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THE CHEMISTRY OF 8-AMINO-BENZANTHRONE AND RELATED COMPOUNDS.

by

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Thesis submitted for the degree of Ph.D.

May 1940. University of Edinburgh.

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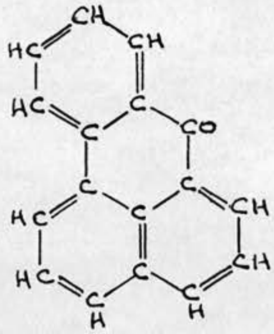
INTRODUCTION

A retrospective study of the investigations carried out on organic aromatic compounds in the past thirty five years, clearly shows that the trend of such work, in recent times, has been more towards the elucidation of problems derived from compounds of complex ring structure, rather than those arising from compounds of a simple nature.

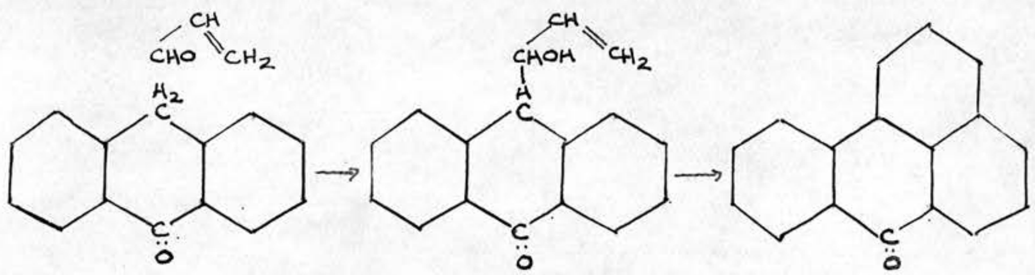
Among the more complex ring structures, the benzanthrone system, first discovered by Bally in 1905, (Ber., 1905, 38, 194), has proved a most fruitful field of investigation.

In an examination of the Skraup reaction on anthraquinone, Bally found that treatment with glycerol and sulphuric acid, in the presence of a reducing agent, led to the isolation of a compound which subsequent investigation proved to be Benzanthrone.

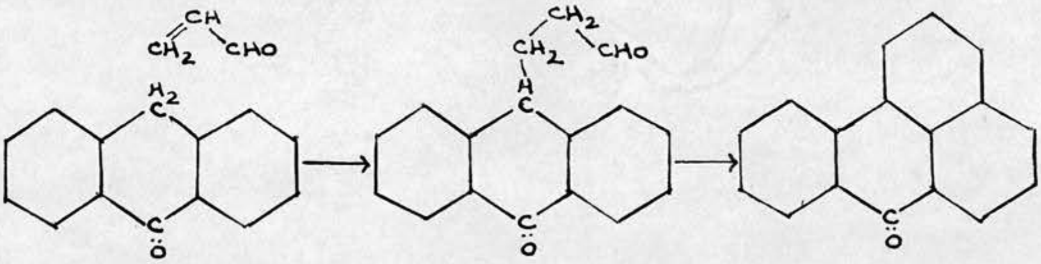


Many compounds, having Benzanthrone as a basic structure, have proved of great commercial value in the production of new dyestuffs, and at present, the benzanthrone colours are among the most important carbocyclic vat dyes known.

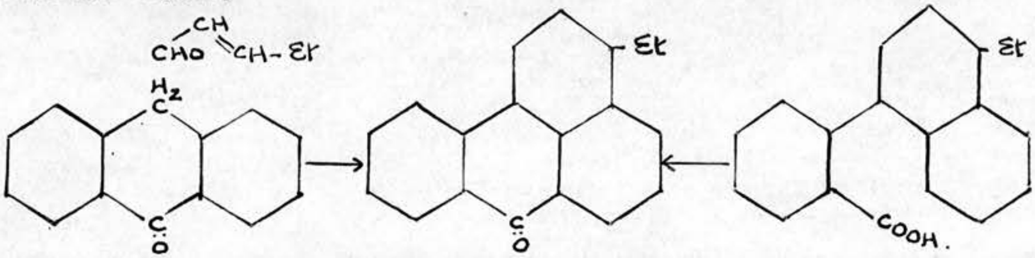
Since the original discovery, the above method of synthesis has been slightly modified, in that anthraquinone is reduced to anthrone by copper powder and sulphuric acid, prior to the introduction of the glycerol. The mechanism of this reaction has aroused considerable discussion. Two interpretations have been put forward. The first by Bally and Scholl, (Ber., 1911, 44, 1656.) postulates that the reaction proceeds in the following stages:- Some anthraquinone is reduced to anthrone, which combines with the acrolein produced from the glycerol and sulphuric acid, to yield an aldol. This proceeds to lose water and hydrogen, giving benzanthrone. The hydrogen is taken up in the reduction of more anthraquinone.



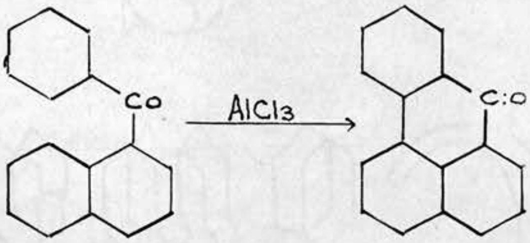
The second theory, due to Meerwein (J. prakt. Chem. 1918, (2) 97, 284) sought to avoid this unusual cyclisation. This author applied the additive property which anthrone possesses towards unsaturated substances such as Benzal malonic ester, to reactions of this type. The anthraquinone nucleus attaches to the C-atom of the double bond further removed from the ester group, and Meerwein suggested that the first stage in benzanthrone formation is of this type, followed by ring closure of the aldehyde group.



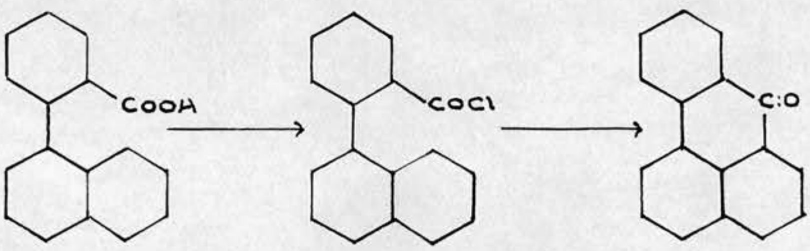
Recent work by Baddar and Warren (J.C.S., 1938, 401.) furnishes positive proof in favour of Bally and Scholl's theories. Condensation of α-ethyl glycerol, which is converted to α-ethyl acraldehyde by concentrated sulphuric acid, with anthrone under the same conditions as Bally's reaction, led to the isolation of Bzl-ethyl benzanthrone, the constitution of which was verified by ring closure of o-4'-ethyl-1'-naphthyl benzoic acid.



An interesting synthesis of benzanthrone in view of the fact that it gives access to various substituted derivatives, was carried out by Scholl and Seer (Ann., 1912, 394, 111,). It consists in "baking" -benzoyl naphthalene with aluminium chloride; a process of aerial oxidation.



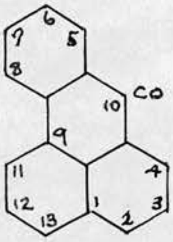
A later synthesis due to Schaarschmidt (Ber., 1918, 51, 1082.), leaves no doubt as to the structure of benzanthrone. This involves the preparation of o-1-naphthyl benzoic acid, the acid chloride of which is converted quantitatively into benzanthrone by treatment with aluminium chloride.



Benzanthrone forms yellow needles melting at 170-171°C., and dissolves in concentrated sulphuric acid to form an orange-red fluorescent solution. This colour reaction with concentrated sulphuric acid is a characteristic of most benzanthrone derivatives. Various halogen and other derivatives of benzanthrone have been fully characterised, and perhaps the hydroxy and methoxy substitution products deserve special mention, as they are of great importance in the dyeing industry and form an integral part of the current investigations.

Confusion is sometimes met with in the systematic nomenclature of benzanthrone and its derivatives. The first systems in use, took the anthracene molecule as their basis, and are given below I and II. The latter, still being the standard used by the J.C.S. and J.A.C.S. will be employed throughout this thesis. The international system III, is perhaps the one most extensively used in present day technical literature.

I



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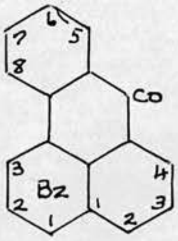

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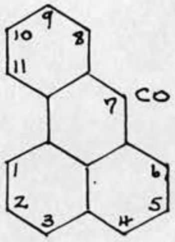
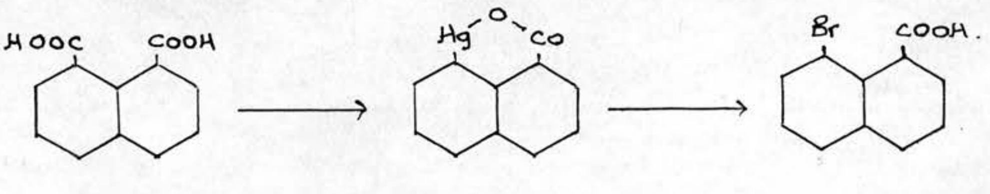


A modern method of wide applicability in the synthesis of benzanthrone, uses as starting materials, certain peri- derivatives of naphthalene.

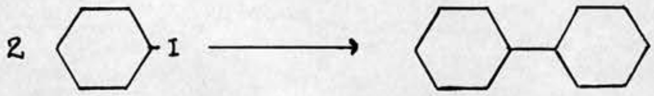
During recent years, the 8-halogeno-1-naphthoic acids have attracted considerable attention. Rule and co-workers (J.C.S., 1934, 170), employed the mercuration method of Whitmore and co-workers (J.A.C.S., 1929, <u>51</u>, 1831, 3363), and have found it an eminently satisfactory source of these acids.



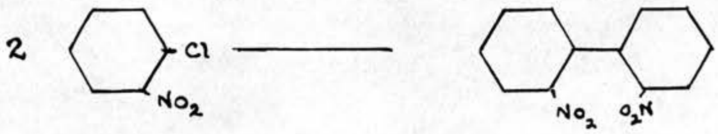
The importance of these acids in benzanthrone synthesis rests in their ability to take part in the now familiar Ullmann reaction. (Ber., 1901, 34, 2174. and Ann., 1904, 332, 38).

Fundamentally, the course of the reaction is due to the readiness with which copper bronze eliminates the halogen as cuprous salt at high temperatures, causing two molecules to condense with the formation of a dinuclear product.

Ullmann's investigations showed that the reaction proceeded smoothly with almost all iodo- compounds, iodobenzene for example, with copper at 230°C in a sealed tube, converting to diphenyl.



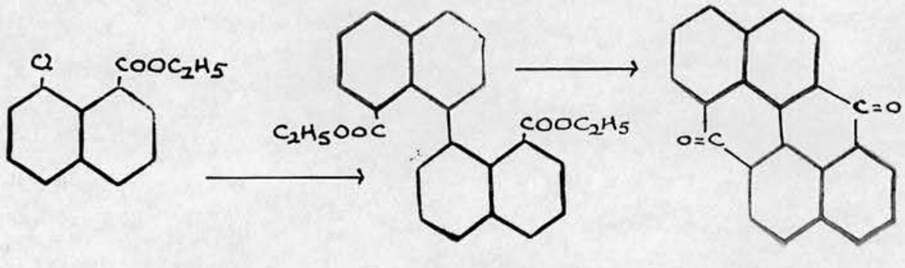
In the case of the corresponding chloro- and bromo-compounds, however, the halogen was found to be unreactive, unless an increased lability was conferred by the presence of other substituents in certain positions. A carboxy or nitro grouping in the ortho position to the halogen has apparently an activating effect, causing the compound to undergo the reaction. In this way 2:2'-dinitro diphenyl can be obtained from o-nitrochlorobenzene.



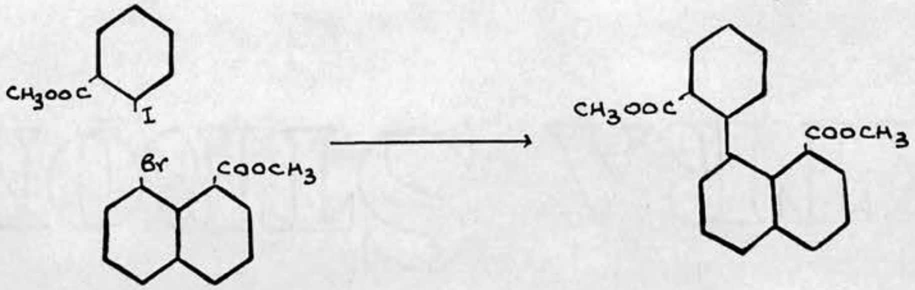
In contrast, the m- and p-nitro-chlorobenzenes are quite unreactive.

An important extension of the Ullmann reaction lies in the utilisation of mixtures of halogeno compounds to give unsymmetrical products.

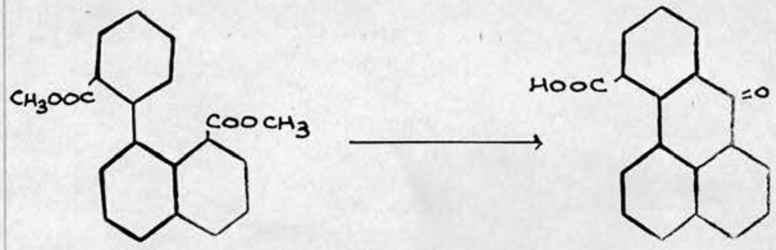
Kalb, (Ber., 1914, 47, 1724) in his synthesis of anthanthrone was the first to employ this procedure, which is now so widely used in the preparation of substituted benzanthrones. The ethyl ester of 8-chloro-1-naphthoic acid was treated with copper powder at 200°C and the diethyl 1:1'-dinaphthyl-8:8'-dicarboxylate which was formed in very small yield, was converted quantitatively to anthanthrone by the action of concentrated sulphuric acid.



Rule and Barnett (J.C.S., 1932, 2728), in an investigation of the reactivity of the bromine atom in 8-bromo-1-naphthoic acid, concluded that the halogens in methyl-8-bromo-1-naphthoate and methyl-o-iodobenzoate were comparable in reactivity with one another. Barnett, (Thesis - Edinburgh, 1932) on subjecting these compounds to the Ullmann reaction at 190-200°C. succeeded in the isolation of methyl-8-(o-carbomethoxyphenyl)-1-naphthoate.

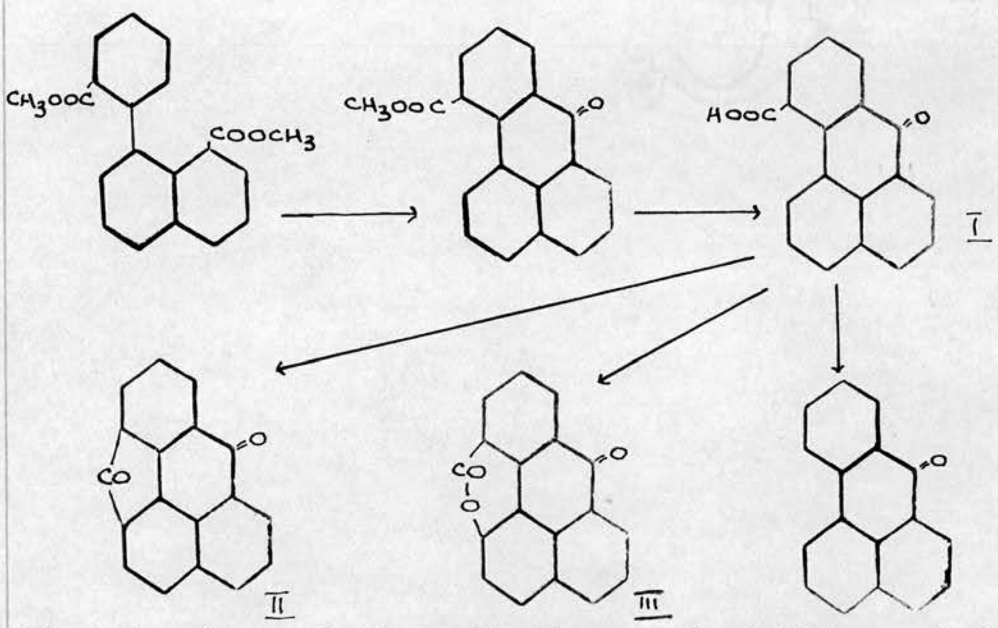


Rule and Pursell (J.C.S., 1935, 571) showed that the phenylnaphthyl-dicarboxylate obtained by Barnett, was, on treatment with concentrated sulphuric acid, converted quantitatively into 8-carboxy benzanthrone.



Barnett's preparation has since been examined more thoroughly, and by carrying through the Ullmann reaction at a lower temperature and using excess of the iodobenzoate, the yield of the unsymmetrical product has been considerably increased (F.R. Smith - Thesis, Edinburgh, 1935).

In an attempt to effect the further cyclisation of the 8-carboxy benzanthrone to Bz3:8-keto-benzanthrone II, Rule and Bigelow (J.C.S., 1935, 373) showed that on more vigorous treatment of the acid with concentrated sulphuric acid, a partial decarboxylation to benzanthrone occurred. This was also accompanied by some oxidation, indicated by the smell of sulphur dioxide, while the yield of the expected keto-benzanthrone was very small. The oxidation product was provisionally formulated as the lactone of the Bz3-hydroxy-8-carboxy benzanthrone III. Treatment of the phenylnaphthyl-dicarboxylate with concentrated sulphuric acid at 50°C. led to the isolation of the intermediate product, 8-carbomethoxy-benzanthrone.

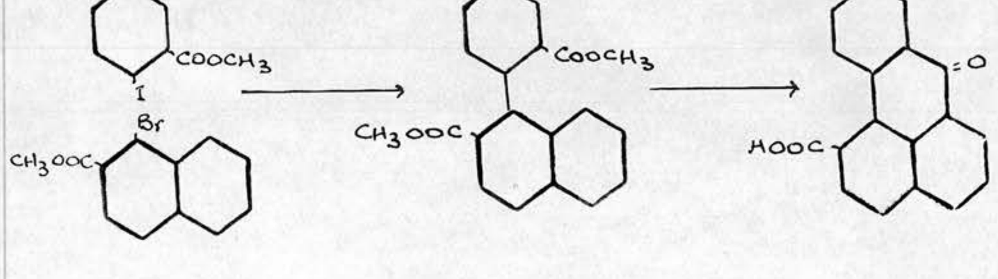


The structure of the oxidation product III was later confirmed by J.L. Grieve (Thesis - Edinburgh, 1936) who performed the Ullmann reaction at 175°C. with methyl-7-methoxy-8-bromo-1-naphthoate and methyl-o-iodo-benzoate, and obtained a yield of 46% of the methyl-7-methoxy-8-(o-carbomethoxy-phenyl)-1-naphthoate which with concentrated sulphuric acid at 100°C. gives the lactone of Bz3-hydroxy-8-carboxy-benzanthrone. This compound was identical with that obtained by the sulphuric acid oxidation of 8-carboxy-benzanthrone.

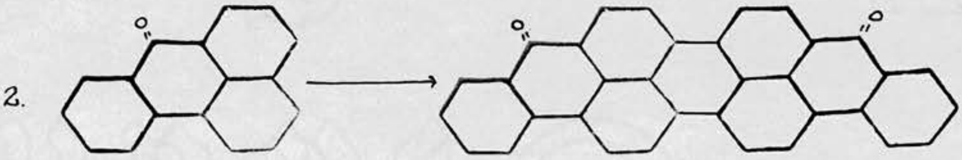
The Bz3:8-keto-benzanthrone was later found to be obtained in good yield by the action of phosphorus pentoxide on 8-carboxy-benzanthrone in molten phthalic anhydride at 200° C.

Bz3:8-keto-benzanthrone, when heated under reflux with dilute alkali, slowly hydrolyses, presumably to give a mixture of Bz3-carboxy-benzanthrone and 8-carboxy-benzanthrone. (Rule and Bigelow, J.C.S., 1935, 574) This mixture of acids defied all efforts at separation, until J.S. Flanders (Thesis - Edinburgh, 1938), obtained a 15% yield of pure ethyl-benzanthrone-8-carboxylate from the reaction by partial separation of the mixed esters by chromatographic adsorption on aluminium oxide from benzene solution.

Bz3-carboxy-benzanthrone has been synthesised by J.L. Grieve (loc. cit.) by coupling methyl-1-bromo-2-naphthoate with methyl-o-iodo-benzoate at 175-180° C. and cyclising the product with concentrated sulphuric acid. The yield was only 3% whereas 90% of the diphenic ester was isolated from the reaction mixture.

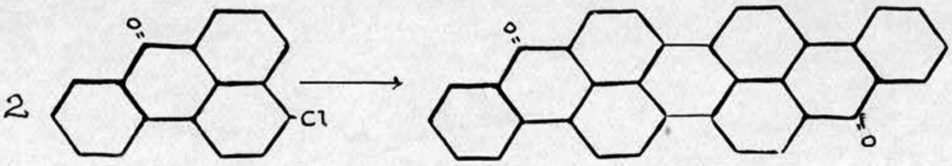


The great technical value of benzanthrone and its derivatives, as aforesaid, lies in their ability to undergo alkaline fusion to yield dibenzanthrones, which are valuable vat dyes. The parent benzanthrones are not highly coloured compounds, and doubt has been cast upon their capacity for vat dye formation. Bally, however, fused benzanthrone with caustic alkali at 230-240°C. and obtained a dark blue vat dye (Ber., 1905, 38, 195; G.P. 185221), which Scholl and Seer (Ann., 1912, 394, 126) showed to have the structure formulated below, the union of the two nuclei occurring at positions Bzl and 2.



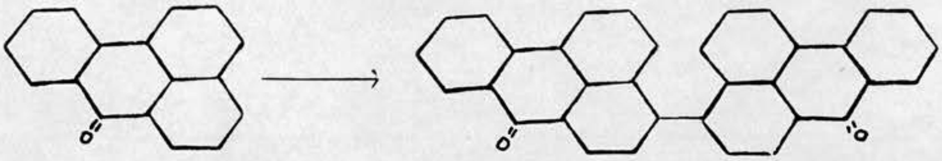
This product, known at first commercially as Violanthrone, now appears on the market as Indanthrene Dark Blue B.O., Caledon Dark Blue B. etc. From a red-violet hydrosulphite bath it dyes cotton in very fast dark blue shades.

The symmetrical isomeride, isodibenzanthrone, is the parent compound of a second class of dyes. It is also known as Isoviolanthrone, and was prepared originally by the action of alcoholic caustic potash on Bzl-chloro-benzanthrone.

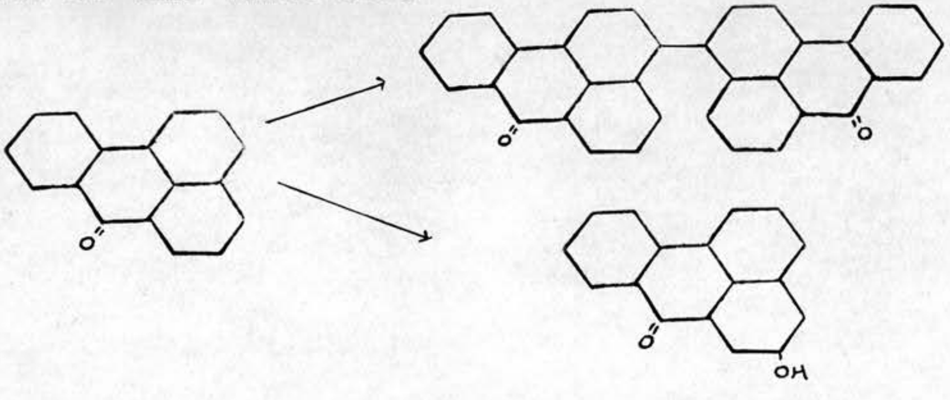


This value of benzanthrone as dyestuffs, has stimulated a vast amount of industrial research, and as a result, many new and valuable dyestuffs have been put on the market.

It has been found that mild treatment of benzanthrone with alcoholic potash at 100 C. yields 2:2'-dibenzanthronyl which can be converted into dibenzanthrone by fusion with caustic potash or oxidation in acid. The yield and purity of the product are better than can be obtained by direct fusion with alkali of benzanthrone. (Lüttringhaus and Neresheimer, Ann., 1929, 473, 259).

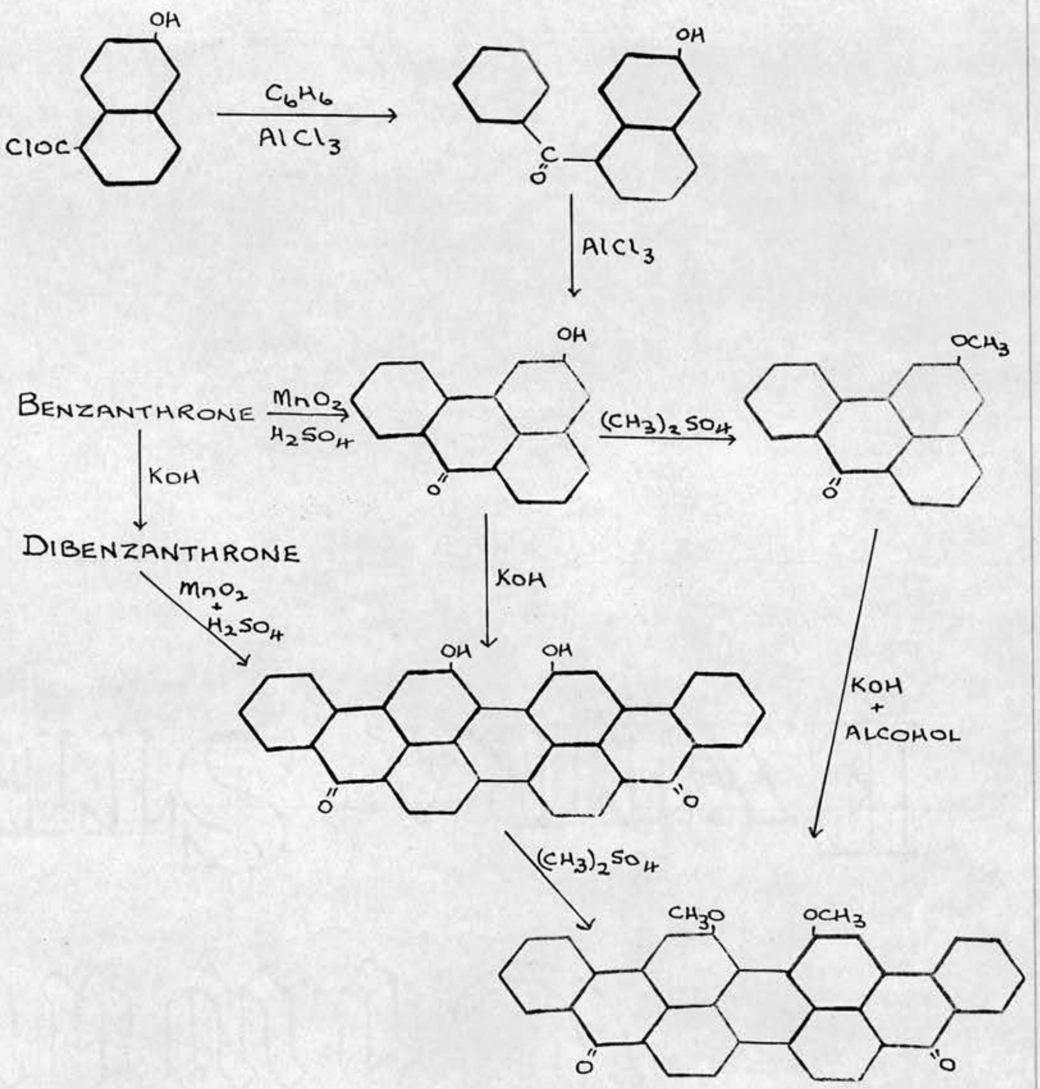


Oxidation of benzanthrone with manganese dioxide and concentrated sulphuric acid at 0 C. yields the Bz1-Bz1'-dibenzanthronyl, which can be converted by the action of alcoholic potash in excellent yield into dibenzanthrone. (Scottish Dyes, E.P. 251313, 278112, 278496). The important Bz2-hydroxy benzanthrone is also formed in this oxidation.



