THE SYNTHESIS OF POLYCYCLIC AROMATIC HYDROCARBONS.

By

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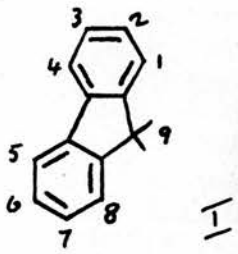
INTRODUCTION

FLUORENE



I

The hydrocarbon fluorene has been known for almost a hundred years. In 1878 (1,2) the structure was established as that of diphenylenemethane I. Since then a considerable amount of research has been devoted to fluorene and its related compounds.

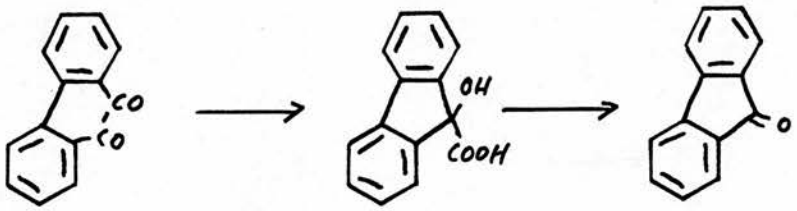
Preparations of fluorenes have been carried out in two general ways:-

(a) by syntheses from suitable starting materials.

(b) by direct substitution on a fluorene skeleton.

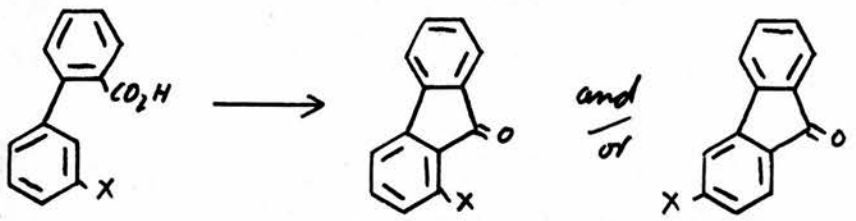
Synthetic methods are numerous and yield primarily substituted fluorenones which are subsequently reduced.

The rearrangement of phenanthraquinones, an application of the benzil-benzilic acid rearrangement, has often been employed. The resulting diphenylene glycollic acids II decompose in boiling water to give fluorenones III.

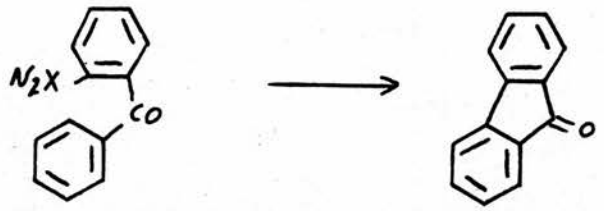


II III

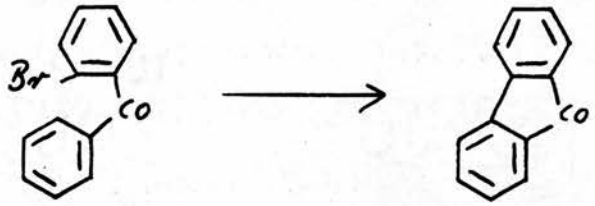
The dehydration of o-carboxydiphenyls has proved of value. This method has the disadvantage that if the substituent in the second ring is in the meta position, ring closure can give rise to two compounds. Often high temperatures are involved and rearrangements have been reported (4,5).



Coupling of diazotised o-aminobenzophenone derivatives has given rise to numerous fluorenones.

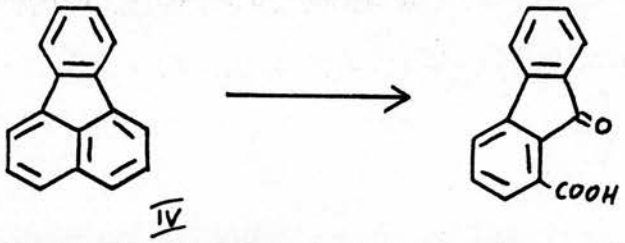


Fluorenones may also be synthesised from o-halogen benzophenones. High temperature is required to effect the elimination of the halogen acid and the method generally gives small yields. Rearrangements are possible.



In the last two mentioned syntheses also a meta substituent in the second ring of the starting material gives two possible modes of ring-closure.

Oxidation of fluoranthene IV by chromic acid gives fluorenone-1-carboxylic acid (7). A number of fluorenones have been prepared from fluoranthene derivatives by this method.



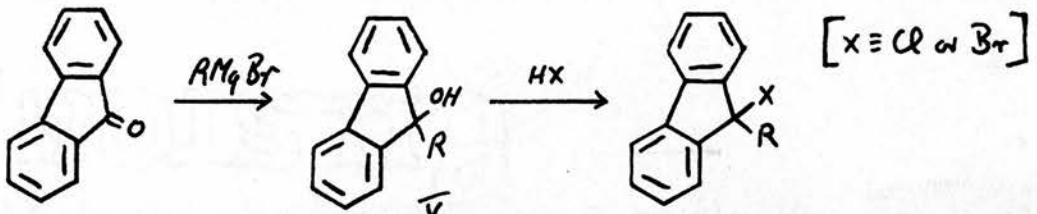
IV

Nuclear substitution on the fluorene skeleton gives mainly 2-substituted derivatives. Further substitution gives 2,7-compounds in all but a few cases.

Fluorene, having the structure of dibenzocyclopentadiene

not surprisingly contains a reactive methylene and derivatives in which one or both of the hydrogen atoms of the 9-carbon atom are replaced by substituents are well known.

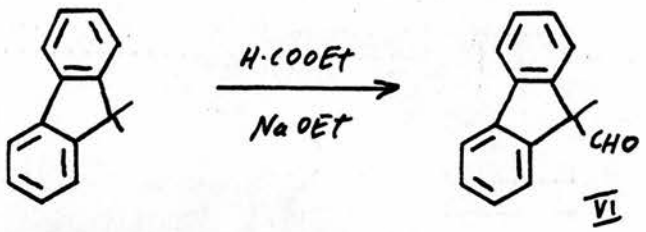
Various 9-substituted derivatives have been prepared from fluorenone by the normal reactions of the carbonyl group. It reacts normally with hydroxylamine and hydrazine derivatives. Fluorenone also undergoes Reformatsky and Stobbe reactions. Reaction with Grignard reagents give substituted fluorenols V. In these the 9-hydroxyl may be replaced by bromine or chlorine by reaction with a suitable hydrogen or phosphorus halide. Hyriodic acid reduces the hydroxyl giving derivatives of the type $(C_6H_4)_2$ CHR.



V

The reactive 9-methylene group of fluorene gives rise to many 9-substituted derivatives. Oxidation gives fluorenone. 9-Sodium and potassium derivatives can be formed. Fluorene also reacts with ethylmagnesium bromide to give 9-fluorylmagnesiumbromide which has all the usual properties of a Grignard reagent. A valuable 9-lithium derivative is formed by reaction with phenyllithium. Fluorene also condenses with a number of carbonyl compounds, particularly aromatic aldehydes giving compounds of the type $(C_6H_4)_2$ C = CHR. Fluorene and derivatives containing an active hydrogen on the 9-position undergo Michael condensation with compounds possessing an activated double bond. This has proved especially valuable in the synthesis of fluoranthenes. Esters can be

condensed with fluorene in a Claisen type of condensation. For example, condensation with ethyl formate (8) gives 9-formylfluorene VI.



VI

1,8-Substituted Fluorenes.

Oxidation of fluoranthene with chromic acid gives fluorenone-1-carboxylic acid. The preparation by Goldschmiedt (9) of 1-amino-fluorenone from fluorenone-1-carbonamide by a Hofmann reaction and subsequent diazotisation provided the basis for the preparation of a number of 1-substituted fluorenones and fluorenes. Since then an impressive list of 1-substituted derivatives has been prepared as a result of oxidative degradation of fluoranthene derivatives.

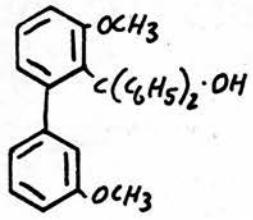
The apparent scarcity of references in the literature to derivatives containing two substituents ortho to the 9-carbon atom is of interest. The few 1,8 fluorene derivatives mentioned are of doubtful structure.

Schmidt and Stützel (10) claimed to have obtained 1,8-dinitrofluorenone by nitration of 9-acetylaminofluorene. On repeating this nitration, Langdecker (11) found the main product to be 2-nitrofluorenone. Huntress and Cliff (12) reinvestigated the work of Schmidt and Stützel and showed their conclusions to be unsound. Repetition of the nitration under similar conditions gave 70% yields of 2-nitrofluorenone, while further nitration gave 2,7-dinitrofluorenone and 13% yield of a new dinitrofluorenone which was neither 2,4- nor 2,5-dinitrofluorenone. It seems unlikely, in view of the relative inactivity

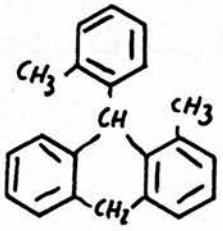
of the 1-position, that this would be 1,8-dinitrofluorenone.

Huntress and Cliff (3) prepared 1,8-dichlorofluorenone by heating 3,3'-dichlorodiphenic anhydride. The action of heat or hot concentrated sulphuric acid on 3,3'-dichlorodiphenic acid and 5,5'-dichlorodiphenic acid (4,5) gave, depending on reaction conditions, a number of compounds involving rearrangements. The designation of structures and postulation of mechanism for the rearrangements involved appear reasonable (6); but in view of the high temperatures involved an independent synthesis of the 1,8-derivative would be of value.

Wittig and Furman (13) during a study of the complicated interaction of m-iodoanisole and phenyllithium, reacted the mixture obtained with benzophenone. A small amount of compound isolated after treatment with glacial acetic acid, was thought to be 1,5- or 1,8-dimethoxy-9-9-diphenylfluorene, presumably formed by dehydration of an intermediate carbinol, VII.



VII



VIII

Theilacker and Wessel-Ewald (14) on reacting o-tolyllithium with the ethyl ester of o-toluic acid obtain an oil, mainly di-o-tolylketone. Treatment with sulphuric acid produced a small amount of a compound, $C_{22}H_{20}$, considered to be 1,8-dimethyl-9-(o-methylphenyl)fluorene or the dihydro-anthracene derivative VIII, presumably formed by dehydration of some tri-o-tolyl-carbinol formed in the mixture.

FLUORANTHENE

IX

The hydrocarbon fluoranthene was first isolated as early as 1877 (15). Since then it has become commercially available from coal tar and fluoranthene derivatives are of importance industrially.

The correct structure was not assigned to the fluoranthene molecule till 1929, when Braun and Anton (16), from the evidence available, suggested a 1,2-benzacenaphthene structure IX, which they proceeded to establish synthetically.

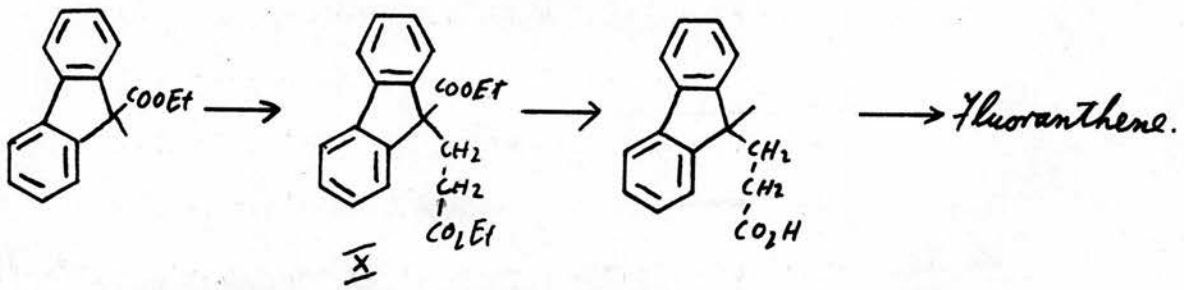
Indirect syntheses of fluoranthene and its derivatives have followed three general routes :-

(a) from a fluorene nucleus, involving synthesis of ring A.

(b) from a naphthalene nucleus, with addition of ring C.

(c) from an acenaphthene skeleton, with synthesis of ring C.

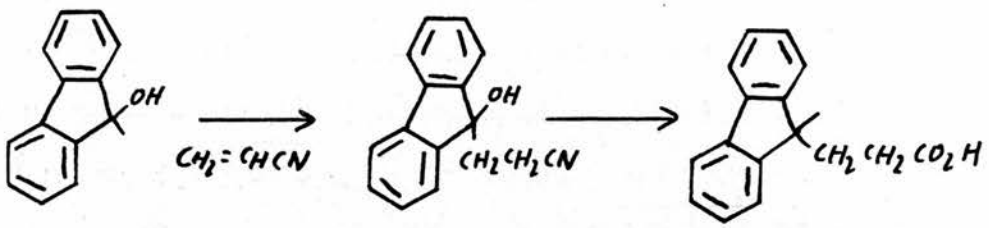
In the original synthesis of Braun and Anton (loc.cit.) ethyl 9-fluorenecarboxylate was condensed with ethyl β-chloropropionate. The product X was hydrolysed and decarboxylated to β-(9-fluorenyl)propionic acid. Ring-closure, reduction and dehydrogenation gave fluoranthene.



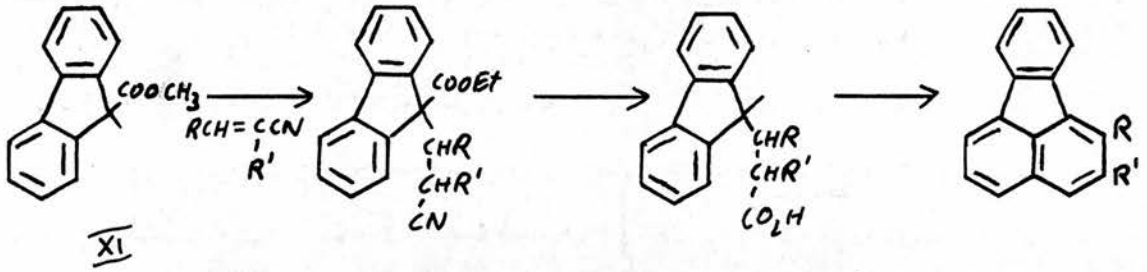
X

This synthesis underwent no modification till Campbell and Fairfull (17) prepared β-(9-fluorenyl)propionic acid by a route involving condensation of fluorenol and acrylonitrile. The resulting β-(9-hydroxy-

9-fluorenyl)propionitrile was hydrolysed, dehydrated and reduced.

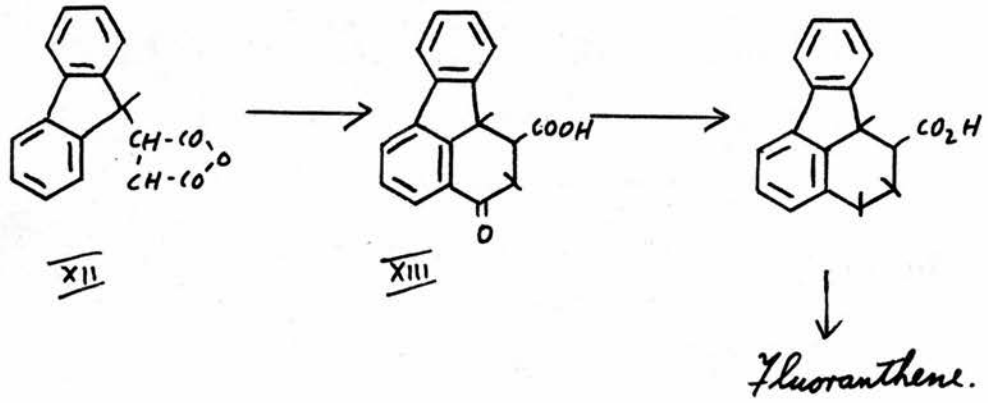


This method was later extended and improved (18). Methyl 9-fluorenecarboxylate XI provides a more reactive hydrogen on the 9-position than fluorenol. Substituted acrylonitriles or acrylic esters gave 2-or 3-substituted fluoranthenes.



XI

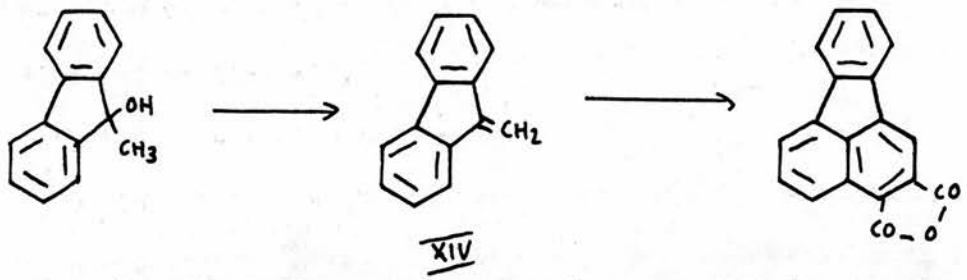
Bergmann and Orchin (19) employed an initial condensation between fluorene and maleic anhydride. Cyclization of the adduct XII gave the keto-acid XIII. Reduction, dehydrogenation and decarboxylation gave fluoranthene.



XII XIII

The Stobbe condensation of fluorenone and ethyl succinate has also been utilised (20) in the preparation of 9-fluorenylsuccinic acid.

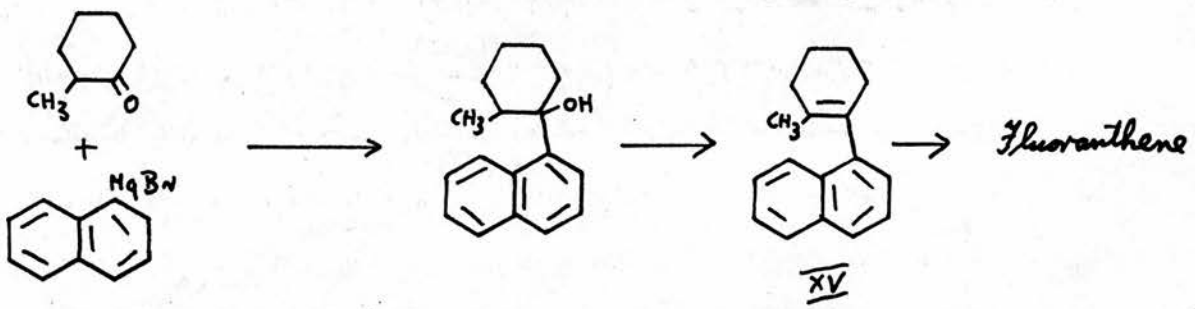
Campbell and Wang condensed 9-hydroxy-9-methylfluorene with maleic anhydride (21) producing fluoranthene-3,4-dicarboxylic acid, presumably by Diels-Alder addition to the intermediate 9-methylenefluorene XIV. Decarboxylation yielded fluoranthene.



XIV

A number of syntheses commencing from a naphthalene nucleus have been recorded.

Cook and Lawrence (22) reacted α-naphthylmagnesium bromide with 2-methylcyclohexanone. Dehydration of the resulting alcohol gave XV. Cyclisation and dehydrogenation gave fluoranthene in poor yield.

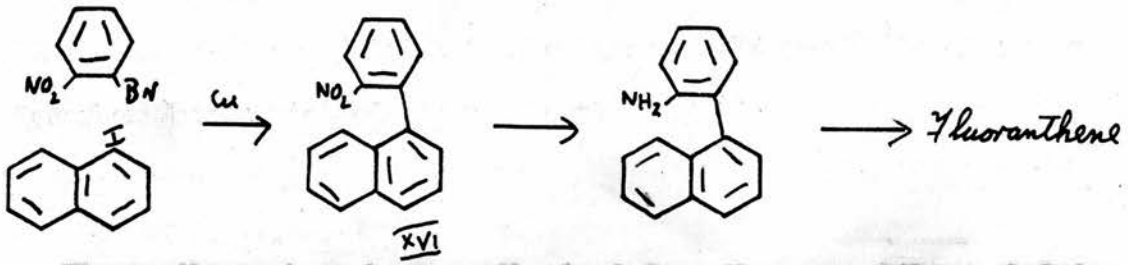


XV

Orchin and Reggel (23) obtained better yields by reacting α-naphthylmagnesium bromide with cyclohexanone. Dehydration gave 1-(2', 3',4',5',-tetrahydrophenyl)naphthalene which was cyclo-dehydrogenated to fluoranthene.

Forrest and Tucker (24) prepared fluoranthene by condensing

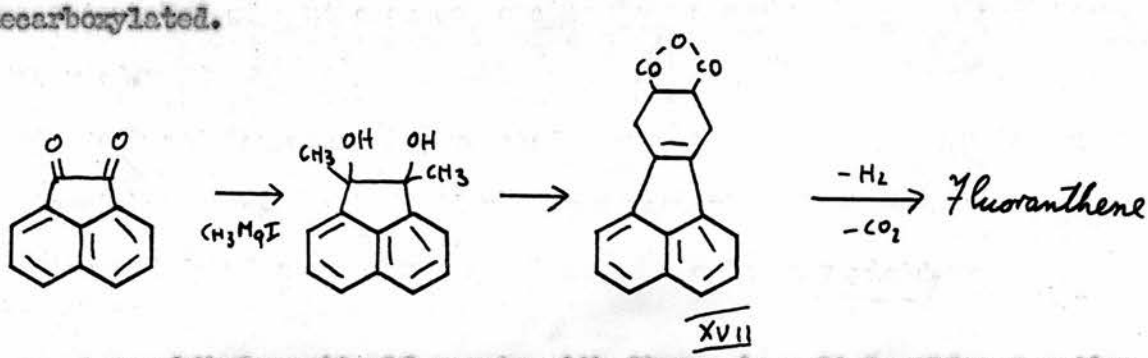
α-iodonaphthalene with O-bromonitrobenzene in an Ullmann reaction. The resulting 1-(2-nitrophenyl)naphthalene XVI was reduced to an amine, diazotised and cyclised with copper bronze.



XVI

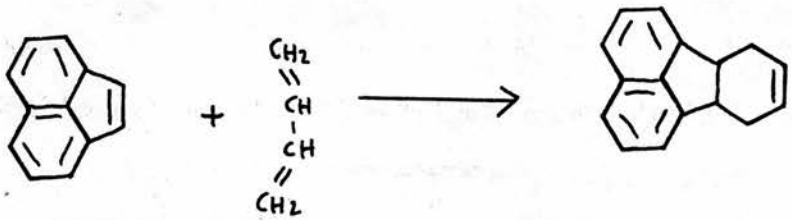
Fluoranthenes have been synthesised from the acenaphthene skeleton.

Campbell and Gow (25) condensed trans 9,10-dimethylacenaphthene-9,10-diol with maleic anhydride to give XVII which was then dehydrogenated, and decarboxylated.



XVII

Acenaphthalene itself reacts with dienes in a Diels-Alder reaction giving hydrogenated fluoranthenes (26).



SUBSTITUTION REACTIONS OF FLUORANTHENE

Substitution reactions of fluoranthene usually give mixtures from which isolation of pure products is often difficult.

Monosubstitution in positions other than 4 and 11 have not been reported. Normally the main product is the 4-isomer with a small amount of 11-isomer sometimes formed. In Friedel-Crafts reactions, however, the 11-position is mainly attacked with a lesser amount of 4-isomer formed.

Dibromination gives a 4,11-dibromofluoranthene, while sulphonation and Friedel-Crafts reactions give 4,12-disubstituted derivatives. Campbell and Keir (27) found 4-carboxy-, 4-methoxycarbonyl-, 4-cyano-, and 4-nitrofluoranthene all brominate in the 12-position. On the basis of the available evidence they suggested fluoranthene may be considered as consisting of two diphenyl nuclei AC and BC, in which rings A and B have equal power of directing substituents to the para positions 11 and 12 respectively.

An ortho-para directing group on ring A would increase its directing power giving a 4,11-isomer, while a meta directing substituent would decrease the directing power of the ring giving a 4,12-isomer.

Nitration of 4-acetylaminofluoranthene (28), however, has been shown to give 4-acetylamino-3-nitrofluoranthene. Kloetzel, King and Menkes suggested the acetylamino group so intensely activates the ring to which it is attached that the second substituent enters the same ring.

