catalyst. These and other facts have been considered in their bearing upon the hypotheses which have been previously advanced to account for the variation in the ratio of competing reactions over various catalysts.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE SULFONATION OF PHENANTHRENE.
I. A NEW MONOSULFONATE

BY LOUIS FREDERICK FIESER

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After a series of careful investigations, the results of which were published in 1902, Werner and his students[1] were able to show that three phenanthrene sulfonic acids may be obtained by the action of concentrated or fuming sulfuric acid on the hydrocarbon. Various methods of separating these isomers were elaborated and the compounds were all carefully identified and characterized. The yields, however, were poor, and the separation was a tedious process. In preparing large quantities of two of the acids according to Werner's methods, it has been found possible to introduce some improvements which render these substances more readily accessible and which also serve to cast further light on the course of the reaction.

Werner records that the best yields of the 2-acid (12%) and the 3-acid (18.6%) were obtained on heating phenanthrene with two molecular equivalents of concentrated sulfuric acid at a temperature of 120–130° for four and one-half to five hours. It was assumed that the greater part of the hydrocarbon was converted into disulfonic acids, and this conclusion has been confirmed by Sandqvist,[2] who found that disulfonic acids accompany the monosulfonic acids even when phenanthrene is sulfonated incompletely at room temperature. At a temperature of 100° or below, a third isomer, phenanthrene-9-sulfonic acid, which was not detected in the reactions carried out at 120–130°, is produced.

Before attempting to extend these observations, it seemed almost necessary to find some new method for the identification and the determination of the purity of the isomeric acids. Reactions such as the alkali fusion, or the preparation of the ester or the chloride, all require a fairly large sample of the dry salt, and they are all rather slow. A much more suitable derivative was found in the *p*-toluidine salt. With this amine, the phenanthrene sulfonic acids all form crystalline salts whose melting points are characteristic and fairly well separated. One can quickly

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[1] Werner, Frey, J. Kunz, M. Kunz, Löwenstein, Rekner and Wack, *Ann.*, **321**, 248 (1902).

[2] Sandqvist, "Studien über die Phenanthrensulfosäuren," Inaugural Dissertation, Upsala, **1912**.

identify a few milligrams of an acid or of any of its metal salts, whether it is in the solid form or in solution, by this method.

In working up the reaction mixture, Werner first neutralized the acid solution with barium carbonate and thus had the tedious task of extracting the rather sparingly soluble salt of the 3-acid, and the very slightly soluble salt of the 2-acid, with water and with dilute sulfuric acid, respectively. It was found much more convenient to prepare first a sodium salt mixture and to treat a solution of this with only enough barium chloride to cause the precipitation of the barium 2-salt. When the reaction mixture was stirred mechanically and the sulfonation conducted at 120° for four hours, the yields of the 2-acid and the 3-acid were 18 and 27%, respectively. When the reaction was stopped after three hours, the amounts of the two acids corresponded to 25 and 27%, respectively, of the theoretical quantity. That the observed yield of the 3-acid did not show an increase proportional to that for the isomer is due probably to the difficulty in separating all of the 3-acid from the disulfonates. The yield of the 2-acid, on the other hand, is easily determined. That the amount of this isomer which is produced decreases with the length of the reaction period doubtless is due to the conversion of the acid into disulfonic acids, as will be shown in the following paper.

The modified method of separation was also applied to the mixtures which result from the low-temperature sulfonation, and which are known to contain the 2-acid, the 3-acid and the 9-acid. Thus Werner[3] obtained these acids in 7, 9 and 6% yield, respectively, by sulfonating at 100° for eight hours, while Sandqvist raised the yield of the 9-acid to 7–14.5% by carrying out the reaction at 20° over a period of fifteen to twenty days.[2,4] In the present work the sulfonation was conducted at 60° for three days and the mixture was stirred mechanically for about half of the time. The 2-acid was easily removed in the form of the barium salt, and a considerable quantity of the 3-acid separated as the least soluble fraction on crystallizing the remaining product in the form of the potassium salt. The further working of the mixture involved many difficulties, most of which have been recognized by the earlier investigators. The mixture, however, is even more complex than these workers have realized, for it contains not only the 3-acid and the 9-acid, but traces of the 2-acid and an appreciable amount of a new isomer, phenanthrene-1-sulfonic acid. The presence of the 1-acid was only established in the present work through a fortunate circumstance. A sulfonate residue, which had yielded no pure products after several crystallizations, was fused with alkali in the hope that the phenanthrol mixture, particularly if it contained

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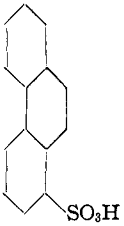
[3] Werner, ref. 1; see also J. Kunz, "Ueber einige Derivate des Phenanthrens," Inaugural Dissertation, Zürich, **1902**, p. 35.

