

STUDIES IN THE FLUORANTHENE SERIES

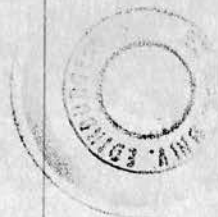
THESIS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

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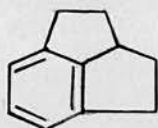
INTRODUCTION

Though the aromatic hydrocarbon, fluoranthene, was discovered more than one hundred years ago, its chemistry has been elucidated only in the last twenty years. The initial lack of interest was no doubt due to its small industrial application though several patents now exist covering its use as a dyestuff intermediate. Now, however, fluoranthene is rapidly taking its place along with naphthalene, anthracene, and the other well-known aromatic hydrocarbons.

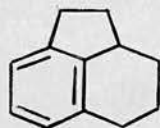
THE SYNTHESSES OF FLUORANTHENE AND ITS DERIVATIVES.

Though fluoranthene, or idryl, as it was then termed, was first isolated in 1844 (1), the systematic study of its chemical properties began only in 1929 when von Braun and his co-workers entered the field.

Von Braun (2) had been unable to synthesise compound I, and he concluded that it was impossible for two five-membered rings to be adjacent and condensed to the same benzene ring. Since compound



I

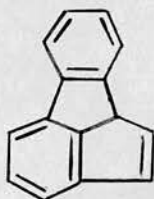


II

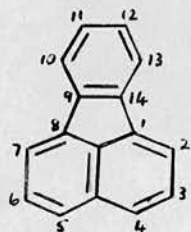
(II) could be obtained easily

he concluded that a five-membered and a six-membered ring could be condensed together, and to another

benzene ring. A survey of the literature showed



III

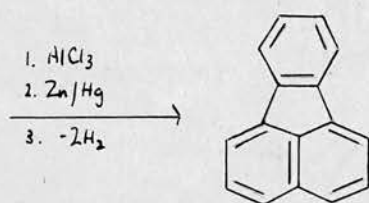
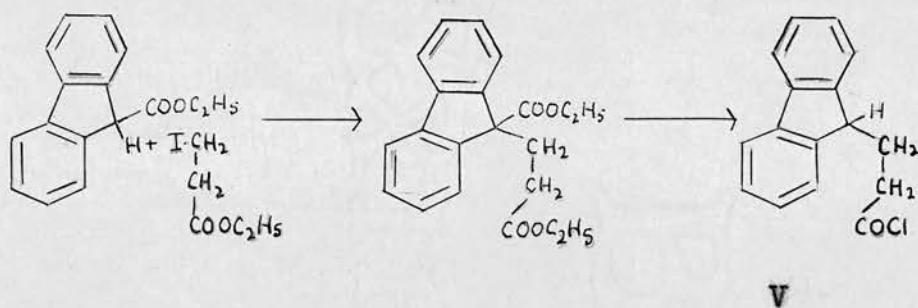


IV

that fluoranthene (III) was the only outstanding substance whose formula violated von Braun's rule, and accordingly, von Braun postulated the naphthalene structure (IV) for the hydrocarbon.

The numbering used throughout the Thesis is shown in formula (IV)

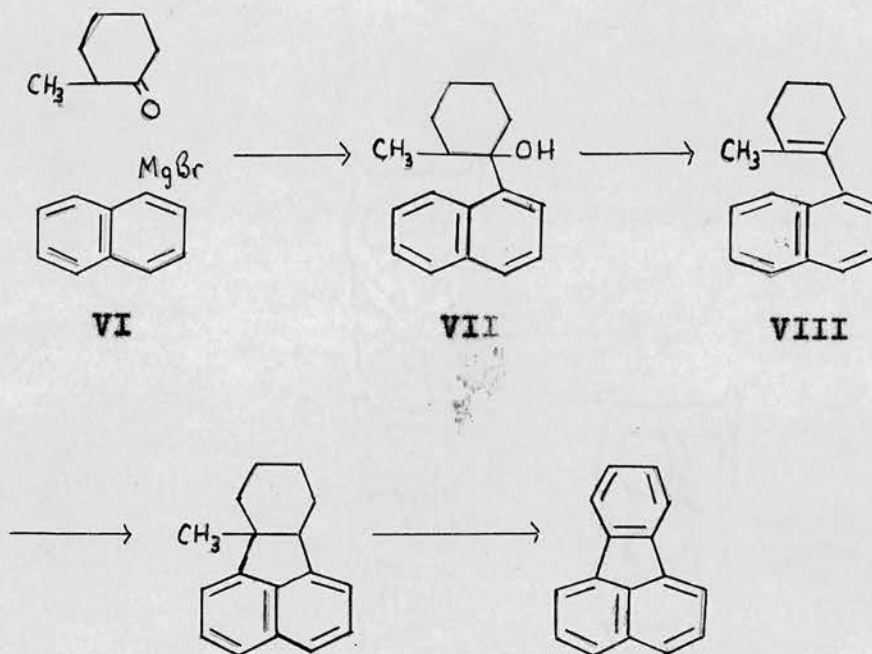
The synthesis of fluoranthene by von Braun and Anton (2) proved this structure.



9-Fluorenyl- β -propionyl chloride (V) was cyclised with aluminium chloride in light petroleum and the resulting ketotetrahydrofluoranthene reduced, then dehydrogenated to fluoranthene.

Though Mayer (3,4) reported the isolation of fluoranthene from the tar obtained by passing acetylene and hydrogen through a porcelain tube at 640°, the first important synthesis was that of von Braun and Anton. Another synthesis was that of Cook & Lawrence (5) who condensed 2-methylcyclohexanone

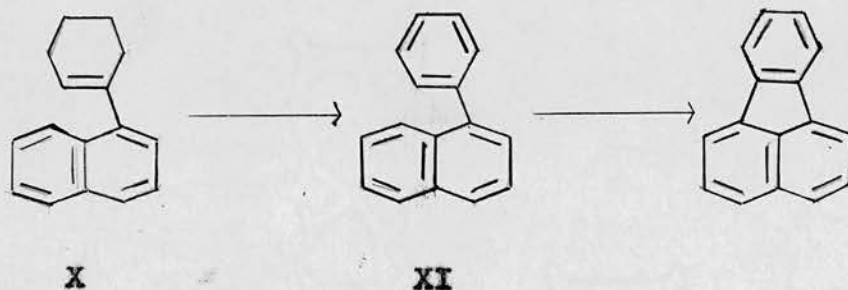
with

**IX**

1-naphthylmagnesium bromide (VI). The cyclohexene derivative (VIII), obtained by dehydration of the resulting carbinol (VII) was cyclised to the methyltetrahydrofluoranthene (IX) by the Friedel-Crafts reaction. Dehydrogenation with selenium gave fluoranthene. The ring-closure was unsuccessful without the methyl group.

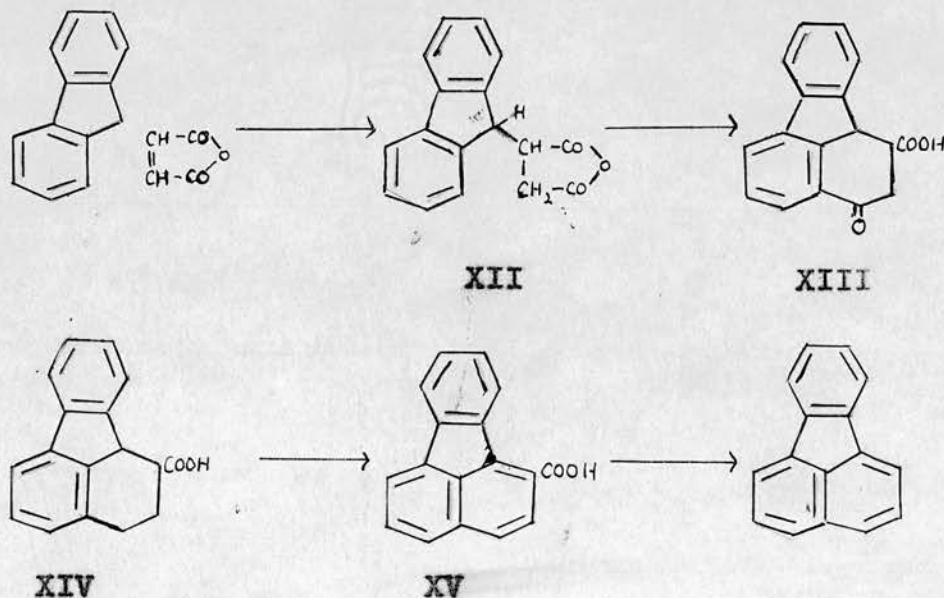
A somewhat similar synthesis was described by Orchin & Reggel (6). The carbinol obtained from the reaction of cyclohexanone and 1-naphthylmagnesium bromide was dehydrated with formic acid to 1-(1-naphthyl)- Δ^1 -cyclohexene (X) which was dehydrogenated with palladium-charcoal to

to 1-phenylnaphthalene (XI).



Cyclodehydrogenation with palladium-charcoal, or better, chromia-alumina, yielded fluorene. Cook & Lawrence found it impossible to cyclise (VI) with aluminium chloride at 0.

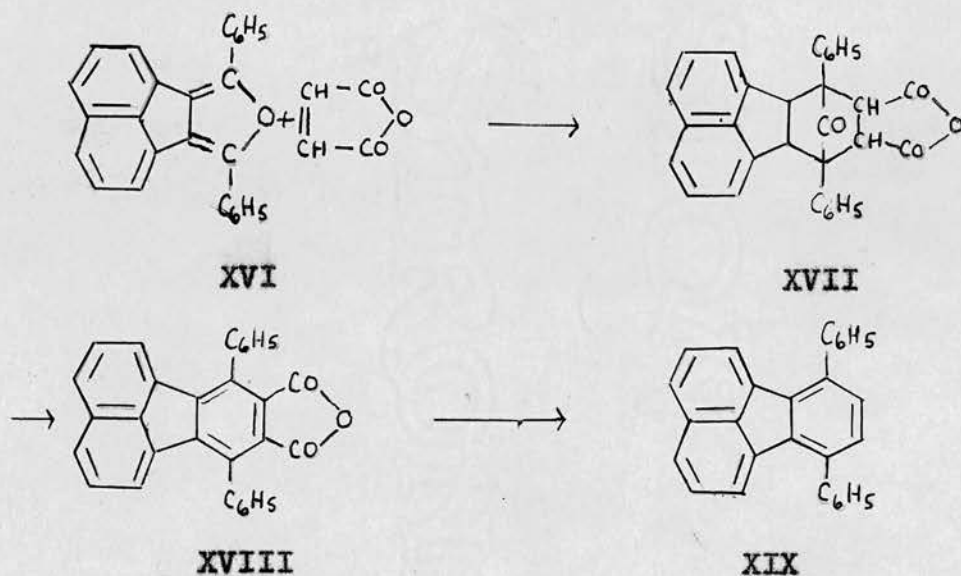
A later synthesis of fluorene, and fluorene-2-substituted derivatives, was that of Bergmann & Orchin (7). The adduct (XII) obtained from the Michael condensation of fluorene with maleic anhydride (8) was cyclised with aluminium chloride to the keto-acid (XIII). Clemmensen reduction of this keto-acid



followed by sulphur dehydrogenation of the resulting 2-carboxy - 1; 2: 3: 4 -tetrahydrofluoranthene (XIV), yielded 2-carboxyfluoranthene, the decarboxylation of which, gave fluoranthene. The acid hydrazide yielded 2- aminofluoranthene.

The Diels -Alder reaction has also proved of value for the synthesis of fluoranthene and its derivatives.

Dilthey and his co-workers (9) condensed acecyclone (XVI) with maleic anhydride. The adduct (XVII) readily gave (XVIII) which

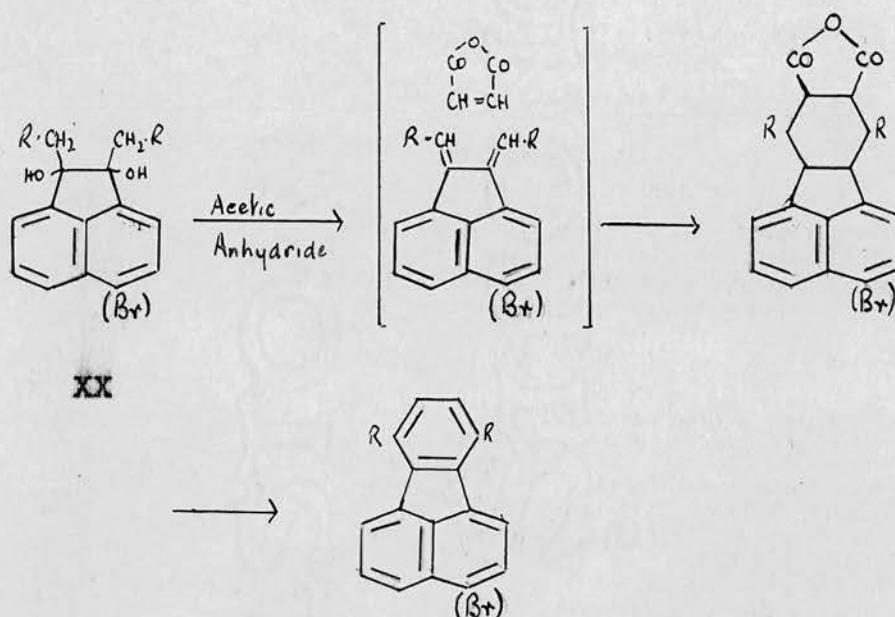


when decarboxylated (soda-lime), gave 10:13 - diphenylfluoranthene (XIX).

Various aryl fluoranthenes have been prepared in this way (10).

10:13 -Diphenyl fluoranthene was also prepared from acecyclone and dibromoethane (11)

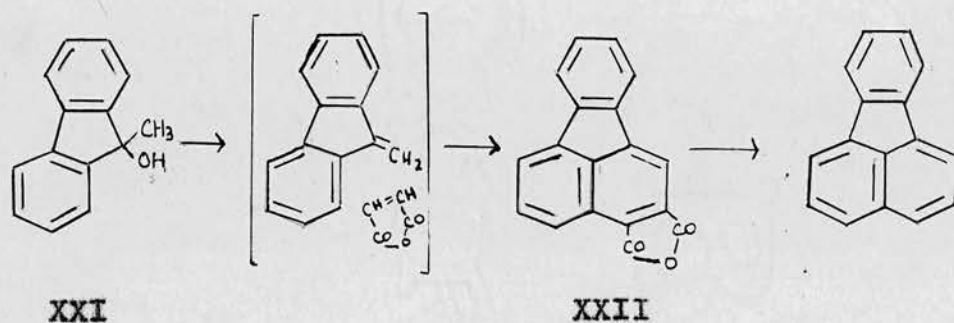
Campbell & Gow (12) showed that when 7:8 - dialkylacenaphthene -7:8 -diols (XX) were dehydrated in acetic anhydride in the presence of dienophiles, condensation readily took place to form fluoranthene derivatives.



Fluoranthene and many of its derivatives were prepared.

The synthesis of 4-bromofluoranthene by this method confirmed von Braun's structure.

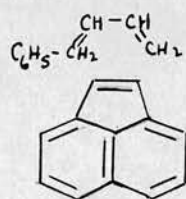
A related synthesis of fluoranthene and its derivatives was that of Campbell & Wang. (13)



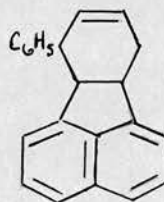
9-Hydroxy-9-methylfluorene (XXI) was boiled with maleic anhydride in acetic anhydride, when a Diels-Alder reaction, (presumably by addition to the intermediate 9-methylenefluorene) took place.

Spontaneous dehydrogenation occurred, yielding fluoranthen-3:4 - dicarboxylic acid anhydride, (xxii) which, when decarboxylated with calcium hydroxide, gave fluoranthen.

Another example of the Diels-Alder reaction was reported by Bergmann (14). 10 Phenyl-9:10:13:14 - tetrahydrofluoranthen (XXIV) was prepared.



XXIII



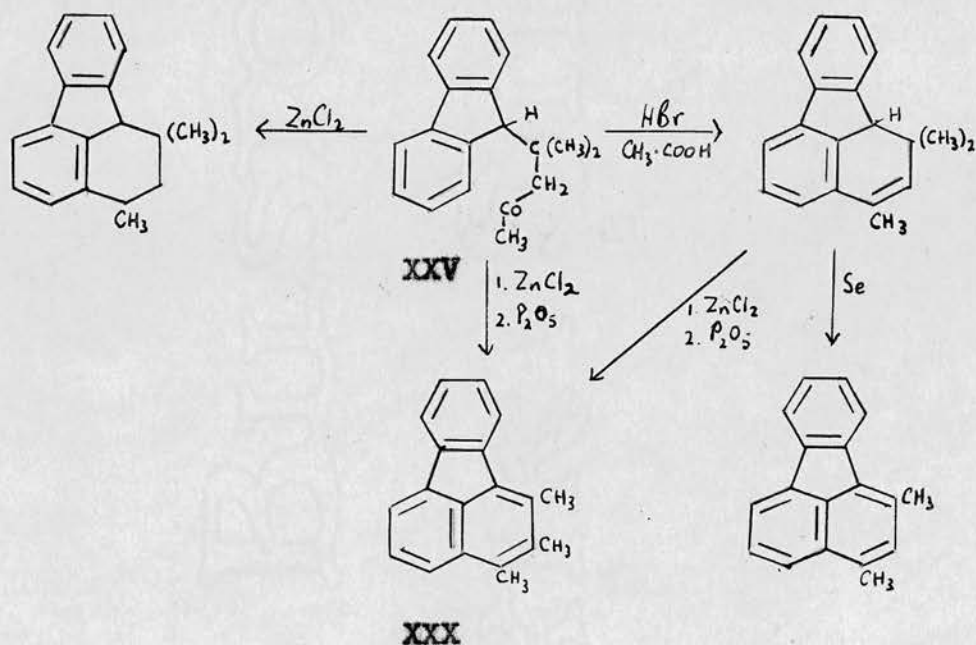
XXIV

by condensing acenaphthylene (XXIII) with 1-phenylbutadiene.

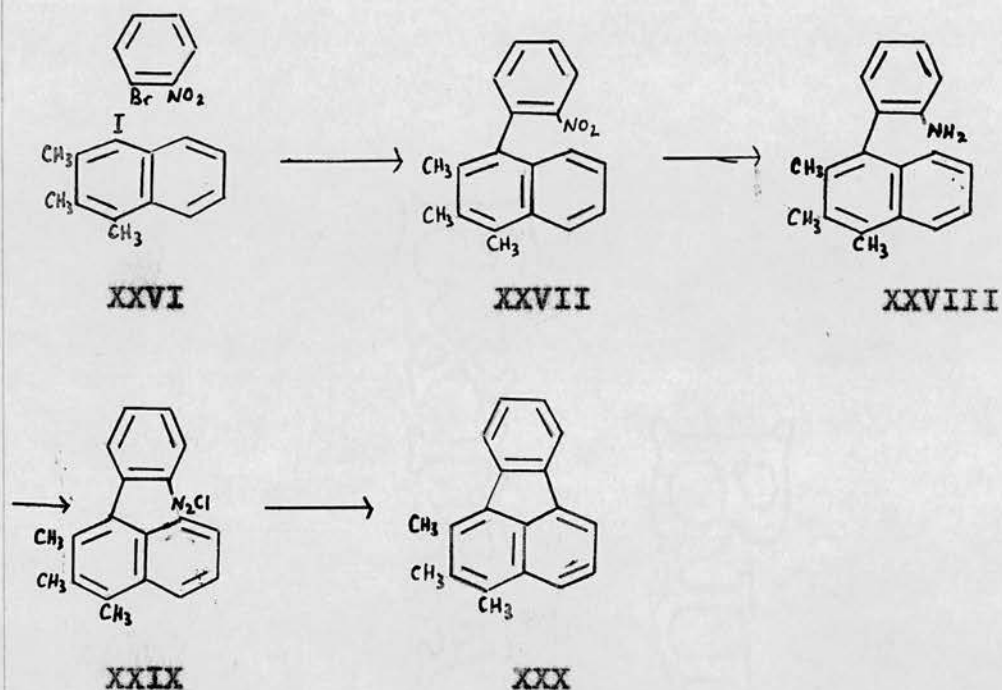
Two other syntheses, based on this reaction, have been reported recently. In one (15) acenaphthylene was condensed with sorbic acid to give 10 methyl-tetrahydrofluoranthene-13-carboxylic acid; in the other (16) acenaphthylene was condensed with methylbutadienes to yield methylfluoranthenes.

Methylfluoranthenes have been the subject of a series of papers by Tucker and co-workers.

Methyl- β -9-fluorenyl- β -methyl-n-propylketone (17) (XXV) underwent the reactions shown below (18)



Tucker & Whalley (20) have confirmed the structure of 2:3:4 trimethylfluoranthene (XXX) by the following synthesis.



1-iodo-2:3:4-trimethylnaphthalene (XXVI) was condensed, in the Ullmann reaction, with o-nitro-bromobenzene and the resulting nitrophenylnaphthalene (XXVII) was reduced to the amine (XXVIII). The diazo salt (XXIX) was cyclised in alkaline solution to 2:3:4-trimethylfluoranthene (XXX).

In a similar way have been synthesised 10- and 11-methylfluoranthenes (21) and 11-methoxyfluoranthene (22)

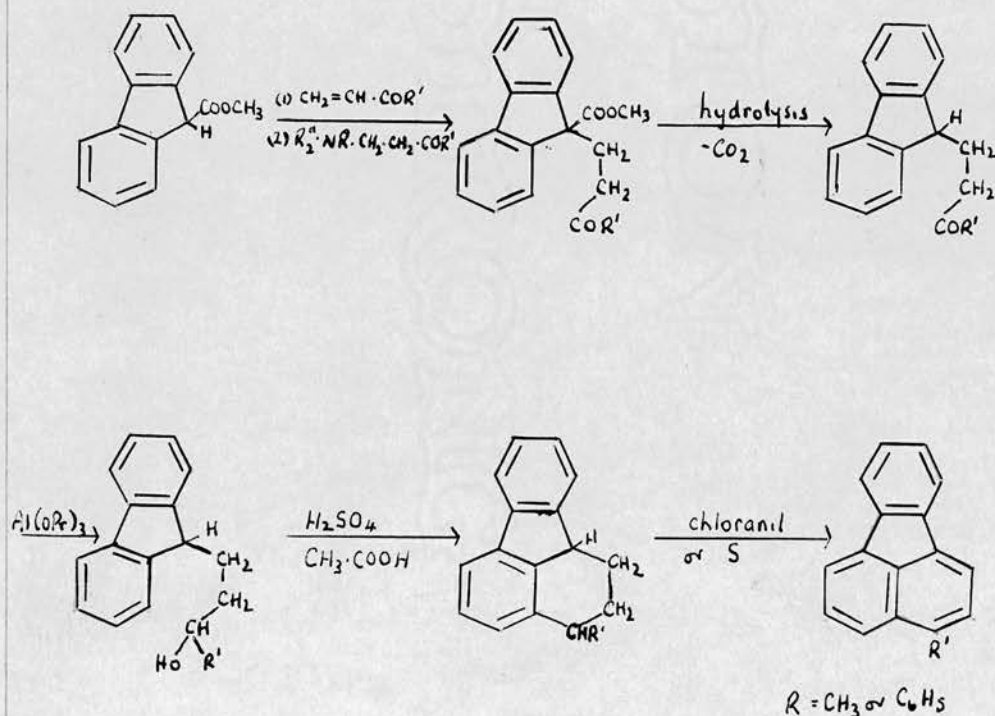
2:4-Diphenylfluoranthene and 2-phenyl-4-methylfluoranthene were described by Tucker & Whalley (19)

Fluorene-9-carboxylate has proved an important intermediate in the synthesis of derivatives of fluoranthene. The reagent is easily prepared (26) and has the added advantage that the single

9-hydrogen atom available has a much enhanced reactivity.

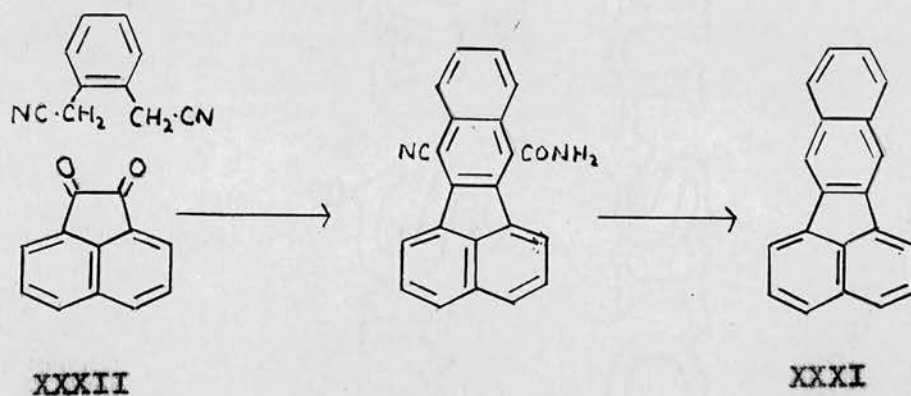
The Michael condensation of fluorene-9-carboxylate with crotononitrile (23) and vinyl Cyanide (24) has yielded further methylfluoranthenes.

Recently Stubbs & Tucker (25) have synthesised 4-methylfluoranthene and 4-phenylfluoranthene from fluorene-9-carboxylate by (1) Michael condensation with vinyl ketones and (2) from the corresponding Mannich bases.

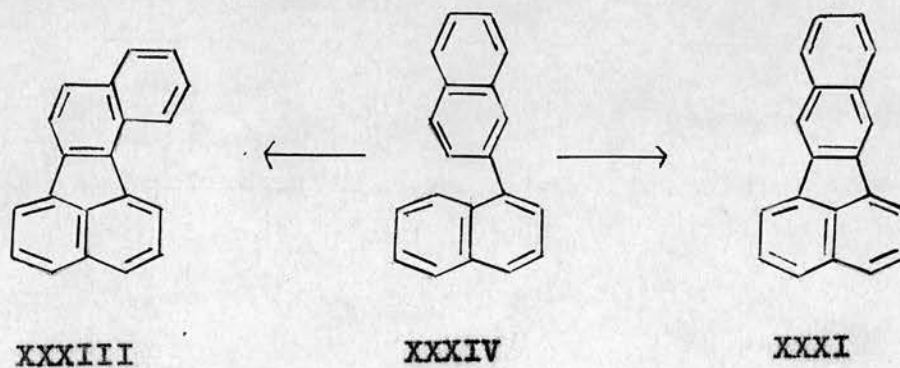


BENZOFLUORANTHENES

11, 12 - Benzofluoranthene (XXXI) has been prepared by two methods. Moureu, Chovin & Rivoal (26) condensed acenaphthene quinone (XXXII) with *o*-xylyenedicyanide, then hydrolysed and decarboxylated, the product.

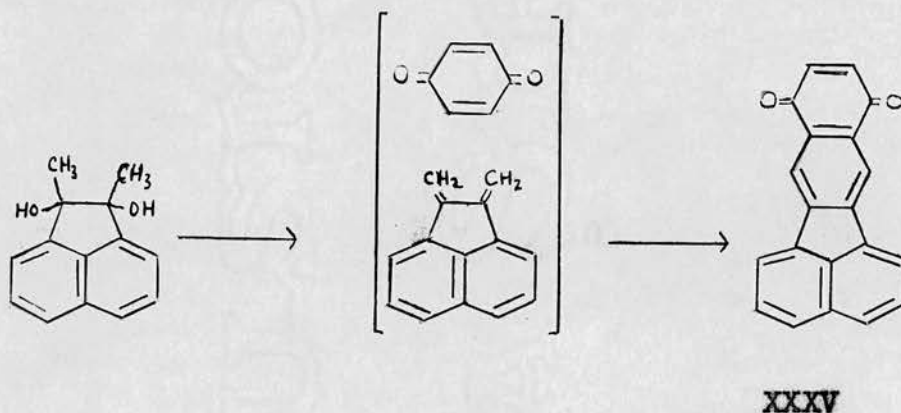


Orchin & Reggel (6) prepared this hydrocarbon, along with its isomer 12:13 - benzofluoranthene (XXXIII), by the cyclodehydrogenation of 1:2-dinaphthyl (XXXIV) over chromia-alumina at 500°.



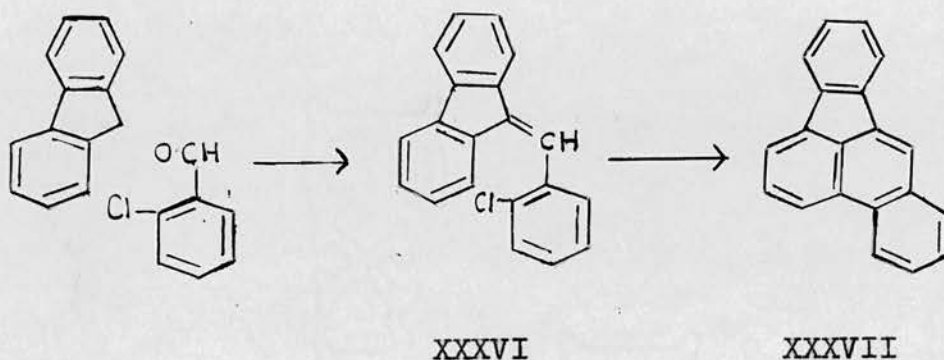
That these authors assigned the reverse structures was pointed out by the French workers. (27) Orchin & Reggel have since synthesised the two isomers verifying the conclusions of Maureu et al (28).

