[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE SULFONATION OF PHENANTHRENE.
II. DISULFONATION

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It was observed as early as 1873 that disulfonic acids are produced in the sulfonation of phenanthrene along with the monosulfonic acids, even when the reaction is stopped before all of the hydrocarbon has been consumed,[1] and yet there is no information available concerning the nature of these disulfonic acids. When the sulfonation is conducted at 120–130°, under the conditions best suited for the preparation of the 2- and the 3-monosulfonates, over 40% of the phenanthrene is converted into disulfonates.[2] Having collected a certain quantity of this material as a by-product, it became a matter of interest to attempt to learn something of the composition of the mixture.

A method of isolating a mixture of the potassium disulfonates in a form free from inorganic salts was found, and some attempts were made to effect a separation of the isomers. This difficult task, however, was not accomplished. Among the obstacles, the extreme solubility of the potassium salts may be mentioned. Potassium sulfate crystallizes out first from a solution of the organic and inorganic salts; even the barium salt is very soluble. The tendency to form supersaturated solutions, so often noted with phenanthrene derivatives, is particularly marked with these salts. In addition to these unfavorable properties, one is confronted with an extremely complex mixture. From the results to be presented below, it may be said that there are probably twelve isomers present in the mixture.

In order to simplify the problem, a study was made of the disulfonic acids produced when pure phenanthrene-2-sulfonic acid and the 3-isomer are treated with sulfuric acid at 120–130°. In each case there was obtained a mixture of extremely soluble disulfonates having the unfavorable properties noted above, and a separation was not achieved. The mixtures were fused with alkali, but the phenanthrol mixtures, though easily purified by distillation at a reduced pressure, likewise resisted efforts to effect a separation. When the phenanthrol mixtures were acetylated, on the other hand, it was possible, by fractional crystallization, to isolate three pure diacetoxyphenanthrenes as the result of each sulfonation. While it is a relatively easy matter to separate the greater part of the chief constituent of each mixture, the isolation of the substances formed in smaller quantity was accomplished only after a great many fractionations.

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[1] Graebe, *Ann.*, **167**, 152 (1873). See the preceding paper for further references.

[2] Fieser, THIS JOURNAL, 51, 2460 (1929).

As in the separation of the phenanthrene-monosulfonic acids, one encounters here the phenomena of supersaturation and of an order of crystallization which is contrary to the solubility relationships. Though the separations were thus incomplete, it will be seen from the following results that a fairly comprehensive account is given of the course of the sulfonations. From potassium phenanthrene-3-sulfonate, there was obtained, on sulfonation and fusion, a phenanthrol mixture corresponding to 83% of the theoretical amount, while the distilled material amounted to 77%. Conversion into the diacetate was quantitative and 70% of this was separated into the pure constituents. The melting points of the isomers, and the amounts which were obtained in pure condition from the mixtures, are given in the following table.

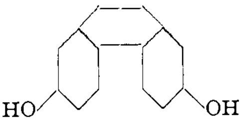
TABLE I

DIACETOXY-PHENANTHRENES OBTAINED

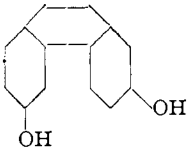
	From phenanthrene-3-sulfonic acid			From phenanthrene-2-sulfonic acid		
	α	β	γ	δ	ε	ζ
M. p., °C.	124.5	122–123	184	122–123	181.5	125
Yield, %	59.1	10.0	0.9	54.1	2.1	1.0

The problem of determining the positions of the substituents in these compounds is to some extent simplified by the fact that they all yield diacetoxy-9,10-phenanthrenequinones on oxidation, showing that the second substituent has in no case entered the 9- or 10-position. While none of the phenanthrene derivatives correspond to known compounds, the quinone obtained from one of them, namely, ε-diacetoxyphenanthrenequinone, was found to be identical with 2,7-diacetoxyphenanthrenequinone which has been described by several investigators.[3,4] This proves that the ε-isomer, melting at 181.5°, is the diacetate of 2,7-dihydroxyphenanthrene, I.

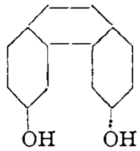
A further fact of value in the elucidation of the structural problem is that two of the substances listed in Table I are identical.



I (ε)



II (β, δ)



III (α)

The β-diacetate, which constitutes 10% of the product obtained from the 3-sulfonic acid, is identical with the δ-diacetate, which is the chief product

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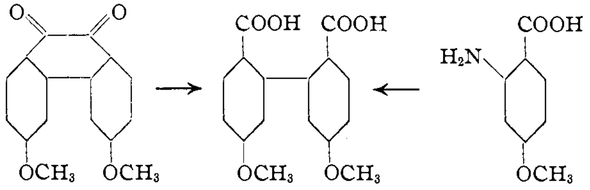
[3] (a) Anschütz and Meyer, *Ber.*, **18**, 1944 (1885); (b) Schmidt and Kämpf, *ibid.*, **36**, 3742 (1903); (c) Werner, *ibid.*, **37**, 3087 (1904); (d) Brass and Nickel, *ibid.*, **58**, 208 (1925).

[4] Through the courtesy of Professor Brass, to whom the author wishes to express his thanks, a direct comparison of the two substances was possible.

resulting from the sulfonation of the 2-sulfonic acid. Assuming that no rearrangement has taken place, the diacetate which is obtained from both the 2-acid and the 3-acid must have a structure corresponding to 2,3-dihydroxyphenanthrene, or to 2,6(or 3,7)-dihydroxyphenanthrene, II. The former structure is not only improbable, but is definitely ruled out because the dimethyl ether and the dihydroxyphenanthrenequinone derived from the new dihydroxyphenanthrene are different from the known 2,3-dimethoxyphenanthrene[5] and 2,3-dihydroxyphenanthrenequinone.[6] The substance, therefore, may be assigned the structure of II.

