THE CHEMISTRY OF ANTHRAQUINONE

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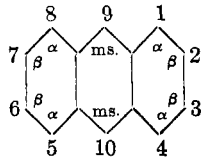
The synthesis of alizarin from anthracene by Graebe and Liebermann (1) in 1868 and the elucidation of the generic relationship between anthracene, anthraquinone, and alizarin by the same investigators, may be said to mark the beginning of a new era in the study of the chemistry of anthraquinone and its derivatives. Although anthraquinone had been prepared by Laurent (2) in 1840 by the oxidation of anthracene with nitric acid and subsequently by Fritzsche (3) by the oxidation of anthracene with chromic acid, little interest was attached to this compound until Graebe and Liebermann announced their epoch-making discovery. This soon led to the technical production of synthetic alizarin (4) and stimulated research to such a marked degree that today we may with propriety speak of an "anthraquinone chemistry." In this paper a review will be presented of the more important facts pertaining to the chemistry of this compound.

CONSTITUTION AND NOMENCLATURE

Constitution. The quinone-like character of anthraquinone was first clearly recognized by Graebe and Liebermann (5), who showed that it bore the same structural relationship to anthracene as benzoquinone did to benzene. The name "anthraquinone" was first proposed by these two investigators (5). The generally accepted diketo formula for this compound was suggested by Fittig (6). The synthesis of anthraquinone from benzoyl-2-benzoic acid, which will be discussed elsewhere in this paper, is a further proof of its structure.

Nomenclature. The generally accepted system of nomencla-

ture is the following. The ten positions in anthracene are numbered as indicated below.



Positions 1, 4, 5 and 8 are frequently referred to as the α positions; and positions 2, 3, 6 and 7, as the β. The 9 and 10 positions are sometimes designated as the meso- or ms-. Of the six theoretically possible monoquinones of anthracene, namely, 1,2; 2,3; 1,4; 1,5; 2,6; and 9,10, the last one only is of any practical importance. When speaking of "anthraquinone" the 9,10 anthraquinone is generally understood.

PREPARATION

From anthracene. The anthracene fraction of "anthracene oil" (280° to 400°C.), obtained in the distillation of coal tar, is allowed to stand, and the crystals which separate out, consisting of anthracene, carbazol, phenanthrene, etc., are subjected to hot pressing and then to purification by washing either with solvent naphtha or pyridine. This process gives a product containing about 50 per cent anthracene. This mixture is distilled in a current of superheated steam, and the vapor condensed by means of fine jets of water, thus reducing the anthracene to a state fine enough for oxidation. The distillate is then oxidized with the calculated amount of sodium dichromate and sulfuric acid, thereby converting the anthracene to anthraquinone without greatly affecting the impurities. In order to free the anthraquinone from these impurities, use is made of a method first proposed by Luck (7), which consists in treating the oxidation product with two to three parts of concentrated sulfuric acid of 66° Bé and heating the mixture at 110°C. This treatment sulfonates the impurities, but not the anthraquinone. The hot sulfonation mass is poured into boiling water, and the anthraquinone is precipitated out in a form suitable for filtration.

The filtrate contains the impurities. The anthraquinone thus obtained is usually further purified by sublimation.

SYNTHETIC

From benzoic acid. When benzoic acid is heated with a suitable dehydrating agent, such as phosphorus pentoxide, anthraquinone is obtained (8). When an hydroxy benzoic acid is used, the condensation proceeds more easily and hydroxy anthraquinones (9) are formed.

From phthalic anhydride directly. This method which is useful in the preparation only of derivatives of anthraquinone, especially hydroxy-anthraquinones, consists in heating phthalic anhydride and a phenol or a phenol derivative with concentrated sulfuric acid and boric acid. Thus p-chlorophenol and phthalic anhydride yield quinizarin (10). Anthraquinone itself can not be prepared by this method.

From phthalic anhydride, benzene, and anhydrous aluminum chloride. This is the only method technically used in the preparation of synthetic anthraquinone. Phthalic anhydride is first condensed with benzene and aluminum chloride to give benzoyl-2-benzoic acid, which when heated with sulfuric acid is converted into anthraquinone. In view of the tremendous technical importance of this method, an historical review of its development may be in place here.

Anthraquinone was first prepared synthetically from o-benzoyl-benzoic acid by Behr and van Dorp (11). By heating one part of o-benzoyl-benzoic acid with two parts of P_2O_5 at 200°C. for several hours, these investigators succeeded in obtaining a 26 per cent yield of anthraquinone.

Liebermann (12) in attempting to improve on the foregoing method substituted fuming sulfuric acid in place of the P_2O_5 and found that this acid acted as a sulfonating agent as well as a condensing agent. The final product obtained was anthraquinone sulfonic acid, which he was able to convert into alizarin.

The fundamental scientific work of the present synthetic anthraquinone process was done by Friedel and Crafts (13). In applying their reaction, now well-known, to phthalic acid chloride

and benzene, they obtained a reaction product consisting of two substances, namely, phthalophenone and anthraquinone. They assumed that in this reaction the benzene and anhydrous aluminum chloride reacted first to give an intermediate compound represented by the formula $C_6H_5 \cdot Al_2Cl_5$ and that this compound then reacted with the phthalic acid chloride to give phthalophenone and anthraquinone (14).

