

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## REDUCTION PRODUCTS OF NAPHTHACENEQUINONE

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Naphthacenequinone is the most interesting of those few anthraquinones which fail to give the characteristic red vat when treated with hyposulfite and alkali in the usual manner. The failure of the Liebermann reaction cannot be attributed to steric interference, as in the case of the poly- $\alpha$ -substituted anthraquinones,<sup>1</sup> and the substance is simpler in structure than its benzologue, *lin.*-dibenzanthraquinone, which presents the same anomaly.<sup>2</sup> It is not generally known that naphthacenequinone belongs to this exceptional class of substances, for although the discoverers<sup>3</sup> made the highly interesting observation that the quinone forms an eosin-red solution on reduction in glacial acetic acid solution, they did not study the alkaline reduction, and the compound has received no attention since the time of their work. Further study perhaps has been delayed by the statement of Mills and Mills<sup>2</sup> that naphthacenequinone reacts in the usual manner with zinc and alkali. This unfortunate statement is probably an incorrect quotation from the paper of Gabriel and Leupold, for there is no indication that the English investigators studied the compound themselves. That there is this error in the very meager literature of the subject, became apparent to the present author in the course of an attempt to measure the reduction potential of naphthacenequinone. This attempt met with no success, and the failure appeared to be due to the unusual instability of the immediate reduction product.

Before any extensive study of the unusual behavior of naphthacenequinone could be conveniently undertaken, it was necessary to find a more suitable method of preparation than those which involve the very unsatisfactory hydrogen iodide-phosphorus reduction of hydroxy-<sup>4</sup> or dihydroxy-naphthacenequinone.<sup>3</sup> Such a method was found in the dehydrogenation of 2,3-tetralanthraquinone with bromine. Pure naphthacenequinone can be obtained in 80% yield by this method in the course of a few hours. It is of interest that the hydrocarbon, naphthacene, results from the zinc-dust distillation of 2,3-tetralanthraquinone.

The reduction of naphthacenequinone has been studied under a variety of conditions, and the main results are summarized in the accompanying chart. Boiled in glacial acetic acid solution with tin, the quinone, I, first gives a deep red solution of the hydroquinone, II, and the latter substance

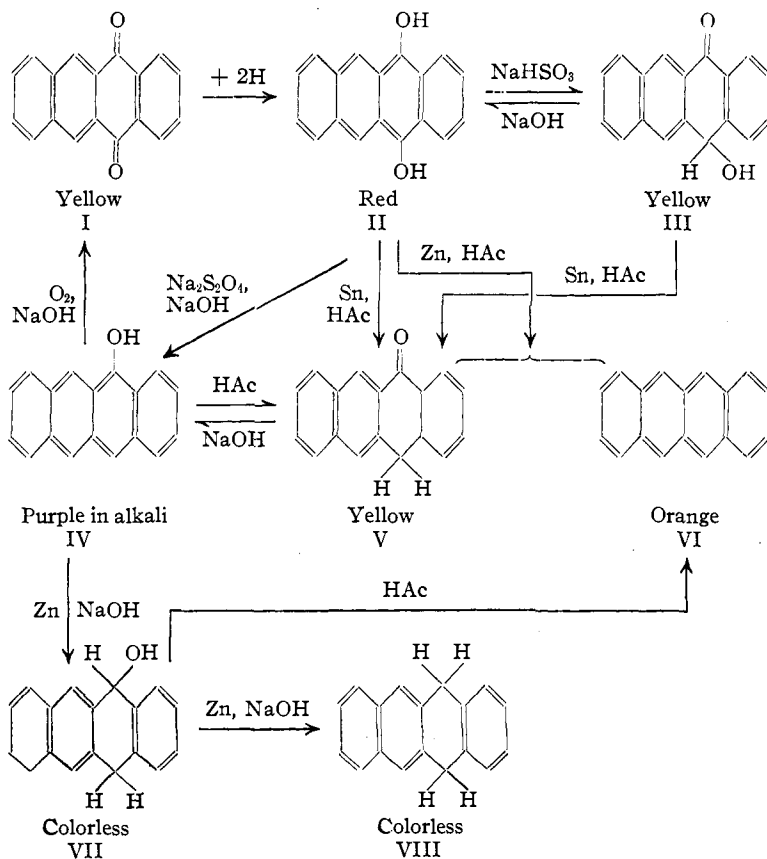
<sup>1</sup> (a) Seer, *Monatsh.*, **33**, 535 (1912); (b) Seer and Ehrenzweig, *ibid.*, **43** (1912); (c) Seer, *ibid.*, **34**, 579 (1913); (d) Philippi and Seka, *ibid.*, **43**, 617 (1922).

<sup>2</sup> W. H. Mills and M. Mills, *J. Chem. Soc.*, 101, 2194 (1912).

<sup>3</sup> Gabriel and Leupold, *Ber.*, **31**, 1277 (1898).

