di-*n*-amyl, di-*iso*-amyl. The energy of activation has been calculated from the temperature coefficient of the reaction velocity.

3. A parallelism has been found between the rates of dissociation and the temperature at which appreciable dissociation first occurs as evidenced by the appearance of color in a dilute solution.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

PHENANTHRENEQUINONES RELATED TO ALIZARIN AND PURPURIN

BY LOUIS FREDERICK FIESER

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It is an interesting indication of the general difference in the chemistry of anthracene and of phenanthrene that alizarin was synthesized, produced commercially and the structure established all in the course of seven years, while over fifty years have elapsed since the first attempt was made[1] to obtain the corresponding phenanthrene derivative and the substance has not yet been described. Phenanthrenequinone is so sensitive to the action of alkalies, acids and oxidizing agents that it is doubtful if many of its derivatives will prove useful as dyestuffs; but the angular alignment possesses a greater chromophoric character than anthraquinone, and it is at least a matter of theoretical interest to know how the phenanthrenequinones having two or more hydroxyl groups in the ortho and para positions compare with the anthraquinone dyes.

Morpholquinone, the first substance of this type to be described, was obtained by Vongerichten[2] from a degradation product of morphine. Because it was a mordant dye similar to alizarin, Vongerichten at first regarded it as 1,2-dihydroxyphenanthrenequinone, but later[3] recognized it as the 3,4-isomer. The aim of several investigators to prepare this quinone from phenanthrene, or by applying the Pschorr synthesis, was finally achieved by Schmidt and Söll.[4] An unsuccessful attempt to synthesize 1,2-dimethoxyphenanthrene, from which 1,2-dihydroxyphenanthrenequinone might be obtainable, has been recorded,[5] and Mukherjee and Watson[6] found it impossible to hydroxylate 2-hydroxyphenanthrenequinone by the methods so useful for the preparation of alizarin and its congeners. Thus no dihydroxyphenanthrenequinones possessing dyeing properties, other than morpholquinone, were known until Brass under-

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[1] Graebe, *Ann.*, **167**, 143 (1873).

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

[3] Vongerichten, *ibid.*, **33**, 352 (1900).

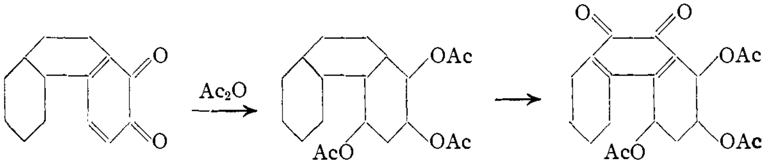
[4] Schmidt and Söll, *ibid.*, **41**, 3696 (1908).

[5] Pschorr and Buckow, *ibid.*, **33**, 1829 (1900).

[6] Mukherjee and Watson, *J. Chem. Soc.*, **109**, 617 (1916).

took a study of the rearrangement of the phenanthrenequinone azides. As a result of this work he was able to prepare 1,4-dihydroxyphenanthrenequinone[7] and the 2,3-isomer.[8] The only other polyhydroxyphenanthrenequinones known are 2,5-[9] and 2,7-dihydroxyphenanthrenequinone,[10] 2,3,4-trihydroxy-[11] and 2,7,?-trihydroxyphenanthrenequinone,[6] and 2,3,6,7-tetrahydroxyphenanthrenequinone.[12] None of these compounds presents any new points of interest.

In view of the scarcity of such compounds and the difficulty in finding methods suitable for their preparation, it seemed worth while to attempt to use the isophenanthrenequinones which recently have become available for the preparation of new 9,10-phenanthrenequinones. Thus an improved method of preparing morpholquinone has been found in the reductive acetylation of 3,4-phenanthrenequinone, followed by oxidation at the 9,10-positions and hydrolysis of the oxidation product.[13] In a similar manner 1,2-phenanthrenequinone[14] has now been converted into 1,2-dihydroxyphenanthrenequinone. The triacetate of 1,2,4-trihydroxyphenanthrenequinone, III, was obtained by hydroxylating 1,2-phenanthrenequinone, I, by the Thiele method and oxidizing the triacetoxy-phenanthrene, II, with chromic acid. 1,3,4-Trihydroxyphenanthrenequinone was prepared in the same way from 3,4-phenanthrenequinone.