From the foregoing it is seen that in three instances, in the production of a disulfonic acid from a monosulfonic acid, the second substituent has entered the unsubstituted, terminal benzene ring. It is not unreasonable to suppose that this rule also holds for the formation of the acid of the α-series, whence the substituents in this series are probably in the 3,5-, the 3,6- or the 3,8-positions, since the 3,7-isomer is already known. It will be observed that the isomer in question is the chief reaction product. Recalling the fact that the monosulfonation of phenanthrene gives the 3- and the 2-acids as the chief products, while a relatively small amount of the 1(or 8)-acid, and none of the 4(or 5)-acid, is formed, it will be seen that the most probable structure for the α-series is represented by III, the 3,6-derivative.

The correctness of this conclusion was proved in the following manner. The dimethyl ether of the α-series was oxidized to a quinone, IV, and this was oxidized by hydrogen peroxide in glacial acetic acid solution. Two products were obtained, one having the properties of a lactone, the other (V) giving reactions characteristic of a diphenic acid, such as the formation of a fluorenone on treatment with sulfuric acid. The same diphenic acid, V, was obtained synthetically from 4-methoxy-2-aminobenzoic acid, VI.



IV V VI

The formation of the lactone in the oxidation of 3,6-dimethoxyphenanthrenequinone represents a somewhat unusual reaction. The substance has the formula $C_{15}H_{12}O_4$. It dissolves in alkali only on long boiling. That this is not due to a lack of solubility of the sodium salt but to the slow opening of a lactone ring is shown by the result of methylation in

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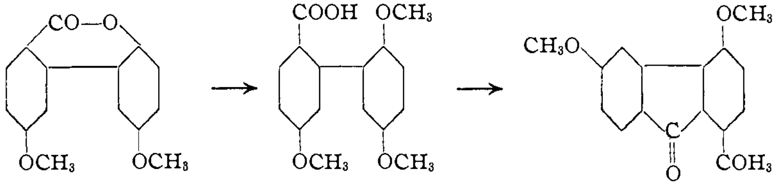
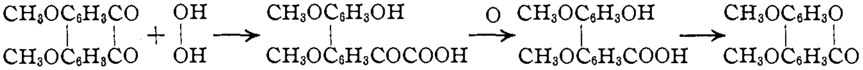
[5] Pschorr and Buckow, *Ber.*, **33**, 1831 (1900).

[6] Brass, Ferber and Stadler, *ibid.*, **57**, 127 (1924).

alkaline solution (followed by boiling with alkali), for a substance differing from the lactone by the elements of methyl alcohol is thus obtained and the new compound dissolves in cold carbonate solution. This methylated derivative yields a trimethoxyfluorenone on dissolution in concentrated sulfuric acid, indicating the presence of a carboxyl group adjacent to a diphenyl linkage. These facts point to the structures VII, VIII and IX for the compounds concerned. The lactone, VII, could not be obtained on treating 5,5′-dimethoxydiphenic acid with hydrogen peroxide, and it must, therefore, come directly from 3,6-dimethoxyphenanthrenequinone. It is probably produced as follows



VII VIII IX



$$\begin{array}{c}CH_3OC_6H_3CO\\ |\\ CH_3OC_6H_3CO\end{array} + \begin{array}{c}OH\\ |\\ OH\end{array} \longrightarrow \begin{array}{c}CH_3OC_6H_3OH\\ |\\ CH_3OC_6H_3COCOOH\end{array} \xrightarrow{O} \begin{array}{c}CH_3OC_6H_3OH\\ |\\ CH_3OC_6H_3COOH\end{array} \longrightarrow \begin{array}{c}CH_3OC_6H_3O\\ |\quad\quad |\\ CH_3OC_6H_3CO\end{array}$$

According to this interpretation, the action of hydrogen peroxide on 3,6-dimethoxyphenanthrenequinone involves not only the usual splitting between the two ketone groups but also a cleavage of the bond between one ketone group and a benzene ring. So far as the author is aware, this type of oxidation has not been observed previously in the phenanthrenequinone series. It finds a certain parallel, however, in the alkaline oxidation of purpurin to 2,5-dihydroxybenzoquinone,[7] and a close analogy is found in the alkaline oxidation of alizarin to 2-hydroxy-1,4-naphthoquinone-3-vinylglyoxylic acid,[8] if it is true that this reaction involves, as the first step, the formation of a diquinone.

To return to the problem of determining the structures of the compounds listed in Table I, it will be seen that only the γ- and the ζ-series remain to be accounted for. If it is again assumed that the second substituent enters the unsubstituted, terminal ring, only two structures remain for the γ-series and two for the ζ-series: the γ-series must have the 3,5- or the 3,8-structure; the substituents in the ζ-derivatives must be in the 2,5- or the 2,8-positions. 2,5-Dihydroxyphenanthrenequinone, however, is a known compound,[9] and the dihydroxyphenanthrenequinone of the

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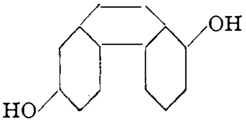
[7] Scholl and Dahll, *Ber.*, **57**, 80 (1924).

[8] Scholl and Zinke, *ibid.*, **51**, 1419 (1918).

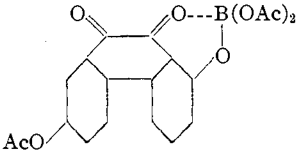
[9] Schmidt and Kämpf, *ibid.*, **36**, 3750 (1903), who first prepared this quinone, regarded it as 4,5-dihydroxyphenanthrenequinone, but the evidence of Christie and Kenner, *J. Chem. Soc.*, 470 (1926), and of Christie, Holderness and Kenner, *ibid.*, 671 (1926), convincingly supports the 2,5-structure.

ζ-series does not have the properties ascribed to this substance. It is probable, therefore, that the ζ-derivatives belong to the 2,8-series, X.

