

ISOCYANATES OF 9-METHYL AND 9,10-DIMETHYL-
1,2-BENZANTHRAcene

By

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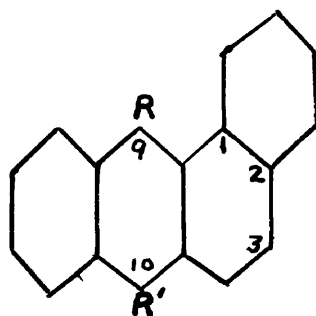
INTRODUCTION

In the early part of this century it was noted that persons doing work which required long exposure to coal tar or related products often developed skin cancer. It was suspected that specific hydrocarbons caused these cancers and in 1930 Kennaway and Meiger²³ found that 1,2,5,6-dibenzanthracene possessed marked carcinogenic activity.

Since that time a large number of hydrocarbons have been tested. One of these, 3,4-benzpyrene, which was isolated from pitch was found to be somewhat more active than 1,2,5,6-dibenzanthracene.

One of the most powerful carcinogenic hydrocarbons is methyl cholanthrene. This can be prepared from desoxycholic acid and from cholesterol, both of which are normal constituents of human bile. The hypothesis has been advanced that cancer-producing hydrocarbons may appear in the organism as a result of abnormal metabolism of bile acids or other normal constituents of the body.¹⁷

An important feature common to all of these compounds is the presence of the nucleus of 1,2-benzanthracene (D). This compound is itself inactive, but derivatives with a methyl group at the 9- or 10- position are of particular interest. 10-Methyl-1,2-benzanthracene (E), produces cancer nearly as rapidly as methyl cholanthrene, and the 9-methyl compound, (F), is only slightly less active. The 9,10-dimethyl-1,2-benzanthracene, (G), is



- | | | |
|-----|-----------------------|----------------------|
| (D) | R = H; | R' = H |
| (E) | R = H; | R' = CH ₃ |
| (F) | R = CH ₃ ; | R' = H |
| (G) | R = CH ₃ ; | R' = CH ₃ |

more potent than either of the monomethyl compounds and in fact it is perhaps the most rapidly acting carcinogen known.¹⁷

In the past several years a study has been made of certain isocyanate derivatives of these active hydrocarbons.¹⁵ Among the most important of the isocyanates which have been described are the 9-isocyanate of 1,2,5,6-dibenzanthracene, the 5-isocyanate of 3,4-benzpyrene, and the 3-isocyanate of 10-methyl-1,2-benzanthracene (E).

It has been shown that these isocyanates may be coupled with amino acids and proteins "in vitro".⁸ The possibility that they may combine with tissue proteins "in vivo" is worthy of consideration.⁷ It may be possible to produce antisera from these hydrocarbon-protein conjugates which are capable of preventing hydrocarbon car-

cinogenesis.* Recent immunological studies on these conjugates have produced results of considerable interest.⁹ The 9-amino derivative of 1,2,5,6-dibenzanthracene shows slight carcinogenic activity^{15(b),6} while the 9-isocyanate prepared from this amine has pronounced activity. Since it seemed very desirable that these studies be extended, the synthesis of 9,10-dimethyl-1,2-benzanthryl-3-isocyanate [(IX), Figure I] and 9-methyl-1,2-benzanthryl-3-isocyanate [(IX A), Figure I] was attempted. These are derivatives of the very active hydrocarbons (F) and (G).

* Dr. H. J. Creech will conduct this work at the Lankenau Hospital Research Institute in Philadelphia.

DISCUSSION

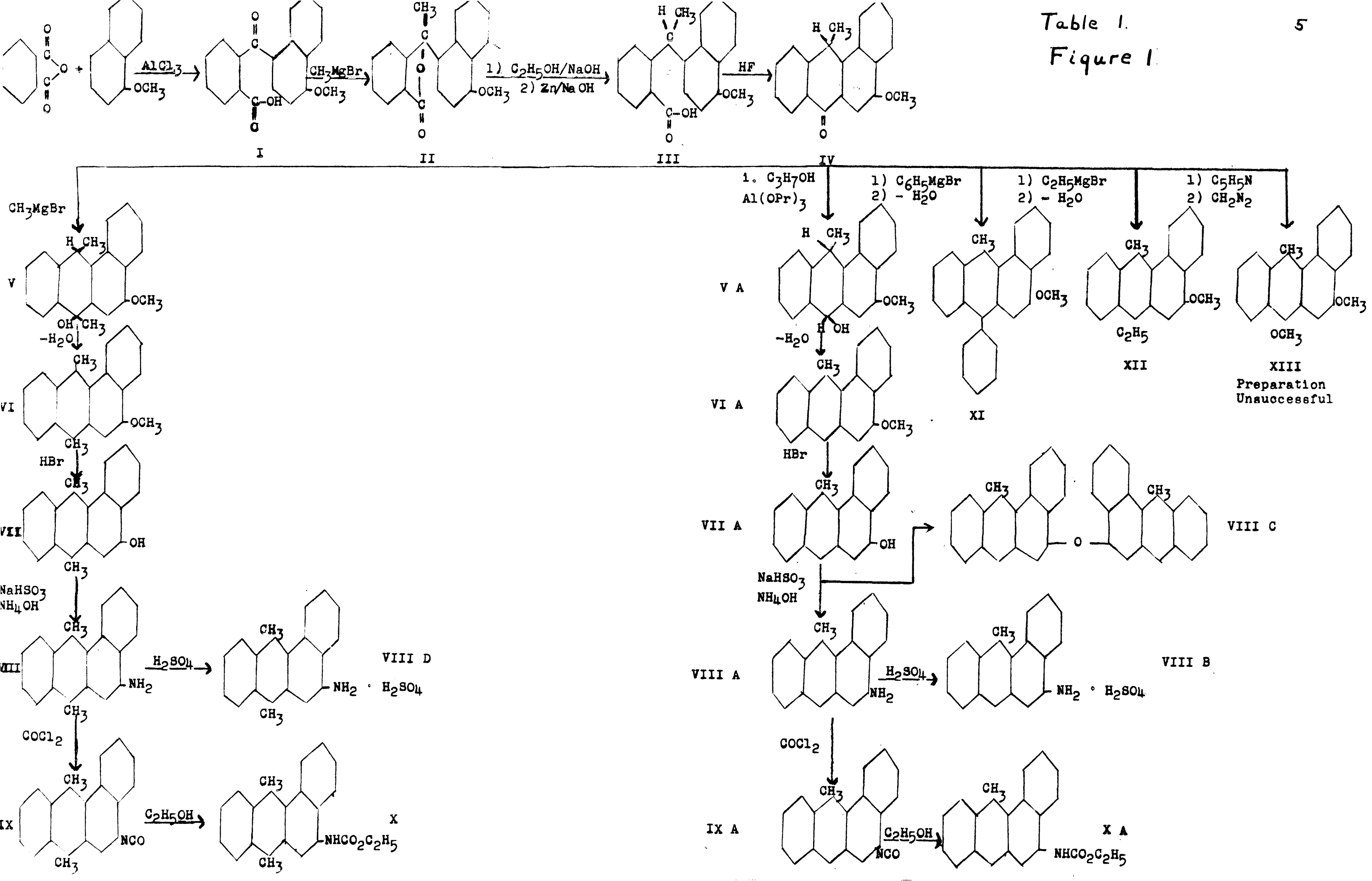
The methods of synthesis of 9,10-dimethyl-1,2-benzanthryl-3-isocyanate and of 9-methyl-1,2-benzanthryl-3-isocyanate are outlined in the following chart (Figure 1). The key intermediate is 3-methoxy-9-methyl-1,2-benz-10-anthrone. It was prepared from phthalic anhydride and α -methoxynaphthalene by the four step synthesis outlined. The anthrone is a versatile intermediate. Not only were the two isocyanates (IX) and (IX A) made from it but two methoxybenzanthracenes (XI) and (XII) which are unsymmetrically substituted in the meso positions were also prepared from this important compound. An attempt to convert the anthrone to 3,10-dimethoxy-9-methyl-1,2-benzanthracene was unsuccessful.

