STUDIES IN THE FLUORANTHENE SERIES

by

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INTRODUCTION

The history of fluoranthene dates back to the first years of classical organic chemistry and to one of the founders of that science as we know it to-day. Friedrich Wohler describes in the Annalen der Chimie und Pharmacie (1) how he set one of his pupils, Boedeker, the task of investigating the sooty deposit, "stupp" obtained by distilling the mercury ores found at Idria. In the paper which follows, Boedeker describes how he isolated a compound, melting at about 360°C and subliming to a colourless iridescent substance which he named idryl. The analysis figures obtained by Boedeker, which compare very favourably with the theoretical values for fluoranthene, led him to assign the formula C_{42}H_{14} to the compound, that is C_{15}H_{10} according to our present-day values of atomic weights.

No further mention of the new hydrocarbon is to be found in the literature until over thirty years later when, in 1877, both Goldschmiedt and Fittig and Gebhard independently reported the existence of the compound. Goldschmiedt (2) isolated it from stupp and retained the original name, idryl, and he proved that Boedeker's sample had been a mixture of anthracene, phenanthrene, pyrene, chrysene as well as idryl. Goldschmiedt was able to show that oxidation of the hydrocarbon gave a quinone which yielded diphenyl when distilled with soda-lime. He prepared a picrate
of idryl and postulated the formula \( \text{C}_{15}^5 \text{H}_{10} \) for the hydrocarbon, based on analysis figures and vapour density determinations.

Fittig and Gebhard (3) isolated the compound from coal tar and named it fluoranthene because of its fluorescence. They too investigated the oxidation of fluoranthene (I) and showed that further oxidation of the quinone (IIA) first formed, gave an acid \( \text{C}_{14} \text{H}_{8} \text{O}_{3} \) (II) which on decarboxylation yielded fluorenone (IV) while distillation with zinc dust gave fluorene (III). Thus the acid (II) was identified as fluorenone-1-carboxylic acid and an indene structure was postulated for fluoranthene.

In the following year Fittig and Gebhard (4) in addition to preparing fluoranthene picrate, dibromo-fluoranthene and trinitro-fluoranthene, showed that the acid (II) obtained on oxidizing fluoranthene gave isodiphenic acid (V) when heated with potassium hydroxide. The structure of isodiphenic acid was later proved by Fittig and Liepmann (5, 6.) when they showed that it could be oxidized to isophthalic acid (VI). They also showed (6.) that fluorenone-1-carboxylic acid could be reduced to the corresponding fluorene acid (VII) which yielded fluorene on distillation with lime; all of which gave support to the postulated structure of fluoranthene. Fittig and Liepmann (6)
obtained fluoranthene quinone, to which they assigned the formula $C_{15}H_{8}O_2$ and they showed that like phenanthraquinone, it formed a molecular compound with two molecules of the parent hydrocarbon.
Fluorenone -1- carboxylic acid was ultimately synthesized by Mayer and Freitag (7.) from isodiphenic acid according to the following scheme of reactions.

The reduction products of fluoranthene were studied by Goldschmidt (8.) who postulated that a dihydro compound $C_{16}H_{12}$ could be obtained by reduction with hydrogen iodide or with sodium amalgam and alcohol. A more vigorous reduction with phosphorus and hydrogen iodide was asserted to give an octahydro derivative $C_{15}H_{18}$. 
The first attempt to synthesise fluoranthene was made by Mayer (9) who accepted Fittig's formula and attempted a cyclisation of 1-fluorenylacetic acid (VIII) which he prepared by the following method:

\[
\begin{align*}
\text{CH}_2 \quad \text{BrCH}_2 \quad \text{COOC}_2\text{H}_5 \\
\text{CH}_2 \quad \text{COOC}_2\text{H}_5 \\
\text{COOC}_2\text{H}_5 \\
\end{align*}
\]

Mayer was unable to bring about a cyclisation of either the acid or the acid chloride, neither did he succeed when he used 2-fluorenylpropionic acid or the acid chloride.

In 1929 von Braun published the first of a series of important papers in which he and his various coworkers investigated the structure and synthesis of fluoranthene and its derivatives. Von Braun had been working on the stability of condensed ring systems where the rings contained more or fewer than six carbon atoms (10,10A). As he was unable to synthesise the compound (IX) von Braun concluded that it was impossible to obtain a structure in which two five-membered rings were adjacent and both condensed to
the same benzene ring.

On the other hand the compound (X) could readily be obtained which showed that a system containing a five and a six-membered ring condensed together and both annealed to a six-membered ring was stable. von Braun later showed that a seven- and a five-membered ring condensed together and both adjacent to a six-membered ring also gave a stable structure (XI). In this case the seven-membered ring was a strainless one.

When he came to apply his theory to known compounds von Braun discovered that fluorethene had been assigned an indene structure (XIII) which was in direct contradiction to his findings. Accordingly he postulated a naphthalene structure for the hydrocarbon (XIII)
Furthermore, von Braun and Anton pointed out that the analysis figures required for a compound C_{16}H_{10} differ but slightly from those required for Fittig's proposed compound C_{15}H_{10}. Similarly in the case of the quinone derived from fluoranthene by oxidation with chromate, the difference between the analysis figures required for C_{16}H_{8}O_2 and for C_{15}H_{8}O_2 is very small.

The final proof that fluoranthene had a naphthalene structure came with its synthesis by these workers (11). Like Mayer (9) they started from fluorene and prepared pared/3-fluorenylpropionic acid (XIII) which they converted to the acid chloride with thionyl chloride and cyclised with aluminum chloride in light petroleum to 4-keto-1:2:3:4-tetrahydrofluoranthen (XIV). This was reduced by the Clemmensen method to 1:2:3:4-tetrahydrofluoranthen (XV) which on dehydrogenation with lead oxide yielded fluoranthene (XVI).

The system of numbering the fluoranthene nucleus is indicated below, as is also the accepted system of conjugated double bonds. The naphthalene nucleus, a resonance hybrid, will have as its main contributing form a structure with the bond system shown below while the third benzene ring of the fluoranthene nucleus will also be a resonance hybrid having two equally probable contributing forms, namely those
shown in fig (XVI) and (XVIA)
Buu-Hoi and Cagniant (20) have suggested however that the bonding in (XVI) does not conform to the Mills-Nixon principle which decrees that indane have the structure (XVII) and not that give in figure (XVIIIA); the formula (XVI) for fluoranthene conforms to this theory. These workers tender as further support to this structure (XVI) the fact that fluoranthene is colourless whereas acenaphthylene (XVIII), which has the opposite bonding in the indene ring, is yellow. Such a comparison, however, of a genuine double bond as the 9:10 bond in acenaphthylene, with a "aromatic" double bond, as the 9:14 bond in fluoranthene is unsound.

The synthetic fluoranthene was oxidized to a quinone (XIX) which was identified with the long known fluoranthene quinone first described by Fittig and Gebhard. Furthermore the new naphthalene structure of fluoranthene made it easy to understand how quinone formation occurred, a fact which was difficult to explain on an indene structure.

von Braun and Anton also repeated Mayer's previous work (9) and confirmed his finding that fluorenylecetic acid cannot be cyclised.

The reduction of fluoranthene was next studied by von Braun. Along with Manz (12) he repeated Goldschmidt's work (8) and showed that four atoms of
hydrogen, and not two, as the earlier worker had claimed, were added to the fluoranthene molecule when reduction with sodium amalgam was carried out, the product being 1:2:3:4 - tetrahydrofluoranthene (XX). This on further reduction with sodium and alcohol yielded 1:2:3:4:9:10:11:12:13:14 - decahydrofluoran-

thene (XXI) which could also be obtained by the direct reduction of fluoranthene with sodium and alcohol, or with hydrogen in the presence of a nickel catalyst. Finally the third ring was reduced to give perhydro-

fluoranthene.

Further support to the structure of fluoranthene was given by Kruber (26) who isolated 1:2:3:4 -tetra-

hydrofluoranthene from coal-tar by treating the neutral tar-oil fraction with sodium in solvent naphtha, and decomposing the sodium derivative so formed, with water. Using sodium dichromate in glacial acetic acid he was able to oxidize tetrahydrofluoranthene to an acid containing the same number of carbon atoms, fluorenone-8:β-propionic acid.

![Diagram of fluoranthene and tetrahydrofluoranthene conversions](attachment:fluoranthene_diagram.png)
A second synthesis of fluoranthene was described by Cook and Lawrence (13). They condensed 2-methylcyclohexanone with 1-naphthylmagnesium bromide and dehydrated the carbinal (XXII) so produced with potassium hydrogen sulphate. The resulting 1:1'-naphthyl-2-methyl-\( \Delta^2 \) cyclohexene (XXIII) was cyclised at 0°C with aluminium chloride and carbon disulphide as solvent giving 9:10:11:12:13:14-hexahydro-9-methylfluorantheno (XXIV) which was dehydrogenated by heating with selenium to give fluoranthene.
Orchin and Reggel (14) carried out a similar synthesis of fluoranthene starting from cyclohexanone and 1:naphthylmagnesium bromide. They used formic acid in place of potassium hydrogen sulphate to dehydrate the alcohol, and dehydrogenated the product 1-(1'-naphthyl) -Δ'-cyclohexene, with palladium on charcoal forming 1-phenynaphthalene which they cyclodehydrogenated, again using palladium on charcoal, to fluoranthene.

Bergmann and Orchin (15) have recently published a new synthesis of fluoranthene starting from fluorene (XXV) with which they carried out a Michael condensation. This reaction, which was studied by Alder, Phorr and Vagt (60) consists of the formation of an adduct (XXVI) of fluorene and maleic anhydride. The adduct was then hydrolysed to the acid which was cyclised with acetyl chloride. The 2-carboxy-4-keto-1,2,3,4-tetrahydrofluoranthene (XXVII) so formed was reduced by the Clemmensen method to 2-carboxy-1,2,3,4-tetrahydrofluoranthene (XXVIII) which was dehydrogenated with sulphur to give 2-carboxyfluoranthene (XXIX). This acid on decarboxylation gave fluoranthene, while the hydrazide of the acid yielded 2-aminofluoranthene.
In addition to these syntheses, a large number of syntheses of derivatives of fluoranthene have been published. One of the earliest papers describes the synthesis of 10:13- diphenyfluoranthen by Dilthey and co-workers (16) by the condensation of acecyclone with maleic anhydride to form a bridged compound. This was readily decomposed to the acid anhydride which on decarboxylation gave 10:13- diphenyfluoranthen.

The preparation of 11:12-benzfluoranthen has also been described by Moureu, Ghevin and Riveal (27).

The Diels-Alder reaction is one which has been widely used in the syntheses of substituted fluoran-
fluoranthenes. Campbell and Gow (17) showed that 7:8-dialkyl-acenaphthene-7:8-diols when heated with dienophiles in dehydrating solvents condense readily to form fluoranthene derivatives, and in this way they were able to synthesize fluoranthene itself and many of its derivatives, such as 10:13-dimethylfluoranthene, fluoranthene (11':12'-2:3) -p- benzoquinone, fluoranthene (11':12'-2:3) naphthaquinone etc. In particular they were able to synthesize 4-bromofluoranthene by the following method which proved the structure assigned to it by von Braun.
A similar synthesis of substituted fluoranthenes is described by Campbell and Wang (18). The starting compound in this case was 9-hydroxy-9-methylfluorenone (XXX) which with acetic anhydride and excess maleic anhydride gave fluoranthene-3:4-dicarboxylic acid presumably by addition to the intermediate 9-methylfluorene (XXXI).

Hydrolysis of the anhydride (XXXII) gave the acid which when heated with calcium hydroxide decarboxylated to fluoranthene. Heating with copper bronze and quinoline removed only the carboxyl group in the 4 position leaving impure fluoranthene-3-carboxylic acid.

Campbell and Wang were able to synthesise 3:4-benzfluorantheine-1:4'-quinone and naphtho(2:3'-3:4') fluoranthene-1:4'-quinone by this method.

Bergmann (19) has also used the Diels-Alder reaction.
for synthesizing fluoranthene derivatives, and by condensing acenaphthylene with 1-phenyl-butadiene he obtained 10-phenyl-9:10:13:14-tetrahydrofluoranthenone.

![Chemical Structure]

In the past few years, Tucker and co-workers have published a number of papers (21,22,23,24,25) dealing with the syntheses of fluoranthene derivatives and tetrahydrofluoranthenone derivatives.

Of the two synthetic routes described, the first has fluorene as a starting point, while the second involves condensations of naphthalene derivatives.

Tucker, France and Maitland (21) originally prepared methyl -β-9-fluorenyl-β-methyl-n-propylketone (XXXIII) by condensing fluorenone with acetone in the presence of potassium hydroxide, and this compound was later used by Tucker (22) to synthesize 2:2:4-trimethyl-1:2:3:4-tetrahydrofluoranthenone (XXXIV) as shown.
Tucker and Forrest (23) converted 2:2:4-trimethyl-1:2-dihydrofluoranthenes (XXXV) into 2:3:4-trimethylfluoranthenes by heating it with phosphorus pentoxide when a molecular rearrangement took place. Dehydrogenation of (XXXV) with selenium gave 2:4-dimethylfluoranthenes.

The synthesis of 2:4-diphenylfluoranthenes and 2:phenyl-4-methylfluoranthenes is described by Tucker and Whalley (24) starting from phenyl-2-phenyl-2:9'-
fluorenylethyl ketone and methyl-2-phenyl-2:9'-fluorenyl ethyl ketone respectively. The ketones were reduced to the corresponding alcohols which were cyclodehydrated with sulphuric acid and glacial acetic acid to the substituted tetrahydrofluoranthenes, dehydrogenation of which was carried out with palladium on charcoal.

Starting from 2:3:4-trimethylnaphthalene (XXXVI) Tucker and Whalley (25) were able to synthesise 1:2:3-tri-methylfluoranthenes (XXXIX) using the Ullmann reaction to condense 1-iodo-2:3:4-trimethylfluoranthenene (XXXVII) obtained by iodination of (XXXVI), with O-nitrobenzene. The resulting substituted naphthalene (XXXVIII) was reduced to the amine and ring closure was carried out by diazotisation and coupling of the diazonium salt intramolecularly in alkaline solution.
These authors also reported the preparation of 2:4:4-trimethyl-1:2:3:4-tetrahydrofluoranthenes and 2:3:4-trimethylfluoranthenes from 4-fluorenylidene - 2-methylpent-2-one.

Turning now to the substituted derivatives of fluoranthenes it is surprising to note that most of the orientations which have been carried out have been confined to the mono-substituted fluoranthenes and
relatively little information has been obtained about the di- and poly-substituted fluoranthenes.

In their early papers Fittig and Gebhard (4) reported the preparation of fluoranthene picrate and trinitro- and dibromofluoranthane. Goldschmiedt (2,8) also prepared the picrate and tri- and di-bromofluoranthane, the latter being an inferior product to that obtained by Fittig and Gebhard. He obtained a di-sulphonoderivative by treating fluoranthene with sulphuric acid and showed that when treated with potassium cyanide this gave a mono-cyanofluoranthane, which he obtained as an oil and hydrolysed to the corresponding monocarboxlyic acid M.P. 185°C, for which he obtained a good analysis.

