The CHEMISTRY OF 1:11-KETOBENZANTHRONE

And The RELATED CARBOXYLIC ACIDS.

By

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Thesis submitted for the degree of Ph.D.

May 1936. University of Edinburgh.

This is to certify that Mr JOHN L. GRIEVE, candidate for the degree of Ph.D., successfully sustained an oral examination on the subject of his thesis, by a committee of the department, on 16 March, 1936.

Chairman of Committee.

1 May, 1936.

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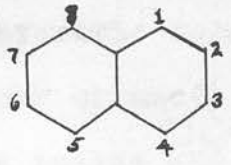
INTRODUCTION

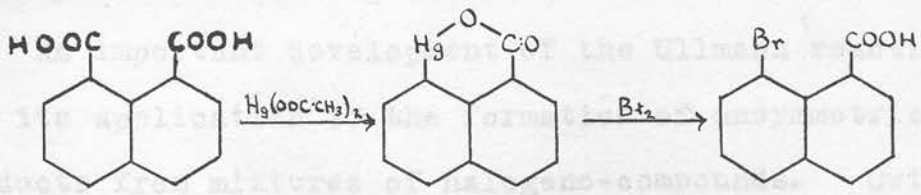
Of the substitution derivatives of naphthalene, the peri-compounds, or those with substituents in the 1:8- (or 4:5-) positions, are of particular importance, having no exact analogues in the benzene series.



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, many of them are readily accessible and have been employed in some remarkable syntheses of more complex compounds.

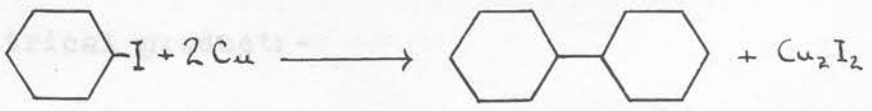
Amongst these peri-derivatives, the 8-halogeno-1-naphthoic acids have attracted special attention during the last few years. The recent mercuration

method of Whitmore and co-workers (J. A. C. S., 1929, 51, 1831, 3363) has proved a satisfactory source of the acids and has been employed with marked success by Rule and co-workers (J., 1934, 170). The method consists in mercurating naphthalic acid by means of mercuric acetate to give anhydro-8-hydroxymercuri-1-naphthoic acid which, on treatment with bromine (or chlorine), yields the halogeno-acid.



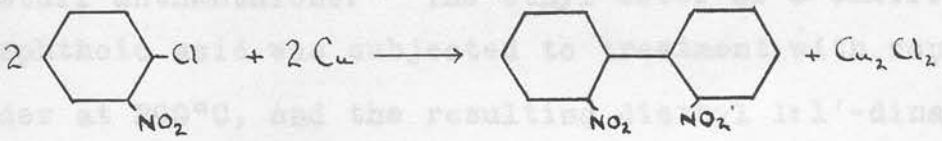
A reaction which has been applied with outstanding results to compounds of this last type is the Ullmann reaction. Discovered by Ullmann in 1900 (Ber., 1901, 34, 2174; Ann., 1904, 332, 38), it consists in heating halogenated aromatic compounds with finely divided copper ("copper bronze") whereby halogen is eliminated as cuprous halide and a dinuclear product results.

It was found by Ullmann that the reaction proceeded smoothly with almost all iodo-compounds. For example, diphenyl was formed by heating iodobenzene with copper powder at 230°C in a sealed tube.



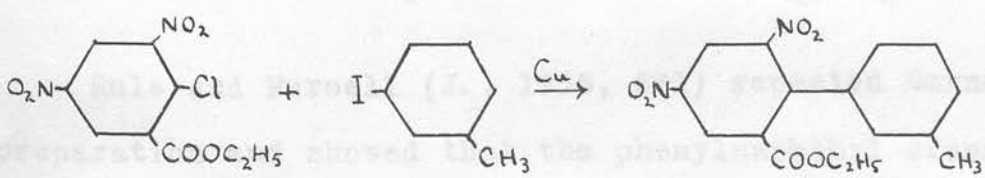
Corresponding bromo- and chloro-compounds, however, were found to react only when an increased lability was

conferred upon the halogen by the presence of other substituents in certain positions. Thus, while m- and p-nitrochlorobenzene were unreactive, the o-nitro-compound reacted readily to give 2:2'-dinitrodiphenyl.

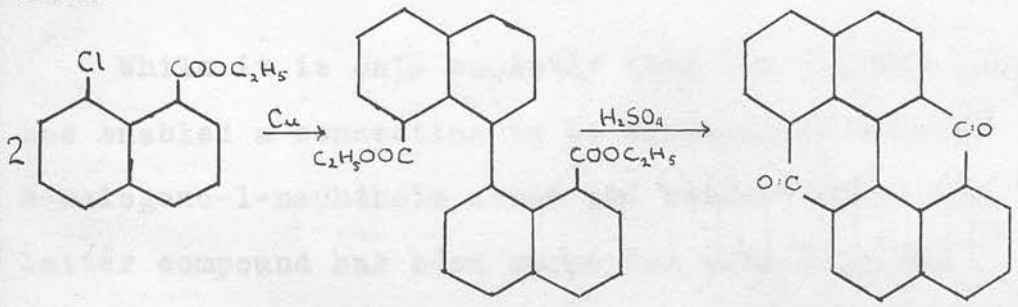


A similar type of activation also appears to be conferred upon the halogen by a carboxyl group in the ortho-position.

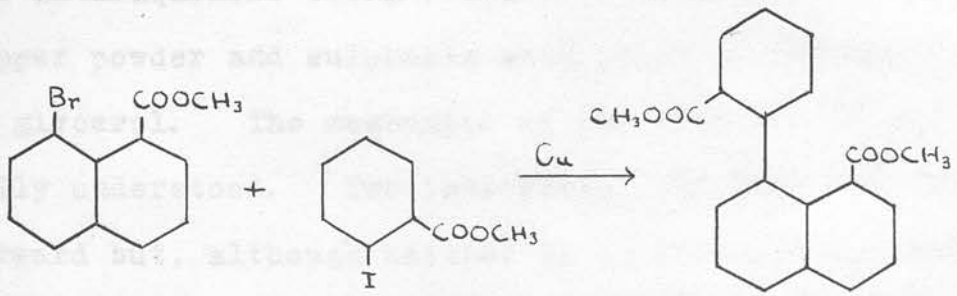
An important development of the Ullmann reaction was its application to the formation of unsymmetrical products from mixtures of halogeno-compounds. Owing partly to the interest in certain unsymmetrical diphenyls with respect to their optical activity, this modification of the reaction has been employed extensively in recent years. Turner and co-workers have shown that the yield of unsymmetrical product is surprisingly large in many instances. For example, Lesslie and Turner (J., 1930, 1785) state that, when equimolecular quantities of ethyl 2-chloro-3:5-dinitrobenzoate and an aromatic iodo-compound are heated together in the presence of copper powder, ethyl 2:4-dinitrodiphenyl-6-carboxylates alone are formed. In this manner, m-iodotoluene gives a 68% yield of the unsymmetrical product:-



The Ullmann reaction was first applied to 8-halogeno-1-naphthoic acids, in the form of their esters, by Kalb (Ber., 1914, 47, 1724) 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:-

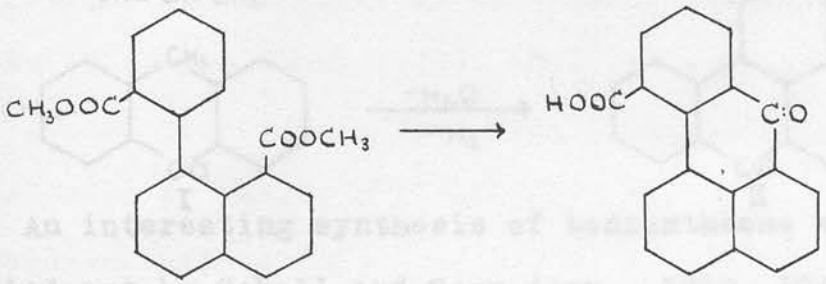


From their investigations, Rule and Barnett (J., 1932, 2728) concluded that the halogens in methyl 8-bromo-1- naphthoate and methyl o-iodobenzoate were comparable in reactivity. Barnett (Thesis, Edinburgh, 1932) carried out the Ullmann reaction with these two compounds and obtained at 190-200°C a 45% yield of methyl 8-(o-carbomethoxyphenyl)-1-naphthoate.



Rule and Pursell (J., 1935, 571) repeated Barnett's preparation and showed that the phenylnaphthyl dicar-

boxylate was converted quantitatively to a benzanthrone carboxylic acid by the action of concentrated sulphuric acid.

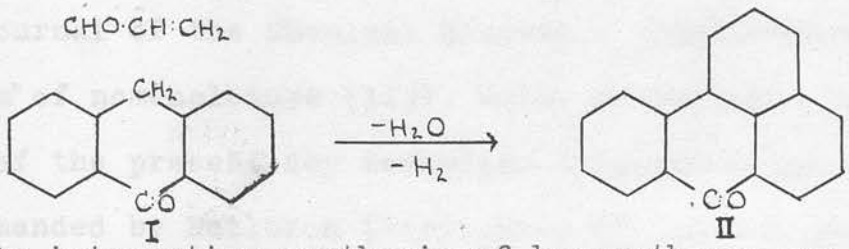


Benzanthrone

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

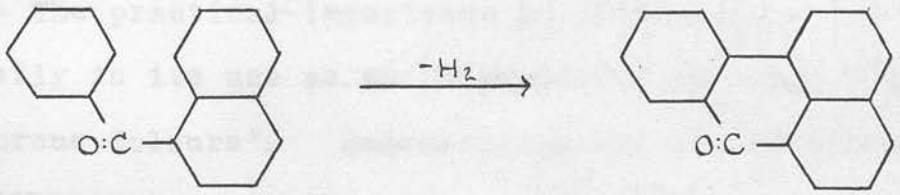
Discovered by Bally (Ber., 1905, 38, 194) during the course of his investigations on the Skraup reaction with substituted anthraquinones, benzanthrone was originally prepared by heating anthraquinone with glycerol and sulphuric acid in the presence of a reducing agent. In modern practice, this method is modified somewhat, the anthraquinone being reduced to anthrone by means of copper powder and sulphuric acid prior to the addition of glycerol. The mechanism of the reaction is not fully understood. Two interpretations have been put forward but, although neither is in complete agreement with experimental evidence, there is no doubt that the reaction involves a condensation between anthrone (I) and acrolein (formed from the glycerol and acid),

followed by loss of water and hydrogen to yield benzanthrone (II).

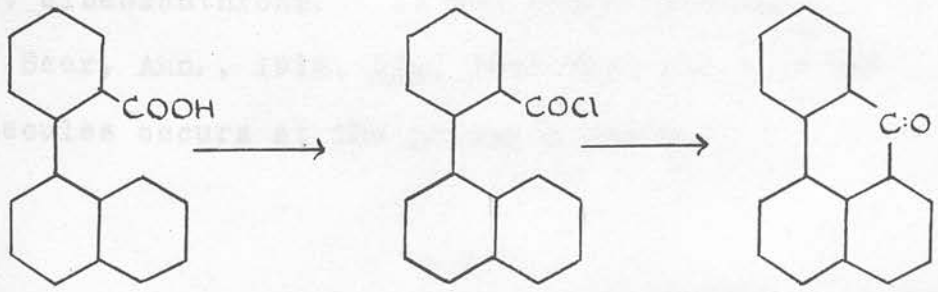


I II

An interesting synthesis of benzanthrone was carried out by Scholl and Seer (Ann., 1912, 394, 111) and the method has been applied to the preparation of various substituted derivatives. It consists in "baking" α-benzoylnaphthalenes with aluminium chloride, a process of aerial oxidation.

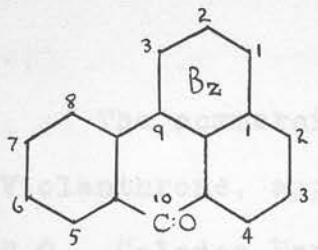


Another synthesis of benzanthrone, due to Schaarschmidt (Ber., 1918, 51, 1082), leaves no doubt as to its structure. This involved the preparation of ortho-1-naphthylbenzoic acid, the acid chloride of which is converted quantitatively into benzanthrone by treatment with aluminium chloride.



The systematic numbering of benzanthrone and its derivatives is somewhat confusing. The systems for-

merly 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 System" of nomenclature (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.



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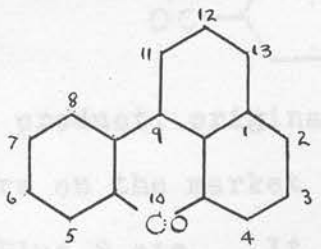
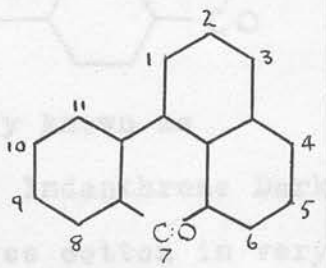
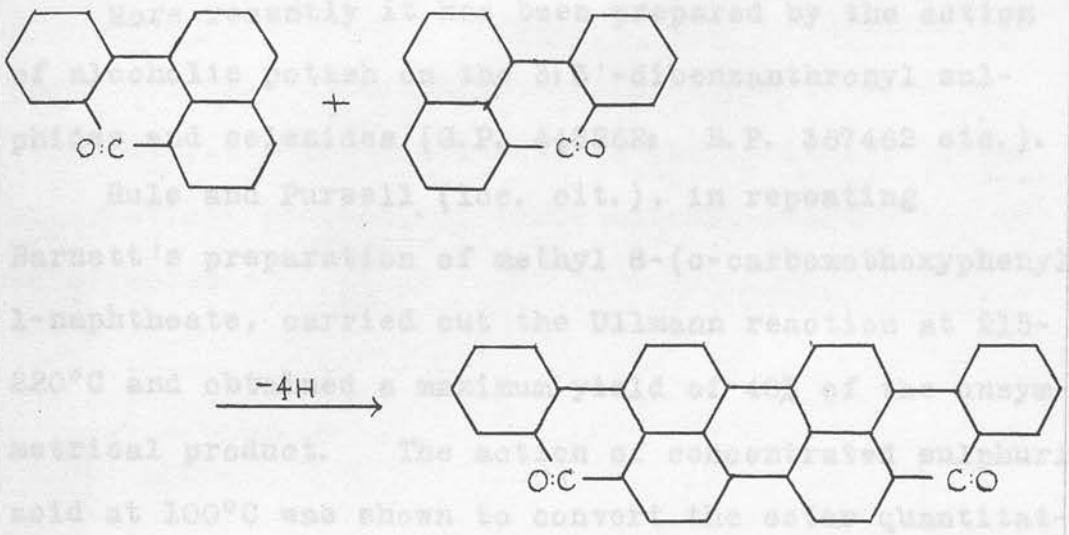


II



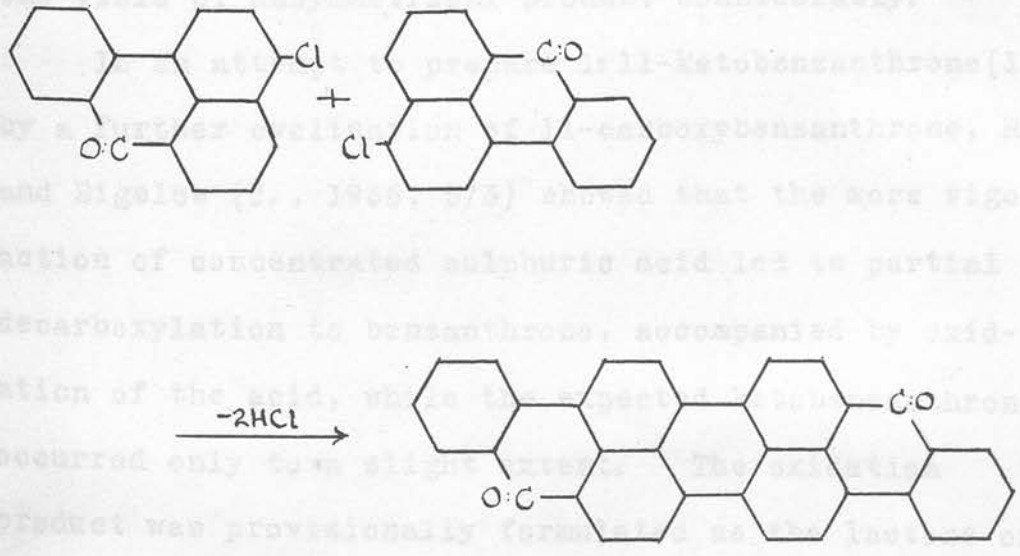
III

The practical importance of benzanthrone lies chiefly in its use as an intermediate for the "Benzanthrone Colours". Benzanthrone and its substituted derivatives are not highly coloured compounds and have found no use as vat dyes. Indeed, it is questionable whether they form true vats with alkaline hydrosulphite. Bally, the discoverer of benzanthrone, found, however, (Ber., 1905, 38, 195; G.P. 185221) that fusion with caustic alkali at 230-240°C produced 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 the points 3 and 4.



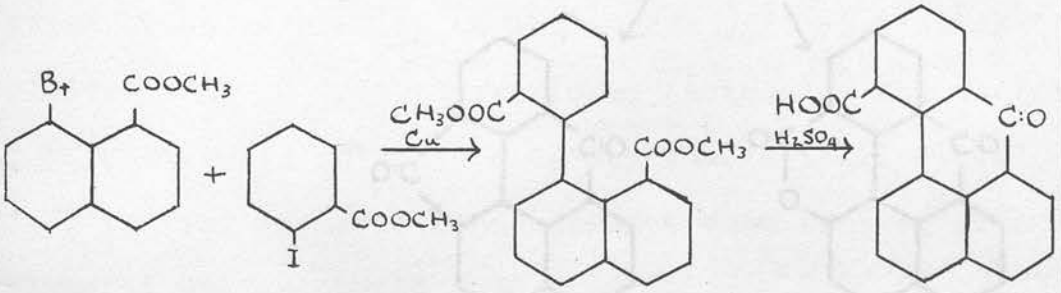
The commercial product, originally known as Violanthrone, appears on the market as Indanthrene Dark Blue B.O., Caledon Dark Blue B etc. It dyes cotton in very fast dark-blue shades from a red-violet hydrosulphite vat.

A second class of dyes has as its parent compound isodibenzanthrone, the symmetrical isomeride of dibenzanthrone. It is also known as Isoviolanthrone and was originally prepared (G.P. 194252) by the action of alcoholic potash on 3-chlorobenzanthrone.



More recently it has been prepared by the action of alcoholic potash on the 3:3'-dibenzanthronyl sulphides and selenides (G.P. 448262; B.P. 367462 etc.).

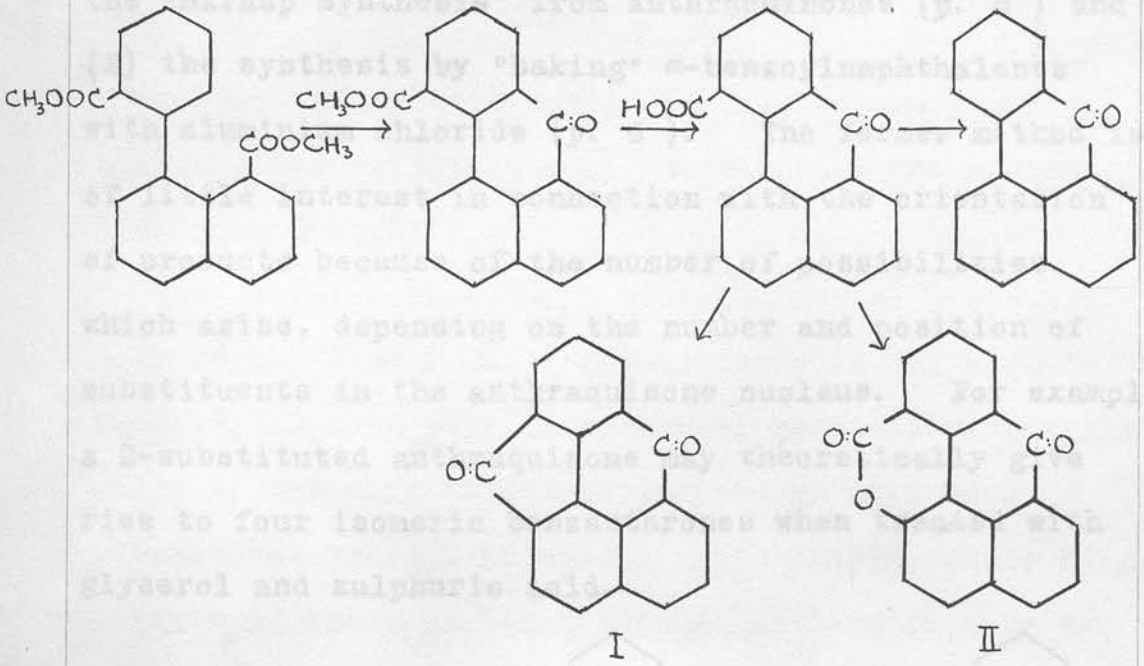
Rule and Pursell (loc. cit.), in repeating Barnett's preparation of methyl 8-(o-carbomethoxyphenyl)-1-naphthoate, carried out the Ullmann reaction at 215-220°C and obtained a maximum yield of 40% of the unsymmetrical product. The action of concentrated sulphuric acid at 100°C was shown to convert the ester quantitatively into 11-carboxybenzanthrone.



The preparation has since been examined more thoroughly and, by carrying out the Ullmann reaction at a lower temperature and employing excess of the iodobenzoate, F.R. Smith (Thesis, Edinburgh, 1935) has increased the yield of unsymmetrical product considerably.

In an attempt to prepare 1:11-ketobenzanthrone(I) by a further cyclisation of 11-carboxybenzanthrone, Rule and Bigelow (J., 1935, 573) showed that the more vigorous action of concentrated sulphuric acid led to partial decarboxylation to benzanthrone, accompanied by oxidation of the acid, while the expected ketobenzanthrone occurred only to a slight extent. The oxidation product was provisionally formulated as the lactone of

1-hydroxy-11-carboxybenzanthrone (II). Treatment of the phenylnaphthyl dicarboxylate with sulphuric acid at temperatures below 100°C allowed the isolation of the intermediate product, 11-carbomethoxybenzanthrone, to be effected.



I II

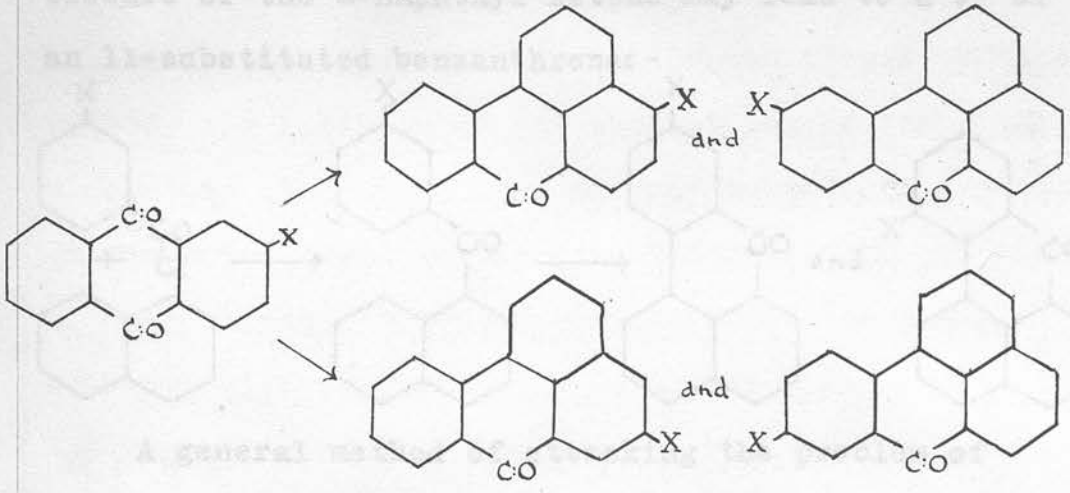
1:11-Ketobenzanthrone was, however, found to be readily prepared by the action of phosphorus pentoxide on a solution of the 11-carboxybenzanthrone in molten phthalic anhydride at 200°C. It is a stable orange-yellow compound, possessing no strong dyeing properties.

This synthetic method of approach to the benzanthrone series was employed (F.R. Smith, loc. cit.) in the preparation of various derivatives and has proved valuable in the problem of orientation of substituted benzanthrones.

The two general methods available for the orientation of substitution derivatives of a parent compound,

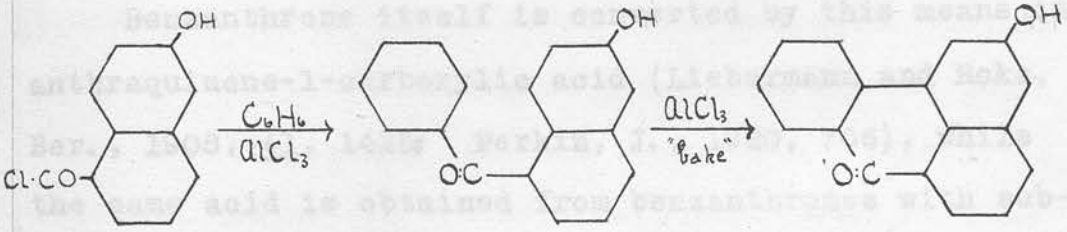
namely graduated synthesis, and degradation to known products, are both applicable to a certain extent in the benzanthrone series.

Two synthetic methods have commonly been employed for the preparation of benzanthrones. These are (1) the "Skraup Synthesis" from anthraquinones (p. 5) and (2) the synthesis by "baking" α-benzoylnaphthalenes with aluminium chloride (p. 6). The former method is of little interest in connection with the orientation of products because of the number of possibilities which arise, depending on the number and position of substituents in the anthraquinone nucleus. For example, a 2-substituted anthraquinone may theoretically give rise to four isomeric benzanthrones when treated with glycerol and sulphuric acid.



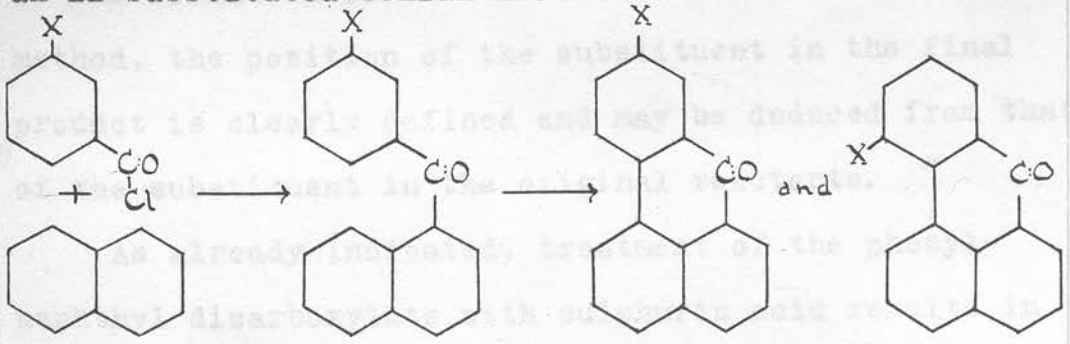
From the point of view of orientation, however, the second synthetic method is much more important, and in many cases the position of the substituent is clearly defined. The synthesis of 2-hydroxybenzanthrone (M.L.B., 1923, D.P. 413738) may be given as an example.

6-Hydroxy-1-naphthoyl chloride is converted to the benzoyl derivative, which, on baking with aluminium chloride, yields the benzanthrone:



When the substituent is in the benzene nucleus, however, the orientation of the benzanthrone may not always be predicted.

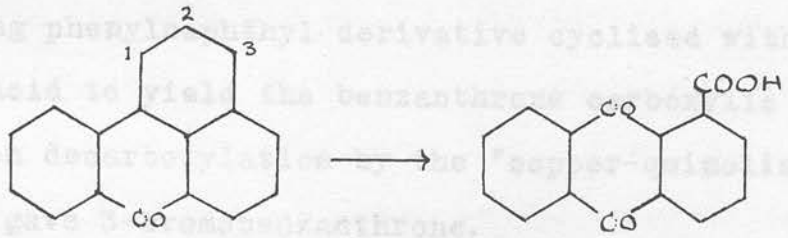
Alternatively, benzoyl chloride may be condensed with naphthalene. With substituents in the naphthalene nucleus, in this case, a number of possibilities again arise. The same objection is present when meta-substituted benzoyl chlorides are employed, since ring-closure of the α-naphthyl ketone may lead to a 9- or an 11-substituted benzanthrone:-



A general method of attacking the problem of orientation of substituted benzanthrones is one involving an oxidation to derivatives of anthraquinone, a degradation which has proved fruitful in establishing the constitution of a number of products. Oxidation may be conveniently carried out by means of chromic

acid, which converts benzanthrones to anthraquinone-1-carboxylic acid or its derivatives, many of which are known or can be synthesised.

Benzanthrone itself is converted by this means into anthraquinone-1-carboxylic acid (Liebermann and Roka, Ber., 1908, 41, 1425; Perkin, J., 1920, 706), while the same acid is obtained from benzanthrones with substituents in the benz-nucleus, i.e. in positions 1, 2 and 3.

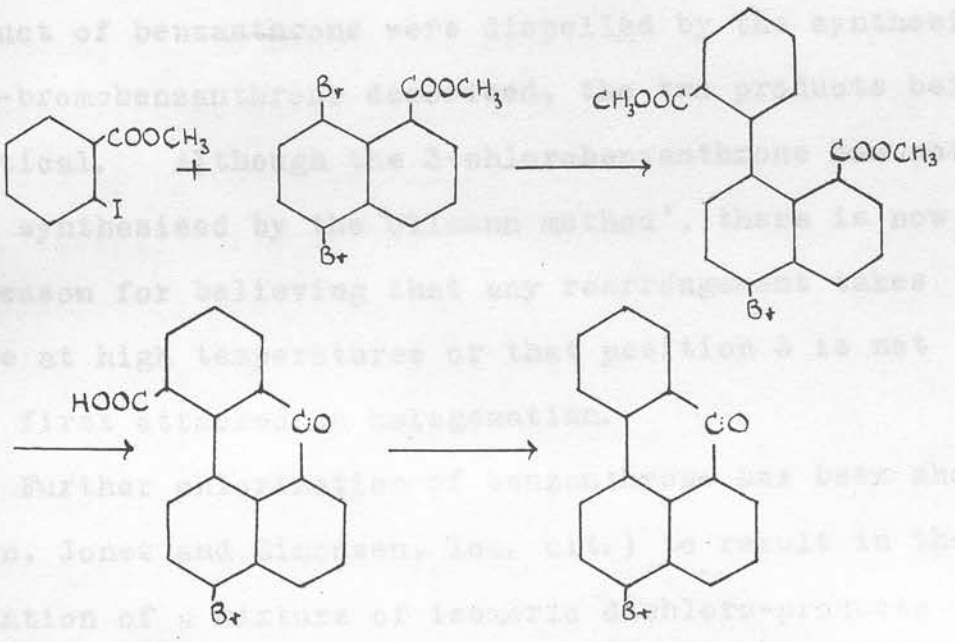


The synthetic preparation of benzanthrones, due to Rule and co-workers (loc. cit.), was a valuable addition to these orientation methods, since it is free from any of the uncertainty characterising the above syntheses. In the formation of substituted benzanthrones by this method, the position of the substituent in the final product is clearly defined and may be deduced from that of the substituent in the original reactants.

As already indicated, treatment of the phenyl-naphthyl dicarboxylate with sulphuric acid results in the formation of a benzanthrone system having the carboxyl group derived from the benzoate in position 11. For the preparation of benzanthrones containing no carboxyl group, the acids may be decarboxylated conveniently by the action of copper bronze in boiling quinoline (Hurtley, J., 1929, 1870; Shephard, Winslaw

and Johnson, J.A.C.S., 1930, 2084; Davies, Heilbron and Irving, J., 1932, 2715).

