[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

1,2-PHENANTHRENEQUINONE

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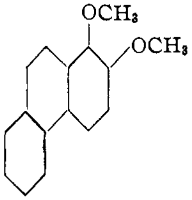
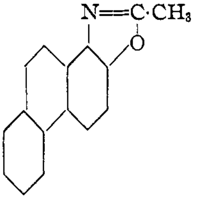
Having found a convenient method of preparing 3,4-phenanthrenequinone from 3-phenanthrol,[1] a similar series of reactions was applied to 2-phenanthrol in the hope of obtaining another isophenanthrenequinone. On reducing with sodium hyposulfite the dyestuff produced by coupling 2-phenanthrol with diazotized sulfanilic acid, an amino-2-phenanthrol was obtained in excellent yield, and the conversion of this substance into a quinone was nearly quantitative. Since both the diacetate and the triacetate of the new amino-2-phenanthrol are easily converted by thermal decomposition into an oxazole derivative, it may be concluded that the coupling has taken place in the ortho position, that is, in either the 1- or the 3-position. Thanks to the valuable synthetical work of Pschorr, a distinction between these two possibilities is not difficult. A dimethoxyphenanthrene was obtained by reducing the phenanthrenequinone and methylating the reduction product. This substance, which must have the structure of either 1,2-dimethoxyphenanthrene or 2,3-dimethoxyphenanthrene, proved to be different from the compound synthesized by Pschorr and Buckow[2] and known to have the structure of the 2,3-isomer. The new substance is thus 1,2-dimethoxyphenanthrene, I, and corresponding structures may be assigned to the oxazole derivative, II, and to the quinone, III.



I



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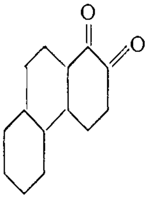

III

The marked chromophoric character of an isophenanthrenequinone nucleus in comparison with 9,10-phenanthrenequinone was noted in the case of the 3,4-isomer; this is also true of 1,2-phenanthrenequinone, for the substance forms large needles which are brilliant red in color. The similarity between the two isophenanthrenequinones is quite pronounced, and in all but one instance the reactions of 1,2-phenanthrenequinone and of its derivatives follow an entirely normal course. A description of these reactions may be found in the Experimental Part, and it will suffice at this time to call attention to the fact that the hydrolytic cleavage of an hydroxyquinone, noted for the first time in the case of 3-hydroxy-1,4-

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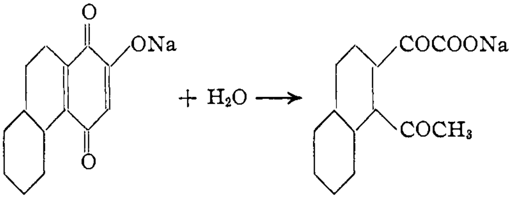
[1] Fieser, THIS JOURNAL, **51**, 940 (1929).

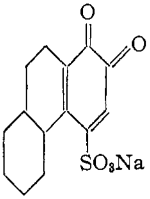
[2] Pschorr and Buckow, *Ber.*, **33**, 1831 (1900).

phenanthrenequinone,[1] takes place with great ease with the isomer, 2-hydroxy-1,4-phenanthrenequinone, IV; the reaction being represented as

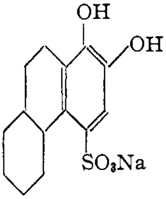


IV V

An interesting deviation from the behavior of other quinones was observed in studying the properties of sodium 1,2-phenanthrenequinone-4-sulfonate, VI. The substance was prepared from the hydroquinone, VII, which, in turn, resulted from the addition of sodium bisulfite to 1,2-phenanthrenequinone. Judging by the properties of other compounds of similar structure, one might expect that VI would react with aromatic amines in such a way that the sulfonate group would be replaced by an arylamino group. Thus the following compounds all yield water-insoluble anilino- or *p*-toluidinoquinones on reaction with the corresponding amine: 1,2-naphthoquinone-4-sulfonate,[3] 1,2-anthraquinone-4-sulfonate,[4] 3,4-phenanthrenequinone-1-sulfonate,[1] 6,7-indazolequinone-4-sulfonate,[5] and 2-phenyl-benzotriazole-4,5-quinone-7-sulfonate.[6] The normal reaction of such quinones with alkali involves, so far as is known,[5] the replacement of the sulfonate group by hydroxyl. 1,2-Phenanthrenequinone-4-sulfonate, on the other hand, undergoes a disproportionation when treated either with *p*-toluidine or with alkali. On adding alkali to a cold, aqueous solution of the quinone, the color changes at once from red to pale yellow and the solution is now found to contain the hydroquinone, VII. A quantitative study of the reaction, carried out in an indifferent atmosphere and under conditions permitting the detection of any hydrogen peroxide or oxygen which might be formed, showed that one molecule of the hydroquinone results from two molecules of the quinone and that no oxidation