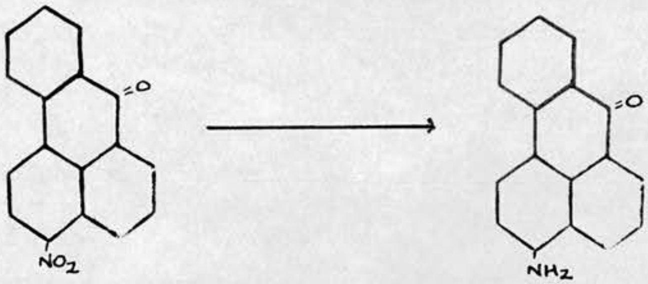
I In 1922, Davies, Fraser-Thomson and Thomas of Scottish Dyes, found that if the Bz2:Bz2'-dihydroxy-dibenzanthrone I, discovered by the B.A.S.F. in 1912 by a similar oxidation, and valueless as a dyestuff, is methylated in nitrobenzene suspension with dimethyl sulphate in the presence of sodium carbonate, a green dye, Bz2:Bz2'-dimethoxy-dibenzanthrone, technically known as Caledon Jade Green, II, is obtained (E.P. 181304, 193431). The same substance can be prepared by methylation of the Bz2-hydroxy-benzanthrone III, which has already been mentioned, and fusing the methoxy benzanthrone so formed with potash and alcohol at 180 C. The position of the hydroxyl groups are fixed by the synthesis of the parent Bz2-hydroxy-benzanthrone from 6-hydroxy-naphthalene-1-carboxylic acid chloride IV, through the benzoyl derivative V, by the Scholl "baking" process (M.L.B. 1923, 413738). Caledon Jade Green is one of the fastest dyes known, and is particularly valuable, as it fills a gap in the range of colours, which is somewhat weak in satisfactory green shades.

The above relationships are indicated in the following scheme.

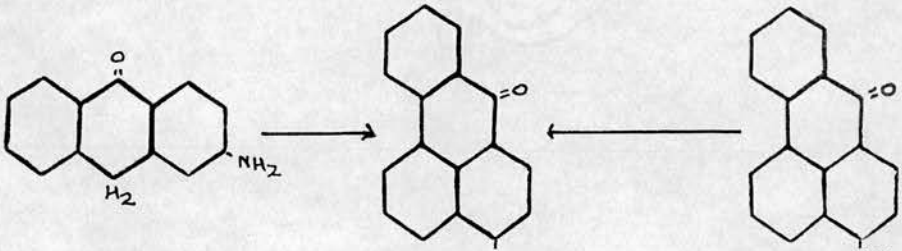


Various references to amino-benzanthrones occur in the patent literature, but their chemical and physical properties are not discussed, the chief concern, being, their practical use as a source of fresh violanthrone dyestuffs. An 8-amino-benzanthrone is noted as being prepared from the 8-chloro compound but it is not further described (C., 1929, (1) 1746, E.P. 301197). Only two mono-amino-benzanthrones appear in the literature proper.

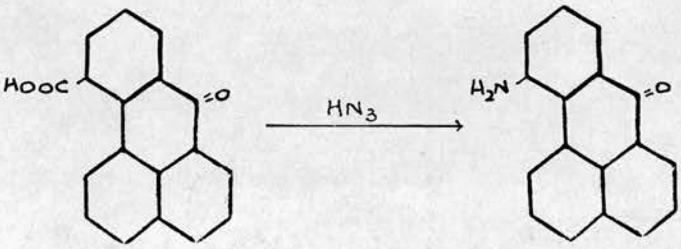
Reduction of the corresponding nitro-compounds has yielded Bz1-amino, Bz1:6-diamino and Bz1:2:6-tri-amino-benzanthrone (C., 1908, (1) 2071, (2) 364). The Bz1-amino-benzanthrone is readily soluble in organic solvents and is obtained as red-brown needles from aqueous pyridine.



The 2-amino-benzanthrone has been prepared by a Skraup synthesis from 3-amino-anthrone (F.P. 23880, cf. Bally and Scholl, Ber., 1911, 44, 1658), and by heating 2-hydroxy-benzanthrone with ammonia in an autoclave (Perkin and Spencer, J.C.S., 1932, 121, 480). It crystallises from alcohol in red needles melting at 223-224° C.



Consequent upon the success attending their efforts to convert Bz3:8-keto-benzanthrone into anthridone employing hydrazoic acid, Rule and co-workers (J.C.S., 1938, 342, 1838) applying the same reagent succeeded in isolating 8-amino-benzanthrone. The method involved the treatment of the carboxy acid in concentrated sulphuric acid and chloroform solution with solid sodium azide at 45-50° C.



The amine crystallises from alcohol in red needles melting at 216-217° C. It is insoluble in aqueous acids, the orange-yellow salts formed being insoluble in water.

The work of the present thesis deals with various derivatives of benzanthrone, and falls mainly into three parts.

(1) The Chemistry of 8-amino-benzanthrone.

(2) Investigations of Dyestuff potentialities of compounds derived from 8-amino-benzanthrone.

(3) Further investigations on Bx3-carboxybenzanthrone and its chemistry.

EXPERIMENTAL SECTION.

The experimental work carried out is described in the following pages. Yields are quoted as percentages of the theoretical amount obtainable, and all melting points are corrected, the thermometers employed having been calibrated against standard short stem thermometers. Since quantities used were for the most part small, the majority of the melting point determinations were performed on a special micro melting point apparatus consisting of an electrically heated plate, with thermometer incorporated, mounted on the stage of a low power microscope.

All new compounds obtained in the pure state have been analysed by micro methods by Mr. W. Brown of the Department of Medical Chemistry of the University of Edinburgh, or by Dr. Weiler of Oxford.

PREPARATIONS.

8-CARBOXY-BENZANTHRONE.

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

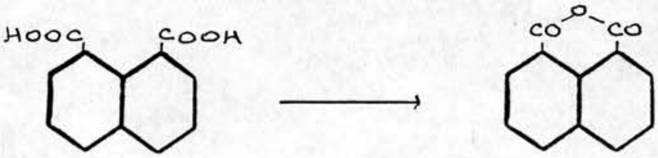
(1) Methyl-8-bromo-1-naphthoate.

(a) Naphthalic anhydride.

100 gm.	naphthalic acid.
800 gm.	nitrobenzene.

The acid was added to the cold nitrobenzene, the mixture heated to 160° C. with stirring, and maintained at that temperature for 2 hours. The product was cooled and the crystalline anhydride filtered, washed with benzene and dried at 80° C.

Yield: 77 gm. (84%) m.p. 274° C.

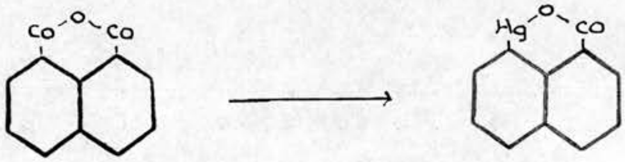


(b) Mercuration.

1.	45.8	gm.	naphthalic anhydride.
	43.4	gm.	caustic potash (88-90%).
	300	ml.	water.
2.	52	gm.	mercuric oxide (98-100%).
	45	gm.	glacial acetic acid.
	200	ml.	water.

Solutions 1. and 2. were made up and mixed when cold to prevent frothing, the precipitated mercury salt being white. A concentrated solution of potassium hydroxide was then dropped in cautiously until the precipitate turned creamy yellow in colour (test - brilliant yellow paper), - pH 7.2. The mixture was then boiled under reflux with stirring for 3 hours, acidified with acetic acid, filtered and the precipitate washed with water and dried.

Yield: 85 gm. (100%).



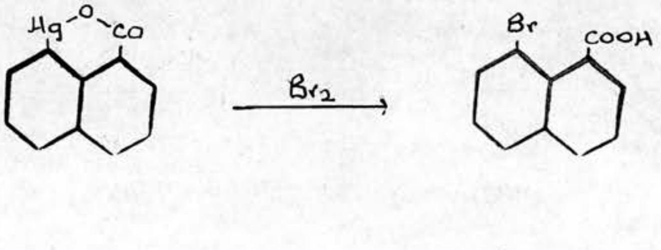
(c) 8-Bromo-1-naphthoic acid.

37 gm.	bromine.
77 ml.	hydrochloric acid (36%).
325 ml.	water.

85 gm.	mercury compound.
18.3 gm.	caustic soda.
500 ml.	water.

The mercury compound was dissolved in the alkali and water, and the solution filtered and cooled with stirring to 0-5°C. To the suspension was added 55 ml. concentrated hydrochloric acid, and the bromine solution run in over one hour, temperature being maintained at 0-5°C. After a further 30 minutes stirring, the bromo-acid was filtered, washed with cold water, and dried.

Yield: 57.5 gm. (100%) m.p. 172-174°C.



(d) Methyl-8-bromo-1-naphthoate.

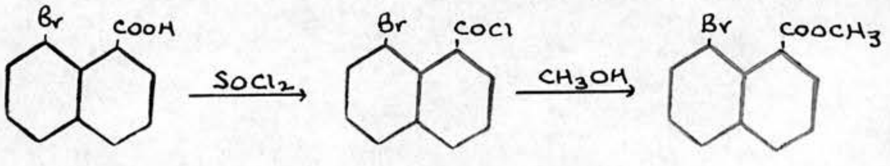
(Rule and Barnett, J.C.S., 1932, 175).

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

The acid and the 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 removed on the steam bath, and finally under reduced pressure. The liquid acid chloride was allowed to cool, and the methyl alcohol added cautiously in small quantities. A vigorous evolution of hydrochloric acid took place, and the reaction was finally completed by boiling the mixture for 30 minutes.

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

Yield: 15 gm. (96%). m.p. 32-33°C.



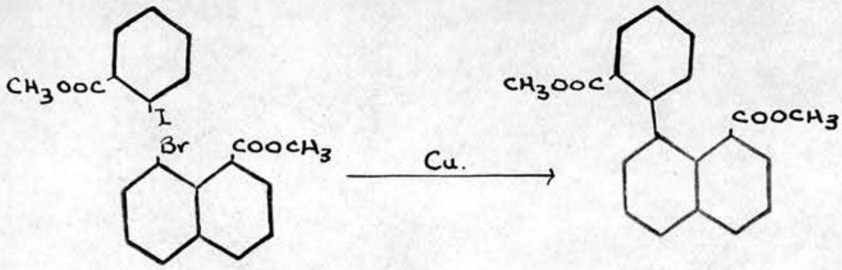
(2). Methyl-8-(o-carbomethoxy-phenyl)-1-naphthoate.

50 gm.	methyl-o-iodo-benzoate.
25 gm.	methyl-8-bromo-1-naphthoate.
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 ml. 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 ml. ether when crystals immediately deposited. After standing overnight, these crystals were filtered off, washed with a little ether and dried.

Yield: 22.5 gm. m.p. 129-131° C.

The pure phenyl-naphthyl-dicarboxylate crystallises from ligroin in colourless rhombs, m.p. 133° C. For conversion to 8-carboxy-benzanthrone, however, there is no need to purify the product.



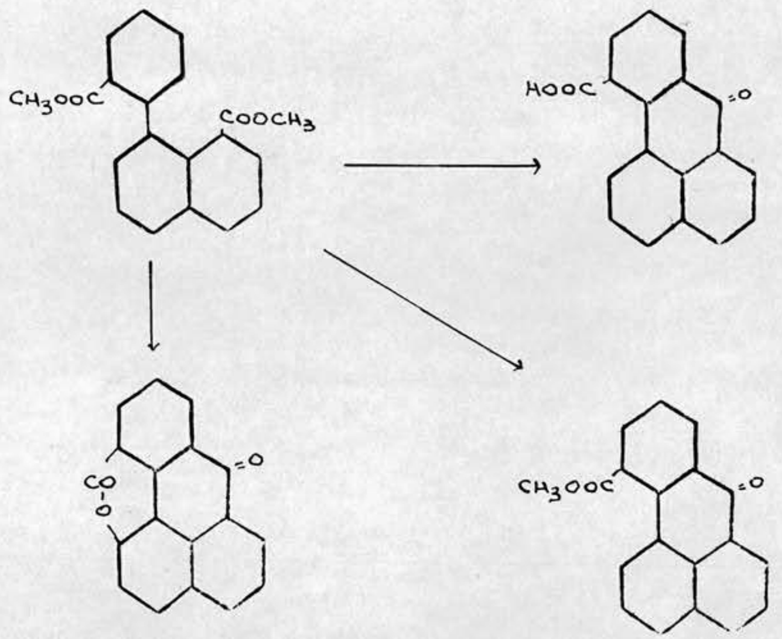
8-Carboxy-benzanthrone.

20 gm. mixed esters from (2).
200 gm. concentrated sulphuric acid.

The mixture was heated with occasional shaking at 100° C. for one hour and the solution poured into water. The yellow precipitate was filtered off, added to 500 ml. water and the mixture made distinctly alkaline with sodium hydroxide. After warming to 60° C. for a few minutes, the insoluble portion was filtered off and washed with warm water. It consisted largely of anthanthrone with a little 8-carbomethoxy-benzanthrone. The filtrate, which was coloured red owing to traces of the lactone of the Bz3-hydroxy derivative, was carefully acidified until the red colour disappeared, and the slight precipitate removed. On further acidification, the filtrate yielded the 8-carboxy-benzanthrone.

Yield of acid: 8 gm. (70%). m.p. 271-272° C.
Yield crude anthanthrone: 0.3 gm. (3%).

The yields quoted are based on the bromo-naphthoate used in (2). 8-Carboxy-benzanthrone crystallises from alcohol or glacial acetic acid in orange-yellow needles melting at 273° C.



Mercuration of 8-carboxy-benzanthrone.

0.5	gm.	8-carboxy-benzanthrone.
0.64	gm.	dry mercuric acetate.
1.5	ml.	glacial acetic acid.

The acid was dissolved in the minimum amount of dilute caustic soda solution, and the mixture made up to 15 ml. The mercuric acetate was dissolved in the glacial acetic acid and 15 ml. water added. The two solutions were carefully mixed in the cold and pH. adjusted to 7.2. The mixture was then boiled under reflux for 100 hours, acidified with acetic acid, and the yellow solid filtered, washed and dried.

Yield: 0.7 gm.

Investigation of the Mercuric salt of 8-carboxy-benzanthrone:

The mercuri compound is a yellow solid which decomposes about 230° C. It is insoluble in organic solvents and water.

0.3 Gm. of the substance were placed in a pyrex test-tube and heated cautiously in vacuo in an oil bath. At 215-220° C. a yellow crystalline sublimate began to form, and further raising of the temperature to 225° C. caused the compound to form a dark melt which effervesced vigorously. The melt was maintained at 230° C. for a further 20 minutes, and then allowed to cool. As much of the crystalline sublimate as possible was removed, and the finely powdered residue and the sublimate remaining in the tube, boiled out with several 5 ml. portions of alcohol. The residue was dried and treated as follows:-

Treatment of Residue:

The dark brown powder had no melting point below 360° C. and proved to be insoluble in dilute acids or alkalis, but gave the characteristic red colour of a benzanthrone derivative with concentrated sulphuric acid. A small portion of the solid was then boiled for 20 minutes with concentrated hydrochloric acid, whereon a pale yellow solution was obtained along with an insoluble organic residue. The solution gave a positive test for mercury with hydrogen sulphide. Recrystallisation of the organic residue from alcohol gave yellow needles melting at 168-169°C. A mixed melting point with pure benzanthrone gave no depression showing that the organic material was benzanthrone. Hence it may be concluded from these tests, that the residue from the sublimation experiment is a mercury compound of benzanthrone.

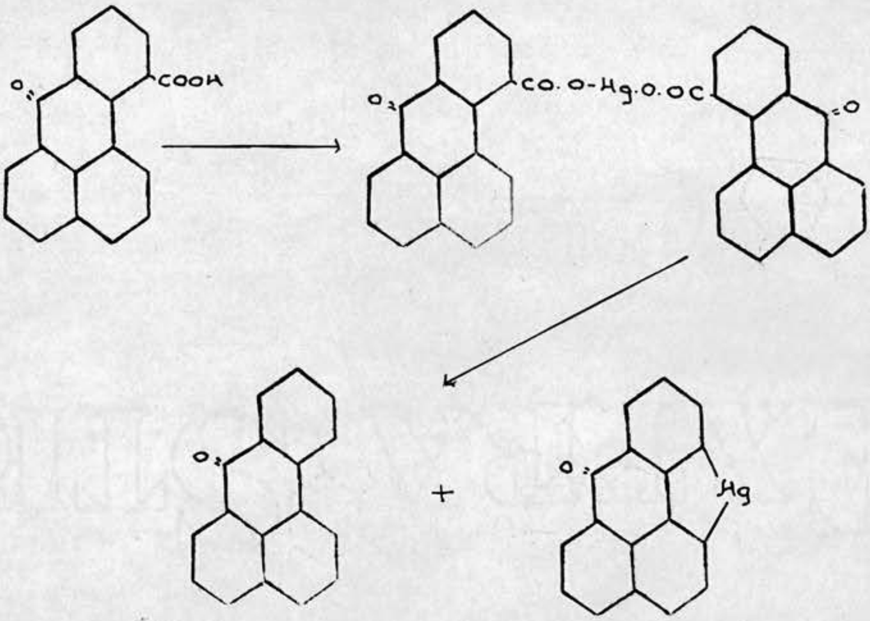
Treatment of the Sublimate.

This yellow crystalline product failed to dissolve in dilute acids or alkalis, but gave the red colour with concentrated sulphuric acid. It melted at 168-169°C., and a mixed melting point with benzanthrone again failed to show any depression, proving that the sublimate was indeed benzanthrone in a fair state of purity. The alcoholic extract of the residue of the sublimation, when evaporated to small bulk, deposited crystals melting at 168-170°C., which on similar treatment to above, were also identified as benzanthrone.

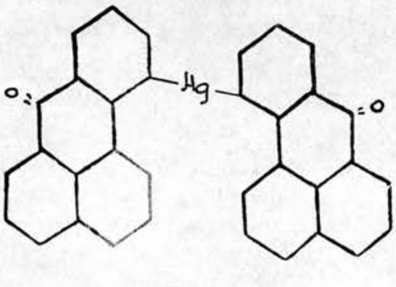
Total weight of Benzanthrone obtained: 0.075 gm.

From a repetition of the sublimation and testing the small amount of gas evolved with lime water, a faint opacity was observed, proving the gas to be carbon dioxide.

An examination of the foregoing investigations leads to the likely conclusion that the mercuri compound links up two molecules of the 8-carboxy-benzanthrone through a mercury atom, as shown in the following scheme.



In the same way it may be reasoned that, since the sublimate of benzanthrone accounts for almost half of the total benzanthrone content, the formula given below for the mercuri compound of benzanthrone remaining as a residue after sublimation, must be excluded.



Bromination:

In an attempt to find the nature of the mercuri compound of benzanthrone left as a residue when the mercuric salt of 8-carboxy-benzanthrone is heated in vacuo at 230°C., 0.1 gm. of the substance was very finely powdered and shaken for several hours with a solution of 0.05 gm. bromine in 5 ml. 20% potassium bromide. The mixture was finally heated at 100°C. for an hour, and on cooling it was found that the solution had been completely decolourised. The solid was filtered off, washed with water and heated with dilute alkali for an hour to remove any traces of lactone which had been formed in the reaction. The alkali-insoluble material was filtered, washed and dried, before extracting with benzene. The residue, insoluble in benzene was very dark coloured and was neglected. After concentration, the benzene solution, which hada reddish brown colour, was passed through a tube containing aluminium oxide and benzene. There seemed to be a narrow band of high adsorption at the top of the tube, and on elution and examination under ultra violet light, three bands could be discerned. The bottom layer was lemon yellow in colour, while the other two were pale and dark brown respectively. The two lower bands were washed out and collected separately, but the third did not move down the tube so readily. Finally it was removed from the tube and boiled out with benzene. This treatment, however, failed to extract the adsorbate, and so this layer was neglected. The other two fractions were evaporated to dryness, and small amounts of a brown solid obtained in each case.

First fraction: m.p. 64-86°C.

Second fraction: m.p. 81-145°C.

Hence it must be concluded that both fractions are still mixtures.

Owing to lack of time and material, this investigation was abandoned at this stage.

8-Amino-benzanthrone.

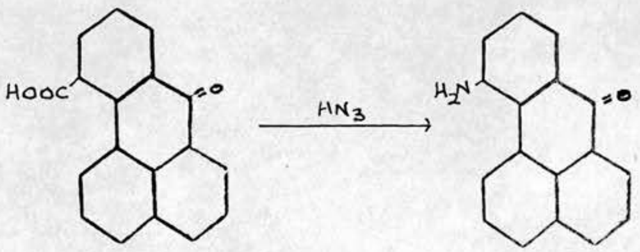
(Rule and Boyes, J.C.S., 1938, 342, 1838).

4 gm.	8-carboxy-benzanthrone.
4.4 gm.	sodium azide.
25 ml.	concentrated sulphuric acid.
100 ml.	chloroform.

The acid was dissolved in the concentrated sulphuric acid and the chloroform added. To this mixture was added solid sodium azide in portions over 2 hours with stirring, at 45-50°C. The mixture was then poured into water, the reddish precipitate filtered off, washed and boiled for a few minutes with dilute caustic soda solution, filtered again and washed. 0.46 Gm. (10%) of the acid was recovered from the alkaline filtrate.

Yield: 3 gm. (85%). m.p. 214-216°C.

Crystallisation from alcohol gave fine red needles melting at 216-217°C.



8-Formamido-benzanthrone.

0.25 gm. 8-amino-benzanthrone.
50 ml. formic acid (90%).

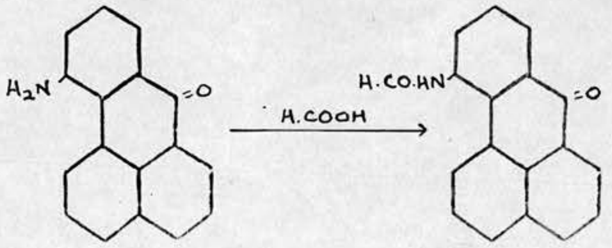
The above were boiled under reflux for 20 minutes, the amine dissolving to a brown solution with a slight green fluorescence. The excess formic acid was removed under reduced pressure, and the residue crystallised as yellow needles from alcohol.

Yield: 0.18 gm. (80%). m.p. 265-267° C.

Three further crystallisations from alcohol gave fine yellow needles which melted at 268° C.

Analysis: found C: 79.02%; H: 3.99%; N: 5.53%.

$C_{18}H_{11}O_2N$ requires C: 79.12%; H: 4.03%; N: 5.13%.



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

8-Acetamido-benzanthrone.

0.4 gm. 8-amino-benzanthrone.
30 ml. acetic anhydride.

The above were boiled under reflux for 15 minutes, and the hot solution filtered from any residue, and poured into 250 ml. water. The aqueous mixture was then heated on the steam bath until the oil solidified to a yellow precipitate which was cooled and filtered off.

Yield: 0.32 gm. (77%). m.p. 155-157° C.

This product seemed to differ from that obtained by Boyes (Thesis - Edinburgh, 1936) in that the melting point is very much lower. Recrystallisation from alcohol gave a yellow crystalline solid which on microscopic examination, was found to consist of two forms of crystals. The melting point of the mixture was 157-158° C. The plate like crystals melted fairly sharply at this temperature, but the crystalline needles which formed the other part of the mixture did not completely melt until a temperature of 260-270° C. was reached.

The same experiment was repeated with another sample of acetic anhydride, but the results were the same.

An attempt was then made to separate the two crystalline components, and this was accomplished to a certain extent by fractional crystallisation from benzene. The lower melting fraction consisted of bright leaflets, m.p. 156-157°C. and the needles which constituted the less soluble fraction melted at 267-269°C. This latter temperature approaches that given by Boyes, (278-279°C.), but further crystallisation failed to make any alteration in the melting point of the latter product. The two samples were sent for analysis, but, as the following details show, no definite proof of constitution was obtained.

Fraction melting 156-157°C.

found:- C: 76.29, 76.54, 76.67%
H: 4.7, 4.66, 4.62%
N: 4.87, 5.16%

Fraction melting 267-268°C.

found:- C: 78.2%; H: 4.67%.
N: 5.02, 5.45%

(a). Acetamino compound.

$C_{19}H_{13}O_2N$ requires:- C: 79.44%; H: 4.53%; N: 4.88%.

(b). Diacetamino compound.

$C_{21}H_{15}O_3N$ requires:- C: 76.59%; H: 4.56%; N: 4.25%.

A small weighed sample of each fraction was boiled for one hour with 50% sulphuric acid, and in each case the only hydrolysis product proved to be the free amine melting at 216-217°C., a mixed melting point showing no depression.

An analysis of Boyes' product, quoted in his thesis, was carried out for nitrogen alone, and this is not in complete agreement with the amount required for the mono-acetyl derivative of the amine. An examination of the figures given above, together with the fact that both products hydrolyse back to the amine, points to the lower melting fraction being the diacetyl derivative, while the other is in moderately good agreement with the analysis required for the mono-acetyl compound.

Another experiment was carried out to try and obtain the mono-acetyl derivative alone, as follows:-

0.1 gm.	8-amino benzanthrone.
30 ml.	glacial acetic acid.

The above were boiled under reflux for 8 hours, and then poured into 100 ml. water. The yellow solid was filtered off, washed and dried.

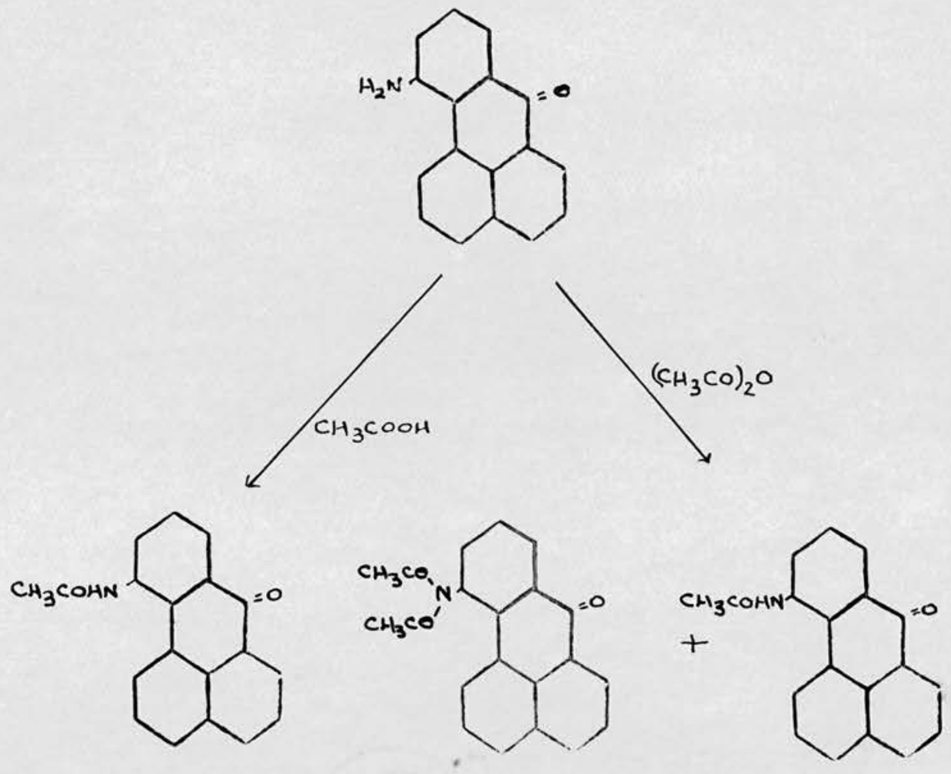
Yield: 0.075 gm. (80%). m.p. 274-276° C.