Studying this fundamental reaction further, these investigators reported in the following year (1878) that when phthalic anhydride was used in place of the phthalic acid chloride, the principal reaction product was o-benzoyl-benzoic acid (15). No information regarding yield obtained or procedure followed in carrying out the reaction is given.

In 1880, v. Pechmann (16) prepared o-benzoyl-benzoic acid by the method of Friedel and Crafts and reported a yield of 60 per cent of the weight of phthalic anhydride used (41 per cent of theory). A small amount of diphenylphthalide (17) was also formed in this reaction.

In 1891 Perkin (18) showed that when o-benzoyl-benzoic acid is heated at 100°C. with concentrated sulfuric acid instead of the fuming sulfuric acid used by Liebermann (12), a quantitative yield of anthraquinone is obtained.

Haller and Guyot (19) in a paper published in 1894 reported that they succeeded in obtaining a 92 per cent yield of o-benzoyl-benzoic acid, using the method of Friedel and Crafts. They failed, however, to give any details concerning the manner in which this reaction was carried out.

Graebe and Ullmann (20) give the following directions for the preparation of o-benzoyl-benzoic acid: Fifty grams phthalic anhydride (1 mole) is dissolved in 250 cc. benzene, and 70 to 75 grams (0.82 mole) finely powdered Al_2Cl_6 is added. This mixture is heated on the water bath until no more HCl is evolved (two hours). The reaction product is decomposed with water and steam distilled to remove the unused benzene, and the residue is digested with Na_2CO_3 solution. The yield amounts only to 85 per cent of the theory, owing to the fact that an insufficient amount of aluminum chloride is used.

Heller (21) was the first to make a systematic study of the reactions involved in the preparation of synthetic anthraquinone from phthalic anhydride, anhydrous aluminum chloride, and benzene. He showed conclusively (1906) that the aluminum chloride does *not* act catalytically but forms an intermediate compound with the phthalic anhydride and benzene. To get the best yield of o-benzoyl-benzoic acid, one mole of Al_2Cl_6 must be added for every mole of phthalic anhydride used. His directions for obtaining the best yield of anthraquinone are as follows:

To 1 kgm. (1 mole) of phthalic anhydride and 3.5 kgm. benzene (6.6 moles), contained in a lead-lined vessel, 1.8 kgm. (1 mole) Al_2Cl_6 is added all at once. The reaction mixture is heated gradually to 70°C. and maintained at this temperature until no more HCl is evolved. Water is added to the reaction mixture, the excess benzene is distilled off, the residue is digested with Na_2CO_3 solution and filtered, and the filtrate is acidified. The yield of o-benzoyl-benzoic acid is 95 to 97 per cent of theory. This acid is converted into anthraquinone by heating it with 5 to 6 parts of sulfuric acid (66° Bé) at 150°C. The yield is quantitative.

In 1908 Heller and Schulke (22) studied the mechanism of the reaction involved in the synthesis of o-benzoyl acid and concluded that the reaction first produces an addition compound having the composition represented by the formula $C_8H_4O_3 \cdot Al_2Cl_6 \cdot C_6H_6$. This product then decomposes with the elimination of HCl, giving the second intermediate compound $C_{14}H_9O_3 \cdot Al_2Cl_5$, which then treated with water forms the aluminum salt of o-benzoyl-benzoic acid.

Rubridge and Qua (23) confirmed Heller's findings with regard to the part played by the aluminum chloride in this reaction. When less than one mole of Al_2Cl_6 was used for each mole of phthalic anhydride, diphenyl phthalide was formed, a result which was found to be due to the action of the excess of phthalic anhydride on the intermediate compound.

Harding (24) carried out the preparation of synthetic anthraquinone on a semiindustrial scale. The process as described by him is essentially the one now used commercially. It will be

noted that it is similar to the method recommended by Heller (21).

One and eight-tenths (1.8) parts Al_2Cl_6 and 1 part benzene by volume are put into the reaction kettle, which is lead-lined, jacketed for cooling, and provided with a good stirrer and reflux condenser. It is connected to a scrubber system for the absorption of the HCl generated. One part of phthalic anhydride is dissolved in 4 parts benzene, and this solution is run into the reaction kettle by means of a jacketed pipe. The temperature is gradually raised to 35°C. and the reaction begins, with the evolution of HCl. This temperature is maintained for twenty to thirty minutes, then slowly increased to 75 to 80°C. within an

TABLE 1

Anthraquinone produced in the United States, 1919–1924

YEAR	POUNDS
1919	294,260
1920	539,619
1921	125,358
1922	395,107
1923	857,910 (about 50 per cent synthetic)
1924	638,755 (about 75 per cent synthetic)

hour, and maintained at this temperature until no more HCl is evolved. The excess benzene is distilled off under reduced pressure. The dry residue, which is easily powdered, is decomposed either with hot water or with hot Na_2CO_3 solution. The yield of o-benzoyl-benzoic acid is about 95 per cent of theory or 145 per cent of the weight of the phthalic anhydride used.

