STUDIES IN THE AROMATIC HYDROCARBONS

by

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ABSTRACT OF THESIS

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Title of Thesis Studies in the Aromatic Hydrocarbons

2-Benzylidene-2,3-dihydrophenalenone and its isomer 2-benzylphenalenone have been prepared and their structures established by ozonolysis. Homo-naphthalic acid has been identified as a product of oxidation. The structure for an unusual product from the addition of benzaldehyde to 2-benzylidene-2,3-dihydrophenalenone has been postulated. Attempts have been made to prepare homo-naphthalic acid reference samples and to prepare 3 substituted 2,3-dihydrophenalenones.

Ethyl acetoacetate has been condensed with 2-benzylidene-2,3-dihydrophenalenone to give three substituted hydrobenzanthrenes (a) an unsaturated hydroxy ester (b) an unsaturated keto-ester (c) an undehydrated form of (b). Structures have been assigned to several reduction products of (b). The unsaturated keto-ester (b) has been reduced to the keto-ester, decarbethoxylated to the ketone, reduced to the hydrocarbon and aromatized to give 8-phenyl-benzanthrene identical with a compound produced by reduction of a sample of 8-phenyl-mesobenzanthrone.

Some other attempts to prepare 8-phenyl-benzanthrene have been reported.

Use other side if necessary.

To My Parents
and Isobel

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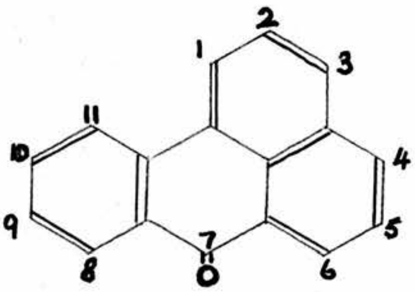
Section V

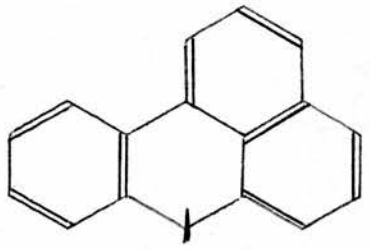
The Structure of Some Intermediates and Reduction Products in the Synthesis of 8-phenylbenzanthrene

INTRODUCTION

The Chemistry of Mesobenzanthrones and Benzanthrenes

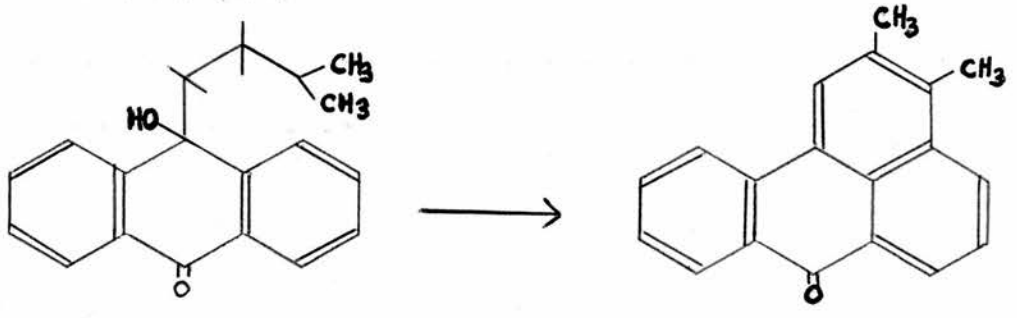
7H-Benz(de)anthracene-7-one consists structurally of anthrone with a benzene ring fused into the 1,9 positions. Reduction of the carbonyl to methylene gives 7H-Benz(de)anthracene. The numbering system of these molecules is shown below.





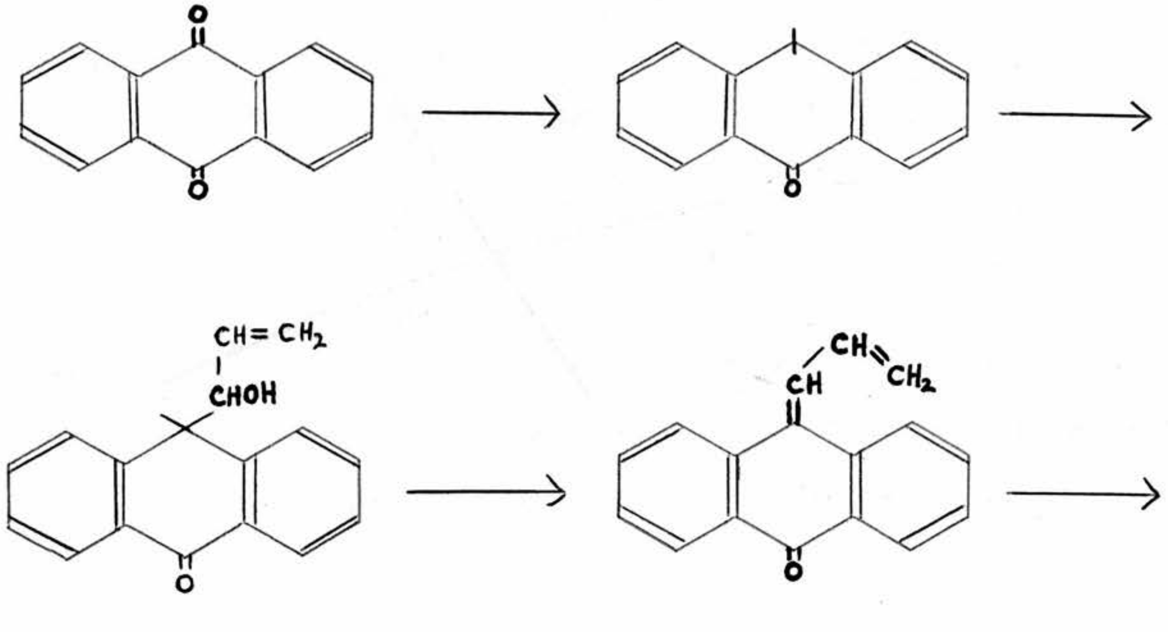
In the literature these two compounds have commonly been termed mesobenzanthrone and benzanthrene and these names will be retained in this thesis except for the systematic naming of new compounds.

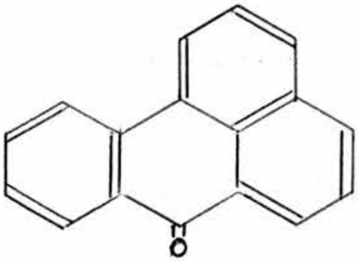
The first recorded synthesis of a mesobenzanthrone nucleus was acheived in 1882 by Liebermann (1) who cyclised meso-isoamyl-oxanthrol I with sulphuric acid to obtain what was subsequently shown to be 2,3-dimethyl-mesobenzanthrone II migration of one of the methyl groups having taken place. Other similar migrations have since been encountered in the series (2)



I II

The first synthesis of unsubstituted mesobenzanthrone III, was carried out by Bally in 1905 (3) by condensation of glycerol with anthraquinone in the presence of sulphuric acid and copper, the anthraquinone first being reduced to the anthrone which then condensed with acrolein produced from the glycerol by sulphuric acid dehydration.



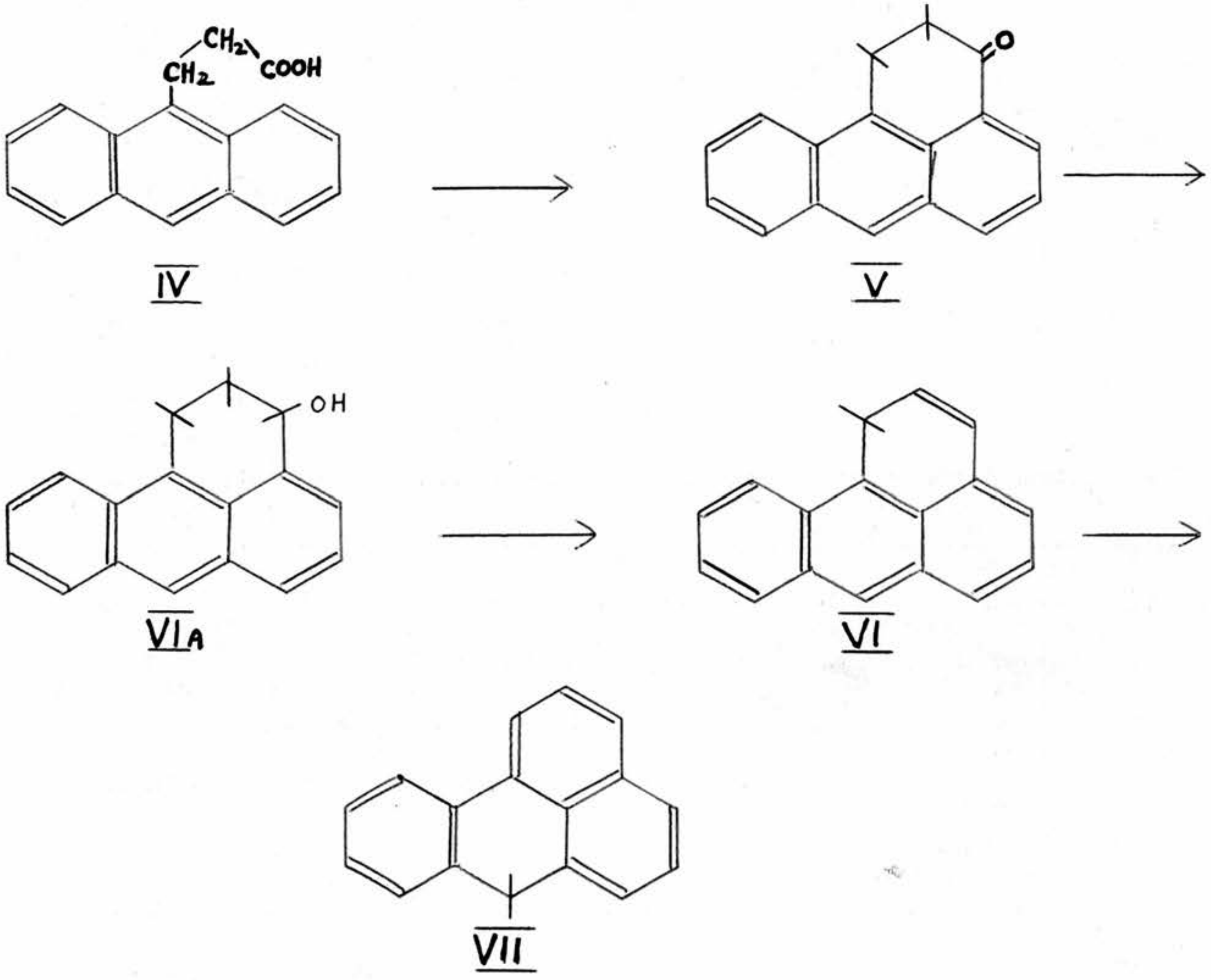


III

This has formed the basis of many subsequent syntheses of mesobenzanthrones substituted in several positions. The mechanism denoted above has been rigidly established (4) as proceeding through a secondary alcohol. This subsequently loses water to yield an alkylidene anthrone which undergoes cyclodehydrogenation.

The mesobenzanthrones are of industrial importance forming the basis of the dibenzanthrone vat dyes. Benzanthrene can be prepared by the reduction of mesobenzanthrone by zinc and pumice (5), by lithium aluminium hydride and aluminium chloride complex (6), or even by heating benzyl-naphthalene at high temperature (7).

Cyclisation of β -(anthranyl-9)-propionic acid IV with stannic chloride to 1'-oxo-1,9-tri-methylene- anthracene V followed by reduction with lithium aluminium hydride and dehydration on an alumina column gave 1H-benz (de)anthracene VI convertible under acid conditions to benzanthrene VII (8).

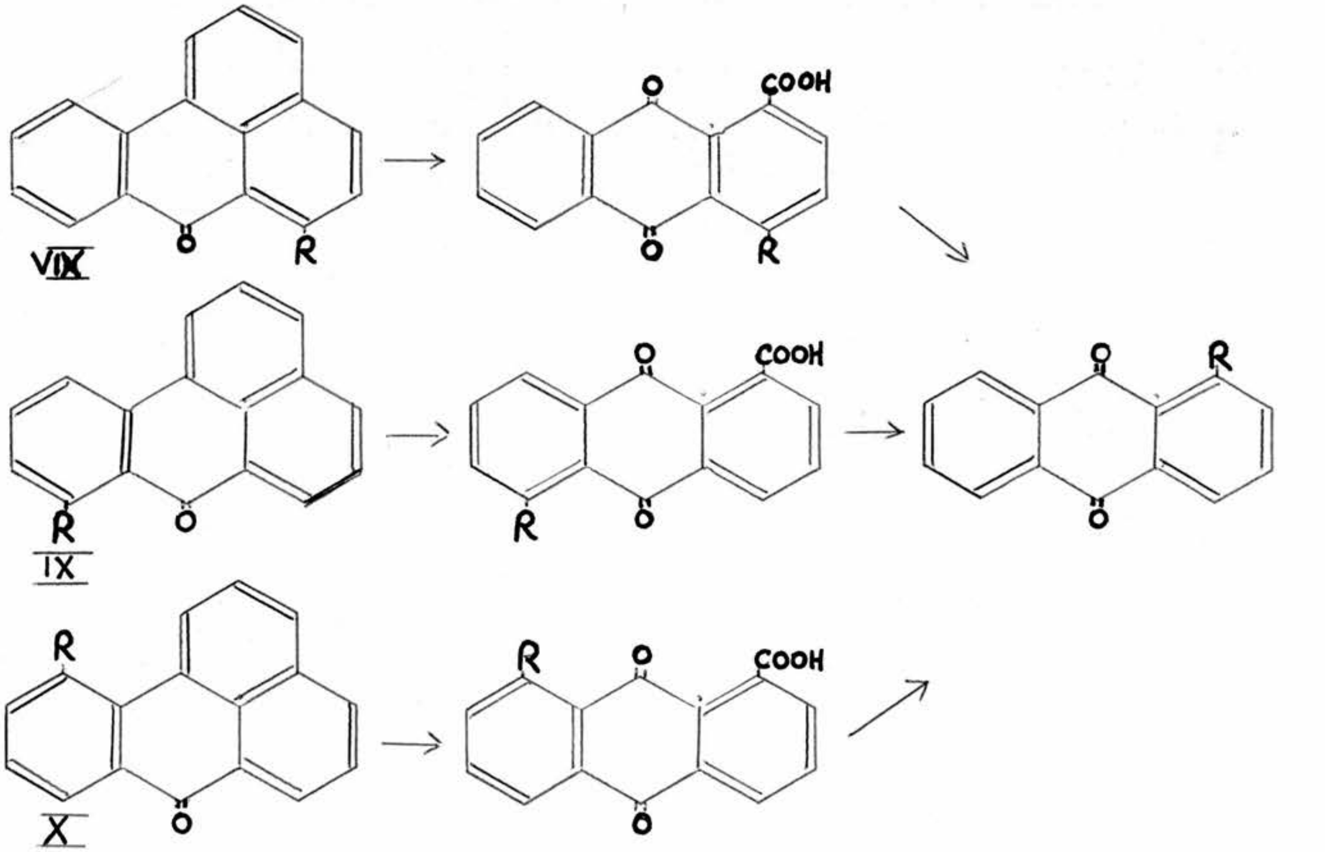


Similar methods have been applied to the synthesis of benzanthrene involving 3H, 4H, 6H, benz(de)anthracenes as intermediates (9).

Benzanthrene is one of the products obtained by heating 1-naphthyl-cycloheptane at 320° with palladium charcoal. (10)

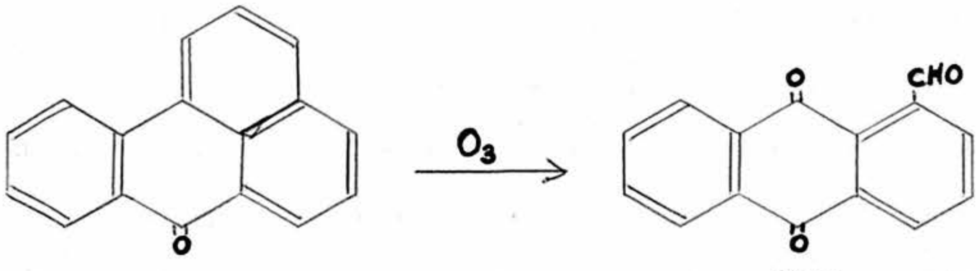
The Properties of Mesobenzanthrones

Mesobenzanthrone is a stable compound, but it can be ruptured with chromium oxide in acetic acid to produce anthraquinone-1-carboxylic acid (11). In the case of a mesobenzanthrone substituted in the anthrone part of the molecule such an oxidation would lead to an anthraquinone-carboxylic acid substituted in the appropriate place, the substituent usually being unaffected by the oxidation (12). Decarboxylation of the acid gives a substituted anthraquinone which may be identified. This degradation technique is limited by the inability to distinguish between 6,8 and 11 substituted mesobenzanthrones VIII, IX and X since identical products are produced in each case.



The yield of substituted products is not always very good (13).

Ozonolysis of mesobenzanthrone is reported (14) as giving the 1-aldehyde XI.



XI

Reductions of Mesobenzanthrones

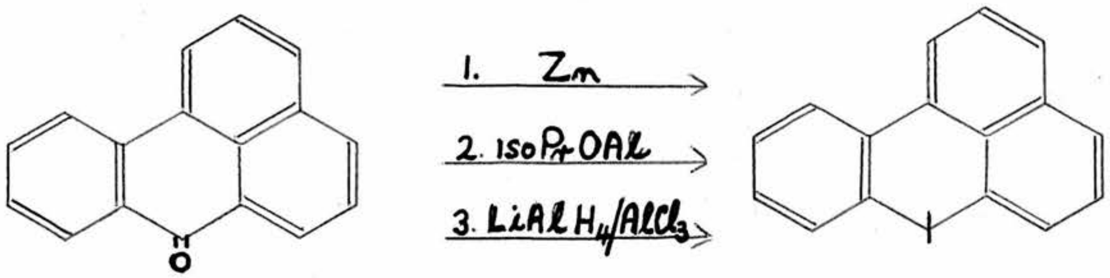
Two types of reduction are possible on a mesobenzanthrone nucleus: (a) reduction of the carbon-carbon skeleton and (b) reduction of the carbonyl group.

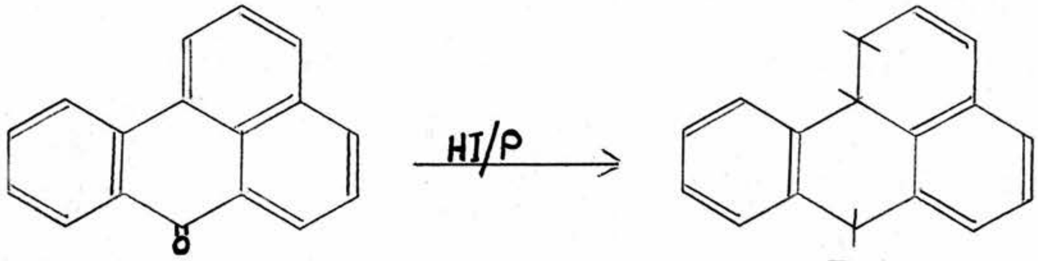
When passed over zinc dust heated on pumice mesobenzanthrone is reduced to benzanthrene (5), while with red phosphorus and hydrogen iodide a dihydro-mesobenzanthrene XII is reported. With zinc dust and alkali another dihydro-mesobenzanthrone was reported XIII (15) but was later shown to be 1,9-trimethylene-10-anthranol (16) which is also formed by the hydrogenation of mesobenzanthrone in the presence of Nickel salts. (17) Further reduction of XIII leads to 1,9-trimethylene-5,6,7,8-tetra-hydro-anthranol. XIIIA Reduction with zinc dust and acetic acid gives a dihydro-mesobenzanthrone XIV (19) which disproportionated to trihydro-mesobenzanthrol XV and mesobenzanthrone in the presence of alkali. Bimolecular reduction products have also been reported (21).

High pressure hydrogenation on the other hand does not attack the angular ring and in the presence of catalysts 1,10-trimethylene-phenanthrene is isolated XVI (22).

Two anomalous reductions have been carried out with a substituted and an unsubstituted mesobenzanthrone. Mesobenzanthrone and aluminium isopropoxide give the hydrocarbon benzanthrene in good yield and not as might be expected the carbinol (23). 6-Hexylmesobenzanthrone is reduced to the hexylbenzanthrene with lithuim aluminium hydride but not with aluminium isopropoxide (24). Lithium aluminium hydride alone is ineffective with mesobenzanthrone.

More recently an excellent reagent for the reduction of the mesobenzanthrone carbonyl cleanly at room temperature has been found in lithuim aluminium hydride and aluminium chloride complex (6).





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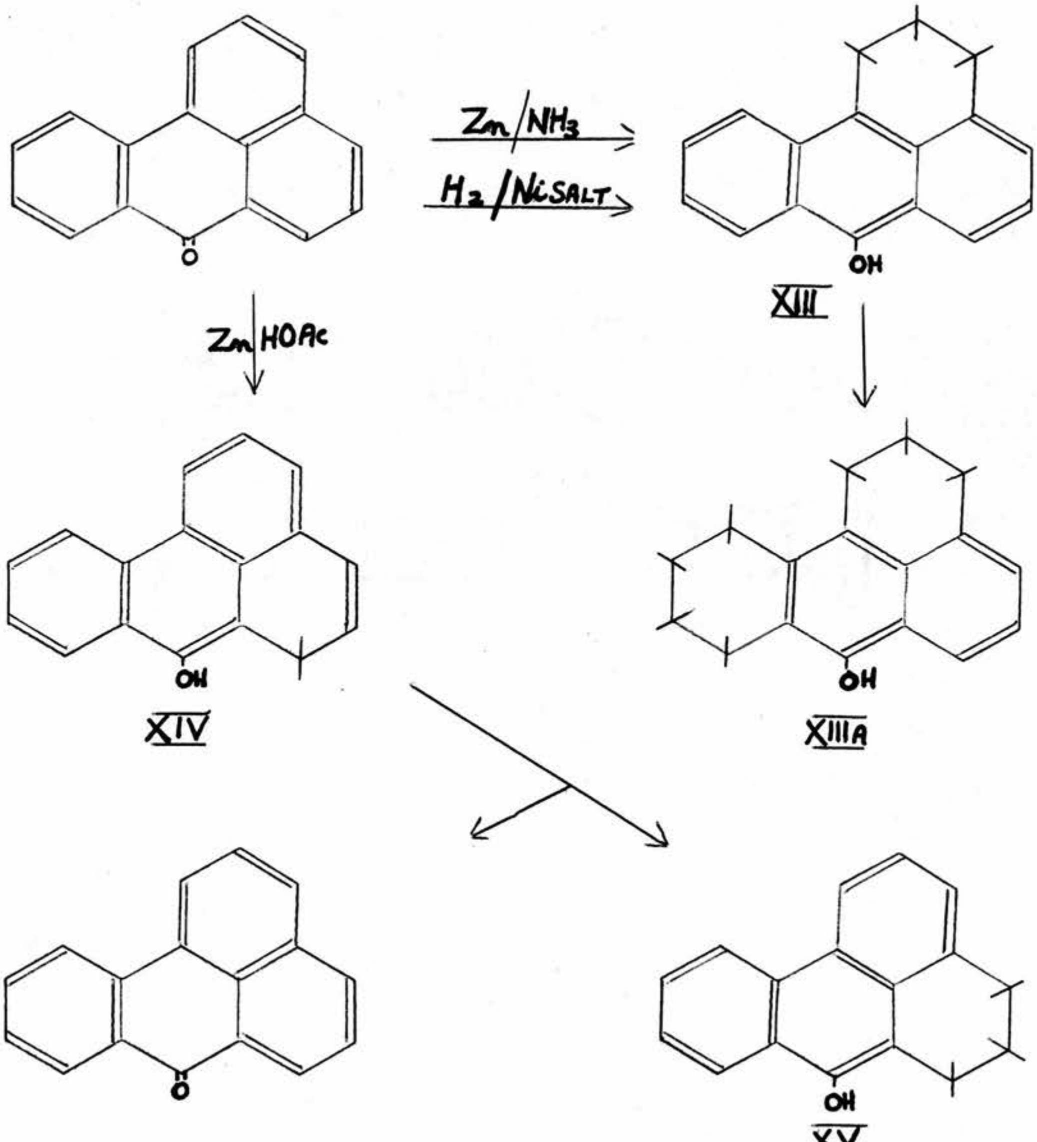
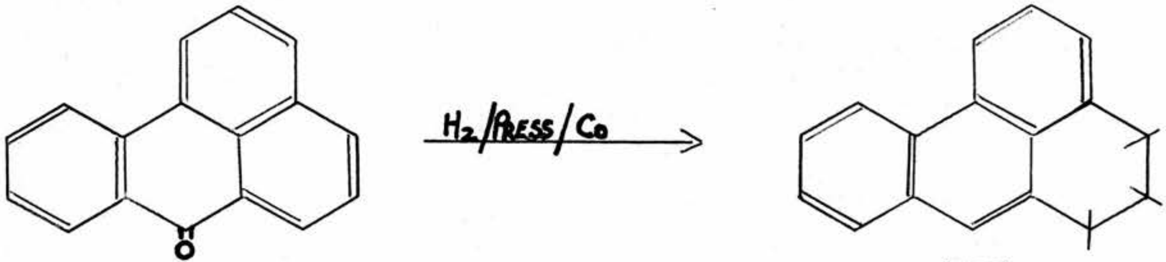


XIII

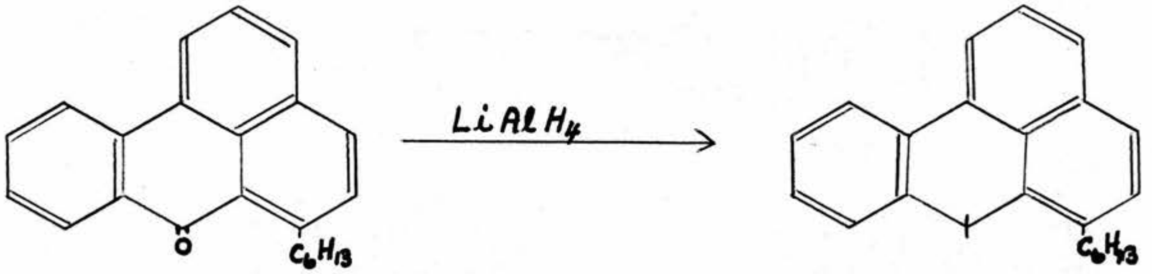
XIV

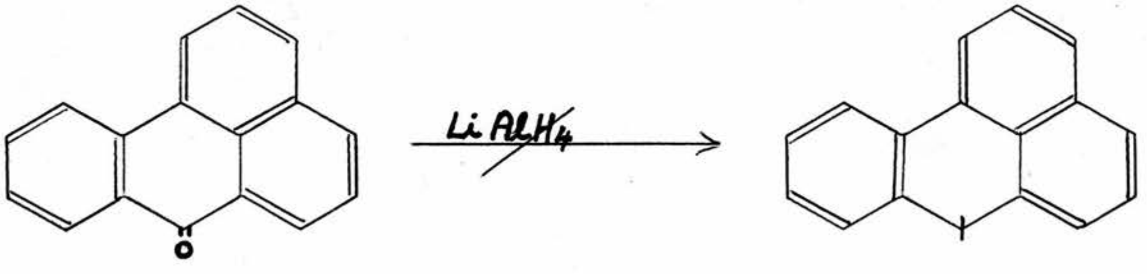
XIIIA

XV



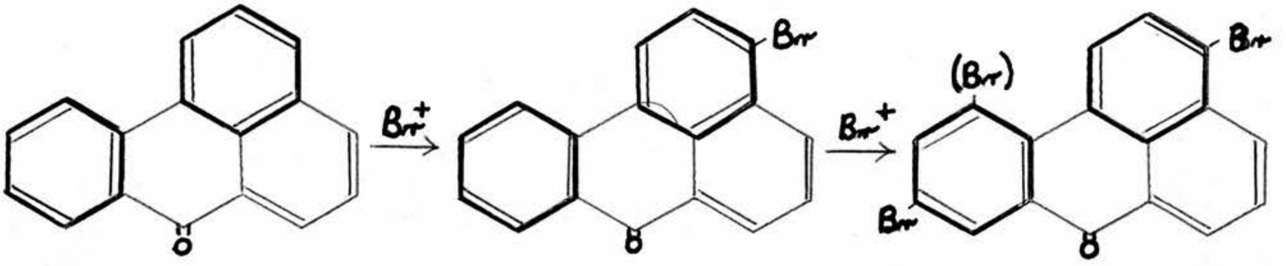
XVI





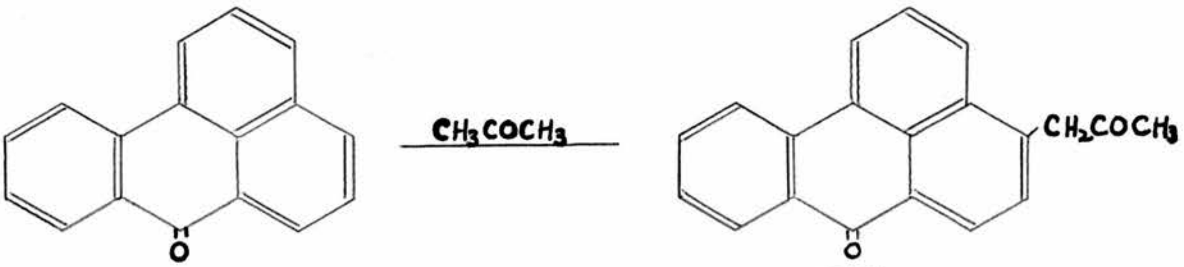
Substitution in the Mesobenzanthrone Nucleus.

Electrophilic substitution occurs in the 3-position (25) but exceptions occur 3-Nitromesobenzanthrone is produced by nitration in nitrobenzene and 2-nitromesobenzanthrone by nitration in acetic acid (26) Disubstitution gives 3.9- or 3.11- products (12, 27, 28).



Electrophilic substitution thus goes as if the diphenyl part of the molecule was the governing factor.

Nucleophilic attack takes place in the 4-position or in the 6-position. Direct amination with sodamide in dimethyl aniline as solvent yields 6-aminomesobenzanthrone with traces of the 4-isomer (29). Reactive methylene groups can be condensed e.g. in the presence of alkali, acetone with mesobenzanthrone gives 4 acetonylmesobenzanthrone XVII (30, 31).