A very delicate means of confirming the structure assigned to the ζ-series, and of distinguishing between the two possible structures for the γ-compounds, was found in the application of the elegant method of Dimroth for the recognition of an hydroxyl group in a position adjacent to a quinone carbonyl group.[10] The method, which has been applied already to a few hydroxyphenanthrenequinones,[10b] consists in comparing the action of acetic anhydride on the quinone with the action of a solution of boro-acetic anhydride in acetic anhydride. With the latter reagent, ordinary acetylation takes place when the hydroxyl group is not adjacent to the carbonyl group, but an hydroxyl group in this favorable position, that is, in the 1- or 8-position in phenanthrenequinone, enters into the formation of a boro-acetate complex, which is characterized by having an intense color. Thus the quinone corresponding to X should yield the substance XI, and the formation of such a complex should be evident from the development of a distinctive color. With the absence of an hydroxyl group in the 1- or 8-position, both boro-acetic anhydride and acetic anhydride can be expected to yield a yellow or orange simple acetate.



X (ζ)



XI

Before applying the Dimroth test to the new dihydroxyphenanthrenequinones, it seemed desirable to extend Dimroth's observations by making at least a brief study of the action of the boro-acetic anhydride reagent on the various hydroxyphenanthrenequinones of known structure which have been prepared recently by the author. Experiment showed that the colors of the solutions in acetic anhydride and in the boro-acetic anhydride reagent were identical (usually pale yellow or orange) with quinones having the hydroxyl groups in the following positions: 2,5-, 2,6-, 2,7- and 3,6-, and to this list may be added, from Dimroth's results, the 2- and 3-derivatives. With the groups in the following positions, on the other hand, a striking change to green was observed in the presence of boro-acetic anhydride: 1,2-, 1,4-,[10b] 1,2,4-; while the color changed to red in the case of 1-hydroxyphenanthrenequinone, and 1,3,4-trihydroxy phenanthrenequinone gave a sparingly soluble red precipitate.

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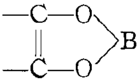
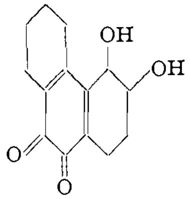
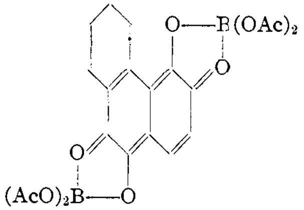
[10] (a) Dimroth and Faust, *Ber.*, **54**, 3020 (1921); (b) Dimroth, *Ann.*, **446**, 97 (1926); (c) Dimroth and Ruck, *ibid.*, **446**, 123 (1926); (d) Dimroth and Roos, *ibid.*, **456**, 177 (1927).

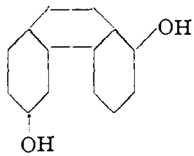
With only one compound was the behavior such as to constitute a possible anomaly. Morpholquinone, XII, though it contains no hydroxyl group in the favorable ortho position, imparts to a cold solution of boro-acetic anhydride a red color which becomes intensely purple on warming, and dark red crystals separate from the solution. On boiling, a deep green solution results. According to the theoretical analysis which Dimroth[10b] has made of the problem, it is possible that the formation of a complex is in this case due to a tautomeric change and that one of the products formed has the amphi-quinonoid structure, XIII, though the failure of 3-hydroxyphenanthrenequinone to form a complex renders this explanation unlikely. It is also possible that the two ortho hydroxyl groups enter into combination with the reagent, forming primary valence compounds of the type  $\begin{matrix}-C-O\\ \| \\ -C-O\end{matrix}\!\!>B-OAc$, or complex compounds of the type described by Böesecken[11] and by Rosenheim and Vermehren.[12] A reaction of this character appears to be the more probable in view of the fact that the red precipitate first formed is not as easily attacked by water as the complexes obtained by Dimroth. Thus the present indications are that the unusual reaction of morpholquinone is connected with the presence of two adjacent hydroxyl groups. Since such a grouping is impossible for the two new dihydroxyphenanthrenequinones, it was felt that the test could be applied with confidence to these substances and the interesting behavior of morpholquinone was not studied further.



XII



XIII



XIV (γ)

When the dihydroxyphenanthrenequinone of the ζ-series was examined, it was found that boro-acetic anhydride produced an intense green coloration in the cold, and that this became purple on warming. The compound, therefore, has one group in the 1(or 8)-position and, since the other group is fixed at 2, and the compound differs from the known 1,2-isomer, the substance may be assigned the formula of the 2,8-derivative, corresponding to X. The isomer of the γ-series also forms a complex with boro-acetic anhydride, evident from the red coloration produced, and it is thus considered to be the 3,8-derivative, corresponding to XIV, though it is possible, if highly improbable, that it is 1,3-dihydroxyphenanthrenequinone.

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[11] Böesecken, *Chem. Zentr.*, II, 1341 (1923).

[12] Rosenheim and Vermehren, *Ber.*, **57**, 1337, 1828 (1924).

The conclusions concerning the new dihydroxyphenanthrenes, and the disulfonic acids from which they were obtained, may be summarized in the following way

$$\text{Phenanthrene-3-sulfonic acid} \longrightarrow \begin{cases} \text{3,6-Disulfonic acid } (\alpha\text{-Series}) \\ \text{3,7(or 2,6)-Disulfonic acid } (\beta\text{-Series}) \\ \text{3,8-Disulfonic acid } (\gamma\text{-Series}) \end{cases}$$

$$\text{Phenanthrene-2-sulfonic acid} \longrightarrow \begin{cases} \text{2,6-Disulfonic acid } (\delta\text{-Series}) \\ \text{2,7-Disulfonic acid } (\epsilon\text{-Series}) \\ \text{2,8-Disulfonic acid } (\zeta\text{-Series}) \end{cases}$$

In the monosulfonation of phenanthrene, the substituent enters the 1-, the 2-, the 3- and the 9-positions; a second substituent, at least in the case of the 2- and the 3-acid, enters the 8-, the 7- and the 6-, or what may be termed the 1′-, the 2′- and the 3′-, positions. In each case, the predominant isomer is that produced by substitution in the 3(or 6)-position. In no instance has substitution in the 4(or 5)-position been observed.