Great difficulty was encountered with two reactions of the synthesis but conditions were finally found under which these reactions were carried out in good yield. Nine successive reactions are required to convert α -methoxynaphthalene to either the mono- or the dimethylbenzanthryl isocyanates (IX) and (IX A). The yields were good for each step; they varied from 68% to 96%. The overall yield for the nine reactions was about 28% in each case. Stated in another way, fifty-one grams of the dimethylbenzanthryl isocyanate (IX) could be obtained from one hundred grams of α -methoxy naphthalene.

2-(4'-Methoxynaphthoyl-1')- benzoic acid (I).

This compound was readily prepared by the method of

Table I.
Figure 1.



Fieser and Dietz.¹⁶ By strictly controlling the reaction temperature and eliminating the extremely wasteful decolorization with carbon, it was possible to improve the purity of the product a great deal and at the same time to raise the yield to 95% from 91%.

This reaction was conveniently handled in the laboratory using twice the quantities reported in the experimental part.

Lactone of 2-[α -hydroxy- α -(1'-(4'-methoxynaphthyl)-ethyl)]-benzoic acid (II).

The preparation of this compound, using Newman's method for synthesis of another lactone,²⁶ was attempted by E. Walton of this University in October, 1942. Repeated attempts to crystallize the reaction product were not successful.

The author also encountered difficulty in this crystallization until the proper technique and solvents were found. Many solvents and solvent mixtures were tried, but only the ones described were found to be satisfactory.

A toluene solution of the lactone was concentrated to a small volume by evaporation under reduced pressure. About one-third volume of alcohol was added and then petroleum ether (30-60°) was very carefully added with almost continuous swirling until just a trace of turbidity appeared. The amount of petroleum ether was found to be critical for the slightest excess caused an oil to separate. Upon cooling in a refrigerator, the product crystallized rapidly once a seed crystal had formed. In subsequent runs

crystallization was easy since seed crystals were available. It was interesting to observe that two liquid phases were present when crystallization occurred. After a 57% yield was obtained, no further lactone would crystallize from the now homogeneous solution. Further manipulation with solvents in attempts to cause more lactone to crystallize was fruitless. It was found, however, that the crude lactone in the mother liquors could be readily purified by molecular distillation. The lactone distilled nicely and the distillate crystallized immediately; these crystals melted at the same temperature as those obtained from the solvents and when a mixture of the crystals from the two sources was melted the melting point was not lowered. The total yield of crystals from both sources was 70%.

2-[α -1'-(4'-Methoxynaphthyl)-ethyl]-benzoic acid (III).

An attempt was made to cleave the lactone to the substituted benzoic acid by the Clemmensen method of reduction.²⁵ Amalgamated zinc was used with a two layer solvent system of hydrochloric acid, water, and toluene. The toluene layer holds most of the compound to be reduced out of contact with the zinc so that any tendency to form polymolecular compounds which coat and thereby inactivate the zinc is decreased. After the reaction mixture was refluxed thirty-one hours, the product was isolated by crystallization. It melted at 143.1-145.8° and when it was mixed with starting material the melting point was

depressed only very slightly to 139-141°; this indicated little reaction had occurred.

Martin's modification of the Clemmensen method²⁴ gave similar results. The lack of reaction may have been due to steric hindrance for Martin was able to reduce δ -phenylbutyrolactone to δ -phenylbutyric acid with amalgamated zinc and hydrochloric acid.

It was found that the desired acid could be obtained in 98% yield by Newman's method.²⁷ The lactone was refluxed twenty-four hours with aqueous sodium hydroxide and alcohol followed by activated zinc and aqueous alkali. The product, which was isolated by standard methods, melted at 197.3-198.1°.

3-Methoxy-2-methyl-1,2-benz-10-anthrone (IV).

Anhydrous hydrofluoric acid was used to cyclize the substituted benzoic acid to the anthrone.¹⁸ It was found that by using an amount of hydrofluoric acid equivalent to ten times the weight of the substituted benzoic acid (III) the desired product was obtained in good yield; the large excess of hydrofluoric acid gave a low viscosity solution which was convenient to handle. Vigorous stirring is essential during the addition of the reaction mixture to pulverized ice if the formation of lumps which interfere with efficient washing is to be avoided. All attempts to crystallize the anthrone led only to tars. Similar results were obtained by Fieser and Gason¹⁴ in their work on the cyclization of o-(7-acenaphthyl)-benzoic acid with hydrofluoric acid. Acetone is the recommended solvent for this

type of compound for it favors the tautomerization of the enol to the keto form.

When the anthrone was prepared as described here, it was found to be stable after all solvent and any other volatile material was removed by distillation. This is in contrast to previous reports¹⁶ in which it is stated that similar anthrones are very sensitive to heat and oxygen and therefore they must be used immediately after preparation. In this investigation anthrone which was several months old was as satisfactory as the freshly prepared material. Consequently it was possible to prepare several batches at one time and store the product until ready for use; in this way much time and effort could be saved.

This anthrone is the important intermediate from which the monomethyl and dimethyl benzanthryl isocyanates (IX) and (IX A) were prepared.

3-Methoxy-9,10-dimethyl-1,2-benzanthracene (VI).

The intermediate tertiary alcohol (V) was prepared by treating the anthrone (IV) with methylmagnesium bromide. The product could not be obtained in pure, crystalline form although small quantities of brown scales melting over a wide range in the vicinity of 200° were often obtained. Possibly the chief impurity was the dehydration product (VI), for upon heating the crude tertiary alcohol on a hot plate at 200° the methoxydimethyl-benzanthracene (VI) was readily obtained. Excessive heating increased

the amount of dark, tarry material produced. This crude dehydrated product was very effectively purified by converting it to the picrate. Impurities were removed from the picrate by adsorbing them from benzene solution on a column of alumina and supercel; at the same time the picrate was dissociated and a solution containing only the desired product passed through the column. This solution showed bright blue fluorescence and it was found that the intensity of the fluorescence decreased as the concentration of the solution increased. The existence of an optimum concentration for maximum fluorescence was noted each time a fluorescent solution was encountered in this investigation. It was found that two adsorption columns eighteen inches long and one and one-half inches in diameter were usually sufficient for the purification of the amount of picrate obtained from cyclization of a twenty-five gram batch of the substituted benzoic acid (III).