Campbell & Gow (14) prepared 2:3 -(11:12-fluoranthene) - benzoquinone (XXXV) by dehydrating trans -7:8 - dimethylacenaphthene -7:8 - diol in presence.



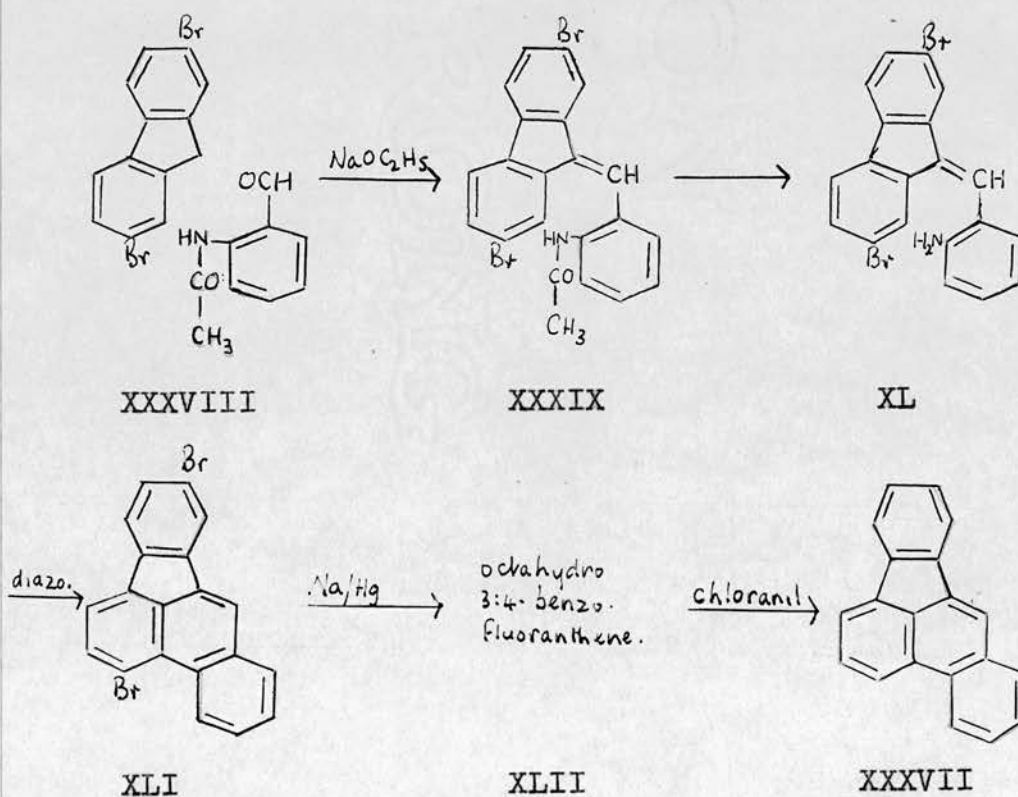
of 1:4 - ^{benzo}naphthoquinone, but they were unable to reduce it to the hydrocarbon.

The synthesis of 3:4 - benzofluoranthene (XXXVII) has been reported in the patent literature (29). Fluorene was condensed with o-chlorobenzaldehyde and the product (XXXVI) cyclised with potassium



hydroxide and quinoline to 3:4 -benzofluoranthene (XXXVIII).

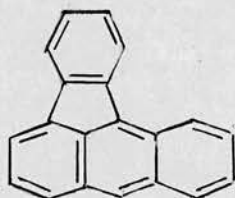
A dibromoderivative of this hydrocarbon was synthesised by Tobler et al (30). 2: 7-Dibromofluorene (XXXVIII) was condensed with o-acetylaminobenzaldehyde and the product (XXXIX) hydrolysed to the



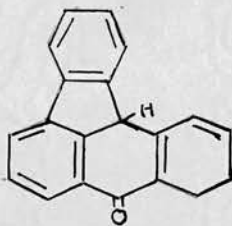
amine (XL). Diazotisation followed by ring-closure gave 5:12- dibromo 3:4 -benzofluoranthene (XLI), the first substituted fluoranthene derivative, in which the positions of both bromine atoms were established.

Reduction with sodium amalgam removed the bromine atoms yielding an octahydroderivative, dehydrogenation of which (chloranil), gave 3:4 - benzofluoranthene.

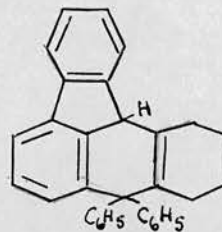
The linear 2:3 -benzofluoranthene (XLIII) remained unknown



XLIII



XLIV



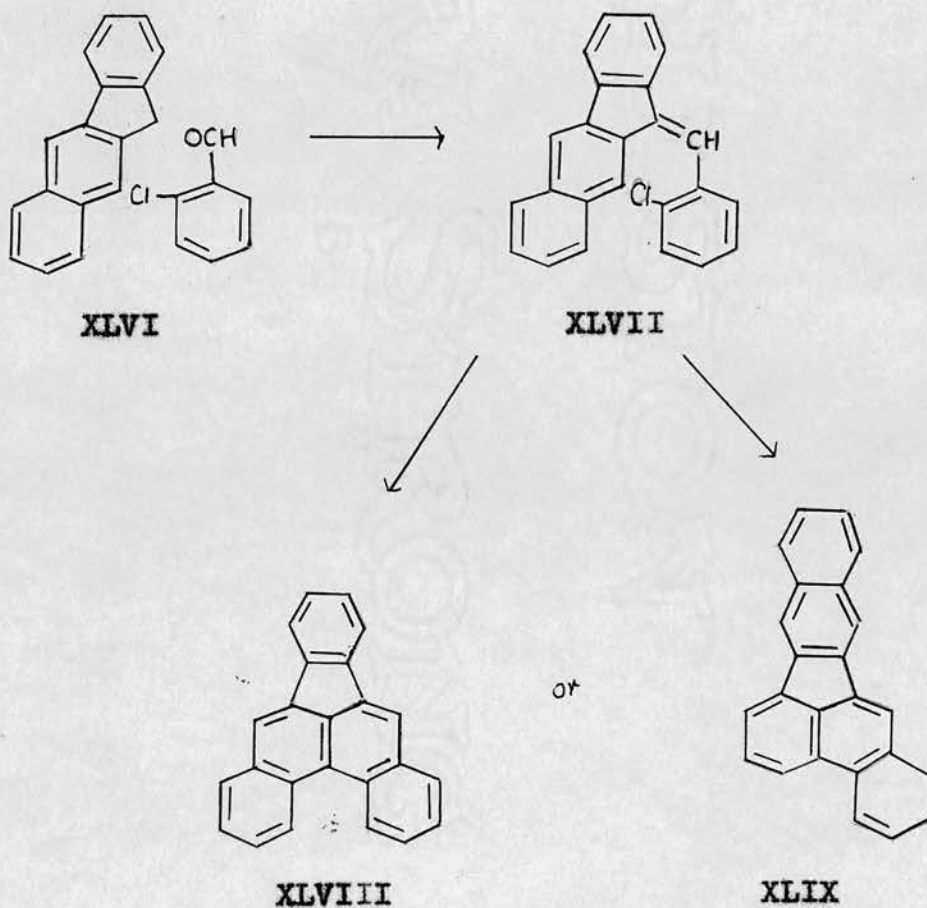
XLV

though the derivatives (XLIV, 31) and (XLV, 32) were known.

DIBENZOFLUORANTHENES

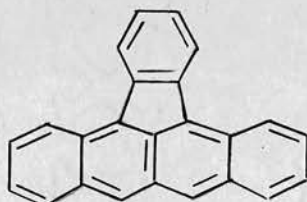
No fully-orientated dibenzofluoranthenes are known.

The patent literature (29) reported the condensation of 2:3-benzofluorene (XLVI) with *o*-chlorobenzaldehyde. The product (XLVII) was cyclised with



alkali and quinoline to give a compound claimed to be 3:4-5:6- dibenzofluoranthene (XLVIII) or 3:4-11:12 -dibenzofluoranthene (XLIX).

The linear dibenzofluoranthene, or indenonaphthacene (L), is unknown.

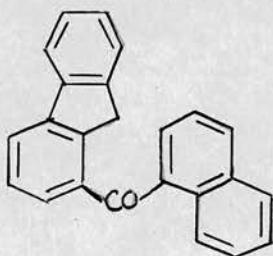


L

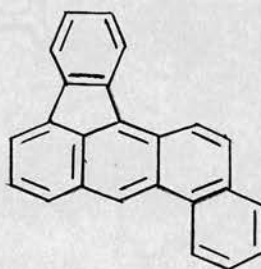
NAPHTHOFLUORANTHENES.

Several naphthofluoranthenes and their derivatives are known.

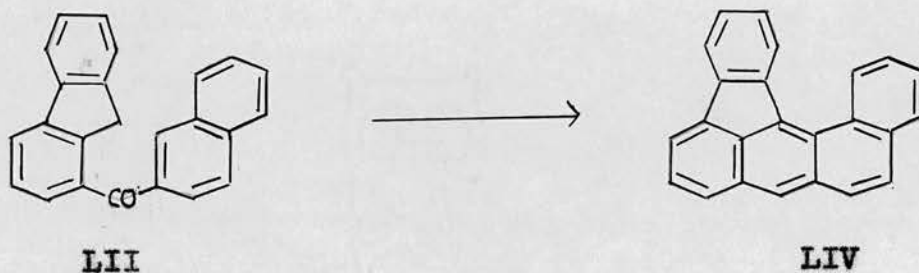
The Friedel-Crafts reaction of fluorene-1-carboxylic acid chloride and naphthalene (33) yielded a mixture of the ketones (LI) & (LII).



LI



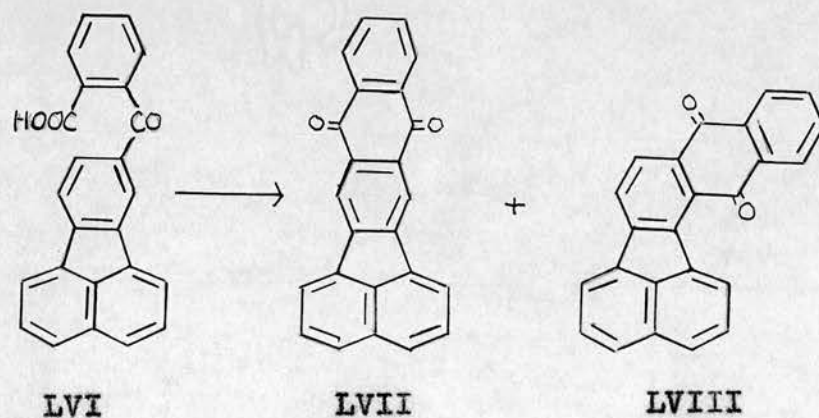
LIII



which pyrolysed to give naphtho -2: 1' -2:3 - fluoranthene (LIII) and naphtho -1' : 2' - 2: 3 - fluoranthene (LIV). The ketone (LI) was also obtained by the reaction of fluorene -1-carboxylic acid chloride with α -naphthylmagnesium bromide.

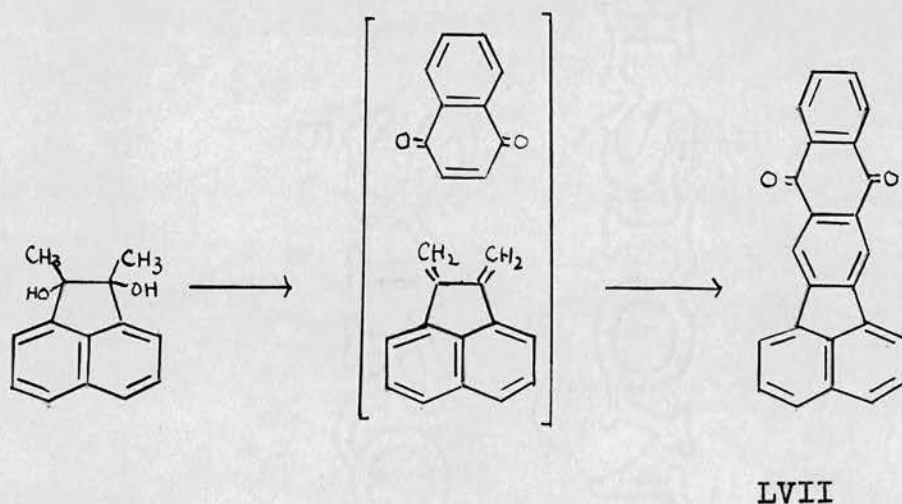
Von Braun & Menz (34) condensed fluoranthene with phthalic anhydride in the Friedel-Crafts reaction and cyclised the resulting 4- and 12 - o-carboxybenzoylfluoranthenes (LV & LVI).

Cyclisation of the 12-isomer (LVI) yielded the two expected quinones (LVII & LVIII), to which they gave structures based on



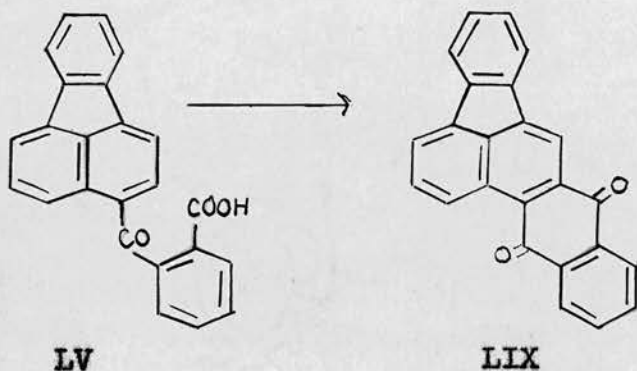
oxidation studies. To the yellow compound, von Braun & Manz gave structure (LVIII), and to the red compound, structure (LVII).

Naphtho (2' : 3' - 11 : 12) -fluoranthene - 1' : 4' - quinone (LVII) was synthesised unequivocally by Campbell & Gow (12) who dehydrated trans - 7 : 8 - dimethylacenaphthene - 7 : 8 - diol in presence of naphthoquinone, when the Diels - Alder reaction, shown below, occurred.

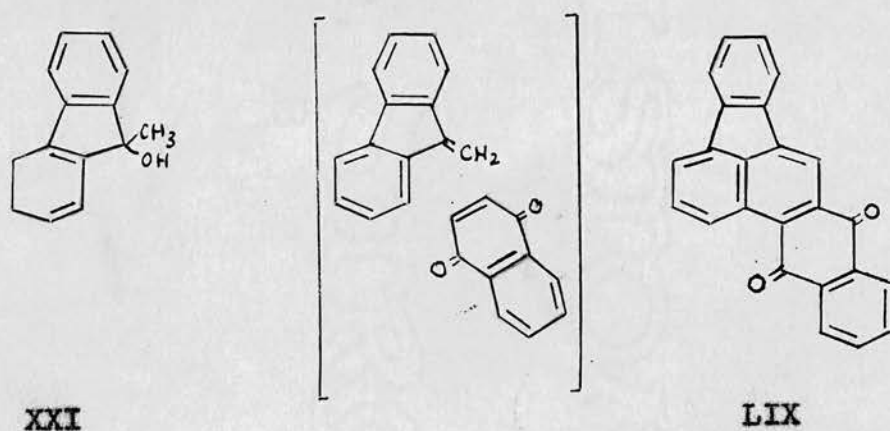


This compound was, in fact, the yellow compound of von Braun & Manz, and, accordingly the structures given by the German workers must be reversed.

By the cyclisation of 4-o-carboxybenzoylfluoranthene (LV) von Braun & Manz obtained a third compound, to which they gave the structure naphtho-(2':3'-3:4) fluoranthene - 1' : 4' - quinone (LIX).



This compound, also, was synthesised unequivocally by Campbell & Wang (13). 9-Methyl-9-hydroxyfluorene (XXI) was dehydrated to 9-methylene-fluorene, in presence of 1 : 4 -naphthoquinone when



naphtho (2':3' - 3:4) fluoranthene - 1':4'-quinone was obtained. This compound was not identical with that of the German investigators, the structure of whose compound, is unknown. It must be pointed out that in their separations of intermediate and final products they had not the help of chromatography.

The cyclisation of the mixture of 4 & 12 -o-carboxybenzoylfluoranthenes was also reported in the patent literature (35). Two products only were

described. One was, apparently, the yellow compound of von Braun & Manz; the other was a red compound, but of different melting point from "(LVIII)".

The subject was somewhat confusing.

Both von Braun & Manz and Campbell & Gow, reduced the yellow quinone to the corresponding 11:12- naphthofluoranthene by zinc dust distillation.

SUBSTITUTION.

Monosubstitution

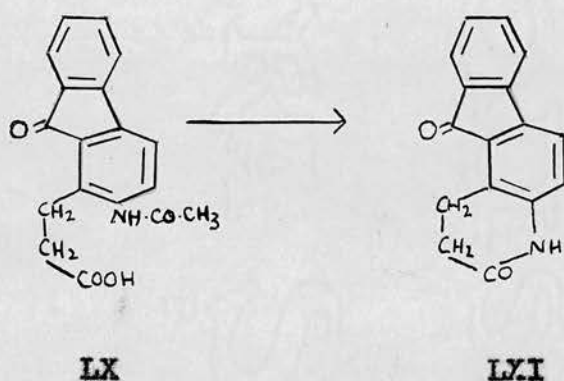
The monosubstitution of fluoranthene has been studied mainly by von Braun and co-workers, who showed it took place in the 4 and 11(12) positions.

Monobromination (36) yielded chiefly the 4-isomer with a little of the 11-isomer. Nitration and sulphonation were similar.

Von Braun showed that monosubstitution took place mainly in the 4 - position by the following series of reactions. The synthetic 4-keto-1:2:3:4 - tetrahydrofluoranthene was reduced to the 4-hydroxy compound apparently stereoisomeric with the product obtained by hydrogenation of 4- hydroxyfluoranthene since they yielded the same phenylcarbamide.

The bromo derivative was converted to the corresponding cyano compound, also obtained from the sulphonic acid prepared directly by the sulphonation of fluoranthene.

The sulphonic acid derivative gave a phenol which, yielded an amine. Reduction of this 4-amino-fluoranthene gave 4-amino-5:6:7:8-tetrahydrofluoranthene, the acetyl derivative of which, oxidised to the keto-carboxylic acid (LX). The deacetylated acid, by loss of water,



yielded the lactam (LXI), which showed the position of the amino group to be 4.

The behaviour of fluoranthene in the Friedel-Crafts reaction was also studied by von Braun & Manz (34). Reaction of fluoranthene with oxalyl chloride yielded mainly fluorenone-12-carboxylic acid, a dicarboxylic acid, and some 4-acid. Reaction with benzoyl chloride yielded 12-benzoylfluoranthene, with a little of the 4-isomer. Similarly, in the reaction with phthalic anhydride, the main product was 12-o-carboxybenzoylfluoranthene with a little of the 4-isomer.

The orientation of these 12-derivatives was carried out by von Braun, as follows. Fluoranthene

-12-carboxylic acid gave the same amine by a Curtius reaction and hydrolysis as did the 12-acyl derivatives by oxime formation, followed by a Beckmann re-arrangement and hydrolysis. This amine was different from 4-amino-fluoranthene obtained from the 4-isomers by a similar series of reactions. Fluoranthene -12-carboxylic acid, on oxidation, gave two isomeric fluorenone dicarboxylic acids and hence fixed the substituting position as 12 or 13. Then since 12-o-carboxybenzoyl fluoranthene cyclised to give two isomeric phthaloylfluoranthenes (p 18), substitution must have occurred at the 12-position.

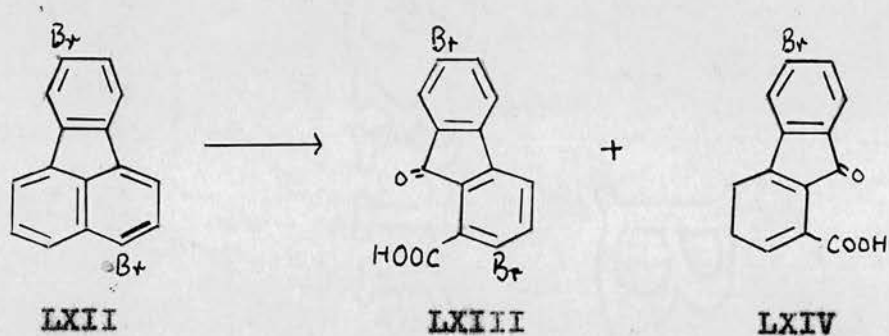
Buu-Hoi & Cagniant (39) reported that acetylation took place mainly at the 12- position, though later work (38) showed the unreliability of their results.

Though both von Braun & Buu-Hoi reported that benzoylation, phthaloylation, and acetylation took place mainly at the 12- position, Campbell & Easton (38), using chromatographic techniques, showed that in each case the 4+12-isomers were produced in equal amounts.

Disubstitution

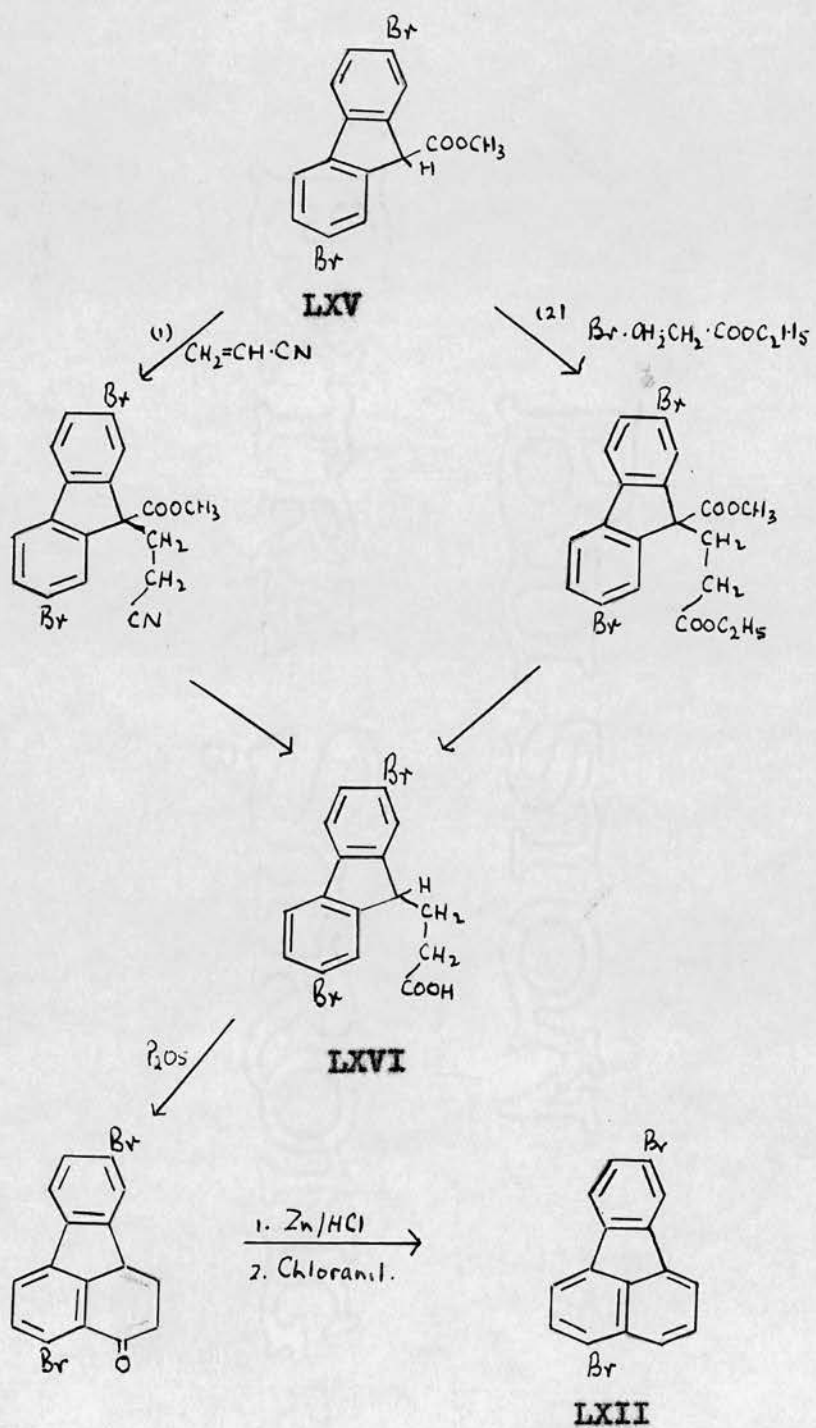
Earlier work suggested that dibromination of fluoranthene occurred at the 4 & 11 -positions (30,39) and the correctness of this prediction has been shown recently by the oxidation of dibromofluoranthene (LXII) to 2:7 - Dibromofluorenone -1-carboxylic acid

(LXII), (40) and 6-bromofluorenone -1-carboxylic acid (LXIV), (4L) and by the



synthesis of dibromofluoranthene (42).

2: 7- Dibromofluorene -9- carboxylic acid ester (LXV) was condensed, with



(1) vinyl cyanide and (2) β -bromopropionic acid ester, and the 9-(2:7 - dibromofluorenyl)-propionic acid (LXVI) obtained in each case, cyclised to 4:11- dibromofluoranthene (LXII).

That disubstitution in the Friedel-Crafts reaction with fluoranthene occurred in the 4 and 12 positions was proved as follows (Campbell, Leadill & Wilshire, 43).

Acetylation of fluoranthene yielded a diacetylfluoranthene, which underwent the Schmidt reaction to give a diaminofluoranthene. This product was converted, by a Sandmeyer reaction, to a dibromofluoranthene not identical with 4:11 - dibromofluoranthene obtained by direct bromination.

A diacid (A) was obtained in the Friedel-Crafts reaction of fluoranthene with oxalyl chloride (39). The dimethyl ester of this acid was different from that obtained from the authentic 4:11 -di-acid (prepared from 4:11- dibromofluoranthene by way of 4:11 - dicyanofluoranthene).

The diacetyl derivative obtained in the Friedel-Crafts reaction (43) was converted to the di-acid (A). Finally since acylation of 4-acetylfluoranthene and 12-acetylfluoranthene gave the above diacetyl - fluoranthene substitution must have occurred in the 4 and 12 positions.

Little is known of polysubstitution.

SECTION AFLUORANTHENE-NAPHTHOQUINONESObject of Research.

As pointed out in the introduction, in view of the importance of 4- & 12-o-carboxybenzoylfluoranthenes in the substitution studies of fluoranthene it is highly desirable that their cyclisations be re-investigated. The need for such studies is emphasised by the unreliability of previous work on the subject.

DISCUSSION OF RESULTS.

The Friedel-Crafts reaction of fluoranthene with phthalic anhydride was influenced by the solvent used. The yield was lowest in carbon disulphide (40%) and was best in methylene chloride (100%) a solvent for the Friedel-Crafts reaction, recommended by Baddeley (44). Tetrachloroethane, as solvent, gave a yield of 75%. The quantitative yield in methylene chloride was due undoubtedly to the complete solution of the reactants in the solvent.

The separation of the 4- & 12-*o*- carboxybenzoyl-fluoranthenes proved tedious and time-consuming and only relatively small amounts of the 4-isomer were obtained.

The first stage of the separation was the fractional crystallisation of the isomer mixture from chloroform. From the mixture of isomers obtained in the reaction with carbondisulphide as solvent, careful concentration yielded a small quantity of pure 12- *o*- carboxybenzoylfluoranthene, m.p. 234°. Further concentration resulted in the product being contaminated with the 4-isomer and the melting point was consequently depressed to 212°. This figure was quoted by von Braun & Manz as the melting point of their 12- isomer.

From the product obtained with methylene chloride as solvent in the Friedel-Crafts reaction, this

operation yielded slightly more than 50% pure 12-isomer, m.p. 234° .

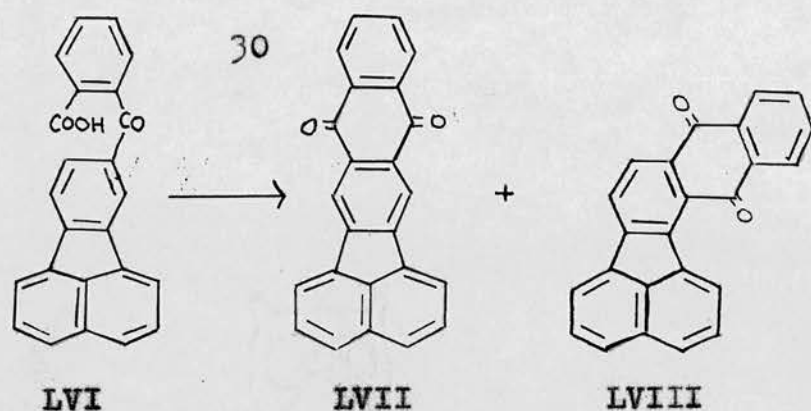
The chloroform filtrate was then evaporated and the residue extracted with cold ether to give an ether soluble fraction, containing a higher proportion of the 4-isomer. This fraction, and the residue, were then esterified, the methyl esters separated chromatographically, and hydrolysed to the free acids. (Campbell & Easton, 38).

The 4-acid had a melting-point of 230° in agreement with von Braun & Manz & Campbell & Easton.

Though the separation obtained from the "carbon disulphide" product agreed with Campbell & Easton in that equal quantities of the isomers were produced in the Friedel-Crafts reaction, the separation of the 'methylene chloride' product showed that the 12-isomer predominated.

This increase in the proportion of the 12-isomer may be due to the influence of the solvent or may arise from the superior yields obtained with this solvent.