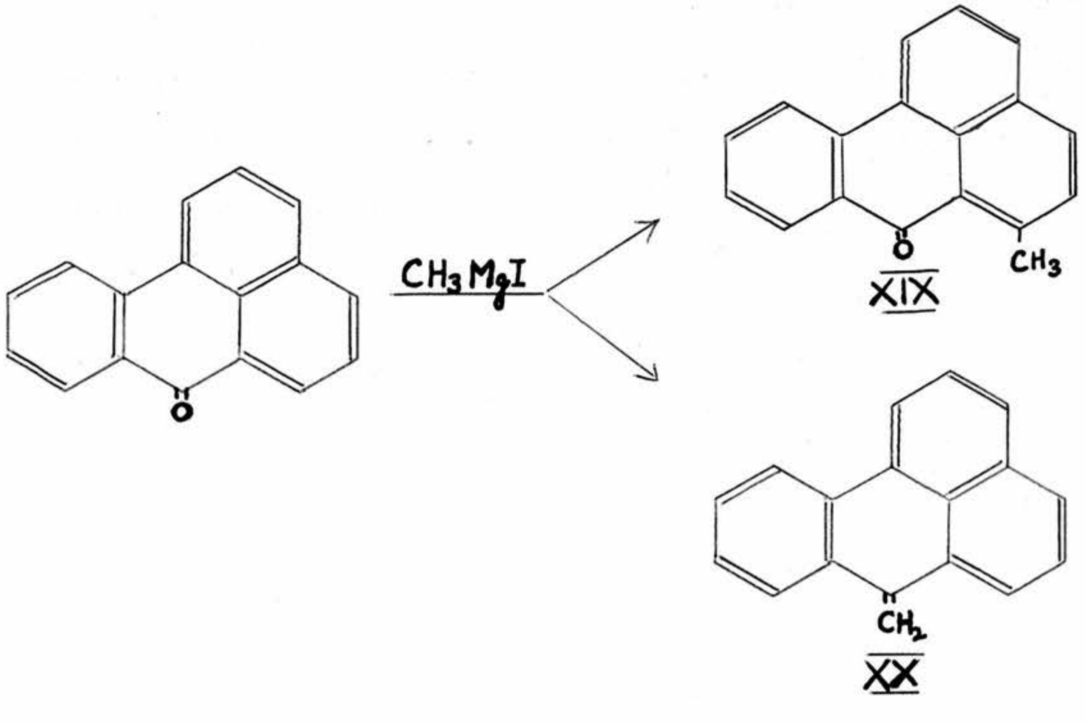


XVII

Properties of the Carbonyl of Mesobenzanthrone.

Apart from its reduction which has been dealt with mesobenzanthrone enters into other carbonyl reactions. Its solution in concentrated sulphuric acid is deep orange with a strong fluorescence probably due to the formation of an oxonium salt. Its weakly basic character is exhibited by its ability to form complex salts with sulphuric acid (32) and trichloro-acetic acid whereas it does not form salts with benzoic or mono chloro-acetic acids. It forms normal carbonyl derivatives - 2,4-dinitrophenyl-hydrazone and oxime - but only under forcing conditions (23).

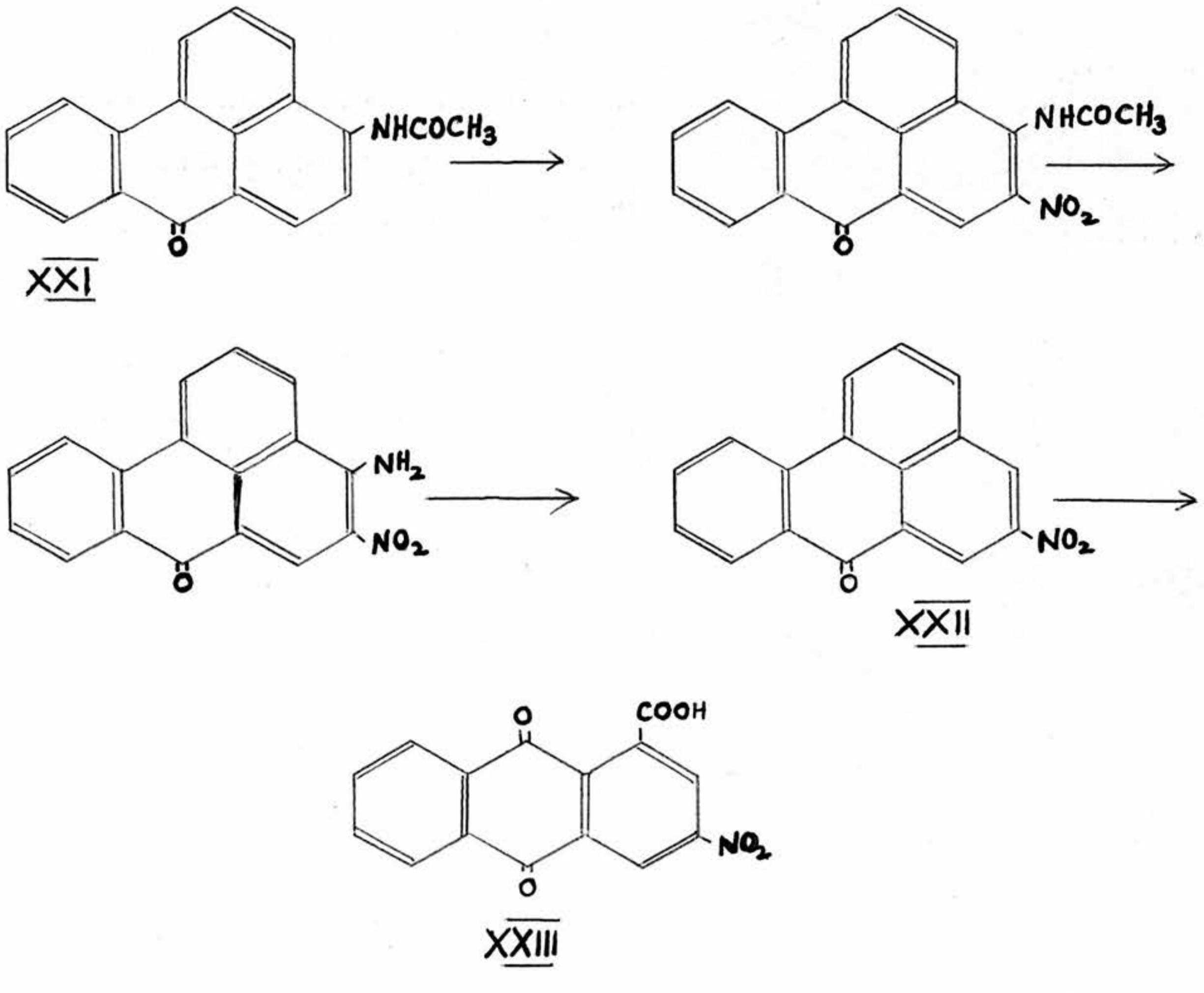
The Grignard reaction of the carbonyl occurs by 1:4 addition to give 6-substituted compounds (13). Methylmagnesium iodide reacts however to give a mixture of 6-methylmesobenzanthrone XIX and 7-methylene-benzanthrene XX (20).



Preparation of Substituted mesobenzanthrones.

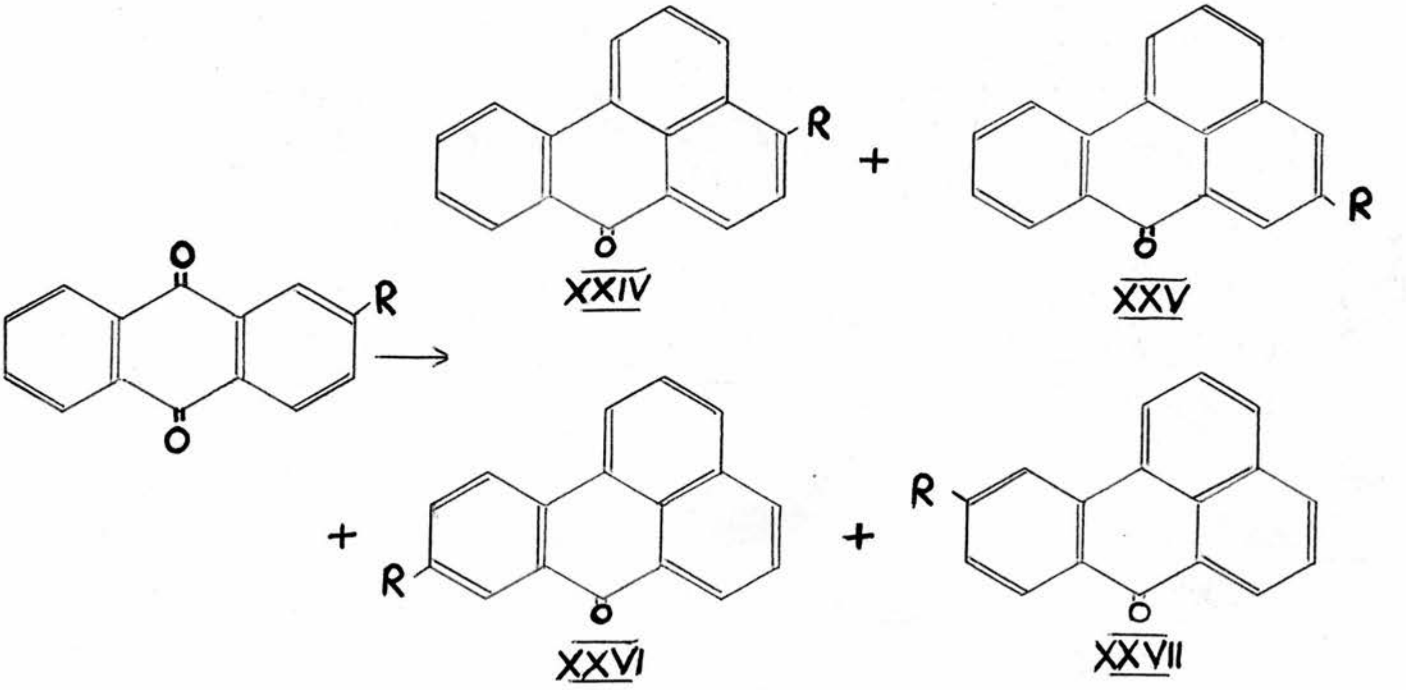
Mesobenzanthrone, then, can be used to prepare 2,3,4,6 and 9 substituted mesobenzanthrones but to prepare 1,5,8,10 and 11 substituted compounds we start from substituted precursors.

5-Nitro-mesobenzanthrone XXII has been prepared (33) by nitration of 4-acetamido--mesobenzanthrone XXI followed by deacetylation and diazotization. The 5-nitro-orientation has been clearly established by oxidation to 3 nitro-anthraquinone-1-carboxylic acid XXIII.

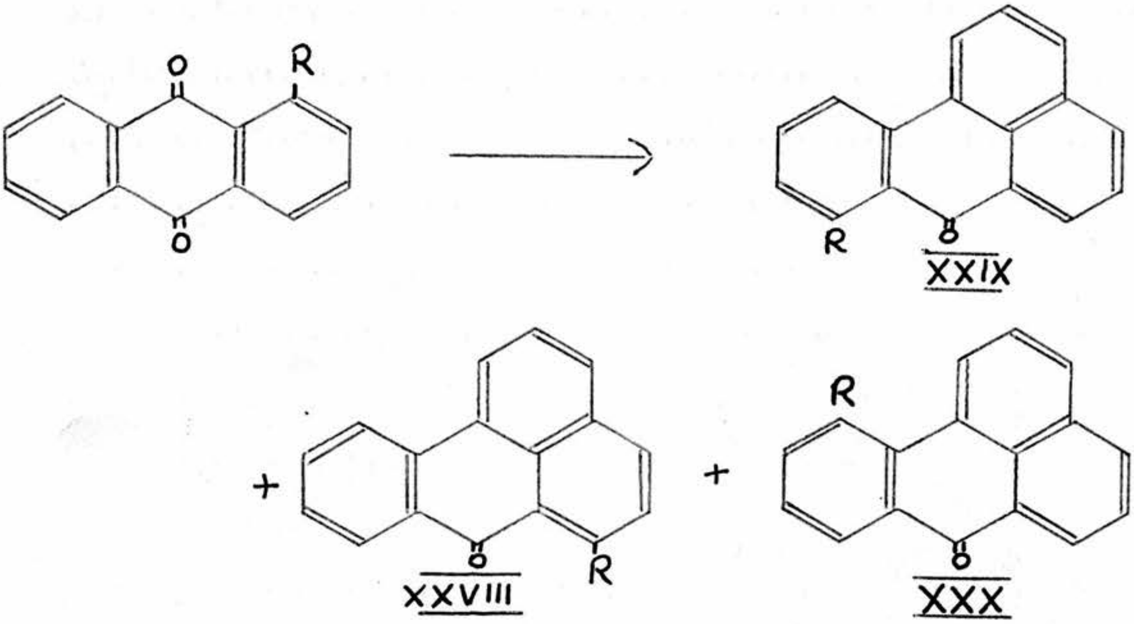


Of the remaining 1,8,10 and 11-substituted compounds which have had to be prepared from the substituted intermediates, unexpected difficulties have occurred only with the 8-substituted compound.

Bally's synthesis from anthraquinones applied to 2-substituted anthraquinones could give a mixture of 4,5,9 and 10 substituted mesobenzanthrones XXIV, XXV, XXVI and XXVII.



In fact 2-chloroanthraquinone yields as the main product 4-chloromesobenzanthrone (34) which was identified by oxidative degradation. The 9- and 10- isomers were also observed although in smaller quantities, but no 5-chloro-mesobenzanthronecarboxylic acids have been isolated from the reaction with anthraquinone-2-carboxylic acid and separated by chromatographing the ethylesters (35). In the same way 1 substituted anthraquinones could yield a mixture of 6,8 and 11 substituted mesobenzanthrones XXVII, XXIX, XXX.



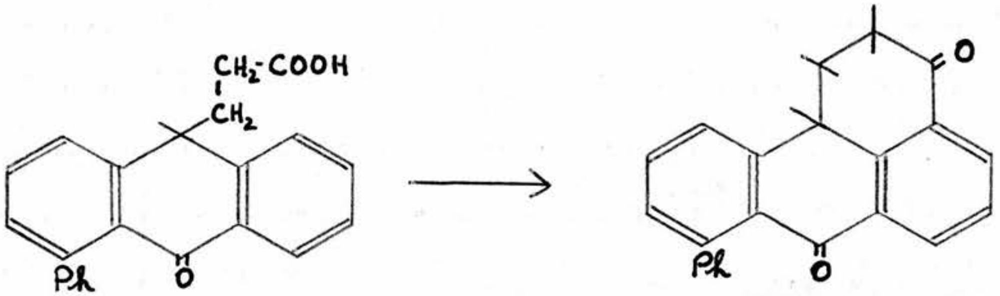
All these isomers have been claimed from 1-chloroanthraquinone although only the 11 chloro mesobenzanthrone was established conclusively by oxidative degradation (36). The amide of anthraquinone-1-carboxylic acid (35) yielded a mixture of the 6-and 8-mesobenzanthrone carboxylic acids separable by chromatography of the esters.

1-Chloro-9-anthrone with glycerol and sulphuric acid (37) yielded a product which was separated into 6- and 8-chloromesobenzanthrone by their differing solubility in alcohol.

A similar synthesis applied to 1-phenyl-anthraquinone gave only sulphonated material (38).

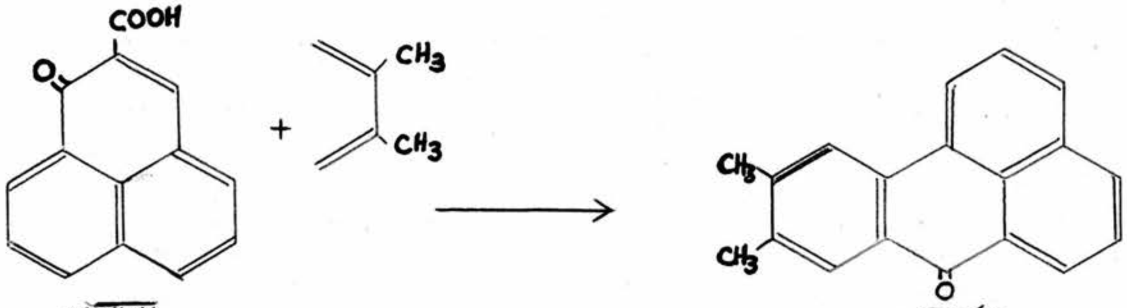
Mono-cyanoethylation of fluorene with acrylonitrile is a facile reaction provided one of the active hydrogens is blocked to prevent dicyano-ethylation. Such a blocking group can be carbomethoxy (39). Mono-cyanoethylation of 9-nitro-anthrone with acrylonitrile is reported to yield 9-nitro-9-cyanoethyl anthrone (40).

An attempt to mono-cyano-ethylate phenylanthrone failed even at elevated temperatures in the presence of triton B in the presence of sodium ethoxide starting material only being recovered (38). Other conditions however are given in the literature where the potassium salt of anthrone is cyanoethylated (41). Hydrolysis followed by ring closure of the mono-cyanoethylated phenylanthrone could have led to 8-phenylmesobenzanthrone.



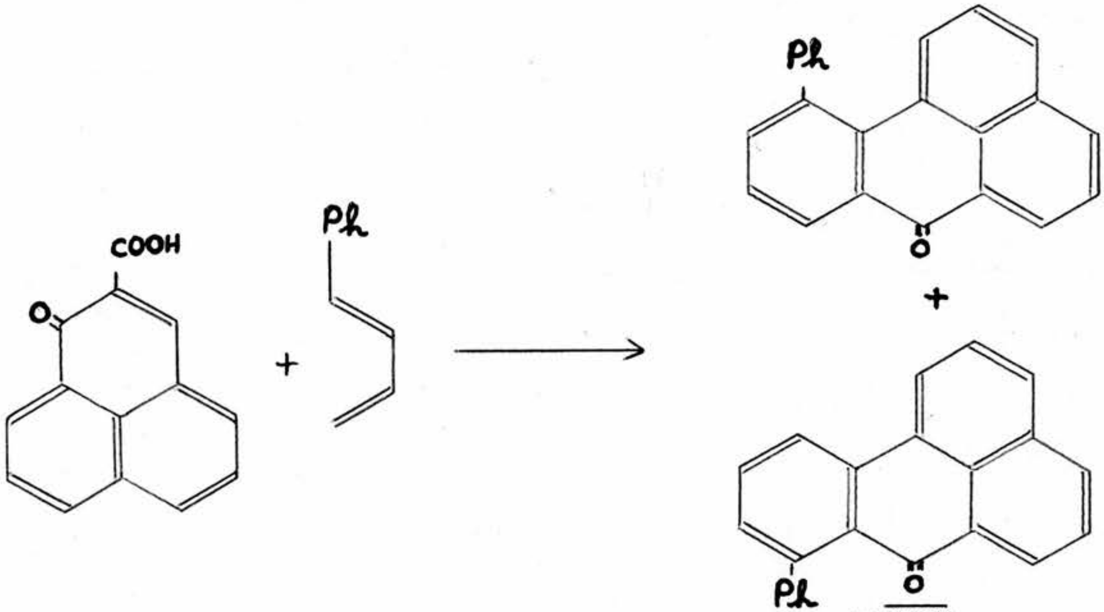
The Diels-Alder reaction has been applied to the synthesis of 8-phenylmesobenzanthrone with some little success (42). Although phenalenone itself does not participate in the Diels-Alder reaction phenalenone-2-carboxylic acid XXXI does.

Condensation of this acid with 2,3-dimethyl-butadiene gave 9,10 dimethyl mesobenzanthrone XXXII (43).



XXXI XXXII

Phenalenone-2-carboxylic acid and 1-phenyl-butadiene could give two products.



XXXIII

Of these two products only one was obtained and from steric considerations it was thought to be the 8-phenyl-mesobenzanthrone XXXIII. Further strength was lent to this belief by the following synthesis.

Condensation of phenanthraquinone with glycerol (44) in the presence of anhydrous ferrous sulphate and

70% sulphuric acid leads to mesobenzanthrone.

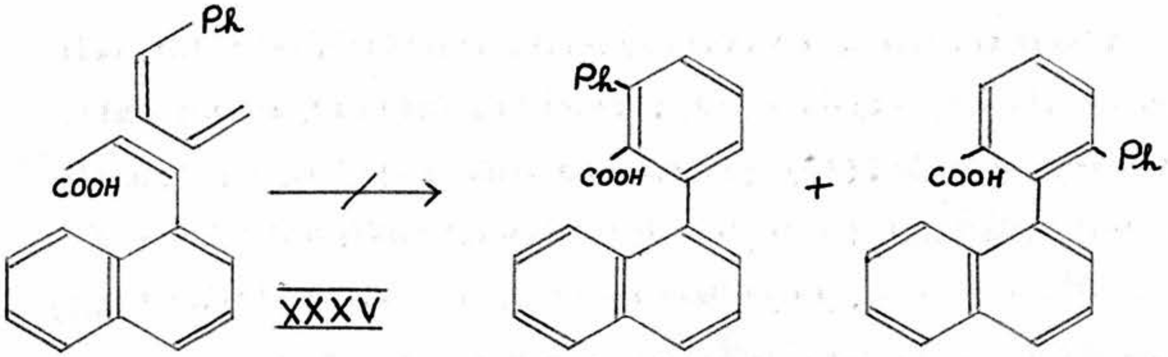
A similar reaction with 1-phenyl-phenanthraquinone XXXIV would lead unequivocally to 8-phenyl-mesobenzanthrone XXXIII. This reaction has been carried out (43) and its product shown to be identical with that from the Diels-Alder reaction which suggests it is the 8-phenyl-mesobenzanthrone. It must be stressed however that in these reactions the yield is very small.

XXXIV XXXIII

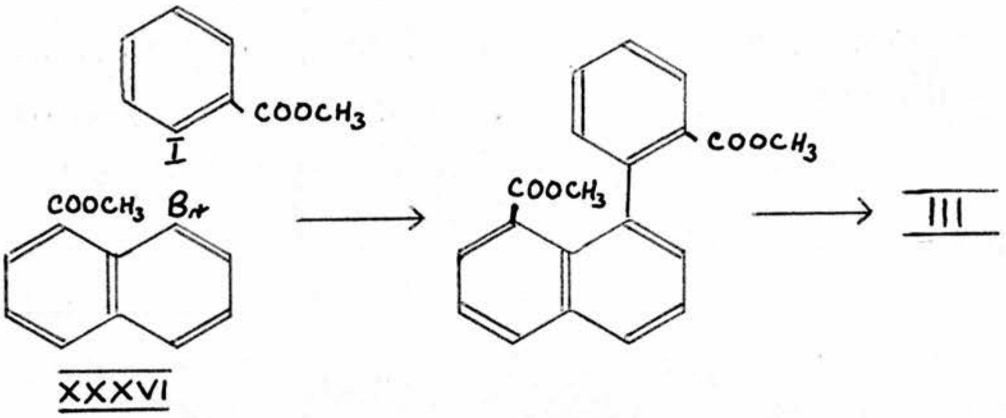
Other attempts to prepare 8-phenyl-mesobenzanthrone may be outlined.

Since reactions between methylene-anthrones and maleic anhydride have been successful (45) an attempt was made to prepare 1-phenyl-9-methylene-anthrone but this did not give a practical yield (38).

2-(α-naphthyl) -acrylic acid XXXV has failed to condense with phenyl butadiene under forcing conditions.

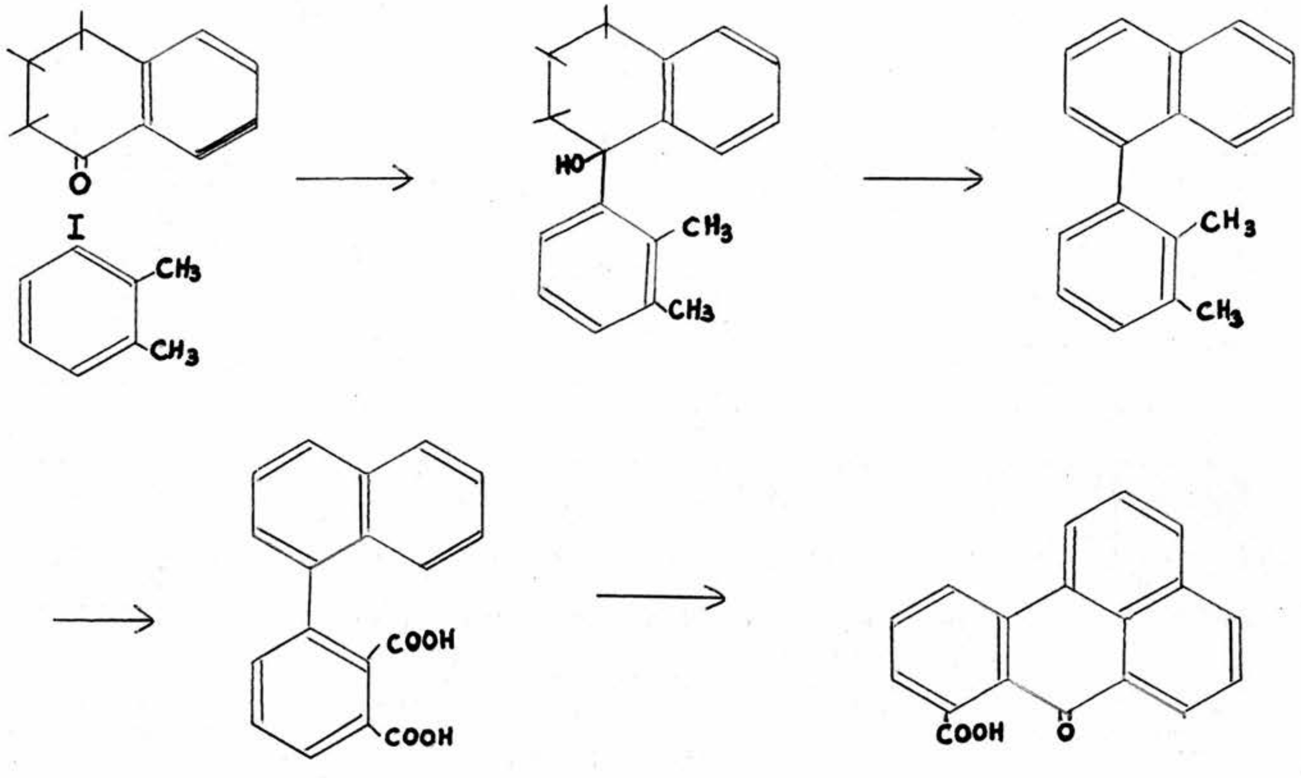

XXXV

A mesobenzanthrone has been prepared by the condensation of methyl 8-bromo-1-naphthoate XXXVI with methyl 2-iodobenzoate. The product was hydrolysed, cyclised and decarboxylated to give mesobenzanthrone.


XXXVI

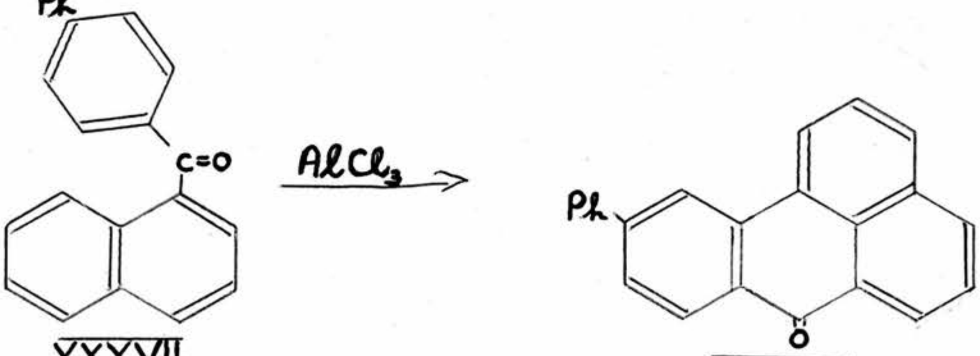
III

A useful variation of this synthesis is the reaction of aryl-halomagnesium compounds and cyclic ketones. Thus tetralone might be expected to give with 2,3-dimethylphenylmagnesiumiodide a possible intermediate for the synthesis of the 8-carboxymesobenzanthrone.



This synthesis was unsatisfactory due to the formation of abnormal Grignard reaction products from the α tetralone (47).

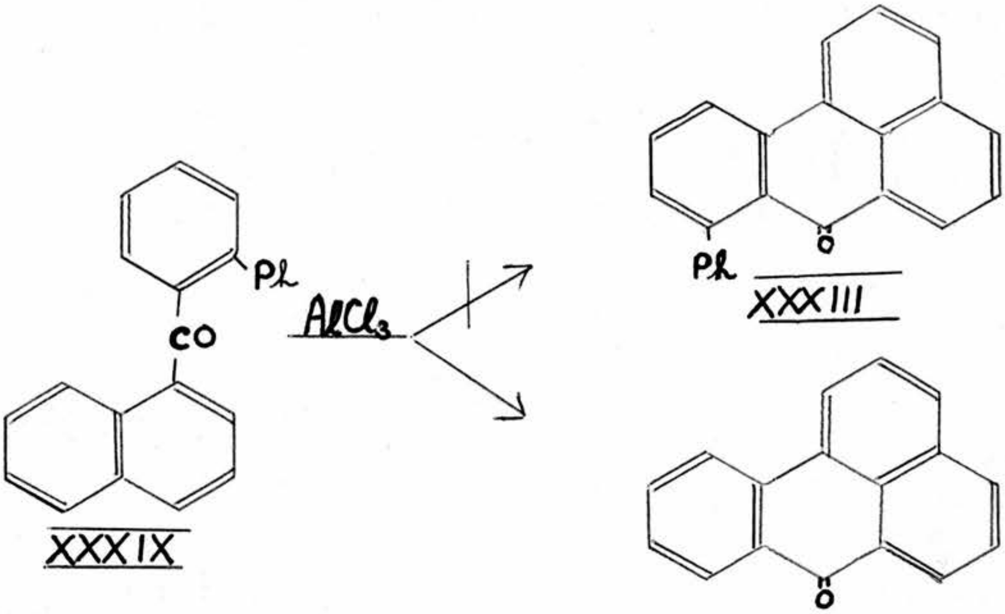
Cyclodehydrogenation of 1-(4 -phenyl-benzoyl)-naphthalene XXXVII to 10-phenyl-mesobenzanthrone XXXVIII has been achieved (48).



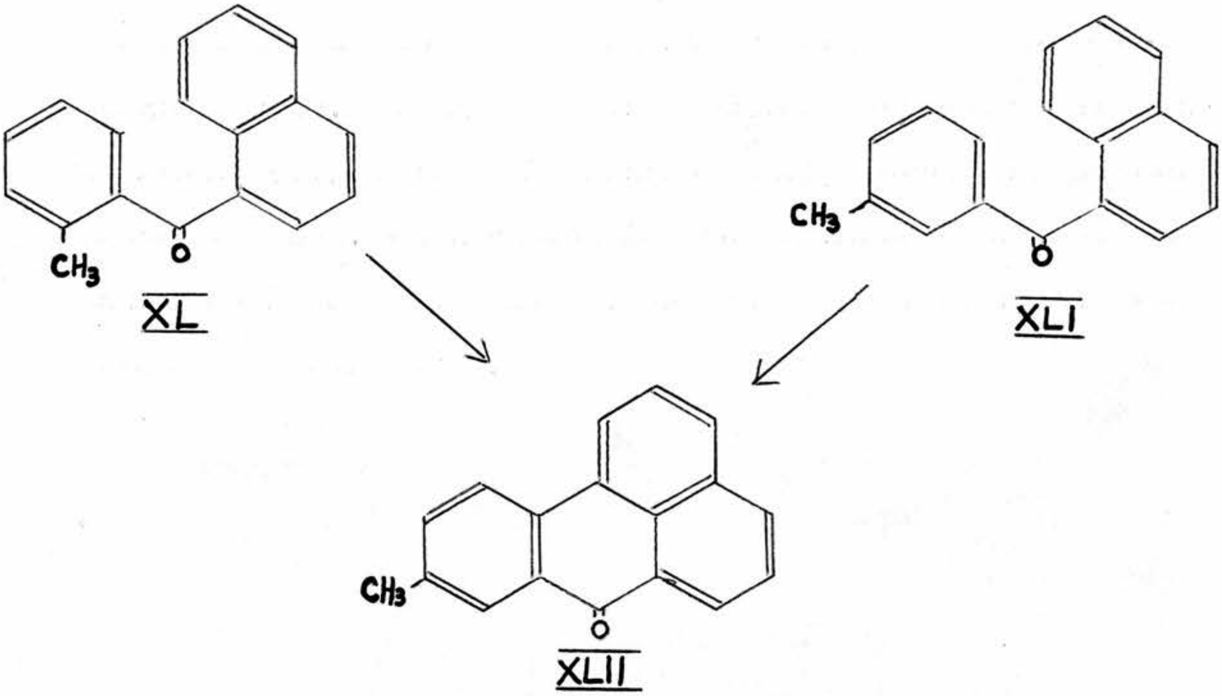
XXXVII

XXXVIII

By analogy the cyclisation of 2 -substituted benzoyl naphthalene XXXIX might produce 8 phenyl-meso-benzanthrone. XXXIII This reaction gave only mesobenzanthrone (47) once again fission having occurred without recombination. Migration in the presence of aluminium chloride is a known phenomenon but complete loss is not normally encountered.