Upon concentration and cooling of the purified benzene solution of the methoxy dimethyl-benzanthracene (VI), well-formed plates were obtained in 62% yield calculated from the substituted benzoic acid (III).

1-Hydroxy-9,10-dimethyl-1,2-benzanthracene (VII).

Extreme difficulty was encountered in finding the proper conditions for carrying out two of the reactions of this investigation. One of these reactions was the splitting of the methoxy compounds (VI) and (VI A) to the corresponding hydroxy compounds. The other reaction was

the replacement of the hydroxy groups of (VII) and (VIIA) by amine groups to give (VIII) and (VIIIA), respectively.

Over one hundred attempts to split the methoxy compounds under various conditions were made without success before the proper conditions were found. This difficulty was wholly unexpected since similar reactions have been carried out satisfactorily.²⁰ The usual conditions for carrying out this reaction and a large number of variations of these gave in every instance products which analyzed low in carbon and high in hydrogen.

Some of the products obtained decomposed slowly when exposed to air or when moistened with benzene while others turned from yellow to ruby-red almost instantly. It is possible that this rapid change was the result of a peroxide bridge forming across the 9,10-positions of the benzenanthracene nucleus. Since qualitative tests for peroxide were negative, any peroxides of this type which formed must have changed rapidly into other decomposition products.

Photo-oxidation of compounds of this type occurs readily.² Cook and Martin³ observed that homologs of 1,2-benzanthracene with a substituent at one or both of the meso positions are oxidized with particular ease. If oxygen is passed through a dilute solution of one of the hydrocarbons dissolved in carbon disulfide in the presence of sunlight, photo-oxidation proceeds rapidly. Irradiation of a benzenanthracene solution with an ordinary gas-filled lamp also produced the photo-oxide. The peroxide of 9,10-

dimethyl-1,2-benzanthracene was identified by hydrogenation over a palladium catalyst to 9,10-dihydroxy-9,10-dimethyl-9,10-dihydro-1,2-benzanthracene.

Other investigators observed peroxide formation with compounds of this type and they encountered great difficulties in testing for and isolating the products. Velluz²⁸ found that 9,10-diphenyl-1,2-benzanthracene and 1,2,3,4-tetrahydro-9,10-diphenyl-1,2-benzanthracene formed peroxides but these were difficult to isolate because of interferences by other products of the reaction. Cook, Martin, and Rice⁴ reported that contaminants interfered with the isolation of peroxides of 1,2-benzanthracene. Dufralase and Gerard¹² state that anthracene itself formed a photo-oxide when irradiated in solution with a carbon arc.

Alkyl ethers of benzanthracenes are usually split by refluxing with hydrogen bromide for one hour in acetic acid solution. Fieser and Hershberg,¹⁹ for example, converted 3-methoxy-10-methyl-1,2-benzanthracene to the corresponding benzanthracene in this way. In contrast to this and other information in the literature, it was found that both methoxy compounds (VI) and (VI A) were split completely when treated with either hydrogen bromide or hydrogen iodide in acetic acid solution for ten minutes at room temperature. The reaction products could not be crystallized, but the methoxyl content of the amorphous material was in all cases nil. With hydrogen chloride, on

the other hand, only partial reaction occurred in one hour at either room or reflux temperature.

The previously mentioned results of the carbon and hydrogen analyses of the reaction products suggested that in addition to cleavage of the ether group some secondary transformation was taking place. It was hoped that the ultra-violet absorption curve for the reaction product would indicate what had occurred. This curve is given in Figure 2 together with the curve for the starting material (VI). The curve for the methoxydimethyl-benzanthracene is very similar to that found for 9,10-dimethyl-1,2-benzanthracene²¹ as was to be expected. It was also to be expected that the curve for the product obtained from splitting the methoxy compound would be almost identical with the curve for the methoxy compound itself. It is obvious from Figure 2, however, that the absorption curves have little in common. The greatly decreased absorption by the product from the splitting of the methoxy compound suggests that the completely aromatic system of double bonds has been destroyed. The probability of the formation of peroxides was discussed above and when peroxides are formed from this type of compound, the aromatic system of double bonds is always disrupted. It is also possible that the hydrogen iodide used to split the ether caused hydrogenation of the double bond at the 3,4-position to give the corresponding secondary alcohol. Upon treatment of the reaction product with palladium-carbon at 200°,

FIGURE II

LOGARITHM OF THE MOLECULAR EXTINCTION COEFFICIENT

4.8

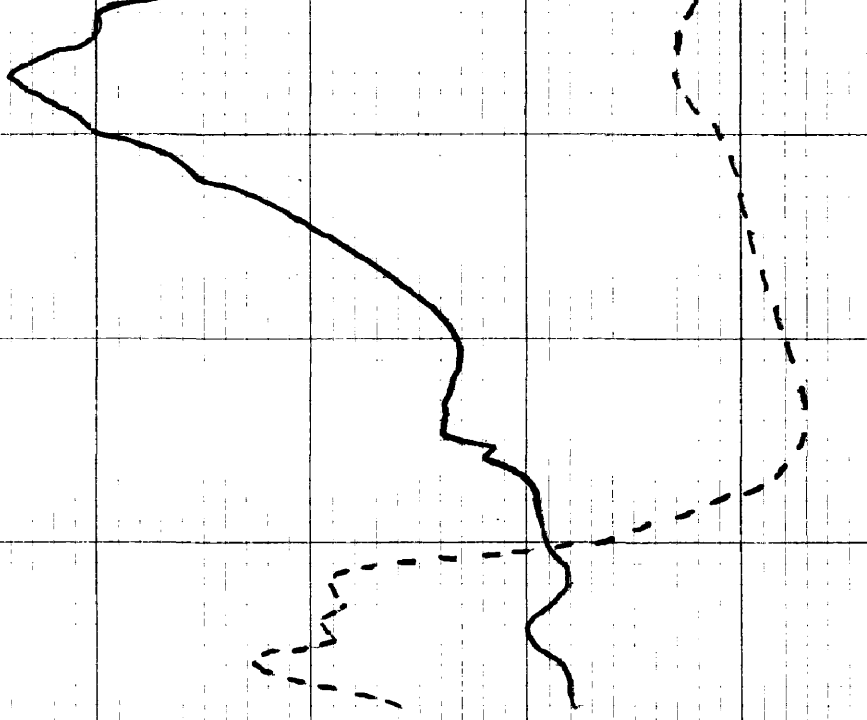
2.4

2300

4100

— 3-METHOXY-9,10-DIMETHYL-1,2-BENZANTHRACENE

- - - CLEAVAGE PRODUCT OF 3-METHOXY-9,10-DIMETHYL-1,2-BENZANTHRACENE



WAVE LENGTH IN ANGSTROMS

some evidence of dehydrogenation was obtained. The desired benzanthrol (VII) could not, however, be isolated as a product of the dehydrogenation reaction.

A successful procedure for splitting the ethers (VI) and (VI A) was finally developed in which pure dioxane was used as the solvent in place of glacial acetic acid. The dioxane must be free of aldehydes as shown by a negative Schiff's test. A nitrogen atmosphere was used and the cleaving agent was hydrogen bromide. It was found to be desirable to have a small amount of hydroquinone present as an anti-oxidant. The reaction product was much more stable when hydroquinone was used and only under these conditions were crystalline products isolated. Even the products obtained under these conditions were, however, quite unstable.

