SYNTHETIC STUDIES IN THE AROMATIC POLYCYCLIC SERIES

By

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T O M Y P A R E N T S

C O N T E N T S

SUMMARY

1. The bromination of 3-methoxyfluoranthene yields 2,8-dibromo-3-methoxyfluoranthene as proved by synthesis. This result is in harmony with the results observed with other 3-substituted fluoranthenes.

2. Various unsuccessful attempts to prepare 2-bromo-3-methoxy-fluoranthene are described. Examples include the interaction of the diazonium salt of 3-amino-2-bromofluoranthene with methanol to give 2-bromo-fluoranthene and the failure of the diazonium salt of 2-amino-3-methoxyfluoranthene to undergo the Sandmeyer reaction with cuprous bromide. It has been found that 3-aminofluoranthenes form stable diazonium salts which can be readily isolated.

3. Bromination of 3-methoxy-2-nitrofluoranthene yields 8-bromo-3-methoxy-2-nitrofluoranthene, the structure of which was established by degradation to 6-bromofluorenone-1-carboxylic acid. In anticipation that the oxidation product might be 2-bromo-7-methoxy-6-nitrofluorenone-1-carboxylic acid, 2-bromo-7-methoxy-6-nitrofluorenone was synthesised.

4. 3-Hydroxyfluoranthene, 2,8-dinitro-3-methoxy-fluoranthene and 3-amino-8-bromofluoranthene have been prepared by improved methods.

5. In the course of the synthesis of substituted fluoranthenes from substituted methyl fluorene-1-carboxylates by the method of Tucker and Campbell it has been found that autoxidation at the 9-position of the fluorene molecule can vitiate the synthesis. It has also been found that, particularly in the synthesis of methoxyfluoranthenes, conditions for each of the several stages of the synthesis are critical.

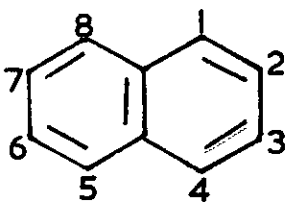
6. Some exploratory work to synthesise substituted fluoranthenes from naphthalene derivatives led to the discovery that nitric acid with 4-iodo-1-methoxynaphthalene yields 2,4-dinitro-1-methoxynaphthalene and examples of the reactivity of halogen in 1-halogeno-8-nitronaphthalenes have been found.

7. Miscellaneous observations include the bromination of 3-oxo-1,2,3,10b-tetrahydrofluoranthene in acetic acid to give a product, possibly 2,8-dibromo-3-oxo-1,2,3,10b-tetrahydrofluoranthene; confirmation of the structure of 1-hydroxy-2-nitro-1,2,3,10b-tetrahydrofluoranthene by its infra-red spectrum; and the preparation of 3,6-dimethylfluorenone.

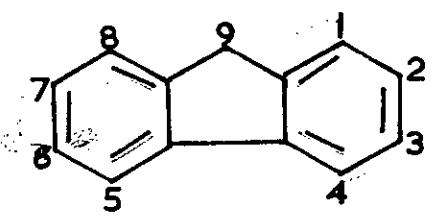
NOMENCLATURE

The names and numbering of the three hydrocarbons employed in this thesis are shown below:

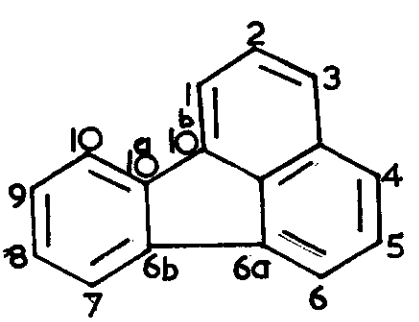
Naphthalene



Fluorene



Fluoranthene



INTRODUCTION

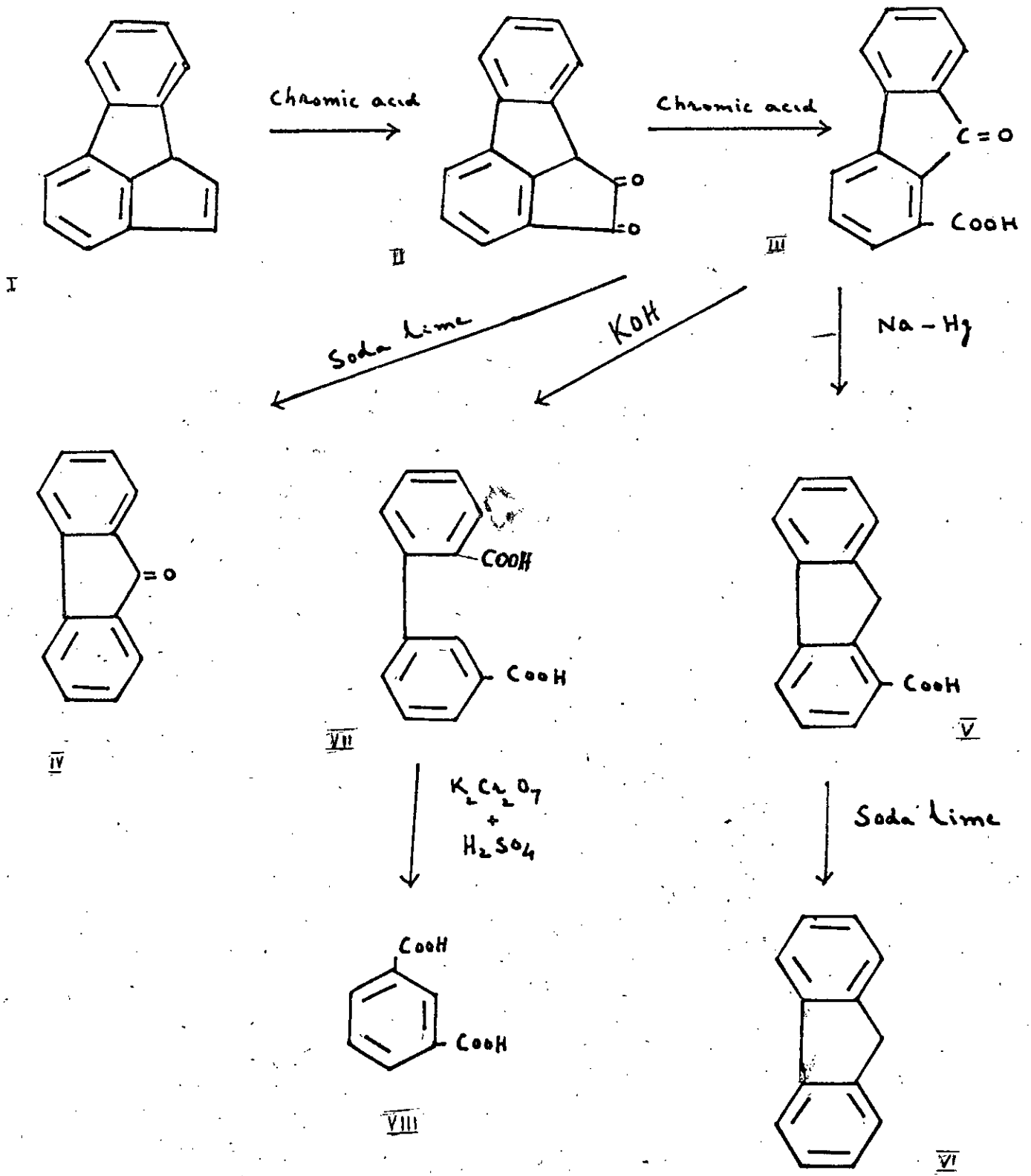
Fluoranthene, a polycyclic hydrocarbon has been known for more than a century, although the structure, orientation of substituted products and synthesis of its derivatives have only been investigated more recently. This hydrocarbon can be detected in many sources, dust (1), food grain (2), tobacco smoke and particularly coal tar from which it is obtained commercially. Although itself not carcinogenic (3), many of its derivatives possess carcinogenic properties (4,5). However, so far no correlation have been found between the electronic characteristics of the active compounds and their carcinogenetic potency.

Discovery and Structure:-

Dumas (6) and later Laurent (7), obtained a hydrocarbon fraction by extracting the mercury ores of idria with oil of terpentine. Boedeker (8) in 1844 obtained the same product by distillation of the ores. This material was called "Idryl". It was later shown by Goldschmiedt (9) to be a mixture of anthracene, phenanthrene, chrysene, pyrene, and a new hydrocarbon to which he gave the formula $C_{15}H_{10}$.

The same hydrocarbon was also obtained by Fittig and Gebhard (10) from the higher boiling fractions of coal tar. They called the hydrocarbon fluoranthene. This was shown to be identical with the compound isolated by Goldschmiedt from the mercury ores.

They prepared dibromo, trinitro derivatives and fluoranthene-quinone. Oxidation of fluoranthene gave fluorenone-carboxylic acid and this with Potassium hydroxide gave diphenyl-2,3'-di-carboxylic acid. On the basis of these results and the analytical



I

II

III

IV

V

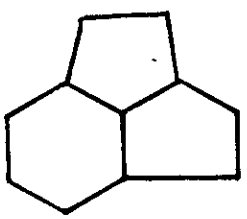
VI

VII

VIII

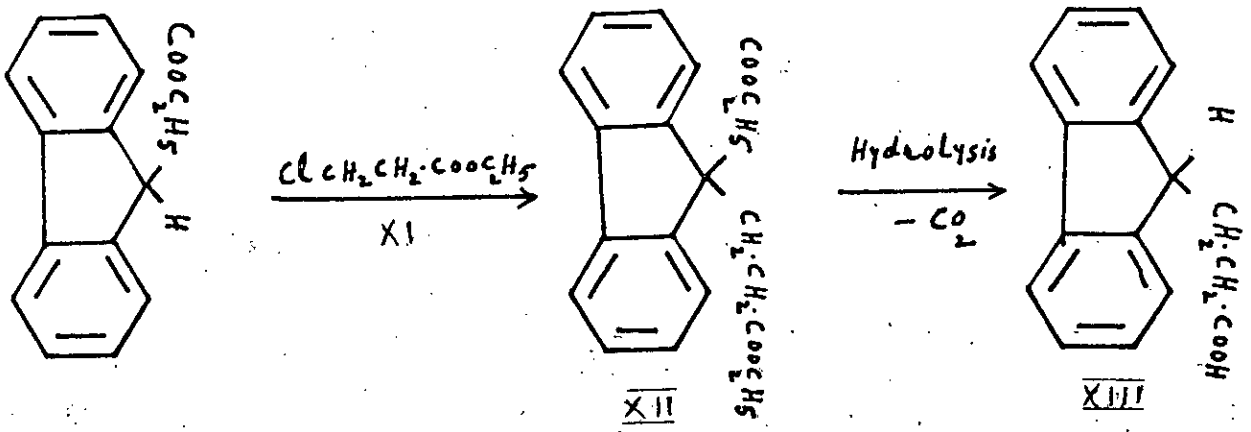
figures, they suggested the formula I for fluoranthene. Their results can be summarised as given on the opposite page.

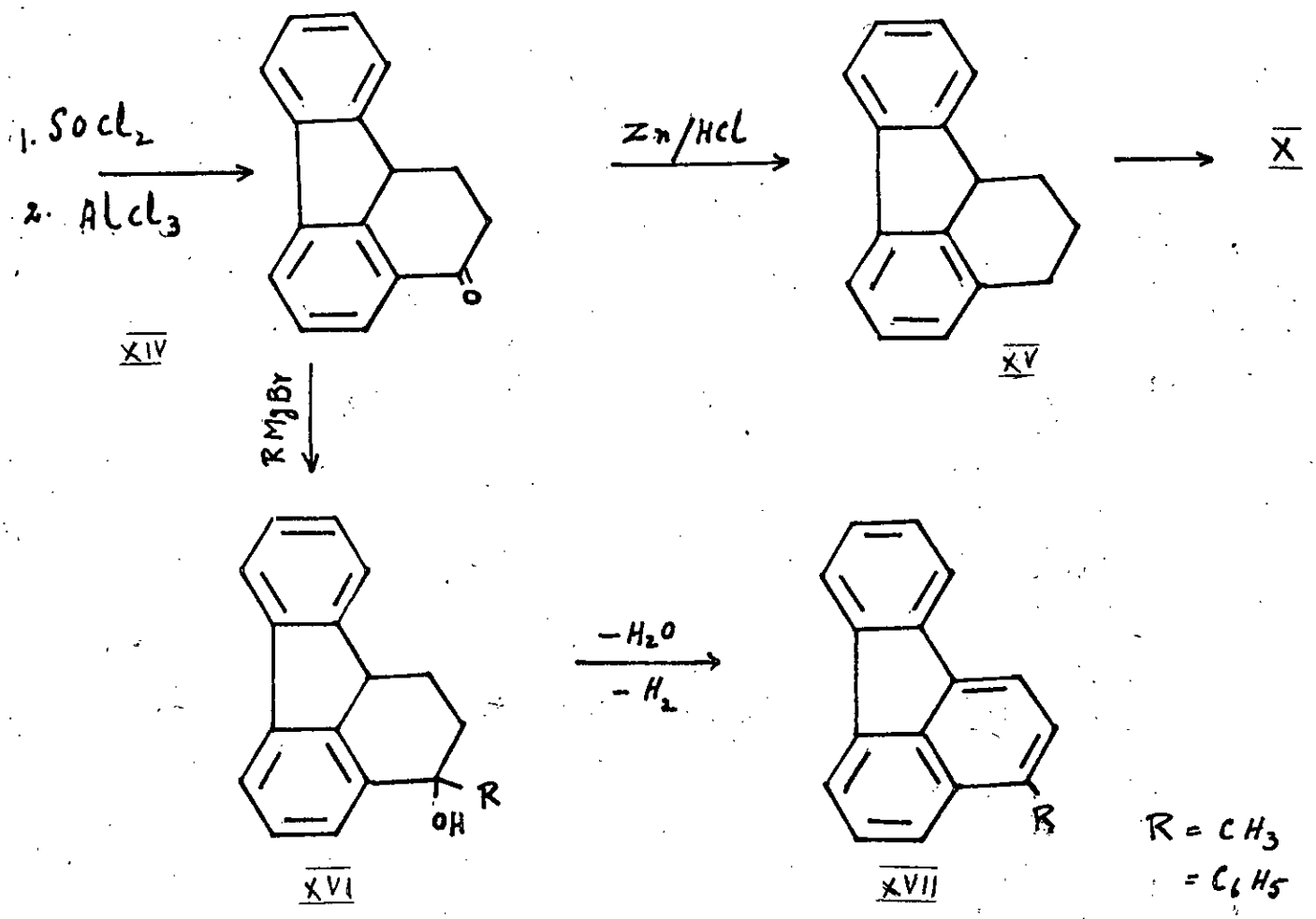
Little work on fluoranthene chemistry was carried out, until Von Braun and Anton (11) in 1929, pointed out that two five membered rings could be fused together to give a stable compound only if the fusion occurs in the 'cis' position, and neither of the five membered rings deviates from the plane model. These conditions could not be satisfied if the two rings were fused adjacently to a benzene nucleus to form a tricyclic compound IX.



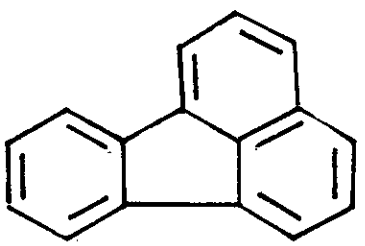
IX

Thus the indene type of structure I, suggested by Fittig and Gebhard would not yield a stable compound. They were unable to synthesise the fluoranthene skeleton from 9-fluorenylacetyl chloride. However, if fluoranthene is regarded as a naphthalene derivative, it would be expected to be quite stable. So they


$ClCH_2CH_2\cdot COOC_2H_5$
XI
Hydrolysis
$-CO_2$
XII
XIII


1. $SOCl_2$
2. $AlCl_3$
XIV
Zn/HCl
XV
X
RMgBr
$-H_2O$
$-H_2$
XVI
XVII
R = CH_3
= C_6H_5

proposed Structure X and confirmed the proposed structure by its synthesis.

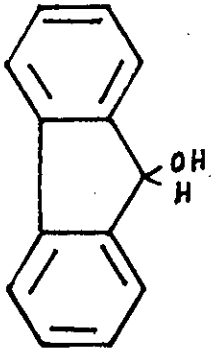


X

Ethyl-β-chloropropionate XI was condensed with 9-carboethoxyfluorene in alcoholic caustic soda, which gave ethyl-9(9'-carboxyfluorenyl)-2-propionate XII. On hydrolysis and decarboxylation 9-fluorenyl-2-propionic acid XIII was obtained. This acid was converted to the acid chloride by thionyl chloride, and ring closure was achieved by aluminium-chloride in light petrol XIV. On Clemmensen reduction 4-Keto-1:2:3:10b-tetrahydro-fluoranthene was converted to 1:2:3:10b-tetrahydro-fluoranthene XV, which on dehydrogenation by lead oxide gave fluoranthene X.

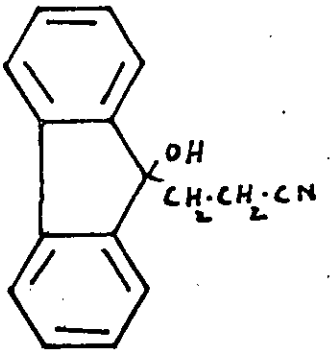
The Ketone XIV, was later used in the synthesis of 3-methyl and 3-phenyl-fluoranthene (12). The carbinol obtained by the action of the appropriate Grignard reagent was dehydrated and dehydrogenated to the required hydrocarbon.

Since the original synthesis of Von Braun, fluoranthene and



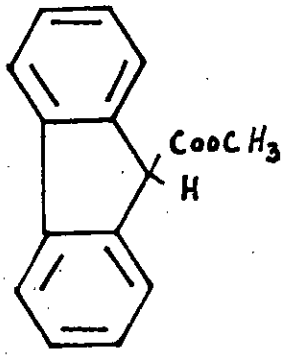
XVIII

$CH_2=CH\cdot CN$ →

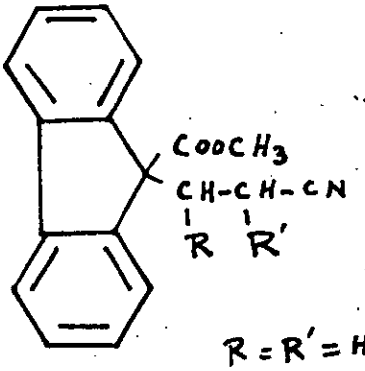


XIX

1. Hydrolysis
2. $-H_2O$
3. $[H]$
→ XIII

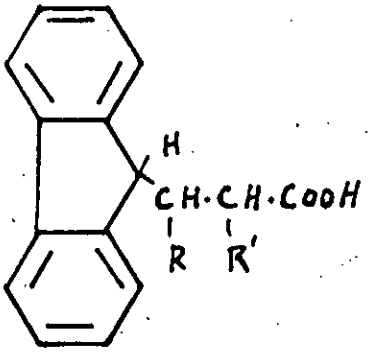


$RCH=\overset{R'}{\underset{|}{C}}-CN$ →

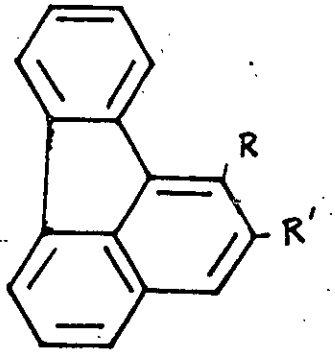


→ XIII

$R = R' = H$



3 stages →



its derivatives have been prepared from fluorene, naphthalene or acenaphthene nuclei.

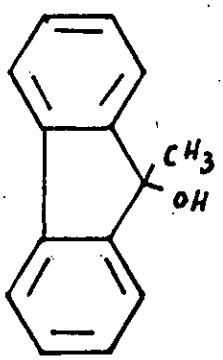
From the fluorene nucleus:-

Fluorene and its derivatives are excellent starting materials for the preparation of fluoranthene and its derivatives, the reason being that methylene group present in the 9-position is very active. Bruson (13) studied the condensation of acrylonitrile in presence of an alkaline catalyst with fluorene and found that two molecules of acrylonitrile condensed most readily with fluorene. Crotononitrile also condensed with fluorene under the above conditions, although in this case only one molecule of crotononitrile condensed with fluorene. Now if one hydrogen atom is blocked initially, suitable substituted acrylonitrile or acrylic ester can replace the remaining hydrogen atom which becomes more labile.

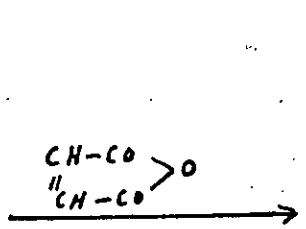
After Von Braun's synthesis, this approach was first utilised by Campbell and Fairfull (14) in the preparation of fluoranthene.

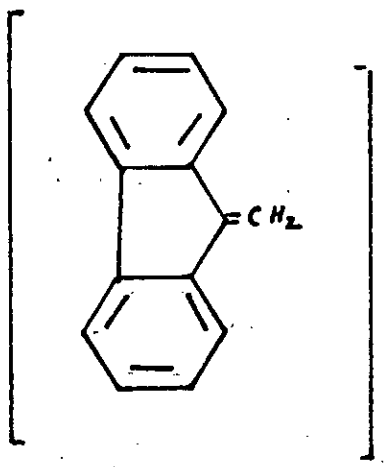
β -(9-Hydroxy-9-fluorenyl)-propiononitrile XIX was obtained by the action of acrylonitrile on fluorene-9-ol XVIII. This on hydrolysis, dehydration and reduction gave β -(9-fluorenyl)-propionic acid XIII, an intermediate in the Von Braun's synthesis.

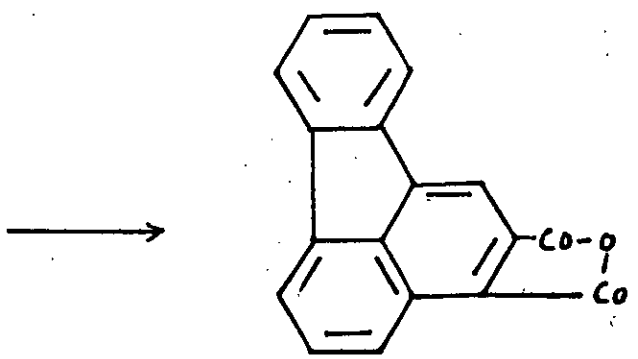
Independently in the same year, A. Campbell and Tucker (15) and Tucker (16) condensed acrylonitrile with methyl fluorene-9-carboxylate. Hydrolysis and decarboxylation gave XIII. The use of crotononitrile (16) and 2-methyl-acrylonitrile (17) in a similar way gave 1- and 2-methylfluoranthene respectively, their synthesis is outlined on the opposite page. This route has been extended for the preparation of 3-hydroxy-fluoranthene (18).



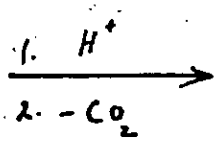
XXIV





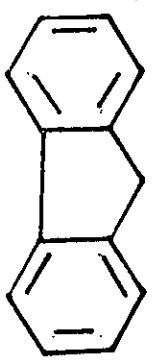


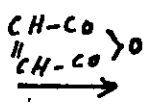
XXV

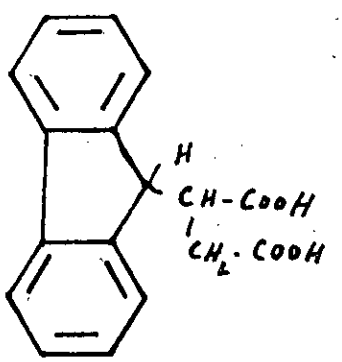


X

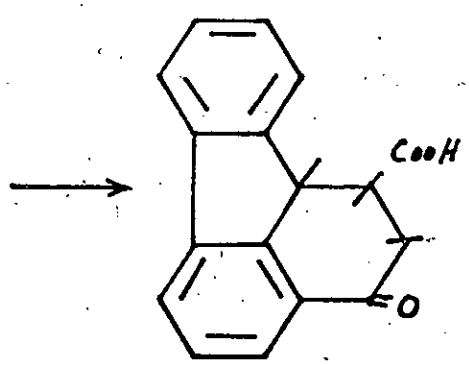
3 stages







XXVI



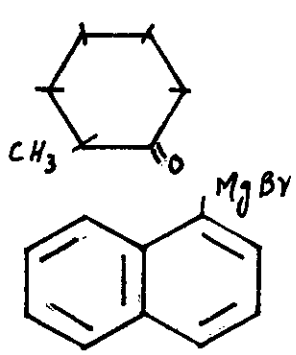
XXVII

Yet another interesting route starts from 9-hydroxy-9-methylfluorene, obtained by the action of methyl-magnesium iodide on 9-fluorenone. This with maleic anhydride gave fluoranthene-2:3-dicarboxylic acid anhydride, from which fluoranthene was obtained (19).

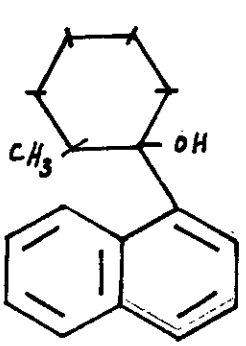
A similar approach was achieved by Bergmann and Orchin (20). They condensed fluorene with maleic anhydride and the resulting adduct was cyclised. After reduction, dehydrogenation and decarboxylation fluoranthene was obtained.

From the naphthalene nucleus:-

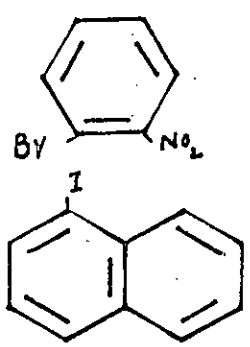
Fluoranthene has been prepared using naphthalene as the parent product. Cook and Lawrence for example (21) reacted α -naphthyl magnesium bromide with 2-methyl cyclohexanone. The resulting alcohol XXIX on dehydration XXX and cyclisation XXXI gave the tetrahydrofluoranthene. This, when dehydrogenated with selenium gave fluoranthene in poor yield. The yield of fluoranthene was improved, when cyclohexanone was used in place of 2-methyl-cyclohexanone (22).



