RESEARCHES ON FLUORANTHENE
AND
RELATED POLYCYCLIC AROMATIC HYDROCARBONS

by

DAVID HERALD REID, B.Sc.

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INTRODUCTION

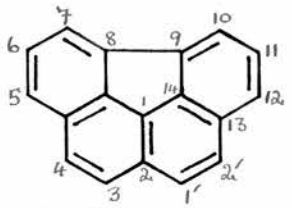
Five polycyclic aromatic hydrocarbons containing five-membered rings have been considered in this thesis. The chemistry of two of these, fluoranthene and 4:5-methylenephenanthrene, has been considered in rather greater detail.

FLUORANTHENE. Little work had been done on this hydrocarbon before its constitution was finally settled by Von Braun and co-workers (Ber., 1929, 62, 145). After Von Braun's pioneer work extending largely over the period 1929 - 1932 the chemistry of fluoranthene continued to engage the attention of an increasing number of investigators. As a result the volume of literature dealing with this hydrocarbon is now quite considerable and no claim is made here that all aspects of its chemistry have been surveyed. Only those topics relevant to the subject matter of the thesis are mentioned. Of the numerous investigators whose work is not directly concerned with the work described in this thesis, the names of Tucker (Glasgow), Bergmann (Rehovoth, Israel) and Tobler (Basel) may be mentioned.

4:5-Methylenephenanthrene. Only two investigators have hitherto studied this hydrocarbon viz. Kruber (Duisburg) and Bachmann (Michigan, U.S.A.). A complete survey of the chemistry of the hydrocarbon has been given in this thesis.

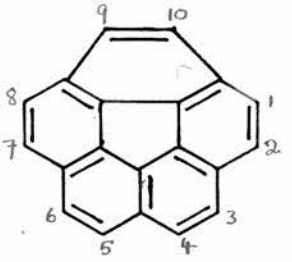
NOMENCLATURE. Two hydrocarbons possessing unusual structures are described in this thesis. In accordance with suggestions made by Dr. Cahn, Editor of the Journal of the Chemical Society, these hydrocarbons are named and numbered as follows -

(a) The hydrocarbon synthesised in the course of work outlined in this thesis and possessing structure A is considered as a derivative of fluoranthene and is accordingly described as 2:13-benzfluoranthene.



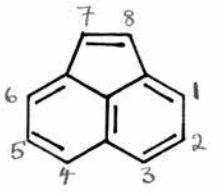
A. 2:13-Benz-fluoranthene

(b) The hypothetical hydrocarbon possessing structure B is described as coronindene.

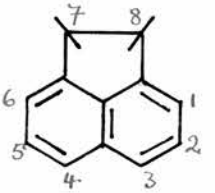


B. Coronindene

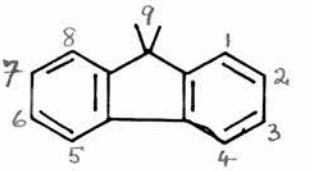
NUMBERING. The system of numbering employed in this thesis is illustrated on the following page.



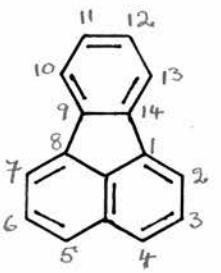
Acenaphthylene



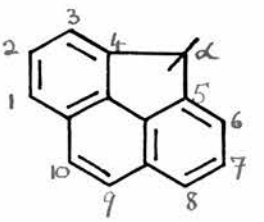
Acenaphthene



Fluorene



Fluoranthene



4:5-Methylenephenanthrene

The scheme of numbering of acenaphthene, acenaphthylene and fluorene is that employed by the Bureau of Abstracts. In order to avoid confusion it was decided to adhere to the older system of numbering of fluoranthene as hitherto used by the Chemical Society.

The hydrocarbon 4:5-methylenephenanthrene is considered as a derivative of phenanthrene and numbered accordingly. This agrees with the system employed by the German and American investigators as used in "Berichte Der Deutschen Chemischen Gesellschaft" and the "Journal of the American Chemical Society", respectively.

In agreement with a suggestion by Dr. Cahn,

Editor/

Editor of the Journal of the Chemical Society, the position of substitution of the methylene carbon atom in this hydrocarbon is designated as the "α-" position.

GENERAL INTRODUCTION

The aromatic hydrocarbons whose chemistry will be touched upon in some aspect or other in this thesis are

1 Acenaphthene

2 Acenaphthylene

3 Fluorene

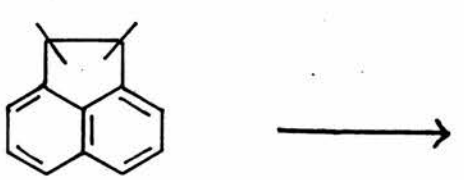
4 Fluoranthene

5 4:5-Methylenephenanthrene

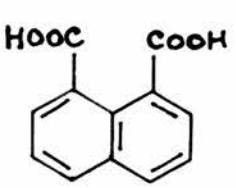
An outline of some of the investigations upon which the accepted structure of each of these hydrocarbons rests will be given immediately below. Only those experiments which are of value as regards the elucidation of the structures of the hydrocarbons will be described, irrespective of the chronological order of these experiments in the history of the hydrocarbons.

ACENAPHTHENE

This hydrocarbon (1) was first isolated by Berthelot (Ann. Suppt., 1867, 5, 372) who prepared it by the action of ethylene on naphthalene at red heat, but more insight into its constitution came from oxidative breakdown by the action of chromic acid to give naphthalic acid (2) (Behr and Van Dorp. Ber., 1873, 6, 60).

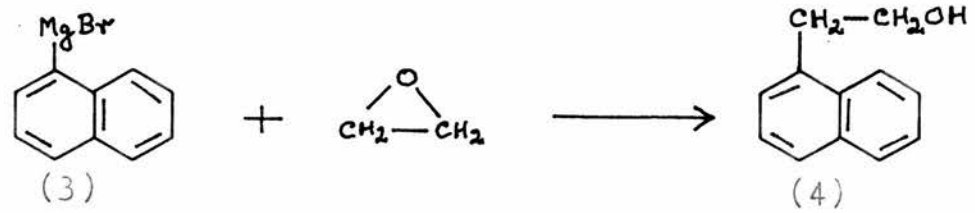


(1)

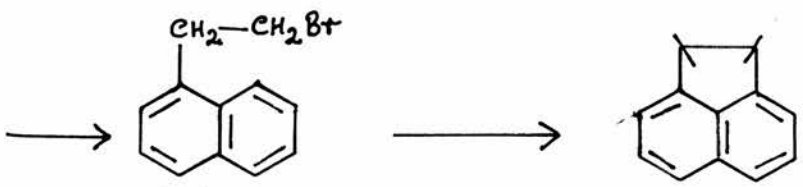


(2)

Synthesis of acenaphthene was achieved by the action of ethylene oxide on α-naphthyl magnesium bromide (3) followed by treatment of the resulting alcohol (4) with phosphorous tribromide. The 1-2'-bromoethylnaphthalene (5) was dehydrobrominated by the action of alcoholic potash to give acenaphthene (1).



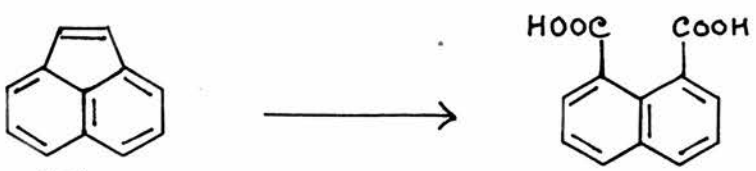
(3) (4)



(5) (1)

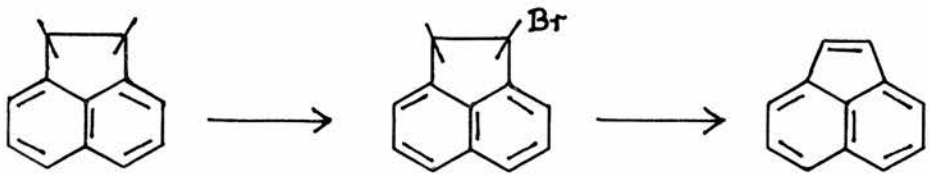
ACENAPHTHYLENE

Acenaphthylene (6) was first isolated by Behr and Van Dorp (Ber., 1873, 6, 753) who prepared it by passing acenaphthene vapour over red hot lead oxide. Conclusive proof of its structure ultimately rests on the same basis upon which the structure of the closely related acenaphthene rests. Oxidation of acenaphthylene with chromic acid yielded naphthalic acid (2).



(6) (2)

Most of the methods used for the preparation of acenaphthylene proceed essentially along the same lines as Behr and Van Dorp's original method viz. heating acenaphthene vapour in the presence of a suitable oxidising agent or dehydrogenation catalyst. The method of Barnes (J.A.C.S., 1948, 70, 145) is the only one of value for purposes of structure determination and involves the bromination of acenaphthene (1) with N-bromosuccinimide followed by dehydrobromination of the resulting 7-bromoacenaphthene (7).



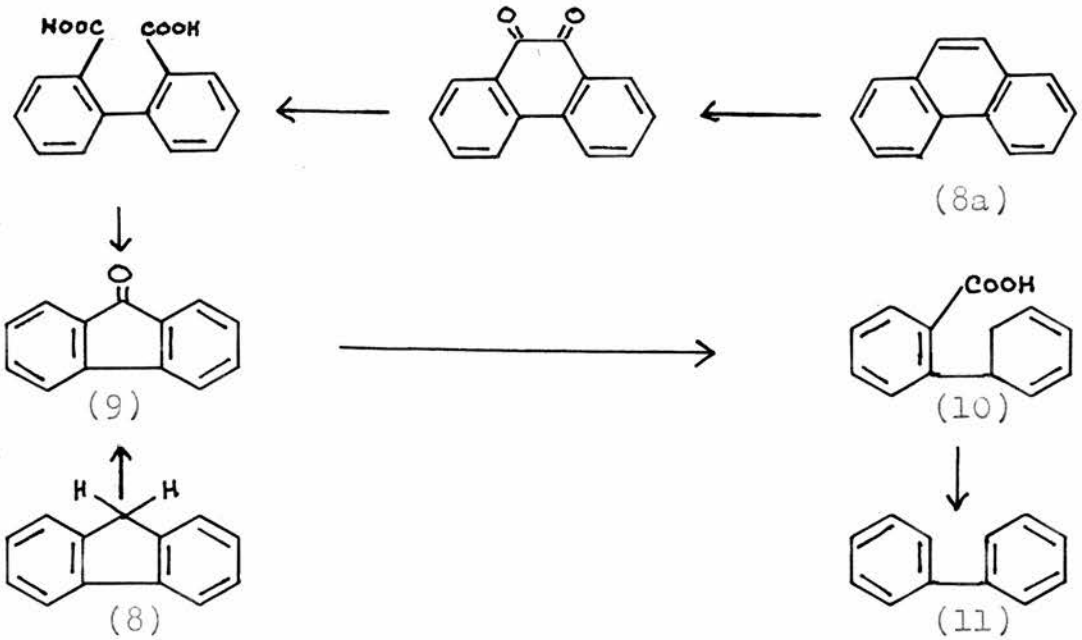
(1) (7) (6)

FLUORENE

First isolated by Berthelot (Ann. chim. Phys., 1867, 12, 222) from the crude anthracene oil fraction of coal tar boiling between 300 and 310°, fluorene (8) owed the rapid elucidation of its structure to the discovery of, and investigations on, phenanthrene which was discovered five years later by Fittig and Ostermeyer and independently by Graebe.

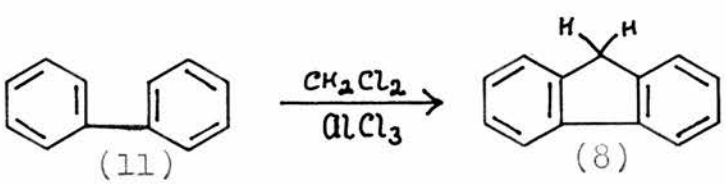
In their investigations on the degradation of phenanthrene (8a) Fittig and Ostermeyer (Ber., 1873, 6, 167) obtained the same ketone, fluorenone (9), as Barbier (Compt. rend., 1874, 79, 1151) obtained a year later/

later by oxidation of fluorene.



Fusion of fluorenone with alkali gave diphenyl-1-carboxylic acid (10) which was decarboxylated to diphenyl (11).

Confirmation of the structure of fluorene as concluded from degradation came at an early date from synthesis. By the reaction of diphenyl (11) with methylene chloride in the Friedel-Crafts reaction Adam (Compt. rend., 1886, 103, 207) prepared fluorene (8) directly.

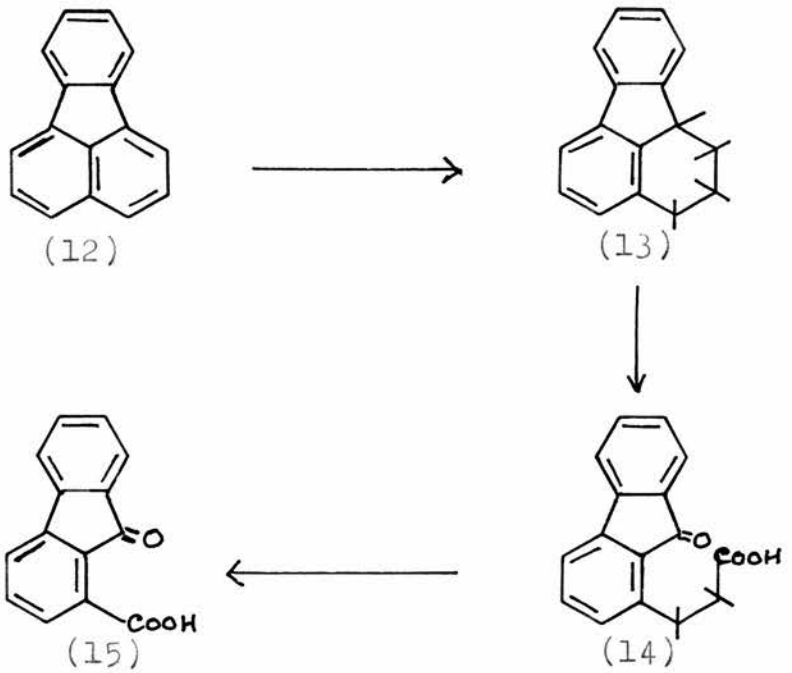


FLUORANTHENE

Though/

Though first isolated pure as early as 1877 by Fittig and Gebhard (Ber., 1877, 10, 2141) from a high-boiling coal tar distillate and by Goldschmiedt (Ber., 1877, 10, 2022) from "stuppfett", a crude hydrocarbon mixture obtained as a side product during the smelting of the mercury ores of Idria, the correct structure was not assigned to fluoranthene until its synthesis was carried out by Von Braun and Anton (Ber., 1929, 62, 145).

Reduction of fluoranthene (12) with sodium amalgam and alcohol led to tetrahydrofluoranthene (13) (Von Braun loc. cit.). Kruber (Ber., 1931, 64, 84) oxidised tetrahydrofluoranthene with chromic acid and obtained fluorenone-1-propionic acid (14) which on further oxidation yielded fluorenone-1-carboxylic acid (15).

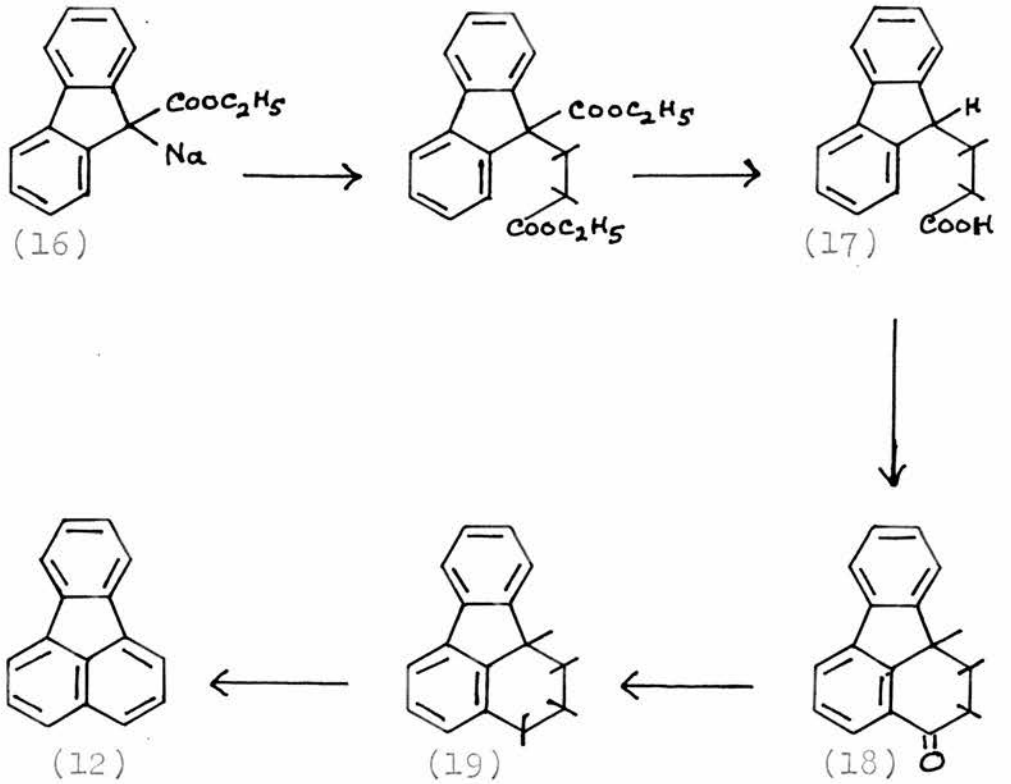


(12) (13) (14) (15)

Evidence for the correct structure first came from synthesis. Von Braun and Anton (loc. cit.) condensed

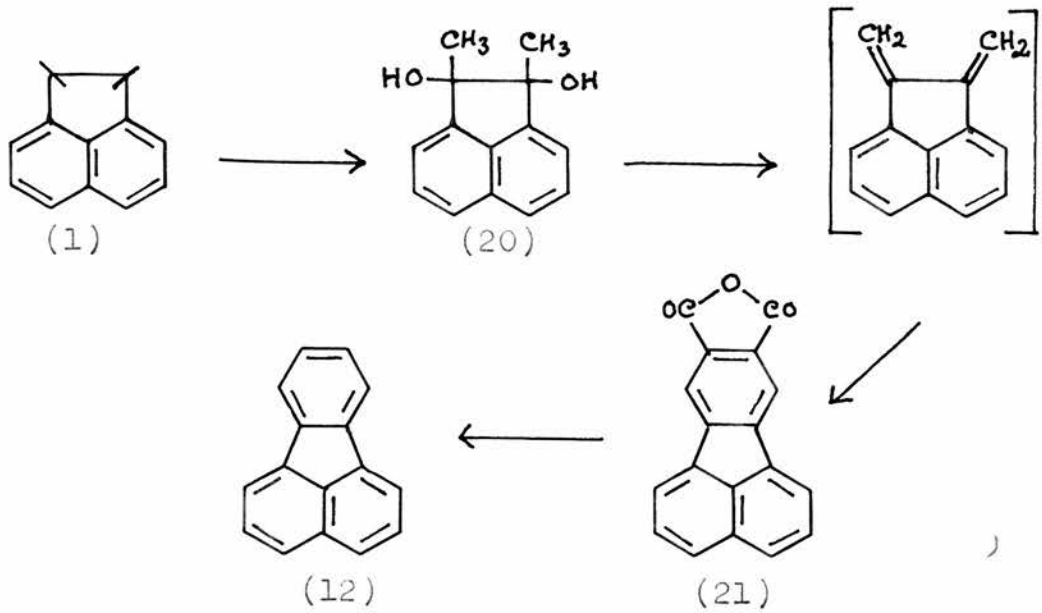
β-chloropropionic/

β-chloropropionic ester with 9-sodio-9-carbethoxyfluorene (16) and obtained β-fluorene-9-propionic acid (17) which was cyclised to 4-keto-1:2:3:4-tetrahydrofluoranthene (18). Clemmensen reduction of this ketone, followed by dehydrogenation of the resulting 1:2:3:4-tetrahydrofluoranthene (19) gave fluoranthene itself (12).



(16) (17) (12) (19) (18)

The synthesis described above started from fluorene. By utilising acenaphthene (1) Campbell and Gow (J., 1949, 1555) prepared trans-7:8-dimethylacenaphthene-7:8-diol (20). The diol (20) dehydrated in acetic anhydride to 7:8-dimethyleneacenaphthene (20a) which condensed immediately with maleic anhydride under Diels-Alder conditions to give fluoranthene-11:12-dicarboxylic acid anhydride (21), decarboxylation of which afforded fluoranthene (12).

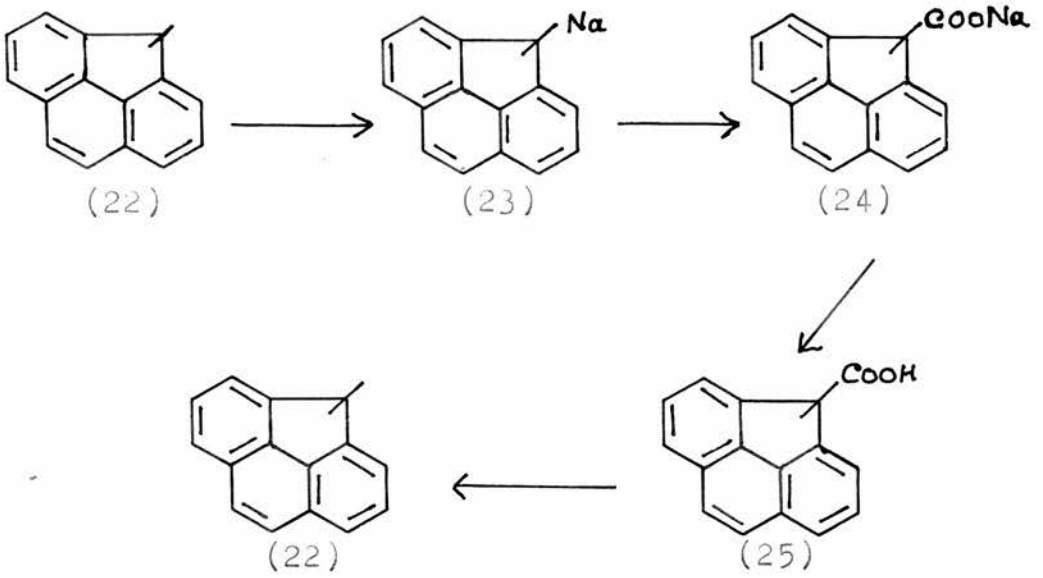


(1) (20) (12) (21)

4:5-METHYLENEPHENANTHRENE

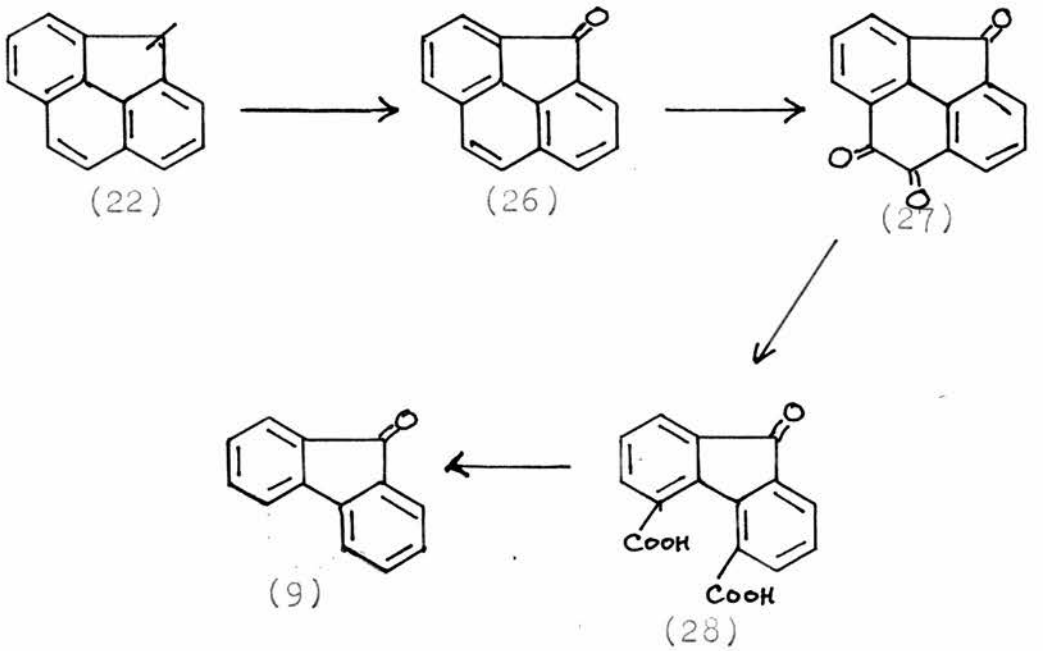
This hydrocarbon (22) whose structure embodies at one and the same time the structures of phenanthrene, acenaphthene and fluorene, was first isolated only relatively recently by Kruber (Ber., 1934, 67, 1000) who obtained it from the crude anthracene oil of coal-tar boiling at 250 - 260°.

Treatment of the coal-tar distillate with sodium gave α-sodio-4:5-methylenephenanthrene (23) which formed the sodium salt of α-carboxy-4:5-methylene-phenanthrene (24) on passing carbon dioxide into the mixture. The sodium salt, separated from the neutral matter accompanying the 4:5-methylenephenanthrene, yielded α-carboxy-4:5-methylenephenanthrene (25) on acidification, decarboxylation of which yielded 4:5-methylenephenanthrene itself.



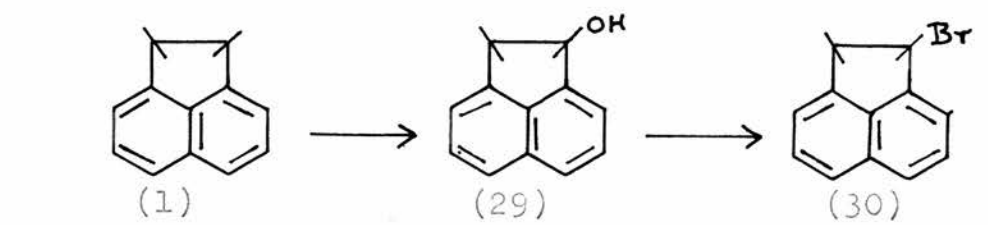
(22) (23) (24) (25) (22)

The structure followed from experiments involving the oxidative breakdown of the hydrocarbon with chromic acid. A ketone, α-keto-4:5-methylenephenanthrene (26) was first produced, which oxidised further to α-keto-4:5-methylene-9:10-phenanthraquinone (27) and finally to fluorenone-4:5-dicarboxylic acid (28). Decarboxylation of this dicarboxylic acid yielded fluorenone (9).

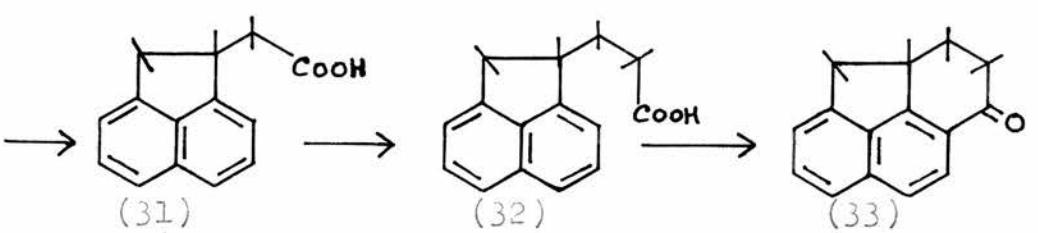


(22) (26) (27) (9) (28)

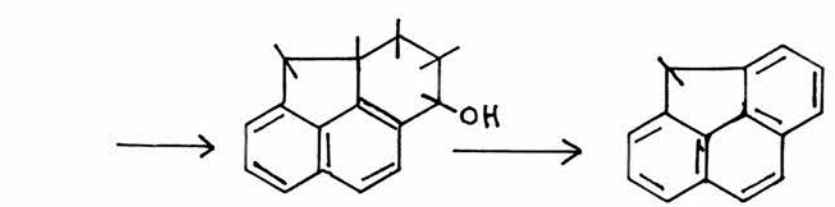
Confirmation of this structure came from synthesis. Bachmann and Sheehan (J.A.C.S., 1941, 63, 204), starting from acenaphthene (1), prepared acenaphthenol (29) and thence 7-bromoacenaphthene (30). Condensation of (30) with sodio-malonic ester followed by hydrolysis and decarboxylation yielded 7-acenaphthenyl acetic acid (31). The homologue (32) of this acid, prepared by the Arndt-Eistert reaction on acid (31), on ring-closure gave 1-keto-1:2:3:4-tetrahydro-4:5-methylenephenanthrene (33), which was reduced by the Meerwein-Ponndorf method to the alcohol (34). Dehydrogenation proceeded smoothly to give the fully aromatic 4:5-methylene-phenanthrene (22).



(1) (29) (30)



(31) (32) (33)



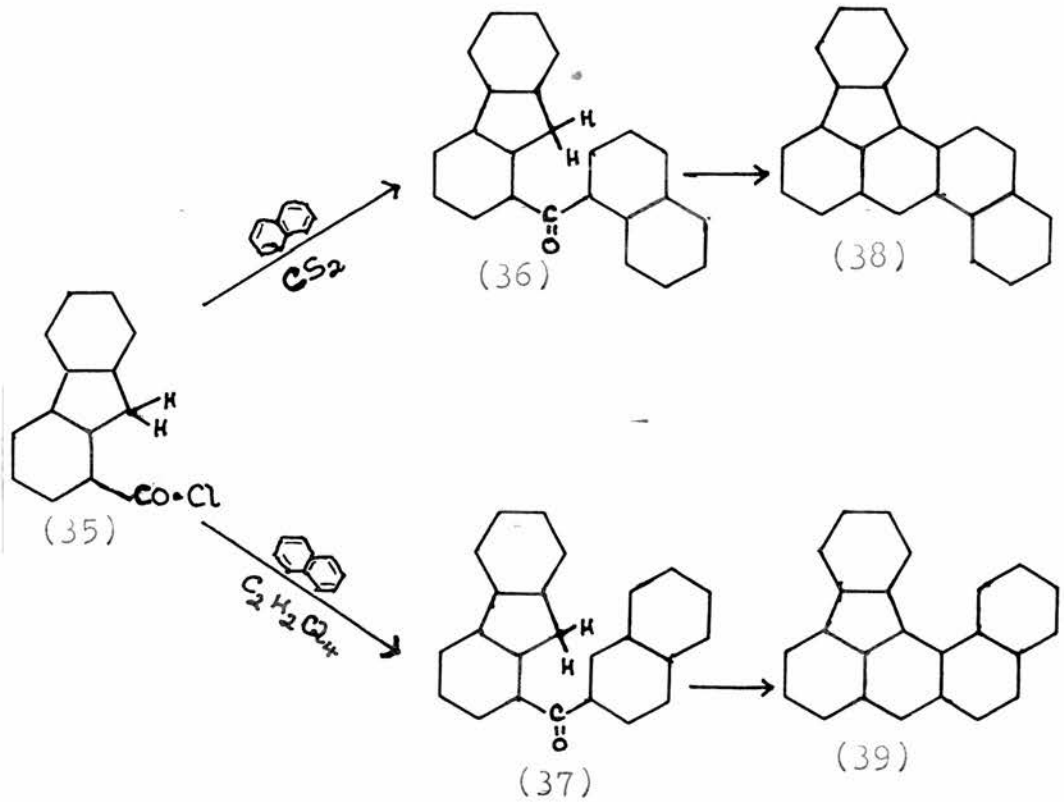
(34) (22)

SECTION A INTRODUCTION

NAPHTHOFLUORANTHENES

Only three naphthofluoranthenes have been reported hitherto in the literature,

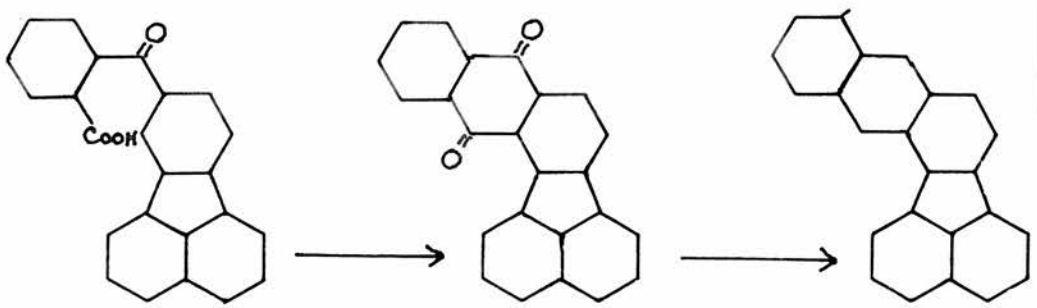
The Friedel-Crafts reaction between fluorene -1-carboxylic acid chloride (35) and naphthalene (Fieser and Seligman. J.A.C.S. 1935, 57, 2175) gave a mixture of ketones (36) and (37). In carbon disulphide as solvent ketone (36) was formed to the greater extent while in tetrachloroethane the ketone (37) preponderated.



The Elbs pyrolysis of ketone (36) formed naphtho (2':1' - 2:3) fluoranthene (38) while the similar pyrolysis of ketone (37) yielded naphtho (1':2' - 2:3) fluoranthene/

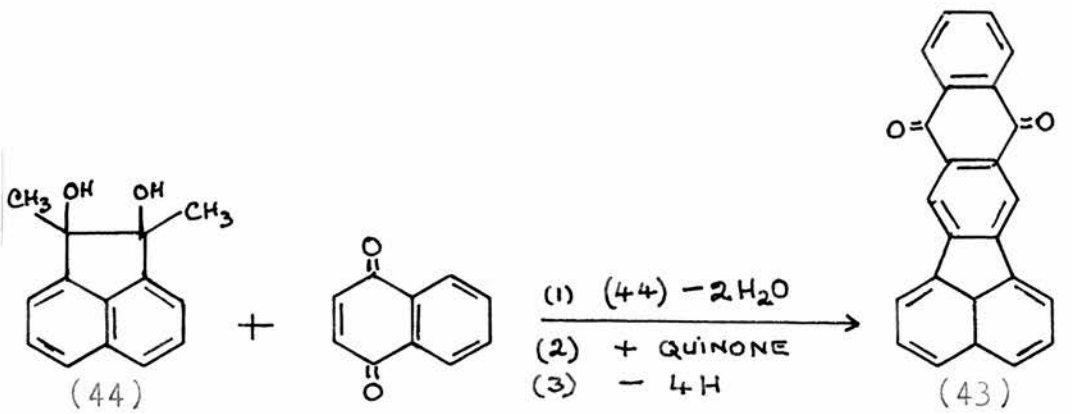
fluoranthene (39).

The third naphthofluoranthene (40) was obtained by Von Braun and Manz (Ann. 1932, 496, 188) by zinc dust distillation of the corresponding quinone (41) which he obtained as one of two quinones from the ring-closure of 11-o-carboxybenzoylfluoranthene (42). From oxidation studies Von Braun concluded that his quinone (41) and hydrocarbon (40) were respectively naphtho (2':3' - 10:11) fluoranthene - 1':4' - quinone and naphtho (2':3' - 10:11) fluoranthene.



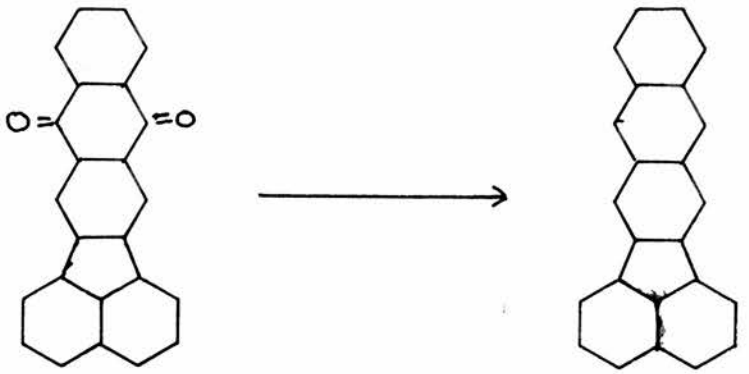
(42) (41) (40)

Later work however by Campbell et. al. showed that Von Braun's compounds were naphtho (2':3' - 11:12) fluoranthene and its quinone. Campbell and Gow (J. 1949, 1555) prepared naphtho (2':3' - 11:12) fluoranthene - 1':4' - quinone (43) by the action of α- naphthaquinone on trans - 7:8 - dimethylacenaphthene - 7:8 - diol (44) in acetic anhydride.



(44) (43)

Distillation of this quinone with zinc dust yielded naphtho (2':3' - 11:12) fluoranthene (45).



(43) (45)

Both the hydrocarbon (45) and the quinone (43) possessed the properties belonging to the hydrocarbon and quinone, respectively, described by Von Braun as the 10:11 - derivatives of fluoranthene viz. (40) and (41). (see below).

MONO = SUBSTITUTION IN FLUORANTHENE

The work described in the Experimental Section A is/

is concerned with an examination of the evidence cited by Von Braun (Ann., 1932, 496, 188) for his contention that mono - substitution of fluoranthene by Friedel-Crafts acylations gave the 4- and 11- derivatives. The constitutions of various key compounds involved in his evidence depend on his work dealing with the orientation of mono-substitution products of bromination, sulphonation and nitration of fluoranthene.

A short outline of the orientation of these latter compounds will therefore be given prior to examining his evidence for 4- and 11- mono - substitution in Friedel-Crafts acylations.

Bromination, Nitration and Sulphonation of Fluoranthene

Von Braun and Manz (Ann., 1931, 488, 111) gave a detailed account of their work on mono - substitution products of fluoranthene obtained by bromination, sulphonation and nitration.

The three products obtained were shown to be correspondingly substituted fluoranthenes by conversion into common compounds as shown below, I, II and III.

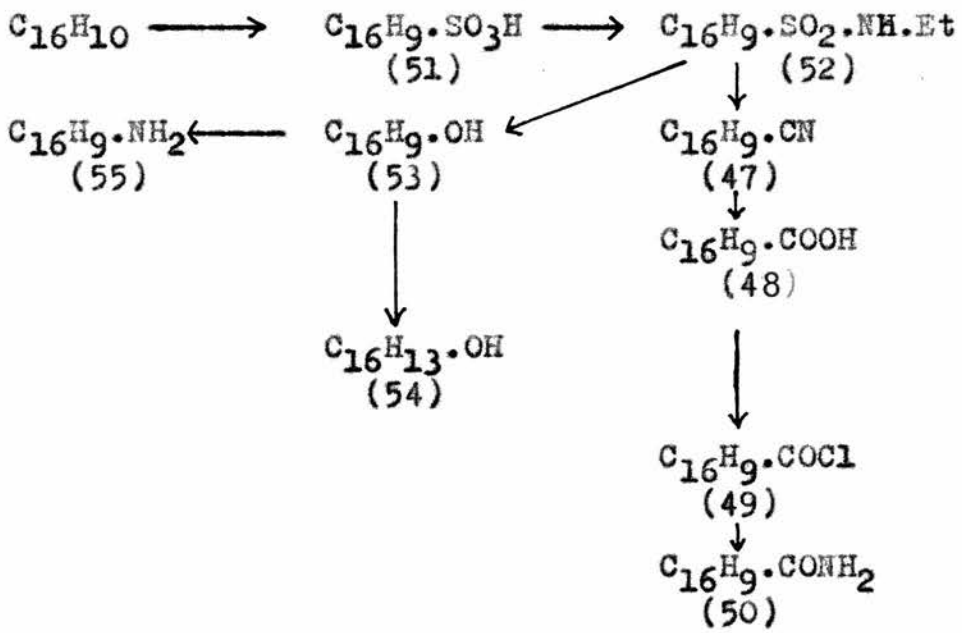
I. The mono - bromofluoranthene (46) obtained by the action of bromine on a boiling solution of fluoranthene in carbon disulphide was isolated by means of its picrate and with potassium cyanide gave a cyano derivative (47) which on hydrolysis was converted into an acid (48). This acid was converted to the amide (50) via. the acid chloride (49).

$C_{16}H_{10}$/

$C_{16}H_{10} \longrightarrow C_{16}H_9Br$ (46) $\longrightarrow C_{16}H_9.CN$ (47) $\longrightarrow$

$C_{16}H_9COOH$ (48) $\longrightarrow C_{16}H_9CO.Cl$ (49) $\longrightarrow C_{16}H_9.CONH_2$ (50)

II. Sulphonation of fluoranthene gave the sulphonic acid (51) which, with ethylamine gave the sulphoethylamide (52). Treatment of (52) with a mixture of sodium and potassium cyanide gave the cyanide (53)[47]? which was identical with (47) above and which also yielded the same acid (48), acid chloride (49) and amide (50) as were obtained from the bromofluoranthene (46) by the series of reactions described in I above.



The action of caustic potash at elevated temperatures on the sulphoethylamide (52) gave a phenol (53) which yielded on reduction a tetrahydrophenol (54) and, on treatment with alcoholic ammonia, an amine (55).

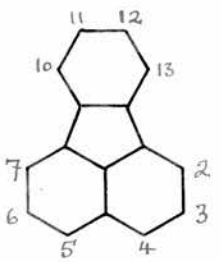
III/

III. Nitration of fluoranthene gave the mono - nitrofluoranthene (56) which was reduced to the amine (57). This amine proved to be identical with (55) above,

$$C_{16}H_{10} \rightarrow \underset{(56)}{C_{16}H_9.NO_2} \longrightarrow \underset{(57)}{C_{16}H_9.NH_2} \longrightarrow \underset{(58)}{C_{16}H_9.OH}$$

while the phenol (58) obtained by action of hot hydrochloric acid on the amine (57) proved to be identical with the phenol (53) obtained from the fluoranthene sulphonic acid (51).

There are five possible positions in fluoranthene for mono - substitution viz. positions 2-, 3-, 4-, 10- (13-) and 11- (12-). Von Braun showed that substitution had taken place in the 4- position. His reasoning and evidence was as follows -



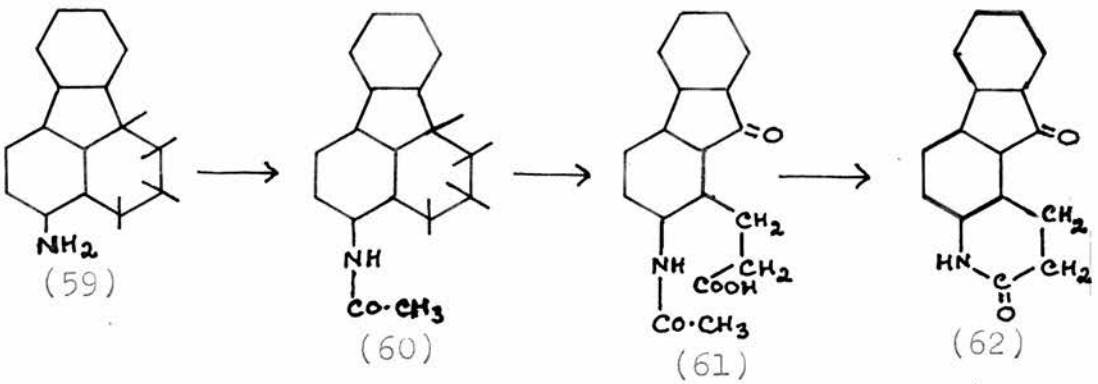
Bromofluoranthene on reduction lost bromine to give the 1:2:3:4-tetrahydrofluoranthene whose structure was established when Von Braun and Anton (Ber., 1929, 62, 145) synthesised fluoranthene. (This synthesis has been described earlier in the General Introduction).

This limited the possibilities of the position of monosubstitution to one of positions 2, 3 and 4. Reduction of 4- keto - 1:2:3:4-tetrahydrofluoranthene (Von Braun and Manz Ann., 1931, 488, 111) also obtained in the synthesis of fluoranthene by Von Braun and Anton (loc. cit.), gave a phenol whose phenylurethane derivative was identical with that of the tetrahydrophenol (54) obtained/

obtained from the fluoranthene - monosulphonic acid (51) (see II above).

The phenols themselves, though not identical (as by mixed m.p.) were believed to be related stereoisomerically. This indicated that substitution of fluoranthene had occurred in position 4.

That this was so, was proved by taking the amine (57) obtained from the nitrofluoranthene (56) and reducing it to the tetrahydroamine (59).



The acetyl derivative of this amine, (60), was oxidised to an acid (61) containing the same number of carbon atoms and this acid on hydrolytic deacetylation passed spontaneously into the lactam (62). With the amino group in any other position than the 4- position this lactamisation could not have been possible.

Friedel-Crafts Acylation of Fluoranthene

Although only one monosubstitution product was isolated from each of the nitration, sulphonation and bromination products of fluoranthene, Von Braun and

Manz/

Manz (Ann., 1932, 496, 188) found that the reaction of oxalyl chloride on fluoranthene under conditions of the Friedel-Crafts reaction gave a mixture consisting of a monocarboxylic acid (7 parts), a dicarboxylic acid (3 parts) and a very small amount of a second monocarboxylic acid.

Benzoyl chloride gave mainly one monocarboxylic acid together with a small amount of a second monocarboxylic acid. Phthalic anhydride reacted with similar results.

The three monosubstitution products obtained in quantity from the acylations of fluoranthene with oxalyl chloride, benzoyl chloride and phthalic anhydride were shown to be similarly substituted. This was done as follows -

I. The ethyl ester (63) of the monocarboxylic acid was converted to the hydrazide (64) by the action of hydrazine hydrate and (64) to the azide (65) by the action of nitrous acid.

$$C_{16}H_9.COOEt \longrightarrow \underset{(63)}{} \quad C_{16}H_9.CO.NH.NH_2 \longrightarrow \underset{(64)}{} \quad C_{16}H_9.CON_3 \underset{(65)}{}$$

$$\longrightarrow \left[C_{16}H_9.N = CO\right] \longrightarrow C_{16}H_9.NH.COOEt \longrightarrow \underset{(66)}{} \quad C_{16}H_9.NH_2 \underset{(67)}{}$$

The azide underwent a Curtius rearrangement to give the urethane (66) which was hydrolysed to the amine (67).

II. The oxime (68) of the benzoylfluoranthene likewise underwent a Beckmann rearrangement to give the amine (69).

C/

$$C_{16}H_9.CO.C_6H_5 \longrightarrow C_{16}H_9.C = NOH.C_6H_5 \longrightarrow C_{16}H_9.NH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad (68) \qquad\qquad\qquad (69)$$

III. and in a similar manner the o-carboxybenzoyl-fluoranthene gave an amine (70).

$$C_{16}H_9.CO.C_6H_4.COOH \longrightarrow C_{16}H_9.NH_2$$
$$\qquad\qquad\qquad\qquad\qquad (70)$$

These three amines (67), (69), and (70) all proved to be identical but were different from the amine (57) obtained by reduction of 4-nitrofluoranthene (56).

However, by a similar series of reaction the other three monosubstitution products obtained in small yield by the Friedel-Crafts reaction of oxalyl chloride, benzoyl chloride and phthalic anhydride on fluoranthene each yielded the same amine which proved to be identical with 4-aminofluoranthene (57). According therefore to Von Braun, Friedel-Crafts acylation of fluoranthene gives the 4-isomer in small yield and a second monosubstitution product, as yet not orientated, in preponderance. It is with the evidence brought forward by Von Braun to support this contention that the second mono - acyl product is the 11- (12-) isomer that we are concerned.

Von Braun's evidence was as follows.

Oxidation of the unorientated fluoranthene-mono-carboxylic acid gave a mixture of two fluorenone-dicarboxylic acids. If the - COOH group had been in the 2- or the/

the 3- position then only one fluorenone-dicarboxylic acid would have been obtained (71) or (72) (see separate page). Since position 4- was already ruled out as being the position of substitution of the other mono-acylation products this leaves the alternative possibilities of positions 10- (13-) or 11- (12-).

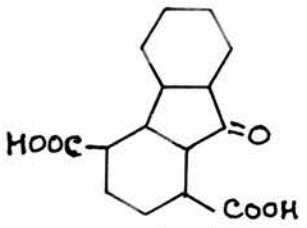
The fact that two fluorenone dicarboxylic acids were obtained thus fixes the position of substitution to by 10- (13-) or 11- (12-), since oxidation of either 10- (13-) carboxyfluoranthene or 11- (12-) carboxy-fluoranthene would give two fluorenone-dicarboxylic acids (73) and (74) or (75) and (76) respectively, the two dicarboxylic acids being due in each case to the fact that the fluoranthene nucleus may be split at either ring A or ring B. (see below)

That substitution had in fact taken place in position 11 (12) was decided when, on cyclisation of the o-carboxybenzoyl fluoranthene, two quinones (78) and (79) were obtained. Had substitution occurred in position 10 then formation of only one quinone would have been possible viz. (79).

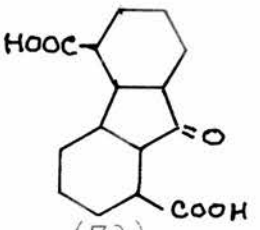
Since here we are dealing with the evidence brought forward by Von Braun to establish his claim that acylation of fluoranthene gave chiefly the 11- acyl derivatives, we may digress at this point to bring forward evidence gathered by later workers (Campbell et. al.) which proved Von Braun's conclusions, qualitatively at least/

ORIENTATION of 11-o-CARBOXYBENZOYLFLUORANTHENE

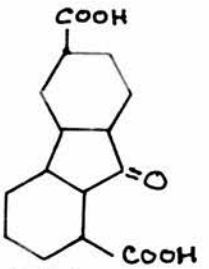
(as by Von Braun and Manz. Ann., 1932, 496, 188)



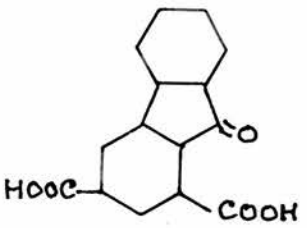
(71)



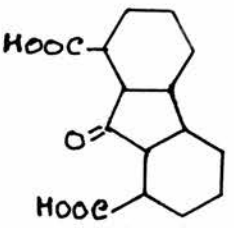
(73)



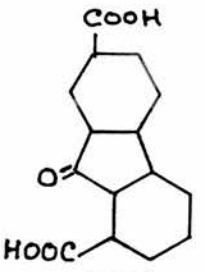
(75)



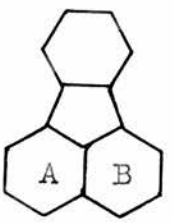
(72)



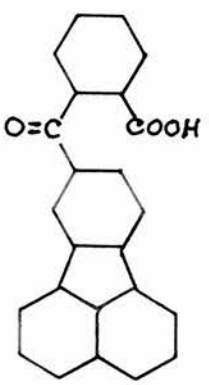
(74)



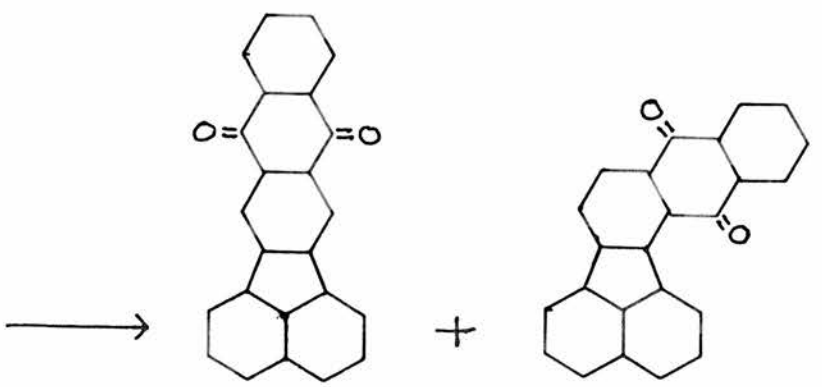
(76)

Fluoranthene 

nucleus



(77)



(78) (79)

least, to be correct with respect to the position of acylation substitution in fluoranthene. As will be discussed later his work on the cyclisation of the o-carboxybenzoylfluoranthene (77) was in error although his conclusions drawn therefrom regarding the position of substitution were essentially correct.

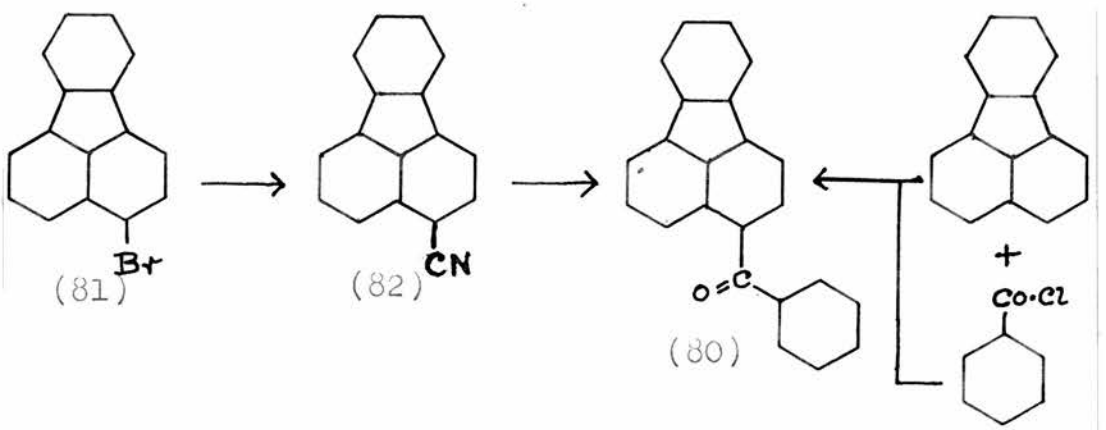
By examination of the products obtained from the benzoylation and phthaloylation of fluoranthene Campbell and Easton (J., 1949, 340) proved quite conclusively that the 4- and 11- (12-) isomers are produced and that, in equal quantities. The action of oxalyl chloride on fluoranthene was however found to give chiefly the 11-monocarboxylic acid (2 parts) together with a dicarboxylic acid (1 part) but, in contrast to Von Braun's results, no 4-monocarboxylic acid was isolated. Campbell's conclusions drawn from studies on the benzoylation and phthaloylation of fluoranthene agreed with Von Braun's as to the positions of substitution (4- and 11-) but not as to the relative quantities of the isomers formed; those drawn from studies on the action of oxalyl chloride on fluoranthene differed only in that no 4-carboxy-fluoranthene was isolated by Campbell and Easton.