It was again von Braun who was responsible for the elucidation of the structure of the simple fluoranthene derivatives. Having proved the structure of the parent hydrocarbon and investigated its hydrogenation products (11,12) von Braun and Manz turned to the preparation and orientation of the mono-substituted fluoranthenes (28). They prepared 4-bromofluoranthane (XI) by direct bromination in carbon di-sulphide and showed that it did not react with magnesium to form a Grignard reagent, but that it could be reduced with sodium amalgam and alcohol to 1:2:3:4-tetrahydro-fluoranthane with the elimination of bromine.
Furthermore, 4-bromofluoranthenone when heated at 260°C with cuprous cyanide gave 4-cyanofluoranthenone (XLI) which was hydrolysed by concentrated hydrochloric acid to fluoranthene-4-carboxylic acid (XLII). Treating the acid chloride with benzene and ammonia gave the amide (XLIII).

The mono-sulphonic derivative (XLIV) was prepared by treating fluoranthene with monochlorosulphonic acid in chloroform. The acid gave with ethylamine, fluoranthene-4-ethylsulphonamide (XLV) which in turn was converted to a cyano compound, identical with that (XLI) obtained from 4-bromofluoranthenone, when heated with a mixture of sodium and potassium cyanides. Again, the amide (XLV) when heated at 330-240°C with potassium hydroxide gave a phenol (XLVI) which could be reduced by sodium amalgam and alcohol to a hydroxy-tetrahydrofluoranthenone (XLVII) M.P. 156-163°C. This latter compound could not be oxidized to a keto-tetrahydrofluoranthenone. Furthermore the 4-hydroxy-1:2:3:4-tetrahydrofluoranthenone, M.P. 130-134, obtained by reducing 4-keto-1:2:3:4-tetrahydrofluoranthenone differed from (XLVII) as a mixed melting point of these two compounds showed a depression of 20 degrees.

When treated with alcohol and ammonia, the phenol (XLVI) gave 4-aminofluoranthenone (XLVIII). Direct nitration of fluoranthene gave 4-nitrofluoranthenene (XLIX)
which was reduced by tin and hydrochloric acid to the corresponding amine (XLVIII) shown to be identical with that obtained from the phenol.

\[
\begin{align*}
C_{16}H_{10} & \rightarrow C_{16}H_{9}E \rightarrow C_{16}H_{9}CH \rightarrow C_{16}H_{9}COOH \rightarrow C_{16}H_{9}CONH_{2} \\
& \rightarrow C_{16}H_{9}SO_{3}H \rightarrow C_{16}H_{9}SO_{2}NHCH_{2}CH_{3} \\
& \rightarrow C_{16}H_{9}NO_{2} \rightarrow C_{16}H_{9}NH_{2} \leftarrow C_{16}H_{9}OH \rightarrow C_{16}H_{13}OH
\end{align*}
\]

In this manner it was possible to orientate all of these fluoranthene derivatives by establishing the constitution of any one particular compound. von Braun and Manz oriented the amino compound (XLVIII) in the following manner. The mono-acetyl derivatives (L) was first formed and this on reduction with 5% sodium amalgam and alcohol gave 4-acetylamino-5:6:7:8-tetrahydrofluoranthene (LI). Oxidizing this with sodium dichromate in glacial acetic acid gave a substituted fluorenone - $\beta$-propionic acid (LII) and on de-acetylation this underwent spontaneous lactam formation (LIII) with the exclusion of a molecule of water. Only if the amino group had been in the 4-position in the original fluoranthene molecule could such lactam formation have occurred.
von Braun and Manz (32.) next turned their attentions to the Friedel-Crafts reaction on fluoranthene and reported that whereas nitration, bromination and sulphonation all take place mainly in the 4-position, acetylation, benzoylation and phthaloylation occur preferentially in the 11-position with only a slight amount of 4-position substitution as a by-product. This work has been repeated recently by Campbell and
Easton (33.) who have shown that in the case of benzo-
ylation and phthaloylation substitution occurs in
both positions and equal quantities of the 4- and 11-
isomers are obtained. In the case of acylation they
agree with the earlier workers that a mono-(11) and
a dicarboxylic acid are produced, in the ratio of
2:1, but failed to find the second mono-substituted
acid reported by the German workers.

von Braun and Manz acetylated fluoranthene with
oxalyl chloride and aluminium chloride in carbon di-
sulphide, and they showed the presence of two monocarb-
oxylc acids, one of which was present only in a small
quantity. The major product, 11-carboxyfluoranthene
was esterified (LIV), converted to the hydrazide (LV)
and thence through the azide (LVI) to the urethane
(LVII) which on hydrolysis yielded an aminofluoran-
thene (LVIII) which could not be identified as no
authentic sample had then been prepared.

\[
\begin{align*}
\text{C}_{16} \text{H}_9 \text{COOC}_2 \text{H}_5 & \rightarrow \text{C}_{16} \text{H}_9 \text{CO.NH.NH}_2 \rightarrow \text{C}_{16} \text{H}_9 \text{CON}_3 \\
\text{LV} & \text{LV} & \text{LVI} \\
\left[ \text{C}_{16} \text{H}_9 \text{N.CO} \right] & \rightarrow \text{C}_{16} \text{H}_9 \text{NH.COOC}_2 \text{H}_5 & \rightarrow \text{C}_{16} \text{H}_9 \text{NH}_2 \\
\text{LVII} & \text{LVII} & \text{LVIII}
\end{align*}
\]
In a similar manner, the second mono-carboxylic acid was converted to an amine which was shown to be identical with that obtained by the reduction of 4-nitrofluoranthenone. Thus the carboxyl group must also have occupied the 4-position.

The constitution of these acids was further elucidated by a study of their oxidation products.
If substitution occurs in the 4-position (LIX) then oxidation gives one fluorenone-dicarboxylic acid (LX) with the two carboxyl groups ortho- to one another. This von Braun and Manz were able to prove since an anhydride was readily formed. The other fluoranthene carboxylic acid could have the acid group in the 2-, 3-, 10- or 11-position. If substitution were in the 2- or 3-position then oxidation would yield a single fluorenone-dicarboxylic acid (LXIV) or (LXV). Since, however, two acids were obtained on oxidation this meant that the fluoranthene must have the carboxyl group in the 10- or 11-position. If the former, the oxidation products would be the acids (LXVI) and (LXVII), and if the latter then the products would be (LXII) and (LXIII). However von Braun and Manz were able to isolate an acid whose methyl ester they identified with methyl\(^7\)-fluorenone.
dicarboxylate prepared by Bamberger and Hooker.\(^\text{61}\)
These workers obtained the fluorenone dicarboxylic acid by the oxidation of retene and thus established its constitution.

Thus von Braun and Manz proved one of the oxidation products of the fluoranthene carboxylic acid to be fluorenone -1:7-dicarboxylic acid (LXII), the other product being presumably the 1:6- isomer (LXIII), and hence they identified the fluoranthene acid as the 11- isomer (LXI). Although the Germans did not claim the orientation of the unknown amine (LVIII) obtained from the acid (LXI) by the method shown above, they had in fact established it as being 11-aminofluoranthenes.

As for the fluoranthene dicarboxylic acid, Campbell and Easton (33) have shown that it can readily be decarboxylated with copper in boiling quinoline, to fluoranthene-11-carboxylic acid. Now fluoranthene-4-carboxylic acid is also readily decarboxylated under these conditions whereas the 11-acid is not; this points to either a 4:11- or a 4:12- dicarboxyfluoranthenes.

The constitution of the two monobenzoylfluoranthenes obtained by von Braun and Manz was investigated by forming the oxime of each, carrying out a Beckmann rearrangement and examining the products of hydrolysis
of the resulting substituted amides.

\[
\text{C}_6\text{H}_5\text{CO.C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{C}:(\text{NOH})\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CO.NH.C}_6\text{H}_5
\]

\[
\text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_2\text{NH}_2
\]

In this manner one of the benzoyl derivatives gave 4-aminofluoranthenene and benzoic acid, showing it to be the 4-benzoylfluoranthenene, while the other derivative gave the yet unidentified 11-aminofluoranthenene and benzoic acid. The o-carboxybenzoylfluoranthenenes gave similar products, when the oximes were examined but when the quinones formed by cyclisation were prepared, they gave the key to the structure of the second isomer.
The acid chloride of the unidentified o-carboxybenzoylfluoranthenone was heated in trichlorebenzene and cyclisation resulted in the production of two quinones (LXXI) and (LXXII). Since the original compound was known to be either 10- or 11-substituted
fluoranthene this meant that it must be the latter since a 10-substituted fluoranthene could only give one quinone (LXX).

The structure of the two quinones was determined by examining their oxidation products. (LXIX) gave on oxidation one phthaloyl-fluorenone carboxylic acid (LXXII) which was decarboxylated to the corresponding so-called anthraquinone-fluorenone. The quinone (LXX) on oxidation yielded two isomeric phthaloyl-fluorenone carboxylic acids (LXXIII) and LXXIV which were decarboxylated to two isomeric "anthraquinone-fluorenones". Furthermore the quinone (LXX) gave the hydrocarbon (LXXI) when subjected to a zinc dust distillation.

In this way it was shown that the original phthaloyl group was in the 11-position, and since the amino-fluoranthenone obtained from this derivative was identical with that obtained from the corresponding benzoyl- and carboxyl-fluorenones these two must also be the 11-derivatives. Furthermore the amino-fluoranthenone is also established as the 11-derivative (cf. p.27).

Campbell and Easton have further substantiated the proof of the structure of the two isomeric benzoyl-fluoranthenes by oxidizing them to the corresponding fluorenone acids, two of which on decarboxylation
yielded the same products, 2-benzoylfluorenone (LXXV).

von Braun and Manz (28) also examined the effect of substitution in tetrahydrofluoranthenes and showed that substituents entered almost exclusively into the 4-position giving 4-substituted-5:6:7:8-tetrahydrofluoranthenes. Only a very small amount of 11-substituted compound could be obtained. They also examined the fluorenone-carboxylic acids obtained by oxidizing 4-bromo- and 4-nitrofluoranthenes.

In their next paper, von Braun, Anton and Manz (29) compared the substitution of fluoranthene with that
of 1-phenylnaphthalene (LXXVI) which only differs from the former in that it has no 8;9 bond.

They showed that not only nitration and bromination but also benzoylation occur in the 4-position in this compound.

In an attempt to prepare 4-aminofluoranthenene direct from the parent hydrocarbon by heating it with soda-mide in naphthalene, von Braun and Manz (30) obtained instead a dimeric compound melting above 360°C. This they called periflanthenene and assigned to it the structure (LXXVII).

Support to this structure was given by the fact that if 4-bromofluoranthenene be heated with copper
powder and sodium iodide, two molecules condense with the exclusion of bromine, to give difluoranthyl which when heated with sodamide yields periflantanene.

Neither 4-methyl nor 4-phenylfluoranthenes (which were prepared by the action of a Grignard reagent on 4-keto-1:2:3:4-tetrahydrofluoranthenes and subsequent dehydrogenation) yields this dimer.

In view of von Braun's findings, namely that the 4- and 11-(or 12-) positions are the most reactive in the fluoranthene molecule, it is reasonable to assume that disubstitution will occur either in the 4:11- or the 4:12-positions. In a paper in which they describe a new method of preparing 4-bromofluoranthenes via the 4-bromo-1:2:3:4-tetrahydro compound, Tobler et al. put forward an argument supporting disubstitution of fluoranthene in the 4:11-positions. They point out that when fluoranthene is sulphonated, a disulphonic acid is formed which on hydrolysis gives a dihydroxy compound (LXXVIII). This in turn can be oxidised to a coloured substance which Tobler et al. claim is possible a quinone (LXXIX); only 4:11-disubstitution can account for such a quinonoid form.

This argument however, though interesting is inconclusive.
Tobler et al. were unable to synthesise 4:11-dibromofluoranthenes from 2:7-dibromofluorene by a method similar to the synthesis of fluoranthenes (11, and ) since they failed to prepare the starting compound ethyl-2:7-dibromofluorene-9-oxalate (LXXX).

They succeeded however, in synthesizing 4:11-dibromo-5:6-benzofluoranthenes in the following way.
By condensing 2:7-dibromofluorenone (LXXXI) with 2-acetylaminobenzaldehyde (LXXXII) in the presence of sodium ethoxide they obtained 2:7-dibromo -9- (2-acetylaminobenzylidene) fluorene (LXXXIII). The free base (LXXXIV) was liberated by hydrolysis with concentrated hydrochloric acid and diazotised with amyl nitrate in sulphuric acid (LXXXV). This compound was cyclised to 4:11-dibromo-5:6-benzofluoranthene (LXXXVI) by heating with copper.
There thus remains no definite proof that disubstitution of the fluoranthene nucleus occurs in the 4:11- positions.
OBJECT OF RESEARCH.

It can readily be seen from the preceding introduction that there has as yet been no rigid orientation of the di-substituted fluoranthene derivatives obtained by direct substitution of the hydrocarbon. Accordingly, the primary aim of this research was to orientate one such derivative, namely dibromofluoran-thene obtained by bromination of fluoranthene; it was shown to be 4:11-dibromofluoran-thene. From this substance a considerable number of disubstituted fluoranthenes can be made by standard methods, and thus their constitution is automatically determined.

The oxidation of 4:11-dibromofluoran-thene and certain other fluoranthene derivatives was studied in an attempt to repeat similar work done by Dr. Easton and hitherto unpublished.

Finally syntheses of two fluorenone derivatives and one fluoranthene derivative were attempted.
EXPERIMENTAL SECTION

INTRODUCTION.

The following section contains a description of the experimental work carried out during the course of the research. All yields are given as the percentage of the maximum theoretical yield.

Melting points were determined by two methods: (a) by the capillary - tube method (Campbell, Qualitative Organic Chemistry, p.7, fig.4); (b) on a micro-melting-point apparatus (Kofler, Mikrochem., 1934,15, 242) The latter gave valuable information about the behaviour of the compound e.g. sublimation etc., prior to melting, and also indicated the sharpness of the melting point.

All analyses were carried out by Drs. Weiler and Strauss of Oxford, using microanalytical methods.
EXPERIMENTAL.

Preparation of 4:11-Dibromofluoranthenone.

The dibromo compound was prepared by direct bromination of fluoranthene by the method described by Tobler, Holbro, Sutter and Kern (Helv. 1941, 24, 1055).

Yield of pure product = 66%, M.P. -205°C.

Oxidation of 4:11-Dibromofluoranthenone.

1st Method.

The method was based on that described by Fieser and Seligman for the oxidation of fluoranthene (J.A.C.S. 1935, 57, 2175) and used by Easton (Thesis, Edinburgh, p. 156).