Little work has been done on higher substitution. A tribromo-derivative has been shown to be the 4,11,12-isomer (29). During this work 4,11-dibromofluoranthene was shown to acetylate in the 12-position.

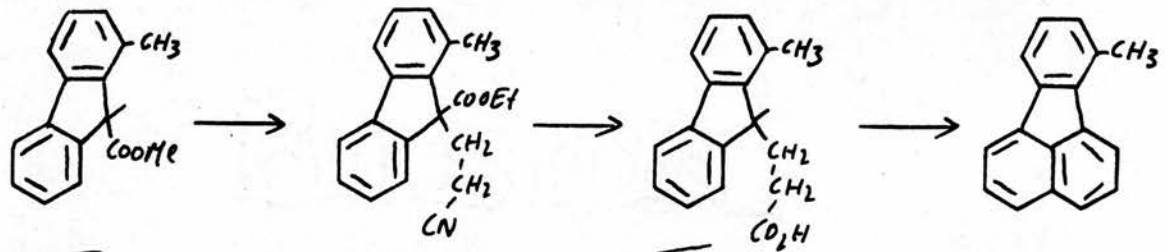
10-SUBSTITUTED FLUORANTHENES.

The synthesis of 10-substituted fluoranthenes is difficult. A number have been reported, mainly derivatives disubstituted in positions 10 and 13, prepared by diene addition reactions involving acenaphthene

skeletons. Only a few compounds have been reported in which fluoranthene carries a single substituent in the 10-position.

Tucker and Whalley (30) synthesised 10-methylfluoranthene by condensing 1-iodonaphthalene with 2-bromo-3-nitrotoluene in an Ullmann reaction. The resulting 1-(2-nitro-6-methylphenyl)naphthalene was reduced to an amine, diazotised and cyclized with copper bronze.

Kloetzel and Mertel (31) prepared the 10-methyl derivative in a number of ways. Metalation and carbonation of 1-methylfluorene gave 1-methyl-9-fluorenecarboxylic acid. The methyl ester XVIII was condensed with acrylonitrile. Hydrolysis and decarboxylation gave 3-(1-methyl-9-fluorenyl)propionic acid XIX which was cyclized, reduced and dehydrogenated.



XVIII XIX

Acenaphthalene underwent a Diels-Alder addition with 1,3-pentadiene and the adduct was dehydrogenated to 10-methylfluoranthene. The condensation of ethyl sorbate with acenaphthylene followed by dehydrogenation gave ethyl 13-methyl-7-fluoranthenecarboxylate which was hydrolysed and decarboxylated.

The melting point reported by Tucker and Whalley differed from that of Kloetzel and Mertel. Repetition of their original synthesis (32) and preparation of the derivative by an analogous series using 3-bromo-2-nitrotoluene gave a purer product with the melting point reported by Kloetzel and Mertel.

A 10-phenylfluoranthene derivative (26) has been prepared by diene addition of acenaphthylene and 1-phenylbutadiene.

Synthesis of 10-methoxyfluoranthene has been effected. The

attempted condensation of 2-bromo-3-nitroanisole with 1-iodonaphthalene (33) gave a yield of 1-(2-methoxy-6-nitrophenyl) naphthalene too poor to be of value. 3-Bromo-2-nitroanisole condensed successfully (34) and the resulting 1-(3-methoxy-2-nitrophenyl) naphthalene was reduced to the corresponding amine which, however, failed to undergo cyclisation. The derivative was finally prepared by condensing 1-bromo-8-nitronaphthalene with o-iodoanisole, followed by reduction and cyclisation.

Attempts to prepare 10-carbomethoxyfluoranthene by analogous routes (33) failed. The attempted condensation of methyl 2-bromo-3-nitrobenzoate with 1-iodonaphthalene gave mainly 2,2'-dinitro-6,6'-diphenate with only a few crystals of the desired 1-(2-carbomethoxy-6-nitrophenyl) naphthalene, while methyl 2-chloro-3-nitrobenzoate failed to react completely.

This method of condensing a naphthalene nucleus with a benzene nucleus although valuable is limited by requiring synthesis of individual starting materials and obviously involves stages which may be capricious or liable to side reactions.

The synthesis of fluoranthenes by the diene addition type of reaction is also limited by preparation of starting materials.

SCHMIDT REACTION

The reaction between equimolar quantities of hydrazoic acid and carbonyl compounds in the presence of strong acid is known as the Schmidt reaction. This interesting reaction provides the initial stage in a series of syntheses in this thesis. A brief description would, therefore, seem desirable.

Carboxylic acids form amines according to the following scheme:-

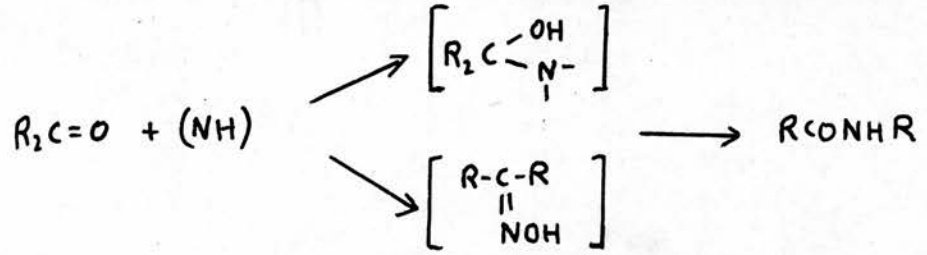
$$RCO_2H + HN_3 \longrightarrow RNH_2 + CO_2 + N_2$$

Aldehydes yield nitriles and formyl derivatives of amines, while ketones yield amides.

$$RCHO + HN_3 \longrightarrow RCN \text{ and } RNHCHO$$

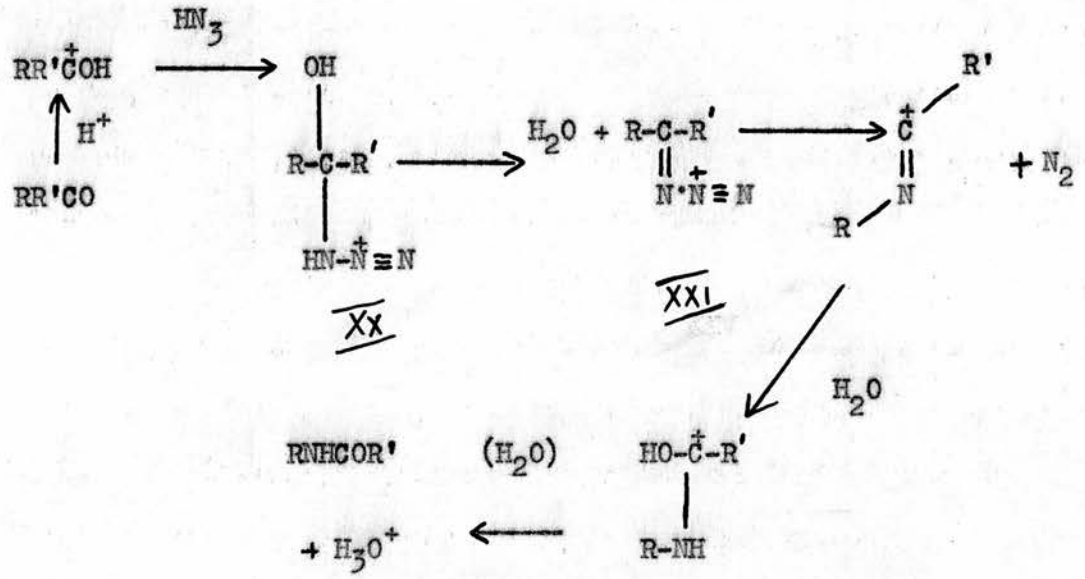
$$RCOR + HN_3 \longrightarrow RCONHR + N_2$$

As yet, the mechanism has not been rigorously established. Schmidt suggested hydrazoic acid first cleaves to nitrogen and the imide radical (NH), which adds to the carbonyl followed by direct rearrangement or by a Beckmann rearrangement of an intermediate oxime to the amide.



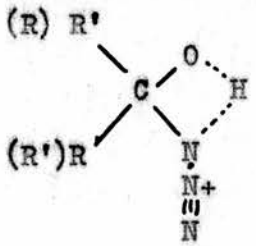
Since then, a number of mechanisms have been proposed for the ketonic Schmidt reaction. The one most favoured in recent years, has been that proposed by Smith (35,36). The initial step previously suggested (37) for an essentially different mechanism consists of formation of a carbonium ion from the carbonyl group and the acid catalyst. The carbonium ion and hydrogen azide form a transitory intermediate XX which loses water with the

preferential formation of one geometric isomer of an iminodiazonium ion XXI which, analogous to the Beckmann rearrangement, undergoes trans rearrangement with loss of nitrogen as shown.



The isomer of XXI having the larger group "anti" to the $\overset{+}{N}_2$ group would be formed preferentially and rearrangement would lead to the observed migration of the larger group.

Since this mechanism was proposed, a number of exceptions to the predicted migration of the larger group has been noted (38) and the migratory aptitudes of groups do not appear to adhere to simple rules. Arcus, Coomb and Evans also suggest that Smith's mechanism, involving dehydration and rehydration of reaction intermediates, is improbable. They suggest that hydrogen bonding between the nitrogen and oxygen atom in the intermediate XX



gives rise to a 4 membered ring. The ring nitrogen is considered to have a pyramidal configuration whence two geometrical isomers are possible. Migration of the group trans to the N_2 group on the separation of the latter would give rise to the final structure.

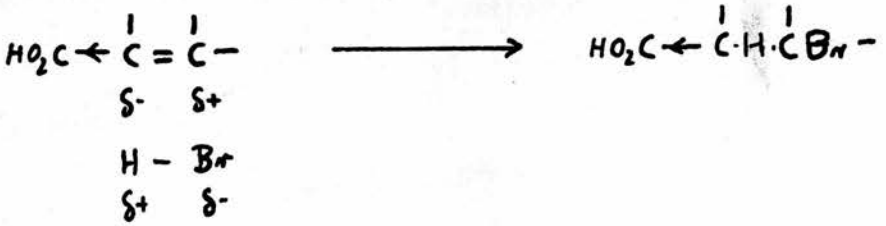
αβ-and βγ-UNSATURATED CARBOXYLIC ACIDS.

A substantial part of this thesis is concerned with investigating the structures of some unsaturated acids of possible value in the synthesis of polycyclic aromatic hydrocarbons, with particular interest in the position of the double bond relative to the carboxyl group. A brief description of some of the reactions and methods concerned seems desirable.

Acids which contain a double bond in the αβ-position differ in many respects from the isomeric acids in which this bond is further removed from the carboxylic group. The introduction of ethylenic unsaturation α to the carboxyl group causes a moderate increase in the strength of a carboxylic acid. This effect is reduced by intercalation of single bonds between the unsaturated centre and the carboxyl. Decarboxylation of αβ-unsaturated acids is apparently more difficult than with the βγ-isomers (39).

The proximity of the carboxyl group also affects the properties of the ethylenic linkage. Electron attracting substituents in ethylene decrease the electron density at the double-bonded carbon and so decrease the velocity of electrophilic additions. Thus, bromine addition to αβ-unsaturated acids occurs 10-100 times more slowly than does similar addition to βγ-unsaturated acids.

Orientation of electrophilic addition is also affected. Thus, the addition of hydrogen halide, which is initiated by the attack of the proton at the centre of higher electron density does not normally obey Markownikoff's rule in the case of αβ-unsaturated acids.



Alkali often effects isomerisation of αβ- and βγ-unsaturated carboxylic ions.

$$-\overset{|}{C}-\overset{|}{C} = C-CO_2^- \quad \rightleftharpoons \quad -\overset{|}{C} = \overset{|}{C}-\overset{|}{C}-CO_2^-$$

The point of equilibrium is normally nearer the left hand side but varies depending upon the substituents on the carbon chain (40). γ-Alkyl substituents tend to shift the equilibrium to the right while γ-Aryl substituents give almost exclusively the βγ-isomer in equilibrium (41).

βγ-Unsaturated acids may often be easily converted to the isomeric γ-lactone by conversion to the hydrobromide followed by treatment with mild alkali. Aqueous mineral acid may often effect this isomerisation directly. The isomerisation by aqueous acid was considered irreversible (42). However, cases of equilibrium between βγ-unsaturated acid and γ-lactone have been reported (43) and this thesis instances isomerisation of a γ-lactone to the acid while the reverse could not be effected.

Differentiation between αβ- and βγ-unsaturated acids is often more satisfactorily accomplished by physical methods. The problem of distinguishing between an αβ-unsaturated acid and the βγ-isomer is normally one of distinguishing between a conjugated and an unconjugated system.

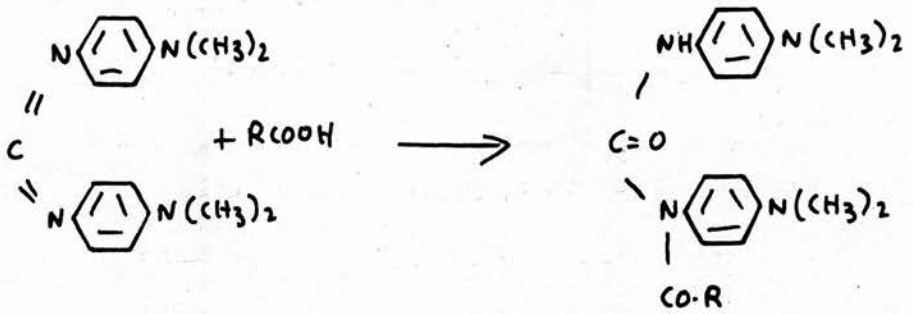
$-CH_2 \cdot CH{:}CH \cdot COOH$ $\qquad$ $-CH{:}CH \cdot CH_2 \cdot COOH$

For this purpose ultraviolet spectra are most generally used, based on the fact that the absorption of chromophores separated by one or more methylene groups is essentially additive whereas conjugated chromophores exhibit a different, typical absorption. Isolated ethylenic linkages and carbonyl groups absorb selectively with high intensity about 185 mμ

(ϵ ca. 10,000), the carbonyl also absorbing with low intensity at 275 mμ (ϵ ca. 15). Conjugation of the two groups results in a bathochromic effect and increased intensity, mesityl oxide, for instance, $(CH_3)_2C{=}CH.CO.CH_3$, absorbing at 225 mμ (ϵ ca. 13,000) and 324 mμ (ϵ ca. 43). The carboxyl group is a weaker chromophore than the carbonyl group, acetic acid exhibiting a band at 225 mμ (ϵ 44·5). Conjugation of the carbonyl group with an ethylenic group on the other hand results in a high intensity band at 204-220 mμ (ϵ ca. 10,000 - 20,000). The unsaturated acids studied in this thesis contained chromophores other than carbonyl and ethylenic groups, and the problem became one of distinguishing between two possible conjugated systems each with its typical absorption. Generally this was easily accomplished by comparison with reference compounds containing similar conjugated systems; for example, β-fluorenylidenepropionic acid was characterised by comparison with fluorenylidene and fluorenyl reference compounds (cf. p.30).

Differentiation of isomeric unsaturated acids by infra-red spectroscopy is less successful. The conjugation of an ethylenic double bond with a carboxyl group results in a lowering of the frequency of absorption associated with the carbonyl stretching vibration. Saturated monobasic acids generally show carbonyl absorption between 1725 cm.$^{-1}$ and 1705 cm.$^{-1}$ and similar values are found for unsaturated carboxylic acids other than $\alpha\beta$-unsaturated acids. In $\alpha\beta$-unsaturated acids the carbonyl absorption falls between 1715 cm.$^{-1}$ and 1690 cm.$^{-1}$.

A reagent which has been suggested as useful for differentiating between $\alpha\beta$- and $\beta\gamma$-unsaturated acids is di-p-dimethylaminophenylcarbodiimide XXII (44,45).



XXII

Aromatic carbodiimides in general react with carboxylic acids to form acylureas (46). Zetsche and co-workers formed a large number of acylureas from di-p-dimethylaminophenylcarbodiimide. It was found the adducts from $\alpha\beta$-unsaturated carboxylic acids were generally coloured while those from $\beta\gamma$-unsaturated acids and other acids unsubstituted in the α-position were generally colourless. These derivatives are highly crystalline and easily formed under mild conditions.

DISCUSSION.

The work carried out in this thesis is in two main sections.

Section I.

Development of a synthetic route to 10-substituted fluoranthenes and 1,8-substituted fluorenones.

Section II.

Structural investigation of some unsaturated acids of possible value in the synthesis of polycyclic aromatic hydrocarbons.

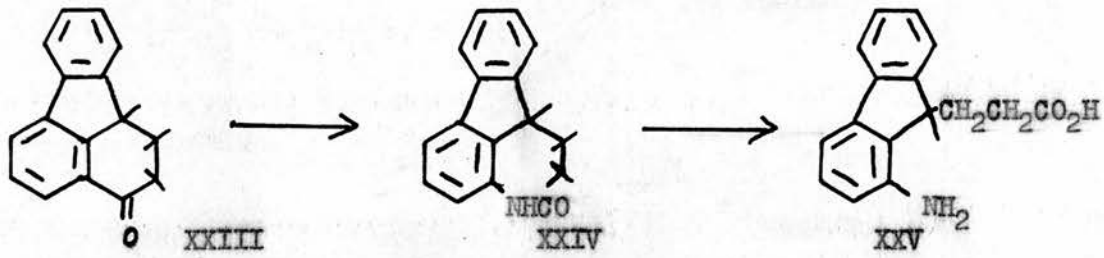
Section I.

Expt. p 45.

The synthesis of substituted fluoranthenes is often difficult and this applies particularly to the preparation of 10-substituted fluoranthenes. So far, only 10-methyl, 10-phenyl and 10-methoxy derivatives have been reported (31,32,26,34). In this section the successful synthesis of 10-bromo and 10-chlorofluoranthenes is described.

The route was suggested by the observation (47) that during the reaction of α-hydrindone and α-tetralone with hydrazoic acid in the ketonic Schmidt reaction, migration of the aryl group is predominant.

4-Keto-1,2,3,4-tetrahydrofluoranthene XXIII was prepared in good yield by the method of Craig (48). Analogous to α-tetralone (35) 4-keto-1,2,3,4-tetrahydrofluoranthene reacted with sodium azide in trichloroacetic acid to give the lactam XXIV which was isolated as its trichloroacetic acid salt. The salt was converted to the lactam by treatment with sodium carbonate solution. Hydrolysis in concentrated hydrochloric acid gave 3-(1-amino-9-fluorenyl)propionic acid XXV.



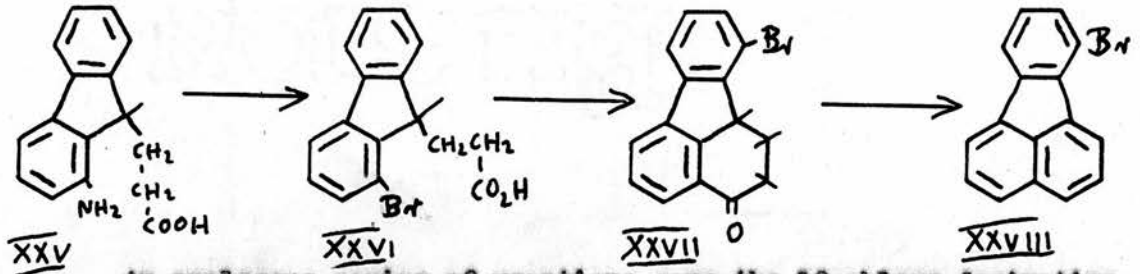
XXIII XXIV XXV

The attempted acetylation of the amino-acid XXV gave the lactam XXIV as did heating the amino-acid above its melting point. The ethyl ester of XXV was prepared and the amino group benzoylated.

3-(1-Amino-9-fluorenyl)propionic acid reacted with phenyl-isothiocyanate to give a phenylthiourea derivative. The attempted

cyclisation of this compound by stannic chloride gave a colourless amorphous solid melting over a wide range. Purification could not be effected. Cyclisation in polyphosphoric acid was unsuccessful. The yellow solid produced gave only slight reaction to dinitrophenylhydrazine, melted over a wide range, and could not be crystallised.

3-(1-Amino-9-fluorenyl)propionic acid was diazotised and reacted in cuprous bromide/hydrobromic acid solution (Sandmeyer reaction) giving 3-(1-bromo-9-fluorenyl)propionic acid XXVI. Cyclisation in polyphosphoric acid gave the ketone XXVII which by Clemmensen reduction yielded 13-bromo-1,2,3,4-tetrahydrofluoranthene. Dehydrogenation by chloranil gave 10-bromofluoranthene XXVIII.



XXV XXVI XXVII XXVIII

An analogous series of reactions gave the 10-chloro derivative. Diazotisation of the amino-acid XXV and reaction in cuprous chloride/hydrochloric acid solution gave 3-(1-chloro-9-fluorenyl)propionic acid. Cyclisation in polyphosphoric acid, Clemmensen reduction and dehydrogenation by chloranil gave 10-chlorofluoranthene.

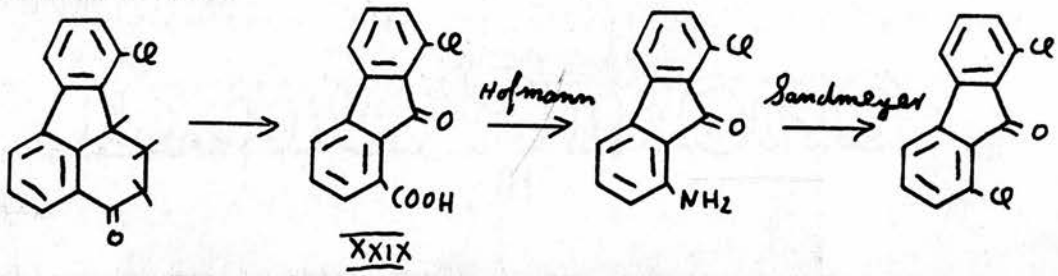
Attempts to prepare the 10-iodo derivative were unsuccessful. The diazotised amino-acid on reaction in potassium iodide solution gave an uncrystallisable tar. Possibly different reaction conditions would be successful.

The diazotised amino-acid reacted in aqueous acid to give

3-(1-hydroxy-9-fluorenyl)propionic acid. Cyclisation in polyphosphoric acid gave ketonic material which could not be purified. Conversion to the methoxy derivative before cyclisation was considered. In view of the poor yield of 3-(1-hydroxy-9-fluorenyl)propionic acid obtained, work along this route was discontinued.

Few 1,8-substituted derivatives of fluorenone and fluorene have been reported and their synthesis is difficult. The only 1,8-derivative whose assigned structure is probably correct is the 1,8-dichlorofluorenone of Huntress (3).

A number of 1-substituted fluorenones and fluorenes have been prepared as a result of oxidative degradation of fluoranthene derivatives (p. 4). By analogy a number of 1,8-substituted derivatives are theoretically accessible by oxidation of the 13-substituted-4-keto-1,2,3,4-tetrahydrofluoranthenes prepared in the foregoing series. In particular, it was hoped to synthesise independently 1,8-dichlorofluorenone by the following series.

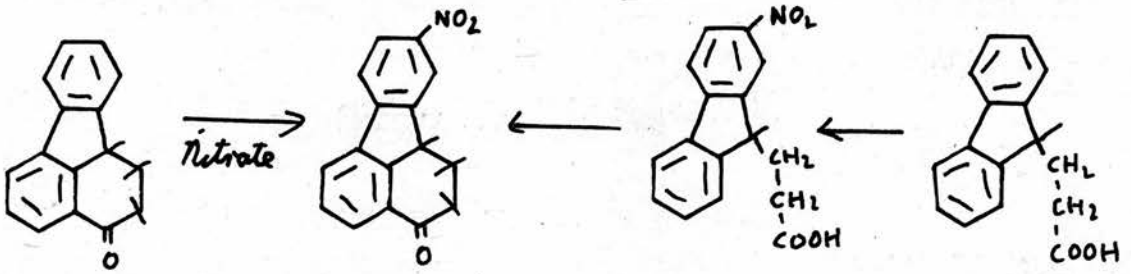


XXIX

13-Chloro-4-keto-1,2,3,4-tetrahydrofluoranthene on oxidation by dichromate gave 1-carboxy-8-chlorofluorenone XXIX. Crystallisation from acetic acid showed two different crystalline forms. No difference in melting-point or mixed melting-point was detected, and crystallisation from benzene showed only one crystalline form. An attempt to convert the carboxyl group to an amino gave a small amount of material with a slight positive reaction to a diazotisation test (49). Purification

could not be effected. The success of the reaction requires preparation of larger amounts of XXIX.

