

melting at 125°.  $[\alpha]^{20}_D$   $-28.0^\circ$ , in alcohol. *Anal.* Calcd. for  $C_{20}H_{19}O_2N$ : C, 78.75; H, 6.23. Found: C, 78.73; H, 6.33.

**Nitroso Derivative of the Urethan.**—This was prepared by passing dry nitrous anhydride into a suspension of the urethan in ether at  $-20^\circ$  for two hours. After standing for thirty minutes the excess gas was removed and the solution poured into water. The nitroso derivative separated and was recrystallized from alcohol; m. p.  $87-89^\circ$  (dec.). An alcoholic solution containing 0.1631 g. in 25 cc. gave in a 2-dm. tube  $\alpha_D +0.12^\circ$ ,  $[\alpha]^{25}_D +9.2^\circ$ . *Anal.* Calcd. for  $C_{20}H_{19}O_3N_2$ : C, 71.83; H, 5.42. Found: C, 72.2; H, 5.8.

**Phenyl- $\alpha$ -naphthyl-diazomethane** was prepared as previously described. The ligroin solution was evaporated in a stream of dry air free from carbon dioxide until the volume was reduced 25%. The solution was cooled to  $-78^\circ$  and filtered. The precipitate was orange colored. This fraction was optically active, as 0.4714 g. in 10 cc. of ether in a 2-dm. tube gave  $\alpha_D -1.03^\circ$ ,  $[\alpha]^{20}_D -9.15^\circ$ . It contained 0.002947 g. of nitrogen corresponding to 5.45% of the diazo compound. On recrystallization *l*-phenyl- $\alpha$ -naphthylcarbinol, m. p.  $86^\circ$ , was obtained.<sup>9</sup>

The second fraction was obtained in a similar manner by evaporation of the solution to half the original volume. This material was small in amount, pink in the solid state, and dissolved to give a deep cherry red solution. It melted at  $50-54^\circ$  with vigorous decomposition.

The third fraction separated from the solution that had been evaporated to 25% of its original volume. It was a pink crystalline substance melting at  $55-58^\circ$  with vigorous decomposition. The rotatory dispersion was determined. The material was then heated until the red color had disappeared. This leads to the formation of symmetrical products of decomposition. The rotatory dispersion was again determined and found to be identical with the previous determination. Evidently the diazo compound had no influence on the rotation.

0.0793 g. in 10 cc. of solution in a one-dm. tube gave:

$\lambda$	Before heating $\alpha$	After heating $\alpha$
486.1	..	-0.19
546.3	..	- .16
577.2	-0.15	- .15
589.3	- .14	- .15
611.4	- .14	..
633.4	- .12	..
656.3	..	- .13

Error = 0.01.

*Anal.* Calcd. for  $C_{17}H_{12}N_2$ : N, 11.5. Found: N, 9.34.

The fourth and last fraction was recrystallized from ligroin and gave the purest material melting sharply at  $58^\circ$  with decomposition. The melt was at first a deep red color which became straw colored with the evolution of gas. The solution was optically inactive in red and yellow light. The deep red color of the solution made it impossible to obtain accurate readings at the shorter wave lengths. The pink colored solid was unstable and gave but 1 to 2% diazo nitrogen after standing twenty-four hours. When quickly dried and combusted it gave: *Anal.* Calcd. for  $C_{17}H_{12}N_2$ : C, 83.7; H, 4.9; N, 11.5. Found: C, 83.5, 83.4; H, 4.6, 4.8; N, 11.2, 11.1.

### Summary and Conclusion

Phenyl- $\alpha$ -naphthyldiazomethane has been prepared from *l*-phenyl- $\alpha$ -naphthylaminomethane and found to be optically inactive.

The diazo compound while rather permanent in ligroin solution is only moderately stable in the solid state at room temperature.