A solution of chromic anhydride (A.R. 10g) in water (20 ml) and glacial acetic acid (24ml) was added cautiously to a solution of dibromofluoranthenone (6g.) in glacial acetic acid (400 ml) just below the boiling point. The dibromofluoranthenone was sparingly soluble in the acid.
The mixture was allowed to stand overnight then heated under reflux for three hours, at the end of which all the dibromofluoranthene had not completely dissolved. A solution of 14g. chromic anhydride (A.R.) in water (20 ml) and glacial acetic acid (100 ml) was added and the whole boiled for a further three hours. Acetic acid was then distilled off until the volume of the solution was about 100 ml and this was poured into water (ca. 200 ml.) when a fine precipitate separated out. After standing, the precipitate was filtered, washed with dilute hydrochloric acid and extracted by boiling with an aqueous suspension of an excess of barium carbonate. The extraction was repeated several times and the solution of the barium salt decomposed with dilute acid. A yellow-orange precipitate was obtained which was recrystallized from glacial acetic acid in long orange needles which sublimed at 200° C. and melted at 266° C. with some slight decomposition.

The barium carbonate residue was decomposed with hydrochloric acid, yielding a red precipitate. This was purified by dissolving it in ether, extracting with 5% potassium carbonate solution and acidifying the extracts to give a yellow-orange precipitate which was crystallized from glacial acetic acid in long orange needles melting, with decomposition, at
A further recrystallization from ethyl alcohol gave yellow-orange needles M.P. 264-265°C, with slight decomposition.

A mixed melting point of the acids obtained from the barium extract and the residue showed no depression.

Total yield of crude acid = 2 g = 31.6%.

The orange needles obtained by crystallization from glacial acetic acid were obtained as bright yellow needles on recrystallization from methyl alcohol or benzene M.P. 266 - 267°C.

**Analysis.**

\[C_{14}H_{20}O_2\text{ requires } C \; 43.27\%; \; H \; 1.57\%; \; Br \; 41.88\% \]

\[\text{found } C \; 42.37\%; \; H \; 2.40\%; \; Br \; 39.70\%; \; 40.90\% \]

From the analysis figures it can be seen that the product was not pure.

**2nd Method.**

An oxidation was carried out exactly as described in the first method but the purification of the product was somewhat different. The impure acid, after filtering and washing with dilute hydrochloric acid, was treated with ether which dissolved most of the residue. The ether solution was extracted several times with a 5% solution of potassium carbonate and these extracts on acidifying, gave a bright orange
precipitate. The acid was filtered, dried and recrystallized from methyl alcohol in long yellow needles M.P. 260 - 262°C after subliming about 200°C to small yellow needles.

The residue which remained after the ether extraction was boiled with an aqueous suspension of excess potassium carbonate and the solution of the potassium salt gave a further crop of the acid, when treated with hydrochloric acid. This was filtered and recrystallized from methyl alcohol as described above and again yellow needles were obtained M.P. 260°- 262°C after subliming at ca200°C. A mixed melting point with the first product showed no depression.

3rd Method.

An oxidation was used based on that described by Forrest and Tucker (J.C.S. 1948, 1140) for the oxidation of trimethylfluoranthenone, and similar to one used by Easton (unpublished results).

Dibromofluoranthenone (1.4g), sodium dichromate (12g) and glacial acetic acid (100ml) were boiled for eighteen hours. Acetic acid was then distilled off until the volume of the solution was about 30 ml and this was poured into water (ca.100 ml) acidified strongly with sulphuric acid. A red-orange precipitate was formed which, after standing, was filtered, then
treated with ether in which it was not completely soluble. The ether solution was extracted with a 5% solution of potassium carbonate and this carbonate extract gave an orange precipitate when acidified. This crystallized from glacial acetic acid in orange needles M.P. 260° - 262°C.

The insoluble residue was boiled with an aqueous suspension of potassium carbonate and the potassium salt decomposed with acid. In this way a further yield of the product was obtained which crystallized from glacial acetic acid also as orange needles M.P. 260° - 262°C. A mixed melting point of the two acids showed no depression.

Total yield of pure acid = 0.3g = 20.3%

Esterification of 2,7-dibromo-1-carboxyfluorenone.

(a) The acid was refluxed with methyl alcohol and 10% sulphuric acid for periods up to forty-eight hours, but on each occasion the starting product was obtained unchanged.

(b) Diazomethane was prepared from methylamine by the following set of reactions.

Stage I

\[ \text{CH}_3\text{NH}_2 + \text{NH}_2\cdot\text{CO}.\text{NH}_2 \rightarrow \text{CH}_3\cdot\text{NH}.\cdot\text{CONH}_2 + \text{H}_2 \]

\[ \text{CH}_3\cdot\text{NH}.\cdot\text{CO}.\text{NH}_2 + \text{HNO}_2 \rightarrow \text{CH}_3\text{N} \cdot (\text{NO}) \cdot \text{CONH}_2 + \text{H}_2\text{O}. \]
Stage II.

\[ CH_3N(\text{NO})CO.NH_2 + KOH \rightarrow CH_2N_2 + KNO + 2H_2O \]

Stage I, the preparation of nitrosomethylurea from \text{N}-methylurea was carried out according to Amdt (Ber. 1940, 73, 607) and stage II as described by the same author in Organic Syntheses, XV,3.

To a solution of 2:7-dibromo-1-carboxyfluorenone (0.1g) in the minimum quantity of ether was added an ethereal solution of diazomethane (ca. 0.9g diazomethane) prepared as above. The solution was left standing for three quarters of an hour by which time all evolution of nitrogen had ceased. The ether was then removed leaving a yellow solid which crystallized from methyl alcohol in long primrose-yellow prisms M.P. 180 -182°C.

Analysis.

\[ C_{15}H_{8}O_3Br_2 \] requires Br 40.4%  
found Br 40.95%

Decarboxylation of 2:7-dibromo-1-carboxyfluorenone.

1st Method.

The dibromo-acid was ground up finely with a large excess of soda-lime and heated to redness in a Pyrex tube. No sublimate was formed and when the residue was treated with acid only charcoal was obtained.
2nd Method.

2:7-dibromo-1-carboxyfluorenone (0.5g.) dissolved in quinoline (15ml) was heated with a small quantity of copper bronze. Bubbles appeared at 180°C indicating decarboxylation, and the mixture was boiled gently for thirty minutes. The cooled product was filtered, and the filtrate treated with hydrochloric acid and extracted with benzene. The benzene extracts were washed with dilute hydrochloric acid and water, dried over anhydrous sodium sulphate, then reduced to a small volume (ca. 20ml) and purified by chromatography. A short column of alumina (3/8 by 1") was used, and the chromatogram developed with benzene. A yellow band separated first, and this on evaporation yielded a yellow solid which crystallized from alcohol in yellow prisms M.P. 141 - 142°.

A mixed melting point with 2-bromofluorenone (M.P. 142-143°) showed no depression proving the decarboxylation product to be 2- bromofluorenone.
3rd Method.

An adaptation was employed of the method described by Dziewonski and Kahl (Chem. Abs. 1935, 29, 2941):

2:7-dibromo-1-carboxyfluorenone (0.5g), freshly precipitated mercuric oxide (0.32g) and water (5ml) were heated in a sealed tube at 185°C for thirty hours. The product was refluxed with concentrated hydrochloric acid (15 ml) for three hours, filtered and the residue extracted with ether then benzene. The extracts were washed with 5% potassium carbonate (A), dried over anhydrous sodium sulphate and finally evaporated, leaving a residue of red, yellow and some white solids. This dissolved in benzene (ca. 5ml) except for a small quantity of the dark red substance — presumably a mercury salt — which was filtered off.

The benzene solution was purified by passing it through a small column of alumina (4" by 3/16") and developing with benzene. A yellow band, brightly fluorescent in ultra-violet light, separated first. On evaporation of the solvent, a fine pale yellow
solid was obtained. A micro-melting point was carried out, and the compound, under the microscope, appeared in long yellow needles which sublimed and melted at 201-202°C.

A mixed melting point (micro) of this compound with an authentic sample of 2:7-dibromofluorenone (201.5 - 202°C) showed no depression.

The potassium carbonate extract was acidified and a yellow-orange precipitate was thrown down. It was filtered, dried and recrystallized from methyl alcohol.

A mixed melting point with the starting substance showed no depression.

**Attempted Dehalogenation of 2:7-Dibromofluorenone.**

2:7-Dibromofluorenone (0.5g) was dissolved in quinoline (15ml) and refluxed for thirty minutes with a small quantity of copper bronze. The resulting product was worked up in the manner described on p.

The benzene extract of the product was purified by running it through a short column of alumina (4" by 2") and developing with benzene. In this way a dark orange band was obtained which on evaporation gave an orange solid. This was recrystallized from glacial acetic acid in small, dark yellow prisms M.P. 194-195°C.

A mixed melting point with the starting substance
showed no depression.

**Dehalogenation of o-Bromobenzoic Acid.**

\[
\begin{align*}
\text{Br} & \\
\text{COOH} & \rightarrow \\
\text{COOH}
\end{align*}
\]

The experiment was carried out as described by Pursell (Thesis, Edinburgh p.134.)

Yield of benzoic acid 60%; M.P. 119-121°C.

**Attempted Dehalogenation of 2:7-Dibromo-1-carboxy-Fluorenone.**

The dibromo-acid (0.05g) and copper bronze (0.05g) were boiled under reflux overnight in toluene (15 ml). No change was observed in the appearance of the copper bronze. The product was worked up as described in the dehalogenation of o-bromobenzoic acid (Pursell, loc.cit). In this case no precipitate of copper oxide was formed and the alkaline extracts on acidification gave a yellow precipitate, which crystallized from methyl alcohol in long yellow needles M.P. 259-261°C. A mixed melting point with the starting substance showed no depression, proving that dehalogenation had not occurred.
Preparation of 4-bromofluoranthene.

1st Method.

The whole preparation was carried out as described by Easton (Thesis, Edinburgh, p.154).

Stage I, the reduction of fluoranthene to 1:2:5:4-tetrahydrofluoranthene was done by the method according to von Braun and Manz (Ber.1930, 63, 2612) with 5% sodium amalgam prepared as described in Fieser's "Experiments in Organic Chemistry" p.329. An excellent yield of a pure product was obtained.
Bromination of 1:2:3:4-tetrahydrofluoranthene gave an 81% yield of 5-bromo-1:2:3:4-tetrahydrofluoranthene according to the method of von Braun and Manz (Ann. 1932, 496, 192).

The method of Tobler, Holbro, Sutter and Kern (Helv. 1941, 24, 104 E) was used for the dehydrogenation of 5-bromo-1:2:3:4-tetrahydrofluoranthene to 4-bromofluoranthene. The yields were low in this case (under 50%) and varied when different samples of chloranil and sulphur-free xylene were used.

2nd Method.

The direct bromination of fluoranthene (20g) as described by von Braun (Ann. 1931, 489, 117) was employed.

A highly impure product (24g) was obtained, melting very low 80-86°C (lit 110°C), and two methods were used to purify it.

(a) Formation of 4-Bromofluoranthene Picrate.

By the formation of a picrate the impure bromocompound could be freed from any dibromofluoranthene since the latter does not form a derivative with picric acid and would remain in solution.

The impure 4-bromofluoranthene was dissolved in the minimum quantity of boiling alcohol, and to this solution was added a boiling, saturated, alcoholic solution of an equal weight of picric acid. The solution
turned deep red and long needles separated out on cooling M.P. 130 - 132°C (Lit. 129-130°C).

The picrate was decomposed by dissolving it in ether and shaking this solution with 10% sodium hydroxide. The ether extracts were dried and the solvent removed to give a white waxy solid. M.P. 90-95°C. Recrystallization from methyl alcohol gave almost colourless prisms M.P. 100 - 102°C.

(b) Sublimation.

The impure 4-bromofluoranthenone was heated in a vacuum sublimation apparatus at 110°C on an oil bath. At this temperature, 4-bromofluoranthenone and any unchanged fluoranthene sublimed out of the melt. The sublimate, which was obtained over a period of hours, was collected and further purified by dissolving it in the minimum volume of benzene and running it through a column of alumina (13" by 1/8") and developing the chromatogram with benzene. A small light blue fluorescent band of fluoranthene, easily visible in ultra-violet light, was removed from the column first. It constituted about 4% of the mixture.

The 4-bromofluoranthenone which was next eluted from the column was recrystallized several times from glacial acetic acid yielding finally small, pale yellow prisms M.P. 105-106°C. Mixed melting point with fluoranthene 45-46°C.
Analysis.

C\textsubscript{16} H\textsubscript{9} Br requires Br 23.47%
found Br 23.93%

Oxidation of 4-bromofluoranthene.

![Chemical structure](image)

The oxidation of 4-bromofluoranthene was carried out in exactly the same manner as the oxidation of 4,11-dibromofluoranthene \cite[p. 39]{ref} and cf. von Braun and Mansz \cite[Ann. 1932, 496, 194]{ref} also Fieser and Seligman \cite[J.A.C.S. 1935, 57, 2175]{ref}.

To a solution of 4-bromofluoranthene (2.5g) in glacial acetic acid (50 ml), just below the boiling point, was added cautiously a solution of chromic anhydride (A.R. 5g.) in water (5 ml.) and glacial acetic acid (5 ml.). The solution was left standing overnight then heated under reflux for three hours when a further solution of chromic anhydride (A.R. 5g.) in water (5 ml.) and glacial acetic acid (5 ml.) was added and the whole boiled for three hours more.
At the end of this period, acetic acid was distilled off till the volume of the solution was about 30 ml; this was poured into water (ca. 90 ml) and left standing overnight. The orange precipitate (A) which formed was filtered, and washed with dilute hydrochloric acid.

The filtrate yielded a further yellow precipitate (B) on standing, and this was also filtered and washed.

Both A and B were recrystallized from glacial acetic acid. Fraction A gave mainly yellow needles but also some amorphous crystals M.P. 252°C.

Fraction B recrystallized as long yellow needles M.P. 252 - 254°C. A mixed melting point of A & B showed no depression.

Total yield of impure product = 0.8 g = 30.5%

Analysis.

\[ C_{14}H_{7}O_3Br \]

Calculated C 53.43%; H 2.32%; Br 26.37%;

Found C 55.09%; H 2.27%; Br 26.50%.

Esterification of 2-Bromo-1-carboxyfluorenone.

(a) As in the case of 2,7-dibromo-1-carboxyfluorenone (p. 45) esterification with methyl alcohol and sulphuric acid was not successful.

(b) To a solution of 2-bromo-1-carboxyfluorenone (0.1g) in the minimum quantity of ether, was added 10ml
of a freshly prepared ethereal solution of diazo-methane ( p. 43 ). The solution was allowed to stand for thirty minutes then the ether was evaporated leaving a yellow solid. The ester was crystallized from methyl alcohol as yellow needles M.P. 140 - 142° C.

Analysis.

\( C_{15}H_{9}O_3Br \) requires C 56.81%; H 2.84%; Br 25.21%.

found C 56.54%; H 3.13%; Br 22.10%.

