[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

HYDROXYL DERIVATIVES OF RETENE

BY LOUIS F. FIESER AND MORRIS N. YOUNG

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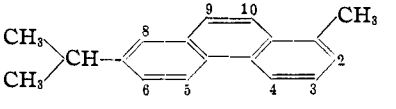
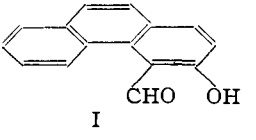
The two new retenols recently described by Komppa and Wahlforss[1] present certain points of interest to the general chemistry of phenanthrene, and one of the compounds is probably the most readily available of the known hydroxyl derivatives of this hydrocarbon. It is thus a matter of importance to establish the structures of the compounds, and this paper records the results of our experiments in this direction, as well as a description of the preparation of one more new retenol.

Following the procedures of Komppa and Wahlforss for the sulfonation of the hydrocarbon and for the alkali fusion, we obtained the two compounds which these authors have called A-retenol and B-retenol in yields of 15 and 29%, respectively. A few new derivatives of these substances were prepared, and some attempts were made to establish the structures by the oxidation of derivatives in which the hydroxyl group was either protected or replaced. While no promising method of degradation was discovered, we believe that, from certain properties of the compounds in the two series, the two retenols may be assigned structures which, if not definitely proved, are highly probable.

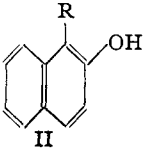
Since it is possible to oxidize suitable A and B derivatives to 9,10-retenequinones without affecting the new substituents,[1] these groups must occupy the 2-, 3-, 4-, 5-, 6- or 8-positions. The 8-position is ruled out by the Dimroth



test. 8-Hydroxyretenequinone should give an intense coloration with boroacetic anhydride, but neither the A nor the B quinone displays such a reaction. The next significant fact is that B-retenol couples with diazotized amines while A-retenol does not. The failure to react is unusual, for all of the known phenanthrols couple: 1-phenanthrol at 4; 2-phenanthrol at 1; 3-phenanthrol at 4. Among the substituted phenanthrols there is only one compound with which the coupling reaction has been found to fail. This is 3-phenanthrol-4-aldehyde, I.[2] The substance has a free



I



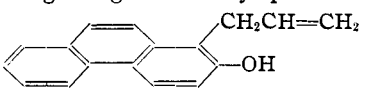
II

[1] Komppa and Wahlforss, THIS JOURNAL, **52**, 5009 (1930).

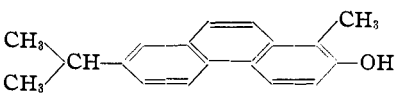
[2] Smith, *J. Chem. Soc.*, **109**, 568 (1916).

position ortho to the hydroxy group, and its inability to couple appears surprising until the behavior of compounds of the type of II is recalled. 1-Methyl-2-naphthol[3] and 1-allyl-2-naphthol[4] do not couple, nor does the allyl ether of the latter compound rearrange on heating. Since the coupling reaction very probably proceeds through an addition to a double bond or a conjugated system, these facts indicate that the double bonds of naphthalene are fixed and that there is no double bond between the 2- and 3-carbon atoms. This point, indeed, has been thoroughly established by the investigations of Zincke[5] and of Fries,[6] and the argument thus might be reversed.

The failure of 3-phenanthrol-4-aldehyde to couple is thus interpreted as an indication that there is a single bond between carbon atoms 2 and 3 of phenanthrene and that the structure of this hydrocarbon is fixed, as shown in the formulas, and not mobile as in the case of benzene. Since this point is one of importance, we have sought to test it further by examining other compounds of structure similar to I. Two such substances were obtained by the rearrangement of 2- and 3-alloxyphenanthrene.[7] Since in the naphthalene series the Claisen rearrangement exactly parallels the coupling reaction, it is safe to assume that the allyl group here enters the 1- and the 4-position, respectively. Neither substance couples, and in the case of 1-allyl-2-phenanthrol, III, it was found that the allyl ether does not rearrange to give a diallyl-phenanthrol.



III



IV

These examples are sufficient to establish the rule that only those phenanthrols can couple which have a free position either para to the hydroxyl group or in an ortho position which is connected by a double bond to the carbon carrying the hydroxyl group. Turning now to retene, it will be seen that there is only one possible hydroxyl derivative which does not fulfil the requirements of the rule. Since A-retenol does not couple, it must have the structure of IV, and it is thus 2-retenol.