Campbell and Easton's orientation experiments were as follows.

Benzoylation of fluoranthene by the action of benzoyl chloride and aluminium chloride on fluoranthene in/

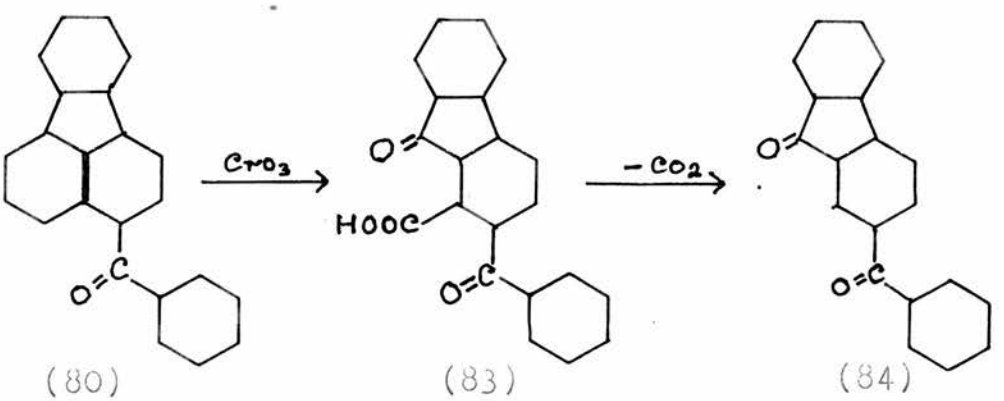
in carbon disulphide gave, after chromatographic analysis, two monobenzoylfluoranthenes.

One of these benzoylfluoranthenes (80) proved to be identical with an authentic sample of 4-benzoyl-fluoranthene (80) which Campbell and Easton (loc. cit.) prepared by the action of cuprous cyanide on 4-bromo-fluoranthene (81) followed by the action of phenyl magnesium bromide on the resulting 4-cyanofluoranthene (82) (c.f. also Von Braun and Manz. Ann., 1931, 488, 111).



(81) (82) (80)

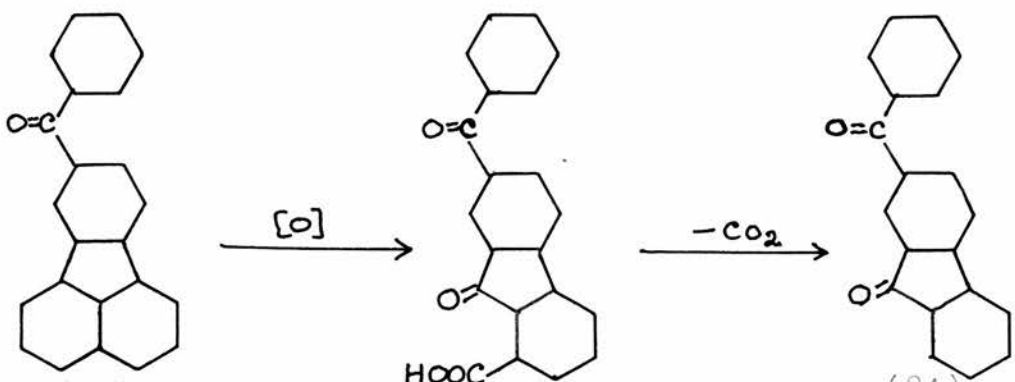
On oxidation of this benzoylfluoranthene (80) and decarboxylation of the resulting benzoyl fluorenone - monocarboxylic acid (83) the 2-benzoylfluorenone (84) was obtained, whose constitution was already known.



(80) (83) (84)

It follows therefore that the benzoylfluoranthene in question is the 4-benzoylfluoranthene.

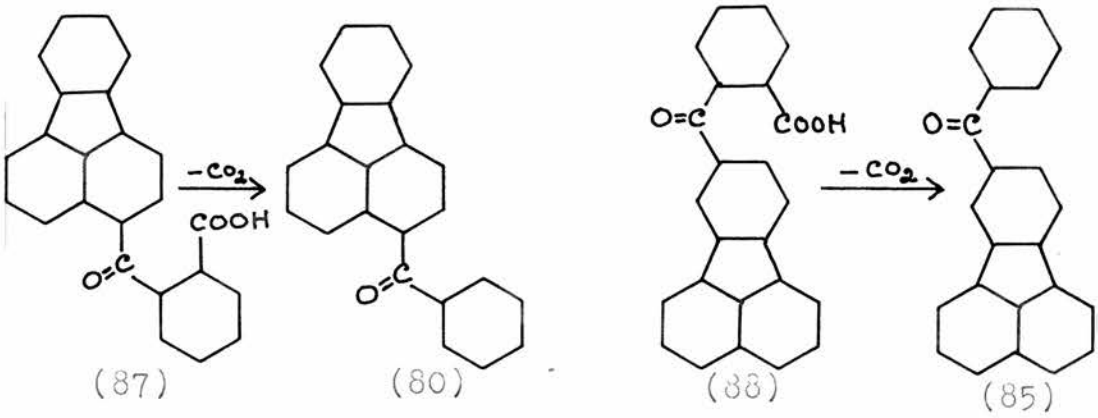
The second benzoylfluoranthene (85) obtained was similarly oxidised and yielded a benzoyl fluorenone-monocarboxylic acid (86) which was not identical with (83) above. This acid (86) however, decarboxylated to give the same (2-) benzoylfluorenone (84) as had been obtained by oxidation of 4-benzoylfluoranthene (80).



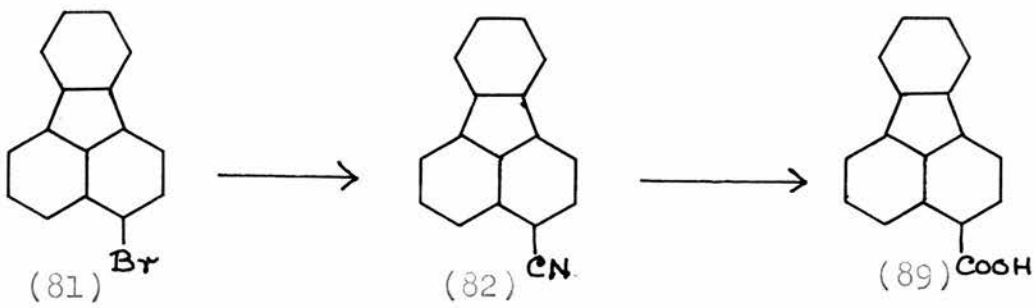
(85) (86) (84)

Since only two benzoylfluoranthenes — the 4- and 11- (12-) benzoylfluoranthenes — could possibly give rise to the same (2-) benzoylfluorenone, it follows that the second benzoylfluoranthene must be 11- (12-) benzoyl-fluoranthene.

Phthaloylation likewise gave two isomeric o-carboxy-benzoylfluoranthenes. One of these acids on decarboxylation yielded 4-benzoylfluoranthene (80) thus showing itself to be 4-o-carboxybenzoylfluoranthene (87). Similarly decarboxylation of the second acid to 11-benzoylfluoranthene (85) showed it to be 11-o-carboxy-benzoylfluoranthene (88).



The fluoranthene monocarboxylic acid obtained by the action of oxalyl chloride on fluoranthene was definitely not the 4- substituted fluoranthene since it was not identical with the fluoranthene -4- carboxylic acid (89) prepared by Campbell and Easton by hydrolysis of 4-cyano-fluoranthene (82).



In all probability it was fluoranthene -11- carboxylic acid since it corresponded in melting point (278 - 280°) to the fluoranthene -11- carboxylic acid (m.p. 283 - 285°) prepared by Von Braun and Manz (Ann., 1932, 496, 188).

Having/

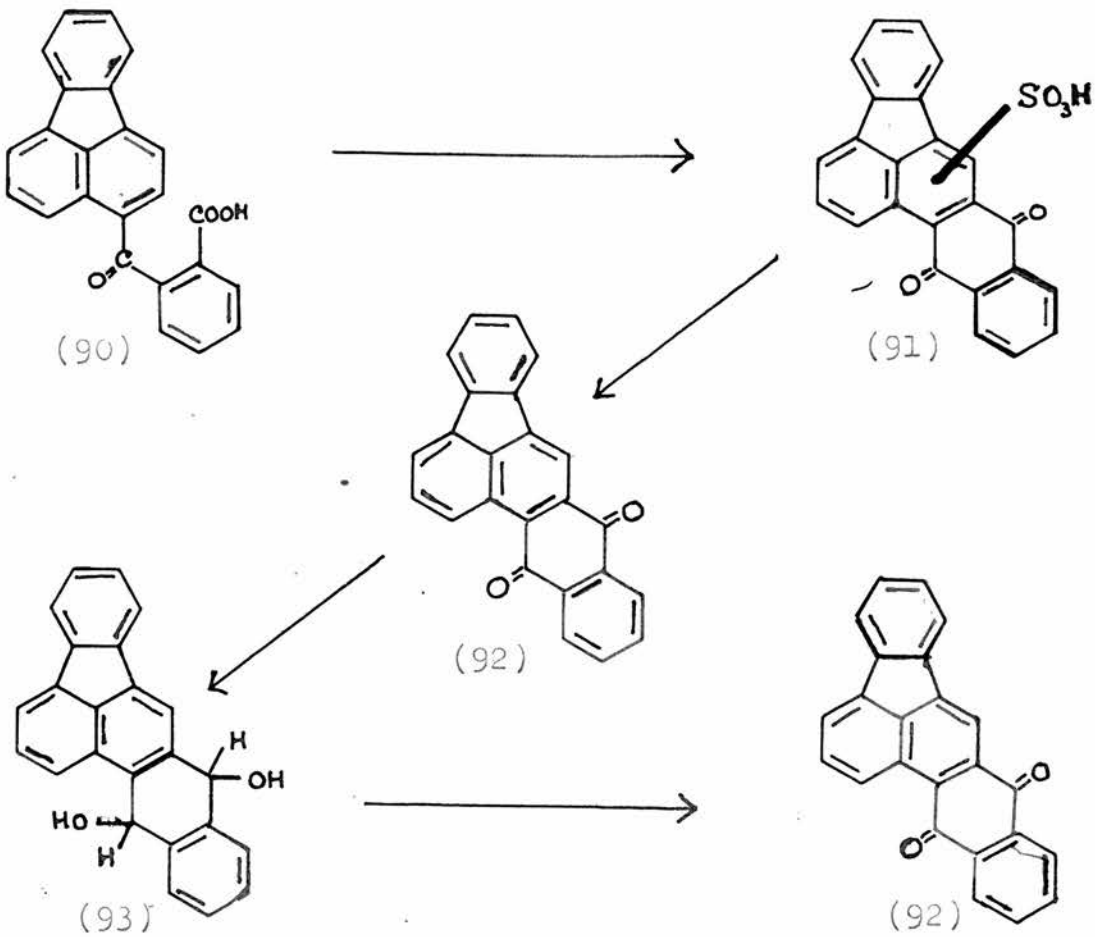
Having established the fact that Friedel-Crafts acylation (in particular phthaloylation) does in fact take place in the 4- and 11- positions of the fluoranthene molecule the stage is now set for returning to a detailed examination of the evidence put forward by Von Braun as grounds for his contention that Friedel-Crafts acylation (in particular phthaloylation) of fluoranthene takes place in the 11- position and not the 10- position. (see above).

Having narrowed the possibilities to either the 10- or the 11- position in which acylation had chiefly occurred (see above) Von Braun and Manz eliminated the former possibility and established the second by their claim to have isolated two quinones on ring-closure of the o-carboxybenzoylfluoranthene. In their conclusions they were correct as has been shown by the confirmatory work of Campbell and Easton just mentioned, but subsequent work by Campbell and co-workers described in a series of papers from 1949 onward has shown that the experimental basis for these conclusions was unsound.

Ring-closure of 4- and 11-o-Carboxybenzoylfluoranthene (as described by Von Braun and Manz. Ann., 1932, 496, 188).

(1) Ring closure of 4-o-carboxybenzoylfluoranthene (90) by sulphuric acid gave the quinone sulphonic acid (91) which was hydrolysed with hydrochloric acid/

acid and barium chloride. The resulting quinone (92), yellow, m.p. 328 - 331°, was purified via. its vat (93) and sublimation in high vacuum.



This quinone (92) was not oxidised to the 2:3-phthaloylfluoranone -1- carboxylic acid.

(2) The second o-carboxybenzoylfluoranthene (94) obtained by the action of phthalic anhydride on fluoranthene gave, on ring closure in trichlorobenzene, two quinones (i) red, m.p. 228° and (ii) yellow, m.p. 332 - 333°. Von Braun assigned the structure (95) to the yellow quinone/

quinone m.p. 332 - 333° and structure (96) to the red quinone m.p. 228°, on the basis of oxidation studies, since oxidation of the yellow quinone m.p. 332 - 333° gave a mixture of phthaloylfluorenone carboxylic acids (97) and (98) while oxidation of the red quinone, m.p. 228°, gave only one phthaloyl fluorenone - carboxylic acid (99) (See next page). Decarboxylation of the acid mixture (97) and (98) gave a mixture of phthaloyl-fluorenones (100) and (101), the melting point of the mixture being 326 - 337°. The m.p. of the mixture they compared with that of the 3:4-phthaloylfluorenone prepared by Schaarschmidt and Herzenberg (Ber., 1918, 51, 1230) which possessed a m.p. 317°, but no mention was made of the vat produced by their mixture although Schaarschmidt and Herzenberg (loc. cit.) stated that their 3:4-phthaloylfluorenone gave an intense red vat with hydrosulphite.

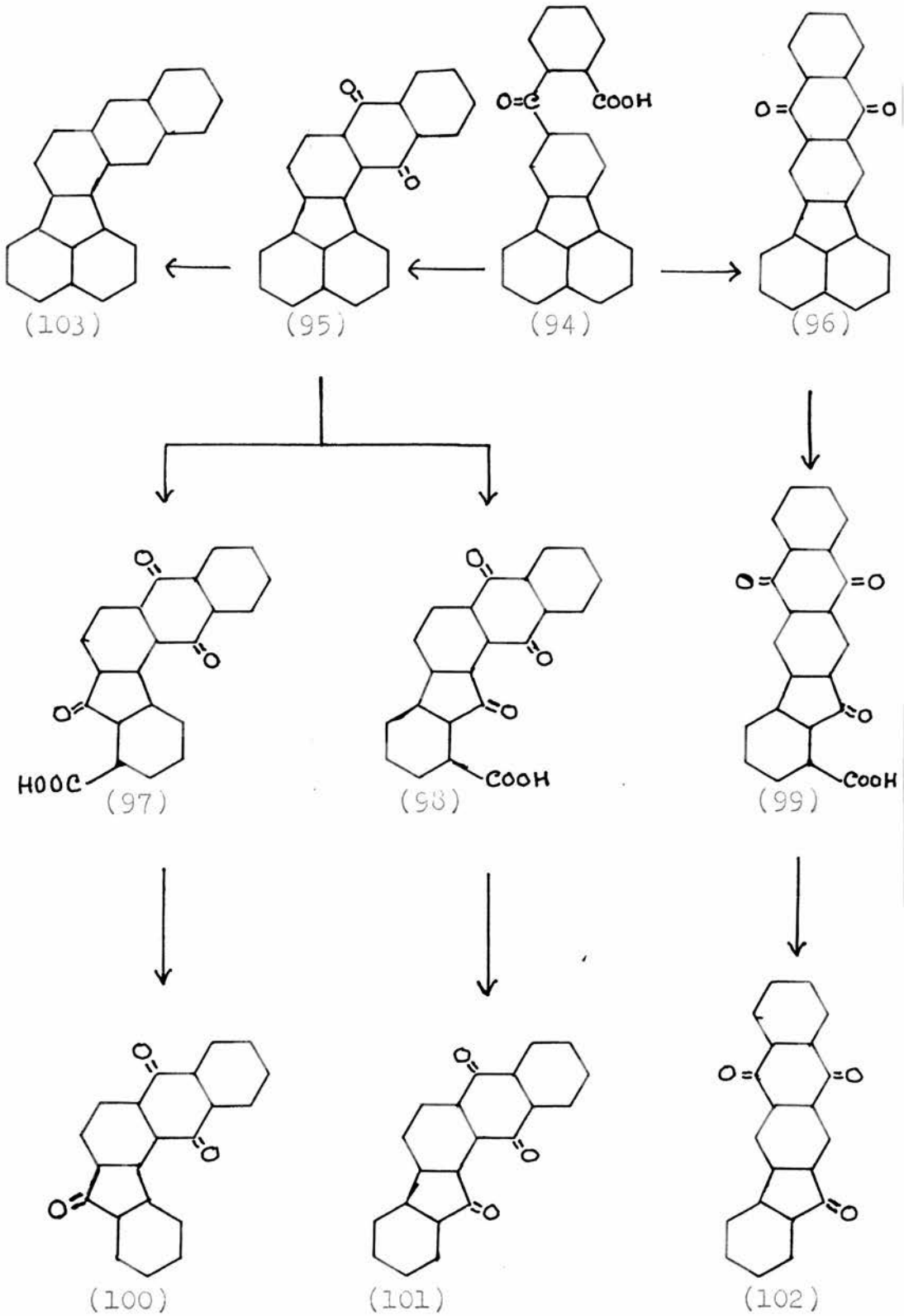
The quinone (95) on fusion with zinc dust gave a yellow hydrocarbon, m.p. 290 - 291°, possessing a yellowish - blue fluorescence in benzene, and to which they assigned the structure (103).

Decarboxylation of the acid (99) gave a single phthaloylfluorenone (102) m.p. 353° which they compared with that of 2:3-phthaloylfluorenone, m.p. 365°, prepared by Ullman and Dasgupta (Ber., 1914, 47, 553). Again, no mention of the vat produced by their compound is made although Ullman and Dasgupta (loc. cit.) describe their compound as giving a green vat with hydrosulphite.

The/

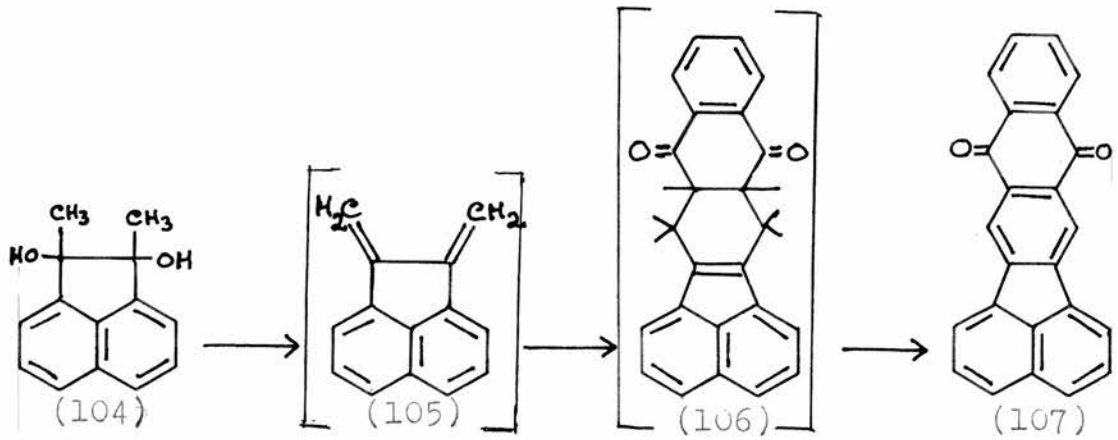
RING-CLOSURE of 11-o-CARBOXY BENZOYL-FLUORANTHENE

(as described by Von Braun and Manz.
Ann., 1932, 496, 188)



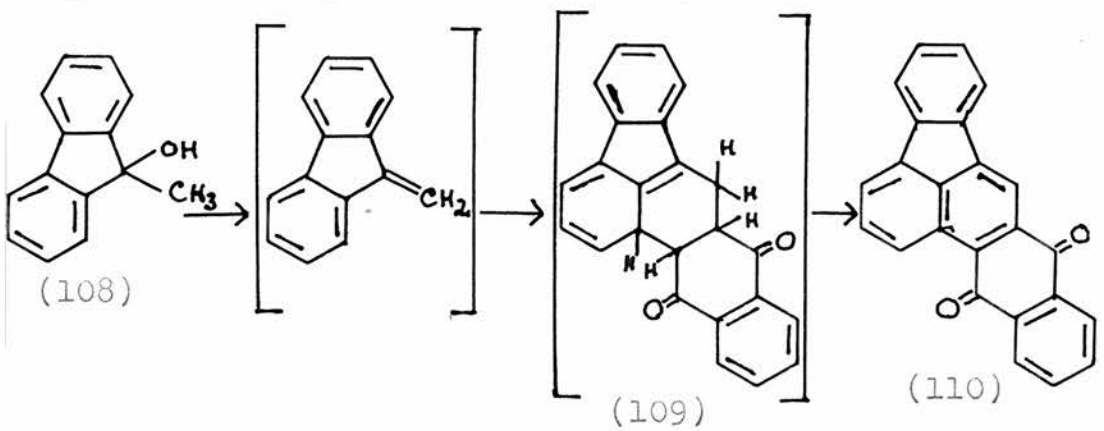
The first hint as to the untenability of the premises for Von Braun's conclusions, correct in themselves, came only when, during the course of investigations on the use of the Diels-Alder reaction for the synthesis of fluoranthene and its derivatives, Campbell and co-workers obtained naphtho (2':3' - 11:12) fluoranthene - 1':4' - quinone (107) and found that its properties did not agree with those of the quinone to which Von Braun had assigned that structure (96).

Having prepared trans -7:8- dimethyl-acenaphthene-7:8-diol (104), Campbell and Gow (J., 1949, 1555) treated this with α-naphthaquinone in boiling acetic anhydride whereupon simultaneous dehydration of the diol and condensation of the thereby arising 7:8-dimethylene-acenaphthene (105) took place. The tetrahydro-intermediate (106) apparently dehydrogenated spontaneously in the boiling solution, for the fully aromatic naphtho (2':3' - 11:12) fluoranthene - 1':4' - quinone (107) was the only product obtained.



(104) (105) (106) (107)

This quinone (107), yellow, m.p. > 310°, was fused with zinc dust and zinc chloride to give a yellow hydrocarbon m.p. >310° displaying in solution a yellowish-blue fluorescence whose constitution naphtho (2':3' - 11:12) fluoranthene, (107), followed from the method of synthesis. It appeared therefore that the assignment of formulae (95) and (96) to the quinones obtained by Von Braun and Manz (i) yellow, m.p. 332 - 333° and (ii) red, m.p. 228° respectively, should at least be reversed. Furthermore, by a similar Diels-Alder reaction involving 9-methyl-9-hydroxy-fluorene (108) and α-naphthaquinone in boiling acetic anhydride, Campbell and Wang (J. 1949, 1513) synthesised unambiguously naphtho (2':3' - 3:4) fluoranthene - 1':4' - quinone m.p. 249 - 251°. This quinone is obviously different from Von Braun's quinone m.p. 328 - 331°, to which he assigned formula (92).



(108) (109) (110)

Here again the tetrahydro-intermediate (109) from the Diels-Alder reaction appeared to be unstable under the reaction conditions, for the fully aromatic quinone (110) was the sole product isolated.

As/

As is seen therefore from the foregoing, the two quinones synthesised by Campbell and co-workers, viz. naphtho (2':3' - 11:12) fluoranthene - 1':4' - quinone (107) and naphtho (2':3' - 3:4) fluoranthene - 1':4'- quinone (110), both differ from the respective quinones obtained by Von Braun and Manz and to which these investigators assigned structures (95) and (92) above.

A relevant paper in the patent literature may be mentioned at this point (Tschech. P.56604. C. 1937, II, 2579). A mixture of 4- and 11-o-carboxybenzoyl-fluoranthenes was cyclised by boiling the mixture with p-toluenesulphonylchloride in trichlorobenzene solution. Two products were obtained, one apparently the yellow quinone (107); the other was red, m.p. 240°. It may be noted here that the colour and m.p. of the latter compound is at once reminiscent of the orange-red quinone, m.p. 228°, obtained by Von Braun and Manz.

SECTION A OBJECT OF RESEARCH

In view of the doubt which had fallen upon the work of Von Braun concerning the structures of the above mentioned naphthofluoranthenequinones it seemed desirable to undertake an unambiguous synthesis of the quinones/

quinones and thereby determine their structures.

The experiments undertaken to this end, involving the Elbs pyrolyses of two isomeric ketones, 4- and 11-o-toluylfluoranthene, also served to prepare the hitherto unknown naphtho (2':3' - 3:4) fluoranthene and naphtho (2':3' - 11:12) fluoranthene.

SECTION A DISCUSSION OF RESULTS

TOLUYLATION of FLUORANTHENE

Since acylation in general had been shown to take place in the 4- and 11- positions of fluoranthene it was anticipated that the toluylation of fluoranthene in carbon disulphide with toluyl chloride in the presence of aluminium chloride would also take place in these positions. Experiment bore this out. The isomeric 4- and 11- o-toluylfluoranthenes, (111) and (110) below, were formed in approximately equal quantities, being separated chromatographically. A considerable amount of tarring occurred during the Friedel-Crafts reaction since the total yield of pure toluylfluoranthenes amounted to only 38%.

ELBS REACTIONS ON 4- and 11- o-TOLUYLFLUORANTHENE

As/

As expected, the Elbs pyrolysis of 11-o-toluyl-fluoranthene gave the two isomeric fully aromatic hydrocarbons.

(112) Naphtho (2':3' - 10:11) fluoranthene (15%)

(113) Naphtho (2':3' - 11:12) fluoranthene (20%)

Each of these hydrocarbons was oxidised to the quinones.

(114) Naphtho (2':3' - 10:11) fluoranthene-1':4'-quinone

(115) Naphtho (2':3' - 11:12) fluoranthene-1':4'-quinone

The Elbs pyrolysis of 4-o-toluylfluoranthene likewise gave the expected hydrocarbon.

(116) Naphtho (2':3' - 3:4) fluoranthene (17%)

together with the corresponding quinone

(117) Naphtho (2':3' - 3:4) fluoranthene-1':4'-quinone (2.5%)

and a peri-condensed hydrocarbon

(118) 4:5-o-xylylenefluoranthene (3%).

The hydrocarbon (116) on oxidation gave the quinone

(119) Naphtho (2':3' - 3:4) fluoranthene-1':4'-quinone

which was identical with (117), while oxidation of the hydrocarbon (118) gave

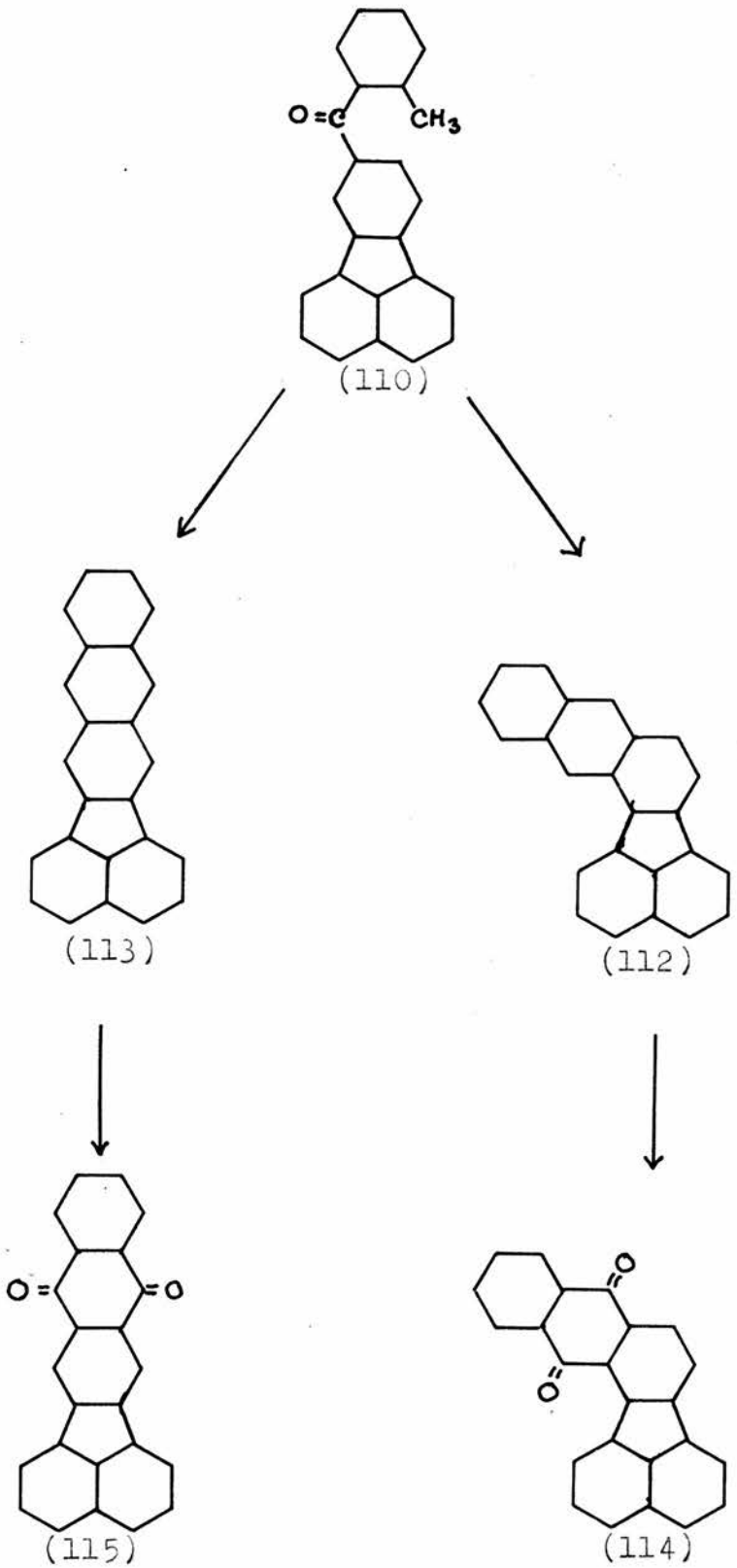
(120) 4:5-phthaloylfluoranthene

This is summarised in equation form. (see separate page).

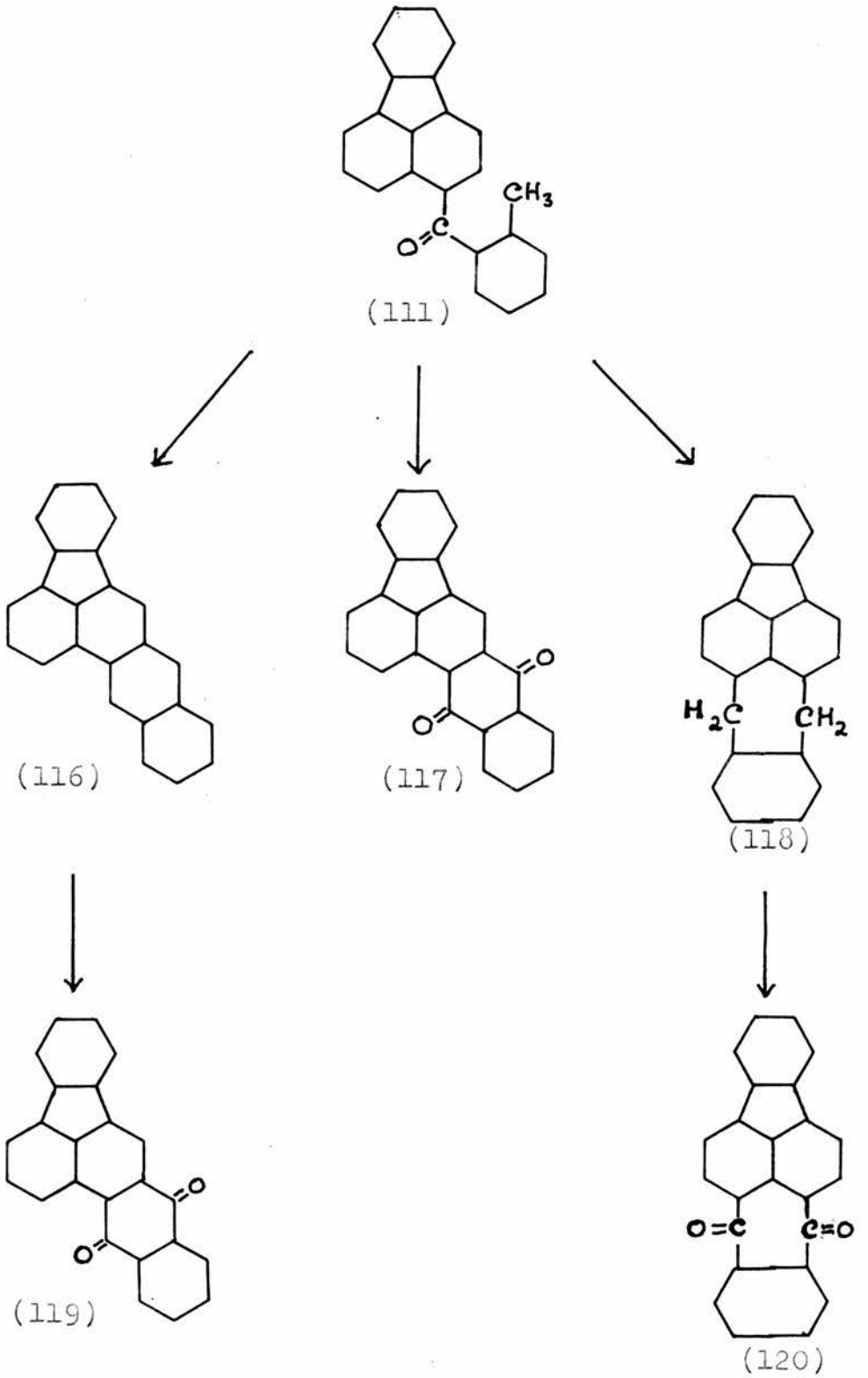
Orientation of these hydrocarbons and their oxidation products was achieved by comparison with the compounds synthesised unambiguously by Campbell and co-workers.

(a) A mixture of hydrocarbon (113) and a sample of naphtho (2':3' - 11:12) fluoranthene prepared by/

ELBS PYROLYSIS of 11-o-TOLUYLFLUORANTHENE



ELBS PYROLYSIS of 4-o-TOLUYLFLUORANTHENE



by Campbell and Gow (loc. cit.) showed no depression of melting point (see Experiemntal Section A).

This serves to orientate the original toluyl-fluoranthene (110) as the 11- isomer as well as orientating the hydrocarbon (113) and quinone (115) as the 11:12-fluoranthene derivatives.

By elimination, the hydrocarbon (112) and the quinone (114) must be naphtho (2':3' - 10:11) fluoranthene and naphtho (2':3' - 10:11) fluoranthene-1':4'-quinone, respectively.

(b) The quinones (117) and (119) each showed no depression of m.p. when mixed with samples of naphtho (2':3' - 3:4) fluoranthene-1':4'-quinone prepared by Campbell and Wang (loc. cit.). This serves to orientate the quinones (117) and (119) and the hydrocarbon (116) as the 3:4-fluoranthene derivatives.

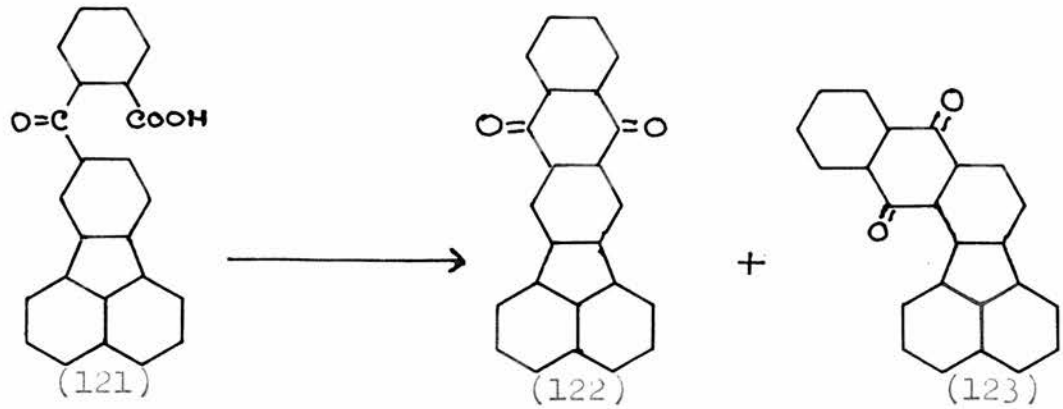
(c) The hydrocarbon (118) was shown to be 4:5-o-xylylenefluoranthene since on oxidation it gave the phthaloylfluoranthene (129), identical (mixed m.p.) with 4:5-phthaloylfluoranthene prepared by ring-closure of 4-o-carboxybenzoyl-fluoranthene (Campbell, Marks and Reid. J., 1951, 3466). (see below).

This serves to orientate the original toluyl-fluoranthene (111) as the 4- isomer.

Support/

Support for these conclusions came from work by Campbell and Marks (Campbell, Marks and Reid. J., 1951, 3466). These investigators prepared 4- and 11-o-carboxybenzoylfluoranthene (124) and (121) respectively, whose constitutions had already been determined by Campbell and Easton (see Introduction, Section A).

(a) Ring-closure of 11-o-carboxybenzoylfluoranthene by boiling it in trichlorobenzene containing toluene-p-sulphonyl chloride gave two quinones (122) and (123) in the proportions of 5 parts (122) to 1 part (123).



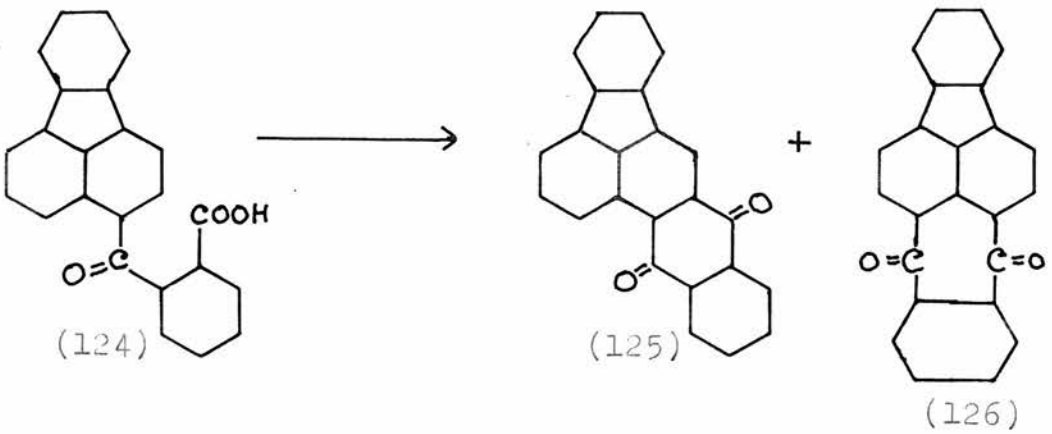
(121) (122) (123)

A mixed m.p. determination showed quinone (122) to be identical with the quinone (115) obtained as described above. The properties of the two quinones (colour and crystalline form, vat, and colouratinn with conc. sulphuric) agreed exactly.

In a similar fashion the quinone (123) proved to be identical with quinone (114) prepared as described above.

(b)/

(b) Ring-closure of 4-o-carboxybenzoylfluoranthene (124) by fusion with aluminium chloride and sodium chloride gave two products, (125) and (126) each having the composition of a naphthofluoranthene quinone.



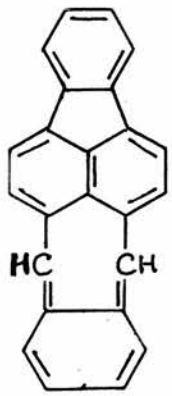
(124) (125) (126)

The compound (125) proved to be identical (mixed m.p.) with the quinones (119) and (117) obtained as described above and agreed entirely with these in its properties.

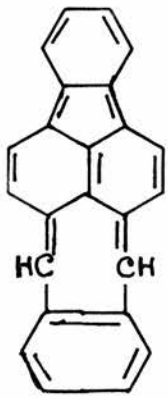
The compound (126), having the same composition as quinone (125), must be regarded as possessing the structure (126) above, having been formed by a peri-ring-closure at the 5- position of the 4-o-carboxybenzoylfluoranthene molecule (124). This theory explains the nature of the hydrocarbon (118) formed by the Elbs pyrolysis of 4-o-toluylfluoranthene since oxidation of (118) gave (120) i.e. (126). The fact that the hydrocarbon (118) is colourless indicates that it possesses the structure (118) assigned to it and not the structure of the fully aromatic system (127) (annexed formulae).

Such/

Such a system as (127) existing with the contributing forms (127) and (128) would be expected to adsorb farther in the visible region than fluoranthene itself, which is pale yellowish - green in colour, the last of the p-bands lying at 3585 Å (Clar and co-workers. Nature, 1950, 166, 1075).

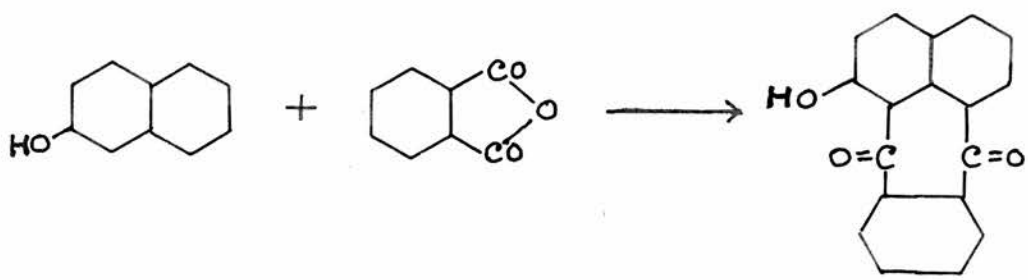


(127)



(128)

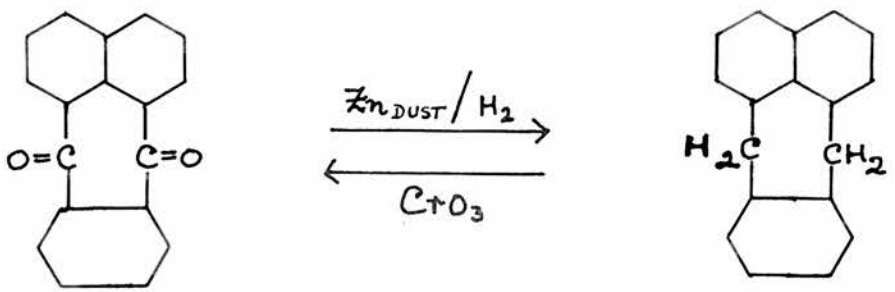
The existance of such peri-condensed phthaloyl compounds in the naphthalene series is already well known. The first example of this type of compound was isolated by Rieche and Frühwald (Ber., 1931, 64, 1603) who obtained 1:8-phthaloyl-β-naphthol (129) as the sole product from the reaction of phthalic anhydride on β-naphthol.



(129)

In a later paper Rieche, Sauthoff and Müller (Ber., 1932, 65, 1371) described the preparation of several hydroxy-1:8-phthaloylnaphthalenes and also the simplest member/

member of this group of compounds viz. 1:8-phthaloyl-naphthalene (130). The evidence aited by Rieche left no doubt as to the correctness of his theory that a seven-membered ring is present in these compounds and arises from a peri-condensation in the naphthalene nucleus. In these compounds the oxygen is present in the form of two non-quinonoid carbonyl groups. As might be expected the carbonyl groups should be reducible and indeed, by distilling 1:8-phthaloylnaphthalene with zinc dust in a stream of hydrogen Rieche and co-workers were able to isolate 1:8-o-zylylenenaphthalene (131) in which the two keto groups are reduced to methylene.



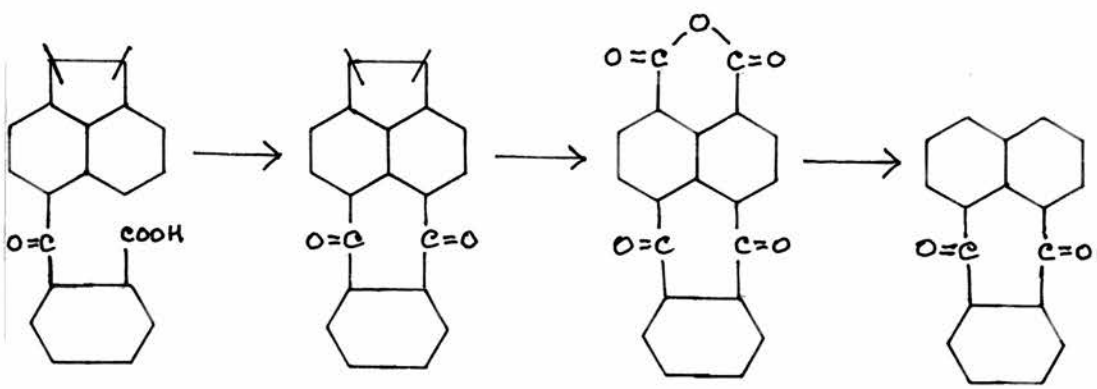
(130) (131)

Oxidation of 1:8-o-xylylenenaphthalene (131) with sodium dichromate in glacial acetic acid regenerated 1:8-phthaloylnaphthalene (130). The latter was also obtained by a similar zinc dust distillation of the phenol (129). It is noteworthy that these compounds containing seven membered rings are quite stable to heat. (c.f. 4:5-o-xylylenefluoranthene below).

Rieche's/

Rieche's assertion that 'man kann wohl mit Recht annehmen, dass auch bei anderen Reaktionen dieser Art Derivative des Phthaloyl-naphthalins als Nebenproducte entstehen' was fully justified by later work on the ring closure of 3-o-carboxybenzoylacenaphthene (132) and 4-o-carboxybenzoylfluoranthene (124) (above).

On fusion of 3-o-carboxybenzoylacenaphthene (132) with a mixture of aluminium chloride and sodium chloride (Peters and Rowe. J. Soc. Dyers and Colourists, 1943, 59, 52) the sole product of the reaction was 3:4-phthaloyl-acenaphthene (133) whose structure was fixed by oxidation to 4:5-phthaloylnaphthalic anhydride (134) which was subsequently decarboxylated to 1:8-phthaloyl-naphthalene (135) (Campbell, Marks and Reid, loc. cit.)



(132) (133) (134) (135)

Furthermore, under the same reaction conditions Campbell and Marks (Campbell, Marks and Reid, loc. cit.) ring-closed 4-o-carboxybenzoylfluoranthene (124) as described earlier and obtained 4:5-phthaloylfluoranthene (126). The formation of this seven-membered ring compound/

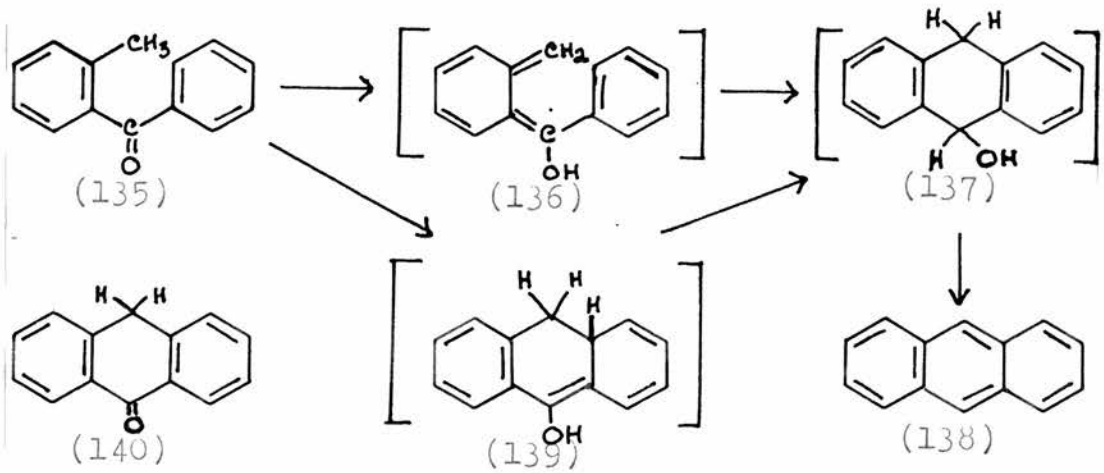
compound on oxidation of the hydrocarbon to which structure (118) has been assigned has been described earlier and parallels the formation of 1:8-phthaloylnaphthalene (131) by oxidation of 1:8-o-xylylenenaphthalene (130), the establishment by Rieche of whose structure has already been discussed. It seems conclusive therefore that the structure (118) assigned to this hydrocarbon is the correct one.

The isolation of 4:5-o-xylylenefluoranthene from the product of the Elbs pyrolysis of 4-o-toluylfluoranthene represents the first case in which a seven-membered ring system has been isolated from the products of an Elbs pyrolysis. The hydrocarbon appears quite stable to heat - a feature belonging to the related hydrocarbon 1:8-o-xylylenenaphthalene - being unscathed by the Elbs pyrolysis temperature (400 - 450°). A peculiar feature of the reaction is that no oxygen appears in the final product while there are present two atoms of hydrogen more than would be present if the oxygen were eliminated from the ketone as water.

As to the actual mechanism of the normal Elbs condensation, Cook (J., 1931, 487) suggested that the diaryl ketone (135) with the methyl or methylene group adjacent to the carbonyl group, may tautomerise to an enolic form (136) having a diene system to which intramolecular addition of the attached aryl group may occur with formation of the dihydroanthranol (137) which at the pyrolysis temperature would lose water at

once/

once to give the fully aromatic hydrocarbon (138).



Fieser and Dietz (Ber., 1929, 62, 1827) suggested that the same dihydroanthranol (137) may alternately be formed by a forced 1:4-addition of the ortho methyl(ene) group to the conjugated system consisting of the carbonyl group and the aryl nucleus via. intermediate (139). These mechanisms, besides explaining the formation of the normal product from the Elbs pyrolysis viz. anthracene or a substituted anthracene, also explain the formation in one or two instances of anthrones, hydrogen being eliminated from (137) or (139) instead of water with ultimate formation of (140). (for discussion see below).

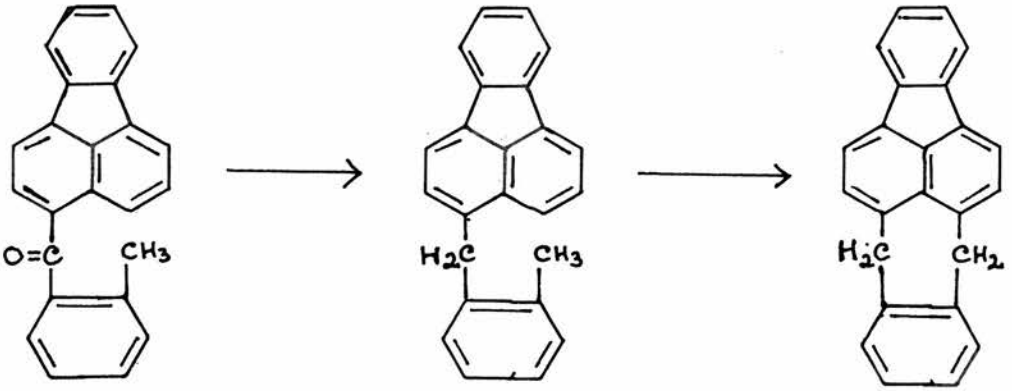
In such cases the final product appears with 2 atoms of hydrogen less than the original ketone - no oxygen is lost, hydrogen is cracked out.

It is however unlikely that either of these mechanisms is in operation during the formation of the peri-condensed hydrocarbon (118) for the double-bond configuration about the carbon atoms which participate in/

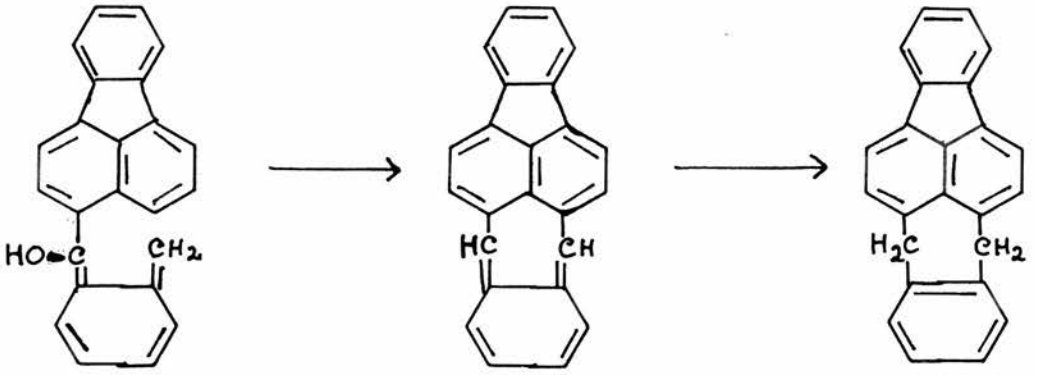
in the ultimate formation of the seven-membered ring in this compound is no longer comparable with that about the carbon atoms involved in the formation of the six-membered ring in the "normal" Elbs pyrolysis products.

Two suggestions may be put forward to describe the mechanism of formation of peri-condensed hydrocarbon during the Elbs pyrolysis of 4-o-toluylfluoranthene.