For the conversion of the o-benzoyl-benzoic acid into anthraquinone, 1 part of the anhydrous acid is heated with 4 parts 95 per cent H_2SO_4 at 130°C. for from three-quarters to one hour with good stirring. An ordinary sulfonator is suitable for this condensation. The sulfuric acid solution of the anthraquinone is poured into water, cooled and centrifuged. This anthraquinone is further purified by sublimation with steam. The overall yield

of sublimed anthraquinone on the phthalic anhydride used is more than 120 per cent by weight (85 per cent of theory).

Table 1 gives the quantity of anthraquinone produced in the United States during the period 1919–1924. These figures are taken from the annual reports issued by the United States Tariff Commission ("Census of Dyes and Other Synthetic Organic Chemicals," United States Tariff Commission, Washington, D. C.).

It is understood that a considerable quantity of anthraquinone was produced during the years 1925 and 1926, but the Tariff Commission could not publish these figures without disclosing the operation of individual firms.

Sulfonation. Anthraquinone does not sulfonate easily with ordinary concentrated sulfuric acid, and fuming sulfuric acid is therefore generally employed. This leads to the formation of the β acid together with a small amount of disulfonic acids, principally the 2,6 and 2,7 acids (25). In the technical production of the β acid an excess of anthraquinone is used, and the formation of the disulfonic acids is then reduced to the minimum. The sulfonation mass is poured into water, the excess anthraquinone is filtered off, and the filtrate is neutralized with sodium carbonate. The rather insoluble sodium salt of anthraquinone-2-sulfonic acid then separates out. Because of its silver-like appearance this salt is technically known as "silver salt."

Until 1903, it was generally held that the anthraquinone-α-sulfonic acid could not be obtained by direct sulfonation of anthraquinone. It was found, however, by Schmidt (26), and also by Iljinsky (27), that if a small amount of mercuric sulfate is added to the sulfonation mixture the α acid is obtained almost entirely (28). On further sulfonation the 1,5 and 1,8 disulfonic acids are produced together with a small amount of trisulfonic acid (29).

As a rule, the anthraquinone sulfonic acids are fairly easily desulfonated by hydrolysis, although the ease with which the sulfonic group is eliminated varies to a great extent in different substances. Ordinarily, the sulfonic acid group in the α position is more easily removed than one in the β position (30). It will be

recalled that the monosulfonic acids of naphthalene behave similarly.

Nitration. When anthraquinone is nitrated the α position is first substituted. No β nitroanthraquinone is formed in this reaction. The nitration is carried out by dissolving the anthraquinone in concentrated sulfuric acid and adding concentrated nitric acid to this solution (31). The β nitroanthraquinone can not be prepared by direct nitration and is generally made by nitrating β aminoanthraquinone and then removing the amino group from the resulting 2-amino-3-nitroanthraquinone by the diazo reaction (32).

Halogenation. Anthraquinone is attacked by halogens only with the greatest difficulty, although the classical synthesis of alizarin from anthraquinone by Graebe and Liebermann was brought about by brominating the anthraquinone in a sealed tube at 100°C. and fusing the resultant dibromo derivative with alkali. A more simple method, however, is first to brominate anthracene and then to oxidize this to the corresponding bromo derivative of anthraquinone (33). In general, the halogen derivatives of anthraquinone are obtained by indirect methods that is, by replacing a substituent already present in the anthraquinone molecule. Thus chloroanthraquinone can be prepared from aminoanthraquinone by the diazo reaction or by the treatment of an hydroxy anthraquinone with phosphorus penta chloride, phosphorus oxychloride, or phosphorus trichloride (34).

Halogen anthraquinones may be readily prepared from the corresponding sulfonic acids. Sulfonic acid groups either in the α or β positions are readily replaced by chlorine or bromine. Thus α-chloroanthraquinone may be obtained in excellent yield by adding sodium or potassium chlorate to an acid solution of anthraquinone α-sulfonic acid. The nascent chlorine liberated in this reaction replaces the sulfonic acid group (35).

Another satisfactory method for preparing halogen derivatives of anthraquinone is the phthalic anhydride synthesis. Thus, if monochlorobenzene is condensed with phthalic anhydride and aluminum chloride, chloro-benzoyl-benzoic acid is obtained, which

on condensation with concentrated sulfuric acid is converted into 2-chloroanthraquinone (36). By starting with p-dichlorobenzene 1,4-dichloroanthraquinone is obtained (37). If o-dichlorobenzene is condensed with phthalic anhydride, however, the principal product of the reaction is 2,3-dichloroanthraquinone, together with a small amount of 1,2-dichloroanthraquinone (38). In a similar manner halogen derivatives of anthraquinone may be obtained by condensing chlorophthalic acids with benzene and aluminum chloride (39).

Amidation. The amino anthraquinones are of great commercial importance, being used as intermediates in the preparation of a number of important anthraquinone dyes. They are generally prepared either by the reduction of the corresponding nitroanthraquinone or by the replacement of negative substituent groups in the anthraquinone molecule, such as halogen atoms, hydroxyl, or sulfonic acid groups.