An example of such a migration although with recombination is seen in the cyclisation of 1 -methyl-benzoyl-naphthalene XL and 2 -methyl-benzoyl-naphthalene XLI in both cases the same compound 9-methyl-benzanthrone XLII being produced (49).

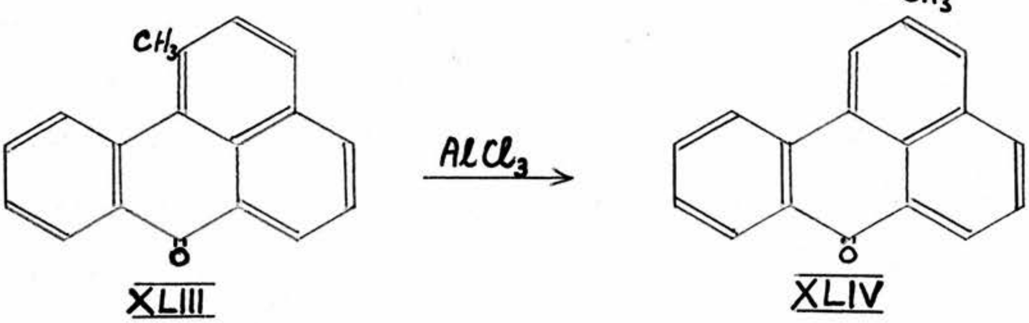


XL

XLI

XLII

Group migrations have also been observed in the conversion of 1-methyl-mesobenzanthrone XLIII into 2-methyl-mesobenzanthrone XLIV in the presence of anhydrous aluminium chloride (50).



XLIII

XLIV

Object of Research.

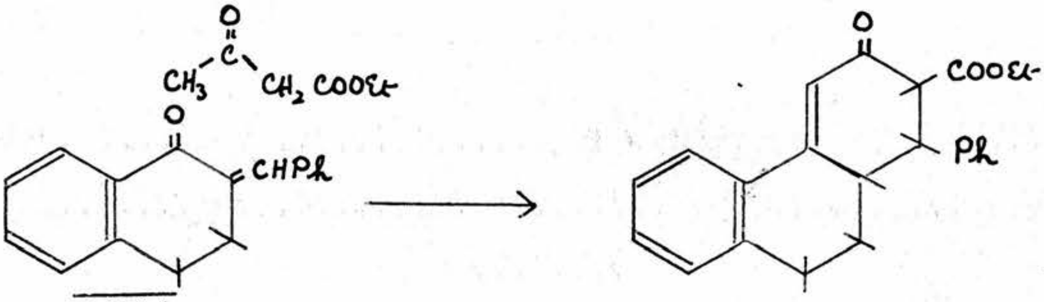
Of the attempts which have been made to synthesise 8-phenyl-mesobenzanthrone only two have been successful and these only in very poor yield (43). One elegant synthesis was doomed at an early stage by the formation of an abnormal product. The benzylidene derivative of 2,3-dihydrophenalenone was required as an intermediate in the synthesis of the 8-phenylmesobenzanthrene. Although V. Brown et al. had reported this compound in the literature (51) no conditions were given for its preparation and attempts to repeat this synthesis led to unexpected results. The object of this research was to investigate the reaction more closely, to prepare the benzylidene compound and to continue the synthesis in an attempt to prepare 8-phenylmesobenzanthrene in an unambiguous and more satisfactory way.

SECTION I

The Preparation of Benzylidene-2,3-dihydrophenalenone and and related compounds and the determination of their structure

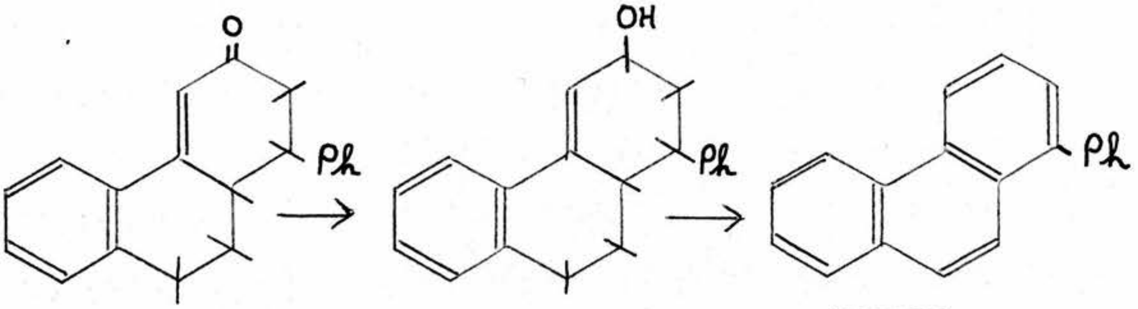
Discussion

The Michael reaction (52) can be applied to the synthesis of alicydic ring systems by condensation of an α ,β -unsaturated carbonyl compound with a second compound containing an active methylene group. The reaction is normally base catalysed and a specific case is the synthesis of 1-phenylphenanthrene from 2-benzylidene-tetralone XLV by the addition of ethyl acetoacetate (69).



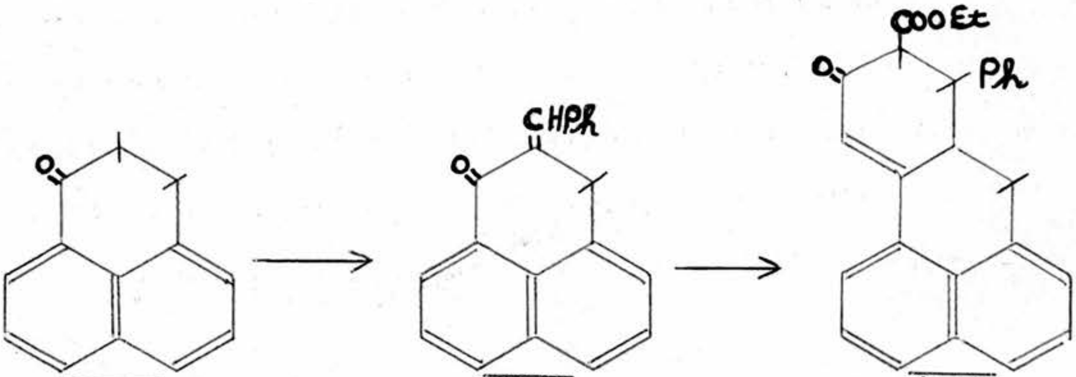
XLV

Decarboxylation and reduction followed by aromatization led to 1-phenylphenanthrene XLVI.



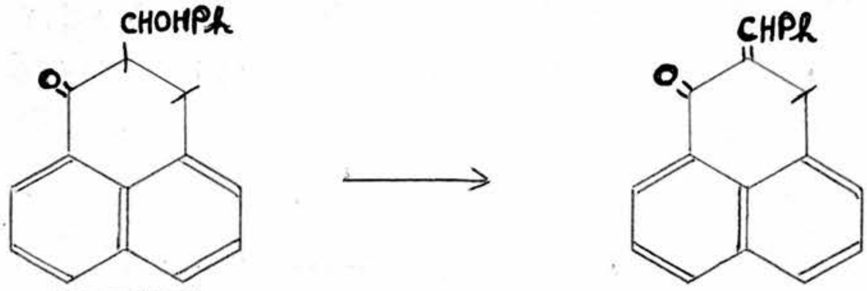
XLVI

Applied to the synthesis of 8-phenylmesobenzanthrene benzylidene 2,3-dihydrophenalenone XLVII provides a suitable starting material and condensation with ethyl acetoacetate would give the keto ester XLVIII



XLIX XLVII XLVIII

V. Braun et al claimed to have prepared benzylidene-2,3-dihydrophenalenone by the condensation of benzaldehyde and 2,3-dihydrophenalenone XLIX (51). No details were given of the preparation and the product was described as melting at 163°, yellow and analysing correctly for benzylidene-2,3-dihydrophenalenone. Neale in an attempt to repeat this (38) tried 4% alcoholic potassium hydroxide, pyridine, 80% sulphuric acid and acetic anhydride as catalysts. Only the first of these gave any product but different from that of V. Braun in that it melted at 204° - 205°. Analysis indicates that this is not benzylidene-2,3-dihydrophenalenone but a product in which two molecules of benzaldehyde have condensed with one of the ketone with the loss of only one molecule of water. In an attempt to produce V. Braun's compound we tried other conditions and reagents dry hydrochloric acid in ethanol, aqueous ethanolic sodium hydroxide, sodium ethoxide and finally extremely dilute ethanolic sodium hydroxide. Of these the last gave in good yield a product melting at 163° but which analysed for $C_{20}H_{16}O_2$ indicating that if condensation had taken place no water had been lost. This result was somewhat surprising until a reinvestigation of V. Brauns results revealed an arithmetical discrepancy in his analysis calculation which when corrected confirmed that his compound was also probably phenyl-2(2,3-dihydraphenalenone)-carbinol L.



L

XLVII

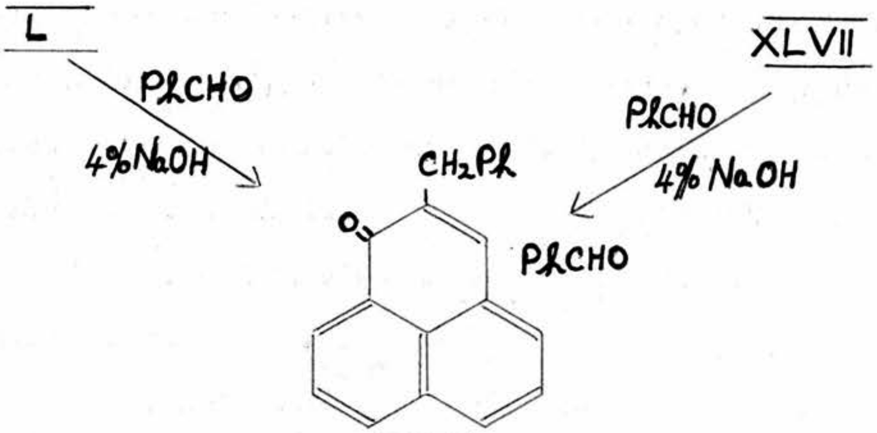
The infra red spectrum of L showed the presence of the carbonyl and the hydroxyl groups.

Dehydration of this compound to XLVII with formic acid and acetic acid resulted only in oils until a catalytic quantity of concentrated hydrochloric acid was added 0.05% being sufficient. The compound so obtained could bd crystallized from acetic acid but retained 1 molecule of acetic acid of crystallization. This complex was stable if crystallized quickly from alcohol. When crystallized from petrol ether after removal of the acetic acid it formed in plates melting at 118° and analysing correctly for benzylidene 2,3-dihydrophenalenone. The compound was subject to decomposition if left in contact with its solution in the light.

The ultra violet and infra red spectra agree with the structure XLVII.

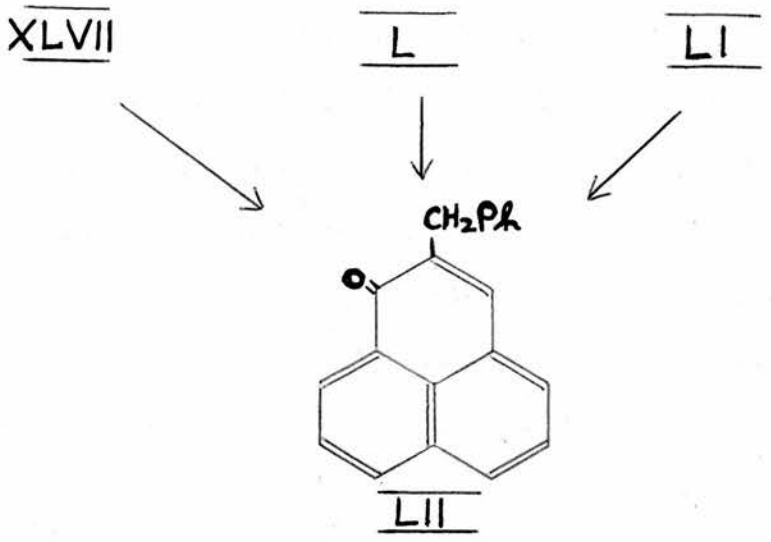
Neale also obtained a compound containing 2 molecules of p-chlorobenzaldehyde with the loss of one molecule of water when he condensed it with 2,3-dihydrophenalenone. Using the mild alkaline conditions which produced the carbinol L we have prepared the corresponding p-chlorophenyl carbinol.

The discrepancy between our results and those of V. Braun is thus accounted for but the constitution of the "dibenzylidene" compound obtained by Neale and melting at 203° remains to be discussed. The work of Neale was repeated and confirmed. The same compound melting at 203° can be synthesised by condensation of benzylidene-2,3-dihydrophenalenone XLVII or the carbinol L with benzaldehyde under the same conditions.



LI

When Neale attempted to condense this compound LI with ethyl acetoacetate with alkali he obtained a compound mp89-90° $C_{20}H_{14}O$ with molecular weight 239-262. When compound LI was refluxed with sodium ethoxide without adding ethyl acetoacetate the same compound was produced. In fact the same compound could be produced by refluxing the benzylidene compound XLVII, and carbinol L with sodium ethoxide in ethanol. On the basis of its origin analysis and ultra violet spectrum which resembles that of phenalenone it has been given the benzyl structure LII rather than the benzylidene structure XLVII.


XLVII

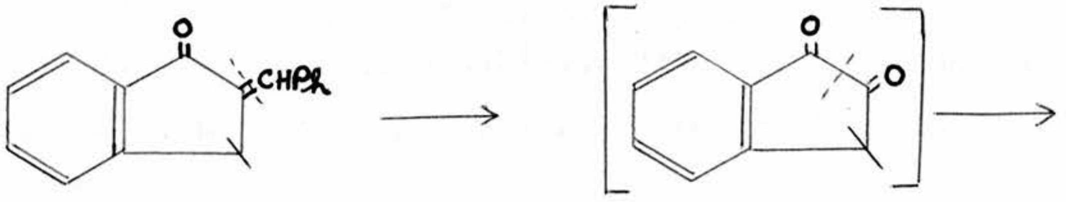
L

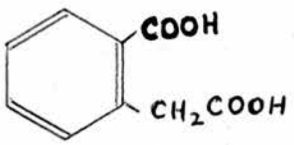
LI

LII

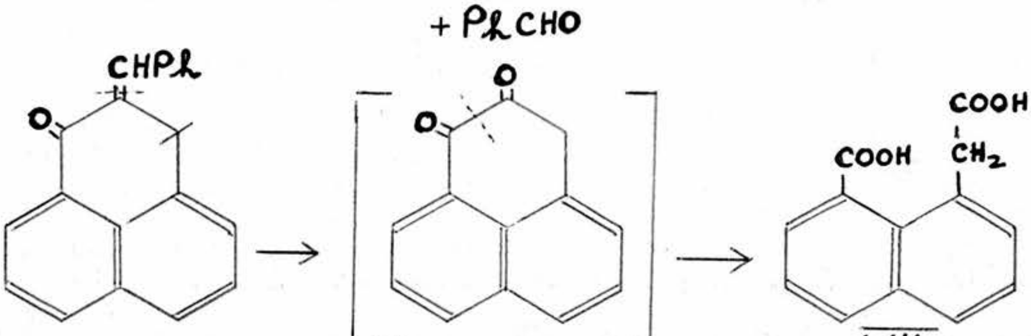
The infra red spectrum shows that the compound is probably an $\alpha:\beta$-unsaturated ketone.

It was decided to rigidly establish the structures of benzylphenalenone LII and of benzylidene-2,3-dihydrophenalenone XLVII before proceeding further. Ozonolysis of XLVII in carbon tetrachloride gave a substance which when removed by steam distillation gave a 2,4-dinitrophenylhydrazone melting at 237° and identical with the 2,4-dinitrophenylhydrazone of benzaldehyde. Also obtained from the solution was an acid which analysed for homonaphthalic acid melting point 213° (53). Such acid products have been observed in the case of benzylideneindanone (54) and of a benzylidenetetralone (55).





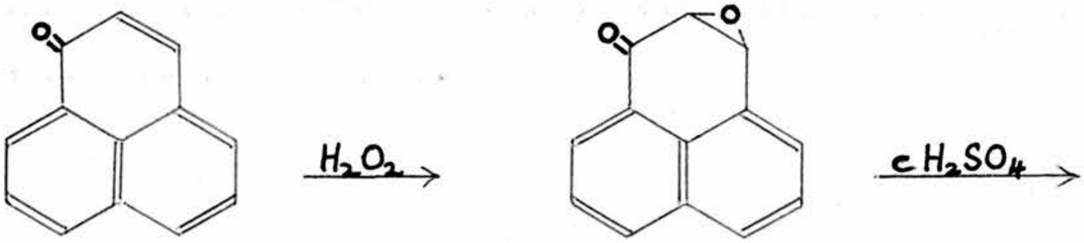
In the case of XLVII we would get benzaldehyde and homonaphthalic acid LIII.



LIII

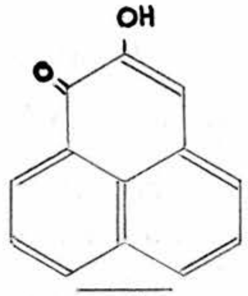
Homonaphthalic acid has been prepared in extremely poor yield and with great difficulty melting point 213° (53). Several attempts were made to prepare a reference sample for comparison by other methods.

Phenalenone-epoxide LV was prepared from phenalenone LIV. The epoxide was ruptured with concentrated sulphuric acid to give 2-oxo-2,3-dihydrophenalenone LVI or alternatively 2-hydroxyphenalenone LVII.



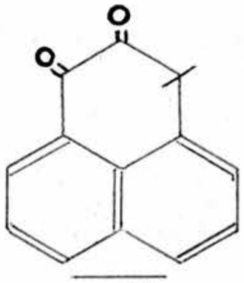
LIV

LV



LVII

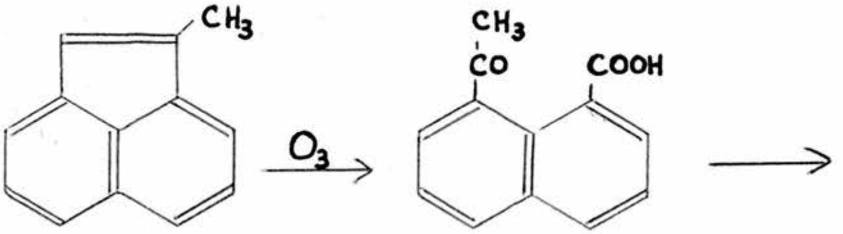
OR



LVI

Ozonolysis of LVI should split between the carbonyls to give homonaphthalic acid but in fact the product was naphthalic acid in good yield. There are two possible conclusions from this (a) that the rearranged compound exists in the form LVII which would be expected to oxidise to naphthalic acid and (b) that the mechanism of the ozonolysis of the benzylidene-2,3-dihydrophenalenone does not involve either forms as an intermediate. The infra red spectrum suggests that the first of these conclusions is true since a strong hydroxyl peak shows. The more likely course of ozonolysis is developed in a later section.

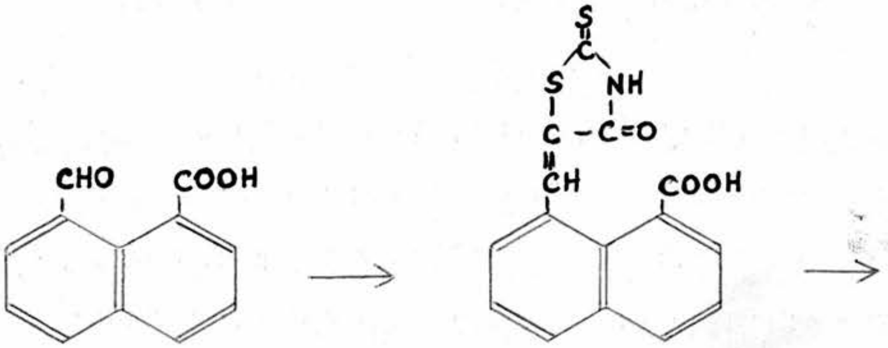
Phenanthrene on ozonolysis gives ketones and acids by oxidation exclusively at the 9.10 double bond (56) Ozonolysis of methylacenaphthylene could give 8-acetyl-1-naphthoic acid which might undergo a Willgerodt reaction to give homonaphthalic acid.



LIII

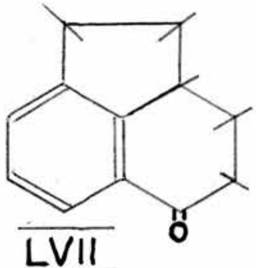
Methylacenaphthylene was prepared but no acid product could be separated from the reaction product of the ozonolysis.

Chain extension of aldehydes has been carried out using rhodanine (57). Applied to naphthaldehydic acid this could lead to homonaphthalic acid. Naphthaldehydic acid was prepared and reacted with rhodanine but the analysis requirements of the product were not met.

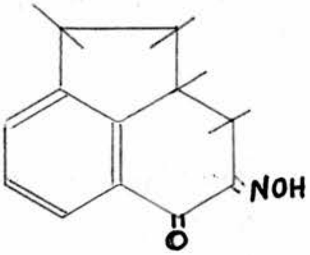


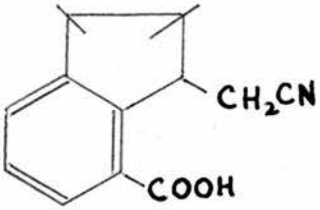
LIII

A facile reaction in the preparation of a cyanocarboxylic acid is one of Rapoports where tetrahydroacenaphthenone LVIII is oximated with butyl nitrite in the presence of potassium t-butoxide then cleaved with benzene sulphonyl chloride in pyridine (59).

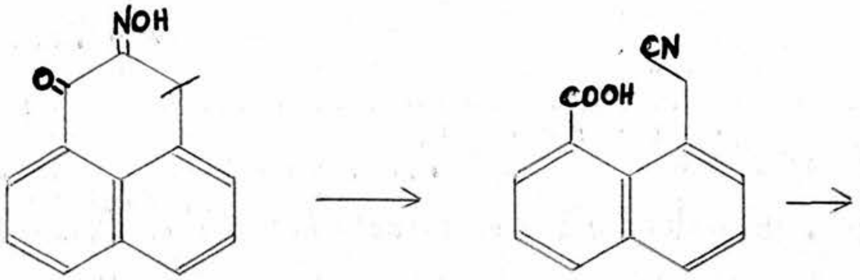


LVII





Oximation of 2,3-dihydrophenalenone should likewise lead to homonaphthalic acid.

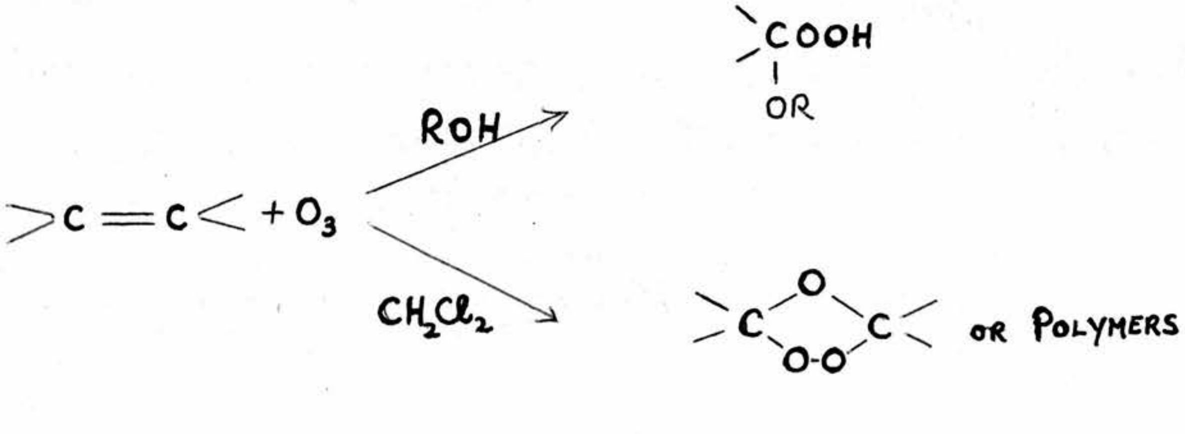


LIII

The oxime could not be prepared with butyl nitrite.

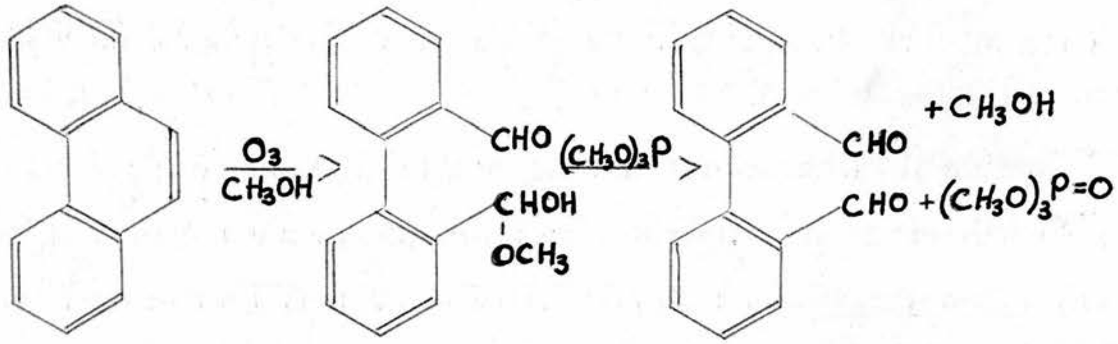
Epoxides react with potassium cyanide to give nitriles (60). Acenaphthylene oxide would give a suitable nitrile but although the product of oxidation contained oxygen it was not the oxide and this synthesis was also abandoned.

The problem of identification of the homonaphthalic acid was circumvented by a new approach. Creigee and coworkers have shown that in hydroxylic solvents, ozonolysis produces a hydroperoxide and a carbonyl fragment whereas in inert solvents we get ozonides and polymeric peroxides (61, 62).



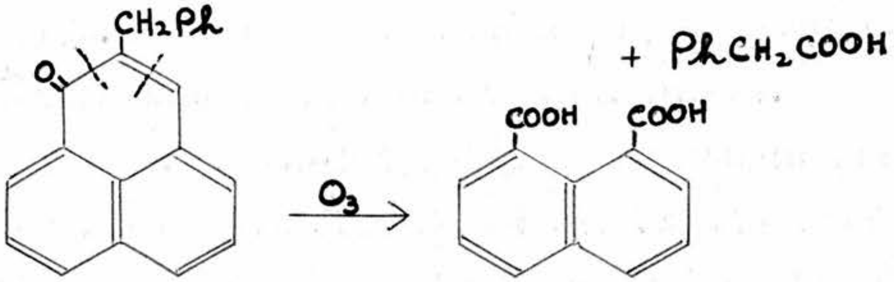
Normally hydrolysis of the peroxides leads to the isolation of a mixture of ketonic and acidic material. More advantageous is reduction at low temperature when only ketonic fragments result.

At about -40° many reducing agents tend to suffer from a loss of activity but trimethylphosphite has proved an effective reducing agent at this temperature (63). Addition of the reagent to the peroxide in the hydroxylic solvent is sufficient to effect the reduction. Phenanthrene thus yields diphenyl dicarboxaldehyde in quantitative yield.



In the case of benzylidene-2,3-dihydrophenalenone we would expect the dione LVI or the enolone LVII. The enolone was isolated in good yield and found to be identical with that obtained from the epoxide of phenalenone (42) by mixed melting point and comparison of infra red spectra.

Ozonolysis of benzyl-phenalenone oxidatively at ordinary temperatures might be expected to give phenylacetic acid and naphthalic acid.



Phenylacetic acid was isolated and identified by a mixed melting point with a commercial sample and by infra red spectra. Naphthalic acid was also easily isolated and identified in the same way.

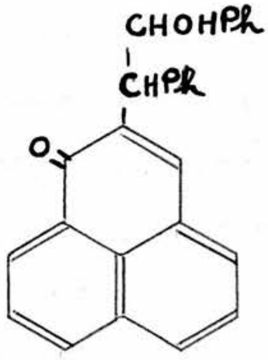
Catalytic hydrogenation of the two isomers should give the same compound but with catalysts selective for double bonds only oils were obtained and there were indications that hydrogenation was taking place in the naphthalene nucleus by the appearance of large peaks around 1620 cm^{-1} in the infra red spectrum.

The oxidative evidence however rigidly establishes the nature not only of these two compounds, but also of V. Braun's compound. It is more difficult to assign a structure to the "dibenzylidene" compound LI.

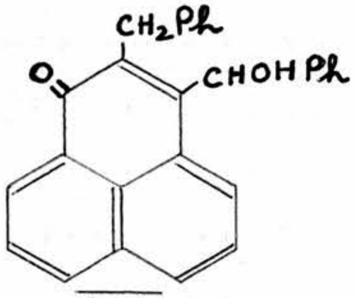
The "dibenzylidene" compound is formed by addition of benzaldehyde to the carbinal L, to the benzylidene compound XLVII, to 2,3-dihydrophenalenone XLIX, but not to benzylphenalenone LII.

Since addition will not take place to the benzyl-compound it seems that the exocyclic double bond is necessary for the reaction to go. On the basis of the ultra violet spectra evidence seems to be in favour of an endocyclic double bond in the dibenzylidene compound since the spectrum is very close to that of phenalenone and benzylphenalenone though this is by no means conclusive. It follows that either the double bond shift takes place after addition of the second molecule of benzaldehyde or is involved in the reaction.

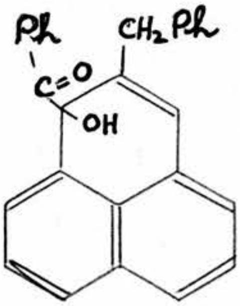
Four structures have been considered, but most of the evidence points to the first structure LIX.



