

SYNTHETIC REACTIONS WITH 11-CARBOXY-BENZANTHRONE.

By


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GENERAL INDEX.

	<u>Page.</u>
Introduction .....	1
I Summary of Experimental Work and Discussion of Results:	
A. The amide of 11-carboxy-benzanthrone and its behaviour on oxidation .....	17
B. Preparation of the oxime of 1:11-keto- benzanthrone and investigation of its behaviour to Beckmann reagents .....	29
C. Other 11-substituted benzanthrones including 11-amino-benzanthrone .....	47
II Experimental Section .....	52
Summary .....	133

---

Index of Tables.

Page.

Summary of action of concentrated sulphuric acid on methyl 8-(o-carbomethoxy)-phenyl-1-naphthoate ..... opposite 13

Properties of certain oxidation products of the amide of 11-carboxy-benzanthrone opposite 26

Reactions of fluorenone, 1:11-ketobenzanthrone and their oximes to various reagents ..... opposite 43

Comparison of diamino-dibenzanthrones .. opposite 126

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INDEX OF PREPARATIONS.

	<u>Page.</u>
<i>o</i> -Iodo-benzoic acid .....	54
Methyl <i>o</i> -iodo-benzoate .....	55
8-Bromo-1-naphthoic acid .....	55
Methyl 8-bromo-1-naphthoate .....	57
Methyl 8-( <i>o</i> -carbomethoxy-phenyl)-1-naphthoate ...	59
11-Carboxy-benzanthrone .....	60
11-Carbomethoxy-benzanthrone .....	61
Ammonium benzanthrone-11-carboxylate .....	62
Amide of 11-carboxy-benzanthrone .....	70
Lactam of 1-amino-11-carboxy-benzanthrone .....	85
Aceto- $\beta$ -naphthalide .....	86
Oxalyl-bis-phenyl-imido-chloride .....	87
1:11-Keto-benzanthrone .....	91
Benzanthrone-1:11-ketoxime .....	92
Lactam of 11-amino-1-carboxy-benzanthrone .....	98
1-Bromo-2-acetonaphthalide .....	109
1-Bromo-2-naphthylamine hydrochloride .....	110
1-Bromo-2-naphthoic acid .....	111
Methyl 1-bromo-2-naphthoate .....	113
11-Amino-benzanthrone .....	119
11-Formamino-benzanthrone .....	122
11-Acetamino-benzanthrone .....	123
11-11'-Diamino-3:3'-4:4'-dibenzanthrone .....	124

## I N T R O D U C T I O N

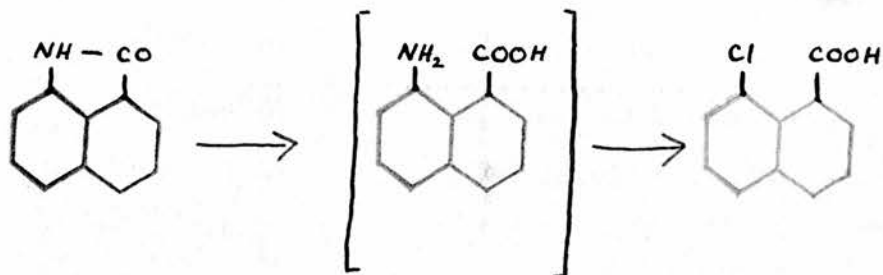
In the relatively wide field of naphthalene chemistry, especial attention has been given to the peri-derivatives, that is, those compounds in which the 1:8- (or 4:5-) positions are substituted.

Their importance lies not only in the fact that, in general, they possess the properties of the corresponding ortho-substituted benzene derivatives to an enhanced degree, but also in their ready accessibility and reactivity, which enables them to be used in the synthesis of numerous and important compounds of a more complex type.

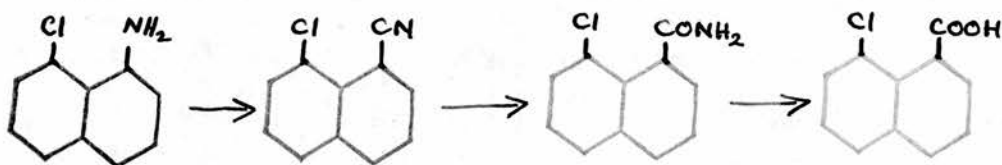
### 8-Halogeno-1-naphthoic Acids.

In recent years, a considerable amount of work has been carried out on those peri-derivatives in which one of the substituents is a halogen atom and the other a carboxyl group. Until recently some trouble was experienced in preparing 8-halogeno-1-naphthoic acids cheaply and in good yield.

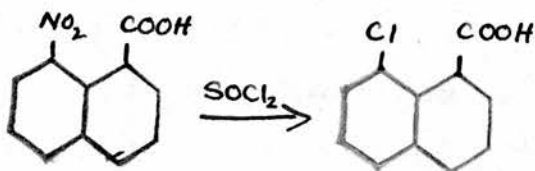
The 8-chloro-acid was prepared almost fifty years ago by submitting naphthastyril to the Sandmeyer reaction (Ekstrand, J. prakt. Chem., 1888, 38, 139, 241).



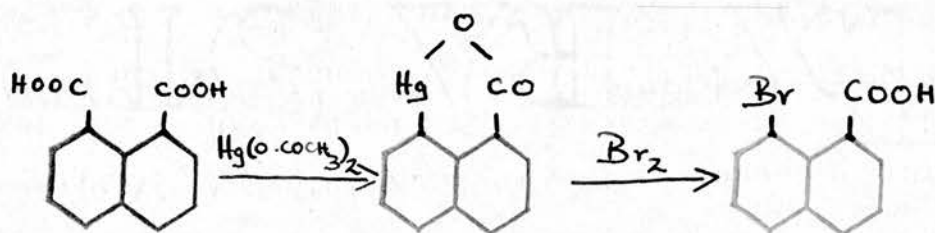
and later from 8-chloro-1-naphthylamine by a modified Sandmeyer reaction (Kalb, Ber., 1914, 47, 1724).



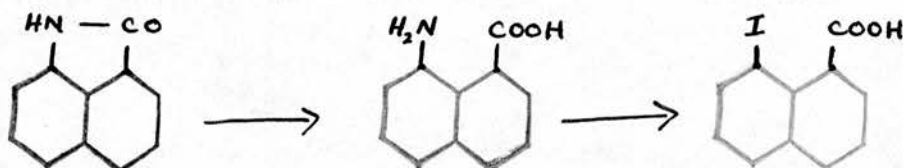
Rule and Spence (J., 1929, 2516) obtained both the chloro- and the bromo-acid by the action of thionyl chloride and bromide respectively on 8-nitro-1-naphthoic acid in benzene solution.



None of these methods could be applied economically on a large scale and the successful preparation of the acids depends on the mercuration method of Whitmore and co-workers (J.A.C.S., 1929, 51, 1831, 3363), later elaborated at Edinburgh (Rule and co-workers, J., 1932, 175; 1934, 170). Prolonged treatment of naphthalic acid with aqueous mercuric acetate gives anhydro-8-hydroxy-mercuri-1-naphthoic acid, which is converted to 8-bromo-1-naphthoic acid by the action of bromine (yield 90%).

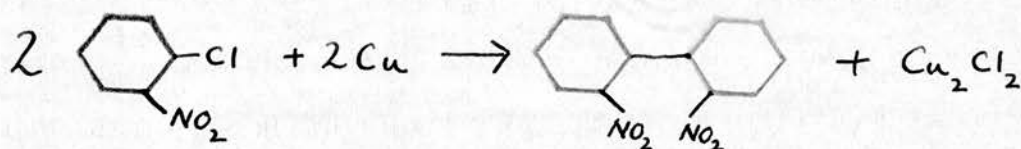


Although the 8-iodo-1-naphthoic acid cannot be prepared by the above methods, it has been obtained from naphthastyril by Goldstein and Francey (Helv., 1932, 15 1362). The naphthastyril is converted by means of caustic soda into 8-amino-1-naphthoic acid, which is then submitted to the diazo-reaction with potassium iodide.



The Ullmann Reaction.

A reaction which has been applied with outstanding results to compounds of the above type is that discovered by Ullmann in 1900 (Ber., 1901, 34, 2174; Ann., 1904, 332, 38). By treatment of iodobenzene with copper bronze at 230°C, two molecules of iodobenzene give one molecule of a dinuclear product, diphenyl, with elimination of iodine as cuprous iodide. While this reaction was found to proceed smoothly with almost all stable iodo-compounds, it was found that bromo- and chloro-compounds only reacted when an increased lability was conferred upon the halogen by the presence of other substituents in certain positions. Thus, although m- and p-nitrochlorobenzene were unreactive, the o-nitro-compound reacted readily to give 2:2'-dinitrodiphenyl.

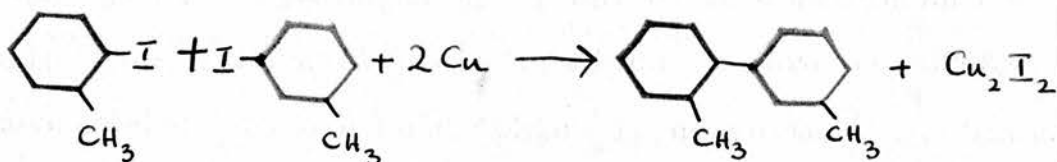


A similar type of activation appears to be conferred upon the halogen by a carbomethoxy group in the ortho-position.

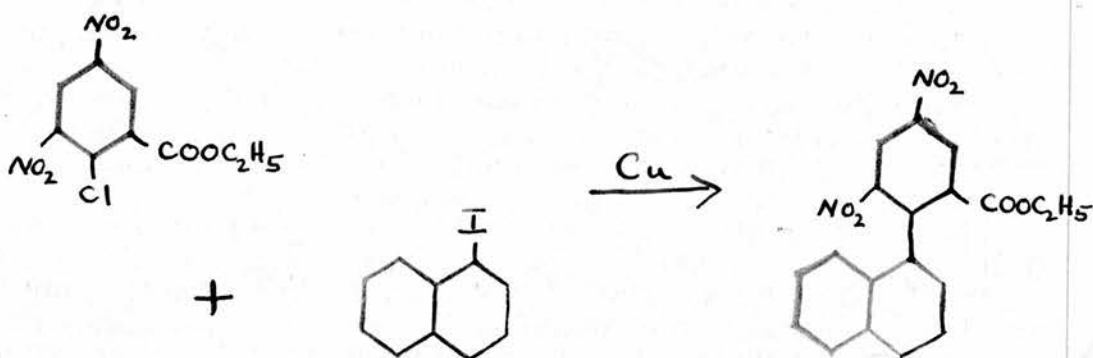
Applications of the Ullmann reaction have been very numerous but especial mention must be made of the production of unsymmetrical derivatives. The first re-



corded instance of such is the formation of 2:3'-ditolyl by treating o-iodo-toluene and m-iodo-toluene with copper bronze and its isolation in 30% yield (Mayer and Freitag, Ber., 1921, 54, 356).

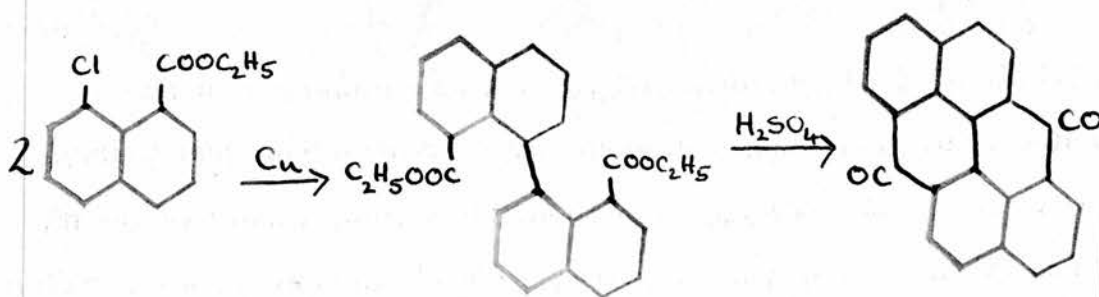


In connection with their work on optical activity, Turner and co-workers have prepared many such compounds. In particular, they obtained a phenyl-naphthyl derivative, ethyl 3:5-dinitro-6-( $\alpha$ -naphthyl)-benzoate by heating ethyl 2-chloro-3:5-dinitro-benzoate and  $\alpha$ -iodo-naphthalene with copper bronze at 180°C (J., 1931, 1188).

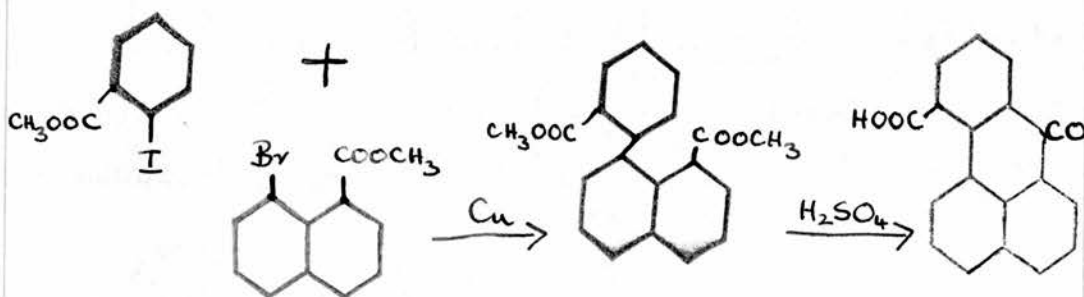


They quote a yield of 53%, and state that no diphenyl or dinaphthyl derivative was obtained as a by-product.

The Ullmann reaction was first applied to 8-halogeno-1-naphthoic acids, in the form of their esters, by Kalb (loc. cit.) in his synthesis of the dyestuff anthanthrone. The ethyl ester of 8-chloro-1-naphthoic acid was subjected to treatment with copper powder at 290°C, and the resulting diethyl 1:1'-dinaphthyl-8:8'-dicarboxylate converted quantitatively to anthanthrone by the action of concentrated sulphuric acid:-



In a similar way, Barnett (Thesis, Edinburgh, 1932; Rule, Pursell and Barnett, J., 1935, 571) obtained a 47% yield of the unsymmetrical compound, methyl 8-(*o*-carbomethoxy-phenyl)-1-naphthoate, by treating methyl *o*-iodo-benzoate and methyl 8-bromo-1-naphthoate with copper bronze at 190-200°C.

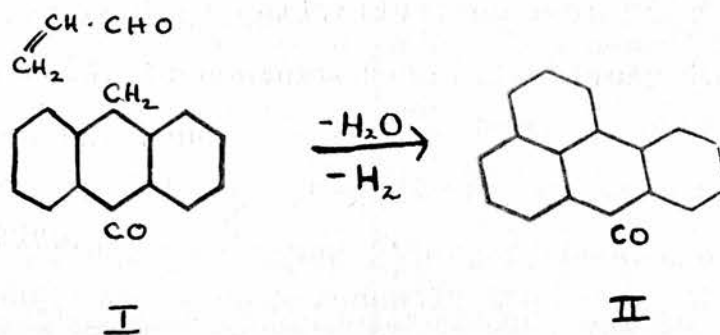


This phenyl-naphthyl derivative, on being warmed with sulphuric acid, is converted quantitatively into 11-carboxy-benzanthrone.

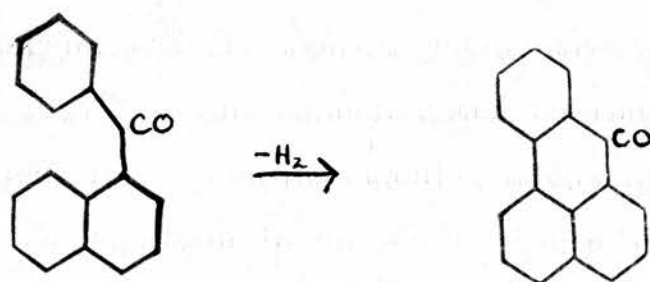
#### Benzanthrone.

Although it is only recently that the Ullmann reaction has enabled a direct connection to be established between 8-halogeno-1-naphthoic acids and benzanthrone, the latter compound has been known for over thirty years and occupies an important position as a dye intermediate.

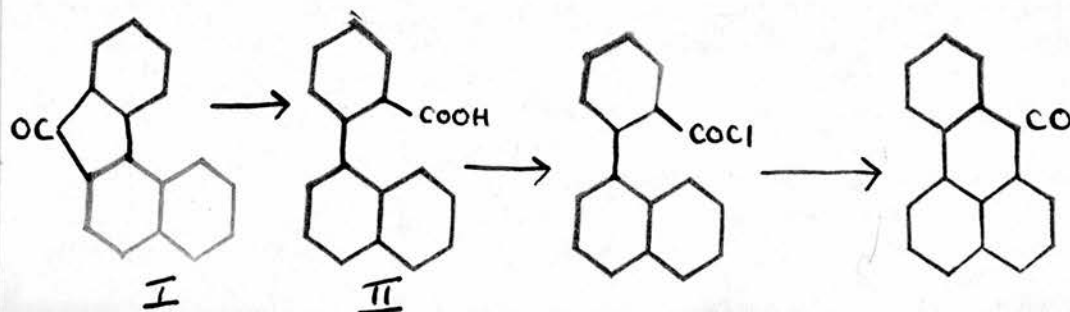
Benzanthrone was first prepared by treating anthraquinone with glycerol and concentrated sulphuric acid in the presence of a reducing agent (Bally, Ber., 1905, 38, 194). The reaction is an adaptation of the Skraup quinoline synthesis, but some doubt exists as to the exact mechanism of the reaction which occurs between the anthrone (I) formed from the reduction of the anthraquinone, and the acrolein, formed from the glycerol and acid (cf. Bally and Scholl, Ber., 1911, 44, 1656; Meerwein, J. prakt. Chem., 1918, 2, 97, 284). Nevertheless there is no doubt that the reaction involves a condensation between the anthrone and acrolein, with loss of water and hydrogen to yield benzanthrone (II).



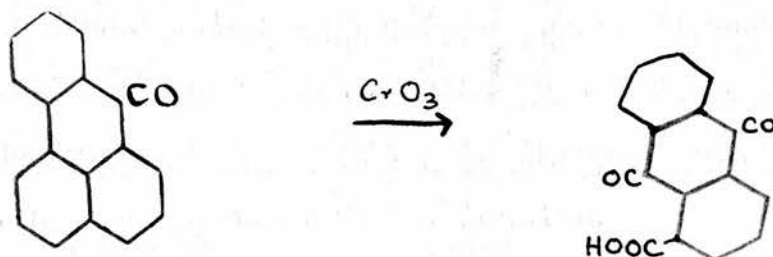
An interesting synthesis of benzanthrone was made by Scholl and Seer (Ann., 1912, 394, 111) by baking 1-benzoyl-naphthalenes with aluminium chloride at 100-150°C, a process of aerial oxidation.



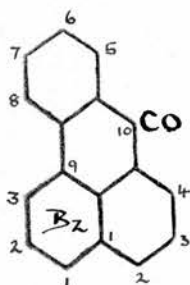
Schaarschmidt (Ber., 1918, 51, 1082) has shown the constitution of benzanthrone by synthesis from benzo-fluorenone (I), which yields *o*-( $\alpha$ -naphthyl)-benzoic acid (II) on mild alkaline fusion. The acid chloride of the latter is converted quantitatively to benzanthrone by treatment with aluminium chloride in benzene solution.



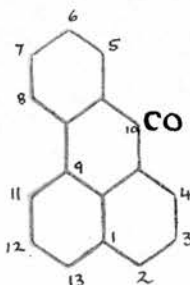
Benzanthrone forms yellow needles of melting-point 170-172°C, dissolving in concentrated sulphuric acid with a deep red colour. On oxidation with chromic acid, it yields anthraquinone-1-carboxylic acid (Liebermann and Roka, Ber., 1908, 41, 1425).



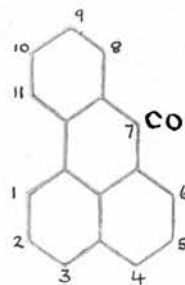
The systematic numbering of benzanthrone and its derivatives is somewhat confusing. The systems formerly in use are based on the anthracene nucleus and are given below (I and II), the second being employed by the Journal of the Chemical Society. The "International Numbering" (III), which is employed in most of the present-day technical literature and is recommended by Heilbron (Dictionary of Organic Compounds), is used throughout this thesis.



I

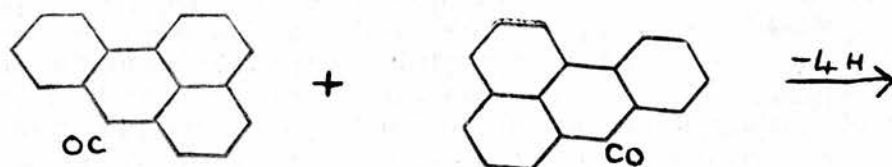


II



III

The importance of benzanthrone and its derivatives lies in their use as intermediates for the "Benzanthrone Colours." Benzanthrone and its substituted derivatives are not highly coloured compounds and have been found of no use as vat dyes. Bally, the discoverer of benzanthrone, found, however, (Ber., 1905, 38, 195; G.P. 185221) that fusion with caustic alkali at 230-240°C yielded a dark-blue vat-dye, dibenzanthrone. It has since been shown (Scholl and Seer, Ann., 1912, 394, 126) that union of two molecules occurs at points 3 and 4.

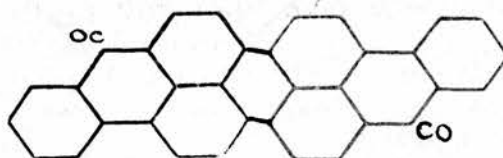
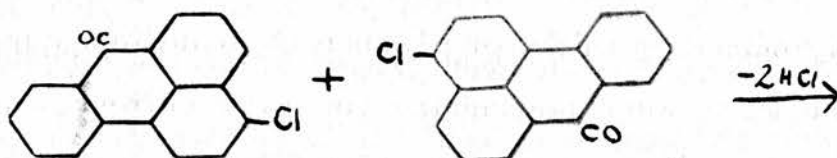


3:3'-4:4'-Dibenzanthrone

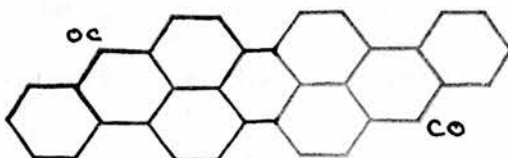
The commercial product, originally known as Violanthrone, appears on the market as Indanthrene Dark Blue B.O., Caledon Dark Blue B etc. It dyes cotton in very fast dark-blue shades from a red-violet hydrosulphite vat.

The symmetrical isomer, isodibenzanthrone, was

originally produced by treating 3-chloro-benzanthrone with alcoholic potash at 140°C (G.P. 194252). It appears on the market as Isoviolanthrone, Caledon Purple R, etc.

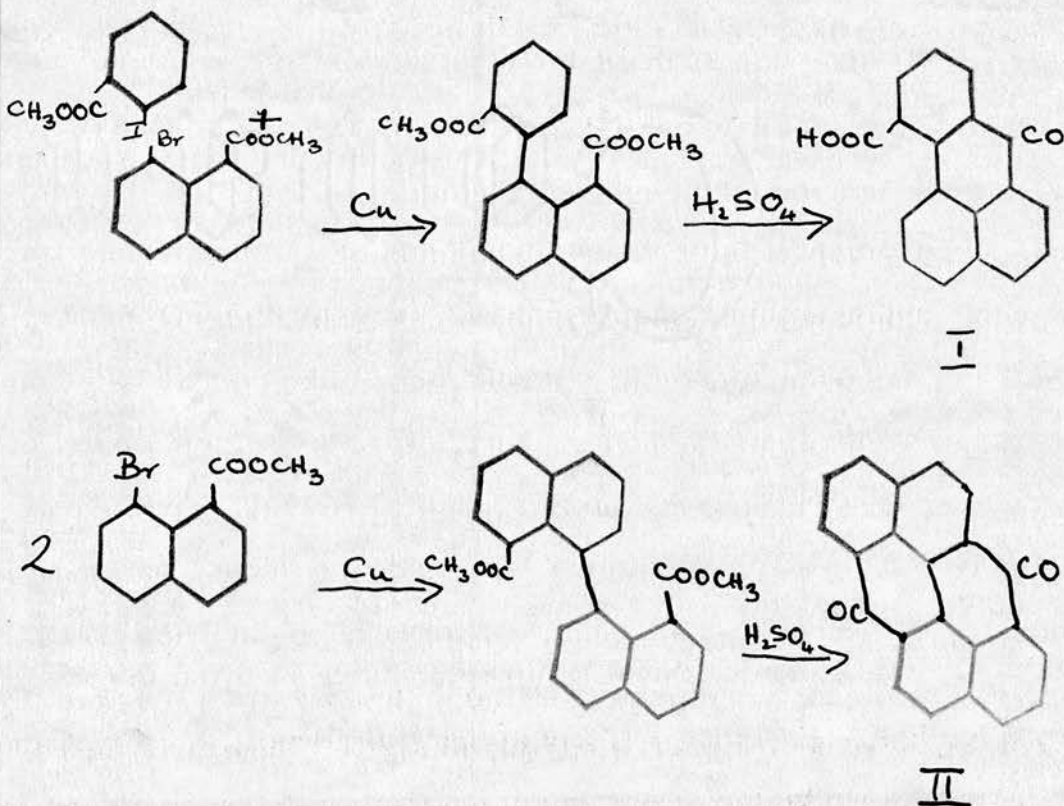


More recently it has been obtained by treating 3:3'-dibenzanthronyl selenides with alcoholic potash (G.P. 448262).



The process of Rule and Barnett (p = 6) has been examined in further detail by carrying out the Ullmann reaction at a lower temperature and employing excess of the iodobenzate. In this manner F.R. Smith (Thesis, Edinburgh, 1955) has increased the yield of unsymmetrical product considerably.

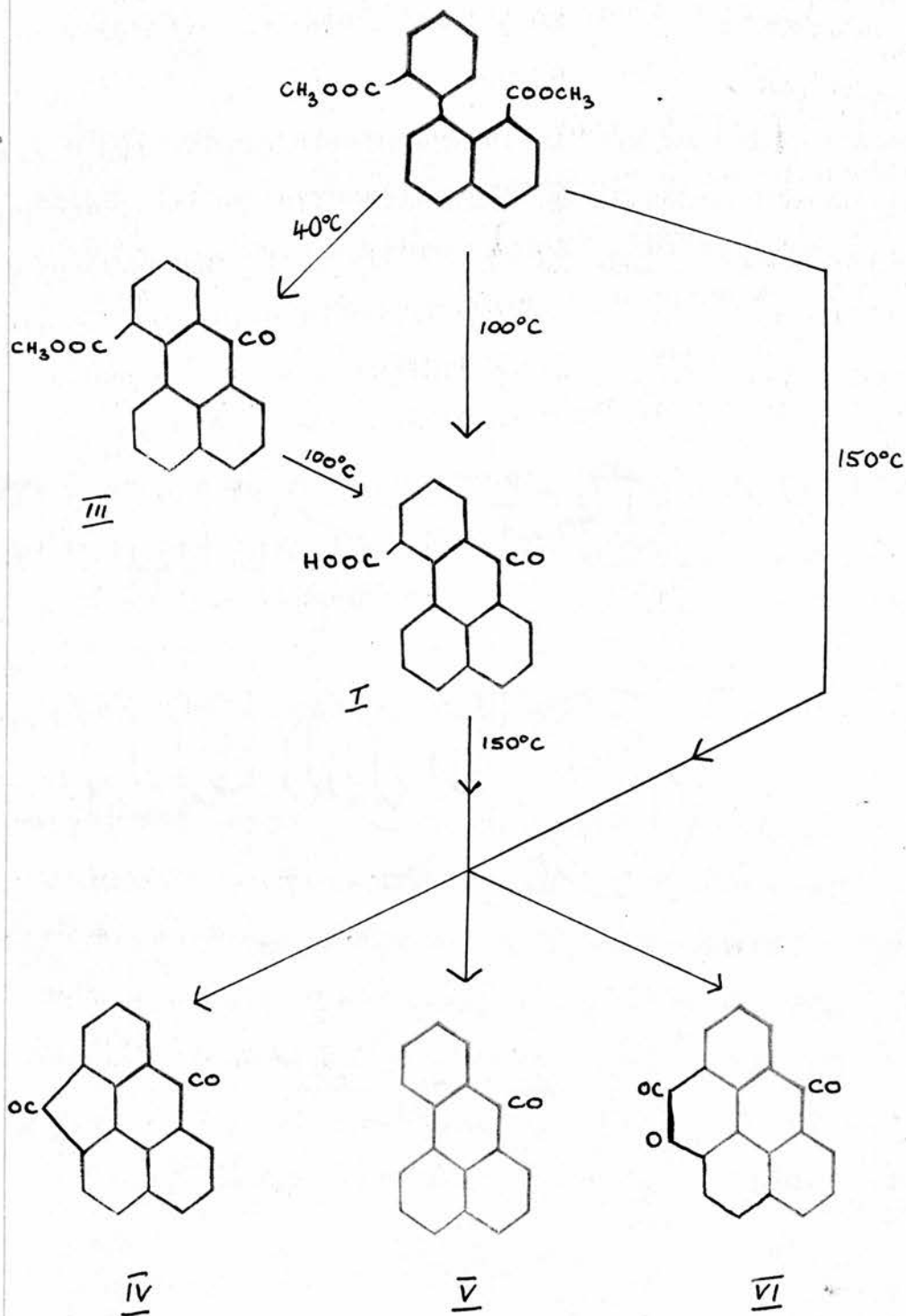
Treatment of the mixed phenyl-naphthyl and di-naphthyl esters with concentrated sulphuric acid at 100°C yields a quantitative mixture of 11-carboxy-benzanthrone (I) and anthanthrone (II) from which the former can be removed by solution in alkali.



