, the second atom entering taking the *ortho*- position. Thus erythrohydroxyanthraquinone when treated with mole-cular or nascent halogen (*e.g.* $NaBrO_4 + HBr$) gives first 4-brom-1-hydroxyanthraquinone and then 2.4-dibrom-1-hydroxyanthraquinone,[4] and anthrarufin and chrysazin behave in the same way.[5] The bromination can be carried out in boiling glacial acetic acid solution, but unless sodium acetate is added the reaction is very slow. In the presence of sodium acetate, however, the reaction is rapid and the bromo- compound crystallizes out on cooling.[6] The reaction can also be conveniently carried out by suspending the

[1] Möhlau, B. **46**, 443. Wieland and Binder, B. **47**, 977.
[2] Soc. **75**, 433 ; **83**, 129. J.S.C.I. **22**, 600. A. **398**, 151. B. **41**, 1062, 3469 ; **44**, 2653 ; **45**, 148, 1116 ; **47**, 738, 977. F.T. **1**, 624 ; **3**, 366 ; **4**, 186.
[3] B. **51**, 1419–1428.
[4] By., D.R.P. 127,532 ; 131,403. Wed., D.R.P. 202,770. *Cf.* Eckert and Steiner, M. **35**, 1144.
[5] Schrobsdorf, B. **35**, 2930. By., D.R.P. 127,699 ; 197,082.
[6] Friess and Schürmann. B. **52**, 2182.

hydroxy compound in boiling dilute sulphuric acid (45–50 per cent. strength) at 140° and then treating with molecular chlorine or bromine,[1] and in many cases molecular halogen can be used in aqueous solution [2] at the ordinary temperature or at 100°. Erythrohydroxyanthraquinone, anthrarufin, and chrysazin have all been chlorinated and brominated by these methods, but the claim that chrysazin is chlorinated in aqueous suspension has been contradicted,[3] although it is said to yield a dichlor compound with great ease if sufficient sulphuric acid is added to raise the boiling point to 120–140°.

Chlorination can also be effected conveniently by heating with sulphuryl chloride in nitrobenzene solution, erythro-hydroxyanthraquinone being readily converted by this means into 1-hydroxy-4-chloranthraquinone and 1-hydroxy-2.4-dichloranthraquinone.[4]

In the case of quinizarin, in which there is no vacant *para*- position, chlorination in glacial acetic acid [5] leads to 3-chlorquinizarin, the same product being obtained by the action of hydrochloric acid on 1.4.9.10-anthradiquinone.[6]

Comparatively little work has been done on the chlorination and bromination of hydroxyanthraquinones in which hydroxyl groups are only present in the β- positions. It is claimed that β-hydroxyanthraquinone and anthraflavic acid are readily brominated by the action of molecular bromine on their aqueous suspensions, and that the bromine atoms first attack those β- positions which are contiguous to the hydroxyl groups, no α- position being entered until all such β- positions have been occupied.[7] Anthraflavic acid is not chlorinated in aqueous suspension at 100°, but if sulphuric acid is added so as to raise the boiling point a dichlor compound is formed.[8] The melting point of this compound and also the melting points of its acetyl and benzoyl derivatives agree with those of the dichlor compound

[1] By., D.R.P. 197,082. Wed., D.R.P. 167,743; 172,300.
[2] By., D.R.P. 127,699.   [3] Wed., D.R.P. 172,300.
[4] Ullmann and Conzetti, B. **53**, 829.   [5] By., D.R.P. 114,199.
[6] Dimroth and Schulze, A. **411**, 348.   [7] Wed., D.R.P. 175,663.
[8] Wed., D.R.P. 187,685.

obtained by the action of sodium hypochlorite on anthraflavic acid, but their solubilities are different and their identity is questionable. If the chlorination of anthraflavic acid is carried out in suspension in calcium chloride solution a totally different reaction takes place, as under these conditions a hexachlor addition product is obtained.[1] This is resinified by treatment with alkali, but when heated with an inert solvent of high boiling point a trichlor-anthraflavic acid is obtained.[2]

But little work has been recorded concerning the behaviour of hystazarin when halogenated, but Schrobsdorff,[3] by heating it to 140° with bromine in a sealed tube, obtained a dibromo compound, but did not determine the positions of the bromine atoms.

Although α-hydroxyanthraquinones are usually completely destroyed by hypochlorites, the β-hydroxy compounds are often easily and smoothly chlorinated by the action of sodium hypochlorite on their alkaline solutions. By this means Decker and Laube[4] obtained 2-hydroxy-1-chlor-anthraquinone from β-hydroxyanthraquinone, and it has been claimed that the action of hypochlorite often leads to the entrance of one, two, or three chlorine atoms into the molecule.[5] The reaction seems to be restrained by alkali, and in the presence of excess of alkali as a rule only one chlorine atom is taken up.

In the case of hydroxyanthraquinones, in which hydroxyl groups are present both in α- positions and in β- positions, the behaviour on halogenation becomes complicated and seems to depend on which hydroxyl groups have the predominating influence in the molecule, but the data available are too scanty to permit the detection of regularities. Flavopurpurin and anthrapurpurin are readily brominated in aqueous suspension,[6] the bromine entering the vacant β- positions, and aqueous suspensions of flavopurpurin when treated with sodium chlorate and hydrochloric acid give a monochlor derivative, the position of the chlorine

[1] Wed., D.R.P. 179,916. [2] Wed., D.R.P. 181,659.
[3] B. **36**, 2938. [4] B. **39**, 112.
[5] Wed., D.R.P. 152,175; 153,194. [6] Wed., D.R.P. 175,663.

being unknown.[1] Xanthopurpurin when brominated also gives a dibromo compound which is probably 1.3-dihydroxy-2.4-dibromanthraquinone.[2] The chlorination of 1.7- di-hydroxyanthraquinone can be effected by sodium hypo-chlorite, but the reaction proceeds with difficulty and only one chlorine atom is taken up.[3] The chlorination of alizarin in aqueous suspension by sodium chlorate and hydrochloric acid leads to 3-chloralizarin.[4]

The bromination of hydroxyanthraquinones such as alizarin, anthrapurpurin and flavopurpurin is often very greatly facilitated by first reducing to the corresponding anthranol and then treating this with bromine. Under these conditions the bromine both enters the nucleus and also becomes attached to the *ms*-carbon atoms; but subsequent oxidation leads to the brominated hydroxyanthraquinone, *e.g.* monobromalizarin.[5]

One of the most convenient methods of chlorinating the hydroxyanthraquinones is to treat them with sulphuryl chloride. The reaction takes place quite readily by heating the hydroxyanthraquinone on the water bath with sulphuryl chloride in nitrobenzene solution, and is facilitated by the presence of a trace of iodine. The method was first described by Ullmann,[6] who by this means obtained 4-chlorerythro-hydroxyanthraquinone and 5.8-dichloranthrarufin, and has been extended by L. B. Holliday and Co., Ltd., to various polyhydroxyanthraquinones such as alizarin, anthraflavic acid, *iso*-anthraflavic acid, Alizarin Bordeaux, etc. Apparently under some conditions one or more of the hydroxyl groups is simultaneously replaced by chlorine.[7]

SULPHONATION

Comparatively little reliable information is available concerning the sulphonation products of the hydroxy-anthraquinones, but it has been claimed that α-hydroxy

[1] Wed., D.R.P. 189,937.   [2] Plath, B. **9**, 1204.
[3] Wed., D.R.P. 152,175; 153,194.   [4] Wed., D.R.P. 189,937.
[5] By., D.R.P. 117,923.   [6] D.R.P. 282,494.
[7] L. B. Holliday and Co., Ltd., and H. D. Law, E.P. 126,727–8[18].

compounds sulphonate in the β- position, and that further sulphonation then leads to αβ-polyhydroxyanthraquinones.[1] Anthrarufin, for example, gives anthrarufin-2.6-disulphonic acid [2] and chrysazin gives chrysazin-2.7-disulphonic acid.[3] Wölbling,[4] on the other hand, by sulphonating chrysazin obtained a disulphonic acid from which a tetrahydroxyanthraquinone was obtained, which may or may not be identical with the 1.2.7.8-tetrahydroxyanthraquinone described in the patent literature.[5] They are both stated to give blue solutions in caustic soda, but whereas Wölbling characterises his product by its melting point and that of its acetyl derivative, the patentees confine themselves to describing the colour of its solutions in various solvents and its tinctorial properties, points concerning which Wölbling gives no information except in so far as the blue solution in caustic soda is concerned. In connection with this it should be noted that simultaneously with Wölbling, Schrobsdorf [6] described a dibromchrysazin which yielded a tetrahydroxyanthraquinone which one would expect to be 1.4.5.8-tetrahydroxyanthraquinone, but which differs widely from this substance in its properties,[7] and also cannot be 1.2.7.8-tetrahydroxyanthraquinone [8] or 1.2.5.8-tetrahydroxyanthraquinone (quinalizarin),[9] although it is conceivable that either of these might have been formed. As Schrobsdorf and Wölbling both carried out their work in the same laboratory at the same period, it is fair to assume that they both used the same sample of chrysazin, so that any error arising from their starting-out substance would vitiate both their results.

The sulphonation of anthraflavic acid [10] and *iso*-anthraflavic acid [11] and their methyl ethers [12] also appears to lead to the entrance of sulphonic acid groups into the β- positions.

[1] By., D.R.P. 141,296. [2] By., D.R.P. 96,364.
[3] By., D.R.P. 100,136. [4] B. **36**, 2941.
[5] By., D.R.P. 103,988. [6] B. **36**, 2936.
[7] B., D.R.P. 125,579; 143,804. [8] By., D.R.P. 103,988.
[9] By., D.R.P. 60,855. [10] M.L.B., D.R.P. 99,611; 99,874.
[11] By., D.R.P. 104,317. M.L.B., D.R.P. 99,612.
[12] M.L.B., D.R.P. 143,858. *Cf.* also M.L.B., D.R.P. 139,425 (sulphonation of anthrachrysazin dimethylether).

In the case of 1.4.5- and 1.4.6-trihydroxyanthraquinone sulphonation under ordinary conditions leads to impure mixtures, but in each case if the sulphonation is carried out in the presence of boric acid a single sulphonic acid group enters at 7.[1]

On account of its technical importance the sulphonation of alizarin has attracted considerable attention, sulphonation with oleum leading to alizarin-3-sulphonic acid [2] (Alizarin Red S), alizarin-6- and -7-sulphonic acids being only obtainable from anthraquinone disulphonic acids by fusion with caustic potash under suitable conditions.[3]   Further sulphonation of alizarin-3-sulphonic acid leads to disulphonic acids,[4] from which, however, one sulphonic acid group can be split off by subsequent hydrolysis at 190° with sulphuric acid of 80 per cent. strength.[5]

When alizarin is sulphonated in the presence of mercury the products obtained are not the same as those which are formed in the absence of mercury.   Both alizarin and alizarin-3-sulphonic acid when sulphonated in the presence of mercury give a mixture of alizarin-3.5- and alizarin-3.8-disulphonic acid, and as purpurin behaves in a similar way it must be concluded that as a rule a hydroxyl group in a ring directs to the β- position more powerfully than the mercury directs to the α- position ; but in the ring free from hydroxyl groups the mercury exerts its usual influence.[6]   Both these disulphonic acids also lose one sulphonic acid group when heated to 180–190° with sulphuric acid of about 80 per cent. strength,[7] alizarin thus yielding alizarin-5- and alizarin 8-sulphonic acids, and purpurin yielding purpurin-8-sulphonic acid.

Dihydroxyanthraquinones such as quinizarin in which the hydroxyl groups are in the *para*- position to one another

[1] By., D.R.P. 165,860.
[2] Graebe and Liebermann, A. **160**, 144.   Graebe, B. **12**, 571.   Perger, J. pr. [2] **18**, 173.   Pryzbram and Co., D.R.P. 3,565.
[3] See p. 241.
[4] By., D.R.P. 56,952.
[5] By., D.R.P. 56,951.
[6] Wed., D.R.P. 205,965 ; 210,863.
[7] By., D.R.P. 172,688. Wed., D.R.P. 210,863. Cf. By., D.R.P. 160,104.

can also be sulphonated by heating with solutions of sulphites.[1] In this case the reaction is no doubt due to oxidation to the anthradiquinone, followed by the addition of sodium sulphite, and as would be expected takes place most rapidly in the presence of an oxidising agent such as manganese dioxide. In the absence of an oxidising agent the necessary oxidation is brought about by the partial reduction of the cyclic carbonyl groups. The 1.4-hydroxy-aminoanthraquinones and the 1.4-diaminoanthraquinones are sulphonated in the same way, the intermediate product in these cases being the quinone imide or di-imide.

Only a few hydroxyanthraquinone sulphonic acids have found application as dyes, as the presence of the sulphonic acid group tends to decrease the fastness of the shades to washing. The best known are Alizarin Red S (alizarin-3-sulphonic acid), which gives scarlet shades on an alumina mordant and is also used to a certain extent in the laboratory as an indicator, and Erweco Alizarin Acid Red BS, which is a mixture of alizarin-5- and alizarin-8-sulphonic acids and gives bordeaux shade on both chrome and alumina. Flavopurpurin-3-sulphonic acid is used to a small extent under the names Alizarin Red 3WS or SSS, and gives brownish-red shades on alumina. The disulphonic acid of 1.2.4.5.6.8-hexahydroxyanthraquinone (Anthracene Blue WR) is obtained by the action of oleum on 1.5-dinitroanthraquinone, the subsequent hydrolysis being omitted. It has received several trade names, such as Acid Alizarin Blue BB, Alizarin Cyanine WRS, BBS, and 3RS, and Anthracene Blue SWX.

NITRATION

The hydroxyanthraquinones being much more stable than the phenols can often be fairly easily nitrated without protecting the hydroxyl groups, but under these conditions there is always considerable chance of simultaneous hydroxylation taking place, *e.g.* both alizarin and quinizarin give 3-nitropurpurin. Protection of the hydroxyl

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[1] By., D.R.P. 287,867 ; 288,474 ; 289,112.

group greatly lessens the danger of simultaneous hydroxylation; but, on the other hand, the directing influence of a protected group is often quite different from that of a free hydroxyl group, and to some extent depends on how the protection is effected.

When hydroxyl groups are present only in a- positions they direct entering nitro groups to the *para*- position, but the *ortho*- position is also readily taken, so that there is usually no difficulty in inserting two nitro groups for each hydroxyl group present. Erythrohydroxyanthraquinone, anthrarufin, and chrysazin [1] are fairly easily nitrated in the free state, although much purer products are obtained by nitrating the boric esters,[2] and the nitration and subsequent demethylation of chrysazin dimethyl ether has been recommended as the best method of obtaining mononitrochrysazin.[3]

In the case of quinizarin the nitration is somewhat more troublesome owing to the tendency to form nitropurpurin, and in this case the boric ester method fails.   By nitrating in an organic solvent, however, such as glacial acetic acid or nitrobenzene, quinizarin can be converted into 2-nitroquinizarin.[4]

When hydroxyl groups are present only in the β- position the entering nitro groups take the *ortho*- positions to them, a-positions usually being preferred to β- positions.   β-Hydroxy-anthraquinone itself readily gives a dinitro compound,[5] the position of the nitro groups being proved by its conversion into anthragallol.   Anthraflavic acid [6] and *iso*-anthraflavic acid [7] give both dinitro and tetranitro compounds, and hystazarin gives a mono and a dinitro compound,[8] both of these latter giving phthalic acid when oxidised.

As would be expected from its technical importance, the nitration of alizarin has received most attention.   If alizarin

[1] By., D.R.P. 98,639.
[2] Eckert and Steiner, M. **35**, 1144.   By., D.R.P. 163,042.
[3] M.L.B., D.R.P. 193,104.
[4] By., D.R.P. 272,299.
[5] Liebermann and Simon, A. **212**, 25, 53.   B. **14**, 464 ; **15**, 692.   Simon, D.R.P. 119,755.
[6] Schardinger, B. **8**, 1487.   M.L.B., D.R.P. 112,179.
[7] Römer and Schwazer, B. **15**, 1040.
[8] Schrobsdorf, B. **36**, 2938.

itself is nitrated in ordinary concentrated sulphuric acid solution a mixture of 3-nitroalizarin, purpurin, and 3-nitro-purpurin is obtained owing to simultaneous hydroxylation taking place.[1] If, however, the boric ester of alizarin is nitrated, *i.e.* if nitric acid is added to a solution of alizarin in concentrated sulphuric acid containing an excess of boric acid, the side reactions are to a large extent avoided and almost pure 3-nitroalizarin results.[2] The same compound is also obtained by nitrating alizarin when dissolved or suspended in some suitable solvent such as ligroin, toluene, nitrobenzene, or, best of all, glacial acetic acid, and also by the action of nitrous acid on alizarin,[3] although the action of nitrous acid in concentrated sulphuric acid solution leads to 7-nitroalizarin.[4]

If the diacetyl derivative of alizarin is nitrated the nitro group enters a different position, and 4-nitroalizarin is obtained,[5] but the nitration is rather troublesome to carry out, as the acetyl groups are readily lost by hydrolysis during the nitration, and for this reason it is better to use the dibenzoyl derivative,[6] the subsequent hydrolysis being very readily effected by cold caustic soda. This method has also been extended to the nitration of other hydroxy-anthraquinones such as anthrapurpurin, flavopurpurin,[7] etc. Instead of protecting the hydroxyl groups by forming an ester with an organic acid, the sulphate[8] or arsenate[9] can be used, *i.e.* the alizarin can be nitrated when dissolved in oleum of 20 per cent. strength at $-5°$ to $-10°$, or when dissolved in concentrated sulphuric acid in the presence of arsenic acid below $0°$. It is very remarkable that whereas the nitration of the sulphate or arsenate gives 4-nitroalizarin,

[1] Schunck and Römer, B. **12**, 583. M.L.B., D.R.P. 150,322. *Cf.* also By., D.R.P. 50,164 ; 50,708.
[2] By., D.R.P. 74,562.
[3] Caro, B. **10**, 1760 ; **12**, 1008. Rosenthiel, C. r. **82**, 1455 ; **83**, 73. Ann. [5] **12**, 519. B. **9**, 1036. *Cf.* also Strobel, Mon. Sci. 1878, 1337. B. **12**, 584.
[4] Grawitz, B. **10**, 1165. Caro, Mon. Sci. 1879, 424. Girard and Pabst, C. r. **91**, 570.
[5] Perkin, Soc. **2**, 578 ; B. **8**, 780. Caro, A. **201**, 353.
[6] M.L.B., D.R.P. 66,811.   [7] M.L.B., D.R.P. 70,515 ; 74,212.
[8] M.L.B., D.R.P. 74,431.   [9] By., D.R.P. 74,598.

the nitration of the borate gives the isomeric β-nitroalizarin, but other hydroxyanthraquinones such as flavopurpurin, anthrapurpurin, and Alizarin Bordeaux exhibit the same peculiarity. The α-nitro compound is also formed when alizarin monomethyl ether is nitrated,[1] although as already stated alizarin itself yields the β-isomer.

Xanthopurpurin is fairly easily nitrated to a dinitro compound,[2] and anthrachrysazin is easily and quantitatively converted into a tetranitro compound.[3]

It is worth observing that methyl ethers are often demethylated during nitration, especially when the methoxy group is in the α- position. Thus O. Fischer and Ziegler [4] found that 1-methyl-4-methoxyanthraquinone when gently warmed with excess of nitric acid of 70 per cent. strength gave a mononitro methyl hydroxy anthraquinone, although they did not determine the position of the nitro- group.

The chief technical interest in the nitroalizarins lies in the fact that they are intermediate products for the production of the important hydroxyanthraquinone quinolines (hydroxy pyridino anthraquinones), but 3-nitroalizarin is used to a considerable extent as a dye under the name Alizarin Orange A, W, SW, Cy, etc. It gives orange shades in both chrome and alumina mordants.

II. AMINOHYDROXY COMPOUNDS

When 1.5-dinitroanthraquinone is reduced in alkaline solution a bishydroxylamine derivative is formed, which under the influence of acids is at once rearranged into 4.8-diaminoanthrarufin,[5] the same product being obtained by oxidising 1.5-diaminoanthraquinone with manganese dioxide, etc., in concentrated sulphuric acid solution.[6] This diaminoanthrarufin has scarcely any tinctorial properties, but these are very greatly increased by the entrance of negative groups or atoms such as sulphonic acid groups

[1] M.L.B., D.R.P. 150,322.   [2] Plath, B. 9, 1204.
[3] M.L.B., D.R.P. 73,605.   [4] J. pr. [2] 86, 292.
[5] By., D.R.P. 81,694.   [6] By., D.R.P. 106,034.

or bromine atoms.[1] The bromo compounds are of but little importance, although it is worth remarking that the entrance of bromine into the molecule is accompanied by an increase in solubility, a phenomenon not infrequently met with in the anthraquinone series. The diaminoanthrarufin sulphonic acids, especially 4.8-diaminoanthrarufin-2.6-disulphonic acid, have met with wide application as acid wool dyes under the name Alizarin Saphirol [2] and give reddish-blue shades which become greener and duller when chromed.

If anthrarufin is sulphonated by treatment with oleum the 2.6-disulphonic acid is obtained. This on nitration gives the 4.8-dinitro compound from which the dye is formed by reduction,[3] but if the reduction is pushed too far one sulphonic acid group is split off.[4] Alizarin Saphirol is also obtained direct from dinitroanthrarufin by heating on the water bath with aqueous solutions of alkali sulphites or bisulphites.[5] Here simultaneous reduction and sulphonation takes place, a reaction which is very common in the aromatic series, and this is probably the most convenient method of obtaining the dye. Of lesser interest is its formation by the action of a sulphite on dibromdinitroanthrarufin, the sulphite reducing the nitro group and at the same time replacing the bromine atoms by sulphonic acid groups,[6] and from dibromanthrarufindisulphonic acid by heating with ammonia and a copper catalyst.[7] The dye can also be obtained by oxidising diaminoanthrarufin disulphonic acid with manganese dioxide and concentrated sulphuric acid,[8] and by the reduction of the quinoneimide sulphonic acid obtained by the action of oleum and sulphur on 1.5-dinitroanthraquinone.[9]

An isomer of Alizarin Saphirol is obtained from chrysazin either by sulphonation, nitration, and reduction,[10] or by heating dinitrochrysazin with sulphites or bisulphites,[11] or

[1] By., D.R.P. 102,532.   [2] Solway Blue (Scottish Dyes, Ltd.).
[3] By., D.R.P. 96,364; 100,137; 105,501; 108,362; 119,228.
[4] By., D.R.P. 108,578.   [5] By., D.R.P. 103,395.
[6] By., D.R.P. 163,647.   [7] By., D.R.P. 195,139.
[8] By., D.R.P. 106,034.
[9] By., D.R.P. 113,724; 116,746.   See also p. 245.
[10] By., D.R.P. 100,136.   [11] By., D.R.P. 103,395.

by heating dinitrodibromchrysazin with a sulphite.[1]   It dyes in rather greener shades than Alizarin Saphirol itself. Isomers are also obtained by successive sulphonation, nitration and reduction of anthraflavic acid [2] and *iso*-anthraflavic acid,[3] that from anthraflavic acid giving fiery red shades and that from *iso*-anthraflavic acid giving yellowish-red shades.

The formulæ of the various dyes are * :—

NH₂ OH	HO OH	NH₂	NH₂ NH₂

NH$_2$ OH | HO OH | NH$_2$ | NH$_2$ NH$_2$
S | S   S | S OH | HO   OH
S | | HO S | S   S
OH NH$_2$ | NH$_2$ NH$_2$ | NH$_2$ |

| Alizarin Saphirol. From anthrarufin. Reddish-blue shades. | From chrysazin. Greener than Alizarin Saphirol. | From anthraflavic acid. Fiery red shades, bordeaux on chrome. | From *iso*-anthraflavic acid. Yellowish-red shades. Bordeaux on chrome. |
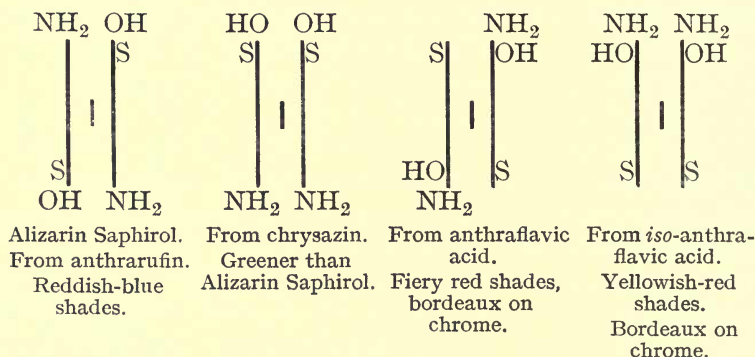
In addition to Alizarin Saphirol one or two hydroxy-aminoanthraquinones have found technical application as dyes.   Of these may be mentioned 4-aminoalizarin (Alizarin Garnet R, Alizarin Cardinal) which is obtained by the reduction of 4-nitroalizarin,[4] and gives bluish-red tones on an alumina mordant.   The corresponding 3-amino-alizarin (Alizarin Maroon W) is used to a small extent in printing, but is of very minor importance.   It gives rather loose shades of red on an alumina mordant.   Alizarin Cyanine G and New Anthracene Blue WR may possibly be hydroxyimino compounds, although they are more probably imides.   The former is obtained by heating Alizarin Cyanine R with ammonia,[5] the latter by heating Anthracene Blue with ammonia and caustic soda.[6]   Both give blue shades on alumina.

The other hydroxyaminoanthraquinones which are of

[1] By., D.R.P. 163,647.   [2] M.L.B., D.R.P. 99,611 ; 99,874.
[3] M.L.B., D.R.P. 99,612.   * S = SO₃H.
[4] By., D.R.P. 66,811.   [5] By., D.R.P. 62,019.
[6] B.A.S.F., D.R.P. 119,959.

technical importance are chiefly secondary amino compounds and are mentioned in Chapter XI.

III. The Ethers

As already stated hydroxyl groups when in the β- position are readily alkylated by heating with the alkyl iodide or dimethyl sulphate and caustic potash in alcoholic or aqueous alcoholic solution.[1] In the case of α-hydroxyl compounds, however, this method fails, and although Plath[2] claimed to have obtained dimethyl and diethyl ethers of xanthopurpurin it is fairly certain that he really obtained only the mono-methyl and monoethyl ethers. Methylation of α-hydroxy compounds, however, can be effected by heating the *dry* potassium salts with dimethyl sulphate,[3] and in many cases the alkylation can be brought about without difficulty by first reducing the hydroxyanthraquinone to the anthrone.[4] These are usually easily alkylated and the resulting ether can then be oxidised to the anthraquinone. The method fails, however, when there are hydroxyl groups in the *ortho*- position to both cyclic carbonyl groups. In spite of the well-known difficulty in alkylating hydroxyl groups when in the α- position, it has been claimed that a cyclic ether is formed when alizarin is heated with ethylene dichloride or ethylene dibromide and sodium acetate, with or without the addition of a catalyst such as copper.[5] This compound has been assigned the structure :
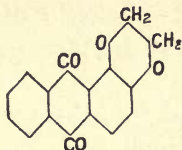
but this can only be accepted with reserve pending further confirmation.

[1] Graebe, A. **349**, 201. Graebe and Aders, A. **318**, 369. M.L.B., D.R.P. 158,277.
[2] B. **9**, 1205.
[3] O. Fischer and Gross, J. pr. [2] **84**, 372. O. Fischer and Ziegler, J. pr. [2] **86**, 297. M.L.B., D.R.P. 242,379.
[4] Graebe, A. **349**, 201 ; B. **38**, 152.   [5] M.L.B., D.R.P. 280,975.

But little work has been done on the direct arylation of hydroxyanthraquinones, although it has been claimed [1] that hydroxyl groups in the α- position are readily arylated when the alkali salt is heated with an alkyl ester of an aryl sulphonic acid, with or without the addition of a basic substance.

Dianthraquinonyl ethers are obtained by condensing a halogen anthraquinone with a hydroxyanthraquinone by heating in an inert solvent such as nitrobenzene with sodium acetate and a copper catalyst.[2] The patent does not state whether the reaction is confined to β-hydroxy compounds, although this is probably the case. From 1-chlor-2-hydroxyanthraquinone and similar compounds cyclic ethers are said to be obtained.[3] These have the structure—
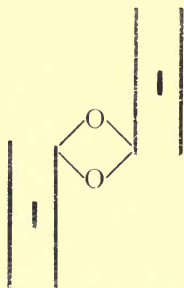
and are yellow vat dyes although apparently of no technical value. In their formation an α-halogen atom reacts with a β-hydroxyl group so that αβ-dianthraquinonyl ethers would seem obtainable by this method. It is very improbable, however, that an α-halogen atom would react with an α-hydroxyl group to produce an αα-dianthraquinonyl ether.

Cyclic dianthraquinonyl ethers are also formed from o_2-dihydroxydianthraquinonyl compounds by heating with condensing agents such as zinc chloride.[4] Here loss of water takes place between two hydroxyl groups with the formation of a furfurane ring :

[1] M.L.B., D.R.P. 243,649.
[2] M.L.B. 216,268.
[3] Wed., D.R.P. 257,832 ; 263,621 ; 265,647 ; 269,215.
[4] Scholl, D.R.P. 274,783.
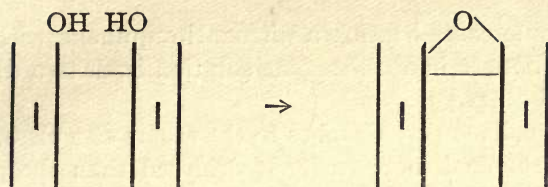
According to one patent specification [1] when quinizarin is heated to about 120° with a salt of a weak acid such as a carbonate, borate, phosphate, or acetate, it is converted into two compounds. These are present in the melt more or less as reduction products, and the patent suggests that they are formed by the union of two molecules by self-oxidation at the expense of the cyclic carbonyl groups. If this is the case they may or may not be ethers. The analytical figures given agree with the formulæ $C_{28}H_{14}O_8$ and $C_{28}H_{13}O_8$. Both substances give blue alkali salts.

Both alkyl and aryl ethers can be obtained directly by the replacement of halogen atoms,[2] or sulphonic acid groups,[3] or nitro- groups.[4] The alkyl ethers are obtained by heating with a solution of caustic potash in the alcohol or with an alcoholic solution of the alkali alcoholate, and in the case of nitro- compounds it is very desirable to exclude all moisture, as otherwise simultaneous reduction takes place. The aryl ethers are formed by heating with the alkali phenolate in alcohol or in some indifferent solvent of high boiling point, such as the phenol. The addition of a catalyst such as copper or copper acetate is often advantageous. In the case of halogen atoms and sulphonic acid groups the replacement takes place most readily when the atom or group is in the α- position, but in the case of nitro groups replacement when in the β- position is most easy.[5] The reaction with nitro compounds, however, although quite common, is by no means a general one.[6] ·

[1] By., D.R.P. 146,223.
[2] Frey, B. **45**, 1359. Ullmann, B. **49**, 2162 ; 2168. By., D.R.P. 158,531 ; 229,316 ; 263,423.
[3] R. E. Schmidt, B. **37**, 10. Laube, B. **39**, 2245. By., D.R.P. 156,762 ; 158,531 ; 166,748.
[4] By., 75,054 ; 77,818 ; 145,188 ; 158,531. M.L.B., D.R.P. 158,278 ; 167,699.
[5] M.L.B., D.R.P. 167,699.   [6] M.L.B., D.R.P. 158,278.

