STUDIES in the mesoBENZANTHrone SERIES.

By

ANTHONY ARTHUR WOODHAM, B.Sc.

Thesis for the Degree of Doctor of Philosophy.

July 1951 University of Edinburgh.
# CONTENTS

## PART 1

4-Substituted mesoBenzanthrones derived from 4-a-Cyano/benzylmesobenzanthrone

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction.</td>
<td>1</td>
</tr>
<tr>
<td>Discussion.</td>
<td></td>
</tr>
<tr>
<td>The Synthesis of 4-Benzoylmesobenzanthrone.</td>
<td>3</td>
</tr>
<tr>
<td>The Oxidation of 4-Benzoylmesobenzanthrone.</td>
<td>6</td>
</tr>
<tr>
<td>The Oxidative Hydrolysis of 4-a-Cyanobenzyl/mesobenzanthrone.</td>
<td>8</td>
</tr>
<tr>
<td>Experimental.</td>
<td>20</td>
</tr>
<tr>
<td>Bibliography.</td>
<td>51</td>
</tr>
</tbody>
</table>

## PART II

Some Reactions of the Carbonyl group of mesoBenzanthrone

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction.</td>
<td>53</td>
</tr>
<tr>
<td>Discussion.</td>
<td></td>
</tr>
<tr>
<td>Oximes and the Beckmann Rearrangement</td>
<td>57</td>
</tr>
<tr>
<td>The Schmidt Reaction.</td>
<td>67</td>
</tr>
<tr>
<td>Oxonium Salts of mesoBenzanthrone.</td>
<td>73</td>
</tr>
<tr>
<td>The Reduction of mesoBenzanthrone with/Aluminium isopropoxide.</td>
<td>78</td>
</tr>
<tr>
<td>The Action of Phosphorus oxychloride and/pentachloride on mesoBenzanthrone.</td>
<td>81</td>
</tr>
<tr>
<td>The Synthesis of 6-Hydroxymesobenzanthrone</td>
<td>88</td>
</tr>
<tr>
<td>Experimental.</td>
<td>92</td>
</tr>
<tr>
<td>Bibliography.</td>
<td>147</td>
</tr>
<tr>
<td>Summary of Research.</td>
<td>149</td>
</tr>
<tr>
<td>Postscript.</td>
<td>151</td>
</tr>
</tbody>
</table>
Introductory Remarks.

The numbering of the mesobenzanthrone nucleus which has been used throughout this thesis, is indicated below. This numbering has now been officially adopted by the Chemical Society, and its use appears to be practically universal at the present time.

In the experimental part of the thesis, all melting points quoted are uncorrected, and, unless otherwise stated, were determined on the apparatus described in "Qualitative Organic Analysis" (p.7, fig.4.) by N. Campbell.

All yields are calculated as a percentage of the maximum theoretically possible.

Chromatographic separations and purifications were invariably carried out using aluminium oxide standardised according to Brockmann.

Fluorescence observations were carried out in the beam of a Hanovia ultra-violet lamp. Absorption spectra work was done on a Hilger ultra-violet absorption spectrophotometer.

All analyses were carried out by Dr's Weiler and Strauss of Oxford.
PART I

4- SUBSTITUTED mesoBENZANTHRONES DERIVED FROM

4-a- CYANOGENYLmesoBENZANTHRONE.
INTRODUCTION.

Under the circumstances which obtain for the ordinary substitution reactions of mesobenzanthrone (I) such as nitration (1) and halogenation (2), the 4-position is not the most reactive. Primary attack occurs at the 3-position and in the chlorination at least, successive chlorine atoms are introduced in the 9- and 11- positions.

There have been a number of references in the patent literature (3) however, to the condensation of mesobenzanthrone with compounds containing a reactive methylene group, in the presence of alkalis. It is claimed that with benzyl cyanide, for example, the product is 4-a-cyanobenzylmesobenzanthrone, (II) and further that this is converted by oxidative hydrolysis into 4-benzoylmesobenzanthrone. (III).

Evidence that this oxidative condensation does occur at the 4-position is to be found in the patent literature, but the reliability of this is difficult to assess. Relevant details, such as the constitution of important intermediates and their origin, methods
of identification, and analytical figures, are omitted.

The condensation and oxidative hydrolysis were studied in this Department by the late Dr. H.G. Rule and A.G. McGregor, independently of the patent literature. They did not, however, establish the constitution of 4-benzoylemesobenzanthrone unequivocally.

The first part of this thesis, then, will deal with the proof of the constitution of the product of the oxidative condensation of mesobenzanthrone and benzyl cyanide, and with some considerations of the manner in which it arises.
DISCUSSION.

The condensation of mesobenzanthrone with benzyl cyanide was carried out according to the method described in B.P. No. 319593, and the oxidative hydrolysis of the resulting 4-a-cyanobenzylmesobenzanthrone was effected by means of the instructions in the Ph.D. thesis of A.G. McGregor (Edinburgh 1941).

The preparation of 4-a-cyanobenzylmesobenzanthrone was not quite as straightforward as it would appear from a study of the patents. On some occasions no reaction whatever appeared to take place, although the materials and conditions employed duplicated exactly a successful condensation previously carried out. No trouble was experienced, however, with the oxidative hydrolysis of 4-a-cyanobenzylmesobenzanthrone.

The structure of the latter compound was proved by synthesis and oxidation.

-------------------

The Synthesis of 4-Benzoylmesobenzanthrone

1-Bromo-4-methylnaphthalene (IV) was prepared from a-methylnaphthalene by the method of Meyer and Sieglitz (4). Oxidation with nitric acid gave 4-bromo-1-naphthoic acid (v), the acid chloride of which was converted into 1-bromo-4-benzoylnaphthalene (VI) by a Friedel-Crafts reaction. (VI) was shown to be identical with the product obtained by direct benzoylation of a-bromonaphthalene by means of a
Friedel-Crafts reaction. Replacement of the bromine by a cyano group gave 4-benzoyl-1-naphthonitrile (VII) which was cyclised to 4-cyanomesobenzanthrone (VIII) with AlCl₃ and NaCl in a current of oxygen. Hydrolysis of the nitrile yielded mesobenzanthrone-4-carboxylic acid (IX) (5), the acid chloride of which was condensed with benzene in the presence of AlCl₃ to give 4-benzoylmesobenzanthrone (X).

(IV) was converted into (XI) by treatment with cuprous cyanide in pyridine, but the preparation of (XII) from this by means of a Grignard reaction yielded a product which contained bromine. Obviously, the bromobenzene used here must have contained some of the dibromo-compound. However, as the alternative synthesis already described, had been brought to a successful conclusion in the meantime, further experiments on the conversion of (XI) into 4-benzoyl/mesobenzanthrone were not carried out.

(XI) was shown to be identical by melting point, mixed melting point and analysis with the compound obtained by oxidative hydrolysis of 4-α-cyanobenzyl/mesobenzanthrone.

The possibility, however, that molecular rearrangement had occurred during the cyclisation had to be considered, and in consequence a further proof that the compound was 4-benzoylmesobenzanthrone was sought, and obtained by oxidation.
The Oxidation of 4-Benzoylmesobenzanthrone

Oxidation of mesobenzanthrone itself with chromic acid is known to cause ring scission with the production of anthraquinone-1-carboxylic acid (XIII), and hence 4-benzoylmesobenzanthrone would be expected to yield 2-benzoyl-anthraquinone-1-carboxylic acid (XIV), under similar treatment.

This compound previously obtained by Scholl Wanka and Dehnert (6) from 1-chloro-2-benzoylanthraquinone, did indeed result from the oxidation, and its structure was unequivocally established as follows:

The carboxyl is in the 1-position and the benzoyl group was shown to be contiguous to it by the fact that reaction occurred with hydrazine hydrate yielding 3-keto-6-phenyl-2:3-dihydroanthraquinone (1':2':4:5) pyridazine (XV). Further the compound reacted with acetic anhydride in pyridine to yield 5'-acetoxy-5'-phenyl-2':5'-dihydofuran-2'-one(3':4':1:2) anthraquinone (XVI).
Control experiments showed that hydrazine hydrate under the same conditions did not react with anthraquinone, and with anthraquinone-1-carboxylic acid gave the hydrazinium salt. These experiments were necessary because Schaarschmidt (7) showed that 1-benzoyl/anthraquinone does react with hydrazine to yield a ketazine XVII.

A model experiment involving the condensation of hydrazine hydrate with o-(p-toluoyl)benzoic acid yielded 3-keto-6-phenyl-2;3-dihydro-4:5-benzpyridazine. XVIII.

Decarboxylation of 2-benzoylanthraquinone-1-carboxylic acid yielded 2-benzoylanthraquinone, previously obtained from 9-benzoylmesobenzanthrone by Moshchinskaya (8) or anthraquinone-2-carboxylic acid by Waldmann (9).

Anthraquinone-2-carboxylic acid and the 1- and 2- naphthoic acids were not decarboxylated by copper in quinoline under the conditions used in the decarboxylation of the 2-benzoylanthraquinone-1-carboxylic acid. 1-nitroanthraquinone-2-carboxylic acid, on the other hand, was readily decarboxylated.

The reduction of 2-benzoylanthraquinone-1-
carboxylic acid to 2-benzyl-anthracene-1-carboxylic acid by means of zinc dust and ammonia was attempted, but the results were unsatisfactory.

It was later found that the reduction of 3-benzoylanthraquinone-2-carboxylic acid by means of zinc dust and ammoniacal CuSO₄ had been attempted by Philippi (10), and that he had found this reduction unsatisfactory.

As a result of the work which has been described, then, the constitution of the product of oxidative hydrolysis of 4-a-cyanobenzylbenzanthrone has been rigidly established as 4-benzoylmesobenzanthrone.

The Oxidative hydrolysis of 4-a-Cyanobenzylmesobenzanthrone

While it is not difficult to visualise a series of reactions by which 4-a-cyanobenzylmesobenzanthrone might be converted into 4-benzoylmesobenzanthrone, the fact that they should all take place together under the relatively mild conditions of hydrolysis and oxidation, which have already been described, is perhaps remarkable. Even more so is the fact that the yield is high and the product is uncontaminated with any by-products such as might be expected with so many stages involved. A possible mechanism for the change is represented by the following scheme:
The first three stages of this mechanism are logical, but the final oxidation of 4-benzylmeso/benzanthrone to 4-benzoylmesobenzanthrone seems unlikely under the mild oxidative conditions used. Kacer (11) has stated that 4-benzylmesobenzanthrone is not easily oxidised, and he used H$_2$SeO$_3$ under pressure. McGregor (12) showed that the benzylcyano-compound (XIX) could be converted into 4-benzylmesobenzanthrone by treatment with CH$_3$COOH and H$_2$SO$_4$, while CH$_3$COOH and Na$_2$Cr$_2$O$_7$ gave 4-benzoylmesobenzanthrone. It seemed, however, that some work was required before such a scheme as that outlined above, could be ruled out.

It was found that 4-a-cyanobenzylmesobenzanthrone could be hydrolysed to 4-a-carbamidobenzylmeso/benzanthrone (XX), by allowing it to stand in H$_2$SO$_4$ solution for a few days, and further, that hydrolysis of the amide either with ethanolic KOH or ethanolic
HCl yielded 4-benzylmesobenzanthrone (XXII). Attempts to isolate the carboxylic acid intermediate (XXI) by employing a less vigorous hydrolysing agent, nitrous acid, failed, a mixture of 4-benzylmesobenzanthrone and unchanged amide being obtained. Oxidative hydrolysis of the amide with methanolic KOH and air, just as in the case of 4-a-cyanobenzylmesobenzanthrone, yielded 4-benzoylmesobenzanthrone XXIII.

These results suggested immediately that air should be sufficient to oxidise 4-benzylmesobenzanthrone to 4-benzoylmesobenzanthrone, and it was found that air in the presence of methanolic KOH did indeed effect the oxidation. On the 0.05g scale 4-benzylmeso/benzanthrone was oxidised quantitatively to 4-benzoylmesobenzanthrone in only three minutes. A similar result was obtained in the case of 4-p-methoxybenzylmesobenzanthrone. In so far as we are aware, this oxidation is unparalleled in organic chemistry. Aerial oxidation of hydrocarbons are known, but they are usually extremely slow, and the yields are not high. The unique aspects of the oxidation of 4-benzylmesobenzanthrone are its speed, and the fact that a quantitative yield of the ketone is obtained.

It has been shown, then, that excepting for the initial hydrolysis of 4-a-cyanobenzylmesobenzanthrone to the amide, each step of the proposed mechanism is possible under the conditions employed in the oxidative hydrolysis of the cyanobenzyl-compound.
There is evidence, too, for an amide intermediate in that the evolution of ammonia was detected during the oxidative hydrolysis of the cyanobenzyl-compound.

A study, next, of the oxidation of 4-benzyl/mesobenzanthrone showed that the suggested mechanism cannot account for all the facts. It would be easy to say that the methanolic KOH is responsible for the first two hydrolytic stages and that the carboxylic acid formed is extremely labile, immediately losing CO₂ to yield 4-benzylmesobenzanthrone, which is then oxidised to 4-benzoylmesobenzanthrone by the air. This does not explain, however, why KOH as well as air, is necessary for the final stage. Omission of either inhibits the oxidation completely or partially. Treatment of 4-benzylmesobenzanthrone with methanol and air alone causes no oxidation. Methanol, piperidine, and air caused partial oxidation, but after 10 hours, most of the material was unchanged. Methanolic KOH and nitrogen caused very slight oxidation after 18 hours, but later experiments indicated that even this was due to a little dissolved oxygen present. If some water was present along with the methanolic KOH and air, the oxidation was inhibited to a great extent. This latter effect was noticed in the case of the cyanobenzyl-compound by McGregor, but he attributed it to a solubility effect. Care was taken in our experiments, not to add sufficient water to cause precipitation of the 4-benzylmesobenzanthrone.

A study of a limited number of benzyl-compounds...
was undertaken to see if any analogous oxidation occurred when these were aerated in methanolic KOH. Diphenylmethane, 2-benzylpyridine prepared by LaForge’s modification of Tschitschibabin’s method (13,14), fluorene, dibenzyl and 4:4’-tetramethylaminodiphenyl/methane were examined thus, and in none was any oxidation observed, although the experiments were carried out for 10 hours. 2-benzylpyridine is particularly interesting as Müller and Dorfmann (15) claimed that it was oxidised to 2-benzoylpyridine merely by exposing it in air to a quartz mercury lamp.

Similar results were obtained with the cyanobenzyl compounds. Treatment of 4-α-cyano-p-methylbenzylmeso/benzenanthrone with methanolic KOH without aeration, resulted in no change after 28 hours refluxing and no NH₃ was evolved. A further 35 minutes aeration gave a quantitative yield of the benzoyl derivative. This result is interesting as it proves that oxygen is necessary before the nitrogen atom can be split off as ammonia.* This does not fit in with the scheme proposed above, where hydrolytic reactions alone are supposed to be involved in the removal of the nitrogen. Refluxing and aeration of the cyanobenzyl-compound in methanol alone caused no change. Oxidative hydrolysis of the cyanobenzyl-compound was found to occur in the cold solution in the presence of methanolic KOH and air. When rigorous precautions were taken to exclude air by boiling the methanolic KOH, cooling in a nitrogen atmosphere, and substituting a stream of nitrogen for
air during the reaction, no oxidation occurred, even after 56 hours refluxing. No oxidation occurred when dioxan was substituted for methanol as the solvent, but this may have been due to the small solubility of KOH in dioxan. A further interesting point is that the alkaline methanolic solution resulting from an apparently complete oxidation of 4-a-cyanobenzylmesobenzanthrone has a striking green fluorescence. This is present also in the case of the amide hydrolysis, and the oxidation of 4-benzylmesobenzanthrone. In every case an apparently quantitative yield of 4-benzoylmesobenzanthrone is obtained, and yet it can be shown that a solution of 4-benzoylmesobenzanthrone in methanolic KOH is a non-fluorescent straw colour. Some material is obviously present in minute quantity, which is responsible for the green fluorescence; on exposure to air for several days, the fluorescence disappears.

The facts now available suggested that the cyanobenzyl-compound, the amide and the 4-benzylmesobenzanthrone were converted to 4-benzoylmesobenzanthrone by a similar mechanism, but that they were not individual intermediates of one mechanism. In none of the oxidations, were traces found of any of the other precursors, but in all of them it was found possible to detect the presence of a peroxide. This can be isolated by evaporation of the alkaline methanolic liquors of a partially complete oxidation, and extraction of the residue with water. A vivid
green fluorescent solution is obtained, which deposits a yellow solid on acidification. This gives a deep-blue colour with starch iodide indicating a peroxide is present. It rapidly deteriorates to a reddish resin on exposure to the air. An alternative test using potassium dichromate, depending on the formation of perchromic acid in the presence of peroxide, did not show a positive reaction with this material.

Comparison of the starch-iodide and perchromic acid tests by using standard solutions containing known amounts of \( \text{H}_2\text{O}_2 \) indicated that the starch-iodide test was more sensitive than the perchromic acid. Notwithstanding this however, the inference is that the solid isolated was not itself a peroxide, as the quantity present should have given a decided positive reaction with potassium dichromate HCl and ether. The conclusion is rather that the material was associated with traces of peroxide.

McGregor (12) mentioned an acidic by-product obtained in small quantity during the conversion of the cyanobenzyl-compound to 4-benzylmesobenzanthrone, by hydrolysis with mixed acids. This material dissolved in \( \text{NaOH} \) to a yellow green-fluorescent solution. On acidification, the colour was discharged and a trace of solid, only, was precipitated. This would seem to be identical with the material that we have found associated with peroxide.

Measurement of the amount of oxygen absorbed during the oxidation of the cyanobenzyl-compound and
4-benzylmesobenzanthrone, by carrying out the oxidation in a gas pipette and measuring the volume of oxygen absorbed directly in a gas burette, gave results corresponding to 2 atoms of oxygen per molecule of benzylmesobenzanthrone in each case. This is consistent with the formation of a peroxide. In the case of 4-benzylmesobenzanthrone, this might have the structure (XXIV).

At this stage, it was thought possible that the results would fit a mechanism similar to those already advanced to explain the autoxidation of hydrocarbons. In these, a hydroperoxide intermediate is postulated, which calls for the presence of a substance both to initiate the chain reaction leading to the formation of the hydroperoxide and catalyse the decomposition of the latter when it is formed. The best known catalysts for this type of oxidation, are said to be the soluble derivatives of the transition metals; e.g. the naphthenates and stearates of Co, Mn, Cu, Ni and Fe.

An attempted aerial oxidation of 4-a-cyano/benzylmesobenzanthrone with cobalt naphthenate in
benzene was entirely unsuccessful, no oxidation being observed, so it would seem that a hydroperoxide capable of being decomposed by a metal catalyst is not involved.

Frank (16) mentions that the ability of alkalies to promote degradative autoxidation at high temperatures is well known. The data are not sufficient to permit more than speculation as to the role of alkalies in the reaction, but there is little doubt that they may exert a selective effect on the course of hydroperoxide decomposition. Against this explanation must be placed the fact that hydroperoxides decompose in the presence of warm alkali to give chiefly alcohols along with some acids.

A reaction involving the use of alkali is the coupling of substituted 4-nitrotoluenes by autoxidation (17). 2-methoxy-4-nitrotoluene in the presence of methanolic KOH and air yields a mixture of 2:2' -dimethoxy-4:4'-dinitrostilbene and the corresponding substituted dibenzyl:

![Chemical Structure](image)

The function of the alkali here, however, is probably to labilise the C-H bond of the methyl group and enhance the stability of the nitrobenzyl radical.

Stephens (18) succeeded in oxidising ethylbenzene
and n-propyl-benzene in small yields to acetophenone and propiophenone respectively by bubbling oxygen through the hydrocarbons heated to 100° for periods of from 24 to 30 days. Other similar aromatic hydrocarbons were also investigated, and it was found that oxidation only occurred at the carbon atom in the side-chain adjacent to the ring, and further, that at least one hydrogen atom must be attached to this carbon atom. Stephens also found that water inhibited the oxidation. Control experiments were not carried out, and in consequence the possibility of the wall of the vessel supplying a trace of an alkaline catalyst cannot be excluded, particularly in view of the length of the experiments. If this is actually the case, then Stephens' work can be considered parallel to the work on 4-benzylmeso/benzanthrone, 4-a-cyanobenzylmesobenzanthrone and its amide, as all these compounds have a free hydrogen atom attached to the carbon atom adjacent to the ring system.