The mixed esters may themselves be separated by fractional crystallisation from ligroin, the phenyl-naphthyl



Summary of Action of Concentrated Sulphuric Acid on  
Methyl-8-(o-carbomethoxyphenyl)-1-naphthoate.

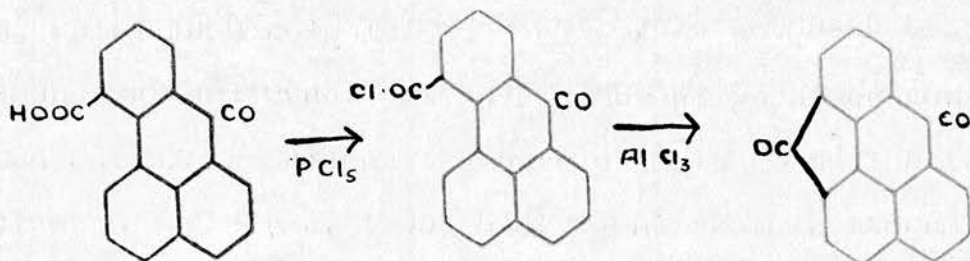


ester being less soluble.

On further investigation of the action of concentrated sulphuric acid on the pure phenyl-naphthyl ester, Bigelow and Rule (J. , 1935, 573) found that treatment at 40°C gave, as primary product, the ester, 11-carbo-methoxy-benzanthrone (III); while at temperatures above 100°C, the reaction became more complex, partial conversion to the expected 1:11-keto-benzanthrone (IV) occurring, accompanied by decarboxylation to benzanthrone (V) and oxidation to an alkali-soluble product which was formulated as the lactone of 1-hydroxy-11-carboxy-benzanthrone (VI).

11-Carboxy-benzanthrone forms golden yellow needles of melting-point 273°C and dissolves in concentrated sulphuric acid to a blood-red solution with yellowish red fluorescence. The solution in alkali is orange with a strong green fluorescence.

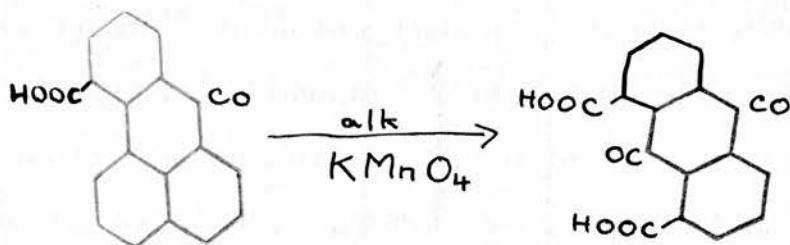
Although only slight conversion of the 11-carboxy-acid to 1:11-keto-benzanthrone was obtained through the agency of concentrated sulphuric acid, good results were obtained by treating the acid in molten phthalic anhydride with phosphorus pentoxide as a dehydrating agent. Partial conversion was also obtained by ring-closure of the acid chloride by means of aluminium chloride.



The diketone forms orange needles of melting-point 327-8°C and dissolves in concentrated sulphuric acid to a cherry red solution without fluorescence. It slowly dissolves in strong boiling alkali, probably forming a mixture of 11-carboxy- and 1-carboxy-benzanthrones but all attempts to separate the mixture have so far failed.

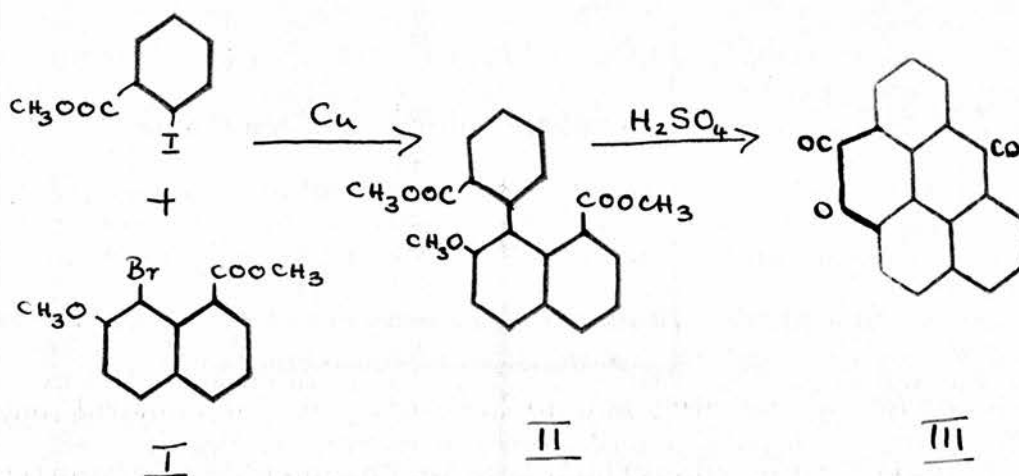
The formulation of the alkali-soluble product (VI p. 13a, obtained in the treatment of the phenyl-naphthyl ester with sulphuric acid at high temperatures) as an oxidation product is supported by the fact that the odour of sulphur dioxide is always noticeable in the reaction mixture. Further, although the oxidation of benzanthrone itself with chromic acid yields anthraquinone-1-carboxylic acid (Liebermann and Roca, loc. cit.), it was found that this treatment converted the 11-carboxy-acid into the lactone (VI) in about 50% yield. Grieve (Thesis, Edinburgh, 1936) has shown that the 11-carboxy-acid is converted into an anthracene derivative, anthraquinone-1:8-dicarboxylic acid, by oxidation with alkaline potassium permanganate.

15.



The lactone of 1-hydroxy-11-carboxy-benzanthrone forms golden yellow needles of melting-point 356-8°C, dissolves in alkali with a characteristic purplish red colour showing red fluorescence and in concentrated sulphuric acid with the same colour as the original 11-carboxy-acid. It has not been possible to prove the existence of any hydroxyl group in the molecule and all attempts at methylation have failed.

The constitution of the lactone has been finally proved by synthesis in these laboratories (J.L. Grieve, loc. cit.). 7-Methoxy-8-bromo-1-naphthoic acid, prepared from oxanilide and  $\beta$ -naphthyl methyl ether by a long synthesis (Davies, Heilbron and Irving, J., 1932, 2715; etc.) was converted into its methyl ester (I) by the thionyl chloride method. On treating this ester with excess of methyl *o*-iodo-benzoate in an Ullmann reaction, there was obtained methyl 7-methoxy-8-(*o*-carbomethoxy-phenyl)-1-naphthoate (II), which was converted quantitatively into the lactone of 1-hydroxy-11-carboxy-benzanthrone (III) by cold concentrated sulphuric acid.



The work of the present thesis deals with various derivatives of benzanthrone and falls into three main sections: -

- a) preparation of the amide of 11-carboxy-benzanthrone and its conversion into the lactam of 1-amino-11-carboxy-benzanthrone;
- b) preparation of the oxime of 1:11-keto-benzanthrone and its conversion into the lactams of 1-amino-11-carboxy-benzanthrone and/or 11-amino-1-<sup>carb</sup>hydroxy-benzanthrone;
- c) preparation of other 11-substituted benzanthrone.

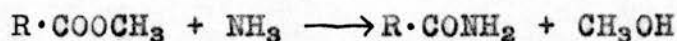
I SUMMARY OF EXPERIMENTAL WORK  
AND DISCUSSION OF RESULTS.

A. The Amide of 11-Carboxy-benzanthrone and its  
Behaviour on Oxidation.

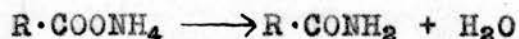
Preparation of the Amide.

Three general methods are available for the preparation of amides: -

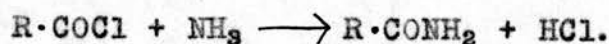
(a) by treatment of the methyl ester of the acid with aqueous, alcoholic or gaseous ammonia;



(b) by heating the ammonium salt of the acid either alone, in the presence of dehydrating agents or under conditions which will favour dehydration;



(c) by treatment of the acid chloride with ammonia;



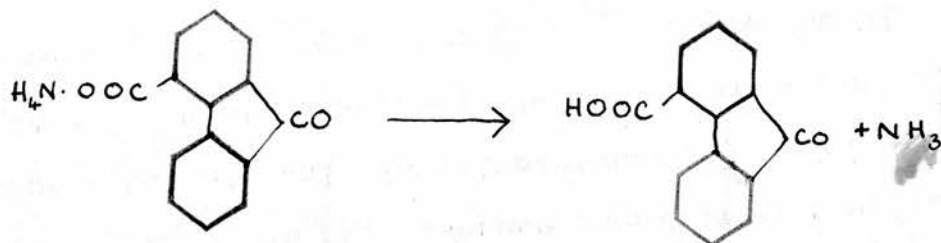
Each of these methods was tried in the case of 11-carboxy-benzanthrone but only the last yielded favourable

results.

Treatment of the methyl ester with concentrated aqueous ammonia or methyl alcohol saturated with the gas in a sealed tube at 100°C for periods up to seventeen hours left the ester unchanged. Dry ammonia gas in methyl alcohol solution in a sealed tube at 200°C for twenty four hours yielded a red powder with no melting-point below 360°C. This appeared to be a condensation product of high molecular weight. It could not be crystallised and gave no reactions indicating the presence of any hydrolysable or alkali-soluble group. Similar treatment to the last but at 150°C for seven hours yielded about 70% of unchanged ester and some unidentified impure solid material of melting-point 215-230°C. At this stage, the process was discontinued as an easier approach to the amide was offered by the acid chloride method.

The ammonium salt was most readily prepared by passing ammonia gas into an alcoholic solution of the acid. It is appreciably soluble in water with a vivid yellow-green fluorescence. The dry salt was found, on heating, to dissociate largely into the free acid and ammonia, and no amide formation could be demonstrated. This behaviour is similar to that of many other carboxylic acids of high molecular weight. Graebe and Aubin (Ann., 247, 275) have shown that, when heated to 100°C, the hydrated ammonium salt of 4-carboxy-fluorenone loses not only water but ammonia to an appreciable extent. Such dissociation also occurs on dry dis-

tillation.



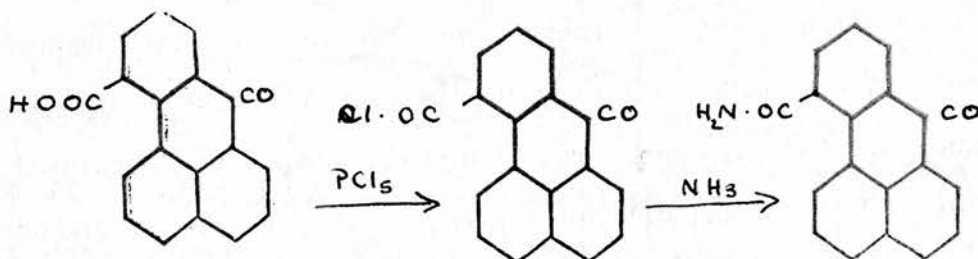
Other attempts to dehydrate the ammonium salt by heating in boiling quinoline and nitrobenzene also failed. In the latter case, it was found that a small quantity of the compound used had undergone oxidation to the lactone of 1-hydroxy-11-carboxy-benzanthrone; this is interesting in view of the fact that Grieve (Thesis, loc. cit.) had been unable to oxidise the free acid by using boiling nitrobenzene.

The 11-carboxy-acid was transformed into the acid chloride by means of phosphorus pentachloride in benzene solution below 50°C; it was found to be reconverted to the acid by caustic soda and also by moist air. If the phosphorus pentachloride treatment was carried out at higher temperatures, there was obtained a complex red substance, insoluble in alkalies or organic solvents. This product was not found capable of purification but, so far as can be judged, it resembles the red compound obtained by Dr. Bigelow (Edinburgh, 1934, unpublished) by treating the acid with thionyl chloride. By carefully controlling the temperature (below 50°C) the



formation of this compound can be avoided.

The amide of 11-carboxy-benzanthrone was finally prepared by treating the solid acid chloride with concentrated aqueous ammonia (yield - 98%).



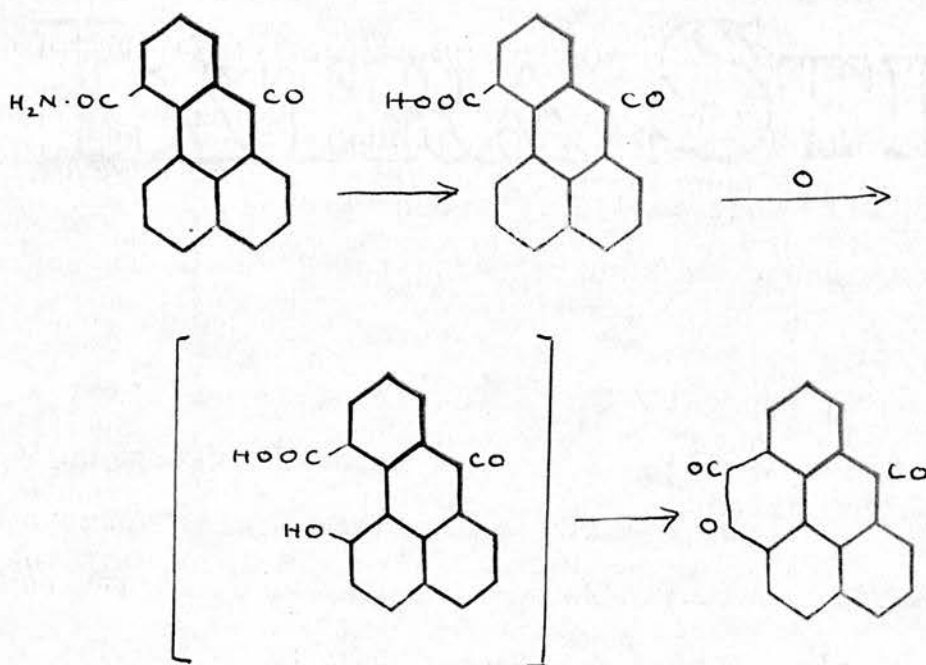
#### Reactions of the Amide.

The amide is much less soluble in organic solvents than the parent acid and crystallises from nitrobenzene in golden yellow needles. Its curious behaviour on fusion is discussed below.

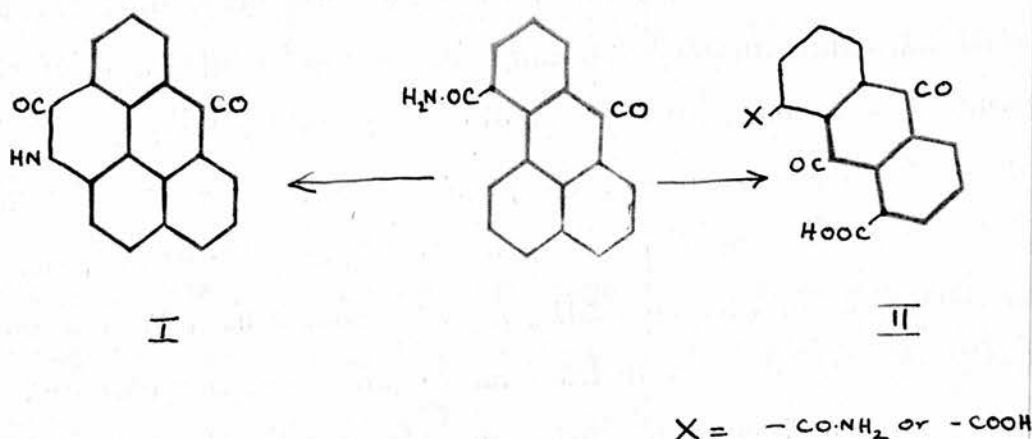
The amide is insoluble in alkalis and is not hydrolysed by them even on prolonged boiling. It is noteworthy that an amide of similar type, that of 4-carboxy-fluorenone, has also been described as insoluble in alkalis (Wegerhoff, Ann., 252, 30); while Leslie and Turner (J., 1931, 1188) were unable to hydrolyse d-3:5-dinitro-6-( $\alpha$ -naphthyl)-benzamide by use of sodium nitrite in hot glacial acetic acid, normal caustic soda solution under reflux or 75% sulphuric acid under reflux. Other examples of this kind also appear in the literature.

In attempts to hydrolyse the amide of 11-carboxy-benzanthrone, it has only been found possible to isolate

the free acid by one method. The amide was quite unaffected by treatment with concentrated sulphuric acid for one hour at 100°C. Hydrolysis was, however, brought about by Bouveault's method (Bull. Soc. chim., 1893, [3], 9, 370) using nitrous acid - the yield of acid in this case was 71% together with a yield of 24% of the lactone of 1-hydroxy-11-carboxy-benzanthrone. The ready formation on this and other occasions of the lactone may indicate that hydrolysis had occurred under conditions which immediately brought about partial oxidation of the acid.



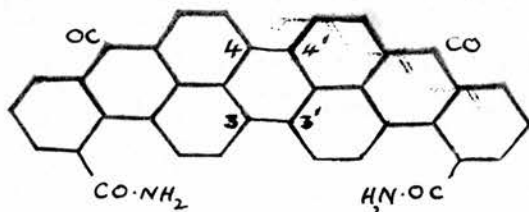
The amide was subjected to treatment with chromic acid in expectation that it might undergo oxidation to give either the lactam of 1-amino-11-carboxy-benzanthrone (I) or an anthraquinone-carboxylic acid (II).



In actual fact the lactone was obtained in 75% yield and no other product. This general method of determining the structure of a benzanthrone derivative cannot therefore be used in this case.

A small quantity (about 10%) of lactone was also obtained on refluxing the amide with moderately concentrated sulphuric acid for 17 hours.

While the amide is thus very resistant to hydrolysis it appears to undergo oxidation comparatively readily. On submitting the compound to potash fusion, condensation to the dibenzanthrone appears to proceed only at very high temperatures (360°C); the violet-black product is hardly soluble in alkaline hydrosulphite and possibly for this reason did not act as a dye.

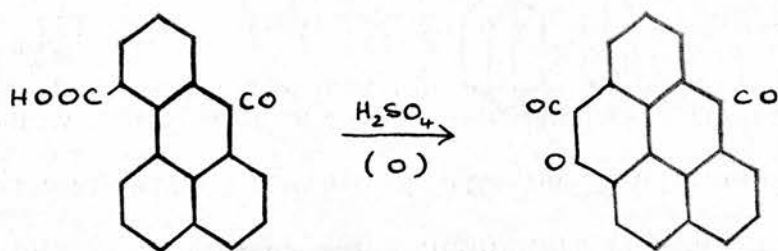


If the fusion is carried out at lower temperatures (250-300°C), there is obtained 70% of a compound crystallising from nitrobenzene in brown needles, m.p. > 360°C. This is believed to be a dibenzanthronyl formed by two molecules coupling up in one position only (i.e. 3:3', 4:4' or 3:4'). Oxidation has not proceeded as far as the dibenzanthrone stage. In the same fusions, there is always a small amount (10-28%) of alkali-soluble material. This presumably results from oxidation of a nuclear hydrogen atom in the amide molecule to a phenolic group (compare Maki, J. Soc. Chem. Ind. Japan, 1932, 35, 577B).

Oxidation also appears to take place when the amide itself is heated. The amide usually sinters over the range 300-310°C, softens at 320°C and appears to melt at 325-7°C. This is followed by subsequent crystallisation at 327-330°C with no further change up to 360°C. The new product is much less soluble in organic solvents. Experiments were carried out heating the amide for various intervals of time at temperatures between 320°C and 360°. Unchanged amide was then removed by boiling with a small quantity of nitrobenzene and the undissolved material was further separated by boiling with a larger quantity of nitrobenzene into brown needles (50% yield: assumed to be a dibenzanthronyl) and a blue black residue (30% yield: a dibenzanthrone?). The purification and identification of small quantities of complex products of this type is extremely difficult owing to their physical properties (lack of determinable melting-point and

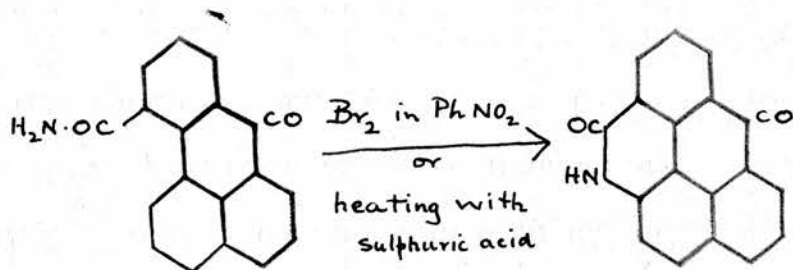
very low solubility) and to the fact that analysis figures are not a reliable means of distinguishing between dibenzanthronyls and dibenzanthrones.

An oxidation of a different type was found to occur when the amide was heated for a considerable period with 50% sulphuric acid. As has already been stated the free benzanthrone-11-carboxylic acid is partly oxidised with hot concentrated sulphuric acid to yield the lactone of 1-hydroxy-11-carboxy-benzanthrone.



The amide under the above conditions was converted into a mixture of products, from which were isolated the lactone (10% yield) and an alkali-insoluble product (40% yield) which did not melt below 360°. From its appearance and colour reactions this compound was concluded to be identical with one obtained later by heating the amide with bromine in nitrobenzene solution. This last treatment has been shown by J. L. Grieve (Thesis, Edinburgh, 1936) to oxidise benzanthrone-11-carboxylic acid to the corresponding 1:11-lactone. It is therefore reasonable to assume the amide will similarly form the

lactam of 1-amino-11-carboxy-benzanthrone. The above product is therefore given the following provisional structure.



Attempts to prepare the lactam of the above formula by heating the lactone with ammonia in a sealed tube and by treating the amide with hypobromite solution were unsuccessful.

It may be useful at this point to summarise the description of the highly complex products mentioned in the foregoing pages. These compounds are all obtained by oxidative changes from the amide of 11-carboxy-benzanthrone. The methods employed were

1. Alkaline fusion at 360°.
2. Alkaline fusion at 250-300°.
3. Heating the amide above its melting point.
4. Prolonged heating with 50% sulphuric acid.
5. Heating with bromine in nitrobenzene.

Reaction 1. leads to the diamide of a dicarboxy-dibenzanthrone; the temperature of fusion, however, is

Properties of Compounds described on pages 23 to 27.

No.	Method of Preparation	Appearance	Colour of Solutions	
			Nitrobenzene	Conc. H <sub>2</sub> SO <sub>4</sub>
II	Alkali-insoluble material from alkaline fusion of the amide at 250-300 °C.	fine dark brown needles	amber, slight red fluorescence	green, strong green fluorescence
III	Heating the amide	fine brown needles	amber, slight red fluorescence	greenish brown, strong green fluorescence
IV	Prolonged action of 50% sulphuric acid on the amide	fine yellow needles	yellow, yellow-green fluorescence	yellow, green fluorescence
V	Action of bromine on the amide in nitrobenzene	fine yellow needles	yellow, yellow-green fluorescence	yellow, green fluorescence
VI	Action of hydrazoic acid on 1:11-ketobenzanthrone or Action of phosphorus pentachloride on oxime	bright yellow powder	yellow, yellow-green fluorescence	red, orange fluorescence

higher than that usually required for this type of change. The compounds obtained from 2. and 3. are assumed to be dibenzanthronyls, in which the condensation has only proceeded half as far as in 1. Reactions 4. and 5. are assumed to yield the lactam of 1-amino-11-carboxy-benzanthrone.

None of these compounds possesses any characteristic melting-point below 360°C and the difficulty of identifying them is increased by the failure of oxidation with chromic acid to yield a substituted anthraquinone, and by the fact that little information is given by the analysis figures, which are in any case usually difficult to obtain with accuracy. The small differences in the elementary composition of the compounds under examination are indicated in the following table:-

		C	H	N
Amide	$C_{18}H_{11}O_2N$	79.1%	4.0%	5.1%
Lactam	$C_{18}H_9O_2N$	79.7	3.3	5.2
Dibenzanthronyl-dicarboxylic diamide	$C_{36}H_{20}O_4N_2$	79.4	3.7	5.15
Dibenzanthrone-dicarboxylic diamide	$C_{36}H_{18}O_4N_2$	79.7	3.3	5.2

A comparison of the colour reactions of the products as given in nitrobenzene and in sulphuric acid solutions respectively is tabulated on p. 26a. This affords some support for the suggestion that II is identical with III and IV with V. The difference between

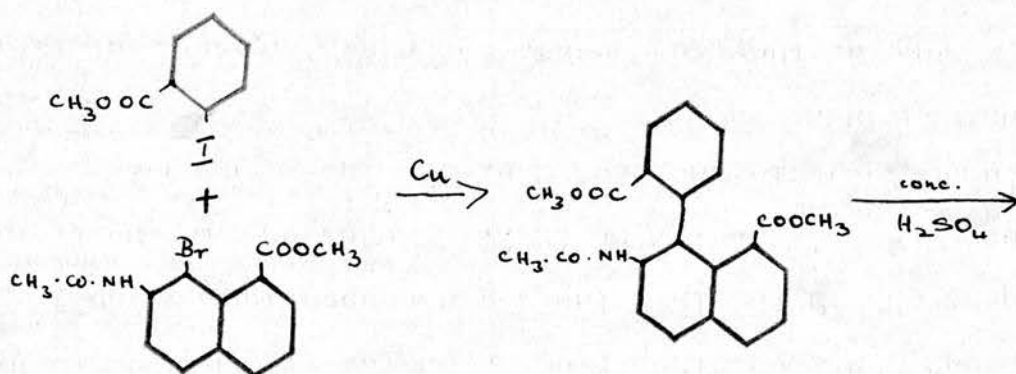


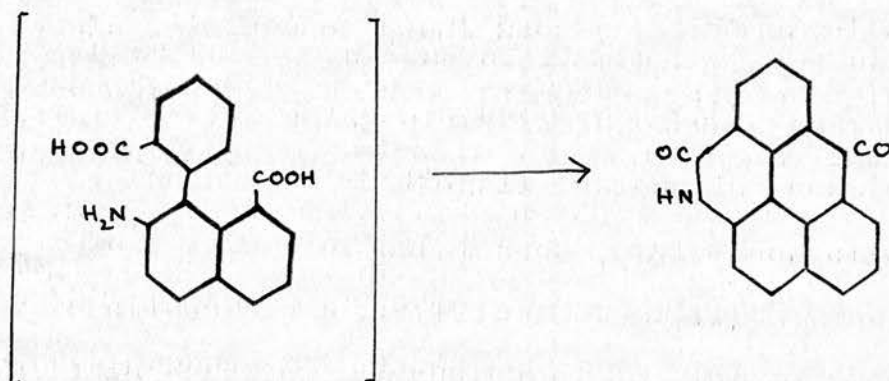
the sulphuric acid reactions of II and III may possibly be due to the difficulty of purifying the products, as it is well known that the alkali fusions in question lead to a complex mixture of substances (Maki, loc. cit.). Colour reactions of an isomeric lactam (VI) described in the following section are also included in the table.

Owing to their extremely low solubilities, it was not found possible to determine the molecular weights of the compounds, either by the boiling-point method or by that of Rast.

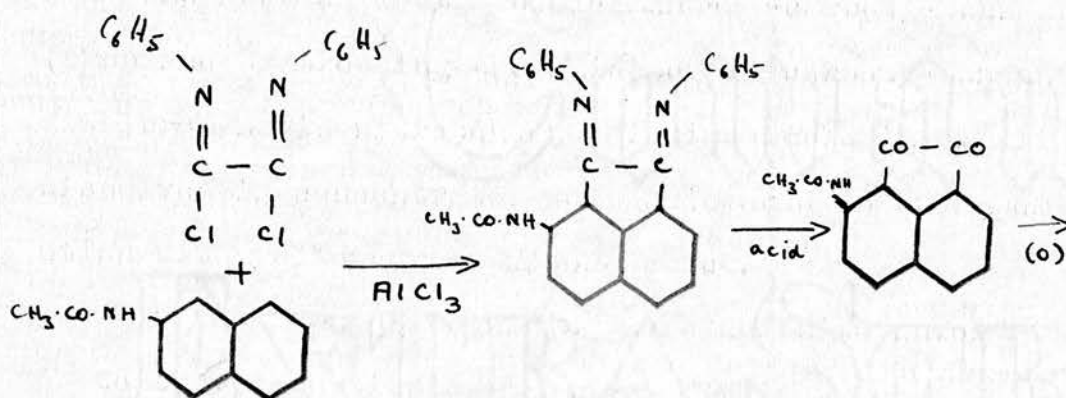
The assumed lactam of 1-amino-11-carboxy-benzanthrone (prepared by treating the amide of 11-carboxy-benzanthrone with bromine in nitrobenzene) is insoluble in alkali and dissolves in concentrated sulphuric acid to an amber solution with yellow-green fluorescence.

In the hope of obtaining more definite information as to the properties of lactams of this type a synthesis was attempted on the following lines. It was proposed to couple methyl *o*-iodo-benzoate with methyl 7-acetamino-8-bromo-1-naphthoate and then to convert the resulting phenyl-naphthyl ester directly to the lactam by concentrated sulphuric acid.

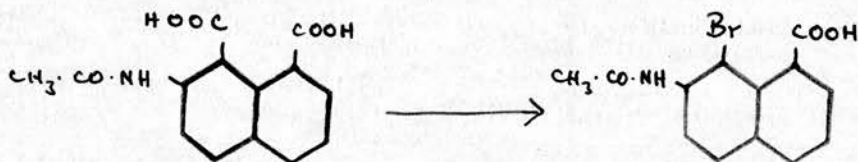




It had been hoped that it would be possible to prepare the substituted naphthoic acid by condensing aceto- $\beta$ -naphthalide with oxalyl-bis-phenyl-imido-chloride,



followed by oxidation, mercuration and bromination.