For B-retenol there remain four possible locations for the hydroxyl group: 3, 4, 5 or 6. A further distinction is possible through a comparison of the reduction potentials of the A(2)- and B-hydroxyretenequinones. It has been shown[8] that there is a considerable difference in the effect of an hydroxyl group on the potential of phenanthrenequinone according to whether the substituent occupies a position which is meta or ortho–para

[3] Fries and Hübner, *Ber.*, **39**, 435 (1906).

[4] Claisen, *ibid.*, **45**, 3157 (1912).

[5] Zincke, *ibid.*, **21**, 3378, 3540 (1888).

[6] Fries, *Ann.*, **389**, 305 (1912).

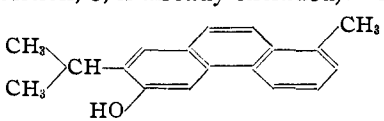
[7] These experiments were carried out by Mr. H. D. Newman.

[8] Fieser, THIS JOURNAL, **51**, 3101 (1929).

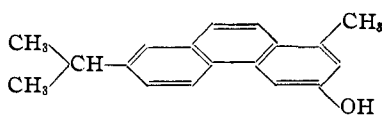
to one of the ketonic oxygen atoms. A single hydroxyl group in the 2- or 4-position is without influence, while such a group at 1 or 3 lowers the potential 51 mv. In the case of the hydroxyretenequinones the situation is slightly altered by the fact that there must be present in one of the terminal benzene rings two substituents (hydroxyl and alkyl) which produce a lowering in the potential of the parent quinone. Comparing the mono- and dihydroxyphenanthrenequinones it is seen that the effect of a second hydroxyl group introduced into the ring carrying the first such group produces a somewhat greater potential lowering: 28 mv. for a meta group; −77 mv. for an ortho–para group. It is reasonable to expect that an hydroxyl group would have a similar effect upon the potential of retenequinone. The potentials of the present compounds, are as follows:[9]

Retenequinone	0.421 v.
A(2)-Hydroxyretenequinone	.385 v; $\Delta = -36$ mv.
B-Hydroxyretenequinone	.348 v; $\Delta = -73$ mv.

The differences, which show the effects of the added hydroxyls, clearly class the A group as meta and the B group as ortho or para. This confirms the structure already assigned to the A-compound and shows that in B-retenol the hydroxyl group must be located at either 3 or 6 (since the ortho position, 8, is already excluded). A choice between V and VI can be made



V



VI

on the basis of the method by which the compound is prepared. It is obtained from the sulfonate, and it is highly improbable that a sulfonic acid group would assume a position meta to an alkyl group (VI), when a position ortho to such a group is available (V). Indeed the formation of retene-2-sulfonic acid in the same reaction is an example of the directive influence of an alkyl group. Thus the B-compound very probably is 6-retenol, V.

The isomers formed in largest amount on sulfonating phenanthrene are the 2-acid and the 3-acid (which also may be called the 6-acid). Retene is attacked in the same positions, yielding the 2- and the 6-acids. The alkyl groups serve only to promote substitution at an adjacent position and thus to hinder the formation of a large number of isomers.

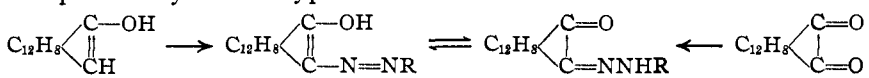
9-Retenol

A third retenol was obtained from retenequinone by reduction with zinc dust and acetic acid. The reaction is rather remarkable, for phenanthrenequinone is reduced only to the hydroquinone under similar conditions. The yield from retene is only 26.3%, but this compares favorably with the

[9] In 95% alcohol, 0.2 *N* in HCl and 0.2 *N* in LiCl at 25° by titration with titanous chloride.