Experimental Part

Experiments with the Disulfonate Mixture.—It was stated in Part I that the neutralization of the sulfonation product with alkali causes the monosulfonates to crystallize out completely, while the disulfonates are largely retained in the mother liquor. When an attempt was made to isolate the disulfonic acids, in the form of their potassium salts, by concentration of such a solution, there separated at the boiling point a substance which appeared to be gelatinous, but which was found to have a fine, hair-like structure and to consist largely of potassium sulfate. The addition of a large quantity of potassium hydroxide, however, brings about the precipitation of a mixture of potassium phenanthrene-disulfonates. The material may be freed from inorganic salts by repeated precipitation with potassium hydroxide, followed by washing with alcohol, and analyses agreed with the values calculated for a disulfonate. The material is extremely soluble in cold water and it could not be crystallized. Even the barium salt is very soluble in water and has little tendency to crystallize; the solutions have a soapy consistency. The *p*-toluidine salt separates as an oil only from a very concentrated solution. By fusion of the disulfonate mixture and distillation of the product, a solid phenanthrol mixture was obtained but this is not well adapted to a separation by fractional crystallization. It is very readily soluble in alcohol and very sparingly soluble in benzene. Crystallization of the mixture obtained on acetylating this material gave some promise of success and this method of separation was adopted in the experiments described below.

The Sulfonation of Potassium Phenanthrene-3-sulfonate.—The sulfonates used in carrying out these reactions were carefully freed not only from all traces of isomers but also from traces of potassium chloride, which interferes with the reaction. Ninety-four grams of the potassium 3-sulfonate was stirred into 94 cc. of concentrated sulfuric acid and the mixture was heated in an oil-bath at 130°. The temperature of the reaction mixture soon reached 125°, and it was then maintained at 125–130° for one and one-half hours.[13] The reaction is exothermic and it is necessary to keep the bath temperature about 10° below that desired for the reaction. The mixture was stirred thoroughly in order to break up the lumps which first formed. A clear, viscous solution usually resulted after about thirty minutes, and at the same time a crystalline salt began to

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[13] The results were the same when the heating was continued for three hours.

separate, so that, at the end of the specified time, a thick, almost solid, crystalline paste resulted. This was dissolved in 700–800 cc. of water and the solution was neutralized with a concentrated solution of about 200 g. of potassium hydroxide and then rendered slightly acid. The solution was next boiled down until the separation of solid material caused too much bumping, when it was poured, in portions, into an evaporating dish and dried in the oven.

The finely powdered mixture of disulfonates and potassium sulfate was fused with 700 g. of potassium hydroxide at a temperature of 280–305°. Fusion took place smoothly, giving a thick, brown melt. This was dissolved in water, to which ice was added, the greater part of the alkali was neutralized, and the hot, filtered solution was then acidified and cooled. The quality of the product was improved by a further precipitation from alkali, though the material slowly undergoes oxidation unless the solution is again acidified without delay. The dried phenanthrol mixture formed a gray powder weighing 55.5 g. and melting at about 175–200°. It was distilled at a pressure of 3 mm., taking care to avoid exposure of the molten material to the air, for it is easily oxidized. The distillate (51 g.) was dissolved in acetic anhydride and the solution was boiled for one hour and then poured into water. The diacetate mixture soon solidified and the crushed and well-washed material dried in the course of two days to a weight corresponding closely with the theoretical weight (71.3 g.). The product was somewhat green and melted at 95–125°.

The mixture of diacetates was first crystallized from a minimum quantity of alcohol in order to remove a small amount of acetic acid and oil, and then was subjected to a systematic fractionation from alcohol. The product at first separated in the form of a stiff paste of amorphous material, but, after six crystallizations, the top fraction formed blades of pure 3,6-diacetoxyphenanthrene (31.5 g.), while a further quantity (5 g.) of this isomer was soon separated as the least soluble of the remaining fractions. This isomer crystallizes in the form of long, flat blades having a characteristic gloss and melting, when perfectly pure, at 124.5°. On further crystallization the 3,8-isomer became concentrated in the top fraction along with the 3,6-derivative. For a time it was difficult to distinguish this mixture, which formed plates, from the pure 3,6-isomer, except that the melting point was a few degrees too low and not sharp. After further crystallization the melting point was raised to about 130°, at which point a fairly complete separation becomes possible. If a solution of the somewhat feathery plates is closely watched, a pause in the progress of the crystallization may be observed. If the solution is quickly filtered without undue disturbance, needles of the 3,8-isomer melting at 182–183° may be obtained, while blades of the nearly pure 3,6-isomer crystallize at once from the filtrate. Pure 3,8-diacetoxyphenanthrene forms long slender needles from alcohol and melts at 184°.

The 2,6-isomer becomes concentrated in the more soluble fractions and may be recognized from the fact that it forms clusters of stout needles melting at about 115–117°. Though the crystals appear to be well-formed, the compound on further purification melts at 122–123° and forms small plates. The needle form, however, is not only characteristic of the material in a certain stage of purification, but it is an aid in effecting a separation. A mixture of these needles with blades of the 3,6-isomer may be warmed with alcohol until the blades are dissolved, without greatly affecting the compact needles.

While alcohol is preferred as a solvent with which to carry out the first crystallizations, a point is reached where further working of the mixture becomes unprofitable and it is then advisable to change to benzene–ligroin. Using the latter solvent, and having removed the greater part of the 3,6-isomer, it is found that the high-melting 3,8-diacetate is the first to crystallize. It first forms a crust of small crystals and then good, prismatic needles. The 2,6-isomer again concentrates in the tail fractions and the 3,6-diacetate was obtained from intermediate fractions.