Two possibilities, therefore, present themselves: first, the diazo group has a symmetrical structure; second, the compound racemized during the time necessary for its preparation and isolation.<sup>4c</sup>

CINCINNATI, OHIO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Structure of Anthracene

BY LOUIS F. FIESER AND WARREN C. LOTHROP

Of the various attempts to account for the special properties of anthracene by means of a special formula, the essentially speculative idea of a reactive para-bond has been found inconsistent<sup>1</sup> with the chemical,<sup>2</sup> electrochemical<sup>3</sup> and optical<sup>4</sup> properties of anthracene derivatives and it has been quite definitely eliminated by the evidence<sup>5</sup> that the carbon atoms of anthracene are practically

co-planar and that the distance separating the meso positions is approximately twice the length of any known carbon-carbon linkage.<sup>6</sup> Studies of the magnetic susceptibility<sup>7</sup> of even the most highly reactive of the linear benzologs of the hydrocarbon have shown that the diradical formula postulated by Clar<sup>8</sup> is inadmissible, except perhaps as a reaction phase. Other formulations suggested for anthracene are based upon the fundamental concept of the centric structure of ben-

(1) Hinsberg, *Ann.*, **319**, 257 (1901).

(2) Clar, *Ber.*, **64**, 2194 (1931).

(3) Fieser and Dietz, *This Journal*, **53**, 1128 (1931).

(4) Goudet, *Helv. Chim. Acta*, **14**, 379 (1931).

(5) Bragg and Bragg, "X-Rays and Crystal Structure," 1924, p. 233; Lonsdale, *Trans. Faraday Soc.*, **26**, 352 (1929).

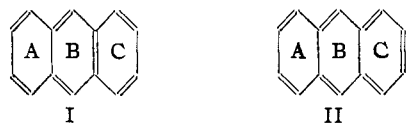
(6) K. H. Meyer, *Z. angew. Chem.*, **41**, 935 (1928).

(7) E. Müller and I. Müller-Rodloff, *Ann.*, **517**, 134 (1935).

(8) Clar and John, *Ber.*, **62**, 3021 (1929); **63**, 2967 (1930).

zene. Whether this is expressed by means of the Armstrong-Baeyer formula, Thiele's second formula, or either of the electronic counterparts suggested by Kauffmann<sup>9</sup> and by Robinson,<sup>10</sup> the essential idea is that all six of the carbon-carbon linkages are equivalent and that they are of a different character from any known type. While there are few observations concerning benzene derivatives which can be regarded as definitely contradictory to this view, there is abundant evidence in the chemistry of naphthalene to indicate that the  $\alpha,\beta$ - and  $\beta,\beta$ -linkages of the hydrocarbon are not equivalent or even qualitatively similar, but that they are as fundamentally different as aliphatic double and single bonds.<sup>11</sup> The evidence on this point definitely excludes any form of centric or centric-electron structure for naphthalene and points to the presence of Kekulé rings with alternate double and single bonds. Since benzene, naphthalene and the higher benzologs all exhibit to a greater or less degree the type of properties characteristic of the aromatic condition, and since the qualitative differences can be adequately interpreted without assuming the existence of more than one kind of ring structure, the evidence indicating that naphthalene is composed of Kekulé rings provides a rational basis for the view that this is the fundamental structural unit of all of the aromatic hydrocarbons, including benzene.

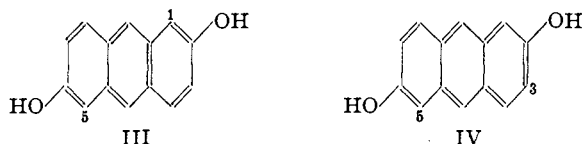
Two formulations (I and II) are possible for anthracene in terms of Kekulé rings and either one of them may be said to express the idea of



Armstrong that there is present in anthracene at least one ring (A) which contains only two double bonds and which, with the ethylenic linkages extending into the central nucleus, constitutes an ortho-quinonoid, or dihydrobenzenoid, system of linkages. This arrangement represents a condition less stable than that of an isolated benzene ring. The ortho-quinonoid formula accounts well for the various manifestations of the comparatively high degree of unsaturation of the hydro-

carbon,<sup>12</sup> above all its ability to function as the diene component in the Diels-Alder reaction.<sup>13</sup> The addition may be said to occur at the diene system of the central nucleus or at the ends of the entire conjugated system including the *o*-quinonoid ring A.

