acid was dissolved in a small amount of water and six times the theoretical amount of sodium amalgam added very slowly with constant stirring. When the reaction was complete the solution was acidified with hydrochloric acid and evaporated to dryness on a water-bath. The residue was taken up with methyl alcohol, the solution filtered and evaporated as before. The product was weighed and the calculated amount of 0.1 *N* sodium hydroxide added to free the acid from the hydrochloride. This was evaporated until crystals began to form and then allowed to stand at 0° for twenty-four hours. This method was used since β-amino-β-phenylpropionic acid is soluble in alcohol and the methods used for the other acids were not applicable. A 65% yield of crude product was obtained which contained no chlorine. The melting point was, however, too low and the compound could not be readily purified. The benzoyl derivative was prepared as described for β-amino-α-chlorobutyric acid. The melting point of the purified product was 194–195° (uncorr.). A mixed melting point was taken with the known compound prepared by another method.

Anal. Subs., 0.0200, 0.0201: 7.65, 7.66 cc. of 0.01 *N* HCl. Calcd. for $C_{16}H_{15}O_3N$: N, 5.21. Found: N, 5.36, 5.34.

Summary

Nitrogen trichloride reacts with crotonic acid to form, among other products, α-chloro-β-dichloro-aminobutyric acid, which is changed by hydrochloric acid to β-amino-α-chlorobutyric acid. The structure of the compound was established by reduction to the corresponding amino acid.

A similar reaction occurs with cinnamic acid. The dichloro-amino group again enters the β-position.

Iowa City, Iowa

[Contribution from the Chemical Laboratory of Bryn Mawr College]

SOME DERIVATIVES OF 3,4-PHENANTHRENEQUINONE

By Louis Frederick Fieser

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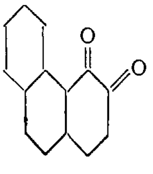
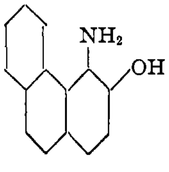
In the belief that a knowledge of the reduction potentials of ortho- or para-quinones derived from phenanthrene, but isomeric with 9,10-phenanthrenequinone, would throw some additional light on the general problem of the relationship between the oxidizing power and the structure of the various quinones, the author undertook to prepare one or two compounds of the isophenanthrenequinone type, and to compare them, by the potentiometric method, with the corresponding naphthoquinones. In the course of this work it soon became evident that the isophenanthrenequinones, which have received scarcely any attention up to the present time, are interesting from several points of view other than that of the original problem, and the work has thus developed into a rather extensive study of the general chemistry and the methods of obtaining various isophenanthrenequinones and compounds derived from them. The presentation of the results of investigations which are concerned solely with the chemistry of phenanthrene derivatives will be followed with an account of the electrochemical data which have accumulated.

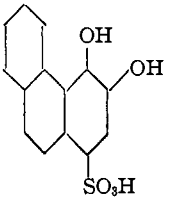
3,4-Phenanthrenequinone (I).—This is the only one of the isophenanthrenequinones of the type indicated which has been described up to the present time. Barger[1] obtained the quinone by oxidizing morphol with silver oxide; the morphol which he employed was prepared by converting 3-phenanthrol into an ortho-aldehyde and oxidizing the latter substance with hydrogen peroxide. A more convenient method was suggested by an unexplained observation of Werner and his students.[2] These investigators, in the course of a careful study of 3-phenanthrol, converted this compound into an amino-3-phenanthrol by coupling with a diazonium salt and reducing the azo dye. When they attempted to diazotize the amino-3-phenanthrol hydrochloride, as the first step in the proposed conversion of the compound into a dihydroxyphenanthrene, they were surprised to find that nitrous acid converted the salt into a sparingly soluble, easily decomposed, yellow substance. Since the substance was obviously not a diazonium salt, their original plan was abandoned, though it is now clear that they were very close to achieving one of the aims of the extensive studies on phenanthrene undertaken by Werner, namely, the preparation of morphol from the hydrocarbon. It appeared probable to the author that the colored substance was a quinone, produced by the oxidizing action of nitrous acid, and investigation has shown that this is the case and that the substance is 3,4-phenanthrenequinone. On reduction it yields morphol, while morpholquinone may be obtained from it by known methods. It is thus clear that 3-phenanthrol couples in the 4-position and that the amine has the structure of II.



I



II



III

It has been found possible to carry out the preparation of 4-amino-3-phenanthrol hydrochloride on a large scale in a simple manner. The dyestuff formed on interaction with diazotized sulfanilic acid is reduced, without being isolated, by means of sodium hyposulfite. The oxidation of the amine hydrochloride is best accomplished by adding an aqueous solution of chromic acid to a suspension of the salt in glacial acetic acid. The yields in all of these reactions are good.

3,4-Phenanthrenequinone is characterized by the brilliant red color of its crystals and by a beautiful color reaction with concentrated sulfuric acid. Though certain precautions must be observed in order to prevent

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[1] Barger, *J. Chem. Soc.*, **113**, 218 (1918).