[4] Sandqvist, *Ann.*, **392**, 76 (1912).

any dihydroxyphenanthrenes, might be separable. While this was not the case, it was found that the acetate mixture obtained on acetylation easily yielded pure 1-acetoxyphenanthrene on crystallization. It was then found possible to isolate the 1-acid from a similar sulfonate mixture, but the process is extremely tedious. The solubilities of the salts of the 1-acid, the 3-acid and the 9-acid all appear to be about the same, and the solutions have a pronounced tendency to remain supersaturated.[5] By carrying out a great many crystallizations of the potassium and ferrous salts, and by identifying the various fractions by means of the melting points of the *p*-toluidine salts, a part, at least, of the sulfonate mixture was separated into the pure components, the yields being as follows: 2-acid, 18%; 3-acid, 18%; 9-acid, 13%; 1-acid, 8%.

The sulfonation of phenanthrene at a low temperature thus gives a mixture of four of the five possible monosulfonic acids. Two of these acids, the 9-acid and the 1-acid, have not been found in mixtures obtained at 120–130°. Experiments with the former acid, as well as with the 2-acid and the 3-acid, failed to reveal any rearrangement on heating with sulfuric acid but indicated that the substances are all sulfonated further with great ease. Thus it is probable that the absence of two of the acids from the products obtained at the higher temperature is due simply to the disulfonation of these substances. The sulfonation of phenanthrene leads to the same number of isomers as the nitration, but neither the relative yields nor the positions of the substituents are the same; nitration, according to Schmidt and Heinle,[6] yields 9-nitrophenanthrene as the chief product, together with smaller quantities of the 2-nitro and 4-nitro and a very small amount of the 3-nitro derivatives.

Phenanthrene-1-sulfonic acid, I, was characterized by the preparation of the potassium and *p*-toluidine salts, the methyl ester and the corresponding quinone, II. The structure was established by conversion into 1-phenanthrol, III, which, unknown at the time of these experiments, has been synthesized recently by Shoesmith and Guthrie.[7] The properties agreed with the description given by these authors, while the methyl ether



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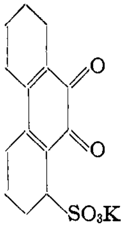

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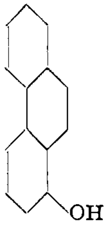

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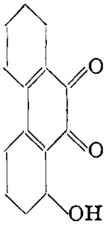

IV

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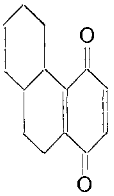
[5] Compare Sandqvist, ref. 2, p. 36.

[6] Schmidt and Heinle, *Ber.*, **44**, 1488 (1911).

[7] Shoesmith and Guthrie, *J. Chem. Soc.*, 2332 (1928).

and its picrate melted at the temperatures given by Pschorr, Wolfes and Buckow[8] for the synthetically prepared 1-methoxyphenanthrene and its picrate. From the acetate, which was oxidized and hydrolyzed, there was obtained 1-hydroxyphenanthrenequinone, IV, which is the last of the four possible compounds of this type to be described.

Another compound obtainable from 1-phenanthrol, and one which is of particular interest in connection with the problem outlined in the first paper of this series,[9] is 1,4-phenanthrenequinone, V. This was prepared in good yield by coupling 1-phenanthrol with diazotized sulfanilic acid, reducing the azo dye and oxidizing the 4-amino-1-phenanthrol. On reductive acetylation to VI, followed by oxidation, the diacetyl derivative of 1,4-dihydroxy-9,10-phenanthrenequinone (VII) was obtained. This compound has been described by Brass and Stadler,[10] who adequately established the positions of the substituent groups, and the author is greatly indebted to Professor Brass for supplying him with a sample of the product. The substance was found to be identical with the material here described. The structure of the new isophenanthrenequinone, V, is thus definitely fixed, and it is also clear that both 1-phenanthrol and 3-phenanthrol[9] couple in the 4-position and behave, in this respect, like naphthols. With the isolation of V, all of the four possible homonuclear phenanthrenequinones are known.