Incidental to this work, the nitration of 4-keto-1,2,3,4-tetrahydrofluoranthene was studied with a view to the preparation of other more highly substituted derivatives. 4-keto-1,2,3,4-tetrahydrofluoranthene, unlike 1,2,3,4-tetrahydrofluoranthene (50) which nitrates in the alicyclic nucleus, gave a mononitro derivative identical with the 12-nitro-4-keto-1,2,3,4-tetrahydrofluoranthene already prepared by a series of reactions from 2-nitrofluorene (51) and by nitration of β-(9-fluorenyl)propionic acid followed by cyclisation (52).

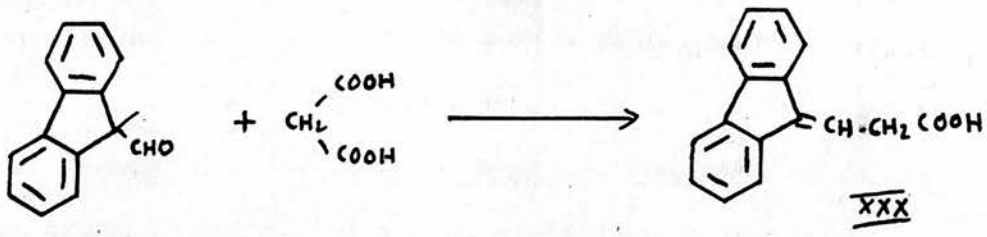


Section II

Aryl substituted unsaturated acids are often intermediates in the preparation of polycyclic aromatic hydrocarbons. A survey of the literature shows there is considerable uncertainty regarding the structure and properties of a number of these acids. The following describes some structural studies on a number of aryl substituted unsaturated acids and their related compounds.

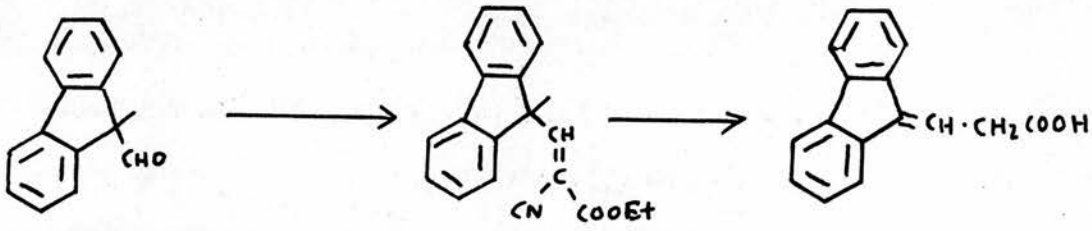
β-Fluorenylidenepropionic acid and its derivatives.

Borsche and Niemann (53) prepared β-fluorenylidenepropionic acid XXX, m.p. 202-203, by condensing 9-formylfluorene and malonic acid in piperidine, but were careful to point out the position of the double bond was uncertain.



XXX

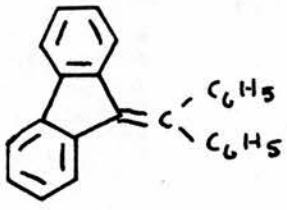
Craig (54) obtained XXX by the interaction of 9-formylfluorene and ethylcyanoacetate followed by hydrolysis and decarboxylation of the product XXXI.



XXXI

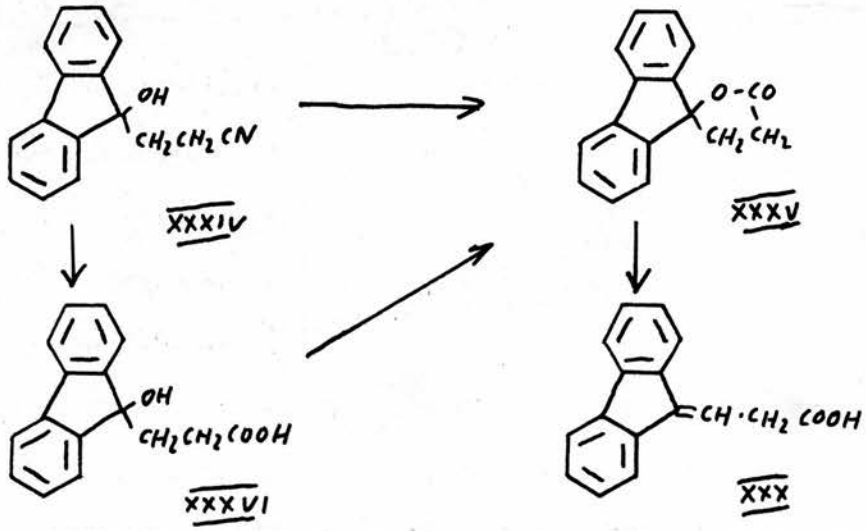
The properties of this intermediate XXXI are interesting. In the solid state or in hexane XXXI was white, while its solution in ethanol or piperidine was yellow. This is probably due to the colourless form having the structure XXXI which tautomerises to the yellow βγ-unsaturated ester form

= CH.CH(CN)·COOEt (55). This was borne out by the resemblance of the ultraviolet spectrum in hexane to that of fluorene (p. 27) a similarity which disappeared when the solvent was changed to ethanol. Similar colour changes, however, have been observed in fluorene derivatives which cannot tautomerise, the colourless 9-diphenylmethylenefluorene for example XXXII giving a yellow solution or yellow melts (56).

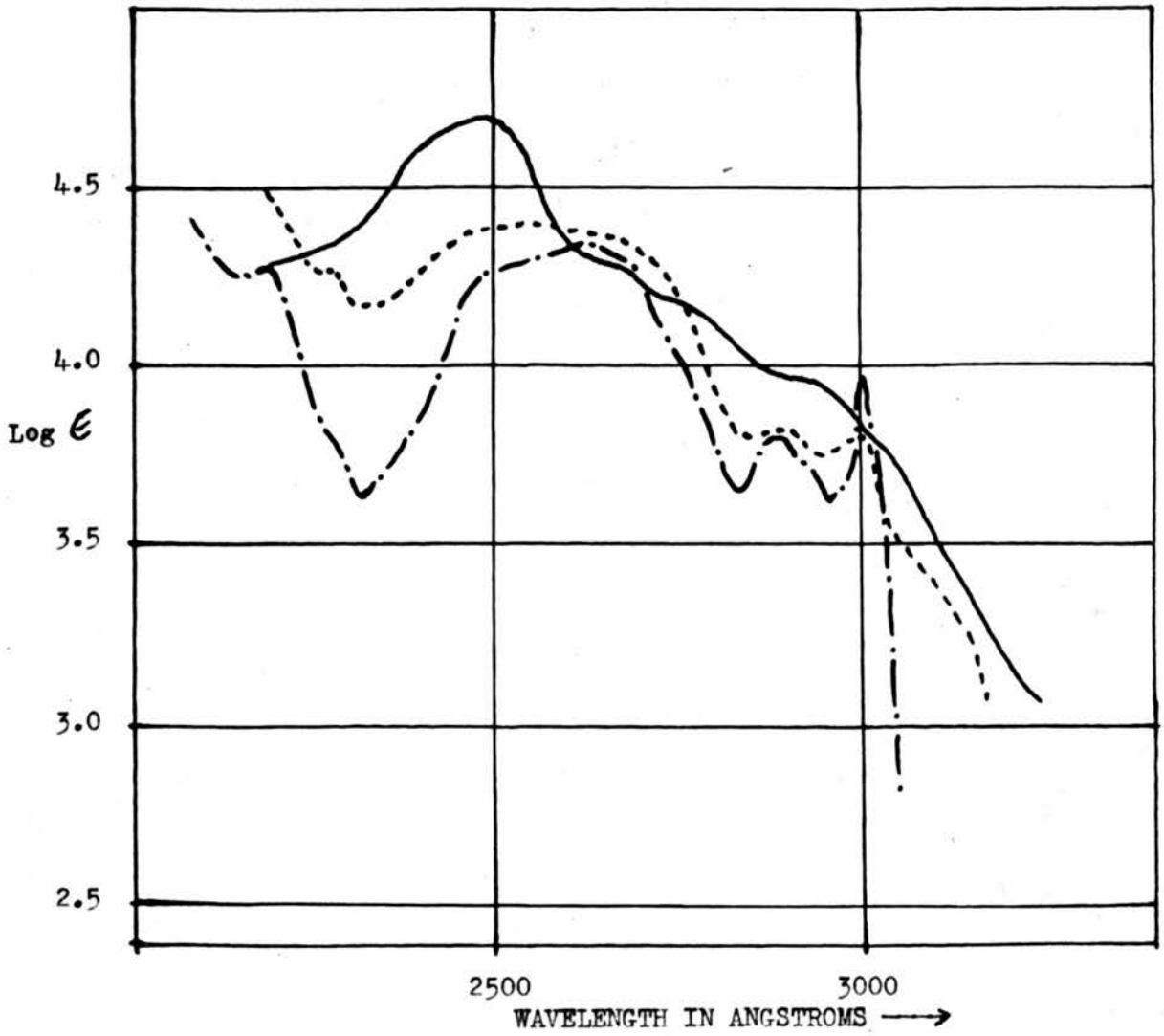


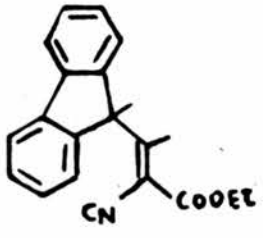
XXXII

The foregoing work is in conflict with the results of Campbell and Fairfull (17) who assigned m.p. 137°C. to the acid XXX, which they prepared by the alkaline hydrolysis of β-(9-hydroxy-9-fluorenyl)propionitrile XXXIV and subsequent treatment with mineral acid; they gave m.p. 202°C. for the corresponding lactone XXXV. Re-investigation of this hydrolysis has shown that some of the data reported by Campbell and Fairfull are erroneous and that depending on the conditions the product may be β-(9-hydroxy-9-fluorenyl)propionic acid XXXVI, m.p. 140°C. or the lactone XXXV, m.p. 133°-134°C.



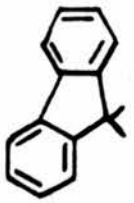
The constitution of the lactone has been well established. It is





——— in ethanol

– – – – – in hexane

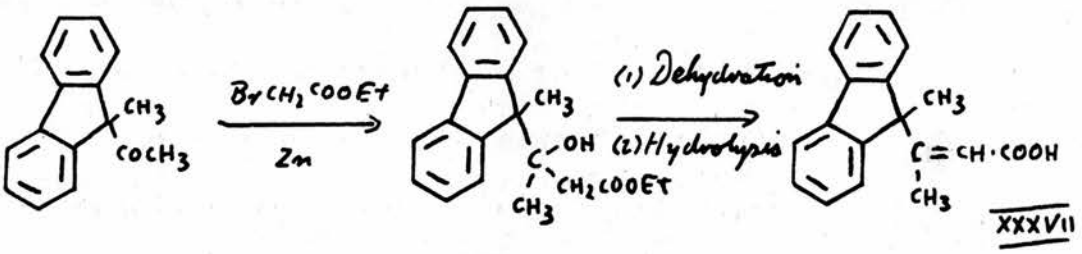


—·—·— (Cf. Ref. 60, Diagram 311)

insoluble in sodium carbonate, gave a positive test with hydroxylamine (57) and showed an infrared band at 1772 cm.$^{-1}$ characteristic of five-membered saturated lactones (58) Its ultraviolet spectrum is similar to those of fluorene and particularly 9-ethylfluorene-9-ol (p. 29). Ring-opening with sulphuric acid gave β-fluorenylidenepropionic acid XXX.

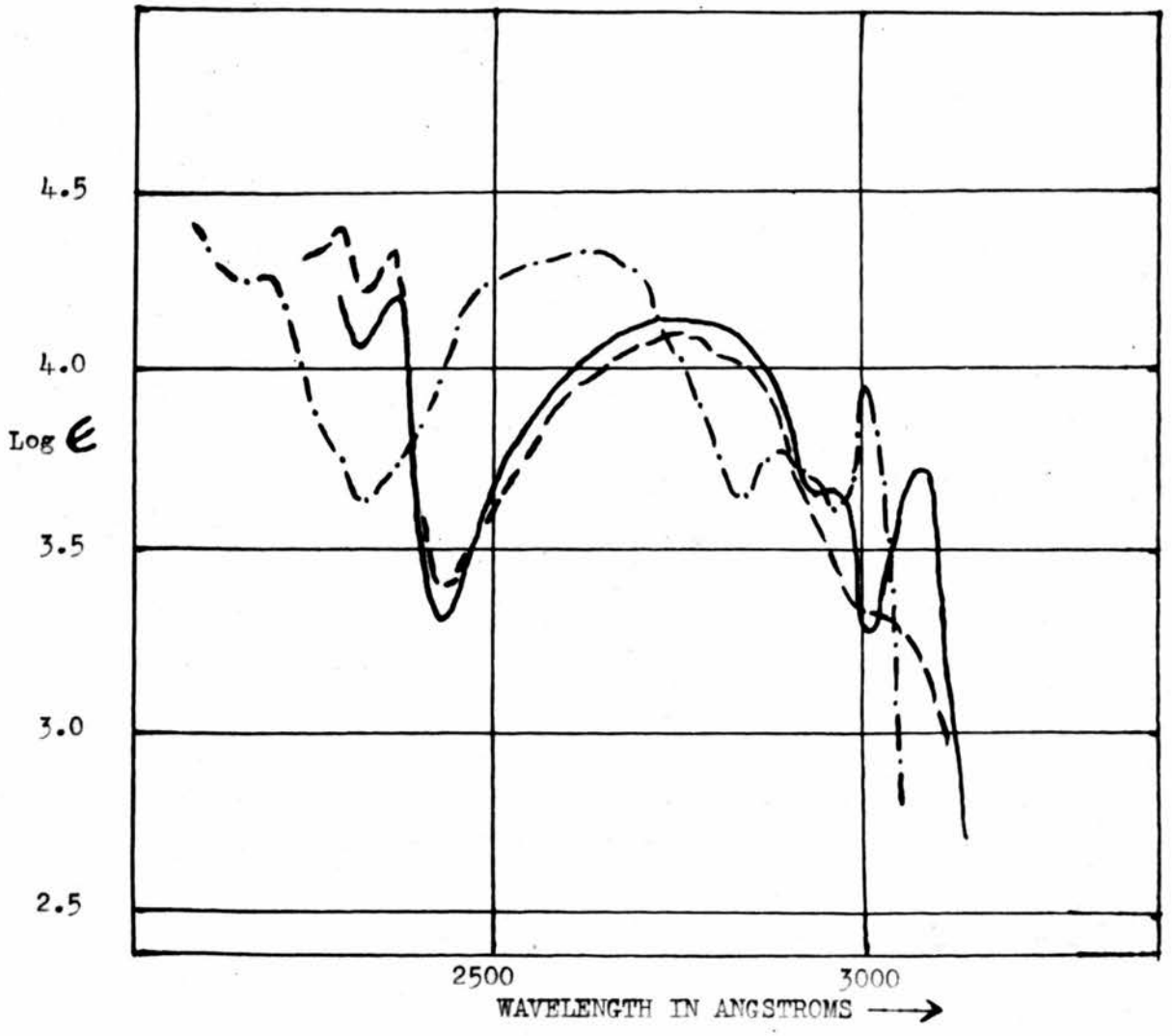
Craig (54) suggested compound XXX may have the αβ-unsaturated structure. Its properties, however, leave little doubt that it has the βγ-structure XXX. It formed a colourless ureide with di-p-dimethylaminophenylcarbodiimide (p. 18) and showed infrared absorption at 1718 cm.$^{-1}$ associated rather with a saturated or βγ-unsaturated acid than with an αβ-unsaturated acid (p. 17). The presence of an αβ-double bond does not greatly alter the ultraviolet absorption of the fluorene system (59) the ultraviolet spectrum of XXX, however, lacks the 250-300 mμ band and the less intense band at 300-310 mμ characteristic of fluorene and fluorenyl derivatives (60) and exhibits absorption similar to that of fluorenylidene derivatives such as 9-ethylidenefluorene (p. 30) and fluorenylideneacetic acid (p. 81).

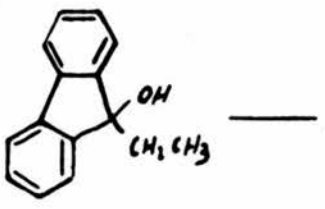
An attempt was made to prepare an acid XXXVII, with the ethylenic double bond stabilised in the αβ-position, and study its physical and chemical properties. 9-Methyl-9-acetylfluorene was reacted with ethyl bromoacetate and zinc (Reformatsky reaction) and the resulting oil dehydrated in benzene/phosphorus pentoxide mixture. Hydrolysis gave a solid which melted over a wide range and could not be purified.

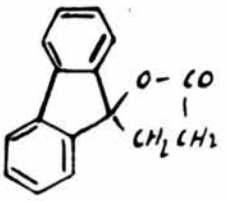


XXXVII

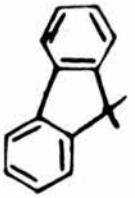
An attempt to prepare XXXVII by condensing malononitrile with



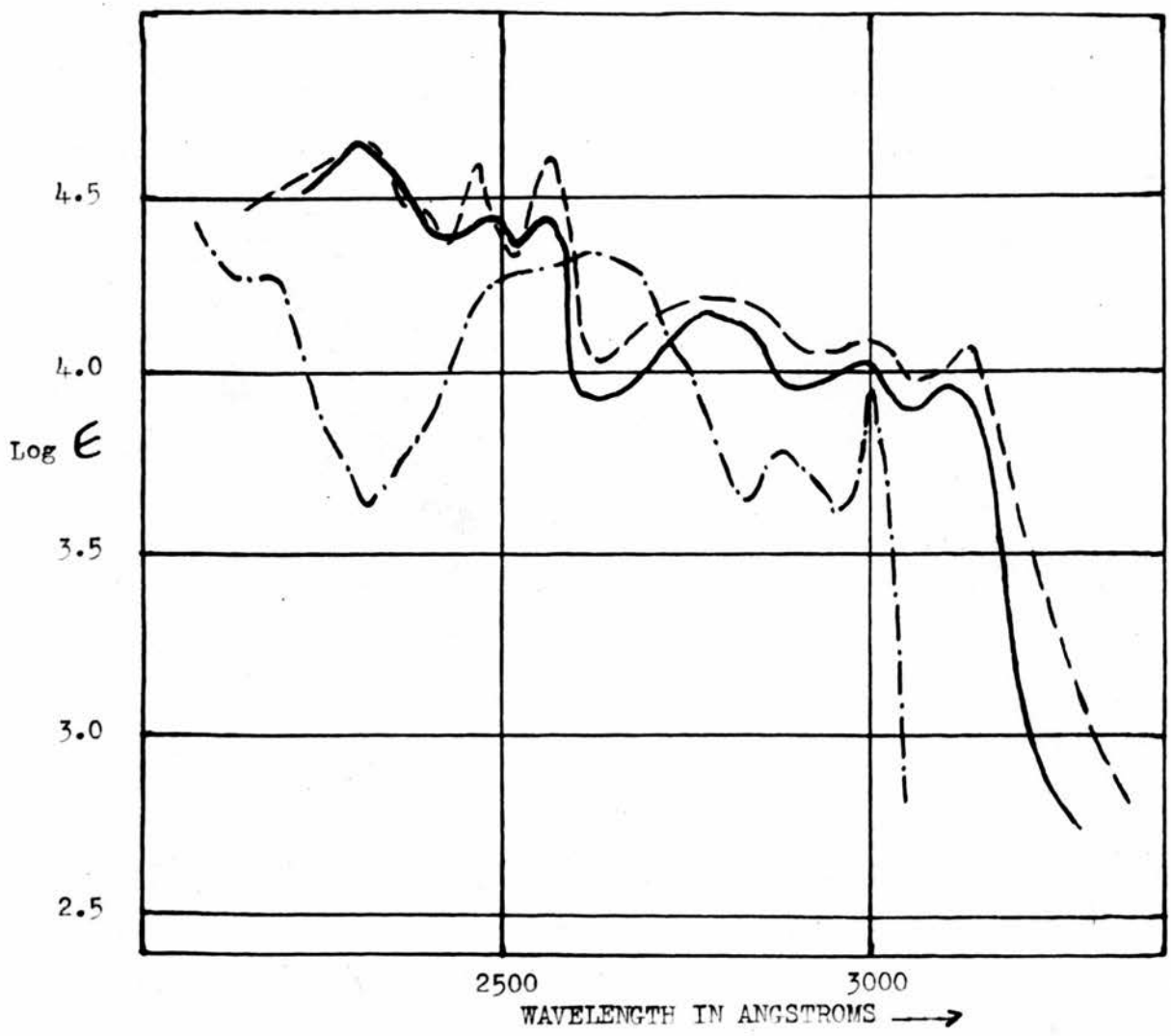


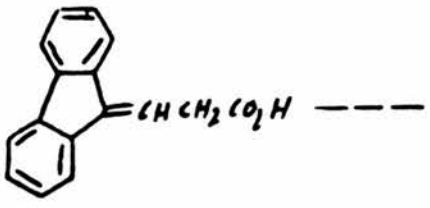


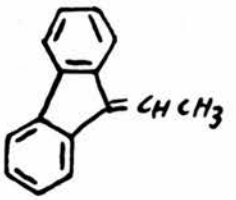
(Cf. Ref. 60, Diagram 324)



(Cf. Ref. 60, Diagram 311)



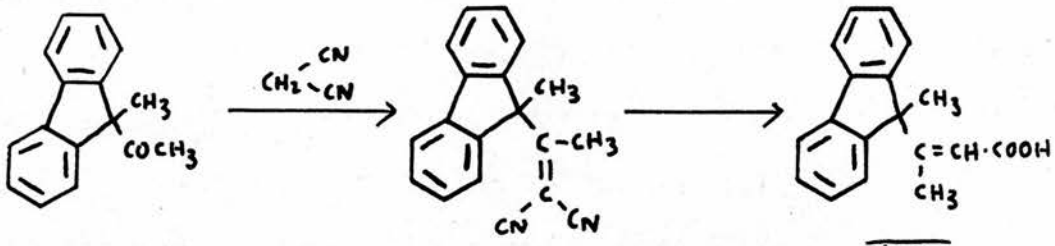




—— (Cf. Ref. 75)

—·—·— (Cf. Ref. 60, Diagram 311)

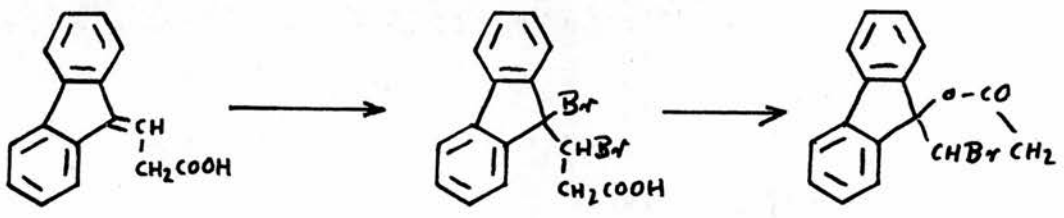
9-methyl-9-acetylfluorene followed by hydrolysis also failed.



XXXVII

Unsuccessful attempts were made to convert the acid XXX into the lactone XXXV, which, however, is easily obtained by dehydration of the hydroxy-acid XXXVI. The acid-catalysed irreversible isomerisation of a γ-lactone to the corresponding βγ-unsaturated acid is novel (42) and is in contrast to the behaviour of the structurally analogous diphenylvinylacetic acid which in acid media is in equilibrium with the lactone and with sulphuric acid gives a 95% yield of the lactone (43). Efforts to isomerise the βγ- to the αβ-unsaturated acid by alkali failed, confirming the conclusions of earlier workers (41) that γ-aryl substituents give almost exclusively the βγ-isomer in the base-catalysed equilibrium between βγ- and αβ-unsaturated carboxylic ions.