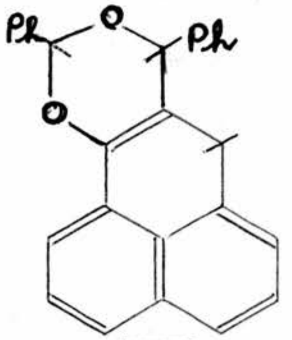
LIX



LX



LXI



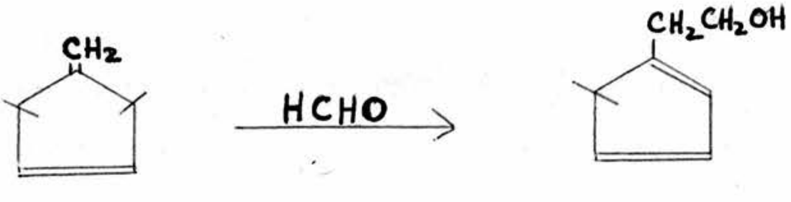
LXII

The infra red spectrum shows the presence of a hydroxyl group which eliminates compound LXII which on analogy is just possible. It would be very difficult to justify the formation of LXI under alkaline conditions and no analogy exists for LX.

Two difficulties in the acceptance of structure LIX are, its ability to split off one molecule of benzaldehyde with alkali and its failure to dehydrate satisfactorily. Dehydration does take place with formic acid or by reflux with p-toluene sulphonic acid as shown by the water which could be azeotroped from the reaction to give a fluorescent green oil which in air rapidly darkens. It would not give an adduct with maleic anhydride even when the diene was produced in situ.

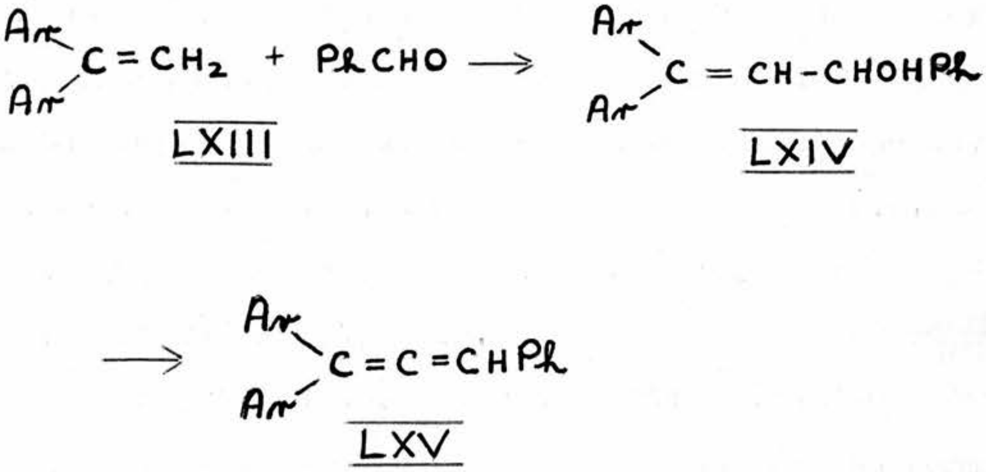
A search of the literature has failed to reveal any product completely analogous to LIX but some similarity has been encountered. The Prins reaction (64) where condensation of an olefin and an aldehyde gives rise to an unsaturated alcohol the formation of which is accompanied by a double bond shift.

With methylenecyclopentene and formaldehyde we get the cyclopentenylethanol (65).



This type of reaction is either thermal or acid catalysed but is not alkali catalysed.

Another such reaction which is acid catalysed but shows the condensation of benzaldehyde with an aromatic olefine with subsequent loss of water is that between LXIII and benzaldehyde. The final product is an allene LXV (66).



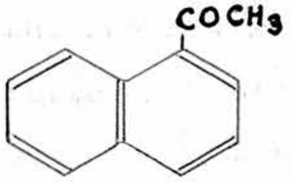
LXIII LXIV LXV

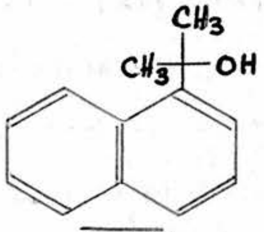
Many examples of vinylogous carbonyl activated methylenes reacting occur but in the case of LIX no true vinylogy occurs.

To show that formula LX was not applicable an attempt was made to produce 2,3-dihydrophenalenones substituted in the 3 position.

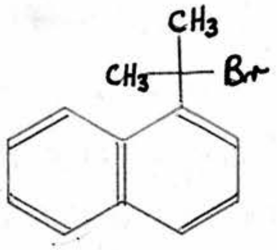
To produce 3,3-dimethyl-2,3-dihydrophenalenone the tertiary alcohol LXVI was prepared by reacting methyl magnesium iodide with 1-acetylnaphthalene.

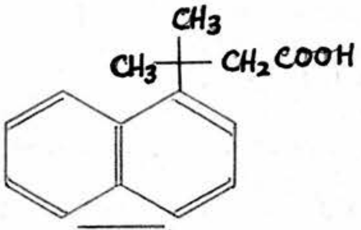
Halogenation and reaction with diethyl malonate would lead to the dimethylpropionic acid LXVII.





LXVI





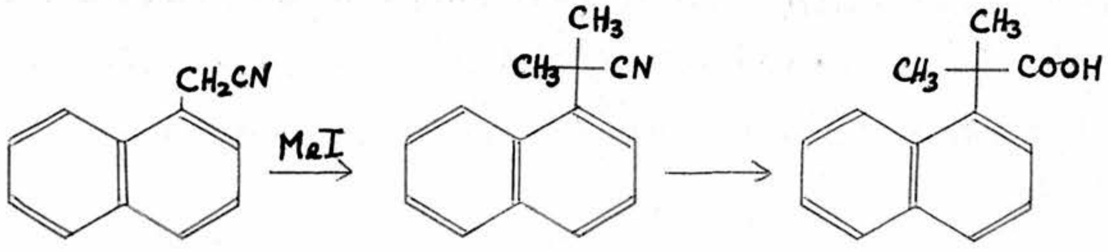
LXVII

Under no conditions could halogenation be accomplished, the olefine being produced at each attempt by dehydration.

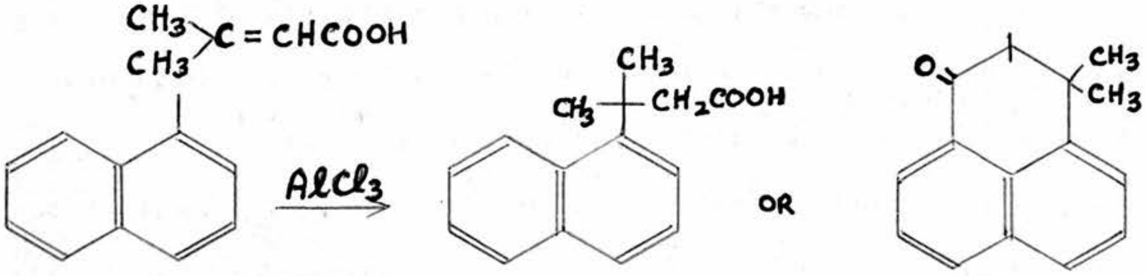
An attempt was made to dimethylate naphthylacetonitrile. Methylenes α to a nitrile group have been methylated with sodamide and methyl iodide (68).

$$RCH_2CN \xrightarrow{MeI} RC(CH_3)_2CN$$

Although reaction occured the product even under the most drastic conditions could not be hydrolysed.



Attempts to condense mesityl oxide or dimethyl acrylic acid with naphthalene gave neither the condensed product nor the cyclised ketone LXVIII.

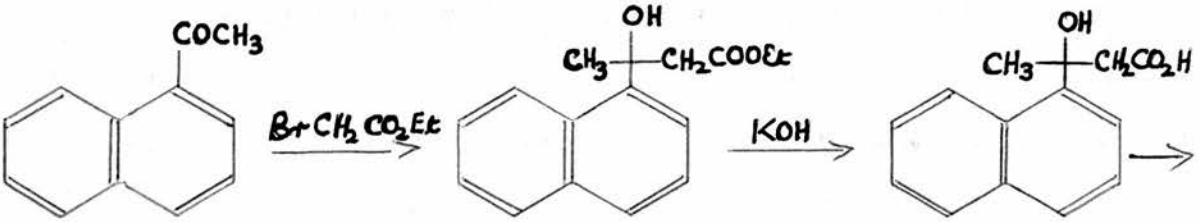


LXVIII

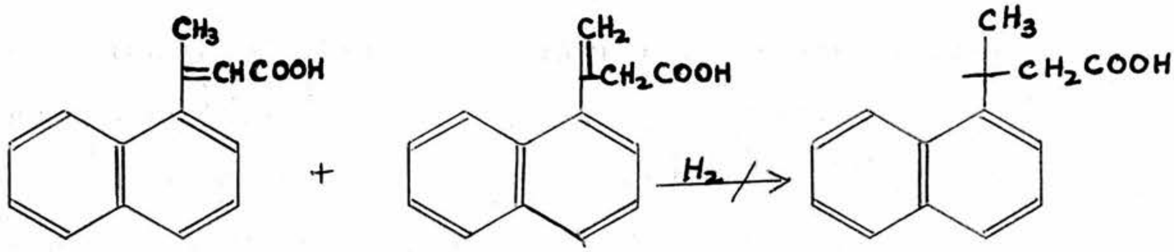
The difficulties encountered in the preparation of the disubstituted compound may be steric and an attempt was made to prepare the mono-methyl 3 substituted 2,3-dihydrophenalenone.

Pure 1-acetylnaphthalene was reacted under Reformatsky conditions with bromoethyl acetate. The liquid product was hydrolysed with potassium hydroxide to give in good yield an acid analysing for 1 naphthyl (β-methyl-β-hydroxy) propionic acid LXIX.

Dehydration of this acid gave an oil possibly due to the formation of two unsaturated isomers. Attempts to reduce this oil catalytically to the fully saturated single acid failed to produce any solid product.



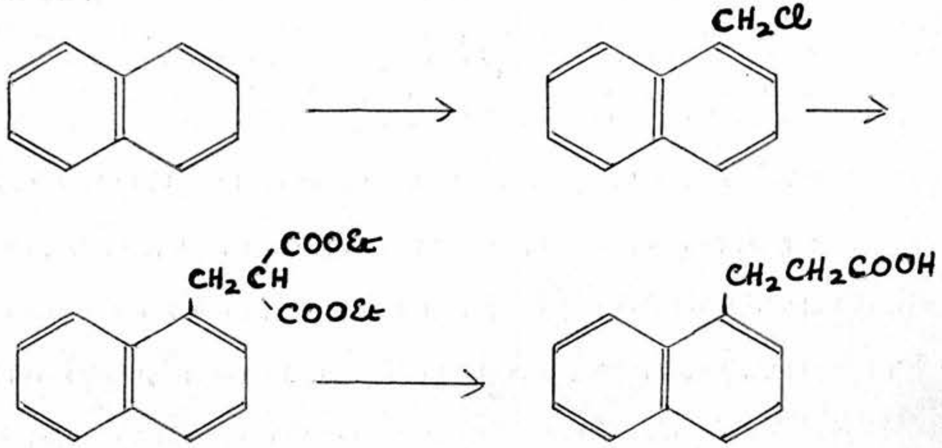
LXIX



Further synthesis along these lines was abandoned since it would only produce negative information.

A monobenzylidene compound has been prepared in small yield from 3-phenyl-2,3-dihydrophenalenone (70) using 4% potassium hydroxide but storic factors do not permit legitimate comparison with the compound without a phenyl in the 3 position.

Preparation of Naphthalene Propionic Acid.



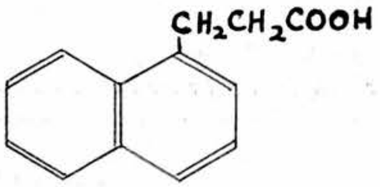
Naphthalene was chloromethylated by the method of Grummit and Buck, Org. Synth. Vo.24 30 (1944). Yield 60% on basis of naphthalene used.

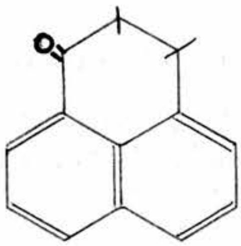
Diethyl naphthyl malonate was produced by the method of Fieser and Gates, J.A.C.S., 1940, 62, 2335. yield 75%.

Hydrolysis and decarboxylation to β (-1.Naphthyl)-propionic acid was by the method of Fieser and Gates except that the final product was distilled at 180° and 3mm. Hg. to give pure white glistening needles yield 80% mp. 157°.

Preparation of 2,3-dihydrophenalenone

c.f. Fieser and Gates J.A.C.S., 1940, 62, 2335.



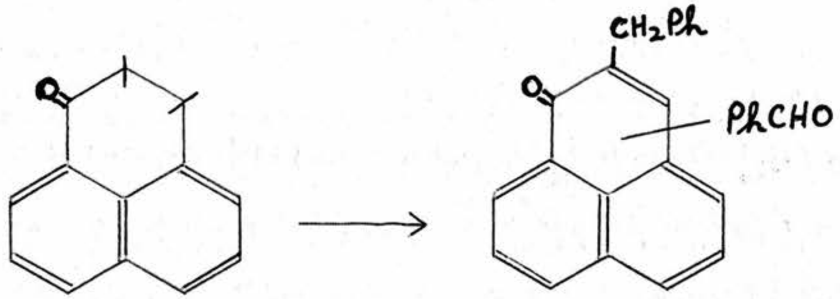


100 gms naphthalenepropionic acid was dissolved in 300 mls hydrogen fluoride in a polythene beaker. A polythene tile was put on top and the mixture was left for three hours. The tile was then removed and overnight the hydrogen fluoride evaporated leaving an oily fuming solid. This product was dissolved in ether/benzene and washed once with water to remove traces of hydrogen fluoride then washed with 10% sodium carbonate to remove any unchanged acid. From the sodium carbonate solution 22 grams of naphthalenepropionic acid were recovered. The organic layer was dried with sodium sulphate, evaporated to dryness, and dissolved in 50 mls of benzene/petrol (1;1) and chromatographed on alumina. The first fluorescent oily fraction was discarded (2 gms.) then came pure 2,3-dihydrophenalenone, followed by a mixture of 2,3-dihydrophenalenone and 4.5 benzindanone. This last fraction when rechromatographed gave 55 gms 2,3-dihydrophenalenone and 2.5 gms of 4.5- benzindanone

mp. 2,3-dihydrophenalenone	82°C
mp. 45. benzindanone	121°C

Yield based on acid used 77%

Condensation of 2,3-dihydrophenalenone with 2 moles benzaldehyde.



R. F. Neale Ph.D. Thesis Edinburgh

2,3-dihydrophenalenone (1gm.) was dissolved in 10 mls of 4% ethanolic KOH. Benzaldehyde (3.5 gms) was added and the solution darkened immediately and overnight yellow crystals separated which were dissolved in ether/benzene (40 mls), washed well with 20 ml portions of sodium carbonate solution, dilute hydrochloric acid and then water. Concentration of the organic layer gave yellow needles which melted at 203° - 204° after two recrystallizations from alcohol. Yield 0.6 gms.

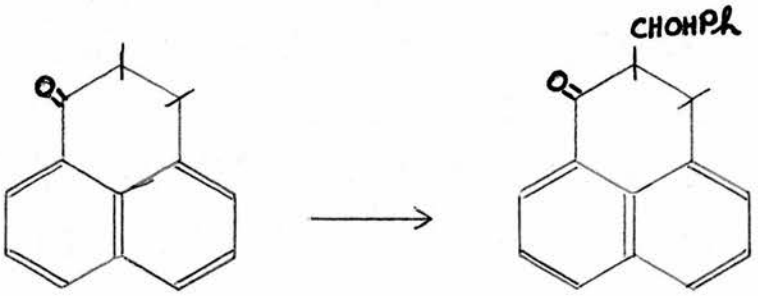
Mixed melting point with Neales product undepressed.

Infra red.	3500 cm^{-1}	hydroxyl
	1660 cm^{-1}	$\alpha\beta$ unsaturated carbonyl
	1630 cm^{-1}	olefinic double bond

Ultra viålet spectrum. Comparison with phenålenone.

See U.V. I.

Preparation of Phenyl-2(2,3-dihydrophenalenone) Carbinol. L



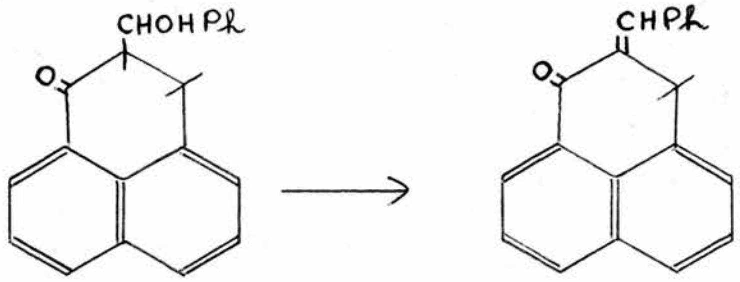
2,3-Dihydrophenalenone (2 gms) was dissolved in 10 mls ethanol and benzaldehyde (1.2 mls) added. The mixture was cooled to 0°C and a 2% solution of potassium hydroxide in ethanol added drop by drop until a slight permanent darkening of the reaction mixture occurred (approx. 6 drops). After two minutes the product started to separate. The mixture was shaken intermittently for half an hour, the temperature being kept at 0°C. The mixture was allowed to stand for three hours at 0°C and the solid product was filtered off and washed with a mixture of ethanol and water at 0°C, finally with a little ethanol. The product was almost pure melting at 162° which was raised to 163° by recrystallization from ethanol.

yield 2.4 gms 76%

Analysis Found.	C	83.4%	H	5.9%
Required $C_{20}H_{16}O_2$	C	83.3%	H	5.6%

Infra red spectrum	1700 cm	carbonyl
	3500 cm	hydroxyl.

Preparation of 2-Benzylidene -2,3-dihydrophenalenone XLVII



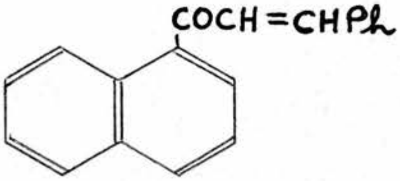
Phenyl -2(2,3-dihydrophenalenone)-carbinol (2 gms.) was dissolved in 20 mls hot acetic acid and 1 drop of concentrated hydrochloric acid was added, causing an immediate darkening in colour. On cooling 2-benzylidene-2,3-dihydrophenalenone was deposited in flat plates. The solution was allowed to stand at 0°C for one hour and the solid is filtered off dissolved in chloroform, washed with sodium bicarbonate solution then dilute hydrochloric acid and finally with water then dried over sodium sulphate. The chloroform was removed and the resulting solid recrystalized from petrol/benzene (3:1) in large flat glistening plates mp 118°C. Yield 1.7 gms 90%

Note:- The product should not be left in contact with its mother liquor particularly in the light as either decomposition or isomerism occurs.

Analysis Found	C 88.9%	H 5.0%
Required $C_{20}H_{14}O$	C 88.7%	H 5.2%

Infra red spectrum 1660 cm^{-1} carbonyl $\alpha\beta$ unsat.
1627 cm^{-1} olefinic double bond.

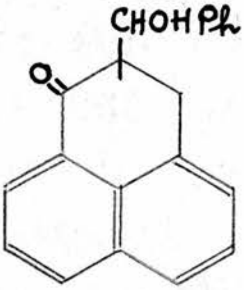
ultra violet spectrum. Comparison with benzylideneacetylnaphthalene is not good though not contradictory U.V. II

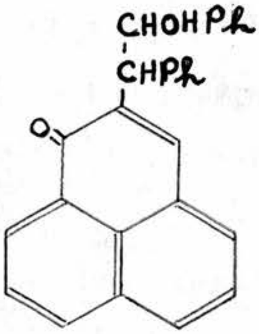


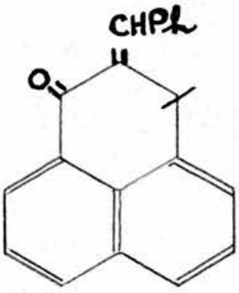
Crystallization from acetic acid gave an excellent product in form but containing one mole of acetic acid of crystallization which remains even after recrystallization from petrol ether.

Analysis of complex. Found C 81.3% H 5.3%
Required $C_{22}H_{18}O_3$ C 80.0% H 5.5%

Preparation of the "dibenzylidene" compound from
(a) Benzylidene - 2,3-dihydrophenalenone
(b) Phenyl 2(2,3-dihydrophenalenone) carbinol.







1 gm of compound (a) or (b) was dissolved in 10 mls ethanol containing 4 gms sodium hydroxide, and 3 gms benzaldehyde were added. After 2-3 hours yellow crystals

appeared which were filtered, redissolved in an ether/benzene mixture washed with sodium carbonate, dilute hydrochloric acid, and water and then crystallized from alcohol.

Yield from (a) 0,7 gms mp 203°
(b) 0.6 gms mp 203°

These compounds were identical with the compound of Neale.

Preparation of Benzylphenalenone from

(a) "Dibenzylidene" c/d mp 203° cf. Ph.D Thesis Neale.
(b) Benzylidene 2,3-dihydrophenalenone
(c) Phenyl 2(2,3-dihydrophenalenone) carbinol

1 gm of the solid (a) or (b) or (c) was dissolved in 10 mls ethanol containing 0.2 gms. sodium and the mixture refluxed for 1 hour then poured into water. The yellow oil was extracted with benzene washed with dilute hydrochloric acid and then water, dried with sodium sulphate, and then chromatographed on alumina to give a homogeneous yellow compound m.p. 89°C.

Yield (a) .3 gms
Yield (b) .7 gms
Yield (c) .6 gms

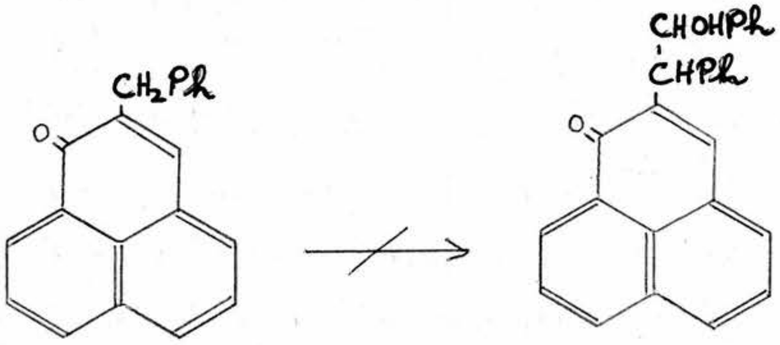
Analysis Found	(Neale)	C	89.0%	H	5.1%
Required	Benzyl cpd	C	88.7%	H	5.2%
	Benzylidene cpd	C	88.9%	H	5.0%

If is not identical to Benzylidene 2,3-dihydrophenalenone but isomeric with it.

Infra red spectrum 1655 cm^{-1} unsaturated carbonyl
1630 cm^{-1} olefinic double bond

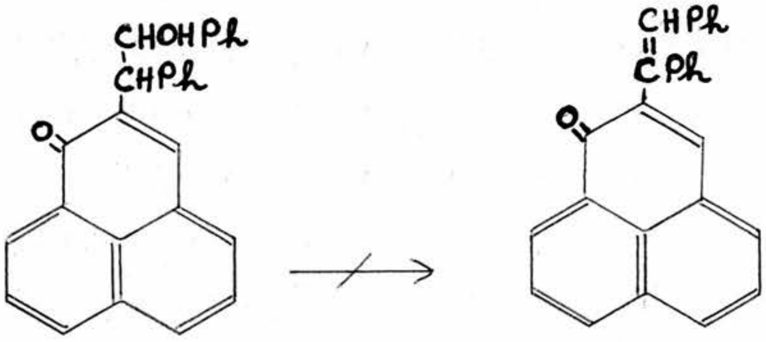
ultra violet spectrum. Very similar to phenalenone U.V. III.

Attempted Preparation of "Dibenzylidene" compound from Benzylphenalenone



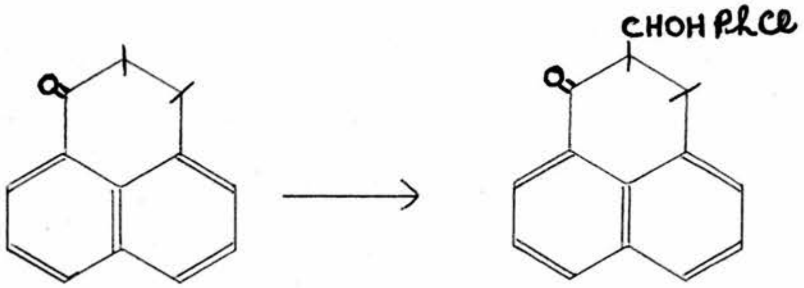
The conditions used were as above for its preparation from benzylidene 2,3-dihydrophenalenone but only starting material was recovered.

Attempted dehydration of "dibenzylidene" compound.



1 gram of the compound was dissolved in 10 mls formic acid containing 1 drop concentrated hydrochloric acid. The mixture was warmed for ten minutes allowed to cool and added to water which precipitated an oil which was extracted with benzene washed with sodium carbonate and water then dried with sodium sulphate. The oil contained by evaporating the solution to dryness was fluorescent and could not be separated even after chromatography on alumina.

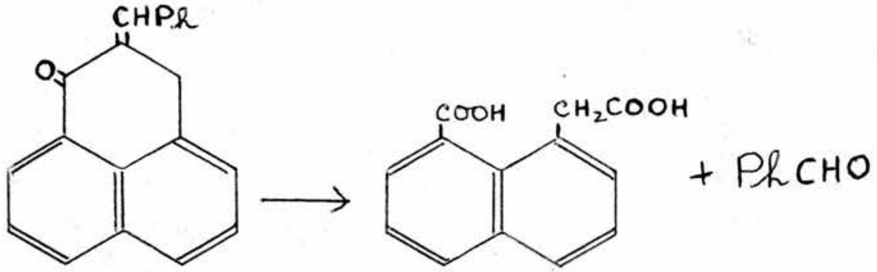
Preparation of p-chlorophenyl 2(2,3-dihydrophenalenone) carbinol.



Conditions used were identical to those used for benzaldehyde and 2,3-dihydrophenalenone.

Yield	0.7 gms	m.p.	126°C
Infra red spectrum		$1680\ cm^{-1}$	carbonyl
		$3500\ cm^{-1}$	hydroxyl.

Ozonolysis of 2,benzylidene -2,3-dihydrophenalenone in carbon tetrachloride..



1 gm of the benzylidene compound was dissolved in 10 mls carbon tetrachloride.. Ozone was passed at $0^{\circ}C$ until excess caused rapid darkening of a potassium iodide solution in dilute hydrochloric acid. Water was added to the solution in chloroform and the chloroform was distilled off. The residue was steam distilled, the distillate extracted with ether and evaporated down. The product formed a 2.4-dinitrophenylhydrazone, m.p. 237°

benzaldehyde 2.4 dinitrophenylhydrozone m.p.237°

mixed melting point, 237°

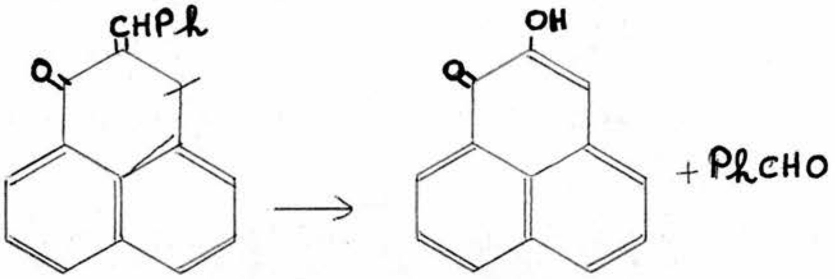
The residue after steam distillation was extracted with chloroform, extracted again with alkali and reprecipitated with acid to give a pink residue which on recrystallization from petrol ether gave a buff coloured precipitate of homonaphthalic acid, m.p. 213°C.

Analysis	Found	C	67.0 %	H	4.3%
	Required $C_{15}H_{10}O_4$	C	67.8%	H	4.3%

Infra red spectrum 1690, 1705 cm^{-1} carbonyls

Compare naphthalic acid 1750 1755 cm^{-1} carbonyls.

Ozonolysis of Benzylidene -2,3-dihydrophenalenone at-70° in methanol



Benzylidene-2,3-dihydrophenalenone was dissolved in methanol cooled to - 70° in dry ice and ozone/oxygen mixture passed in until no more was absorbed as indicated by the darkening of a potassium iodide and acid mixture. While the reaction mixture was still at - 70° trimethyl phosphite (1 ml.) was added.

The mixture was then allowed to warm up to room temperature. Benzene was added and from the benzene was extracted with sodium hydroxide the dione (or enolone). The solution was acidified and the precipitate collected.

Crude yield of enolone 0.4 gms. This was purified by dissolving in concentrated sulphuric acid pouring on ice, extracting first with ether and then sodium carbonate. Acidification of the alkaline extract gave a red compound, (0.3 gms) which was crystallized from methanol-water, m.p. 182°.

Infra red spectrum	1660 cm^{-1}	unsaturated Carbonyl
	1625 cm^{-1}	olefinic double bond
	3350 cm^{-1}	unsaturated alcohol

Preparation of phenalenone.

Fieser and Hershberg J.A.C.S., 1938, 60, 1658. Fieser's method was used with 50 gms β -naphthol, 125 gms. glycerol, 170 cc. concentrated sulphuric acid and 60 gms sodium nitrobenzene sulphonate. The product distilled at 200°/2 mm., and was crystallized from petrol:benzene (1:1)

Yield 20 gms. m.p. 155°C.

Preparation of 2-hydroxyphenalenone.

Fieser, J. A. C.S., 1942, 64, 919

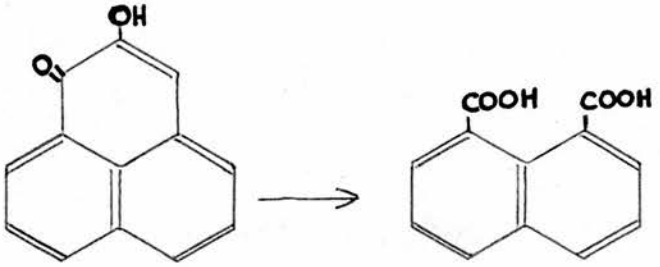
2,3-Dihydrophenalenone (1 gm) was dissolved in 10 cc ethanol and treated with 1cc 30% H_2O_2 and 0.2 gms sodium carbonate in 5 cc water. The solution was warmed to 50° for 20 minutes and then cooled to give 0.6 gms oxide. This was dissolved in concentrated sulphuric acid 10 cc to give a homogeneous red solution. The solution when poured onto ice gave a red precipitate. Recrystallization from methanol gave red needles, m.p. 182° - 183°

Yield 0.4 gms.

Infra red spectrum	3350 cm $^{-1}$	Hydroxyl
	1660 cm $^{-1}$	Carbonyl
	1625 cm $^{-1}$	olefinic double bond

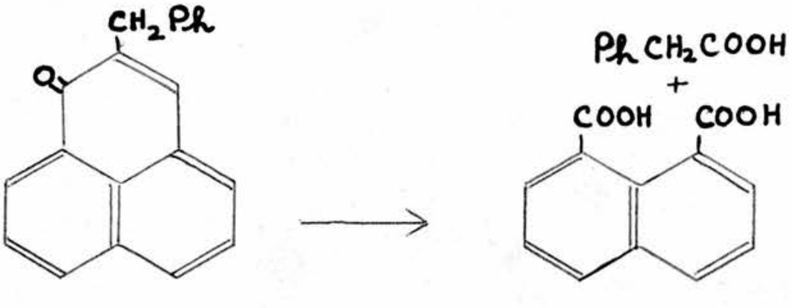
The hydroxylphenalenone was identical with the compound prepared by the ozonolysis of benzylidene -2,3-dihydrophenalenone. This was confirmed by mixed melting point - no depression.