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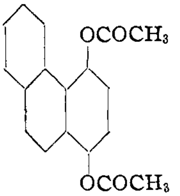
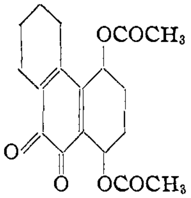


VI



VII

Experimental Part

p-Toluidine Salts of the Phenanthrene Sulfonic Acids.—In order to prepare such a salt the aqueous solution of the free acid, or of the sodium, potassium or ferrous salt, is treated with an excess of p-toluidine and hydrochloric acid, enough water is added to bring all of the material into solution at the boiling point and crystallization is allowed to take place. A barium salt should be boiled with dilute sulfuric acid, a little animal charcoal added and the filtered solution treated with p-toluidine. If the amine salt separates in an oily condition, the walls of the containing vessel should be thoroughly scratched, for these salts, particularly that of the 3-acid, may remain as oils for a short time even when nearly pure.

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[8] Pschorr, Wolfes and Buckow, *Ber.*, **33**, 170 (1900).

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

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

On the other hand, a fairly impure acid, or a mixture of pure isomers, gives a *p*-toluidine salt which remains as an oil almost indefinitely. This property characterizes a mixture of isomers nearly as definitely as the depression in the melting point, though this is large. In determining the melting point of one of the salts, the sample may be dried by pressing the material on a filter paper, but the capillary should not be placed in the melting-point bath when the temperature is greater than 130°, for, if the heating is commenced at a higher temperature, the material melts 20–30° below the true melting point. When the material is thoroughly dried in a vacuum at 100°, this behavior is not noted. The salts all sinter at temperatures slightly below the melting points. They are all moderately soluble in hot water, sparingly soluble in cold water and very readily soluble in alcohol.

TABLE I

p-TOLUIDINE SALTS, $C_{21}H_{19}O_3NS$

Salt of phenanthrene-( )-sulfonic acid	Melting point, °C.	Appearance	Analyses, % C (calcd., 69.01)	Analyses, % H (calcd., 5.24)
-1-	260 (267 corr.)	Needles	68.75	5.47
-2-	282 (291 corr.)	Flat needles or plates	68.82	5.17
-3-	217 (222 corr.)	Thick needles	68.85	5.47
-9-	229 (235 corr.)	Small needles	68.68	5.47

Sulfonation at 120–125° for Four Hours.—Three hundred and twenty-seven cc. of concentrated sulfuric acid was added to 500 g. of pure phenanthrene[11] in a 2-liter flask and the mixture was heated in an oil-bath and stirred by hand until it became sufficiently liquid to permit mechanical stirring. The temperature of the reaction mixture soon reached 120° and a temperature of 120–125° was maintained for just four hours. The reaction is exothermic, even after the disappearance of all of the phenanthrene, and the bath must be kept at a temperature about 4° below that of the mixture. The product first became green and some sulfur dioxide was formed; a dark brown sirup finally resulted. After heating and stirring for the time specified, this solution, while still hot, was dissolved in 3.5–4 liters of water and a concentrated solution of 400 g. of sodium hydroxide was added. After thorough cooling in an ice-bath, the precipitated sodium salt was collected on a large funnel, pressed well and washed well with a half-saturated sodium chloride solution. The filtrate contains a mixture of disulfonates.

The crude mixture of sodium salts was dissolved in 6–7 liters of water, to which there was added enough hydrochloric acid to render the solution slightly acid,[12] and a solution of 100 g. of barium chloride dihydrate was added to the boiling solution. After digestion of the fine precipitate of barium phenanthrene-2-sulfonate for a short time, the mixture was brought onto the funnel while at the boiling point. The filtrate, from which some material crystallized at once, was set aside to cool. The precipitated barium salt was digested at the boiling point with 6–7 liters of water and again collected. The filtered wash water contained, as shown by the melting point of a sample of the *p*-toluidine salt, only barium phenanthrene-3-sulfonate, which crystallized out after concentration of the solution. The main barium salt precipitate still contained a small amount of the 3-

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[11] From the Gesellschaft für Teerverwertung, Duisberg-Meiderich.