(a) Oxygen of the carbonyl group may be removed initially by reduction at the high temperature of the pyrolysis, with subsequent elimination of hydrogen and ring formation as follows -



(b) Alternatively initial enolisation of the ketone may take place as postulated by Cook followed by removal of water and formation of the aromatic system (140) which might then be



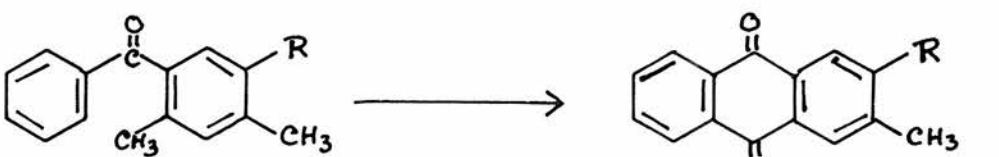
(140) (118)

reduced to 4:5-o-xylylenefluoranthene(118).

The formation of such a peri-condensed hydrocarbon being quite novel, an attempt was made to detect the formation of 1;8-o-xylylenenaphthalene in the Elbs pyrolysis of 1-o-toluylnaphthalene. Despite careful search none was observed.

Some Observations on the Elbs Reaction

As has already been mentioned the formation of anthrones has in one or two rare cases been observed to take place during the Elbs pyrolysis. It may be remarked here that during his researches on the uses of the reaction bearing his name, Elbs (J. prakt. Chem., 1887, 35, 471 and 492) observed the formation of 2-methyl and 2:3-dimethyl-anthraquinone (143) and (144) from the pyrolyses of 4-benzoyl-m-xylene (141) and 2-benzoyl-1:4:5-trimethylbenzene (142), respectively.



(141) R ≡ H
(142) R ≡ CH_3-

(143) R ≡ H
(144) R ≡ CH_3-

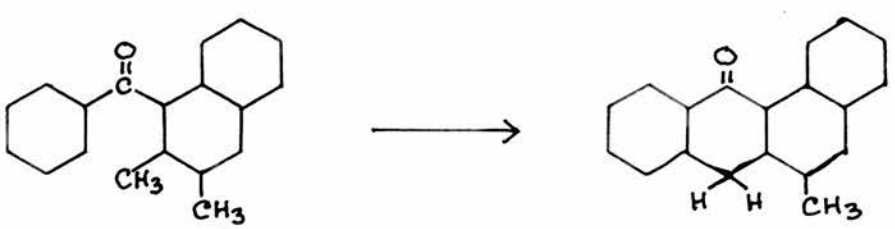
Elbs attributed this to aerial oxidation of the corresponding anthracenes formed, during the long boiling of the ketones.

Apart from these two cases where the simple explanation given is very likely correct, only three other/

other cases have been reported out of some 160 pyrolyses carried out of anthrones arising from Elbs pyrolyses. These were -

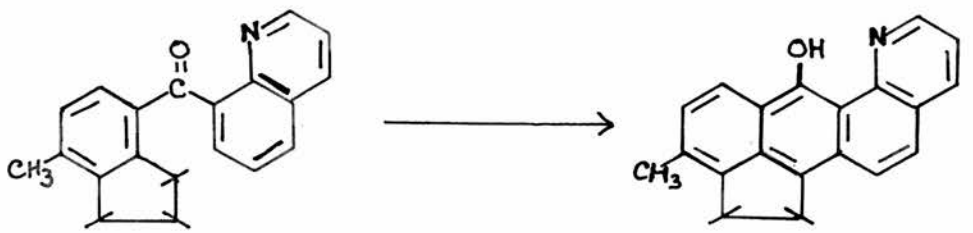
(a) the formation of 2:3:6-trimethyl-9-anthrone, along with the main reaction product, 2:3:6-trimethylanthrace, from the pyrolysis of 2:4:5:4'-tetramethylbenzophenone (Morgan and Coulson. J., 1929, 2551) thus

(b) the formation of 4-methyl-1:2-benz-9-anthrone together with the main reaction product, 4-methyl-1:2-benzanthracene, from the pyrolysis of 2':3'-dimethyl-1'-benzoylnaphthalene (Fieser and Peters. J.A.C.S., 1932, 54, 3742) thus



and

(c) the formation of 11-hydroxy-20-methyl-1-azacholanthrene (147) as the sole product from the Elbs pyrolysis of 8-quinolyl-(7-methyl-4-hydrindyl)-ketone (145) (Fieser and Hershberg., J.A.C.S., 1940, 62, 1640) thus



(145) (147)

This reaction was favoured by the presence of palladised-charcoal and proceeded in good yield (50%).

It is extremely interesting therefore that in three out of four Elbs pyrolyses carried out in our laboratories, as well as the normal products from the reactions viz. the fully aromatic hydrocarbons, the corresponding quinones were also isolated (see Experimental Section A).

A control experiment carried out on 1:2-benzanthracene (c.f. Experimental Section A) yielded, besides unchanged 1:2-benzanthracene, a mere 0.5% yield of an orange syrup which could not be identified definitely as 1:2-benzanthraquinone, while a yield of not less than 7% of 1:2-benzanthraquinone, and even as high as 13%, was obtained when Elbs pyrolyses were carried out on 1-o-toluylnaphthalene. This, coupled with the fact that the pyrolyses were all carried out in an inert atmosphere, shows conclusively that the quinones were not produced by oxidation of the hydrocarbon when once formed, either by aerial oxidation during the pyrolyses or by subsequent/

subsequent oxidation on the alumina columns used for the analyses of the products of the pyrolyses.

It seems fairly certain that the quinones arose from the corresponding anthrones by oxidation on the alumina. A yellow compound, possessing the same analysis figures as would be given by 1:2-benz-9-anthrone, was actually isolated from the product obtained by the Elbs pyrolysis of 1-o-toluylnaphthalene.

This substance, although giving a positive Liebermann test for anthrone (anthranol), had an unusually high melting point (310 - 313°). 1:2-benz-9-anthrone has been described by Cook (J., 1930, 1087) who however did not obtain it analytically pure, but characterised it by preparing its benzoate. Unfortunately, not enough of the yellow compound was obtained to allow of the preparation of a derivative.

This substance dissolves in boiling alcoholic alkali to give a yellow solution possessing a strong greenish - yellow fluorescence in U.V. radiation. Acidification quenches the fluorescence and almost decolourises the solution. Both colour and fluorescence reappear on addition of excess alkali to the acid solution, followed by boiling of the solution. Although no solid was isolated from the product of the Elbs pyrolysis on 4-o-toluylfluoranthene a small quantity of a yellowish - brown solid was obtained from the pyrolysis of 3-o-toluylacenaphthene. The substance had no definite melting point and could not be obtained pure/

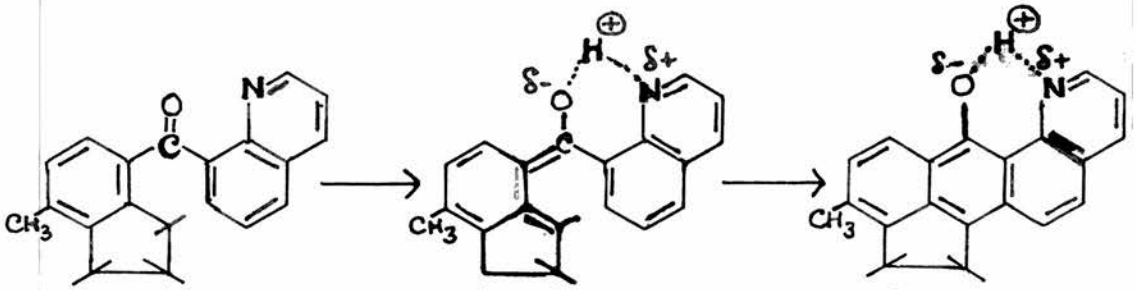
pure on account of the small amount of material available. It did dissolve partially in alcoholic alkali and completely on boiling the alcoholic alkaline solution. The solution displayed the same colour and fluorescence in alkali as did a solution of the solid described above and again, on acidification decolourisation of the solution and quenching of the fluorescence occurred.

Likewise an alkaline extraction of the pyrolysis product of 4-o-toluylfluoranthene gave a solution (from which no solid could be extracted) which behaved similarly.

The behaviour of all these solutions indicates the presence of anthrones or their tautomeric forms, anthranols. The formation of the anthrones probably takes place by dehydrogenation of the intermediate (136) postulated by Cook or, in the case of the mechanism postulated by Fieser and Dietz, the intermediate (139). Either mechanism, both of which postulate the formation of an enolic form of the oxygen atom, is in accord with the behaviour of 8-quinolyl-(7-methyl-4-hydrindyl)-ketone (145) when subjected to the Llbs pyrolysis and it is significant that the best yields were obtained when the pyrolysis were carried out in the presence of palladised-charcoal, a dehydrogenation catalyst.

Examination of the U.V. spectrum of the product of this pyrolysis, (147), indicated that the nitrogen was bound in an ionic form probably as an inner salt formed/

formed by the interaction of the nitrogen atom with the hydroxyl group which is in close proximity to it.



(145) (146) (147)

The presence of this structural feature would increase the extent of enolisation of the ketone (145) to the intermediate form (146) and at the same time stabilise the product (147) towards the reaction temperature. Two atoms of hydrogen would split out with formation of the final product (147), a process which, as might be expected, would be assisted by the presence of palladised-charcoal.

The fact that the presence of anthrones has hitherto been observed in only three instances is no indication of the number of cases where formation actually took place. Owing to the complex nature of the products the analysis of these pyrolyses products is a difficult matter unless the products are present in reasonable quantity, and as has been found the anthrones (or quinones) have been isolated in relatively small quantities. It is significant that the detection of the quinones obtained from the three pyrolyses carried out in our laboratories was due entirely to the use of

chromatography/

chromatography for the purification of the pyrolyses products. It seems safe to predict that with a more general application of the chromatographic analysis technique to Elbs reaction products the presence of anthrones will be found to be the rule and not the exception.

A Critical Analysis of Von Braun's Results

As mentioned earlier in the discussion the results of the work carried out on the 4- and 11-o-toluylfluoranthenes agree exactly with those obtained by Campbell and Marks on the cyclisation of the 4- and 11-o-carboxybenzoylfluoranthenes. A satisfactory interpretation of the results is obtained if the orientation of all the compounds obtained (hydrocarbons and their oxidation products) is based on the key syntheses

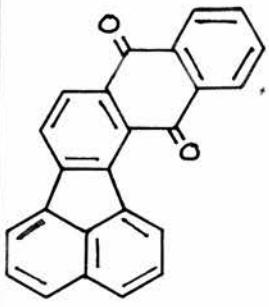
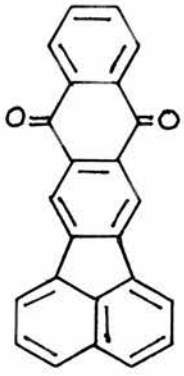
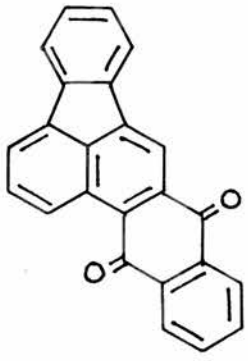
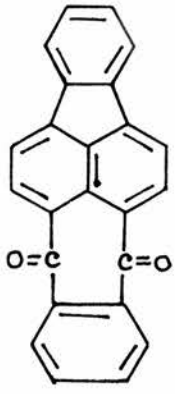
(a) that of naphtho (2':3' - 3:4) fluoranthene-1':4'-quinone by Campbell and Wang.

(b) that of naphtho (2':3' - 11:12) fluoranthene-1':4'-quinone by Campbell and Gow.

The results of Campbell and co-workers and those of Von Braun and Manz are set out in the table on the next page and are discussed thereafter.

As mentioned in the Experimental Section A the quinone m.p. 332 - 333° which Von Braun concluded was naphtho (2':3' - 10:11) fluoranthene-1':4'-quinone gave, on distillation with zinc dust, a hydrocarbon, m.p. 290-291° which from its m.p. and properties corresponded to the/

Campbell, Marks and Reid

				
m.p.	316-318°	338-340°	250-253°	296-297°
Colour	yellow	yellow	orange-red	yellow
Vat	none	blue	blue-violet	none
Conc.H_2SO_4	purple	blue	blue-green	red
	Von Braun and Manz			
m.p.	332-333°	228°	328-331°	
Colour	golden-yellow	red	yellow	NOT
Vat	bluish-violet	violet	blue-violet	ISOLATED
Conc.H_2SO_4	deep blue	deep violet	---	

zinc dust distillation of naphtho (2':3' - 11:12) fluoranthene-1':4'-quinone. It appeared therefore that von Braun's quinone, m.p. 332-333° was really naphtho (2':3'- 11:12) fluoranthene-1':4'-quinone. This however leaves unsolved the identity of the other quinone m.p. 228° obtained by von Braun on ring closure of his 11-o-carboxybenzoylfluoranthene (94), for this quinone shows no resemblance whatever to naphtho (2':3' - 10:11) fluoranthene-1':4'-quinone (see table above). Furthermore von Braun's quinone, m.p. 328-331°, obtained by ring-closure of 4-o-carboxybenzoylfluoranthene (90) does not correspond to Campbell's naphtho (2':3' - 3:4) - fluoranthene - 1':4' - quinone.

In the first place it is seen that van Braun's 11-o-carboxybenzoylfluoranthene (94) was impure having a m.p. of 212° as compared with 234° found by Campbell and Marks. It is also noteworthy that the m.p. 230°, of 4-o-carboxybenzoylfluoranthene as determined by both Campbell and von Braun lies very close to that of Campbell and Marks 4-o-carboxybenzoylfluoranthene. Again, Campbell and Marks found that ring-closure of 11-o-carboxybenzoylfluoranthene produced the 10;11 - and the 11:12 - quinones in the ratio of 1:5 by weight.

From/

From these observations a reasonable explanation can be given which accounts on the whole for the facts.

Von Braun's 11-o-carboxybenzoylfluoranthene (94), being very impure, probably contained some of the 4-o-carboxybenzoylfluoranthene (90). On ring closure of the impure 11-acid (94) there would result therefore some naphtho (2':3' - 3:4) fluoranthene - 1':4' - quinone together with the mixture of quinones arising from the 11-acid. Since however there arises only one part of naphtho (2':3' - 10:11) fluoranthene - 1':4' - quinone for every five parts of naphtho (2';3' - 11:12) fluoranthene - 1':4' - quinone formed, the amount of the former quinone present would be small and might well have escaped detection. The net result would be that ring closure of the impure 11-acid would give naphtho (2':3' - 3:4) - and naphtho (2':3' - 11:12) - fluoranthene - 1':4' - quinone. A comparison of these quinones with the two quinones isolated by von Braun indeed shows a parallelism between the two pairs of quinones.

Again, von Braun obtained his 4-acid (90) by working up the motherliquors from which he obtained his 11-acid, and after a lengthy process of crystallisation obtained it with a m.p. of 230°.

Now/

Now this acid could not be the 4-acid since ring closure of the acid gave a quinone m.p. 328-331° obviously entirely different from that synthesised by Campbell and co-workers whose quinone gave a m.p. of 250-253°. It seems extremely likely that von Braun, far from obtaining the 4-acid (90) had actually isolated the 11-acid (94) in a relatively pure form - much purer than his supposed pure 11-acid (94) of m.p. 212°. Ring closure of this acid (94) should however give two quinones whereas von Braun obtained only one quinone, m.p. 328-331°. This objection however is removed when the method is considered by which von Braun isolated his quinone. For, ring-closure of his supposed 4-acid (90) by the use of conc. sulphuric acid resulted in the formation of a quinone sulphonic acid. This was hydrolysed with hydrochloric acid - barium chloride to the quinone which was purified by formation of its vat and subsequent sublimation in high vacuum. Two possibilities present themselves to account for the non-appearance of a second quinone from the ring-closure.

(a) The ring-closure process might have led to the formation of an 11:12- quinone sulphonic acid alone.

(b) Assuming the formation of both the 10;11- and the 11:12- quinone sulphonic acids it is conceivable that/

that the 10:11- quinone sulphonic acid could hydrolyse much less readily than the 11:12 quinone sulphonic acid.

Whatever the explanation the fact remains that the 10:11-quinone, if present, would never survive the purification process involving the formation of the vat, because it does not form a vat. Accordingly, only the 11:12- quinone, which is soluble in alkaline hydrosulphite, would pass into solution and be obtained subsequently as the sole product from the ring-closure. A comparison of the properties of this quinone and those of Campbell's naphtho (2':3' - 11:12) fluoranthene - 1':4' - quinone shows the two quinones to have similar properties.

Briefly, it appears extremely probably that

(a) von Braun's supposed 10:11 - quinone was really naphtho (2':3' -11:12) fluoranthene - 1':4' - quinone.

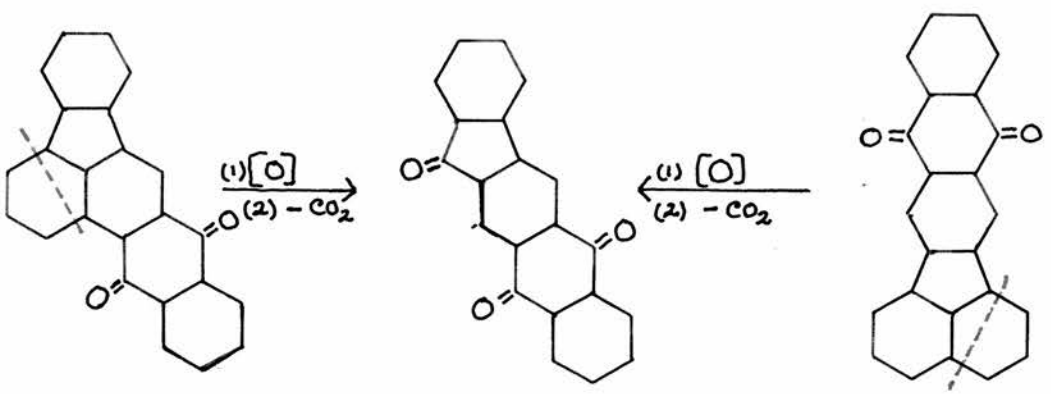
(b) likewise, his supposed 11:12- quinone was really naphtho (2':3' -3:4) fluoranthene - 1':4' - quinone.

(c) and again, his supposed 3:4- quinone was really naphtho (2':3' - 11:12) fluoranthene - 1':4' - quinone.

It only remains to discuss the oxidation products of von Braun's quinones.

In/

In the first place, oxidation of the supposed 11:12- quinone followed by decarboxylation of the resulting acid yielded a phthaloylfluorenone m.p. 353° which von Braun indicated was identical with 2:3- phthaloylfluorenone m.p. 365° described by Ullmann and Dasgupta (loc. cit.). The proposal that von Braun's supposed 11:12- quinone is in reality the 3:4- quinone does not clash with this oxidation result of von Braun since both the 11:12- and the 3:4- quinone would give the same (2:3-) phthaloylfluorenone on oxidation thus



Secondly, oxidation of the supposed 10:11- quinone gave finally a so-called mixture of phthaloyl- fluorenones of melting range 326 - 337°, This they indicated would contain the 3:4- phthaloylfluorenone m.p. 317° prepared by Schaarschmidt and Herzenberg (loc. cit.). It is obvious that this comparison really means nothing since von Braun's product had too wide a range of melting (326-337°) to allow of a legitimate comparison with Schaarschmidt's

3/

3:4- phthaloylfluorenone. It has already been stated that von Braun's supposed 10:11- quinone was in all probability the 11:12- quinone, oxidation of which would give eventually 2:3- phthaloylfluorenone, m.p. 365°. The order and range of the melting point of von Braun's oxidation product (326-337°) is in good agreement with the belief that this substance was impure 2:3- phthaloylfluorenone obtained by oxidation of the 11:12 quinone.

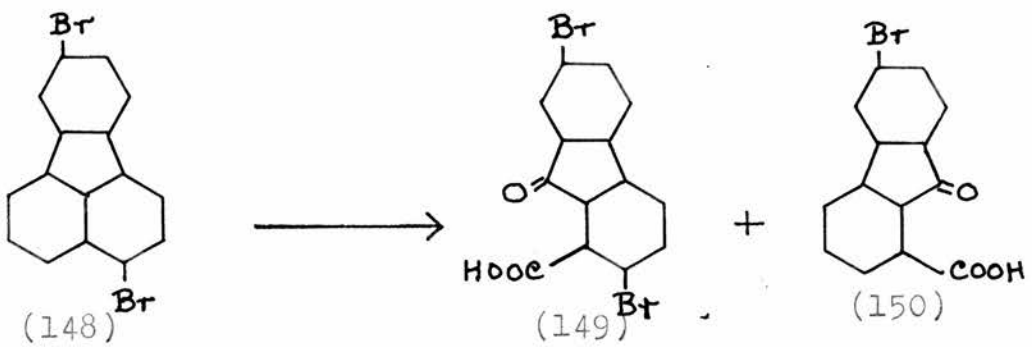
Finally, with regard to the ring closure of the mixture of 4- and 11-o-carboxybenzoylfluoranthenes described in the patent literature it appears probable that the red quinone m.p. 240° was actually naphtho (2':3' - 3:4) fluoranthene - 1':4'- quinone (orange - red, m.p. 250-253°).

SECTION B INTRODUCTION

DISUBSTITUTION IN FLUORANTHENE

Bromination. Earlier work by Tobler (Helv. Chim. Acta., 1941, 24, 101 E) and Campbell (Nature 1950, 165, 76) suggested that dibromination of fluoranthene took place in the 4- and 11- positions. Proof of this came from both degradative and synthetic work.

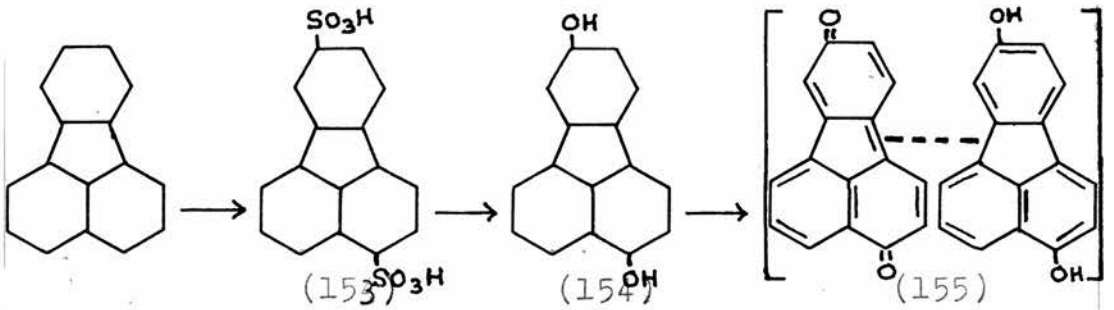
(a) Oxidation of dibromofluoranthene (148) by Campbell, Easton, Rayment and Wilshire (J., 1950, 2784) gave 2:7-dibromofluorenone-1-carboxylic acid (149) together with 6-bromo-fluorenone-1-carboxylic acid (150).



(b) Holbro [redacted] and Tagmann [redacted] (Helv. Chim. Acta., 1950, 33, 2178) synthesised 4:11-dibromofluoranthene by starting from 2:7-dibromofluorene-9-carboxylic acid ester (151) which they condensed (a) with acrylonitrile and (b) with ethyl 2-bromopropionate, each condensation ultimately/

ultimately giving β - 2:7 - dibromofluorene - 9 - propionic acid (152). This acid was cyclised, reduced and dehydrogenated to 4:11 - dibromofluoranthene (148). (Scheme of synthesis on next page).

Sulphonation. The action of conc. sulphuric acid on fluoranthene resulted in the formation of a disulphonic acid (153) (von Braun & Manz. Ann., 1931, 488, 111). This diacid (153) was fused with potash (I.G. Farbenindustrie A.G., D.R.P. 575,953) to give a dihydroxyfluoranthene (154) oxidation of which gave a green quinhydrone type of compound (155).



(153) (154) (155)

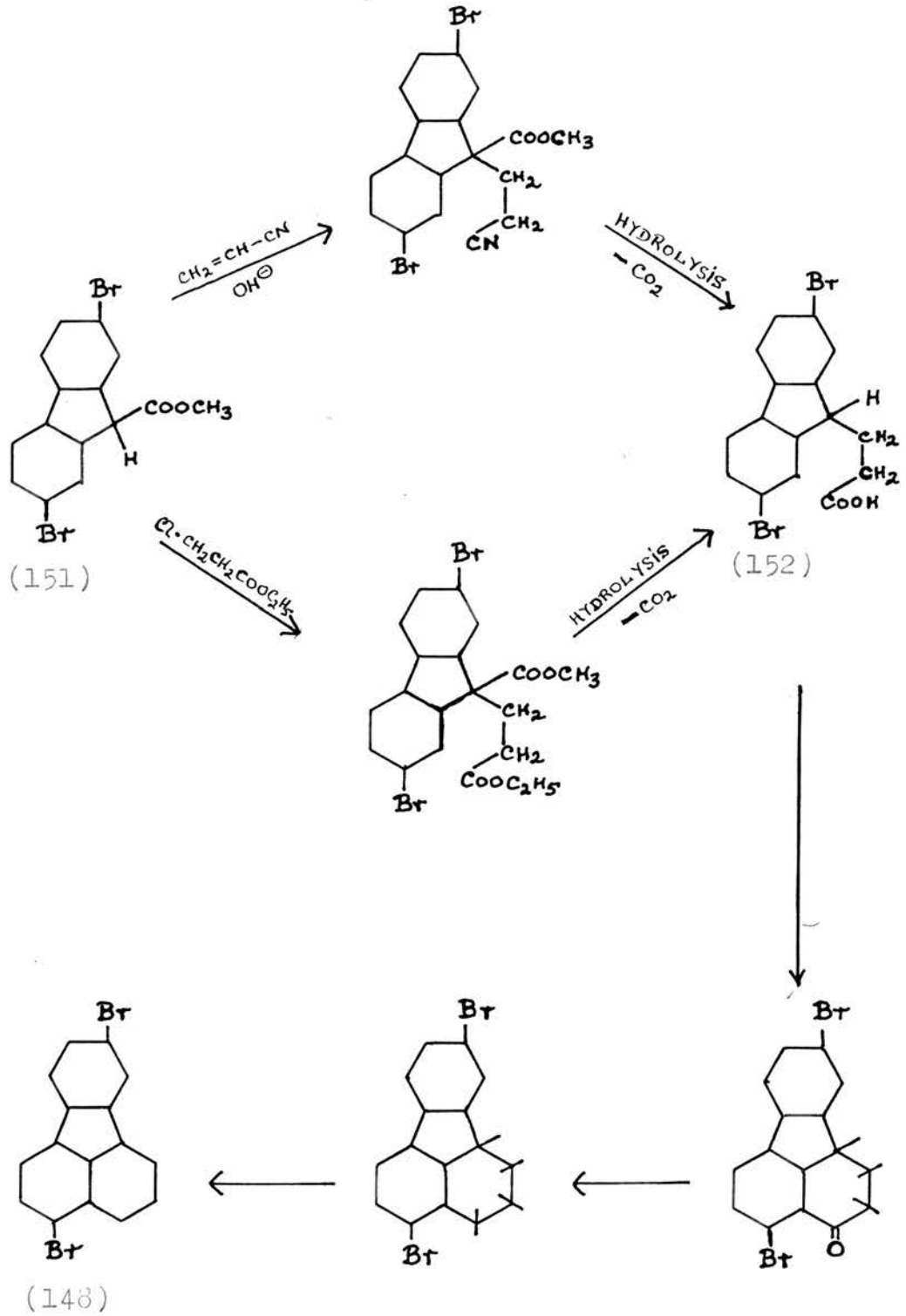
Tobler (loc. cit.) argued that with the sulphonic acid groups in any other positions than the 4- and 11- positions such a quinonoid structure as exists in (155), would not be possible. It followed that the diacid (153) was fluoranthene - 4:11 - disulphonic acid.

Nitration. No dinitration product of fluoranthene is known. The action of nitric acid on fluoranthene

in/

SYNTHESIS of 4:11-DIBROMOFLUORANTHENE

(as described by Holbro and Tagmann. Helv. Chim. Acta, 1950, 33, 2178)



in acetic acid (von Braun & Manz. Ann. 1931, 488, 188) gives a mixture of 4- and 11- nitrofluoranthene while the use of fuming nitric acid (Fittig and Gebhard. Ann., 1878, 193, 147) gives an as yet not orientated, trinitrofluoranthene.

Acylation. While dibromination of fluoranthene was shown quite conclusively to take place in the 4- and 11- positions and in all probability disulphonation took place likewise in the 4- and 11- positions, nothing definite was known concerning other disubstituted fluoranthenes and, in particular, diacylfluoranthenes as obtained from the Friedel - Crafts reactions on fluoranthene. Two diacylfluoranthenes had previously been characterised but not orientated (a) a fluoranthene - dicarboxylic acid and (b) a diacetyl fluoranthene.

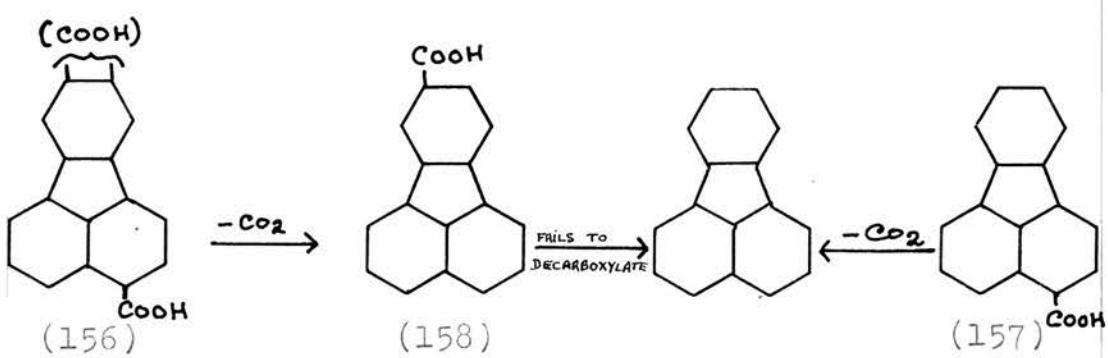
Carboxylation of fluoranthene by the action of oxalyl chloride and aluminium chloride on fluoranthene (von Braun and Manz. Ann., 1932, 496, 170) gave mainly 11 - carboxyfluoranthene, a considerable quantity of a dicarboxyfluoranthene and a small amount of 4 - carboxyfluoranthene. Repetition of this work by Campbell and Easton (J. 1949, 340) gave essentially the same results except that no 4- acid was found.

Campbell and Easton (loc. cit.) likewise obtained

4/

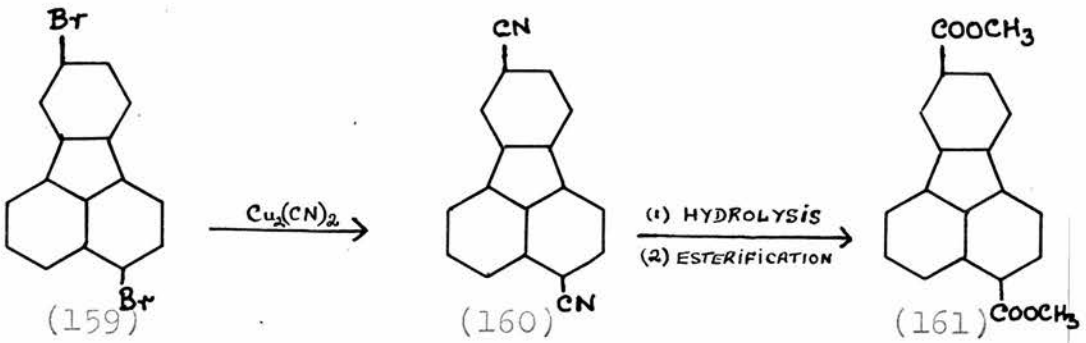
4- and 11- acetylfluoranthene and a diacetylfluoranthene by the action of acetyl chloride and aluminium chloride on fluoranthene. This was a repetition of the work of Buu - Hoi and Cagniant (Rect. Trav. Chim., 1943, 62, 719) who claimed to have isolated pure 11- acetylfluoranthene but no diacetylfluoranthene, by this procedure.

While no definite evidence existed as to the positions of substitution of these diacylfluoranthenes, certain observations on the behaviour of the fluoranthene dicarboxylic acid (156) on decarboxylation indicated that this diacid was either the 4:11- or the 4:12- dicarboxylic acid. Since fluoranthene - 4 - carboxylic acid (157) is readily decarboxylated with copper in boiling quinoline whereas the 11- acid (158) is unaffected, the fact that the dicarboxylic acid was decarboxylated to fluoranthene - 11 - carboxylic (158) acid was a good indication that it was either the 4:11- or the 4:12- dicarboxylic acid.



(156) (158) (157)

Furthermore, Campbell et. al. converted authentic 4:11- dibromofluoranthene (159) to 4:11- dicyano-fluoranthene (160)which hydrolysed to give fluoranthene - 4:11 - dicarboxylic acid whose methyl ester (161) appeared to be identical with the methyl ester of the dicarboxylic acid prepared by Campbell and Easton.



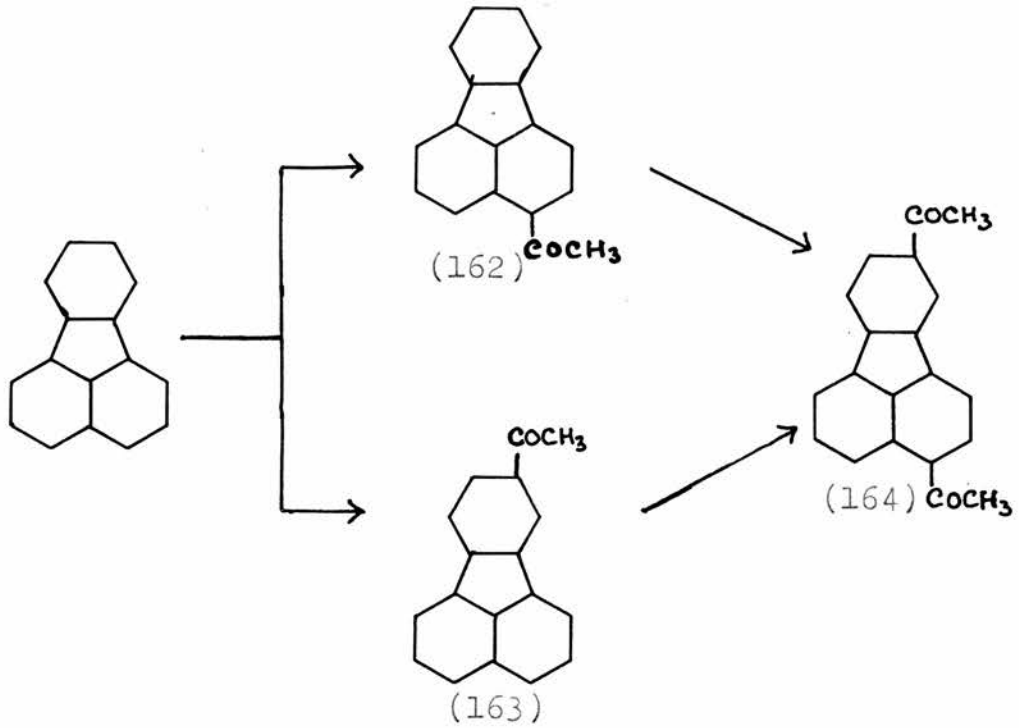
(159) (160) (161)

Owing to the small quantity of material obtained, however, the results could not be considered conclusive. The work was therefore repeated by Campbell and Wilshire (J. 1950, 2784) when it was shown quite definitely that the dicarboxylic acid of Campbell and Easton and the German investigators was not the 4:11- dicarboxylic acid. (m.p. and mixed m.p.)

This was the state of affairs existing when the synthesis described in experimental Section B was undertaken. While this work was being carried out/

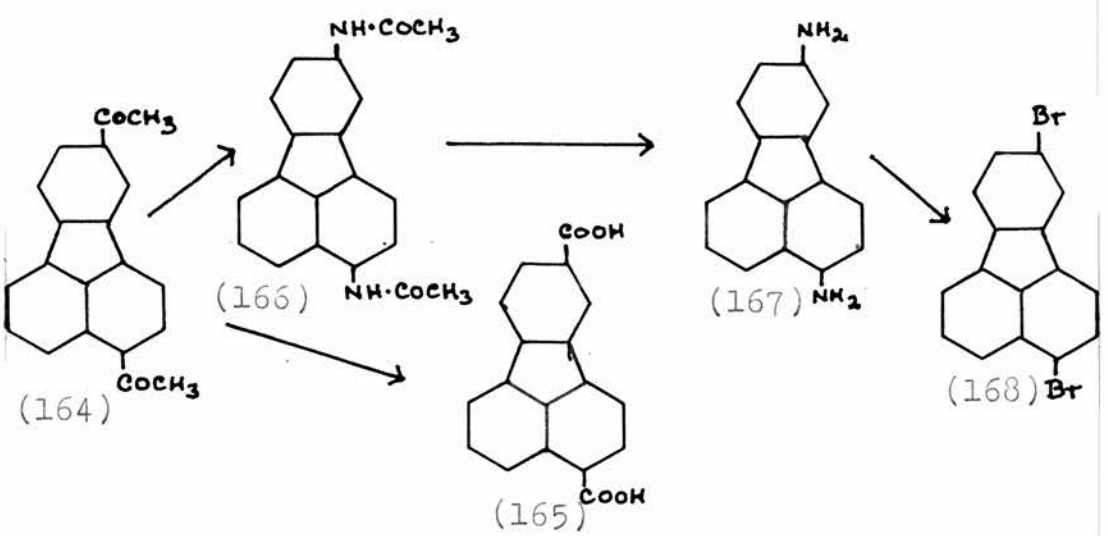
out however, investigations by Campbell, Leadill and Wilshire (J. 1951, 1404) established the fact that diacylation of fluoranthene resulted in 4:12-disubstitution.

Acetylation of fluoranthene by the action of acetyl bromide in the presence of aluminium chloride in carbon disulphide solution gave a mixture of 4- and 11- acetylfluoranthenes which were separated and purified chromatographically.



Both 4- and 11- acetylfluoranthene (162) and (163), respectively, on further acetylation yielded the same diacetylfluoranthene (164). It followed therefore that the diacetylfluoranthene (164) must have/

have been either the 4:11- or the 4:12- compound. That it was actually the latter was shown by hypochlorite oxidation of the diacetylfluoranthene to a fluoranthene - dicarboxylic acid (165) which was different from fluoranthene - 4:11 - dicarboxylic acid prepared from authentic 4:11 - dibromofluoranthene via 4:11 - dicyanofluoranthene (see above, Campbell and Wilshire, J. 1950, 2784). It follows therefore by elimination that the dicarboxylic acid (165) is fluoranthene 4:12 - dicarboxylic acid and the diacetylfluoranthene (164), 4:12 - diacetylfluoranthene, Confirmation of this came from conversion of the 4:12 - diacetylfluoranthene (164) into 4:12 - diacetamidofluoranthene (166) by the Schmidt reaction, hydrolysis of which gave 4:12 - diaminofluoranthene (167). Diazotisation of the diamine followed by the Sandmeyer reaction afforded 4:12 - dibromo - fluoranthene (168) which was found to be different from 4:11 - dibromofluoranthene (Campbell et. al. J. 1950, 2784).



SECTION B OBJECT OF RESEARCH

No disubstituted acyl fluoranthenes being orientated when the work described in this section was begun, it was felt desirable to establish the constitution of one, and thereby all, of the diacylfluoranthenes and the compounds derived from them.

Exploratory work was therefore carried out with the object of finding, if possible, a suitable route to fluoranthene - 4:12 - dicarboxylic acid. It was proposed to carry out the synthesis of this dicarboxylic acid according to the scheme outlined below (see next page).

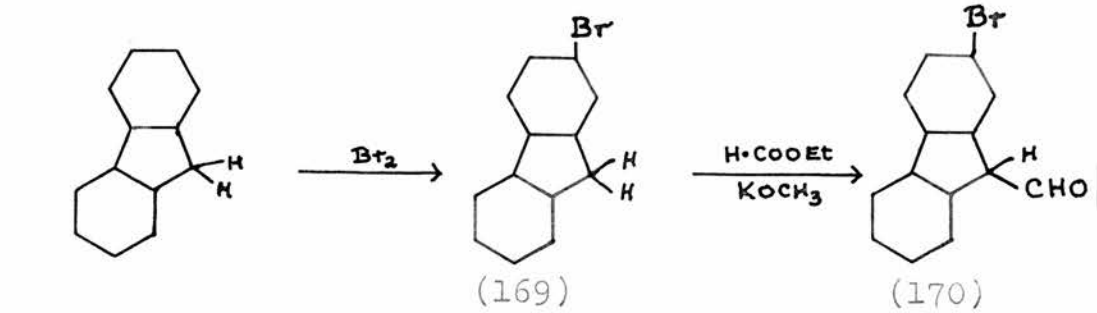
SECTION B DISCUSSION OF RESULTS

Four out of the eleven stages involved in the proposed synthesis of fluoranthene - 4:12 - dicarboxylic acid were carried out successfully.

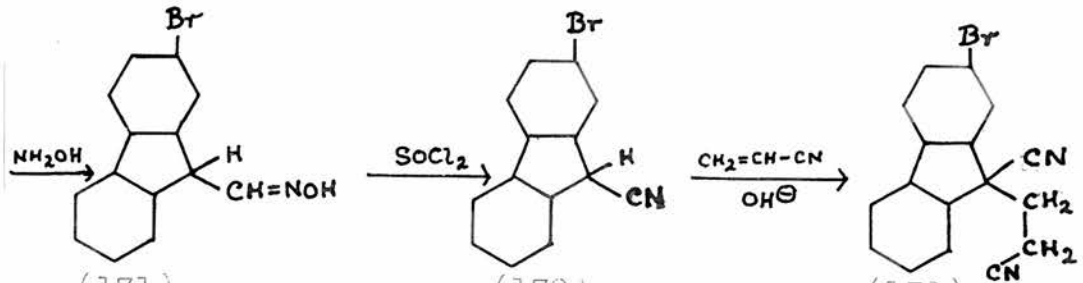
Bromination of fluorene proceeded easily to give 2 - bromofluorene (169) together with a small quantity of 2:7 - dibromofluorene which was separated from (169) by high vacuum distillation.

2 - Bromofluorene - 9 - aldehyde (170) was obtained/

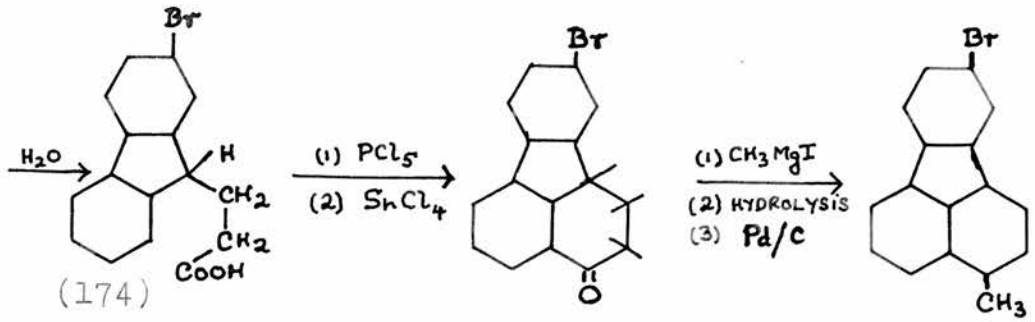
PROPOSED SYNTHESIS of FLUORANTHENE-4:12-DICARBOXYLIC ACID



(169) (170)



(171) (172) (173)



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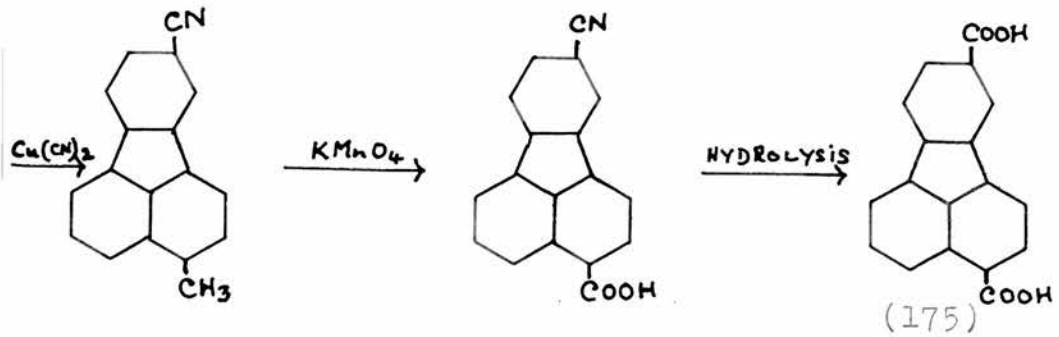
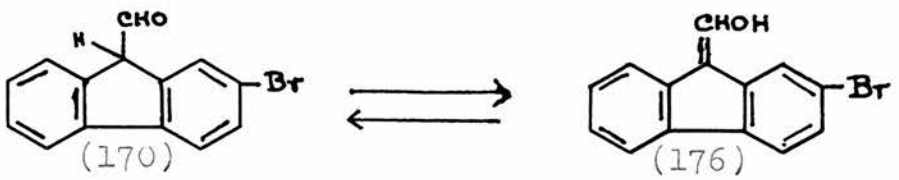


(175)

obtained as a bright yellow oil which would not solidify and was therefore utilised directly, without purification, for the preparation of 2 - bromo - fluorene - 9 - aldoxime (171).

The deep yellow colour of the aldehyde (170) is presumably due to the presence of the enolic form (176), which owing to the presence of the reactive hydrogen atom at the 9 - position of the 2 - bromofluorene - 9 - aldehyde molecule could theoretically exist in equilibrium with the purely keto form (170).



(170) (176)

Such a structure as (176) is seen to possess the "cross" conjugation type of structure belonging to the theoretical fulvene molecule, a fact which would account for the high colour of the aldehyde.

Dehydration of the aldoxime (171) proceeded smoothly in thionyl chloride to give 2 - bromo - 9 - cyanofluorene (172).

Difficulties were encountered in attempting to condense 2 - bromo - 9 - cyanofluorene with acrylonitrile. Three unsuccessful attempts were made under varying conditions to effect the condensation/

condensation with trimethylbenzyl - ammonium hydroxide.

A fourth attempt, using potassium hydroxide in 2 - ethoxyethanol, gave a yellow resinous material which could not be obtained analytically pure, but which was quite different from the starting material, 2 - bromo - 9 - cyanofluorene, and was presumably β - 2 - bromo - 9 - cyanofluorene - 9 - propionitrile (173). This compound had no definite melting point but commenced to soften at 110° and appeared to be completely liquid at 210°.

The compound on treatment under hydrolysis conditions with alcoholic alkali gave an acid m.p. 188 - 190° which was analysed for β - 2 - bromofluorene - 9 - propionic acid (174). While the bromine content was found to agree exactly with that required by β - 2 - bromofluorene - 9 - propionic acid (174) the figures found for carbon and hydrogen differed considerably from those required by (174).

No explanation can yet be offered for these observations and the matter requires further investigation.

The orientation in the meantime of the fluoranthene dicarboxylic acid as the 4:12 - derivative/

derivative of fluoranthene (Campbell, Leadill and Wilshire, J. 1951, 1404) made further work in the direction of the synthesis of fluoranthene - 4: 12 - dicarboxylic acid (175) less important and the synthesis was therefore abandoned.

SECTION C.

INTRODUCTION

CHEMISTRY of 4:5-METHYLENEPHENANTHRENE

Isolated as recently as 1934 (Kruber., Ber., 1934, 67, 1004) this interesting hydrocarbon, which embodies at one and the same time the structures of acenaphthene, fluorene and phenanthrene, has not been studied extensively, no doubt due to its relative inaccessibility. At present only two methods are known by which it may be obtained in workable quantities -

(a) treatment with sodium of the crude anthracene oil from coal-tar boiling over the range 250 - 260°, a procedure by which it was first isolated by Kruber (loc. cit.).

(b) synthesis from 7-acenaphthenol as employed by Bachmann and Sheehan (J.A.C.S., 1941, 63, 204).

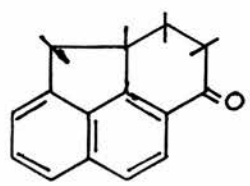
It will be of interest therefore to outline the known facts of the chemistry of 4:5-methylenephenanthrene for this outline together with the details concerning the hydrocarbon drawn from part of the work set out in this thesis forms the basis for part of the discussion on the chemistry of 4:5-methylenephenanthrene (Section C).

ALKYL DERIVATIVES

Only three alkyl derivatives of 4:5-methylenephenanthrene/

threne are known and all three have been prepared by synthesis from a suitably substituted acenaphthene.

(a) By proceeding from 1-keto-1:2:3:4-tetrahydro-4:5-methylenephenanthrene (177) obtained as an intermediate in the synthesis of the parent hydrocarbon (see structure of 4:5-methylenephenanthrene, General Introduction), Bachmann and Sheehan (J.A.C.S., 1941, 63, 2598) prepared the carbinol (178) using methyl magnesium iodide, dehydration and dehydrogenation of which carbinol led to 1-methyl-4:5-methylenephenanthrene (179).



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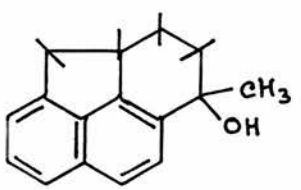

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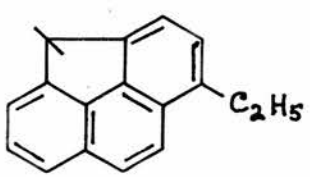

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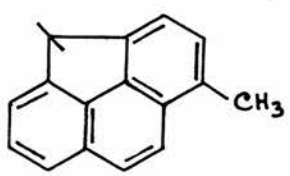
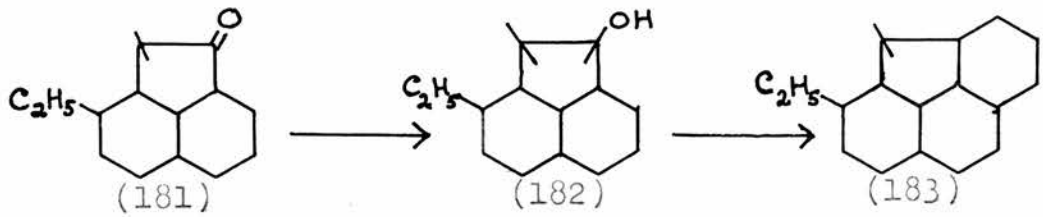


(179)

(b) the use of ethyl magnesium bromide instead of methyl magnesium iodide in the above procedure led to 1-ethyl-4:5-methylenephenanthrene (180).

(c) The same investigators were able to synthesise 3-ethyl/

ethyl-4:5-methylenephenanthrene (183) by starting from 1-ethyl-7-acenaphthenone (181). This ketone was reduced by the Meerwein-Ponndorf method to 1-ethyl-7-acenaphthenol (182) which was converted to 3-ethyl-4:5-methylenephenanthrene (183) using the same series of reactions by which 4:5-methylenephenanthrene itself had been prepared from 7-acenaphthenol.



(181) (182) (183)

Both 1-ethyl- and 3-ethyl-4:5-methylenephenanthrene were also prepared by Clemmensen reduction of the corresponding acetyl-4:5-methylenephenanthrenes, the products from the acetylation of 4:5-methylenephenanthrene (see immediately below).

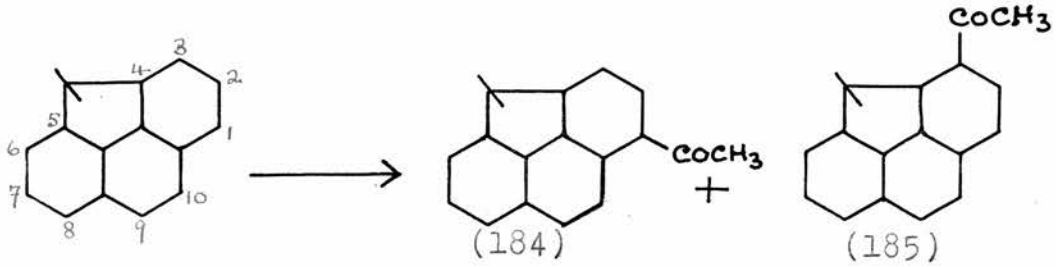
FRIEDEL-CRAFTS ACYLATIONS

Acetylation.

By the action of acetyl chloride and aluminium chloride on 4:5-methylenephenanthrene in nitrobenzene,

Bachmann/

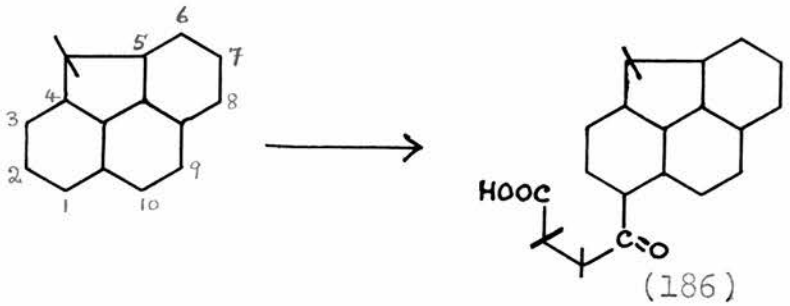
Bachmann and Sheehan (loc. cit.) were able to prepare 1- and 3-acetyl-4:5-methylenephenanthrene (184) and (185) in yields of 30% and 20%, respectively.



(184) (185)

Succinoylation.