I II III

The oxidation of an acetoxyl or alkoxyl derivative of phenanthrene seldom proceeds smoothly and in good yield, and the results are often negative. Thus Pschorr reports the failure to obtain a quinone from 1- or 4-methoxyphenanthrene, or from 1,5-dimethoxy-6-acetoxyphenanthrene,[15] and the author was unable to oxidize 3-methoxy-1,4-diacetoxyphenanthrene or 1-(*p*-toluidino)-3,4-diacetoxyphenanthrene.[13] The difficulty is partly due to the fact that the quinones are about as easily oxidized as the starting materials,[3] while a poor yield in some cases has been traced

[7] Brass and Stadler, *Ber.*, **57**, 134 (1924).

[8] Brass, Ferber and Stadler, *ibid.*, **57**, 121 (1924).

[9] Schmidt and Kämpf, *ibid.*, **36**, 3750 (1903).

[10] Anschütz and Meyer, *ibid.*, **18**, 1944 (1885).

[11] Schmidt and Spoun, *Ber.*, **55**, 1194 (1922).

[12] Brass and Nickel, *ibid.*, **58**, 204 (1925).

[13] Fieser, This Journal, **51**, 940 (1929).

[14] Fieser, *ibid.*, **51**, 1896 (1929).

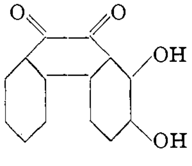
[15] Pschorr, *Ber.*, **33**, 161, 176, 1826 (1900).

to the formation of a diphenanthryl derivative as a by-product.[16] In the present case the chief side reaction appeared to consist in the hydrolysis of the acetoxyquinones or of the starting materials, but, by carrying out the oxidation with an equal weight of chromic acid in glacial acetic acid solution at 40°, yields of from 30 to 60% were obtained.

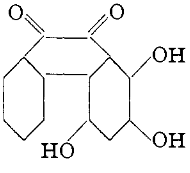
The new trihydroxyphenanthrenequinones are very easily oxidized by the air in alkaline solution. The intensely green solutions lose their color in a short time and it is thus necessary to hydrolyze the acetates in an indifferent atmosphere. 1,2-Dihydroxyphenanthrenequinone and morpholquinone are also oxidized under these conditions, though not as rapidly. Since this sensitivity to oxygen is characteristic only of the quinones having hydroxyl groups in the ortho or para positions, it is probable that the first step in the oxidation is the formation of a diquinone.

It may be noted that the new quinones exhibit no tendency to exist in any of the possible tautomeric forms, for they are all reconvertible into the original acetates, whose structures are fixed.

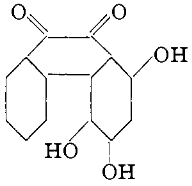
The new hydroxyphenanthrenequinones are in general inferior in dyeing properties to the isomers of the anthraquinone series. The trihydroxy-*o*-quinones, V and VI, are very poor dyes in comparison with purpurin. 1,2-Dihydroxyphenanthrenequinone, IV, which corresponds in structure to alizarin, dyes mordanted wool deep green, but it has little affinity for unmordanted cloth. The colors produced with IV are, to be sure, deeper than those from alizarin, just as 1,4-dihydroxyphenanthrenequinone surpasses quinizarin in tinctorial properties.[17] This is a further indication that phenanthrenequinone is a more powerful chromophore than anthraquinone.



IV



V



VI

On comparing the descriptions of the dyeing produced with the three *o*-dihydroxyphenanthrenequinones, it is found that there is a deepening in color on passing from the 2,3-isomer (brown-red),[8] to the 3,4-isomer (blue),[2] to the 1,2-isomer (green). It is rather surprising that the isomer having the true "alizarin structure" has less affinity for the fiber and gives less brilliant colors than morpholquinone. An hydroxyl group adjacent to the carbonyl group of phenanthrenequinone does not appear to favor

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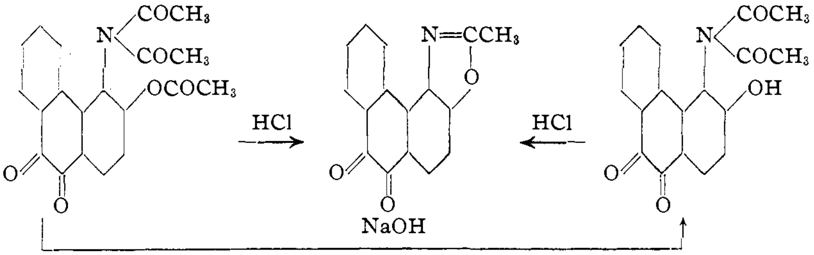
[16] (a) Vongerichten, *Ber.*, **30**, 2441 (1898); (b) Werner, *Ann.*, **322**, 135 (1902).