Although the percentage of bromine obtained by analysis was rather low, the ester was presumed to be pure since the acid from which it was obtained gave a good analysis.

Decarboxylation of 2-Bromo-1-carboxyfluorenone.

\[ \text{2-bromo-1-carboxyfluorenone (0.05g) dissolved in quinoline (5 ml) was heated with a small quantity of copper bronze. Bubbles appeared at about 190°C indicating decarboxylation, and the mixture was boiled gently for thirty minutes. The product was worked} \]
up in the same manner as before (p. 45).

The benzene extract was purified by running it through a short column of alumina (3" by ½") and developing with benzene. A yellow band separated quickly which, when the solvent was evaporated, yielded a yellow oily solid in a fawn pattern. A melting point was most indefinite due to the oily nature of the compound.

A little of the compound was heated on a clean piece of copper wire but no green flame could be seen, indicating the absence of halogen.

A 2:4-dinitrophenylhydrazone was prepared and its melting point compared with similar derivatives of fluorenone and 2-bromofluorenone.

2:4-dinitrophenylhydrazone of compound  295-297°C.
2:4-dinitrophenylhydrazone of fluorenone (Lit 284°C)  299-300°C.
2:4-dinitrophenylhydrazone of 2-bromofluorenone  275-278°C.

**Analysis.**

\[ C_{19}H_{12}O_4N_4 \] calculated N  15.56%
found N  15.20%

From the melting point and analysis of the 2:4-dinitrophenylhydrazone the compound was identified as fluorenone.
Attempted Dehalogenation of 2-Bromofluorenone.

(cf. p. 47)

2-bromofluorenone (0.1g) was dissolved in quinoline (5ml) and heated under reflux with a small quantity of copper bronze for thirty minutes. The solution was cooled, filtered free from copper, acidified with hydrochloric acid and extracted with benzene. This extract was run through a short column of alumina (4" by \frac{1}{2}") and developed with benzene. A yellow band separated which on evaporation yielded a yellow compound M.P. 141-142°C. A mixed melting point with the starting material showed no depression.

Attempted Bromination of 2-bromo-1-carboxyfluorenone.

2-bromo-1-carboxyfluorenone (0.1g) was dissolved in the minimum volume of glacial acetic acid and bromine (0.067g) was added dropwise to the solution whilst stirring vigorously. The mixture was left standing overnight in a corked vessel, and yellow crystals separated out which were filtered, M.P. 254-255°C. A mixed melting point with the starting substance showed a depression of a few degrees whereas a mixed melting point with 2,7-dibromo-1-carboxyfluorenone showed a considerable depression 223 - 225°C: indicating that bromination had not taken place.
Oxidation of 4-Bromacenaphthene.

The method used was that due to Dashewskii and Karishin (C.A. 1938, 32, 4974)

4-bromacenaphthene (4g) was dissolved in 90% glacial acetic acid (60ml) and digested with sodium dichromate (20g) in a water-bath for one hour. A red substance remained which was filtered off. The filtrate was diluted with three volumes of water and the precipitate which formed was filtered and extracted from an ether solution with 2.5% potassium carbonate. On acidifying the alkaline layer a white precipitate was formed which was filtered and dried. M.P. 200-202°C with decomposition. Recrystallization from benzene yielded long white crystals M.P. 213-219°C (lit 220°C)

The red insoluble portion was crystallized from glacial acetic acid M.P. 135-144°C.

It was presumed to be a mixture of the acid and the anhydride (M.P. 210°C lit.) since the same condensation product with o-phenylenediamine was obtained with this
mixture as with the pure acid.

**Attempted Esterification of 4-bromonaphthalic acid.**

Several attempts were made to esterify the acid by refluxing it with methyl alcohol containing 10% concentrated sulphuric acid for periods up to fifty-six hours, but none was successful.

The method of esterification with diazomethane (p. 43) was also tried without success.

**Condensation of 4-bromonaphthalic acid with O-phenylenediamine.**
Equimolecular quantities of o-phenylenediamine and either the white or the red compound (p. 57) were dissolved in glacial acetic acid and boiled for a few minutes. In each case the same yellow amorphous solid separated out on cooling. It charred on heating and gave no definite melting point. Recrystallization from glacial acetic acid yielded a yellow amorphous solid subliming at about 165°C and melting over a wide range 228–266°C. This indicated the formation of the two isomers A and B.

**Analysis.**

C₁₈H₉NO₂Br requires N 8.02%; Br 22.88%.
found N 7.96%; Br 23.61%.

An attempt was made to separate the isomers by chromatography.

The crude mixture (0.38g) was dissolved in hot benzene (ca.60ml) and on cooling, a flocculent yellow precipitate settled out and was filtered off (0.25g). The remainder of the benzene solution was run through a column of alumina (13” by ½”) prepared with benzene, which was also used to develop the chromatogram.

The compound showed a particularly vivid greenish-yellow fluorescence in benzene solution in daylight and this was even more marked in ultra-violet light. As the column was developed a colour gradient was set up – dark yellow at the top of the column diffusing
into paler yellow at the bottom.

Unfortunately no complete separation was brought about; the various 100 ml portions of eluate yielding, on evaporation of the solvent, yellow solids exhibiting a gradual decrease in melting point but no depression when a mixed melting point was determined. This indicated that the first fractions were richest in one isomer and the last richest in the other.

A separation based on the different solubilities of the isomers in benzene was carried out.

All the fractions from the chromatogram were treated with the minimum volume of benzene, boiled for a few minutes then filtered hot. Yellow needles separated from the filtrate on cooling and were purified by further recrystallization from benzene M.P. 219-221°C.

Analysis.

C\textsubscript{18} H\textsubscript{9} N\textsubscript{2} OBr. requires N 8.02 %; Br.22.88%.

found N 8.30%; Br.21.81%.

The portion filtered off before chromatographing the benzene solution was examined. It sublimed at 228°C and melted at 258-265°C and was purified by repeated recrystallizations from toluene yielding, finally, rosettes of yellow needles M.P. 270-272°C.
Analysis.

C₁₈H₉N₂O₃Br required N 3.02%; Br 22.88%.

found N 3.12%; Br 19.05%

As in a previous case (p.54) the percentage of bromine obtained by analysis was low. In spite of this fact and in view of the figure obtained for nitrogen, the compound was presumed to be pure.

Oxidation of Fluoranthenes.

\[ \text{The method used was based on that described by Forrest and Tucker (J.C.S.1948,1140) for the oxidation of trimethylfluoranthenes (cf.p.42).} \]

\[ \text{A solution of fluoranthenes (10g) and sodium dichromate (150g) in glacial acetic acid (500 ml) was boiled for 13 hours. Acetic acid was then distilled off till the volume of the solution was about 200 ml and this was poured into about 700 ml sulphuric acid (1:4) and water. A bright orange precipitate was thrown down which, after standing for a few hours, was filtered and washed with dilute sulphuric acid.} \]
The acid was purified by recrystallization from glacial acetic acid M.P. 191.5°C (lit 192°C)

**Bromination of Fluorenone-1-carboxylic acid.**

Fluorenone-1-carboxylic acid (2g) was left standing overnight in bromine (25 ml). At first the mixture turned into a thick paste, but after standing overnight it became liquid again.

The solution was poured into water (ca. 200ml) and air bubbled through to remove excess hydrogen bromide and bromine. An orange solid was obtained which was filtered and washed with alcohol M.P. 224-226°C.

The compound was recrystallized from glacial acetic acid in long red prisms M.P. 224-226°C and finally from benzene M.P. 226-228°C. A mixed melting point with the starting acid showed a depression of sixty degrees. Yield of pure compound = 1.6g = 59.2%.

**Analysis.**

C_{14}H_{7}O_{3}Br 
requires C 55.49%; H 2.32%; Br 26.37%
found C 55.30%; H 2.76%; Br 27.90%

23.78%
Esterification of 7-bromo-1-carboxyfluorenone.

(a) 7-bromo-1-carboxyfluorenone (0.6g) was refluxed for thirty minutes with ethyl alcohol (25 ml) and concentrated sulphuric acid (10 drops) and a clear yellow solution was obtained. Alcohol was removed until the volume of the solution was about 10-12 ml and from this, yellow prisms separated out on cooling. M.P. 98°C.

The ester was purified by crystallization from a mixture of benzene and light petroleum (40-60) M.P. 102-103°C.

Analysis.

C_{16}H_{11}O_3Br requires Br 24.13%  
found Br 23.75%

(b) 7-bromo-1-carboxyfluorenone (0.25g) was refluxed for thirty minutes with methyl alcohol (15 ml) and concentrated sulphuric acid (5 drops) and a clear solution obtained. The volume of the solution was reduced to 10 ml and yellow prisms were obtained. M.P. 148-158°C. Crystallization from benzene gave prisms M.P. 164°C.

Analysis.

C_{15}H_{9}O_3Br requires Br 25.21%  
found Br 25.40%

Decarboxylation of 7-bromo-1-carboxyfluorenone.
Decarboxylation of 7-bromo-1-carboxyfluorenone.

7-bromo-1-carboxyfluorenone (0.15 g) was dissolved in quinoline (15 ml) and heated with a small amount of copper bronze. Bubbles were evolved at 160°C and heating was continued up to 180°C for forty-five minutes. The solution was cooled, filtered free from copper, and the filtrate, after acidifying with dilute hydrochloric acid, was extracted with ether. The ether solution was extracted with 5% potassium carbonate solution then dried over anhydrous sodium sulphate. On evaporation, the ether extract yielded yellow prisms which were crystallized from ethyl alcohol M.P. 136°C. A mixed melting point with 2-bromo-fluorenone showed no depression.

On heating a small portion of the decarboxylation product on a clean piece of copper wire a bright green flame was obtained showing the presence of halogen.
Attempted Bromination of 7-bromo-1-carboxyfluorenone.

Several attempts were made to brominate this acid - by refluxing with bromine in the absence of a solvent and in the presence of a halogen carrier, e.g. iodine or an iron nail; by leaving the acid in solution in bromine in the presence of a halogen carrier - but none of these was successful. In each case the starting product was obtained back unchanged.

Preparation of 4:11-dicyano-fluoranthenone.

1st Method.

(a) A solution of 4:11-dibromofluoranthenone (6g; 1mol) in pyridine (18 ml) and cuprous cyanide (3.3g; 2.2 mol) were heated at 200-230°C for six hours in a sealed Carus tube. When the tube was cool, the contents were removed with dilute hydrochloric acid, and filtered. Both the filtrate and the residue were extracted with benzene and the combined extracts were purified by running them through a column of alumina
alumina (9" by ½"), developing with benzene. A very small quantity of a yellow fluorescent compound was obtained M.P. 217-219°C.

(b) A similar experiment was carried out only the Carius tube and contents were heated for twenty-four hours at 200-230°C. On acidifying the product a certain amount of the starting material was obtained. The filtrate was extracted with glacial acetic acid and the extract on dilution with water, yielded a very small amount of a compound M.P. 219-223°C.

(c) 4:11-dibromofluoranthene (1g.), cuprous cyanide (0.7g.) and pyridine (25 ml) were heated in a sealed tube for twenty-four hours at 260°C.

The product was extracted with glacial acetic acid and on diluting the extracts with water a compound M.P. 340°C was obtained.

2nd Method.

The method outlined in the German patent (533,962) was also tried.

4:11-dibromofluoranthene (30 parts) was melted in a boiling tube immersed in a metal bath at 500°C and whilst stirring the melt, cuprous cyanide (26 parts) was added in small portions, a process taking fifteen minutes. The melt kept at 320 - 330°C for fifteen minutes longer. On cooling, a hard brown mass was
obtained which was pulverised then added to boiling dilute nitric acid to remove copper salts. When free from copper, the residue was extracted with glacial acetic acid and a yellow solid obtained. This was crystallized from glacial acetic acid giving a compound M.P. 310 - 315°C.

3rd Method.

A method was employed analogous to that used by von Braun and Manz (Ann.1931, 488,117) for the conversion of 4-bromofluoranthenone to 4-cyanofluoranthenone.

4:11-dibromofluoranthenone (1 mol) and cuprous cyanide (2.2 mol) were mixed thoroughly then heated in a boiling tube in a metal bath at 260°C for six hours. The hard chocolate brown mass obtained on cooling was ground up finely and extracted with various solvents; the extracts yielded the following products.

(I) Chloroform extract: a small quantity of unchanged dibromofluoranthenone.

(II) Xylene extract: some impure fluoranthene.

(III) Chlorobenzene extract: a yellow solid which sublimed at ca. 200°C, started to decompose about 280°C and had not melted up to 320°C.

4th Method.
4th Method.

4,11-dibromofluoranthene (3g.) was dissolved in benzyl cyanide (40 ml) and refluxed for twenty-four hours with cuprous cyanide (1.8g.). The product was cooled thoroughly then filtered, and the residue washed with alcohol and ether. The residue was extracted, first with chloroform then xylene to remove any dibromofluoranthene or fluoranthene and finally with chlorobenzene. The latter extracts gave a dirty yellow compound subliming at about 200°C which did not melt up to 320°C but showed distinct charring.

It was recrystallized from chlorobenzene.

Analysis.

C₁₈H₈N₂ requires N 11.11%.
found N 10.30%

Oxidation of 4,11-dicyanofluoranthene.

The procedure was identical with that used for the oxidation of 4,11-dibromo- and 4-bromo-fluoranthene (p. 39, 52)
4:11-dicyanofluoranthene (1.5g) was suspended in glacial acetic acid (200 ml) and a solution of chromic anhydride (A.R. 4g) in water (3ml) and glacial acetic acid (6ml) was added to the suspension just below its boiling point. The mixture was allowed to stand overnight, then heated under reflux for three hours. All the solid was not in solution at the end of this period, so a solution of chromic anhydride (A.R. 4g) in water (8 ml) and glacial acetic acid (100 ml) was added and boiling continued for a further three hours. Acetic acid was distilled off until the volume of the solution was about one third of the original volume and this was poured into water (ca. 150-200 ml). The precipitated acid was filtered then extracted with potassium carbonate. The carbonate extracts on acidifying threw down a yellow, somewhat gelatinous precipitate which, after standing, was filtered and dried.

No solvent could be found from which to recrystallize this acid though many were tried: methyl alcohol, ethyl alcohol, benzene, xylene, chlorobenze, glacial acetic acid.

A micro-melting point showed sublimation at 260°C to yellow needles which did not melt up to 360°C.

Yield = 0.56 g.
Analysis.

\[ \text{C}_{16} \text{H}_8 \text{O}_7 \]

requires C 61.53\%; H 2.56\%; N 0\%

found C 50.82\%; H 3.21\%; N 0.4\%

It is obvious from the above analysis that oxidation of dicyanofluoranthenes does not proceed in the usual manner. If this were so the product would presumably be fluorenone-1:2:7-tricarboxylic acid \[ \text{C}_{16} \text{H}_8 \text{O}_7 \] (the two cyano groups having been hydrolysed). Clearly this is not the case.

Attempted Esterification of Oxidation Product.