In some cases heating a nitroanthraquinone with potassium carbonate in nitrobenzene solution leads to a dianthraquinonyl ether.[1]

No great interest attaches to the ethers as a class. They are a great deal more easily hydrolysed than the phenolic ethers of the benzene or naphthalene series, and hence their formation is often a useful means of protecting hydroxyl groups during nitration. On sulphonation the alkyl ethers are dealkylated, but the aryl ethers are more stable and can be sulphonated in the aryl group.[2]

The methyl ethers of the α-hydroxyanthraquinones show considerable tendency to form oxonium salts such as hydrobromides, zincibromides, and perchlorates.[3] The hydrobromides, however, are unstable and readily undergo spontaneous demethylation.

[1] Agfa, D.R.P. 283,482.   [2] By., D.R.P. 164,129.
[3] O. Fischer and Ziegler, J. pr. [2] **86**, 297.

CHAPTER XIII

PYRIDINE AND QUINOLINE DERIVATIVES

COMPOUNDS containing both an anthracene or anthraquinone residue and a pyridine ring can be conveniently divided into two classes, viz. compounds in which the *ms*-carbon atom of the anthracene residue forms part of the pyridine ring, and compounds in which the pyridine ring is fused into one of the benzene rings of the anthracene nucleus, both *ms*-carbon atoms remaining intact. Compounds of the former class are very similar in structure to the benzanthrenes and benzanthrones and are known as pyridanthrenes and pyridanthrones—
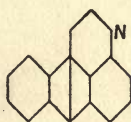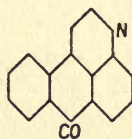
1(N).9-Pyridanthrene.   1(N).9-Pryidanthrone.

Compounds of the latter class are similar in structure to the benzanthracenes and benzanthraquinones and are known as anthraquinolines (pyridinoanthracenes) and anthraquinone quinolines (pyridinoanthraquinones) :
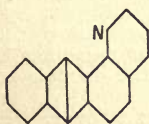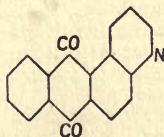
Anthraquinoline   Anthraquinonequinoline
1(N).2-Pryidinoanthracene.   1.2(N)-Pyridinoanthraquinone.

A third class of compound is also known in which two anthracene residues are united by one or two pyridine rings. In these each pyridine ring is present as a pyridanthrene with reference to one anthracene nucleus, and as an anthraquinoline with reference to the other anthracene nucleus. The most important compounds of this nature are the pyranthridones and flavanthrones * :
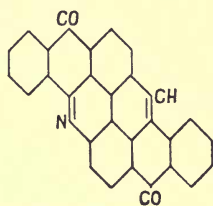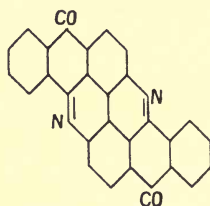
Pyranthridone.   Flavanthrone.

I. THE PYRIDANTHRONES

When an α-acetylaminoanthraquinone is heated alone at 200–280°, or when it is boiled with aqueous caustic alkali, loss of water takes place with the formation of a pyridanthrone : [1]
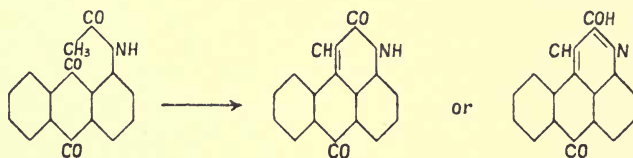
A similar reaction is also brought about when the α-acetyl amino compound is heated with a formate or acetate,[2] or with an acid chloride such as sulphuryl chloride or phos-

* In the literature the term usually employed is "flavanthrene." Owing to the ketonic nature of the body the name should terminate in -one, and consequently the word "flavanthrone" has been adopted in the sequel. The term "flavanthrene" is reserved to denote the oxygen free reduction product. Flavanthrone itself was originally known commercially as Flavanthrene, spelt with a capital, but as the name has been altered to Indanthrene Yellow G confusion will not arise on this score. See also footnote on p. 342.

[1] By., D.R.P. 185,548; 192,201; 199,713; 203,752. B.A.S.F., D.R.P. 212,204; 216,597. M.L.B., D.R.P. 280,190.
[2] B.A.S.F., D.R.P. 191,111; 192,970. By., D.R.P. 209,033.

phorus oxychloride.[1] In a great many cases it is not necessary to isolate the acetyl derivative as pyridone formation takes place simultaneously with acetylation when an α-aminoanthraquinone is boiled with acetic anhydride,[2] or is heated with acetic anhydride and concentrated sulphuric acid or oleum.[3]

Several variations of the above method of forming pyridanthrones have been described. Thus the α-aminoanthraquinone can be condensed with one molecule of diethyl malonate and the product then boiled with caustic alkali.[4] Under these conditions the pyridoneanthrone carboxylic acid is first formed, but this readily passes into the pyridanthrone itself by loss of carbon dioxide :
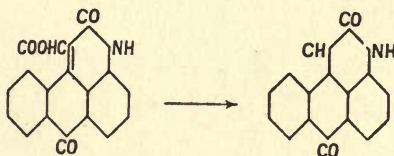
Another variation consists in condensing an aryl sulphone acetyl chloride of the type $ArSO_2.CH_2COCl$ with a primary or secondary α-aminoanthraquinone and then boiling the product with aqueous alcoholic alkali.[5] Under these conditions the arylsulphone group is split off, and at the same time the pyridine ring is closed, the product being a hydroxypyridone anthrone :
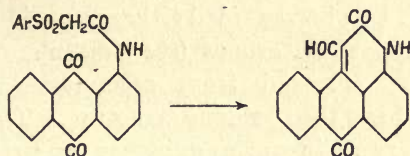
Pyridoneanthronepyridinium chlorides are obtained when α-chloracetylaminoanthraquinones are treated with pyridine, formation of the pyridinium chloride and of the pyridone ring taking place simultaneously[6] :

[1] B.A.S.F., D.R.P. 198,048.
[2] By., D.R.P. 209,033.
[3] B.A.S.F., D.R.P. 198,025 ; 200,015.
[4] M.L.B., D.R.P. 250,885.
[5] M.L.B., D.R.P. 284,209.
[6] By., D.R.P. 290,984.
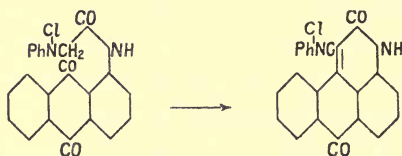
Other tertiary bases behave in the same way.

The C-alkyl and aryl pyridanthrones can be obtained by condensing a primary α-aminoanthraquinone with a ketone which has at least one methyl group directly attached to the carbonyl group,[1] such as acetone, acetoacetic ester, acetophenone, etc. When acetone itself is used the product is Py.α-methyl-1(N).9-pyridanthrone :
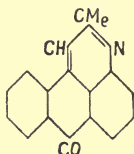
The above methods of preparing the pyridanthrones are of very general application and have been extended to α-aminoindanthrones, α-aminodianthraquinonylamines [2] and 1.4-diaminoanthraquinone, although in this last case it is not certain whether pyridanthrone formation takes place with both amino groups.[3]

It will be observed that the compounds prepared from primary aminoanthraquinones by all the above methods except the last can be regarded either as pyridoneanthrones or as hydroxypyridanthrones (see formulæ on p. 290), although those prepared from secondary aminoanthraquinones must have the pyridone structure. Those prepared from the primary aminoanthraquinones are probably tautomeric, and react in the enolic form when treated with phosphorus pentachloride, passing under these conditions in Py.α-chlor-1(N)-9-pyridanthrones.[4] The Py-chlorpyridanthrones are also readily obtained by chlorinating the pyridanthrones.[5] In them the chlorine atom is very

[1] By., D.R.P. 185,548.   [2] B.A.S.F., D.R.P., 198,025; 200,015.
[3] By., D.R.P. 185,548.   [4] M.L.B., D.R.P. 256,297.
[5] By., D.R.P. 264,c10.

reactive and is readily replaced by a hydroxyl group by boiling with 10 per cent. alcoholic alkali,[1] and by an arylamino group by boiling with a primary aromatic amine.[2]

The Bz-amino, alkylamino and arylaminopyridanthrones and the Bz-anthraquinonylaminopyridanthrones are easily obtained by the usual methods, *e.g.* by replacing negative groups attached to the benzene rings by heating with ammonia or with a primary secondary amine,[3] or by condensing a Bz.-halogen or Bz.-aminopyridanthrone with halogen compounds or amino compounds.[4] Some of the products thus obtained have been described as vat dyes and their sulphonic acids as acid wool dyes,[5] but they do not seem to have found any technical application.

II. THE ANTHRAQUINONE QUINOLINES

There are three possible anthraquinone quinolines (pyridinoanthraquinones) viz. :
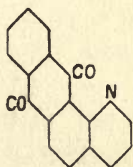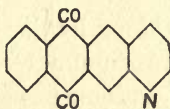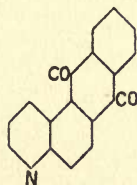
1(N).2-Pyridinoanthra-   2.3-Pyridinoanthra-   2(N).1-Pyridinoanthra-
quinone, m.p. 169°.   quinone, m.p. 322°.   quinone, m.p. 185°.

and all three have been prepared although they have been comparatively little studied, the chief interest centring round the technically valuable hydroxy compounds.

The preparation of quinolines from aminoanthraquinones by Skraup's method often gives very satisfactory results, but in other cases the quinoline is only obtained under special conditions. Mejert[6] claimed to have obtained a quinoline from aminoanthraquinone by Skraup's method, but his specification contains no details and his claims must

[1] By., D.R.P. 268,793.   [2] M.L.B., D.R.P. 256,297.
[3] By., D.R.P. 201,904.   B.A.S.F. 205,095.
[4] B.A.S.F., D.R.P. 217,395–6 ; 218,161.   By., D.R.P. 194,252.
[5] By., D.R.P. 194,253 ; 233,126.   [6] D.R.P. 26,197.

be accepted with considerable reserve. Bally [1] was unable to obtain a quinoline from α-aminoanthraquinone by carrying out Skraup's synthesis under the usual conditions, but a quinoline is readily obtained if sulphuric acid of 78 per cent. strength is used in place of concentrated sulphuric acid, and if nitrobenzene sulphonic acid is used as an oxidising agent.[2] By this means 1(N).2-pyridinoanthraquinone has been obtained from α-aminoanthraquinone and 1(N).2.5(N).6-dipyridinoanthraquinone has been obtained from 1.5-diaminoanthraquinone. In the case of β-aminoanthraquinone the tendency to form a benzanthrone compound [3] is so great that it is almost impossible to obtain the pyridinoanthraquinone. A small amount of a substance which melts at 322°, and which has the formula $C_{17}H_9O_2N$, is obtained, however, and this is probably 2.3-pyridinoanthraquinone [4] although it has never been properly investigated. The third isomer, 2(N).1-pyridinoanthraquinone is best obtained from the corresponding 2(N).1-pyridinoanthracene (anthraquinoline) by oxidation by chromic acid.[5] The pyridinoathracene can be obtained by distilling Alizarin Blue with zinc dust,[6] or from β-anthramine by Skraup's method.[7]

The pyridinoanthraquinones have been but little investigated, although a certain amount of work has been recorded in connection with the technically important hydroxy derivatives. All three isomers are smoothly nitrated, the nitro group entering the benzene ring to which the quinoline group is not attached.[8] Dinitro compounds do not appear to have been described.

The *hydroxyanthraquinone quinolines* can be obtained from the corresponding aminohydroxyanthraquinones by Skraup's method, and by this means quinolines have been prepared from 3-aminoalizarin,[9] 4-aminoalizarin,[10] amino-

[1] B. **38**, 194. [2] M.L.B., D.R.P. 189,234.
[3] See p. 332. [4] B.A.S.F., D.R.P. 171,939.
[5] Graebe, A. **201**, 349. [6] Graebe, A. **201**, 344.
[7] Graebe, B. **17**, 170. Knüppel, B. **29**, 708.
[8] B.A.S.F., D.R.P. 218,476.
[9] Prud'homme, Bl. **28**, 62. Graebe, B. **11**, 522, 1646; **12**, 1416; **15**, 1783; A. **201**, 333. Knüppel, B. **29**, 708. Auerbach, Chem. Ztg. **3**, 525, 682. *Cf.* Ort, M.L.B., D.R.P. 62,703. [10] M.L.B., D.R.P. 67,470.

flavopurpurin, aminoanthrapurpurin,[1] aminoquinalizarin,[2] and other similar compounds.[3] They are nearly all mordant dyes and several of them have found technical application, *e.g.*

Alizarin Blue.   Alizarin Green.   Alizarin Black P.
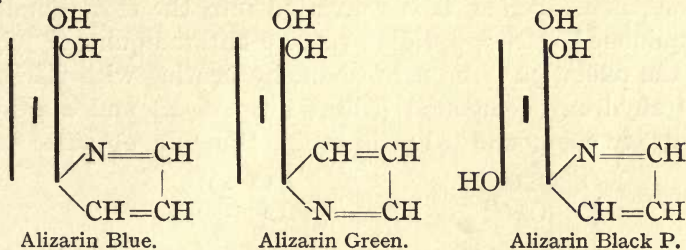
Of these Alizarin Blue is by far the most important and numerous brands are placed on the market, viz. Alizarin Blue AB1, X, R, RR, A, F, GW, WA, etc. It is manufactured from β-aminoalizarin by Skraup's method. The isomeric dye, Alizarin Green, is obtained from α-amino-alizarin, but is of much less importance, although it finds some little application in printing, being then used in connection with a nickel-magnesium mordant. Alizarin Black P is only very little used.

Another method of synthesising hydroxyanthraquinone quinolines has been described by Niementowski,[4] who states that 3.7-dihydroxy-1.2(N).4.5(N)-dipyridinoanthraquinone is obtained when 8-hydroxyquinoline-6-carboxylic acid is heated with concentrated sulphuric acid and phosphorus pentoxide. He describes it as an orange vat dye. Other dipyridinoanthraquinones have also been described.[5]
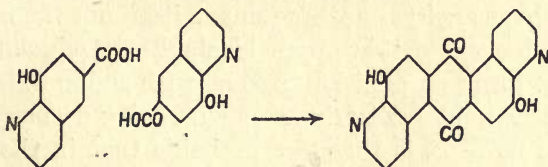
Hydroxyl groups can be introduced into the anthraquinoline molecule by sulphonating and then heating the

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[1] M.L.B., D.R.P. 54,624 ; 70,665.   [2] B.A.S.F., D.R.P. 58,480.
[3] Schaarschmidt and Stahlschmidt, B. **45**, 3452. By., D.R.P. 50,164 ; 50,708. M.L.B., D.R.P. 149,781.
[4] B. **49**, 23.   [5] M.L.B., D.R.P. 189,234.

sulphonic acid with milk of lime at 180°, but more important results are obtained by direct hydroxylation by oxidation. If Alizarin Blue is oxidised under carefully controlled conditions, *e.g.* by treatment with bromine, nitric acid, or manganese dioxide, it is converted into the corresponding diquinone [1] (3(N).4-pyridino-1.2.9.10-anthradiquinone) ; but if the oxidation is brought about by heating with oleum a tetrahydroxy compound (Alizarin Green X) and a penta-hydroxy compound (Alizarin Indigo Blue) are obtained [2] :
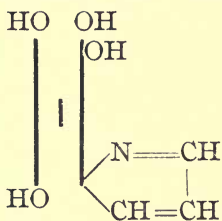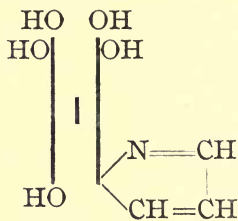
Alizarin Green X.   Alizarin Indigo Blue.

This last on oxidation with nitric acid very readily yields quinolinic acid.

When Alizarin Blue and similarly constituted dyestuffs are allowed to remain in contact with concentrated aqueous solutions of sodium bisulphite for several days they combine with two molecules of the bisulphite and pass into water-soluble products which are very largely used in printing [3] (Alizarin Blue S, Alizarin Green S, etc.). In text-books on tinctorial chemistry these soluble products are usually represented as being formed by union of the bisulphite with the cyclic carbonyl groups, but such a structure is very improbable as neither anthraquinone itself nor the hydroxy-anthraquinones combine with bisulphite. Quinoline itself, however, forms an addition product with sodium bisulphite, and this resembles Alizarin Blue S by being decomposed by water at 60°. It is therefore probable that in the soluble dyes the bisulphite is united to the quinoline ring and not to the cyclic carbonyl groups.[4]

[1] By., D.R.P. 171,836.
[2] Graebe and Philips, A. **276**, 21.   B.A.S.F., D.R.P. 46,654 ; 47,252.
[3] B.A.S.F., D.R.P. 17,695 ; 23,008.
[4] Brunck and Graebe, B. **15**, 1783.

III. Anthraquinone Phenanthridones

The anthraquinone phenanthridones are of no particular interest but are quite readily obtained from those benzoyl-aminoanthraquinones in which there is a halogen atom in the *o*-position to the nitrogen atom, either in the anthraquinone nucleus or in the benzene ring :
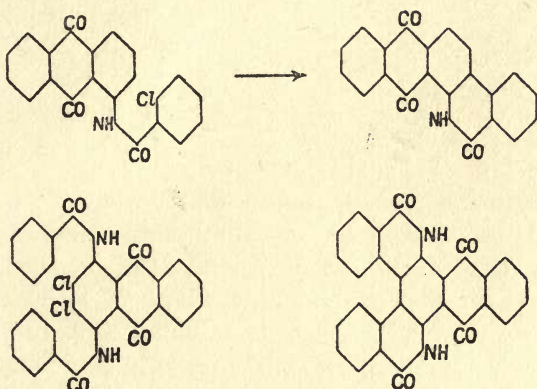
The reaction is brought about by boiling with sodium carbonate or sodium acetate, preferably in naphthalene solution. It is not necessary to isolate the benzoylamino anthraquinone as the phenanthridone is formed by the prolonged boiling of an aminoanthraquinone with *o*-chlor-benzoyl chloride in nitrobenzene solution in the presence of sodium carbonate.[1]

IV. The Pyranthridones

The pyranthridones are intermediate in structure between the pyranthrones (p. 335) and the flavanthrones (p. 300), and were studied by Scholl during his investigations on these substances. Scholl [2] found that when a mixture of 2-methyl-1-chloranthraquinone and 2-benzylideneamino-1-chloranthra-quinone is heated with copper powder, a mixture of three different dianthraquinonyl derivatives is formed, although

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[1] B.A.S.F., D.R.P. 236,857 ; 238,158.
[2] B. **51,** 441. D.R.P. 307,399. *Cf.* Ullmann, A. **399,** 332 ; D.R.P. 248,999.

he was unable to separate them. When the mixture was heated with sulphuric acid, however, the benzylidene group was split off and simultaneous loss of water took place, and from the product he was able to isolate flavanthrone and 2'-methyl-1.2.α.β-pyridanthrone anthraquinone. These two compounds had obviously been formed from two of the dianthraquinonyls thus :

Flavanthrone

2'-Methyl-1·2·α·β-pyridanthrone
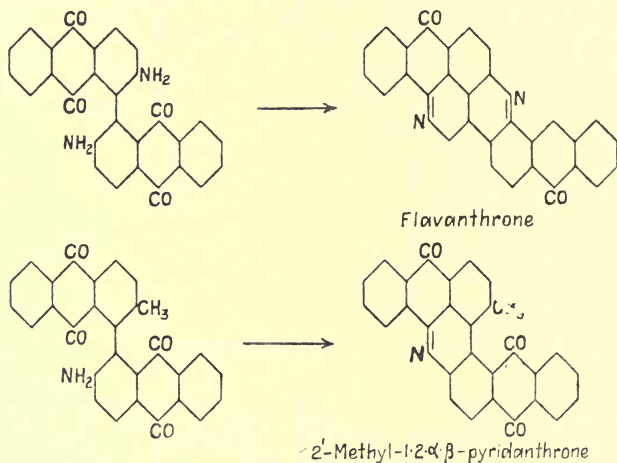
The third dianthraquinonyl derivative was unaffected by the sulphuric acid under the conditions of the experiment, and was, of course, 2.2'-dimethyl-1.1'-dianthraquinonyl.

The pyridanthrone anthraquinone was found to be a yellow vat dye although the tinctorial properties were very feeble. When reduced with sodium hydrosulphite in alkaline solution it gives first a comparatively stable red vat and then a very easily oxidised blue vat. As each of these gives a di-brombenzoyl derivative they probably have the structures :

Red product.

Blue product.
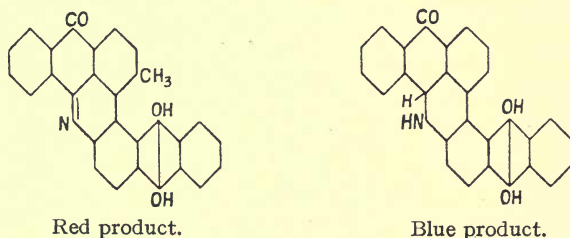
The chief interest attached to methylpyridanthrone-anthraquinone lies in its behaviour when heated alone or with concentrated sulphuric acid or with alcoholic caustic potash, as under these conditions another molecule of water is lost and pyranthridone is formed :
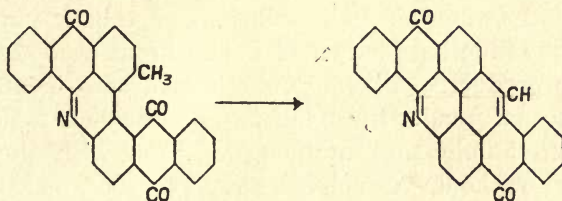
This is a powerful vat dye which dyes in orange-red shades which are somewhat yellower than those obtained from pyranthrone itself, but much redder than those obtained from flavanthrone. Its bromo derivatives are also orange-red dyes.

Pyranthridone when reduced by sodium hydrosulphite in alkaline solution gives a violet-coloured vat, and since this gives a di-brombenzoyl derivative it probably has the formula :
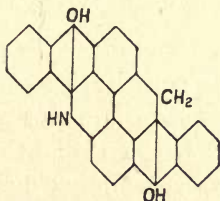
Reduction with hydriodic acid and phosphorus leads to dihydropyranthridene, which when heated with copper powder loses two atoms of hydrogen and passes into pyranthridene itself :
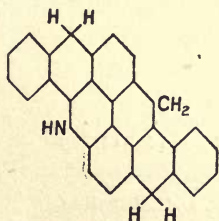
Dihydropyranthridene.
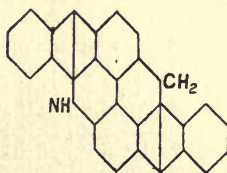
Pyranthridene.

V. THE FLAVANTHRONES *

When β-aminoanthraquinone is fused with caustic alkali a mixture of the reduction products of indanthrone and flavanthrone is obtained,[1] although when the fusion is carried out in the presence of a reducing agent, or more particularly when alcoholic solutions of caustic potash are used, the reduction product of flavanthrone becomes almost the sole product.[2] Flavanthrone, mixed with indanthrone, can also be made by oxidising β-aminoanthraquinone,[3] and when β-aminoanthraquinone is heated with aluminium chloride without a solvent at 250–280° considerable quantities of flavanthrone are obtained.[4] Curiously enough the use of an indifferent solvent such as nitrobenzene leads to quite a different result, as under these conditions little or no flavanthrone is formed, the chief product consisting of a reddish-brown vat dye of unknown constitution.[5] The best method, both for laboratory and for manufacturing purposes, of obtaining flavanthrone is to boil β-aminoanthraquinone with antimony pentachloride in nitrobenzene solution.[6]

None of the above methods of preparing flavanthrone throw any light on the constitution of the dyestuff, and the first direct proof of its structure was given by Scholl.[7] He started with 2.2'-dimethyl-1.1'-dianthraquinonyl and first oxidised this to the corresponding dicarboxylic acid. This he then converted into its amide and then endeavoured to obtain diaminodianthraquinonyl from this by Hofmann's method. In this he was not successful as the diamino-dianthraquinonyl proved to be unstable under the experimental conditions and at once lost two molecules of water and passed into flavanthrone :

* See footnote on p. 290.
[1] See p. 343.
[2] B.A.S.F., D.R.P. 133,686 ; 135,408.
[3] B.A.S.F., D.R.P. 139,633 ; 141,355 ; 211,383.
[4] B.A.S.F., D.R.P. 136,015.
[5] B.A.S.F., D.R.P. 138,119 ; 206,464.
[6] Scholl, B. **40**, 1691.　B.A.S.F., D.R.P. 138,119.
[7] B. **41**, 1691.
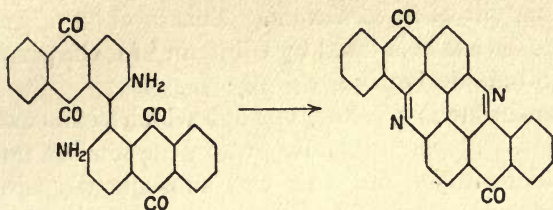
At a later date Scholl [1] showed that 1.1'-dianthraquinonyl when nitrated gave a mixture of nitro compounds from which small quantities of flavanthrone could be obtained by reduction with sodium sulphide, the production of flavanthrone being no doubt due to the instability of 2.2'-diamino-1.1'-dianthraquinonyl. Benesh [2] also found that diaminodianthraquinonyl was unstable, as he obtained only flavanthrone by heating 2.2'-dimethoxy-1.1'-dianthraquinonyl with ammonia.

To establish the structure of flavanthrone beyond all possible doubt it was desirable if possible to isolate the diaminodianthraquinonyl and prove that it did readily pass into flavanthrone. If 2-amino-1-bromanthraquinone is heated with copper powder this last acts as a catalyst and splits out two molecules of hydrobromic acid, the product being indanthrone (see p. 345). If this catalytic effect could be prevented it should be possible to split out the two atoms of bromine and thus obtain diaminodianthraquinonyl. Scholl [3] first tried to achieve this result by using the acetyl derivative of the aminobromanthraquinone, but was not successful. By using the benzylidene derivative,[4] however, he succeeded in preparing the dibenzylideneaminodianthraquinonyl and was then able to hydrolyse this in alcoholic solution at the ordinary temperature. The resulting 2.2'-diamino-1.1'-dianthraquinonyl was found to pass into flavanthrone when heated alone to 250° or when warmed to 50° with concentrated sulphuric acid. Boiling with solvents such as nitrobenzene, pyridine, or glacial acetic acid also effected flavanthrone formation, and reduction with sodium hydrosulphite in alkaline solution led at once

[1] B. **43**, 1740.
[3] B. **40**, 1699.
[2] M. **32**, 447.
[4] B. **51**, 452.

to the blue vat of flavanthrone.   This method of preparing flavanthrones has been used by Ullmann [1] for the preparation of the dibromo derivative.

Flavanthrone is a yellow vat dye which yields extremely fast shades.   It was originally put on the market under the name Flavanthrene, but this was subsequently altered to Indanthrene Yellow G.[2] The dibrom derivative gives orange shades.   Flavanthrone itself is very stable towards nitric acid, but by prolonged heating a mixture of substances is obtained from which Scholl [3] has isolated a dihydroxy-dinitrosodinitro compound.   This on reduction gives the corresponding tetraminodihydroxy compound, and if boiled with a primary aromatic amine such as aniline or *p*-toluidine the nitro groups can be replaced by arylamino groups.

The reduction products of flavanthrone have been very fully investigated by Scholl and his co-workers.   Scholl [4] finds that reduction in alkaline solution with sodium hydrosulphite gives a blue vat which is readily oxidised by the air.   From this solution acetic acid precipitates a greenish-blue hydrate which loses water slowly at 110° and rapidly at 150°.   It gives a disodium salt but only a monobenzoyl derivative, and this monobenzoyl derivative is insoluble in alkali.   Scholl therefore concludes that in the blue vat there is only one true hydroxyl group present, and represents the hydrate by formula I and its disodium salt by formula II :
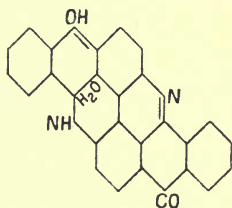
I. Flavanthranol hydrate.[5]   II.
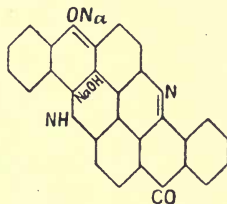
Reduction of flavanthrone with zinc dust and caustic soda leads to a brown vat which is extremely easily oxidised

[1] A. **399**, 332.   D.R.P. 248,999.   *Cf.* By., D.R.P. 172,733.
[2] Caledon Yellow G (Scottish Dyes, Ltd.).   [3] B. **43**, 340.
[4] B. **41**, 2304, 2534.   *Cf.* Potschiwauscheg, B. **43**, 1748.   By., D.R.P. 139,634.   [5] Dihydroflavanthrene hydrate (Scholl).

by the air. This vat seems to consist of at least four hydrated substances which lose their water at 160°. In alkaline solution they are all red, but are blue when precipitated by acids, so that salt formation is probably accompanied by enolisation. Scholl represents them by formulæ III, IV, V, and VI :
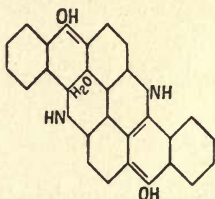
III. *Flavanthraquinol Hydrate.*[1]   IV.α-*Dihydroanthraquinol Hydrate.*[2]
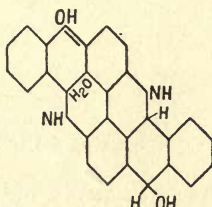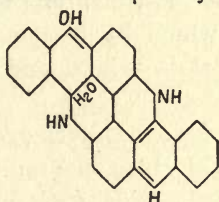
V. *Flavanthrenol Hydrate.*[3]   VI. *Flavanthrene Hydrate.*[4]
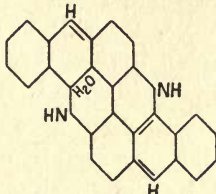
When flavanthrone is reduced with hydriodic acid and phosphorus, non-hydrated products are obtained. When the reduction is carried out at 170° a product is formed which is not particularly sensitive to oxidation by the air, and which is green when in the solid state, but red when in solution, particularly in the presence of alkali. The red and green forms are probably due to keto-enol tautomerism (formulæ VII and VIII).
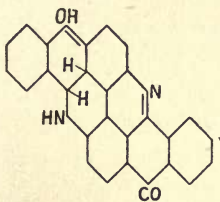
VII   Dihydroflavanthranol.[5]   VIII
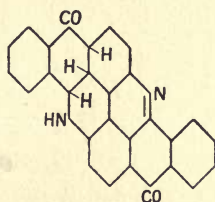
[1] α-Tetrahydroflavanthrene hydrate (Scholl).   [2] α-Hexahydroflavanthrene hydrate (Scholl).   [3] Flavanthrinol hydrate (Scholl).   [4] Flavanthrine hydrate (Scholl).   [5] β-Tetrahydroflavanthrene (Scholl).

