When 1.0688 g. of sequoyite was heated with hydriodic acid in a small distilling flask, 0.9192 g. or 86.0% of the sequoyite was recovered as *i*-inosite and a sufficient amount of the methyl iodide was collected for a boiling-point determination. It boiled between 43 and 44°. A maximum yield of 93.1% of the theoretical amount of *i*-inosite or 89.4% of the weight of the sequoyite was obtained from a hydriodic acid residue remaining from a methoxyl determination.

A careful investigation of the chemical literature indicates that no compound with the properties here described has been previously reported. We are therefore convinced that we have isolated a new cyclose. Since methyl iodide and *i*-inosite are the only decomposition products obtained and since they are obtained in the proportion corresponding to a compound having the molecular formula $C_6H_6(OH)_5OCH_3$, sequoyite must be a monomethyl ether of inactive inosite.

Summary

1. The isolation of a new cyclose from the heartwood of redwood has been described.
2. Experimental results show that this compound is a monomethyl ether of *i*-inosite.
3. Upon heating with hydriodic acid, two decomposition products are obtained and have been identified as methyl iodide and *i*-inosite.
4. The pentacetate derivative has been prepared and described.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

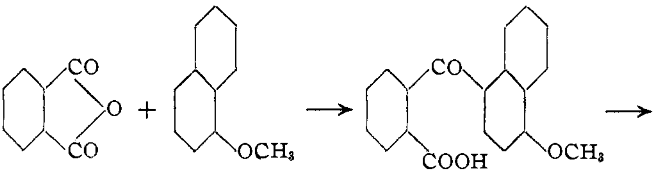
1,2-BENZ-3,4-ANTHRAQUINONE

BY LOUIS F. FIESER AND EMMA M. DIETZ

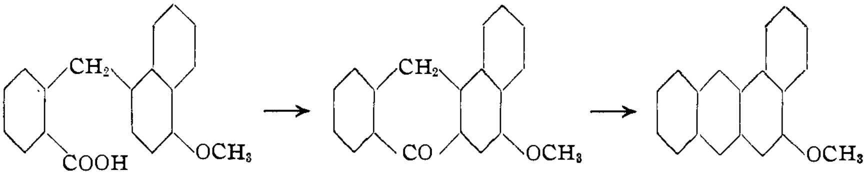
RECEIVED JUNE 10, 1929 PUBLISHED OCTOBER 5, 1929

In connection with a study of the reduction potentials of some of the higher benzologues of anthraquinone and phenanthrenequinone, we became interested in securing the compound named in the title. A suitable method of preparing the quinone was found in the oxidation of 4-amino-3-hydroxy-1,2-benzanthracene, which, in turn, was obtained from 3-hydroxy-1,2-benzanthracene.

The synthesis of the methyl ether of 3-hydroxy-1,2-benzanthracene, IV, was accomplished in the following manner



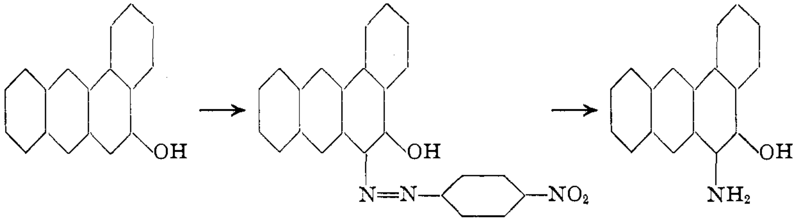
I



II III IV

2-(4′-Methoxy-naphthoyl-1′)-benzoic acid, I, has been described by Scholl, Seer and Zincke,[1] and the structure which they assumed for the acid is established by the present work. By using tetrachloro-ethane rather than nitrobenzene as the solvent in carrying out the Friedel and Crafts reaction, their method of preparation became easily applicable to quantity production. While the keto-acid, I, failed to condense easily to give an anthraquinone, the condensation of the reduction product, II, to the anthrone, III, was accomplished readily by dissolution in cold, concentrated sulfuric acid. 3-Methoxy-1,2-benz-10-anthrone, III, is a rather unstable compound and it was isolated only in the form of the acetyl derivative of the enol modification. It was reduced to 3-methoxy-1,2-benzanthracene, IV, with aluminum amalgam and ammonia in alcoholic suspension, according to the general method of Hall and Perkin.[2] Owing to side reactions, the yield was only about 55%.