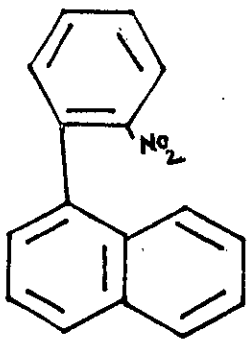
XXVIII



XXIX

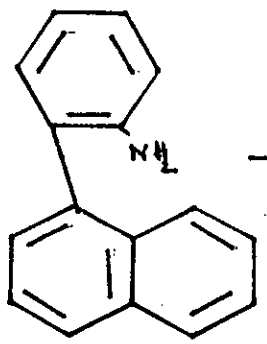


Cu →



XXXII

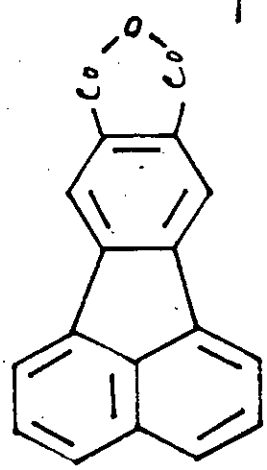
LHJ →



XXXIII

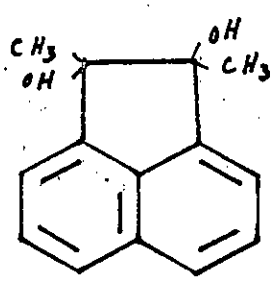
→ X

2 steps ↑



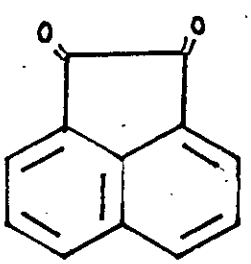
XXXVI

1. Ac_2O
2. $CH_2(CO)_2CH_2$

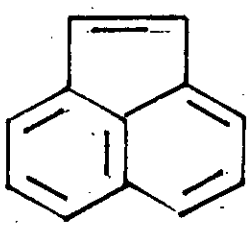


XXXV

CH_3MgI →

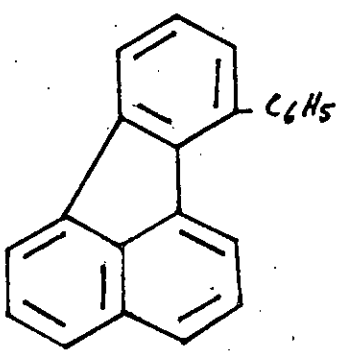


XXXIV



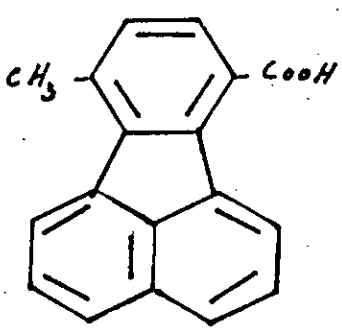
XXXVIII

←

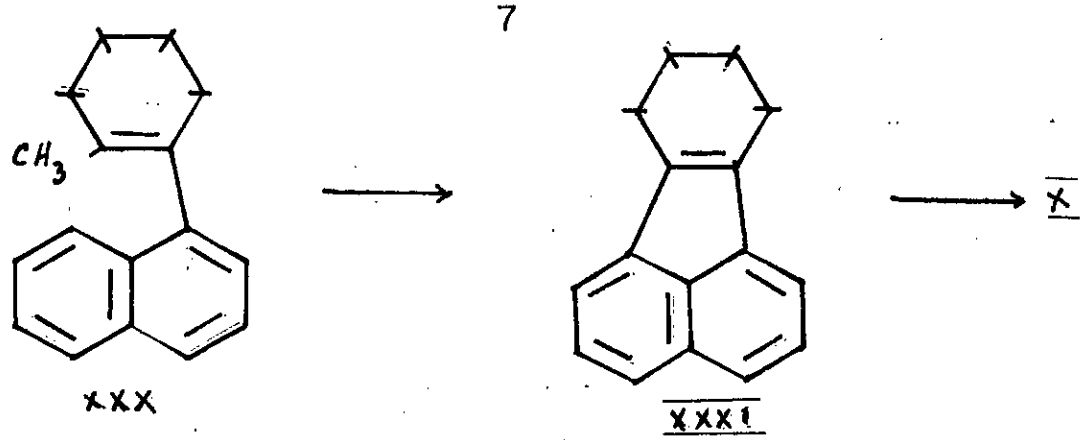


XXXVII

→



XXXIX



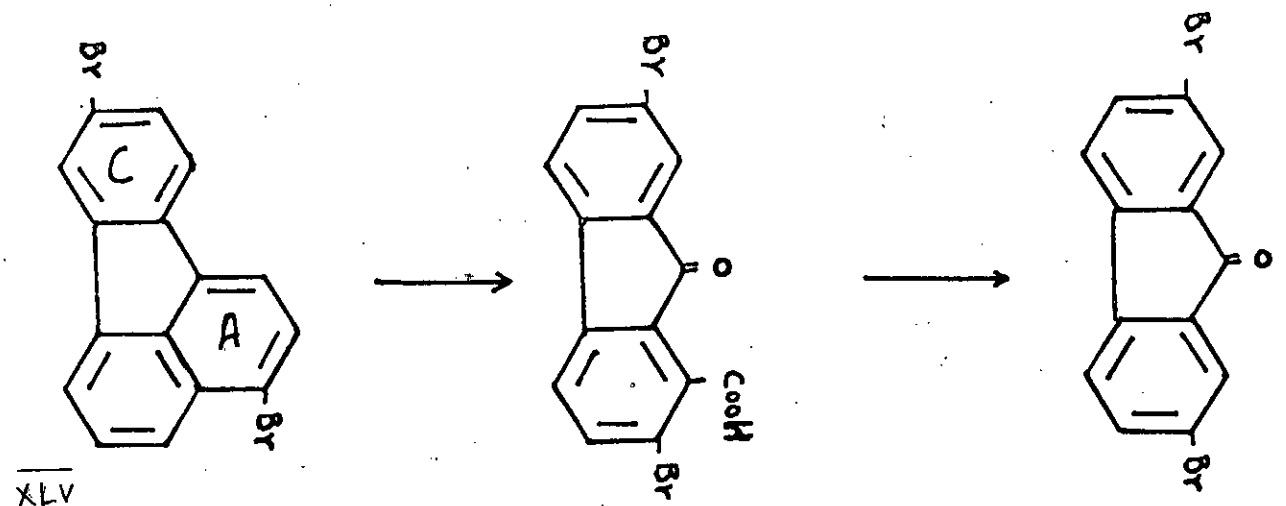
Similarly when 1-iodo-naphthalene was allowed to react with o-bromo-nitro-benzene in presence of copper powder (Ullmann synthesis) it gave 1-(o-nitro-phenyl)-naphthalene XXXII. This on reduction to amine XXXIII, followed by diazotisation and treatment with copper powder gave the corresponding fluoranthene.

The use of suitable substituted benzenes and naphthalenes by Tucker and co-workers gave the corresponding substituted fluoranthenes (23-29).

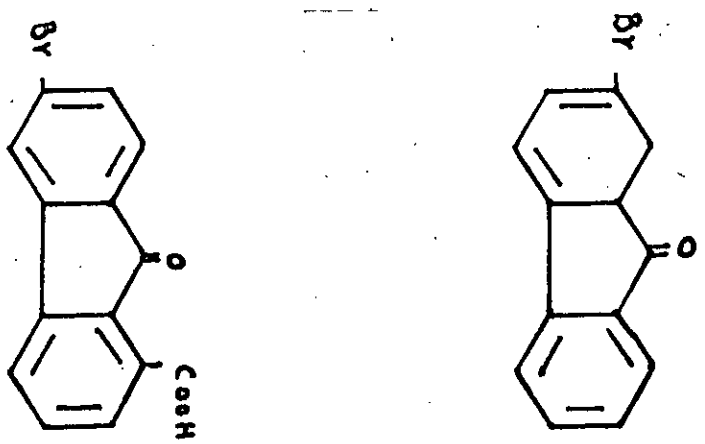
From the acenaphthene nucleus:-

Campbell et al. (30) made use of the acenaphthene nucleus for the preparation of fluoranthene. They condensed 1,2-dihydroxy-1-2 dimethyl acenaphthalene XXXV with maleic anhydride in presence of acetic anhydride to give XXXVI. The product on dehydrogenation and decarboxylation yielded fluoranthene.

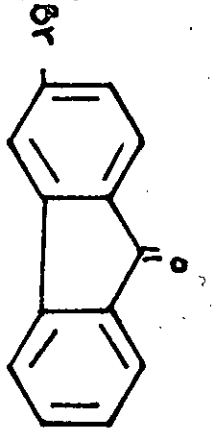
Fluoranthene derivatives may also be synthesised by other ways from an acenaphthene nucleus. Acenaphthylene XXXVIII undergoes a Diels-Alder reaction with certain dienes to give substituted fluoranthene. For example, Bergmann and Orchin (31) obtained 7-phenyl-fluoranthene from 1-phenyl-butadiene. Similarly methyl butadienes gave 7- and 8-methylfluoranthene (32), while sorbic acid yielded 7-methyl-fluoranthene-10-carboxylic acid (33) XXXIX.



XLV XL XLII



XLIII XLI



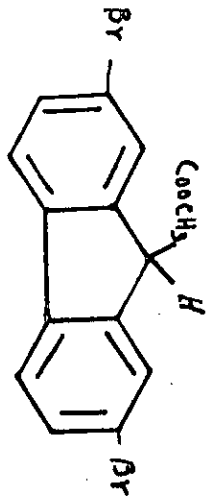
XLIV

Mono-substitution:-

Von Braun and Manz, in 1931, published an important paper (34) on the mono-substitution of fluoranthene derivatives. Under mild conditions they prepared and orientated several mono-substituted products. Their studies revealed that although there are five possibilities (1,2,3,7 or 8) for substitution, the main product in each case was the 3-isomer, with a small amount of 8-isomer as a by-product. They pointed out later on that Friedel-crafts reaction, (35) however, is an exception to this rule, where the main substitution occurs in 8-position and a small amount of 3-isomer and a disubstituted product are obtained as by-products. The influence of reaction conditions on the relative yield of isomers has been stressed by Steitwieser and Fahey (36). They nitrated fluoranthene at 0° and 50° in acetic acid. The measurement of the intensity of the selected bands in infra red spectra and the correlation showed that although the order of reactivities in both cases was the same, yet there was a sharp increase in percentage yield of 3-isomer (from 43·5% to 69·6%) at 50°, at the expense of 1 and 7 isomers.

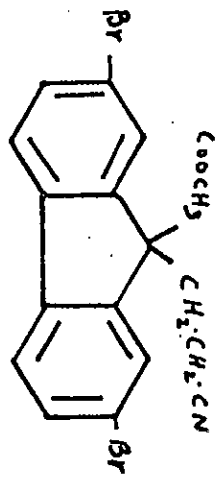
Disubstitution:-

Bromination of fluoranthene in nitrobenzene gave a dibromo product (37). This on oxidation yielded a dibromo-fluorenone-1-carboxylic acid (XL). Obviously this result proved that substitution took place in rings 'A' and/or 'C' of fluoranthene (38). Decarboxylation with copper and quinoline resulted in partial debromination to give 2-bromofluorenone, XLI, while decarboxylation



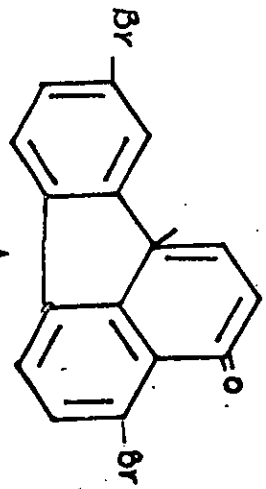
XLVI

$CH_2=CH\cdot CN$



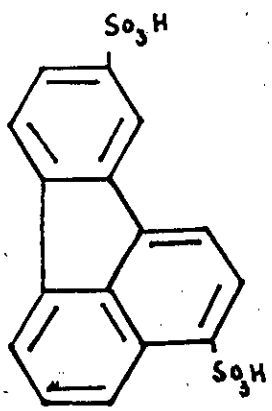
XLVII

1. Hydrolysis
2. cyclisation



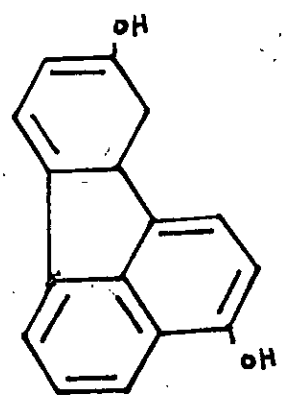
XLVIII

XLV



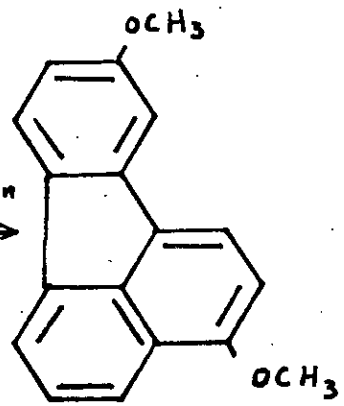
XLIX

KOH
Fusion

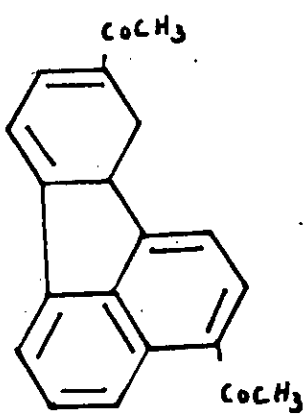


L

methylation

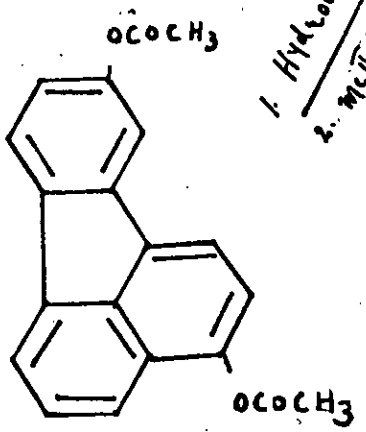


LI



LII

C_6H_5COOOH



LIII

1. Hydrolysis
2. methylation

with mercuric oxide gave 2,7-dibromofluorenone XLII. This work led to the only conclusion that the positions of bromine atoms were 3 and 8 in fluoranthene molecule XLV. Further evidence to support this claim was given by Campbell et al. in their later work (39). Oxidation of the ring A yielded a mono-bromo-fluorenone-carboxylic acid XLIII, decarboxylation of which gave the known 3-bromo-fluorenone XLIV.

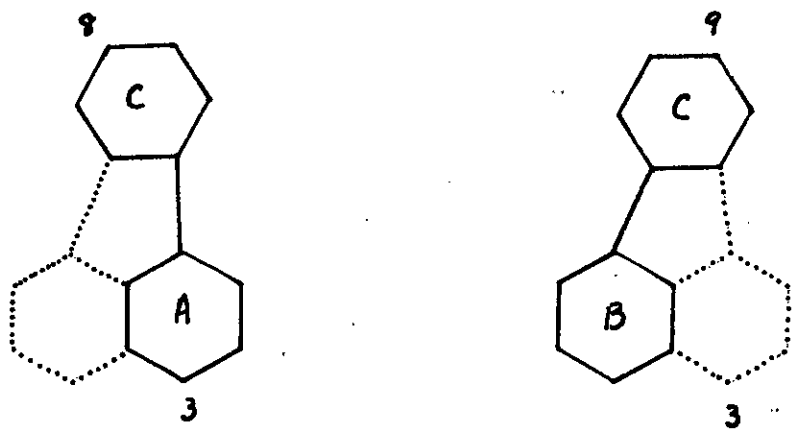
Holbro and Tagmann (40) gave the final proof by synthesising it from 2:7-dibromo-9-carbomethoxyfluorene XLVI. The outlines of the synthesis were those which were employed by Tucker (15, 16).

When diacetyl derivatives of fluoranthene were orientated (41), it was found that in Friedel-crafts reaction the second group occupies the 9-position, giving a 3,9 disubstituted product. In order to establish the 9-position of the second substituent, the diacetyl derivative was converted to diacetamino-fluoranthene by the Schmidt reaction. This on hydrolysis, tetrazotisation and treatment with cuprous bromide gave a dibromo-fluoranthene, which was different from the 3,8-dibromo-fluoranthene.

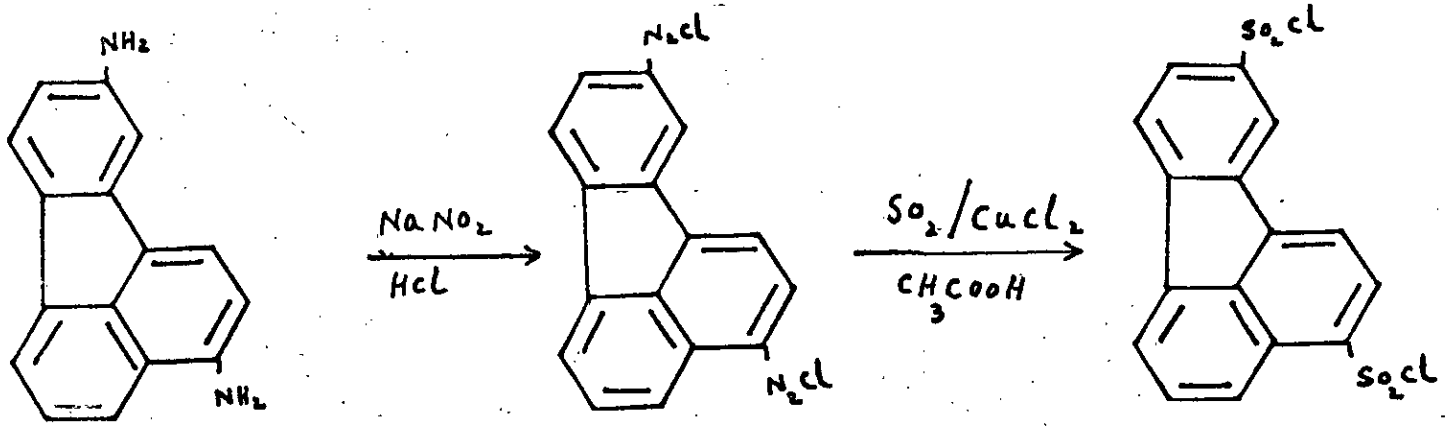
Sulphonation of fluoranthene with (42) conc. H_2SO_4 yields a disulphonic acid XLIX, which on fusion with potassium hydroxide gave the corresponding phenol L. Methylation of this gave a dimethyoxy-fluoranthene LI. Now, 3,9-diacetyl-fluoranthene LII by perbenzoic acid oxidation, followed by hydrolysis and methylation gave also a dimethoxyfluoranthene which was found to be identical with the previous one. This confirmed that disulphonation had occurred in 3,9-position of fluoranthene.

When 3-nitro, 3-carbomethyoxy and 3-cyano-fluoranthene were brominated, in each case, the bromine atom was found to occupy the 9-position.

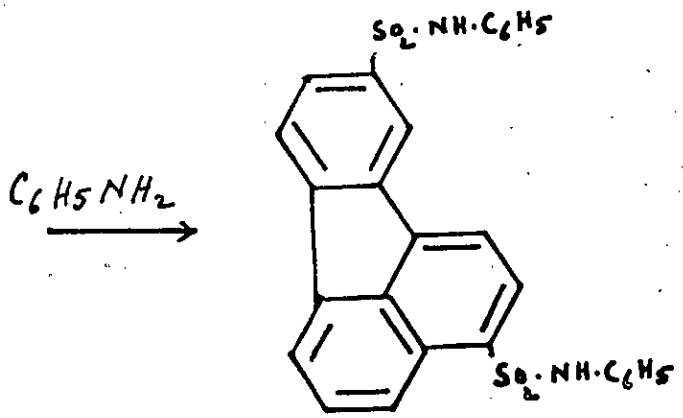
Campbell and Keir (42), from the studies of these orientations concluded that a meta directing group in 3-position of fluoranthene will direct a second substituting group into the 9-position. These authors proposed that the molecule can be regarded as two diphenyl nuclei fused together and possessing a common ring, i.e. ring A and C from one diphenyl nucleus and B and C the other.



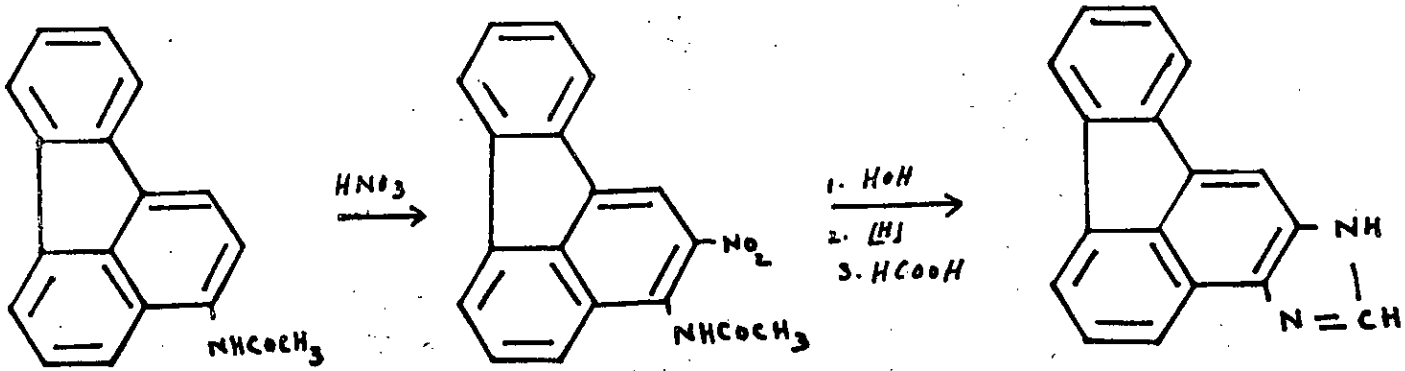
Ring 'A' and 'B' are considered as phenyl groups, each exerting an ortho-para directing effect on substituents entering to ring 'C'. 'A' directing the position 8 and 'B' to position 9. In the unsubstituted molecule both effects are the same and position '8' and '9' are identical. However, if ring 'A' is activated by an ortho-para directing substituent, then it will take over the directing role, and electrophilic substitution will occur in 8-position. On the other hand, if ring 'A' is



LIV LV LVI



LVII



LVIII LIX LX

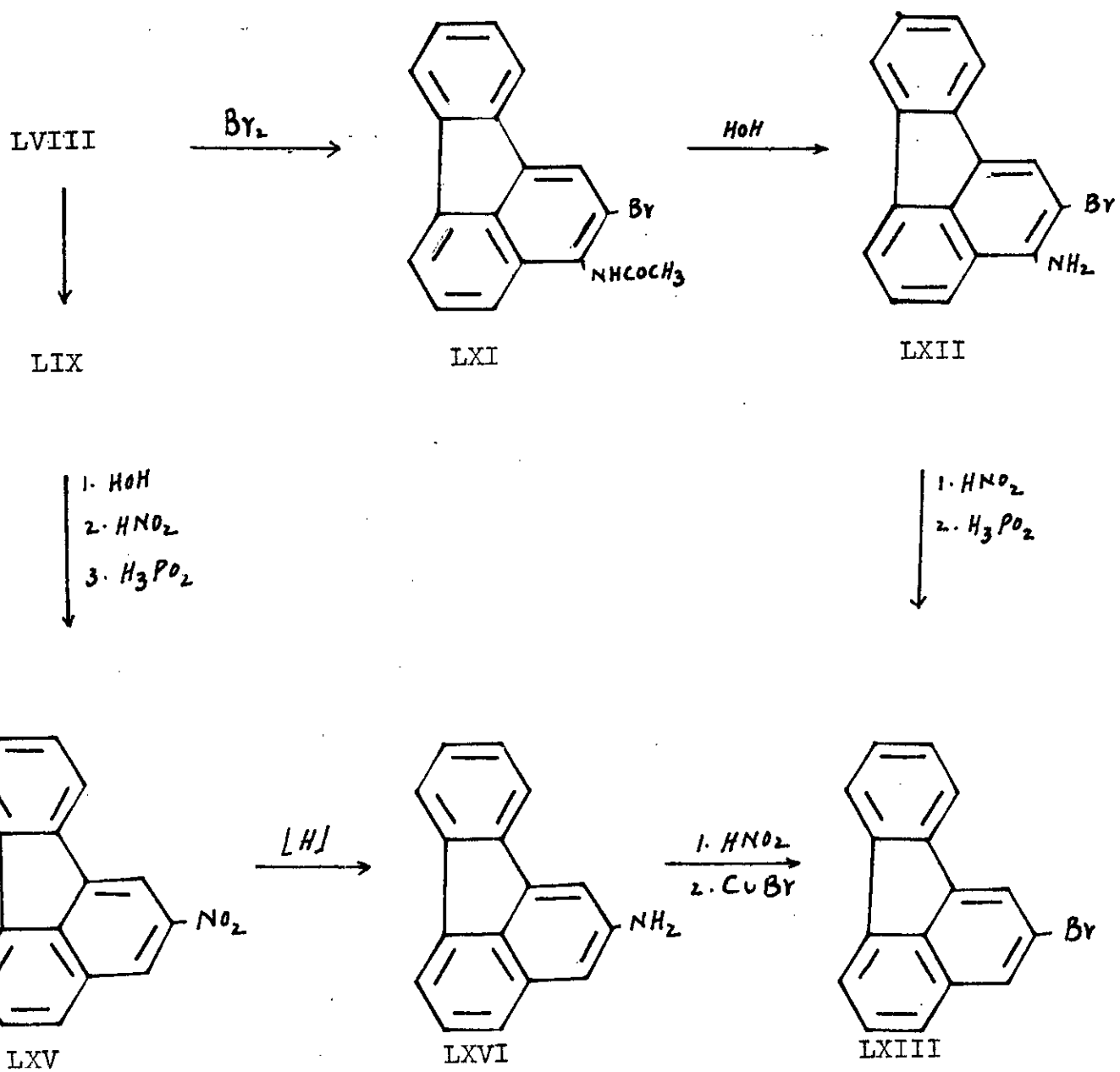
deactivated by meta-directing substituent, ring 'B' will be dominant and will direct further substitution to position 9.

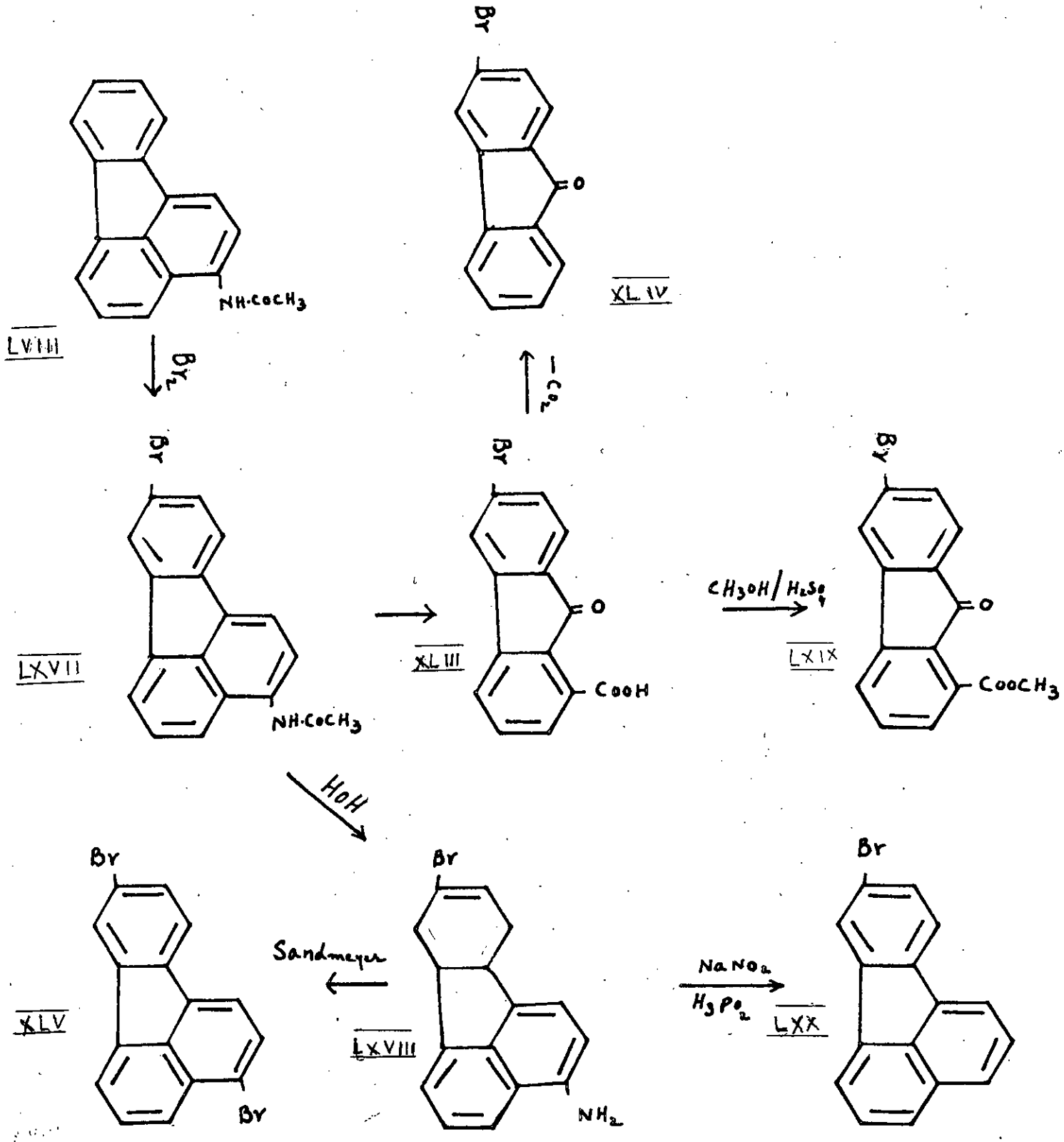
The orientation study of 3:8- and 3:9-disulphonanilides by Campbell and Holbro (43) supported and confirmed the results of Campbell and Keir on disulphonation. 3:9 Diamino fluoranthene LIV was tetrazotised. Treatment of this with sulphurdioxide and cupric chloride in glacial acetic acid gave 3:9-disulphonyl chloride LVI, which with aniline yielded the corresponding 3:9 disulphonanilide LVII.