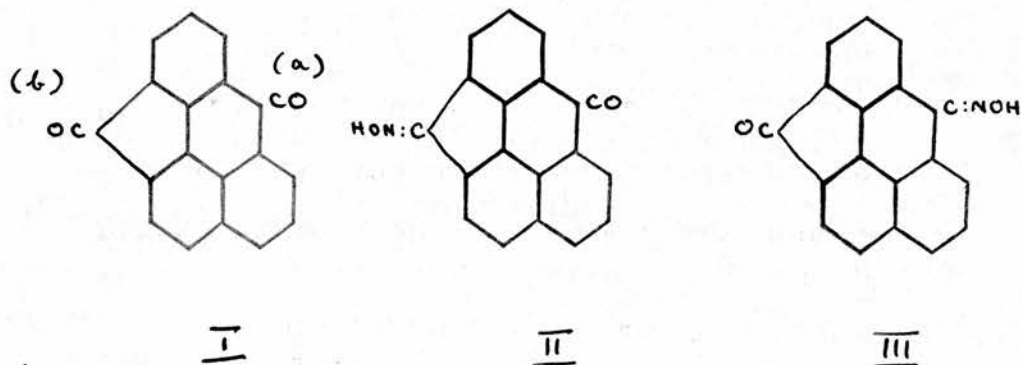


It was found however that the initial condensation with the oxalyl derivative could not be effected, even under varying conditions as to temperature and solvent.

In this respect aceto- $\beta$ -naphthalide thus differs markedly from the methyl ether of  $\beta$ -naphthol, which reacts almost quantitatively in the desired direction. It has been recorded in the literature that scarcely any substituted acenaphthene quinone is obtained from oxalyl-bis-phenyl-imido-chloride and dimethyl- or benzoyl- $\beta$ -naphthylamines (Staudinger, Schlenker and Goldstein, *Helv.*, 1921, 4, 342).

B. Preparation of the Oxime of 1:11-Keto-benzanthrone and Investigation of its Behaviour to Beckmann Reagents.

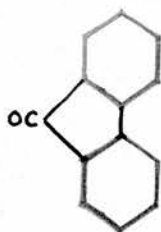
The Oxime.



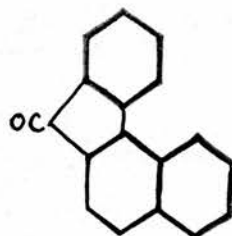
1:11-Keto-benzanthrone (I) possesses two ketonic groups, one (a) in a 6-membered ring in the original

benzanthrone nucleus and the other (b) in a new 5-membered ring which may be formed by dehydration of 11-carboxy-benzanthrone. The existence of these two ketonic groups would indicate that the usual reagents for testing the presence of such groups might attack the molecule in two ways: e.g. hydroxylamine might yield either benzanthrone-1:11-ketoxime (II) or (1:11-keto)-benzanthrone-oxime (III) or a mixture of both compounds.

Certain factors suggest that the ketonic group in the new 5-membered ring will be the less stable and, therefore, the more reactive; this ring, for example, is easily opened by boiling alkali. Now oxime formation is found to occur readily with both fluorenone (IV) (Spiegler, *Monats.*, 5, 195; Schmidt and Söll, *Ber.*, 1907, 40, 4258; Wislicenus, *Ber.*, 1908, 41, 3335) and 3:4-benzofluorenone (allochrysoketone) (V) (Schaarschmidt, *Ber.*, 1916, 49, 1450), both of which contain a ketonic group in a 5-membered ring;



IV



V

but no reference to the formation of an oxime of benz-

anthrone has been discovered. A reaction involving benzanthrone and hydroxylamine hydrochloride appears in the literature (Shepherdson and Thornley, E.P. 279205; C., 1928, I, 757) but the experimental conditions would seem to indicate a more complex reaction than simple oxime formation, - probably some sulphonation occurs. In this instance, a solution of benzanthrone in concentrated sulphuric acid was treated with ferrous sulphate and then, after cooling, with hydroxylamine hydrochloride, treated for 4 hours at 150°C, and poured into iced water. The solid product so obtained was subsequently submitted to an alkaline fusion to yield a blue-green vat dye, but nothing is said about its constitution. In the present work, an attempt was made to prepare an oxime of benzanthrone by boiling an alcoholic solution with hydroxylamine hydrochloride in the presence of alkali, but the ketone was recovered unchanged in quantitative yield.

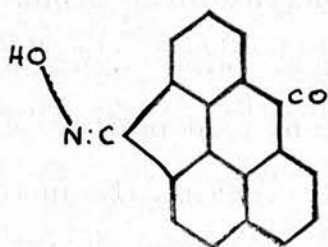
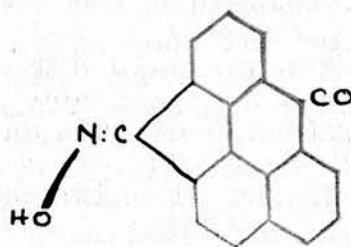
It thus appears that in ketobenzanthrone oxime formation is more likely to occur in the 5-membered than in the 6-membered ketonic ring. In agreement with this conclusion, 1:11-keto-benzanthrone has now been converted into an oxime by a method similar to that used in the case of fluorenone (Spiegler, loc. cit.), and the resulting compound is formulated as benzanthrone-1:11-ketoxime (II, p. 29).

According to the directions of the above author, an alcoholic solution of 1:11-keto-benzanthrone was heated under reflux with one molecular proportion of hydroxyl-

amine hydrochloride and the oxime crystallised out on cooling. The method has two disadvantages however: the volume of alcohol necessary to dissolve the original ketone is large, while the oxime is rather more soluble than the parent substance. A modified method has been found preferable in practice. An alcoholic suspension of the ketone and the hydrochloride is heated under reflux and a dilute aqueous solution of caustic soda slowly run in. The base is liberated, and the oxime passes into solution as it forms, apparently as a red sodium salt. As the salt is readily soluble, a suspension of the ketone can be used and the volume of liquid cut down considerably. The solution is filtered free of any unchanged ketone and the oxime precipitated by acidification.

As mentioned above, the oxime forms a red sodium salt. This is insoluble in cold water but fairly soluble in boiling water to give a deep pink solution with orange fluorescence.

The crude oxime is orange in colour and as usually isolated melts at 306-9°C. It was subsequently found that treatment with various solvents under certain conditions separated the product into two different crystalline solids of melting-points 314°C and 322°C respectively. These were at first assumed to be the two stereochemically possible benzanthrone-1:11-ketoximes (I and II) arising from the unsymmetrical form of the molecule.

III

An orange-yellow microcrystalline solid of melting-point  $314^{\circ}\text{C}$  also was obtained by subliming the crude oxime under reduced pressure or by dissolving the crude solid in boiling xylene or decalin (solubility only 0.2 gm. in 100 ml.), filtering the hot solution and treating with light petroleum ether. This proved by reactions and analysis to be an oxime of 1:11-ketobenzanthrone.

As the crude oxime is so very difficultly soluble in decalin but dissolves readily in nitrobenzene, the latter solvent was on several occasions used as a crystallising agent. But the loss involved was considerable and the resultant orange needles melted lower and over a wide range,  $306\text{-}317^{\circ}\text{C}$ . Eventually it was found that no product of sharp melting-point could be isolated with this reagent.

The use of animal charcoal in the above process in an attempt to purify the crude oxime or to isolate a possible isomer yielded unexpected results. Animal charcoal has actually been employed in the interconversion of stereoisomeric oximes by Taylor and co-workers (J.,

1930, 2305 et seq.). In the present case, treatment of the crude oxime with animal charcoal and boiling nitrobenzene gave over 50% of fine orange needles (m.p. 319-322°C). Further treatment did not raise the melting-point above 322°C. The experiment could not be reproduced exactly - later samples having lower melting-points in the range of 306-317°C. A mixed melting-point of the above sample with a sample (m.p. 314°C) deposited from decalin showed a large depression. As the compound was also proved to contain nitrogen by a sodium fusion, it was concluded to be the isomeric oxime and sent away for analysis.

Meanwhile, however, it was found that although both compounds, A (m.p. 314°C) and B (m.p. 322°C), contained nitrogen, the resemblance went no further. On treatment for one hour at 100°C with concentrated sulphuric acid in an attempt to bring about a Beckmann rearrangement of the oxime, A was recovered unchanged in quantitative yield but B gave a 75% yield of 1:11-keto-benzanthrone. Again, while A is soluble in boiling alkali and is recovered on acidification, B was found to be insoluble. Finally, when the analysis results came to hand, A gave agreement with the theoretical values for the oxime but B did not. It was also discovered that while mixtures of A with B or the parent ketone gave appreciable melting-point depressions, mixtures of B with the parent ketone gave only slight depressions.

These results suggested that the compound B was



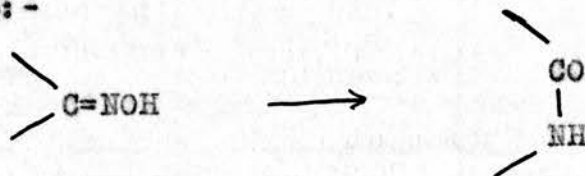
some other nitrogenous derivative of the ketone. The animal charcoal might possibly have contained an acidic impurity such as might bring about hydrolysis, and it was considered that the nitrogen detected in the analysis might be due to an association between the ketone and nitrobenzene employed as solvent. Calculation showed that the elementary analysis figures for a molecular compound composed of one molecule of ketone and one molecule of nitrobenzene agreed with the actual values obtained, and the matter was conclusively proved by showing that quantitative loss of nitrobenzene occurred after heating for two hours in an oven at 220°C. The stability of the molecular compound in this case is unusual and unexpected.

In an attempt to isolate an isomeric oxime, a later experiment was carried out heating the oxime with nitrobenzene saturated with hydrochloric acid, but the original oxime was recovered unchanged. On subsequently crystallising this from nitrobenzene in the presence of animal charcoal, similar results were obtained to those already mentioned. It thus appears that only one form of benzanthrone-1:11-ketoxime has been isolated, notwithstanding the two theoretical possibilities.

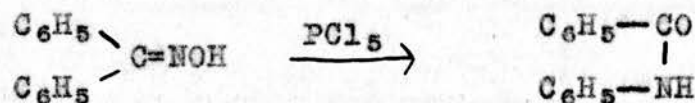
#### The Beckmann Reaction.

To elucidate the structure of stereo-isomeric oximes, it is customary to use the Beckmann reaction. Under the influence of certain reagents (e.g. phosphorus

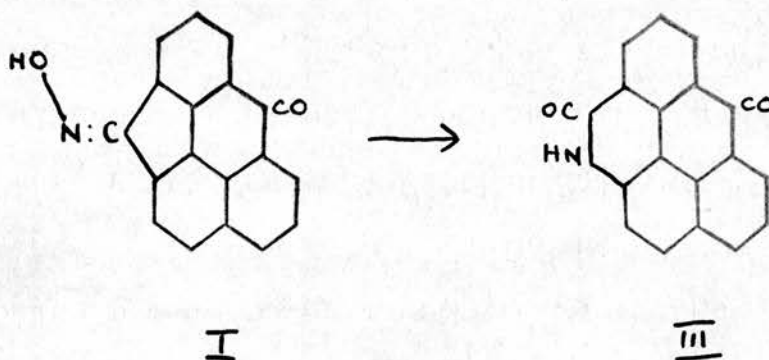
pentachloride, concentrated sulphuric acid, acetyl chloride, benzene sulphonic chloride, hydrochloric acid in glacial acetic acid), oximes of ketones can be converted into amides: -

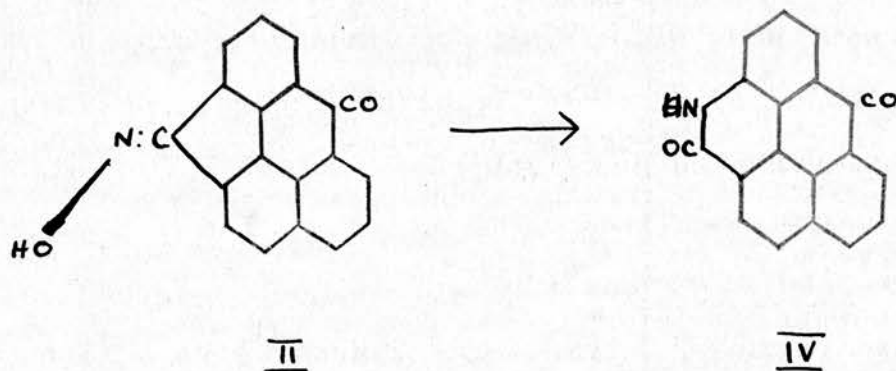


thus, benzophenone oxime gives benzanilide (Beckmann, Ber., 1886, 19, 988).



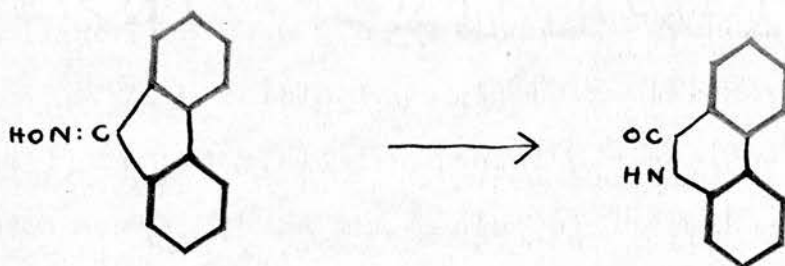
Adopting the modern views for the mechanism of the Beckmann change involving a trans-interchange between the hydroxyl of the oximino-group and a group attached to the ketonic carbon atom (Meisenheimer, Ber., 1921, 54, 3206), the two possible isomeric benzanthrone-1:11-ketoximes (I and II) should yield the lactam of 1-amino-11-carboxy-benzanthrone (III) and the lactam of 11-amino-1-carboxy-benzanthrone (IV) respectively, thus: -





These lactams are of interest from their structural relation to the lactone of 1-hydroxy-11-carboxy-benzanthrone, the acidic oxidation product obtained in the preparation of 11-carboxy-benzanthrone.

In searching for a suitable reagent for the Beckmann conversion reference was made to the analogous conversion of fluorenone oxime into phenanthridone.

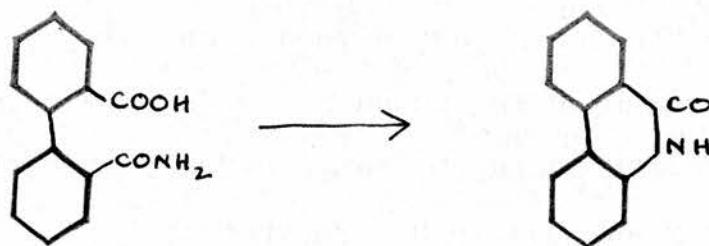


In this case, however, stereo-isomeric oximes cannot exist and only one product of the Beckmann change is possible.

Shortly after the discovery of the Beckmann rearrangement in 1884, Beckmann and Wegerhoff (*Ann.*, 1889, 252, 35) tried to expand the scope of the reaction to the oximes of cyclic ketones. In the case of fluorenone oxime, they showed that two of the typical reagents

were ineffective, a mixture of acetic anhydride and hydrochloric acid in a sealed tube only led to acetylation, while the use of concentrated sulphuric acid resulted in sulphonation. Nevertheless, treatment with a solution of phosphorus pentachloride in phosphorus oxychloride gave an oil, which with water resulted in a yellow solid of melting-point  $287^{\circ}\text{C}$ . Owing to difficulties involved in purifying the substance, the subject was not pursued further. Even when phenanthridone (m.p.  $293^{\circ}\text{C}$ ) was prepared four years later, no connection was traced between it and Beckmann's product.

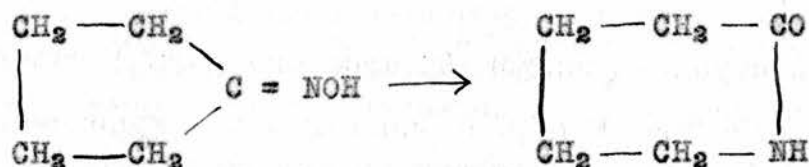
Phenanthridone was first prepared as such and its constitution shown in 1893 by Graebe and Wander (Ann., 1893, 276, 245), who obtained it by the action of alkaline hypobromite upon diphenamic acid.



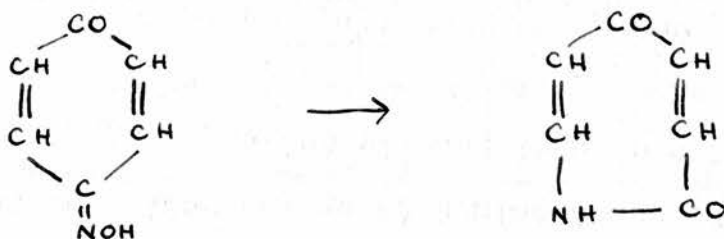
The same year, it was prepared from fluorenone oxime by a zinc chloride fusion (Pictet and Patry, Ber., 1893, 26, 1964).

Although this latter treatment is more vigorous than a normal Beckmann reagent, it was almost twenty five years later before Moore and Huntress (J. A. C. S., 1927, 49, 2618) put forward the theory that Beckmann's product obtained from fluorenone oxime was also phenanthridone.

This was supported by the fact that Wallach (Ann., 1899, 309, 1; 1900, 312, 171; 1906, 346, 249) was able to show that cyclomethylene ketoximes were rearranged by concentrated sulphuric acid into lactams of amino-acids, e.g. cyclopentanone oxime gives piperidone, (the lactam of  $\delta$ -amino-valeric acid),



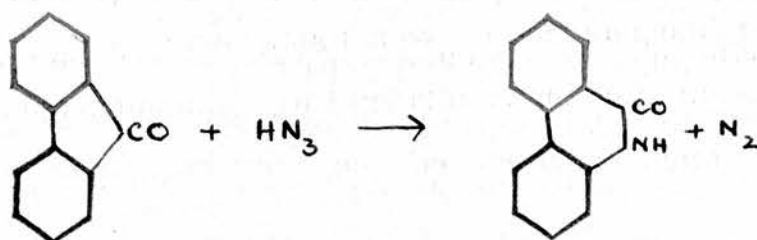
while Beckmann in collaboration with Liesche had rearranged quinone monoxime to a 7-membered ring compound (Ber., 1923, 56, 1):



Moore and Huntress repeated Beckmann and Wegerhoff's experiment on the rearrangement of fluorenone oxime and proved the product to be phenanthridone.

More recently various phenanthridones have been prepared directly from the parent fluorenones by the use of hydrazoic acid. In the original German paper (C., 1930, II, 2959; E.P. 333173) it is stated that a solution of the ketone in concentrated sulphuric acid and benzene was treated with a benzene solution of hydrazoic acid at 30°C. The mixture was poured on to ice, filtered and the solid product crystallised from nitrobenzene

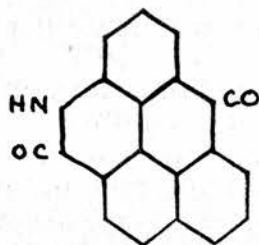
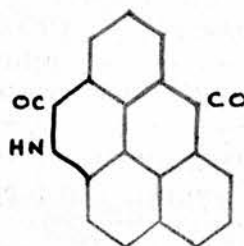
or other suitable solvent. By this method fluorenone was converted to phenanthridone in 93% yield: the highest yield from the oxime by other methods was 84%. Walls (J., 1935, 1405) has since introduced a modified method. The solution of the ketone in concentrated sulphuric acid is cooled in ice and treated dropwise with an aqueous solution of sodium azide, and the phenanthridone isolated as above. The author states that "the reaction is analogous to a Beckmann change."



By Walls' method, 1:11-keto-benzanthrone has now been converted into an alkali-insoluble, high melting compound isomeric with the oxime, which is assumed to be of the anthridone type. The compound is much less soluble than the ketone or its oxime and crystallises from nitrobenzene as a bright yellow powder which does not melt below 360°C. It has not been possible to show the formation of any intermediate oximino-compound in the above reactions: this point will be taken up at a later stage when discussing the mechanism of the change.

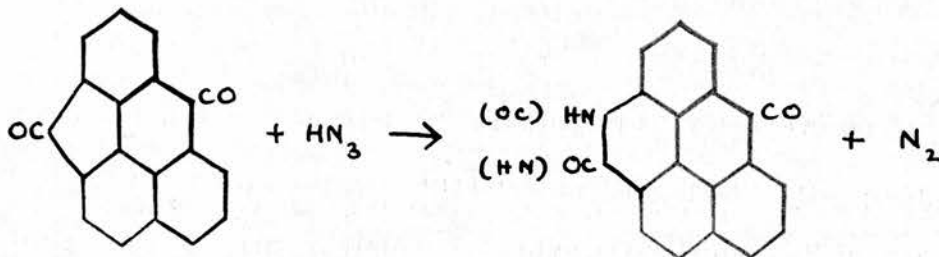
From its high melting-point and general insolubility, it appears to be of the anthridone type (cf. phenanthridone, m.p. 293°C, insoluble in alkalis). As to its constitution

it may have either of the following formulae:

III

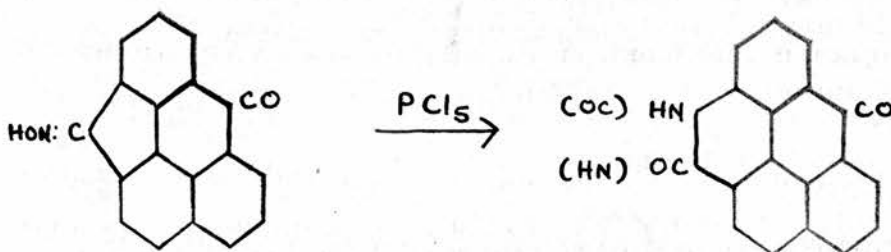
Formula I is however considered the more probable, as in appearance and colour reactions the compound differs from the substance described on p. 24 and assumed to be the lactam of 1-amino-11-carboxy-benzanthrone. For convenience of comparison these colour reactions have been included in the table on p. 26a.

There still remains the possibility that some product of type II may have formed during the above reaction and been removed during the purification. The 75% yield of pure lactam which was isolated is similar to the results obtained by Walls in the phenanthridone series.

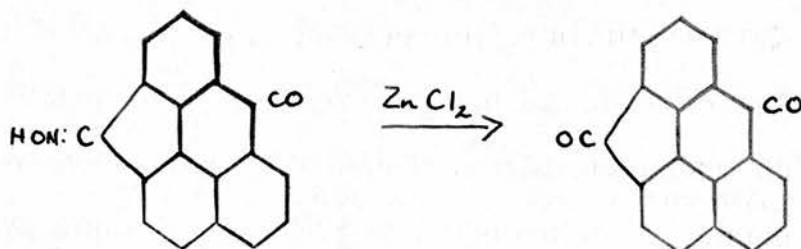


An identical compound was obtained in good yield by treating the oxime of 1:11-keto-benzanthrone (m. p. 314°C) with phosphorus pentachloride in anisole at 60°C

for 5 hours - no reaction occurred at 0°C. The yield (70%) compares favourably with the yield (84%) of phenanthridone obtained by Moore and Huntress (*loc. cit.*) from the action of phosphorus pentachloride in phosphorus oxychloride on fluorenone oxime. Thus the interesting fact emerges that the same isomer is obtained by use of phosphorus pentachloride as by the hydrazoic acid method.



An unexpected result was obtained when the oxime was submitted to a zinc chloride fusion. Whereas Pictet and Patry (*loc. cit.*) converted fluorenone oxime into phenanthridone by this means, it was found that in this case the parent ketone was obtained. Presumably the high temperature and the acidic nature of the medium combined in this case to bring about hydrolysis.



Although concentrated sulphuric acid at 100°C had no effect on the oxime, extensive sulphonation appeared



Reactions of Fluorenone, 1:11-Keto-benzanthrone and Their Oximes to Various Reagents.

Reagent	Fluorenone Series	1:11-Keto-benzanthrone Series
Ketone and hydrazoic acid	93% phenanthridone <sup>1</sup>	75% anthridone derivative (crystallised)
Oxime and phosphorus pentachloride	phenanthridone small yield <sup>2</sup> 84% <sup>3</sup>	70% anthridone derivative (crystallised)
Oxime and conc. sulphuric acid	sulphonation <sup>2</sup>	sulphonation at high temperature
Oxime and acetic anhydride	acetylation <sup>2</sup>	—
Oxime and zinc chloride	phenanthridone 30% <sup>4</sup>	1:11-keto-benzanthrone 74%
Oxime and benzene sulphonic chloride	—	no change

References:

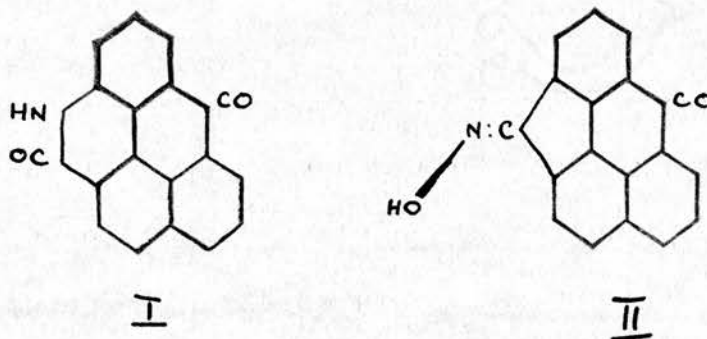
- <sup>1</sup> Walls, J., 1935, 1405.
- <sup>2</sup> Beckmann and Wegerhoff, Ann., 1889, 252, 35.
- <sup>3</sup> Moore and Huntress, J.A.C.S., 1927, 49, 2618.
- <sup>4</sup> Pictet and Patry, Ber., 1893, 26, 1964.

to take place at 150°C. This is in agreement with the observation of Beckmann and Wegerhoff (*loc. cit.*) that fluorenone oxime underwent sulphonation under the action of concentrated sulphuric acid.

Another reagent often used in the Beckmann transformation is benzene sulphonic chloride in solution in alkali or pyridine (Wege, *Ber.*, 1891, 24, 3539; Werner and Piquet, *Ber.*, 1904, 37, 4295; Beckmann, *Ber.*, 1923, 56, 6). In the case under review treatment with this reagent in pyridine solution at 100°C for six hours had no effect upon the oxime.

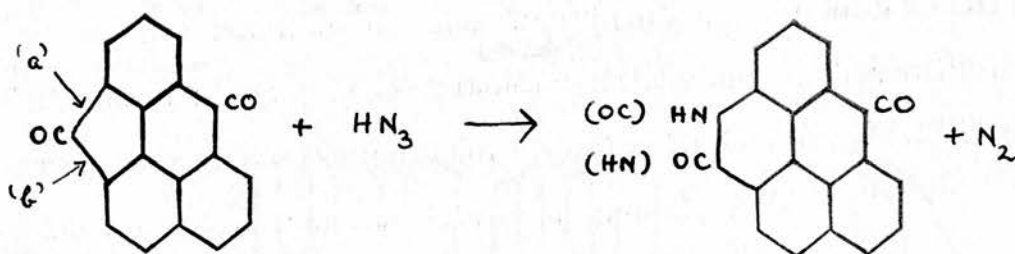
The results of the treatment of the oximes of fluorenone and 1:11-keto-benzanthrone with various reagents are summarised opposite. Only in the case of zinc chloride, do the results diverge greatly.

If the anthridone derivative is accepted as being the lactam of 11-amino-1-carboxy-benzanthrone, (I) then the oxime (m.p. 314°C) must be given the following configuration (II) (*cf.* p. 37).



At this point it is appropriate to discuss the mechanism of the reaction of hydrazoic acid on fluorenone and 1:11-keto-benzanthrone. Intermediate oximino-

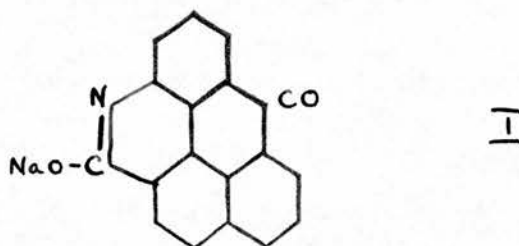
formation has been assumed, but this is not in agreement with the fact that both oximes are unaffected by concentrated sulphuric acid alone at the temperature of the experiment (0°C). There does not appear to be any reason why an oxime should be assumed as an intermediate except that the anthridones have generally been obtained through a compound of this type. The action of the hydrazoic acid seems to be rather due to an ability to lose nitrogen and to the instability of the 5-membered ring in both ketones:



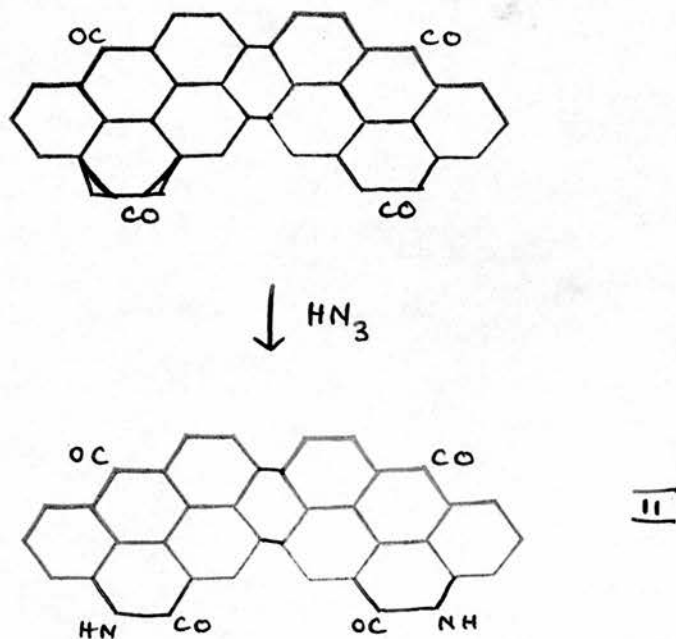
for it was found that hydrazoic acid had no effect upon benzanthrone itself under similar conditions. The preferential formation of one of the two possible anthridones indicates that one bond (probably "a") is more liable to break than the other ("b").