The separation was not carried to completion, but was interrupted when the following quantities of the pure isomers had been collected: 3,6-diacetoxyphenanthrene, 42.2 g.; 2,6-diacetoxyphenanthrene, 7.2 g.; 3,8-diacetoxyphenanthrene, 0.7 g.[14]

The Sulfonation of Sodium Phenanthrene-2-sulfonate.—A mixture of 63 g. of the salt and 63 cc. of concentrated sulfuric acid was heated at a temperature of 125–130° for just thirty minutes, when the reaction was found to be complete. The material in this case dissolved very easily and crystallization of the acid sodium salt did not take place. The reaction mixture was worked up and converted into a diacetate mixture in exactly the same manner as with the isomer. The crude phenanthrol mixture (39.5 g.) gave 37.5 g. (71%) of distilled product, while the yield of the diacetate mixture was quantitative (47.3 g.). The latter substance was somewhat oily until it was triturated with dilute sodium hydroxide solution.

The diacetate mixture was again fractionally crystallized from alcohol. On the first crystallization the material separated as an oil which soon solidified, but it thereafter formed crystals. After seven crystallizations, the greater part of the 2,6-diacetoxyphenanthrene was obtained from the top, or "less soluble," fractions (23 g.). The compound has been described above. The tendency to form needles when slightly impure was again noted.

2,7-Diacetoxyphenanthrene (m. p. 181.5°) made its initial appearance in the very first mother liquor. The solution, which contained about one-fifth of the total product, was dark brown and contained ethyl acetate. On long standing it deposited hard crystalline clusters melting at about 120–140°. Once obtained in this condition, the diacetate was easily purified by crystallization from alcohol, for it now appears to be distinctly less soluble than either of the other isomers present. It forms small, thin plates when completely pure and when the solution cools slowly, though needle-like crystals were often obtained on rapidly cooling a solution.

The intermediate fractions, after the removal of small additional quantities of the 2,6-isomer, deposited a few of the hard clusters of the impure 2,7-diacetate, and the third isomer then made its appearance. 2,8-Diacetoxyphenanthrene first crystallized in the form of round clusters of needles radiating from a common base. The material had the appearance of a pure compound and melted fairly sharply at 117–118°, but after several crystallizations from alcohol and from benzene–ligroin, a constant melting point of 125° was found. The compound forms long slender needles from either solvent.

The amounts of the pure isomers which could be collected at a time were usually not over 0.1–0.2 g., and when the returns fell below this limit the solvent was changed. Before using benzene–ligroin, however, it seemed expedient to distil the collected material at a diminished pressure in order to remove moisture and some coloring matter. The glass-like product so obtained was caused to crystallize only by the use of alcohol, but it could then be crystallized from benzene–ligroin. From this solvent-pair, the 2,7-isomer separated first, followed by the 2,8-diacetate, while none of the 2,6-derivative could be collected.

The separation was discontinued when the following quantities of the pure isomers had been obtained: 2,6-diacetoxyphenanthrene, 25.6 g.; 2,7-diacetoxyphenanthrene, 1.0 g.; 2,8-diacetoxyphenanthrene, 0.5 g.

The 2,6-diacetoxyphenanthrene thus obtained was carefully compared with the product resulting from the sulfonation of phenanthrene-3-sulfonic acid, and the two substances, as well as their hydrolysis products and the dimethyl ethers, were found to be identical.

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[14] The presence of this last isomer was overlooked in earlier experiments carried out on a smaller scale.

Diacetoxyphenanthrenes.—Since each of the five isomers has been described in the foregoing passages, it is sufficient to record here the analyses.

TABLE II

DIACETOXYPHENANTHRENES, $C_{18}H_{14}O_4$

Positions of substituents	M. p., °C.	Appearance	Analyses, % C, calcd.: 73.45	Analyses, % H, calcd.: 4.79
2,6	122–123	Plates	73.18	4.86
2,7	181.5 (183.5 corr.)	Plates	73.65	4.95
2,8	125	Needles	73.66	4.80
3,6	124.5	Blades	73.35	4.84
3,8	184 (186 corr.)	Needles	73.42	4.81

Dihydroxyphenanthrenes.—The diacetates were hydrolyzed by warming a suspension of the material in alcoholic sodium hydroxide solution. When the dissolution was complete, the solution was diluted with water and slowly acidified at the boiling point. The product then separated in a crystalline condition.

TABLE III

DIHYDROXYPHENANTHRENES, $C_{14}H_{10}O_2$

Positions of substituents	M. p., °C.	Appearance	Analyses, % C. calcd.: 79.98	Analyses, % H, calcd.: 4.80
2,6	234 (239, corr.)	Plates	79.82	4.91
2,7	258 (265, corr.)	Needles	79.65	4.90
2,8	202 (205, corr.)	Small needles	...	...
3,6	221 (225, corr.)	Large gray plates	79.69	4.77
3,8	247 (253, corr.)	Pink needles	80.06	4.88

The dihydroxyphenanthrenes are only sparingly soluble in toluene; they dissolve very readily in alcohol and they are moderately soluble in boiling water. They are conveniently crystallized from dilute alcohol or from a xylene–toluene mixture. No means was found for separating a mixture of isomers. The compounds may be distilled without loss if precautions are taken to avoid much contact of the molten material with the air. The specimens were colorless except as noted; attempts to remove the color in the cases of the last two compounds in the table were without avail. The dihydroxyphenanthrenes all form orange or yellow solutions in concentrated sulfuric acid. The alkaline solution exhibited a blue fluorescence with the 2,8-, the 3,6- and the 3,8-isomers, and all of the alkaline solutions slowly darkened on exposure to the air. Though it is theoretically possible to formulate quinones derivable from three of the compounds, none of the five isomers possesses the properties of a hydroquinone. 2,7-Dihydroxyphenanthrene, for example, might be expected to yield 2,7-phenanthrenequinone; but it is not attacked by silver oxide even in a boiling nitrobenzene solution. The other isomers are equally indifferent.