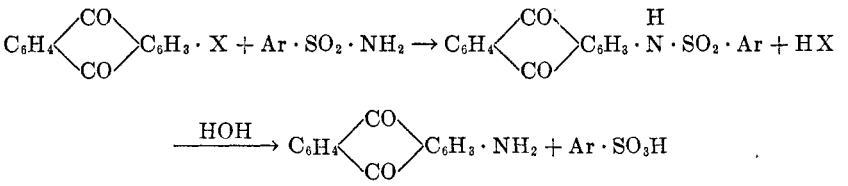
The most satisfactory reagent for the reduction of the nitroanthraquinones is sodium sulfide, and, as a rule, the yields obtained by this method are very good (40). The reduction may also be brought about with tin and hydrochloric acid (41), sodium stannite, zinc dust, and sodium hydroxide or ammonia (42).

REPLACEMENT OF NEGATIVE GROUPS

Replacement of halogen atoms. When heated with aqueous ammonia under pressure halogen anthraquinones are converted into the corresponding amino derivatives. Thus, when heated with aqueous ammonia in an autoclave, 2-chloroanthraquinone is converted into 2-aminoanthraquinone (43). If, in place of ammonia, an alkyl or aryl amine is used, the corresponding secondary aminoanthraquinone is formed (44).

The reaction between ammonia or alkyl amines and halogen anthraquinones will generally take place only when the substances are heated together in an autoclave under pressure. Ullmann (45) in 1910 discovered that sulfonamides will condense with halogen anthraquinones at ordinary pressure. On hydrolysis the condensation product gives the aminoanthraquinone.

This reaction may be represented as follows:



The sulfonamide generally employed in this reaction is p-toluene sulfonamide, a by-product in the manufacture of saccharin. If in place of p-toluene sulfonamide an N-alkyl or N-aryl substitution product is used in this reaction, the corresponding secondary aminoanthraquinone is obtained.

Replacement of hydroxyl groups. The hydroxyl group can generally be replaced by an amino group by heating the hydroxy compound with ammonia or with an alkyl or aryl amine (46). This reaction is made use of in the preparation of a number of dyes, such as Quinizarin Green; Alizarin Irisol; Alizarin Direct Green G, and Alizarin Brilliant Green G. The condensation is brought about by first reducing the hydroxy anthraquinone to the leuco compound, then condensing with the aromatic amine in the presence of boric acid, and finally oxidizing this product to the amino anthraquinone derivative (47).

Replacement of sulfonic acid groups. Another important method of preparing aminoanthraquinones is by replacing the sulfonic acid groups. Thus, 2-aminoanthraquinone, which is extensively used in the preparation of anthraquinone vat colors, is obtained from sodium anthraquinone-2-sulfonate ("silver salt" of commerce) by heating it with aqueous ammonia in an autoclave under pressure. In order to obtain the best yields of 2-aminoanthraquinone it is necessary to destroy the sodium sulfite formed as a by-product in this reaction. This is usually done either by the addition of barium chloride (48), which reacts to form the insoluble barium sulfite, or by the addition of manganese dioxide (49), which oxidizes the sulfite to the inactive sulfate.

The aminoanthraquinones may be alkylated or arylated in the

usual manner by heating the amino compound with alkyl or aryl halide. The arylation, however, is preferably conducted in the presence of a copper catalyst and sodium acetate or potassium carbonate (50).

HYDROXYLATION

The hydroxyanthraquinones are of considerable technical importance; like alizarin they are used as dyes and as intermediates in the preparation of other anthraquinone derivatives. They are phenolic in character giving soluble phenolates with the fixed alkalies. These soluble phenolates form "lakes" with iron, tin, antimony, and aluminum. The hydroxyl group in any position can be readily acylated, but an hydroxyl in the α position can not be alkylated.

There are four general methods for introducing an hydroxyl group into the anthraquinone nucleus. They are:

(1) Replacement of a sulfonic acid group.
(2) Replacement of an halogen atom.
(3) Replacement of an amino group.
(4) Direct oxidation.

The replacement of a sulfonic acid group by fusion with caustic alkali is an important method and is used commerically for the production of alizarin from sodium anthraquinone-2-sulfonate. The alkali fusion of this sulfonate proceeds abnormally, in that during the alkali melt simultaneous oxidation takes place, and usually the number of hydroxyl groups in the product is greater than the number of sulfonic acid groups in the original sulfonic acid. In the alkali fusion of sodium anthraquinone-2-sulfonate, hydrogen is liberated, reducing a part of the alizarin to monohydroxyanthraquinone or even to anthraquinone itself. This used to occur in the early days of the manufacture of synthetic alizarin, but is now obviated by adding sodium chlorate or nitrate to the melt, an improvement introduced by Koch (51). When the sulfonic acid group is in the α position, fusion with alkali usually leads to the rupture of the benzene ring. Sulfonic acid groups in any position in the anthraquinone molecule,

however, can be replaced by hydroxyl groups (without simultaneous oxidation taking place as in alkali fusion) by heating the sulfonic derivative with an aqueous solution of calcium or barium hydroxides at a temperate of 150 to 180°C. (52).

Replacement of halogen atoms. When attached to the anthraquinone nucleus halogen atoms may be replaced with hydroxyl groups by the fusion with alkali. Thus Graebe and Liebermann effected the first synthesis of alizarin by the fusion of dibromoanthraquinone with potassium hydroxide. The reaction, however, proceeds abnormally, in that an intramolecular migration takes place. For example, by the alkali fusion of 2,3-dichloroanthraquinone, the chief product of the reaction is alizarin and not hystazarin (53).