[2] Werner, Löwenstein, Wack and Kunz, *Ann.*, **321**, 297 (1902).

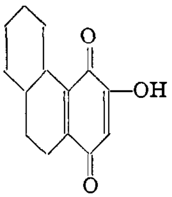
the destruction of a considerable quantity of the material during the course of its preparation, the pure quinone is a quite stable substance. Like other ortho-quinones it adds a molecule of sodium bisulfite with the formation of a sulfonic acid derivative of the hydroquinone. In consideration of the nature of this reaction, the substance must have the structure of 3,4-dihydroxy-phenanthrene-1-sulfonic acid, III, and this is confirmed by the conversion of the substance into the para-quinone described below. The sulfonic acid was isolated in the form of the *p*-toluidine salt and was converted into the corresponding quinone by oxidation.

3-Hydroxy-1,4-phenanthrenequinone.—A fairly satisfactory method of preparing this compound, which is the first representative 1,4-phenanthrenequinone to be described, was found in the oxidation of 3,4-dihydroxy-phenanthrene-1-sulfonic acid in alkaline solution with hydrogen peroxide. The quinone separates in the form of a sparingly soluble sodium salt. Much poorer yields of the hydroxyquinone were obtained by the addition of acetic anhydride to 3,4-phenanthrenequinone and by hydrolyzing and oxidizing the 1,3,4-triacetoxyphenanthrene produced, or by hydrolyzing 3,4-phenanthrenequinone-1-sulfonic acid, though these methods are serviceable in several other instances.

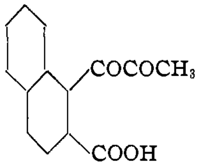
3-Hydroxy-1,4-phenanthrenequinone is very similar in properties to other compounds of the same type, such as hydroxynaphthoquinone or 2-hydroxy-1,4-anthraquinone. Thus the methyl ether may be obtained by the Fischer method of esterification, while interaction of the silver salt of the quinone with allyl bromide yields a mixture of the C-alkylation product, 2-allyl-3-hydroxy-1,4-phenanthrenequinone (63%) and the ortho-quinone ether, 1-alloxy-3,4-phenanthrenequinone (17%).

The Cleavage of 3-Hydroxy-1,4-phenanthrenequinone by Alkali.—While the above-mentioned reactions of the isophenanthrenequinones all belong to well-known types, an entirely novel behavior was discovered when 3-hydroxy-1,4-phenanthrenequinone was subjected to the prolonged action of dilute alkali. The red sodium salt of this quinone is only moderately soluble in water, but when a suspension of the salt in very dilute sodium hydroxide solution was boiled for a few hours in an open beaker the material all dissolved and gave a dull brown-red solution. On acidification a substance separated which dissolved readily in water and crystallized in the form of colorless plates.

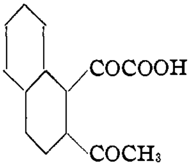
The empirical formula of this compound corresponds to that of 3-hydroxy-1,4-phenanthrenequinone plus the elements of water. The substance displaces carbonic acid from its salts, it may be esterified with an alcohol and hydrogen chloride and titration reveals the presence of a single carboxyl group. From these facts it would appear that the quinonoid ring of the hydroxyquinone, IV, has suffered cleavage by the action of a molecule of water. The nature of this cleavage is further elucidated by the fact



IV



V



VI

that the acidic substance yields naphthalene-1,2-dicarboxylic acid on oxidation in alkaline solution by means of hydrogen peroxide. From this it may be concluded that the cleavage of the hydroxyquinone has occurred between the carbon atoms at positions 1 and 2 or at the 2- and 3-positions, or at the 3- and 4-positions. A distinction among these three possibilities is furnished by a consideration of other properties of the cleavage product. This acid melts at 195° and at that temperature loses carbon dioxide; it is not affected by prolonged boiling of its solutions either in dilute acids or alkalies. It is conceivable that the quinone, reacting in a tautomeric, ortho-quinonoid form, might undergo ring rupture at the 1,2-bond, giving V, but this formula is not consistent with the fact that the acid evolves carbon dioxide on melting. The possibility of cleavage between 3 and 4 is ruled out because this would give rise either to a β-keto acid or a β-keto aldehyde (or their enolic forms), and such substances would not possess the observed stability toward mineral acids and alkalies.