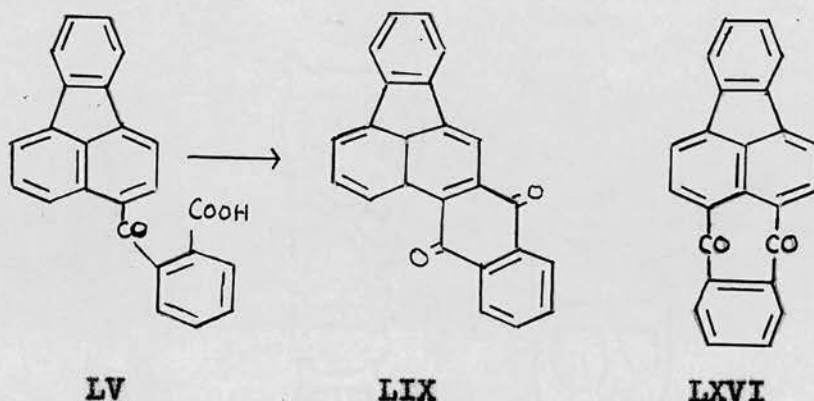
As already mentioned (p. 18) Von Braun & Manz (34) by ring-closure of the acid chloride of 12-*o*-carboxybenzoylfluoranthene (LVI) obtained the two quinones (LVII) & LVIII), to which structures were given,



based on oxidation studies. LVII was red m.p. 228°; LVIII was yellow, m.p. 330° .

With the synthesis of the authentic naphtho (2': 3' - 11:12) - fluoroanthene - 1' : 4' - quinone (LVII, p19) Campbell & Gow (12) showed that the structures (LVII) & (LVIII) should, at least, be reserved. They pointed out that von Braun's evidence, based on oxidation studies, was unreliable, since the products were not obtained pure, and no mixed melting points were carried out with authentic samples.

Von Braun & Manz cyclised 4 -o- carboxybenzoyl-fluoroanthene (LV) in sulphuric acid. Hydrolysis with barium chloride-hydrochloric acid yielded a yellow quinone, m.p. 328° , to which the authors gave the anthraquinone structure (LIX) because the compound vatted easily. This compound, naphtho (2' : 3' - 8:4) fluoroanthene - 1' : 4' - quinone, yellow-orange, m.p. 250° , was synthesised



unequivocally by Campbell & Wang (13), and was clearly not identical with that obtained by the German workers. Campbell & Wang therefore suggested that the compound obtained by von Braun & Manz might have been 4:5-phthaloylfluoranthene (LXVI).

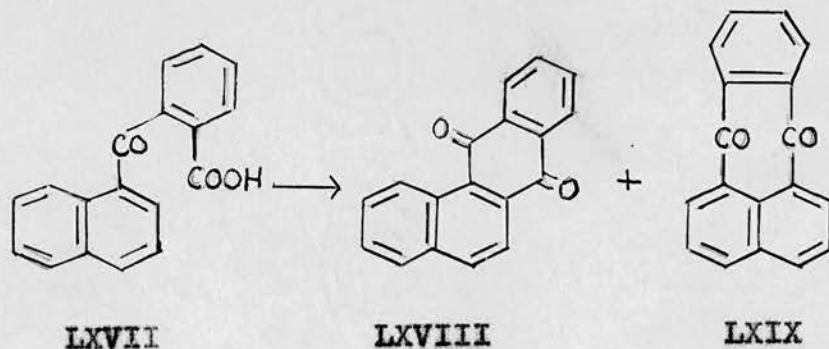
The cyclisation of the mixture of 4 & 12 -o - carboxybenzoylfluoranthenes has been reported in the patent literature. By boiling the mixture with toluenesulphonylchloride in trichlorobenzene solution, two products were obtained, one, apparently the yellow compound (LVIV); the other a second red compound m.p. 240° .

Cyclisation of pure 12-o-carboxybenzoylfluoranthene by this toluenesulphonylchloride method did yield two quinones which were separated chromatographically. One was shown to be, by melting point and mixed melting point determinations, the orange-yellow naphtho (2' : 3' - 11 : 12) - fluoranthene of Campbell & Gow. The other naphtho - (2':3' - 12:13) fluoranthene - 1': 4' -quinone (LVIII), was yellow, m.p. 319° ,

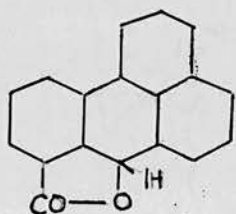
and strangely, for such an anthraquinone derivative, gave no vat with alkaline hydrosulphite. There was no trace of the red compound m.p. 228° claimed by von Braun & Manz. Nor was there a red compound m.p. 240°

4-0- carboxybenzoylfluoranthene did not cyclise at all by this method.

To determine the constitution of the cyclisation product of 4-0-carboxybenzoylfluoranthene, 4 : 5 - phthaloylfluoranthene was synthesised. The formation of peri-condensed phthaloyl compounds in the naphthalene series is well known. Rieche et. al. (45) found that the cyclisation of o-(1-naphthoyl) benzoic acid (LXVII), by fusion with sodium and aluminium chlorides in an inert atmosphere, yielded the two theoretically



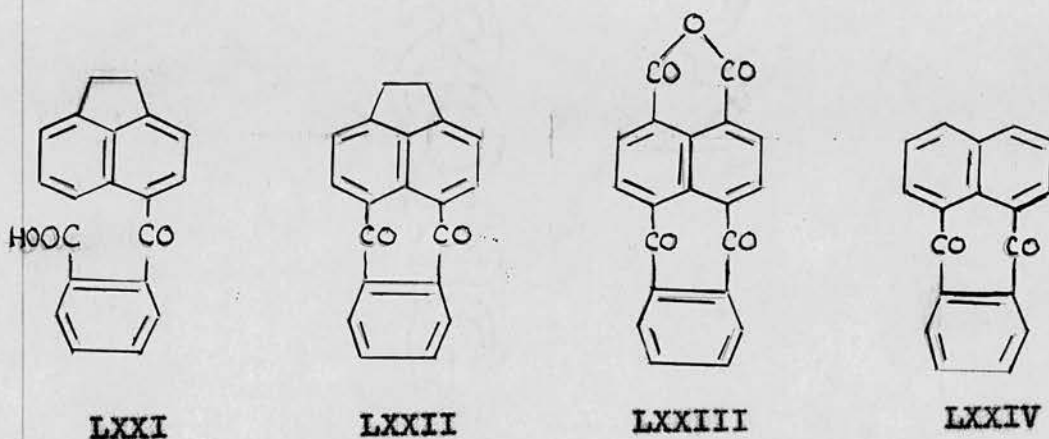
possible products, 1 : 2-benzanthraquinone (LXVIII) and 1 : 8 - phthaloyl naphthalene (LXIX). That the patent literature (46) erroneously suggested the formation of a benzanthrone derivative (LXX) .



LXX

in this reaction, was shown by Rieche.

Cyclisation of 3-o-carboxybenzoylacenaphthene (LXXI), by this method, yielded only 3:4-phthaloylacenaphthene (LXXII),

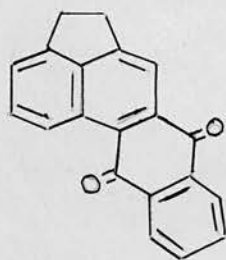


the structure of which was proved by oxidation to 4:5: phthaloyl -1:8 -naphthalic anhydride (LXXIII), followed by decarboxylation with mercuric oxide to 1:8 -phthaloylnaphthalene (LXXIV).

This result was later found to be in agreement with the observations of Peters & Rowe (47), who

did not, however, achieve the decarboxylation to 1:8 - phthaloylnaphthalene. This, however, has been accomplished by a Russian worker (48).

Attempts to prepare naphtho (2': 3' - 2: 3)
 acenaphthene -1':4' - quinone (LXXV) from
 3-o-carboxybenzoylbenzoylacenaphthene (LXXI)



LXXV

by the toluenesulphonylchloride method failed as did the benzoyl chloride method of Clar (49).

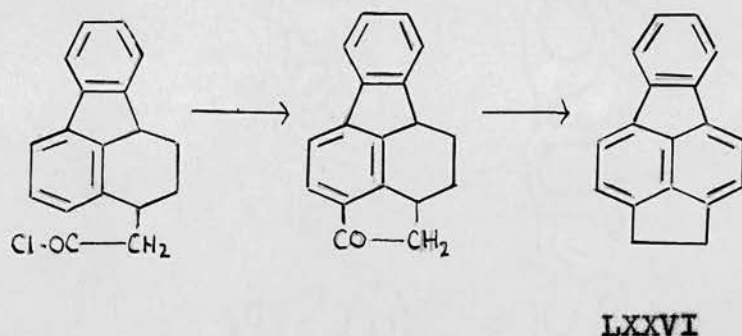
Cyclisation of pure 4-6-carboxybenzoyl fluoranthene by the sodium-aluminium chlorides fusion

did yield two products, separated chromatographically, one of which was shown, by melting-point and mixed melting-point, to be identical with the authentic naphtho (2': 3' - 3:4) fluoranthene -1': 4' - quinone of Campbell & Wang. The other product, 4:5 - phthaloylfluoranthene m.p. 296° , was yellow-orange (LXVI) and, in accordance with its structure, gave no vat with alkaline hydrosulphite. There was no trace of any compound, m.p. 328° , nor of the red compound, m.p. 246° , of the patent literature.

An interesting observation on the formation of peri-condensed naphthalene derivatives was that of Kloetzel & Chubb (50). These authors pointed out that 5-membered rings could be closed readily across

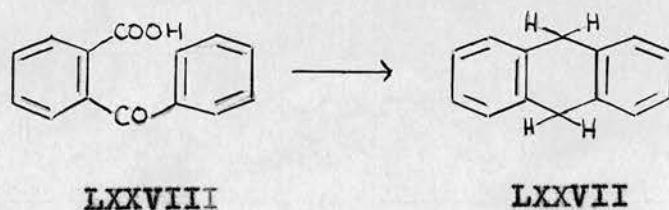
both peri-positions of the partially hydrogenated naphthalene nucleus while there was resistance to the closing of a second five-membered peri-ring in the naphthalene nucleus.

They prepared the fluoranthene derivative (LXXVI)



This observation may perhaps be extended to the preparation of 4:5 phthaloylfluoranthene in better yield by cyclisation of the 5-*o*-carboxybenzoyl -1:2:3:4 - tetrahydrofluoranthene.

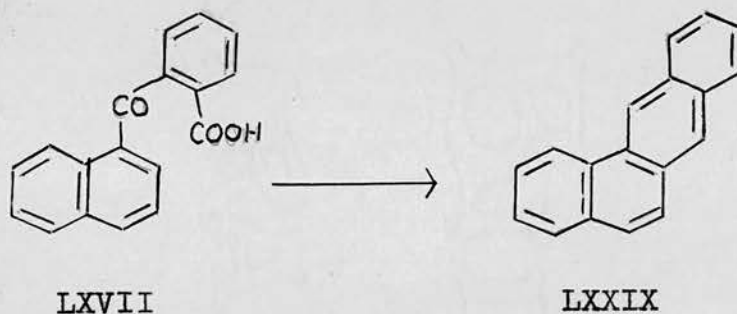
The preparation of 9:10 - dihydroanthracene (LXXVII) by reductive ring-closure of *o*-benzoylbenzoic acid (LXXVIII) by Miescher & Billeter (51) suggested an alternative way to obtain the fluoranthenenaphthoquinones by oxidation of the corresponding



dihydro compounds.

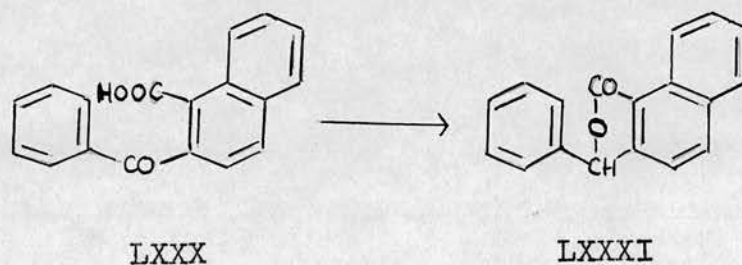
The method consisted of boiling the acid with

potassium iodide and red phosphorus in phosphoric acid, and by this reaction o-naphthoylbenzoic acid (LXVII) gave a reduced



product which dehydrogenated to 1:2-benzanthracene (LXXIX).

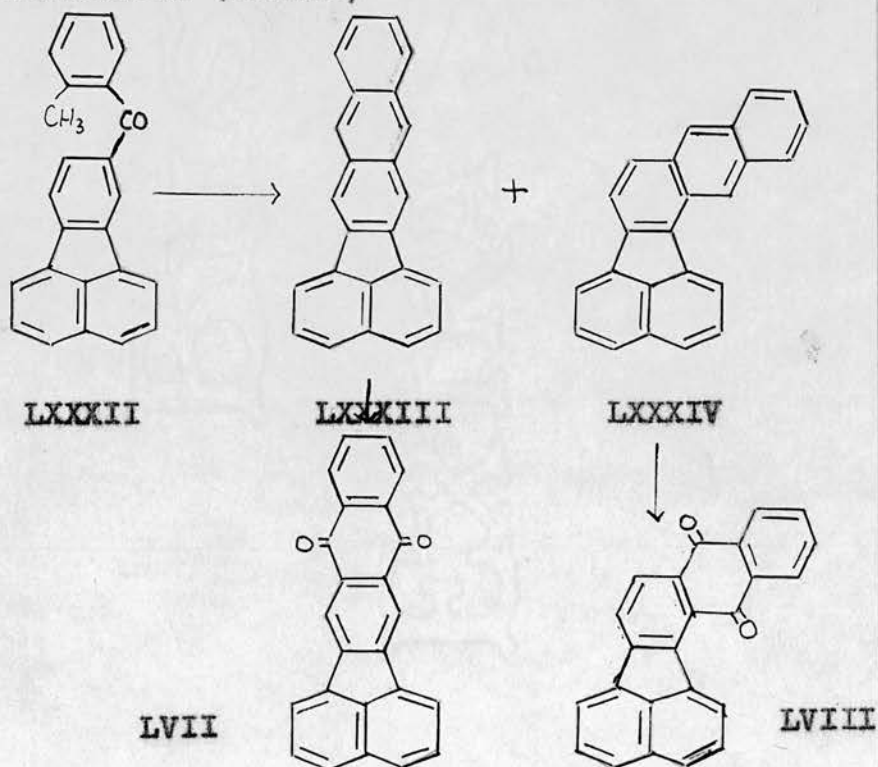
Newman & Gaertner (52) carried out a similar type of reaction in the synthesis of substituted benzanthraenes. Ring-closure of compounds of type (LXXX) with red phosphorus, potassium iodide, phosphoric and acetic acids yielded lactones of the type (LXXXI)



which were converted to benzanthracenes by way of the anthraquinones.

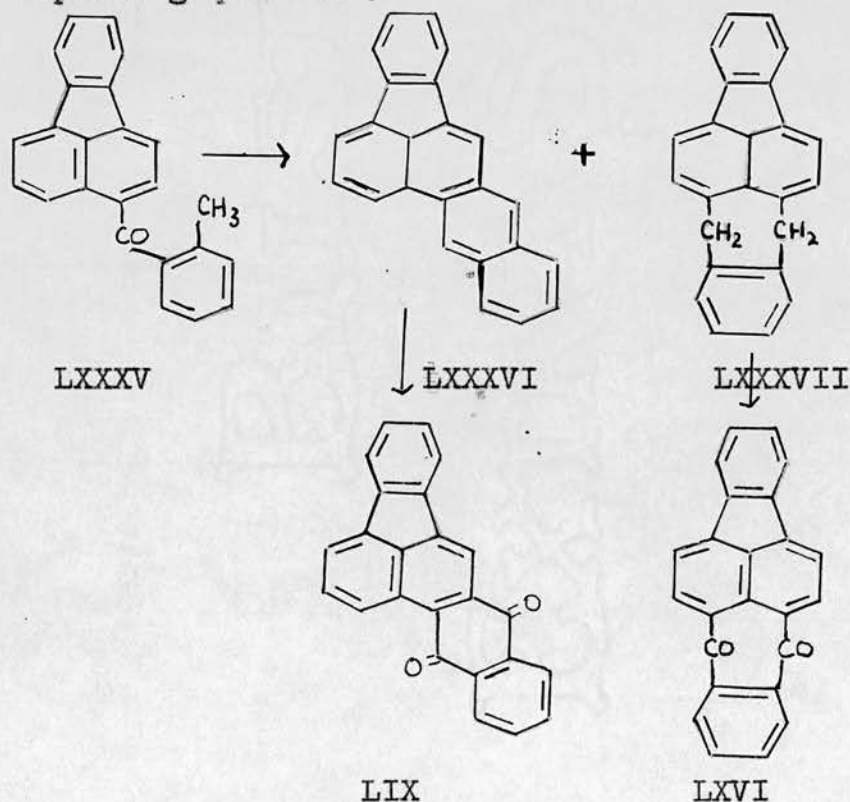
3-o-Carboxybenzoylacenaphthene (LXXI) and the mixture of o-carboxybenzoylfluoranthenes (LV, LVI) yielded only black intractable products by the original method of Miescher & Billeter. The addition of acetic acid to the mixture, in the case of 3-o-carboxybenzoylacenaphthene, resulted only in the return of the unreacted acid.

While these experiments were being carried out Reid (53) also isolated the three quinones and 4:5-phthaloylfluoranthene. Fluoranthene and o-toluoyl chloride in carbon disulphide gave a mixture of the 4- and 12-Toluoylfluoranthenes which were separated chromatographically. Elbs pyrolysis of the 12-o-toluoylfluoranthene (LXXXII)



gave two naphthfluoranthenes (LXXXIII) and (LXXXIV), which were oxidised to the two quinones (LVII) and (LVIII). One was identical with the naphtho (2':3' - 3:4) fluoranthene - 1': 4- quinone (LVII) of Campbell & Gow (so thus orientating the 12-toluyfluoranthene) and the other, naphtho (2':3' - 12:13) fluoranthene -1': 4'- quinone (LVIII) was yellow, m.p. 316^o . Both compounds were identical with those obtained from the ring-closure of 12-o-carboxybenzoylfluoranthene by the toluenesulphonylchloride method.

Elbs pyrolysis of the 4-toluyfluoranthene (LXXXV) again resulted in two hydrocarbons (LXXXVI) (LXXXVII) which were then oxidised to the corresponding quinones.

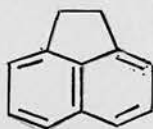


One was the naphtho (2':3' -3:4) fluoranthene -1': 4' - quinone (LIX) of Campbell & Wang (also orientating the 4-*o*-toluylfluoranthene); the other was yellow, m.p. 295° , and was 4:5-phthaloyl-fluoranthene. Again, these two compounds were identical with those obtained from the cyclisation of 4-*o*-carboxybenzoylfluoranthene by the sodium chloride/aluminium chloride fusion method.

SECTION BATTEMPTED DIELS -ALDER REACTIONS BY DEHYDRATION
of ACENAPHTHENE -7:8 -DIOL & ACEANTHRENE -1:2 -DIOL.Object of Research

By dehydrating acenaphthene -7:8-diols in presence of dienophiles, Campbell & Gow found that a Diels-Alder reaction took place, presumably by addition to the intermediate 7:8 -dimethyleneacenaphthene. If suitable substituted acenaphthene-quinones could be obtained, the synthesis would be of value in the understanding of the substitution of fluoranthene. Also the reaction might be extended to other 6- diketones, particularly aceanthraquinone, to yield substituted benzofluoranthenes.

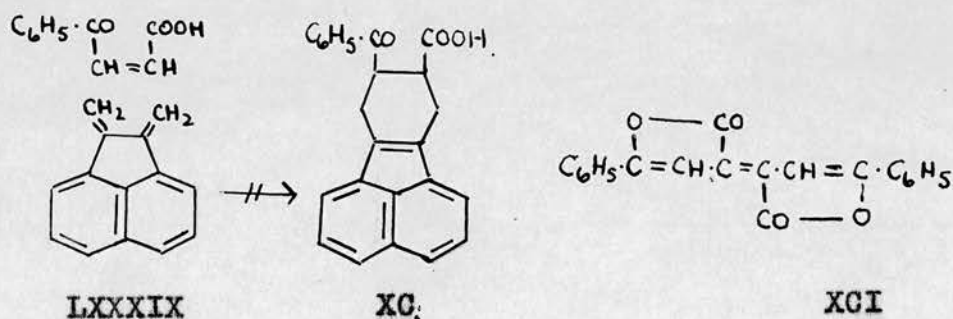
As pointed out by the authors, this synthesis was limited because of a competitive reaction. If the dienophile was reactive enough, then the Diels-Alder reaction took place; if not, then polymerisation of the transient dimethylene - acenaphthene (LXXXVIII) occurred, and only polymeric



LXXXVIII

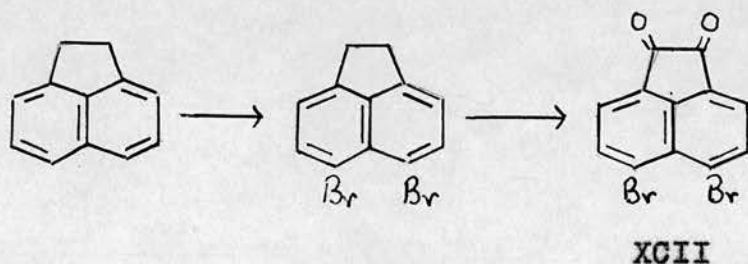
material was isolated. Maleic anhydride, benzoquinone, 1:4 - naphthoquinone, and many other dienophiles, condensed satisfactorily. Crotonic acid and other less reactive dienophiles did not.

Neither citraconic anhydride nor β -benzoylacrylic acid (LXXXIX)



gave a Diels-Alder product with the diol. With the latter compound a crimson, crystalline product was obtained, its colour immediately suggesting that it was not the desired tetrahydrobenzoylfluoranthene carboxylic acid (XC). Nor did it analyse for (XC). It appeared, however, to be identical with the compound obtained by von Pechmann (54). Later work suggested that this so called "Pechmann dye" had the structure (XCI, 55), arising from the dehydration and bimolecular coupling of two molecules of β -benzoylacrylic acid. This reaction had taken place in preference to the Diels-Alder. Had the reaction been successful an authentic 11-benzoylfluoranthene would have resulted.

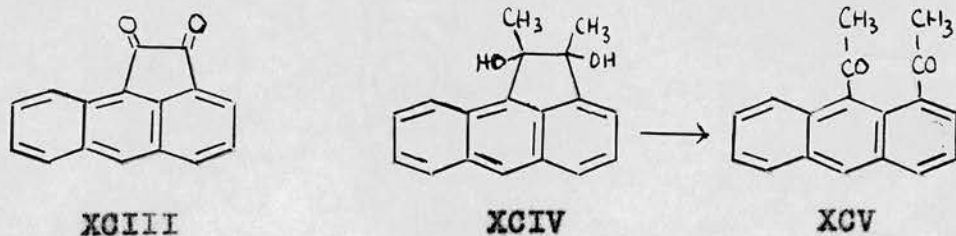
The preparation of 3:4-dibromoacenaphthenequinone (XCII) has been reported in the literature (56). Acenaphthene was brominated in 75% alcohol and the resulting 3:4-dibromoacenaphthene oxidised to 3:4-dibromoacenaphthenequinone (XCII). Under these



conditions bromination yielded an oil, distillation of which, at reduced pressure, immediately resulted in rapid decomposition to give much hydrogen bromide and a polymeric glass.

In nitrobenzene, as solvent, bromination took place rapidly and from the yellow semi-solid obtained on removal of the solvent, was obtained a solid, apparently the dibromoacenaphthenetetra-bromide of Mayer & Kaufmann (57), though boiling with alcoholic potash yielded a crystalline material which melted 10° below that reported by the above investigators.

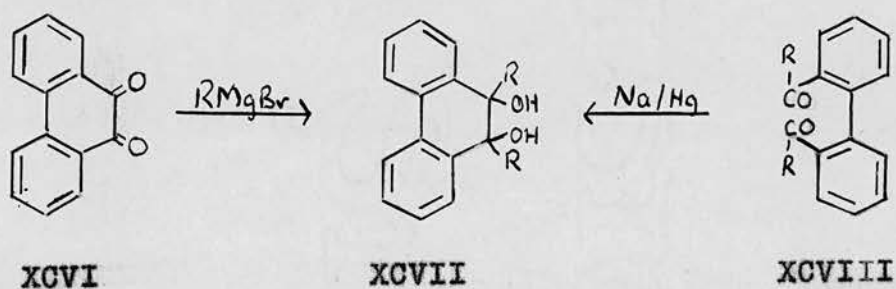
The investigation was not carried further because of the difficulty of obtaining authentically substituted acenaphthenequinones and attention was turned to another diketone, aceanthraquinone (XCIII)



The dimethylglycol (XCIV) apparently consisted of one isomer only, and with maleic anhydride it did not yield a Diels-Alder product from which it had been hoped to obtain the 2:3 -benzofluoranthene, hitherto unprepared.

In the phenanthraquinone (XCVI) series (58), the corresponding glycol isomers (XCVII) were obtained in two ways. Normal Grignard

This ref. deals with dimethyl glycol.



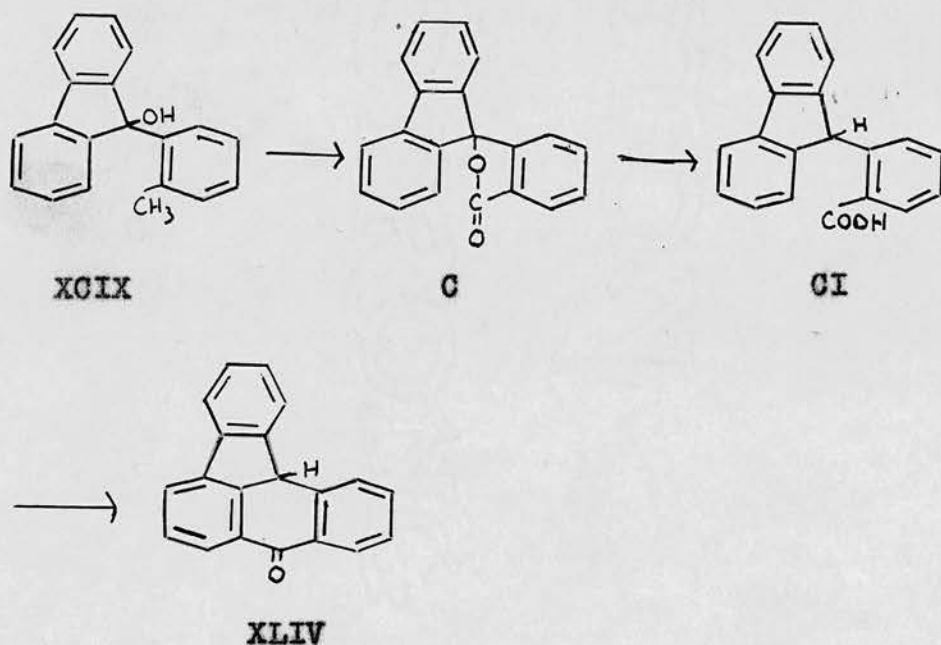
reaction with phenanthraquinone yielded one isomer; reduction of the corresponding 2:2'-diacylbiphenyls (XCVIII) gave the other.

Though the dimethylacanthraquinoneglycol was oxidised with lead tetra-acetate to 1:9 -diacetyl-anthracene (XCV), no attempt was made at the lengthy reduction. Attention was turned to other syntheses of 2':3 - benzofluoranthene.

*Cregee et al., Ber., 1940, 73, 571
mp. 165° ans.*

SECTION C.THE SYNTHESIS OF 2:3 -BENZOFLUORANTHENE

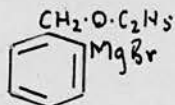
A suitable intermediate for the preparation of 2:3 -benzofluoranthene (XLIII) appeared to be the 1:9 -o-phenyleneanthrone (XLIV) prepared by Weiss & Anapp (31). Fluorenone was condensed with o-toluylmagnesium bromide and the carbinol (XCIX) obtained, was oxidised with alkaline



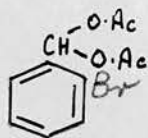
permanganate to the phthalide (C). Reduction to o-9-fluorenylbenzoic acid (CI) was followed by cyclisation (phosphorus pentoxide) to 1:9 - o-phenyleneanthrone (XCIV).

Noelsch (59) reported that he had been unable to repeat this synthesis at one stage and he replaced o-toluylmagnesium bromide with the Grignard reagent

of o-bromobenzylethylether (CII).



CII

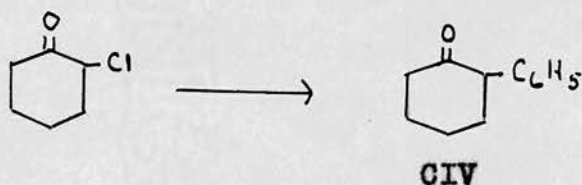


CIII

In attempting to repeat this synthesis the correct conditions for the formation of this Grignard reagent were inadvertently overlooked and with the failure of this preliminary reaction, attention was turned to other attempted syntheses. o-Bromo-

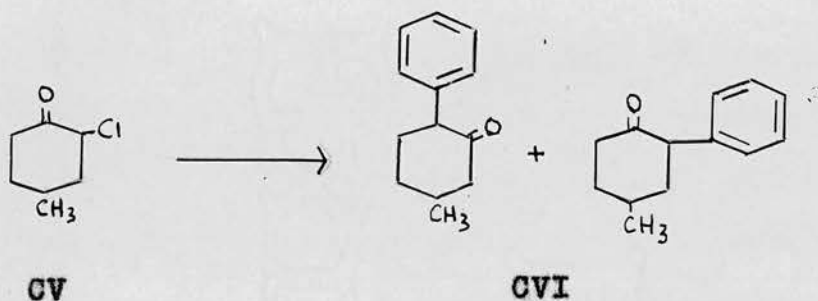
toluene diacetate (CIII), likewise, did not form a Grignard reagent under the conditions employed.