Replacement of amino groups. Amino groups can be replaced with hydroxyl groups in the usual manner, through the diazo reaction. As a rule, it is best to diazotize the amino compound in concentrated sulfuric acid, and then break off the diazo group by heating to 90° to 100°C. (54). This method of introducing hydroxyl groups is, however, of no great technical importance.

Direct oxidation. Anthraquinone differs from the aromatic compounds in the great ease with which hydroxyl groups can be introduced into the anthraquinone molecule. The simultaneous oxidation of anthraquinone-2-sulfonic acid to alizarin by fusion with alkali has already been referred to. Another reaction used in the introduction of hydroxyl groups into the anthraquinone nucleus is what is known as the Bohn-Schmidt reaction (55). This reaction consists in introducing hydroxyl groups into the anthraquinone molecule by the oxidizing action of fuming sulfuric acid. Subsequently Schmidt (56) discovered that if boric acid is added to the reaction mixture, ordinary concentrated sulfuric acid may be used in place of the oleum. The boric acid forms esters with the hydroxyanthraquinones and prevents the oxidation from going too far. The importance of this reaction can be appreciated from the fact that it is used in the technical preparation of such important dyes as Alizarin Green S, Alizarin Bordeaux, Alizarin Cyanine R, and Alizarin Cyanin Black.

OXIDATION AND REDUCTION

Anthraquinone is stable to oxidizing agents. If too severe oxidation is resorted to, complete disruption of the molecule takes place. Alkyl side chains when present may, however, be readily oxidized with nitric acid (57) to the corresponding carboxylic acids.

Reduction. Unlike benzoquinone, anthraquinone can not be reduced with sulfurous acid. Tin and hydrochloric acid reduces it to anthranol (58). It can be reduced with several alkaline reducing agents, such as zinc dust and ammonia, and glucose and alkali, but the most important reducing agent is "sodium hydrosulfite" (hyposulfite). On reduction with "hydrosulfite" the carbonyl groups are reduced to hydroxyl groups, or anthranols. These anthranols are alkali-soluble and are reoxidized to the corresponding anthraquinone by atmospheric oxygen. This property of undergoing reversible oxidation and reduction makes it possible to use many of the anthraquinone derivatives as vat dyes.

HOMOLOGUES

The alkyl anthraquinones are generally prepared via the phthalic anhydride synthesis. Thus from toluene, phthalic anhydride and aluminum chloride, 2-methyl anthraquinone is obtained (59). From the xylenes, the corresponding dimethyl anthraquinones are obtained (57). p-Cymeme yields 1,4-methyl isopropyl anthraquinone (60). With the exception of 2-methyl anthraquinone, the alkyl anthraquinones are of no technical importance.

REFERENCES

(1) GRAEBE, C., AND LIEBERMANN, C.: Ueber Alizarin und Anthracen. Ber., **1**, 49 (1868).

GRAEBE, C., AND LIEBERMANN, C.: Ueber künstliche Bildung von Alizarin. Ber. **2**, 14 (1869).

GRAEBE, C., AND LIEBERMANN, C.: Ueber künstliches Alizarin. Ber. **2**, 332 (1869).

GRAEBE, C., AND LIEBERMANN, C.: Ueber Anthracen und Alizarin. Ann. Supplementband, **7**, 257 (1870). For a detailed account of the events and circumstances that led to the synthesis of alizarin from anthracene, the reader is referred to C. Graebe's "Geschichte der organischen Chemie," i, p. 333, Julius Springer, Berlin, 1920.

(2) LAURENT, A.: Ueber verschiedene Verbindungen des Anthracen's. Ann. **34**, 287 (1840).

(3) FRITZSCHE, J.: Jahresbericht über die Fortschritte der Chemie. (A. Strecker) **1868**, p. 403.

(4) CARO, H., GRAEBE, C., AND LIEBERMANN, C.: Improvements in Preparing Coloring Matter. E. P. No. 1936 (1869).

CARO, H., GRAEBE, C., AND LIEBERMANN, C.: Ueber Fabrikation von künstlichem Alizarin. Ber., **3**, 359 (1870).

PERKIN, W. H.: Improvements in the Manufacture of Coloring Matter Suitable for Dyeing and Printing. E. P. No. 1948 (1869).

(5) GRAEBE, C., AND LIEBERMANN, C.: Ueber Anthracen und Alizarin. Ann. Supplementband, **7**, 284 (1870).

(6) FITTIG, R.: Ueber Phenanthren und Anthracen. Ber., **6**, 167 (1873).

(7) LUCK, E., in FRIEDLAENDER, P.: Fortschritte der theerfarbenfabrikation, i, p. 301. Julius Springer, Berlin, 1888.

(8) BEHR, A., AND VAN DORP, W. A.: Ueberführung von β-Benzoylbenzoësäure in Anthrachinon. Ber., **7**, 578 (1874).

(9) SCHUNCK, E., AND ROEMER, H.: Ueber Anthraflavon und über ein neues Bioxyanthrachinon. Ber., **10**, 1225 (1877).

SCHUNCK, E., AND ROEMER, H.: Ueber Metabenzbioxy-Anthrachinon und Anthraflavinsäure aus Metaoxybenzoësäure. Ber., **11**, 969 (1878).