<sup>4</sup> Deichler and Weizmann, *ibid.*, **36**, 547 (1903).

is then slowly converted into 2,3-benz-9-anthrone, V, and the reaction stops at this point. With the more active metal zinc, a mixture of the anthrone and naphthacene, VI, is obtained and, since the anthrone cannot be converted into naphthacene under similar conditions, it is concluded that the hydrocarbon is produced by the direct reduction of the hydroquinone. In order to prepare the diacetate of the hydroquinone in good yield, it is necessary to modify the standard method of reductive acetylation by substituting tin for zinc. Otherwise the product is contaminated with the anthrone and the hydrocarbon.



Crystalline naphthacenequinone may be boiled indefinitely with alkaline hyposulfite solution without developing the red color characteristic for most anthraquinones. When it is prepared in a finely divided condition by pouring a solution in concentrated sulfuric acid into boiling water, the quinone rapidly dissolves in alkaline hyposulfite solution and the latter acquires a deep green color. The usual red vat is obtained only by the use

of alcohol as the solvent. When hyposulfite solution and a rather large quantity of alkali are added to a suspension of the quinone in boiling alcohol, the material dissolves in a few minutes to give a deep red solution of naphthacene hydroquinone, II. The color then slowly changes to an intense purple for which the anthranol, IV, is responsible. On acidification, the substance ketonizes and is obtained in the form of the anthrone.

While the anthrone, V, is a very stable substance, the enol form, IV, is sensitive to both oxidation and reduction. The purple solution in alcoholic alkali oxidizes readily in the air to give naphthacenequinone. It is not attacked by hyposulfite, but it is easily reduced by zinc in the presence of alcoholic alkali to the dihydro-anthranol, VII, which in turn is converted by the same reagent into dihydronaphthacene, VIII. The dihydroanthranol, VII, very easily loses the elements of water with the formation of naphthacene, VI. The dehydration takes place instantly in a boiling alcoholic solution on adding a trace of a mineral acid, and it is likely to occur in the process of crystallizing the compound from alcohol or ligroin unless a trace of a basic substance such as pyridine is added to stabilize it.

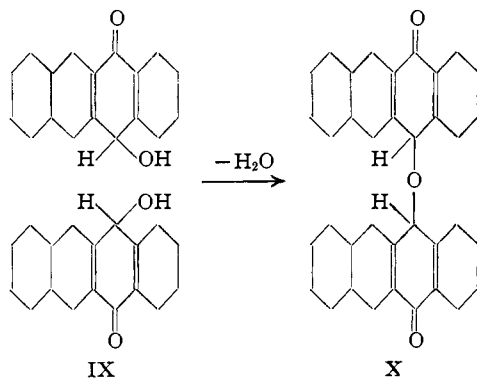
Naphthacenehydroquinone (II) is unstable in solution not only because it is easily reduced by the reagents ordinarily used to produce it, but also because it easily undergoes two other reactions, namely, disproportionation and ketonization. In a solution of the substance prepared by the hydrolysis of its diacetate, in order to eliminate the possibility of reduction, the hydroquinone undergoes mutual oxidation and reduction with the formation of the quinone and the anthrone. The reaction is quite rapid in an alcoholic solution which is either strongly acidic or weakly alkaline; it is very slow in a strongly alkaline medium. The striking color changes accompanying the disproportionation are described in the Experimental Part.

Under conditions which are not easily specified, naphthacenehydroquinone ketonizes and passes into 2,3-benz-9-hydroxyanthrone, III. The keto form may be obtained quantitatively from the quinone by adding hyposulfite solution and a certain small quantity of alkali to a boiling alcoholic suspension of the quinone. The deep red solution of naphthacenehydroquinone which first results suddenly changes within a few minutes to brown and then to a pale pink and the solution is now found to contain the hydroxyanthrone as the sole product. With more alkali present, the substance remains in the enolic form until it is slowly converted by reduction into the anthranol. The keto form can be enolized by the action of pyridine or, more slowly, by alcoholic alkali. Although the equilibrium appears to favor the keto form in neutral or acid solution, the quantitative ketonization of the hydroquinone has not been accomplished

except in the course of the preparative method described. When working in the absence of reducing agents, the disproportionation reaction appears to be more rapid than the ketonization.

The failure of naphthacenequinone to form a red vat in an aqueous medium is probably due in large part to the great instability of naphthacenehydroquinone.