VI



VII

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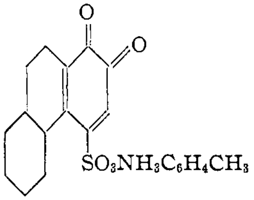
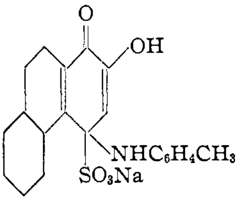
[3] Böniger, *Ber.*, **27**, 25 (1894).
[4] Fieser, THIS JOURNAL, **50**, 470 (1928).
[5] Fieser, *ibid.*, **48**, 1103 (1926).
[6] Fieser and Ames, *ibid.*, **49**, 2614 (1927).

products of water are produced. Thus, while an organic oxidation product was not isolated, there can be little doubt that such a product is formed and that the reaction is of the Cannizzaro type. This reaction is not unusual for all quinones, but only for the particular type of sulfonated quinone under discussion. The unusual feature is that the normal replacement reaction does not occur.

The exceptional character of 1,2-phenanthrenequinone-4-sulfonic acid is even more evident in the reaction with *p*-toluidine. In neutral aqueous solution a disproportionation again takes place and the *p*-toluidine salt of the hydroquinone, VII, may be obtained by acidifying the solution. In the presence of mineral acids the disproportionation does not occur, but even under these conditions the replacement of the sulfonic acid group by the *p*-toluidino group does not take place, for the only reaction product is the *p*-toluidine salt of the quinone-sulfonic acid, VIII.



VIII



IX

The remarkable stability of the sulfonic acid group of this one quinone is probably due to the spatial arrangement of the molecule, for the presence of a benzene nucleus adjacent to the sulfonic acid group is the only structural feature which distinguishes the quinone from all of the similar compounds listed above. If it is supposed that the formation of a *p*-toluidinoquinone involves, as the first step, the 1,4-addition of the amine to a sulfonated quinone, the influence of the neighboring phenylene group in preventing the formation of an intermediate addition product, IX, is understandable, and this hypothesis appears to afford the most plausible explanation of the phenomenon.

Experimental Part[7]

1-Amino-2-phenanthrol.—The coupling of 2-phenanthrol with diazotized sulfanilic acid and the reduction of the dye by means of sodium hyposulfite proceeded in so nearly the same manner as in the case of 3-phenanthrol[1] that it is only necessary to state the modifications of the method already described, which are required in the present instance. The chief difference is that somewhat more water is required to dissolve sodium 2-phenanthrolate and 1-amino-2-phenanthrol hydrochloride than the isomers. The azo compound was first prepared by Werner and Rekner.[8] Like these investigators, I was unable to obtain it in a crystalline condition; the coupling reaction gave a

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[7] The Dennstedt contact star was employed in carrying out most of the analyses here reported, compare ref. 1, footnote 11.

[8] Werner and Rekner, *Ann.*, **321**, 307 (1902).

very viscous, colloidal solution of the dye. On reduction with hyposulfite, the aminophenanthrol separated in a very finely-divided condition but the solution filtered without difficulty. The product was often pink, rather than colorless, but this did not interfere with the preparation of the pure hydrochloride. In converting the amine into its salt, it was found expedient to use 6-7 liters of water and 130 cc. of concentrated hydrochloric acid to dissolve the material obtained from 97 g. of 2-phenanthrol. The yield was very close to the theoretical amount.

The free amine was obtained by drying the crude product on a porous plate and crystallizing it from alcohol containing a little sulfur dioxide. It formed glistening plates which were somewhat gray, but which have not undergone further change in nearly a year. The substance begins to darken at about 210°, and there is no definite point of decomposition. It dissolves well in alcohol, but is only very sparingly soluble in benzene or ether. The xylene solution darkens on boiling.

Anal. Calcd. for $C_{14}H_{11}ON$: C, 80.35; H, 5.30. Found: C, 80.08; H, 5.51.