The unsaturated acid XXX with bromine in acetic acid yielded a dibromide XXXVIII which decomposed so rapidly that it could not be obtained pure. There seems little doubt, however, that the pure dibromo-acid melts considerably lower than the m.p. 166-167°C. reported (17). The dibromo-acid when kept yielded the bromo-lactone XXXIX.



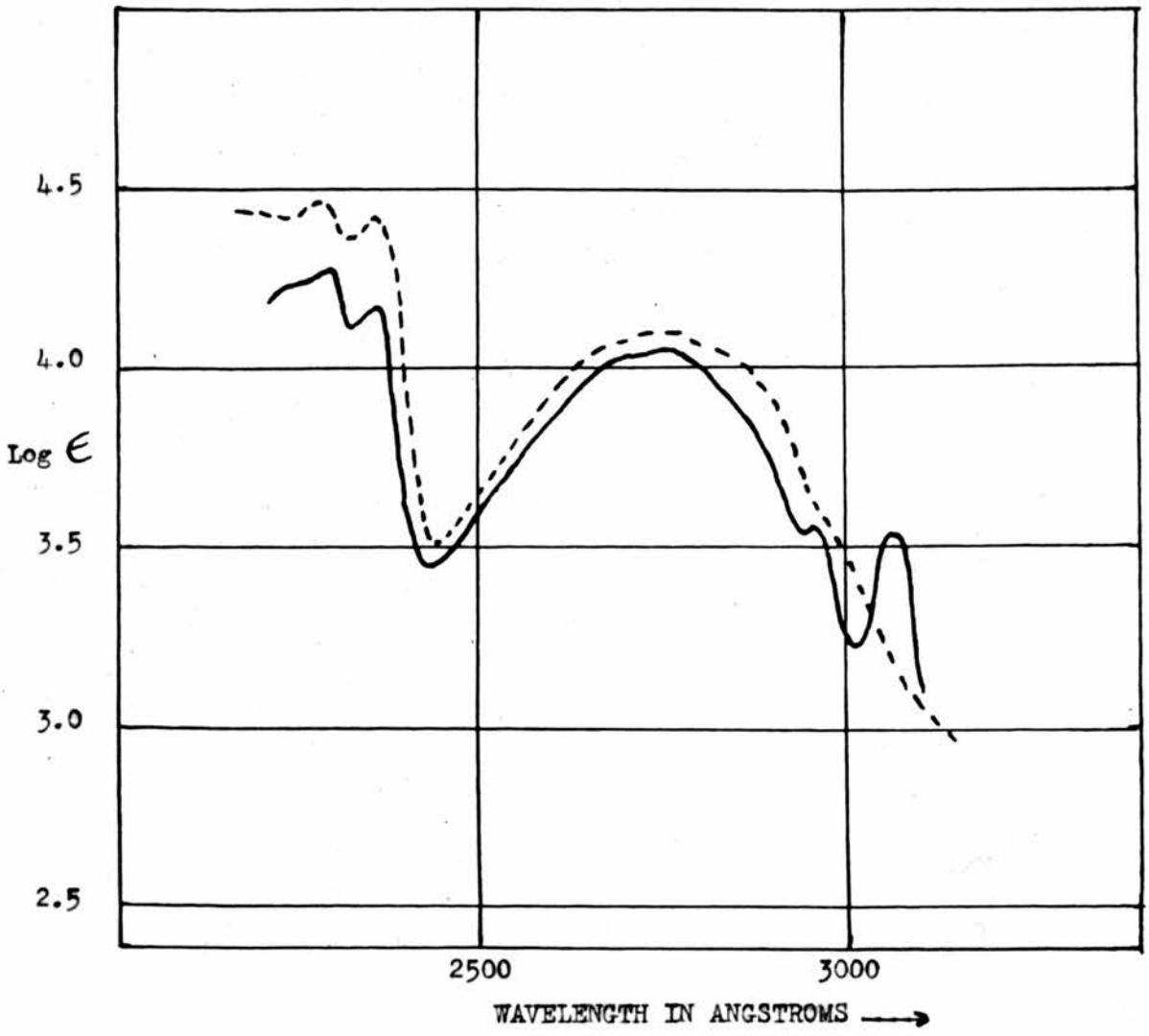
XXX XXXVIII XXXIX

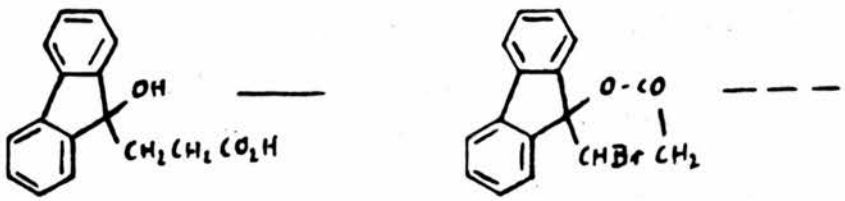
The bromo-lactone XXXIX gives an ultraviolet spectrum resembling

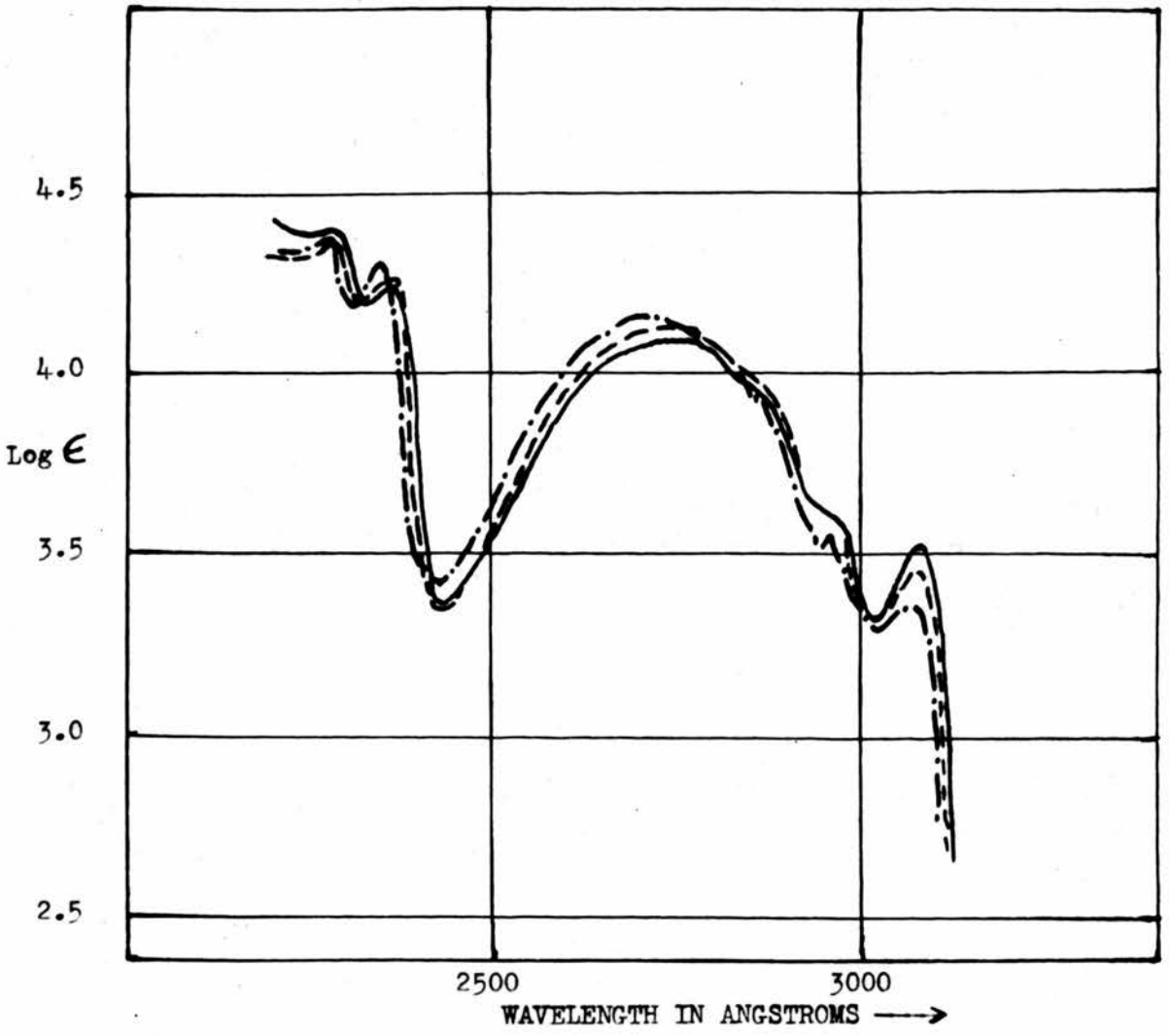
that of the lactone XXXV (p.33), but exhibited a strong infrared band at 1795 cm.$^{-1}$, differing from the 1775 cm.$^{-1}$ exhibited by five-membered lactones (58). The lactone XXXV with bromine in acetic acid on standing gave finally the bromo-lactone; probably the acid catalysed isomerisation of the lactone XXXV to the unsaturated acid XXX is the initial step. The bromo-lactone and the dibromo-acid gave rise to the unsaturated acid XXX when boiled for a short time with zinc and acetic acid.

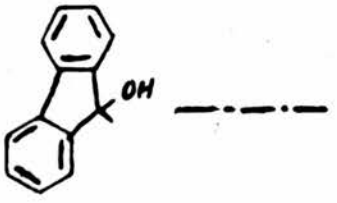
Both the $\beta\gamma$-unsaturated acid XXX and the hydroxy-acid showed carboxyl absorption at 1718 cm.$^{-1}$ typical of dimerised carboxylic acids (61), while the hydroxy-acid possesses a sharp hydroxyl band (62) at 3460 cm.$^{-1}$. The ultraviolet spectrum of the hydroxy-acid (p.33) is typical of a fluorene derivative and almost identical with that of 9-ethylfluorene-9-ol (p.29).

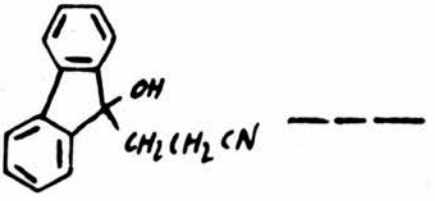
The ultraviolet spectra of a number of fluorenol derivatives have been investigated. The spectra of fluoren-9-ol, 9-benzylfluoren-9-ol, β-(9-hydroxy-fluorenyl)propionitrile (p.34) β-(9-hydroxy-9-fluorenyl)-propionic acid and 9-ethylfluorene-9-ol are all similar and illustrate the bathochromic influence of the 9-hydroxyl group on the fluorene spectrum (63), giving rise to the characteristic band at 307-310 mμ by which fluorenols can be differentiated from their derivatives such as alkyl ethers or lactones.

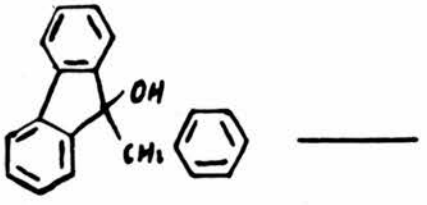

4.5
4.0
Log ∈
3.5
3.0
2.5
2500
3000
WAVELENGTH IN ANGSTROMS


OH
CH2CH2CO2H
O-CO
CHBrCH2


4.5
4.0
Log ∈
3.5
3.0
2.5
2500
3000
WAVELENGTH IN ANGSTROMS ⟶

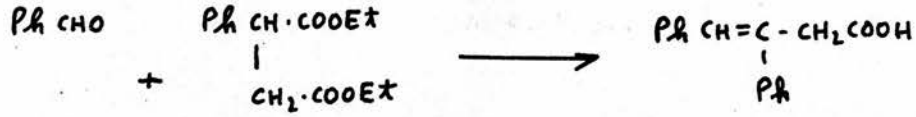

OH


OH
CH2CH2CN


OH
CH3

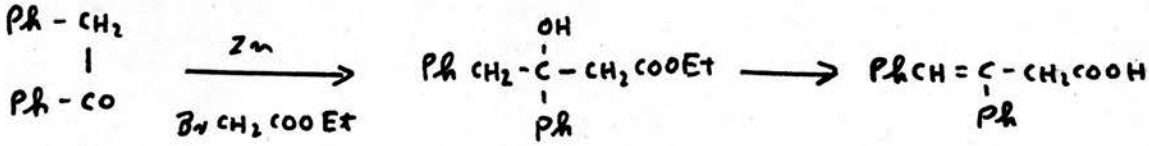
3,4-Diphenylbutenoic acids.

Fichter and Latzko (64) prepared 3,4-diphenylbutenoic acids by condensing benzaldehyde with diethyl phenylsuccinate in a Stobbe reaction, the condensation apparently taking place on the α-carbon atom activated by the phenyl group.



Two 3,4-diphenylbut-3-enoic acids were obtained, one of m.p. 172-173°C. and an 'allo' compound of m.p. 142°C. Isomerisation of both compounds by alkali gave the αβ-isomer m.p. 130°C.

A 3,4-diphenylbutenoic acid (quoted m.p. 168°C.) has been prepared by a Reformatsky reaction between deoxybenzoin and ethyl bromoacetate followed by dehydration and hydrolysis of the intermediate hydroxy-ester XL. Both the βγ-unsaturated (66,67) and the αβ-unsaturated structure (65, 76) have been assigned to this compound.



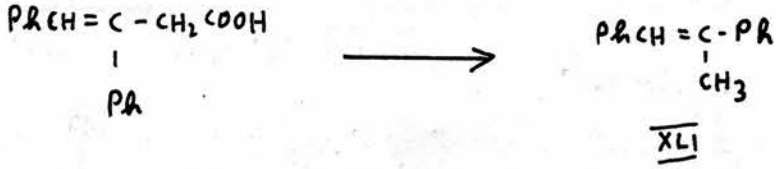
XL

Phalnikar and Nargund (67) also obtained a 3,4-diphenylbut-2-enoic acid by hydrolysis of XL and dehydration of the resulting hydroxy-acid in acetic anhydride (quoted m.p. 114°C.).

According therefore to the above researches, it seems that at least four 3,4-diphenylbutenoic acids have been isolated. This is not impossible, since the acids might be αβ-or βγ-unsaturated acids, each existing in two geometrically isomeric forms. It seems unlikely that all four forms would be easily isolated. That the hydroxy-ester XL should dehydrate in the βγ-position

while the corresponding hydroxy-acid dehydrates in the $\alpha\beta$-position (67) also seems unlikely. This could possibly be accounted for by the change in dehydrating reagents (Cf. Ref. 77). However, this is not probable and it was therefore decided to repeat the investigation both of the Stobbe and the Reformatsky reactions.

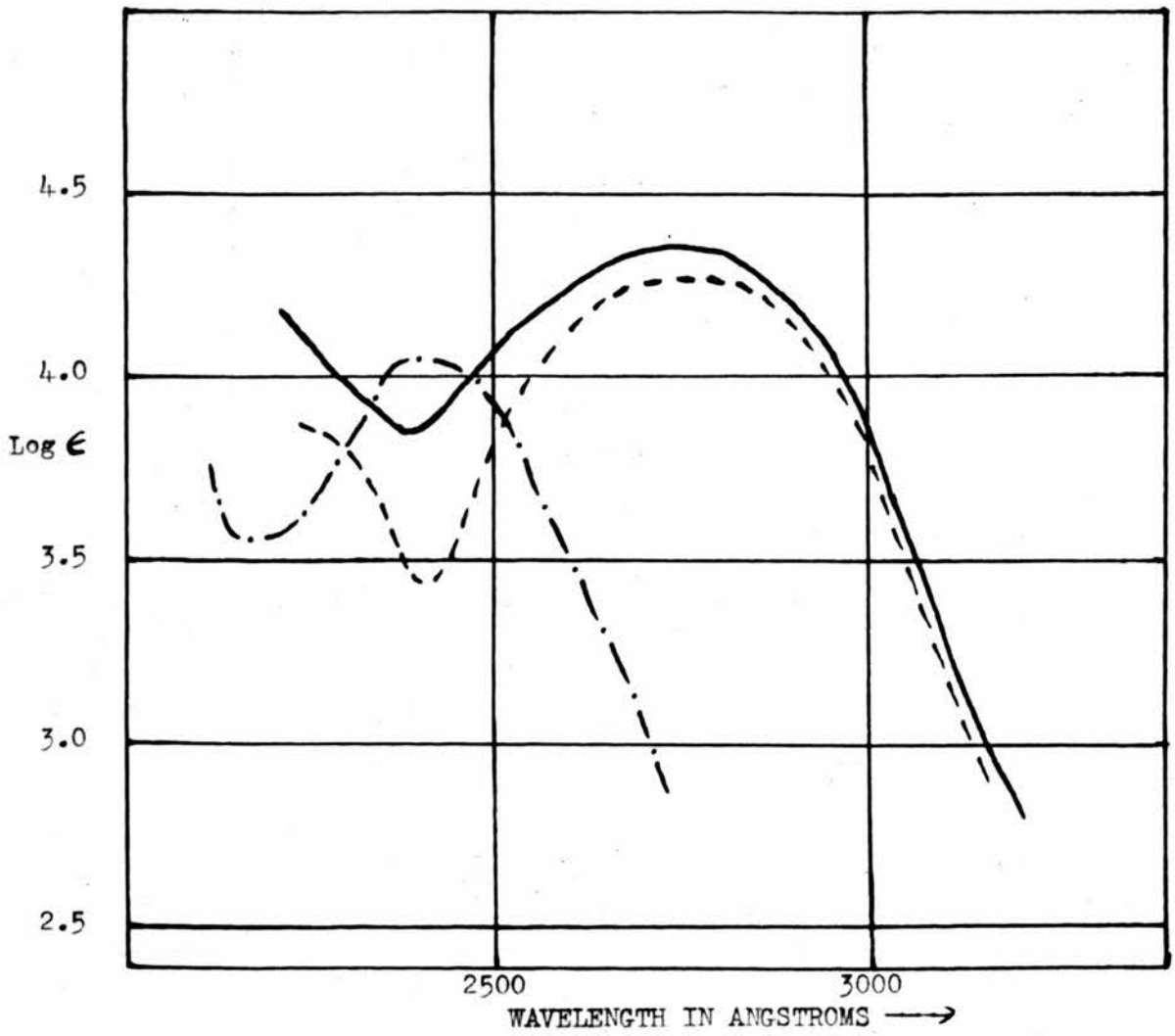
A Reformatsky reaction between deoxybenzoin and ethyl bromoacetate gave XL. Dehydration by phosphorus pentoxide and hydrolysis of the resulting unsaturated ester gave 3,4-diphenylbut-3-enoic acid, m.p. 169° C., whose structure was confirmed by the colourless ureide formed with di-p-dimethylaminophenylcarbodiimide (Cf. p.18), the similarity of its ultraviolet spectrum to that of α-methylstilbene, and its difference from that of α-methylstyrene (p.37). The attempted lactonisation of the unsaturated acid by boiling in sulphuric acid, b.p. 140°C., resulted in decarboxylation to α-methylstilbene XLI. In this ease of decarboxylation 3,4-diphenylbut-3-enoic acid differs from styryl- and $\alpha\alpha'$-dimethylstyrylacetic acid which are resistant to decarboxylation (39).



XLI

The attempted addition of hydrobromic acid followed by ring-closure gave back the original unsaturated acid. In an attempted isomerisation to the 2-enoic acid (64) only unchanged $\beta\gamma$-unsaturated acid was obtained.

Hydrolysis of the hydroxy-ester XL gave $\beta\gamma$-diphenyl-β-hydroxybutyric acid. An attempted dehydration in acetic anhydride (67) gave an oil which could not be crystallised. Boiling the hydroxy-acid in sulphuric acid, b.p. 140°C., gave a mixture of 3,4-diphenylbut-3-enoic acid and α-methylstilbene XLI. Despite a number of attempts no unsaturated acid



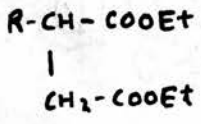
$PhCH{=}C(Ph)\text{-}CH_2COOH$ ——————→ - - - - - -

$PhCH{=}C(Ph)\text{-}CH_3$ ——————— (Cf. Ref. 60, Diagram 127)

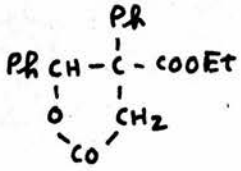
$CH_3\text{-}C(Ph){=}CH_2$ -.-.-.-.- (Cf. Ref. 60, Diagram 25)

of m.p. 114°C. could be detected or isolated. It is concluded that Phalnikar and Nargund probably isolated only an impure unsaturated acid.

Attention was then directed to the Stobbe condensation between benzaldehyde and diethyl phenylsuccinate carried out by Fichter and Latzko (64). It is known that in the Stobbe condensation between substituted succinic esters XLII where R = CH_3, CH_2Ph, CH_2CH_2Ph, and aldehydes condensation occurs at the methylene groups. Fichter's contention (64) that benzaldehyde condenses at the substituted carbon atom (see above) of diethyl phenylsuccinate (XLII, R = Ph) giving 3,4-diphenylbut-3-enoic acid, possibly through hydrolysis and decarboxylation of an intermediate paraconic ester XLIII (68), is therefore unlikely. This view is strengthened by recent work which showed that cycloheptanone condenses with diethyl phenylsuccinate at the methylene group (69).

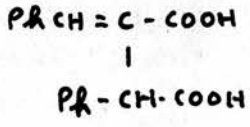


XLII



XLIII

Repeated attempts to obtain the diphenylbutenoic acid of Fichter and Latzko led only to oily products, alkaline hydrolysis of which yielded a compound whose properties indicate that it is benzylidenephenylsuccinic acid XLIV.



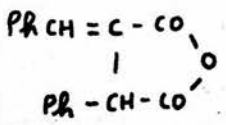
XLIV

It is soluble in sodium carbonate solution. With ethanol and sulphuric acid it gave a monoethyl ester which was soluble in sodium carbonate solution, and with p-nitrobenzyl bromide yielded a di-p-nitrobenzyl ester. The dicarboxylic acid showed an infrared absorption band at 1625 cm.$^{-1}$ which

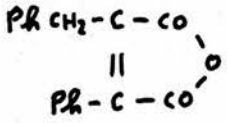
is not present in the spectrum of phenylsuccinic acid and which is assigned to the ethylenic linkage, cinnamic acid, for instance, exhibiting a band at 1626 cm.$^{-1}$ (70). Ozonolysis gave an oil from which was isolated benzaldehyde (identified by dinitrophenylhydrazone). Decarboxylation of the dibasic acid was attempted without success.

Attempts to repeat Fichter's condensation of benzaldehyde with the sodium salt of phenylsuccinic acid (64) gave only uncrystallisable oily products.

Benzylidenephenylsuccinic acid gave two cyclic anhydrides, m.p. 76° and 114°C. It is unlikely that these are cis- and trans- isomers of the anhydride XLV, since they are easily obtained from one geometric form XLIV, and it is probable that the two isomers are benzylidenephenylsuccinic anhydride XLV, m.p. 76°C., and α-benzyl-β-phenylmaleic anhydride XLVI respectively.

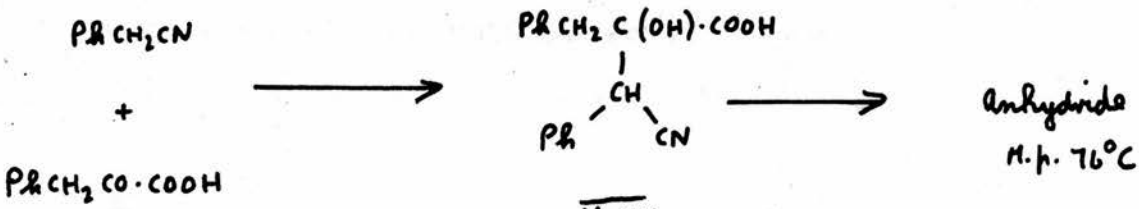


XLV



XLVI

The low melting anhydride was obtained by heating the dicarboxylic acid XLIV above its melting point and was occasionally isolated along with the dibasic acid XLIV from the Stobbe reaction. It is probably identical with the anhydride obtained by the condensation of phenylpyruvic acid with benzyl cyanide followed by hydrolysis and dehydration of the product XLVII (71). To this anhydride Cordier (loc.cit.) tentatively assigned the structure XLVI.