The reaction of phenylmagnesium bromide and 2-chlorocyclohexanone yielded 2-phenylcyclohexanone (CIV,60), though it was not known if the phenyl group was

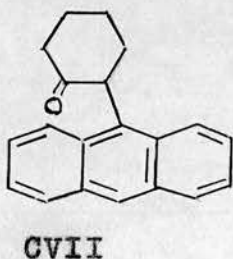


CIV

joined to the carbon atom which originally formed the keto group or to the carbon atom containing the chlorine. To elucidate this point 2-Chloro-4-methyl-cyclo



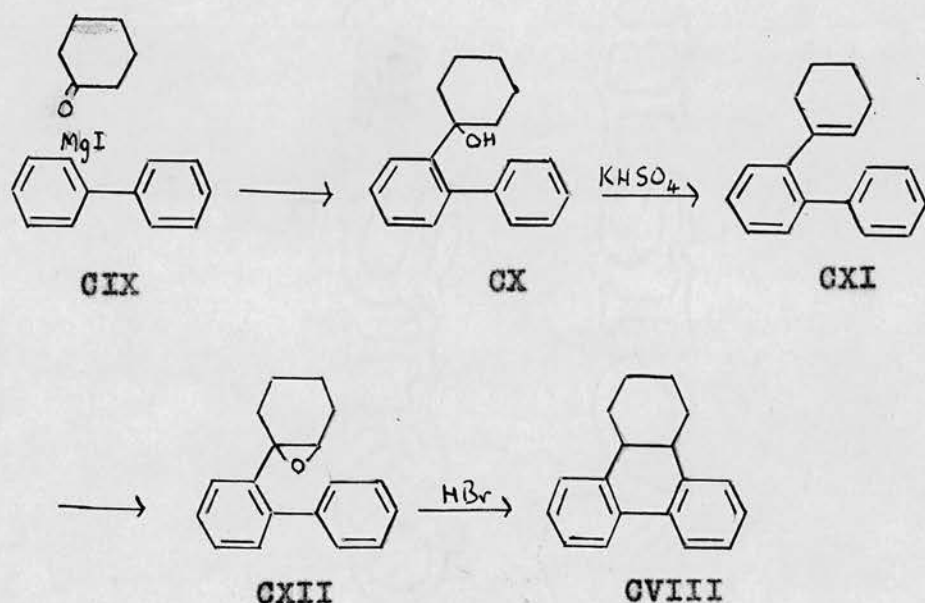
hexanone (CV) was condensed with phenylmagnesium bromide (61) and a mixture of isomeric 2-phenyl-methylcyclohexanones were obtained. This mixture of isomers proved that the bromomagnesium derivative of the 1-phenyl-2-chloro-4-methylcyclohexanol, initially formed in the Grignard reaction, rearranged in part, to produce a product in which the phenyl group was attached to the carbon atom which originally held the chlorine atom. Though unsuitable for preparing authentic derivatives substituted in the idene part of the 2:3-benzofluoranthene molecule, the method did suggest a means of preparing the parent hydrocarbon.



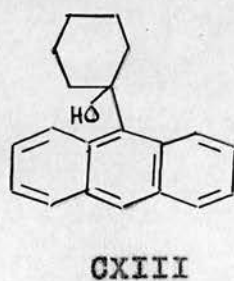
By condensing 2-chlorocyclohexanone with 9-anthrylmagnesium bromide (62) there might have been obtained the derivative (CVII), which could then have been cyclised to the required hydrocarbon. The condensation, however, was unsuccessful since

the only product isolated was anthracene.

The synthesis of tetrahydro-9:10-benzophenanthrene (CVIII) by Bradsher (63), suggested another synthesis of 2:3-benzofluoranthene. Condensation of cyclohexanone with diphenyl-2-magnesium iodide (CIX) yielded the corresponding carbinol (CX), which was dehydrated to the

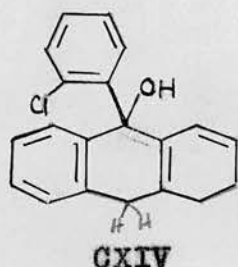


cyclohexene (CXI) Treatment of this material with monopero-phthalic acid yielded the oxide (CXII) which was cyclodehydrated with hydrobromic acid to the tetrahydro-9:10-benzophenanthrene (CVIII). The



preparation of 9-anthrylcyclohexylcarbinol (CXIII), however, from cyclohexanone and 9-anthrylmagnesium bromide was unsuccessful.

The other anthracene derivative used in an attempted synthesis of 2:3-benzofluoranthene was anthrone, which readily undergoes reaction with Grignard reagents to form the corresponding carbinols (64,65). It was surprising, therefore, that when



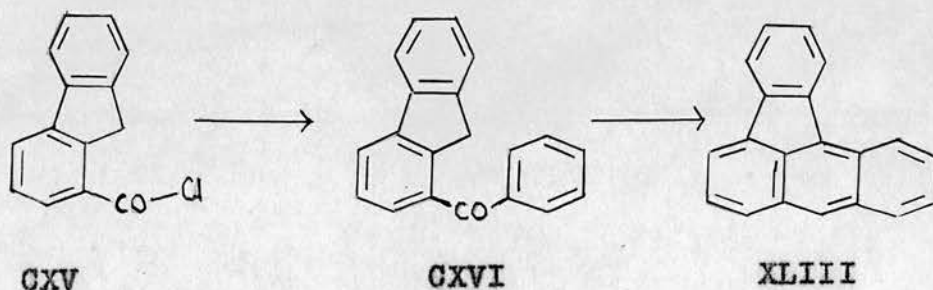
anthrone was treated with *o*-chlorophenylmagnesium bromide, the expected carbinol (CXIV) was not formed. The sole product of the reaction was anthra^{9,10}quinone.

A survey of the literature showed no parallel.

The synthesis of 2:3-benzofluoranthene was finally achieved by two methods, the first of which gave the desired hydrocarbon in very low yield.

Though fluorenone-1-carboxylic acid and chloride reacted easily with benzene in the Friedel-Crafts reaction (66), fluorene-1-carboxylic acid chloride (CXV) did not. This acid chloride, however, condensed easily with the more reactive anisole.

The preparation of 1-benzoylfluorene (CXVI)



See also
L. F. Fieser &
A. W. Szymanski
(J. Am. Chem. Soc., 1935, 57,
2174) who
condensed
fluorene-1-carboxyl
with naphthalene

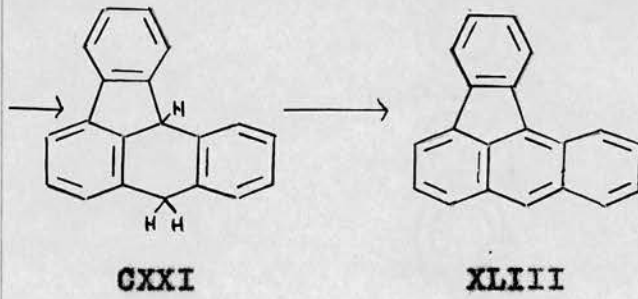
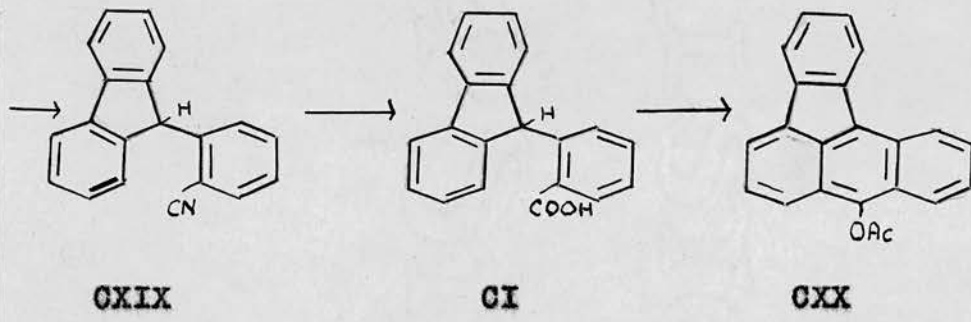
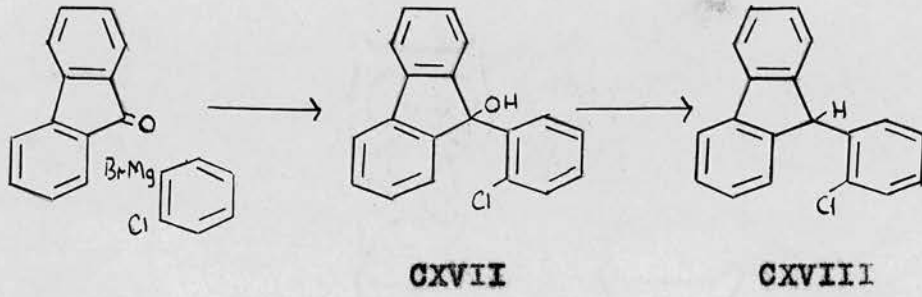
was achieved in good yield by treating the acid chloride with an excess of diphenylcadmium, one of the organocadmium compounds much favoured by Cason (67) for the preparation of ketones from acid chlorides.

Elbs pyrolysis of 1-benzoylfluorene yielded the required hydrocarbon (XLIII) which was separated chromatographically. The hydrocarbon fraction contained, also, an oxygenated substance which analysed to give an empirical formula $C_{40}H_{24}O$, suggesting that two benzofluoranthene molecules were in some way, oxygen-linked.

2:3-Benzofluoranthene was separated from this compound by means of its picrate. The yield in this reaction was too poor to be of value and another synthesis, suggested by one of Fieser & Cason (68), was achieved. In outline, it was as follows.

Fluorenone was condensed, with the Grignard reagent o-chlorophenylmagnesium bromide, and the resulting 9-o-chlorophenylfluoren-9-ol (CXVII) was converted to 9-(o-chlorophenyl)fluorene (CXVIII) by the Clemmensen reduction (cf Ullmann 69). Hydrolysis of the corresponding nitrile (CXIX), yielded o-(9-fluorenyl)benzoic acid (CI)

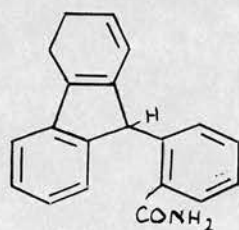
51



which was cyclised to the 4-acetate of 2;3 benzofluoranthene (CXX) by the method of Fieser & Hershberg (70). Reductive hydrolysis with zinc and caustic soda (Martin 71) yielded a hydrogenated product, probably the dihydrocompound (CXXI), which was then dehydrogenated (chloranil) to 2;3 - benzofluoranthene (XLIII).

Fluorenone reacted satisfactorily with 3 moles of Grignard reagent. With 1.5 to 2 moles was formed a complex, which decomposed to yield fluorenone. Such reversible complex formation with benzophenone and phenylmagnesium bromide has been reported by Pfeiffer & Blank (72)

The yield, in the Rosenmund reaction of the chloro-compound with cuprous cyanide, was best when the reaction was carried out in a sealed tube, in pyridine, with acetonitrile as catalyst.



CXXII

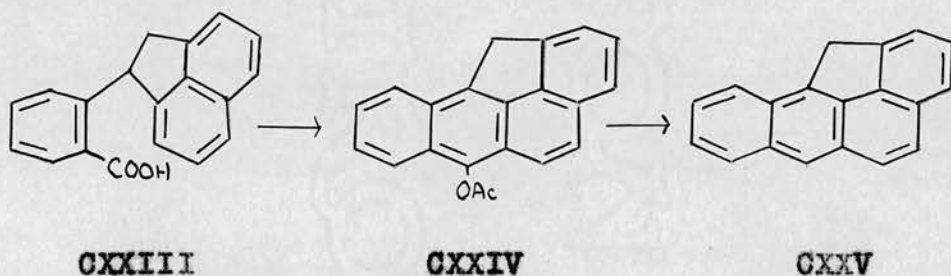
The addition of copper sulphate and tolunitrile (Koelsch & Whitney 73) gave rise to a higher proportion of the amide (CXXII), at the expense of the nitrile.

Hydrolysis of the nitrile (XIX) was achieved, in good yield, by boiling with an acetic acid/sulphuric acid/water mixture, but a far superior yield was obtained on hydrolysis with caustic soda and ethylene

glycol.

Since the cyclisation of *o*-(9-fluorenyl)benzoic acid (CI) by the phosphorus pentoxide method of Weiss & Knapp, gave only a yield of 16%, another method seemed desirable, and a suitable one was found in the zinc-chloride/acetic acid/acetic anhydride method of Fieser & Hershberg (70). No attempt was made to purify the crude acetate obtained; it was immediately reduced by the alkaline modification of the Clemmensen reduction.

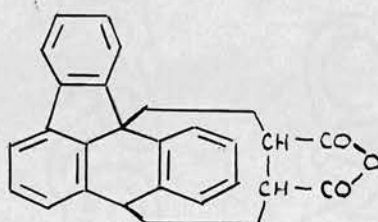
When *o*-(7-acenaphthyl)benzoic acid (CXXII^I) was cyclised in this



way, (68), the acetate (CXXIV) ^{was} reduced to 1':9-methylene-1:2-benzanthracene (CXXV). However, when the yellow acetate of *o*-(9-fluorenyl)benzoic acid (CI) was reduced, the product was not 2:3-benzofluoranthene. Crystallisation of the product obtained from the reduction, after chromatographic purification, gave a mixture of colorless and golden yellow prisms. Mechanical separation showed the golden yellow material to be 2:3-benzofluoranthene,

identical in melting point and mixed melting point with the Elbs reaction product. It was assumed, therefore, that the colorless product was 1:4-dihydro -2:3 -benzofluoranthene (CXXI), since it had already been observed (Exp. sect. A. p \times) that dihydroanthracene suffered some dehydrogenation on being chromatographed. Dehydrogenation with chloranil gave an almost quantitative yield of 2:3- benzofluoranthene.

2:3 - Benzofluoranthene is golden-yellow m.p. $144^{\circ}-5^{\circ}$ and readily gives a deep red picrate and with maleic anhydride a colorless Diels-Alder adduct, presumably (CXXVI)



CXXVI

Boiling o-(9-fluorenyl)benzoic acid with red phosphorus/potassium iodide, and phosphoric acid, did not yield a hydrogenated product. Unreacted starting material was recovered.

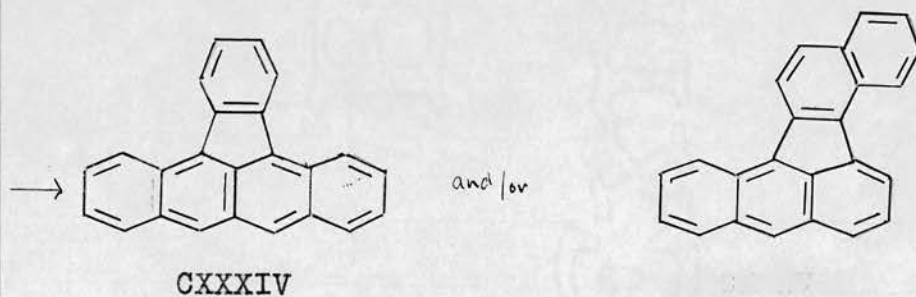
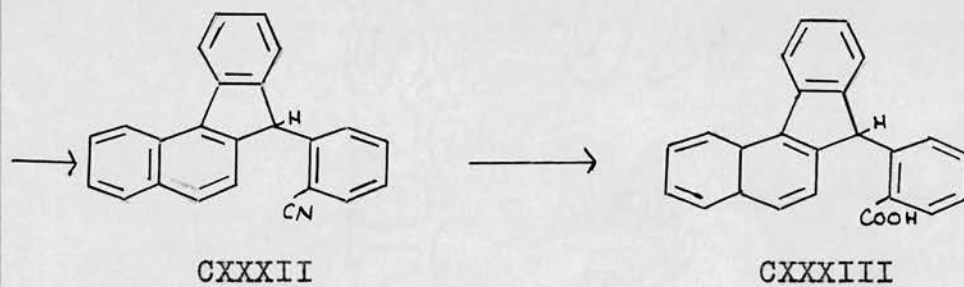
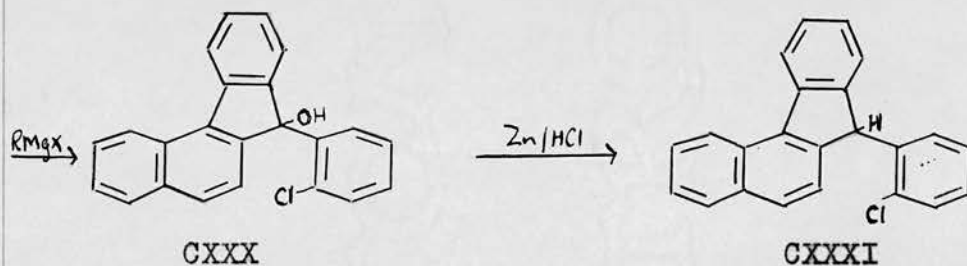
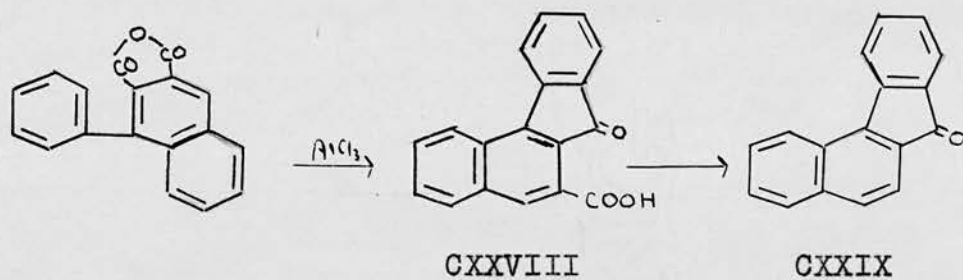
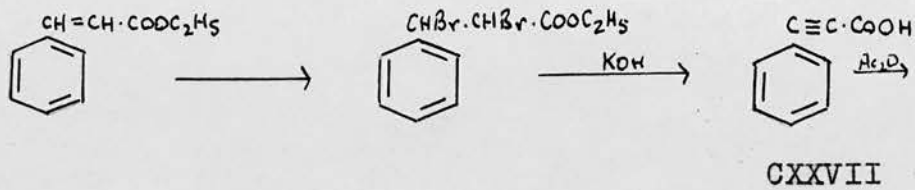
Some attempts at cyclisation were made by the Friedel-Crafts reaction. The acid chloride, when treated with aluminium chloride in nitrobenzene gave only intractable oils.

When the reaction was repeated with stannic chloride and benzene as solvent, there was obtained a golden-yellow compound melting some thirty degrees higher than the 1:9-o-phenyleneanthrone of Weiss & Knapp. The compound analysed for 1:9-o-phenylene anthrone. Unfortunately the investigation had to be abandoned for the want of time and material.

To be repeated.

After the successful synthesis of 2:3-benzofluoranthene it was decided to attempt to extend the reactions to the synthesis of 2:3-6:7-dibenzofluoranthene (CXXXIII) from 3:4-benzofluorenone (CXXIX). The proposed total synthesis was that shown below.

55a.



3:4-Benzofluorenone was prepared from phenylpropionic acid (CXXVII) by the method of Schaarschmidt (74), except that 3:4-benzofluorenone-1-carboxylic acid (CXXVIII) was decarboxylated with copper and quinoline. Though the reaction was satisfactory, the decarboxylation was lengthy, particularly when larger quantities were being used. The very rapid decarboxylation with basic copper carbonate (75) appears to be the more desirable.

The yield in the Grignard reaction with 3:4-benzofluorenone was lower than that obtained in the reaction with the simple fluorenone. The large reaction volume of benzene/ether may have been a contributory factor to the lower yield of the carbinol (CXXX). With two moles of Grignard reagent, there separated a pink complex which decomposed to yield the unreacted benzofluorenone. Though three moles of Grignard reagent yielded the required carbinol the best results were obtained with four moles.

The Clemmensen reduction of 9-(o-chlorophenyl)-3:4-benzofluoren-9-ol resulted in a yield of over 80%, though in this case, the product did not crystallise from the acetic acid-hydrochloric acid concentrate. The mixture was poured into water and the colorless complex, which precipitated, was dissolved in benzene and chromatographed. 9-(o-chloro-phenyl)-3:4-benzofluorene (CXXI) separated.

The conversion of this compound to the nitrile (CXXII), with acetonitrile as catalyst was achieved in 70% yield. No amide was characterised in this reaction (cf the 9-o-chlorophenylfluorene reaction).

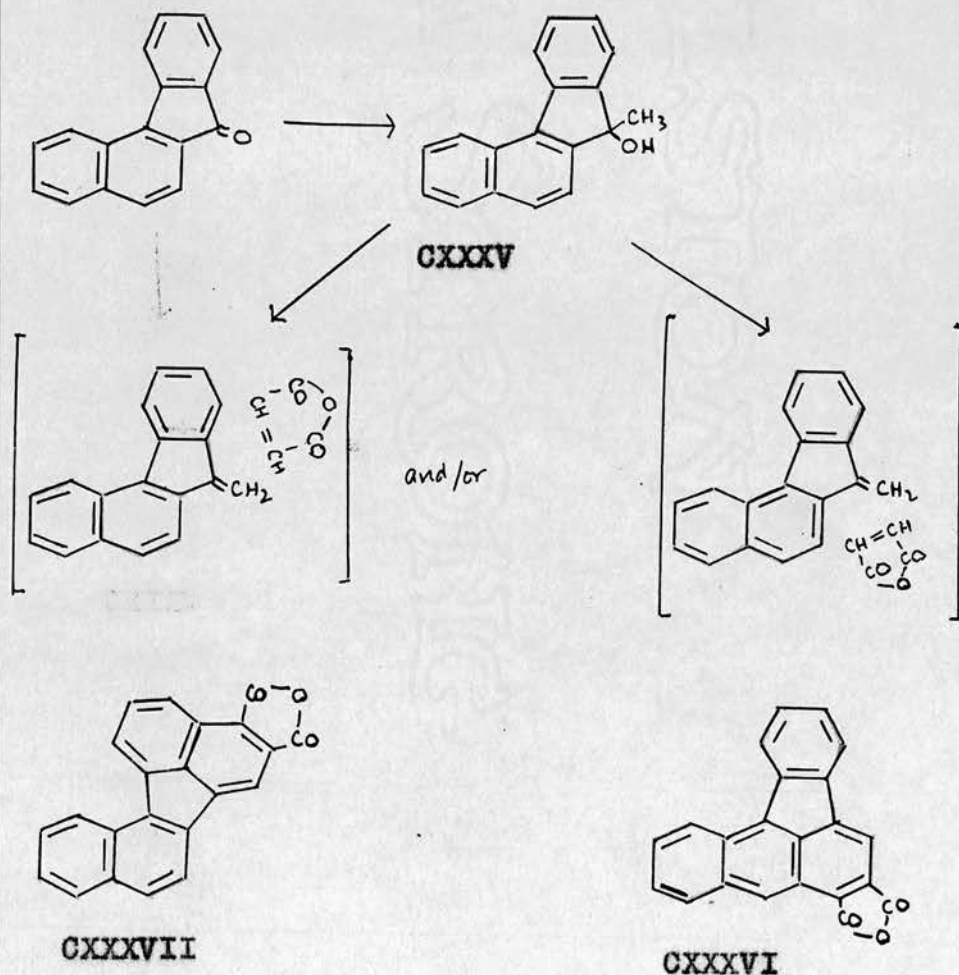
9-(o-Cyanophenyl) -3:4 -benzofluorene (CXXII) was hydrolysed quantitatively by caustic soda and ethylene-glycol. Acid hydrolysis gave a much diminished yield.

9-(o-Carboxyphenyl) -3:4 -benzofluorene (CXXXIII) melted over a large range (200° - 30°). Since all the intermediates in this benzofluorenone synthesis melted some 30° higher than the corresponding fluorenone derivatives it was expected that this acid would melt about 270° . Though the material was completely soluble in dilute carbonate repeated crystallisation did not raise the melting point to the expected figure. The methyl ester of the acid was chromatographed and then hydrolysed back to the parent acid without any change in the melting point.

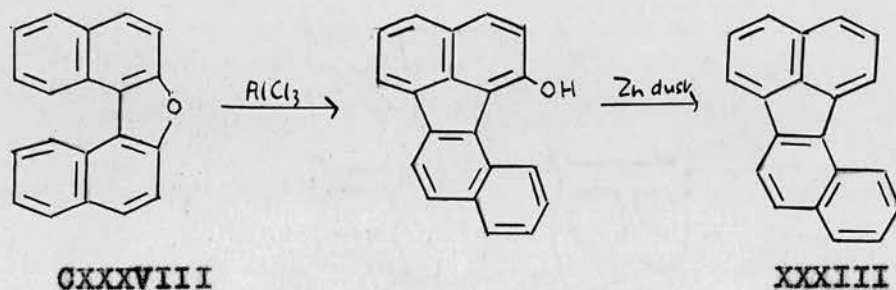
In spite of this apparent contradiction in melting point some attempts at cyclisation were made. The zinc chloride/acetic anhydride method was unsuccessful no quantity of product being isolated from the alkaline reduction. Boiling with phosphorus pentoxide in benzene, and heating the acid with phosphorus pentoxide in phosphoric acid, were also unsuccessful.

Unfortunately for scarcity of material further attempts at cyclisation could not be carried out. The stannic chloride method seems worthy of investigation.

With the availability of 3:4-benzofluorenone, another synthesis of 2:3-benzofluoranthene was attempted by the method of Campbell & Wang (13)

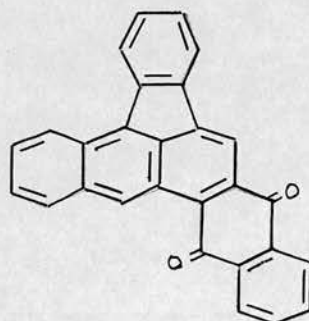
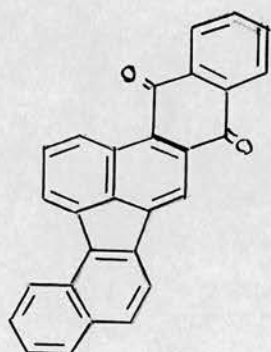


9-Methyl-3:4-benzofluoren-9-ol (CXXXV) was dehydrated in acetic anhydride in presence of excess maleic anhydride, when a Diels-Alder reaction occurred. Analysis of the product indicated that spontaneous dehydrogenation had occurred as Campbell & Wang had found in their synthesis of Fluoranthene-3:4-dicarboxylic acid anhydride. It was expected that the Diels-Alder addition would take place at the naphthalene portion of the molecule to yield 6:7-benzofluoranthene-3:4-dicarboxylic acid anhydride (CXXXVI), but decarboxylation did not yield 2:3-benzofluoranthene. Their addition, therefore, must have taken place at the benzene portion of the molecule to yield 10:11-benzofluoranthene-3:4-dicarboxylic acid anhydride (CXXXVII). Decarboxylation yielded a yellow hydrocarbon melting point $163^{\circ} - 4^{\circ}$ which must be the 10:11-benzofluoranthene, m.p. 166° of Orchin & Reggel (28). The compound dissolved in warm sulphuric acid with an olive green colour and organic solution of the hydrocarbon showed a yellow green fluorescence under the ultra violet lamp. These properties were in agreement with those of the hydrocarbon* claimed to be 10:11-benzofluoranthene (XXXIII) prepared by Zinke & Pack (76) by the zinc dust distillation of one of the products obtained from the treatment of β -dinaphthylene oxide (CXXXVIII)



with aluminium chloride. The hydrocarbon may also be identical with the compound obtained by Dansi & Ferri (77), by dehydrogenation of the product from the action of aluminium chloride on tetralin.

By analogy, the Diels-Alder addition of 1:4 -naphthoquinone to 9-methylene -3:4 -benzofluorene probably gave the 10:11 -benzofluoranthenenaphthoquinone (CXXXIX), rather than



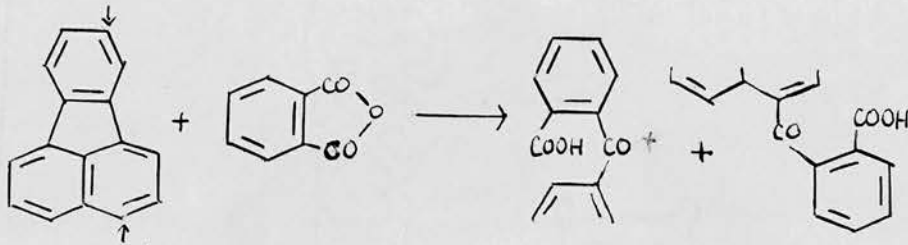
the corresponding naphthoquinone (CXL).

*NOTE - A mixed melting point of 10:11-benzofluoranthene with the compound prepared by Zinke & Pack gave no depression. The structure of their compound was thus established.

EXPERIMENTALINTRODUCTION.

Melting points (micro) of all compounds were determined as described in Campbell's Qualitative Chemistry (p.7) and (micro) on a Kofler apparatus (Kofler, Mikrochem, 1934, 15, 242)

Preparations already described in the literature are reported in outline only. Analyses were carried out by Drs. Weiler, and Strauss, Oxford.

SECTION A.Phthaloylation of Fluoranthene (I)

von Braun & Manz Ann. 1932,496,186. Campbell & Easton J.1949,340.