This on alkaline reduction gives a product which is very sensitive to oxidation by the air, and which is probably represented by formula IX :
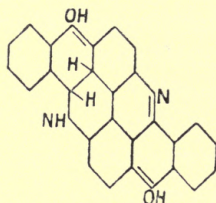
IX. β-Dihydroflavanthraquinol.[1]

When the reduction of flavanthrone with hydriodic acid and phosphorus is carried out at 200° flavanthrene hydrate (formula VI, p. 303) is obtained, which by loss of water yields flavanthrene [2] itself. This last is a base and is not sensitive to oxidation by the air.

Attention may here be directed to a bluish-grey vat dye which is obtained by converting chlorbenzanthraquinone, obtained by condensing phthalic anhydride with α-chlornaphthalene, into the corresponding amino compound by heating with ammonia, and then boiling this with antimony pentachloride in nitrobenzene solution.[3] Nothing is known of its structure, but it is improbable that it is a flavanthrone.

[1] β-Hexahydroflavanthrene (Scholl).   [2] Flavanthrine (Scholl).
[3] G.C.I.B., D.R.P. 230,455.

CHAPTER XIV

THE ACRIDONES, XANTHONES, AND THIOXANTHONES

I. The Acridones *

THE anthraquinone acridones are almost invariably obtained by loss of water from arylaminoanthraquinones or dianthraquinonylamines in which there is a carboxyl group in the *ortho-* position to the imino group, although this carboxyl group may be either in the anthraquinonyl group or in the aryl group. Such carboxylic acids can be obtained (*a*) by condensing an *o*-aminoanthraquinone carboxylic acid with an aromatic halogen compound or halogen anthraquinone; (*b*) by condensing an *o*-halogen anthraquinone carboxylic acid with a primary aromatic amine or aminoanthraquinone; (*c*) by condensing an aminoanthraquinone with an aromatic *o*-halogen carboxylic acid; (*d*) by condensing a halogen anthraquinone with an aromatic *o*-amino carboxylic acid. Of these the last two methods lead only to acridones in which the heterocyclic ring lies between one anthraquinone residue and one aromatic ring. Such compounds, however, are readily obtained owing to the easy accessibility of *o*-chlorbenzoic acid and anthranilic acid. When the condensation is being carried out with *o*-chlorbenzoic acid Ullmann [1] finds that improved yields are obtained by using the methyl ester in place of the free acid. In cases in which the carboxyl group is attached to the anthraquinone nucleus (methods (*a*) and (*b*)) the use of sodium acetate as a

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* These can be named either as anthraquinone acridones or as phthaloyl acridones, and both methods of nomenclature are in use.

[1] B. **51**, 9. *Cf.* M.L.B., D.R.P. 254, 475.

condensing agent often leads to very poor yields owing to the tendency of this substance to cause loss of carbon dioxide. This, however, can be avoided by replacing the sodium acetate by the carbonate, acetate, or hydroxide of calcium or magnesium.[1]

The final closing of the acridone ring can usually be brought about by heating with sulphuric acid,[2] but in many cases it is sufficient to boil the carboxylic acid with some indifferent solvent of high boiling point, such as nitrobenzene,[3] with or without the addition of acetic anhydride or acetyl chloride.[4] The fact that the acridone ring can sometimes be closed merely by boiling with a solvent has enabled Eckert and Halla [5] to obtain an acridone by boiling 1-aminoanthraquinone-2-carboxylic acid with β-chloranthraquinone in nitrobenzene solution in the presence of cuprous chloride and sodium acetate.

In spite of the ease with which the acridone ring is often closed by the above methods, Ullmann [6] in many cases prefers to convert the carboxylic acid into its chloride by treatment with phosphorus pentachloride and then to obtain the acridone by boiling this with nitrobenzene. It has also been stated that the ring is closed when an ester of the acid is reduced by sodium hydrosulphite or by zinc dust and ammonia.[7]

The above methods of preparing the acridones have given rise to several minor variations. Thus *o*-methyl dianthraquinonylamines when oxidised in alkaline solution pass into the corresponding carboxylic acid, from which simultaneous loss of water takes place with the immediate production of the acridone.[8] In a very similar way *o*-methylarylamino anthraquinones, in which the methyl group may be either in the anthraquinone residue or in the aryl group,

[1] B.A.S.F., D.R.P. 268,219.

[2] Ullmann and Billig, A. **381**, 1 ; B. **43**, 538. Ullmann, B. **49**, 2160. Ullmann and Dootson, B. **51**, 9. Ullmann and Conzetti, B. **53**, 836. Ullmann, D.R.P. 221,853. B.A.S.F., D.R.P. 240,002 ; 269,850 ; 287,614. M.L.B., D.R.P. 240,327 ; 243,586 ; 245,875 ; 254,475 ; 256,626. Brass, B. **46**, 2907 ; D.R.P. 268,646.

[3] B.A.S.F., D.R.P. 248,170.   [4] Ullmann, B. **47**, 748.   [5] M. **35**, 755.

[6] A. **381**, 1. B. **43**, 538 ; **47**, 553, 562. D.R.P. 221,853.

[7] B.A.S.F., D.R.P. 246,966.   [8] B.A.S.F., D.R.P. 192,436.

pass into the acridone when treated with halogens or with sulphuryl chloride.[1] Schaarschmidt,[2] on the other hand, prepares acridones from the *o*-nitriles of the arylamino-anthraquinones or dianthraquinonylamines, the nitrile group being attached either to the anthraquinone nucleus or to the aryl group. Acridone formation takes place on heating with sulphuric acid, and according to Schaarschmidt is not preceded by hydrolysis of the nitrile, as he claims that acridones are formed in excellent yield under conditions under which little or no hydrolysis takes place. Ullmann, on the contrary, is convinced that acridone formation only takes place subsequent to the hydrolysis of the nitrile to the carboxylic acid, and a lively and somewhat heated polemical discussion has taken place between the two investigators.[3]

A further variation consists in condensing an amino-anthraquinone with 1.2-naphthoquinone-3-carboxylic acid by warming on the water-bath in aqueous solution, and then closing the ring by heating with sulphuric acid [4] :
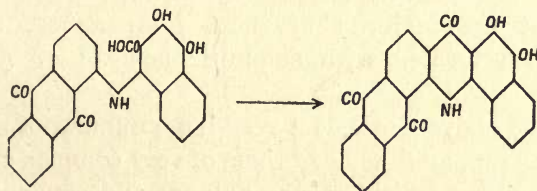
The yields obtained at both stages are said to be almost quantitative and the method would appear to deserve more attention than it has received. A somewhat more complicated variation consists in first preparing an anthraquinonyl isatin, either by condensing a halogen anthraquinone with isatin, or by the action of oxalyl chloride on an arylamino-anthraquinone. The isatin is then converted into the acridone by treatment with aluminium chloride, sulphuric acid or alkali [5] :

[1] B.A.S.F., D.R.P. 272,296 ; 275,671 ; 283,724.
[2] A. **405**, 95. D.R.P. 269,800.
[3] B. **49**, 735 ; **50**, 164, 403, 1356, 1360, 1526.
[4] Cas., D.R.P. 280,712.   [5] By., D.R.P. 286,096.
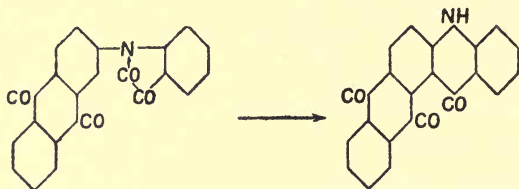
In all the above methods the acridone ring is closed through the carbonyl group. In some cases, however, the ring can be closed through the imino group, although as a rule this method is only of minor importance. Thus aryl anthraquinonyl ketones in which there are amino groups present in the *ortho-* position to the ketonic carbonyl group both in the aryl group and in the anthraquinonyl residue pass readily into acridones by loss of ammonia, and compounds like 2-*o*-chlorbenzoyl-1-chloranthraquinone pass directly into the acridone when treated with toluene-*p*-sulphonamide.[1]

The *purification* of the anthraquinone acridones can often be conveniently effected by taking advantage of the fact that the majority of them form almost insoluble salts when treated with sulphuric acid of 78 per cent. strength.[2]

By the above methods a very large number of acridones have been prepared, some of them of very complex structure. Starting with 1.5-dichloranthraquinone and condensing this with anthranilic acid, Ullmann and Billig [3] were able to obtain a compound containing two acridone groups (formula I.), but from 1.4-dichloranthraquinone could only obtain a compound containing one anthraquinone ring, and only a monoacridone was obtained from 1.4-diaminoanthraquinone and *o*-chlorbenzoic acid.[4] From this it would appear that two carbonyl groups in the *ortho-* position hinder one another (*cf.* p. 337); but Schaarschmidt [5] claims to have obtained a compound corresponding to formula II by his nitrile method :

[1] B.A.S.F., D.R.P. 272,297. [2] B.A.S.F., D.R.P. 253,090.
[6] A. **381**, 1. [4] M.L.B., D.R.P. 243,586.
[5] A. **405**, 95.

I.   II.
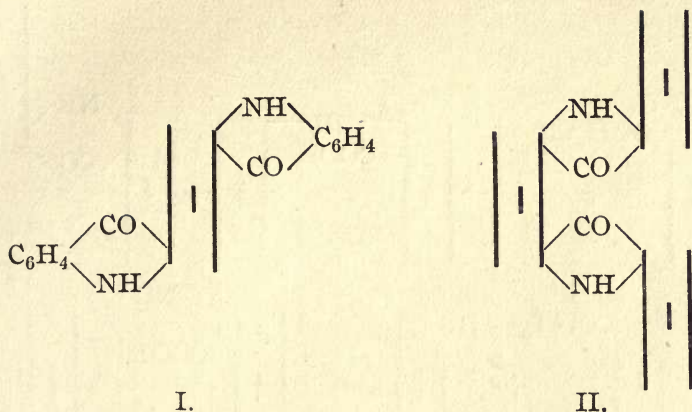
An acridone containing two anthraquinonyl residues (1.2.5.6-diphthaloyl acridone) is obtained by oxidising 2 - methyl - 1 . 2' - dianthraquinonylamine,[1] and Schaarschmidt [2] has obtained the same substance by his nitrile method :
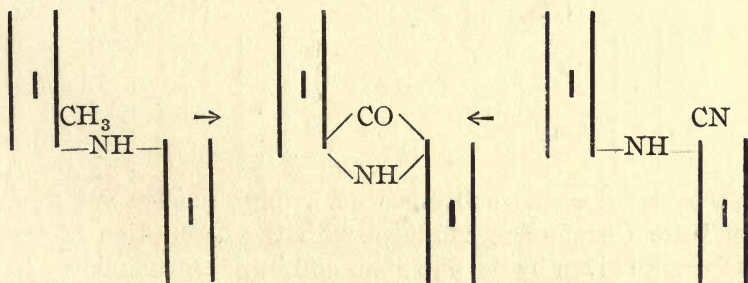
Both in the patent and in Schaarschmidt's paper this is described as an orange-red vat dye. On the other hand, Eckert and Halla [3] prepared the substance by two methods, viz. (1) by condensing 1-aminoanthraquinone-2-carboxylic acid with β-chloranthraquinone and then causing loss of water, and (2) by condensing 2-brom-3-benzylidene amino-anthraquinone with 1-aminoanthraquinone-2-carboxylic acid and then removing the amino group by diazotising and reducing :

[1] B.A.S.F., D.R.P. 192,436.   [2] A. 405, 95.
[3] M. 35, 755.
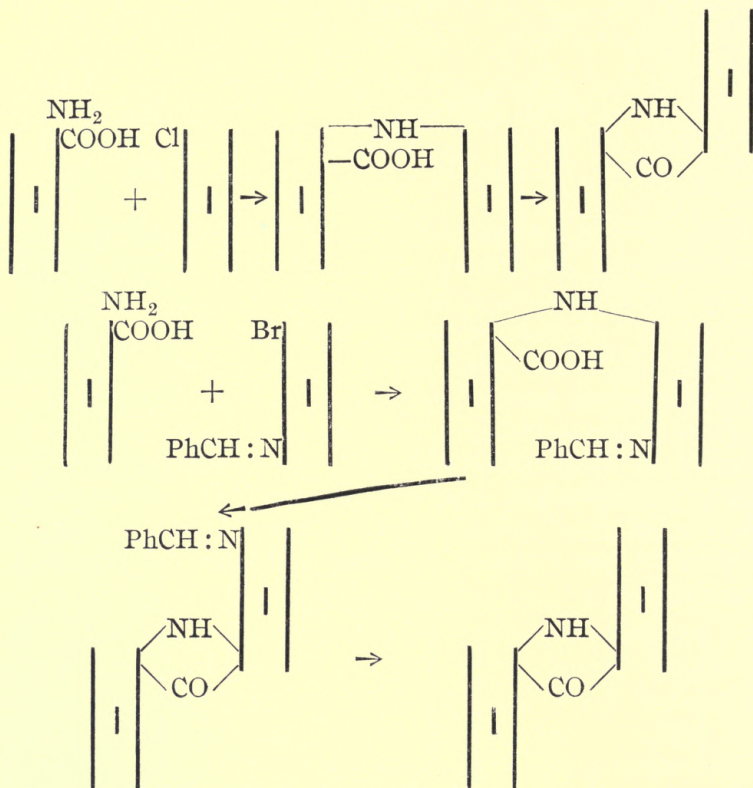
They describe the substance as a bluish-violet vat dye, and are therefore at variance with the description of the substance given by the patentees and by Schaarschmidt. In Eckert and Halla's first synthesis the ring might close in two ways, giving either

or
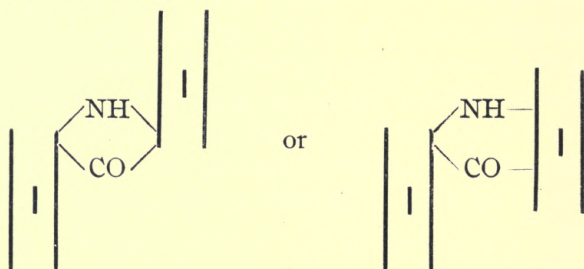
The second synthesis, however, leaves no doubt that the

former structure is the correct one. In the patented method two alternatives are also possible :
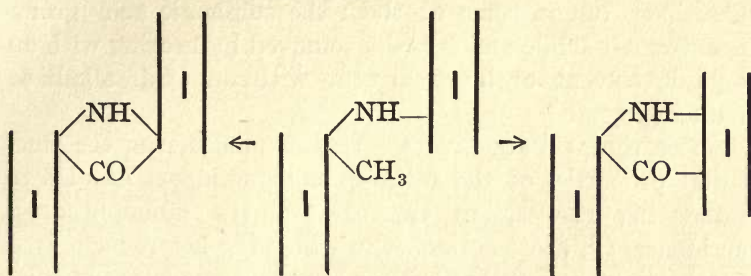
but as the product is different from that obtained by Eckert and Halla the latter must be the correct one. This conclusion is supported by the preparation of an acridone by Ullmann [1] by condensing 1-chloranthraquinone-2-carboxylic acid with β-aminoanthraquinone. Here again two alternatives are possible :
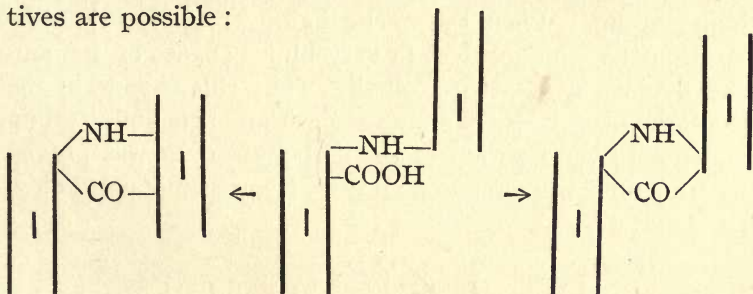
but as the product formed is an orange vat dye it must be concluded that the former structure is correct. It is difficult to see how Schaarschmidt's product could have any structure other than that which he assigns to it ; but the weight of evidence is against this, and consequently Schaarschmidt's claims cannot be accepted.

Substituted acridones of the anthraquinone series are usually built from the substituted anthraquinones. Halogen atoms when present in the anthraquinone nucleus are readily replaced by arylamino or anthraquinonyl amino groups by heating with primary aromatic amines or aminoanthraquinones in the usual way,[2] and the same compounds

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[1] B. **47**, 553.   [2] Ullmann and Billig, A. **381**, 1.   B. **43**, 538.

can also be obtained by condensing an aminoacridone with a halogen compound.[1]   Very few sulphonic acids have been described, but in some of them the sulphonic acid group is extremely labile and is easily removed by heating with an organic solvent or by treatment with an acid, alkali, or reducing agent.[2]

TINCTORIAL PROPERTIES.—The examination of the tinctorial properties of the anthraquinone acridones has led to interesting results.   In the case of the monophthaloyl acridones, *i.e.* those acridones in which the heterocyclic ring lies between one anthraquinone ring and one benzene ring, when the imino group is in the β- position to one of the cyclic carbonyl groups of the anthraquinone nucleus the product is a yellow or orange vat dye, but the shades obtained are very loose to alkali, and there are no data available to say whether the fastness is improved by alkylating the cyclic imino group.   When the cyclic imino group is in the α-position the product dyes in very bluish shades of red and the dyeings are fast to alkali.   That this change in the tinctorial properties is due to the position of the imino group and not to the position of the carbonyl group was proved by Ullmann,[3] who prepared all three isomeric monophthaloyl acridones :

Bluish-red.   Orange.   Brownish-yellow.
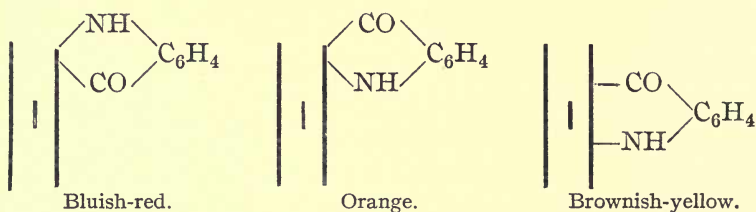
Only the first of these (Indanthrene Red BN Extra [4]) is fast to alkali, both the others being extremely loose.   The formation of a second acridone ring with the imino group in the α- position shifts the colour still more towards the violet end of the spectrum [5] :

[1] M.L.B., D.R.P. 239,543.   [2] B.A.S.F., D.R.P. 287,614–5.
[3] A. **381**, 1 ; B. **43**, 538 ; **47**, 553, 748.   *Cf.* Schaarschmidt, A. **405**, 95.
By., D.R.P. 286,095.
[4] Caledon Red (Scottish Dyes, Ltd.).   [5] B.A.S.F., D.R.P. 234,977.
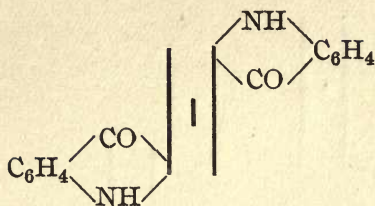
Indanthrene Violet RN Extra.[1]

The entrance of halogen atoms into the molecule greatly increases the affinity for the fibre, and at the same time brightens the shade and shifts it towards the red end of the spectrum.[2] Amino and methoxy groups when in the *para*-position to the cyclic imino group shift the colour towards the violet end of the spectrum, but when in the *para*- position to the acridone carbonyl group they have the opposite effect, the anthraquinone acridones thus behaving like the indigoid and thioindigoid dyes.[3] The presence of an aryl-amino or anthraquinonyl amino group in the *para*- position to the cyclic imino group often gives rise to a green or greenish-grey vat dye,[4] and the same result is frequently obtained by the introduction of an aryl mercapto group.[5]

In the case of acridones in which the heterocyclic ring lies between two anthraquinone ring systems (diphthaloyl acridones), the colour seems to depend very largely on constitution, as will be seen from the following formulæ :

Bluish-violet.[6]   Violet.[7]   Orange.[8]
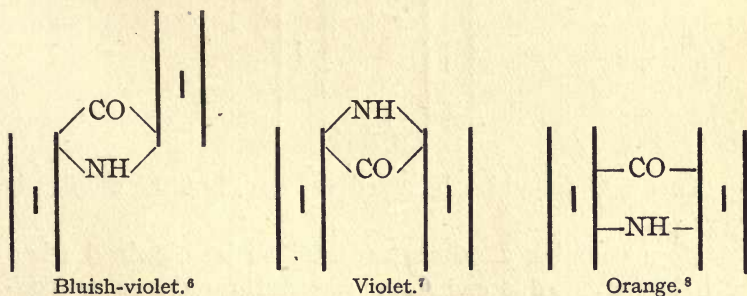
[1] Caledon Violet RN Extra (Scottish Dyes, Ltd.).
[2] Schaarschmidt, A. **405**, 95. B.A.S.F., D.R.P. 242,063.
[3] Ullmann, B. **51**, 9. *Cf.* Ullmann, B. **49**, 2168. M.L.B., D.R.P. 239,543 ; 243,586 ; 256,626.
[4] B.A.S.F., D.R.P. 263,078. [5] B.A.S.F., D.R.P. 248,996. [6] See p. 309.
[7] Eckert and Halla, M. **35**, 755. [8] Ullmann, B. **47**, 553, 562.

Reddish-brown.[1]   Reddish-brown.[1]   Blue.[1]
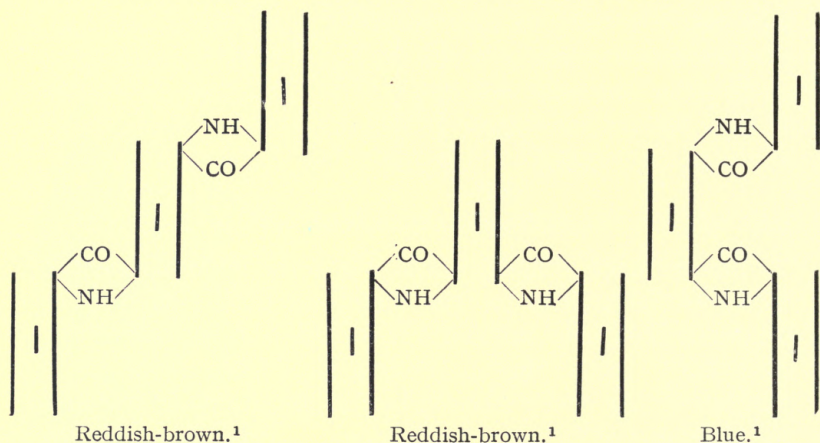
Very little is known of the *anthraquinone acridines*, but Ullmann [2] by heating 2.2'-dihydroxy-1.1'-dianthryl-methane with ammonia obtained a dianthrylacridine which on oxidation passed into the anthraquinone acridine :
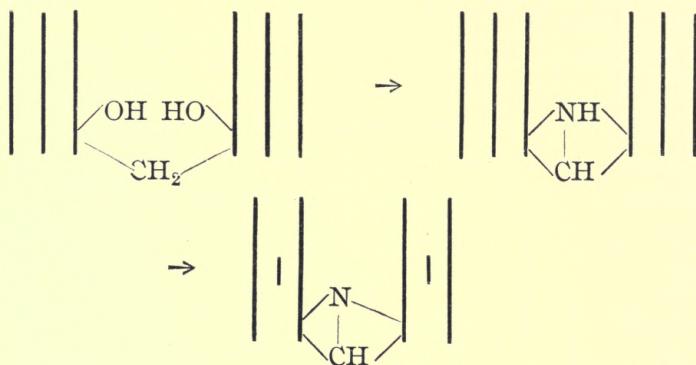
This was found to be a red vat dye, but the affinity is very poor.

More complex acridines are said to be obtained when a halogenated fluorenone or phenanthraquinone is condensed with an aminoanthraquinone and the product then dehydrated.[3]

Closely related to the acridones and acridines are the

[1] Schaarschmidt, A. **405**, 109.   [2] B. **45**, 2259.
[3] B.A.S.F., D.R.P. 269,194.

bluish-green vat dyes which are obtained by condensing two molecules of an aminoanthraquinone with one molecule of *o*-chlorbenzaldehyde.[1]

II. THE XANTHONES

The anthraquinone xanthones (phthaloylxanthones) are rather troublesome to prepare, as attempts to condense a halogen anthraquinone with salicylic acid generally leads to loss of the carboxyl group. Salicylic aldehyde, however, will condense with α-chloranthraquinone and the resulting aldehyde can then be oxidised to the carboxylic acid, the xanthone ring being subsequently closed by treatment with phosphorus pentachloride [2] :
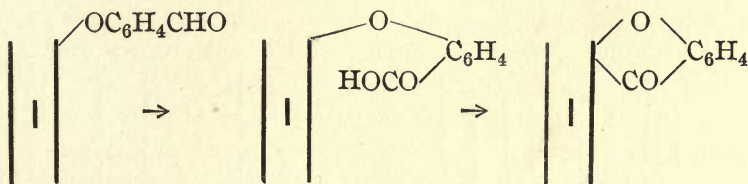
The method, however, is not a very satisfactory one, as the aldehyde is extremely stable and very difficult to oxidise. In the above case, for example, the aldehyde could only be oxidised by boiling it for five hours with chromic acid in a mixture of glacial acetic acid and sulphuric acid.

A more satisfactory method of preparing the xanthones is to condense an anthrol with formaldehyde and then to close the ring by treatment with phosphorus pentachloride. The xanthone is then obtained by subsequent oxidation : [2]

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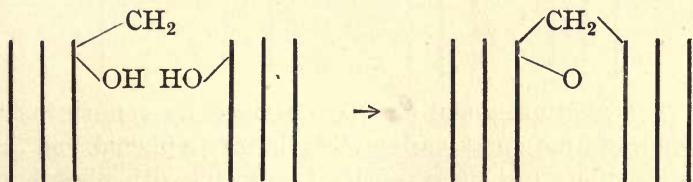
[1] Kalischer and F. Mayer, B. **49**, 1994. F. Mayer and Stein, B. **50**, 1306. F. Mayer and Lever, B. **52**, 1641. Cas., D.R.P. 280,711.
[2] Ullmann and Ürményi, B. **45**, 2259.

→
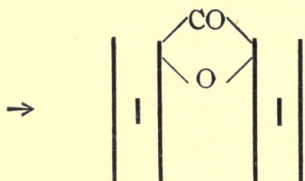
The condensation of the anthrol with formaldehyde takes place quite readily at 70° in aqueous solution, or in a mixture of acetic acid and alcohol to which a little hydrochloric acid has been added. Acetaldehyde can be substituted for formaldehyde, the condensation then being best effected in glacial acetic acid solution at 50° in the presence of a little hydrochloric acid. The methyl group is lost when the methyl xanthene is oxidised :

→
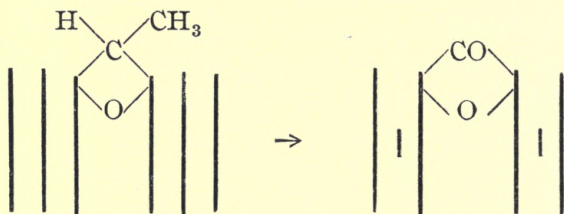
Benzaldehyde also condenses with β-anthrol, but in this case subsequent oxidation of the phenyl xanthene leads only to the anthraquinone phenyl xanthene (diphthaloyl phenyl xanthene) :

→
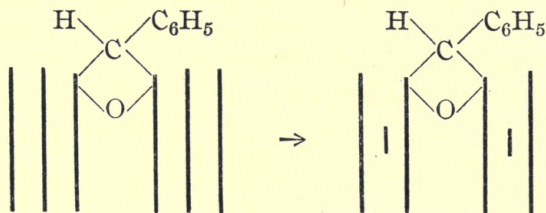
The xanthones can also be obtained by condensing an o-chloranthraquinone carboxylic acid with a phenol, and then closing the xanthone ring by treatment with phosphorus pentachloride [1] :

[1] Ullmann, B. 47, 566. B.A.S.F., D.R.P. 251,696.

The xanthones are of no particular interest. They are usually yellow substances but are devoid of tinctorial properties.

III. THE THIOXANTHONES

The anthraquinone thioxanthones (phthaloyl thioxanthones) are always obtained from the corresponding sulphide in which a carboxyl group is present in the *ortho-* position to the sulphur atom. This carboxyl group may be in the anthraquinone ring, in which case the sulphide is prepared either by condensing an *o*-mercapto anthraquinone carboxylic acid with a halogen compound, or by condensing an *o*-halogen anthraquinone carboxylic acid with a mercaptan,[1] or the carboxyl group may be present in the aryl group. In this case the sulphide can be prepared by condensing an anthraquinone mercaptan with an *o*-halogen carboxylic acid ; but as a rule it is more convenient to condense the halogen anthraquinone with thiosalicylic acid.[2]

The closing of the thioxanthone ring can usually be effected by heating with concentrated sulphuric acid, but as a rule much better results are obtained by the use of phosphorus pentachloride or toluene sulphochloride.[3] Schaarschmidt [4] has also prepared a number of thioxanthones from the corresponding nitrile by the action of sulphuric acid, and claims that the formation of the thioxanthone is not preceded by the formation of the carboxylic acid.[5]

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[1] B.A.S.F., D.R.P. 243,750. Sanders, D.R.P. 253,983.
[2] Ullmann, B. 43, 539 ; 44, 3125. Frey, B. 45, 1361. By., D.R.P, 216,480. B.A.S.F., 234,977. M.L.B., D.R.P. 243,587.
[3] Ullmann, B. 43, 539 ; 44, 3125. D.R.P. 238,983. B.A.S.F., D.R.P 243,750.
[4] A. 409, 59. D.R.P. 269,800.
[5] *Cf.* p. 307.

Halogenated thioxanthones are usually best prepared by direct halogenation either before or after closing the thioxanthone ring.[1] They can be converted into *arylamino-* and *anthraquinonylamino-anthraquinone thioxanthones* by treatment with a primary aromatic amine or aminoanthraquinone.[2] *Primary amino* compounds can be obtained by the nitration and subsequent reduction of the thioxanthones themselves.[3]

Tinctorial Properties.—The thioxanthones of the anthraquinone series are all vat dyes, but it is only those in which the cyclic sulphur atom is attached to the anthraquinone ring system in the α- position which are of any value.

The relationship between the shades obtained and the constitution of the dye is of interest. It is well known that in the indigoid dyes the replacement of the cyclic imino group by a sulphur atom is accompanied by a shifting of the colour towards the red end of the spectrum, and a precisely similar effect is noticeable when the anthraquinone acridones are compared with the corresponding thioxanthones. The thioxanthones are decidedly less highly coloured than the corresponding acridones and, as a rule, dye in yellow, orange, or red shades. Those compounds in which the sulphur atom is in the α- position are more highly coloured than the isomeric substances in which the sulphur atom is in the β- position :

Yellow.   Orange.   Red.
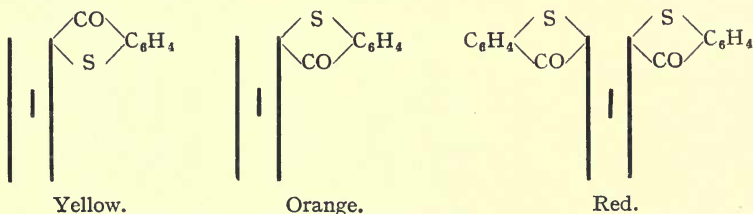
[1] Ullmann, D.R.P. 242,386. B.A.S.F., 258,561.
[2] Ullmann, D.R.P. 242,386. *Cf.* M.L.B., D.R.P. 231,854 ; 248,996.
[3] Schaarschmidt, D.R.P. 250,271–2. *Cf.* M.L.B., D.R.P. 243,587 ; 248,469.