(10) BAEYER, A., AND CARO, H.: Synthese von Anthrachinon-abkömmlingen aus Benzolderivaten und Phthalsäure. Ber., **8**, 152 (1875).

LIEBERMANN, C., AND GIESEL, F.: Die Reduction des Chininzarins. Ann., **212**, 9 (1882).

Friedr. Bayer & Co.: Verfahren zur Darstellung von Chininzarin. D. R. P. 255,031 (1912).

REYNOLDS, H. H., AND BIGELOW, L. A.: A Study of the Preparation of Quinizarin. J. Am. Chem. Soc., **48**, 420 (1926).

(11) BEHR, A., AND VAN DORP, W. A.: Ueberführung von β-Benzoylbenzoësäure in Anthrachinon. Ber., **7**, 578 (1874).

(12) LIEBERMANN, C.: Synthese der Anthrachinonsulfosäure. Ber., **7**, 805 (1874).

(13) FRIEDEL, C., AND CRAFTS, J. M.: Sur une méthode générale nouvelle de synthése d'hydrocarbures, d'acétones, etc. Compt. rend., **84**, 1450 (1877).

(14) FRIEDEL, C., AND CRAFTS, J. M.: Sur une méthode générale nouvelle de synthése d'hydrocarbures, d'acétones, etc. Compt. rend., **85**, 74 (1877).

(15) FRIEDEL, C., AND CRAFTS, J. M.: Fixation directe de l'acide carbonique, de l'acide sulfureux, de l'anhydride phtalique sur la benzine, synthese de l'acide benzöique, de l'hydrure sulfophenyle et de l'acide benzoylbenzöique. Compt. rend., **86**, 1368 (1878). See also Ann. Chim. phys. (6), **14**, 446 (1888).

(16) v. PECHMANN, H. F.: Ueber die Verbindungen der Orthobenzoylbenzoësäure mit Phenolen. Ber., **13**, 1612 (1880).

(17) v. PECHMANN, H. F.: Condensation der Orthobenzoylbenzoësäure mit aromatischen Kohlenwasserstoffen. Ber., **14**, 1865 (1881).

(18) PERKIN, JR., W. H.: Note on the Formation of Anthraquinone from Orthobenzoylbenzoic Acid. J. Chem. Soc., **59**, 1012 (1891).
(19) HALLER, A., AND GUYOT, A.: Sur de nouveaux dérivés obtenus en partant de l'acide benzoylbenzöique. Compt. rend., **119**, 139 (1894).
(20) GRAEBE, C., AND ULLMANN, F.: Ueber o-Aminobenzophenon. Ann., **291**, 8 (1896).
(21) HELLER, G.: Ueber die Möglichkeit der technischen Darstellung von Anthrachinon aus Benzoylbenzoesäure. Z. Angew. Chem., **19**, 669 (1906).
(22) HELLER, G., AND SCHULKE, K.: Ueber die Friedel-Craftsche Reaktion. Ber., **41**, 3627 (1908).
(23) RUBIDGE, C. R., AND QUA, N. C.: Friedel and Craft's Reaction—The Preparation of Orthobenzoyl-Benzoic Acid and Benzophenone. J. Am. Chem. Soc., **36**, 732 (1914).
(24) HARDING, E. R.: The Synthesis of Anthraquinone from Phthalic Anhydride and Benzene. Color Trade J., **9**, 184 (1921).
(25) GRAEBE, C., AND LIEBERMANN, C.: Ueber Anthracenderivate. Ann., **160**, 130 (1871).
CARO, H., GRAEBE, C., AND LIEBERMANN, C.: Ueber Fabrikation von künstlichem Alizarin. Ber., **3**, 359 (1870).
PERKIN, W. H.: Ueber einige Derivate des Anthracens. Ann., **158**, 319 (1871).
LIEBERMANN, C., AND DEHNST, J.: Ueber die Constitution des Anthrarufins und des Oxyanthrarufins. Ber., **12**, 1287 (1879).
CROSSLEY, M. L.: Separation of the Mono-β-, 2,6, and 2,7-Sulfonic Acids of Anthraquinone. J. Am. Chem. Soc., **37**, 2178 (1915).
(26) SCHMIDT, R. E.: Ueber Anthrachinon-α-sulfosäuren. Ber., **37**, 66 (1904).
Friedr. Bayer & Co.: Verfahren zur Darstellung von Anthrachinon-α-monosulfosäure. D. R. P. 149,801 (1904).
(27) ILJINSKY, M.: Darstellung isomerer Sulfosäuren mittels Katalyse. Ber., **36**, 4194 (1903).
(28) FIERZ-DAVID, H. E., KREBSER, A., AND ANDERAU, W.: Ueber die Anthrachinonsulfosäuren. Helv. Chim. Acta, **10**, 197 (1927).
(29) MEYER, A.: Sur la sulfonation de l'anthraquinone en présence du mercure. Comp. rend., **184**, 609 (1927).
(30) Friedr. Bayer & Co.: Verfahren zur Darstellung von Anthrachinon und dessen Derivaten. D. R. P. 160,104 (1905). See also Ref. 29.
(31) ULLMANN, F., AND V. D. SCHALK, W.: Untersuchungen in der Anthrachinonreihe. VII. Ueber Anthrachinon-l-carbonsäure. Ann., **388**, 199 (1912).
(32) SCHOLL, R., SCHNEIDER, G., AND EBERLE, F.: Ueber die Nitroamine der Anthrachinonreihe. Ber., **37**, 4434 (1904).
(33) GRAEBE, C., AND LIEBERMANN, C.: Ueber Anthracen und Alizarin. Ann. Supplementband, **7**, 288 (1870).
(34) ULLMANN, F., AND CONZETTI, A.: Ueber 1-Oxy-4-chlor-Anthrachinon. Ber., **53**, 826 (1920).
(35) ULLMANN, F., AND OCHSNER, P.: Untersuchungen in der Anthrachinonreihe. IV. Ueber Anthrachinon-2,1-acridon und Anthrachinondiacridon. Ann., **381**, 1 (1911).