As an example of the application of the "Ullmann Synthesis" to the formation of substituted benzanthrones, the preparation of 3-bromobenzanthrone (F.R. Smith, loc. cit.) may be given. In this case, methyl o-iodobenzoate and methyl 5:8-dibromo-1-naphthoate were subjected to treatment with copper powder and the resulting phenylnaphthyl derivative cyclised with sulphuric acid to yield the benzanthrone carboxylic acid which, on decarboxylation by the "copper-quinoline" method, gave 3-bromobenzanthrone.



Substitution of benzanthrone

Direct halogenation of benzanthrone in glacial acetic acid solution, or in aqueous suspension (B.A.S.F., D.P. 193959; C., 1908, I, 1112), yields the 3-halogeno-derivatives. Proof of the orientation of the products formerly rested on (1) oxidation to halogen-free anthra-

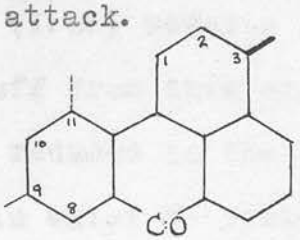
quinone-1-carboxylic acid, which established that the halogen was situated in the benz-nucleus, and (2) the formation of isodibenzanthrone by elimination of two molecules of hydrogen halide on treatment with alkali. While the latter could only occur if the halogen did actually occupy the 3-position, Cahn, Jones and Simonsen (J., 1933, 444) hold that this argument is inconclusive owing to (a) the great mobility of halogens attached to the benz-nucleus of benzanthrone and (b) the peculiar tautomerism of benzoyldinaphthyls reported by Luttringhaus and Neresheimer (Ann., 1929. 473, 259).

Doubts as to the structure of the bromination product of benzanthrone were dispelled by the synthesis of 3-bromobenzanthrone described, the two products being identical. Although the 3-chlorobenzanthrone has not been synthesised by the "Ullmann method", there is now no reason for believing that any rearrangement takes place at high temperatures or that position 3 is not that first attacked on halogenation.

Further chlorination of benzanthrone has been shown (Cahn, Jones and Simonsen, loc. cit.) to result in the formation of a mixture of isomeric dichloro-products to which the constitution of 3:9- and 3:11-dichlorobenzanthrones can be assigned. Dibromination, however, would appear to give a homogeneous product which has been designated as the 3:9-dibromo-derivative (B.A.S.F., 1908, D.P. 193959). That this formulation is correct was proved by means of an "Ullmann synthesis" of 3:9-dibromobenzanthrone, in this case employing methyl 2-iodo-

5-bromobenzoate and methyl 5:8-dibromo-1-naphthoate (F.R. Smith, loc. cit.).

Although halogenation of benzanthrone takes place primarily in the 3-position, it is evident, therefore, that position 9 and, to a less extent, position 11 are also open to attack.



Halogenation.

It has been established (cf. Martinet and Drobatscheff, Chem. et Ind., 1929, 21, 227) that two mono-nitration products of benzanthrone may be formed, depending on the conditions of nitration employed. In nitrobenzene at 40-50°C, a nitrobenzanthrone melting at 248-9°C is produced (B.A.S.F., Addn. no. 6435 to F.P. 349531), while nitration in boiling glacial acetic acid solution yields an isomeric product melting at 305-7°C. In sulphuric acid solution, a mixture of the two isomerides is said to be produced.

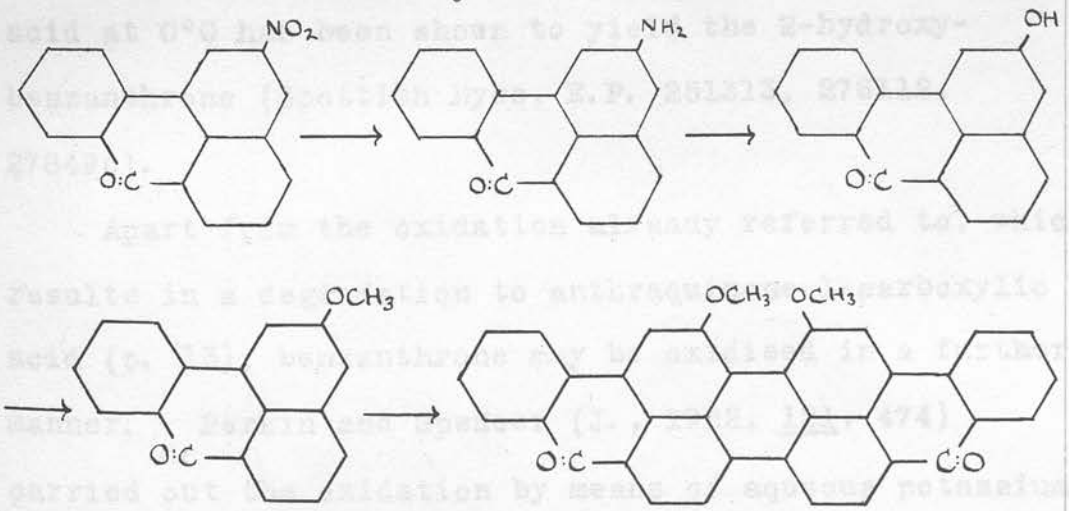
The lower-melting nitration product has been designated as the 3-nitrobenzanthrone and confirmation of the structure has been obtained, amongst other methods, by an "Ullmann synthesis" employing methyl o-iodobenzoate and methyl 5-nitro-8-bromo-1-naphthoate (F.R. Smith, loc. cit.).

The second nitration product, melting at 305-7°C, was believed for some time to have the nitro-group in position 9 (Martinet and Drobatscheff, loc. cit.).

Recently, however, it has been established that the compound is 2-nitrobenzanthrone.

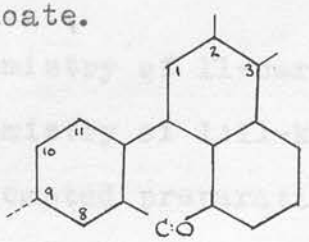
Proof of the structure of this product has not been arrived at by any of the normal orientation methods applicable to benzanthrones.

B.P. 278651 (I.G.) reports the formation of a jade-green dyestuff from this nitrobenzanthrone. The latter was first reduced to the amine, which was diazotised and boiled in water to yield the hydroxybenzanthrone. Methylation, followed by fusion with alkali produced the dimethoxydibenzanthrone, which, by comparison with the synthetic dyestuff of B.P. 218255 (M.L.B.) can be assigned the constitution of 2:2'-dimethoxy-3:3':4:4'-dibenzanthrone. The original nitro-group must, therefore, have occupied the 2-position, and the stages of its conversion to the dyestuff are briefly as follows:-



Further nitration of 3-nitrobenzanthrone or dinitration of benzanthrone in nitric acid solution yields a dinitro-product for which the constitution of 3:9-dinitrobenzanthrone has been suggested. This

suggestion has been substantiated by the formation of the same dinitro-compound by further nitration of the 9-nitrobenzanthrone, the latter having been synthesised by F.R. Smith (loc. cit.) by applying the Ullmann reaction to methyl 2-iodo-5-nitrobenzoate and methyl 8-bromo-1-naphthoate.



Nitration.

Although positions 3 and 9 are attacked on nitration as on halogenation, the formation of 2-nitrobenzanthrone in glacial acetic acid solution appears as an exception to the normal rule of substitution in benzanthrone.

Position 2, however, is not attacked only by nitric acid, for oxidation with manganese dioxide in sulphuric acid at 0°C has been shown to yield the 2-hydroxybenzanthrone (Scottish Dyes, E.P. 251313, 278112, 278496).

Apart from the oxidation already referred to, which results in a degradation to anthraquinone-1-carboxylic acid (p. 13), benzanthrone may be oxidised in a further manner. Perkin and Spencer (J., 1922, 121, 474) carried out the oxidation by means of aqueous potassium hydroxide and potassium chlorate in the presence of anthraquinone at about 250°C, the main product being 4-hydroxybenzanthrone.

The behaviour of the benzanthrone molecule on

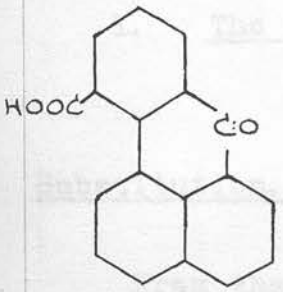
substitution can therefore only be described as irregular.

The work described in the present thesis falls into three parts:

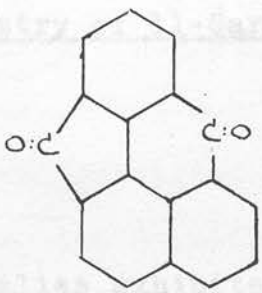
(a) the chemistry of 11-carboxybenzanthrone (I)

(b) the chemistry of 1:11-ketobenzanthrone (II)

and (c) the attempted preparation of 1-carboxybenzanthrone (III) and a summary examination of its chemistry.



I



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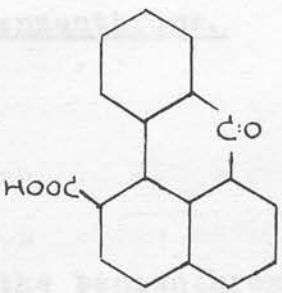


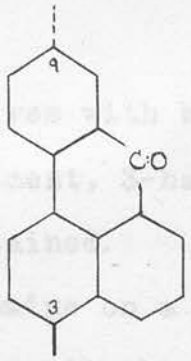
III

SUMMARY OF EXPERIMENTAL WORK AND DISCUSSION OF RESULTS.

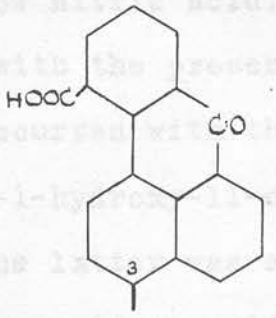
I. The Chemistry of 11-Carboxybenzanthrone.

Substitution.

From the anomalies exhibited by the benzanthrone molecule on substitution, there emerges the fact that position 3 is the most reactive of the system. A consideration of the structure of the molecule shows that this is not an unexpected result for, apart from the fact that it is situated in the only ring-system which does not contain a chromophore tending to prevent substitution, the position may be regarded as related alternatively to an α-naphthalene or a 4-diphenyl position, each the most reactive in the corresponding system.



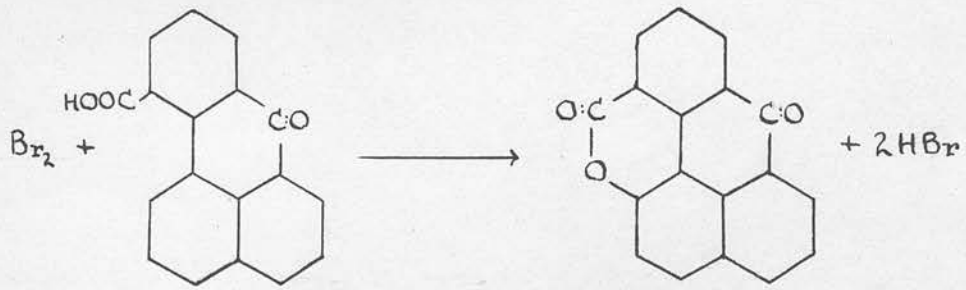
The general effect of the introduction of a carboxyl group into the 11-position may to a certain extent be predicted, in as much as it is a group whose presence in an aromatic nucleus tends to prohibit further substitution. It might be expected, for instance, that 11-carboxybenzanthrone would be more resistant to reagents than the parent compound but that position 3 would still be primarily attacked on halogenation and nitration. A second substituent, however, would not be expected to enter the 9-position, as is the case with benzanthrone itself, since the ring-system containing this position has now two carbonyl groups attached.



The behaviour of 11-carboxybenzanthrone towards halogen and nitric acid was examined in the present work and the results of the examination were in agreement with these considerations. It was found that the acid was not attacked by halogen under conditions which yield

3-substituted derivatives with benzanthrone but that, on more vigorous treatment, 3-halogeno-11-carboxybenzanthrones were obtained.

The action of bromine on a solution of 11-carboxybenzanthrone in boiling nitrobenzene gave a somewhat unexpected result, the acid being oxidised to the lactone of 1-hydroxy-11-carboxybenzanthrone (see p. 24) with evolution of hydrogen bromide.

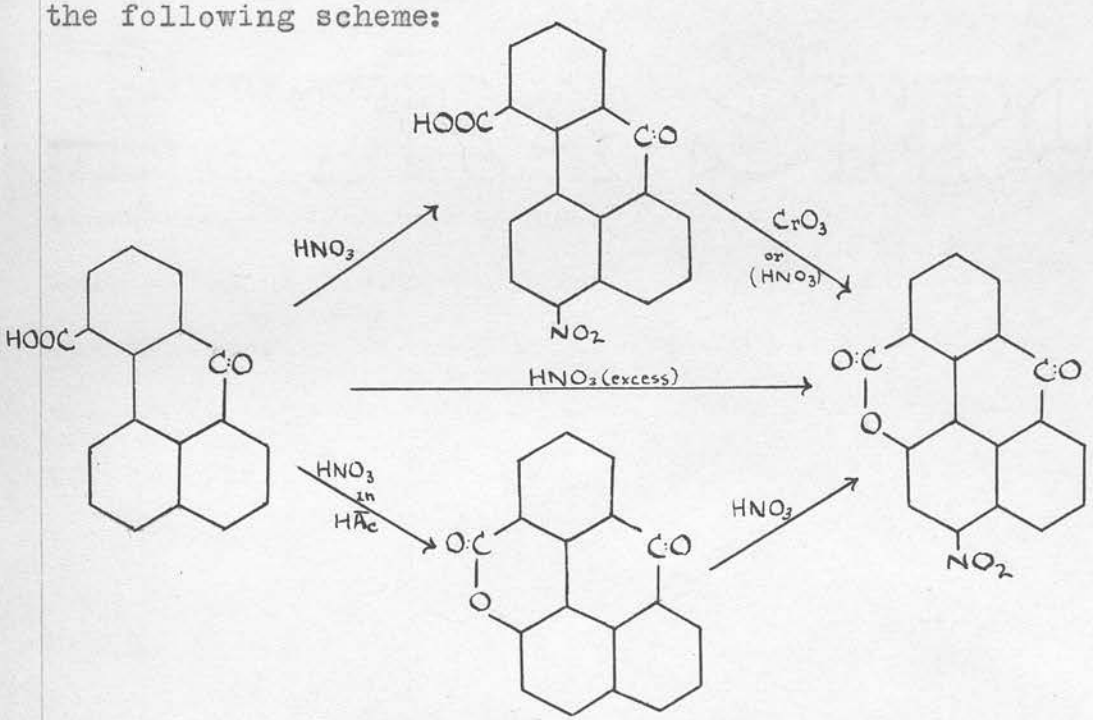


Treatment with nitric acid under various conditions was found to bring about some interesting reactions. A solution of 11-carboxybenzanthrone in concentrated sulphuric acid at 0°C yielded, on treatment with the calculated amount of nitric acid, 3-nitro-11-carboxybenzanthrone, but with the presence of excess reagent a further reaction occurred with the formation of the lactone of 3-nitro-1-hydroxy-11-carboxybenzanthrone. The structure of the latter was shown by its formation (a) from the 3-nitro-acid on oxidation with chromic acid and (b) from the unsubstituted lactone on treatment with excess nitric acid.

Perhaps the most interesting result arising from the study of the action of nitric acid on 11-carboxy-

benzanthrone was the formation of the unsubstituted lactone when glacial acetic acid was employed as solvent. Under the conditions in which this reaction took place, benzanthrone itself yields the 2-nitro-derivative and it might have been expected that the lactone, containing what is virtually a hydroxyl group in the adjacent 1-position, would nitrate the more readily in position 2. Oxidation alone appeared to take place, however, the entrance of a nitro-group into the molecule apparently being inhibited by the presence of the acetic acid.

The reactions with nitric acid are summarised in the following scheme:



Apart from the side-reactions which occurred, apparently owing to the ease of formation of the lactone-ring, the substitution of 11-carboxybenzanthrone was found to follow the expected course in that 3-substituted derivatives alone were formed. In no case was

there evidence of a second substituent entering the molecule even under vigorous conditions of treatment.

The substituted benzanthrone carboxylic acids, of which the 3-chloro-11-carboxybenzanthrone was previously unknown, are all yellow crystalline compounds of high melting point. They dissolve in sulphuric acid with a blood-red colouration and in aqueous alkali give yellow solutions.

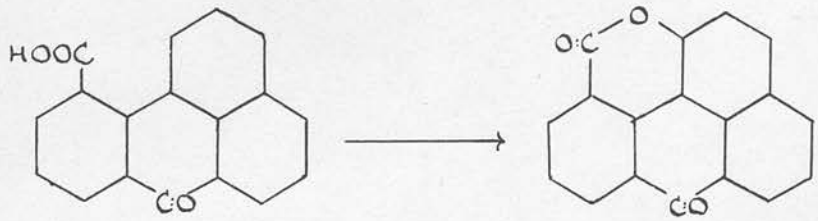
Orientation of the substitution products was simplified by the fact that the 3-bromo- and 3-nitro-11-carboxybenzanthrones had already been synthesised by the Ullmann reaction in these laboratories (F.R. Smith, Thesis, Edinburgh, 1935). A comparison of properties and mixed melting points with specimens of these compounds was sufficient to identify the products. In the case of the 3-chloro-derivative, however, orientation was effected by decarboxylation to the chlorobenzanthrone and identification of the latter with the product of direct halogenation of benzanthrone.

Oxidation.

a) The lactone of 1-hydroxy-11-carboxybenzanthrone.

In an examination of the behaviour of 11-carboxybenzanthrone towards concentrated sulphuric acid at high temperatures, Rule and Bigelow (J., 1935, 573) observed the formation of a high-melting compound for

which the structure of the lactone of 1-hydroxy-11-carboxybenzanthrone was suggested. That it was actually an oxidation product was shown by its formation from the 11-acid on treatment with chromic acid under conditions which normally lead to the oxidation of benzanthrones to anthraquinone-1-carboxylic acids.



Although the compound reacted in the expected manner with alkalis, it proved very resistant to methylation, treatment with dimethyl sulphate or with silver oxide and methyl iodide leaving it unchanged. Perkin and Bradshaw, however, record (J., 1922, 121, 911) that difficulty was experienced in methylating the lactone of 4-hydroxy-3-carboxybenzanthrone (formed by the action of a sugar on 2-hydroxyanthraquinone) and it seemed possible that the 6-membered ring would be even more resistant to methylation.

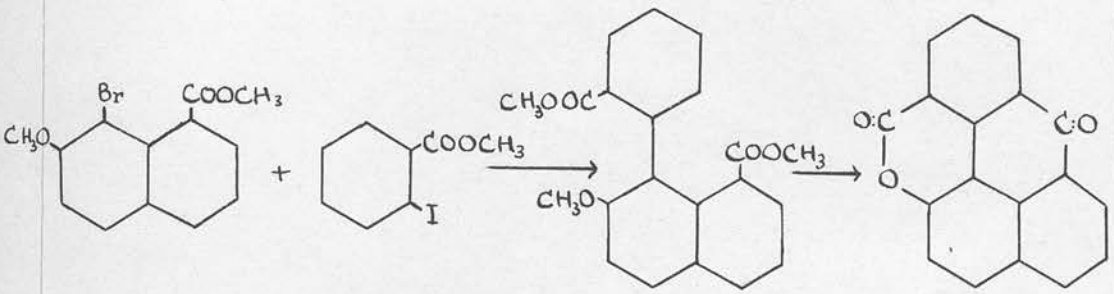
On the other hand, oxidation in the 1-position would appear as a novel and unexpected phenomenon since benzanthrone may be oxidised in positions 2 and 4 but in no case is there evidence of reagents attacking position 1. Such an oxidation is the more unusual when it is remembered that the 2:2'-positions in the diphenyl system (corresponding to the 1:11-positions in benzanthrone) are considered to resemble ortho-positions

(Kenner and Turner, J., 1911, 99, 2101; Kenner, J., 1913, 103, 613) and the presence of a carboxyl group in the 11-position would hardly be expected to favour attack in position 1.

In the present work, the frequent occurrence of compounds having the supposed lactone structure, during the examination of the substitution of 11-carboxybenzanthrone, led to an attempt to confirm the orientation of this interesting oxidation product. A successful synthesis of the compound was carried out, leaving no doubt as to the structure and proving conclusively that oxidation of 11-carboxybenzanthrone takes place in the 1-position.

The method involved the application of the Ullmann reaction to methyl o-iodobenzoate and methyl 7-methoxy-8-bromo-1-naphthoate. Two molecular proportions of the former and one of the latter were used and the mixture treated at 175°C with copper bronze. The copper, employed in this and other Ullmann reactions, was supplied by Imperial Chemical Industries, Limited, and possessed a typical copper-red colour in contrast to less reactive specimens from other sources which had a brassy tint. From the reaction mixture, the unsymmetrical product of coupling, methyl 7-methoxy-8-(o-carbomethoxyphenyl)-1-naphthoate, was isolated in 50% yield. The colourless, crystalline ester, on treatment with concentrated sulphuric acid at 100°C, was converted quantitatively into the lactone of 1-hydroxy-11-carboxy-

benzanthrone, identical with the oxidation product of 11-carboxybenzanthrone.



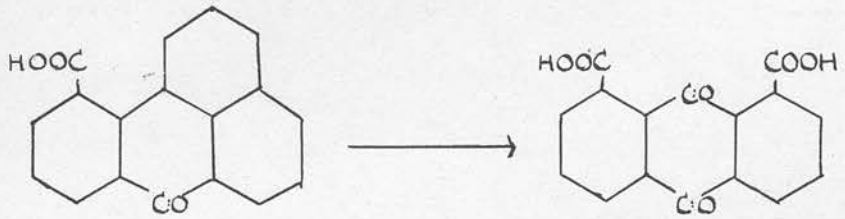
The lactone is a yellow, crystalline compound which dissolves in aqueous alkali only on boiling to give a very characteristic purple solution having a green fluorescence.

b) Anthraquinone-1:8-dicarboxylic acid.

It has already been noted that the oxidation of 11-carboxybenzanthrone with chromic acid does not proceed in the usual manner to yield an anthraquinone derivative. The formation of the lactone ring, which apparently requires an acid medium, would appear to stabilise the system towards this reagent, for further treatment does not bring about the expected degradation.

Recently, a second reagent, alkaline potassium permanganate, has been employed (Allen and Overbaugh, J.A.C.S., 1935, 57, 740) to effect the degradation of certain benzanthrones to derivatives of anthraquinone-1-carboxylic acid. When this reagent was applied to 11-carboxybenzanthrone, a small yield of a free acid, very soluble in polar organic solvents, was obtained.

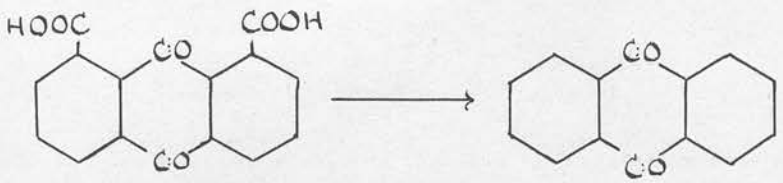
The acid crystallised from alcohol in the form of light-yellow octahedra which melted with decomposition at 316-317°C. From the manner of oxidation employed and the properties of the acid, it was concluded that the compound was anthraquinone-1:8-dicarboxylic acid, an interesting derivative not listed in the literature.



To confirm this structure, however, it was necessary to show that the acid was indeed an anthraquinone derivative, the most obvious method being by decarboxylation.

Decarboxylation experiments were first carried out with the anthraquinone-1-carboxylic acid, obtained by oxidising benzanthrone. This acid melts at 293-294°C and it was thought that heating to the melting point under diminished pressure might be sufficient to remove the carboxyl group, but the acid was found to sublime unchanged at 270°C and 12 mm. pressure. If, however, a trace of copper bronze were added prior to melting the acid, rapid gas-evolution was observed and the product, on sublimation under reduced pressure, gave yellow needles of anthraquinone. This convenient method of decarboxylation, which dispenses with the use of a solvent and gives an almost quantitative yield of the neutral product, was applied to the new acid with a like result, a specimen of pure anthraquinone being

obtained.

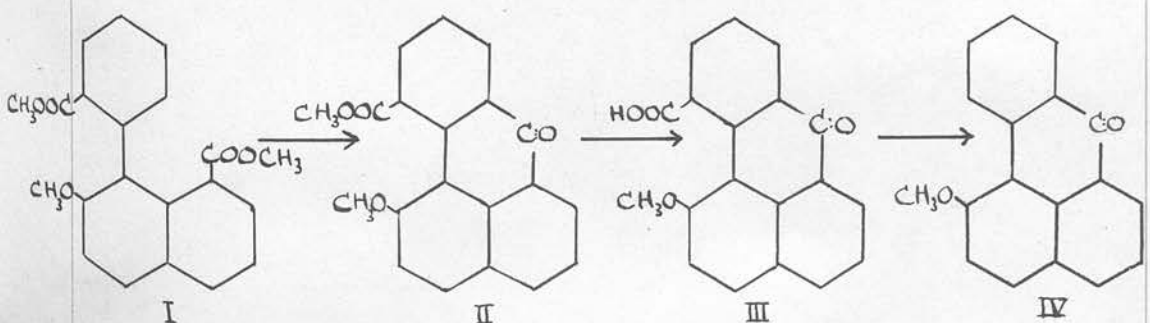


An analysis for carbon and hydrogen content left no doubt as to the structure of the acid.

The decarboxylation method would appear, from several small experiments (not reported in the experimental section of this work), to be of fairly wide application, although the presence of halogen probably interferes with the reaction.

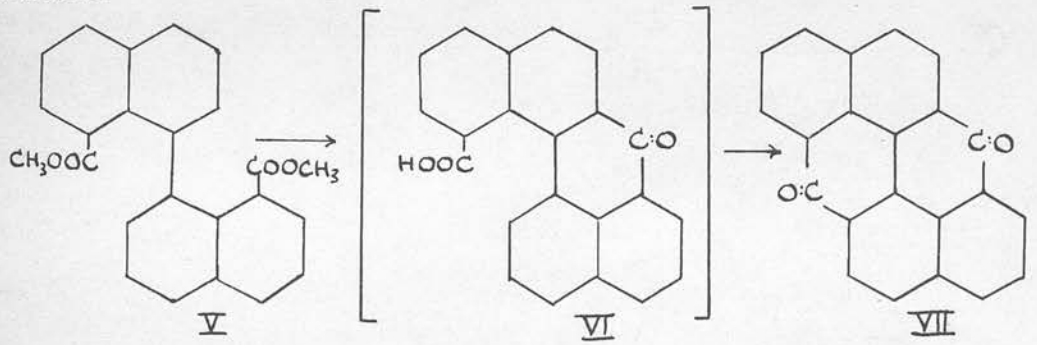
The Hydrolysis and Cyclisation of Phenylnaphthyl and Dinaphthyl Dicarboxylic Esters.

During the synthesis of the lactone of 1-hydroxy-11-carboxybenzanthrone, a study was made of the behaviour of the intermediate 7-methoxy-8-(o-carbomethoxyphenyl)-1-naphthoate (I) towards sulphuric acid and alkalis. It was hoped to supplement the synthesis by partially cyclising the phenylnaphthyl derivative to 1-methoxy-11-carbomethoxybenzanthrone (II) and, by hydrolysis of the latter to the free acid (III), followed by decarboxylation, to obtain the hitherto unknown 1-methoxybenzanthrone (IV).



The preparation failed owing to the peculiar behaviour of the intermediate products but valuable information regarding the cyclisation of such compounds was afforded. In the hydrolysis and cyclisation of phenylnaphthyl and dinaphthyl dicarboxylates, Rule and coworkers have already encountered some interesting facts, a brief résumé of which may be given.

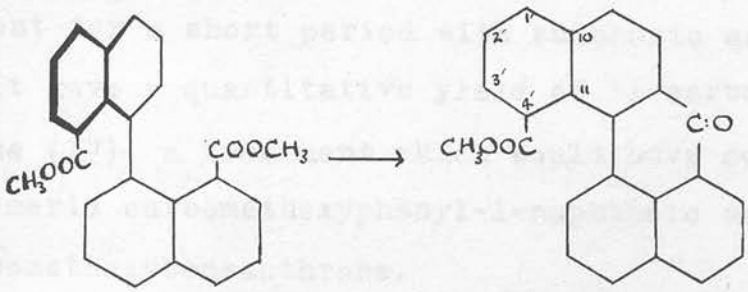
The conversion of 1:1'-dinaphthyl-8:8'-dicarboxylates into anthanthrone by treatment with sulphuric acid (Kalb, Ber., 1914, 47, 1724) is known to proceed in two stages as indicated by colour changes; the almost colourless cold solution becomes first an intense red which changes gradually, or more rapidly on heating, to a pure green. Anthanthrone is precipitated as an orange-yellow solid on pouring the green solution into water.



V VI VII

Kalb (loc. cit.) suggested that the intermediate product, giving rise to the red colour, is the carboxybenzobenzanthrone (VI). During an examination of this reaction, however, F.R. Smith (Thesis, Edinburgh, 1935) succeeded in arresting the course of the cyclisation by pouring the still red solution into water and showed

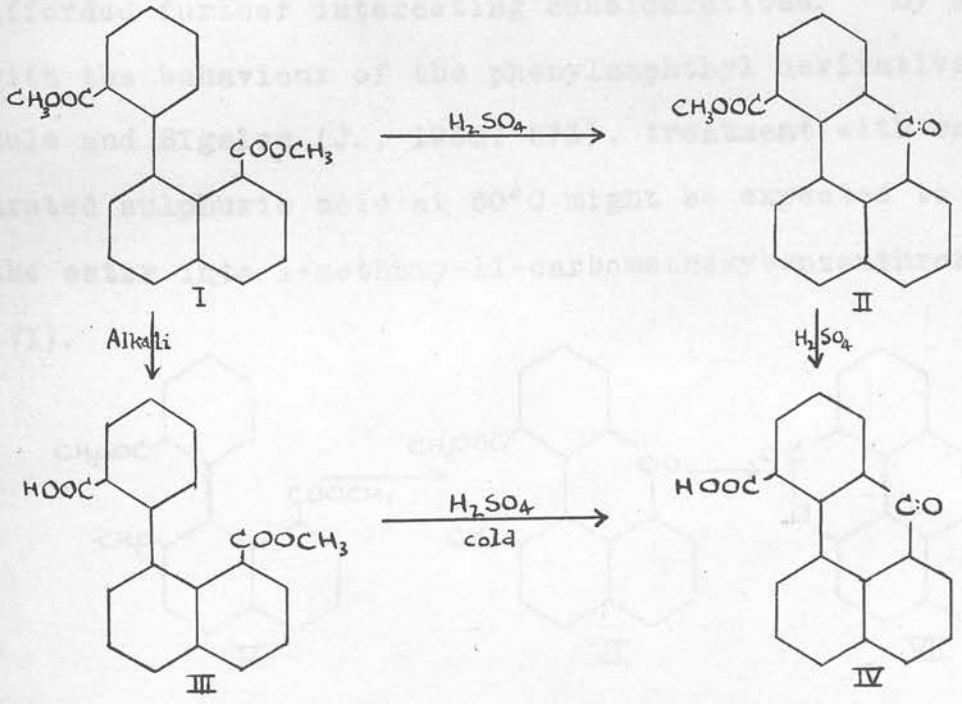
that the intermediate compound is not the acid but the ester, methyl 10:11-benzobenzanthrone-4'-carboxylate. The partially cyclised product was found to be comparatively stable towards sulphuric acid, the suggestion being made that this is due to increased steric hindrance, consequent on the elimination of the possibility of free rotation about the bond joining the two dinaphthyl nuclei, the remaining ester group thus being screened by the second naphthyl nucleus.



The monomethyl ester dissolves in concentrated sulphuric acid to give a red solution (characteristic of benzanthrone derivatives) which is relatively stable under conditions of temperature and concentration in which the free acid rapidly gives the green colour characteristic of anthanthrone. It has been suggested (F.R. Smith, loc. cit.) that the free acid is the immediate precursor of anthanthrone, but Kalb's assumption that the red intermediate colour corresponds to the existence of free monocarboxylic acid is not correct. It may be pointed out, however, that there is no experimental evidence to show that the cyclisation involves a hydrolysis followed by dehydration, and the direct removal of methyl alcohol by the sulphuric acid, though less

likely, is a possibility.