On the other hand, the rupture of the ring at the double bond between positions 2 and 3 would yield the α-keto acid, VI, and the properties of the cleavage product are entirely consistent with this formulation. A further confirmation of this structure is furnished by the application of a reaction typical of α-keto acids. It is known that aniline, at an elevated temperature, converts phenylglyoxylic acid into benzalaniline,[3] and α-naphthylglyoxylic acid into the anil of α-naphthaldehyde.[4] In the present instance the cleavage product reacts with one equivalent of aniline at 180° to give a substance having the analysis and properties to be expected for the anil of 2-aceto-1-naphthaldehyde, which indicates that the reaction has followed the normal course

$$C_{10}H_6(COCH_3)(COCOOH) + C_6H_5NH_2 \longrightarrow C_{10}H_6(COCH_3)(CH{=}NC_6H_5) + CO_2 + H_2O$$

A further reaction of 2-aceto-1-naphthylglyoxylic acid (VI) follows a course which is probably novel. While oxidation in alkaline solution yields naphthalene-1,2-dicarboxylic acid, the action of hydrogen peroxide in glacial acetic acid solution, or of chromic acid in dilute sulfuric acid solution, yields 1,2-naphthindandione, VIII. The identity of this product was established by comparison with an authentic sample prepared by

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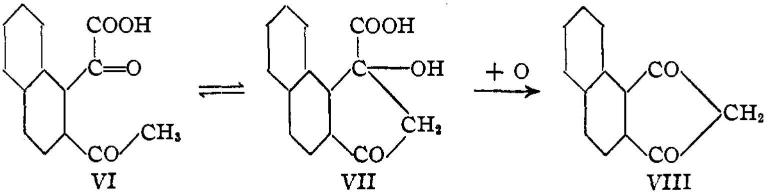
[3] Bouveault, *Bull. soc. chim.*, [3] **15**, 1020 (1896); Simon, *Ann. chim.*, [7] **9**, 509 (1896).

[4] Rousset, *Bull. soc. chim.*, [3] **17**, 303 (1897).

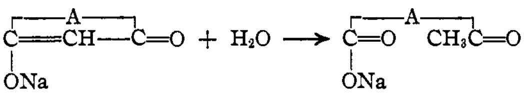
Noto's method.[5] A possible explanation of this rather surprising reaction is given in the following



VI VII VIII

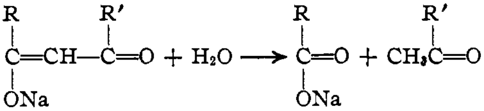
The known ability of the carbonyl group of α-keto acids to enter into aldol condensations lends some plausibility to the hypothesis that the α-keto acid, VI, exists in solution in equilibrium with a small amount of the α-hydroxy acid, VII, while there are many parallels to the conversion of VII into VIII. Thus α-hydroxy-*iso*butyric acid yields acetone on oxidation,[6] benzilic acid yields benzophenone[7] and α-phenyl-lactic acid, which is the most closely related to the hypothetical acid VII, yields acetophenone.[8]

Only further investigation can determine whether the alkaline cleavage of hydroxyquinones with the production of a carboxyl group and a ketone group in the same molecule is a general reaction, though results to be published shortly demonstrate that at least one other phenanthrene derivative, namely, 2-hydroxy-1,4-phenanthrenequinone, reacts with alkali in the manner indicated with particular ease. It will be noted that these reactions may be represented as follows



$$\overbrace{\underset{\mathrm{ONa}}{\mathrm{C}}{=}\mathrm{CH}{-}\mathrm{C}}^{\mathrm{A}}{=}\mathrm{O} + \mathrm{H_2O} \longrightarrow \overbrace{\underset{\mathrm{ONa}}{\mathrm{C}}{=}\mathrm{O} \quad \mathrm{CH_3C}}^{\mathrm{A}}{=}\mathrm{O}$$

from which the similarity to the alkaline cleavage of a β-diketone, reacting in its enolic form is apparent.



$$\underset{\mathrm{ONa}}{\overset{\mathrm{R}}{\mathrm{C}}}{=}\mathrm{CH}{-}\overset{\mathrm{R'}}{\mathrm{C}}{=}\mathrm{O} + \mathrm{H_2O} \longrightarrow \underset{\mathrm{ONa}}{\overset{\mathrm{R}}{\mathrm{C}}}{=}\mathrm{O} + \mathrm{CH_3}\overset{\mathrm{R'}}{\mathrm{C}}{=}\mathrm{O}$$

The similarity between the two classes of compounds is not limited to the alkaline hydrolysis; it is quite generally true that hydroxyquinones yield C-alkylation products when the alkylation is carried out with certain particularly reactive alkyl halides[9] and 3-hydroxy-1,4-phenanthrenequinone forms no exception to this rule.

In connection with a recent study of the alkaline hydrolysis of β-diketones, Bradley and Robinson[10] have advanced a theory of the mechanism

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[5] Noto, *Gazz. chim. ital.*, **45**, II, 126, 427 (1915).

[6] Markownikow, *Ann.*, **153**, 235 (1870).

[7] Jena, *ibid.*, **155**, 83 (1870).

[8] Benrath, *ibid.*, **382**, 226 (1911).

[9] Fieser, This Journal, **48**, 3201 (1926); **50**, 465 (1928).