Acid (0.1g) was boiled for twenty four hours with methyl alcohol (15 ml) and concentrated sulphuric acid (10 drops). A suspension of a fine yellow solid was obtained and filtered, and from the filtrate a fine yellow flocculent precipitate separated out on cooling. It was filtered, dissolved in ether and extracted with 5% potassium carbonate when the yellow colour was transferred from the ether to the carbonate layer. Acidification of the carbonate layer gave back the yellow flocculent precipitate which was filtered and dried. A micro melting point showed that the compound sublimed at approximately 260\(^\circ\)C to yellow prisms, which did not melt below 360\(^\circ\)C. It was presumed to be the starting substance.
Hydrolysis of $\beta$-Naphthonitrile to $\beta$-Naphthoic acid.

The method of hydrolysing nitriles to the corresponding acids by way of the imino-ethers due to Hager, von Arendonk and Shonle (J.A.C.S. 1944, 66, 1932) was employed.

$\beta$-naphthonitrile (1g) was dissolved in alcohol (20 ml) and the solution was saturated with dry hydrogen chloride at 5°C. The flask was then stoppered tightly and left in a warm place overnight. On chilling the solution and filtering, the imino-ether hydrochloride (0.32g) M.P. 180-191°C, was obtained. By diluting the mother liquor with ether a further crop of crystals (0.37g) was obtained. M.P. 190-191°C.

The imino-ether was suspended in water (10ml) and
heated on a steam bath for one to two hours whilst stirring all the time. A yellow oil was thus obtained which, on chilling, yielded the solid ethyl-β-naphthoate (0.65g.).

The ester was hydrolysed by boiling for one to one and a half hours with a 4% solution of alcoholic sodium hydroxide (25 ml), which was prepared by dissolving sodium hydroxide (1g) in water (1ml) and diluting to 25 ml with alcohol.

The acid obtained was purified by recrystallization from alcohol. M.P. 180 - 184°C.

Yield = 0.5g = 44%

**Attempted Hydrolysis of α-Naphthonitrile.**

The above method was applied to α-naphthonitrile. No hydrolysis occurred and only unchanged starting material was obtained.

**Attempted Hydrolysis of 4:11-Dicyanofluoranthenone.**

The above method of hydrolysis was tried on 4:11-dicyanofluoranthenone but only unchanged starting material was obtained.

**Hydrolysis of 4:11-Dicyanofluoranthenone.**
4:11-Dicyanofluoranthene (0.1g) was boiled for one hour with glacial acetic acid (2ml), concentrated sulphuric acid (1 ml) and water (1ml). The dicyano compound was not itself soluble but after an hour its colour had changed to brown. The precipitate was filtered off and dried. A micromelting point showed that the compound sublimed at ca. 230°C to tiny yellow needles which did not melt up to 360°C. As no suitable solvent could be found from which to recrystallise the acid, it was purified by esterification.

**Esterification of 4:11-Dicarboxyfluoranthene.**

4:11-Dicarboxyfluoranthene (0.35g) was heated under reflux overnight with methyl alcohol (1.75 ml) and concentrated sulphuric acid (3 drops). The resulting solution was filtered and dark yellow flocculent crystals separated out of the filtrate on cooling. After filtering and drying the product, a micro melting point showed that most of the solid melted at 130°C but there was also a small amount of unchanged acid.

The ester was purified by dissolving it in benzene (ca. 10ml), running this solution through a small column of alumina (4" by ½") and developing with benzene. The alumina retained the acid and the pure ester was obtained on evaporating the eluate.

A micro melting point showed that the ester
sublimed at 140°C to small yellow prisms which melted finally at 173 - 180°C.

Analysis.

C₂₀ H₁₄ O₄ requires C 75.47%; H 4.40%
found C 75.34%; H 4.38%

Decarboxylation of 4:11-Dicarboxyfluoranthenes.
Kenton (Thesis Edinburgh p.54)

Fluoranthenes 4:11-dicarboxylic acid (ca. 0.05 g) was dissolved in quinoline (10 drops), and when the solution was cool, a small amount of copper bronze was added. The mixture was heated in a metal block, and at 205°C bubbles began to appear, indicating that decarboxylation was taking place. The mixture was kept at this temperature for about twenty minutes then it was treated with dilute hydrochloric acid when a dirty brown precipitate formed which was filtered and dried. As the yield of product was so small, purification was achieved by carrying out a micro-sublimation in the following manner:

A small quantity of the impure acid was placed on a cover slip on top of a microscope slide, and a second cover slip was placed above the first, but separated from it by means of two thin pieces of glass arranged as shown below:
Thus when the compound was heated on the micro melting-point apparatus to a suitable temperature, the sublimate formed on the upper, somewhat cooler cover-slip.

From 170°G onwards, fine clear needles formed on the top cover-slip, and from about 210°G an oily yellow solid was deposited. Finally the whole substance melted to a yellow liquid at 272-274°G.

Since the acid thus obtained was present in such small quantity and as it was impure, mixed micro-melting-points with 4-carboxy- and 11-carboxy-fluoranthenes, which were also slightly impure, were inconclusive.

**Attempted Preparation of 4-Bromo-11-carboxyfluoranthenes.**

**Stage I: Attempted Preparation of a Grignard Reagent from 4;11-Dibromofluoranthene.** (cf. von Braun Ann. 1931, 432, 116)

**1st Method.**

4;11-Dibromofluoranthene (2g, 1 mol) was suspended in anhydrous ether (75 ml), and a few drops of the suspension were added to Grignard magnesium (0.17g, 1mol) and a crystal of iodine. As there was no immediate reaction, a few drops of methyl iodide were added. The remainder of the dibromofluoranthene suspension was added but even after prolonged heating on a water bath, no interaction between the magnesium and the
halogen compound occurred.

2nd Method.

The above experiment was repeated with anisole as solvent in which the dibromofluoranthenes was readily soluble. The reaction mixture, which contained excess magnesium (2.5 mol.) was refluxed for twenty-four hours on a water bath. At the end of this period, dry solid carbon dioxide was added to the filtered solution, but only unchanged dibromofluoranthenes separated out.

Debromination of 4:11-Dibromofluoranthenes.

![Debromination of 4:11-Dibromofluoranthenes](image)

Although Raney nickel-aluminium alloy was used for the dehalogenation the methods described by Papa, Schwenk and Whitrom (J. Org. Chem. 1942, 7, 587) and Papa, Schwenk and Ginsberg (Ind. Eng. Chem. (Anal.) 1943, 15, 576) were found to be unsuitable for dibromofluoranthenes and the following method was used.

To a boiling solution of 4:11-dibromofluoranthenes
(0.3g) in alcohol (10ml) and 10% alcoholic potassium hydroxide (75 ml) was added Raney nickel-aluminium alloy (3.5g). The alloy was added in four portions over a period of ten minutes, and the flask and contents were shaken vigorously at each addition. The mixture was then heated until all the alloy had reacted (1-1½ hours), and the flask was occasionally shaken.

The hot solution was filtered and the product precipitated by adding water to the filtrate which was next made acid to Congo Red paper with concentrated hydrochloric acid and heated to keep all aluminium salts in solution. On cooling, the precipitate was filtered, washed with water and crystallized from alcohol to give impure fluoranthene M.P. 100-104°C.

Yield 0.1g = 60%

Recrystallization from alcohol gave pure fluoranthene M.P. 110°C.

Preparation of 4-and 11-methylfluoranthene.

Preparation of 4- and 11-chloromethylfluoranthene

Stage I

\[ \text{Molecule A} \rightarrow \text{Molecule B} + \text{Molecule C} \]
Many attempts were made to prepare these compound of which two are here reported.

1st Method.

A method analogous to that used by Cook and Preston (J.C.S.1944, 560) for the chloromethylation of 9:10-dihydrophenanthrene was tried without success.

Paraformaldehyde (3.4g) was added to an ice-cold suspension of fluoranthene (10g) in glacial acetic acid (30ml) and dry hydrogen chloride passed through the mixture for two days. No visible change took place, and the fluoranthene was recovered unchanged.

An attempt was made to obtain the fluoranthene in solution and the experiment was repeated with 100 ml glacial acetic acid. Even then the fluoranthene separated out on cooling and saturation with dry hydrogen chloride had to be done at room temperature to prevent the glacial acetic acid from solidifying.

Again, neither the paraformaldehyde nor the fluoranthene went into solution and the latter was recovered by pouring the mixture into water and extracting with benzene. The extract was well washed, dried over anhydrous sodium sulphate and the solvent evaporated.

2nd Method.

The method used is to be found in Fieser's Organic Reactions, Vol I p.65 (cf. Horn and Warren J.C.S. 1946, 144.)
Fluoranthene (10g; 0.05 mol), paraformaldehyde (6g; 0.067 mol), glacial acetic acid (17g), concentrated hydrochloric acid (19g) and syrupy phosphoric acid (9g) were heated at 100°C, with stirring, for eight to nine hours. Shorter periods (viz. three to four hours) were insufficient to complete the reaction, and yielded unchanged fluoranthene.

The reaction mixture was poured into water (ca. 200ml) and a lump of plastic solid was obtained. The supernatant liquid was decanted and the solid dissolved in a small volume of benzene as it was not readily soluble in ether. Ether added to the benzene solution precipitated a small quantity of a brown substance which was removed during the washing of the extract, first with water then with 5% potassium carbonate. The extract was dried over anhydrous sodium sulphate then the ether and benzene were evaporated off to yield a mixture of 4- and 11-chloromethylfluoranthenes in the form of a dark brown oil which was not purified at this stage.

Yield 13 g = 96.9%

Analysis:

\[ \text{C}_{17} \text{H}_{11} \text{Cl} \] requires Cl 13.95%
found Cl 15.22%

Stage II: Reduction of 4- and 11-chloromethylfluoranthenes.
Stage II: Reduction of 4- and 11-chloromethylfluoranthene.

The reduction was carried out with Raney nickel-aluminium alloy and the method was a modification of that of Papa, Schwenk and Whitman (J. Org. Chem. 1942, 7, 537) (cf. Schwenk, Papa and Ginsberg (Ind. Eng. Chem. (Anal.) 1943, 15, 576)).

A mixture of impure 4- and 11-chloromethylfluoranthene (15g) was heated to boiling with 10% potassium hydroxide (350 ml). Raney nickel-aluminium alloy (40g) was added to the boiling solution in small portions over a period of thirty minutes; the flask was shaken vigorously after each addition. The
mixture was heated under reflux until all the alloy had ceased to react - about two hours - and again the flask and contents were frequently shaken. The solution was cooled slightly then filtered; the filtrate was poured into water (ca.300ml), acidified to Congo Red paper with concentrated hydrochloric acid, then heated slightly to dissolve any potassium chloride or aluminium salts.

On cooling the solution an oil separated which, after decanting off the aqueous layer, was extracted with ether, dried over anhydrous sodium sulphate, and the ether then removed. To ensure complete dryness, the product was next taken up in benzene, again dried over anhydrous sodium sulphate and the solvent removed.

A light brown oil, a mixture of 4- and 11- methylfluoranthene was thus obtained.

Yield = 6g = 55%

Attempts to Separate 4- and 11- methylfluoranthene.

The first method of separation tried was chromatography. The oil obtained as described above, was dissolved in benzene (ca. 100 ml) and run through a column of alumina (18" by 1½") prepared with benzene. The chromatogram was developed with a mixture (1:5) of benzene and light petroleum (100 - 120°C).
A bright yellow-green fluorescence was visible in ultra-violet light, but no separation into bands was observed.

15 ml portions of eluate were collected and in all cases a brown syrup was obtained on evaporation of the solvent. This syrup could not be obtained crystalline either by trituration or by treatment with the usual solvents.

**Analysis.**

\[ C_{17}H_{12} \text{ requires } C \ 94.42\%; \ H \ 5.56\% \]

\[ C_{17}H_{12} \text{ found } C \ 90.9\%; \ H \ 6.04\% \]

No picrate could be isolated at this stage as mixtures of the picrate and picric acid were obtained. Recrystallization was impossible as the picrate decomposed.

About 1 ml of the syrup was steam distilled, and a yellow substance formed on the walls of the condenser. It was extracted with ether, the extract dried and the solvent removed to give a waxy, greenish-yellow solid M.P. 68-72°C. A picrate was prepared in alcohol M.P. 119-120°C. A mixed melting point with picric acid showed no depression, but the compound was thought to differ from picric acid as it crystallized from alcohol in a felt of orange needles.

The residue from the steam-distillation was extracted with ether; the extract dried and the ether removed
leaving an oil. An attempt at picrate formation was not successful. The mixture obtained was dissolved in benzene and chromatographed through a short column of alumina \( (8" \text{ by } \frac{3}{4}"") \) made up and developed with benzene. The alumina held back all the picric acid at the top of the column, as a yellow non-fluorescent band. The hydrocarbon, from the decomposed picrate, passed through the column exhibiting the characteristic yellow-green fluorescence of fluoranthene in ultra-violet light. The eluate on evaporation gave a syrup which defied all attempts at crystallization.

The remainder of the syrup obtained from the reduction of 4- and 11-chloromethylfluoranthene was distilled in a high vacuum and two fractions were obtained.

A. Yellow syrup B.P. 178-182°C at 0.05 mm Hg.
B. Yellow syrup B.P. 210-214°C at 0.01 mm Hg.

Crystals formed in the yellow syrup A. on long standing but they could not be separated. All attempts at trituration and crystallization also failed. A picrate was prepared in ethyl alcohol and recrystallized from the same solvent in orange needles which sublimed about 85°C and melted at 165°C.

(cf. lit. M.P. picrate of 4-methylfluoranthene 172°C).

Analysis.

\[ C_{23}H_{15}N_3O_7 \text{ requires } C \ 62.01\%; H 3.37\%; N 9.43\% \]

\[ \text{found } C \ 61.14\%; H 3.34\%; N 8.90\% \]
The yellow syrup B could not be obtained in crystalline form either and yielded neither a picrate nor a 1:3:5-trinitrobenzene derivative.

1st scheme for Attempted Synthesis of 2:7-dibromo-1-carboxyfluorenone.
Preparation of 2;3'-Azotoluene.

The condensation of m-nitrotoluene and o-toluidine in the presence of sodium hydroxide was carried out in the manner described by Mayer and Freitag (Ber. 1921, 54, 347).

A dark red liquid was obtained B.P. 190-195°C at 8 mm. Yield = 55%

Preparation of 3;2'-Dimethylbenzidine.

2;3'-Azotoluene was reduced in alcoholic solution by stannous chloride (A.R.) and concentrated hydrochloric acid as described by Mayer and Freitag (loc. cit.).

A reddish-brown glassy solid was obtained, B.P. 243-246°C at 12 mm. Yield = 57%

Preparation of 4;4'dibromo-3;2'-dimethylidiphenyl.

1st Method.

The method consisted of a tetrazotisation of 3;2'-dimethylbenzidine followed by the formation and subsequent decomposition of the mercury double salt as described by Schmechten (Ber. 1932, 65, 1605).