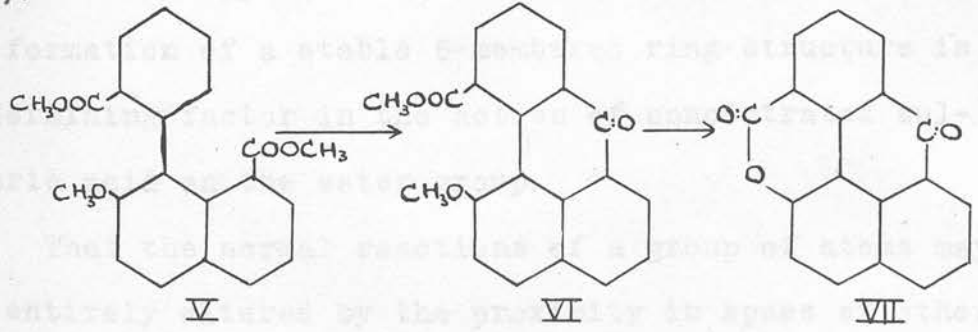
Rule and co-workers (J., 1935, 571, 573), in a study of the hydrolysis of methyl 8-(o-carbomethoxyphenyl)-1-naphthoate (I), showed that the primary product, obtained by the action of concentrated sulphuric acid, is 11-carbomethoxybenzanthrone(II). From the alkaline hydrolysis of the dimethyl ester, an ester-acid was isolated to which the structure of methyl 8-(o-carboxyphenyl)-1-naphthoate (III) could be assigned since, on treatment for a short period with sulphuric acid in the cold, it gave a quantitative yield of 11-carboxybenzanthrone (IV), a treatment which would have converted the isomeric carbomethoxyphenyl-1-naphthoic acid into 11-carbomethoxybenzanthrone.



Although this result is not commented upon in the above papers, it may be noted that it presents an interesting anomaly. While alkaline hydrolysis has taken

the course to be expected on the usual ideas of steric hindrance, the ester group attached to the phenyl nucleus being attacked before the peri-ester group, reaction with sulphuric acid has taken the opposite course. The 11-carbomethoxybenzanthrone has, indeed, been shown (F.R. Smith, loc. cit.) to be remarkably resistant to hydrolysis with concentrated sulphuric acid, in contrast, not only with the ready ring-closure of the ester group in the peri-position but also with the cyclisation of the carbomethoxy group in methyl 10:11-benzobenzanthrone-4'-carboxylate mentioned above.

The examination of methyl 7-methoxy-8-(o-carbomethoxyphenyl)-1-naphthoate (V) in the present work afforded further interesting considerations. By analogy with the behaviour of the phenylnaphthyl derivative of Rule and Bigelow (J., 1935, 573), treatment with concentrated sulphuric acid at 50°C might be expected to convert the ester into 1-methoxy-11-carbomethoxybenzanthrone (VI).



V VI VII

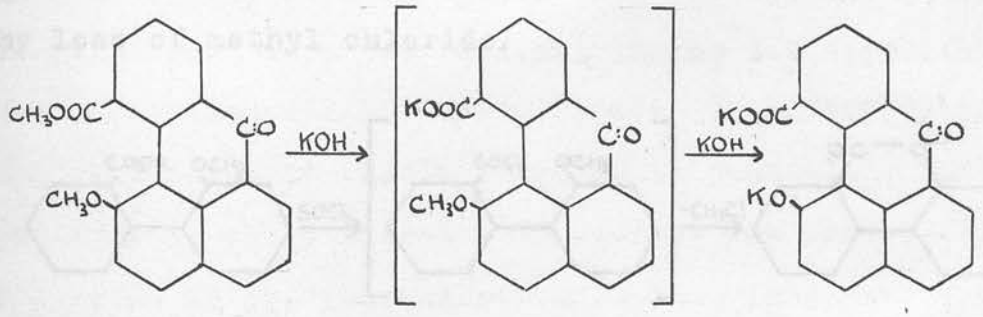
Not only did such treatment bring about a complete cyclisation to the lactone (VII), however, but the action of concentrated sulphuric acid even for a short period at room temperature was sufficient to produce

the lactone in quantitative yield. A variety of other reagents were found to effect this complete cyclisation but eventually the partially cyclised product was isolated by treatment with sulphuric acid, diluted with glacial acetic acid. Even with this reagent, it was found difficult to arrest the course of the cyclisation, the lactone ring seemingly being formed almost as readily as the benzanthrone structure. The 1-methoxy-11-carbomethoxybenzanthrone so obtained was a brilliant yellow, crystalline product, dissolving in most organic solvents with a vivid green fluorescence. It was rapidly converted to the lactone on treatment with cold concentrated sulphuric acid.

The behaviour of the phenylnaphthyl derivative and of 1-methoxy-11-carbomethoxybenzanthrone is the more surprising considering the resistance to acid hydrolysis normally offered by an ether grouping as well as by the ester group of 11-carbomethoxybenzanthrone already noted. It would now appear that the possibility, or otherwise, of formation of a stable 6-membered ring-structure is a determining factor in the action of concentrated sulphuric acid on the ester group.

That the normal reactions of a group of atoms may be entirely altered by the proximity in space of other groups is indicated by the behaviour of 1-methoxy-11-carbomethoxybenzanthrone on mild hydrolysis with alkali. A portion of this ester was refluxed with alcoholic potash for 5 hours when it was found to be largely

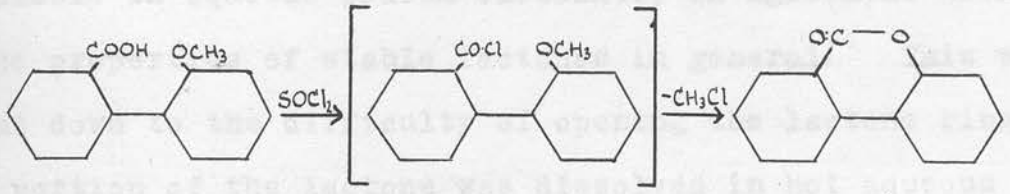
converted to the lactone.



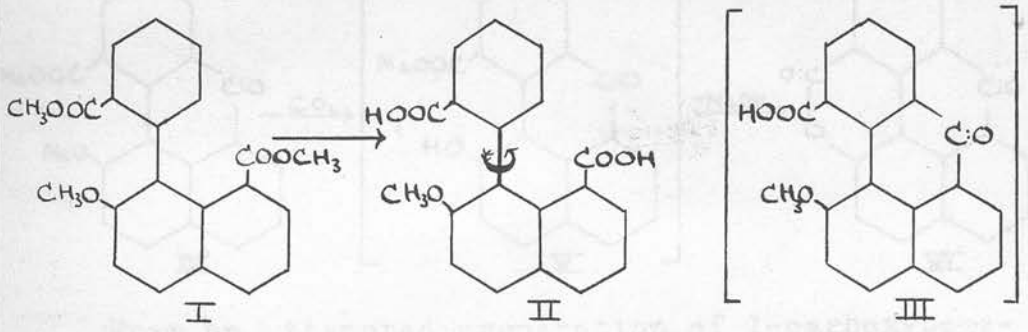
Considering the reputed resistance of the methoxyl group to such treatment, it would appear that the intermediate methoxy-acid, which could not be isolated, is quite unstable. It is possible that potassium methylate is eliminated during the treatment to form the lactone ring but, since the reaction took place in alkaline medium, the lactone structure, if formed, must have been reopened immediately to form the double potassium salt. The actual mechanism can not therefore be decided upon but, by some means, an apparent hydrolysis of both methoxyl and carbomethoxyl groups results. The behaviour, although unexpected, is, however, in good agreement with the failure to methylate the lactone reported by Rule and Bigelow (loc. cit.).

Although no exactly analogous compounds appear to have been examined previously, a peculiar reaction of 2-methoxy-2'-carboxydiphenyl reported by Rule and Bretscher (J., 1927, 925) may be mentioned as further illustrating the effect which spatial arrangement may have on the normal reactions of certain groups. In an attempt to esterify this acid by way of the acid chloride, these authors found that the latter was unstable

even at -16°C and was rapidly converted to the lactone by loss of methyl chloride.



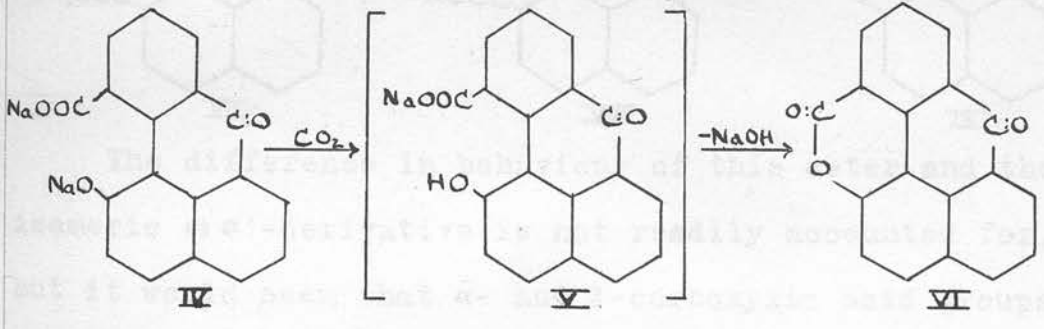
The difference in the two cases is probably one of degree only for, in the rigid benzanthrone structure, the methoxyl and carboxyl groups are constantly held in close contact and it is possible that methyl alcohol may split off in a similar manner. This is supported by the result of alkaline hydrolysis of the phenylnaphthyl derivative (I) which gave the stable 7-methoxy-8-(o-carboxyphenyl)-1-naphthoic acid (II), in which the acid and methoxyl groups may once more be separated by rotation round the phenylnaphthyl bond.



All attempts to bring about the partial cyclisation of this product to the methoxy-acid (III) resulted in failure, the lactone only being obtained.

A further consequence of the close proximity of substituents in the 1:11-positions in benzanthrone was shown by an experiment carried out with the lactone itself (not given in the experimental section).

According to Rule and Bigelow (loc. cit.), the lactone of 1-hydroxy-11-carboxybenzanthrone is not appreciably soluble in aqueous sodium carbonate, in agreement with the properties of stable lactones in general. This was put down to the difficulty of opening the lactone ring. A portion of the lactone was dissolved in hot aqueous sodium hydroxide solution and, on passing in carbon dioxide, was found to be completely reprecipitated, leaving no trace of the characteristic red colour in the solution. Since 11-carboxybenzanthrone is a comparatively strong acid, it can only be concluded that the mono-sodium salt (V) of the hydroxy-acid is unstable and loses sodium hydroxide to give the lactone. The insolubility of the lactone in water is probably a factor in allowing this reaction to proceed to a finish.

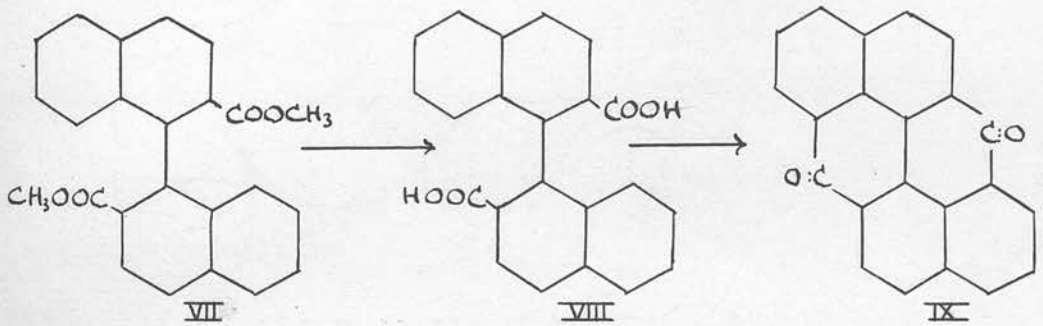


IV V VI

From an attempted preparation of 1-carboxybenzanthrone (p. 52), a portion of dimethyl 1:1'-dinaphthyl-2:2'-dicarboxylate (VII) was isolated and the cyclisation of the compound with concentrated sulphuric acid briefly examined. The conversion of this ester to anthanthrone by sulphuric acid treatment is described by Kuhn and Albrecht (Ann., 1928, 465, 282) but no comment is made regarding the course of the cyclisation. It was found

that the compound required much more vigorous treatment to convert it to anthanthrone than the isomeric product of Kalb (loc. cit.). The colourless solution in concentrated sulphuric acid, on heating above 50°C, changed to a pale green which gradually deepened and it was noticeable that no intermediate red (benzanthrone) colour made its appearance.

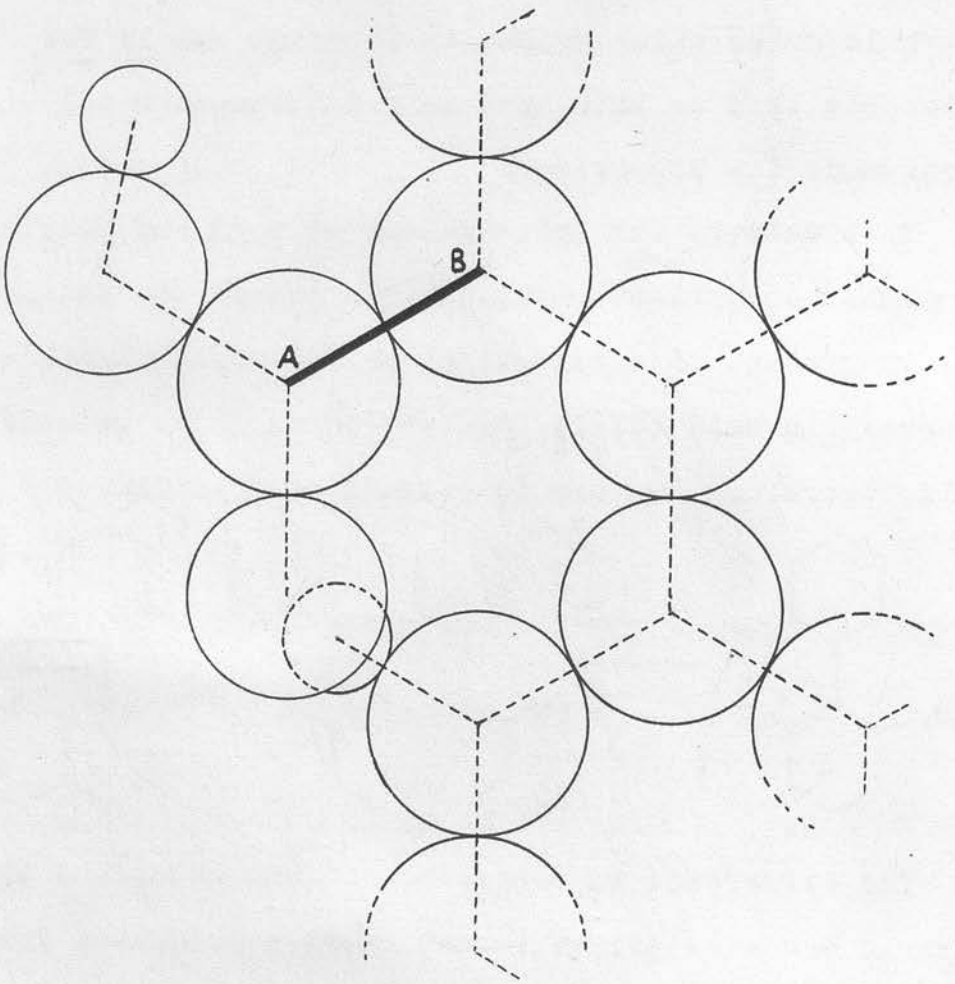
By treatment for half-an-hour at 50°C and pouring the almost colourless solution into water, the intermediate product of cyclisation, 1:1'-dinaphthyl-2:2'-dicarboxylic acid (VIII), was obtained. The reaction would, therefore, appear to proceed as follows:

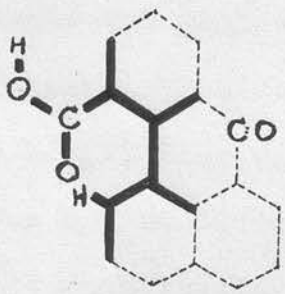


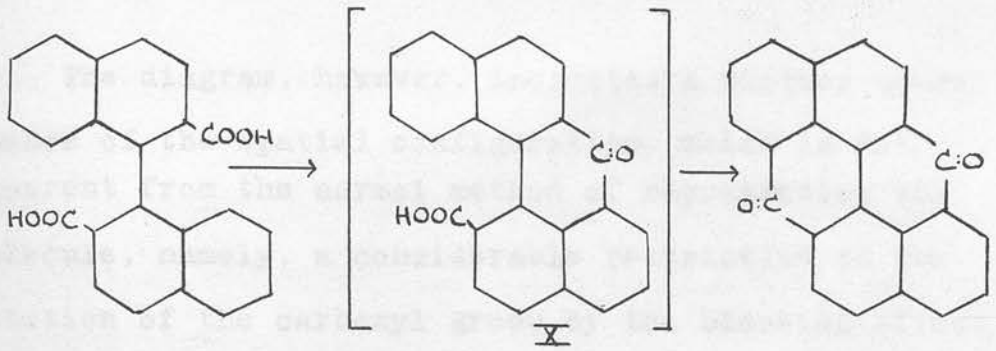
The difference in behaviour of this ester and the isomeric $\alpha:\alpha'$-derivative is not readily accounted for, but it would seem that α- and β-carboxylic acid groups are not cyclised with the same ease. The absence of any intermediate red colour corresponding to a benzanthrone derivative would indicate that the benzobenzanthrone carboxylic acid (X) is quite unstable under the conditions of temperature and concentration necessary to effect the first cyclisation.

Atomic Scale Model of Part of the 11-Carboxybenzanthrone Molecule.

The thick line, AB, represents the bond joining the carboxyl group to the benzanthrone nucleus.







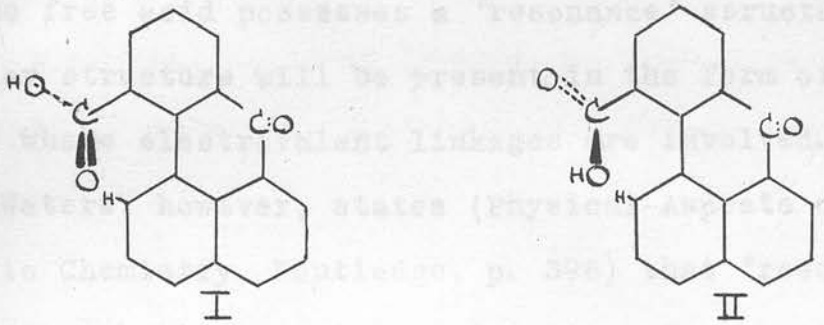
X

This last example is of importance, being the only case encountered in which there is definite experimental evidence that the cyclisation proceeds by way of hydrolysis. The examination serves to indicate the diversity of the factors which govern the hydrolysis and cyclisation of such compounds.

The Attempted Resolution of 11-Carboxybenzanthrone.

The reactions of 1-methoxy-11-carbomethoxybenzanthrone described above may be attributed to the close proximity of the substituents in the 1: 11-positions. The scale diagram opposite, which represents part of the 11-carboxybenzanthrone molecule according to atomic radii quoted by Boys (Proc. Roy. Soc., 1934, 144, 683), emphasises the proximity of the two positions in the benzanthrone system. Not only so, but the ready formation of the lactone on oxidation of the acid is made comprehensible, it being obvious from the model that, since the oxygen atoms of the carboxyl group may approach very closely to the 1-carbon atom, practically no additional strain is imposed on the structure by the formation of the lactone ring.

The diagram, however, indicates a further consequence of the spatial configuration, which is not apparent from the normal method of representing the molecule, namely, a considerable restriction to the rotation of the carboxyl group by the blocking effect of the hydrogen atom in position 1. Indeed, the restriction to rotation is of much greater magnitude than in the case of many resolvable diphenyl derivatives and the question of the existence of stereoisomeric forms of 11-carboxybenzanthrone immediately arises. The possible enantiomorphs are represented diagrammatically in figs. I and II, where in the former the ketonic oxygen is above the plane of the paper and in the latter it lies below:

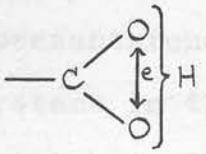


I II

This consideration led to an attempt to resolve the acid. The brucine salt and ℓ-menthyl ester were prepared but repeated crystallisation of these derivatives failed to effect any separation of isomers, the specific rotations remaining constant throughout. The brucine salt also failed to show mutarotation when dissolved in pyridine and a portion, after repeated crystallisation, yielded an inactive specimen of the original acid on hydrolysis. The examination, therefore,

gave no indication of the existence of stereoisomeric forms of 11-carboxybenzanthrone.

Recently, the suggestion has been put forward, on physical considerations, that the carboxyl group, in the free state at least, is a symmetrical one involving an electron "resonance" state, represented as follows:



If this is the case, then the existence of stereoisomeric forms of 11-carboxybenzanthrone obviously becomes impossible. The failure to resolve the acid in the form of the brucine salt was, therefore, not entirely unexpected since it is highly probably that, if the free acid possesses a "resonance" structure, a similar structure will be present in the form of its salts where electrovalent linkages are involved.

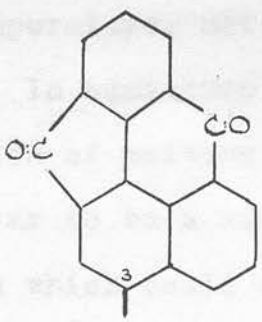
Waters, however, states (Physical Aspects of Organic Chemistry, Routledge, p. 396) that "resonance" is also probable in esters and amides of carboxy acids and the failure to resolve the menthyl ester would appear to be in support of the "resonance" state.

On so scanty evidence, however, it is impossible to draw definite conclusions. A more thorough examination of the acid and related compounds is desirable and might lead to an experimental method of establishing more precisely the constitution of the carboxyl group.

II The Chemistry of 1:11-Ketobenzanthrone.

Substitution

The position at which substituents will enter the 1:11-ketobenzanthrone molecule is not readily predicted for, in contrast to benzanthrone and 11-carboxybenzanthrone, all ring systems in the diketo-derivative have ketonic groups attached, tending to retard substitution. From the previously noted reactivity of the 3-position in benzanthrone, however, it might be expected that this position would still be primarily attacked on substitution and the fact that it is meta to a ketonic grouping is in support of this suggestion. It is also reasonable to suppose that substituents will not readily enter the 1:11-ketobenzanthrone molecule.



The results of an examination of the halogenation and nitration of 1:11-ketobenzanthrone were in general agreement with these considerations. Halogenation, carried out on an aqueous suspension of the compound, was found to yield the 3-halogeno-derivative exclusively. Prolonged treatment with excess bromine under these conditions gave, rather unexpectedly, a quantitative

yield of pure 3-bromo-1:11-ketobenzanthrone. The compound crystallised from glacial acetic acid in stout red needles and proved identical with the synthetic product obtained by F.R. Smith (loc. cit.) by means of an "Ullmann Synthesis". The pure chloro-derivative was obtained in somewhat smaller yield than that recorded for the bromo-compound but the presence of isomeric products was not detected. It was orientated by identification with the product of cyclisation of 3-chloro-11-carboxybenzanthrone.

The action of chlorine on the ketone in glacial acetic acid solution at 100°C also yielded 3-chloro-1:11-ketobenzanthrone but in this solvent there was a tendency for a second chlorine atom to enter the molecule. For example, further treatment with chlorine gave a dichlorination product which melted over a small range of temperature, not appreciably altered on crystallisation. In admixture with the 3-chloro-derivative, no depression of melting point occurred and the product would appear to be a mixture of isomeric dichloro-compounds which could not be separated by the methods employed.

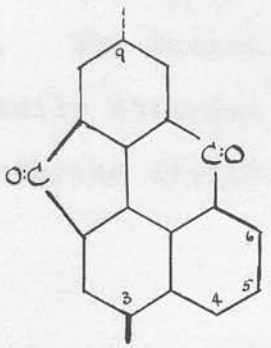
In contrast to the behaviour with chlorine, the ketone was unaffected by prolonged treatment with bromine in glacial acetic acid. Dibromination, however, was readily effected by treatment with liquid bromine at the boiling point. From the product, a specimen

of 3:9-dibromo-1:11-ketobenzanthrone was isolated after repeated crystallisation, the compound being shown to be identical with that synthesised by F.R. Smith (loc. cit.).

The action of nitric acid on 1:11-ketobenzanthrone was also examined, nitration with the calculated amount of the reagent in concentrated sulphuric acid yielding the 3-nitro-derivative. The small yield of pure product recorded would indicate that other isomers were formed during the reaction. Treatment with excess nitric acid alone or in sulphuric acid led to an oxidation of the ketone and a mixture of products of the lactone-type was obtained from which no pure compound could be isolated. Attempts to increase the yield of 3-nitro-ketone were unsuccessful.

In glacial acetic acid solution, treatment of the ketone with a large excess of nitric acid left it unchanged, the entrance of a nitro-group into the molecule again appearing to be inhibited by the presence of the solvent. It may be noted that in concentrated sulphuric acid or nitric acid solution a considerable proportion of the ketone probably exists in the form of the oxonium salt. The presence of the resulting positively charged pole or poles would be expected to still further diminish the ease with which substituents could be introduced. A consideration of this factor, however, does not appear to throw any light on the behaviour of benzanthrone and its derivatives on sub-

stitution in concentrated sulphuric acid, nitric acid and glacial acetic acid respectively.



The position at which substituents enter the 1:11-ketobenzanthrone molecule on monosubstitution is not unexpected. The entrance of a second bromine atom at position 9, however, is rather surprising since it might be thought that the ring system containing positions 4, 5 and 6, and having only one ketonic group attached, would be more readily attacked. It is possible that the original mixtures obtained on dihalogenation contained compounds with substituents in that ring, even though none could be isolated by crystallisation methods.

The substituted ketobenzanthrones are highly coloured compounds but are of no use as vat dyes. Although they appear to form vats with alkaline hydrosulphite, the leuco-compounds show little affinity for cotton and any colour which does adhere is largely removed with soap treatment. The halogenated compounds dissolve in concentrated sulphuric acid with blood-red colouration, very dilute solutions of the disubstituted derivatives showing a blue colour. On treatment with aqueous alkali at the boiling point, all gradually go

into solution, presumably owing to the opening of the 5-membered ketone ring to give a mixture of carboxylic acids (see below). The substituted derivatives, however, are less readily attacked on such treatment than is 1:11-ketobenzanthrone itself.

Oxidation

It has already been noted that the presence of the lactone ring in the lactone of 1-hydroxy-11-carboxybenzanthrone appears to stabilise the system towards oxidising agents. The same would seem to apply to the 5-membered ketone ring, for 1:11-ketobenzanthrone proved very resistant to oxidation with chromic acid. Although on prolonged treatment a considerable loss of material occurred, no solid oxidation product could be obtained.

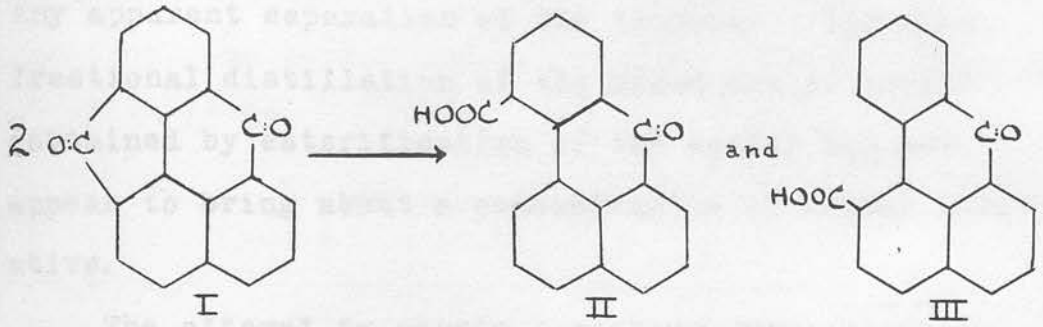
The effect of alkaline oxidising agents was not examined, since a mixture of products would undoubtedly result owing to the opening of the ketone ring which occurs in the presence of alkalis (see below).

III 1-Carboxybenzanthrone.

Attempts to prepare 1-carboxybenzanthrone.

Rule and Bigelow (J., 1935, 573) observed that 1:11-ketobenzanthrone (I) is slowly attacked by aqueous alkali at the boiling point to give a mixture of acids consisting presumably of 11-carboxybenzanthrone (II)

and 1-carboxybenzanthrone (III).



I II III

This instability towards alkalis contrasts strongly with the behaviour of fluorenone which is not appreciably attacked by aqueous alkali. The difference probably arises from the greater tension in the 1:11-ring in the benzanthrone derivative. In fluorenone, "the strain in the 5-membered ring may be relieved by a slight adjustment of the loose diphenyl system, a distortion which is not so readily tolerated by the more rigid benzanthrone molecule" (Rule and Bigelow, loc. cit.).

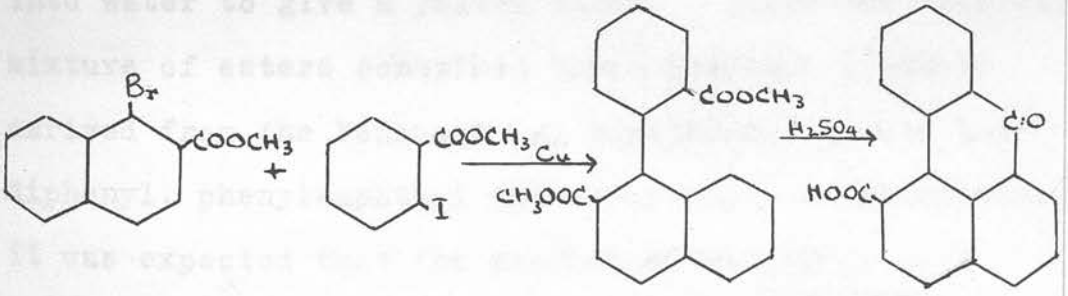
In an attempt to isolate 1-carboxybenzanthrone, Rule and Bigelow (unpublished) carried out an examination of the acid mixture obtained from ketobenzanthrone and showed that repeated crystallisation of the acids or their metallic salts resulted in a concentration of the 11-carboxybenzanthrone and eventually led to the isolation of a pure specimen of that isomeride. Treatment of the mother liquors also failed to yield the 1-acid.

In the present work, the examination of the acid mixture was resumed. Attempts to obtain the 1-acid by partial esterification and by partial acidification of

an alkaline solution of the mixture failed to effect any apparent separation of the isomers. Likewise, fractional distillation of the mixed methyl esters (obtained by esterification of the acids) did not appear to bring about a concentration of either derivative.

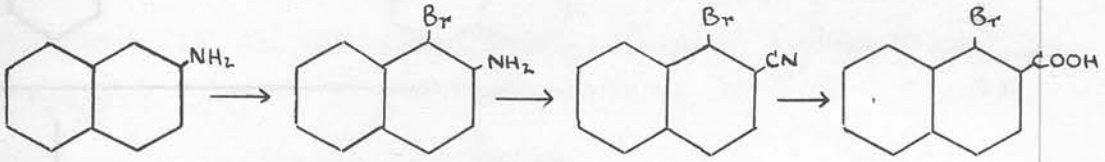
The attempt to obtain 1-carboxybenzanthrone by way of the ketone was therefore given up in favour of an "Ullmann Synthesis" similar to that of Rule and co-workers (loc. cit.) for the preparation of 11-carboxybenzanthrone.