[17] Brass, *Z. angew. Chem.*, **37**, 67 (1924).

particularly the formation of a color lake.[18] Dimroth and Roos recently have recorded a similar observation concerning the dihydroxynaphthoquinones.[19] It is also surprising that the trihydroxyphenanthrenequinones, V and VI, are much poorer dyes than the ortho or para dihydroxy compounds from which they may be considered to be derived.

Since Brass[7,8] has found that 2-amino-3-hydroxy- and 4-amino-1-hydroxyphenanthrenequinone possess some dyeing properties, an attempt was made to prepare the quinone corresponding to 4-amino-3-hydroxyphenanthrene.[13] The triacetate of this substance was converted without difficulty into the triacetate of 4-amino-3-hydroxyphenanthrenequinone, VII, but the complete hydrolysis of the latter compound was not accomplished. On acid hydrolysis, or by dissolution of the quinone in bisulfite solution, the substance was converted into the oxazole derivative, VIII, which is very resistant to the action of either acids or alkalies. The triacetate was easily hydrolyzed by alkalies, but the product obtained was the N,N-diacetate, IX. This compound was easily converted into the oxazole derivative, VIII, by the action of acids, but it was only very slowly attacked by alkalies and then only with the complete destruction of the molecule. Thus the desired aminohydroxyphenanthrenequinone was not obtained.



VII VIII IX

The stability of the diacetylamino group in the 4-position is somewhat surprising, but it is not unlike the unusual stability of the sulfonic acid group of 1,2-phenanthrenequinone-4-sulfonic acid.[14] In the latter case the phenomenon was attributed to the configuration of the molecule, and it is possible that the resistance of the above diacetate to alkaline hydrolysis is due to the blocking effect of the neighboring phenyl group.

Experimental Part

1,2-Diacetoxyphenanthrene.—A mixture of equal parts of 1,2-phenanthrenequinone,[14] zinc dust and sodium acetate, with 5 parts of acetic anhydride, was boiled until the solution became pale yellow, the mixture was diluted with glacial acetic acid,

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[18] 1-Hydroxyphenanthrenequinone, which will be described in a forthcoming paper, imparts only a faintly pink color to mordanted wool.

[19] Dimroth and Roos, *Ann.*, **456**, 177 (1927).

filtered and carefully treated with water. The crude diacetate, m. p. 140°, was thus obtained in 89% yield. After repeated crystallization from dilute acetic acid and from ligroin–benzene, small, colorless needles melting at 146–147° were obtained. The compound is very readily soluble in benzene or glacial acetic acid and sparingly soluble in ligroin.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.45; H, 4.79. Found: C, 73.24; H, 4.82.

1,2-Diacetoxyphenanthrenequinone.—Five grams of the diacetate was oxidized in glacial acetic acid solution at 40° with 5.2 g. of chromic acid. The mother liquor contained some unchanged diacetate, for a further quantity of the quinone was obtained by adding more chromic acid after collecting the first crop of crystals. The yield was 3.3 g. (60%). The quinone dissolves readily in glacial acetic acid and forms small orange needles which melt with decomposition at 251° (257°, corr.).

Anal. Calcd. for $C_{18}H_{12}O_6$: C, 66.65; H, 3.73. Found: C, 66.89; H, 3.85.

1,2-Dihydroxyphenanthrenequinone.—When the diacetate was covered with a mixture of sodium hydroxide and alcohol, hydrolysis took place at once. A dark green solution resulted and some of the sodium salt of the quinone separated. The mixture was diluted with water in order to bring the salt into solution, and acidified. The flocculent, dark red precipitate was digested for a short time at the boiling point and the more compact product was then easily collected and washed. The substance is only sparingly soluble in water, and very readily soluble in alcohol, acetone or glacial acetic acid. Clusters of small, very dark red crystals were obtained from acetone. The substance decomposes on heating. The alkaline solution is chrome green, and a green salt is easily precipitated by an excess of alkali. The solution in concentrated sulfuric acid is red; in pyridine it is crimson.