Ozonolysis of 2-hydroxylphenalenone.



2-Hydroxyphenalenone (1 gm) was dissolved in carbon tetrachloride and cooled to 0°C Ozone was passed until a potassium iodide solution was rapidly coloured. The resultant solution was poured into water and the carbon tetra chloride removed. The acid portion was extracted from the residue by making alkaline and washing with ether. The acid was precipitated and was found to have a melting point 260° and an infra red identical with that of naphthalic acid.

Ozonolysis of Benzylphenalenone in carbon tetrachloride at 0°C.



Benzylphenalenone (1 gm) was dissolved in 20 mls carbon tetrachloride and ozone was passed at 0°C until a potassium iodide/acid solution was rapidly soloured by excess ozone.

The solution of the ozonide was poured into water and the carbon tetrachloride was removed. The aqueous residue was made alkaline extracted with ether and the acid precipitated by addition of dilute hydrochloric acid then extracted with ether. The ether soluble acid fraction crystallized on evaporation of the ether and was found to melt at 76°. The melting point was not depressed when it was mixed with an authentic sample of phenylacetic acid.

The fraction not soluble in ether was identified as naphthalic acid by comparison of its infra red with that of an authentic sample of naphthalic acid.

Attempted preparations of homonaphthalic acid

Preparation of acenaphthenone.

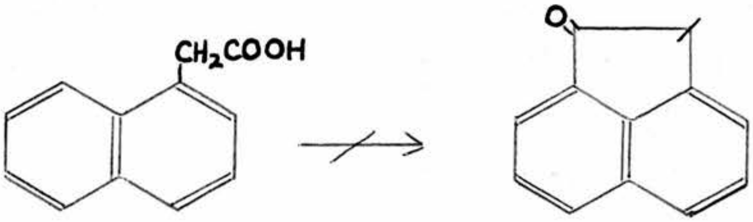
Fieser and Cason J.A.C.S., 1940, 62, 434.

The method of Fieser was used with half the quantities and a proportionate yield was obtained.

Yield 32 gms. m.p. 121°C.

Attempted preparation of acenaphthenone by cyclisation of naphthalene acetic acid with hydrogen fluoride.

c.f. Fieser and Gates J.A.C.S. 1940 62 2335.



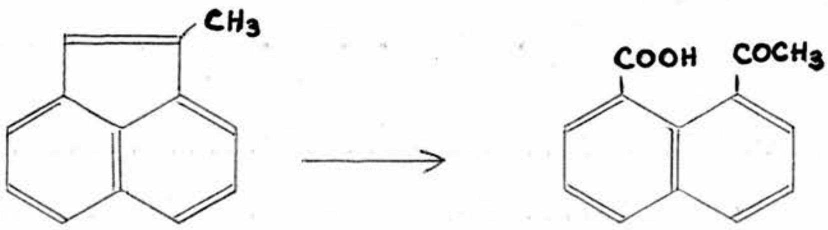
Naphthalene acetic acid (20 g) was dissolved in anhydrous hydrogen fluoride 100 mls. The mixture was covered and allowed to stand for 24 hours. The cover was removed and the hydrogen fluoride allowed to evaporate. On working up as with 2,3-dihydrophenalenone only starting material was recovered in 95% yield.

Preparation of 1-methyl acenaphthylene.

Brown and Hammick, J.C.S., 1948, 1395

A Grignard reagent wasobtained from magnesium (3 gms) methyl iodide (17 gms) in 100 ccs ether. 17 gms acenaphthenone in dry ether were added. Removal of ether and decomposition with hydrochloric acid gave an oil. Recrystallization of the picrate m.p. 176° (lit 176°) and decomposition gave the yellow orange oil found by Brown and Hammick.

Ozonolysis of 1-methyl acenaphthylene.



The methyl acenaphthylene was dissolved in carbon tetrachloride. Excess ozone was passed in and decomposition of the ozonide gave some acid material from which no pure product could be separated.

Preparation of naphthaldehydic acid.

Cason and Wordie J. Org. Chem., 1950, 15, 608. The reaction was carried out as in reference to give 2.5 gms of 1,8-naphthaldehydic acid, m.p 167° (lit m.p 167°).

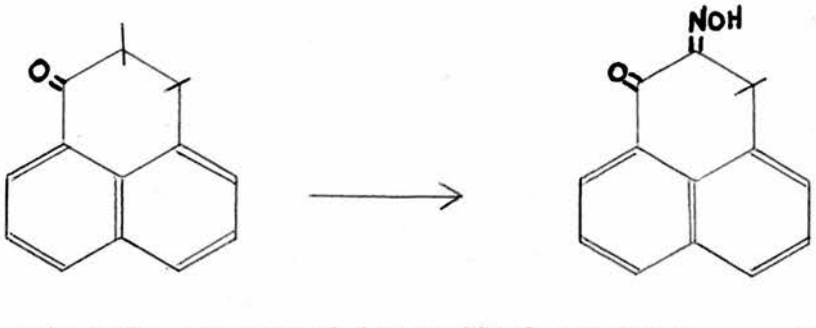
Attempted preparation of Rhodanine compound of 1.8 naphthaldehydic acid.

c.f. Campbell and McKail J.C.S. 1948, 1251

Naphthaldehydic acid (0.1 mol) and rhodanine (0.1 mol) were refluxed in an oil bath, in 50 mls glacial acetic acid and sodium acetate. (15 gms) for thirty minutes. The product was washed with water then glacial acetic acid and dried at 70°. The compound was not the required product.

Attempted preparation of 2,3-dihydro-2-oxo-phenalenone oxime.

c.f. Hartung and Munch J.A.C.S. 1929, 51, 2262

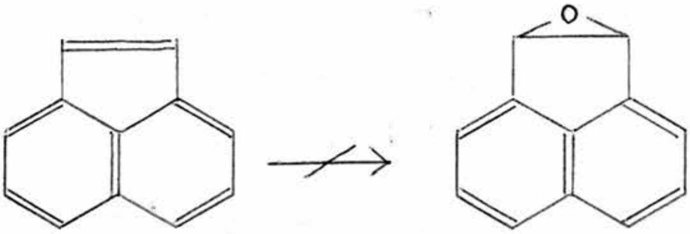


Butyl nitrite prepared by method of Noyes Org. Synth. 16, 7, (1936)

2,3-Dihydrophenalenone (3.6 g) in 50 cc. ether were stirred and dry hydrochloric acid gas passed at the rate of 2-3 bubbles per second and 2.5 gms. butyl nitrite were added slowly. The mixture warmed and darkened. It was allowed to stand overnight. The ethereal solution was added to 2N sodium hydroxide and the ether layer separated. The alkaline layer was added to 6N hydrochloric acid, but only a small amount of oily precipitate was obtained which could not be induced to crystallize.

Attempted preparation of acenaphthylene oxide.

C.F. Org. Synth. 8 102 (1928).



To 4.2 gms of benzoyl hydroperoxide in 50 cc chloroform was added acenaphthylene (4.5 g). The solution was kept at 0° for 24 hours then allowed to warm up to room temperature. Titration of a portion by addition of potassium iodide followed by titration with sodium thio sulphate showed that the benzoyl hydroperoxide had been consumed. Addition of excess sodium hydroxide removed the benzoic acid and the chloroform solution was washed with water and dried over sodium carbonate. Removal of the chloroform left a solid which analysis showed contained more than carbon and hydrogen but not enough oxygen for the

required oxide.

Preparation of 1-acetylnaphthalene.

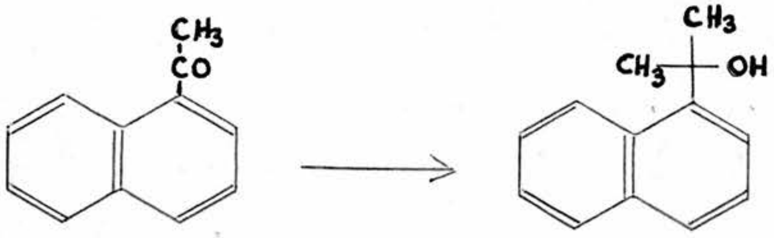
Baddeley, J.C.S., 399, 1949.

To 8 gms acetyl chloride, and 14 gms aluminium chloride in dichloroethane was added naphthalene (13 gms) in 30 mls dichloroethane. Stirring was continued for 1 hour at 35°. Hydrolysis, washing of the organic layer and removal of the dichloroethane gave a residue distilling at 150° at 5 mm. Hg.

Some difficulty was experienced in obtaining the solid material but once seeded it melted at 9°C the melting point of the α isomer .

Yield 15 gms % yield 88%

Preparation of naphthyl propanol.



cf. Inglis J.C.S., <u>99</u>, 540, (1911).

Magnesium (2.4 gms) and methyl iodide (14.2 gms) in 50 ccs dry ether were used to prepare a Grignard reagent. 17 gms of acetyl naphthalene in 50 ccs ether were added to the stirred Grignard reagent, the temperature not being allowed to rise above 10°. The mixture was allowed to stand for one hour and excess ice and hydrochloric acid was added slowly. The ether solution was washed with aqueous sodium hydroxide and dried over sodium sulphate. On evaporation of the ether a solid alcohol was obtained which crystallized from petrol ether mp 64°

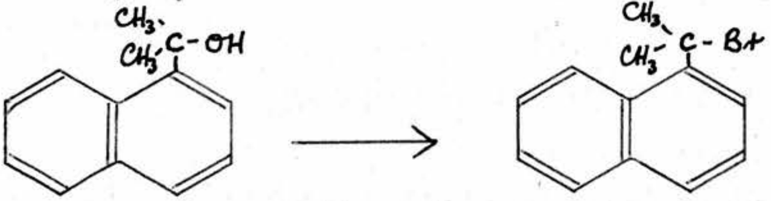
Yield 11 gms % yield 60%

Infra red spectrum 3500 cm^{-1} hydroxyl.

Prep from peroxide mp 62° Capp and Hawkins J.C.S., 1953, 4106.

Attempted Esterification of naphthyl propanol.

with HBr/H_2SO_4 Hey et al. J.C.S., 1953, 2021



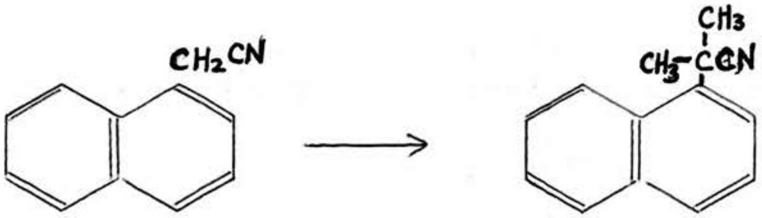
The alcohol (6 gms) and 48% hydrobromic acid (10g) and sulphuric acid (3.5 g) were heated for two hours at 100°C. The organic layer was separated washed in ether and concentrated to an oil which could not be crystallized. A Beilstein test indicated no bromine was present and the infra red spectrum showed no hydroxyl but an olefinic band. Several recrystallizations of the oil from alcohol gave a solid m.p.47°C. c.f. dehydration of the alcohol Caff and Hawkins J.C.S. 1953, 4106.

Preparation of Naphthyl acetonitrile.

M.S. Newman, Org. Synth, 21, 89, 1941.

The yield was 70% c.p. 150°, 3 mm. Hg.

Attempted Dimethylation of naphthonitrile



cf. Knabe and Kubitz Naturwissenschafter

1961 48 669

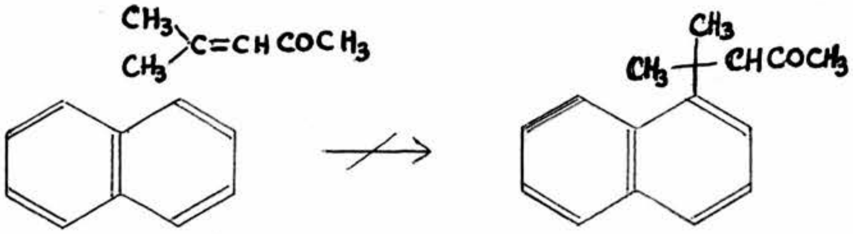
To 5 gms sodamide in 100 ccs. dry ether was added over the course of 2 hours 12 gms of naphthylacetonitrile. After refluxing for 1 hour 20 gms of methyl iodide in 50 ccs ether were added in two hours. After two hours reflux the organic layer was washed with water and the solvent was removed. Yield 11 gms.

Attempted hydrolysis of product of dimethylation

The product was refluxed with 10% potassium hydroxide in aqueous ethanol for twenty four hours in the hope of obtaining an identifiable product. No ammonia was evolved, no acid was produced and the material recovered appeared to be the unchanged starting material.

Attempted condensation of naphthalene and mesityl oxide

c.f. Hoffman, J.A.C.S. 1929, 51, 2542.

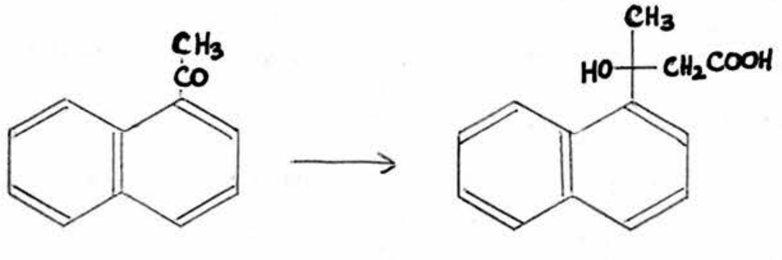


50 grams anhydrous aluminium chloride, 200 mls. of ethylene dichloride and 60 grams of naphthalene were placed in a flask cooled to 0°, and 25 grams mesityl oxide were dropped in over the period of one hour with stirring. Stirring was continued for three hours at room temperature. The mixture was poured on ice, the water separated, and a benzene solution of the product was washed. The benzene and excess mesityl oxide were distilled off leaving largely naphthalene. No other product could be found.

Attempted condensation of dimethyl-acrylic acid and naphthalene.

The conditions employed were the same as those above and only dimethyl-acrylic acid and naphthalene were recovered.

Preparation of β (1 Naphthyl) β hydroxybutyrie acid



Ethylbromoacetate (16.7 g) was added over the course of one hour to acetylnaphthalene (17 gms), zinc wool (13.5 g) and benzene (100 mls) with one crystal of iodine, contained in a round bottomed flask fitted with a reflux condenser. Boiling was continued for two hours on the steam bath and the mixture was then cooled, treated with a mixture of ice and acetic acid and the organic layer separated. The zinc was washed with benzene ether mixture and the washings combined with the organic layer. The combined extracts were washed with three 50 ml portions of dilute ammonium hydroxide then with water and evaporated to dryness to yield an almost colourless oil. This oil when chromatographed on alumina and eluted with petrol/benzene gave a discrete fraction as a colourless oil which did not crystallize. Yield 7 gms.

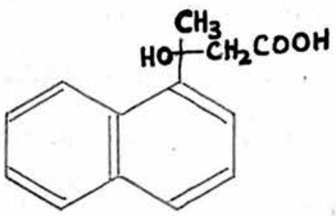
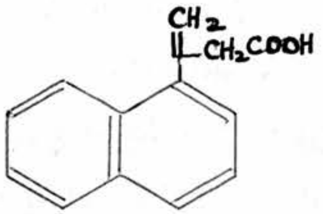
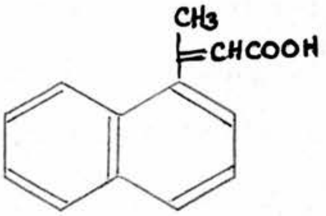
Infra red spectrum.	1680 cm^{-1}	carbonyl
	3450 cm^{-1}	hydroxyl

The hydroxy ester was hydrolysed by dissolving in a mixture of potassium hydroxide (6 gms), ethanol (50 mls), water (10 mls) and boiling for three hours. The alcohol was then distilled off with simultaneous addition of 20 mls water. The solution was extracted with ether to remove any unhydrolysed material and the aqueous alkaline layer was acidified with dilute hydrochloric acid to give a yellow solid. This solid was filtered, washed with water, dried and recrystallized from petrol to give the pure acid m.p. 140° Yield 4 gms.

Infra red spectrum	1700 cm^{-1}	carboxylic acid
	3450 cm^{-1}	hydroxyl.

Analysis	Found	C	73.6%	H	6.1%
	Required $C_{14}H_{14}O_3$	C	73.0%	H	6.1%

Attempted dehydration of the above acid.

The acid (3 gms) was dissolved in formic acid (20 mls) containing 1 drop concentrated hydrochloric acid. The solution was maintained at 60° for one hour and then left to stand overnight. Addition of water precipitated an oil which was extracted with ether and washed with water. After drying over sodium sulphate the ether was removed and the residual oil failed to crystallize. Yield 2.1 gms.

Infra red spectrum. 1680 cm^{-1} carboxylic acid
1630 cm^{-1} olefinic double bond
No hydroxyl

Attempted reduction of the naphthyl-methyl-acrylic acid and isomer.

The mixture of acids (2 gms), was dissolved in ethanol (50 mls) and introduced into a hydrogenator with 50 mls ethanol containing previously hydrogenated platinum oxide. (200 mg.) The mixture was shaken for about six hours until the uptake of hydrogen was equivalent to the amount required to saturate the double bonds. When the catalyst was filtered and the ethanol removed a colourless oil was left which failed to crystallize in any solvent.

Infra red spectrum	1700 cm^{-1} carboxylic acid
	No olefinic double bond.

Summary of Section I

Benzylidene-2,3-dihydrophenalenone has been prepared and the structure of this compound has been established along with that of its isomeric benzyl form. Homonaphthalic acid and other ozonolysis products of these two isomers have been prepared. The structure of the abnormal "dibenzylidene" compound has been discussed. Attempts have been made to synthesise homonaphthalic acid and to prepare mono- and di-substituted 2,3-dihydrophenalenones.

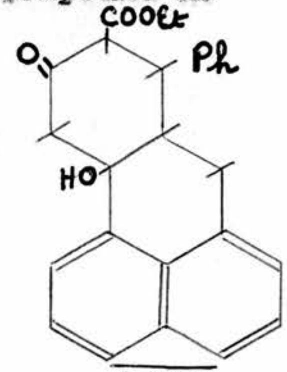
SECTION II

The Preparation of 8-phenylbenzanthrene

Discussion

The condensation of 2,3-dihydro-2-benzylidenephenalenone XLVII led as in the case of the condensation of benzylidenetetralone with ethylacetoacetate to more than one product (69). No fewer than four products were produced depending on the conditions under which the reaction was carried out. The catalyst employed was sodium ethoxide and the concentration was critical. In the first attempt with 1% sodium ethoxide in ethanol no condensation took place and only benzylphenalenone LII was produced in good yield. When the alkali concentration was reduced to 0.1% sodium ethoxide a mixture of two compounds A and B was produced. With an alkali concentration of 0.2% less of A was produced and B along with a fourth compound C resulted. The finer structure of these compounds will be discussed in Section IV but briefly on the basis of ultra violet spectra infra red spectra and analyses the following formulae were assigned.

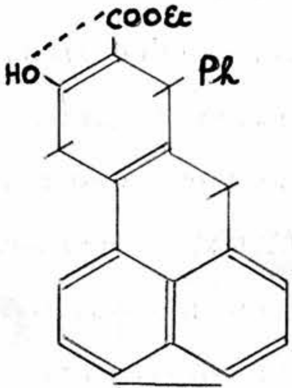
Compound A.



LXX

The ultra violet spectrum U.V.IV was similar to naphthalene and the infra red contained 2 carbonyl peaks and one hydroxyl. Dehydration in formic acid gives a compound identical to B.

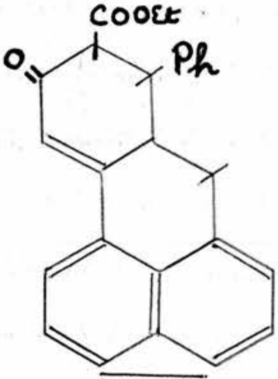
Compound B



LXXI

The ultra violet spectrum similar to that of phenalene U.V.V and an infra red spectrum with only one carbonyl peak indicate this structure. The hydroxyl does not appear in the infra red spectrum but this is consistent with this type of chelated compound. Two olefinic double bonds appear.

Compound C



LXXII

The ultra violet spectrum of a naphthylidene ketone U.V.VI and two carbonyls in the infra red indicate this structure.

Separation of these compounds was achieved by difference in solubility and by chromatography.

B was more soluble in benzene than A. B and C could be separated on silica gel or on alumina. B could be obtained pure from silica gel by elution with benzene leaving C on the column - C could be eluted from alumina with benzene leaving B on the column.

Since at this stage B was more easily produced attempts were made to hydrolyse and decarboxylate it with sulphuric acid, acetic acid and water in varying proportions. The milder of these conditions gave only starting material the stronger a dark purple highly insoluble resin from which no pure product could be obtained. A similar product was obtained with sodium hydroxide.

Compound C was treated in the same way with identical results.

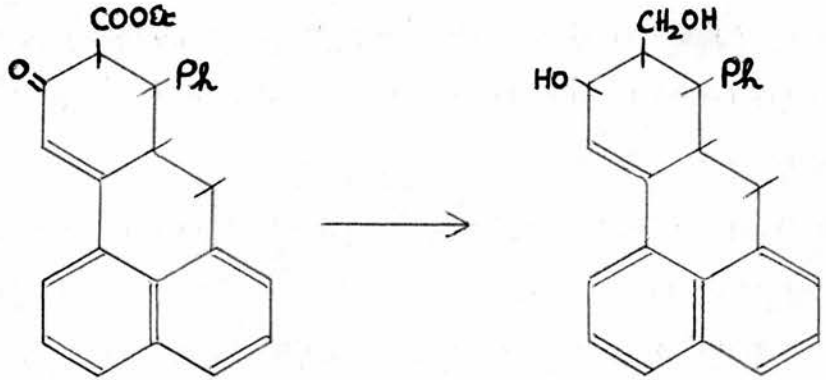
Attempted aromatization with palladium charcoal and selenium dioxide gave no identifiable product.

Attempts were made to reduce compounds B and C with a variety of reagents. Since B appeared more resistant to reduction than C a new synthesis for C was worked out to give it in preference to B.

Higher alkaline concentrations give C but also give benzylphenalenone. A catalyst was found which did not cause isomerism - alcohol free sodium ethoxide. Since a large excess of ethylacetoacetate favoured condensation rather than isomerism this was used as solvent. By this means the unchelated ester was produced in very satisfactory yield. Removal of other products was easy as the ester crystallised out on addition of ether.

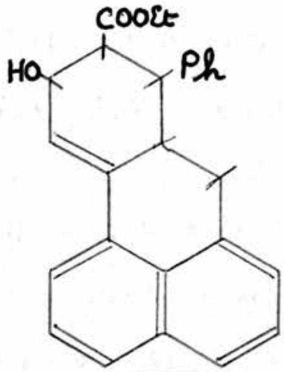
Reduction of C.

Lithium Aluminium Hydride gave as expected a diol.



LXXII LXXIII

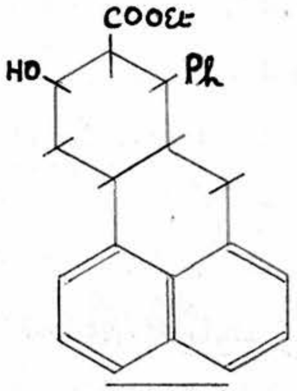
Sodium borohydride gave an identical diol but by choosing conditions carefully it could be reduced to give a hydroxy ester LXXIV.



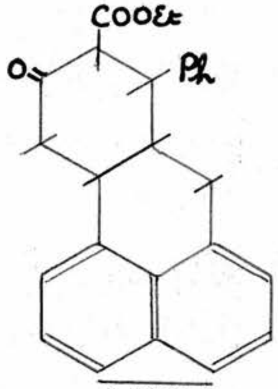
LXXIV

The nature of this alcohol will be discussed in section V. All these alcohols were resistant to decarbethoxylation. If the ketone is essential for decarbethoxylation and the double bond causes the polymerisation which previously hindered the decarbethoxylation selective reduction of the double bond could remove the difficulties. Selective catalysts for double bonds such as palladium on barium sulphate or palladium on charcoal were ineffective in producing any reduction.

Hydrogenation of C in the presence of platinum oxide in ethanol caused the saturated hydroxyester LXXV to precipitate out but in ethyl acetate it was possible after one mole of hydrogen had been taken up to isolate some saturated ketoester. LXXVI In an attempt to get a catalyst slightly milder Raney Nickel was used, but gave the same result as platinum oxide, until a three year old batch was tried. This went at such a speed that a good yield of ketoester LXXVI was obtained.

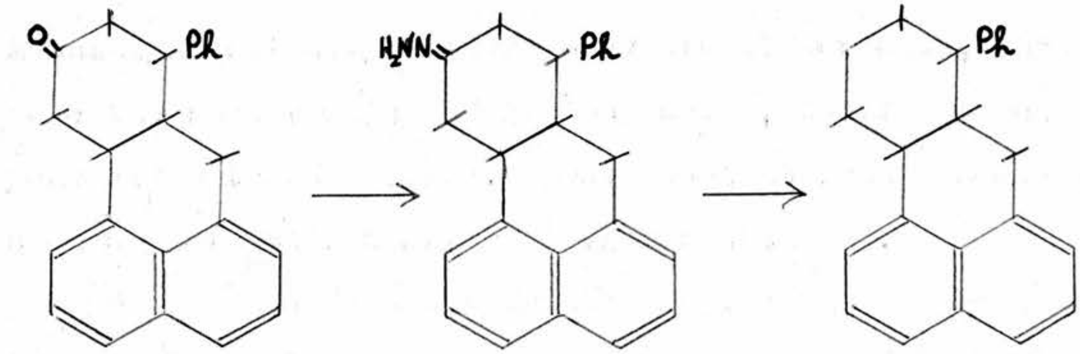


LXXV



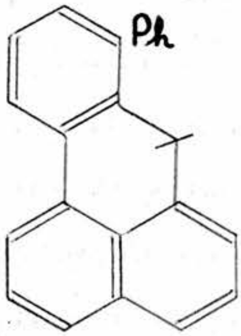
LXXVI

The ketone LXXVI was decarbethoxylated with a mixture of acetic acid, sulphuric acid and water. The physical properties and analysis were consistent with decarbethoxylation having taken place. The resultant ketone LXXVII was reduced to the saturated hydrocarbon by a two stage Huang Minlon modification of the Wolff Kishner reduction. The hydrazone was prepared without alkali and without being isolated was decomposed with potassium hydroxide. The hydrocarbon was easily extracted and the physical characteristics and analysis were consistent with the hydrocarbon structure LXXVII. No functional group bands were present in the infra red spectrum.



LXXVII LXXVIII

Dehydrogenation was effected by refluxing in benzene with tetrachloro ortho quinone for twelve hours under nitrogen. This gave a hydrocarbon which after chromatography on alumina melted at 89° and the analysis figures corresponded to 8-phenylbenzanthrene LXXIX.

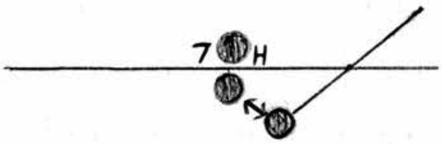


LXXIX

The analysis and the infra red spectrum suggest that this is the hydrocarbon. The ultra violet spectrum showed a very close similarity to that of benzanthracene.

R. N. Jones in a review of ultra violet (75) spectra has shown that substituents such as phenyl substituents which are prevented from taking up a planar position with the rest of the molecule do not alter the ultraviolet spectrum to any great extent from the unsubstituted molecule. Thus if the phenyl is not planar in 8-phenylbenzanthracene then the ultra violet spectrum will tend rather to a summation of the spectra of benzene and benzanthracene.

A Catalin model indicates considerable interference occurs in the 8-phenylbenzanthracene molecule. This then is consistent with the ultra violet spectrum recorded.



A comparative case is that of 9,10-diphenylanthracene which has a spectrum very close to that of anthracene itself (76).

The 8-phenylmesobenzanthrone synthesised by Wall (47) in small yield from phenylphenanthraquinone and glycerol was available and reduction of this to 8-phenylbenzanthracene would provide a confirmation of both syntheseses. Brown and White (67 have described a suitable reducing agent - the complex of lithium aluminium hydride and aluminium chloride. Addition of this reagent to the ketone gave almost immediate reduction in high yield to the phenylbenzanthracene. The excess complex was destroyed by addition of ethyl acetate which was then used as a solvent for the hydrocarbon.

The hydrocarbon obtained by this reduction was identical to that obtained by the synthesis from 2,3-dihydrophenalenone.

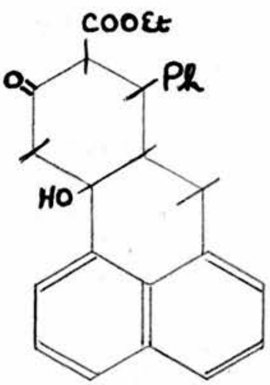
The melting point was 89° and this was undepressed by admixture of the two samples. Identical ultra violet and infra red spectra confirm the identity of the two compounds.

Experimental

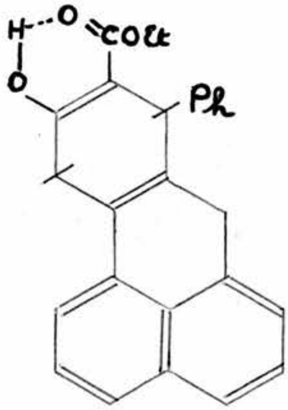
Attempted condensation of Benzylidene-2,3-dihydrophenalenone and ethyl-acetoacetate.

c.f. Campbell, Leaver et al J.C.S. 1959, 3992. 2-Benzylidene-2,3-dihydrophenalenone (10.89) and ethyl acetoacetate (5.29) were dissolved in ethanol (50 mls) containing sodium (19). The mixture was boiled for three hours and poured into water (100 cc) containing acetic acid (15 mls). Extraction with ether and evaporation gave a solid. m.p. 89° Yield 8 gms. This was indentical with benzylphenalenone by mixed melting point and identical infra red spectrum.

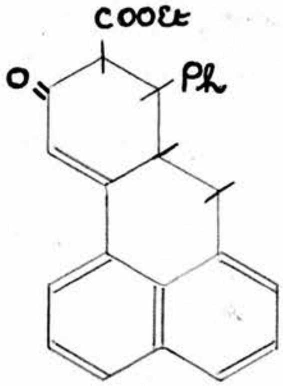
Preparations of A. 7H 7a. 8, 9,10,11, 11a-hexahydro-11a-hydroxy-8-phenyl-9-carbethoxy-10-oxo-benz(de)anthracene B. 7H 8. 11,-dihydro-8-phenyl-9-carbethoxy-10-hydroxy-benz(de)anthracene C. 7H 7a 8, 9, 10-tetra-hydro-8-phenyl-9-carbethoxy-10-oxo-benz(de)anthracene.



A



B



C

Preparation of A B.