3-Amino-9,10-dimethyl-1,2-benzanthracene (VIII).

The Bucherer reaction was employed to convert the dimethyl benzanthrol (VII) to the dimethylbenzanthrylamine (VIII). This conversion proved to be almost as difficult as the splitting of the methoxy compounds. Most of the difficulties with the Bucherer reaction were later found to be the result of attempting to use products from the splitting of the methoxy compounds which were not the expected benzanthrols (VII) and (VII A) but were actually by-products resulting from oxidation or hydrogenation or both as discussed above. In every case in which the supposed 3-hydroxy-9,10-dimethyl-1,2-benzanthracene was isolated

as a non-crystalline solid, the products of the application of Bucherer reaction conditions to this solid failed to give a positive test for nitrogen. The temperature of the Bucherer reaction was varied from 125 to 250° and the time from 12 to 60 hours, but in no case was any product obtained which was soluble in dilute hydrochloric acid. The higher temperature gave carbonaceous, granular solids.

Some of the benzene soluble organic reaction products could be isolated as a brownish solid which melted at 160.9-161.4°. This solid contained no nitrogen and it was thought that possibly it was the dimethyl-benzanthrol (VII), although it was not soluble in aqueous alkali and was only sparingly soluble in Claisen's alkali. When this solid was again treated with ammonia and sodium bisulfite under the conditions of the Bucherer reaction, no nitrogen could be detected in the product and it could not be converted to a salt.

The possibility that the product obtained upon cleavage of the dimethylmethoxy-benzanthracene (VI) was a ketone or diketone was considered, but a negative test was obtained with 2,4-dinitrophenyl-hydrazine. The Beilstein test for halogens and the bromine water test for olefinic double bonds were both negative. As mentioned above the peroxide test was also negative. It was observed by Dufraisse¹¹ that peroxides of anthracenes with hydrogen atoms or aryl groups in the meso positions readily lose oxygen. Since alkyl groups at the meso positions as in (VII) do not favor

this loss of oxygen from the peroxides, it may be difficult to obtain a positive test for peroxides with these compounds.

Since the methoxy benzanthracenes (VI) and (VI A) are cleaved so readily, it seemed possible that these ethers could be used directly in the Bucherer reaction. The products from two attempts at carrying out this reaction contained no nitrogen.

Acetylation of the products from cleavage of the ether (VI) was also tried in the hope that the acetates might be used directly in the Bucherer reaction. The product from attempted acetylation with acetic anhydride and a drop of sulfuric acid as a catalyst was a yellow-tan solid which melted over a wide range. Since the results of carbon and hydrogen analysis of this material were also widely different from the values calculated for the desired acetate, this approach was abandoned.

It was finally discovered that it was preferable not to attempt to isolate the pure crystalline dimethyl benzanthrol. Most of the solvents were distilled from the reaction mixture obtained in the cleavage of the methoxy compound (VI) as described above. The green oil remained in the flask as the residual solvent containing dissolved hydroquinone was decanted. This crude product was dissolved in dioxane and used directly in the Bucherer reaction. Upon cooling the sealed reaction tube, the crude amine separated as either a liquid or a solid. From this a pure,

crystalline product was obtained. The yield calculated from the methoxy compound (VI) was 67%.

The sulfate (VIII D) of this amine was prepared as a derivative. When a dilute alcoholic solution of sulfuric acid was added to an ethereal solution of the amine, the amine sulfate crystallized out immediately.

2,10-Dimethyl-1,2-benzanthryl-3-isocyanate (IX).

This isocyanate could be prepared from either the crude Bucherer reaction product or from the pure, recrystallized amine (VIII). A solution of phosgene in toluene was added to a solution of the amine in ether. The product (IX) isolated by crystallization from a mixture of toluene and petroleum ether was obtained in 68% yield calculated from the methoxy compound (VI).

In order to establish the identity of the isocyanate more completely, it was converted to the urethane. This crystalline derivative was readily prepared by refluxing a solution of the isocyanate in absolute alcohol.

3-Methoxy-9-methyl-1,2-benzanthracene (VI A).

This compound was made from the crude anthrone (IV) via the dihydroanthranol (V A). The anthranol was prepared by the Meerwein-Ponndorf-Verley²⁹ reaction which employs aluminum isopropoxide in isopropyl alcohol as the reducing agent. As with the analogous dimethyl compound (V), it was impossible to obtain the product in pure, crystalline form. The crude material could be dehydrated, however, to give a good yield of (VI A).

Dehydration of the secondary alcohol (V A) could be carried out by heating at 200° on the hot plate as described for (VI). Since considerable tar formed under these conditions, an improved method was developed. After the completion of the reduction with aluminum isopropoxide, most of the volatile material was distilled off and replaced with xylene. The mixture was refluxed for one-half hour and then distillation was renewed. Dehydration occurred and as the water formed it was removed azeotropically with the xylene. This method eliminates the danger of overheating. A 67% yield, calculated from (III), of pure, white plates was obtained.

3-Amino-9-methyl-1,2-benzanthracene (VIII A).

The methoxy compound (VI A) was split in exactly the same way as given above for (VI). It was found best to treat only two grams of material at a time in order to keep decomposition at a minimum.

The crude methylbenzanthrol (VII A) was used without purification for the preparation of the aminomethyl benzanthracene (VIII A) by the Bucherer reaction as previously described for the analogous compound (VIII). The yield of purified amine was 64%, calculated from (VI A), while the yield of crude amine was 93%, also calculated from (VI A). The crude material gave a good yield of the isocyanate.

The amine was converted to the sulfate (VIII B) as described above for (VIII).

From some of the Bucherer reaction mixtures there was

isolated in a small amount long, silky needles which decomposed at 270-271°. The amount obtained was never more than about one-tenth per cent of the amount of the amine (VIII A). A similar compound was never isolated in the preparation of the related aminodimethyl compound (VIII). The structure of this high melting compound was not established, but the results of carbon and hydrogen analyses and molecular weight determinations by the Rast method agreed very closely with the values calculated for the symmetrical ether (VIII C).

2-Methyl-1,2-benzanthryl-1-isocyanate (IX A).

This isocyanate could be made from either the crude or the purified amine (VIII A). When a solution of the crude amine was treated with a solution of phosgene, the crystalline isocyanate (IX A) was obtained in 72% yield. This isocyanate often crystallized with difficulty; it was necessary to concentrate a solution of it in toluene almost to a syrup and to add petroleum ether carefully. The mother liquors from this crystallization were sent to Dr. Creech at the Lankenau Hospital Research Institute. He was able to isolate small amounts of material which melted above 200°. It was his opinion that this material was a di-substituted urea.⁵

The methylbenzanthryl-isocyanate (IX A) was converted to the urethane (X A) by refluxing a solution of it in absolute alcohol.

3-Methoxy-9-methyl-10-phenyl-1,2-benzanthracene (XI)
and 3-methoxy-9-methyl-10-ethyl-1,2-benzanthracene (XII).