Four further crystallisations from alcohol gave fine yellow needles melting at 278-279° C.

Analysis: found:- C: 79.7%; H: 5.1%; N: 5.27%.

$C_{19}H_{13}O_2N$ requires:- C: 79.5%; H: 4.53%, N: 4.9%.

The analysis figures for this compound are acceptable and the melting point is in agreement with that quoted by Boyes.



Attempted preparation of 8-hydroxy-benzanthrone.

(Kogan and Nikolaeva, J. Appl. Chem. Russ., 1938, 11, 652-659)

The above workers were successful in replacing an amino by a hydroxy grouping in a few naphthylamine derivatives, by heating the compound with aqueous sodium bisulphite at pH. 4.2. The following experiment is based on this work.

0.02 Gm. 8-amino-benzanthrone were "pasted" by pouring the alcoholic solution into water, filtering and washing. The moist solid was added to a solution of 0.17 gm. sodium bisulphite in a minimum amount of water, and well shaken. The pH. value was adjusted to 4.2 by the addition of water, and the mixture refluxed for 2 hours. At this stage a small test portion of the mixture was removed and warmed with dilute alkali, and any colour change to blue or red, denoting the presence of a phenolic group, observed. No such reaction, however, took place, the whole of the starting material being recovered unchanged.

The experiment was repeated in a sealed tube which was heated to 150°C. for 8 hours, and when this proved unsuccessful, at increasing temperatures to 250°C. for a similar period. The amine was recovered unchanged, however, in each case.

Attempted oxidation of 8-amino-benzanthrone.

(Rule and co-workers, J.C.S., 1938, 342, 1834).

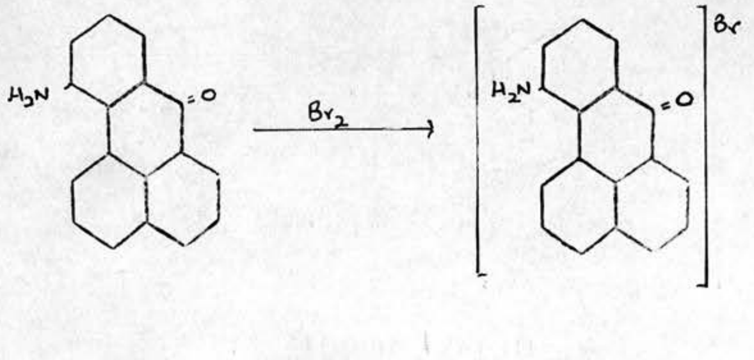
0.4 gm.	8-amino-benzanthrone.
0.125 gm.	bromine.

The amine was dissolved in the minimum amount of nitrobenzene, and the bromine added by means of a small pipette. The mixture became semi-solid in the cold, and was finally refluxed for one hour to complete the reaction. The nitrobenzene was then steam distilled, and the dark coloured residue filtered and dried.

Yield: 0.36 gm. m.p. 165-185° C.

The solid was then extracted with boiling alcohol, and the minute amount of residue neglected. The red alcoholic solution was evaporated to dryness, and the red solid which remained weighed 0.31 gm. and melted at 175-190° C. Exhaustive crystallisation from alcohol gave a very small amount of a red crystalline compound melting at 204-206° C. On testing for bromine with copper wire, the compound was found to volatilise at the temperature of the wire, and the characteristic green flame pointed to the presence of bromine in the molecule.

On boiling the substance for a few minutes with acetic anhydride and pouring into water, a brown oil was obtained which soon solidified to a brown solid, which melted at 240-245° C. Consequently it would appear that the oxidation to the secondary amine had not taken place, but that bromination had occurred, leaving the amino group free in the molecule, hence the formation of the acetyl compound with acetic anhydride.



Bromination of 8-amino-benzanthrone.

x-Bromo-8-amino-benzanthrone.

Since the attempted oxidation of 8-amino-benzanthrone with bromine resulted in the formation of a bromo-amine, the procedure was repeated on a larger scale in an attempt to identify the product.

0.4 gm.	8-amino-benzanthrone.
0.25 gm.	bromine (1 mol.).

The amine was dissolved in the minimum amount of nitrobenzene with warming, allowed to cool with stirring, and the bromine added gradually in the cold. The mixture was then poured into 250 ml. light petroleum (40-60) and the solid filtered off and washed with the same solvent.

Yield: 0.45 gm. (86%) m.p. 202-205° C.

After three crystallisations from alcohol, the product was obtained as red-brown needles melting at 205-206° C.

Analysis: found Br: 24.3%

$C_{17}H_{10}ONBr$ requires Br: 24.6%

Subsequent work on this product showed it to be a mixture of isomers, despite the sharp melting point.

The bromo-amine dissolves readily in alcohol and benzene but very sparingly in light petroleum. The solutions in alcohol and benzene are red in colour and exhibit no fluorescence.

Bzl-Bromo-8-amino-benzanthrone.

This preparation was carried out on a small sample of Bzl-bromo-8-carboxy-benzanthrone prepared by a previous worker. The procedure was exactly the same as that employed in the formation of the 8-amino-benzanthrone.

0.3	gm.	Bzl-bromo-8-carboxy-benzanthrone
0.26	gm.	sodium azide.
2	ml.	concentrated sulphuric acid,
7	ml.	chloroform.

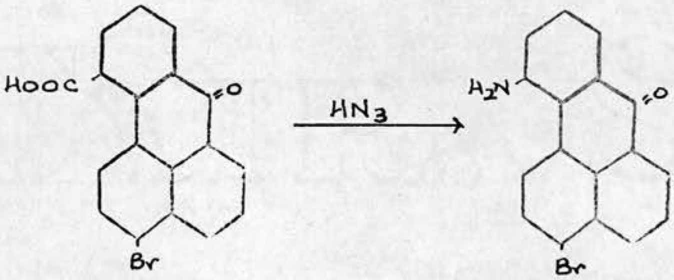
The solid azide was added in the usual manner to the solution of the acid in concentrated sulphuric acid to which the chloroform had been added, over a peroid of 2½ hours, and then allowed to stir for a further 30 minutes. The solution was poured into 50 ml. water and the precipitate filtered off. The red-brown solid was digested with dilute caustic soda, filtered once more, well washed and dried.

Yield: 0.25 gm. (91%) m.p. 245-251° C.

The suspected Bzl-bromo-8-amino-benzanthrone dissolves sparingly in alcohol, readily in nitrobenzene from which solution it is precipitated by light petroleum. Successive crystallisations from alcohol gave the compound in the form of fine red needles melting at 257-259°C.

Analysis: found:- Br: 24.1% N: 4.6%

$C_{17}H_{10}ONBr$ requires:- Br: 24.7% N: 4.3%

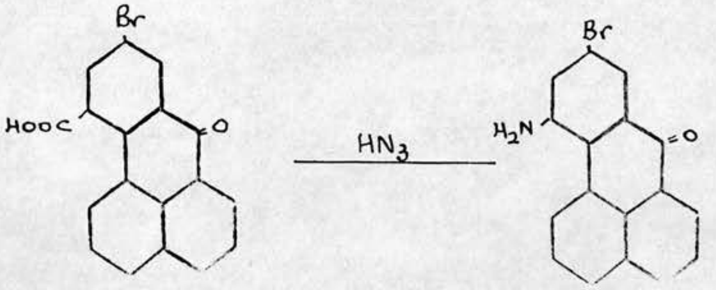


6-Bromo-8-amino-benzanthrone.

As in the previous experiment the 6-bromo-8-carboxy-benzanthrone used as starting material had been prepared by a former worker. The procedure and quantitties were exactly the same as those employed for the isomeric compound.

Yield: 0.2 gm. (75%) m.p. 226-228°C.

The properties of the compound were similar to the Bzl-bromo derivative, and after crystallising several times from alcohol the compound was obtained pure as fine red needles melting at 229-230°C.



Analysis: found:- Br: 24.73%

$C_{17}H_{10}ONBr$ requires:- Br: 24.7 %

Neither of these bromo-amines proved to be identical with that compound obtained by the direct bromination of the 8-amino-benzanthrone, so it may be assumed that in the latter compound the bromine atom does not occupy either of positions Bz1 and 6 in the benzanthrone molecule.

<u>Attempted elimination of amino group from 8-amino- benzanthrone.</u>

0.2 gm.	8-amino-benzanthrone.
0.1 gm.	sodium nitrite.
1.5 ml.	concentrated sulphuric acid.

The solid sodium nitrite was added to the concentrated sulphuric acid with stirring at 0° C., the temperature being later raised to 70° C. until all the nitrite had dissolved, after which the solution was again cooled to 0° C. The solution of the amine in glacial acetic acid (20 ml.) was also cooled and the resulting suspension added with stirring and in a thin stream to the nitrous acid mixture.

At 0° C. this was semi-solid due to the separation of acetic acid crystals, but a clear solution was obtained at ordinary temperatures. This diazo solution was added to 300 ml. alcohol, and refluxed for one hour. The alcohol was then reduced in bulk by distillation (25 ml.). The characteristic odour of acetaldehyde which normally accompanies such reactions with diazo salts could not be detected at this stage. The alcoholic solution was then drowned with water, and the brown precipitate filtered off and washed.

Yield: 0.15 gm.

The dark brown solid dissolved in dilute alkali to a great extent, giving a carmine coloured solution. Extraction of the whole with boiling dilute caustic soda was then carried out, and the dark tacky residue neglected on this occasion, since quantities were too small for successful purification. Acidification of the filtrate precipitated a light brown solid which was filtered off, washed and dried.

Yield: 0.1 gm. m.p. 260-270° C.

An elements test on the crude product showed that nitrogen and sulphur were absent.

Recrystallisation was carried out several times with dilute alcohol, and finally a very small amount of a yellow crystalline compound melting at 269-271° C. with decomposition, was isolated.

The experiment was repeated with 0.1 gm. of the amine, and enough of the pure product was obtained for analysis. The properties of this compound led to the suspicion that it was the 8-hydroxy derivative, a theory which was borne out by analysis.

Analysis: found:- C: 82.4%; H: 4.27%.

$C_{17}H_{10}O_2$ requires:- C: 82.9%; H: 4.0 %.

Boyes, (Thesis - Edinburgh, 1936) tried unsuccessfully to prepare this compound from the 8-amino-benzanthrone by boiling the diazo solution with water, this being the usual method employed for the replacement of an amino with a hydroxyl grouping.

The experiment was then repeated under optimum conditions with a larger quantity of the amine as follows:-

<u>8-Hydroxy-benzanthrone. 8-Ethoxy-benzanthrone.</u>

2 gm.	8-amino-benzanthrone.
1.2 gm.	sodium nitrite.
15 ml.	concentrated sulphuric acid.

The amine was diazotised as in the previous experiment, and the diazo solution refluxed for one hour with 1 litre of alcohol. The alcoholic mixture was then reduced in bulk (100 ml.) and poured into a litre of cold water. The mixture was made alkaline with strong sodium hydroxide solution, and warmed for a few minutes before filtering. The brown residue of alkali-insoluble material was washed and dried. The carmine filtrate gave, on acidification, 1.2 gm. of the crude hydroxy compound.

The alkali-insoluble product weighed 0.6 gm. and melted at 145-155°C. Purification was carried out by crystallisation from alcohol, and a pure compound melting at 159°C. was isolated in the form of orange needles.

Analysis: found:- C; 83.32%; H: 5.20%.
$C_{19}H_{14}O_2$ requires:- C: 83.20%; H: 5.11%.

Yield of 8-hydroxy-benzanthrone: 55%
Yield of 8-ethoxy-benzanthrone: 25%

The hydroxy derivative dissolves in dilute alcohol and most organic solvents, while in dilute alkali a carmine solution is obtained. Concentrated sulphuric acid gives a deep violet-red colour without fluorescence.

8-Ethoxy-benzanthrone gives a more violet colour with concentrated sulphuric acid than the phenol.

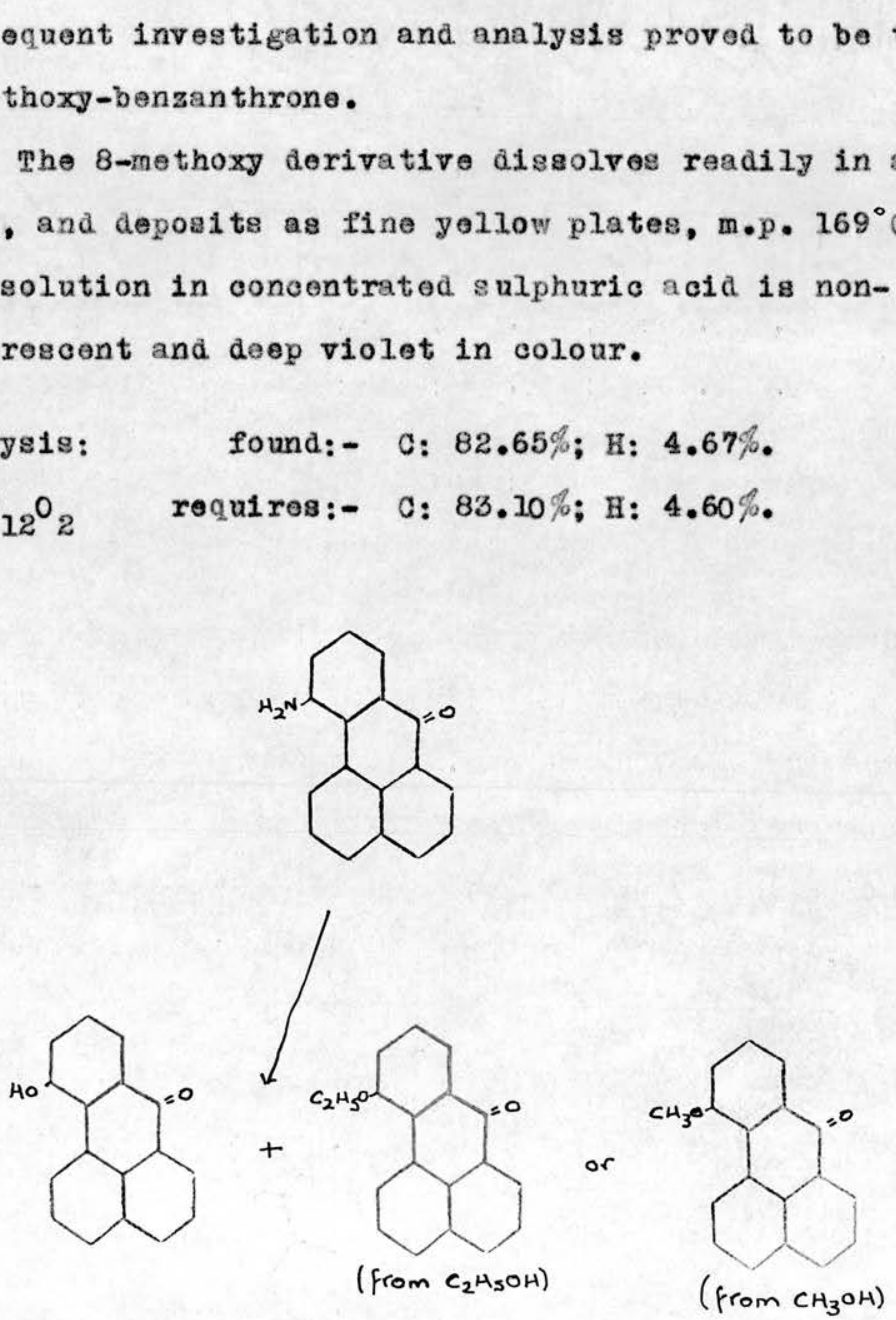
8-Methoxy-benzanthrone.

The procedure in this experiment was identical with that employed in the previous case, but with the exception that ethyl alcohol was replaced by methyl alcohol.

This led to the yield of the phenol being reduced to 35%, while the alkali-insoluble product accounted for 50% of the starting material. Purification of this latter fraction by crystallisation from alcohol gave a pure substance melting at 169°C. and which subsequent investigation and analysis proved to be the 8-methoxy-benzanthrone.

The 8-methoxy derivative dissolves readily in alcohol, and deposits as fine yellow plates, m.p. 169°C. The solution in concentrated sulphuric acid is non-fluorescent and deep violet in colour.

Analysis: found:- C: 82.65%; H: 4.67%.
$C_{18}H_{12}O_2$ requires:- C: 83.10%; H: 4.60%.



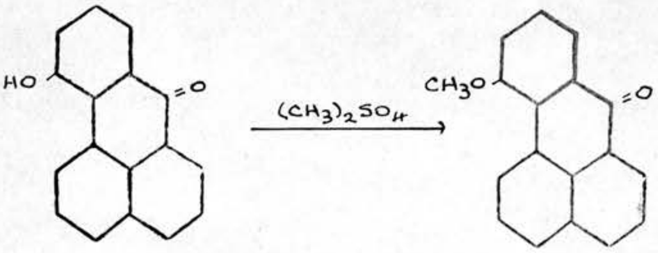
Methylation of 8-hydroxy-benzanthrone; 8-Methoxy-benzanthrone.

0.2	gm.	8-hydroxy-benzanthrone.
1	ml.	dimethyl sulphate.
20	ml.	20% sodium hydroxide solution.

The phenol was dissolved in the alkali solution, and warmed with stirring to 60°C. The dimethyl sulphate was then added and the stirring continued at this temperature until the carmine colour of the solution disappeared. The mixture was then heated on the steam bath for 30 minutes to destroy any excess dimethyl sulphate, and allowed to cool. The yellow precipitate was filtered off, washed well with water and dried.

Yield: 0.2 gm. (86%) m.p. 166-167°C.

Crystallisation from alcohol gave the pure compound as yellow plates melting at 169°C. An admixture with the methoxy derivative obtained from treatment of the diazonium salt with methyl alcohol failed to show any depression in the melting point, thus showing that the two compounds were identical.



Methyl-1-bromo-2-naphthoate.

(Rule and Grieve, J.C.S., 1938, 342, 1836).

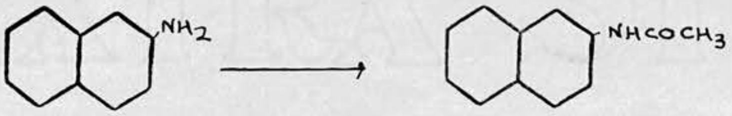
(a) Aceto-β-naphthalide.

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

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

The naphthylamine was dissolved in 250 ml. 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 filtered, 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.).

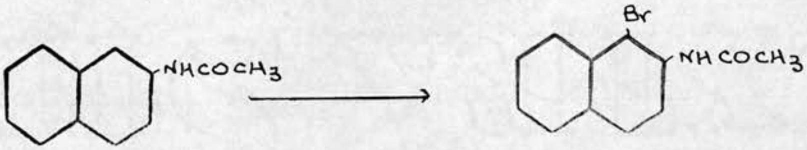
37 gm.	aceto-β-naphthalide.
33 gm.	bromine.

The aceto-β-naphthalide was dissolved in 200 ml. chloroform with heating, and bromine, dissolved in

40 ml. 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 ml. dilute sodium carbonate solution until effervescence ceased, 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.



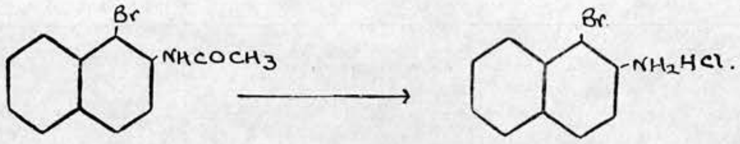
(c) Hydrolysis of the bromonaphthalide.

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 ml. alcohol with heating. Concentrated hydrochloric acid

(25 ml.) 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 filtered off, washed with a little alcohol and dried.

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



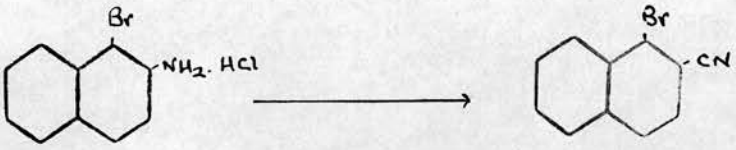
(d) 1-Bromo-2-naphthonitrile.

50 gm. bromonaphthylamine hydrochloride.
20 gm. sodium nitrite in 25 ml. water.
(1) 120 gm. sodium cyanide in 300 ml. water.
(2) 100 gm. copper sulphate in 400 ml. water.

The finely powdered hydrochloride was suspended in 150 ml. water and 60 ml. concentrated hydrochloric acid were added. The suspension was cooled to 0-5° C. and diazotised in the usual manner until a slight excess of nitrous acid was present.

A solution of cuprous cyanide was prepared by adding solution (1) to (2) with shaking and the mixture filtered from any residue.

The clear diazo solution was added in portions to the vigorously stirred cuprous cyanide on the steam bath. The brown precipitate which formed was stirred for a further 3 hours on the steam bath, when the oily drops of the nitrile were formed. After standing over-night the solid nitrile was filtered off and hydrolyses to the acid without preliminary purification.



(e) 1-Bromo-2-naphthoic acid.

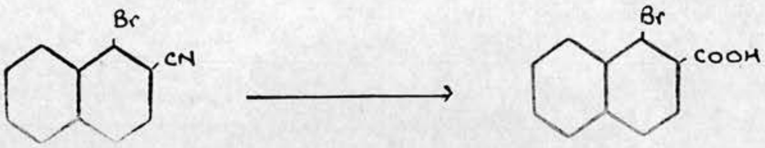
The crude nitrile was refluxed for 24 hours with an acid hydrolysing mixture consisting of:-

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

The brown liquid was poured into 2 litres of cold water, and the crude acid which was precipitated, filtered off. The solid was added to 500 ml. water, made distinctly alkaline with caustic soda, heated to 50° C. for a few minutes and then 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 melting at 191°C. For conversion to the ester, however, it was found more economical to esterify the crude acid and purify the ester.



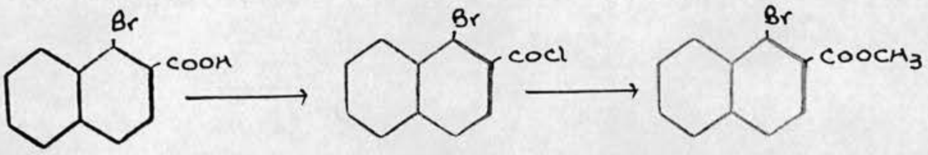
Methyl-1-bromo-2-naphthoate.

15 gm. 1-bromo-2-naphthoic acid.
30 ml. thionyl chloride (purified).
50 ml. methyl alcohol (dry).

The ester was formed by way of the acid chloride, as described in the preparation of the 8-bromo-1-naphthoic ester. 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 light petroleum (b.p. 40-60°C.).

Yield: 14 gm. (90%) m.p. 58-59°C.

The ester crystallises from light petroleum in colourless plates melting at 60°C.



Bz3-Carboxy-benzanthrone.

An attempt to prepare this acid was made by Rule and Grieve (J.C.S., 1938, 342, 1836), but the chief product of the reaction was fluorenone 4-carboxylic acid, and this interfered to a great extent in the purification of the small amount of the Bz3-carboxy-benzanthrone which was formed. These workers, after many attempts, finally obtained the required acid in a yield of 3%.

The procedure employed in the following experiment is the same as that used by the above workers, with the exception that methyl-o-bromo-benzoate was substituted for methyl-o-iodo-benzoate, in the hope that the reduced activity of the halogen atom might lead to a reduction in the amount of diphenic ester produced in the Ullmann coupling, with a corresponding increase in the yield of the required phenyl-naphthyl ester.

25 gm.	methyl-1-bromo-2-naphthoate.
50 gm.	methyl-o-bromo-benzoate.
30 gm.	copper bronze.

The mixed esters were stirred in a small flask, heated in an oil bath at 160° C. and 15 gm. of the copper added over one hour. The temperature was then raised to 200° C. and the remainder of the copper added in portions. After 6-7 hours, the product was extracted with acetone in the usual manner, and the inorganic material removed. Acetone was distilled off and the syrupy residue transferred to a Claisen flask fitted with a long fractionating column. The mixed esters were then distilled in vacuo, and several fractions collected. The first fraction consisted of a little methyl-o-bromo-benzoate at 145° C./20 mm., but the temperature rapidly rose to 195° C. when a fraction was collected, distilling at 195-210° C. and which was chiefly diphenic ester. It solidified on standing to a low melting solid which crystallised from ether in plates, m.p. 73-74° C. A third fraction distilling at 225-275° C. was collected (17 gm.), and took the form of a very viscid yellow liquid which solidified on proponged chilling. A small dark residue remained in the flask, presumably the dinaphthyl ester.

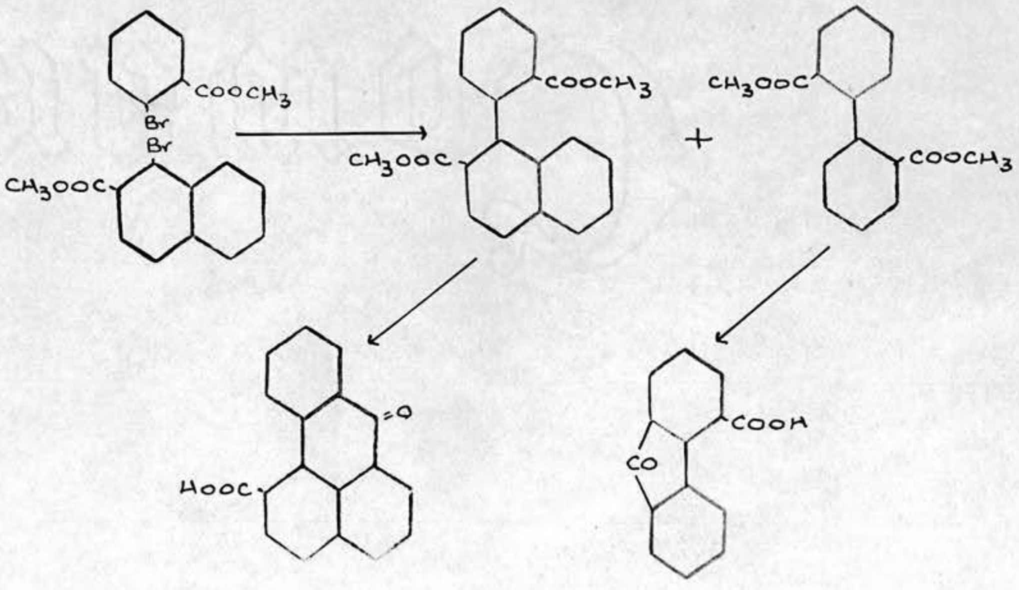
The fraction distilling at 225-275° C. was treated with concentrated sulphuric acid (300 ml.) with stirring at 100° C. for one hour. The red fluorescent solution was poured into water, the brown precipitate filtered off and well washed with water. It was dissolved in dilute caustic soda solution with heating, and the yellow-brown fluorescent solution filtered from a small insoluble residue. On acidification, the filtrate yielded a yellow solid which consisted of the required acid along with some fluorenone derivative. The dry solid (3.35 gm.) was boiled with 200 ml. chlorobenzene for a short period and filtered hot. The hot solution on cooling gave crude fluorenone 4-carboxylic acid, and the light brown insoluble residue now dissolved in caustic soda solution with a vivid green fluorescence.