[12] The solubility of the sulfonates is increased by the presence of a mineral acid but phenanthrene itself dissolves in a too strongly acidic solution.

salt, but the latter was removed, along with a little of the 2-salt, by a further boiling with 6–7 liters of water. This left the barium salt of the 2-acid in an essentially pure condition. The salts remaining in the last wash water were recovered by concentrating the solution, and they were separated by converting the barium salt mixture into a mixture of the potassium salts, dissolving this in boiling water, and adding 2 g. of barium chloride dihydrate. The precipitated salt, after washing with hot water, was the pure barium 2-sulfonate (2 g.), while the mother liquor yielded 9 g. of the 3-sulfonate.

The first filtrate from the precipitation of the main portion of the barium 2-sulfonate deposited crystals of the pure barium 3-sulfonate on cooling. The mother liquor was concentrated to a fairly small volume and saturated sodium chloride solution was added. The precipitated sodium salt was found to consist chiefly of the 3-sulfonate, and it was easily purified, after conversion into the potassium salt, by crystallization (76 g.). The mother liquor remaining from the salting-out with sodium chloride contained an appreciable amount of the 3-sulfonate, mixed probably with disulfonates, but its recovery is not easily accomplished. On boiling down the solution to a volume of 1 liter, a crystalline paste was obtained, and this was converted into the potassium salt and crystallized several times. It finally yielded 31 g. of the pure 3-sulfonate.

The total yield of barium phenanthrene-2-sulfonate was 175 g., while 146 g. of the barium salt and 107 g. of the potassium salt of phenanthrene-3-sulfonic acid were obtained. Determinations of the melting points of the *p*-toluidine salts showed that the products were free from all but traces of isomers, and the salts of the 3-acid, having been crystallized, were free from much inorganic material. The barium salt of the 2-acid contained only a small amount of barium sulfate, and from the results of alkali fusions it was judged that the material was 95% pure. On this basis the yields were: 2-acid, 18%; 3-acid, 27%.

Sulfonation at 120–125° for Shorter Periods of Time.—When the sulfonation was carried out in the manner described above, with the exception that the reaction was stopped after two and one-half hours, a small amount of phenanthrene was unsulfonated. Only traces of phenanthrene remained when the reaction proceeded for three hours, and the yields were practically the same as for the shorter period. It is thus considered that *the conditions most suitable for the preparation of the 2-acid and the 3-acid are: sulfonation for three hours with two molecular equivalents of concentrated acid at 120–125°.*

Owing to the increase in the yields when operating under the conditions specified, the washing of the precipitate of barium phenanthrene-2-sulfonate is not easily accomplished when working on a large scale and a slight modification of the above procedure is advisable. Instead of precipitating the barium salt from a solution of the crude sodium salt, the sodium salt was dissolved in water containing 50 cc. of concentrated hydrochloric acid (to aid in the dissolution of the salt) and the filtered solution was then neutralized with sodium hydroxide and allowed to crystallize. The crystals, consisting largely of the salt of the 2-acid, were dissolved in about 8 liters of water, 100 g. of barium chloride dihydrate was added, and the precipitate was collected and then digested with 6–7 liter portions of boiling water until the residual salt was found to be free from the isomers. It was often found that a single washing was sufficient for this purpose. The washings were concentrated to a small volume, sulfuric acid was added to precipitate the barium and the filtered solution was treated with potassium hydroxide to bring down a potassium salt mixture, which was set aside. The mother liquor from the sodium salt crystallization was concentrated and the product converted into the potassium salt. This was combined with the other batch of potassium salt and crystallized from water, giving a large quantity of the pure potassium 3-salt. The mother liquor, containing more of this salt together with some of the 2-salt, was concentrated, and the product was salted out with potassium chloride and washed free of sulfate ion.

A solution of this material was then treated with 10 g. of barium chloride dihydrate, the precipitate of the barium 2-salt was washed free of isomers and the washings were discarded. From the mother liquor there was obtained an additional quantity of the potassium 3-salt. The yields were: barium phenanthrene-2-sulfonate, 232 g. (25%); potassium phenanthrene-3-sulfonate, 225 g. (27%).