In order to demonstrate the versatility of the anthrone (IV) as an intermediate, two representative methoxybenzanthracenes with unsymmetrical substitution in the meso positions were synthesized, (XI) and (XII).

The 10-phenyl compound (XI) was prepared by the action of phenylmagnesium bromide on the anthrone. The intermediate tertiary alcohol was dehydrated and the product was converted to the picrate in benzene solution. This picrate was purified and at the same time cleaved to give free methoxy compound (XI) by chromatographic adsorption with alumina. The product could not be crystallized but purification by molecular distillation gave a glassy solid which had the proper carbon and hydrogen content for the desired compound (XI). The yield was 81% calculated from (III).

The 10-ethyl compound (XII) was prepared in an entirely analogous fashion using ethylmagnesium bromide in place of phenylmagnesium bromide. Considerable difficulty was encountered in its crystallization, but it was finally obtained from ligroin solution as fine rosettes; yield 60% calculated from (III).

Attempted preparation of 3,10-dimethoxy-9-methyl-1,2-benzanthracene (XIII).

The crude anthrone was dissolved in pyridine; this base facilitates tautomerization of the anthrone to the anthrol. The solution was treated with excess diazomethane and after considerable difficulty a crystalline product was obtained. The analytical results, however, did not

agree with those calculated for the dimethoxymethyl-benzanthracene (XIII).

According to the analytical results the product had the composition of the intermediate anthrol plus one atom of oxygen. It appears that a peroxide may have been formed. According to the works of Julian and Cole,²² however, the peroxide obtained from the anthrol would be expected to contain two additional atoms of oxygen instead of only one. It appears, therefore, to be impossible from the evidence at hand to assign a definite structure to the compound obtained here.

EXPERIMENTAL*

2-(4'-Methoxynaphthoyl-1')-benzoic acid (I):-This acid was made by the method of Fieser and Dietz.¹⁶ It was found that by keeping the temperature at 15-20° during the addition of the aluminum chloride, the yield was increased to 95% from 91% and the product was much less contaminated with sodium chloride. Higher temperatures cause greater darkening of the product and make its purification more difficult.

Four hundred grams of aluminum chloride was added in small portions over a period of about one hour to a solution of 234 g. (1.48 moles) of *α*-methoxynaphthalene and 234 g. (1.58 moles) of phthalic anhydride in 1200 ml. of tetrachloroethane. The temperature was kept below 20° by stirring vigorously in an ice bath. After the addition of the aluminum chloride was completed, the reaction mixture was allowed to warm up to room temperature, stirred for an additional eight hours, and allowed to stand for twenty hours. After decomposition of the complex with hydrochloric acid and ice, the tetrachloroethane was removed by steam distillation. The brown, granular acid was filtered off and dissolved in aqueous alkali from which the sodium salt crystallized on cooling. Purification was best accomplished by dispersing this salt in cold water and precipitating the free acid with dilute sulfuric

* All melting points are corrected. Microanalyses by Miss Eleanor Werble of this University.

acid; the precipitate was washed thoroughly with very dilute acid and then with water. The product must be carefully dried in a vacuum oven allowing the temperature to rise from 35° to 105° as the process proceeds. If further purification is required, the acid may be converted to the sodium salt and the above process repeated. A yield of 431.6 g. (95%) of a white, flocculent powder was obtained; m.p. 196.5-197.0°.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.49; H, 4.60
 Found: C, 74.55; H, 4.58.

Lactone of 2-[α -hydroxy- α -1'-(4'-methoxynaphthyl)-ethyl]-benzoic acid (I): Methylmagnesium bromide was prepared from 121 g. (5.0 moles) of magnesium, 4 liters of anhydrous ether, and an excess of methyl bromide. The solution was filtered in a nitrogen atmosphere through a cotton plug to remove traces of magnesium and admitted under the surface of a well stirred suspension of 519 g. (1.66 moles) of the acid (I) in 5 liters of anhydrous toluene. A chalky yellow color appeared which changed to greenish-yellow, orange, and finally to a muddy yellow or red. The final color varied from preparation to preparation, but most often it was a muddy yellow. The reaction mixture was refluxed four hours during which time the amount of insoluble material appeared to increase rather than decrease. Stirring without heating was continued overnight; some material still remained undissolved. The complex was decomposed with ice and hydrochloric acid and the layers separated. Extraction of the aqueous layer with

benzene-ether (2:1) was continued until the extract was colorless. These extracts were added to the original non-aqueous layer and the combined solution was washed with aqueous sodium carbonate until the washings, which originally were blood-red, were no longer colored. After washing with saturated sodium chloride solution, the organic layer was dried over magnesium sulfate. The solvent was removed by distillation under reduced pressure until the red, syrupy lactone in a small amount of toluene remained and further distillation became difficult. Anhydrous ethanol was added in an amount equal to one-fourth the volume of the concentrated lactone. Petroleum ether (30-60°) was then added until a faint turbidity appeared. Chilling in an ice bath precipitated 286 g. (57%) of a yellow-white powdery product. Cooling and concentrating the mother liquor did not cause further crystallization of lactone, but by molecular distillation of the residue left upon evaporation of the solvents, an additional 57 g. of an immediately crystallizable distillate was obtained. The total yield was 343 g. or 70%; m.p. 139.8-140.5°.

Anal. Calc'd. for $C_{20}H_{16}O$: C, 78.93; H, 5.30
 Found: C, 78.82; H, 5.57.

2-[α -1'-(4'-Methoxynaphthyl)-ethyl]-benzoic acid (III):-

Hydrolysis and reduction of the lactone (II) with zinc and hydrochloric acid did not proceed in good yield, but alkaline hydrolysis and reduction gave an almost quantitative yield of (III). The orange solution obtained by dissolving 363.8 g. (1.19 moles) of the lactone in 8500 ml. of 95% alcohol was

treated with 850 ml. of 55% aqueous sodium hydroxide, whereupon the color changed to a deep red or violet. The solution was refluxed gently for twenty-four hours. Approximately 3 liters of the solvents were distilled off and replaced by water; distillation was then continued until violent bumping prohibited further removal of solvent. Zinc dust (850 g.) activated by copper sulfate, 1700 ml. of 55% sodium hydroxide, and 4000 ml. of water were added and the mixture was refluxed a second twenty-four hours. The grayish to creamy-white material was then filtered off using a thick glass wool plug and gentle suction. In contrast to Newman's procedure, acidification of the filtrate produced no solid since the sodium salt of the substituted benzoic acid was insoluble in alkali under the above conditions. The precipitate in the filter was extracted by washing with hot water until the washings, which at first gave a heavy precipitate when acidified with dilute sulfuric acid, no longer gave any precipitate upon acidification. The sulfuric acid contaminated acid (III) was collected and washed with small quantities of hot water until no test for the sulfate ion was obtained upon addition of barium chloride to the washings. The product was dried in a vacuum oven at not more than 40° until almost all of the water was removed in order to prevent decomposition. Drying was then completed at 105° . A 98% yield (358 g.) of white, microscopic needles melting at $197.3-198.1^{\circ}$ was obtained.

Anal. Calc'd. for $C_{20}H_{19}O_3$: C, 78.41; H, 5.92
 Found: C, 78.33; H, 5.98.