Red.   Yellowish-orange.   Reddish-orange.
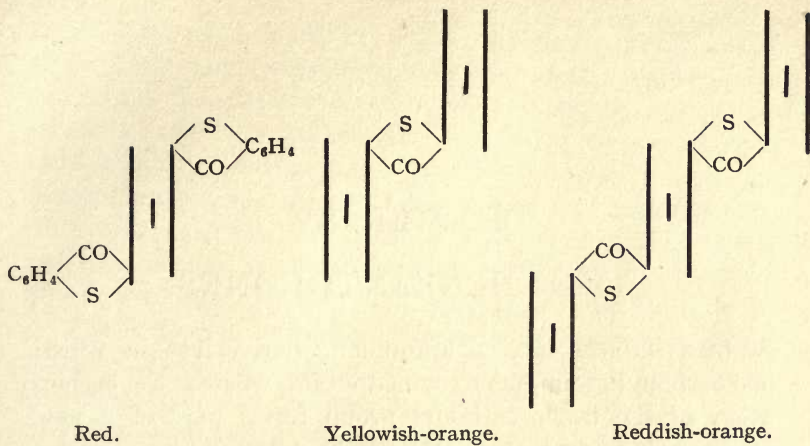
The entrance of halogen atoms into the molecule renders the shades lighter :

Indanthrene Yellow GN.   Indanthrene Orange GN.
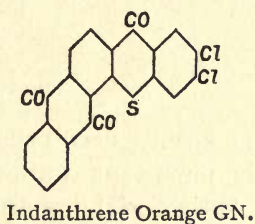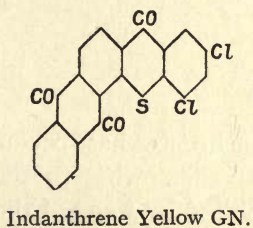
CHAPTER XV

THE BENZANTHRONES

Benzanthrones are anthraquinone derivatives in which one carbonyl group has remained intact, whereas the carbon atom of the other carbonyl group forms part of a new benzene ring in which is also involved one of the α-carbon atoms :
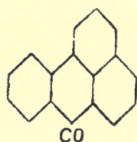
9.10-Benzanthrone.

The chemistry of the benzanthrones has become extremely important during recent years, owing to the very valuable tinctorial properties exhibited by some of the more complex members.

I. Simple Benzanthrones

The discovery of the benzanthrones originated in the observation [1] that only very little anthraquinonequinoline (pyridinoanthraquinone) is obtained when β-aminoanthraquinone is treated with glycerine, sulphuric acid and an oxidising agent (Skraup's quinoline synthesis), the main product of the reaction being a compound which melts at 251°, and which has the formula $C_{20}H_{11}ON$. The same compound is obtained by treating anthraquinone quinoline with sulphuric acid and glycerine,[2] and Bally and Scholl [3]

[1] B.A.S.F., D.R.P. 171,939.   [2] Bally, B. **38**, 194.
[3] B. **44**, 1656.

found that anthraquinone itself condenses readily with glycerine in the presence of sulphuric acid to produce a compound (benzanthrone) with the formula $C_{17}H_{10}O$. In all these cases it is obvious that one of the cyclic carbonyl groups has become involved in the condensation, and as benzanthrone itself on oxidation yields anthraquinone a-carboxylic acid, it follows that one of the a-carbon atoms has also become involved in the reaction. The formula given above is the only one which explains these facts.

The formation of benzanthrones by treating an anthraquinone derivative with glycerine and a dehydrating agent is a very general one, and in addition to anthraquinone itself [1] is also shown by anthraquinone homologues,[2] 1.2-benzanthraquinone,[3] hydroxyanthraquinones,[4] halogen anthraquinones,[5] and other anthraquinone derivatives, provided always that there is a free a- position available. The best yields, however, are usually obtained by reducing the anthraquinone to the corresponding anthraquinol or anthranol.[6] Anthracene itself will undergo benzanthrone formation, but in this case it is almost certain that condensation is preceded by oxidation.[7] Benzanthrone formation is not limited to the anthraquinone series as a similar type of compound, naphthindenon, is obtained when a-naphthol is treated with glycerine and an oxidising agent.[8] The mechanism of benzanthrone formation has been discussed by Bally and Scholl,[9] who conclude that the first reaction consists in the formation of an aldol-like condensation product from one molecule of anthranol and one molecule of acroleïn, that this then loses a molecule of water, and that the final closing of the ring is brought about by the loss of two atoms of hydrogen. This hydrogen is not, of course, evolved as such, but is utilised in reducing a further quantity of the anthraquinone to the anthranol. This view of the

[1] Bally, B. 38, 194. Bally and Scholl, B. 44, 1656. B.A.S.F., D.R.P. 176,018.
[2] B.A.S.F., D.R.P. 200,335.   [3] B.A.S.F., D.R.P. 181,176.
[4] B.A.S.F., D.R.P. 187,495. A. G. Perkin, Soc. 117, 697.
[5] B.A.S.F., D.R.P. 205,294.   [6] B.A.S.F., D.R.P. 176,018, etc.
[7] B.A.S.F., D.R.P. 176,019.   [8] B.A.S.F., D.R.P. 283,066.
[9] B. 44, 1656.

reaction is supported by the fact that it has been found impossible to induce benzanthrone formation to take place with both carbonyl groups.
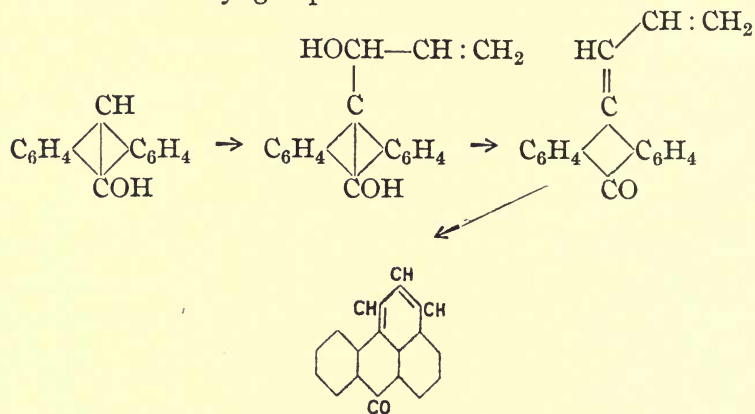
In place of glycerine it is, of course, possible to use mono- or di-chlorhydrin, epichlorhydrin, triacetin,[1] etc., and Jacob Meyer[2] has prepared benzanthrones by condensing anthraquinone with ketones of the type $R.COCH_3$.

In the above method the benzanthrone is formed by building the benzene ring on to the anthraquinone nucleus. Benzanthrones, however, can also be formed by building up the anthraquinone residue, and extremely important results have been obtained by reactions of this type. The methods used for achieving this result fall broadly into two classes, viz. methods in which the anthraquinone ring system is completed through the cyclic carbonyl group, and methods in which the anthraquinone ring system is completed through the other central carbon atom.

The first method originated in the preparation of a highly condensed benzanthrone, anthranthrone, by loss of two molecules of water from 1.1'-dinaphthyl-8.8'-dicarboxylic acid, or from 1.1'-dinaphthyl-2.8-dicarboxylic acid,[3] the product being an orange-yellow vat dye.

[1] B.A.S.F., D.R.P. 204,354.   [2] D.R.P. 247,187.
[3] Kalb, B. **47**, 1724.   *Cf.* Weitzenböck, M. **39**, 307.
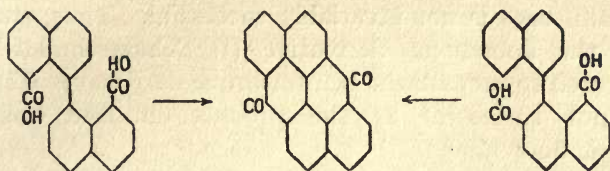
Schaarschmidt [1] extended the method by showing that allochrysoketone (3.4-benzfluorenone) on fusion with caustic potash gives two monocarboxylic acids, one of these by loss of water passing back into allochrysoketone, whereas the other yields benzanthrone :
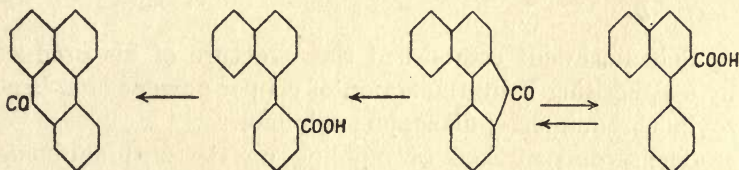
He also found that 1-phenylnaphthalene-2.3-dicarboxylic acid by loss of water gave both allochrysoketone carboxylic acid [2] and benzanthrone carboxylic acid,[3] the latter acid being obtained by heating for three hours with sulphuric acid of 91 per cent. strength. In this case the benzanthrone could only have been formed by the series of reactions shown below, *i.e.* by the opening of the fluorenone ring followed by loss of water in another direction :
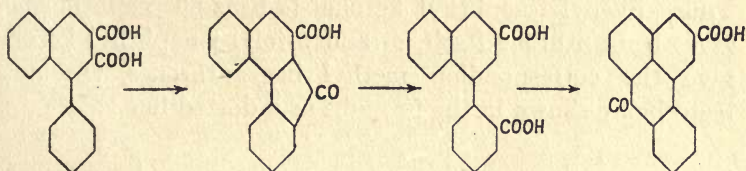
In confirmation of this Schaarschmidt showed that the cyclic imide of 1-phenylnaphthalene-2.3-dicarboxylic acid can be converted into the amide of allochrysoketone carboxylic acid, and that this in turn gives the amide of the benzanthrone carboxylic acid. This method of preparing

[1] B. **51**, 1082.   [2] B. **48**, 1827.   [3] B. **50**, 294 ; **51**, 1074.

benzanthrones is not invariably successful. Thus, starting with the fluorenone derivative (I) Schaarschmidt [1] endeavoured to prepare the benzanthrone derivatives (II), but was not successful as the product obtained was the isomeric fluorenone (III) :
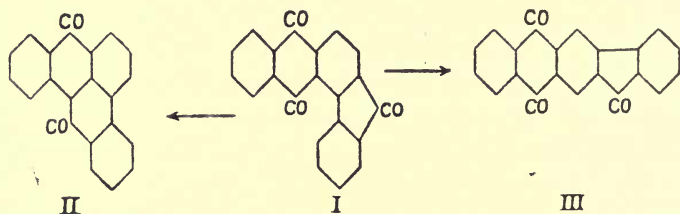
Schaarschmidt established the structure of his product by synthesising it by the action of copper powder on 2-benzoylanthraquinone-3-diazonium sulphate.

The second method of building up the anthraquinone ring system so as to produce a benzanthrone is due to Scholl,[2] and is generally known as " Scholl's *peri*-method." It has proved of the utmost value in the study of the more complex benzanthrones, as will be seen later. The method is based on the fact that aromatic ketones in which there is at least one pair of free positions in the *peri*- position to one another evolve hydrogen when heated with anhydrous aluminium chloride to about 140°, the two carbon atoms in the *peri*- position to one another becoming united. Thus, phenyl-1-naphthyl ketone (α-benzoyl naphthalene) gives benzanthrone itself, *o*- and *p*-tolyl-1-naphthyl ketone give the corresponding methyl benzanthrones, the new bond being shown in the formulæ as a dotted line :
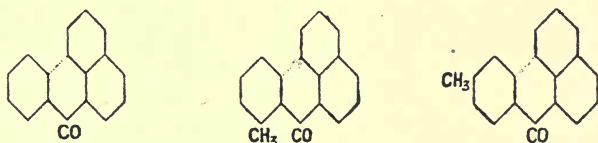
In the case of *m*-tolyl-1-naphthyl ketone, two possible isomers (A and B) might be formed :

[1] B. **51**, 1230.   [2] Scholl, A. **394**, 111 ; B. **44**, 1656 ; M. **33**, 1.

A   B
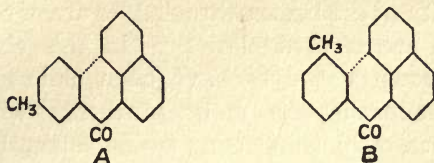
As the compound obtained is identical with that obtained from 2-methylanthrone by the glycerine method,[1] formula A must be the correct one.

Benzanthrone on reduction [2] with sodium hydrosulphite yields dihydrobenzanthrone (I), which is very sensitive to oxidation by atmospheric oxygen. Further reduction leads to benzanthrene (II or III), and then to dihydrobenzanthrene (IV or V) :

I   II   III

IV   V
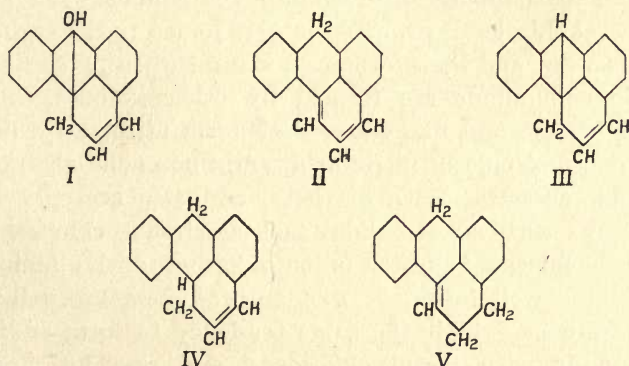
This last compound is identical with the *iso*-chrysofluorene which Graebe [3] obtained by passing benzyl naphthalene over red-hot pumice.

When benzanthrone is halogenated [4] by means of molecular or nascent halogen either in aqueous suspension or in the presence of an organic solvent such as acetic acid or nitrobenzene, the halogen atoms first enter the *Bz.*-ring, the products giving unsubstituted anthraquinone-α-carboxylic acid on oxidation. Halogen atoms in this position are much more reactive than those attached to the anthraquinone nucleus.

Bertram Meyer, F.P. 407,593 (G.C.I.B.).
[2] Bally and Scholl, B. **44**, 1656.   [3] B. **27** 953.
[4] B.A.S.F., D.R.P. 193,959.

The majority of the benzanthrone dyes are of complicated structure and are treated elsewhere in this chapter, but orange and brown vat dyes have been claimed as being obtained by condensing halogen benzanthrones with primary aromatic amines, or by condensing aminobenzanthrones with halogen compounds.[1] A black vat dye of unknown structure is said to be obtained when nitrobenzanthrone is fused with caustic potash.[2] It is probably a violanthrone derivative.

The benzanthrones yield highly coloured solutions when dissolved in concentrated sulphuric acid, although they are precipitated unchanged on the addition of water. From benzanthrone itself, however, a crystalline ferrichloride, stannichloride and platinichloride can be obtained, and other benzanthrones form similar compounds.[3] In these the metal chloride is probably loosely joined to the carbonyl oxygen atom, and their formation is not surprising as similar double compounds are formed by other ketones. Thus, benzophenone and fluorenone both form nitrates by union with one molecule of nitric acid, and fluorenone also forms a trichloracetate. Both of them, and also acetophenone, form salts with metal halides such as stannic chloride and mercuric chloride,[4] and the union of ketones with aluminium chloride is well known.[5] Phenanthraquinone, benzil and other ketones exhibit the same tendency to form addition compounds with metal chlorides [6] and perchloric acid,[7] but in anthraquinone and its derivatives this tendency is not so well marked. Thus, neither anthraquinone nor alizarin forms a perchlorate, although the former unites with two molecules of antimony pentachloride. It is not known whether the benzanthrones form perchlorates or not, but it is extremely probable that they would, and as the ketone perchlorates are usually well crystallised and sparingly soluble substances, they would probably furnish a useful means of purifying the benzanthrones.

The hydroxybenzanthrones have been but little studied

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[1] By., D.R.P. 200,014. [2] G.C.I.B., D.R.P. 262,478.
[3] A. G. Perkin, Soc. **117**, 696. [4] Kurt Meyer, B. **43**, 157.
[5] See p. 130. [6] Kurt Meyer, B. **41**, 2568.
[7] K. A. Hofmann and Metzler, B. **43**, 178.

up to the present. The dihydroxybenzanthrone (benzalizarin) obtained from alizarin has been prepared by Perkin,[1] who finds that both hydroxyl groups can easily be methylated by treatment with methyl iodide and caustic potash. Consequently benzalizarin is probably 7.8-dihydroxy-1.9-benzanthrone :
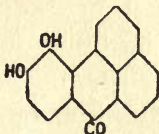
Curiously enough its tinctorial properties are very similar to those of alizarin, and a more detailed study of the hydroxy benzanthrones would probably lead to valuable information as regards the constitution of the hydroxy ketone dyestuffs.

II. THE COMPLEX BENZANTHRONES

The complex benzanthrones can be broadly divided into two classes, viz. derivatives of perylene and derivatives of pyrene. The former class comprises violanthrones, *iso*-violanthrones, cyanthrones, and helianthrones, whereas the latter class comprises the pyranthrones.* In the following formulæ the characteristic ring system is shown by heavy lines.[2]

Violanthrone.   iso—Violanthrone.
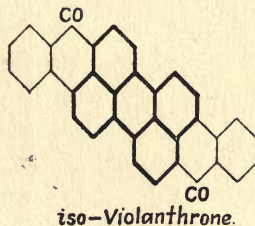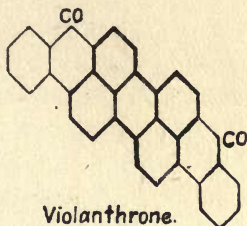
[1] Soc. **117**, 696.

* In the literature these compounds are almost invariably given names terminating in -ene, *e.g.* violanthrene, pyranthrene, etc. In the following pages the termination -one has been adopted to denote their ketonic structure the termination -ene being reserved for the parent hydrocarbon which can usually be obtained by reduction. This nomenclature is merely an extension of the system proposed by Scholl in connection with the helianthrones, and in all cases where confusion seems likely to arise a footnote has been added. The same system has been adopted when dealing with the indanthrones (indanthrenes), the change in this case being particularly advisable owing to Indanthrene being a registered trade name.

Helianthrone

Pyranthrone.
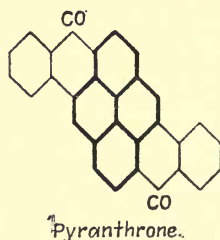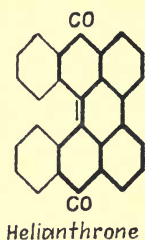
The hydrocarbons, perylene and pyrene, themselves have been studied by Scholl. The former he obtained by heating naphthalene, or better 1.1'-dinaphthyl, with anhydrous aluminium chloride.[1] The latter has, of course, been known for many years, but has also been investigated by Scholl, who has pointed out that in the case of condensed hydrocarbons which are readily oxidised to a quinone, the hydrogen atoms which are attacked during quinone formation are always those which are split out when the hydrocarbon undergoes a Friedel-Crafts reaction. On this basis, and with regard to the structure of the mono-, di-, and tri-benzoyl derivatives formed by the action of benzoyl chloride in the presence of aluminium chloride,[2] he concludes that pyrene quinone must have formula I or II, and not formula III, as proposed by Bamberger,[3] and as usually given in the literature :

I

II

III
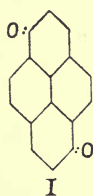
By oxidising dibenzoyl pyrene Scholl obtained what he thought was probably impure pyrene quinone, and therefore he gives preference to formula I. Goldschmidt,[4] on the other hand, gives preference to formula II.

[1] B. **43**, 2202.
[3] A. **240**, 158.

[2] See p. 337.
[4] A. **351**, 230.

VIOLANTHRONES.—When benzanthrone is fused with caustic potash [1] a dark blue vat dye is obtained which was originally given the trade name of Violanthrene BS, this being subsequently altered to Indanthrene Dark Blue BO (Caledon Dark Blue B).[2] The constitution of the dye was definitely proved by Scholl,[3] who synthesised it by his *peri-* method by heating 4.4'-dibenzoyl-1.1'-dinaphthyl with aluminium chloride, three pairs of *peri-* positions becoming united as shown by the dotted lines in the following formula :
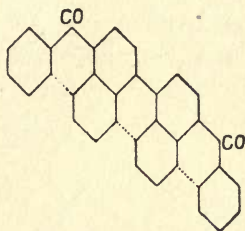
The formation of violanthrone by fusing benzanthrone obviously consists in the linking up of two molecules by the union of two pairs of carbon atoms as indicated by the dotted lines (formula I, page 330). Such reactions are not uncommon, and the appended formulæ illustrate cases in which they have been observed, although several of the substances obtained have not yet been submitted to scientific examination, so that the structure assigned to them is more or less guesswork. The substance represented by formula V is a green dye, whereas that represented by IV gives only bordeaux shades. From this it is probable that in V union has taken place at three points, the extra bond being denoted by the line of crosses. In VI it is probable that union at either two or four points can take place, as when the fusion is carried out at 220–300° a reddish-brown dye (dotted bonds only) is obtained, whereas the dye obtained at higher temperatures is greyish-blue (dotted bonds and cross bonds).

[1] B.A.S.F., D.R.P. 185,221 ; 188,193 ; 290,079. A. G. Perkin, E.P. 126,765 (1918).
[2] Scottish Dyes, Ltd.   [3] B. 43, 2208.

I	II[1]	III[2]	IV[3]
Benzanthrone.	Naphthindenon.	Naphthindandion.	
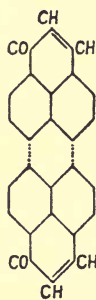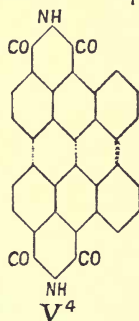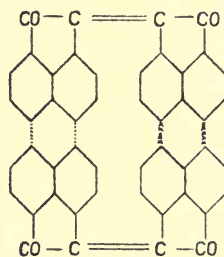
V[4]   VI[5]

A violanthrone is also obtained when the benzanthrone prepared from 1.2-benzanthraquinone is fused with caustic alkali.   It dyes in rather greener shades than violanthrone itself.   Its structure, however, is doubtful, as 1.2-benzanthra-quinone might form three isomeric benzanthrones.[6]

Nitration of violanthrone [7] yields a green vat dye, which was formerly known as Viridanthrene B, although the name was subsequently altered to Indanthrene Green B (Caledon Green B).[8]   It is rather remarkable that a nitro compound should be capable of being used as a vat dye

[1] Errera. G. (1911), 190.   B.A.S.F., D.R.P. 283,066.
[2] B.A.S.F., D.R.P. 283,365.
[3] Kardos, D.R.P. 276,357–8; 276,956; 286,098. B.A.S.F., D.R.P. 280,880.
[4] Kardos, D.R.P. 275,220; 278,660; 280,839; 282,711; 284,210.
[5] Kardos, D.R.P. 286,468.   *Cf.* Graebe, A. **276,** 17.
[6] B.A.S.F., D.R.P. 185,223.
[7] B.A.S.F., D.R.P. 185,222; 226,215.
[8] Scottish Dyes, Ltd.

without the nitro group being reduced. From nitroviolan-throne the corresponding amino- compound can be prepared, and this can be alkylated, arylated, or combined with alde-hydes. These amino compounds dye in rather greener shades than violanthrone itself, but are of no technical value.[1]

When violanthrone is oxidised, *e.g.* with sulphuric acid and boric acid, a product is formed which has very feeble tinctorial properties. By heating this with a condensing agent such as boric acid at 160°, however, it is converted into a powerful green dye, the tinctorial properties of which are improved by bromination, although the shade becomes somewhat yellower.[2] Violanthrone itself can be halogenated,[3] the halogenated product being placed on the market as Indanthrene Violet RT.

iso-VIOLANTHRONES.—*iso*-Violanthrone is isomeric with violanthrone, and is obtained when brombenzanthrone is fused with caustic akali.[4] The patentees assigned to it formula I, but Scholl regards it as a perylene derivative and prefers formula II.
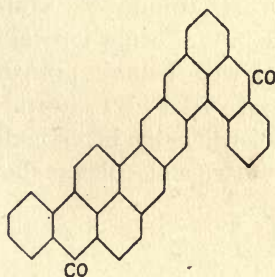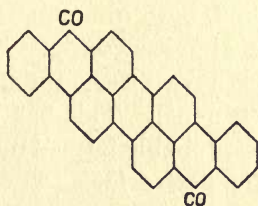
I   II

Scholl[5] endeavoured to confirm his formula by effecting a synthesis of the dyestuff from dibenzoyl perylene by his *peri*- method, thus :

[1] B.A.S.F., D.R.P. 267,418 ; 268,224 ; 284,700.
[2] B.A.S.F., D.R.P. 259,370 ; 260,020 ; 280,710.
[3] B.A.S.F., D.R.P. 177,574.
[4] B.A.S.F., D.R.P. 194,252.
[5] B. **43,** 2208.
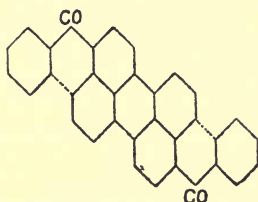
The synthesis, however, was not successful, and probably the carbonyl groups in dibenzoyl perylene are not in the positions in which they are shown in the above formula. *iso*-Violanthrone itself is a powerful vat dye, and was formerly known as Violanthrene R Extra, this being subsequently changed to Indanthrene Violet R Extra (Caledon Brilliant Purple R).[1] Its dichlor derivative is Indanthrene Violet RR Extra (Caledon Brilliant Purple RR) [1] and its dibrom derivative Indanthrene Violet R Extra.[2] Its nitro derivative is of no value.[3]

CYANTHRONES.—These are complex quinoline derivatives of benzanthrone, and have been but little investigated. Benzanthrone quinoline itself (3(N).4-pyridino-1.9-benzanthrone) is obtained from β-aminoanthraquinone by Skraup's method, both quinoline and benzanthrone formation taking place simultaneously.[4] When fused with caustic potash it gives a vat dye, Indanthrene Dark Blue BT (formerly Cyanthrene). This has not been scientifically investigated, but is probably formed by the union of two molecules as shown by the dotted lines : [5]
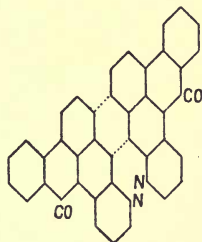
Its halogen derivatives have also been described.[6]

[1] Scottish Dyes, Ltd.   [2] B.A.S.F., D.R.P. 217,570.
[3] B.A.S.F., D.R.P. 234,749.   [4] B.A.S.F., D.R.P. 171,939.
[5] Baely, B. 38, 196.   B.A.S.F., 172,609.   [6] B.A.S.F., D.R.P. 177,574.

A much more simple benzanthrone quinoline is obtained by condensing *Bz.*-chlorbenzanthrone with α-aminoanthraquinone and then fusing the benzanthronyl-α-aminoanthraquinone with caustic potash. Apparently the alkali causes closing of the quinoline ring as shown by the dotted line.[1] The product is a green vat dye, although it is not used commercially :
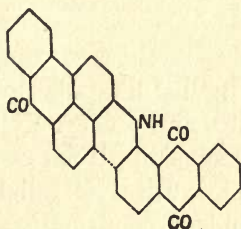
HELIANTHRONES.—When 1.1′-dianthraquinonyl is reduced, preferably by means of copper bronze and concentrated sulphuric acid at 40-50°, ring formation takes place by union of two *ms*-carbon atoms. The product is *ms*-benzdianthrone or helianthrone, a yellow vat dye, which, however, has not found technical application : [2]
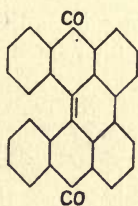
Helianthrone.

By the same method Scholl has prepared dihydroxy and tetrahydroxy derivatives.[3]

It will be observed that in helianthrone there is a pair of carbon atoms in the *peri-* position to one another, so that a new ring, as indicated by the dotted line, should be formed by heating with aluminium chloride :

[1] B.A.S.F., D.R.P. 212,471.
[2] Scholl, B. **43**, 1734. D.R.P. 190,799 ; 197,933. *Cf.* Eckert and Tomaschek, M. **39**, 839.
[3] B. **44**, 1091. *Cf.* Seer, M. **34**, 631.
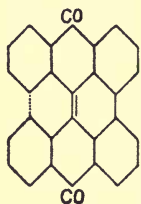
ms-Naphthadianthrone.

This Scholl has found to be the case, and he has also prepared the same compound by distilling dianthraquinonyl with zinc dust.[1] Meyer, Bondy, and Eckert [2] claim that it is more readily obtained by exposing glacial acetic acid solutions of dianthrone to sunlight or ultra-violet light, but their observations require independent confirmation as they deduce the formula from four analyses in which values obtained for carbon vary from 87·8 to 88·7 per cent., and those for hydrogen from 3·2 to 3·8 per cent.[3] In a later paper, however, Eckert and Tomaschek [4] describe several halogen derivatives which they have obtained by similar means. *ms*-Naphthadianthrone acts as an orange vat dye, although reduction to the vat is very difficult.

The reduction products of helianthrone itself have been investigated by Potschiwauscheg,[5] who obtained three products :
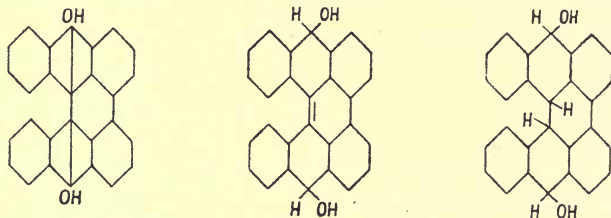
The first of these he was only able to isolate in the form of its diacetate. He was unable to obtain the parent hydrocarbon.

Attention may here be drawn to a series of olive and brown vat dyes of unknown constitution which are obtained by

B. **52**, 1829.   [2] M. **33**, 1451.   [3] $C_{28}H_1O_2$ requires C=88·4, H=3·16.
       [4] M. **39**, 839.   [5] B. **43**, 1746.

the action of concentrated sulphuric acid and copper powder on anthraquinone derivatives.[1] They are probably helianthrone derivatives, although their structure has never been investigated. The brown and bronze vat dyes which are obtained from 1.2-benzanthraquinone, dianthrone and dianthrol by heating with aluminium chloride are also probably helianthrones.[2]

PYRANTHRONES.—When 2.2'-dimethyl-1.1'-dianthraquinonyl is heated alone at 380°, or with zinc chloride at 280°, or, better, with alcoholic caustic potash at 145°, a very fast orange vat dye is obtained,[3] which was formerly known as Pyranthrene, but was later named Indanthrene Golden Orange G. The dichlor derivative (Indanthrene Golden Orange R) and the dibrom derivative (Indanthrene Scarlet G) dye in redder shades and can be obtained either by halogenating pyranthrone, or, synthetically, from the corresponding halogen dimethyldianthraquinonyl.[4]

Pyranthrone formation also takes place when 1.1'-dianthraquinonyl-2.2'-dialdehyde is reduced, *e.g.* with sodium hydrosulphite and the *leuco*-product thus formed then oxidised,[5] and advantage has been taken of this reaction in printing, the pattern being printed on to the cloth with the aldehyde and the colour then developed in a hydrosulphite bath followed by oxidation. The corresponding dianthraquinonyl diketones also yield pyranthrones on reduction, *e.g.* 2.2'-dibenzoyl-1.1'-dianthraquinonyl gives diphenylpyranthrone.[6] These diarylpyranthrones are yellow vat dyes, and Scholl has found that alkyl groups also decrease the colour.[7] The structure of pyranthrone was definitely established by Scholl by synthesis by his *peri*-method, but as Scholl used the same methods for preparing some highly complex pyranthrones it will be best to postpone the discussion of the synthesis from pyrene, and first consider

[1] B.A.S.F., D.R.P. 190,656. By., D.R.P. 203,436; 205,442.
[2] E., D.R.P. 237,751; 241,631.
[3] Scholl, B. **43**, 346, 512; **44**, 1448, 1662; M. **32**, 687. B.A.S.F., D.R.P. 174,494; 175,067; 212,019; 287,270.
[4] Scholl, B. **43**, 352; M. **39**, 231. B.A.S.F., D.R.P. 186,596; 211,927; 218,162.   [5] B.A.S.F., D.R.P. 238,980.
[6] B.A.S.F., D.R.P. 278,424.   [7] M. **32**, 687.

the mechanism of pyranthrone formation from 2.2′-dimethyl-1.1′-dianthraquinonyl.