In another set of experiments, 3:8 dibromofluoranthene was converted to the nitrile which on subsequent hydrolysis gave the diacid. With Schmidt reaction the corresponding 3:8 diamine was obtained. Further work on similar lines as above, gave 3:8-disulphonanilide, which was found to be different from the corresponding isomer.

Kloetzel, King and Menkes (44) criticised the Campbell-Keir rule for its over simplification, and pointed out a new third type of substitution. They nitrated 3-acetamidofluoranthene in acetic acid. The resulting product LIX on hydrolysis and subsequent reduction gave the diamine. When it was treated with formic acid an Imidazole LX was obtained. This is only possible if the two amines are 'ortho' to each other, and hence the nitro group occupies 2-position. This experiment proved, they argued, that a strongly o-p directing group so much activates the ring 'A' that substitution takes place in the same ring.

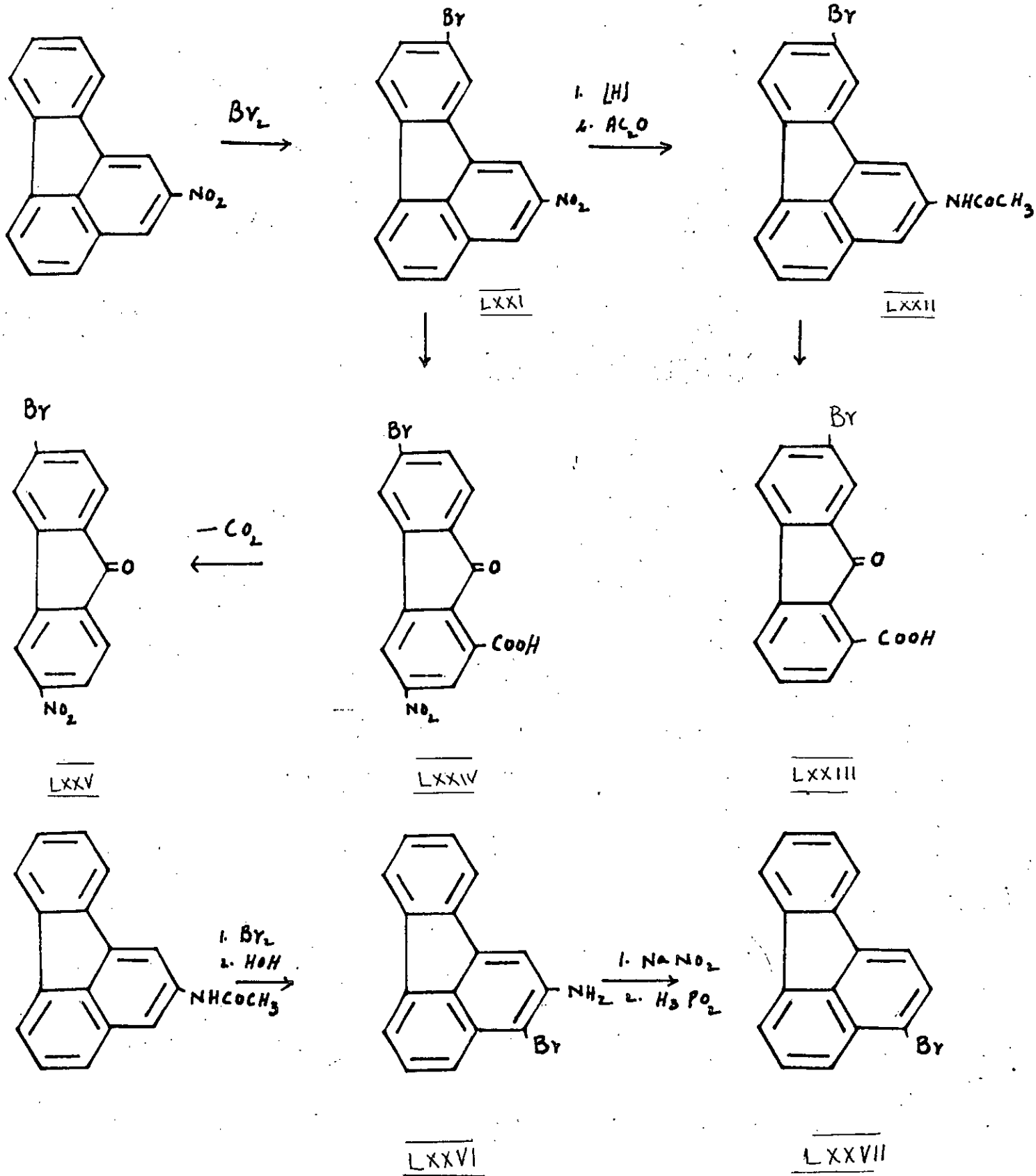
Further support to this view was given by Charlesworth and Blackburn (45). Using pyridine as solvent they brominated 3-acetamidofluoranthene and proved quite conclusively that bromination also takes place in the 2-position. Their results can be summarised as:-




Br
O
NH·COCH3
LVIII
XLIV
Br2
-CO2
Br
Br
O
COOH
LXVII
XLIII
CH3OH/H2SO4
Br
O
COOCH3
LXIX
HOH
Br
Br
Br
Sandmeyer
NaNO2
H3PO2
NH2
XLV
LXVIII
LXX

Barbara Kaminska and Tadeusz Mazonski (46) reported a very interesting observation. When they brominated 3-acetamido-fluoranthene using acetic acid/carbon tetrachloride as solvent mixture, they obtained a mono-bromo-acetamidofluoranthene LXVII which was different from 2-bromo-3-acetamidofluoranthene LXI prepared by Charlesworth et al. The oxidation of the bromo-acetamidofluoranthene yielded 6-bromofluorenone 1-carboxylic acid XLIII, which on decarboxylation gave 3-bromofluorenone. This proved that bromine occupied the 8-position. Further they hydrolysed the 8-bromo-3-acetamidofluoranthene to the corresponding amine LXVIII. The Sandmeyer reaction gave 3,8-dibromofluorenone XLV. The deamination of 3-amino-8-bromofluoranthene gave the new 8-bromofluoranthene LXX. These results confirmed conclusively the 8-position of bromine.

Bromination of 2-nitro-fluoranthene LXV in nitro-benzene gave 9-bromo-2-nitrofluoranthene LXXI (47). Oxidation of this with chromic acid cleaved ring 'B' to give 3-nitro-6-bromo-fluorenone-1-carboxylic acid LXXIV and decarboxylation yielded 3-bromo-6-nitro-fluorenone LXXV. Further confirmation for the position of bromine was made when the above nitro-bromo-fluoranthene was reduced and subsequently acetylated LXXII. The product thus obtained, on oxidation gave 7-bromo-fluorenone-1-carboxylic acid LXXIII. These experiments proved that bromine atom must be in the 'C' ring and at 9-position.


Br
NO2
Br2
1. [H]
2. Ac2O
NHCOCH3
LXXI
LXXII
LXXIII
LXXIV
LXXV
LXXVI
LXXVII
O
COOH
-CO2
1. Br2
2. HOH
NH2
1. NaNO2
2. H3PO2

The 2-acetamidofluoranthene on bromination and removal of acetyl group gave 3-bromo-2-aminofluoranthene LXXVI. Deamination of this product gave the 3-bromofluoranthene LXXVII. These experiments of Charlesworth and Dolenko suggest that Campbell-Keir rule for deactivating substituents and the rule of Kloetzel et al. for strongly activating substituents are also applicable to substituents in the 2-position.

Higher Substitution:-

The tribromo-derivative has been orientated (48) and was shown to be the 3:8:9 tri-isomer. 3:8 Dibromofluoranthene reacted with acetyl bromide and aluminium chloride to give a dibromo-acetyl-fluoranthene. This was shown to be 3:8-dibromo-9-acetyl fluoranthene by Campbell and Leadill.(49). The conversion of this trisubstituted product to tribromo-fluoranthene was achieved by Campbell and Wilshire (50). They converted the acetyl group to the amine and then to the tribromo-fluoranthene and found it to be identical with 3:8:9 tribromo-fluoranthene. Hence acetylation took place at 9-position.

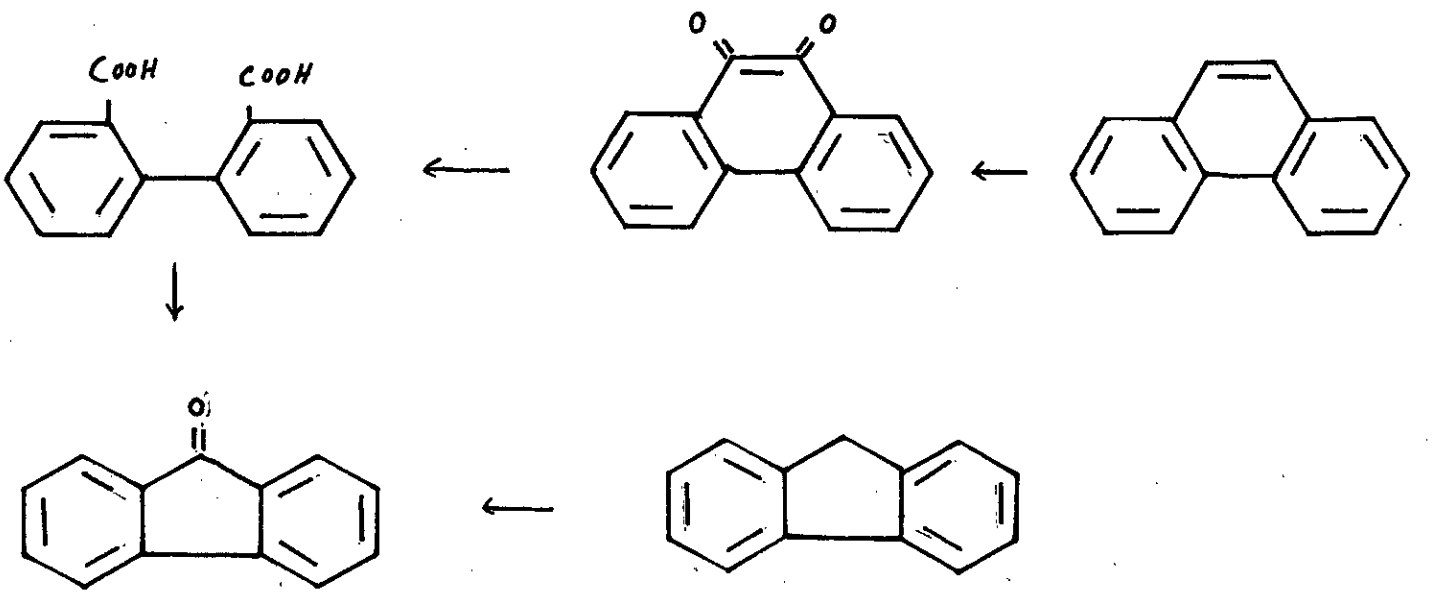
The nitration of 3-methoxy-2-nitro- and 3-methoxy-8-nitro-fluoranthene gave 3-methoxy-2:8-dinitrofluoranthene (51).

The trinitrofluoranthene (9) and trichlorofluoranthene(10) have been prepared in the earlier work, but not orientated.

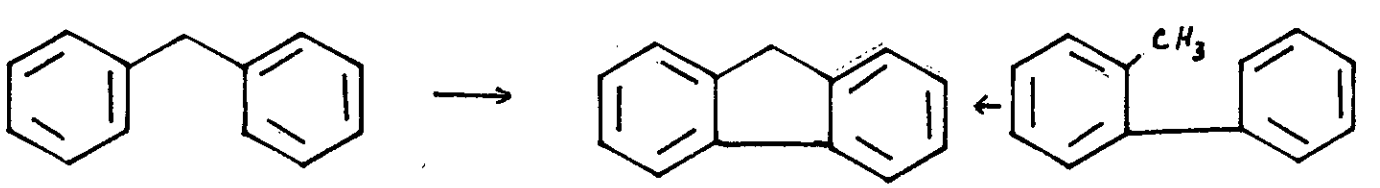
Fluorene:-

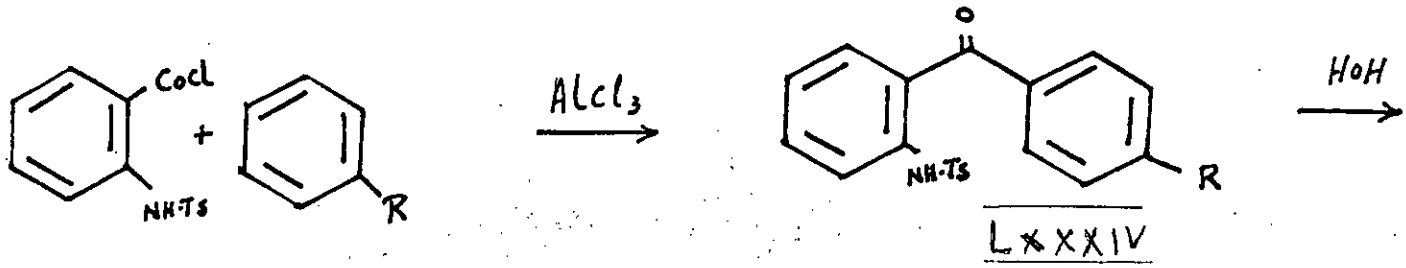
Fluorene was first isolated by Berthelot (52) in 1867, from the crude anthracene oil of coal-tar distillation. The structure of this hydrocarbon was established at an early date by

chemical methods. Barbier (53) obtained a ketone from the oxidation of fluorene which was identical with the Ketone of Fittig and Ostermeyer (54) by the degradation of phenanthrene.

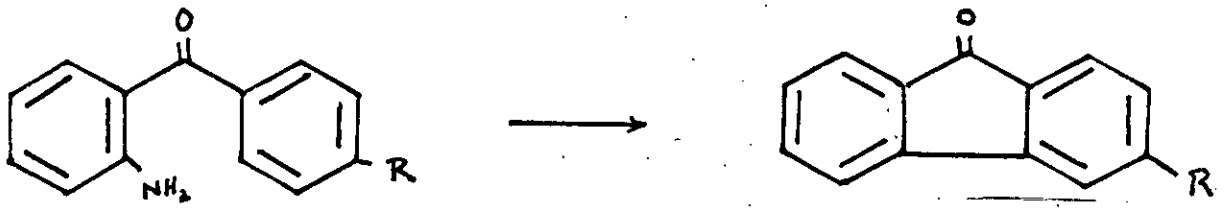


Other methods confirmed the assigned structure. For example Cook et al. (55) and Swain and Todd (56) obtained fluorene when they carried out catalytic cyclodehydrogenation at high temperature of 2-methyl-diphenyl and diphenyl-methane.

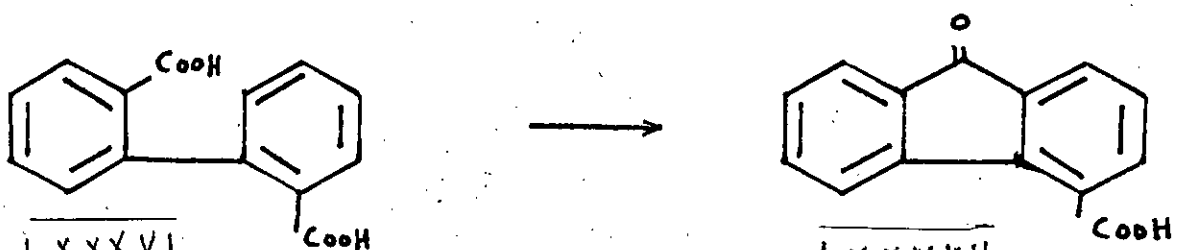




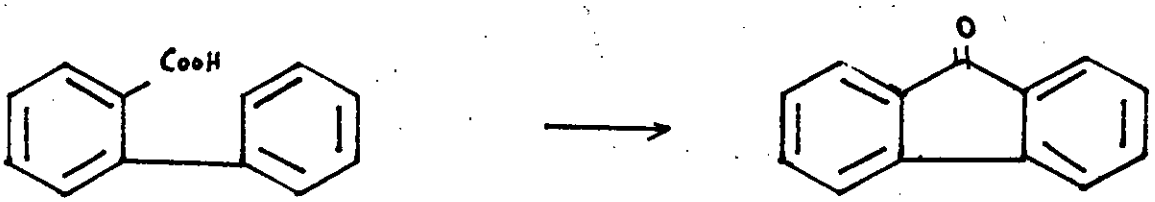
LXXXIV

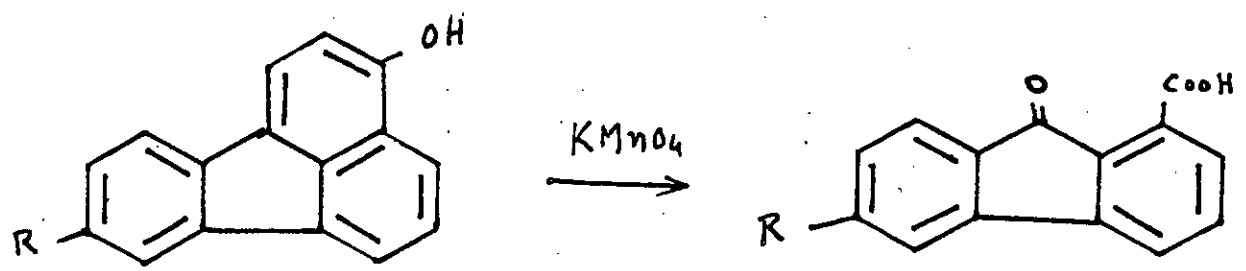


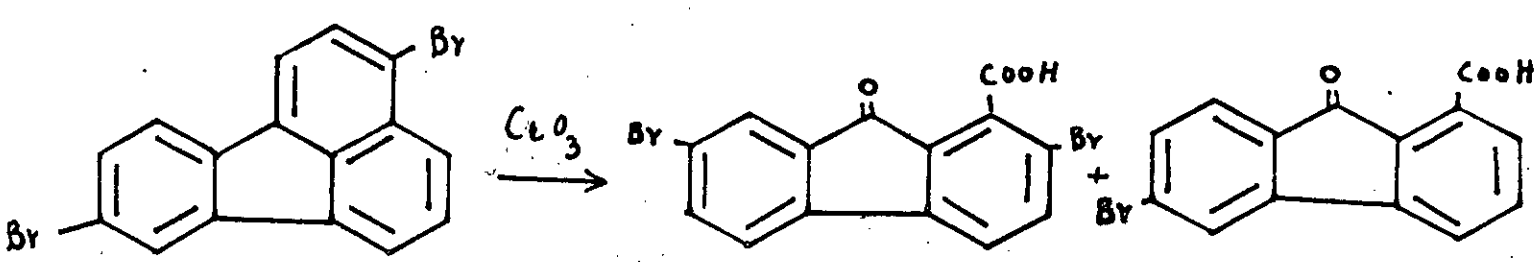
LXXXV



LXXXVI LXXXVII







A method of choice for the preparation of fluorene and its derivatives starts from 2-aminobenzophenone or its substituted derivatives, which can be readily obtained by a three stage synthesis involving a Friedel-Crafts reaction with a protected anthranilic acid. Diazotisation of the former, with subsequent ring closure (57) gives the corresponding fluorenone.

Diphenic acid and diphenyl-2-carboxylic acids have been employed successfully to obtain fluorenones (58, 59).

Oxidation of fluoranthene and its derivatives provide a useful and a general method for the preparation of fluorenone and its derivatives. The route is more valuable since suitable substitution in fluoranthene give the hitherto, rather inaccessible 1,6-disubstituted fluorenones. For example Andrew (60) obtained 6-nitrofluorenone-1-carboxylic acid by oxidising 3-hydroxy-8-nitrofluoranthene.

Similarly, oxidation of 3,8-dibromofluoranthene with chromic acid gives 2,7-dibromofluorenone-1-carboxylic acid as well as 6-bromo-fluorenone-1-carboxylic acid (39).

Fluorene is oxidised to fluorenone when heated with sodium dichromate in glacial acetic acid. Fluorenones, and substituted fluorenones are important intermediate compounds in synthetic work, as they undergo many reactions such as Stobbe, Reformatsky and Grignard reactions and provide the principal route for the corresponding fluorenols and fluorenes.

Substitution:-

A remarkable property of fluorene is the reactivity of its

methylene group at 9-position, with the result that all the reactions belong to one or other of two distinct classes. (1) Those involving the 9-aliphatic methylene group, and (2) those where substitution takes place in the aromatic nucleus.

Reactivity of methylene group:-

It was shown that the reactivity of the methylene group decreased in the order cyclopentadiene-indene-fluorene (61) due to the inactivating influence of the fused benzene nuclei. Nevertheless the methylene group in fluorene is reactive.

Fluorene forms alkali metal derivatives with lithium (62, 63), Sodium (64) and potassium (15). These are prepared by the exchange of metal from the corresponding derivatives of less acidic hydrocarbons. These derivatives are not only used in the synthesis of substituted fluorenes, but they also play an important role in the synthesis, study and orientation of substituted higher aromatic hydrocarbons, such as fluoranthene and its derivatives.

Fluorene also undergo base catalysed reactions due to the acidity of the methylene group. For example when it is heated with potassium hydroxide and benzyl chloride, 9, 9'-dibenzyl-fluorene is formed. Fluorene readily reacts in presence of a catalyst, with acrylonitrile to form a disubstituted 9, 9'-bis-(cyano-ethyl)-fluorene, although with crotononitrile it forms a monosubstituted product.

Fluorene when heated with lead oxide is dimerised, to give first bifluorenyl and then bifluorenylidene. It reacts with aromatic aldehydes in presence of sodium alkoxide to form 9-

arylidenefluorene (65). The condensation of fluorene with propionaldehyde, butyraldehyde and iso-butyraldehyde have been reported (66), although the reaction is not very common.

Von and Wagner obtained 9-formyl-fluorene (67) by condensing it with ethyl-formate. Similarly on reacting with maleic anhydride (68) it gives 9-fluorenyl-succinic anhydride. When refluxed with N-bromo-succinimide in carbon tetrachloride it gives 9-bromo-fluorene (67).

Substitution in the aromatic nucleus:-

The substitution in fluorene nucleus generally occurs at the 2-position e.g. 2-nitro fluorene (69) 2-bromofluorene (70). An electron attracting group in the 2-position directs the 2nd substituent into 7- and to some extent to the 5-position, while an electron releasing group directs the 2nd substituent into 7, and/or 3, and/or to a much smaller extent the 1-position (71). However, only 2;2,7 and 2,3 derivatives of fluorene are readily obtained and of synthetic value, and the same applies also to the corresponding fluorenone. In other cases, usually indirect methods of synthesis are employed. For example 2-nitrofluorenone on reduction and subsequent bromination gives 2-amino-3-bromo-fluorenone (72). This on deamination gives 3-bromofluorenone. Another example is 3-nitrofluorenone which is obtained by the following indirect route. 2-Tosyl-aminobiphenyl is nitrated and then hydrolysed to the free amine. The Sandmeyer reaction on the amine gives the corresponding nitrile which is converted to the corresponding carboxylic acid. When this is heated with

conc. H_2SO_4 it yields 3-nitrofluorenone (73) 74).

NAPHTHALENE

The structure and chemistry of naphthalene or its derivatives have been thoroughly studied and it has been found that substitution takes place far more readily in the α - than in the β -position. Thus when naphthalene is halogenated or nitrated, α -substituted derivatives are obtained almost exclusively. Sulphonation of naphthalene at moderate temperature gives mainly the α -sulphonic acid, which changes to β -isomer, when heated at high temperature. The course of Friedel-Crafts acetylation of naphthalene varies more with the nature of reagent and solvent than with temperature. The hydrocarbon is converted by acetyl chloride or acetic anhydride in carbondisulphide into a mixture of α and β -aceto-derivatives in the ratio of about 3:1, while in nitrobenzene the β -acetonaphthalene is the chief product

Naphthalene $\xrightarrow{CH_3CO.Cl, AlCl_3, CS_2}$ α -acetonaphthalene + β -isomer (3 : 1)

Naphthalene $\xrightarrow{CH_3COCl, AlCl_3, C_6H_5NO_2}$ α-isomer + β-isomer (1 : 9)

The hydrolysis of 1-naphthylamine gives α -naphthol, while the β -isomer is prepared efficiently by alkali fusion of sodium naphthalene- β -sulphonate. α , and β -naphthylamine can be prepared by heating the corresponding derivative with aqueous ammonium sulphite or bisulphite. This reaction, known as Bucherer

reaction, is reversible.

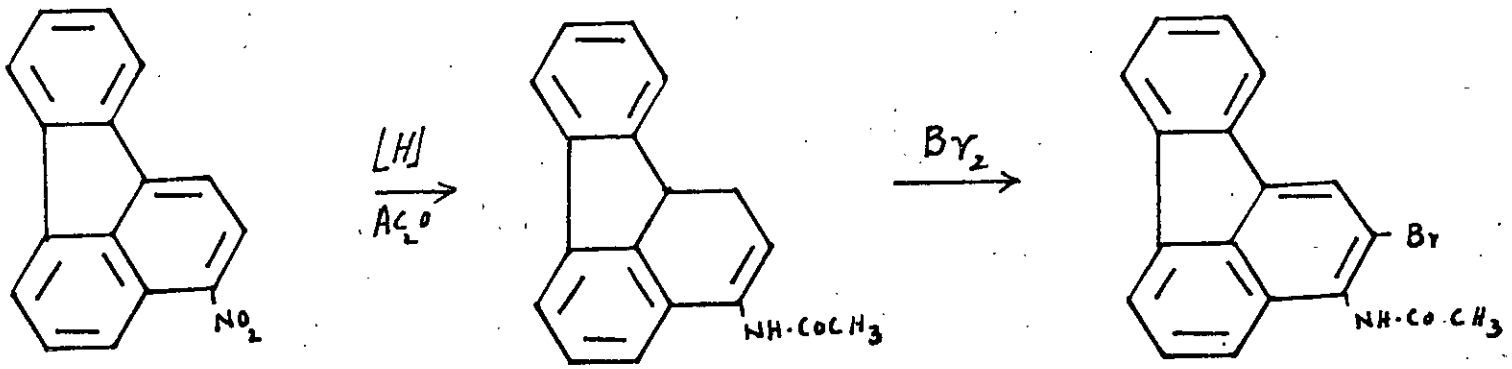
The formation of disubstituted and trisubstituted derivatives is more complicated and is governed by several factors, such as the nature of substituent already present, the position α -, or β - occupied by the group already present, the nature of the entering group and the reaction conditions. In general groups such as CH_3, Cl, OH, NHAC in α -position direct the entering group into 4- and 2-position. (The difficulty of generalising, however, is shown later in the thesis by the nitration of 1-bromonaphthalene in which nitration occurs at the 4,5,8-positions). While the above mentioned groups when present in 2-position of naphthalene direct the entering group into 1-position or into unsubstituted nucleus. Groups like NO_2, SO_3H, when present either in α -, or β -position direct the second group to the unsubstituted nucleus. This is understandable since these groups deactivate the ring to which they are attached towards electrophilic reagents.