From purely theoretical considerations it would appear that the first of the two alternate structures is the more likely because it represents a more stable system. Formula I contains an *o*-benzoquinonoid ring (A) and two benzenoid rings combined to form a normal naphthalene nucleus (BC), while in formula II two of the rings are dihydride and constitute a 2,3-naphthoquinonoid grouping of linkages (AB) and there is only one benzenoid ring (C). As Fries<sup>14</sup> has stated the case, there is a closer average approach in the first instance to the stable condition of an isolated benzene ring and consequently I is the preferred structure. Fries sought to test this conclusion by studying the bromination of 2,6-dihydroxyanthracene. If the structure is that of III the bromine atoms should be directed to the two enolic ortho positions 1 and 5, whereas the alternate structure IV should lead to 3,5-substitution.



It was found that bromination occurs at the 1- and 5-positions, as predicted for a substance of the structure III, but the observation hardly proves that III is the only species present in the solution submitted to reaction. The solution might well contain a tautomeric mixture of III and IV in which III is either the predominant tautomer or the one most easily substituted. It might be argued that the rate of bromination would be greater at the 1-position of III than at the 3-position of IV because the former is adjacent to a second ring while the latter is a  $\beta$ -position.

In order to extend the observations of Fries and submit the matter to a rigid test, we have applied

(9) Kauffmann, "Die Valenzlehre," 1911, p. 539.

(10) Kermack and R. Robinson, *J. Chem. Soc.*, **121**, 427 (1922); Armit and R. Robinson, *ibid.*, **127**, 1604 (1925); R. Robinson, *Inst. Internat. Chim. Solvay*, 4 Conseil, 423 (1931).

(11) Fieser and Lothrop, *THIS JOURNAL*, **57**, 1459 (1935).

(12) Kehrman, *Ber.*, **27**, 3348 (1894); Scholl, *ibid.*, **41**, 2312 (1908); Schlenk, Appenrodt, Michael and Thal, *ibid.*, **47**, 479 (1914); K. H. Meyer and Schlösser, *Ann.*, **420**, 126 (1920); v. Auwers, *Ber.*, **53**, 941 (1920); v. Auwers and Krollpfeiffer, *Ann.*, **430**, 254 (1923); Fieser and Ames, *THIS JOURNAL*, **49**, 2604 (1927); Fieser, *ibid.*, **50**, 465 (1928).

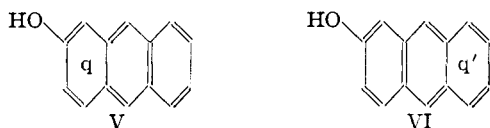
(13) Diels and Alder, *Ann.*, **486**, 191 (1931); Clar, *Ber.*, **64**, 1676 (1931).

(14) Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935).

to the anthracene problem the method used in the case of naphthalene.<sup>11</sup> The 1,5-dimethyl and 1,5-diallyl derivatives of 2,6-dihydroxyanthracene were prepared, in the first case by a synthesis which leaves no doubt as to the structure, and investigated for their ability to couple with diazotized amines. The structure III for such a compound would permit of no reaction, since both of the normal ortho positions are blocked by alkyl groups, but if the substance can exist to any appreciable extent in the tautomeric form having the bond structure of IV coupling should occur at the available ortho position C<sub>3</sub>, for this is connected to the hydroxylated carbon atom by an enolic double bond. There was in no case any indication of a reaction, and consequently it is concluded that the substances exist entirely in the forms corresponding to III and that tautomerization is negligible. The bond structure appears to be immobile, and the double linkages in the terminal ring C are not free to oscillate as in an isolated benzene ring. The views of Fries clearly are substantiated by the more rigid evidence.

That the bond structures determined for symmetrically substituted derivatives of polynuclear hydrocarbons apply equally well to the parent substances is an entirely rational assumption because the theoretical considerations are the same in each case. The alternate thesis would have to bear the full burden of proof, since there is at present no reason to suppose that the structures are different.