On hydrolysis of the ether with a hydrobromic acid–glacial acetic acid mixture, 3-hydroxy-1,2-benzanthracene (V) was obtained. This phenol, which was characterized by the preparation of a number of derivatives, is



V VI VII

only very sparingly soluble in alkali and it failed to couple with diazotized sulfanilic acid under a variety of conditions. An azo compound was obtained only by the use of the method which Meyer, Irschick and Schlösser developed for carrying out the coupling reaction with phenol ethers.[3] By the interaction of 3-hydroxy-1,2-benzanthracene and *p*-nitrobenzene diazonium sulfate in glacial acetic acid solution the dyestuff, VI, was produced without difficulty. Being only very sparingly soluble in organic solvents or in alkali, the dyestuff is not easily reduced by the usual methods, but a satisfactory means of preparing the amine, VII, was found in the re-

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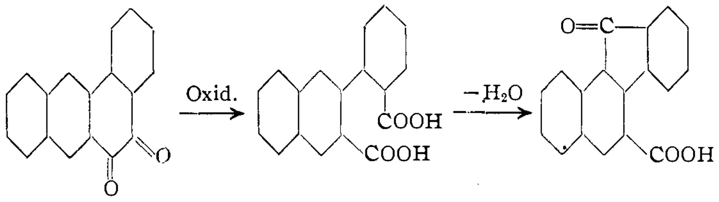
[1] Scholl, Seer and Zincke, *Monatsh.*, **41**, 598 (1920).

[2] Hall and Perkin, *J. Chem. Soc.*, **123**, 2029 (1923).

[3] Meyer, Irschick and Schlösser, *Ber.*, **47**, 1747 (1914).

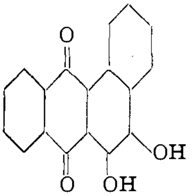
duction of the azo compound with stannous chloride in a boiling butyl alcoholic suspension.

The hydrochloride of 4-amino-3-hydroxy-1,2-benzanthracene yielded 1,2-benz-3,4-anthraquinone, VIII, on oxidation in glacial acetic acid solution. The quinone crystallizes in bright red needles and forms a bisulfite addition product. It was converted by oxidation with hydrogen peroxide in glacial acetic acid solution into a substance having the properties of a diphenic acid derivative. This acid, to which the structure of 4,5-benzodiphenyl-2,2′-dicarboxylic acid, IX, may be assigned, was condensed by the action of concentrated sulfuric acid to a yellow fluorenone-carboxylic acid which probably has the structure of X, though the structure of 2,3-benzofluorenone-5-carboxylic acid is also possible. These facts indicate that the quinone in question is of the ortho type and similar to 9,10-phenanthrenequinone, hence that it has the structure of VIII.

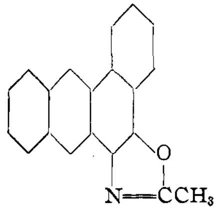


VIII IX X

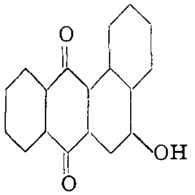
The structure of the hydroxybenzanthracene, V, is fixed by the method of synthesis and the structure of the above ortho-quinone; but the following independent evidence also may be cited. By the reductive acetylation of 1,2-benz-3,4-anthraquinone, followed by oxidation and by hydrolysis of the oxidation product, there was obtained the dihydroxy-1,2-benz-9,10-anthraquinone, XI. The compound gives an intense coloration with Dimroth's boro-acetic anhydride reagent,[4] showing that one hydroxyl group is adjacent to a quinonoid carbonyl group. The second hydroxyl group must be ortho to the first, for the hydroxybenzanthracene couples in the ortho position, as shown by the formation of an oxazole derivative, XII, from 4-amino-3-hydroxy-1,2-benzanthracene. The dihydroxyquinone, XI, could be formed from either 3- or 4-hydroxy-1,2-benzanthracene, but the latter possibility is excluded by the fact that the monohydroxy-1,2-



XI



XII



XIII

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[4] Dimroth and Faust, *Ber.*, **54**, 3020 (1921); Dimroth, *Ann.*, **446**, 97 (1926).

benz-9,10-anthraquinone (XIII), prepared by the oxidation of the acetyl derivative and the hydrolysis of the oxidation product, gives a negative result in the Dimroth test.