The anthridone in question forms a bright yellow powder which does not melt below 360°C and dissolves in concentrated sulphuric acid to an orange-red solution with slight green fluorescence. Although the lactam is unlike the oxime in that it does not dissolve appreciably in boiling alkali, nevertheless it appears to form a red sodium salt in contact with aqueous sodium hydroxide.

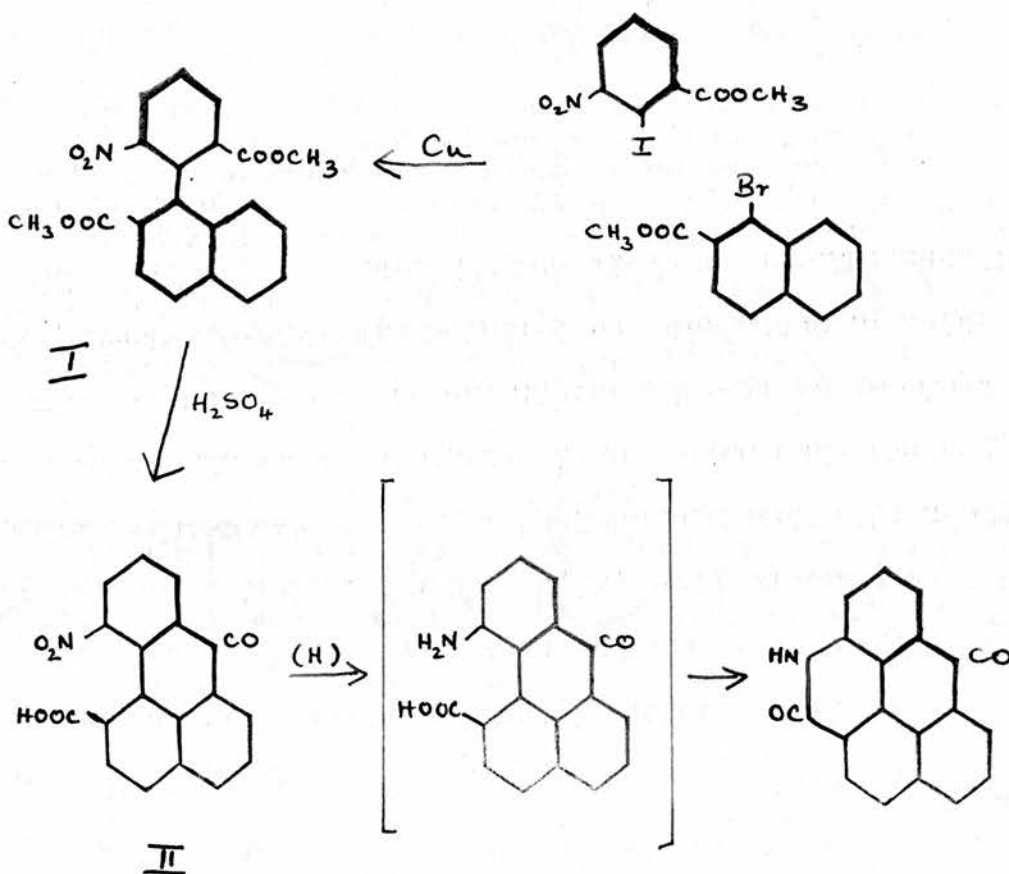
The yellow colour is restored by acidification or even by filtration and treatment with water. This unstable sodium salt is probably of the enolic type (I).



Alkaline fusion of the anthridone for one hour at 280°C gave an almost quantitative yield of the dibenzanthrone derivative (II). The latter forms a bluish green alkaline hydrosulphite vat only with difficulty and dyes cotton a soft purple grey, fast to alkalis. An attempt was made to obtain the same compound by the action of hydrazoic acid on 1-11:1'-11'-diketo-3-3':4-4'-dibenzanthrone but without effect.



An attempted synthesis of the lactam of 11-amino-1-carboxy-benzanthrone proved unsuccessful. It was proposed to obtain 11-nitro-1-carboxy-benzanthrone (II) by sulphuric acid treatment of the unsymmetrical product (I) from an Ullmann reaction between methyl 3-nitro-2-iodo-benzoate and methyl 1-bromo-2-naphthoate. Subsequent mild reduction of the nitro-carboxy-benzanthrone was expected to yield the lactam.



Unfortunately no nitro-carboxy-benzanthrone could be isolated. The mixture of, presumably, diphenyl, dinaphthyl and phenyl-naphthyl esters from the Ullmann reaction could not be separated; treatment of the mixture with concentrated sulphuric acid at 100°C gave anthanthrone (from the dinaphthyl derivative), and a nitro-acid of

melting-point 267-9°C. The latter appeared to be a dinitro-diphenic acid, although it was in an impure form as its analysis figures and melting-point did not agree very closely with the expected values. In an analogous coupling between ethyl 3:5-dinitro-2-chloro-benzoate and iodobenzene, Lesslie and Turner (J., 1931, 1188) obtained 57% of unsymmetrical product and could not isolate any dinaphthyl or diphenic ester. They did not however submit the product to sulphuric acid treatment. This matter is discussed in greater detail in the experimental section (p.117).

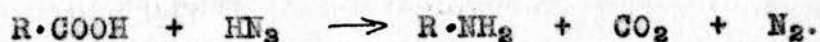
### C. Other 11-Substituted Benzanthrones.

#### 11-Amino-benzanthrone.

Consequent upon the success attending the use of hydrazoic acid in the conversion of 1:11-keto-benzanthrone into the anthridone, it was decided to see if the same reagent could be used to convert the carboxy-group in benzanthrone-11-carboxylic acid into an amino-group.

(Oesterlin, Z. angew. Chem., 1932, 45, 536; compare also Schmidt, C., 1930, I, 1536; and von Braun, Ber., 1931, 64, 2866; Ann., 1931, 490, 100). The method involves treating a solution of the carboxy-acid in concentrated

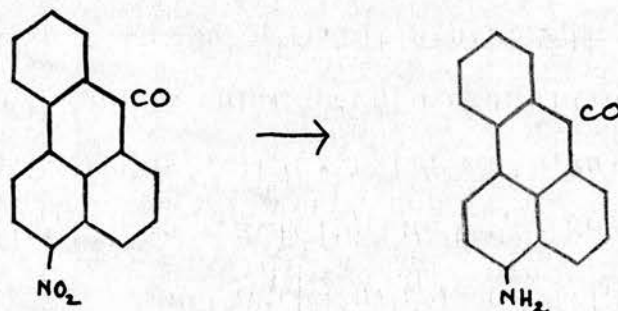
sulphuric acid and chloroform with solid sodium azide at 45-55°C.



Using this method 11-carboxy-benzanthrone has now been converted into 11-amino-benzanthrone in 86% yield.

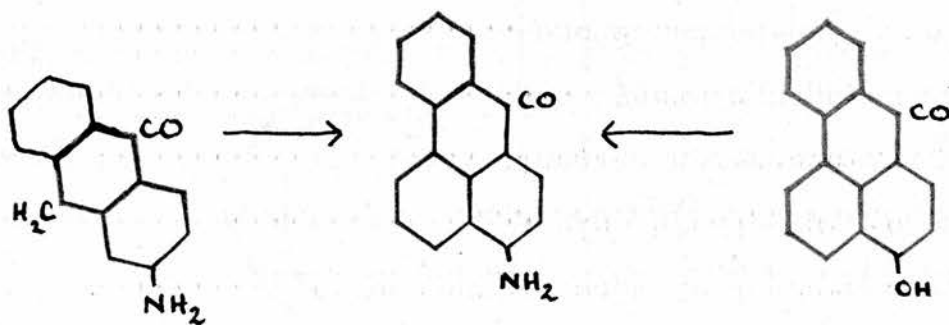
Various references to amino-benzanthrones occur in the patent literature but their chemical and physical properties are not discussed, the chief concern being their practical use as a source of fresh violanthrone dyestuffs. An 11-amino-benzanthrone is noted as being obtained from the 11-chloro-compound but it is not further described (C., 1929, I, 1748; E.P. 301197). Only two mono-amino-benzanthrones appear in the literature proper.

Reduction of the corresponding nitro-compounds has yielded 3-amino-, 3-9-diamino- and 3-4-9-triamino-benzanthrones (C., 1908, I, 2071; II, 364); the 3-amino-benzanthrone (m. p. 239-240°C) is readily soluble in organic solvents and is obtained in red-brown needles from aqueous pyridine.

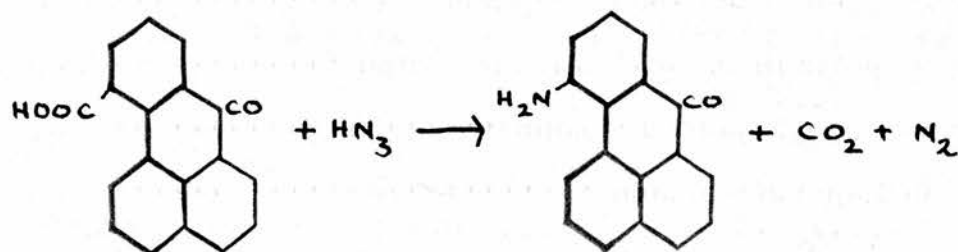


4-Amino-benzanthrone has been prepared by a Skraup

synthesis from 3-amino-anthrone (F.P. 23880; cf. Bally and Scholl, Ber., 1911, 44, 1658) and by heating 4-hydroxy-benzanthrone with ammonia in an autoclave (Perkin and Spencer, J., 1932, 121, 480). It crystallises from alcohol in red needles, m.p. 223-4°C.



In the present work, a solution of 11-carboxybenzanthrone in concentrated sulphuric acid and chloroform was treated with solid sodium azide at 40-50°C and the reaction mixture poured into water. The crude precipitate was boiled with alkali and the alkali-insoluble amine crystallised from alcohol as red needles, m.p. 215-7°C.

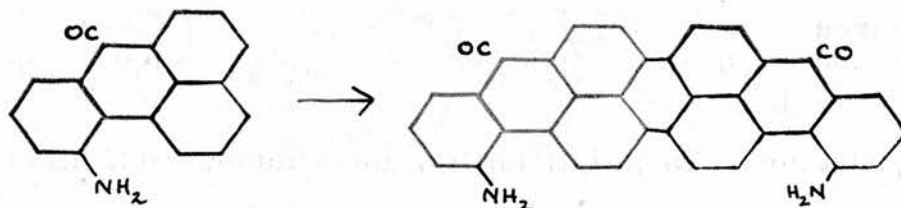


The amine is not soluble in aqueous acids, the orange-yellow salts formed being insoluble in water. It has been characterised by the preparation of two



derivatives, namely 11-formylamino-benzanthrone (golden yellow needles, m.p. 268-271°C) and 11-acetamino-benzanthrone (golden yellow needles, m.p. 278-9°C). The coupled product obtained from an alkaline solution of  $\beta$ -naphthol and the diazotised amine was found to act as a pale pink azo-dye, not very fast to alkali.

When the amino-compound was fused with alkali, an 80% yield of a diamino-dibenzanthrone was formed.



This compound dissolved in alkaline hydrosulphite with even greater difficulty than the dibenzanthrone prepared from the lactam of 11-amino-1-carboxy-benzanthrone. It dyes cotton a fast pale grey-green colour. A very small quantity of an alkali-soluble product was also formed in the fusion: it was assumed to be 11-hydroxy-benzanthrone but conclusive proof was lacking.

An attempt was made to prepare this hydroxy-compound by diazotisation of the amine. The means employed was the diazotisation method of Hodgson and Walker (J., 1933, 1620) and the solution of the diazonium sulphate was finally boiled. The method used by Perkin and Spencer (J., 1922, 480) for the preparation of 4-hydroxy-benzanthrone was also tried but gave a less pure product. The

crude acidic product isolated by both methods proved difficult to purify but eventually a small quantity of orange needles (m.p. 249-251°C) was obtained from alcohol. Perkin (J., 1920, 698; 1922, 474) reports that he was unable to purify 4-hydroxy-benzanthrone and quotes no melting-point. The analysis figures obtained in the present case did not agree with the calculated values for a hydroxy-benzanthrone, the carbon value being too low.

Methylation of the crude product by means of dimethyl sulphate and anhydrous sodium carbonate in boiling xylene gave two alkali-insoluble products after a tedious process of crystallisation. One was obtained as greenish yellow needles (m.p. 269-274°C) from alcohol; the other as a bright yellow powder (m.p. 152-4°C) from benzene. On analysis, neither compound gave the expected carbon and hydrogen values for a methoxy-benzanthrone.

In conclusion, it would appear that the diazotisation has proceeded in an abnormal manner probably forming a mixture of products as indicated by the methylation experiment. Notwithstanding the analysis figures both the acidic and alkali-insoluble materials described above behave as would be expected if they were 11-hydroxy- and 11-methoxy-benzanthrone respectively.

## II. EXPERIMENTAL SECTION.

The experimental work carried out is described in the following pages. Yields are quoted as percentages of the theoretical amount obtainable. Melting-points are corrected, the thermometer used having been calibrated against short-stemmed standard thermometers. All new compounds have been analysed where possible and the method of analysis noted.

### Methods of analysis.

Nitrogen was estimated in every case by the micro-Dumas method, but in the case of benzanthrone derivatives heating to a higher temperature than usual was necessary. It was not found practicable to analyse satisfactorily compounds of the dibenzanthrone type as the values were generally low owing to the high temperature necessary for combustion. Only in one case, the diamino-dibenzanthrone from 11-amino-benzanthrone, was the expected value ob-

tained.

Specimens of some of the more important compounds were sent for micro-analysis to Dr. Schoeller (Berlin) or Dr. Weiler (Oxford). The carbon values for benzanthrone derivatives have been found to be generally low, presumably due to their stability to heat. Dr. Weiler reported that he had great difficulty with the nitrogen determination of several compounds of the dibenzanthrone type by the micro-Dumas method.



P R E P A R A T I O N S.

Methyl o-Iodo-benzoate.

(Cohen and Raper, J., 1904, 1272)

a) o-Iodo-benzoic acid.

80 gm. anthranilic acid.

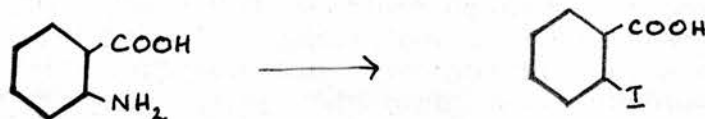
40 gm. potassium nitrite in 100 ml. water

120 gm. potassium iodide in 300 ml. water.

The acid was suspended in dilute sulphuric acid (125 ml. concentrated acid in 625 ml. water) and cooled in ice to 0°C. The sodium nitrite solution was dropped in with stirring, the temperature being maintained at 0°C until excess was present. This was tested by means of starch-potassium iodide paper. A little urea was added to destroy excess nitrous acid. The potassium iodide solution was then added in a thin stream with stirring at ordinary temperature, the stirring continued for several hours, and the mixture allowed to stand overnight. It was then warmed on the steam-bath until effervescence ceased. After cooling, and the addition of sodium bisulphite to destroy the excess of iodine, the product was filtered, washed with warm sodium thiosulphate solution till buff-coloured, and finally with warm water.

After drying, it was crystallised from strong aqueous acetic acid (3:2).

Yield: 108 gm. (75%). M.p. 161°C.



b) Methyl o-Iodo-benzoate.

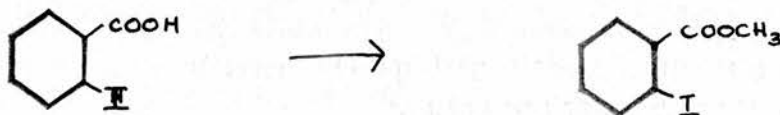
50 gm. o-iodo-benzoic acid

200 gm. methyl alcohol

20 gm. concentrated sulphuric acid.

The mixture was refluxed for 15 hours and the excess methyl alcohol removed by distilling on the water-bath. The residue was poured onto ice and neutralised with solid sodium carbonate. The ester was extracted with ether, and the ethereal extract shaken with dilute alkali, water (twice) and then dried over calcium chloride. The ether was removed and the crude ester distilled in vacuo.

Yield: 45 gm. (85%). B.p. 145°C/15 mm.



Methyl 8-Bromo-1-naphthoate.

a) Mercuration of Naphthalic Acid.

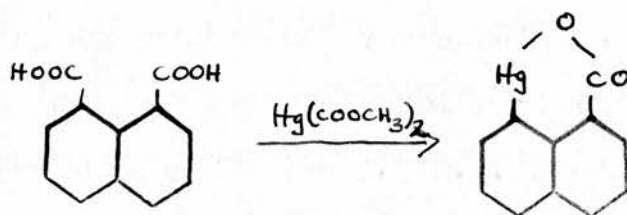
(Rule and co-workers, J., 1934, 170).

56.

54 gm. naphthalic acid  
21 gm. sodium hydroxide  
55 gm. yellow mercuric oxide.

The sodium hydroxide and naphthalic acid were dissolved in 1200 ml. of water with heating. The solution was filtered and placed in a 2-litre flask fitted with a reflux condenser. The mercuric oxide was dissolved in a mixture of 40 ml. glacial acetic acid and 150 ml. water with heating, filtered and added to the flask. The contents were then made distinctly acid, when a light suspension formed. The mixture was boiled for 96 hours, after which a test portion (containing solid in suspension) was completely soluble in sodium hydroxide solution. The precipitate was filtered off, well washed with water and dried at 110°C.

Yield: 88 gm. (97%).



b) Bromination of Mercury Compound.

(Rule and co-workers, loc. cit.)

80 gm. anhydro-8-hydroxy-mercuri-1-naphthoic acid  
34 gm. bromine.

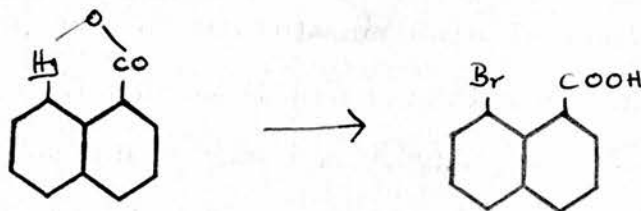
The mercury compound was suspended in 300 ml. of acetic glacial acid and 50 ml. of water were added. The mixture

was cooled in ice and water and efficiently stirred. Bromine, dissolved in 150 ml. concentrated sodium bromide solution, was then added drop by drop over three hours, after which the mixture was warmed to 90°C and the clear solution poured into 2 litres of cold water. After standing overnight, the crystalline solid was filtered off and extracted with 8-9 litres of boiling water. The crystals which deposited on cooling the filtrate were filtered off and dried.

Wt. 39 gm. M.p. 160-170°C.

The crude acid was then recrystallised from benzene.

Yield: 33 gm. (57%). M.p. 178°C.



c) Esterification of the acid.

(Rule and Barnett, J., 1932, 175)

- 15 gm. 8-bromo-1-naphthoic acid
- 30 ml. purified thionyl chloride
- 50 ml. dry methyl alcohol.

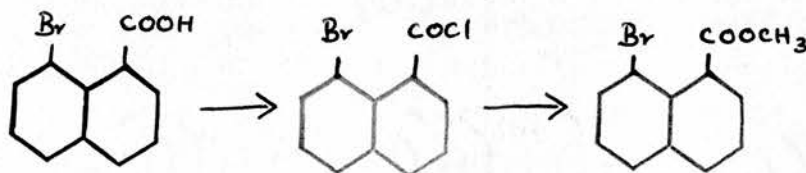
The acid and thionyl chloride were boiled under reflux on the water-bath until a clear solution was obtained and fumes ceased to be evolved. Excess thionyl chloride was distilled off on a boiling water-bath and finally under reduced pressure. The liquid acid chloride



was allowed to cool and the methyl alcohol cautiously added in small quantities. A large evolution of hydrochloric acid took place and the reaction was finally completed by boiling the mixture for half-an-hour.

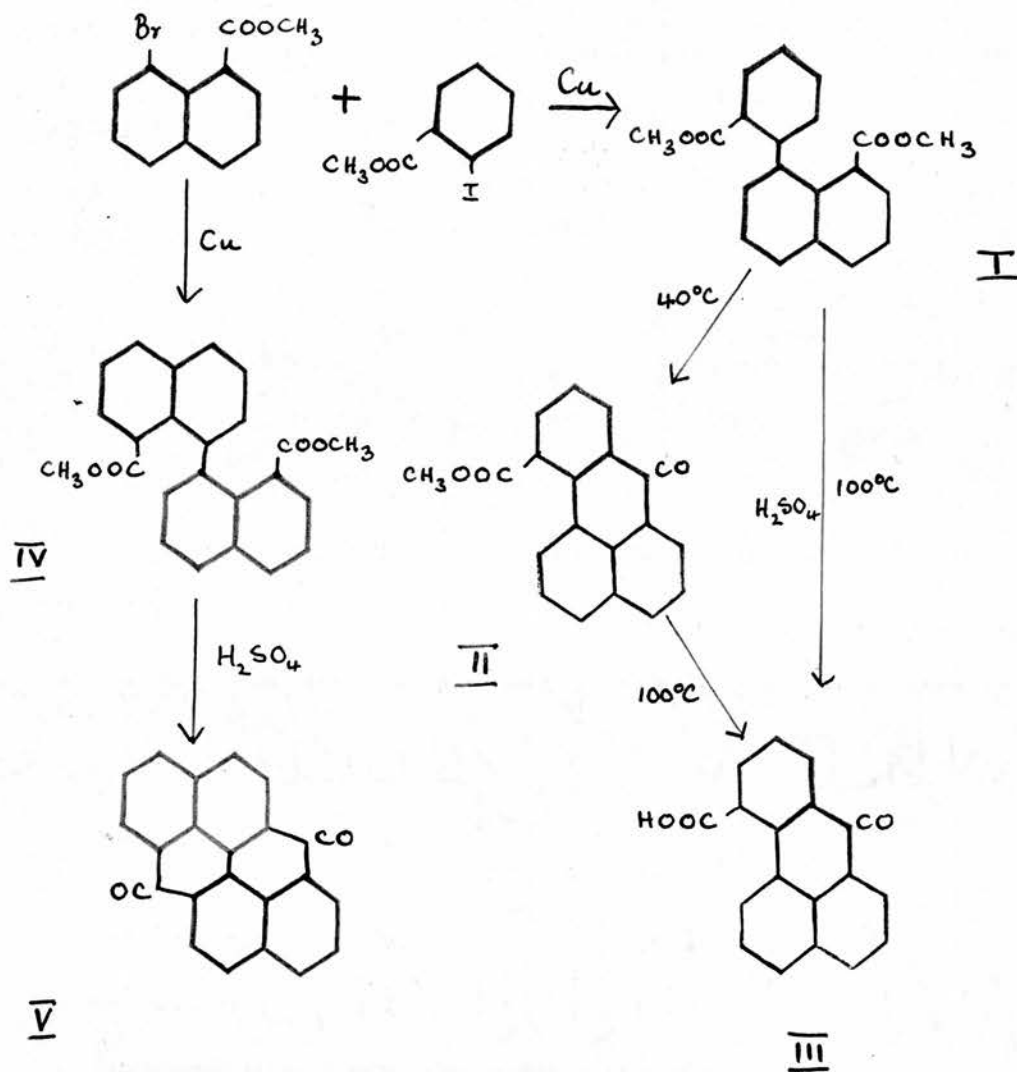
Most of the methyl alcohol was removed on the steam-bath and the liquid ester taken up in ether, washed with dilute caustic soda, and then twice with water. The solution was dried over calcium chloride and the ether removed in a vacuum desiccator. A light brown liquid was obtained which solidified on standing to a cream coloured solid.

Yield: 15 gm. (96%). M.p. 32-33°C.



Ullmann Reaction between Methyl 8-Bromo-1-naphthoate and Methyl o-Iodo-benzoate: Methyl 8-(o-Carbomethoxy-phenyl)-1-naphthoate, 11-Carboxy-benzanthrone and 11-Carbomethoxy-benzanthrone.

(Rule and co-workers, J., 1935, 571)



1) Methyl 8-(*o*-Carbomethoxy-phenyl)-1-naphthoate (I).

25 gm. methyl 8-bromo-1-naphthoate (1 mol.)

50 gm. methyl *o*-iodo-benzoate (2 mols.)

18 gm. copper bronze.

The above materials were heated together for 5 hours at 180°C with stirring. The reaction product was boiled out with 175 ml. acetone (in three portions) and insoluble inorganic material filtered off. The acetone was removed from the filtrate by heating in vacuo, and the warm syrupy

residue treated with 25 ml. ether when crystals were immediately deposited. After standing overnight, these were filtered off and washed with 20 ml. ether.

Yield: 22 gm., m.p. 127-132°C, consisting almost entirely of methyl 8-(*o*-carbomethoxy-phenyl)-1-naphthoate (I) and dimethyl 8:8'-dinaphthyl-1:1'-dicarboxylate (IV).

The mixed esters need not be separated if it is intended to prepare 11-carboxy-benzanthrone (II) as this can be separated from anthanthrone (V) by solution in alkali.

For the preparation of 11-carbomethoxy-benzanthrone (III), the phenyl-naphthyl ester was purified by dissolving the mixed esters in 250 ml. ligroin and allowing the solution to cool. After standing for two hours, the clear liquid was quickly decanted and the crystals remaining in the flask were crystallised from 165 ml. ligroin. Longer standing may give the dinaphthyl ester. The phenyl-naphthyl ester crystallises in colourless rhombs, m.p. 133°C, and the loss in purification is considerable.

Yield: 12 gm. (40%, calculated on the naphthoate used).

## 2) 11-Carboxy-benzanthrone (III).

10 gm. mixed esters.

80 ml. sulphuric acid (96%).

The mixture was heated at 100°C for one hour. The blood-red mixture was digested for a few minutes with dilute aqueous caustic soda at 60°C, and the resulting purplish-red suspension of anthanthrone filtered off.

The filtrate was treated carefully with concentrated sulphuric acid until the first small precipitation discharged the red colour leaving an orange solution of sodium benzanthrone-11-carboxylate. The precipitated lactone of 1-hydroxy-11-carboxy-benzanthrone was filtered off and the clear liquid acidified with sulphuric acid when it deposited lactone-free 11-carboxy-benzanthrone.

Yield: 11-carboxy-acid - 8.2 gm. (71%). M.p. 271-2°C.  
anthanthrone - 0.2 gm. (2%).

(quoted on the bromo-naphthoate used).

The acid crystallises from glacial acetic acid or alcohol in orange-yellow needles, m.p. 273°C.

### 3) 11-Carbomethoxy-benzanthrone (II).

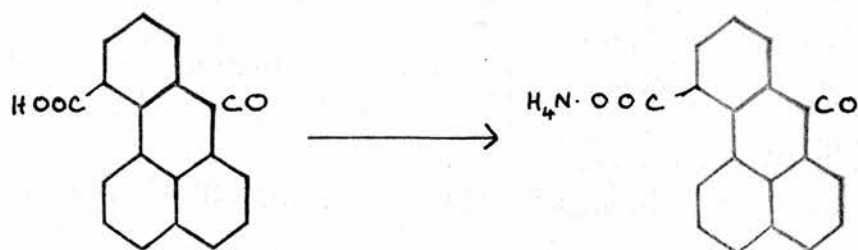
1 gm. pure methyl 8-(o-carbomethoxy-phenyl)-1-naphthoate,  
8 ml. sulphuric acid (96%).

The above were heated at 50°C for one hour, the mixture poured into 200 ml. water and the solid product filtered off, digested with caustic soda solution and the solid filtered off.

Yield: 0.90 gm. (90%). M.p. 160°C.

Acidification of the alkaline filtrate always yields some 11-carboxy-benzanthrone.

The ester crystallises from alcohol in orange needles, m.p. 161°C.

Ammonium Benzanthrone-11-carboxylate.

3 gm. 11-carboxy-benzanthrone were dissolved in 200 ml. alcohol and dry ammonia gas passed in to the solution, which took on a strong greenish yellow fluorescence. After twenty minutes the yellow solid was filtered off and washed with alcohol.

Yield: 2.2 gm.

The salt is soluble in warm water with a strong green fluorescence. It sinters at 225°C and melts at 254-6°C.

Attempts to Prepare the Amide of 11-Carboxy-benzanthrone.1. By treating 11-carbomethoxy-benzanthrone with ammonia.

a) 2 gm. 11-carbomethoxy-benzanthrone

6 ml. concentrated aqueous ammonia (S.G. 0.88).

The mixture was heated for 5 hours in a sealed tube at 100°C. The tube was opened, the contents filtered and the solid washed with water until the filtrate was no longer fluorescent. There remained 2 gm. of orange solid (m.p. 159°C) which proved to be unchanged ester.

- b) 1 gm. 11-carbomethoxy-benzanthrone  
30 ml. dry methyl alcohol saturated with  
ammonia gas at 0°C.