Yield: 2.15 gm. m.p. 275-281°C.

Successive crystallisations from glacial acetic acid gave the pure product in the form of yellow needles, melting at 283-284°C.

A mixed melting point with a pure sample of the acid prepared by Grieve failed to show any depression, so that the two products were identical.

Yield: 7%.



Bz3-Amino-benzanthrone.

1	gm.	Bz3-carboxy-benzanthrone.
1.1	gm.	sodium azide.
7	ml.	concentrated sulphuric acid.
25	ml.	chloroform.

The procedure employed here was similar to that used in the preparation of the 8-amino-benzanthrone. The yield of crude amine obtained was 0.4 gm. and 0.47 gm. of Bz3-carboxy-benzanthrone was recovered from the alkali filtrate.

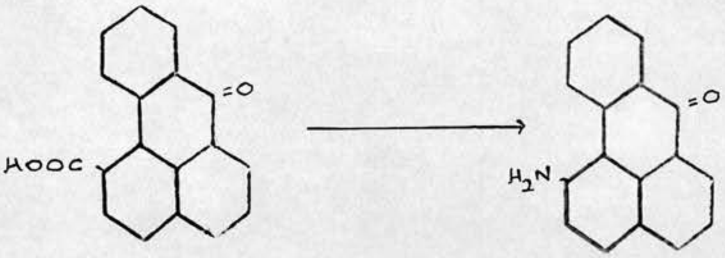
Yield: 45-50%. m.p. 230-234° C.

The same experiment was repeated, but in this case the period of addition of the sodium azide was extended to 3 hours. This resulted in a yield of almost 95% being obtained.

The amine crystallises from chlorobenzene in red needles melting at 235-236° C., decomposition taking place slightly below the melting point. It dissolves readily in alcohol to form a vivid yellow fluorescent solution, while the solution in benzene shows a vivid green fluorescence. Concentrated sulphuric acid gives a yellow solution with vivid yellow fluorescence.

Analysis: found:- C; 82.5%; H: 4.7%; N: 5.7%.

$C_{17}H_{11}NO$ requires:- C: 83.3%; H: 4.5%; N: 6.02%.



Bz3-Acetamido-benzanthrone.

0.05 gm. Bz3-amino-benzanthrone.
5 ml. acetic anhydride.

The above were refluxed for 15 minutes and then poured into water (40 ml.). The oil which separated solidified after a short time on the steam bath. The solid was filtered off, washed and dried.

Yield: 0.06 gm. (90%) m.p. 204-210° C.

Crystallisation from alcohol gave a crystalline product which microscopic examination showed to consist of small plates mixed with a smaller amount of needles. The two fractions were separated from alcohol, the plates being relatively more soluble than the needles. The plates constituted about 75% of the mixture and melted at 238-239° C. while the needles melted at 240-241° C. The small quantities available did not allow of the higher melting fraction being analyses for C. and H., but the figures for the other form point to the probability that the same reaction has occurred here as took place on treatment of the 8-amino-benzanthrone with acetic anhydride. The fraction melting at 238-239 °C. is most likely the diacetyl derivative while the other is the mono compound.

Analysis:

Fraction m.p. 238-239 C. (diacetyl compound).

found:- C: 76.24%; H: 4.52%; N: 5.08%.

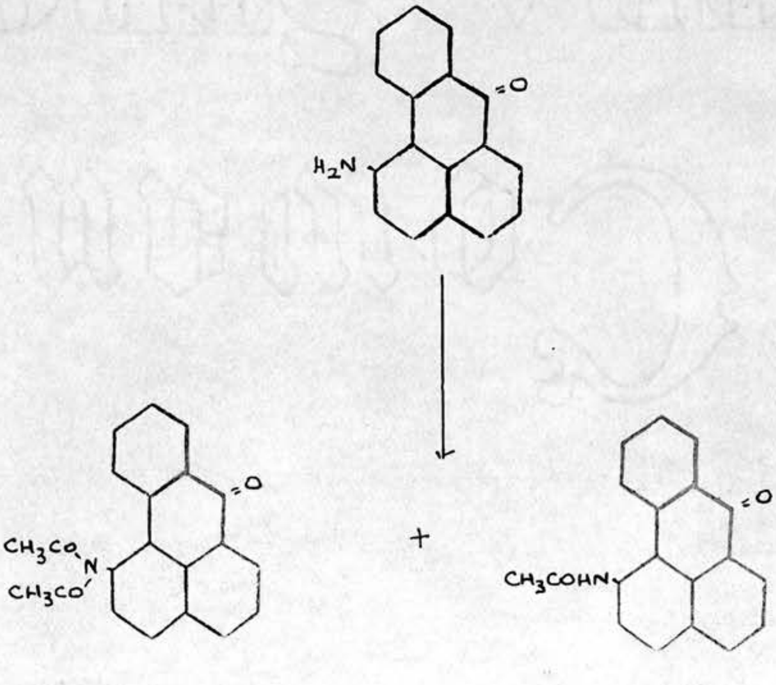
$C_{21}H_{15}O_3N$ requires:- C: 76.59%; H: 4.56%; N: 4.25%.

Fraction m.p. 240-241 C. (monoacetyl compound).

found:- N: 3.8%.

$C_{19}H_{13}O_2N$ requires:- N: 4.88%.

Owing to lack of material the investigation was abandoded at this stage.



Bz3-formamido-benzanthrone.

0.25 gm. Bz3-amino-benzanthrone.
50 ml. formic acid (90%).

The above were boiled under reflux for 20 minutes. The amine dissolved to a red-brown solution with a crimson fluorescence. The excess formic acid was removed under reduced pressure, and the residue crystallised from alcohol. The alcoholic solution is pale yellow in colour and exhibits vivid yellow fluorescence.

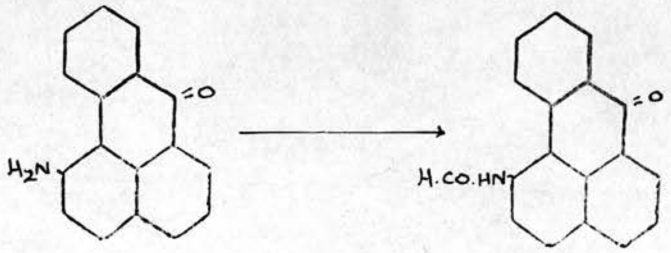
Yield: 0.25 gm. (90%) m.p. 270-273°C. (decomp).

After three crystallisations from alcohol, the product was obtained as yellow brown needles melting at 273-275°C. with decomposition.

Analysis:

found:- C: 78.98%; H: 4.08%; N: 5.43%.

$C_{18}H_{11}O_2N$ requires:- C: 79.10%; H: 4.03%; N: 5.13%.



Attempted preparation of x-Bromo-8-methoxy-benzanthrone and x-Bromo-8-hydroxy-benzanthrone.

1 gm.	x-bromo-8-amino-benzanthrone.
0.5 gm.	sodium nitrite.
25 ml.	concentrated sulphuric acid.

The diazotisation was carried out in exactly the same manner as that employed for the 8-amino-benzanthrone. The bromo-amine was dissolved in glacial acetic acid (250 ml.) and the cold suspension added slowly to the nitrous acid solution, keeping the temperature between the usual diazo limits.

The mixture was stirred for 30 minutes after all the amine had been added, and poured into 500 ml. methyl alcohol, the mixture being then boiled for one hour.

The bulk of the alcohol was then removed and the residue drowned with water and cooled. The cold mixture was filtered and the brown solid boiled for a few minutes with dilute alkali. The alkaline mixture was again filtered and the residue washed and dried.

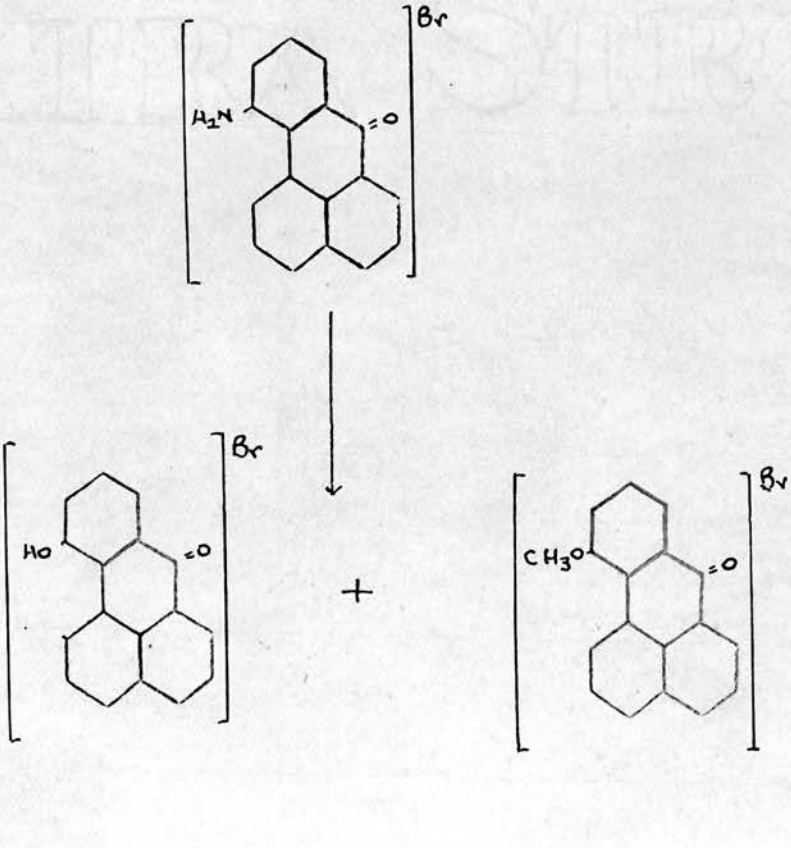
Weight of supposed methoxy derivative: 0.75 gm.

m.p. 190-200°C.

Weight of supposed hydroxy derivative: 0.15 gm.

Purification of the alkali-insoluble compound was carried out and although a seemingly pure compound was obtained from glacial acetic acid, no sharp melting point could be procured. At this point it was discovered that the starting material, also of sharp melting point and of analytical purity, consisted of a mixture of isomeric bromo-amino-benzanthrones, and so the investigation of the above products was not carried further.

However, results obtained up to this point would point to the formation of the methoxy and hydroxy bromo benzanthrones, and there should be no difficulty in isolating a pure product from a similar series of reactions on a homogeneous sample of authentic bromo-amino-benzanthrone.



8-Bromo-benzanthrone.

0.5 gm.	8-amino-benzanthrone.
0.3 gm.	sodium nitrite.
10 ml.	concentrated sulphuric acid.
8 gm.	copper sulphate.
6.5 gm.	sodium bromide.
37 gm.	hydrobromic acid (S.G. 1.49).
4 gm.	copper filings.

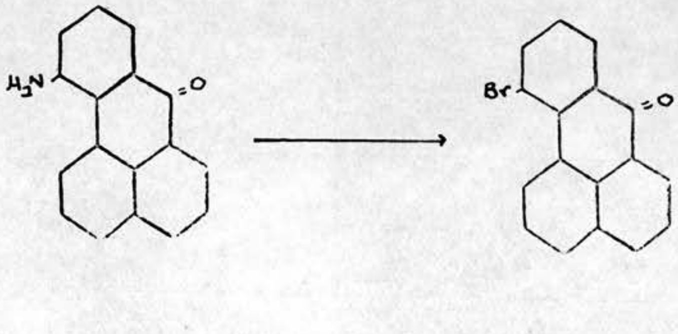
The amine was diazotised in glacial acetic acid solution by the usual method, and the cooled solution added fairly rapidly to a warm (40-50°C.) cuprous bromide solution prepared as follows:- The copper sulphate, sodium bromide, hydrobromic acid and copper filings were boiled together under reflux until colourless, and the clear solution decanted from solid residue. The mixture was allowed to stand for 30 minutes, and finally heated on the steam bath until effervescence ceased. On pouring the product into 500 ml. water, a yellow solid was precipitated which was filtered off, washed and dried. The yellow solid was then extracted three times with 100 ml. alcohol and the red-brown solution evaporated to dryness. The dark brown solid remaining weighed 0.5 gm. and melted at 165-175°C. Crystallisation did not give a pure product, since the impurity seemed to be less soluble than the compound required, and so chromatographic analysis was resorted to, employing benzene as solvent and aluminium oxide as adsorbent. This was carried out with complete success, a broad yellow band separating with relative ease from the narrow band of deep adsorption at the top of the tube. On washing this band out, a yellow benzene solution was obtained, which on evaporation to dryness yielded 0.35 gm. of a yellow crystalline compound which melted at 175-177° C. Crystallisation from glacial acetic acid gave the pure substance melting at 178 C.

Yield: 0.3 gm. (50%) m.p. 178° C.

Analysis: found: Br: 25.45%.

$C_{17}H_9OBr$ requires: Br: 25.80%.

The compound dissolves readily in alcohol and benzene to give a yellow solution. Concentrated sulphuric acid yields a crimson non-fluorescent solution.

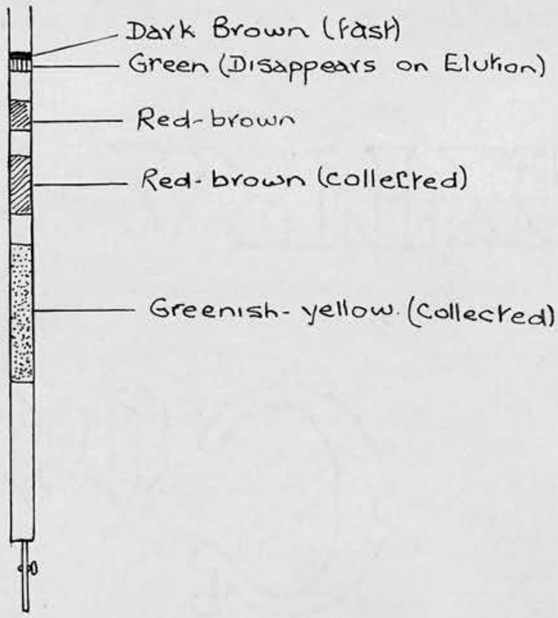


x:8-Dibromo-benzanthrone.

0.6 gm.	x-bromo-8-amino-benzanthrone.
0.3 gm.	sodium nitrite.
5 ml.	concentrated sulphuric acid.
12 gm.	copper sulphate.
9.6 gm.	sodium bromide.
55.2 gm.	hydrobromic acid (S.G. 1.49).
6 gm.	copper filings.

The bromo-amine, subsequently found to be a mixture of isomerides, was diazotised as formerly by the Hodgson and Walker method, and the diazo solution allowed to stir for a further 30 minutes. Meanwhile, a solution of cuprous bromide was prepared as in the previous experiment. The diazo solution was run into the warm solution fairly rapidly, and the product heated on the steam bath until effervescence ceased. The mixture was then poured into water and the pale yellow precipitate filtered off, washed and dried. The product was then extracted with 100 ml. alcohol, and on evaporation of the alcoholic solution to dryness, a brownish residue remained which weighed 0.6 gm. and melted at 145-150° C.

Repeated crystallisation from alcohol did not lead to the isolation of a pure product, and it was decided as with the previous Sandmeyer reaction, to try chromatographic means for purification. This was carried out on a benzene solution of the crude compound using aluminium oxide as the adsorbent. Adsorption took place to a great extent and elution with benzene caused the chromatogram to spread out into several bands as shown in the following diagram.



Elution led to the greenish yellow band being washed down and the other layers spreading down the column. The bottom layer, however, separated from the others, and complete elution was effected. The orange-red band was also washed out, but more slowly than the greenish-yellow layer. These were the only two fractions collected, since the others obviously consisted solely of small amounts of impurities. during the elution, the tube stood for some time in the direct rays of the sun, and a smoky appearance was observed on the sun-ward side of the tube. This effect seemed to be confined to the orange-red band,

and the brown layer next the glass failed to move down the tube on continued elution. The brown colour could not be removed from the aluminium oxide by boiling with benzene, and so was neglected, since it comprised only a very thin layer on the side of the tube.

The yellow and red benzene solutions were evaporated to dryness and the resulting solids examined. The yellow solution gave 0.5 gm. of a bright yellow crystalline compound which melted at 148-149°C. The red solution gave a reddish-brown solid which weighed 0.04 gm. and melted at 195-205°C.

Crystallisation of the yellow compound from alcohol gave bright yellow needles melting at 149°C. The product also gave a positive test for bromine with copper wire, and gave a crimson fluorescent solution with concentrated sulphuric acid. Analysis of this compound was carried out for bromine and was in complete agreement with the amount required for a dibromo-benzanthrone, although subsequent investigations proved that this supposedly pure compound was in reality a mixture of isomerides.

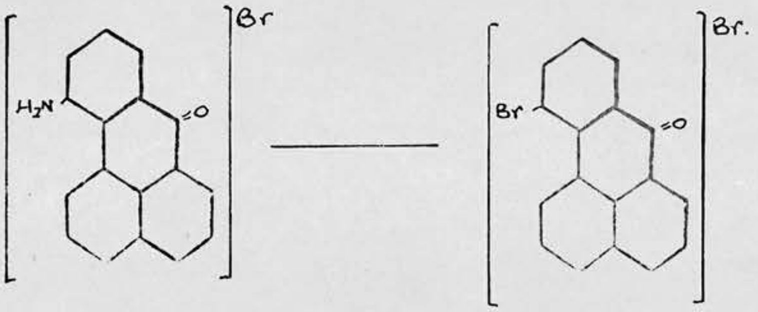
Crystallisation of the red-brown solid from alcohol gave red needles melting at 204-205°C., and admixture with the starting material gave no depression in the melting point, proving it to be some unchanged bromo-amine.

Yield: 0.5 gm. (75%) m.p. 149°C. (isomeric mixture)

Analysis: found:- Br: 41.34%.

$C_{17}H_8OBr_2$ requires:- Br: 41.24%.

The compound dissolves readily in alcohol and benzene, but sparingly in light petroleum.



The failure in subsequent investigations to identify this dibromo-benzanthrone with other prepared dibromo derivatives led to the suspicion that the product was an isomeric mixture. On submitting a sample to chromatographic analysis with aluminium oxide, and collecting several fractions, a variety of melting points were obtained which proved the supposition to be an actual fact. The matter is treated fully in the discussion section.

Attempted elimination of the amino group from 8-amino-benzanthrone.

(Chamberlain, Amer. Chem. J. 1897, 19, 531).

The above worker, employing a procedure similar to that given below, was successful in isolating toluene alone from p-diazo-toluene sulphate, the formation of the ether being inhibited in this case.

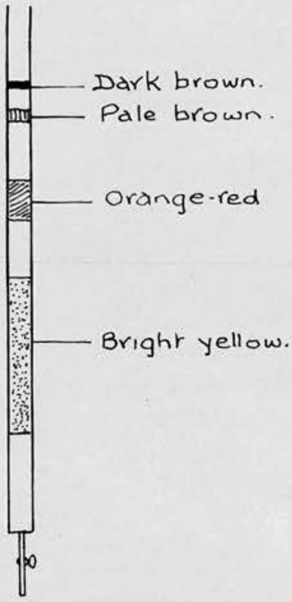
0.5 gm.	8-amino-benzanthrone.
0.3 gm.	sodium nitrite.
5 ml.	concentrated sulphuric acid.

The amine was diazotised by the usual Hodgson and Walker modification, but in this instance the amine was dissolved in 10 ml. concentrated sulphuric acid in the cold with stirring. The solution was added slowly to the nitrous solution, also in concentrated sulphuric acid, the temperature being maintained below 5°C. When mixture was complete, stirring was continued for a further 30 minutes and in the meantime a solution of 30 gm. caustic soda in 500 ml. methyl alcohol was prepared. 10 ml. of this solution were diluted with 100 ml. methyl alcohol, and transferred to a litre beaker fitted with a stirrer. To this solution the diazo solution was added very slowly through a dropping funnel drawn to a fine point. At the same time the remainder of the alcoholic caustic soda was added through another dropping funnel, the rate of dropping being adjusted so that the mixture just remained on the alkaline side. This was tested with an occassional drop on litmus paper.

When the mixture was complete, it was allowed to stand overnight and then boiled for an hour, before filtering off the solid precipitate of sodium sulphate. The solid was washed with methyl alcohol until colourless and the washings added to the filtrate. Most of the alcohol was then distilled off, and the residue evaporated to dryness, when it was digested for a few minutes with 50 ml. dilute caustic soda solution. The carmine solution was filtered off and the residue washed and dried. Acidification of the filtrate gave 0.05 gm. of a light brown solid which had all the characteristics of 8-hydroxy-benzanthrone.

The reddish brown alkali-insoluble fraction weighed 0.35 gm. and melted at 115-145°C. The colour obtained with concentrated sulphuric acid was a red-violet, not unlike that given by the 8-methoxy derivative, but totally different from that exhibited by benzanthrone. Crystallisation did not give a satisfactory purification and so the whole was dissolved in benzene and submitted to chromatographic analysis with aluminium oxide. A separation was obtained but there seemed to be a number of fractions in the product.

As shown in the following diagram, elution led to the separation of various bands (4). The lower two washed out completely, while the others, although spreading to some extent, failed to respond to prolonged elution.



The yellow band gave a yellow solution from which 0.05 gm of a yellow solid were obtained. This substance which had a needle crystal structure melted at 156-158 C. and a mixed melting point with pure 8-methoxy-benzanthrone showed no depression, thus proving it to be identical with the latter compound. The orange-red solution on evaporation gave 0.1 gm. of a red solid melting at 210-215 C. which subsequent purification and investigation proved to be unchanged starting material. No trace of benzanthrone could be isolated.

(2).

By treatment of diazonium salts with alkaline formaldehyde, Brewster and Poje (J.A.C.S., 1939, 61, 2418). have been successful in converting various amines into the corresponding hydrocarbons. The method is stated as being particularly efficacious with amines which tend to give the ether on submitting to the usual procedure for such conversions. The following experiment is based on their work.

0.5 gm.	8-amino-benzanthrone.
0.3 gm.	sodium nitrite.
5 ml.	concentrated sulphuric acid.

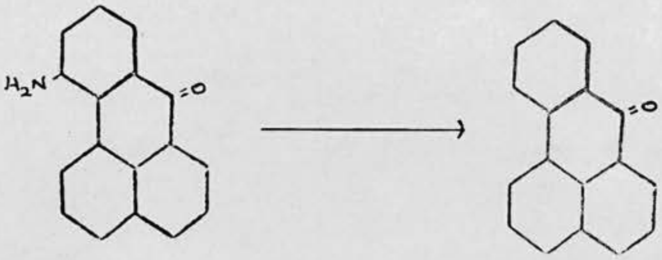
The amine was diazotised in the same manner as previously using concentrated sulphuric acid as solvent.

150 gm. caustic soda were dissolved 800 ml. water, and 100 ml. formalin (37% formaldehyde) added, the mixture being cooled by the addition of 500 gm. shaved ice. To the vigorously stirred alkaline formaldehyde solution, the diazo solution was added slowly. No frothing was observed, and the mixture became reddish-brown in colour. After standing for an hour, the dark brown precipitate was filtered off, washed and dried. The alkaline filtrate again yielded a large proportion of the 8-hydroxy derivative on acidification, but of a very impure nature.

Purification of the product was again effected by chromatographic means and a good separation was obtained. A dark band of deep adsorption was observed at the top of the tube, and a relatively broad band of a yellow colour spread down the column on elution. This latter band was washed out and the yellow benzene solution evaporated to dryness, when 0.05 gm. of a yellow crystalline solid was obtained which melted at 160-165° C. Crystallisation from glacial acetic acid gave fine yellow needles melting at 169-171°C., admixture of which with pure benzanthrone produced no melting point depression.

Yield of Benzanthrone: 0.05 gm.

Yield of 8-hydroxy-benzanthrone (crude): 0.3 gm.



5:8-Dibromo-benzanthrone.

(a) 1:4-Dibromo-anthraquinone.

(Battegay and Claudin, Bull. Soc. Ind. Mulhouse 1920).

The above workers are quoted as having prepared 1:4-dibromo-anthraquinone by a Sandmeyer reaction from 1:4-diamino-anthraquinone, but no particulars are given.

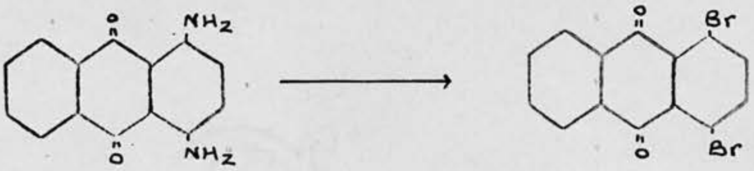
4 gm.	1:4-diamino-anthraquinone.
4 gm.	sodium nitrite.
50 ml.	concentrated sulphuric acid.
14.25 gm.	copper sulphate.
12 gm.	sodium bromide.
68 gm.	hydrobromic acid (S.G. 1.49).
8 gm.	copper filings.

The amine was diazotised in glacial acetic acid solution by the same procedure as was employed with 8-amino-benzanthrone, and the diazo solution allowed to stir for 30 minutes. To the warm solution of cuprous bromide, prepared as in previous experiments, the diazo solution was added fairly rapidly, and the mixture allowed to stand for 24 hours, finally being heated on the steam bath until effervescence ceased. The dark coloured product was then poured into water, and the brown precipitate filtered off, washed and dried.

The solid was then extracted three times with 100 ml. portions of alcohol, and the black insoluble residue rejected. On evaporating to dryness, the red-brown alcoholic solution gave 3.9 gm. of a red-brown solid melting at 175-187°C. Crystallisation from alcohol with the addition of animal charcoal led to the isolation of 3 gms. of fairly pure 1:4-dibromo-anthraquinone, melting at 194-196°C.

Yield: 66%.

The above workers quote the melting point as 196°C.



(b) <u>1:4-dibromo-anthrone.</u>

2 gm.	1:4-dibromo-anthraquinone.
50 ml.	glacial acetic acid.
2.2 gm.	tin.
10 ml.	fuming hydrochloric acid.

The dibromo-anthraquinone was dissolved in the glacial acetic acid with warming, tin and a crystal of copper sulphate added, and the mixture boiled gently under reflux. Fuming hydrochloric acid (prepared by passing dry hydrochloric acid gas into the cooled concentrated acid until its density is 1.5), was then added in portions at such intervals as to maintain a steady evolution of hydrogen. At the end of two hours the clear solution was decanted from the solid residue, and allowed to cool, when yellow crystals were deposited. These proved to be the required anthrone.

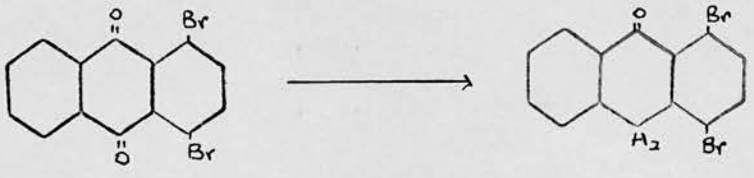
Yield: 1.6 gm. (85%) m.p. 168-169°C.