The proposed synthesis involved the application of the Ullmann reaction to methyl 1-bromo-2-naphthoate and methyl o-iodobenzoate, followed by hydrolysis and cyclisation of the resulting phenylnaphthyl derivative with concentrated sulphuric acid:

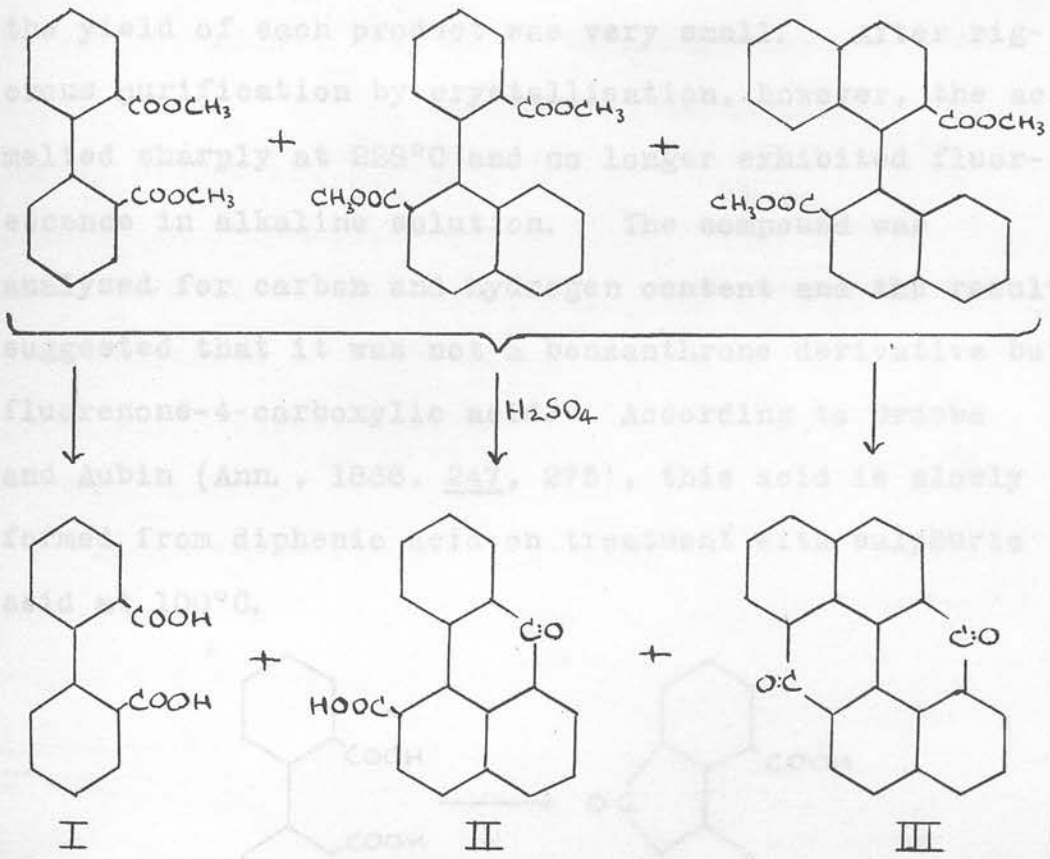


A preparation of 1-bromo-2-naphthoic acid is reported by Mayer and Sieglitz (Ber., 1922, 55, 1836, 1859) by oxidation of the corresponding methylnaphthalene or the aldehyde. A more satisfactory preparation was devised during the present work, employing β-naphthylamine as the starting material. The amine was brominated according to the method of Franzen and Eidis

(J. pr. Chem., 1913, 88, 755) and the bromoamine converted to the nitrile by application of the Sandmeyer reaction, the latter yielding 1-bromo-2-naphthoic acid on hydrolysis.



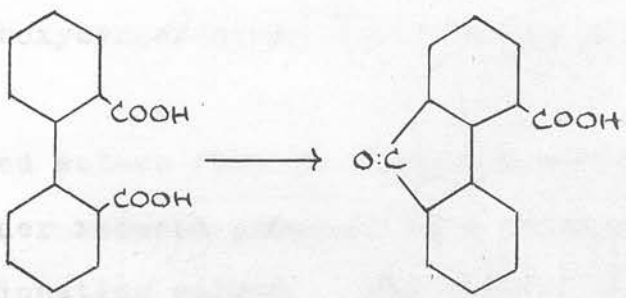
The Ullmann reaction was first carried out between the methyl ester of this acid and methyl o-iodobenzoate, two molecular proportions of the former and one of the latter being employed. The resulting mixture of esters did not deposit any solid on treatment with ether and chilling, and various attempts to isolate the phenylnaphthyl dicarboxylate proved unsuccessful. The mixed product was therefore treated with concentrated sulphuric acid at 100°C for one hour and the red solution poured into water to give a yellow solid. Since the original mixture of esters contained three possible products derived from the benzoate and naphthoate, namely the diphenyl, phenylnaphthyl and dinaphthyl dicarboxylates, it was expected that the product of sulphuric acid treatment would consist of diphenic acid (I), 1-carboxybenzanthrone (II), and anthanthrone (III).



I II III

The product of such treatment was therefore boiled out with water to remove diphenic acid, and the residue then extracted with alkali, leaving anthanthrone as an insoluble solid which was filtered off. In this manner was obtained a light yellow acid product which crystallised from glacial acetic acid in needles, melting at 225-227°C. It dissolved in concentrated sulphuric acid with a blood-red colouration and in alkalis gave a yellow solution with green fluorescence. The acid appeared to be homogeneous and was at first thought to be 1-carboxybenzanthrone, a conclusion supported by the fact that decarboxylation and further cyclisation gave, respectively, specimens of benzanthrone and 1:11-ketobenzanthrone, although it was noted that

the yield of each product was very small. After rigorous purification by crystallisation, however, the acid melted sharply at 228°C and no longer exhibited fluorescence in alkaline solution. The compound was analysed for carbon and hydrogen content and the results suggested that it was not a benzanthrone derivative but fluorenone-4-carboxylic acid. According to Graebe and Aubin (Ann., 1888, 247, 275), this acid is slowly formed from diphenic acid on treatment with sulphuric acid at 100°C.



The fluorenone carboxylic acid is a yellow compound possessing some of the properties of benzanthrones. It dissolves in concentrated sulphuric acid with a blood-red colouration but differs from the benzanthrone carboxylic acids in showing no fluorescence in alkaline solution.

The properties of the original acid mixture before crystallisation, however, suggested that 1-carboxybenzanthrone was formed to some extent in the preparation. Renewed attempts were made to isolate the intermediate phenylnaphthyl derivative, but without success and Ullmann reactions were then modified in an endeavour to minimise the formation of the diphenyl derivative.

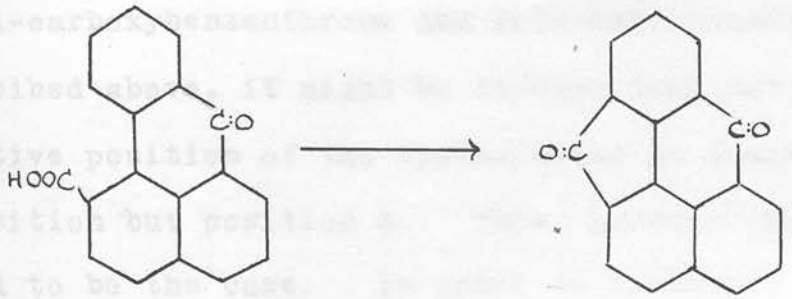
In one experiment, two molecular proportions of the naphthoate and one of the benzoate were treated with copper bronze and from the reaction product a considerable quantity of the dinaphthyl derivative separated. After removal of this compound, the residue was treated with sulphuric acid and again an acid portion was isolated which appeared to be mainly the fluorenone derivative.

After various unsuccessful attempts to remove the fluorenone derivative from the acid mixtures, a specimen of 1-carboxybenzanthrone was obtained in the following manner:

The mixed esters from an Ullmann coupling were distilled under reduced pressure in a flask fitted with a long fractionating column. The bulk of the diphenic ester distilled at 200°C at 12 mm. pressure and a second fraction was collected, distilling at 225-240°C, which contained the required phenylnaphthyl derivative. This fraction, forming a yellow syrup, was treated with sulphuric acid and from the product, by repeated crystallisation, a yellow acid was obtained which melted at 285°C. The very small yield recorded (5% theory) would indicate that the unsymmetrical product of coupling was formed only to a slight extent during the Ullmann treatment.

The structure of the acid was confirmed by treating a portion with phosphorus pentoxide in molten phthalic anhydride at 200°C, a treatment which con-

verted it quantitatively into 1:11-ketobenzanthrone.



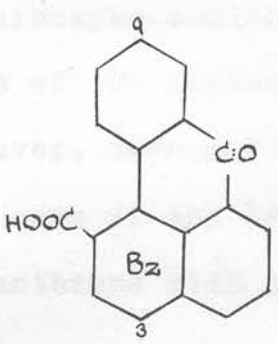
A carbon-hydrogen analysis further confirmed the identity of the acid.

1-Carboxybenzanthrone possesses typical benzanthrone properties and resembles 11-carboxybenzanthrone very closely. It dissolves in alkalis to give a deep yellow solution having a vivid green fluorescence and its solubility in water and in the usual organic solvents is very similar to that of the 11-isomeride.

Chemistry of 1-carboxybenzanthrone.

Owing to the difficulty experienced in preparing 1-carboxybenzanthrone and the small yield obtained, only a brief examination of its reactions could be undertaken.

A portion of the acid was successfully brominated by prolonged treatment of an aqueous suspension with bromine and a bright yellow mono-bromo-acid was formed in good yield.



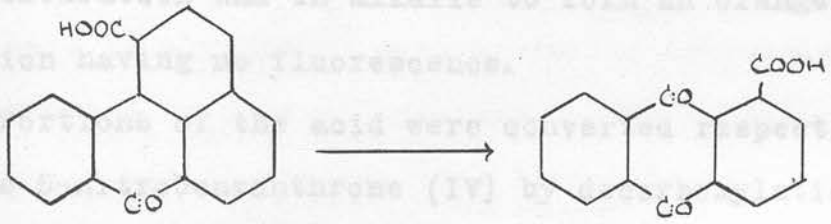
From a consideration of the substitution reactions of 11-carboxybenzanthrone and 1:11-ketobenzanthrone described above, it might be thought that the most reactive position of the system would no longer be the 3-position but position 9. This, however, was not found to be the case. In order to orientate the bromo-1-carboxybenzanthrone, it was cyclised with phosphorus pentoxide treatment and red needles of the ketone were obtained which melted at 325-326°C. The compound proved identical, not with 9-bromo-1:11-keto-benzanthrone which melts at 239-240°C (F.R. Smith, loc. cit.), but with the 3-bromo-derivative.

Unfortunately, chlorination and nitration of the acid could not be examined but it would appear that the influence of the carboxyl group in position 1, tending to prevent substitution in the Bz-ring, is not sufficient to overcome the normal reactivity of the 3-position in the benzanthrone system.

A small experiment with nitric acid yielded a yellow product, melting at 257°C, which dissolved in alkali only on boiling to give a blue solution. The compound, which could not be obtained in sufficient quantity for examination, was probably a nitro-lactone of 11-hydroxy-1-carboxybenzanthrone.

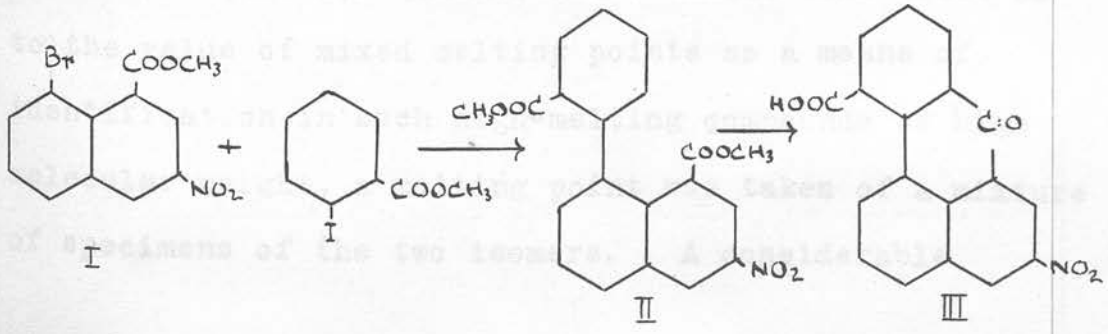
The formation of the lactone ring with 1-carboxy-benzanthrone, however, does not appear to occur so readily as in the case of the 11-acid. Oxidation of the 1-carboxybenzanthrone with chromic acid gave a

good yield of anthraquinone-1-carboxylic acid and no lactone appeared to be formed during the treatment.



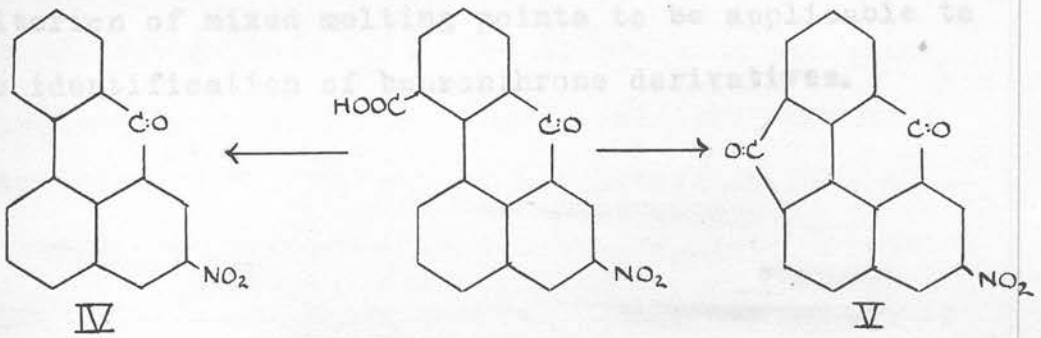
During the early attempts to prepare 1-carboxybenzanthrone, a portion of the fluorenone carboxylic acid was nitrated in the belief that it was the required benzanthrone derivative. In an attempt to orientate the nitration product, 5-nitrobenzanthrone was prepared by means of an "Ullmann Synthesis" and this preparation is given in the experimental section.

The synthesis consisted in coupling methyl 3-nitro-8-bromo-1-naphthoate (I) and methyl o-iodobenzoate in the presence of copper bronze. From the reaction mixture, the unsymmetrical product of coupling, methyl 3-nitro-8-(o-carbomethoxyphenyl)-1-naphthoate (II) was isolated and on treatment with sulphuric acid was converted into the 5-nitro-11-carboxybenzanthrone (III).



The acid is a light brown, crystalline compound, dissolving in concentrated sulphuric acid to give a red colouration and in alkalis to form an orange-yellow solution having no fluorescence.

Portions of the acid were converted respectively to the 5-nitrobenzanthrone (IV) by decarboxylation and to the 5-nitro-1:11-ketobenzanthrone (V) by further cyclisation.



IV V

The nitrobenzanthrone, which is not listed in the literature, forms light brown needles, melting at 287°C, and possesses the normal benzanthrone properties. The diketone is an orange compound which gives a purple vat with alkaline hydrosulphite but it appears to be of no use as a vat dye, having little affinity for the cotton fibre.

5-Nitro-11-carboxybenzanthrone has the melting point 309°C, almost identical with that of the 3-nitro-derivative (310°C). Since there exists some doubt as to the value of mixed melting points as a means of identification in such high-melting compounds of high molecular weight, a melting point was taken of a mixture of specimens of the two isomers. A considerable

depression, approximately 20°C, was observed. Specimens of 3-chloro-11-carboxybenzanthrone and the lactone of 3-nitro-1-hydroxy-11-carboxybenzanthrone, both of which melt at 317-318°C, gave a similar depression of melting point when mixed together. The behaviour of the dichlorination product of 1:11-ketobenzanthrone in admixture with 3-chloro-1:11-ketobenzanthrone reported above would therefore appear to be an exception and the criterion of mixed melting points to be applicable to the identification of benzanthrone derivatives.

EXPERIMENTAL SECTION.

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

Methods of Analysis.

Halogen was determined by the method of Ter Meulen (Ter Meulen and Heslinga, Rec. Trav. Chim., 1923, 42, 1093) which consists in the hydrogenation of the compound in the presence of ammonia and estimation of the resulting ammonium halide by Volhard's volumetric method. For high-melting compounds (above 250°C), however, the method proved unsatisfactory and that of Hein, Hoyer and Klar (Zeit. analyt. Chem., 1928, 75, 161) was resorted to. In this semi-micro method, the halogeno-

compound is oxidised by means of sodium peroxide, a small steel bomb being employed, and the sodium halide estimated by Volhard's method.

Nitrogen was estimated by the micro-Dumas method, but in the case of benzanthrone derivatives heating to a higher temperature than usual was necessary and results were generally low.

Specimens of the more important compounds, however, were sent to Dr Schoeller (Berlin) or Dr Weiler (Oxford) for micro-analysis.

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

8-Bromo-1-naphthoic acid.

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

a) Mercuration of naphthalic acid.

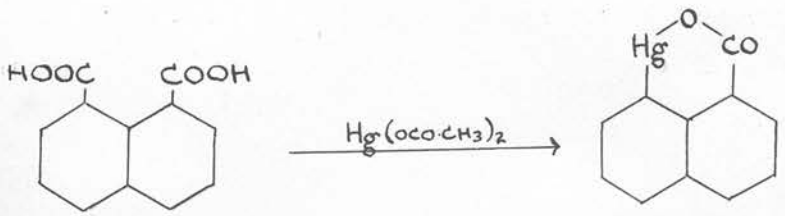
54 gm. naphthalic acid.

21 gm. sodium hydroxide.

55 gm. yellow mercuric oxide.

The sodium hydroxide and naphthalic acid were dissolved in 1200 c.c. 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 c.c. glacial acetic acid and 150 c.c. water with heating, the solution filtered and added to the flask. The contents were then made distinctly acid with acetic acid when a light coloured 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, washed well with water and dried at 110°C.

Yield: 88 gm. (97%).



b) Bromination of mercury compound.

80 gm. anhydro-8-hydroxymercuri-1-naphthoic acid.

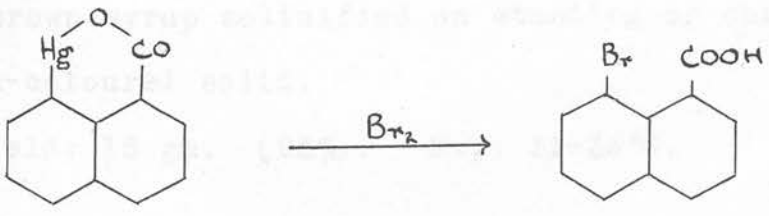
34 gm. bromine.

The mercury compound was suspended in 300 c.c. glacial acetic acid and 50 c.c. water were added. The mixture was cooled in ice and water, efficiently stirred and the bromine, dissolved in 150 c.c. concentrated sodium bromide solution, was added drop by drop over three hours. The mixture was then heated to 90 °C and the clear brown solution poured into 2 litres of cold water. After standing overnight, the crystalline precipitate was filtered off and extracted with 8-9 litres of boiling water. The crystals which deposited on cooling the extract were filtered off and dried.

Wt. 39 gm. M.p. 160-170 °C.

The crude acid was recrystallised from benzene.

Yield: 33 gm. (57%). M.p. 178 °C.



Methyl 8-bromo-1-naphthoate.

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

15 gm. 8-bromo-1-naphthoic acid.

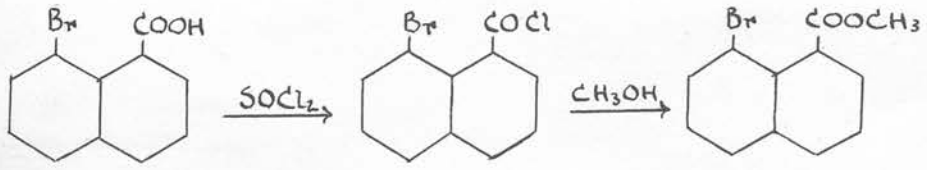
30 c.c. thionyl chloride (purified).

50 c.c. methyl alcohol (dry).

The acid and thionyl chloride were boiled together under reflux on the water-bath until a clear solution was obtained and fumes ceased to be evolved. Excess thionyl chloride was then removed by distillation, finally under reduced pressure. The acid chloride was allowed to cool and the methyl alcohol carefully added in portions. Vigorous evolution of hydrochloric acid occurred and the reaction was completed by boiling the mixture for half-an-hour.

Most of the methyl alcohol was then removed on the steam-bath and the liquid ester taken up in ether. The ethereal extract, after washing with dilute sodium hydroxide followed by water, was dried over calcium chloride and the ether removed in vacuo. The residual light-brown syrup solidified on standing or chilling to a cream-coloured solid.

Yield: 15 gm. (95%). M.p. 31-32°C.



7-Methoxy-8-bromo-1-naphthoic acid.

(Davies, Heilbron and Irving, J.C.S., 1932, 2715).

a) Oxalyl-bis-phenylimidochloride.

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

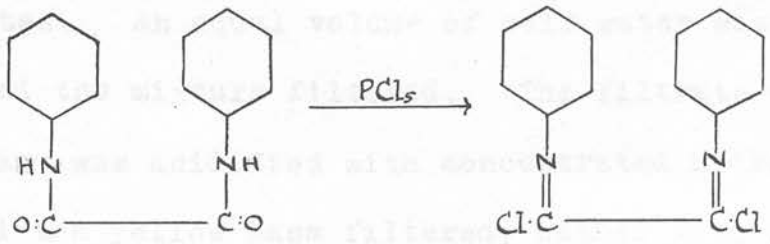
50 gm. oxanilide.

100 gm. phosphorus pentachloride.

The oxanilide was suspended in 150 c.c. toluene, the phosphorus pentachloride added and the mixture heated gradually to the boiling point under reflux. Hydrogen chloride was evolved and a clear solution gradually resulted. After refluxing for three hours, about 100 c.c. of the toluene were distilled off and the residue was allowed to cool. The green solid which separated was filtered and washed with petroleum ether (b.p. 40-60°C).

Yield: 45 gm. (80%). M.p. 113-114°C.

The product, which was pure enough for the present purpose, crystallises from ligroin in yellow needles, melting at 115°C.



b) 2-Methoxyacenaphthenequinone.

(Staudinger, Goldstein and Schlenker, Helv. chim. acta, 1921, 4, 342)

81 gm. aluminium chloride.

90 gm. β-naphthyl methyl ether (nerolin).

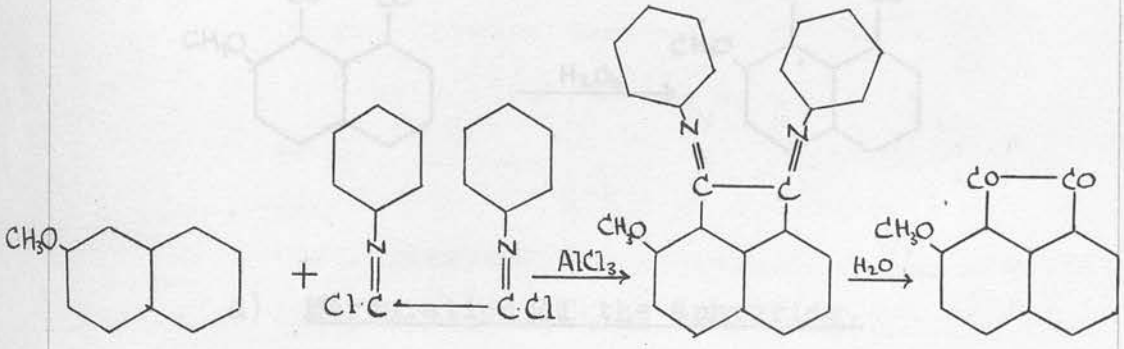
82·2 gm. oxalyl-bis-phenylimidochloride.

The aluminium chloride, finely powdered but not freshly prepared, was suspended in 100 c.c. benzene and a solution of the nerolin and imidochloride in 500 c.c. benzene run in with vigorous stirring over a period of 2 hours. During the addition, the temperature was prevented from rising by cooling the mixture in water. After a further 4 hours at ordinary temperature, the mixture was heated at 50-55°C for half-an-hour, the stirring being continued throughout. The product was then treated with 400 gm. ice and 80 c.c. concentrated hydrochloric acid, the benzene was removed in steam and the red residue filtered.

The solid residue, containing the quinone and excess nerolin, was treated with 500 c.c. of a 40% solution of sodium bisulphite and heated at 70-80°C for 15 minutes. An equal volume of cold water was then added and the mixture filtered. The filtrate while still warm was acidified with concentrated hydrochloric acid and the yellow mass filtered, washed with water and dried.

Yield: 45 gm. (75%). M.p. 219-220°C.

The quinone crystallised in yellow needles from glacial acetic acid, m.p. 222-223°C.



c) 2-Methoxynaphthalic anhydride.

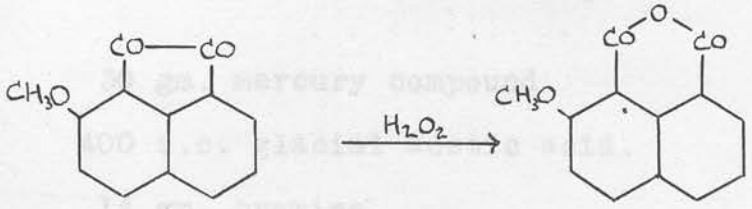
Staudinger and co-workers (loc. cit.) carried out the oxidation of the quinone with potassium chromate. The oxidation method of Whiston (J. Soc. Chem. Ind., 1924, 43, 370), employing hydrogen peroxide, was tried in the present work and proved more satisfactory.

The quinone (25 gm.) was ground to a smooth paste with 100 c.c. water and then stirred to a fine suspension with 150 c.c. sodium hydroxide solution (10%). The suspension was heated to 40°C and 250 c.c. hydrogen peroxide solution (3%) were run in, the temperature being raised to the boiling point during the addition. The resulting yellow solution was filtered and the filtrate acidified. The product, which appeared to be in the form of the anhydride, weighed 26·5 gm. and melted at 259°C.

The pure anhydride was obtained in the form of

colourless needles by crystallisation from nitrobenzene.

Yield: 90-95 % theory. M.p. 260°C.



d) Mercuration of the anhydride.

(Davies, Heilbron and Irving, loc. cit.)

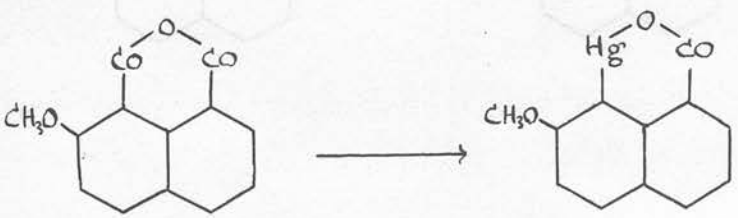
50 gm. 2-methoxynaphthalic anhydride.

17·6 gm. sodium hydroxide.

48·5 gm. yellow mercuric oxide.

The sodium hydroxide and naphthalic anhydride were dissolved in a litre of water with heating. A solution of the mercuric oxide in 140 c.c. of 20% acetic acid was added and the resulting suspension boiled under reflux until completely soluble in dilute sodium hydroxide (100 hrs.). The anhydro-7-methoxy-8-hydroxymercuri-1-naphthoic acid was filtered off, washed with water and dried.

Yield: 79·5 gm. (90%).



e) Bromination of the mercury compound.

(Davies, Heilbron and Irving, loc. cit.)

30 gm. mercury compound.

400 c.c. glacial acetic acid.

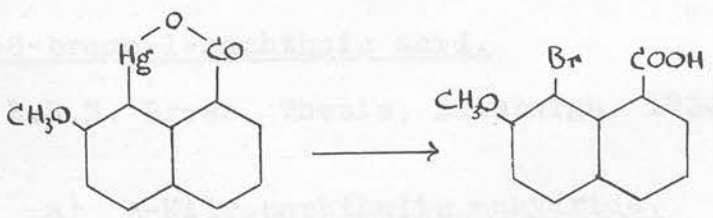
14 gm. bromine.

The mercury compound was suspended in the boiling glacial acetic acid and a solution of the bromine in 75 c.c. concentrated aqueous sodium bromide run in over 15 minutes. The suspension gradually went into solution and, when no solid remained, the solution was poured into a litre of cold water and the light brown precipitate filtered off, washed well with water and dried.

Weight: 18 gm. M.p. 191-194°C (decomp.).

The product was crystallised from alcohol (100 c.c.) to give almost colourless needles of the pure 7-methoxy-8-bromo-1-naphthoic acid.

Yield: 14 gm. (65%). M.p. 196-197°C.



Methyl 7-methoxy-8-bromo-1-naphthoate.

25 gm. 7-methoxy-8-bromo-1-naphthoic acid.

50 c.c. thionyl chloride (purified).

90 c.c. methyl alcohol (dry).

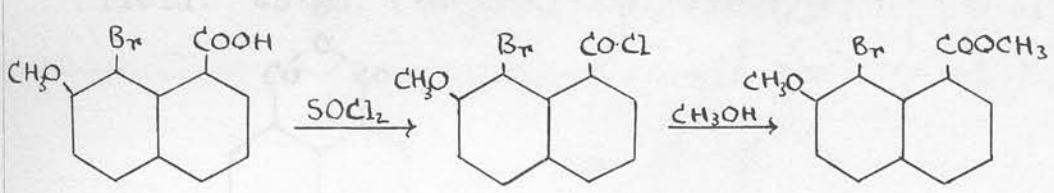
The acid chloride was formed as described in the preparation of the 8-bromonaphthoate (p. 62). After treatment with methyl alcohol, the ester was extracted as before and the dry ethereal solution yielded the solid ester on evaporation.

Yield: 25 gm. (95%). M.p. 73-75°C.

The ester crystallises in stout colourless needles from petroleum ether (b.p. 60-80°C), m.p. 79°C.

Analysis (Ter Meulen): found, Br, 27·0% ;

calculated for $C_{13}H_{11}O_3Br$ 27·1%.



3-Nitro-8-bromo-1-naphthoic acid.

(cf. R.R.H. Brown, Thesis, Edinburgh, 1934).

a) 3-Nitronaphthalic anhydride.

(Leuck, Perkins and Whitmore, J.A.C.S., 1929, 51, 1831).

50 gm. naphthalic acid.

500 c.c. concentrated sulphuric acid.

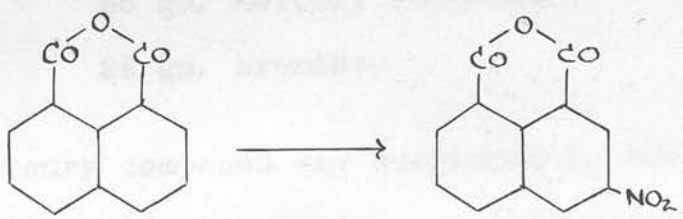
22 gm. sodium nitrate.

The naphthalic acid used was that supplied by British Drug Houses, Ltd., and contained a proportion of the anhydride. It was dissolved in the sulphuric acid and the sodium nitrate gradually added with stirring, the temperature being maintained below 20 °C. After the addition, the mixture was heated on the boiling water-bath for 15 minutes, allowed to cool and poured on ice when a yellow solid separated. It was filtered off, washed acid-free and dried at 100 °C. The crude product was then heated with 250 c.c. toluene to the boiling point, filtered hot and washed with benzene and dried.

Yield: 48 gm. M.p. 247-250 °C.

The pure anhydride was obtained by crystallisation from nitrobenzene (100 c.c.).

Yield: 45 gm. (75-80%). M.p. 252-253°C.



b) Mercuration of the naphthalic anhydride.

(Leuck, Perkins and Whitmore, loc. cit.)

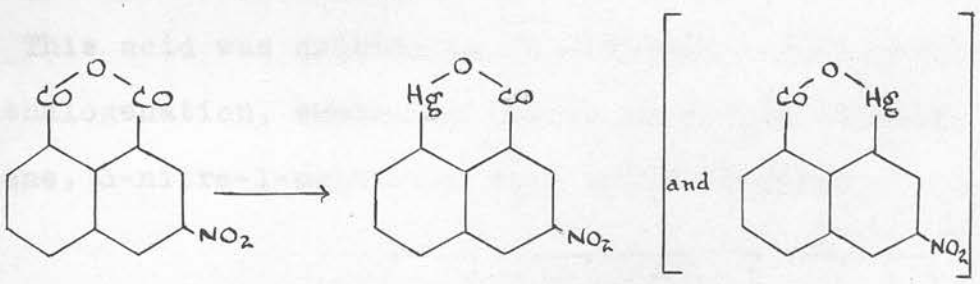
40 gm. 3-nitronaphthalic anhydride.

