SYNTHESIS

of

COMPOUNDS RELATED TO FLUORANTHENE

THESIS

presented by

H. W. D. STUBBS, B.Sc.(Glasgow),

for the DEGREE of

DOCTOR OF PHILOSOPHY

of the

UNIVERSITY OF GLASGOW.

I wish to express my great indebtedness to my supervisor, Dr. S. Horwood Tucker, for his invaluable advice, help, and encouragement during the period of this research. I am also very grateful to Dr. E. Clar of this Department for his help in the interpretation of the ultra-violet absorption spectra, and for measuring the absorption spectra of 1:2:5:6—dibenzpyracylene, fluoranthene, 2:3- and 3:4-benzfluoranthene, the green hydrocarbon, and 9-phenylanthracene; to the Department of Scientific and Industrial Research for a grant during the period of this research; and to Mr. J. M. L. Cameron and Miss R. H. Kennaway of this Department for microanalyses. I thank Miss R. H. Hutchins, B.Sc., for her assistance with the work on ethyl chloroformate (Part Ia) and Mr. W. Hamill for his assistance in part of the synthesis of 2-methoxyfluoranthene (Part 3).

Department of Chemistry,
The University,
Glasgow, W.2.

September, 1951.

PUBLICATIONS

The following papers have been, or are about to be, published. Reprints are enclosed at the back.

1. Bisperiphenylenenaphthalene.

   (Received, August 17th, 1950). Nature, 1950,166,1075.

2. Synthesis of Fluoranthenes. Part VI. Utilisation of the Mannich Reaction.

   (Received, August 28th, 1950). J., 1950,3288.

3. Synthesis of Fluoranthenes, Part VII. 1:2:5:6-Dibenzpyracylene.

   (Received, May 10th., 1951).

4. Synthesis of Fluoranthenes. Part VIII. 2:3-Benzfluoranthene.

   (Received, July 9th, 1951).

CONTENTS

Pages

Part 3. 3:4-Dimethylfluoranthene -

2-Methoxyfluoranthene -

Part 4. Ultra-violet Absorption Spectra of Substituted Fluoranthenes.

SUMMARY

Part 1a. The known 4-methylfluoranthene and 4-phenylfluoranthene have been synthesised by condensation of methyl and phenyl vinyl ketones, or the corresponding Mannich bases, methyl 2-morpholinoethyl ketone and 2-diethylaminoethyl phenyl ketone respectively, with methyl fluorene-9-carboxylate, followed by hydrolysis and decarboxylation, reduction, cyclisation, and dehydrogenation. Unsuccessful attempts to evolve a new synthesis of methyl fluorene-9-carboxylate were made.

Part 1b. 1:2:5:6-Dibenzpyracylene was synthesised by a crossed Ullmann reaction between 4-iodofluoranthene and 2-bromonitrobenzene, followed by reduction, diazotisation, and ring-closure. An attempt at synthesis by the method described in Part 1a failed. The ultra-violet absorption spectrum is reported and discussed, especially in relation to Clar's Anellation Theory.

Part 2. 2:3—Benzfluoranthene has been synthesised from *o*-diphenylenephthalide by Clar's zinc dust-zinc chloride fusion method. An attempt to synthesise 2:3—benzfluoranthene by cyclisation of 9-bromo-9-ω-bromo-*o*-tolylfluorene gave a compound believed, in the light of spectrographic and analytical evidence, to be 1:9-diphenylanthracene. The spectrum

of 2:3—benzfluoranthene is reported and discussed, especially in relation to the Anellation Theory.

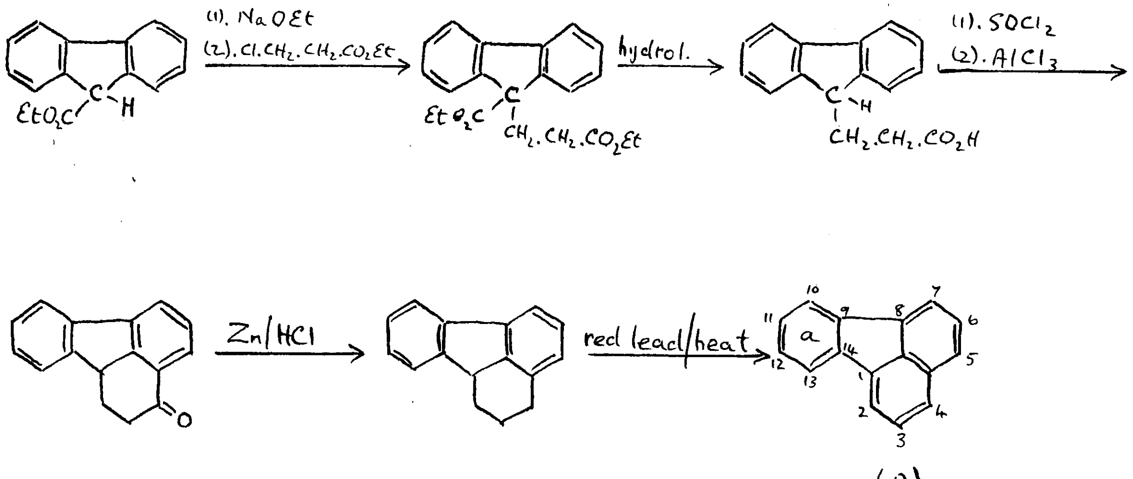
Part 3. 3:4—Dimethylfluoranthene was obtained by the Grignard reaction on 4-keto-3-methyl—1:2:3:4-tetrahydrofluoranthene, followed by dehydration-dehydrogenation.

2-Methoxyfluoranthene was synthesised by a crossed Ullmann reaction between 1-iodo-2-methoxynaphthalene and o-bromonitrobenzene, followed by reduction, diazotisation, and ring-closure.

Part 4. The ultra-violet absorption spectra of several mono-, di-, and trimethylfluoranthenes, methoxyfluoranthenes, and 4-phenylfluoranthene, not previously recorded, have been measured. They are shown to be of value in characterisation of the pure compounds. Distortion due to overlapping of the substituent methyl- or methoxyl- group with a hydrogen atom in the 2- or 10- substituted derivatives appears to produce corresponding distortions in the ultraviolet absorption curve.

INTRODUCTION

Fluoranthene (A) (76) was first isolated in the pure state by Goldschmiedt (1), and almost simultaneously by Fittig (2) in 1877. The structure was elucidated by von Braun and Anton (3) by degradative studies, and their conclusions confirmed by synthesis from the fluorene skeleton by the following route:-



(A).

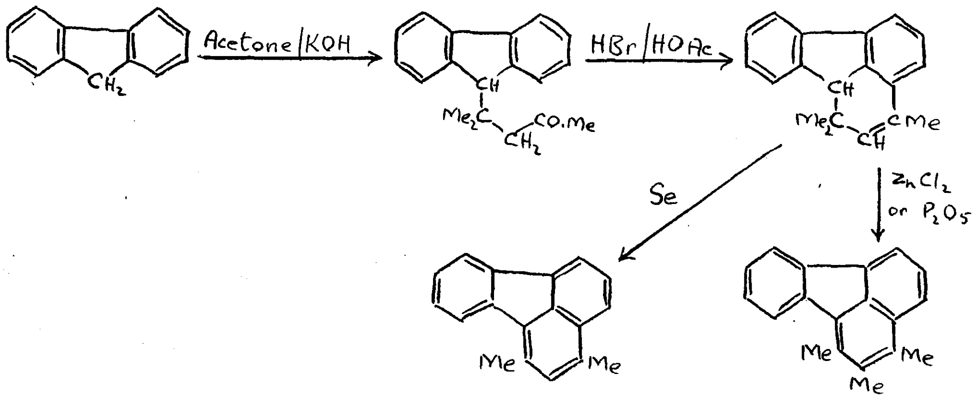
The system of numbering used in this thesis is that finally adopted by von Braun and Anton (4) and illustrated in formula (A).

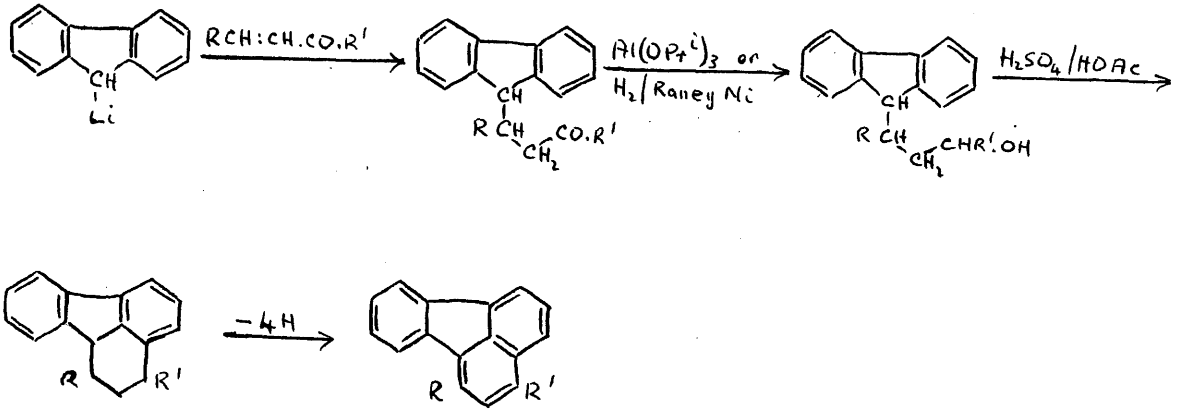
Alkyl- and Aryl-substituted Fluoranthenes.

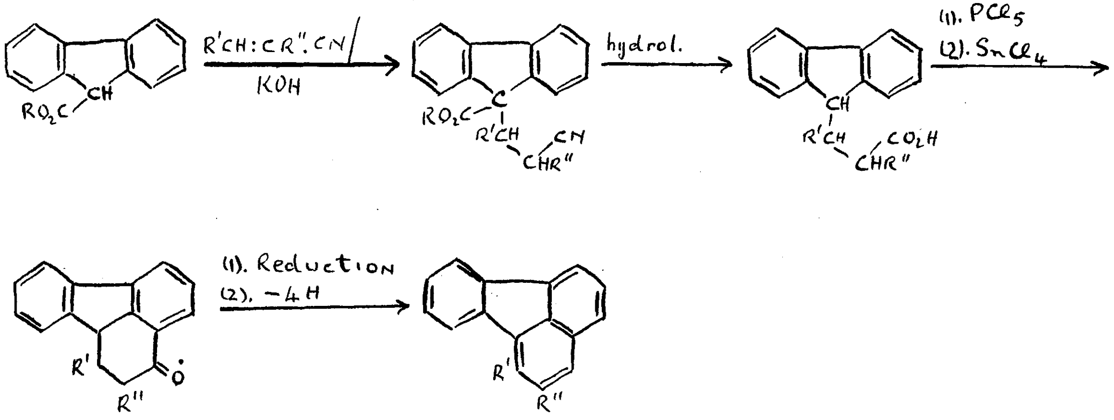
The synthesis of substituted fluoranthenes, namely the 4-methyl- and 4-phenyl-derivatives, is first described by von Braun and Manz (5). They reacted on 4-keto-1:2:3:4-

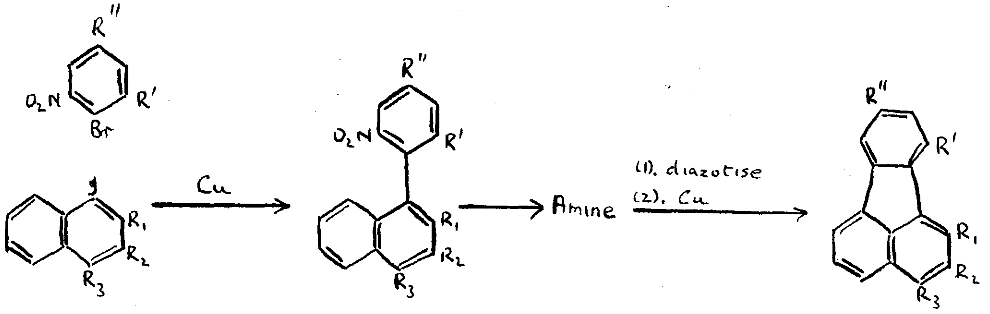
tetrahydrofluoranthene, an intermediate in the synthesis of fluoranthene described above, with the appropriate Grignard reagent, and converted the product to the substituted fluoranthene by dehydration and dehydrogenation.

Tucker and co-workers (6-12) describe the synthesis of various mono-, di-, and trimethylfluoranthenes, and of other alkyl-, aryl-, and methoxy-substituted fluoranthenes by various modifications of the following general methods:-









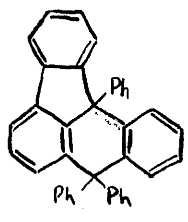
By this last (crossed Ullmann) method have been prepared fluoranthene ($R_1 = R_2 = R_3 = R^1 = R^{11} = H$) and 2:4-dimethylfluoranthene ($R_1 = R_3 = Me$; $R_2 = R^1 = R^{11} = H$) (7); 2:3:4—trimethylfluoranthene ($R_1 = R_2 = R_3 = Me$; $R^1 = R^{11} = H$) (9); ethyl fluoranthene-11-carboxylate ($R^{11} = CO_2Et$; $R^1 = R_1 = R_2 = R_3 = H$), 11-methylfluoranthene ($R^{11} = Me$; $R^1 = R_1 = R_2 = R_3 = H$), and 10—methylfluoranthene ($R^1 = Me$;

$R^{11} = R_1 = R_2 = R_3 = H$) (11); and 11-methoxyfluoranthene ($R^{11} = OMe$; $R^1 = R_1 = R_2 = R_3 = H$) (12). As will be seen, this method is capable of application to a wide range of naphthalene and *o*-bromonitrobenzene derivatives, and provided the required 1-iodonaphthalene and *o*-bromonitrobenzene derivatives are available, it affords the most direct route for synthesis of fluoranthene derivatives. The method has been further extended to the formation of the second *peri*-phenylene bridge (see Part 1b).

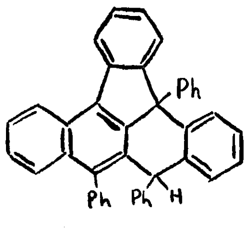
Higher Ring-systems Related to Fluoranthene.

1. Benzfluoranthenes.

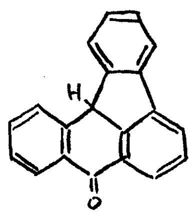
While the ring-system of 2:3—benzfluoranthene (E) has been mentioned several times in the literature, the parent hydrocarbon seems not to have been prepared. Bergmann (56), and Dufraisse and Amiard (57) confirmed that the compounds obtained by the action of metallic chlorides on tetraphenylanthracene and tetraphenyltetracene were (B) and (C) respectively.



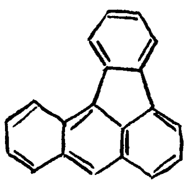
(B).



(C).

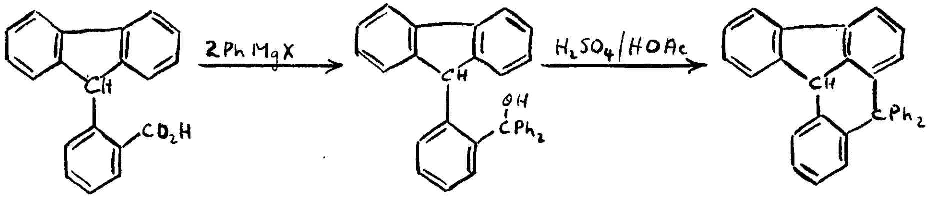


(D).



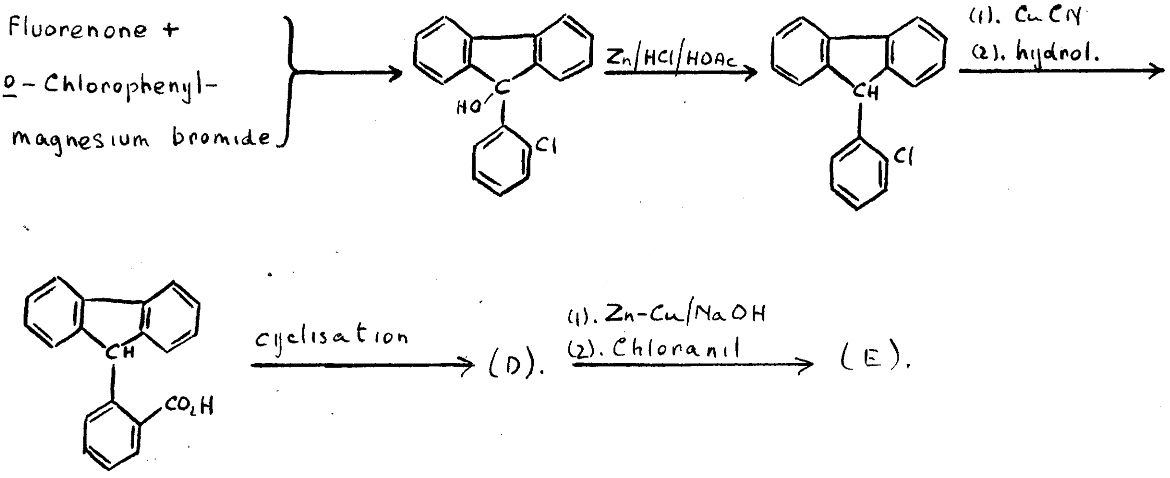
(E).

Although Weiss and Knapp (19) synthesised 1:9-phenylene-10-anthrone (D), they failed to convert it to 2:3—benzfluoranthene (E). Koelsch (20) prepared 4:4—diphenyl-1:4—dihydro-2:3-benzfluoranthene (F) by the following method:-

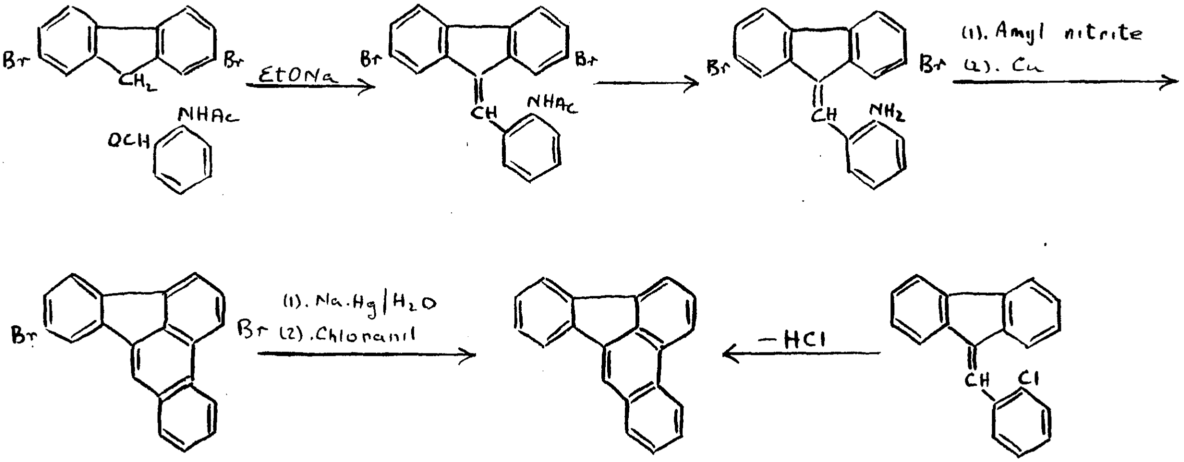


(F).

but makes no mention of the parent hydrocarbom. Concurrently with the work on the synthesis of 2:3-benzfluoranthene described later (Part 2), N. Campbell and Marks (21) accomplished a synthesis of the same compound independently by an alternative route, as outlined below.



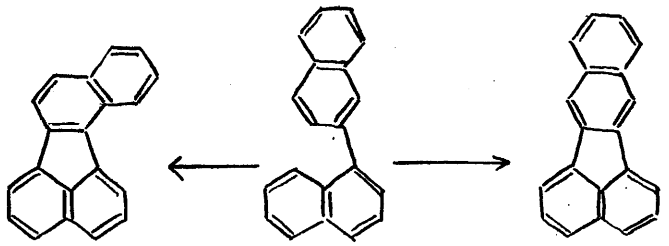
Tobler and co-workers (58) failed in attempts to prepare 4:11—dibromofluoranthene from 2:7—dibromofluorene, but synthesised 5:12—dibromo—3:4—benzfluoranthene, and from this obtained 3:4—benzfluoranthene (G), as shown:-



(G).