One other reduction product, and one of an unusual type, was isolated by H. D. Newman in the course of some preliminary experiments described in the Experimental Part. It was later found that the same compound may be produced in quantity by the oxidation of 2,3-benz-9-anthranol, IV, in alcoholic alkaline solution by the action of sulfur. The substance has the molecular formula  $C_{36}H_{22}O_3$ . It yields naphthacenequinone on oxidation and 2,3-benz-9-anthrone on acid reduction, and it corresponds in the state of oxidation to naphthacenehydroquinone. The substance is obviously composed of two  $C_{18}$  residues, but an adequate basis for a choice between several possible formulas was only furnished by the results of a quantitative study of the action of the Grignard reagent. This showed that the compound has no active hydrogen atoms, but that it adds this reagent. From these facts it was concluded that the substance has the structure of di-(2,3-benz-9-anthronyl)-ether, X. If this formula is correct,



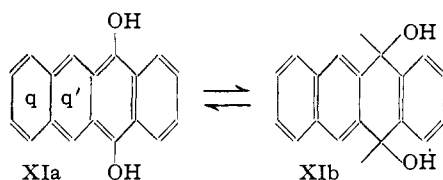
it should be possible to obtain the compound by the dehydration of two molecules of 2,3-benz-9-hydroxyanthrone, IX, and this was indeed found to be the case. The conversion is easily brought about by the action of acetic anhydride and a trace of sulfuric acid. The ether structure is thus confirmed, and the compound represents a type which is probably novel in the anthraquinone series.

**The Theoretical Significance of the Results.**—When the various naphthacene derivatives here described are compared with the corresponding derivatives of anthracene, it becomes apparent that there is a marked difference between the two series. Naphthacenehydroquinone, II, is

more easily reduced than is anthrahydroquinone, and it has a much greater tendency to ketonize. This statement applies equally well to 2,3-benz-9-anthranol (IV); it readily forms a dihydride on reduction, and the ketonization takes place with such facility that the isomerization can only be reversed by the action of alcoholic alkali. Pyridine and aqueous alkali, reagents which readily enolize anthrone, are without effect on 2,3-benz-9-anthrone, V. In each of the instances cited it is seen that the naphthacene derivatives possess an enhanced tendency to react in such a way as to produce derivatives of dihydronaphthacene. A further example of the greater stability of the dihydride structure in the naphthacene as compared with the anthracene series is that, while dihydroanthranol becomes dehydrated in alkaline solution to give anthracene, its 2,3-benz-derivative (VII) does not lose water under similar conditions, but retains the dihydride structure and is easily reduced to dihydronaphthacene.

The disproportionation of naphthacenehydroquinone is a reaction which may be classed with those already cited. While anthrahydroquinone reacts in a similar manner only on prolonged boiling in an alcoholic solution containing hydrochloric acid,<sup>5</sup> naphthacenehydroquinone is completely decomposed in a few minutes even in a weakly alkaline solution. Here again a substance having a completely aromatic structure appears to be peculiarly unstable and it undergoes mutual oxidation and reduction to form products which, in their most stable condition, possess the dihydride structure.

The ortho quinonoid structure for anthracene and its benzologues furnishes the simplest explanation of the facts observed. As compared with anthrahydroquinone, naphthacenehydroquinone, XIa, has, in place of a



single ortho quinonoid ring, two rings which are quinonoid. The combined system presented by rings q and q' is similar to that of the unknown 2,3-naphthoquinone, and the lack of stability of this substance shows that such a system is one of great strain or of great reactivity. This furnishes an adequate interpretation of the pronounced tendency of the compound in question to pass into substances having the dihydride structure either by ketonization, reduction or disproportionation, for the condition of strain in the molecule is thereby relieved. The striking colors of those naphthacene derivatives which have the completely aromatic

<sup>5</sup> K. H. Meyer, *Ann.*, 379, 61 (1911).

structure may also be attributed to the quinonoid grouping, though the relationship of the different substances is not clear (see chart).

One may also regard naphthacene as a substance having a conjugated system of six double bonds and with consequent enhanced reactivity<sup>6</sup> at the meso carbon atoms, which are at the ends of this long system. Regarded thus as a condensed derivative of *o*-phenylenedodeca-hexa-ene, the orange hydrocarbon corresponds well in color with diphenyl-dodeca-hexa-ene, which is brown-orange.<sup>7</sup> There is also a rough correlation between the aromatic and aliphatic compounds having systems of eight conjugated double bonds with phenyl groups at the two ends, for Clar and John<sup>8</sup> have described *lin.*-dibenzanthracene as a blue hydrocarbon, while Kuhn and Winterstein<sup>7</sup> have found diphenyl-hexadeca-octa-ene to be bluish copper-red.

Since the *o*-quinonoid formula and the poly-ene formula are one and the same, the two points of view regarding the anthracene hydrocarbons are in no way antagonistic, but they rather supplement each other.