1-Amino-2-phenanthrol Hydrochloride.—The salt was purified for analysis by crystallization from an alcoholic solution to which considerable hydrochloric acid was added. A cotton-like mass of colorless micro-needles was thus obtained. The sample became slightly gray during drying; it decomposes in the vicinity of 250°. The salt is only moderately soluble in water, but very readily soluble in alcohol. It gives a cherry-red solution on warming with concentrated sulfuric acid.

Anal. Calcd. for $C_{14}H_{12}ONCl$: C, 68.42; H, 4.93. Found: C, 68.59; H, 5.28.

The Acetylation of 1-Amino-2-phenanthrol

When the amine is heated with acetic anhydride for about three minutes, a thick paste consisting chiefly of crystals of the N-monoacetate results. If the heating is continued until the crystals just dissolve, the solution contains chiefly the diacetate, together with a little of the triacetate. Prolonged boiling, preferably with the use of sodium acetate as a catalyst, leads to the complete acetylation of the amine. Both the diacetate and the triacetate are converted quantitatively into the N-monoacetate on boiling the alcoholic solutions with hydrochloric acid. Thus this compound may be prepared from a mixture of the diacetate and the triacetate, while the triacetate is most conveniently prepared from the monoacetate.

1-Amino-2-phenanthrol Diacetate.—A mixture of 1 g. of the amine and 10 cc. of acetic anhydride was boiled until the crystals of the monoacetate just dissolved and the solution was cooled and poured into water. The product was crystallized from benzene until the melting point became constant at 222° (227°, corr.). The compound formed a cotton-like mass of fine, colorless needles; yield, 0.5 g. It is only sparingly soluble in benzene and insoluble in acids or alkalies.

Anal. Calcd. for $C_{18}H_{15}O_3N$: C, 73.69; H, 5.16. Found: C, 73.38; H, 5.18.

1-Acetylamino-2-phenanthrol.—The method of acetylation just described yields, as the crude product, a mixture of the di- and triacetates suitable for the preparation of the monoacetate, but it is convenient to add a little sodium acetate in order to hasten the reaction. The crude product, without being dried, was dissolved in alcohol, hydrochloric acid was added and the solution was boiled until there was no increase in the quantity of the glistening white plates of the monoacetate. The yield was practically quantitative. The substance may be dissolved in alkali and recovered without change. It is very sparingly soluble in alcohol, benzene or glacial acetic acid and it crystallizes from nitrobenzene, in which it dissolves readily, in the form of plates melting at 295°.

Anal. Calcd. for $C_{16}H_{13}O_2N$: C, 76.46; H, 5.22. Found: C, 76.56; H, 5.12.

1-Amino-2-phenanthrol Triacetate.—A mixture of equal parts of the monoacetate and fused sodium acetate with ten parts of acetic anhydride was boiled for one and one-half hours and the solution was then poured into water. The triacetate soon separated in the form of a clean solid melting at 122–123°, and the yield was close to that called for by theory. The substance, which dissolves very readily in alcohol or benzene, is best crystallized from ligroin, when it forms colorless scales melting at 125°.

Anal. Calcd. for $C_{20}H_{17}O_4N$: C, 71.62; H, 5.11. Found: C, 71.63; H, 5.01.

Oxazole Derivative of 1-Amino-2-phenanthrol (II).—This compound was obtained from both the diacetate and the triacetate. The material was heated in a distilling flask with a sealed-on receiver until no more acetic acid or anhydride was given off and then distilled at a pressure of 3 mm. The oxazole is very readily soluble in alcohol, benzene or ligroin, but insoluble in acids or alkalies. It was crystallized from methyl alcohol, forming slender colorless needles on rapidly cooling the solution, and very large thick needles on slow cooling. The substance melted at 120°.

Anal. Calcd. for $C_{16}H_{11}ON$: C, 82.37; H, 4.76. Found: C, 82.03; H, 4.95.

Oxidation Experiments.—Attempts to convert the above oxazole derivative into a quinone were unsuccessful. It appeared that the substance is oxidized with difficulty and that, when the reaction does proceed, it quickly passes beyond the quinone stage. The triacetate of 1-amino-2-phenanthrol, treated with an equal weight of chromic acid in glacial acetic acid solution at 60°, gave a very small amount of a substance which appeared to be a quinone (orange color, green solution in alcoholic alkali), but the only product isolated in any quantity was aminophenanthrol diacetate. Thus the partial hydrolysis of the starting material is at least partly responsible for the failure to obtain a good yield of the quinone in this case.