3-Methoxy-9-methyl-1,2-benz-10-anthrone(IV):—When 25 g. (0.082 moles) of the substituted benzoic acid (III) was treated in a copper vessel with 250 g. of anhydrous hydrofluoric acid cyclization proceeded without difficulty. The reaction mixture was swirled occasionally for ten minutes; volatilization of the hydrogen fluoride controlled the temperature. The dark red solution was slowly added to about two liters of finely chopped ice with vigorous stirring. It is essential that excess ice remains after the addition is complete since stirring with this ice prevents the anthrone from forming balls which interfere with thorough washing. The brownish, sandy anthrone was washed free of acid with ice water, dissolved in two liters of boiling acetone and the solution was rapidly concentrated. Since attempts at crystallization were unsuccessful the acetone was completely evaporated and the product dried to constant weight under reduced pressure. This crude anthrone weighed 23.0 g. (93% yield). The proportion of impurities present was not determined, but the crude anthrone was entirely satisfactory for use in both Grignard and Meerwein-Ponndorf reactions.

3-Methoxy-9,10-dihydro-9,10-dimethyl-10-hydroxy-1,2-benzanthracene (V):—A total of 69 g. (0.24 moles) of the crude anthrone was dissolved in 1500 ml. of benzene producing a dark red solution. This solution was slowly added to a solution of methylmagnesium bromide in 2400 ml. anhydrous ether prepared from 23.2g. (0.956 moles) of magnesium turnings, and an excess of methyl bromide. The

color changed to a dark green. The solution was refluxed one hour and the complex decomposed with dilute sulfuric acid and ice. After separation of the layers, the aqueous layer was extracted with benzene-ether (2:1). The extract was added to the original non-aqueous layer and the combined solutions were thoroughly washed with water until free of acid. After further washing with saturated sodium chloride solution, the organic layer was dried over magnesium sulfate. The solvent was removed under reduced pressure, and the tertiary alcohol crystallized from toluene-petroleum ether. The brownish scales could not be obtained pure, possibly because of dehydration to (VI). Removal of all the solvent under very low pressure gave a total of 65.3 g. (90%) of the crude tertiary alcohol (V).

3-Methoxy-9,10-dimethyl-1,2-benzanthracene (VI):—A total of 75.0 g. (0.244 moles) of the substituted benzoic acid (III) was converted to the crude anthrone (IV) (69.0 g.; 0.24 moles) by the procedure described above. It was found best to do this in three 25 g. portions. Upon treating the total crude anthrone with methylmagnesium bromide, 65.3 g. (0.214 moles) of crude (V) was obtained. When this was heated for about five minutes at 200° dehydration proceeded rapidly and an acrid odor was evolved. The crude 3-methoxy-9,10-dimethyl-1,2-benzanthracene was best purified by chromatographic adsorption of the picrate on a 1:1 mixture of alumina and supercel. The dark, tarry material adhered to the adsorption medium while the blue highly

fluorescent solution of (VI) in benzene passed through. The process was repeated until all the dark red to red-black impurities were removed. Upon concentration and cooling of the benzene solution, 43.0 g. of lustrous yellow-white plates were deposited; m.p. 129.9-130.9°. The overall yield of the methoxydimethyl compound (VI) from the substituted benzoic acid (III) was 61.5%.

Anal. Calc'd. for $C_{21}H_{19}O$: C, 88.06; H, 6.30; CH_3O -, 10.83
 Found: C, 88.07; H, 6.41; CH_3O -, 10.79.

3-Hydroxy-2,10-dimethyl-1,2-benzanthracene (VII):—Great difficulty was encountered in finding proper conditions for splitting the methoxydimethyl compound (VI) and the methoxymonomethyl compound (VI A). It was found that if purified dioxane was used as a solvent and if the reaction was carried out in a nitrogen atmosphere and in the presence of hydroquinone, a satisfactory product was obtained. A round-bottom 125 ml. flask equipped with a gas inlet tube and a water cooled condenser was used. Forty milliliters of dioxane was placed in the flask and nitrogen bubbled through it for some time. Hydroquinone (0.10 g.) was added followed by 2.0 g. of the methoxydimethyl compound (VI). The clear yellow solution became turbid upon the addition of 6 ml. of 48% hydrogen bromide (analytical reagent). The mixture was heated in a boiling water bath for one hour during which time nitrogen was constantly admitted under the surface of the liquid. The color changed to reddish and finally to dark green. Most of the solvent was removed by distillation and the remaining solvent de-

cented from the green oil which separated. Hydroquinone was discarded in this decantation. If the solvent to be decanted was still very turbid after much of the solvent had been distilled off, a few milliliters of water was added to aid separation of the green oil. Since it was found to be impractical to attempt to crystallize this crude dimethylbenzanthrol (VII), it was dissolved in the required amount of dioxane and used directly in the Bucherer reaction.¹⁰

A detailed description of the ultra-violet absorption study on 3-methoxy-9,10-dimethyl-1,2-benzanthracene (VI) and its cleavage product (VII) was given in the discussion part.

Dioxane used as a solvent for these compounds was carefully purified. The commercial grade dioxane was refluxed in dilute hydrochloric acid for twenty-four hours; a slow stream of nitrogen being constantly admitted. The acid was then neutralized by sodium hydroxide and the dioxane dried over anhydrous sodium hydroxide and distilled from sodium ribbon. The purity of this distilled dioxane was such that a negative Schiff's test was obtained. Pure iron wire was placed in the dioxane, and the solvent was stored in a refrigerator for its use in the spectrophotometer.

3-Amino-9,10-dimethyl-1,2-benzanthracene (VIII):—The above dimethyl benzanthrol (VII) prepared from 2.0 g. of (VI) was dissolved in 28 ml. of dioxane in a tube prepared for sealing. Ten grams of analytical reagent sodium bi-

sulfite, 16 ml. of water, and 40 ml. of analytical reagent ammonium hydroxide (28%) were added. The mixture was chilled in a dry ice-alcohol bath and the tube sealed and placed in a small, electrically heated rocking bomb provided with a device for automatic temperature control. The tube was heated at $125^{\circ} \pm 5^{\circ} \text{C.}$, for from twenty-four to thirty-three hours. Before heating was begun two liquid phases were present in the tube, but at the end of the heating period the hot liquid existed as only one phase. Upon cooling in a refrigerator for several hours, the amine (VIII) separated out as a dark red band of solid in a translucent fluorescent solution. In certain cases the amine separated as a red oil and this proved to be just as satisfactory as the solid. The dioxane-water phase was decanted from the solid or oil and extracted with ether; the ether extract was added to the original amine phase. The highly fluorescent, blue ethereal solution was thoroughly washed with water, dried over magnesium sulfate, and the drying agent and any other insoluble matter filtered off. Twenty milliliters of toluene was added and the ether was evaporated on the steam bath. Low-boiling ($30-60^{\circ}$) ligroin* was added until the first slight turbidity appeared or until a precipitate which dissolved with difficulty formed. Upon cooling overnight in a refrigerator, 1.27 g. (67% calculated from VI) of fluffy, wool-like, bright yellow needles deposited; m.p. $128.9-130.8^{\circ}$.