Experimental Part

2-(4′-Methoxynaphthoyl-1′)-benzoic Acid (I).[1]—To a solution of 78 g. of α-methoxynaphthalene and 78 g. of phthalic anhydride in 400 cc. of tetrachloro-ethane there was added 150 g. of powdered aluminum chloride in three portions. The mixture was stirred mechanically at room temperature for twelve hours and allowed to stand for an equal period of time. The dark addition product was decomposed with ice and hydrochloric acid and the solvent was removed by steam distillation. This operation was completed in a small fraction of the time required when nitrobenzene was employed as the solvent. The granular, brown residue was dissolved in the requisite quantity of hot sodium carbonate solution, the solution was treated with animal charcoal and then 50 cc. of 6 *N* sodium hydroxide solution was added. The sodium salt of the acid separated from the cooled solution in the form of colorless crystals. When washed with sodium chloride solution and dried, the product contained a small quantity of sodium chloride but it was otherwise pure and the salt was well suited for carrying out the following reaction; yield, 147 g. (91%). The acid obtained from this sodium salt melted at 196–197° (Scholl, Seer and Zincke, 193–194°).

(4-Methoxynaphthyl-1)-phenylmethane-2′-carboxylic Acid (II).—A solution of 86 g. of the sodium salt of 2-(4′-methoxynaphthoyl-1′)-benzoic acid and 104 g. of sodium hydroxide in 1.5 liters of water was treated with 145 g. of zinc dust and the mixture was heated so as to maintain a lively evolution of gas for ten hours. The hot solution was filtered, the zinc was extracted with several portions of boiling water and 50 cc. of 6 *N* sodium hydroxide was added to the filtrate. The sodium salt often separated in an oily condition but it soon crystallized. The material was washed with sodium chloride solution, dissolved in water and converted into the free acid. Prepared by precipitation, the acid was not easily collected by filtration until it had been coagulated somewhat by heating the mixture to the boiling point. A colorless product melting at 215–219° and requiring no further purification was obtained; yield, 75 g. (91%).

The acid dissolves readily in alcohol, benzene or glacial acetic acid. It forms colorless plates melting at 217–219° (221–223°, corr.).

Anal.[5] Calcd. for $C_{19}H_{16}O_3$: C, 78.07; H, 5.52. Found: C, 78.01; H, 5.62.

3-Methoxy-1,2-benz-10-anthrone (III).—The above acid dissolves in cold, concentrated sulfuric acid to give a deep red solution and ring closure takes place without side reactions. Twenty grams of the powdered acid was stirred into 220 cc. of concentrated sulfuric acid at 20° and after forty-five minutes the solution was slowly poured into 1.2 liters of a well-stirred mixture of ice and water. This precipitated a finely divided, pale yellow product which was collected and washed with dilute ammonia solution. The anthrone is very sensitive to heat and to oxygen, particularly when in solution, and it was not purified for analysis. A glacial acetic acid solution rapidly turned dark green and deposited a brown, amorphous material while still well below the boiling point. The anthrone dissolves readily in alcohol or benzene, but the solutions darken rapidly; it dissolves slowly in alkali.

For purposes of identification the **acetyl derivative** of the anthranol form was prepared by boiling for a short time a solution of 0.7 g. of the anthrone in 3 cc. of pyridine and 5 cc. of acetic anhydride. The product, crystallized from benzene–ligroin and from alcohol, formed colorless needles melting at 194° (197° corr.).

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[5] The Dennstedt platinum contact star was employed in carrying out all of the analyses reported.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72, H, 5.10. Found: C, 79.76; H, 5.14.