(36) PHILLIPS, M.: The Preparation of 2-Aminoanthraquinone from Phthalic Anhydride and Chlorobenzene. Ind. Eng. Chem., **17**, 721 (1925).

(37) PHILLIPS, M.: Preparation of 1,4-Dichloroanthraquinone from Phthalic Anhydride and p-Dichlorobenzene. J. Am. Chem. Soc., **48**, 3198 (1926).

(38) SENN, E.: Ueber die Verwendung von o- und p-Dichlorbenzol zur Synthese von dichlorierten Anthrachinonderivaten. Dissertation: Eidgenössischen Technischen Hochschule in Zürich, 1923.

PHILLIPS, M.: The Preparation of Alizarin from Phthalic Anhydride and Ortho-Dichlorobenzene. J. Am. Chem. Soc., **49**, 473 (1927); Ibid., **49**, 2335 (1927).

(39) ULLMANN, F., AND BILLIG, G.: Ueber Dichloranthrachinone. Ann., **381**, 11 (1911).

(40) LAUTH, C.: Colorants azoiques, solides, dérivés de l'α-aminoanthraquinone. Compt. rend., **137**, 661 (1903).

(41) BÖTTGER, R., AND PETERSEN, T.: Ueber einige Stickstoffverbindungen des Anthrachinons. Ann., **160**, 148 (1871).

ROEMER, H.: Ueber ein neues Nitroanthrachinon und Amidoanthrachinon, sowie eine neue Darstellungsweise des Erythrooxyanthrachinons. Ber., **15**, 1790 (1882).

(42) CLAUS, A.: Ueber Nitro-und Amidoanthrachinonsulfosäuren. Ber., **15**, 1514 (1882).

(43) Badische Anilin & Soda Fabrik: Verfahren zur Darstellung von 2-Aminoanthrachinon und seinen Derivaten. D. R. P. 295,624 (1916).

PHILLIPS, M.: The Preparation of 2-Aminoanthraquinone from Phthalic Anhydride and Chlorobenzene. Ind. Eng. Chem., **17**, 721 (1925).

(44) Friedr. Bayer & Co.: Verfahren zur Darstellung neuer stickstoffhaltiger Farbenstoffe der Anthracenreihe. D. R. P. 107,730 (1899).

Friedr. Bayer & Co.: Verfahrung zur Darstellung von tertiären Basen der Anthrachinonreihe. D. R. P. 136,777 (1902).

ULLMANN, F., AND SCHMIDT, W.: Ueber die Kondensation von Phthalsäureanhydrid mit Phenolen durch Aluminiumchlorid. Ber., **52**, 2109 (1919).

(45) ULLMANN, F.: Verfahren zur Herstellung von Arylsulfaminoanthrachinonen. D. R. P. 224, 982 (1910).

ULLMANN, F.: Verfahren zur Herstellung von N-Alkyl- und N-Arylarylsulfaminoanthrachinonen. D. R. P. 227, 324 (1910).

ULLMANN, F.: Studien in der Anthrachinonreihe. Ber., **43**, 536 (1910).

ULLMANN, F., AND FODOR, O.: Untersuchungen in der Anthrachinonreihe. I. Ueber α-Aminoanthrachinon. Ann., **380**, 317 (1911).

ULLMANN, F., AND BILLIG, G.: Ueber Dichloranthrachinone. Ann., **381**, 17 (1911).

ULLMANN, F., AND BINCER, H.: Ueber die 1-Chloranthrachinon-2-Carbonsäure. Ber., **49**, 741 (1916).

ULLMANN, F., AND EISER, O.: Ueber 1,3-Dibrom-anthrachinon. Ber., **49**, 2157 (1916).

(46) Friedr. Bayer & Co.: Verfahren zur Einführung von Aminresten in Oxyanthrachinone. D. R. P. 86,150 (1896).