The Friedel-Crafts reaction of 4:5-methylenephenanthrene with succinic anhydride and either anhydrous aluminium chloride or hydrogen fluoride in nitrobenzene (Fieser and Cason. J.A.C.S., 1940, 62, 1293) gave a mixture of keto-acids from which only one isomer, β-(4:5-methylene-1-phenanthroyl)-propionic acid (186) could be isolated. Reduction of the keto acid (186) to γ-(4:5-methylene-1-phenanthryl) -butyric acid (187) followed by cyclisation resulted in ring-closure taking place in the 2-position to give ketone (188).



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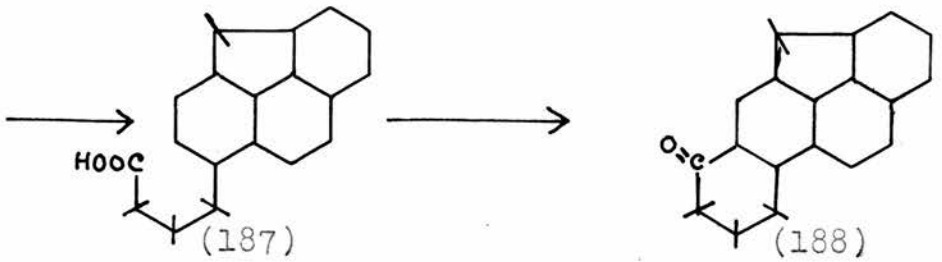
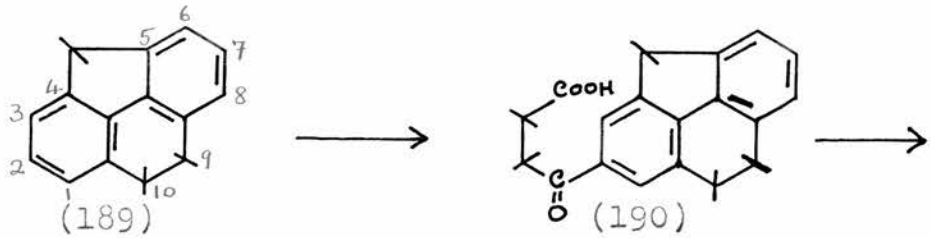


(187) (188)

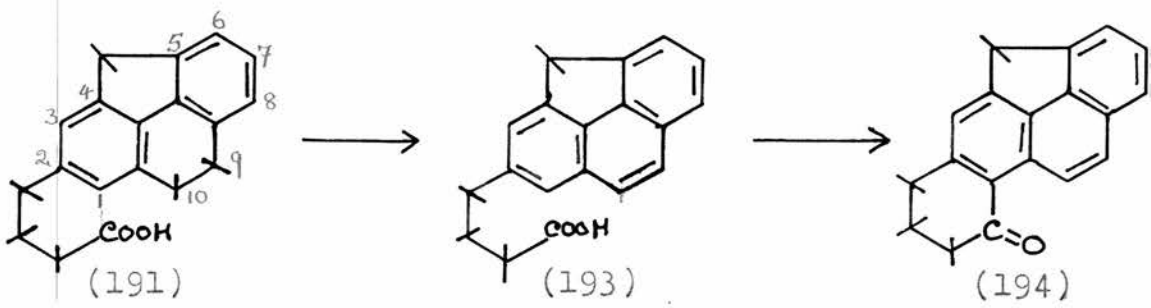
Different results were obtained if the 4:5-methylene-phenanthrene had first been reduced to 9:10-dihydro-4:5-methylenephenanthrene (189). Succinoylation of this dihydride under the same conditions as described above gave a single keto acid (190) in nearly quantitative yield. This was reduced to the acid (191) which cyclised in poor yield (49%) to the ketone (192). The keto acid was the 2-acid and cyclisation of (191) had taken place in the 3-position.



(189) (190)

(191) (192)

However, if the dihydro-acid (191) had first been aromatised to the acid (193) and this ring-closed, cyclisation took place at the 1-position to give ketone (194)



(191) (193) (194)

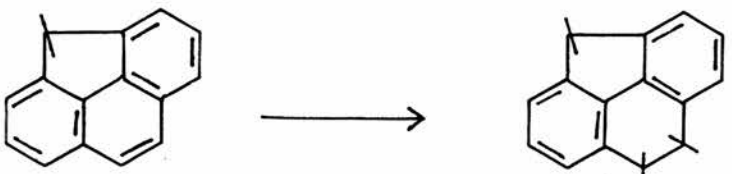
Briefly then, succinoylation of 4:5-methylenephenanthrene takes/

takes place in the 1-position — that of 9:10-dihydro-4:5-methylenephenanthrene in the 2-position.

Furthermore, cyclisation of γ-(4:5-methylene-2-phenanthryl)-butyric acid (193) takes place in the 1-position — that of γ-(9:10-dihydro-4:5-methylene-2-phenanthryl)-butyric acid (191) in the 3-position.

HYDROGENATION

Only one hydrogenation derivative of 4:5-methylene-phenanthrene has been obtained directly from the parent hydrocarbon, viz. the 9:10-dihydride (189) which resulted from the action of hydrogen gas on 4:5-methylene-phenanthrene in the presence of copper chromite catalyst (Fieser and Cason. loc. cit.).

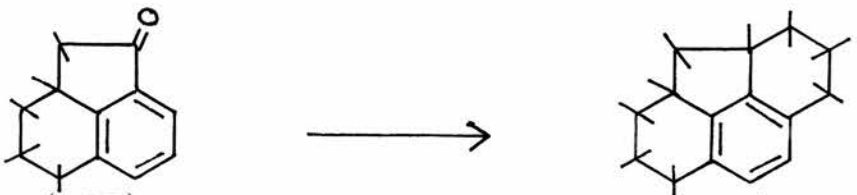


(189)

Two other reduced forms of 4:5-methylenephenanthrene have been obtained in the course of synthetic work.
(a) 1:2:3:4-tetrahydro-4:5-methylenephenanthrene which was obtained in the course of the synthesis of the parent hydrocarbon (Bachmann and Sheehan loc. cit.) and which has already been described (General Introduction).

(b)/

(b) 1:2:3:4:5:6:7:8-octahydro-4:5-methylenephenanthrene (196) which was obtained from tetrahydro-7-acenaphthenone (195) (von Braun and Rath, Ber. 1928, 61, 956).



(195) (196)

This hydrocarbon (196) could not be dehydrogenated to 4:5-methylenephenanthrene, a fact attributed to steric strain which von Braun believed would arise on aromatisation.

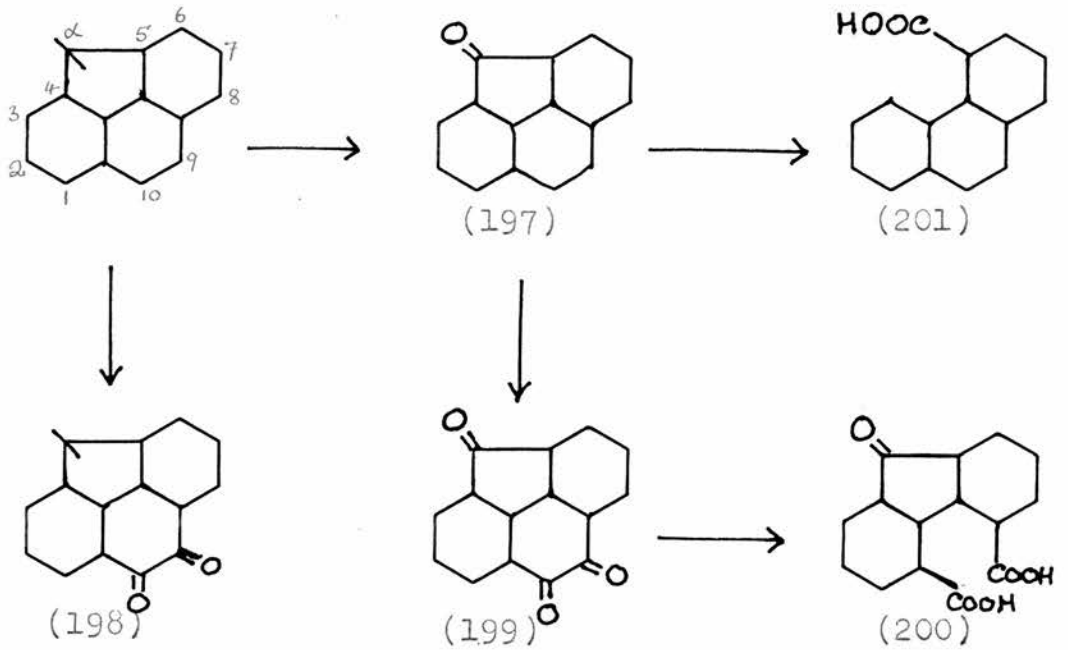
OXIDATION

Investigations on the behaviour of 4:5-methylene-phenanthrene on oxidation have all been carried out by Kruber (loc. cit.) who utilised the results of these investigations for the determination of the structure of the hydrocarbon (See General Introduction).

Oxidation of 4:5-methylenephenanthrene with sodium dichromate in glacial acetic acid at 70° for 2 days gave α-keto-4:5-methylenephenanthrene (197) while stronger oxidation over a shorter period resulted in the formation of 4:5-methylene-9:10-phenanthraquinone (198). Oxidation of α-keto-4:5-methylenephenanthrene (197)

(197) by boiling under reflux with chromic acid in glacial acetic acid resulted in the formation of a small quantity of α-keto-4:5-methylene-9:10-phenanthraquinone (199) but give chiefly fluorenone-4:5-dicarboxylic acid (200).

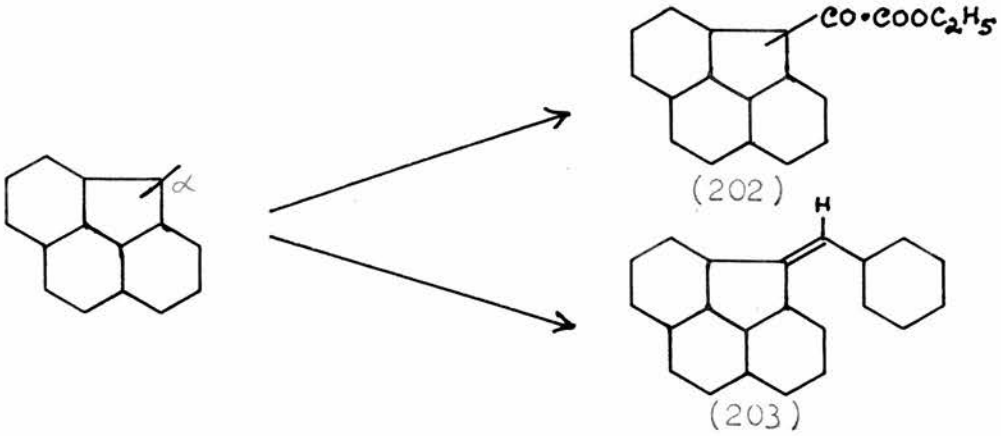
Fusion of α-keto-4:5-methylenephenanthrene with potash yielded phenanthrene-4-carboxylic acid (201).



REACTIONS INVOLVING the METHYLENE GROUP

Indications that the methylene group of 4:5-methylenephenanthrene possessed a reactivity comparable with that of the methylene group in fluorene came at an early date when Kruber (loc. cit.) found that the hydrocarbon/

hydrocarbon condensed with diethyl oxalate in the presence of ethoxide ion to give ethyl 4:5-methylene-Phenanthrene-α-glyoxalate (202) and further, with benzaldehyde in the presence of ethoxide ion to give α-benzal-4:5-methylenephenanthrene (203).

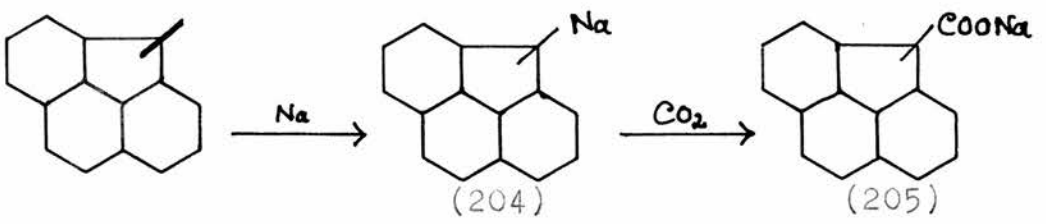


(202)

(203)

The results of these experiments, together with the mode of isolation of the hydrocarbon by treatment of the coal tar distillate, boiling range 250 - 260°, with formation of α-sodio-4:5-methylenephenanthrene, gave a good indication of the acidic nature of the methylene group present in the hydrocarbon.

The sodio-derivative, α-sodio-4:5-methylene-Phenanthrene (204), which Kruber obtained gave, on treatment with carbon dioxide, the sodium salt (205) of α-carboxy-4:5-methylenephenanthrene. This acid readily splits off carbon dioxide when heated above its melting point, a property which Kruber utilised in his isolation of the h drocarbon.



(204) (205)

SECTION C.

OBJECT OF RESEARCH

From stereochemical considerations it appeared desirable to achieve, if possible, the synthesis of the previously unknown hydrocarbon, 2:13-benzfluoranthene or a derivative thereof.

This hydrocarbon represents a new type of compound in which there is present a central five-membered ring, fused on each of four sides of which is a benzene ring.

The stereochemical considerations which prompted the synthesis of this hydrocarbon are given in detail in the discussion on the stereochemistry of fluoranthene and related aromatic systems containing five-membered rings.

It was seen that the work which would be carried out in the course of the synthesis of 2:13-benzfluoranthene would also serve to extend the then existing knowledge of

the/

the chemistry of 4:5-methylenephenanthrene, the hydrocarbon which seemed the most advantageous starting point for this synthesis.

SECTION C.

DISCUSSION OF EXPERIMENTAL RESULTS

ATTEMPTED SYNTHESES of 2:13-BENZFLUORANTHENE.

(1) From Fluorenone.

Difficulty was experienced in hydrolysing the dicyanide, diphenylene-dicyano-ethylene. In an attempted hydrolysis of the cyano groups to carboxyl by the use of 50% alcoholi alkali the sole product was a highly impure yellow solid, which was found to consist essentially of fluorenone.

An attempted hydrolysis with a water-sulphuric acid-glacial acetic acid mixture gave only unchanged di-nitrile.

When finally hydrolysis was achieved by the use of a mixture of hydriodic acid in glacial acetic acid reduction took place at the double bond in the "9-position" of the fluorene nucleus, accompanied by loss of one of the two carboxyl groups which had been formed by hydrolysis of the cyano-groups. The synthesis had therefore to be abandoned.

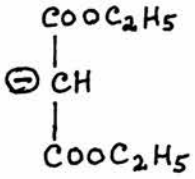
(2) From Acenaphthylene

This synthesis had also to be abandoned after unsuccessful attempts to condense 7:8-dibromoacenaphthene with sodio-malonic ester.

Since sodio-malonic ester condensed readily with 7-bromoacenaphthene to give 7-acenaphthenyl malonic ester, an attempt was made to introduce two malonic ester residues into acenaphthene at the 7- and 8-positions by a similar procedure utilising 7:8-dibromoacenaphthene. No condensation took place. The observed phenomena (See Experimental Section C, I (b)) are accounted for by the following explanation.

The 7:8-dibromoacenaphthene, as a result of its formation by addition of bromine to acenaphthylene, will probably be the trans isomer.

While the negatively charged ion (206) can approach the bromine - carrying carbon atom C_1 from the rearward side without any hindrance from the relatively small hydrogen atom on the adjacent carbon atom C_2 (207) this will not be so when this hydrogen atom on C_2 is replaced by a bulky bromine atom (208). Steric hindrance of the approaching ion (206) by the bromine atom on C_2 will prevent the bimolecular nucleophilic/



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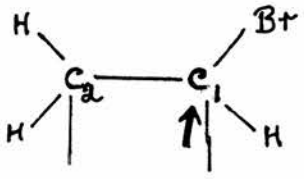

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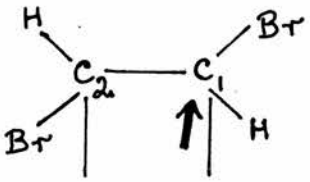


(208)

nucleophilic displacement from occurring. No substitution can therefore take place at either carbon atom.

The alcoholic solution containing 7:8-dibromoacenaphthene, sodio-malonic ester and ethoxide ion is completely favourable to the elimination reaction, involving splitting out of hydrogen bromide with formation of 7-bromoacenaphthylene, taking place. As is well known from experience the use of a medium of low dielectric constant facilitates elimination, a process also aided by the use of a relatively strong base which has a greater tendency to attack hydrogen rather than carbon.

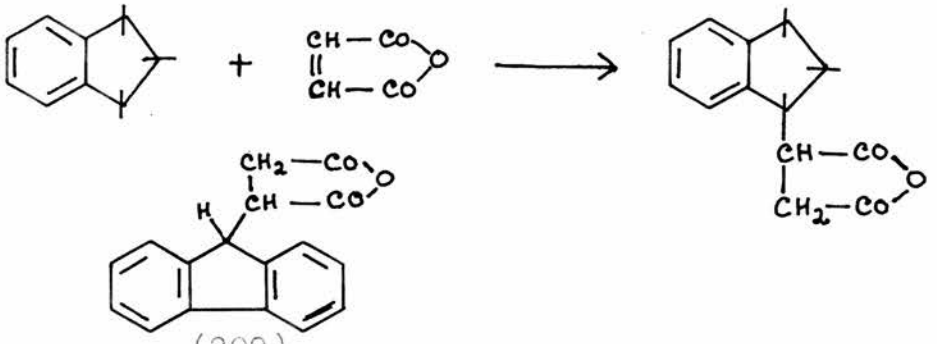
The solvent (anhydrous ethanol) and the base (ethoxide ion) used in this reaction therefore tend to result in elimination of hydrogen bromide with formation of acenaphthylene which subsequently polymerises in the boiling alcoholic alkaline solution.

(3) From 4:5-Methylenephenanthrene

On account of the presence of the methylene group in 4:5-methylenephenanthrene there seemed a promising possibility of introducing into 4:5-methylenephenanthrene the 3-carbon atom chain necessary for formation of the fourth benzene ring of 2:3-benzfluoranthene by the same procedure as that employed by Alder, Pascher and Vagt (Ber., 1942, 75, 1501) for the preparation of fluorene/

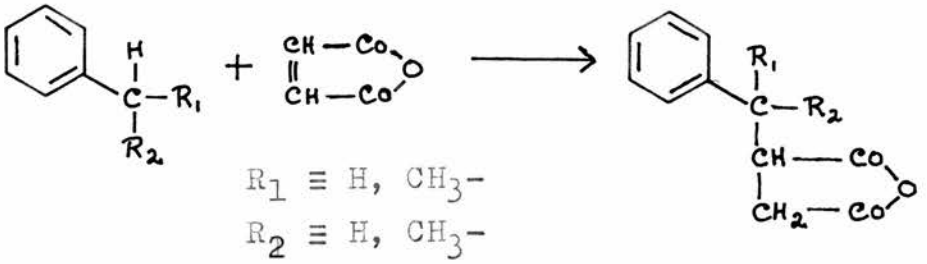
fluorene-9-succinic anhydride (209).

In the course of studies on the diene synthesis involving maleic anhydride and indene, Alder (loc. cit.) found that hydrindene and fluorene reacted with maleic anhydride according to a "substitution-addition" process, e.g.



(209)

These reactions represented an extension of an already known type of reaction which involved maleic anhydride and a simple homologue of benzene such as toluene ethylbenzene, isopropylbenzene, thus.



$R_1 \equiv H, CH_3-$

$R_2 \equiv H, CH_3-$

In all these reactions migration of a hydrogen atom takes place from the carbon atom attached directly to the aromatic nucleus to one end of the double bond in the maleic anhydride molecule, the other end of the double/

double bond attaching itself to the carbon atom from which the hydrogen atom migrates. A substituted succinic anhydride is thereby formed.

Comparatively good yields of fluorene-9-succinic anhydride were obtained from fluorene and maleic anhydride (Alder u. Mitarbeiter. loc. cit.). On allowing 4:5-methylenephenanthrene and maleic anhydride to react under the conditions as employed by Alder a small quantity of the desired acid, α-(1':2'-dicarboxyethyl)-4:5-methylenephenanthrene was indeed obtained but the low yield (3.6%) prohibited the use of the reaction owing to the scarcity of the hydrocarbon, 4:5-methylenephenanthrene, 32g. of which were prepared only after six months of continuous work, according to the synthesis of Bachmann and Sheehan (loc. cit.).

SYNTHESES OF 2:13-BENZFLUORANTHENE

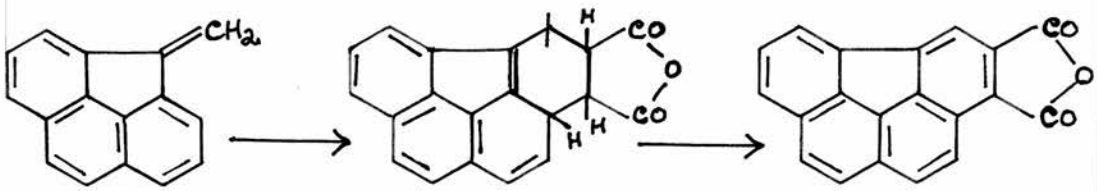
This hydrocarbon, important from the stereochemical point of view, was prepared by two unambiguous syntheses.

(1) From α-Keto-4:5-Methylenephenanthrene

The ketone, α-keto-4:5-methylenephenanthrene, underwent the Grignard reaction with methylmagnesium iodide to give the carbinol, α-hydroxy-α-methyl-4:5-methylenephenanthrene in good yield. 4:5-Vinylidenephenanthrene, (210), the diene involved in the Diels-Alder addition/

addition with maleic anhydride, was not isolated but was simultaneously prepared and condensed with maleic anhydride by heating the reactants, carbinol and maleic anhydride, together in acetic anhydride.

The expected product from the reaction, 10:11:12:13-tetrahydro-2:13-benzfluoranthene-11:12-dicarboxylic acid anhydride (211) was not obtained. Instead the fully



(210) (211) (212)

aromatic 2:13-benzfluoranthene-11:12-dicarboxylic acid anhydride (212) was obtained, arising apparently from spontaneous dehydrogenation of the tetrahydro-acid anhydride (211). Decarboxylation of the anhydride (212) gave 2:13-benzfluoranthene in relatively good yield. The Diels-Alder addition of maleic anhydride to 4:5-vinylidenephenanthrene gave an extremely poor yield of the acid anhydride (212), amounting to a mere 3.6%. The use of nitrobenzene as solvent in place of acetic anhydride made no appreciable difference to the yield.

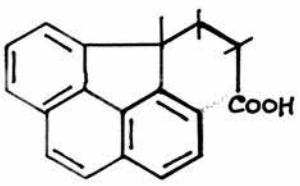
In both cases a considerable quantity of a buff-coloured/

coloured precipitate was obtained from the reaction solution on addition of light petroleum. This solid which had no definite melting point and was insoluble in boiling alkali and the common organic solvents, appeared to have been formed by polymerisation of the 4:5-vinylidene-phenanthrene. It appears therefore that besides the normal Diels-Alder addition reaction taking place a side reaction, one of polymerisation, also occurs, a reaction which, in predominating over the Diels-Alder addition, accounts for the low yield of 2:13-benzfluoranthene-11:12-dicarboxylic acid anhydride.

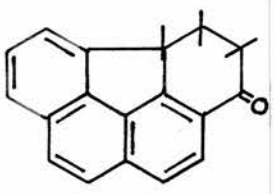
(2) From α-Carbomethoxy-4:5-Methylenephenanthrene

Acrylonitrile and α-carbomethoxy-4:5-methylene-phenanthrene reacted under conditions of the Michael reaction to give an excellent yield of α-2'-carboxyethyl-4:5-methylenephenanthrene (214), the intermediate cyanide (213) not being isolated.

(213)



(214)



(215)

Cyclisation of this acid (214) to 12-keto-9:10:11:12-tetrahydro-2:13-benzfluoranthene (215) proceeded without/

without any difficulty under Friedel-Crafts conditions employing stannic chloride as the cyclising agent. From the stereochemical point of view it is interesting to compare the ease of ring-closure of this acid with that of β-fluorene-9-propionic acid (Campbell and Tucker. J., 1949, 2625). In both cases the yields of the propionic acid derivatives lay around 45-50%. It seems therefore that the presence of the additional benzene ring in 4:5-methylenephenanthrene makes no difference stereochemically to the ease of cyclisation.

Reduction of the ketone (215) to 9:10:11:12-tetrahydro-2:13-benzfluoranthene and dehydrogenation of the latter to 2:13-benzfluoranthene proceeded without any difficulty.

SYNTHESIS of 2:13-11:12-DIBENZFLUORANTHENE

This hydrocarbon was prepared by dehydrohalogenation of either α-(o-chlorobenzal)- or α-(o-bromobenzal)-4:5-methylenephenanthrene both of which were prepared in good yield from 4:5-methylenephenanthrene and the corresponding halogen-substituted aldehyde in the presence of ethoxide ion.

Attempts to dehydrohalogenate the halogen substituted α-benzal-4:5-methylenephenanthrenes by fusion with potash were unsuccessful and resulted either in a large quantity of unchanged starting material being/

being recovered or in the complete destruction of the starting material. In one case, that of the fusion of α-(o-bromobenzal)-4:5-methylenephenanthrene with potash, a very small quantity of the expected 2:13-11:12-dibenzfluoranthene was obtained but it was obvious that the molten potash was destroying completely either the α-(o-halogenobenzal)-4:5-methylenephenanthrene or any 2:13-11:12-dibenzfluoranthene which might have been formed.

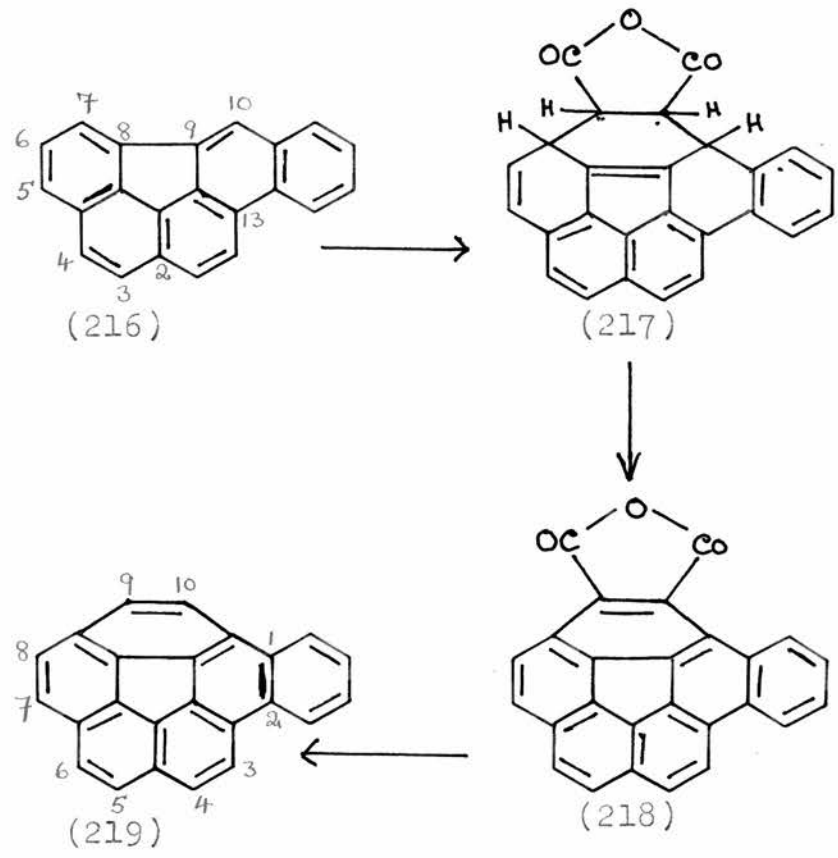
The use of the basic solvent quinoline however, reduced the destructive effect of the pure potassium hydroxide itself for on treatment of the α-(o-halogenobenzal)-4:5-methylenephenanthrene with a concentrated solution of caustic potash in quinoline at the boiling point of the quinoline solution it became possible to isolate the hydrocarbon, 2:13-11:12-dibenzfluoranthene in relatively good yield.

The nature of the halogen atom in the α-(o-halogenobenzal)-4:5-methylenephenanthrene was found to affect the yield of hydrocarbon, higher yields being obtained from the bromo-substituted α-benzal-4:5-methylenephenanthrene.

ATTEMPTED SYNTHESIS OF 1:2-BENZCORONINDENE.

An attempt was made to synthesise 1:2-benzcoronindene (219) by carrying out a forced Diels-Alder addition involving/

involving maleic anhydride and 2:13-11:12-dibenzfluoranthene according to the following scheme -



It was expected that addition (if possible) of maleic anhydride would take place at the 7- and 10-Positions of the 2:13-11:12-dibenzfluoranthene molecule (216).

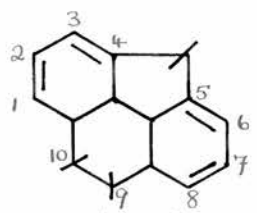
No trace however of the expected 1:2-benzcoronindene-3:4-dicarboxylic acid anhydride (218) or its tetrahydro-derivative (217) could be detected. The only solid material isolated from the reaction solution consisted of a brown solid of large and variable melting range.

SECTION C.

DISCUSSION ON THE CHEMISTRY OF 4:5-METHYLENEPHENANTHRENE

I. REDUCTION OF 4:5-METHYLENEPHENANTHRENE

As mentioned earlier (General Introduction) only one reduction product of 4:5-methylenephenanthrene has been obtained by direct hydrogenation. As might be expected this hydrocarbon resulted from attack of the double bond at the 9:10-position and proved to be 9:10-dihydro-4:5-methylenephenanthrene (220) (Fieser and Cason. J.A.C.S., 1940, 62, 1293). Attack at the 9:10- double bond of this molecule therefore is reminiscent of the mode of reduction of the closely related phenanthrene.



(220)

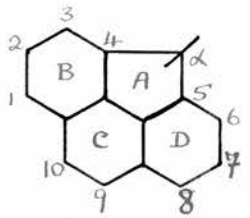
Only two other reduction products of 4:5-methylene-phenanthrene are known and were obtained in the course of syntheses from acenaphthene and its derivatives (See Section C. Introduction).

II. OXIDATION OF 4:5-METHYLENEPHENANTHRENE

All oxidation investigations were carried out by Kruber (Ber., 1934, 67, 1000).

Since the hydrocarbon (221) embodies the structures of both fluorene (rings A, B and D) and phenanthrene (rings/

(rings B, C and D) it is interesting to compare the relative susceptibilities of the methylene group and the 9:10-positions in the molecule towards oxidation. Mild oxidation over a somewhat long period of time leads to oxidation at the methylene group resulting in the formation of α-keto-4:5-methylenephenanthrene (222) while oxidation over a shorter period but under stronger conditions involving the same oxidant, chromic acid, yields 4:5-methylene-9:10-phenanthraquinone (223).



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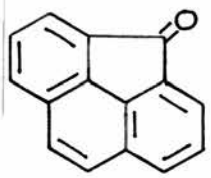
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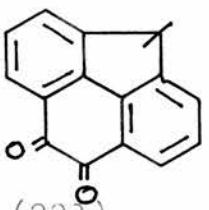
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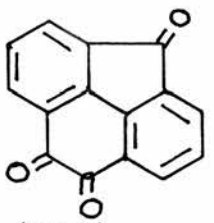
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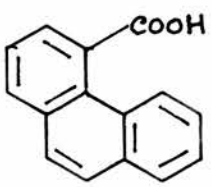


(226)

(225)

Oxidation of the ketone (222) leads to the formation of α-keto-4:5-methylene-9:10-phenanthraquinone (224)/

(224) but it is extremely difficult to prevent oxidation from proceeding further with formation of fluorenone-4:5-dicarboxylic acid (225) which is also obtained by strong oxidation of quinone (223).

It is apparent therefore that the methylene group of 4:5-methylenephenanthrene is more sensitive towards oxidation than the 9:10-positions. In contrast however, oxidation of the triketone (224) results in further oxidation at the 9:10-positions, the fluorenone nucleus displaying its characteristic resistance towards further oxidation. α-keto-4:5-methylene-9:10-phenanthraquinone (224) behaves therefore like phenanthraquinone in respect of oxidation. The presence of the fluorene structure in this hydrocarbon comes into evidence in its oxidised form, α-keto-4:5-methylenephenanthrene (222). This ketone reacts in the same fashion as fluorenone on fusion with potash, a procedure which results in fission of the five-membered ring and formation of phenanthrene-4-carboxylic acid (226).

III. AROMATIC SUBSTITUTION IN 4:5-METHYLENEPHENANTHRENE.

Very little work has been carried out on the subject of aromatic substitution in 4:5-methylenephenanthrene, investigations in this direction having been limited to Friedel-Crafts acylations.

Friedel-Crafts Acylation.

As indicated earlier (General Introduction) acylation has been carried out twice, the one being an acetylation and the other a succincylation.

Acetylation with acetyl chloride and aluminium chloride in nitrobenzene resulted in the formation of 1-acetyl-4:5-methylenephenanthrene (227) and 3-acetyl-4:5-methylenephenanthrene (228) in yields of 30% and 20%. respectively. (formulae 47 - 53 on next page).

Succinoylation of 4:5-methylenephenanthrene under conditions similar to those employed for acetylation gave a mixture from which only one acid, β-(4:5-methylene-1-phenanthroyl)-propionic acid (229), could be isolated (45% yield). Acylation of 4:5-methylene-phenanthrene in nitrobenzene therefore takes place in the 1-position with the formation of smaller quantities of other isomers, in the case of acetylation the 3-isomer.

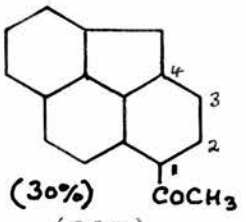
A comparison of these results with those obtained from experiments on the acylation (under the same conditions) of related hydrocarbons is interesting.

(a) Phenanthrene (230) is attacked chiefly at the 3-position with formation of lesser amounts of the 2-isomer, both on acetylation and succinoylation.

(b) Acetylation of fluorene results in the molecule being attacked exclusively at the 2-position (231).

(c)/

ACYLATION of 4:5-METHYLENEPHENANTHRENE and RELATED HYDROCARBONS



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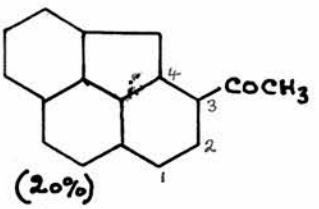

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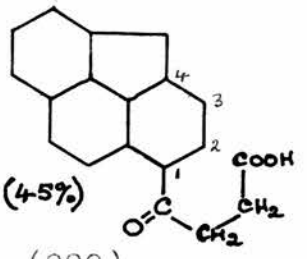

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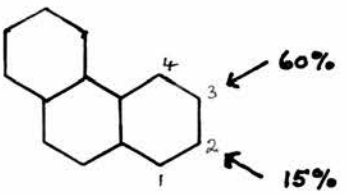

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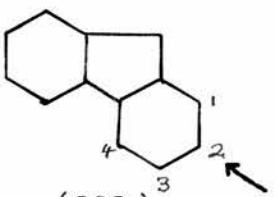

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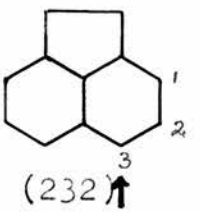

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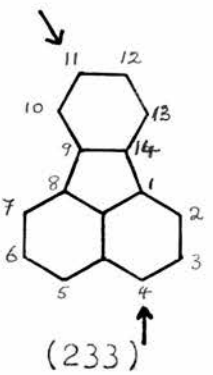


(233)

(c) Acetylation of acenaphthene (232) and fluoranthene (233) results in attack taking place at the 3-position of acenaphthene and the 4-position of fluoranthene. Acetylation of fluoranthene (233) also occurs to a considerable extent in the 11-position.

It appears therefore that those aromatic systems of the acenaphthene type containing a five-membered ring are acetylated preferentially in a position para to the five-membered ring, i.e. in position 3 of acenaphthene, in position 4 of fluoranthene and in position 1 of 4:5-methylenephenanthrene.

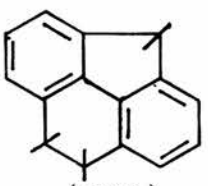
Fieser and Cason (loc. cit.) have attributed the preferential formation of 1-acetyl-and 1-succinoyl-4:5-methylenephenanthrene to the strong para directing influence of the methylene group. In the light of the more general considerations outlined above it may well be that this orientation effect in the para positions to the five-membered ring of these molecules is due to the strain present in these molecules caused by the presence of the five-membered ring, this strain resulting in increased electron density at the para positions.

Substitution in fluorene occurs exclusively in the 2-position of the molecule (231). In view of the fact that the fluorene nucleus is present in the fluoranthene/

fluoranthene molecule it is perhaps not surprising that substitution of fluoranthene (233), besides occuring in the 4-position, also takes place in the 11-position, which position corresponds to the 2-position of fluorene (231). Phenanthrene (230) is attacked chiefly in the 3-position but also to a small extent in the 2-position of fluorene (231). We might therefore expect secondary substitution (if any) of 4:5-methylenephenanthrene to take place in either the 2-position (corresponding to the 2-position of fluorene) or in the 3-position (corresponding to the 3-position of phenanthrene). From the fact that secondary substitution of 4:5-methylenephenanthrene actually takes place in the 3-position it seems that the directive influence of the phenanthrene moiety in 4:5-methylenephenanthrene is greater than that due to the fluorene moiety.

Succinoylation of 9:10-dihydro-4:5-methylene-phenanthrene (220) resulted in the formation of γ- (9:10-dihydro-2-phenanthryl)-butyric acid (191) i.e. substitution occurred in the 2-position. This result is to be expected from the fact that 9:10-dihydro-phenanthrene (234) substitutes in the 2-position (corresponding to the 2-position of 4:5-methylenephenanthrene) and flucrene (231) also substitutes in the 2-position (corresponding to the 2-position of 4:5-methylenephenanthrene. Here/

Here the directive effects of the fluorene and 9:10-dihydrophenanthrene moieties (231) and (234) in 9:10-dihydro-4:5-methylenephenanthrene reinforce one another.



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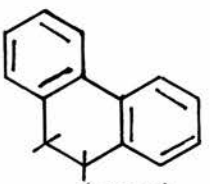

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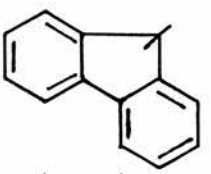


(231)

To summarise this discussion on the Friedel-Crafts acylation of 4:5-methylenephenanthrene we may state that:-

(a) it is substituted chiefly in the 1-position in which respect it resembles acenaphthene and fluoranthene.

(b) substitution also occurs to a lesser extent in the 3-position in which behaviour it resembles phenanthrene.

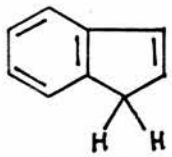
(c) if reduction is first carried out to give 9:10-dihydro-4:5-methylenephenanthrene this compound is acylated in the 2-position exclusively, in which behaviour it corresponds exactly to both 9:10-dihydrophenanthrene and fluorene.

IV. CHEMICAL REACTIVITY of the METHYLENE GROUP in 4:5-METHYLENEPHENANTHRENE

In view of the fact that the 4:5-methylenephenanthrene molecule contains the fluorene nucleus it would not be surprising to find it displaying the nucleophilic properties associated with fluorene itself. That it actually does so will become evident from the discussion below.

The structural features in cyclopentadiene (235) indene (236) fluorene (237) and 4:5-methylenephenanthrene (238) which are responsible for the nucleophilic properties displayed in basic media by the methylene carbon atoms in these molecules are the conjugated double bond systems.

(235)



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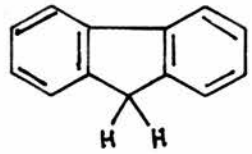

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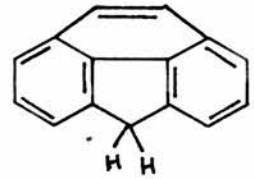
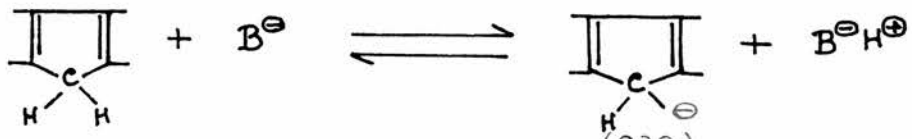


(238)

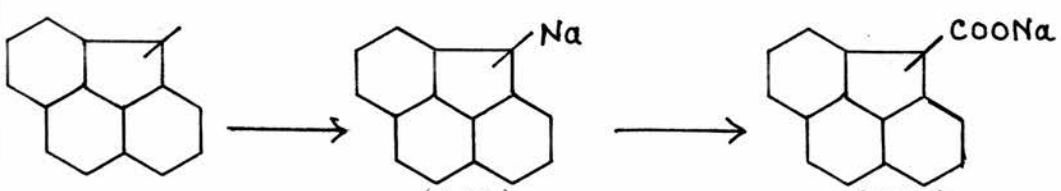
The tendency of the $\geq CH_2$ group in saturated hydrocarbons to ionise in the presence of a base cannot be detected and must be considered as extremely small. The presence of the conjugated systems in the molecules just considered however results in resonance stabilisation of the carbanion (239) formed in the equilibrium



(239)

This equilibrium is accordingly displaced unusually far over to the right.

It is found therefore that cyclopentadiene, fluorene and indene all form sodium or potassium salts. As would be expected 4:5-methylenephenanthrene likewise forms a sodium salt (240) and indeed it was by utilisation of this property that Kruber (loc. cit.) isolated the hydrocarbon from the crude anthracene oil of coal tar. Treatment of the crude oil with sodium allowed by interaction of the resulting sodio-derivative (240) with carbon dioxide resulted in the formation of the sodium salt (241) of α-carboxy-4:5-methylenephenanthrene.

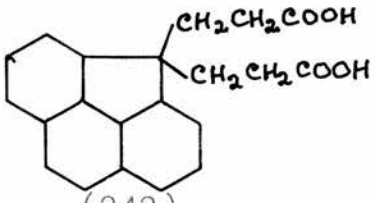


(240) (241)

The reactivity of the methylene group in 4:5-methylenephenanthrene in its behaviour towards acrylonitrile in the presence of a base (proton acceptor) was found to be high (cf. experimental Section C) for

condensation/

condensation involving both hydrogen atoms of the methylene group took place with ultimate formation of α-α-bis-(2'-carboxyethyl)-4:5-methylenephenanthrene (242).



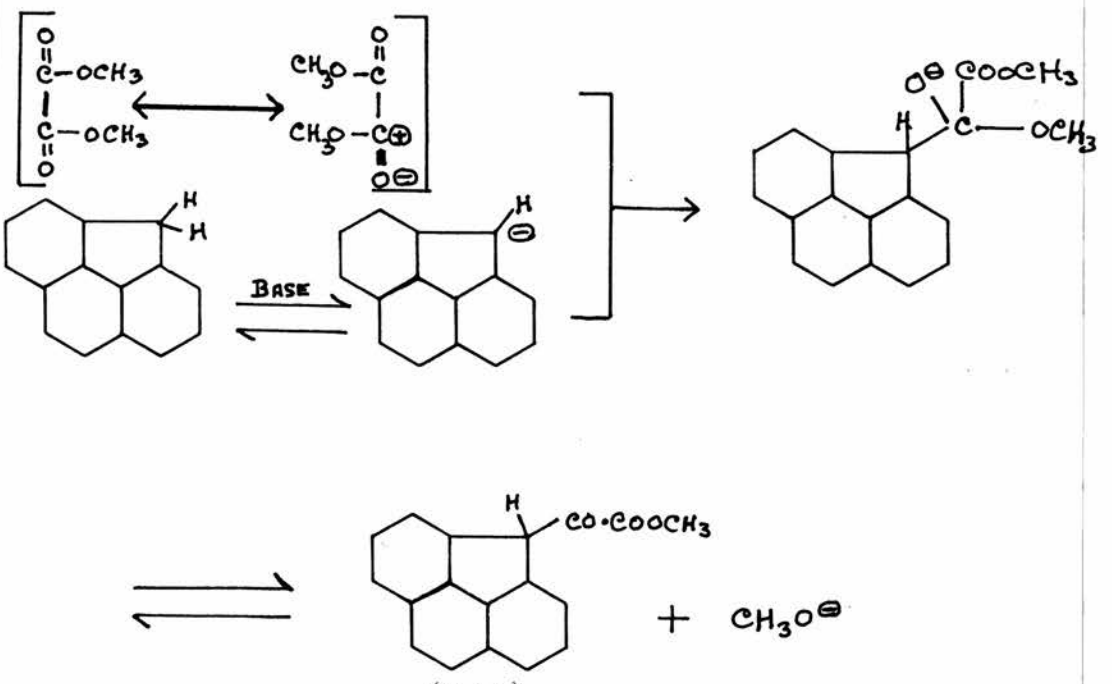
(242)

This parallels the reactivity of fluorene towards acrylonitrile (Bruson. J.A.C.S. 1942, 64, 2457).

Strangely enough attempted condensations of 4:5-methylenephenanthrene with cinnamonitrile failed, although Campbell and Fairfull (J. 1949. 1239) obtained a 50% yield of β-phenyl-β-9-fluorenyl-propionitrile by condensing fluorene with cinnamonitrile.

Reactions with Oxalic Esters.

The potential nucleophilic reactivity of the methylene carbon atom of 4:5-methylenephenanthrene again found expression in the condensation with dimethyl-oxalate in the presence of alkali to give methyl 4:5-methylenephenanthrene-α-glyoxalate (243), which was obtained as an intermediate in the synthesis of 2:13-benzfluoranthene, (see overpage).



(243)

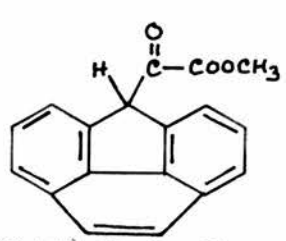
This condensation took place with the utmost ease in ethanolic solution in the presence of sodium or potassium ethoxide and corresponds to the condensations under similar conditions of oxalic ester with cyclopentadiene (Thiele. Ber., 1900, 33, 666), with indene (Thiele. Ber., 1900, 33, 851 and Wislicenus. Ber., 1900, 33, 771) and with fluorene (Thiele. Ber., 1900, 33, 851 and Wislicenus. Ber., 1900, 33, 771 and 1902, 35, 759). Interesting observations were made concerning this ester, methyl 4:5-methylenephenanthrene-α-glyoxalate. Crystallisation of the ester from light petroleum gave the ester as bright yellow plates which melted partially at 122°. Very pale yellow needles formed in the liquid and/

and the whole semi-molten mass melted to a clear, rather deep yellow liquid at 129°. This behaviour was not altered by repeated crystallisation from light petroleum.

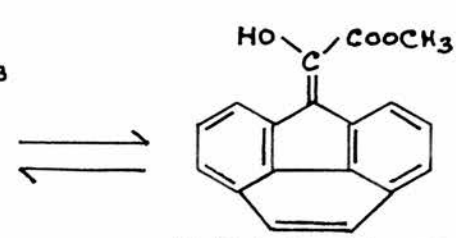
In one case, crystallisation from a light petroleum -acetone mixture resulted in the formation of very pale yellow needles which did not alter in colour or crystalline form at 122°, but melted sharply at 129° to give a deep yellow liquid.

Crystallisation of the ester from glacial acetic acid resulted in the formation of very pale greenish-yellow crystals melting at 129°. Both crystalline forms of the ester dissolved in aqueous alkali with production of a deep yellow solution.

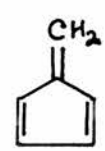
This behaviour is in accord with the supposition that the ester is capable of existing in two tautomeric forms arising from a keto-enol tautomerism. It seems probable that the pale coloured form corresponds to the keto tautomer (244) while the deep yellow form corresponds to the enolic form (245). This is supported by the observation that in alkaline solution the ester is deep yellow. This colour is characteristic of the fulvene type of structure (246), a structure which the enolic form would possess.



(244) Keto Form



(245) Enolic Form



Fulvene
(246)

The corresponding acid, 4:5-methylenephenanthrene-α-glyoxalic acid, which is obtained by hydrolysis of the methyl ester (245) behaves in a similar manner. Crystallisation from glacial acetic gives a greenish-yellow solid (needles) which changes colour somewhat below 100° to a deep yellow, melting taking place with decomposition. The acid crystallises from glacial acetic acid with one molecule of solvent of crystallisation. The acid dissolves in cold alkali with formation of an intensely yellow solution from which a deep yellow solid is precipitated on acidification. This solid possesses the same melting point as the original greenish-yellow acid. Presumably the same tautomerism exists here as in the case of the methyl ester.

That the ester is capable of reacting in both the keto and enolic forms was shown by the formation on the one hand of a 2:4-dinitrophenylhydrozone and on the other, of a benzoyl derivative.

This behaviour of methyl 4:5-methylenephenanthrene-α-glyoxalate parallels that of the corresponding fluorene derivative, methyl fluorene-9-glyoxalate (c.f. Kuhn and Levy, Ber., 1928, 61, 2240).

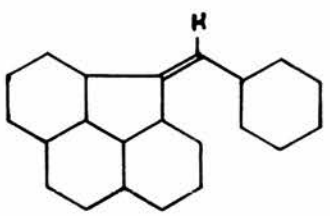
The Clemmensen reduction of 4:5-methylenephenanthrene-α-glyoxalic acid resulted in the formation of the hydroxy acid, a course taken under these conditions by α-keto acids. The corresponding fluorene derivative behaves/

behaves similarly (Wislicenus and Weitemeyer. Ber., 1921, 54, 978).

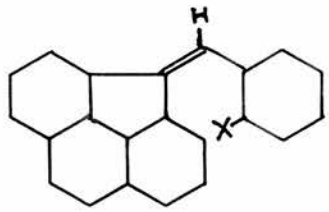
α-carboxy-4:5-methylenephenanthrene was conveniently prepared by oxidative decarbonylation of 4:5-methylene-phenanthrene-α-glyoxalic acid with hydrogen peroxide in glacial acetic acid according to the method developed by Tucker and Co-workers (J. 1949, 2625) for the formation of fluorene-9-carboxylic acid from fluorene-9-glyoxalic acid. The glyoxalic acid derivative of 4:5-methylenephenanthrene however required 5-7 days for completion of the reaction as compared with only several hours in the case of fluorene-9-glyoxalic acid.

Reactions with Aromatic Aldehydes.

The pioneer workers in the field of 4:5-methylene-phenanthrene chemistry, Kruber, within a short time of isolating the hydrocarbon had tested its reactivity towards benzaldehyde in the presence of alkali and obtained α-benzal-4:5-methylenephenanthrene (annexed formula).



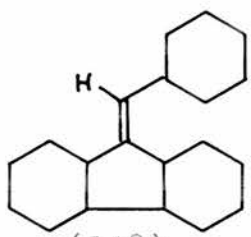
In subsequent investigations carried out in the course of work described in this thesis this reaction was extended to condensation involving o-halogeno-benzaldehydes for the purpose of preparing α-(o-



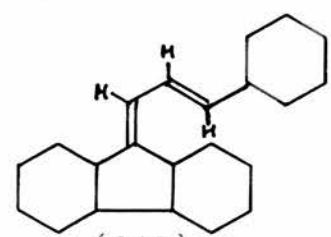
(247)

halogenobenzal)-4:5-methylene-phenanthrenes, general formula (247). With o-chloro- and o-bromo-benzaldehyde the reactions proceeded to give good yields of the normal products (247) but in both condensations (~~247~~), besides the normal products, a smaller quantity of a deeper yellow compound was obtained on chromatographic purification of the crude condensation product.

Now a similar phenomenon was encountered by De Fazi (Gazz. chim. ital, 1921, 51, 328) in the course of condensations of fluorene with aromatic aldehydes and subsequently by Bergmann (Ber., 1930, 63, 1617 and 2598) who was able to prove by synthesis that these more deeply coloured compounds were vinylene homologues of the normal condensation products. The products of the condensation of fluorene with benzaldehyde were then -



(248)

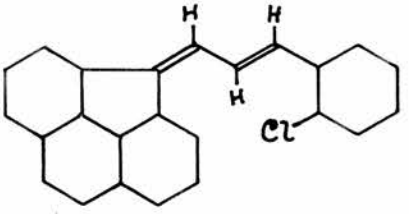


(249)

9-benzalfluorene (248) and 9-cinnamylidene-fluorene (249).

Reasoning by analogy therefore it was expected that the deep yellow compounds obtained as side products in the condensations of o-chloro- and o-bromobenzaldehyde with 4:5-methylenephenanthrene would be respectively, 1-(o-chlorophenyl)-4:4-(4:5-phenanthrylene)-butadiene (250) and 1-(o-bromophenyl)-4:4-(4:5-phenanthrylene)-butadiene (251).

The analysis figures obtained for these two compounds were in agreement with this expectation.