XLVII

The anhydride showed three characteristic absorption bands, two of which at 1842 cm.$^{-1}$ and 1764 cm.$^{-1}$ are found in cyclic anhydrides (72) Cf. succinic anhydride, 1865 cm.$^{-1}$ and 1782 cm.$^{-1}$; maleic anhydride 1848 cm.$^{-1}$ and 1790 cm.$^{-1}$. The third band at 1640 cm.$^{-1}$ is assigned to the double bond and was missing in the spectrum of a specimen of phenylsuccinic anhydride prepared, which showed only absorption at 1858 cm.$^{-1}$ and 1780 cm.$^{-1}$ typical of cyclic anhydrides (72).

Benzylidenephenylsuccinic acid on heating in acetyl chloride gave the higher melting anhydride, which showed the two carbonyl absorptions typical of anhydrides at 1832 cm.$^{-1}$ and 1762 cm.$^{-1}$ and a band at 1647 cm.$^{-1}$ associated with the double bond. Ozonolysis of the two anhydrides gave oils from which were isolated dinitrophenylhydrazones which could not be purified. The ultraviolet spectra of the dicarboxylic acid XLIV (λmax 265 mμ, log ϵ 4.13) the high melting anhydride (λmax 285 mμ, log ϵ 4.5) and the low melting anhydride (λmax 309 mμ, log ϵ 4.05) did not contain sufficient fine structure to be of value. In ethanol the spectra of the anhydrides tended to "wander" and were recorded in cyclohexane.

The condensation of benzaldehyde with diethylphenylsuccinate by potassium t-butoxide gave mixtures of acid XLIV and the low melting anhydride. In one run a small amount of material of m.p. 206°C. was isolated. The compound analysed for $C_{19}H_{18}O_4$ but could be neither hydrolysed nordecarboxylated and surprisingly gave no infrared carbonyl absorption. The substance has so far not been identified.

It can be concluded that the claims of both Fichter and Latzko, and Phalnikar are open to grave doubt and this is in harmony with other work carried out in the department.

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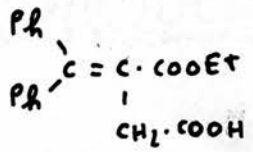
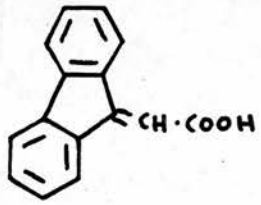
The ureides from di-p-dimethylaminophenylcarbodiimide and a number of other aryl substituted unsaturated acids have been prepared. 4,4-Diphenylbut-3-enoic acid XLVIII, prepared by condensing diphenylacetaldehyde with malonic acid (73) crystallised from petrol in two forms, elongated plates and short prisms. Its structure follows from its ease of lactonisation (43) and is confirmed by the similarity of its spectrum to that of 1,1-diphenylprop-1-ene (p.42). With di-p-dimethylaminophenylcarbodiimide it gave a colourless ureide.

XLVIII

The acid-ester tentatively assigned structure XLIX prepared in the Stobbe condensation of benzophenone (20) and diethyl succinate gave a colourless ureide with di-p-dimethylaminophenylcarbodiimide, thus confirming its structure.

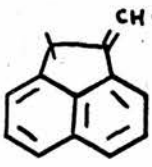


XLIX

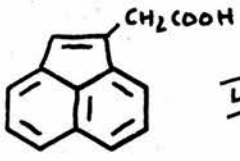


L

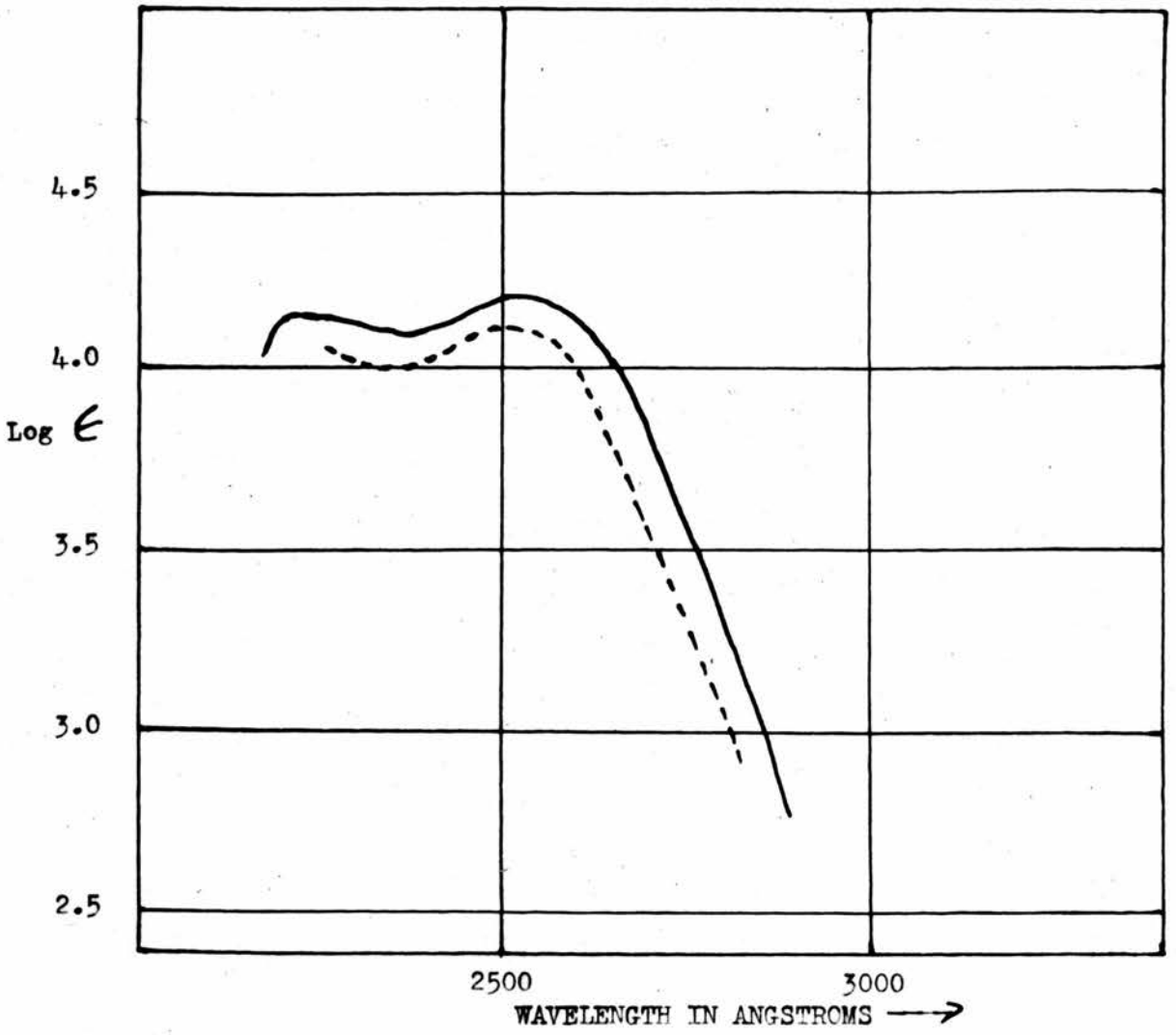
With coloured $\alpha\beta$-unsaturated acids it seems di-p-dimethylaminophenylcarbodiimide gives ureides more deeply coloured than the parent acid. The yellow fluorenylideneacetic acid L for example gave an orange yellow prismatic ureide. The yellow acenaphthylideneacetic acid LI with di-p-dimethylaminophenylcarbodiimide gave orange coloured needles while the yellow isomeric 7-acenaphthyleneacetic acid LII gave a yellow prismatic ureide.



LI



LII



Ph
C = $CHCH_2COOH$ ———
Ph

Ph
C = $CHCH_3$ ------ (Cf. Ref. 60, Diagram 119)
Ph

EXPERIMENTAL

1. Analysis were carried out by Drs. Weiler and Strauss, Oxford.

2. All melting points are uncorrected and were determined by a capillary melting point apparatus (using butyl phthalate) except in a few cases in which a Kofler micro-melting point apparatus was used.

3. Unless otherwise stated the petrol used was of b.p. 100-120°C.

4. Ultraviolet spectra were determined with a Unicam SP 500 Spectrophotometer with ethanol as solvent unless otherwise stated.

5. Infrared spectra were obtained with a Hilger H 800 double beam Spectrometer.

Section I

Fluorene-9-carboxylic acid

Campbell and Tucker, J.C.S., 2624, (1949).

62 gm. Fluorene gave 52 gm. fluorene-9-carboxylic acid after crystallisation from acetic acid.

M.p. = 220-225°C.

Methyl fluorene-9-carboxylate

Tucker J.C.S., 2182, (1949).

52 gm. Fluorene-9-carboxylic acid gave 43 gm. methyl fluorene-9-carboxylate.

M.p. = 60-61°C.

β-(9-Fluorenyl)propionic acid

Campbell and Tucker, loc.cit.

43 gm. Methyl fluorene-9-carboxylate gave 40 gm. β-(9-fluorenyl)-propionic acid.

M.p. = 139-143°C.

4-Keto-1,2,3,4-tetrahydrofluorenthene

Craig, Ph.D. Thesis, p.68.

Phosphorus pentoxide (750 gm.) was dissolved in syrupy phosphoric acid (600 ml.) by heating at 140°C. for 1 - 2 hours. β-(9-Fluorenyl)propionic

acid (40 gm.) was added and the mixture heated at 150°C. for 35 minutes. The solution was poured into water and the crude ketone obtained by extraction with benzene. A sample of pure ketone was obtained by chromatographing crude ketone (4 gm.) on alumina (80 gm.). Evaporation of the first 100 ml. benzene eluted gave a sample of reasonable purity (2 gm.) for the next stage.

M.p. = 90-93°C.

In succeeding large scale experiments crude ketone was used.

Schmidt reaction on 4-keto-1,2,3,4-tetrahydrofluoranthene

The reaction was initially carried out on the pure ketone. In succeeding experiments, as reported here, crude ketone was used with little change in yield.

A mixture of crude ketone (22 gm.), sodium azide (10 gm.) and trichloroacetic acid (130 gm.) was heated at 60°C. (fume-cupboard) with occasional shaking for 5 hours. The dark mixture was poured into water (800 ml.) precipitating a brown solid, or oil which solidified on standing. The trichloroacetic acid salt of the lactam was filtered off, dried and crystallised from benzene.

Yield = 15 gm.

M.p. = 159-169°C.

Two further crystallisations gave straw coloured needles.

M.p. = 172-173°C. (decomp.)

$C_{18}H_{14}NO_3Cl_3$ requires:- C = 54.2% H = 3.5% N = 3.5% Cl = 26.7%.

Found:- C = 54.2% H = 3.7% N = 4.2% Cl = 25.8%.

Powdered trichloroacetic acid salt (11 gm.) was thoroughly shaken with sodium carbonate solution. The lactam of 3-(1-amino-9-fluorenyl)propionic acid was filtered off, washed and dried.

Yield = 6.2 gm.

M.p. = 225-230°C.

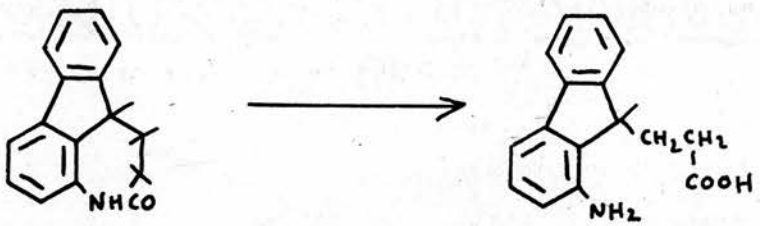
Three crystallisations from glacial acetic acid gave dark yellow prisms.

M.p. = 234-236°C. (decomp.).

$C_{16}H_{13}NO$ requires:- C = 81.7% H = 5.6% N = 5.9%

Found:- C = 81.0% H = 5.7% N = 5.5%.

3-(1-Amino-9-fluorenyl)propionic acid.



Powdered lactam (6 gm.) was heated under reflux with concentrated hydrochloric acid (150 ml.) for 1 hour. The solution was cooled, and the hydrochloride of the amino-acid filtered off. After washing with a little water, the precipitate was boiled in saturated sodium acetate solution. On hot filtering and cooling the solution, 3-(1-amino-9-fluorenyl)propionic acid was deposited as a white crystalline solid.

Yield = 4 gm.

M.p. = 161-163°C. (loses water) 228-233°C. (decomp.).

Two crystallisations in aqueous alcohol gave colourless needles.

M.p. = 162-163°C. (loses water) 234-235°C (decomp.).

$C_{16}H_{15}NO_2$ requires:- C = 75.9% H = 6.0% N = 5.5%.

Found:- C = 76.1% H = 6.0% N = 5.7%.

Amino-acid (0.1 gm.) was heated at 180°C. for 5 minutes. Two crystallisations from glacial acetic acid gave yellow prisms.

Yield = 0.06 gm.

M.p. and Mixed M.p. with lactam = 232-234°C.

Attempted acetylation of the amino-acid.

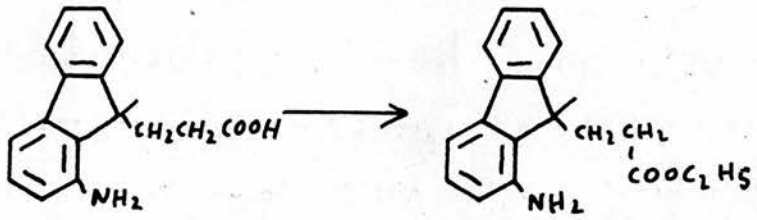
Amino-acid (0.2 gm.) was boiled with acetic anhydride (1 ml.) and concentrated sulphuric acid (1 drop). Addition of water to the cooled solution precipitated a pale yellow oil which solidified overnight. Crystallisation from alcohol gave dark yellow prisms.

M.p. = 228-232°C.

Mixed M.p. with lactam = 228-232°C.

Evaporation of the ethanol left an oily residue which could not be crystallised.

Ethyl 3-(1-amino-9-fluorenyl)propionic acid.



Amino-acid (0.3 gm.) was refluxed in ethanol (8 ml.) with concentrated sulphuric acid (4 drops) for 2½ hours. The solvent was removed and addition of water yielded a white oil. The mixture was made alkaline by addition of sodium carbonate solution and the oil induced to crystallise by scratching on the side of the tube.

Yield = 0.24 gm.

The ethyl ester was twice dissolved in ether/petrol mixture and the ether allowed to evaporate overnight. Colourless needles.

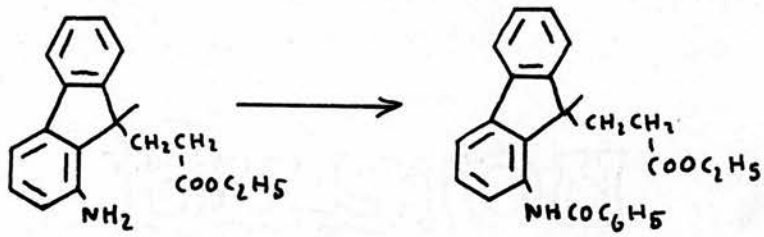
Yield = 0.16 gm.

M.p. = 63-64°C.

$C_{18}H_{19}NO_2$ requires:- N = 5.0%.

Found:- N = 5.0%.

Benzoylation of ethyl 3-(1-amino-9-fluorenyl)propionic acid.



The ethyl ester (0.1 gm.) was dissolved in pyridine (0.5 ml.), benzoyl chloride (0.06 ml.) added, and the solution allowed to stand overnight. Dropwise addition of water precipitated a pale yellow oil which was washed by decantation with dilute hydrochloric acid, sodium carbonate solution, and water. The oil, dried under vacuum, was dissolved in ether, and petroleum added. Scratching the sides of the tube induced crystallisation. Recrystallisation from aqueous ethanol gave colourless needles.

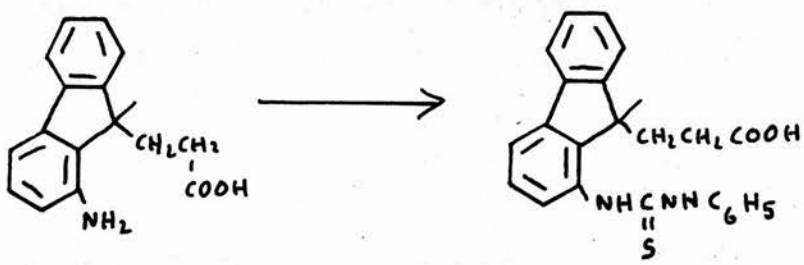
Yield = 0.08 gm.

M.p. = 148°C.

$C_{25}H_{23}NO_3$ requires:- N = 3.6%.

Found:- N = 3.3%.

Phenylthiourea of 3(1-amino-9-fluorenyl)propionic acid.



The amino-acid (0.6 gm.) and phenyl isothiocyanate (0.3 gm.) were heated in ethanol (8 ml.) for 5 minutes. Water was added until the solution became milky below its boiling-point. The product crystallised on standing.

Yield = 0.7 gm.

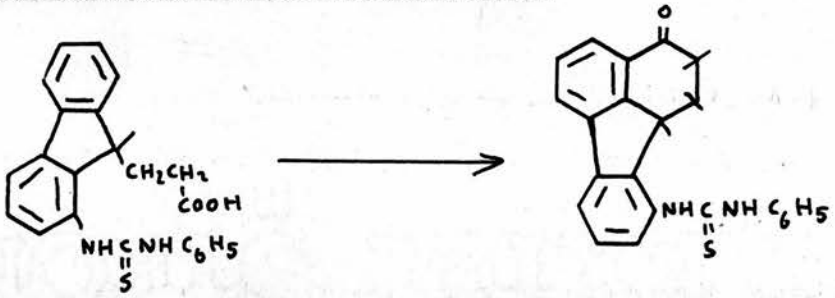
Three crystallisations from aqueous ethanol gave white needles.

M.p. = 164°C.

$C_{23}H_{20}N_2SO_2$ requires:- N = 7.2% S = 8.2%.

Found:- N = 6.6% S = 7.3%.

Attempted cyclisation of the phenylthiourea.



(1) Phosphorus pentoxide (3.5 gm.) was dissolved in syrupy phosphoric acid (3 ml.) by heating the mixture at 140°C. The phenylthiourea (0.3 gm.) was added and the mixture heated at 130°C. until the solid dissolved and then for a further 15 minutes. Pouring the deep red solution into water (40 ml.), gave a yellow precipitate which was filtered off and washed thoroughly with sodium carbonate solution.

Yield = 0.2 gm.

The solid melted over a wide range between 100-200°C., could not be crystallised, and yielded a dinitrophenylhydrazone which also melted over a wide range and could not be purified.

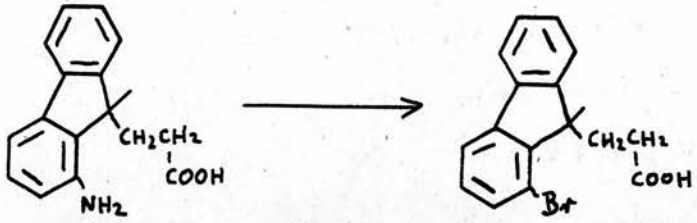
(2) The phenylthiourea (0.3 gm.) was dissolved in benzene (10 ml.). Phosphorus pentachloride (0.3 gm.) was added and the mixture boiled for 5 minutes. On adding stannic chloride (0.2 ml.) a yellow complex separated. After standing for 24 hours with occasional shaking, the mixture was poured

into concentrated hydrochloric acid, the white amorphous solid filtered off, and washed thoroughly with sodium carbonate solution.

Yield = 0.2 gm.

The solid showed only slight reaction to dinitrophenylhydrazine solution, melted over a wide range and could not be purified.

3-(1-Bromo-9-fluorenyl)propionic acid.



The amino-acid (4 gm.) was stirred into glacial acetic acid (70 ml.) and hydrobromic acid (18 ml., 40%) added. The amino-acid immediately dissolved and the hydrobromic acid salt precipitated a few minutes later. The mixture was stirred for 20 minutes, water (24 ml.) added, and the solution quickly cooled to 2°C. Diazotisation was carried out by adding over 10 minutes a solution of sodium nitrite (1.44 gm.) in water (20 ml.). After 45 minutes, urea was added and stirring continued for a further 5 minutes. The mixture was quickly filtered and added in a fine stream over 10-15 minutes to a solution of freshly prepared cuprous bromide (4 gm.) in hydrobromic acid (160 ml., 40%) at 40°C. The sticky product was separated and dissolved in ether. The ethereal solution was washed and dried over sodium sulphate. Evaporation gave the crude 3-(1-bromo-9-fluorenyl)propionic acid.

Yield = 2.4 gm.

The product was crystallised by dissolving it in petrol/ether mixture and allowing the ether to evaporate overnight.

M.p. = 146-150°C.

Two recrystallisations from petrol gave colourless needles.

M.p. = 150-152°C.

$C_{16}H_{13}BrO_2$ requires:- Br = 25.1%.

Found:- Br = 25.3%.

13-Bromo-4-keto-1,2,3,4-tetrahydrofluoranthene.

The experiment described here was made on pure bromo-acid. In other experiments crude bromo-acid was used.

Phosphorus pentoxide (12 gm.) was dissolved in syrupy phosphoric acid (10 ml.) by heating at 140°C. Bromo-acid (0.6 gm.) was added and the mixture heated for 30 minutes at 140°C. The solution was poured into water (40 ml.) and the dark brown product filtered off, washed, and dried. The solid was boiled with petrol and hot filtered. On cooling the solution 13-bromo-4-keto-1,2,3,4-tetrahydrofluoranthene was deposited as yellow balls.

Yield = 0.36 gm.

M.p. = 197-200°C.

One recrystallisation from petrol (charcoal) and two further re-crystallisations gave colourless needles.

M.p. = 204°C.

$C_{16}H_{11}BrO$ requires:- Br = 26.8%.

Found:- Br = 27.3%.

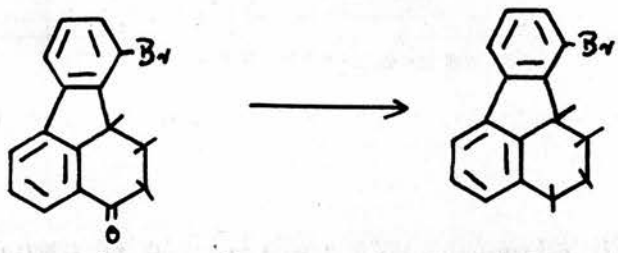
Dinitrophenylhydrazone. Crystallised from benzene as orange needles.

M.p. = 264°C. (decomp.).

$C_{22}H_{15}N_4O_4Br$ requires:- N = 11.7%.

Found:- N = 10.9%.

13-Bromo-1,2,3,4-tetrahydrofluoranthene.



Zinc dust (4.5 gm.) and mercuric chloride (0.45 gm.) were shaken with water (6 ml.) and concentrated hydrochloric acid (3 drops) for 5 minutes. The zinc amalgam formed was washed by decantation. The bromo-ketone (0.3 gm.) in sulphur free toluene (6 ml.), and concentrated hydrochloric acid (6 ml.) were added and the mixture refluxed for 9 hours. The solution was decanted into a separating funnel, the amalgam washed with ether, and the washings added to the separating funnel. After thorough extraction, the ethereal solution was washed and dried over anhydrous sodium sulphate. The ether/toluene solvent was removed and the residue dissolved in the minimum of ether. On cooling the solution in a cardice/acetone mixture 13-bromo-1,2,3,4-tetra hydrofluoranthene was deposited as fine crystals and quickly filtered.

Yield = 0.17 gm.

M.p. = 90-96°C.

Two further crystallisations gave colourless crystals.