Stephens (19) advanced a mechanism for the oxidation which avoided the postulation of an intermediate alcohol, and also accounted for the inhibitory action of water. However, difficulties arise if we attempt to apply this in the case of the mesobenzanthrone derivatives. For example, it has been shown that oxidation of the cyanobenzyl-compound, which has only one hydrogen attached to the a-carbon atom, is inhibited by water, (McGregor), but Stephens found that water did not inhibit the oxidation of compounds in which there was only one hydrogen atom attached to
the α-carbon atom. Oxidation was only inhibited when there were two or more of these. Further, Stephens' proposed mechanism is based in part on the slowness of the oxidation; while in the case of 4-benzylmeso/benzanthrone at least, the oxidation is extremely rapid. Thirdly, he does not allow for a peroxide intermediate.

A reference has recently appeared (20) to a base-catalysed decomposition of a dialkyl peroxide. In this work Kornblum and de la Mare found that KOH, piperidine, and sodium ethoxide catalyse the decomposition of 1-phenylethyl-tertiary butyl peroxide (XXV) to give a ketone and an alcohol.

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{C}_6\text{H}_5-\text{C}-\text{O}-\text{O}-\text{C}-\text{CH}_3 & \quad \rightarrow \quad \text{CH}_3 \\
\text{H} & \quad \text{CH}_3
\end{align*}
\]

\[\text{XXV}\]

The reaction takes place smoothly at room temperature. The peroxide corresponds of course, to that suggested for 4-benzylmesobenzanthrone, and decomposition of this similarly would yield 4-benzoyl/mesobenzanthrone and water.

As has already been mentioned, the substitution of piperidine for KOH in the oxidation of 4-benzyl/mesobenzanthrone caused only partial oxidation to occur. An interesting point about this experiment was the pronounced fluorescence that developed. This indicated that the peroxide intermediate was being formed, but...
the intensity suggested that the piperidine did not break it down so quickly to the 4-benzoylmeso/benzanthrone.

On the whole, the most satisfactory explanation of the oxidative hydrolysis of 4-a-cyanobenzylmeso/benzanthrone and the oxidation of 4-benzylmesobenzanthrone would seem to be peroxide formation in each case, followed by a base-catalysed decomposition to give 4-benzoylmesobenzanthrone. The base seems to function both as an initiator in the peroxide-formation stage, and as a catalyst for the peroxide decomposition.

Corrigendum: In a subsequent repetition of the experiment described on page 12, on a larger scale, the slow evolution of ammonia was detected, and in consequence the conclusion that oxygen is necessary for the removal of the nitrogen atom is erroneous.
The Condensation of Benzyl cyanide with mesoBenzanthrone

The condensation of benzyl cyanide with mesoBenzanthrone

Mesobenzanthrone (18g.) finely powdered KCl (36g.) and anhydrous pyridine (60g.) were mixed and stirred vigorously as benzyl cyanide (20g.) was slowly dropped in over half an hour. The temperature rose from 15° to 20° of its own accord and was maintained at 20-21°C by careful external cooling of the flask. Stirring was continued for a further 1½ hours after all the benzyl cyanide had been added, and the reaction mixture was then diluted with 120ml. alcohol, and the whole poured into a mixture of 60ml. conc. HCl and 200 ml. water with some ice. A brownish resinous solid deposited which was collected, washed with a little acetone, and dried. After two recrystallisations from benzene, 4g of 4-a-cyanobenzylmesobenzanthrone m.p. 202-4°C was obtained.

A further preparation on the 9g. scale using the above method, yielded also 4g. of product, m.p. 200-2°C.

In all, twenty-one attempted condensations of mesobenzanthrone with benzyl cyanide, were carried out. Of these, seven were reasonably successful, giving yields of 4-a-cyanobenzylmesobenzanthrone ranging from
25 to 40%. Five experiments yielded only traces of the cyanobenzyl-compound with good recoveries of unchanged mesobenzanthrone. Two experiments yielded a red product which was highly soluble in acetone, benzene, etc., and gave no colour with methanolic KOH. The remaining eight experiments were entirely unsuccessful, only unchanged mesobenzanthrone being obtained.

Although conditions were varied considerably, reproducible results were never obtained, a repetition of a successful condensation under seemingly identical conditions, and with identical materials, often yielding no cyanobenzyl-compound, or only a trace. A survey of the experiments carried out, however, shows that all the successful condensations were carried out at a temperature of 20°C, in the absence of a nitrogenous atmosphere, using anhydrous pyridine, and in a reaction time of 2-3 hours. The quality of the mesobenzanthrone did not seem to matter, as successful condensations were carried out with both pure and commercial mesobenzanthrone. In particular, low temperatures (<18°C) which are especially recommended in the patents, invariably caused no condensation to occur. The two experiments which yielded the red, low-melting, acetone-soluble product, were carried out at 21°C with a long reaction time; 3½ hours in one case, and 7 hours in the other.

The directions in the patent literature for carrying out the condensation are straightforward
without being detailed, and no hint is given that difficulty might be encountered. Previous workers in this Department, however, have found the reaction troublesome.

The results of the present work confirm that the condensation is highly capricious. Some factor, or combination of factors, which have not yet been recognised must be responsible, and it seems that until this position is clarified, reproducibility will not be obtained.

The Hydrolysis of 4-a-Cyanobenzylmesobenzanthrone

4-a-Cyanobenzylmesobenzanthrone (4.0g.) was refluxed with 2N methanolic KOH (320m.l.) for 7 hours, air being bubbled through the mixture throughout, and the flask was then left open to the air overnight. By next morning the deep blue colouration of the solution was discharged and the flask was filled with yellow crystals. These were collected, washed well with water and dried.

The crude product of two such hydrolyses were recrystallised together from benzene to yield 5.9g. of 4-benzoylmesobenzanthrone m.p. 175-6°c.
The Synthesis of 4-Benzoylmesobenzanthrone.

1-Bromo-4-methylnaphthalene

\[
\begin{align*}
\text{CH}_3 & \quad \text{Br}_2 \\
\text{CH}_3 & \quad \text{Br}
\end{align*}
\]

\(\alpha\)-Methylnaphthalene (47.4 g.) was dissolved in carbon disulphide (25 m.l.) and bromine (53.2 g.) dissolved in carbon disulphide (10 m.l.) was added over a period of \(\frac{1}{2}\) hour through a reflux condenser. The reaction flask was well wrapped with cloths to exclude light. A vigorous reaction occurred, the flask becoming warm and much HBr being evolved. When all the bromine had been added, the solution was allowed to stand for 2 hours and the carbon disulphide distilled off. The residue was distilled in vacuo and separated into three fractions as follows:

1st Fraction; boiling range 178-190°/80 m.m. Hg - 10 g.
2nd Fraction; " " 190-192°/40 m.m. Hg - 53 g.
3rd Fraction; " " 195-204°/40 m.m. Hg - 8.5 g.

Assuming the second fraction to be pure 1-bromo-4-methylnaphthalene, this represents a 72% yield based on
the α-methylnaphthalene used. The product was a pale yellow oil.

---------------

**4-Bromo-1-naphthoic acid**

![](image)

1-Bromo-4-methylnaphthalene (15g.) conc. HNO₃ (110g.) and water (1200m.l.) were refluxed for 95 hours. The supernatant liquid was poured off and the residual solid repeatedly extracted with warm Na₂CO₃ solution. Much of the material did not dissolve and remained as an oil after the extraction. The extracts were acidified with dil. HCl and the precipitated acid collected, dried, and recrystallised, first from glacial acetic acid, and finally from aqueous alcohol. m.p.: 211-12 °C. Yield 2.0g. (12%).

Meyer and Sieglitz (4) quote 212 °C as the melting point, but do not state a yield for the oxidation.

---------------

**1-Bromo-4-Benzoylnaphthalene**

![](image)
4-Bromo-1-naphthoic acid (1g.) was refluxed with thionyl chloride (2g.) for 1 hour and the excess thionyl chloride then distilled off at atmospheric pressure. The residual acid chloride was dissolved in benzene.

To the benzene solution was added anhydrous AlCl₃ (1g.) and the solution refluxed on the steam-bath for 3½ hours. While still warm, the contents of the flask were poured into a mixture of conc. HCl and ice. This was thoroughly extracted with benzene and the benzene solution chromatographed on alumina, the column being developed with a 1:1 mixture of benzene and 60-80 light petroleum. Elution of the various zones with alcohol showed that the bulk of the solid was in the dark ring at the top of the column. Recrystallisation from alcohol yielded material m.p. 73°C. On further recrystallisation from a mixture of benzene and light petroleum, the melting point was raised to 77°C. A mixed melting point with the product of a direct benzoylation of 1-bromonaphthalene (m.p. 87-89°C) was 81-3°C. The two products must be the same, therefore, and hence it was possible to prepare a large quantity of the 1-bromo-4-benzoylnaphthalene directly from 1-bromonaphthalene, to continue the synthesis.

-------------------

1-Bromo-4-benzoylnaphthalene

\[
\begin{align*}
\text{Br} & \quad \xrightarrow{\text{Ph.COCI}} \\
\text{AlCl₃} & \quad \xrightarrow{} \\
\text{Br} & \quad \text{CO.PH}
\end{align*}
\]
Benzoyl chloride (14g.) and AlCl₃ (14g.) were mixed, and carbon disulphide (80c.c.) was added. When the mixture was cold 1-bromonaphthalene (21g.) was added in small portions with shaking. The mixture was heated on the water bath for 2 hours with occasional shaking, and then poured into 250g. ice. The mixture was extracted with ether and the ether-CS₂ extract filtered to remove precipitated solid, and dried with CaCl₂. The solvent was removed by distillation, and the last traces taken off on the steam-bath. On cooling, the product partially solidified, and the solid was filtered off. 11g. of the crude 1-bromo-4-benzoylnaphthalene were obtained. m.p. 66-9°C. A pure sample has m.p. 87-8°C after recrystallisation from ethanol.

Vacuum distillation of the residual oil removed the benzoyl chloride and some solid sublimed into the neck of the flask. This melted at 117-3°C, but was not identified. Some of the oil was now caused to solidify by extraction with hot alcohol, decantation of the alcoholic solutions from the insoluble portion, removal of the solvent on the steam bath and seeding the residual oil. A further 3g. was obtained in this manner, giving a total yield of 14g. (45%).

**Analysis:** Found Br: 25.9. C₇H₈OBr requires Br: 25.7%

Two further preparations carried out in the same manner as described above but using less pure a-bromonaphthalene gave lower yields of crystalline material. In each case much oil was produced which could not be induced to crystallise.
1-Benzoyl-4-naphthonitrile

1-Bromo-4-benzoylnaphthalene (9g.) CuCN (5.5g) and freshly distilled pyridine (15 m.l.) were mixed in this order and refluxed in an oil bath at 210-220°C for 17 hours. The reaction mixture was poured into a mixture of conc. NH₄OH (25 m.l.) and water (25 m.l.), and the whole well stirred. Benzene (25 m.l.) was added, the mixture well shaken and ether (25 m.l.) added, when cold. The whole was then stirred again and filtered through a sintered glass funnel. The ether-benzene layer was separated and washed with 25 m.l. dil. NH₄OH solution four times; twice with 25 m.l. portions of 6N HCl; twice with 20 m.l. portions of water, and finally twice with 20 m.l. portions of saturated NaCl solution. The solvent was then removed on the steam-bath, and the residual oil quickly solidified on cooling to a brownish solid m.p. 67-9°C. Yield 5g. (66%).

Analysis: Found - N: 5.2  C₁₈H₁₄ON requires: N: 5.4%

A second preparation on the same scale as the above was carried out, but the temperature in this one was allowed to rise to 250°C for a short period. Yield: 5.5g. (72%). M.p. 69-74°C.
4-Cyanomesobenzanthrone

1-Benzoyl-4-naphthonitrile (2g.), anhydrous AlCl₃ (16.5g.) and NaCl (3.5g.) were well ground together and heated in an oil bath at 115-20°C for 24 hours, care being taken to exclude all moisture from the apparatus. The product was decomposed with water. The tarry deposit was dissolved in glacial acetic acid, from which crystals m.p. 65-70°C, separated. This was dissolved in benzene, chromatographed on alumina, and the column developed with benzene-light petroleum. A pale yellow band which separated quickly, gave an elution with alcohol, the bulk of the material present. m.p. 68-90°C. This was shown to be unchanged starting material by m.p. and mixed m.p. Elution of a narrow dark zone at the top of the column, however, yielded a small quantity of brownish-yellow material, m.p. 234°C. This was the 4-cyanomesobenzanthrone.

The preparation was repeated, using a stream of oxygen to remove the HCl split off during the reaction. Heating was continued for 23 hours at 110°C, and oxygen was bubbled slowly through the melt. The hot mixture was then poured into water, and the whole extracted.
with ether. Concentration of the ethereal extract caused the deposition of a crop of yellow crystals m.p. 226-30°C. This was the 4-cyanomesobenzanthrone. Evaporation of the ethereal liquors, however, yielded chiefly unchanged nitrile m.p. 74-8°C.

Yield of 4-cyanomesobenzanthrone 0.1 g. (5%) 

A third cyclisation on 6.6 g. of the nitrile at a temperature of 110-135°C for 24 hours, yielded 0.8 g. (12%) of 4-cyanomesobenzanthrone m.p. 234° after recrystallisation from glacial CH₃COOH.

Analysis: Found - N: 5.45. C₁₈H₁₄CN requires N: 5.5%

mesoBenzanthrone-4-carboxylic acid

![Chemical structure](attachment:chemical_structure.png)

4-Cyanomesobenzanthrone (0.2 g), water (2.0 m.l.), H₂SO₄ (2.0 m.l.) and CH₃COOH (2.0 m.l.) were refluxed for 5 hours and poured into water. The precipitated solid was filtered off and extracted with aqueous Na₂CO₃ solution. The portion which did not dissolve in Na₂CO₃ was subjected to a further 9 hours hydrolysis with a fresh quantity of hydrolysing mixture. No Na₂CO₃-insoluble material remained at the end of this time. The combined alkaline extracts were filtered and acidified and the precipitated acid was collected.
Yield of mesobenzanthrone - 4 - carboxylic acid:
0.22 g. (quantitative) m.p. 304°C.

Recrystallisation from nitrobenzene raised the melting point to 314-15°C.

Analysis: Found C: 78.5 H: 3.7. Calc. for C_{12}H_{10}O_3
C: 78.8, H: 3.7%

---------------

4-Benzoylmesobenzanthrone

\[
\begin{align*}
\text{mesoBenzanthrone-4-carboxylic acid} & (0.2 g.) \text{ and} \\
\text{redistilled thionyl chloride} & (5.0 \text{ m.l.}) \text{ were refluxed for 1 hour. The excess thionylchloride} \\
\text{was then} & \text{distilled off on the water bath and the residue} \\
\text{dissolved in benzene.} & \text{AlCl}_3 (0.5 g.) \text{ was added and} \\
\text{the whole refluxed for 4 hours. The contents of the} & \text{flask were then poured into a mixture of conc. HCl and} \\
\text{ice, and well stirred. The benzene layer was} & \text{separated off, the aqueous layer was extracted three} \\
\text{times with benzene, and the combined benzene extracts} & \text{were dried over Na}_2\text{SO}_4 \text{, concentrated to small volume} \\
\text{and chromatographed on an alumina column} (3" \times \frac{1}{2}""). \\
\text{A yellow zone passed rapidly down the column and on} & \text{washing through and removing the solvent, 0.21 g. of} \\
\text{yellow solid m.p. 136-40° was obtained. Recrystallisation}
\end{align*}
\]
first from benzene and then from alcohol, yielded yellow crystals of 4-benzoylmesobenzanthrone m.p. 176°C.

**Analysis:** Found C = 85.7 ; H = 4.3. \( C_{24}H_{14}O_2 \) requires C = 86.2 ; H = 4.5.

---

A mixed m.p. of the above product, with that obtained by the oxidative hydrolysis of 4-a-cyanobenzyl/mesobenzanthrone (m.p. 176°C) was 176°C. There is therefore no doubt that the compounds are identical.

---

**4-Methyl-1-naphthonitrile.**

\[
\begin{align*}
\text{CH}_3 & \quad \text{CuCN} \\
\text{Br} & \quad \text{CN} \\
\end{align*}
\]

1-Methyl-4-bromonaphthalene (10 g.) CuCN (6 g.) and freshly distilled pyridine (10 m.l.) were mixed in that order and heated in an oil bath at 215-25°C for 18 hours under reflux. The dark reaction mixture was poured into a mixture of conc. aqueous ammonia (25 m.l.) and water (25 m.l.). Benzene (25 m.l.) was added and the whole well agitated until all lumps had disintegrated. Ether (20 c.c.) was added when the mixture had cooled somewhat, and the whole was filtered through a sintered glass funnel. The ether-benzene layer was separated and washed with 4 x 20 m.l. portions of dil. \( \text{NH}_2\text{OH} \); 2 x 20 m.l. portions of 6 M HCl; 2 x 20 m.l. portions of water.
and finally with 2 x 20 m.l. portions of saturated NaCl solution. The ether and benzene were removed by distillation on the water-bath, and the residue fractionated in vacuo. 5g. of a faintly yellow oil were obtained distilling at 210-20° C/40 m.m. Hg. (oil-bath temperature was 290°C). The oil solidified to a white crystalline mass on cooling. Yield, 80% m.p. 44-9°C. Recrystallisation from 40 - 60 petroleum ether gave colourless needles m.p. 53-4°C.

**Analysis:** Found - N = 8.1. C_{12} H_{9} N requires N = 8.4%.

The preparation of 4-methyl-1-benzoylnaphthalene was not successful. Although a product was obtained by a Grignard reaction, viz. PhMgBr on 4-methyl-1-naphthonitrile, it contained 13% of bromine, and it seems likely that the bromobenzene used was not pure, but contained some dibromobenzene.

The Oxidation of 4-Benzoylmesobenzanthrone

4-Benzoylmesobenzanthrone (0.5g.) chromic acid (1.0g.) and glacial acetic acid (10.0 m.l.) were refluxed for 3/4 hour and poured into 50 m.l. water. The precipitate
was filtered off and extracted with Na₂CO₃ solution. The solution was filtered, acidified and the product collected and dried. 0.1g. m.p. 231-3°C.

The aqueous liquors were concentrated to half volume and the precipitated acid collected and dried. 0.1g. m.p. 234°C.

The aqueous liquors were finally extracted with hot benzene, the benzene layer separated and concentrated to 5 ml. On cooling, a further 0.2g. of 2-benzoyl-anthraquinone-1-carboxylic acid m.p. 234°C were obtained. (lit: 224°.)

The total yield represents 80% of the theoretical.

Analysis: Found - C = 72.9 ; H = 3.3. Calc. for C₂₁H₁₂O₂:

C = 74.2 ; H = 3.3

The Action of Hydrazine Hydrate on O-(p-Toluoyl)benzoic acid

O-(p-Toluoyl)benzoic acid m.p. 144°C, (1g) was mixed with hydrazine hydrate 50% w/w. (3 ml.) to give a clear solution. This was gently heated over a small flame for 30 minutes. The contents of the flask solidified quickly. The white solid was filtered off and dried. Yield 0.95g (95%) m.p. 254-5°C.
Crystallisation from glacial CH₃COOH yielded colourless rectangular plates m.p. 258-9°C. The product was unaffected by HCl and was insoluble in aqueous Na₂CO₃ solution.

**Analysis:** Found - N = 11.3 ; C₁₅H₁₀ON₂ requires : N = 11.9%

The Action of Hydrazine hydrate on Anthraquinone

Under the same conditions as those used for O-(p-toluoyl)benzoic acid, unchanged anthraquinone only was obtained (m.p. and mixed m.p.)

The Action of Hydrazine hydrate on Anthraquinone-1-carboxylic acid.

Anthraquinone-1-carboxylic acid, m.p. 284-8°C (0.2g) was treated under the same conditions as above, with hydrazine hydrate (3.0 m.l.) The product melted above 360°C.

Treatment of the product with HCl, regenerated anthraquinone-1-carboxylic acid (m.p. and mixed m.p.), so it must be the hydrazinium salt.

**Analysis confirmed this.** Found - N = 10.3 ; C₁₅H₁₀O₄N₂ requires : N = 9.9%

The Action of Hydrazine hydrate on 2-Benzoylanthraquinone-1-Carboxylic acid
2-Benzoylanthraquinone-1-carboxylic acid m.p. 234°C (0.2g) was mixed and heated as before, with hydrazine hydrate 50% w/w. (3.0 m.l.), for 30 minutes. A dark brown crystalline solid was obtained (0.2g.) m.p. 298°C. Recrystallisation first from glacial CH₃COOH and then from alcohol, gave yellowish crystals, m.p. 324-7°C. The alcoholic solution had a pronounced olive-green fluorescence.