Anal. Calcd. for $C_{14}H_8O_4$: C, 69.99; H, 3.36. Found: C, 69.77; H, 3.48.

1,2-Dihydroxyphenanthrenequinone dyes unmordanted wool a pale bluish gray. Wool or silk mordanted with aluminum or chromium is dyed dark green. The tones are not as brilliant as those with morpholquinone.

1,2,4-Triacetoxyphenanthrenequinone.—In early experiments on the oxidation of 1,2,4-triacetoxyphenanthrene[14] it was found that the product was partially hydrolyzed when the reaction was carried out in glacial acetic acid solution at the boiling point, with the result that most of it was destroyed by further oxidation. The use of acetic anhydride, or of mixtures of this with acetic acid, was then tried but a somewhat elevated temperature was required and again hydrolysis products of the quinone, as well as of the starting material, were obtained. Thus 2-acetoxy-1,4-phenanthrenequinone (m. p. 146°) was identified in one experiment. More satisfactory results were obtained by dissolving 5 g. of the triacetate in 75 cc. of glacial acetic acid, cooling to 40° and adding a solution of 5 g. of chromic acid. The product, which separated after standing for some time, was washed with alcohol and crystallized from toluene, giving 1.7 g. (32%) of pure material. It forms orange plates melting with decomposition at 227–228°. The quinone is only moderately soluble in toluene and readily soluble in glacial acetic acid.

Anal. Calcd. for $C_{20}H_{14}O_8$: C, 62.82; H, 3.69. Found: C, 62.63; H, 3.72.

1,2,4-Trihydroxyphenanthrenequinone.—While the triacetate is very easily hydrolyzed, the extreme sensitivity of the hydroxyquinone to oxygen in the presence of alkali makes it imperative to exclude all air while carrying out the reaction. When the triacetate was covered with alcoholic sodium hydroxide solution in an atmosphere of nitrogen, hydrolysis proceeded without heating, giving a deep green solution. The green solution was diluted with water, filtered and acidified. The precipitate was at first somewhat gelatinous, but it coagulated on heating to give an easily filterable suspension. The dried material is black and decomposes on heating. No satisfactory method of crystallizing the compound was discovered. It is sparingly soluble in most solvents other than alcohol, in which it is extremely soluble. The red alcoholic solution deposited a red crystalline crust on slow evaporation, but this product, dried in vacuum at 100°, appeared to contain alcohol of crystallization.

Anal. Calcd. for $C_{14}H_8O_5 \cdot C_2H_5OH$: C, 66.24; H, 4.32. Found: C, 66.18; H, 4.31.

The precipitated material gave the following analytical results.

Anal. Calcd. for $C_{14}H_8O_5$: C, 65.62; H, 3.15. Found: C, 65.30; H, 3.20.

This quinone gives a green solution in alkali, but in the presence of air the color rapidly disappears and gives place to a pale red. The change may be noted in the film formed on shaking the green solution in a test-tube. A completely oxidized solution gives off carbon dioxide on acidification. The quinone dissolves in concentrated sulfuric acid with a green color. The solution in pyridine is cornflower-blue when fresh, but soon becomes brown on exposure to the air and deposits a black, sparingly soluble substance which has the properties of a quinone. The trihydroxyquinone is easily acetylated with acetic anhydride and sulfuric acid without heating, giving the original triacetate.

1,2,4-Trihydroxyphenanthrenequinone has scarcely any dyeing properties. A poor, dull brown is produced on aluminum-mordanted wool.

1,3,4-Triacetoxyphenanthrene.—This compound was obtained in good yield by the reductive acetylation of 3-hydroxy-1,4-phenanthrenequinone[13] with zinc dust, sodium acetate and acetic anhydride. It dissolves very readily in alcohol, readily in benzene and only sparingly in ligroin. Fluffy clusters of silken white needles melting at 138° were obtained on crystallization from benzene–ligroin.