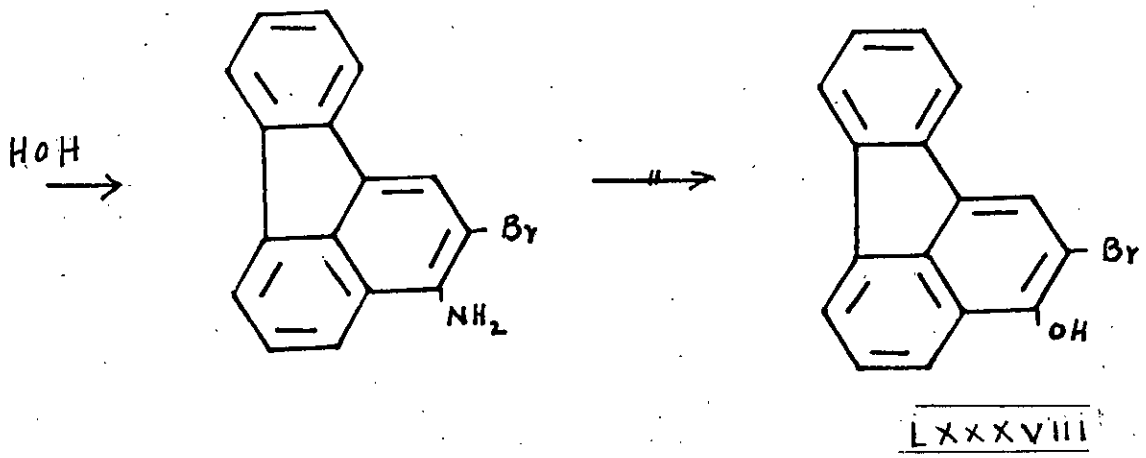
OBJECT OF RESEARCH

3-Methoxyfluoranthene on bromination in acetic acid gives a dibromo-3-methoxyfluoranthene. The object of this research was to establish the structure of this compound, which has now been found by synthesis to be 2,8-dibromo-3-methoxyfluoranthene.

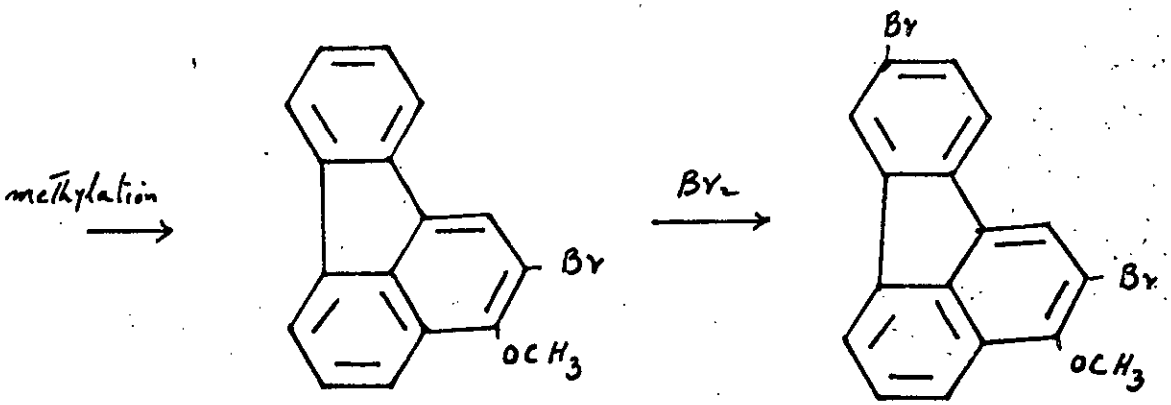
The research necessitated the preparation and structural determination of a number of fluoranthene, fluorene and naphthalene derivatives.

D I S C U S S I O N





LXXXVIII



LXXXIX

XC

Part I: Attempted synthesis 2:8-dibromo-3-methoxy fluoranthene from 3-amino-2-bromo-fluoranthene

A promising route for the preparation of 2:8-dibromo-3-methoxyfluoranthene from fluoranthene is given on the opposite page.

3-Nitrofluoranthene was prepared by the method of Carascia, Fries and Ching (75). This was reduced with Raney nickel to the amine, which was acetylated in almost quantitative yield (44). The bromination of this 3-acetaminofluoranthene in pyridine, with subsequent hydrolysis gave 3-amino-2-bromo-fluoranthene (45). Different standard methods (76, 77) were tried to obtain a clear diazonium solution, but success was achieved only by using the method of Charlesworth et al. (45). A large number of attempts under various conditions were made for converting the diazonium solution into the corresponding phenol. For instance it was heated with dilute acid of various concentration for different intervals of time. The diazonium solution was found to be very stable, no improvement was achieved when steam was passed through the boiling dilute acid solution. Boiling dilute sulphuric acid containing sodium sulphate (78) or corresponding other metallic salts (79) have been employed quite successfully for decomposing stable diazonium solutions. By this means, more elevated temperatures are achieved for decomposition purposes, and phenols are formed quite smoothly. Unfortunately this also failed. In each of the above cases tar formation was observed. Another

method of diazotisation and phenol formation which was used and found later satisfactory for conversion of 2-amino-fluorene and 2-amino-7-bromo-fluorene, to the corresponding phenols (Page 55) was also attempted, but no success was achieved. An experiment was conducted on 3-amino-fluoranthene in order to obtain some information as to the best reaction conditions. It was diazotised by the method of Charlesworth (loc.cit.) heating with dilute acid gave the corresponding phenol in only about 10% and considerable tar formation was observed. This extraordinary resistance of diazonium solution of fluoranthene derivatives to undergo the usual replacement reactions was also reported by other workers. For instance, Nichol (80) although he could diazotise 3-amino-2-nitrofluoranthene, failed to convert it to the corresponding phenol. Tucker et al. (29) also reported only a partial success in obtaining 3-methoxyfluoranthene from 3-aminofluoranthene. It is interesting to note that most of the hydroxy-fluoranthenes derivatives reported in the literature have either been prepared by more drastic methods or by indirect methods. For example, Von Braun (81) prepared 3-hydroxy-fluoranthene by heating the corresponding amine with dilute acid in a seal tube at 200°. Nichol (loc. cit.) took advantage of the position of the nitro group and converted 3-amino-2-nitro-fluoranthene by heating with sodium hydroxide; a number of phenols are prepared, from substituted 3-Keto-1,2,3,10b tetra-hydrofluoranthene, which themselves were obtained by the cyclisation of substituted 9-(2 -carboxyethyl)-fluorene (18, 82). Similarly Campbell and Keir (42) prepared 3:9-dihydroxyfluoran-thene by fusing the disulphonic acid derivative of fluoranthene

with Potassium hydroxide.

It was thought, therefore, that more vigorous conditions might be required for phenol formation. Now, Franzen et al. (83) converted amino-naphthalene and a number of substituted amino-naphthalenes into corresponding phenols, by heating with 20% HCl in sealed tubes at high temperatures in good yield. Similarly, Newman and Cathcart (84) obtained 6-hydroxy-chrysene by heating 6-amino-chrysene with 10% H_2SO_4 at 220° in a seal tube, and the yield obtained was quite high. These methods were applied with various modifications to 3-amino-2-bromo-fluoranthene. Under the more vigorous conditions, the resultant product was found to be either a black residue or solid products whose m.ps. were above 350°, and which were not soluble in the usual solvents. When less vigorous conditions were employed charring also occurred and unchanged starting material was obtained.

The decomposition of stable diazonium salts is sometimes achieved by carefully boiling the fluoro-borates with acetic acid or acetic anhydride to give nitrogen and the acetoxy-derivative (85). From this the phenol can be readily obtained by subsequent hydrolysis with alkali.

The fluoro-borate salt from the diazotised solution of 3-amino-2-bromofluoranthene was easily obtained. This was heated with acetic anhydride and then was refluxed with alkali. The resultant oil obtained could not be solidified. As the phenols are usually found to be comparatively more unstable and difficult to purify, the oil was refluxed with dimethyl sulphate with the hope of obtaining a bromo-methoxy-fluoranthene. Working

up and passing through a short column again gave an oil. Attempts to solidify, including triturating with solvents and keeping for long intervals (1 month) in cold storage did not meet with success.

The direct formation of ether from the diazonium salt is another method, which has been used quite successfully. For example, Hantzsch and Jochem (86) obtained the methyl ether, when a diazonium salt was gradually added to excess of absolute methyl alcohol at room temperature and then boiled for a short time.

In general, the method is avoided if other methods can be successfully used. One obvious reason is the difficulty in isolating the diazonium salt; however, stable and easily isolated zinc chloride double salts of a number of diazonium chlorides have been obtained by Hodgson and Foster (87).

Accidentally, it was found that a stable diazonium salt of 3-amino-2-bromo-fluoranthene can be obtained most easily, if the diazonium solution obtained by the method of Charlesworth et al. (loc. cit.) is simply kept for about three to four hours in ice water. The diazonium salt thus obtained was filtered, and in order to test the stability a small amount of the salt was kept for four days at room temperature and was found to be quite stable. The remaining diazonium salt was filtered, most of the adhering water removed by suction, and then added, at room temperature to an approximately ten fold amount of methyl alcohol. It was later refluxed for one hour on a water bath. Next day, the quantity of methanol was reduced to a small bulk, which on

cooling gave beautiful cream coloured crystals. It was thought to be initially the 2-bromo-3-methoxy-fluoranthene. Surprisingly I.R. and N.M.R. spectra showed no characteristic methoxy group peak. The melting point of the product after recrystallisation from methanol was 101-103°, in exact agreement with that of 2-bromofluoranthene (45).

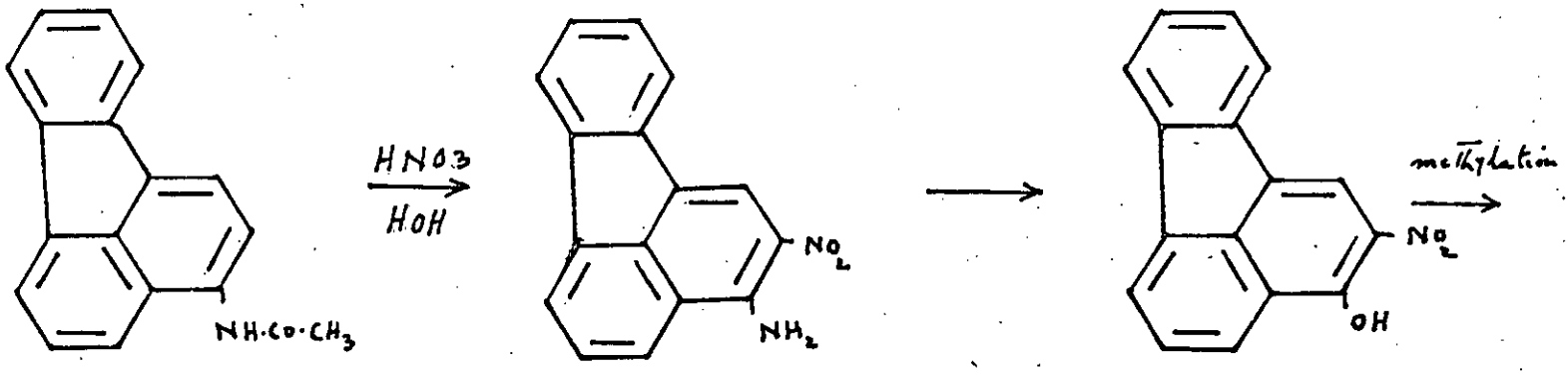
The replacement of the diazo-group by hydrogen when ethanol is used as solvent is a common observation. Griess (88) discovered many years ago that benzene diazonium nitrate in ethanol is converted into benzene and dinitrophenol. The examples of this type of replacement by hydrogen using methanol are more rare. Although, for example, Griess obtained benzoic acid from diazotised anthranilic acid with methanol, in the case of m-aminobenzoic acid and p-aminobenzoic acid, the products obtained were m- and p-methoxybenzoic acid respectively.

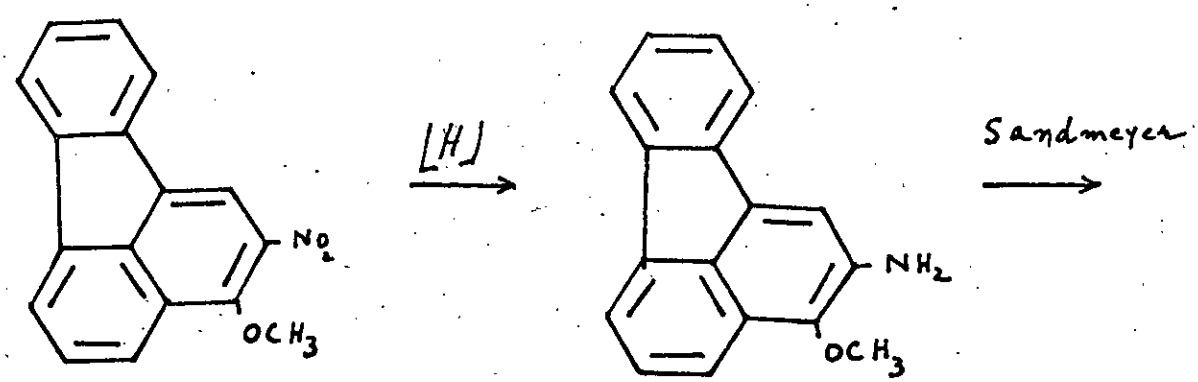
As might be expected in many cases decomposition of diazonium salts with alcohols gives a mixture of phenol ether and hydrocarbon. For example, α-naphthalene diazonium sulphate in boiling ethanol afforded naphthalene (40%) and α-ethoxynaphthalene (23%) (89).

It has been noted that the addition of water to alcohol increases hydrocarbon formation (90). Another example of the influence of water was afforded by Ridge (91) who found that when 2:6-dichloro-4-nitroaniline was diazotised slowly in cold concentrated sulphuric acid and alcohol was then added the product was 2:2'6:6'-tetrachloro-4:4'-dinitrodiphenyl, but if a little water was added before the alcohol then the product was 3:5-

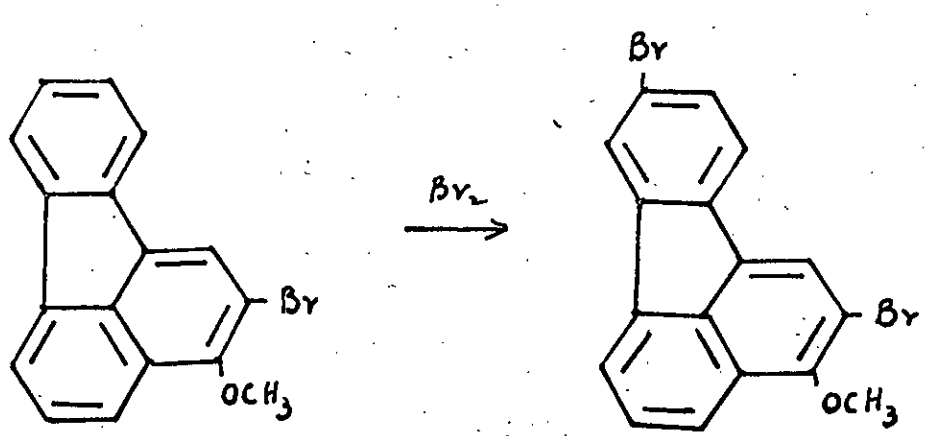
dichloro-1-nitrobenzene. Since in the previous experiment the diazonium salt was not quite anhydrous and undried methanol was used, it was thought worthwhile to repeat the experiment with the exclusion of moisture. The diazonium salt, obtained as in the previous case, was dried by pressing between the folds of filter paper. The process was repeated a number of times, until an almost dry salt was obtained. This was added to the dried methanol. A change of colour from orange to colourless was observed after half an hour when the solution was boiled. 2-Bromofluoranthene, however, again resulted. Although the formation of 2-bromo-fluoranthene was somewhat unexpected it has long been known that negative substituents in the aryl nucleus, especially if ortho to the diazo-group, encourage the formation of hydrocarbons, and this fact has been generalised in the remark of Hodgson (92) that the greater the induced positivity on the carbon to which the diazonium group is attached, the greater the ease with which the group is replaced by hydrogen. Thus halogenodiazonium compounds especially such as 2:4:6 trichloro or tribromo-benzene diazonium salts are converted into 1:3:5 trichloro or tribromo-benzene (93) in high yield.

It is noteworthy that Charlesworth (loc. cit.) obtained 2-bromo-fluoranthene by diazotisation and subsequent deamination with hypo-phosphorous acid and keeping the whole mixture for four days at 0-5°, whereas the method described above gives a simpler and quicker method.


HNO3
HOH
NH·CO·CH3
NO2
NH2
methylation
NO2
OH


NO2
OCH3
[H]
NH2
OCH3
Sandmeyer

XCI


Br
OCH3
Br2
Br
Br
OCH3

XC

Part 2: Attempted preparation of 2:8-dibromo-3-methoxy fluoranthene from 3-acetamino-2-nitro-fluoranthene

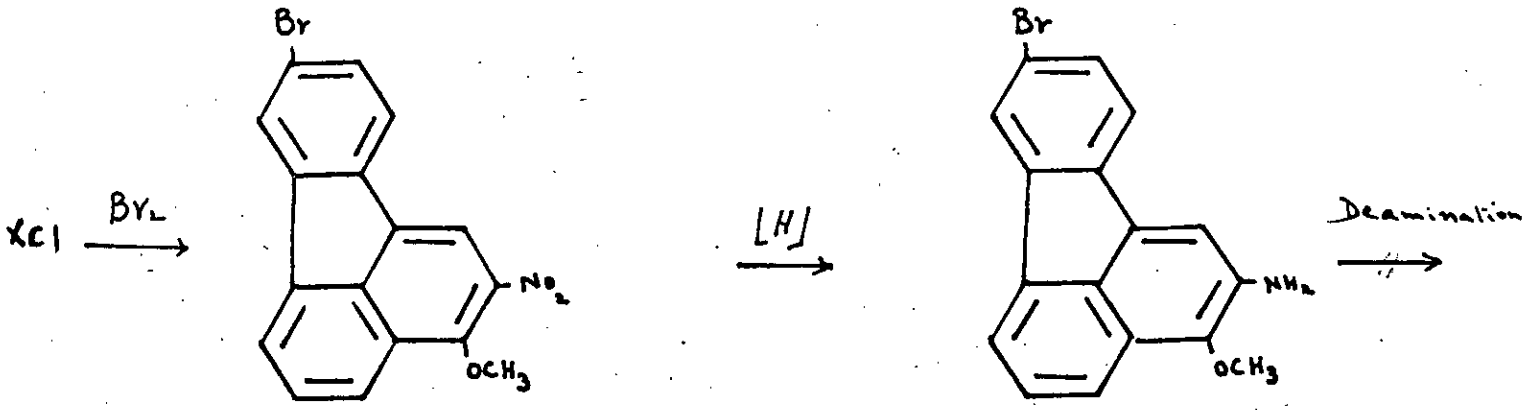
A possible preparation of 2,8-dibromo-3-methoxy-fluoranthene was made by the scheme given on the opposite page.

3-Acetaminofluoranthene was nitrated (44) and later the acetyl group was removed by boiling with HCl. The nitro-amine was hydrolysed with sodium hydroxide in ethanol to give 3-hydroxy-2-nitrofluoranthene (94). The hydrolysis of 3-acetamino-2-nitro-fluoranthene with 10% sodium hydroxide also gave the phenol directly. It formed a sodium or potassium salt very readily when it was merely shaken with the corresponding alkali. The phenol was methylated with dimethylsulphate and anhydrous potassium carbonate in chlorobenzene and passed through a column of alumina with benzene as solvent. Evaporation of the solvent and recrystallisation from benzene/light petroleum gave yellow long needles of 3-methoxy-2-nitrofluoranthene, m.p. 120-121°, 8° higher than that reported by Nichol (94). The N.M.R. spectrum showed the characteristic methoxy group peak at 5·85, with a ratio 3 methyl protons to 8 aromatic protons.

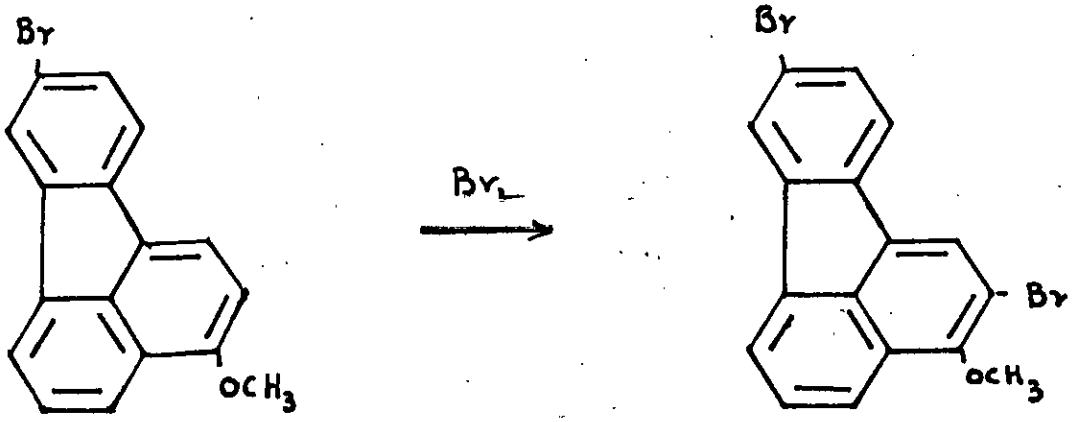
As a side reaction 3-methoxy-2:8-dinitrofluoranthene was prepared. This was achieved by dissolving the above methoxynitro-fluoranthene in glacial acetic acid and nitrating it with fuming nitric acid at room temperature. The mixture was kept standing for 18 hours. The yellow precipitate obtained was recrystallised twice from toluene-1-methylnaphthalene which gave yellow needles of m.p. 282°-284°. It might be pointed out, that the compound

was initially prepared by Craig and others (95,96,97) who gave the m.p. over a range. Moreover, the analytical result of nitrogen, obtained by Craig was rather poor.

3-Methoxy-2-nitro-fluoranthene was reduced catalytically with Raney nickel as catalyst to 2-amino-3-methoxyfluoranthene. It was expected that the Sandmeyer reaction would give 2-bromo-3-methoxy-fluoranthene. However, when attempts were made to diazotise the above amine in hydrobromic acid (98), it was found to be completely insoluble, even on heating, and diazotisation yielded a mixture of products. In another experiment, the amine was initially dissolved in the minimum quantity of acetic acid, then HBr (38%) was added dropwise with stirring, immediately a salt was formed, which was quite resistant to diazotisation. A repeat experiment was made with the variation that the previous mixture was heated to 85° and then cooled rapidly. Still no clear diazonium solution was obtained. An attempt at diazotisation using the Hodgson and Walker (77) method was made. The thick viscous diazonium solution, without filtration was added gradually to freshly prepared cuprous bromide in hydrobromic acid solution (38%). The resultant product was found to be a mixture m.p. 150°-350°, which could not be separated. Similarly an experiment with tetrahydrofuran as solvent also failed (99). This led once again to the more useful method of Charlesworth and Blackburn. The clear diazonium solution was added gradually with stirring to freshly prepared cuprous bromide in hydrobromic acid (38%) and then heated slowly to 95°. The resultant product was found to be a mixture. From a fairly large amount of material


XCl
Br_2
Br
NO_2
OCH_3
[H]
Br
NH_2
OCH_3
Deamination

XC II


Br
OCH_3
Br_2
Br
Br
OCH_3

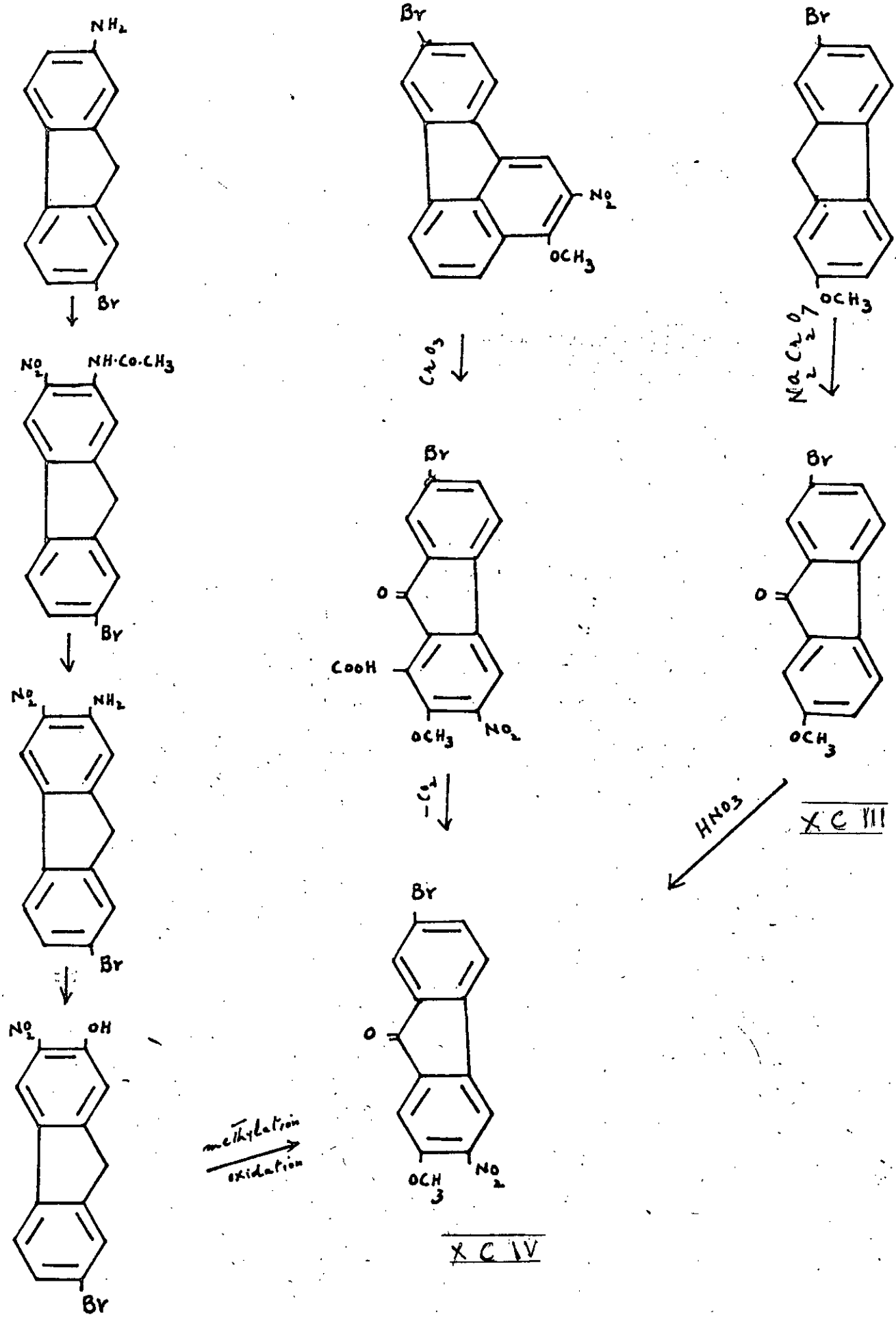
XC

only a few milligrams of a product m.p. 110°-115° was obtained which were analysed for bromine. However, the percentage of bromine was found to be higher than theoretically required which suggested that probably the required product was formed but contained still some impurity. It was thought that a temperature of 95° was too high, since sulphuric acid might have reacted with hydrobromic acid to liberate some bromine, which caused some dibromination. So two sets of experiment at 35° and 60° were conducted, but no success was achieved. It might be pointed out that Charlesworth and Blackburn (45) have reported a failure of the Sandmeyer reaction on 2-amino-3-acetamidofluoranthene. Similarly Barbara Kaminska (46) obtained a yield of only 8% of 3,8-dibromofluoranthene from 3-amino-8-bromofluoranthene.