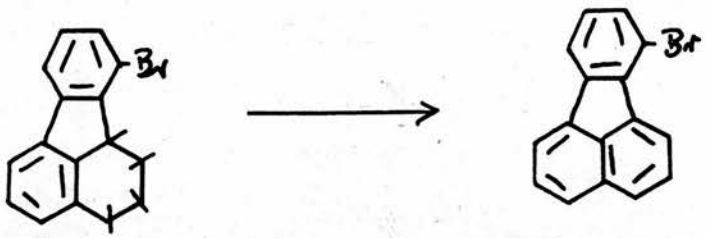
M.p. = 107-109°C.

$C_{16}H_{13}Br$ requires:- Br = 28.0%.

Found:- Br = 26.3%.

Higher bromine analysis could not be obtained, probably due to the deficiencies of the crystallisation procedure.

10-Bromofluoranthene.



13-Bromo-1,2,3,4-tetrahydrofluoranthene (0.12 gm.) was refluxed for 3 hours with chloranil (0.22 gm.) in sulphur free xylene (2 ml.) during which the blood-red solution became dark brown. The cooled solution was filtered and the precipitate washed with xylene (2 ml.). The combined filtrates were diluted with ether and extracted with N sodium hydroxide solution. The organic layer was washed, dried over anhydrous sodium sulphate and evaporated. The red sticky residue in the minimum of warm benzene was chromatographed on a column (5" x 1") of alumina (20 gm.). The chromatogram was developed using a 3:1 by volume mixture of petrol and benzene. Evaporation of the first colourless eluate (20 ml.) gave 10-bromofluoranthene.

Yield = 0.06 gm.

M.p. = 138-144°C.

Two crystallisations in petrol gave pale yellow needles.

M.p. = 157-158°C.

$C_{16}H_9Br$ requires:- Br = 28.4%.

Found:- Br = 27.9%.

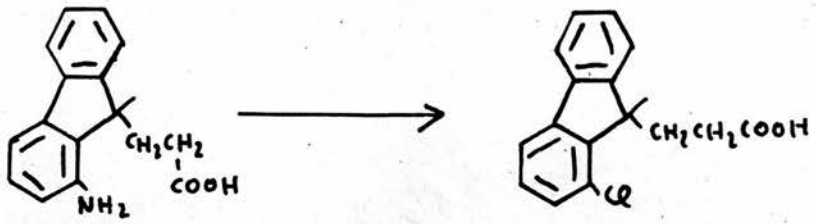
A picrate was deposited on addition of a warm ethanolic solution of 10-bromofluoranthene to a saturated ethanolic solution of picric acid. Crystallisation from ethanol gave yellow needles.

M.p. = 172-173°C.

$C_{22}H_{12}N_3O_7Br$ requires:- N = 8.2%.

Found:- N = 8.1%.

3-(1-Chloro-9-fluorenyl)propionic acid.



The amino-acid (4 gm.) was stirred into glacial acetic acid (70 ml.). Concentrated hydrochloric acid (9.6 ml.), was added and the mixture stirred for 20 minutes. Water (24 ml.) was added and the solution quickly cooled to 2°C. Diazotisation was carried out by adding over a period of 10 minutes a solution of sodium nitrite (1.44 gm.) in water (20 ml.). After 45 minutes urea was added and stirring continued for a further 5 minutes. The diazo mixture was quickly filtered and added in a fine stream over a period of 10-15 minutes to a solution of freshly prepared cuprous chloride (2 gm.) in 6 N hydrochloric acid (100 ml.) at 45°C. The product was filtered off, washed with 6 N hydrochloric acid and then water.

Yield = 2.4 gm.

M.p. = 123-128°C.

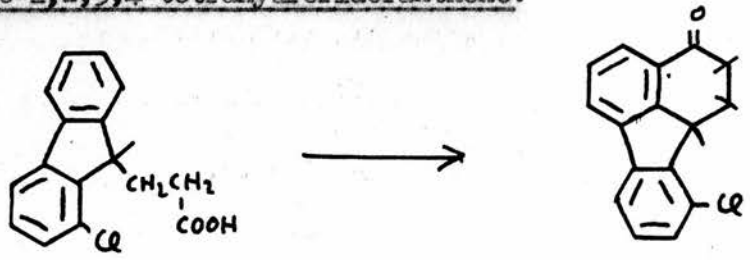
Three crystallisations from aqueous alcohol gave colourless needles.

M.p. = 137°C.

$C_{16}H_{13}O_2Cl$ requires:- Cl = 13.0%.

Found:- Cl = 13.0%

13-Chloro-4-keto-1,2,3,4-tetrahydrofluoranthene.



Phosphorus pentoxide (30 gm.) was dissolved in syrupy phosphoric

acid (25 ml.) by heating at 140°C. The chloro-acid (1.6 gm.) was added, the mixture heated at 140°C. for 30 minutes and poured into water (80 ml.). The precipitate was filtered off, washed, dried, and extracted with hot petrol. On adding charcoal, hot filtering and cooling the solution, the chloro-ketone was deposited as yellow elongated prisms.

Yield = 0.9 gm.

M.p. = 198-202°C.

Two crystallisations gave colourless elongated prisms.

M.p. = 200-202°C.

$C_{16}H_{11}OCl$ requires:- Cl = 14.0%.

Found:- Cl = 14.2%.

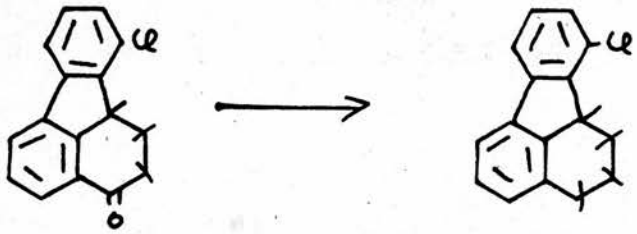
Dinitrophenylhydrazone. Crystallised from benzene as orange needles.

M.p. = 258°C.

$C_{22}H_{15}N_4O_4Cl$ requires:- Cl = 8.2%.

Found:- Cl = 7.7%.

13-Chloro-1,2,3,4-tetrahydrofluoranthene.



The chloro-ketone (0.4 gm.) was reduced by a toluene/zinc amalgam/hydrochloric acid mixture for 6 hours and the tetrahydro compound isolated as before (p.53). Crystallisation was effected by dissolving the product in ether and cooling the solution in a cardice/acetone mixture.

Yield = 0.28 gm.

M.p. = 92-98°C.

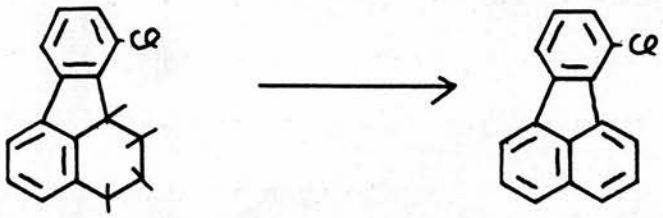
One recrystallisation gave fine colourless crystals.

M.p. = 98-100°C.

$C_{16}H_{13}Cl$ requires:- Cl = 14.8%.

Found:- Cl = 13.6%.

10-Chlorofluoranthene.



The tetrahydro compound (0.24 gm.) was refluxed with chloranil (0.49 gm.) in sulphur free xylene (4 ml.). The cooled solution was filtered and the precipitate washed with xylene (4 ml.). The combined filtrates were diluted with ether and extracted with N sodium hydroxide. The organic layer was washed, dried and evaporated, leaving a red oily product which was crystallised from benzene.

Yield = 0.15 gm.

M.p. = 145-147°C.

One recrystallisation gave colourless plates.

M.p. = 149-150°C.

$C_{16}H_9Cl$ requires:- Cl.= 15.0%.

Found:- Cl. = 15.0%.

Picrate. Crystallised from ethanol as yellow needles.

M.p. = 172°C.

$C_{22}H_{12}N_3O_7Cl$ requires:- N = 8.8%.

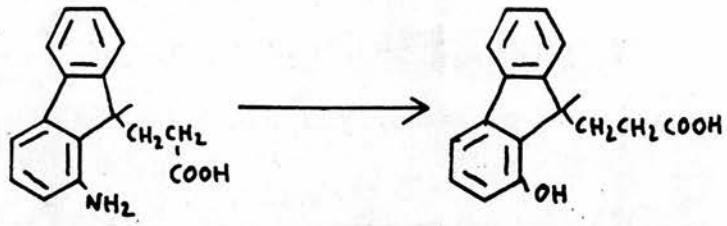
Found:- N = 8.9%.

Attempted preparation of 3-(1-iodo-9-fluorenyl)propionic acid.

3(1-Amino-9-fluorenyl)propionic acid (1 gm.) was diazotised (p.55) and added in a fine stream over 10 minutes to a solution of potassium iodide (8 gm.) in water (30 ml.) at 45°C. A tarry solid (0.6 gm.) which could not

be crystallised, was filtered off.

3-(1-Hydroxy-9-fluorenyl)propionic acid.



3(1-Amino-9-fluorenyl)propionic acid (1 gm.) was diazotised in hydrochloric acid/glacial acetic acid solution (p.55) and added in a fine stream over a period of 30 minutes to a boiling solution of concentrated sulphuric acid (0.5 ml.) in water (50 ml.). The cooled mixture was extracted with ether. The organic layer was washed with a little water and extracted with sodium carbonate solution. Acidification of the extract precipitated a dark oil which crystallised on standing.

Yield = 0.45 gm.

M.p. = 135-140°C.

Four crystallisations from benzene gave fawn coloured needles.

M.p. = 149°C. (decomp.).

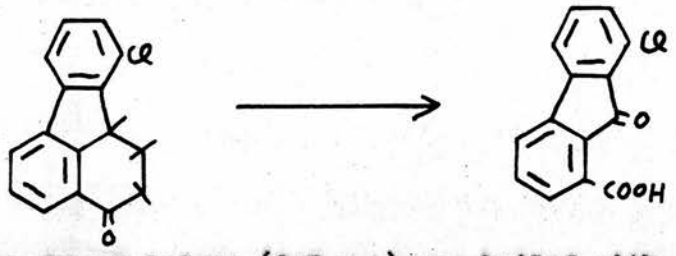
$C_{16}H_{14}O_3$ requires:- C = 75.6%. H = 5.5%.

Found:- C = 75.2%. H = 5.4%.

Attempted cyclisation of 3-(1-hydroxy-9-fluorenyl)propionic acid.

Phosphorus pentoxide (3 gm.) was dissolved in syrupy phosphoric (2.5 ml.) acid by heating at 140°C. The hydroxy-acid (0.13 gm.) was added and the mixture heated at 130°C. for 30 minutes during which the dark brown solution became blood-red. Pouring the mixture into water (25 ml.) gave a dark brown solid. The product melted over a wide range and could not be crystallised. A dinitrophenylhydrazone obtained also melted over a wide range and could not be purified.

1-Carboxy-8-chlorofluorenone.



The chloro-ketone (0.5 gm.) was boiled with sodium dichromate (1.5 gm.) for 2 hours in glacial acetic acid (12 ml.). The dark green solution was reduced to one-third its volume and poured into water (40 ml.). The precipitate was filtered off and thoroughly shaken with sodium carbonate solution. Filtration left a tarry residue which could not be crystallised. Acidification of the filtrate precipitated a pale yellow solid.

Yield = 0.13 gm.

Crystallisation from acetic acid gave two forms of crystals, small prisms and needles. No difference in melting point or mixed melting point was detected. Two crystallisations from benzene gave one form, yellow needles.

M.p. = 239-240°C. (decomp.).

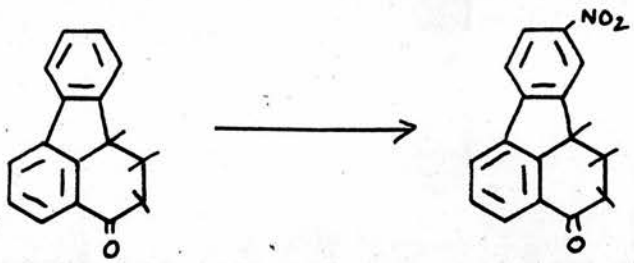
$C_{14}H_7O_3Cl$ requires:- C = 65.0% H = 2.7% Cl = 13.7%.

Found:- C = 65.3% H = 2.9% Cl = 13.7%.

Attempted Hofmann reaction on 1-carboxy-8-chlorofluorenone.

The chloro-acid (0.2 gm.) was boiled briefly with thionyl chloride. The excess thionyl chloride was removed, concentrated ammonia added and the mixture allowed to stand overnight. The resulting amide was filtered off and added to an ice cold solution of bromine (0.06 ml.) in water (2 ml.) and sodium hydroxide (0.24 gm.). The temperature was slowly raised to boiling-point and the mixture boiled for 45 minutes. The dark brown solid which was filtered off melted over a wide range and various attempts at purification were unsuccessful.

Nitration of 4-keto-1,2,3,4-tetrahydrofluoranthene.



Powdered ketone (3 gm.) was added with vigorous stirring to concentrated nitric acid (50 ml.). The solid became oily and after 5 minutes recrystallised. The mixture was stirred for a further 30 minutes and poured into water (150 ml.). The yellow precipitate was filtered off, washed, dried, and dissolved in the minimum of benzene. The solution was chromatographed on alumina (80 gm.) using benzene as solvent. Evaporation of the first 60 ml. of eluate gave only oily impurities. The next 250 ml. on evaporation gave a pale yellow solid which was boiled in a little alcohol cooled and filtered off.

Yield = 1.9 gm.

M.p. = 186-202°C.

One crystallisation in acetic acid and two in benzene gave pale yellow prisms.

M.p. = 224-226°C. (decomp.). Softens 208°C. upwards.

$C_{16}H_{11}NO_3$ requires:- C = 72.4% H = 4.2% N = 5.3%.

Found:- C = 71.9% H = 4.6% N = 5.2%.

A mixed melting point with 12-nitro-4-keto-1,2,3,4-tetrahydrofluoranthene (prepared by Nichol, Cf. Ref. 52) = 223-226°C.

Dinitrophenylhydrazone. Crystallised from benzene as orange prisms.

M.p. = 270°C. (decomp.).

$C_{22}H_{15}N_5O_6$ requires:- N = 15.7%.

Found:- N = 15.7%.

Succeeding elutions from the column gave only oily material which could not be crystallised.

Section II.

Fluorenone

Huntress, Hersberg and Cliff, J.A.C.S., 53, 2720, (1931).

100 gm. Fluorene gave 65 gm. fluorenone.

M.p. = 82-83°C.

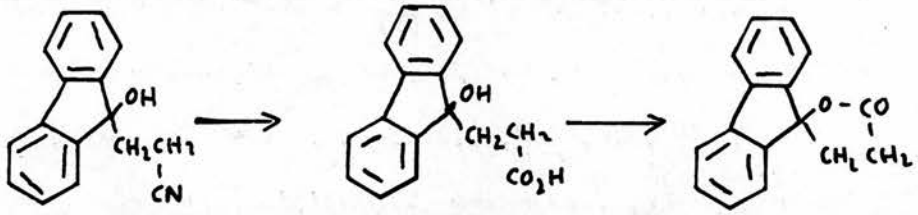
Fluorenol

Fluorenone (10 gm.) and zinc dust (35 gm.) were refluxed in ethanol (160 ml.) and sodium hydroxide solution (7.5 gm. in 100 ml.) till the solution became colourless (30 minutes) then for a further 30 minutes. The solution was filtered, diluted with water and the product filtered off, dried and crystallised from benzene as colourless prisms.

Yield = 8 gm.

M.p. and mixed M.p. with authentic fluorenol = 150-153°C.

Hydrolysis of β-(9-hydroxy-9-fluorenyl)propionitrile



In each of three experiments fluorenol (8 gm.) and vinyl cyanide (3 ml.) were added to a solution of potassium hydroxide (0.53 gm.) in methoxyethanol (48 ml.) and the mixture heated at 50°C. for 20 minutes then boiled for 30 minutes with potassium hydroxide (40 gm.) in water (72 ml.) and methoxyethanol (48 ml.). The dark mixture was poured into water (600 ml.) and filtered.

(a) In one run the solution was acidified with hydrochloric acid and extracted with ether. The ethereal solution was washed, dried and evaporated, leaving an oil which crystallised on standing. Crystallisation from benzene/petrol gave colourless prisms of β-(9-hydroxy-9-fluorenyl)propionic acid lactone

Yield = 2 gm.

M.p. = 133-134°C.

$C_{16}H_{12}O_2$ requires:- C = 81.3% H = 5.1%.

Found:- C = 81.15% H = 5.0%.

(b) In another run evaporation of the ethereal extract left an oil which crystallised from benzene/petrol as colourless prisms of β-(9-hydroxy-9-fluorenyl)propionic acid.

Yield = 2 gm.

M.p. = 143-144°C.

$C_{16}H_{14}O_3$ requires:- C = 75.6% H = 5.55%.

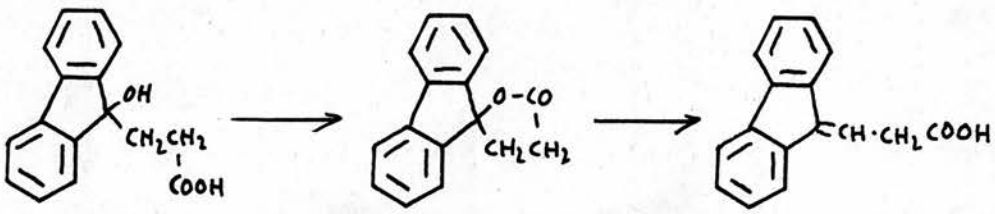
Found:- C = 76.8% H = 5.5%.

(c) The ethereal extract was extracted with sodium carbonate solution. Acidification of the aqueous layer precipitated an oil which crystallised on standing. Crystallisation gave colourless prisms of β-(9-hydroxy-9-fluorenyl)propionic acid.

Yield = 2.5 gm.

M.p. = 143-144°C.

β-Fluorenylidenepropionic acid.



(i) The hydroxy-acid (0.5 gm.) was refluxed in dilute sulphuric acid (12 ml.) for 10 minutes during which the solid became oily. The mixture was poured into water (12 ml.) and extracted with ether. The ethereal solution was washed and extracted with sodium carbonate solution. After washing and drying the ether was evaporated giving β-(9-hydroxy-9-fluorenyl)propionic

acid lactone, recrystallised from benzene/petrol.

Yield = 0.3 gm.

M.p. and mixed M.p. = 131-133°C.

Acidification of the sodium carbonate extract gave a white solid which was filtered off. Crystallisation from benzene gave white needles of β-fluorenylidenepropionic acid, fluorescing blue in ultraviolet light.

Yield = 0.025 gm.

M.p. = 202-204°C., not depressed when admixed. with the acid obtained by the interaction of 9-formylfluorene and ethyl cyanoacetate followed by hydrolysis and decarboxylation, (Cf. Ref. 54).

(2) The lactone (0.5 gm.) was boiled in dilute sulphuric acid (12 ml.) for 2½ hours during which the solid became oily then gradually solidified. The mixture was poured into water (12 ml.) and extracted with ether. The ethereal solution was washed and extracted with sodium carbonate. Evaporation of the ether gave unchanged lactone, recrystallised from benzene/ petrol.

Yield = 0.18 gm.

M.p. and mixed M.p. = 132-134°C.

Acidification of the sodium carbonate extract gave β-fluorenylidenepropionic acid, recrystallised from benzene.

Yield = 0.25 gm.

M.p. and mixed M.p. = 202-204°C.

Ureide with di-p-dimethylaminophenylcarbodiimide. The unsaturated acid with a slight excess of carbodiimide was dissolved in ether. The ureide crystallised out on standing and was recrystallised from acetone.

M.p. = 173-174°C.

$C_{33}H_{32}O_2N_4$ requires:- N = 10.9%.

Found:- N = 10.5%.

Attempted Lactonisation of β-fluorenylidenepropionic acid.

(1) The unsaturated acid (0.2 gm.) was boiled in a mixture of concentrated sulphuric acid (3 ml.) and water (3 ml.) for 1 hour, poured into water, and extracted with ether. The ethereal solution was extracted with sodium carbonate solution, acidification of which gave β-fluorenylidenepropionic acid, crystallised from benzene.

Yield = 0.15 gm.

M.p. and mixed M.P.= 202-203°C.

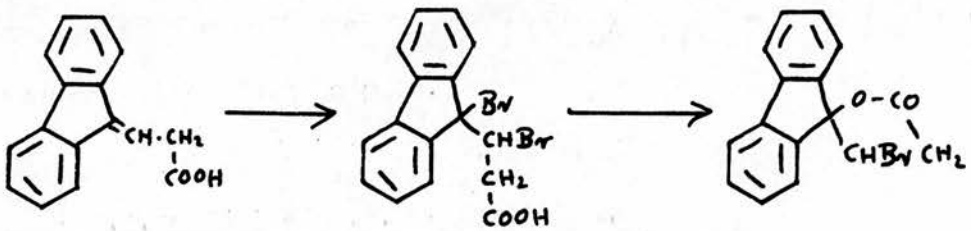
Evaporation of the ether layer gave nothing.

(2) The unsaturated acid (0.2 gm.) was dissolved in hydrobromic acid/glacial acetic acid 1:1 by weight (6 ml.). After standing overnight the solution was poured into water precipitating a white solid, crystallised from benzene.

Yield = 0.16 gm.

M.p. and mixed M.p. with β-fluorenylidenepropionic acid = 202-203°C.

Bromination of β-fluorenylidenepropionic acid.



The reaction was capricious.

(1) The unsaturated acid (0.15 gm.) dissolved on standing in carbon disulphide (6 ml.) and bromine (0.1 gm.) mixture for a few minutes. The bromine was decolourised and impure dibromo-acid crystallised out as hexagonal prisms during 3 hours. The product was filtered off and washed

with a little carbon disulphide.

Yield = 0.17 gm.

M.p. = 128-134°C. lit., 166-167°C.(17).

$C_{16}H_{12}O_2Br_2$ requires:- Br = 40.4%.

Found:- Br = 38.3%.

The dibromo-acid decomposed readily in organic solvents to the bromo-lactone and better bromine analysis could not be obtained.

(2) The unsaturated acid (0.35 gm.) was dissolved in acetic acid (13 ml.) and bromine (0.2 gm.). After 30 minutes the bromine was decolourised. The solvent was removed at room temperature under vacuum. Addition of petrol precipitated a white solid.

Yield = 0.25 gm.

M.p. = 163-165°C.

The bromo-lactone crystallised from benzene as compact prisms.

M.p. = 165-166°C.

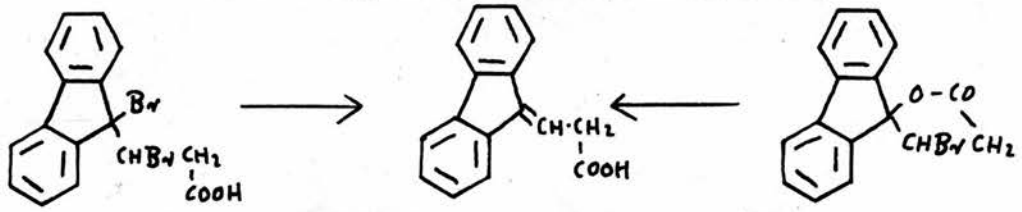
$C_{16}H_{11}BrO_2$ requires:- C = 61.0% H = 3.5% Br = 25.4%.

Found:- C = 60.8% H = 3.6% Br = 25.5%.

Frequently the product was a mixture of dibromo-acid and bromo-lactone.

(3) The lactone of β-(9-hydroxy-9-fluorenyl)propionic acid (0.3 gm.) was dissolved in acetic acid (6 ml.) and bromine (0.2 gm.). The solution which was almost completely decolourised overnight was poured into water precipitating a white sticky solid. Three crystallisations from benzene/petrol gave impure bromo-lactone.

M.p. and mixed M.p. = 159-162°C.



(1) Dibromo-acid (0.17 gm.) was refluxed in acetic acid (1 ml.) with

zinc dust (0.6 gm.) for 4 minutes. Hot filtration and dilution with water gave β-fluorenylidenepropionic acid, crystallised from benzene.

Yield = 0.05 gm.

M.p. and mixed M.p. = 201-202°C.

(2) Bromo-lactone (0.15 gm.) was refluxed in acetic acid (1 ml.) with zinc dust (0.6 gm.) for 4 minutes. Hot filtration and dilution with water gave β-fluorenylidenepropionic acid, crystallised from benzene.

Yield = 0.045 gm.