Anal. Calcd. for $C_{20}H_{16}O_6$: C, 68.16; H, 4.58. Found: C, 68.19; H, 4.67.

1,3,4-Triacetoxyphenanthrenequinone.—The above triacetate was oxidized in glacial acetic acid solution at 40° with an equal weight of chromic acid. After maintaining the specified temperature until yellow crystals of the quinone began to separate, the mixture was cooled and the nearly pure product was collected; yield, 47%. The compound dissolves readily in glacial acetic acid and crystallizes from this solvent in the form of well-shaped yellow needles. The substance softens at about 220° and decomposes at about 240°.

Anal. Calcd. for $C_{20}H_{14}O_8$: C, 62.82; H, 3.69. Found: C, 62.66; H, 3.92.

1,3,4-Trihydroxyphenanthrenequinone.—Working in an atmosphere of nitrogen, 1,3,4-triacetoxyphenanthrenequinone was covered with cold alcoholic sodium hydroxide solution. Hydrolysis took place readily and the solution became deep red and then green. A dark red, rather voluminous precipitate was thrown down on acidification. The product is only sparingly soluble in water but very readily soluble in alcohol, and it was obtained in the form of small, very dark red crystals on allowing the intensely red alcoholic solution to evaporate slowly.

Anal. Calcd. for $C_{14}H_8O_5$: C, 65.62; H, 3.15. Found: C, 65.47; H, 3.25.

The solution in alkali is intensely green when viewed in thin layers, but greenish-red when a considerable volume of the solution is viewed against a source of light. When exposed to the air, the color of the alkaline solution fades rather rapidly to a pale pink. The solution in concentrated sulfuric acid is deep red, while with pyridine a deep red solution is obtained which becomes green on dilution with water. The substance is easily acetylated by acetic anhydride, either in pyridine solution or with the aid of a few drops of concentrated sulfuric acid.

1,3,4-Trihydroxyphenanthrenequinone has poor dyeing properties. It dyes aluminum-mordanted wool or silk a dull green; with a chromium mordant a brown-gray is produced.

4-Amino-3-phenanthrol Diacetate.—This substance was prepared by adding acetic anhydride to a cold solution of 4-amino-3-phenanthrol hydrochloride[13] in pyridine. The product was precipitated by water and crystallized repeatedly from alcohol. It formed small, colorless plates melting at 208° (211°, corr.). It is sparingly soluble in benzene, moderately soluble in alcohol 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, 5.11.

Oxazole Derivative of 4-Amino-3-phenanthrol.—Aminophenanthrol diacetate readily loses the elements of acetic acid on heating, with the closing of an oxazole ring. Since the same substance is formed by the loss of acetic anhydride from the triacetate,[20] a mixture of the di- and triacetates may be used for the preparation.

A mixture of 24.5 g. of 4-amino-3-phenanthrol hydrochloride, 9 g. of fused sodium acetate and 50 cc. of acetic anhydride was heated for one hour on the water-bath and the product was poured into water. The rather oily solid was heated in a distilling flask until all of the adhering water and all of the acetic acid formed in the reaction had been removed. The residue was then distilled at a pressure of 3 mm. The distillate solidified at once, giving 20 g. (86%) of a pale yellow product melting at 152°. Repeated crystallization from glacial acetic acid failed to remove the color, but yielded small, pale yellow plates melting at 155°.

Anal. Calcd. for $C_{16}H_{11}ON$: C, 82.37; H, 4.76. Found: C, 82.23; H, 5.02.

The substance dissolves readily in glacial acetic acid or benzene; it is moderately soluble in alcohol and insoluble in acids or alkalies.

Oxazole Derivative of 4-Amino-3-hydroxyphenanthrenequinone.—A solution of 4.7 g. of the above phenanthrene derivative in 150 cc. of glacial acetic acid was cooled to 70° and a solution of 8 g. of chromic acid (twice the theoretical quantity) in water, diluted with glacial acetic acid, was added in the course of ten minutes, while maintaining the initial temperature by cooling. In the early stages of the oxidation a brown precipitate was produced but this soon dissolved and orange crystals began to separate. After cooling the solution the product was collected and washed with alcohol. It was nearly pure; yield, 2.4 g. (47%).