In this case, the mixture was heated for seventeen hours in a sealed tube at 100°C. The tube was opened and the mixture filtered. There was obtained 0.78 gm. of the ester (m. p. 161°C), while on evaporation of the filtrate a further quantity of the ester was recovered. It was decided to employ more vigorous treatment.

c) The above experiment was repeated with 0.5 gm. of the ester for twenty-four hours at 200°C. On opening the tube and filtering the solid material, there was obtained 0.35 gm. of a red-brown powder with no melting-point below 360°C. It could not be crystallised from the usual organic solvents, even chlorobenzene and nitrobenzene being ineffective. It had no dyeing properties. No fluorescence was obtained on heating for twenty hours with caustic soda on the steam-bath; nor was any alkali-soluble material obtained by heating with concentrated sulphuric acid (brown solution with no fluorescence) for one hour at 100°C and subsequently pouring into water. There cannot therefore be any acidic or readily hydrolysed group present. The product may possibly be of a complex type formed by condensation of two molecules; it cannot be the lactam of 1-amino-11-carboxy-benzanthrone as this exhibits a fluorescence in concentrated sulphuric acid (cf. p. 27). The subject was not pursued further, but

the experiment was repeated again under less drastic conditions.

d) In this experiment, the above procedure was followed but the heating was carried out for seven hours at 150°C. The insoluble solid proved to be the original ester (0.16 gm.), but the filtrate on concentration gave a small quantity of an impure yellow solid of melting-point 220-233°C. The problem of preparing the amide by this method was discarded at this point, an easier method of approach being through the acid chloride.

2. By fusion of 11-carboxy-benzanthrone with ammonium carbonate.

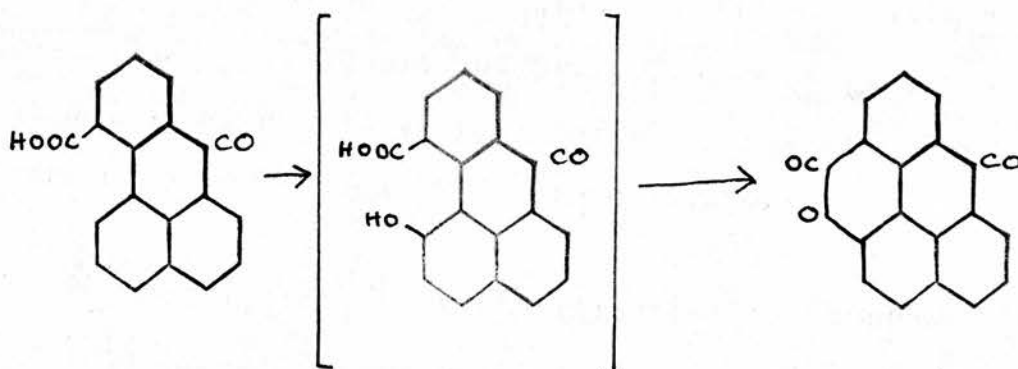
It was thought that the amide might be obtained by fusing the parent acid with ammonium carbonate.

- 1 gm. 11-carboxy-benzanthrone
- 3 gm. ammonium carbonate.

The materials were heated until just molten and the cooled melt extracted with warm water, and filtered. A small quantity of unchanged acid was recovered from the filtrate on acidification.

The solid (0.71 gm.), insoluble in warm alkali, when crushed appeared to be a red powder which melted with decomposition at 220-228°C after sintering at 190°C. A small quantity was crystallised with difficulty from alcohol (m.p. 291-301°C). The solid was soluble in concentrated sulphuric acid to give a brown colour with

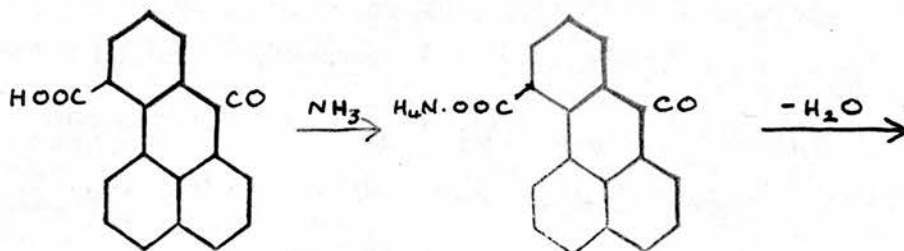
deep green fluorescence; it was soluble in boiling alkali to give a deep red fluorescent solution reminiscent of the lactone of 1-hydroxy-11-carboxy-benzanthrone. No nitrogen could be detected by a sodium fusion. It is believed to be impure lactone formed possibly by aerial oxidation in the presence of alkali.



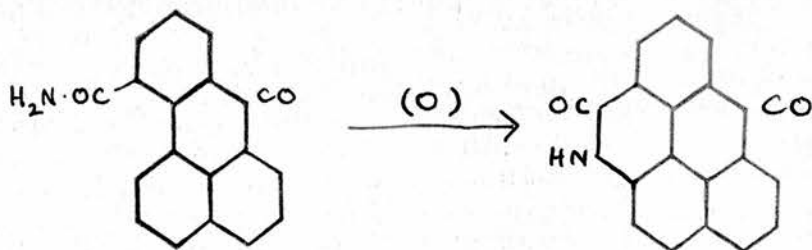
The reaction was not investigated further.

### 3. By dehydration of the ammonium salt.

a) in boiling nitrobenzene: it was proposed to pass ammonia gas into a solution of 11-carboxy-benzanthrone in the hope that, at this high temperature, the ammonium salt would be converted into the amide which might possibly undergo oxidation to the lactam thus:-



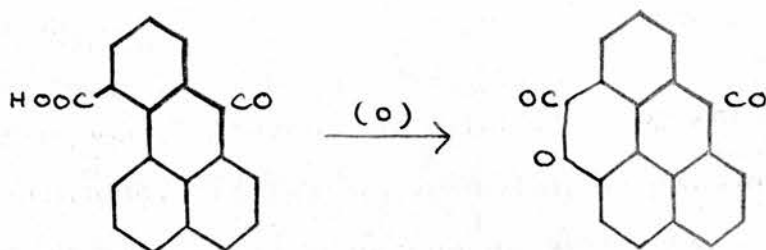




1 gm. 11-carboxy-benzanthrone was dissolved by heating in 35 ml. nitrobenzene, and dry ammonia gas passed in. The nitrobenzene on distillation showed no turbidity, hence apparently no loss of water had occurred. On cooling and filtering, 0.61 gm. of solid (softening at 234°C and melting at 239-248°C) was obtained. This solid was heated in vacuo at 250-255°C for half-an-hour in the hope that, if it was the ammonium salt, dehydration would occur. The solid darkened and the melt was extracted with warm water to remove any unchanged acid or ammonium salt. The filtrate exhibited a strong yellow-green fluorescence but did not yield any appreciable quantity of 11-carboxy-benzanthrone on acidification.

The residue after this treatment weighed only 0.38 gm. and had melting-point 242-250°C. By repeatedly boiling with quantities of hot alcohol and filtering, there was obtained from the filtrate on cooling 0.04 gm. orange needles, sintering at 285°C, softening at 341° and melting at 345-6°C. A further crystallisation raised the melting-point to 353-5°C and the compound was identified as the lactone of 1-hydroxy-11-carboxy-benzanthrone by mixed melting-point and its colouration in alkali and concentrated sulphuric acid. This small quantity pro-

bably resulted from oxidation of the acid by the boiling nitrobenzene, although J. L. Grieve (Thesis, Edinburgh, 1936) was unable to prepare the lactone in quantity by such a means.

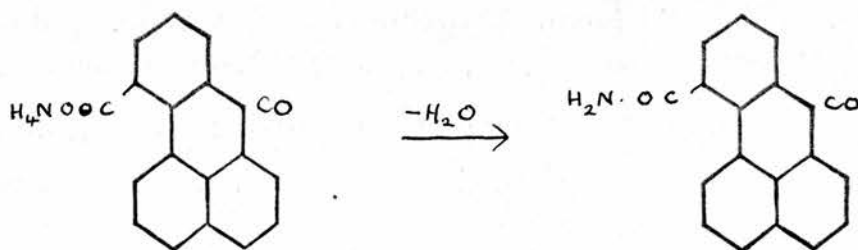


The impure residue (m. p. 290-310°C) was insoluble in alcohol. It exhibited no fluorescence in water and no typical benzanthrone colouration in concentrated sulphuric acid. It was not examined further.

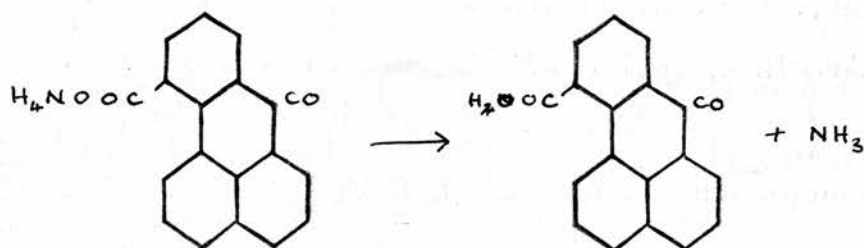
This method was abandoned as the only recognisable product was the lactone in small quantity; it is probable that no ammonium salt formed at all owing to the slight solubility of ammonia in boiling nitrobenzene.

b) in boiling quinoline; no result could be obtained by heating 0.25 gm. ammonium benzanthrone-11-carboxylate in boiling quinoline for three hours. In fact, no solid product could be recovered at all. It had been hoped that quinoline would provide a high-boiling solvent without the oxidising property of nitrobenzene.

c) by direct heating of the ammonium salt.



Ammonium benzanthrone-11-carboxylate (0.3 gm.) was heated in vacuo for two hours in an oil-bath at 240-245°C. Vigorous sublimation occurred. After this treatment, there was recovered from the tube a yellow crystalline solid (0.25 gm., m.p. 271-3°C). The product was much less soluble in water than the original salt and crystallisation from alcohol and mixed melting-point proved it to be the parent acid. Thus the heating of the ammonium salt resulted in dissociation into the free acid and ammonia.



#### 4. By Treating the Acid Chloride with Ammonia.

1) In an early experiment, 11-carboxy-benzanthrone was treated with phosphorus pentachloride in benzene at 75°C. After passing ammonia gas in excess into the solution, distillation of the benzene and treatment with water, there was obtained about 40% yield of a complex red com-

pound, which could be crystallised from nitrobenzene with difficulty as a red powder, m.p.  $> 360^{\circ}\text{C}$ . By sodium fusion it was proved to contain both nitrogen and halogen. It was insoluble in alkali. The subject was not pursued, but the compound may be comparable to a red compound obtained by treating the 11-carboxy-acid with thionyl chloride (Dr. Bigelow, in these laboratories, unpublished).

2) Preparation of the Acid Chloride of 11-Carboxy-benzanthrone and Regeneration of the Parent Acid.

1 gm. finely powdered 11-carboxy-benzanthrone  
 1.3 gm. dry phosphorus pentachloride  
 30 ml. benzene (A. R.).

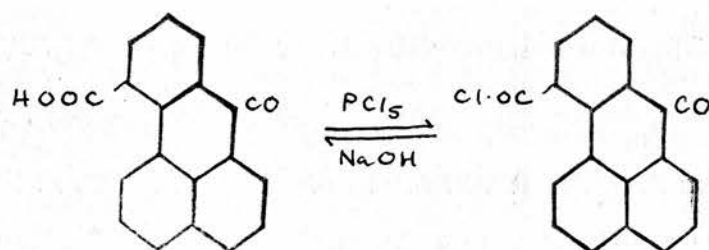
The reagents were warmed together at  $40^{\circ}\text{C}$  until the reaction appeared to be complete. The hot red solution was filtered and the benzene distilled off under reduced pressure and at as low a temperature as possible. The ochre solid remaining was collected.

Yield: 0.87 gm. (80%). M.p.  $111-114^{\circ}\text{C}$ .

It was very soluble in organic solvents and crystallised from petrol-ether (b.p.  $60-80^{\circ}\text{C}$ ) in yellow nodules, m.p.  $154-6^{\circ}\text{C}$  (sintering at  $140^{\circ}\text{C}$ ) - 0.6 gm. dissolves in 10 ml. of solvent.

The acid chloride is readily converted back into the parent acid. 0.2 gm. of the chloride was treated with 2 ml. 2N. caustic soda solution and warmed on the steam-bath for 10 minutes. A small residue ( $< 0.01$  gm.)

was filtered off and the reddish solution acidified. On drying the precipitate, there was obtained 0.15 gm. acid, m.p. 266-8°C. On crystallisation from glacial acetic acid, this was identified as 11-carboxy-benzanthrone (m.p. and mixed m.p. 272-3°C).



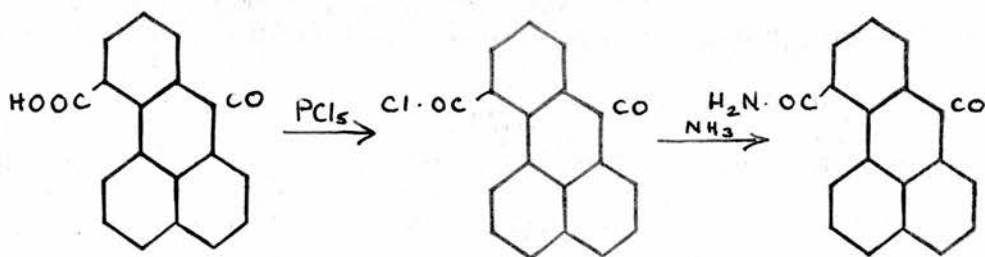
### 3) Benzanthrone-11-carboxylic Amide.

4 gm. powdered 11-carboxy-benzanthrone  
 5 gm. dry phosphorus pentachloride  
 150 ml. pure dry benzene.

The reagents were warmed together at 40°C until a reddish solution was obtained, the benzene and phosphorus oxychloride were removed under diminished pressure (temperature not greater than 50°C) and the solid residue quickly added to a concentrated aqueous ammonia solution. The solution was boiled and filtered, the filtrate rendering 0.20 gm. 11-carboxy-benzanthrone on acidification. The residue was the crude amide.

Yield: 3.95 gm. (96%).

Crystallisation from nitrobenzene gave 2.58 gm. (65%) of yellow needles.



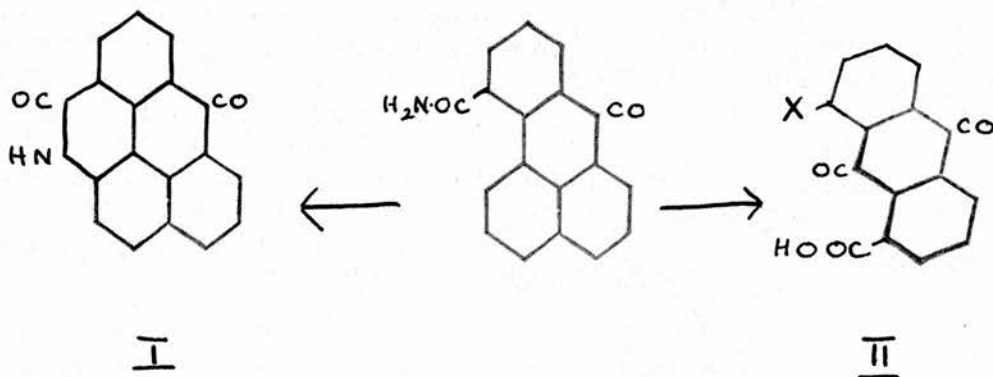
The amide dissolves in concentrated sulphuric acid with a blood-red colour and yellowish red fluorescence similar to the parent acid; only a very faint pink colour is developed even in boiling alkali. There is no vatting property and its behaviour in a melting-point tube is mentioned below.

Analysis: found (Schoeller) C 78.2%, H 4.2%, N 5.2%

$\text{C}_{18}\text{H}_{11}\text{O}_2\text{N}$  requires C 79.1%, H 4.0%, N 5.1%.

Treatment of the Amide with Chromic Acid: Oxidation to the Lactone of 1-Hydroxy-11-carboxy-benzanthrone.

This treatment was carried out in the hope that oxidation might take place to either the lactam of 1-amino-11-carboxy-benzanthrone (I) or an anthraquinone-carboxylic acid (II).



1 gm. amide of 11-carboxy-benzanthrone.  
1.4 gm. chromic acid.

The amide was dissolved in 10 ml. concentrated sulphuric acid and an equal volume of water added. The mixture was raised to the boiling-point and the chromic acid added in small portions. After boiling for two hours, the mixture was filtered and the precipitate dried.

Yield: 0.78 gm. (83%). M.p. 351-4°C.

It was slowly but almost wholly soluble in warm alkali to a purple fluorescent solution. The yield on acidification of filtrate was 0.67 gm. Crystallisation of this product from glacial acetic acid gave 0.46 gm. of golden yellow needles, melting-point and mixed melting-point with an authentic specimen of the lactone of 1-hydroxy-11-hydroxy-benzanthrone, 356-7°C.

No trace of any other product could be isolated.

#### Behaviour of the Amide above its Melting-Point.

Even after several crystallisations the same unusual behaviour is observed in a melting-point tube. Sintering occurs usually over the range 300-310°C, softening at 320°C, with melting at 325-7°C, followed by subsequent crystallisation at 327-330°C. A slight red sublimate invariably appears but no further change below 360°C. Sometimes there appears to be gas evolution about 325-330°C, but this is by no means general. The

residue in the tube usually contains some black particles, and, whereas the original amide exhibits the typical behaviour of a benzanthrone derivative in concentrated sulphuric acid (blood-red colour with yellowish red fluorescence), the residue in the tube shows a brown colour with an extraordinary vivid green fluorescence. Sublimation of some crystals of the amide under reduced pressure gave a product with behaviour in the melting-point tube similar to the original amide.

An examination of the melting-point of the amide was carried out in an atmosphere of carbon dioxide. No running or melting was observed but there was a darkening of the material in the tube over the range 325-333°C; a reddish sublimate also formed.

It was hoped that it might be possible to separate the mixture of yellow and blackish particles obtained after heating the amide at 327°C. Experiments on heating small quantities (about 0.10 gm.) at temperatures between 320°C and 360°C have always yielded a mixture of products.

Unchanged amide was first removed by boiling with a small quantity of nitrobenzene (about 10 ml. per 0.5 gm.). The residue was further separated by boiling 0.5 gm. with 200 ml. nitrobenzene and filtering hot. From the solution, there deposited 0.25 gm. of fine brown needles, melting-point  $> 360^{\circ}\text{C}$ . They were insoluble in alkali and gave a greenish brown colour with intense green fluorescence in concentrated sulphuric acid.

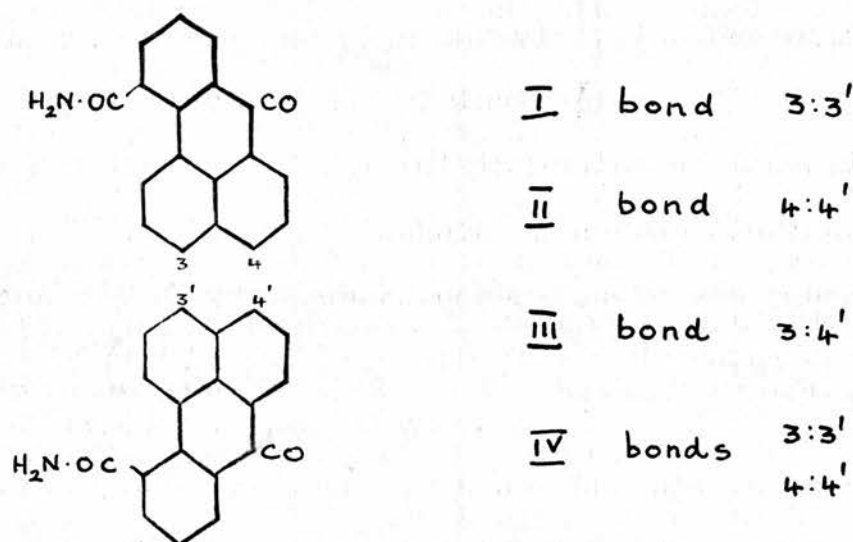
The compound is believed to be a diamide of a di-



carboxy-dibenzanthronyl (formulae I, II or III), similar to that obtained in the mild alkaline fusion of the amide.

Analysis: found N 5.4%

$C_{23}H_{20}O_4N_2$  requires N 5.15%.



The residue (0.15 gm.), insoluble in nitrobenzene, was boiled with alcohol and filtered hot to remove nitrobenzene. The dry solid was blue black in colour, melting-point  $> 360^\circ C$ ; it was insoluble in alkali and gave a red-brown colour and green fluorescence in concentrated sulphuric acid. Although it had no vatting property, it is believed to be a dibenzanthrone (IV).

Analysis: found (Weiler) N 3.8% (reported very difficult to combust)

$C_{36}H_{18}O_4N_2$  requires N 5.2%.

The low value is not unexpected due to the resistance of such compounds to heat (compare the similar compounds of this type obtained by alkaline fusion of the amide and of the lactam of 11-amino-1-hydroxy-benzanthrone, see pp. 78, 106).

Apparently the heating of the amide results in the elimination of hydrogen from positions 3 or 4 in a similar manner to that resulting from alkaline fusions. No phenolic derivative resulted; and the properties of the compound do not resemble those of the lactam of 1-amino-11-carboxy-benzanthrone (obtained later by oxidation with bromine in nitrobenzene solution).

#### Alkaline Fusion of the Amide.

##### 1) At 250°C.

0.5 gm. amide, 1.5 gm. caustic potash and a few drops of water were fused together for one hour in a nickel crucible at 250°C (outside temperature of bath). The reddish melt was then boiled with 250 ml. of water and filtered.

The dry residue (0.35 gm., about 70%) was brown in colour, had no melting-point below 360°C and gave a green colour with green fluorescence in concentrated sulphuric acid. There was no vatting property.

From the alkaline filtrate there was obtained, on acidification, 0.07 gm. (about 14%) of a green powder. It had no melting-point below 360°C, gave a similar colour in concentrated sulphuric acid though rather more strongly fluorescent. It gave a red brown alkaline hydrosulphite vat showing green fluorescence, and feebly dyed cotton a brown colour which was not fast to alkali.

The constitution of the products is discussed below.

2) At 280°C.

In an attempt to convert the above "brown product" to a blue vat dye, the material (0.35 gm.) was fused for a further 20 minutes with 1.5 gm. caustic potash at 280°C (outside temperature). The melt was then treated as above:

alkali-insoluble, brown product	0.31 gm.
alkali-soluble material	a trace.

3) the fusion was repeated with the amide at 300°C, and the same results obtained:

0.5 gm. amide was added to 5 gm. sodium hydroxide in a nickel crucible at 200°C, the temperature raised to 300°C and there maintained for 30 minutes. The bluish melt was then boiled for 15 minutes with 150 ml. water and filtered. The brown residue was boiled with a further quantity of alkali to remove all acidic products and filtered off.

Yield: alkali-insoluble - 0.32 gm. (about 70% as above)

The brown residue, insoluble in alkali, was crystallised from 100 ml. nitrobenzene to give 0.20 gm. of fine brown needles. These did not melt below 360°C, dissolved in concentrated sulphuric acid to a green liquid with strong green fluorescence, but were insoluble in alkaline hydrosulphite. The compound is formulated as a diamide of the dibenzanthronyl type similar to if not identical with the brown crystalline compound obtained by heating the amide above its melting-point (cf. p. 73).

Analysis:

found N 5.6%.

$C_{36}H_{20}O_4N_2$  requires N 5.2%.

Acidification of the alkaline filtrate (brown with strong green fluorescence) yielded a precipitate which, after drying, appeared as a green powder - 0.14 gm. (about 28%). It was more soluble in nitrobenzene than the alkali-insoluble material giving a brown solution with reddish fluorescence, and crystallised from 35 ml. to yield 0.11 gm. of a green powder, m.p. > 360°C. The colour reactions were as already mentioned (fusion at 250°C).

Nitrogen analysis precludes the possibility that this compound might be of the dibenzanthronyl type with one amide group hydrolysed; the solubility in alkali is

therefore supposed to be due to oxidation of a hydrogen atom to a phenolic group, a change which commonly occurs during alkaline fusions in this group. The nitrogen analysis figures are insufficient to show whether this product is of the benzanthrone or of the dibenzanthronyl type but its colour suggests the former.

Analysis:

found N 5.2%

$C_{18}H_{11}O_3N$  requires N 4.8%.

4) At 360°C.

A final fusion was carried through at the abnormally high temperature of 360°C.

10 gm. caustic potash were fused in a nickel crucible at 200°C and 0.5 gm. amide (pasted from concentrated sulphuric acid solution) added. The temperature was raised to 360°C (outside temperature) and maintained for 3 hours. The bluish melt was extracted with 500 ml. water, warmed on the steam-bath for 2 hours and filtered hot.

Residue: 0.22 gm. (> 50%). M.p. < 360°C.

The blue residue was boiled with 10 ml. nitrobenzene to remove any unchanged amide and filtered; the residue was subsequently refluxed for some time with 10 ml.

alcohol to remove nitrobenzene. The final product was a violet-black crystalline powder (0.15 gm., m.p. > 360°C) only very slightly soluble in nitrobenzene (green solution, red fluorescence). It dissolves with some difficulty in concentrated sulphuric acid to a green solution; it forms a greenish alkaline hydrosulphite vat only with great difficulty and hardly affects cotton. Sodium fusion showed the presence of nitrogen. These properties indicate a dibenzanthrone structure and the product is formulated as the diamide of 11:11'-dicarboxy-dibenzanthrone

Analysis:

found (Weiler) N 3.2% (reported difficult to combust)

$C_{36}H_{18}O_4N_2$  requires N 5.2%.

The yield of alkali-soluble material was only 0.05 gm. It was similar to that obtained at lower temperatures.

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Fusion of the amide of 11-carboxy-benzanthrone with alkali seems, therefore, to yield the dibenzanthrone only at high temperatures. At lower temperatures, the oxidation apparently stops at the dibenzanthronyl stage and is similar to that which occurs on heating the amide alone above its melting-point. Oxidation also occurs to a minor extent to give a phenolic derivative.

These statements are supported by the work of Maki

and co-workers (J. Soc. Chem. Ind., Japan, 1932, 35, 577 B) who were able to isolate dibenzanthrone, dibenzanthronyl and 4-hydroxy-benzanthrone from the alkaline fusion of benzanthrone itself.

Attempts to Convert the Amide into the Parent Acid.

1) By concentrated sulphuric acid at 100°C.

0.4 gm. benzanthrone-11-carboxylic amide

4 ml. concentrated sulphuric acid.

The above were heated at 100°C for 1 hour, the solution poured into 100 ml. water and the solid filtered off. It proved to be quite inert to alkali and a practically quantitative recovery of amide was obtained: the alkaline solution with which the precipitate was digested was a pale pink with faint greenish fluorescence but neither the strong green fluorescence of the 11-carboxy-acid nor the characteristic tint of the lactone was evident. No solid was obtained on acidification.

It had been hoped that the above treatment would bring about conversion of the amide to the acid, since the methyl ester (11-carbomethoxy-benzanthrone) is readily hydrolysed in this manner. It was decided to employ stronger reagents.

2) Using the method of Bouveault.

Ref: Bull. Soc. chim., 1893, [3], 9, 370.

1 gm. benzanthrone-11-carboxylic amide, in 16 ml. concentrated sulphuric acid

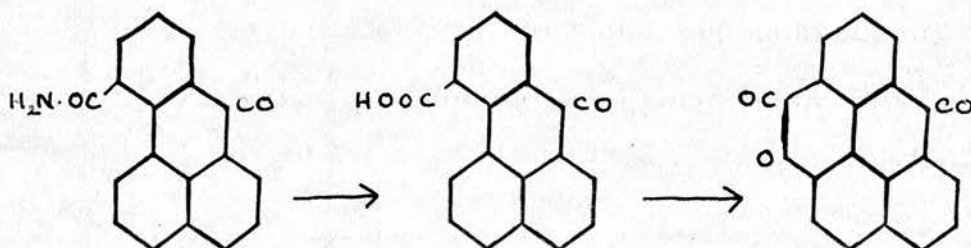
1 gm. sodium nitrite in 15 ml. water.

The solution of the amide in concentrated sulphuric acid was cooled and the sodium nitrite solution slowly run in with cooling. The mixture was then warmed and finally heated for 1 minute at 100°C. It was poured into water (200 ml.) and the solid filtered off.

The solid was digested twice with warm dilute alkali and filtered hot. The residue (0.07 gm.) proved to be unchanged amide. The alkaline solution was treated as described under the preparation of 11-carboxy-benzanthrone (p. 61) and separated thus into the acid and the lactone of 1-hydroxy-11-carboxy-benzanthrone.

Yield: acid - 0.70 gm. (71%), m.p. 267-270°C, confirmed as such by crystallisation from glacial acetic acid, m.p. and mixed m. p. with authentic specimen, 272-3°C.

lactone - 0.22 gm. (24%), m.p. 340-346°C, confirmed as above m.p. and mixed m.p. 354-6°C.



### 3) Prolonged Heating with 50% Sulphuric Acid.

0.5 gm. amide was dissolved in 15 ml. concentrated sulphuric acid and the solution poured into 75 ml. water.



The resulting suspension was boiled for 17 hours; as the water boiled off, it was frequently renewed. Tests were made hourly for alkali-soluble material: as time went on, the reddish colour developed in alkali became deeper (it resembled the "lactone" colour). After 17 hours boiling, the solution was poured into 200 ml. water, boiled and the greenish solid filtered off. The dirty green solid was several times digested with alkali at 60°C, filtered off and washed with warm water. From the alkaline filtrate (pink with strong purplish fluorescence) acidification gave some orange solid.

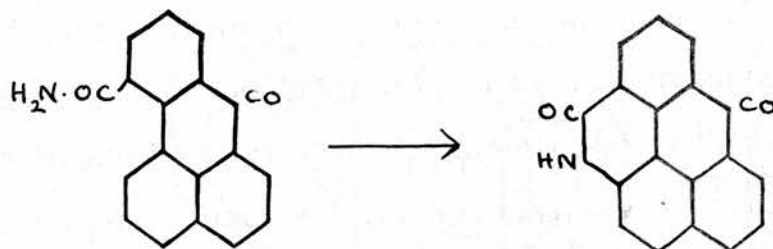
Alkali-insoluble: 0.40 gm. (80% approx.).

Alkali-soluble: 0.06 gm. (12% approx.).