Part 3. Attempted preparation of 2:8-dibromo-3-methoxy-fluoranthene from 8-bromo-3-methoxy-2-nitro-fluoranthene.

Bromination of 3-methoxy-2-nitrofluoranthene gave a bromo-3-methoxy-2-nitrofluoranthene the optimum yield being obtained, when bromination was carried out at 80° in acetic acid. Now if the bromination has taken place at the 8th position of fluoranthene, this would provide another approach for the preparation of 2:8-dibromo-3-methoxyfluoranthene, according to the scheme given on the opposite page.

Obviously, to determine the position of bromine is of prime importance. A possible approach is the oxidation of the above

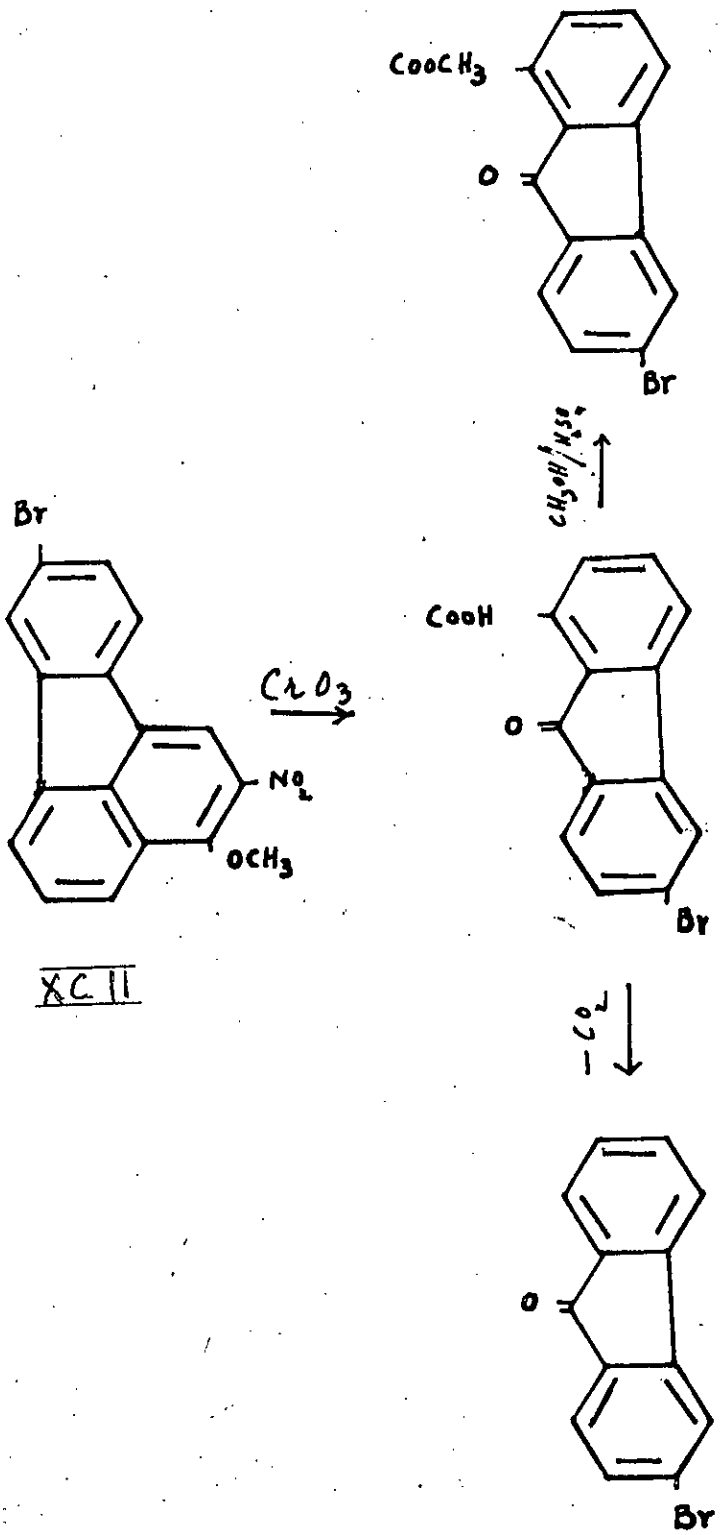

NH2
Br
NO2
NH·Co·CH3
Br
NO2
NH2
Br
NO2
OH
Br
methylation
oxidation
Br
NO2
OCH3
CrO3
Br
O
COOH
OCH3
NO2
-CO2
Br
O
OCH3
NO2
XCIV
Br
OCH3
Na2Cr2O7
Br
O
OCH3
HNO3
XCIII

fluoranthene derivative to the corresponding fluorenone with chromic anhydride. Campbell and Wilshire (100) who oxidised 1-nitro-fluoranthene obtained 4-nitrofluorenone-1-carboxylic acid. It was hoped that if bromination occurred at 8th position then analogous to the above results, the oxidation of this 8-bromo-3-methoxy-2-nitrofluoranthene would rupture the unsubstituted ring 'B' to give 7-bromo-2-methoxy-3-nitrofluorene-9-one-1-carboxylic acid. This on decarboxylation would yield 7-bromo-2-methoxy-3-nitrofluorenone.

The aforesaid fluoranthene derivative was oxidised with chromic anhydride which gave a substituted fluorenone-1-carboxylic acid in good yield. Owing to the low solubility of the product no N.M.R. spectrum could be obtained.

In order to establish the structure of the above decarboxylated fluorenone it was necessary to prepare 7-bromo-2-methoxy-3-nitrofluorenone. In an attempted short cut, 2-amino-7-bromofluorene (prepared for the main synthesis page 55) was acetylated, nitrated and hydrolysed to the corresponding 2-amino-7-bromo-3-nitrofluorene. It was hoped that with alkali the corresponding phenol (Nichol Thesis, page 23) would be obtained. However, when the reaction was carried out only tar formation was observed. This failure forced to adopt the other approach. 2-Methoxy-7-bromofluorene (prepared for the main synthesis page 55) was oxidised with sodium dichromate (101) to the corresponding ketone. This was nitrated with conc. HNO_3, most probably which yielded 7-bromo-2-methoxy-3-nitrofluorenone.

The analytical results of the oxidation product of bromo-3-



XCII

methoxy-2-nitrofluoranthene gave a surprise. No nitrogen was found which showed that the ring containing the methoxy and nitro groups in the fluoranthene (Ring A) had been ruptured. This was substantiated as the analytical figures were in good agreement with those required for 6-bromofluorene-9-one-1-carboxylic acid. For confirmation the methyl ester was prepared by refluxing with methanol containing 5% sulphuric acid (by weight). On recrystallisation from methanol, yellow needles m.p. 125°-127° were obtained. The N.M.R. spectrum showed only one methoxy peak at 6·0 . The integral ratio was 6 aromatic protons to 3 methyl protons. This is only possible if the compound in question has a structure of 6-bromo-1-carbomethoxy-9-fluorenone. The final proof was made, when a mixed m.p. with an authentic sample of 6-bromo-1-carbomethoxy-9-fluorenone m.p. 125° was found undepressed (m.p. 125°).

Further confirmation was made by the decarboxylation of 6-bromo-fluorene-9-one-1-carboxylic acid which gave the known 3-bromo-fluorenone. The m.p. was 160°-161°, and the mixed m.p. with 3-bromo-fluorenone (160°-162°) was undepressed. These experiments established that bromine atom had occupied the 8th position in fluoranthene and hence the product was 8-bromo-3-methoxy-2-nitro-fluoranthene.

The next step of the synthesis, reduction of the nitro-group by catalytic hydrogenation with Raney nickel as catalyst, gave an oil which could not be recrystallised. It was, therefore, converted into its acetyl derivative. The yield thus obtained was extremely poor, and the analysis revealed that bromine has been removed to a great extent. This hydrogenolysis has been reported by other workers. For instance, Busch et al. (102)

reported that when the substituted aromatic halogeno-compounds were treated with Raney nickel and hydrogen at room temperature, hydrogenolysis took place to variable extent in a number of compounds.

Weizmann (103) pointed out that the loss of halogen can be retarded by the use of non-polar solvents such as ethyl acetate, benzene or cyclohexane. So an experiment was made using platinum oxide as catalyst and ethyl-acetate as the solvent medium. Again, an oil was obtained which could not be recrystallised and hence was converted into the acetyl derivative. The analytical results for this were reasonable, but the yield was very poor. Charlesworth and Dolenko (47) presumably encountered the same difficulty in the reduction of 3-bromo-2-nitrofluoranthene. They failed to isolate the pure amine, and converted it to the acetyl derivative.

It has been stressed by other workers that groups like alkoxy, amino or carboxy in the aryl ring facilitate the dehalogenation of phenyl halide in catalytic reductions and the relative positions of the activating group to the departing halide has little effect on the amount of halogen lost (104). It is also said that this activation of the ring by an amino group explains the large amount of dehalogenation which occurs during the hydrogenation of halo-aryl-nitro, azo and hydazo compounds. So it might be probable, that in 8-bromo-3-methoxy-2-nitrofluoranthene during the process of reduction, both methoxy and the amino groups (formed during reduction) have their influence on the departure of halogen.

Attempts were made to increase the yield of the amine by avoiding the two wasteful steps (conversion into the acetyl derivative and then hydrolysis). In one case a picrate was formed which was decomposed by passing through a column of alumina. Although the amine was obtained in a solid state still it melted over a range (five to six degrees). As the yield was again poor, other methods of reduction were sought. It was found that for aryl-halo-nitro compounds most predominently metal/acid reduction has been used (105,106). In the event the amine was obtained in high yield by refluxing the compound with iron powder, ethanol, and acetic acid.

Once the amine was obtained the crucial step was deamination. Unfortunately this did not work. Two unsuccessful attempts for deamination were made. When the deamination was attempted following the direction of Charlesworth (45) only a black product was obtained which was insoluble in the usual solvents and did not melt up to 350°. In the second trial, the amine was diazotised and kept for four hours in ice-water. A diazonium salt separated out and was filtered. It appears that this easy isolation of diazonium salts is a characteristic feature of fluoranthene derivatives. However, no reaction took place when the salt was refluxed with methanol containing a little water for even eight hours.

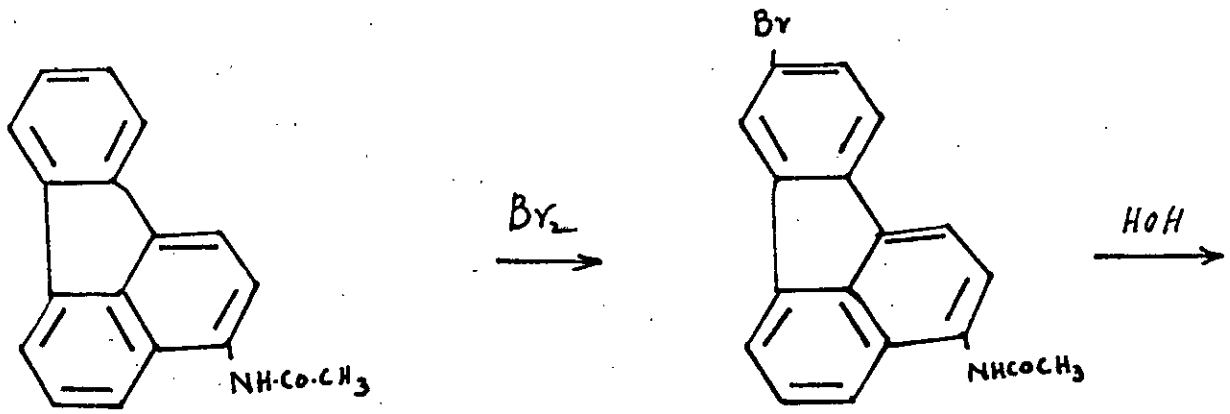
Part 4. Attempted preparation of 2:8-dibromo-3-methoxy-fluoranthene from 3-amino-8-bromo-fluoranthene.

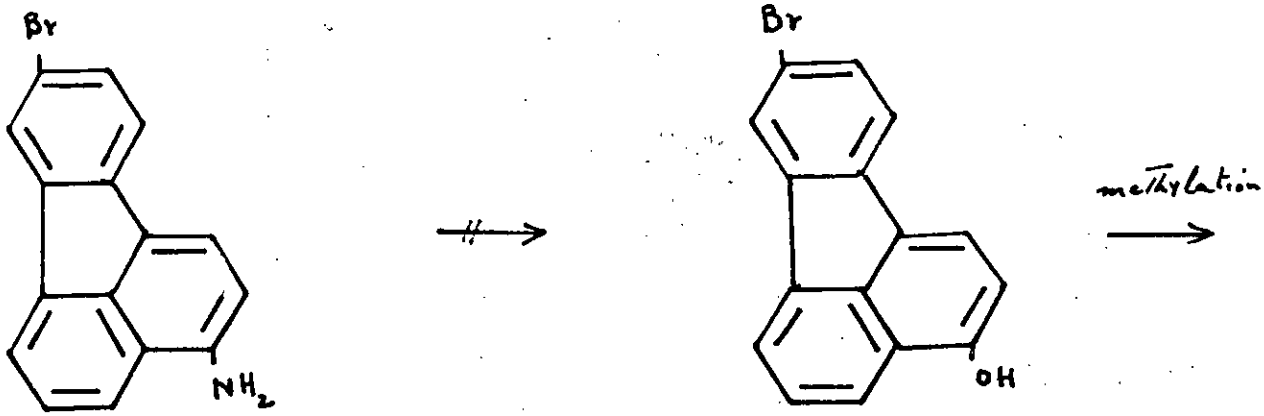
Frank Bell (107) reported an interesting observation. When he brominated 4-p-toluenesulphonamidodiphenyl in pyridine he obtained 3,5-dibromo-4-p-toluenesulphonamidodiphenyl, while in chloroform 3,4'-dibromo-4-p-toluenesulphonamidodiphenyl was formed.

Later in 1932, he reported (108) that the bromination of p-toluenesulphon-2-naphthalide in pyridine gave 1,3-dibromo-p-toluenesulphon-2-naphthalide while when chloroform was used as solvent 1,6-dibromo-p-toluenesulphon-2-naphthalide was obtained.

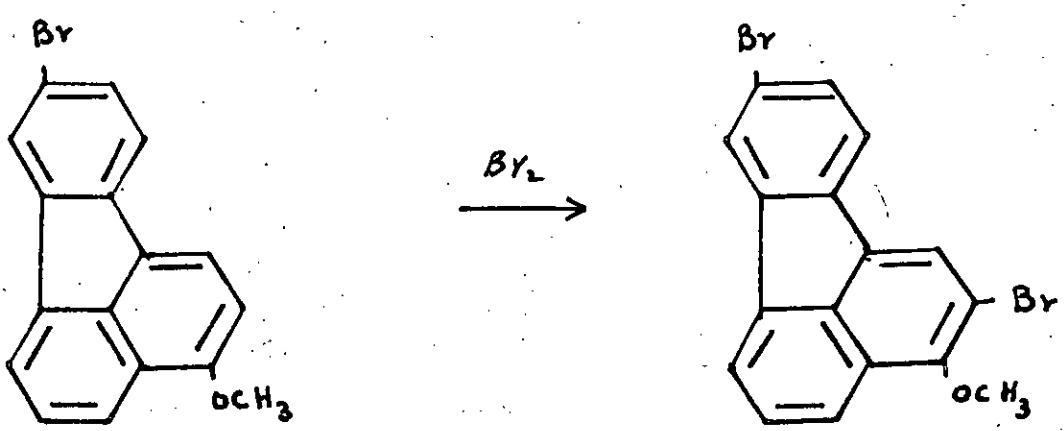
In fluorene, Bell and Mulholland (109) provide a most remarkable example. They reported that position of entry of bromine atom into 2-toluene-p-sulphonamidofluorene is largely governed by the choice of chloroform or pyridine as a solvent. With one molecular proportion of bromine in chloroform, there was produced a 60% yield of 7-bromo-2-toluenesulphonamido fluorene and impure 3-bromo-2-toluene-p-sulphonamidofluorene. With 2 molecular proportions of bromine in chloroform there was obtained a 70% yield of the 3,7-dibromo-derivative. While when pyridine was used as solvent, with 1 molecular proportion of bromine the main product was the 3-bromo-drivative. With 2-molecular proportions 1,3-dibromo-2-toluene-p-sulphonamidofluorene was obtained. A small amount of 1-bromo-2-toluene-p-sulphonamidofluorene was also present in the crude 3-bromo derivative, for on further bromination in chloroform it gave the 1-7-dibromo-derivative.

It is scarcely surprising that some similar results are


NH·Co·CH3
Br2
Br
NHCOCH3
HOH


Br
NH2
Br
OH
methylation

XCV


Br
OCH3
Br2
Br
Br
OCH3

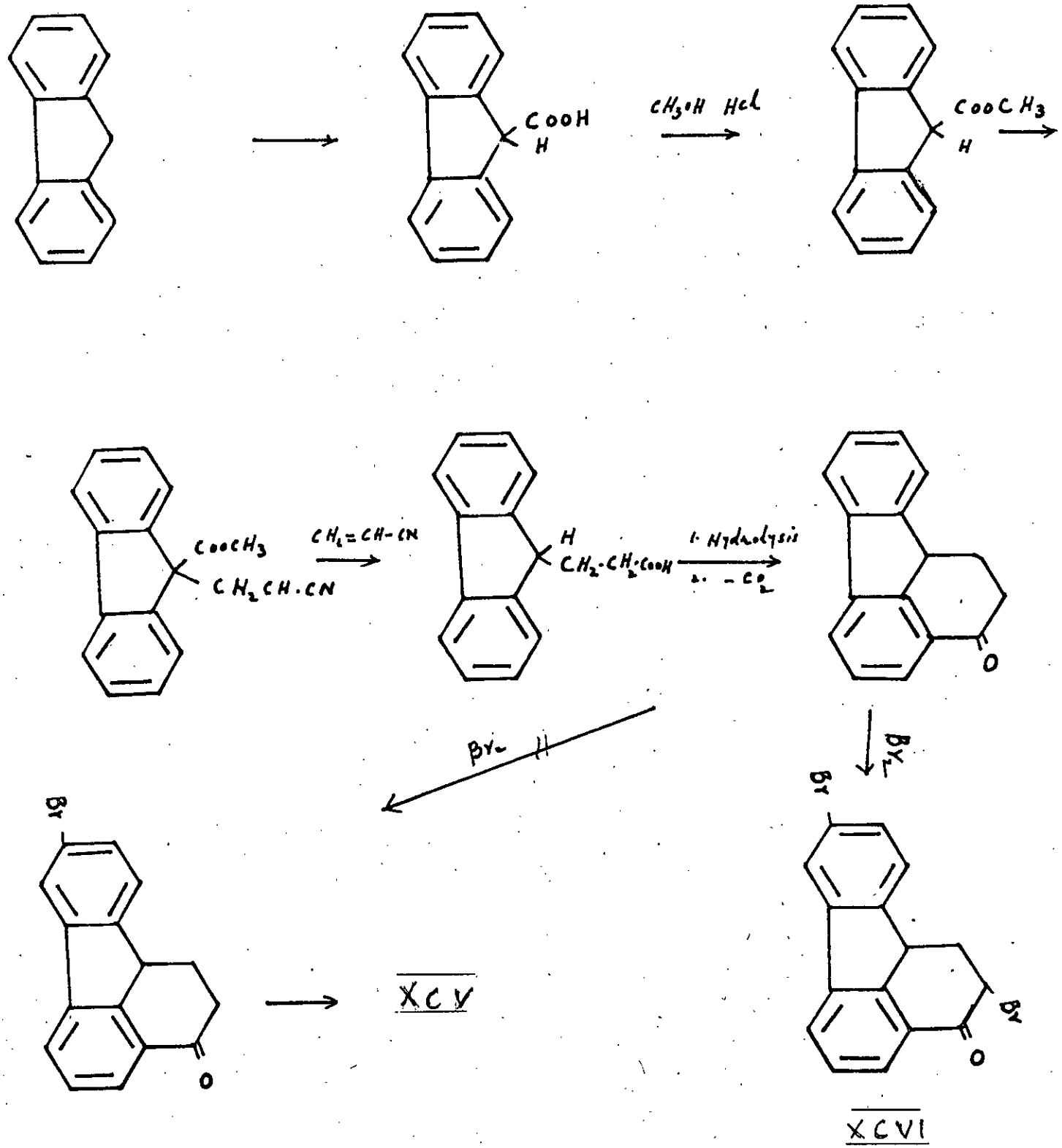
XC

observed in fluoranthene. Charlesworth (45) carried out bromination in pyridine of 3-acetylaminofluoranthene and obtained 2-bromo-3-acetaminofluoranthene. Later Barbara Kaminska (46) brominated 3-acetaminofluoranthene, however, in a mixture of CCl_4/CH_3COOH at room temperature and obtained 3-acetamino-8-bromo-fluoranthene.

Now, if the work of Barbara Kaminska could be repeated, it would provide another possible route for the preparation of 2,8-dibromo-3-methoxyfluoranthene.

When the bromination was carried out according to the conditions specified a mixture m.p. 210°-225° was obtained. However, when the reaction conditions were modified and bromination was done at 50° a product was obtained, which after recrystallisation from acetic acid and then from chlorobenzene gave a m.p. 265°-267°. The mixed m.p. with 3-acetamino-2-bromofluoranthene (m.p. 265-266°)was depressed (233°-237°). Bromine was analysed for mono-substitution and found in agreement with the calculated requirement. It was found more advantageous to remove the acetyl group by refluxing it with alkali in ethylene glycol. The reported m.p. of the amine was 186°. However in our case the amine melted at 178°-180° and repeated recrystallisation did not increase the m.p. The mixed m.p. of this amine with 3-amino-2-bromo-fluoranthene (m.p. 176°) was depressed (155°-160°). As a check, the amine was oxidised, which gave 6-bromo-fluorene-9-one-1-carboxylic acid, m.p. 248°. Mixed m.p. was undepressed with an authentic sample.

Unfortunately this approach also failed for the conversion of amine to the corresponding phenol was once again unsuccessful.


COOH
H
CH3OH HCl
COOCH3
H
COOCH3
CH2CH.CN
CH2=CH-CN
H
CH2-CH2-COOH
1. Hydrolysis
2. -CO2
O
Br2
Br
Br
O
Br2
Br
O

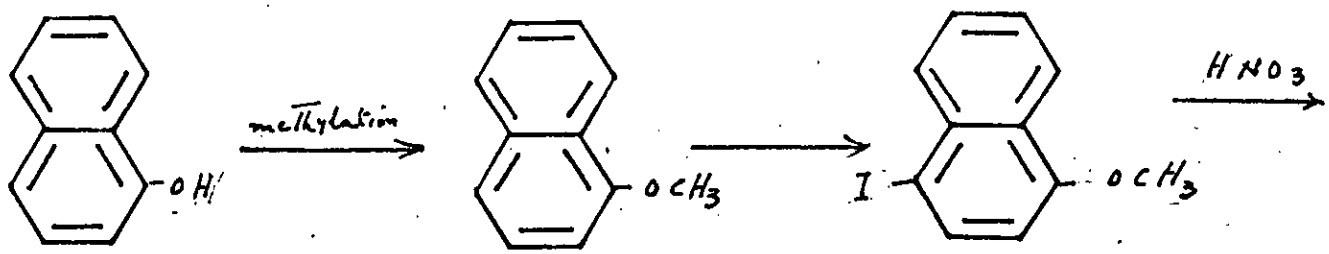
XCV

XCVI

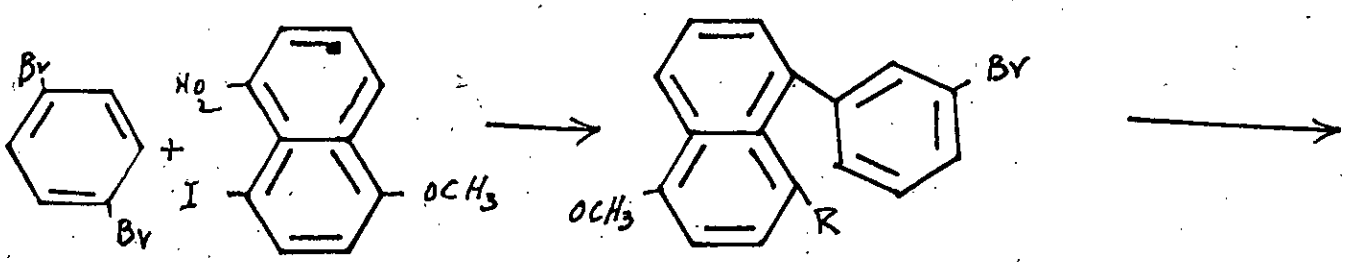
Part 5. Attempted preparation of 2:8-dibromo-8-methoxy-fluoranthene from 3-oxo-1:2:3:10b-tetrahydro-fluoranthene.

Craig (110) reported that bromination of 3-oxo-tetrahydro-fluoranthene with N.B.S. in CCl_4 gave only tar. This was confirmed but it was thought that bromination in acetic acid might give 8-bromo-3-keto-1:2:3:10b-tetrahydrofluoranthene which could be eventually converted to 2,8-dibromo-3-methoxy-fluoranthene by a known method.

3-Oxo-1:2:3:10b-tetrahydrofluoranthene was prepared in five steps from fluorene by following the method of Craig. However on bromination a dibromo product was obtained. As the yield was very poor this was not further investigated.

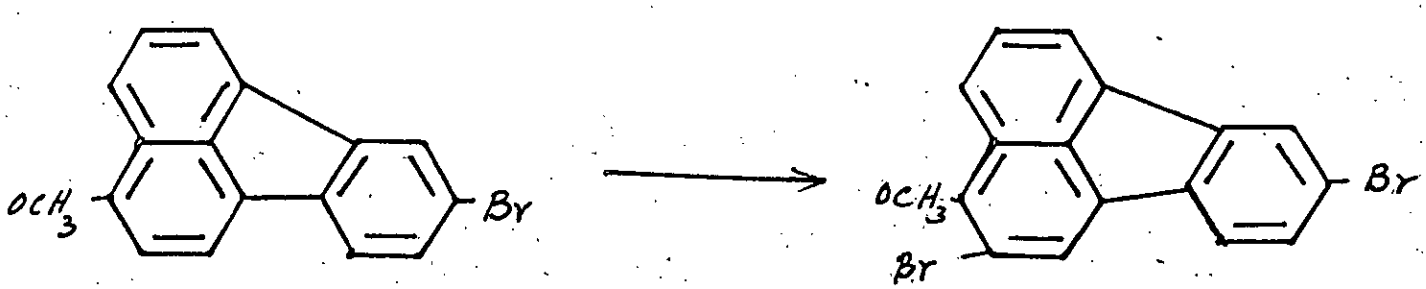


XCVII



R = NO_2

= NH_2



XC

Attempted synthesis of 2:8-dibromo-3-methoxy-fluoranthene from 1-iodo-4-methoxy-naphthalene.

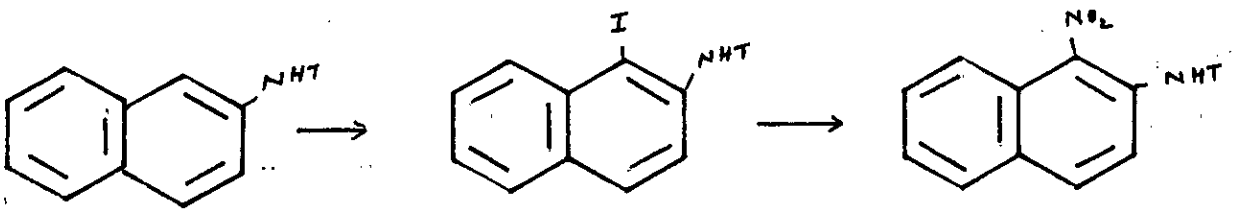
Reactivity of the 1-halogeno-nitro-naphthalene

As already mentioned in the introduction Tucker and his school (23,25,28) made use of suitable substituted iodonaphthalenes for the preparation of fluoranthene and substituted fluoranthenes. It was therefore decided to carry out analogous experiments according to the scheme given on the opposite page. However, the aim was not achieved as the nitration step took an unexpected course.