Crystallisation from glacial acetic acid gave fine yellow needles melting at 171°C.

The compound gives a yellow non-fluorescent solution with concentrated sulphuric acid, and is fairly soluble in most organic solvents.

Analysis: found:- Br: 45.2%.

$C_{14}H_8OBr_2$ requires:- Br: 45.4%.

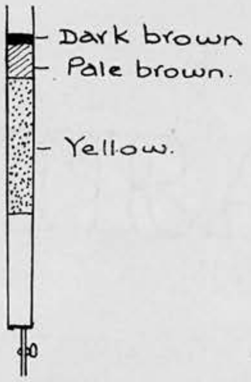


5:8-Dibromo-benzanthrone.

1.2 gm.	1:4-dibromo-anthrone.
14 ml.	82% sulphuric acid.
1.5 ml.	glycerol.

The above were mixed and heated cautiously to 120°C. in an oil bath for four hours. After cooling, the liquid was poured into 200 ml. water, and the dark brown solid filtered off, washed and dried. It was then boiled with 50 ml. 1% caustic soda solution, filtered, washed and dried.

The product at this point was a dark brown-red solid which gave no good melting point. Extraction with benzene was then carried out and the reddish brown solution passed through an aluminium oxide column. A separation into bands was obtained and is shown diagramatically in the illustration below.

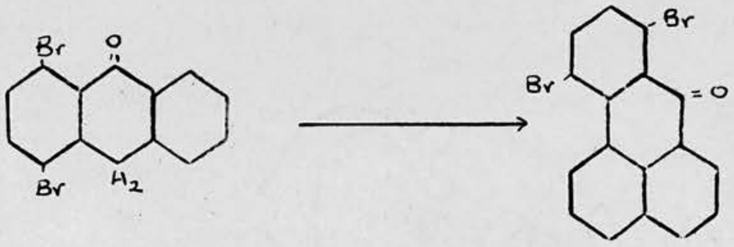


The elution with benzene, led to the two bottom layers moving down the tube, the yellow band, however, being completely separated from the pale brown layer which ultimately remained fixed halfway down the column. The former band was completely washed out, and the yellow benzene solution evaporated to dryness. The yellow solid obtained weighed 0.65 gm. and melted at 174-176 °C. Crystallisation from glacial acetic acid finally gave the pure compound as fine yellow needles melting at 176 °C. Analysis confirmed the nature of the product.

Yield: 50%.

Analysis: found:- Br: 41.27%.

$C_{17}H_8OBr_2$ requires:- Br: 41.24%.



The compound dissolves in concentrated sulphuric acid to give a violet non-fluorescent solution, and is also fairly soluble in most organic solvents.

7:8-Dihydroxy-benzanthrone. Benzalizarin.

(Perkin, J.C.S., 1920, 700).

The above worker succeeded in the isolation of this compound from alizarin by the glycerol condensation, but gives no details for the preparation.

(a) 3:4-Dihydroxy-anthrone. Deoxyalizarin.

(Graebe and Thode, Ann., 1906, 349, 207).
(Römer, Ber., 14, 1260).

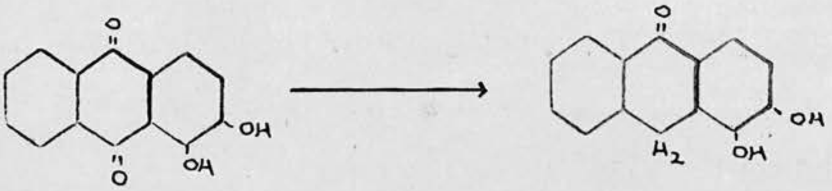
5.5 gm.	alizarin.
100 ml.	ammonia (25%).
500 ml.	water.
50 gm.	zinc dust.

The above were warmed on the water bath for 30 minutes with frequent shaking, and then filtered into a mixture of 350 ml. concentrated hydrochloric acid and 700 ml. water. The yellow precipitate was filtered off and well pressed on the filter. Crystallisation was carried out with aqueous alcohol, animal charcoal being added to remove impurities.

Yield: 5 gm. m.p. 198-202°C.

It is difficult to obtain a good melting point of the compound since the crystals contain water of crystallisation. However, the product was pure enough for further treatment. A previous attempt to prepare this compound by reduction of alizarin in acid solution failed to give a good product since the reaction results in the formation of a mixture of the 1:2 and 3:4 dihydroxy-anthrones. Alkaline reduction results in the formation of the 3:4 isomer alone.

The compound dissolves in alkali to give an orange red solution, entirely different from the deep purple colour exhibited by alizarin.



7:8-Dihydroxy-benzanthrone. Benzalizarin.

3.5 gm.	3:4-dihydroxy-anthrone.
3 gm.	glycerol.
45 gm.	sulphuric acid (82%).

The above were heated cautiously in an oil bath to 120 C. for 4 hours, cooled and poured into water. A black resinous powder was obtained which was filtered, washed and dried. Extraction was then carried out with four 100 ml. portions of alcohol. The extract was red-brown in colour, and on evaporation to 25-30 ml. was poured into 1500 ml. ether. A black sludge was precipitated and filtered off. The clear ethereal solution was washed repeatedly with water until the aqueous layer was colourless, dried over calcium chloride and evaporated to dryness. This led to the isolation of 2.5 gm. of a red-brown solid. The total product was boiled for 20 minutes with 100 ml. acetic anhydride, poured when cold into 300 ml. water, and heated on the steam bath until the oil solidified. When cold the yellow precipitate was filtered off, washed with water and dried.

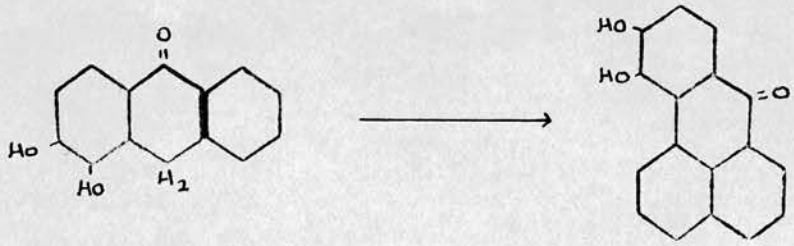
Yield of ~~Benzalizarin~~ diacetate: 2 gm. m.p. 198-200° C. Benzanthrone

Hydrolysis of the diacetate with an acid mixture comprising 4 parts of glacial acetic acid, 2 parts concentrated sulphuric acid and 1 part of water, at the boiling point for 15 minutes, and pouring into water gave a quantitative yield of the required 7:8-dihydroxybenzanthrone in a good state of purity.

Yield: 1.5 gm. (40%) m.p. 308-309° C. (decomp).

Perkin (J.C.S., 1920, 700) is quoted as aforesaid as having prepared these compounds, but gives no yields. The melting points given by him, however, are in complete agreement with those quoted above.

The dihydroxy derivative dissolves in concentrated sulphuric acid to give a crimson solution. In alkali an intense deep blue solution is obtained.



7:8-Dimethoxy-benzanthrone.

1 gm.	7:8-dihydroxy-benzanthrone.
1 ml.	dimethyl sulphate.
25 ml.	caustic soda solution (20%).

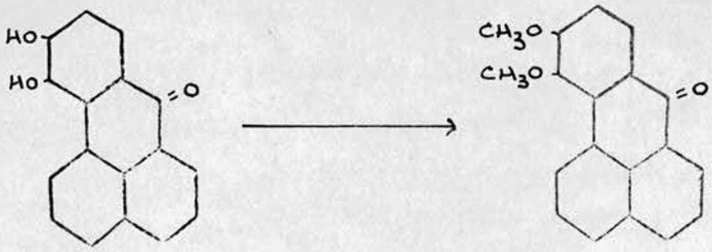
The dihydroxy compound was dissolved in the alkali and warmed to 55-60° C. The dimethyl sulphate was then added with stirring at this temperature and stirring continued until the blue colour of the solution was dispersed. A yellow precipitate came down in the alkaline solution and after heating the mixture on the steam bath for a few minutes to destroy excess dimethyl sulphate, this was filtered off, washed and dried.

Yield: 1 gm. (95%) m.p. 139-141° C.

Crystallisation from dilute alcohol gave the pure compound in the form of fine needles melting at 142 C.

Perkin (loc.cit.) also prepared this compound but by the more tedious method employing methyl iodide. He had some difficulty in purifying his product, and does not quote yields. The melting point is given by this worker as 139-141° C.

The dimethoxy derivative dissolves in concentrated sulphuric acid to give an orange non-fluorescent solution.



1:4-Dihydroxy-anthrone.

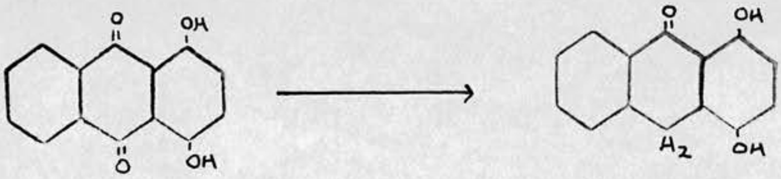
23 gm.	quinizarin.
800 ml.	glacial acetic acid.
50 gm.	tin.
100 ml.	fuming hydrochloric acid (S.G. 1.4).

The quinizarin and the glacial acetic acid were brought to boiling point and the tin added along with a crystal of copper sulphate. To the gently boiling solution the fuming hydrochloric acid was added in such portions as to produce a constant evolution of hydrogen. After two hours the yellow solution was poured into 2 litres of water, cooled and filtered.

Yield: 21 gm. (100%) m.p. 153-155° C.

Crystallisation from alcohol, in which medium the compound gives a yellow solution with a slight green fluorescence, gave orange needles melting at 156° C.

Pleus (Ber., 35, 2924) is quoted as having prepared this compound by reduction with hydriodic acid and red phosphorus. He quotes a melting point of 156° C. but yields are not reported.



Attempted preparation of 5:8-dihydroxy-benzanthrone.

3.5 gm.	1:4-dihydroxy-anthrone.
3 gm.	glycerol.
45 gm.	sulphuric acid (82%).

The above were heated cautiously in an oil bath to 120 C. for 4 hours, cooled and poured into water. A black-brown resinous powder was precipitated which was filtered, washed and dried. Extraction with alcohol gave a red-brown solution which was evaporated to small bulk and poured into much ether. The dark brown solid was filtered off, and the clear ethereal solution evaporated to dryness, when 1.3 gm. of a red oil was obtained. This oil solidified to a red solid on standing. The total product was then boiled for a few minutes with acetic anhydride and poured into water. The small amount of red solid obtained dissolved completely in cold caustic soda solution, and prolonged boiling with acetic anhydride failed to give the alkali-insoluble diacetate of the required product. The solid obtained in this way proved to be quinizarin itself. No trace of benzanthrone derivative could be observed.

The matter is treated at length in the discussion section.

2-Iodo-4-nitro-benzoic acid.

(Haldane, Thesis Edinburgh 1934).

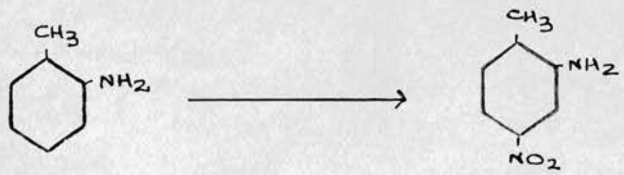
(a) 2-amino-4-nitro-toluene.

(Cohen and Dakin, J.C.S., 1902, 81, 1333).

50 gm.	o-toluidine.
500 gm.	concentrated sulphuric acid.
50 gm.	potassium nitrate.
10 ml.	fuming nitric acid.

The o-toluidine dissolved in concentrated sulphuric acid was cooled to 0°C. and finely powdered potassium nitrate added in portions so that the temperature rose to 10°C. Finally the fuming nitric acid was added to complete the reaction. The mixture was poured on to ice and the sulphate of the base separated and drained from excess acid. The sulphate was then suspended in water and decomposed with solid sodium carbonate. The 2-amino-4-nitro-toluene crystallised from alcohol in monoclinic prisms.

Yield: 53 gm. (92%) m.p. 107°C.



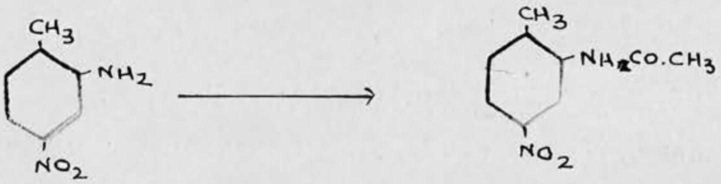
(b) **2-Acetamino-4-nitro-toluene.**

(Noelting and Collin, Ber., 1884, 17, 269).

50 gm.	2-amino-4-nitro-toluene.
75 gm.	acetic anhydride.

The above were refluxed together for 10 minutes, cooled and poured into water. The yellow precipitate was filtered off, washed and dried. Crystallisation from dilute alcohol gives the compound in the form of yellow prisms melting at 150-151° C.

Yield: theoretical.



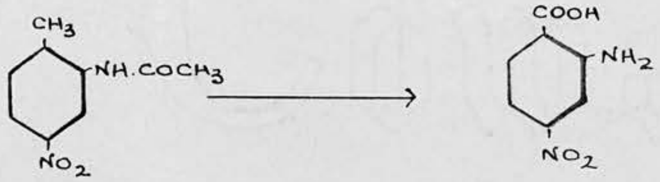
(c) **2-amino-4-nitro-benzoic acid.**

(Wheeler and Johns, A.C.J., 1910, 14, 445).

35 gm.	2-acetamino-4-nitro-toluene.
90 gm.	crystalline magnesium sulphate.
90 gm.	potassium permanganate.

The nitrotoluene was suspended in a litre of hot water and the magnesium sulphate added. Steam was passed in and the potassium permanganate, dissolved in 2 litres of water, added in portions from time to time. Oxidation was complete in 3 hours. The contents of the flask were filtered hot, and the filtrate evaporated to a volume of 500 ml. The solution was made alkaline with ammonia and again filtered. On acidification, the filtrate yielded a bulky precipitate of the acetamino acid. This was filtered off, dissolved in 200 ml. alcohol containing 15 ml. concentrated sulphuric acid, and digested on the steam bath. The amino acid separates as a bright orange crystalline deposit.

Yield: 29 gm. (88%). m.p. 264°C.



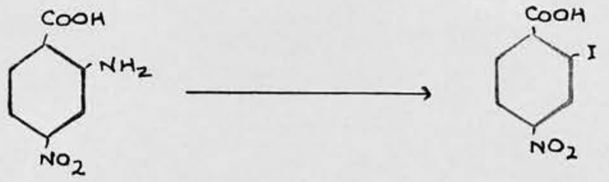
2-Iodo-4-nitro-benzoic acid.

(Wheeler and Johns, A.C.J., 1920, 44, 445).

24 gm.	2-amino-4-nitro-benzoic acid.
300 ml.	sulphuric acid (40%).
12 gm.	sodium nitrite.
30 gm.	potassium iodide.

The diazo solution of the 2-amino-4-nitro-benzoic acid was poured on to ice and treated with potassium iodide. The brown product was filtered off and washed free from iodine. On crystallisation from hot water, the pure iodo acid was obtained in the form of slender prisms.

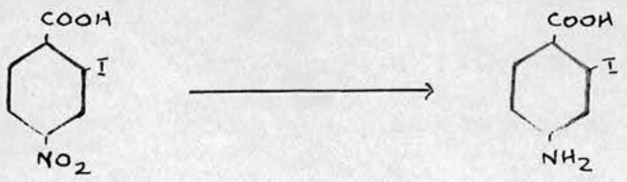
Yield: 50 gm. (90%) m.p. 143°C.



2-Iodo-4-amino-benzoic acid.

(Wheeler and Johns, A.C.J., 1920, 44, 446).

2 Gm. 2-iodo-4-nitro-benzoic acid were dissolved in 25 ml. concentrated ammonia and this solution mixed with one containing 12.2 gm. ferrous sulphate. There was a slight evolution of heat andvreduction seemed to take place rapidly. The mixture was then heated on the steam bath and filtered after 5 minutes. The filtrate was evaporated to dryness and the residue extracted with alcohol. Evaporation of the alcohol and treatment with water should have led, according to the literature, to the isolation of the amino acid in 75% yield. No such success, however, attended repeated efforts to isolate the acid in this way. Owing to the poor yield, if any, and by reason of the many subsequent stages to be carried out, this line of attack was abandoned at this stage.



Dibenzanthrone derivatives of 8-hydroxy and 8-methoxy-benzanthrone and their vatting properties.

In a series of investigations to see whether or not dibenzanthrone derivatives could be obtained from the 8-hydroxy and 8-methoxy-benzanthrones, a number of caustic potash fusions were carried out under various conditions.

Details of the procedure in each case with the attendant results are given in the following reports. The experiments are listed in the order in which they were carried out.

Fusion No. 1.

Attempted preparation of 8:8'-dimethoxy-dibenzanthrone.

A very small portion of 8-methoxy-benzanthrone was fused with 2-3 gm. caustic potash in a nickel crucible, and the temperature raised gradually to 250° C., any colour change in the melt being carefully noted. No such change was evident and the temperature was finally raised to 300° C. At this temperature the melt finally became black, and further treatment showed this to be due to carbonisation. A repetition was carried out and the melt tested for vatting properties at various temperatures, but none could be observed.

Fusion No.2.

Attempted preparation of 8:8'-dihydroxy-dibenzanthrone.

0.2 gm. 8-hydroxy-benzanthrone were used with 5 gm. caustic potash in a nickel crucible and the temperature gradually raised to 235-240°C. The melt became dark brown-purple in colour, and was maintained at this temperature for 30 minutes. The melt was then boiled out with 100 ml. water and filtered from the small insoluble residue. The brown filtrate was acidified and the dark greenish brown solid filtered off, washed and dried. This dark powder forms a blue hydrosulphite vat from which cotton dyes a bluish green shade. The vat exhibits a vivid crimson fluorescence.

Attempted preparation of 8:8'-dimethoxy-dibenzanthrone.

The small amount of alkali-soluble material obtained in the previous experiment was treated with dimethyl sulphate in 20% sodium hydroxide solution. A dark green alkali-insoluble solid was obtained which formed a similar vat to the starting material, and dyed cotton in somewhat greener shades of blue.

Fusion No. 3.

This was similar in every way to the previous fusion with 8-hydroxy-benzanthrone, except that a larger quantity of the hydroxy compound was used (4 gm) and proportionate amounts of caustic potash. However, difficulties were encountered in this instance. There appeared to be a fairly large proportion of alkali-insoluble material. The alkaline solution was finally obtained free from any suspended solid, and acidified. This procedure yielded a bluish green precipitate which dyed cotton in bluish green shades from a blue hydrosulphite vat which showed vivid crimson fluorescence. The alkali-insoluble material gave a colour with boiling caustic soda solution and repeated extraction always gave a coloured alkaline solution. In proportion, the alkali-insoluble part seemed by far to be the greater. It would seem that the sodium salt of the dihydroxy derivative is only slightly soluble in water, and for this reason, organic solvents were resorted to for purification purposes. The total product was first extracted with alcohol to remove any benzanthrone derivative remaining, and then with butyl alcohol, which gave a dirty green solution yielding a small amount of a dirty green solid which had no good vatting properties. The residue seemed to be fairly soluble in pyridine, and so was extracted with this medium several times until no more colour was observed in the extract. The pyridine solution was a clean deep blue colour and the residue left, black. This residue ultimately proved to be carbon. The pyridine solution was reduced in bulk and drowned with water, giving a dark blue-black precipitate which formed a blue hydrosulphite vat with crimson fluorescence from which cotton was dyed a clean dark blue shade.

8:8'-Dimethoxy-dibenzanthrone.

Assuming that the product from the last experiment is the dihydroxy-dibenzanthrone, alkylation was carried out. The dihydroxy derivative was pasted with water and the moist solid suspended in nitrobenzene along with excess sodium carbonate. The mixture was then heated above 100°C. until all the water had been driven off, and then excess dimethyl sulphate added, care being taken that sufficient sodium acrbonate was present to keep the mixture alkaline. The temperature was then raised to 120°C. and maintained at that level for 3 hours. Steam distillation removed the nitrobenzene and the dark blue-black insoluble residue was filtered, washed and dried. The product was totally insoluble in alkali, but formed a blue-violet hydrosulphite vat with vivid crimson fluorescence from which cotton was dyed in clean shades of blue.

This supposed dimethoxy-dibenzanthrone dissolved in nitrobenzene to form a blue solution which had a very strong crimson fluorescence when hot, less so when cold. Purification was attempted by crystallisation from nitrobenzene, but no crystals could be obtained. The final product was sent for analysis, the results of which did not agree in any way with the requirements.

Analysis: found:- C: 78.6%; H: 4.2%.
$C_{34}H_{16}O_4$ requires:- C: 83.2%; H: 3.3%.

Fusion No. 4.

Treatment of 8-hydroxy-benzanthrone with alcoholic potash.

A very small amount of 8-hydroxy-benzanthrone was fused with 2-3 gm. caustic potash and 2 ml. ethyl alcohol at 180°C. for 30 minutes. The melt became a dark purple-brown colour, and boiling out with water gave a dark brown solution along with a fairly large proportion of alkali-insoluble material. The insoluble solid was separated and washed. On testing for vatting properties, this latter product was found to give the familiar blue vat with crimson fluorescence, and dyed cotton the usual blue shade. The alkali-soluble fraction was too small to isolate and could not be filtered. Concentration of the solution however, and testing in a vat gave a blood red solution without fluorescence, from which cotton emerged a pink shade which rapidly oxidised in air to a brownish green shade. Prolonged exposure to the atmosphere brought no colour change, but on washing with water, a clean pale green shade was obtained which did not deteriorate on standing.

Fusion No. 5.

A very small portion of 8-methoxy-benzanthrone was fused under the same conditions as in No. 4. The results were very similar except that the alkali-insoluble part was greater and dyed a cleaner blue, while the alkali-soluble fraction could not be isolated for examination. A test vat, however, on the concentrated solution gave a pale green shade as in the previous case.

Fusion No. 6.

Similarbto the above with the exception that methyl alcohol was used in place of methyl alcohol. Results were similar.

Fusion No 7.

Similar to the above fusions, but 8-ethoxy-benzanthrone was used in place of the 8-methoxy derivative. The results were similar, but the shade on cotton was a slightly brighter blue.

Fusion No. 8.

A very small portion of 8-hydroxy-benzanthrone was fused with 2-3 gm. caustic potash and 2 ml. ethyl alcohol at 120° C. for 30 minutes. The melt became purple in colour, and boiling out with water gave a deep reddish brown solution with no vatting properties. Acidification gave a brown solid which was found to contain a proportion of the starting material, the remainder being presumed to be the 8:8'-dihydroxy-dibenzanthronyl. No alkali-insoluble material was obtained in this instance.

The same procedure was carried out on a larger quantity of material and the theoretical amount of the supposed dibenzanthronyl derivative was obtained. The solution of the product in concentrated sulphuric acid has a violet colour.

When this latter product was subjected to fusion with alcohol and caustic potash at 180° C. no dibenzanthrone derivative could be isolated and the black product had no vatting properties.

Fusion No. 9.

0.1 gm.	8-methoxy-benzanthrone.
5 gm.	caustic potash.
5 ml.	methyl alcohol.
1 gm.	potassium nitrate.

The above were fused at 180° C., the methoxy compound being added in small portions to the melt at that temperature. Effervescence occurred and the melt became dark brown in colour, gradually darkening to an almost black shade. After 20 minutes at this temperature, the effervescence ceased and the melt became semi-solid. After a further 10 minutes treatment the melt was boiled out with water. Once more an alkali-soluble and alkali-insoluble fraction were obtained. The alkaline solution was a brown colour with a vivid green fluorescence. A test vat of the mixture of alkali-soluble and insoluble portions gave a blue-green vat with a vivid red fluorescence, cotton being dyed a green shade.

The two fractions were separated on the centrifuge and treated separately. The alkali-insoluble product was a blue-black powder which formed a blue hydrosulphite vat with the familiar red fluorescence, cotton being dyed a clean blue shade from this bath. The alkali-soluble product was a dark brown colour and formed a brown-purple vat. From this vat cotton emerged a purplish pink shade which rapidly oxidised to a pink shade, unchanged on washing. Acid on a pink dyed sample brings up a green shade which washed to an unsatisfactory yellow green colour. This latter shade is not fast, but fades on exposure, to a brown tint.

Attempted oxidation of supposed Dimethoxy-dibenzanthrone with manganese dioxide and concentrated sulphuric acid.

A small portion of the supposed dimethoxy-dibenzanthrone obtained from the potash fusion of 8-methoxy-benzanthrone, was dissolved in 5 ml. concentrated sulphuric acid, and 0.5 gm. manganese dioxide added at 0°C. This temperature was maintained for 36 hours, and the mixture then drowned with water and the solid filtered off. The resulting solid which contained a large proportion of residual manganese dioxide, was boiled with sodium bisulphite and again filtered. The state of the product was too fine and the yield too small to see whether or not an alkali-soluble fraction was present.

A test vat with the total product gave a deep blue non-fluorescent solution from which cotton was dyed a clean grey shade. This would point to the fact that oxidation has taken place, probably with the formation of an alkali-soluble fraction.

Fusion No. 10.

0.2 gm.	8-methoxy-benzanthrone.
2.5 gm.	caustic potash.
0.5 gm.	water.
1.0 gm.	phenol.

The phenol and the caustic alkali were fused at

190°C. in a nickel crucible and the methoxy derivative added in a finely powdered state. The mixture was then heated at 210°C. for 30 minutes, and the dark purple-blue melt rapidly dissolved in 250 ml. water, and centrifuged.

The dark blue-black insoluble material was extracted several times with boiling alkali, and then washed well with water. The dry solid weighed 0.12 gm. and gave a blue hydrosulphite vat with crimson fluorescence from which cotton dyed a clean blue shade which had just a hint of green in it.

The brown alkaline solution exhibited a vivid green fluorescence and acidification precipitated a dark green solid which was centrifuged and well washed with water. This green solid when dry weighed 0.03 gm. and gave a reddish brown hydrosulphite vat with crimson fluorescence. From this bath cotton emerged a brown-green colour which rapidly oxidised to a yellow-green shade. Washing with water eliminated the yellow tint and resulted in a bright green colour being left on the cotton. This green shade, however, was not quite stable with acid, the green being somewhat dulled in tint. Boiling with soap solution also had a marked effect on a dyed specimen. The green colour was removed, as would be expected, and a pale blue shade left on the cotton. This latter fact would point to the green dyestuff being a mixture, consisting of, for the most part, the green alkali-soluble compound, along with a small proportion of the blue alkali-insoluble dyestuff which was so finely divided as to pass through a filter and escape notice.

The blue colour given by the alkali-insoluble material is completely fast to soap boiling, no change in shade being observed, even on prolonged boiling with a strong solution.

A repetition of the fusion was carried out on a larger quantity, and a supply of the two fractions obtained for purification purposes.

The green solid is relatively soluble in pyridine, but concentration of the solution did not lead to any crystal formation, and so the whole of the material was precipitated with water.

The blue dyestuff was not so soluble in pyridine as the above, but eventually a concentrated solution was obtained which on standing for some time deposited a fine blue-black powder which was dried and sent for analysis. The data obtained in this way did not satisfy the requirements for a dimethoxy-dibenzanthrone.

Analysis:- found:- C: 71.7%; H: 4.64%.
$C_{36}H_{20}O_4$ requires:- C: 83.72%; H: 3.87%.