Crystallized from glacial acetic acid, in which it is only moderately soluble, this quinone formed small, orange needles melting at 275° (282°, corr.). It dissolves in concentrated sulfuric acid with a red-brown color and may be recovered unchanged from the solution. It dissolves to a slight extent in hot concentrated bisulfite solution and is recovered on the addition of acid or alkali to the solution. Attempts to hydrolyze this oxazole derivative with alcoholic sodium hydroxide solution were unsuccessful. The substance was attacked with such difficulty that the primary products were apparently destroyed during the process.

Anal. Calcd. for $C_{16}H_9O_3N$: C, 72.99; H, 3.45. Found: C, 72.78; H, 3.71.

4-Amino-3-hydroxyphenanthrenequinone Triacetate.—Werner[20] obtained triacetylaminophenanthrol by heating the aminophenanthrol with acetic anhydride in a sealed tube. It may be prepared more easily by boiling a mixture of 12 g. of 4-amino-3-phenanthrol hydrochloride, 4 g. of fused sodium acetate and 90 cc. of acetic anhydride for one hour. The mixture was poured into water and the product crystallized from alcohol; yield, 12.5 g. (76%); m. p., 170.5° (Werner, 169–170°).

The conversion of the triacetate into a quinone was best accomplished by oxidizing a solution of 4 g. of material in 30 cc. of glacial acetic acid with a solution of 4 g. of chro-

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[20] Werner, *Ann.*, **321**, 298 (1902).

mic acid in 4 cc. of water and 8 cc. of glacial acetic acid at 55–60°. After ten minutes a little water was added gradually to the red solution; the quinone then separated in crystalline condition and was practically pure. The compound slowly dissolves on boiling with a rather large quantity of alcohol, but the resulting solution deposits crystals only after it has been concentrated to about one-tenth of the initial volume. Feather-shaped clusters of yellow needles melting at 204° (207°, corr.), with decomposition, are thus obtained.

Anal. Calcd. for $C_{20}H_{15}O_6N$: C, 65.74; H, 4.14. Found: C, 65.84; H, 4.45.

The only compounds isolated as the result of the hydrolysis of this substance were the oxazole derivative and a diacetate. The former is produced by boiling the alcoholic solution with hydrochloric acid, or by dissolving the quinone in bisulfite solution and adding hydrochloric acid.

4-Diacetylamino-3-hydroxyphenanthrenequinone.—This was obtained by the alkaline hydrolysis of the triacetate. Working in an atmosphere of nitrogen, 2 g. of the triacetate was covered with 5 cc. of alcohol and 8 cc. of $3N$ sodium hydroxide solution. The material rapidly dissolved to give a clear, deep red solution. When the solution was diluted with water and then acidified, a yellow solution resulted and in a short time yellow needles began to separate. The product (1.4 g.) did not dissolve easily in 95% alcohol, but the addition of a little water to a suspension which had been boiled for some time caused the material to go into solution rapidly. Crystallization now took place only after the solution had been well concentrated. Brown-yellow needles of what appeared to be the N,N-diacetate were thus obtained. The compound decomposes on heating at about 255–260°.

Anal. Calcd. for $C_{18}H_{13}O_5N$: C, 66.86; H, 4.05. Found: C, 66.81, 66.85; H, 4.64, 4.52.

The substance dissolves in alkali with a pure, intensely red color. The compound is slowly oxidized in alkaline solution by the air. It is not at all easily hydrolyzed. A strongly alkaline solution, heated on the water-bath in an atmosphere of nitrogen in order to prevent oxidation, still contained unchanged material after two hours. Hydrolysis products could not be isolated in pure condition. It is probable that further changes occur as rapidly as the hydrolysis. Acid hydrolysis of the diacetate yielded only the oxazole derivative. This reaction is easily brought about by boiling an alcoholic solution or suspension of the diacetate with hydrochloric acid. Orange needles of the oxazole soon separate.

Summary

A description is given of the preparation of 1,2-dihydroxyphenanthrenequinone and of 1,2,4- and 1,3,4-trihydroxyphenanthrenequinone from certain isophenanthrenequinones. An attempt to prepare 4-amino-3-hydroxyphenanthrenequinone met with failure owing to the resistance to hydrolysis of a diacetylamino group in the 4-position.

BRYN MAWR, PENNSYLVANIA