Dimethoxyphenanthrenes.—The ethers were prepared by methylation with dimethyl sulfate in alkaline solution. Their properties are all quite similar: they are very readily soluble in alcohol or benzene, and they form excellent, long, colorless needles on crystallization from methyl alcohol. In the case of the 2,6-isomer it is necessary to induce crystallization, best by seeding, for otherwise a sponge of amorphous material separates from the supersaturated solution. A mixture of benzene and ligroin is a less suitable solvent; with the 3,8-derivative, compact clusters of ill-formed crystals resulted. It is possible to effect a separation of mixtures of the isomeric ethers by fractional crystallization.

TABLE IV

DIMETHOXYPHENANTHRENES, $C_{16}H_{14}O_2$

Positions of substituents	M. p., °C.	Appearance	Analyses, % C, calcd.: 80.64	Analyses, % H, calcd.: 5.92
2,6	87	Needles	80.41	5.89
2,7	167–168	Needles	80.43	6.10
3,6	105	Needles	80.52	5.77
3,8	117	Needles	80.75	6.14

Diacetoxyphenanthrenequinones.—The conditions found most suitable for carrying out the oxidation of the diacetoxyphenanthrenes were as follows: 1 g. of the diacetate was dissolved in 8–10 cc. of glacial acetic acid and, while controlling the temperature to 60°, a solution of 1.1 g. of chromic acid in the minimum quantity of water, and diluted with glacial acetic acid, was added. A red solution resulted and in most cases it deposited the quinone, on cooling, in a crystalline condition. With the 2,7-isomer it was necessary to use more glacial acetic acid (19 cc.) in order to keep the diacetate in solution. The 2,8-isomer did not crystallize from the glacial acetic acid solution, and the addition of water caused the precipitation of an oil. When this was triturated with alcohol, a clean, solid product was obtained. With the other compounds it was only necessary to collect the crystalline material and to wash it thoroughly with alcohol, water, and again with alcohol, in order to obtain a good product. The yield, in the case of the 2,6-, 2,7- and 3,6-derivatives, was 0.5–0.7 g. of crystallized product, while the yield of the 2,8-isomer was much poorer. 3,8-Diacetoxyphenanthrenequinone was produced

TABLE V

DIACETOXY-9,10-PHENANTHRENEQUINONES, $C_{18}H_{12}O_6$

Positions of substituents	M. p., °C.	Appearance	Analyses, % C, calcd.: 66.65	Analyses, % H, calcd.: 3.73
2,6	216–217 (220–221 corr.)	Golden-yellow plates	66.42	3.80
2,7	238 (244 corr.)	Long slender orange needles	66.35	3.80
2,8	219–220 (223–224 corr.)	Orange plates	66.75	3.81
3,6	217 (232 corr.)	Fine yellow needles	66.39	4.01
3,8	217–218 (221–222 corr.)	Flat orange-yellow needles	66.43	3.82

in quantitative yield, which was a fortunate circumstance in view of the small amount of material available.

The isomers differ considerably in appearance and in their solubility relationships. The 2,6-derivative is moderately soluble in alcohol and crystallizes well from this solvent. With the 2,7- and the 3,6-derivatives, the solubility in alcohol is slight and the best solvent for the crystallization is glacial acetic acid. 2,8-Diacetoxyphenanthrenequinone dissolves readily in benzene and crystallizes well from a benzene–ligroin mixture. The 3,8-isomer gives a paste of poor crystals from glacial acetic acid but forms excellent crystals from alcohol or benzene. With all of the compounds several crystallizations are usually necessary before a pure product is obtained. Since the color reactions of these quinones are reactions characteristic of their hydrolysis products, they will be described below.

Dihydroxyphenanthrenequinones.—The diacetoxyphenanthrenequinones were hydrolyzed with alcoholic sodium hydroxide solution. The reaction proceeds in the cold, with the formation of an intensely colored solution, and a sodium salt soon begins to precipitate. The mixture is diluted with water and heated until all of the material passes into solution, and the filtered solution is acidified. The product often separates in a highly dispersed condition, but it becomes more easily filterable on digestion at the boiling point. A very good product was obtained in each case. Only two of the isomers were available in quantity sufficient for analysis.

2,6-Dihydroxyphenanthrenequinone.—While no solvent suitable for the crystallization of this material was found, the reprecipitated material gave satisfactory analytical figures. It was obtained as a reddish-brown powder, readily soluble in glacial acetic acid or alcohol, very sparingly soluble in xylene and rather hygroscopic. It is easily acetylated by acetic anhydride in conjunction with either pyridine or concentrated sulfuric acid.

Anal. Calcd. for $C_{14}H_8O_4$: C, 69.99; H, 3.36. Found: C, 69.88; H, 3.56.

3,6-Dihydroxyphenanthrenequinone.—As precipitated from an alkaline solution, the material formed a light orange powder. It is very sparingly soluble in water, alcohol or glacial acetic acid, and only moderately soluble in nitrobenzene. Crystallization from the latter solvent gave orange-red micro-needles.

Anal. Calcd. for $C_{14}H_8O_4$: C, 69.99; H, 3.36. Found: C, 69.81; H, 3.81.

An account of the color reactions of the five dihydroxyphenanthrenequinones is given in Table VI, while Table VII summarizes a series of

TABLE VI

COLOR REACTIONS OF THE DIHYDROXYPHENANTHRENEQUINONES

Positions of substituents	Color	Color of the solution in			
		H_2SO_4	0.1 *N* NaOH	6 *N* NaOH	Pyridine
2,6	Brown-red	Yellow-green	Red	Intense red	Orange
2,7	Dull red	Brown	Green	Yellow	Red
2,8	Dull red	Green	Intense purple	Purple	Red
3,6	Orange	Red	Red	Red	Orange-yellow
3,8	Red	Pale purple	Light red	Light red	Yellow

tests in which the action on the quinones of acetic anhydride and of boro-acetic anhydride is compared. The latter reagent consisted of a solution of 0.5 g. of pyroboro-acetate[10] in 10 cc. of acetic anhydride. In those cases in which the color of the solution changes on warming, the color of the solution at about 25° and at about 60° has been noted.