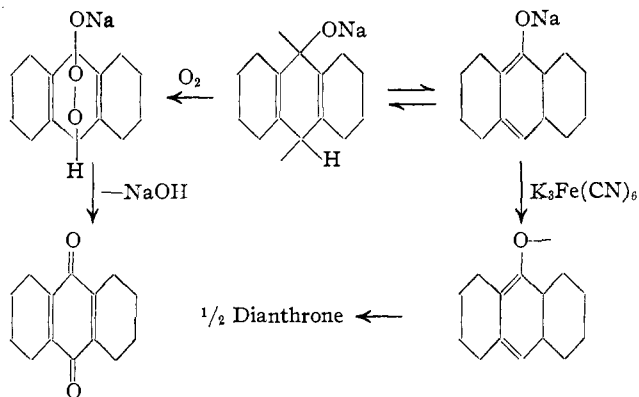
Clar and John<sup>8</sup> have recently advanced evidence to show that their blue *lin.*-dibenz-anthracene has the properties of a bivalent radical. According to their views, naphthacenehydroquinone in solution should consist of an equilibrium mixture containing the radical XIb. Naphthacene itself can hardly be formulated as a bivalent radical, for it is not attacked by moist oxygen in high-boiling solvents in the manner characteristic of the pentacyclic hydrocarbon. There is reason to believe, however, that the hydroxyl or metal-oxyl groups of naphthacenehydroquinone would promote radical dissociation at the meso carbon atoms. The red color of acid solutions of the substance is unusual among the anthrahydroquinones, and the suggestion that the color is due to the presence of a certain quantity of the bivalent radical is an attractive one. The reactions by which the compound stabilizes itself also find a ready explanation in terms of this hypothesis.

It may be pointed out in this connection that the assumption of free radicals furnishes the basis for a comprehensive interpretation of the alkaline oxidation of anthrahydroquinones and anthranols. It is generally agreed that the oxidation of sodium anthranolate to dianthrone by reagents other than oxygen proceeds through the intermediate formation of a univalent oxygen radical. The reaction with molecular oxygen must follow a different course, for the product is anthraquinone and not dianthrone. If the solution consists of an equilibrium mixture containing the trivalent carbon radical, this could form a peroxide which, by loss of sodium hydroxide, would yield anthraquinone. The reactions may be formulated as follows

<sup>6</sup> Wittig and Wiemer, *Ann.*, **483**, 144 (1930).

<sup>7</sup> Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

<sup>8</sup> Clar and John, *Ber.*, **63**, 2967 (1930).



Applied to the action of oxygen on anthrahydroquinone in alkaline solution, the same mechanism may serve to account for the great speed of the reaction,<sup>9</sup> and it agrees well with the facts. The peroxide in this case would yield anthraquinone by the elimination not of sodium hydroxide but of sodium peroxide, and it is well known that this is one of the reaction products.

It must be recognized that the results presented in this paper neither confirm nor contradict the interesting hypothesis that anthracene derivatives partially isomerize to substances with trivalent meso carbon atoms and that the isomerization increases with the number of linear rings. Since any isomerization to radicals must be the result of a strained condition within the molecule for which the ortho quinonoid structure may be considered responsible, the ortho quinonoid theory may be extended to include the possibility of radical formation, and it is thus both the sounder and the more fundamental of the two views.

### Experimental Part

**2,3-Tetralanthraquinone.**—As a result of the preparation of large quantities of this material, the following procedure can be recommended as representing some improvement of Schroeter's procedure for the preparation of *o*-[tetroyl-2]-benzoic acid.<sup>10</sup> A mixture of 250 g. of phthalic anhydride, 350 g. of tetralin, 1200 cc. of benzene and 400 g. of aluminum chloride was stirred and heated at the boiling point for three hours. After cooling, the benzene layer was decanted from the addition product and discarded. The addition product was decomposed by adding ice and 400 cc. of concentrated hydrochloric acid, and then treated with steam until most of the adhering benzene and tetralin was removed. After removal of the aqueous solution, the product was treated with a solution of 150 g. of sodium carbonate monohydrate and digested with steam until all but a small residue had dissolved and the remaining tetralin was evaporated. The solution yielded 459 g. (97%) of good product on acidification.

In the condensation to the tetralanthraquinones, it was found expedient to use two

<sup>9</sup> Fieser, *THIS JOURNAL*, **46**, 2639 (1924).

<sup>10</sup> Schroeter, *Ber.*, **54**, 2242 (1921).

to three times the quantity of sulfuric acid employed by Schroeter, though there was no improvement in the yield.

**Naphthacenequinone.**—A boiling solution of 50 g. of *lin.*-tetralanthraquinone in 350 cc. of glacial acetic acid was treated with 65 g. of bromine in the course of one-half hour. Most of the solvent was removed by distillation and the thick sirup which remained was washed out while still hot into a distilling flask with sealed-on receiver. The remaining solvent was distilled off, and the heating was continued cautiously in order to promote the evolution of hydrogen bromide. The reaction should be carried out as slowly as possible, for it easily becomes too vigorous. As the formation of naphthacenequinone reached completion, the contents of the flask suddenly solidified. The product was then distilled under diminished pressure with the use of an oil pump, and then redistilled. The crude product (44 g.) is best crystallized from tetrachloroethane, which has marked solvent power for the polycyclic quinones and hydrocarbons. A single crystallization gave 37 g. of the pure quinone, while a further 3-g. portion was recovered from the mother liquor; yield (pure), 81%.