1,2-Phenanthrenequinone

In preparing this quinone it is advisable to start with 2-phenanthrol and to carry out the various operations, including the oxidation of the aminophenanthrol, without isolating any of the intermediates. Quantities of the materials found convenient for the preparation are given below, while reference has already been made to the details of the coupling reaction and the reduction.

To a solution of 30 g. of 2-phenanthrol and 18.5 g. of sodium hydroxide in about 1 liter of water, ice was added until the mixture half filled a 4-liter beaker. After coupling with a suspension of an equivalent quantity of diazotized sulfanilic acid, in about 1 liter of water, reduction with a solution of sodium hyposulfite was carried out, the aminophenanthrol was collected and then washed back into the beaker. A little sodium bisulfite was added, the volume was made up to 2.5 liters with boiling water and 40 cc. of concentrated hydrochloric acid was added. The material rapidly passed into solution and left only a trace of residue on filtration. The solution was cooled rapidly, with stirring, in order that the amine hydrochloride which separated should come down in a finely-divided condition. After cooling to room temperature, an aqueous solution of 13.3 g. (1.3 Th.) of chromic acid and 11 cc. of concentrated sulfuric acid was added all at once. A dark precipitate was first produced, but this soon changed to a bright, finely-divided red product. In order to facilitate the collection and washing of this material, the mixture was heated to the boiling point, while stirring constantly, for this treatment serves to increase greatly the particle size without destruction of the quinone. Thoroughly washed and dried, the 1,2-phenanthrenequinone formed a red powder weighing 29–31 g. (90–96%). This material is not quite pure, but it is satisfactory for many reactions.

The quinone was purified by crystallization from toluene, in which it dissolves fairly readily. A small amount of black material remained undissolved, and the solution was at first dull red; but by further crystallization from this solvent, with the use of animal charcoal, a brilliant red product was obtained which crystallizes in the form of needles. The substance is moderately soluble in alcohol or benzene and readily soluble in glacial acetic acid; it crystallizes well from the red solutions in all of these solvents. It softens at about 195° and melts with decomposition at 216° (222° corr.). The reaction with concentrated sulfuric acid is both characteristic and beautiful: the solution is at first brilliant blue in color but changes within a few seconds to an intense sap-green. In this respect the substance is similar to 3,4-phenanthrenequinone, though the two are easily distinguished by the test. The two quinones, in crystalline condition, are almost identical in appearance, but the 1,2-isomer is much the less soluble of the two.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.76; H, 3.88. Found: C, 80.62; H, 4.08.

1,2-Dihydroxyphenanthrene.—On warming an aqueous suspension of the quinone, best in the finely-divided condition in which it is first obtained, with a solution of sodium hyposulfite, the material soon became reduced and a somewhat dark precipitate of the hydroquinone was formed. Enough alcohol was added to bring the material into solution at the boiling point and the solution, after treatment with animal charcoal, was filtered and quickly cooled. The hydroquinone was thus obtained in the form of small, colorless needles which, however, darkened considerably on long storage. The compound melts at 178°. The alkaline solution is at first yellow, but the action of the air soon gives a precipitate of a green quinhydrone, or its salt. In a solution of alcoholic alkali the oxidation soon proceeds beyond this stage and the red sodium salt of 2-hydroxy-1,4-phenanthrenequinone soon separates.

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.80. Found: C, 79.63; H, 4.77.

1,2-Dimethoxyphenanthrene.—1,2-Dihydroxyphenanthrene was methylated in an atmosphere of nitrogen with dimethyl sulfate and alkali. The product was distilled at diminished pressure and crystallized from ligroin. It forms feathery clusters of short, colorless needles melting at 102°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.60; H, 5.88.

Attempts to convert the compound into a quinone were not successful.