14 gm. sodium hydroxide.

36 gm. yellow mercuric oxide.

The anhydride and sodium hydroxide were dissolved in a litre of water with heating. The mercuric oxide, dissolved in 120 c.c. water and 40 c.c. glacial acetic acid, was added to the first solution and the mixture made acid with acetic acid. The yellow suspension was refluxed for 100 hours and the mercury compound filtered off, washed with water and dried at 110°C.

Yield: 65 gm. (95%).



c) Bromination of the mercury compound.

(R.R.H. Brown, loc. cit.)

65 gm. mercury compound.

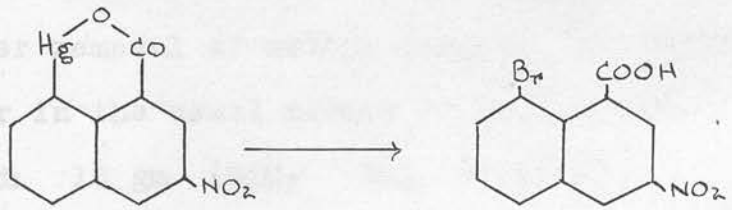
26 gm. bromine.

The mercury compound was suspended in 600 c.c. glacial acetic acid at ordinary temperature and the bromine, dissolved in 160 c.c. concentrated aqueous sodium bromide solution, run in with stirring over one hour. The mixture was then heated at 90°C for 15 minutes and the clear solution poured into 1500 c.c. cold water. The yellow precipitate was filtered, washed with water and dried.

Weight: 36 gm. M.p. 218-225°C.

The product was crystallised twice from glacial acetic acid when pure 3-nitro-8-bromo-1-naphthoic acid was obtained in the form of yellow plates.

Yield: 19 gm. (40%). M.p. 239-241°C.



This acid was orientated (R.R.H.Brown, loc. cit.) by dehalogenation, employing copper bronze in boiling toluene, 3-nitro-1-naphthoic acid being obtained.

Methyl 3-nitro-8-bromo-1-naphthoate.

(cf. R.R.H. Brown, loc. cit.)

15 gm. 3-nitro-8-bromo-1-naphthoic acid.
30 c.c. thionyl chloride (purified).
50 c.c. methyl alcohol (dry).

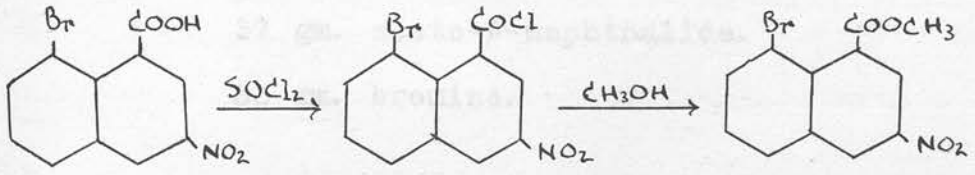
R.R.H. Brown (loc. cit.) reports that difficulty was experienced in forming the acid chloride of the nitro-acid. After several attempts to improve the yield, it was found that the acid chloride formed as readily as in the case of the 8-bromonaphthoic acid, provided the nitro-acid was first moistened with a few drops of water.

The moistened acid was refluxed with the thionyl chloride for half-an-hour, when complete solution

occurred. On removing the thionyl chloride by distillation the solid acid chloride was obtained. It was powdered in a mortar, placed in a flask with the methyl alcohol and refluxed for 30 minutes. The product, after removal of methyl alcohol, was extracted with ether in the usual manner to give a yellow solid.

Yield: 15 gm. (95%) M.p. 171-172°C.

The pure ester was obtained in yellow needles by crystallising from glacial acetic acid, m.p. 173°C.



1-Bromo-2-naphthoic acid.

a) Aceto-β-naphthalide.

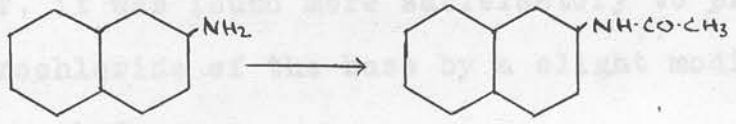
(Franzen and Eidis, J.,pr. Chem., 1913, 88, 755)

100 gm. β-naphthylamine.
70 gm. acetic anhydride.

The naphthylamine was dissolved in 250 c.c. benzene by heating on the water-bath and the acetic anhydride was added in portions with stirring, a vigorous reaction occurring. After the addition, the mixture was allowed

to cool and the colourless crystalline mass was filtered. The precipitate was washed with benzene and dried.

Yield: 120 gm. (95-100%). M.p. 133°C.



b) Aceto-1-bromo-2-naphthalide.

(Franzen and Eidis, loc. cit.)

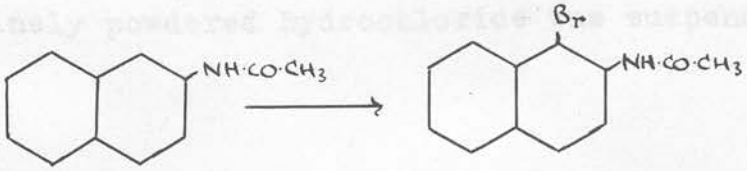
37 gm. aceto-β-naphthalide.

33 gm. bromine.

The aceto-β-naphthalide was dissolved in 200 c.c. chloroform with heating and the bromine, dissolved in 40 c.c. chloroform, was run in with stirring over 15 minutes. The stirring was continued until the mixture had cooled and the precipitate was filtered off. The product weighed 60-65 gm. at this stage and appeared to contain some of the hydrobromide of the naphthalide. It was stirred with 200 c.c. dilute sodium carbonate solution till effervescence ceased then filtered off, washed well with water and dried.

Yield: 52 gm. (95-100%). M.p. 138°C.

The compound crystallises from alcohol in colourless needles, m.p. 140°C.

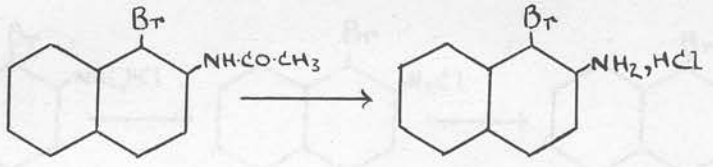


c) Hydrolysis of the bromonaphthalide.

The hydrolysis to the free base is described by Franzen and Eidis (loc. cit.). For the present purpose, however, it was found more satisfactory to prepare the hydrochloride of the base by a slight modification of the method.

The naphthalide (20 gm.) was dissolved in 100 c.c. alcohol with heating. Concentrated hydrochloric acid (25 c.c.) was added and the mixture refluxed for one hour when crystals of the hydrochloride separated. Most of the alcohol was then removed on the steam-bath and the hydrochloride was filtered off, washed with a little alcohol and dried.

Yield: 19 gm. (95-100%). M.p. 219-220°C (decomp.)



d) 1-Bromo-2-naphthonitrile.

50 gm. bromonaphthylamine hydrochloride.

20 gm. sodium nitrite in 25 c.c. water.

(i) 120 gm. sodium cyanide in 300 c.c. water

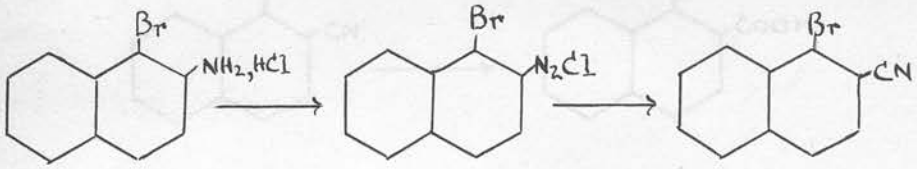
(ii) 100 gm. copper sulphate ($CuSO_4,5H_2O$) in 400 c.c. water.

The finely powdered hydrochloride was suspended

in 150 c.c. water and 50 c.c. 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 3 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.



e) 1-Bromo-2-naphthoic acid.

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

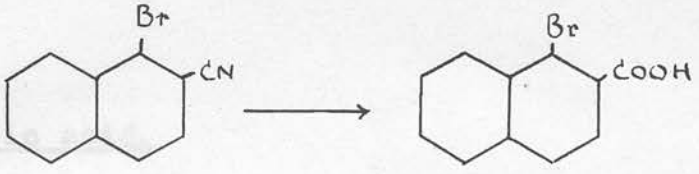
400 c.c. glacial acetic acid.
200 c.c. concentrated sulphuric acid.
100 c.c. water.

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 c.c. 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. For conversion to the ester, however, it was found more economical to esterify the crude acid and purify the ester. The acid has already been prepared (Mayer and Sieglitz, Ber., 1922, 55, 1836) by oxidising the corresponding aldehyde, the melting point quoted being 186°C.



Methyl 1-bromo-2-naphthoate.

15 gm. 1-bromo-2-naphthoic acid (m.p. 187-189°C).
30 c.c. thionyl chloride (purified).
50 c.c. methyl alcohol (dry).

The ester was formed by way of the acid chloride

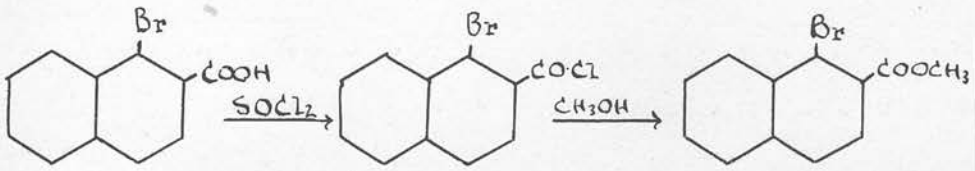
as described in the preparation of the 8-bromo-1-naphthoate. It was necessary, however, to filter the ethereal extract and the ester was obtained as a red solid on removing the ether. It was purified by extraction with petroleum ether (b.p. 40-60°C).

Yield: 14 gm. (90%). M.p. 58-59°C.

The ester crystallised from light petroleum ether in colourless plates, melting at 60°C.

Analysis (Ter Meulen): found, Br, 30·0%;

calculated for $C_{12}H_9O_2Br$ 30·2%.



o-Iodobenzoic acid.

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

80 gm. anthranilic acid.

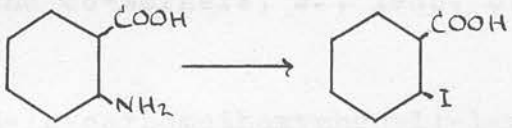
40 gm. sodium nitrite in 100 c.c. water.

100 gm. potassium iodide in 250 c.c. water.

The anthranilic acid was dissolved in dilute sulphuric acid (125 c.c. conc. acid in 625 c.c. water) and cooled to 0-5°C in ice. The fine suspension which formed was diazotised in the normal manner until a slight excess of nitrite was present. The potassium

iodide solution was then run in with stirring and the mixture allowed to stand overnight. The reaction was completed by warming on the steam-bath till effervescence ceased. Free iodine was then removed with sodium bisulphite and the iodo-acid was filtered off and crystallised from dilute acetic acid.

Yield: 120 gm. (80%). M.p. 160°C.



Methyl o-iodobenzoate.

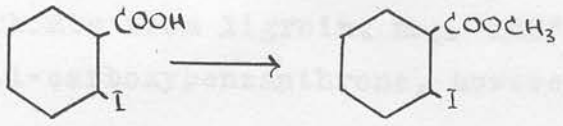
(Cohen and Raper, loc. cit.)

50 gm. o-iodobenzoic acid.
200 gm. methyl alcohol.
20 gm. concentrated sulphuric acid.

The mixture was boiled under reflux for 15 hours, after which most of the alcohol was removed on the steam-bath. The residue was poured into water and the liquid ester taken up in ether. The ethereal extract was washed with dilute alkali, then with water and dried.

Ether was removed on the steam-bath and the ester distilled under reduced pressure to give a colourless liquid.

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



11-Carboxybenzanthrone and 11-Carbomethoxybenzanthrone.

(Rule and co-workers, J., 1935, 571, 573)

a) Methyl 8-(o-carbomethoxyphenyl)-1-naphthoate.

50 gm. methyl o-iodobenzoate (2 mol.).

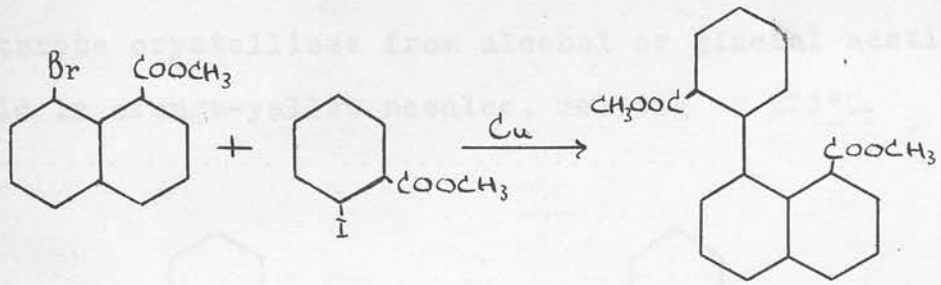
25 gm. methyl 8-bromo-1-naphthoate (1 mol.).

30 gm. copper bronze.

The mixed esters were heated with stirring in an oil-bath at 160°C. The copper was added in portions over a period of one hour and when addition was complete the temperature of the bath was raised to 175-180°C. The mixture was maintained with stirring for a further 4 hours at the latter temperature. The reaction product was boiled out with 200 c.c. acetone (in 3 portions) and the insoluble inorganic matter filtered off. Acetone was removed from the filtrate by heating in vacuo and the warm syrupy residue was treated with 25 c.c. ether when crystals immediately deposited. After standing overnight, these were filtered off, washed with a little ether and dried.

Yield: 22.5 gm. M.p. 131-132°C.

The pure phenylnaphthyl dicarboxylate crystallises in colourless rhombs from ligroin, m.p. 133°C. For conversion to 11-carboxybenzanthrone, however, there is no need to purify the product.



b) <u>11-Carboxybenzanthrone.</u>

10 gm. mixed esters from a).
80 c.c. sulphuric acid (96%).

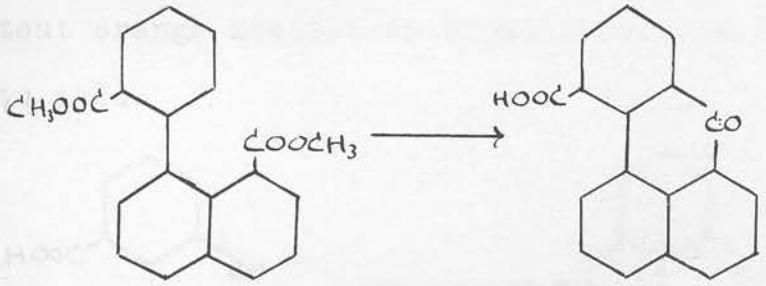
The mixture was heated with stirring at 100°C for one hour and the red solution poured into water. The yellow precipitate was filtered off, added to 500 c.c. water and the mixture made distinctly alkaline with sodium hydroxide. The insoluble portion, after warming to 60°C for a few minutes, was filtered off and washed with warm water. It consisted largely of anthanthrone. The filtrate, which was coloured red owing to traces of lactone, was carefully acidified till the red colour disappeared and the slight precipitate was removed. On further acidification, the filtrate

yielded the 11-carboxybenzanthrone.

Yield acid: 8·2 gm. (71%). M.p. 271-272°C.

Yield crude anthanthrone: 0·2 gm. (2%).

The yields quoted are based on the bromonaphthoate used in the previous experiment. 11-Carboxybenzanthrone crystallises from alcohol or glacial acetic acid in orange-yellow needles, melting at 273°C.



By carrying out the cyclisation of the mixed esters at 50°C instead of 100°C and crystallising the product obtained on pouring into water, 11-carbomethoxybenzanthrone was obtained. Crystallisation from alcohol gave the pure exter in orange needles.

Yield: 65% theory. M.p. 160°C.

1:11-Ketobenzanthrone.

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

4 gm. 11-carboxybenzanthrone.

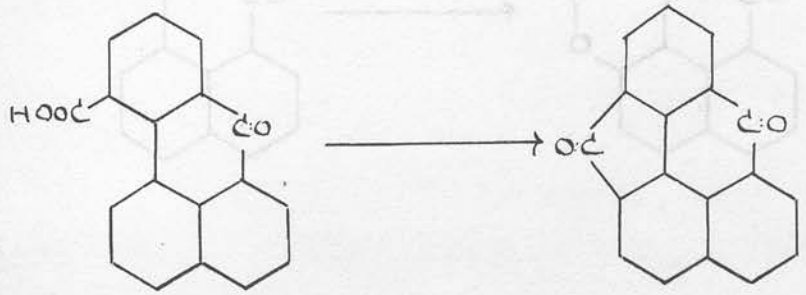
80 gm. phthalic anhydride.

4·7 gm. phosphorus pentoxide.

The acid was dissolved in the phthalic anhydride with stirring at 200°C and the phosphorus pentoxide added in two portions at an interval of 30 minutes. After 2 hours, the dark mixture was cooled somewhat and poured into a solution of 50 gm. sodium hydroxide in 450 c.c. water. The orange precipitate was filtered off, washed well with hot water and dried.

Yield: 3.45 gm. (92%). M.p. 325-327°C.

The pure ketone, melting at 327-328°C, was obtained in stout orange needles on crystallisation from glacial acetic acid.



The lactone of 1-hydroxy-11-carboxybenzanthrone.

(Rule and Bigelow, loc. cit.)

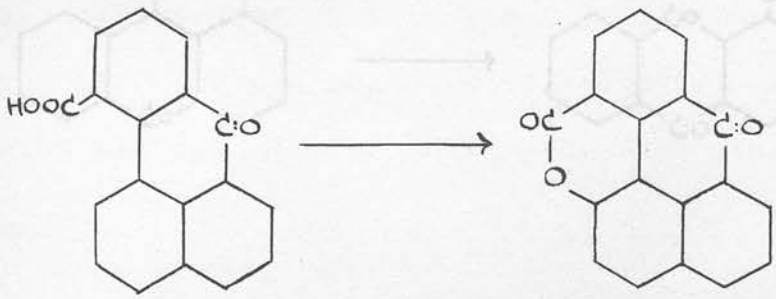
2 gm. 11-carboxybenzanthrone.
20 c.c. concentrated sulphuric acid.
8 gm. chromic acid.

The carboxybenzanthrone was dissolved in the sulphuric acid with heating and a fine suspension obtained

by adding 160 c.c. water. To this suspension at the boiling point, the chromic acid was added in portions and the mixture was gently refluxed for 12 hours. The product was then diluted with water and the pink precipitate of lactone filtered off.

Yield: 1·20 gm. (60%). M.p. 340-350°C.

It was crystallised from glacial acetic acid thrice to form fine yellow brown needles, m.p. 356°C (40% yield).



Anthraquinone-1-carboxylic acid.

(Perkins, J., 1920, 706)

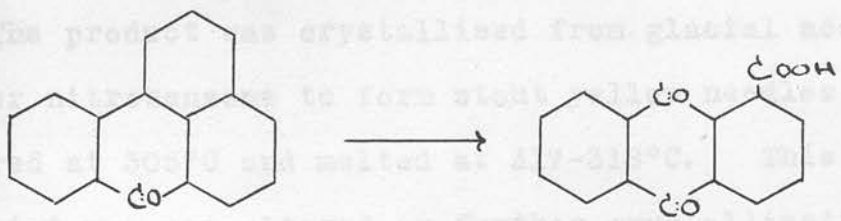
2 gm. benzanthrone.

10 gm. chromic acid.

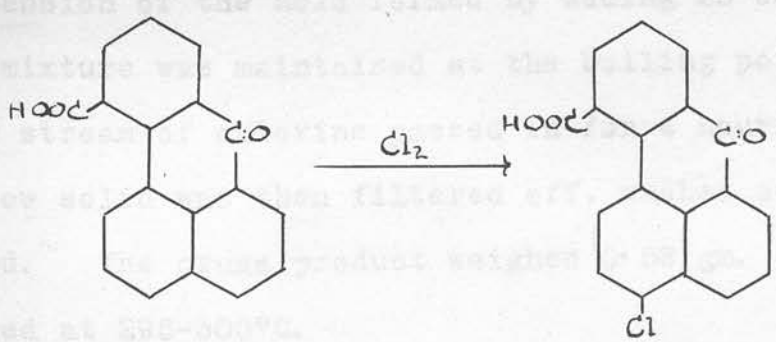
A solution of the benzanthrone in 20 c.c. boiling glacial acetic acid was slowly treated with a solution of the chromic acid in 20 c.c. of 50% acetic acid over 3 hours. The product was then diluted with water and cooled overnight. The precipitate was collected, extracted with the minimum of dilute ammonia and filtered.

On acidification with hydrochloric acid, the filtrate deposited a light yellow precipitate of the carboxylic acid. The pure anthraquinone-1-carboxylic acid was obtained in fine, almost colourless needles by crystallisation first from concentrated nitric and then from alcohol.

Yield: 1·0 gm. (46%). M.p. 293-294°C.



Chlorination of 11-Carboxybenzanthrone: 3-Chloro-11-carboxybenzanthrone.



1) Chlorination in glacial acetic acid.

11-Carboxybenzanthrone (1 g.) was dissolved in glacial acetic acid (50 c.c.) with heating. The solution was maintained at 100°C on the boiling water-bath

and chlorine slowly passed in. After a few minutes, a yellow crystalline deposit formed and the chlorine stream was stopped after a further 10 minutes. The mixture was then allowed to cool and the crystals were filtered off, washed with a little acetic acid and dried.

Yield: 0·73 gm. (63%). M.P. 307-309°C.

The product was crystallised from glacial acetic acid or nitrobenzene to form stout yellow needles which sintered at 305°C and melted at 317-318°C. This melting point was not altered on further crystallisation.

2) Chlorination in aqueous suspension.

11-Carboxybenzanthrone (0·5 gm.) was dissolved in 5 c.c. concentrated sulphuric acid by warming and a fine suspension of the acid formed by adding 25 c.c. water. The mixture was maintained at the boiling point and a slow stream of chlorine passed in for 4 hours. The yellow solid was then filtered off, washed acid-free and dried. The crude product weighed 0·58 gm. (100%) and melted at 295-300°C.

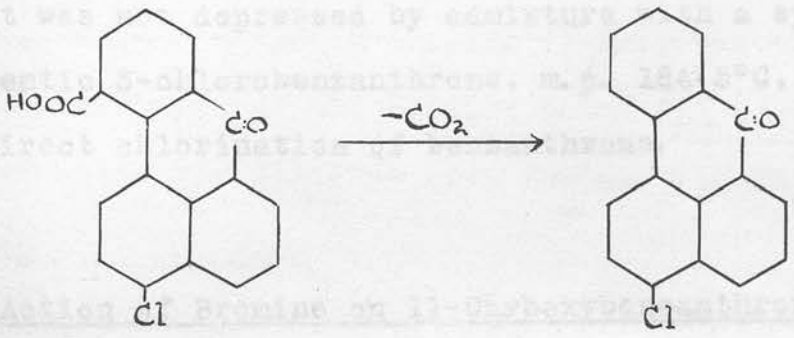
The pure 3-chloro-11-carboxybenzanthrone was obtained in yellow needles by crystallisation from nitrobenzene.

Yield: 0·42 gm. (74%). M.p. 317-318°C.

Analysis (Hein): found, Cl, 11·3%;
calculated for $C_{18}H_9O_3Cl$, 11·5%.

The products from experiments 1) and 2) were identical, a mixed melting point with specimens of the two showing no depression. The 3-chloro-acid dissolves in alkalis to give a yellow solution with a vivid green fluorescence. In concentrated sulphuric acid, a bright red colouration is produced, the solution also showing a green fluorescence.

Decarboxylation of 3-Chloro-11-carboxybenzanthrone: 3-Chlorobenzanthrone.



1 gm. 3-chloro-11-carboxybenzanthrone.
10 c.c. dry quinoline.
0·3 gm. copper bronze.

The acid was dissolved in the quinoline in a pyrex test-tube and the mixture heated to the boiling point in an oil-bath. The copper was then added in portions when vigorous effervescence occurred and after 5 minutes the mixture darkened somewhat. The tube was

immediately removed from the bath and the cooled contents were poured into dilute hydrochloric acid. The brown solid which separated was filtered off, washed with warm alkali, then with water and dried. It was dissolved in 20 c.c. glacial acetic acid by boiling and the solution was filtered from the copper. The filtrate on cooling deposited fine brown needles.

Yield: 0·48 gm. (56%). M.p. 181-182°C.

The compound was crystallised from glacial acetic acid and chlorobenzene to give light brown needles of pure 3-chlorobenzanthrone, m.p. 184°C. This melting point was not depressed by admixture with a specimen of authentic 3-chlorobenzanthrone, m.p. 184·5°C, prepared by direct chlorination of benzanthrone.

The Action of Bromine on 11-Carboxybenzanthrone.

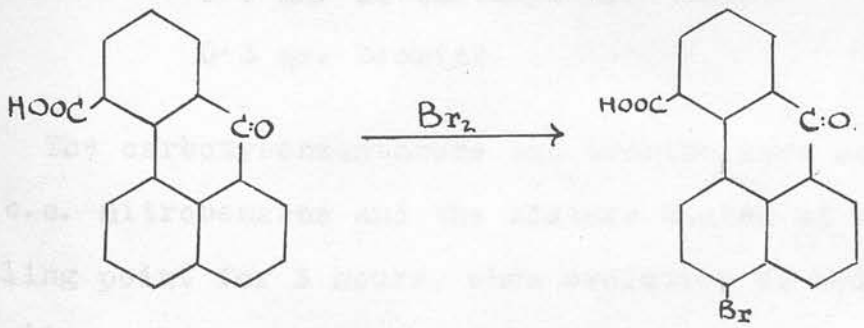
A variety of experiments were carried out before a successful bromination of the acid was obtained. Treatment of the acid with excess bromine in boiling glacial acetic acid resulted only in bromination of the solvent and the 11-carboxybenzanthrone was recovered unchanged. The action of the calculated amount of bromine under pressure at 150°C led to the formation of a mixture of 3-bromo-11-carboxybenzanthrone and the lactone of 1-hydroxy-11-carboxybenzanthrone.

1) Bromination in aqueous suspension: 3-bromo-11-carboxybenzanthrone.

A first experiment, in which 0·5 gm. 11-carboxybenzanthrone in aqueous suspension was boiled with 0·3 gm. bromine for one hour, resulted in the recovery of the material unchanged. Under these conditions, benzanthrone is readily brominated, according to D.P.193959 (C., 1908, I, 1112).

In a later experiment, a fine suspension of 11-carboxybenzanthrone (0·5 gm.) was formed by dissolving the acid in 5 c.c. concentrated sulphuric acid and adding 25 c.c. water. Excess bromine (1 gm.) was added and the mixture kept at the boiling point for 5 hours. The yellow solid was filtered off, washed with water and dried.

Yield: 0·63 gm. (98%). M.p. 293-298°C.



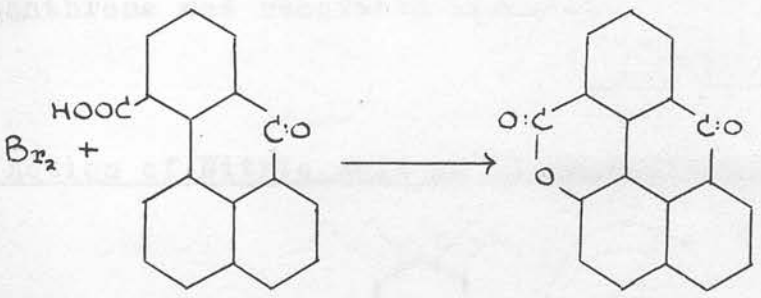
The pure 3-bromo-11-carboxybenzanthrone was obtained by crystallisation of the product from nitro-

benzene when it formed yellow needles, sintering at 305°C and melting at 315-316°C.

Yield: 0·45 gm. (70%).

The acid was identical with the synthetic product of F.R. Smith (loc. cit.) admixture with a specimen of which, melting at 315-316°C, did not depress the melting point.

2) Action of bromine in nitrobenzene: the lactone of 1-hydroxy-11-carboxybenzanthrone.



0·5 gm. 11-carboxybenzanthrone.

0·3 gm. bromine.

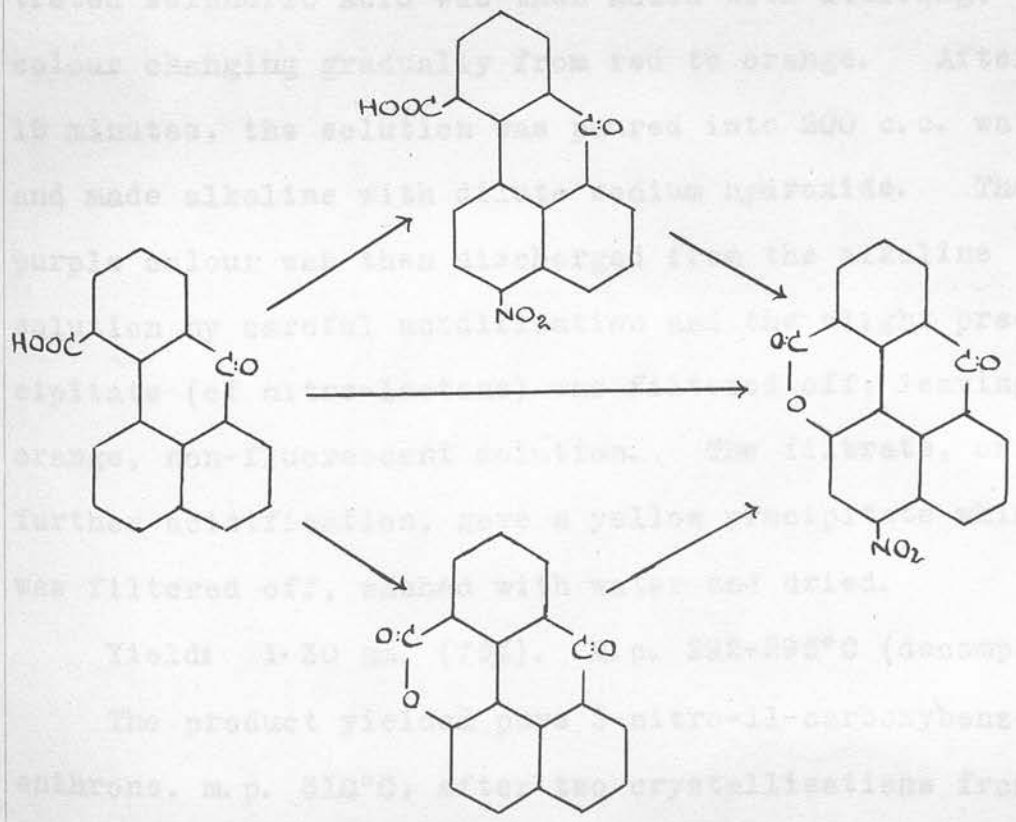
The carboxybenzanthrone and bromine were added to 25 c.c. nitrobenzene and the mixture heated at the boiling point for 3 hours, when evolution of hydrogen bromide could no longer be detected. The solution was allowed to cool, ether (5 c.c.) was added and the mixture chilled in ice when fine yellow needles separated. These were filtered off, washed with ether and dried.

Yield: 0·30 gm. (60%). M.p. 348-351°C.

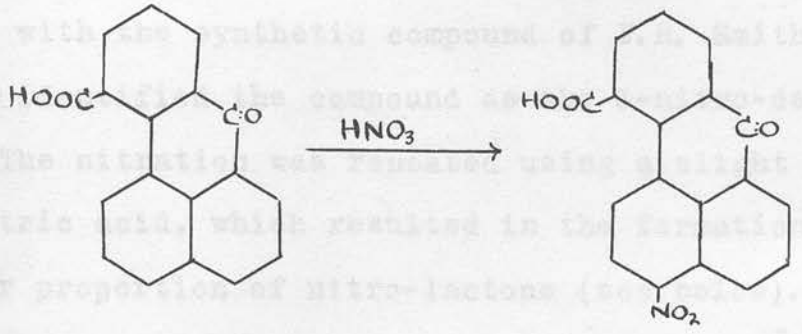
The product on repeated crystallisation from glacial acetic acid gave yellow needles, melting at 356°C. It dissolved in aqueous alkali only on boiling to give a purple, fluorescent solution and was identical with the product of chromic acid oxidation of 11-carboxybenzanthrone (p. 82), a mixed melting point with which confirmed the identity, there being no depression.