(a) Tetrazotisation and Formation of Mercury Double Salt.

A suspension of dimethylbenzidine (16g) in concentrated hydrochloric acid (120 ml) and water (100 ml) was cooled to below 0°C and tetrazotised with a
solution of sodium nitrite (13g) in water (50 ml) with the temperature of the reaction mixture maintained at -5°C to 0°C. An orange coloured solution containing a small amount of orange solid was obtained, and to this was added the suspension obtained by adding mercuric nitrate (56g) to a solution of potassium bromide (32g) in water (1,000 ml). The temperature was kept below 0°C and an orange powder separated out which was washed well with water by decantation, then filtered and dried. The powder darkened on standing and lost its amorphous appearance after a short time.

(b) Decomposition of Mercury Double Salt.

The mercury double salt (10g) was powdered with potassium bromide (2.5g) and the mixture introduced into a long narrow Carus tube - 2' by $\frac{3}{8}$" - sealed at one end and fitted with a long thick stirring rod. The tube was heated gently, from the open end downwards in such a way that a brown oil, which was produced, just distilled from the portion which was being heated. Stirring was continued throughout the operation and when heating was complete white needles appeared at the bottom end of the tube. The tube was cut and the solid extracted with ether. The extract was treated with charcoal to purify it, and when the solvent was removed a white residue remained which was crystallized from methyl alcohol in long needles M.P.
M.P. 230 - 231°C. The yield was very poor.

Analysis:

\[ \text{C}_{14}\text{H}_{12}\text{Br}_2 \text{ requires: Br } 47.05\% \]
\[ \text{found: Br } 44.24\% \]

This direct fusion did not always yield a crystalline product; in several instances a brown oil was formed which was extracted with ether, and, after removing the solvent, was used in the next stage of the synthesis, namely the preparation of 4:4'-dibromo-3:2'-dicarboxyldiphenyl.

2nd Method.

A tetrazotisation followed by a Sandmayer reaction was used as described by Hodgson and Walker (J.C.S. 1933, 1620). The cuprous bromide was freshly prepared by one of the standard methods.

Finely powdered sodium nitrite (6.4g) was added with vigorous stirring to ice-cold concentrated sulphuric acid (70 ml). The temperature of the mixture was raised to 70°C until all the nitrite was dissolved, then the solution was cooled to room temperature, and to it was added a cold solution of dimethylbenzidine (9g) in glacial acetic acid (125ml) with vigorous stirring, the temperature being kept below 20°C. A brown, somewhat viscous solution and a considerable
amount of dark coloured solid were obtained and the mixture was added, again with vigorous stirring, to a solution of cuprous bromide (23g) in 40% hydrobromic acid (230ml). A violet liquid resulted which was poured into water (2 litres), when the colour changed to green, and extracted with ether. The extracts were dried and the solvent removed leaving a purple oil which defied all attempts at recrystallization.

Preparation of 4:4'-dibromo-3:3'dicarboxyldiphenyl.

The method was an adaptation of that used by Freitag and Mayer for the oxidation of 2:3'-dimethyl-diphenyl (Ber.1921, 54, 351.)

A 2% solution of potassium permanganate (9.5 g) in water (475 ml) was added gradually to a slowly boiling suspension of impure dibromodimethyldiphenyl (5g) in water (100 ml), with continual stirring. The mixture was refluxed for eighteen hours and alcohol then added until all the purple colour was discharged. The solution was cooled, filtered, and the filtrate acidified with hydrochloric acid. A white precipitate formed which, after standing for a short while, was filtered, washed then crystallized from glacial acetic acid.

Analysis.

C₁₄ H₉ O₄ Br₂ requires C 42.00%; H 2.00%; Br 40.00%.
found C 44.05%; H 2.30%; Br 37.27%
Due to the very small yield of acid finally obtained, the method was abandoned.

2nd Scheme for Attempted Synthesis of 2:7-dibromo-1-carboxyfluorenone.
Preparation of m-tolyhydroxylamine.

The method used was adapted from that described by Gattermann and Wieland for the preparation of phenylhydroxylamine (Laboratory Methods of Organic Chemistry p. 165).

Yield = 60%

Preparation of m-nitrosotoluene.

Again the method was adapted from one described by Gattermann and Wieland (ibid., p. 169) for the preparation of nitrosobenzene.

Yield = 60%  M.P. 55-56°C.

Preparation of 2:3'-Azotoluene.

The condensation of m-nitrosotoluene and o-toluidine was carried out in a manner similar to that described by Gattermann and Wieland (ibid., p. 171) for the preparation of azobenzene.

A solution of m-nitrosotoluene (1 g) in glacial acetic acid (10 ml) was added to a solution of o-toluidine (1 ml) in glacial acetic acid (3 ml) and the mixture was heated on a water bath for twenty-four hours, at the end of which time the colour had changed to a reddish violet. This product was poured into water (ca. 50 ml) and extracted with ether; the extracts were washed, dried over anhydrous sodium sulphate then the solvent removed leaving a dark red oil. This was purified by dissolving it in benzene
ca. 10 ml), running it through a column of alumina (18" by \(\frac{3}{8}\"\)), and developing with benzene. A red, eluate was obtained first which on evaporation gave a clear dark red oil.

\[
\text{Yield} = 1.6 \text{ g} = 97\%
\]

Preparation of 2,3-dimethylhydrazobenzene (in solution)

The method was adapted from that described by Gattermann and Wieland (ibid., p. 174) for the reduction of azobenzene.

2,3'-azotoluene (1.6g) was dissolved in alcohol (15 ml) containing sodium hydroxide (1.8g). Zinc dust (5g) was added portionwise to the solution with vigorous shaking at each addition, then the mixture was heated on a water bath, again with frequent shaking, until the solution became colourless (about one hour). More alcohol (20 ml) was added and the solution heated to boiling and filtered.

Benzidine Transformation on 2,3'-dimethylhydrazobenzene

The alcoholic solution obtained in the preceding preparation was added gradually, with constant shaking, to ice-cold 7. N hydrochloric acid (50 ml: obtained by diluting concentrated hydrochloric acid with an equal volume of water). A white solid began to separate out after five minutes shaking and more concentrated hydrochloric acid (25 ml) was added and
the mixture was allowed to stand overnight when the liquid acquired a purple colour. 3:2'-dimethylbenzidine hydrochloride was filtered off, washed with dilute acid and crystallized from water containing two or three drops of hydrochloric acid. Long colourless needles were obtained.

Yield = 1.2g = 55%

Analysis.

\[ \text{C}_4\text{H}_8\text{N}_2\text{Cl}_2 \] requires Cl 24.35%; N 9.83%

found Cl 24.95%; N 10.05%

**Attempted Preparation of 4:4'-dibromo-3:2'-dimethyl-diphenyl.**

The methods of Hodgson and Walker (J.C.S. 1933, 1602 and also this thesis p. 87) and Schnechten (Ber., 1932, 65, 1605 and also this thesis p. 85) were employed.

(a) **Modified Sandmeyer method.**

3:2' dimethylbenzidine hydrochloride (1.2g) was added gradually to a cold solution of sodium nitrite (0.7g) in concentrated sulphuric acid (8 ml) prepared as described on p. 87. The reaction mixture was stirred vigorously throughout the addition and the temperature maintained below 20°C. When all the solid had been added, glacial acetic acid (10 ml) was added slowly and again the temperature was kept below 20°C. The resulting dark red solution of the
tetrazonium salt was added, with stirring, to a solution of freshly prepared cuprous bromide (2.6g) in 40% hydrobromic acid (26 ml) and a brown solid in a violet solution was obtained. The product was poured on to ice (ca. 100g) when a dark brown solid formed which was left standing overnight then filtered. The product was purified by dissolving it, incompletely, in benzene, washing the benzene extract with acid, 5% carbonate then finally drying it and reducing the volume to about 10 ml. This solution was then run through a short column of alumina (3" by 3"), developing with benzene. A yellow-orange band separated which, on evaporation of the solvent, yielded a bright dark red oil, presumably an azo compound (cf. p. 88).

(b) Attempted Substitution of Bromine through the Mercury Double Salt.

3-2′-dimethylbenzidine hydrochloride (2g) was added gradually to a cold solution of sodium nitrite (1g) in concentrated sulphuric acid (p. 87) with the temperature below 20°C. When tetrazotisation was complete the temperature of the solution was lowered to -5°C, and the suspension obtained by adding mercuric nitrate (6.5g) to a solution of potassium bromide (7.2g) in water (25 ml) was run in cautiously keeping the temperature as low as possible. The
temperature was maintained as near 0°C as possible and only once rose to 12°C.

A rather sticky red amorphous solid was obtained which was washed well with water, then alcohol and ether to dry it. The mercury double salt was decomposed by grinding it finely with potassium bromide (2.5g) then heating the mixture directly in a long tube as described on p. 36.

The product was extracted with ether but no dibromo compound was obtained on evaporation of the extracts.

**Attempted Synthesis of 7-bromo-1-carboxyfluorenone I.**
Preparation of methyl-3-aminophthalate.

Methyl 3-nitrophthalate was prepared by the method described by Butterworth, Hey, Heilbron and Wilkinson (J.C.S 1939, 1386). The ester was obtained as a slightly yellowish-white waxy solid which was not purified at this stage. Yield = 94%

Methyl 3-nitrophthalate was reduced according to Bogert and Renshaw (J.A.C.S. 1906, 28, 618).

The ester (42 g) was suspended in alcohol (210 g) and concentrated hydrochloric acid (420 g) and the suspension cooled to 0°C allowing one to two hours at this temperature to ensure complete chilling. Zinc dust (ca. 20 g) was added in small quantities to the stirred solution, and the temperature was kept low at about 0°C. When all the precipitate had dissolved, a slight excess of zinc (ca. 3-4 g) was added to ensure complete reduction. A concentrated solution of sodium hydroxide was added gradually until the solution was almost neutral, and ice was added simultaneously in order to keep the temperature down. Finally a solution of sodium carbonate was added which resulted in the formation of an insoluble white precipitate, presumably zinc carbonate. The neutral solution was next extracted with ether and the extracts, after drying over anhydrous sodium sulphate, were evaporated to yield a dark brown oil.
Attempted Preparation of methyl 4'-bromo-2,3-dicarboxydiphenyl.

The method was adapted from that used by Butterworth, Hey, Heilbron and Wilkinson (J.C.S.1938,1388) for the preparation of 2,3-dicarboxydiphenyl. (cf. Heilbron, Hey and Wilkinson J.C.S.1938, 116).

Methyl 3-aminophthalate (2.7g) suspended in concentrated hydrochloric acid (5.4 ml) and water (12 ml) was diazotized with a solution of sodium nitrite (1g) in water (4 ml). To the solution of the diazonium salt was added dropwise a solution of sodium hydroxide (2g) in water (8 ml) over a period of ten minutes, care being taken not to allow the temperature of the reaction mixture rise above 50°C. Freshly distilled bromobenzene (32g) was run into the solution at a temperature of 5-10°C and the mixture was left stirring at room temperature overnight. The product was extracted with benzene and the extracts after washing and drying, were evaporated leaving a bright red oil which defied all attempts at trituration.

**Proposed Scheme for Synthesis of 7-bromo-1-carboxyfluorenone II.**
Proposed Scheme for Synthesis of 7-bromo-1-carboxyfluorenone II

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

Preparation of p-bromobenzaldehyde.

The method of oxidising p-bromotoluene (62g) to the corresponding aldehyde given in Organic Syntheses XVIII, 62 was used.

Yield of diacetate = 57 g, M.P. 90°C.
Yield of aldehyde = 20 g, M.P. 56-58°C.

Preparation of p-bromocinnamaldehyde.

The procedure was similar to that given by Strauss (Ann. 1912, 393, 311).
To a solution of p-bromobenzaldehyde (5 g.) in ethyl alcohol (25 ml) was added acetaldehyde (2.5 g.) and diethylamine (2 drops). The solution was allowed to stand for twenty-four hours then more diethylamine (3 drops) was added and the solution left standing for a further three days.

Alcohol was then distilled off until the solution was one third of its original volume. This was diluted with water and extracted with ether. The extracts were washed with water, acid and 5% potassium carbonate and after drying, the solvent was removed.

The residue was distilled in vacuo and the fraction coming over at 140-170°C (24 mm) gave white crystals which rapidly turned yellow. The product was recrystallized from a mixture of ether and light petroleum (40 - 60°) M.P. 72-74°C (A). A further recrystallization gave a purer product, colourless prisms M.P. 76-77°C (lit 81°C) in poor yield.

Analysis.

C₉H₇BrO calculated C 51.10%; H 3.32%; Br 37.59%
found C 51.13%; H 3.32%; Br 37.90%

A 2:4-dinitrophenylhydrazone was prepared in alcohol and recrystallized from tetralin as dark red needles M.P. 266°C.

Analysis.

C₁₅H₁₂O₄BrN₄ requires N 14.23%
found N 13.40%
The filtrate from A was cooled in a freezing mixture and a second crop of long prisms obtained M.P. 37-39°C. Presumably this was a mixture of p-bromobenzaldehyde and p-bromocinnamaldehyde.

Several attempts were made to improve the above method of preparing p-bromocinnamaldehyde. The condensation mixture was heated on a water bath for 4, 6, 18, 24 hours but no product was obtained.

**Preparation of p-chlorocinnamaldehyde.**

A method based on the standard laboratory method of preparing dibenzalacetone was employed (cf. Mann and Saunders Practical Organic Chemistry p.156)

To a solution of p-chlorobenzaldehyde (3.2g) and acetaldehyde (4 ml) in methyl alcohol (50 ml) was added a solution of sodium hydroxide (5 ml of 10% sodium hydroxide diluted with 20 ml water) and the mixture was shaken vigorously for ten minutes. The solution was allowed to stand for a further forty-five minutes with occasional shakings, and finally it was left in a freezing mixture. The product was extracted with ether and the extract was dried then evaporated yielding an oil which was distilled in vacuo. A yellow liquid was obtained which solidified in long colourless needles on cooling. This was recrystallized from a mixture of ether and light petroleum (40-60) M.P. 58-59°C (lit. 62-62.5°C)
Attempted Preparation of p-bromocinnamaldehyde.

The above method was attempted using p-bromobenzaldehyde in place of p-chlorobenzaldehyde, but it was not successful.

Proposed Synthesis of 11-Bromofluoranthena.
Preparation of 5-Aminotetralin.

5-Aminotetralin was prepared by the reduction of 2-naphthylamine with sodium and alcohol, according to the method of Morgan, Mucklethwaite and Winfield (J.C.S. 1904, 85, 744).

A liquid B.P. 270 - 275°C (lit. 275-277°C) was obtained. Yield = 65%.

Preparation of 5-Iodotetralin.

A suspension of 5-aminotetralin (15 g) in concentrated hydrochloric acid (28 ml) and water (50 ml) was cooled to 0°C and diazotised, whilst stirring, with a solution of sodium nitrite (8.5 g) in water (10 ml).