When 1-iodo-4-methoxy-naphthalene in acetic acid was nitrated with fuming nitric acid at room temperature a product m.p. 96-97°, was obtained. It was thought initially to be an iodo-methoxy-nitro-naphthalene derivative, but surprisingly, the analytical result revealed that no iodine was present. However, the analytical figures were quite in agreement with a methoxy-dinitronaphthalene, and the product was in fact 1-methoxy-2:4-dinitronaphthalene identical with the product prepared in 2 steps by the nitration of 1-methoxynaphthalene (111,112). The mixed melting point of these two products was found to be undepressed. Similarly on comparison, the I.R. and N.M.R. spectrums were found to be identical.

Examples of such liberation of iodine during nitration have been cited in the literature. For instance Meldola (113) reported the easy liberation of iodine when he attempted nitration of 2-hydroxy-4-iodonaphthalene. Similarly Hodgson and Moore, and Hodgson and Crook (114, 115) have also made the same observation

in their iodobenzene and iodonaphthalene derivatives. These products have generally, however, not been identified. Consden and Kenyon (116) appear to be notable exceptions. They prepared the 1-iodo derivative of p-toluensulphon-2-naphthalide which readily reacted with nitrous acid to give the 1-nitro-naphthalide.



This easy replacement of iodine by the nitro group determines the constitution of the product.

Moreover, it has long been established that halogen atoms in aromatic nuclei are no longer inactive if nitro groups are present in the ortho or para positions (relative to the halogen atom) and advantage is often taken of this property for preparation and identification purposes. For instance, 3,5-dinitrobenzoic acid is obtained from 2-chloro-3:5-dinitrobenzoic acid when the latter is heated with copper in phenol (117). Similarly Lesslie and Turner (118) reported that when a mixture of ethyl 2-chloro-3, 5-dinitrobenzoate and 1-iodo-tetrahydronaphthalene is heated at 200-220^{o} with copper bronze, ethyl 3,5-dinitrobenzoate is obtained as the main product. They interpreted their results by assuming that initially catalytic dehydrogenation of iodotetrahydronaphthalene

takes place in presence of copper with subsequent dechlorination of the ester. A somewhat similar reagent is employed by W.T. Smith jr. (119), who found that dehalogenation could be effected in aromatic halogeno-nitro compounds by heating with copper powder and benzoic acid at about 200°. In this way 1-chloro-2:4-dinitronaphthalene yielded 1:3-dinitronaphthalene (74%) while 2-chloro-3:5-dinitrotoluene gave 3:5-dinitrotoluene (83%) (120). It is quite possible that both nitro groups have exerted their influence and enhance the ease of dehalogenation, thereby giving a better result in these cases. Smith (120) also reported that with this reagent preferential removal of halogen could be effected, and showed that a chlorine or bromine ortho to a nitro group can be removed without the removal of chlorine or bromine located meta to the same nitro group. Thus 2:5-dibromo-1-nitro-benzene and 2:5-dichloro-1-nitrobenzene yielded m-bromo-nitro and m-chloro-nitro benzene respectively (38%).

Not unexpectedly, similar results are observed in the naphthalene series. Salkind (121) found that heating 1-bromo-4-nitronaphthalene with piperidine readily removed the halogen atom, and this method was used by Campbell and McLeish (122) and Campbell, Anderson and Gilmore (123) to obtain information about the fine structure of naphthalene.

The mobility of halogen due to the influence of nitro group is observed similarly in other less drastic methods. For example Blatt and Gross (124) used hydroiodic acid or hypophosphorous acid together or separately with picryl halide and obtained trinitro-benzene. Stannous chloride (125) has been used successfully in

obtaining dehalogenated products in various yield from a number of amino-bromo derivatives of naphthalene. The halogen in these cases was always ortho or para to an amino-group.

However, there are limitations of these methods. For instance Blatt and Gross (loc. cit.) reported the failure of their method when applied to 2:4-dinitro-iodobenzene. Similarly p-nitrobromobenzene remained intact when copper-benzoic acid mixture was used (120).

It was, therefore, thought desirable to obtain further information on the mobility of halogen in some halogeno-nitro-naphthalene compounds.

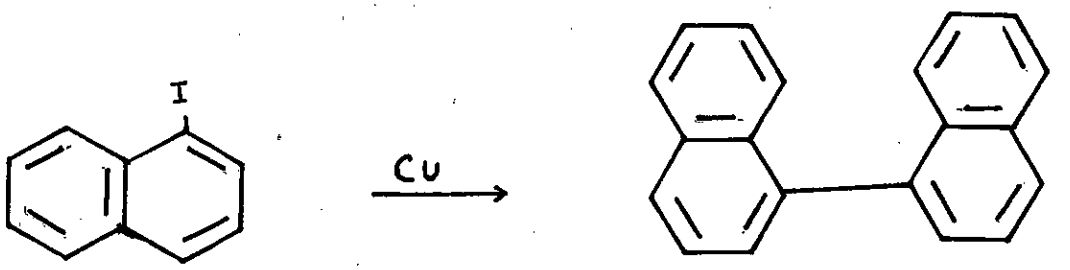
Bromination of naphthalene gave (126) 1,4-dibromonaphthalene, which when nitrated yielded 1:4-dibromo-5-nitronaphthalene (122). Dehalogenation with stannous chloride (125) proved to be a failure and an amine was formed. However, preferential dehalogenation was achieved when 1:4-dibromo-5-nitronaphthalene was heated with copper-benzoic acid mixture at about 210°, to give 1-bromo-5-nitro-naphthalene. This was characterised by an undepressed mixture m.p. with a sample prepared by the bromination of 1-nitronaphthalene (127). α-Bromo-naphthalene under similar conditions yielded no naphthalene. It is interesting to note that Salkind (121) also could not obtain any naphthalene even after heating 1-bromonaphth-alene with piperidine for 24 hours.

In another set of experiments α-naphthylamine was converted to phthalo-α-naphthylimide (128). After nitration and hydrolysis, 8-nitro-1-naphthylamine was separated from the corresponding 4- and 5- isomers, according to the method of Hodgson

and Ratcliffe (129). This was converted to 1-iodo-8-nitronaphthalene (115). In one case, 8-nitro-1-naphthylamine was prepared by the method of Morgan and Jones (130), but the overall results were not satisfactory.

1-Iodo-8-nitronaphthalene when heated with copper powder and benzoic acid as in the previous case, yielded 1-nitronaphthalene, which was again characterised by mixed m.p. with an authentic sample.

This activating influence of a nitro group situated in the ring not containing the halogen was less expected, although other examples are found in the literature. For instance 1-iodonaphthalene undergoes the Ullmann reaction with copper only at a high temperature to form 1-1'-dinaphthyl, whereas 1-iodo-8-nitronaphthalene gives the corresponding nitro-binaphthyl by merely boiling in nitrobenzene for $1\frac{1}{4}$ hours.



It is of course realized that the 8-position in naphthalene ring is sometimes regarded as 'ortho' to the 1-position, and the activation in consequence is perhaps not so surprising. On the other hand, the activating effect of a nitro group in the 5-position

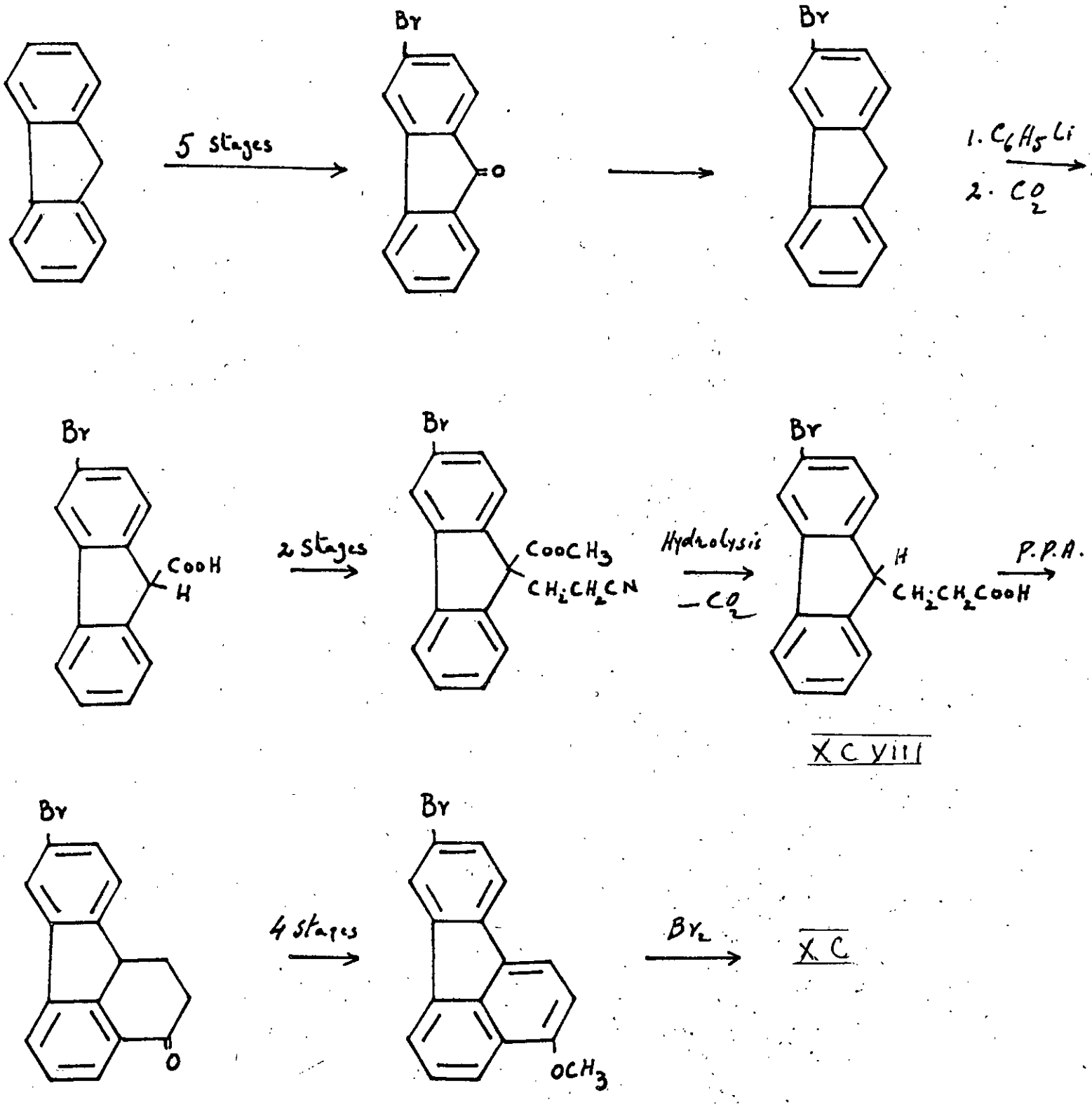
is less easily explained. This effect has been quite definitely established. Salkind (loc. cit.) for instance, found that 1-bromo-4:5-dinitronaphthalene exhibits greater reactivity towards piperidine than 1-bromo-4-nitro-naphthalene. Simonetta and Beltrame (131) measured the reactivity of various halogeno-compounds towards alkali and found that the 5-nitro group exerted a definite activating effect.

Now when each of the two isomers 1-bromo-4:8-dinitronaphthalene m.p. 141°, and 1-bromo-4:5-dinitronaphthalene m.p. 167° obtained by the nitration of 1-bromonaphthalene (132) was heated with copper-benzoic acid mixture, the expected results were achieved. 1-Bromo-4:8-dinitronaphthalene yielded 1:5-dinitronaphthalene and 1-bromo-4:5-dinitronaphthalene gave 1:8-dinitronaphthalene. Mixed melting points with the authentic purchased samples were undepressed. It may be pointed out that the structure of 1-bromo-4:8-dinitronaphthalene has never been rigidly established and its implicit acceptance rests on a statement in Beilstein's Handbuch der Organischen Chemie, v, 562. The above reaction provides a simple and unambiguous confirmation of the structure (133) of this compound. It is probable that in the above cases, the nitro groups located at the 5 and 8 position have also exerted their influence over the replacement of the halogen atom.

Bassilios et al. (134) reported that 1-chloronaphthalene with fuming nitric acid gave 1-chloro-4:5-dinitronaphthalene. From the mother liquor, they claimed to obtain 1-chloro-4:8-dinitronaphthalene in reasonable good yield. However, when this

experiment was repeated, the mother liquor gave a crude product m.p. 65-95°. It was found difficult, even after six recrystallisations to isolate the pure product. Another trial was made, by conducting the experiment at a slightly elevated temperature. The mother liquor again gave a mixture, and attempts to purify it by recrystallisation met with no success.

However 1-chloro-4:8-dinitronaphthalene was obtained in good yield by a two steps process. 1-Nitronaphthalene was converted to 1-chloro-8-nitronaphthalene (135), which on nitration gave 1-chloro-4:8-dinitronaphthalene. When 1-chloro-4:8-dinitronaphthalene was heated with sodium methoxide in methanol 1-methoxy-4:8-dinitronaphthalene was obtained.

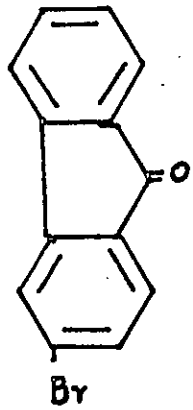

5 stages
Br
O
1. C_6H_5Li
2. CO_2
Br
COOH
H
2 stages
Br
$COOCH_3$
CH_2CH_2CN
Hydrolysis
$-CO_2$
Br
H
CH_2CH_2COOH
P.P.A.
XCVIII
Br
O
4 stages
Br
OCH_3
Br_2
XC

Part I: Synthesis of 2-8-dibromo-3-methoxy-fluoranthene from 3-bromo-fluorene nucleus

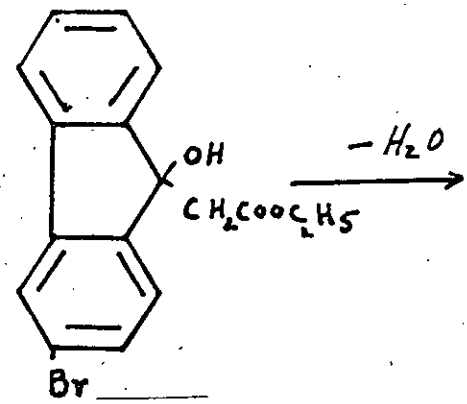
The failure of a synthetic route to 2,8-dibromo-3-methoxy-fluoranthene from the foregoing routes prompted an investigation of synthesis from the fluorene nucleus. It was thought that if 3-bromo-9-(2'-carboxyethyl)-fluorene could be prepared, this, on cyclisation, would provide a possible way for the required product. Hence attention was placed for introducing a suitable side chain to the substituted fluorene, and the scheme given on the opposite page was investigated.

Schultz (136) claimed to obtain 2-nitro-fluorenone by the direct nitration of fluorenone. When the work was repeated, the m.p. of the main product was found to be 290° (137) (which was probably 2,7-dinitrofluorenone). The mother liquor was poured into water and the precipitate recrystallised twice from the minimum quantity of glacial acetic acid. The product melted at 238°-240° (presumably it was 2,5-dinitrofluorenone m.p. 241°). The acetic acid filtrate from the above was distilled under vacuum. The crude product was dissolved in benzene and passed through a column of alumina. The fractions (2-4) were collected together and repeated recrystallisation from acetic acid gave a small amount of 2-nitrofluorenone (m.p. 218°-220°). The m.p. was undepressed with 2-nitrofluorenone prepared by other route.

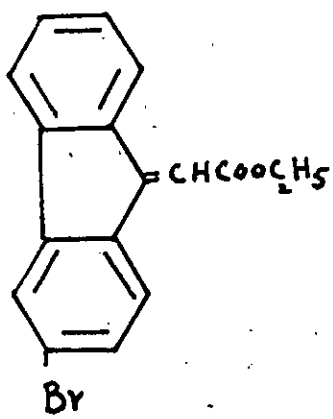
However, 2-nitro-fluorenone was obtained in high yield by a two step process. Fluorene was nitrated (138) and then oxidised (139). The conversion into the corresponding amine was found satisfactory by the method of Aecus and Coomb (74) as well as by



$BrCH_2COOC_2H_5$ →

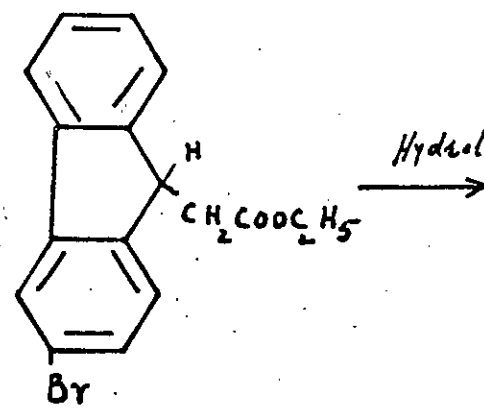


XCIX

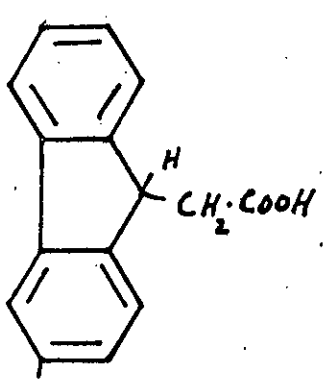


C

[H] →



CI



CII

Arndt-Eistert → XCVIII

Gray et al. (140) procedure. Bromination was effected by following the directions of Suzuki and Momoi (72). Although the yield claimed by them was never achieved, nevertheless 2-amino-3-bromofluorenone was obtained in fairly good yield. Deamination by their method gave the 3-bromo-fluorenone. This was converted to 3-bromo-fluorene in about 50% yield by refluxing it with hydrazine hydrate and glycol at 200°-210° without alkali (141). 3-Bromofluorenyl lithium, prepared by the exchange of phenyllithium, was added to a mixture of solid CO_2 and ether (142). The yield of the 3-bromo-fluorene-9-carboxylic acid was so variable by this process that it was thought more appropriate to seek other routes for the introduction of a side chain.

The Reformatsky reaction by the interaction of 3-bromo-fluorenone and ethyl bromo-acetate in the presence of zinc foil (143) (which was washed with 2% HCl, then water, alcohol, acetone and dried ether and then dried at 100° in a vacuum oven) and iodine gave 3-bromo-9-hydroxy (9'-ethyl acetate)-fluorene as a light brown oil. This hydroxy ester was dehydrated by refluxing with 98-100% formic acid for 45 minutes (144) and formic acid removed by blowing air through the hot solution. Extraction of the residue with light petroleum gave small yellow needles of ethyl 3-bromo-9-fluorylidene acetate. This was hydrolysed easily with alkali to 3-bromo-9-fluorenylidene-acetic acid.

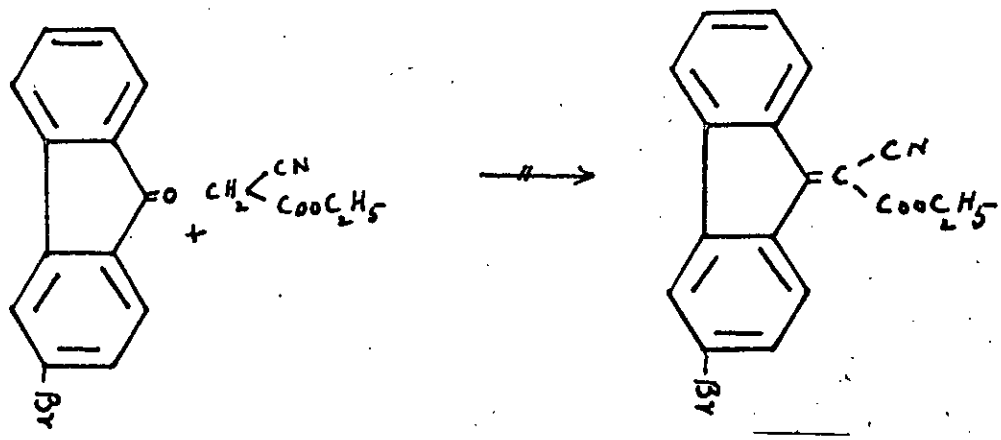
Saturation of the double bond of the ester before hydrolysis

to the corresponding saturated acid has been recommended (143). However, difficulties were faced when the saturation of the double bond was attempted with Raney nickel. Only an extremely small yield of an oil was obtained. Attempts to obtain a solid product by trituration with solvents met with no success. The above oil was hydrolysed with alkali with the hope of obtaining 3-bromo-9-fluorene-acetic acid, which might be more easily purified. Unfortunately this acid appeared to be a mixture with a wide range of melting point (100°-125°) and could not be purified. The yield also was low. It is probable that during reduction, hydrogenolysis took place to some extent, thus accounting for the low yield and mixture formation.

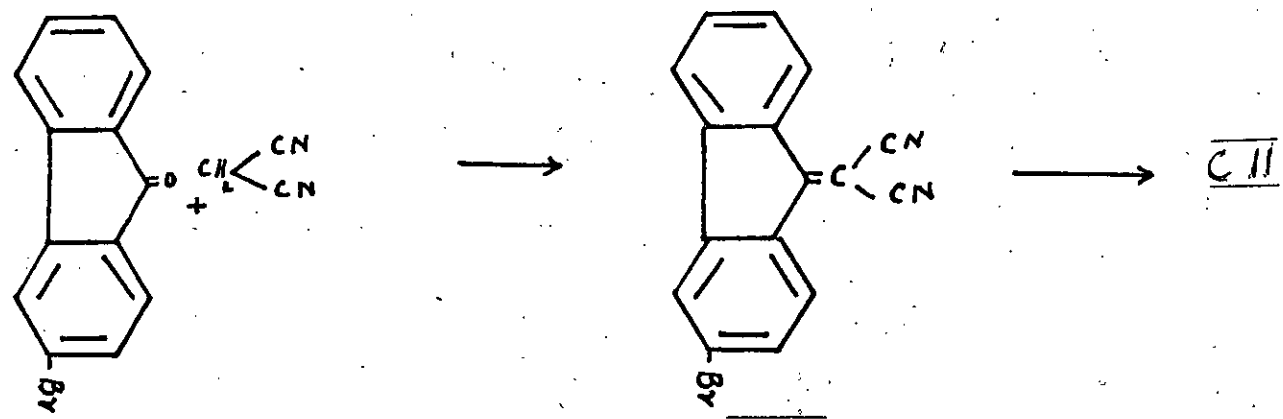
The failure of various attempts to increase the carbon chain by the Ardnt-Eistert reaction on 9-fluorenylidene-acetic acid has been reported (145) so it is most unlikely that an analogous reaction would work with 3-bromo-9-fluorenylidene-acetic acid. Hence no attempt was made in this direction. So this scheme was discarded.

Fluorenone when refluxed for 22 hours with ethyl cyano-acetate gave ethyl (9-fluorenylidene)-cyano-acetate in good yield (87%) (146). It was thought that 3-bromo-fluorenone would also behave in the same manner, and a scheme was outlined.

When the ketone was refluxed with ethyl cyano-acetate in benzene with ammonium acetate as catalyst, after 24 hours some



C III



C IV

C II

unreacted bromofluorenone along with intractable material was obtained. It has been pointed out that for less active ketones it is advisable to add a fresh and equal amount of catalyst once or twice to obtain a good yield. A repeat experiment was therefore made with the variation that after 24 hours a fresh and equal amount of catalyst was added portionwise and the period of heating was increased to 46 hours, but was unsuccessful.

Increasing the time to 66 hours with two additions of catalyst was likewise unsuccessful, and the method was abandoned. It has been pointed out by other workers that the general inertness of aryl ketones is increased by substitution and an increase in molecular weight.

Fluorenone on condensation with malononitrile gives 9-fluorenyl dicyanoethylene (147). As this reaction appears to be a promising one for the introduction of a side chain at 9-position, the scheme on the opposite page was outlined.

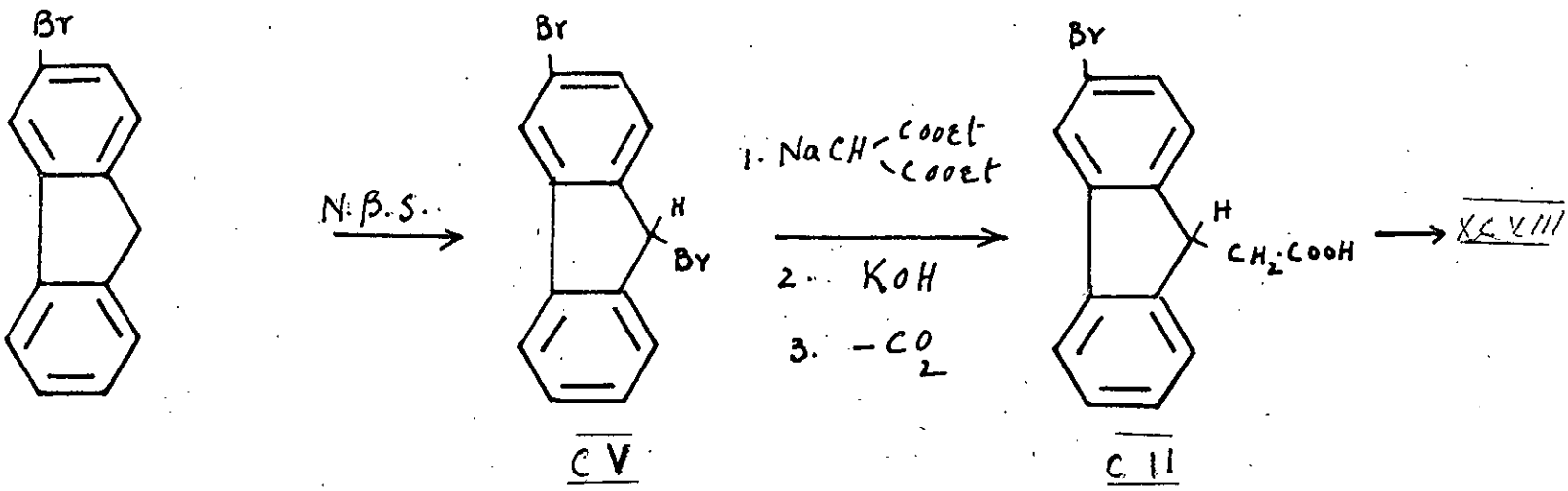
3-Bromo-fluorenone with malononitrile in the presence of diethylamine gave 3-bromo-9-fluorenyldicyanoethylene, in good yield, but hydrolysis of the product presented difficulties.

Acid hydrolysis with conc. HCl/ethanol and with sulphuric acid-acetic acid-water mixture in the ratio of 1:1:1 (by weight) gave the unchanged starting material, while with phosphoric acid, tar formation was observed. When alcoholic alkali was used, a light yellow impure product was obtained, which on recrystallisation was

found to be 3-bromofluorenone m.p. 158°-161° (mixed m.p. with 3-bromofluorenone 160°, and I.R. identical in both cases). It is of interest to note that Reid (148) in an attempted alkaline hydrolysis of 9-fluorenyldicyanoethylene also obtained impure fluorenone. Another case of this type of fission is reported by Campbell and Fairfull (14). They pointed out that during the alkaline hydrolysis of β-9-fluorenylidene-propionitrile, fluorene is formed.