As for unsymmetrical derivatives such as 2-anthrol, for example, the traditional explanation of the existence of only one isomer perhaps would be that the bonds are capable of oscillation between the structures V and VI, and Fries has observed that the oscillation need involve only the



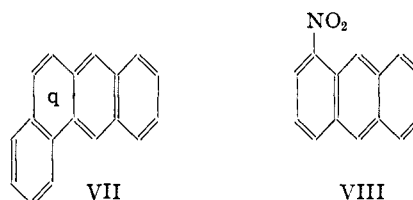
central ring. We are inclined, however, to view the two forms as tautomers, rather than as mere phases in an oscillation, and since quinonoid structures are involved it is rational to apply to the problem the principles governing the equilibria in tautomeric systems of quinones.<sup>15</sup> The idea is not new but is essentially that expounded by Kehrman<sup>16</sup> in a brilliant but little recognized paper of 1898 dealing with phenazonium salts.

(15) Fieser, *THIS JOURNAL*, **50**, 439 (1928).

(16) Kehrman, *Ber.*, **31**, 977 (1898).

Since a hydroxyl group lowers the oxido-reduction potential of a quinone, and consequently decreases the free energy of reduction, the hydroxy-quinonoid grouping (q) of V should have a greater thermodynamic stability than the quinonoid nucleus (q') of VI, and the first formula therefore represents the structure of the predominant tautomer in solution, and probably the structure of the solid compound. The less stable tautomer VI doubtless is capable of existing, but the isolation of the substance probably would present even greater difficulties than that of obtaining the still unknown tautomer of 2-hydroxy-1,4-naphthoquinone. The idea of an oscillation in the central nucleus merely provides a mechanism for the dynamic equilibrium between the tautomers.

Alkyl groups influence quinone potentials in the same direction as hydroxyl groups but to only about half the extent, and consequently the less stable forms of 1- and 2-alkylanthracenes probably are present in the equilibrium mixtures in somewhat larger amounts. The amino group is considerably more potent than the hydroxyl group and the much debated  $\beta$ -anthramine must exist very largely in the aminoquinonoid form corresponding to V. That the substance is a weak base and resists diazotization<sup>17</sup> except under special conditions<sup>14</sup> is easily understood on the basis of such a structure, for aminoquinones exhibit similar properties. Considering the low energy of reduction of  $\beta$ -naphthoquinone as compared with *o*-benzoquinone, 1,2-benzanthracene must have the naphthoquinonoid structure VII.



Unsaturated groups, and to a lesser extent halogen atoms, can be expected to shift the equilibrium in the other direction, the more stable form of a compound such as 1-nitroanthracene probably being that in which the substituent is located in the benzenoid ring (VIII). The enhanced reactivity of the linear benzologs of anthracene is explained by the presence in these hydrocarbons of multiple quinonoid rings.<sup>18</sup>

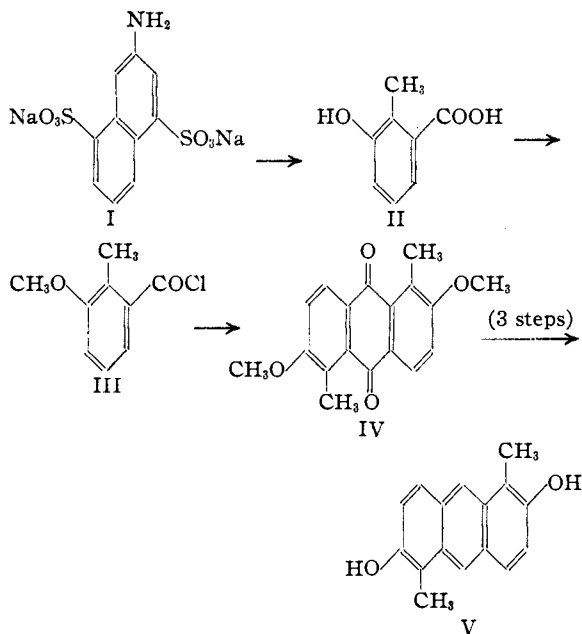
(17) Bollert, *ibid.*, **16**, 1635 (1883); Bamberger and Hoffmann, *ibid.*, **26**, 3068 (1893).