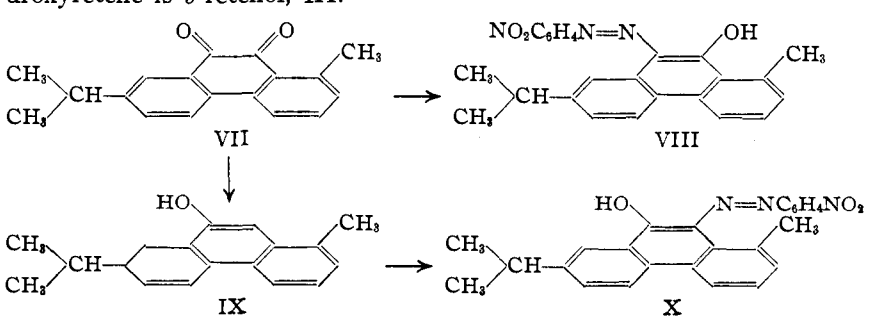
yield of 9-phenanthrol,[10] and the preparation is decidedly simpler. The substance is easily obtainable in the form of colorless needles and it is more stable than 9-phenanthrol. In solution it is slowly oxidized by the air and it combines with the quinone so produced to form bright red crystals of a molecular compound.

As a means of deciding between the two possible locations of the hydroxyl group in the new retenol, we made a study of the 9,10 (or 10,9)-hydroxyazo derivatives of retene. In the case of phenanthrene such a substance may be prepared in two ways: by coupling 9-phenanthrol with a diazotized amine, or by condensing phenanthrenequinone with a phenylhydrazine. It has been shown[11] that the same product is obtained in each case; there is the usual mobile equilibrium between the hydroxyazo and the quinone–hydrazone types:



With retene, on the other hand, the two reaction products are different and, in view of the facts just cited, it may be inferred that the substances are position isomers, the isomerism arising from the unsymmetrical structure of the hydrocarbon.

The structure of the product from the new retenol depends, of course, upon the structure of this substance and not upon the nature of the reaction by which it is produced. On the other hand, the course of the reaction between retenequinone and the hydrazine determines the structure of the reaction product. Since the reaction is probably one involving an addition, and since it is known to be subject to steric influence, it is reasonable to assume that condensation at the ketonic group closest to the methyl group is retarded and, consequently, that the product formed has the structure of VIII. The compound obtained from the retenol, being isomeric with this substance, must have the alternate structure of X, whence the new hydroxyretene is 9-retenol, IX.



[10] (a) Schmidt and Lumpp, *Ber.*, **41**, 4215 (1908); (b) Japp and Findlay, *J. Chem. Soc.*, **71**, 1115 (1897).

[11] Werner and Frey, *Ann.*, **321**, 298 (1902).

It is thus the oxygen atom closest to the methyl group in retenequinone which is eliminated on reduction. It may at first appear odd that the methyl group wards off one reagent (*p*-nitrophenylhydrazine) and attracts another (hydrogen); but it must be remembered that the two reactions are entirely different. The reduction is not an addition reaction, but involves only the replacement by hydrogen of a hydroxyl group of the retenehydroquinone first formed. The methyl simply activates the bond holding the hydroxyl group. That this actually is the case is demonstrated by the following facts. With conditions under which one oxygen is easily eliminated from retenequinone, phenanthrenequinone is unaffected. The difference must be attributed to the influence of the methyl or isopropyl groups, or to both. To settle this point we examined 1-methylphenanthrenequinone and found that in this case also a monohydroxy compound is formed easily. This shows that it is the 1-methyl group of retenequinone which is responsible for the activation, and confirms the above reasoning.

Experimental Part

B(6)-Series

Potassium 6-retene sulfonate was prepared according to Komppa and Wahlforss,[1] with the following slight changes. The reaction mixture, rather than the oil-bath, was maintained at 200°, and the sulfonation was continued for two and one-half minutes (50-g. lot). The end of the reaction is marked by a cease in the copious evolution of sulfur dioxide. After pouring the reaction mixture into water, unreacted retene was removed by extraction with ether. After boiling off the ether, potassium hydroxide was added to the hot solution to precipitate the potassium salt (yield, 28 g.). The product is nearly pure and is suitable for any of the reactions studied.

The *p*-toluidine salt furnishes a convenient derivative with which to identify the acid and to test its purity. Prepared by adding the amine to a hot solution of the potassium or ammonium salt in dilute hydrochloric acid and crystallized from dilute methyl alcohol containing hydrochloric acid, the salt formed large plates melting at 233–234°. When slightly impure it first separates as an oil, but may be caused to solidify by rubbing.

Anal.[12] Calcd. for $C_{25}H_{27}O_4NS$: C, 71.20; H, 6.46. Found: C, 71.62, 71.00; H, 6.64, 6.47.