Fluoranthene (20 gm) and phthalic anhydride (16.3 gm) were stirred in carbon disulphide (100 ml) while powdered anhydrous aluminium chloride (33.4 gm) was added portionwise with stirring. After boiling for 60 hours the brownish mass was decomposed with ice and water and the solvent distilled off on the water bath. Sodium hydroxide (10%) liquor was added until the mother liquor was alkaline and the sodium salts of the organic acids filtered off. The free acids were obtained by acidification. Yield 14 gms. (40%)

Separation of Isomers.

The acids mixture (12 gm) was taken up in chloroform and allowed to crystallise after careful concentration. Yellow prisms separated. 1.3 gm m.p. 228°. Crystallisation from acetic acid raised the m.p. to 234°. There was no depression with the sample m.p. 228° prepared by Campbell and Easton.

Analysis for 12-o-carboxybenzoylfluoranthene.

C	H	O	Calc for	C	82.5	H	4.0
24	13	3	Found	C	81.5	H	4.2

Concentration of the chloroform filtrate yielded a further 0.8 gm.

The chloroform filtrate was then evaporated and the residue (9.5 gm), (m.p. 174°-84°) was shaken in the cold, with ether (150 ml), and filtered. The residue (3.1 gm) crystallised from glacial acetic acid in yellow prisms m.p. 234° giving no depression with the material obtained above.

The ether extract enriched in 4-isomer was taken to dryness and the yellow brown oil fused with anhydrous aluminium chloride (36 gm), and sodium chloride (9 gm), for 1 hour 125°, and then at 150° for 1 hour (oil bath temperatures). The mixture was decomposed with ice and hydrochloric acid, filtered, and the residue dried, after extraction with hot 5% potassium carbonate.

The dark residue (4.7 gm) was extracted with hot benzene (leaving 3.2 gm insoluble material) and the benzene extract chromatographed on a column 16" x $\frac{3}{4}$ ". Development with benzene led to a diffuse brownish appearance over the whole column. Fractions (100 ml) were collected but only dark intractable oils were obtained from them.

Phthaloylation of Fluoranthene⁽¹¹⁾

Fluoranthene (20 gm) and phthalic anhydride (16.3 gm) were stirred in tetrachloroethane (150 ml) while anhydrous aluminium chloride (33.4 gm)

was added portionwise with stirring. The mixture warmed slightly and a dark red colour developed. A fairly rapid evolution of hydrogen chloride occurred. Stirring was continued, at room temperature, for 48 hours, when the mixture was decomposed with ice and acid. The solvent was removed by steam distillation and the chocolate brown semi-solid cake was extracted with hot 5% potassium carbonate. The carbonate extract was acidified and filtered hot.

Yield 26 gm. (75%)

Separation of Isomers.

The acids mixture (18 gm.) was taken up in chloroform and carefully concentrated.

12 - o- Carboxybenzoylfluoranthene (3 gm.) separated, m.p. 234° after crystallisation from glacial acetic acid.

The chloroform was removed, the residue shaken with cold ether (250 ml) and filtered (residue A and filtrate B)

Residue A.

Residue A. (9 gm.) was extracted with glacial acetic acid (150 ml), filtered, concentrated, and left to crystallise.

Yield 6 gm. m.p. $206-12^{\circ}$ (A)

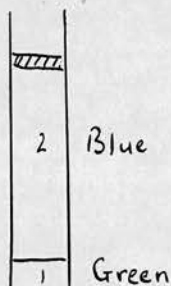
Esterification (A)

Fraction A. (5.8 gm), methanol (150 ml.) and concentrated sulphuric acid (15 ml.) were boiled for 1 hour. A small amount of tarry material was filtered off and the solution left to crystallise.

Yield 4.5 gm. Methyl esters m.p. 136° - 46°
 Addition of water to the filtrate yielded a further 1.0 gm. m.p. 134° - 146°

The crude esters (4.3 gm) were dissolved in the minimum of cold benzene and chromatographed in a column 20" x 0.86". The solution was adsorbed as a yellow band with a dark band of impurities at the top. Development was carried out with benzene light petroleum 80° - 100° (3/1.)

The column then appeared as below.



Fraction 1. The green band yielded 0.3 gm solid
 m.p. 136° - 40°

Fraction 2. The blue band, after elution with alcohol, gave 2.2 gm. solid m.p. 160° - 66° Crystallisation from light petroleum benzene raised the m.p.

to 172° (lit. 12-ester m.p. 174° ; 4-ester 104°)

Residue A was therefore essentially the 12-
o-carboxybenzoylfluoranthene.

Hydrolysis of the 12-ester.

The ester (m.p. 160° -66° 2.1 gm.) was boiled with 10% caustic soda (70ml) and ethanol (70ml) for 4 hours. Acidification yielded 12- o-carboxybenzoyl-fluoranthene, 1.9 gm. (crude) m.p. 217° - 20°

Crystallisation from acetic acid raised the melting point to 234°

The ether soluble fraction (B)

The ether soluble fraction (2.8gm.) was esterified as before.

Yield of methyl esters 2.1 gm.

The crude esters (2.0 gm) was chromatographed on a column 10" x 0.8" as for fraction A. esters.

The column appeared in the u.v. as shown below.

3	Bluish. yellow.
2	Deeper yellow.
1	Blue.

Fraction 1. The blue fluorescent band yielded a very small quantity of oil, not enough to be investigated further.

Fraction 2. The deeper yellow band. This

band yielded 0.75 gm. solid, m.p. 90° - 98° , obviously the 4-ester (Lit 104°)

Fraction 3. The column now fluoresced blue and this band was eluted with alcohol.

Yield 0.4 gm., m.p. 95° - 160° .

This column was not investigated further in view of the small amount of the desired 4-methyl ester, which might be present in the 3rd fraction.

Phthaloylation of Fluoranthene (iii)

Phthalic anhydride (16.3 gm.) and aluminium chloride (33.4 gm.) were stirred in methylene chloride (75ml) at room temperature. To the clear solution which resulted, was added, dropwise, with stirring a solution of fluoranthene (20 gm.) in the same solvent. A dark colour spread rapidly throughout the solution and hydrogen chloride was briskly evolved as the addition continued. The mixture was left overnight and was then decomposed with ice and hydrochloric acid. The solvent was removed with steam and the residue extracted with hot 5% potassium carbonate.

Acidification yielded the free acids (35 gm., quantitative)

Separation of the Isomers.

From the acids mixture (25 gm.) was obtained 12, o- carboxybenzoylfluoranthene (13 gm.) by careful crystallisation from chloroform as before.

Separation of the esterified portions as before, including re-columning of impure fractions yielded only 2.5 gm. of the 4-ester, hydrolysis of which yielded 4-o-carboxybenzoylfluoranthene (2 gm.) m.p. 230° , after crystallisation from alcohol. Mixed m.p. with the 12- acid was 212° .

A. CYCLISATIONS OF THE o-CARBOXYBENZOYLFLUORANTHENES
by the TOLUENESULPHONYLCHLORIDE METHOD.

(C.1937,II,2597)

(1) The Mixture

The mixture of 4- & 12-o-carboxybenzoyl-fluoranthenes (1.0 gm.) and toluenesulphonylchloride (0.55gm.) was boiled in trichlorobenzene (5ml) for 1 hour. The clear yellow solution changed to a dark red at the boiling point. The solution was reduced to half-volume and allowed to crystallise. The solid separating out was filtered off, washed with a little benzene, and then with a little hot acetone.

Yield 0.50gm., which after crystallisation from chlorobenzene had a m.p. of 255° - 330° . Under the microscope there could be seen a mixture of orange yellow elongated plates, and light yellow needles.

This mixture (50 mg.) was dissolved in chlorobenzene and chromatographed in that solvent. The solution was strongly adsorbed as a narrow orange band. Development gave a yellow band which moved away

from an orange band. The column was cut and the two bands eluted with chloroform.

The orange band gave a compound crystallising in long lathes from chlorobenzene m.p. $> 330^{\circ}$. It gave a blue vat with alkaline hydrosulphite, a deep blue colour with concentrated sulphuric acid, and was identical in m.p. & mixed m.p. with naphtho (2' : 3' - 11 : 12) - fluoranthene-1' : 4' - quinone prepared by Campbell & Gow (sec p. 19).

The yellow band gave, in smaller quantity, yellow needles m.p. $297^{\circ} - 300^{\circ}$. This compound gave no vat with alkaline hydrosulphite and with concentrated sulphuric acid gave a cherry red colour.

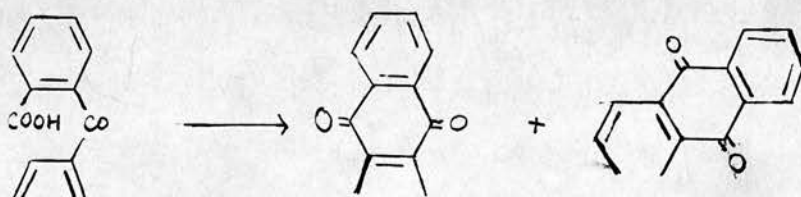
Analysis, however, did indicate a quinone or phthaloyl compound.

Analysis (on the crude material)

C	H	O	requires	C = 86.7	H = 3.7
24	12	2	found	C = 85.5	H = 4.1

The trichlorobenzene filtrate was steam distilled to remove the solvent and the residue was chromatographed. No other material was found. There was no sign of any red material m.p. 240° (patent) or 228° (von Braun)

2. Cyclisation of 12-o- Carboxybenzoylfluoranthene



Pure 12-o- carboxybenzoylfluoranthene (3gm) and toluenesulphonylchloride (1.65gm) were boiled in trichlorobenzene (15ml) for 1 hour. The solution was allowed to crystallise and the product filtered off and washed as before.

Yield 1.7 gm.

Crystallisation from chlorobenzene gave the same mixture, and yellow orange lathes and yellow needles could be seen under the microscope.

The mixture of cyclised products (1.0 gm) was boiled with chlorobenzene (400 ml). On cooling 0.4 gm material was deposited, and filtered off. The filtrate was chromatographed on a column 18" x 7/8" on which it was strongly adsorbed as a narrow orange band. On development the column assumed the appearance as before - a yellow band (1) moving away from a more strongly adsorbed orange band (2).

The column was cut and the two bands eluted with chloroform.

(1) The yellow band eluate, on removal of the chloroform, yielded 0.1 gm of a yellow solid, crystallising from chlorobenzene in long yellow lathes, m.p. 319°-20°. This compound gave a red colour with concentrated sulphuric acid, but no vat with alkaline hydrosulphite. In the solid state and in solution this compound showed a yellow-green fluorescence in ultra-violet light.

It was analysed for naphtho 2 (2': 3' - 12:13) fluoranthene - 1': 4'-quinone.

C H O required C) 86.7 H 3.7
24 12 2

found C 85.8 H 3.8

This quinone was identical with that obtained from the cyclisation of the mixture of acid isomers (expt. 1.)

(2) The orange band eluate gave 0.3 gm of the known naphtho (2':3' - 11:12) fluoranthene - 1'-4' quinone, m.p. > 330°. It gave a blue colour with concentrated sulphuric acid and a blue vat with alkaline hydrosulphite.

Both products were identical with the corresponding compounds from the pyrolysis of 12-toluoylfluoranthene (Reid p. 37)

A mixture of the two quinones was separated by an alkaline hydrosulphite and indicated that the 11:12 - quinone and the 12: 13 - quinone were formed, approximately, in the ratio 5/1.

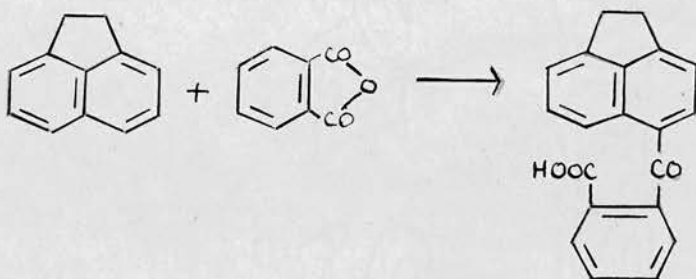
The fact that both quinones obtained from the cyclisation of the mixtures of acids were identical with those obtained from the 12 - acid suggested that 4 - o-carboxybenzoylfluoranthene did not cyclise by this method. This was found to be true. Unreacted starting material was recovered

B. CYCLISATION of the o-CARBOXYBENZOYL ACIDS by
the SODIUM CHLORIDE - ALUMINIUM CHLORIDE METHOD

(cf. Rieche et. al. Ber. 1932,65,1371)

Model Experiments

Preparation of 3-o-carboxybenzoylacenaphthene

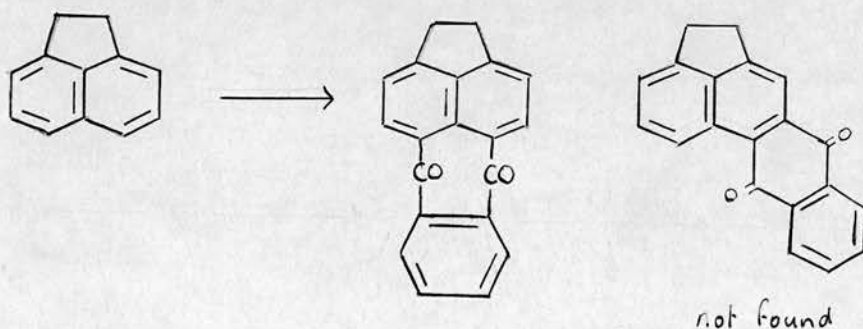


The Friedel- Crafts reaction of acenaphthene with phthalic anhydride in benzene yielded the desired product.

25 gm. acenaphthene yielded 42 gm. 3- o- carboxybenzoylacenaphthene, white plates m.p. 200°

(Peters and Rowe. J. soc. Dyers and Colorists 1943, 59, 52)

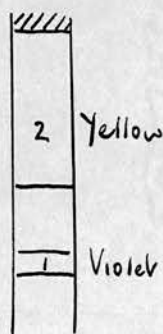
Cyclisation of 3-o-carboxybenzoylacenaphthene



Anhydrous aluminium chloride (48gm) and

Sodium chloride (12 gm) were fused in a nickel crucible at 125° . To the clear melt was added 3 - o - carboxybenzoylacenaphthene (5.5 gm), all at once, and the temperature of the oil bath was raised to 160° . The melt was maintained at this temperature, in a stream of nitrogen, for 2 hours, and then decomposed with ice and hydrochloric acid. The product was filtered off, extracted with carbonate, washed and dried. (4.7 gm)

The crude material was extracted with hot benzene (residue 1.2 gm), and after concentration the benzene extract was chromatographed on a column 17" x 0.75". Development was carried out with a mixture of benzene/ light petroleum 60/80 $^{\circ}$, (4/1) . When the column was fully developed it appeared as shown



Fraction 1 : The violet band was rapidly eluted. Removal of the solvent yielded a very small quantity of a solid which was not investigated further.

Development was continued until the yellow band reached the foot of the column, which was then cut.

Fraction 2. The yellow band was eluted with alcohol and concentration yielded long, straw coloured prismatic needles of 3:4- phthaloylacenaphthene m.p. $196^{\circ} - 7^{\circ}$.

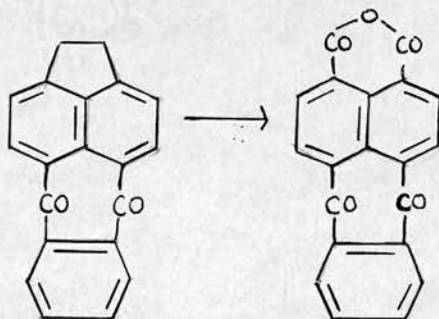
The 2:3- phthaloylacenaphthene was not formed.

In concentrated sulphuric acid 3:4- phthaloyl acenaphthene gave an orange coloured solution with a strong green fluorescence. As expected from its structure it gave no vat with alkaline hydrosulphite.

Analysis. C H O. calc for C 84.5 H 4.2
20 12 2

Found C 84.5 H 4.5

Oxidation of 3:4- Phthaloylacenaphthene to 4:5- phthaloyl - 1:8- Naphthalic Anhydride.



3:4- Phthaloylacenaphthene (1gm) was heated in glacial acetic acid to 60° and chromic anhydride(see below, 36 ml.) was added. The solution was boiled for 30 minutes, and more chromic

anhydride solution (54ml.) was added. After further boiling for two hours the mixture was concentrated to half - volume and the precipate, obtained on cooling, washed with alcohol and water, and then digested with hot glacial acetic acid.

Yield 0.75 gm, bright yellow needles m.p. > 310°

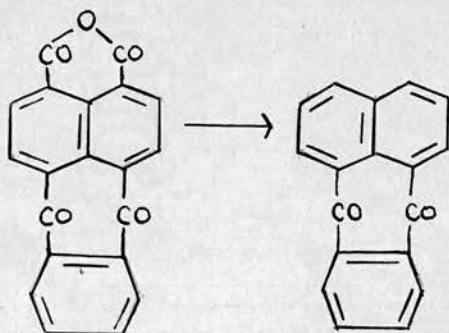
This compound gave a deep orange colour with concentrated sulphuric acid.

Analysis. Calc. for C₂₀ H₈ O₅ C 73.2 H 2.37

Found C 73.2 H 2.35

Chromic anhydride solution: Chromic anhydride (9gm) was dissolved in water (14ml) and made up to 90 ml with glacial acetic acid.

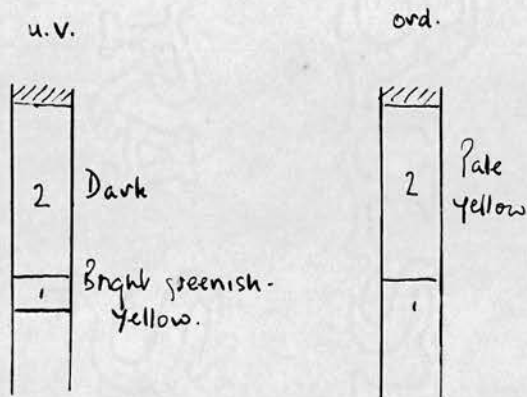
Decarboxylation of 4:5 - Phthaloyl-1:8 - naphthalic anhydride to 1:8 - Phthaloylnaphthalene.



4:5- Phthaloyl - 1:8- naphthalic anhydride
(0.75gm), water (20ml), and mercuric oxide, freshly prepared from mercuric acetate (1.5gm) by precipitation with sodium hydroxide and washing until neutral, were heated in a sealed tube at 250 for 4 hours. The resulting dark material

was boiled with concentrated hydrochloric acid for 2 hours, filtered, washed, and dried (1.1gm).

The dried material was extracted with benzene. (residue 0.4 gm) and the benzene solution chromatographed on a column 6" x $\frac{1}{8}$ ". Development was carried out with benzene. The column appeared as below.



Fraction 1. -The narrow strongly fluorescent band . The eluate did not retain its fluorescence. Removal of the solvent yielded a white solid(0.15 gm) m.p. 168° - 72°

Fraction 2. The column was then cut and the visible pale yellow band eluted with alcohol. A further quantity of the white solid (0.15 gm) was obtained.

Total Yield (crude) 0.30gm.

Crystallisation from alcohol/glacial acetic acid gave 1:8 - phthaloylnaphthalene, colorless

clusters of needles, m.p. $176^{\circ} - 7^{\circ}$ (Lit. 178°), soluble in concentrated sulphuric acid to give a canary yellow solution with a green fluorescence. There was no colour with zinc dust and ammonia and no vat was produced with alkaline hydrosulphite.

Analysis. Calc for C₁₈ H₁₀ O₂ C 83.7 H 3.9

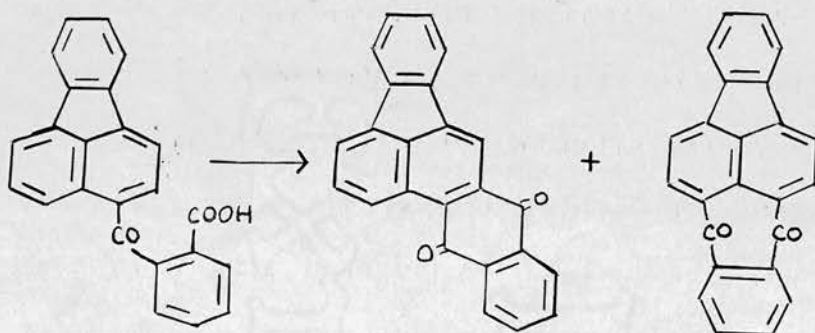
Found. C 83.6 H 4.1

Two attempted cyclisations of 3-o- Carboxybenzoyl-acenaphthene.

(1) 3-o-Carboxybenzoylacenaphthene (4.0 gm) and toluenesulphonyl chloride (3.0 gm) were boiled in trichlorobenzene (25ml.) for 1 hour. The clear yellow solution darkened at the boiling point. Removal of the solvent by steam distillation yielded a black intractable solid.

(2) 3-o-Carboxybenzoylacenaphthene (1.0 gm), benzoyl chloride (3.0 gm) and concentrated sulphuric acid (1 drop) were boiled for thirty minutes in nitrobenzene (30 ml.). A black colour soon appeared and only a black intractable solid resulted.

(cf. Clar J. 1949, 2073, 2440.)

Cyclisation of 4-o- Carboxybenzoylfluoranthene

Pure 4-o-Carboxybenzoylfluoranthene (1.1gm), aluminium chloride (3.3gm.), and sodium chloride (2.75 gm.), were intimately mixed. The mixture was heated in an oil bath, the temperature being raised to 140° over 30 minutes. It was maintained there for three hours while dry nitrogen was passed through the melt.

After decomposition with ice and hydrochloric acid the black product was extracted with 5% carbonate washed and dried. It was then extracted with and the benzene concentrate chromatographed on a column 12" x 0.75".

The reddish brown solution was adsorbed as a dark band with a yellow green forerun. On developing with benzene, a yellow band separated, and was rapidly eluted. The lime yellow eluate had a weak green fluorescence in the u.v.

Removal of the solvent yielded a solid (20mg), m.p. 248.53° (micro) with sublimation.

Crystallisation from chlorobenzene gave yellow-orange prisms m.p. 252.3° (micro). The compound

gave a bluish green colour with concentrated sulphuric acid and a blue - violet vat with alkaline hydrosulphite.

By m.p. and mixed m.p., this compound was shown to be naphtho-(2':3'-3:4) fluoranthene - 1':4'-quinone.

(Campbell and Wang)

After the elution of this yellow band, a deeper yellow band could be seen separating from the band of dark impurities. After suitable development, the column was cut, and the deep yellow band eluted with chloroform, removal of which yielded a solid (30mg) m.p. $293^{\circ}5'$ (micro). Crystallisation from chlorobenzene yielded yellow elongated prisms of 4:5- phthaloyl-fluoranthene, m.-p. $296^{\circ}7'$.

This compound gave a red colour with concentrated sulphuric acid but no vat with alkaline hydrosulphite.

Analysis	C	H	O	req.	C	H	O
	24	12	2		86.7	3.7	
				Fd.	86.3	3.6	

Both products were identical in m.p. and mixed m.p. with the corresponding products from the pyrolysis of 4-toluoylfluoranthene (cf Reid p. 38)

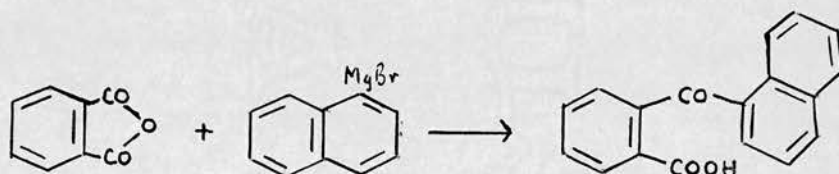
The material obtained by von Braun from the cyclisation of 4-o-carboxybenzoylfluoranthene with sulphuric acid was neither of the products described above.

C CYCLISATION of the o-CARBOXYBENZOYLACIDS by the
POTASSIUM- IODIDE- HYDROGEN IODIDE METHOD.

Miescher and Billeter *Helv. Chim. Acta*, 1939, 22, 601
Model Experiments.

(1) Cyclisation of 1-o-Carboxybenzoylnaphthalene

Preparation of 1-o-Carboxybenzoylnaphthalene.



Fieser & Hershberg *JACS*, 1932, 59, 1028

The Grignard reagent from 2-bromonaphthalene (21 gm) was added to phthalic anhydride (10 g,) in benzene.

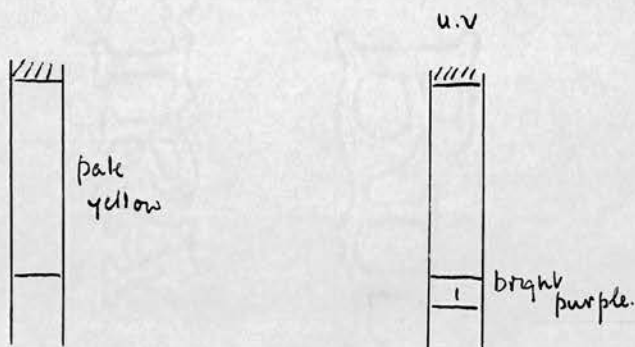
The yield was poor - 10 gm (Lit.75%)

Cyclisation of 1-o-Carboxybenzoylnaphthalene

1-o-Carboxybenzoylnaphthalene (4.6 gm) potassium iodide (5.5 gm), red phosphorus (1.5 gm) and phosphoric acid (20 ml) were boiled for 4 hours. On cooling water was added to dissolve inorganic salts and the product filtered off. The residue was extracted with alcohol, the filtrate being yellow with a green fluorescence. Removal of the solvent yielded a solid (2.0 gm, 52%)

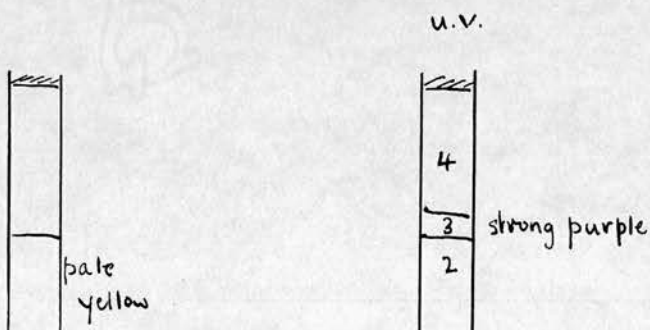
This material (1.9 gm) was dissolved in the minimum of cold benzene and chromatographed on a column 14" x 0.75".

After development with benzene the column appeared as below.



Fraction 1. The bright purple band was eluted and the greenish yellow eluate on removal of the solvent gave a solid (0.6 gm) m.p. $110^{\circ} - 120^{\circ}$ (micro) crude and $112^{\circ} - 120^{\circ}$ after crystallisation from acetic acid.

The column then appeared



Fraction 2. The visible pale yellow band. The green eluate on removal of the solvent yielded a solid (0.9 gm) m.p. $135^{\circ} - 45^{\circ}$ (micro). Crystallisation from acetic acid raised the m.p. only slightly - $138^{\circ} - 145^{\circ}$.

Fraction 3. The second narrow purple fluorescent band gave only a very small amount of solid not investigated further.

Fraction 4. The column was then cut and eluted with alcohol. No more material was obtained.

Total recovery 1.5 gm.

Fractions 1 & 2 were again chromatographed separately.

Fraction 1. 0.5 gm was dissolved in benzene and chromatographed in benzene on a column 5" x 0.5". The column appeared as before.

(1) The first fraction gave 0.15 gm solid
m.p. $108^{\circ} - 120^{\circ}$ (Micro)

(2) The second fraction gave 0.25 gm solid
m.p. $130^{\circ} - 45^{\circ}$ (micro)

Fraction 2. 0.75gm chromatographed in benzene on a column 9" x 0.5"

(1) The first fraction gave 0.05 gm m.p. $95^{\circ} - 100^{\circ}$ (micro)

(2) The second fraction gave 0.65 gm., m.p. $144^{\circ} - 50^{\circ}$ (micro)

Dehydrogenation of the main fraction.

The fraction m.p. $146 - 50^{\circ}$ (0.14 gm) and chloranil (0.10gm) were boiled in sulphur free xylene (2ml.) for 3 hours. Benzene was added on cooling and the mix

the mixture shaken with cold 5% sodium hydroxide to remove tetrachlorohydroquinone. The benzene/xylene layer was separated, washed and dried. Removal of the solvent yielded an off-white solid (0.11 gm) which on crystallisation from acetic acid gave white crystals of 1:2-benzanthracene, m.p. 156° (Lit, 158°)

There was no depression with an authentic sample

Analysis. Calc for C₁₈ H₁₂ C 94.7 H 5.3

Found. C 94.2 H 5.3

The other fractions (0.75 gm) was similarly dehydrogenated to 1:2-benzanthracene.

Yield 0.65 gm.

There appeared to be some dehydrogenation on the column and accordingly pure 9:10-dihydroanthracene was prepared and chromatographed.

Preparation of 9:10-Dihydroanthracene

Clemmensen Ber.1914,47,684.

9:10-Anthraquinone was reduced by boiling with zinc amalgam and concentrated hydrochloric acid. The dihydroanthracene distilled off with the steam and was crystallised.

9:10-Dihydroanthracene (m.p. 106° Lit 107°) (0.5 gm) was chromatographed on a column 5" x 0.5" in benzene. The solution was adsorbed as ^a wide band with a deep violet fluorescence in the u.v.

Yield 0.45 gm m.p. 90° - 100°

*what other
fractions?
all 1/2
residue*

Dehydrogenation, therefore, was occurring on the column. !!!