M.p. and mixed M.p. = 201-203°C.

9-Hydroxyfluorene-9-carboxylic acid.

Schmidt and Bauer, Ber., 38, 3757, (1905).

20 gm. Phenanthraquinone gave 13 gm. 9-hydroxyfluorene-9-carboxylic acid.

M.p. = 164-165°C.

Ethyl 9-hydroxyfluorene-9-carboxylate.

Miller and Wagner, J.Org.Chem., 16, 286, (1951).

10 gm. 9-Hydroxyfluorene-9-carboxylic acid gave 6 gm. ethyl-9-hydroxyfluorene-9-carboxylate.

M.p. = 93-94°C.

9-Hydroxy-9-(α-hydroxyisopropyl)fluorene.

Meerwein, Ann., 396,241, (1913).

6 gm. Ethyl 9-hydroxyfluorene-9-carboxylate gave 5 gm. 9-hydroxy-9-(α-hydroxyisopropyl)fluorene.

M.p. = 100°C.

9-Methyl-9-Acetylfluorene.

Miller and Wagner, J.Org.Chem., 16, 287, (1951).

4 gm. 9-Hydroxy-9-(α-hydroxyisopropyl)fluorene gave 2 gm. 9-Methyl-9-acetylfluorene, crystallised by dissolving in ethanol and cooling in cardice/acetone mixture. White needles.

M.p. = 88°C.

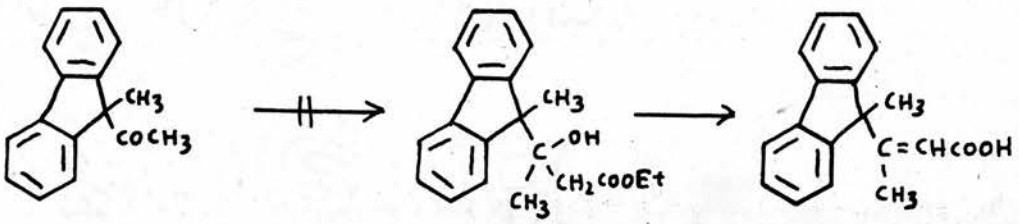
Dinitrophenylhydrazone. Crystallised from ethanol as orange prisms.

M.p. = 219°C.

$C_{22}H_{18}N_4O_4$ requires:- N = 13.9%.

Found:- N = 13.7%.

Attempted Reformatsky reaction on 9-Methyl-9-acetylfluorene.



The ketone (1 gm.) was dissolved in dry benzene (40 ml.) and added to previously cleaned and dried (74) zinc wool (0.5 gm.). A crystal of iodine was added and ethyl bromoacetate (0.75 gm.) slowly run in. As reaction began to subside the mixture was warmed and finally refluxed for 2 hours. After filtering through glass wool the solution was added to 10% sulphuric acid (80 ml.) and ether (20 ml.). After thorough extraction the organic layer was washed, dried and evaporated leaving an oil which could not be crystallised.

The oil was refluxed in benzene (10 ml.) with phosphorus pentoxide (1 gm.) for ½ hour. After filtration and removal of the solvent, sodium hydroxide (20 ml.) was added and the mixture refluxed for 2 hours. After extraction with ether, the aqueous layer was acidified and the resulting oily solid filtered off.

Yield = 0.6 gm.

The solid melted over a wide range and could not be purified.

Attempted condensation of 9-Methyl-9-acetylfluorene with Malononitrile.

The ketone (0.4 gm.) with malononitrile (0.16 gm.) and ammonium acetate (0.06 gm.) was refluxed in benzene (8 ml.) and glacial acetic acid (0.4 ml.) for 5 hours. Ether was added and the organic layer washed and evaporated leaving an oil which was dissolved in ethanol. Dropwise addition of water gave back 9-methyl-9-acetylfluorene.

Yield = 0.23 gm.

M.p. and mixed M.p. = 78-80°C.

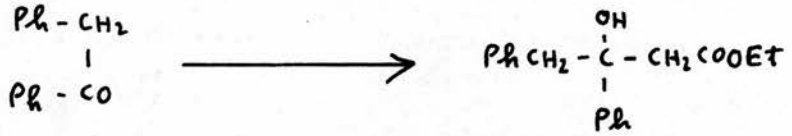
Deoxybenzoin.

Allen and Barker, Org. Syntheses, XII, 16, (1932).

68 gm. Phenylacetic acid gave 45 gm. deoxybenzoin.

M.p. = 54-55°C.

Reformatsky reaction on deoxybenzoin.



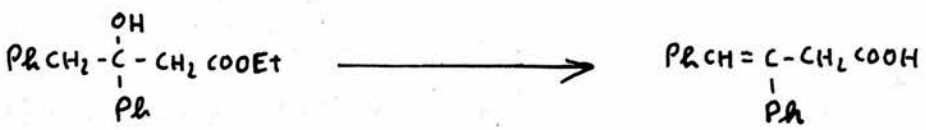
The ketone (15 gm.) was dissolved in dry benzene (80 ml.) and previously cleaned and dried (74) zinc wool (5 gm.) added along with a crystal of iodine. Ethyl bromoacetate (12 gm.) was slowly run in, the mixture allowed to react, and finally refluxed for 2 hours. After filtering through glass wool, the solution was added to 10% sulphuric acid (160 ml.) and ether (50 ml.). After thorough extraction the organic layer was washed, dried over anhydrous sodium sulphate, and evaporated, leaving the crude hydroxy-ester.

Yield = 16 gm.

Crystallised from ethanol as colourless needles.

M.p. = 58°C. (lit. 57-58°C.).

3,4-Diphenylbut-3-enoic acid.



The hydroxy acid (8 gm.) was refluxed in benzene (40 ml.) with

phosphorus pentoxide (7 gm.) for 3 hours. The solution was filtered, evaporated and the resulting unsaturated ester hydrolysed by refluxing in sodium hydroxide (80 ml.) for 1 hour. Acidification of the solution gave 3,4-diphenylbut-3-enoic acid which crystallised from petrol as colourless needles fluorescing pale blue in ultraviolet light.

Yield = 5 gm.

M.p. = 168-169°C. (lit. 168-169°C.).

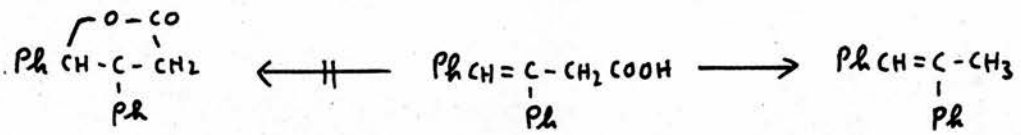
Ureide with di-p-dimethylaminophenylcarbodiimide. The unsaturated acid with a slight excess of carbodiimide was dissolved in dry ether. The ureide crystallised out overnight and was recrystallised from acetone as colourless elongated prisms.

M.p. = 175°C.

$C_{33}H_{34}O_2N_4$ requires:- N = 10.8%.

Found:- N = 10.2%

Attempted Lactonisation of 3,4-diphenylbut-3-enoic acid.



(a) The unsaturated acid (2 gm.) was refluxed in an approximately 50% by volume sulphuric acid/water mixture (35 ml., b.p. 140°C.) for 40 minutes. The mixture was diluted with water, extracted with ether and the organic layer extracted with sodium carbonate solution. Acidification of the sodium carbonate extract gave back 3,4-diphenylbut-3-enoic acid crystallised from petrol.

Yield = 0.8 gm.

M.p. and mixed M.p. = 167-168°C.

Evaporation of the ethereal solution gave a colourless solid which crystallised from ethanol as colourless plates, light blue fluorescence in ultraviolet light.

M.p. = 80-81°C.

Analysis showed the compound to be a hydrocarbon.

Found:- C = 93.1% H = 7.1%.

$C_{15}H_{14}$ requires:- C = 92.7% H = 7.3%.

A mixed M.p. with a sample of α-methylstilbene showed no depression.

(b) The unsaturated acid (0.5 gm.) was dissolved in hydrobromic acid/glacial acetic acid 1:1 by weight (12 ml.). After standing overnight the solution was poured into water precipitating a white solid, crystallised from petrol.

M.p. and mixed M.p. with starting material = 167-168°C.

Attempted isomerisation of 3,4-diphenylbut-3-enoic acid to the 2-enoic acid (64).

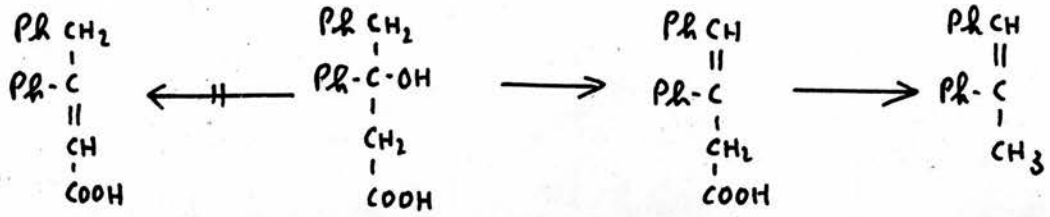
The unsaturated acid (1 gm.) was added to sodium hydroxide (7 gm.) in water (28 ml.). The solid was immediately converted to an oil (probably the sodium salt, since dilution of the mixture caused the oil to dissolve). The mixture was refluxed for 24 hours, acidified, and extracted with ether. A sodium carbonate extract of the ether solution on acidification gave back the original acid, crystallised from petrol.

Yield = 0.8 gm.

M.p. and mixed M.p.= 167-168°C.

Evaporation of the washed, dried, ether solution gave nothing.

Dehydration of $\beta\gamma$-Diphenyl-β-hydroxybutyric acid (Cf. Ref. 67).



Crude ethyl $\beta\gamma$-diphenyl-β-hydroxybutyrate (8 gm.) was refluxed with sodium hydroxide (100 ml.) for 1 hour. Acidification of the solution gave the hydroxy-acid, crystallised from petrol as colourless needles.

Yield = 6 gm.

M.p. = 120°C. (lit. M.p. = 121°C.).

(a) The hydroxy-acid (4 gm.) was refluxed in acetic anhydride (7 gm.) for 3 hours. The acetic anhydride was distilled off under vacuum leaving an oil. Various attempts at crystallisation and purification failed.

(b) The hydroxy-acid (2 gm.) was refluxed in an approximately 50% by volume sulphuric acid/water mixture of b.p. 140°C. (35 ml.) for 20 minutes. The mixture was diluted with water, extracted with ether, and the organic layer extracted with sodium carbonate solution. Acidification of the sodium carbonate extract gave 3,4-diphenylbut-3-enoic acid, crystallised from petrol.

Yield = 1.2 gm.

M.p. and mixed M.p. = 166-168°C.

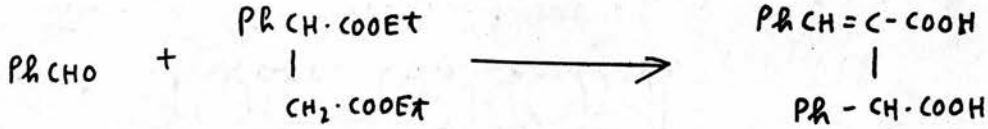
Evaporation of the washed and dried ethereal solution gave α-methylstilbene, crystallised from ethanol.

Yield = 0.2 gm.

M.p. and mixed M.p. = 80-81°C.

Stobbe condensation between benzaldehyde and phenylsuccinic acid.

(a) Dry phenyl sodium succinate (29 gm.) benzaldehyde (14.1 gm.) acetic anhydride (13.6 gm.) were heated at 125-130°C. for 15 hours. The resinous mass was freed from benzaldehyde by steam distillation. Dilute hydrochloric acid was added and the mixture extracted with ether. The organic layer was extracted with sodium carbonate solution, acidification of which gave an oil which was separated by ether extraction. All attempts at purification (Cf. Ref. 64) gave only phenylsuccinic acid and uncrystallisable oil.



(b) Diethyl phenylsuccinate (15.3 gm.) benzaldehyde (6.3 gm.) and ethanol free sodium ethoxide (8 gm.) were added to dry ether (80 ml.) and the mixture kept at room temperature, with occasional shaking, for 5 days, then poured into water (100 ml.). Acidification of the aqueous layer gave an oil which was extracted into ether. The ethereal solution was washed, dried and evaporated to an oil.

Yield = 8 gm.

The oil, which could not be crystallised, was refluxed for 1 hour in sodium hydroxide solution (80 ml.). The mixture was acidified, extracted with ether, and the organic layer washed, dried and evaporated. The resulting oil on standing in petrol/ether mixture overnight deposited white crystals of benzylidenephenylsuccinic acid.

Yield = 2.2 gm.

Two crystallisations from aqueous alcohol gave colourless plates.

M.p. = 175°C. (decomp., rapid heating).

$C_{17}H_{14}O_4$ requires:- C = 72.3% H = 5.0%.

Found:- C = 72.4% H = 5.0%

The remaining oily material could not be crystallised.

Occasionally, some benzylidenephenylsuccinic acid was obtained from the oil before alkaline hydrolysis and in other runs some of the low melting anhydride (Cf. p.77) was also isolated.

(c) Benzaldehyde (6.3 gm.) and diethyl phenylsuccinate (15.3 gm.) were added to a solution of potassium (2.4 gm.) in t-butyl alcohol (50 ml.) under an atmosphere of nitrogen, and the mixture was refluxed for 45 minutes. The cold reaction mixture was just acidified with hydrochloric acid and the bulk of the t-butyl alcohol removed under reduced pressure. Hydrochloric acid was added and the oily product extracted into ether. The organic layer was extracted with sodium carbonate solution which, on acidification, gave an orange coloured oil.

Yield = 7 gm.

The oil was hydrolysed by refluxing in sodium hydroxide (70 ml.) for 1 hour. The solution was acidified, extracted with ether and the organic layer evaporated to an oil which, on standing in petrol/ether mixture overnight, deposited benzylidenephenylsuccinic acid in varying amounts but in each case in poorer yield than in (b). In one run a small amount of material was deposited which crystallised from aqueous alcohol in small granular crystals.

M.p. = 206°C.

Found:- = C = 73.5% H = 5.6%

Analysis for the monoethyl ester of benzylidenephenylsuccinic acid

$C_{19}H_{18}O_4$ requires:- C = 73.5% H = 5.8%.

However, all attempts to hydrolyse, decarboxylate or dehydrate the compound failed, and an infrared spectrum of the material surprisingly showed no carbonyl absorption to any extent. The compound has not been identified.

Monoethyl ester of benzylidenephenylsuccinic acid.

The dicarboxylic acid (0.2 gm.) ethanol (4 ml.) and concentrated sulphuric acid (3 drops) were refluxed for 2 hours. The volume was reduced, water added, and the mixture extracted with ether. The ethereal layer was washed and extracted with sodium carbonate solution. Acidification of the aqueous layer gave a white oil which was induced to solidify by scratching on the sides of the tube.

Yield = 0.1 gm.

Three crystallisations in benzene petrol mixture gave white needles.

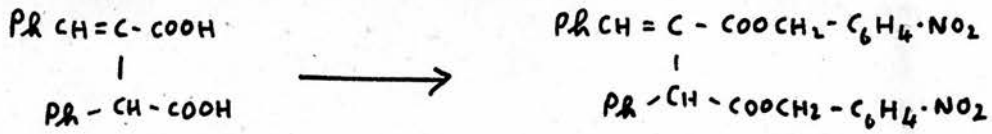
M.p. = 124°C.

$C_{19}H_{18}O_4$ requires:- C = 73.5% H = 5.8%.

Found:- C = 73.3% H = 5.8%.

Evaporation of the ethereal layer gave an oil which could not be crystallised.

Di-p-nitrobenzyl ester of benzylidenephenylsuccinic acid.



The dicarboxylic acid (0.2 gm.) in water (3 ml.) was neutralised by sodium hydroxide (phenolphthalein). p-Nitrobenzyl bromide (0.32 gm.) in ethanol (12 ml.) and hydrochloric acid (3 drops) was added and the solution refluxed for 2 hours. The sticky solid obtained on diluting the mixture with water was crystallised from ethanol as colourless needles.

Yield = 0.15 gm.

M.p. = 127°C.

$C_{31}H_{24}O_8N_2$ requires:- C = 67.4% H = 4.4% N = 5.1%.

Found:- C = 67.0% H = 4.7% N = 5.2%.

Ozonisation of benzylidenephenylsuccinic acid.

A solution of the dicarboxylic acid (0.3 gm.) in purified ethyl acetate (40 ml.) was cooled in a freezing mixture and a slow stream of ozonised oxygen (approximately 2% ozone) passed through from a multiple electrode ozoniser for 10 minutes. The mixture was thoroughly shaken with a solution of water (40 ml.) and concentrated hydrochloric acid (4 drops). The organic layer was washed, dried over anhydrous sodium sulphate and evaporated to an oil which was extracted with ethanol. The ethanolic extract on boiling with stock dinitrophenylhydrazine solution containing a few drops of concentrated hydrochloric acid deposited a voluminous red precipitate of benzaldehyde dinitrophenylhydrazone, crystallised from glacial acetic acid.

M.p. and mixed M.p. = 237°C.

Attempted decarboxylation of benzylidenephenylsuccinic acid.

The dicarboxylic acid (0.2 gm.) was refluxed in a mixture of glacial acetic acid (15 ml.) concentrated hydrochloric acid (7 ml.) and water (10 ml.) for 4 hours. After concentration to 5 ml. the mixture was extracted with ether and the ether layer extracted with sodium carbonate solution. Acidification of the aqueous extract gave back benzylidene-phenylsuccinic acid, crystallised from aqueous ethanol.

M.p. and mixed M.p. = 174-175°C.

The ethereal solution on evaporation gave nothing.

Refluxing the dicarboxylic acid (0.2 gm.) in glacial acetic acid (3 ml.) and hydrobromic acid (2 ml., 48%) mixture had a similar effect.

Dehydration of benzylidenephenylsuccinic acid.

(a) The dicarboxylic acid (0.2 gm.) was heated at 180°C. for 10 minutes during which effervescence was noted. The resulting oil crystallised from petrol as colourless needles which on standing in the mother liquor became colourless prisms. Both forms had similar melting-points which showed no depression on admixing. Recrystallisation from ethanol or petrol gave colourless prisms.

Yield = 0.12 gm.

M.p. = 76°C.

Found:- C = 76.7% H = 4.8%.

The anhydride of benzylidenephenylsuccinic acid $C_{17}H_{12}O_3$

requires:- C = 77.3% H = 4.6%.

(b) The dicarboxylic acid (0.2 gm.) was boiled in acetyl chloride (4 ml.) for 15 minutes. The solution was concentrated and careful addition of water precipitated an oil which solidified on standing. On boiling the solid in petrol and cooling, the solution became milky then deposited white crystals. Two further crystallisations from petrol gave white needles.

Yield = 0.11 gm.

M.p. = 114°C.

Found:- C = 76.8% H = 4.7%

$C_{17}H_{12}O_3$ requires:- C = 77.3% H = 4.6%

The infrared spectra of both the above compounds indicated they are

anhydrides (Cf. p.40). Ozonolysis of both compounds was carried out (as on page 76) giving oils from which dinitrophenylhydrazone precipitates were obtained. These dinitrophenylhydrazones melted over a wide range and could not be purified.

Di-p-dimethylaminophenylthiourea.

Cf. Baur, Ber., 12, 533, (1879).

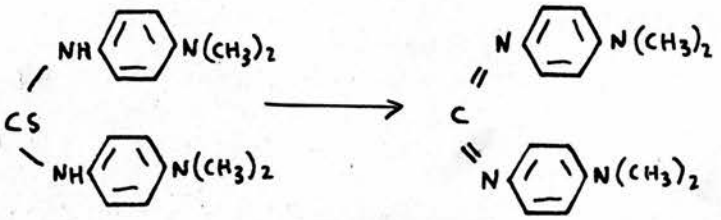
Dimethyl-p-phenylenediamine (10 gm.) and carbon disulphide (8 gm.) were refluxed in ethanol (100 ml.) until no more hydrogen sulphide was evolved (lead acetate paper). On cooling the solution the product which separated was filtered off and recrystallised from benzene as colourless needles.

Yield = 8 gm.

M.p. = 186-187°C.

Di-p-dimethylaminophenylcarbodiimide.

Cf. Rotter, Monats., 47, 355, (1926).



Di-p-dimethylaminophenylthiourea (8 gm.) was refluxed in benzene (50 ml.) with a mixture of yellow mercuric oxide (20 gm.) and anhydrous calcium chloride (4 gm.). The mixture was filtered and the solvent removed under vacuum leaving a white crystalline mass, which was dissolved in ether. On cooling and reducing the volume of the cold solution the carbodiimide crystallised out and was filtered off in stages.

Yield of pure material = 3 gm.

M.p. = 87°C.

Hydrobenzoin.

Burtner and Cusic, J.A.C.S., 65, 262, (1943)

In the reduction ethanol was used as the solvent.

18 gm. Benzoin gave 15 gm. of hydrobenzoin.

M.p. = 138°C.

Diphenylacetaldehyde.

Danilov, Ber., 59, 1032, (1926).

14 gm. Hydrobenzoin gave 6 gm. of diphenylacetaldehyde.

B.p. = 184-186°C./20 m.m.

4,4-Diphenylbut-3-enoic acid.

Burtner and Cusic, loc.cit.

5 gm. Diphenylacetaldehyde gave 3.5 gm. 4,4-diphenylbut-3-enoic acid. Crystallisation from petrol showed two forms, prisms and elongated plates. No depression of melting-point was noted on mixing the two.

M.p. = 117-118°C.

Ureide with di-p-dimethylaminophenylcarbodiimide. The unsaturated acid with a slight excess of carbodiimide was dissolved in ether. The ureide crystallised out on standing and was recrystallised from acetone as colourless needles.

M.p. = 152°C.

$C_{33}H_{34}O_2N_4$ requires:- C = 76.5% H = 6.6% N = 10.8%.

Found:- C = 76.7% H = 6.9% N = 10.9%.

The ureides of the following compounds were prepared by dissolving the acids with a slight excess of the carbodiimide in ether. On standing, the ureide crystallised out.

Fluorenylideneacetic acid. The ureide crystallised from acetone as orange-yellow prisms.

M.p. = 180°C.

$C_{32}H_{30}O_2N_4$ requires:- N = 11.1%.

Found:- N = 11.0%.

$Ph_2C = C(CO_2Et)CH_2CO_2H$. The ureide crystallised from acetone as colourless prisms.

M.p. = 178-179°C.

$C_{36}H_{38}O_4N_4$ requires:- N = 9.5%.

Found:- N = 9.1%.

Acenaphthylideneacetic acid. The ureide crystallised from acetone as orange coloured needles.

M.p. = 173-174°C.

$C_{31}H_{30}O_2N_4$ requires:- N = 11.4%.

Found:- N = 11.1%

7-Acenaphthyleneacetic acid. The ureide crystallised from acetone as yellow compact prisms.

M.p. = 165-166°C.

$C_{31}H_{30}O_2N_4$ requires:- N = 11.4%.

Found:- N = 11.4%.

ULTRAVIOLET SPECTRA.

Wavelength in mμ ($\log \epsilon_{max}$ in parentheses), solvent ethanol unless otherwise stated.

Ethyl α-cyano-β-9-fluorenylacrylate.	250(4.68)				
In hexane	228(4.28)	258(4.40)	288(3.84)	300(3.80)	
Lactone of β-(9-hydroxy-fluorenyl)propionic acid.	228(4.38)	235(4.36)	273(4.10)	302(3.34 inflexion)	
β-Fluorenylidene-propionic acid.	230(4.66)	246(4.59)	257(4.61)	280(4.23)	300(4.1) 314(4.09)
Fluorenylideneacetic acid.	228(4.60)	250(4.46)	258(4.46)	288(4.22)	302(4.13) 315(4.12)
Lactone of β-(9-hydroxy-fluorenyl)-β-bromopropionic-acid.	228(4.49)	235(4.44)	274(4.14)		
β-(9-Hydroxy-9-fluorenyl)-propionic acid.	228(4.29)	234(4.18)	275(4.05)	296(3.56)	307(3.55)
Fluoren-9-ol.	228(4.38)	234(4.29)	271(4.14)	296(3.56)	307(3.35)
9-Benzylfluoren-9-ol.	228(4.37)	236(4.24)	276(4.07)	307(3.51)	
β-(9-Hydroxyfluorenyl)-propionitrile.	228(4.35)	236(4.25)	274(4.12)	307(3.45)	
3,4-Diphenylbut-3-enoic acid.	270(4.3)				
4,4-Diphenylbut-3-enoic acid.	254(4.22)				

BIBLIOGRAPHY.