The Preparation of the Phenanthrols.—Werner[1] prepared 2-phenanthrol from the potassium salt of the 2-acid. If it is desired to prepare this salt from the barium salt, it is highly advisable to use the salt in the moist and finely divided condition in which it is first obtained; but the reaction with sulfuric acid is slow at best, and one should employ several fresh portions of acid. Barium sulfate carried through the filter is easily removed with animal charcoal. It is not necessary, however, to follow this rather tedious procedure, for the barium salt, prepared as described above, may be fused without difficulty. Thus 150 g. of the finely powdered salt was stirred into a melt from 450 g. of potassium hydroxide at a temperature of 290–300° in the course of fifteen minutes; the temperature was then raised to 325° and held there for five minutes. The fusion was then complete and a brown, oily layer of the phenanthrolate appeared at the top of the melt. After some cooling, but before solidification, the mass was added in small portions to a mixture of 1 liter of concentrated hydrochloric acid and about 2 kg. of ice. After thorough stirring, the phenanthrol, which was mixed with some barium sulfate, was collected, dissolved in dilute alkali and reprecipitated. The material at first separates in a finely divided condition, but when it is digested at the boiling point the particles soon become more compact and the material may be collected and washed very easily. The crude product is most conveniently purified by distillation at a pressure of 3 mm. If the barium salt used is free from any isomers, the 2-phenanthrol so prepared is completely pure and melts at 168°. The average yield was 65 g. (72%), about 8–10% of the precipitated material having been lost in the distillation. Pure 2-phenanthrol may be obtained from a mixture containing the more soluble 3-phenanthrol by crystallization from benzene, but only with the loss of a considerable amount of material. 3-Phenanthrol may be prepared in a similar manner, or from the potassium salt, and purified as suggested by Smith,[13] by distillation *in vacuo.*

Sulfonation at 60°.—Four hundred grams of finely powdered phenanthrene was mixed with 160 cc. of concentrated sulfuric acid and the temperature was kept at 60°. The mixture, which was frequently stirred, soon became pasty and somewhat green, and some sulfur dioxide was formed. After twenty-four hours, 80 cc. of concentrated acid was added and the mixture was stirred mechanically throughout that, and the following, day. After the reaction had proceeded for a total of three days, a viscous, bluish-green, homogeneous sirup resulted; this was dissolved in water and the solution was treated with an excess of sodium hydroxide (400 g.). The product contained some phenanthrene, which was removed by boiling a solution of the salt with animal charcoal. The filtered solution was allowed to cool and the crystalline product was subjected to the usual process of separating out the pure barium salt of phenanthrene-2-sulfonic acid, using 40 g. of barium chloride dihydrate. All mother liquors and washings were then concentrated and the material converted into the potassium salt, which was precipitated several times with potassium chloride solution in order to remove all sulfates and disulfonates. After three crystallizations of this potassium salt, a considerable quantity (95 g.) of the pure potassium 3-salt was obtained. The mother liquors were then combined and the product was converted into a ferrous salt mixture by the action of ferrous sulfate and dilute sulfuric acid. On crystallizing this salt several times, excellent needles of the ferrous salt of the 9-acid finally resulted, and from this material 70 g. of pure potassium phenanthrene-9-sulfonate was obtained by the action of po-

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[13] Smith, *J. Chem. Soc.*, 109, 569 (1916).

tassium hydroxide. The material in the mother liquors was then converted into the potassium salt and this, after being freed from sulfates, was dissolved in water and treated with 5 g. of barium chloride dihydrate in order to precipitate a small quantity of the 2-acid still present.[14]

From this point on the separation of the combined product, which was collected in the form of the purified potassium salt, is extremely difficult and no systematic method of procedure can be specified. The mixture contains the 3-acid, the 9-acid and the 1-acid and, as stated in the introduction, the solubilities of the salts of these acids are all very nearly the same, and the separation is greatly complicated by the tendency to form supersaturated solutions. A systematic fractionation was undertaken at the outset, and potassium phenanthrene-1-sulfonate was first isolated from an intermediate fraction. The concentration of a preponderant quantity of this salt in a given fraction becomes apparent from the character of the *p*-toluidine salt which is obtained from it. The amine salt of this impure acid usually separates in the form of oily shreds which fail to solidify or else the solution sets to a gel. On further crystallization of the potassium salt a purification can be effected until excellent, large plates of the 1-salt are obtained, and the *p*-toluidine salt now has little tendency to remain in an oily or colloidal condition, but forms small, fine needles.