3-Methoxy-1,2-benzanthracene (IV).—The reduction of the anthrone was carried out in alcoholic suspension with aluminum amalgam and ammonia, a method employed extensively by Hall and Perkin.[2] In the present case the reaction is difficult to control and the formation of by-products greatly decreases the yield. It was found advisable to work with no more than 20 g. of material at one time and to prepare the amalgam very carefully, according to the directions of Wislicenus.[6] Twenty grams of aluminum turnings was etched with 10% sodium hydroxide, washed with water, shaken for one-half minute with a 0.5% mercuric chloride solution, washed again, and the whole process was repeated. The resulting amalgam was added to 960 cc. of alcohol and the mixture was heated to obtain a lively gas evolution. The cake of moist anthrone obtained as above from 20 g. of (4-methoxynaphthyl-1)-phenylmethane-2′-carboxylic acid was broken into large pieces and introduced into the mixture. Sixty cc. of concentrated ammonia solution was then added gradually. The mixture was boiled under the reflux condenser for four hours, 30 cc. of ammonia solution and the amalgam from 10 g. of aluminum being added after the second and third hours. The light yellow solution rapidly became deep red and later pale yellow or pink, while much aluminum hydroxide separated. At the end of the reaction the liquid was decanted, treated with 250 cc. of concentrated hydrochloric acid and heated to the boiling point in order to dissolve the hydroxide, which otherwise occludes much material. An equal volume of water was added, the solution was cooled and the material which separated was collected and again digested with hydrochloric acid. The dried residue (17 g.) contained some inorganic material. It was extracted twice with benzene and the well-concentrated, dark red solution deposited 10 g. of straw-colored needles, m. p. 165–167°.

3-Methoxy-1,2-benzanthracene is very soluble in benzene or chloroform, moderately soluble in alcohol or glacial acetic acid, and the solution in the latter solvent has a violet fluorescence. The pure material forms colorless needles melting at 167–168°.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.47. Found: C, 88.03; H, 5.47.

When the preparation was carried out exactly as described above, the yield was usually from 45 to 55% of the theoretical, though in two instances it rose to 65%. The results were much poorer (25%) when the mixture was stirred and when the anthrone was added in very small portions. In this instance it was possible to isolate a considerable quantity of a yellow by-product which melted at 272° and which was less soluble than 3-methoxy-1,2-benzanthracene. The yellow substance contains a higher percentage of oxygen than the original material and it is probably a dimolecular product. Traces of the substance were always present in the residue after extracting the main product with benzene.

3-Methoxy-1,2-benz-9,10-anthraquinone.—3-Methoxy-1,2-benzanthracene was oxidized in glacial acetic acid solution at 90° with chromic acid. The oxidation product, precipitated by the addition of water after one-half hour, was crystallized from methyl ethyl ketone and from benzene. It forms brown-red needles melting at 188.5°. It forms a red vat with alkaline hyposulfite solution, while the solution in concentrated sulfuric acid is intensely blue-green. The quinone is moderately soluble in benzene or glacial acetic acid and only slightly soluble in alcohol.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.13; H, 4.20. Found: C, 78.96; H, 4.19.

3-Hydroxy-1,2-benzanthracene (V).—The hydrolysis of 3-methoxy-1,2-benzanthracene was accomplished by the use of hydrobromic acid. Aluminum chloride had no effect in carbon disulfide solution and when heated with the solid material it caused decomposition. A hot, stirred solution of 33 g. of the ether in 1 liter of glacial acetic

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[6] Wislicenus, *J. prakt. Chem.*, [2] **54**, 54 (1896).

acid was treated with 43 cc. of 40% hydrobromic acid and boiled for one and three-quarters hours. The color changed from yellow to dark green to red-brown and finally to a pale orange. On adding 50 cc. of water to the solution and cooling, 27.2 g. (87.5%) of nearly pure, greenish-yellow needles separated. Recrystallization from toluene removed a trace of green material and small, orange-yellow needles were obtained. The substance melts with decomposition at about 196–205° and imparts an orange color to the glass capillary. It is moderately soluble in toluene, less soluble in alcohol, and the sodium salt, which is yellow, is very sparingly soluble. The solutions darken on long heating. The material may be distilled at a reduced pressure without much decomposition if care is taken to avoid contact of the hot material with the air.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.50; H, 4.96. Found: C, 88.47; H, 4.81.

3-Acetoxy-1,2-benzanthracene.—Prepared by boiling a solution of the hydroxy compound in acetic anhydride for one hour, and crystallized from benzene and from benzene–ligroin, the acetate formed colorless needles melting at 129°.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.93; H, 4.93. Found: C, 83.67; H, 4.99.

3-Acetoxy-1,2-benz-9,10-anthraquinone.—The oxidation of the acetate with chromic acid in glacial acetic acid proceeded smoothly and in nearly quantitative yield when the solution was kept at a temperature of 70°. The quinone, which is moderately soluble in toluene or glacial acetic acid, formed small, yellow crystals melting at 232°.

Anal. Calcd. for $C_{20}H_{12}O_4$: C, 75.93; H, 3.83. Found: C, 76.13; H, 4.00.