[10] Bradley and Robinson, *J. Chem. Soc.*, 2356 (1926).

of the reaction based upon the assumption that the cleavage is a reaction characteristic of the ketonic modification, even though the concentration of this form in an alkaline solution is very small, and without regard to the possible mechanism, or the rate, of the formation of the ketonic modification from the enol. In order to apply these ideas to the cleavage of a hydroxyquinone, one would have to suppose that the salt of this strongly acidic substance undergoes hydrolysis even in the presence of alkali, that the free enol or its ion rearranges into a triketone, and that the latter, purely hypothetical, substance undergoes cleavage. There is little justification for such a view. At the time of the publication of the paper by Bradley and Robinson, their statement that "substances having fixed keto–enolic structures and related to β-diketones are relatively stable to hydroxyl ions," which they cite as evidence in support of their hypothesis of ketonic cleavage, was doubtless justified; but the discovery of the ready cleavage of compounds of fixed enolic structure lends support to the alternate view that it is the enolic modification which suffers cleavage in those cases in which the existence of such a modification is possible.

Experimental Part[11]

4-Amino-3-phenanthrol Hydrochloride.—The amine was prepared by Werner and his students[2] by coupling 3-phenanthrol with diazotized sulfanilic acid and reducing the azo compound with stannous chloride. The process was tedious and in order to convert the aminophenanthrol, which they isolated by extraction with ether, into the hydrochloride, it was necessary to use small quantities of the material. It has now been found that much better results may be obtained by reducing the un-isolated dyestuff with sodium hyposulfite, and that the amine hydrochloride may be prepared on a large scale if proper precautions are taken to prevent oxidation.

Ninety-seven grams of 3-phenanthrol[12] was dissolved in a warm solution of 60 g. of sodium hydroxide in 1.5 liters of water and the solution was cooled by the addition of about 500 g. of ice. A suspension of the diazonium salt was prepared by dissolving 105 g. of crystalline sulfanilic acid in 500 cc. of water and the requisite quantity of alkali, adding 37 g. of sodium nitrite, and pouring the solution into a mixture of 127 cc. of concentrated hydrochloric acid, 200 cc. of water and 500 g. of ice. When diazotization was complete the suspension was poured into the well-stirred phenanthrolate solution. The thick, bright-red solution of the azo compound was allowed to stand for one-half hour, when some solid matter separated, and then a solution of 230 g. of 85% sodium hyposulfite was added and the mixture heated and stirred until the red color disappeared and the aminophenanthrol which separated became very nearly colorless. The product sometimes separated in the form of colorless needles which became slightly yellow on drying and which melted with decomposition at 162° (Werner, 159–161°).

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[11] The melting points recorded below are all uncorrected. Difficulty was experienced in the analysis of several phenanthrene derivatives, the values for carbon often being as much as 1% too low. This trouble was completely eliminated by the use of a Dennstedt contact star, as recommended by Scholl, *Ber.*, 43, 342 (1910).

[12] New observations concerning the preparation and the alkali fusion of the sulfonates of phenanthrene will be reported in a future communication.

In order to obtain the hydrochloride, the moist amine was made into a fine paste with 2.5 liters of water containing a little sulfur dioxide, 95 cc. of concentrated hydrochloric acid was added and the mixture was heated and stirred until all but a very small quantity of black, tarry material dissolved. On adding hydrochloric acid to the filtered solution, while still hot, 4-amino-3-phenanthrol hydrochloride separated in the form of pale gray needles; yield, 113 g. (92%).

The material prepared in the manner indicated may be preserved indefinitely without undergoing any change, but a less pure product rapidly becomes green. The free amine is very sensitive to the oxidizing action of the air and to heat and it is largely destroyed if an attempt is made to dissolve the dry material in water containing just one equivalent of hydrogen chloride. A considerable excess of acid is required to prevent hydrolysis. These facts may serve to explain Werner's difficulty in preparing the pure salt in quantity.

3,4-Phenanthrenequinone.—Oxidation of 4-amino-3-phenanthrol hydrochloride with chromic acid in aqueous solution or suspension gave a product which was contaminated by considerable black, insoluble material. Though this may be removed by extracting the quinone with alcohol and precipitating it with water, the following method of oxidation gives a product which is practically pure at the outset, provided that the amine salt is pure and that the conditions are carefully controlled as specified.

Twelve grams of 4-amino-3-phenanthrol hydrochloride was made into a fine paste with 120 cc. of glacial acetic acid at room temperature. A thermometer was placed in the mixture, an ice-bath was made ready and a solution of 5 g. of chromic anhydride in water was added all at once. The mixture was stirred vigorously and the temperature was not allowed to rise above 40°. The salt rapidly dissolved and formed a deep red solution. After ten minutes the solution was poured into 500 cc. of water, thus precipitating the quinone in the form of a very fine, orange-red suspension which soon coagulated to a spongy precipitate which was easily collected and washed free of acid. The yield was 8.9 g. (87%) and the quinone was very nearly pure.

Slight variations from these conditions, such as a change in the initial or the maximum temperature or the gradual addition of the oxidizing agent, gave, in poorer yield, a darker product which was collected and washed with great difficulty, for a very fine, black substance partially clogged the filter paper and rendered the filtrate black. The quinone is also produced by the action of nitrous acid on a suspension of the amine hydrochloride but it rapidly undergoes decomposition to a black tar.