2-Benzylidene-2,3-dihydrophenalenone (5.4 gms) ethyl acetoacetate (2.6 gms) were dissolved in 100 mls. ethanol containing 0.05 gms sodium. The mixture was refluxed for three hours then cooled where upon a solid separated. This was filtered off and partially dissolved in acetone. The insoluble fraction was compound A and the fraction soluble in acetone compound B.

mp. A. 208° mp. B 191°

Analyses.

A.	Found	C	76.7%	H	5.8%
	Required $C_{26}H_{24}O_4$	C	78.0%	H	6.0%
B	Found	C	82.3%	H	6.0%
	Required $C_{26}H_{22}O_3$	C	81.7%	H	5.8%

Preparation of B from A by dehydration

Compound A (0.5 gms) was dissolved in 90% formic acid (5 mls). The compound went into solution when the mixture was warmed on the steam bath but almost immediately reprecipitation took place. On cooling to 0° a solid was precipitated further and when the pink compound was filtered, washed with water and recrystallized from ethanol was found to melt at 191°.

Mixed melting point with B undepressed.

Infra red spectrum identical with B.

Preparation of Esters B and C.

2-Benzylidene-2,3-dihydrophenalenone (5.4 gms) ethyl acetoacetate (2.6 gms) were dissolved in 100 mls ethanol containing 0.2 gms sodium. The mixture was boiled on the steam bath for three hours and became red in colour. On cooling and addition of water a solid separated. This was filtered off and dissolved in benzene.

Chromatography on silica gel gave two compounds B and C. B is eluted with benzene and comes off in a pink band. C is eluted with benzene containing a little methanol. C crystallizes from ethanol in yellow needles 0.9 gms mp. 203°.

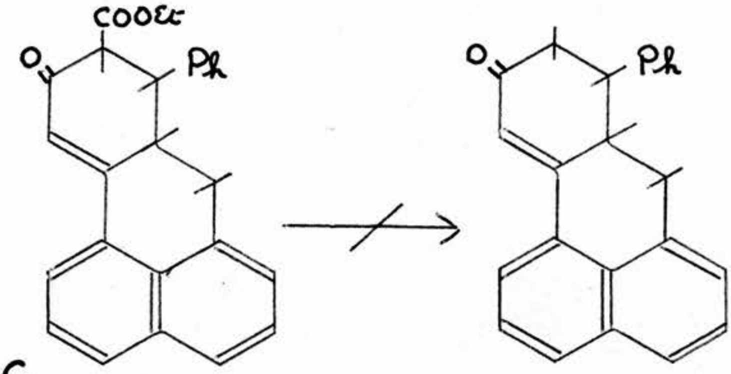
Analysis of C. Found	C	81.9%	H	5.9%
Required $C_{26}H_{22}O_3$	C	81.7%	H	5.8%

The physical characteristics of these esters is given in Section V of the discussion

Preparation of Ester C preferentially

A solution of sodium ethoxide was prepared from 0.1 gm sodium and 2.5 mls ethanol. To this solution was added 5 mls ethyl acetoacetate and 1 gram of 2-benzylidene-2,3-dihydrophenalenone. The mixture was heated on the steam bath under reflux for one hour then cooled and 20 mls of water added. The resultant oil was extracted with ether benzene (1:1) and washed three times with 2N sodium hydroxide and then once with water. The ether/benzene was removed and 20 mls of ether added. The ester precipitated in needles from the ether and was filtered off and recrystallized from ethanol 25 ccs per gram. Yield 0.7 gms mp. 203°.

Attempted decarbethoxylation of B and C.



C

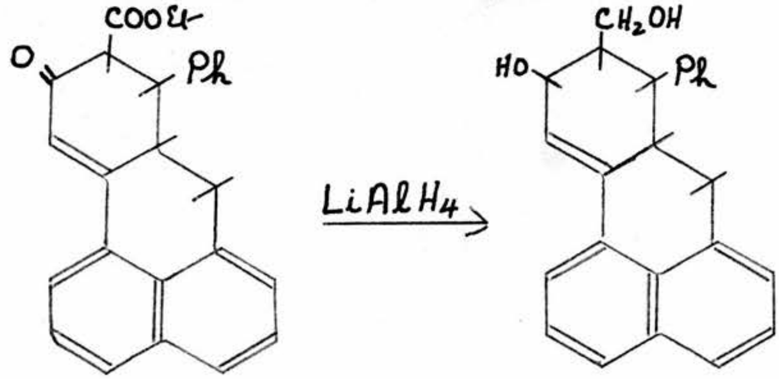
Esters B and C were warmed or boiled with

(a) Sulphuric acid/acetic acid/water 2/4/1 wt.
(b) Sulphuric acid/acetic acid/water 2/5/1 wt.
(c) 4% sodium hydroxide in ethanol.

Both esters gave an unidentifiable purple insoluble material with methods (b) and (c) while with (a) starting material was recovered.

Reductions of Ester C.

(a) Lithium aluminium hydride



Ester C (1 gm.) was slowly added to lithium aluminium hydride (0.25 gms) in 25 cc ether and the mixture was boiled for ten minutes. Excess lithium aluminium hydride was destroyed with ethyl acetate, the mixture was filtered and the solvent removed. The product was recrystallized from ethanol. Yield 0.8 gms m.p. 180°

Infra red spectrum	No carbonyl
$3300 - 3400\ cm^{-1}$	hydroxyl

(b) Sodium Borohydride

To ester C suspended in ethanol was added excess sodium borohydride in ethanol and the mixture was warmed. On destruction of excess borohydride and washing with dilute ethanol an alcohol was obtained identical to the diol above.

(c) Sodium Borohydride

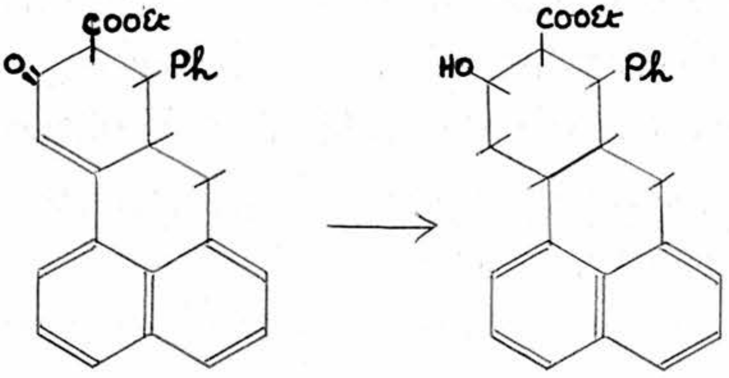
c.f. Brown and Rapoport. J. Org. Chem 1963, 28, 3261.

To the ester C was added 1.1 moles sodium borohydride at room temperature in propanol and the mixture allowed to stand for 48 hours. Washing of the mixture and extraction of the product in ether gave the alcohol. m.p. 185°C.

Infra red spectrum	$3380\ cm^{-1}$	hydroxyl
	$1720\ cm^{-1}$	ester carbonyl
	$1640\ cm^{-1}$	olefine double bond.

Analysis	Found.	C 80.9	H 6.1
	Required $C_{26}H_{24}O_3$	C 81.3	H 6.3

(d) Reduction of keto ester C with platinum oxide.



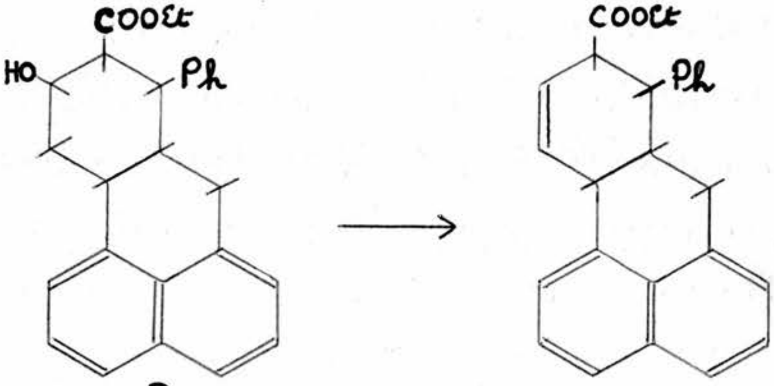
D + E 2 ISOMERS

2 gms ester C in alcohol were added to a hydrogenator containing 200 mg. platinum oxide catalyst. The uptake was very slow and a white compound started to precipitate before 1 mole of hydrogen was taken up. The hydrogenation was allowed to go to completion when 2 moles had been taken up. The product was a white solid fairly insoluble in ethanol which was separated easily into two isomers D and E. D being insoluble and E being soluble in petrol ether D: mp. 254° E: mp. 194°

Analysis of D	Found	C	80.4%	H	6.9%
	Required $C_{26}H_{26}O_3$	C	80.8%	H	6.8%
Analysis of E	Found	C	80.9%	H	6.9%
	Required $C_{26}H_{26}O_3$	C	80.8%	H	6.8%

The other physical characteristics are dealt with in Section V of the Discussion.

Dehydrations of the hydroxy esters D and E.



D

0.2 gm portions of esters C and D were each heated with formic acid containing a drop of concentrated hydrochloric acid. In each case a new compound was produced and although no analyses were carried out the infra red spectrum clearly showed that compound E had formed a formate and compound D had undergone dehydration.

(e) <u>Reduction of unsaturated keto ester C with Raney Nickel.</u>

The compound reduced with Raney Nickel in the same way as with platinum oxide.

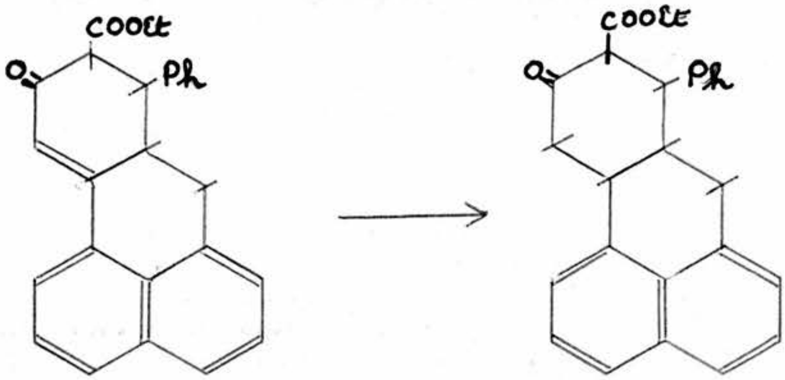
(f) <u>Reduction of C with 5% Palladium on Barium sulphate.</u>

No reduction took place.

(g) <u>Reduction with platinum oxide in ethyl acetate.</u>

With this solvent the conditions were as with platinum oxide in ethanol but some keto ester was isolated after one mole of hydrogen had been taken up. For characteristics see section (h) below.

(h) Reduction of unsaturated keto ester C with old non-pyrophoric Raney Nickel.



The reduction was carried out in ethyl acetate with hydrogen and 3 year old Raney Nickel. A fairly rapid uptake of 1 mole of hydrogen was followed by a slower uptake. When 1.1 moles of hydrogen were taken up the solution was filtered free of catalyst and the solvent removed the product was chromatographed with benzene on alumina to give the pure white keto ester m.p. 210° in 65% yield.

Analysis of keto ester Found: C, 81.4%; H, 6.5%

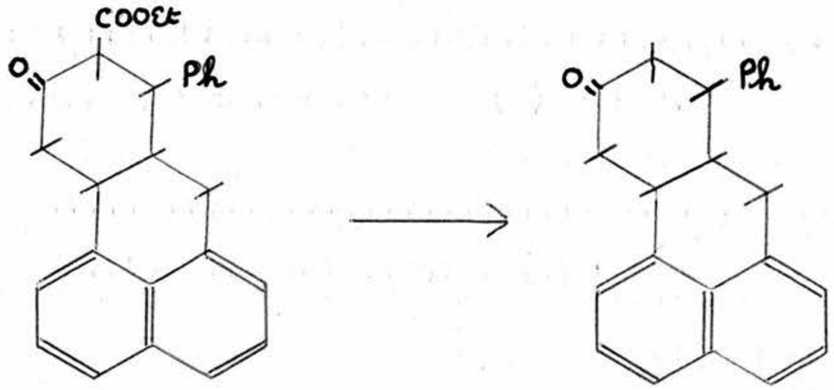
Required $C_{26}H_{24}O_3$ C, 81.3%; H, 6.3%

Infra Red spectrum 1705 cm^{-1} carbonyl unconjugated

1725 cm^{-1} carbonyl of ester.

Decarbethoxylation of saturated keto ester.

Campbell, Leaver et al J.C.S., 1959, 3992.

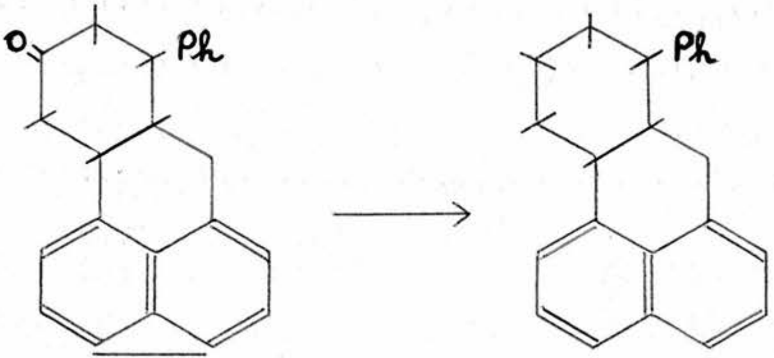


The keto ester (1 gm) was refluxed in a mixture of 5 mls. acetic acid, 2 mls. concentrated sulphuric acid and 1 ml. water in an oil both for 30 minutes. If the ketone is pure almost no colouration takes place, but if impure intense colouration results and a small yield is obtained. The mixture was poured into water to give an orange precipitate, which was taken up in benzene, the benzene layer washed, dried with sodium sulphate, and evaporated to small volume. When chromatographed in benzene on alumina it gave the pure ketone m.p. 180° after recrystallization from petrol 80°/100°. Yield 0.5 gms.

Analysis

Found	C, 87.4%; H, 6.4%
Required $C_{23}H_{20}O$:	C, 88.4%; H, 6.4%

Huang Minlon Modification of Wolff Kishner Reduction to hexahydrophenylbenzanthrene.



LXXVII

c.f. C. Djerassi et al., J.A.C.S. 1953, 75, 3505

1 ml. Hydrazinehydrate was added to the ketone LXXVII (0.4 gms) in 10 mls ethylene glycol and the whole refluxed for one hour then cooled. Potassium hydroxide (0.5 g) in 3 mls. water was added to the cold solution and the temperature was gradually raised to reflux, the water being removed in a separator. When the temperature had risen to 180° it was maintained there for three hours. A small amount of hydrocarbon was collected from the water in the separator and was extracted with benzene (10 mls). The same benzene was used to extract the rest of the hydrocarbon from the diluted ethylene glycol. The benzene extract was washed with water three times, dried with sodium sulphate and chromatographed in benzene on alumina (10 gms). A small amount of fluorescent oil was collected first, followed by the hydrocarbon, which crystallized in pure white needles from petrol ether 40°/60°.

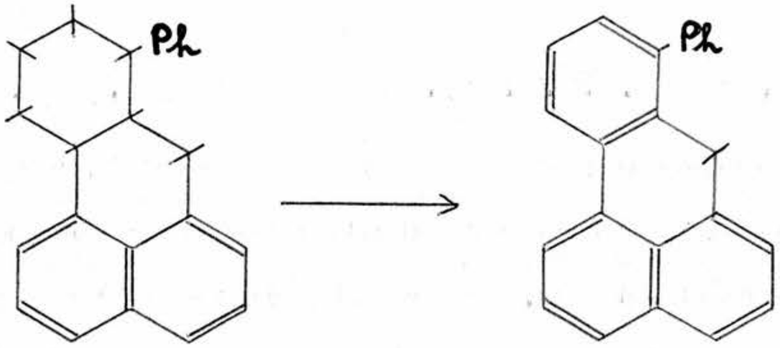
Yield 0.2 gms m.p. 158°

Infra red spectrum. No carbonyl peak.

Analysis Found: C, 91.7%; H 6.9%

Required $C_{23}H_{22}$: C, 92.6%; H 7.4%

Preparation of 8-phenylbenzanthracene from the hexahydro compound.



c.f. Braude, Brook, and Linstead J.C.S., 1954, 3569

The hexahydro-hydrocarbon (0.1 gms) was dissolved in sulphur free xylene and tetra-chloro-orthoquinone (Jackson and Carleton Amer. J. Chem. 1908, 39.) was added. The solution was refluxed for three hours then cooled. The hydrocarbon solution containing also the excess tetrachloro-ortho-benzoquinone and tetrachlorocatechol was put through an alumina column to retain the last two compounds. The solution was evaporated to dryness and the hydrocarbon crystallized from petrol in yellow plates melting point 89°. Yield 0.06 gms.

Infra red spectrum. No functional groups present.

Analysis. Found: C, 93.3%; H 5.3%

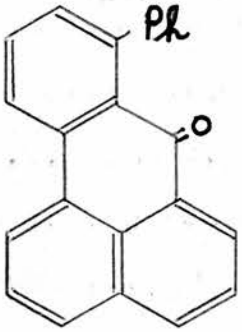
Required $C_{23}H_{10}$: C, 94.5%; H 5.5%

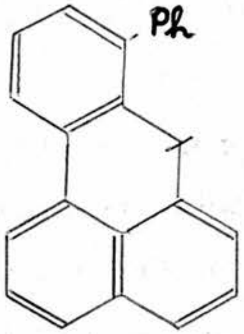
Assuming that the 1.4% missing is slight oxidation or inorganic material e.g. alumina from the column, the carbon hydrogen content would be C, 94.6%; H, 5.4%.

The ultra violet spectrum is similar to that of benzanthrene.

Reduction of the Phenylmesobenzanthrone synthesised by R. A. Wall, with Lithium aluminium Hydride/aluminium Chloride comples.

c.f. Brown and White J.C.S., 1957, 3755.





Lithium aluminium hydride (.074g) was added to a solution of 0.4 gms aluminium chloride in ether (5 mls). After the reaction had subsided the phenyl-mesobenzanthrone (0.05 gms) was added to the solution of the complex. A vigorous reaction occurred. accompanied by a transient orange colour. When the addition was complete the mixture was warmed for a few moments on the steam bath. The excess complex was destroyed by the addition of ethyl acetate first until no more reaction occurred then a further 20 mls as solvent. The ethyl acetate solution of the hydrocarbon was washed with 2N sulphuric acid and then dried over sodium sulphate. The ethyl acetate was distilled off and the hydrocarbon crystallized immediately and was dissolved in 60/80 petrol and chromatographed on alumina (5 gms). The pale yellow plates from petrol melted at 89° and the mixed melting point with the 8-phenylbenzanthrene showed no depression. Yield 0.025 gms. The ultra violet spectra of the compound synthesised from 2 benzylidene-2,3-dihydrophenalenone and the compound obtained by the reduction were the same.

Summary of Section II.

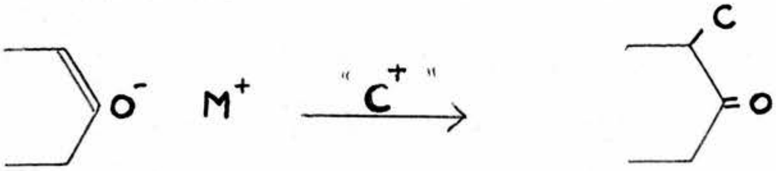
The synthesis of 8-phenylbenzanthrene has been achieved by condensation of ethylacetoacetate with benzylidene -2,3-dihydrophenalenone and reduction, decarbethoxylation, reduction and aromatization of the product. Some isomers and reduction products were also observed, and structures assigned to them.

SECTION III

Some attempted syntheses of 8-phenylmesobenzanthrone

Discussion

In the synthesis of new ring systems a major reaction system employed is the condensation of an enolate derived from a carbonyl group with an electrophilic carbon as in the aldol condensation Claisen condensation and related reactions.

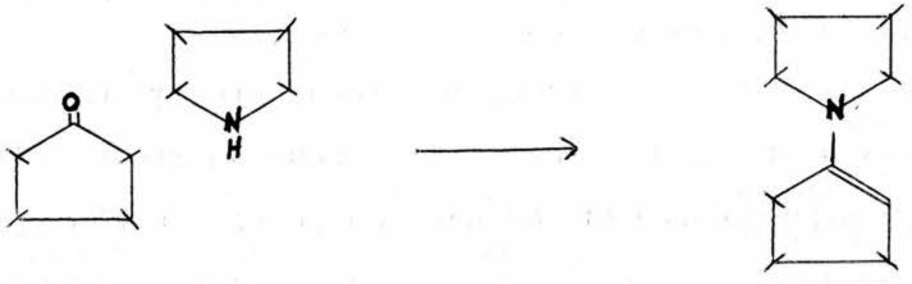


The serious limitations to such reactions are normally self condensation due to the necessity of a strong base and dialkylation instead of mono-alkylation (77).

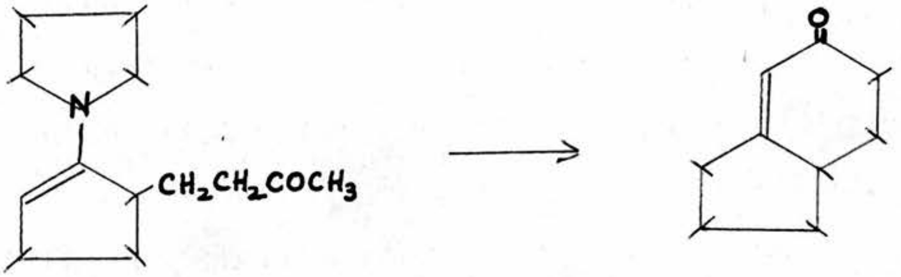
G. Stork et al have suggested a method to avoid these problems and have applied it to many carbonyl compounds to which such condensations could not previously be applied.

The enamine formed by an ordinary aldehyde or ketone and an amine, (frequently pyrrolidine) is allowed to react with an electrophilic reagent. No basic catalyst is normally necessary.

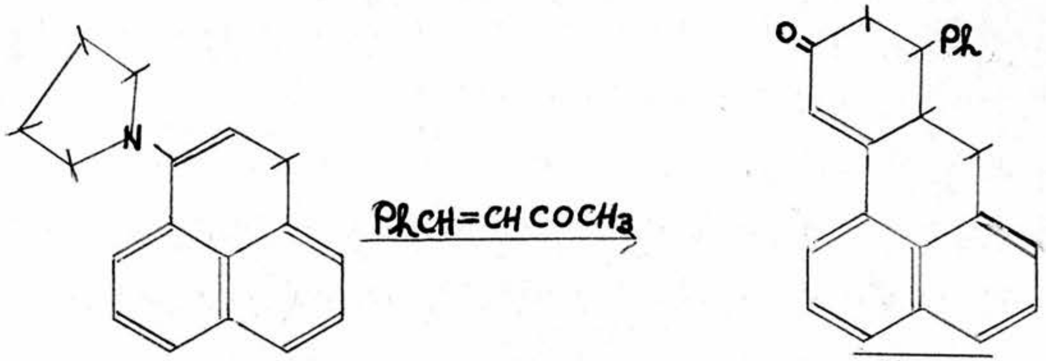
This base and cyclopentanone (which normally condenses with itself under Michael reaction conditions) yield pyrrolidine cyclopentenamine LXXX. Such enamines condense with $\alpha\beta$ -unsaturated ketones without alkali to give substituted enamines and hence by hydrolysis diketones which then cyclise.



LXXX



Thus if the enamine of 2,3-dihydrophenalenone should condense with methyl styryl ketone to give tetrahydrophenylbenzanthrone LXXXI.

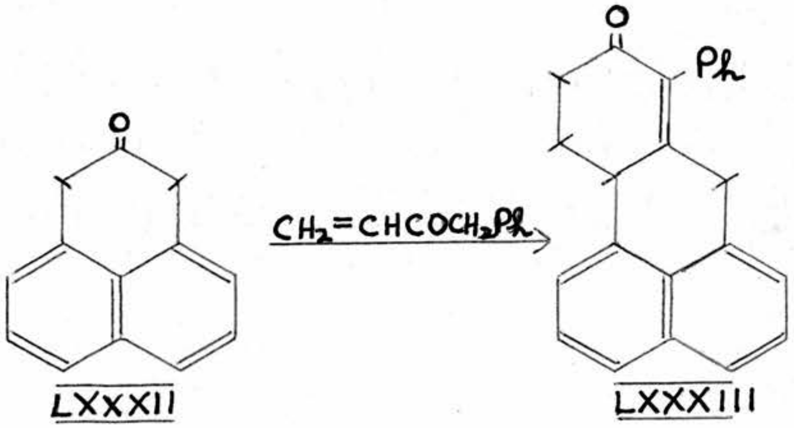


LXXXI

The attempt to prepare the enamine resulted only in a deep purple insoluble uncrystallizable product which could not be completely removed from the glass ware by any normal solvents.

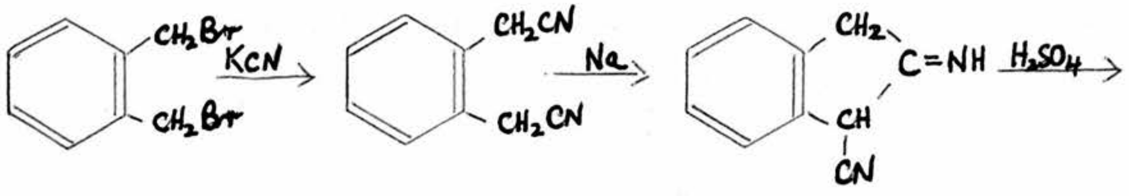
Consideration of the ketones employed by Stork suggests that for the method to be successful two carbons to the carbonyl should have at least one hydrogen atom. For instance Stork quotes β -tetralone but not α -tetralone. If this indeed is an essential factor it is clear that 2,3-dihydrophenalenone does not have the necessary hydrogens.

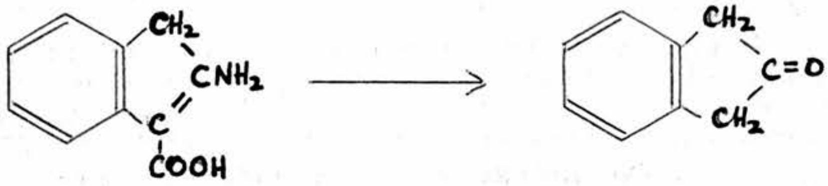
One way of solving this problem is to use 2,3-dihydrophenalene-2-one LXXXII. This could be used to prepare the ketone LXXXIII.



LXXXII LXXXIII

LXXXII has not been prepared but an elegant synthesis used by Thorpe to prepare β -indanone was considered (78).





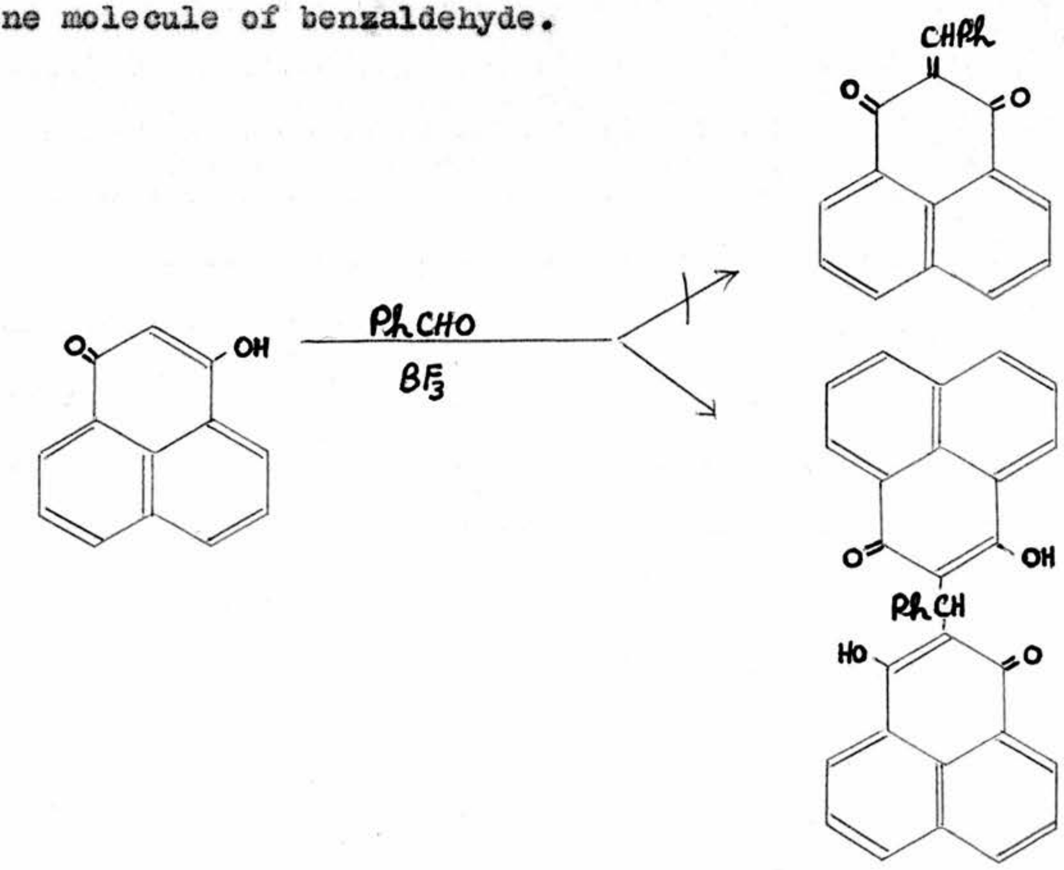
Reduction of naphthalic anhydride to give napthalene-1.8-dimethanol provided suitable starting material.

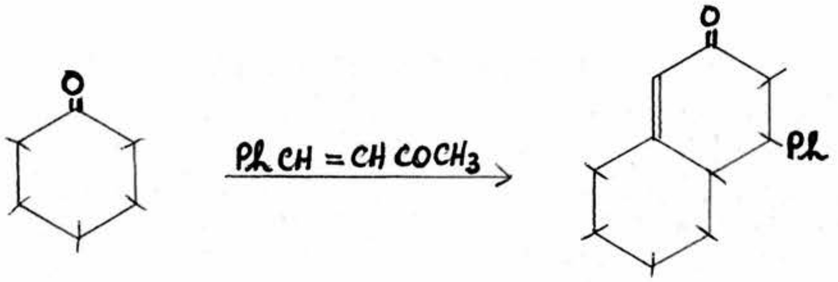
The alcohol with hydrobromic acid gave a compound containing bromine but analysis showed that it contained less bromine than required for the dibromo compound and just more than enough for the monobromo compound.

Attention was turned now to certain diones. 2-Benzylideneindandione has been prepared from 1.3-indandione (79).