At first sight it would seem probable that pyranthrone formation was preceded by a wandering of hydrogen atoms to the neighbouring cyclic carbonyl groups with the formation of an aldol-like product, pyranthrone formation taking place by subsequent loss of water :
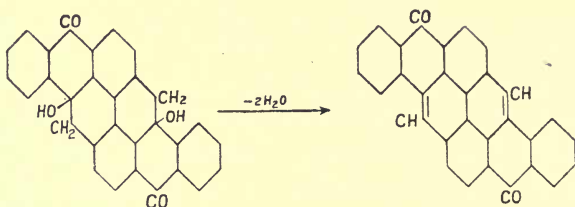
If this were the case, the corresponding diethyl and di-*n*-propyl dianthraquinonyls should behave in exactly the same way, giving rise to dimethyl and diethyl pyranthrone. In the case of di-*iso*-propyldianthraquinonyl there is no reason why the first of the above steps should not take place, but the aldol-like product could not pass into a pyranthrone by loss of water owing to the necessary hydrogen being absent. Scholl [1] has examined the behaviour of all three substances, and finds that diethyl and di-*iso*-propyl dianthraquinonyl both give pyranthrones, although not nearly so readily as dimethyldianthraquinonyl. In the case of 2.2′-di-*iso*-propyl-1.1′-dianthraquinonyl, however, no reaction whatsoever took place, although it was to be expected that the aldol-like substance would be obtained. It is therefore very probable that pyranthrone formation is a direct loss of water and is not preceded by a migration of hydrogen atoms. The dimethyl and diethyl pyranthrones which Scholl obtained are very similar to pyranthrone itself in their tinctorial properties although they give paler shades.

The synthesis of pyranthrone and of many very complex pyranthrone derivatives has been achieved by Scholl [2] by means of his *peri*- method. Starting with pyrene he first condensed it with benzoyl chloride in the presence of

[1] M. **32**, 687.   [2] A. **394**, 111 ; M. **33**, 1.   D.R.P. 239,671.

aluminium chloride, and in this way obtained mono-, di-, and tribenzoyl pyrene. From dibenzoyl pyrene by heating with aluminium chloride he obtained pyranthrone (I), whereas the tribenzoyl derivative gave benzoyl pyranthrone (II) :

I   II
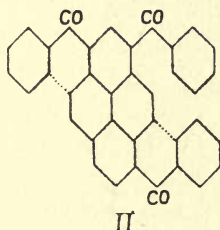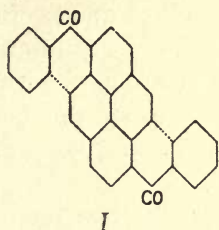
In benzoyl pyranthrone it will be noticed that there is still a pair of carbon atoms in the *peri-* position to one another. It was found impossible, however, to cause these to unite, and it seems to be a general rule that in the case of six-membered rings *peri-* condensation cannot take place twice at the same side of the pyrene nucleus. This is probably to be attributed to steric influences, for, as will be seen below, in the case of five-membered rings such double *peri-* condensation is possible.

By condensing α-naphthoyl chloride and β-naphthoyl chloride with pyrene Scholl obtained dinaphthoyl pyrenes, which when heated with aluminium chloride passed into complex pyranthrones (III and IV) :

III   IV
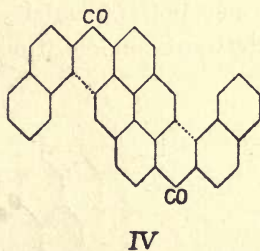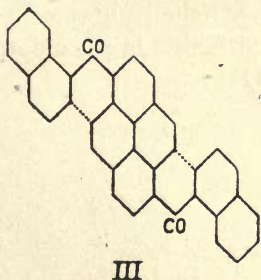
In the case of di-α-naphthoyl pyrene, pyranthrone formation can only take place as indicated by formula III. In the case of di-β-naphthoyl pyrene, however, pyranthrone

22

formation might take place through the α-carbon atoms of the naphthalene nuclei, as indicated in formula IV, or it might possibly take place through the β-carbon atoms. The α-carbon atoms, however, are always the most reactive, and it has been shown definitely in the case of phenyl naphthyl ketone that the α-carbon atom is capable of undergoing *peri*-condensation,[1] and also that in the case of β-anthraquinonyl-α-naphthyl ketone it is the α-carbon atom which reacts.[2] Hence, in the absence of all evidence to the contrary, formula IV must be accepted as representing what actually takes place.

Scholl has also employed his *peri*- method for building up complex pyranthrones containing five-membered hetero-cyclic rings. He first showed that α-thienyl-1-naphthyl ketone gives a condensation product (V) when heated with aluminium chloride, and that α-furyl-1-naphthyl ketone behaves in the same way (VI), although in this latter case he was unable to isolate the product in the pure condition :

V   VI
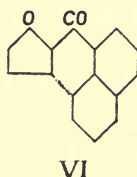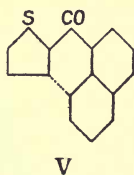
By condensing two molecules of α-thienylcarbonyl chloride with one molecule of pyrene, Scholl obtained two ketones, both of which when heated with aluminium chloride underwent condensation (VII and VIII) :

VII   VIII
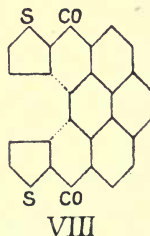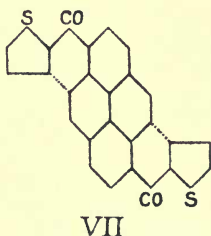
[1] See p. 324.   [2] See p. 156.

It will thus be seen that in the case of five-membered rings a double *peri-* condensation at the same side of the pyrene nucleus is possible.

As regards the tinctorial properties of these complex pyranthrones, the pyranthrones derived from both naphthoyl pyrenes dye in redder shades than pyranthrone itself, this being particularly noticeable in the case of the β- compound (formula IV, page 337). Both thiophene pyranthrones are brown vat dyes, but the one represented by formula VII is the most powerful.

Pyranthrone itself on reduction in alkaline solution gives only a purple red vat, and in this way differs from many of the other complex anthraquinonoid vat dyes, such as indanthrone and flavanthrone, which are capable of giving two different vats. The pyranthrone vat is very unstable towards atmospheric oxygen, and Scholl [1] was only able to isolate it in the form of its brombenzoyl derivative, which he found to correspond to formula IX. Further reduction leads to the parent hydrocarbon, pyranthrene, which is represented by formula X :
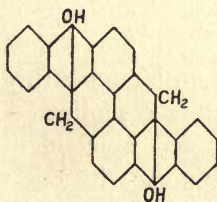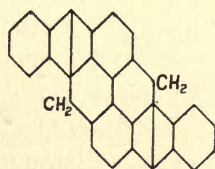
IX   X

Brown and green dyes can be obtained by the nitration and reduction of pyranthrone.[2]

[1] B. **43**, 346.
[2] Scholl, B. **43**, 346.   By., D.R.P. 220,580.   B.A.S.F., D.R.P. 268,504.

THE CYCLIC AZINES AND HYDRO-AZINES

THE cyclic azines and hydroazines of the anthraquinone series can be conveniently divided into two groups, viz. mixed compounds in which only one anthraquinone ring system is present, and simple compounds in which the azine ring lies between two anthraquinone residues. Of these two groups the latter has been studied most fully, as some extremely important vat dyes have been found to be simple anthraquinone hydroazines.

I. THE MIXED AZINES AND HYDROAZINES

Mixed azines are obtained by condensing an o-diaminoanthraquinone with an α-diketone. The simplest azine obtainable by this method is the pyrazino- compound (I), which is formed by condensing 1.2-diaminoanthraquinone with ethyl oxalate.[1] Somewhat more complicated are the blue-black vat dyes which are obtained by condensing two molecules of an o-diamino anthraquinone with one molecule of glyoxylic acid by boiling in glacial acetic acid solution, or in alcoholic solution in the presence of a little sulphuric acid.[2] Their structure probably corresponds to formula II :
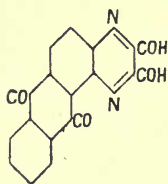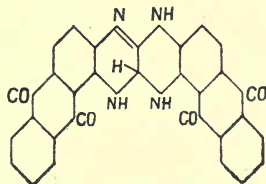
I   II

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[1] Ertl, M. **35**, 1427. Scholl, B. **44**, 1729. Terres, B. **46**, 1644.
[2] G.E., D.R.P. 264,043.

The first of these compounds is of some interest, as it is also obtained by the oxidation of indanthrone.

Mixed azines have been obtained by condensing both 1.2-diaminoanthraquinone and 2.3-diaminoanthraquinone with a large number of α-diketonic compounds such as benzil, phenanthraquinone, β-naphthaquinone and isatin.[1] With the latter substance under certain conditions yellow and red vat dyes are obtained the structure of which is quite uncertain, as, unlike other azines, they give almost colourless vats.[2]

The azines obtained from 1.2-diaminoanthraquinone are, of course, *angular* in structure, whereas those obtained from 2.3-diaminoanthraquinone must be *linear*. The former on reduction in alkaline solution give blue vats, whereas the latter give brown solutions. As the azines obtained from 1.2.3-triaminoanthraquinone give brown solutions on alkaline reduction it is probable that they are *linear* in structure and that the free amino group is in the α- position.[3]

N-Substituted cyclic hydroazines are said to be obtained by condensing *o*-aminoarylamino anthraquinones with aldehydes and ketones, and it has been claimed that their sulphonic acids are blue wool dyes.[4] *o*-Aminoazo- compounds are also said to yield cyclic azines under certain conditions.[5]

Of greater importance is the cyclic azine synthesis devised by Ullmann.[6] He found that when an *o*-nitrophenyl-1-amino-anthraquinone is reduced with sodium hydrosulphite the corresponding primary amino- compound is formed, but that if the reduction is brought about by means of sodium sulphide an almost quantitative yield of the cyclic hydroazine is obtained. The mechanism of this reaction consists, no doubt, primarily in the production of a hydroxylamine derivative, the azine ring being then closed by loss of a molecule of water :

[1] Scholl, M. **32**, 1043. Scholl and Kacer, B. **37**, 4531. Terres, B. **46**, 1634. By., D.R.P. 170,562.
[2] By., D.R.P. 251,956.
[3] Scholl, M. **32**, 1043.
[4] By., D.R.P. 184,391 ; 252,529.
[5] M.L.B., D.R.P. 230,005 ; 232,526.
[6] A. **380**, 324.
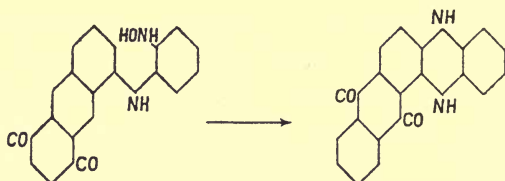
A somewhat similar synthesis has been devised by Ull-mann and Medenwald [1] who obtain azines by oxidising *o*-aminoaryl aminoanthraquinones with lead dioxide.

The hydroazines are blue substances which are capable of use as vat dyes although the mixed hydroazines are of no technical value. The imino hydrogen atoms cannot be replaced by acetyl groups,[2] all attempts at acetylation leading to the diacetate of the anthraquinol derivative owing to the cyclic carbonyl groups of one molecule becoming reduced at the expense of the imino hydrogen atoms of another molecule. On oxidation the hydroazines pass into the corresponding azine. These are yellow compounds and are much more stable than the hydroazines. As will be seen later, this is the reverse of what is found to be true in the case of the simple azines and hydroazines.

II. The Simple Azines and Hydroazines

Simple azines and hydroazines (indanthrones *) can be obtained by methods very similar to those employed for the production of the mixed compounds. Thus simple cyclic azines or hydroazines are obtained when *o*-diamino-

[1] B. **46**, 1809.   [2] Ullmann, A. **380**, 324.

* The first cyclic azine of the anthraquinone series to be prepared was *trans. bisang.*-anthraquinonedihydro azine. This was placed on the market under the name Indanthrene Blue, and the name " indanthrene " has come into general use in the literature. The word " indanthrene," however, is a registered trade name (B.A.S.F.) and is applied to many vat dyes which are not azines. Indanthrene Blue is an anthraquinone derivative and ketonic in structure, and in order to denote its ketonic nature the name should terminate in -one. In the following pages, therefore, the word " indanthrone " is used to denote the ketonic hydroazine, indanthrene (without a capital) being used for the parent, oxygen free hydroazine (*trans. bisang.*-dihydroanthrazine). Where " Indanthrene " is used as a registered trade name it is spelt with a capital. This system of nomenclature should not lead to any confusion as the dihydroanthrazine is of very little importance. Where any confusion seems possible a footnote has been added.

anthraquinones are condensed with o-dihydroxyanthra-quinones such as alizarin, best by heating with boric acid and a solvent of high boiling point,[1] or with 1.2-anthra-quinone.[2] In the latter case, of course, the product is an anthracene anthraquinone azine (*trans. bisang.*-anthroanthra-quinone azine), but the anthracene residue is readily oxidised to the quinone. Cyclic azines are also obtained by oxidising o-aminodianthraquinonylamines by heating alone in the air, or by heating with a nitro- compound, oleum or sulphuric acid and manganese dioxide.[3] The o-nitrodianthraquinonyl-amines also give cyclic hydroazines on reduction with sodium sulphide, although in this case it is necessary to carry out the reduction by fusion with crystallised sodium sulphide, as treatment with aqueous solution leads only to brown substances of unknown constitution.[4] Better results are usually obtained by reducing o_2-dinitrodianthraquinonyl-amines with stannous chloride and hydrochloric acid in acetic acid solution, one nitro group being split out.[5] This method is of very general application for the preparation of azines and by it phenazine itself can be obtained in excellent yield from o_2-dinitrodiphenylamine.[6]

From a practical point of view by far the most important method of obtaining the indanthrones is by fusing the β-aminoanthraquinones with caustic alkali, and this method has been very widely applied not only to β-aminoanthra-quinone itself,[7] but also to diaminoanthraquinones[8] and β-aminoanthraquinone sulphonic acids,[9] although in the latter case the sulphonic acid group is often lost. Even β-anthramine is said to yield a cyclic hydroazine (anthrazine) when fused with caustic alkali.[10] The anthraquinonyl-β-hydroxylamines, however, do not give cyclic azines.[11]

[1] By., D.R.P. 178,130.
[2] Terres, B. **46**, 1634.
[3] B.A.S.F., D.R.P. 186,465. By., D.R.P. 239,211.
[4] By., D.R.P. 178,129 ; 213,501.
[5] Eckert and Steiner, M. **35**, 1129.
[6] Eckert, M. **35**, 1153. *Cf.* also B. **38**, 2975 ; Soc. **95**, 577.
[7] Scholl, B. **36**, 3427. B.A.S.F., D.R.P. 129,845 ; 135,407–8 ; 287,270.
[8] B.A.S.F., D.R.P. **157**,685.
[9] B.A.S.F., D.R.P. 129,846.
[10] By., D.R.P. 172,684. *Cf.* B. **34**, 3410.   [11] M. **32**, 1035.

The mechanism of the conversion of β-aminoanthraquinone into indanthrone is not understood. At one time it was thought probable that the first product formed was a hydrazo compound, and that this then underwent an *ortho*-semidine rearrangement. This, however, can hardly be the case, as it has been found that no indanthrone is formed when β-azoxyanthraquinone is reduced. It is possible that one molecule of the β-aminoanthraquinone reacts in the p-quinonoid form and then adds on another molecule reacting in the ordinary form, the azine ring being completed by a second condensation of a similar nature :
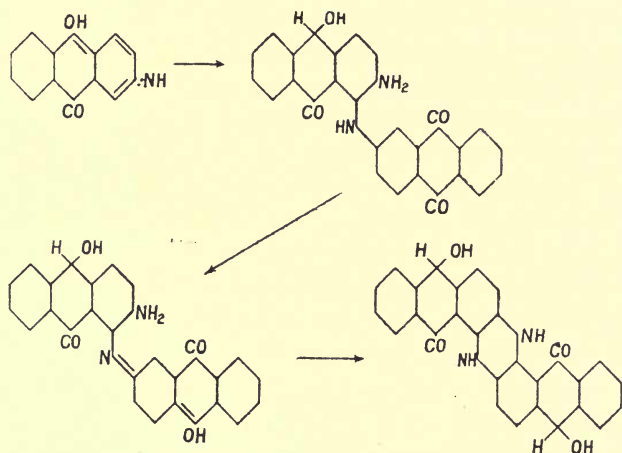
Theories of this nature, however, are merely speculative and lack experimental verification.

In the alkali melt of β-aminoanthraquinone the indanthrone is not present as such but as its reduction product (vat), from which, however, the indanthrone is readily obtained by blowing air through the aqueous solution. Also in addition to indanthrone, flavanthrone (pages 300–304) is formed, and when the melt is carried out with caustic alkali alone the reduction products of indanthrone and flavanthrone are produced in the ratio of about two to one. If a reducing agent is added to the alkali, indanthrone forma-

tion is greatly hindered, and the reduction product (vat) of flavanthrone is then almost exclusively produced.[1] If, on the other hand, the melt is carried out in the presence of an oxidising agent such as potassium nitrate or chlorate,[2] flavanthrone formation is prevented and only indanthrone is obtained. In this case, of course, it is the dye itself and not its vat which is produced. On this observation has been based a series of patents [3] claiming the production of indanthrone by oxidising β-aminoanthraquinone with lead dioxide, manganese dioxide, chromic acid, nitric acid, etc., although these methods are of no practical importance.

Indanthrones can also be obtained from α-aminoanthra-quinones by treating them with halogens,[4] or by fusing them with caustic alkali in the presence of a phenol or naphthol,[5] or by heating them with acids or metallic salts such as chromium sulphate or copper sulphate.[6] The yields, however, are usually very poor although the last method has been extended to the preparation of complex indanthrones from aminobenzanthrones and amino-benzanthrone quinolines.[7]

Another method of obtaining indanthrones, and one which has been of value in proving their structure and in preparing N-substituted indanthrones, consists in splitting out two molecules of halogen acid from two molecules of an o-amino halogen anthraquinone. Thus indanthrone itself is obtained when 1-amino-2-bromanthraquinone is heated in some indifferent solvent of high boiling point with anhydrous sodium acetate and either cuprous chloride or copper powder [8] :

[1] B.A.S.F., D.R.P. 135,408.
[2] Morton, Dandridge, and Morton Sundour Fabrics, Ltd., E.P. 126,112 (1918). In spite of this A. G. Perkin claims in E.P. 126,764 (1918) that the yield and purity of the indanthrone is improved by carrying out the alkali fusion in the presence of sucrose, glucose, lactose, or the like.
[3] B.A.S.F., D.R.P. 139,633 ; 141,355 ; 238,979.
[4] By., D.R.P. 161,923.
[5] By., D.R.P. 175,626.
[6] B.A.S.F., D.R.P. 186,636–7 ; 238,979.
[7] B.A.S.F., D.R.P. 198,507 ; 204,905 ; 210,565.
[8] By., D.R.P. 158,287 ; 193,121.
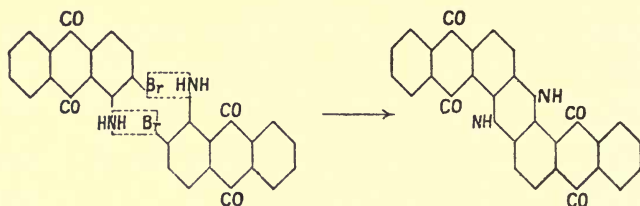
For the extension of this method to the preparation of indanthrone derivatives the reader is referred to the original literature.[1]

The cyclic hydroazines or indanthrones are blue compounds which act as powerful vat dyes. They are fairly easily oxidised to the yellow azines, but these are very stable substances and strongly resist further oxidation although they are readily reduced to the cyclic hydroazine. The most important member of the series is indanthrone itself (Indanthrene Blue R), and as this has been investigated in detail it will be described at some length, as it serves as a general type.

In spite of the numerous methods which have been proposed for the manufacture of indanthrone, the only one which is of any practical importance consists in fusing β-aminoanthraquinone with caustic alkali.[2] The dye itself forms an insoluble blue powder which usually occurs in commerce in the form of a 20 per cent. paste.

Indanthrone is rather easily oxidised to the yellow azine, so that material dyed with Indanthrene Blue R is apt to become slightly yellow on washing, although the original blue shade can be restored by treatment with a mild reducing agent. The oxidation to the azine is best carried out in the laboratory by means of nitric acid, a bimolecular product in which the two molecules are joined through the nitrogen atoms being formed as an intermediate product.[3] The azine itself is yellow and is much more stable than the hydroazine, the simple anthraquinone azines in this respect

[1] Ullmann, A. **399**, 341. By., D.R.P. 158,287; 158,474; 167,255; 193,121.
[2] For laboratory details see Scholl, B. **36**, 3427.
[3] Scholl, B. **36**, 3431; **40**, 320.

differing from the mixed azines. So stable in fact is the azine obtained from indanthrone that Scholl [1] was only able to oxidise it by boiling it for forty hours with chromic acid in glacial acetic acid solution. Under these conditions it passes into the pyrazinoanthraquinone mentioned on p. 340.

Indanthrone itself is a very feeble base and its salts even with strong acids are very readily decomposed. For a long time it was believed that the imino-hydrogen atoms could not be replaced by acyl groups, as treatment with acyl chlorides always lead to the entrance of halogen atoms into the molecule with simultaneous reduction and acylation of the cyclic carbonyl groups. [2] In this way indanthrone resembles indigo, [3] benzoquinone, [4] chloranil, [5] and the oxazines and thiazines, [6] but Scholl [7] succeeded in preparing a dibenzoyl indanthrone by boiling indanthrone for a few minutes with a great excess (70 parts) of benzoyl chloride. This derivative must have been N-dibenzoyl indanthrone, as on hydrolysis indanthrone itself and not its reduction product was obtained. It was found to be a stable red substance, so that indanthrone, like indigo, changes from blue to red on acylation, both diacetyl indigo [8] and dibenzoyl indigo being red.

The behaviour of indanthrone on reduction has been carefully investigated by Scholl and his students. When the reduction is carried out by means of sodium hydrosulphite in alkaline solution, first a blue vat and then a brown vat is obtained, both being very readily oxidised by the air and thereby being changed back to indanthrone. The *blue vat* consists of the sodium salt of anthraquinolanthraquinone dihydroazine (formula I) and under the name Indanthrone Blue RS [9] has been used in printing. [10]   Scholl,

[1] B. **44**, 1727.
[2] Scholl and Berblinger, B. **40**, 395.   B.A.S.F., D.R.P. 229,166.
[3] Heller, B. **36**, 2762.
[4] Buchka, B. **14**, 1327.   Sarauw, A. **209**, 129.
[5] Graebe, A. **146**, 12.
[6] Scholl, B. **40**, 399.   Private communication from Bernthsen.
[7] B. **44**, 1732.   [8] Liebermann and Dickhuth, B. **24**, 4133.
[9] Caledon Blue R (Scottish Dyes, Ltd.).   [10] B.A.S.F., D.R.P. 129,848.

Steinkopf and Kabacznik [1] have prepared the dibenzoyl derivative, and Scholl and Stegmuller [2] have shown that if the sodium salt is heated to 220°–230° with concentrated caustic soda, or if it is heated alone at 250° in an indifferent atmosphere, auto-oxidation and reduction takes place with the production of a mixture of anthraquinoneanthranol-dihydroazine (formula II) and indanthrone :

$$
2C_6H_4
\begin{array}{c} CO \\ \diagdown \\ CO \end{array}
C_6H_2
\begin{array}{c} NH \\ \diagdown \\ NH \end{array}
C_6H_2
\begin{array}{c} OH \\ | \\ C \\ \diagdown \\ C \\ | \\ OH \end{array}
C_6H_4
$$

$$I$$

$$
=\quad C_6H_4
\begin{array}{c} CO \\ \diagdown \\ CO \end{array}
C_6H_2
\begin{array}{c} NH \\ \diagdown \\ NH \end{array}
C_6H_2
\begin{array}{c} OH \\ | \\ C \\ \diagdown \\ C \\ | \\ H \end{array}
C_6H_4
$$

$$
+\ C_6H_4
\begin{array}{c} CO \\ \diagdown \\ CO \end{array}
C_6H_2
\begin{array}{c} NH \\ \diagdown \\ NH \end{array}
C_6H_2
\begin{array}{c} CO \\ \diagdown \\ CO \end{array}
C_6H_4 + H_2O
$$

$$II$$
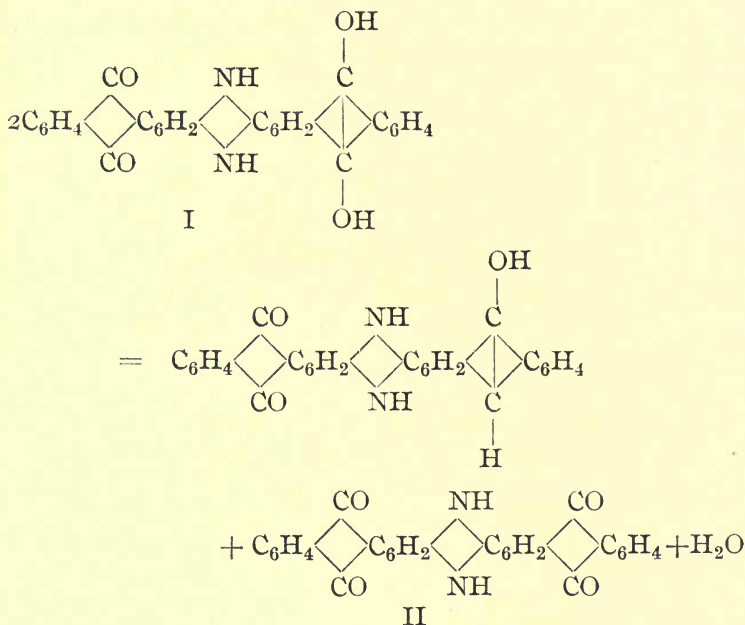
The former compound, however, is much more readily obtained by reducing indanthrone with boiling alkaline sodium hydrosulphite solution and then oxidising the anthraquinol anthranol dihydroazine thus formed by exposure to the air. On oxidation with sodium hypochlorite it passes into the azine.

The *brown vat* obtained by the alkaline reduction of indanthrone consists of the sodium salt of anthraquinol-dihydroazine [3] and Scholl, Steinkopf, and Kabacznik [4] have prepared a tetrabenzoyl derivative.

[1] B. **40**, 390.
[2] B. **40**, 924.
[3] Scholl, B. **36**, 3410.
[4] B. **40**, 390.

Exhaustive reduction of indanthrone by means of zinc and caustic soda gives N-dihydroanthrazine. The dihydroazine group in this is less stable than in indanthrone, so that heating alone suffices to split off two atoms of hydrogen, the product left being anthrazine. Both anthrazine and dihydroanthrazine on oxidation with chromic acid give anthraquinone azine. Anthrazine when boiled with nitric acid (D=1400) gives a compound which is probably pentanitrotetrahydroxy anthrazine, although it has not been obtained in a state of purity.[1]

The reduction of indanthrone by hydriodic acid has been studied by Scholl[2] and by Kaufler,[3] who find that three products are formed, viz. $C_{28}H_{16}O_2N_2$, $C_{28}H_{18}O_2N_2$ and

Anthronazine, $C_{28}H_{16}O_2N$

N-Dihydroanthronazine, $C_{28}H_{18}O_2N_2$

Anthrazine, $C_{28}H_{16}N_2$
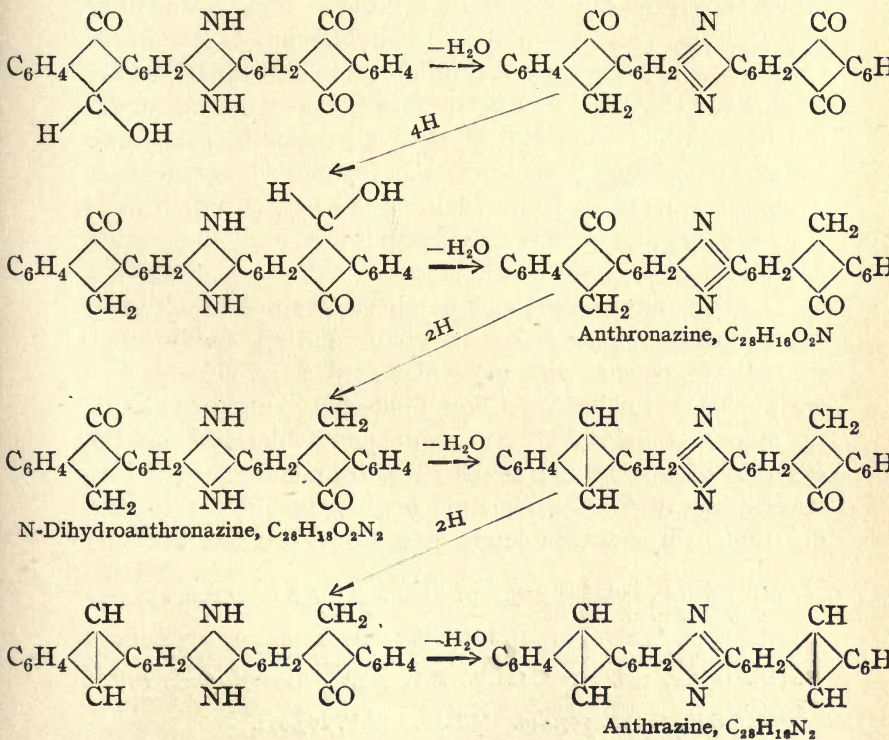
[1] Scholl, B. **40**, 933. *Cf.* Scholl, B. **36**, 3442. By., D.R.P. 172,684.
[2] B. **36**, 3410.   [3] B. **36**, 930.

$C_{28}H_{16}N_2$. The last of these is anthrazine, and of the two former, the second is readily oxidised to the first either by loss of hydrogen when heated alone to 340°, or by boiling with nitrobenzene, and hence is probably a dihydroazine. Neither compound is soluble in aqueous caustic alkali, but both are soluble in alcoholic alkali, and this points to an anthrone structure. If this be assumed the reduction of indanthrone would appear to consist in an alternate adding on of hydrogen and splitting off of water.