2-Hydroxy-1,4-phenanthrenequinone

1,2,4-Triacetoxyphenanthrene.—This compound was easily obtained by applying the Thiele reaction to 1,2-phenanthrenequinone, but the yield was poor. Twenty-five grams of the finely powdered quinone was slowly stirred into a mixture of 160 cc. of acetic anhydride and 5 cc. of concentrated sulfuric acid, while cooling to room temperature. The quinone dissolved rapidly to give a dark brown solution, from which crystals of the triacetoxyphenanthrene began to separate within a few minutes. After standing for two hours, the mixture was cooled well, the walls of the vessel were scratched to relieve supersaturation and the product was then collected and washed with glacial acetic acid and with alcohol. The material (16 g.) melted at 180–182°, and gave 15.5 g. (36%) of pure 1,2,4-triacetoxyphenanthrene on crystallization. The acetic anhydride mother liquor, on decomposition with water, gave a very dark-colored, tarry product which is not profitably worked for the triacetate. It may be heated with alcohol and sodium hydroxide solution, when the sodium salt of 2-hydroxy-1,4-phenanthrenequinone separates, due to hydrolysis and oxidation. This salt, though mixed with much black material, is easily converted into the pure hydroxy compound, for the impurities are insoluble in water. In this way it is possible to obtain the equivalent of about 5 g. of the triacetate. 1,2,4-Triacetoxyphenanthrene crystallizes well from glacial acetic acid, benzene or benzene–ligroin and forms colorless needles melting at 186° (189°, corr.).

Anal. Calcd. for $C_{20}H_{16}O$: C, 68.16; H, 4.58. Found: C, 68.23; H, 4.65.

2-Hydroxy-1,4-phenanthrenequinone.—Since this quinone is destroyed very rapidly by boiling its alkaline solution, special precautions must be observed in preparing it by the hydrolysis and oxidation of the above triacetate. In the method which follows the process of hydrolysis, which requires either an elevated temperature or a prolonged period of reaction, was carried out separately, and then advantage was taken of the ease of oxidation of the cold hydroquinone solution and the slight solubility of the sodium salt of the oxidation product.

A suspension of 12 g. of 1,2,4-triacetoxyphenanthrene in 100 cc. of alcohol was swept free of oxygen with a stream of nitrogen and 50 cc. of oxygen-free 6 *N* sodium hydroxide was added. On warming to the boiling point, hydrolysis soon took place with the formation of an orange solution. The solution was then cooled, diluted with 100 cc. of water and treated with a stream of air until there was no further increase in the amount of the red precipitate of the sodium salt of 2-hydroxy-1,4-phenanthrenequinone. This material was then collected, washed with alcohol and dried; yield, 7.4 g. (88%). In order to obtain the free hydroxy compound, the sodium salt was added to 2 liters of boiling water, the solution was stirred vigorously in order to bring the salt into solution as quickly as possible and then filtered into dilute sulfuric acid. The quinone was thus obtained in a pure condition, in the form of an orange-yellow mass of micro-needles.

2-Hydroxy-1,4-phenanthrenequinone is only sparingly soluble in water, very readily soluble in alcohol and readily soluble in benzene or glacial acetic acid. The yellow solutions deposit cotton-like clusters of small, orange-yellow needles melting at 188° (190°, corr.) with decomposition. The solution in concentrated sulfuric acid is intensely green, the alkaline solution is red.

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.99; H, 3.60. Found: C, 74.78; H, 3.62.

2-Methoxy-1,4-phenanthrenequinone.—The hydroxy compound is easily converted into the ether by boiling with methyl alcohol and hydrogen chloride. The ether separates from the hot solution in the form of long, yellow needles and the yield is quantitative. The ether is easily hydrolyzed by hot alkali; it is moderately soluble in alcohol and readily soluble in benzene; m. p., 172.5°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.61; H, 4.23. Found: C, 75.37; H, 4.27.

The Allylation of 2-Hydroxy-1,4-phenanthrenequinone

This reaction proceeded less smoothly than is usually the case, and a considerable amount of tarry material was not identified. A suspension of 4.9 g. of the silver salt of the quinone in 70 cc. of benzene was boiled with 2 g. of allyl bromide for one hour and the benzene solution of the reaction products was concentrated in vacuum to a very small volume. From the very dark red solution there separated a solid product which was rather tarry but which was obtained in a fairly clean condition by washing with benzene. This was triturated with successive portions of dilute ammonia solution until no further material dissolved. The residue was found to contain chiefly 4-alloxy-1,2-phenanthrenequinone, of which 1 g. (26%) was obtained, while 1 g. of the product of C-alkylation was recovered from the ammonia solution.

4-Alloxy-1,2-phenanthrenequinone.—The crude material, which is readily soluble in alcohol or benzene, was crystallized repeatedly from ligroin. It formed dark red rather ill-formed needles melting at 128°. The quinone dissolves easily in sodium bisulfite solution with the formation of a rather sparingly soluble addition product.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 76.93; H, 4.64.