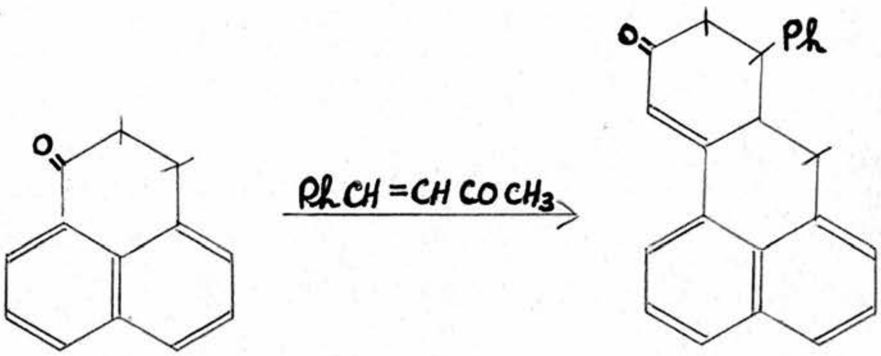
If a similar benzylidene compound could be obtained from 2,3-dihydrophenalenone-1,3-dione it might be possible to condense it with ethylacetoacetate to produce a substituted 7-benzanthrone instead of the benzanthrene which might be more stable when subsequent attempts at decarbethoxylation were made.

Errera (80) had trouble with this condensation an abnormal product being produced due to the tendency for the 1,3-dione to exist in the enol-one form, but by using an acid catalyst such as boron trifluoride (81), which has been used on the pentenedione, it was hoped that a normal benzylidene compound could be prepared. The product of the reaction however was of the form described by Errera where two molecules of enol-one condensed with one molecule of benzaldehyde.





Rapson and Robinson in the face of the probability of self condensation reacted cyclohexanone and methylstyryl ketone to give a mixture of compounds which gave without chromatography a phenyl decalenone (82).



With 2,3-dihydrophenalenone under similar conditions it is possible that a ketone could be isolated by chromatography and converted to the phenylbenzanthrene more easily than with the ester.

The product was a yellow plastic mass which could not be separated into components by chromatography or crystallization.

Experimental

Attempted Preparation of pyrrolidine-2,3-dihydrophenalenoneenamine.

c.f. Stork et al. J.A.C.S., 1963, 85, 207.

2,3-Dihydrophenalenone (9.1g) and pyrrolidine (79) in 50 mls benzene were refluxed using a water separator until no more water separated. Since after six hours very little water had separated a little p. toluene sulphonic acid was added and the boiling continued for 24 hours. No more water separated and toluene was added slowly and the benzene removed. Still no more water separated. The solvent was removed and the excess amine but only an extremely insoluble intensely purple product was obtained which permanently coloured some of the glass ware.

Attempted hydrolysis of the above product.

The product was refluxed with acetic acid (25 mls) sodium acetate (12.5 g) and water (25 mls) for four hours. At the end of this time no 2,3-dihydrophenalenone could be extracted from the gummy mixture by chromatography on alumina.

Attempted Preparation of 2,3-dihydrophenalen-2-one

Preparation of Naphthalene 1.8 Dimethanol.

Beyler and Sannet J.A.C.S. 1952, 74, 1406.

The reaction was carried out as in the reference.

Yield 4.59 g. m.p. 157^{o}

Attempted preparation of 1.8 dihyomomethyl naphthalene.

c.f. Hey et al J.C.S. 1953, 2021.

Naphthalene 1.8 dimethanol (4.25 gms) was heated with 48% hydrobromic acid (10.59) and concentrated sulphuric acid (3.5 gms) for three hours. When cold the heavy bromo-compound was washed with water and dissolved in ether. The ethereal solution was washed dried and concentrated. The residue crystallized from petrol 40^{o}/60^{o}. Yield 2 gms m.p. 80^{o}.

Analysis	Found:	Bromine,	36.9%
	Required:	$C_{12}H_{10}Br_2$,	51%
	Required:	$C_{12}H_{11}O\,Br$,	31.9%

Preparation of 2,3-dihydrophenalenone 3 one - or 3-hydroxy-phenalenone.

G. Errera Gazz. Chim. Ital. 41I 190 (1911)

The method of Errera was used but the yield was reduced.

m.p. 250 - 262^{o} Yield 25 gms.

Infra red hydroxyl present

Attempted preparation of 2-benzylidene-2,3-dihydrophenalene-1,3-dione.

c.f. De Puy and Wells J.A.C.S. 1960, 82, 2909.

The "dione" (2 gms) in anhydrous ether 25 mls was treated with 5 gms benzaldehyde and 25 mls boron trifluoride/ether complex (redistilled at 120°) and refluxed for one hour. On cooling the resulting solution was carefully washed with saturated aqueous sodium chloride solution, dried over anhydrous sodium sulphate and evaporated to dryness. Extraction of the yellow semi solid product, with 40°/60° petrol removed the excess benzaldehyde to leave a yellow compound which crystallized from alcohol as a yellow powder. m.p 295°

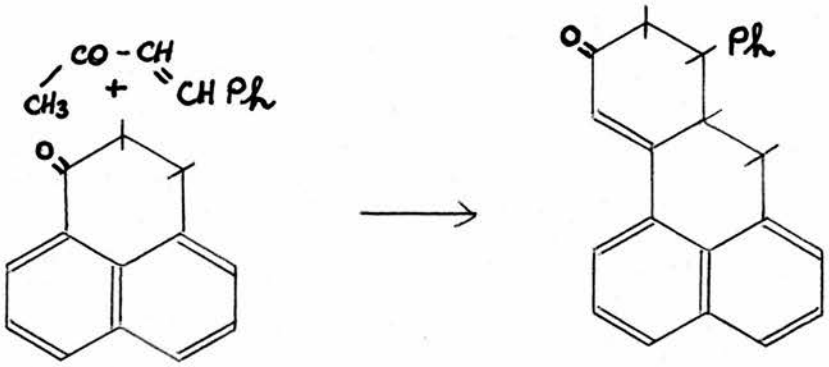
Yield 1 gm. c.f. Errera and Cuffaro Gazz Chim. Ital. 41 II 807.

Attempted Preparation of 2 benzylidene 2,3-dihydrophenalene 1,3 dione.

Using the conditions of mild alkali used in the preparation of 2-benzylidene-2,3-dihydrophenalenone only starting material was recovered.

Attempted Condensation of 2,3-dihydrophenalenone and methyl styryl ketone.

c.f. Rapson and Robinson J.C.S. 1935, 1285

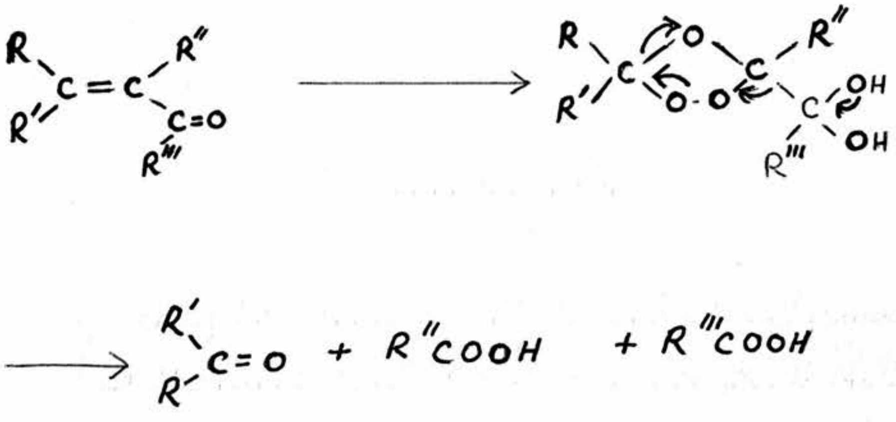


Sodio-2,3-dihydrophenalenone was prepared from 2,3-dihydrophenalenone (3.6 gms) sodamide (1 gm) in 25 cc ether. The ammonia was removed in a stream of dry hydrogen. Styryl methyl ketone (2.3 gms) dissolved in 10 cc ether was added slowly with shaking and cooling. After 12 hours water was added and the ether layer was shaken with dilute sulphuric acid, washed with water then dried. The residue after removal of the solvent was chromatographed on alumina in petrol without achieving any separation.

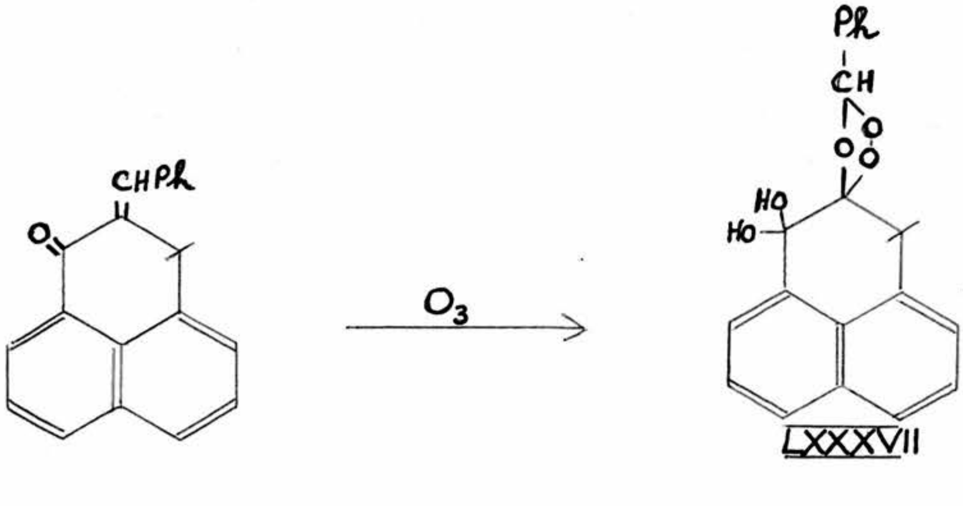
SECTION IV

The Mechanisms of the ozonolysis of benzylidene 2,3-dihydrophenalenone and related compounds

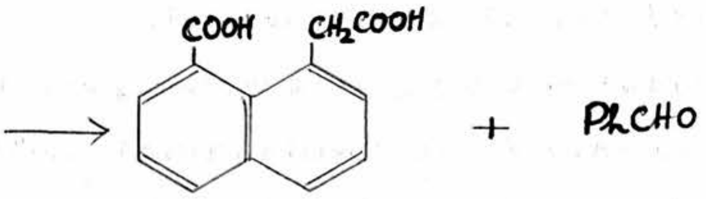
The products of the type isolated from benzylidene-2,3-dihydrophenalenone by ozonolysis are listed as "abnormal products" in a review by Bailey (62). According to Barton and Sloane (83) these products are to be expected in varying degrees from $\alpha\beta$ -unsaturated ketones and the mechanism suggested is by formation of the hydrate of the carbonyl.



Thus with 2,3-dihydrophenalenone we have LXXXVIII.

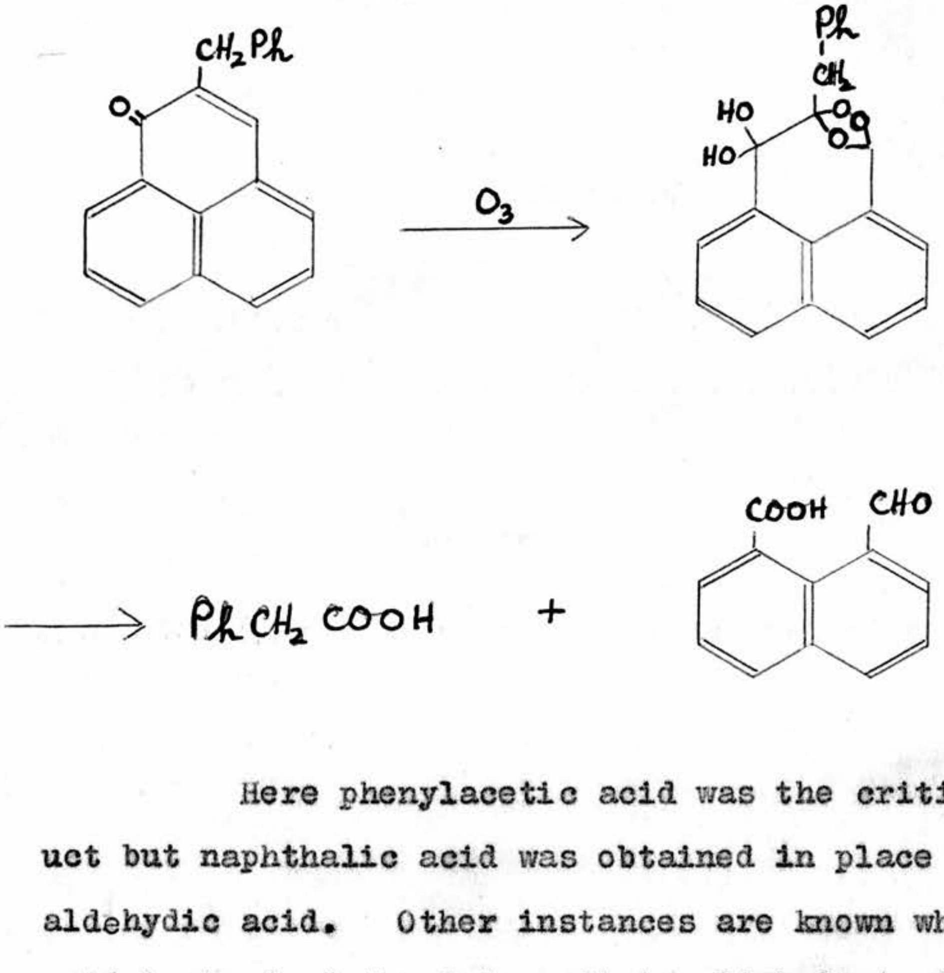


LXXXVII



Homonaphthalic acid is the product of the reaction and as suggested earlier it does not involve any dione.

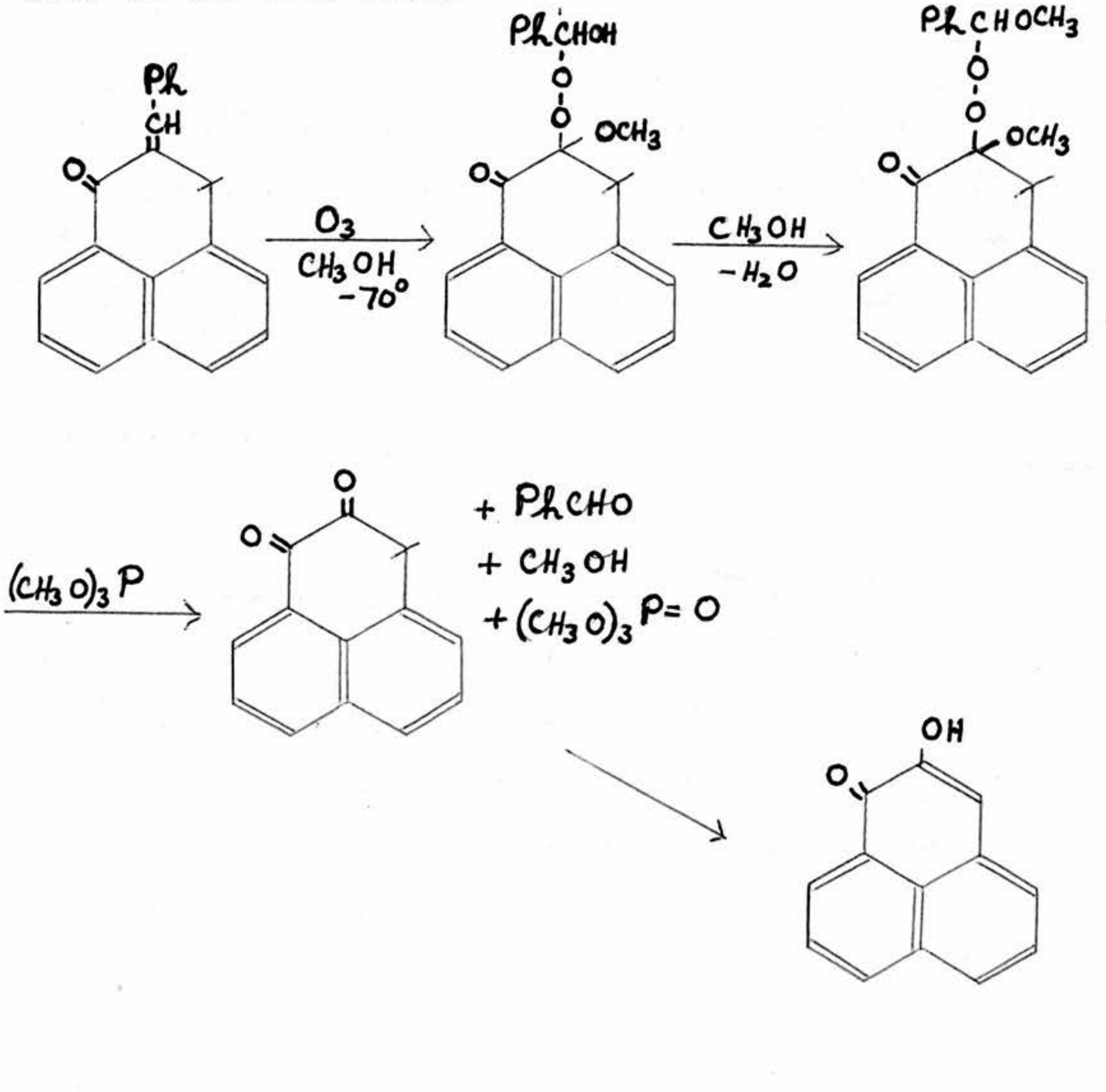
Similarly with benzylphenalenone.



Here phenylacetic acid was the critical product but naphthalic acid was obtained in place of naphthaldehydic acid. Other instances are known where the acid instead of the intermediate aldehyde is isolated and we found that decomposition of the ozonide with hydrogen peroxide solution led to a higher yield of the acid.

On this basis we can explain the formation of naphthalic acid as the result of the ozonolysis of 2-hydroxyphenalenone.

Ozonolysis of the benzylidene compound in methanol with trimethyl phosphate yields the diketone (keto-enol form). Formation of the ozonide is followed by addition of methanol at -70°. As the temperature rises addition of more methanol with loss of water takes place and reduction with the phosphite leads to the diketone and benzaldehyde. The diketone immediately isomerises to the keto-enol.



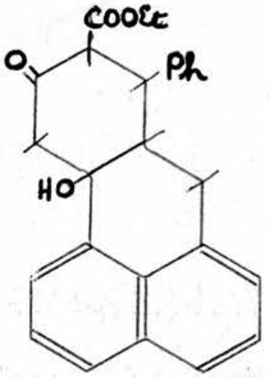
SECTION V

The Structure of Some Intermediates and Reduction Products in the Synthesis of 8-Phenylbenzanthrene

Discussion

The structure of three esters (p 67) has been deduced from their physical characteristics and chemical reactions. These esters, the products of the condensation of benzylidene-2,3-dihydrophenalenone with ethylacetoacetate were A LXX B LXXI and C LXXII.

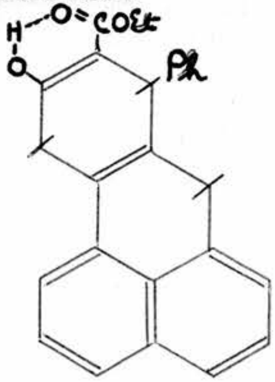
Compound A



Since no conjugation exists between the phenyl group and the 2,3-dihydrophenalene nucleus the ultra violet spectrum might be expected to be close to that of 2,3-dihydrophenalene but with an increase in adsorption intensity around 260 mμ corresponding to the benzene ultra violet spectrum (U.V. IV). The infra red spectrum shows two peaks at 1735 cm^{-1} for an ester carbonyl and at 1700 cm^{-1} for an unconjugated ketone.

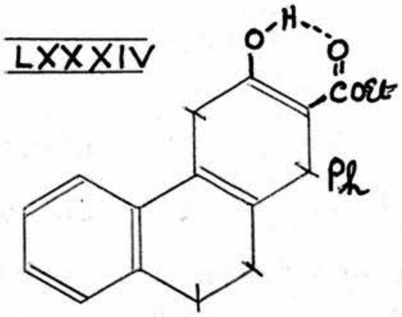
A peak at 3400 cm^{-1} corresponds to the hydroxyl. Dehydration with formic acid takes place across the interannular junction to give B.

Compound B



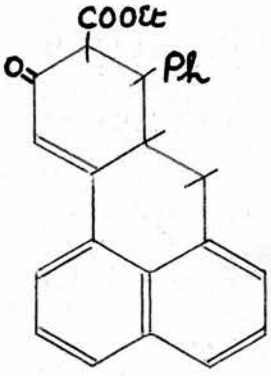
Once again there is no conjugation between the phenyl and the phenalene nucleus, and the ultra violet spectrum might be expected to be similar to that of phenalene with an increase in adsorption intensity around 260 mμ

LXXXIV

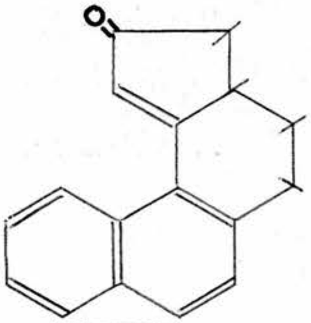


corresponding to the phenyl U.V. V. The infra red spectrum shows a single band at 1672 cm^{-1} for a conjugated ester and two olefinic double bond bands at 1620 cm^{-1} and 1640 cm^{-1} . There is no hydroxyl peak. The infra red spectrum is very similar to that of compound LXXXIV which has its carbonyl band at 1665 cm^{-1} and olefinic double band bands at 1635 cm^{-1} and 1605 cm^{-1} . It also shows no hydroxyl because of the strong chelation.

Compound C

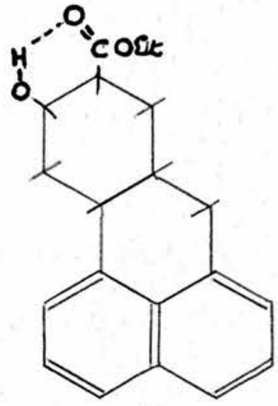


This compound has an ultra violet spectrum resembling that of nephthal acetone with increase in adsorption intensity due to the phenyl group around 260 mμ . An even stronger resemblance is found with that of compound LXXXV (U.V VI). The infra red spectrum has two carbonyl bands one at 1722 cm^{-1} for the ester and the other at 1660 cm^{-1} for an unsaturated ketone.

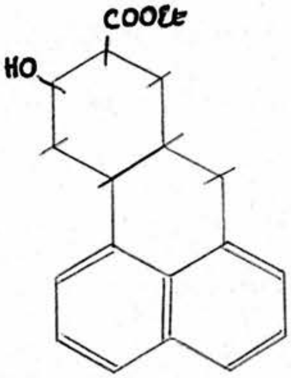


LXXXV

Reduction of ester C LXXII gave two isomeric saturated hydroxy esters - D and E.



D

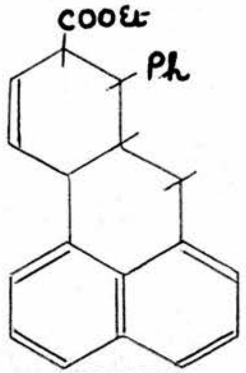


E

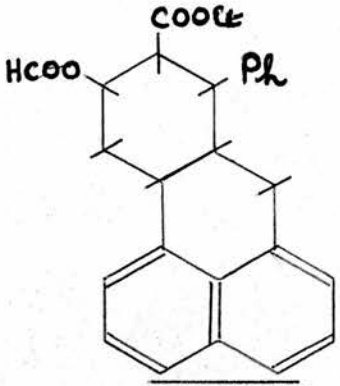
Analysis shows that these two compounds are isomeric. The melting point of E is 254° and that of D is 194°. The infra red spectra are distinct. Both show one hydroxyl peak and one carbonyl peak but the hydroxyl of D is at 3400 cm^{-1} and sharp suggesting chelation as does the melting point, the solubility in petrol ether and the low carbonyl band at 1685 cm^{-1} E on the other hand has a broad hydroxyl peak at 3500 cm^{-1} suggesting inter molecular bonding. The carbonyl band appears at 1730 cm^{-1} showing that the compound is unchelated. The compound is insoluble in petrol ether.

Dehydration of these two compounds led to two new compounds on which no analyses were carried out but the infra reds showed clearly that E had given a formate with two carbonyls one at 1715 cm^{-1} and one at 1730 cm^{-1} LXXXVI whereas D had dehydrated to give a compound showing no hydroxyl and with a single carbonyl at 1720 cm^{-1} LXXXVII.

Since dehydration is normally trans then D must be the trans isomer of the reduction and E the cis isomer.

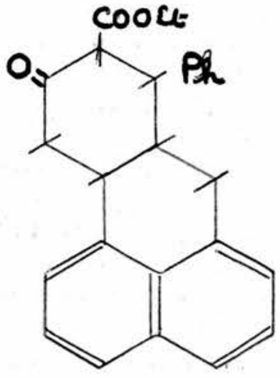


LXXXVI



LXXXVII

Reduction of the olefinic double bond only of C led to a keto ester LXXVI. The ultra violet spectrum was similar to that of 2,3-dihydrophenalene and the infra red spectrum showed the ester band at 1725 cm^{-1} but the carbonyl had risen from 1660 cm^{-1} for the unsaturated ketone to 1705 cm^{-1} for the saturated ketone.



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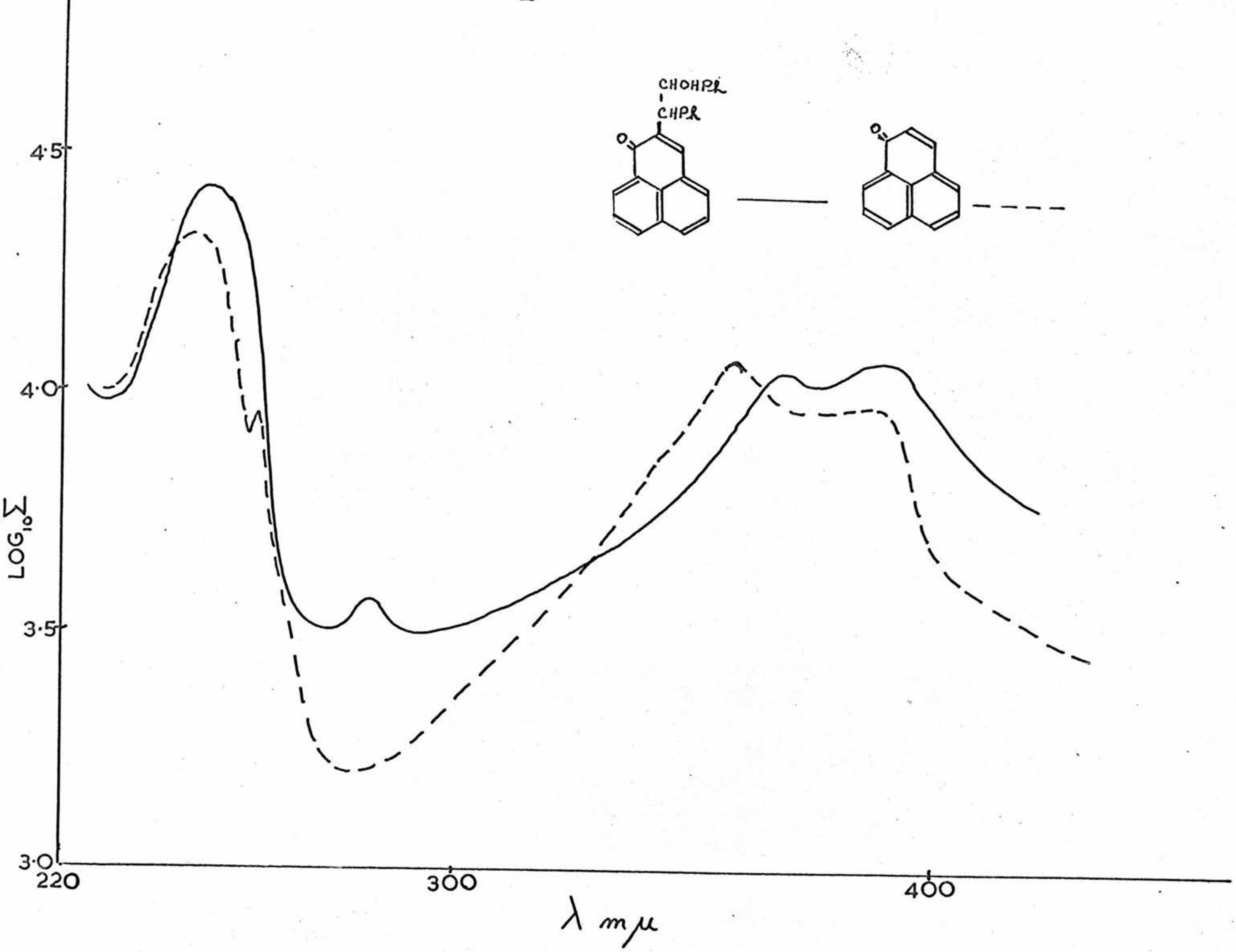

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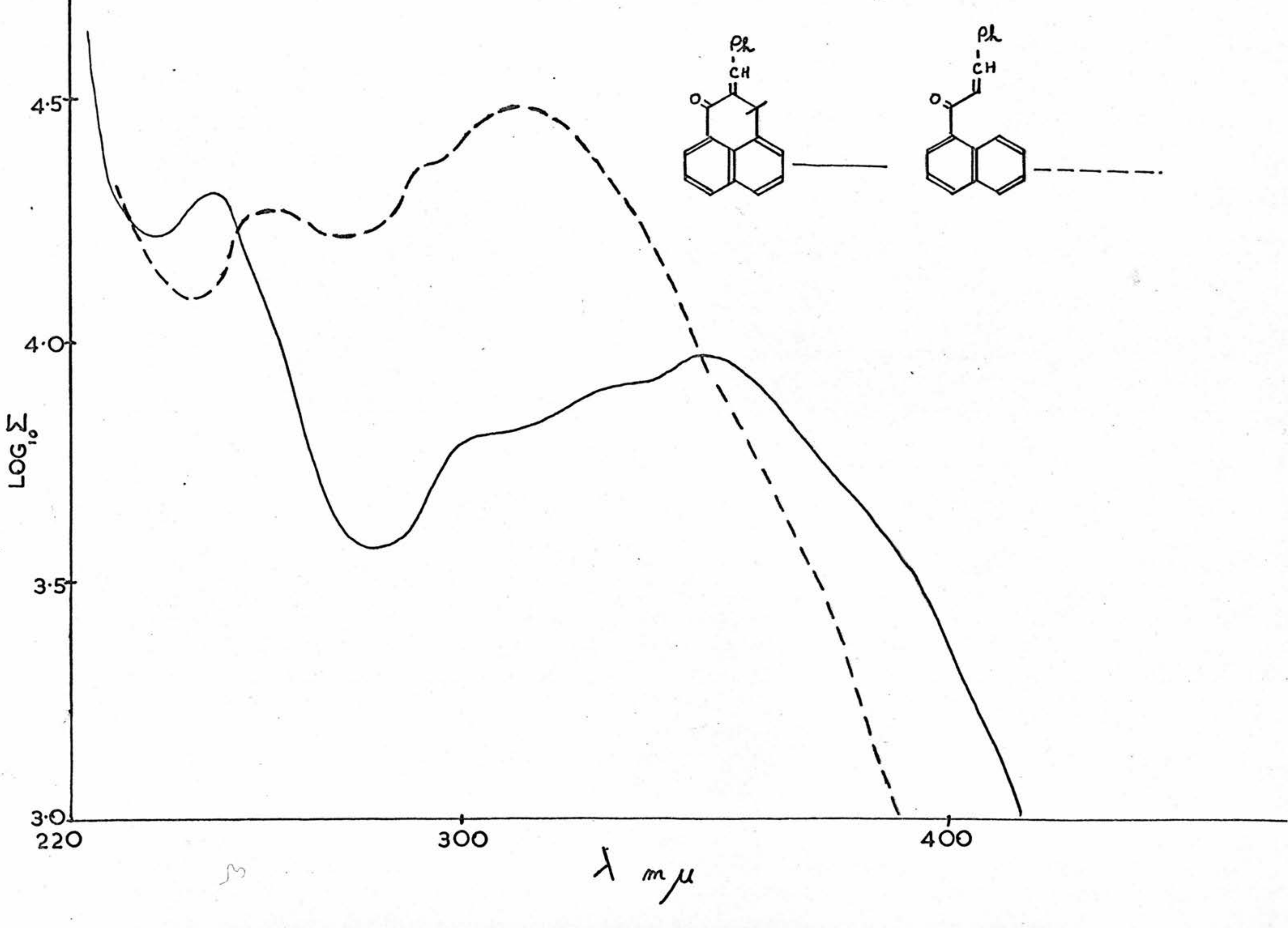