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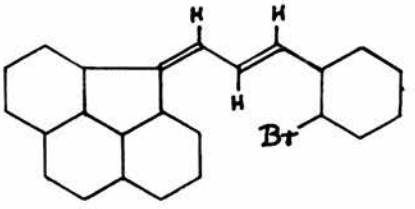


(251)

It has been proposed by Rieveschl and Ray (Chem. Reviews, 1938, 23, 314)that the formation of such compounds is due to the intermediate formation of acetaldehyde from the sodium ethylate used as the condensing base in these reactions. The acetaldehyde would undergo condensation with the aromatic aldehyde and the resulting cinnamaldehyde or derivative (252) then condense with the reactive methylene- containing compound/

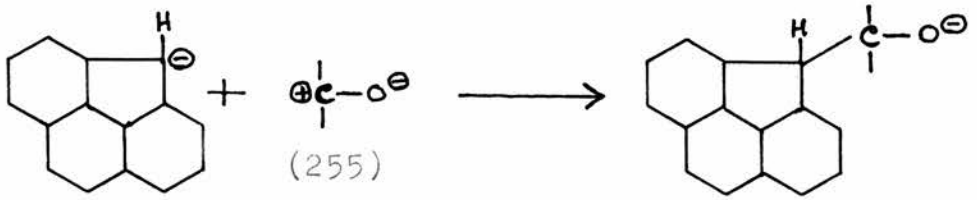
compound (253) according to the following scheme -

$$R.CHO + CH_3CHO \longrightarrow \underset{(252)}{R.CH = CH-CHO} + H_2O$$

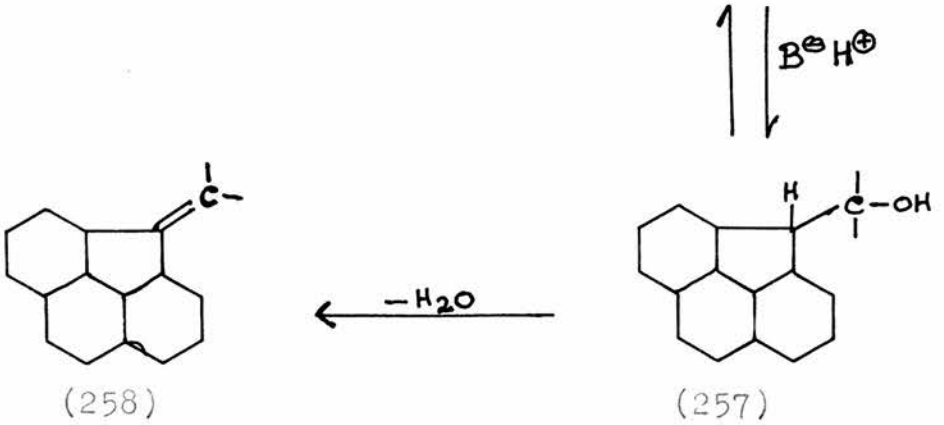
$$\underset{(252)}{R.CH = CH-CHO} + \diagup\!\!\diagdown CH_2 \longrightarrow \underset{(253)}{R.CH = CH-CH = C}\diagup\!\!\diagdown$$

(R ≡ C_6H_5 - or substituted C_6H_5-)

In general, these reactions of 4:5-methylenephenanthrene with aldehydes involve the reversible formation of the 4:5-methylenephenanthrene carbanion (254) on removal of proton by the base present and irreversible addition of this resonance-stabilised carbanion (254) to the carbon atom of the polarised form (255) of the carbonyl group in the aldehyde.



(254) (255) (256)



(258) (257)

The normal product (258) of these reactions is then formed/

formed on dehydration of the intermediate alcohol (257) present in equilibrium with its ionised form (256).

SUMMARY.

From the foregoing discussion it is evident that 4:5-methylenephenanthrene behaves like one of the hydrocarbons acenaphthene, fluorene or phenanthrene, due to the fact that the structure of 4:5-methylene-phenanthrene incorporates at one and the same time the structures of these three hydrocarbons. Which of these hydrocarbons 4:5-methylenephenanthrene will resemble in any given reaction depends on the nature of the reaction.

(a) On hydrogenation 4:5-methylenephenanthrene resembles phenanthrene, the 9:10-bridge being attacked.

(b) On oxidation it resembles both fluorene and phenanthrene, the methylene group or the 9:10-bridge or both being attacked.

(c) In Friedel-Crafts acylations it behaves as if it were an acenaphthene derivative. The presence of the phenanthrene structure also is manifested for in secondary substitution it resembles phenanthrene.

(d) In its reactions involving the methylene group, 4:5-methylenephenanthrene behaves, down to almost the last detail, like fluorene.

SECTION C

STEREOCHEMISTRY OF 2:13-BENZFLUORANTHENE AND RELATED AROMATIC HYDROCARBONS

Kekule's assumption that the benzene molecule possesses the geometrical form of a regular hexagon has in recent years received ample support from x-ray and electron-diffraction experiments, infra-red and Raman spectra. As a result of conjugation in the molecule the six carbon-carbon bonds become indistinguishable and identical, each pair of carbon atoms being bound primarily by a σ-bond superimposed up which are six π-electrons evenly distributed about the carbon atoms in the ring. It is due to these π-electrons that the peculiar properties of aromatic molecules are due; moreover the different chemical behaviour of different bonds in all aromatic molecules except the electronically completely symmetrical benzene is due to the unequal distribution about these bonds of the electrical atmosphere composed of the mobile or π-electrons.

Benzene therefore has the form of a regular hexagon whose sides and angles are all equal, being 1.39Å and 120°, respectively.

The application of the resonance theory to aromatic molecules has explained the peculiar non-reactivity of the double bonds in benzene. In a resonating system all bonds acquire double-bond character. It follows that resonance in a molecule occurs only if all the atoms involved lie in the same plane. Accordingly, an explanation/

explanation is at hand for the fact that the benzene molecule is planar. The non-reactivity towards normal double bond reagents is reflected in the resonance energy of benzene.

Now it was assumed that in the condensed benzene ring systems, of which we shall take naphthalene as an illustrative case, the bond lengths and bond angles were, to all intents and purposes, the same as those in the simplest aromatic molecule benzene itself, viz. 1.39Å and 120°, respectively. Although no experimental proof of this was available, the resonance theory (see Pauling "Nature of the Chemical Bond" p. 141) indicated from resonance energy considerations that naphthalene would be coplanar with 120° bond angles. Considerable resonance must occur in naphthalene since it possesses resonance energy of 77 kcal./mole as compared with 41 kcal./mole for benzene.

With the acquirement through resonance of double-bond character by every bond in the naphthalene molecule adjacent bonds would strive to be coplanar and the molecule would therefore be brought into a completely coplanar configuration with bond angles of 120°. Robertson (Proc. Roy. Soc., 1933, A140, 79 and 1933, A142, 674) by x-ray work showed that naphthalene and anthracene were indeed coplanar molecules with 120° bond angles.

More recent work on polycyclic aromatic hydrocarbons has led to the conclusion that the different bonds in aromatic/

aromatic molecules have slightly different lengths.

Naphthalene (with whose dimensions we shall be concerned later in greater detail) has bond lengths shown (Fig. I) (Abrahams, Robertson and White, Acta Cryst., 1949, 2, 233). Nothing has actually been said concerning the bond angles but from the fact that differences in bond lengths are small (max. 4% difference) it seems likely that the bond angles do not differ appreciably from the classical angle of 120° of the benzene molecule itself.

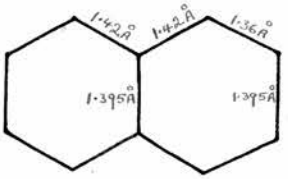


Fig. I

No exact x-ray analysis has yet been worked out for phenanthrene (resonance energy 130 kcal./mole) but on the basis of the observations made on the above-mentioned hydrocarbons together with those made on a number of other polycyclic aromatic systems viz. pyrene, coronene and 1:12-benzperylene (Robertson, Acta Cryst., 1938, 1, 101) it might be inferred that phenanthrene also possesses bond angles in the close vicinity of 120° and bond lengths of approximately 1.42Å, the molecule being coplanar.

It is only fair to mention that the variations in bond length in different parts of the molecules are in many cases not much greater than the possible experimental error involved in the x-ray analyses (±0.03Å) so that it would be unwise to base any detailed calculations on/

on these findings. It seems however to be fairly certain that variations in bond length do exist even in a symmetrical molecule such as coronene.

These x-ray analyses however, have all been carried out on aromatic molecules containing only six-membered rings. The important point however in this discussion, is the stereochemistry of condensed benzene ring systems containing a five-membered ring in the molecule and interest therefore centres round the possible stereochemical effects that such a five-membered ring will produce in the molecule containing it. The foregoing discussion is a necessary basis for the following discussion.

From the facts gathered from x-ray analyses of various polynuclear hydrocarbons it seems that aromatic bond lengths are slightly greater or slightly less than 1.39Å. Little mention however is made in the literature concerning the size of the bond angles in those molecules which contain only six-membered rings. As indicated earlier the fact that the bond lengths differ relatively little among themselves probably means that the bond angles will not differ very appreciably from 120°. Any differences will most likely be of the same order of magnitude as the possible errors involved in the measurements.

Quite different is the case when a five-membered ring is present in the molecule.

In these molecules at least one bond is common to

the/

the five-membered ring and a six-membered ring present in the molecule. In the simplest molecule of this kind, hydrindene (Fig. II), this bond is shown AB.

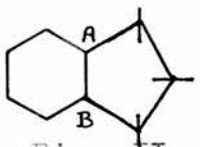


Fig. II

Two such bonds, mutually adjacent, are present in acenaphthene (Fig. III) viz. AB and BC, while in fluorene (Fig. IV) in which there are likewise two such bonds AB and CD these bonds are non-adjacent.

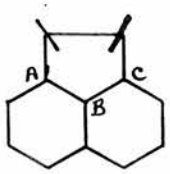


Fig. III

The structure of one or both of these molecules, fluorene and acenaphthene, is present in the systems whose stereochemistry will be discussed.

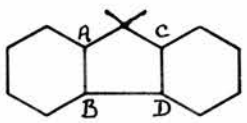


Fig. IV

The geometrical requirements of the five-membered rings present in these molecules result of necessity in the departure of either the peripheral or internal ring bonds of the benzene ring(s) from their normal configurations in which they lie in one plane and at an angle of 120° to one another. The stereochemistry of the following molecules will be considered

1 Acenaphthene
2 Acenaphthylene
3 Fluorene
4 Fluoranthene
5 4:5-Methylenephenanthrene

ACENAPHTHENE

ACENAPHTHENE

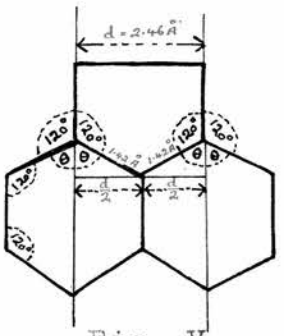


Fig. V

The implications incurred by the presence of a five-membered ring fused onto the naphthalene nucleus may be found by assuming that the naphthalene portion of the molecule possesses nearly the same bond lengths and angles as naphthalene itself (see above). We then find by simple calculation (Fig. V) that the distance between the centres of the two peri-carbon atoms is given by

$$d = 2 \cdot 1{\cdot}42 \cdot \sin\theta$$

Assuming that the bond angles in naphthalene are 120° then $\theta = \frac{1}{2} \cdot 120^\circ = 60^\circ$

This gives $d = 2 \cdot 1{\cdot}42 \cdot \sin 60^\circ = 2{\cdot}46\text{Å}$

Now if the peri-bonds in acenaphthene are, as in naphthalene, directed at an angle of 120° with each adjacent C–C bond then the distance between the centres of the two bridge carbon atoms must also be $2{\cdot}46\text{Å}$. But the normal single bond is $1{\cdot}54\text{Å}$ in length. Hence to preserve the bond angles in the naphthalene portion of the molecule we must assume a stretching of the bond between the bridge carbon atoms of $(2{\cdot}46 - 1{\cdot}54)$ or 0.92Å i.e. 60%!
This is however ridiculous.

It seems much more reasonable to assume that the peri-valence bonds are deviated through an angle (Fig. VI) such that the bridge C–C bond length is that of/

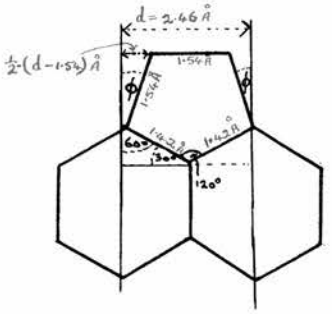


Fig. VI

of a normal single bond viz. 1·54Å. Assuming that the peri-bond lengths are also 1·54Å we have ϕ given by

$$\text{Sin } \phi = \frac{\frac{1}{2}(d - 1{\cdot}54)}{1{\cdot}54}$$

$$= \frac{\frac{1}{2}(2{\cdot}46 - 1{\cdot}54)}{1{\cdot}54} = \frac{0{\cdot}46}{1{\cdot}54} = 0{\cdot}299$$

Whence $\phi = 17{\cdot}5^{\circ}$

There is therefore a considerable amount of strain at the five-membered ring in acenaphthene, This strain is measured by the angle 17·5° through which each of the peri-bonds must be distorted in order to conform to the requirements of the normal single bond, length 1·54Å, of the bridge carbon atoms of the five membered ring.

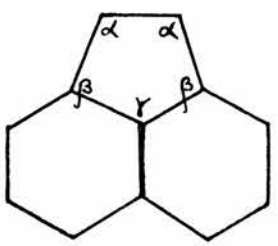


Fig. VII

The various angles in the five membered ring are accordingly given (Fig. VII) by

$$\alpha = 107{\cdot}5^{\circ}$$

$$\beta = 102{\cdot}5^{\circ}$$

$$\gamma = 120^{\circ}$$

The distortion of 17·5° through which the peri-bonds are deviated from the normal is not however unusually great when we consider the magnitudes of the deviations from the natural tetrahedral angle of the bonds in simple

cyclic/

cyclic molecules such as cyclopropane and cyclobutane these deviations being 49°28' and 19°28', respectively.

ACENAPHTHYLENE

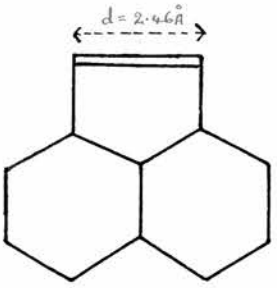


Fig. VIII

Similar considerations apply here as in the case of the acenaphthene molecule.

The distance d being 2·46Å (Fig. VIII) and the normal ethylenic bond length being 1·34Å it follows that in order to maintain the peri-bonds at their normal angle of 120° with each of the adjacent bonds, then the double bond must be stretched from 1·34Å to 2·46Å i.e. 1·12Å or 84%.

Again, it seems more reasonable to assume (Fig. IX) that the peri-bonds of acenaphthylene are distorted through an angle ϕ such that the distance between the bridge carbon atoms has the same value (1·34Å) as the length of the normal ethylenic bond.

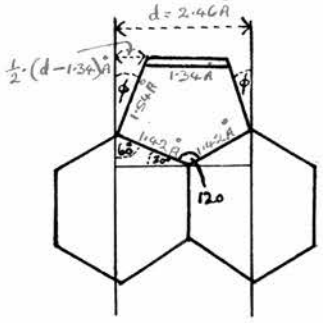


Fig. IX

A similar calculation to that above for the case of acenaphthene leads to the value

$$\phi = 21{\cdot}5^\circ$$

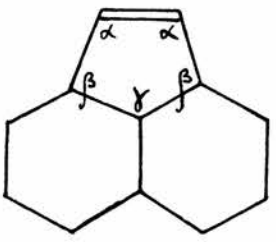


Fig. X

The various angles in the five-membered ring are accordingly given (Fig. X) by

$$\alpha = 111{\cdot}5^\circ$$

$$\beta = 98{\cdot}5^\circ$$

$$\gamma = 120^\circ$$

The same comments apply here as were made concerning the distortion in acenaphthene.

FLUORENE

This molecule differs from the two discussed above in that the two benzene nuclei in fluorene are united, as in diphenyl, by a covalent bond while in acenaphthene and acenaphthylene the benzene nuclei are united by ortho-fusion. Since the benzene nuclei in fluorene are united as in diphenyl a short account of the bond lengths and bond angles in diphenyl itself will be given.

Different values for the bond lengths were given by different methods of measurement.

From x-ray data (Dhar. Ind. J. Phys. 1932, 7, 43) the bond lengths were given (Fig. XI) as

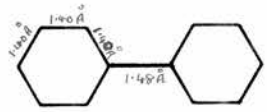


Fig. XI

(a) ring bonds 1·40Å

(b) inter-ring bond 1·48Å

Different results were obtained from electron diffraction experiments (Karle and Brockway. J.A.C.S., 1944, 66, 1974)

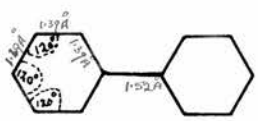


Fig. XII

The bond lengths were given (Fig. XII) as

(a) ring bonds 1·39Å

(b) inter-ring bond 1·52Å

while bond angles of 120° appeared to give the best agreement with the results.

In the former case the molecule was considered to be coplanar; in the latter case Karle and Brockway considered that a non-coplanar structure for diphenyl was/

was more probable because such a structure would avoid steric hindrance between the ortho hydrogen atoms in the planar structure and because it was compatible with the electron diffraction data.

Returning to the question of fluorene we shall make the assumption that the benzene ring bond lengths, the inter-ring distance and the bond angles are the same as in diphenyl (data from electron diffraction investigations).

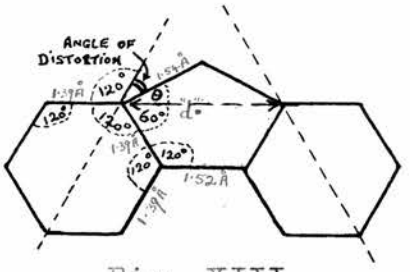


Fig. XIII

To find a measure of the strain introduced into the fluorene molecule by the replacement of two adjacent ortho hydrogen atoms with methylene we shall calculate the angle through which each ortho bond participating in the formation of the five-membered ring must be distorted, assuming all the while that the assumptions mentioned immediately above hold (see Fig. XIII).

The angle of distortion is then $120^\circ - (\theta+60^\circ)$.

Assuming also that the two bonds uniting the methylene carbon atom to the benzene rings in the diphenyl moiety are single bonds in character then θ is given by the equation

$$\cos\theta = \frac{\frac{1}{2}\cdot(\text{distance, d, between two "ortho" carbon atoms})}{1\cdot54}$$

$$= \frac{\frac{1}{2}\cdot(1\cdot52 + 2.1\cdot39.\cos 60^\circ)}{1\cdot54}$$

$$= 0\cdot9455$$

whence $\theta = 19^\circ$

and the deviation is therefore 41°.

The angles in the five-membered ring are given (Fig. XIV) as

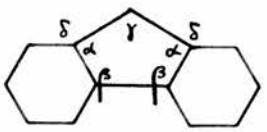


Fig. XIV

$\alpha = 79^\circ$

$\beta = 120^\circ$

$\gamma = 142^\circ$

$\delta = 161^\circ$

If we calculate the distortion angle using the data obtained from x-ray measurements then we find, by a calculation similar to that given immediately above, that the angle of distortion is nearly the same as the value obtained using data from electron diffraction experiments.

It is seen also that the normal tetrahedral angle at the methylene group has been strained from 109·5° to 142° i.e. through 32·5°.

The strain in a molecule possessing the structure assumed for fluorene in the above calculations is therefore seen to be quite considerable. This strain centres round the five membered ring.

FLUORANTHENE

This case may be considered in the light of the results obtained for acenaphthene and acenaphthylene. Two cases arise.

(a) The phenylene group in the fluoranthene molecule has/

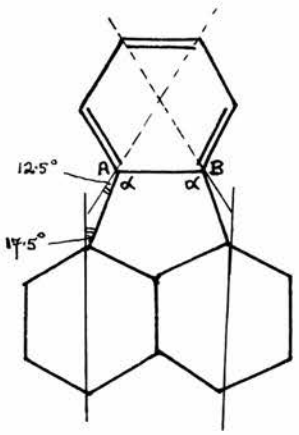


Fig. XV

has the bond structure shown (Fig. XV) in which bond AB is a single bond (1·54Å). The distortion of the peri-bonds from the normal position is the same as in acenaphthene viz. 17·5°.

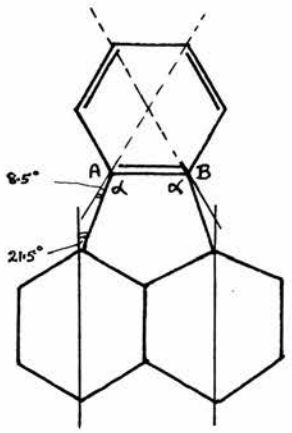


Fig. XVI

(b) The bond AB (Fig. XVI) is a double bond (1·34Å) which means that the angle of distortion of the peri-bonds is the same as in acenaphthylene viz. 21·5°.

It is seen that the two bonds external to the benzene and naphthalene nuclei and common to both rings are also distorted through a small angle from the normal position.

If structure (a) (Fig. XV) is real then this angle of deviation is given by $120^\circ - \alpha$

$= 120^\circ - 107{\cdot}5^\circ$

$= 12{\cdot}5^\circ$

and if structure (b) (Fig. XVI) is real the angle of deviation is $120^\circ - \alpha$

$= 120^\circ - 111{\cdot}5^\circ$

$= 8.5^\circ$

The/

The same comments which apply to the results derived for acenaphthene and acenaphthylene apply here.

4:5-METHYLENEPHENANTHRENE

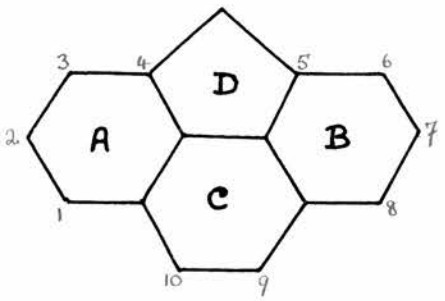


Fig. XVII

Owing to the presence of the additional benzene ring C in this molecule (Fig. XVII) it is a more reasonable assumption to make, that the length of the bond between rings A and B is closer to that of the benzene ring itself than the inter-ring distance in diphenyl.

If we assume

(a) an average value of 1·41Å for the bond between rings A and B and

(b) that the bond angle of 120° obtains in the three benzenoid rings A, B and C

then we can calculate the angle of distortion of the bonds at the 4- and the 5- positions in the molecule (Fig. XVII) by a process similar to that used in the calculation on fluorene above.

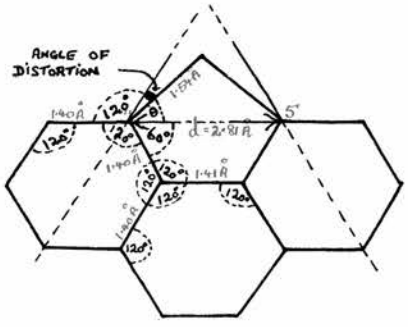


Fig. XVIII

The distance between C_4 and C_5 (Fig. XVIII) is given by

$$d = 1{\cdot}41 + 2.1{\cdot}40.\cos 60^{\circ}$$
$$= 1{\cdot}41 + 1{\cdot}40$$
$$= 2{\cdot}81\text{Å}$$

The angle of distortion of the C_4 or C_5 external bond which results from the formation of the five-membered ring by replacement of hydrogen on C_4 and C_5 by methylene is given by $120^\circ - (\theta + 60^\circ)$

$$\text{Now} \quad \cos\theta = \frac{\frac{1}{2}\cdot d}{1\cdot 54} = \frac{\frac{1}{2}\cdot 2\cdot 81}{1\cdot 54}$$

$$= 0.912$$

$$\text{whence} \quad \theta = 24^\circ$$

and so the angle of deviation $= 35^\circ$.

The various angles in the five-membered ring are accordingly given (Fig. XIX) by

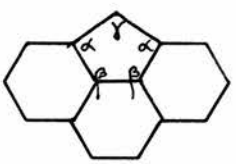


Fig. XIX

$$\alpha = 84^\circ$$

$$\beta = 120^\circ$$

$$\gamma = 132^\circ$$

The strain in this molecule is therefore not very much different from the strain in the fluorene molecule if we consider that the angle of deviation of the bonds in the five-membered rings is a measure of this strain.

With regard to the foregoing discussions on the geometry of those hydrocarbons containing five-membered rings two observations may be made here

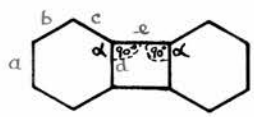
(a) the molecules were assumed to be coplanar

(b) the calculations assumed that the geometrical form of all benzene rings in the molecules was to all intents and purposes that of benzene itself. Small differences in bond lengths were taken into account where necessary, but were of the order of only 1 to 2%.

It/

It was necessary to alter only those bond angles external to the benzene rings in order to meet the requirements of the geometry of the five membered rings, and at the same time maintain coplanarity of the molecules and 120° angles within the benzene rings. The reasonable assumption was made that the bond angles in the molecules would alter at the demand of steric strain rather than the bond lengths.

The strain in the molecules was considered as related to the angles of distortion of these bonds. It has been shown that these angles of distortion are not excessively great when molecules such as cyclopropane are considered. A more analogous case might be the consideration of the aromatic hydrocarbon biphenylene (annexed formula) which differs from fluorene in that it contains a central four-membered ring instead of a five-membered ring. In this hydrocarbon the dimensions as obtained from electron diffraction data (Waser and Schomaker. J.A.C.S., 1943, 65, 1451) are as follows



Biphenylene

$$a = b = c = d = 1{\cdot}41\text{Å} \quad (\pm\ 0{\cdot}02\text{Å})$$
$$e = 1{\cdot}46\text{Å} \quad (\pm\ 0{\cdot}02\text{Å})$$
$$= 121^\circ \quad (\pm\ 3^\circ)$$

As is seen the benzene nuclei possess dimensions close to those of benzene itself.

The angle of distortion of the inter-ring bonds is at once seen to be

121°/

$$121^\circ - 90^\circ \pm 3^\circ$$

or $$31^\circ \pm 3^\circ$$

which is of the order of magnitude of the angles of distortion in the molecules discussed above. Like the hydrocarbons previously discussed, biphenylene is a stable molecule.

DATA ON FIVE-MEMBERED RING SYSTEMS

A short account of the results obtained and the conclusions reached by various investigators concerning the stereochemistry of those systems just considered which contain five-membered rings, will be given below.

These condensed benzene ring systems containing five-membered rings have not hitherto been examined in any great detail regarding their spatial configurations and the evidence existing at present is unconclusive and self-contradictory.

ACENAPHTHENE

The molecular geometry of this molecule has been studies by two schools of investigators, each of which utilised x-ray analyses. The conclusions arrived at regarding not only the molecular geometry but the crystal structure of the substance differ widely.

Banerjee and Sinha (Ind. J. Phys., 1937, 11, 21 and C.A. 1937, 31, 4546) concluded that their results were best explained by assuming a co-planar structure for the molecule. The bond lengths and angles were given (Fig. XX)/

(Fig. XX) as

$a = 2{\cdot}01\text{Å}$

$b = 1{\cdot}47\text{Å}$

$\alpha = 114^\circ$

$\beta = 97^\circ$

$\gamma = 126^\circ$

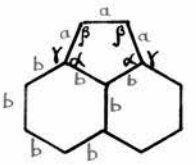


Fig. XX

More recent work by the Russian investigator Kitaigorodskii (J. Phys. Chem. U.S.S.R., 1947, 21, 1085) and C.A., 1948, 42, 2488) disagrees quite considerably with the Indian investigators' results with regard to the bond lengths and angles in the five membered ring. The bridge c-c bond was found to be $1{\cdot}80\text{Å}$ (Fig. XXI) and the molecule to be coplanar. It is evident that in the light of the presently accepted views regarding c-c bond lengths in organic compounds both of these results must be treated with extreme reserve.

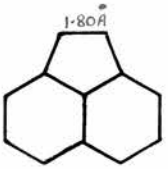


Fig. XXI

Apart from acenaphthene the only other hydrocarbon of this type which has been studied in any detail is fluorene.

FLUORENE

Quite a considerable controversy has, however, taken place regarding the stereochemistry of fluorene. The various opinions may be classified into two sets (a) those which hold that fluorene is coplanar and (b) those which maintain that the best representation of/

of fluorene is a non-coplanar structure with the benzene rings inclined at an angle to the five-membered ring and to one another.

(a) According to Hughes, Lefevre and Lefevre (Chem. and Ind., 1936, 55, 545) dipole moment studies on 2:7-dinitrofluorenone provides evidence that fluorene is best represented by a uniplanar structure with the two benzene rings co-axial. They regard the molecule as a resonance hybrid to which the structure (XXIIa) and (XXIIb) below are the chief contributing forms.

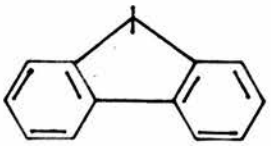


Fig. XXIIa

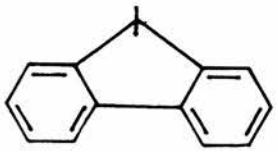


Fig. XXIIb

This structure it will be noted is the same as that assumed in the calculations above.
Pinck and Hilbert (J.A.C.S., 1937, 59, 8) however, while considering that the molecule was uniplanar, concluded from the general results of x-ray and electron diffraction studies as summarised at that time by Robertson (Chem. Reviews, 1935, 16, 417) that the benzene rings in fluorene would not be co-axial but would have the configuration shown (Fig. XXIII).

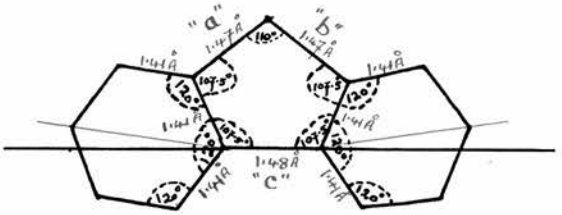


Fig. XXIII

Each of the bonds a, b and c were considered to be bent through an angle of 12·5° from the normal. The molecule was considered to be under considerable strain owing to this bond distortion.

(b) Cook and Iball (Chem. and Ind., 1936, 55, 467) on the other hand considered that the structure in best agreement with their data was non-planar with the benzene rings inclined at an angle of 20° to the plane of the five-membered ring and at 40° to one another (Fig. XXIV) (cf. also Iball., Zeit. für Krist., 1936, 94, 397). A head-on view of the fluorene molecule of Fig. XXIV is shown in Fig. XXV in which the configuration is obtained by moving the planes of the benzene rings about sides BC and DE through an angle of 20° from the planar configuration.

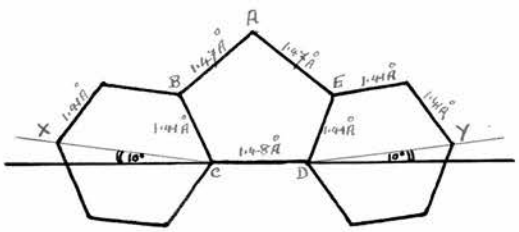


Fig. XXIV

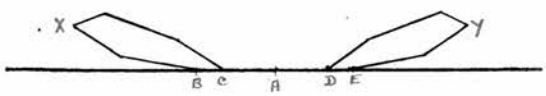
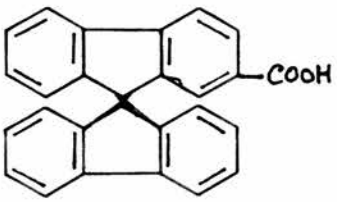


Fig. XXV

The position has been summarised recently by Weisburger, Weisburger and Ray (J.A.C.S., 1950, 72, 4250) who, from considerations of resonance energy, bond lengths, bond angles and absorption spectra, concluded that fluorene was planar. These investigators considered that their failure to resolve 9:9'-spirobifluorene/



spirobifluorene-2-carboxylic acid (Annexed formula) supported these conclusions.

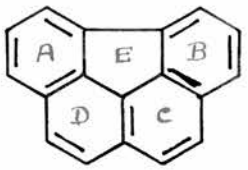
Finally it may be mentioned that Sandorfy (Compt. Rend., 1948, 227, 198 and C.A. 1948, 42, 8035) from a consideration of acenaphthylene and fluoranthene by the method of molecular orbitals came to the conclusion that the distortion of the naphthalene nucleus in these molecules does not greatly depend on the size of the rest of the molecule.

SIGNIFICANCE OF THE SYNTHESIS OF 2:13-BENZFLUORANTHENE

In all those ring systems considered above three sides at most of the five-membered ring present in the molecule are each common to the five-membered ring and a six-membered (benzene)ring. It was shown that there was no need to depart from the concept of a coplanar molecule in which the bond angles in every benzene ring present were of the same size as those in benzene itself viz. 120°. The only necessity for this to hold was that the external valence bonds of the benzene rings should depart from their normal directions relative to the valence bonds constituting the rings themselves.

The existence of the newly synthesised 2:13-benz-fluoranthene/

fluoranthene forces a departure from these ideas. In this compound (annexed formula) there are present four benzene rings A, B, C and D fused on adjacent sides of a five-membered ring E. It is evident that in this molecule there are embodied the structures of acenaphthene (rings E, D and C), fluorene (rings A, E and B), fluoranthene (rings A, E, D and B) and 4:5-methylenephenanthrene (rings A, D, C and E).



2:13-Benz-fluoranthene

Now if, as before, it is assumed that the molecule is coplanar with the internal angles of the benzene rings lying approximately at 120° then we are forced to the conclusion that the bond length "a" (Fig. XXVI) is 2·46Å, assuming an average value of 1·42Å for the lengths of bonds "b" and "c" as is present in naphthalene.

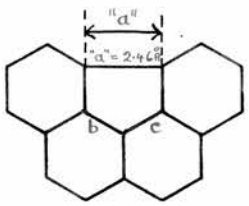


Fig. XXVI

This value for the length of bond "a" however cannot be accepted since the normal c-c single bond length is 1·54Å. It is proposed that in the following the value of 1·54Å shall be taken as the length of the c-c single bond. Even a stretching of this bond to 1·60Å, a process which would incur a considerable effort, would still fall far short of the requirements of the above molecule.

It is necessary therefore to give up either

(a) the idea of coplanarity in 2:13-benzfluoranthene

or/

or (b) the assumption that in the benzene rings the internal angles are all 120° or very nearly so or it may be necessary to give up both ideas.

The consequences of relinquishing completely one of these alternatives while retaining the other will now be outlined.

2:13-BENZFLUORANTHENE IS COPLANAR

Several possibilities then present themselves, depending on the manner in which the molecule is built up.

Coplanar Structure I

2:13-benzfluoranthene may be considered as built up on the acenaphthene structure as basis. Rings A, B and C (Fig. XXVII) possess the same bond angles as acenaphthene itself. The data for the molecule then is

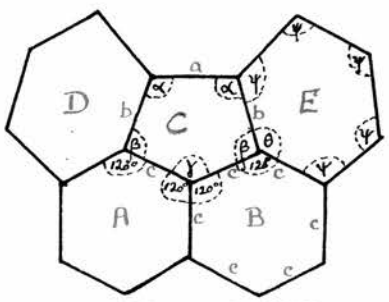


Fig. XXVII

$$a = b = 1{\cdot}54\text{Å}$$
$$c = 1{\cdot}42\text{Å}$$
$$\alpha = 107{\cdot}5^\circ \quad \beta = 102{\cdot}5^\circ \quad \gamma = 120^\circ$$

From this data $\theta = (360^\circ - 120^\circ - \beta)$

$= (360^\circ - 120^\circ - 102{\cdot}5^\circ)$

$= 137{\cdot}5^\circ$

Then the sum S of the remaining five internal angles/

angles of ring E is given by

$$S = 720^\circ - \theta$$
$$= 720^\circ - 137{\cdot}5^\circ$$
$$= 582{\cdot}5^\circ$$

If we assume an average value of ψ for each of these remaining five angles in ring E then

$$\psi = \frac{S}{5}$$
$$= \frac{582{\cdot}5^\circ}{5}$$
$$= 116{\cdot}5^\circ$$

Accordingly, in the benzene rings E and D there are five angles of average size $116{\cdot}5^\circ$ and one angle of $137{\cdot}5^\circ$.

Coplanar Structure II

In like manner the 2:13-benzfluoranthene nucleus may be considered as built up on the fluoranthene nucleus. Rings A, B, C and D (Fig. XXVIII) are then assumed to possess the same bond angles as the corresponding angles in fluoranthene itself. The data for the molecule then is

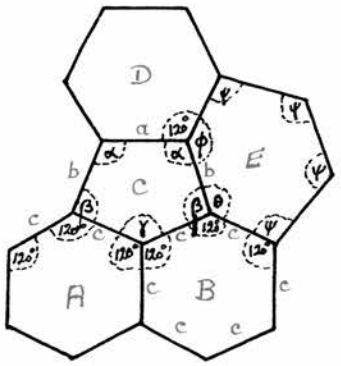


Fig. XXVIII

$$a = b = 1{\cdot}54\text{Å}$$
$$c = 1{\cdot}42\text{Å}$$
$$\alpha = 107{\cdot}5^\circ \quad \beta = 102{\cdot}5^\circ \quad \gamma = 120^\circ$$

whence
$$\theta = (360^\circ - 120^\circ - \beta)$$
$$= (360^\circ - 120^\circ - 102{\cdot}5^\circ)$$
$$= 137{\cdot}5^\circ$$

and $$\phi = (360^\circ - 120^\circ - \alpha)$$
$$= (360^\circ - 120^\circ - 107{\cdot}5^\circ)$$
$$= 132{\cdot}5^\circ$$

Denoting the sum of the remaining four internal angles of ring E by S it follows that

$$S = (720^\circ - 137{\cdot}5^\circ - 132{\cdot}5^\circ)$$
$$= 450^\circ$$

and if we assume an average value of ψ for each of these four angles then

$$\psi = \frac{S}{4}$$
$$= \frac{450^\circ}{4}$$
$$= 112{\cdot}5^\circ$$

According therefore to this model of the 2:13-benzfluoranthene molecule there are four angles in ring E of average value $112{\cdot}5^\circ$, a fifth angle of $137{\cdot}5^\circ$ and a sixth of $132{\cdot}5^\circ$.

In the above two calculations it has been assumed that the angles α and β were of the same magnitude as those present in acenaphthene. Assuming that the rings A, B and C possessed the same dimensions as were assigned to acenaphthylene viz.

$$a = 1{\cdot}34\text{Å}$$
$$\alpha = 111{\cdot}5^\circ \quad \beta = 98{\cdot}5^\circ$$

then by substituting these values of α and β in the co-planar structures I and II above it is found that

in I above $\psi = 115{\cdot}7^\circ$

and in II above $\psi = 112{\cdot}5$, as before.

Coplanar/

Coplanar Structure III

However, if the molecule of 2:13-benzfluoranthene is coplanar it is unlikely that the strain imposed upon the molecule by the formation of four benzene rings about the sides of the five-membered ring will be confined to one (or two) of these rings alone. It seems logical to assume that the strain will be distributed evenly throughout the whole molecule.

The assumption can now be made for the third possibility for the structure of 2:13-benzfluoranthene viz. that the external angles of the five-membered ring, θ_1 θ_2-----θ_8 are all equal (Fig. XXIX).

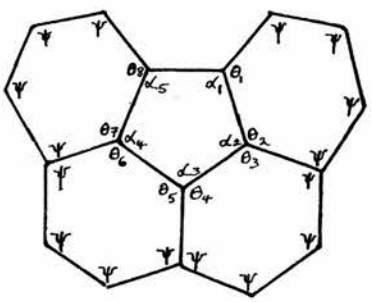


Fig. XXIX

Since $\alpha_1 = \alpha_2 = \alpha_3 --- = \alpha_5$ it follows that $\theta_1 = \theta_2 = \theta_3 --- = \theta_8$ assuming again that the five-membered ring is a regular pentagon.

Also since $\theta_1 = \theta_2 = 126^\circ$

$\theta_3 = \theta_4 = 126^\circ$

etc.

then, assigning an average value of ψ to each of the four remaining angles in the benzene rings, it follows that

$$\psi = \tfrac{1}{4}(720^\circ - 126^\circ - 126^\circ)$$

$$= 117^\circ$$

In/

In this representation of the 2:13-benzfluoranthene molecule there are accordingly four benzene rings in each of which are two angles of 126° and four angles of average size 117° each.

Even if the molecule were coplanar, it is not likely that any of the three representations thus described is correct although it would appear safe to say that the last representation would be nearest the actual state of the molecule.

Nevertheless it does not matter what the relative magnitudes of the bond angles are in the benzene rings; the important point to be gathered from the foregoing is that in none of the possible coplanar representations of the molecule can the bond angles in all the benzene rings remain at or close to 120°. The representation involving the highest degree of symmetry in the molecule would seem to be most likely in the event of the molecule being coplanar. In such a case the maximum angle of distortion in the benzene rings is from 120° to 126° i.e. through 6°.

2:13-BENZFLUORANTHENE IS NON-COPLANAR

The most reasonable assumption to make is that the strain is distributed evenly throughout the molecule and that as a result the planes of all the benzene rings present in the 2:13-benzfluoranthene molecule lie in different planes to that of the five-membered ring. It will/

will now be shown that all the bond angles in the four benzene rings present in the molecule may possess angles of 120° if a non-coplanar structure is assumed for the molecule.

Consider (Fig. XXX, see next page) the regular pentagon F, sides a, b, c, d and e. Let lines l, m, n, p and q be drawn from the corners, and in the plane, of the pentagon F and let each of these lines make equal angles θ with the sides of the pentagon adjacent to it.

Let the lengths of the lines l, m, n, p and q be the same and equal to the length of the sides of the pentagon.

Hence $l = m = \text{---} = q$

$= a = b = \text{---} = e$

Consider one of these lines, say l.

Since the pentagon is regular the five internal angles ϕ of the pentagon will all be equal and of magnitude 108°.

Since l makes equal angles θ with the adjacent sides a and b, it follows that

$$\theta = \tfrac{1}{2}(360^{\circ} - \phi)$$
$$= \tfrac{1}{2}(360^{\circ} - 108^{\circ})$$
$$= 126^{\circ}$$

Denoting the angle of inclination of l with the plane F by ψ, it follows that when l lies in the same plane as pentagon F then (Fig. XXX and XXXI)

$$\psi = 0^{\circ} \text{ and } \theta = 126^{\circ}$$

When however l is perpendicular to the plane of pentagon/

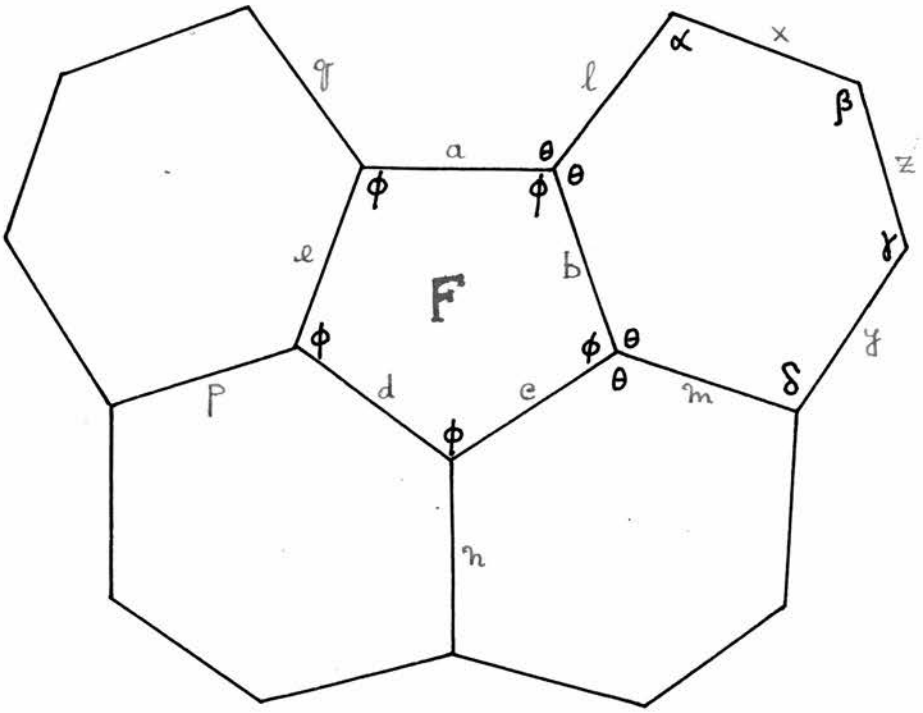


Fig. XXX

Fig. XXXI

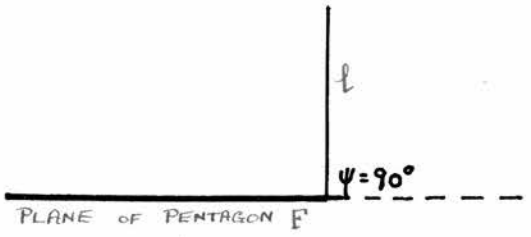


Fig. XXXII

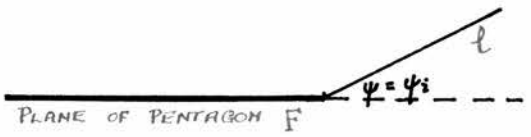


Fig. XXXIII

pentagon F then (Figs. XXX and XXXII)

$$\psi = 90^\circ \text{ and } \theta = 90^\circ$$

There will be some value of ψ lying between 126° and 90° for which $\theta = 120^\circ$. Denote this angle by ψ_i (Fig. XXXIII).

Each of the lines l, m, n, p and q (Fig. XXX) may in turn be moved through an angle ψ_i on the same side of the plane of the pentagon F such that they make equal angles of 120° with the two concurrent sides of the pentagon.

Draw a line x from the end of line l parallel to line m and equal in length to m. Similarly draw a line y parallel to l from the end of m and equal in length to l. Join the ends of lines x and y and denote the resulting line by Z.

Then from the constructions of the figure outlined above

$$l = m = b = x = y = z$$

Also since the angle contained by sides l and b is of the same magnitude as the angle contained by sides m and b viz. 120° it follows (Fig. XXX) that

$$\alpha = \beta = \gamma = \delta = 120^\circ$$

i.e. the figure whose sides are l b m y z x is a regular hexagon.

Similar figures may in like manner be described about the sides c, d and e of the pentagon F.

If we consider this figure as a geometrical representation of the 2:13-benzfluoranthene molecule in space/

space then the regular hexagons of the geometrical figure represent the benzene rings - the regular pentagon, the five-membered ring - in 2:13-benzfluoranthene.

The angle of inclination ψ_i of the peripheral valence bonds of the five-membered ring to the plane of the five-membered ring is related to the angle of inclination ϵ of the planes of the six-membered rings to the five-membered ring by the equation

$$\sin \epsilon = \frac{\sin \psi_i}{\sin 60^\circ}$$

while the angle ψ_i is given by

$$\cos \psi_i = \tfrac{1}{2} \cdot \sec 54^\circ$$

These two relationships give the values

$$\psi_i = 31^\circ 42' \approx 32^\circ$$
$$\epsilon = 37^\circ 23' \quad 37^\circ$$

and the angle λ between the planes of each adjacent benzene ring is given by

$$\lambda = 59^\circ 59' \approx 60^\circ$$

In short, this geometrical representation of the 2:13-benzfluoranthene molecule describes the molecule as consisting of a central five-membered ring with bond lengths and bond angles respectively of the same magnitude, and on four sides of this central five-membered ring are fused benzene rings having the forms of regular hexagons, these rings being inclined at an angle of 37° to the plane of the five-membered ring and at 60° to one another.

The/

Coronindene

The as yet hypothetical coronindene molecule (annexed formula) differs from 2:13-benzflucranthene in that a fifth benzene ring is fused on the remaining "open" side of the five-membered ring in 2:13-benzfluoranthene. The coronindene molecule would, according to this non-coplanar representation of 2:13 benzfluoranthene, consist of a central five-membered ring possessing the form of a regular pentagon, fused upon the sides of which are five benzene rings with the forms of regular hexagons.

DISCUSSION ON ALTERNATIVE PROPOSED STRUCTURES

It must be emphasised that no claim is made here that the geometrical representations of 2:13-benz-fluoranthene considered above are exact representations, even if one of the two possible (coplanar and non-coplanar) structures considered likely proved to be essentially correct. In both representations which are considered as likely alternatives viz. the non-coplanar structure on the one hand and the coplanar structure III on the other, no account has been taken of possible, and indeed probable, small variations in bond lengths which will occur in the 2:13-benzfluoranthene molecule. The calculations are at best semi-quantitative.

It is clear in any case that the 2:13-benzfluoranthene molecule will either be non-coplanar or will possess bond angles/

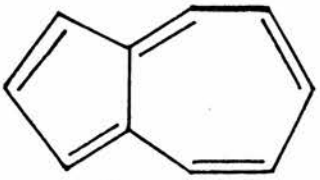
angles in the benzene rings considerably different from those in the aromatic hydrocarbons hitherto encountered. A third possibility for the structure of this hydrocarbon is a combination of both features involving a compromise between distortion due to alteration of the bond angles and that due to non-coplanarity. No new feature is encountered in this possibility which has not already been considered in one or other of the two extreme possibilities already discussed and the case need not be considered by itself. Such a possibility still does not maintain the classical 120° angles in the benzene rings and, at the same time, coplanarity of the molecule.

The non-coplanar structure considered above for the 2:13-benzfluoranthene molecule at once raises the question of resonance in the molecule.

According to theory planarity of a molecule is a necessity for resonance to be appréciable. Resonance in 2:13-benzfluoranthene should therefore be considerably reduced if the molecule possesses the non-coplanar structure.

The alternative coplanar structure for this hydrocarbon would also be expected to have a considerably reduced resonance energy since the bond angles for such a structure have departed from 120° which is the undistorted and natural valency angle of Sp_2 hybridised carbon. The bond angles for this coplanar structure were given as 117° (four bond angles) and 126° (two bond angles). It may be relevant to compare these angles with/

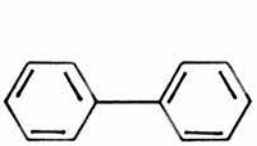
with the angles present in azulene, a substance which satisfies the quantum-mechanical conditions for aromaticity. If the rings present in this molecule (annexed formula) are assumed to possess the forms of regular polygons then the bond angles in the five-membered ring will be 108° while those in the seven-membered ring will be 128·6°. Both angles are considerably removed from the valency angle of Sp_2 hybridised carbon viz. 120°. It is interesting to find that the resonance energy of azulene amounts to 46 kcal./mole (Heilbronner and Wieland., Helv. Chim. Acta, 1947, 30, 953) while that of the strainless naphthalene is 77 kcal/mole.



Azulene

According to theoretical considerations we may therefore expect to find a not very high value for the resonance energy of 2:13-benzfluoranthene.

It is a known fact that the introduction of a methyl or a methylene bridge across part of a polycyclic aromatic hydrocarbon molecule may result in a pronounced sharpening of the resolution of the fine structure bands of the hydrocarbon. This effect, described by Jones (J.A.C.S., 1945, 67, 2132) as the Fs (fine structure) effect, is well illustrated in a comparison of the spectra of diphenyl (259), 9:10-dihydrophenanthrene (260) and Fluorene (261).



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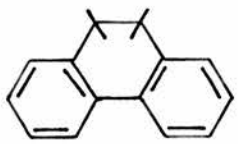
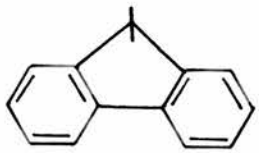


(260)



(261)

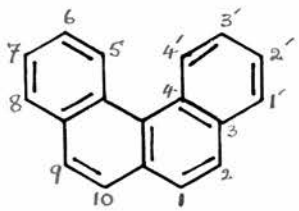
The spectrum of diphenyl is practically structureless, the maximum intensity of absorption of the single band occurring at 2450Å. With the introduction of the dimethylene bridge, as in 9:10-dihydrophenanthrene, this band is displaced to 2700Å while a second band appears at longer wavelengths viz. around 3000Å.

With the introduction of the dimethylene bridge into the diphenyl molecule little strain has been introduced and apart from the bathochromic shift due to the introduction of the dimethylene bridge into the diphenyl the spectrum of diphenyl and 9:10-dihydrophenanthrene are very similar. The strain associated with the five-membered ring in fluorene however, causes a considerable difference in the appearance of the spectrum of fluorene as compared with diphenyl.

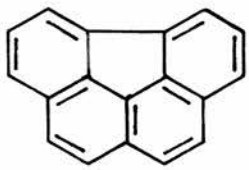
Two sets of bands can be distinguished, one appearing in the same region as that in which the shorter wavelength band of 9:10-dihydrophenanthrene appears, the other in the same region as that in which the longer wavelength band of 9:10-dihydrophenanthrene appears. Much greater resolution occurs in the spectrum of fluorene and whereas in 9:10-dihydrophenanthrene the/

the two bands (at 2700Å and 3000Å) are structureless, those of fluorene show very prominent fine structure with production of a number of subsidiary maxima.

It will be interesting, therefore to compare the known spectra of 3:4-benzphenanthrene (262) with that of 2:13-benzfluoranthene (263)



(263)



(262)

for the former differs from the latter only in that no bridge bond is present between the 4' and 5 positions of the 3:4-benzphenanthrene molecule.

EXPERIMENTAL . INTRODUCTION

(1) Unless otherwise stated all yields are reported as the percentage of the theoretical yield.

(2) All melting points are corrected and were determined by the use of a Kofler micro melting point apparatus (Kofler. Mikrochem., 1934, 15, 242). In most cases the melting points were checked by the capillary tube method (Campbell. "Qualitative Organic Chemistry", p. 7).

(3) Fluorescence observations were made in U.V. radiation generated by a Hanovia lamp.

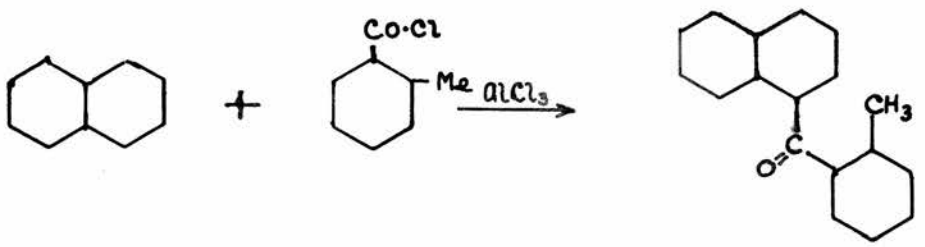
(4) Chromatographic analyses and purifications of organic compounds were performed with Brockmann standardised alumina.

(5) Analyses of organic compounds were carried out by Drs. Weiler and Strauss, Oxford.

SECTION A.