Analysis: Found - C = 73.7, H = 3.6, N = 7.4. C₁₁H₁₂O₃N₂ requires:

C = 74.9, H = 3.4; N = 8.0%

The product was insoluble in aqueous Na₂CO₃ solution and was unaffected by HCl.

---------------

The Preparation of the Acetoxy-lactone of 2-Benzoylanthraquinone-1-carboxylic acid

2-Benzoylanthraquinone-1-carboxylic acid (0.1g.) pyridine (0.7 m.l.) and acetic anhydride (0.35 m.l.) was heated on the steam bath for 3 hours. A clear solution was immediately obtained, which changed quickly on heating, to an orange-brown colour. On pouring the clear reaction mixture into water, a white crystalline solid immediately precipitated.
This was collected and dried. m.p. 248-9°C.
Recrystallisation from glacial acetic acid yielded
pale yellow needles, m.p. 255-6°C.

Analysis: Found - C - 71.8; H - 3.8 C<sub>24</sub>H<sub>14</sub>O<sub>6</sub> requires:
C - 72.4; H - 3.5

The Attempted Decarboxylation of α-naphthoic acid

α-Naphthoic acid (0.3g.), quinoline (4.0 ml.) and
a pinch of copper bronze were heated in an oil bath, the
temperature being slowly raised to 225°C and maintained
there for 1 hour. No bubbles of CO<sub>2</sub> could be observed
at all. The product was poured into dilute HCl and
the solid which was precipitated, collected and dried.
It was found to be completely soluble in aqueous Na<sub>2</sub>CO<sub>3</sub>
solution, and was shown to be unchanged α-naphthoic acid.

2-Naphthoic acid and anthraquinone-2-carboxylic
acid were treated similarly to the above, but unchanged
material was obtained in each case.

The Decarboxylation of Anthraquinone-1-carboxylic acid

![Chemical structure](image)

Anthraquinone-1-carboxylic acid (0.3g.), quinoline
(4.0 ml.) and a pinch of copper bronze were heated in
an oil-bath. At a temperature of 160-5°C, a vigorous evolution of bubbles commenced. The oil-bath temperature was maintained at 175°C for 3/4 hour, and the product was poured into 50 m. l. dil. HCl. After three hours, the solid was filtered off and found to be insoluble in aqueous Na₂CO₃ solution. Crystallisation from glacial CH₃COOH gave a buff crystalline product with m.p. 285°C. This was identical with an authentic specimen of anthraquinone, (m.p. and mixed m.p.)

The Decarboxylation of 2-Benzoylanthraquinone-1-carboxylic acid

2-Benzoylanthraquinone-1-carboxylic acid (0.3g.), quinoline (4.0 m. l.) and a pinch of copper bronze were heated in an oil-bath as before. CO₂ was evolved at a temperature of 170°C and the oil-bath temperature was maintained at this level for 3/4 hour. The reaction mixture was poured, hot, into dil. HCl and the precipitated material collected after two hours. The product was found to be insoluble in aqueous Na₂CO₃ solution. Recrystallisation from glacial CH₃COOH with charcoal gave colourless needles, m.p. 216-17°C.

Analysis: Found ... ... ... ... C = 80.3; H = 3.6

C₂H₁₂O₃ requires ... C = 80.7; H = 3.8%
Moshchinskaya (8) quotes the m.p. for 2-benzoyl/anthraquinone derived from 9-benzoylmesobenzanthrone as 215-18°C.

The Decarboxylation of 1-Nitroanthraquinone-2-Carboxylic Acid

The decarboxylation was carried out as described for 2-benzoylanthraquinone-1-carboxylic acid. After recrystallisation from glacial CH₃COOH with charcoal, orange-red needles of 1-nitroanthraquinone were obtained m.p. 228°C (Houben: 228°C).

The Action of H₂SO₄ on 4-a cyanobenzylmesobenzanthrone

4-a-Cyanobenzylmesobenzanthrone (0.5g) was dissolved in conc. H₂SO₄ (10 m.l.) and allowed to stand at room temperature for 4 days, before being poured into water. The yellow precipitate was collected, washed well with water till it was free
from sulphate, and then air-dried at room temperature.
Yellow crystals were obtained m.p. 255-65°C. Two
recrystallisations from glacial CH₃COOH yielded pale
yellow elongated prisms, m.p. 278-80°C.

Analysis: Found  
\[ C = 81.5; \quad H = 4.7; \quad N = 4.5 \]

C₂₅H₁₇O₂N requires:  
\[ C = 82.6; \quad H = 4.7; \quad N = 3.9\% \]

A Lassaigne test on this product showed S to be
absent but N to be present. It was insoluble in hot or
cold alkali. Subsequent hydrolysis of the compound
proved it to be an amide, for NH₃ was readily detected.

The Hydrolysis of 4-a-Carboxybenzylmesobenzanthrone

4-a-Carboxybenzylmesobenzanthrone (0.1g.) was
refluxed for 4½ hours with 10% ethanolic KOH (10 m.l.)
A deep green fluorescent solution was first formed,
and much ammonia was evolved. When the fluorescence had
disappeared and the evolution of ammonia had practically
ceased, the now red solution was poured into water (50 m.l.)
The whole was thoroughly extracted with ether, and the
ethereal extract concentrated to small volume, whereupon
pale yellow blunted needles crystallised, m.p. 176-8°C.

A mixed melting point determination, carried out
with 4-benzylmesobenzanthrone (m.p. 177-8°C) was 177-8°C.

The colour given by the product with conc. H₂SO₄.
(orange, with orange fluorescence under the UV lamp) was identical with that given by 4-benzylmesobenzanthrone.

Acid hydrolysis with ethanolic HCl also yielded 4-benzylmesobenzanthrone.

The Oxidative Hydrolysis of 4-a-Carbamidobenzylmesobenzanthrone

![Chemical Structure]

4-a-Carbamidobenzylmesobenzanthrone (0.05 g) and 3N methanolic KOH were refluxed for 10 hours, with a current of air passing through the solution, which was then cooled. Yellow crystals deposited and these were filtered off, dried and recrystallised from benzene. m.p.: 172-3°C.

Mixed m.p. with pure 4-benzoylmesobenzanthrone (m.p. 176°): 175-6° C.

Mixed m.p. with pure 4-benzylmesobenzanthrone (m.p. 178°): 140-5°C.

There is therefore no doubt that the product this time is 4-benzoylmesobenzanthrone, and this was confirmed by the H₂SO₄ colour test.

The Oxidation of 4-Benzylmesobenzanthrone

![Chemical Structure]
4-Benzylmesobenzanthrone (0.025 g.) was refluxed for 15 minutes with 2 N methanolic KOH (10 m.l.) with a current of air passing through the solution. The solution was cooled, and the yellow crystalline material which separated out, was collected, dried, and recrystallised from benzene. m.p. 174-5°C.

Mixed m.p. with 4-benzoylmesobenzanthrone, (m.p.176°): 175-6°C.

Mixed m.p. with 4-benzylmesobenzanthrone, (m.p. 178°): 143-5°C.

A further experiment in which the time of aeration and heating was shortened to three minutes, also yielded 4-benzoylmesobenzanthrone quantitatively.

----------

The Oxidation of 4-(p-Methoxybenzyl)-mesobenzanthrone

Oxidation was quantitative under conditions which were identical with those used in the previous experiment.

----------

The Hydrolysis of 4-a-Carbamidobenzylmesobenzanthrone with HNO₃.
4-α-Carbamidobenzylmesobenzanthrone (0.08g.), conc. HCl (3 m.l.), ethanol (10 m.l.) and NaNO₂ (0.5g.) were refluxed for 8 hours, additional NaNO₂ being added from time to time. After dilution with water and ether-extraction, 4-benzylmesobenzanthrone was obtained, with some unhydrolysed amide.

The Attempted Oxidation of 2-Benzylpyridine

2-Benzylpyridine (0.2g.), 2 N methanolic KOH (10 m.l.) and methanol (5 m.l.) were refluxed for 12 hours, air being passed through the mixture continually. The methanol was then evaporated off, the inorganic material removed by extraction with water, and the residual oil added to a solution of p-nitrophenylhydrazine (0.05g.) in ethanol (2 m.l.) and glacial CH₃COOH (1 drop). This solution was refluxed gently for 20 minutes and allowed to cool. No p-nitrophenylhydrazine separated even on dilution with water. Unchanged 2-benzylpyridine was recovered from the solution by further dilution, and was identified as its picrate.

No oxidation had occurred under these conditions.

Similar experiments were carried out on diphenylmethane, fluorene, dibenzyl, and 4:4'-tetramethylidiaminodiphenylmethane, and in none was any oxidation observed.

The Attempted Oxidation of 4-Benzylmesobenzanthrone in neutral solution

4-Benzylmesobenzanthrone (0.03g.) and methanol
(10 m.l.) was refluxed for 30 minutes, air being bubbled through the solution throughout. The solution was then concentrated to small volume and the yellow crystalline deposit collected and dried. m.p. 177-8°C.

Mixed m.p. with 4-benzoylmesobenzanthrone (m.p. 176°) was 145-50°C.

Mixed m.p. with 4-benzylmesobenzanthrone (m.p. 178°) was 177-8°C.

No oxidation has occurred, then, in the absence of KOH.

The Attempted Oxidation of 4-Benzylmesobenzanthrone in the presence of water

I. 4-Benzylmesobenzanthrone (0.05g.) was refluxed with 2 N aqueous KOH for 2 hours, the suspension being aerated throughout. No oxidation occurred, but for this the water-insolubility of 4-benzylmesobenzanthrone might have been responsible.

II. 4-Benzylmesobenzanthrone (0.02g.) was dissolved in methanol (10 m.l.). 2 N methanolic KOH (5 m.l.) was added and then water (3 m.l.) until the 4-benzylmesobenzanthrone began to separate. Refluxing and aeration was then carried out for 35 minutes. The solution was concentrated down and the yellow deposit well washed with water and dried. m.p. 155-60°C.

Mixed m.p. with 4-benzylmesobenzanthrone (m.p. 178°) was 160° (softening about 150°C.)

Mixed m.p. with 4-benzoylmesobenzanthrone (m.p. 176°) was 140-5°.
The indication (confirmed by H₂SO₄ test) is that the product is a mixture of 4-benzylmesobenzanthrone and 4-benzoylmesobenzanthrone, the former predominating. Water, then, has had an inhibiting effect upon the oxidation.

The Attempted Oxidative Hydrolysis of 4-a-Cyano-p-methylbenzylmesobenzanthrone in neutral solution

4-a-Cyano-p-methylbenzylmesobenzanthrone (0.05g.) was refluxed with methanol (10 m.l.), air being bubbled through the solution continually. A little of the solution was withdrawn from time to time and tested with 2 N methanolic KOH. The benzylcyano-test was still strongly positive however, at the end of two hours.

The Oxidative Hydrolysis of 4-a-Cyano-p-methylbenzylmesobenzanthrone in the cold

4-a-Cyano-p-methylbenzylmesobenzanthrone (0.05g), methanol (10 m.l.) and 2 N methanolic KOH (2 drops) were stoppered in an air-filled tube. After 6 hours, the blue colour had practically disappeared, and after standing overnight, oxidation was complete.

The Effect of Aeration on the Oxidative Hydrolysis of 4-a-Cyano-p-methylbenzylmesobenzanthrone

4-a-Cyano-p-methylbenzylmesobenzanthrone (0.1g) was refluxed with 2 N methanolic KOH for 28 hours, without aeration of the solution. The deep-blue benzylcyano-colour persisted throughout and no evolution of NH₃ could be detected.
Aeration was commenced, and within a further 35 minutes the blue colour had disappeared. Evaporation of the solution followed by extraction of the residue with benzene and chromatographing on a short column of alumina yielded pure 4-\textit{p}-methylbenzylmesobenzanthrone. (m.p. and mixed m.p.)

---------

The Effect of Air on the Oxidation of 4-Benzylmeso-benzanthrone

4-Benzylmesobenzanthrone (0.02g.), methanol (10 m.l.) and 2 M methanolic KOH (2 drops) were shaken and stoppered in an air-filled tube. A duplicate mixture was placed in a stoppered nitrogen-filled tube. After 6 hours, the air-filled tube exhibited a strong greenish fluorescence, while the nitrogen-filled tube showed none.

After 18 hours, oxidation was complete in the air-filled tube, but the nitrogen-filled tube showed only a faint fluorescence and contained chiefly unchanged 4-benzylmesobenzanthrone.

---------

To Find if Complete absence of Air inhibits the Oxidation

Methanol (15 m.l.) and 2 M methanolic KOH (2 drops) were mixed and refluxed for 30 minutes, concentrated to about 10 m.l. and then allowed to cool in an atmosphere of nitrogen. When cold, 4-\textit{a}-cyano-\textit{p}-/methylbenzylmesobenzanthrone (0.02g.) was added and nitrogen was bubbled through the blue solution.

No change occurred after 56 hours, so it can
be concluded that complete exclusion of air does inhibit the oxidative hydrolysis.

----------

To Show that Ammonia is evolved during the Oxidative Hydrolysis of 4-a-Cyanobenzylmesobenzanthrone

4-a-Cyanobenzylmesobenzanthrone (0.5 g.) was refluxed with aeration, with \( \frac{2}{\text{N}} \) methanolic KOH (60 m.l.). After passing through the solution the air passed up a vertical condenser at the top of which was suspended a piece of moist red litmus paper. This quickly became blue, indicating that ammonia was being evolved.

----------

The Attempted Oxidation of 4-a-Cyano-p-methylbenzylmesobenzanthrone in Dioxan

4-a-Cyano-p-methylbenzylmesobenzanthrone (0.02 g.) was refluxed in dioxan solution with a little powdered KOH for 20 minutes. Aeration was carried out meanwhile, and subsequently for a further 5 hours in the cold. No oxidation occurred.

----------

The Detection of a Peroxide Intermediate in the Oxidation of 4-a-Cyano-p-methylbenzylmesobenzanthrone

4-a-Cyano-p-methylbenzylmesobenzanthrone (0.05 g.), methanol (10 m.l.) and \( \frac{2}{\text{N}} \) methanolic KOH (2 drops) were refluxed and aerated for 15 minutes. After standing overnight, the yellow, green-fluorescent solution was evaporated to dryness and extracted with a little water. The aqueous solution exhibited a striking green fluorescence. A little of this solution was added to an aqueous solution of KI and starch and acidified with dil. \( \text{H}_2\text{SO}_4 \). A deep-blue colour appeared immediately,
indicating the presence of a peroxide. This was confirmed by comparison with standards containing known amounts of hydrogen peroxide.

The rest of the aqueous extract was now acidified and extracted with ether which dissolved the scanty flocculent precipitate. Evaporation of the ether on a watch glass left a very small quantity of a yellow solid, m.p. 220°C. (micro m.p.): with H₂SO₄ this gave a yellow solution with a green fluorescence. On exposure to the air, the yellow solid slowly deteriorated into a reddish resin.

The Attempted Oxidation of 4-a-Cyanobenzylmeso/benzanthrone with Cobalt Naphthenate in benzene

4-a-Cyanobenzylmesobenzanthrone (0.1g.) and cobalt naphthenate (0.03g.) were dissolved in benzene (20 m.l.), and air was bubbled through the gently refluxed solution for 28 hours. A little of the solution was removed from time to time, evaporated down and tested with 2 M methanolic KOH. After 28 hours, however, the test still gave a definite positive reaction indicating the presence of the cyanobenzyl-group.

To See if Peroxide is formed in the absence of KOH

4-Benzylmesobenzanthrone (0.05g.) was treated with methanol (10 m.l.) and refluxed for 60 hours with aeration. A little of the solution was removed from time to time, and tested for peroxide with starch-iodide. The test remained negative throughout, and a quantitative
recovery of unchanged 4-benzylmesobenzanthrone was obtained.

------------------

**The Oxidation of 4-Benzylmesobenzanthrone with Piperidine instead of KOH**

4-Benzylmesobenzanthrone (0.03 g.) was dissolved in a mixture of methanol (10 m.l.) and piperidine (4 m.l.), and the solution was gently refluxed for 10 hours, air being passed through continually. A pronounced green fluorescence appeared after about 30 minutes, suggesting that oxidation was occurring. The solution was finally evaporated down to dryness, and the residue well washed with water. m.p. 140-155°C.

Mixed m.p. with 4-benzylmesobenzanthrone (m.p. 178°C) was 147-50°C.

Mixed m.p. with 4-benzoylmesobenzanthrone (m.p. 176°C) was 138-40°C.

The indication is that while some oxidation has undoubtedly occurred, the product contains more unchanged 4-benzylmesobenzanthrone, than 4-benzoylmeso/benzanthrone.

------------------

**The Measurement of the Oxygen absorbed during the Oxidation of 4-a-Cyanobenzylmesobenzanthrone, and 4-Benzylmesobenzanthrone**

A 50 m.l. gas burette was filled with methanol, previously saturated with oxygen, and connected at the top by means of a short piece of rubber tubing fitted with a screw clip, to an ordinary double bulb gas pipette. The burette was fitted with a methanol reservoir which could be conveniently raised and lowered as necessary.
To carry out the oxidation, a weighed quantity of the 4-aminobenzylmesobenzanthrone, or the 4-benzylmesobenzanthrone was sealed in a small specimen tube closed with a ground glass cover which was held in place by a rubber band. This was introduced into the lower bulb of the gas-pipette and the latter then filled completely with 2 M methanolic KOH previously saturated with oxygen. A measured quantity of oxygen was then admitted from the gas burette by manipulating the reservoir, and this was sealed in the pipette by tightly closing the screw clip. A capillary U-tube between the clip and the "reaction bulb" of the pipette was allowed to fill with methanol before finally tightening the clip, and this acted as a seal. The pipette was now disconnected from the burette, and the cover removed from the specimen tube in the reaction bulb, by a sharp jerk on a piece of string, previously attached to the rubber band. The mesobenzanthrone to be investigated was then brought into contact with the methanolic KOH and the oxygen. The pipette was shaken vigorously from time to time to ensure complete removal from the tube, and thorough mixing with the reagents.

The volume of the oxygen in the reaction bulb was measured at intervals by returning it to the gas burette. A blank experiment was carried out after those on the 4-aminobenzylmesobenzanthrone and 4-benzylmeso/benzanthrone. For this, the tube of material was omitted, but the pipette was filled with 2 M methanolic KOH as before, and the measured quantity of oxygen was admitted. The result showed that a steady loss was
occurring, and as the pipette was sealed at both ends with methanol traps, it must involve a continual loss at the outer surface of the methanol, followed by absorption of oxygen at the surface in the reaction bulb to resaturate the solution.

**Blank:** Oxygen absorbed after 1 week: 9.9 m.l.

Oxygen absorbed after 2 weeks: 13.6 m.l.

4-a-Cyanobenzylmesobenzanthrone: - Volume of oxygen absorbed at N.T.P. after 1 week was 35.2 m.l.

The 'blank' must be subtracted from this figure to give a value of approximately 25 m.l. oxygen; i.e. 2 atoms of oxygen have been absorbed, as the amount of 4-a-cyanobenzylmesobenzanthrone used was 0.345 g. (1/1000 mole).

4-Benzylmesobenzanthrone. The volume of oxygen absorbed at N.T.P. after 2 weeks was 41 m.l.

Applying the correction for the blank we obtain a figure of approximately 22 m.l. oxygen; i.e. 2 atoms of oxygen have been absorbed again by the oxidation, as the weight of 4-benzylmesobenzanthrone used was 0.320 g. (1/1000 mole).
BIBLIOGRAPHY.

(2) Cahn, Jones and Simonsen. J.C.S. (1933). 447
(3) B.P. ...........319,593; GP. 568,783 and 501,082.
(19) " J.A.C.S. (1928) 50 2523.
(20) Kornblum and De La Mare. J.A.C.S. (1951). 73 880.
PART II.

SOME REACTIONS OF THE CARBONYL GROUP OF

mesoBENZANTHRONE.
INTRODUCTION

A study of the literature of mesobenzanthrone from the time of its discovery in 1905 up to the present day, reveals the interesting fact that comparatively little work has been carried out on reactions directly affecting the carbonyl group. This may well be due to the circumstance that most of the published work appears in patents, and has been carried out by industrial firms chiefly concerned with those derivatives of meso/benzenanthrone which might have applications in the dyestuffs field. In consequence, most of the work has been done on reactions such as the halogenation of mesobenzanthrone, the synthesis of mesobenzanthrone and substituted mesobenzanthrones, and the fusion of meso/benzenanthrone with alkali to yield violanthrones and isoviolanthrones. It will be convenient to summarise briefly here the published work on reactions of the carbonyl group.