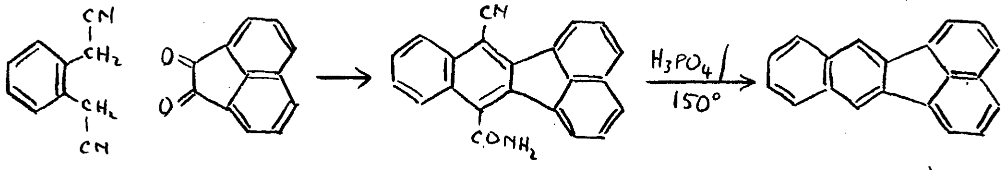
The compound (G), obtained thus, proved identical with that previously formed by cyclisation of 9—(o-chlorobenzal)—fluorene with alkali (59,60).

There are two possible benzfluoranthenes with the benz-ring fused to ring a of fluoranthene (A). These two isomers, 10:11- and 11:12—benzfluoranthene, (H) and (J) respectively, were first obtained by Orchin and Reggel (17) by cyclodehydrogenation of 1:2'—dinaphthyl:-



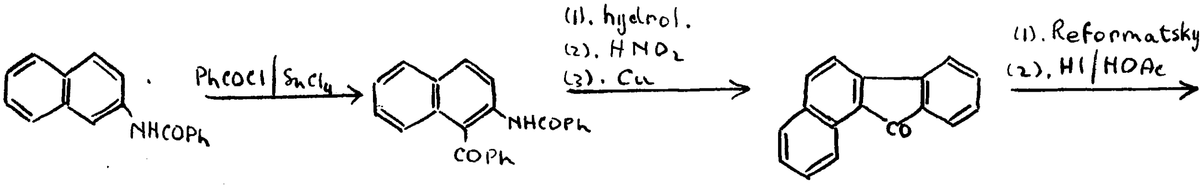
(H). (J).

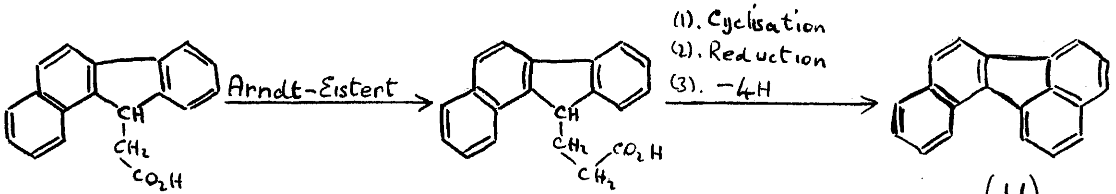
Maurea, Chovin, and Riveal (61-64) obtained 11:12—benzfluoranthene (J) by the following method,



(J).

while Orehin and Reggel (18) synthesised the 11:12- isomer by a method essentially the same as Maurea, Chovin, and Riveal's, and the 10:11- isomer by the method shown below. More recently N. Campbell, Khanna, and Marks (97) have described a new synthesis of 10:11—benzfluoranthene.

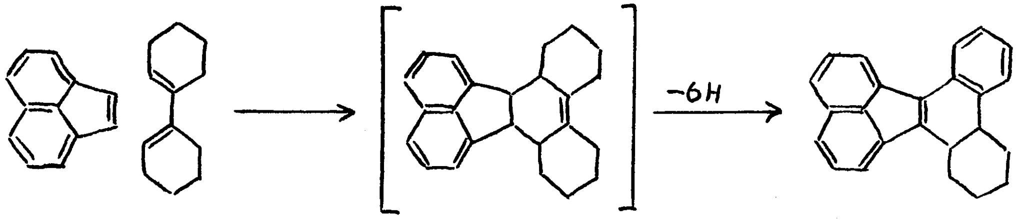




(H).

2:Dibenzfluoranthenes.

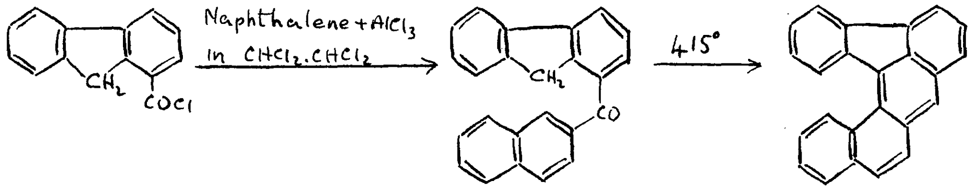
Of the dibenzfluoranthenes described in the literature, mention has already been made (p. 4) of 1:4:5—triphenyl-1:4-dihydro-2:3:6:7—dibenzfluoranthene (C), whose constitution was confirmed by conversion to 4:5—diphenyl—2:3:6:7-dibenzfluoranthene (55,29). Bergmann (65) carried out the Diels-Alder addition of dicyclohexenyl to acenaphthylene, and obtained, presumably by partial dehydrogenation, a compound with analysis corresponding to the formula (K).



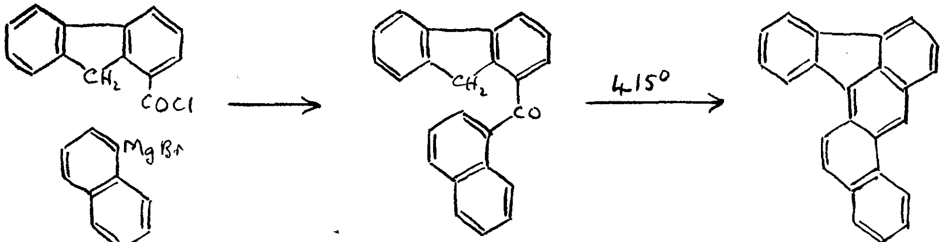
(K).

3. Naphthofluoranthenes.

The isomeric 1':2':2:3—naphthofluoranthene (L) and 2':1':2:3—naphthofluoranthene (M) were prepared by Fieser and Seligman (16) from fluorene-1-carboxylic acid (derived from fluoranthene) by the following methods:-

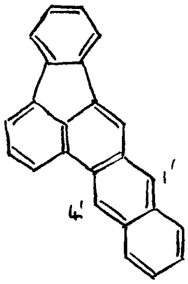


(L).

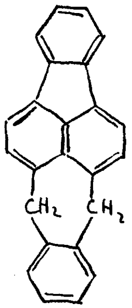


(M).

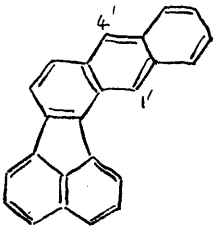
Pyrolysis of 4-o—toluoylfluoranthene (66) gave a mixture of 2':3':3:4—naphthofluoranthene (N) and its 1':4'-quinone with a hydrocarbon which gave 4:5—phthaloylfluoranthene on oxidation, indicating the probable structure (O), 4:5-o-xylylenefluoranthene, for this substance. In the same paper, N. Campbell, Marks, and Reid describe the



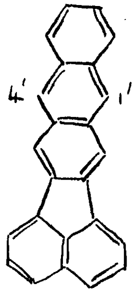
(N).



(O).

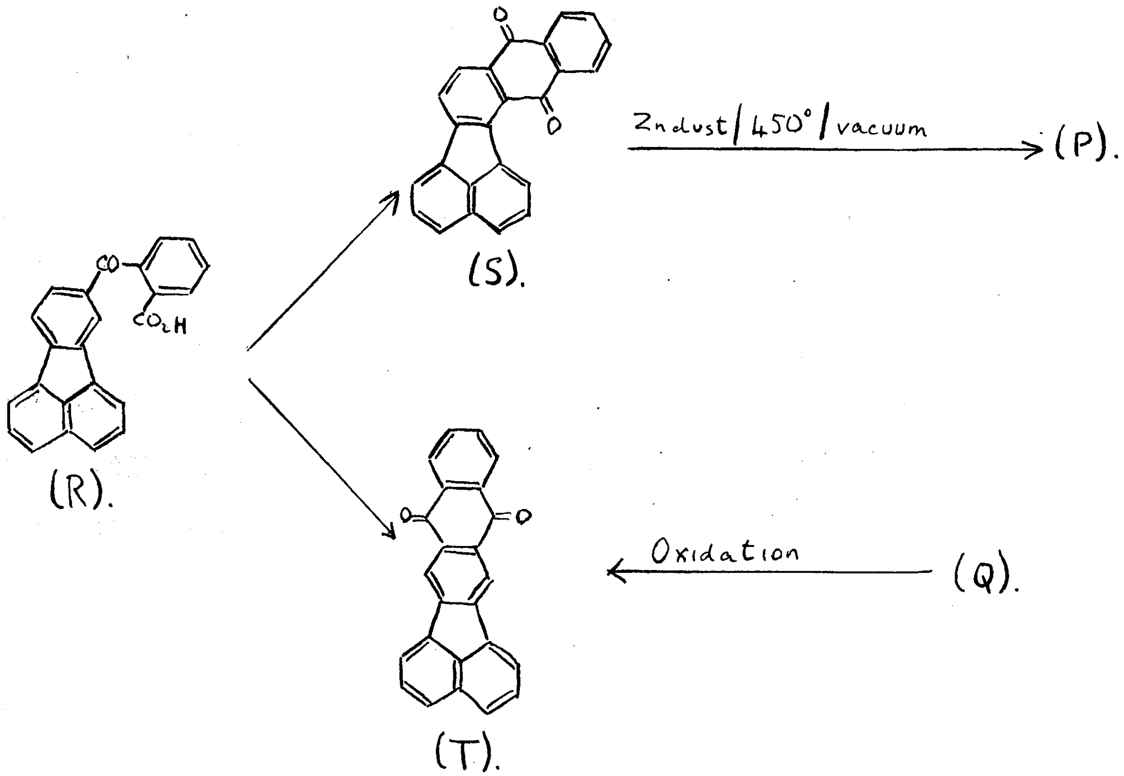


(P).



(Q).

pyrolysis of 11-*o*-toluoylfluoranthene to give 2':3':10:11-(P) and 2':3':11:12—naphthofluoranthene (Q). The two 1':4'-quinones, (S) and (T) respectively, derived from these hydrocarbons, were synthesised by von Braun and Manz (15) by dehydration of the compound (R) in boiling trichlorobenzene. Distillation of the quinone (S) from zinc dust in vacuum gave 2':3':10:11—naphthofluoranthene (P). Oxidation of the hydrocarbon (Q),

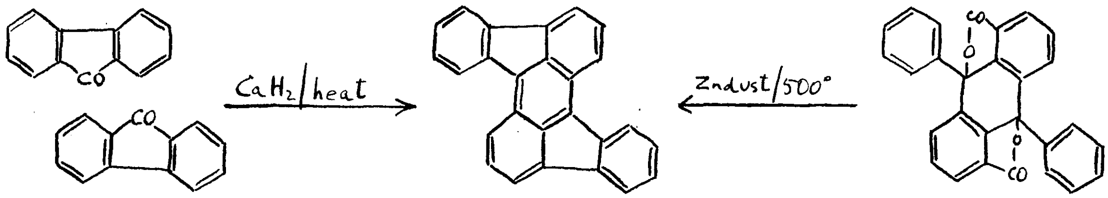


obtained by Campbell and co-workers (66), gave the corresponding quinone (T), identical with that obtained by von

Braun and Manz (15).

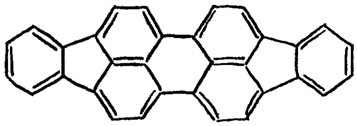
4. Compounds containing Two Five-membered Rings.

The preparation of rubicene (U) has been described several times (13,14,67-72), the usual method being a high temperature reaction on fluorene or one of its derivatives. Schlenk and Karplus (13) obtained rubicene by heating fluorenone with calcium hydride, while Scholl and Meyer (14) obtained it by reduction of the dilactone of 9:10-diphenyl-9:10—dihydroxy—9:10—dihydroanthracene—1:5—dicarboxylic acid with zinc dust.

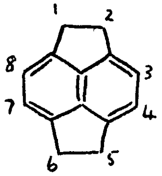


(U).

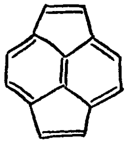
Von Braun and Manz (5,74), attempting to aminate fluoranthene by heating with sodamide - a method successful in the case of naphthalene - failed to obtain any amino-compound, but along with unchanged fluoranthene obtained a new hydrocarbon. Since 4:4'—difluoranthyl (obtained by an Ullmann reaction on 4—bromofluoranthene) gave the same compound, and 4-methyl- and 4—phenylfluoranthene failed to react in an analogous manner, they assigned the name di-perifluoranthene (or periflanthene) and the formula (V) to the hydrocarbon.



(V).



(W).

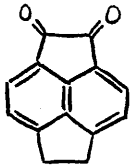


(X).

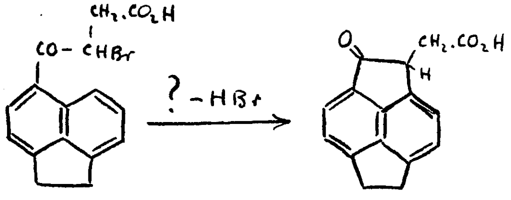
In view of the work reported later (Part 1b.) on the synthesis of 1:2:5:6—dibenzpyracylene (or bisperiphenylenenaphthalene, see note at end of paragraph), the most interesting members of the class with two five-membered rings are the derivatives of pyracene (W).

NOTE. The name bisperiphenylenenaphthalene was originally (31) adopted for compound (AD). The Journal of the Chemical Society preferred to name the compound after pyracylene (X), whose name is derived systematically from that of pyracene (W) (32). Hence (AD) becomes 1:2:5:6—dibenzpyracylene. This name has been adopted in this thesis for the sake of simplicity.

Mayer and Kaufmann (22) distilled 5—ethylacenaphthene from zinc dust, but instead of the hoped-for pyracene (W), obtained only acenaphthylene. Fleischer and Wolff (23), by the action of oxalyl bromide on acenaphthene in the presence of aluminium chloride, obtained a yellow compound to which they assigned the structure (Y) - "pyracene hemiquinone" - without confirmatory evidence.

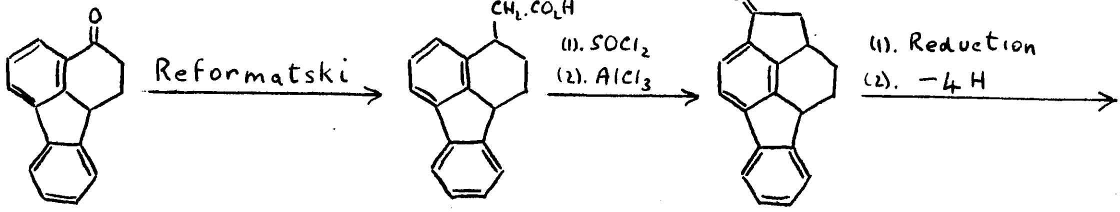


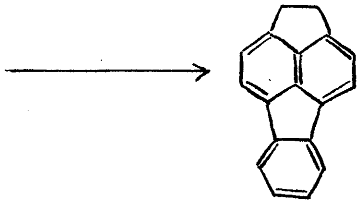
(Y).



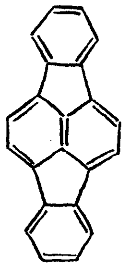
(Z).

Fieser and Peters (24) attempted to obtain the pyracene derivative (Z) by dehydrobromination of β-(5-acenaphthoyl)-β-bromopropionic acid, but reported that this cyclisation could not be accomplished. In view of this list of failures, Kloetzel and Chubb (25) utilised the tetrahydrofluoranthene derivative (AB), in the belief that the greater flexibility of the hydrogenated ring would facilitate cyclisation. They synthesised 1:2-benz-5:6-dihydropyracylene (4:5—dimethylene-fluoranthene) (AC) as follows:-



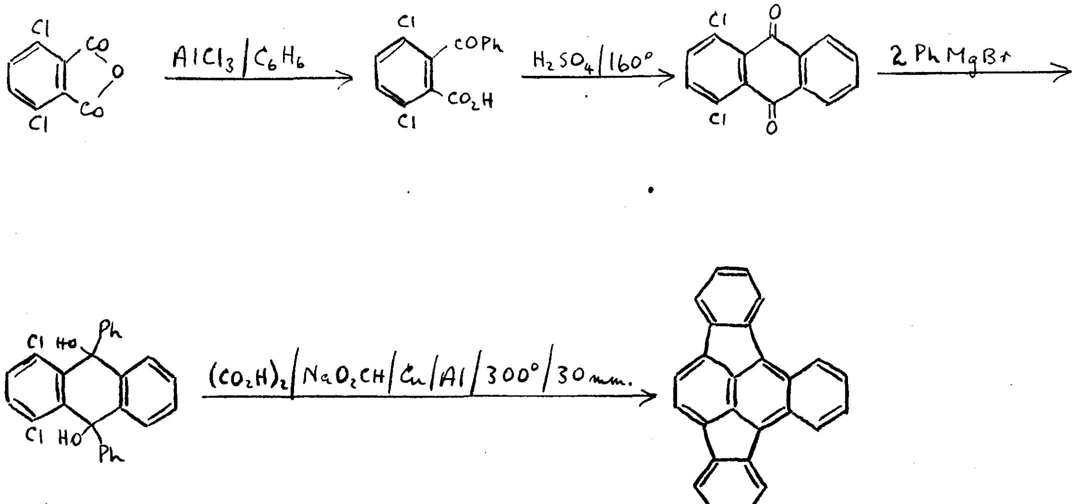


(AC).



(AD).

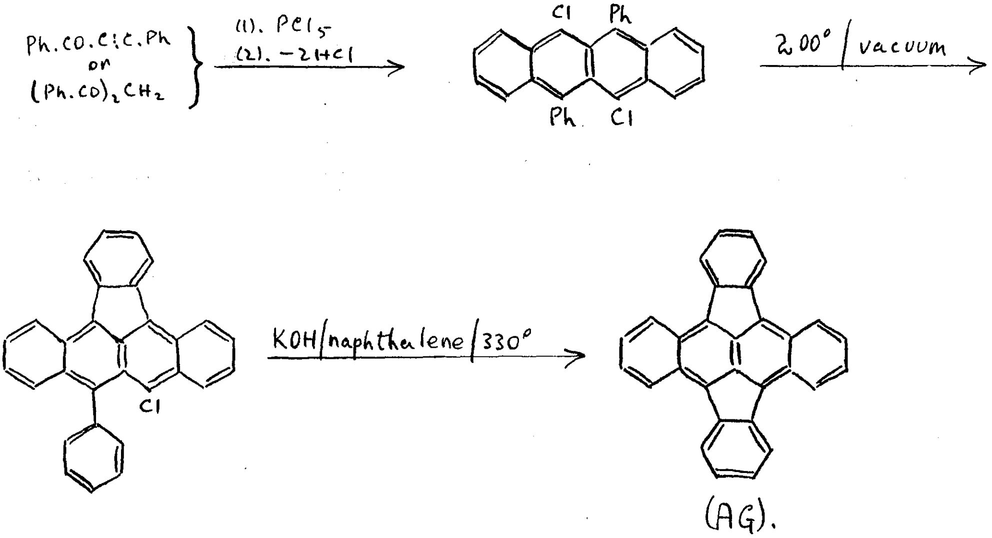
Federov (26) describes the synthesis of isorubicene (AF) by heating together 1:4-dichloro-9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene (AE), oxalic acid, sodium formate, copper powder, and aluminium powder:-



(AE).

(AF).

Dufraisse and co-workers (28-30) describe the synthesis of 5:6:11:12-diphenylenetetracene (AG) by the following series of reactions:-



Thus it would appear that, while formation of pyracene (W) or pyracylene (X) may be difficult (if not impossible), formation of benz- (e.g. AC), and more especially of poly-benzpyracylene derivatives (e.g. AF + AG), can be accomplished with varying degrees of readiness. This latter conclusion is supported by the smooth formation of 1:2:5:6—dibenzpyracylene (AD) described later (Part 1b).

Ultra-violet Absorption Spectra.