That the oxidation was not brought about by the nitrobenzene was shown by a repeat experiment in which the bromine was omitted. In this case the 11-carboxybenzanthrone was recovered unchanged.

The Action of Nitric Acid on 11-Carboxybenzanthrone.



1) <u>3-Nitro-11-carboxybenzanthrone.</u>



1·5 gm. 11-carboxybenzanthrone.

0·42 cc. nitric acid (S.G. 1·42).

The 11-carboxybenzanthrone was dissolved in 30 c.c. concentrated sulphuric acid and the solution cooled to 0°C in ice. A cooled solution of the nitric acid (the calculated amount for mono-nitration) in 5 c.c. concentrated sulphuric acid was then added with stirring, the colour changing gradually from red to orange. After 15 minutes, the solution was poured into 200 c.c. water and made alkaline with dilute sodium hydroxide. The purple colour was then discharged from the alkaline solution by careful acidification and the slight precipitate (of nitro-lactone) was filtered off, leaving an orange, non-fluorescent solution. The filtrate, on further acidification, gave a yellow precipitate which was filtered off, washed with water and dried.

Yield: 1·30 gm. (75%). M.p. 292-295°C (decomp.).

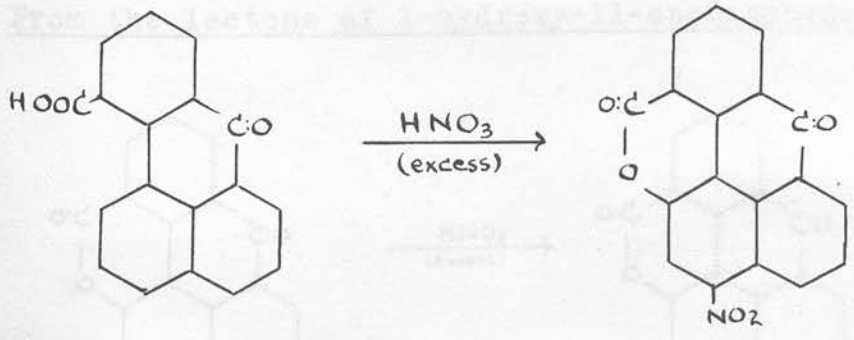
The product yielded pure 3-nitro-11-carboxybenzanthrone, m.p. 310°C, after two crystallisations from

nitrobenzene, the yield being reduced to 45-50%. A comparison of colour reactions and a mixed melting point with the synthetic compound of F.R. Smith (loc. cit.) identified the compound as the 3-nitro-derivative.

The nitration was repeated using a slight excess of nitric acid, which resulted in the formation of a larger proportion of nitro-lactone (see below). The lactone was also formed to a larger extent if the temperature of the nitration were allowed to rise. Attempts were made to increase the yield of 3-nitro-acid by nitration in nitrobenzene solution. Under conditions in which benzanthrone is readily nitrated, however, the acid was not attacked and on heating to 120°C, a vigorous reaction occurred accompanied by oxidation. No pure compound could be isolated from the product, which dissolved in alkali on boiling to give a purple solution similar to that of the nitro-lactone.

2) The lactone of 3-nitro-1-hydroxy-11-carboxybenzanthrone.

a) From 11-carboxybenzanthrone.



11-Carboxybenzanthrone (0·5 gm.) was added to 10 c.c. concentrated nitric acid and the temperature raised to the boiling point, when solution occurred. The yellow, non-fluorescent solution was maintained at the boiling point for 15 minutes when nitrous fumes ceased to be evolved. It was then poured into water and the yellow precipitate collected. The product weighed 0·55 gm. and melted at 279-290°C (decomp.). It was crystallised from glacial acetic acid (twice) to give yellow needles.

Yield: 0·36 gm. (62%). M.p. 317-318°C (decomp).

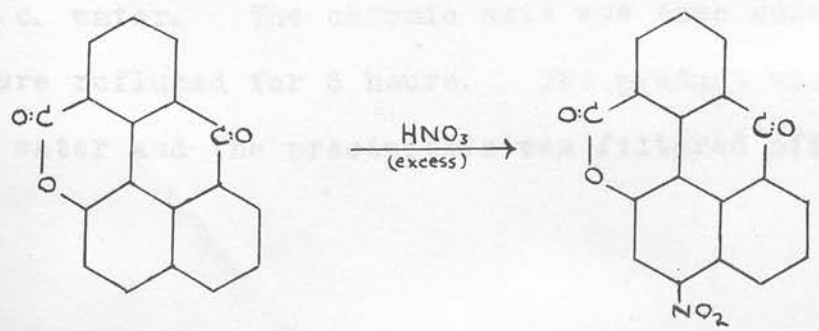
Analysis (micro-Dumas): found, N, 4·4%;

calculated for $C_{18}H_7O_5N$, 4·4%.

The nitro-lactone dissolves in aqueous alkali only on boiling to give a purple, non-fluorescent solution. In concentrated sulphuric acid, it forms an orange solution also showing no fluorescence.

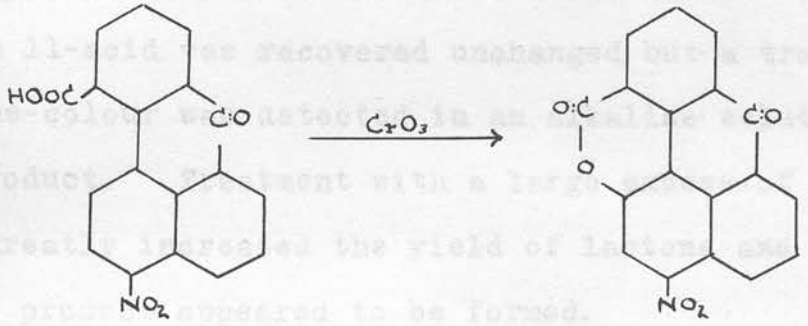
A less pure product was obtained on treating the 11-carboxybenzanthrone, dissolved in concentrated sulphuric acid, with a large excess of nitric acid. On repeated crystallisation the 3-nitro-lactone was again obtained.

b) From the lactone of 1-hydroxy-11-carboxybenzanthrone.



The lactone (0·25 gm.) was treated with concentrated nitric acid (5 c.c.) for 15 minutes at the boiling point. The yellow solution was then poured into water and the precipitated nitro-lactone collected. The crude product weighed 0·26 gm. (90%) and melted at 280-287°C (decomp.). After two crystallisations from glacial acetic acid, the product gave yellow needles of the pure 3-nitro-lactone, m.p. 317-318°C. This melting point was not depressed by admixture with the product of experiment a).

c) <u>From 3-nitro-11-carboxybenzanthrone.</u>



0·2 gm. 3-nitro-11-carboxybenzanthrone.

1 gm. chromic acid.

The nitro-acid was dissolved in 5 c.c. concentrated sulphuric acid and a fine suspension formed by adding 25 c.c. water. The chromic acid was then added and the mixture refluxed for 3 hours. The product was diluted with water and the precipitate was filtered off, washed

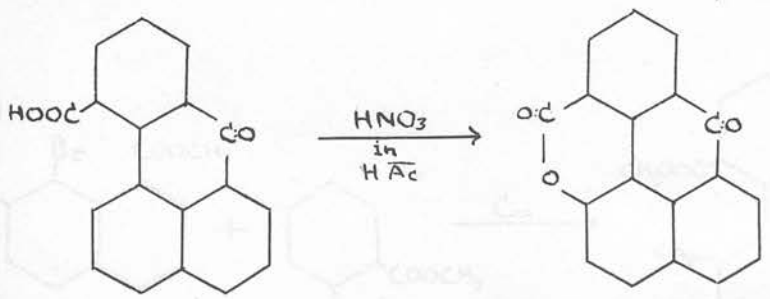
with water and dried.

Yield: 0·12 gm. (60%). M.p. 280-290°C (decomp.).

The product on crystallisation from glacial acetic acid gave yellow needles of the 3-nitro-lactone, m.p. 317-318°C (decomp.), identical with the products of experiments a) and b).

3) The lactone of 1-hydroxy-11-carboxybenzanthrone.

In an attempt to nitrate 11-carboxybenzanthrone in glacial acetic acid, under conditions which yield the 2-nitro-derivative with benzanthrone, a portion of the acid was treated with a slight excess of nitric acid in glacial acetic acid and refluxed for 1 hour. The bulk of the 11-acid was recovered unchanged but a trace of lactone-colour was detected in an alkaline solution of the product. Treatment with a large excess of nitric acid greatly increased the yield of lactone and no nitration product appeared to be formed.



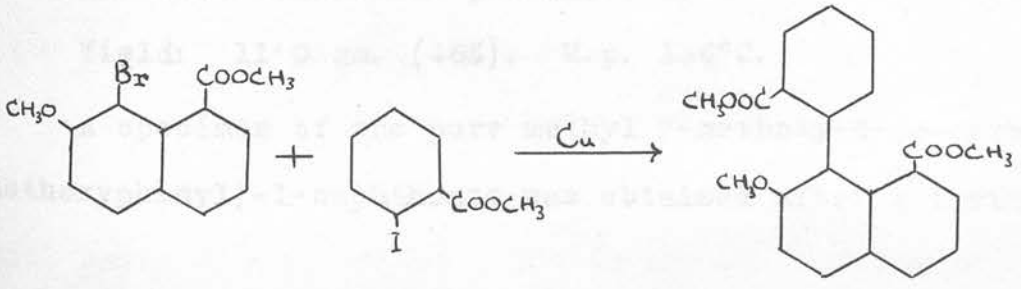
0·5 gm. 11-carboxybenzanthrone
25 c.c. glacial acetic acid.
10 c.c. nitric acid (S.G. 1·42).

A solution of the acid in the acetic acid at the boiling point was treated with 5 c.c. of the nitric acid and after 2 hours the remainder of the nitric acid was added. Refluxing was continued for a further 2 hours when nitrous fumes ceased to be evolved. The solution was poured into water and the yellow precipitate was filtered off, washed with water and dried. The product weighed 0·48 gm. and melted at 340-345°C. It was crystallised thrice from glacial acetic acid to give the pure lactone of 1-hydroxy-11-carboxybenzanthrone in light brown needles.

Yield: 0·23 gm. (46%). M.p. 355-356°C.

Synthesis of the Lactone of 1-Hydroxy-11-carboxybenzanthrone and Proof of the Structure of the Oxidation Product of 11-Carboxybenzanthrone.

1) Methyl 7-methoxy-8-(o-carbomethoxyphenyl)-1-naphthoate.



20 gm. methyl 7-methoxy-8-bromo-1-naphthoate.

40 gm. methyl o-iodobenzoate.

25 gm. copper bronze.

The esters were placed in a small flask fitted with an efficient stirrer and the mixture was heated in an oil-bath at 150°C (outside temperature). The copper was added in portions over one hour and when addition was complete the temperature of the bath was raised to 175°C, the stirring being continued throughout. After 3 hours at this temperature, the product was allowed to cool and the inorganic matter removed by extracting with 150c.c. acetone (in 3 portions) and filtering. Acetone was removed from the filtrate by distillation on the water-bath, finally under reduced pressure, and the syrupy residue was treated with 25 c.c. ether. The mixture was "seeded" with a minute crystal of methyl 8-(o-carbomethoxyphenyl)-1-naphthoate and agitated until a crystalline precipitate began to form. After standing overnight, the crystals were filtered off, washed with a little cold ether and dried.

Yield: 12·3 gm. (52%). M.p. 131-133°C.

The product was crystallised from ligroin (150 c.c.) to form stout colourless prisms.

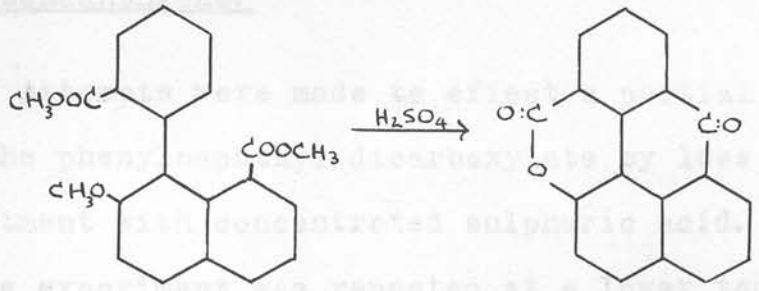
Yield: 11·0 gm. (46%). M.p. 136°C.

A specimen of the pure methyl 7-methoxy-8-(o-carbomethoxyphenyl)-1-naphthoate was obtained after a further

crystallisation from ligroin, the compound melting at 137°C.

Analysis (Schoeller): found, C, 71·9%, H, 5·2%;
calculated for $C_{21}H_{18}O_5$, C, 72·0%, H, 5·2%.

2) The lactone of 1-hydroxy-11-carboxybenzanthrone.



1·5 gm. phenylnaphthyl derivative.
15 c.c. concentrated sulphuric acid (95%).

The phenylnaphthyl derivative was heated with the sulphuric acid at 100°C for half-an-hour with stirring and the blood-red solution was then poured into 150 c.c. water. The yellow precipitate of the lactone was filtered off, washed acid-free and dried.

Yield: 1·17 gm. (100%). M.p. 354-355°C.

The product crystallised from glacial acetic acid (150 c.c.) in fine yellow needles, m.p. 356°C, weighing 1·09 gm. (93%). It proved identical in its properties with the product of oxidation of 11-carboxybenzanthrone with chromic acid (p. 82), giving the characteristic

purple solution in boiling aqueous alkali. A mixed melting point confirmed the identity.

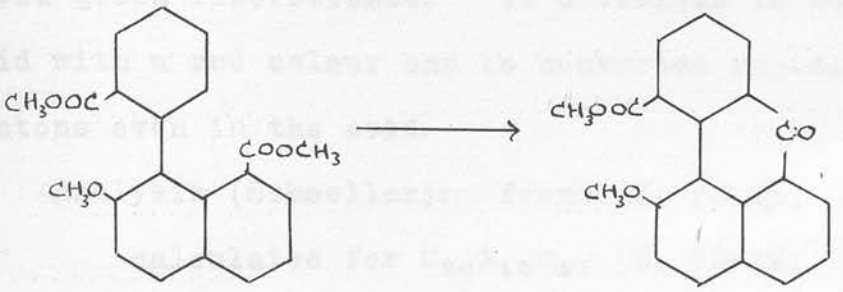
Reactions of Methyl 7-methoxy-8-(o-carbomethoxyphenyl)-1-naphthoate and 1-Methoxy-11-carbomethoxybenzanthrone.

1) Partial cyclisation: 1-methoxy-11-carbomethoxybenzanthrone.

Attempts were made to effect a partial cyclisation of the phenylnaphthyl dicarboxylate by less vigorous treatment with concentrated sulphuric acid. The previous experiment was repeated at a lower temperature but, after 30 minutes at 50°C, the lactone was again obtained in quantitative yield. A portion of the dicarboxylate was treated with concentrated sulphuric acid for 5 minutes at ordinary temperatures and was also converted quantitatively to the lactone. Several small experiments were carried out employing other reagents but the lactone was again obtained by treatment with (a) zinc chloride, on mild fusion in the presence of water, (b) phosphorus pentoxide in nitrobenzene at the boiling point and (c) thionyl chloride on warming for a short period.

Eventually a portion of the methoxy mono-carboxylic ester was obtained by treating the phenylnaphthyl derivative with sulphuric acid, diluted with glacial acetic acid. The yield recorded below, however, was not

always reproduceable, as very slight changes in conditions appeared to affect the reaction strongly.



0·5 gm. phenylnaphthyl derivative.

10·0 c.c. glacial acetic acid.

2·0 c.c. concentrated sulphuric acid.

The ester was dissolved in the acetic acid with heating and the sulphuric acid was added to the warm solution. The temperature was raised to 80°C and the solution maintained at this temperature for 15 minutes. The orange-red solution was then poured into 100 c.c. water to give a semi-solid, yellow precipitate and the mixture was made distinctly alkaline with concentrated sodium hydroxide. After boiling for 10 minutes to dissolve any lactone, the precipitate, which became solid on such treatment, was filtered off, washed with water and dried.

Yield: 0·21 gm. (46%). M.p. 178-190°C.

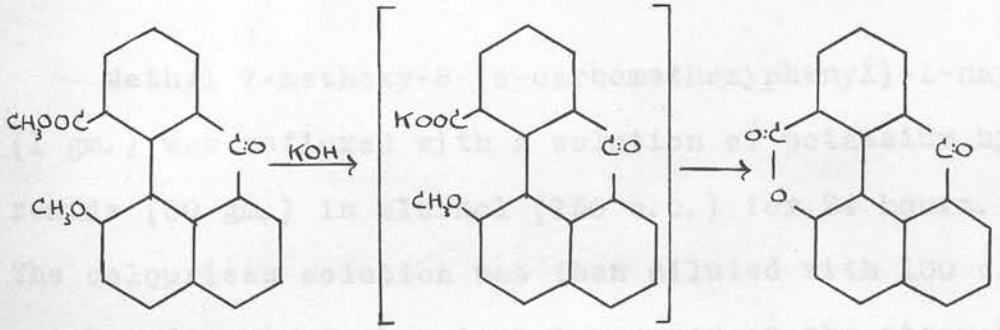
The product crystallised from alcohol in brilliant yellow needles and after two crystallisations, the pure methoxy-carbomethoxy-benzanthrone was obtained.

Yield: 0·06 gm. (13%). M.p. 194°C.

The ester dissolves in alcohol, glacial acetic acid and other solvents to give yellow solutions with a vivid green fluorescence. It dissolves in sulphuric acid with a red colour and is converted rapidly to the lactone even in the cold.

Analysis (Schoeller): found, C, 75·4%, H, 4·4%;
calculated for $C_{20}H_{14}O_4$, C, 75·1%, H, 4·5%.

2) Hydrolysis of 1-methoxy-11-carbomethoxybenzanthrone.



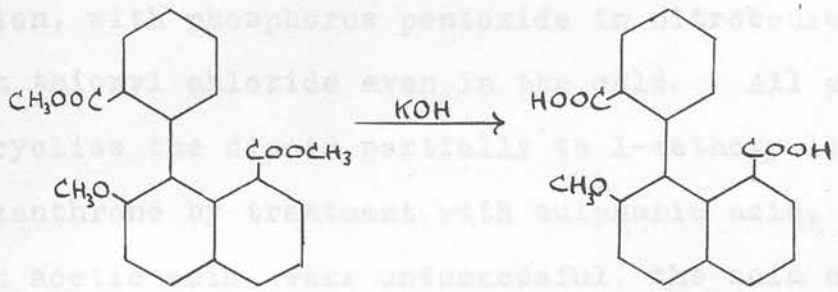
The 1-methoxy-11-carbomethoxybenzanthrone (0·56 gm.) was refluxed with a solution of potassium hydroxide (10 gm.) in alcohol (50 c.c.). The solution gradually assumed the lactone colour and after 5 hours the purple product was diluted with a little water, acidified with hydrochloric acid and the yellow precipitate collected.

Yield: 0·32 gm. (67%). M.p. 345-348°C.

The pure lactone of 1-hydroxy-11-carboxybenzanthrone, m.p. 356°C, was obtained by crystallisation of the product from glacial acetic acid. By further dilution

of the alcoholic filtrate with water, a portion of the unhydrolysed ester (0·10 gm.) was recovered.

3) 7-Methoxy-8-(o-carboxyphenyl)-1-naphthoic acid.



Methyl 7-methoxy-8-(o-carbomethoxyphenyl)-1-naphthoate (1 gm.) was refluxed with a solution of potassium hydroxide (50 gm.) in alcohol (150 c.c.) for 24 hours. The colourless solution was then diluted with 100 c.c. water and most of the alcohol removed on the steam-bath. The residue was acidified with hydrochloric acid and, after cooling, the colourless crystalline deposit which formed was filtered off, washed with cold water and dried.

Yield: 0·75 gm. (82%). M.p. 238-239°C.

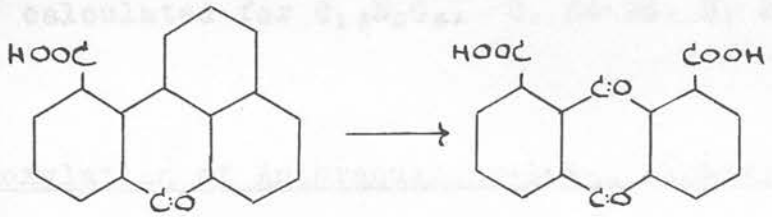
The diacid crystallised from alcohol in colourless rhombs which appeared to contain alcohol of crystallisation, since on rapid melting gas evolution occurred. The crystals were therefore dried at 150°C for 30 minutes and then melted sharply without decomposition at 239°C.

Analysis (Schoeller): found, C, 70·8%, H, 4·4%;
calculated for $C_{19}H_{14}O_5$, C, 70·8%, H, 4·4%.

The acid dissolves in concentrated sulphuric acid with a red colouration, being rapidly converted to the lactone. The lactone of 1-hydroxy-11-carboxybenzanthrone was also formed by treatment with zinc chloride on mild fusion, with phosphorus pentoxide in nitrobenzene and with thionyl chloride even in the cold. All attempts to cyclise the diacid partially to 1-methoxy-11-carboxybenzanthrone by treatment with sulphuric acid, diluted with acetic acid, were unsuccessful, the acid either being left unchanged or converted to the lactone.

Alkaline Oxidation of 11-Carboxybenzanthrone:

Anthraquinone-1:8-dicarboxylic Acid.



1 gm. 11-carboxybenzanthrone.
1 gm. sodium hydroxide.
2 gm. potassium permanganate.

The acid, sodium hydroxide and potassium permanganate were dissolved in 150 c.c. water and the mixture

refluxed for 20 hours. The product was filtered and the yellow, fluorescent filtrate acidified to give a small precipitate of unchanged 11-carboxybenzanthrone (0·2 gm.) which was filtered from the hot solution. The filtrate was then evaporated on the steam-bath almost to dryness and the light yellow precipitate collected.

Yield: 0·095 gm. (9%). M.p. 305-312°C (decomp.)

The acid, which is very soluble in alcohol and hot water, was taken up in 3 c.c. alcohol and the solution allowed to stand overnight. The light yellow octahedra which separated were collected, washed with a little ether and dried.

Yield: 0·042 gm. (4%). M.p. 316-317°C (decomp.).

This melting point was not altered on further crystallisation.

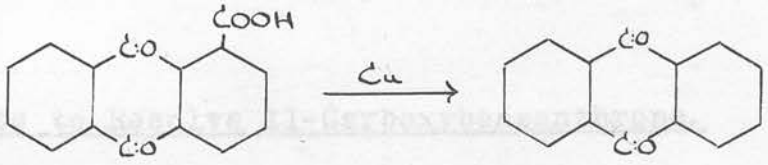
Analysis (Weiler): found, C, 65·0%, H, 2·9%;

calculated for $C_{16}H_8O_6$, C, 64·9%, H, 2·7%.

Decarboxylation of Anthraquinone-1:8-dicarboxylic Acid to Anthraquinone.

Decarboxylation experiments were first carried out with anthraquinone-1-carboxylic acid. A portion of this acid, which melts at 293-294°C, was first heated under reduced pressure in a small sublimation apparatus in the hope that this treatment might prove sufficnent

to remove the carboxyl group. The acid, however, sublimed unchanged at 270°C and 12 mm. pressure, yellow needles melting at 293-294°C being obtained. The unsublimed acid, however, slowly decomposes when maintained above its melting point but the purified product is stable, the decomposition apparently being due to traces of impurities. A trace of copper bronze added to the sublimed product again caused decomposition to occur on melting and, since anthraquinone is a very stable compound, it seemed possible that the decomposition simply involved a loss of carbon dioxide. This proved to be the case.



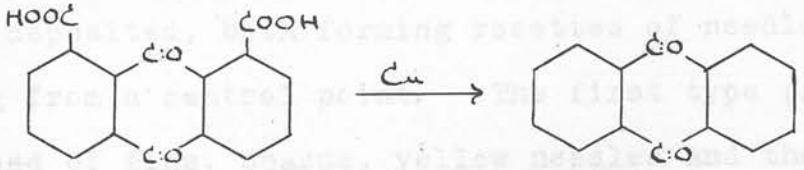
Anthraquinone-1-carboxylic acid (0·1 gm.) was mixed with a few milligrams of copper bronze and the mixture heated at 300°C for 15 minutes in a wide tube placed in a metal-bath. The tube was then removed from the bath and a cooling surface was inserted above the product. The pressure in the tube was then reduced to 12 mm. and the mixture was heated to 270°C when bright yellow needles of anthraquinone collected on the cold surface.

Yield: 0·065 gm. (80%). M.p. 285°C.

The experiment was repeated with the anthraquinone-1:8-dicarboxylic acid (0·1 gm.). It was heated with a trace of copper at 320°C for 5 minutes and the product, on sublimation under reduced pressure, gave yellow needles of a neutral compound.

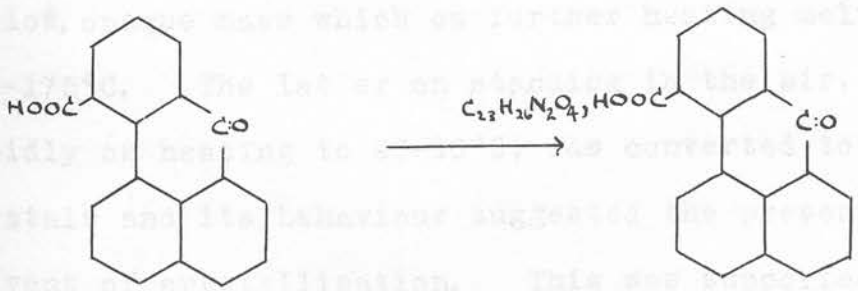
Yield: 0·06 gm. (85%). M.p. 285°C.

In admixture with an authentic specimen of anthraquinone (m.p. 285°C), the melting point was not depressed.



Attempts to Resolve 11-Carboxybenzanthrone.

1) The brucine salt of 11-carboxybenzanthrone.



1 gm. 11-carboxybenzanthrone.

1·3 gm. brucine.

100 c.c. ethyl acetate.

The brucine was dissolved in the ethyl acetate by warming and the solution at the boiling point was treated with the 11-carboxybenzanthrone in portions. The acid gradually dissolved and the yellow solution was filtered from the small residue, evaporated to half its volume and left overnight. Two distinct sets of crystals deposited, both forming rosettes of needles radiating from a central point. The first type (a) was composed of fine, opaque, yellow needles and the second (b) of transparent, orange crystals. These sets of crystals were readily separated under the lens.

(a) Yield: 0·81 gm.

(b) Yield: 0·68 gm.

The product (a) melted over a range of 170-175°C whereas the second (b) decomposed at 100-120°C to give a yellow, opaque mass which on further heating melted at 170-175°C. The latter on standing in the air, or more rapidly on heating to 80-90°C, was converted to opaque crystals and its behaviour suggested the presence of solvent of crystallisation. This was supported by the fact that each set of crystals gave again a mixture of the two types on crystallisation from ethyl acetate.

The specific rotation of the products was deter-

mined in the following manner. A portion of the material (ca. 0·1 gm.) was dissolved in methyl alcohol, which had been purified by refluxing with metallic magnesium and repeated distillation, and the solution was made up to 5 c.c. in a standard flask. The solution was placed in a 2-decimetre polarimeter tube and the rotation, α, was measured using the sodium D line (5893 Å U). The specific rotation was obtained by applying the following formula, where w represents the weight of brucine salt used:

$$\left[\alpha_D\right] = \frac{\alpha \times 5}{w \times 2}$$

In this manner, the products (a) and (b) gave the rotations:

$$\text{(a)} \quad \left[\alpha_D\right] = -18{\cdot}2°$$

$$\text{(b)} \quad \left[\alpha_D\right] = -15{\cdot}9°.$$

If it is assumed that the product (b) contains one molecular proportion of ethyl acetate of crystallisation, i.e. has the formula $C_{41}H_{36}N_2O_7, CH_3COOC_2H_5$, and that the small proportion of ethyl acetate does not affect the rotation in methyl alcohol, then the true specific rotation of the brucine salt in the product (b) is given by:

$$\frac{15{\cdot}9 \times (\text{M.W. of } C_{41}H_{36}N_2O_7, CH_3COOC_2H_5)}{(\text{M.W. of } C_{41}H_{36}N_2O_7)}$$

$$= \frac{15{\cdot}9 \times 756}{668} = -18{\cdot}0°.$$

The similarity of this figure to the specific rotation of the product (a) again suggests that the two compounds are not stereoisomeric forms but that, on crystallisation from ethyl acetate, two forms are simultaneously deposited, one of which contains solvent of crystallisation. This was confirmed by crystallisation of the products from methyl alcohol, which gave identical specimens of the salt in the form of yellow rhombs having the same specific rotation (- 18·2).

The preparation of the brucine salt was repeated on a larger scale and the product was filtered off and dried at 80-90°C. The compound (6·5 gm.) was crystallised repeatedly from methyl alcohol, the rotation in that solvent being taken after each crystallisation. The final product, after 6 crystallisations, weighed 1·5 gm. The specific rotations were practically constant throughout, varying only between the limits - 18·0° and - 18·4°. From methyl alcohol, the salt crystallises in yellow rhombs of one type only, the pure compound melting at 170-175°C.

A portion of the final product was hydrolysed by heating at 60°C with dilute sulphuric acid and after 15 minutes, the 11-carboxybenzanthrone was filtered off, washed free of brucine and dried. It melted at 272-273°C and gave no rotation in alcoholic solution.

A second portion (0·1250 gm.) was examined for mutarotation. It was placed in a small standard

flask, dissolved in pure pyridine and the solution was made up to 5 c.c. with that solvent. It was immediately transferred to the polarimeter tube and the rotation was examined at intervals over 24 hours. The specific rotation, - 67·0°, remained constant during that time.

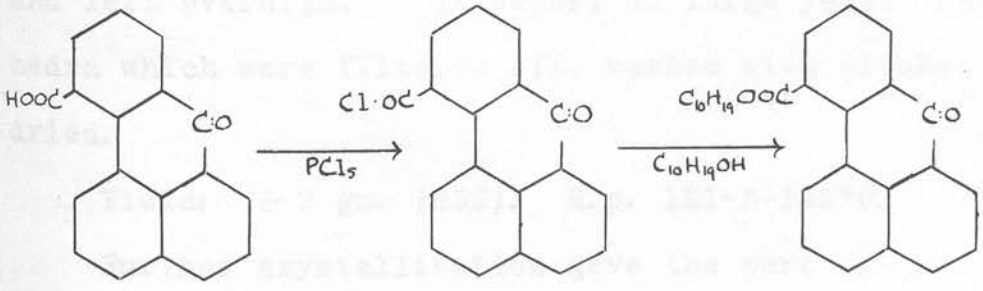
Analysis (Ter Meulen): found, N, 4·0%;

calculated for $C_{41}H_{36}N_2O_7$, 4·2%.

2) The ℓ-menthyl ester of 11-carboxybenzanthrone.

A first attempt to prepare the ester by use of the Fischer-Speier method resulted in the recovery of the acid unchanged. ℓ-Menthol (30 gm.) was heated to 130°C, 11-carboxybenzanthrone (2 gm.) was added and allowed to dissolve. Dry hydrogen chloride was passed in over 30 hours and the menthol was then distilled off in steam. The residue was completely soluble in alkali and the acid was recovered quantitatively.

The ester, however, was readily prepared via the acid chloride.



5 gm. 11-carboxybenzanthrone.

150 c.c. dry benzene (A.R.)

6·5 gm. purified phosphorus pentachloride.