TABLE VII

THE ACTION OF BORO-ACETIC ANHYDRIDE ON HYDROXYPHENANTHRENEQUINONES

Positions of substituents	Color of the solutions (25 to 60°) in Acetic anhydride	Boro-acetic anhydride
1	Yellow	Red
1,2	Red to orange	Green to red
3,4	Pale orange	Red to purple[15]
2,5	Pale red to orange	Pale red to orange
2,6	Yellow	Yellow
2,7	Yellow	Yellow
2,8	Pink to orange-yellow	Chrome-green to purple
3,6	Yellow	Yellow
3,8	Yellow	Red
1,2,4	Faint purple to yellow	Green to red
1,3,4	Red to yellow	Red[16]

Comparison of ε-Diacetoxyphenanthrenequinone with 2,7-Diacetoxyphenanthrenequinone.—Since the ε-quinone, which, for convenience, has been called 2,7-diacetoxyphenanthrenequinone in the above passages. corresponded closely in properties with the substance known to have this structure,[3] a direct comparison was desirable. This was greatly facilitated by Professor Brass, who kindly supplied a sample of the material, in an impure condition. After repeated crystallization from glacial acetic acid, the substance formed brown-red lumps of indefinite shape and the melting point was raised to 234°. The sample obtained in the present work had an entirely different appearance (long, orange needles) and melted at 238°, but mixtures of the two specimens always melted between these two temperatures. After assuring myself that other diacetoxyphenanthrenequinones which melt at about the same temperature exhibit a very decided depression when mixed with each other, I became convinced that the two specimens were identical, but that the material prepared from the diacetoxyphenanthrene was purer than that previously obtained. This conclusion was supported by the results of comparative color tests with the dihydroxyphenanthrenequinones obtained by hydrolyzing the two diacetates. The new compound, as precipitated from an alcoholic alkaline solution, has a dull blue color under certain lighting conditions, but the true color, clearly seen on rubbing the material on a glass slide, is dull red. The microscope revealed a mass of well-formed needles. The compound of known structure, which may be called the Anschütz compound, after the discoverer, was also dull red when rubbed on glass but the crystalline structure was not well developed. The most characteristic color reaction of the Anschütz compound, as described by Werner,[3c] is that the yellow-green solution in very dilute alkali becomes yellow on adding more concentrated alkali. Table VI shows that the present compound likewise gives this test. The only difference observed in a direct comparison was that the solutions of the Anschütz compound were less bright than the others, and this was true of the solutions in concentrated sulfuric

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[15] Dark red crystals separated on gently heating; the solution became brown and then intensely green on boiling.

[16] Dark red crystals were deposited.

acid and in pyridine. All of these observations indicate the identity of the two compounds and show that the method of preparation here described yields a better product than has yet been obtained by the older method of hydrolyzing the tetrazonium salt of 2,7-diaminophenanthrenequinone.

Proof of the Structure of the α-(3,6)-Dihydroxyphenanthrene

3,6-Dimethoxyphenanthrenequinone.—Thirty-two grams of 3,6-diacetoxyphenanthrene was hydrolyzed with alcoholic sodium hydroxide solution and the product was methylated with dimethyl sulfate in alkaline solution. The ether was purified by distillation at a pressure of 3 mm., when it melted at 102°; yield, 25 g. (96%). This material was dissolved in 170 cc. of glacial acetic acid, the solution was cooled to 60° and a solution of 27 g. of chromic acid was slowly added while the temperature was kept below 70° by cooling in an ice-bath. In the early stages of the reaction a tarry brown precipitate formed, but this soon dissolved and crystals of the quinone were deposited from a dark red solution. On completion of the reaction the solution was well cooled and the product was collected and washed with alcohol. A single crystallization from glacial acetic acid gave a pure product; yield, 16.2 g. (60%).

The quinone is sparingly soluble in alcohol and only moderately soluble in glacial acetic acid. It crystallizes well from the latter solvent, forming yellow needles melting at 235° (241° corr.).

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.62; H, 4.51. Found: C, 71.36; H, 4.46.

Oxidation of 3,6-Dimethoxyphenanthrenequinone.—A solution of 9 g. of this quinone in 450 cc. of glacial acetic acid was prepared and cooled to 90°. Six cc. of 30% hydrogen peroxide solution was then added and the solution was allowed to stand at 60–90° for two hours. Part of the quinone had crystallized at the end of this time; this was dissolved and the solution was again treated with 6 cc. of hydrogen peroxide solution. While the quinone did not again separate, it was found advisable to repeat this process after a further two hours and then to allow the solution to stand in a warm place overnight. The greater part of the acetic acid was then removed from the pale brown solution by distillation and water was added. This caused the separation of a dark brown oil, but this partially dissolved and partly solidified on adding an excess of alkali. After prolonged boiling the solid was all brought into solution, but the solution had such a dark brown color that it was treated with a little hydrogen peroxide and warmed until it become pale yellow.[17] The yellow product which precipitated on acidifying the solution, and after very thorough cooling, was triturated with a cold, dilute sodium carbonate solution until no more material dissolved. The residue was only slightly colored, and it was found to consist of the lactone described below in nearly pure form; yield, 0.9 g.; m. p. 190°. From the carbonate solution there was obtained 3.6 g. of 5,5′-dimethoxydiphenic acid, which was somewhat yellow, but fairly pure.

5,5′-Dimethoxydiphenic Acid (V).—Like the parent acid, this substance has a pronounced tendency to form supersaturated solutions. It dissolves very readily in alcohol or glacial acetic acid, moderately in water and is practically insoluble in benzene. The crude material was crystallized several times from dilute alcohol and then from methyl alcohol, when it was obtained in the form of colorless needles melting at 229° (234° corr.).

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.56; H, 4.67. Found: C, 63.27; H, 4.69.