* Ligroin was purified by refluxing with potassium permanganate and then with sodium hydroxide; it was then distilled.

Anal. Calc'd. for $C_{20}H_{17}N$: N, 5.16
 Found: N, 5.13.

Sulfate of 3-amino-9,10-dimethyl-1,2-benzanthracene

(VIII D):—It was found that the sulfate of the amine was a convenient derivative. It was prepared by dropwise addition of a solution of 5 drops of concentrated sulfuric acid in 10 ml. of anhydrous alcohol to a solution of 50 mg. of the amine in 10 ml. of anhydrous ether. The alcoholic sulfuric acid was added until no more amine precipitated. The greenish-yellow granular sulfate melted at 206–207°.

Anal. Calc'd. for $C_{20}H_{19}NSO_4$: N, 3.79
 Found: N, 3.77.

9,10-Dimethyl-1,2-benzanthryl-3-isocyanate (IX):—The isocyanate could be readily prepared without isolation of the pure, crystalline amine. Two grams (0.007 moles) of the methoxydimethyl compound (VI) was converted to the dimethylbenzanthrol (VII) and this was employed in the Bucherer reaction as described above. The dried ether solution of the amino-dimethyl compound (VIII) obtained as previously described was diluted with 40 ml. of benzene and the ether evaporated from a steam bath. A solution of phosgene prepared by absorbing 14 g. of the gas in 55 g. of cooled toluene was added to the warmed benzene solution of the amine.¹⁵ A flocculent precipitate formed immediately which disappeared when the solution was refluxed five to ten minutes. After removal of about two-thirds of the solvent by distillation at atmospheric pressure, purified petroleum ether (30–60°) was added until a faint turbidity appeared. Upon cooling in ice, 1.34 g. [67% yield calculated from (VI)]

of glistening, yellow needles separated. The isocyanate was also prepared in 68% yield from 0.10 g. of the pure amine (VIII). Both preparations melted at 115.4-115.8°.

Anal. Calc'd. for $C_{21}H_{15}ON$: C, 84.82; H, 5.08; N, 4.71
 Found: C, 84.61; H, 5.33; N, 4.91.

Ethyl-2,10-dimethyl-1,2-benzanthryl-3-carbamate (X):-

The carbamate proved to be a suitable derivative of the isocyanate (IX). A solution of 0.025 g. (0.000084 moles) of the isocyanate in 25 ml. of absolute alcohol was refluxed twenty hours; a reflux period of one hour left some unchanged isocyanate. Five milliliters of toluene was added and the solution extracted with water and dried over magnesium sulfate. Petroleum ether (50-60°) was added and upon cooling 0.018 g. (63%) of pale yellow needles crystallized. The melting point was 113.3-114.1°; admixture with (IX) gave a marked lowering.

Anal. Calc'd. for $C_{23}H_{21}O_2N$: N, 4.07
 Found: N, 3.91.

3-Methoxy-2,10-dihydro-2-methyl-10-hydroxy-1,2-benzanthracene (V A):- A solution of 29.4 g. (0.102 moles) of crude anthrone (IV), prepared as described above, in 250 ml. of anhydrous isopropyl alcohol was stirred efficiently during the addition of three molar equivalents (62.4 g.) of aluminum isopropoxide. After the mixture had been refluxed for seven hours, volatile material was slowly removed by distillation. At first the distillate gave a precipitate with 2,4-dinitrophenylhydrazine, but this test was negative after most of the volatile material was removed. In order to insure complete reduction, fresh anhydrous isopropyl

alcohol was added and refluxing continued for seven hours more. When the volatile material was again removed, the distillate gave no test for acetone. Three hundred milliliters of water-hydrochloric acid (3:1) was added to the reaction mixture and the anthrol was then extracted into benzene. After the dark red fluorescent extract was washed well with water, it was dried over magnesium sulfate and the benzene was removed by distillation. An 87% yield (25.8 g.) of crude product was obtained which resisted attempts at crystallization.

3-Methoxy-9-methyl-1,2-benzanthracene (VI A):-The above monomethylanthrol could be dehydrated as previously described for the dimethylanthrol (V), but an improved method which eliminates overheating and excessive formation of tars was devised. After the acetone and most of the isopropyl alcohol were distilled from the Meerwein-Ponndorf reaction mixture, as described above, xylene was added. Upon further distillation the anthrol dehydrated, and the water was removed azeotropically without danger of decomposition of the methoxymethyl benzanthracene (VI A). Impurities were removed from a benzene solution of the crude product as described for the analogous compound (VI). Upon concentration and cooling of the benzene solution which showed blue fluorescence under ultra-violet light, 18.9 g. (78%) of shining pale yellow plates appeared; m.p. 123.9-124.3°. Since 32.0 g. (0.104 moles) of the substituted benzoic acid (III) was used to make the crude anthrone used here, the overall yield calculated from (III) was 66.5%.

Anal. Calc'd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92; CH_3O- , 11.39
 Found: C, 88.14; H, 6.07; CH_3O- , 11.36.

3-Hydroxy-9-methyl-1,2-benzanthracene (VII A):-The conversion of (VI A) to (VII A) was carried out exactly as described for the corresponding dimethyl compounds, (VI) and (VII). In order to facilitate handling the product so as to avoid decomposition, only 2.0 g. (0.0073 moles) of the methoxy compound was treated at a time.

3-Amino-9-methyl-1,2-benzanthracene (VIII A):-The methylbenzanthrol (VII A) prepared from 2.0 g. of the methoxy compound as just described, was dissolved in dioxane and treated as previously described for the analogous dimethyl compound (VIII). After completion of the reaction, the sealed tube was placed in the refrigerator overnight. The free amine crystallized out as beautiful yellow-white rosettes and long, nicely-shaped needles. A disc of solid also formed which was found upon microscopic examination to be composed of well-formed needles. This amine was washed well with water and then dried in a vacuum desiccator at room temperature. Since the amine is sensitive, it must be dried carefully at low temperatures until practically all of the water is removed. The product melted at 112.1-115.9° and weighed 1.76 g.; this corresponds to a 93% overall yield from (VI A). Although this material gave good yields when converted to the isocyanate, absolutely pure amine was prepared by recrystallization. The amine was dissolved in ether and a slight amount of material believed to be (VIII C) was removed by filtration. After the

addition of toluene most of the ether was evaporated. Upon cooling the solution of amine in dry ice-alcohol bath, needles were obtained which had to be filtered off rapidly since they redissolved readily. By recooling the filtrate and refiltering a total of 1.21 g. [64.5% calculated from (VI A)], of pure amine which melted at 116.6-117.4° was obtained. It should be emphasized that the unrecrystallized amine, obtained as described above in 93% yield, could be used to better advantage for conversion to the methylbenzanthryl-isocyanate (IX A) as described below.

Anal. Calc'd. for $C_{19}H_{15}N$: N, 5.44
 Found: N, 5.35.

Di-(9-methyl-1,2-benzanthryl-3) ether (VIII C):-A

material believed to be this compound remained as nicely crystalline, very long, silky, yellow needles when the slightly impure amine (VIII A) was dissolved in ether as just described. In various runs the amount of this material obtained varied from none up to 0.13% of the weight of the desired amine compound (VIII A). The elementary composition and the molecular weight by the Rast method agreed closely with that calculated for (VIII C). The compound decomposed at 270-271°.