Naphthacenequinone forms yellow needles from tetrachloroethane, very long yellow or orange-yellow needles from glacial acetic acid. The purest samples melted at 285°. Gabriel and Leupold<sup>3</sup> have described the characteristic color tests with concentrated sulfuric acid and with glacial acetic acid and zinc dust

**2,3-Benz-9-anthrone (5-Oxo-naphthacene), V.**—The best method of preparing the anthrone from naphthacenequinone is by reduction with tin in glacial acetic acid solution. Zinc is too energetic in its action and invariably leads to the production of some naphthacene. It is of interest that the hydrocarbon produced by reduction with zinc and acetic acid does not come from 2,3-benz-9-anthrone, for this substance, though easily reduced when in the anthranol condition (alkaline solution), is not affected by prolonged boiling in glacial acetic acid solution with zinc and hydrochloric acid. It thus must result above from the reduction of benz-anthrahydroquinone.

Four grams of naphthacenequinone was suspended in 100 cc. of glacial acetic acid and boiled under the reflux with 8 g. of granular tin. The quinone slowly dissolved with the formation of a deep red solution; the color faded to a pale yellow-brown in about one hour, when the reduction was complete. The solution was filtered, treated with 10 cc. of concentrated hydrochloric acid, concentrated to half its volume, and allowed to cool. The anthrone separated in nearly pure condition (3.5 g.).

A second satisfactory method of preparing 2,3-benz-9-anthrone is by reduction in alkaline solution with sodium hydrosulfite. This will be described below.

The anthrone is readily soluble in glacial acetic acid or benzene and moderately soluble in alcohol. It forms yellow needles melting at about 196°, the temperature being dependent upon the rate of heating.

*Anal.* Calcd. for  $C_{18}H_{12}O$ : C, 88.49; H, 4.96. Found: C, 88.21; H, 5.16.

The solution of the anthrone in concentrated sulfuric acid is bright red. The compound is not soluble in aqueous alkali, but dissolves readily in alcoholic sodium hydroxide solution. The solution is intensely purple; when shaken with air it rapidly loses this color and naphthacenequinone precipitates. The anthrone is not enolized by pyridine, for the material was recovered unchanged after boiling a pyridine solution with acetic anhydride.

**Naphthacenehydroquinone Diacetate (9,10-Diacetoxy-2,3-benz-anthracene).**—Liebermann's method of reductive acetylation with zinc dust, sodium acetate and acetic anhydride gave a very poor yield in the present case owing to the great ease of reduction of naphthacenehydroquinone. The desired product was invariably contaminated with the anthrone and with naphthacene. A satisfactory preparation was found in the substitution of granular tin for zinc and proceeding in the usual manner. A pure product



was thus easily obtained in good yield. The substance crystallizes well from glacial acetic acid, forming orange needles melting at 269°. Dilute solutions of the substance are yellow with a green fluorescence. The hydrolysis of the diacetate will be described below.

*Anal.* Calcd. for  $C_{22}H_{16}O_4$ : C, 76.72; H, 4.69. Found: C, 76.33; H, 4.98.

**2,3-Benz-9-hydroxyanthrone (5-Hydroxy-12-oxo-5,12-dihydronaphthacene), III.**—

This compound was first obtained by adding successive portions of sodium hyposulfite solution to a boiling alcoholic suspension of naphthacenequinone. Each addition of reagent caused the solution to take on a red color which, however, disappeared suddenly in the course of a few minutes (ketonization of the hydroquinone); but even after several hours the reduction of the quinone was not complete. It was then found that the presence of a limited quantity of alkali materially assists in the reduction and in the formation of the desired compound. With a still larger quantity of alkali present the reduction does not stop at the hydroxyanthrone stage but converts this into the anthranol. The hydroxyanthrone also may be reduced with tin in glacial acetic acid solution, forming the anthrone.

To a suspension of 6 g. of naphthacenequinone in 400 cc. of boiling alcohol, there was added a concentrated aqueous solution of 12 g. of sodium hyposulfite and 10 cc. of 6 *N* sodium hydroxide. The quinone rapidly dissolved, giving a deep red solution having the appearance characteristic of an anthraquinone vat. After about two minutes, the color suddenly changed to a dark greenish-brown and then as suddenly cleared to a pale pink, with the separation of inorganic salts. The inorganic material, together with a small amount of unreacted quinone, was removed by filtering the hot solution and the latter was poured into an equal volume of water to precipitate the reaction product. The material was pale pink in color and very nearly pure. The yield depends somewhat upon the character of the starting material. If a crystalline sample of the quinone is used, about 10% of it is recovered unchanged. When the naphthacenequinone is prepared in finely divided condition by pouring a sulfuric acid solution of the substance into boiling water, the conversion is quantitative.