Little regularity was observed in the order in which the three potassium salts crystallize from the mixtures; the 3-salt may separate first, followed by the 1-salt, and then by more of the 3-salt. After dividing the material into six fractions, all solutions appeared to contain all three acids, with the exception of the "least soluble" fraction, which contained none of the 9-acid. It appears that the potassium 9-salt has somewhat less tendency to crystallize from the mixture than the other two, while the ferrous salt of the 9-acid tends to separate first. As a consequence, it is advisable to change occasionally to the ferrous salt and thus remove some of the 9-acid. The 1-acid and the 3-acid were isolated in pure condition only in portions of 0.5–2 g. at a time. This was done by carrying out numerous crystallizations, by carefully noting the appearance of the crystals separating, interrupting the process whenever a change or a pause in the crystallization was observed, and by identifying the products by means of their *p*-toluidine salts.

The separation finally effected was far from being complete; it was interrupted with 110 g. of the potassium salt mixture still on hand. The amounts of the salts isolated in pure condition were as follows: barium phenanthrene-2-sulfonate, 131 g. (18%); potassium phenanthrene-3-sulfonate, 127 g. (19%); potassium phenanthrene-9-sulfonate 86 g. (13%); potassium phenanthrene-1-sulfonate, 27 g. (4%).

The residual sulfonate mixture was partially identified as follows. It was subjected to alkali fusion and the phenanthrol mixture was distilled and then acetylated. After crystallizing this acetate mixture twice from alcohol, 20 g. of pure 1-acetoxyphenanthrene, m. p. 135–136°, was obtained, which brings the amount of phenanthrene-1-sulfonic acid which is known to have been produced in the sulfonation up to 8%.

Phenanthrene-1-sulfonic Acid

Metal Salts.—The potassium salt crystallizes from water in the form of large plates. The solubility in water is about the same as that of the 3-isomer. The salt is only sparingly soluble in alcohol, but dissolves readily in glacial acetic acid.

Anal. Calcd. for $C_{14}H_9O_3SK$: K, 13.19. Found: K, 13.22.

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[14] It may be noted that the salts of the 2-acid remain in solution up to this point even though they are much less soluble than the salts of the isomers. According to Sandqvist (ref. 2, p. 8), the ferrous 2-sulfonate is but one-fourth as soluble at 20° as the ferrous 9-sulfonate.

The barium salt dissolves with difficulty in boiling water, but it only crystallizes from the well-concentrated solution. The ferrous salt crystallizes in the form of needles; it appears to be slightly more soluble than ferrous phenanthrene-9-sulfonate.

Methyl Ester.—A suspension of the potassium salt in dimethyl sulfate was boiled gently until all of the salt dissolved, and then heated on the water-bath for one hour. The solution was poured into water, the mixture was boiled for a few minutes in order to decompose the dimethyl sulfate and well cooled. The product was purified by crystallization from methyl alcohol, in which it dissolves readily; it formed colorless plates melting at 102°.

Anal. Calcd. for $C_{15}H_{12}O_3S$: C, 66.15; H, 4.45. Found: C, 65.87; H, 4.47.

Potassium Phenanthrenequinone-1-sulfonic Acid.—Three grams of potassium phenanthrene-1-sulfonate was dissolved in 25 cc. of glacial acetic acid and a solution of 3 g. of chromic acid in water, diluted with glacial acetic acid, was added while the temperature was kept at 100° by cooling. The yellow quinone, which began to separate after a few minutes, was brought into solution and allowed to crystallize slowly. The product (1.7 g.) was washed with alcohol and purified by adding about one volume of alcohol to four volumes of an aqueous solution and allowing crystallization to take place very slowly. Under these conditions large, orange-yellow plates were formed.

Anal. Calcd. for $C_{14}H_7O_5SK$: K, 11.98. Found: K, 11.94.

The quinone is very readily soluble in water and the yellow aqueous solution rapidly loses its color on the addition of alkali. The solution in concentrated sulfuric acid is deep red.