3-Allyl-2-hydroxy-1,4-phenanthrenequinone.—On crystallization from ligroin, in which it dissolves readily, the compound forms long, slender orange needles melting at 157°.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.27; H, 4.85.

The alkaline solution of this quinone is grape-purple but the color disappears completely on boiling the solution for a short time and the acidification of the colorless solution causes the separation of an oil. The quinone thus appears to behave in a manner similar to that described below for 2-hydroxy-1,4-phenanthrenequinone. The allyl derivative dissolves in concentrated sulfuric acid with the formation of an intensely green solution; a dark purple-red substance precipitates on adding water.

The Cleavage of 2-Hydroxy-1,4-phenanthrenequinone by Alkali

In describing the preparation of this quinone, it was stated that the substance is extremely sensitive to the hydrolytic action of hot alkali. An aqueous solution of the pure sodium salt rapidly loses its color on boiling and becomes pale yellow, and the change is hastened by the presence of an excess of alkali. On acidifying the hot solution, after it has been somewhat concentrated, the cleavage product crystallizes in the form of large, well-formed, somewhat yellow plates. The substance has the composition of the starting material plus the elements of one molecule of water, and the properties of an α-keto acid. It is in every way similar to the isomeric substance obtained in the same way from 3-hydroxy-1,4-phenanthrenequinone,[1] and the structure follows from the same considerations as those detailed in the earlier paper. The cleavage occurs more rapidly in the present case than with the 3-hydroxyquinone.

1-Aceto-2-naphthyl-glyoxylic Acid (V).—The cleavage product is readily soluble in water and crystallizes best from an acidified aqueous solution. Several crystallizations are required to remove a trace of yellow coloring matter, though the melting point is little affected by the process. The compound melts at 181° with the evolution of carbon dioxide.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.41; H, 4.16. Found: C, 69.02, 69.48; H, 4.24, 4.28. *Neut. equiv.* Subs. 0.2038: 6.81 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 ether was prepared by esterification with methyl alcohol and hydrogen chloride. It dissolves very readily in alcohol or benzene and fairly readily in ligroin. It is easily purified by the use of the latter solvent, but the crystals are not good; a paste of micro-crystals melting at 112° results.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.19; H, 4.76.

Oxidation of 1-aceto-2-naphthyl-glyoxylic acid with hydrogen peroxide in alkaline solution gave naphthalene-1,2-dicarboxylic acid, while the same reagent, in glacial acetic acid solution, yielded 1,2-naphthindanedione. The oxidation products are thus the same as those obtained from the isomeric acid, 2-aceto-1-naphthyl-glyoxylic acid.[1] The present reactions were carried out in the same manner and the products were carefully compared and their identity established.

1,2-Phenanthrenequinone-4-sulfonic Acid

Salts of 1,2-Dihydroxyphenanthrene-4-sulfonic Acid.—The addition of sodium bisulfite to 1,2-phenanthrenequinone does not proceed as smoothly as is usually the case with *o*-quinones of this type because some of the material always undergoes reduction to the hydroquinone before the addition reaction has gone to completion. When the quinone was treated with concentrated bisulfite solution, very little reaction of any sort took place until a small volume of alcohol was added. Nearly all of the material then dissolved, but a considerable part of it was converted into 1,2-dihydroxyphenanthrene, which soon separated in an impure condition. The formation of this substance was to some extent hindered by using a mixture of sodium bisulfite and sodium sulfite.

Twenty grams of 1,2-phenanthrenequinone was ground to a fine paste with 60 cc. of water and a solution of 40 g. of sodium bisulfite and 4 g. of sodium hydroxide in 90 cc. of water was added. The quinone rapidly disappeared, giving a dark brown solution containing some suspended matter. After a few hours it was diluted to a volume of 400 cc., warmed to about 80° in order to coagulate the particles of 1,2-dihydroxyphenanthrene and filtered. A solution of 27 cc. of concentrated sulfuric acid in water was then added, together with a few drops of caprylic acid to prevent foaming, and the sulfur dioxide was boiled off. The solution, on cooling, now deposited crystals of sodium 1,2-dihydroxyphenanthrene-4-sulfonate. This material was dissolved in water containing some sodium hyposulfite, and salted out with a solution of sodium chloride. An almost colorless product resulted; yield, 19.7 g. (65%). A further crystallization gave a sample containing the calculated percentage of sodium, though the compound does not crystallize well but forms a faintly gray crystalline powder. It is very readily soluble in water.