The reaction of Grignard reagents with meso/benzenanthrone has been studied by Charrier and Ghigi, (1, 2.) and by Allen and Overbaugh (3). In 1932, the former obtained a mixture of 6-methylmesobenzanthrone and 7-methylenemesobenzanthrone by treating meso/benzenanthrone with MeMgl and heating the 7-methylene-3:4-dihydrumesobenzanthrene thus formed with activated charcoal. With EtMgl, only 6-ethylmesobenzanthrone was obtained. Allen and Overbaugh obtained 6-phenylmesobenzanthrone and 6-benzylmesobenzanthrone by treating mesobenzanthrone with PhMgBr and PhCH2MgCl.
respectively. The structures of the products were settled by chromic acid oxidation to the corresponding substituted anthraquinone-1-carboxylic acid. Exceptions have been noted; for example, tertiary butyl magnesium bromide on 3-phenylmesobenzanthrone yielded a carbinol. (4). The reaction is however, a useful method for obtaining 6-substituted meso/benzanthrones, and it must be explained by 1,4-addition to a conjugated system.

The reduction of mesobenzanthrone was investigated in 1911 by Bally and Scholl (5), who obtained meso/benzanthrene (I) by distillation of mesobenzanthrone over glowing pumice and zinc dust in a current of hydrogen. They also reduced mesobenzanthrone with zinc dust and aqueous NaOH, NH₃ or alkaline hyposaluthe to dihydromesobenzanthrone (II). HI and red phosphorus on mesobenzanthrone yielded dihydromesobenzanthrene. (III).

Clar and Furmari (6) reinvestigated the above compounds in 1932, and showed that some of the properties attributed by Scholl and Bally were erroneous. By reducing mesobenzanthrone with zinc dust and NaOH, zinc and HCl, or alkaline Na₂S₂O₄, they obtained a substance which was apparently identical with the
1,9-trimethylene-10-anthranol (IV) obtained by von Braun and Bayer (7) in 1925 through the catalytic hydrogenation of mesobenzanthrone:

\[
\text{IV}
\]

Clar and Furnari suggested that the remarkable ease with which mesobenzanthrone can be reduced, could be explained only by assuming that it is in equilibrium with a diradical form in which it first takes up two hydrogen atoms, and the product is at once further hydrogenated to IV at the reactive 5,6-double bond.

The most recent work on the reduction of mesobenzanthrone has been carried out by Zinka and co-workers (8, 9). They obtained mesobenzanthrene by distillation of mesobenzanthrone with Zn dust and as by-products, several dibenzanthrones, one of which appears to be violanthrone.

Only one reference could be found in the literature to the formation of oxonium salts of mesobenzanthrone. In 1920, A.G. Perkin prepared the ferrichlorides, stannichlorides and platinichlorides of mesobenzanthrone and some substituted mesobenzanthrones (10). Perkin presumed that these were oxonium salts and pointed out that if this were so, their formation could only originate from the oxygen of the carbonyl group. He stated further that acetophenone and benzophenone did
not yield these salts, and hence, when the carbonyl group forms part of a 6-membered ring, there was evidence that its basicity was increased.

Finally, mention must be made of a recent paper by Clemo, Munday and Swan (11) in which it is claimed that mesobenzanthrone reacts with ethyl succinate under the conditions of the Stobbe condensation, to give an aldol type product (V). The possibility of the reaction occurring at the 4-position is discussed and discarded, but the possibility that the product is (VI) is evident from the work described in the first part of this thesis. (12).
**DISCUSSION**

**Oximes**

The starting point in this work was an attempt to prepare an oxime of 4-benzoylmesobenzanthrone. A preliminary survey of the literature having indicated that no oxime of mesobenzanthrone was known, it was anticipated that 4-benzoylmesobenzanthrone would yield a monoxime only. However the product obtained gave very variable analyses for nitrogen even after several recrystallisations, and accordingly control experiments were carried out on mesobenzanthrone itself, in order to find out if oximation could occur at the meso/benzanthrone carbonyl group. It was found that while little if any oximation occurred on heating meso/benzanthrone with hydroxylamine in pyridine solution for periods of up to 8 hours, a yield of 30-50% of mesobenzanthrone oxime was obtained by continuing the heating for a total of 20 hours. If the time of heating was increased to 50-70 hours, the yield could be increased to well over 80%. Some unchanged meso/benzanthrone was always obtained. The oxime of 3-chloromesobenzanthrone was prepared similarly.

Attention was then turned again to 4-benzoylmeso/benzanthrone, and it was found that the product obtained by heating this with hydroxylamine and pyridine for 8 hours was principally the monoxime. Some dioxime was however present and the two could be separated chromatographically. Methylation of the product gave a mixture of two compounds, and these
also could be separated by chromatography. If the time of heating was increased to 50 hours, the product consisted entirely of the dioxime.

It was possible to differentiate unequivocally the monoxime and dioxime by mixed melting points, analyses, and the colours given with conc. $\text{H}_2\text{SO}_4$. A table of these colours is quoted in the experimental part of the thesis, and it will be noticed that while mesobenzanthrone, 3-chloromesobenzanthrone, 4-benzoyl/mesobenzanthrone and its monoxime all give red colours with $\text{H}_2\text{SO}_4$, mesobenzanthrone oxime, 3-chloromesobenzanthrone oxime and 4-benzoylmesobenzanthrone dioxime all give yellow colours. As the red colour is assumed to be due to oxonium salt formation at the carbonyl group, it follows that 4-benzoylmesobenzanthrone monoxime has no oxime group on the mesobenzanthrone carbonyl. The structure of 4-mesobenzanthrone monoxime also follows from the fact that it is formed after only 8 hours heating, while the dioxime and mesobenzanthrone oxime require about 50 hours.
Having established the fact that mesobenzanthrone did react with hydroxylamine, it was felt that reaction with another typical ketone reagent should be attempted. It was found that reaction did occur with 2:4-dinitrophenylhydrazine when drastic conditions were employed, but even then, the yields were small.

It is definitely established then, that mesobenzanthrone will react with at least some of the ordinary ketone reagents, but that the conditions require to be considerably more drastic than those which suffice for most ketones.

The Beckmann rearrangement of mesobenzanthrone oxime

The oximes of some cyclic ketones on rearrangement undergo ring enlargement and yield lactams. Examples
are cyclohexanone oxime (13), fluorenone oxime (14) and anthraquinone monoxime (15).

\[
\begin{align*}
\text{CH}_2\text{-CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{C}=\text{N} \cdot \text{OH} \quad \longrightarrow \quad \text{CH}_2\text{-CH}_2\text{-CO} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} \cdot \text{OH} \quad \longrightarrow \quad \text{O} \cdot \text{H} \\
\end{align*}
\]

meso-Benzanthrone is obviously interesting from this stand-point because it is an example of that class of cyclic ketones in which the molecule is unsymmetrical about the carbonyl group. Theory predicts the possible existence of two stereoisomers according to whether the naphthalene nucleus is on the same or opposite side of the carbon-nitrogen double bond as the oxime hydroxyl group:
The Beckmann rearrangement, of the oxime of mesobenzanthrone should indicate whether it consists of a mixture of the two forms or not. In the first case we shall obtain a mixture of two lactams, while in the second, only one will be isolable.

Moore and Huntress, (14) have investigated the rearrangement of 2-nitrofluorenone oxime (VII) as well as that of fluorenone oxime itself, and they found that only one of the two possible isomers was formed. This was 7-nitrophenanthridone (X). They found also that a chlorine-containing compound was formed, and that this analysed fairly well for the 2-nitrofluorenone-9-iminochloride (VIII) or its rearrangement product 7-nitro-9-mesochloro-phenanthridine (IX). From this they concluded that their original 2-nitro-fluorenone oxime consisted mainly, if not entirely, of one of the possible stereoisomers, and proposed the following scheme for the Beckmann rearrangement:

This work represents the only case that is comparable to that of mesobenzanthrone, which has so
far been published. Chardomens and Wurmli (16) have carried out a Beckmann rearrangement of 1:3-dimethylfluorenone oxime, but they did not identify the product.

Several methods for the rearrangement of mesobenzenanthrone oxime were tried in preliminary experiments, including PCl₅ in ether, benzene, and acetyl chloride, but all proved unsatisfactory. The procedure eventually adopted was substantially that of Moore and Huntress (14) with PCl₅ in POCl₃.

Chromatographic purification of the product so obtained, showed that it consisted of only one lactam, and a chlorine-containing compound. Analysis indicated that these were respectively one of the possible mesobenzenanthrone lactams (XI) and (XII), and an oxime chloride (XIII) or its rearrangement product (XIV or XV).
The results were, in fact, parallel to those obtained by Moore and Huntress for 2-nitrofluorenone oxime.

Attempts were next made to elucidate the structure of the mesobenzanthrone lactam by hydrolysis, but these were not successful, and this is not surprising as phenanthridone is completely resistant to hydrolysis. (17).

Following this, the synthesis of the two possible isomers was attempted. Meyer and Hofmann (18) cyclised benzanilide to phenanthridone by heating the vapour of the molten anilide with a glowing platinum spiral. It was found possible to repeat this as a model reaction, but the best yield obtained was only 3%. All attempts, however, to cyclise N-benzoyl-1-naphthylamine (XVI) and a-naphthylamide (XVII) were unsuccessful.

\[
\begin{align*}
\text{XVI} & : \quad \text{CO—NH} \\
\text{XVII} & : \quad \text{NH—CO}
\end{align*}
\]

The former yielded a small quantity of a high melting compound which was easily purified by its sparing solubility in most solvents, but no deductions as to its structure could be made from the analytical figures, except that it was not a mesobenzanthrone lactam.

Only naphthalene and unchanged starting material
could be isolated from the attempted pyrocyclisation of a-naphthanilide.

The possibility of synthesising the lactams by an intramolecular Ullmann condensation was now considered. Not much work has been done on this type of Ullmann reaction. In a recent review (19) only three successful applications of the reaction are mentioned. (20, 21, 22).

8-Bromo-1-naphthoic acid 2'-bromanilide (XVIII) was first synthesised and subjected to an intramolecular Ullmann condensation. The chief product was N-phenylnaphthastyril (XIX) which must have been formed by the splitting out of HBr from the anilide, with subsequent dehalogenation. Two other products were also isolated, one of them pure and in reasonable quantity. Although the analysis of this compound suggested one of the isomeric mesobenzanthrone lactams, its low melting point, extremely high solubility in most organic solvents, and the blue fluorescence of its
solutions do not support this conclusion, and rather suggest that it is a diphenylamine derivative. The third product of the Ullmann reaction was obtained in only minute yield, but the circumstances of its isolation suggest that this was one of the isomeric mesobenzanthrone lactams.

![Chemical structures](attachment:image.png)

Success was, however, obtained with the intramolecular Ullmann condensation of N-(o-bromobenzoyl)-8-bromo-1-naphthylamine (XX). A small yield of material was obtained which was shown to be identical with the product of the Beckmann rearrangement of meso/ benzanthrone oxime.

Finally, the lactam was oxidised with alkaline KMnO₄ by a similar method to that used by Moore and Huntress for the oxidation of 2-nitrophenanthridone (23) and an almost quantitative yield of phthalic acid was obtained. No naphthalic acid could be detected in the product, even when the oxidation was repeated on some unpurified Beckmann rearrangement product.

It can be definitely stated, then, that Beckmann rearrangement of mesobenzanthrone Oxime yields a lactam corresponding to the structure XI, and that the chloro-compound found with it has one of the structures XIII or XV.
The Beckmann Rearrangement of 4-Benzoylmesobenzanthrone Oximes

This work is only fragmentary, and was carried out on material obtained by oximation of 4-benzoyl/mesobenzanthrone for 8 hours. The starting material, therefore, was a mixture consisting chiefly of the monoxime, but undoubtedly also containing some dioxime. It was found that $\text{H}_2\text{SO}_4$ caused no rearrangement, but with $\text{PCl}_3$ in ether a product was obtained which was later shown to have the constitution XXI, by the fact that on admixture with the product obtained by the action of hydrazoic acid on 4-benzoylmesobenzanthrone, the melting point suffered no depression. These two compounds were identical, and as the constitution of the product of the Schmidt reaction was conclusively established by hydrolysis, the constitution of the Beckmann product of the 4-benzoylmesobenzanthrone oxime was also fixed:

![Chemical Structure](attachment:image.png)

In the work of Moore and Huntress on the rearrangement of 2-nitrofluorenone oxime, an attempt was made to verify Meisenheimer's theory that a trans-interchange was involved. The result was inconclusive as only one oxime could be obtained.

The same difficulty is true regarding the work on
mesobenzanthrone oxime, but as there appears to be an overwhelming amount of evidence now that a trans-interchange is involved in the Beckmann rearrangement of oximes, all the formulae are drawn with configurations appropriate to a trans-change. For example, XXI above must have arisen, from an oxime with a configuration XXII.

\[
\text{XXII}
\]

The Schmidt Reaction

The reaction between hydrazoic acid and carbonyl compounds in the presence of acids is known generally as the Schmidt reaction. This has found probably its widest application in the preparation of amines from acids, and two examples of this use of the method have already been described in the experimental part of the section on the Beckmann rearrangement, namely, the preparations of \(\alpha\)-naphthylamine and \(\beta\)-bromo-\(\alpha\)-naphthylamine from \(\alpha\)-naphthoic acid and \(\beta\)-bromo-\(\alpha\)-naphthoic acids respectively. The procedure can also be used however to prepare amides from ketones and particularly, lactams from cyclic ketones. As an example of this latter reaction we may instance cyclohexanone (24) and fluorenone (25).
The reaction with fluorenone is also described in the experimental part of the section of the thesis dealing with the Beckmann rearrangement. Quantitative yields of phenanthridone are obtained, and it might be anticipated therefore that the reaction would be applicable to mesobenzanthrone. Two lactams would be possible just as in the Beckmann rearrangement of the oxime, already considered. It was found, however, that this reaction could not be applied to mesobenzanthrone. Although numerous variations of the standard procedure were carried out only unchanged mesobenzanthrone was obtained. The attempts included the use of NaN₃ in trichloroacetic acid (25, 26), in H₂SO₄ (25, 27), in a mixture of trichloroacetic and sulphuric acids (26), and by dropwise addition of H₂SO₄ to a stirred solution of mesobenzanthrone and HN₃ in chloroform (28, 29). Reaction temperatures were also varied but without success, and it was concluded that the mesobenzanthrone
carbonyl was immune to attack by hydrazoic acid.

An investigation was now commenced into the reaction of hydrazoic acid with 4-benzoylmesobenzanthrone. From the preceding work it was evident that any reaction that occurred would do so only at the carbonyl group attached to the 4-position, and in consequence only two isomers (XXIII and XXIV) were theoretically possible, instead of the four that might have resulted if the mesobenzanthrone carbonyl had reacted as well.

![Equivalents XXIII and XXIV](image)

Examples of the application of the Schmidt reaction to unsymmetrical diaryl ketones are not numerous. A recent review (30) includes none. Sanford and co-workers (31) have since showed that phenyl-p-tolyl ketone, the simplest unsymmetrical diaryl ketone, yielded 82% of phenyl-p-toluidide. This was estimated by determination of the benzoic acid formed on hydrolysis:

![Equivalence of reaction](image)

Sanford showed that, where different groups were attached to the carbonyl, a certain order was noticeable in their respective tendencies to migrate, both under the influence of hydroxylamine o-sulphonic acid and
hydrazoic acid. The order can be roughly indicated thus:-

\[ p\text{-tolyl} \gg \text{phenyl} \gg \text{alkyl radicals.} \]

Dice and Smith (26) investigated the action of hydrazoic acid on 1-benzoylphenanthrene and found that 1-phenanthranilide (XXV) was the principal product, being obtained in 72% yield, while 15% of benz-1-phenanthrylamide (XXVI) estimated as 1-phenanthrylamine, was also produced.

\[
\text{XXXV} \\
\text{XXXVI}
\]

Dice and Smith pointed out, also, that this result was similar to that obtained by Bachmann and Boatner (32) for the Beckmann rearrangement of 1-benzoylphenanthrene oxime. These workers obtained 82% of 1-phenanthranilide and 18% of benz-1-phenanthrylamide. This result is interesting because it has been claimed (33, 34) that the Beckmann rearrangement and the Schmidt reaction do not involve similar mechanisms. According to these papers, the latter does not involve oxime intermediates with subsequent rearrangement, and there is no evidence for the postulation of imino intermediates. Recent work however by Smith (35) suggests a mechanism for the Schmidt reaction involving --
an iminocarbonium ion which could also arise under the conditions of the Beckmann rearrangement.

Alexander, in a recently published book (36) suggests that the more bulky group tends to migrate in preference to the other, and quotes a number of examples in support of this. It appears from these that, where one group is aryl and the other alkyl, the former does indeed migrate preferentially, but in cases where both groups are aryl, there is little difference in their relative tendencies to migrate.

Badger and Howard (37) have found that o-benzoyl/benzoic acid reacts with hydrazoic acid to give two products, N-benzoyleanthranilic acid (XXVII) and anhydro-N-benzoyleanthranilic acid (XXVIII). The yield of the two products was very nearly quantitative, so the reaction must have occurred exclusively by migration of the benzoic acid radical, rather than the phenyl radical.

\[
\text{XXVII} \quad \text{XXVIII}
\]

In the first experiment o-benzoylmesobenzanthrone sodium azide in trichloroacetic acid was used. No reaction occurred, and the trichloroacetic acid was replaced by H\textsubscript{2}SO\textsubscript{4} in the subsequent successful reactions. No attempt was made to purify the product of the
reaction, although it was found to be pure enough to establish its identity with the product of the Beckmann rearrangement of 4-benzoylmesobenzanthrone oxime by mixed melting point. The procedure of Eachmann and Boatner, and Dice and Smith, was adopted to determine the course of the reaction, namely, hydrolysis to the corresponding acid and amine.

Hydrolysis was attempted with alcoholic sulphuric acid, HCl and KOH, but the most satisfactory agent was found to be a I:1:1:1 (by wt.) mixture of CH₃COOH, H₂SO₄, and water. A 96% yield of mesobenzanthrone-4-carboxylic acid was obtained, identified by comparison with an authentic synthetic sample. Approximately 1% of 4-aminomesobenzanthrone was obtained, also. It can be concluded, then, that treatment of 4-benzoylmeso/benzanthrone with hydrazoic acid, leads to a 96% yield of 4-mesobenzanthrone anilide XXIII with about 1% of 4-benzoylaminomesobenzanthrone XXIV.

It will be noticed that this result is similar to that obtained by Dice and Smith. In each case the phenyl radical has migrated in preference to the phenanthryl and mesobenzanthronyl radicals. Also, the chief product of the Schmidt reaction on 4-benzoylmeso/benzanthrone is identical with the only product isolated from the Beckmann rearrangement of 4-benzoylmeso/benzanthrone oxime.

The reaction of hydrazoic acid with 1-benzoyl/naphthalene was similarly investigated to see if this gave a comparable result to the others. It was found that in H₂SO₄, no reaction occurred, but when a
mixture of trichloroacetic acid and $\text{H}_2\text{SO}_4$ was used, excellent yields of a Schmidt product were obtained. This was hydrolysed with $\text{CH}_3\text{COOH}$, $\text{H}_2\text{SO}_4$, and water to give a yield of $a$-naphthoic acid corresponding to 79% of $a$-naphthylamide (XXIX) and a yield of $a$-naphthylamine corresponding to 5% of $N$-benzoyl-$a$-naphthylamine (XXX). 

This result, then, is in agreement with the two other cases already mentioned where one of the radicals constitutes a condensed ring system. In each case, the phenyl group migrates preferentially.

---------

**The Oxonium Salts of mesoBenzanthrone**

In the course of the experiments on the action of hydrazoic acid on mesobenzanthrone in the presence of trichloroacetic acid, already described, it was noted that the crude reaction product was red in colour and melted below 90°C. Purification of this material by recrystallisation from alcohol, or by chromatography on alumina followed by elution with alcohol, yielded only pure mesobenzanthrone, m.p. 171°C. It was found that by merely pouring alcohol or water onto the red material and shaking for a few seconds, the red colour disappeared and the yellow product was now mesobenzanthrone. The material could, however, be recrystallised from petrol
ether, and yielded orange needles melting at 95°C. Halogen was found to be present and it was concluded that the orange product consisted of a complex containing mesobenzanthrone and trichloroacetic acid.

Perkin (10) found that mesobenzanthrone formed a ferrichloride, stannichloride and platinichloride, and noted that these were decomposed by water, leaving a suspension of mesobenzanthrone. He noted also that mesobenzanthrone dissolved in conc. H₂SO₄ to give a red solution which deposited mesobenzanthrone on dilution with water, and he concluded that a double compound was formed here also, but he was unable to isolate it. He assumed that these compounds were oxonium salts involving linkage at the carbonyl group in mesobenzanthrone.