The acid, benzene and phosphorus pentachloride were warmed together on the water-bath at 40°C. The acid gradually dissolved and after 30 minutes the benzene and phosphorus oxychloride were distilled off under diminished pressure, the temperature being maintained below 45°C. The greenish-brown solid residue was dissolved in 100 c.c. dry benzene (A.R.) and excess menthol (6 gm.) added, the solution assuming a green tint. After refluxing for 10 hours, the benzene and excess menthol were removed in steam to leave a light brown, oily product. Dilute sodium hydroxide (20 c.c. of 10% solution) was added and the steam was passed in for a further 15 minutes to dissolve any acid residue. On cooling, the brown oil solidified to a hard cake. It was powdered and dried, the product weighing 7·5 gm. (100%). The crude product was dissolved in 200 c.c. absolute alcohol with heating, the solution filtered and left overnight. It deposited large yellow octahedra which were filtered off, washed with alcohol and dried.

Yield: 6·2 gm. (83%). M.p. 121·5-122°C.

Further crystallisation gave the pure ester melting at 122·5°C.

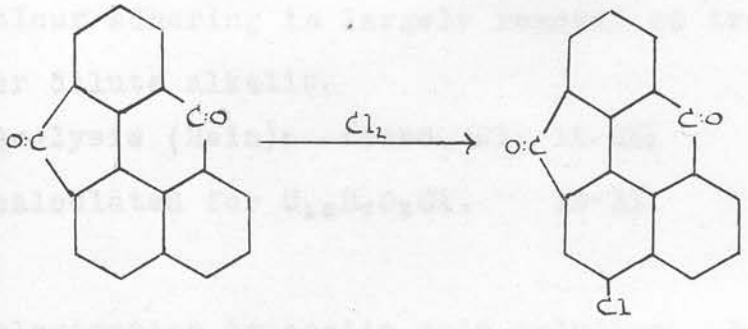
Analysis: found, C, 81·2%, H, 6·6%;
calculated for $C_{28}H_{28}O_3$, C, 81·5%, H, 6·8%.

The ester is readily soluble in chloroform and rotations in this solvent were determined. Approximately 0·1 gm. of the ester was weighed out, dissolved in purified chloroform and the solution was made up to 5 c.c. in a standard flask. The original product, after one crystallisation from alcohol, gave the specific rotation -148·0°. The bulk of the ester (5·5 gm.) was crystallised repeatedly using 150 c.c. absolute alcohol in each case, the rotation being taken after each crystallisation. The product after 6 crystallisations, weighed 1·5 gm. The rotation remained practically constant throughout, varying only between the limits of experimental error, 147·7° — 148·3°, The examination therefore gave no evidence of the existence of stereoisomeric forms of the ester.

Action of Chlorine on 1:11-Ketobenzanthrone.

1) Chlorination in aqueous suspension: 3-chloro-1:11-ketobenzanthrone.

In a first experiment, a portion of 1:11-ketobenzanthrone in aqueous suspension was treated at ordinary temperature with chlorine for 4 hours and the ketone was largely recovered unchanged.



The ketone (0·5 gm.) was dissolved in concentrated sulphuric acid (5 c.c.) by warming and a fine suspension formed by adding 25 c.c. water. To this suspension at the boiling point a slow stream of chlorine was passed in for 3 hours, the orange colour of the solid deepening somewhat. The product was filtered off, washed acid-free and dried. It weighed 0·57 gm. (100%) and melted at 328-332°C with previous sintering at 190°C. It was crystallised twice from glacial acetic acid to form red needles, sintering at 245°C and melting at 335-336°C.

Yield: 0·38 gm. (67%).

Further crystallisation from glacial acetic acid or nitrobenzene did not alter this melting point. The sintering of compounds of this type at temperatures considerably below the melting point has been noted by F.R. Smith (loc. cit.) and appears to be a property of the crystalline form.

3-Chloro-1:11-ketobenzanthrone dissolves in concentrated sulphuric acid to give a red-purple solution. It is incompletely attacked by alkaline hydrosulphite to

give a purplish vat which dyes cotton only faintly orange. The colour adhering is largely removed on treatment with soap or dilute alkalis.

Analysis (Hein): found, Cl, 12·2%;

calculated for $C_{18}H_7O_2Cl$, 12·3%.

2) Chlorination in acetic acid solution: 3-chloro-1:11-ketobenzanthrone, dichloro-1:11-ketobenzanthrones.

0·5 gm. 1:11-ketobenzanthrone.

25 c.c. glacial acetic acid.

The ketone was dissolved in the acetic acid and the solution was maintained at 100°C on the boiling water-bath. Chlorine was slowly passed in for 10 minutes, an orange precipitate appearing after 5 minutes. The mixture was cooled and the precipitate collected.

Yield: 0·30 gm. (53%). M.p. 333-335°C.

Crystallisation from chlorobenzene or glacial acetic acid gave the pure 3-chloro-1:11-ketobenzanthrone in red needles which sintered at 245°C and melted at 335-336°C (Yield: 45%). The compound was identical in its properties with the product of experiment 1, and a mixed melting point showed no depression. The original acetic acid filtrate from the experiment gave a further 0·2 gm. crude product on dilution with water.

The experiment was repeated, the chlorine stream being passed for one hour when the solid gradually

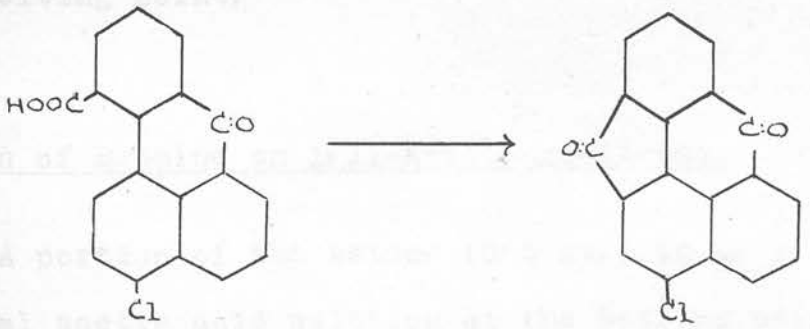
deepened in colour to red-orange. The product weighed 0·48 gm. and melted at 334-339°C, a range of temperature not appreciably altered on repeated crystallisation from nitrobenzene. The product was only slightly soluble in glacial acetic acid and in concentrated sulphuric acid gave a purple solution which, on dilution with sulphuric acid, changed to blue.

Analysis (Hein): found, Cl, 21·3%;

calculated for $C_{18}H_6O_2Cl_2$, 21·8%.

The product, the melting point of which was not depressed by admixture with the 3-chloro-derivative, would appear to be a mixture of isomeric dichloro-compounds.

Cyclisation of 3-Chloro-11-carboxybenzanthrone: 3-Chloro-1:11-ketobenzanthrone.



0·75 gm. 3-chloro-11-carboxybenzanthrone.

15 gm. phthalic anhydride.

1·0 gm. phosphorus pentoxide.

The chloro-acid was dissolved in the phthalic anhydride with heating and the yellow solution was maintained at 200°C with stirring. The phosphorus pentoxide was added in two portions at an interval of 30 minutes, the solution gradually darkening in colour. After 2 hours, the mixture was cooled somewhat and poured into a solution of 10 gm. sodium hydroxide in 100 c.c. water. After digesting for a few minutes at 80-90°C, the orange precipitate was collected, washed well with hot water and dried.

Yield: 0·70 gm. (99%). M.p. 322-326°C.

It was crystallised from chlorobenzene then glacial acetic acid to give red needles which sintered at 245°C and melted at 335-336°C. In its properties, the 3-chloro-1:11-ketobenzanthrone was identical with the mono-chlorination products of 1:11-ketobenzanthrone described above, admixture with specimens of which did not depress the melting point.

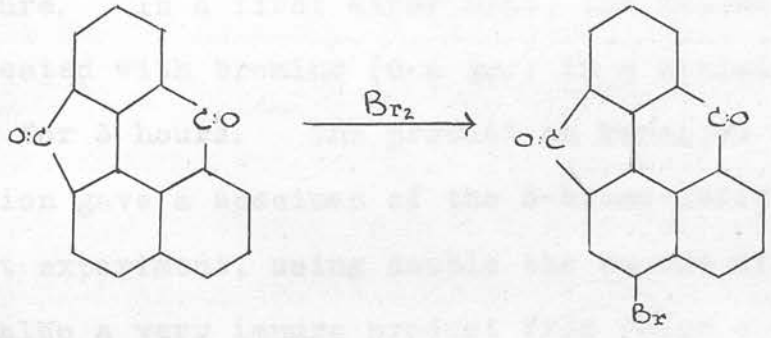
Action of Bromine on 1:11-Ketobenzanthrone.

A portion of the ketone (0·5 gm.) in 25 c.c. glacial acetic acid solution at the boiling point was treated with bromine (0·3 gm.) and the mixture refluxed for 3 hours. The solution on cooling deposited orange needles of the original compound, the evolution of hydrogen bromide which was observed during

the treatment apparently arising from bromination of the solvent.

A second portion was treated in the same manner, nitrobenzene being employed as solvent in place of the acetic acid. The product melted at a lower temperature than the original and probably contained a trace of the halogeno-derivative. On crystallisation, however, the original 1:11-ketobenzanthrone was obtained.

1) 3-Bromo-1:11-ketobenzanthrone.



Pure 1:11-ketobenzanthrone (1·0 gm.) was dissolved in concentrated sulphuric acid (10 c.c.) and a fine suspension obtained by adding water (50 c.c.). Excess bromine (1·0 gm.) was added and the mixture was maintained at the boiling point for 4 hours. The solid was then filtered off, washed well with water and dried.

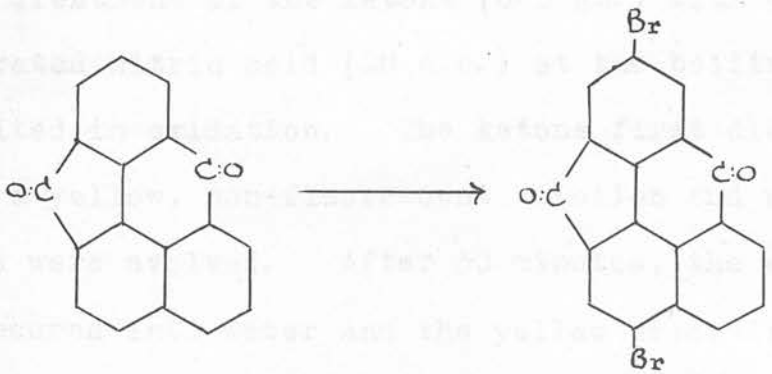
Yield: 1·30 gm. (100%). M.p. 323-325°C.

It was crystallised from glacial acetic acid to form bright red needles which sintered at 200°C and

melted at 326-327°C, further crystallisation not altering this melting point. The compound dissolved in concentrated sulphuric acid with purple colouration and was identical with the synthetic 3-bromo-1:11-ketobenzanthrone of F.R. Smith (loc. cit.), admixture with a specimen of which gave no depression of melting point.

2) 3:9-Dibromo-1:11-ketobenzanthrone.

Attempts were made to brominate and dibrominate 1:11-ketobenzanthrone by treating with bromine under pressure. In a first experiment, the ketone (1·0 gm.) was heated with bromine (0·6 gm.) in a sealed tube at 150°C for 3 hours. The product on repeated crystallisation gave a specimen of the 3-bromo-derivative. A repeat experiment, using double the amount of bromine, gave also a very impure product from which a specimen of 3:9-dibromo-1:11-ketobenzanthrone was isolated after 10 crystallisations from nitrobenzene. The yield of 3:9-dibromo-derivative, however, was improved by brominating in liquid bromine.



0·5 gm. 1:11-ketobenzanthrone.

10 gm. bromine.

The bromine and the ketone were mixed in a small flask, fitted with a ground-in reflux condenser, and the mixture was gently boiled by placing in the water-bath at 50-60°C for 2 hours. Bromine was then distilled off and the red residue collected. It weighed 0·85 gm. and melted at 274-280°C. After 5 crystallisations from nitrobenzene, the pure 3:9-dibromo-1:11-ketobenzanthrone was obtained in small, deep-red needles.

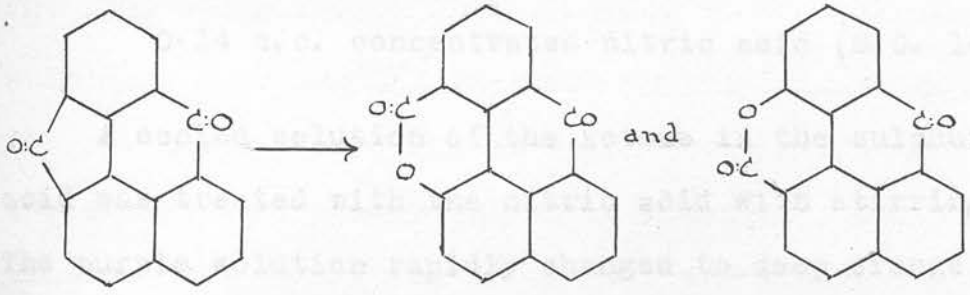
Yield: 0·40 gm. (48%). M.p. 298-299°C.

It was identical with the synthetic product of F.R. Smith (loc. cit.), a mixed melting point with which showed no depression. The compound dissolved in concentrated sulphuric acid with a purple colouration and on dilution with the solvent showed a blue tint.

Action of Nitric Acid on 1:11-Ketobenzanthrone: 3-Nitro-1:11-ketobenzanthrone.

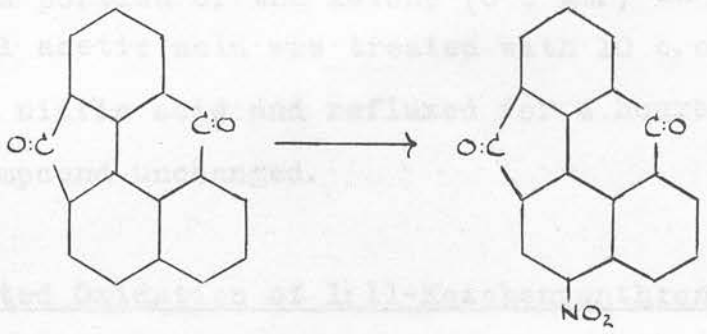
Treatment of the ketone (0·5 gm.) with excess concentrated nitric acid (20 c.c.) at the boiling point resulted in oxidation. The ketone first dissolved to give a yellow, non-fluorescent solution and nitrous fumes were evolved. After 30 minutes, the solution was poured into water and the yellow precipitate collected. It had the properties of a nitro-lactone, dis-

solving in alkalis only on boiling to give a purple solution, without fluorescence. The product melted over a wide range of temperature, 250-270°C (with decomp.), and repeated crystallisation from nitrobenzene or glacial acetic acid failed to give a sharp-melting compound. It probably consisted of a mixture of nitro-derivatives of the lactones of 1-hydroxy-11-carboxy-benzanthrone and 11-hydroxy-1-carboxybenzanthrone, formed from the ketone on oxidation:



An attempt to nitrate the ketone in nitrobenzene solution, employing a slight excess nitric acid and heating to 40°C, resulted in the recovery of the compound unchanged. Heating the solution to 120°C, however, again brought about an oxidation to a product with lactone-like properties. Repeated crystallisation again failed to give a pure compound.

A successful nitration of the ketone was effected by treating a sulphuric acid solution with the calculated amount of nitric acid.



0·5 gm. 1:11-ketobenzanthrone.

15 c.c. concentrated sulphuric acid.

0·14 c.c. concentrated nitric acid (S.G. 1·42).

A cooled solution of the ketone in the sulphuric acid was treated with the nitric acid with stirring. The purple solution rapidly changed to deep orange and after 15 minutes was poured into 100 c.c. water. The yellow precipitate, which was insoluble in alkalis, was filtered off, washed with water and dried. It weighed 0·57 gm. and melted at 240-250°C. After 3 crystallisations from nitrobenzene, pure 3-nitro-1:11-ketobenzanthrone was obtained in greenish-yellow needles.

Yield: 0·16 gm. (27%). M.p. 284-285°C.

In admixture with a specimen of the synthetic product of F.R. Smith (loc. cit.), the melting point was not depressed.

An attempt was made to nitrate 1:11-ketobenzanthrone in glacial acetic acid under conditions in which benzanthrone yields the 2-nitro-derivative. The ketone, however, was unaffected. More vigorous treatment, in

which a portion of the ketone (0·5 gm.) in 25 c.c. glacial acetic acid was treated with 10 c.c. concentrated nitric acid and refluxed for 4 hours, also left the compound unchanged.

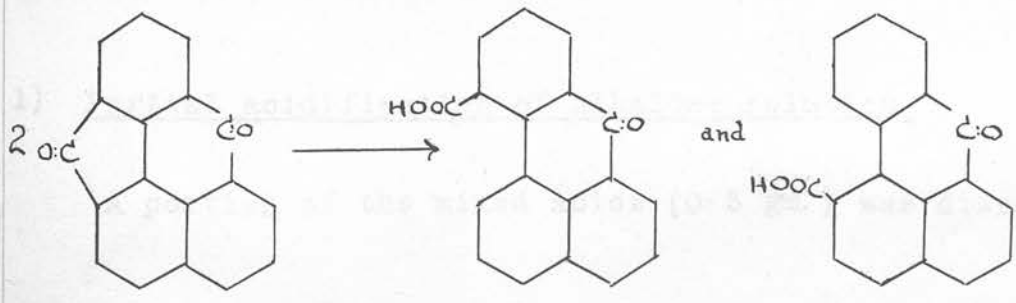
Attempted Oxidation of 1:11-Ketobenzanthrone.

1 gm. 1:11-ketobenzanthrone.
8 gm. chromic acid.

The ketone was dissolved in 10 c.c. concentrated sulphuric acid and a fine suspension formed by adding 30 c.c. water. The chromic acid was added in portions and the mixture was refluxed for 6 hours. The product was filtered and the ketone (0·65 gm.) was recovered unchanged. Evaporation of the filtrate failed to yield any oxidation product.

Longer treatment with chromic acid resulted in a larger loss of material. An attempt to oxidise the ketone with chromic acid in acetic acid gave a similar result.

Hydrolysis of 1:11-Ketobenzanthrone.



1:11-Ketobenzanthrone (2·5 gm.) was dissolved in concentrated sulphuric acid (10 c.c.) by warming, the solution poured into water and the finely divided solid filtered off. It was added to 250 c.c. dilute sodium hydroxide solution (10%) and the mixture boiled under reflux. The solid gradually dissolved to give a red solution, hydrolysis being complete after 8 hours. The solution was filtered from any residue and the filtrate acidified to give an orange-yellow precipitate of the mixed acids. It was filtered off, washed well with water and dried.

Yield: 2·4 gm. M.p. 220-240°C.

Attempts to Isolate 1-Carboxybenzanthrone from the Mixed Acids.

Rule and Bigelow (unpublished) showed that repeated crystallisation of the acid mixture led to the isolation of pure 11-carboxybenzanthrone. The product recovered from the mother liquors also failed to yield the 1-acid on crystallisation. Attempts to isolate the 1-carboxybenzanthrone by crystallisation of the metallic salts of the mixed acids resulted in failure. Further attempts were made to separate the mixture in the present work.

1) Partial acidification of alkaline solution.

A portion of the mixed acids (0·5 gm.) was dissolved

in dilute alkali and the solution made up to 200 c.c. with water. Dilute sulphuric acid was then carefully added with stirring until approximately half of the solid was reprecipitated. It was filtered off and the remainder obtained by further acidification of the filtrate. Both fractions melted over the range 220-240°C and on repeated crystallisation from glacial acetic acid specimens of pure 11-carboxybenzanthrone, melting at 273°C, were obtained.

2) Partial esterification.

1·85 gm. mixed acids.

50 c.c. methyl alcohol.

2·5 c.c. concentrated sulphuric acid.

The mixed acids, methyl alcohol and concentrated sulphuric acid were boiled together under reflux for 30 hours when approximately one half of the solid had dissolved. Most of the methyl alcohol was removed on the steam-bath and the residue was diluted with water. Dilute sodium hydroxide was added till distinctly alkaline and, after digesting for a few minutes at 60°C, the insoluble esterified fraction was filtered off, washed with water and dried. The filtrate on acidification yielded the unesterified acid portion.

Yield esters: 0·74 gm. M.p. 125-140°C.

Yield acids: 1·10 gm. M.p. 230-245°C.

The esterified portion was crystallised from alcohol, the melting point rising. After 6 crystallisations, a specimen was obtained in the form of orange needles

which melted at 159-160°C and proved identical with 11-carbomethoxybenzanthrone (p. 81). The acid portion, after 5 crystallisations from glacial acetic acid, yielded a specimen of 11-carboxybenzanthrone.

Although there was a slight difference between the melting point of the recovered acid portion and the original mixture, suggesting a possible difference in rate of esterification of the two isomerides, there was not a sufficient concentration of the 1-isomeride in either fraction to permit of its isolation by crystallisation.

3) Fractionation of the mixed esters.

The mixture was esterified by the silver salt method.

The mixed acids (2·0 gm.) were dissolved in the minimum of dilute ammonium hydroxide and the solution was diluted to 250 c.c. with water and boiled till ammonia could no longer be detected. The yellow solution at 60°C was then treated with dilute silver nitrate solution (2 gm. in 25 c.c. water), the mixture being stirred to allow coagulation of the silver salts which separated. The yellow solid was filtered off, washed with a little water and dried.

Yield: 1·4 gm.

The salts appeared to be appreciably soluble in water, the filtrate depositing 1·0 gm. of the original

acid mixture, m.p. 220-240°C, on acidification with nitric acid.

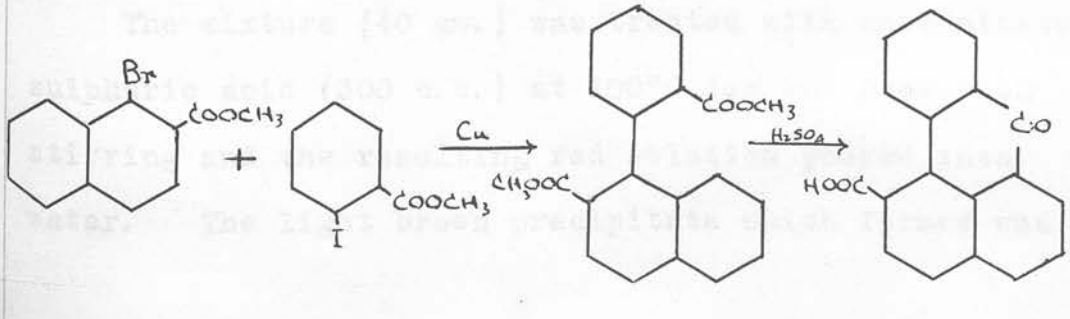
The silver salts were shaken in a stoppered flask with methyl iodide (20 c.c.) for a few minutes, some heat being developed. The mixture was filtered from silver iodide and the methyl iodide solution evaporated to give the mixed esters in the form of a yellow solid.

Yield: 1·0 gm. M.p. 119-125°C.

The ester mixture was placed in a small Anschutz flask and heated under diminished pressure in an oil-bath. At approximately 1 mm. pressure, a portion of yellow liquid distilled at 200°C and when roughly one third had collected in the receiver, the distillation was stopped. The distillate and residue solidified to orange needles on cooling. Both portions melted at 119-125°C, the melting point of the original mixture.

Repeated crystallisation of either portion from alcohol led to the isolation of pure 11-carbomethoxybenzanthrone.

<u>The Ullmann Reaction between Methyl 1-bromo-2-naphthoate and Methyl o-iodobenzoate: 1-Carboxybenzanthrone.</u>



1) A first attempt was made to prepare 1-carboxybenzanthrone on lines similar to those described for the preparation of the 11-isomeride (p. 79).

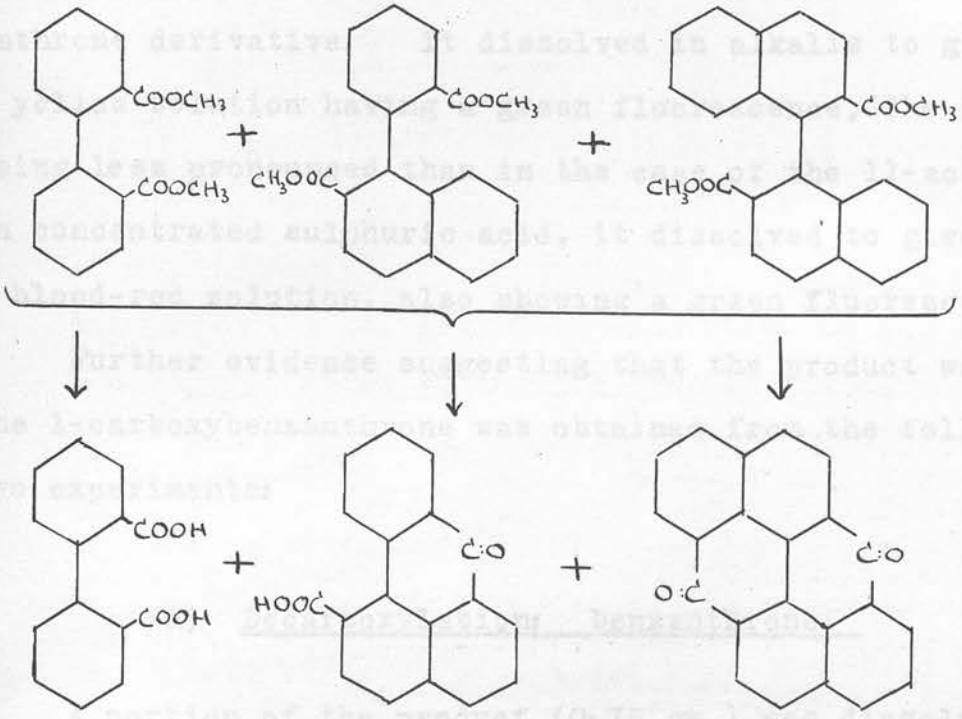
25 gm. methyl 1-bromo-2-naphthoate (1 mol.)
50 gm. methyl o-iodobenzoate (2 mol.).
30 gm. copper bronze.

The mixed esters were stirred together in a small flask, heated in an oil-bath at 160°C, and the copper was added in portions over one hour. The temperature was then raised to 175-180°C and the mixture stirred for a further 5 hours. The product was extracted with 250 c.c. acetone (in 3 portions) and the inorganic material filtered off. Acetone was removed by distillation on the water-bath, finally under reduced pressure, to leave a yellow syrup which weighed 44 gm.

All attempts to obtain a solid product from the syrup resulted in failure. Treating with ether and leaving for several days, or chilling to low temperatures (-16°C) gave no crystalline deposit. Beside the required phenylnaphthyl derivative, the product might be expected to contain quantities of the diphenyl and dinaphthyl dicarboxylic esters, derived respectively from the benzoate and naphthoate.

The mixture (40 gm.) was treated with concentrated sulphuric acid (300 c.c.) at 100°C for one hour with stirring and the resulting red solution poured into water. The light brown precipitate which formed was

filtered off. It consisted, presumably, of diphenic acid, 1-carboxybenzanthrone and anthanthrone.



It was therefore boiled with 4 litres of water to dissolve the diphenic acid and the mixture filtered hot. The yellow residue was suspended in water (500 c.c.) and made distinctly alkaline with sodium hydroxide. After digesting at 60°C for a short period, the insoluble anthanthrone was filtered off (1·4 gm.) and the deep yellow, fluorescent filtrate was acidified. The yellow solid which precipitated was filtered off, washed with water and dried.

Yield: 16·9 gm. M.p. 213-218°C.

On crystallisation from glacial acetic acid, the product formed light yellow needles which appeared to be homogeneous and melted at 225-227°C.

Although this melting point was lower than expected by comparison with 11-carboxybenzanthrone, the properties of the product suggested that it was the required benzanthrone derivative. It dissolved in alkalis to give a yellow solution having a green fluorescence, the latter being less pronounced than in the case of the 11-acid. In concentrated sulphuric acid, it dissolved to give a blood-red solution, also showing a green fluorescence.

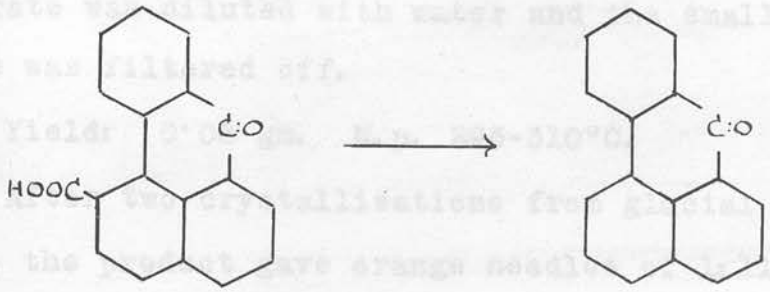
Further evidence suggesting that the product was the 1-carboxybenzanthrone was obtained from the following two experiments:

a) Decarboxylation: benzanthrone.

A portion of the product (0·75 gm.) was dissolved in dry quinoline (7·5 gm.) and the solution maintained at the boiling point while copper bronze (0·3 gm.) was added in portions. Some effervescence occurred and after 10 minutes the solution darkened somewhat. It was cooled, poured into dilute hydrochloric acid and the brown precipitate collected and washed well with water. Alkali soluble material was removed by warming with dilute sodium hydroxide solution and the solid was filtered off. It was boiled up in alcohol (10 c.c.) and filtered hot from copper. On cooling, the filtrate deposited fine brown needles which weighed 0·08 gm. and melted at 130-150°C.

After two crystallisations from the minimum of alcohol, yellow needles of benzanthrone were obtained.

Yield: 0·02 gm. M.p. 171-172°C.



b) Cyclisation to 1:11-ketobenzanthrone.

A first experiment in which the acid was treated with phosphorus pentoxide in molten phthalic anhydride at 200°C resulted in the recovery of the material unchanged. More vigorous conditions were therefore employed.

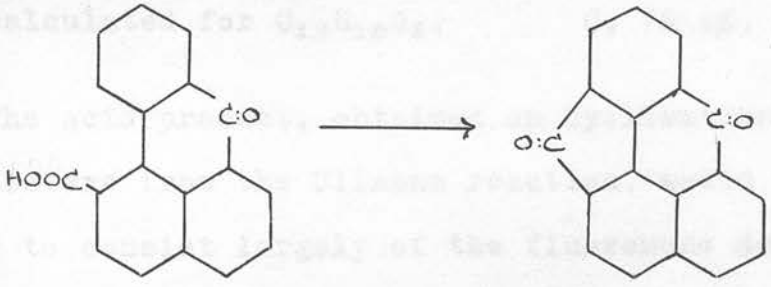
1·5 gm. supposed 1-carboxybenzanthrone.
20 gm. phthalic anhydride.
3 gm. phosphorus pentoxide.

The acid was dissolved in the phthalic anhydride at 215°C and the phosphorus pentoxide was added in 3 portions at intervals of 30 minutes. After 3 hours, the orange product was cooled somewhat and poured into a solution of 20 gm. sodium hydroxide in 200 c.c. water. The mixture was heated to the boiling point and the insoluble orange solid collected. It weighed 0·75 gm. and melted at 265-280°C but was largely insoluble in glacial acetic acid. It was refluxed with 20 c.c.

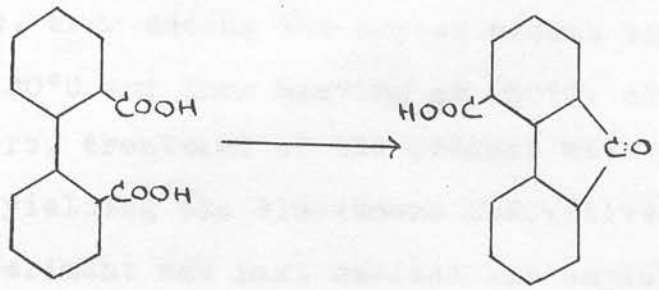
glacial acetic acid. and filtered hot. The orange filtrate was diluted with water and the small precipitate was filtered off.

Yield: 0·08 gm. M.p. 295-310°C.

After two crystallisations from glacial acetic acid, the product gave orange needles of 1:11-ketobenzanthrone, m.p. 327-328°C.