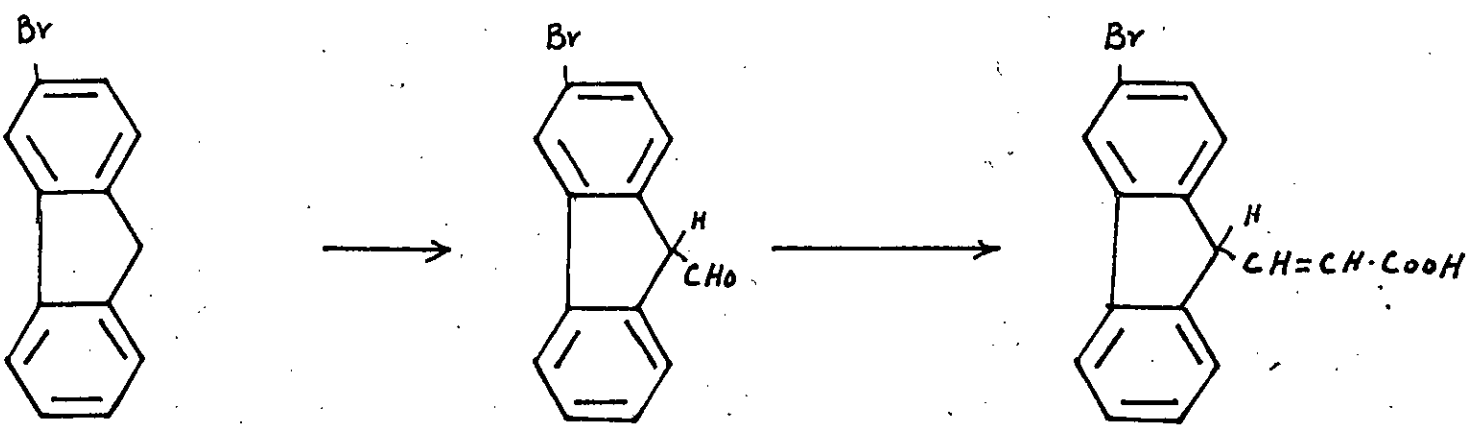
The hydrolysis was achieved, finally by the use of a mixture of hydriodic acid (sp. gr. 1·92) in glacial acetic acid. Reid (loc. cit.) who initially used this process of hydrolysis for 9-fluorenyldicyonoethylene obtained fluorene-9-acetic acid and suggested that during hydrolysis of the di-nitrile reduction and decarboxylation took place. The analysis figures for the product were in good agreement with those required for 3-bromo-fluorene-9-acetic acid. As the process was not very clean and the yield was not promising, the approach was abandoned.

3,9-Dibromo-fluorene was prepared in moderate yield by refluxing a solution of 3-bromo-fluorene in carbon tetrachloride with N.B.S. in the presence of benzoyl peroxide. It was hoped that this would condense with sodio-malonic ester, and the resulting product on hydrolysis and subsequent decarboxylation would yield 3-bromo-9-fluorene-acetic acid which by Arndt-Eistert reaction would be converted to β-(3-bromo-9-fluorenyl)-propionic



CV

CII



CVI

[H]

XCVII

acid. However, when the former reaction was carried out, the yield was very poor. This result is surprising since 9-bromo-fluorene under the same conditions reacted smoothly with sodio-malonic ester and gave an excellent yield (89%) of 9-fluorene acetic acid (149).

Von and Wagner (67) reported a yield of 90% of crude 9-formyl-fluorene by reacting fluorene with ethyl formate. If the reaction could be repeated with 3-bromo-fluorene, it would provide a useful method for the introduction of a suitable side chain at the 9-position and the ultimate preparation of β -(3-bromo-9-fluorenyl)-propionic acid.

3-Bromo-fluorene with ethyl formate under conditions described by Von and Wagner, gave a yellow oil. The I.R. spectrum indicated the presence of an aldehyde group ($1705\ cm^{-1}$), but no solid product could be obtained. It is of interest to point out that the isomeric 2-bromo-fluorene-9-aldehyde was also reported by Dr. Reid (150) as a yellow oil, which could not be solidified.

It was thought worthwhile to proceed to the next stage of condensation with malonic acid (151) in the hope of obtaining β -(3-bromo-9-fluorenyl)-acrylic acid. However, the synthesis broke down at this stage. An oil was obtained and various attempts to solidify it, including placing the oil in cold storage for three weeks gave only a few crystals. The amount was so small that only an analysis for carbon and hydrogen could be performed.

Dickinson and Eaborn (62) by refluxing a number of 2-substituted fluorenes with n-butyl-lithium and subsequent carboxylation obtained the corresponding 2-substituted fluorene-9-carboxylic acids, in excellent yield. However, when the process was carried out in case of 3-bromofluorene a very small amount of carboxylic acid was obtained by the acidification of the aqueous layer. The ether layer on evaporation gave a red oil, which was not further investigated.

The failure of all these attempts to obtain a promising route for the introduction of a side chain at the 9-position renders the first synthesis of 3-bromo-fluorene-9-carboxylic acid by the use of phenyl-lithium more valuable, and efforts were made to improve it. Fortunately success was achieved by passing carbon dioxide from a cylinder first through conc. sulphuric acid and then into an ethereal solution of 9-lithio-3-bromo-fluorene, for a few minutes. The reaction took place immediately as was observed by the change of colour. To ensure that the reaction was complete the gas was bubbled for 10-15 minutes. This process which was repeated several times always gave an average yield of 65-70%. the method is found simple, most promising and as will be seen later, applicable to other substituted fluorenes which were converted to the corresponding fluorene-9-carboxylic acids in fairly good yield. On the face it has an advantage where rather comparatively big quantities of material may be used for conversion

to the corresponding carboxylic acids. For it would be appropriate to mention that Delahunt used a 'bath process' for carbonating his 4-lithio-4H-cyclopenta-(def.)-phenanthrene and stressed that "otherwise addition of the ethereal solution of the above compound to a stirred mass of finely crushed solid carbon-dioxide resulted in greatly reduced yield of the corresponding acid." (152)

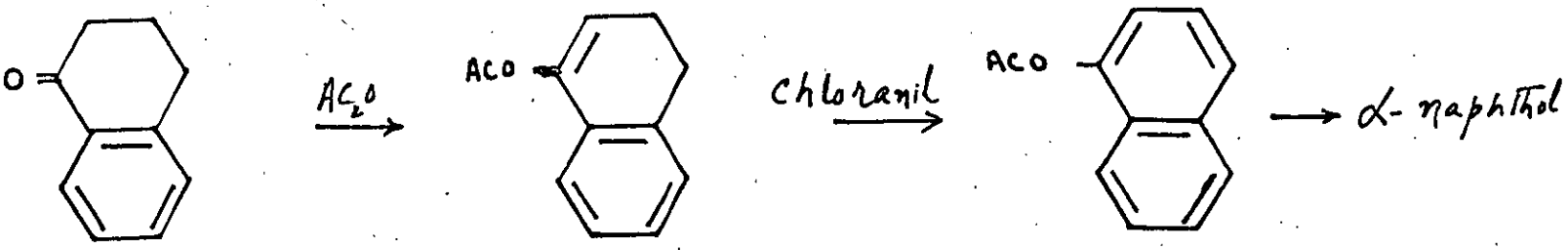
3-Bromo-9-carboxyfluorene was then converted into its methyl ester by following the method of Tucker (16). The next step was the condensation with acrylonitrile. It was found that condensation goes quite smoothly by the procedure of Campbell and Fairfull (14). Hydrolysis with alkali gave β -9-(3-bromo-fluorenyl)-propionic acid.

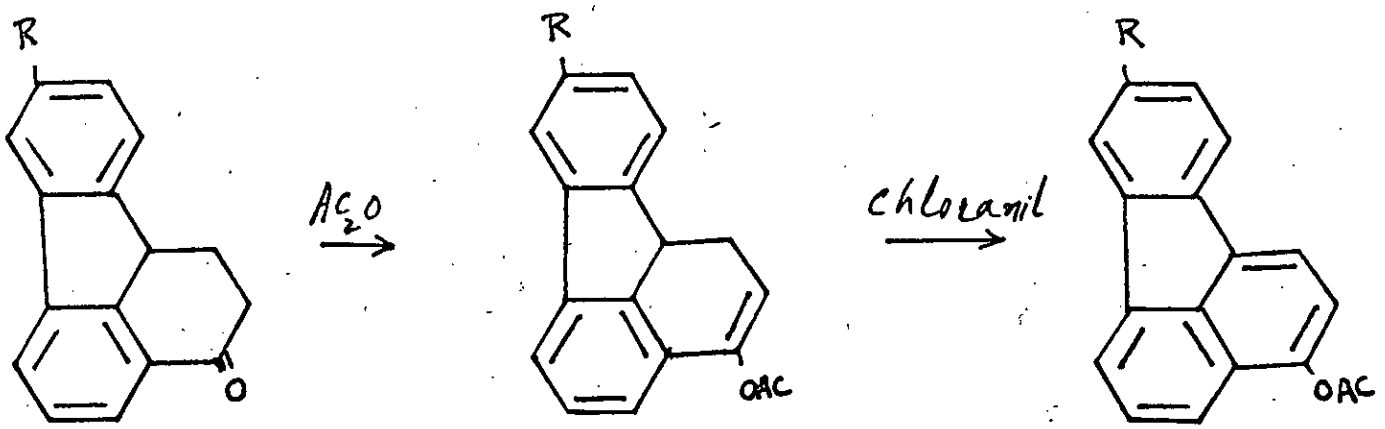
Cyclisation with HF gave a pure product but in poor yield, while with PPA the yield was better.

Possible routes for conversion of 8-bromo-3-keto,1:2:3:10b tetrahydro-fluoranthene to 8-bromo-3-hydroxy-fluoranthene were considered.

In steroid chemistry various methods have been used for the conversion of such ketones to a corresponding enol-acetate form. It was realised that subsequent aromatisation and hydrolysis would give a phenol.

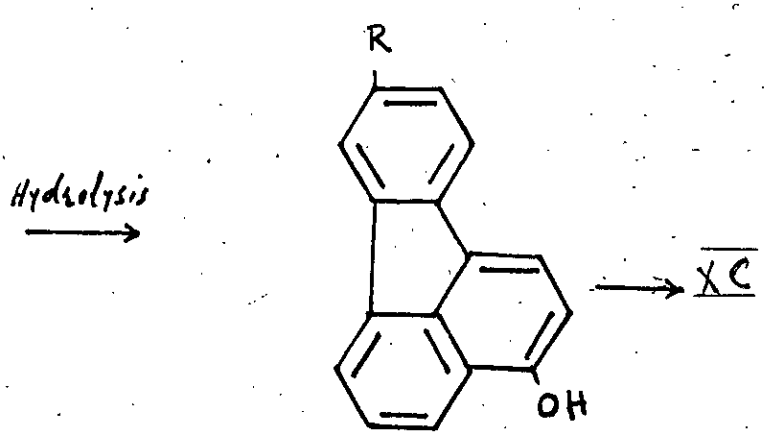
A simple and mild procedure is developed by Edwards et al. (153) using absolute ethyl acetate and perchloric acid. As a preliminary experiment, tetralone was subjected to the conditions specified by these workers. Although a number of attempts by using other methods (154, 155) and with modified conditions were





CVII

CVIII



XCV

R = H

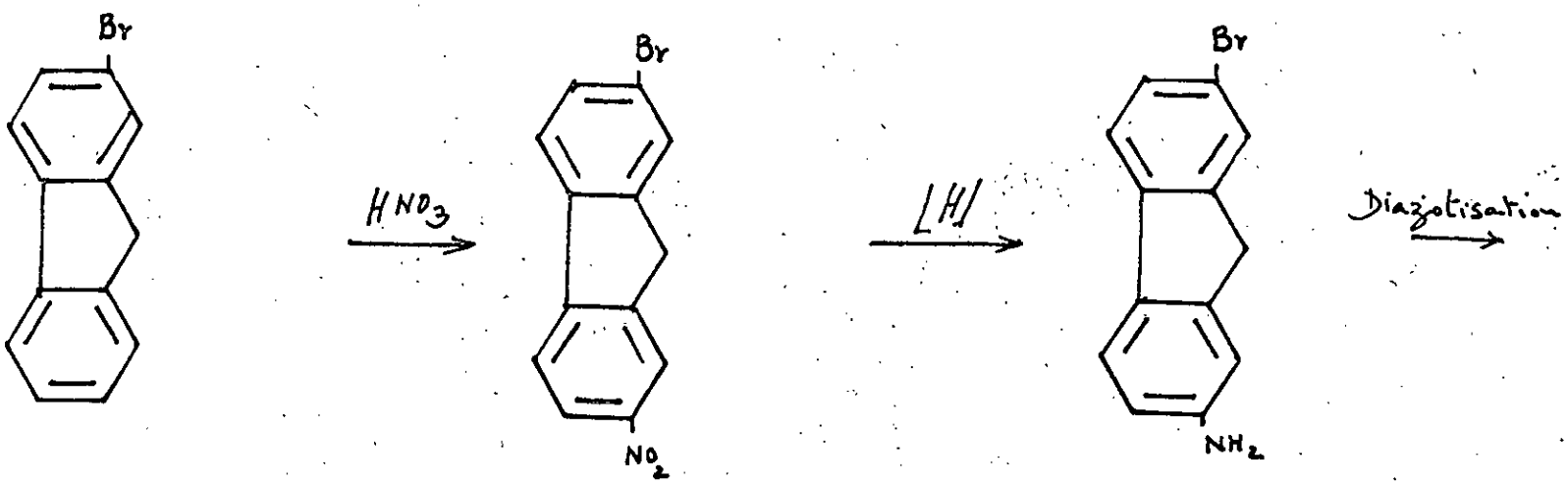
= Br

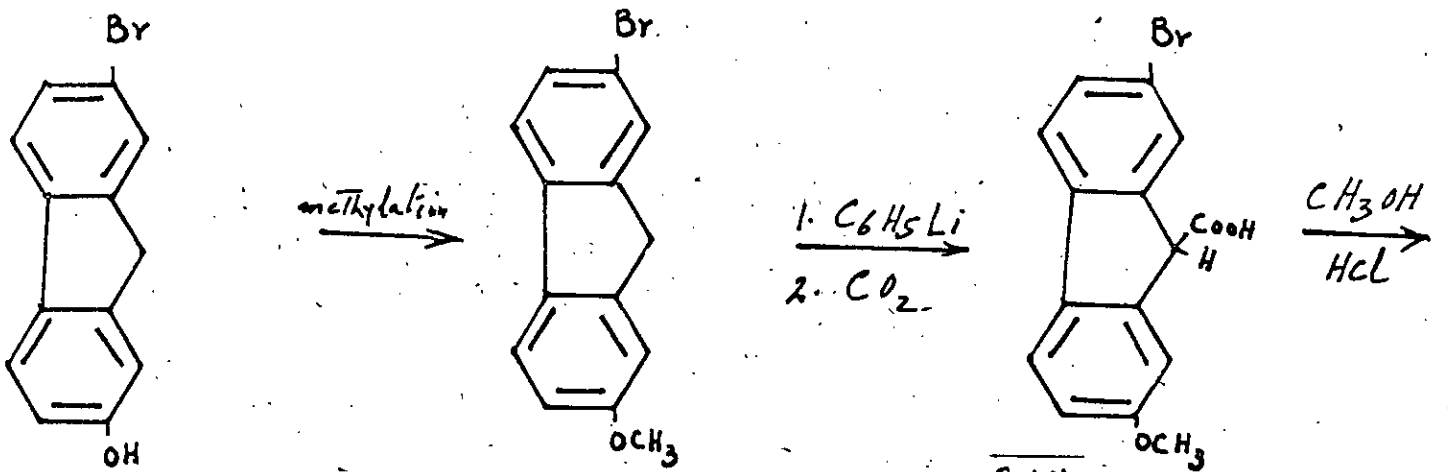
made, the product was always found to be predominantly the unchanged starting material. Better results were obtained under more vigorous conditions. Tetralone, acetic anhydride and toluene-p-sulphonic acid were heated under a short column and slowly distilled (156). From time to time, fresh quantities of acetic anhydride were added. The infra red spectrum (1760 cm^{-1}) supported the formation of enol-acetate as the characteristic enol-acetate bands (157) appeared along with the ketonic peaks already present. I.R. Spectrum and G.L.C. data suggested that about 30% unchanged ketone was still present. However, the mixture was refluxed with chloranil in sulphur free xylene and thus the aromatisation was achieved. This was subsequently hydrolysed, without any purification at this stage, to 1-naphthol.

Another prototype experiment with 3-keto-1:2:3:10b tetrahydrofluoranthene was carried out under similar conditions. The mixture was aromatised and subsequently hydrolysed to give 3-hydroxyfluoranthene. Next 8-bromo-3-keto-1:2:3:10b tetrahydrofluoranthene was treated similarly. The intensity of the carbonyl I.R. band indicated the presence of about 40% unchanged ketone. Still the strong characteristic peaks of enol-acetate were present at 1749 cm^{-1} and 1220 cm^{-1}. Aromatisation by refluxing with chloranil in sulphur-free xylene, and hydrolysis of the product with alkali gave 8-bromo-3-hydroxyfluoranthene. The phenol was refluxed with dimethyl sulphate and anhydrous potassium carbonate in chlorobenzene. After cooling the solution was diluted with ether, washed with dil. sodium hydroxide solution and water. After drying it was passed in benzene through a short column of alumina. A

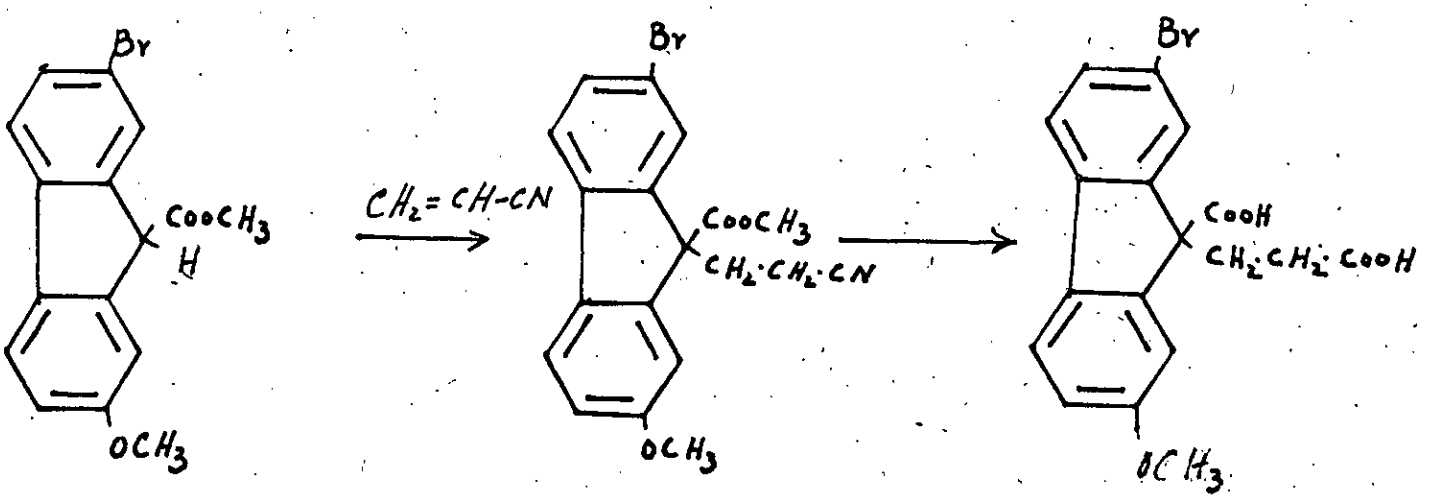
yellow band was eluted with benzene to give a light yellow product, crystallisation of which was not very successful, as it melted over a range of five degrees (m.p. 168°-173°).

A second successful preparation was made by a simpler route. Jarrett and Louden (158) obtained 3-hydroxy-1:2-benzofluorenone from 3:4:10:11-tetrahydro-3-oxo-1:2-benzofluorenone by refluxing it with nitrobenzene containing a crystal of iodine. The same procedure was adopted by Nichol (82) who successfully converted 9-nitro-3-oxo-1:2:3:10b-tetrahydrofluoranthene to 3-hydroxy-9-nitrofluoranthene. 8-Bromo-3-hydroxyfluoranthene was made by refluxing the 8-bromo-3-oxo-1:2:3:10b-tetrahydrofluoranthene in nitrobenzene with a crystal of iodine, followed by removal of the solvent by steam distillation. The product was dissolved in ether and extracted with aqueous alkali, subsequent acidification of which gave the required phenol. This was converted to its methyl ether with dimethylsulphate and anhydrous potassium carbonate with sulphur free xylene as solvent. The product was passed through a column of alumina and after evaporation of the solvent was recrystallised twice from acetic acid which gave light yellow needles of 8-bromo-3-methoxyfluoranthene m.p. 173°-175°. The bromination of this gave 2,8-dibromo-3-methoxyfluoranthene.





CIX



CX CXI CXII

Part II: Attempted synthesis of 2,8-dibromo-3-methoxyfluoranthene from 2-bromo-7-methoxyfluorene:-

The successful formation of 3-bromofluorene-9-carboxylic acid from 3-bromofluorene led to a fresh approach to the synthesis of 8-bromo-3-methoxyfluoranthene which on further bromination would yield the required 2,8-dibromo-3-methoxyfluoranthene. This synthesis from 2-bromo-7-methoxyfluorene would also confirm the results of the previous synthesis. In the event, however, difficulties were encountered at every stage of the synthesis.

Fluorene was brominated in chloroform (159) at 0°, to give 2-bromo-fluorene contaminated with 2,7-dibromofluorene. The former was separated by repeated recrystallisations from ethanol. The product was dissolved in glacial acetic acid and nitrated with conc. HNO_3.(2). Although Temple (160) obtained a 67% 2-bromo-7-nitrofluorene, in our case after two successive recrystallisations from glacial acetic acid only 45% was obtained. The conversion into the corresponding 7-amino-2-bromo-fluorene was done by following the method of Berkovic (161). Conversion into the phenol was effected by diazotising according to the method of Charlesworth (45). This method was successful, but was unsuitable for larger quantities due to the large volumes of acid required. Two other unsuccessful attempts at phenol formation were made. A survey of the literature revealed, however, that Weisburger (162) using smaller volumes of acid converted 2-amino-7-nitrofluorene into 2-hydroxy-7-nitrofluorene in excellent yield. This method with a slight modification gave 2-bromo-7-hydroxyfluorene, with a 'batch process' in 60% yield. The phenol was found to be only sparingly soluble in alkali. This was converted into the methyl ether by

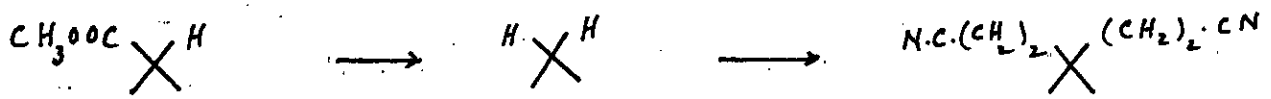
Br
H3COOC
CH2.CH2.CN
OCH3
Hydrolysis
− CO2
Br
H
CH2.CH2.COOH
OCH3
Cyclisation
Br
O
OCH3
NaBH4
Br
OH
OCH3
HCOOH
Br
OCH3
chloranil
Br
OCH3

the method described elsewhere (P. 75). The I.R. spectrum showed the methoxyl peak at 1290$^{cm^{-1}}$. Similarly the N.M.R. spectrum showed the singlet at 6·2τ (corresponding to the methoxyl group) Singlet at τ 6·35 (methylene protons at 9c) with the proton ratio 6 aromatic:3 methyl:2 methylene as expected. The conversion into the corresponding 2-bromo-7-methoxyfluorene-9-carboxylic acid was achieved via the lithium derivative, in 62% yield, the acid was converted into its methyl ester by suspending in methanol and passing in dried hydrogen chloride. The characteristic peaks of methoxyl and ester groups appeared at 1280$^{cm^{-1}}$ and 1715$^{cm^{-1}}$ respectively. The N.M.R. spectrum showed an aromatic multiplet at 2·25 - 3·2 τ and singlets at 5·25τ (C_9 - proton), 6·2τ (OCH_3) and 6·3τ ($COOCH_3$) with the proton ratio 6:1:3:3. This ester was dissolved in dioxan and condensed with acrylonitrile with benzyl trimethyl-ammonium hydroxide as catalyst at 40-45° to yield 2-bromo-7-methoxy-9-carbomethoxy-9-cyanoethylfluorene; m.p. 162°. Peaks in I.R. spectrum appeared at 1290$^{cm^{-1}}$, 1715 $^{cm^{-1}}$ and 2220$^{cm^{-1}}$ corresponding to methoxyl, ester and nitrile groups respectively. Likewise the N.M.R. showed singlets at 6·1 τ and 6·35 τ (methyl groups) and triplets of methylene protons at 7·0 - 7·4 τ and 8·2 to 8·55 τ with the ratio 1:1. The integral ratio of aromatic:methyl:methyl:methylene:methylene was 6:3:3:2:2 as expected.

Now in one experiment, where by chance a greater quantity of catalyst and excess of acrylonitrile were added under similar conditions at 40°, quite unexpectedly a product m.p. 218° was obtained. Thus the m.p. was 56° higher than that previously

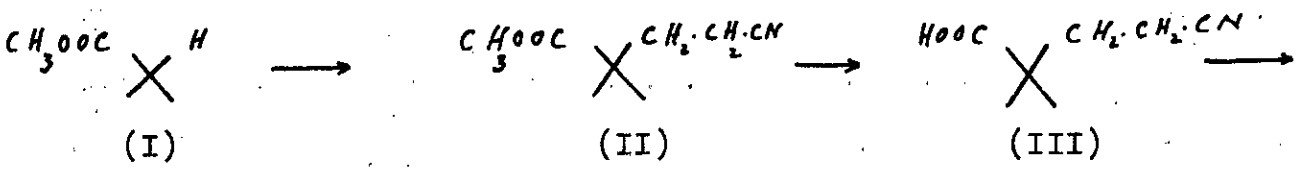
obtained. The infra-red spectrum showed peaks at 1290 cm^{-1} and a much stronger peak at 2240 cm^{-1} for methoxyl and nitrile groups respectively, but surprisingly there was no ester peak at 1715 cm^{-1}. Similarly the N.M.R. spectrum showed a singlet at 6·15 τ and triplets of methylene groups in two bands as before with the ratio 1:1 at 7·4 - 7·75 τ and 8·2 - 8·6 τ but there was no singlet at 6·3 τ corresponding to methoxy ester, as in the previous case. The proton ratio was 6:3:4:4. These results suggested that the product must be 2-bromo-7-methoxy-9,9-di-(2-cyanoethyl)-fluorene. This was confirmed by analysis and by hydrolysing the compound with a sulphuric acid-acetic acid-water mixture to the corresponding dicarboxylic acid.

In view of the mild conditions employed the result was unexpected and it was thought profitable to carry out other experiments. Under the same conditions methyl fluorene-9-carboxylate yielded 9,9-di-(2-cyanoethyl)-fluorene, as did 9-carbomethoxy-9-(2-cyanoethyl)-fluorene. It is clear that under the influence of the catalyst at 40° three reactions occur: hydrolysis of the ester, decarboxylation of the resulting carboxylic acid, and condensation with vinyl cyanide. Similar observations have been made by previous workers. For example. A. Campbell and H.S. Tucker (15) on two occasions obtained 9,9-di-2-carboxyethylfluorene, no attempt being made to isolate the intermediate dinitrile. They thought that the methyl fluorene-9-carboxylate had failed to react with the vinyl cyanide and initially underwent hydrolysis and decarboxylation to give fluorene, which then reacted to give

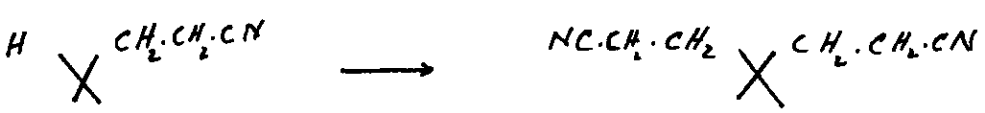


the dinitrile. Andrew (163) obtained similar results with methyl 3-bromo-(chloro)-fluorene-9-carboxylate and came to the same conclusion as Campbell and Tucker.