Derivatives of 1-Phenanthrol

Most of the material used for the following reactions was prepared from the acetate, which, in turn, was obtained from the mixture of the phenanthrene monosulfonates. The acetate appears to be much less soluble in alcohol than any of the isomers present and the isolation of the pure material is accomplished with ease. A fairly large quantity (6–10 g. from 100 g. of phenanthrene) may be obtained from the sulfonate mixture which remains after separating the greater part of the 2-acid, the 3-acid and the 9-acid.

1-Acetoxyphenanthrene crystallizes from alcohol or benzene in the form of long needles melting at 135–136°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.00; H, 5.14.

1-Phenanthrol.—Twenty grams of the acetate was warmed with 80 cc. of alcohol and 15 cc. of 6 *N* sodium hydroxide until the material dissolved. The solution was diluted with an equal volume of water and acidified, when the phenanthrol separated in the form of small, colorless needles; yield, 16 g. (97%), m. p., 155°. Fusion of pure potassium phenanthrene-1-sulfonate (10 g.) with potassium hydroxide (35 g.) at 300° gave a product which, after crystallization from benzene–ligroin, formed cotton-like clusters of colorless needles melting at 155° (157° corr.) and identical with the above product.

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.34, H, 5.27.

The properties are in conformity with the observations of Shoesmith and Guthrie,[7] who prepared 1-phenanthrol synthetically.

1-Methoxyphenanthrene was prepared by the action of dimethyl sulfate and alkali. It formed long needles melting at 105° and the picrate melted at 154° corr. Pschorr, Wolfes and Buckow[8] give 105–106° and 153° corr., as the melting points of these substances.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.50; H, 5.81. Found: C, 86.35; H, 5.68.

1-Acetoxyphenanthrenequinone.—A solution of 1 g. of 1-acetoxyphenanthrene in

6 cc. of glacial acetic acid was treated with a solution of 1.2 g. of chromic acid at 70° and the temperature was kept at this point until the solution required no further cooling. The quinone, which separated on cooling, was washed with alcohol and with water, when it was nearly pure; m. p. 201°; 0.6 g. It dissolved readily in glacial acetic acid and the solution deposited orange, cluster-forming needles melting at 202° (206° corr.).

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 72.17; H, 3.79. Found: C, 71.80; H, 4.08.

1-Hydroxyphenanthrenequinone.—The above acetate forms a soluble bisulfite addition product which, in a hot solution, readily undergoes hydrolysis with the formation of hydroxyphenanthrenequinone. The latter substance, being insoluble in sodium bisulfite solution, thus separates in crystalline condition. The red product which was obtained in this way was crystallized from alcohol. It dissolves readily in this solvent and the orange solution deposits very long, fiery red needles melting at 220° (227° corr.).

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.98; H, 3.60. Found: C, 74.64; H, 3.89.

The solution of the quinone in concentrated sulfuric acid has an intense green color. The material dissolves in very dilute sodium hydroxide solution with the development of a grape-purple color, and the slightest excess of alkali precipitates an indigo-blue sodium salt.

The Preparation of 1,4-Phenanthrenequinone

The conversion of 1-phenanthrol into this quinone, through the azo dye and 4-amino-1-phenanthrol, was accomplished in the manner found useful for the isomeric ortho quinones,[9,15] though the yield was poorer, and the aminophenanthrol is more sensitive, than in the other cases. In the preparation of the quinone it is advisable to carry out the complete series of reactions without isolating any of the intermediates.

A solution of 2.1 g. of crystalline sulfanilic acid in 16 cc. of 0.6 *N* sodium hydroxide was diazotized by adding 0.7 g. of sodium nitrite and pouring the solution into a mixture of 2.5 cc. of concentrated hydrochloric acid and ice. This was coupled with a solution of 1.94 g. of 1-phenanthrol in 30 cc. of water and 5 cc. of 6 *N* sodium hydroxide. To the deep red solution of the azo dye which resulted, sodium hyposulfite solution was added and the mixture was heated until the 4-amino-1-phenanthrol which separated was completely colorless. The product was collected in an atmosphere of nitrogen, for it is extremely sensitive to air-oxidation, it was quickly made into a very fine paste with about 100 cc. of water containing sulfur dioxide and 2.0 cc. of concentrated hydrochloric acid was added. The mixture was stirred very vigorously and heated to a temperature just below the boiling point. The pink solution was filtered from a small amount of undissolved material and this was warmed with a fresh quantity of dilute acid. The combined filtrates were cooled to room temperature, when a part of the amine hydrochloride was deposited as a fine powder. A solution of 1.2 g. of chromic acid and 1.2 cc. of concentrated sulfuric acid was then added, causing the separation of the yellow quinone in a finely divided condition. The mixture was warmed to 45° to increase the particle size and to complete the oxidation, before collecting the product. The crude material (1.2 g.) melted at 147° and contained a small amount of a black, insoluble substance. It is best purified by crystallization from ligroin with the use of animal charcoal. Pure 1,4-phenanthrenequinone forms light, fluffy, yellow needles melting at 153° (155° corr.); yield, 0.8 g. It dissolves readily in alcohol, benzene or glacial acetic acid; the solution in concentrated sulfuric acid is violet-red in color. The quinone dissolves only very slowly in acetic anhydride containing sulfuric acid.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.76; H, 3.88. Found: C, 80.42; H, 3.88.