Little seems to have been published on the ultra-violet absorption spectra of fluoranthene and its derivatives. Seshan (33) describes the spectrum of fluoranthene, and Orchin and Woolfolk (75) compare its spectrum with that of its 2:4:7—trinitrofluorenone complex. Kloetzel and Chubb

(25) found that the spectra of fluoranthene and 4:5—dimethylenefluoranthene (AC) were similar, and Orchin and Reggel (17,18) report the spectra of 10:11- and 11:12—benzfluoranthene.

These are all isolated reports, however, and there appears to have been no attempt made to carry out a survey of the spectra of fluoranthene and its derivatives.

While Clar (93) applied his Anellation Theory to a wide variety of polycyclic hydrocarbons, he was unable to apply it to fluoranthene-type compounds as there were too few available. The purpose of the work described in Parts 1 and 2 of this thesis was, the preparation of two such hydrocarbons, previously unknown. As will be seen from the discussion in Parts 1b and 2, comparison of the absorption spectra of these two compounds, 1:2:5:6—dibenzpyracylene and 2:3—benzfluoranthene, with the absorption spectra of other related compounds conforms to theoretical predictions and affords further evidence of the validity of the Anellation Theory.

PART 1a. SYNTHESIS OF 4-METHYLFLUORANTHENE AND 4-PHENYLFLUORANTHENE

Von Braun and Manz (5) synthesised 4-methyl-(V) and 4-phenylfluoranthene (VI) by the action of the appropriate Grignard reagent on 4-keto-1:2:3:4-tetrahydrofluoranthene (3,34,35), followed by dehydration-dehydrogenation of the resulting compound. This method is not very suitable, particularly as the keto-compound presents difficulties in preparation. Robinson's adaptation of the Michael reaction using the Mannich base methiodides, has been applied to the synthesis of these two compounds, as described below.

Fluorene undergoes Michael addition to one molecular equivalent of an $\alpha\beta$-unsaturated ketone such as mesityl oxide, chalcone, or benzylideneacetone (8,36-40), but in practice the conditions of the reaction must be varied to suit each individual ketone: use of 9-fluorenyllithium extended the applicability of the reaction (8). In the course of the work described in this thesis, it was found that methyl vinyl and phenyl vinyl ketones failed to combine with fluorene - presumably due to polymerisation of the vinyl compound, under the prevailing alkaline conditions, before addition could occur. This failure is in striking contrast to the great reactivity of vinyl cyanide, which reacts with fluorene to give the di-addition product 9:9-di(2-cyanoethyl)-fluorene (41). On the other hand 2-methylvinyl cyanide (crotononitrile) combines with fluorene directly in 1:1-molecular proportion (41). On account of these results attention was directed towards the fluorene-9-carboxylic esters, which, as far as the Michael reaction is concerned, have a double advantage: they possess only one reactive hydrogen atom, and that is more reactive than either of the two hydrogen atoms on position 9 in fluorene (10,35). N. Campbell and Fairfull (38) have shown that 9-phenylfluorene and 9-fluorenol will also undergo Michael addition to vinyl cyanide.

Condensation of fluorene-9-carboxylic esters (particularly the methyl ester) with $\alpha\beta$-unsaturated ketones and cyanides has been uniformly successful, qualitatively and quantitatively, in providing 1:1 adducts uncontaminated by 1:2 addition products. Moreover, the products are readily cyclised to give rise to definitely oriented derivatives of fluoranthene (10,35). While it was found, as stated above, in the course of this work that methyl vinyl and phenyl vinyl ketones failed to react with fluorene, it was established at the same time that these vinyl ketones react quite readily with methyl fluorene-9-carboxylate (see below).

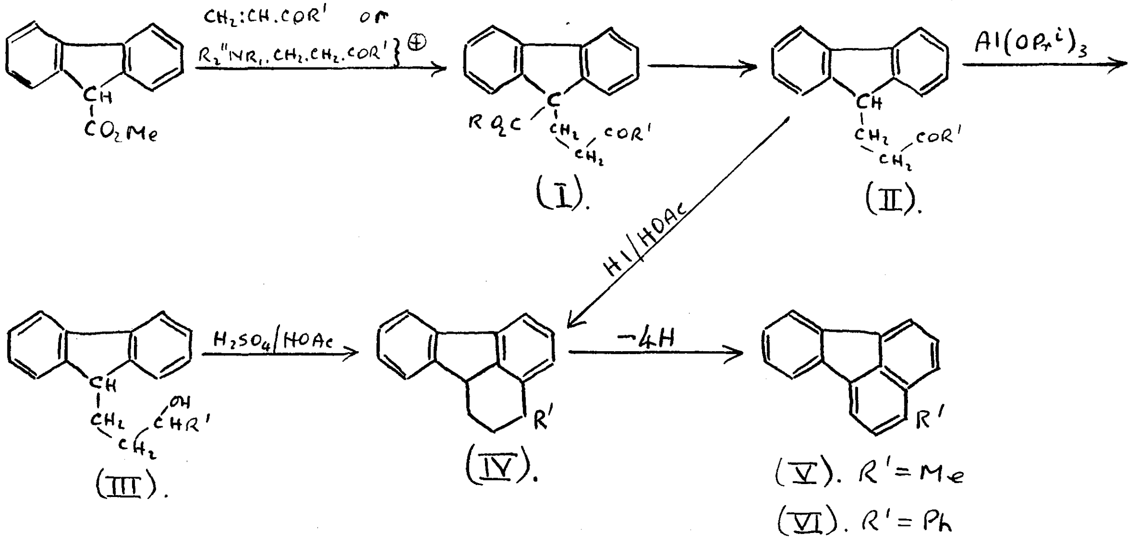
Vinyl compounds are, however, prone to polymerise. Accordingly attention was turned to the Mannich bases (42), which may, on appropriate treatment, give rise to vinyl ketones, or, better, may be used directly in place of vinyl derivatives. Du Feu, McQuillin, and Robinson (43), investigating substances "capable of ready decomposition with formation of the unsaturated ketones........ in minimal concentration and at optimal reactivity," in connection with their work on steroid synthesis, found that the β-chloralkyl methyl ketones were not suitable, but that the methiodides of the Mannich bases condensed with the sodio-derivatives of reactive methylene groups to give the required ketones in good yield.

The methiodide of methyl 2-morpholinoethyl ketone reacted smoothly with methyl fluorene-9-carboxylate in presence of sodium methoxide in boiling methanol to give 2—(9-carbomethoxy-9-fluorenyl) ethyl methyl ketone (I; $R = R' = Me$). Care was taken to remove excess methyl iodide from the methiodide for reasons outlined in the following paragraph.

The use of methyl sulphate in place of methyl iodide gave unexpected results. With the quaternary salt formed from methyl sulphate and either methyl 2-morpholinoethyl ketone or 2-morpholinoethyl phenyl ketone, methyl fluorene-9-carboxylate in presence of sodium methoxide in cold methanol, (and in the case of the former quaternary salt, in boiling methanol also), gave as sole product methyl 9-methylfluorene-9-carboxylate. This was identified by hydrolysis to the previously described (44,45) 9-methylfluorene-9-carboxylic acid, and decarboxylation of this to yield 9-methylfluorene

(46). In the case of the quaternary salt formed from methyl sulphate and 2-morpholinoethyl phenyl ketone (or 2-diethylaminoethyl phenyl ketone), when the reaction was carried out in <u>boiling</u> methanol, 2-(9-carbomethoxy-9-fluorenyl) ethyl phenyl ketone (I; R = Me; R' = Ph) was formed in excellent yield. In spite of the striking contrast in the products from the reaction of the methyl sulphate quaternary salts of the methyl keto— and the phenyl keto— compounds in boiling methanol, that there is no fundamental difference in the mode of reaction of the two Mannich bases is shown by the fact that, as shown above, when the quaternary salt of the methyl keto-compound is free of potential methylating agent (in the methiodide salt), reaction occurs in the same direction as in the case of the phenyl keto-compound. It may be that there is competition between methylation by $MeSO_4^{\ominus}$ and Michael addition to the incipiently formed vinyl compound. In the case of the phenyl keto-base the release of the vinyl compound must occur very rapidly, excluding the methylation reaction, whereas in the case of the methyl keto-base the release of the vinyl compound must occur so slowly that methylation takes place almost exclusively. That no methylation can occur when the quaternary salt is formed by the action of methyl iodide is a strong argument for its use in all cases in preference to methyl sulphate.

Methyl fluorene-9-carboxylate underwent Michael addition smoothly to both methyl vinyl and phenyl vinyl ketones in dioxan, using 0.2 mole of potassium hydroxide as catalyst. As found in previous work (10,35) increasing the amount of potassium hydroxide to one mole and/or adding pyridine lowered the yield of addition product. The addition products (I) were converted to 4-methyl- and 4-phenylfluoranthene as shown in the scheme.



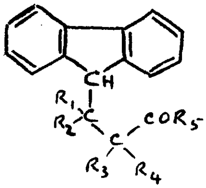
Conversion of (I) to (II) followed the established route (10,35) of hydrolysis by potassium hydroxide in warm aqueous ethanol, followed by decarboxylation on hot 10N-potassium hydroxide solution. In each case the reaction proceeded smoothly and in nearly theoretical yield. Attempts at hydrolysis and decarboxylation by boiling with aqueous-ethanolic barium hydroxide or potassium hydroxide, or with

10N-potassium hydroxide in 2-methoxyethanol (10,35) led to decreased yields of (II).

Reduction of 2-9'-fluorenylethyl methyl ketone (II, $R' = Me$) with aluminium *iso*propoxide in *iso*propanol solution gave 4-9'-fluorenylbutan-2-ol (III, $R' = Me$) as a low-melting solid, which liquified on keeping for a few days. Treatment of this solid with hot sulphuric acid-acetic acid gave 4-methyl-1:2:3:4-tetrahydrofluoranthene (IV, $R' = Me$), characterised as its 2:4:7-trinitrofluorenone addition complex. Dehydrogenation by means of chloranil in boiling xylene (10,47,48) gave 4-methylfluoranthene (V), identical (m.p., mixed m.p., and picrate m.p.) with that prepared by the method of von Braun and Manz (5).

Reduction of 2-9'-fluorenylethyl phenyl ketone (II, $R' = Ph$) with aluminium *iso*propoxide in *iso*propanol solution gave an uncrystallisable oil, which, on treatment with hot sulphuric acid-acetic acid, gave 4-phenyl-1:2:3:4-tetrahydrofluoranthene (IV, $R' = Ph$). This was readily dehydrogenated on fusion with sulphur to give 4-phenylfluoranthene (VI), identical (m.p. and mixed m.p.) with that prepared by the method of von Braun and Manz (5). 4-Phenyl-1:2:3:4-tetrahydrofluoranthene was dehydrogenated by chloranil in boiling xylene, but reaction was slow (*ca.* 24 hours) and accompanied by a side reaction. This may be due to a

Diels-Alder type reaction between chloranil and 4-phenylfluoranthene on prolonged contact in boiling xylene.



(IIa).

Ketones of the type (IIa) with substituents on the carbon atom(s) α and/or β to the keto group have been cyclised directly to give di- or tetrahydrofluoranthene derivatives, by the action of hydrogen bromide or hydrogen iodide respectively in acetic acid (6,7, cf. 49,50). Treatment of the ketones (II, $R' = Me$ or Ph) with hydrogen bromide in glacial acetic acid failed to produce any fluoranthene derivative. Cyclisation of (II, $R' = Me$) to give (IV, $R' = Me$) was accomplished in poor yield by boiling the ketone with a mixture of acetic and hydriodic acids.

Attempts to cyclise the amine corresponding to the carbinol (III, $R' = Ph$; NH_2 in place of OH) failed. The amine was prepared by hydrogenation of the oxime of (II, $R' = Ph$) in presence of palladium-charcoal catalyst (51-54).

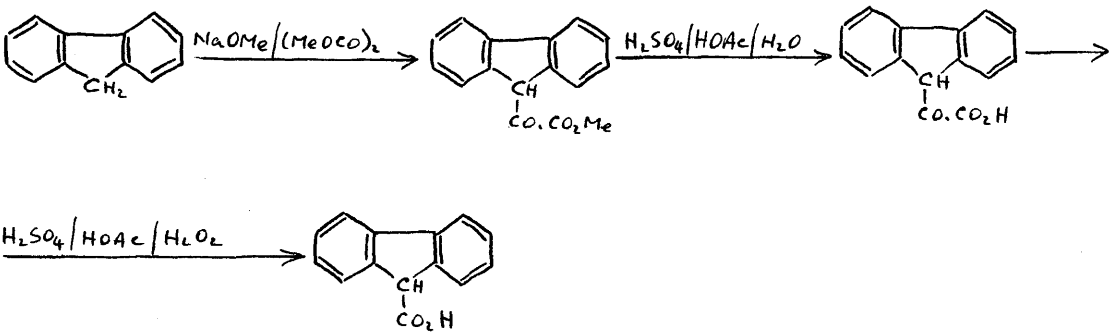
Methyl Fluorene-9-Carboxylate.

Although this compound is readily available, for theoretical reasons two new methods of preparation were attempted.

Arnold, Parham, and Dodson (98) dehydrated benzilic acid with aluminium chloride in benzene and obtained fluorene-

9-carboxylic acid in 82% yield, while Yost and Hauser (99) carbonated 9-fluorenylpotassium to give the acid in 72% yield (on the half-molar scales). Tucker and Whalley (8) carried out the similar reaction with 9-fluorenyllithium, the yield of acid in this case being 100% on unrecovered fluorene.

A synthesis of the acid from fluorene, in 76% yield, by the route shown below (without isolation of intermediates) is described by A. Campbell and Tucker (35).



An attempt to prepare the acid by an analogous oxidation of 9-formylfluorene (101) gave only an unidentified compound, insoluble in dilute alkali.

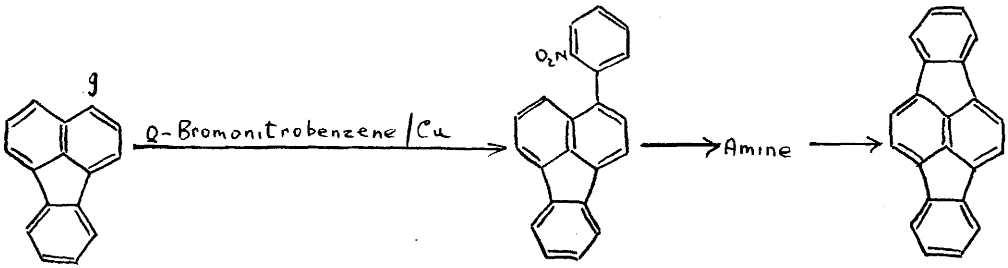
Blum-Bergmann (100) obtained methyl fluorene-9-carboxylate directly by the action of 9—fluorenyllithium on methyl carbonate. An attempt to carry out the analogous reaction between 9-fluorenylpotassium and ethyl carbonate failed: ethyl chloroformate and 9-fluorenylpotassium gave ethyl fluorene-9-carboxylate (36%).

PART 1b. SYNTHESIS OF 1:2:5:6-DIBENZPYRACYLENE

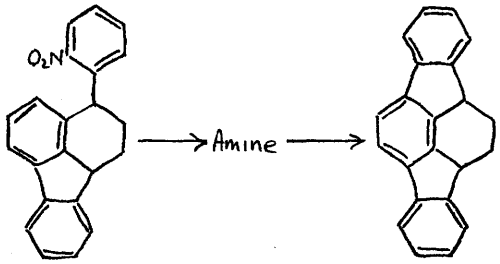
It was originally thought that cyclodehydrogenation of 4-phenylfluoranthene might, by analogy with Orchin and Reggel's work (17,18) (see p. 6), give 1:2:5:6—dibenzpyracylene (IX) directly. Attempts to accomplish this by heating 4-phenylfluoranthene with a mixture of anhydrous aluminium chloride and sodium chloride at 110-140° failed, however. In view of Kloetzel and Chubb's (25) opinion that the second five-membered ring might be closed more easily across the peri-positions of naphthalene if one of the naphthalene rings is in the tetra-hydro form, an attempt was made to cyclise 4-phenyl—1:2:3:4—tetrahydrofluoranthene (IV, R' = Ph) by treatment with aluminium chloride in boiling nitrobenzene, but the sole isolable product from this reaction was 4-phenylfluoranthene.

In view of these failures, attention was turned to two alternative routes. The first, and successful, method was by means of a crossed Ullmann reaction between 4-iodofluoranthene and 2-bromonitrobenzene, followed by reduction, diazotisation, and treatment with copper (formulae VII to IX) - an adaptation of the method of fluoranthene synthesis previously described (p. 3). The second, and unsuccessful, route was synthesis of 4-o-nitrophenylfluoranthene (VIII) by the method used for synthesis of 4-methyl- and 4-

phenylfluoranthene (Part 1a). This method would have the advantage of providing an opportunity for further investigation into the relative ease of cyclisation of naphthalene and tetralin derivatives, by comparison of the cyclisation of (IV, R' = o-nitrophenyl-) and (VIII) to give, respectively, 1:2:5:6-dibenz-2a:3:4:4a—tetrahydropyracylene (X) and 1:2:5:6-dibenzpyracylene (IX).



(VII). (VIII). (IX).



(IV, $R' = o\text{-}C_6H_4.NO_2$). (X).

Synthesis by the Ullmann Reaction.

The first stage in the synthesis required the previously unknown 4-iodofluoranthene (VII). Naphthalene and certain of its derivatives are readily iodinated (79) in the α-position by a variety of reagents, e.g. sodium iodide - sodium nitrate (7), potassium iodide - potassium iodate (9,80), iodine - nitric acid (77), iodine - silver perchlorate (78), and iodine - mercuric oxide (81,82). Attempts by these and other methods to iodinate fluoranthene all failed to yield 4-iodofluoranthene in workable quantity. This is in striking contrast to the facile bromination of fluoranthene (83) to give the 4-bromo-derivative. The bromo-compound was rejected in favour of the iodo- on account of the sparing reactivity of the former towards copper (5). 4-Iodofluoranthene was finally obtained by the usual method - reduction, diazotisation, and treatment with hydriodic acid - from the known 4-nitrofluoranthene (83). This method of preparation of the starting material established the orientation of compounds (VII) and (VIII), and hence the structure of 1:2:5:6-dibenzpyraclene (IX), since cyclisation of the diazonium compound is far more likely to take place with the reactive 5-position, forming a five-membered ring, than with the less reactive 3-position, of fluoranthene, forming a four-membered ring.

On heating to 210° in the presence of copper, 4-iodofluoranthene and o-bromonitrobenzene condensed to form 4-o-nitrophenylfluoranthene (VIII). Reduction of (VIII) to the corresponding amine was accomplished by hydrogenation in the presence of either 10% palladium-charcoal (in glacial acetic acid) or Raney nickel (in ethanol). The amine, an uncrystallisable oil, was characterised as the picrate, the hydrochloride having a wide melting range (210-250°) and indefinite analysis.

The amine, prepared as above and without further purification, was diazotised in sulphuric acid solution. Warming of this diazo solution with copper powder gave, after chromatographic purification, 1:2:5:6—dibenzpyracylene (IX) as orange needles, m.p. 261-262°. Rather unexpectedly the complexes formed with picric acid and 2:4:7—trinitrofluorenone were found to be unstable to crystallisation, presumably due to the relative insolubility of the hydrocarbon.

Attempted Synthesis by the Mannich Reaction.

For this synthesis, o-nitroacetophenone was required as starting material. Direct nitration of acetophenone (73,84,85) was unsuitable due to the difficulty of complete removal of the m-isomer. A modification of the synthesis from o-nitrobenzoic acid (86-88) was adopted, and found to give very pure o-nitroacetophenone in high yield, the method being applicable to large-scale runs with little trouble.

The Mannich base formed from o-nitroacetophenone, paraformaldehyde, and diethylamine hydrochloride (89), reacted explosively with methyl iodide in the absence of solvent.