Anal. Calcd. for $C_{14}H_9O_5SNa$: Na, 7.36. Found: 7.19.

The **potassium** salt is somewhat less soluble but it also forms poor crystals. The sample was dried at 80°.

Anal. Calcd. for $C_{14}H_9O_5SK \cdot 2H_2O$: K, 10.73. Found: 10.83.

The **p-toluidine** salt was precipitated by adding *p*-toluidine and an excess of hydrochloric acid to a solution of the sodium or the potassium salt. It crystallizes well from water acidified with hydrochloric acid, forming faintly yellow, lustrous plates melting at 240° (248°, corr.), with decomposition. It darkens somewhat on exposure to the sunlight.

Anal. Calcd. for $C_{21}H_{19}O_5NS$: C, 63.45; H, 4.82; S, 8.07. Found: C, 63.25; H, 5.01; S, 8.04.

Sodium 1,2-Phenanthrenequinone-4-sulfonate.—The oxidation of sodium 1,2-dihydroxyphenanthrene-4-sulfonate in aqueous solution with a slight excess of chromic acid–sulfuric acid solution takes place readily at room temperature, but some caution is necessary in purifying the product for it decomposes rather easily when in an impure condition. The deep red solution which resulted from the oxidation was treated with an equal volume of saturated sodium chloride solution, causing the separation of the red sodium salt of the quinone. This material, which was rather finely divided, was collected and dissolved, while still moist, in boiling water. The solution was filtered without delay, treated with about one-third of its volume of alcohol and at once cooled. This time the quinone separated in the form of fine crystals, so that the material could be thoroughly washed. It was then dissolved in a minimum quantity of water, a small amount of alcohol was added to the filtered solution and crystallization was allowed to proceed slowly. The quinone then separated in the form of large, bright red plates. The pure material shows little tendency to undergo decomposition in solution, but solutions of less pure samples rapidly lose their bright red color on standing, even at room temperature, and deposit a very dark, or even black, product. The quinone dissolves readily in hot water, but it is much less soluble than sodium 3,4-phenanthrenequinone-1-sulfonate. The sample for analysis was dried at 100° in a vacuum.

Anal. Calcd. for $C_{14}H_7O_5SNa \cdot H_2O$: Na, 7.01. Found: 6.76.

The behavior of this quinone toward alkalies and amines is unique. When dilute sodium hydroxide solution is added to a suspension of the quinone in water, the red crystals lose their color at once and become green. On warming the material all dissolves to give a yellow solution. If a saturated solution of the quinone in water is treated with an equal volume of 6 *N* sodium hydroxide, the color changes at once from red to yellow. If such a solution is acidified at once, the red color reappears, but if the alkaline solution is allowed to stand for about one hour, acidification causes only a change to a paler yellow. If this solution is sufficiently concentrated, the sodium salt of 1,2-dihydroxyphenanthrene-4-sulfonate will separate. The identity of the substance was established by adding *p*-toluidine hydrochloride to the pale yellow solution, when the *p*-toluidine salt of 1,2-dihydroxyphenanthrene-4-sulfonate crystallized in the form of plates of characteristic appearance; it was identified by mixed melting point determinations.

The reaction of the quinone with *p*-toluidine follows a similar course. When a solution of the quinone in hot water was treated with an equivalent quantity of the amine, a very small amount of dark red tar was formed, but in about five minutes the solution lost its red color and became pale yellow. On concentrating the solution and adding hydrochloric acid, the *p*-toluidine salt of 1,2-dihydroxyphenanthrene-4-sulfonic acid, which was again identified by melting-point determinations, separated.