(18) Fieser, *THIS JOURNAL*, **53**, 2329 (1931); Fieser and Martin, *ibid.*, **57**, 1844 (1935).

## Experimental Part

### 1. 1,5-Dimethyl-2,6-dihydroxyanthracene

2-Methyl-3-hydroxybenzoic acid (II), the starting material for the synthesis, was prepared by heating technical sodium 2-naphthylamine-4,8-disulfonate (250 g.), I, with four parts of 50% sodium hydroxide solution at 250–275° for eleven hours, following the procedure of Baudisch and Perkin.<sup>19</sup> The yield was considerably better than reported by these investigators, possibly because of the method of recovery. The contents of the autoclave was dissolved in the least amount of hot water, the solution was rendered barely acidic by the addition with cooling of 800 cc. of crude concentrated hydrochloric acid, and treated with Norite. A troublesome oil, which remains dissolved when the solution is weakly alkaline, was in this way eliminated, and on strongly acidifying the yellow filtrate and cooling the product separated as pale brown needles. After recrystallization, and extraction of the mother liquors with ether, the yield of acid melting at 141–142° was 20–30 g. (18–27%).



The claim<sup>20</sup> that this acid (II) can be condensed to an anthraquinone by means of zinc chloride could not be verified. We were unable to effect the "ruff"-condensation with this reagent, with sulfuric acid, with sulfuric and boric acids or with phosphorus pentoxide. It was thought that the acid chloride might give better results, but although the phenolic acid reacts fairly smoothly with thionyl chloride in ethereal solution the chief product, obtained after extraction of the residue with sodium bicarbonate solution, had the properties of an ester-acid:  $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})\text{COOC}_6\text{H}_3(\text{CH}_3)\text{COOH}$ . The compound forms fine, colorless needles from dilute alcohol, m. p. 211°. (*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_5$ : C, 67.10; H, 4.93. Found: C, 66.85; H, 5.00.)

(19) Baudisch and Perkin, *J. Chem. Soc.*, **95**, 1883 (1909).

(20) Ger. patent 87,620 (1894); Friedlaender, *Fortschr. Teerfarb. Fabrik.*, **4**, 336 (1894).

2-Methyl-3-hydroxybenzoic acid was then methylated and converted into the acid chloride III and it was found that this substance can be condensed to an anthraquinone by the action of aluminum chloride in carbon bisulfide solution. The yield was poor, however, because a part of the starting material is demethylated before it can undergo condensation. The dihydroxy- and dimethoxyanthraquinones were both isolated from the reaction mixture, but only the latter substance could be reduced satisfactorily. The results were no better using nitrobenzene or tetrachloroethane. As in analogous cases, the di- $\alpha$ -substituted quinone IV does not give a vat test. Reduction to an anthracene was best accomplished in two steps, and the desired dihydroxy compound V was obtained on demethylation.

**2-Methyl-3-methoxybenzoic acid**, prepared in 80% yield from the hydroxy compound with the use of dimethyl sulfate in a warm, alkaline solution, followed by alkaline hydrolysis, forms characteristically jagged, colorless plates from dilute alcohol, m. p. 145–146°.

*Anal.* Calcd. for  $\text{C}_9\text{H}_{10}\text{O}_3$ : C, 65.02; H, 6.08. Found: C, 64.99; H, 6.07.