1. Barbier, Ann.chim.phys., (5), 7, 472, (1876).

2. Fittig and Schmitz, Ann., 193, 134, (1878).

3. Huntress and Cliff, J.A.C.S., 55, 2559, (1933).

4. Huntress, Cliff and Atkinson, J.A.C.S., 55, 4262, (1933).

5. Huntress and Atkinson, J.A.C.S., 58, 1514, (1936).

6. Huntress and Seikel, J.A.C.S., 61, 1066, (1939).

7. Fittig and Gebhard, Ber., 10, 2141, (1877).

8. Von and Wagner., J.Org. Chem., 9, 155, (1944).

9. Goldschmiedt, Monats., 23, 886, (1902).

10. Schmidt and Stutzel, Ann., 370, 1, (1909)

11. Langdecker, J. Prakt. Chem., 132, 145, (1931).

12. Huntress and Cliff, J.A.C.S., 54, 826, (1932).

13. Wittig and Furman, Ber., 73, 1197, (1940).

14. Theilacker and Wessel-Ewald, Ann., 594, 214, (1955).

15. Goldschmiedt, Ber., 10, 2022, (1877). Ber., 11, 1578, (1878). Monats., 1, 221, (1880).

16. Braun and Anton, Ber., 62, 145, (1929).

17. Campbell and Fairfull, J.C.S., 1239, (1949).

18. Tucker, J.C.S., 2182, (1949). Campbell and Tucker, J.C.S., 2623, (1949).

19. Bergmann and Orchin, J.A.C.S., 71, 1917, (1949).

20. Campbell and Fairfull, J.C.S., 1102, (1949).

21. Campbell and Wang, J.C.S., 1513, (1949). Nature, 162, 857, (1948).

22. Cook and Laurence, J.C.S., 1431, (1936).

23. Orchin and Reggel, J.A.C.S., 69, 505, (1947).

24. Forrest and Tucker, J.C.S., 1137, (1948).

25. Campbell and Gow, J.C.S., 1555, (1949). Nature, 162, 857, (1948).

26. Bergmann, Nature, 161, 889, (1948).

27. Campbell and Keir, J.C.S., 1233, (1955).

28. Kloetzel, King and Menkes, J.A.C.S., 78, 1165, (1956).

29. Campbell, Leadhill and Wilshire, J.C.S., 4615, (1952).

30. Tucker and Whalley, J.C.S., 3213, (1949).

31. Kloetzel and Mertel, J.A.C.S., 72, 4786, (1950).

32. Tucker and Whalley, J.C.S., 3187, (1952).

33. Hawkins and Tucker, J.C.S., 3286, (1950).

34. Stubbs and Tucker, J.C.S., 227, (1954).

35. Smith, J.A.C.S., 70, 320, (1948).

36. Smith and Ashby, J.A.C.S., 72, 2503, (1950).
Smith and Horwitz, J.A.C.S., 72, 3718, (1950).

37. Sanford, Blair, Arroya and Sherk, J.A.C.S., 67, 1941, (1945).

38. Arcus, Coombs and Evans, J.C.S., 1498, (1956).

39. Arnold, Elmer and Dobson, J.A.C.S., 72, 4359, (1950).

40. Ingold, "Structure and Mechanism in Organic Chemistry". G. Bell & Sons, Ltd., London., 562, 563, (1953).

41. Linstead and Williams, J.C.S., 2735, (1926).

42. Farmer, Ann. Reports, 29, 108, (1932).

43. Johnson, Petersen and Schneider, J.A.C.S., 69, 74, (1947).

44. Zetsche, Meyer, Overbeck and Lindlar, Ber., 71B, 1516, (1938).

45. Zetsche and Rottger, Ber., 72B, 1599, (1939).

46. Khorana, Chem. Revs., 53, 154, (1953).

47. Briggs and De Ath, J.C.S., 456, (1937).

48. Craig, Ph.D.Thesis, 68, (1955).

49. Campbell, "Qualitative Organic Chemistry", Macmillan & Co., Ltd., London, 2nd Edition, 41, (1946).

50. Campbell and Wilshire, J.C.S., 867, (1954).

51. Craig, Ph.D. Thesis, 61, (1955).

52. Nichol, Ph.D. Thesis, 31, (1958).

53. Borsche and Niemann, Ber., 69, 1998, (1936).

54. Craig, Ph.D. Thesis, 37, (1955).

55. Cf. Meyer and Gottlieb-Billroth, Ber., 54, 575, (1921).

56. Klinger and Lonnes, Ber., 29, 2157, (1896).

57. Feigl, "Qualitative Analysis by Spot Tests" Elsevier, Amsterdam, 3rd Edition, 358, (1947).

58. Bellamy, "The Infrared Spectra of Complex Molecules", Methven & Co., London, 2nd Edition, 186, (1958).

59. Miller and Wagner, J. Org. Chem., 16, 279, (1951).

60. Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds", J. Wiley & Co., Inc., New York, diagrams 311-315, (1951).

61. Ref., 58, p.165.

62. Ref., 58, p.96.

63. Coombs, J.C.S., 3454, (1958).

64. Fichter and Latzko, J. Prakt. Chem., 74, 327, (1906).

65. Spring, J.C.S., 1332, (1934).

66. Bergmann, Hofmann, and Meyer, J. Prakt. Chem., 135, 265, (1932).

67. Phalnikar and Nargund, J. Univ., Bombay, 8, Part 3, 184, (1939).

68. Cf. Johnston and Daub, Organic Reactions, Vol. VI, p.18-19.

69. Islam and Zemaity, J.A.C.S., 80, 5806, (1958).

70. Ref. 58, p.41.

71. Cordier, Compt. Rend., 200, 1412, (1935).

72. Ref. 58, p.127-128.

73. Burtner and Cusic, J.A.C.S., 65, 262, (1943).

74. Cf. Fieser and Johnson, J.A.C.S., 62, 575, (1940).

75. Bergmann, Heller and Weiler-Feilchenfeld, Bull Soc. Chim. France., 634(1959) Greenhow, McNeill and White, J.C.S., 986, (1952), 3099, (1953).

76. Ruhemann, J.C.S., 459, (1910).

77. Kon and Nargund, J.C.S., 2461, (1932).

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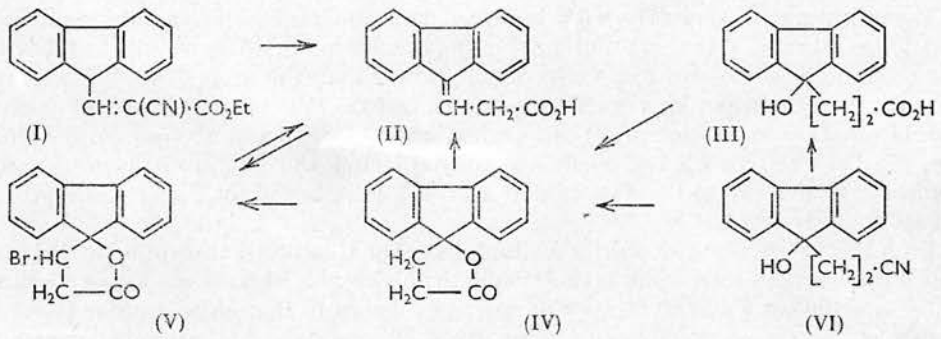
158. *The Preparation and Properties of β-9-Fluorenylidenepropionic Acid.*

By D. M. W. Anderson, Neil Campbell, J. T. Craig, and D. A. Crombie.

The constitution of β-9-fluorenylidenepropionic acid (II) has been established and the chemical and spectral properties of the acid and its derivatives are reported.

9-Formylfluorene and malonic acid in piperidine condense to give β-9-fluorenylidenepropionic acid [1] (II), m. p. 202—203°, which is also obtained by the interaction of 9-formylfluorene and ethyl cyanoacetate followed by hydrolysis and decarboxylation of the product (I). This intermediate is colourless in the solid state and in hexane, but gives a yellow solution in ethanol or piperidine, probably owing to the colourless form's having structure (I) which tautomerises [2] to the yellow βγ-unsaturated ester form, :CH·CH(CN)·CO_2Et. This is substantiated by the ultraviolet spectrum in hexane which resembles that of fluorene, a similarity which disappears when the solvent is changed to ethanol. Similar colour changes, however, are sometimes observed in fluorene derivatives which cannot tautomerise, the colourless, crystalline 9-diphenylmethylenefluorene, for



(I) (II) (III) (V) (IV) (VI)

instance, giving yellow solutions or melts.[3] The position of the double bond in the unsaturated acid (II) is suggested by the colourless ureide formed by the acid with di-*p*-dimethylaminophenylcarbodi-imide.[4] These results are in conflict with those of Campbell and Fairfull,[5] who assigned m. p. 137° to the acid (II), which they prepared by the alkaline hydrolysis of β-(9-hydroxy-9-fluorenyl)propionitrile (VI) and subsequent treatment with mineral acid; they gave m. p. 202° for the corresponding lactone (IV). We have therefore re-investigated this hydrolysis and find that some of the data reported by Campbell and Fairfull are erroneous and that depending on the conditions the product may be β-(9-hydroxy-9-fluorenyl)propionic acid (III), m. p. 140°, or the lactone (IV), m. p. 133—134°. The constitution of the lactone (IV) is established by the infrared band at 1772 $cm.^{-1}$ characteristic of five-membered saturated lactones,[6] by the similarity of its ultraviolet spectrum to those of fluorene and particularly 9-ethylfluorene-9-ol [7] (see Table), by the positive test with hydroxylamine,[8] and by ring-opening with sulphuric acid to give β-9-fluorenylidenepropionic acid (II).[9] The lactone with bromine in acetic acid gives the bromo-lactone (V). That the acid (II) is a βγ-unsaturated acid is proved by catalytic hydrogenation or reduction with hydriodic acid and phosphorus to β-9-fluorenylpropionic acid,[10] and by the ultraviolet spectrum (see Table) which lacks the 250—300 mμ band and

ethyl α-cyano-β-9-fluorenylacrylate which separated from methanol in needles (11 g.), m. p. 93—94·5° (Found: C, 79·0; H, 5·2; N, 5·0. $C_{19}H_{15}O_2N$ requires C, 78·9; H, 5·2; N, 4·8%), $\lambda_{max.}$ 250 mμ (log ε 4·68) in ethanol, and 228 (log ε 4·28), 258 (log ε 4·40), 288 (log ε 3·84), and 300 mμ (log ε 3·80) in hexane. The ester (2·23 g.) when boiled for 3 hr. with ethanol (180 ml.) and concentrated hydrochloric acid (180 ml.) yielded β-9-fluorenylidenepropionic acid (1·18 g.), m. p. 198—201° (not depressed when admixed with the acid obtained by the condensation of 9-formylfluorene and malonic acid with pyridine as catalyst [1]), and the *ethyl ester* (1·21 g.), m. p. 73—74° (after trituration and crystallisation from ethanol) (Found: C, 81·3; H, 6·3. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%). The ester was hydrolysed to the acid by boiling with methanol and sodium hydroxide in ½ hr. Boiling the acid (0·5 g.) for ½ hr. with 50% aqueous potassium hydroxide gave fluorene (0·3 g.), m. p. and mixed m. p. 115°.

Hydrolysis of β-(9-Fluorenyl-9-hydroxy)propionitrile.—In each of three experiments fluorenol (8 g.) and vinyl cyanide (3 ml.) were added to potassium hydroxide (0·53 g.) in methoxyethanol (48 ml.), and the mixture was heated at 50° for 20 min. and then boiled for 30 min. with potassium hydroxide (40 g.) in water (72 ml.) and 2-methoxyethanol (48 ml.). The mixture was poured into water.

(*a*) In one run the solution was acidified with hydrochloric acid, extracted with ether, and evaporated to give *β-(9-fluorenyl-9-hydroxy)propionic acid lactone* (2 g.), m. p. 133—134°: after crystallisation from benzene–light petroleum (Found: C, 81·15; H, 5·0. $C_{16}H_{12}O_2$ requires C, 81·3; H, 5·1%), $\nu_{max.}$ 1772 cm.$^{-1}$ (cf. Table).

(*b*) In another run 2 g. of crude material yielded *β-(9-hydroxy-9-fluorenyl)propionic acid*, m. p. 143—144° after crystallisation from benzene–light petroleum (Found: C, 76·8; H, 5·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·55%), $\lambda_{max.}$ 228 (log ε 4·29), 234 (log ε 4·18), 275 (log ε 4·05), 296 (log ε 3·56), and 307 mμ (log ε 3·55).

(*c*) The crude product after acidification with hydrochloric acid was extracted with ether, and the extract shaken with aqueous sodium carbonate. The carbonate layer with acid gave the hydroxy-acid which, crystallised from benzene–light petroleum, had m. p. 143—144°. The hydroxy-acid (0·5 g.) was boiled for 10 min. with dilute sulphuric acid (12 ml.) and poured into water (12 ml.). The mixture was extracted with ether, and the ether layer shaken with sodium carbonate solution. The ether on evaporation gave the lactone (0·3 g.), m. p. and mixed m. p. 131—133°, while acidification of the sodium carbonate solution yielded β-9-fluorenylidenepropionic acid (0·025 g.), m. p. and mixed m. p. 202—204° (from benzene–light petroleum), subliming in prisms. The acid has a blue fluorescence. The lactone (0·5 g.) was boiled for 2½ hr. in dilute sulphuric acid and poured into water (12 ml.); extraction with ether was followed by shaking the ether with sodium carbonate; evaporation of the ether gave unchanged lactone (0·18 g.), m. p. 132—134°, and acidification of the sodium carbonate layer yielded β-9-fluorenylidenepropionic acid (0·25 g.), m. p. 202—204° (from benzene).

Bromination of β-9-Fluorenylidenepropionic Acid.—The reaction is capricious. The unsaturated acid in carbon disulphide with bromine yielded the impure dibromo-acid, m. p. 128—134° (lit., 166—167° [5]) (Found: Br, 38·3. $C_{16}H_{12}O_2Br_2$ requires Br, 40·4%), which decomposed in organic solvents to give the bromo-lactone. Bromine (0·2 g.) in acetic acid (3 ml.) was added to the unsaturated acid (0·35 g.) in acetic acid (10 ml.) until the colour persisted and most of the solvent was removed at room temperature in a vacuum. Addition of light petroleum gave the *bromo-lactone* (0·25 g.), compact prisms (from benzene–light petroleum), m. p. 165—166° (Found: C, 60·8; H, 3·6; Br, 25·5. $C_{16}H_{11}BrO_2$ requires C, 61·0; H, 3·5; Br, 25·4%), $\lambda_{max.}$ 228 (log ε 4·49), 235 (log ε 4·44), and 274 mμ (log ε 4·14), $\nu_{max.}$ 1795 cm.$^{-1}$. Frequently the product was a mixture of dibromo-acid and bromo-lactone, each (0·16 g.) of which when heated with zinc dust (0·6 g.) and acetic acid for 4 min. yielded β-9-fluorenylidenepropionic acid. Keeping the lactone (0·3 g.) of β-(9-hydroxy-9-fluorenyl)propionic acid suspended in acetic acid (4 ml.) overnight with bromine (0·2 g.) in acetic acid (2 ml.) and adding water gave impure bromo-lactone, m. p. and mixed m. p. 159—162° (after three crystallisations from benzene–light petroleum).

9-Fluorenylidenacetic Acid.—Fluorenone (9 g.) and ethyl bromoacetate (10 g.) in dry benzene (40 ml.) were heated for 2 hr. with zinc wool (3·3 g.) which had been washed with hydrochloric acid, ethanol, and ether, and dried. The oily product, obtained in the usual way, was boiled with 85% formic acid (75 ml.) for 1 hr., and water and formic acid were removed under reduced pressure. The residual red oil when dissolved in boiling methanol and cooled yielded ethyl 9-fluorenylideneacetate, yellow needles (8 g.), m. p. 72° (lit., 77°). The ester (8 g.) was boiled

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ZETSCHE'S TEST FOR αβ-UNSATURATED ACIDS

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We have verified Zetsche's claim that di-*p*-dimethylamino-phenylcarbodiimide (I) reacts with αβ-unsaturated acids to give coloured *N*-acyl ureides (II) whereas βγ-unsaturated acids afford colourless ureides,[1] and we now report further examples of the use of this reagent.

The test can be applied to coloured αβ-unsaturated acids since the resulting ureides are more deeply coloured than the parent acids. The yellow fluorenylideneacetic acid gives an orange-yellow

$$\begin{matrix} N{\cdot}C_6H_4{\cdot}NMe_2 \\ \diagup \\ C \\ \diagdown \\ N{\cdot}C_6H_4{\cdot}NMe_2 \\ \text{(I)} \end{matrix} + R{\cdot}CO_2H \rightarrow \begin{matrix} CO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2 \\ \vdots \\ N{\cdot}C_6H_4{\cdot}NMe_2 \\ COR \\ \text{(II)} \end{matrix}$$

ureide, prisms, m.p. 180° (Found: N, 11·0. $C_{32}H_{30}O_2N_4$ requires N, 11·1%). Acenaphthylideneacetic acid affords an orange coloured ureide, needles, m.p. 173–174° (Found: N, 11·1. $C_{31}H_{30}O_2N_4$ requires N, 11·4%), whereas the isomeric 7-acenaphthyleneacetic acid gives a yellow ureide, compact prisms, m.p. 165–166° (Found: N, 11·4%).

It is established that a γ-aryl group in the butenoic acids stabilises the double bond in the βγ-position,[2] and as anticipated such acids give colourless ureides. 3 : 4-Diphenylbut-3-enoic acid (III) (sublimes, prisms, m.p. 171–173° (lit., 173°)) prepared by the Reformatsky reaction between deoxybenzoin and ethyl bromacetate followed by dehydration, gives a colourless ureide, m.p. 175° and then resolidifying (Found: N, 10·2. $C_{33}H_{34}O_2N_4$ requires N, 10·8%). The constitution (III) of the acid, assigned without rigid proof by Phalnikar and Nargund,[3] has been confirmed by heating the acid for 40 minutes with sulphuric acid, b.p. 140°, to give α-methylstilbene (IV), and by the similarity of its spectrum ($\lambda_{max.}$ 270 mμ, log ε 4·3) to that of α-methylstilbene (IV) ($\lambda_{max.}$ 270 mμ, log ε 4·4)[4] and its difference from that of α-methylstyrene (VI) ($\lambda_{max.}$ 242 mμ, log ε 4·08).[4] Efforts to prepare the isomeric 3 : 4-diphenylbut-2-enoic acid (V) by the method of Phalnikar and Nargund were unsuccessful as were efforts to prepare it by isomerising the acid (III) with alkali.[5]

$PhCH : CPh{\cdot}CH_2{\cdot}CO_2H$ (III) $\qquad$ $PhCH_2{\cdot}CPh : CH{\cdot}CO_2H$ (V)

$PhCH : CPhMe$ (IV) $\qquad$ $Me{\cdot}CPh : CH_2$ (VI)

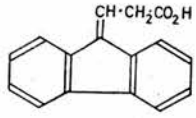
4 : 4-Diphenylbut-3-enoic acid (VII), plates, m.p. 121–122°, whose structure follows from its ease of lactonisation[6] and is confirmed by the similarity of its spectrum ($\lambda_{max.}$ 254 mμ, log ε 4·22) to that of 1 : 1-diphenylprop-1-ene (VIII) ($\lambda_{max.}$ 250 mμ, log ε 4·1)[7] yields a colourless ureide, m.p. 152° (Found: C, 76·7; H, 6·9; N, 10·9. $C_{33}H_{34}O_2N_4$ requires C, 76·5; H, 6·6; N, 10·8%).

The acid ester $Ph_2C : C(CO_2Et){\cdot}CH_2{\cdot}CO_2H$ gives a colourless ureide, m.p. 178–179° (Found: N, 9·1. $C_{36}H_{38}O_4N_4$ requires N, 9·5%).

The acid described variously in the literature as β-fluorenylidenepropionic acid[8] (IX) or the isomeric γγ-diphenylenecrotonic acid gives a colourless ureide, needles, m.p. 173–174° (Found: N, 10·5. $C_{33}H_{32}O_2N_4$ requires N, 10·9%) and hence the acid has the structure (IX) tentatively assigned by Borsche[8] but disregarded by Burtner and Cusic.[9] We have confirmed this structure by other methods which will be reported later.

$Ph_2C : CH{\cdot}CH_2{\cdot}CO_2H$ (VII)

$Ph_2C : CH{\cdot}Me$ (VIII)



(IX)

The ureides were prepared by mixing the reactants in ether, keeping overnight, and recrystallising the precipitate from acetone. The melting-points of the ureides vary with the rate of heating. Those reported above were obtained by means of a Kofler hot-stage microscope with samples inserted about twenty degrees below the melting-point determined in the usual way.

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References

[1] Zetsche, F. & Röttger, G., *Ber. dtsch. chem. Ges.*, 1939, **72**, 1599
[2] Linstead, R. P. & Williams, L. T. D., *J. chem. Soc.*, 1926, 2735
[3] Phalnikar, N. L. & Nargund, K. S., *J. Univ. Bombay*, 1939, **8**, part 3, 184
[4] Ramart-Lucas, P. & Amagat, P., *Bull. Soc. Chim.*, 1932, [iv], **51**, 119
[5] cf. Fichter, Fr. & Latzko, W., *J. prakt. Chem.*, 1906, **74**, 327
[6] Johnson, W. S., Petersen, J. W. & Schneider, W. P., *J. Amer. chem. Soc.*, 1947, **69**, 74
[7] Ramart-Lucas, P. & Hoch, M. J., *Bull. Soc. Chim.*, 1935, v, **2**, 1276
[8] Borsche, W. & Niemann, J., *Ber. dtsch. chem. Ges.*, 1936, **69**, 1998
[9] Burtner, R. R. & Cusic, J. W., *J. Amer. chem. Soc.*, 1943, **65**, 265

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ABSTRACT OF THESIS

Name of Candidate Douglas Alexander Crombie

Degree Ph.D. *Date* July 1960.

Title of Thesis The Synthesis of Polycyclic Aromatic Hydrocarbons.

A synthetic route to 10-substituted fluoranthenes and 1,8-substituted fluorenones has been developed. The ketonic Schmidt reaction on 4-keto-1,2,3,4-tetrahydrofluoranthene and hydrolysis of the resulting lactam gave 3-(1-amino-9-fluorenyl)-propionic acid. A Sandmeyer reaction on this amino-acid followed by cyclisation, reduction and dehydrogenation yielded 10-bromo-fluoranthene. 10-Chlorofluoranthene was similarly prepared. Oxidation of 13-bromo-4-keto-1,2,3,4-tetrahydrofluoranthene gave 1-carboxy-8-chlorofluorenone.

Aryl substituted unsaturated acids are often intermediates in the preparation of polycyclic aromatic hydrocarbons. A number of these intermediates of uncertain structure has been investigated. The constitution of β-fluorenylidene-propionic acid has been established and the chemical and spectral properties of the acid and a number of related compounds have been investigated. The structure of 3,4-diphenylbut-3-enoic acid (m.p. 168°C) produced by a Reformatsky reaction on deoxybenzoin has been confirmed. The reported preparation of other isomeric 3,4-diphenylbutenoic acids by this reaction and by the Stobbe condensation of benzaldehyde on diethyl phenylsuccinate could not be substantiated. The latter reaction gave a compound whose structure has been established as benzylidenephenylsuccinic acid. The properties of this dicarboxylic acid and a number of its derivatives have been investigated. The reported reaction of di-p-dimethylaminophenylcarbodiimide with αβ-unsaturated acids to give coloured acylureas, while βγ-unsaturated acids give colourless adducts has been utilised in these investigations. The acylureas of the unsaturated acids already mentioned and a number of other aryl substituted unsaturated acids have been prepared as additional evidence of their structures.

Use other side if necessary.