3-Hydroxy-1,2-benz-9,10-anthraquinone (XIII) was prepared, but not purified for analysis, by warming the acetate with alcoholic alkali. The intensely purple solution which resulted deposited a light brown product on acidification. The quinone dissolves in concentrated sulfuric acid with an intense blue-green color; in pyridine it forms a dark orange-red solution; while the solution in boro-acetic anhydride is pale yellow. The alkali salts of the quinone dissolve with difficulty in water but give purple solutions in alcohol; the vat is orange.

4-Amino-3-hydroxy-1,2-benzanthracene (VII).—This compound was prepared in the form of the hydrochloride and analyzed as the triacetate. It was obtained from 3-hydroxy-1,2-benzanthracene by the formation and reduction of an azo dye. Attempts to couple this phenol with diazotized sulfanilic acid in aqueous or alcoholic suspension or in pyridine solution were unsuccessful, but it was found possible to prepare **4-(*p*-Nitrobenzene-azo)-3-hydroxy-1,2-benzanthracene** (VI) in the following manner. Sixteen and seven-tenths g. of *p*-nitro-aniline was converted into *p*-nitrobenzene diazonium sulfate as described by Meyer, Irschick and Schlösser[3] and dissolved in glacial acetic acid. On adding this solution to a well-stirred, cooled solution of 15 g. of 3-hydroxy-1,2-benzanthracene in 1250 cc. of glacial acetic acid, a dark red dyestuff separated immediately. On completion of the reaction the solution was diluted with water and the product was collected. The substance is insoluble in alkali and sparingly soluble in most organic solvents. It dissolves fairly readily in nitrobenzene but does not form good crystals suitable for analysis.

For the reduction of the dye it is advisable to use the moist material. The above product was suspended in 850 cc. of *n*-butyl alcohol containing 100 g. of stannous chloride and 200 cc. of concentrated hydrochloric acid. The mixture was stirred mechanically and heated at the boiling point for four to five hours, when all of the dye had dissolved to give a clear orange solution. On adding 150 cc. of concentrated hydrochloric acid and cooling, pale yellow crystals of the amine hydrochloride separated. A further quantity (3 g.) was obtained on concentrating the mother liquor in a vacuum; yield, 21 g. Dried at room temperature, the material contained some solvent, but only traces of tin. In solution the substance decomposes very easily in the absence of a reducing agent and an analytically pure sample was not obtained. It is sparingly soluble in water but soluble in alcohol. For purposes of characterization it was converted into the following derivatives.

Triacetate of 4-amino-3-hydroxy-1,2-benzanthracene.—This was prepared by boiling for one hour an acetic anhydride solution of equal parts of the amine hydrochloride and fused sodium acetate. The product was not homogeneous but the less soluble fraction yielded, after repeated crystallization, a substance crystallizing in colorless plates and melting constantly at 199–201° (203–205°, corr.). The compound is insoluble in acids or alkalies and dissolves readily in benzene or glacial acetic acid. It is converted by distillation into the oxazole derivative.

Anal. Calcd. for $C_{24}H_{19}O_4N$: C, 74.78; H, 4.97. Found: C, 74.27, 74.13; H, 5.13, 5.22.

Oxazole Derivative of 4-amino-3-hydroxy-1,2-benzanthracene (XII).—The crude product obtained on acetylating in the manner described above was distilled *in vacuo.* After the removal of acetic acid and anhydride, the oxazole distilled as a yellow oil which soon solidified. It is only moderately soluble in glacial acetic acid but it dissolves easily in benzene and separates in clusters of light yellow needles, m. p. 175.5°.

Anal. Calcd. for $C_{20}H_{13}ON$: C, 84.78; H, 4.63. Found: C, 84.99, 85.05; H, 5.05, 5.00.

1,2-Benz-3,4-anthraquinone (VIII).—The 4-amino-3-hydroxy-1,2-benzanthracene obtained from 15 g. of 3-hydroxy-1,2-benzanthracene was largely dissolved in 670 cc. of glacial acetic acid, a solution of 5 g. of chromic anhydride was added at 100° and the temperature was held there for fifteen minutes. On adding water a dull red product was obtained. The quinone was extracted with toluene from some dark brown material, giving 8.1 g. of bright red needles. The yield from 3-hydroxy-1,2-benzanthracene was 57% of the theoretical.