In methanol solution, however, it formed a methiodide which condensed very readily with methyl fluorene-9-carboxylate (cf. pp. 19, 20) to form 2-(9-carbomethoxy-9-fluorenyl)-ethyl o-nitrophenyl ketone (I, R = Me, R' = o-$C_6H_4NO_2$). Attempts to hydrolyse and/or decarboxylate this by means of alkaline reagents gave only tarry products. Hydrolysis to 2-(9-carboxy-9-fluorenyl) ethyl o-nitrophenyl ketone (I, R = H, R' = o-$C_6H_4NO_2$) was accomplished by boiling with sulphuric acid in aqueous acetic acid. Decarboxylation occurred on heating to 170-180°, but the yield was low (21%); solution of the acid in boiling methyl cyanide was accompanied by smooth decarboxylation, in good yield (66%), to give 2-9'-fluorenylethyl o-nitrophenyl ketone (II, R' = o-$C_6H_4NO_2$). Neither the ketone (II, R' = o-$C_6H_4NO_2$) nor the ester (I, R = Me, R' = o $C_6H_4NO_2$) could be cyclised by means of anhydrous hydrogen bromide in glacial acetic acid (6,7,49,50), while treatment of the ketone (II, R' = o-$C_6H_4NO_2$) with hydriodic acid in boiling acetic acid gave an unidentified product (cf. p. 23). Furthermore, attempts to reduce the ketone by means of aluminium *iso*propoxide, so successful in the cases of similar compounds (pp. 2, 21, 22), failed, as did attempts to prepare an oxime [cf. v. Auwers, Lechner, and Bundesmann (90), who prepared the oxime of o-nitroacetophenone by boiling the latter for 24 hours with twice the theoretical amount of aqueous-alcoholic hydroxylamine sulphate]. This reluctance towards reduction and oxime formation may be due to enolisation and hydrogen-bonding of the resultant hydroxyl group with the o-nitro group.

Hydrogenation of 2-9'-fluorenylethyl o-nitrophenyl ketone in presence of Raney nickel (in ethyl acetate solution) proceeded smoothly with absorption of the theoretical volume of hydrogen required for reduction of the keto-nitro to carbinol-amine, but neither the latter nor its picrate could be isolated, and treatment of the oily hydrogenation product with sulphuric acid in acetic acid failed to yield any isolable 4-o-aminophenyl-1:2:3:4-tetrahydrofluoranthene (IV, R' = o-$C_6H_4NO_2$) (cf. pp. 2, 22).

Ultra-Violet Absorption Spectrum.

In Fig. 1 the ultra-violet absorption spectra of 4-phenylfluoranthene and of 1:2:5:6-dibenzpyracylene are compared. It will be seen that, although the curves show the same general form, that of the latter compound has considerable fine structure. In addition, the p-bands and β'-bands (91) of 1:2:5:6-dibenzpyracylene show a bathochromic shift in relation to those of 4-phenylfluoranthene. The comparison of the absorption curves of fluoranthene and 1:2:5:6-dibenzpyraclene in Fig. 2 is more informative. The proximity of the main β-bands in all three compounds (Figs. 1 and 2) is probably due to almost complete lack of

TABLE 1. Absorption Spectra of 1:2:5:6—Dibenzpyracylene and Fluoranthene in Ethanol. λ in Å.

	p-bands						β-bands							β'-bands	
Dibenzpyracylene	4100	4020	3870	3795	3670	3490	3170	3040	2925	2865	2810	2760	2705	2625	2530
Fluoranthene	3585	-	3420	-	3230	3090	-	-	2870	2820	2760	2715	-	2360	-

FIG. I.

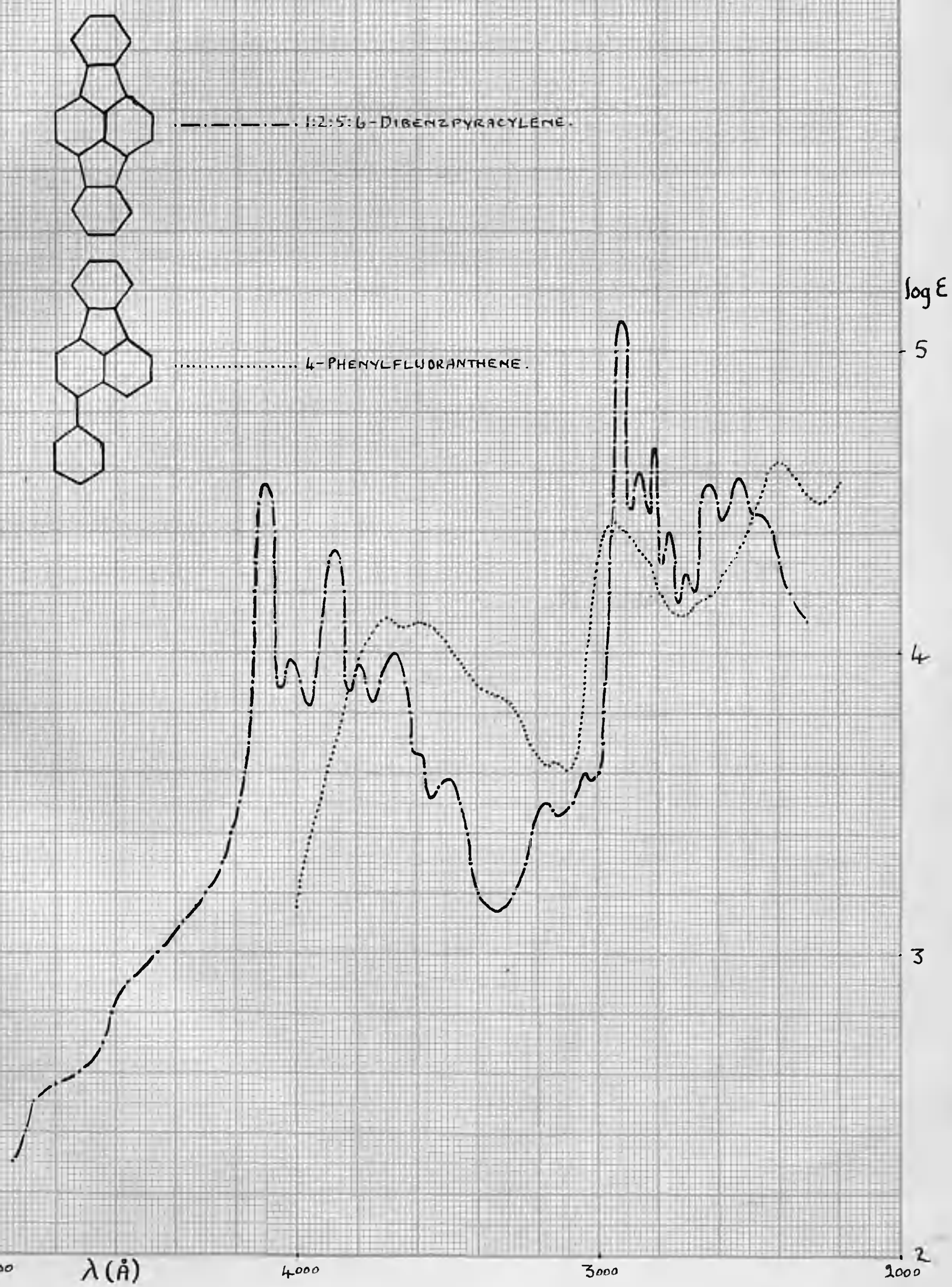
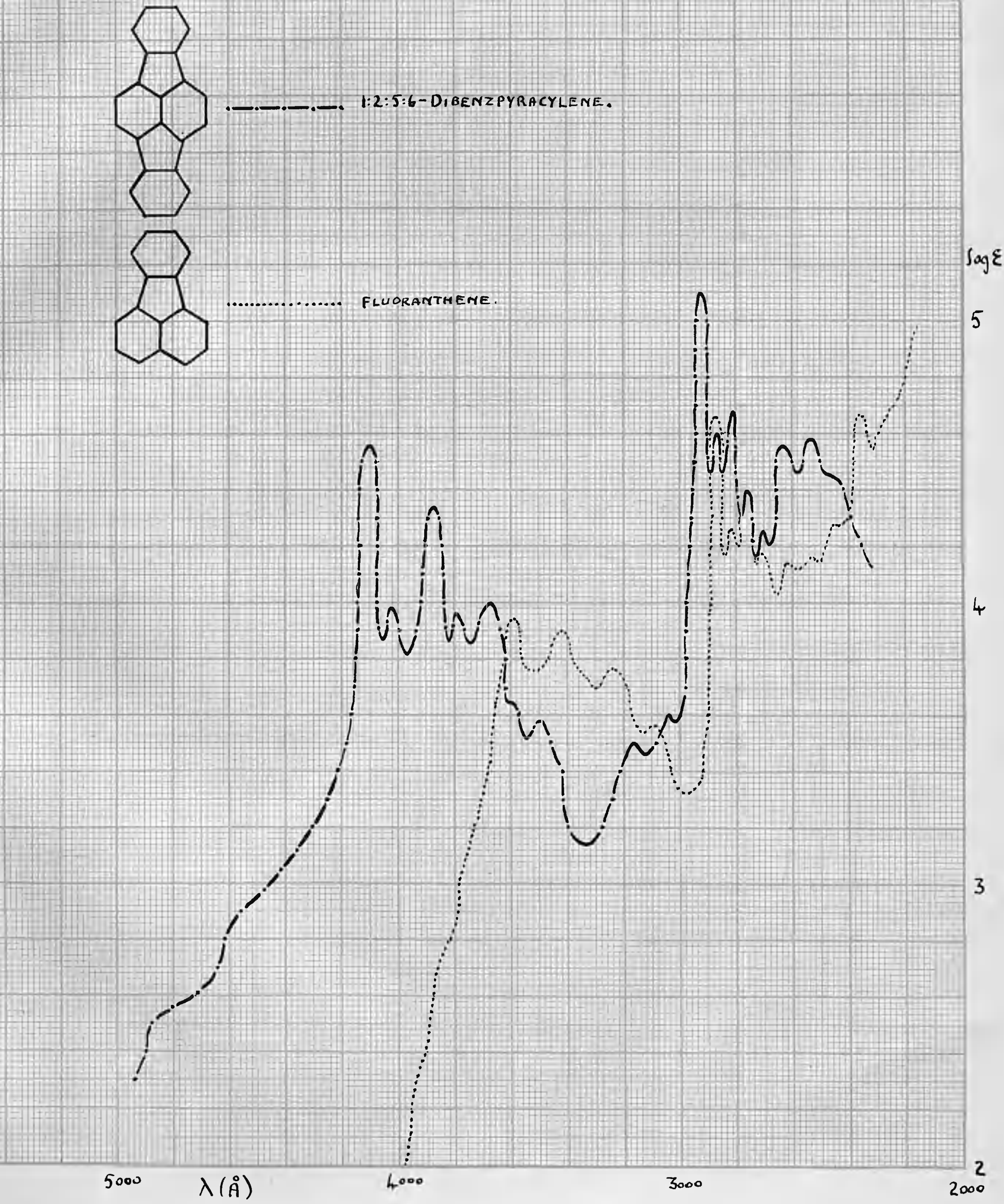
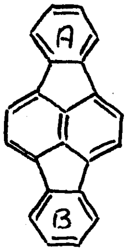

1:2:5:6-DIBENZPYRACYLENE.
4-PHENYLFLUORANTHENE.
log ε
5
4
3
2
5000
λ (Å)
4000
3000
2000

FIG 2.


1:2:5:6-DIBENZPYRACYLENE.
FLUORANTHENE.
log ε
5
4
3
2
5000
λ (Å)
4000
3000
2000

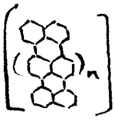
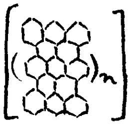
interaction between the π-electrons of rings A and B in 1:2:5:6—dibenzpyracylene, i.e. π-electron absorption in the three compounds mentioned above is restricted to the naphthalene rings.



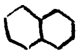
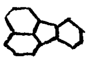
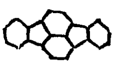
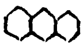
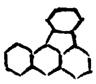
On the other hand, the much more intense fine structure of the spectrum of dibenzpyracylene, compared with that of fluoranthene, is similar to that observed with other hydrocarbons at very low temperatures (92), and is probably due to the molecule of dibenzpyracylene being rigidly planar at room temperature.

The first p-band in the spectrum of 5:6:11:12-diphenylenetetracene (AG) (27-30) occurs at 6100 Å, whereas that of 1:2:5:6—dibenzpyracylene is at 4100 Å. This difference corresponds approximately to two anellation units (93) and coincides with the relative data for naphthalene and tetracene: i.e. if $K_p = \sqrt{R_p . \lambda}$, where Kp is the anellation number for the p-band, R_p = 1,712,800, and λ (cm.) is the wavelength of the first p-band,

Kp (dibenzpyracylene)	= 8.380	Kp (naphthalene)	= 7.021
Kp (diphenylenetetracene)	= 10.222	Kp (tetracene)	= 9.006
	1.842		1.985

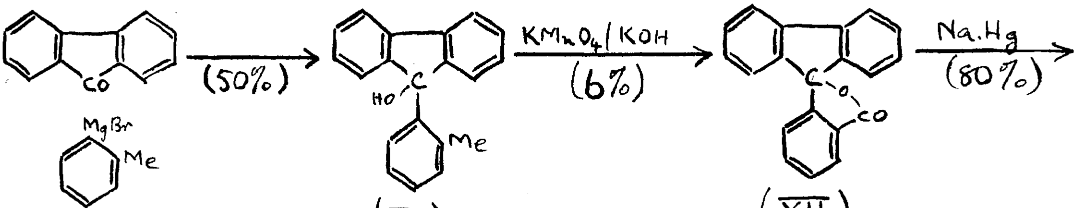
Clar (104) compared the spectra of the polyphenyls and found that, when wavelengths were measured in cm.$^{-1}$, the numerical differences between the values for the wavelengths of the first p-bands of succeeding members of the series were approximately in the ratio 1:½:¼:⅛:1/16......... Similar relationships were found for the polyrylene  and polyanthene  series, which had different ratios. Similar calculations applied to naphthalene, fluoranthene, and dibenzpyracylene give rise to the same geometrical progression as is obtained in the polyphenyl series, but it is doubtful whether any significance can be attached to these calculations. The relationship between anthracene and 2:3—benzfluoranthene is similar to that between fluoranthene and dibenzpyracylene. The results of these calculations are summarised in Table 2.

<u>TABLE 2</u>.

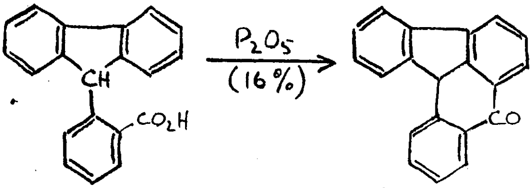
Compound	First p-band	Difference
	35,090 cm^{-1}	7200 (1)
	27,890 cm^{-1}	3500 (½)
	24,390 cm^{-1}	
	26,750 cm^{-1}	3390
	23,360 cm^{-1}	

PART 2. SYNTHESIS OF 2:3-BENZFLUORANTHENE

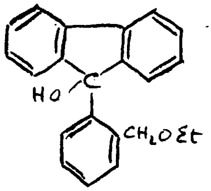
Weiss and Knapp (19) synthesised 1:9-phenylene-10-anthrone (XIV) as shown below, but the method left much



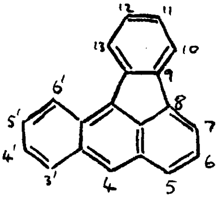
(XI). (XII).



(XIII). (XIV).



(XV).



(XVI).

to be desired, as two stages were accomplished in very low yield: Adams and Campbell (95) describe the preparation of (XI) in 78% yield by a modification of Weiss and Knapp's method. Koelsch (94) failed to accomplish the oxidation of (XI) to (XII), but (20) prepared o-diphenylenephthalide (XII) in 55-60% yield by chromic acid oxidation of 9-hydroxy-9-(ω-ethoxy-o-tolyl) fluorene (XV); Weiss and Knapp report that attempts to oxidise (XI) with fuming nitric acid gave nitration products only.

When attempts were made to oxidise 9-hydroxy-9-o-tolylfluorene (XI) with chromic acid in acetic acid, the only isolable product was fluorenone. Potassium permanganate in acetone (96) had no effect on (XI), while heating at 210° with 30% nitric acid gave a low-melting compound, presumably due to breakdown of the molecule. Long boiling (70 hours) of (XI) with 30% nitric acid in presence of manganese dioxide and nitrobenzene gave the phthalide (XII) in 50-55% yield.

Reduction of the phthalide to the free acid (XIII), cyclisation to the anthrone (XIV) and reduction of this to give 2:3-benzfluoranthene (XXI) was accomplished (in very low yield) in one step by fusion of the phthalide at 340° with zinc dust, zinc chloride, and sodium chloride (97). Confirmation of this, by reduction and dehydrogenation of the anthrone (XIV), was rendered superfluous by comparison of the zinc dust melt product with a sample kindly supplied by N. Campbell and Marks (see p. 5). The two samples were identical in appearance and m.p., and showed no depression on mixed m.p.

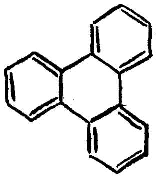
Reduction of the phthalide (XII) with hydriodic acid and red phosphorous failed to give any of the expected 2:3—benz-1:4-dihydrofluoranthene (XXII); the products were mainly 9-*o*-carboxyphenylfluorene (XIII) and a very small amount of 2:3-benzfluoranthene (XVI).

2:3—Benzfluoranthene dissolves immediately in concentrated sulphuric acid to give a yellow solution, which rapidly changes to violet, there being no further change on warming. A solution of 2:3—benzfluoranthene in light petroleum (b.p. 60-80°) when exposed to light and air deposited pale yellow crystals m.p. 208-211°. There was no sign of decomposition (e.g. loss of oxygen) on heating to the m.p.

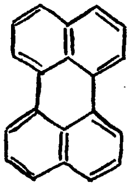
The ultra-violet absorption spectrum of 2:3—benzfluoranthene in ethanol is shown in Fig. 3. While the positions of the first p-bands (91) in fluoranthene (Fig. 2) and in 2:3—benzfluoranthene correspond approximately to the shift expected from the Anellation Theory (93), and the overall shape of the curves is similar, there are striking differences between the two compounds.

Using the relationship (93) $Kp = \sqrt{Rp.\lambda}$ (see p. 32), the values obtained for Kp for fluoranthene and 2:3-benzfluoranthene are 7.830 and 8.526 respectively, a difference of 0.732 anellation units. This is rather less than the theoretical value of 1, but the divergence is accounted for by the diffuse nature of the p-bands of 2:3—benzfluoranthene. Due to this effect, the true first p-band may be masked, and accordingly the value for Kp be lowered.

The diffuse nature of the p-bands, and more especially of the β- and β'-bands, of 2:3—benzfluoranthene is probably due largely to interference between the hydrogen atoms on the 13- and 6'-carbon atoms of (XVI), causing distortion of the molecule from the planar configuration. A similar effect is noted in triphenylene (XVII) and perylene (XVIII) (92), and also in certain fluoranthene derivatives substituted in the 2- or 10- positions (see Part 4). A considerable difference is observed between the curves of 2:3—benzfluoranthene and of 1:2:5:6—dibenzpyracylene (Fig. 2), which is more rigidly planar and shows greater complexity in its absorption curve (see p.32). The curve of 3:4—benzfluoranthene, superimposed on that of 2:3—benzfluoranthene in Fig. 3, shows less bathochromic shift in its p-bands than the 2:3- isomer, in relation to fluoranthene. This is in accordance with what is generally observed in linear and angular anellation (93). The α-bands, at 3630 Å for the 2:3- isomer and 3690 Å for the 3:4-, are very close, but 3:4—benzfluoranthene shows much more fine structure, especially in the β-bands. It will be observed that there is no opportunity for steric interference in this compound.