Mol. Wt. Calc'd.: 498.6; Found: 496

Anal. Calc'd. for $C_{38}H_{26}O$: C, 91.53; H, 5.23
 Found: C, 91.30; H, 5.11.

Sulfate of 3-amino-9-methyl-1,2-benzanthracene (VIII E):-

This salt was prepared in a manner exactly analogous to that previously described for (VIII D). Upon addition of sulfuric acid in alcohol to the ether solution of (VIII A), a

grayish white, granular solid precipitated. This compound decomposed very sharply without melting at $218.7-219.0^{\circ}$.

Anal. Calc'd. for $C_{19}H_{17}NSO_4$: N, 3.94
 Found: N, 3.85.

9-Methyl-1,2-benzanthryl-3-isocyanate (IX A):—The slightly impure amine (VIII A) melting at $112.1-115.9^{\circ}$ was the starting material for the preparation of this isocyanate. Three-tenths of a gram (0.00116 moles) of this amine was dissolved in ether, any insoluble material was filtered off, and 10 ml. of benzene added. A solution of 2.65 g. of phosgene in 11 ml. of toluene was added to the warm solution of the amine. The precipitate which first appeared, redissolved after the mixture was refluxed five to ten minutes. After removal of most of the solvent by distillation at atmospheric pressure, petroleum ether ($30-60^{\circ}$) was added until a slight turbidity appeared. Upon cooling overnight in a refrigerator, long, slender, well-formed needles appeared which became bulky and compact upon further growth. The product weighed 0.238 g. (73% yield) and melted at $63.0-64.2^{\circ}$. Frequently it was necessary to concentrate the solution further and to use seed crystals in order to obtain a crystalline product.

Anal. Calc'd. for $C_{20}H_{17}ON$: C, 84.77; H, 4.62; N, 4.94
 Found: C, 84.39; H, 4.84; N, 4.82.

Ethyl-9-methyl-1,2-benzanthryl-3-carbamate (X A):—A solution of 0.04 g. (0.00014 moles) of the isocyanate (IX A) in 10 ml. of anhydrous alcohol was refluxed for ten hours. Six milliliters of toluene was added and the carbamate crystallized as described above for (X). A 65% yield

(0.030 g) of pale yellow needles which melted at 174.2-174.9° was obtained.

Anal. Calc'd. for $C_{22}H_{19}O_2N$: N, 4.25
Found: N, 4.19.

3-Methoxy-9-methyl-10-phenyl-1,2-benzanthracene (XI):-

Crude anthrone (IV) prepared from 25 g. (0.082 moles) of the substituted benzoic acid, as described above, was dissolved in one liter of benzene. This solution was added to a solution of phenylmagnesium bromide prepared from 3.0 g. of magnesium and 20.0 g. of bromobenzene in one liter of anhydrous ether. After the suspension of the mud-yellow complex was refluxed for twelve hours, the mixture was decomposed with sulfuric acid and ice. The layers were separated, the aqueous layer was extracted with benzene-ether (1:1), and the extracts were added to the original non-aqueous layer. The combined solutions were washed with dilute sodium carbonate, and then with water and dried over magnesium sulfate. After removal of the solvent by distillation, the intermediate tertiary alcohol was dehydrated by heating for a few minutes on a hot plate. Considerable purification was accomplished by converting the desired product to the picrate and separating it from impurities by chromatographic adsorption as previously described for the analogous dimethyl compound (VI). Attempts to obtain pure crystals from the yellow solution in benzene gave only oil or highly impure solid. It was found that sublimation followed by molecular distillation gave 23.0 g. [81% calculated from (III)] of an orange,

glassy solid which had no definite melting point. This compound in benzene solution showed intense blue fluorescence under ultra-violet light. The glassy product was, according to elementary and methoxyl analysis, of high purity even though it could not be crystallized.

Anal. Calc'd. for $C_{26}H_{20}O$: C, 89.62; H, 5.78; CH_3O -, 8.90
 Found: C, 89.84; H, 6.04; CH_3O -, 8.93.

3-Methoxy-9-methyl-10-ethyl-1,2-benzanthracene (XII):-

Ten grams (0.0326 moles) of the substituted benzoic acid was converted to the crude anthrone (IV) in the usual manner. This anthrone dissolved in 200 ml. of benzene was added to an excess of ethylmagnesium bromide prepared in 500 ml. of anhydrous ether from 1.2 g. of magnesium and 5.3 g. of ethyl bromide. A precipitate formed and a green color appeared which changed to yellow when the mixture was refluxed fifteen hours. The complex was decomposed and the tertiary alcohol intermediate was isolated and dehydrated to (XII) as described for (XI) just above. The picrate was formed and the dark red, viscous oil was chromatographed. Good separation was obtained on the adsorption column. A benzene solution of the desired product showed intense blue fluorescence. It was necessary to use a large volume of petroleum ether (30-60°) for crystallization. The compound separated as fine rosettes in 60% yield (5.9 g.) calculated from (III); m.p. 86.4-87.2°.

Anal. Calc'd for $C_{22}H_{20}O$: C, 87.96; H, 6.67; CH_3O -, 10.33
 Found: C, 87.97; H, 6.77; CH_3O -, 10.26.

Attempted preparation of 3,10-dimethoxy-9-methyl-1,2-benzanthracene (XIII):-Crude anthrone (IV) prepared from

10 g. (0.0326 moles) of the substituted benzoic acid in the usual manner was refluxed for six hours in 150 ml. of analytical reagent pyridine. This basic treatment tautomerizes the anthrone to the anthrol.¹⁹ The pyridine solution of the anthrol was added to a large excess of diazomethane dissolved in benzene. The diazomethane was prepared from 0.1 mole of N-nitrosomethylurea by a well known method.¹ The temperature was kept at 5-10° during the addition and for three hours more; nitrogen was evolved copiously during this period. After the solution was allowed to warm up and stand at room temperature for twelve hours, an attempt was made to extract the pyridine into water. Since this produced an emulsion the solvents were distilled off, the brown-black residue was treated with benzene, insoluble matter was filtered off, and the filtrate was treated with picric acid. When this benzene solution of the picrate was passed through a column of alumina, the resulting solution showed a bright green fluorescence. After considerable difficulty 6.67 g. of large, yellow rectangular plates crystallized from a highly concentrated benzene solution; m.p. 148.2-149.6°.

Anal. Calc'd. for $C_{21}H_{18}O_2$: C, 83.41; H, 6.00
 Calc'd. for $C_{20}H_{16}O_3$: C, 78.80; H, 5.30
 Found: C, 78.79; H, 5.48.

The above analysis shows that the expected dimethoxy compound (XIII) was not obtained. It is indicated that instead of substituting a hydrogen atom of the anthrol by a methoxy group, an atom of oxygen was added. This addition of oxygen might have been expected since Dufraisse and

Fricou¹³ found that 9,10-dimethoxy anthracene was the most easily photo-oxidized of a large number of related compounds which he studied. No proof of structure or other characterization of the compound obtained here has been attempted.

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