When the above procedure was altered only to the extent of using twice the specified quantity of alkali the course of the reduction was entirely different. The red, vat color persisted for about one-half hour, when a change to reddish-purple became apparent. After one hour the solution had the purple color characteristic of the anthranol salt, and it showed no further change on prolonged reaction. On acidifying and diluting the solution, 2,3-benz-9-anthrone was obtained in excellent yield. Reduction in an alcoholic medium in the presence of a large amount of sodium carbonate also led to the formation of the anthrone. When in a finely divided condition, naphthacenequinone may be reduced with hyposulfite and alkali in an aqueous medium. The solution first becomes deep green; the color then suddenly fades and a mixture of the anthrone and the hydroxyanthrone separates.

2,3-Benz-9-hydroxyanthrone dissolves readily in benzene or glacial acetic acid; it is moderately soluble in alcohol and sparingly soluble in ligroin. It forms excellent, long, hair-fine, yellow needles and decomposes at about 230°. A characteristic test for the compound is furnished by the deep red color which it imparts to alcoholic sodium hydroxide solution (see below). It is insoluble in aqueous alkali.

*Anal.* Calcd. for  $C_{18}H_{12}O_2$ : C, 83.05; H, 4.65. Found: C, 82.55; H, 4.57.

This benz-hydroxyanthrone enolizes readily in boiling pyridine solution and the solution rapidly acquires the deep red color characteristic of naphthacenehydroquinone. The color fades on shaking with the air and naphthacenequinone crystallizes from the solution. When heated with a mixture of equal parts of pyridine and acetic anhydride, the benz-hydroxyanthrone is converted largely into naphthacenehydroquinone diacetate,

m. p. 269°, though a part of the naphthacenehydroquinone becomes oxidized to the quinone before it can be acetylated.

**2,3-Benz-9,10-dihydro-anthranol (5-Hydroxy-5,12-dihydronaphthacene), VII.**—This compound has been obtained as the first product of the reduction of 2,3-benz-9-anthrone in alcoholic alkaline solution with zinc dust, but it is most readily prepared directly from naphthacenequinone. The velocity of reduction increases very rapidly with an increase in the concentration of alkali. Under the conditions of the experiment 2,3-benz-9,10-dihydro-anthranol is in turn easily reduced to dihydronaphthacene, and the formation of a small amount of this material could not be avoided. The best yields were obtained in the following manner.

A suspension of 1 g. of naphthacenequinone in 100 cc. of alcohol and 10 cc. of 25% sodium hydroxide was boiled with 5 g. of zinc dust for one hour. The quinone rapidly dissolved to give a deep red solution; this became deep green within a few minutes and then the color slowly faded. At the end of the time specified the solution was pale greenish-yellow. It was cooled and the residue, consisting chiefly of zinc, was washed with water, dried and extracted with benzene. The benzene extract contained dihydronaphthacene (0.2 g.). The 2,3-benz-9,10-dihydro-anthranol was precipitated with water from the alcoholic solution. In order to remove a trace of zinc hydroxide and dihydronaphthacene, the crude product was dissolved in alcohol containing one drop of sodium hydroxide; the solution was cooled well, filtered and the product was precipitated with water. The material cannot be further purified by crystallization from pure solvents such as alcohol or ligroin because it is partially converted by the boiling solvents into naphthacene. A trace of an alkaline reagent, however, prevents this dehydration. The substance thus crystallizes well from benzene-ligroin containing a drop of pyridine. The solvent completely removes an otherwise persistent yellow color, and the compound forms colorless silken needles which form cottony clusters of great beauty.

*Anal.* Calcd. for  $C_{18}H_{14}O$ : C, 87.77; H, 5.73. Found: C, 87.40; H, 5.75.

The benz-dihydro-anthranol has no melting point but decomposes even on very gentle heating with the formation of naphthacene. The dehydration occurs slowly on boiling an alcoholic solution of the substance, and it is completed within a few seconds if a trace of mineral acid is added. This is a good way of preparing pure naphthacene.

**Dihydronaphthacene, VIII.**—A good method of preparing this substance consists in reducing naphthacenequinone with zinc dust and alcoholic alkali in exactly the manner described above, with the exception that the heating is continued for six hours. Water is added to the now pale yellow solution and the product is extracted from the zinc with benzene. The purified material was yellow and melted at 207°. Like Gabriel and Leupold,<sup>8</sup> I was unable to remove the colored impurity.

**Naphthacene.**—This hydrocarbon was obtained both from 2,3-benz-9,10-dihydro-anthranol and by the zinc dust distillation of 2,3-tetralanthraquinone. The zinc serves to hydrogenate one part of the molecule, while it dehydrogenates another part.

One gram of 2,3-tetral-anthraquinone was dissolved in benzene in a small distilling flask and treated with 50 g. of zinc dust. After evaporation of the benzene, a further 25 g. of zinc dust was added and the flask was strongly heated. The distillate (0.5 g.) crystallized from tetrachloroethane, forming orange plates melting at 331°; it was identical with naphthacene.