As stated on p. 346 fabric dyed with Indanthrene Blue R (indanthrone) tends to become yellow on washing owing to the oxidation of the dihydroazine to the azine. Such oxidation is obviously impossible if the iminohydrogen atoms are replaced by methyl groups, and N-dimethyl indanthrone, made from 1-methylamino-2-bromanthra-quinone by heating with sodium acetate and copper powder or cuprous chloride,[1] has been placed on the market under the name Algol Blue K. It is much faster to soap than Indanthrene Blue R, and has the further advantage that dyeings can be made from a cold vat,[2] whereas Indanthrene Blue R only gives satisfactory results if used at a temperature of at least 50°.

Halogen indanthrones can be obtained from halogenated aminoanthraquinones,[3] or by halogenating indanthrone itself by treatment with molecular or nascent chlorine,[4] or with sulphuryl chloride,[5] thionyl chloride,[6] sulphur chloride or stannous chloride,[7] antimony pentachloride,[8] or the chloride of an organic acid.[9] The bromination of indan-throne, however, only takes place with great difficulty, and chlorindanthrones completely free from bromine are said

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[1] By., D.R.P. 158,287; 193,121; 234,294; B.A.S.F., D.R.P. 238,979.
[2] By., D.R.P. 240,265.
[3] Ullmann, A. **399**, 341. By., D.R.P. 158,474; 167,255.
[4] Scholl and Berblinger, B. **40**, 320. B.A.S.F., D.R.P. 138,167; 155,415. M.L.B., D.R.P. 296,841. G.C.I.B., E.P. 113,783 (1918). G.E., D.R.P. 292,127.
[5] B.A.S.F., D.R.P. 157,449. M.L.B., D.R.P. 293,971.
[6] M.L.B., D.R.P. 287,590.
[7] M.L.B., D.R.P. 289,279. G.E., D.R.P. 296,192; 271,947. *Cf.* also M.L.B., D.R.P. 224,500; 240,792; 245,768; 246,867.
[8] B.A.S.F., D.R.P. 168,042. [9] B.A.S.F., D.R.P. 229,166.

to be obtained when indanthrone is suspended in bromine and then treated with chlorine.[1] Halogen indanthrones can also be obtained by boiling the corresponding azines with halogen acid.[2] The reaction in this case is merely the usual addition of a molecule of halogen acid to a quinonoid compound. The resulting monohalogen hydroazine can then be oxidised to the azine and a second atom of halogen introduced in the same way.

The halogen indanthrones are much less easily oxidised to the azine than is indanthrone itself,[3] and consequently the shades obtained by their use are fast to soap. Various halogenated indanthrones have been introduced as vat dyes, of which Indanthrene Blue GCD[4] and Indanthrene Blue GC[5] are the most important. The former consists chiefly of dichlorindanthrone, whereas the latter seems to be a mixture of dibromindanthrone and tribromindanthrone. They are both fast to soap and dye in somewhat greener shades than indanthrone itself.

Hydroxy indanthrones can be synthesised from the corresponding aminohydroxy halogen anthraquinone. Thus 1-amino-4-hydroxy-2-bromanthraquinone when heated with sodium acetate and a contact substance such as cuprous chloride or copper powder gives dihydroxy indanthrone[6] (Algol Blue 3G). Hydroxyl groups can also be introduced into the indanthrone molecule by direct oxidation with a mixture of nitric and sulphuric acids, but nitroso and nitro groups enter at the same time. Thus from indanthrone Scholl and Mansfield[7] obtained a nitrodinitrosotrihydroxy derivative and also a tetranitrotetrahydroxy compound. Both, of course, were azines and on reduction yielded the corresponding triaminotrihydroxy - N - dihydroazine and tetraminotetrahydroxy - N - dihydroazine. Sulphonic acid groups when present in the indanthrone molecule also seem

[1] G.C.I.B., E.P. 113,783 (1918).
[2] Scholl, B. 36, 3436. Scholl and Berblinger, B. 40, 320. By., D.R.P. 147,872.
[3] Scholl and Berblinger, B. 40, 320.
[4] Caledon Blue GCD (Scottish Dyes, Ltd.).
[5] Caledon Blue GC (Scottish Dyes, Ltd.).
[6] By., D.R.P. 193,121.   [7] B. 40, 326.

capable of being replaced by hydroxyl groups. Thus indanthrone sulphonic acid when heated with concentrated sulphuric acid gives a vat dye which dyes in rather greener shades than indanthrone itself and is probably a hydroxy indanthrone. The same dye is obtained by heating indanthrone with sulphuric acid, with or without the addition of boric acid, at a temperature insufficient to cause sulphonation.[1]

Amino indanthrones can be built up from polyamino-anthraquinones by the usual methods, or the amino group can be introduced into the indanthrone molecule by taking advantage of the quinonoid character of the azine. Thus Scholl[2] found that the azine obtained from indanthrone by oxidation reacts with aqueous ammonia at 200° or with boiling aniline and is converted into amino or phenylamino indanthrone. These are vat dyes and dye cotton in greenish shades of blue.

A few *indanthrone sulphonic acids* have been described. They can be obtained from aminoanthraquinone sulphonic acids[3] or by sulphonating indanthrone.[4] They are soluble in water and are acid dyes for wool or silk but are of no importance.

Brief reference may be made to two vat dyes of unknown constitution which have been obtained from indanthrone. One is a greenish-blue dye obtained by condensing indanthrone with formaldehyde in the presence of sulphuric acid.[5] The other is a green dye obtained by treating indanthrone with nitric acid in the presence of nitrobenzene.[6] Neither are of any technical value.

[1] B.A.S.F., D.R.P. 227,790.   [2] B. **36**, 3438.
[3] B.A.S.F., D.R.P. 129,846.
[4] B.A.S.F., D.R.P. 129,847; 216,891; 220,361.
[5] By., D.R.P. 159,942.   [6] By., D.R.P. 198,024.

CHAPTER XVII

MISCELLANEOUS HETEROCYCLIC COMPOUNDS

I. THE PYRIDAZINEANTHRONES

PYRIDAZONEANTHRONE is prepared by treating the ethyl ester or the chloride of anthraquinone-α-carboxylic acid with hydrazine [1] :
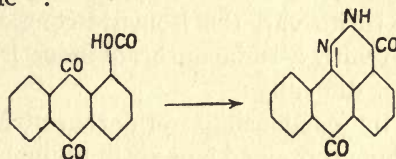
and N-phenylpyridazoneanthrone can be obtained by using phenylhydrazine in place of hydrazine itself.[2] By treating anthraquinone-α-ketones with hydrazine Schaarschmidt [3] has prepared C-arylpyridazineanthrones :
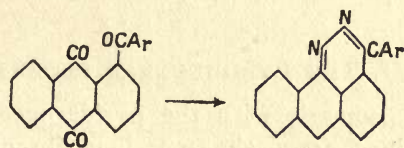
Pyridazineanthrones of more complicated structure are obtained by a similar reaction from the anthraquinone-1.2(N)-acridones,[4] and the anthraquinone-1.2(S)-thioxanthrones,[5] the pyridazine ring being formed by bridging the two carbonyl groups, e.g.

[1] Ullmann, A. **388**, 211 ; B. **44**, 129.
[2] Ullmann, D.R.P. 230,454.
[3] B. **48**, 836.
[4] Ullmann and Sone, A. **380**, 336 ; B. **43**, 537. B.A.S.F., D.R.P. 248,582.
[5] B.A.S.F., D.R.P. 254,097.
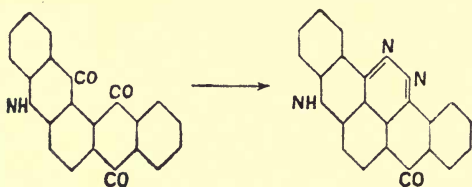
Derivatives of pyridazoneanthrone have been prepared by converting 1-chloranthraquinone-4-carboxylic acid into the pyridazone and then replacing the chlorine atom by an amino, alkylamino, arylamino, or anthraquinonylamino group.[1] They are valueless yellow or brown vat dyes. It is interesting to notice, however, that whereas the anthraquinonylaminopyridazoneanthrone obtained by condensing the above chloro compound with β-aminoanthraquinone is easily reduced to its vat, the isomeric compound obtained by combination with α-aminoanthraquinone is only reduced with the utmost difficulty.

Ullmann[2] by condensing pyridazoneanthrone with α-chloranthraquinone obtained N-α-anthraquinonylpyridazoneanthrone ; but it proved to be of no interest, and although a vat dye its tinctorial properties were extremely feeble. The same remarks apply to the compounds obtained by condensing N-p-bromphenylpyridazoneanthrone with aminoanthraquinone.

II. The Pyrimidoneanthrones

These are isomeric with the pyridazoneanthrones and can be obtained from the α-aminoanthraquinone or α-alkylamino-anthraquinone by treatment with a urethane[3] :
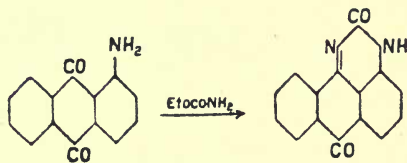
The reaction is a very general one and can be brought about

[1] Ullmann, **A. 388**, 217 ; D.R.P. 248,998.   Agfa, D.R.P. 271,902.
[2] A. **388**, 211.   [3] M.L.B., D.R.P. 205,035.

simply by boiling the amine with the urethane, although the condensation is more rapid in the presence of zinc chloride or other condensing agent. The method can be modified by first converting the α-aminoanthraquinone into its urea chloride or urethane and then treating this with ammonia.[1] A somewhat similar method of preparation consists in heating the α-aminoanthraquinone with an acid amide in an indifferent solvent, pyrimidone ring formation then taking place very readily by loss of two molecules of water.[2] Urea itself acts as an acid amide, but in this case, of course, a molecule of ammonia is lost, the reaction taking place most readily in the presence of copper acetate.[3]

A bipyrimidone compound has been obtained from 1.4-diamino anthraquinone. The pyrimidone derivatives have been very little studied and do not seem to be of any particular interest.

III. The Oxazines

A few yellow vat dyes of ketomorpholine structure have been obtained by boiling *o*-hydroxy chloracetylamino-anthraquinones with dilute aqueous caustic soda solutions of 5 per cent. strength.[4] The formation of the morpholine ring is due to loss of hydrochloric acid, but the resulting compounds are of no particular interest :
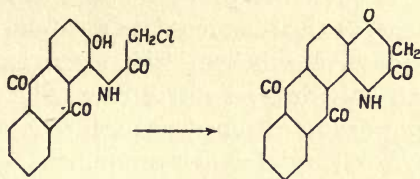
The oxazines themselves are obtained when *o*-hydroxy-arylamino anthraquinones are oxidised by means of manganese dioxide, lead dioxide, chromic acid, oleum, or an organic nitro compound,[5] and consequently are often

[1] By., D.R.P. 225,982.   [2] By., D.R.P. 220,314.
[3] M.L.B., D.R.P. 205,914.   [4] M.L.B., D.R.P. 290,983.
[5] By., D.R.P. 141,575.

produced when reactions which should lead to *o*-hydroxy-arylamino compounds are carried out in the presence of an oxidising agent.　Thus purpurin when boiled with a primary aromatic amine in the presence of boric acid and an oxidising agent such as mercuric oxide or nitrobenzene gives an oxazine.[1]　This method can also be used for preparing oxazines in which the oxazine ring lies between two anthraquinone groups.　Thus 2-methoxy-1.1'-dianthraquinonyl-amine when heated with concentrated sulphuric acid at 170–180° in the presence of boric acid gives an oxazine, the sulphuric acid in this case acting as the oxidising agent.[2]

A somewhat similar reaction also takes place when an *a*-amino anthraquinone is heated with a 1-amino-2-halogen anthraquinone in nitrobenzene solution in the presence of a basic substance such as potassium acetate, and a contact substance such as copper acetate.[3]　In this case the di-anthraquinonylamine is first formed and is then oxidised to the oxazine :
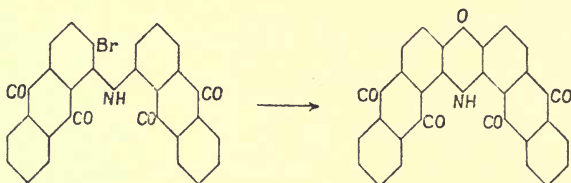
The oxidation is obviously brought about at the expense of the nitrobenzene, as the reaction does not take place if amyl alcohol is used as a solvent.　The same oxazine is also obtained when 2-hydroxy-1-nitroanthraquinone is heated with copper powder in nitrobenzene solution.[4]

If the *o*-hydroxyarylaminoanthraquinone is obtained by heating an *o*-hydroxynitroanthraquinone with a primary aromatic amine, oxazine formation often takes place without the use of an oxidising agent, the necessary oxygen being supplied at the expense of the nitrous acid liberated during the formation of the arylaminoanthraquinone.　Thus an oxazine is obtained when 2-hydroxy-1-nitroanthraquinone

[1] By., 153,770.
[2] M.L.B., D.R.P. 273,444.
[3] M.L.B., D.R.P. 266,945.
[4] M.L.B., D.R.P. 266,946.

is boiled with a primary aromatic amine, and 2.4-dihydroxy-1-nitroanthraquinone undergoes oxazine formation particularly easily under similar conditions.[1]

Alizarin might be expected to condense with *o*-aminophenol to give an oxazine, but this is not found to be the case unless there is an amino or a hydroxyl group present in the anthraquinone molecule at 4. When such a group is present, however, oxazine formation takes place extremely readily, the reaction being brought about by heating under pressure with *o*-aminophenol in alcoholic solution in the presence of boric acid, or in aqueous solution when the aminoanthraquinone contains a sulphonic acid group. According to the patent[2] in which this reaction is described, purpurin gives a hydroxyoxazine which has one of the following formulæ :
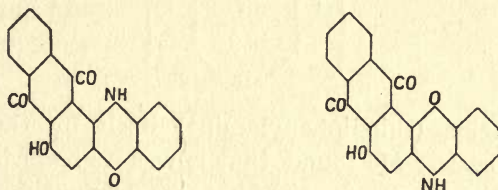
This statement, however, must be accepted with some reserve pending further confirmation, as it seems more probable that a dihydroxyoxazine would be produced.

A very curious case of oxazine formation has been described as taking place when 1-arylamino-2-hydroxy-3-halogen anthraquinones are heated alone or with basic substances.[3] The resulting oxazines contain no halogen, so that oxazine formation seems to be brought about by oxidation at the expense of the halogen atom :

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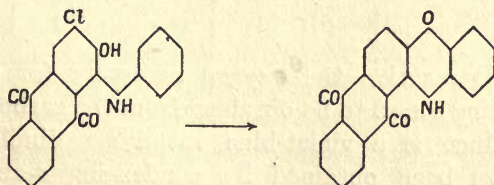
[1] By., D.R.P. 141,575.   [2] M.L.B., D.R.P. 156,477.
[3] By., D.R.P. 153,517.

There is no need to isolate the arylamino compound, as oxazine formation takes place when 3-halogenalizarin is boiled with a primary aromatic amine.

Little or nothing is known of the substituted anthraquinone oxazines, but sulphonic acids can be obtained by sulphonation.[1]

IV. The Thiazines

Very little is known of the thiazines of the anthraquinone series although a few such compounds have been described. Scholl[2] obtained what was probably *lin*-thiodianthraquinonylamine
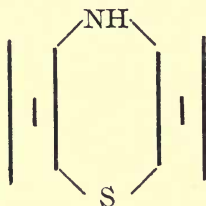
from thiazine (thiodiphenylamine) itself by the phthalic acid synthesis. He found that it was a greenish-blue dye, but that the affinity for the fibre was extremely poor. The same was also found to be the case with the N-methyl derivative. Ullmann[3] found that a thiazine was formed when 2-amino-1.3-dibromanthraquinone was boiled with anthraquinone-α-mercaptan in nitrobenzene solution:
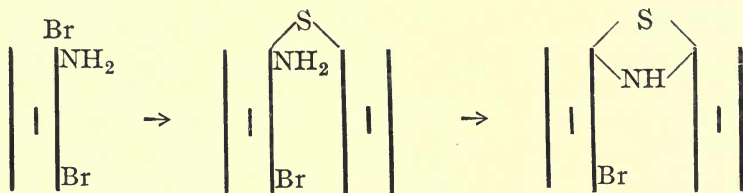
In this reaction the oxygen necessary for closing the thiazine ring seems to be obtained from the carbonyl groups. The product is a violet-blue vat dye. Similar thiazine dyes have been obtained by condensing *o*-aminoanthraquinone mercaptans with halogen anthraquinones, or by

---

[1] By., D.R.P. 141,982.   [2] B. **44**, 1241.   [3] B. **45**, 832.

condensing *o*-aminohalogen anthraquinones with anthra-
quinone mercaptans. In either case thiazine formation can
be brought about by self-oxidation (heating alone or with a
solvent of high boiling point) or by heating with concentrated
sulphuric acid and boric acid.[1] Thiazines are also formed
when an *o*-aminoanthraquinone mercaptan is condensed
with a halogen anthraquinone in which the *ortho*- position
with reference to the halogen atom is occupied by an amino,
methoxy, or carboxyl group, the group being split off during
the condensation.[2]

Thiazine formation takes place very readily, it merely
being necessary to heat the components together in some
suitable solvent such as nitrobenzene, pyridine or naphthalene,
no catalyst or condensing agent being required.

As would be expected a thiazine is also obtained when
1.2-dichloranthraquinone is condensed with 1-aminoanthra-
quinone-2-mercaptan.[3]

A few thiazines containing only one anthraquinone
residue have been prepared. Thus Laube and Libkind [4]
obtained a green vat dye by condensing 1-chlor-2.4-dinitro-
benzene with α-aminoanthraquinone, reducing the nitro
groups and finally fusing the diaminophenylaminoanthra-
quinone with sulphur and sodium sulphide at 150° :

$$NHC_6H_3(NH_2)_2$$

$$\rightarrow$$
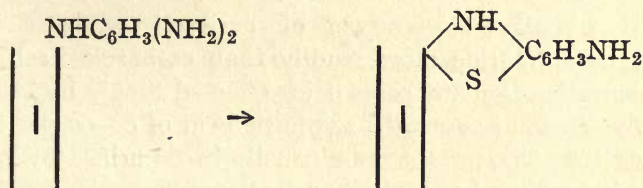
It will be observed that thiazine formation takes place by
loss of an amino group. From β-aminoanthraquinone a
thiazine could not be obtained by this method.

Ullmann [5] has also obtained a thiazine containing only
one anthraquinone residue by condensing 2-amino-1.3-di-
bromanthraquinone with thio-*p*-cresol and then treating

[1] B.A.S.F., D.R.P. 248,169.   [2] B.A.S.F., D.R.P. 266,952.
[3] B.A.S.F., D.R.P. 248,171.   [4] B. **43**, 1730.   [5] B. **49**, 2163, 2165.

the product with formaldehyde and concentrated sulphuric acid :
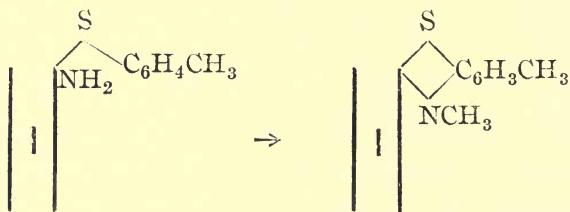
V. THE CARBAZOLS

Compounds in which a pyrrol ring lies between two anthraquinone rings, or between one anthraquinone ring and one benzene ring, are best designated as phthaloyl carbazols. They can be obtained from carbazol by condensation with phthalic anhydride in the presence of aluminium chloride (phthalic acid synthesis, pp. 130–141), carbazol itself giving a diphthaloyl derivative which is probably *linear* in structure although this has not yet been definitely proved [1] :
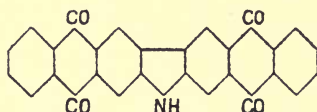
The N-alkyl derivatives of carbazol condense with phthalic anhydride more readily than carbazole itself, the condensation in many cases being effected simply by heating for five to ten hours with sulphuric acid of 80–90 per cent. strength.[2] The products are usually best purified by washing with sodium hypochlorite solution.

Phthaloyl carbazols can also be obtained by building up the pyrrol ring. Thus, 1.1'-diamino-2.2'-dianthraquinonyl when heated with concentrated sulphuric acid loses a molecule of ammonia and passes into the diphthaloyl carbazol [3] :

[1] Scholl, B. **44**, 1249.
[2] Ehrenreich, M. **32**, 1113. Cas., **D.R.P. 261,495**. B.A.S.F., **D.R.P. 275,670**.
[3] M.L.B., **D.R.P. 267,833**.
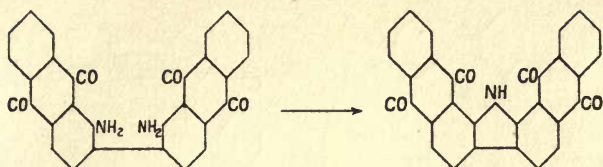
and the same compound is also obtained from 1.1'-dianthraquinonylamine by fusion with aluminium chloride, or by oxidation with sodium hypochlorite.[1] This latter method has also been applied to the preparation of monophthaloyl carbazols, as it has been found that these are obtained by the oxidation of those α-arylaminoanthraquinones in which the *ortho-* position in the aryl group is unoccupied [2]:
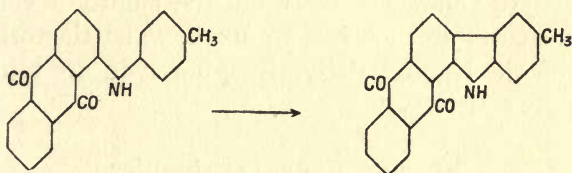
As a rule, the oxidation is effected by means of chromic acid, ferric chloride, or hydrogen peroxide; but if an acylamino group is present in the *para-* position in the anthraquinone nucleus the reaction takes place so easily that the carbazol is formed on heating in the air at ·60–70°.

Monophthaloyl carbazols have also been synthesised by Ullmann [3] by a somewhat different method. He found that the diazotisation of 2-amino-1-arylamino anthraquinones led to osotriazoles, similar compounds also being readily formed by condensing α-chloranthraquinones with aziminobenzene in the presence of potassium and copper acetates. These osotriazoles on heating, preferably in diphenylamine solution, split off nitrogen and pass into monophthaloyl carbazols :

[1] M.L.B., D.R.P. 240,080 ; 251,021 ; 251,350. *Cf.* also 267,522. These compounds were formerly wrongly regarded as complex indanthrones.
[2] By., D.R.P. 288,824.
[3] B. **47**, 380.
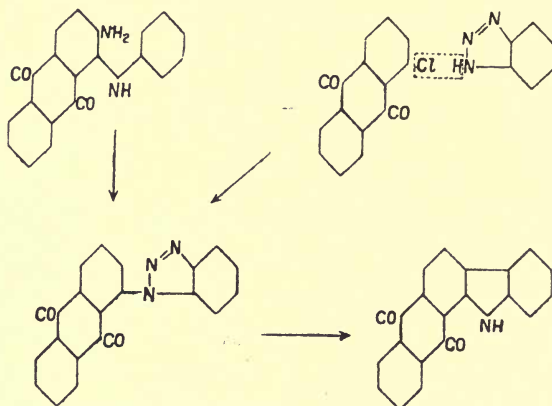
Both the monophthaloyl carbazols and the diphthaloyl carbazols are yellow vat dyes, but the affinity is very poor and the shades are not fast to alkali. The tinctorial properties of the N-alkyl derivatives, however, are said to be much more satisfactory.[1]

VI. THE PYRROLANTHRONES

If an α-arylaminoanthraquinone is condensed with chloracetic acid, a glycine is obtained which passes into a pyrrolanthrone when boiled with acetic anhydride [2] :
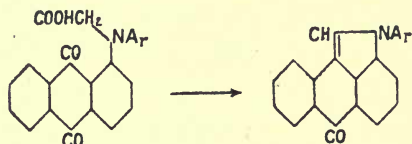
In this case the formation of the pyrrol ring is accompanied by simultaneous loss of carbon dioxide. If the glycine is esterified and the ester then heated with an alkali and an indifferent solvent such as xylene, this loss of carbon dioxide is avoided and a pyrrolanthrone carboxylic acid obtained which can be used as an acid wool dye.[3] If this carboxylic acid is heated with a dehydrating agent such as oleum or chlorsulphonic acid a further loss of water takes place with the formation of a second pyrrol ring :

[1] Cas., D.R.P. 261,495.   [2] M.L.B., D.R.P. 270,789 ; 272,613.
[3] M.L.B., D.R.P. 280,190.
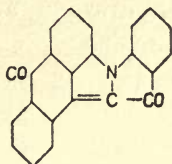
the resulting compound being a red vat dye.[1]

The C-aryl pyrrolanthrones can be obtained by condensing an arylchloracetic acid with an α-aminoanthraquinone and then boiling the product with acetic anhydride [2] :
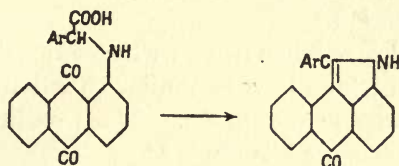
An *indolanthrone* has been obtained by Scholl [3] by nitrating and reducing 3-methyl-1.2-benzanthraquinone, in this case reduction being accompanied by loss of water and formation of a pyrrol ring. The compound thus formed behaves as a true quinone and is readily reduced by sulphurous acid, phenylhydrazine and cold hydriodic acid :
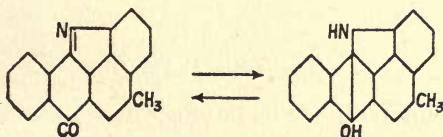
The reduction product is soluble in alkali and is readily oxidised to the indolanthrone by atmospheric oxygen. The indolanthrone can, therefore, be used as a vat dye. It gives violet-brown shades, but the affinity is very poor.

VII. The Pyrrazols

The α-anthraquinonylhydrazines when boiled with water or glacial acetic acid readily lose water and pass into pyrazol compounds,[4] a monopyrazol being obtained

[1] M.L.B., D.R.P. 284,208. [2] M.L.B., D.R.P. 279,198.
[3] B. **44**, 2370 ; M. **32**, 1001. [4] By., D.R.P. 171,293.

from anthraquinone-1-hydrazine and a dipyrazol from anthraquinone-1.5-dihydrazine :
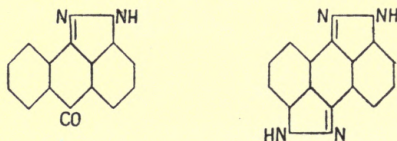
In the case of 1.8-dichloranthraquinone a pyrazol is formed by boiling with hydrazine in pyridine solution, one chlorine atom being unaffected, but it is not certain if this is a general reaction.[1]

Pyrazolanthrone when fused with caustic alkali undergoes a condensation which is very similar to indanthrone formation from aminoanthraquinone. The product is a yellow vat dye which has the structure [2] :
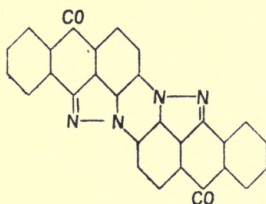
VIII. The Indazols

Anthraquinone indazols having the structure :
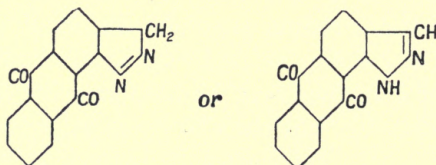
are readily obtained from o-methylanthraquinone diazonium salts. The formation of the pyrazol ring takes place quite readily either by boiling the diazonium sulphate with water, or by heating it to 50° with sodium carbonate, or by treating

[1] Möhlau, B. **45**, 2233, 2244.
[2] G.E., D.R.P. 255,641 ; 301,554 ; 302,259 ; 302,260.

it with cold pyridine. In some cases diazotisation and indazol formation can be combined in one operation, *e.g.* an indazol is formed when 2-methyl-1-aminoanthraquinone is treated with sodium nitrite in boiling glacial acetic acid solution.[1]

The simple indazols have only extremely feeble tinctorial properties, but yellow vat dyes are said to be obtained when they are oxidised by treatment with halogens [2] or ferric chloride.[3] The structure of these oxidation products is unknown, but they are probably formed by the union of two molecules through the carbon atom of the pyrazol ring.

IX. THE IMIDAZOLS

The imidazols are always obtained from *o*-diaminoanthra-quinones and are formed when the acyl derivatives of these substances are heated with dehydrating agents such as sulphuric acid, zinc chloride, or the anhydride or chloride of an organic acid.[4] Imidazol formation therefore takes place when *o*-diamino anthraquinones are boiled for some time with acid chlorides or anhydrides,[5] or when the base is heated with a carboxylic acid in the presence of sulphuric acid.[6] As would be expected the nitrile can be used in place of the carboxylic acid, but it is not certain that in this case imidazol formation is due to the preliminary formation of the carboxylic acid, as according to Schaarschmidt imidazols are often formed under conditions which are insufficient to bring about the hydrolysis of the nitrile.

A variation of the above method has been introduced by Ullmann and Medenwald,[7] who find that 2-acetamino-1-nitroanthraquinone passes directly into the imidazol on reduction with sodium sulphide :

[1] By., D.R.P. 269,842.
[2] By., D.R.P. 268,505.
[3] By., D.R.P. 280,840.
[4] Schaarschmidt, A. **407**, 176.
[5] By., D.R.P. 238,981. *Cf.* Ullmann, A. **380**, 322.
[6] Schaarschmidt, A. **407**, 176. D.R.P. 251,480 ; 254,033.
[7] B. **46**, 1807.
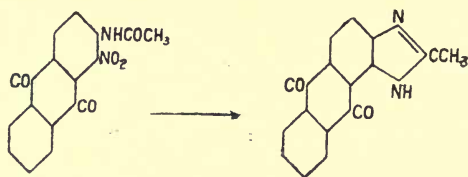
C-Methylanthraquinone-1.2-imidazol.

Another variation consists in heating an *o*-acylamino halogen anthraquinone with a primary aromatic amine in the presence of copper powder. In this case an arylamino group first replaces the halogen atom, the imidazol being then formed by loss of water through the acylamino group reacting in the enolic form [1] :
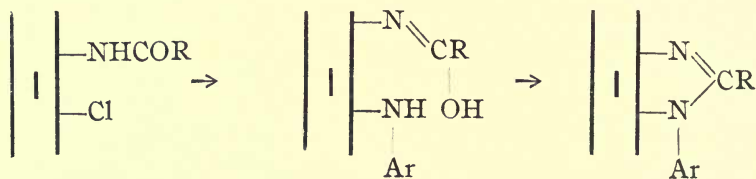
A somewhat different method of preparing imidazols consists in condensing *o*-diaminoanthraquinone with an aliphatic or aromatic aldehyde or with an ω-dichlor compound such as benzalchloride, or, more particularly, ω-dichlor-β-methyl anthraquinone.[2] In this reaction the primary product formed is a dihydroimidazol, but if sulphuric acid is used as a condensing agent this is at once oxidised to the imidazol itself. The dihydroimidazol can, however, be isolated if pyridine is used as a condensing agent. When the aldehyde used is chloral a much more complicated reaction takes place, and blue or black vat dyes of unknown constitution are obtained.[3]

If a ketone is substituted for an aldehyde in the above reaction compounds are obtained which, after sulphonation, can be used as acid wool dyes. The dyes obtained from acetone and acetophenone are red, whereas that obtained

[1] M.L.B., D.R.P. 298,706.
[2] Schaarschmidt, A. **407**, 176. Ullmann, A. **399**, 332. By., D.R.P. 238,982 ; 247,246. B.A.S.F., D.R.P. 261,737.
[3] M.L.B., D.R.P. 284,207.

from anthrone is violet and that from benzophenone blue. Nothing is known of the structure of these dyes, and it is doubtful if they contain the imidazol ring system.[1]

Schaarschmidt [2] has examined the tinctorial properties of a number of anthraquinone imidazols and finds that neither anthraquinone-1.2-imidazol nor anthraquinone-2.3-imidazol has any affinity for the fibre. Slight affinity, however, is shown by those imidazols in which a phenyl group is attached to the carbon atom of the imidazol ring, and the corresponding anthraquinonyl derivatives, the C-anthraquinonyl anthraquinone imidazols, have good affinity.