It seems obvious that the orange compound that has been isolated is a similar type of complex to the ones prepared by Perkin. To investigate the formation of the complexes more thoroughly, recourse was had to a technique described by Kofler and Kofler in "Mikromethoden" (1948), for the detection of molecular compounds, involving the use of a microscope with an electrically heated stage.

Briefly, this method consists in melting the two compounds that are suspected of forming a complex, onto a microscope slide in such a way that they just come into contact with one another. A cover-slip is placed over the whole, the slide is placed under the microscope on the cold stage, and adjusted so that the interface runs across the centre of the field.
On looking through the microscope now, crystals of pure substance A are seen on one side of the field, pure B on the other, and any complex A.B. is present at the interface. It is often possible to see, immediately, if a complex has been formed by the individual crystalline structure at the interface. The slide is now heated gradually, and examined, preferably through crossed nicols. If a complex has been formed there will of course, be two eutectics (corresponding to A-M and B-M where M is the molecular complex), and these are observed as molten strips across the field on either side of the interface. These strips appear black through crossed nicols and are unmistakable in comparison with the beautiful polarisation colours of the unmelted crystals. In this way the temperatures of the eutectics and of the melting points of the two pure substances, and the complex, can all be accurately determined at once.

It was found that complexes were formed by mesobenzanthrone with picric acid, trichloroacetic acid, trinitrobenzene and $H_2SO_4$, but not with monochloro/acetic or adipic acid or benzoic acid. Benzalacetophenone did not form a complex either with picric acid or trichloroacetic acid, while fluorenone formed complexes with picric acid, trichloroacetic acid and trinitrobenzene. Phenanthraquinone also formed a complex with trichloroacetic acid.

By melting together mesobenzanthrone and trichloroacetic acid in various proportions, it was shown that the complex had the composition $C_{17}H_{10}O$. 
A mixture made up with this proportion had the same melting point as that of the complex, determined by the microscope technique.

Sudborough and Beard (38) investigating compound-formation with trinitrobenzene, mentioned that ketones did not form complexes with this reagent, but that compounds with oxygen in the ring, such as coumarone did. However, they appear to have confused fluorenone with diphenylene oxide, for they quote fluorenone as an example of a compound with cyclic oxygen, and mention that it does form a complex.

Fluorenone trichloroacetate was also investigated, and found to melt at 37°C. This was confirmed by preparing it from a mixture of trichloroacetic acid and fluorenone in light petroleum, when yellow plates m.p. 37°C were obtained. Meyer (39) reported that fluorenone trichloroacetate crystallised in long orange needles m.p. 58°C.

An attempt to show by means of the ultra-violet absorption spectrophotometer whether or not the mesobenzanthrone carbonyl was directly involved in the linking of the complex, and hence whether the complexes were true oxonium salts, failed, because it was found that, in the dilute solutions necessary for the employment of the technique, the complexes were completely broken down into their components. The spectrum obtained was identical with that of mesobenzanthrone itself, and a similar result was obtained with fluorenone trichloroacetate. This
confirms the result obtained by Hunter Qureishy and Samuel (40), who found that in the case of four definite molecular compounds, naphthalene/picric acid, iodoform/quinoline, and the 1- and 2-naphthylamines/m-dinitrobenzene, the two components retained their chemical individuality in the addition complex in each case. The absorption curve of a-naphthylamine, for example, was almost identical with that of the a-naphthylamine/m-dinitro/ benzene complex.

The results obtained, then, in this work suggest that mesobenzanthrone does form oxonium salts with strong acids like trichloroacetic acid and sulphuric acid, but is not basic enough to combine with comparatively weak acids such as benzoic acid, adipic acid and monochloroacetic acid. The complexes formed with picric acid and trinitrobenzene are more likely to be molecular compounds of the same type as naphthalene picrate, rather than oxonium salts, as it is difficult to envisage any type of direct linkage between these compounds and the mesobenzanthrone carbonyl.

So Perkin was probably correct when he suggested that the carbonyl group in the six-membered ring of mesobenzanthrone conferred a certain basicity on the compound, but it seems unlikely that all the complexes formed by mesobenzanthrone can be classed as oxonium salts.
The Reduction of mesoBenzanthrone with Aluminium isopropoxide

During the work already described in the first part of the thesis, on the mechanism of the oxidative hydrolysis of 4-a-cyanobenzylmesobenzanthrone, the possibility of a carbinol intermediate (XXXI) was tentatively considered.

Several attempts to prepare this by reducing 4-benzoylmesobenzanthrone with aluminium isopropoxide, according to the well known Meerwein-Ponndorf method, were unsuccessful as the product appeared to be a mixture which could not be separated into individual components by chromatography. Remembering that previous workers (6) had shown that mesobenzanthrone was easily reduced, it was thought possible that some reduction of the mesobenzanthrone carbonyl had occurred. A search of the literature revealed that no mesobenzanthrone carbinol was known, and as far as could be ascertained, reduction of mesobenzanthrone by the Meerwein-Ponndorf method had not been attempted.

On treatment with aluminium isopropoxide in isopropyl alcohol, mesobenzanthrone gave a good yield of a compound which was proved by analysis, picrate-formation, etc., to be mesobenzanthrene. The
properties of the compound were identical with those described for the latter substance by Clar and Furnari (6).

This result is of great interest, firstly because it affords an excellent preparative method for mesobenzanthrene which has only been obtainable hitherto by rather drastic reactions; e.g. by the distillation of mesobenzanthrone over red hot pumice and zinc dust in a current of hydrogen (5); by the treatment of mesobenzanthrone with HI and red phosphorous to yield dihydromesobenzanthrene which is then reduced to mesobenzanthrene by treatment with \( \text{H}_2\text{SO}_4 \) (5); or by the passage of a-benzylnaphthalene through a reaction chamber heated to 800°C, (42). The isopropoxide reduction is elegant and affords yields of 70-80%.

Secondly, only one case of the reduction of a ketone to the corresponding hydrocarbon by the use of aluminium isopropoxide has so far been reported. Adkins and Rossow (43) found that 9:9'-dimethylanthrene-10 (XXXII) was slowly reduced to the corresponding hydrocarbon (XXXIII) in the course of 2 days, on treatment with aluminium isopropoxide and isopropyl alcohol.

![Chemical structure](image)
In the present work it was found that anthrone (XXXIV) yielded anthracene on reduction with aluminium isopropoxide, and not dihydroanthracene, as might be expected by analogy with mesobenzanthrone. This can be explained by the preliminary formation of dihydro/anthranol (XXXV), which is known (44) to be unstable in air losing water to give anthracene (XXXVI). This could not happen of course, in the case of (XXXII).

Experimental evidence was obtained for the formation of dihydroanthranol.

The unsuitability of the older methods of mesobenzanthrone reduction for application to substituted meso/benzanthrones is obvious, and it was thought that the usefulness of the isopropoxide method would be much enhanced if it could be shown that it was applicable to the preparation of substituted mesobenzanthrones.

Good yields of 3-chloro- and 3-bromomesobenzanthrones were obtained by the reduction of the corresponding mesobenzanthrones, but 4-benzylmesobenzanthrone yielded a small quantity only, of a product which appeared to be the carbinol, from its analysis. 3-Nitro and 11-aminomesobenzanthrones gave unsatisfactory results, unchanged material only being obtained. It is thought that a solubility factor was possibly responsible for
this, as the starting material did not dissolve readily in isopropyl alcohol. Better results might be obtained with these compounds if other solvents were tried.

---------

Thanks are due to Mr W. McKinnon for preparations of 3-chlor- and 3-bromomesobenzanthrene.

---------

The Action of Phosphorus Oxychloride and Pentachloride on mesoBenzanthrone

The Beckmann rearrangement of mesobenzanthrone oxime led to the formation of small quantities of by-products along with the lactam. The chief by-product was the high melting chlorine-containing compound which was later found to be analogous to the chlorine-containing substance isolated by Moore and Huntress during the Beckmann rearrangement of 2-nitrofluorenone oxime. At the time, however, it was thought that it might have arisen by nuclear chlorination of the oxime by the reagents used and, accordingly, experiments were carried out to see if PCl₅ and POCl₃ had any effect upon mesobenzanthrone itself.

When mesobenzanthrone was treated with PCl₅ and POCl₃, under the same conditions as those used in the Beckmann rearrangement of the oxime, a mixture of two products was obtained, both of which dissolved in benzene, ethanol, esters, etc., to give yellow solutions with a vivid green fluorescence. The purest of the two compounds isolated crystallised in orange micro-needles melting at 390°C. It did not dissolve in concentrated sulphuric acid, even on standing for a
considerable time. The material contained chlorine which was not removed by boiling alcoholic KOH.

Molecular weight determinations by the Rast method gave values of about 500. The evidence, then, suggested that this was a dibenzanthrenyl, the link between the molecules being at the 7:7'-position in view of the absence of colour with conc. H₂SO₄. The structure indicated was as follows (XXXVII), and this was confirmed by the analysis.

![XXXVII]

The second product of the reaction was a red solid melting at 320°C, which, however, sintered below this temperature and was obviously not pure. This dissolved in sulphuric acid on long standing to a pale orange solution, which became green on warming.

**Dechlorination of the higher melting compound with Raney nickel alloy (45) gave a yellow crystalline solid** which seemed too highly soluble in most solvents for it to be a dibenzanthrenyl. Analysis confirmed this conjecture and indicated that the compound now contained oxygen. It is difficult to imagine where this has come from, and the structure of this product was not settled.

Amongst the known dibenzanthronyls, only
only violanthrone (XXXVIII) and isoviolanthrone (XXXIX) appear to have been well investigated. 3:3′-
-Dibenzanthronyl (XL) and 4:4′-dibenzanthronyl (XLI) are also known (46).

All of these substances give red or violet colours with conc. H₂SO₄.

A German patent (47) refers to the preparation of condensation products of mesobenzanthrene, by heating mesobenzanthrene and dihydremesobenzanthrenes substituted with halogen in the 7- position, to high temperatures in the presence of metal oxides. These products are said to have a high colouring power and usually a green fluorescence, and are useful for colouring lubricating oils, etc. In the case of mesobenzanthrene itself, the product must be 7:7′-dibenzanthronyl (XLII).
This compound dissolved in hydrocarbon solvents to a solution with an intense green fluorescence.

When mesobenzanthrone is heated with iron powder to 300-50°C for 20 hours, a product is formed which dissolves in hydrocarbon solvents giving a solution with vivid green fluorescence. (48). Further, when mesobenzanthrene, or a mixture of mesobenzanthrene and mesobenzanthrone is treated above 300°C with a condensing reagent such as phosphoric acid, a yellow compound is obtained which dissolves in hydrocarbon solvents to give an intensely green-fluorescent solution. (49). Clar (50) suggests that the product of both these condensations has the structure XLII.

Data such as the melting point, colour with concentrated sulphuric acid, and analysis figures, appear to be completely lacking, however, for this compound.

Recently, Zinke and co-workers (8, 9) have investigated the distillation of mesobenzanthrone over zinc dust. As primary products they obtained mesobenzanthrene and dihydromesobenzanthrene, but with them they obtained smaller quantities of materials which dissolved in hydrocarbon solvents to give yellow solutions with a green fluorescence. In their first paper (8) they
reported the separation of the mixture of by-products into two compounds, a yellow and a red hydrocarbon. In the second paper, however, (9), they reported that the red hydrocarbon was in fact a mixture of three compounds, a second yellow hydrocarbon, and two red compounds which they did not separate.

The first yellow hydrocarbon to which Zinke gave the structure (XLIII) dissolved in benzene to give a yellow solution with a blue-green fluorescence, from which it crystallised in yellow needles m.p. 341-2°C. This material dissolved in $\text{H}_2\text{SO}_4$ to a violet-blue solution. The analysis accorded with the structure proposed. The second yellow hydrocarbon dissolved in xylene to a bright yellow solution with a blue-green fluorescence, from which it crystallised in yellow needles, m.p. 407-8°C. This material gave a reddish-yellow colour in concentrated $\text{H}_2\text{SO}_4$. For this compound one of the structures (XLIV) or (XLV) was proposed.
Finally the mixture of red compounds obtained as dark red plates from nitrobenzene or quinoline, melted at 416-18°C. It dissolved in warm concentrated sulphuric acid to a blue solution and the analysis indicated a violanthrene structure. On oxidation, this yielded a substance which from sulphuric acid colouration data, etc., was concluded to be a mixture of violanthrene (XXXVIII) and isoviolanthrene (XXXIX). Zinke concluded therefore, that the red product of the zinc dust distillation was a mixture of the corresponding hydrocarbons, violanthrene (XLVI) and isoviolanthrene (XLVII).

The similarity in properties between these hydrocarbons of Zinke, and the chlorine-containing compound obtained by the action of POCl₃ and PCl₅ on mesobenzanthrone, was noted, and it was thought that if the introduction of the chlorine atoms could be avoided, the product might be identical with one of Zinke's hydrocarbons.
An experiment to determine whether the chlorine atoms had been introduced into the 3-position of the mesobenzanthrone nucleus, by treating 3-chloromeso-benzanthrone under the same conditions with \( \text{POCl}_3 \) and \( \text{PCl}_3 \), yielded no pure product, but the compound obtained was shown to be dissimilar from the compound obtained from mesobenzanthrone.

Treatment of mesobenzanthrone with \( \text{POCl}_3 \) alone, was found to yield a product which did not contain halogen. Chromatographic purification, while not completely successful, yielded a pure product which crystallised from a yellow, bluish-green-fluorescent benzene solution in the form of yellow needles, m.p. 346-7°C. This dissolved in conc. \( \text{H}_2\text{SO}_4 \) to a blue-violet solution, and the analysis suggested a dibenzanthrenyl. Comparison of this product with a sample of the yellow hydrocarbon, m.p. 341-2°C, kindly supplied by Professor A. Zinke of Graz University, showed that the two compounds were identical. The mixture of the two melted at 343-6°C.

Although Zinke has suggested the formula (XLIII) for this hydrocarbon, he has stated in a private communication to us that he is doubtful of this. The product we obtained appeared to be rather purer than his, and our analysis indicated the structure (XLII). Further, as we have shown that the compound can be prepared merely by the action of phosphorus oxychloride on mesobenzanthrone, there seems to be no reason for the postulation of a 6:6'- or 6:7'- bond. The evidence available to us at the present, then, rather favours the
structure (XLII) for this hydrocarbon.

********

The Synthesis of 6-Hydroxymesobenzanthrone

Difficulty was experienced in obtaining a positive test for nitrogen in mesobenzanthrone oxime when it was first prepared. Before an analysis was obtained, in consequence, there was some dubiety regarding the structure of the product. A publication by Bradley (51) was noted, dealing with the direct amination of mesobenzanthrone by sodamide in dimethylaniline in which 6-aminomesobenzanthrone was obtained. This hydrolysed partially, in the alkaline solution to 6-hydroxymesobenzanthrone. The possibility of the oximation product being actually 6-hydroxymesobenzanthrone was therefore considered, and the latter compound was synthesised for comparison. The synthesis proved to be unnecessary as the confirmation of the oxime structure was soon forthcoming from the analysis, and from hydrolysis experiments etc.

6-hydroxymesobenzanthrone has been synthesised by Fieser (52) by the following route.

\[ \text{Ph.COCI} \xrightarrow{\text{AlCl}_3} \text{Ph.} \xrightarrow{\text{AlCl}_3} \text{NaCl} \]

Fieser obtained a 53% yield of the 1-benzoyl-2-naphthol from the Friedel-Crafts reaction along with
22\% of the methoxy-compound. When an attempt was made to repeat this work however, our product consisted almost entirely of the 1-benzoyl-2-methoxynaphthalene. A 3\% yield of the naphthol was obtained in one experiment, but repetition on a larger scale yielded none of this product. Accordingly we attempted to demethylate the 1-benzoyl-2-methoxynaphthalene using HBr and acetic acid. This, however, was also unsuccessful, because debenzylation also occurred and the product obtained in good yield was 2-naphthol.

1-Benzoyl-2-methoxynaphthalene was next cyclised to 6-methoximesobenzanthrone by the Scholl procedure, and this was demethylated in small yield to 6-hydroxy/mesobenzanthrone. This was compared with an authentic specimen prepared by the method of Bradley (51) and found to be identical with it. 6-Hydroximesobenzanthrone was shown to be a different compound from the product of the oximation of mesobenzanthrone.
The loss of the benzoyl group on treatment of 1-benzoyl-2-methoxynaphthalene is interesting. It was discovered when this work was completed, that this compound has been successfully demethylated by Baddar (53), using quinoline hydriodide or aniline hydriodide in boiling quinoline, and no mention is made of any debenzoylation. Analogous cases are known, however, in which 2-naphthol results from the treatment of 1-substituted 2-naphthols with acids. As an example, the case of 2-naphtholphenylmethylamine may be quoted. Treatment of this compound with dil. HCl (54) or nitrous acid (55) yields 2-naphthol.

\[
\begin{align*}
\text{Ph} & \quad \text{CH} \cdot \text{NH}_2 \\
\text{H} & \quad \text{O} \\
\text{OH} & \quad \text{HCl} \\
\text{H} & \quad \text{O} \\
\text{HNO}_2
\end{align*}
\]

The possibility that a reversed Fries rearrangement might be involved here, must not be ignored. In the normal Fries rearrangement, a phenolic ester of a carboxylic acid rearranges to give a mixture of o- and p- acyl phenols under the influence of a condensing agent such as aluminium chloride. The reverse change can occur and in the case of 1-benzoyl/-2-methoxynaphthalene, the resulting ester could be hydrolysed under the conditions employed, to yield 2-naphthol.
It must be said that Wheland in "Advanced Organic Chemistry" Wiley (1949) p. 566, claims that examination of a considerable number of examples leads to the rule that the reverse Fries rearrangement occurs generally if, and only if, the hydroxyl group is para to the acyl group, and if, and only if, some further substituent in the hydroxy ketone is ortho to the acyl group. The existence of exceptions to this rule is, however, not excluded.
EXPERIMENTAL

The Preparation of mesoBenzanthrone oxime.

mesoBenzanthrone (10g.), hydroxylamine hydrochloride (50g.) and pyridine (250 m.l.), were mixed, and the resulting clear yellow solution boiled gently for 70 hours under reflux. The bulk of the pyridine was then distilled off and the residue poured into 150 m.l. water. The product was extracted from the resulting oily suspension by thorough shaking with ether, and the combined ether extracts concentrated down until only a dark solution of the oxime in a small volume of pyridine remained. This was now diluted with an equal volume of boiling ethanol, whereupon the oxime rapidly crystallised out. When cold, this was collected and the liquor evaporated down and triturated with a further quantity of ethanol to yield a second crop.

The yield of crude material m.p.: 160°C varied in a number of experiments from 85-96%. Smaller yields were obtained when uncrystallised mesobenzanthrone was used. The crude product contained some mesobenzanthrone as a rule, and it was found advisable to purify the oxime chromatographically, although this lowered the yield.
The product was dissolved in the minimum amount of benzene and adsorbed onto a column of alumina (18"x1"). Pure benzene was used for development of the chromatogram. Unchanged mesobenzanthrone rapidly passed down the column and was washed through, leaving the oxime adhering close to the top of the column, as a dull yellow band with a faint yellow fluorescence under the ultra-violet lamp. The oxime zone was removed, dried, and thoroughly extracted with successive portions of boiling ethanol until the latter was no longer coloured yellow. Concentration of the combined ethanolic extracts down to approximately 80 m.l. followed by cooling, yielded a first crop of material, and two more crops of good material were obtained by further concentration.

Finally the whole was recrystallised from methanol to give pale yellow rhombohedral plates m.p. 171° C. The yield of pure material was 6.8g. (65%) and recovered mesobenzanthrone 0.45g. (8%).

Analysis Found -

\[ \text{C} = 82.8; \quad \text{H} = 4.5; \quad \text{N} = 5.5. \]

\[ C_{17}H_{11}ON \text{ requires: } \quad \text{C} = 83.3; \quad \text{H} = 4.5; \quad \text{N} = 5.7. \]

The oxime is readily hydrolysed to mesobenzanthrone by refluxing with alcoholic \( \text{H}_2\text{SO}_4 \), and even recrystallisation from glacial \( \text{CH}_3\text{COOH} \) is to be avoided, as it causes partial hydrolysis.

-------------
The Preparation of 4-Benzoylmesobenzanthrone monoxime

4-Benzoylmesobenzanthrone (1g.), hydroxylamine hydrochloride (5g.) and pyridine (50 m.l.) were heated over a small flame for 8 hours, and pyridine (40 c.c.) was then distilled off under slightly diminished pressure. The residue was poured into 100 m.l. water, and the product extracted with ether. The ethereal extract was concentrated down and finally evaporated on the steam bath, and the residue was taken up in boiling ethanol and allowed to crystallise. Two further crops were obtained by successive concentrations of the liquors. A total yield of 0.83g. of crude oxime was obtained, m.p. 234-5°C.