3,4-Phenanthrenequinone is best crystallized from a mixture of benzene and ligroin. On rapid cooling the solution deposits a spongy product; excellent, long, brilliant red needles are produced on cooling slowly. In agreement with the observation of Barger,[1] the substance was found to melt with decomposition at 133°.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.76; H, 3.88. Found: C, 80.35; H, 4.06.

The reaction of this quinone with sulfuric acid constitutes a highly characteristic test, for a solution of the substance in the concentrated acid at first has a beautiful Prussian blue color which changes in a few minutes to a clear, chrome green. The rate of the change is dependent upon the purity of the sample and also upon the amount of acid employed. Mixed with a very small quantity of acid, the pure quinone gives a blue color which lasts less than one minute; using a large volume of acid, it persists for several minutes. When the uncrystallized quinone is added to a large volume of acid, the blue stage has only a momentary existence.

Morphol is conveniently prepared by reducing the quinone with an aqueous solution of sodium hyposulfite or sulfur dioxide, while diacetylmorphol is best obtained by boiling a mixture of 10 g. of the quinone, 10 g. of zinc dust, 10 g. of fused sodium acetate and 80 cc. of acetic anhydride until no further color change occurs. The mixture is then diluted with glacial acetic acid, filtered and cautiously treated with water. Crystallization from benzene gives a pure product (10.8 g.) melting at 158° (Barger, 158°). Vongerichten has described the conversion of this substance into diacetylmorpholquinone.[13] The author's experiments confirmed his statement regarding the yield and the pure material was found to melt at 197° (Vongerichten, 196°).

The Addition of Sodium Bisulfite to 3,4-Phenanthrenequinone.—This reaction, which proceeds so readily in the case of β-naphthoquinone, at first presented some difficulties. Since the phenanthrenequinone is very easily destroyed by acids, much of the material is converted into an insoluble, black substance unless the bisulfite solution is concentrated enough so that the addition reaction becomes very rapid. Thus, while the quinone dissolves only partially in dilute bisulfite solution, it is almost completely soluble in a saturated solution and, after time has been allowed for the rearrangement of the primary addition product, the sulfonic acid formed may be isolated in the form of an amine salt or else oxidized to a sulfonated quinone.

Ammonium 3,4-Phenanthrenequinone-1-sulfonate.—Twenty and eight-tenths grams of uncrystallized 3,4-phenanthrenequinone was ground to a fine paste with 150 cc. of water and 41.6 g. of sodium bisulfite was added all at once while the mixture was stirred thoroughly. Nearly all of the quinone dissolved, giving a thick, dark-brown solution. After standing for a few hours, it was diluted with water to a volume of 250 cc., 8.5 cc. of concentrated sulfuric acid was added cautiously, together with a few drops of caprylic alcohol to disperse the foam, and the solution was heated until the sulfur dioxide had been driven off. The solution was then filtered through a folded paper in order to remove a little dark material, cooled to room temperature and treated with a chromic acid solution containing 15 g. of the anhydride and 15 cc. of concentrated sulfuric acid. To the deep-red solution of the quinone a saturated solution of sodium chloride was added, causing the separation of a partially gelatinous precipitate of sodium 3,4-phenanthrenequinone-sulfonate. In spite of the dispersed character of the precipitate, no difficulty was experienced in collecting it and in pressing it free of most of the water, though it was not obtained in a condition satisfactory for analysis. The ammonium salt, although it is rather unstable, forms good crystals. It was prepared by adding saturated ammonium chloride solution to a hot solution of the sodium salt and cooling the solution rapidly. Small, glistening, dark red plates were thus obtained; yield: 18.5 g. (about 53% of the theoretical amount).

The salt is not easily crystallized. A hot solution in pure water turns dark before crystals begin to separate and even when an ammonium salt is added to decrease the solubility, a dark red, insoluble substance is formed unless the solution is cooled rapidly and unless the crystals are separated from the solvent without delay. The air-dried material contained about 13% of water and the anhydrous salt is very hygroscopic.

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[13] Vongerichten, *Ber.*, **32**, 1521 (1899).

Anal. Calcd. for $C_{14}H_{11}O_5NS$: S, 10.50. Found: S, 10.58.

p-Toluidine Salt of 3,4-Dihydroxyphenanthrene-1-sulfonic Acid.—The sodium and potassium salts of the acid are extremely soluble in water, but the p-toluidine salt crystallized readily on adding a solution of the amine hydrochloride to the solution of the dihydroxyphenanthrene-sulfonate obtained by the addition of sodium bisulfite to 3,4-phenanthrenequinone or by the reduction of the sulfonated quinone. The compound dissolves readily in water and crystallizes in the form of colorless needles which become slightly gray on drying and which decompose at about 182°.

Anal. Calcd. for $C_{21}H_{19}O_5NS$: C, 63.45; H, 4.82. Found: C, 63.44; H, 5.03.