The alkali-insoluble, green solid was boiled with 20 ml. nitrobenzene to remove any unchanged amide and filtered hot. The solution deposited 0.07 gm. fine brown hairs of amide: sintering 318°C, collapsing 328°C but not melting below 360°C. The green residue was now boiled with alcohol and filtered. The solid weighed 0.19 gm., m.p. > 360°C. The colour in concentrated sulphuric acid was amber with a green fluorescence. Crystallisation from a larger quantity of nitrobenzene (80 ml.) gave 0.10 gm. greenish needles, m.p. > 375°C giving a yellow colour with green fluorescence in concentrated sulphuric acid (similar to the product obtained by treating the amide with bromine in nitrobenzene, see below). Further crystallisations from 120 ml. nitrobenzene gave fine yellow needles giving the colour as before. The

product is assumed to be the lactam, but proof is not conclusive.

Analysis:                    found N 5.3%  
 $C_{18}H_{19}O_2N$  requires N 5.2%.



The small amount of alkali-soluble material (0.06 gm.) was crystallised from alcohol as fine orange hairs and proved to be the lactone of 1-hydroxy-11-carboxy-benzanthrone.

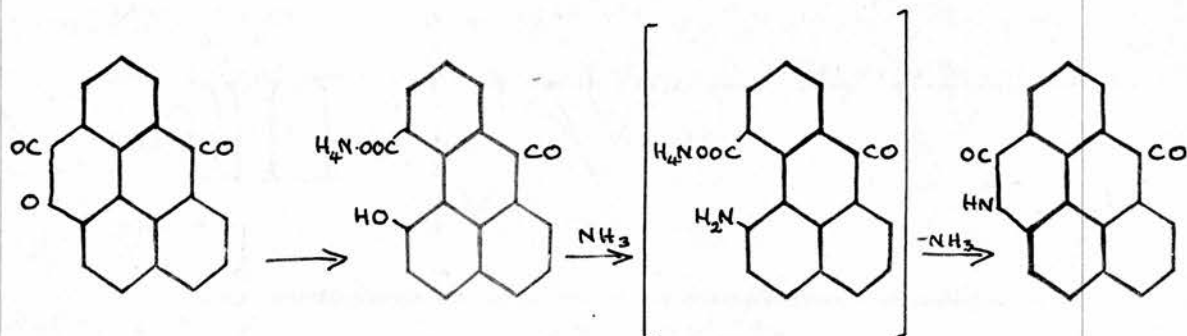
Alone:                    sinters at 310°C, softens 356°C, melts 357°C.

Mixed with  
 lactone:                    310°C,                    354°C,                    355-7°C.

It is concluded that the above treatment has resulted chiefly in an oxidation of the amide to the lactam: the formation of a small amount of lactone indicates that a little hydrolysis of the amide also occurred followed by oxidation to the lactone. This last product is formed in large quantities when the free acid is oxidised with concentrated sulphuric acid.

Attempt to Convert the Lactone of 1-Hydroxy-11-carboxy-benzanthrone into the Lactam of 1-Amino-11-carboxy-benzanthrone.

There was available a quantity of the lactone which had been prepared by chromic acid oxidation of 11-carboxy-benzanthrone according to the method of Bigelow and Rule (J., 1935, 513). It was thought that it might be possible to convert the lactone into the analogous lactam by prolonged treatment with strong ammonia in the presence of ammonium sulphite in a sealed tube. Reactions of this type occur with the naphthols.



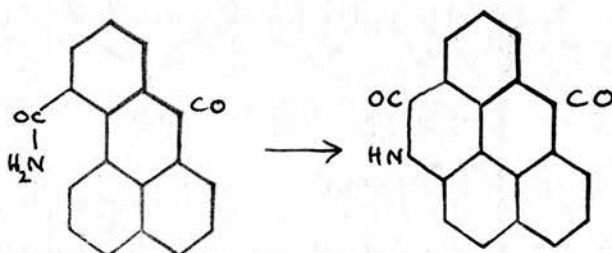
0.5 gm. lactone of 1-hydroxy-11-carboxy-benzanthrone  
 3 ml. concentrated aqueous ammonia (S. G. 0.88)  
 5 ml. ammonium sulphite solution.

The above materials were heated in a sealed tube at  $150^\circ\text{C}$  for five hours. After cooling, opening the tube and filtering off the yellow solid, the alkaline filtrate yielded no solid product on acidification. The insoluble residue weighed 0.5 gm. and melted at  $353-6^\circ\text{C}$ . It proved, in fact, to be wholly soluble in boiling caustic soda, and on acidification and crystallisation,

there was obtained 0.44 gm. of the lactone - identified by m. p. and mixed m. p. 356-7°C.

Preparation of the Lactam of 1-Amino-11-carboxy-benzanthrone by Ring-closure of the Amide of 11-Carboxy-benzanthrone.

1) using sodium hypobromite.



0.5 gm. of the amide was dissolved in concentrated sulphuric acid and the solution poured into water. After filtration, the paste was added to a solution of 0.01 ml. of bromine in 10 gm. caustic soda and 25 ml. water. The pasty mass showed no change after warming under reflux for 3 hours at 60°C, followed by a further 5 hours on a boiling water-bath. Finally, a further proportion of sodium hypobromite was added and the boiling continued for another 3 hours. There appeared to be two layers of suspended material; accordingly, as far as possible, the light brown solid was separated from some rather darker heavier material. The former weighed 0.16 gm. and the latter 0.27 gm. (0.43 gm. in all) and, on crystallisation from nitrobenzene, both proved to be the original amide.

No solid was isolated on acidifying the alkaline filtrate.

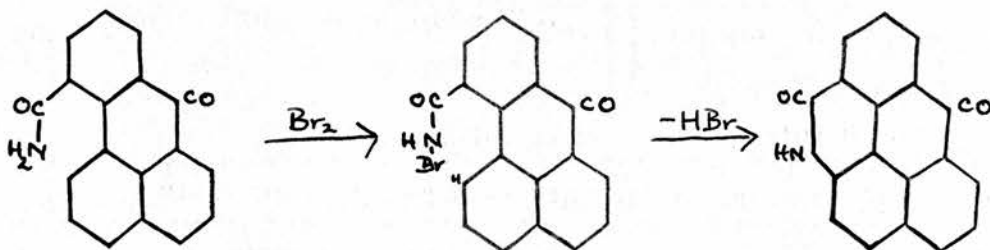
2) using bromine in nitrobenzene solution.

The method was similar to that used by Grieve (Thesis, Edinburgh, 1935) resulting in oxidation of the 11-carboxy-acid to the lactone.

0.5 gm. of the amide was pasted as before and the dried paste treated with 0.1 ml. of bromine and 50 ml. nitrobenzene and maintained at the boiling-point for 3 hours. On cooling, greenish needles were deposited and were filtered off.

Yield: 0.26 gm., 52%.

They did not melt below 360°C although a slight sublimate formed about 330°C (cf. the amide, p. 72). The product was quite insoluble in alkali, but readily in concentrated sulphuric acid to give a yellow solution with green fluorescence. It was extraordinarily insoluble in organic solvents: 0.25 gm. needs 160 ml. of boiling nitrobenzene (0.25 gm. amide dissolves in 20 ml.). Two further nitrobenzene crystallisations were carried out, and a sodium fusion on this purified product demonstrated presence of nitrogen but absence of halogen. From considerations of solubility the compound appears to be the related lactam and this is supported by the analysis figures given below. The substance differs in appearance and colour reactions from the isomeric lactam obtained by treatment of 1:11-keto-benzanthrone with hydrazoic acid.



Analysis:

found (Schoeller) C 78.6%, H 3.3%, N 5.3%  
 C<sub>18</sub>H<sub>9</sub>O<sub>2</sub>N requires C 79.7%, H 3.3%, N 5.2%.

The tendency of these complex derivatives to give low analysis figures for carbon has already been noted.

Attempted Synthesis of the Lactam of 1-Amino-11-carboxybenzanthrone from Aceto- $\beta$ -naphthalide and Methyl o-Iodo-benzoate.

An attempt was made to prepare the lactam by a synthesis analogous to that used in the case of the lactone of 1-hydroxy-11-carboxy-benzanthrone (see p. 14). This would have involved the preparation of 7-amino (or acetamino) -8-bromo-1-naphthoic acid similar to the 7-methoxy derivative used by Grieve. Unfortunately, unlike the case of  $\beta$ -naphthyl methyl ether, aceto-naphthalide could not be converted into an acenaphthene quinone, and the synthesis had to be abandoned.

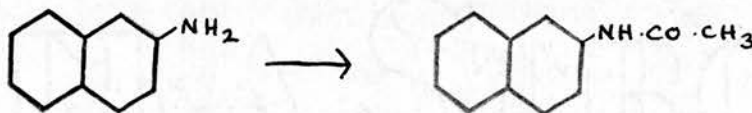
1) Aceto- $\beta$ -Naphthalide.

(Kaufmann, Ber., 1909, 42, 3482).

100 gm.  $\beta$ -naphthylamine  
 250 ml. benzene  
 70 gm. acetic anhydride.

The  $\beta$ -naphthylamine was dissolved in the benzene by warming on the steam-bath. The acetic anhydride was then added in small portions with stirring and the mixture was finally allowed to cool and the precipitate filtered off and washed with benzene.

Yield: 120 gm. (94%). M.p. 132°C.



2) Oxalyl-bis-phenyl-imido-chloride.

(Bauer, Ber., 1907, 40, 2650).

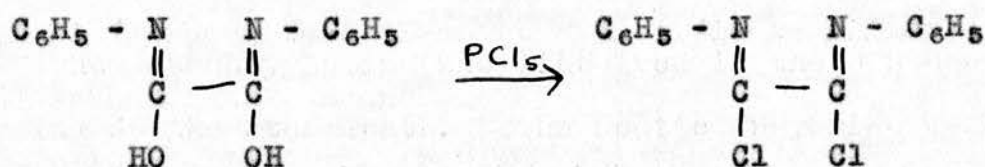
50 gm. oxanilide  
 100 gm. phosphorus pentachloride  
 150 ml. toluene.

The phosphorus pentachloride was added to the suspension of oxanilide in toluene and the mixture heated to the boiling-point under reflux. After three hours, 100 ml. of the toluene was distilled off and the solid, deposited on cooling, was filtered and dried in a vacuum desiccator.

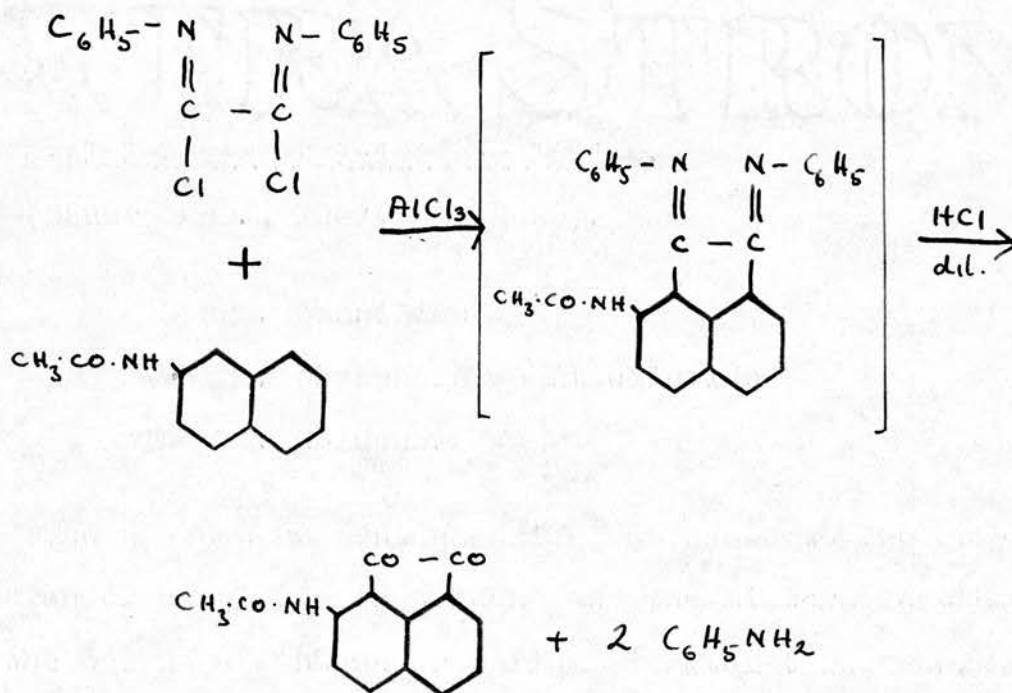
Yield: 40 gm. (70%).

It can be crystallised from ligroin in greenish yellow needles, m.p. 115°C, but it must be kept out of

contact with air as far as possible or extensive hydrolysis occurs.



3) Attempted Preparation of 2-acetamino-acenaphthene quinone by a Friedel-Crafts reaction between aceto- $\beta$ -naphthalide and oxalyl-bis-phenyl-imido-chloride.



a) 1 gm. (2x mols.) powdered but not freshly prepared aluminium chloride was suspended in 10 ml. benzene and a solution of 1 gm. aceto- $\beta$ -naphthalide (2x mols.) and 1 gm. of the phenyl-imido-chloride (x mols.) in 100 ml. benzene was run in over a period of thirty minutes with



stirring, the mixture being maintained at room temperature. A yellowish suspension was seen and the aluminium chloride showed only a faint redness in colour. After standing overnight, the mixture was warmed at 50-60°C for half-an-hour; as the solution began to redden and some evolution of hydrochloric acid now became evident, it was decided to continue the heating for some time (2½ hours). The reaction appearing to be now complete, the mixture was treated with 20 gm. of ice and 8 ml. concentrated hydrochloric acid to decompose any aluminium chloride complex, the benzene removed by distillation in steam and the black residue filtered from the red solution.

The residue (0.97 gm.) was unaffected by extraction with 10 ml. warm 40% sodium bisulphite solution (which would extract any quinone formed) and proved to be chiefly tarry matter and oxanilide (the latter identified by crystallisation from alcohol and mixed melting-point).

The acidic filtrate, on standing some time, deposited a little aceto- $\beta$ -naphthalide but was not further examined for any basic products which might arise from hydrolysis of the acetamino group (e. g.  $\beta$ -naphthylamine).

b) The experiment was repeated on a larger scale (3 gm. quantities) with carbon disulphide as solvent, but, even after refluxing for 1 hours, no action appeared to have occurred. Subsequent removal of the solvent by distillation and its substitution by benzene gave similar results as previously - oxanilide, aceto- $\beta$ -naphthalide,

some tar but no quinone.

c) Finally, more vigorous conditions were employed. 3 gm. of powdered aluminium chloride and 3 gm. aceto- $\beta$ -naphthalide were suspended in 150 ml. benzene and 3 gm. of the phenyl-imido-chloride in 20 ml. benzene slowly run in. The mixture was boiled under reflux for five hours and allowed to stand overnight. It was then poured onto 50 gm. ice and 10 ml. concentrated hydrochloric acid added. The benzene was removed by a steam-distillation and the solution filtered hot.

The tarry residue (4 gm.) was warmed with a saturated solution of sodium bisulphite and filtered hot. On cooling, the filtrate deposited 0.18 gm., m.p. 128-130°C (confirmed as aceto- $\beta$ -naphthalide), but yielded nothing on treatment with acid. The tarry residue (3.72 gm., m.p. 164-190°C) was boiled several times with benzene and from the benzene extract, on cooling, there was obtained 0.90 gm., m.p. 246°C (confirmed as oxanilide by benzene crystallisation and mixed melting-point). From the residue by boiling with water and hot filtering from the tar (of which there was a considerable amount) there was isolated 0.55 gm. of aceto- $\beta$ -naphthalide.

On this occasion, on cooling the hot acidic filtrate, there was obtained 0.45 gm. aceto- $\beta$ -naphthalide. On making the acidic solution alkaline and boiling the precipitate of aluminium hydroxide with alcohol and filtering the solution hot, there was isolated a very small quantity

of organic material rather reddish in colour. Although it could not be identified, it appeared to be impure  $\beta$ -naphthylamine.

1:11-Keto-benzanthrone.

(Bigelow and Rule, J., 1935, 573)

4 gm. 11-carboxy-benzanthrone (lactone free)

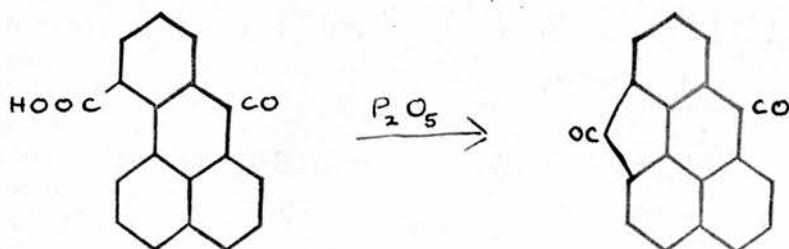
4.7 gm. phosphorus pentoxide

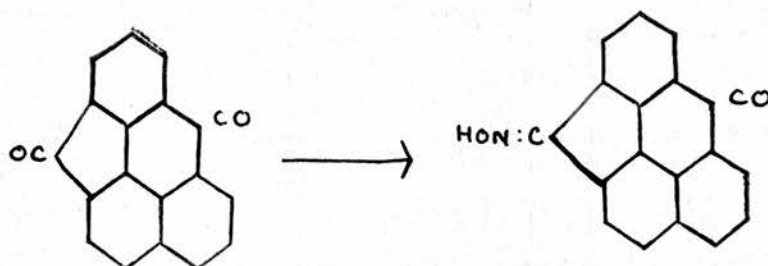
80 gm. phthalic anhydride.

The acid was dissolved in the phthalic anhydride at 200°C, and the phosphorus pentoxide added in two portions at an interval of thirty minutes. After two hours at 200°C, the dark red mixture was cooled somewhat and poured rapidly into a solution of 50 gm. caustic soda in 450 ml. water. It was boiled for a few minutes, filtered hot and the residue liberally washed with hot water.

Yield: 3.45 gm. (92%). M.p. 300-325°C.

It crystallised from glacial acetic acid in fine orange needles, m.p. 327-8°C (sintering at 290°C), and solidifying again sharply at 325°C.



Benzanthrone-1:11-ketoxime.

- 1)            2 gm. 1:11-keto-benzanthrone  
               0.56 gm. hydroxylamine hydrochloride  
               550 ml. alcohol.

The mixture was refluxed and 50 ml. dilute caustic soda solution run in slowly. The solution changed in colour from orange to a deep red, and most of the ketone went into solution. Any unchanged ketone was removed by filtration and the filtrate carefully acidified. The yellow, rather gelatinous precipitate was filtered off.

Yield: 1.91 gm. (90%). M.p. 298-308°C.

Purification was found to be difficult. Crystallisation from 25 ml. boiling nitrobenzene gave 1.27 gm. orange needles, m.p. 309°C, but nitrobenzene is not a suitable solvent for final purification (cf. below). The oxime is not very soluble in alcohol, though more so than the parent ketone; it is very soluble in pyridine; and dissolves readily in glacial acetic acid, but can only be recovered after addition of water. Other solvents also proved unsatisfactory (chlorobenzene, anisole). The best crystallising agents have been found to be decalin or xylene (solubility: 0.2 gm. per 100 ml.);

on filtering the hot solution and allowing to cool, or on adding petroleum ether (b.p. 40-60°C), the oxime is deposited in the form of orange micro-needles melting sharply at 313-4°C and unaltered by further treatment. Sublimation under reduced pressure likewise gives a product of m.p. 314°C.

The oxime dissolves in alkali, but the red sodium salt is not very soluble except in boiling water, when it gives a deep pink solution with orange fluorescence. The colour in concentrated sulphuric acid is as for the parent ketone (purple).

Analysis:

found (Schoeller) C 78.8%, H 3.5%, N 4.74%.

$C_{18}H_9O_2N$  requires C 79.7%, H 3.3%, N 5.16%.

2) An experiment was carried out to see if the oxime could also be prepared by simply boiling a solution of the ketone in alcohol with hydroxylamine hydrochloride under reflux. It was found to be possible, but the alkali method is to be preferred as the volumes required are smaller and less time is taken.

0.3 gm. 1:11-keto-benzanthrone was dissolved by boiling in 250 ml. alcohol and the solution heated for some time under reflux with 0.25 gm. hydroxylamine hydrochloride. After all the latter had passed into solution, the solution was allowed to cool. As no crystals deposited, the solution was concentrated somewhat and eventually 0.33 gm. reddish needles obtained melting at 313-4°C with

vigorous decomposition. Recrystallisation from decalin confirmed these as the oxime (m.p. and mixed m.p. with oxime prepared by method 1, 313-4°C).

3) An attempt to prepare an oxime of benzanthrone by a method similar to that used in the case of 1:11-keto-benzanthrone.

0.5 gm. benzanthrone  
0.25 gm. hydroxylamine hydrochloride  
100 ml. alcohol.

The mixture was boiled under reflux and 30 ml. dilute caustic soda slowly run in. The yellow solution turned to a deep red. After refluxing for 15 minutes it was filtered hot. On cooling, the hot filtrate deposited 0.47 gm. of fine yellow needles which, on crystallisation from alcohol, proved by m.p. and mixed m.p. (171°C) to be unchanged benzanthrone. No alkali-soluble material was obtained.

This experiment shows that benzanthrone does not form an oxime under these conditions and supports the view that the 1:11-keto-benzanthrone most readily forms an oxime by interaction of the ketonic group in the five-membered fluorenone ring.

Attempts to isolate an isomeric oxime: discovery of the formation of a molecular compound between 1:11-ketobenzanthrone and nitrobenzene.

Although decalin proves a good agent for purifying the oxime, the treatment is tedious owing to the slight solubility in this medium. As a result, resort was frequently had to nitrobenzene for crystallising the crude product or samples which had already been boiled with several successive portions of decalin and still remained undissolved. When nitrobenzene was so used it was found that quite a considerable loss occurred, and the product had not a sharp melting-point (usually over a range 306-310°C). It was thought that this might be due to the presence of a less soluble isomer in the crude mixture (see p. 33). In an attempt to prepare a specimen and to purify crude mixtures, use was made of boiling nitrobenzene together with a little animal charcoal. Several successive treatments of this kind gave a product with variable melting-point in the range 306-322°C. In the experiment detailed below the best result was obtained and, as a result of certain differences between the two compounds, A (the oxime, m. p. 314°C) and B (m. p. 322°C) (see p. 34), it was decided that the latter was not an oxime. In fact analysis shows it to be a molecular compound between the ketone (presumably derived from the oxime through the agency of the animal charcoal) and the solvent nitrobenzene.

1) 3 gm. 1:1-keto-benzanthrone, 1.62 gm. hydroxylamine hydrochloride and 500 ml. alcohol were boiled under reflux and 30 ml. caustic soda solution slowly run in. The mixture was filtered from 0.78 gm. unchanged ketone and the filtrate carefully acidified and the orange precipitate filtered off. The yield of crude product (2.49 gm.) had melting-point 307-13°C. It was dissolved in nitrobenzene with a small quantity of animal charcoal added, and filtered hot. It was found necessary to distil off some of the nitrobenzene from the solution when 1.93 gm. orange needles were obtained (m.p. 311-7°C). A second treatment gave 1.40 gm. (m.p. 319-22°C) and a third 0.95 gm. orange-brown needles (m.p. 320-2°C). A mixed melting-point with the oxime (m.p. 314°C, crystallised from decalin) showed a large depression (m.p. 299-311°C). The compound was found to contain nitrogen by a sodium fusion and was sent away for analysis, but the results did not agree with those of the oxime. It was later discovered that the compound was insoluble in alkali, gave little depression in melting-point when mixed with authentic ketone and gave the ketone after treatment with concentrated sulphuric acid at 100°C for one hour (p.101): the oxime (m.p. 314°C) was soluble in boiling alkali and was recovered in quantitative yield after treatment with concentrated sulphuric acid under similar conditions. As stated above, the compound is formulated as a molecular compound of one molecule of ketone and one molecule of nitrobenzene. The analysis figures



support this supposition.

Analysis:

a) found (Schoeller) C 76.1%, H 3.5%, N 3.9%  
 ( $C_{18}H_8O_2, C_6H_5NO_2$ ) requires C 76.0%, H 3.4%, N 3.7%  
 oxime,  $C_{18}H_9O_2N$  requires C 79.7%, H 3.3%, N 5.2%.

b) after heating for two hours at 220°C, 0.2838 gm.  
 lost 0.0968 gm. loss 34.1%.

for quantitative loss of nitrobenzene;

$C_{18}H_8O_2, C_6H_5NO_2$  requires 32.5%.

The results are in good agreement after making due allowance for the sublimation of a trace of the ketone itself.

2) An attempt was also made to form a second oxime through the catalytic effect of hydrochloric acid gas.

0.75 gm. oxime was boiled under reflux for two hours with 50 ml. nitrobenzene which had been saturated with hydrochloric acid gas. On cooling and filtering, there was obtained 0.15 gm. fine orange-brown needles (m. p. 313-4°C). Subsequent treatment with nitrobenzene and animal charcoal gave a product of melting-point 317-22°C. It thus appears that the animal charcoal facilitates conversion of the oxime to the ketone and that neither of the reagents used produces a second oxime.

As a result of the above experiments, nitrobenzene is avoided as a reagent for crystallising the oxime although it is suitable from solubility considerations.

The Lactam of 11-Amino-1-carboxy-benzanthrone: the  
Action of Hydrazoic acid on 1:11-Keto-benzanthrone.

The experiment was carried out by the method used by Walls (J., 1935, 1405) for the conversion of fluor-enones into phenanthridones.

0.5 gm. 1:11-keto-benzanthrone (in 5 ml. concen-  
trated sulphuric acid)

0.5 gm. sodium azide (in 5 ml. water).

The solution of the ketone was cooled in ice and treated dropwise with stirring with the aqueous solution of sodium azide. A vigorous evolution of nitrogen took place. After thirty minutes, the mixture was poured into 150 ml. water and the precipitate filtered off. The light brown solid, when dried, weighed 0.53 gm. (100%) and had a melting-point above 360°C.

The crude residue was boiled under reflux for half-an-hour with 50 ml. alcohol and filtered hot. From the alcohol solution, there was deposited 0.05 gm. of yellow powder, but it did not appear to be pure. The undis-solved residue crystallised from nitrobenzene as a yellow crystalline powder (0.38 gm., yield 75%). Neither of these products melted below 360°C, but the former had a deep pink colour in boiling alkali, and a deep red with deep green fluorescence in concentrated sulphuric acid) while the latter exhibited only a faint pink in alkali and red with yellowish green fluorescence in concentrated

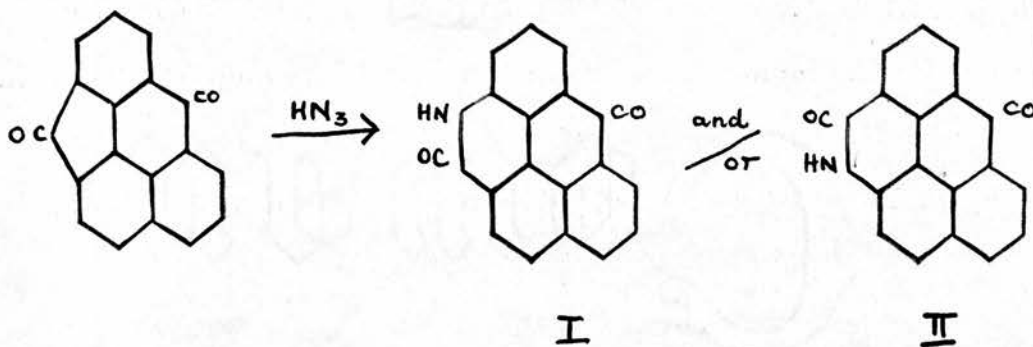
sulphuric acid.

In a subsequent experiment, 0.90 gm. of the crude compound was boiled with 30 ml. glacial acetic acid and it was found that this solvent also removed most of the alkali-soluble material. 0.77 gm. Insoluble residue, finally purified by recrystallisation from nitrobenzene.

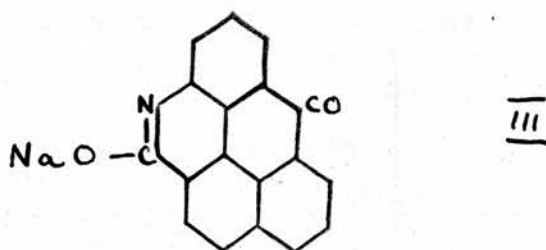
The final product is believed to be the lactam of formula I rather than II (cf. p. 41). It may be a mixture of the two forms, but no information on this point can be obtained in the usual manner as the product has no determinable melting point.

Analysis:

found (Schoeller)	C 79.0%,	H 3.4%,	N 5.4%
$C_{18}H_9O_2N$ requires	C 79.7%,	H 3.3%,	N 5.2%



The anthridone appears to form a red sodium salt when treated with alkali; the yellow colour changes to red and it dissolves to a very slight extent on boiling (orange to pink colour, with pink fluorescence). The yellow colour is restored by making acid once more or on filtering and washing the red salt with water. It would appear that the sodium salt is of the enolic type III.



It was decided to see whether there was any possibility that, in the reaction between hydrazoic acid and 1:11-keto-benzanthrone, the point of attack might possibly be the keto-group in the benzanthrone nucleus and not that in the five-membered ring: to this end benzanthrone was submitted to similar treatment to that used in the case of 1:11-keto-benzanthrone.

0.2 gm. benzanthrone was dissolved in 5 ml. concentrated sulphuric acid and the cooled solution treated dropwise with a solution of 0.2 gm. sodium azide in 5 ml. water with stirring. The solution was then poured into 100 ml. water and the solid (0.18 gm., m. p. 155-70°C) filtered. After crystallisation from glacial acetic acid, it was identified by melting-point and mixed melting point 171-2°C, as the starting material.