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[15] Fieser, THIS JOURNAL, **51**, 1896 (1929).

The hydrochloride of 4-amino-1-phenanthrol may be precipitated by adding hydrochloric acid to a solution of the salt, but it separates in the form of a gray powder and does not crystallize well. It was characterized by the preparation of a triacetyl derivative.

Triacetyl-4-amino-1-phenanthrol.—The hydrochloride (0.5 g.) was heated for one hour on the water-bath with an excess of acetic anhydride (5 cc.), 0.3 g. of fused sodium acetate was then added to complete the reaction and, after five minutes, the solution was poured into water. The product solidified rapidly and, when triturated with a little ether to remove some brown material, it was nearly pure. The substance dissolves very readily in methyl alcohol and the solutions have a decided tendency to remain in a supersaturated condition. When the solution is cooled rapidly and seeded, small colorless plates melting at 143° are obtained.

Anal. Calcd. for $C_{20}H_{17}O_4N$: C, 71.63; H, 5.11. Found: C, 71.56; H, 5.33.

1,4-Diacetoxyphenanthrene.—This compound was obtained by heating equal parts of 1,4-phenanthrenequinone, zinc dust and sodium acetate with 5 parts of acetic anhydride until the solution became practically colorless. The solution was diluted with glacial acetic acid, filtered, and poured into water, when the diacetate soon separated in nearly pure condition; yield, 95%; m. p. 137–138°. It crystallizes well from ligroin, forming slender long needles melting at 140°.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.45; H, 4.79. Found: C, 73.17; H, 4.89.

1,4-Diacetoxy-9,10-phenanthrenequinone.—The oxidation of the diacetoxyphenanthrene does not proceed smoothly and care must be taken to avoid the hydrolysis of the product during crystallization. The oxidation was carried out in glacial acetic acid solution at 40°, using 1 g. of chromic acid to 1 g. of the diacetate. On completion of the reaction, the solution was diluted with water. An orange, semi-solid oil separated and this was triturated with cold alcohol in order to dissolve the oil and leave a clean yellow solid (0.3 g.). After two crystallizations from benzene–ligroin, golden yellow prisms melting at 181° (184° corr.) were obtained.

Anal. Calcd. for $C_{18}H_{12}O_6$: C, 66.65; H, 3.73. Found: C, 66.54; H, 3.81.

This compound has been described by Brass and Stadler,[10] who report a melting point of 183°. Through the kindness of Professor Brass in supplying a sample of 1,4-dihydroxyphenanthrenequinone, a direct comparison of the two products was possible. The sample was acetylated and the product crystallized from benzene–ligroin, when it melted at 181° and gave no depression on admixture with the above quinone. Color tests confirmed this identification.

Summary

Some improvements have been effected in the method of separating and identifying phenanthrene-2-sulfonic acid and phenanthrene-3-sulfonic acid, the chief products resulting from the sulfonation of the hydrocarbon at 120–130°. It was known that phenanthrene-9-sulfonic acid is also produced when the reaction is carried out at a lower temperature. In the course of the present work, a fourth isomer was discovered among the products of the low-temperature sulfonation and the new substance was found to be phenanthrene-1-sulfonic acid. It has been used in the preparation of a few new phenanthrene derivatives, the most interesting of which are 1-hydroxy-9,10-phenanthrenequinone and 1,4-phenanthrenequinone.

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