Attempted cyclisation of 3-o-Carboxybenzoylacenaphthen

3-o-Carboxybenzoylacenaphthene (2.0 gm), potassium iodide(2.2 gm), and red phosphorus(0.6 gm), were boiled with phosphoric acid (10 ml.) for 4 hours. An intractable dark product resulted.

The experiment was repeated with acetic acid as solvent. Unreacted starting material was recovered.

Attempted cyclisation of the o-Carboxybenzoylfluoranthenes.

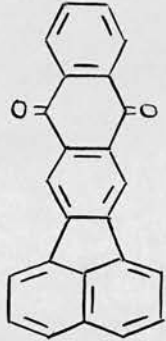
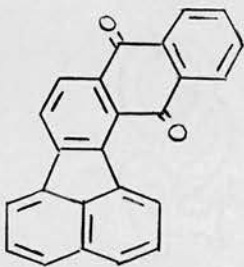
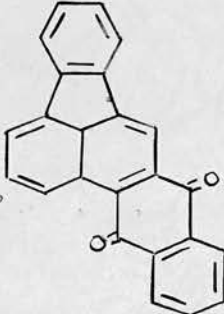
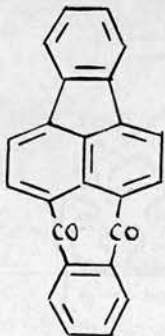
A sample of the 4-+12-o-carboxybenzoylfluoranthenes obtained in the Friedel - Crafts reaction was esterified passed through a short "cleaning" column and hydrolysed back to the free acid mixture.

This acid mixture (1.1gm), potassium iodide (1.1gm), and red phosphorus (0.3 gm) were heated with phosphoric acid in an oil bath at 160°. After 3 hours water was added to the mixture and the dark solid filtered off. Carbonate extraction showed no free acid.

Extraction of the residue with alcohol removal of the solvent yielded 0.2 gm solid A.

Further extraction with benzene , as solvent yielded 0.3 gm solid B.

The two fractions A & B. were combined boiled with chloranil (0.4 gm) in sulphur - free xylene (10ml) for 3 hours. After extraction with cold 5% sodium hydroxide the xylene solution was washed, dried, concentrated and chromatographed on a column 11" x 0.6". From one fraction was obtained a very dirty solid which was not investigated further because of its quality and poor yield.

			Conc. H ₂ SO ₄ 2 4	Vat.
Naphtho(2':3'- 11:12)fluoran- thene-1':4'- quinone.	yellow orange m.p. 330° (sub)		Blue	Blue
Naphtho(2':3'- 12:13)fluoran- thene-1':4'- quinone	yellow m.p. 319° 20° (sub)		Red	none
Naphtho(2':3'- 3:4)fluoran- thene-1':4'- quinone	yellow orange m.p. 252-3° (sub)		Bluish green	Blue violet
4:5-Phthaloyl- fluoranthene	yellow m.p. 296-7°		Red	none

(sub) - Sublimation.

Summary of Results.

12-o-carboxybenzoylfluoranthene is cyclised to yield the two expected naphthofluoranthenequinones. This necessitates considerable revision of ~~the~~ von Braun's results. 4-o-carboxybenzoylfluoranthene is cyclised to yield the expected naphthofluoranthenequinone and the phthaloylfluoranthene neither of which corresponds to the compound obtained by the German Workers.

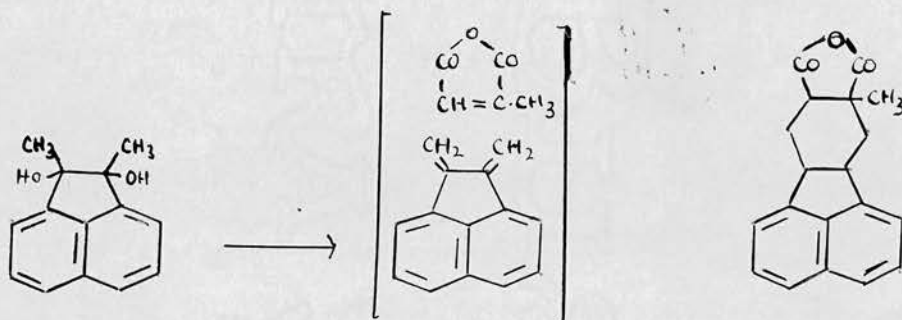
All four compounds are identical with those obtained by oxidation of the hydrocarbons prepared by the ~~Elbs~~ reaction on 4- & 12-toluoylfluoranthene (Reid).

The structure of 4 :5-phthaloylacenaphthene is shown by its conversion to 1:8- phthaloylnaphthalene.

Cyclisation of 1-o-carboxybenzoylnaphthalene by potassium iodide/hydrogen iodide yields a hydrogenated product which is dehydrogenated to 1:2- benzanthracene.

SECTION B.Attempted Diels-Alder Reactions with trans - 1:2-Dimethylacenaphthene quinoneglycol.

Trans - 1:2 - dimethylacenaphthenequinoneglycol was prepared by the method of Campbell & Gow, J.1949, 1555.

(1) Attempted condensation with Citraconic anhydride

(a) Trans-acenaphthenequinoneglycol (0.1 gm), citraconic anhydride (0.4 gm) and hydroquinone (.001 gm) were boiled for 30 minutes in acetic anhydride (3 ml). The solution turned orange. No crystallisation occurred on cooling. Addition of water resulted in the precipitation of an intractable amorphous powder, probably a polymer.

(b) On boiling overnight a thick intractable oil resulted.

(2) Attempted condensation with β -Benzoylacrylic acid

(a) Trans-acenaphthenequinoneglycol (0.1gm), X
 β -benzoylacrylic acid (0.4 gm) were boiled in acetic anhydride (2ml) for 2 hours. No product was isolated.

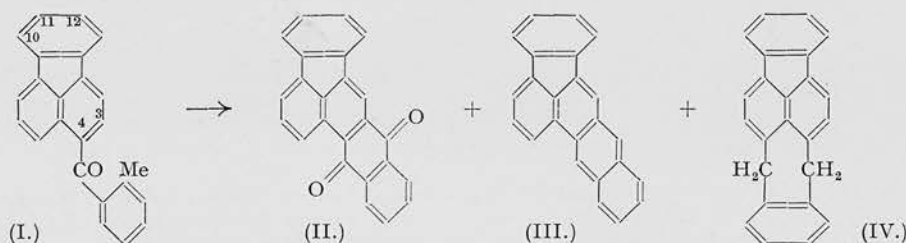
(b) The experiment was repeated adding the glycol portionwise and boiling for 30 minutes. On cooling

680. The Preparation of Some Naphthofluoranthenes and their Quinones.

By NEIL CAMPBELL, A. MARKS, and D. H. REID.

The syntheses of naphtho(2':3'-3:4)-, naphtho(2':3'-10:11)-, and naphtho(2':3'-11:12)-fluoranthenes and their quinones and of 4:5-phthaloylfluoranthene are described.

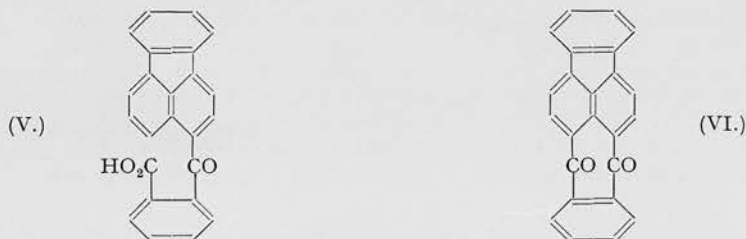
o-TOLUOYL chloride and fluoranthene with aluminium chloride yield a mixture of 4- and 11-*o*-toluoylfluoranthene, m. p. 115—116.5° and 148.5—150°, respectively (I and VII), each of which was subjected to the Elbs reaction. The first ketone gave three products: (1) an orange-coloured quinone which proved to be naphtho(2':3'-3:4)fluoranthene-1':4'-quinone (3:4-



phthaloylfluoranthene) (II) since it gave no m. p. depression with an authentic sample (Campbell and Wang, *J.*, 1949, 1513); (2) a yellow hydrocarbon, m. p. 229—230°, which was shown to be naphtho(2':3'-3:4)fluoranthene (III) since on oxidation it yielded the quinone (II); (3) a colourless hydrocarbon, m. p. 208—210°, which is presumably 4:5-*o*-xylylene-fluoranthene (IV) and whose skeleton structure follows from its oxidation to 4:5-phthaloylfluoranthene (VI). The isolation of the hydrocarbon (IV) and the quinone (II) serves to orientate the original ketone.

1:2-Benzanthracene and its quinone, but no 1:8-phthaloylnaphthalene derivatives, were isolated from the pyrolysis of 1-*o*-toluoylnaphthalene.

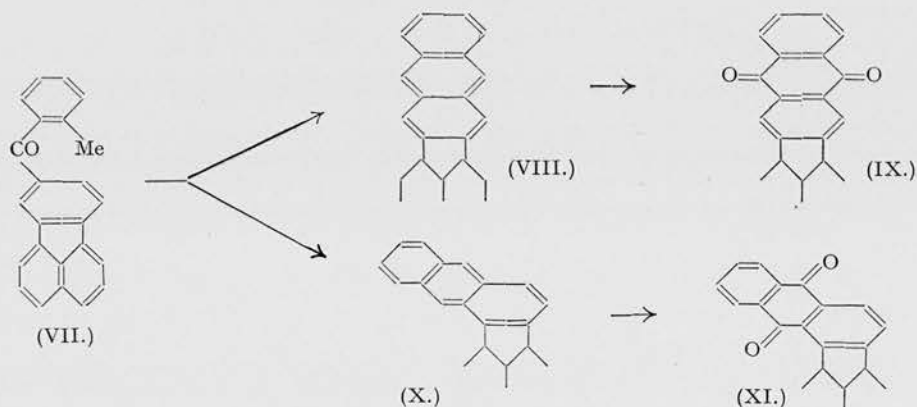
11-*o*-Toluoylfluoranthene (VII) on pyrolysis gave two isomeric hydrocarbons: (1) a yellow hydrocarbon, m. p. 301—303°, which was oxidised to the known naphtho(2':3'-11:12)fluoranthene-1':4'-quinone (IX) (Campbell and Gow, *J.*, 1949, 1555) and is therefore naphtho(2':3'-



11:12)fluoranthene (VIII)—the structure of the original ketone follows from this identification; (2) a red hydrocarbon, m. p. 225.5—227°, which must by elimination be naphtho(2':3'-10:11)-fluoranthene (X) and whose structure was confirmed by oxidation to the quinone (XI) (for preparation, see below).

4-Benzoylfluoranthene-2'-carboxylic acid (V) did not undergo ring-closure when heated in trichlorobenzene with toluene-*p*-sulphonyl chloride (cf. the 11-isomer described below), but did so when fused with aluminium chloride and sodium chloride and yielded two products: (1)

naphtho(2' : 3'-3 : 4)fluoranthene-1' : 4'-quinone (II) and (2) an isomeric compound, m. p. 296°, which gave a cherry-red colour with concentrated sulphuric acid and no vat with sodium dithionite. These facts are evidence that the substance is 4 : 5-phthaloylfluoranthene (VI). Now von Braun and Manz (*Annalen*, 1932, 496, 170) by the ring closure of the above acid obtained a substance, m. p. 328—331°, which they claimed to be the quinone (II), but which Campbell and Wang (*loc. cit.*) showed must have some other structure, and might be the 4 : 5-phthaloyl compound. This is now excluded by the preparation of this substance. It is impossible to say what von Braun and Manz's substance was, but they did not have the advantage of chromatography to aid them in their separations and purifications. As a result their 11-acid, for example, was impure with a m. p. 212° as compared to our product, m. p. 234°.



Pure 11-*o*-carboxybenzoylfluoranthene (cf. von Braun and Manz, *loc. cit.*; Campbell and Easton, *J.*, 1949, 340) was cyclised by boiling it with toluene-*p*-sulphonyl chloride in trichlorobenzene to give the two expected quinones : (1) a yellow-orange quinone, m. p. >335°, found to be identical with naphtho(2' : 3'-11 : 12)fluoranthene-1' : 4'-quinone (IX), and (2) a yellow isomer, m. p. 316°, which must be naphtho(2' : 3'-10 : 11)fluoranthene-1' : 4'-quinone (XI). We could detect no sign of the red substance, m. p. 228°, claimed by von Braun and Manz (*loc. cit.*) to be this quinone (cf. also G.P. 624,918; Friedländer, 1937, 21, 1189; Tschech.P., 56,604; *Centr.*, 1937, II, 2597).

It is unlikely that the quinones isolated from the Elbs products were formed during the pyrolysis for so far as we are aware quinones have not been thus obtained. They probably resulted from the oxidation of anthrones on the chromatographic columns used to purify the products. Control experiments showed that they were not produced by oxidation of the corresponding hydrocarbons on the column (cf. Levy and Campbell, *J.*, 1939, 1442).

Attempts to cyclise 4- and 11-benzoylfluoranthene-2'-carboxylic acids and 5-benzoylacenaphthene-2'-carboxylic acid by heating with potassium iodide and hydrogen iodide (Miescher and Billeter, *Helv. Chim. Acta*, 1939, 22, 601) failed, although 1-benzoylnaphthalene-2'-carboxylic acid yielded a hydrogenated product, which on chloranil dehydrogenation furnished 1 : 2-benzanthracene.

5-Benzoylacenaphthene-2'-carboxylic acid when fused with aluminium chloride gave 3 : 4-phthaloylacenaphthene whose structure was proved by oxidation to 4 : 5-phthaloylnaphthalic anhydride, decarboxylation of which afforded 1 : 8-phthaloylnaphthalene. We have thereby confirmed the structure of 3 : 4-phthaloylacenaphthene which Peters and Rowe (*J. Soc. Dyers Col.*, 1943, 59, 52) had advanced from a consideration of its synthesis and properties.

EXPERIMENTAL.

M. p.s were determined on the Kofler heating-stage microscope, and unless otherwise stated the fluorescence observations were made in the ultra-violet light of a Hanovia lamp. All chromatographic purifications were effected on alumina (Brockmann).

4- and 11-*o*-Toluoylfluoranthenes.—Fluoranthene and *o*-toluoyl chloride in carbon disulphide with aluminium chloride gave by the method of von Braun and Manz (*loc. cit.*) a 91% yield of mixed toluoylfluoranthenes. Partial separation was effected by passing a benzene solution through a column (40 g. of alumina per 1 g. of material) and development with benzene-light petroleum. Three lots of crystals were obtained, m. p.s 100—130°, 130—140°, and 140—155°. The first fraction on further chromato-

graphic purification gave complete separation into a lower and an upper yellow zone. The lower zone on elution with ethanol gave 4-toluoylfluoranthene, which was crystallised first from ethanol and then from benzene-light petroleum (b. p. 60–80°), forming yellow crystals, m. p. 115–116.5° (Found: C, 90.3; H, 5.1. C₂₄H₁₆O requires C, 90.0; H, 5.0%). The third fraction, m. p. 140–155°, on repeated crystallisation from ethanol or benzene-light petroleum afforded 11-toluoylfluoranthene, m. p. 148.5–150° (Found: C, 89.4; H, 5.0%). Both isomers gave with concentrated sulphuric acid an orange-green coloration in reflected and an orange colour in transmitted ultra-violet light.

Elbs Pyrolysis of 11-o-Toluoylfluoranthene.—The ketone (1.30 g.) was pyrolysed in an atmosphere of carbon dioxide at 440° as described by Fieser ("Organic Reactions," Vol. I, p. 129). The dark red product was dissolved in the minimum volume of benzene and passed through a column 40 × 1.3 cm. Development with benzene gave a lower yellow zone, an intermediate orange zone, and a top dark band. The orange zone gave a product, m. p. 190–220° (0.46 g.), which on crystallisation from benzene and then glacial acetic acid furnished compact red prisms of naphtho(2': 3'-10 : 11)fluoranthene, m. p. 225.5–227.5° (0.18 g., 15%) (Found: C, 95.4; H, 4.7. C₂₄H₁₄ requires C, 95.3; H, 4.7%). which has an orange fluorescence and gives a purplish-blue colour with concentrated sulphuric acid which becomes crimson when kept. Continued development of the column gave a buff-coloured band which was extracted with acetone. The top dark band was extracted with cold glacial acetic acid and the combined extracts gave naphtho(2': 3'-11 : 12)fluoranthene, which separated as a yellow powder from benzene-acetic acid, m. p. 301–303° (0.25 g., 20%) (Found: C, 95.1; H, 4.8%). The m. p. differs from those previously recorded, namely, 290–291° (von Braun and Manz, *loc. cit.*) and >310° (Campbell and Gow, *loc. cit.*). The hydrocarbon sublimes in yellow needles, fluoresces with a bright yellow colour, and in benzene or acetic acid has a strong bluish-green fluorescence in daylight. When heated with sulphuric acid it gives a pink colour, changing successively to brown, green, and brown. The hydrocarbon (50 mg.) in boiling acetic acid (10 c.c.) was oxidised by "AnalaR" chromic anhydride (70 mg.) in acetic acid (1 c.c.). The cooled solution deposited an orange-brown substance which was dissolved in chlorobenzene and passed through a column (20 × 1.2 cm.). Development with the same solvent gave an orange band, which was cut and extracted with chloroform. The extract yielded naphtho(2': 3'-11 : 12)fluoranthene-1': 4'-quinone (33 mg.), which crystallised in yellow needles from chlorobenzene, m. p. 338–340°, showing no depression when admixed with a sample prepared as below. It sublimes, gives a blue vat with sodium dithionite, and a blue colour with concentrated sulphuric acid, and has a dull golden-yellow fluorescence. The isomeric naphthofluoranthene (0.07 g.), m. p. 225.5–227.5°, when similarly oxidised, gave naphtho(2': 3'-10 : 11)fluoranthene-1': 4'-quinone (34 mg.), yellow needles (chlorobenzene), m. p. 316–318°, giving no depression with the quinone prepared as below. It sublimes, gives a purple coloration with sulphuric acid, gives no vat with sodium dithionite, and has a bright greenish-yellow fluorescence.

Pyrolyses of 4-o-Toluoylfluoranthene.—The ketone (1.00 g.) was pyrolysed for 30 minutes at 450° in carbon dioxide and the resulting solid was dissolved in benzene and passed through a column, 40 × 1.9 cm. Development with light petroleum-benzene (2 : 3 by vol.) gave (a) a bottom, colourless zone with a bright blue fluorescence, (b) a yellow zone, (c) an orange-pink zone with a green fluorescence, and (d) a top, reddish-black band. (a) This band gave a pale yellow solid, m. p. 80–150°, which was passed in benzene through a column, 25 × 1.3 cm., and was developed as above. When the whole column showed a blue fluorescence, it was cut, and the lower half extracted with acetone. Evaporation gave 4 : 5-oxylylenefluoranthene (0.03 g.), colourless crystals (light petroleum, b. p. 80–100°), m. p. 208–210° (Found: C, 94.3; H, 5.2. C₂₄H₁₆ requires C, 94.7; H, 5.3%). The hydrocarbon has a pale greenish-yellow fluorescence, and when heated with concentrated sulphuric acid gives a pink colour turning to brown. The hydrocarbon (30 mg.) was oxidised with chromic acid (60 mg.) in glacial acetic acid to 4 : 5-phthaloylfluoranthene, m. p. 285–287°, undepressed when mixed with the substance prepared as below. (b) The yellow band on elution gave a yellow solution with a strong blue fluorescence, and concentration of the solution afforded naphtho(2': 3'-3 : 4)fluoranthene (0.16 g.), m. p. 229–230° (Found: C, 94.9; H, 4.9%). It sublimes in yellow needles, and has a blue fluorescence in solution and a greenish-yellow fluorescence in the solid state. On oxidation with chromic anhydride in glacial acetic acid it gave the quinone, m. p. 250–253°, not depressed when admixed with Campbell and Wang's quinone (*loc. cit.*). (c and d) Continued development brought through a filtrate with a greenish-yellow fluorescence in daylight, from which nothing could be isolated, and then an orange-coloured filtrate. This was combined with the acetone eluate of the column and on evaporation gave naphtho(2': 3'-3 : 4)fluoranthene-1': 4'-quinone (3 : 4-phthaloylfluoranthene), orange crystals (benzene), m. p. 250–253°, undepressed with the above quinone; yield 0.025 g. It gave a blue vat with sodium dithionite and a green colour with concentrated sulphuric acid.

Pyrolysis of 1-o-Toluoylnaphthalene.—1-o-Toluoylnaphthalene (5 g.) was pyrolysed with zinc dust (1.4 g.) in carbon dioxide at 415° for 3 hours. The product was dissolved in benzene, and the filtered solution passed through a column, 50 × 2.3 cm. Development with benzene-light petroleum (b. p. 80–100°) (1 : 2 by vol.) gave a colourless bottom zone with a purple fluorescence, and an upper yellow layer with a blue fluorescence. Washing through the filtrates from both layers yielded 1 : 2-benzanthracene (1.98 g.), m. p. and mixed m. p. 160–161°. Development was continued with benzene and gave first a yellow filtrate with a strong yellowish-green fluorescence in daylight which deposited a small quantity of impure 1 : 2-benzanthraquinone. Finally, a deep golden-yellow filtrate without fluorescence in daylight was collected; it deposited on evaporation 1 : 2-benzanthraquinone (0.38 g.), m. p. 168–169°. It gave a green colour with concentrated sulphuric acid and an orange-red vat with sodium dithionite. The solid fluoresced with a dull scarlet-red colour. The pyrolysis was repeated at 440° without zinc dust and gave similar products but in different quantities, *i. e.*, 36% of hydrocarbon and 13% of quinone. No xylylenenaphthalene or derivative was detected in either experiment.

Ring-closure of 4- and 11-Benzoylfluoranthene-2'-carboxylic Acids.—Phthaloylation was best effected as follows. Fluoranthene (20 g.) in methylene chloride was added with stirring at room temperature to phthalic anhydride (16.3 g.) and aluminium chloride (33.4 g.) in methylene chloride (75 c.c.). Stirring

was continued overnight and the mixture was then decomposed with hydrochloric acid and ice. The solvent was removed by steam and the residue was extracted with potassium carbonate. Acidification yielded a mixture of acids (35 g.). The acids (25 g.) were dissolved in chloroform, concentration of which gave 11-benzoylfluoranthene-2'-carboxylic acid (13 g.), m. p. 234°, showing no depression when mixed with an authentic sample. Complete evaporation of the chloroform gave a residue which was esterified with methanol and sulphuric acid, and the esters separated chromatographically. The 4-ester (2.5 g.) thus obtained on hydrolysis gave the 4-acid, m. p. 230°, giving a m. p. depression when mixed with the 11-acid.

Pure 11-acid (3 g.) and toluene-*p*-sulphonyl chloride (1.65 g.) were boiled in trichlorobenzene (15 c.c.) for 1 hour. The cold solution deposited a solid which when washed with acetone afforded a mixture (1.7 g.) of yellowish-orange plates and yellow needles. The mixture (0.6 g.) was dissolved in chlorobenzene (400 ml.) and chromatographed on a column, 18 × $\frac{7}{8}$ in. Development with the same solvent gave a strongly orange adsorbed zone and a lower, yellow band. The orange zone on extraction gave naphtho-(2' : 3'-11 : 12)fluoranthene-1' : 4'-quinone, m. p. >335°, which gave a blue colour with concentrated sulphuric acid and a blue vat with sodium dithionite. The yellow band gave naphtho(2' : 3'-10 : 11)-fluoranthene-1' : 4'-quinone (10 : 11-phthaloylfluoranthene) (0.1 g.), yellow elongated plates, m. p. 319—320° (Found : C, 85.8; H, 3.7. C₂₄H₁₂O₂ requires C, 86.7; H, 3.6%). It gave a red colour with concentrated sulphuric acid and no vat with sodium dithionite. A mixture of the two quinones was separated by sodium dithionite and indicated that the 11 : 12-quinone and the 10 : 11-quinone are formed approximately in the ratio 5 : 1.

Pure 4-benzoylfluoranthene-2'-carboxylic acid (1.1 g.), aluminium chloride (3.3 g.), and sodium chloride (2.75 g.) were intimately mixed and heated in an oil-bath the temperature of which was raised to 140° during 30 minutes. Nitrogen was passed through at this temperature for 3 hours. The product was decomposed with ice and hydrochloric acid and the black solid was then extracted with 5% sodium carbonate and dried. The dry product was extracted with benzene, and the benzene concentrate chromatographed on a column 12 × $\frac{3}{4}$ in. Development with benzene gave a yellow zone which quickly passed down the column. The filtrate on evaporation furnished a solid (20 mg.) which crystallised from chlorobenzene in yellow-orange prisms, m. p. 252—253° with sublimation, and was proved to be naphtho-(2' : 3'-3 : 4)fluoranthene-1' : 4'-quinone (Campbell and Wang, *loc. cit.*). It gave a bluish-green colour with concentrated sulphuric acid and a bluish-violet vat with alkaline sodium dithionite. Further development of the column gave a deep yellow zone below the top dark band. The column was cut and the yellow zone eluted with chloroform which on evaporation gave 4 : 5-phthaloylfluoranthene, yellow elongated prisms (chlorobenzene), m. p. 296—297° (Found : C, 86.3; H, 3.6. C₂₄H₁₂O₂ requires C, 86.7; H, 3.6%). It gave a red colour with concentrated sulphuric acid and no vat with alkaline dithionite.

3 : 4-Phthaloylacenaphthene.—Crude 3 : 4-phthaloylacenaphthene (Peters and Rowe, *loc. cit.*) (3.5 g.) was purified by passing a benzene solution down a column, 17 × $\frac{3}{4}$ in., and development with benzene-light petroleum (b. p. 60—80°) (4 : 1 by vol.). A yellow zone separated and afforded on elution 3 : 4-phthaloylacenaphthene (1.3 g.), yellow elongated prisms (ethanol), m. p. 196—197° (lit., 194—195°) (Found : C, 84.5; H, 4.5. Calc. for C₂₀H₁₂O₂ : C, 84.5; H, 4.2%). The phthaloylacenaphthene was oxidised by chromic anhydride ("AnalaR") and glacial acetic acid to 4 : 5-phthaloyl-1 : 8-naphthalic anhydride which, after purification by being washed successively with ethanol, water, and glacial acetic acid, was isolated as bright yellow needles, m. p. >310° (lit., 368°) (Found : C, 73.2; H, 2.4. Calc. for C₂₀H₈O₅ : C, 73.2; H, 2.3%). The anhydride (0.75 g.), water (20 c.c.), and mercuric oxide, freshly prepared from mercuric acetate (1.5 g.), were heated in a sealed tube at 250° for 4 hours. The product was refluxed with concentrated hydrochloric acid for 2 hours, washed with water, and dried. The dry material (1.1 g.) was extracted with benzene, and the benzene extract passed through a column, 6 × $\frac{1}{2}$ in. A pale yellow zone separated, below which was a band with a bright yellow fluorescence. Both zones yielded 1 : 8-phthaloylnaphthalene, colourless needles (ethanol-acetic acid), m. p. 176—177° (lit., 178°), yield 0.30 g. (Found : C, 83.6; H, 4.1. Calc. for C₁₈H₁₀O₂ : C, 83.7; H, 3.9%). In concentrated sulphuric acid it gave a yellow solution with a green fluorescence. No colours were obtained with zinc and ammonia or alkaline sodium dithionite.

Ring-closure of 1-Benzoylnaphthalene-2'-carboxylic Acid.—The acid (4.6 g.), potassium iodide (5.5 g.), red phosphorus (1.5 g.), and phosphoric acid (20 ml.) were refluxed for 4 hours. Water was added, and the residue extracted with ethanol. Evaporation gave a solid (2.0 g.), which was dissolved in the minimum volume of benzene and passed through a column, 14 × 0.75 in. Development with the same solvent gave a bottom zone with a bright purple fluorescence which gave 0.6 g. of a solid, m. p. 112—120° after crystallisation from glacial acetic acid, and a yellow zone which afforded a solid, m. p. 138—145° (0.9 g.) after crystallisation from acetic acid. The second substance (0.75 g.) in benzene was passed through a column, 9.5 × 0.45 in., and a yellow zone which separated yielded a substance, m. p. 146—150° (0.65 g.) after crystallisation from acetic acid. Dehydrogenation with chloranil in xylene (3 hours) gave 1 : 2-benzanthracene, m. p. and mixed m. p. 156° (lit., 158°) (Found : C, 94.2; H, 5.3. Calc. for C₁₈H₁₂ : C, 94.7; H, 5.3%).

Thanks are expressed to the Carnegie Trust for the Universities of Scotland for the award of a scholarship to one of us (D. H. R.), and to the Anglo-Iranian Oil Company Limited for a grant.

THE UNIVERSITY OF EDINBURGH.

[Received, August 24th, 1950.]

elongated crimson prisms crystallised.

Yield 0.04 gm.

Analysis For α -11-benzoylfluoranthene - 12 - Carboxylic acid.

Req. C 81.3 H 5.1

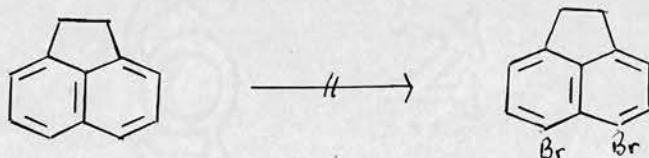
Fd. C 76.1 H 4.0

von Pechman Ber. 1882, 15, 886 (C H O
10 6 2)2

Req. C 76.0 H. 3.8

Analysis indicated that polymerisation of the β -benzoylacrylic acid was taking place in preference to the Diels-Alder reaction.