A portion of the original acid was purified for the purpose of analysis. After repeated crystallisation from glacial acetic acid, it gave yellow needles, m.p. 228°C. It was observed that the green fluorescence in alkaline solution was almost absent in the purified compound although it still dissolved in concentrated sulphuric acid with red colouration. The acid proved to be not the expected benzanthrone derivative but fluorenone-4-carboxylic acid. According to Graebe and Aubin (Ann., 1888, 247, 275), this acid is slowly formed from diphenic acid on treatment with sulphuric acid at 100°C. It dissolves in concentrated sulphuric acid with blood-red colouration.



Analysis (Schoeller): found, C, 74·4%, H, 3·5%;
calculated for $C_{14}H_8O_3$, C, 75·0%, H, 3·6%.
(calculated for $C_{18}H_{10}O_3$, C, 78·8%, H, 3·7%.)

The acid product, obtained on cyclisation of the mixed esters from the Ullmann reaction, would therefore appear to consist largely of the fluorenone derivative, but the above experiments and the green fluorescence of the original product in alkaline solution pointed to the presence of some 1-carboxybenzanthrone.

Attempts were made to separate the original acid mixture by forming the dinitrophenylhydrazone of the fluorenone derivative, benzanthrone and its derivatives not being attacked by hydrazines. Treatment of an alcoholic solution of the mixture with dinitrophenylhydrazine, however, gave an incomplete precipitation of the fluorenone derivative and no benzanthrone derivative could be isolated.

2) Several unsuccessful attempts were made to reduce the proportion of diphenyl derivative formed during the Ullmann reaction. Carrying out the reaction at a higher

temperature, e.g. adding the copper bronze to the mixed esters at 180°C and then heating at 200°C, did not improve matters, treatment of the product with sulphuric acid again yielding the fluorenone derivative.

An experiment was next carried out employing two molecular proportions of the bromonaphthoate and one proportion of the iodobenzoate.

30 gm. methyl 1-bromo-2-naphthoate.

15 gm. methyl o-iodobenzoate.

25 gm. copper bronze.

The mixed esters were stirred at 160°C and 15 gm. of the copper were added over one hour. The temperature was then raised to 200°C and the remainder of the copper added in portions. After 5 hours, the product was extracted with acetone in the usual manner and the inorganic matter removed. Acetone was removed from the product and the syrupy residue was treated with 15 c.c. ether and left overnight. The colourless crystals which deposited, proved to be the dimethyl 1:1'-dinaphthyl-2:2'-dicarboxylate. They were filtered off, washed with a little ether and dried.

Weight: 9·9 gm. M.p. 150-152°C.

Crystallisation from ligroin gave the compound in fine colourless needles.

Yield: 8·95 gm. (43%). M.p. 156°C.

It dissolved in concentrated sulphuric acid on heating to give immediately the green colour of anth-

anthrone (see below).

The reaction product, after removal of the dinaphthyl derivative, was treated with concentrated sulphuric acid (150 c.c.) at 100°C for one hour and the red solution poured into water. The precipitate, after boiling with water to remove diphenic acid and extraction with alkali, yielded again the crude fluorenone derivative. It weighed 4·95 gm. and melted at 209-214°C. Repeated crystallisation again failed to give the benzanthrone carboxylic acid.

3) Attempts were therefore made to isolate the intermediate phenylnaphthyl dicarboxylate from the product of the Ullmann reaction. Experiment 1 was repeated and the mixed esters were subjected to distillation in superheated steam, the containing flask being suspended in an oil-bath. When the temperature of the bath reached 150°C, the product began to distil but no apparent separation occurred. Fractions were collected, but each yielded the crude fluorenone carboxylic acid on cyclisation with concentrated sulphuric acid.

A specimen of 1-carboxybenzanthrone was eventually isolated in the following manner, a concentration of the phenylnaphthyl derivative being first effected by distillation of the mixed esters under reduced pressure:

50 gm. methyl o-iodobenzoate.

25 gm. methyl 1-bromo-2-naphthoate.

30 gm. copper bronze.

The esters were treated with the copper bronze as in experiment 1 and the mixed esters from the reaction isolated in the usual manner. The mixture was placed in a 100 c.c. distilling flask, which was fitted with a long fractionating column, and distilled at 12 mm. pressure. A little unchanged iodobenzoate first distilled but the temperature rapidly rose to 195°C and a large fraction (23 gm.) of colourless distillate was collected at 195-200°C. This solidified on standing to give a low-melting solid which crystallised from ether in plates, m.p. 73-74°C, and proved to be diphenic ester. A second fraction (10 gm.) was collected, distilling at 225-240°C. It formed a yellow viscid liquid which did not solidify on treating with ether and chilling. A small dark residue remained in the flask.

The fraction distilling at 225-240°C was treated with concentrated sulphuric acid (150 c.c.) with stirring at 100°C for one hour. The red, fluorescent solution was poured into water (300 c.c.) and the brown precipitate which formed was filtered off and washed with water. It was dissolved in dilute sodium hydroxide solution with heating and the yellow-brown solution filtered from a small insoluble residue. On acidification, the filtrate yielded a yellow solid which softened at 225°C and melted at 234-239°C.

Weight: 4·50 gm.

It appeared to contain a considerable proportion of the fluorenone derivative and crystallisation from glacial

acetic acid led to a concentration of that compound. The product was boiled with chlorobenzene (150 c.c.) for 10 minutes and filtered hot, the filtrate on cooling depositing fairly pure fluorenone-4-carboxylic acid. The light brown insoluble portion now dissolved in alkali to give a vivid green fluorescent solution. It weighed 1·02 gm. and melted at 272-275°C.

The product was dissolved in boiling nitrobenzene (25 c.c.) and the solution filtered hot, the filtrate on cooling depositing yellow needles of the 1-carboxybenzanthrone.

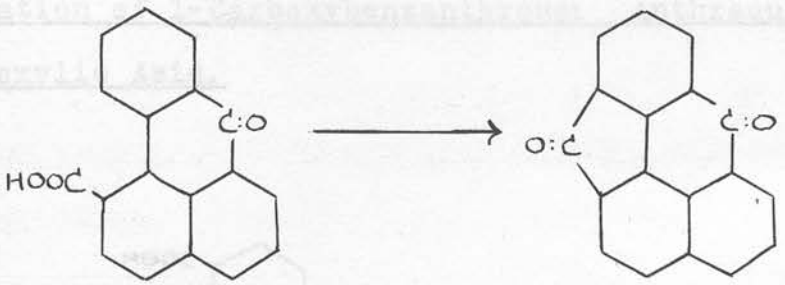
Yield: 0·85 gm. (3%). M.p. 283-4°C.

Further crystallisation from nitrobenzene or glacial acetic acid gave the pure acid, m.p. 285°C.

Analysis (Weiler): found, C, 78·8%, H, 3·8%;
calculated for $C_{18}H_{10}O_3$, C, 78·8%, H, 3·7%.

The acid is readily soluble in alkalis to give a deep yellow solution with bright green fluorescence. In concentrated sulphuric acid it gives a red solution also having a green fluorescence. Owing to the difficulty of obtaining the acid, only a brief examination of its reactions could be undertaken. The behaviour of the acid left no doubt as to its structure.

Cyclisation of 1-Carboxybenzanthrone to 1:11-Keto-benzanthrone.



0·1 gm. 1-carboxybenzanthrone.
5 gm. phthalic anhydride.
0·2 gm. phosphorus pentoxide.

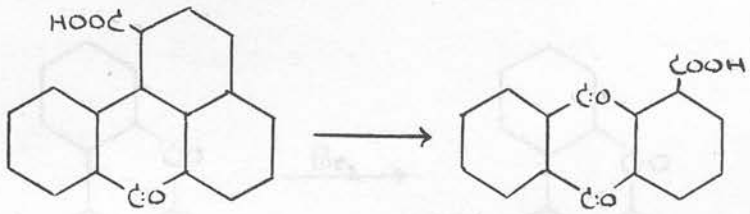
The acid was dissolved in the phthalic anhydride with heating and the yellow solution maintained at 200°C with stirring. The phosphorus pentoxide was added in two portions at an interval of 30 minutes, the solution deepening in colour. After 2 hours, the mixture was cooled somewhat and poured into a solution of 5 gm. sodium hydroxide in 50 c.c. water. After digesting at the boiling point for a few minutes, the orange precipitate was filtered off, washed well with hot water and dried.

Yield: 0·084 gm. (90%). M.p. 323-325°C.

The product was crystallised from glacial acetic acid to form orange needles, m.p. 327-328°C, identical with 1:11-ketobenzanthrone obtained by cyclising 11-car-

boxybenzanthrone.

Oxidation of 1-Carboxybenzanthrone: Anthraquinone-1-carboxylic Acid.



0·1 gm. 1-carboxybenzanthrone.
1 gm. chromic acid.

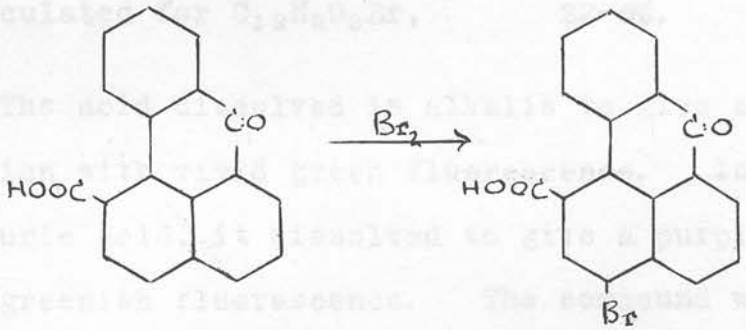
The 1-carboxybenzanthrone was dissolved in concentrated sulphuric acid (3 c.c.) by warming and water (10 c.c.) added. The fine suspension which formed was treated with the chromic acid in portions and the mixture boiled under reflux for 6 hours. The product was diluted with water and the brown precipitate was filtered off, washed with water and dried.

Yield: 0·055 gm. (64%). M.p. 287-290°C.

The product, on crystallisation from dilute alcohol, gave a specimen of pure anthraquinone-1-carboxylic acid, m.p. 293-294°C, in fine, almost colourless needles. In admixture with a specimen of authentic anthraquinone-1-carboxylic acid, the melting point was not depressed.

The crude product from the reaction showed no trace of the lactone of 1-hydroxy-11-carboxybenzanthrone when in alkaline solution.

Bromination of 1-Carboxybenzanthrone: 3-Bromo-1-carboxybenzanthrone.



In a preliminary experiment, a portion of 1-carboxybenzanthrone in aqueous suspension was treated with the calculated amount of bromine and the mixture refluxed for 3 hours. The original material was largely recovered on crystallisation of the product.

0·3 gm. 1-carboxybenzanthrone.

1·5 gm. bromine.

The acid was dissolved in concentrated sulphuric acid (3 c.c.) by warming and a fine suspension formed by adding water (25 c.c.). The bromine was added and the mixture was maintained at the boiling point for 6 hours. Excess bromine was then removed by distillation and the orange solid was filtered off, washed well with water and dried.

Yield: 0·37 gm. (96%). M.p. 305-308°C.

Two crystallisations from nitrobenzene gave the pure 3-bromo-1-carboxybenzanthrone in fine yellow needles, melting at 319-320°C.

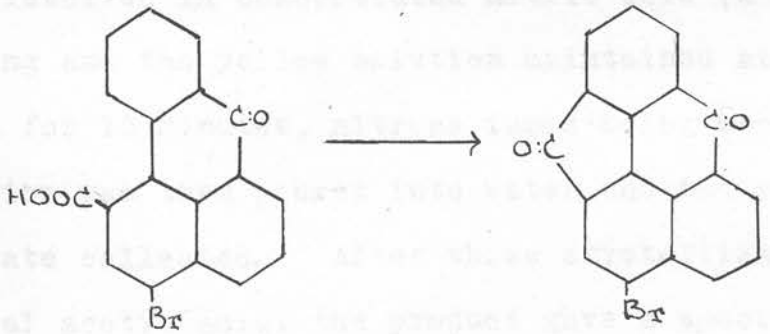
Yield: 0·20 gm. (51%).

Analysis (Hein): found, Br, 22·5%;

calculated for $C_{18}H_9O_3Br$, 22·6%.

The acid dissolved in alkalis to give a yellow solution with vivid green fluorescence. In concentrated sulphuric acid, it dissolved to give a purple solution with greenish fluorescence. The compound was orientated by conversion to 3-bromo-1:11-ketobenzanthrone.

Cyclisation of 3-Bromo-1-carboxybenzanthrone to 3-Bromo-1:11-ketobenzanthrone.



0·2 gm. 3-bromo-1-carboxybenzanthrone.

10 gm. phthalic anhydride.

0·3 gm. phosphorus pentoxide.

A solution of the acid in phthalic anhydride at 200°C was treated with phosphorus pentoxide in the usual manner and after two hours, the mixture was poured into dilute sodium hydroxide (10 gm. in 100 c.c. water). The resulting mixture was digested at the boiling point for a few minutes and the orange solid collected.

Yield: 0·17 gm. (90%). M.p. 323-325°C.

The pure ketone was obtained in the form of orange needles, m.p. 325-326°C, by crystallisation of the product from glacial acetic acid. In admixture with authentic 3-bromo-1:11-ketobenzanthrone, the melting point was not depressed and colour reactions in sulphuric acid confirmed the identity.

Action of Nitric Acid on 1-Carboxybenzanthrone.

A small specimen of 1-carboxybenzanthrone (< 0·1 gm.) was dissolved in concentrated nitric acid (2 c.c.) by heating and the yellow solution maintained at the boiling point for 15 minutes, nitrous fumes being evolved. The solution was then poured into water and the yellow precipitate collected. After three crystallisations from glacial acetic acid, the product gave a specimen of fine yellow needles, melting at 256-257°C.

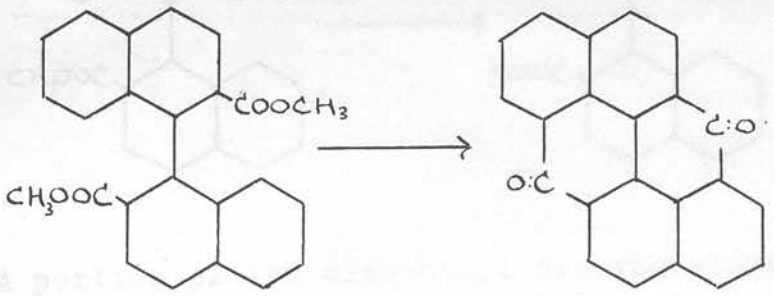
These dissolved in aqueous alkali very slowly on boiling to give a pure blue, non-fluorescent solution. This behaviour suggested that the product was a lactone, probably a nitro-lactone of 11-hydroxy-1-carboxybenzanthrone.

A further examination of the product could not be made owing to lack of material.

Hydrolysis and Cyclisation of Dimethyl-1:1'-Dinaphthyl-2:2'-dicarboxylate.

During attempts to prepare 1-carboxybenzanthrone (p. 133), a specimen of dimethyl 1:1'-dinaphthyl-2:2'-dicarboxylate was obtained. This compound has been prepared and its conversion to anthanthrone by sulphuric acid treatment carried out by Kuhn and Albrecht (Ann., 1928, 465, 282) but these authors do not comment on the course of the cyclisation.

1) Anthanthrone.



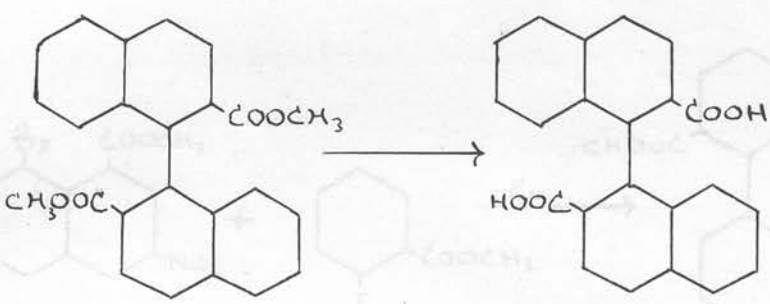
The dinaphthyl derivative (1·0 gm.) was dissolved in concentrated sulphuric acid (10 c.c.) with stirring and the temperature of the colourless solution was raised. At 50°C, the solution showed no sign of any intermediate benzobenzanthrone compound, i.e. no red colour, but

immediately assumed a green tint which gradually deepened on further heating. After stirring at 100°C for one hour, the dark green product was poured into water and the red-orange precipitate was filtered off, washed with water and dried. It was completely insoluble in alkalis and did not melt below 360°C.

Yield: 0·85 gm. (100%).

The product crystallised from alcohol in orange needles. It was identified as anthanthrone, forming a magenta-coloured vat with alkaline hydrosulphite, which dyed cotton in orange shades.

2) 1:1'-Dinaphthyl-2:2'-dicarboxylic acid.



A portion of the dinaphthyl dicarboxylate (1·0 gm.) was heated in concentrated sulphuric acid (10 c.c.) at 50°C for one hour with stirring. The resulting light green solution was poured into water to form a pink precipitate which was filtered off and added to 20 c.c. dilute sodium hydroxide solution (10%). The mixture was heated to the boiling point and the slight residue of anthanthrone (0·035 gm.) was filtered off. The cooled filtrate on acidification yielded a colourless precip-

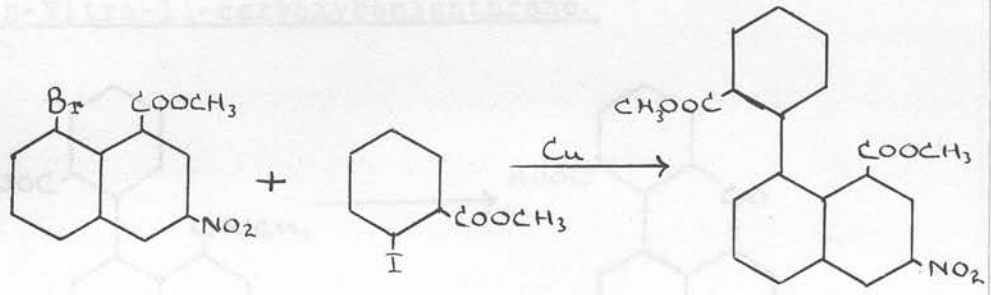
itate of the dinaphthyl dicarboxylic acid.

Yield: 0·78 gm. (84%). M.p. 270-271°C.

The acid crystallised from dilute acetic acid in colourless needles, m.p. 272°C. It has already been prepared (Kuhn and Albrecht, loc. cit.) by alkaline hydrolysis of the dimethyl ester, the melting point quoted being 268·5-270°C.

Synthesis of 5-Nitrobenzanthrone.

1) Methyl 3-nitro-8-(o-carbomethoxyphenyl)-1-naphthoate.



20 gm. methyl 3-nitro-8-bromo-1-naphthoate.

40 gm. methyl o-iodobenzoate.

25 gm. copper bronze.

The mixed esters were heated with stirring at 155-160°C and the copper was added in portions over one hour. The product was then stirred for a further 3 hours at 175-180°C and the inorganic matter was removed by extraction with 200 c.c. acetone in the usual manner.

Acetone was removed from the extract by distillation on the water-bath under reduced pressure and the brown residue was treated with 25 c.c. ether and left overnight. A light brown crystalline deposit separated. It was filtered off, washed with a little ether and dried. It weighed 12·8 gm. and melted at 138-141°C. Crystallisation from alcohol (300 c.c.) gave the phenylnaphthyl derivative in yellow-brown needles, m.p. 141-142°C.

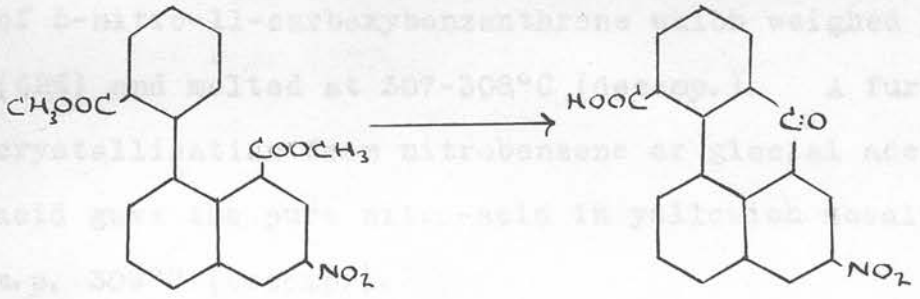
Yield: 9·37 gm. (40%).

A further crystallisation gave the pure ester in yellow needles, melting at 143°C.

Analysis (micro-Dumas): found, N, 3·7%;

calculated for $C_{20}H_{15}O_6N$, 3·8%.

2) 5-Nitro-11-carboxybenzanthrone.



In a preliminary experiment, a portion of the phenylnaphthyl derivative was treated with sulphuric acid at 100°C for one hour and the product, obtained on pouring the red solution into water, contained a high-melting compound which was insoluble in the usual sol-

vents. It was probably the anhydride of the nitro-acid since on prolonged boiling with dilute alkali it was converted to 5-nitro-11-carboxybenzanthrone. The formation of this product was avoided by carrying out the cyclisation at a lower temperature.

The phenylnaphthyl derivative (2 gm.) was treated with concentrated sulphuric acid (20 c.c.) and the mixture maintained with stirring for 30 minutes at 80°C. The resulting blood-red solution was poured into water and the brown precipitate which formed was filtered off, washed with hot water and dried.

Yield: 1·72 gm. (98%). M.p. 298-301°C (decomp.)

The product was dissolved in 50 c.c. boiling nitrobenzene and the slight insoluble residue filtered off. The filtrate on cooling deposited yellow-brown needles of 5-nitro-11-carboxybenzanthrone which weighed 1·08 gm. (62%) and melted at 307-308°C (decomp.). A further crystallisation from nitrobenzene or glacial acetic acid gave the pure nitro-acid in yellowish needles, m.p. 309°C (decomp.).

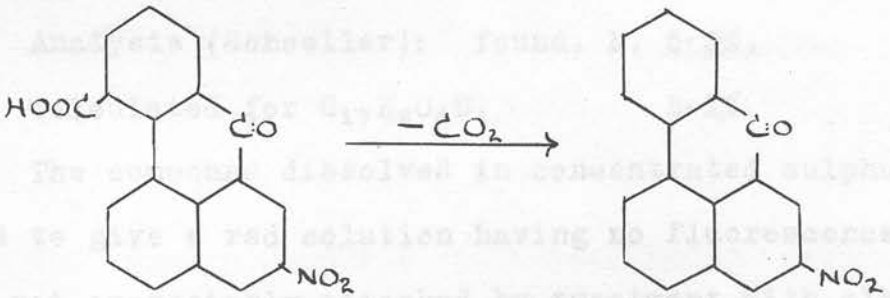
Analysis (micro-Dumas): found, C, 4·0%;

calculated for $C_{18}H_9O_5N$, 4·4%.

5-Nitro-11-carboxybenzanthrone dissolves in alkalis to give a yellow non-fluorescent solution and in concentrated sulphuric acid forms a blood-red colouration, the solution also showing no fluorescence. In

admixture with 3-nitro-11-carboxybenzanthrone which melts at 310°C (decomp.), a specimen of the 5-nitro-derivative gave the melting point 288-291°C, a depression of approximately 20°C.

3) Decarboxylation of 5-nitro-11-carboxybenzanthrone to 5-nitrobenzanthrone.



0·75 gm. 5-nitro-11-carboxybenzanthrone.

7·5 c.c. dry quinoline.

0·3 gm. copper bronze.

The carboxy acid was dissolved in the boiling quinoline and the copper bronze added in small portions. Effervescence occurred and boiling was continued for two minutes longer. (Further boiling was found to give a product which could only be purified with difficulty). The cooled mixture was poured into dilute hydrochloric acid to dissolve the quinoline and filtered. The residue was washed with water, warmed with dilute alkali and again filtered, washed with water and dried. The

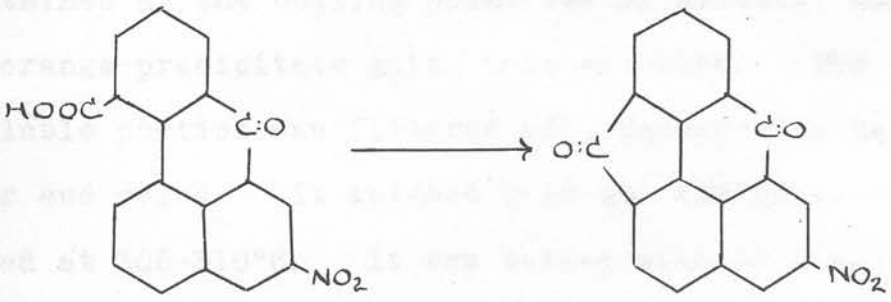
brown solid was refluxed with boiling acetic acid (200 c.c.), filtered from copper and the nitrobenzanthrone recovered by dilution of the filtrate with water. It weighed 0·49 gm. (75%) and melted at 281-285°C. After two crystallisations from glacial acetic acid, fine brown beedles were obtained (40% yield), m.p. 287°C. Further crystallisation from glacial acetic acid or chlorobenzene did not alter this melting point.

Analysis (Schoeller): found, N, 5·3%,

calculated for $C_{17}H_9O_3N$, 5·1%.

The compound dissolved in concentrated sulphuric acid to give a red solution having no fluorescence. It was not appreciably attacked by treatment with alkaline hydrosulphite, in which it remains insoluble.

Cyclisation of 5-Nitro-11-carboxybenzanthrone to 5-Nitro-1:11-ketobenzanthrone.



Difficulty was experienced in cyclising the carboxy acid to the ketone by means of phosphorus pentoxide treatment. The product from such treatment appeared

to consist largely of an insoluble, high-melting compound. This compound, however, was slowly attacked with aqueous alkali to give the original carboxy acid. It was probably the anhydride of the acid, already encountered in the cyclisation of the phenylnaphthyl derivative with sulphuric acid. The formation of this product greatly reduced the yield of the ketone.

0·75 gm. 5-nitro-11-carboxybenzanthrone.
20 gm. phthalic anhydride.
1 gm. phosphorus pentoxide.

The carboxy acid was dissolved in the phthalic anhydride with heating and the yellow solution maintained at 200°C with stirring. The phosphorus pentoxide was added in two portions at an interval of 30 minutes and after two hours the product was cooled somewhat and poured into a solution of 15 gm. sodium hydroxide in 150 c.c. water. The resulting mixture was maintained at the boiling point for 15 minutes, much of the orange precipitate going into solution. The insoluble portion was filtered off, washed with hot water and dried. It weighed 0·18 gm. and partially melted at 305-310°C. It was boiled with 10 c.c. nitrobenzene for a short period and the insoluble portion filtered off. On cooling, the filtrate deposited fine orange needles of the nitro-ketone.

Yield: 0·09 gm. (13%). M.p. 319-320°C.

Further crystallisation did not affect this melting point. The compound dissolved in concentrated sulphuric acid to give a purple non-fluorescent solution. The ketone was incompletely attacked by alkaline hydrosulphite to give a purplish vat which showed no dyeing properties. Probably partial reduction of the nitro group also occurs in this case.

Analysis (micro-Dumas): found, N, 4·3%,

calculated for $C_{18}H_7O_4N$, 4·65%.

S U M M A R Y.

The substitution reactions of 11-carboxybenzanthrone have been examined and successful chlorinations, brominations and nitrations carried out. 3-Substituted derivatives are shown to be formed in every case but the action of bromine and nitric acid under certain conditions led to oxidation of the molecule in the 1-position, lactones of 1-hydroxy-11-carboxybenzanthrone being obtained. The oxidation of 11-carboxybenzanthrone with chromic acid had previously been carried out by Rule and co-workers, who had suggested the lactone structure for the product. The frequent occurrence of the supposed lactones during the examination of the substitution reactions of 11-carboxybenzanthrone in the present work, led to an attempt to prove the structure of these interesting oxidation products. A successful synthesis of the lactone of 1-hydroxy-11-carboxybenzanthrone was carried out by applying the Ullmann reaction to methyl 7-methoxy-8-bromo-1-naphthoate and methyl o-iodobenzoate and cyclising the resulting phenylnaphthyl derivative with concentrated sulphuric acid. The compound obtained was identical with the product of

oxidation of 11-carboxybenzanthrone and the lactonic structure of the latter was therefore confirmed.

The behaviour of the intermediate 7-methoxy-phenyl naphthyl dicarboxylic ester towards alkalis and concentrated sulphuric acid has been further examined and some interesting observations have been made regarding the hydrolysis and cyclisation of the compound and related products. The suggestion is put forward that the possibility or otherwise of formation of a stable 6-membered ring-system is a determining factor in the behaviour of carbomethoxyl groups in compounds of this type towards hydrolysis with concentrated sulphuric acid. It is shown that the normal reactions of certain groups of atoms such as OCH_3 are fundamentally modified by the proximity in space of other groups in the same structure. These deviations from the normal are greatly emphasised if the groups are held rigidly in close spatial proximity and the possibility of separation by rotation round a bond in the system is absent.

A second oxidation product of 11-carboxybenzanthrone was obtained by use of an alkaline oxidising reagent. The acid on treatment with alkaline potassium permanganate gave a small yield of anthraquinone-1:8-dicarboxylic acid, an interesting compound not listed in the literature. A useful method of decarboxylation was employed in orientating the product.

The examination of the 7-methoxy-phenylnaphthyl

dicarboxylic ester, obtained during the synthesis of the lactone of 1-hydroxy-11-carboxybenzanthrone, gave an indication of the proximity in space of the 1:11-positions in the benzanthrone structure. This proximity is clearly observed in an atomic scale model of the 11-carboxybenzanthrone molecule, which also makes apparent a considerable restriction to the rotation of the 11-carboxyl group by the blocking effect of the hydrogen atom in position 1. This restriction is so marked as to suggest the possibility of the existence of stereoisomeric forms of the carboxy acid. An examination of the brucine salt and the ℓ-menthyl ester of the acid was made but gave no evidence of the existence of diastereoisomeric forms of these derivatives. Some consequences of the restriction to rotation were pointed out and a further study of the acid and its derivatives recommended.

The behaviour of 1:11-ketobenzanthrone on substitution was examined and on mono-substitution, chloro-, bromo- and nitro- derivatives were obtained with substituents in the 3-position. Further bromination led to the production of a mixture from which 3:9-dibromo-1:11-ketobenzanthrone was isolated. The 1:11-ketobenzanthrone was shown to be very resistant to oxidation and no oxidation product was obtained by use of aqueous chromic acid mixtures.

Various attempts were made to obtain the related 1-carboxybenzanthrone. An examination of the acid

mixture formed by alkaline hydrolysis of 1:11-ketobenzanthrone failed to give the required acid. A synthesis of the acid was undertaken, on lines similar to those employed by Rule and co-workers in the preparation of 11-carboxybenzanthrone. Methyl 1-bromo-2-naphthoate and methyl o-iodobenzoate were treated with copper bronze but the unsymmetrical product of coupling could not be isolated in solid form. Eventually a very small yield of 1-carboxybenzanthrone was obtained, the product from the Ullmann reaction appearing to contain very little of the corresponding phenylnaphthyl derivative.

A brief examination of the chemistry of 1-carboxybenzanthrone was made. Bromination of the acid was again shown to yield the 3-bromo-derivative, the primary position of attack in the benzanthrone nucleus not being affected by the presence of the carboxyl group. Treatment of the acid with concentrated nitric acid gave a product with properties suggesting that oxidation had taken place in the 11-position to give a lactone. The lactone structure, however, did not appear to be formed on oxidation of the 1-acid with chromic acid, anthraquinone-1-carboxylic acid being obtained.

A successful "Ullmann Synthesis" of 5-nitrobenzanthrone was carried out by coupling methyl 3-nitro-8-bromo-1-naphthoate with methyl o-iodobenzoate in the presence of copper. The intermediate phenylnaphthyl dicarboxylate was isolated in good yield from the reaction

product and converted to the nitro-11-carboxybenzanthrone by treatment with concentrated sulphuric acid. The acid was decarboxylated and further cyclised to give respectively the new nitrobenzanthrone and 5-nitro-1:11-ketobenzanthrone.

In conclusion, the author desires to express his gratitude to Dr H. G. Rule for his continued interest and advice during the course of this work. Thanks are also due to the Carnegie Trust for a Scholarship and to the Imperial Chemical Industries, Ltd., for a grant and chemicals.