1-(p-Toluidino)-3,4-phenanthrenequinone.—This compound soon precipitated when aqueous or alcoholic solutions of equivalent quantities of ammonium 3,4-phenanthrenequinone-1-sulfonate and p-toluidine were combined and heated for a short time. A brick-red product was thus obtained in 60% yield. It is sparingly soluble in alcohol; somewhat more so in glacial acetic acid or toluene. It dissolves in alcoholic sodium hydroxide solution with a red color but it is insoluble in aqueous alkali. Crystallized from xylene the substance formed a crust of small, dark red crystals which melted with decomposition at 260°.

Anal. Calcd. for $C_{21}H_{15}O_2N$: C, 80.48; H, 4.83. Found: C, 80.29; H, 5.01.

1-(p-Toluidino)-3,4-diacetoxyphenanthrene was prepared by the reductive acetylation of the above quinone with zinc dust, sodium acetate and acetic anhydride. It is only sparingly soluble in alcohol, but readily soluble in benzene or glacial acetic acid. The benzene solution is fluorescent and it deposits short, colorless needles melting at 208°.

Anal. Calcd. for $C_{25}H_{21}O_4N$: C, 75.16; H, 5.30. Found: C, 75.09; H, 5.60.

3-Hydroxy-1,4-phenanthrenequinone.—Several methods of hydroxylating 3,4-phenanthrenequinone were investigated and the less successful procedures may be mentioned briefly. The Thiele reaction, which involves the addition of acetic anhydride to the quinone molecule under the influence of sulfuric acid, gave very poor results, probably because the quinone is extremely sensitive to the action of mineral acids. Even at room temperature the reaction yielded only a black, tarry product which gave a certain amount (30%) of the hydroxyquinone on hydrolysis, air oxidation and purification through the sodium salt, but from which pure 1,3,4-triacetoxy-phenanthrene could not be isolated.

A second method, which has given good results with similar compounds,[9b,14] consisted in the conversion of ammonium 3,4-phenanthrenequinone-1-sulfonate into 3-methoxy-1,4-phenanthrenequinone (see below), and hydrolyzing this ether. Thus a suspension of 5 g. of the ammonium salt in 25 cc. of methyl alcohol was treated with 4 cc. of concentrated sulfuric acid, while shaking, and the mixture was then allowed to cool. The ether which separated, washed with water and with a little alcohol, was nearly pure, and it gave a 97% yield of the pure hydroxyquinone on hydrolysis. The yield was only 2 g., or 59% of the theoretical amount, so that the overall yield of the hydroxy compound from 3,4-phenanthrenequinone was only 30%.

[14] Fieser, This Journal, 48, 2929 (1926).

A much simpler process, which gave a better yield of material, consisted in oxidizing 3,4-dihydroxyphenanthrene-1-sulfonic acid in alkaline solution with air or, better, with hydrogen peroxide. It is convenient to start with 4-amino-3-phenanthrol hydrochloride and not to isolate any of the intermediates in dry form.

Twelve grams of this amine salt was oxidized in the manner indicated above and the 3,4-phenanthrenequinone (average dry weight, 8.9 g.) was made into a paste with 100 cc. of water; 16 g. of sodium bisulfite was added and, after one-half hour, 4 cc. of concentrated sulfuric acid was added cautiously; the sulfur dioxide was boiled off and the filtered solution of sodium 3,4-dihydroxyphenanthrene-1-sulfonate was treated with 70 cc. of 6 *N* sodium hydroxide solution and 100 cc. of 3% hydrogen peroxide solution. A red precipitate of the sodium salt of 3-hydroxy-1,4-phenanthrenequinone soon began to separate and it was collected after a few hours. The addition of more peroxide to the filtrate usually gave a further quantity of the salt. The combined product was dissolved in boiling water, the red solution was quickly filtered from a small amount of black material and acidified, when the hydroxy compound separated in the form of a very fine yellow suspension. This material is very pure. The yield was 5.6 g., or 58% of the theoretical amount based on the weight of aminophenanthrol hydrochloride.

3-Hydroxy-1,4-phenanthrenequinone is only very sparingly soluble in water; it dissolves readily in alcohol or benzene and very readily in glacial acetic acid. The solution in concentrated sulfuric acid is brown-red, while the alkaline solution is red. The sodium salt is very sparingly soluble in the presence of an excess of alkali. The hydroxy compound is a strong acid, being soluble in sodium acetate solution. It was crystallized repeatedly from benzene and from dilute acetic acid, when it formed small, orange-yellow needles which sintered at 200° and melted, with some decomposition, at 230°.

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.99; H, 3.60. Found: C, 74.87; H, 3.67.

3-Methoxy-1,4-phenanthrenequinone.—The preparation of this ether from ammonium 3,4-phenanthrenequinone-1-sulfonate has been described above. It was also obtained by boiling a solution of the hydroxy compound in methyl alcohol containing a little hydrogen chloride. The ether soon separated in crystalline condition. It was crystallized from alcohol and from benzene-ligroin, forming light yellow needles melting at 170°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.61; H, 4.23. Found: C, 75.69; H, 4.40.