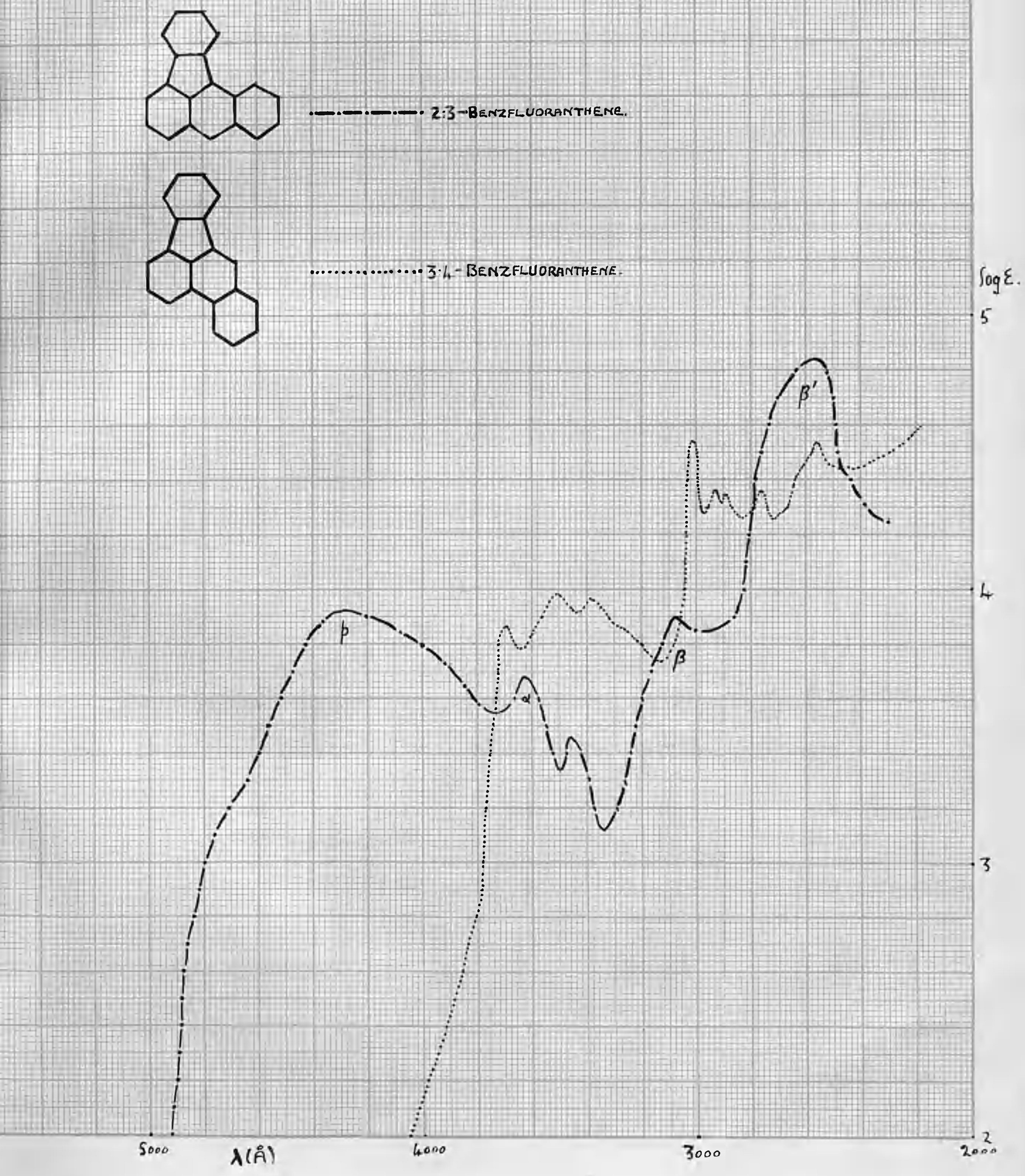


(XVII).



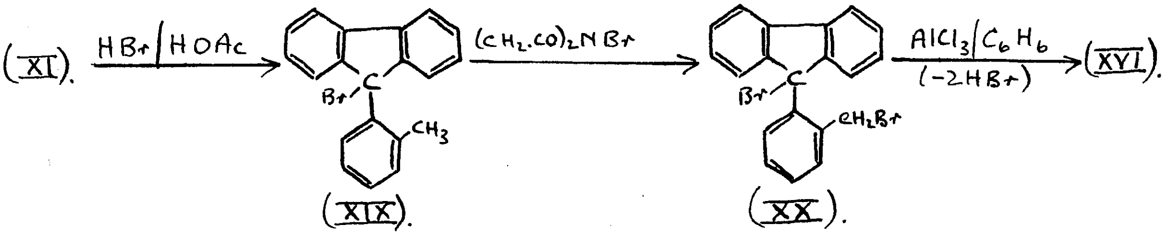
(XVIII).

FIG. 3.

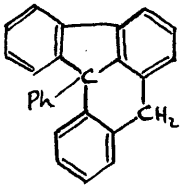

2:3-Benzfluoranthene.
3:4-Benzfluoranthene.
log E.
5
4
3
2
p
α
β
β'
5000
λ(Å)
4000
3000
2000

Synthesis of the Green Hydrocarbon.

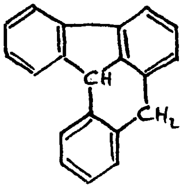
An attempt to synthesise 2:3—benzfluoranthene (XVI) by the following route failed: the main product was a pale green, strongly fluorescent, hydrocarbon, which may be 1:9-diphenylanthracene.



(XIX). (XX).



(XXI).



(XXII).

Bromination of 9-bromo-9-*o*-tolylfluorene (XIX) with N-bromosuccinimide in carbon tetrachloride with light/peroxide catalyst gave a crude product which could not be purified completely, but which consisted essentially of 9-bromo-9-(ω—bromo-*o*-tolyl) fluorene (XX). Treatment of this with aluminium chloride in boiling benzene gave a small amount of a yellow compound believed to be (XVI), but the major yield was the green hydrocarbon, m.p. 135-138°. Comparison of its spectrum with that of 9-phenylanthracene (Fig. 4) shows that the two are very similar, the green hydrocarbon showing a bathochromic shift compatible with the addition of one aryl group to 9-phenylanthracene. A comparison of the main absorption bands of these two compounds and of anthracene is shown in Table 3. 9-Phenylanthracene was synthesised by the method of Krollpfeiffer and Branscheid (102).

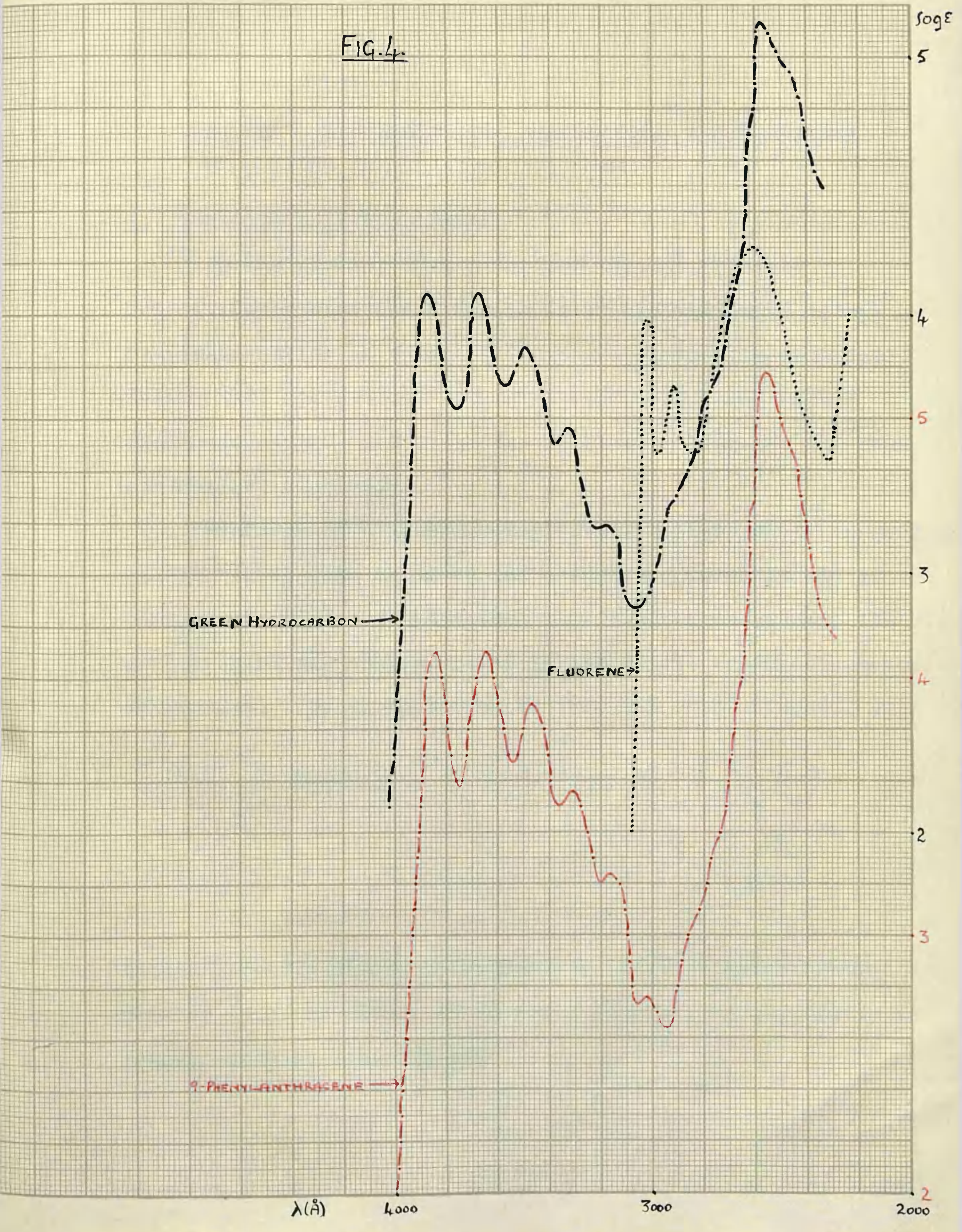
TABLE 3. Absorption spectra of Green Hydrocarbon, 9-Phenylanthracene, and Anthracene in Ethanol λ in Å.

Green hydrocarbon	3870	3670	3490	3320	3170	2580
9-Phenylanthracene	3840	3645	3465	3305	3160	2555
Anthracene	3745	3545	3380	3230	3080	2515

The green hydrocarbon (m.p. 135-138°) cannot be 1-phenylanthracene (m.p. 110°): that it is not 9-phenylanthracene (m.p. 155-157°) is shown by its different m.p. and ultra-violet absorption spectrum, while the spectrum of 2:3-benz-1:4—dihydrofluoranthene (XXII) would almost certainly resemble that of fluorene rather than of anthracene. The absorption curve for fluorene (103) is superimposed on that of the green hydrocarbon in Fig. 4.

Formation of an anthracene derivative from (XX) is understandable if, after cyclisation involving the bromomethyl group, the five-membered ring splits. Reaction of the 9-bromine atom in (XX) with the solvent, benzene, would give rise, after cyclisation, to 2:3-benz-1-phenyl-1:4-dihydrofluoranthene (XXI), which, due to molecular overcrowding round the 9-carbon atom of the fluorene nucleus, might rearrange to form 1:9-diphenylanthracene. This structure for the green hydrocarbon is supported by analysis and molecular weight determinations as well as by the ultraviolet absorption spectrum.

FIG. 4.

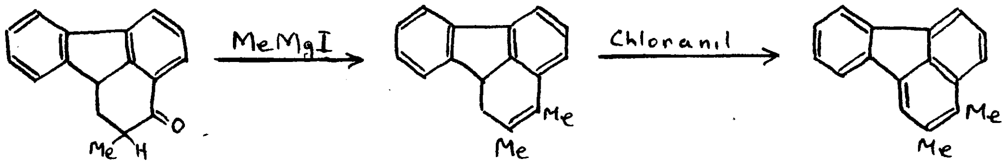

log ε
5
4
3
2
5
4
3
2
GREEN HYDROCARBON
FLUORENE
9-PHENYLANTHRACENE
λ(Å)
4000
3000
2000

PART 3. SYNTHESIS OF SUBSTITUTED FLUORANTHENES

1. 3:4-Dimethylfluoranthene.

As has already been described (pp. 1, 2, 17), 4-methylfluoranthene can be prepared by the action of methyl magnesium halide on 4-keto-1:2:3:4—tetrahydrofluoranthene. Tucker (10) synthesised 2:4—dimethylfluoranthene in an analagous manner, and 3:4—dimethylfluoranthene has now been synthesised similarly.

Treatment of 4-keto-3-methyl-1:2:3:4-tetrahydrofluoranthene (XXIII) (105) with an excess of methyl magnesium iodide in benzene-ether gave 3:4-dimethyl-1:2-dihydrofluoranthene (XXIV), an oil which was characterised as its 2:4:7-trinitrofluorenone derivative. Dehydrogenation of this oil with chloranil in xylene gave 3:4-dimethylfluoranthene (XXV) as bright green needles, m.p. 83-85°. It formed a picrate, crystallising as orange needles, m.p. 181-182°.



(XXIII). (XXIV). (XXV).

2. 2-Methoxyfluoranthene.

Hawkins and Tucker (12) synthesised 11-methoxyfluoranthene by the crossed Ullmann method (pp.3,4). This was the only known methoxyfluoranthene, and as others were required for spectrographic comparison, the 2-isomer was synthesised in a similar manner.

1-Iodo-2-methoxynaphthalene was obtained by the method of Jurd (82), i.e. treatment of β-naphthyl methyl ether with iodine and yellow mercuric oxide in 95% ethanol. Fusion of this iodo-compound with o-bromonitrobenzene and copper gave, as expected, 2-methoxy-1-o-nitrophenylnaphthalene (XXVI). Hydrogenation of this in presence of Raney nickel in ethanol gave the amine (XXVII), which could not be crystallised, but which was purified and characterised as its picrate. After recovery from the pure picrate - by decomposition of the salt with aqueous ammonia and extraction of the amine with ether - the amine was diazotised and the scarlet diazo-solution warmed with copper powder, yielding 2-methoxyfluoranthene (XXVIII) as green feathers, m.p.111-113°. Determination of the methoxyl content eliminated the possibility of cyclisation involving the methoxyl group.

PART 4. ULTRA-VIOLET ABSORPTION SPECTRA OF SUBSTITUTED FLUORANTHENES

In a review (109) on the ultra-violet absorption spectra of aromatic hydrocarbons, Jones was "concerned primarily with an assessment of the possibilities and limitations of ultra-violet spectraphotometry as a method of characterising aromatic hydrocarbons." It was with a similar aim that the compilation of data on the absorption spectra of the known simply substituted fluoranthenes was undertaken, and the results and deductions are set out in the following pages. While more fluoranthene derivatives are still in the process of being synthesised and will be examined spectroscopically in due course, a sufficient number have been examined to show that the spectra conform to a simple pattern. This thesis is concerned primarily with a study of empirical relationships, rather than of theoretical interpretations, of the ultra-violet absorption spectra.

It is generally recognised (109) that replacement of a hydrogen atom by a methyl group in an aromatic hydrocarbon has little effect on the general shape of the absorption curve, but usually produces a shift of the main absorption bands to longer wavelengths. This shift is, in general, slight. Brade and Patterson (110) found that the monomethylchrysenes conformed to this rule, but also discovered that steric hindrance effects in 4- and 5-methylchrysene caused greater variations in the curve than was observed in the case of the other methylchrysenes. They found that there were sufficient differences in the absorption spectra of the monomethylchrysenes to make the use of absorption spectra a practical method of characterisation in the pure state.

The mono-, di-, and trimethylfluoranthenes studied (Table 4; Figs. 5-7) show similar results. It will be seen that the substitution of one or more methyl groups in the fluoranthene nucleus produces a shift towards the red end of the spectrum of most of the absorption maxima, the effect being in general the greater the more substituent methyl groups there are present. Substitution of a methyl group in either the 2- or the 10- position, where steric hindrance between this group and the hydrogen in the alternative position is possible - producing distortion of the molecule from its normal planar configuration - causes flattening of the curve, particularly in the region of the first two p-bands, in each of the four possible cases of this type (Figs. 5-7). Where the substituent is the bulkier methoxyl group (see below) the effect is much more pronounced, and is similar to that observed in 2:3—benzfluoranthene (p. 36).

The introduction of groups capable of greater electronic interaction with the nucleus, viz., phenyl- or methoxyl-, produces greater variations in the absorption curve. Comparison of the spectrum of 4-phenylfluoranthene with that of

TABLE 4. Ultra-violet absorption spectra in ethanol.

Bands	Fluoranthene	Methyl-					dimethyl-		tri-methyl			
		2-	3-	4-	10-	11-	2:4-	3:4-	2:3:4-	4-Ph	2-OMe	11-OMe
p-	3620	3635	3620	3640	3670	3620	3680	3660	3670	3700	3720	3610
	3600	-	-	-	-	-	-	-	-	-	-	-
	3440	3480	3460	3480	3530	3460	3520	3495	3520	3580	-	3440
	-	-	-	-	-	-	-	-	3410	-	-	-
	3230	3270	3265	3275	3280	3260	3280	3290	3300	-	3275	3240
	3090	3130	3115	3120	3135	3100	3140	3135	3150	3145	3120	3100
β-	2870	2865	2895	2905	2900	2900	2905	2930	2925	2940	2855	2950
	2810	-	-	2850	-	2840	-	-	-	-	-	-
	2770	2765	2790	2800	2800	2790	2795	2815	2810	-	2760	2850
	2715	-	-	-	-	-	-	-	-	-	-	-
β′-	2615	-	2620	2640	-	2660	2630	2680	2640	-	-	-
	2530	-	2535	-	-	-	-	2545	-	-	-	-
	2450	-	-	-	-	-	-	-	-	-	-	-
	2360	2390	2365	2390	2420	2360	2420	2405	2430	2405	2465	2360
	-	-	-	2300	-	-	-	-	-	-	-	-

fluoranthene (Fig. 8) shows that several prominent maxima present in the latter compound have disappeared or become points of inflexion in the former, the whole curve, while retaining the general fluoranthene pattern, showing much less fine structure. Other aryl-substituted aromatic hydrocarbons show analogous effects in their spectra (109).

Comparison of the curves of 2- and 11-methoxyfluoranthene with that of fluoranthene (Fig. 9) shows several interesting points. The 2-isomer, with the possibility of distortion due to steric hindrance, shows a considerable red-shift (100Å) of the p-bands, disclosing an α-band at 3275Å, whereas the maxima of the 11-isomer, with no possibility of steric hindrance, are very near to those of fluoranthene. Furthermore, the p-bands of the 2-isomer are considerably broadened, while the β-bands are depressed and the β'-band increased in intensity. This is very similar to the effect observed in the absorption curve of 2:3-benzfluoranthene (Fig. 3), likewise attributed to steric hindrance distorting the planarity of the molecule.

Thus it may be concluded that:

(1) The ultra-violet absorption spectra of the mono-, di-, and trimethylfluoranthenes measured are very similar to that of fluoranthene, but are sufficiently distinct to make their use of practical value in characterisation of the pure compounds.

(2) Substitution by phenyl or methoxyl groups produces greater variations in the curves, which still retain the

fluoranthene form.

(3) The possibility of overlapping of hydrogen and substituent groups is probably reflected in the spectra.

Details of the method used to measure the absorption spectra are given in the Experimental Section.