The majority of the imidazols are yellow, but Schaarschmidt states that C-β-anthraquinonyl-anthraquinone-1.2-imidazol :

$$\text{N} \diagdown \text{C}(\beta)\text{C}_{14}\text{H}_7\text{O}_2 \diagup \text{NH}$$
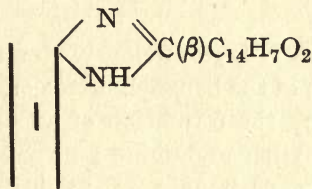
which he prepared in three ways, viz. from 1.2-diaminoanthraquinone and anthraquinone-β-carboxylic acid, anthraquinone-β-nitrile and ω-dichlor-β-methyl anthraquinone, is red, whereas in a patent specification [3] the same substance is described as being prepared from 1.2-diaminoanthraquinone and is stated to be a violet dye.

The only *imidazolon* of the anthraquinone series which has been described up to the present was obtained by Ullmann [4] by treating 1.2-diamino-3-bromanthraquinone with chloroformic ester. It has the formula :

$$\text{NH} \diagdown \text{CO} \diagup \text{NH} \quad \text{Br}$$
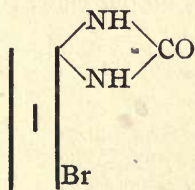
[1] By., D.R.P. 264,290.
[3] B.A.S.F., D.R.P. 261,737.
[2] A. **407**, 176.
[4] A. **399**, 332.

and is a yellow vat dye with good affinity although the shades are very loose to alkali.

X. The Oxazols

Oxazol formation takes place when *o*-hydroxyacylamino anthraquinones are heated with dehydrating agents, β-amino-alizarin, for example, giving an oxazol when boiled with excess of benzoyl chloride [1] :

Oxazol formation is here obviously due to loss of water from the enolic form of the benzoylamino compound, and this view is supported by the formation of an oxazol by loss of nitrous acid when 1-benzoylamino-2-nitroanthraquinone is boiled with sodium carbonate in naphthalene solution,[2] and also by the production of oxazols by the oxidation of acylamino-anthraquinones by lead dioxide in glacial acetic acid solution, or by nitric acid in nitrobenzene solution.[3]

A somewhat similar reaction has been described by Ullmann,[4] who finds that when 2-amino-1.3-dibromanthraquinone is benzoylated very little of the benzoyl derivative is produced, the chief product being an oxazol. In this case it is the bromine atom in the α- position which is lost, the structure of the oxazol being proved by its decomposition into 2-amino-1-hydroxy-3-bromanthraquinone when heated with sulphuric acid of 80 per cent. strength :

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[1] By., D.R.P. 252,839; 259,037. M.L.B., D.R.P. 284,181 ; 288,842.
[2] M.L.B., D.R.P. 286,094. [3] M.L.B., D.R.P. 286,093. [4] A. **339**, 330.

2.6-Diamino-1.3.5.7-tetrabromanthraquinone reacts in exactly the same way and gives a dibromanthraquinone dioxazol.

Oxazols and dihydro-oxazols are also formed by condensing *o*-aminohydroxyanthraquinones with aldehydes, ketones or the corresponding *ω*-dichlor compounds. The reaction is brought about by heating the substances together with or without an indifferent solvent of high boiling point such as nitrobenzene.[1]

XI. THE ISOXAZOLS

Isoxazols of the anthraquinone series in which one or both of the *meso-* carbon atoms form part of an isoxazol ring have been prepared by Freund and Achenbach[2] and by Schaarschmidt.[3] The former investigators found that the oximes prepared from *α*-chloranthraquinones existed in two forms, one of which was unaffected by alkali whereas the other was converted into an isoxazol. By this means they prepared both a mono- and a di-isoxazol :
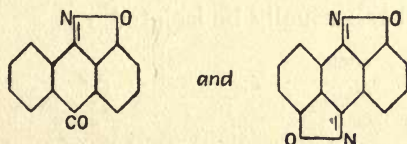
The isoxazols prepared by Schaarschmidt were isomeric with these, and were obtained by boiling anthraquinone-*α*-azides with water. By this means one mono-isoxazol and two di-isoxazols were obtained :
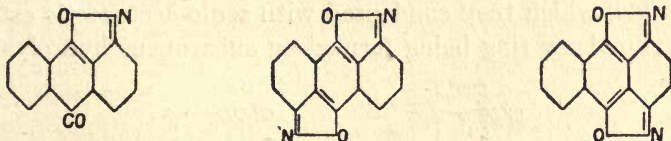
Gattermann[4] also obtained these compounds from the azides but named them "semi-azo" compounds, and suggested, with some reserve, that they contained monovalent

[1] By., D.R.P. 252,839.   [2] B. **43**, 3251.
[3] B. **49**, 1632.   [4] B. **49**, 2117.

nitrogen, although he has offered no evidence whatsoever in support of this view :
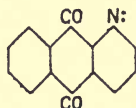
XII. The Thiophenes

The 1(S)-9-thiopheneanthrones have been prepared by Gattermann,[1] who found that the anthraquinonyl-*a*-thioglycollic acids, obtained by condensing anthraquinone-*a*-mercaptans with chloracetic acid, lose water and carbon dioxide when boiled with acetic anhydride. This tendency to form a thiophene ring is greatly enhanced by the presence of a methyl group in the *a*- position to the mercaptan group, and in such cases it is usually impossible to isolate the anthraquinonyl thioglycollic acid owing to the ease with which it passes into the thiopheneanthrone. In these cases, however, the loss of carbon dioxide only takes place slowly, so that the carboxylic acid can usually be isolated, *e.g.* :
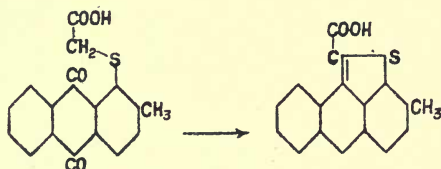
Friess and Schürmann [2] also prepared thiopheneanthrones. Their starting-out substance was anthraquinone-*a*-sulphur chloride, which they condensed with sodio-acetoacetic ester, the thiophene ring being formed on subsequent hydrolysis :
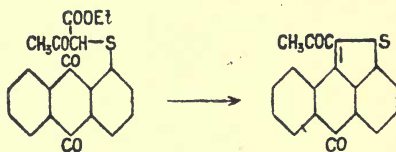
They also found that a thiophene anthrone is produced

[1] A. 393, 122, 190.   [2] B. 52, 2172.

when sodium anthraquinone-α-mercaptide is condensed with
p-hydroxy-ω-chloracetophenone :
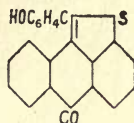
This reaction is by no means a general one, as no thio-
phene derivative is formed from either o-nitrobenzyl chloride
or p-nitrobenzylchloride.

XIII. The Thiazols

Anthraquinone thiazols are obtained from o-acylamino
anthraquinone mercaptans by loss of water, the reaction
being brought about by heating with a suitable dehydrating
agent, such as acetic anhydride or, in many cases, merely
by heating with an indifferent solvent of high boiling point,
such as nitrobenzene.[1] There is no need to isolate the
acylamino mercaptan, as acylation and thiazol formation
take place simultaneously when the amino mercaptan is
heated with a carboxylic acid or its chloride, anhydride,
amide, ester, or nitrile.[2] Even the isolation of the amino
mercaptan can often be avoided, as in many cases thiazols
are formed when o-amino or o-acylamino halogen anthra-
quinones are treated with a sulphide, thiocyanate or other
substance capable of replacing the halogen atom by a mer-
captan group, the reaction being usually best carried out in
pyridine solution.[3]

In the above reactions carbon disulphide would seem to
act to some extent as an acid anhydride, as it has been
claimed [4] that 1-aminoanthraquinone-2-mercaptan when
heated with carbon disulphide in alcoholic solution at 95° is
converted into a thiazol mercaptan in which the mercaptan
group is attached to the carbon atom of the thiazol ring :

[1] By., D.R.P. 250,090.
[2] B.A.S.F., D.R.P. 260,905.
[3] B.A.S.F., D.R.P. 260,905.   M.L.B., D.R.P. 311,906.
[4] By., D.R.P. 250,090.
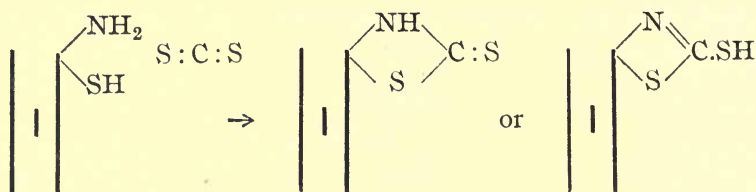
Thiazol formation also takes place when *o*-aminoanthraquinone mercaptans are condensed with an aldehyde or the corresponding ω-dichlor compound.[1] The reaction is brought about by heating in a suitable solvent and is exactly analogous to the formation of oxazols from *o*-aminohydroxyanthraquinones mentioned on p. 369, and to the formation of imidazols from *o*-diaminoanthraquinones (p. 366). As in the case of the oxazols, dihydro compounds (thiazolines) are often formed, this, of course, always being the case when a ketone is substituted for an aldehyde.[2]

Somewhat similar to the above methods is the formation of thiazols from *o*-aminohalogenanthraquinones by means of thiolbenzoic acid [3] :
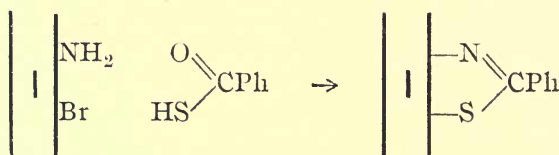
The reaction takes place extremely easily, but the method has the disadvantage that the thiol acids are troublesome to prepare and are apt to react with other groups present in the molecule. Thus, 2-amino-1.3-dibrom anthraquinone gave the anthraquinone thiazol disulphide :
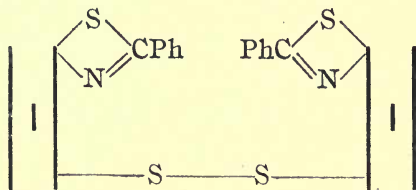
[1] By., D.R.P. 252,839; 259,037. B.A.S.F., D.R.P. 260,905.
[2] M.L.B., D.R.P. 253,089.
[3] Ullmann, A. **399**, 345. D.R.P. 254,743.

Benzyl and benzylidene aminoanthraquinones in which an *ortho-* position, which is preferably also an α- position, with reference to the amino group is vacant pass into thiazols when fused with sulphur.[1]   Here again there is no need to isolate the benzyl or benzylidene derivative as the reaction can be carried out by heating the amine with benzalchloride or benzo-trichloride, preferably in the presence of an indifferent solvent such as naphthalene.[2]

bis-Thiazolines in which the two molecules are joined by the carbon atoms of the thiazoline rings can be obtained by fusing the *o*-acetamino chloranthraquinones with sulphur,[3] or by treating the *o*-aminoanthraquinone mercaptans with oxalyl chloride.[4]   They are vat dyes and have the structure
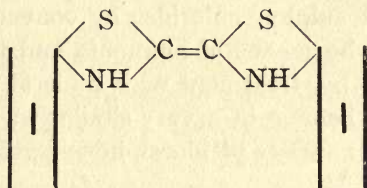
but have not been studied in detail.

A series of vat dyes giving red, bordeaux or violet shades has been described [5] as being obtained by heating 2-methyl-1-aminoanthraquinone with sulphur and an aromatic monamine or diamine.   The patents give no information as to the structure of these substances, but it is quite possible that they are complex thiazols.

XIV.   The *iso*-Thiazolanthrones

The *iso*-thiazolanthrones are formed when an anthraquinone mercaptan is heated with ammonia and a polysulphide,[6] and   consequently can be obtained by heating any suitable α-substituted anthraquinone, such as an α-chloranthraquinone, an anthraquinone-α-sulphonic acid, or

[1] Ullmann, A. **399**, 345.   Agfa, D.R.P. 229,165 ; 232,711–2 ; 233,072.
[2] B.A.S.F., D.R.P. 264,943 ; 267,523.
[3] B.A.S.F., D.R.P. 280,882.   [4] B.A.S.F., D.R.P. 280,883.
[5] Cas., D.R.P. 283,725 ; 287,005 ; 287,523.   [6] By., D.R.P. 216,306.

an α-anthraquinonyl xanthate, with an alkali polysulphide and ammonia. The α-anthraquinonyl thiocyanates are particularly suitable as starting-out substances as they pass into the *iso*-thiazolanthrone on heating with ammonia at 140°, preferably in alcoholic solution, no polysulphide being required.[1] By their use Gattermann has prepared one mono and two isomeric dithiazols :
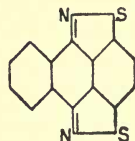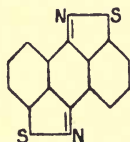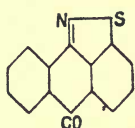
iso-Thiazolanthrones can also be prepared from the anthraquinone-α-sulphur chlorides by converting these into the sulphamide by means of ammonia and then closing the *iso*-thiazol ring by treatment with mineral acids.[2] The α-sulphochlorides behave in a very similar way, as the corresponding sulphonamides yield sulphone *iso*-thiazolanthrones by loss of water [3] :

The *iso*-thiazols are pale yellow substances which are of no particular interest. The *iso-selenazolanthrones* have also been described.[4] They are obtained by treating the anthraquinone-α-selenocyanides [5] with ammonia.

XV. CŒROXENE DERIVATIVES

When pyrogallol is condensed with phthalic anhydride a pyronine dye, galleïn, is produced which forms a monomethyl ester, isomeric colourless and coloured tetramethyl

[1] Gattermann, A. **393**, 123, 192. By., D.R.P. 217,688.
[2] Friess and Schürmann, B. **52**, 2172.
[3] Ullmann, B. **52**, 545.
[4] By., D.R.P. 264,139.
[5] By., D.R.P. 256,667.

derivatives, a tetra-acetyl derivative, and a compound with three molecules of phenyl *iso*-cyanate.[1] There can be no doubt that this substance has the ordinary pyronine dye structure, the coloured tetramethyl compound being derived from the quinonoid form (I), and the colourless tetra-alkyl derivative from the lactone form (II) :

I   II
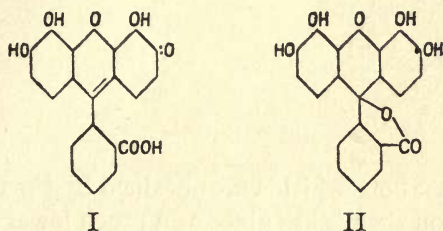
When galleïn is heated with concentrated sulphuric acid at 190–200° a molecule of water is lost and a new dye, cœruleïn (Alizarin Green, Anthracene Green), is obtained.[2] This forms a triacetate, two monomethyl ethers which are soluble in caustic alkali, and a trimethyl ether which is insoluble in caustic alkali. The carboxyl group present in galleïn seems to have disappeared so that the new dye is no doubt represented by formula III :

III
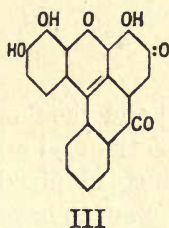
This, it will be seen, contains the anthrone ring system, and the formation of similar compounds, cœroxenes, from other pyronine dyes has been recorded.[3]

[1] Orndorff and Brewer, Am. **23**, 425 ; **26**, 96.
[2] Baeyer, B. **4**, 595, 663. Buchka, A. **207**, 272 ; B. **14**, 1329. Most of Buchka's work has been contradicted by Orndorff and Brewer, Am. **23**, 425 ; **26**, 96.
[3] M.L.B., D.R.P. 86,225. *Cf.* By., D.R.P. 196,752.

Very similar to the above synthesis is the preparation of the highly coloured cœroxonium sulphate (IV) by Decker [1] by heating fluorane with concentrated sulphuric acid :

IV
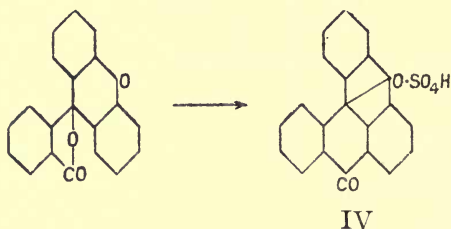
In this case better yields are obtained by the use of oleum, as the reaction then takes place at a much lower temperature and sulphonation is avoided.

A third method [2] of preparing cœroxonium salts consists in heating the aryl ethers of erythrohydroxyanthraquinone with sulphuric acid of 70 per cent. strength, or with zinc chloride at 160-180° :
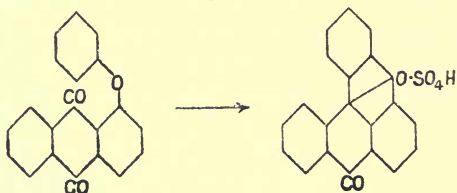
Both the α-naphthyl and the β-naphthyl ethers react in the same way, as do also the aryl ethers of di-α-hydroxyanthraquinone. The products obtained from these dihydroxyanthraquinones do not seem to have been studied in detail, and Decker does not state whether they contain one or two pyronine rings, neither is it clear whether he prepared them from quinizarin or anthrarufin or both.

The cœroxonium salts are highly coloured, but on neutralisation or when their solutions are sufficiently diluted

[1] A. **348**, 214, 223.
[2] Laube, B. **39**, 2245.   Decker, A. **348**, 232, 245.   By., D.R.P. ₁86,882.

with water the colourless carbinol base, cœroxonol, formula
V, is obtained :
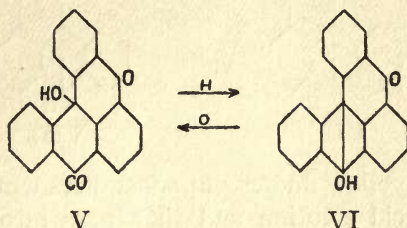
These carbinols are decomposed by light and atmo-
spheric oxygen, but when boiled with alcohol, or when the
cœroxonium sulphate is recrystallised from alcohol,[1] the
corresponding ethyl ether is obtained, and this is much more
stable.

On reduction [2] with zinc dust and acetic acid or am-
monia, stannous chloride or cold hydriodic acid, the carbinol
base first passes into the cœroxenol, formula VI. These
coeroxenols are soluble in caustic alkali, and do not form
salts with acids. They are rapidly re-oxidised to the
carbinol base by atmospheric oxygen, and hence are best
isolated in the form of their stable acetyl derivatives. They
can also be obtained direct from the phenyl xanthene
carboxylic acids by loss of water, the reaction being effected
by concentrated sulphuric acid at the ordinary temperature
or, more rapidly, at 100° :
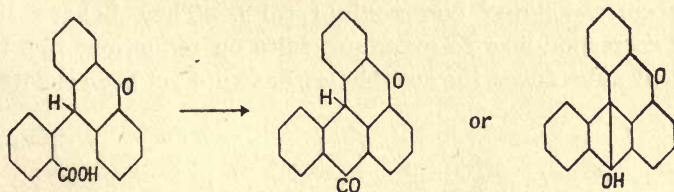
Further reduction of the cœroxenols by boiling with
hydriodic acid and phosphorus leads to the parent com-
pounds, the cœroxenes, formula VII :

[1] Laube, B. **39**, 2245.
[2] Laube, B. **39**, 2245.   Decker, A. **348**, 217.
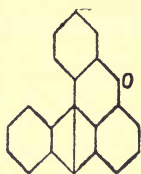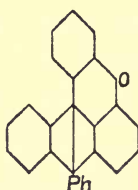
VII   VIII

These are yellow fluorescent substances which are readily oxidised in acid solution and then pass into cœroxonium salts. By treating the ethyl-ether of cœroxonol with magnesium phenylbromide, 10-phenyl cœroxene, formula VIII, has been obtained, simultaneous reduction taking place. This is a very stable fluorescent yellow substance.

XVI. THE CŒRTHÏENE DERIVATIVES

Cœrthionium salts are obtained when α-anthraquinonyl aryl sulphides are heated for thirty hours at 160° with sulphuric acid of 70 per cent. strength.[1] The dianthraquinonyl sulphides also undergo a similar reaction although as a rule more vigorous treatment is required, *e.g.* heating to 150–180° with concentrated sulphuric acid. In some cases, however, the reaction takes place extremely easily and may take place with evolution of heat under the influence of sulphuric acid monohydrate at the ordinary temperature.[2]

The cœrthionium salts are more highly coloured than the corresponding cœroxonium salts. They behave like the corresponding cœroxonium salts on reduction, but the parent substances, the cœrthïenes, have not yet been isolated:

Cœrthionium salt.   Cœrthionol.   Cœrthienol.

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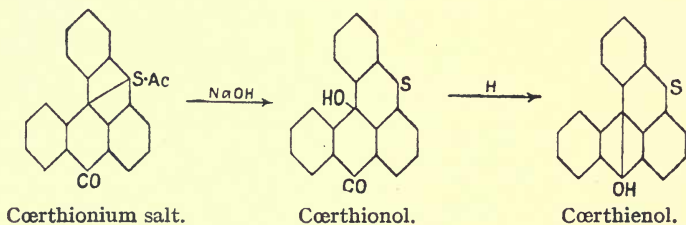
[1] Decker and Würsch, A. **348**, 238. By., D.R.P. 186,882.
[2] By., D.R.P. 252,530.

XVII. The Cœramidine Derivatives

Cœramidines can be obtained by treating α-arylamino anthraquinones with suitable dehydrating agents, such as sulphuric acid of 60–80 per cent. strength at 150°, crystallised phosphoric acid at 200° or zinc chloride in glacial acetic acid, and when a 1.4- or 1.5-diarylamino anthraquinone is used compounds can be obtained in which two acridine ring systems are present [1] :
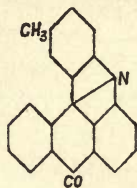
| From 1-tolylamino anthraquinone. Yellowish-brown. | From 1.4-ditolylamino anthraquinone. Dark red. | From 1.5-ditolylamino anthraquinone. Dark blue. |
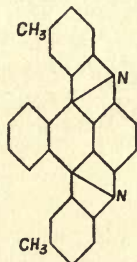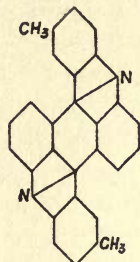
1.1′-Dianthraquinonylamine and 1.2′-dianthraquinonylamine also give cœramidine derivatives when treated with dehydrating agents, the products being yellow or orange vat dyes.[2] The reaction is a very general one and has been applied to the preparation of complex compounds from α-anthraquinonylamino acidrone and from α-anthraquinonylamino thioxanthone.[3] It has also led to the preparation of cœramidine carboxylic acids from α-arylamino anthraquinone carboxylic acid, but when the carboxyl group is in the *ortho*-position to the arylamino group acridone formation takes place simultaneously and, as would be expected, the acridone is usually the predominant product.[4]

The simplest cœramidine can also be prepared by condensing phthalic acid with diphenylamine in the presence of zinc chloride,[5] converting the resulting acridyl benzoic acid into its acid chloride, and finally treating this with aluminium chloride [6] :

[1] By., D.R.P. 126,444.   [2] By., D.R.P. 239,544.   [3] Agfa, D.R.P. 258,808.
[4] By., D.R.P. 262,469.   [5] Bernthsen, A. **224**, 45.   [6] Dammann and Gattermann, F.T. **1**, 325.   *Cf.* Decker and Schenk, A. **348**, 242.
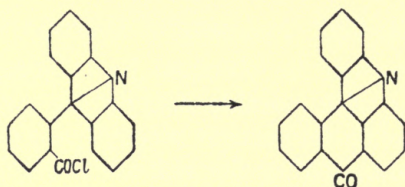
When treated with dimethyl sulphate this gives the quaternary ammonium sulphate from which caustic alkali liberates the carbinol base, N-methylcœramidonol [1] :
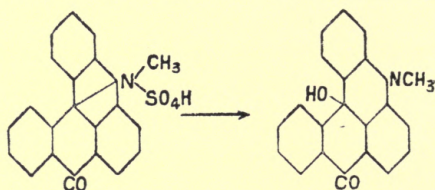
XVIII. MISCELLANEOUS COMPOUNDS

Anthraquinone-α-sulphochloride when treated with hydrazine yields a sulphohydrazine [2] :
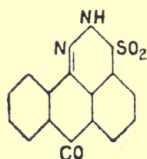
Anthrone condenses with true *p*-quinones such as benzo-quinone or chloranil to give blue or green vat dyes.[3] The reaction is brought about by boiling in some indifferent solvent such as nitrobenzene or xylene, but it is doubtful if the dyes obtained are single substances. For the blue dye obtained from anthrone and *p*-benzoquinone the patentees suggest the formula
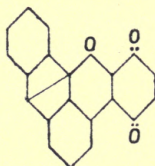
[1] Decker and Shenk, A. **348**, 242.   [2] Ullmann, B. **52**, 545.
[3] M.L.B., D.R.P. **251,020** ; 267,417.

Oxazoneanthrones are obtained when anthraquinone-α-carboxylic acids are warmed with hydroxylamine in aqueous solution [1]:
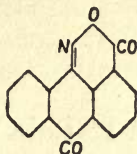
An anthraquinonyl thioglycollic acid can be obtained either by condensing 1-alkyl (or aryl) amino-2-chloranthraquinone with thioglycollic acid or its ester, chloride or amide, or by condensing 1-alkyl (or aryl) aminoanthraquinone-2-mercaptan with chloracetic acid. Such anthraquinonyl thioglycollic acids when heated alone or in an indifferent solvent, with or without the addition of a condensing agent such as phosphorus pentachloride, zinc chloride or thionyl chloride, pass into orange or brownish-red vat dyes [2]:
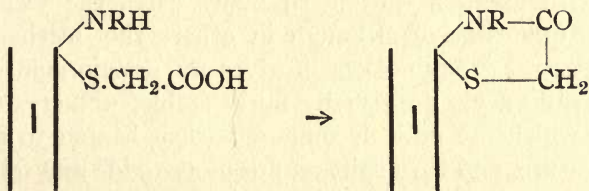
When an anthraquinone mercaptan is condensed with a hydroxyanthraquinone by treatment with concentrated sulphuric acid at 160°, compounds are obtained which probably have the structure :
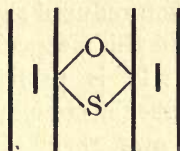
Instead of the mercaptan the disulphide, thiocyanate or xanthate can be used. The products are usually red vat dyes.[3]

[1] Ullmann, A. **388**, 211; B. **44**, 129.   [2] By., D.R.P. 232,076.
[3] By., D.R.P. 235,094.

CHAPTER XVIII

MISCELLANEOUS COMPOUNDS

I. ARSENIC COMPOUNDS

VERY little is known of the arsenic derivatives of anthraquinone, although a few compounds have been described by Benda.[1] The aminoanthraquinones are not arsinated when heated with arsenic acid,[2] but the anthraquinone arsinic acids can be readily obtained from the amino compounds by Bart's method, *i.e.* by treating the diaozonium salts with alkali arsenite. In many cases the yields are almost quantitative although in others the method fails completely, *e.g.* aminoalizarin gives no arsinic acid at all. The arsinic acids are usually fairly stable, well-crystallised bodies which are only decomposed when heated to a high temperature, and then split off arsenious oxide and form the hydroxyanthraquinone. They differ from the arsinic acids of the benzene series by being precipitated in the cold both by magnesia mixture and by calcium chloride. They can be nitrated but with some difficulty, it being necessary to employ a large excess of nitrating acid.

The arsinic acids when reduced show a great tendency to split off their arsenic, and this is especially true of the anthraquinone-α-arsinic acids. It is probably to this tendency to liberate inorganic arsenic compounds that the anthraquinone arsinic acids owe their great toxidity. If the reduction is carried out with sodium hydrosulphite arsenoanthraquinols are formed. These in caustic alkali solution are very rapidly reoxidised by the air to the arsinic acids, and in this way differ from the arseno compounds of the benzene

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[1] J. pr. [2] **95**, 74.   [2] Bechamp, C. r. **56**, 1172.

series which under similar conditions only form arsenoxides, the use of hydrogen peroxide or iodine being necessary in order to convert an arseno benzene into the corresponding arsinic acid. The anthraquinone arsenoxides can, however, be obtained by oxidising the arsenoanthraquinols in sodium carbonate solution by atmospheric oxygen. Oxidation by hydrogen peroxide converts these into the arsinic acid, whereas when reduced with sodium hydrosulphite they revert to the arsenoanthraquinols.

II. ACEANTHRENEQUINONES

By the action of oxalyl chloride on anthracene in the presence of aluminium chloride Liebermann and Zsuffa [1] obtained aceanthrenequinone (I), the structure being proved by the fact that oxidising agents convert it into anthraquinone-α-carboxylic acid :
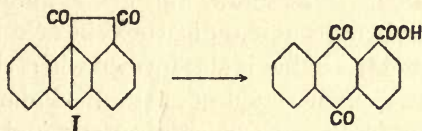
At a later date the same investigators described several substituted aceanthrenequinones,[2] and Liebermann, Kardos and Mühle [3] by the action of oxalyl-chloride on dianthryl obtained similar compounds, the diquinone (II) and the monoquinone dicarboxylic acids (III) being the most interesting compounds obtained, although dianthryl tetracarboxylic acid was also formed :
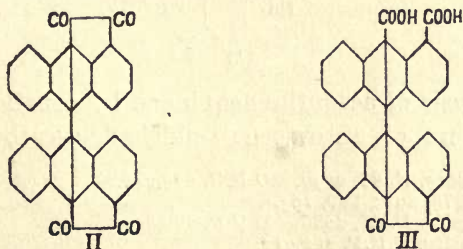
[1] B. **44**, 202.   [2] B. **44**, 852, 1213 ; **45**, 1187, 1213.   [3] B. **48**, 1648.