**Di-(2,3-benz-9-anthronyl) Ether, X.**—This compound first made its appearance when a mixture of naphthacenequinone and naphthanthraquinone was being separated by vatting the latter compound with alkaline hyposulfite solution. Naphthacenequinone does not vat in the usual way, but as a result of the repeated treatment with hyposulfite, a small portion of the material was converted into the new ether. The substance concentrated in the mother liquors from the crystallization of the naphthacenequinone

from glacial acetic acid. It was later found that the substance is produced in good yield when a very weakly alkaline solution of 2,3-benz-9-anthrone in alcohol is boiled for about one week in an atmosphere of nitrogen in a three-necked flask carrying rubber stoppers. The observation that the anthrone solution is perfectly stable when boiled in an all-glass apparatus led me to suspect that the observed reaction is an oxidation brought about by the sulfur in the stoppers. This was confirmed by experiment, and a suitable method of preparation thus became available.

Three grams of 2,3-benz-9-anthrone was dissolved in 450 cc. of alcohol, the solution was swept free of oxygen, and 1 g. of sulfur was added. A few drops of alkali were added to produce a purple solution, and more was added later to maintain a weakly alkaline solution. Crystals of the ether soon began to deposit on the walls of the flask and the reaction was complete in about three hours. The product was collected from the hot solution, which was very dark in color, and smelled of hydrogen sulfide. The material so prepared was very nearly pure; yield, 2 g.

The ether is very sparingly soluble in alcohol or benzene. It is very soluble in chloroform, but dissolves quite slowly. It may be purified by dissolving in chloroform, concentrating the solution and precipitating the product with petroleum ether. Good crystals are formed from glacial acetic acid, though the substance dissolves very slowly in this solvent and crystallizes only after considerable concentration. Thus naphthacenequinone, which crystallizes first from a mixture with the ether, can be dissolved out of such a mixture with glacial acetic acid, without dissolving the ether. The latter substance also crystallizes well from pyridine, in which it is very soluble. The ether forms small, salmon-colored plates melting at 295°. Crystals from chloroform are colorless, but acquire the above color on drying. A characteristic property of the ether is its color in concentrated sulfuric acid. The cold solution is bright red; on standing, or on gentle heating, it changes to an intense, pure blue.

*Anal.* Calcd. for  $C_{36}H_{22}O_2$ : C, 86.03; H, 4.42. Found: C, 86.03, 86.22; H, 4.79, 4.50. *Mol. Weight.* Calcd.: 502.2. Found (Rast): 498, 496.

In the modified Zerewitinoff "machine" of Kohler<sup>11</sup> the substance showed no active hydrogen atoms, but added well over one mole of Grignard reagent in five minutes, even though it did not completely dissolve. The ether is converted quantitatively into naphthacenequinone by chromic acid, or into 2,3-benz-9-anthrone by tin and glacial acetic acid.

The relationship of the ether to 2,3-benz-9-hydroxyanthrone was established by the following experiment. To a suspension of 0.6 g. of the latter compound in 5 cc. of acetic anhydride a drop of concentrated sulfuric acid was added. The material rapidly dissolved to give a dark brown solution and crystals of the ether soon began to separate. After heating for one-half hour on the steam-bath, the product was collected and purified. It formed the characteristic salmon-colored plates melting at 295°, and was identical with the material prepared previously.

**The Properties of Naphthacenehydroquinone (II).**—This substance is the primary reduction product of naphthacenequinone in acid or alcoholic alkaline medium, and it imparts a red color to the solvent in either case. The solution in alcoholic alkali is deep blood-red; the alcoholic or glacial acetic acid solution is only slightly brighter. The action of zinc dust and acetic acid on naphthacenequinone produces only an eosin-red solution, because the hydroquinone is reduced further nearly as rapidly as it is formed, but by the substitution of tin for zinc a solution can be obtained which approaches in intensity the usual anthraquinone vat color. Because of its sensitivity to further reduction, solutions of the hydroquinone are best prepared from its diacetate or from its ketonic modification, though in neither case is it possible to prepare an unquestionably

<sup>11</sup> Kohler and collaborators, *THIS JOURNAL*, 49, 3181 (1927); 51, 3736 (1930).

pure solution, for the substance very readily undergoes a disproportionation. The reaction is best described by quoting a few experiments.

A suspension of 0.5 g. of naphthacenehydroquinone diacetate in 150 cc. of alcohol was boiled in an all-glass apparatus in an atmosphere of nitrogen and then cooled to room temperature, when only a part of the material remained in solution (yellow). On adding 15 cc. of 6 *N* sodium hydroxide the solution became deep green. In a few seconds this changed to blue and this as rapidly changed to reddish-purple. On warming, the solution became deep red. These striking color changes are interpreted as follows. The blue solution probably contains the monoacetate, which is a derivative of 2,3-benz-9-anthranol and which might well exhibit a similar color. The final red color is without doubt due to the presence of the hydroquinone salt or ion. The green and purple solutions thus represent mixtures of the diacetate and monoacetate and of the monoacetate and the hydroquinone. The red color was not permanent but changed in the course of three to four days (at the boiling point) to the intense purple characteristic of solutions of the anthranol. When this solution was acidified, it became pale yellow at once and it was found to contain naphthacenequinone and the corresponding anthrone. The experiment shows that disproportionation of the hydroquinone takes place slowly in strongly alkaline solution.