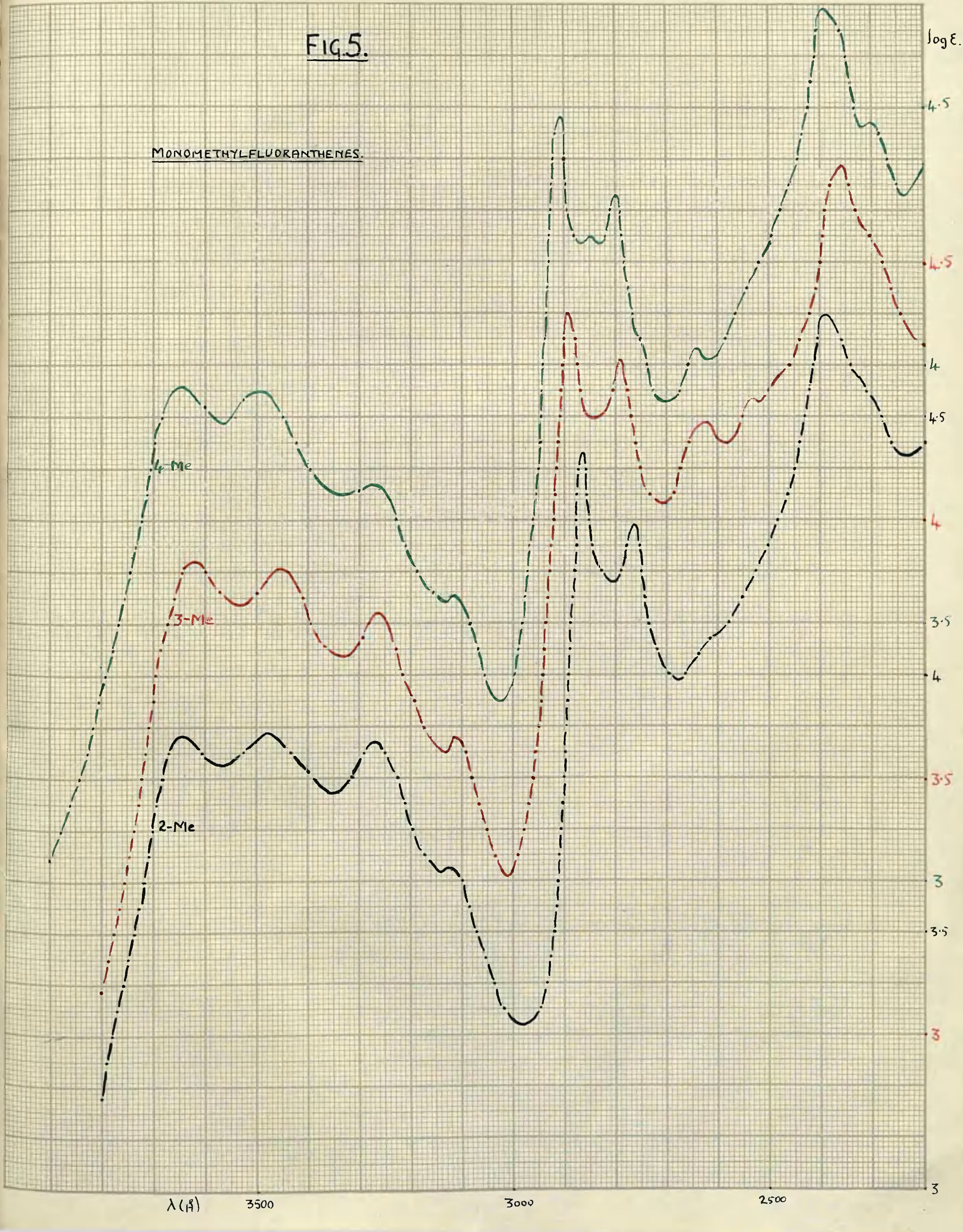


FIG.5.

MONOMETHYLFLUORANTHENES.

FIG. 6.

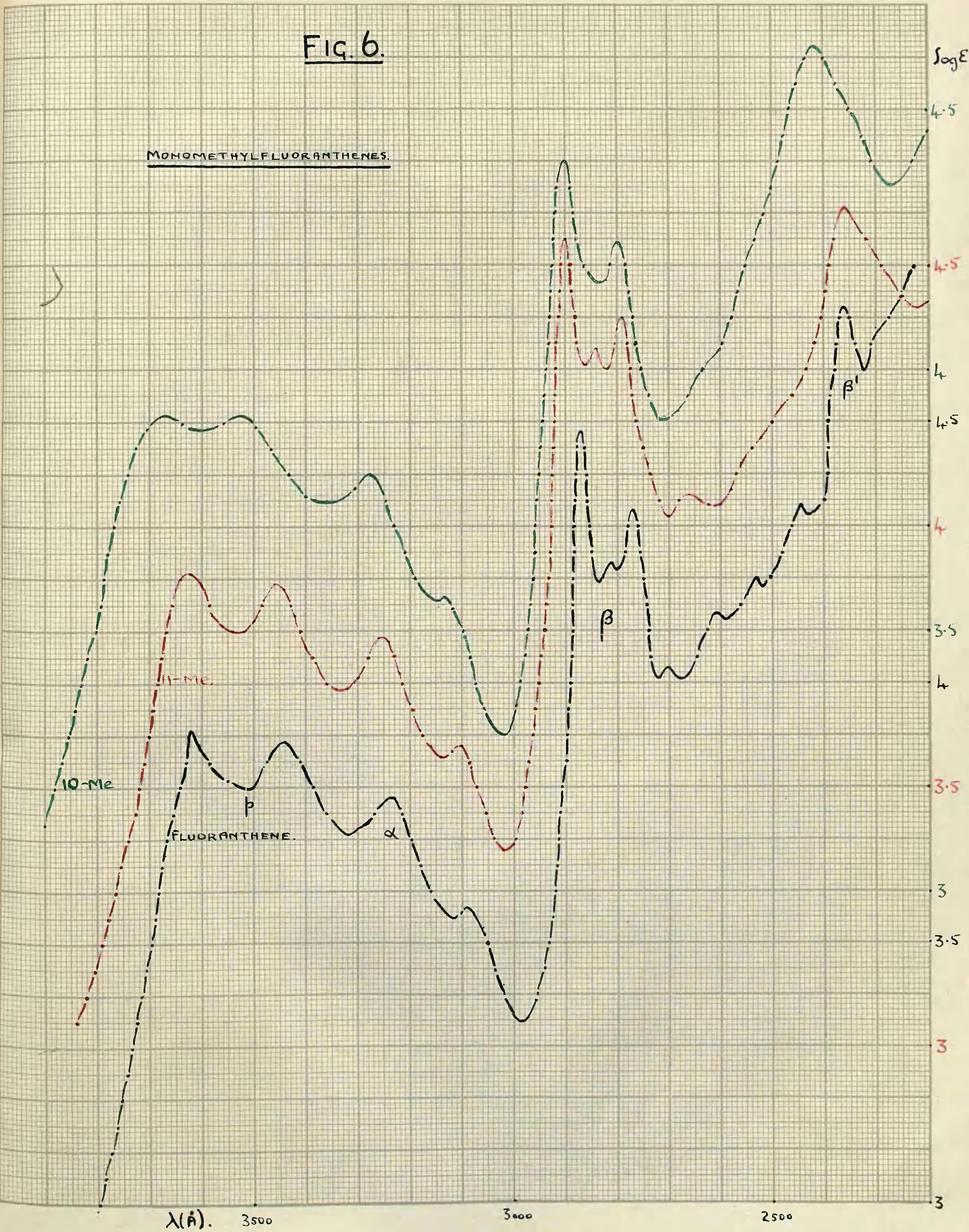

MONOMETHYLFLUORANTHENES.
log ε.
4·5
4·5
4
4·5
4
3·5
4
3·5
3
3·5
3
3
10-Me
11-Me.
FLUORANTHENE.
p
α
β
β'
λ(Å).
3500
3000
2500

FIG. 7.

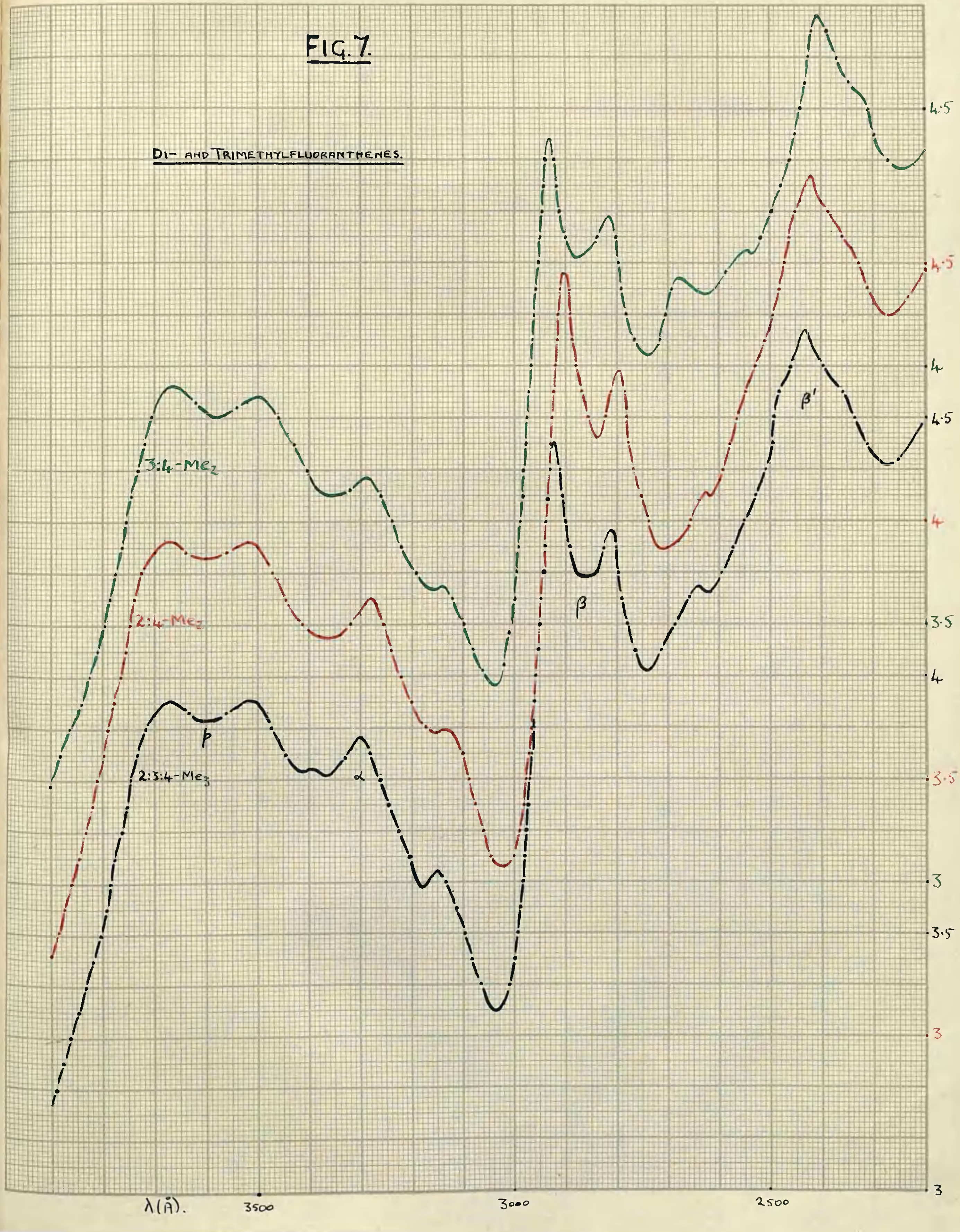

DI- AND TRIMETHYLFLUORANTHENES.
3:4-Me$_2$
2:4-Me$_2$
2:3:4-Me$_3$
p
α
β
β'
4·5
4·5
4
4·5
4
3·5
4
3·5
3
3·5
3
3
λ(Å).
3500
3000
2500

FIG. 8.

4-PHENYLFLUORANTHENE.

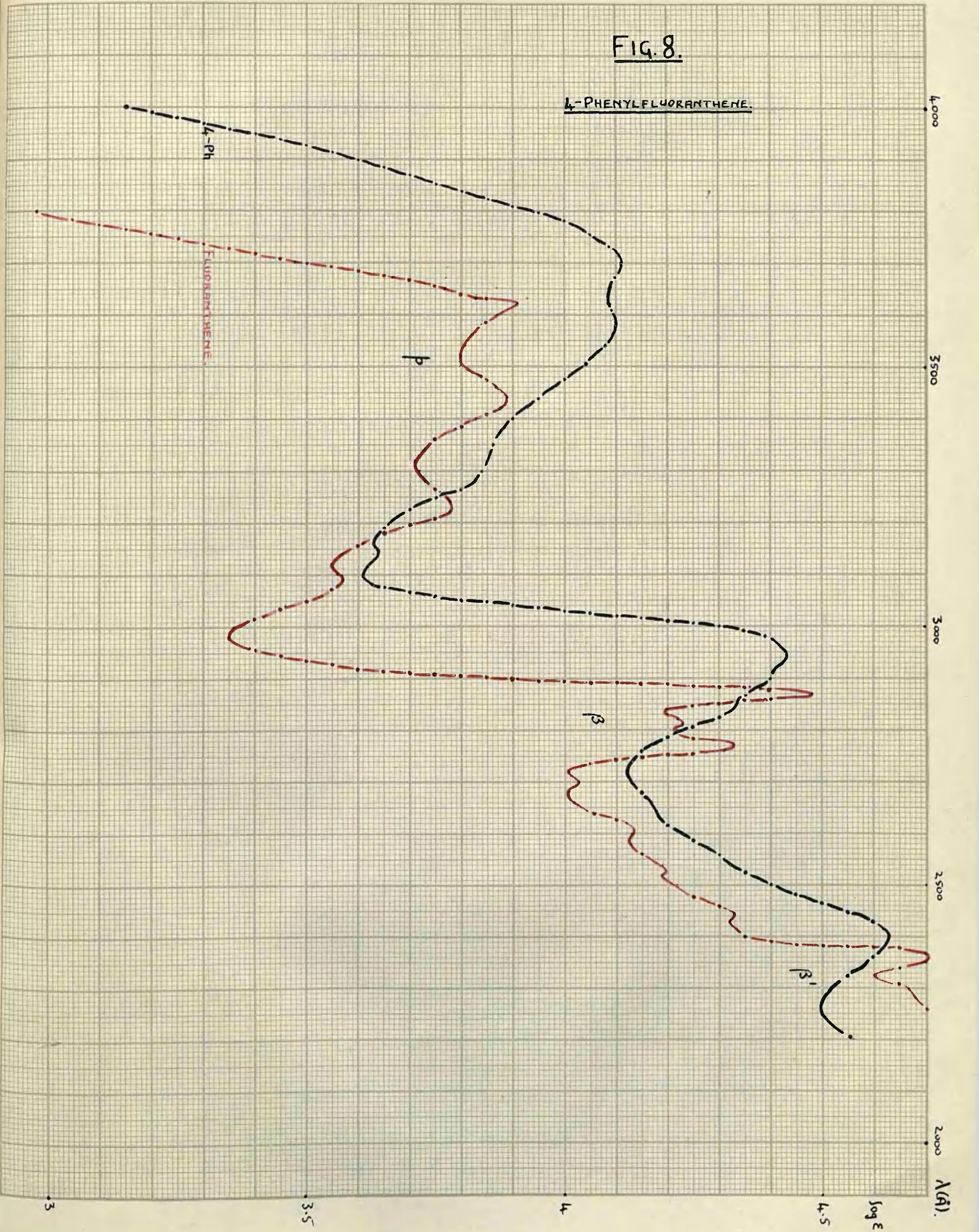
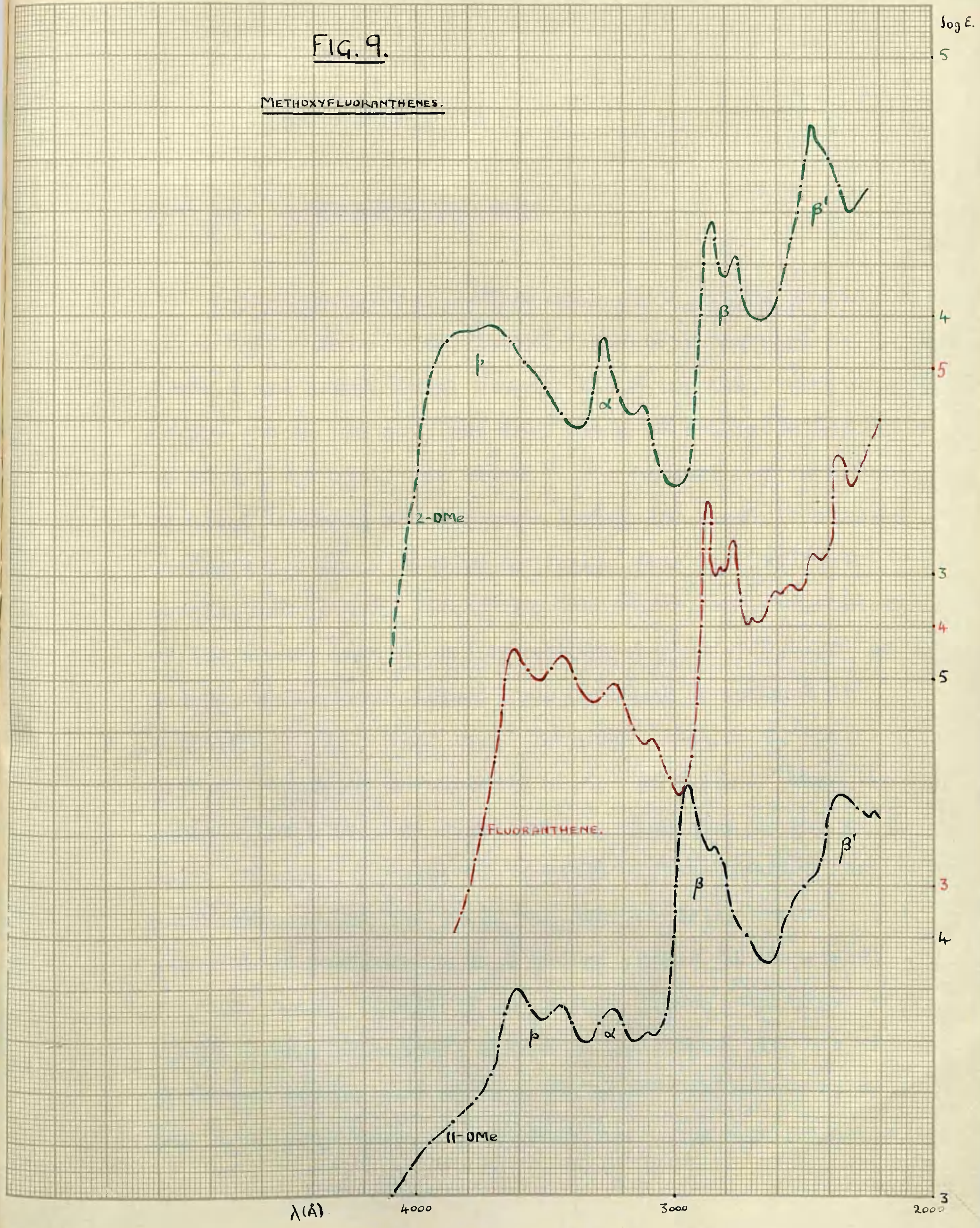


FIG. 9.

METHOXYFLUORANTHENES.



EXPERIMENTAL

PART 1a; 4-METHYLFLUORANTHENE.

2-(9-Carbomethoxy-9-fluorenyl) ethyl Methyl Ketone

(I, R = R' = Me). (a) Methyl fluorene-9-carboxylate (11.2 g., 1 mol.) and methyl vinyl ketone (3.5 g., 1 mol.) were dissolved in dry dioxan (55 ml.) and dry, powdered potassium hydroxide (0.56 g., 0.2 mol.) was added. The mixture was kept for 24 hours (warming was observed during the first 15 minutes), during which the potassium hydroxide went into solution. Pouring into water, extraction with ether, and evaporation of the ether, gave 2-(9-carbomethoxy-9-fluorenyl)ethyl methyl ketone, which crystallised from methanol or ethanol in leaflets (10.5g., 71%), m.p. 101-103° (Found: C,77.5; H, 6.2. $C_{19}H_{18}O_3$ requires C, 77.5; H, 6.2%). When the quantity of potassium hydroxide was increased to 2.8 g. (1 mol.) the product required repeated crystallisation for purification, and the yield was substantially lower. The addition of pyridine (1 ml.) had no effect on the yield.

(b) Methyl iodide (1 g., slight excess) was mixed with methyl 2-morpholinoethyl ketone (1 g.) (106), and the excess of methyl iodide removed from the pasty methiodide by applying water-pump vacuum for 30 minutes. The methiodide, which had a slight smell of methyl vinyl ketone, was washed with methanol (5 ml.) into a solution of methyl fluorene-9-carboxylate (1.42g.) and sodium (0.15g.) in methanol (5 ml.), and the resulting mixture boiled (90 minutes). On cooling, crystals (0.8 g., 45%) were deposited, the m.p. of which and of a mixture with an authentic specimen of 2-(9-carbomethoxy-9-fluorenyl)ethyl methyl ketone was 101-102°.

2-(9-Carboxy-9-fluorenyl)ethyl Methyl Ketone (I, R = H, R' = Me). The above methyl ester was dissolved in hot ethanol and a small amount of ION-potassium hydroxide solution added. Working up in the usual manner gave 2-(9-carboxy-9-fluorenyl)ethyl methyl ketone, which crystallised from methyl cyanide in prisms, m.p. 108-113° (decomp.) (Found: C, 72.2, 72.4; H, 5.8, 5.9. Calc. for $C_{18}H_{16}O_3$; C, 77.1; H, 5.8%).