A suspension of a dark brown solid in a brown solution was obtained and to this was added a solution of potassium iodide (24 g) in water (30 ml) portion-wise, whilst shaking the flask vigorously at each addition. Nitrogen was evolved, and after fifteen minutes shaking the flask and contents were heated on a water bath for a further twenty minutes. 10% Sodium hydroxide (20 ml) was added to remove any phenol, and the 5-iodotetralin was obtained by steam distilling the mixture.

The oil was separated from the aqueous portion of the distillate, dried over anhydrous sodium sulphate, then distilled under reduced pressure to give a
slightly yellow oil B.P. 130 - 135°C at 10 mm
(lit. 150°C at 17 mm) Yield = 6 g = 23%

Preparation of 1-nitro-2,5-dibromobenzene.

p-Dibromobenzene (5 g) was heated under reflux for thirty minutes with fuming nitric acid (40 ml). The resulting solution was poured on to ice and the solid which separated was filtered, washed and crystallized from alcohol as needles M.P. 83°C (lit 85°C).

Attempted Condensation of 5-iodotetralin and 1-nitro-2,5-dibromobenzene.

An Ullman synthesis was attempted based on the methods described by Fanta (Chem. Reviews 1946, 38, 139).

Copper Bronze (1 g) was added, portionwise, with stirring to a mixture of 5-iodotetralin (1 g) and 1-nitro-2,5-dibromobenzene heated to 220°C, and heating was continued for five minutes after all the copper had been added. The whole operation was conducted over a period of fifteen to twenty minutes and the temperature was maintained at 220 - 230°C throughout.

The product, an oily sludge, was extracted with alcohol and the brown extracts were evaporated down to give a small quantity of a solid M.P. 34-37°C.

A mixed melting point of this substance and 1-nitro-2,5-dibromobenzene showed a depression and melting occurred over a wide range 60-75°C.

There was insufficient product for an analysis.
DISCUSSION.

The central theme of the foregoing section has been the orientation of 4:11-dibromofluoranthenone, but before turning to the discussion of these experimental results it would be advisable to give a brief survey of the theoretical aspect of the substitution of fluoranthene by heterolytic (i.e. ionic or polarised) reagents.

Waters (62) claims that the only correct way to predict substitution in polycyclic compounds lies in an evaluation of the energy difference between the mesomeric ground state of the compound and the transition state; substitution occurring preferentially when this difference is a minimum. Furthermore he points out that the transition state is essentially quinonoid, having a considerable degree of bond localisation, and he uses the oxidation-reduction potential of the corresponding quinone to give an indication of the energy of this transition state.

Although Waters can apply this theory direct to explain such phenomena as the ortho-para ratio; naphthalene substitution etc., where the prediction of the position of substitution is possible, he states that such a prediction based on a consideration of the partial double bond character of the hydrocarbon, is impossible in the case of polycyclic
compounds such as phenanthrene, chrysene, pyrene and perylene. However Waters does point out that polar substitution does occur in these molecules at the same points as those which are converted into carbonyl groups in the most stable quinones which can be derived from these hydrocarbons by oxidation.

Clearly if this theory be applied to fluoranthene only one form can be postulated having the quinonoid structure shown in I.

Thus di-substitution would be expected to occur in the 4:11-positions.

Tobler et al. (31.) claim to have formed such a quinone. These workers postulated 4:11-di-substitution in fluoranthene from their investigation of a dihydroxyfluoranthene (II) obtained from the corresponding disulphonic acid which they prepared by direct sulphonation of fluoranthene. II on oxidation gave a coloured compound of quinonoid nature which Tobler et al. postulated to be I, (p. 33) a compound whose structure was only possible assuming
4:11-di-substitution. Thus there are good theoretical grounds for 4:11-di-substitution in the fluoranthenone nucleus.

Turning now to the preceding experimental section it can be seen that much attention has been focussed on the products obtained by oxidizing dibromofluoranthene and other derivatives of fluoranthenone.

Easton (34,35) reported that on oxidizing dibromofluoranthene with chromic anhydride and glacial acetic acid he obtained a monobromofluorenone-1-carboxylic acid which crystallized from methyl alcohol as yellow needles M.P. 238-241°C. This acid gave a fairly satisfactory analysis.

\[ C_{14}H_{7}O_3Br \] requires Br 26.40%; found 27.52%.

When Easton's work was repeated it was therefore surprising to find that the acid obtained by oxidizing dibromofluoranthene had quite different properties, subliming at 200°C to minute yellow needles M.P. 266 - 267°C. This acid gave a reasonable analysis for a dibromofluorenone-1-carboxylic acid, and the methyl ester analysed even more favourably.

\[ C_{14}H_7O_3Br \] requires Br 41.88%; found 39.70% 40.90%
\[ C_{15}H_8O_3Br \] requires Br 40.40%; found 40.95%.

It was only with difficulty that this methyl ester was prepared. The ordinary methods of boiling the acid with methyl alcohol and 10% sulphuric acid
failed and esterification was finally achieved with diazomethane. The difficulty encountered in esterifying both this acid and 2-bromo-1-carboxyfluorenone (p. 53) is due presumably to the steric hindrance caused by the bromine in the 2-position since 7-bromo-1-carboxyfluorenone can readily be esterified in the ordinary way (p. 63).

From the analysis figures it is clear that the oxidation product was a dibromo acid, 2:7-dibromo-1-carboxyfluorenone (IV) (see p.111) formed by the oxidation of ring A of dibromofluoranthenone (III). To account for the production of a monobromofluorenone carboxylic acid Easton (34) postulated that the ring B of the starting substance was oxidized to give, presumably, 6-bromo-1-carboxyfluorenone (V).

\[
\begin{align*}
\text{III} & \quad \rightarrow \quad \text{IV} \\
& \quad \text{V}
\end{align*}
\]

This monobromo acid Easton isolated by means of the barium salt which he decomposed with acid. When he treated the insoluble residue left after the extract-
extraction, with water and hydrochloric acid he was able to extract with ether a mixture of his original product (V) and a second acid M.P. 264-266°C; a mixed melting point of this acid with a sample of our product (IV) showed no depression (35). Although he obtained a small quantity of the dibromo acid, the bulk of Easton's oxidation product was the monobromo acid.

The oxidation of dibromofluoranthene was repeated but a different method of purifying the product (p. 41) was used, namely extracting an ether solution with carbonate. Only one acid could be isolated - 2:7-dibromo-1-carboxyfluorenone. Easton too, tried this method of purification but again his findings were entirely different. He was only able to isolate an acid M.P. 238-240°C which gave no depression when a mixed melting point was carried out with an analysed sample of 6-bromo-1-carboxyfluorenone, showing it to be the monobromo acid as before.

Oxidation of dibromofluoranthene with sodium dichromate and glacial acetic acid, similar to that used by Tucker and Forrest for the oxidation of trimethylfluoranthene (36), yielded the dibromofluorenone-carboxylic acid, though in somewhat poorer yield than by the previous method. It is interesting to note that when Easton carried out a similar oxidation (35 cf. 36) he too was able to isolate only the dibromo acid.
It can only be concluded that there must have been some experimental detail by which our work differed from Easton's and which was sufficient to cause in his case a more vigorous rupture of the molecule.

The orientation of 2:7-dibromofluorenone-l-carboxylic acid proved to be rather more complex than had been expected. A decarboxylation with quinoline and copper bronze was carried out and the product obtained was not the anticipated dibromofluorenone but 2-bromofluorenone M.P. 141-142°C. A mixed melting point with an authentic sample of 2-bromofluorenone showed no depression. Clearly if the original acid were 2:7-dibromo-l-carboxyfluorenone then decarboxylation and the simultaneous removal of either of the bromine atoms would result in the production of 2-bromofluorenone (V).

In view of the activation of halogen atoms by negative groups on adjacent carbon atoms, it was considered...
considered highly probable that it was the bromine atom in position 2- which was removed. To confirm this view several experiments were carried out.

(a) 2:7-Dibromofluorenone and 2-bromofluorenone were both treated with copper bronze and quinoline in exactly the same manner as the acid had been treated. In both cases the starting product was obtained back unchanged.

(b) 2-bromo-1-carboxyfluorenone was treated in the same manner (p. 56,113) and in this instance the product was fluorenone.

(c) 7-bromo-1-carboxyfluorenone was also similarly treated (p. 115) when decarboxylation alone took place yielding 2- (7) bromofluorenone.

All of this evidence indicated that in 2:7-dibromo-1-carboxyfluorenone the carboxyl group must influence the mobility of the halogen. As a result the neighbouring carboxyl group and bromine atom are both removed by copper bronze and quinoline yielding 2-bromofluorenone.

Several workers have shown that a carboxyl group in the ortho-position to a halogen facilitates considerably the replacement of the latter in the presence of copper. Hurtley (37) described how the bromine in o-bromobenzoic acid may be replaced by a phenylacetylacetone group by boiling the acid with acetylacetone and copper bronze. Rule, Pursell and
Brown (38) used a similar reaction in the orientation of substituted peri-naphthoic acids when they removed the halogen in the 8-position by boiling the acid with toluene and copper bronze. Pursell also showed (39) that dehalogenation occurred when o-chloro, o-bromo and o-iodobenzoic acids were similarly treated, the product in each case being benzoic acid. The hydrogen for the reduction appears to come from the carboxyl group since the esters of these acids when boiled with copper bronze and toluene remained unchanged.

Rule used this reduction or dehalogenation to facilitate the decarboxylation of peri-naphthalene derivatives. Treatment of the substituted 1-carboxyl-8-halogen naphthalene with copper bronze and quinoline did not bring about decarboxylation, but when the halogen had been removed by the method described above, decarboxylation occurred readily since the steric hindrance effect caused by the halogen had been removed.

This method was applied to 2:7-dibromo-1-carboxyfluorenone but no removal of bromine took place. Since the reduction depends on the availability of the hydrogen in the carboxyl group, it is most likely that in the fluorenone acid this hydrogen is bound in a hydrogen-bond linkage by chelation with oxygen of the keto group.
This gives a seven-membered ring which is not often encountered. It may be noted that this ring is adjacent to a five-membered ring and that both are condensed to a benzene ring; this gives a system of condensed rings similar to those which von Braun (10,10a) found to be completely stable.

A successful decarboxylation of 2:7-dibromo-l-carbocycluorone was finally achieved by the method of Dzielewski and Kahl (40) and 2:7-dibromofluorenone (VII) was obtained thus proving the structure of the original acid.
With the proof of the structure of this acid came the final orientation of 4,ll-dibromofluoranthenone from which it had been obtained by direct oxidation.

To investigate further the decarboxylating and dehalogenating action of copper bronze and quinoline, the oxidation product of 4-bromofluoranthenone (VIII) was studied. Some slight difficulty was met with in preparing very pure 4-bromofluoranthenone. The last stage in the synthesis described by Tobler et al. (41) consists of a dehydrogenation of 5-bromo-1;3;3;4-tetrahydrofluoranthenone and it was found that the yield varied greatly depending on the chloranil used, and on the purity of the sulphur-free xylene. The second preparation used, that due to von Braun (28) gave a very impure product and purification was rather wasteful.

The acid M.P. 252-4°C obtained by oxidizing 4-bromofluoranthenone (p. 52) was identical with that described by von Braun (32) namely 2-bromo-1-carboxyfluorenone (IX) (lit M.P. 252°C)
A decarboxylation of this acid with copper bronze and quinoline again resulted in dehalogenation as well as decarboxylation (cf., p. 108), and fluorenone (X) was obtained and identified by means of its 2:4-dinitrophenylhydrazone.

\[ \text{Br} \quad \text{COOH} \quad \xrightarrow{\text{CuBr}} \quad \text{CO} \]

This gives support to the structure advanced for the oxidation product (IV) of dibromofluoreanthene (p. 108) since if 2-bromo-1-carboxyfluorenone on treatment with copper bronze and quinoline loses both bromine and carbon dioxide, from the 2- and 1-position respectively, then presumably 2:7-dibromo-1-carboxyfluorenone, under the same conditions, behaves similarly, i.e. the bromine in the product, 2-bromo-fluorenone, must originally have occupied the 7-position.

To clinch this argument the behaviors of 7-bromo-1-carboxyfluorenone (XI) was studied. The acid was obtained by direct bromination of 1-carboxyfluorenone.
The acid obtained M.P. 226-228 °C, analysed for a monocarboxylic acid, and from its melting point differed from (IX) and (V). Furthermore it could readily be esterified with methyl alcohol and 10% sulphuric acid to give an ester M.P. 164°C; in this it differed from 2-bromo-1-carboxyfluorenone (IX) which could only be esterified with diazomethane (p 53, 106).
As the two reactive positions in the fluorenone molecule are the 2- and the 7- position it was concluded that since bromination had not yielded 2-bromo-1-carboxyfluorenone it must have occurred in the 7-position. This was finally proved by treating the acid with copper bronze and quinoline when only decarboxylation occurred yielding 2-bromofluorenone. Not only did this confirm the structure of the original acid (XI) but it showed also that copper-bronze and quinoline could not remove the bromine from the 7-position and hence would not remove it from the 7-position in 2:7-dibromo-l-carboxyfluorenone on similar treatment (p. 108).

From the above table it can be seen that the monobromocarboxylic acid (V) obtained by Easton differs from 7-bromo and 2-bromo-l-carboxyfluorenone; it can only be assumed that it is 6-bromo-1-carboxyfluorenone.

Attempts to prepare 2:7-dibromo-l-carboxyfluorenone by direct bromination of 2-bromo-and 7-bromo-l-carboxyfluorenone were not successful.

Returning to Easton's findings on the oxidation of dibromofluoranthenes, it might be argued from the analysis figures shown below, that the monobromo acid he obtained was not 6-bromo-l-carboxyfluorenone but 4-bromonaphthalic acid (XXII)
The melting point of this acid (XII) does not correspond however to that obtained by Easton; furthermore Easton's acid was obtained as small yellow needles whereas (XII) crystallizes as long white needles and is readily converted to the anhydride (XIII), yellow needles M.P. 210°C.

4-bromonaphthalic acid was prepared and its properties contrasted with 2-bromo- and 2,7-dibromo-1-carboxyfluorenone. Unlike these acids it could not be esterified even with diazomethane, however derivatives were formed with o-phenylenediamine. According to Bistrzycki and Risi (41) and later Peters (42), o-phenylenediamine condenses with ortho- or peri-dicarboxylic acids to give benziminazol derivatives,
derivatives, e.g. with phthalic acid.

Thus in the case of 4-bromonaphthalic acid two isomers (XIV) and (XV) would be formed.
This was found to be so, and the isomers were separated by means of their different solubilities in benzene. The two final products melting at 219-221°C and 270 - 272°C respectively. No attempt was made to identify these isomers.

A substance closely related to 4:11-dibromofluoranthenes is 4:11-dicyanofluoranthenes (XVI) which was obtained from the former direct by replacement of the bromine atoms. It was hoped to support the above orientation studies by oxidizing the dicyano-compound to 2:7-dicyano-1-carboxyfluorenone (XVII) followed by decarboxylation to 2:7-dicyanofluorenone (XVIII).