Attempted preparations of 5:6- Dibromoacenaphthene



Dashevskii & Karishin C.A. 32, 1975

(1) Acenaphthene (20 gm) was dissolved in 75% alcohol while bromine (21.3 m.) was blown in (air and nitrogen). The solution was kept in the water bath during this addition and for a further 30 minutes when it was poured into water. The resulting dark oil was extracted with ether, the extract washed and dried and the solvent removed.

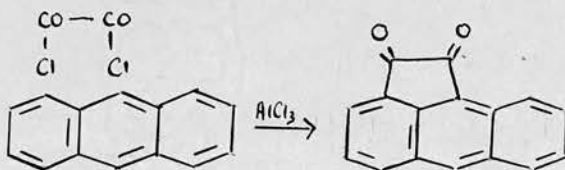
Further work required.

Distillation at 25 m.m. resulted in immediate decomposition with copious evolution of hydrogen bromide to give a dark intractable glass.

(2) Acenaphthene (10 gm) was dissolved in nitrobenzene at room temperature and bromine (10.6 ml) was added dropwise with stirring. A very vigorous evolution of hydrogen bromide occurred and the reaction appeared completed in a very short time. The nitrobenzene was removed by steam distillation, and the golden yellow semi-solid obtained, on trituration with ether, gave a pale yellow solid (4.5 gm, m.p. $172^{\circ}-6^{\circ}$) The ether deposited further solid material on standing (1.4 gm).

Crystallisation from glacial acetic acid yielded long slender needles, m.p. 178° , with decomposition and liberation of hydrogen bromide.

This material appeared to be the dibromoacenaphthenetetrabromide of Mayer & Kaufmann (Ber. 53, 289) though the orange needles (benzene) obtained by boiling it for 30 minutes with concentrated alcoholic potash melted at $170^{\circ}-1^{\circ}$ (Lit 180°).

Preparation of Aceanthraquinone

Liebermann. Ber. 1911, 44, 208.

From anthracene (16 gm) and oxalyl chloride (40 gm) was obtained a dark product (17 gm) after extraction of anthroic acid. This crude product was extracted with hot chlorobenzene, the filtrate yielding, on cooling, crimson prisms of aceanthraquinone (8.5 gm) m.p. 268° - 70° (Lit 270°) It gave a green colour with concentrated sulphuric acid.

Very condensed with Sulphur

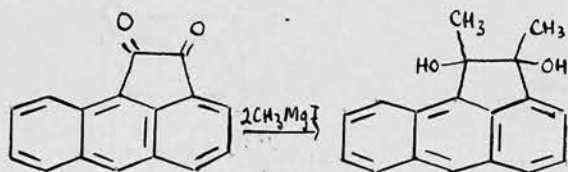
The dark residue (4.0 gm) from the chlorobenzene extraction showed no signs of melting even at 330° .

Crystallisation of aceanthraquinone from an "aged" sample of tetralin yielded pale orange prisms m.p. 285° - 6° which gave a red colour with concentrated sulphuric acid. Melting point, colour test, and analysis showed it to be anthracene 1:9-dicarboxylic acid anhydride.

very - yellow? what about purified tetralin? has done

Calc. for.	C	H	O	C	77.4	H	3.2
					16	8	3

Found.	C	76.4	H	3.4
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Preparation of 1:2-Dimethylaceanthracene-1:2-diol.

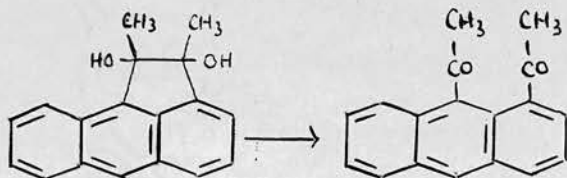
To a well stirred mixture of magnesium turnings (0.84 gm) in dry ether (10 ml) was added, dropwise, methyl iodide (5.0 gm) in dry ether (20 ml). When the formation of the Grignard reagent was complete, aceanthraquinone (2.0 gm) was added portionwise, visible signs of reaction occurring with each addition. The mixture was then boiled for 4 hours and left overnight. After decomposition with ice and hydrochloric acid the ether was removed and the yellow product filtered off.

Yield 2.1 gm (crude)

Crystallisation from alcohol yielded pale yellow needles m.p. $230^{\circ} - 1^{\circ}$, which both in solid state and solution showed a violet fluorescence in the u.v.

Analysis. C H O req. C 81.8 H 6.1
18 16 2

Found. C 81.1 H 5.9

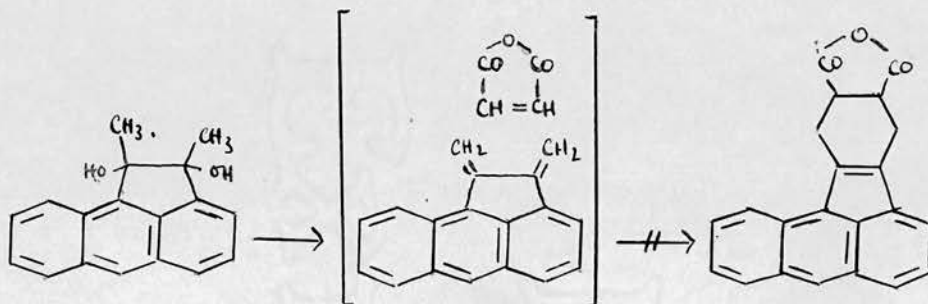
Preparation of 1:9- Diacetylanthracene

~~Aceanthraquinone~~ glycol (0.5 gm) was suspended in dry benzene (100 ml) and dry lead tetraacetate (1.0 gm), (10% xs) was added. Excess of lead tetraacetate was show by starch- iodide paper. A flocculent precipitate appeared but after 15 minutes standing and shaking, a few drops of ethylene glycol were added to remove the excess reagent. The flocculent precipitate disappeared leaving a clear golden brown solution which was shaken with water (10ml), separated and dried. The solvent was removed and the residue was taken up in acetone, filtered, and water added until crystallisation occurred. Yellow needles m.p. 154° - 5°.

A second crystallisation for analysis raised the m.p. 156° - 7°.

Analysis	C	H	O	req.	C	82.4	H	5.3
	18	14	2					

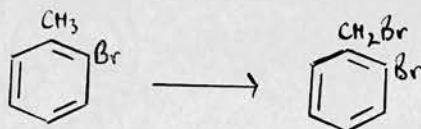
Found. C 81.6 H 5.5

Attempted Diels-Alder Reactions.

(1) Aceanthraquinoneglycol (0.1 gm) , and maleic anhydride (0.4 gm) were boiled in acetic anhydride (2ml). No adduct was isolated.

(2) The reaction was repeated in nitrobenzene as solvent . No aduct was obtained.

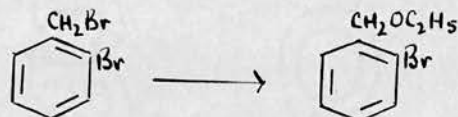
(3) The reaction was repeated in a sealed tube at 150° . A dark intractable mass resulted.

SECTION C.Preparation of o-Bromobenzylbromide

Jackson. J.A.C.S. 1880,1 , 101

Bromine (32 ml) was airblown into boiling o-bromotoluene (100 gm). When all the bromine had been added the dark solution was fractionated under reduced pressure.

The yield of highly lachrymatory o-bromobenzylbromide was 84 gm b.p. $134^{\circ} - 40^{\circ} / 20$ mm.

Preparation of o-bromobenzylethylether

Blicke & Weinkauff. JACS. 1932, 54,

o-Bromobenzylbromide (84 gm) was heated for 2 hours on the steam bath with sodium ethoxide (absolute alcohol 200 ml and sodium 10 .0 gm) . The sodium bromide was filtered off and the alcoholic solution was poured into water. The resulting oil was fractionated under reduced pressure.

Yield 60 gm b.p. $126^{\circ} - 7^{\circ} / 27$ mm.

When this ethylether was added to a well stirred mixture of magnesium turnings in dry ether, no reaction occurred. The addition of a little methylmagnesium iodide appeared to start a reaction which

soon slowed down and finally stopped. Fresh addition of the bromo compound had no effect nor had boiling. The metal lost its lustre and was obviously coated and sticky.

Preparation of o-Bromotoluenediacetate

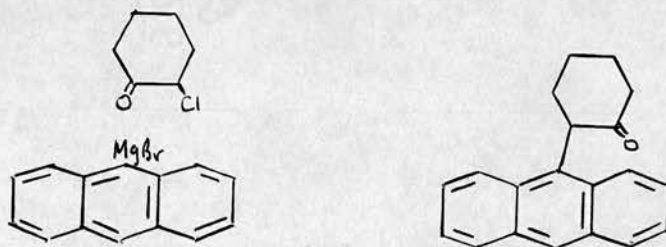
Brady et.al. J. 1925,2429.

Acetic anhydride (40 gm), acetic acid (30 gm), concentrated sulphuric acid (15 gm) and o-bromo-toluene (5 gm) were mixed carefully in that order, and the mixture cooled to 0° . Chromic oxide (10 gm) in acetic acid (30 gm) was slowly added so that the temperature remained below 10° . After 30 minutes the mixture was poured onto ice. Water was added to precipitate the diacetate which was crystallised from alcohol.

Yield 2 gm.

Grignard formation did not occur with this derivative.

Attempted reaction of 2- Chlorocyclohexanone with 9- anthrylmagnesiumbromide



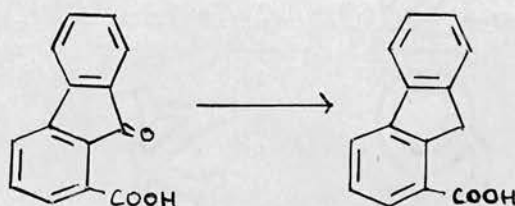
A Grignard reagent was prepared from 9-bromoanthracene (2.57 gm) by the method of Bachmann & Kloetzel, J. Org. Chem. 1939,3,55.

To the cold reagent in ether was added 2-chloro-cyclohexanone (0.7 gm) and after 4 hours the mixture was decomposed with ice and hydrochloric acid.

No product other than anthracene was observed.

The reaction with cyclohexanone was similar.

Preparation of Fluorene-1-carboxylic acid.



Bergmann & Orchin J.A.C.S. 1949, 71, 1111.

Fluorenone -1-carboxylic acid (5.5 gm) was reduced by the modified Wolff-Kishner method.

Yield 4.5 gm m.p. 247° - 9°

Attempted Friedel - Crafts Reactions, with Fluorene-1 Carboxylic acid chloride and benzene

(1) Benzene as solvent

(a) Fluorene-1-carboxylic acid (2 gm) was boiled with thionyl chloride, the excess of which was removed in vacuo. Traces of the reagent were removed by repeated distillation with benzene.

To the acid chloride residue was added dry benzene (10 ml) and then powdered anhydrous aluminium chloride (1.4 gm) , portionwise with stirring. The mixture was left overnight, decomposed with ice and hydrochloric acid and filtered.

The benzene layer was separated, extracted with carbonate, washed and dried. Removal of the solvent yielded a small amount of a viscous oil which was not investigated.

(b) Rep^etitition of the experiment with the reactants maintained at 50° for 4 hours yielded only dark intractable material.

(2) Tetrachloroethane as solvent

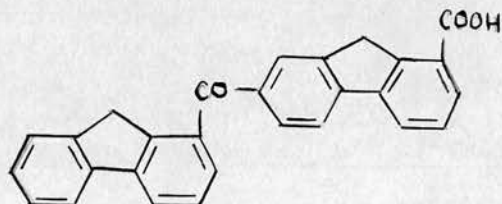
To the reactants was added tetrachloroethane (30 ml). After standing overnight the dark red gel was decomposed as before and the solvent was removed with steam.

A small quantity of a product crystallising from benzene in pale yellow needles, m.p. 182° - 4°, was obtained and this was analysed for 1-benzoyl-fluorene.

Analysis. C H O req C 88.9 H 5.2
20 14

Found. C 83.8 H 4.4

Analysis suggested a condensation product of the acid chloride with itself, probably in the 7-position.



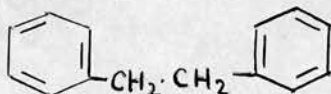
C H O req. C 83.4 H 4.5
28 18 3

(3) Ethylendichloride as solvent

A solution of fluorene -1-carboxylic acid chloride (from 2 gm acid) in ethylendichloride (20 ml) was added dropwise to a well stirred mixture of powdered anhydrous aluminium chloride (2.7 gm), drybenzene (5ml), and ethylendichloride (5 ml). The solution warmed slightly and there separated a thick brownish red precipitate which redissolved after 30 minutes. There was a vigorous evolution of hydrogen chloride. Stirring was continued for 2 hours and the mixture left overnight. After decomposition with ice and hydrochloric acid the solvent was removed with steam. The residual oil was taken up in benzene, shaken with carbonate, washed and dried. The solvent was removed and the residue distilled in vacuo.

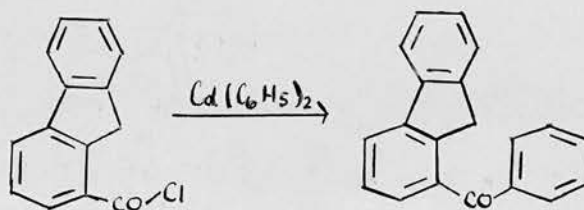
Two fractions resulted.

(1) A white crystalline solid distilled up to 250 (bath) /0.05 mm, m.p. $50^{\circ} - 1^{\circ}$. This compound was dibenzyl (m.p. & m.m.p. with authentic sample),



The solvent had, therefore, reacted with the benzene.

(2) The rest of the material distilled as an oil which, even after chromatographic purification, yielded no solid.

Preparation of 1-Benzoylfluorene

A Grignard reagent was made from magnesium turning (1.8 gm) and bromobenzene (10 ml) in dry ether (50 ml). When the formation of the Grignard reagent was complete, anhydrous cadmium chloride (7 gm) was added portionwise to the well stirred, cold, mixture. When a Michler's ketone test (Gilman, J.A.C.S. 1925, 47 2002) showed the absence of Grignard reagent the ether was distilled off and replaced with dry benzene (20 ml). The acid chloride of fluorene-1-carboxylic acid (2 gm) was dissolved in dry benzene and added dropwise to the benzene solution of the organocadmium compound. The mixture was boiled 4 hours on the water bath and left overnight. After decomposition with ice and hydrochloric acid the benzene layer was separated, washed with carbonate, then water, and dried. The solvent was removed and the residual pale yellow oil, when triturated with light petroleum, yielded a white solid.

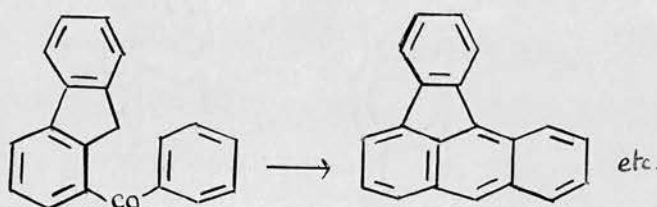
Yield 1.9 gm m.p. $35^\circ - 7^\circ$ (76%)

Crystallisation from methanol yielded glistening white plates m.p. $90^{\circ}1'$

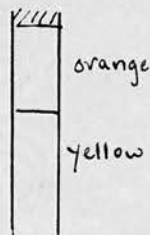
Analysis	C	H	O	req	C	88.9	H	5.2
	20	14						
				Found.	C	88.4	H	5.1

A dinitrophenylhydrazone could not be prepared.

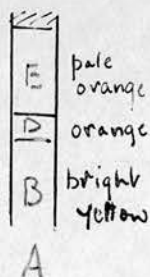
The Elbs pyrolysis of 1-benzoylfluorene



1-Benzoylfluorene (3.0 gm) was pyrolysed at 420° in an atmosphere of carbon dioxide, for 15 minutes, during which time the characteristic effervescence occurred. The reddish brown residue was dissolved in benzene and chromatographed on a column $36'' \times 1''$. The brownish yellow fluorescent solution was adsorbed as shown.



After some development with benzene the column appeared as in diagram.



Fractions were taken as follows.

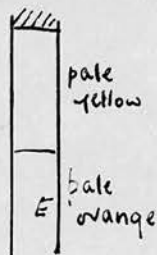
(A) The forerun to the bright yellow band. No material was isolated.

(B) The bright yellow band which separated from the orange band as development proceeded.

From this band was obtained a pale yellowish solid (0.75 gm) m.p. $140^{\circ} - 200^{\circ}$.

(C) Cut to the orange band. No material was isolated.

(D) The orange band. The eluate was orange with a yellow green fluorescence. Removal of the solvent yielded an oil which on trituration with methanol/light petroleum gave a solid (0.4 gm) which was obviously a mixture of colorless, yellow, and reddish materials. The column then appeared.



(E) The oily solid from this band was triturated with methanol and filtered.

Yield 0.8 gm m.p. (Micro)
 $80^{\circ} - 5^{\circ}$

Under the microscope this material appeared to be a mixture of orange and colorless material.

(F) The alcohol washings of the column yielded no quantity of solid.

Total recovery from the column was 1.95 gm.

Fractions B, D, & E were recollected separately.

Fraction B. The yellowish white material when crystallised from methanol/light petroleum yielded an obvious mixture of yellow prisms and small white prisms. No separation was obtained on recolumning.

The mixture was separated as follows. By boiling with light petroleum (60° - 80°) the yellow material dissolved leaving the colorless solid which was taken up in a small volume of chlorobenzene. Addition of light petroleum until a turbidity in the hot was obtained yielded small colorless prisms m.p. 232° - 3°.

Analysis for 2:3-benzofluoranthene.

C	H	req	C	95.2	H	4.8
20	12					

Found. C	92.2	H	4.8
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Though a molecular weight determination was not carried out this analysis yielded an empirical formula of $\begin{matrix} 6 & H & 0, \\ 40 & 24 \end{matrix}$ which suggested a molecule built up from 2 benzofluoranthene residues but containing oxygens. This colorless solid did not form a picrate. e/

The light petroleum filtrate was evaporated and the residue treated with picric acid in benzene. Deep red needles resulted. Decomposition of this picrate with ammonia yielded a yellow solid crystallising from aqueous methanol in golden prisms m.p. 144° - 5°.

It was slowly soluble in concentrated sulphuric acid giving a dark reflecting yellow solution.

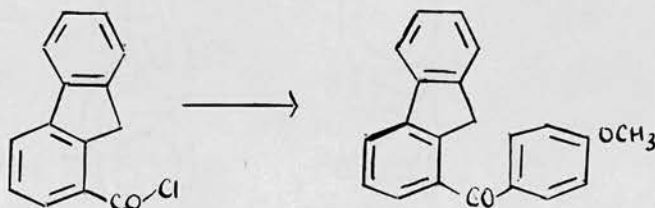
Analysis for 2:3- benzofluoranthene

C	H	req	C	95.2	H	4.8
20	12					
			Found. C	94.3	H	4.9

Because of the low yield the method was abandoned.

Recolumning of fractions D & E. did not lead to any separation and they were not investigated further.

Preparation of 1-(p-methoxybenzoyl)fluorene.



Fluorene -1-carboxylic acid chloride (from 2 gm acid) was dissolved in the minimum of anisole at room temperature and powdered anhydrous aluminium chloride (2.7 gm) was added. The mixture was stirred for 2 hours and left overnight. The colour darkened in the course of the reaction from a golden yellow to a dark reddish brown. After decomposition with ice and hydrochloric acid the excess solvent was removed with steam. An oil was obtained, setting solid on cooling.

Crystallisation from alcohol yielded clusters of colorless prisms m.p. $104^{\circ} - 5^{\circ}$, yield 1.9 gm.

Analysis	C	H	O	req.	C	84.0	H	5.0
	21	16	2					
				Found.	C	82.7	H	5.6

Preparation of o-Chlorobromobenzene

Org. Synth. 24,22

o-Chlorobromobenzene was prepared by treating small o-chlorobenzenediazonium bromide with cuprous bromide. The yield from 127 gm o-chloraniline was 165 gm o-chlorobromobenzene.

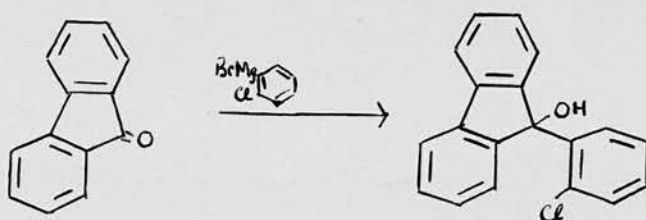
Reaction of o-Chlorophenylmagnesium bromide with anthrone

A Grignard reagent was made from magnesium turnings (0.7 gm) and o-chlorobromobenzene (5.86 gm) in dry ether (50 ml). When the formation of the Grignard reagent was complete, anthrone (2 gm), suspended in dry benzene (20 ml) was added portionwise with vigorous stirring. The first few additions resulted in an intense cherry red colour with a blue fluorescence, which faded to a pale yellow while still retaining a blue fluorescence. When all the anthrone had been added, the mixture was boiled for 1 hour during which time a small amount of a yellow flocculent precipitate separated.

The mixture was cooled and decomposed with iced ammonium chloride. The organic layer was separated

filtered, washed and dried and the solvent removed. Trituration of the residual oil, with methanol, yielded a pale yellow solid, 1.2 gm.

It crystallised from alcohol/benzene in pale yellow prisms m.p. 285° (micro) with rapid sublimation. The material contained no chlorine and gave a red colour with zinc dust and caustic soda. This colour test and m.m.p. with an authentic sample showed it to be anthraquinone. Preparation of 9-o-Chlorophenylfluorene-9-ol.



*Quantity?
(3.5g)*

o-Chlorobromobenzene (29.3 gm) in dry ether (80 ml) was added dropwise with stirring to magnesium turnings in dry ether (20 ml). Fluorenone (9 gm) was dissolved in the minimum of dry benzene and dry ether (50 ml) was added. This solution was then added dropwise with stirring to the Grignard Reagent, when an orange yellow colour resulted on each addition. After all the fluorenone had been added the mixture was boiled on the steam bath for 1 hour. A small amount of white precipitate separated from the pale yellow ethereal solution during this hour.

After decomposition with ice and dilute hydrochloric acid, the ether layer was separated, washed and dried.

Removal of the solvent gave an oil, which on trituration, with light petroleum, yielded the required product.

Yield 11 gm (75%)

Crystallisation from methanol gave colorless plates turning opaque at 60° and melting $138^{\circ} - 40^{\circ}$.

A second crystallisation raised the m.p. to $140^{\circ} - 1^{\circ}$ Dried at 80° for analyses.

C	H	O	Cl	req.	C	H	Cl
19	13				77.9	4.4	12.1

Found C	H	Cl
78.6	4.4	11.6

The carbinol showed a pale helio fluorescence in the u.v. and gave a wine red colour with concentrated sulphuric acid.

From the light petroleum mother liquors was obtained a thick oil not investigated further.

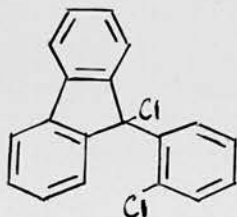
On one occasion the yield was 82%.

Derivative

On warming the carbinol with a little acetyl chloride a vigorous reaction occurred and white prisms were deposited m.p. $143^{\circ} - 4^{\circ}$ M.m.p. with the carbonal $120^{\circ} - .$

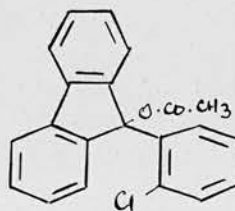
Crystallisation from alcohol/ acetic acid to which 1 drop of water is added yielded colorless prisms m.p. 145° A red colour was obtained with concentrated sulphuric acid.

Analysis There are two possibilities (cf triphenylcarbanol).



C H Cl 2 req. Cl 22.6
19 12 2

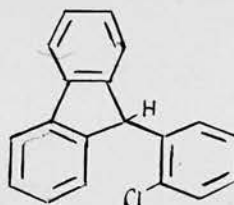
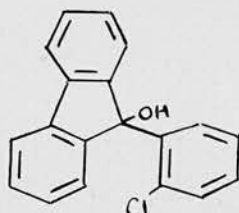
(cf triphenylmethylchloride)



C H O Cl req Cl 10.4
21 15 2

Found Cl 11.4

Preparation of 9-o-Chlorophenylfluorene



9-o-Chlorophenylfluorene-9-ol (17.8 gm) was boiled for 3 hours with lightly amalgamated zinc dust (9 gm) and zinc metal (18 gm) in acetic acid (500 ml) and concentrated hydrochloric acid (100 ml) . At the start of the reaction there appeared a yellow colour which eventually disappeared to yield a clear solution. Concentration of this clear solution yielded globules of oil which crystallised on cooling and scratching.

Colorless prisms m.p. 75° - 6°.

A second crop was obtained on further concentration.
m.p. 74° - 6°.

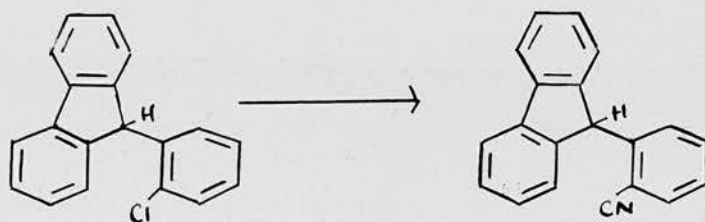
Total yield 14 . 5 gm (85%)

The chlorohydrocarbon crystallised from methanol in colorless prisms m.p. $76^{\circ} - 7^{\circ}$, insoluble in concentrated sulphuric acid.

Analysis C H Cl req C 82.4 H 4.7 Cl 12.8
19 13

Found C 82.0 H 4.8 Cl. 4.7

Attempted preparations of o-(9-Fluorenyl)benzonitrile



(1) Boiling with cuprous cyanide in pyridine led only to the recovery of unreacted starting material.

(2) Fusing with cuprous cyanide in oil bath yielded no product.

(3) Heating with cuprous cyanide in quinoline for 8 hours at 250° in a sealed tube yielded only a dark intractable product.

(4) Heating with cuprous cyanide (no solvent), with the addition of catalytic quantities of copper sulphate and tolunitrile in a sealed tube at 250° led to no recognisable product.

Preparation of o-(9-Fluorenyl)benzotrile.First Method

9-o-Chlorophenylfluorene (0.5 gm) , dry cuprous cyanide (0.5 gm), copper sulphate and toluenitrile (small spatula) and dry pyridine (1 ml) were heated in a sealed tube for 20 hours at 230. The mixture was poured into dilute acid and extracted with benzene. The benzene layer was washed with ammonia, water, acid and water and then dried. The concentrate was chromatographed on a column 140 cm x 12 cm and developed with benzene. m/

After some developpment the column appeared as below.



Fraction 1. Removal of the solvent yielded a small quantity of oily solid too small to be investigated further.

Fraction 2. The eluate of the pale helio band showed a weak violet fluorescence in the u.v. and yielded a colorless solid (0.2 gm)m.p.104° -110°

Crystallisation from light petroleum (80° - 100°) raised the m.p. to 114° - 5° The product gave a blue green colour with concentrated sulphuric acid. It contained nitrogen and analysed for the required nitrile(see next experiment)

Fraction 3 The column was cut and the upper band eluted with chloroform. Removal of the solvent yielded a colorless solid (0.15 Gm) m.p.(crude) $125^{\circ} - 30^{\circ}$. It crystallised from light petroleum (120°) in colorless prisms m.p. $142^{\circ} - 3^{\circ}$. This product also contained nitrogen and analysed for the amide (see next experiment).

Second Method.

9-o-Chlorophenylfluorene (5.5 gm), dry cuprous cyanide (5.5 gm) and dry pyridine (10 ml) were heated in sealed tube for 24 hours at 230° . The product was treated as above.

Fraction 1. The deep violet band. The eluate had a bright blue fluorescence in the u.v. and yielded unreacted 9-o-chlorophenylfluorene (0.6 gm).

Fraction 2. The pale helio band yielded a solid (2.6 gm) which crystallised from light petroleum ($80^{\circ} - 100^{\circ}$) in rosettes of colorless short prisms m.p. $112^{\circ} - 4^{\circ}$. The solid showed no fluorescence in the u.v. though the solution showed a weak violet.

With concentrated sulphuric acid, on standing the colour changed from red - violet- blue- blue green where it remained.

A second crystallisation raised the m.p. to $115^{\circ} - 6^{\circ}$.

Analysis. (for nitrile)

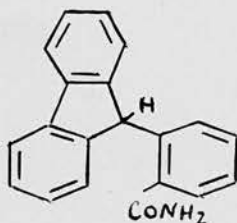
C	H	N	req	C	89.9	H	4.9	N	5.2
20	13								

Found	C	90.0	H	4.9	N	5.2
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The yield of nitrile was therefore 51%.

Fraction 3. The upper violet band yielded a colorless solid (0.65 gm) which crystallised from light petroleum (120°)/benzene in long slender elongated prisms m.p. 142° - 3°. It was immediately soluble in concentrated sulphuric acid to yield a pale helio colour.

Analysis (for the amide)



C	H	NO	req.	C	84.2	H	5.0	N	5.0
20	15								

Found.	C	84.5	H	5.3	N	4.9
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From a run of chlorocompound (14.5 gm) and cuprous cyanide (6.5 gm), (1.2 M) the nitrile (8 gm) was obtained in 56% yield.

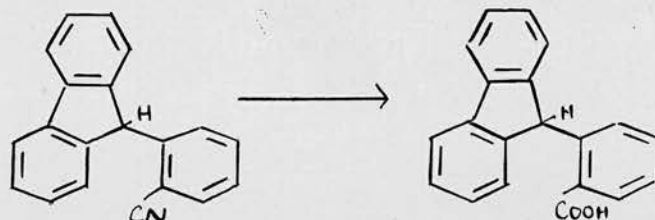
Third Method.