Attempts to Submit Benzanthrone-1:11-ketoxime to a Beckmann Change using Various Reagents.

- 1) Concentrated sulphuric acid.
  - a) with the oxime (compound A, m. p. 314°C)

0.2 gm. oxime and 2 ml. concentrated sulphuric acid

were heated for one hour at 100°C, the mixture allowed to cool somewhat and poured into 100 ml. water. The solid was filtered off (0.19 gm., m.p. 307-8°C with vigorous decomposition), dissolved in boiling alkali and filtered hot. On acidifying the filtrate, there was obtained 0.18 gm. identified by crystallisation from decalin as almost quantitative recovery of the oxime.

- b) With the ketone-nitrobenzene compound (B,  
m.p. 320-2°C, see p. 96).

Similar treatment with concentrated sulphuric acid gave 0.18 gm. (m.p. 323-5°C), insoluble in boiling alkali and identified on crystallisation from glacial acetic acid as 1:11-keto-benzanthrone (m.p. and mixed m.p. with ketone, 324-6°C). This was one of the steps towards disproving the possibility that B was a second oxime.

- c) With the oxime (at a higher temperature).

0.25 gm. oxime (m.p. 314°C) and 3 ml. concentrated sulphuric acid were heated together for one hour at 150°C, the mixture allowed to cool and poured into 150 ml. water. The yellow precipitate was colloidal in character and it was found impossible to isolate it. The liquid itself was an orange-yellow colour and it appeared that the more vigorous treatment at the higher temperature had resulted in extensive sulphonation.

2) By zinc chloride fusion.

The procedure adopted was similar to that used in the conversion of fluorenone oxime into phenanthridone (Pictet and Patry, Ber., 1893, 26, 1964; Moore and Huntress, J.A.C.S., 1927, 49, 2618).

0.50 gm. oxime was fused with 3 gm. zinc chloride for 20 minutes at 280°C in a Pyrex test-tube; the red melt was boiled with two successive 100 ml. portions of water to remove zinc compounds and the residue filtered off. The residue was then boiled with dilute caustic soda solution and filtered hot: from the filtrate there was recovered 0.05 gm. alkali-soluble material, which was unchanged oxime.

The residue (0.36 gm.), insoluble in alkali, contained no nitrogen when tested by a sodium fusion; it partially melted at 313-7°C with softening at 300°C. The solid was recrystallised from nitrobenzene giving needles with melting-point 317-20°C and softening at 300°C (0.29 gm.). Further crystallisations from nitrobenzene (0.10 gm., m.p. 318-20°C) and glacial acetic acid gave finally 0.08 gm. fine orange needles, identified as 1:11-keto-benzanthrone by m.p. and mixed m.p. 323-6°C.

3) By phosphorus pentachloride.

This reagent is usually employed in ice-cold or warm ether solution for converting oximes into substituted amides. Owing to the insolubility of benzanthrone-1:11-ketoxime in ether, anisole was used as solvent medium.

a) 0.2 gm. oxime was dissolved in 80 ml. anisole, cooled to 0°C and treated with 0.2 gm. phosphorus pentachloride. The mixture was allowed to stand 24 hours in the cold and shaken at intervals. The anisole was distilled in steam and the solid residue filtered off, washed and dried. It weighed 0.18 gm., had a melting-point 305-11°C and dissolved almost completely in dilute boiling caustic soda. The slight insoluble residue had m. p. 305-8°C - and was probably unchanged oxime.

From the alkaline filtrate, there was obtained, on acidification, 0.12 gm. which, on crystallisation from decalin, had melting-point 310-2°C not depressed by admixture with the starting material.

As treatment at 0°C had thus no effect on the oxime, the experiment was repeated at a higher temperature.

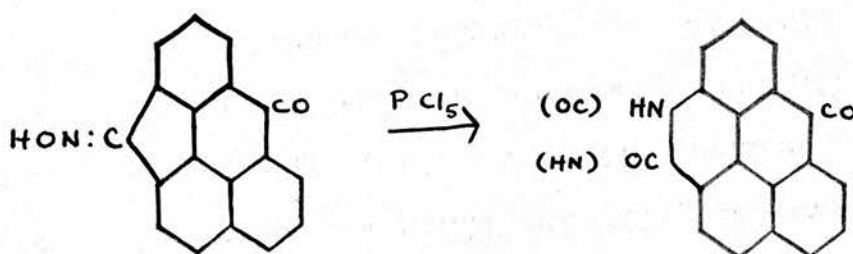
b) The above experiment was carried out for 1½ hours at 60°C. The product was mainly alkali-insoluble and with melting-point above 360°C. It appeared to be the anthridone; so the experiment was repeated on a larger scale.

c) 0.5 gm. oxime was dissolved in 150 ml. anisole, treated with 0.5 gm. phosphorus pentachloride and maintained at 75°C for 5 hours. Some solid which had separated was filtered and washed with ether. It was then boiled with water, filtered and dried. There was obtained 0.05 gm. of a yellow-green powder softening at 356°C and partially melting at 365°C. After removal of the anisole from the filtrate by steam-distillation

and filtration of the solid, there was obtained a further 0.30 gm. which melted incompletely at 313-326°C.

The total solid (0.35 gm., 70%) was boiled with dilute caustic soda solution and filtered hot. No appreciable solution occurred, and the filtrate gave only a very small quantity of solid on acidification. The alkali-insoluble material weighed 0.32 gm. and had a rather indefinite melting-point about 340°C. Crystallisation from 50 ml. nitrobenzene gave 0.12 gm. of yellow powder with no melting-point below 360°C. This was shown by colour reaction in concentrated sulphuric acid and analysis to be identical with the product obtained by treating 1:11-keto-benzanthrone with hydrazoic acid.

Analysis: found N 5.0%  
 $C_{18}H_9O_2N$  requires N 5.2%.



4) By treatment with benzene sulphonic chloride.

0.5 gm. benzanthrone-1:11-ketoxime

0.3 gm. benzene sulphonic chloride

10 ml. pure pyridine.



The oxime was dissolved in the pyridine and the benzene sulphonic chloride added; the solution was then heated on a water-bath at 100°C for six hours and allowed to stand overnight. After treatment with dilute sulphuric acid and filtration of the yellow solid, followed by washing with hot water, there was obtained 0.50 gm. A test portion showed this to be completely soluble in alkali - apparently indicating that no Beckmann change had taken place. Crystallisation from nitrobenzene and xylene gave 0.32 gm. of an orange powder, m.p. 308-9°C which proved to be unchanged oxime, for on treatment with phosphorus pentachloride in anisole for five hours at 60°C it gave the same anthridone as the starting material.

Alkaline Fusion of the Lactam of 11-amino-1-carboxy-benzanthrone.

5 gm. caustic potash were fused at 200°C in a narrow nickel tube and 0.5 gm. of the anthridone added. The temperature (inside) was then raised to 280°C and maintained for one hour. The cooled melt was then boiled for half-an-hour with one litre of water and filtered.

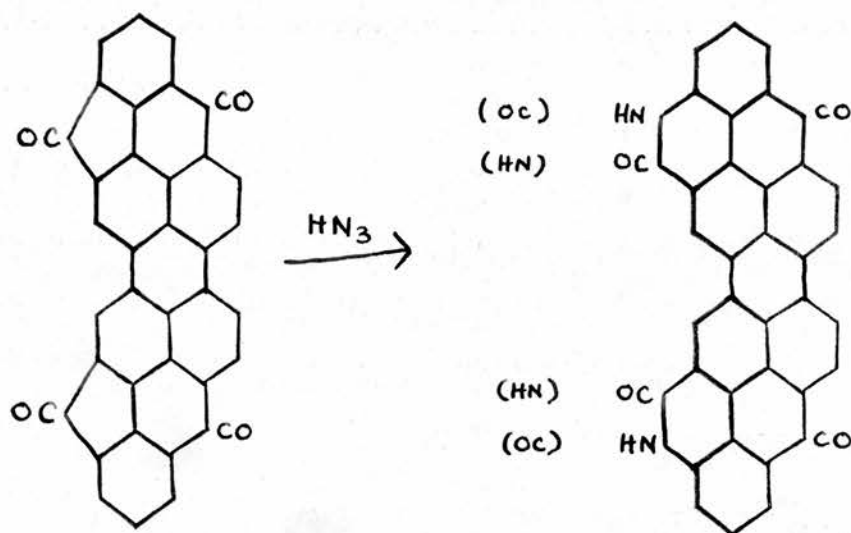
The alkali-insoluble material, when dry, appeared as a blue-black crystalline powder (0.50 gm.). It was boiled with 100 ml. nitrobenzene to remove any unchanged anthridone and filtered hot; the residue was further boiled with 50 ml. alcohol and filtered off. The blue-black crystalline solid itself is very diffi-



concentrated sulphuric acid is brown with a strong green fluorescence and a brownish precipitate was obtained on adding water. It forms a brown vat with green fluorescence and dyes cotton brown not fast to soap solution. The compound is presumably phenolic in character due to oxidation of the molecule at some point (cf. Maki, J. Soc. Chem. Ind. Japan, 1932, 35, 579B).

Treatment of Diketo-dibenzanthrone with Hydrazoic Acid.

Some pure 1-11:1'-11'-diketo-3-3':4-4'-dibenzanthrone was available and an attempt was made to see if hydrazoic acid would convert it to a product identical with that obtained above, thus:-



Accordingly, 0.2 gm. of the pure dyestuff was dissolved in 75 ml. concentrated sulphuric acid in the cold. To the stirred and cold solution was run in a solution of 0.1 gm. sodium azide in 5 ml. water. No

Alk. fusion of anthridone      Product described on p. 107      Diketo-dibenzanthrone

Appearance	blue-black crystalline powder	violet crystalline powder	violet crystalline powder
Sodium fusion	nitrogen	nitrogen detected	nil
Colour in concentrated sulphuric acid	greenish blue	violet	violet
+ water	blue green ppt.	violet ppt.	violet ppt.
Hot nitrobenzene - colour	green, no fluorescence	reddish violet, red fluorescence	bluish violet, red fluorescence
Colour of vat	bluish green	purplish blue	purplish blue
Colour on cotton	purple-grey	violet-blue	blue-violet
Effect of 30 minutes boiling with 1% soap solution	fast	fast	fast

visible change at all took place. The mixture was then poured into 300 ml. water and the violet precipitate filtered off. The process was long and tedious. There was finally obtained 0.15 gm. of a violet powder, which contained nitrogen but resembled the starting material rather than the alkali-insoluble fraction from the alkaline fusion of the lactam, as shown opposite. Apparently the hydrazoic acid has only brought about a partial conversion into the anthridone.

Analysis: found (Weiler) N 1.3% (reported difficult to combust)

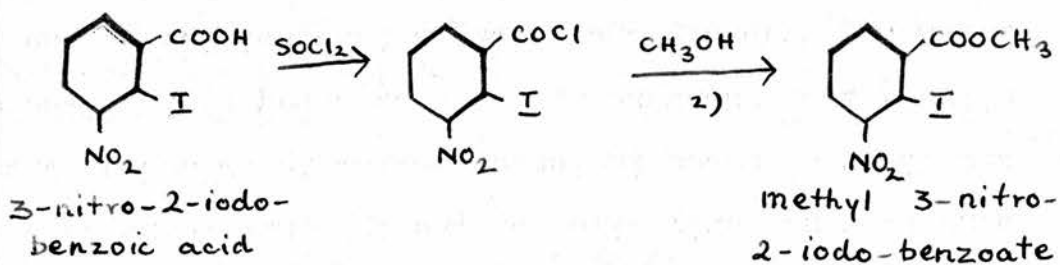
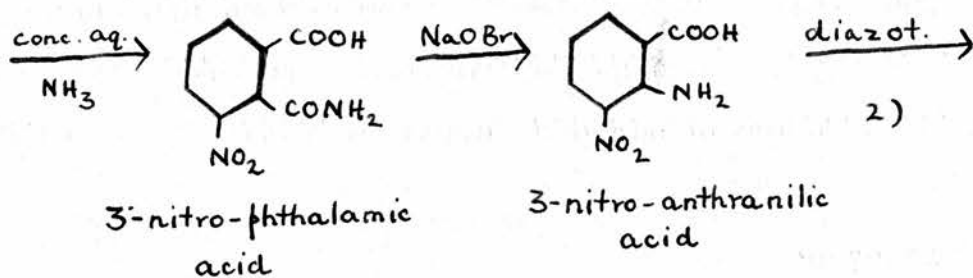
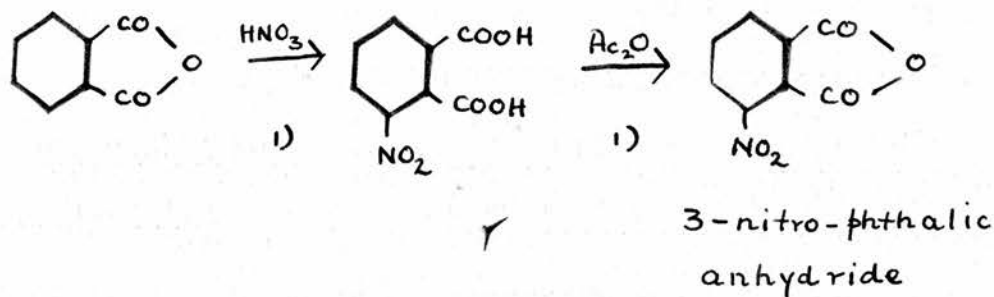
$C_{36}H_{14}O_4N_2$  requires N 5.2%

As the nitrogen analysis figures for all complex benzanthrone derivatives of the type are found to be low, the figures quoted indicate that at least 30% of the diketo-dibenzanthrone has been transformed into the dilactam. Probably the extreme insolubility of the starting material accounts for the small percentage conversion.

Ullmann Reaction between Methyl 3-Nitro-2-iodo-benzoate and Methyl 1-Bromo-2-Naphthoate: Attempted Synthesis of the Lactam of 11-Amino-1-Carboxy-benzanthrone.

1) Methyl 3-Nitro-2-iodo-benzoate.

A supply of this ester was available, which had been prepared from phthalic anhydride according to the following scheme (details are to be found in Haldane's Thesis, Edinburgh, 1934):



## References: -

- 1) Clark, Organic Syntheses, Vol. 7, p. 74.
- 2) James, Kenner and Stubbing, J., 1920, 773.

2) Methyl 1-Bromo-2-naphthoate.

(Grieve, loc. cit.)

(a) 1-Bromo-2-acetonaphthalide.(Franzen and Eidis, J. pr., 1913, 88, 755)

37 gm. aceto- $\beta$ -naphthalide (see p. 86)

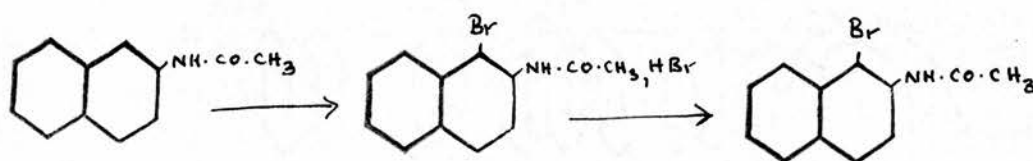
33 gm. bromine in 40 ml. chloroform

200 ml. chloroform.

The aceto- $\beta$ -naphthalide was dissolved in the chloroform by warming on the steam-bath. The bromine solution was then run in with stirring, the mixture allowed to stand for half-an-hour till cold and the solid filtered off. At this stage, the compound is in the form of the hydrobromide of the required compound; the hydrobromic acid is removed by shaking up with dilute sodium carbonate or caustic soda solution, filtering and drying the white 1-bromo-2-acetonaphthalide.

Yield: 53 gm. (95%). M.p. 138°C.

It can be crystallised from alcohol in colourless needles, m.p. 140°C.



(b) 1-Bromo-2-naphthylamine Hydrochloride.

(Claus and Philipson, J. pr., [2], 43, 47;

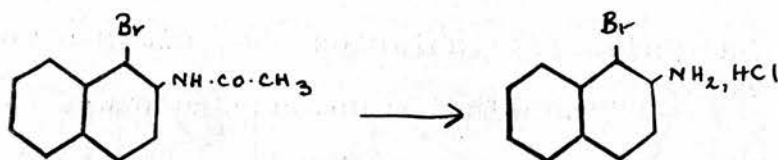
Morgan, J., 1900, 77, 819)

It has been found most convenient to prepare the hydrochloride of the base for diazotisation at a later stage.

20 gm. 1-bromo-2-acetonaphthalide.  
 25 ml. concentrated hydrochloric acid  
 100 ml. alcohol.

The bromo-aceto-compound was dissolved in the alcohol and the hydrochloric acid added. The solution was then refluxed for an hour, most of the alcohol removed on the steam bath, and the crystals of the hydrochloride filtered off, washed with alcohol and dried.

Yield: 20 gm. (100%). M.p. 219-20°C.



(c) 1-Bromo-2-naphthoic Acid.

(Grieve, loc. cit.)

50 gm. 1-bromo-2-naphthylamine hydrochloride  
 20 gm. sodium nitrite in 25 ml. water  
 (i) 120 gm. sodium cyanide in 300 ml. water  
 (ii) 100 gm. copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in 400 ml. water.

The finely powdered hydrochloride was suspended in 150 ml. water and 50 ml. concentrated hydrochloric acid were added. The suspension was cooled to 0-5°C and diazotised with the sodium nitrite solution in the usual manner till a slight excess was present.

A solution of cuprous cyanide was prepared by adding



solution (i) to (ii) with shaking and the mixture filtered from any residue.

The clear diazo-solution was added in portions to the vigorously stirred cuprous cyanide solution on the steam-bath. The brown precipitate which formed was stirred for a further three hours on the steam-bath, when brown oily drops of the nitrile formed. After standing overnight, the solid nitrile was filtered off and hydrolysed to the acid without preliminary purification.

The crude nitrile was refluxed for 24 hours with an acid hydrolysing mixture consisting of:

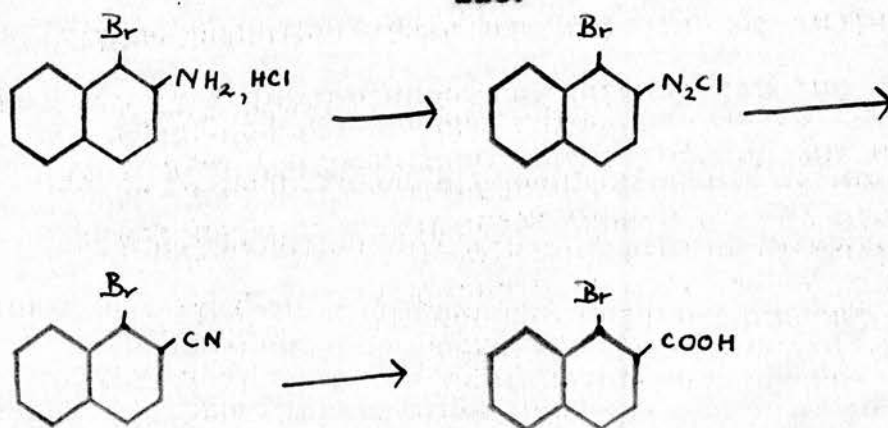
- 400 ml. glacial acetic acid
- 200 ml. concentrated sulphuric acid
- 100 ml. water.

The brown liquid was poured into 2 litres of cold water and the crude acid which precipitated was filtered off. It was added to 500 ml. water, made distinctly alkaline with sodium hydroxide and heated at 50°C for a short period and filtered. The filtrate on acidification yielded a light brown acid which was filtered off, washed well with water and dried.

Yield: 21 gm. (43%). M.p. 187-189°C.

The acid was obtained, on crystallisation from benzene, in the form of colourless needles, m.p. 191°C. As the loss in purification was considerable, it was found more convenient to esterify the crude acid and purify the ester.

113.

(d) Methyl 1-Bromo-2-naphthoate.

(Grieve, loc. cit.)

15 gm. 1-bromo-2-naphthoic acid (m.p. 187-9°C)

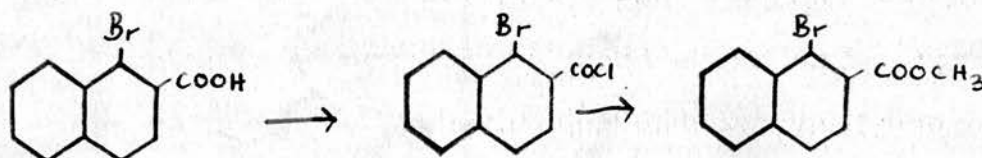
30 ml. thionyl chloride (purified)

50 ml. dry methyl alcohol.

The ester was formed by way of the acid chloride as described in the preparation of the 8-bromo-1-naphthoate. It was necessary, however, to filter the ethereal extract and the ester was obtained as a red solid on removing the ether. It was purified by boiling out with petroleum ether (b.p. 40-60°C).

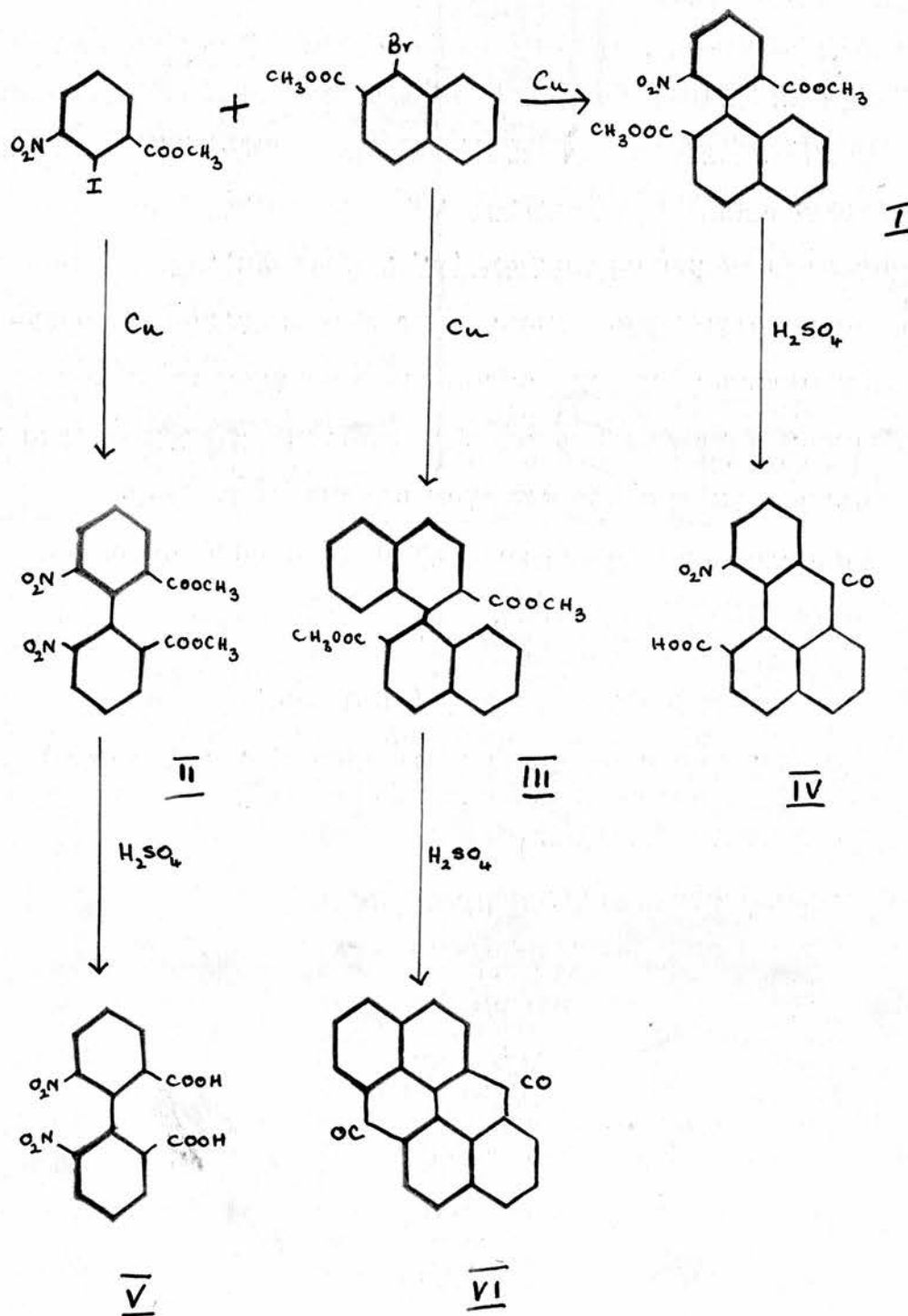
Yield: 14 gm. (90%). M.p. 58-59°C.

The ester crystallises from light petroleum ether in colourless plates, m.p. 60°C.



3) Ullmann Reaction between Methyl 3-Nitro-2-iodo-benzoate and Methyl 1-Bromo-2-Naphthoate.

The products which may theoretically be formed in this reaction are indicated in the following scheme: -



10 gm. methyl 3-nitro-2-iodo-benzoate  
10 gm. methyl 1-bromo-2-naphthoate  
20 gm. copper bronze.

The above materials were heated together with stirring for  $4\frac{1}{2}$  hours at  $180^{\circ}\text{C}$ , and the organic matter extracted with three portions (40ml.) of boiling acetone. On cooling, the acetone solution deposited some solid which was filtered off and washed with a little ether.

The whitish solid (1.47 gm.) had melting-point  $139-40^{\circ}\text{C}$ . Since the colour developed in concentrated sulphuric acid was green with no trace of red, this was concluded to be largely the dinaphthyl ester, dimethyl 1:1'-dinaphthyl-2:2'-dicarboxylate, (III) which yields a green solution of anthanthrone (VI) on being warmed with concentrated sulphuric acid. It was to be expected that in the Ullmann reaction, in addition to the formation of any of the desired phenyl-naphthyl ester (I), some dinaphthyl ester and some diphenic ester (II) would form. The melting-points of the last two compounds are given respectively as  $155-6^{\circ}\text{C}$  (Grieve, loc. cit.) and  $131-2^{\circ}\text{C}$  (Beilstein's Handbuch). Crystallisation of the above crude solid from petroleum ether of different boiling-points failed to yield any pure product - the samples had variable melting-points between  $123^{\circ}\text{C}$  and  $152^{\circ}\text{C}$  and all gave a pure green colour in concentrated sulphuric acid even on warming. The phenyl-naphthyl ester ought to give some trace of a red colour if any benzanthrone (IV) is formed.

The filtrate was next examined. The acetone was removed completely by distillation under reduced pressure and the brown oily residue treated with 15 ml. ether and allowed to stand overnight. The brownish solid was filtered off and washed with a little ether: weight - 9 gm.

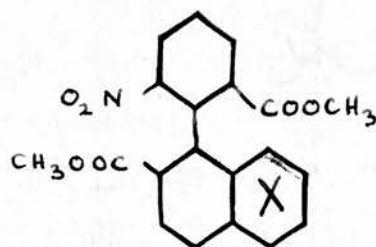
All attempts to crystallise this crude product gave indefinite results similar to those already recorded. It was therefore thought best to submit the mixture of esters to concentrated sulphuric acid treatment for one hour at 100°C, and to attempt to separate the free carboxylic acids from the neutral anthanthrone produced from the dinaphthyl dicarboxylic acid.

4) Treatment of the mixed esters with concentrated sulphuric acid.

8 gm. of the crude mixed esters were heated at 100°C for one hour with 60 ml. concentrated sulphuric acid, the cooled mixture poured into 220 ml. water and the solid filtered off. The reddish solid was boiled with dilute alkali and filtered hot. The alkali-insoluble material (0.30 gm. only) proved to be anthanthrone by its green colouration in concentrated sulphuric acid and by its formation of a magenta vat with alkaline hydrosulphite. The alkaline filtrate (brown-red with no fluorescence) gave, on acidification and filtration, only 1.40 gm. of material, consisting of buff needles, m. p. 267-9°C with decomposition. Only a very faint

green was developed in concentrated sulphuric acid, but no trace of a typical benzanthrone red was evident. A sodium fusion indicated the presence of nitrogen. A crystallisation from 40 ml. alcohol gave cream coloured plates, m.p. 269-270°C. Further crystallisation did not affect the melting-point.

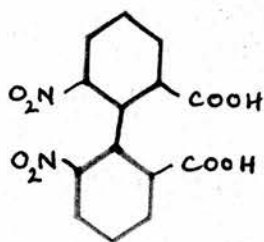
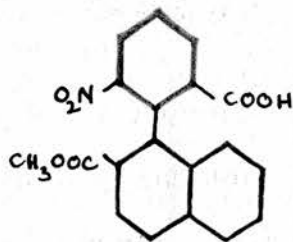
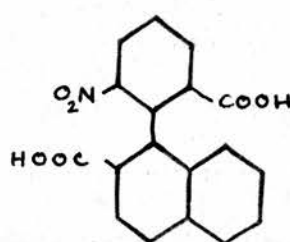
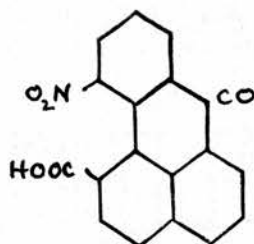
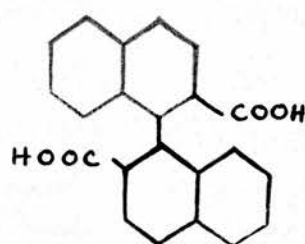
The appreciable solubility of this product in water may to some extent account for the large loss in material observed in the experiment, but it may be due to even greater extent to the phenyl-naphthyl ester (probably with melting-point between 120°C and 160°C) undergoing sulphonation in the unprotected ring (X) in the naphthalene nucleus to form water soluble derivatives before hydrolysis of the ester groupings to a benzanthrone derivative can take place.