The crude monoxime was dissolved in benzene and chromatographed on a column of alumina. After long development with benzene the oxime zone - which had precisely the same appearance and position as that of mesobenzanthrone oxime - separated into two portions. The upper one, on elution with boiling ethanol, yielded a trace only of material m.p. 240°C which was later identified as the dioxime. The lower portion yielded the bulk of the product on elution with ethanol and this was shown on analysis, to be the monoxime. It was crystallised from ether and had m.p. 245-6°C.
The Preparation of 4-Benzoylmesobenzanthrone dioxime

The scale, materials and method were the same as used in the previously described preparation of the monoxime, but heating was continued for 50 hours. After concentration of the ether extract, the residual pyridine solution was rubbed this time with ether, to give fine yellow crystals 0.95g. m.p.: 246-7°C (decomp.)

Analysis: Found - C = 78.5; H = 4.2; N = 7.8.
C_{24}H_{16}O_N requires - C = 79.1; H = 4.4; N = 7.7%
4-Benzoylmesobenzanthrone mixed oximes from an 8-hour oximation (0.68 g.) were dissolved in about 50 m.l. hot ethanol and a little powdered NaOH was added. 3 m.l. of dimethyl sulphate were added dropwise, with more solid NaOH whenever the solution became acid (indicated by the solution becoming yellow). When all the dimethyl sulphate had been added, the alkaline solution was refluxed for three hours, concentrated by distillation, and the concentrate poured into about 100 m.l. water. The yellow ppt was collected and dried; m.p.: 190-200°C.

The product was dissolved in benzene and chromatographed on alumina. Two yellow bands washed through the column on development with benzene, but they were not widely separated from one another. In consequence, the material obtained from each band was not quite pure. The lower band yielded the bulk of the product in the form of yellow crystalline material, m.p.: 196-202°C (0.40 g.) This gave a scarlet colour with conc. H₂SO₄. The upper band yielded yellow material also, m.p. 160-170°C. This gave a pink colour only with conc. H₂SO₄. There was not enough of this material for analysis.

The analysis of the material from the lower band was not good, but it did indicate the methylated monoxime, and this fitted in with the H₂SO₄ colouration. The fact that the material from the upper band gave only a pink colour with H₂SO₄ indicated that this was probably the methylated dioxime.
Analysis of lower band material:

**Found** - C = 81.0; H = 6.4; N = 4.2.

Methylated monoxime C$_{25}$H$_{17}$O$_2$N requires:
C = 82.6; H = 4.7; N = 3.9

Methylated dioxime C$_{26}$H$_{20}$O$_2$N$_2$ requires:
C = 79.6; H = 5.1; N = 7.1.%

----------

**The Preparation of 3-Chloromesobenzanthrone Oxime**

3-Chloromesobenzanthrone (5g.), hydroxylamine hydrochloride (25g.) and pyridine (250 m.l.) were heated gently for 72 hours, and the crude oxime was obtained as in previous experiments (4g.). This was dissolved in benzene and chromatographed on alumina. This time, exactly 2g. (40%) of unchanged 3-chloro/mesobenzanthrone was obtained from the column. The oxime was left in a narrow orange zone at the top of the column, and it was eluted with boiling ethanol. Concentration of the ethanol caused the oxime to crystallise out in orange prisms 1.8g. (35%).

The oxime crystallised from methanol with a little charcoal, in beautiful pale orange prisms. m.p. 205°C.

**Analysis:**

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>C$<em>{17}$H$</em>{10}$NOCl requires</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>5.2</td>
<td>N = 5.0; Cl = 12.7.%</td>
</tr>
<tr>
<td>Cl</td>
<td>13.3</td>
<td></td>
</tr>
</tbody>
</table>
mesoBenzanthrone-2:4-dinitrophenylhydrazone

mesoBenzanthrone (0.5 g.), 2:4-dinitrophenylhydrazine (1 g.), \( \text{H}_2\text{SO}_4 \) conc. (2.0 m.l.) and ethanol (50 m.l.) were refluxed for 15 hours and the solution allowed to cool. The reddish solid which crystallised out was collected and extracted with 15 m.l. portions of boiling ethanol, till the melting point of the residue was constant. The dinitrophenylhydrazone was obtained as a dark-red crystalline solid, m.p. : 259-60°.

Yield: 15 m.g.

Analysis: Found \( N = 13.4 \%

\[ \text{C}_{23}\text{H}_{14}\text{O}_9\text{N}_7 \text{ requires: } N = 13.7 \%

Attempts to prepare the 2:4-dinitrophenylhydrazone by less drastic methods led to the recovery of unchanged mesobenzanthrone only.

---------------

Sulphuric acid colour test for mesoBenzanthrones.

The test is carried out by adding about 1 m.g. of the substance to 1-2 m.l. of conc. \( \text{H}_2\text{SO}_4 \) in a test-tube and shaking for a minute or two.

mesoBenzanthrone \( \text{Orange red solution with reddish orange fluorescence.} \)
4-Benzoylmesobenzanthrone | Crimson solution. Non fluorescent.
---|---
3-Chloromesobenzanthrone oxime | Rose-red solution.
mesoBenzanthrone oxime | Yellow solution. Non fluorescent.
4-benzoylmesobenzanthrone dioxime | Yellow solution. Non fluorescent.
4-Benzoylmesobenzanthrone monoxime | Rose-red solution. Non fluorescent.
mesoBenzanthrone-2:4-dinitrophenylhydrazone | Pale orange-brown solution.
3-Chloromesobenzanthrone oxime | Golden yellow solution. Non fluorescent

-------------

The Beckmann rearrangement of mesoBenzanthrone oxime

\[
\text{mesoBenzanthrone oxime} + \text{POC}_{13} \rightarrow \text{Beckmann rearranged product}
\]
mesoBenzanthrone oxime (3.0g.), PCl₅ (3.8g.) and POCl₃ (50 m.l.) were refluxed gently for 1½ hours, at the end of which time the HCl evolution had almost ceased, and the POCl₃ was then distilled off at atmospheric pressure from an oil-bath. The residue was stirred with a little water and the whole was then refluxed with successive portions of benzene. After thorough benzene extraction - about 600 m.l. in all - the combined benzene extracts were allowed to stand overnight, and the material which had crystallised out was collected, dried, and recrystallised from a large volume of ethanol. Colourless needles 0.17g.
m.p. 288°C.

Analysis:

Found

C = 70.3;  H = 3.7;  N = 4.9;  Cl = 13.1

C₁₇H₁₆NOCl requires - C = 77.4;  H = 3.8;  N = 5.3;  Cl = 13.4%

The poor C analysis is difficult to explain, as the compound appeared to be absolutely pure. The m.p. was sharp, whereas the corresponding chlorine-containing compound obtained by Huntress and Moore from 2-nitro/fluorenone melted over a wide range (15 - 35°). A bad analysis seems the only explanation.

The filtrate from this product was now adsorbed onto a column of alumina (12" x 1") and development carried out with benzene. A yellow zone quickly passed down the column and was washed through. This was found to yield mesobenzanthrone (0.24g.), and showed that a certain amount of hydrolysis of the oxime had occurred during the reaction, probably by the
HCl liberated. This zone was followed by another yellow zone which yielded only a small residue on evaporation. A colour test with $\text{H}_2\text{SO}_4$ indicated that this was probably 3-chloromesobenzanthrone. (mesoBenzanthrone is known to yield 3-chloromeso/benzanthrone on treatment with $\text{PCl}_3$).

Development was continued till four more distinct bands were clearly separated on the column, and the latter was then cut and each zone eluted separately. The column had this appearance before cutting.

<table>
<thead>
<tr>
<th>Daylight</th>
<th>Ultra-violet light</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dull yellow</td>
<td>1 — Greenish fluorescence</td>
</tr>
<tr>
<td>Yellow</td>
<td>2 — Yellow fluorescence</td>
</tr>
<tr>
<td>Buff</td>
<td>3 — Non-fluorescent</td>
</tr>
<tr>
<td>Buff</td>
<td>4 — Slight indeterminate fluorescence</td>
</tr>
</tbody>
</table>

Each section of alumina was dried and then extracted with boiling ethanol till the extracts were colourless.

Zones 1 and 2 yielded only small residues on evaporation of the alcohol. $\text{H}_2\text{SO}_4$ colour tests on these were similar to that given by mesobenzanthrone oxime. The position of the bands is in agreement with this theory, and it is suggested that one is mesobenzanthrone oxime.

Zone 3 yielded material which contained chlorine, and
on recrystallisation from ethanol, it was shown to be identical with the material already isolated, m.p. 283°C. The amount on the column was small - about 20 m.g.

Zone 4 yielded the bulk of the product: 1.55g. of solid melting at 220-6°C (52% yield). This, on recrystallisation from ethanol yielded colourless feathery needles, m.p. 234°C. This was found to contain no halogen and was, in fact, the desired mesobenzanthrone lactam. No trace of any other isomeric compound could be detected.

Analysis:

**Found**

\[
\begin{align*}
C &= 82.9; \quad H = 4.6; \quad N = 5.7 \\
C_{11}H_{17}O \quad \text{N requires} \quad C &= 83.3; \quad H = 4.5; \quad N = 5.7\%
\end{align*}
\]

The total yield of the chloro-compound is 5% and the recovered mesobenzanthrone represents 8% based on the starting material.

----------------

The attempted Hydrolysis of mesobenzanthrone lactam

Hydrolysis of the lactam was attempted by boiling it for long periods with 10% aqueous NaOH solution, aqueous alcoholic NaOH solution, dilute HCl, and finally, by heating it with 50% aqueous HCl solution in a sealed tube. No hydrolysis was observed. Good recoveries of unchanged mesobenzanthrone lactam were invariably obtained.

----------------
The apparatus consisted of a Pyrex 50 m.l. R.B. bolthead flask with a 50 c.m. Pyrex neck 30 m.m. in diameter. Two 1.5 m.m. diameter copper wires were led down the neck, insulated from one another by enclosing one in a long piece of Pyrex glass tubing, and the ends joined by a platinum spiral inside the belly of the flask. This spiral was made from a 25 c.m. length of 0.25 m.m. diameter wire shaped by winding round a \( \frac{1}{4} \)" diameter glass rod. The other ends of the wire were connected through a variable resistance transformer and ammeter to the 230 volts A.C. mains. The flask was immersed in a metal bath so that the spiral was below the surface of the metal.

3.0g. of pure benzanilide, m.p.: 161°C were placed in the flask and melted by raising the temperature of the metal bath to 240°C. A gradually increasing current was now passed through the spiral, and, when it reached 4.5 amp., the wire glowed brilliantly. The current was maintained at this level for six hours with a metal-bath temperature of 240-260°C. For the first three hours, benzanilide continually sublimed up into the neck of the flask and it was necessary to heat the
outside of the neck with a gentle flame from time to time to drive it back down into the region of the spiral.

When the contents of the flask had cooled somewhat, benzene was introduced. The contents, except for a little charred material, all dissolved in about 40 m.l. Nothing crystallised out on cooling so the solution was adsorbed onto an alumina column (18" x 4"). After development with benzene, two zones became apparent. At the top of the column was a small dark-brown region, and below it an extensive grey region. Neither showed any fluorescence under the ultra-violet lamp. The column was cut and the zones separated, dried, and eluted with boiling ethanol. The grey zone yielded 0.63g. material, which, after recrystallisation from aqueous methanol with charcoal, melted at 160°C, and was not depressed on admixture with benzanilide.

The brown-black zone yielded 100 m.g. buff material after charcoalisation of the ethanolic solution, m.p. 286°C. This represents a 3% yield of phenanthridone. This was further purified by sublimation to give long colourless needles, m.p. 293°C.

Another experiment in which the above conditions were maintained but the contents of the flask worked up after only one hour, in an attempt to minimise charring, yielded only 3 m.g. of phenanthridone.

An initial experiment in which the platinum wire was merely caused to glow dull-red (2.6 amps), and a
bath temperature of 280-320°C was maintained for 3 hours, yielded no phenanthridone.

The Preparation of \textit{N-Benzoyl-l-naphthylamine}

\[ \text{NH}_2\text{CO}_2\text{Ph.} \]

1-Naphthylamine (10g.) was dissolved in the minimum volume of dry pyridine, and benzoyl chloride (12g.) was added. The reddish solution was allowed to stand overnight and the solid which had separated was then collected, washed well with water and dried. A second crop was obtained by dilution of the pyridine liquors with water. The crude product was recrystallised from ethanol with charcoal to give needles, m.p. 164.5°C. Yield 10.2g.

The Attempted Pyrocyclisation of \textit{N-Benzoyl-l-naphthylamine}

3.0g. of \textit{N}-benzoyl-l-naphthylamine were melted in the flask, the metal bath being maintained at 240-260°C for 19 hours with a heating spiral current of 3.25-3.75 amps.

On cooling, the flask was rinsed out with boiling ethanol. Some white material was observed which appeared to be very sparingly soluble in hot
ethanol, so it was filtered off. 0.20g. m.p.: 270-90 °C. The ethanolic extract on cooling deposited some more of this material, m.p. 260-270 °C, and on complete evaporation of the ethanolic solution, approximately one gramme of N-benzoyl-l-naphthylamine was recovered.

The high melting product was dissolved up in a considerable quantity of boiling ethanol, concentrated down to about 150 m.l. charcoalised, and the solution filtered. Colourless needles crystallised, m.p. 295 °C. 0.16g. (5% yield).

These were very sparingly soluble in methanol, a little more soluble in ethanol, and moderately soluble in benzene.

**Analysis:**

**Found**  
C = 80.0; H = 5.3; N = 8.3; 3.1

C₁₇H₁₄O N (a mesobenzanthrone lactam) requires:

\[ C = 83.3; \quad H = 4.5; \quad N = 5.7\% \]

This analysis requires an empirical formula of

\[ C_{3\gamma}H_{7\gamma}N_3O_{\alpha\beta} \]

It is certain, therefore, that whatever the product is, it is not one of the two isomeric lactams of mesobenzanthrone.

----------

Another reaction carried out under approximately the same conditions, unaccountably gave a much smaller yield of the high melting compound - 25 m.g. However, it will be realised that it is difficult to maintain absolutely standard conditions in an experiment of this type.

Only unchanged material was obtained from an
initial experiment in which the reaction time was 2 hours.

The Preparation of 1-Naphthanilide

1-Naphthonitrile (15g.) was hydrolysed by boiling with a mixture of 30 m.l. CH₃COOH, 30 m.l. water and 30 m.l. H₂SO₄ until a sample obtained by pouring a little into cold water proved to be completely soluble in alkali. The whole was then poured into cold water, the solid collected and dissolved up in warm Na₂CO₃ solution. The alkaline solution was filtered, the filtrate acidified and the acid collected. It was dried and recrystallised from 80/100 light petroleum. m.p. 160°C.

The pure 1-naphthoic acid (5.5g.) was refluxed with thionyl chloride (20 m.l.) for 30 minutes, and the thionyl chloride was distilled off under diminished pressure.

The crude 1-naphthoyl chloride was dissolved in a little dry benzene and aniline (5.5g.) also in dry benzene, was added gradually with stirring. The flask was then heated in the steam bath for a few minutes and allowed to cool.
The anilide was collected and washed well with water to remove aniline hydrochloride. Yield 6.0g. m.p. 160°C.

The Attempted Pyrocyclisation of 1-Naphthanilide

3.0g. of the anilide were melted in the flask with the bath temperature maintained at 245-60°C for 24 hours. The platinum (heating) spiral current was 4-5 amps.

The cooled reaction mixture was extracted thoroughly with boiling ethanol, the combined extracts concentrated to about 10 m.l. charcoalised, and filtered. A little buff material crystallised which melted at about 60°C. The solvent was now removed completely, and the residue dissolved in benzene and adsorbed onto an alumina column (18" x $\frac{3}{4}"$). On development with benzene three bands appeared. A brown band at the top of the column and a grey band immediately below it, yielded on elution with ethanol, unchanged 1-naphthanilide (m.p. and mixed m.p.). The bottom band was faintly yellow in colour and had a vivid purple fluorescence under the ultra-violet lamp. On elution, this yielded yellowish material m.p. 50-60°C. A Lassaigne test indicated that no nitrogen was present. Recrystallisation from 40/60 petrol ether gave white material, m.p. 70-75°C. Naphthalene was now suspected, and confirmed by a mixed melting point. (78-80°C).

In another experiment, the time of heating was
18 hours, the current 3.25 amp. and the bath temperature range was as above. This yielded only unchanged l-naphthanilide. (m.p. and mixed m.p.).

It seems, therefore, that Meyer and Hofmann's pyrocyclisation method is not applicable to our compounds.

The Preparation of 8-Bromo-l-naphthoic acid 2'-bromanilide

8-Bromo-naphthoic acid (5g.) was refluxed with thionyl chloride (15 m.l.) for half an hour, the excess thionyl chloride distilled off, and the residual acid chloride dissolved in benzene.

o-Bromaniline (8g.) was dissolved in dry benzene and the acid chloride solution added slowly to it with frequent shaking. The clear golden yellow solution was heated on the steam bath for a few minutes and allowed to cool. The benzene solution was washed twice with dil. HCl, and then thoroughly with water. Material which precipitated during the water washing weighed 3.3g. and had m.p.: 143-6°C. Evaporation of the benzene yielded further material making 7.2g. in all. This was recrystallised from
aqueous methanol with charcoal, to give colourless feathery needles, m.p. 145-6°C.

Analysis: Found

_\text{C}_{17}\text{H}_{17}\text{NOBr}_2 \text{ requires: Br} = 39.5; \text{N} = 3.5\%_

---

The Intramolecular Ullmann Condensation of 8-Bromo-1-naphthoic acid 2'-bromanilide

8-Bromo-1-naphthoic acid 2'-bromanilide (2.0g.) and copper bronze (1.8g.) were stirred together in an oil bath maintained at 255-60°C for 2 hours.

The flask was rinsed out with acetone and the copper thoroughly extracted with boiling acetone. The extract was evaporated to dryness, the residue dissolved in benzene and adsorbed onto an alumina column. Benzene alone was used for development.

The first zone to wash through was colourless in daylight, but had a strong blue fluorescence under the ultra-violet lamp. The benzene solution, on washing through, had a strong blue fluorescence even in daylight. Concentration to small volume caused crystallisation to occur, colourless prismatic needles being obtained, m.p. 100-1°C. These were recrystallised from 60/80 light petroleum and the m.p. became 102°C.

A Beilstein test on this material indicated the
absence of halogen, and this was confirmed by a Lassaigne test, which also showed that nitrogen was present.

**Analysis:** Found

\[ C = 82.5; \quad H = 4.6; \quad N = 5.5 \]

\[ C_{17}H_{17}O_N \text{ requires } C = 83.3; \quad H = 4.5; \quad N = 5.7\% \]

Although the analysis suggests that the material could be one of the desired isomeric mesobenzanthrone lactams, the low melting point, comparatively high solubility in organic solvents, and the blue fluorescence of its solutions, do not support this view. 1-Naphthanimide melts at 160°C.

The next zone to wash through appeared on the column as an extensive yellow region with a yellow fluorescence under the ultra-violet lamp, and it did in fact yield the bulk of the product. On evaporation of the benzene solution to small volume, a yellow crystalline material was obtained, m.p. 100-2°C. (0.29g.) This, on recrystallisation from 80/100 light petroleum, gave beautiful pale yellow needles, m.p. 105°C. A further recrystallisation raised the m.p. to 106°C. Beilstein and Lassaigne tests indicated the absence of halogen and the Lassaigne test again showed nitrogen to be present. The material was soluble in hot conc. HCl, and also in hot aqueous NaOH, but insoluble in cold NaOH. All the information obtained therefore about the compound suggested that it was N-phenyl/naphthastyril (Heilbron), and analysis gave confirmation. (Lit. m.p.: 105°C.)

**Analysis:** Found

\[ C = 83.1; \quad H = 4.5; \quad N = 5.7\]

\[ C_{17}H_{17}O_N \text{ requires } C = 83.3; \quad H = 4.5; \quad N = 5.7\% \]
After these two zones had been washed through, the column was cut and the three remaining zones were eluted separately.

The lowest of the three bands appeared yellow on the column and on elution with ethanol, followed by concentration of the ethanolic extract, yielded only a trace of yellowish oily material which contained no halogen.

The middle zone which was an orange-brown colour on the column, yielded on elution with methanol, followed by evaporation of the extract, 0.1g. buff material. This was halogen-free and melted about 90°C. It was obviously a mixture, for recrystallisation did not improve the melting point, but a separation was not effected.