6-Retenol.—The potassium salt of the acid is better adapted for conversion to the retenol than the ammonium salt, as used by Komppa and Wahlforss. For each gram of the crude salt, 7.6 g. of potassium hydroxide was employed, and the fusion was carried out at a temperature just below the point where boiling occurs (about 280°). The crude retenol was distilled at diminished pressure and crystallized once from xylene; yield, 73.5%; m. p. 161–162°.

6-Acetoxyretenequimone.—To a solution of 8 g. of 6-acetoxyretene in 150 cc. of glacial acetic acid a solution of 10 g. of chromic acid in water and acetic acid was added in small portions in the course of twenty minutes, not allowing the temperature to rise above 60°. After standing for an hour, the product was precipitated with water, washed with water and then alcohol, and crystallized from alcohol or glacial acetic acid; yield, 5.4 g. The compound forms flat, orange needles melting at 200°.

[12] The semi-micro method was used for all carbon and hydrogen determinations.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.50; H, 5.63. Found: C, 74.48; H, 5.61.

6-Hydroxyretenequnione.—Warmed for a short time with alcoholic alkali, the acetate dissolved to give a cherry-red solution. On acidification, and short digestion at the boiling point, an orange precipitate of the hydroxyquinone was obtained. The compound dissolves readily in alcohol and crystallizes from this solvent in the form of flat, orange needles. Ordinarily the material becomes very dark after a few crystallizations; but a trace of hydrogen chloride prevents this darkening and even causes the dark material to form light orange needles. The compound has no characteristic melting point. The solution in concentrated sulfuric acid is yellow-green.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.10; H, 5.76. Found: C, 76.98; H, 5.78.

6-Methoxyretene.—Prepared by alkylation with dimethyl sulfate, distilled and crystallized from alcohol, the ether formed colorless plates, m. p. 115–116°.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.30; H, 7.63. Found: C, 86.33; H, 7.88.

6-Methoxyretenequinone was prepared by the oxidation of the above ether, or, better, by methylation of 6-hydroxyretenequinone with dimethyl sulfate. The crude material is conveniently purified through the bisulfite addition product and crystallized from alcohol (moderately soluble), giving fine, orange needles melting at 196°.

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.52; H, 6.17. Found: C, 77.42; H, 6.38.

5-(*p*-Nitrobenzeneazo)-6-retenol.—Probably because it dissolves with difficulty in alkali, 6-retenol does not couple easily with diazotized amines when the standard procedure is used. The above compound was thus prepared by adding an excess of *p*-nitrobenzenediazonium chloride to a solution of 6-retenol in glacial acetic acid. After seven hours the mixture was diluted with water, which gave a brown precipitate of the azo compound. It formed very dark red needles from glacial acetic acid. The substance decomposes on heating.

Anal.[13] Calcd. for $C_{24}H_{21}O_3N_3$: N, 10.5. Found: N, 10.8.

Derivative of 5-Amino-6-retenol.—The reduction of the above azo compound did not proceed smoothly and we were unable to isolate the amine. Somewhat better results were obtained with the sodium azobenzene sulfonate derivative. This was prepared by slowly adding alkali to a mixture of an aqueous solution of diazotized sulfanilic acid and a solution of 6-retenol in glacial acetic acid. The dye precipitated as the red sodium salt. This was easily reduced with sodium hyposulfite, but the aminoretenol was not obtained in pure condition. It is very sensitive to air oxidation and it does not form a stable hydrochloride. Treated with acetic anhydride and sodium acetate and then distilled, it was converted into the **oxazole derivative,** which formed pale yellow plates, m. p. 112°, from methyl alcohol.

Anal. Calcd. for $C_{20}H_{19}ON$: N, 4.85. Found: N, 5.22.

Attempted Degradations.—We may record here a few preliminary experiments in this direction. 6-Methoxy- and 6-acetoxyretenequinone were both oxidized with hydrogen peroxide in glacial acetic acid solution, but only in the latter case was a crystalline acid isolated, and this in only minute amount. Hoping for better results with a chlororetenequinone, we experimented with a few phenanthrenequinone sulfonates to see if the sulfonic acid group can be replaced with chlorine by boiling with potassium chlorate and hydrochloric acid, a reaction which gives excellent results with the anthraquinones.[14] 3-Chlorophenanthrenequinone, m. p. 253–254° (given: 253°)[15] was obtained by this method, and the 1-sulfonate was converted into **1-chlorophenanthrene-**

[13] Micro method.