![Diagram of the chemical structures of XVI, XVII, and XVIII]

The oxidation of (XVI) however, produced somewhat surprising results. An acid (A) was formed which sublimed at about 260°C to small yellow needles which did not melt below 360°C: it contained no nitrogen and could not be esterified when boiled with methyl
methyl alcohol and 10% sulphuric acid. Clearly the cyano group had been hydrolysed during the oxidation.
The most probable product was 1:2:7-tricarboxyfluorenone (XIX) or its anhydride (XX), but the analysis figures did not give any support to this theory. Other possible oxidation products are diphenyl 2:4:3':4'-tetracarboxylic acid (XXI), naphthalene 1:4:5-tricarboxylic acid (XXII), benzene 1:2:3-tricarboxylic acid (XXIII), benzene 1:3:4-tricarboxylic acid (XXIV) and benzene 1:2:3:4-tetracarboxylic acid (XXV) whose analyses and melting points are listed below.

![Chemical structures](image-url)
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Analysis</th>
<th>Melting Point.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>fd. 50.82 3.21</td>
<td>360°C; sublimes ca. 260°C.</td>
</tr>
<tr>
<td>XIX</td>
<td>req. 61.20 2.50</td>
<td>-</td>
</tr>
<tr>
<td>X</td>
<td>65.30 2.05</td>
<td>-</td>
</tr>
<tr>
<td>XXI</td>
<td>59.18 3.23</td>
<td>-</td>
</tr>
<tr>
<td>XXII</td>
<td>55.49 3.21</td>
<td>forms anhydride M.P. 274°C</td>
</tr>
<tr>
<td>XXIII</td>
<td>51.40 2.90</td>
<td>190°C</td>
</tr>
<tr>
<td>XXIV</td>
<td>51.40 2.90</td>
<td>238°C</td>
</tr>
<tr>
<td>XXV</td>
<td>46.95 2.36</td>
<td>238°C</td>
</tr>
</tbody>
</table>

From the above table it can be seen that compounds (XXIII) and (XXIV) are the most probable from the analysis figures, however their melting points do not conform with that obtained for the oxidation product (A). Thus no satisfactory conclusion can be drawn as to the constitution of this acid. It is likely that it contains at least three carboxyl groups since it is insoluble in all the usual organic solvents but is very slightly soluble in aqueous alcohol, cf. Acids (XXIII) and (XXV) which can both be recrystallized from water while (XXIV) can be recrystallized from aqueous alcohol.

By carrying out a hydrolysis of 4:11-dicyanofluoranthene the corresponding dicarboxylic acid (XXVI) was obtained.
This acid appeared to be identical with that obtained by Easton (43) by the action of oxalyl chloride on fluoranthene. The methyl ester was prepared and shown to be identical with Easton's, but decarboxylation experiments were not successful due to the very small quantities of pure compounds available. Easton, however, showed that decarboxylation gave 11-carboxyfluoranthene in agreement with expectation since 4-carboxyfluoranthene is easily decarboxylated whereas the 11-acid is not (43).

It is interesting to note that the first method tried of hydrolysing dicyanofluoranthene was one used by Hager et al (44) for the hydrolysis of β-naphtho-nitrite (XXVI) to β-naphthoic acid through the imino-ether. Hager showed that while the method was successful in the case of the β-compound it failed when the ω-nitrile (XXVIII) was used.
If dicyanofluoranthene be compared with these naphthonitriles it can be seen that the cyano group in the 4-position corresponds to (XXVIII) whereas the 11-substituent more closely resembles $\beta$-substitution (XXVII). In this way it was expected to hydrolyse only one of the cyano groups, viz. that in the 11-position, but it too remained unchanged.

The failure of 4:11-dibromofluoranthene to form a Grignard reagent is not altogether surprising. von Braun (23) showed that 4-bromofluoranthene did not give such a compound but it was hoped that the bromine in the 11-position might prove somewhat more reactive. This however, was not the case and even when anisole was used as solvent - the dibromocompound being almost insoluble in ether - no reaction took place between the magnesium and dibromofluoranthene.

In order to throw some light on to the problem of the disubstitution of fluoranthene an attempt was made to synthesize 4-bromo-11(?)-methyl and 11(?)-bromo-4-methylfluoranthene. The first stage was the preparation of 4- and 11(?)-chloromethylfluoranthene (XXIX), (XXX)
which were reduced to the corresponding methylfluoranthenes (XXXI, XXXII) with Raney nickel-aluminium alloy (45, 46 and p. 30). It was hoped that these two isomers might then be brominated to, presumably 11(?)-bromo-4-methylfluoranthen (XXXIII) and 4-bromo-11(?)-methylfluoranthen (XXXIV) which in turn could be orientated by a study of their oxidation products.

Unfortunately no separation of the isomeric methylfluoranthenes could be effected. Chromatography was completely unsuccessful; steam distillation gave a waxy substance M.P. 68-72°C which formed a picrate M.P. 119-120°C. Although the melting point of this picrate did not show any depression when mixed with picric acid it was thought to differ from the latter since it crystallized from alcohol in a felt of orange needles. Although the melting point of this isomer is in good agreement with that quoted by von Braun (30) for 4-methylfluoranthen (lit. M.P. 66°C) it is doubtful if it is the 4-isomer since the latter forms a picrate M.P. 172°C (30). It cannot definitely be stated to be the 11-isomer since no authentic sample of this compound has been prepared.

When the mixture of methylfluoranthenes was distilled in vacuo two fractions were obtained, but neither could be crystallized. The lower boiling fraction, 178-182°C /0.05 mm., formed a picrate in
alcohol as long orange needles which sublimed at 35°C and melted at 165°C. As no authentic sample of 4-methylfluoranthene was available no mixed melting point of its picrate (lit. M.P. 172°C) and this compound could be carried out.
The second fraction, 210-214°C/0.01 mm, failed to form either a picrate or a 1:3:5-trinitrobenzene derivative.

Since the mixture of isomers was obtained as an oil this suggests either two low-melting compounds or even an oil and a low-melting substance. If we consider the isomeric β-methylnaphthalene and α-methylnaphthalene we find that the β-compound is a solid M.P. 35°C while the α-compound is a liquid B.P. 243°C. By analogy we might expect 11-methylfluoranthenone to be a liquid or a very low-melting solid, since the other isomer, 4-methylfluoranthenone, is a solid M.P. 66°C. This would fit in with Easton’s findings that, in general, 4-substituted fluoranthenone derivatives have relatively higher melting points than the corresponding 11-substituted isomers.

The latter part of the experimental section is devoted to some attempted syntheses of substituted fluorenone-1-carboxylic acids and also an attempt to synthesize 11-bromofluoranthenone with a view to preparing 4:11-dibromofluoranthenone.

The two methods tried to prepare 2:7-dibromo-1-carboxyfluorenone were essentially identical with that by Mayer and Freitag to prepare isodiphenic acid (7 also p. 4). In the first method m-nitrosotoluene was not isolated, the condensation being carried
out by heating m-nitrotoluene with o-toluidine in the presence of sodium hydroxide. Both the 2:3'-azotoluene thus produced and the 3:2-dimethylbenzidine obtained from it were purified by distillation in vacuo as the earlier workers described. Parsons and Ballard (47) in a later paper state that 2:3'-azotoluene cannot be distilled even in vacuo without decomposition, and this was confirmed. Thus when the second method of preparing 2:3'-azotoluene was used - this time preparing the nitroso compound first then condensing it with o-toluidine - the product was purified by chromatography. The benzidine rearrangement was carried out in two stages, first reduction of the azo compound to 2:3-hydrazotoluene followed by rearrangement to 3:2-dimethylbenzidine dihydrochloride which was purified by recrystallization.

The substitution of bromine in 3:2'-dimethylbenzidine did not prove to be easy. Schmechten (48) described a modification of the Sandmeyer method of introducing bromine by means of a complex mercury double salt of the tetrazonium compound which was decomposed by heating with potassium bromide. Two methods of tetrazotisation were employed, the first in hydrochloric acid was a standard method, and the second, in which the amine was added to a solution of sodium nitrite in concentrated sulphuric acid, was
described by Hodgson and Walker (49). In each case some difficulty was encountered in forming the mercury complex with the tetrazonium salt. No pure mercuric nitrate (or bromide) could be obtained, and all the material available had been converted, on standing, into basic salts. Consequently, when added to a solution of potassium bromide this produced a suspension which did not give highly satisfactory results. The decomposition of the complex by direct heating with potassium bromide was also disappointing and a crystalline compound was isolated on only one occasion. From the analysis figures of this compound, 4:4'-dibromo-3:2'-dimethyldiphenyl (XXXV) and of the acid it gave on oxidation (XXXVI) it can be seen that some halogen-free 3:2'-dimethyldiphenyl (and the corresponding acid) was also obtained.

XXXV \[\text{XXXV} \quad \begin{array}{c}
\text{CH}_3 \\
\vdots \\
\text{Br} \\
\text{CH}_3 \\
\end{array}
\]

XXXVI \[\text{XXXVI} \quad \begin{array}{c}
\text{Br} \\
\text{COOH} \\
\vdots \\
\text{Br} \\
\text{COOH} \\
\end{array}
\]

\[
\text{XXXV} \quad \text{C}_{14} \text{H}_{12} \text{Br}_2 \quad \text{requires} \quad \text{Br} 47.05\% \quad \text{found} \quad 44.24\%
\]

\[
\text{XXXVI} \quad \text{C}_{14} \text{H}_{12} \text{Br}_0 \quad \text{requires} \quad \text{Br} 40.00\% \quad \text{found} \quad 37.27\%
\]

A second method of halogen substitution was
attempted, namely, treating the solution of the tetrazonium salt with a solution of cuprous bromide in hydrobromic acid. Although Hodgson and Walker (49) reported the success of this method a red oil was obtained which suggested the formation of an azo-compound.

The proposed synthesis of 7-bromo-1-carboxyfluorenone (p. 94) was based on a condensation reaction originally carried out by Gomberg (50, 51), who showed that a diazonium salt (XXXVII) will couple up in alkaline solution with benzene, or its derivatives, to give a substituted diphenyl.

\[
\begin{align*}
\text{XXXVII} & \quad \begin{array}{c}
\text{XXXVII} \\
\text{XXXVII}
\end{array} \\
\end{align*}
\]

With a substituted benzene coupling always takes place mainly in the ortho- and para- positions irrespective of whether the substituent group R is ortho- and para- or meta-directing. The explanation is that the reaction involves free radicals (52.)

Heilbron, Hey and their co-workers (53, 54) have.
used this reaction extensively for the syntheses of substituted fluorenones as shown below.
Methyl anthranilate (XXXVIII $R = H$) is diazotised and coupled with benzene in alkaline solution, and the resulting methyl diphenyl-2-carboxylate (XXXIX) is hydrolysed, converted to the acid chloride and cyclised to fluorenone (XL $R = H$). Using substituted anthranilic acids Hey et al. were able to prepare fluorenones of known constitution, substituted in one ring only.

If however, a derivative such as bromobenzene (XLI) be used in place of benzene, a mixture of the two isomeric diphenyl-1-carboxylic acids (XLII) and (XLIII) is obtained (53). Consequently Hey et al. were not able to prepare satisfactorily, fluorenones having substituents in both rings, as they were unable to separate the two isomers.

Starting from methyl 3-nitrophthalate which they reduced to the corresponding amino acid, these workers were able to synthesise fluorenone-1-carboxylic acid (54). By a similar method it was hoped to synthesise 7-bromo-1-carboxyfluorenone, condensing the diazonium salt with bromobenzene. This would of course give a mixture of isomers (XLIV) and (XLV), probably separable by chromatography.
The preparation of methyl 3-aminophthalate by the reduction of methyl 3-nitrophthalate was carried out according to Bogert and Renshaw (55 cf. 54). The yields were not good and it was felt that the addition of sodium carbonate for the final stages of neutralization of the reduction mixture was inadvisable since it resulted in the formation of insoluble zinc carbonate (p. 95). The coupling of the diazonium salt with bromobenzene was not successful, and although a large excess of the latter was used it may not have been sufficient. Hey (54) does not quote the quantity of bromobenzene that he used in the preparation of 2-carboxy-4'-bromo- and 2-carboxy-2'-bromodiphenyl and this is a most important factor since Grive and Hey (56) have shown that the success of the reaction depends on the production of a two-phase system.

A second scheme for the synthesis of 7-bromo-1-carboxyfluorenone was briefly investigated. In this case the difficulty lay in the preparation of p-bromo-cinnamaldehyde by condensing p-bromobenzaldehyde with acetaldehyde in the presence of diethylamine. The condensation described by Straus (57) though rather a slow process, gave a pure product but in very poor yield. Condensation by heating the mixture had no advantageous effect. p-Chlorocinnamaldehyde can be prepared by a method analogous to that for the
preparation of dibenzalacetone (58) by carrying out a Claisen condensation on p-chlorobenzaldehyde with acetaldehyde in the presence of alkali; but p-bromo-
benzaldehyde did not undergo the condensation.

An attempt was also made to synthesise 11-bromo-
fluoranthene ( p. 97 ). The main objection to the
method was the low yield of 5-iodotetralin obtained
from 5-aminotetralin by the method described by
Morgan (59). An Ullmann synthesis was carried out,
on a very small scale, with this iodo-compound and
2:5-dibromonitrobenzene, and while a solid M.P.34-37°C
was obtained there was not sufficient for an analysis.

Since this work was carried out, a paper has been
published by Tucker and Whalley ( 25, also p.18 )
describing a synthesis of 2:3:4-trimethylfluoranthene
in which the first stage is an Ullmann synthesis with
1-iodo-2:3:4-trimethylnaphthalene ando-nitrobenzene.
In view of the success of these workers it is felt
that a similar synthesis of 11-bromofluoranthene
should be possible and that work in this direction
would be highly profitable.
SUMMARY OF DISCUSSION.

4:11-Dibromofluoranthe has been orientated by an investigation of its oxidation products.

7-bromo-1-carboxyfluorenone and 2-bromo-1-carboxyfluorenene have been prepared, and a study of their decarboxylation products has been used to confirm the constitution of 4:11-dibromofluoranthe.

4:11-Dibromofluoranthe has been converted to 4:11-dicyanofluoranthe and 4:11dicarboxyfluoranthe, and the structures of these di-substituted fluoranthenes are thus established. This orientated fluoranthene-dicarboxylic acid has been shown to be identical with that obtained by Easton by a Friedel-Crafts reaction with oxalyl chloride on fluoranthene.

No trace has been found in the oxidation product of 4:11-dibromofluoranthe of the monobromo-fluorenone-1-carboxylic acid obtained by Easton which is presumed to be 6-bromo-carboxyfluorenone.

The oxidation of 4:11-dicyanofluoranthe yielded an acid whose structure could not be ascertained.

The syntheses of 11-bromofluoranthe and 7-bromo-1-carboxy-, and 2:7-dibromo-1-carboxyfluorenene were attempted.
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