The following experimental work is concerned particularly with the Elbs syntheses of three isomeric Naphthofluoranthenes from 4- and 11-O-Toluylfluoranthene. In addition the Elbs Reaction on 3-O-Toluylacenaphthene and 1-O-Toluylnaphthalene, two ortho methyl aryl ketones structurally similar to 4- and 11-O-Toluylfluoranthene, is described.

1-O-TOLUYLNAPHTHALENE



The conditions used in the preparation of 1-O-Toluylnaphthalene were essentially those under which Acree (Ber., 1904, 37, 625) prepared α-Benzoylnaphthalene. Granulated magnesium (3.6g. - 0.157mols.) was added to a solution of α-Bromonaphthalene (31g. - 0.15mols.) in ether (50 c.c.). On addition of a crystal of Iodine a reaction set in and the mixture was then boiled under reflux for 30 minutes, at the end of which time the magnesium had gone into solution. A further 50 c.c. ether together with 100 c.c. benzene were slowly added while the solution was maintained at the boiling point.

The/

The resulting solution, after cooling, was slowly added to a solution of O-Toluyl chloride (24g. - 0.156 mols.) dissolved in a mixture of 25 c.c. ether and 25 c.c. benzene. After complete addition, the resulting solution was slowly raised to the boiling point and thereafter boiled under reflux for 4 hours.

At the end of the reaction the mixture was poured into dilute hydrochloric acid (250 c.c.) and the resulting mixture steam-distilled for 5 hours when the benzene and ether, and later a little naphthalene, were removed from the reaction product. The residue was extracted with ether; the ether solution so obtained was washed free of acid with sodium carbonate solution (100 c.c.), twice with water and finally dried over calcium chloride. The bulk of the ether was evaporated off and the residue taken up in a 1:1 mixture of methanol-petrol ether (b.p. 60-80°). Concentration of this solution to 20 c.c. followed by cooling in the refrigerator resulted in the deposition of colourless flat prisms of 1-O-Toluylnaphthalene

m.p. 55 - 57°C. (Lit. m.p. 59° - 61°C.)

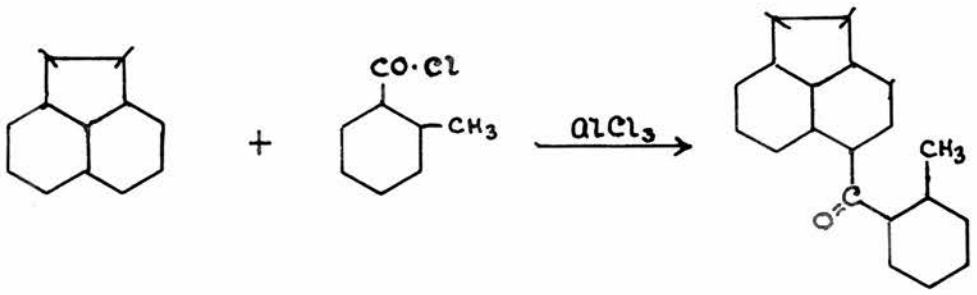
Yield 14g. (38%)

The ketone gives a golden-yellow coloration with concentrated sulphuric acid.

3-O-TOLUYLACENAPHTHENE

The method used for the preparation of 3-O-Toluyl-acenaphthene was essentially that as used by Geyer and Zuffanti/

Zuffanti (J.A.C.S. 1935, 57, 1787).



Anhydrous aluminium chloride (30g.) was added in small quantities at a time to an ice-cold solution of acenaphthene (30g.) and o-Toluyl chloride (30g.) in carbon disulphide (75 c.c.). After standing at 0-5°C. for 6 hours, the solution was allowed to warm to room temperature and then carefully treated with water and cracked ice.

The dark brown ketone was steam-distilled for 12 hours first in the presence of HCl and then dil. NaOH, whereupon a considerable amount of unchanged acenaphthene passed over. The residue was extracted with benzene, and the benzene layer washed with water until free of alkali, dried over anhydrous calcium chloride and taken down to small volume. This solution contained a considerable quantity of tarry material and, on cooling, deposited a brownish crystalline solid. This was recrystallised twice from ethanol to give 3-o-Toluyl-acenaphthene, pale yellow plates,

m.p. 137 - 139°C. (Lit. m.p. 139 - 140°C.)

Yield 10g. (19%).

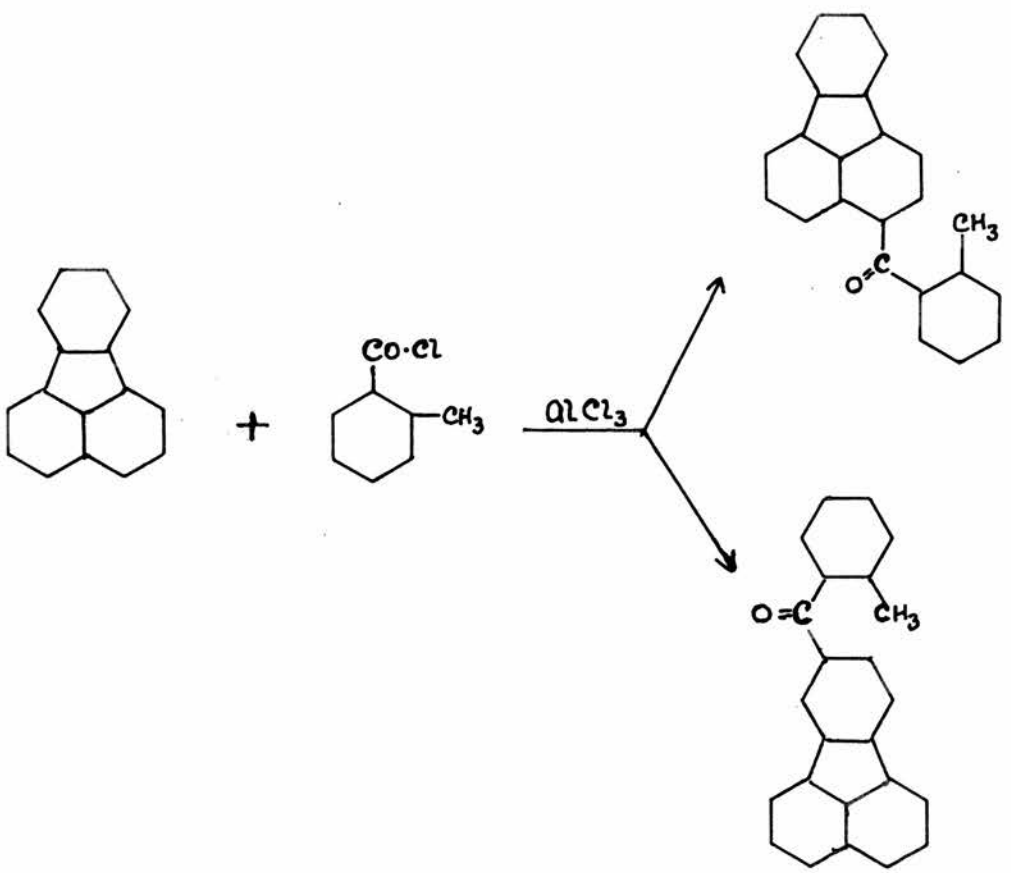
The/

The ketone gives an orange colouration with conc. sulphuric acid.

4- and 11-o-TOLUYLFLUORANTHENE

Toluylation of Fluoranthene

The toluylation of fluoranthene was carried out under conditions similar to those employed for the benzoylation of fluoranthene (c.f. von Braun u. Manz. Ann., 1932, 496, 184. and Campbell and Easton. J. 1949, 340).



Fluoranthene (30g.) and powdered aluminium chloride (24g.) were shaken up in carbon disulphide (180 c.c.) with ice-cooling. o-Toluyl chloride (24g.) was run into the mixture dropwise with vigorous stirring and/

and the whole agitated at room temperature for 8 hours. The reaction mixture was boiled under reflux for a further 6 hours on the water bath and the carbon disulphide then removed by distillation. The orange-brown mass thus obtained was decomposed by ice to give a yellowish-brown oily solid. This solid was extracted with ether, washed with sodium carbonate solution and then with water and finally dried over anhydrous $CaCl_2$. Removal of the ether by distillation yielded a dark yellowish-brown solid. Yield (crude) 43g. (90%).

Attempted separation of 4- and 11-o-Toluylfluoranthene by Fractional Crystallisation

The crude ketone mixture (43g.) obtained as described above was dissolved in the minimum volume of boiling benzene, and on cooling, a considerable amount of very dark brown tarry material settled out of solution as a semi-solid mass. This was filtered off and the light-brown filtrate was evaporated to dryness. The residual sticky solid was redissolved in the minimum volume of boiling methylated spirits. On cooling, this solution deposited a yellow, crystalline solid (11.7g.) which was filtered off. Concentration of the filtrates so obtained yielded a second crop of yellow crystals (4.2g.).

Repetition of this process on the second batch of filtrates produced a third crop of yellow crystals (7.0g.). Examination of the three crops of crystals obtained in this way showed each to have the same colour and melting/

melting range viz. 103 - 150°C. It was thus obvious that this attempt at purification of the isomeric ketones had been unsuccessful. Resort was then made to chromatography on activated alumina.

CHROMATOGRAPHIC SEPARATION OF 4- and 11-o-TOLUYLFLUORANTHENE

As described above, the following batches of material were obtained from the attempted separation of the 4- and 11-o-Toluylfluoranthenes by fractional crystallisation.

A. The semi-solid mass of tarry material obtained from benzene solution.

B. The first crop (11.7g.) of yellow crystals from the methylated spirits solution.

C. The second crop (4.2g.) of yellow crystals from the methylated spirits solution.

D. The third crop (7.0g.) of yellow crystals from the methylated spirits solution.

E. The residual filtrate obtained after filtering off the third (7.0g.) crop of crystals. The methylated spirits in this filtrate was exchanged for benzene preparatory to chromatographing it.

The tarry material, described under A, was discarded. Batches B, C, D and E were individually chromatographed on alumina columns of suitable dimensions. Since all four chromatograms of B, C, D and E gave similar results, only one chromatogram (here B) need/

need be described in detail. Tables giving the weight and m.p. of each fraction obtained will be given for each chromatogram (see separate pages.).

Chromatogram I (see Table I and Fig. I.)

The mixed toluylfluoranthenes (11.7g.) were dissolved in the minimum volume of cold benzene and adsorbed onto a column of alumina (40 x 4.5 cms.). The column was developed with benzene-light petroleum (b.p. 60 - 80°) mixture (1:1 by vol.). When the adsorbed material had occupied the whole length of the column, the latter had the appearance shown in Fig. I (see separate page). Continued development was carried out until no more solid material came through in the filtrates. The filtrates so obtained were collected 100 c.c. at a time, and each 100 c.c's. reduced to small volume and allowed to evaporate to dryness in a crystallising dish at room temperature. In each case the m.p. and weight of the residue was determined, while the fluorescence in U.V. radiation of the filtrates, before concentration and evaporation to dryness, was also noted. The results are given in Table I. (separate page). As can be seen from Table I., the first 100 c.c. fraction possessed a blue fluorescence in U.V. radiation and by a mixed melting point determination (no depression of m.p.) of its residue with fluoranthene proved itself to contain unchanged fluoranthene. The fluorescences of successive fractions proved to be very much/

TABLE I.

(11.7 g. mixed ketones chromatographed)

	Wt. (g.)	m.p.	Colour - visible	Colour - U.V.
1	0.19	107 - 112°	Very pale yellow	Blue fluorescence
2	2.83	112 - 119°	Lemon yellow	Bluish-yellow
3	0.40	124 - 129°	" "	yellow
4	0.13	125 - 130°	" "	"
5	1.32	128 - 134°	" "	"
6	2.57	142 - 144°	" "	"
7	0.91	---	orange syrup	orange

Recovery from column = 9.43 g. (80%)

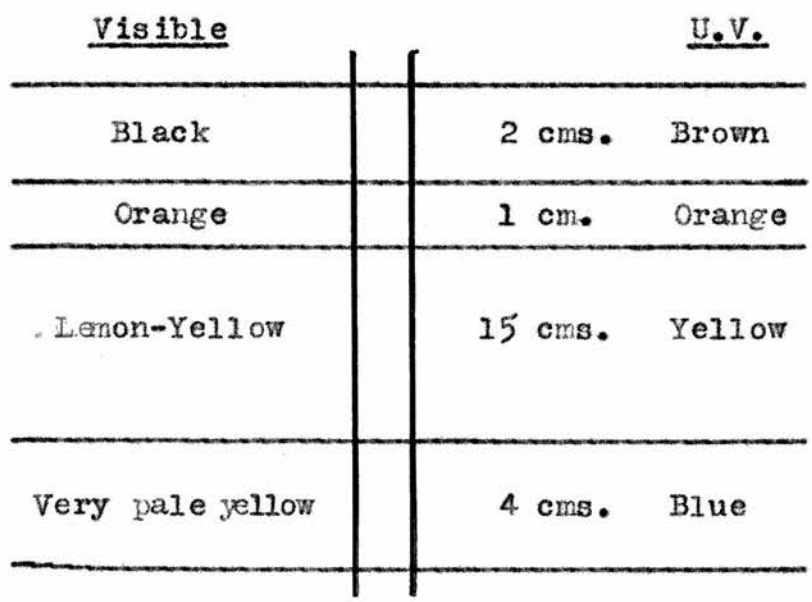


Fig. I.

TABLE II.

(4.15 g. mixed ketones chromatographed)

	Wt. (g)	m. p.	Colour
1	0.05	105 - 116°	Pale Yellow
2	0.62	125 - 128°	Lemon Yellow
3	0.72	127 - 131°	" "
4	0.43	135 - 139°	" "
5	0.43	139 - 143°	" "
6	0.27	143 - 146°	" "
7	0.21	146 - 148°	" "
8	0.22	147 - 150°	" "
9	0.13	146 - 150°	" "
10	0.36	146 - 150°	" "
11	0.01	---	Orange Syrup

Recovery from column = 3.45 g. (82%)

TABLE III.

(7.0 g. mixed ketones chromatographed)

	Wt. (g)	m. p.	Colour
1	0.10	103 - 114°	Pale Yellow
2	0.19	117 - 120°	Lemon Yellow
3	0.65	118 - 121°	" "
4	0.65	130 - 133°	" "
5	0.51	135 - 138°	" "
6	0.52	142 - 144°	" "
7	0.34	143 - 145°	" "
8	0.24	146 - 149°	" "
9	0.37	147 - 150°	" "
10	0.41	148 - 151°	" "
11	0.36	148 - 151°	
12	0.87	---	Orange Syrup

Recovery from column = 5.21 g. (74%)

TABLE IV.

(Residual filtrate chromatographed)

	Wt. (g)	m. p.	Colour
1	1.59	109 - 118°	Lemon Yellow
2	0.99	123 - 136°	" "
3	0.86	139 - 144°	" "
4	0.58	145 - 148°	" "
5	0.31	149 - 151°	" "
6	2.75	170 - 210°	Orange

TABLE V.

(showing three groups of fractions combined according to their melting points)

Material chromatographed	m.p. < 130° Wt. (g.)	m.p. 130-140° Wt. (g)	m.p. > 140° Wt. (g.)
11.70g.	3.36	1.32	2.57
4.15g.	1.34	0.43	1.62
7.00g.	0.84	1.16	2.24
Residual filtrate	1.59	0.99	1.75
Total Wt. (g.)	7.13	3.90	8.18

much alike and were of no diagnostic value in the separation of the isomeric ketones. The fluorescence in U.V. radiation of successive fractions taken off the remaining three columns is therefore omitted from Tables II, III and IV (separate page).

As is seen from the results intTable I., the m.p's., of the isomeric ketones lie somewhere between 100° and 150°C. Therefore the fractions obtained from all four chromatograms were divided into three batches; the first containing all fractions possessing m.pts. below 130°C., the second containing all fractions possessing m.pts. above 140°C., and the third containing all fractions with m.pts. lying between 130 and 140°C. The result is given in Table V. (separate page). Finally, the combined fractions, m.p. 130 - 140°C., (total 3.90g.) were chromatographed and yielded a further 1.77g. crude ketone m.p. < 130°C., and 0.98g. m.p. > 140°C.

The final result is therefore as follows -

crude ketone,	m.p. < 130°C.	8.9	grams.
" "	m.p. > 140°C.	9.2	"

This corresponds to a total of 18g. (38%) of semi-pure ketones.

Conclusion

A partial separation of the isomeric 4- and 11-O-toluylfluoranthenes has been achieved by chromatographic methods.

Purification of 4-o-Toluylfluoranthene

Crude ketone (1.0g.) of m.p. < 130°C. was

dissolved/

dissolved in the minimum volume of cold benzene and adsorbed onto a column of alumina (36 x 1.4 cms.). On development with a 1:1 mixture of benzene - petrol - ether (b.p. 60 - 80°) the column presented the appearance shown in Fig. II.

Visible		U.V.
Yellow	5 cms.	Yellow
Colorless	3 cms.	Colorless
Yellow	10 cms.	Yellow

Fig. II.

Development was continued with light petroleum - benzene mixture (described above) until the whole of the lower band had been washed down to the foot of the column. The column was then cut at the intermediate colorless zone, the lower band extracted and eluted with ethanol. Concentration of the eluate gave 4-o-Toluylfluoranthene, which crystallised, first from ethanol and then from benzene - light petroleum (b.p. 60 - 80°), in yellow plates, m.p. 115 - 116·5°C.

Analysis found C = 90.3%; H = 5.1%
$C_{24}H_{16}O$ requires C = 90.0%; H = 5.0%

Purification of 11-o-Toluylfluoranthene

This/

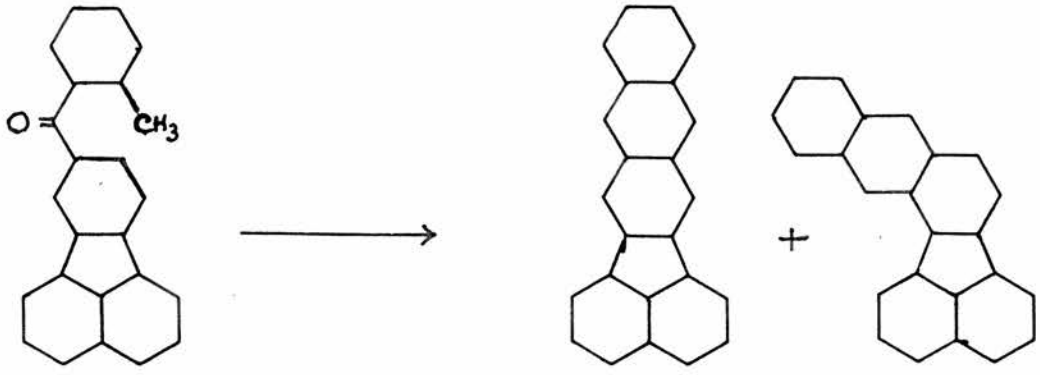
This was easily accomplished by fractional crystallisation. The crude ketone (1.0g.) m.p. > 140°C. was crystallised four times from benzene - light petroleum or ethanol until constant melting point was attained. This afforded finally 11-o-Toluylfluoranthene, yellow prisms, m.p. 148.5 - 150°C. (0.50g. pure ketone).

Analysis found C = 89.4%; H = 5.0%
$C_{24}H_{16}O$ requires C = 90.0%; H = 5.0%

Properties of 4- and 11-o-Toluylfluoranthenes

Both ketones give an orange coloration with conc. sulphuric acid. Both ketones in conc. sulphuric acid possess an orange - green coloration in reflected and an orange color in transmitted ultra-violet radiation.

ELBS PYROLYSIS OF 11-o-TOLUYLFLUORANTHENE



The ketone (1.30g.) was pyrolysed in an atmosphere of carbon dioxide at 440°C. for 20 min. in the manner as described by Fieser ("Organic Reactions", Vol. I, p. 129). During the reaction time the colour of the reactant/

reactant changed from yellow to dark red, and the colour change was accompanied by considerable charring. When no more water was liberated (as seen by the cessation of bubbling at the surface of the liquid) the product was cooled and thereafter set to an amorphous dark red solid. This was dissolved in the minimum volume of cold benzene and adsorbed onto a column of activated alumina (40 x 1.3 cms.). The column, developed with benzene, had the appearance as shown in Fig. IIIa (below).

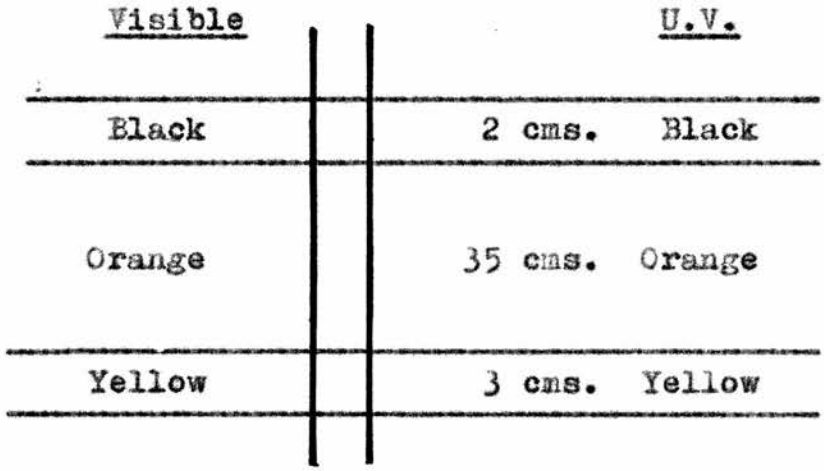


Fig. IIIa

The material on the column was analysed into its pure components as will now be described.

(1) The whole of the lower yellow band was washed through by continued development with benzene until the orange band reached the foot of the column. On evaporation of the filtrates comprising this yellow band, a negligible quantity of a yellow syrup was obtained which could not be induced to crystallise. The yellow syrup was therefore/

therefore discarded.

(2) Development with benzene was continued until the whole of the orange band had been washed through the column. Following the orange band came a buff coloured band with a very strong greenish-yellow fluorescence in U.V. radiation. This is described below in paragraph (3) (q.v.).

The filtrates comprising the orange band, on evaporation to dryness overnight, left an orange-red solid (0.46g.) with well-defined crystalline form and melting range approx. 190 - 220°. The solid was crystallised once from benzene to give an orange-red solid m.p. 220 - 227°C. Recrystallisation of this orange-red solid first from benzene and then glacial acetic acid furnished compact red prisms, m.p. 225.5 - 227.5°, which were analysed for Naphtho (2':3' - 10:11) - fluoranthene as follows -

	found	C = 95.4%; H = 4.7%
$C_{24}H_{14}$	requires	C = 95.3%; H = 4.7%

The mother liquors obtained from the crystallisations involved in the final purification of the hydrocarbon were combined in benzene solution and purified by passage through a short column of alumina (12 x 1.3cms.) to yield a further small quantity of pure hydrocarbon thus making a total yield of pure Naphtho (2':3' - 10:11) fluoranthene of 0.18g. (15%).

(3)/

(3) Immediately following on the orange band came the buff-coloured band which possessed a very strong greenish-yellow fluorescence in U.V. radiation. This band came through very slowly, appeared homogeneous, since no further zone formation could be observed at the top of the column, and was cut and worked up in two parts (a) the buff coloured band was eluted with acetone and the acetone exchanged for benzene (b) the black band at the top of the column was extracted with cold glacial acetic acid until the extracts no longer appeared yellow. The glacial acetic acid was exchanged for benzene, the benzene solution washed with water (twice), with sodium carbonate solution (once) and finally with water until free of alkali. The benzene solution was then dried over anhydrous calcium chloride and combined with the eluate from (a) to give a yellow solution with a bluish-green fluorescence in daylight. On concentration of this solution, a yellow solid separated out very easily which was then crystallised successively from a benzene - acetic acid mixture and from toluene. The yellow solid thus purified separated as a microcrystalline powder, m.p. 301 - 303°, and was analysed for Naphtho (2':3' - 11:12) fluoranthene as follows -

	found	C = 95.1%;	H = 4.8%
$C_{24}H_{14}$	requires	C = 95.3%;	H = 4.7%

Chromatographic/

Chromatographic purification of the mother liquors obtained from the crystallisations involved in the purification of the yellow hydrocarbon yielded a further small quantity of the latter making a total yield of 0.25g. (20%) of naphtho (2':3' - 11:12) fluoranthene.

Summary

The Elbs pyrolysis of 11-o-Toluylfluoranthene yields the two expected hydrocarbons

(i) Naphtho (2':3' - 10:11) fluoranthene m.p. 225.5 - 227.5°C. yield 0.18g. (15%)

(ii) Naphtho (2':3' - 11:12) fluoranthene m.p. 301 - 303°C. yield 0.25g. (20%)

Properties

(1) Naphtho (2':3' - 10:11) fluoranthene - compact orange - red prisms, soluble in common organic solvents. The solid fluoresces orange in U.V. radiation. With conc. H_2SO_4 the hydrocarbon gives a purple - blue coloration which turns dull crimson on standing.

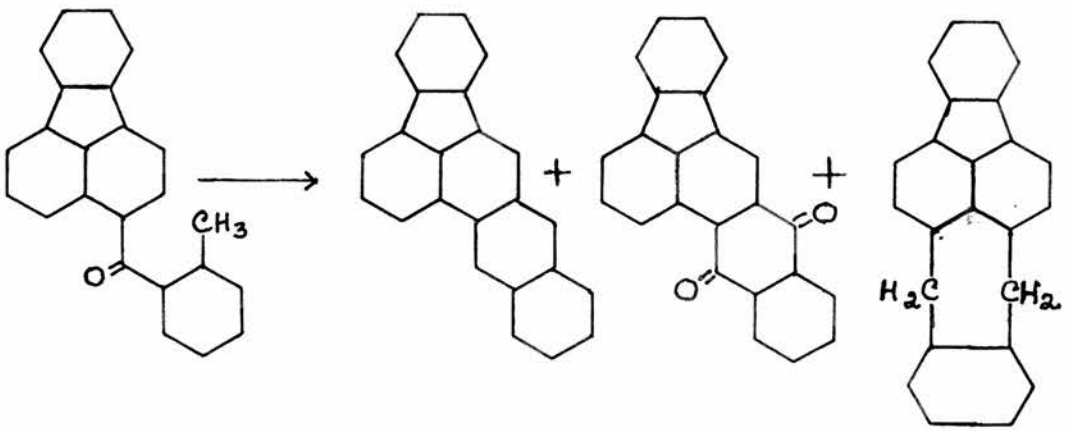
(2) Naphtho (2':3' - 11:12) fluoranthene - sublimes into yellow needles. which are fairly insoluble in benzene, glacial acetic acid and alcohol but soluble in toluene.

In dilute solution (C_6H_6) the hydrocarbon fluoresces bluish - green in daylight. The solid has a bright yellow fluorescence in U.V. radiation, On heating with conc. H_2SO_4 the hydrocarbon gives

a/

a pink colour changing successively to brown, green and brown.

ELBS PYROLYSIS OF 4-o-TOLUYLFLUORANTHENE



The ketone (1.00g.) was pyrolysed for 30 min. at 450° in an atmosphere of carbon dioxide in the same manner as described for the Elbs pyrolysis of 11-o-Toluylfluoranthene. During the heating the colour of the melt changed from yellow to orange, a change accompanied by some charring. The product was dissolved in the minimum volume of cold benzene and adsorbed onto a column of alumina (40 x 1.9 cms.). On development with light petroleum (b.p. 60 - 80°)-benzene (2:3 by vol.) the column had the appearance as shown in Fig. IIIb (see below)

(D)	Reddish - Black		2cms.	Brown
(C)	Orange - Pink		8cms.	Green
(B)	Yellow		10cms.	Yellow
(A)	Colorless		20cms.	Light-blue fluorescence

Fig. IIIb

Four distinct bands could be observed. The column was therefore analysed as follows -

(1) The whole of band (A) was washed through the column until the yellow band (B) had moved to the foot of the column. Evaporation to dryness of all the filtrates comprising band (A) yielded 0.30g. of pale yellow needles of melting range 80 - 150° which were dissolved in benzene, passed through a column of alumina, (25 x 1.3 cms.), and developed as above. When the whole column showed a blue fluorescence in U.V. radiation, it was cut and the lower half eluted with acetone. This acetone eluate on exchanging acetone for light petroleum (b.p. 60 - 80°) gave 4:5-o-Xylylenefluoranthene, colourless needles from petrol - ether, m.p. 208-210°C. Yield 30 mgm. (3%).

Analysis/

Analysis

	found	C= 94.3%;	H = 5.2%
$C_{24}H_{16}$	requires	C= 94.7%;	H = 5.3%

(2) Collection of the filtrates was begun as soon as the yellow band (B) came through the column. This was accompanied by the development of a characteristic, strong, blue fluorescence of the yellow filtrates. Collection of the filtrates was continued until the latter had lost their yellow colour and the blue fluorescence. The filtrates comprising band (B) were concentrated to low volume and, without any need for further purification, yielded Naphtho (2':3' - 3:4) fluoranthene, yellow needles, m.p. 229 - 230°. Yield 0.16g. (17%).

Analysis

	found	C = 94.9%;	H = 4.9%
$C_{24}H_{16}$	requires	C = 95.3%;	H = 4.7%

(3) Following immediately on the filtrates comprising band B came filtrates possessing a deep yellow colour and a strong greenish - yellow fluorescence in both daylight and U.V. radiation. Development was continued until the issueing filtrates had lost their greenish - yellow fluorescence. The filtrates thus collected contained the material comprising band (c) and were evaporated to dryness. A red sticky solid of wide melting range (170 - 250°) was thus obtained and an attempt to purify it chromatographically failed. The red material

was/

was therefore discarded.

(4) Continued development of the column brought an orange band down the column but the rate of travel down the column of this orange coloured material was very small, even when the developing solvent hitherto used (light petroleum - benzene, 2:3 by vol.) was replaced by benzene. The column, which showed no further zone formation, was therefore eluted with acetone and the latter exchanged for benzene. On concentration of this solution there crystallised Naphtho (2':3' - 3:4) fluoranthene - 1':4' - quinone, orange prisms, m.p. 250 - 253°, undepressed with the quinone prepared in an unambiguous synthesis by Campbell and Wang, (J. 1949, 1513). Yield 25 mgm. (2.5%).

Summary

The Albs pyrolysis of 4-o-Toluylfluoranthene yields -

(i) the expected hydrocarbon, Naphtho (2':3' - 3:4) fluoranthene m.p. 229 - 230°. yield 17%.

(ii) the corresponding quinone, Naphtho (2':3' - 3:4) - fluoranthene - 1':4' - quinone m.p. 250 - 253°. yield 2.5%.

(iii) 4:5 - o - xylylenefluoranthene m.p. 208 - 210°. yield 3%.

Properties

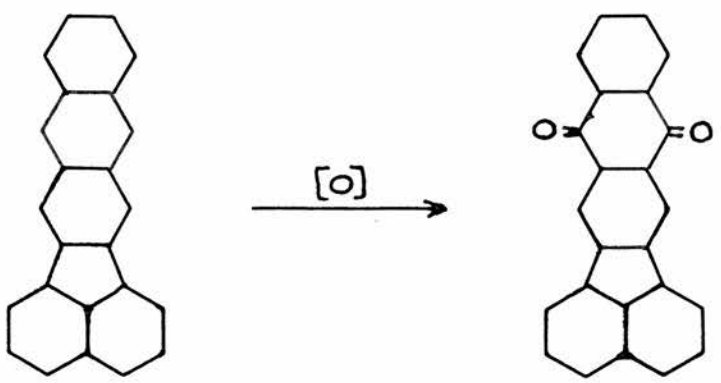
(1) Naphtho (2':3' - 3:4) fluoranthene - sublimes into yellow needles, easily soluble in benzene in which/

which it possesses a strong blue fluorescence in U.V. radiation. The solid shows an intense greenish - yellow fluorescence in U.V. radiation. With conc. H_2SO_4 it gives a lime - green coloration.

(2) 4:5-o-xylylenefluoranthene - colourless needles from petrol - ether, easily soluble in benzene. In U.V. radiation the hydrocarbon fluoresces a light blue colour in solution and pale greenish - yellow in the solid state.
With hot conc. H_2SO_4 the hydrocarbon gives a pink colouration changing to brown.

(3) Naphtho (2':3' - 3:4) fluoranthene - 1':4' - quinone - see oxidation product of Naphtho (2':3' - 3:4) fluoranthene (below).

OXIDATION OF NAPHTHO (2':3' - 11:12) FLUORANTHENE

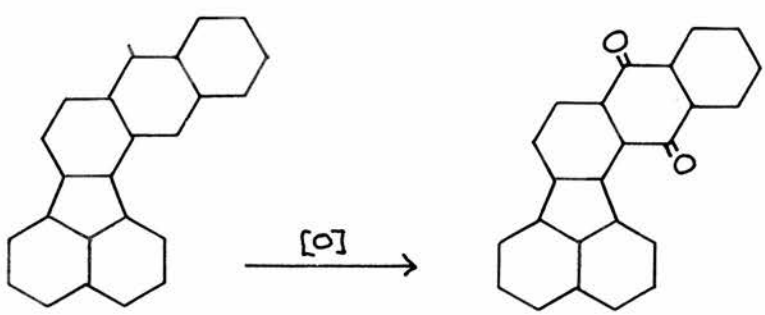


The hydrocarbon (50mgm.) was dissolved in boiling glacial acetic acid (10 c.c.) and a solution of AnalaR chromic anhydride (70 mgm.) in glacial acetic acid (1 c.c.)/

(1 c.c.) allowed to run into the solution dropwise at the boiling point. The solution was then boiled under reflux for 30 min. and on cooling deposited an orange-brown substance. This was washed with cold alkali, followed by boiling water, filtered and dried. The solid was dissolved in chlorobenzene and adsorbed onto a column of alumina (20 x 1.2 cms.). A homogeneous orange band passed down the column on development with chlorobenzene, leaving a brown residue at the top. The column was cut and the orange band eluted with chloroform. The extract, after exchange of chloroform for chlorobenzene, yielded Naphtho (2':3' - 11:12) fluoranthene - 1':4'-quinone, yellow needles, m.p. 338 - 340°, not depressed when mixed with the substance prepared by ring-closure of 11-benzoylfluoranthene -2'- carboxylic acid (Marks, Thesis, Edinburgh, 1951 and Campbell, Marks and Reid. J. 1950, 3466).

Yield 33 mgm. (60%).

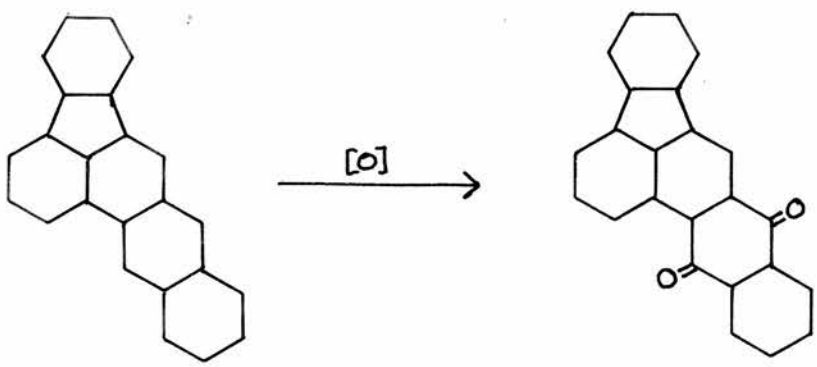
OXIDATION OF NAPHTHO (2':3' - 10:11) FLUORANTHENE



The hydrocarbon (70 mgm) dissolved in boiling glacial acetic acid (10 c.c.) was oxidised by a solution of AnalaR chromic anhydride (100 mgm.) in glacial acetic acid (1 c.c.) in the same manner as Naphtho (2':3' - 11:12) fluoranthene and the product purified also in the same manner as above to give Naphtho (2':3' - 10:11) fluoranthene - 1':4'-quinone, yellow needles (chlorobenzene), m.p. 316 - 318°, giving no depression/in m.p. with the quinone prepared by ring-closure of 11-benzoylfluoranthene -2'- carboxylic acid (Marks, loc. cit.)

Yield 34 mgm. (47%).

OXIDATION OF NAPHTHO (2':3' - 3:4) FLUORANTHENE



The hydrocarbon (50 mgm.) dissolved in glacial acetic acid (10 c.c.) was oxidised as above with AnalaR chromic anhydride (70 mgm.) in glacial acetic acid (1 c.c.)/

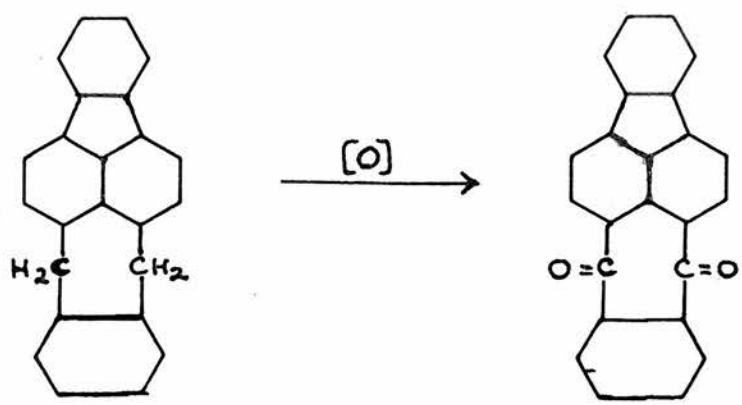
(1 c.c.) and the product purified in a similar manner as were the above mentioned quinones to yield Naphtho (2':3' - 3:4) fluoranthene - 1':4' - quinone, orange prisms, m.p. 250 - 253°. yield 44 mgm. (80%). No depression in m.p. was found when mixed melting points were done with -

(i) Campbell and Wang's quinone (J. 1949, 1513) m.p. 249 - 251°.

(ii) the quinone prepared by Marks (loc. cit.). m.p. 252 - 253°.

(iii) the quinone m.p. 250 - 253° isolated from the product of the Elbs Reaction on 4-o-Toluyl-fluoranthene as described above (c.f. also Campbell, Marks and Reid. J. 1950, 3466).

OXIDATION OF 4:5-o-XYLYLENEFLUORANTHENE



The hydrocarbon (30 mgm.) dissolved in boiling glacial acetic acid (10 c.c.) was oxidised with analar chromic anhydride (60 mgm.) in glacial acetic acid (1 c.c.) in the same manner as described above for the oxidation/

oxidation of the three isomeric naphthofluoranthenes. The resulting 4:5 - phthaloylfluoranthene crystallised from chlorobenzene in yellow - orange elongated prisms, m.p. 285 - 287°, undepressed when mixed with the diketone obtained on ring - closure of 4-benzoyl-fluoranthene - 2' - carboxylic acid (Marks, loc. cit., and Campbell, Marks and Reid, loc. cit.).

Properties

(1) Naphtho (2':3' - 11:12) fluoranthene - 1':4' - quinone - sublimes in yellow needles, sparingly soluble in benzene, fairly soluble in chlorobenzene. The quinone (solid) has a dull golden - yellow fluorescence in U.V. radiation. It gives a blue vat with sodium dithionite and a blue coloration with conc. sulphuric acid.

(2) Naphtho (2':3' - 10:11) fluoranthene - 1':4' - quinone - sublimes in yellow needles, soluble in chlorobenzene, which give a bright greenish - yellow fluorescence in U.V. radiation. It gives no vat with sodium dithionite but with conc. H_2SO_4 gives a purple coloration which turns crimson - red on standing.

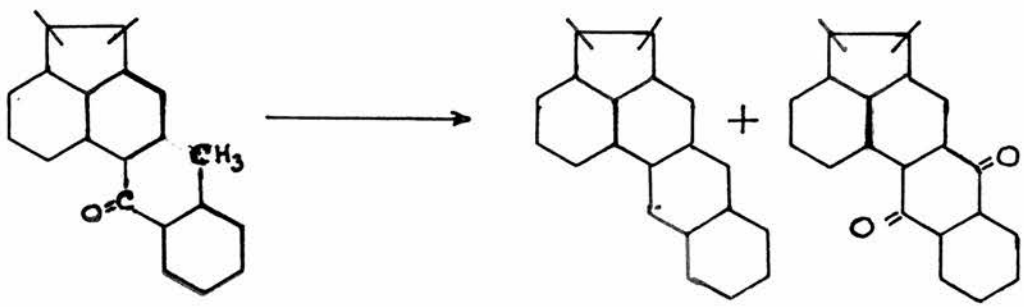
(3) Naphtho (2':3' - 3:4) fluoranthene - 1':4' - quinone - sublimes in yellow - orange prisms, soluble in chlorobenzene. It gives a blue vat with sodium dithionite and a green colouration with conc. H_2SO_4.

(4)/

(4) 4:5 --phthaloylfluoranthene — yellow-- orange elongated prisms, soluble in chlorobenzene. It gives no vat with alkaline dithionite but gives a pink colouration with conc. H_2SO_4.

ELBS PYROLYSIS OF 3-o-TOLUYLACENAPHTHENE

Geyer and Zuffanti. J.A.C.S., 1935, 57, 1787.



The ketone 1.0g.) was pyrolysed in an atmosphere of carbon dioxide at 410° for 40 min. The dark - red product was dissolved in the minimum volume of cold benzene and passed through a column of alumina (30 x 1.8 cms.). Development of the column gave three well defined bands; (A) a very pale yellow lower band with a strong blue fluorescence; (B) an intermediate orange band; (C) a top black band.

(1) Development was continued until the lower band (A) was completely washed through. Evaporation of the filtrates obtained caused a yellow material to come out of solution. Recrystallisation of this from glacial acetic acid and then from benzene gave/

gave Naphtho (2':3' - 2:3) acenaphthene, pale yellow plates, m.p. 188 - 190° (Lit. m.p. 192.5 - 193.5°). Yield 0.21g. (23%).

The hydrocarbon gives a pink colour in reflected, and a blue colour in transmitted daylight with conc. H_2SO_4. This solution has a strikingly beautiful pinkish - scarlet fluorescence in U.V. radiation.

(2) The orange band which came down the column fairly slowly was removed by cutting the column and eluting with acetone. The top black band of the column was discarded. The acetone of the eluate was exchanged for glacial acetic acid and concentration of the resulting solution yielded Naphtho (2':3' - 2:3) acenaphthene - 1':4' - quinone. The quinone sublimes in orange needles, m.p. 222 - 224°. Yield 9.0 mgm. (0.9%).

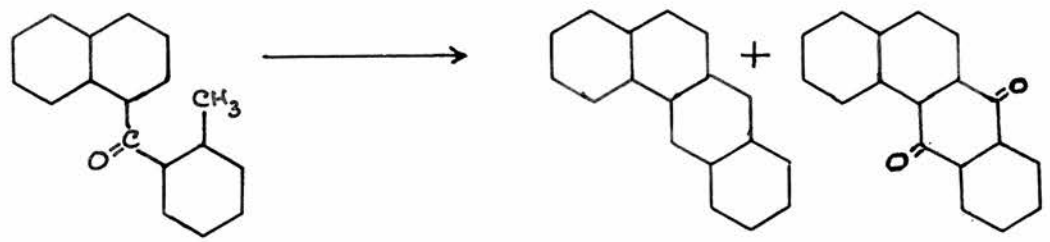
Analysis

	found	C = 83.5%; H = 4.1%
$C_{20}H_{12}O_2$	requires	C = 84.5%; H = 4.3%

The quinone gives a deep orange vat with sodium dithionite. Graebe (Ann. 1903, 327, 99) describes his Naphtho (2':3' - 2:3) acenaphthene - 1':4' - quinone as greenish - yellow crystals, m.p. 215 - 220°, which give a red vat with zinc dust and alkali.

With conc. sulphuric acid the quinone gives a dark-green colouration.

ELBS PYROLYSES OF 1-o-TOLUYLNAPHTHALENE



The pyrolyses were carried out as described by Fieser and Hershberg (J.A.C.S. 1937, 59, 2502) but the products were analysed by chromatographic methods in order to avoid the omission of any compounds which might be present in relatively small quantities.

Two pyrolyses were carried out: I. with zinc dust II. without zinc dust.

I. The ketone (5g.) in the presence of zinc dust (1.4g.) was pyrolysed in an atmosphere of carbon dioxide for 3 hours at 415°. The dark orange coloured product was dissolved in the minimum volume of cold benzene and passed through a column of alumina (50 x 2.3 cms.), Development was begun with benzene - light petroleum (b.p. 80 - 100) (1:2 by vol.), the column assuming the appearance shown, Fig. IV.

Visible	U.V.
Band A. Black (Tar)	6 cm. Black
" B. Greenish-Blue	4 cm. Green fluorescence
" C. Yellow	35 cm. Blue fluorescence
" D. Colorless	5 cm. Purple fluorescence

Fig. IV.

The issueing filtrates were taken off in small portions to begin with, since the desired hydrocarbon (1:8-o-xylylenenaphthalene) would, by analogy with 4:5-o-xylylenefluoranthene, be expected to come through early in the filtrates.

(1) The purple band (A) was washed through the column in two 50 c.c. portions. (i) 50 c.c. of the filtrates on concentration to low volume gave 50 mgm. of a white crystalline solid, m.p. 155 - 158°. This material gave a pink colouration with conc. sulphuric acid and a mixed m.p. determination with an authentic sample of 1:2 - benzanthracene showed no depression of melting point. (ii) The second 50 c.c. portion of the filtrates comprising the purple band A gave 70 mgm. colourless crystalline solid, m.p. 158 - 160°, undepressed with an authentic sample of 1:2 - benzanthracene. With conc. sulphuric acid this material also gave a pink colouration.

(2) The yellow band (B), which possessed a blue fluorescence in U.V. radiation, was almost entirely washed through and yielded 1.86g., 1:2 - benzanthracene, m.p. 160 - 161°. The crystals had, however, a very pale yellow colour presumably due to the crysogen, naphthacene, being present in very small amount. With conc. sulphuric acid, 1:2 - benzanthracene gives a cherry - red coloration changing to deep crimson on/

on standing.

(3) The greenish - yellow band (C) which hitherto moved down the column rather slowly was then developed with pure benzene and the issueing filtrates collected until they had lost their green fluorescence in U.V. radiation. The filtrates thus obtained yielded 20 mgm. of a red crystalline solid, m.p. 159 - 173°. Examination of this solid, however, showed that it consisted essentially of 1:2 - Benzanthraquinone and owed its characteristic greenish - yellow fluorescence in daylight to a small amount of a red substance, of which there was too little to purify. The solid was therefore discarded.

(4) The succeeding filtrates were golden - yellow in colour, displayed a dull orange fluorescence in U.V. radiation, and on evaporation deposited 0.38g. 1:2 - Benzanthraquinone, small cubic crystals, m.p. 168 - 169°, giving an orange - red vat with sodium dithionite and a green coloration with conc. sulphuric acid.

The solid fluoresces scarlet - red in U.V. radiation.

II. The experiment was repeated on a further 5g. ketone without zinc dust and using a higher pyrolysis temperature, 440°. The products were similar but were obtained in slightly different yields viz. 1.69g. 1:2 - benzanthracene and 0.68g. 1:2 - benzanthraquinone. A summary/

summary of the results of the two experiments is given in Table VI. (see below).

Table VI.

Conditions	1:2 - Benzanthracene	Quinone
Zinc present	1.98g. (43%)	0.38g. (7%)
Zinc absent	1.69g. (37%)	0.68g. (13%)

No 1:8-o-xylylenenaphthalene or derivative was detected in either experiment. (The products from the Elbs reaction were on the alumina columns for approx. 3 days - vide infra).

ATTEMPTED OXIDATION OF 1:2 - BENZANTHRACENE ON AN ALUMINA COLUMN

One gram of pure white 1:2 - benzanthracene, m.p. 160 - 161°, was adsorbed from benzene solution onto a column of alumina (36 x 1.2 cm.) which was subsequently developed with benzene until the adsorbed hydrocarbon had occupied half of the column. The column was allowed to stand in sunlight under exactly the same conditions as were involved in the chromatographic analysis of the product from the Elbs reaction on 1-o-toluylnaphthalene. (c.f. above). After 4 days the column appeared to have developed an orange coloration. The column was allowed to stand for 10 days in all, and the adsorbed material then washed through with benzene - light petroleum/

petroleum (1:1 by vol.). The filtrates yielded 0.95 g. 1:2 - benzanthracene. The column, when completely freed from 1:2 - benzanthracene, was then eluted with chloroform and the eluate on evaporation to dryness yielded a trace (5 mgm.) of orange material which could not be crystallised.

This substance, which could not be definitely identified as 1:2 benzanthraquinone, was formed in a mere 0.5% yield over a period of 10 days exposure to sunlight of 1:2 - benzanthracene adsorbed on alumina.

ISOLATION of 1:2 - BENZ - 9 - ANTHRONE

An attempt was made to isolate 1:2 - benz - 9 - anthrone from the product of the Elbs Reaction on 1 - o - toluylnaphthalene.

The Elbs pyrolysis of 1 - o - toluylnaphthalene was carried out on 2.5 g. ketone as described earlier in the experimental section.

The crude product from the reaction was distilled in high vacuum (180° / 0.5 mm.) to give an orange crystalline solid (1.2 g.) which was dissolved in the minimum volume of boiling acetone - ethanol (1:1 by vol.). A boiling solution of potassium hydroxide (2 g.) in ethanol - water (10:1 by vol.) (20 c.c.) was added to the solution whereupon the solution turned a deep yellow colour. The solution was boiled for 10 minutes and then drowned in water (200 c.c.)/

(200 c.c.). The mixture was extracted with benzene (3 x 200 c.c.)until the aqueous layer was free from organic alkali - insoluble material and the resulting yellow alkaline solution, which displayed a strong greenish - yellow fluorescence in U.V. radiation, was acidified (conc. hydrochloric acid). The fine yellow precipitate which came out of solution was extracted from the acidic solution with benzene (50 c.c.). The benzene extract, washed with alkali and then with water, was dried (anhydrous sodium sulphate) and distilled to low volume. A yellow crystalline solid came out of solution on cooling and was recrystallised from benzene, yellow plates,

m.p. 310 - 313°

The substance was analysed for 1:2 - benz - 9 - anthrone ($C_{18}H_{12}O$) as follows -

Found C = 89.6%; H = 4.6%

$C_{18}H_{12}O$ requires C = 88.5%; H = 5.0%

This compound gave a positive answer to the test described by Liebermann (Ann. 1882, 212, 6) for anthrone (anthranol). A small quantity of the substance was treated with fuming nitric acid. Addition of water produced a precipitate which was filtered, washed free of acid with water, and dried. The residue dissolved in alcohol to give an orange colouration which changed to violet on addition of a drop of alkali.

Likewise/

Likewise a solution of the compound in conc. sulphuric acid gave a violet colouration on treatment with a small drop of fuming nitric acid.

By carrying out the Elbs pyrolysis on 3 - o - toluylacenaphthene and working up the product in a similar manner as described above an alkaline solution was obtained which possessed a yellow colour and displayed a strong greenish-yellow fluorescence in U.V. radiation. Acidification decolourised this solution, quenched the fluorescence and precipitated a yellowish-brown solid from solution. This solid had an indefinite m.p. and could not be purified on account of the smallness of the amount of material. The solid was partially soluble in cold alkali, completely so in warm alkali giving a solution behaving in the same manner as did that from which the solid was precipitated.

An alkaline solution obtained from the pyrolysis product of 4 - o - toluylfluoranthene behaved in a similar fashion to the solution described above, obtained from the Elbs pyrolysis product of 3 - o - toluylacenaphthene. No solid however was obtained on acidification of the alkaline solution.

SECTION B

This section is concerned with exploratory investigations on the possibility of finding a suitable route for the synthesis of 4:12- disubstituted fluoranthenes from fluorene.

PREPARATION OF 2-BROMOFLUORENE

Thurston and Shriner. J.A.C.S., 1935, 57, 2164.

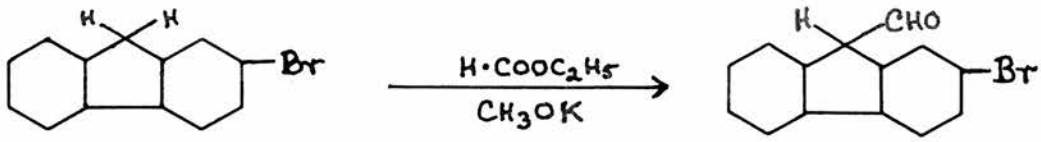
Dry bromine (120g.) dissolved in cold benzene (200 c.c.) was added during the course of 3 hours to a boiling solution of fluorene (125g.) and iodine (1g.) in benzene (350 c.c.). The solution was boiled under reflux for a further 1 hour, cooled, washed with water, sodium bicarbonate solution and water and dried over anhydrous sodium sulphate. After removal of benzene by distillation, the product was fractionated by high vacuum distillation, the 2-bromofluorene distilling at 130 - 140° (0.1 - 0.2 mm.) with a m.p. 109 - 112°. Crystallisation once from ethanol yielded pure 2-bromofluorene, colourless plates m.p. 111 - 113° (Lit. m.p. 113). Yield 71.5g. (39%).

PREPARATION/

PREPARATION OF 2-BROMOFLUORENE-9-ALDOXIME

The 2-bromofluorene-9-aldoxime was prepared directly without isolation of the 2-bromofluorene-9-aldehyde. Formylation of 2-bromofluorene was carried out by essentially the same procedure as described by Von and Wagner (J. Org. Chem., 1944, 9, 162) for the formylation of fluorene.