[14] Ullmann, *Ann.*, **381**, 1 (1911).

[15] Sandquist and Hagelin, *Ber.*, **51**, 1515 (1918).

quinone: orange needles, m. p. 217–218°. (*Anal.* Calcd. for $C_{14}H_7O_2Cl$: C, 69.25; H, 2.91. Found: C, 69.55; H, 2.81.) The yields, however, were very poor and no product could be isolated from either phenanthrenequinone-2-sulfonate or retenequinone-6-sulfonate. We also attempted to prepare a nitrile by distillation of retene-6-sulfonate with potassium ferrocyanide, but no good product could be isolated.

A(2)-Series

On following the directions of Komppa and Wahlforss for the preparation of the A-sulfonate, we obtained a crude product which was found to contain a considerable quantity of the B-sulfonate. We found it expedient to fuse this mixture and to make the separation with the retenols. 2-Retenol crystallizes first from a solution of the two isomers in xylene, and it may be obtained thus in completely pure form as colorless plates: m. p. 200–202°; yield, from retene, 15%.

2-Acetoxyretene.—The acetate forms small plates, m. p. 160°, from alcohol.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.90. Found: C, 82.48, 82.08; H, 6.95, 7.16.

2-Acetoxyretenequinone.—This was obtained in 50% yield by the oxidation of 2-acetoxyretene (0.7 g.) with an excess of chromic acid (1.1 g.) in glacial acetic acid solution at about 50–60°. The compound forms flat, orange needles from alcohol, m. p. 171–172°.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.50; H, 5.63. Found: C, 74.70, 74.60; H, 5.78, 5.71.

2-Hydroxyretenequinone.—Prepared by hydrolysis of the acetate with alcoholic alkali and crystallized from alcohol, this quinone formed dark red needles. The substance shows signs of decomposition at 200°, but melts rather sharply at 229–231°. It gives a dark green solution in concentrated sulfuric acid; the alkaline solution is blue-green.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.10; H, 5.76. Found: C, 77.08; H, 5.91.

A Color Test for Substituted Phenanthrenequinones.—In the course of the preparation of the two hydroxyretenequinones, we were impressed by the marked difference in the behavior of these substances toward alcoholic alkali. The solution of 6-hydroxyretenequinone in the reagent is red, and shows no change on heating. On the other hand, 2-hydroxyretenequinone imparts to cold, dilute alcoholic alkali an intense blue-green color which changes to reddish-brown on heating. On cooling, the blue-green color is restored, and the change can be repeated several times. That retenequinone displays a similar color reaction, has already been noted by Bamberger and Hooker.[16] The cold solution is pale yellow; it becomes deep red on heating, and this color is lost on cooling. Phenanthrenequinone is similar, the solution changing from a practically colorless condition to pink. Tests with some substituted phenanthrene-

COLOR REACTIONS OF HYDROXYQUINONES

	Position of hydroxyl group		Solution in dil. alcoholic alkali: Cold	Hot
Phenanthrenequinones	1	ortho	Violet	
	3	para	Red	
	2	meta	Blue	⇌ Faint brown
	4	meta	Green	⇌ Blue
Retenequinones	6	ortho	Red	
	2	meta	Blue-green	⇌ Red-brown

[16] Bamberger and Hooker, *Ann.*, **229**, 102 (1885).

and retenequinones revealed a surprising regularity, as the table will demonstrate. It appears that when a hydroxyl group is in a position meta to one of the ketonic oxygen atoms of the quinone the reversible color change is exhibited; but when the group is in an ortho or para position no change in color occurs.

Preparation of 9-Retenol

The retenequinone employed was prepared by oxidizing retene in the manner described by Bamberger and Hooker,[16] and it was purified through the bisulfite addition compound. As Ekstrand[17] observed, retenequinone dissolves only with great difficulty in a boiling, saturated solution of sodium bisulfite. The addition product, however, is readily formed by adding bisulfite solution to a suspension of the quinone in hot alcohol. A clear solution results on diluting the mixture with water and filtering. From this the quinone is precipitated by acidifying, and it may be coagulated by short heating at the boiling point. Crystallized once from glacial acetic acid, this gives an excellent product melting at 197°; yield: 53%.