(47) Friedr. Bayer & Co.: Verfahren zur Einführung von Aminresten in hydrirte Oxyanthrachinone. D. R. P. 91,149 (1897).
Meister Lucius & Brüning: Verfahren zur Darstellung von blauen Farbstoffen der Anthrazenreihe. D. R. P. 205,096 (1908).
Meister Lucius & Brüning: Verfahren zur Darstellung von Leuko-diaminoanthrachinonen, bezw. Diaminoanthrachinonen und ihren hydroxylierten oder sulfurierten Derivaten. D. R. P. 205,149 (1908).
Meister Lucius & Brüning: Verfahren zur Darstellung von blauen Farbstoffen der Anthrazenreihe. D. R. P. 205,551 (1908).
(48) Meister Lucius & Brüning: Verfahren zur Darstellung von 2-Aminoanthrachinon. D. R. P. 267,212 (1913).
(49) Badische Anilin & Soda Fabrik: Verfahren zur Darstellung von α-Amino-α-Alkylamino-, α-Arylamino- und β-Aminoanthrachinonen oder deren Derivaten aus Anthrachinonsulfosäuren. D. R. P. 256,515 (1913).
(50) Friedr. Bayer & Co.: Verfahren zur Darstellung von Arylaminoanthrachinonen und deren Derivaten. D. R. P. 175,069 (1906).
Laube E.: Ueber neue Anthrachinonderivate. Ber., **40**, 3562 (1907).
(51) Koch, J. J.: In P. Friedlaender's Fortschritte der theerfarben-fabrikation. i, p. 301.
(52) Schmidt, R. E.: Ueber Anthrachinon-α-sulfosäuren. Ber., **37**, 66 (1904).
Friedr. Bayer & Co.: Verfahren zur Darstellung von Erythrooxyanthrachinon. D. R. P. 172,642 (1906).
Friedr. Bayer & Co.: Verfahren zur Darstellung von 1,5- und 1,8-Oxyanthrachinonsulfosäuren. D. R. P. 197,607 (1908).
Meister Lucius & Brüning: Verfahren zur Darstellung von Oxyanthrachinonen und Oxyanthrachinonsulfosäuren. D. R. P. 106,505 (1899).
Meister Lucius & Brüning: Verfahren zur Darstellung von o-Methoxyanthrachinonsulfosäuren. D. R. P. 145,188 (1903).
(53) Phillips, M.: The Preparation of Alizarin from Phthalic Anhydride and Ortho-Dichlorobenzene. J. Am. Chem. Soc., **49**, 477 (1927).
(54) Eckert, A.: Zur Kenntnis des β-Anthrachinonaldehydes. Monatsch., **35**, 289 (1914).
Ullmann, F., and Conzetti, A.: Ueber 1-Oxy-4-chlor-anthrachinon. Ber., **53**, 826 (1920).
Meister Lucius & Brüning: Verfahren zur Ueberführung von Amido-in Oxyanthrachinone. D. R. P. 97,688 (1898).
Badische Anilin & Soda Fabrik: Verfahren zur Darstellung von Oxyanthrachinonsulfosäuren. D. R. P. 108,459 (1899).
(55) Bohn, R.: (Badische Anilin & Soda Fabrik.) Verfahren zur Darstellung von baluen bis grünen Schwefelsäurederivaten des Alizarinblaus. D. R. P. 46,654 (1889).
Badische Anilin & Soda Fabrik: Neuerungen in dem Verfahren zur Darstellung von blauen bis grünen Schwefelsauredervaten des Alizarinblaus. D. R. P. 47,252 (1889).
Schmidt, R. E.: (Friedr. Bayer & Co.) Verfahren zur Darstellung neuer Derivate des Alizarins und seiner Anologen. D. R. P. 60,855 (1891).

(56) SCHMIDT, R. E.: (Friedr. Bayer & Co.) Verfahren zur Einführung von Hydroxylgruppen in Anthrachinonderivate mittelst Schwefelsäure in Gegenwart von Borsäure. D. R. P. 81,481 (1895).

SCHMIDT, R. E.: (Friedr. Bayer & Co.) Verfahren zur Einführung von Hydroxylgruppen in die Anthrachinonchinoline mittelst Borsäure. D. R. P. 81,961 (1895).

(57) ELBS, K., AND EURICH, H.: Ueber (2.3)-Dimethylanthrachinon. Ber., **20**, 1361 (1887).

ELBS, K.: Beiträge zur Kenntnis der Homologen des Anthracens und Anthrachinons. J. prakt. Chem. (2), **41**, 1 (1890).

HELLER, G.: Färbung und beizenziehende Eigenschaften der Anthrachinon-Derivate. Ber., **43**, 2890 (1910).

WILLGRODT, C., AND MAFFEZZOLI, F.: Beiträge zur Kenntnis des Anthrachinon-o-dicarbonsäureanhydrids. J. prakt. Chem. (2), **82**, 205 (1910).

(58) LIEBERMANN, C., AND GIMBEL, A.: Ueber eine bequeme Darstellungsweise von Anthranol und Dianthryl. Ber., **20**, 1854 (1887).

(59) HELLER, G., AND SCHÜLKE, K.: Ueber die Friedel-Craftsche Reaktion. Ber., **41**, 3627 (1908).

ELBS, K.: Notiz über ein Verfahren zur Synthese von Homologen des Anthrachinons. J. prakt. chem., (2), **33**, 318 (1886).

LIMPRICHT, H., AND WIEGAND, O.: Ueber die p-Toluyl-o-benzoësäure. Ann., **311**, 178 (1900).

(60) PHILLIPS, M.: The Preparation of Methyl-Isopropyl-Anthraquinone. J. Am. Chem. Soc., **46**, 2533 (1924).