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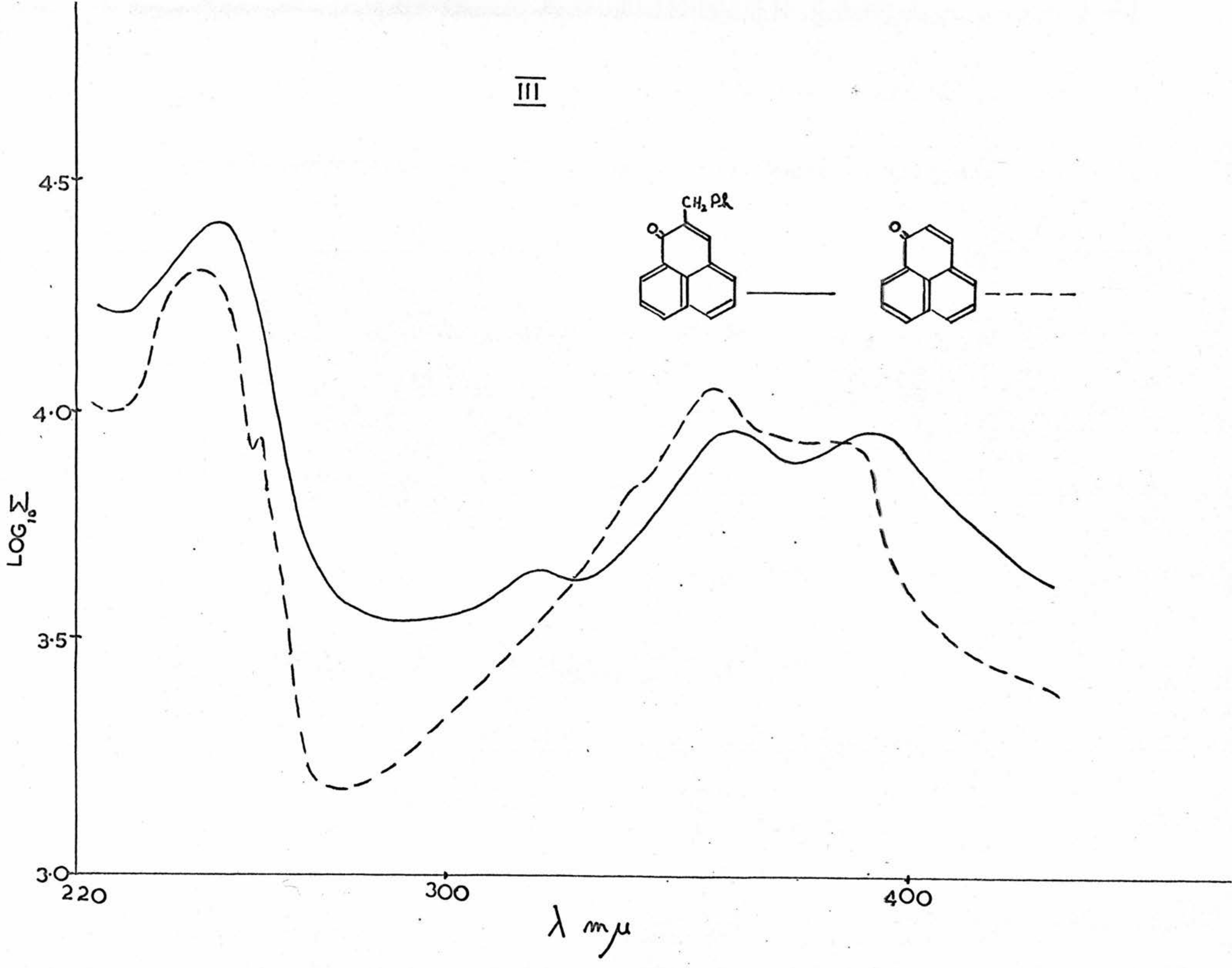

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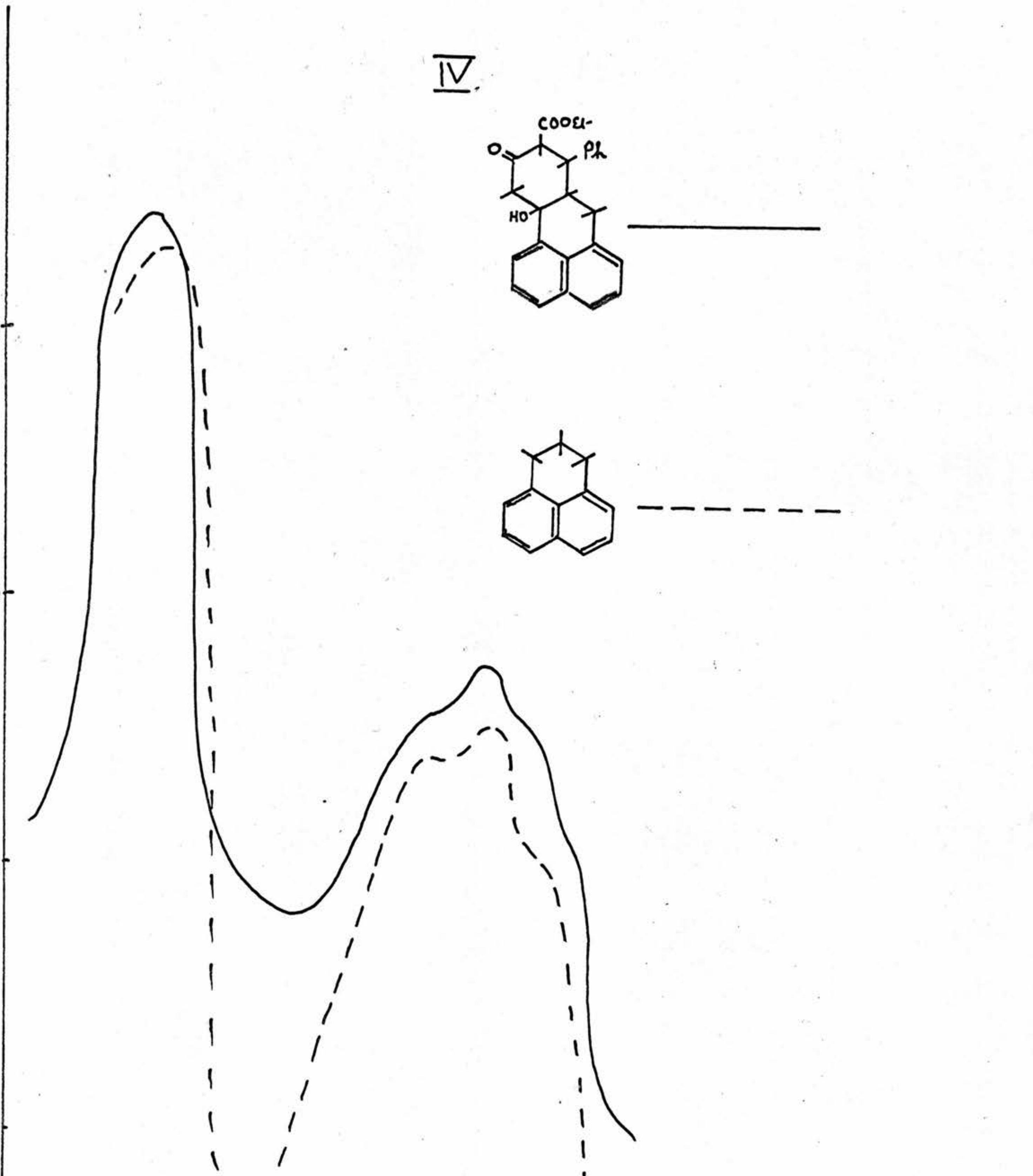

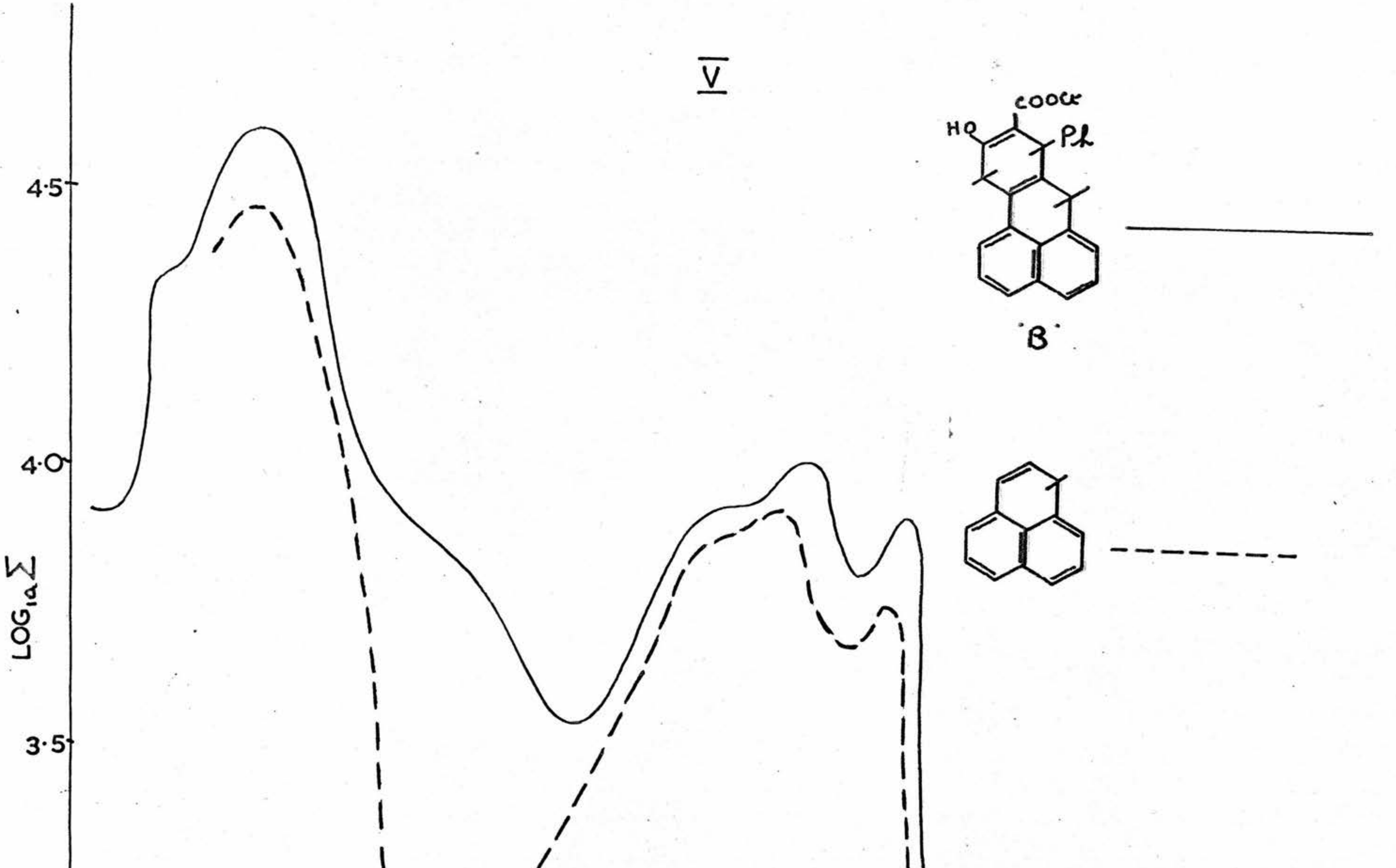
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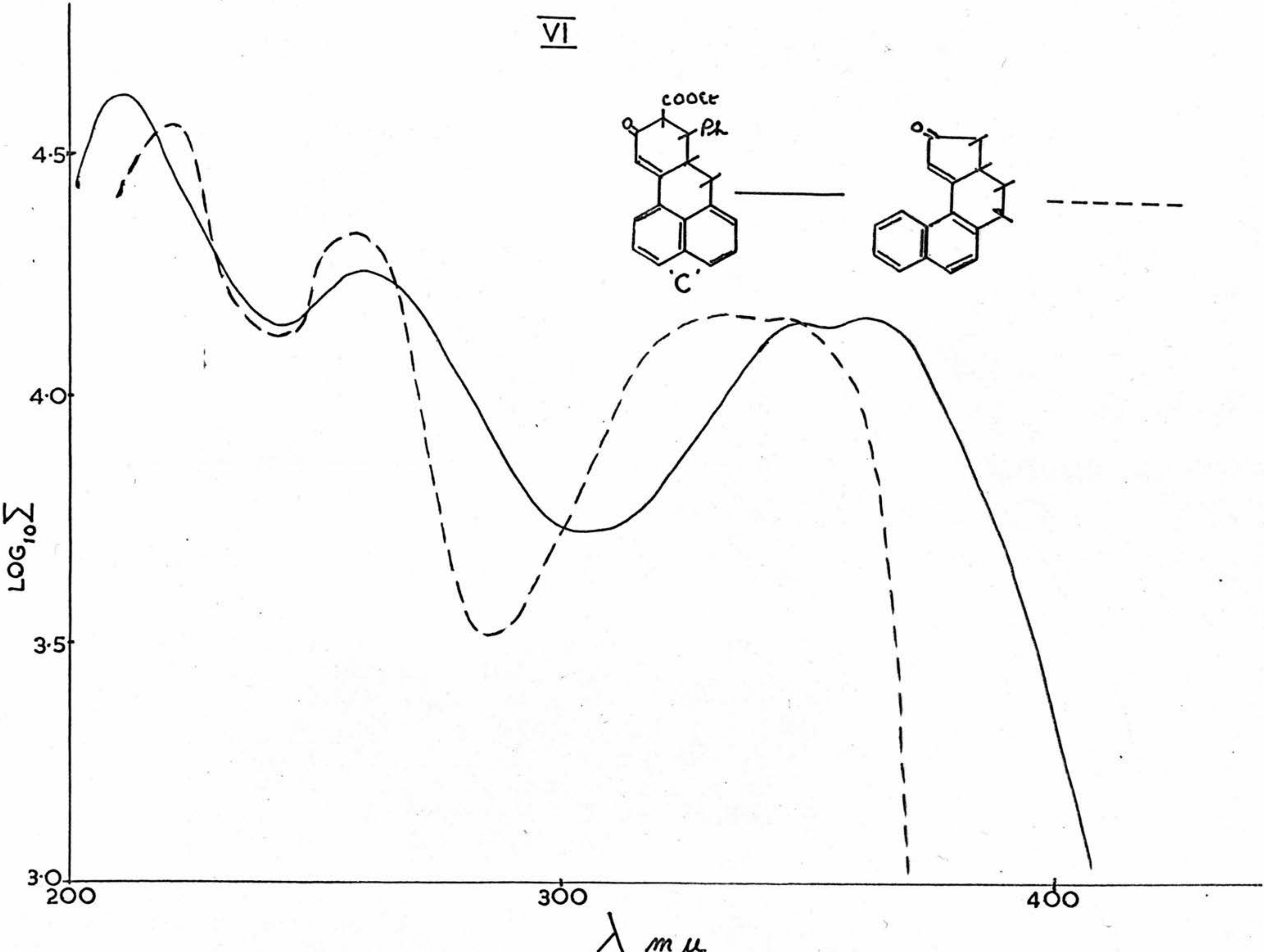
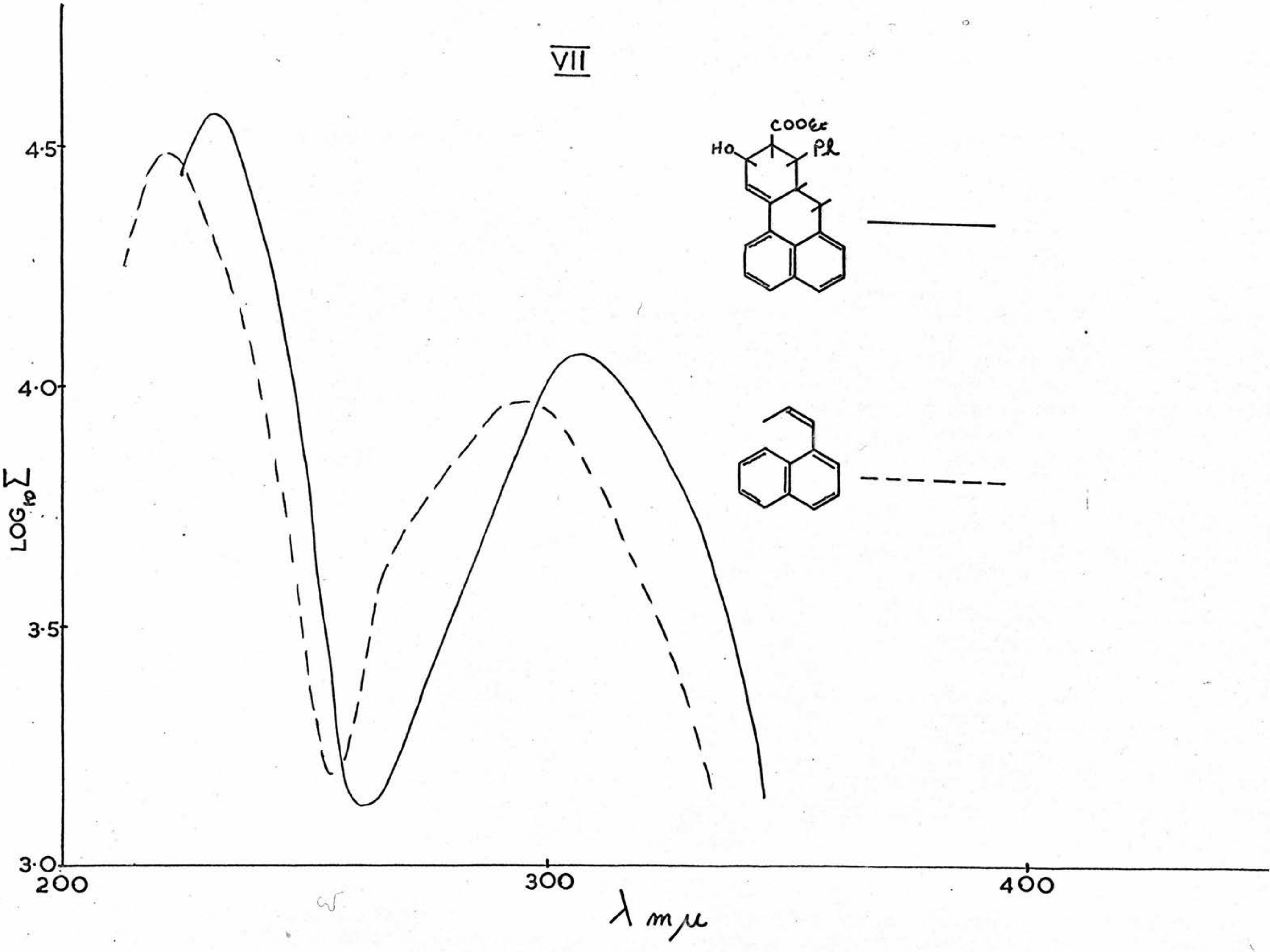
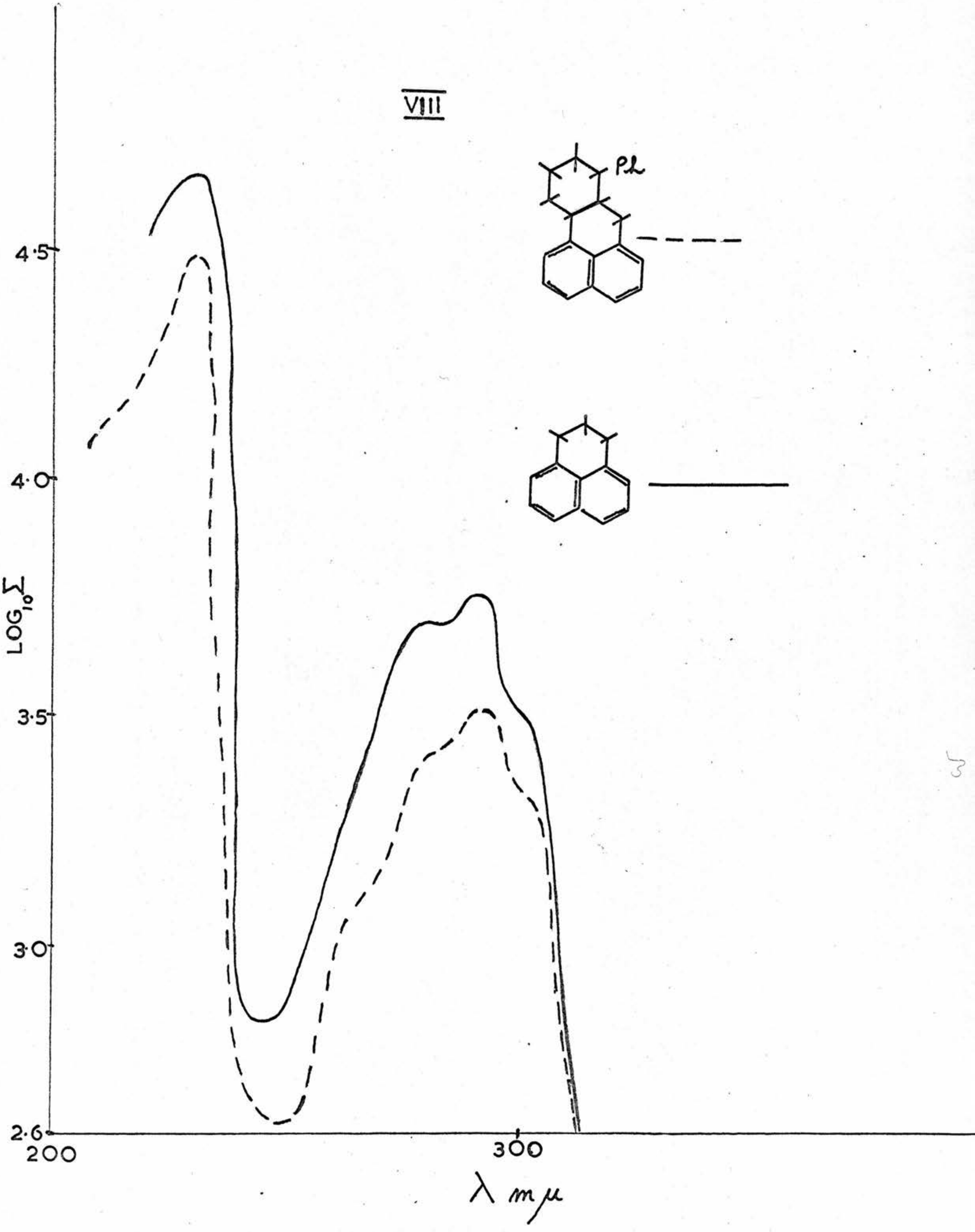


VII

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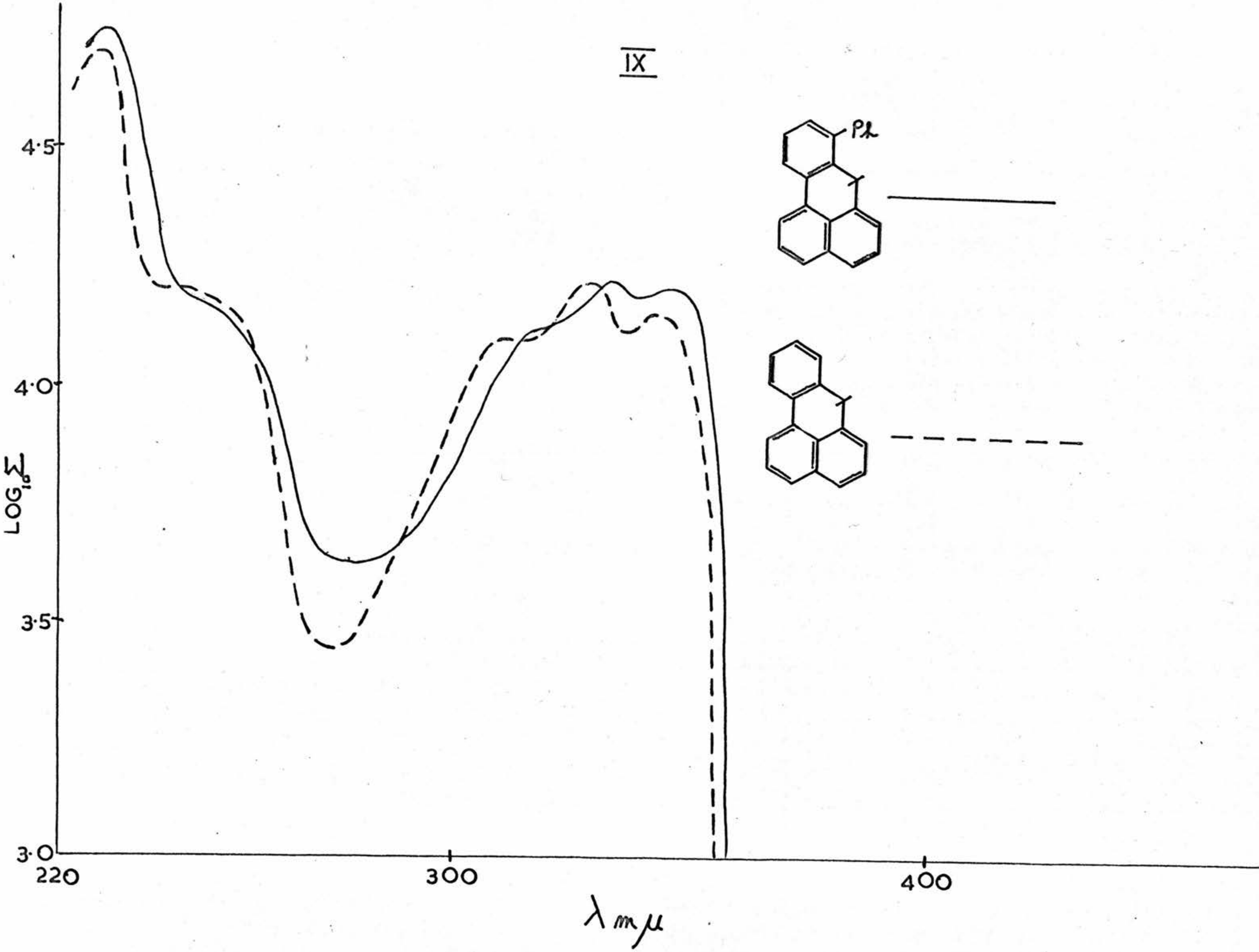IX
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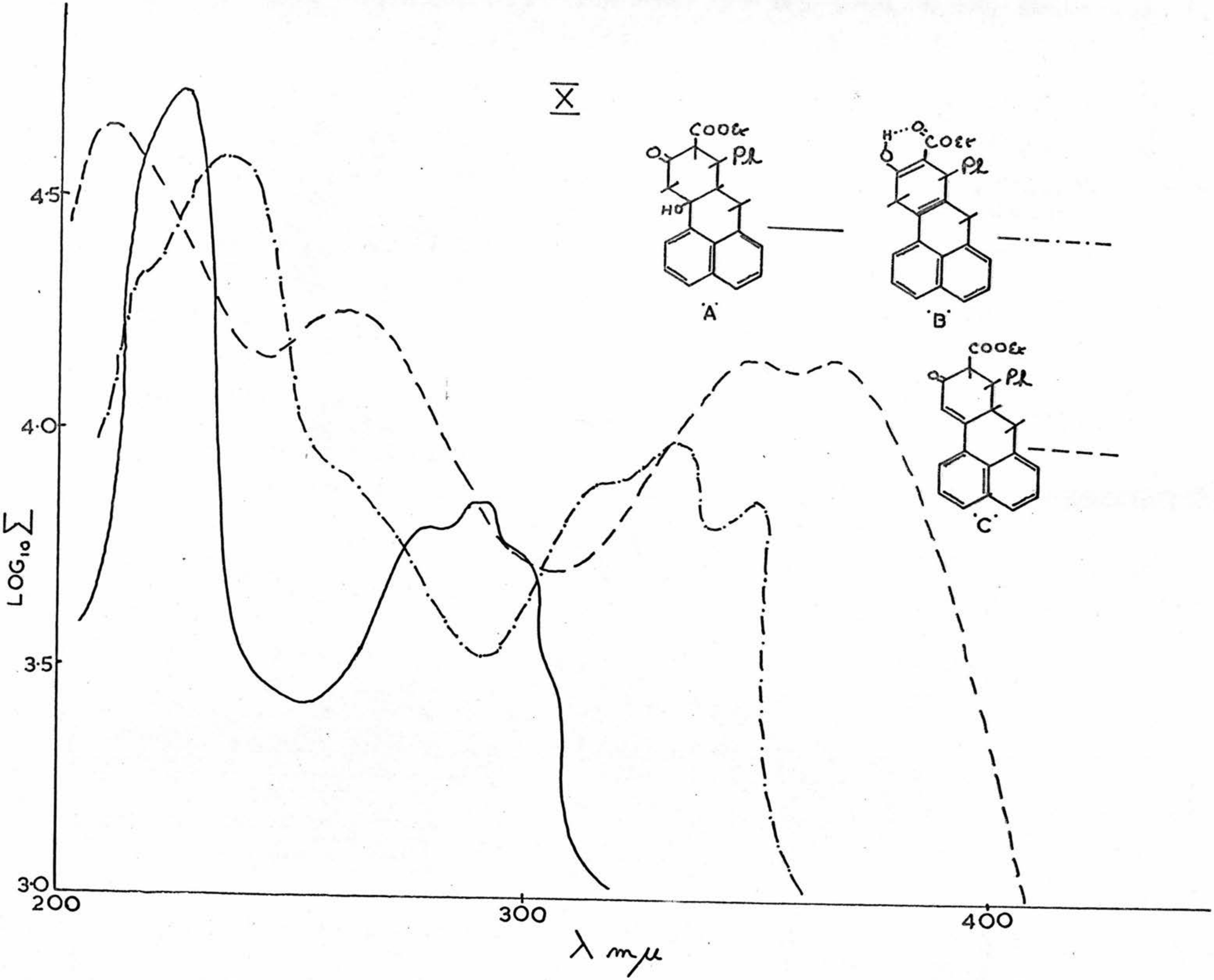
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λ mμ

Acknowledgements

I wish to record my sincere thanks to Dr. Neil Campbell for his helpful advice and encouragement during the course of this work, to Professor E. L. Hirst for the provision of laboratory facilities and the University of Edinburgh for a maintenance grant.