As to the identity of the acidic product of melting-point 269-270°C, the presence of nitrogen indicates that it contains either one or two nitrated phenyl groups. Analysis figures point to it being a diphenyl derivative, although the agreement is by no means good.

Analysis:                    found N 9.3% 8.9, 9.1%  
 $C_{14}H_8O_8N_2$  (I) requires N 8.4%.

The three possible phenyl-naphthyl derivatives (II, III and IV) require N 4.0, 4.2, 4.4% respectively.

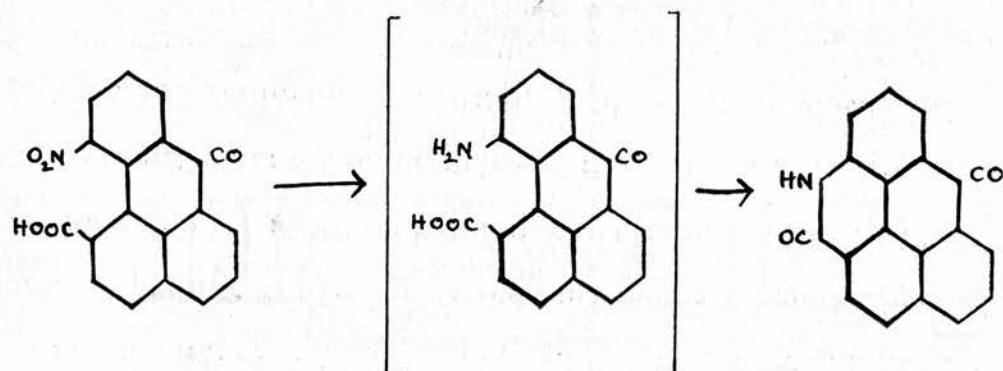
IIIIIIIVV

The melting-point of the acid obtained could not be raised above 269-270°C. The melting-point of 6:6'-dinitro-diphenyl-2:2'-dicarboxylic acid is given variously as 297°C, 303°C (Schultz, Ann., 203, 111; Beckenkamp, Ann., 203, 112), while 1:1'-dinaphthyl-2:2'-dicarboxylic acid is given as 267-8°C (Kuhn and Albrecht, Ann., 465 284).

From the results, it has been assumed that all three products are formed in the Ullmann reaction. The dinaphthyl compound is indicated by the later production of anthanthrone; the diphenyl compound is believed to form and later be hydrolysed despite anomalies of melting-point and analysis figures; while the large loss of material

in the sulphuric acid treatment cannot be wholly due to the solubility of the diphenic acid and is believed to be due to rapid sulphonation of the phenyl-naphthyl derivative.

Had the desired nitro-carboxy-benzanthrone been isolated, it was expected that subsequent mild reduction would give the lactam of 11-amino-1-carboxy-benzanthrone:



11-Amino-benzanthrone.

A preliminary experiment was carried out treating a solution of 11-carboxy-benzanthrone in concentrated sulphuric acid at 0°C with a concentrated aqueous solution of sodium azide according to the method of Walls (J., 1935, 1405) for converting fluorenones into phenanthridones (cf. p. 39). From an experiment using 0.5 gm of acid, there was an almost quantitative recovery of the starting material.

At a later date the procedure was modified according to the method of Oesterlin (Z. angew. Chem., 1932, 45, 536).



4 gm. 11-carboxy-benzanthrone  
 4.4 gm. sodium azide  
 25 ml. concentrated sulphuric acid  
 100 ml. chloroform.

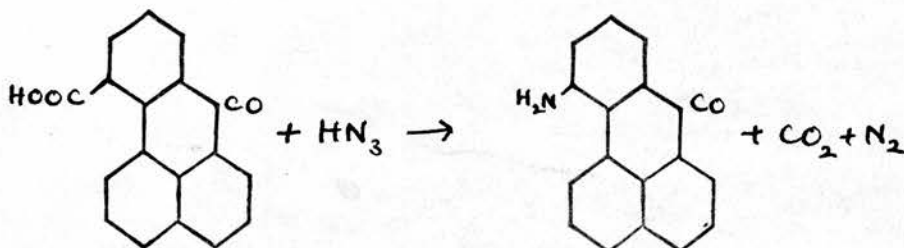
The acid was dissolved in the concentrated sulphuric acid and the chloroform added. To this mixture was added the solid sodium azide in portions with stirring over two hours at 45-50°C. The mixture was then poured into 200 ml. water, the reddish precipitate filtered off and boiled with dilute caustic soda for a few minutes, and the mixture again filtered. 0.46 gm. (10%) of the acid was recovered from the alkaline filtrate. The red alkali-insoluble material proved to be the desired amine.

Yield: 3.04 gm. (86%). M.p. 207-211°C.

Crystallisation from alcohol gave fine red needles melting at 215-7°C and unaltered in melting-point by further crystallisation.

Analysis: found (Weiler) C 82.0%, H 4.6%, N 5.8%

C<sub>17</sub>H<sub>11</sub>ON requires C 83.2%, H 4.5%, N 5.7%.

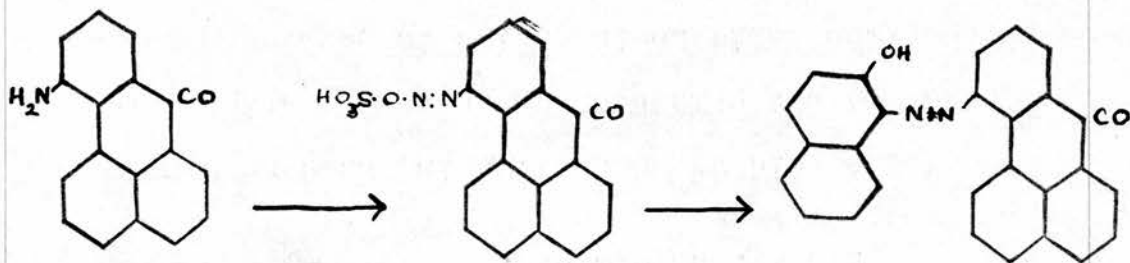


The amine dissolves readily in boiling alcohol to give a red solution, and is moderately soluble in benzene

and in ethyl acetate. The colour in concentrated sulphuric acid resembles that of the 11-carboxy-acid (blood-red with yellowish red fluorescence). It is not appreciably soluble in dilute mineral acids but the colour changes from red to orange-yellow presumably due to the superficial formation of insoluble salts (e.g. the hydrochloride and sulphate), the colour being restored on rendering the solution once more alkaline. Perkin (J., 1922, 121, 480) apparently found the same phenomenon in the case of 4-amino-benzanthrone for he had to use concentrated sulphuric acid to obtain a solution suitable for diazotisation.

Coupled Azo-Dye with  $\beta$ -Naphthol.

0.1 gm. amine in 10 ml. glacial acetic acid was cooled to 0°C and added with stirring and cooling to a solution of 0.1 gm. sodium nitrite in 1 ml. concentrated sulphuric acid. This diazo-solution was then added to a strongly alkaline solution containing 0.5 gm.  $\beta$ -naphthol. The red precipitate formed was found to dye cotton a pale pink, not fast to alkali.



11-Formamino-benzanthrone.

0.25 gm. 11-amino-benzanthrone

50 ml. formic acid (90%).

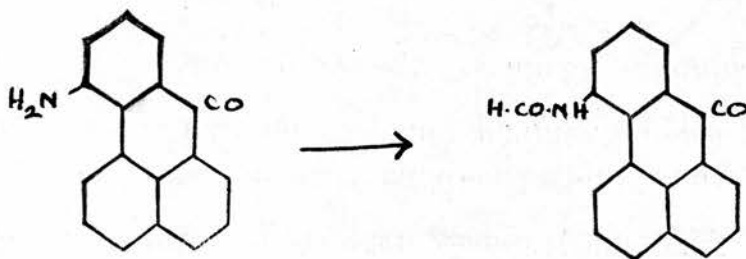
The above were boiled under reflux for twenty minutes, the amine dissolving to a brown solution with slight green fluorescence. The excess formic acid was removed under reduced pressure and the residue crystallised as golden yellow needles from alcohol (orange solution, slight green fluorescence).

Yield: 0.15 gm. (60%). M.p. 268-271°C.

A further crystallisation from alcohol gave 0.14 gm. of fine golden yellow needles with no change in the melting-point.

Analysis: found (Weiler) N 5.2%

$C_{18}H_{11}O_2N$  requires N 5.1%.



The formyl compound is readily soluble in alcohol though rather less so than the parent amine; it is practically insoluble in benzene. It is insoluble in alkalis and dissolves in concentrated sulphuric acid to a blood-red solution with no fluorescence.

11-Acetamino-benzanthrone.

0.4 gm. 11-amino-benzanthrone

30 ml. acetic anhydride.

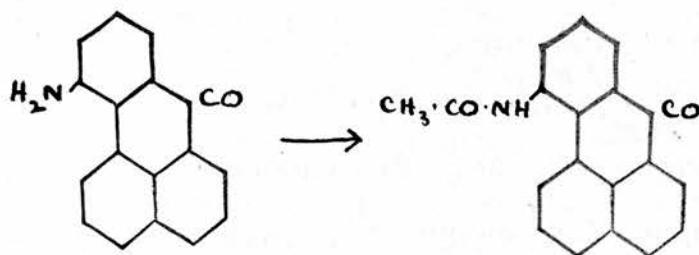
After boiling the above under reflux for 15 minutes, the hot solution was first filtered from a slight residue and then poured into 250 ml. water and warmed on the steam-bath until the oil solidified to a solid mass which was filtered off.

Yield: 0.32 gm. (77%). M.p. 249-252°C (softening at 228°C).

After four successive crystallisations from alcohol, the acetyl compound was obtained in fine golden yellow needles, m.p. 278-9°C (sharp).

Analysis: found (Weiler) N 4.6%

$C_{19}H_{13}O_2N$  requires N 4.9%.



The acetyl derivative is readily soluble in methyl and ethyl alcohol and in glacial acetic acid, moderately soluble in benzene and ethyl acetate but practically insoluble in ligroin.

Alkaline Fusion of 11-Amino-benzanthrone: 11:11'-Diamino-3:3'-4:4'-dibenzanthrone.

0.5 gm. 11-amino-benzanthrone  
4 gm. caustic potash.

The alkali was fused at 220°C in a nickel crucible and the amine slowly added. The temperature was maintained for half-an-hour, the bluish melt boiled with 250 ml. water for two hours, diluted to 500 ml. and filtered. The residue was washed with hot water, alcohol and dried.

The alkali-insoluble material (0.43 gm.) was a blue-black crystalline powder with no melting-point below 360°C. It was boiled with 50 ml. alcohol to remove any unchanged amine and filtered hot: the insoluble residue weighed 0.40 gm. It was now boiled with 50 ml. nitrobenzene and filtered hot - an appreciable amount dissolved. The insoluble blue-black residue weighed 0.19 gm., while the nitrobenzene solution deposited 0.12 gm. of a blue-black crystalline powder on treatment with light petroleum ether. The diamino-dibenzanthrone dissolves in concentrated sulphuric acid with a brown colour and green fluorescence.

Analysis: found (Weiler) N 6.0%

$C_{34}H_{18}O_2N_2$  requires N 5.8%.

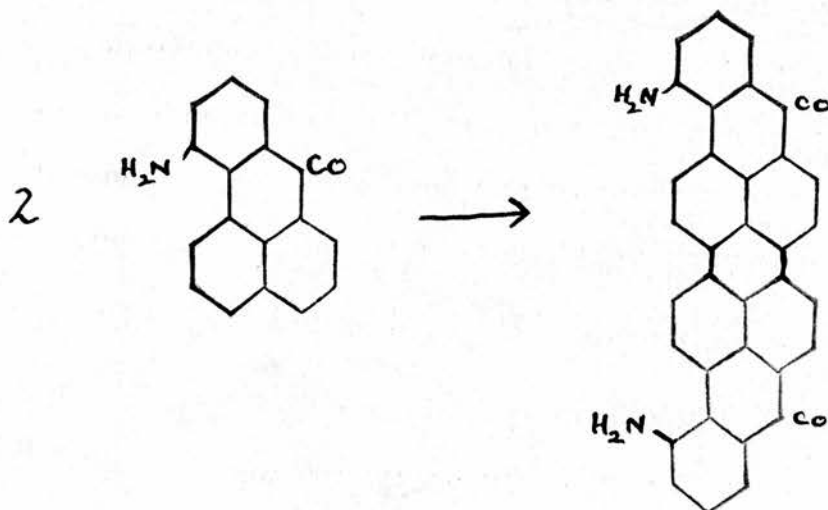
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In this case the diamine has a relatively low melting-point and is more readily combusted. Hence the analysis figures agree more closely with the theoretical values.

It has, rather surprisingly, little vatting property. In a test experiment, 0.05 gm. was warmed at 50°C for 15 minutes with a mixture as follows:-

5 ml. dilute caustic soda  
 400 ml. water  
 100 ml. ethyl alcohol  
 5 gm. sodium hydrosulphite.

and then filtered: almost quantitative recovery of solid was obtained. The faintly coloured vat solution hardly affected cotton at all - a pale grey-green, fast to alkali, developed after reducing for half-an-hour at 70°-80°C. The vat solution deposited very little solid on being allowed to stand in the air. Both the other diamino-dibenzanthrones quoted in the literature are good vat dyes.

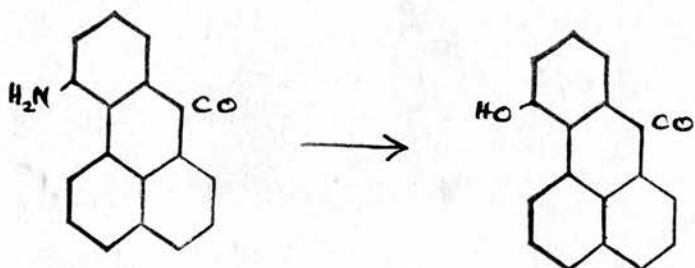


## Comparison of Diamino-dibenzanthrones

	1:1'-derivative	2:2'-derivative	11:11'-derivative
Appearance	violet-black powder	blue-black powder	blue-black powder
Colour in concentrated sulphuric acid	violet	violet	brown, green fluorescence
Solubility and colour in nitrobenzene	insoluble; blue, strong red fluorescence	slight; blue green, red fluorescence	fairly soluble; brown, blue fluorescence
Ease of formation and colour of the alkaline hydro-sulphite vat	readily; blue, red fluorescence	readily; clear blue, red fluorescence	very difficult; green, red fluorescence
Colour on cotton	dark violet-blue	pure green	pale grey-green

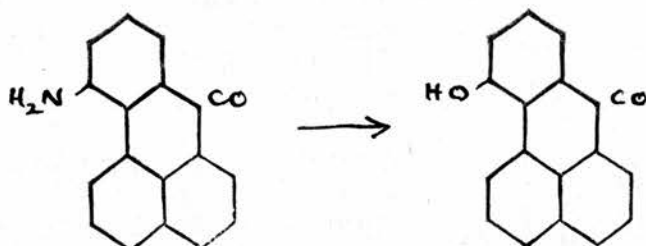
The table opposite shows a comparison between this 11:11'-diamino-dibenzanthrone and the two other known isomers. The constitutions of the latter are due to Maki and co-workers. The 1:1'-diamino-compound (Maki and Aoyama, J. Soc. Chem. Ind. Japan, 1935, 38, 636B) was obtained by treating the dichlorination product of violanthrone with aqueous ammonia in an autoclave at 200°C for seven hours in the presence of a copper catalyst; the 2:2'-diamino-compound (Maki, Nagai and Hayashi, J. Soc. Chem. Ind. Japan, 1935, 38, 715B) was obtained by reducing the dinitration product of violanthrone with alkaline hydrosulphite. The constitution of these two diamino-violanthrones depends on the truth of the formulation of the dichlorination and dinitration products mentioned.

The alkaline filtrate from the above fusion was orange-red with a slight green fluorescence; on acidification, there was obtained 0.08 gm. of orange solid, melting incompletely about 150°C and dissolving in concentrated sulphuric acid to give a red solution showing slight green fluorescence. The product could not be purified by crystallisation. Although conclusive proof is lacking, this compound may be 11-hydroxy-benzanthrone.





Attempts to Prepare 11-Hydroxy-benzanthrone by Diazotisation of 11-Amino-benzanthrone.



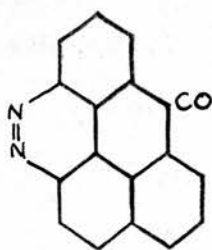
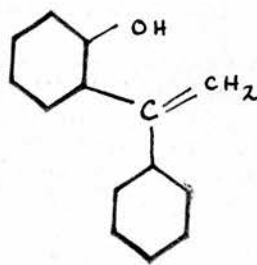
(1) An attempt was made to form 11-hydroxy-benzanthrone by diazotisation of the amine using a method similar to that employed by Perkin and Spencer (J. , 1922, 121, 480) in the case of 4-hydroxy-benzanthrone.

1 gm. 11-amino-benzanthrone (in 8 ml. concentrated sulphuric acid)

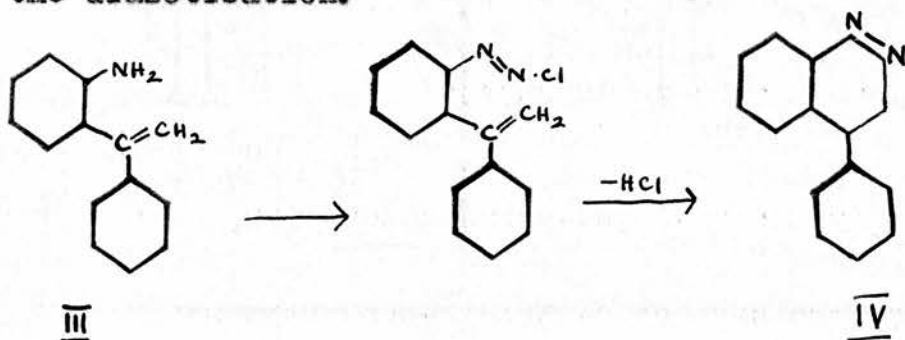
0.5 gm. sodium nitrite.

The solution of the amine was cooled to 0°C and the sodium nitrite added in portions with stirring. After one hour, the mixture was poured into 100 ml. water, boiled and the solid filtered off. This tarry residue was then boiled with several portions of dilute caustic soda solution and filtered.

The residue, insoluble in alkali, was very tarry and could not be satisfactorily purified. It might possibly be a compound of the diazine type (I).

III

This possibility is supported by the fact that Stoemer and Finke (Ber., 1909, 42, 3115) in an attempt to obtain the phenol (II) from the corresponding amine, *o*-amino-diphenyl ethylene III, obtained an almost quantitative yield of the hydrochloride of 4-phenyl-cinnoline (IV). They used hydrochloric acid not sulphuric acid in the diazotisation.

IIIIV

The alkaline filtrate obtained from the diazotised *o*-amino-benzanthrone was large in volume and carmine in colour. On acidification, there was obtained 0.49 gm. of a brown powder (m.p. about 140°C), presumably containing the hydroxy-benzanthrone. Attempts to crystallise this solid did not give a clean product but the melting-point was raised to 212-6°C (with vigorous decomposition). The colour in sulphuric acid solution was reddish violet.

(2) Since so much tarry matter was obtained by the above method, the method of Hodgson and Walker (J., 1933, 1620) for difficultly diazotisable amines was used subsequently.

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1 gm. 11-amino-benzanthrone (in 100 ml. glacial  
acetic acid)

0.5 gm. sodium nitrite

8 ml. concentrated sulphuric acid.

The solid sodium nitrite was added to the concentrated sulphuric acid with stirring at 0°C, the temperature being later raised to 70°C until the nitrite had dissolved, after which the solution was cooled to 0°C. The solution of the amine in glacial acetic acid was also cooled to 0°C and the resulting suspension added with stirring and in a thin stream to the nitrous acid mixture. The red solution was diluted with water to 800 ml. and the mixture boiled for one hour. The solid was filtered off, the yield being quantitative.

The insoluble residue after extraction with several quantities of dilute boiling caustic soda could not be purified and was not further examined (as in the previous experiment).

Acidification of the above alkaline extracts yielded 0.63 gm. (63% by weight of the starting material). This acidic material was a brown powder, m.p. 227-235°C similar

to that obtained before but much cleaner in appearance. Difficulty was experienced, however, in purifying the product but eventually a small quantity (0.11 gm.) of a solid (m. p. 249-251°C) was obtained. It crystallises from benzene as a bright yellow powder and as fine orange needles from alcohol; the latter sample was sent for analysis. The acidic material is readily soluble in organic solvents and dissolves in concentrated sulphuric acid to a crimson solution; the solution in alkali is carmine. Perkin (loc. cit.) appears to have encountered difficulties in purifying 4-hydroxy-benzanthrone for he quotes no melting-point for it and also states that "it is not readily crystallised" (J., 1920, 119, 698).

Analysis: found (Weiler) C 69.7%, H 3.3%

$C_{17}H_{10}O_2$  requires C 82.9%, H 4.0%.

It was discovered that the crude product gave a positive result in a sodium fusion test for the presence of nitrogen. The matter is discussed in the "discussion" section.

#### Methylation of the Crude Acidic Material

Owing to the large volume of solution involved, it was found undesirable to carry out the methylation using dimethyl sulphate and caustic soda solution. Accordingly the method adopted was to reflux the organic compound with dimethyl sulphate in xylene in the presence of anhydrous sodium carbonate.

- 1 gm. crude acidic product from the foregoing experiment (in 300 ml. xylene)
- 25 ml. dimethyl sulphate
- 10 gm. anhydrous sodium carbonate.

The above materials were refluxed for 5 hours and allowed to stand overnight. The xylene was distilled off in steam, a little sodium hydroxide added, the mixture boiled and filtered. Acidification of the filtrate gave 0.10 gm. of the starting material unchanged.

The alkali-insoluble residue (0.68 gm., about 65% methylation by weight) was inclined to be tarry. As in the case of the previous experiment, great difficulty was experienced in purifying the solid. After a tedious process using various solvents (in which the solubility is relatively large) it was found possible to isolate two different compounds. The less soluble was isolated as 0.11 gm. of greenish yellow needles (m.p. 269-274°C) from alcohol. The colour in concentrated sulphuric acid is red with faint violet fluorescence.

Analysis: found (Weiler) C 70.5%, H 4.1%.

The more soluble material was obtained as a bright yellow powder (0.08 gm.) of melting-point 152-4°C from alcohol or benzene. The solution in concentrated sulphuric acid was similar to the high melting product.

132.

Analysis: found (Weiler) C 78.6%, H 4.6%.

$C_{18}H_{12}O_2$  requires C 83.1%, H 4.6%.

No nitrogen could be detected in either case by a sodium fusion.

## SEMI-MICRO METHOD FOR THE DETERMINATION OF HALOGEN IN ORGANIC COMPOUNDS.

Reference: Hein, Hoyer and Clar, Zeit. für Anal. Chem., 1928, 75, 160.

General. The organic compound is heated with sodium peroxide and the halogen determined by reduction and volumetric estimation of the halide by Volhard's method.

Reagents required.

- (1) Sodium peroxide A.R.
- (2) Concentrated nitric acid
- (3) Sulphurous acid solution
- (4) 3% Hydrogen peroxide solution
- (5) Standard solutions of silver nitrate and ammonium thiocyanate, 0.02N.
- (6) Ferric indicator solution.

Procedure. Weigh out accurately about 40 to 50 mgm. of the substance in a glass scoop and cover it with 2 gms. of sodium peroxide. Carefully sweep the mixture into the dry steel bomb and thoroughly mix with a finely pointed glass rod. Weigh out a further 2 gms. of sodium peroxide in the scoop and transfer it to the bomb to form a covering layer. Screw the top of the bomb on firmly and heat it, gently at first and then for ten minutes in the full Bunsen flame. Partially unscrew the top of the bomb while it is still hot and place the bomb in cold water. Wash the outside of the bomb and place it in a 600 ml. beaker. Unscrew the top and wash its underside with hot water, allowing the washings to fall into the beaker. Place a clock-glass on the beaker and blow water from a wash-bottle into the bomb. When the violent reaction has subsided, wash down the clock-glass and sides of the beaker. Grasp the bomb firmly and wash it thoroughly inside and out with hot water.

Make the contents of the beaker definitely acid with concentrated nitric acid (about 7-8 c.c.), add 2 c.c. of sulphurous acid solution and digest the solution on the water-bath or over a very small flame for about an hour. Add 3% hydrogen peroxide solution (this may be made up from 30% A. R. solution) drop by drop until the smell of sulphur dioxide disappears (2 or 3 drops should always be added as precaution against the presence of traces of sulphite) and then 3 c.c. of concentrated nitric acid. The solution is then transferred to a conical flask, cooled to room-temperature and a measured excess of standard silver nitrate added. Add a few c.c. of ether and shake to coagulate the silver halide. Back-titrate with ammonium thiocyanate using ferric indicator solution. The usual precautions must be exercised in the case of chloride and iodide.

A blank determination must be performed on the sodium peroxide, using the same quantities of the other reagents.

Example. Silver nitrate, standardised with KBr, 1 c.c. = 0.001589 g. Br.  
Ammonium thiocyanate, 23.75 c.c. = 25 c.c. silver nitrate.  
Blank determination: 25 c.c. silver nitrate; back-titration 23.2 c.c. i.e. 0.55 c.c. thiocyanate, corresponding to 0.58 c.c. silver nitrate are to be allowed for, leaving 24.42 c.c. silver nitrate.

0.0473 gm. of compound, 25 c.c. silver nitrate, back-titration 11.55 c.c.

Volume of silver nitrate used =  $24.42 - \frac{11.55 \times 25}{23.75} = 12.26$  cc.

% Br =  $\frac{12.26 \times 0.01589}{0.0473}$

.0473

S U M M A R Y.

The amide of 11-carboxy-benzanthrone has been prepared by way of the acid chloride using phosphorus pentachloride followed by treatment with strong aqueous ammonia. It was found that the amide could not be prepared simply by heating the ammonium salt as this treatment led to dissociation into ammonia and the free carboxylic acid; this appears to be a not uncommon phenomenon among complex organic acids.

An examination of the behaviour of the amide on oxidation yielded some unusual results. Oxidation to the dibenzanthrone derivative by fusion with alkali was found to occur only at high temperatures, the process appearing to stop at the dibenzanthronyl stage if the temperature of fusion was below 360°C. Fusion of the amide itself, even in absence of alkali, appears to yield a similar product of the dibenzanthronyl type. Prolonged treatment with moderately concentrated sulphuric acid or with bromine in nitrobenzene leads to the formation of a



compound which is assumed to be the lactam of 1-amino-11-carboxy-benzanthrone. The latter reaction appears to be analogous to the oxidation of the parent acid to the lactone of 1-hydroxy-11-carboxy-benzanthrone which may be effected by use of bromine in nitrobenzene. The lactone itself was obtained from the amide by oxidation with chromic acid, hydrolysis presumably first occurring. A small quantity of the lactone was also isolated by the prolonged treatment with moderately concentrated sulphuric acid already mentioned.

Identification of these complex oxidation products of the amide has been rendered difficult owing to their insolubility and lack of determinable melting-point. The analysis figures are difficult to obtain with accuracy and do not give much information as to slight variations in composition.

Owing to initial failure to condense aceto- $\beta$ -naphthalide with oxalyl-bis-phenyl-imido-chloride in presence of aluminium chloride, it has not been found possible to synthesise the lactam of 1-amino-11-carboxy-benzanthrone. Had this been achieved it would have helped in the identification of the oxidation product of the amide.

The oxime of 1-11-keto-benzanthrone has been shown to form readily but some difficulty was encountered in the purification of the crude product. During the latter process and in an attempt to isolate the two

possible isomeric forms of benzanthrone-1-11-ketoxime it was found that under the influence of animal charcoal in boiling nitrobenzene, the oxime underwent hydrolysis to the ketone, which led to the deposition of an unexpected molecular compound of 1-11-keto-benzanthrone and nitrobenzene.

The behaviour of the oxime to Beckmann reagents has been examined. Treatment with benzene sulphonic chloride in pyridine solution and with concentrated sulphuric acid at 100°C had no effect; extensive sulphonation occurred at high temperatures in the latter case. Fusion with zinc chloride at 280°C has been shown to bring about hydrolysis: this action is in contrast to the case of fluorenone oxime which was converted to phenanthridone in the above manner by Pictet and Patry. The Beckmann change was successfully brought about on the oxime of 1-11-keto-benzanthrone through the agency of phosphorus pentachloride in anisole solution. The anthridone isolated is assigned the structure of the lactam of 11-amino-1-carboxy-benzanthrone as it differs from the compound obtained by treating the amide of 11-carboxy-benzanthrone with bromine in nitrobenzene (assumed to be the isomeric lactam). This anthridone is identical with the product from the action of hydrazoic acid on 1-11-keto-benzanthrone. On alkaline fusion it gave an almost quantitative yield of the dibenzanthrone derivative. A synthesis of the lactam of 11-amino-1-carboxy-

benzanthrone was attempted by carrying out an Ullmann reaction between methyl 3-nitro-2-iodo-benzoate and methyl 1-bromo-2-naphthoate; unfortunately no 11-nitro-1-carboxy-benzanthrone could be isolated by sulphuric acid cyclisation of the mixed esters.

Hydrazoic acid treatment of 11-carboxy-benzanthrone has been shown to yield 11-amino-benzanthrone in good yield. This amino-compound has been characterised by the preparation of the formylamino- and acetylamino-derivatives. When fused with alkali the amine readily gave a diamino-dibenzanthrone.

Attempts to prepare the 11-hydroxy- and 11-methoxy-benzanthrones by diazotisation of the amine followed by methylation have failed to give pure specimens of these compounds, although the products obtained have the expected properties.

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