(1) 2-Bromofluorene-9-Aldehyde

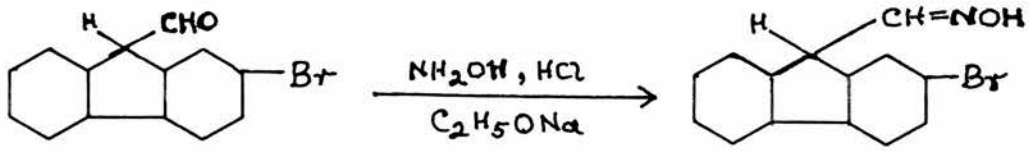


Potassium methoxide (7.2g. freshly prepared from 4.0g. potassium) was transferred to a solution of 2-bromofluorene (2.5g.) and ethyl formate (7.6g.) dissolved in anhydrous ether (150 c.c.) and the mixture boiled under reflux for 6 hours. The solution, which developed a golden - yellow colour, was then cooled, extracted with water (150 c.c.) and the aqueous extract washed with ether (3 x 20 c.c. portions). The aqueous extract on acidification with dilute sulphuric acid precipitated a yellow oil which was extracted with ether. The ether layer was washed once with dilute sodium bicarbonate solution, then with water and dried over anhydrous magnesium sulphate.

An/

An attempt to isolate the 2-bromofluorene-9-aldehyde from the ether extract by removal of the ether did not succeed. A yellow oil was obtained which would not crystallise - this oil was utilised directly for the preparation of 2-bromofluorene-9-aldoxime.

(2) 2-Bromofluorene-9-Aldoxime



The yellow oil obtained from the formylation of 2-bromofluorene (see above), consisting of impure 2-bromofluorene-9-aldehyde, was dissolved in ethanol (200 c.c.). Hydroxylamine hydrochloride (6.4g.) dissolved in water (25 c.c.) was set in reaction with sodium ethoxide (6.3g. prepared from 2.1g. sodium) in ethanol (50 c.c.) and without regard for the sodium chloride which had separated out, the mixture was added to the above solution of 2-bromofluorene-9-aldehyde in ethanol. The resulting mixture was boiled under reflux for a total time of 20 hours. During this period white precipitates which crystallised out from time to time were filtered off and boiling of the filtrate thereafter continued.

The volume of the solution was finally reduced to 50 c,c, whereupon a further quantity of white crystalline

material/

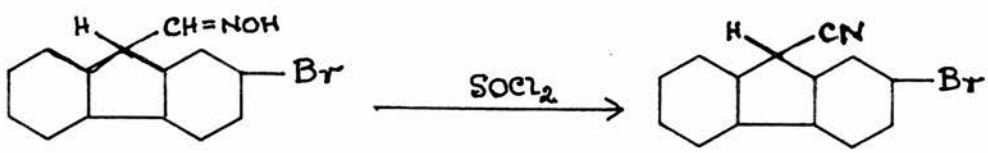
material came out of solution. This was combined with the white precipitates which had separated out of solution during the boiling under reflux and after washing with hot water, the combined precipitates were crystallised from ethanol. The 2-bromofluorene-9-aldoxime thus obtained, crystallised in small colourless needles turning-reddish brown in colour below the melting point and melting to a clear reddish - brown liquid at 234 - 236°.

Yield - 9.7g. (33% over 2 stages).

Analysis

Found	$C_{14}H_{10}O$ Br N requires
C = 57.8%	C = 58.3%
H = 3.8%	H = ,3.5%
Br= 28.5%	Br = 27.7%
N = 4.7%	N = 5.0%

PREPARATION OF 2-BROMO-9-CYANOFLUORENE



A solution of 2-bromofluorene-9-aldoxime (9.5g.) dissolved in thionyl chloride was boiled under reflux for 3 hours, at the end of which time the excess thionyl chloride was removed under reduced pressure on a water-bath. Benzene (25 c.c.) was added to the residue and subsequently removed at reduced pressure. The residue

was/

was allowed to stand for 30 minutes in dilute sodium carbonate solution in order to remove traces of thionyl chloride and its hydrolysis products, and then filtered and dried. The resulting greyish - white solid was crystallised once from chlorobenzene thus affording 2-bromo-9-cyanofluorene, colourless needles, m.p. 264-267°.

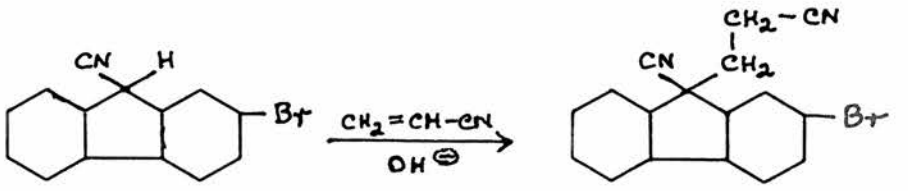
Yield - 7.4g. (82%).

The compound was analysed for bromine and nitrogen as follows -

	found	Br = 30.4%;	N = 6.2%
$C_{14}H_8$ Br N	requires	Br = 29.6%;	N = 5.2%

ATTEMPTED MICHAEL ADDITION OF 2-BROMO-9-CYANOFLUORENE TO ACRYLONITRILE IN THE PRESENCE OF TRIMETHYLBENZYLAMMONIUM HYDROXIDE

The nitrogen base used as catalyst in the attempted addition of 2-bromo-9-cyanofluorene to acrylonitrile consisted of a 20% solution of trimethylbenzylammonium hydroxide prepared by interaction of equivalent amounts of trimethylbenzylammonium chloride and potassium hydroxide in methanol.



(1) Acrylonitrile (0.1g. - 0.125 c.c.) was added to a suspension of 2-bromo-9-cyanofluorene (0.5g.) in dioxan/

dioxan (3 c.c.) containing the above mentioned catalyst (0.1 c.c.). The temperature of the mixture was raised to, and thereafter maintained at, 40° for 90 minutes after which time the solution was poured into water (25 c.c.). The white granular solid which came out of solution, was filtered and dried, m.p. 262 - 265°, undepressed with authentic 2-bromo-9-cyanofluorene (mixed m.p. 263 - 267°).

The substance was therefore unchanged 2-bromo-9-cyanofluorene, recovery of which was nearly quantitative.

(2) The same procedure was again carried out in a second attempt to add 2-bromo-9-cyanofluorene to acoylonitrile with this difference however that after addition of all the reactants, the temperature was slowly raised over a period of 30 minutes to that of boiling dioxan, and boiling thereafter maintained for a further 30 minutes. The resulting dark - brown liquid was then poured into water (25 c.c.) whereupon a dirty brown solid came out of solution. This solid was filtered off, dried, and boiled with ether (100 c.c.) in order to remove tarry material adhering to the solid. On evaporating the ether solution to low volume (20 c.c.) unchanged 2-bromo-9-cyanofluorene came out of solution, m.p. 261 - 265°.

mixed m.p. with 2-bromo-9-cyanofluorene — 262-266°.

The quantity of recovered starting material amounted to only 0.1g. (20%).

(3)/

(3) A third attempt was carried out using the same procedure as described in (2) above. When the temperature of the solution had been thus raised to the boiling point a solution of 40% aqueous sodium hydroxide (2.5 c.c.) was added and the resulting solution boiled under reflux for 60 minutes. The solution, on pouring into water (30 c.c.), deposited an intractable sticky solid, insoluble in water. This was filtered off and the filtrates acidified (dilute sulphuric acid).

No acid came out of solution.

(4) Acrylonitrile (0.10 g. - 0.125 c.c.) was added to a suspension of 2 - bromo - 9 - cyanofluorene (0.5 g.) in 2 - ethoxyethanol (3 c.c.) containing potassium hydroxide (11.20 g. / litre solution). After standing for thirty minutes the solution was raised to the boiling point whereupon the 2 - bromo - 9 - cyanofluorene dissolved completely with production of a green colouration. The solution was boiled for two minutes, cooled, and poured into water (100 c.c.). A brown oil came out of solution and set to a resinous solid. This solid could not be induced to crystallise from any solvent but invariably settled out from solution as brown oil which eventually set to an amorphous brown solid. Melting range 110° (with softening) - 210°

Yield 0.40 g. (crude).

The/

The amorphous solid thus obtained was boiled under reflux for 30 minutes in ethanol (5 c.c.) containing water (2 c.c.) and potassium hydroxide (1.50 g.). The solid dissolved readily on boiling, and the resulting solution, after cooling, was poured into water (30 c.c.). Acidification of the resulting solution caused a white solid to come out of solution. This solid, crystallised twice from a benzene - methanol (3:1 by vol.) mixture, was obtained pure in the form of white needles

m.p. 188 - 190°

This acid was analysed for β-2-bromo - fluorene - 9 - propionic acid ($C_{16}H_{13}O_2Br$) as follows

Found C = 55.4%; H = 3.6%; Br = 25.2%

$C_{16}H_{13}O_2Br$ requires C = 60.6%; H = 4.1%; Br = 25.2%

SECTION C.

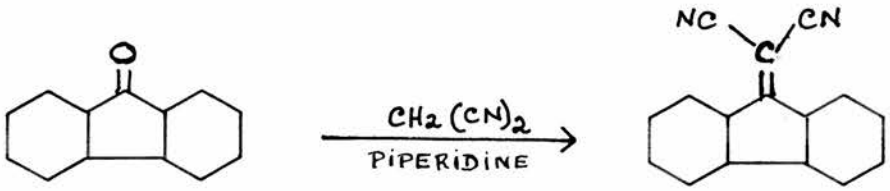
I (a)

ATTEMPTED SYNTHESIS OF

2:13 - BENZFLUORANTHENE FROM FLUORENONE

CONDENSATION of FLUORENONE with MALONITRILE

Schenck and Finken. Ann., 1928, 462, 267.



A solution of malonitrile (6.6g.) in absolute ethanol (100 c.c.) was added to a solution of fluorenone (18g.) and piperidine (0.5 c.c.), also in absolute ethanol (800 c.c.). The solution turned red at once and within five minutes a precipitate consisting of fine red needles began to separate out from the solution. The solution was allowed to stand overnight and the resulting diphenylene-dicyano-ethylene filtered, washed with alcohol and dried.

m.p. 211-212° (Lit. m.p. 213°)
Yield 20.6g. (91%)

HYDROLYSIS of DIPHENYLENE-DICYANO-ETHYLENE

(1) A mixture of diphenylene-dicyano-ethylene (5.0g.) suspended in mixture of water (50 c.c.) and ethanol (50 c.c.) containing potassium hydroxide (50g.) was boiled under reflux for 24 hours. The diphenylene-dicyano-ethylene slowly dissolved. The brown alkaline solution was poured into water (300 c.c.), the resulting yellow precipitate/

precipitate filtered and the filtrate acidified (dilute hydrochloric acid). No precipitate was obtained. The yellow precipitate previously filtered from the alkaline solution was found to be impure fluorenone.

(2) A mixture of diphenylene-dicyano-ethylene (1.0g.) and 50 c.c. of a water-sulphuric acid-glacial acetic acid mixture (1:1:1 by weight) was boiled under reflux for 48 hours, at the end of which time the mixture was poured into excess water (200 c.c.). The resulting precipitate, red needles, m.p. 212°, proved to be unchanged diphenylene-dicyano-ethylene.

Mixed m.p. with diphenylene-dicyano-ethylene 211-212°. The diphenylene-dicyano-ethylene was recovered almost quantitatively (0.97g. - 97%).

(3) The diphenylene-dicyano-ethylene was finally hydrolysed by a mixture of hydriodic acid (S.G. 1.96) and glacial acetic acid (1:1 by vol.). Diphenylene-dicyano-ethylene (7.4g.) was added to a solution of hydriodic acid (110 c.c.) in glacial acetic acid (110 c.c.) and the mixture boiled under reflux for 12 hours. At the end of this period the diphenylene-dicyano-ethylene had completely dissolved, and the solution, on pouring into excess sulphurous acid, deposited a white crystalline precipitate, which on crystallising from boiling water, yielded 4.7g. of colourless needles, m.p. 132-133°.

Analysis./

Analysis.

	Found	C = 80.2% ; H = 5.9%
$C_{16}H_{10}O_4$	requires	C = 72.2% ; H = 3.8%

The compound is therefore not the expected 9-fluorenylidene-malonic acid ($C_{16}H_{10}O_4$).

The low oxygen content found for the acid suggested that decarboxylation involving one of the carboxyl groups had taken place.

Further, the absence of the yellow colour characteristic of compounds possessing the fulvene type of structure at once indicated that a double bond was no longer present at the "9-position" of the fluorene.

The analysis figures found are in good agreement with those calculated for fluorene-9-acetic acid ($C_{15}H_{12}O_2$).

	Found	C = 80.2 ; H = 5.9%
Calculated for $C_{15}H_{12}O_2$		C = 80.4% ; H = 5.4%

Wislicenus and Eble (Ber., 1917, 50, 250) described their fluorene-9- acetic acid as occurring in the form of flat colourless needles, m.p. 138-139°. The related diphenylene-acrylic acid described by Wislicenus and Weitemeyer (Ber., 1921, 54, 978) is, as expected of compounds possessing the fulvene type of structure, yellow, m.p. 222-223°.

The acid obtained gives with conc. sulphuric acid a dirty green colouration which changes to a deep green on standing. These observations are in exact agreement with the properties of fluorene-9-acetic acid (Wislicenus and Eble. loc. cit.).

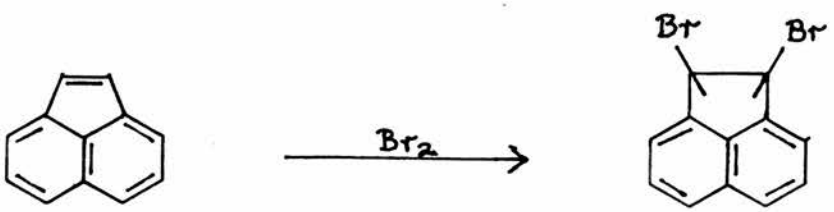
SECTION C.

I (b).

ATTEMPTED SYNTHESIS OF 2:13 - BENZFLUORANTHENE FROM ACENAPHTHYLENE

PREPARATION of 7:8 - DIBROMOACENAPHTHENE

Blumenthal. Ber., 1874, 7, 1093.



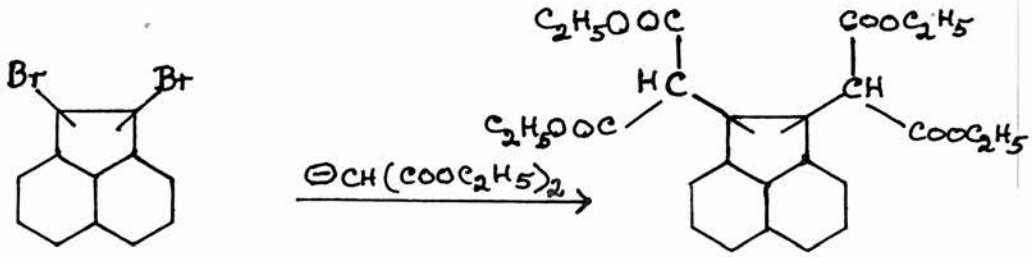
Bromine (2.10g. - 0.67 c.c.) dissolved in anhydrous ether (2 c.c.) was added dropwise to a solution of acenaphthylene (2.0g.) also in anhydrous ether (8 c.c.). The yellow colour of the solution of acenaphthylene in ether disappeared and on allowing the ether to evaporate at room temperature an orange coloured, crystalline solid was obtained. This was dissolved in light petroleum/

petroleum (b.p. 40-60°) from which 7:8 - dibromoacenaphthene crystallised in white needles.

m.p.	120-121° (Lit. m.p. 121-123°)
yield	2.98g. (73%)

The 7:8 dibromoacenaphthene readily decomposes within a few hours after preparation to give an orange sticky solid accompanied by hydrogen bromide fumes.

ATTEMPTED CONDENSATIONS of 7:8 - DIBROMOACENAPHTHENE with SODIO-MALONIC ESTER.



(1) A solution of 7:8-dibromacenaphthene (1.50g.) in anhydrous benzene (5 c.c.) was added to a solution of sodio-malonic ester in absolute ethanol, prepared from sodium (0.33g.), malonic ester (2.31g.) and absolute ethanol (20 c.c.). The solution was sealed off from the atmosphere and allowed to stand at room temperature for 72 hours.

No precipitation of sodium bromide occurred. The solution was then boiled under reflux for 60 minutes during which time the solution developed a yellow colour which changed rapidly to a deep orange.

The/

The solvents were removed under reduced pressure on a water bath and 40% aqueous potassium hydroxide (10 c.c.) added to effect hydrolysis. The solution was warmed on a steam-bath for 30 minutes, then boiled under reflux for a further 60 minutes. On heating the alkaline solution immediately after addition of the potassium hydroxide solution the colour changed to a dark brown and a considerable quantity of black tarry material came out of the solution as an oil on the surface of the boiling liquid.

The liquid was thoroughly cooled, filtered through a sinter glass funnel and the dark brown filtrate acidified (conc. hydrochloric acid). The acidified solution turned turbid in appearance but no solid separated out.

The residue on the sinter glass filter funnel was a sticky, brownish-black plastic-like material.

Blumenthal (loc. cit.) isolated 7-bromoacenaphthylene by boiling 7:8 - dibromoacenaphthene in ethanol. It seems therefore that the 7:8 - dibromoacenaphthene failed to condense with the sodio-malonic ester and on boiling the alcoholic solution before addition of alkali, the 7:8-dibromoacenaphthene split out hydrogen bromide with simultaneous formation of 7-bromoacenaphthylene which subsequently polymerised in the presence of the alkali.

(2)/

(2) A second attempt was made under different conditions to bring about the condensation of 7:8 - dibromoacenaphthene with Sodio-malonic ester. A solution of 7:8 - dibromoacenaphthene (1.0g.) dissolved in anhydrous benzene (3 c.c.) was added to an alcoholic solution of Sodio-malonic ester prepared from sodium (0.22g.) and malonic ester (1.54g.) in absolute ethanol (12 c.c.)

The solution, sealed off from the atmosphere, was allowed to stand at room temperature for 14 days, after which period it was worked up as described above. Exactly the same results were obtained, no acid being obtained.

The synthesis was therefore abandoned. The failure of the 7:8 - dibromoacenaphthene and Sodio-malonic ester to condense and the phenomena observed are examined in the discussion.

SECTION C.

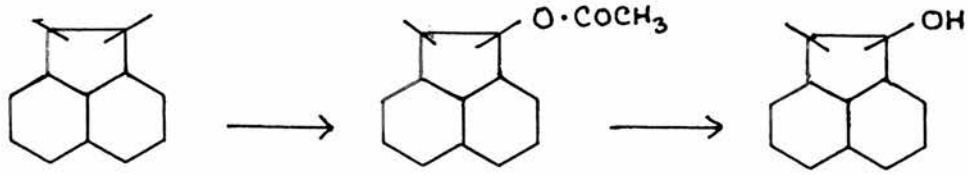
I (c)

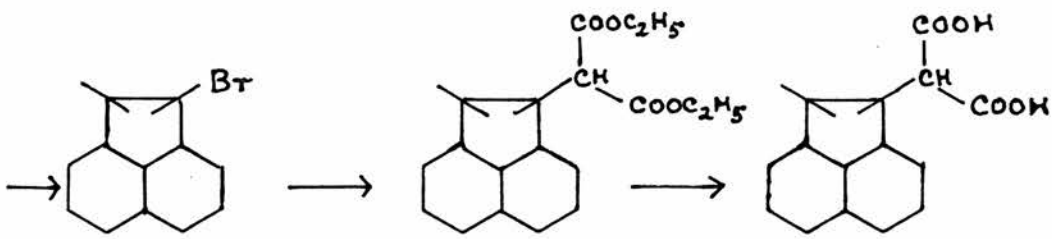
ATTEMPTED SYNTHESIS OF 2:13 - BENZFLUORANTHENE FROM 4:5 - METHYLENEPHENANTHRENE AND MALEIC ANHYDRIDE.

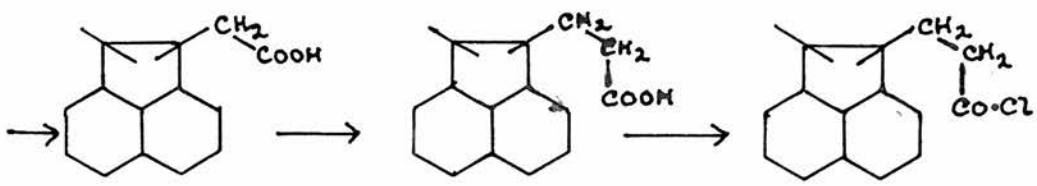
The hydrocarbon 4:5 - methylenephenanthrene was prepared by synthesis from acenaphthene as described by Bachmann and Sheehan (J.A.C.S., 1941, 63, 204) according to the scheme on the following page.

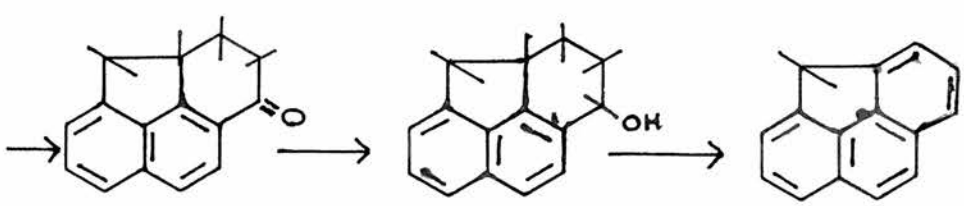
The experimental procedure leading to the preparation/

SYNTHESIS of 4:5-METHYLENEPHENANTHRENE from ACENAPHTHENE (According to Bachmann and Sheehan. J.A.C.S., 1941, 63, 204)









preparation of 4:5 - methylenephenanthrene has already been described in detail by Bachmann and Sheehan (loc. cit.); only a short outline of the synthesis need, therefore, be described here.

PREPARATION OF 7-ACENAPHTHENYL ACETATE

Organic Syntheses. Vol. 21, p.1.

The acetate was prepared from acenaphthene (154g.) dissolved in glacial acetic acid (1100 c.c.) by oxidation with red lead (820g.). Purification was effected by distillation in vacuo (165°/5 mm.) when the 7-acenaphthenyl acetate was obtained as a mobile yellow oil.

Yield 154 g. (73%)

HYDROLYSIS of 7-ACENAPHTHENYL ACETATE

The acetate obtained above (154g.) was hydrolysed by boiling under reflux with 10% sodium hydroxide. The 7-acenaphthenol was crystallised from benzene in colourless needles.

m.p. 145-146° (Lit. m.p. 144.5-145.5°)
yield 120.5g. (98%)

PREPARATION of 7-BROMOACENAPHTHENE

Bachmann and Sheehan. J.A.C.S. 1941, 63, 204.

A solution of 7-acenaphthenol (10g.) in anhydrous ether (80 c.c.) was treated with phospherous tribromide (2.05 c.c.). After washing the ether extract and removal of the ether at reduced pressure a yellow solid was obtained. On digestion of this solid with light petroleum (b.p. 40-60°) the 7-bromoacenaphthene was obtained as colourless leaflets.

m.p./

m.p. 70-71° (Lit. m.p. 70.5-71.5°)

7-Bromoacenaphthene decomposes on standing in air with liberation of hydrogen bromide and development of a yellow colour due to acenaphthylene. The 7-bromoacenaphthene thus prepared was condensed at once with Sodio-malonic ester as described immediately below.

PREPARATION of 7-ACENAPHTHENYLMALONIC ACID.

The 7-bromoacenaphthene prepared as described above was dissolved in anhydrous benzene (40 c.c.) and added to a solution of sodium (3.53g.) and malonic ester (17.8 c.c.) dissolved in absolute ethanol (125 c.c.).

The resulting ester was hydrolsed with 40% aqueous potassium hydroxide (60 c.c.). The 7-acenaphthenyl-malonic acid crystallised from benzene as colourless needles.

m.p. 178-180° (Lit. m.p. 174-175°)
yield (from 157.5g. acenaphthenol) = 194g. (82%).

7-ACENAPHTHENYLACETIC ACID.

The 7-acenaphthenylmalonic acid (194g.) was heated at 190° with vigorous stirring until liberation of carbon dioxide ceased. The 7-acenaphthylacetic acid crystallised from light petroleum - acetone (5:1 by Vol.) as very pale yellow plates.

m.p. 114-115° (Lit. m.p. 115-116°)
yield 134g. (83%).

β-7-ACENAPHTHENYLPROPIONIC ACID/

β-7-ACENAPHTHENYLPROPIONIC ACID

The required β-7-acenaphthenylpropionic acid was prepared from the lower homologue by the Arndt-Eistert reaction.

The acid chloride of 7-acenaphthenylacetic acid was prepared by the action of thionyl chloride (4.4 c.c.) on a suspension of the acid (10g.) in anhydrous ether (50 c.c.) containing a few drops of pyridine.

The acid chloride was thus prepared, dissolved in anhydrous ether (50 c.c.), was added to a solution of diazomethane in ether (300 c.c.) prepared from N-nitroso-N-methylurea (30g.). The resulting diazoketone was treated with two 0.5g. portions of silver oxide in anhydrous methanol (50 c.c.).

Hydrolysis of the methyl ester thus formed was accomplished with 40% Sodium hydroxide solution (10 c.c.). Acidification gave the β-7-acenaphthenylpropionic acid which was crystallised from light petroleum (b.p. 60-80°) - acetone (5:1 by vol.) by allowing the solvents to evaporate at room temperature.

The acid crystallised in the form of pale yellow plates.

m.p. 101 - 104° (Lit. m.p. 108.5 - 109.5°)

A mixed melting point with 7-acenaphthenylacetic acid gave a melting range 65 - 100°.

Yield (from 134g. of 7-acenaphthenylacetic acid) = 87g. (61%)

RING-CLOSURE of β-7-ACENAPHTHENYLPROPIONIC ACID./

RING-CLOSURE of β-7-ACENAPHTHENYLPROPIONIC ACID

β-7-Acenaphthenylpropionic acid chloride was prepared by the action of phosphorous pentachloride (13.10g.) on the acid (10g.) in anhydrous benzene (30 c.c.). Ring-closure was effected by addition of stannic chloride (10 c.c.) to the solution of the acid chloride in benzene. The resulting ketone, 1-keto-1:2:3:4-tetrahydro-4:5-methylenephenanthrene, crystallised from light petroleum (b.p. 60 - 80°) - benzene (4:1 by vol.) as almost colourless prisms.

m.p. 120-121° (Lit. m.p. 124.5-125.5°)
Yield (from 87g. acid) = 66g. (83%)

The ketone gives a light orange colouration with conc. sulphuric acid.

4:5-METHYLENEPHENANTHRENE.

The abovementioned ketone was reduced by the Meerwein-Ponndorf method to 1-hydroxy-1:2:3:4-tetrahydro-4:5-methylenephenanthrene which, without isolation, was dehydrogenated to the fully aromatic hydrocarbon.

The ketone (10g.) was dissolved in 250 c.c. of a molar solution of aluminium isopropoxide in anhydrous isopropyl alcohol and solvent slowly distilled from the solution until acetone ceased to come over in the distillates. After decomposition of the aluminium complex with sulphuric acid the resulting alcohol was heated at 300° for 60 minutes in the presence of 20% palladium-charcoal catalyst (2.0g.). The product was extracted/

extracted with chloroform and after removal of solvent the hydrocarbon was distilled in vacuo (165°/0.5 m.m.).

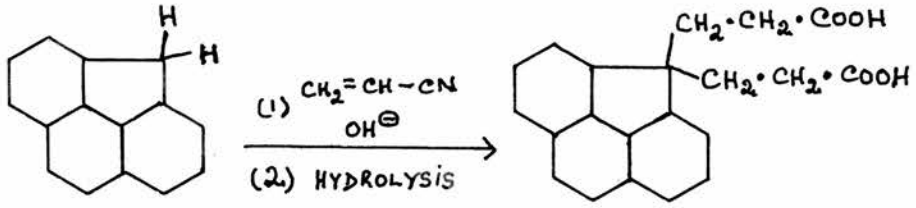
The 4:5-methylenephenanthrene crystallised from ethanol in large colourless plates.

m.p. 115-116° (Lit. m.p. 115-116°)
yield (from 66g. ketone) = 32.8g. (54%)

The hydrocarbon, suspended in conc. sulphuric acid, gives, on addition of a drop of benzal chloride, a cobalt blue colouration changing to a deep prussian blue.

Overall yield of 4:5-methylenephenanthrene from 157.5g. of acenaphthenol = 32.8g. (19%).

MICHAEL ADDITION of 4:5-METHYLENEPHENANTHRENE to ACRYLONITRILE.



The addition was carried out under the conditions described by Campbell and Tucker (J. 1949, 2623) for the condensation of the methyl ester of fluorene-9-carboxylic acid with acrylonitrile.

Acrylonitrile (0.106g. - 0.002 mol.) was added to a solution 4:5-methylenephenanthrene (0.19g. - 0.001 mol.) in 2-ethoxyethanol (3 c.c.) containing potassium hydroxide (11.20g./litre of solution). The temperature of the solution/

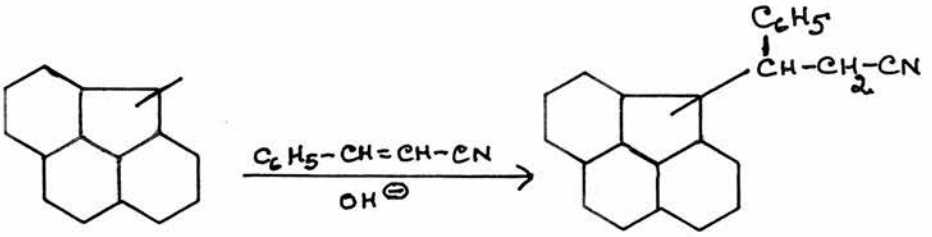
solution rose and after standing for 30 minutes a further 2 c.c. solvent together with 20 $\bar{N}$ potassium (1.5 c.c.) were added, the solution boiled for 60 minutes to effect hydrolysis and poured into water (100 c.c.). The solution was charcoal screened, filtered and acidified (dil. hydrochloric acid). The colourless crystalline precipitate, crystallised from light petroleum-benzene (5:1 by vol.) yielded α-α-bis-(2'-carboxyethyl)-4:5-methylenephenanthrene, colourless needles,

m.p. 239-242°
yield 0.19g. (57%).

Analysis

	Found	C = 75.2%; H = 5.4%
$C_{21}H_{18}O_4$	requires	C = 75.4%; H = 5.4%

ATTEMPTED CONDENSATION of 4:5-METHYLENEPHENANTHRENE with CINNAMONITRILE



(1) The same conditions were employed as described above for the condensation of 4:5-Methylenephenanthrene with acrylonitrile.

4:5-Methylenephenanthrene (0.19g. - 0.001 mol.) was dissolved/

dissolved in 1 c.c. of a solution of potassium hydroxide dissolved in 2-ethoxyethanol (11.20g./litre). After addition of cinnamonitrile (0.129g. - 0.001 mol. - 0.124 c.c.) the solution was allowed to stand overnight at room temperature, and then poured into water. An oily white solid was thereby precipitated. This solid was filtered, dried and crystallised from ethanol, giving colourless plates m.p. 113 - 116°.
Mixed with 4:5-methylenephenanthrene this gave a m.p. 113 - 116°.
The white solid was therefore unchanged 4:5-methylene-Phenanthrene.
Weight of recovered 4:5-methylenephenanthrene = 0.16g. (84%).

(2) The same procedure was repeated on a further 0.19g. 4:5-methylenephenanthrene but after allowing the mixture to stand overnight a further 2 c.c. 2-ethoxy-ethanol were added and the solution then boiled under reflux for one hour. The solution, poured into water (100 c.c.), yielded an orange oil which was extracted with ether. The ether extract was washed with dilute Sodium carbonate solution and water, dried over anhydrous Sodium Sulphate, and taken to low volume. On allowing the residual solvent to evaporate at room temperature an orange-red oil was obtained which, on trituration with a small quantity of ethanol, yielded impure 4:5-methylene-phenanthrene/

phenanthrene, m.p. 105 - 112°.

The quantity of recovered hydrocarbon was too small to permit of further purification.

No trace of the expected α-(2'-cyano-1'-phenylethyl)-4:5-methylenephenanthrene was found.

α-(1'2'-Dicarboxyethyl)-4:5-METHYLENE-PHENANTHRENE.

A mixture of 4:5-methylenephenanthrene (1g. - 0.0052 mol.) and maleic anhydride (0.53g. - 0.0054 mol.) were ground up together and heated in an autoclave for 7 hours at 250°. The product, a brown amorphous solid, was digested with dilute sodium carbonate solution, the resulting alkaline extract filtered free from a considerable quantity of insoluble matter and acidified (dil. HCl), The light yellow solid which came out of solution was filtered, dried and crystallised from a light petroleum - benzene mixture (5:1 by vol.) to give α-(1'2'-dicarboxyethyl)-4:5 methylenephenanthrene in the form of a light yellow, micro-crystalline powder.

m.p. 191 - 194°.
Yield 35 mgm. (3.2% based on reacted hydrocarbon)

Analysis

Found C = 74.4%; H = 5.1%
$C_{19}H_{14}O_4$ requires C = 74.5%; H = 4.6%

The alkali - insoluble material obtained (see above) was dried, dissolved in ethanol and the alcoholic solution charcoal-screened. The clear, pale yellow filtrate/

filtrate thereby obtained, yielded 0.31g. of unchanged 4:5-methylenephenanthrene.

m.p. and mixed melting point with 4:5-methylene-phenanthrene - 112 - 116°.

The quantity of converted hydrocarbon therefore amounted to 0.69g.

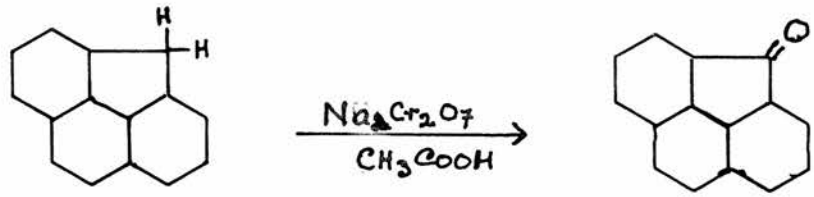
SECTION C.

II.

SYNTHESIS OF 2:13-BENZFLUORANTHENE FROM α-KETO-4:5-METHYLENEPHENANTHRENE

PREPARATION of α-KETO-4:5-METHYLENEPHENANTHRENE.

Kruber. Ber., 1934, 67, 1000.

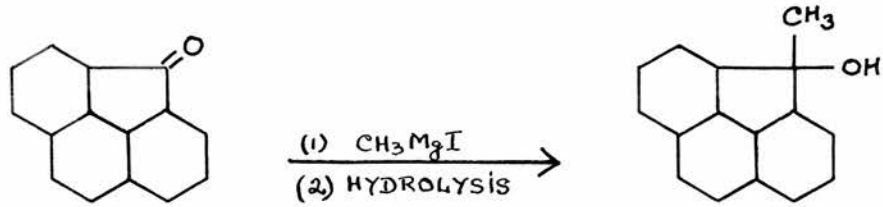


Sodium dichromate (2.4g.) dissolved in glacial acetic acid (10 c.c.) was added to a solution of 4:5-methylenephenanthrene (2.0g.) dissolved in glacial acetic acid (40 c.c.) and the resulting solution maintained at 70 - 75° with stirring for 60 hours. The solution slowly turned green and at the end of the reaction period was poured into water (250 c.c.). The resulting orange coloured precipitate was filtered, washed/

washed with hot water (100 c.c.), dried, and distilled at 150 - 180° with superheated steam. The ketone came over completely in 2 hours and crystallised from glacial acetic acid in orange-yellow needles.

m.p. 165-168° (Lit. m.p. 170°)
yield 0.921g. (43%).

PREPARATION of α-HYDROXY-α-METHYL-4:5-METHYLENE-PHENANTHRENE.



The carbinol was prepared by the action of methyl magnesium iodide on α-keto-4:5-methylenephenanthrene in a mixture of dry ether and benzene.

Magnesium (0.130g. - 0.0054 atom) and methyl iodide (0.768g. - 0.0054 mol.) were allowed to interact at room temperature in anhydrous ether (3 c.c.). When formation of the organometallic complex was complete, a solution of α-keto-4:5-methylenephenanthrene (0.75g. - 0.0036 mol.) in a mixture of ether (4 c.c.) and benzene (6 c.c.) was added to the Grignard reagent, whereupon the resulting solution turned a transient purple-red and finally a pale yellow colour.

The/

The solution was boiled under reflux for 40 minutes and then poured onto crushed ice (2.0g.). The mixture, acidified with dilute sulphuric acid, was thoroughly shaken up to decompose the organometallic complex and the organic layer separated, washed with dilute Sodium Carbonate Solution and then water, and dried with anhydrous Sodium Sulphate. Evaporation of the solvents gave ∝-hydroxy-∝-methyl-4:5-methylene-Phenanthrene in the form of colourless flat prisms.

m.p. 170° (Sharp).
yield 0.615g. (76%).

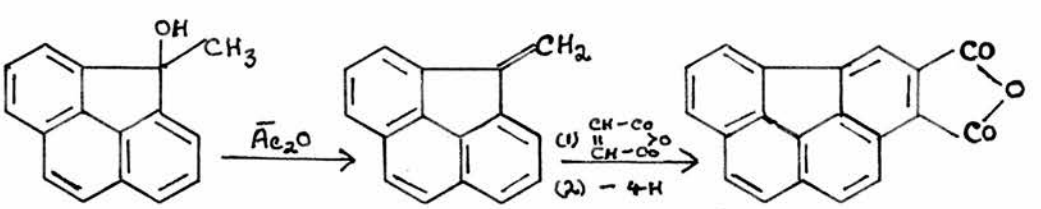
The carbinol sublimes in colourless flat prisms.

Analysis.

	Found	C = 86.9%; H = 5.7%
$C_{16}H_{12}O$	requires	C = 87.2%; H = 5.5%

The carbinol fluoresces blue, both in the solid state and in benzene solution. With conc. Sulphuric acid it gives a green colouration.

PREPARATION of 2:13-BENZFLUORANTHENE-11:12-DICARBOXYLIC ACID ANHYDRIDE.



A mixture of α-hydroxy-β-methyl-4:5-methylene-phenanthrene (0.812g.) and maleic anhydride (3.6g.) was dissolved in acetic anhydride (12 c.c.) and the temperature of the solution raised to the boiling point. The solution was boiled under reflux for 60 minutes, during which time the colour of the solution changed to a dark brown. On cooling and allowing to stand overnight at room temperature, the solution deposited a small crop of yellow-orange crystals, which were filtered, dried, and purified by sublimation. The compound sublimes in beautiful orange-yellow needles whose melting point varies with the rate of heating.

m.p. (slow heating) 335-340° (with decomposition below the melting point).
yield 38.8 mgm. (3.6%).

The compound dissolves in alkali to give a solution fluorescing blue in U.V. radiation. Acidification of the alkaline solution quenches the blue fluorescence and causes precipitation of a yellow solid which possesses a bright yellow fluorescence in U.V. radiation.

This solid, which is presumably a dicarboxylic acid, loses water readily to give the anhydride since, on filtration, it yielded the anhydride alone (melting point found - 335°).

The compound thus behaves in an analogous manner to the closely related fluoranthene -3:4-dicarboxylic acid anhydride (Campbell and Wang. J., 1949, 1513).

Analysis./

Analysis

Found C = 81.1%; H = 2.9%
$C_{20}H_8O_3$ requires C = 81.1%; H = 2.7%
$C_{20}H_{12}O_3$ requires C = 80.0%; H = 4.0%

The behaviour and analysis of the compound is therefore consistent with that of 2:13-benzfluoranthene-11:12-dicarboxylic acid anhydride. This is to be considered as formed by dehydrogenation of its reduced form, 10:11:12:13-tetrahydro-2:13-benzfluoranthene-11:12-dicarboxylic acid anhydride, which should be the normal product obtained by addition of maleic anhydride to the abovementioned carbinol in the presence of acetic anhydride.

The anhydride gives a yellow colouration with conc. sulphuric acid and in U.V. radiation displays an intense yellow-green fluorescence in solution (benzene, ethanol).

Preparation of the anhydride was also carried out with nitrobenzene as solvent. A solution of α-hydroxy-α-methyl-4:5-methylenephenanthrene (0.11g.) and maleic anhydride (0.49g.) in nitrobenzene (2 c.c.) gave, after boiling under reflux for 2 hours, 5.7 mgm. (3.9%) crude 2:13-benzfluoranthene-11:12-dicarboxylic acid anhydride.

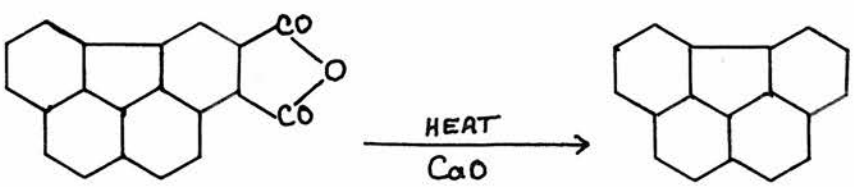
A lower yield of pure anhydride was obtained after purification than was obtained when using acetic anhydride as dehydrating solvent.

It appeared therefore that the use of nitrobenzene as a dehydrating solvent in place of acetic anhydride was/

was to no advantage.

In both methods of preparation addition of light petroleum to the reaction solution after filtration of the anhydride, caused precipitation of a buff coloured, non-crystalline powder of wide melting range viz. - 150 - 250°. This substance, insoluble in boiling alkali and in all the low boiling solvents e.g. benzene, chloroform, appeared to have been formed by polymerisation of 4:5-vinylidenephenanthrene, which is the diene involved in the Diels-Alder addition. Of the two reactions taking place side-by-side that of polymerisation seems to predominate.

DECARBOXYLATION of 2:13-BENZFLUORANTHENE-11:12-DICARBOXYLIC ACID ANHYDRIDE with FORMATION of 2:13-BENZFLUORANTHENE.



The acid anhydride (19.3 mgm.), intimately mixed with lime (4.0g.), was heated to red heat in a sublimation tube. A heavy colourless vapour condensed at the cold end of the tube to a pale yellow crystalline solid/

solid m.p. 136-143°, which was adsorbed from light petroleum (b.p. 60 - 80°) onto a column of alumina (0.6 x 20 cms.). Development with light petroleum (b.p. 60 - 80°) gave pale yellow filtrates which, concentrated to 1 c.c. volume, yielded 2:13-benzfluoranthene, yellow needles.

m.p. 147 - 149° (sublimes)
yield 4.0 mgm. (27%)

Analysis

Found C = 95.2%; H = 4.7%
$C_{18}H_{10}$ requires C = 95.5%; H = 4.5%

The mother liquor from which the 2:13-benzfluoranthene crystallised was evaporated to dryness and the residue dissolved in 1 c.c. absolute ethanol. To this solution at the boiling point was added a similar solution saturated with picric acid, whereupon a yellow crystalline solid came out of the solution at once. Recrystallisation from absolute ethanol gave golden-yellow needles.

m.p. 205 - 210° (Sublimes)

The compound, which partially decomposes below the melting point, was analysed for nitrogen content as the picrate of 2:13-Benzfluoranthene, thus

Found N = 12.3%
Mono-picrate requires N = 9.2%
Di-picrate " N = 12.3%

The compound is, as seen from the analysis figures the di-picrate of 2:13-benzfluoranthene.

The/

The weight of the di-picrate isolated, 5.3 mgm., corresponded to 1.8 mgm. 2:13-benzfluoranthene. The overall yield of hydrocarbon from the decarboxylation therefore amounted to 5.8 mgm. (39%).

Properties

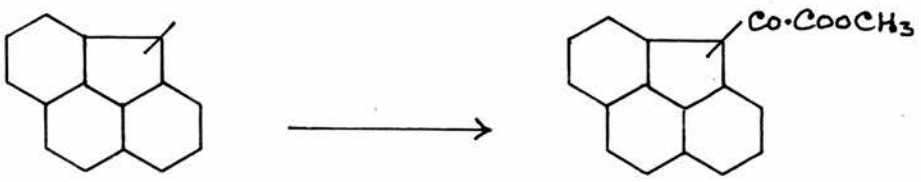
A solution of 2:13-benzfluoranthene in the common organic solvents gives a blue fluorescence in U.V. radiation while the solid fluoresces greenish-yellow. The hydrocarbon gives a green colouration on warming with conc. sulphuric acid.

Addition of a drop of benzyl chloride to a suspension of 2:13-benzfluoranthene in conc. sulphuric acid gives a heliotrope colouration which changes to a deep purple on standing.

SECTION C.

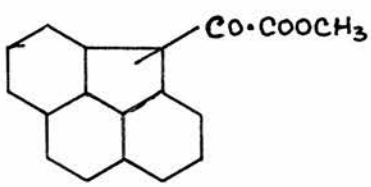
III. SYNTHESIS OF 2:13-BENZFLUORANTHENE FROM α-CARBOMETHOXY-4:5-METHYLENEPHENANTHRENE.

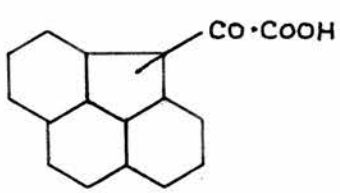
CONDENSATION of 4:5-METHYLENEPHENANTHRENE with DIMETHYL OXALATE



Potassium (2.35g. - 0.006 mol.) was dissolved in anhydrous methanol (24 c.c.) and to the solution was added 4:5-methylenephenanthrene (5.70g. - 0.003 mol.) and dimethyl oxalate (7.09g. - 0.006 mol.). On warming the mixture, a deep yellow colour developed. The mixture was warmed on the steam-bath until the whole was homogeneous, after which the bulk of methanol was slowly distilled off over a period of 40 minutes and finally the residual methanol together with excess dimethyl oxalate removed at 100° under reduced pressure (10 m.m.). The residue consisted of a very viscous yellow liquid which set to a yellow crystalline solid on cooling. This crude Methyl 4:5-Methylenephenanthrene-α-Glyoxalate was hydrolysed as described immediately below.

HYDROLYSIS of METHYL 4:5-METHYLENEPHENANTHRENE-α-GLYOXALATE





The crude yellow solid obtained above was dissolved in warm glacial acetic acid (40 c.c.) and to the solution was added conc. sulphuric acid (5 c.c.) and water/

water (20 c.c.). A yellow precipitate came out at once but dissolved on boiling the mixture under reflux for 60 minutes. The resulting yellow solution on pouring into water (200 c.c.) deposited a heavy yellow precipitate which was filtered and washed at the pump, first with water (100 c.c.), then with ethanol (50 c.c.) and dried.

Crystallisation of the deep yellow solid from glacial acetic acid yielded 4:5-methylenephenanthrene-α-glyoxalic acid, greenish-yellow needles.

m.p. 231 - 234° (dec.)

The compound, on heating above 70°, changes from a greenish-yellow colour to a deep yellow and after slowly turning reddish-brown below the melting point, finally melts to a dark reddish-brown liquid accompanied by vigorous bubbling. The keto-acid appears to crystallise with one molecule of acetic acid of crystallisation thus -

Analysis

Found C = 71.1%; H = 4.4%
$C_{17}H_{10}O_3$ requires C = 77.8%; H = 3.8%
$C_{17}H_{10}O_3.CH_3COOH$ " C = 70.8%; H = 4.4%.

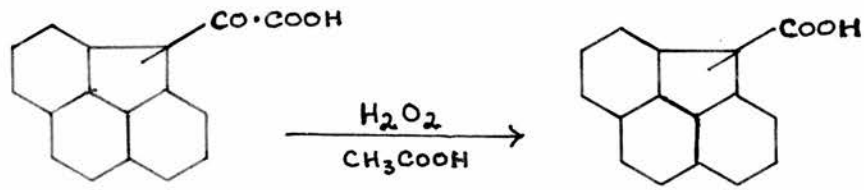
Yield of $C_{17}H_{10}O_3.CH_3COOH$ = 8.6g. (89%)

When sodium was used in place of potassium for the condensation of 4:5-methylenephenanthrene with dimethyl oxalate and the resulting methyl 4:5-methylenephenanthrene-α-glyoxalate hydrolysed as above, the yield of 4:5-methylenephenanthrene-α-glyoxalic acid was almost identical/

identical with that obtained when using potassium methoxide as condensing base.

Yield from 3.8g. 4:5-methylenephenanthrene = 5.6g. (88%).

α-CARBOXY-4:5-METHYLENEPHENANTHRENE



This acid was prepared by oxidation of the above keto-acid with hydrogen peroxide in glacial acetic acid.

The keto-acid (0.20g.) was dissolved in glacial acetic acid (2 c.c.) and on addition to the solution of 30% hydrogen peroxide (1 c.c.) a fine yellow precipitate of the keto-acid settled out from solution. The mixture was allowed to stand at room temperature for 120 hours during which time the colour of the precipitate slowly changed from a yellow to a straw colour.

On filtration a straw-coloured crop of needles was obtained which was crystallised from ethanol giving almost colourless needles of α-carboxy-4:5-methylenephenanthrene.

m.p. 251 - 252° (Lit. 253°).

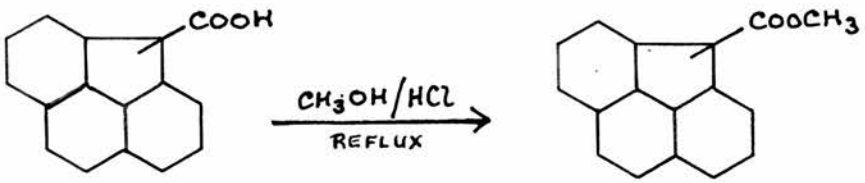
The acid melts with liberation of a gas, presumably carbon dioxide since Kruber (Ber., 1934, 67, 1000) obtained 4:5-methylenephenanthrene by heating this acid

above/

above its melting point.

Yield 100 mgm. (56%)

ESTERIFICATION of α-CARBOXY-4:5-METHYLENE-PHENANTHRENE.



A stream of dry hydrogen chloride was passed into a suspension of the acid (1.10g.) in absolute methanol (80 c.c.) until the weight of the mixture had increased by 3 grams. During this time, which extended over a period of 40 minutes, the acid dissolved completely. The solution was boiled under reflux for 12 hours, then distilled under reduced pressure (15 mm.) until 50 c.c. of methanol had been removed and the residual liquid poured into water (100 c.c.), whereupon a pale yellow turbid emulsion resulted. The emulsion was extracted with benzene until the aqueous layer was quite clear and the pale yellow benzene extracts combined, washed with dilute sodium carbonate until quite free from unchanged acid, then with water, and finally dried with anhydrous Sodium Sulphate.

The benzene was exchanged for light petroleum (b.p. 80-100°)/

(b.p. 80-100°) and the resulting solution of the ester in light petroleum distilled to low volume (10 c.c.). On cooling, an oil separated out from solution which could not be crystallised.

Therefore, the oil was dissolved in light petroleum (b.p. 80 - 100°) at the boiling point and when, on cooling, the first signs of turbidity were observed the flask containing the liquid was plunged into a bath of acetone cooled to - 70° (solid carbon dioxide) with vigorous shaking. The ester crystallised from the solution at once in the form of colourless needles.

m.p. 61 - 62°.

The ester was analysed for α-carbomethoxy-4:5-methylenephenanthrene as follows

	Found	C = 81.5%	H = 5.1%
$C_{17}H_{12}O_2$	requires	C = 82.2%	H = 4.9%

Yield 0.80g. (69%)

The dilute sodium carbonate solution used to wash the benzene extract gave, on acidification, a small quantity (90 mgm.) of unesterified α-carboxy-4:5-methylenephenanthrene.

METHYL 4:5-METHYLENEPHENANTHRENE-α-GLYOXALATE

The crude ester was prepared as described above for the condensation of 4:5-methylenephenanthrene with dimethyl oxalate in the presence of potassium methoxide.

The crude ester thus prepared from 4:5-methylene-phenanthrene/

phenanthrene (1.90g.) and dimethyl oxalate (2.36g.) in a solution of potassium (0.78g.) in absolute methanol (8 c.c.), was dissolved with warming in glacial acetic acid (12 c.c.) and to the resulting solution was added a solution of conc. sulphuric acid (2 c.c.) in water (8 c.c.) whereupon a voluminous yellow precipitate separated out of solution.

This precipitate was filtered, washed at the pump with water (100 c.c.), dried, and crystallised from petrol-ether (b.p. 60 - 80°) to give bright yellow plates which partially melt at 122° to give almost colourless needles, the whole semi-molten mass then melting completely at 129°.

Analysis

	Found	C = 78.3%; H = 4.4%
$C_{18}H_{12}O_3$	requires	C = 78.3%; H = 4.4%

Yield 2.02g. (73%)

The two differently coloured, distinct crystalline forms probably correspond to the two (theoretically) possible isomers arising from a keto-enolic tantomerism. In one case, indeed, crystallisation from a light petroleum-acetone mixture gave the very pale yellow product in the form of needles, which melted sharply at 129° to give a deeper yellow liquid without any change in colour or form at 122°. The pale yellow body, needles, m.p. 129° (Sharp) is very likely the keto form/

form while the deep yellow body, plates m.p. 122°, corresponding in colour to those compounds possessing the fulvene type of structure, (a structure which the enolic form would possess) is probably the enolic form of the ester. That the ester is capable of reacting in both the keto and the enolic forms was demonstrated by the preparation of two derivatives of the ester, one of which involved the keto group and the other the enolic hydroxyl group.

2:4-Dinitrophenylhydrazone.

The ester was dissolved in boiling glacial acetic acid with a slight molar excess of 2:4-dinitrophenylhydrazine and a small drop of conc. hydrochloric acid added to the solution. The 2:4-dinitrophenylhydrazone of Methyl 4:5-Methylenephenanthrene-α-Glyoxalate began to separate out of solution at once in the form of bright yellow needles, which were recrystallised from glacial acetic acid. m.p. 240-243° (dec. below m.p.)