9-o-Chlorophenylfluorene (12.3 gm) , cuprous cyanide (6 gm) , pyridine (15 ml) and acetonitrile (1.5 ml) were heated in a sealed tube for 24 hours at 240° .

The yield of nitrile was 7.5 gm (70%).

(Recovered chlorocompound 1.2 gm; amide 0.2 gm).

Preparation of o-(9-Fluorenyl)benzoic acid.



(1) o-(9-Fluorenyl)benzonitrile (5.0 gm), acetic acid (25ml), concentrated sulphuric acid (12.2 ml) and water (12.2 ml) were boiled for 24 hours. The acid precipitated from this mixture. At the end of the boiling the mixture was poured into dilute acid and extracted with ether. The required acid was obtained by carbonate extraction of the ether extract.

Yield(crude) 3.8 gm) 74%)

Crystallisation from acetic acid (charcoal) yielded colorless plates m.p. 239° - 40° (Lit 242°).

Recrystallised for analysis m.p. 242° - 3°

Analysis. Calc. for C H O C 83.9 H 4.9
20 14 2

Found.C 82.7 H 4.9

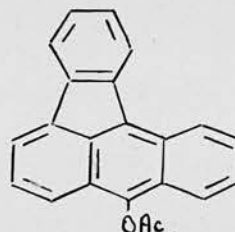
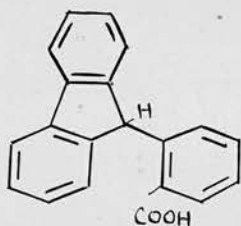
The acid gave a red colour with concentrated sulphuric acid.

(2) *o*-(9-Fluorenyl)benzonitrile (9.3 gm), caustic soda (3.6 gm), water (9 ml) and ethylene glycol (36 ml) were boiled for 24 hours. The clear solution was diluted with water and acidified. *o*-(9-fluorenyl) benzoic acid separated.

Yield 8.8 gm (crude) 88%

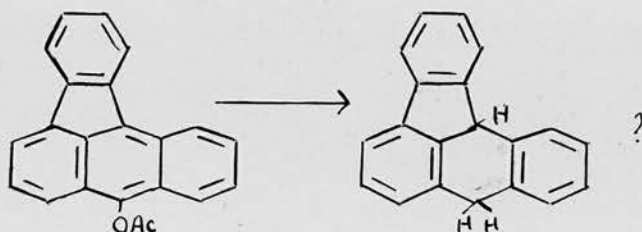
It crystallised from acetic acid in colorless plates m.p. $241^{\circ} - 2^{\circ}$

Preparation of 2:3-Benzofluoranthene .



cf Fieser and Gason J.A.C.S. 1940,62,432.

o-(9-Fluorenyl)benzoic acid (1 gm), acetic acid (6 ml), acetic anhydride (5 ml) and a trace of zinc chloride were boiled for 2 hours. The solution turned yellow with a strong green fluorescence. Water was added to the hot solution until crystallisation occurred. The fluffy orange material (0.95 gm) m.p. $215^{\circ} - 24^{\circ}$ which resulted, did not look pure under the microscope. It contained some colorless material.



The acetate was reduced by the method of Martin (J.A.C.S.)(1936, 58, 1438).

The zinc dust (1.5 gm) was shaken with 0.1% copper sulphate solution for a few minutes. The solution was then decanted from the zinc and to the residue was added caustic soda(30 ml), toluene (10 ml), and finally the crude acetate (0.9 gm). The mixture was boiled for 22 hours.

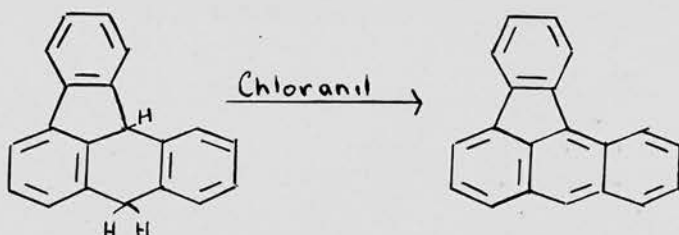
The orange yellow toluene layer assumed a strong green fluorescence. After 4 hours boiling the fluorescence disappeared and the toluene layer paled. After 22 hours the toluene was colorless but as the solution cooled the yellow colour and green fluorescence returned. Benzene was added and the organic layer was separated and washed. The dry concentrate was then chromatographed and the greenish yellow band which separated was eluted. The solvent was removed and the residue (0.25 gm) was crystallised from light petroleum. There resulted a mixture of orange and colorless prisms, some of which were separated mechanically.

The orange material, m.p. $144^{\circ} - 5^{\circ}$ was 2:3- benzo-

fluoranthene identical in m.p. and mixed m.p. with the product obtained in the Elbs reactio of 1-benzoylfluorene.

The colorless material m.p. $139^{\circ} - 40^{\circ}$ therefore was assumed to be the corresponding dihydro compound, since it had already been noted that dihydroanthracene was partially dehydrogenated on a column. (experimental p 85)

Dehydrogenation



The mixture (0.20 gm), chloranil (0.20 gm) and sulphur-free xylene (10 ml) were boiled for 3 hours. The cold solution was diluted with benzene and the organic layer was shaken with cold 5% caustic soda solution containing some hydrosulphite to remove tetrachlorhydroquinone and excess chloranil. After washing and drying, the benzene-xylene concentrate was chromatographed, the rapidly moving yellow band eluted and the solvent removed.

Yield 0.19 gm (quantitative)

Crystallisation from light petrol yielded beautiful orange-yellow lathes, m.p. $144^{\circ} - 5^{\circ}$.

Analysis. $\begin{matrix} \text{C} & \text{H} & \text{req.} & \text{C} & \text{H} \\ 20 & 12 & & 95.2 & 4.8 \end{matrix}$
 (Elbs product) Found. $\begin{matrix} \text{C} & \text{H} \\ 94.8 & 4.9 \end{matrix}$

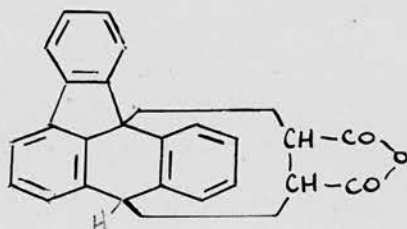
Derivatives.

(1) Picrate (benzene) deep crimson prisms m.p. 215

Analysis. $\begin{matrix} \text{C} & \text{H} & \text{O} & \text{N} & \text{req.} & \text{N} \\ 26 & 15 & 7 & 8.3 & & 8.7 \end{matrix}$

Found. N 8.9

(2) The hydrocarbon also formed a maleic anhydride adduct, thus showing the retention of the meso-position activity of the anthracene nucleus of the molecule.



Benzofluoranthene (50 mg) and maleic anhydride (40 mg), were boiled in xylene for 30 minutes. The product obtained on cooling, after washing with a little ether, was crystallised from xylene.

Colorless prisms, turning yellow at 210° and melting with dec. $220^{\circ} - 35^{\circ}$

Analysis $\begin{matrix} \text{C} & \text{H} & \text{O} & \text{req.} & \text{C} & \text{H} \\ 24 & 16 & 3 & & 82.2 & 4.0 \end{matrix}$
 Found. $\begin{matrix} \text{C} & \text{H} \\ 81.3 & 4.1 \end{matrix}$

The caustic soda solution, on acidification, yielded 0.3 gm of uncyclised o-(9-fluorenyl)benzoic acid.

The yield of hydrocarbon was therefore 50%.

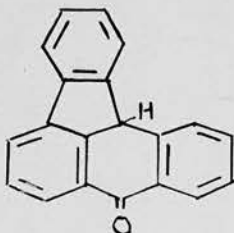
Cyclisation of o-(9-Fluorenyl)benzoic acid (2nd Method)

To o-(9-fluorenyl)benzoic acid (0.5 gm) in dry benzene (5ml) , was added phosphorus pentachloride (0.45 gm) and the mixture gently warmed to start the reaction. A golden-yellow solution of the acid chloride was quickly produced and after standing 15 minutes to it, was added stannic chloride (0.2 ml) in dry benzene (3 ml). A dark colour spread throughout the solution and a dark brown complex separated. After standing 30 minutes the mixture was decomposed with ice and hydrochloric acid and the yellow-orange material which was precipitated was filtered off.

Yield 0.22 gm.

Crystallised from xylene in bright orange stub prisms m.p. $280^{\circ} - 2^{\circ}$ with charring.

Analysis for 1:9-(o-phenylene)anthrone.



C	H	O req.	C	89.6	H	4.5
20	12					

Found.C	89.6	H	4.3
---------	------	---	-----

This compound was reduced easily by the acid *Reinmann*
Clémensen method (toluene) to a colorless crystalline
solid m.p. 240° . Unfortunately there was not
enough of this material for analysis.

Other attempted cyclisations of o-(9-Fluorenyl)benzoic Acid

(1)(a) Replacing the acetic acid with phosphoric acid
led to a dark intractable oil.

(b) Addition of phosphoric acid to the mixture
caused only the precipitation of the acid which did
not cyclise.

(c) When the acid (0.3 gm) was boiled with
hydriodic acid (2 drops) in acetic anhydride (5 ml)
an intractable oil resulted.

(2) Boiling the acid with red phosphorus, potassium
iodide and phosphoric acid did not lead to cyclisation
Unreacted acid was recovered.

(3) The acid chloride was prepared by boiling with
excess thionyl chloride. Removal of the solvent
yielded an oily product to which nitrobenzene and
aluminium chloride were added. After standing
overnight the mixture was decomposed and the solvent
removed with steam. The residue was chromatographed
but only dark oily fractions were obtained.

The Attempted Synthesis of 2:3-6:7-DibenzofluoranthenePreparation of Ethyl Cinnamate

Fischer & Speier Bev. 1895, 28, 3254.

Cinnamic acid was esterified with alcohol and sulphuric acid

Yield. 80%

Preparation of Ethyl α - β -dibromo- β -phenylpropionate

Org. Syn. 1932, XI, 37

Ethyl cinnamate was brominated in carbon tetrachloride

Yield 85%

Preparation of Phenylpropionic Acid

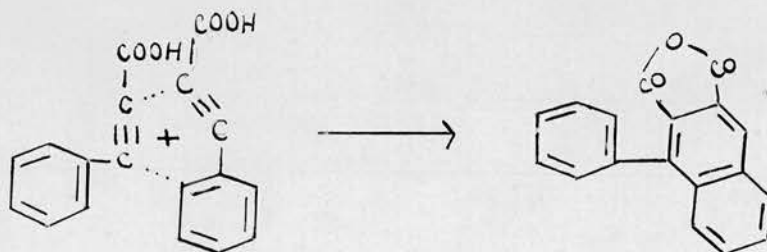
Abbott. Org. Syn. 1932, XI, 60.

Ethyl α - β -dibromo- β -phenylpropionate was hydrolysed and dehydrobrominated with alcoholic potash.

Yield 75%

Preparation of 1-Phenylnaphthalene-2:3-dicarboxylic anhydride

Schaarschmidt Bev. 1915, 48, 1826.



Phenylpropionic acid was gently boiled with acetic anhydride. The literature yield could not be repeated.

50 gm phenylpropionic acid yielded 25 gm anhydride

(3 hours boiling Lit 38^m)

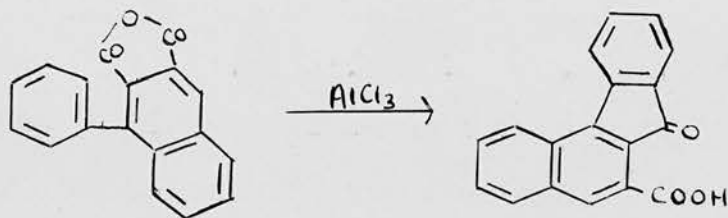
50 gm phenylpropionic acid yielded 35 gm anhydride

(2 hours boiling)

Pale yellow crystals m.p. $258^{\circ} - 9^{\circ}$ Colorless when pure.

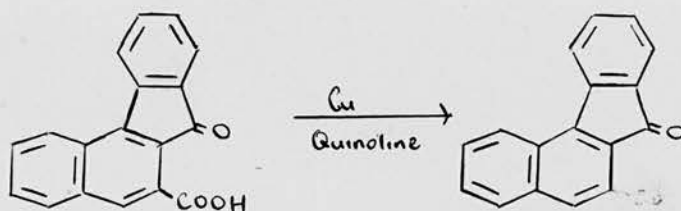
Preparation of 3:4-Benzofluorenone-1-Carboxylic acid

Schaarschmidt Bev. 1915, 48, 1826.



The internal Friedel-Crafts reaction of the phenylphthalic anhydride yielded 3:4-Benzofluorenone-1-carboxylic acid. The acid was extracted with hot 5% carbonate instead of ammonia.

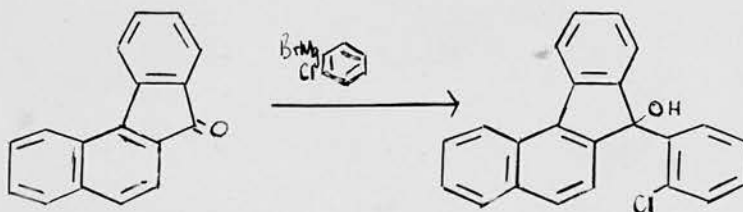
Yield Quantitative

Preparation of 3:4-Benzofluorenone.

3:4-Benzofluorenone-1-carboxylic acid (30 gm),
 (crude as obtained in the last experiment) was
 decarboxylated with copper bronze and quinoline at
 220° - 5°. The quinoline solution was poured into
 acid and the precipitate filtered. Extraction
 with benzene (Charcoal) and concentration yielded
 orange crystals of 2:3-benzofluorenone. 3:4

Yield 19 gm m.p. 158° - 60° (Lit. 161) 72%

The compound gave a green colour with concentrated
 sulphuric acid.

Preparation of 9-(p-Chlorophenyl)-3:4-benzofluoren-9-ol

A Grignard reagent(4M) was prepared from magnesium
 turnings(4.7 gm) and o-chlorobromobenzene (24 ml) in
 ether. It was diluted to a volume of 700 ml.

2:3-Benzofluorenone (11.5 gm was dissolved in dry benzene

(250 ml) and the warm solution added dropwise with efficient stirring. A red coloration was locally produced with each addition. At the end of the addition a clear brownish-yellow solution was boiled for 2 hours on the water bath and then decomposed with ice and hydrochloric acid. After washing and drying the organic layer was taken to dryness and the resulting oil triturated with light petroleum when a pale yellow solid was obtained.

Yield 9.7 gm (55%)

It crystallised from alcohol in colorless prisms melting with effervescence at 100° and resolidifying with melting at 170° . It gave a red colour with concentrated sulphuric acid.

Analysis. (1) air dried.

C	H	O	Cl,	H O	req.	C	76.6	H	4.7	Cl	9.8
23	15			20							

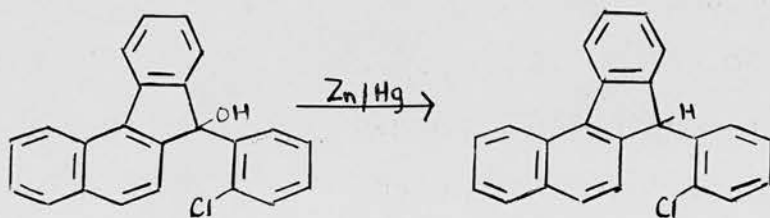
Found C 76.4 H 5.0 Cl 9.6

(2) dried.

C	H	O	Cl		req.	C	80.6	H	4.3	Cl	10.4
23	15										

Found. C 80.2 H 4.1 Cl 10.7

A poorer yield of the carbinol was obtained with 3 moles of Grignard reagent. With 2 moles of Grignard reagent a pink precipitate separated on addition of the benzofluorenone solution. This precipitate decomposed to yield unreacted ketone.

Preparation of 9-o-Chlorophenyl-3:4-benzofluorene

9-o-Chlorophenyl-3:4-benzofluoren-9-ol (11.9 gm), lightly amalgamated zinc (10 gm) and zinc dust (5 gm), concentrated hydrochloric acid (75 ml) and acetic acid (500 ml) were boiled for 3 hours. At the start of reaction a deep red colour was produced which gradually faded to a pale pink after 3 hours. A further quantity of zinc dust (2 gm) was added and the boiling was continued for a further 1 hour when the solution was completely colorless.

Concentration yielded globules of oil which would not solidify. On pouring into water there resulted a copious white precipitate which contained inorganic material. This precipitate was dissolved in benzene and the benzene concentrate chromatographed. The column showed the peculiar phenomenon of a transparent band which displayed a strong blue fluorescence in u.v. This band yielded a clear oil setting solid at once on trituration with light petroleum.

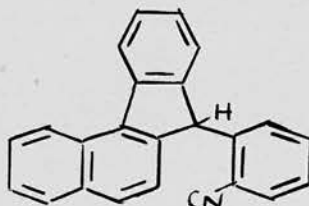
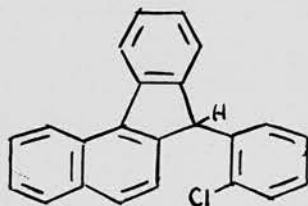
Yield 9.9 gm (82%)

Crystallisation from light petroleum (80° - 100°) gave colorless prisms m.p. 106° - 7°, insoluble in concentrated sulphuric acid.

Analysis. C H Cl req Cl 10.9
23 15

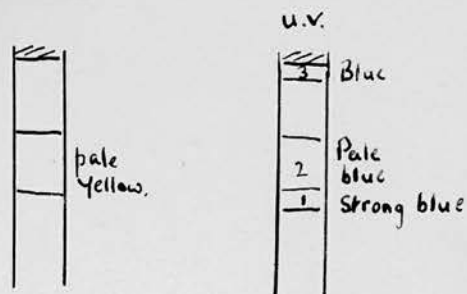
Found. Cl 11.5

Preparation of 9-(o-Cyanophenyl)-3:4-benzofluorene



9-(o-Chlorophenyl)-3:4-benzofluorene (8.6 gm), cuprous cyanide (3.6 gm), pyridine (20 ml) and aceto nitrile (2 ml) were heated in a sealed tube for 24 hours at 240° . On opening the mixture was poured into dilute acid and extracted with benzene. The benzene was washed with ammonia, water, acid and water and then dried. The concentrate was then chromatographed.

The column appeared as shown after some development with benzene.



Fraction 1. The strong blue fluorescent band yielded only a small amount of unreacted chloro compound.

Fraction 2. The visible pale-yellow band yielded an oil which immediately solidified on trituration with light petroleum.

Yield 6.3 gm (74%).

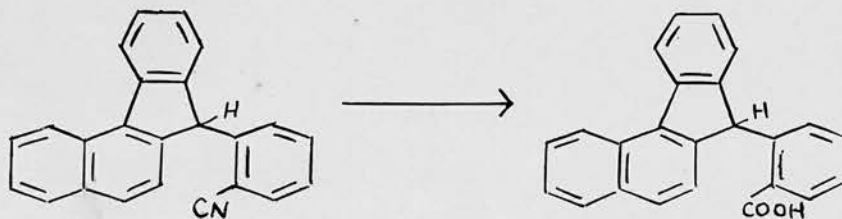
It crystallised from light petrol 80° - 100°/benzene in colorless prisms m.p. 140° soluble on standing, in concentrated sulphuric acid with an olive green colour. The solution eventually turned reddish-brown with a green fluorescence.

Analysis. C H N req. N 4.4
 24 15

Found. N 3.9

Fraction 3. The column was then eluted with alcohol. Removal of the solvent yielded a dark oily solid (0.6 gm) which could not be identified.

Preparation of 9-(o-Carboxyphenyl)-3:4-benzofluorene



(1) 9-(o-Cyanophenyl)3:4-benzofluorene (2.0 gm),
acetic acid (18 ml), concentrated sulphuric acid (9 ml)

was boiled for 24 hours. Solid separated in the course of this boiling. The mixture was poured into dilute acid and the precipitate filtered. Extraction with hot carbonate, followed by acidification yielded the required acid.

Yield 0.9 gm.

It crystallised from acetic acid(Charcoal) in colorless nodules m.p. 200° but not clearing until 230° .

Analysis.	C	H	O	req.	C	85.7	H	4.8
	24	16	2					

Found.	C	84.0	H	5.3
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(2) 9-(o-Cyanophenyl)-3:4-benzofluorene (3.5 gm), caustic soda (1.4 gm), water,(3.5 ml) and ethylene glycol (17 .5 ml) were boiled for 24 hours. The scarlet colour which appeared at the start of the boiling gave way to a clear pale green solution at the end of the reaction. On pouring into acid a white precipitate settled. This precipitate was completely soluble in dilute carbonate.

Yield 3.7 gm (Quantitative)

The methyl ester (methanol, sulphuric acid): colorless nodules(light petrol) m.p. 110° - 11° .

Analysis. C H O req. C 85.7 H 5.1
25 18 2

Found. C 84.7 H 5.3

The methyl ester was chromatographed and hydrolysed back to the parent acid. There was no difference in m.p.

Attempted cyclisations of 9-(o-Carboxyphenyl)-3:4-benzofluorene

(1) The acid (0.85 gm) , acetic acid (6 ml) and acetic anhydride (5 ml) and zinc chloride (trace) were boiled for 2 hours. To the hot deep crimson solution water was added until crystallisation occurred. The crimson acetate was filtered.

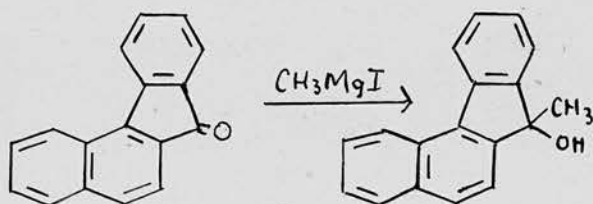
The acetate (crude) was boiled with zinc and alkali as before (p 116) for 24 hours. When the toluene layer was chromatographed a reddish-orange band separated and was eluted. Removal of the solvent yielded a small quantity of reddish oily material which was not investigated further.

(2) The acid (1.0 gm) and phosphorus pentoxide (7 gm) were boiled on the water bath for 3 hours in dry benzene(150 ml). The deep crimson coloured mixture was distilled to dryness and dilute caustic soda added. There was no insoluble residue of cyclised

cyclised product. Acidification of the caustic soda filtrate yielded a black intractable solid.

(3) cf Birch, Jaeger and Robinson. J.1945,582.

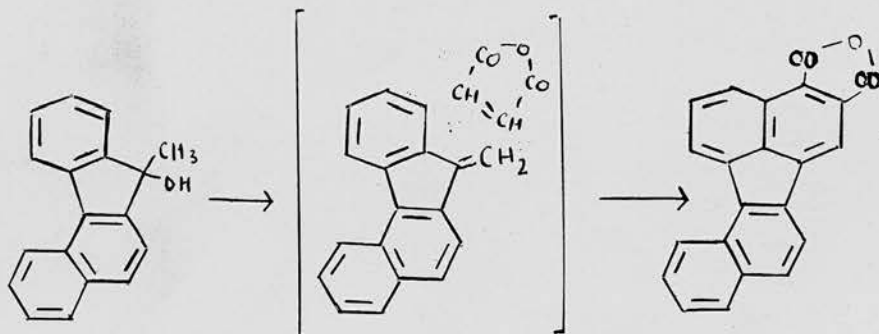
The acid (0.2 gm) was added to a solution of phosphorus pentoxide (0.2 gm) in phosphoric acid (2 ml) and the mixture maintained at 150 for 5 minutes. The mixture was then poured onto ice. Uncyclised acid was recovered.

Preparation of 9-Methyl-3:4-benzofluoren-9-ol

Fieser & Joshel. J.A.C.S. 1940, 62, 957.

3:4-Benzofluorenone (in benzene) was added to methylmagnesiumiodide (4 M).

Yield 80%

Preparation of 10:11-Benzofluoranthene-3:4-dicarboxylic acid anhydride.

9-Methyl-3:4-benzofluoren-9-ol (1.0 gm), maleic anhydride (3.0 gm) and acetic anhydride (1.0 ml) were boiled for 4 hours. The yellow solution gradually reddened. On cooling orange red needles separated

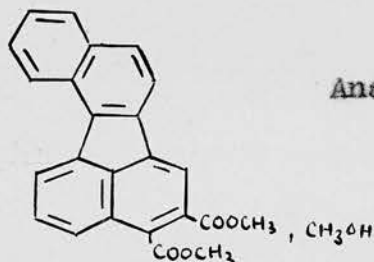
Yield 0.2 gm

It crystallised from α -methylnaphthalene in long thin orange red needles m.p. > 330 .

Analysis. C H O req. C 82.0 H 3.1
22 10 3

Found. C 81.2 H 2.9

When the anhydride was boiled for some hours with methanol and concentrated sulphuric acid there was obtained a yellow solution which on cooling deposited slender yellow needles m.p. $203^{\circ} - 4^{\circ}$ on crystallisation from methanol/benzene. The compound analysed for the expected dimethyl ester with 1 molecule of methanol attached.

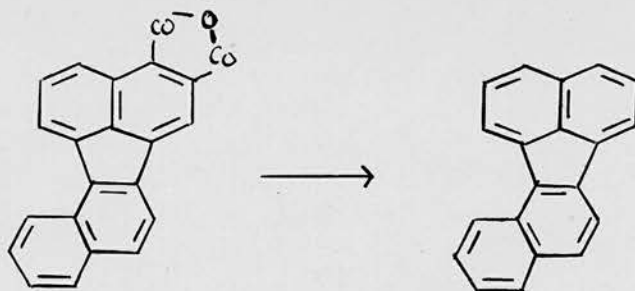


Analysis. C H O, CH OH
24 16 4 3

req. C 76.1 H 4.7

Found. C 75.0 H 5.0

Decarboxylation



The anhydride (100 mg) was intimately mixed with a large excess of calcium oxide and the mixture heated to a dull redness. The yellow sublimate which rapidly appeared was chromatographed in benzene.

Development was carried out with light petrol 120. The yellow band was eluted and the solvent was removed. The bright yellow solid (70 mg) obtained, crystallised from light petrol in compact prisms m.p. $162^{\circ} - 4^{\circ}$.

Solutions showed a bright green fluorescence under the u.v. lamp. The compound dissolved in warm concentrated sulphuric acid to give an olive-green solution.

A mixed m.p. with a sample of the compound prepared by Zinke & Pack (p 60) gave no depression. Analysis for 10:11-benzofluoranthene.

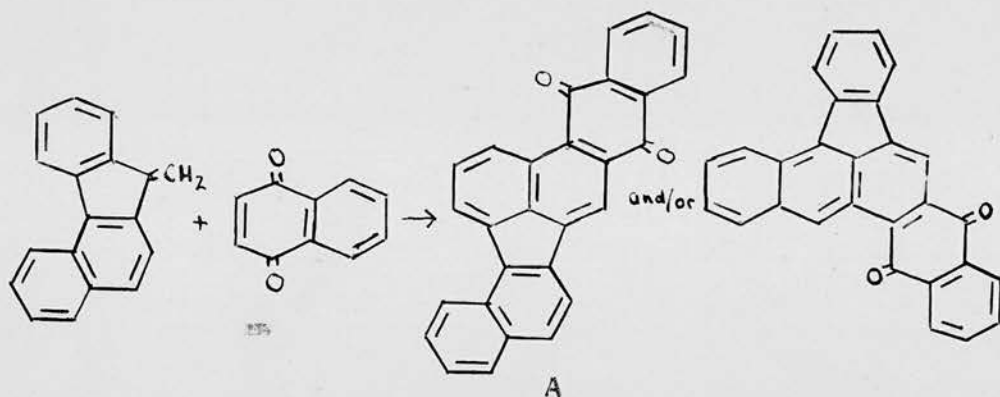
C	H	req.	C	95.2	H	4.8
20	12					

Found. C 93.5 H 5.1

Note. The analysis was carried out on 2 mg.

The anhydride did not decarboxylate by the alkaline ferricyanide method (Campbell & Gow J. 1949,1555.). The probable cause of this failure was the insolubility of the anhydride in caustic solution.

The Dehydration of 9-Methyl-3:4-benzofluoren-9-ol
in presence of 1:4- Naphthoquinone



9-Methyl-4:5-benzofluoren-9-ol (1.0 gm), 1:4-Naphthoquinone (4.0 gm) and acetic anhydride (20 ml) were boiled for 2 hours. The fluffy crystals of the adduct were filtered before the excess naphthoquinone crystallised.

Yield 50 mg.

The product was purified by sublimation. From the mass grew a felt of scarlet prisms m.p. > 330°

Analysis	C.	H	O	req	C	87.9	H	3.7
	28	14	2					
				Found.	C	87.5	H	3.9

By analogy with the preceding Diels-Alder reaction this compound was probably the 10;11-benzofluoranthene naphthoquinone derivative A.

It gave a greenish brown colour with concentrated sulphuric acid and a deep blue vat with alkaline hydrosulphite.

SUMMARY OF RESULTS.

2:3-Benzofluoranthene is synthesised from fluorenone. The method could be extended to the syntheses of dibenzofluoranthenes from benzofluorenones if a general method of cyclisation is evolved.

9-Methyl-4:5-benzofluoren-9-ol yields Diels-Alder addition products with Maleic anhydride and 1:4-Naphthoquinone when dehydrated in presence of the dienophile. With maleic anhydride the addition takes place at the benzene portion of the benzofluorenone nucleus. 10:11-Benzofluoranthene is synthesised in this way.

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POSTSCRIPT.

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