Analysis figures showed that a residue left after combustion accounted for fully 30% of the weight taken. In the light of the fact that the sodium salt of the alkali-soluble green compound is sparingly soluble in water, it might be that the residue is due to the presence of some of this salt.

Extraction of the analytical specimen with boiling water gave a clear water solution which was slightly green in colour and on evaporation left an appreciable quantity of salt-like material. Extraction with boiling water was then continuously carried out for three days, and the blue solid then returned for analysis.

Analysis:- found:- C: 81.5%; H: 5.13%.
$C_{36}H_{20}O_4$ requires:- C: 83.7%; H: 3.87%.

This is the most satisfactory analysis yet obtained for this compound, and is quite close to the required values. The residue left after combustion in this case accounted for a little more than 1% of the weight taken, showing that treatment with boiling water had removed some inorganic material.

Methoxyl determinations on the blue dyestuff were also very unsatisfactory, as the following data will show.

Analysis:- found:- CH_3O- 4.39%.
$C_{36}H_{20}O_4$ requires:- CH_3O- 12.0%.

Methylation of the Green alkali-soluble material.

This was first attempted with dimethyl sulphate in alkaline solution, but the reaction could not be carried through to completion. A very small amount of a dark green-black solid was obtained which was completely insoluble in alkali. This solid also gave no Hydrosulphite vat.

The recovered material was then treated in nitrobenzene solution with dimethyl sulphate in the presence of sodium carbonate as acid adsorbing agent.

The compound was suspended while still wet, in nitrobenzene (20 parts on dry weight) and excess sodium carbonate added. The mixture was then heated above 100°C. until all the water had been driven off, and excess dimethyl sulphate then added, care being taken to ensure of sufficient sodium carbonate being present to keep the mixture alkaline. The temperature was then raised to 160°C. and maintained at that level for three hours, after which time the mixture was steam distilled to remove nitrobenzene, and the dark coloured solid filtered off. When dry, the solid was green-black in colour, and dissolved sparingly in pyridine to give a dark green solution. Treatment with concentrated sulphuric acid gave a red brown solution without fluorescence. As in the case of the previous methylation product, no vatting properties could be observed.

DISCUSSION.

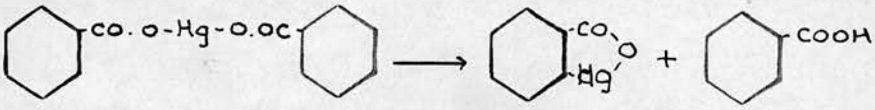
OF

EXPERIMENTAL RESULTS.

When the present investigations were begun, it was intended to submit the 8-amino-benzanthrone to several standard chemical reactions such as oxidation, halogenation, nitration etc. A number of unexpected results, however, were obtained, with the result that although in the main, work has been confined to the reactions in question, so many controversial points have arisen in the course of the research, that in the time allotted, only a few salient points could be dealt with. Many new subjects for investigation have been opened up in the present work, some of which are separately worthy of an entirely new attack.

Mercuration of 8-carboxy-benzanthrone.

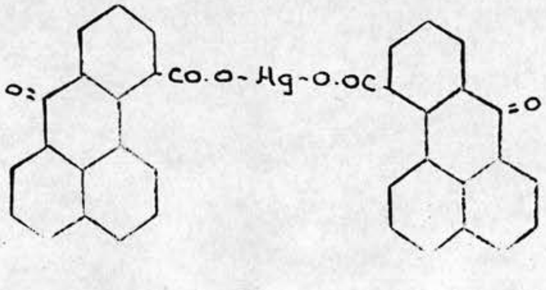
In a series of mercuration experiments with benzoic acid, Dimroth (Ber., 1902, 35, 2870) found that by heating anhydrous mercuric benzoate a few degrees above its melting point, decomposition took place to the mercuri anhydride of the acid. The benzoic acid also formed, sublimed off at the temperature used. (See also Pesci, Cent., 1900, 1, 1097; 1901, 2, 108; 1909, 1, 1092).



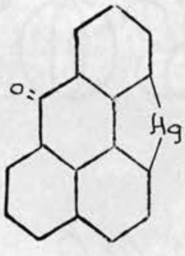
Since a supply of the 8-carboxy-benzanthrone was necessary for the preparation of the 8-amino-benzanthrone, it was decided to submit the acid to a series of reactions similar to that applied by Dimroth, in the hope that, should similar decomposition occur, the mercuri anhydride would give access to some new benzanthrone derivatives.

The 8-carboxy-benzanthrone was mercurated in a manner similar to that used in respect of naphthalic acid in the preparation of the 8-halogeno naphthoic acid, and a yellow mercuri compound obtained. The product melted above 230° C. with decomposition, and in an investigation as to whether this reaction was similar to that discovered by Dimroth, a small quantity of the substance was heated to 230°C. in vacuo for a time. A yellow sublimate formed on the sides of the tube, and decomposition was accompanied by frothing in which carbon dioxide was evolved. Subsequent investigation proved the sublimate to be benzanthrone, while the dark coloured residue was found to be a mercuri compound of benzanthrone. No trace of benzanthrone carboxylic acid could be detected on the hydrolysis of the latter product with hydrochloric acid.

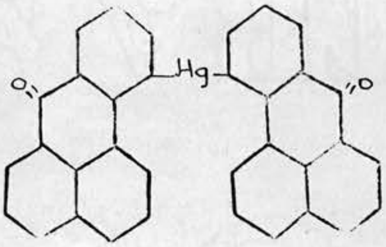
From the results obtained, it would seem that total decarboxylation had occurred with the formation of a mercury benzanthronyl, whilst benzanthrone itself is set free. The most likely supposition is that the mercuric salt of 8-carboxy-benzanthrone has the same formula as that given for the benzoic acid derivative, viz:-



and that decomposition might take place to benzanthrone (sublimes) and a mercury benzanthronyl of the form 1. given below.



1.



2.

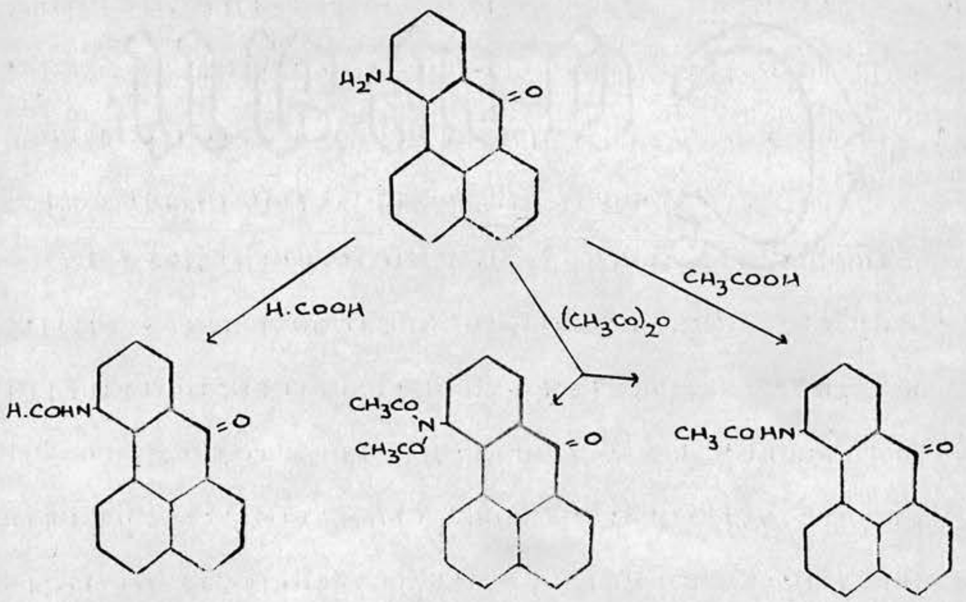
The dimolecular form 2., however, is virtually excluded since the amount of benzanthrone isolated from the sublimate accounts for almost half of the starting material. In all probability therefore, the mercury compound has the structure 1.

In an attempt to elucidate the nature of the mercury compound, it was brominated in aqueous suspension, and the product examined. A sodium fusion "elements test" proved that bromine was present, while reactions for the detection of mercury were entirely negative. Attempts at purification, however, met with no success. Chromatographic analysis with aluminium oxide using benzene as solvent gave a partial separation into two fractions, but from the wide range of melting point obtained, these were evidently still impure.

Owing to excessive losses in purification, and lack of time, further investigations in the matter were not attempted.

The Chemistry of 8-Amino-benzanthrone.

When this compound was first prepared by Rule and Boyes (J.C.S., 1938, 342, 1835) it was observed to be somewhat anomalous in its reactions. Treatment with dilute acid caused a colour change in the compound from red to yellow, but no solution could be detected. This phenomenon is probably due to the formation of a surface coating of the acid salt of the base which is insoluble in water. The same workers quoted the amine as having been fully characterised by the formation of the formyl and acetyl derivatives. A repetition, however, of those preparations showed that in the case of the acetyl compound, a mixed product was obtained by the treatment of the amine with acetic anhydride. Various attempts were made to separate the two components present, but this could not be effected with complete success. An analysis of the partially separated fractions did not furnish conclusive proof of the nature of the compounds, but values obtained point to the lower melting fraction (157-158°C.) being the diacetyl amine, while the higher melting component (268-269°C.) corresponds more or less to the compound quoted by Boyes as being the mono-acetyl derivative melting at 278°C. A number of experiments were carried out in an attempt to obtain the mono-acetyl derivative alone. Prolonged treatment with glacial acetic acid was finally successful and gave the mono-acetyl amine in analytical purity and with a melting point identical with that quoted by Boyes. The formyl amine was obtained in good yield by boiling the amine with 90% formic acid for a short period.

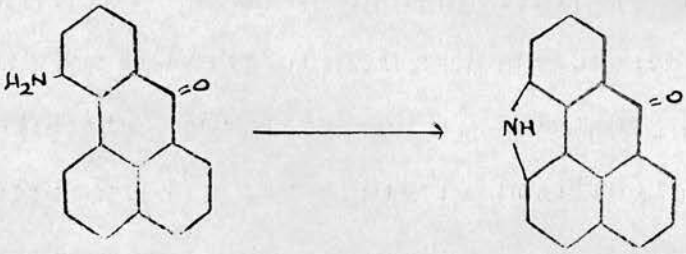


The above workers also found that 8-amino-benzanthrone required special treatment for diazotisation, since solution in the customary dilute acid does not occur. The means employed was the diazotisation method of Hodgson and Walker (J. 1933, 1620). This involves the addition of a cooled solution of the amine in glacial acetic acid to a solution of sodium nitrite in concentrated sulphuric acid at 0° C.

When the amino compound was fused with alkali, a diamino-dibenzanthrone was formed which vatted with difficulty and dyed cotton a fast pale grey-green shade.

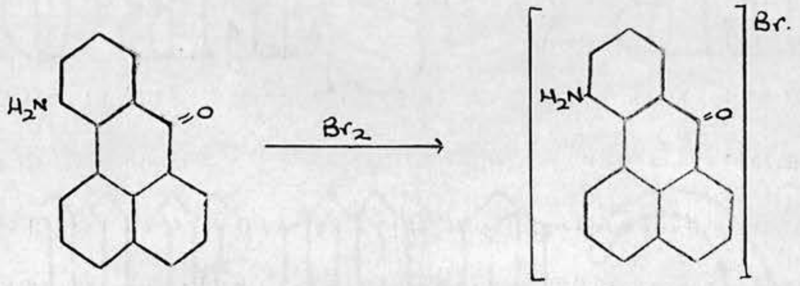
Bromination.

Employing a solution of bromine in nitrobenzene, Rule and Grieve (J.C.S., 1938, 342, 1835) were successful in oxidising the 8-carboxy-benzanthrone to the lactone of Bz3-hydroxy-8-carboxy-benzanthrone; bromination did not take place under those conditions. The amino derivative was submitted to similar treatment in the hope that oxidation might occur to the carbazole compound.



However, as was not unexpected, in this case, bromination occurred almost exclusively, and in the presence of a molecular proportion of bromine, total conversion to the mono-bromo amine was obtained. Oxidation in the case of the carboxy acid was carried out with relative ease and most reactions carried out on this substance resulted in the formation of a small amount of lactone. With the amine, however, such a conversion is a very difficult matter, and so far, all attempts to isolate the cyclised product have resulted in failure.

Purification of the halogenated product gave a supposedly (see later) homogeneous product, the analytical data for which agreed with those for a mono-bromo amino-benzanthrone.



Proof that the amino group was free in the molecule was furnished by the fact that treatment with acetic anhydride gave a yellow-brown compound melting at 230-250° C. Purification was not carried out owing to the mixed product obtained from acetic anhydride, and also for reasons which are treated fully in a later section.

Bromination in the unsubstituted benzanthrone molecule takes place in the Bz1- position, but, an amino grouping being strongly ortho and para directing, it would be more reasonable to suspect the bromo group as occupying either of positions 5 or 7, rather than positions 6 or Bz1.

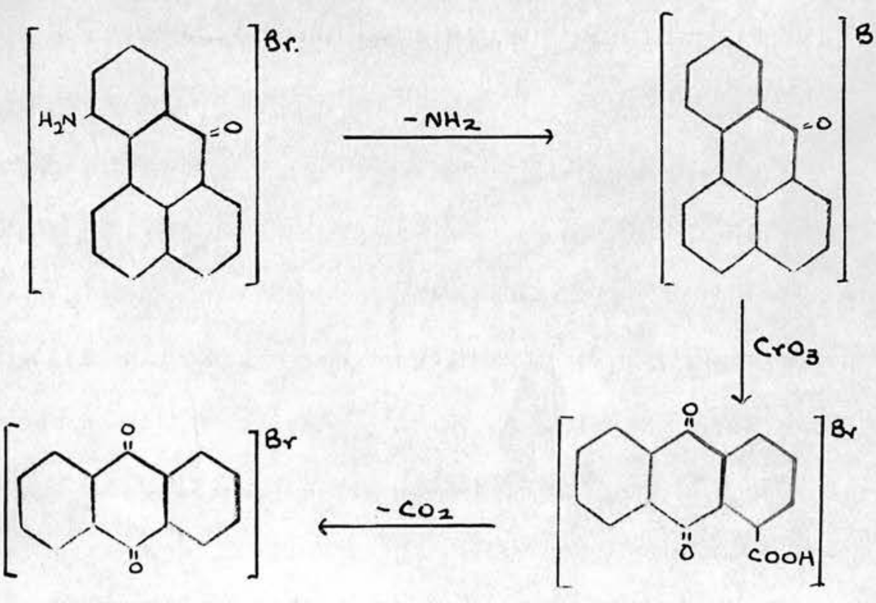
However, since samples of 6-bromo-8-carboxy-benzanthrone and Bz1-bromo-8-carboxy-benzanthrone had been prepared by a previous worker, these were converted to the corresponding 6-bromo-8-amino and Bz1-bromo-8-amino-benzanthrones, a change effected with relative ease by treatment with sodium azide in the usual manner. In this way two new bromo-amino-benzanthrones were obtained, but neither proved to be identical with the product obtained by bromination of the parent amine. The 6-bromo-8-amino compound melted at 229-230°C. while the Bzl- isomeride melted at 258-259°C.

Identification of x-Bromo-8-amino-benzanthrone.

A close examination of the current literature failed to produce a reference to any bromo-amino derivative of benzanthrone. When this procedure failed to give any clue to the nature of the bromo-amine, it was thought that elimination of the amino group might lead to the isolation of a known bromo-benzanthrone. Here again, however, the literature did not give complete information, since only a few bromo-benzanthrones are quoted, these being the 6-bromo-benzanthrone (Cent., 1937, 2, 2833), the Bz2-bromo-benzanthrone (Cent., 1927, 1, 3225), and the Bzl-bromo-compound (Cent., 1938, 2, 2832). The 6-bromo derivative was obtained from an Ullmann coupling of methyl-5-bromo-2-iodo-benzoate and methyl-8-bromo-1-naphthoate with the subsequent decarboxylation of the bromo-carboxy-benzanthrone thus obtained, (Rule and Smith, J.C.S., 1937, 2, 1096). The same workers prepared the Bzl-bromo-benzanthrone by the direct bromination of benzanthrone, this being the normal position for such substitution. A Sandmeyer reaction carried out on the Bz2-amino-benzanthrone resulted in the formation of the corresponding bromo compound.

It may be seen that even if deamination was carried out with success, the resulting bromo benzanthrone would not likely be one of the three quoted above, two of which are automatically ruled out from the experiments with the bromo-carboxy benzanthrones as aforementioned. Such elimination of the amino group, however, might prove of value in the formation of a previously unknown mono-bromo benzanthrone.

It was then decided to attempt this experiment with a double view in mind; firstly to obtain the mono-bromo derivative, known or unknown, and then to attempt disruptive oxidation on this latter compound in the hope that a bromo-anthraquinone carboxylic acid might be formed which might be known, or which could be decarboxylated to a known bromo-anthraquinone, as shown in the following scheme.



However, a preliminary examination of the properties of bromo-carboxy-anthraquinones showed that all efforts at decarboxylation of such a compound resulted in the removal of the halogen also. Hence the only hope in the second part of the investigation, was that the product constituted a known bromo-carboxy-anthraquinone.

The deamination was first tried out on the unsubstituted amine to obtain the optimum conditions for such a conversion.

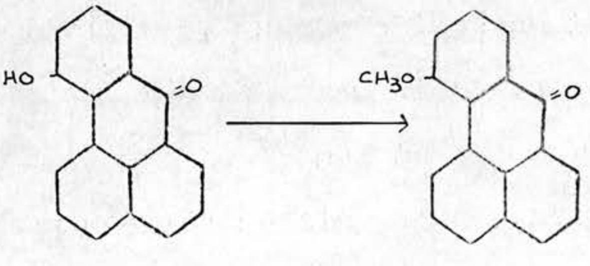
There are several methods quoted for the removal of an amino group, but the one most often used is that in which the diazo solution is boiled for a period with an excess of alcohol.

When this procedure was carried out on the 8-amino-benzanthrone, however, the expected deamination did not occur, and no trace of benzanthrone could be detected. The product of the reaction consisted of an alkali-soluble and an alkali-insoluble fraction. The alkali-soluble portion gave a carmine solution and on acidification, a yellow solid was obtained, which, on purification and analysis proved to be the 8-hydroxy-benzanthrone. Previous workers are quoted (Perkin) as having had great difficulty in purifying such phenolic benzanthrone derivatives, and in this case it was only after repeated crystallisation from dilute alcohol that the compound was finally obtained in the pure state, as golden yellow needles melting at 269-271°C. with decomposition.

The alkali-insoluble product was also a yellow compound, and on crystallisation several times from alcohol, the compound was shown by analysis to be the 8-ethoxy-benzanthrone, melting at 159° C.

Neglecting the main purpose of the investigation for the moment, the same procedure was repeated, methyl alcohol, however, being substituted for ethyl alcohol. Whereas, previously, the alkali-soluble product had accounted for 55% of the starting material, and the alkali-insoluble 25%, in the latter experiment the alkali-soluble percentage was decreased to 35% and the alkali-insoluble correspondingly raised to 50% of the starting material. Here again, the alkali-soluble compound proved to be the 8-hydroxy-benzanthrone, while purification of the alkali-insoluble material gave a compound melting at 169° C., and which analysis proved to be the 8-methoxy-benzanthrone.

Methylation of the hydroxy derivative with dimethyl sulphate gave a compound identical in every respect with the methoxy derivative obtained as alkali-insoluble fraction from treatment of the diazonium solution with methanol.



The isolation of this methoxy derivative of benzanthrone is most interesting in view of the fact that it may give rise to new dibenzanthrone derivatives which are isomeric with Caledon Jade Green. Many experiments in this direction have been carried out and are discussed in a later section. In addition, the method by which the 8-hydroxy-benzanthrone was obtained is somewhat surprising, since when Rule and Boyes (Thesis - Edinburgh, 1936) attempted to prepare it from 8-amino-benzanthrone by boiling the diazonium solution with water, a carmine alkaline solution was obtained, but no pure product could be isolated. Methylation of the crude acidic material was also attempted by the same workers, but, although the acidic properties disappeared, no definite product could be obtained.

With the failure of this attempt at the deamination of 8-amino-benzanthrone, other methods were examined. The second procedure carried out was that of the well known Gatterman reaction in which copper bronze is employed with the alcohol, the metal acting as a catalyst for the reduction of the alcohol to acetaldehyde with the attendant elimination of the amino grouping. No acetaldehyde, however, could be detected and the products of the reaction were the same as those obtained in the previous experiment, namely the hydroxy and ethoxy derivatives.

Chamberlain (Amer. Chem. J., 1897, 19, 531) is quoted as having been successful in isolating toluene alone from p-diazo toluene sulphate by treatment with a solution of caustic soda in methyl alcohol. This method gave good yields of the hydrocarbon and seemed to be very satisfactory with other amino compounds which did not respond to the usual alcohol treatment. When a similar procedure was carried out with the compound in question, however, no trace of benzanthrone could be isolated, or if it was present, could not be separated from the methyl ether which was also a product of the reaction in this case. An alkali-soluble fraction was also obtained which proved to be the hydroxy derivative as before.

Another method for such conversion, which seems to be particularly efficacious with such compounds as tend to give the ether on submitting to the usual procedure, has recently been outlined by Brewster and Poje (J.A.C.S., 1939, 61, 2418). This method involves the treatment of the diazonium salt with alkaline formaldehyde solution, and the absence of any alcohol excludes the possibility of ether formation. Treatment of diazotised 8-aminobenzanthrone in this way gave a small amount of alkali-insoluble material which on purification by chromatographic means, gave pure benzanthrone in a yield of 7%. The bulk of the starting material was again obtained in the form of the hydroxy derivative.

Although this last experiment was successful in the partial conversion of the amine to benzanthrone, the yields are not sufficiently great to warrant its application to the unknown bromo-amino compound. The fact that the possible results are pure conjecture also decreases the value of such an operation.

Another field which might prove of value in the identification of the x-bromo-8-amino-benzanthrone is supplied by the submission of the compound to the Sandmeyer reaction with cuprous bromide, in the hope that a dibromo derivative might be obtained, and which might be listed in the current literature. In this respect, however, particulars relating to the dibromo-benzanthrones are hardly more complete than those pertaining to the mono compounds. References are given for five such compounds, those being the 2:6-dibromo (Cent., 1930, _1_, 3241), the 4:8-dibromo (Cent., 1933, _2_, 3696), the 6:7-dibromo (Cent., 1933, _2_, 3696), the 7:8-dibromo (Cent., 1933, _2_, 3696), and the Bzl:6-dibromo-benzanthrone (Cent., 1936, _1_, 2218). Since the amino group occupies the 8- position, only two of the above compounds are of any value in the orientation of the unknown bromo-amine, namely the 4:8- and the 7:8-dibromo derivatives. Of those two, the 7:8 isomeride is the most valuable in this respect, since the position 4- is very unlikely for the bromine substitution of the 8-amino-benzanthrone.

The 7:8-dibromo-benzanthrone was obtained by a glycerol condensation with 1:2-dibromo-anthraquinone, and melted at 217-218° C.

As aforesaid, the two most likely positions for the bromine atom in the x-bromo-8-amino-benzanthrone are the 5- and 7-. If such is the case, then the dibromo-benzanthrone obtained by the conversion of the amino group into a bromo, should be identical with the known 7:8 isomeride or the 5:8-dibromo derivative, which may possibly be synthesised in a similar manner from 1:4-dibromo-anthraquinone.

Consequently, the diazo solution of the bromo-aminewwas treated in the usual manner with cuprous bromide solution, and the organic product purified by chromatographic analysis. This led to the isolation of a yellow crystalline compound melting at 149° C. (sharp), the analysis of which agreed with that of a dibromo-benzanthrone. The melting point is definitely not in agreement with that of the 7:8 isomeride, and so it does not appear that the bromine is in position 7-, and in order to prove that the substituent is in position 5-, the preparation of the 5:8-dibromo compound is necessary.

Since a supply of the required 1:4-dibromo-anthraquinone for this preparation could not be obtained, the necessary compound was procured from 1:4-diamino-anthraquinone. Battegay and Claudin (Bull. Soc. Ind. Mulhouse, 1920.) are quoted as having prepared the dibromo compound from a Sandmeyer reaction on 1:4-diamino-anthraquinone, but, apart from recording the melting point as 196°C., they give no details of the method or the yields obtained. On experiment, the usual Sandmeyer procedure gave the required 1:4-dibromo-anthraquinone in a yield of 66% and in a sufficiently pure state for further treatment.

Prior to this latter compound being condensed with glycerol, it was first reduced to the corresponding anthrone with tin and fuming hydrochloric acid (Liebermann and Gimbel, Ber., 1887, <u>20</u>, 1854). No reference to this particular disubstituted anthrone could be found, but analysis of the pure compound was entirely in agreement with the figures required for 1:4-dibromo-anthrone. The compound melted at 171 C., and was obtained in 85% yield.

This compound was then condensed with glycerol in accordance with the method outlined by Bally (Ber., 1911, <u>44</u>, 1656), and the condensation product purified by chromatographic means. This resulted in the required 5:8-dibromo-benzanthrone being obtained in 50% yield. The 5:8-dibromo derivative melted at 176°C. and analysis confirmed the nature of the product.

It may be seen that the melting point of this compound is also not in agreement with that of the dibromo derivative obtained by the Sandmeyer reaction on the x-bromo-8-amino-benzanthrone, This fact would at first point to the conclusion that the bromine atom in the latter compound does not occupy either of the expected 5- or 7- positions in the 8-amino-benzanthrone molecule. However, since directive influence theories strongly point to these positions as being the actual seats of substitution, and since bromination was carried out under somewhat crude conditions, it may be that bromination has taken place partially in both of the suspected positions, giving, after submitting to the Sandmeyer reaction, a mixture of the 5:8-and the 7:8-dibromo derivatives.

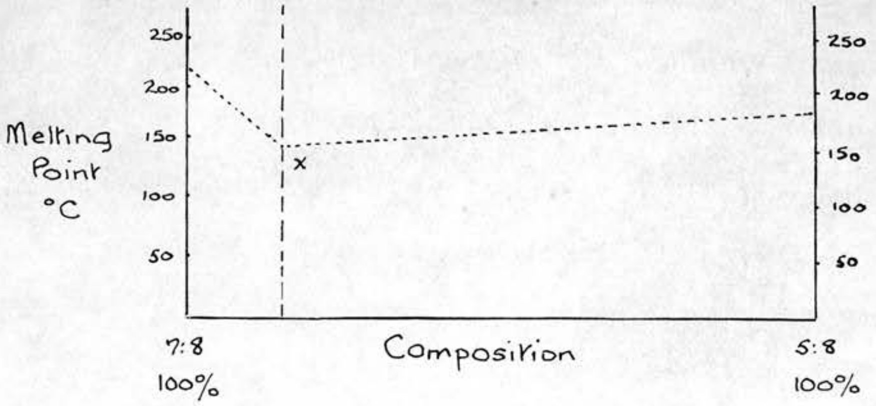
It is difficult to justify this assumption in view of the sharp melting points of the bromo-amine and the corresponding dibromo compound, but instances have been met with, where two complex isomeric compounds, when mixed or crystallised from the same solvent, formed mixed crystals which have a sharp melting point. An analysis at this point would furnish no proof of the homogeneity of the product, although it gives satisfactory proof that only dibromo derivatives are present.