In another experiment the diacetate was hydrolyzed in exactly the same manner, but as soon as the solution reached the pure red stage (five minutes) it was acidified with an excess of hydrochloric acid. The color changed from the deep, vat red to a less intense, bright red. This rapidly faded and in fifteen minutes it had become pure yellow. The alcoholic solution was found to contain about equal parts of naphthacenequinone and the anthrone. This shows that the disproportionation of the hydroquinone takes place much more rapidly in acid than in alkaline solution. The fading of the red solution of the hydroquinone as the result of the disproportionation was less rapid in the presence of acetic acid.

When a much smaller amount of alkali (1-2 cc.) was used to hydrolyze the diacetate (0.5 g.) in alcoholic suspension, the solution became green, then blue and finally purple, and the red color characteristic of the anthrahydroquinone was never reached. The acidified solution was only faintly pink and it contained the usual products of oxidation and reduction. The conclusion drawn from this observation is that the disproportionation occurs as rapidly in a weakly alkaline solution as in the presence of acids. The anthrahydroquinone disappears about as rapidly as it is produced by hydrolysis.

The benz-anthrahydroquinone may also be produced in solution by the enolization of 2,3-benz-9-hydroxyanthrone by alcoholic alkali, but the process is so slow that some of the material is probably destroyed by disproportionation during the period required. Thus when a boiling solution of 0.5 g. of the material in 150 cc. of alcohol was treated with 15 cc. of 6 *N* sodium hydroxide, the solution became deep brown and only acquired the intensely red color after one and one-half hours. On adding hydrochloric acid, the bright red solution which rapidly changes to yellow was again obtained. An observation for which I cannot account is that the addition of a few drops of alkali to an alcoholic solution of the hydroxy-anthrone produces at once a light red solution, while with a large amount of alkali the solution changes from red to brown to red only slowly. The light red solution can hardly contain a large amount of the anthrahydroquinone, because it undergoes disproportionation only after several days.

### Summary

A satisfactory method of preparing naphthacenequinone consists in the dehydrogenation of 2,3-tetralanthraquinone with bromine. By choosing suitable reagents and conditions, naphthacenequinone may be converted

in good yield into any one of the following reduction products: the keto form of the hydroquinone, the anthrone, a di-anthranyl ether, the dihydroanthranol, naphthacene or dihydronaphthacene. Naphthacenehydroquinone, known only in solution or in the form of derivatives, is a remarkably unstable substance. It may be reduced with great ease, it ketonizes readily and it also undergoes a disproportionation.

All of the naphthacene derivatives which have a completely aromatic structure show a marked tendency to pass into derivatives of dihydronaphthacene. This is interpreted in terms of the ortho quinonoid structure for anthracene. The theory of bivalent radical formation is also discussed.

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## THE PREPARATION AND SOME PROPERTIES OF THE CHLOROMANDELIC ACIDS, THEIR METHYL ESTERS AND AMIDES

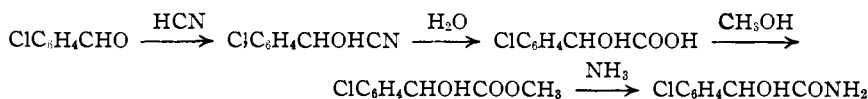
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In connection with another research<sup>2</sup> some derivatives of the chloromandelic acids were desired. Apparently only the ortho<sup>3</sup> and para<sup>4</sup> acids and the para<sup>5</sup> amide have been described heretofore. It was thus decided to prepare the three acids with the corresponding methyl esters and amides.

The method of Karrer,<sup>3</sup> in which *o*-chloromandelic acid was obtained from the aldehyde through the cyanohydrin, was employed. Certain modifications described in the experimental part, however, greatly increased the yield. For the esterification the method of Fischer and Speier<sup>6</sup> was employed. The amides were obtained by treating alcoholic ether solutions of the esters with anhydrous ammonia. The reactions are



### Experimental

**Preparation of the Chloromandelic Acids.**—Into a 500-cc. Claisen flask standing in an ice-bath were placed 100 g. of the chlorobenzaldehyde, 48 g. of 96–98% potassium

<sup>1</sup> Graffin Scholar, 1930–1931.

<sup>2</sup> To be published.

<sup>3</sup> Karrer, *Helv. Chim. Acta*, **4**, 144 (1921).

<sup>4</sup> Collet, *Bull. soc. chim.*, [3] **21**, 70 (1899); Straus, *Ann.*, **393**, 320 (1912).

<sup>5</sup> Rule, *J. Chem. Soc.*, **113**, 17 (1918).

<sup>6</sup> Fischer and Speier, *Ber.*, **28**, 3252 (1895).