2-9'-Fluorenylethyl Methyl Ketone (II, R' = Me). The above acid was warmed gently with ION-potassium hydroxide solution. When the vigorous effervescence ceased the mixture was diluted with water and the precipitated oil extracted with ether. Evaporation of the ether, after its washing with water, gave *2-9'-fluorenylethyl methyl ketone* (96%), which crystallised from methanol in prisms, m.p. 75-76° (Found: C, 86.1; H, 6.8. $C_{17}H_{16}O$ requires C, 86.4; H, 6.8%). The *oxime* crystallised from ethanol in a mixture of sword-blades and feathery needles (possibly the two stereoisomers), m.p. 121-123° (Found: C, 81.1; H, 6.5; N, 5.4. $C_{17}H_{17}ON$ requires C, 81.2; H, 6.8; N, 5.6%).

4-9'-Fluorenylbutan-2-ol (III, R' = Me). The above ketone was heated with three molecules (9 equivs.) of aluminium *iso*propoxide in *iso*propanol till no more acetone was present in the distillate (*ca*. 1 hour). Most of the remaining *iso*propanol was distilled off under slightly reduced pressure and, after acidification and extraction with ether, the oily residue from evaporation of the ether crystallised at 0° from light petroleum (b.p. 60-80°) in needles, m.p. 45-49° (Found: C, 82.9, 83.1; H, 7.6, 7.4. Calc. for $C_{17}H_{18}O$: C, 85.7; H, 7.6%).

4-Methyl-1:2:3:4-tetrahydrofluoranthene (IV, R' = Me). The above carbinol (1.7 g.) was dissolved in glacial acetic acid (7 ml.), and a mixture of acetic acid (7 ml.) and sulphuric acid (7 ml.) added. The mixture was warmed on the steam-bath (5 minutes) and diluted with water. The precipitated oil was extracted with ether, washed with sodium hydrogen carbonate solution and water, and the ether evaporated. The residue distilled at 120-130° (bath-temp.) at 1 mm., yielding 4-methyl-1:2:3:4-tetrahydrofluoranthene (1.25g., 80%), m.p. 32-37°, which liquified when mixed with the carbinol at room temperature. With 2:4:7-trinitrofluorenone in acetic acid it formed a complex, crystallising from acetic acid in orange needles, m.p. 131-133° (Found: C, 67.5; H, 4.0: N, 7.9. $C_{17}H_{16}$, $C_{13}H_5O_7N_3$ requires C, 67.3; H, 3.95; N, 7.85%).

4-Methylfluoranthene (V). The above tetrahydro-compound (0.11 g.), chloranil (0.245 g.), and xylene (1 ml.) were boiled for 1 hour, during which the solution changed from blood-red to pale brown with deposition of pale brown needles of tetrachloroquinol. After cooling and filtration, the filtrate was diluted with ether, extracted with 5% sodium hydroxide solution, washed with water, and evaporated. The residue (0.09 g., 83%) crystallised from ethanol in pale green sword-blades of 4-methylfluoranthene, m.p. 65-66°. The picrate crystallised from ethanol in orange needles, m.p. 171-173°.

Methyl 9-Methylfluorene-9-carboxylate. Methyl sulphate (3.15 g.) was added slowly with cooling to a solution of sodium methoxide (from 0.575 g. of sodium), methyl 2-morpholinoethyl ketone (3.925 g.), and methyl fluorene-9-carboxylate (5.6 g.) in methanol (80 ml.). Colourless crystals (2.5 g.) of methyl 9-methylfluorene-9-carboxylate were deposited during 4 days' storage, at room temperature. Dilution of the filtrate with water gave, on crystallisation of the oily residue, a further 2.5 g. (total yield, 84%). Crystallisation from methanol gave sword-blades, m.p.108-109°

(Found: C, 80.7; H, 5.8. $C_{16}H_{14}O_2$ requires C, 80.7; H, 5.9%).

9-Methylfluorene-9-carboxylic Acid. The above ester was hydrolysed by the addition of 10N-potassium hydroxide solution to a hot ethanolic solution. The acid crystallised from carbon tetrachloride in needles, m.p. 168-169° (Found: C, 80.6; H, 5.2. Calc. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4%).

9-Methylfluorene. Boiling (15 minutes) either the above ester or the acid with 2-methoxyethanol and an equal volume of 10N-potassium hydroxide solution, dilution with water, and extraction with ether gave, on evaporation of the ether, 9-methylfluorene, which, crystallised from ethanol, had m.p. 45-47°.

4-PHENYLFLUORANTHENE.

2-(9-Carbomethoxy-9-fluorenyl)ethyl Phenyl Ketone (I, R = Me, R' = Ph). (a) Methyl fluorene-9-carboxylate (2.24 g., 1 mol.) and phenyl vinyl ketone (1.32 g., 1 mol.) (107) were dissolved in dry dioxan (11 ml.), and dry powdered potassium hydroxide (0.11 g., 0.2 mol.) was added. On being kept for 7 days with occasional shaking and worked up in the usual manner, this gave 2-(9-carbomethoxy-9-fluorenyl)ethyl phenyl ketone (2 g., 56%) in prisms (from methanol), m.p. 110-111° (Found: C, 80.9; H, 5.6. $C_{24}H_{20}O_3$ requires C, 80.9;

H, 5.7%).

(b) Methyl fluorene-9-carboxylate (28.4 g., 1 mol.) was added to a solution of sodium (2.92 g., 1 atom) in anhydrous methanol (125 ml.), and to this was added a mixture of 2-diethylaminoethyl phenyl ketone (26.1 g., 1 mol.) (107), anhydrous methanol (64 ml.), and methyl sulphate (15.9 g., 1 mol. - added cautiously with cooling). After the mixture had been boiled (30 minutes) and then cooled in ice, prisms (34.5 g., 83%) of practically pure 2-(9-carbomethoxy-9-fluorenyl)ethyl phenyl ketone, m.p. 110-111°, were deposited.

(c) The use of 2-morpholinoethyl phenyl ketone (106) in place of 2-diethylaminoethyl phenyl ketone gave a lower yield of the above product.

The Mannich bases used above were prepared from their hydrochlorides immediately before use, since the hydrochlorides were stable and could be kept for several months, whereas the free bases decomposed on storage and their use after some weeks led to decreased yields.

<u>2-(9-Carboxy-9-fluorenyl)ethyl Phenyl Ketone</u> (I, R = H, R' = Ph). The above ester, dissolved in hot ethanol, was hydrolysed in the usual manner by addition of 10N-potassium hydroxide solution, to give the <u>acid</u>, which crystallised from acetic acid in colourless sword-blades, m.p. 174-179° (Found: C, 80.1, 80.3; H, 5.1, 5.5. $C_{23}H_{18}O_3$ requires

C, 80.7; H, 5.3%).

2-9'-Fluorenylethyl Phenyl Ketone (II, R' = Ph). The above acid (3.2 g.) was warmed with ION-potassium hydroxide solution till the vigorous effervescence ceased (5 minutes). Dilution of the mixture with water and extraction with ether gave, on evaporation of the ether, *2-9'-fluorenylethyl phenyl ketone* (2.7 g., 96%), which crystallised from ethanol or light petroleum (b.p. 60-80°) in needles, m.p. 80-81° (Found: C, 88.9; H, 6.3. $C_{22}H_{18}O$ requires C, 88.6; H, 6.1%). The *oxime* crystallised from light petroleum (b.p. 60-80°) in needles, m.p. 135-140° (Found: C, 84.3; H, 6.1; N, 4.5. $C_{22}H_{19}ON$ requires C, 84.3; H, 6.1; N, 4.5%). Reduction of an ethanolic solution of the oxime (containing at least 3 equivs. of dry hydrogen chloride), with hydrogen in the presence of a palladium-charcoal catalyst gave *3-9'-fluorenyl-1-phenylpropylamine hydrochloride* (III, R' = Ph, NH_2 in place of OH). Crystallisation from ethanol-ether yielded needles, m.p. 240-242° (Found: C, 78.7; H, 6.7; N, 4.1. $C_{22}H_{22}NCl$ requires C, 78.7; H, 6.6; N, 4.2%).

4-Phenyl-1:2:3:4-tetrahydrofluoranthene (IV, R' = Ph). 2-9'-Fluorenylethyl phenyl ketone in *iso*propanol solution was heated with three moles (9 equivs.) of aluminium *iso*propoxide till no more acetone was present in the distillate. Working up in the usual manner gave an uncrystallisable oily residue. Warming (5 minutes) the oil in solution in acetic acid (1 vol.) with a mixture of acetic acid (1 vol.) and sulphuric acid (1 vol.) gave, after the usual treatment, an oily solid, which, when mixed with acetone and crystallised from ethanol or acetone, gave prisms of 4-phenyl-1:2:3:4-tetrahydrofluoranthene, m.p. 110-112° (Found: C, 93.8; H, 6.5. $C_{22}H_{18}$ requires C, 93.6; H, 6.4%).

4-Phenylfluoranthene (VI). (a) By use of chloranil. The above tetrahydro-compound (0.141 g.), chloranil (0.246 g.), and xylene (1 ml.) were boiled till no more tetrachloroquinol was deposited (ca. 24 hours). Working up in the usual manner gave a yellow solid, m.p. 120-134°. A solution of this in light petroleum (b.p. 60-80°) was chromatographed (alumina). The first colourless eluate, fluorescing pale blue in daylight and strong green-blue in ultra-violet light, yielded 4-phenylfluoranthene, which crystallised from ethanol in pale green needles, m.p. 141-143°.

(b) By use of sulphur. The above tetrahydro-compound (0.5 g.) and sulphur (0.12 g.) were heated at 190-200°, a vigorous evolution of hydrogen sulphide occurring. The effervescence slackened after 45 minutes, and no further evolution of gas took place when the temperature was raised to 230°. After cooling the residue was dissolved in light petroleum (b.p. 60-80°) and chromatographed (alumina).

Sulphur-containing compounds were retained as yellow and brown bands, 4-phenylfluoranthene passing through as a colourless, pale blue-fluorescent solution, evaporation of which gave 0.42 g. (84%), m.p. 142-144°. Sublimation from zinc dust in vacuum, and crystallisation, failed to separate 4-phenylfluoranthene from sulphur-containing compounds.

METHYL FLUORENE-9-CARBOXYLATE.

Oxidation of 9-Formylfluorene. 9-Formylfluorene (2.8g.), acetic acid (10 ml.), and hydrogen peroxide (5 ml.; 30% solution) were mixed and kept (4-5 hours) at room temperature. A pale yellow solid separated, and crystallisation from benzene gave a product as colourless needles, m.p. 130-135° (with reddening and decomp.). It became pink in air and was not acidic. (Found: C, 77.4; H, 5.4. $C_{12}H_{10}O_2$ requires C, 77.4; H, 5.4%).

Action of 9-Fluorenylpotassium on Ethyl Chloroformate. 9-Fluorenylpotassium, prepared from fluorene (1.66 g.) and potassium (0.43 g.) in liquid ammonia, was suspended in dry ether (50 ml.), which was boiled (15 minutes) to remove all the ammonia, and ethyl chloroformate (1.1 g., theoretical quantity) added. After the boiling solution had been stirred for 30 minutes it was kept at room temperature overnight, then poured into water and separated, and the ethereal layer evaporated. Hydrolysis of the residue in the normal manner gave fluorene-9-carboxylic acid (0.34 g.) and fluorene (1 g.). (Yield, 36% of ethyl fluorene-9-carboxylate, calculated on unrecovered fluorene).

PART 1b; 1:2:5:6-Dibenzpyracylene.

4-Iodofluoranthene (VII). 4-nitrofluoranthene (8 g.) (83), suspended in glacial acetic acid (150 ml.) with the addition of 10% palladium-charcoal catalyst (0.8 g.), was reduced by hydrogen (theoretical volume absorbed in 3-4 hours) to give a green-fluorescent solution. After filtration, the catalyst was extracted several times with boiling glacial acetic acid, the combined filtrates diluted with water (150 ml.), concentrated sulphuric acid (10 ml.) added, and the solution diazotised at -5° to 0° by the addition of sodium nitrite (2.5 g.) in water. After destruction of excess nitrite with urea (1 g.), the solution was poured into a solution of potassium iodide (30 g.) in water (150 ml.) and allowed to stand at room temperature overnight. After filtration, thorough washing, and drying, the residue was extracted by light petroleum (b.p. 60-80°). Iodine was removed by washing with dilute sodium thiosulphate solution, and the organic layer, after treating with charcoal, was evaporated and the residue crystallised from ethanol as cream micro-leaflets of 4-iodofluoranthene, m.p. 109-110° (2.95 g., 28%). (Found: C, 58.6; H, 2.9; I, 38.35. $C_{16}H_9I$ requires C, 58.6; H, 2.8; I, 38.7%).

4-o-nitrophenylfluoranthene (VIII). 4-Iodofluoranthene

(1 g.) and *o*-bromonitrobenzene (0.65 g.) were heated to 210-220°, and copper bronze (0.5 g., washed with carbon tetrachloride) added in portions during two hours, with frequent stirring. Heating was continued for a further two hours, the cooled mass extracted with acetone, and the residue from evaporation of the acetone dissolved in light petroleum (b.p. 60-80°) and chromatographed (alumina). A mixture of benzene and light petroleum (1:1 v/v) gave a yellow eluate with a green fluorescence, from which a yellow solid, crystallising from ethanol, was obtained (0.85 g., 83%). Recrystallisation, with loss of material, by solution in ethyl acetate and then addition of an equal volume of methanol gave lemon-yellow needles melting at 157-160° (softening at 155°) of *4-o-nitrophenylfluoranthene* (Found: C, 81.3; H, 4.1. $C_{22}H_{23}O_2N$ requires C, 81.7; H, 4.05%). The use of three times the above amount of *o*-bromonitrobenzene facilitated mixing and gave similar results but removal of excess was troublesome, as well as removal of *oo*'-dinitrodiphenyl formed.

4-o-Aminophenylfluoranthene. Reduction of the nitro-compound (VIII) was accomplished by hydrogenation with either (a) 10% palladium-charcoal/glacial acetic acid, or (b) Raney-nickel/ethanol. Since the isolated amine, a pale brown oil, could not be crystallised, it was dissolved in ether and dry hydrogen chloride passed to precipitate the hydrochloride, reprecipitated by addition of ether to an ethanol solution to give pale green needles, melting at 210-250° (Found: C, 79.3; H, 4.8. $C_{22}H_{16}NCl$ requires C, 80.1; H, 4.9%). The picrate of the amine, prepared in ethanol, gave golden-brown cubes from chloroform, m.p. 217-219° (softening at 200°) (Found: C, 64.4; H, 3.6; N, 10.6. $C_{22}H_{15}N.C_6H_3O_7N_3$ requires C, 64.4; H, 3.5; N, 10.7%).

1:2:5:6-Dibenzpyracylene (IX). 4-*o*-nitrophenylfluoranthene (0.46 g.) was reduced (H_2/Raney Ni/Et OH) and the uncrystallised amine obtained was dissolved in glacial acetic acid and poured with stirring into excess of 10% (v/v) sulphuric acid solution. A solution of sodium nitrite (0.12 g.) in water (3 ml.) was added all at once to the slightly warm solution. After diazotisation was complete, urea was added, then copper bronze (washed with carbon tetrachloride), and the occasionally stirred mixture allowed to stand. During *ca*. 1 hour an orange solid grew out of the solution. Reaction was completed by heating on the steam bath for 30 minutes, and after filtering, washing, and drying, the precipitate was extracted with benzene and the red-green fluorescing solution chromatographed (alumina). The concentrated orange eluate gave orange needles of 1:2:5:6-dibenzpyracylene, m.p. 261-262° (0.15 g., 38% yield from

4-o-nitrophenylfluoranthene). Picric acid and 2:4:7-trinitrofluorenone gave unstable complexes.

o-Nitroacetophenone. Magnesium turnings (10.7 g., 1.1 atom) were allowed to react vigorously with anhydrous ethanol (10 ml.) and carbon tetrachloride (1 ml.) for a few minutes, then anhydrous benzene (150 ml.) was added. The mixture was heated to the boiling point, the source of heat removed, and the contents of the flask stirred vigorously while ethyl malonate (70.4 g., 1.1 mol.), anhydrous ethanol (40 ml.) and anhydrous benzene (50 ml.) were added at such a rate that vigorous refluxing was maintained, heating if necessary. The mixture was stirred under reflux till all the magnesium was in solution (ca. 30 minutes), the source of heat removed, and vigorous stirring maintained while o-nitrobenzoyl chloride (74.2 g., 1 mol.) in anhydrous benzene (100 ml.) was added as rapidly as the violence of the reaction would allow. After boiling (30 minutes) the mixture was cooled slightly and dilute sulphuric acid added cautiously with stirring. The mixture at first became very pasty, but further addition of acid gave two clear layers. The whole was then submitted to distillation till the temperature of the vapour reached 95°, a mixture of glacial acetic acid (120 ml.), concentrated sulphuric acid (15 ml.), and water (80 ml.) added, and the mixture boiled (4 hours).

It was cooled (ice-salt), made strongly alkaline with solid potassium hydroxide, shaken with ether, the whole filtered and the residue washed well with ether. The organic layer of the filtrate was separated, washed well with water, dried and distilled. The fraction boiling at 158.5-159°/16 mm. (166.5°/21 mm.) was pure o-nitroacetophenone (58.2 g., 88%). [o-Nitrobenzoyl chloride was prepared as required from the acid (67 g.) by boiling the latter with thionyl chloride (100 ml.) till all the acid was in solution. Excess thionyl chloride was removed under reduced pressure, last traces being removed by addition and distillation of anhydrous benzene (50 ml., 3 times). The acid chloride was used without further purification as distillation under reduced pressure led to explosive decomposition].

2-(9-Carbomethoxy-9-fluorenyl)ethyl o-Nitrophenyl Ketone (I, R = Me, R' = o-$C_6H_4NO_2$). 2-Diethylaminoethyl o-nitrophenyl ketone hydrochloride (3.6 g., 1.5 mol.) (89) was dissolved in dry methanol (7 ml.) and a solution of sodium (0.3 g., 1.5 atom) in methanol (3 ml.) added. After stirring for a few minutes, sodium chloride was filtered, washed with a little methanol, and the combined filtrates mixed with methyl iodide (1.6 g., 1.3 mol.) and added to a warm solution of methyl fluorene-9-carboxylate (2.4 g., 1.3 mol.) and sodium (0.24 g., 1.3 atom) in methanol (10 ml.). Crystals appeared immediately and on cooling practically pure 2-(9-carbomethoxy-9-fluorenyl)ethyl *o*-nitrophenyl ketone (3 g., 71%) was deposited. Crystallisation from methyl cyanide gave needles, m.p. 168-169° (Found: C, 71.6; H, 4.95; N, 3.5. $C_{24}H_{19}O_5N$ requires C, 71.8; H, 4.8; N, 3.5%).

2-9'-Fluorenylethyl *o*-Nitrophenyl Ketone (II, R' = *o*-$C_6H_4NO_2$). The above keto-ester (3 g.) was boiled (1 hr.) with a mixture of acetic acid (90 ml.), concentrated sulphuric acid (6 ml.) and water (30 ml.), poured into water (300 ml.), filtered, and washed with water. The acid thus obtained decarboxylated too readily for purification, but boiling (15 min.) this acid in methyl cyanide (30 ml.), and diluting at the boiling point till crystallisation commenced gave, on cooling, 2-9'-fluorenylethyl *o*-nitrophenyl ketone (1.7 g., 66%). Crystallisation from ethanol or methyl cyanide gave needles, m.p. 147-149° (Found: C, 77.2; H, 4.8; N, 4.1. $C_{22}H_{17}O_3N$ requires C, 77.0; H, 5.0; N, 4.1%).

The acid was also decarboxylated by heating at 170-180° till evolution of carbon dioxide ceased (21%). Attempted hydrolysis of the ester by aqueous-alcoholic sodium hydroxide gave a tarry product.

PART 2; 2:3-BENZFLUORANTHENE.