In glacial acetic acid solution retenequinone is reduced by zinc dust very rapidly to the hydroquinone. In the course of one hour this is largely reduced further to 9-retenol. The product is not easy to isolate, however, for it becomes oxidized by air very readily when it is in a slightly impure condition. We thus isolated it as the acetate by adding acetic anhydride to the reduced solution. Time, of course, must be allowed for the reduction of the dihydroxy compound, for if the acetic anhydride is present from the start the sole product is the hydroquinone diacetate, m. p. 170°.

9-Acetoxyretene.—Ten grams of retenequinone was suspended in 70 cc. of hot glacial acetic acid and to this was added 4 g. of zinc dust, the addition being made slowly, and with stirring, in order to avoid the formation of lumps. After boiling for half an hour, 3 g. of zinc dust was added, and a further 9 g. was added at intervals of fifteen minutes. Then 15 g. of fused sodium acetate and 225 cc. of acetic anhydride were added and the mixture was refluxed for one hour. The mixture was then diluted with glacial acetic acid and filtered into water. The slightly green solid thus obtained was distilled at diminished pressure and crystallized from methyl alcohol. The product crystallizes with some difficulty until seed is available; it then forms good, colorless needles, m. p. 141°; yield, 6.2 g. (56%). It dissolves easily in benzene, ether or alcohol.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.90. Found: C, 81.98, 82.18; H, 6.76, 7.15.

9-Retenol was prepared by hydrolysis of the pure acetate with alcoholic alkali, and it was crystallized from xylene; yield, 87.5%. The substance forms very fine, colorless needles melting at 176°. It is very readily soluble in alcohol or glacial acetic acid, moderately soluble in xylene. A yellow color is imparted to concentrated sulfuric acid, the solution acquiring a yellow-green fluorescence on heating.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.22, 86.12; H, 7.50, 7.57.

Molecular Compound with Retenequinone.—9-Phenanthrol is a rather unstable substance which darkens rapidly on storage and becomes oxidized easily in solution. 9-Retenol is more stable. No difficulty is experienced in crystallizing the material, and it was only after exposing a solution in glacial acetic acid to the air for three days that an oxidation was observed. At the end of this time small, dark red crystals had deposited. On crystallization, orange plates of retenequinone were obtained.

The red, crystalline material is a molecular compound composed of equal parts of 9-retenol and retenequinone. It is easily prepared by mixing saturated solutions of

[17] Ekstrand, *Ann.*, **185**, 75 (1877).

equal parts of the two components. The solution becomes red and deposits small, dark red plates, m. p. 160–161°.

The compound is similar to that prepared from phenanthrenequinone and 9-phenanthrol by Japp and Findlay.[10b]

Anal. Calcd. for $C_{36}H_{34}O_3$: C, 84.00; H, 6.66. Found: C, 83.83; H, 6.95.

9-Methoxyretene.—Prepared by the use of dimethyl sulfate and purified by distillation, this substance formed colorless plates from methyl alcohol, m. p. 108°.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.30; H, 7.63. Found: C, 86.28; H, 7.74.

9-Alloxyretene.—This ether was prepared by allylation in acetone solution in the presence of potassium carbonate. The crude product was oily and crystallized at first with some difficulty. It eventually formed good needles, m. p. 84°, from methyl alcohol.

Anal. Calcd. for $C_{21}H_{22}O$: C, 86.84; H, 7.64. Found: C, 86.66, 86.72; H, 7.96, 7.89.

9-Acetoxy-10-allylretene.—The allyl ether rearranged easily on being heated at 150° for one and one-half hours in an atmosphere of nitrogen. The resulting oil was distilled in vacuum, but it could not be caused to solidify. The product was thus isolated as the acetate, which crystallizes from methyl alcohol as colorless needles melting at 102°.

Anal. Calcd. for $C_{23}H_{24}O_2$: C, 83.08; H, 7.29. Found: C, 82.82, 83.08; H, 7.22, 7.36.

9-Hydroxy-10-(*p*-nitrobenzeneazo)-retene (X).—9-Retenol couples readily in alkaline solution with diazotized *p*-nitro-aniline. It may be remarked that a large volume of water must be used (150 cc. for each 0.1 g. of retenol) because of the sparing solubility of the retenol salt. The orange precipitate was crystallized from glacial acetic acid, giving large, orange-red needles melting at 243.5–244.5°. The substance imparts a purple color to concentrated sulfuric acid and a blue color to alcoholic alkali.