**1,5-Dimethyl-2,6-dimethoxyanthraquinone.**—A 2-g. portion of the methoxy acid was warmed with thionyl chloride and the excess reagent was removed at the suction pump, leaving a residue which solidified easily and which could be crystallized from carbon bisulfide (needles, m. p. 40°). A solution of the material in this solvent was cooled in an ice-bath and 4 g. of aluminum chloride was added all at once. After a few minutes a viscous red oil separated, and on gentle warming hydrogen chloride was evolved copiously. After refluxing for two hours the mixture was treated with water and the solvent removed by steam distillation. The aqueous solution was decanted from a gummy, yellow product and extracted with ether, yielding about 1 g. of a mixture of 2-methyl-3-hydroxybenzoic acid and its methyl ether, both of which were identified. The yellow product on treatment with dilute alkali gave a cherry-red extract which on acidification and digestion yielded a fine yellow precipitate of the dihydroxyanthraquinone; yield, 3–7% (not considering the recovered material). The extraction with alkali left a grayish residue of 1,5-dimethyl-2,6-dimethoxyanthraquinone; yield, 4–10%. The ether forms pale yellow needles from glacial acetic acid and melts with decomposition at approximately 305°.

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}_4$ : C, 72.94; H, 5.47. Found: C, 72.82; H, 5.72.

**1,5-Dimethyl-2,6-dihydroxyanthraquinone.**—The crude product was digested with bicarbonate solution and the residue was crystallized from glacial acetic acid or from nitrobenzene, forming thick, yellow needles. The substance decomposes at about 330°. The diacetate, prepared with acetic anhydride and sulfuric acid, forms slender, pale yellow needles, m. p. 253°, from glacial acetic acid.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{12}\text{O}_4$ : C, 71.62; H, 4.51. Found: C, 71.29; H, 4.70. *Anal.* (diacetate). Calcd. for  $\text{C}_{26}\text{H}_{18}\text{O}_6$ : C, 68.18; H, 4.57. Found: C, 68.23; H, 4.90.

**1,5-Dimethyl-2,6-dimethoxyanthracene.**—In the preliminary reduction a mixture of the quinone (0.66 g.), stannous chloride (4 g.), concentrated hydrochloric acid (7 cc.)

and glacial acetic acid (20 cc.) was boiled for thirty minutes, when solution was complete. This solution on cooling deposited a paste of small yellow-green crystals. Although this method of reduction usually leads to the formation of anthrones, analyses of the reaction product, which crystallizes from acetic acid as pale yellow needles, dec. about 295°, agree more closely with the formula of a hydroxyanthrone (*Anal.* Calcd. for  $C_{18}H_{18}O_4$ : C, 72.49; H, 6.07. Found: C, 71.85; H, 5.68). It was found best to use the moist product for the next step, which consisted in reduction by Perkin's method,<sup>21</sup> using aluminum foil etched with alkali and amalgamated according to Wislicenus.<sup>22</sup> The first reduction product was added to a mixture of 3 g. of amalgam, 25 cc. of alcohol, and 15 cc. of 25% ammonia solution. After boiling for five hours the greenish paste was decanted, acidified, and digested for several hours, and the collected solid was digested with alcohol to remove green impurities and crystallized from glacial acetic acid; yield, 0.25 g. (50%). The substance crystallizes as slightly greenish-yellow plates, m. p. 250° (dec.), and the solutions exhibit a blue fluorescence.

*Anal.* Calcd. for  $C_{18}H_{18}O_2$ : C, 81.18; H, 6.80. Found: C, 81.02; H, 7.23.

**1,5-Dimethyl-2,6-dihydroxyanthracene.**—The ether (0.25 g.) was demethylated by refluxing a solution in glacial acetic acid (25 cc.) with 1 cc. of 48% hydrobromic acid for three hours, when the brilliantly fluorescent solution had deposited fine, light yellow crystals of the reaction product; yield, 0.15 g. The substance is sparingly soluble in glacial acetic acid and forms pale yellow plates from this solvent. The alkaline solution has a brilliant green-yellow fluorescence, while the solution in sulfuric acid is orange-brown. The compound begins to decompose at about 340°. The diacetate forms nearly colorless leaflets from glacial acetic acid, m. p. 266°, dec.

*Anal.* Calcd. for  $C_{18}H_{14}O_2$ : C, 80.64; H, 5.92. Found: C, 80.32; H, 6.22. *Anal.* (diacetate). Calcd. for  $C_{26}H_{18}O_4$ : C, 74.50; H, 5.62. Found: C, 74.49; H, 5.91.