***o*-Diphenylenephthalide** (XII). 9-Hydroxy-9-*o*-tolylfluorene (XI) (10 g.), manganese dioxide (0.25 g.), concentrated nitric acid (170 ml.), water (340 ml.), and sufficient nitrobenzene to render the organic layer readily mobile, were boiled together (70 hours). The nitrobenzene was removed by steam distillation, the residue cooled, filtered, and dissolved in alcoholic sodium hydroxide solution. After dilution with four times its volume of water and filtration, the filtrate was acidified. The precipitate was filtered, washed, and dried, giving the phthalide (XII) (5.5 g., 53%), m.p. 216-220°. Crystallisation from acetic acid raised the m.p. to 226°, with considerable loss of material. The use of vanadium pentoxide (108) in place of manganese dioxide was of no advantage.

2:3-Benzfluoranthene (XVI). The phthalide (3 g.) and pure zinc dust (6 g.) were ground together very thoroughly and mixed with powdered sodium chloride (6 g.). To this was added powdered zinc chloride (30 g.), ten drops of water, and the temperature raised to 270° with vigorous stirring. During eight minutes the temperature was allowed to rise to 340° with stirring (a yellow sublimate appearing), the mass cooled, decomposed with boiling water and a little acetic acid, filtered, washed well with hot water, dilute ammonia solution, and water. After drying the residue was extracted with light petroleum (b.p. 60-80°) and this solution chromatographed (alumina, heated strongly in vacuum and cooled under dry CO_2). A mixture of benzene and light petroleum (1:1 v/v) gave a yellow eluate (green fluorescence) which gave on evaporation a yellow residue, crystallising from light petroleum (b.p. 60-80°) in long golden yellow needles of 2:3—benzfluoranthene, m.p. 145-146° (evacuated capillary). (Found: C, 95.15; H, 4.9. $C_{20}H_{12}$ requires C, 95.2; H, 4.8%).

Reduction of o-Diphenylenephthalide (XII) with Hydriodic Acid and Phosphorus. The phthalide (1.9 g.), constant boiling hydriodic acid (50 ml.), red phosphorus (7 g.), and xylene (20 ml.) were boiled (72 hours). After filtration, the residue was extracted well with hot dilute sodium hydroxide solution, and the organic layer of the filtrate washed with water and then dilute sodium hydroxide solution. The combined alkaline solutions gave, on acidification, 9-o-carboxyphenylfluorene (XIII) (19,20,21). The residue from evaporation of the organic layer gave, on chromatographing in the usual manner, a very small amount of 2:3-benzfluoranthene.

THE GREEN HYDROCARBON, m.p. 135-138°.

9-Bromo-9-o-tolylfluorene (XIX). 9-Hydroxy-9-o-tolylfluorene (XI) (10 g.) was dissolved in glacial acetic acid (200 ml.), the solution cooled to room temperature, and saturated with dry hydrogen bromide (from Br_2/tetralin, and purified by red P, then P_2O_5). The product (9.7 g., 79%) gave (glacial acetic acid) yellow platelets of 9-bromo-9-o-tolylfluorene (XIX), m.p. 142° (softening at 120°) (Found: C, 71.8; H, 4.4. $C_{20}H_{15}Br$ requires C, 71.7; H, 4.5%).

9-Bromo-9-ω-bromo-o-tolylfluorene (XX). 9-Bromo-9-o-tolylfluorene (XIX) (1 g., 1.05 mol.) was dissolved in carbon tetrachloride (10 ml.), N-bromosuccinimide (0.5 g., 1 mol.) and benzoyl peroxide (trace) added, and the mixture boiled under light irradiation till all the N-bromosuccinimide had reacted (several hours). After filtration whilst hot and extraction of the succinimide residue with boiling carbon tetrachloride, the combined filtrates were evaporated and the residue crystallised from acetic acid (1 g., 86% crude). Crystallisation from methyl cyanide or acetic acid slowly raised the m.p. to 158-161° (softening at 140°), giving yellow prisms of essentially 9-bromo-9-ω-bromo-o-tolylfluorene (XX), contaminated with a little more highly brominated impurity. (Found: C, 54.1; H, 3.45. Calc. for $C_{20}H_{14}Br_2$: C, 58.0; H, 3.4%).

Attempted Cyclisation of (XX). (XX) (2 g.) was dissolved in dry benzene (50 ml.) and finely-powdered aluminium chloride (10 g.) added. A purple complex formed, and the mixture was boiled until evolution of hydrogen halide ceased (20 minutes). After decomposition of the complex in the usual manner, the benzene solution was evaporated, the residue dissolved in light petroleum (b.p. 60-80°) and chromatographed (alumina). The first colourless eluate (showing a violet fluorescence) gave, on evaporation, a residue which crystallised from ethanol in pale green needles (0.3 g.) m.p. 135-138°. [Found: C, 94.3; H, 5.5; M.Wt., Rast (camphor) 311,313; Ebullioscopic (benzene) 341. Calc. for $C_{20}H_{14}$: C, 94.45; H, 5.55%; M.Wt. 254. Calc. for $C_{26}H_{18}$: C, 94.5; H, 5.5%; M.Wt. 330]. Further treatment of the column with a mixture of light petroleum and benzene (1.1 v/v) gave a yellow eluate with a green fluorescence, probably a very small quantity of 2:3—benzfluoranthene.

PART 3: 3:4-DIMETHYLFLUORANTHENE.

3:4-Dimethyl-1:2-dihydrofluoranthene (XXIV). 4-Keto-3-methyl-1:2:3:4-tetrahydrofluoranthene (XXIII) (0.78 g., 1 mol.) was dissolved in dry benzene (10 ml.) and added to a solution of methyl magnesium iodide, prepared from magnesium (0.25 g., 3 atoms) and methyl iodide (1.4 g., 3 mol.) in ether (5 ml.). After boiling (1 hour), dilute hydrochloric acid was added, and the organic layer washed with dilute hydrochloric acid and water. On distillation of the benzene, the colour of the solution changed from red to yellow-green: the yellow oily residue was dissolved in light petroleum (b.p. 60-80°) and chromatographed (alumina). The pale green (blue fluorescent) eluate gave, on evaporation, a green strongly fluorescent oil which, with 2:4:7-trinitrofluorenone in acetic acid, yielded a *complex* crystallising in orange needles from ethyl acetate, m.p. 177-178° (softening at 170°). (Found: C, 68.1; H, 4.0; N, 7.8. $C_{18}H_{16}\cdot C_{13}H_5O_7N_3$ requires C, 68.0; H, 3.9; N, 7.7%).

3:4-Dimethylfluoranthene (XXV). 3:4-Dimethyl-1:2-dihydrofluoranthene (XXIV) was dehydrogenated with chloranil in the usual manner. Chromatography [light petroleum (b.p. 60-80°)/alumina] of the product gave a green (blue fluorescent) solution, evaporation of which gave *3:4-dimethylfluoranthene*, crystallising from light petroleum (b.p. 60-80°) in bright green needles, m.p. 83-85° (Found: C, 93.9; H, 5.9. $C_{18}H_{14}$ requires C, 93.9; H, 6.1%). The picrate crystallised from benzene in orange needles, m.p. 181-182° (softening at 150°) (Found: C, 63.05; H, 4.0; N, 9.2: $C_{18}H_{14}.C_6H_3O_7N_3$ requires C, 62.7; H, 3.7; N, 9.15%).

2-METHOXYFLUORANTHENE.

2-Methoxy-1-o-nitrophenylnaphthalene (XXVI). 1-Iodo-2-methoxynaphthalene (82) (2 g.) and o-bromonitrobenzene (1.6 g.) were heated to 220-230°, and copper powder (2.4 g., washed with carbon tetrachloride) added with stirring during 30 minutes. Heating was continued with occasional stirring during a further 90 minutes, then the cooled mass was extracted with benzene and this extract chromatographed (alumina). The first brown band gave a yellow eluate, the residue from evaporation of which crystallised from ethanol in yellow needles (1 g., 50%), m.p. 132-133° (Found: C, 72.9; H, 4.7; N, 5.1. $C_{17}H_{13}O_3N$ requires C, 73.1; H, 4.7; N, 5.0%).

1-o-Aminophenyl-2-methoxynaphthalene (XXVII). The above nitro-compound (XXVI) was hydrogenated in presence of Raney nickel in ethanol. After filtration and extraction of the catalyst with boiling ethanol, the combined filtrates were evaporated, giving 1-o-aminophenyl-2-methoxynaphthalene as an oil. It formed a picrate in ethanol, crystallising from benzene in globular clusters of yellow needles, m.p. 205° (decomp.) (Found: C, 57.7; H, 4.0; N, 11.7. $C_{17}H_{15}ON.C_6H_3O_7N_3$ requires C, 57.7; H, 3.8; N, 11.7%).

2-Methoxyfluoranthene (XXVIII). 1-o-Aminophenyl-2-methoxynaphthalene (XXVII) (1.9 g.), recovered from the pure picrate by decomposition of the latter with ammonia and extraction of the amine with ether, was dissolved in warm dilute sulphuric acid, cooled below 0°, and diazotised by the addition of sodium nitrite (0.6 g.) in water. After destruction of excess nitrite with urea, copper powder (washed with carbon tetrachloride) was added and the scarlet diazo-solution stirred at room temperature (45 minutes), then warmed on the steam-bath (30 minutes) to complete the discharge of the colour. Filtration, extraction of the residue with benzene, and chromatography [light petroleum (b.p. 60-80°)/alumina] of the residue from evaporation of the benzene, gave a colourless eluate with a blue fluorescence, from which was obtained 2-methoxyfluoranthene, crystallising in faintly-green feathers from light petroleum (b.p. 60-80°), m.p. 111-113° (Found: C, 88.0; H, 5.4; OMe, 13.8. $C_{17}H_{12}O$ requires C, 87.9; H, 5.2; OMe, 13.4%).

PART 4; ULTRA-VIOLET ABSORPTION SPECTRA.

The ultra-violet absorption spectra described in Part 4 were measured on a Unicam Spectrophotometer, ethanol being used as solvent. No correction was made for the fluorescence of the test solution.

PURIFICATION OF SOLVENT.

Benzene-free rectified spirits was used as solvent. Drying by distillation from calcium oxide gave a product which showed very strong absorption below 2500Å. A solvent sufficiently transparent over the range 2000-4000Å was obtained as follows:- Sodium (10 g.) was dissolved in benzene-free rectified spirits (1 l.), and the solution allowed to stand for 2 days at room temperature. It was then distilled slowly through a Widmer fractionating column, the first and last 200 ml. being rejected and only the middle fraction of 600 ml. retained for use.

The solutions used contained approximately 0.00025 g. mol./l. of the pure substituted fluoranthene. The higher values of log ε were obtained by successive dilutions.

The values of log $\frac{I_0}{I}$ for different wavelengths were obtained by direct reading from the instrument. The value of log ε was obtained from the relationship

$$\log \frac{io}{i} = \varepsilon cl$$

where io is the intensity of light of a particular wavelength transmitted through pure solvent,

i " " " " " of the same wavelength transmitted through the test solution.

ε is the molecular extinction coefficient

c is the concentration of the test solution (g.mol./l.)

l is the length of the path through the test solution traversed by the light.

REFERENCES

1. Goldschmiedt, Ber., 1877, 10, 2022.
2. Fittig and Gebhard, Ber., 1877, 10, 2141.
3. von Braun and Anton, Ber., 1929, 62, 145.
4. von Braun and Anton, Ber., 1934, 67, 1051.
5. von Braun and Manz, Ber., 1937, 70, 1603.
6. France, Tucker, and Forrest, J., 1945, 7.
7. Forrest and Tucker, J., 1948, 1137.
8. Tucker and Whalley, J., 1949, 50.
9. Tucker and Whalley, J., 1949, 632.
10. Tucker, J., 1949, 2182.
11. Tucker and Whalley, J., 1949, 3213.
12. Hawkins and Tucker, J., 1950, 3286.
13. Schlenk and Karplus, Ber., 1928, 61, 1675.
14. Scholl and Meyer, Ber., 1932, 65, 926.
15. von Braun and Manz, Ann., 1932, 496, 170.
16. Fieser and Seligman, J. Amer. Chem. Soc., 1935, 57, 2174.
17. Orchin and Reggel, J. Amer. Chem. Soc., 1947, 69, 505.
18. Orchin and Reggel, J. Amer. Chem. Soc., 1951, 73, 436.
19. Weiss and Knapp, Sitz. der Wiener Akad., IIB (Chemie), 1932, 141, 432.
20. Koelsch, J. Amer. Chem. Soc., 1933, 55, 3394.
21. N. Campbell and Marks, J., 1951,
22. Mayer and Kaufmann, Ber., 1920, 53, 289.

23. Fleischer and Wolff, *Ber.*, 1920, *53*, 925.

24. Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, *54*, 4347.

25. Kloetzel and Chubb, *J. Amer. Chem. Soc.*, 1950, *72*, 150.

26. Federov, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 1947, 397: *Chem. Abs.*, 1948, *42*, 1585.

27. Badoche, *Ann. chim.*, 1933, *20*, 200.

28. Dufraisse and Girard, *Bull. soc. chim.*, 1934, [5] *1*, 1359.

29. Dufraisse, *Bull. soc. chim.*, 1936, [5] *3*, 1857.

30. Dufraisse and Horclois, *Bull. soc. chim.*, 1936, [5] *3*, 1894.

31. Clar, Stubbs, and Tucker, *Nature*, 1950, *166*, 1075.

32. Patterson and Capell, "Ring Index", 1940, 2331.

33. Seshan, *Proc. Indian Acad. Sci.*, 1936, A*3*, 148.

34. Wislicenus and Mocker, *Ber.*, 1913, *46*, 2789.

35. A. Campbell and Tucker, *J.*, 1949, 2623.

36. Maitland and Tucker, *J.*, 1929, 2559.

37. France, Maitland, and Tucker, *J.*, 1937, 1739.

38. N. Campbell and Fairfull, *J.*, 1949, 1239.

39. Taylor and Connor, *J. Org. Chem.*, 1941, *6*, 696.

40. Pinck and Hilbert, *J. Amer. Chem. Soc.*, 1946, *68*, 2015.

41. Bruson, *J. Amer. Chem. Soc.*, 1942, *64*, 2475.

42. Blicke; "Organic Reactions", 1942, *1*, p. 303.

43. Du Feu, McQuillin, and Robinson, *J.*, 1937, 53.

44. Meerwein, *Ann.*, 1913, *396*, 243.

45. Wieland and Probst, *Ann.*, 1937, *530*, 274.

46. "Elsevier's Encyclopedia of Organic Chemistry", 1946, *13*, p. 29.

47. Clar and John, *Ber.*, 1930, **63**, 2967.

48. Clar and John, *Ber.*, 1931, **64**, 981.

49. Bradsher and Smith, *J. Amer. Chem. Soc.*, 1943, **65**, 854, 1643.

50. Bradsher and Kittila, *J. Amer. Chem. Soc.*, 1950, **72**, 277.

51. Hartung, *J. Amer. Chem. Soc.*, 1928, **50**, 3370.

52. Hartung, *J. Amer. Chem. Soc.*, 1931, **53**, 2248.

53. Fodor *et al.*, *J.*, 1948, 885.

54. Fodor *et al.*, *J.*, 1949, 1681.

55. Dufraisse and Badoche, *Compt. rend.*, 1931, **193**, 529.

56. Bergmann, *Bull. soc. chim.*, 1948, [5] **15**, D27.

57. Dufraisse and Amiard, *Bull. soc. chim.*, 1945, [5] **12**, 1044.

58. Tobler, Holbro, Sutter and Kern, *Helv. chim. acta*, 1941, **24**, 100E.

59. I. G. Farbenind. A.-G.; British Patent 459,108: *Centr.*, 1937, **11**, 2262.

60. Zerweck and Schütz; U.S. Patent 2,109,833: *Chem. Abs.*, 1938, **32**, 3629.

61. Mourea, Chovin, and Rivaal, *Bull. soc. chim.*, 1946, 106.

62. Mourea, Chovin, and Riveal, *Compt. rend.*, 1946, **223**, 951.

63. Mourea, Chovin, and Riveal, *Bull. soc. chim.*, 1948, 99.

64. Mourea, Chovin, and Rivoal, *Compt. rend.*, 1947, **225**, 501.

65. Bergmann, *Nature*, 1948, **161**, 889.

66. N. Campbell, Marks, and Reid, *J.*, 1950, 3466.

67. Fittig and Ostermayer, *Ann.*, 1873, **166**, 361, 372.

68. Fittig and Schmitz, *Ann.*, 1878, **193**, 115, 117.

69\. Pummerer, *Ber*., 1912, *45*, 294.

70\. Dziewoński and Suszko, *Bull. intern. acad. polon*. A1921, 67.

71\. Pummerer and Ulrich, *Ber*., 1925, *58*, 1806.

72\. Eckert, *J. pr. Chem*., 1924, [2] *121*, 278.

73\. Elson, Gibson, and Johnson, *J*., 1930, 1128.

74\. I. G. Farbenind, A.-G.; German Patent 595,024: *Chem. Abs*., 1934, *28*, 4069.

75\. Orchin and Woolfolk, *J. Amer. Chem. Soc*., 1946, *68*, 1727.

76\. Tucker and Whalley, *Chem. Rev*., awaiting publication.

77\. Datta and Chatterjee, *J. Amer. Chem. Soc*., 1917, *39* 435.

78\. Birckenbach and Goubeau, *Ber*., 1932, *65*, 395.

79\. Weygand, "Organic Preparations", 1945, p. 89.

80\. Tucker, *J*., 1926, 546.

81\. Jurd, *Austr. J. Sci. Res*., 1949, *2A*, 111; *Br. Ch. Abs*., 1950, AII, 526.

82\. Jurd, *Austr. J. Sci. Res*., 1949, *2A*, 246; *Br. Ch. Abs*., 1950, AII, 647.

83\. von Braun and Manz, *Ann*., 1931, *488*, 111.

84\. Morgan and Moss, *J. Soc. Chem. Ind*., 1923, 461T.

85\. Simpson, Atkinson, Schofield, and Stephenson, *J*., 1945, 646.

86\. Walker and Hauser, *J. Amer. Chem. Soc*., 1946, *68*, 1386.

87\. Schofield and Swain, *J*., 1948, 384.

88\. Bowman, *J*., 1950, 324.

89\. Mannich and Dannehl, *Arch. Pharm*., 1938, *276*, 206.

90. v. Auwers, Lechner, and Bundesmann, Ber., 1925, 58, 50.

91. Clar, J. Chem. Phys., 1949, 17, 741; Ber., 1949, 82, 495.

92. Clar. Spectrochim. Acta, 1950, 4, 116.

93. Clar, "Aromatische Kohlenwasserstoffe", 1941, p. 20.

94. Koelsch, J. Amer. Chem. Soc., 1932, 54, 3389 (note 9).

95. Adams and Campbell, J. Amer. Chem. Soc., 1950, 72, 154.

96. Forrest, Liddell, and Tucker, J., 1946, 454; Forrest, Tucker, and Whalley, J., 1951, 303.

97. N. Campbell, Khanna, and Marks, J., 1951, awaiting publication.

98. Arnold, Parham, and Dodson, J. Amer. Chem. Soc., 1949, 71, 2439.

99. Yost and Hauser, J. Amer. Chem. Soc., 1947, 69, 2326.

100. Blum-Bergmann, Ann., 1930, 484, 47.

101. Von and Wagner, J. Org. Chem., 1944, 9, 155; cf. Wislicenus et al., Ber., 1909, 42, 785; 1910, 43, 2719.

102. Krollpfeiffer and Branscheid, Ber., 1923, 56, 1617.

103. Ramart-Lucas and Hoch, Bull. soc. chim., 1935, [5] 2, 1376.

104. Clar, Ber., 1948, 81, 52.

105. Tucker, unpublished work.

106. Harradence and Lions, J. Proc. Roy. Soc. N.S. Wales, 1938, 72, 233.

107. Young and Roberts, J. Amer. Chem. Soc., 1946, 68, 651; Leslie and Henze, J. Amer. Chem. Soc., 1949, 71, 3480.

108. Rieve and Myers, J. Amer. Chem. Soc., 1951, 73, 1371.

109. Jones, Chem. Rev., 1943, 32, 1.

110. Brode and Patterson, J. Amer. Chem. Soc., 1941, 63, 3252.