1,6-Dimethoxyfluorenone-4-carboxylic Acid.—The dimethoxydiphenic acid forms a brown solution in concentrated sulfuric acid which rapidly becomes deep red on warming. Such a solution was warmed at about 50° for one-half hour and then poured into

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[17] The results were the same when this treatment was omitted, or when the crude oil was first treated with carbonate solution.

water. This caused the separation of a finely divided yellow substance. The compound is only moderately soluble in glacial acetic acid, but it forms good, small, bright yellow crystals if the solution is cooled rapidly or seeded; otherwise an amorphous product slowly separates from a highly supersaturated solution. The compound decomposes alkali carbonates; it melts at 295° (303° corr.) and gives off carbon dioxide at that temperature.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.59; H, 4.26. Found: C, 67.32; H, 4.28.

For further characterization the fluorenonecarboxylic acid was converted into *the amide*, as follows: 1.2 g. of the acid was heated with 1 g. of phosphorus pentachloride at 130° until most of the phosphorus oxychloride had been removed. The crude acid chloride was dissolved in benzene, the solution was filtered from a small amount of the unchanged acid, and treated with dry ammonia. A heavy precipitate of the amide soon separated. This was triturated with dilute ammonia solution and crystallized from glacial acetic acid. Rapid cooling was again necessary for the production of good crystals as small, yellow needles, 0.6 g.; m. p. 261° (268° corr.).

Anal. Calcd. for $C_{16}H_{13}O_4N$: C, 67.83; H, 4.63. Found: C, 67.66; H, 4.97.

The Synthesis of 5,5′-Dimethoxydiphenic Acid.—4-Methoxy-2-aminobenzoic acid was prepared according to the excellent directions of Ullmann and Dootson,[18] starting with *p*-toluidine, and the diazonium salt was reduced with an ammoniacal solution of cuprous hydroxide according to the general method of Vorländer and Meyer.[19] A cuprous hydroxide solution was prepared by adding a solution of 2.7 g. of hydroxylamine hydrochloride and 6.5 cc. of 6 *N* sodium hydroxide to a solution of 6.3 g. of copper sulfate and 7.5 cc. of concentrated ammonia water in 30 cc. of water. A suspension of 1.7 g. of 4-methoxy-2-aminobenzoic acid in 1.8 cc. of glacial acetic acid and 4 cc. of water was diazotized with a solution of 0.7 g. of sodium nitrite. The amine dissolved slowly on shaking the mixture, but a small amount of the azo compound was produced. The filtered solution of the diazotized amine was added in small portions to the well-cooled cuprous hydroxide solution, each portion producing a green foam which soon dissolved. The dark yellow-green solution became pale yellow on warming to the boiling point, when it was made acid to Congo Red paper and cooled well. The product, which contained much copper salt, was digested with sodium carbonate solution and the crude dimethoxydiphenic acid was recovered on acidifying the filtered solution.

The product was quite yellow, melted at about 190° and was only obtained in a pure condition after numerous crystallizations from methyl alcohol. It then formed colorless needles melting at 228°.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.56; H, 4.67. Found: C, 63.70; H, 4.63.

Mixtures of this acid with the acid, m. p. 229°, obtained from 3,6-dimethoxyphenanthrenequinone showed no depression in the melting point. The identity of the two substances was further confirmed by the conversion of the synthetic acid into 1,6-dimethoxyfluoreneone-4-carboxylic acid, which was found to melt at 295° and to be identical with the material already described.

Lactone of 1-Hydroxy-4,4′-dimethoxydiphenyl-1′-carboxylic Acid (VII).—The carbonate-insoluble product resulting from the oxidation of 3,6-dimethoxyphenanthrenequinone was easily purified by crystallization from alcohol, in which it is moderately soluble, and from which it separates in the form of long, colorless needles melting at 191° (194° corr.).

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.29; H, 4.72. Found: C, 70.21, 70.12; H, 4.67, 4.56.

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[18] Ullmann and Dootson, *Ber.*, **51**, 19 (1918).

[19] Vorländer and Meyer, *Ann.*, **320**, 122 (1902).

The substance may be distilled without decomposition. The crystalline material dissolves only very slowly on boiling with alkali, though the resulting salt is very readily soluble in water. On acidifying the solution, even at a low temperature, the lactone and not the free acid results.

Since it is conceivable that the lactone is formed not from the dimethoxyquinone but from the dimethoxydiphenic acid, the latter compound was subjected to the action of hydrogen peroxide in glacial acetic acid solution; in no case was a trace of the lactone obtained, and the greater part of the dimethoxydiphenic acid could be recovered after the prolonged action of a large excess of hydrogen peroxide.

1,4,4′-Trimethoxydiphenyl-1′-carboxylic Acid (VIII).—This was produced by shaking an alkaline solution of the above lactone with dimethyl sulfate until a precipitate began to separate from the alkaline solution. The solution, which was kept strongly alkaline, was then boiled until traces of the ester were hydrolyzed and then acidified. An oily product separated and soon solidified. This was precipitated from a carbonate solution and then crystallized from alcohol and from benzene–ligroin. It formed small, colorless prisms melting at 147–148°.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.65; H, 5.60. Found: C, 66.57; H, 5.42.

1,4,6-Trimethoxyfluorenone (IX).—The above acid dissolved in cold concentrated sulfuric acid to give an intensely crimson solution. After ten minutes the solution was poured into water, when an orange oil resulted. This soon changed to a yellow solid. It was washed with dilute alkali and crystallized from alcohol. It dissolves readily in this solvent and separates in the form of light clusters of small yellow needles melting at 157°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22. Found: C, 70.97; H, 4.85.

Summary

In order to gain an idea of the composition of the mixture of disulfonates which is produced by the action of sulfuric acid on phenanthrene, two of the pure monosulfonic acids were sulfonated and the products were at least partly identified by separating the mixtures of diacetoxyphenanthrenes which were obtained as the result of alkali fusion and acetylation. Derivatives of five new dihydroxyphenanthrenes were thus obtained, and it was possible to determine the structures of all of these compounds. From the results of this study, it was concluded that, when either the 2- or the 3-sulfonic acid derivative of phenanthrene is sulfonated, the second substituent enters the unsubstituted, terminal nucleus in the 6-, the 7- and the 8-positions.

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