3-Methoxy-1,4-diacetoxyphenanthrene was obtained in 91% yield by the reductive acetylation of the above ether. Crystallized repeatedly from benzene–ligroin, it formed clusters of stout, colorless needles, m. p. 168.5°.

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.35; H, 4.98. Found: C, 70.14; H, 5.15.

An attempt to obtain a pure oxidation product of this substance was unsuccessful, though there were indications of the formation of a small amount of a phenanthrenequinone.

The Allylation of 3-Hydroxy-1,4-phenanthrenequinone.—The hydroxy compound was converted into its dark red silver salt by adding silver nitrate to a neutral solution of the ammonium salt at 60°.

Anal. Calcd. for $C_{14}H_7O_3Ag$: Ag, 32.59. Found: Ag, 32.60.

A suspension of 6.7 g. of this salt in 100 cc. of benzene was treated with 2.7 g. of allyl bromide and heated to boiling for forty-five minutes, when the reaction was complete. Only two products were isolated: 1-alloxy-3,4-phenanthrenequinone and 2-allyl-3-hydroxy-1,4-phenanthrenequinone. The former crystallized on concentrating the benzene solution, while the latter was extracted from the benzene solution with ammonia solution; yields: 63 and 17%, respectively. A *p*-quinone ether appeared to be present in small quantity, but it was not obtained in pure form.

1-Alloxy-3,4-phenanthrenequinone is readily soluble in alcohol or benzene and crystallizes in the form of brilliant orange needles melting at 161°. While it is not soluble in bisulfite solution, it is completely hydrolyzed by dissolution in alcohol containing a little hydrochloric acid, a reaction characteristic of *o*-quinone ethers of this type.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.10; H, 4.55.

2-Allyl-3-hydroxy-1,4-phenanthrenequinone dissolves readily in glacial acetic acid or alcohol but it does not crystallize well from these solvents. The solution in ligroin deposits light sponges of small, orange needles, m. p. 155°.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.22, H, 4.60.

This C-alkylation product may also be prepared in good yield by heating 1-alloxy-3,4-phenanthrenequinone to a temperature just above the melting point. Like other substances of this type the compound dissolves in alkali with a red color and it is converted into the following heterocyclic derivative by sulfuric acid.

1-Methyl-5,6-(1,2-naphtho)-3,4-quinone resulted when 1 g. of the above quinone was dissolved in 5 cc. of cold, concentrated sulfuric acid and the solution poured into a large volume of water. The flocculent, red precipitate was crystallized several times from benzene–ligroin with the use of animal charcoal and it was thus freed of a little tar and obtained in the form of brilliant red, flat needles melting at 198–199°. It is insoluble in bisulfite solution.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 76.98; H, 4.56.

The Action of Alkali on 3-Hydroxy-1,4-phenanthrenequinone.—The hydrolytic cleavage of this quinone may be accomplished by prolonged boiling of a solution of the sodium salt in water, but the reaction is hastened by the presence of an excess of alkali. Thus a suspension of 8 g. of the pure sodium salt in 3 liters of water containing 20 cc. of 6 *N* sodium hydroxide solution was boiled gently in an open beaker until all of the solid had dissolved, the clear red color had given place to a dull red-brown and the volume had been dimished to about 400 cc. This required about four hours. A small amount of dark material was then separated by filtration and the solution was acidified with hydrochloric acid while still hot. A part of the material separated in the form of an oil which soon solidified, while part formed large plates. Concentration of the mother liquor yielded an additional quantity of this substance. The combined product, on crystallization from dilute hydrochloric acid with the use of animal charcoal, yielded 5.7 g. (82%) of slightly brown, but essentially pure, material.

This substance, which has been identified as **2-aceto-1-naphthylglyoxylic acid (VI)**, was freed of all traces of coloring matter only after repeated crystallization from acidified water, though this process did not alter the melting point. The pure material melts at 196° with the rapid evolution of carbon dioxide and passes into a glassy substance. It dissolves readily in hot water and crystallizes, best in the presence of a mineral acid, in the form of large, colorless plates. The solubility in cold water is quite appreciable. On acidification of a dilute aqueous solution of the sodium salt the compound separates very slowly but in the form of excellent crystals. The acid decomposes sodium carbonate; it is very sparingly soluble in benzene, moderately soluble in ether and very readily soluble in alcohol.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.41; H, 4.16. Found: C, 69.41; H, 4.26. *Neut. Equiv.* Subs., 0.1716: 5.74 cc. of 0.1242 *N* $Ba(OH)_2$. Calcd. for $C_{14}H_{10}O_4$: mol. wt., 242.1. Found: 240.7.

The methyl ester was easily obtained by boiling a solution of the acid in methyl alcohol containing hydrogen chloride. After removal of most of the alcohol the addition of water caused the separation of an oil which soon solidified. The ester dissolves readily in benzene and only sparingly in ligroin; it crystallizes well from a mixture of the two solvents, forming small, colorless prisms melting at 181°. It does not react with sodium bisulfite to any appreciable extent and it is indifferent toward bromine or ferric chloride.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.56; H, 4.88.