The uppermost band of all, which appeared on the column as a fawn, non-fluorescent region directly below a black zone of impurity at the top of the column, gave a brown solution on elution with methanol which deposited a little material, m.p.: 220-40°C. Recrystallisation from methanol with charcoal, yielded off-white crystalline material, m.p. 240-50°C. A Beilstein test showed that this contained no halogen.

A mixture of this material with mesobenzanthrone lactam, m.p. 234°C., melted at about 170°C., so the two are definitely not the same. They are similar however, in several respects: They are both only slightly soluble in hot methanol and almost insoluble in the cold; their melting points are in the same
region. Furthermore, the region on the column where this product was found is roughly the same as that from which was obtained material in the corresponding Ullmann condensation of N-(o-bromobenzoyl)-8-bromo-l-naphthylamine, described hereafter. This latter product was shown to be identical with the product of the Beckmann rearrangement of mesobenzanthrone oxime.

It does seem reasonable to suppose, then, that this product is the second of the two possible isomers. Unfortunately, there was not enough of this material for an analysis.

The Synthesis of N-(o-bromobenzoyl)-8-bromo-l-naphthylamine.

8-Bromo-l-naphthoic acid (12g.) was dissolved in H$_2$SO$_4$ conc. (100 m.l.) and sodium azide (5g.) added in small portions, the evolution of gas from each addition being allowed to subside before further azide was introduced. The temperature was maintained between 40° and 55° C. by controlling the rate of the addition of azide, no external heating being required. The addition was complete in about $\frac{1}{2}$ hour, and the solution was then poured with stirring into an
aqueous solution of 150g. NaOH and ice. The precipitated amine was extracted by shaking with ether. Removal of the ether by distillation left 10.6g. of 8-bromo-1-naphthylamine, m.p. 82.6°C. This represents a quantitative yield. The material was used without further purification. A sample was however crystallised up from 40/60 light petroleum. It deposited in colourless needles, m.p. 89°C. (Heilbron quotes 89-90°C.).

A model reaction with 1-naphthoic acid gave similarly a 93% yield of 1-naphthylamine.

c-Bromobenzoic acid (3g.) was refluxed gently with 10 m.l. of thionyl chloride for 1/2 hour and the excess thionyl chloride distilled off under diminished pressure. The residue was dissolved in benzene and added slowly, with stirring, to a solution of 8-bromo-1-naphthylamine (6g.) in 35 m.l. dry benzene. The suspension was finally heated for a few minutes on the water bath to complete the reaction. After standing for two hours, the amine hydrochloride was filtered off and washed well with benzene. (3.8g. m.p. 235°C.). The benzene washings were added to the filtrate, and the whole washed twice with about 15 m.l. of dil. HCl, and then with distilled water. The benzene was removed by distillation and the residue dried. The material crystallised from methanol with charcoal in colourless rosettes of elongated prisms. m.p. 142°C.
Analysis:  Found -  
Br = 38.9;  N = 3.3.  
C<sub>17</sub>H<sub>11</sub>NOBr<sub>2</sub> requires -  Br = 39.5;  N = 3.5. %

The Intramolecular Ullmann Condensation of N-(o-Bromo-
benzoyl-)-8-bromo-1-naphthylamine

\[
\begin{array}{c}
\text{Br} \\
\text{Br} \\
\text{CO} - \text{NH} \\
\end{array}
\rightarrow_{\text{Cu}}^{250-60^\circ\text{C}}
\begin{array}{c}
\text{CO} - \text{NH} \\
\end{array}
\]

N-(o-bromobenzoyl-)-8-bromo-1-naphthylamine (1.8g.) and copper bronze 1.6g.) were heated together in an oil bath at 250-60° C. for 2 hours. On cooling, the contents of the flask were dissolved out with acetone, the copper thoroughly extracted as before, the acetone extract evaporated down and the residue dissolved in benzene. A very little black tar failed to dissolve. The cold benzene solution was chromatographed on alumina.

Three yellow bands washed through, first, on development with benzene, and these all yielded mere traces on evaporation of the solvent. Following these came two brown bands, the lower of which yielded 0.22g. buff material, m.p. 137-147° C. Recrystallisation of this from methanol yielded material which was still impure, m.p. 150-60° C. The upper of the two brown bands yielded 0.10g. material, m.p. 95-8° C. This also could not be purified.
satisfactorily. Both of these brown bands contained no halogen.

Five less definite bands were now left on the column and these were cut out. A band was noted in the same place as the one in the corresponding Ullmann condensation already described, which had yielded high melting material. Accordingly, this band was eluted with ethanol to yield a pale yellow solution, which on evaporation, left approximately 10 m.g. of slightly off-white halogen-free material, m.p. 224-30°C. This, on mixing with the product of the Beckmann rearrangement of mesobenzanthrone oxime (m.p. 234°C) melted at 225-8°C. With H₂SO₄, both compounds gave yellow solution with a faint yellow fluorescence.

It appears therefore, that these two compounds are identical and hence the Beckmann product must have the structure shown above.

---

An initial Ullmann condensation in which the temperature was maintained at 210-20°C yielded six more or less pure compounds, but all contained halogen, and it was concluded that a higher temperature was necessary for the condensation to occur.

---

The Preparation of Phenanthridone

Fluorenone (5.4g.) was dissolved in conc. H₂SO₄ (60 m.l.) and sodium azide (3g.) was added to the deep red solution over a period of half an hour. The
flask became warm, and only small portions could be added at a time owing to considerable frothing. This slackened towards the end of the addition. Stirring was continued for a further \( \frac{1}{2} \) hour, when the addition was complete and the contents of the flask were poured onto ice, with stirring. After standing overnight, the white ppt was collected, washed well with water and dried. Yield of phenanthridone, m.p. 293°C was 5.8g. (quantitative).

The Oxidation of Phenanthridone

Phenantridone (1g.) was dissolved in conc. H₂SO₄ (5 m.l.) and the solution poured into 100 m.l. water. The finely divided suspension thus obtained was made alkaline with 10% aqueous NaOH and made up to about 200 m.l. KMnO₄ (6g.) was now added and the whole refluxed for 17 hours. The MnO₂ was then filtered off and the filtrate concentrated down to about thirty m.l. It was acidified with conc. HCl, the resulting suspension allowed to cool, and thoroughly extracted with ether. The solid which had separated, was finally heated on the steam bath with ether, and the combined ethereal extracts were evaporated down to
leave 0.45g. buff material. This was washed well with water and on drying, this melted at 180-195°C., on slow heating, and 208-12°C. on quick heating. There was no depression of melting point on admixture with an authentic sample of phthalic acid.

----------

Preliminary experiments in which the initial solution in H₂SO₄ was omitted, but the phenanthridone was merely finely ground, yielded no phthalic acid.

----------

The Oxidation of mesoBenzanthrone lactam

\[
\begin{align*}
\text{mesoBenzanthrone lactam (0.5g.)} & \quad \xrightarrow{\text{Alk., KMnO}_4} \quad \text{carboxylic acids} \\
\end{align*}
\]

mesoBenzanthrone lactam (0.5g.) was dissolved in conc. H₂SO₄ (4 m.l.) and the solution added with stirring to 50 m.l. of water. The suspension was made alkaline with a little 6 N aqueous NaOH and the whole diluted to about 125 m.l. KMnO₄ (3g.) was added and the whole refluxed for 17 hours. The suspension was filtered hot, and the alkaline filtrate concentrated down to small volume, acidified, and ether-extracted. Removal of the ether left a pale yellow oil, which solidified to a white crystalline solid on solid/trituration with 1 m.l. of water. This melted
(quick heating) at 205-10°C, and was proved to be phthalic acid by the fact that the melting point was not depressed on admixture with an authentic sample. The material gave a strongly positive fluorescein test, on fusing with resorcinol and ZnCl₂, and making alkaline. As final confirmation, the aniline salt was prepared. m.p.: 154°C.

The product gave no colour with conc. H₂SO₄, indicating the complete absence of naphthalic acid, a trace of which gives a deep red colour with purple fluorescence in H₂SO₄. No naphthalic acid was obtained in a second oxidation of some crude Beckmann product, so there seems little doubt that the lactam has the structure given above, and that none of the other isomer is formed as a result of the Beckmann rearrangement of mesobenzanthrone oxime.

The Beckmann Rearrangement of 4-Benzoylmesobenzanthrone oximes

4-Benzoylemesobenzanthrone oximes (0.1g.), the product of an 8 hour oximation of 4-benzoylemeso-benzanthrone, was dissolved in dry ether (10 m.l.), and PCl₅ (0.15g.) was added in portions with shaking.
The whole was then refluxed for 10 minutes, a clear yellow-brown solution resulting, and the ether was then removed by evaporation on the steam bath. The residual brown oil yielded an orange solid on trituration with water. Extraction now with ether dissolved only a part of this orange solid, and purification of the ether-soluble part by passage through a short alumina column (3" x ½") gave a yellow solution which deposited material, m.p. 230-40°C. This gave no depression with the starting material on mixed melting point.

Extraction of the ether-insoluble portion with benzene, followed by evaporation of the solvent, yielded yellow needles, m.p. 268°C. There was not enough of this material for analysis.

The melting point of a mixture of this material with the product of the reaction of hydrazoic acid on 4-benzoylmesobenzanthrone (m.p. 265-70°C) was 265-7°C. As the constitution of this product was proved by hydrolysis, the Beckmann product must have the structure shown above.

An initial attempted rearrangement, using H₂SO₄ instead of PCl₅ in ether, yielded only unchanged oximes, as did another experiment with PCl₅ in acetyl chloride.

The rearrangement has not gone to completion in the experiment described above, as the amount of unchanged material was considerably more than that of the anilide.
The Schmidt Reaction

The Action of Hydrazoic acid on 4-Benzoylmesobenzanthrone

4-Benzoylmesobenzanthrone (0.5g.) was dissolved in conc. $\text{H}_2\text{SO}_4$ (10 m.l.) and sodium azide (0.5g.) added to the well stirred solution. After three hours stirring at room temperature, the solution was poured into 80 m.l. water. The dark yellow precipitate was collected, and washed well with water to remove sulphate. On drying in the oven, this melted at 265-70°C. Yield 0.43g. (85%).

A mixture with the Beckmann rearrangement product of 4-benzoylmesobenzanthrone oxime (m.p. 268°C) had a melting point of 265-7°C.

Recrystallisation from glacial $\text{CH}_3\text{COOH}$ with a little charcoal gave yellow prisms, m.p. 268-70°C.
Analysis: Found -  
C = 79.6;  H = 4.6  N = 4.7.

\[ C_{1r5}H_{4r}NO_2 \] requires  
C = 82.5;  H = 4.3;  N = 4.0%  

As the sample sent for analysis appeared to be pure, a bad analysis seems to be indicated.

**Hydrolysis:** The reaction product (0.3g.) was boiled under reflux with a 1:1:1 mixture by weight of CH\(_3\)COOH, H\(_2\)SO\(_4\), and water (60 m.l.), for 50 hours, and the whole was then poured into water (450 m.l.). The precipitate was collected and dried, and extracted with cold aqueous \( \text{Na}_2\text{CO}_3 \) solution. It dissolved completely, and acidification yielded after drying, 0.228g. mesobenzanthrone-4-carboxylic acid (96.5%), m.p. 310-15\(^\circ\)C. There was no depression on mixed melting point with a synthetic sample, m.p. 314-15\(^\circ\)C.

The original aqueous acidic liquors were now made alkaline with \( \text{NaOH} \), and thoroughly shaken out with ether. The ethereal extract was dried and evaporated to yield red prisms, m.p. 160-170\(^\circ\)C. This was extracted with warm conc. HCl and filtered. The clear acid solution was made alkaline and extracted with ether, to give 0.003g. pure 4-aminomesobenzanthrone, m.p. 220-2\(^\circ\)C. (literature 223/4\(^\circ\)C.). This represents a total yield of amine of approximately 1%.
The Action of Hydrazoic acid on 1-Benzoylnaphthalene

1-Benzoylnaphthalene (0.5g.) was dissolved in a mixture of CCl₃COOH (7.5g.) and H₂SO₄ (0.75 m.l.) at 50°C. Sodium azide (0.2g.) was added and the temperature rose spontaneously to 93°C. When this initial vigorous reaction had ceased, gentle heating was continued, the temperature being maintained at about 60°C. The addition of a further 0.1g. of sodium azide after ½ hour produced no further rise in temperature, so after a total of 1 hour, the reaction mixture was poured into 150 m.l. water. The precipitated solid was collected and resuspended in about 50 m.l. of water to ensure complete removal of sulphate. It was collected and dried. Yield 0.43g. (85%).
Hydrolysis: The reaction product (0.3g.) was boiled under reflux for \( \frac{1}{2} \) hours with a 1:1:1 mixture by weight of \( \text{CH}_3\text{COOH} \), \( \text{H}_2\text{SO}_4 \) and water (5.0 m.l.). At the end of this time all oily material had disappeared leaving a clear brown solution. On cooling, buff needles crystallised out (0.16g.) This was extracted with boiling water (5 m.l.) and the water-insoluble material crystallised from ethanol to give colourless needles, m.p. 150-1\textdegree\text{C}. There was no depression on mixed melting point with an authentic sample of 1-naphthoic acid.

The original acid liquors were now made alkaline and steam distilled. Ether extraction of the aqueous distillate removed 0.07g. of a brown oil, which was shown to be aniline by Runge’s test. It was completely acid-soluble.

The amount of aniline obtained is in agreement with the quantity of 1-naphthoic acid, and both indicate the presence in the Schmidt product of approximately 80\% of 1-naphthanilide.

Ether extraction of the alcoholic liquors from which the aniline was removed by steam distillation, yielded 0.01g. of a brownish-purple solid. This formed a hydrochloride, m.p. 240-250\textdegree\text{C}. (1-naphthylamine hydrochloride melts at 260\textdegree\text{C}.).

This quantity of 1-naphthylamine indicates the presence of approximately 5\% of \( \text{N} \)-benzoyl-1-naphthylamine in the Schmidt product.
The Detection of Oxonium salts of mesoBenzanthrone.

The Kofler contact technique described on page 74 yielded the data embodied in the following diagrams:

- **mesoBenzanthrone** vs. **Picric acid**
  
  - Data points:
    - 171
    - 138
    - 142
    - 115
    - 122

- **mesoBenzanthrone** vs. **Trichloroacetic acid**
  
  - Data points:
    - 171
    - 88
    - 95
    - 47
    - 55

- **mesoBenzanthrone** vs. **Trinitrobenzene**
  
  - Data points:
    - 171
    - 138
    - 140
    - 116
    - 123

- **mesoBenzanthrone** vs. **mesoBenzanthrone-H₂SO₄ complex**
  
  - Data points:
    - 171
    - 140
    - 184
Goldschmiedt and Schmidt (41) quote m.p. for fluorenone picrate of 94°C. Meyer (39) quotes m.p. for phenanthraquinone trichloroacetate of 138°C. and fluorenone trichloroacetate of 58°C.

The preparation of fluorenone trichloroacetate by the same method as that used by Meyer, yielded yellow plates, m.p. 37°C, confirming the melting point indicated by the microscope experiment, and not long orange needles, m.p. 58°C as reported by Meyer.

**Experiment to determine the proportion of mesobenzanthrone and trichloroacetic acid in the complex.**

0.23g. (1/1000 mole) mesobenzanthrone were melted with 0.1635g. (1/1000 mole) of trichloroacetic acid, the melt thoroughly mixed by stirring, and then cooled. A sample of this melted over a range from 94°C to 150°C.

0.23g. of mesobenzanthrone was melted with 0.3270g. (1/500 mole) of trichloroacetic acid as above. A sample of the cooled melt melted at 94-5°C.

0.23g. of mesobenzanthrone was melted with 0.4905g (1/333 mole) of trichloroacetic acid. A sample of the cooled melt melted over a range from 63-80°C.

Hence it can be concluded that the complex must have the composition \( \text{C}_{17}\text{H}_{10}\text{O(CCl}_3\text{COOH)}_2 \).

**The Reduction of mesobenzanthrone with Aluminium isopropoxide**

**The Preparation of Aluminium isopropoxide**
Isopropyl alcohol (200 m.l.) was refluxed over quicklime (10 g.) for two hours on a water-bath, and then distilled off. The dry alcohol (100 m.l.) was immediately boiled under reflux with a CaCl₂ guard tube on the condenser. Aluminium turnings (5 g.) and a small crystal of mercuric chloride were added to the vigorously boiling alcohol, and the whole refluxed for 5 hours. The flask was cooled, stoppered and kept in a desiccator. When required, the solid cake of isopropoxide was heated on the steam bath and the appropriate quantity poured into a measuring cylinder.

The Reduction of 4-Benzoylmesobenzanthrone

Aluminium isopropoxide solution (4 m.l.) was diluted with anhydrous isopropyl alcohol (20 m.l.) and 4-benzoylmesobenzanthrone (0.2 g.) was added. The solution was heated on the steam-bath with a Hahn condenser set for slow distillation. After three hours, tests with the "acetone test reagent" - 2:4-dinitrophenylhydrazine (0.25 g.) in HCl (42 m.l.) and water (200 m.l.) - indicated that no further acetone was being produced, and the remaining isopropyl alcohol was distilled off. The cooled residue was treated with dilute H₂SO₄ and thoroughly extracted with benzene. The benzene extract was concentrated and chromatographed on alumina. A small quantity of a yellowish-brown solid was obtained, m.p. 60-90°C, but most of the
product consisted of non-crystallisable oil.

The Reduction of mesoBenzanthrone

mesoBenzanthrone (0.5 g.), aluminium isopropoxide solution (10 m.l.) and anhydrous isopropyl alcohol (20 m.l.) were refluxed for 20 hours. The flask was then fitted with a Hahn condenser containing methanol and slow distillation was carried out till all the acetone present was removed and the volume was reduced to approximately 10 m.l. A further quantity of isopropoxide solution (5 m.l.) and isopropyl alcohol (20 m.l.) was then added and the solution refluxed for a further 20 hours. The acetone was then distilled off again and the solution concentrated to about 10 m.l. When cold, the residue was treated with dilute H$_2$SO$_4$ and the acid suspension extracted with hot benzene. The concentrated benzene extract was chromatographed on alumina, and the chromatogram developed with benzene. A colourless zone exhibiting strong purple fluorescence under the ultra-violet lamp passed rapidly down the column yielding a white solid on washing through and removing the solvent. 0.37 g. (75%) m.p. 75-7° C. This was recrystallised from ethanol to give almost
colourless plates: m.p. 80-2°C.

**Analysis:** Found: \( C = 94.3; \ H = 5.3 \)

\( C_{17}H_{12} \) requires \( C = 94.4; \ H = 5.6 \%

The product formed a picrate; red needles from alcohol, m.p. 110-1°C (lit: mesobenzanthrene picrate. m.p. 110-1°C).

The hydrocarbon dissolved in conc. \( \text{H}_2\text{SO}_4 \) to a red solution with faint red fluorescence.

---

An initial experiment in which 0.2g. of meso/benzanthrone was refluxed with aluminium isopropanoxide solution for only three hours yielded 0.10g. (52%) of mesobenzanthrene, with 0.08g. (40%) of unchanged mesobenzanthrone.

A further reduction of 5g. of mesobenzanthrone in which alternate refluxing and slow distillation was carried out till no further acetone was formed (40 hours) yielded 3.5g. of mesobenzanthrene (75%).

---

**The Reduction of Anthrone.**

![Anthrone reaction diagram]

Anthrone (0.5g.) aluminium isopropanoxide solution
(10 m.l.) and anhydrous isopropyl alcohol (20 m.l.) were refluxed for 40 hours and slow distillation was then carried out with a Hahn condenser containing methanol. When the volume was small, dilute $\text{H}_2\text{SO}_4$ was added, and the acid solution extracted with hot benzene. On cooling, the benzene extract deposited pale yellow needles of anthracene, m.p.: 215-16° C. There was no depression on a mixed melting point determination with an authentic specimen of anthracene.

Evaporation of the benzene yielded more anthracene, corresponding in all to a practically quantitative yield.

--------

A further reduction in which isopropyl alcohol was replaced by xylene, but the conditions were otherwise the same, gave a quantitative yield of anthracene.

A third reduction was worked up chromatographically, and a yellow zone was noted on the column after the anthracene had washed through. This became pink on exposure to light for some time. It washed through to give a yellow non-fluorescent solution which soon became a straw colour on exposure to the air, and developed a blue fluorescence when viewed under the ultra-violet lamp. Removal of the solvent yielded a further trace of anthracene (m.p. and mixed m.p.). It is suggested that this material was a little dihydroanthranol which was dehydrated on exposure to the air, to anthracene.