In order to determine what substance becomes oxidized in the course of the reduction of the quinone in these two cases, the following experiment was carried out. A weighed sample of the quinone was dissolved in water in an oxidation–reduction vessel in which the potential of the solution could be measured. Pure nitrogen was passed through a definite volume of alkali, then into the quinone solution and then into a second oxidation–reduction vessel containing an alkaline solution of sodium anthraquinone-β-sulfonate and its reduction product. Since this solution is very sensitive to oxygen, the presence of even a trace of this gas could be detected by a change in the potential of the solution. After all of the oxygen had been removed from the system, the alkali was transferred under a pressure of nitrogen into the vessel containing the quinone solution. It had seemed possible that either oxygen or hydrogen peroxide might be produced in the reduction of the quinone, but no oxygen was detected even when the mixture of the quinone and alkali was boiled. After the solution had stood for ten to fifteen hours, always protected by an atmosphere of nitrogen, a volume of sulfuric acid calculated to give a $N/10$ acid solution was added and the amount of the hydroquinone present was determined by electrometric titration with a dichromate solution. From 0.2009 g. of the quinone there was found present an amount of hydroquinone equivalent to 0.0980 g. of quinone, which indicates that 48.7% of the quinone had been converted into the hydroquinone. This indicates that one molecule of the hydroquinone is produced from two molecules of the quinone. The conclusion was supported by the results of a somewhat cruder experiment in which the amount of the hydroquinone formed was determined by precipitating it in the form of its *p*-toluidine salt. From 0.511 g. of the sodium salt of the quinone, there was obtained 0.317 g. of the nearly pure *p*-toluidine salt (m. p. 234°); on the basis of the above hypothesis, 0.309 g. should result.

The *p*-Toluidine Salt of 1,2-Phenanthrenequinone-4-sulfonic Acid (VIII).—The disproportionation of the sulfonated quinone in a solution containing a basic substance such as sodium hydroxide or *p*-toluidine does not occur in a neutral or acidic solution. One thus might expect that the quinone would react with *p*-toluidine in an acidic solution in a manner similar to other sulfonated quinones of the same type, that is, with the formation of a water-insoluble *p*-toluidine-quinone. It was found, however, that no such substance is produced, but that a simple amine salt of the quinone sulfonic acid is the sole reaction product. The salt was prepared by adding a solution of *p*-toluidine in an excess of dilute hydrochloric acid to an aqueous solution of sodium 1,2-phenanthrenequinone at the boiling point. On cooling, the salt separated in the form of slender, flat, bright red needles which, washed with a little cold water, were analytically pure. The substance decomposes very easily and it darkened considerably when crystallized even from an acidic solution containing *p*-toluidine hydrochloride to decrease the solubility. The salt is very readily soluble in water and it decomposes on heating at an indefinite temperature.

Anal. Calcd. for $C_{21}H_{17}O_5SN$: C, 63.77; H, 4.34. Found: C, 63.58; H, 4.33.

Summary

1,2-Phenanthrenequinone has been prepared for the first time and it has been used in securing various other phenanthrene derivatives, notably 2-hydroxy-1,4-phenanthrenequinone and sodium 1,2-phenanthrenequinone-4-sulfonate. The former compound exhibits an interesting type of hydrolytic cleavage by alkalies, observed heretofore in only one other case, while the sulfonated quinone is characterized by a remarkable stability of the sulfonic acid group, a property which appears to be connected with the spatial arrangement of the molecule.

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SYNTHESIS OF EPHEDRINE AND STRUCTURALLY SIMILAR COMPOUNDS. II. THE SYNTHESIS OF SOME EPHEDRINE HOMOLOGS AND THE RESOLUTION OF EPHEDRINE

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In Paper I of this series the authors described some new reactions which led to the synthesis of ephedrine. For the benefit of anyone desirous of repeating the synthesis emphasis is to be laid on the importance of using highly purified methylamine. Owing to the presence of undetermined impurities in the different preparations supplied for our research the most satisfactory results have been obtained only from Kahlbaum's hydrochloride of this base.

It was desirable to determine the generality of the reaction and to ascertain its limitations. Thus far the chief drawback has been the difficulty of preparing certain desired 1,2-diketones, although 1-phenylpropane-1,2-dione itself may be easily prepared. The troublesome cases are those in which methoxyl or hydroxyl groups are attached to the benzene nucleus. It has been found that ketonic aldehydes as well as the diketones may be used, and all primary aliphatic amines so far tried have given the expected product. In the case of aniline the product had somewhat indefinite properties, and no ephedrine-like substance was obtained from *p*-amidophenol.

Details of the synthetic products are given in the annexed table.

It is of some interest to mention that only in one or two cases was there any evidence of the presence of a second isomer, presumably related to ψ-ephedrine. An extensive search was made in the case of the N-ethyl analog of ephedrine but no isomer could be isolated.

The preparation of the *p*-ethyl derivative (see table) yielded a small

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