This may be the case here, and exhaustive crystallisation may lead to a preponderance of one component being obtained with a consequent variation in melting point. A more satisfactory and more economical procedure, however, would be to pass a small portion of the substance in benzene solution, through an aluminium oxide column in the hope that one component of the mixture if such it be, will be more strongly or more rapidly adsorbed than the other. Elution of the chromatogram should then lead to at least a partial separation of the two isomers. It may be argued that the compound was, in the first place, purified by chromatographic means, and a separation, if any, should have been obtained at that point. However, since a clean yellow band was obtained at that juncture, and since it separated completely from the other bands, it was collected as a whole, thus allowing the formation of mixed crystals.

Accordingly, a small amount of the suspected substance was dissolved in benzene and passed slowly through an aluminium oxide column. Uniform adsorption seemed to take place and no differences in colour could be observed in the yellow band. Careful elution, however, with benzene, caused the band to spread down the tube, still without any band separation or colour differences. Ultra violet illumination also failed to show any appreciable difference, although the top part of the yellow band appeared to fluoresce to a slightly greater extent than the bottom. This may be due, of course, to deeper adsorption. Elution was continued and although the band remained unbroken, several fractions were collected, until the colour had been completely removed from the tube. In all, seven fractions of the benzene solution were thus taken, each evaporated to dryness, and the melting points of the resulting solids determined. The results obtained are tabulated below:-

Fraction.	Melting Point.
1.	185-216 °C. very small.
2.	167-190 °C. very small.
3.	143-157 °C.
4.	163-168 °C. softens 160 °C.
5.	168-170 °C. softens 163 °C.
6.	160-169 °C.
7.	158-170 °C. very small.

From the results obtained, it is quite evident that the supposition that the x:8-dibromo-benzanthrone is a mixture is correct, since, had it been homogeneous, all the above fractions would have had the same melting point. The melting point obtained for the mixture, 149 °C., is very near that given for the third fraction above, and apparently corresponds to the minimum on the eutectic curve of the mixture which may take some form such as that illustrated below.



Although the melting point of the very small first fraction, 185-216°C. approaches that of the 7:8-dibromo compound (217-218°C.), the small amounts obtained exclude the possibilty of crystallisation raising the melting point to the desired level. The combination of fractions 4 and 5, however, constitutes the bulk of the starting material and gives purification possibilities. Since the higher melting component was the first to be collected, it is reasonable to suppose that it is the more soluble of the two, and hence crystallisation of fractions 4 and 5 might lead to its elimination in the mother liquor, leaving the lower melting fraction as a crystalline solid. This crystallisation was carried out, but the melting point was found to be lowered, that is, it would appear that the proportion of the 7:8-isomer had been increased to a slight extent. Amounts were too small to allow of any further treatment at this point.

Another column was set up, however, and a further quantity of the mixture passed through, in this case the benzene being replaced by a mixture of benzene and 10% light petroleum (60-80). Elution again caused the band to spread, to a slightly greater extent, however, than in the previous experiment. Fractions were collected and treated as before, results obtained being given in the following table:-

Fraction.	Melting Point.
1.	175-215° C.
2.	169-185° C.
3.	158-179° C.
4.	145-147° C.
5.	159-160° C.
6.	156-158° C.

Although the final melting points are lower than those previously obtained, the lowest melting point approaches very near to that given by the mixture. A mixed melting point taken with a mixture of the untreated substance and fraction 4. gave no depression, thus showing the identity of the two substances. Hence it would seem that the mixture is actually the eutectic of the two components.

Since crystallisation of the final fractions did not give satisfactory separation,in this case, they were again passed through a column and fractions isolated as before. The final fraction gave a very small amount of a yellow crystalline solid melting at 172-175°C. A mixed melting point with the pure 5:8-dibromo-benzanthrone was determined as 174-176° C. Therefore it appears that this final fraction consists of the practically pure 5:8-dibromo-benzanthrone.

From the melting point obtained for the initial fraction and the fact that the second component has been proved to be the 5:8-dibromo derivative, it is most likely that the other part is the 7:8 isomer.

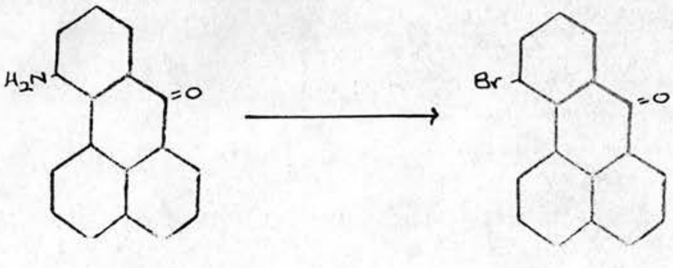
Since the dibromo-benzanthrone is not homogeneous, it then follows that the bromo-amine from which it was prepared must also be a mixture. An attempt at separation of this latter compound by the means employed above, failed to give any differentiation.

Owing to lack of time and material, the investigation was not carried beyond this point.

Sandmeyer reaction on 8-Amino-benzanthrone.

8-Bromo-benzanthrone.

Consequent on the success attending the conversion of the bromo-amine mixture into the corresponding dibromo derivatives, the procedure was repeated with the 8-amino-benzanthrone. Here again a pure compound was obtained by chromatographic separation, and analysis proved it to be the 8-bromo-benzanthrone, melting at 178 °C., and previously unknown. There is no possibility of a mixture occurring here, since the starting material was definitely homogeneous.

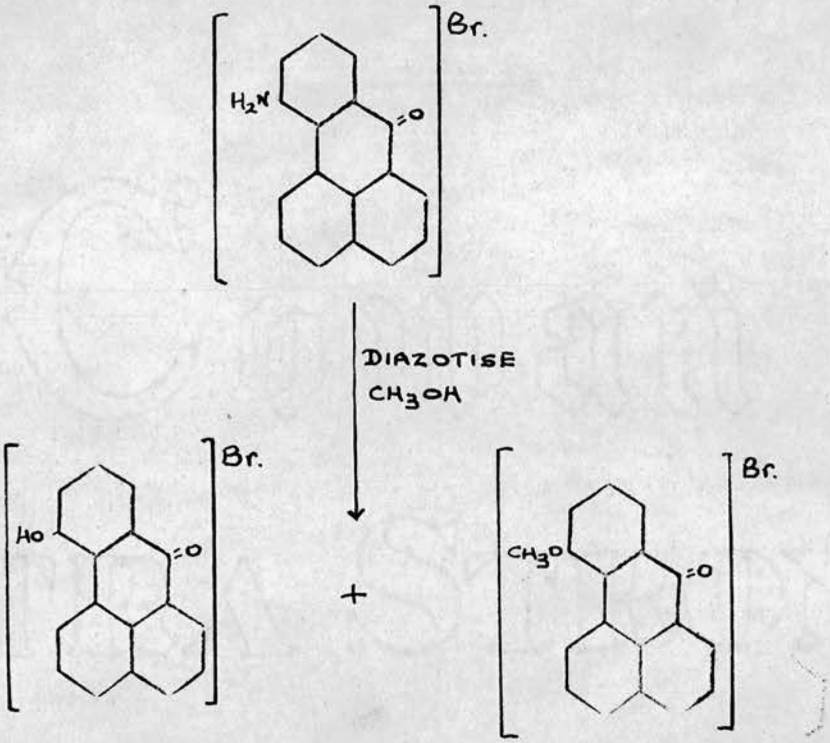


Reactions with the Diazonium Salt of the supposed x-Bromo-8-amino-benzanthrone.

Prior to the discovery of the fact that the x-bromo-8-amino-benzanthrone was not homogeneous, it was thought that treatment of the diazo solution with methyl alcohol might lead to the interesting bromo-methoxy and bromo-hydroxy-benzanthrones, instead of the bromo-benzanthrone which was the original aim of the investigations.

Consequently the bromo-amine was submitted to the same treatment as the 8-amino-benzanthrone, with methyl alcohol, and the products of the reaction examined. As in the previous experiment, an alkali-soluble and an alkali-insoluble fraction were isolated, the former accounting for 20% of the starting material and the latter, 20%.

While the purification of the above products was proceeding, the fact that the bromo-amine used as starting material was a mixture, was discovered, and so further work in this direction was not completed. The facts obtained up to this stage, however, clearly point to the conversion of the amino group to the hydroxy and methoxy having taken place. The methoxy-bromo compound which is of course not homogeneous, was purified to the stage where a yellow crystalline solid was obtained, but without a definite melting point. The melting point obtained for the compound was 182-186° C., which is higher than that of the bromo-amine mixture, and copper wire tests definitely showed the presence of halogen.



2. Investigation of Dyestuff Potentialities of Compounds derived from 8-Amino-benzanthrone.

8-Hydroxy-benzanthrone.

Prior to the isolation of this compound by the treatment of the diazotised amine with alcohol, the importance of such a substance was fully recognised, and an effort was made to prepare it from the amine.

As mentioned in an earlier passage, Boyes (Thesis, Edinburgh - 1936) attempted the preparation by diazotisation of the amine and boiling with water. No pure product, however, could be obtained.

A method has recently been devised by Kogan and Nikolaeva (J. Appl. Chem. Russ., 1938, 2, 652-659) whereby a few naphthylamine derivatives have been converted to the corresponding naphthols. The process involves the boiling of the amine with aqueous sodium bisulphite at pH 4.2. A repetition of the experiment with 8-amino-benzanthrone, however, gave no results, even on changing the pH and temperature conditions, the whole of the starting material being recovered unchanged.

Maki (Ber., 1938, 2, 2038) also mentions the 8-hydroxy-benzanthrone, but did not purify the compound or investigate its properties to any extent.

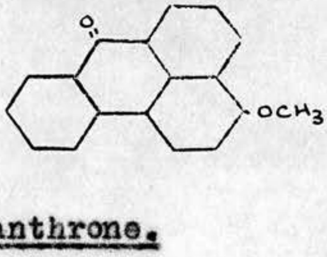
8-Methoxy-benzanthrone.

With the isolation of this compound unexpectedly, in the attempted deamination of 8-amino-benzanthrone, a field of wide possibilities was at once opened up, since it might be expected that the substituted amine would behave in a similar manner. We also have to reckon with the dyestuff potentialities of such compounds, Caledon Jade Green being a dimethoxy-dibenzanthrone obtained by the alkali fusion of the Bz2-methoxy benzanthrone.

Several methoxy-benzanthrones are quoted in the current literature, but few have been submitted to fusion with caustic potash. Five derivatives of this type are given as follows.

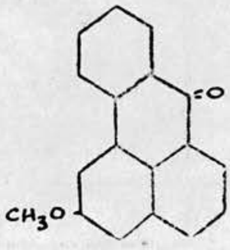
Bz1-methoxy-benzanthrone.

Prepared by Wolff (Cent., 1928, 2, 1625; 1930, 1, 131) from the corresponding chloro derivative by treatment with methanol and alkali in an autoclave.



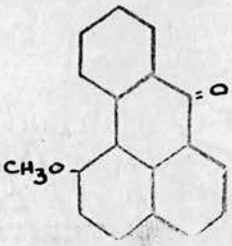
Bz2-methoxy-benzanthrone.

(Cent., 1927, 2, 1087). Prepared from the corresponding hydroxy-benzanthrone which is a valuable bye-product of the oxidation carried out on benzanthrone with manganese dioxide and concentrated sulphuric acid, to form the dibenzanthronyl which subsequently yields violanthrone.



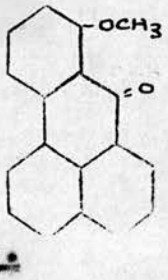
Bz3-methoxy-benzanthrone.

Heilbron (J.C.S., 1938, 699) prepared this derivative by the ring closure of the required phenyl-naphthyl-carboxylic acid.



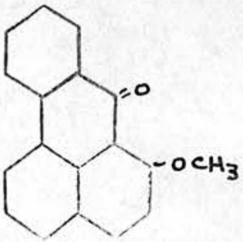
5-Methoxy-benzanthrone.

(Maki, J. Soc.Chem. Ind. Japan, 38, 636B). Obtained from the 5-chloro derivative by treatment with methanol and alkali in an autoclave.



4-Methoxy-benzanthrone.

(Cent., 1926, 1, 2249). Prepared from the required methoxy derivative of phenyl-naphthyl-carboxylic acid by cyclisation with chloro-sulphonic acid below 10° C.



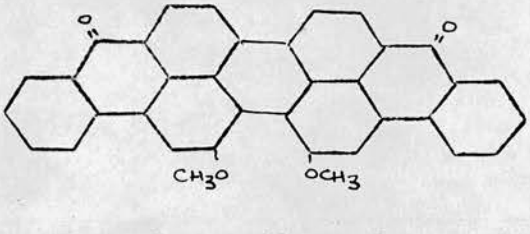
In addition to those compounds, the 8-methoxy-benzanthrone is also listed as having been prepared by Maki and Kikuchi (Ber., 1938, 2, 2038). These workers used the 8-chloro derivative as starting material, and by subjecting this compound to treatment with methanol and alkali in an autoclave at 150° C. for 7 hours, they isolated an alkali-insoluble compound melting at 158.5° C. and which they state, analysis proved to be the 8-methoxy-benzanthrone. Some of the 8-hydroxy-benzanthrone was also obtained, but, for unstated reasons, purification and analysis was not carried out.

Maki obtained his necessary 8-chloro-benzanthrone from a glycerol condensation carried out on the 1-chloro-anthraquinone. The crude product of this latter preparation contained a mixture of the 8-chloro, 5-chloro, and 4-chloro-benzanthrones, as might be expected, and the above workers claim to have obtained a complete separation of the three fractions by refluxing with various dilutions of 94% alcohol, in three stages. Proof of the formulation of the 8-chloro-benzanthrone was obtained by chromic acid oxidation to the 1-chloro-8-carboxy-anthraquinone. The 8-methoxy-benzanthrone prepared in the current work, however, does not agree in melting point with Maki's specimen. The product obtained by the treatment of the diazo salt of 8-amino-benzanthrone with methyl alcohol melts at 169 C. almost 10° above that quoted by Maki, which curiously enough, is the same as that found currently for the 8-ethoxy-benzanthrone, prepared by the present workers in a manner similar to that employed for the 8-methoxy derivative.

Dyestuff Potentialities of 8-Hydroxy and 8-Methoxy-benzanthrone.

Since the field of benzanthrone colours is of great value in modern dyestuff production, it was considered worth while to test the above compounds for any potential dyeing properties to which they might give rise.

One of the main reasons why the methoxy and hydroxy derivatives of benzanthrone obtained in the current work were thus examined arises from the fact that the most important of the benzanthrone colours is Caledon Jade Green, the Bz2:Bz2'-dimethoxy-dibenzanthrone.

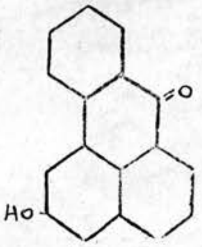


Although a few methoxy-benzanthrones are known, the number of dimethoxy-dibenzanthrone derivatives is extremely limited, and to date, Caledon Jade Green is the only one which has received much attention.

The most familiar procedure for the preparation of these dinuclear compounds from benzanthrone derivatives, consists in the fusion of the compound with caustic potash at temperatures between 150° and 250° C. This method was first applied to benzanthrone by Bally (Ber., 1905, 38, 195; G.P. 185221) when he obtained the now familiar dyestuff violanthrone or dibenzanthrone, at a temperature of 230-240° C. The yield of the dyestuff was small, and subsequent work has given more successful processes. It has been found that mild treatment of benzanthrone with alcoholic potash at 100° C. yields the 2:2'-dibenzanthronyl which can be further converted into violanthrone by fusion with potash or oxidation in acid. The yield and purity of the compound are better than can be obtained by the direct alkali fusion of benzanthrone.

A dibenzanthronyl, probably the Bz1:Bz1' is also obtained by the oxidation of benzanthrone with manganese dioxide and concentrated sulphuric acid at 0° C. (Scottish Dyes) and is converted into dibenzanthrone in excellent yield by the action of alcoholic potash.

The important Bz2-hydroxy-benzanthrone which ultimately led to the discovery of Caledon Jade Green, is also formed in this oxidation.



All the methods outlined above have been applied during the present work, to the 8-hydroxy and 8-methoxy-benzanthrones, and although dyestuffs have been obtained, the true nature of the compounds themselves, however, is open to critiscism.

Investigations on the preparation of such dibenzanthrone derivatives has also been done by Maki and Kikuchi (loc. cit.) but, as in the case of the 8-methoxy-benzanthrone, results obtained in the current work do not completely agree with those published by the above workers.

Prior to his discovery of the 8-methoxy-benzanthrone, Maki, while working with the 8:8'-dibromo-dibenzanthrone, formed the corresponding 8:8'-dimethoxy-dibenzanthrone by treatment with methyl alcohol and caustic alkali in an autoclave. Proof of the formulation of such a compound of necessity depends upon the accurate orientation of the dibromo derivative. Maki proceeds to do this by eliminating all the other possibilities by comparison of ease of vat formation, colour of vat and shade applied to cotton. Actual orientation of the compound by the usual criteria was not obtained.

Maki's analysis of the suspected dimethoxy-violanthrone gave confirmation of the nature of the product, which crystallised from nitrobenzene in blue-black crystals. Treatment with alkali and hydrosulphite at 55-60° C. gave a violet vat with crimson fluorescence from which cotton dyed a violet-blue shade. This ease of vat formation at 60°C. was employed by Maki as a means of purification, filtration of the clear vat solution and subsequent aeration gave a cleaner sample of the dyestuff.

The same workers submitted the 8-methoxy-benzanthrone prepared in a manner similar to that by which they obtained the dimethoxy-violanthrone, to an alkali fusion. The product was found to be exactly similar to that obtained from the dibromo-violanthrone.

Experimental Discussion.

Although a great many alkali fusions have been carried out, at no time could a pure compound be isolated for analytical purposes. Nevertheless, a few analyses have been done, the results of which are not at all satisfactory.

Since the real aim of the current experiments was the isolation of a compound isomeric with Caledon Jade green, the first fusion was carried out on 8-methoxy-benzanthrone with pure caustic potash, a little water being added to facilitate melt formation. Temperatures up to 250°C. were employed, but no colour change in the melt could be observed. No vatting properties were exhibited by the black solid which remained after drowning with water, and this product was shown to be due to carbonisation.

With the view that a better approach could be made by way of the hydroxy derivative, the same fusion was carried out on the 8-hydroxy-benzanthrone. At a temperature of 230-240° C. the melt became dark brown-purple in colour, and finally a dark bluish-green alkali soluble powder was obtained. This vatted with relative ease and the bath was blue in colour with a vivid crimson fluorescence. Cotton emerged from the vat a purple shade which rapidly oxidised to a bluish-green shade, brightening somewhat on washing. The colour was not fast to soap, however, the blue colour becoming rather insipid and very much paler.

The small amount of alkali-soluble material thus obtained was treated with dimethyl sulphate in alkaline solution, and a small amount of a green alkali-insoluble product obtained. This vatted similar to the starting material, but the shade applied to cotton was a somewhat greener shade of blue.

These experiments were carried out on a very small preliminary scale, and when more workable quantities of the necessary benzanthrone derivatives were obtained, repetitions were made on a much larger scale. The products obtained subsequently, however, did not corroborate the evidence obtained above, and conflicting results were the consequence.

A repeat fusion with 8-hydroxy-benzanthrone on a large scale gave rise to considerable difficulties, since it was found that the bulk of the product was alkali-insoluble. No satisfactory explanation of this can be given, unless that the sodium salt of the phenolic compound is extremely sparingly soluble in water. Repeated extraction with alkali seemed to confirm this point, since a coloured solution was always obtained.

At this stage it may be mentioned that very great difficulty was met with in the filtration of these products, the particles being of so fine a nature as to pass through a filter paper and finally to choke the pores. As a result, this tedious process was finally abandoned in favour of centrifuging, which was more rapid and seemed to give solutions free from suspended solid.

Owing to the sparing solubility of the suspected dihydroxy-dibenzanthrone sodium salt in water, it can be seen that the previous methylation with dimethyl sulphate in alkaline solution was not satisfactory. Hence it was decided to attempt purification of the product before carrying out the methylation. Pyridine was found to tbe the most satisfactory solvent, and repeated extraction with this medium was carried out finally leaving a black insoluble residue which proved to be carbon. Crystallisation from the clean blue pyridine solution could not be obtained, even on the concentration of the solution, and the compound was finally recovered by drowning with water. The blue-black powder thus obtained vatted with ease and gave the same blue bath as before from which cotton dyed a clean blue shade. An analysis for C. and H. was done at this stage but the results were unsatisfactory.

Methylation in nitrobenzene suspension was then carried out on this sample and a similar blue-black powder obtained, which gave the same clean blue colour on cotton. This product, as was to be expected, proved to be completely insoluble in alkali. Attempted crystallisation from nitrobenzene did not give any crystals, although a clean blue solution was obtained which exhibited a vivid crimson fluorescence when hot. The material was finally recovered by precipitation with light petroleum. Analytical data here also were not in agreement with the requirements for a dimethoxy-dibenzanthrone.

The incorporation of some alcohol in the fusion mixture had been employed with success in various experiments, and it was decided to try this modification with the compounds in hand, in the hope that improved results might be obtained.

It was found that this procedure did not require such high temperatures as had previously been necessary, and results obtained were more enlightening.

Subjected to this treatment, the 8-hydroxy-benzanthrone at 180°C. gave mostly an alkali-insoluble material with a very small proportion of an alkali-soluble product. The former was a blue-black powder, and from the very small amount of the latter which was obtained, it appeared to be a dark green substance. Test vats were made with each component, and while the blue compound gave a blue vat with the customary crimson fluorescence, the alkali-soluble material gave a brown vat with crimson fluorescence. The first applied a clean blue shade to cotton with a trace of green present, while from the latter bath, cotton emerged a brown-pink shade which rapidly oxidised to a yellow-green colour. Washing this latter specimen caused a change in colour to a bright green, treatment with acid, however, diminishing the brightness of the shade.

The 8-methoxy-benzanthrone was treated in a similar manner, and the results, curiously enough, were the same as those given by the 8-hydroxy compound. The alkali-insoluble product was greater in proportion to the alkali-soluble material, the latter being too small for examination. Concentration of this last alkaline solution, and vatting, however, gave the same green shade on cotton as in the previous case.

When ethyl alcohol in the above experiments was replaced with methyl alcohol, results were exactly similar. Likewise, treatment of the 8-ethoxy-benzanthrone gave practically no difference in product or colour, although the blue shade was slightly brighter and seemed to have lost the green tint.

The occurrence of an alkali-soluble and alkali-insoluble portion in all these experiments, even when the 8-hydroxy-benzanthrone was replaced with the 8-methoxy derivative, was somewhat surprising and various hypotheses may be put forward in explanation.

In the preliminary experiments, since no other agent except caustic potash, is present, the only reasonable explanation for the occurrence of an alkali-insoluble product with 8-hydroxy-benzanthrone, is that reduction has taken place to dibenzanthrone. This theory, however, is incompatible with the nature of the reaction taking place, which has always been considered a process of aerial oxidation. Also, the blue colour applied to cotton is not similar in shade to that given by violanthrone.

If the preliminary experiments are neglected, since subsequent work had failed to give an exact repetition of the results then obtained, and attention confined to those fusions in which alcohol played an important part, some salient points may be observed which are common to each procedure. For instance, each fusion resulted in the isolation of a very small, but quite definite green alkali-soluble product which dyed cotton a bright green colour. Also, the blue dyestuff was common to the lot, the only difference being with the 8-ethoxy-benzanthrone with which a purer blue shade was obtained.

If reactions had only involved the formation of a homogeneous dinuclear compound, them it would have been expected that 8-hydroxy-benzanthrone would have given only the dihydroxy-violanthrone, and the 8-methoxy compound the corresponding dimethoxy-violanthrone alone. On the assumption that the alkali-soluble product is the dihydroxy-dibenzanthrone, and the blue alkali-insoluble product is the dimethoxy-dibenzanthrone, then it would appear that the introduction of the alcohol (methyl or ethyl) has had a marked effect on the course of the reaction. It may be that the methoxy groups have been hydrolysed to hydroxy groupings with the consequent formation of an alkali-soluble portion, the alcohol causing the reaction to proceed at lower temperatures than would be possible with caustic alkali alone. The part played by the alcohol, however, may not stop at this point, and other reactions may be going on with the interchange of methoxy and hydroxy groups, and perhaps even oxidation, with the introduction of other hydroxy groups into the molecule, this last point also accounting for alkali solubility.

Comparison with Maki's work on these compounds gives no clue to the changes in progress, since the preparation of the dyestuffs by him did not involve the use of alcohol in the fusion mixture.

Oxidation, which has been suggested, may involve the introduction of more than two hydroxy groups, perhaps four and even six. Hence it may be seen that a number of controversial points arise from the above experiments.

If oxidation has taken place, then it might be supposed that the green dyestuff is the oxidation product while the blue is the actual dimethoxy-dibenzanthrone. Evidence somewhat in favour of this theory was furnished by a later methylation of the green dyestuff, this product having different properties entirely from the blue alkali-insoluble dyestuff. In an effort to facilitate such oxidation, a little potassium nitrate was introduced into the fusion mixture with 8-methoxybenzanthrone, and the reaction products examined for dyeing properties. Once again the two familiar fractions were obtained, and the blue-black alkali-insoluble material gave the same clean blue shade on cotton. The alkali-soluble material, however, was of a different nature from that previously obtained. It formed a purple-brown vat with crimson fluorescence from which cotton emerged a purplish-pink shade which rapidly oxidised to pink, unaltered on washing. Acid on a pink-dyed sample brought up a green shade which washed to an unsatisfactory yellow green. This latter colour was not fast to exposure, giving finally a brownish tint.

As can be seen from a general review of the methods of preparation of dibenzanthrone derivatives, oxidation is sometimes effected by manganese dioxide and concentrated sulphuric acid at low temperatures. Benzanthrone itself has been found to to give a hydroxy derivative on submission to this procedure. Accordingly, some of the blue dyestuff, presumably the 8:8'-dimethoxy-dibenzanthrone, was treated in this way. The small amount of product obtained did not allow of a very thorough examination, but a test vat of the crude product gave some interesting results. A blue hydrosulphite vat was obtained, but in this case without any fluorescence. From the bath, cotton dyed a clean grey shade. This would point to the fact that oxidation has taken place, with the formation of an alkali-soluble compound.

So far, treatment with oxidising agents has not led to the isolation of a homogeneous alkali-soluble dyestuff, and it would seem probable that differing conditions give correspondingly different oxidation products.

With the failure of the above experiments to furnish any concrete facts as to the nature of the dyestuff products, it was decided to apply Maki's fusion procedure to the same compounds to see whether or not any similarity could be drawn with the compounds listed by him as being the 8:8'-dimethoxy-dibenzanthrone. This method (Ber., 1938, 2, 2039) involves the use of phenol in the fusion mixture, since it has been found that this modification improves the yield of the desired dinuclear compound.

Treatment in this way at 210 C. gave much more amenable products, fundamentally the same, however, as those obtained in previous experiments. The blue alkali-insoluble material vatted in exactly the same manner as the previous samples to give a clean blue shade on cotton. However, in this case, the shade was more bright and showed a hint of green. Peacock blue is a term which might be applied to it. Treatment with acid caused no change in tint, and boiling for various periods with a strong soap solution also failed to produce any deterioration in colour. The soap, however, seemed to take out a small amount of another compound similar to the green dyestuff, since the solution took on a slight green fluorescence.