The quinone is moderately soluble in toluene or glacial acetic acid, less soluble in benzene or alcohol. The solution in concentrated sulfuric acid is purple in color; in pyridine it is red-orange. The quinone dissolves slightly in hot concentrated bisulfite solution and precipitates on the addition of sodium carbonate. The pure material forms red needles melting with some decomposition at 254–255° (262–263°, corr.).

Anal. Calcd. for $C_{18}H_{10}O_2$: C, 83.70; H, 3.90. Found: C, 83.56; H, 3.79.

3,4-Diacetoxy-1,2-benzanthracene.—The quinone was reduced and acetylated by heating a mixture with equal parts of zinc dust and fused sodium acetate and with 10 parts of acetic anhydride for one-half minute, when the original dark green color was replaced by a clear orange. An equal volume of glacial acetic acid was added and the heating continued until all of the quinone had dissolved and the solution had lost all red color, but the heating was discontinued at the first sign of darkening. A pale yellow product was obtained on decanting into water. The substance dissolves readily in benzene and forms plates containing solvent of crystallization. From methyl alcohol, in which it is much less soluble, small, faintly pink needles were obtained. The solution in benzene has a marked blue fluorescence. The melting point is 197° (201°, corr.).

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.72; H, 4.69. Found: C, 76.47; H, 4.69.

3,4-Diacetoxy-1,2-benz-9,10-anthraquinone.—The oxidation of the above diacetate was carried out with an equal weight of chromic anhydride in glacial acetic acid solution at 70°, the yield being nearly quantitative. The quinone crystallizes from benzene or glacial acetic acid in the form of small, yellow prisms melting at 198–199°.

Anal. Calcd. for $C_{22}H_{14}O_6$: C, 70.58; H, 3.77. Found: C, 70.75; H, 3.83.

On hydrolysis of the quinone with alcoholic alkali, **3,4-dihydroxy-1,2-benz-**

9,10-anthraquinone (XI) was obtained as a purplish black powder. The solutions of the quinone in organic solvents are red or purple. The color in concentrated sulfuric acid is an intense Prussian blue and in warm pyridine it is orange red. The alkaline solution is bluish green; the solution in acetic anhydride is pale red and in boro-acetic anhydride it is an intense chrome green. The structure of this dihydroxyquinone is a combination of those of alizarin and of 1,2-benzanthraquinone, both of which are valuable dyes; but the compound is too sparingly soluble in water to be applied to mordanted cloth and the greenish blue dyeing imparted to cotton on vatting is not fast to washing with soap.

4,5-Benzodiphenyl-2,2′-dicarboxylic Acid (IX).—This acid resulted from the oxidation of 1,2-benz-3,4-anthraquinone. A solution of 3 g. of the quinone in 300 cc. of glacial acetic acid was treated with 2 cc. of 30% hydrogen peroxide and the temperature was maintained at 90° for one hour, when the original red color had paled somewhat. After a second addition of peroxide, the solution was allowed to stand for ten hours and then it was concentrated to a small volume and diluted with water. A light brown oil separated and soon crystallized. After precipitation from a sodium carbonate solution, the material was crystallized from dilute methyl alcohol, when it formed slightly tan microcrystals melting at 246° (252°, corr.). The yield was 2.6 g.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 73.96; H, 4.14. Found: C, 74.08; H, 4.18.

1,2-Benzofluorenone-4-carboxylic Acid (X) (or 2,3-Benzofluorenone-5-carboxylic Acid).—A solution of 0.6 g. of 4,5-benzodiphenyl-2,2′-dicarboxylic acid in 50 cc. of concentrated sulfuric acid was allowed to stand for several hours; the dark green solution was then poured into water and the fine yellow precipitate was collected. The product appeared to be homogeneous. It dissolved readily in glacial acetic acid and the solutions tended to remain supersaturated. It crystallizes well from toluene, in which it is moderately soluble, forming slender, yellow needles melting at 261° (268°, corr.).

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.83; H, 3.68. Found: C, 78.79; H, 3.90.

Summary

3-Methoxy-1,2-benzanthracene has been synthesized from phthalic anhydride and α-methoxynaphthalene and converted into 3-hydroxy-1,2-benzanthracene. The latter compound was converted, through the *p*-nitrobenzene-azo derivative, into the 4-amino derivative, which yielded 1,2-benz-3,4-anthraquinone on oxidation.

BRYN MAWR, PENNSYLVANIA