The action of malonyl chlorine on anthracene [1] is very similar to that of oxalyl chloride and leads to anthracene 1.9-indandion, but according to Freund and Fleisher [2] the reaction in the case of dimethyl malonyl chloride takes a different course and leads to either IV or V, from which the corresponding anthraquinone can be obtained by oxidation :
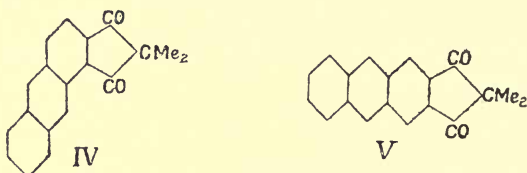
Aceanthrenequinone gives a monoxime [3] which is capable of dyeing wool yellow from an acid bath.   If this monoxime is treated with concentrated sulphuric acid, or with hydrochloric acid gas, glacial acetic acid and acetic anhydride, it is converted into anthracene-1.9-dicarboxylic acid and its monamide and cyclic imide.[4]   The amide and cyclic imide can also be obtained from anthracene-1.9-dicarboxylic acid by the action of ammonia, and the imide is also formed when the monoxime of aceanthrene quinone undergoes the Beckmann rearrangement.[5]   When fused with caustic potash and the solution subsequently oxidised by exposure to the air a green vat dye is obtained which has been named aceanthrene green [6] and probably has the structure represented by formula VI :
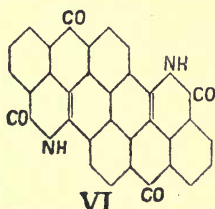
Hydrolysis of aceanthrenequinone by caustic soda leads to a mixture of anthracene-1-aldehyde-9-carboxylic acid,

[1] Kardos, B. **46**, 2090.   D.R.P. 275,248.
[2] A. **373**, 291 ; **399**, 193.
[3] Kardos, B. **46**, 2086.   D.R.P. 280,839.
[4] Kardos, D.R.P. 282,711.
[5] Kardos, B. **46**, 2086.
[6] Kardos, B. **46**, 2086.   D.R.P. 275,220 ; 278,660 ; 284,210.

the anhydride of anthracene-1.9-dicarboxylic acid and anthracene hydroxydion (VII or VIII). This latter gives a monoxime from which a cyclic imide (IX or X) can be obtained by the Beckmann rearrangement. The cyclic imide on fusion with caustic potash gives a green vat dye (XI or XII) which has been named *iso*-aceanthrene green.[1]
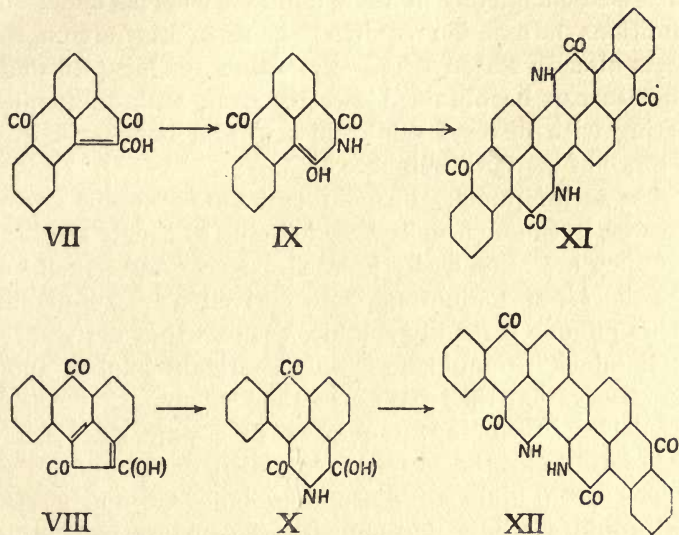
III. Diazonium Salts

Primary amino-anthraquinones can usually be diazotised in suspension in dilute sulphuric acid by dissolving the amine in concentrated sulphuric acid and then precipitating by the addition of water. The majority of the acid is then removed by filtration and the precipitate, without drying or washing, suspended in water and treated with sodium nitrite.[2] In most cases, however, it is much better to carry out the diazotisation in concentrated sulphuric acid solution by slowly adding a solution of sodium nitrite in the same solvent. In some cases the reaction takes place rapidly, but in others it is rather slow, so that as a rule it is best to allow

[1] Liebermann and Kardos, B. **47**, 1203.   [2] Lauth, C. r. **137**, 662.

the solution to stand in the ice chest overnight. Benda [1] finds that a large number of primary aminoanthraquinones are most easily diazotised by dissolving in concentrated sulphuric acid and then rapidly adding a large excess of nitrosyl sulphuric acid, no artificial cooling being used. By this means he claims that β-aminoanthraquinone can be diazotized completely in a few minutes, whereas under other conditions the reaction requires 12 hours to become complete.[2]

As already stated 1-hydroxy-anthraquinone-4-diazonium sulphate can be obtained directly from anthraquinone by heating with nitrosyl sulphuric acid and boric acid in the presence of mercuric sulphate.[3]

The anthraquinone diazonium salts are sometimes soluble in water, but more usually they are only sparingly soluble, so that they are often easily isolated. Kacer and Scholl [4] find that the *bis*-diazonium sulphate derived from 1.8-diaminoanthraquinone is readily soluble, whereas that derived from 1.5-diaminoanthraquinone is only sparingly soluble, and on this observation they base a method of preparing 1.5- and 1.8- derivatives of anthraquinone in a pure state from a crude mixture of the corresponding nitro compounds.

The anthraquinone diazonium salts are fairly stable bodies and are only decomposed by comparatively drastic treatment. Thus, 1-hydroxyanthraquinone-4-diazonium sulphate is only converted into quinizarin when heated to 170–180° with concentrated sulphuric acid.[5] Anthraquinone-1-diazonium sulphate chars if slowly heated, and only explodes feebly if rapidly heated.[6] Even anthraquinone-1.5-*bis*-diazonium sulphate only explodes when heated to 172°. The α-diazonium salts are somewhat more stable than the corresponding β- compounds.[7]

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[1] J. pr. [2] **95**, 76.

[2] Detailed directions for diazotising a large number of aminoanthraquinones will be found in the following papers and patents. Benda, J. pr. [2] **95**, 76. Böttger and Petersen, A. **160**, 151 ; **166**, 149. Gattermann, A. **393**, 132, 149. Kacer and Scholl, B. **37**, 4185. Lauth, C. r. **137**, 662. Schaarschmidt, A. **405**, 115. B. **49**, 2678. Scholl, M. **32**, 708. Ullmann and Conzetti, B. **53**, 828. By., D.R.P. 131,538.

[3] By., D.R.P. 161,954. See also p. 261.

[4] B. **37**, 4185.   [5] By., D.R.P. 161,954.

[6] Kacer and Scholl, B. **37**, 4185.   [7] Schaarschmidt, B. **49**, 2678.

The diazonium group can be replaced by other atoms or groups by the usual methods, the yields usually being satisfactory. It should be noted, however, that the action of cuprous salts sometimes has a tendency to produce dianthraquinonyls.[1] According to Schaarschmidt[2] 1-chloranthraquinone-4-diazonium chloride when warmed gives a nitrogenous, chlorine free product. To this he gives the formula $C_{14}H_6O_2 \underset{O}{\overset{N_2}{\diagup\!\!\!\diagdown}}$, but further confirmation is necessary before this can be accepted. When anthraquinone-2-diazonium sulphate is heated with ammonia a product is obtained which contains 6·11 per cent. of nitrogen. Owing to the meagre information given in the patent[3] it is hardly possible to hazard a guess at the structure of this body, if indeed it is a single substance, but nitrogen content corresponds to that required by hydroxy azoanthraquinone. The diazonium sulphates also give nitrogenous condensation products with primary aromatic diamines[4] and with primary aminoanthraquinones.[5] In the former case at least nitrogen is evolved during the condensation, and in the latter case the products are yellow or orange vat dyes.

IV. Azo, Azimino, and Azoxy Compounds

Hydroxy and amino *azo compounds* can be obtained by coupling anthraquinone diazonium salts with phenols or aromatic amines in the usual way but are of no interest.[6] Azo compounds are also formed when either α-amino anthraquinone or β-aminoanthraquinone is oxidised with bleaching powder.[7]

The o-amino azo compounds when oxidised, especially when oxidised with chromic acid, give triazols,[8] *e.g.* :

[1] B.A.S.F., D.R.P. 215,006.
[2] B. **46**, 2678. [3] M.L.B., D.R.P. 253,238.
[4] M.L.B., D.R.P. 246,085. [5] M.L.B., D.R.P. 255,340.
[6] Lauth, C. r. **137**, 662. Kauffler, F.T. **2**, 469. *Cf.* also G.E., D.R.P. 245,973; 250,274.
[7] M.L.B., D.R.P. 247,352.
[8] G.E., D.R.P. 238,253; 245,191; 250,274; 253,088. M.L.B., D.R.P. 245,191.

$$C_{10}H_6\genfrac{[}{]}{0pt}{}{[\alpha]N:NC_{14}H_7O_2}{[\beta]NH_2} \quad \rightarrow \quad C_{10}H_6\overset{N}{\underset{N}{\diagup\!\!\diagdown}}NC_{14}H_7O_2$$
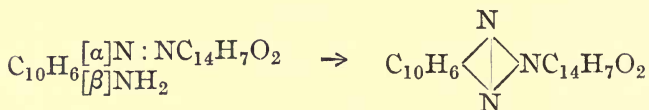
Some of these have been claimed as vat dyes, but they are of no practical importance. They are also formed when the *o*-amino azo compounds are heated with a metallic catalyst, such as copper or iron, and a suitable solvent such as nitro benzene,[1] and when *o*-diamino anthraquinones are treated with nitrous acid.[2]

Aximino compounds (azides) are obtained when diazonium salts are treated with sodium azide,[3] and Gattermann[4] has prepared α-aziminoanthraquinone by treating anthraquinone-α-diazonium sulphate with hydroxylamine and then causing loss of water from the resulting diazo-hydroxyamino compound by treatment with acetic anhydride :

$$C_{14}H_7O_2N_2HSO_4 \rightarrow C_{14}H_7O_2N:N.NHOH \rightarrow C_{14}H_7O_2N\overset{N}{\underset{N}{\diagup\!\!\|}}$$
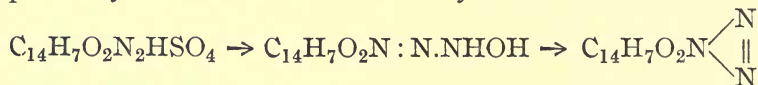
The β-aziminoanthraquinones are more stable than the α-azimino compounds, these latter when heated losing a molecule of nitrogen and passing into oxazols,[5] although Gattermann[6] has suggested that the product formed is a " semiazo " compound containing monovalent nitrogen :

Oxazol.   " Semiazo " compound.
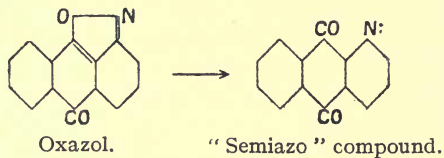
There seems to be no justification for the " semiazo " formula which Gattermann has never developed since he proposed it in a " Preliminary Note."

Very little is known of the *azoxy anthraquinones*, although

[1] G.E., D.R.P. 273,443.   [2] By., D.R.P. 254,745.
[3] Schaarschmidt, B. **49**, 1632.   [4] B. **49**, **2117**.
[5] Schaarschmidt, B. **49**, 1632. See also p. 369.
[6] B. **49**, **2117**.

Scholl [1] obtained β-azoxyanthraquinone by reducing β-nitroanthraquinone with glucose and caustic soda.

V. Hydroxylamines, Hydrazines, and Hydrazo Compounds

Hydroxylamines can be obtained by the alkaline reduction of nitroanthraquinones either by sodium stannite [2] or by glucose and caustic soda,[3] although they are not easy substances to prepare owing to the tendency of the reduction to go too far. Hydroxylamines are also formed by reducing nitro compounds with a solution of sulphur in oleum, but in this case they are extremely difficult to isolate owing to the acid causing a very rapid rearrangement to the amino hydroxy compound.[4] Phenyl hydrazine can also be used as a reducing agent, and by this means R. E. Schmidt and Gattermann [5] were able to confine the reduction to one nitro group in the case of 1.5-dinitroanthraquinone and 1.8-dinitroanthraquinone. The hydroxylamines are of very little interest. They are usually orange or red in colour, but give intensely green solutions in alkali. On oxidation with ferricyanide they give the nitroso- compound, and on reduction in alkaline solution the primary amine. Acids rapidly rearrange them into aminohydroxyanthraquinones.

Hydrazines can be obtained by the reduction of the anthraquinone diazonium salts. The diazonium salts themselves are not particularly easily reduced, so that it is best first to prepare the sulphonic acid by treating the diazonium sulphate with sodium sulphite, and then to reduce this to the hydrazine sulphonic acid by treatment with stannous chloride, sodium hydrosulphite or sulphurous acid.[6] Use of sulphurous acid as a reducing agent, however, often leads to

[1] M. **32**, 1040.
[2] R. E. Schmidt and Gattermann, B. **29**, 2934. *Cf.* By., D.R.P. 100,137; M.L.B., D.R.P. 135,409.
[3] Scholl, M. **32**, 1033. Wacker, B. **35**, 666.
[4] By., D.R.P. 119,229. See also p. 244.
[5] B. **29**, 2934.
[6] Möhlau, B. **45**, 2233, 2244. By., D.R.P. 163,447

the entrance of a second sulphonic acid group, a hydrazine-$\alpha\beta$-disulphonic acid being produced. The hydrazines themselves are readily prepared from the sulphonic acids by hydrolysis with dilute hydrochloric acid.

Hydrazines can also be prepared by condensing halogen anthraquinones with hydrazine, the reaction being best carried out in the presence of pyridine.[1] As would be expected halogen atoms when in α- positions react most easily. Thus, 1.5-dichloranthraquinone when boiled with hydrazine in pyridine solution gives 1-chloranthraquinone-5-hydrazine, and when heated with hydrazine in pyridine solution at 145° it yields anthraquinone-1.5-dihydrazine. 2.6-Dichloranthraquinone only reacts with hydrazine in pyridine solution at 170°, and then gives anthraquinone-2.6-dihydrazine. It should be noted that in the preparation of α-hydrazines by this method there is always a chance of the cyclic carbonyl group becoming involved in the reaction. Thus, 1.8-dichloranthraquinone when boiled with hydrazine in pyridine solution gives a pyrazol.

The anthraquinone hydrazines show much the same reactions as other aromatic hydrazines, and readily condense with aldehydes and ketones to form hydrazones. Many of these hydrazones when derived from aromatic aldehydes or ketones have tinctorial properties, but vat dyes are only produced when there is at least one hydroxyl group present in the aryl group.[2] When this is the case the hydrazones are capable of dyeing cotton either from a hydrosulphite vat or from their solution in sodium sulphite. The hydrazone formed from anthraquinone-1.5-dihydrazine with p-hydroxybenzaldehyde gives greenish-blue shades, blueish-red shades being obtained with the hydrazone derived from m-hydroxybenzaldehyde, and blue shades with that from 2.4-dihydroxyacetophenone. The corresponding hydrazones derived from anthraquinone-2.6-dihydrazine give brown shades.

Both α- and β-anthraquinone hydrazines form hydrazones when treated with acetoacetic ester. When heated with acetic anhydride the β-hydrazone loses water and undergoes

[1] **Möhlau**, B. **45**, 2245.   [2] M.L.B., D.R.P. 256,761

pyrazalon formation in the normal way. The α- compound, on the other hand, does not, but when heated with a mixture of acetic anhydride and sulphuric acid is converted into a pyrazol, acetoacetic acid being split off.[1]

The hydrazine sulphonic acids have tinctorial properties and are capable of being used as acid wool dyes, although these are of no technical importance. Thus, anthraquinone-1.8-di-hydrazine-β-sulphonic acid, $C_{14}H_6O_2[1.8](NH.NHSO_3H)_2$, gives scarlet shades.[2] The introduction of hydroxyl groups into the molecule tends to shift the colour towards the violet end of the spectrum.

Simple *hydrazo- compounds* in which the hydrazo group is joined to two anthraquinone residues, such as

$$C_{14}H_7O_2.NHNH.C_{14}H_7O_2,$$
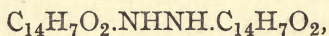
do not seem to have been prepared, although one or two mixed hydrazo compounds have been described. Thus, dichloranthrachrysazin disulphonic acid condenses very readily with phenylhydrazine to produce a hydrazo compound [3] (di-phenylhydrazo-anthrachrysazin disulphonic acid ?), and a mixed hydrazo- compound is also formed by condensing phenylhydrazine, or phenylhydrazine sulphonic acid, with *leuco*- quinizarin.[4]

[1] Möhlau, B. **45**, 2233. See also p. 363.   [2] By., D.R.P. 163,447.
[3] M.L.B., D.R.P. 99,078.   [4] M.L.B., D.R.P. 204,411.

ADDENDA

Page 38. *Cf.* also pp. 31–32.—Rây [1] has stated that anthra-
cene derivatives are obtained from aromatic hydrocarbons
and chloroform, benzal chloride, or carbon tetrachloride
by a modification of the Friedel and Crafts reaction in
which the catalyst is prepared from aluminium and mer-
curic chloride by a special process. From benzene and
chloroform or benzal chloride he states that he prepared
9.10-diphenyl-9.10-dihydroanthracene, but gives its melting
point as 159° as compared with 164·2° found by Linebarger,[2]
who prepared it from benzal chloride and benzene by means
of aluminium chloride. Haller and Guyot [3] have also
prepared the compound by reducing 9.10-diphenyl anthra-
cene, but give the melting point as 218°. Their product
evolved hydrogen when heated, whereas that obtained by
Linebarger does not appear to have done so. Rây's product
prepared from chloroform appears to have been impure
(found : C=93·2, H=6·7. $C_{26}H_{20}$ requires C=94·0, H=6·0),
although the analysis of that obtained from benzal chloride
agrees closely with the theoretical. Rây states that his
product on oxidation with chromic acid gave anthraquinone,
whereas Simonis and Remmert [4] found that 9.10-diphenyl-
anthracene itself does not give anthraquinone on oxidation.
Rây also states that his product when treated with acetic an-
hydride and pyridine gave a diacetyl derivative. It is difficult
to see how a diacetyl derivative could be obtained from a
hydrocarbon by the method employed, and in any case such
a diacetyl compound would contain thirty carbon atoms and
not twenty-eight as Rây states. (Found : C=85·3, H=7·4.

[1] Soc. **117**, 1335.
[2] Am. **13**, 554.
[3] C. r. **138**, 1252.
[4] Page 20.

$C_{28}H_{24}O_2$ requires $C=85\cdot7$, $H=6\cdot8$; $C_{30}H_{24}O_2$ requires $C=86\cdot5$, $H=5\cdot8$.)

From benzene and carbon tetrachloride or benzotrichloride Rây obtained a hydrocarbon which melted at 159° and which he designates as 9.9.10.10-tetraphenyldihydroanthracene. It should be noted that the melting point is the same as that of the product obtained from chloroform or benzal chloride. Rây does not give any facts serving to differentiate them, and analytical data for carbon and hydrogen are insufficient. (Found: $C=94\cdot0$, $94\cdot0$; $H=6\cdot8$, $5\cdot1$. $C_{38}H_{28}$ requires $C=94\cdot2$, $H=5\cdot8$; $C_{26}H_{20}$ requires $C=94\cdot0$, $H=6\cdot0$.)

Page 68.—*ms*-N-Methyl anthramine cannot be obtained by methylating *ms*-anthramine either by treatment with methyl iodide or dimethyl sulphate. It is, however, readily obtained by heating anthrone with aqueous methylamine solution at 220°. It forms sulphur-yellow needles which sinter at 85° and melt at 90°. It is very easily oxidised and its solutions exhibit an intense green fluorescence.

Page 81.—When anthraquinone is reduced by heating at 230° with glucose, sucrose, lactose, or other sugar in the presence of aqueous, caustic soda of 30 per cent. strength, anthranol is produced.[1]

Page 99.—When anthranol is treated with a cold concentrated solution of formaldehyde, it passes readily into methylene anthrone (methylene anthraquinone)[2] :

$$
\begin{array}{c}
\text{CO} \\
C_6H_4 \diagdown \diagup C_6H_4 \\
\text{C} \\
\vdots \\
\text{CH}_2
\end{array}
$$
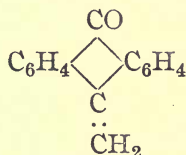
This forms pale yellow prisms which melt at 148°. It unites instantaneously with one molecule of bromine to form brom-methylbromanthrone, also obtained by the action of bromine on methylanthranol methyl ether.[3]

[1] A. G. Perkin, E.P. 151,707[19]. *Cf.* M.L.B., D.B.P. 249,124.
[2] K. Meyer, A. 420, 134.   [3] K. Meyer and Schlösser, A. 420, 131.

Page 112.—The alkylation of anthranol has been further studied by Kurt Meyer and Schlösser.[1] They find that alkylation with dimethyl sulphate or diethyl sulphate leads to the formation of O-alkyl compounds (anthranol methyl and ethyl ethers), whereas alkylation with alkyl iodides leads to the production of C-alkyl derivatives. From anthranol and methyl iodide the chief product was methylanthranol methyl ether (I) together with dimethyl anthrone (II) :
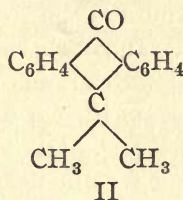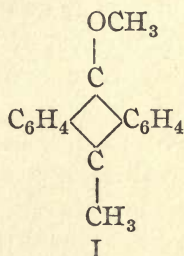
Similar products were obtained by means of ethyl iodide.

Page 118.—Kurt Meyer [2] has extended his investigations on the tautomerism of the anthraquinone reduction products to the corresponding compounds obtained from some hydroxy anthraquinones. The reduction of erythrohydroxy anthraquinone by sodium hydrosulphite and alkali or by tin and hydrochloric acid [3] leads to a product which must be regarded as the anthrone, as the equilibrium mixture in alcohol ($\cdot$1–$\cdot$2 gram in 100 c.c.) contains only 3 to 4 per cent. of the enole (anthranol). Reduction of erythrohydroxy-anthraquinone with zinc dust and caustic soda leads to 1-hydroxyanthraquinol. The corresponding enole, 1(?4).9-dihydroxy anthrone can be obtained by brominating 1-hydroxy anthrone and then replacing the bromine atom by the hydroxyl group by treatment with aqueous acetone. In alcoholic solution the equilibrium mixture contains only about 10 per cent. of the enole (anthraquinol). The reduction products of quinizarin show an even more marked tendency to become ketonised. Reduction of quinizarin with tin and hydrochloric acid in glacial acetic acid solution

[1] A. **420**, 126.   [2] K. Meyer and Sander, A. **420**, 113.
[3] M.L.B., D.R.P. 242,053.

leads to 1.4.9-trihydroxy anthrone, whereas reduction with zinc and caustic soda leads to the isomeric dihydroxy anthraquinol. This latter substance, however, is extremely unstable and is ketonised merely by recrystallisation. The anthranol obtained by the reduction of β-hydroxyanthra-quinone was also examined, but quantitative results as to the state of the equilibrium mixture could not be obtained, as even excess of bromine did not cause the disappearance of the fluorescence. The substance, however, was probably chiefly enolic, so that the ketonising influence of hydroxyl groups would seem to be confined to those occupying α-positions. In connection with this it is interesting to notice that Willstätter and Wheeler [1] have found that hydro-juglone exists in two forms. One of these is probably the true phenol (1.4.5-trihydroxynaphthalene), whereas the other is probably 1.4-dihydroxy-5-keto-5.8-dihydronaphthalene :
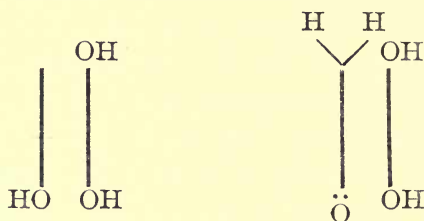
the presence of the two hydroxyl groups in α- positions rendering the ketonic form stable.

Page 136.—Phthalic anhydride will condense with hydrindene [2] to give a ketonic acid which on treatment with ten parts of 15 per cent. oleum at 60–70° yields a mixture of two isomeric phthaloyl hydrindenes (I and II) :
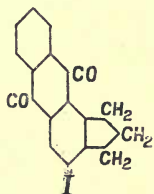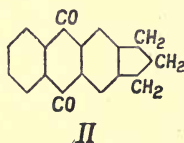
M.p. 108–110°.   M.p. 181°.

[1] B. **47**, 2796.   [2] Braun, Kirschbaum and Schuhmann, B. **53**, 1165.

The second of these substances on reduction with zinc dust and ammonia passes into the corresponding anthracene derivative (m.p. 242–243°), whereas the former yields a product which melts at about 150° but which could not be obtained pure. It therefore behaves on reduction in the same way as the α-methyl anthraquinones.

Page 140.—3-Nitrophthalic acid, 4-nitrophthalic acid, and the corresponding acetyl aminophthalic acids will condense with benzene under the influence of aluminium chloride to form ketonic acids.[1] It is not stated whether or not dehydrating agents will convert these into anthraquinone derivatives.

Page 159.—1-Chlor-2-dichlormethyl anthraquinone is converted into 1-chloranthraquinone-2-aldehyde by heating with concentrated sulphuric acid and boric acid.[2]

Page 160.—2-Methyl-1-aminoanthraquinone when heated with an aromatic nitro compound and an alkali, with or without the addition of a primary aromatic amine, gives an azomethine derivative from which 1-aminoanthraquinone-2-aldehyde can be obtained by hydrolysis with an acid.[3]

Page 163.—1-Chloranthraquinone-2-aldehyde is readily oxidised to the carboxylic acid by chromic acid.[4]

Page 168.—By nitrating anthraquinone to the dinitro compound Dhar [5] obtained 1.5-dinitroanthraquinone (m.p. 360°), 1.3-dinitroanthraquinone (m.p. 240°) and two other isomers which he was unable to identify. For the analysis of the 1.3-dinitro compound he gives the figures : found $N=4\cdot2$; calculated, $N=9\cdot39$.

Page 171.—2-Methyl-1-chloranthraquinone when chlorinated gives 2-dichlormethyl-1-chloranthraquinone.[6]

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[1] Lawrence, Am. Soc. **42**, 1871.
[2] Schaarschmidt and Herzenberg, B. **53**, 1809.
[3] Cas. E.P. 148,339 (1915).
[4] Schaarschmidt and Herzenberg, B. **53**, 1809.
[5] Soc. **117**, 1001.
[6] Schaarschmidt and Herzenberg, B. **53**, 1809.

Page 173.—1-Amino-2-methylanthraquinone can be converted into 2-methyl-1-chloranthraquinone by Sandmeyer's method, but the reaction must be carried out in the cold in order to avoid the formation of anthraquinone-1.2-indazol.[1]

Page 208.—Both α-aminoanthraquinone and β-aminoanthraquinone can be methylated by boiling with dimethyl sulphate and a mild alkali such as sodium carbonate, in the presence of an inert solvent of high boiling point such as nitrobenzene or tetrachlorethane.[2]

Pages 265–266.—Kurt Meyer and Sander have examined *leuco*-quinizarin I and *leuco*-quinizarin II. The former can also be obtained from *leuco*-purpurin by warming with glacial acetic acid, but will not give purpurin by oxidation. Its conversion into quinizarin is not brought about by oxidation but by loss of water, and can be effected by alkali even in the absence of atmospheric oxygen. In view of these facts Meyer and Sander consider that *leuco*-quinizarin I must be 2-hydroxy-1.4-diketo-1.2.3.4-tetrahydroanthraquinol (I). Loss of a molecule of water from this substance would give rise to 9.10-dihydroxy-1.4-anthraquinone (II), which would pass into the 1.4-dihydroxy-9.10-anthraquinone (quinizarin, formula III) by ketonisation of the hydroxyl groups and simultaneous enolisation of the quinonoid carbonyl groups :

$$\text{I} \quad\longrightarrow\quad \text{II} \quad\longrightarrow\quad \text{III}$$
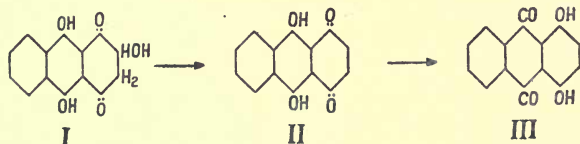
Page 324.—By condensing the chloride of 1-chloranthraquinone-2-carboxylic acid with *p*-xylene, Schaarschmidt and Herzenberg [3] obtained the xylyl chloranthraquinonyl ketone, from which they were able to prepare the corresponding amino ketone (I) by heating with ammonia. This when diazotised and then treated with copper powder

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[1] *Loc. cit.*   [2] Atack and Haworth, E.P. 147,964.
[3] B. **53**, 1807.   *Cf.* also B. **53**, 1388.

gave four products, viz. (*a*) traces of xylyl hydroxyanthra-quinonyl ketone; (*b*) about 20 per cent. of xylyl anthraquinonyl ketone itself, also obtained by condensing the chloride of anthraquinone-2-carboxylic acid with *p*-xylene; (*c*) a fluore-none derivative (formula II) in about 25 per cent. yield; and (*d*) a benzanthrone derivative (formula III) in about 50 per cent. yield:
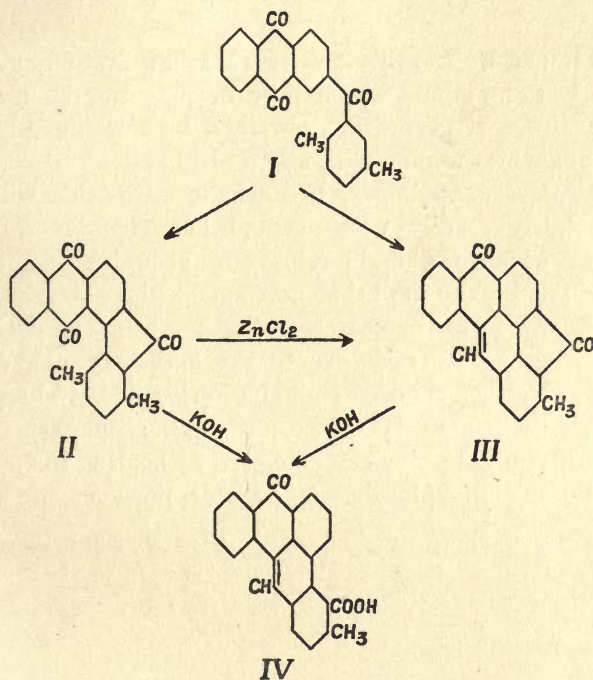
The phthaloyl fluorenone (II) passed into the benzanthrone derivative (III) when heated with zinc chloride. Both II and III yielded the carboxylic acid (IV) when fused with caustic alkali, the carboxyl being formed by the opening of the fluorenone ring.

Page 328.—An investigation of perylene and its deriva-tives has been commenced.[1]

[1] Hansgirg and A. Zinke, M. **40**, 403.   A. Zinke and Unterkreuter, M. **40**, 405.

Page 370.—Compounds which are probably isoxazols of the type :

N
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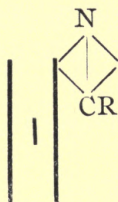
are obtained by treating 1-nitro-2-alkylanthraquinones with oleum.[1] Compounds which may or may not be isoxazols of the above structure are obtained by treating 2-methyl-1-aminoanthraquinone with alkali alcoholates.[2]

Phthaloyl acenaphthene.[3]—Phthalic anhydride will condense fairly readily with acenaphthene to give a ketonic acid in which the carbonyl group occupies one of the α-positions of the naphthalene ring. This substance, however, differs from the corresponding naphthalene derivative in showing great resistance to the action of dehydrating agents. Neither concentrated sulphuric acid nor phosphorus pentoxide will convert it into phthaloyl acenaphthene, but the anthraquinone ring can be closed by heating to 200° with phosphorus pentachloride. The yields, however, are poor.

[1] M.L.B., E.P. 147,001 (1918).   [2] M.L.B., D.R.P. 293,576.
[3] Grœbe, A. 327, 99.

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For index purposes the prefix "mono" is not used. Where two or more substituents are present they are usually arranged in ascending order of mass, substituted amino groups being treated as amino groups, alkoxy groups as hydroxyl, and all alkyl groups as methyl. Both bromine and iodine are treated as equivalent to chlorine.

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