## 2. 1,5-Diallyl-2,6-dihydroxyanthracene

This compound was obtained as the acetyl derivative by the rearrangement of 2,6-dihydroxyanthracene diallyl ether. For the preparation of the ether the direct allylation of the dihydroxy compound was first investigated, but with unfavorable results. It was found better to allylate anthraflavinic acid and to reduce this to the desired ether.

**Anthraflavinic acid diallyl ether** was prepared by refluxing for sixty hours a mixture of 4.1 g. of anthraflavinic acid,<sup>23</sup> 5 g. of allyl bromide, 8 g. of anhydrous potassium carbonate and 100 cc. of acetone. Fresh allyl bromide was added to compensate for some losses and at the end of the period indicated the suspension had assumed a homogeneous orange appearance. After adding water and evaporating the acetone, unchanged material was removed with alkali and the product was crystallized from glacial acetic acid; yield, 4.3 g. (79%). The substance forms long, bright yellow needles, m. p. 149°.

(21) Hall and Perkin, *J. Chem. Soc.*, **123**, 2029 (1923).

(22) Wislicenus, *J. prakt. Chem.*, **54**, 54 (1896).

(23) We are indebted to E. I. du Pont de Nemours & Co. for kindly supplying this material.

*Anal.* Calcd. for  $C_{20}H_{18}O_4$ : C, 74.97; H, 5.03. Found: C, 74.84; H, 5.08.

The ether is extensively decomposed at temperatures above 230–240° and there were no indications of a rearrangement at lower temperatures.

**2,6-Dihydroxyanthracene Diallyl Ether.**—The quinone was reduced as in the above series, stannous chloride giving an unstable, oily, anthrone-like product which was at once reduced further with aluminum amalgam and alcoholic ammonia. The crude product was crystallized from glacial acetic acid, giving pale yellow plates, m. p. 201°, in 21% yield.

*Anal.* Calcd. for  $C_{20}H_{18}O_2$ : C, 82.70; H, 6.27. Found: C, 83.02; H, 6.33.

**1,5-Diallyl-2,6-dihydroxyanthracene Diacetate.**—Attempts to rearrange the diallyl ether by heating the substance alone or in diethylaniline solution (nitrogen atmosphere) gave only very unpromising gums, but it was found possible to isolate the product as the acetyl derivative by carrying out the rearrangement in the presence of acetic anhydride. A mixture of 0.2 g. of the diallyl ether and 1 cc. each of diethylaniline and acetic anhydride was heated for two and one-half hours at 160–180° under nitrogen. On cooling, the solution set to a paste of crystals and the product was collected, washed with hexane and ether, and recrystallized from acetic acid; yield, 0.15 g. (55%). The substance forms faintly buff colored plates, m. p. 179°.

*Anal.* Calcd. for  $C_{24}H_{22}O_4$ : C, 76.97; H, 5.93. Found: C, 76.66; H, 6.05.

The diacetate is easily hydrolyzed by alcoholic alkali giving, in the absence of oxygen, a light red-brown solution with a greenish fluorescence. An intractable, oily product separated on careful acidification and the free dihydroxy compound was not isolated.

## 3. Coupling Tests

Alkaline, oxygen-free solutions were prepared from 1,5-dimethyl-2,6-dihydroxyanthracene and from 1,5-diallyl-2,6-diacetoxyanthracene and tested for coupling with diazotized sulfanilic acid and diazotized *p*-nitroaniline. There was no indication of the formation of azo compounds at 0°, the solutions retaining the original appearance.

## Summary

Derivatives of 2,6-dihydroxyanthracene having substituents in the 1- and 5-positions do not couple with diazotized amines although ortho positions are available for such a reaction. It is concluded that these positions are connected by single linkages and are incapable of forming parts of enolic systems. The evidence indicates that anthracene exists to an appreciable extent in only one of the two possible ortho-quinonoid forms. The position of the equilibrium between the tautomeric forms of unsymmetrical derivatives of anthracene can be inferred from oxido-reduction potential data for quinones.