Anal. Calcd. for $C_{24}H_{21}O_3N_3$: N, 10.5. Found: N, 11.1, 11.2.

The isomeric compound, 10-hydroxy-9-(*p*-nitrobenzeneazo)-retene (VIII) has been prepared by Cheung[18] from retenequinone and *p*-nitrophenylhydrazine. Repeating his preparation, we obtained red micro needles melting at 222–223°. A mixture of the two isomers melted at 185–187°.

Reduction of 1-Methylphenanthrenequinone.—The starting material was prepared by the Pschorr synthesis.[19] Before attempting to isolate a monohydroxymethylphenanthrene by the method used above, we prepared the other possible reduction product for comparison. The **hydroquinone diacetate of 1-methylphenanthrenequinone,** obtained by ordinary reduction acetylation, formed stout needles from alcohol; m. p. 189°; green coloration in concentrated sulfuric acid.

Anal. Calcd. for $C_{19}H_{16}O_4$: C, 74.00; H, 5.24. Found: C, 73.86, 73.98; H, 5.52, 5.48.

1-Methyl-9-acetoxyphenanthrene.—Reduced by the method described under the preparation of 9-retenol, 1-methylphenanthrenequinone was converted into the acetate of a 1-methylphenanthrol. By analogy with the behavior of retenequinone, we assume that the acetoxy group here occupies the 9-position. The product forms colorless needles, m. p. 99–100°; red in hot, concd. sulfuric acid.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.75; H, 6.01.

Allylphenanthrols (Work of H. D. Newman).—2-Phenanthrol and 3-phenanthrol were alkylated with the use of allyl bromide, acetone and potassium carbonate. The

[18] L. M. Cheung, "Dissertation," Bordeaux, 1928.

[19] Pschorr and Hofmann, *Ber.*, **39**, 3110 (1906).

two allyl ethers rearrange with unusual ease, being largely converted into allylphenanthrols at the temperature of the steam-bath. It thus was not possible to purify them by vacuum distillation, and the 3-ether was not obtained in solid form and was characterized only by its picrate, m. p. 101°. The other compounds of the 3-series are all lower melting than the corresponding 2-derivatives; but after distillation they can be caused to solidify. The coumarane derivatives were prepared by heating the allylphenanthrols with a mixture of hydrobromic and acetic acids. Neither of the allylphenanthrols could be caused to couple with diazotized amines. The allyl ether of 1-allyl-2-phenanthrol did not rearrange on moderate heating and only decomposed as the temperature was raised. Analytical data for the new compounds are included in the table.

ALLYLPHENANTHROLS AND DERIVATIVES

	Calcd., % C	H	Found, %[20] C	H	M. p., °C.	Description
2-Alloxyphenanthrene	87.14	6.03	87.13	6.24	92	Flat needles
1-Allyl-2-phenanthrol	87.14	6.03	87.06	6.23	125.5	Needles
Acetate	82.58	5.84	82.44	5.93	105	Needles
Coumarane derivative	87.14	6.03	86.98	6.24	155	Micro crystals
Allyl ether	87.55	6.62	87.50	6.79	91.5	Plates
4-Allyl-3-phenanthrol	87.14	6.03	87.15	6.15	91	Micro crystals
Acetate	82.58	5.84	82.42	5.95	56	Prisms
Coumarane derivative	87.14	6.03	87.02	6.23	89	Small plates

Summary

The double bonds of phenanthrene occupy fixed positions, as in the case of naphthalene. Carbon atoms 2 and 3 are connected by a single bond and hence a 2(or 3)-phenanthrol cannot couple with diazonium salts if the 1 (or 4)-position is blocked, for a double bond is required for the formation of the intermediate addition product.

Using this principle, reduction potential data and the Dimroth test for α-hydroxyquinones, it has been shown that the hydroxyretenes recently described by Komppa and Wahlforss are to be regarded as 2- and 6-retenol.

A third retenol was obtained by the reduction of retenequinone. From reasoning based upon the assumption that a 1-methyl group causes a condensing reagent to attack a phenanthrenequinone at the 9- rather than the 10-ketone group, and upon analogy experiments with 1-methylphenanthrenequinone, it is concluded that the new substance is 9-retenol.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

[20] We are indebted to Mr. Charles L. Bickel for carrying out these analyses.