--------
The Reduction of 3-Chloromesobenzanthrone

Pure 3-Chloromesobenzanthrone (1g.), aluminium isopropoxide solution (15 m.l.) and anhydrous isopropyl alcohol (30 m.l.) were gently refluxed for 18 hours. Alternate distillation and refluxing was then carried out until no acetone was produced after 1 hour's refluxing. The solution was then concentrated down and the cooled residue treated with dil. H₂SO₄. The acid suspension was then thoroughly extracted with hot benzene. The benzene extract was concentrated down, cooled and chromatographed on an alumina column (18" x ½"). A 4:1 mixture of 60/80 light petroleum and benzene was used for development. A blue-fluorescent zone rapidly passed down the column and on washing through and removing the solvent 0.63g. (65%) of buff material was left, m.p. 106-9°C. This was recrystallised from 60/80 light petroleum to give slightly off-white rosettes, m.p. 110°C.

Analysis:

Found: C = 81.2; H = 4.4; Cl = 13.8.

C₁₇H₁₁Cl requires: C = 81.4; H = 4.6; Cl = 14.2%.

An initial experiment with commercial 3-chloro/
mesobenzanthrone gave a small yield of impure material.

A further reduction in which the quantity of isopropoxide solution was doubled, but the method was otherwise similar to the experiment detailed above, gave a 20% yield of 3-chloromesobenzanthrene.

The Reduction of 3-Bromomesobenzanthrene

![Chemical Structure](image)

The quantities of materials, time of reaction and method of purification were all identical with those described above for the reduction of 3-chloromesobenzanthrone. The yield of pure 3-bromomesobenzanthrene, m.p. 116°C, was 0.7g. (70%). 20% of unchanged 3-bromomeso/benzanthrone was also obtained.

The product crystallised from 100/120 light petroleum with a little charcoal, as clusters of buff needles, m.p. 116°C.

Analysis: Found

\[ C = 69.2; \quad H = 3.7; \quad Br = 26.4 \]

\[ C_{17}H_{13}Br \] requires: \[ C = 69.1; \quad H = 3.7; \quad Br = 27.1\% \]

An initial experiment with commercial 3-bromo/mesobenzanthrone yielded a small quantity of impure material.

A further reduction in which the quantity of the
isopropoxide solution was doubled, but the method was otherwise similar to the experiment described above, gave a 40% yield of 3-bromomesobenzanthrene.

Thus in both of the halogenomesobenzanthrones we have dealt with, an excess of isopropoxide reagent is not desirable.

--------

The Reduction of 4-Benzylmesobenzanthrone

![chemical structure](image)

4-Benzylmesobenzanthrone (0.5g.), aluminium isopropoxide solution (15 m.l.) isopropyl alcohol (20 m.l.) and benzene (100 m.l.) were refluxed for 30 hours, alternate distillation and refluxing being carried out over the last 5 hours of the heating. The solution was concentrated, and the residue treated with dilute H₂SO₄. The benzene layer was separated off and further quantities of hot benzene were added in order to thoroughly remove all organic material from the aqueous phase. The benzene extracts were combined and concentrated down to 15-20 m.l. and the cold solution chromatographed on alumina (12" x 1"). On development with benzene three zones appeared on the column. A colourless zone with the purple fluorescence
typical of the mesobenzanthrene, washed through first and yielded only a trace of solid. A yellow zone followed which deposited yellow prisms on washing through and concentration of the solution to small volume. m.p. 127-8°C. (20 m.g.)

Analysis:

Found

$C = 90.8; H = 6.0$

$C_{24}H_{12}$ requires

$C = 94.1; H = 5.9$

The carbinol $C_{24}H_{12}O$ however requires: $C = 89.5; H = 5.6%$

The analysis suggests, then, that in this case, the carbinol has actually been formed. The uppermost zone was yellow and yielded 0.2g. of unchanged 4-benzylmesobenzanthrone.

The Attempted Reduction of 3-Nitromesobenzanthrone

3-Nitromesobenzanthrone (0.5g.) - prepared by the nitration of mesobenzanthrone in acetic acid-aluminium isopropoxide solution (10 m.l.), and anhydrous isopropyl alcohol (10 m.l.) were refluxed for 6 hours. The solution rapidly became brown in colour, and dark coloured material began to separate towards the end of the heating. The reduction was stopped before acetone had ceased to be formed because of the decomposition which seemed to be occurring. The product was worked up in the usual manner, and the purple fluorescent zone on the column yielded only a trace of solid. The only substantial amount of material obtained from the column proved to be unchanged 3-nitromesobenzanthrone.
The Attempted Reduction of 11-Aminomesobenzanthrone

11-Aminomesobenzanthrone (1g.), aluminium isopropoxide solution (15 m.l.) and anhydrous isopropyl alcohol (25 m.l.) were refluxed for 60 hours, when no further acetone could be detected on distillation. The reaction mixture was worked up as before, but only a little unchanged 11-aminomesobenzanthrone was obtained on chromatographic purification.

---------------

The Action of POC1₃ and PCl₅ on mesoBenzanthrone

mesoBenzanthrone (0.5g.) was dissolved in POC1₃ (10 m.l.) and refluxed gently for 5 hours with PCl₅ (0.65g.). The POC1₃ was then distilled off at atmospheric pressure from an oil bath and the residue was triturated with water to yield a dark coloured solid. This was extracted with boiling benzene to give a solution with a deep-green fluorescence in daylight. Concentration of the solution followed by chromatography on a column of alumina (8" x 1") gave a yellow zone which moved rapidly down the column and was washed through to give a yellow solution with vivid green fluorescence. Concentration of the solution to about 10 m.l. gave orange micro-needles, m.p. 390°C. This material did not vat with alkaline hydrosulphite; gave a strongly positive Beilstein test for halogen; and did not dissolve in H₂SO₄ even on standing for an hour. The H₂SO₄ suspension
exhibited a faint yellow fluorescence under the ultra-violet lamp. The chlorine was not removed by boiling with alcoholic KOH.

Molecular weight determination by the Rast method gave values of 460 and 520.

Analysis:

\[
\text{Found} \quad C = 81.8; \quad H = 3.4; \quad Cl = 14.1.
\]

\[
\text{C}_3\text{H}_2\text{Cl}_2 \text{ requires } C = 81.8; \quad H = 4.0; \quad Cl = 14.2\%.
\]

The analysis proves the absence of oxygen, and this, coupled with the absence of the red meso/benzanthrone colour with conc. H\(_2\)SO\(_4\), suggests a 7:7'-dibenzanthronyl, with two chlorine atoms somewhere in the molecule.

Further development of the column caused material to pass through which gave a deeper yellow solution in benzene, and also had a green-fluorescence. There was no clear separation between this and the preceding material. This second zone yielded red material, m.p. 160\(^\circ\)C approximately, which was separated by benzene extraction into the orange material already isolated, m.p.: 390\(^\circ\)C, and a red solid melting at 320\(^\circ\)C, with sintering at 290-3\(^\circ\)C. The material dissolved slowly in conc. H\(_2\)SO\(_4\) to a very pale orange coloured solution with a yellow fluorescence under the ultra-violet lamp. On warming, the solution became green.

The total yield of material was 0.40g, of which rather more than half appeared to be the orange compound melting at 390\(^\circ\)C.
The Action of POCl₃ and PCl₅ on 3-Chloromesobenzanthrone

3-Chloromesobenzanthrone (0.5g.) was dissolved in POCl₃ (10 m.l.) and refluxed for 5 hours with PCl₅ (0.65g.). The POCl₃ was distilled off from an oil-bath and the residue was triturated with cold water, collected, and dried. Extraction with hot benzene gave a deep green fluorescent solution, which was concentrated down to about 150 m.l. This was a greater volume than had been chromatographed in the previous experiment, but even so, much of the dissolved material crystallised out on cooling and had to be filtered off, before transferring the solution to the column of alumina. No separation was obtained on development with benzene, and a greenish-yellow zone with yellow fluorescence under the ultra-violet lamp washed right through. Removal of the solvent yielded dark brown material, m.p. 160-80°C. Extraction with a large volume of 40/60 light petroleum dissolved out a considerable quantity of the solid, and this petroleum-soluble fraction proved to be unchanged 3-chloromesobenzanthrone, (m.p., H₂SO₄ test, etc.). The material, which was insoluble in light petroleum, now melted at 190-200°C, and in H₂SO₄ solution, slowly developed a purple colour. The amount of this material was small, but it was sufficient to differentiate it from either of the products of the action of POCl₃ and PCl₅ on mesobenzanthrone, with reasonable certainty.

The result suggests, then, that the chlorine atoms in the orange compound obtained in the previous
experiment, are not in the 3:3'- positions.

The Dechlorination of the Dichlorodibenzanthrenyl

The dichlorodibenzanthrenyl (0.1g.) was dissolved in 10% ethanolic KOH (35 m.l.) and Raney nickel alloy (1.0g) was added in portions over a period of ten minutes. Heating was continued for 1½ hours and the hot, filtered, solution was diluted with water and acidified. After standing overnight, the yellow precipitate was collected and dried: 0.08g. m.p. 129-31° C.

The material gave a negative Beilstein test for halogen, and dissolved in H_2SO_4 to a clear yellow-brown solution. It was readily soluble in benzene, alcohol and ether. Recrystallisation from alcohol gave pale yellow crystals, m.p. 128-9° C.

**Analysis:**  Found - C = 83.1; H = 6.1% 

This analysis requires an empirical formula of C_{10}H_7O.

A dibenzanthrenyl would require C = 95.8 and H = 4.2, so this is ruled out immediately. The high solubility of the material is not in agreement with the dibenzanthrenyl structure in any case. The strange aspect is, however, that the analysis does not indicate a hydrocarbon and it is difficult to imagine where oxygen has come from, if this is present in the molecule.
The action of POCl₃ on mesoBenzanthrone

mesoBenzanthrone (0.5g.) and POCl₃ (10 m.l.) were refluxed for 1½ hours. The solution, which was initially red, became dark green after about half an hour. The POCl₃ was distilled off from a water-bath under slightly diminished pressure and the residue cooled and triturated with water. The product after drying was a black solid with greenish lustre.

Extraction of this with hot benzene (1·1½ litres) dissolved only a portion of the solid. Concentration of the solution to about 100 m.l. was accomplished without any dissolved material crystallising out, and the cold solution was chromatographed on an alumina column (30" x 1"). Development was carried out with a 4:1 mixture of benzene 60-80 light petroleum. A greenish yellow zone with a bluish-green fluorescence under the ultra-violet lamp was the first to wash through. It gave a yellow solution with a striking blue-green fluorescence in daylight. On concentration to about 5 m.l. beautiful long silky yellow needles crystallised, m.p. 346-7°C (Townson and Mercer electrical apparatus). This material dissolved slowly in conc. H₂SO₄ to a violet-blue solution and gave a negative Beilstein test for halogen.

Analysis: Found:

\[ \text{C} = 95.0; \quad \text{H} = 4.6. \]

\[ \text{C}_{34} \text{H}_{18} \text{ requires:} \quad \text{C} = 95.3; \quad \text{H} = 4.2. \]

\[ \text{C}_{34} \text{H}_{120} \text{ requires:} \quad \text{C} = 95.3; \quad \text{H} = 4.6\% \]

A zone very similar in appearance to the first one and contiguous with it, but having a rather more
greenish fluorescence than the latter under the ultra-violet lamp, yielded a small dark residue of indefinite melting point. A further green zone above this yielded a negligible amount of material. A yellow zone above this, having a bright yellow fluorescence under the ultra-violet lamp, yielded orange material crystallising from benzene in feathery crystals which did not look pure and had m.p.: 300-10°C. Sublimation of this yielded a little mesobenzanthrone, but the bulk of the material did not sublime at 360°C and remained as a dark glass with a greenish sheen.

A mixture of the pure yellow product (m.p. 346-7°C) with a sample of the yellow hydrocarbon (m.p. 341-2°C) kindly supplied by Professor Zinke, melted at 345-6°C, and it can therefore be deduced that the hydrocarbons are identical.

---------

**The Synthesis of 6-Hydroxymesobenzanthrone**

**The Benzoylation of 2-Naphthyl methyl ether**

2-Naphthyl methyl ether (10g.) was dissolved in tetrachloroethane (50 m.l.) and powdered AlCl₃ (10g.)
added. Benzoyl chloride (10g.) was gradually dropped into the mixture, the temperature being maintained at 25°C. After the addition, which took ½ hour, the reaction mixture was allowed to stand for 2 hours and then poured onto ice. The tetrachloroethane layer was separated and evaporated down to leave a brown oil. This was distilled at atmospheric pressure (B.P. > 360°C) to give a pale yellow oil which solidified on cooling to a yellowish solid: (12.5g.)

This crude product was powdered and extracted five times with hot dilute NaOH solution and finally with hot distilled water. The alkali-insoluble material was dried and weighed (12.0g.) and recrystallised from 60 m.l. of 100/120 light petroleum to yield 9.0g (55%) of 1-benzoyl-2-methoxynaphthalene. m.p. 120-5°C.

The acidified NaOH extracts yielded 0.4g (3%) of 1-benzoyl-2-naphthol. m.p. 130°C.

A second preparation using 50g. of 2-naphthyl methyl ether, gave a 60% yield of the 1-benzoyl-2-methoxynaphthalene, but no 1-benzoyl-2-naphthol was formed.

The Cyclisation of 1-Benzoyl-2-methoxynaphthalene
An intimate mixture of 1-benzoyl-2-methoxy/naphthalene (4g.), AlCl₃ (24g.) and NaCl (6g.) was heated in an oil-bath for 2 hours. The temperature was maintained at 200-10°C. The hot melt was then poured into 750 ml. of dilute HCl, and the suspension allowed to stand overnight. It was then filtered and the clear orange filtrate was made strongly acid by the addition of more conc. HCl. On standing, a yellow precipitate deposited. This was collected and dried, m.p. 110-130°C. Extraction of this material with a large volume of boiling 40/60 light petroleum, followed by filtration and concentration of the petroleum solution yielded yellow needles, m.p. 167-8°C.

Analysis: Found

\[ C = 82.6; \quad H = 4.3. \]

\[ C_{18}H_{12}O_2 \] requires \[ C = 83.1; \quad H = 4.6 \%

The 6-methoxymesobenzanthrone dissolved in conc. H₂SO₄ to a yellow solution with a brilliant green fluorescence.

The Action of Hydrogen bromide on 1-Benzoyl-2-methoxy-naphthalene
l-Benzoyl-2-methoxynaphthalene (5.0g.) was refluxed with glacial acetic acid (75 m.l.) and 48% aqueous HBr (75 m.l.) for 7 hours. The solvent was distilled off till the volume was down to about 100 m.l. A white solid deposited on cooling, m.p. 85-94°C. This product dissolved completely in cold NaOH solution. Acidification followed by recrystallisation of the product from 80/100 light petroleum gave colourless plates, m.p. 118°C.

Mixed melting point determination with 2-naphthol (m.p. 123°C) was 119-23°C. The material gave a green colour with FeCl₃, identical with a 2-naphthol standard.

Treatment of l-benzoylnaphthalene with HBr and CH₃COOH under exactly similar conditions, did not effect removal of the benzoyl-group. A quantitative recovery of unchanged material was obtained.

The Preparation of 6-Hydroxymesobenzanthrone.

6-Methoxymesobenzanthrone (0.2g.) was refluxed with HI (10 m.l.) for one hour and poured into 80 m.l. water. The precipitated solid was collected, dried, and dissolved in benzene. The benzene solution was
passed through a short column of alumina. A yellow zone which passed through yielded unchanged 6-methoxy/mesobenzanthrone, (m.p. and mixed m.p.). A yellow zone at the top of the column resisted elution with alcohol, acetone, pyridine, etc.; was removed by warm aqueous NaOH solution. Acidification yielded material which on recrystallisation from ether gave no depression on mixed melting point with an authentic specimen of 6-hydroxymesobenzanthrone, prepared by the method of Bradley (51).
BIBLIOGRAPHY

(1) Charrier and Ghigi........Gazz Chim Ital. (1932) 62 928.
(2) " Ber. (1936) 69.B. 2211.
(4) " J.A.C.S. (1935) 57. 1322.
(5) Bally and Scholl..........Ber. (1911) 44. 1656.
(7) von Braun and Bayer......Ber. (1925) 58.B. 2667.
(8) Zinke, Ott and Weinhardt..Monatshefte (1950) 81. 878.
(9) Zinke and Ott............Monatshefte. (1950) 81. 1137.
(10) A.G. Perkin..............J.C.S. (1920) 696.
(11) Clemo, Munday and Swan....J.C.S. (1950) 1513.
(15) Beckmann and Liesche......Ber. (1923) 56. 1.
(20) Lothrop....................J.A.C.S. (1941) 63. 1187.
(22) Erdtmann...................Ann. (1933) 505. 195.
(23) Moore and Huntress........J.A.C.S. (1927) 49. 1333.
(24) Schmidt....................Ber. (1924) 57. 704.
(29) von Braun and Heymons...Ber. (1930) 63 502.
(31) Sanford, Blair, Arroya & Sherk. J.A.C.S. (1945) 67 1941
(32) Bachmann and Boatner...J.A.C.S. (1936) 58 2097.
(33) Spielman and Austin...J.A.C.S. (1937) 59 2658.
(34) Briggs and Lyttleton...J.C.S. (1943) 421.
(35) Smith................J.A.C.S. (1943) 70 320.
(36) Alexander......Principles of Ionic Organic Reactions
(1950. Wiley.
(38) Sudborough and Beard.....J.C.S. (1911). 217.
(41) Goldschmidt and Schmidt..Monatshefte (1881).2 15.
(42) Scholl and Seer.........Ber. (1911) 44 1673.
(44) Houben..Das Anthracen und die Anthracinone..p.167.
(47) Chem. Abstr. (1935) 29 2177
(49) Chem. Zent. (1936) 1. 1312.
(50) Clar...........Aromatische Kohlenwasserstoffe (1941) p.299.
(51) Bradley...............J.C.S. (1948) 1178.
(52) Fieser...............J.A.C.S. (1931. 53 3558.
(54) Kharasch et al.......J.A.C.S. (1934) 56 1370.
SUMMARY OF RESEARCH.

1. The benzylcyanation of mesobenzanthrone has been studied and the constitution of the product obtained by hydrolysis of the resulting cyanobenzyl compound has been rigidly established as 4-benzoyl/mesobenzanthrone by synthesis and oxidation.

2. The mechanism of the oxidative hydrolysis of the cyanobenzyl compound has been investigated. Traces of a peroxide intermediate were found to be present, and the reaction appears to involve peroxide formation followed by base catalysed decomposition to yield the ketone.

3. An apparently unique oxidation has been discovered, namely, the conversion of 4-benzylmesobenzanthrone into 4-benzoylmesobenzanthrone under the influence of air in the presence of methanolic KOH. The speed and high yield of this oxidation seem to be unparalleled in the literature. Again, a peroxide intermediate is probably involved.

4. Ketonic derivatives of mesobenzanthrone, the oxime and 2:4-dinitrophenyldrazones have been prepared, as far as we are aware, for the first time. The former has been subjected to a Beckmann rearrangement, and the one resulting lactam identified by synthesis and oxidation. Two oximes of 4-benzoyl/mesobenzanthrone have been prepared and differentiated.

5. mesoBenzanthrone has been found to be resistant to hydrazoic acid, but 4-benzoylmesobenzanthrone has
been found to undergo the Schmidt reaction. The product has been identified by hydrolysis, and shown to be identical with the product of a Beckmann rearrangement of 4-benzoylmesobenzanthrone monoxide. The Schmidt reaction has also been studied with reference to 1-benzoylnaphthalene and the product again identified by hydrolysis.

6. Some molecular complexes of mesobenzanthrone have been investigated using the contact method of Kofler and it was concluded that oxonium salts were formed with certain acids.

7. Reduction of some mesobenzanthrones with aluminium isopropoxide has been found to yield the corresponding mesobenzanthrenes in good yield. Only in one case was there any evidence of carbinol formation.

8. Treatment of mesobenzanthrone with phosphorus oxychloride was found to yield a dibenzanthrenyl which has been shown to be identical with a hydrocarbon obtained by Zinke by the distillation of mesobenzanthrone over zinc dust. In the presence of phosphorus pentachloride a corresponding product was obtained, which contained two chlorine atoms.

9. An interesting removal of a benzoyl group by the action of hydrobromic acid and acetic acid on 1-benzoyl-2-methoxynaphthalene was noted during a synthesis of 6-hydroxymesobenzanthrone. The possibility of this being an example of a reverse Fries reaction has been discussed.
In conclusion, the author wishes to express his gratitude to Dr. N. Campbell, for constant encouragement and valuable advice throughout the period of this work.