Analysis

$C_{24}H_{16}O_6N_4$ Found N = 12.2%
requires N = 12.3%

Benzoyl Derivative

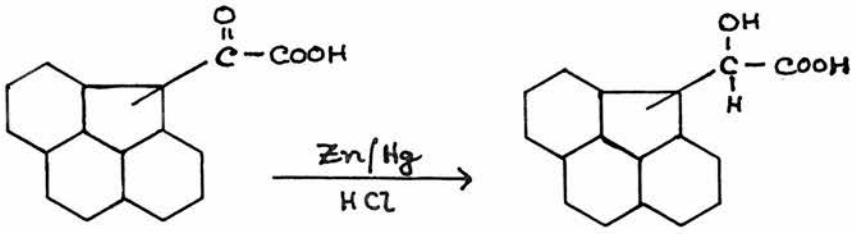
This was prepared extremely easily by addition of a slight excess of benzoyl chloride to a solution of equivalent quantities of the ester and sodium in absolute ethanol. The benzoyl derivative of Methyl 4:5-Methylenephenanthrene-α-Glyoxalate which separated out/

out from solution at once, was recrystallised from ethanol, yellow plates m.p. 167 - 168° (Sharp).

Analysis.

	Found	C = 78.5%; H = 4.3%
$C_{24}H_{16}O_3$	requires	C = 78.9%; H = 4.2%

CLEMMENSEN REDUCTION of 4:5-METHYLENEPHENANTHRENE-α-GLYOXALIC ACID.



The acid (0.40g.) dissolved in toluene (10 c.c.) was boiled under reflux for 60 hours in the presence of conc. hydrochloric acid (6 c.c.), water (2 c.c.), glacial acetic acid (3 c.c.) and 10% zinc amalgam (2g.). Two additional 2 c.c. portions of conc. hydrochloric acid were added 6 hours and 18 hours respectively, after the beginning of the reflux period.

The toluene layer was washed with water until free of mineral acid and the organic acid then extracted from the toluene layer with dilute sodium hydroxide (3 x 25 c.c.), precipitated from the alkaline solution by addition of excess conc. hydrochloric acid, filtered and dried. The acid crystallised from benzene in colourless/

colourless needles.

m.p. 211 - 212° (sublimes)

The acid was analysed for α-carboxymethyl-4:5-methylenephenanthrene ($C_{17}H_{12}O_2$) as follows -

Found C = 77.3%; H = 4.3%

$C_{17}H_{12}O_2$ requires C = 82.2%; H = 4.9%

It is obvious that the keto group in the original keto-acid has not been reduced to methylene - the oxygen content found by difference (18.4%) is considerably higher than that expected from α-carboxymethyl-4:5-methylenephenanthrene (12.9%).

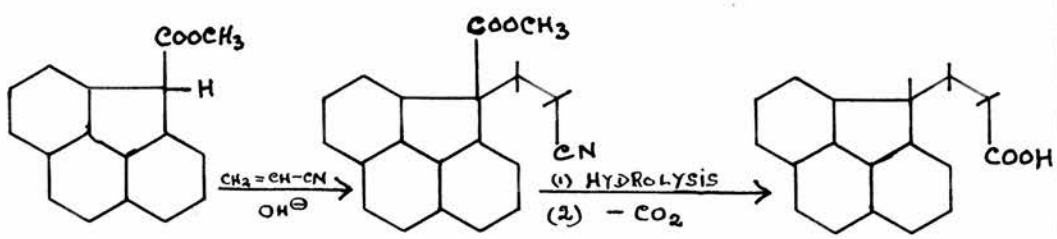
This suggests that the acid, m.p. 211 - 212°, is the hydroxy acid formed by reduction of carbonyl group of the keto-acid to secondary alcohol. A comparison of the analysis figures required for α-(1'-hydroxy-1'-carboxymethyl)-4:5-methylenephenanthrene ($C_{17}H_{12}O_3$) with those found confirms this.

Found C = 77.3%; H = 4.3%

$C_{17}H_{12}O_3$ requires C = 77.3%; H = 4.6%

Yield 0.32g. (79%).

PREPARATION OF α-2'-CARBOXYETHYL-4:5-METHYLENEPHENANTHRENE



Acrylonitrile (0.17g. - 0.22 c.c.) was added to a solution of α-carbomethoxy - 4:5-methylenephenanthrene (0.79g.) in 2-ethoxyethanol (3 c.c.) containing potassium hydroxide (11.20g./litre of solution). The temperature of the solution rose at once and after standing for 60 minutes a further 2 c.c. of 2-ethoxyethanol together with 10 N potassium hydroxide (4.5 c.c.) were added and the mixture boiled under reflux for 60 minutes to effect hydrolysis. The product, on pouring into water (50 c.c.), gave a slightly brown coloured solution, which was treated with charcoal, filtered and acidified. The precipitate obtained was filtered, dried and crystallised from benzene-acetone (4:1 by vol.). The resulting α-2'-carboxyethyl-4:5-methylenephenanthrene had the form of colourless needles.

m.p. 149 - 153°
yield 0.75g. (90%)

Analysis

	Found	C = 80.9%	H = 5.6%
$C_{18}H_{14}O_4$	requires	C = 82.4%;	H = 5.4%

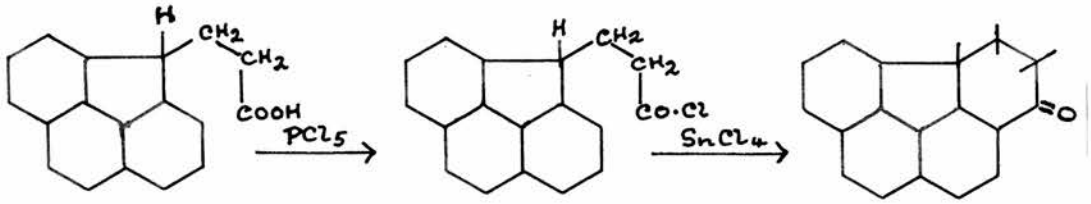
CYCLISATION of α-2'-CARBOXYETHYL-4:5-METHYLENEPHENANTHRENE

Cyclisation was effected by the action of stannic chloride on the acid chloride.

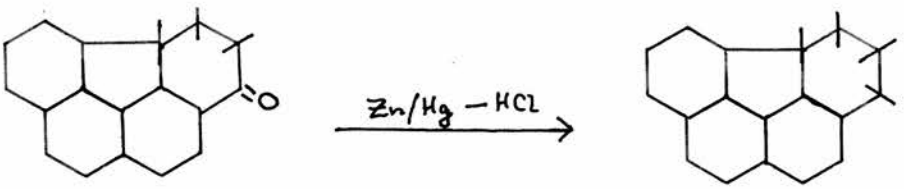
Phosphorus pentachloride (0.63g. - 10% excess) was added to a solution of the acid (0.72g.) in anhydrous benzene (4 c.c.) and the mixture allowed to stand for

30/

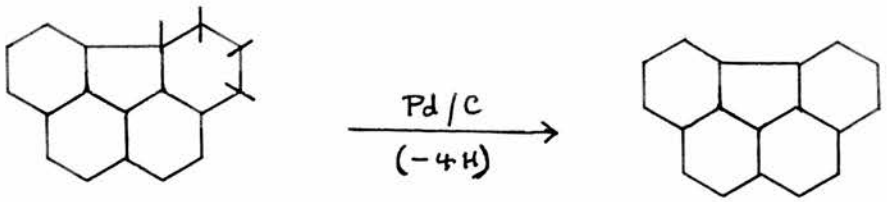
CYCLISATION of α-2'-CARBOXYETHYL-4:5-METHYLENEPHENANTHRENE



CLEMMENSEN REDUCTION of 12-KETO-9:10:11:12-TETRAHYDRO-2:13-BENZFLUORANTHENE



DEHYDROGENATION of 9:10:11:12-TETRAHYDRO-2:13-BENZFLUORANTHENE



30 minutes at room temperature. Fumes of hydrogen chloride were liberated. The solution was boiled under reflux on a water bath for 5 minutes, cooled to 5° and stannic chloride (0.64 c.c. - 100% excess) added. A green solid separated out from solution at once. After allowing the mixture to stand for 40 minutes at room temperature the complex was decomposed by pouring the mixture into conc. hydrochloric acid (30 c.c.). The organic material present was extracted with benzene (40 c.c.) and chloroform (10 c.c.); the extract was washed with dilute sodium carbonate solution (twice) then with water and dried over anhydrous Sodium Sulphate. Exchange of solvent for petrol-ether (b.p. 80 - 100°) containing a little benzene followed by distillation to low volume gave a yellow solid which, crystallised from light petroleum-benzene (3:1 by Vol.), yielded 12-keto-9:10:11:12-tetrahydro-2:13-benzfluoranthene, pale yellow plates.

m.p. 159 - 161°
yield 0.35g. (52%)

Analysis

	Found	C = 87.7%	H = 5.0%
$C_{18}H_{12}O$	requires	C = 88.5%;	H = 5.0%

The 2:4-dinitrophenylhydrazone of 12-keto-9:10:11:12-tetrahydro-2:13-benzfluoranthene was readily formed. The ketone (10 mgm.) was dissolved in glacial acetic acid (2 c.c.) and a slight excess of 2:4-dinitrophenylhydrazine added/

added. The solid material was dissolved by raising the solution to the boiling point and a small drop of conc. hydrochloric acid added. A red solid began to separate out from solution at once. This was crystallised from glacial acetic acid giving the 2:4-dinitrophenylhydrazone in the form of orange-red needles.

m.p. 293-296° (sublimes) (dec. at m.p.)

Analysis

Found N = 13.4%
$C_{24}H_{16}O_4N_4$ requires N = 13.2%

The ketone dissolves in conc. sulphuric acid to give a bright yellow solution which fluoresces greenish-yellow in U.V. radiation. On warming the solution the colour changes from bright yellow to a clear yellowish-green.

CLEMMENSEN REDUCTION of 12-KETO-9:10:11:12-TETRAHYDRO-2:13-BENZFLUORANTHENE

The ketone (0.33g.) was dissolved in toluene (4 c.c.) to which was added conc. hydrochloric acid (4 c.c.), water (6 c.c.), glacial acetic acid (2 c.c.) and 10% zinc amalgam (2g.). The three phase system was boiled under reflux for 60 hours, two 2 c.c. portions of conc. hydrochloric acid being added respectively 6 hours and 18 hours after the beginning of the reflux period. The toluene layer was separated from the acid layer, washed with dilute sodium carbonate, then with water/

water and dried over anhydrous Sodium Sulphate. The toluene was exchanged for ethanol from which the tetrahydro-derivative was precipitated by cooling in an ice-bath. The resulting white solid, crystallised from ethanol, gave the expected 9:10:11:12-tetrahydro-2:13-benzfluoranthene as colourless prisms.

m.p. (Sharp) 78 - 79.5°

Analysis

Found C = 93.6%; H = 6.1%
$C_{18}H_{14}$ requires C = 93.9%; H = 6.1%

A sample of the hydrocarbon was retained for analysis and the remainder combined with the filtrates obtained during the purification of the hydrocarbon. The solvent was removed completely by distillation and the residual 9:10:11:12-tetrahydro-2:13-benzfluoranthene dehydrogenated as described immediately below.

DEHYDROGENATION of 9:10:11:12-TETRAHYDRO-2:13-BENZFLUORANTHENE

The hydrocarbon residue obtained above was heated in an atmosphere of nitrogen for 90 minutes in a metal bath at 300° in the presence of 20% palladium-charcoal catalyst (40 mgm.). The product was extracted with chloroform (2 x 20 c.c.), the solvent exchanged for petrol-ether (b.p. 80 - 100°), and the resulting solution distilled to low volume. The yellow crystalline precipitate obtained, crystallised from light petroleum/

petroleum (b.p. 80 - 100°), yielded the expected 2:13-benzfluoranthene in the form of yellow needles.

m.p. 145 - 148° (sublimes)
Yield 116 mgm. (38% over two stages).

A mixed m.p. determination with the 2:13-benzfluoranthene prepared by the previously described Diels-Alder reaction involving α-hydroxy-α-methyl-4:5-methylenephenanthrene and maleic anhydride in acetic anhydride, followed by decarboxylation of the resulting 2:13-benzfluoranthene-11:12-dicarboxylic acid anhydride, gave a mixed m.p. 145 - 148°. The two hydrocarbons are therefore identical.

SECTION C.

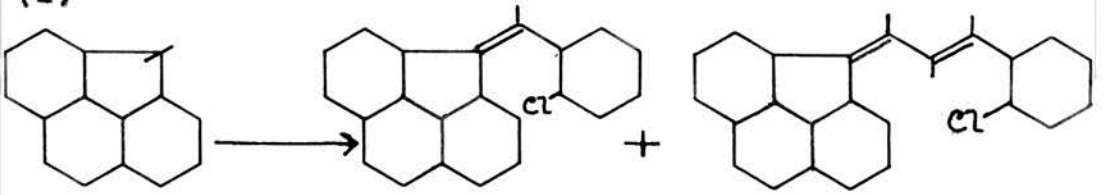
IV.

SYNTHESIS OF 2:13-11:12-DIBENZFLUORANTHENE

CONDENSATIONS of 4:5-METHYLENEPHENANTHRENE with o-HALOGENOBENZALDEHYDES

The condensations were carried out with both o-chloro- and o-bromobenzaldehyde and 4:5-methylenephenanthrene. Only one condensation, that one involving o-chlorobenzaldehyde, will be described in detail, since, in both condensations the procedures were identical.

(1)



To a solution of sodium (0.081g. - 0.0035 atom) in absolute ethanol (5 c.c.) was added 4:5-methylenephenanthrene (0.452g. - 0.0024 mol.) and the temperature of the solution raised to 75° whereupon the 4:5-methylenephenanthrene dissolved completely. The temperature was maintained at 75° while a solution of o-chlorobenzaldehyde (0.335g. - 0.0024 mol.) in absolute ethanol (2 c.c.) was allowed to run into the solution dropwise over a period of 5 minutes. A deep yellow colour developed immediately and after complete addition of the o-chlorobenzaldehyde the solution became turbid, while oily droplets condensed on the sides of the flask.

The solution was then boiled under reflux for 30 minutes, during which time a yellow solid slowly settled out from solution and the oily droplets solidified.

The mixture was then cooled, poured into water (50 c.c.) and the resulting yellow precipitate extracted with benzene (50 c.c.). The extract was washed with water, dried with anhydrous Sodium Sulphate and distilled to low volume, whereupon a deep yellow solid came out of solution, m.p. 128 - 134°.

After three crystallisations from light petroleum (b.p. 60 - 80°) the melting point of the solid was constant at 136 - 137°, (the crystalline form being that of pale lime-green needles.

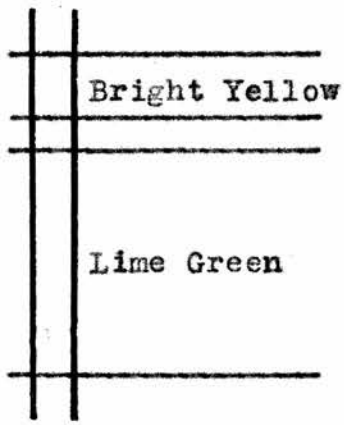
It was evident then, that there were at least two substances/

substances present in appreciable quantity.

(a) a pale lime-green compound, needles, m.p. 136-137°.

(b) a deep yellow substance, as yet not isolated, which confers the deep yellow colour on the crude condensation product.

Accordingly, the combined filtrates from the above crystallisations were passed through a coloumn of alumina (20 x 2.2 cms.) and the adsorbed material thereafter developed with light petroleum (b.p. 60-80°). The adsorbed material spread out into two separate bands, each of which was washed through in turn. (see diagram below).



The lower band, lime green in colour and possessing a yellow fluorescence in U.V. radiation, was washed through with light petroleum (b.p.60-80°) from which it crystallised in lime-green needles, m.p.136-137°. The upper bright yellow band, fluorescing golden-yellow in U.V. radiation, was washed through with light petroleum (b.p. 60 - 80°)-benzene (5:1 by vol.) and yielded compact yellow prisms, m.p. 182 - 184°.

The Lime-green coloured compound, m.p. 136 - 137°, was analysed for α-(o-chlorobenzal)-4:5-methylenephenanthrene as follows -

Found/

Found C = 84.2%; H = 4.3%; Cl = 11.4%
$C_{22}H_{13}Cl$ requires C = 84.5%; H = 4.2%; Cl = 11.3%

The compound decolourised a solution of bromine in carbon tetrachloride.

A solution of the compound in methanol decolourised a dilute aqueous solution of potassium permanganate. The presence of a double bond was thereby indicated.

Yield 0.614g. (83%)

The compound isolated in the form of yellow prisms, m.p. 182 - 184°, was analysed for 1-(o-chlorophenyl)-4:4-(4:5-phenanthrylene)-butadiene as follows -

Found C = 84.4%; H = 4.4%; Cl = 11.2%
$C_{24}H_{15}Cl$ requires C = 85.1%; H = 4.5%; Cl = 10.5%

Yield 51 mgm. (6.3%)

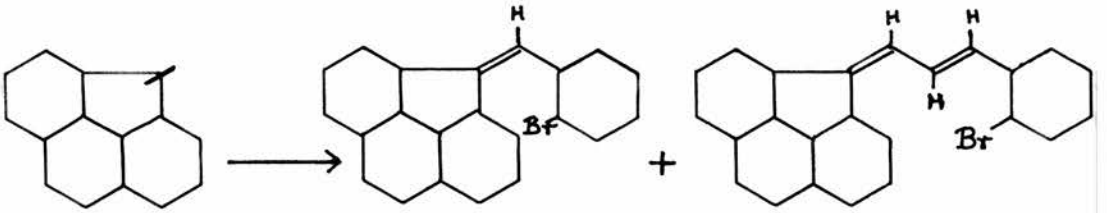
Properties

(1) ∝-(o-chlorobenzal)-4:5-methylenephenanthrene gives a yellow fluorescence in the solid state and a pale bluish-green fluorescence in solution, in U.V. radiation.

(2) 1-(o-chlorophenyl)-4:4-(4:5-phenanthrylene)-butadiene gives a canary-yellow fluorescence in the Solid State and an intense yellow-green fluorescence in Solution in U.V. radiation.

In Sulphuric acid it gives a green colouration turning olive-green on warming.

(2)



A similar condensation involving 4:5-methylene-phenanthrene (0.50g. - 0.0026 mol.) and o-bromobenzaldehyde (0.49g. - 0.0026 mol.) dissolved in a solution of Sodium (0.09g. - 0.0039 atom) in absolute ethanol (5 c.c.) likewise gave two products -

(a) α-(o-bromobenzal)-4:5-methylenephenanthrene, lime-green needles, from light petroleum (b.p. 60 - 80°) m.p. 147 - 149°, identical in appearance with α-(o-chlorobenzal)-4:5-methylenephenanthrene

Yield 0.620g. (66%)

Analysis

	Found	C = 73.7%;	H = 3.5%; Br = 21.8%
$C_{22}H_{13}Br$	requires	C = 74.0%;	H = 3.7%; Br = 22.4%

The compound decolourised a solution of bromine in carbon tetrachloride and when dissolved in methanol decolourised a dilute aqueous solution of potassium permangenate.

The compound fluoresces with a yellowish-green colour in the Solid State and with a pale bluish-green colour in solution.

(b)/

(b) 1-(o-bromophenyl)-4:4-(4:5-phenanthrylene)-butadiene, bright yellow prisms from light petroleum (b.p. 60 - 80°),

m.p. 198 - 200°
Yield 48 mgm. (4.8%)

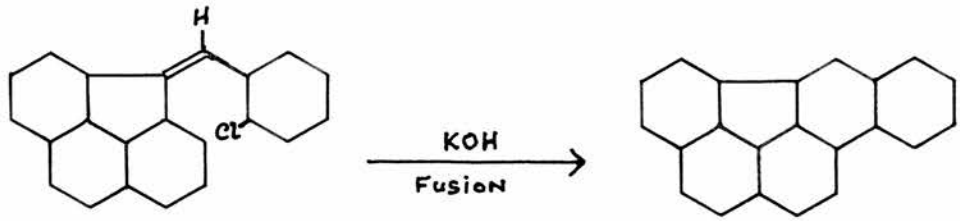
Analysis

Found C = 75.1%; H = 3.6%; Br = 20.8%
$C_{24}H_{15}Br$ requires C = 75.2%; H = 4.0%; Br = 20.8%

The compound in U.V. radiation gives a golden-yellow fluorescence in the Solid State, an intense yellow-green fluorescence in Solution.

In conc. Sulphuric acid the compound gives a greenish-yellow colouration, changing successively to yellow and then to brown.

ATTEMPTED SYNTHESIS of 2:13-11:12-DIBENZFLUORANTHENE by FUSION of α-(o-CHLOROBENZAL)-4:5-METHYLENEPHENANTHRENE with KOH.



(1) A mixture of α-(o-chlorobenzal)-4:5-methylenephenanthrene (0.50g.) and potassium hydroxide (2.5g.) was fused and the resulting two-phase liquid heated for 4 minutes at 240° with vigorous stirring. The organic phase/

phase, which had turned dark brown in colour, was dissolved in benzene (50 c.c.), washed first with dilute hydrochloric acid, then with dilute Sodium carbonate solution, finally with water and dried over anhydrous Sodium Sulphate. The volume of the Solution was reduced to 20 c.c. by distillation, and thence passed through a coloumn of alumina (16 x 2.2 cms.). Development with light petroleum (b.p. 60 - 80°) resulted in formation of two well defined zones, A and B.

Zone A. The lower zone, consisting of a lime-green coloured band with a yellow fluorescence in U. V. radiation, was washed through and the filtrates therefrom gave, on evaporation, 0.36g. of lime-green coloured needles, m.p. 135 - 137°.
Mixed m.p. with α-(o-chlorobenzal)-4:5-methylenephenanthrene 135 - 137°.

The substance was therefore unchanged α-(o-chlorobenzal)-4:5-methylenephenanthrene.

Zone B. This upper zone, consisting of an illdefined orange band, appeared to be heterogeneous judging from its appearance in U. V. radiation. Development with light petroleum (b.p. 60 - 80°)-benzene (5:1 by Vol.) gave several highly coloured bands from which nothing crystalline could be isolated. It was therefore neglected.

(2)/

(2) The same procedure was repeated, using a longer reaction period (12 minutes). When analysed chromatographically the product gave a single dark brown band which virtually remained stationary at the top of the coloumn. Development in turn with light petroleum (b.p. 60 - 80°) and benzene gave no zone formation whatever.

It appeared that all the starting material had been destroyed by the hydroxide.

ATTEMPTED SYNTHESIS of 2:13-11:12-DIBENZFLUORANTHENE by FUSION of α-(o-BROMOBENZAL)-4:5-METHYLENEPHENANTHRENE with KOH.

A mixture of α-(o-bromobenzal)-4:5-methylenephenanthrene (0.18g.) and potassium hydroxide (0.80g.) was fused and heated at 240° for 8 minutes. The product, after extraction with benzene and washing, was passed through a coloumn of alumina (25 x 1.6 cms.) which, on development with light petroleum (b.p. 60 - 80°), showed three distinct zones A, B and C.

Zone A. The lower zone, lime-green in colour with a yellowish-green fluorescence in U.V. radiation, when washed through with light petroleum (b.p. 60 - 80°) yielded 25 mgm. of a lime-green Solid, needles, m.p. 146 - 148°, undepressed with α-(o-bromobenzal)-4:5-methylenephenanthrene.

This substance was, therefore, unchanged α-(o-bromobenzal)/

bromobenzal)-4:5-methylenephenanthrene.

Zone B. This intermediate zone, pale yellow in daylight and displaying a strong purple-blue fluorescence in U.V. radiation, was washed through the coloumn with light petroleum (b.p. 60 - 80°)-benzene (4:1 by vol.) and on distillation of the filtrates to low volume yielded 2 mgm. of a pale lime-green coloured substance, needles, m.p. 144 - 148°. Mixed m.p. with α-(o-Bromobenzal)-4:5-methylenephenanthrene 116 - 142°.

The compound is therefore not unchanged α-(o-Bromobenzal)-4:5-methylenephenanthrene.

The compound, when dissolved in the common organic Solvents, displays a strong purple fluorescence in daylight or U.V. radiation.

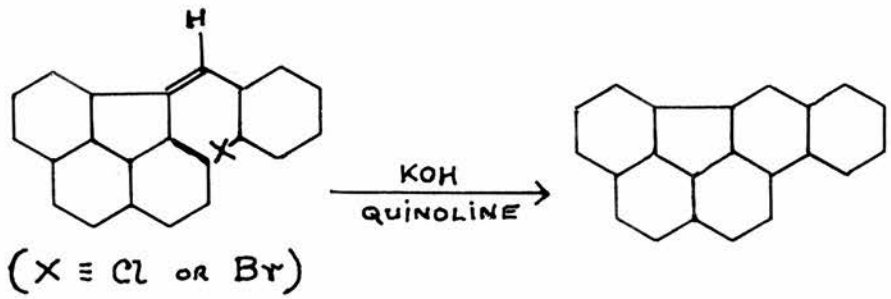
Zone C. The upper zone, consisting of a dark brown band, resisted development with petrol-ether or benzene and appeared to be organic debris from the reaction.

It was therefore discarded.

It was evident that the procedure involving fusion of the α-(o-halogenobenzal)-4:5-methylenephenanthrene with caustic potash was too drastic and resulted in destruction of the halogen-containing compounds.

SYNTHESIS/

SYNTHESIS of 2:13-11:12-DIBENZFLUORANTHENE by DEHYDROHALOGENATION of α-(o-HALOGENOBENZAL)-4:5-METHYLENEPHENANTHRENE with KOH in QUINOLINE.



(X ≡ Cl or Br)

(1) To a solution of α-(o-chlorobenzal)-4:5-methylene-phenanthrene (0.27g.) in quinoline (2.0 c.c.) was added a 25-fold molar excess of potassium hydroxide (0.78g.) and the mixture raised to the boiling point of quinoline. The two phase liquid was thereafter heated under reflux with vigorous stirring for 90 minutes, during which time the colour of the mixture gradually darkened.

The product was poured into excess concentrated hydrochloric acid (50 c.c.) and the resulting brown precipitate extracted with much benzene (500 c.c.) in five 100 c.c. portions. The combined extracts were washed, first with water, then with dilute Sodium Carbonate solution and finally with water and dried over anhydrous Sodium Sulphate. The extract, yellow in colour and displaying a magnificent purple fluorescence in daylight was distilled to low volume (40 c.c.) and passed/

passed through a coloumn of alumina (20 x 2.1 cms.) in order to remove organic debris.

A dark brown zone remained at the top of the coloumn while development with light petroleum (b.p. 60 - 80°) caused a pale yellow band to spread down the coloumn. This latter band, fluorescing purple in U.V. radiation, was washed through completely and on concentration of the filtrates yielded the expected 2:13-11:12-dibenzfluoranthene, pale green needles from light petroleum (b.p. 60 - 80°).

m.p. 147 - 149°

A further small crop of slightly less pure hydrocarbon was obtained from the mother liquors.

Yield 84 mgm. (35%)

Analysis

Found C = 95.0%; H = 4.8%
$C_{22}H_{12}$ requires C = 95.6%; H = 4.4%

PICRATE The Picrate was obtained from a solution of hydrocarbon and picric acid in benzene. It could not, however, be obtained pure since there is a considerable degree of dissociation of the picrate in benzene.

m.p. 150 - 175° (dec.)

The picrate was isolated from a solution of the hydrocarbon and excess picric acid in absolute ethanol as orange-red needles.

m.p. 165 - 175° (dec.)

Recrystallisation from absolute ethanol caused dissociation/

dissociation of the picrate into free hydrocarbon, crystals of which could be observed under the microscope alongside of the picrate.

The sample, m.p. 165 - 175°, on analysis gave a high nitrogen content, which probably indicated the presence of free picric acid.

Analysis

Mono-picrate $C_{28}H_{15}O_7N_3$ Found N = 9.8% requires N = 8.3%

s-TRINITROBENZENE DERIVATIVE. This was formed readily from a solution of the hydrocarbon in absolute ethanol to which a similar solution of s-trinitrobenzene had been added.

Bright yellow needles, m.p. 170 - 175° (dec.)

Analysis

$C_{28}H_{15}O_6N_3$ Found N = 8.8% requires N = 8.6%

Properties

2:13-11:12-Dibenzfluoranthene gives a strong purple fluorescence in both daylight and U.V. radiation. The solid fluoresces a light greenish-yellow colour.

On heating with conc. sulphuric acid, the hydrocarbon gives a pale green colouration changing to olive-green and finally to a brown colour. At the last-mentioned stage the solution fluoresces purple in daylight. Addition of benzal chloride to a suspension of the hydrocarbon in conc. Sulphuric acid gives a blue colouration.

The compound isolated in small yield from the fusion of α-(o-Brombenzal)-4:5-methylenephenanthrene with/

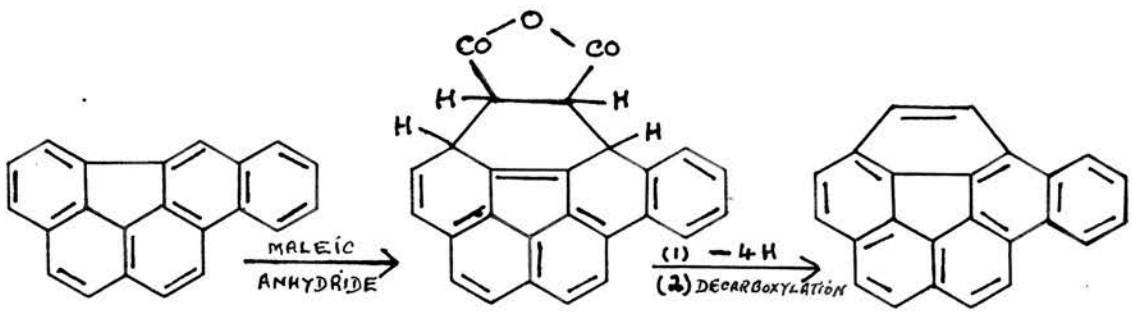
with potassium hydroxide corresponded in properties to 2:13-11:12-dibenzfluoranthene.

The identity of the two compounds was proved by their mixed melting point viz. 144 - 149°.

(2) A repetition of the foregoing experimental procedure was carried out on α-(o-bromobenzal)-4:5-methylenephenanthrene (1.06g.) dissolved in quinoline (10 c.c.) to which potassium hydroxide (4.2g.) was subsequently added. Extraction and purification of the product also as described above gave a considerably greater yield of 2:13-11:12-dibenzfluoranthene than had been obtained from α-(o-chlorobenzal)-4:5-methylenephenanthrene.

Yield 0.40g. (49%)

DIELS-ALDER REACTION on 2:13-11:12-DIBENZFLUORANTHENE - ATTEMPTED SYNTHESIS of 1:2-BENZCORONINDENE



A solution of 2:13-11:12-dibenzfluoranthene (0.1g.) and maleic anhydride (0.107g. — 200% excess) in/

in nitrobenzene (1 c.c.) was boiled under reflux for 24 hours. The colour of the solution slowly changed to a dark brown. No solid separated out from solution during the reaction period. On cooling the resulting dark brown solution, a very small quantity of a brown, crystalline solid deposited on the sides of the reaction vessel. Isolation of this solid showed that it had no definite composition. The substance melted over a variable range, the melting point being dependent on the sample taken and lying between 200 and 300°.

The solid showed no characteristic fluorescence as would have been possessed by the desired 1:2-benz-coronindene - 3:4-dicarboxylic acid anhydride or its tetrahydro derivative.

On addition of light petroleum (b.p. 60 - 80°) to the reaction solution a similar brown solid was precipitated.

The solution possessed the characteristic purple fluorescence of 2:13 - 11:12-dibenzfluoranthene. No trace of the above mentioned anhydride was detected.

SUMMARY OF RESULTS

SECTION A.

(1) In accordance with the general course of the Friedel-Crafts acylation of fluoranthene, toluylation of same gave a mixture of 4- and 11-o-Toluylfluoranthenes in approximately equal quantities. Separation of the individual ketones was achieved by the use of chromatography.

(2) The Elbs pyrolysis of 4-o-Toluylfluoranthene yielded, after chromatographic analysis -

(a) Naphtho (2':3'-3:4) fluoranthene, which was oxidised to the quinone naphtho (2':3'-3:4) fluoranthene - 1':4'-quinone.

(b) Naphtho (2':3'-3:4) fluoranthene - 1':4'-quinone.

(c) 4:5-o-xylylenefluoranthene, which was oxidised to 4:5-phthaloylfluoranthene.

(3) The Elbs pyrolysis of 11-o-Toluylfluoranthene yielded, after chromatographic analysis -

(a) Naphtho (2':3'-10:11) fluoranthene, which was oxidised to naphtho (2'3':10:11) fluoranthene - 1':4'-quinone.

(b) Naphtho (2':3'-11:12) fluoranthene, which was oxidised to naphtho (2':3'-11:12) fluoranthene - 1':4'-quinone.

(4) The orientation of the compounds given in (2) and (3) followed indisputably from earlier work by Campbell/

Campbell and co-workers viz. the unambiguous syntheses of the two quinones:-

(i) naphtho (2':3'-3:4) fluoranthene - 1':4'-quinone.

(ii) naphtho (2':3'-11:12) fluoranthene - 1':4'-quinone.

and the hydrocarbon -

naphtho (2':3'-11:12) fluoranthene.

(5) In the light of these results an interpretation of the results of Von Braun and Manz has been put forward.

(6) The isolation of the peri-condensed hydrocarbon, 4:5-o-xylylenefluoranthene, represents the first instance of such a peri-condensation with formation of a seven-membered ring taking place in an Elbs pyrolysis.

(7) In three out of four Elbs pyrolyses carried out viz. those of 1-o-toluylnaphthalene, 3-o-toluylacenaphthene and 4-o-toluylfluoranthene, besides the hydrocarbons the corresponding quinones were isolated.

It was shown that the quinones probably arise by oxidation, on the alumina columns, of the corresponding anthrones formed as side products of the Elbs pyrolyses.

(8) The Elbs pyrolyses of 4- and 11-o-toluylfluoranthene served as the first known methods of preparation of the hitherto unknown naphtho (2':3'-3:4) fluoranthene and/

and naphtho (2':3'-10:11) fluoranthene, respectively.

(9) The isolation of naphtho (2':3'-2:3) acenaphthene - 1':4'-quinone from the Elbs pyrolysis of 3-o-toluylacenaphthene confirms the tentative suggestion of Graebe that the product from his ring-closure of 3-o-carboxybenzoyl-acenaphthene was the quinone just mentioned.

SECTION B.

An attempt to find a suitable synthetic route from fluorene to fluoranthene - 4:12-dicarboxylic acid met with only partial success. Owing to the failure in ascertaining the correct structure of the products from the Michael reaction involving acrylonitrile and 2-bromo-9-cyanofluorene the synthesis had to be abandoned.

SECTION C.

(1) Attempts to synthesise thehitherto unknown hydrocarbon, 2:13-benzfluoranthene, starting from -

(a) fluorenone

(b) acenaphthylene

(c) 4:5-methylenephenanthrene

met with no success.

(2) Two unambiguous syntheses of 2:13-benzfluoranthene were carried out successfully starting from -

(a)/

(a) α-keto-4:5-methylenephenanthrene

(b) α-carbomethoxy-4:5-methylenephenanthrene

(3) An unambiguous synthesis of 2:13-11:12-dibenzfluoranthene was carried out starting from 4:5-methylenephenanthrene.

(4) An outline of, and a discussion on, the chemistry of 4:5-methylenephenanthrene has shown the close resemblance of its chemical behaviour to that of fluorene and phenanthrene.

(5) The stereochemistry of 2:13-benzfluoranthene and related hydrocarbons has been discussed and an outline of the stereochemical implications brought about by the synthesis of 2:13-benzfluoranthene given.

APPENDIX

PROPOSED NON-COPLANAR STRUCTURE FOR 2:13- BENZFLUORANTHENE

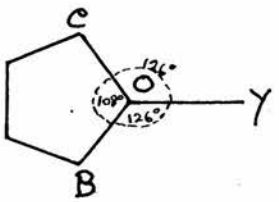


Fig. A

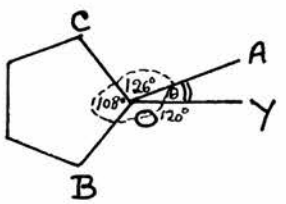


Fig. B

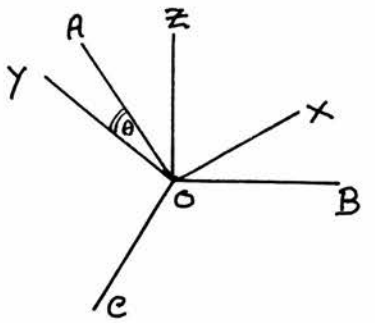


Fig. C

Since the pentagon is regular $\angle COB = 108^\circ$ (Figs. A, B and C). When OY lies in the same plane as OB and OC (Fig. A) and makes equal angles with OB and OC then

$$\angle COY = \angle YOB = 126^\circ$$

Let θ be the angle of inclination of OY (Fig. A) to the plane of the pentagon when $\angle COY = 120^\circ$.

Let OA be the new position of OY (Fig. B)

Then in Fig. B $\angle AOY = \theta$

$$\angle COA = 120^\circ = \angle BOA$$

$$\text{and } \angle COY = 126^\circ = \angle BOY$$

Considering Fig. C, let OY be one of the axes of co-ordinates.

Let OX and OZ be the remaining two rectangular axes such that the two sides of the pentagon, OC and OB, and/

and OY and OX are all in the same plane while OZ is perpendicular to the plane containing these lines. Then the co-ordinate axes are OX, OY and OZ.

Hence $\angle ZOY = \angle ZOX = \angle YOX = 90^\circ$

Since OY, OX and OB lie in the same plane

$\therefore \angle XOB = \angle YOB - \angle YOX$

$= 126^\circ - 90^\circ$

$= 36^\circ$

Also $\angle COY = \angle YOB = 126^\circ$

Since AO, YO and ZO lie in the same plane and since ZO is perpendicular to YO

then $\angle AOZ = (90^\circ - \theta)$

Again since OA lies in the plane YOZ and both OY and OZ are perpendicular to OX

then $\angle AOX = 90^\circ$

Let l_1, m_1, n_1, be the direction cosines of the line OA with OX, OY and OZ, respectively.

We have therefore

$l_1 = \cos\angle AOX = \cos 90^\circ = 0$

$m_1 = \cos\angle AOY = \cos\theta$

$n_1 = \cos\angle AOZ = \cos(90 - \theta) = \sin\theta$

Similarly, if l_2, m_2, n_2 are the direction cosines of the line OB with OX, OY and OZ, respectively then

$l_2 = \cos\angle XOB = \cos 36^\circ$

$m_2 = \cos\angle YOB = \cos 126^\circ$

$n_2 = \cos\angle ZOB = \cos 90^\circ = 0$

Now/

Now the formula for the angle θ between two straight lines whose direction cosines (with fixed rectangular axes) are l_1, m_1, n_1 and l_2, m_2, n_2, respectively, is given by

$$\cos\theta = l_1.l_2 + m_1.m_2 + n_1.n_2$$

Substituting the above values we have

$$\cos 120^\circ = \cos\theta . \cos 126^\circ$$

whence $\cos\theta = \frac{1}{2} \cdot \text{Sec. } 54^\circ$

and so $\theta = 31^\circ 42'$, which is the angle of inclination of the peripheral bonds of the five-membered ring to the plane of the five-membered ring.

Again, since angle AOB = 120° it follows at once that the angle of inclination ϵ of the planes of the six-membered rings to that of the five-membered ring is given by

$$\frac{\text{Sin } \epsilon}{\text{Sin } \theta} = \frac{1}{\text{Sin } (\frac{120^\circ}{2})} = \frac{1}{\text{Sin } 60^\circ}$$

$$\text{Whence Sin } \epsilon = \frac{\text{Sin } \theta}{\text{Sin } 60^\circ} = \frac{\text{Sin } 31^\circ 42'}{\text{Sin } 60^\circ}$$

and so $\epsilon = 37^\circ 23' \approx 37^\circ$

Finally, if l, m, n are the direction cosines of the normal to the plane containing OA and OB

$$1.0 + m.\cos\theta + n.\sin\theta = 0$$

and $1.\cos 36^\circ + m.\cos 126^\circ + n.0 = 0$

./.

$$\therefore \quad \frac{l}{\text{Sin}\,\theta\,.\text{Sin}\,36^{\circ}} = \frac{m}{\text{Sin}\,\theta\,.\text{COS}\,36^{\circ}} = \frac{n}{-\text{COS}\,\theta\,.\text{COS}\,36^{\circ}}$$

and $l^2 + m^2 + n^2 = 1$

$\therefore \quad n = \text{COS}\,59^{\circ}59'$

$\approx \text{COS}\,60^{\circ}$ which is the cosine of the angle of inclination of the benzene rings to one another.

ACKNOWLEDGEMENTS

Sincerest appreciation is expressed to Dr. Neil Campbell for the helpful advice and encouragement given to the author both as an undergraduate and as a Postgraduate student.

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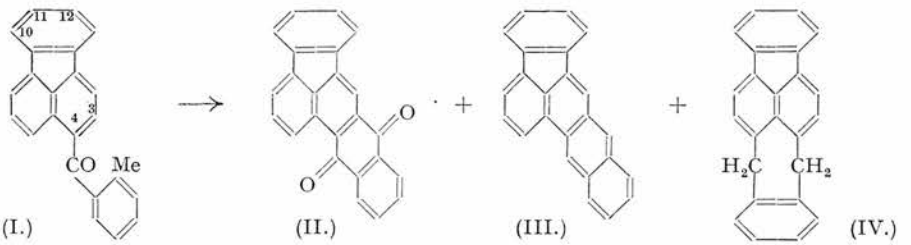
680. *The Preparation of Some Naphthofluoranthenes and their Quinones.*

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

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

o-TOLUOYL chloride and fluoranthene with aluminium chloride yield a mixture of 4- and 11-*o*-toluoylfluoranthene, m. p. 115—116·5° and 148·5—150°, respectively (I and VII), each of which was subjected to the Elbs reaction. The first ketone gave three products : (1) an orange-coloured quinone which proved to be naphtho(2′ : 3′-3 : 4)fluoranthene-1′ : 4′-quinone (3 : 4-



(I.) (II.) (III.) (IV.)

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

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

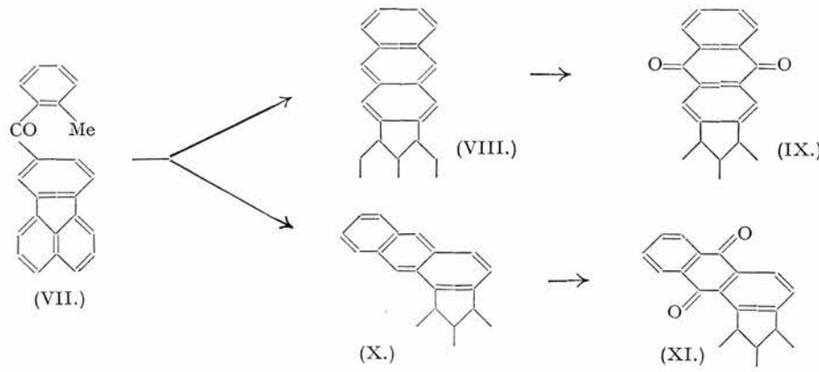
11-*o*-Toluoylfluoranthene (VII) on pyrolysis gave two isomeric hydrocarbons : (1) a yellow hydrocarbon, m. p. 301—303°, which was oxidised to the known naphtho(2′ : 3′-11 : 12)fluoranthene-1′ : 4′-quinone (IX) (Campbell and Gow, *J.*, 1949, 1555) and is therefore naphtho(2′ : 3′-

(V.) (VI.)

11 : 12)fluoranthene (VIII)—the structure of the original ketone follows from this identification; (2) a red hydrocarbon, m. p. 225·5—227°, which must by elimination be naphtho(2′ : 3′-10 : 11)-fluoranthene (X) and whose structure was confirmed by oxidation to the quinone (XI) (for preparation, see below).

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

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



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Pyrolyses of 4-o-*Toluoylfluoranthene.*—The ketone (1·00 g.) was pyrolysed for 30 minutes at 450° in carbon dioxide and the resulting solid was dissolved in benzene and passed through a column, 40 × 1·9 cm. Development with light petroleum–benzene (2 : 3 by vol.) gave (*a*) a bottom, colourless zone with a bright blue fluorescence, (*b*) a yellow zone, (*c*) an orange-pink zone with a green fluorescence, and (*d*) a top, reddish-black band. (*a*) This band gave a pale yellow solid, m. p. 80—150°, which was passed in benzene through a column, 25 × 1·3 cm., and was developed as above. When the whole column showed a blue fluorescence, it was cut, and the lower half extracted with acetone. Evaporation gave 4 : 5-o-*xylylenefluoranthene* (0·03 g.), colourless crystals (light petroleum, b. p. 80—100°), m. p. 208—210° (Found : C, 94·3; H, 5·2. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%). The hydrocarbon has a pale greenish-yellow fluorescence, and when heated with concentrated sulphuric acid gives a pink colour turning to brown. The hydrocarbon (30 mg.) was oxidised with chromic acid (60 mg.) in glacial acetic acid to 4 : 5-phthaloylfluoranthene, m. p. 285—287°, undepressed when mixed with the substance prepared as below. (*b*) The yellow band on elution gave a yellow solution with a strong blue fluorescence, and concentration of the solution afforded *naphtho*(2′ : 3′-3 : 4)*fluoranthene* (0·16 g.), m. p. 229—230° (Found : C, 94·9; H, 4·9%). It sublimes in yellow needles, and has a blue fluorescence in solution and a greenish-yellow fluorescence in the solid state. On oxidation with chromic anhydride in glacial acetic acid it gave the quinone, m. p. 250—253°, not depressed when admixed with Campbell and Wang's quinone (*loc. cit.*). (*c* and *d*) Continued development brought through a filtrate with a greenish-yellow fluorescence in daylight, from which nothing could be isolated, and then an orange-coloured filtrate. This was combined with the acetone eluate of the column and on evaporation gave naphtho(2′ : 3′-3 : 4)fluoranthene-1′ : 4′-quinone (3 : 4-phthaloylfluoranthene), orange crystals (benzene), m. p. 250—253°, undepressed with the above quinone; yield 0·025 g. It gave a blue vat with sodium dithionite and a green colour with concentrated sulphuric acid.

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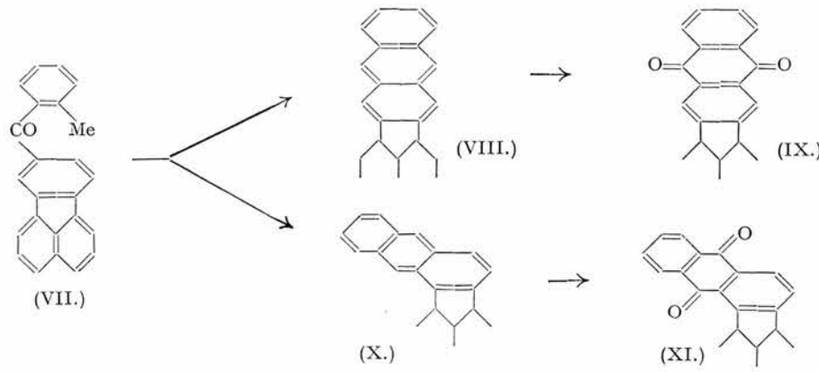

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was continued overnight and the mixture was then decomposed with hydrochloric acid and ice. The solvent was removed by steam and the residue was extracted with potassium carbonate. Acidification yielded a mixture of acids (35 g.). The acids (25 g.) were dissolved in chloroform, concentration of which gave 11-benzoylfluoranthene-2′-carboxylic acid (13 g.), m. p. 234°, showing no depression when mixed with an authentic sample. Complete evaporation of the chloroform gave a residue which was esterified with methanol and sulphuric acid, and the esters separated chromatographically. The 4-ester (2·5 g.) thus obtained on hydrolysis gave the 4-acid, m. p. 230°, giving a m. p. depression when mixed with the 11-acid.

Pure 11-acid (3 g.) and toluene-*p*-sulphonyl chloride (1·65 g.) were boiled in trichlorobenzene (15 c.c.) for 1 hour. The cold solution deposited a solid which when washed with acetone afforded a mixture (1·7 g.) of yellowish-orange plates and yellow needles. The mixture (0·6 g.) was dissolved in chlorobenzene (400 ml.) and chromatographed on a column, 18 × $\frac{7}{8}$ in. Development with the same solvent gave a strongly orange adsorbed zone and a lower, yellow band. The orange zone on extraction gave naphtho-(2′ : 3′-11 : 12)fluoranthene-1′ : 4′-quinone, m. p. >335°, which gave a blue colour with concentrated sulphuric acid and a blue vat with sodium dithionite. The yellow band gave *naphtho*(2′ : 3′-10 : 11)-*fluoranthene*-1′ : 4′-*quinone* (10 : 11-*phthaloylfluoranthene*) (0·1 g.), yellow elongated plates, m. p. 319—320° (Found : C, 85·8; H, 3·7. $C_{24}H_{12}O_2$ requires C, 86·7; H, 3·6%). It gave a red colour with concentrated sulphuric acid and no vat with sodium dithionite. A mixture of the two quinones was separated by sodium dithionite and indicated that the 11 : 12-quinone and the 10 : 11-quinone are formed approximately in the ratio 5 : 1.

Pure 4-benzoylfluoranthene-2′-carboxylic acid (1·1 g.), aluminium chloride (3·3 g.), and sodium chloride (2·75 g.) were intimately mixed and heated in an oil-bath the temperature of which was raised to 140° during 30 minutes. Nitrogen was passed through at this temperature for 3 hours. The product was decomposed with ice and hydrochloric acid and the black solid was then extracted with 5% sodium carbonate and dried. The dry product was extracted with benzene, and the benzene concentrate chromatographed on a column 12 × $\frac{3}{4}$ in. Development with benzene gave a yellow zone which quickly passed down the column. The filtrate on evaporation furnished a solid (20 mg.) which crystallised from chlorobenzene in yellow-orange prisms, m. p. 252—253° with sublimation, and was proved to be naphtho-(2′ : 3′-3 : 4)fluoranthene-1′ : 4′-quinone (Campbell and Wang, *loc. cit.*). It gave a bluish-green colour with concentrated sulphuric acid and a bluish-violet vat with alkaline sodium dithionite. Further development of the column gave a deep yellow zone below the top dark band. The column was cut and the yellow zone eluted with chloroform which on evaporation gave 4 : 5-*phthaloylfluoranthene*, yellow elongated prisms (chlorobenzene), m. p. 296—297° (Found : C, 86·3; H, 3·6. $C_{24}H_{12}O_2$ requires C, 86·7; H, 3·6%). It gave a red colour with concentrated sulphuric acid and no vat with alkaline dithionite.

3 : 4-*Phthaloylacenaphthene*.—Crude 3 : 4-phthaloylacenaphthene (Peters and Rowe, *loc. cit.*) (3·5 g.) was purified by passing a benzene solution down a column, 17 × $\frac{3}{4}$ in., and development with benzene–light petroleum (b. p. 60—80°) (4 : 1 by vol.). A yellow zone separated and afforded on elution 3 : 4-phthaloylacenaphthene (1·3 g.), yellow elongated prisms (ethanol), m. p. 196—197° (lit., 194—195°) (Found : C, 84·5; H, 4·5. Calc. for $C_{20}H_{12}O_2$: C, 84·5; H, 4·2%). The phthaloylacenaphthene was oxidised by chromic anhydride ("AnalaR") and glacial acetic acid to 4 : 5-phthaloyl-1 : 8-naphthalic anhydride which, after purification by being washed successively with ethanol, water, and glacial acetic acid, was isolated as bright yellow needles, m. p. >310° (lit., 368°) (Found : C, 73·2; H, 2·4. Calc. for $C_{20}H_8O_5$: C, 73·2; H, 2·3%). The anhydride (0·75 g.), water (20 c.c.), and mercuric oxide, freshly prepared from mercuric acetate (1·5 g.), were heated in a sealed tube at 250° for 4 hours. The product was refluxed with concentrated hydrochloric acid for 2 hours, washed with water, and dried. The dry material (1·1 g.) was extracted with benzene, and the benzene extract passed through a column, 6 × $\frac{1}{2}$ in. A pale yellow zone separated, below which was a band with a bright yellow fluorescence. Both zones yielded 1 : 8-phthaloylnaphthalene, colourless needles (ethanol–acetic acid), m. p. 176—177° (lit., 178°), yield 0·30 g. (Found : C, 83·6; H, 4·1. Calc. for $C_{18}H_{10}O_2$: C, 83·7; H, 3·9%). In concentrated sulphuric acid it gave a yellow solution with a green fluorescence. No colours were obtained with zinc and ammonia or alkaline sodium dithionite.

Ring-closure of 1-*Benzoylnaphthalene*-2′-*carboxylic Acid*.—The acid (4·6 g.), potassium iodide (5·5 g.), red phosphorus (1·5 g.), and phosphoric acid (20 ml.) were refluxed for 4 hours. Water was added, and the residue extracted with ethanol. Evaporation gave a solid (2·0 g.), which was dissolved in the minimum volume of benzene and passed through a column, 14 × 0·75 in. Development with the same solvent gave a bottom zone with a bright purple fluorescence which gave 0·6 g. of a solid, m. p. 112—120° after crystallisation from glacial acetic acid, and a yellow zone which afforded a solid, m. p. 138—145° (0·9 g.) after crystallisation from acetic acid. The second substance (0·75 g.) in benzene was passed through a column, 9·5 × 0·45 in., and a yellow zone which separated yielded a substance, m. p. 146—150° (0·65 g.) after crystallisation from acetic acid. Dehydrogenation with chloranil in xylene (3 hours) gave 1 : 2-benzanthracene, m. p. and mixed m. p. 156° (lit., 158°) (Found : C, 94·2; H, 5·3. Calc. for $C_{18}H_{12}$: C, 94·7; H, 5·3%).

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