The green alkali-soluble fraction also gave the same brown-red vat with crimson fluorescence, from which cotton dyed a bright green shade. Soap boiling in this case, however, removed the colour which might be expected. On removal from the soap solution, the cotton was found to have retained a pale blue tint, probably due to a small amount of the blue dyestuff mixed with the green. Acid on a green sample also had a slight dulling effect. although essentially the shade remained the same.

Samples of the two dyestuffs on mercerised cotton thread are given below, the effects of acid and soap boiling being also shown.

1.

2.

1, 2, + 3 are suceessive Dyeings from same vat.

3.

4.

4. is effect of boiling specimen 3. with 1% soap.

1.

2.

1. + 2. are same dyed specimen, 2, having been boiled for 1 hour with 1% soap.

The amounts of the two fractions obtained in the foregoing experiment were much larger and allowed purification to be attempted.

Pyridine appeared to be the most suitable solvent, and crystallisation was tried from that medium. The green dyestuff was relatively soluble, but concentration of the clear green solution failed to cause any crystal formation, and consequently the whole of the material was recovered by drowning with water. The blue compound was more difficult to get into solution, but final concentration of the clear blue solution gave a small amount of a blue-black powder, although no crystals were formed. Complete solution was once again effected and a small amount of the saturated solution boiled for a few minutes with animal charcoal in an effort to bring about purification. Unfortunately, the charcoal adsorbed the whole of the dye, leaving a colourless pyridine liquor. All efforts to recover the dyestuff were unavailing, and the powder previously obtained was dried and sent for analysis. The results obtained, however, were again far from satisfactory, and a residue which was left after combustion, accounted for almost 30% of the weight taken. Possibly this residue may be due to some of the sodium salt of the green dyestuff which has been adsorbed by the blue compound. Extraction with boiling water was found to remove some salt-like material which had a faint green colour. After repeated extraction in this way, the sample was returned for analysis, the results of which are given below.

Analysis:

found:- C: 81.5%; H: 5.13%.

$C_{36}H_{20}O_4$ requires:- C: 83.7%; H: 3.87%.

This analysis, although not sufficiently correct for acceptance is by far the best which has been obtained during the present work for a compound of the dibenzanthrone type.

Methoxyl determinations with the blue dyestuff were equally unsatisfactory, the values obtained being far short of the requirements.

Since crystallisation of the green dyestuff could not be effected, the whole of the material was then subjected to methylation in alkaline solution with dimethyl sulphate. The reaction, however, did not go to completion, the bulk of the starting material being recovered unchanged on acidification. The small amount of alkali-insoluble product obtained, was isolated and examined. It was a green-black powder which dissolved in pyridine to give a dark green solution, but gave no solution in a hydrosulphite vat.

The recovered material was then treated in nitrobenzene solution with dimethyl sulphate, sodium carbonate being employed as acid adsorbing agent. Complete conversion was obtained in this case and the alkali-insoluble product was exactly similar to that found in the previous attempt at alkylation.

This latter product differs from the other compounds obtained, in the fact that it has no vatting properties. From this evidence some conclusions may be drawn regarding the nature of the green and blue dyestuffs.

The most reasoable assumption to be made is that the blue dyestuff is in actual fact the 8:8'-dimethoxy-dibenzanthrone, although the greenish blue shade which it gives on cotton is quite different from the violet-blue shade claimed by Maki for the same compound. Nevertheless, it may be said in Maki's favour that his specimens furnished the necessary analytical confirmation, a criterion which cannot be given with the compounds found in the current work. If such a hypothesis is correct, then the alkali-soluble dyestuff must either be a hydrolysis or oxidation product. If the former were correct, then methylation should at once give the same blue dyestuff as constitutes the alkali-insoluble product. Results, however, do not support this theory since the methylation product is entirely different. Thus from an examination of all the results obtained up to this point, various theories may be postulated for the formulation and constitution of the green alkali-soluble dyestuff.

Direct hydrolysis of the dimethoxy-dibenzanthrone to the dihydroxy derivative may be excluded, since if such had been the case, subsequent methylation in the ordinary way would have at once given the familiar blue dyestuff. Such a theory, however, depends on the truth of the assumption that the blue dyestuff is in actual fact the 8:8'-dimethoxy-dibenzanthrone. The necessary analytical confirmation for such a hypothesis has not been obtained, with the result that any explanation offered in this way is open to critiscism.

The fact that methylation of the green solid gave another green solid which was insoluble in alkali and formed no hydrosulphite vat is somewhat surprising, since formation of a soluble leuco compound is a normal characteristic of these dibenzanthrone derivatives. A few, however, are met with, in which the presence of substituents appears to hinder the formation of the leuco compound. This inhibition is specially marked if the substituent occupies the position ortho to the keto group; i.e. position 5 of the benzanthrone nucleus. If, as has already been suggested, oxidation has taken place with the introduction of other hydroxy groups, then it is quite feasible that position 5 has been attacked in this way. This hypothesis would account for the alkaline solubility of the green dyestuff, but the apparent formation of a vat does not agree with the theory given above. A closer examination of the vat solution, however, showed that addition of the sodium hydrosulphite to the alkaline solution did not produce any matked change in the colour of the solution. The faint crimson fluorescence which was noticed at this point, may be due to a small amount of the blue dye which always interferes to a slight extent. Hence it may be seen that the green colour on cotton may quite possibly be due to direct dyeing, very little change due to oxidation being noticed on taking a sample from the vat and exposing to the air. Washing eventually brings up the bright green colour, which fact is probably due to the elimination of alkali.

Beyond complete break down of the benzanthrone system, with the consequent formation of a coloured degradation product, oxidation in this way appears to be the only likely possibility. The number of introduced hydroxy groups of course, may quite possibly be more than two, since four or six are equally probable.

A repetition of these fusions with the 8-ethoxybenzanthrone gave similar results, the blue shade on cotton, however, being more of a pure blue than was obtained from the methoxy derivative. Samples of these dyeings are given below.

From these facts it is evident that the elucidation of the formulation and constitution of these compounds must entail a great deal of work, more than can be accomplished at the present stage. Although definite confirmed results are lacking in this latter branch of the work, further investigations on the subject would be of great interest in the light of the facts already obtained. Unfortunately, the preparation of the starting materials for these products involves a very long procedure, hence the small amounts of the compounds which have been used. Larger quantities would obviously lend more scope to the work.

Benzalizarin. 7:8-Dimethoxy-benzanthrone.

In the examination of the literature which was entailed by the preceding investigations, particulars were found pertaining to the 7:8-dihydroxy-benzanthrone (benzalizarin) and the corresponding dimethoxy derivative. Perkin (J.C.S., 1920, 700) isolated benzalizarin by the usual glycerol condensation carried out on alizarin, but if he investigated the results of alkali fusion on the product, the results he obtained were not published.

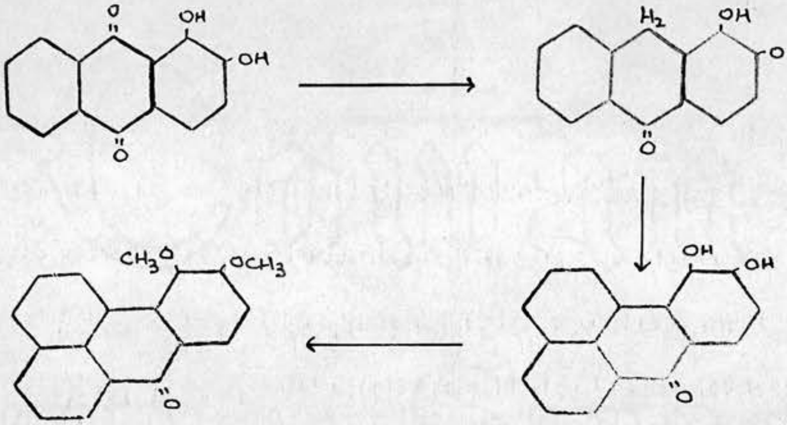
In the hope that some light might be thrown on the nature of the two dyestuffs already obtained, it was decided to repeat Perkin's preparations, and submit the products to fusion experiments.

Prior to the glycerol condensation, the alizarin was reduced to the corresponding anthrone derivative. The usual method with fuming hydrochloric acid and tin was not satisfactory on application to alizarin, the product consisting of a mixture of the 1:2-dihydroxy and the 3:4-dihydroxy-anthrones.

As no details of Perkin's procedure were given, he no doubt used another method for the preparation of the anthrone. Finally, a close examination of the literature gave particulars for this preparation in which alizarin was reduced in alkaline solution (Graebe and Thode, Ann., 1906, 349, 207; Römer, Ber., 14, 1260). Under these conditions, the alizarin was completely converted to the 3:4-dihydroxy-anthrone, which is the necessary intermediate for the preparation of 7:8-dihydroxy-benzanthrone.

After a glycerol condensation and purification by way of the diacetate of the compound, benzalizarin was finally obtained in the pure state in a yield of 40%. Perkin quoted no yields, but melting points obtained currently, agree with those published by the above worker.

Methylation of the phenolic derivative was effected by Perkin with methyl iodide, but a more efficient method lies in the use of dimethyl sulphate applied to an alkaline solution of the compound. This latter method resulted in 7:8-dimethoxy-benzanthrone being obtained in 95% yield and in a good state of purity.



Alkali fusion of 7:8-dimethoxy-benzanthrone.

When the 7:8-dimethoxy-benzanthrone was submitted to fusion with pure caustic potash, no dibenzanthrone derivative could be isolated, decomposition occurring when the temperature was taken too high. Repetition of the procedure with phenol in caustic potash caused a hydrolytic reaction, the first product being completely soluble in alkali to give a red-brown colour. Maintained at 210°C. for 30 minutes, the melt became green-black in colour, and when this was rapidly dissolved in water, a deep red solution was obtained which on acidification gave a small amount of a yellow substance. A deep purple solid was also obtained which appeared to be insoluble in alkali, and which formed a deep blue non-fluorescent hydrosulphite vat from which cotton was dyed an unsatisfactory purple shade. Treatment of a dyed sample with acid, caused the colour to change to a pale yellow green, neither colour being fast to soap boiling.

Owing to lack of time this matter was not treated further.

Attempted preparation of 5:8-dihydroxy-benzanthrone.

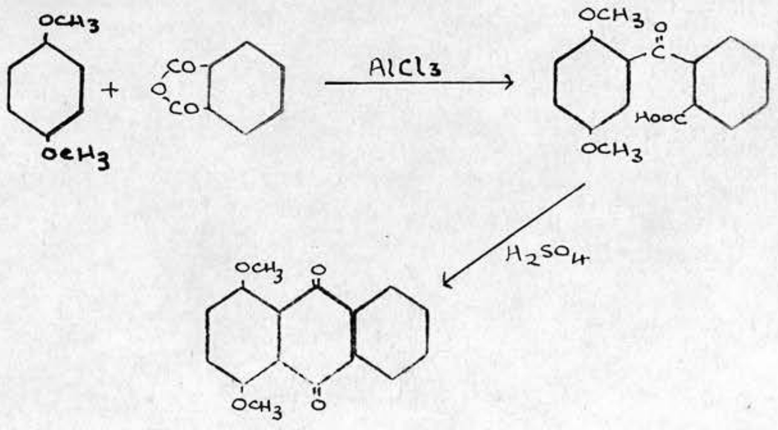
During the current investigations, considerable interest has attached to the 7:8 and 5:8 disubstitution products of benzanthrone, and so an attempt was made to prepare the 5:8-dihydroxy-benzanthrone while the isolation of the 7:8 isomeride was proceding.

For this purpose the starting material was quinizarin or 1:4-dihydroxy-anthraquinone. As in the case of alizarin, reduction to the anthrone is a necessary preliminary to the condensation with glycerol, and treatment of a solution of quinizarin in glacial acetic acid with tin and fuming hydrochloric acid, resulted in the isolation of 1:4-dihydroxy-anthrone in 100% yield, melting at 156° C. Pleus (Ber., 35, 2924), is quoted as having prepared this compound from quinizarin by reduction with hydriodic acid and red phosphorus, and although yields are not given, the melting point reported is also 156° C.

No particulars could be found for the glycerol condensation, and no reference to 5:8-dihydroxy-benzanthrone was given in the literature.

Treatment in the same way as the 3:4-dihydroxyanthrone gave no trace of a benzanthrone derivative, decomposition being the apparent cause.

In the belief that the dimethyl ether of quinizarin might respond better to such treatment, the preparation of this compound was then attempted. No particulars, however, could be found in which quinizarin yielded the dimethyl ether by direct methylation. The only method which could be found was that in which hydroquinone dimethyl ether was converted to 2:5-dimethoxybenzophenone-carboxylic acid, which on treatment with concentrated sulphuric acid gave the required dimethoxyanthraquinone.

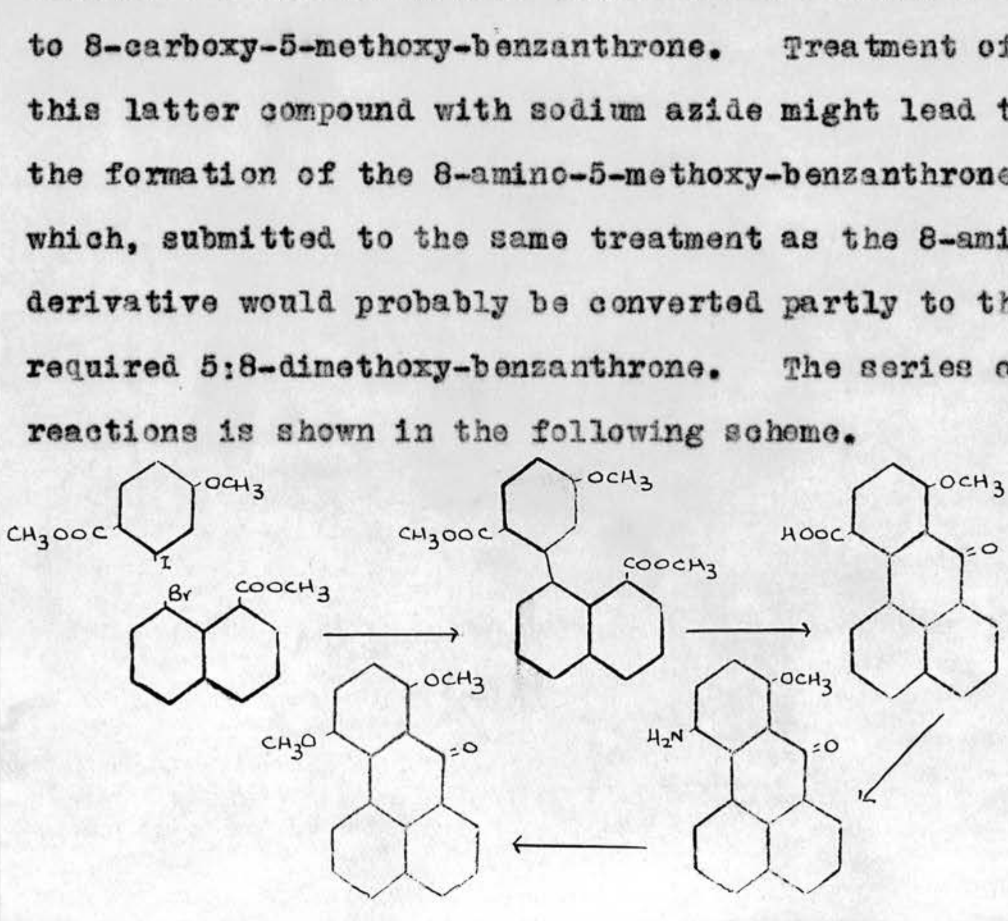


Heating this latter compound with concentrated sulphuric acid gave quinizarin, and for this reason, the whole scheme was abandoned since the 82% sulphuric acid used in the glycerol condensation would no doubt cause the same disruption, thus giving the same results as the condensation carried out on the quinizarin derivative itself.

The only means left for the preparation of 5:8-dimethoxy-benzanthrone would appear to be the synthesis by means of an Ullmann coupling with the required phenyl and naphthyl esters.

The series of reactions which were thought might give the necessary compound were as follows:-

Methyl-1-iodo-3-methoxy-benzoate, submitted to an Ullmann reaction with methyl-8-bromo-1-naphthoate should give dimethyl-8-(1-carboxy-4-methoxy-phenyl)-1-naphthoate, cyclising with concentrated sulphuric acid to 8-carboxy-5-methoxy-benzanthrone. Treatment of this latter compound with sodium azide might lead to the formation of the 8-amino-5-methoxy-benzanthrone, which, submitted to the same treatment as the 8-amino derivative would probably be converted partly to the required 5:8-dimethoxy-benzanthrone. The series of reactions is shown in the following scheme.



This projected scheme, however, had to be abandoned owing to the great difficulty in preparing the required methyl-1-iodo-3-methoxy-benzoate.

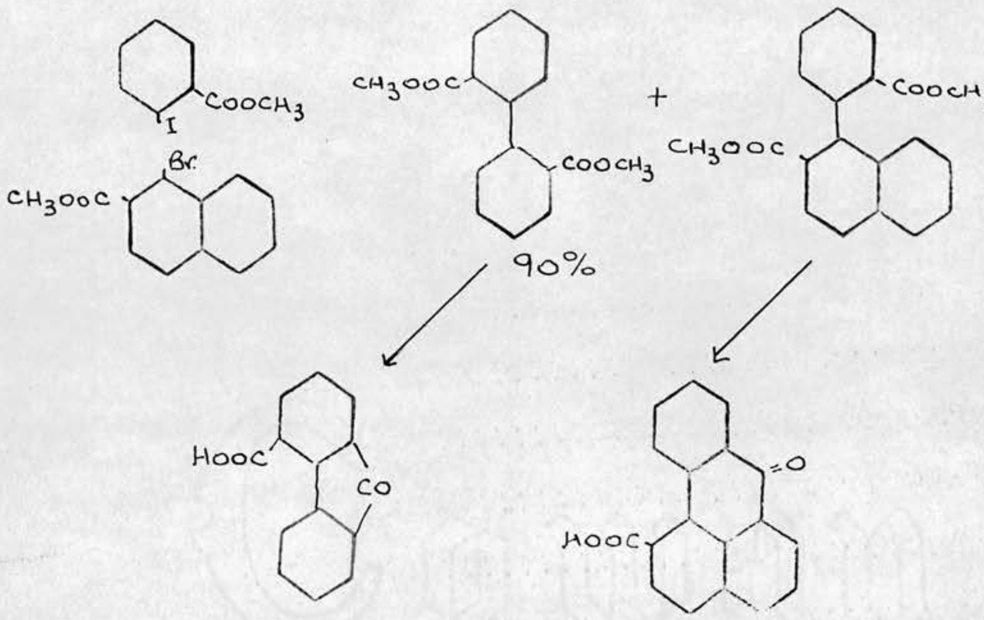
Various methods are given for the preparation of this substituted benzoic acid, but as most of them are protected by patent, (Hodgson and Jenkinson, J.C.S., 1927, 3044), no particulars were available. A great many stages were involved the first of which required the extensive use of phosgene gas. Under the present war-time conditions, a supply of this commodity could not be obtained. Other methods were attempted, and are outlined in the preparative section, but owing to the involved procedure, these also had to be dropped, the time factor also being of importance.

Bz3-Carboxy-benzanthrone: Bz3-Amino-benzanthrone.

Consequent on the ease with which the 8-carboxy-benzanthrone responds to treatment with sodium azide to give the 8-amino derivative, it was decided to attempt a similar conversion with Bz3-carboxy-benzanthrone to the previously unknown Bz3-amino derivative.

For such an investigation, however, a moderate supply of the Bz3-carboxy-benzanthrone was a primary necessity, and previous research has shown this to be no easy matter.

After completing a great number of experiments, Rule and Grieve (J.C.S., 1938, 342, 1836) were ultimately successful in isolating Bz3-carboxy-benzanthrone in 3% yield. Although the basis of the method was an Ullmann coupling between methyl-1-bromo-2-naphthoate and methyl-o-iodo-benzoate, the reaction products did not correspond to those obtained in the preparation of the isomeric 8-carboxy-benzanthrone. In this latter preparation, the reactants, methyl-o-iodo-benzoate and methyl-8-bromo-1-naphthoate, contain halogens which are relatively equal in reactivity, thus causing the required phenyl-naphthyl ester to be the chief product of the reaction. With the Bz3-isomeride, however, the reactivity of the bromine in methyl-1-bromo-2-naphthoate appears to be much inferior to that of the iodine in methyl-o-iodo-benzoate. Consequently in Grieve's preparation, diphenic ester accounted for almost 90% of the reaction product. The very small amount of the required phenyl-naphthyl ester also formed was extremely difficult to isolate. If the whole of the reaction product is treated with concentrated sulphuric acid at 100° C., along with the small amount of Bz3-carboxy-benzanthrone is also produced a vastly greater proportion of the fluorenone-4-carboxylic acid as shown in the following scheme.



The fluorenone derivative is a yellow solid similar to the carboxylic benzanthrone, and since the solution of the mixture in caustic soda exhibits a green fluorescence due to the small amount of benzanthrone derivative present, the above workers were misled into purifying the mixture. Crystallisation from glacial acetic acid led to the elimination of the carboxy-benzanthrone, and unwittingly a pure sample of the fluorenone acid was obtained. Only when analysis figures were obtained, was the real nature of the compound actually discovered.

A tentative separation of the products of the Ullmann was finally achieved by vacuum distillation with the collection of various fractions. The phenylnaphthyl ester was finally obtained as a very viscid high boiling liqid which failed to solidify. Complete removal of the diphenic ester, however, could not be effected, and on subsequent ring closure of the product, fluorenone carboxylic acid still interfered to a great extent. Crystallisation from glacial acetic acid was not successful since it resulted in the concentration of the fluorenone derivative. Extraction with chlorobenzene at the boiling point was finally successful in the preferential solution of the impurity, and in this way a pure sample of the Bz3-carboxy-benzanthrone was finally obtained, the total yield being, howeverm only 3%.

The yields obtained by Rule and Grieve being exceedingly small, some modifications in the procedure were attempted in an effort to increase the amount isolated.

Since as aforesaid, the reactivity of the halogen in the benzoic ester appears to be relatively much greater than that in the naphthoate, the methyl-o-iodobenzoate was replaced by the corresponding bromo compound. This process should cause a reduction in the percentage of the diphenic ester and a corresponding increase in the yield of the required phenyl-naphthyl ester. The subsequent treatment was exactly the same as that used in Grieve's investigations, and although the fluorenone derivative again interfered, the pure acid was finally obtained in 7-8% yield. Admixture of the compound with a sample prepared by Grieve failed to show any melting point depression, thus proving the identity of the compound.

Bz3-amino-benzanthrone.

On treatment of the Bz3-carboxy-benzanthrone with sodium azide in a manner exactly similar to that employ-in the preparation of the 8-amino derivative, a red solid was obtained which proved to be the desired Bz3-amino-benzanthrone. By increasing the reaction period from two to three hours, the yield of the amine was increased from 45-50% to 95%. The compound melted at 234-236°C. with decomposition slightly below the melting point, and formed red needles from chlorobenzene, of a slightly darker shade than the 8-amino-benzanthrone. In its behaviour towards solvents, however, the new amine differed considerably from the latter compound. Vivid fluorescence always accompanied solution in organic solvents, the yellow alcoholic solution showing bright yellow fluorescence, whilst benzene gave a yellow solution with an extremely vivid green fluorescence.

Although the mononuclear compound has so far not been previously prepared, the corresponding dibenzanthrone is already known, having been prepared by Maki and Aoyama (J. Soc. Chem. Ind. Japan, 1935, 38, 636B) by the treatment of the chorination product of violanthrone with aqueous ammonia in an autoclave at 200 C. for 7 hours, in the presence of a copper catalyst. The constitution of this dinuclear compound depends, however, on the truth of the formulation of the dichlorination product mentioned.

Characterisation of the new amine was carried out in the usual manner by the formation of the formyl and acetyl derivatives. Treatment with formic acid resulted in the Bz3-formamino-benzanthrone being obtained with relative ease, a yellow crystalline solid melting at 273-275°C. with decomposition. When the preparation of the acetyl derivative, however, was attempted by the usual acetic anhydride method, the same difficulties were met with as in the case of the 8-amino-benzanthrone. The two fractions in this instance were of definitely different crystalline structure, although in the crude separation, the melting points were very near to each other, mixture of the two however, producing a depression. Analytical data was somewhat confusing, but the values obtained pointed to the components being the mono and diacetyl derivatives of the amine. In this case prolonged boiling with glacial acetic acid failed to give any substitution product, the whole of the starting material being recovered unchanged.

The small amount of amine obtained excluded the possibility of any further work being done on this subject within a reasonable time limit.

SUMMARY.

The 8-amino-benzanthrone has been submitted to several standard reactions, and although the results obtained were somewhat exceptional, considerable interest attaches thereto.

Attempted oxidation with bromine and nitrobenzene to the carbazole derivative did not take place, but bromination occurred exclusively. Subsequent attempts to determine the orientation of the mono-bromo-amine thus obtained gave rise to several new compounds and opened up valuable fields for research.

The new Bzl-bromo-8-amino and 6-bromo-8-amino-benzanthrones have been obtained from treatment of the corresponding carboxy acids with sodium azide.

By a Sandmeyer reaction, the new 8-bromo-benzanthrone has been prepared from the parent amine, while similar treatment of the brominated amine resulted in the formation of a supposedly homogeneous dibromo-benzanthrone. Although this latter product had a sharp melting point, chromatographic analysis showed that it was really a mixture of two isomeric dibromo-benzanthrones. One of the components was proved to be the 5:8-dibromo-benzanthrone while the data obtained appeared to point to the other fraction being the 7:8 isomeride.

The new 5:8-dibromo-benzanthrone has also been prepared from a glycerol condensation on 1:4-dibromo-anthraquinone.

Perhaps the most interesting part of the work is that which has been carried out on the 8-hydroxy and 8-methoxy-benzanthrones. Attempts to prepare these compounds directly from the amine by the usual methods were unsuccessful, but attempted elimination of the amino group by diazotisation and boiling with methyl alcohol gave the hydroxy and methoxy derivatives somewhat unexpectedly.

Alkali fusions have been carried out on these two compounds, and although pure substances have not been obtained, and analytical data was unsatisfactory, the products were very interesting in view of the rather pleasing shades which were applied to cotton.

Elimination of the amino group from the 8-amino-benzanthrone was finally accomplished to the extent of 10% by treatment of the diazonium salt with an alkaline solution of formaldehyde.

Perkin's preparation of benzalizarin has been repeated, and fusion experiments carried out on that compound, results, however, being entirely negative. Attempts were also made to prepare the isomeric 5:8-dihydroxy derivative, but without success.

Grieve's preparation of the Bz3-carboxy-benzanthrone has been modified to a slight extent, and the yield increased from 3% to 7-8%. Hydrazoic acid was successful in converting this latter compound to the new Bz3-amino-benzanthrone.

Mercuration experiments have also been carried out on the 8-carboxy-benzanthrone and a mercury salt of the acid obtained. Treatment of this compound failed to give any mercuri anhydride of the acid, but instead, appeared to result in the formation of a mercuri-benzanthronyl, while benzanthrone was set free.

Mention may be made here of the extensive use which has been made of chromatographic means of separation and purification. It appears to be particularly applicable to compounds of the types dealt with in the present work, and has been the means of saving much valuable material which would otherwise have been lost in tedious crystallisation procedures.

POSTSCRIPT.

An acknowledgement at this stage can only pay small tribute to the encouragement and advice which has been given the author by Dr. H. G. Rule. The able way in which he helped to tackle the many problems which have arisen in the current work, deserves the most sincere thanks.

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