Oxidation of the Cleavage Product in Alkaline Solution.—A solution of 0.5 g. of 2-aceto-1-naphthylglyoxylic acid in 4 cc. of 5% sodium hydroxide was treated with 2 cc. of perhydrol and the solution was kept at a temperature of 60° for several hours. The oxidation was not complete, for some of the unchanged acid separated in the form of a dark tar on acidification. After this had been removed and the solution boiled with animal charcoal and well concentrated, small, colorless crystals of naphthalene-1,2-dicarboxylic acid melting at 175° were obtained. The material was purified by crystallization of the sparingly soluble acid potassium salt and then crystallized from water. The acid melted at 175° with loss of water; the anhydride so produced melted at 165°. These properties agree with Cleve's description[15] of naphthalene-1,2-dicarboxylic acid.

Anal. Calcd. for $C_{12}H_8O_4$: C, 66.66; H, 3.73. Found: C, 66.46; H, 3.76.

Oxidation of the Cleavage Product in Acid Solution.—To a boiling solution of 1 g. of 2-aceto-1-naphthylglyoxylic acid in a mixture of 75 cc. of water and 4 cc. of concentrated sulfuric acid, a solution of 0.4 g. of potassium dichromate was gradually added. Oxidation took place rapidly with the evolution of carbon dioxide and the separation of a yellow substance which was found to be **1,2-naphthindandione** (VIII). After one crystallization from alcohol, long, slender, yellow needles melting at 174–175° were obtained; yield, 0.6 g. The same substance was obtained, though in poorer yield, by boiling a solution of 2 g. of the glyoxylic acid in 12 cc. of glacial acetic acid with 5 cc. of perhydrol for one hour.

Samples of 1,2-naphthindandione were crystallized from a variety of solvents such as alcohol, glacial acetic acid and benzene-ligroin; the melting point always remained constant at 174–175° and the crystals were distinctly yellow. On solution of the crystallized material in alkali, however, a small amount of colored impurity remained undissolved and the material precipitated by acidification and crystallized from benzene–ligroin was now only very faintly yellow but still melted at the same temperature.

Anal. Calcd. for $C_{13}H_8O_2$: C, 79.57; H, 4.02. Found: C, 79.45; H, 4.18.

The alkaline solution of the compound is deep red; the solution in concentrated sulfuric acid is yellow. It reacts with benzaldehyde in the presence of a trace of pyridine to give a product which forms small, lemon-yellow needles melting at 179°. The properties of the diketone correspond very closely with the description of 1,2-naphthin-

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[15] Cleve, *Ber.*, **25**, 2475 (1892).

dandione given by Noto,[5] who synthesized this compound from naphthalene-1,2-dicarboxylic acid, except that the melting point of 174–175° is lower than the figure of 180° recorded by the Italian investigator, and that the benzal derivative was found to melt at 179°, instead of at 190°. The identity of the two compounds was definitely established, however, by comparing the material obtained in the present research with a sample prepared by Noto's method. Each sample, as well as a mixture of the two, melted at 174–175°.

The Action of Aniline on 2-Aceto-1-naphthylglyoxylic Acid.—Two and one-half grams of the acid was dissolved in ether, 0.98 g. of aniline added and the solution evaporated to dryness. The solid residue was transferred to a small flask and this was evacuated with the use of an oil pump and heated in an oil-bath. At 175° the material commenced to fuse with the evolution of gas and a thick, dark-brown liquid soon resulted. After heating at 175–180° for ten minutes, the flask was cooled and the product crystallized from benzene. The dark-brown impurities are largely retained in the mother liquor, for clean, yellow crystals of the nearly pure reaction product separated from the solution on cooling and a further quantity was obtained on concentrating the mother liquor; yield, 1 g.

2-Aceto-1-naphthalaniline is readily soluble in benzene, moderately soluble in alcohol or ether and sparingly soluble in ligroin or water. A sample for analysis, crystallized from benzene and from ethyl acetate, formed small, yellow needles melting at 202°.

Anal. Calcd. for $C_{19}H_{15}ON$: C, 83.48; H, 5.53. Found: C, 83.14; H, 5.72.

The compound is insoluble in alkali; it dissolves in concentrated sulfuric acid to give a solution exhibiting an intense green-yellow fluorescence. On addition of a small amount of water, the fluorescence disappears and a colorless salt soon crystallizes from the clear solution. The salt decomposes on further dilution with the formation of the yellow anil.

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Summary

1. 3,4-Phenanthrenequinone may be obtained in quantity and in good yield by converting 3-phenanthrol into an azo dye, reducing the azo compound and oxidizing the 4-amino-3-phenanthrol so produced. The quinone adds a molecule of sodium bisulfite and the resulting product may be converted into 3-hydroxy-1,4-phenanthrenequinone. The alkylation of this hydroxyquinone follows the normal course.

2. When 3-hydroxy-1,4-phenanthrenequinone is boiled with dilute alkali, the quinonoid ring suffers hydrolytic cleavage in a manner entirely analogous to the cleavage of β-diketones.

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