It is difficult to see, however, why methyl esters with the very reactive C_9 hydrogen atom should not react with vinyl cyanide and our results, while not precluding Tucker's mechanism, suggest a possible if not probable alternative, namely:-



(I) (II) (III)



(IV) (V)

This is confirmed by three observations.

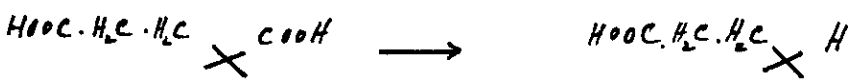
(1) When the ester (I) with a molecular quantity of vinyl cyanide was treated with Triton B (0·1 ml.) in dioxan (2·5 ml.) the ester-nitrile (II) resulted.

(2) When the experiment was repeated with Triton B (1·0 ml.) in dioxan (2·5 ml.) the dinitrile (V) resulted, probably through the intermediate (IV).

(3) The same results as in (2) were obtained with methyl 2-bromo-7-methoxy-fluorene-9-carboxylate.

Further work on the mechanism of the reaction is obviously required, but from the practical point of view it is essential not to use too much catalyst or excess vinyl cyanide.

The next stage in the main synthesis involved the hydrolysis and decarboxylation of 2-bromo-7-methoxy-9-carbomethoxy-9-cyanoethylfluorene and this also proved to be far from simple. Hydrolysis with acetic acid-sulphuric acid-water mixture (2:1:1 by weight) gave 2-bromo-7-methoxy-9-carboxyethylfluorene-9-carboxylic acid (VI). When this was heated with sodium hydroxide in methanol an oil was obtained. Attempts to decarboxylate the 9-carboxylic acid group of (VI) by heating with sodium carbonate or sodium bicarbonate solution did not meet with success.

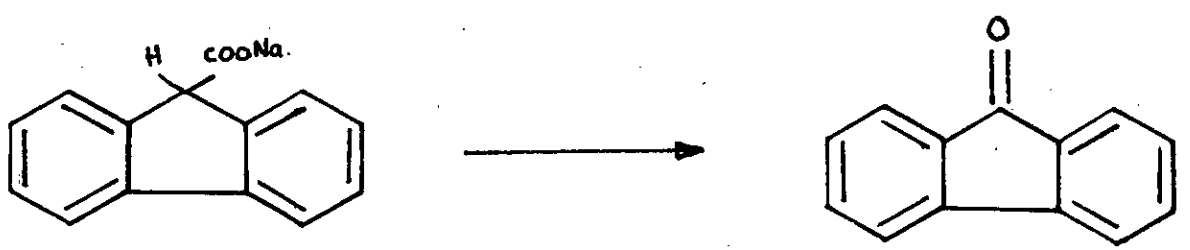


(VI) (VII)

The desired acid VII was obtained by heating the di-acid VI in pyridine with a trace of copper, but the reaction was not clean and the yield was poor. When hydrolysis was carried out with potassium hydroxide in 2-methoxyethanol good yields of the acid VII were obtained after many unsuccessful attempts, but only if the reaction was carried out in an atmosphere of nitrogen. Without this precautionary step, oils were invariably obtained presumably as the result of autoxidation at C_9.

As this observation was interesting a few experiments were carried out. The 9-carboxylic acids of fluorene, 2-methoxy-fluorene, 3-bromo-fluorene, and 2-bromo-7-methoxyfluorene with Triton B at 45° reacted to yield the corresponding fluorenones. Fluorene itself underwent no change. When the carboxylic acids were treated as above but in an atmosphere of nitrogen unchanged acids were recovered in good yield. It seems clear that fluorene-9-carboxylic acids in alkaline solution undergo autoxidation and subsequent decarboxylation.

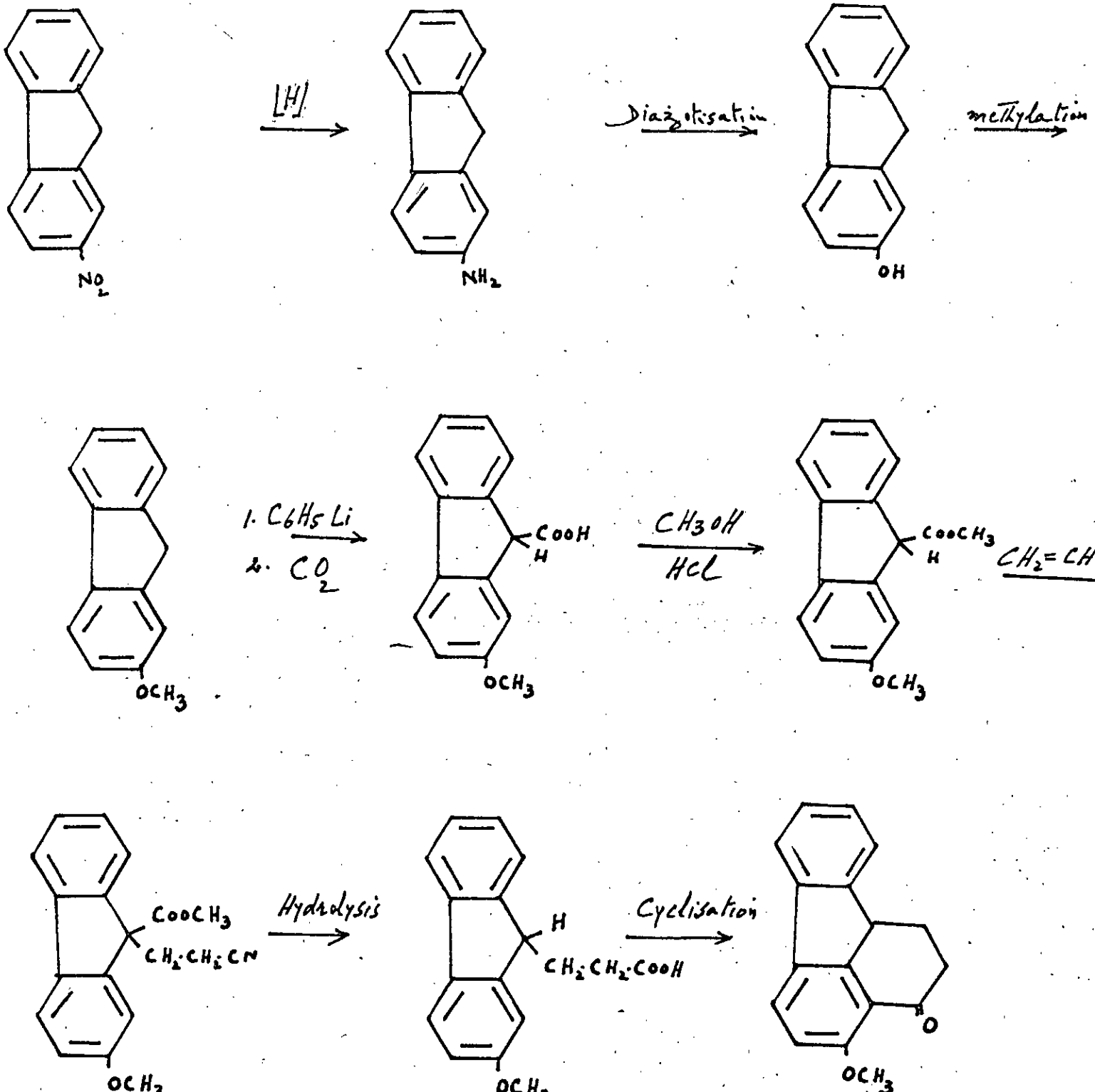
It is of interest that Wislicenus and Ruthing (164) observed the formation of fluorenone from the sodium salt of fluorene-9-carboxylic acid



and pointed out that in an atmosphere of hydrogen, the sodium salt was not attacked. Further interesting results were obtained by Sprinzak (165) who reported that fluorene and some of its derivatives with Triton B in pyridine and in an atmosphere of oxygen gave the corresponding fluorenones, and suggested that the reaction proceeded through hydroperoxide formation. It is probable that in our examples the reaction took a similar path. The inertness of fluorene was not surprising. As Sprinzak has already mentioned that when fluorene was treated in pyridine with Triton B in a flask where only side necks were open to atmospheric air, the reaction was very slow. It must be emphasised that these experiments can only be regarded as preliminary and much more work would obviously be needed before any generalisation could be made. It is equally certain that many of our abortive experiments were results of failure to realise the ease with which autoxidation could occur at the 9-position of the fluorene molecule.

In this present synthesis, difficulties continued to occur at each stage and the next step of cyclisation of 2-bromo-7-methoxy-9-(2-carboxyethyl)-fluorene to 4-methoxy-9-bromo,1,2,3,10b tetrahydro-3-oxo-fluoranthene was at first unsuccessful. The cyclisation of the acid with PPA did not work. One attempt was made by heating the acid at 160° for 20 minutes. A product of indefinite m.p. was obtained, while when the acid was heated at 100°, starting material was recovered. This result was surprising as cyclisation of 3-bromo-9-(2-carboxyethyl)-fluorene with PPA was successful.

A survey of the literature revealed that so far no methoxy


NO2
[H]
NH2
Diazotisation
OH
methylation
OCH3
1. C6H5Li
2. CO2
COOH
H
OCH3
CH3OH
HCl
COOCH3
H
OCH3
CH2=CH-CN
COOCH3
CH2·CH2·CN
OCH3
Hydrolysis
H
CH2·CH2·COOH
OCH3
Cyclisation
O
OCH3

substituted 9-(2-carboxyethyl)-fluorene has been cyclised. To obtain the best reaction conditions for cyclisation, it was thought essential to prepare 2-methoxy-9-(2-carboxyethyl)-fluorene the cyclisation of which would serve as a prototype.

2-Hydroxy-fluorene was obtained in 52% yield by the method used in the previous case (Page 124). It may be mentioned that Gray et al. (140) obtained a yield of 45% of 2-hydroxy-fluorene from the amine. The phenol was converted to 2-methoxy-fluorene and yielded via the lithium derivative 2-methoxy-fluorene-9-carboxylic acid in 50%. This was converted to the methyl ester. Condensation with acrylonitrile in dioxan with benzyl-trimethyl ammonium hydroxide as catalyst gave the corresponding ester-nitrile. This was hydrolysed and decarboxylated with 10N KOH in 2-methoxy-ethanol under an atmosphere of nitrogen to the corresponding 2-methoxy-9-(2-carboxyethyl)-fluorene.

When the hydrolysis was attempted by sulphuric acid-acetic acid-water mixture a product m.p. 194-197° was obtained, which could not be recrystallised. It was thought to be a mixture of di-acid and mono-acid, but when it was further refluxed for eight hours decomposition was observed.

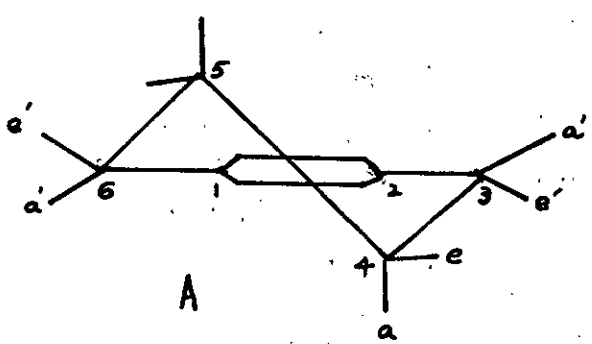
2-Methoxy-(9'-carboxyethyl)-fluorene with PPA at 160° gave a product of indefinite m.p. Presumably the conditions were too harsh. It was noted that Bachmann and Thomas (166) cyclised γ-m-anisylbutyric acid to 6-methoxy-1-Keto-1,2,3,4-tetrahydro-naphthalene under very mild conditions, with stannic chloride. The method was successfully applied to the methoxyfluorenyl-propionic acid to give a 25% yield of 4-methoxy-3-oxo-1,2,3,10b-

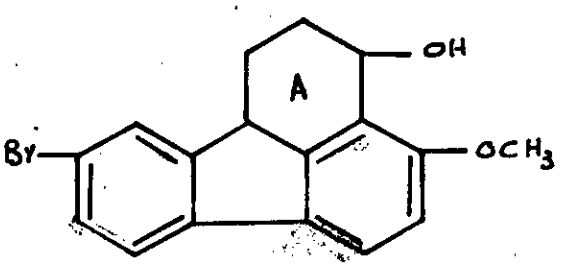
tetrahydrofluoranthene. In similar fashion 9-bromo-4-methoxy-3-oxo-1,2,3,10b-tetrahydrofluoranthene was obtained.

With sodium borohydride the ketone was converted to the corresponding alcohol. To achieve dehydration it was heated at 100° on a steam bath with 98% formic acid. The product was dehydrogenated without any purification. The dehydrogenation was done by heating the di-hydro-derivative with chloranil in sulphur free xylene. Unfortunately the product was not pure and was contaminated with some high melting substance.

It is most probable that contamination of the impurity took place at the dehydration step. This inference may be deduced, if the stereochemical nature of the molecule is considered.

The model of the cyclised ketone showed that the hydrogen





atoms at 4 and 5 occupy normal equatorial (e) and axial (a) positions and are normally staggered, but those attached to

atoms 3 and 6 are imperfectly staggered and are pseudoequatorial (e') and pseudoaxial (a').

Further it is known that:

1. In most cases of metal hydride reduction of ketones the more stable equatorial alcohol predominates (167).

2. Dehydration of cyclic alcohols is favoured when the groups are in trans axial positions.

3. The esterification of equatorial alcohols takes place more readily than that of axial alcohols (168).

With these observations in mind it is probable that the reduction of 9-bromo-4-methoxy-3-oxo-1,2,3,10b-tetrahydrofluoranthene yielded predominantly the pseudoequatorial form of the alcohol, 9-bromo-3-hydroxy-4-methoxy-1,2,3,10b-tetrahydrofluoranthene. Now as all the above factors in such a case favour esterification more than dehydration, it is probable that with formic acid both dehydration and esterification took place. It may be of interest to point out that Delahunt (169) has also reported the formation of formyl ester when he treated 1-methyl-3-hydroxy-1, 2,3,10b-tetrahydrofluoranthene with formic acid. Moreover our assumption of possible esterification is further strengthened by the presence of a weak carbonyl peak in the spectrum of 8-bromo-3-methoxy-fluoranthene. It is therefore not surprising that dehydrogenation yielded an intractable product.

Throughout this synthesis it appeared that the methoxyl group has some influence which has created complications and difficulties,

as in the unsubstituted fluoranthene no such complications have been observed.

It is hoped that a repeat experiment on the cyclised ketone by Clemmensen reduction and dehydrogenation will yield 8-bromo-3-methoxy-fluoranthene.

E X P E R I M E N T A L

EXPERIMENTAL

1. Melting points were determined on a Kofler micromelting-point apparatus with a calibrated thermometer, and fitted with a polariser.

2. Infrared spectra (IR) were recorded on a Perkin-Elmer "Infracord". In the IR data given, the wave numbers of absorption maxima are expressed in cm^{-1}, the corresponding group being in parenthesis.

3. Nuclear magnetic resonance spectra (NMR) were recorded on a Perkin-Elmer R10 (60 m/c) instrument.

4. Alumina was of Type-H as supplied by Peter Spence and Sons, Widnes.

5. Light petroleum refers to that b.p. 60-80°, unless otherwise stated.

6. Analyses were carried out by Drs. Weiler and Strauss, Oxford: or A.H. Baird, Ltd., Edinburgh.

3-Nitro-fluoranthene:-

This was prepared by the method of Garascia, Fries and Ching. Fluoranthene (20 gm.) gave 3-nitro-fluoranthene (11·0 gm.).

m.p. 159 - 162°.

3-Amino-fluoranthene:-

Kloetzel, King and Meekes, J.A.C.S. 78, 1165.

Raney nickel (2 gm.) was used in place of platinum oxide. 11·0 gm. of 3-nitro-fluoranthene gave 5·2 gm. of 3-aminofluoranthene.

m.p. 116°.

I.R. Spectrum: $3310^{cm^{-1}}$ (w), $3390^{cm^{-1}}$ (w) (NH_2) Nujol.

3-Acetaminofluoranthene:-

Kloetzel et al. loc.cit.

3-Aminofluoranthene (5 gm.) gave 3-acetaminofluoranthene (5·4 gm.)

m.p. 244 - 245°.

3-Acetamino-2-bromofluoranthene:-

Charlesworth and Blackburn, C.J.C. 42, 353.

3-Acetaminofluoranthene (15 gm.) gave 3-acetamino-2-bromofluoranthene (10 gm.).

m.p. 265 - 266° (decomposed)

3-Amino-2-bromofluoranthene:-

Charlesworth and Blackburn loc.cit.

3-Acetamino-2-bromofluoranthene (10 gm.) gave 3-amino-2-

bromofluoranthene.

m.p. 176 - 177°.

I.R. Spectrum: 3315$^{cm^{-1}}$ (w), 3400$^{cm^{-1}}$ (NH_2) Nujol.

Attempted preparation of 2-bromo-3-hydroxy-fluoranthene
(First method)

(1) The diazotisation was attempted by following the method of Hodgson and Walker, J.C.S. 1933, 1620. 3-Amino-2-bromofluoranthene (1·0 gm.) was heated with glacial acetic acid (25 ml.), but was only sparingly soluble. The suspension after cooling was added to a stirred solution of nitrosyl-sulphuric acid, prepared from 7 c.c. of H_2SO_4 and 1·0 gm. of sodium nitrite and treated according to the directions of Hodgson and Walker. However no clear solution was obtained.

(2) Nitrosyl-sulphuric acid was prepared by adding sodium nitrite (0·8 gm.) in small portions to a stirred, ice cold mixture of sulphuric acid (8 c.c.) and water (4 c.c.), and warming the mixture on a water bath to about 40° until a clear solution resulted. To this well stirred solution which was cooled with ice and salt to 0° was added (10 minutes) a solution of 1 gm. of the amine in 5·2 c.c. of pyridine. The temperature of the mixture was maintained at 0°. The mixture was stirred for an additional hour at 0° and diluted with ice and water to a volume of about 50 ml. An aqueous solution of 0·2 gm. of urea was added and stirring was continued for another hour at 0°. The cold diazonium solution was filtered from the orange scum which

had formed, and was poured in a thin stream to 200 ml. of boiling water. Heating was continued for another half hour. Cooling deposited no phenol and the solution remained orange red in colour.

(3) 3-Amino2-bromo-fluoranthene (1·0 gm.) was heated to 60° in acetic acid (15 ml.) and 10N sulphuric acid (4 ml.) was added dropwise with stirring. It was cooled to 8° and diazotised with sodium nitrite (0·45 gm.) in water (1 ml.). Urea (0·11 gm.) in water (12 ml.) and 2·5N sulphuric acid (12 ml.) were added after 1 hour. The suspension was added in portions to a boiling stirred mixture of xylene (9 ml.) and 2·1N sulphuric acid (36 ml.). The mixture was boiled for 30 minutes longer. On cooling a dark red coloured solution contaminated with tar was obtained.

(4) 3-Amino-2-bromo-fluoranthene (1·0 gm.) was stirred in dry ether (250 ml.), and the insoluble material was filtered off. Conc. sulphuric acid (0·5 ml.) was added with stirring. The amine sulphate formed was separated by filtration, allowed to dry and finely ground. The salt was added in portions to a vigorously stirred solution of conc. H_2SO_4 (38 ml.) and glacial acetic acid (38 ml.) with gentle warming to 60°. The solution was allowed to cool to room temperature and 75 c.c. of ice cold water was added rapidly with stirring to precipitate the amine salt in a finely divided condition. The salt was diazotised at 15 - 20° by the addition of sodium nitrite (0·8 gm.) in water (5 ml.) and after stirring for five minutes was filtered. A clear diazonium

solution was thus successfully obtained.

I. The diazonium solution was added gradually to 5% H_2SO_4 (boiling) and heated for another half hour, but no decomposition was observed. On prolonged heating (6 hours) tar was formed.

The following attempts and modifications were also made without success.

II. The diazonium solution (50 ml.) was heated at 40-50° with 5% or 10% H_2SO_4 (150 ml.) over night.

III. The diazonium solution (50 ml.) was heated at 75-85° with 5% or 10% H_2SO_4 (150 ml.) for 10 hours.

IV. The diazonium solution (50 ml.) was added gradually to a solution of 5% H_2SO_4 (200 ml.) containing sodium sulphate (10 gm.) and refluxed for ½ hour.

V. The diazonium solution (100 ml.) was added in three portions to boiling 5% H_2SO_4, through which steam was passed for 1 hour.

VI. The diazonium solution was added gradually to 50% boiling sulphuric acid and heated for 10 minutes.

In the above cases, either the solution underwent no change or tar was formed or intractable products, insoluble in alkali were obtained.

3-Hydroxy-fluoranthene:-

The diazotisation of 3-aminofluoranthene was conducted as in the case of 3-amino-2-bromo-fluoranthene (page 69). 3-Amino-fluoranthene (1·0 gm.) was diazotised with sodium nitrite (0·7 gm.)

at 15 - 20°. The clear solution obtained was added slowly to 5% boiling H_2SO_4 and was heated for half hour. After cooling, the product which was contaminated with a considerable quantity of tar, was extracted with benzene. The benzene layer was washed with water, and shaked twice with 2% NaOH (30 ml.). Acidification of the aqueous layer with hydrochloric acid gave a white precipitate of 3-hydroxyfluoranthene. This was filtered, washed with water and recrystallised from methanol.

m.p. 187-189° (rapid heating)

mixed m.p. with authentic sample 186-189°

yield 0·1 gm.

Attempted preparation of 2-bromo-3-hydroxyfluoranthene
(Second method)

3-Amino-2-bromofluoranthene was heated in sealed tubes with HCl or H_2SO_4.

I. With HCl.

	Quantity	Acid	Temperature	Time	Result
1.	0·4 gm.	1N HCl (3 ml.)	220° - 230°		Tube exploded after ½ hour.
2.	0·2 gm.	10% HCl (2 ml.)	150° - 160°	24 hours	A reddish yellow product was obtained, which on dissolving in benzene and passing through a column gave the unchanged compound (0·1 gm.). m.p. and mixed m.p. 173-176°.
3.	0·4 gm.	20% HCl (4 ml.)	150° - 160°	18 hours	Reddish black product m.p. 200-330°. No pure product could be isolated.

II. With H_2SO_4

No.	Quantity	Acid	Temperature	Time	Result
1.	0·2 gm.	10% H_2SO_4 (2 ml.)	210 - 225°	4 hours	Black product
2.	0·4 gm.	10% H_2SO_4 (4 ml.)	190 - 200°	6 hours	Black product m.p. > 350°
3.	0·4 gm.	10% H_2SO_4 (4 ml.)	150 - 160°	16 hours	Black product
4.	0·5 gm.	10% H_2SO_4 (4 ml.)	150 - 160°	4 hours	Black product and unchanged starting material (70 mg.). m.p. 174° and mixed m.p. 171°.

Attempted preparation of 2-bromo-3-methoxy-fluoranthene (Third method)

3-Amino-2-bromo-fluoranthene (0·5 gm.) was diazotised again by the procedure given on page 69 . Fluoroboric acid (10 ml.) was added gradually to the clear diazonium solution. The precipitate formed was filtered, and was refluxed with acetic anhydride (20 ml.) for 20 minutes. This was then concentrated under reduced pressure to 8 ml. and after being diluted with water (25 ml.) was extracted with ether. The ether layer was washed with sodium bicarbonate solution and then with water and dried over anhydrous sodium sulphate. Ether was distilled off and the oil obtained was refluxed in 10 c.c. of ethyl alcohol and 3 c.c. of 10% aq. KoH for two hours. The solution was concentrated under reduced pressure (5 ml.), acidified with dil. HCl and extracted with ether. The ether solution was washed with water

and dried. On evaporation of the solvent an oil was obtained (0·40 gm.). Attempts to obtain the product in a crystalline form failed. The oil (0·35 gm.), anhydrous potassium carbonate (4 gm.), dimethyl sulphate (2 ml.) and sulphur free xylene (20 ml.) were heated under reflux for 2 hours. The volume was reduced, the product was filtered and the residue was washed with a little hot xylene. This was passed through a short column of alumina with benzene as solvent. Evaporation of benzene gave a yellow oil. Attempts to solidify it met with no success.

Attempted preparation of 2-bromo-3-hydroxyfluoranthene and formation of 2-bromo-fluoranthene:

(Fourth method)

The diazonium solution (from 1gm. of the amine) was prepared as in previous cases (Page 69). This was kept in ice water for four hours. A precipitate of the diazonium salt separated out. This was filtered and dried by suction and pressed between the folds of filter paper. The product thus obtained was added in portions with stirring to dry methanol (20 ml.) at room temperature. The suspension thus formed was heated on the water bath for one hour. During this heating a colourless solution formed. It was left overnight and then concentrated to a small volume (7 ml.). The crystals deposited on cooling were filtered off and recrystallised from methanol in pale yellow needles.

m.p. 101 - 103°.

Literature m.p. of 2-bromofluoranthene 102 - 104°

I.R. Spectrum: (No methoxyl peak)

N.M.R. Spectrum: τ 2·0 - 2·8 (Aromatic complex)

No methoxyl peak.

Analysis: $C_{16}H_9Br$ requires C = 68·4%; H = 3·2%; Br = 28·4%.

found C = 68·4%; H = 3·6%; Br = 26·9%.

3-Acetylamino-2-nitro-fluoranthene:-

This was prepared by the method of Kloetzel et al. 3-Acetylaminofluoranthene (4 gm.) in glacial acetic acid (200 ml.) was nitrated by conc. HNO_3 (1·7 ml., d. 1·42) at 75° to give 3-acetylamino-2-nitrofluoranthene (3·8 gm.)

m.p. 282 - 283°.

Literature m.p. 282 - 283°.

Yield 3·8 gm. (80%).

2-Nitro-3-aminofluoranthene:-

Kloetzel, King and Menckes, loc. cit.

5·0 gm. 2-nitro-3-acetaminofluoranthene gave 2·5 gm. of 2-nitro-3-aminofluoranthene. Needles from chlorobenzene,

m.p. 253 - 254°.

I.R. Spectrum: 3310, 3420 cm^{-1} (NH_2)(m) (Two bands)

2-Nitro-3-hydroxyfluoranthene:-

Nichol, Thesis, Edinburgh, 1958, 48.

3·0 gm. of 2-Nitro-3-aminofluoranthene gave 2·2 gm. of 2-nitro-3-hydroxyfluoranthene.

m.p. 187 - 189°.

This was also obtained, when 2-nitro-3-acetaminofluoranthene (3·0 gm.) in ethanol (300 ml.) and 10% sodium hydroxide (200 ml.)

were refluxed overnight, filtered and acidified (1·1 gm.); It recrystallised from xylene as yellow prisms,

m.p. 186 - 188°.

I.R. Spectrum: 3350 cm^{-1} (w) (OH) Nujol.

3-Methoxy-2-nitro-fluoranthene:-

Anhydrous potassium carbonate (4 gm.) and dimethyl sulphate (2 ml.) were added to 2-nitro-3-hydroxy-fluoranthene (0·5 gm.) in chlorobenzene (20 ml.). The mixture was refluxed for 45 minutes, filtered hot and the residual potassium carbonate was washed twice with a little hot chlorobenzene. The filtrate and washings were concentrated to a small volume (10 ml.) under reduced pressure, and was passed through a column of alumina (6" x 1") with benzene as solvent. A yellow band developed. Evaporation of the solvent gave an oil which on trituration with light petroleum became solid. This was recrystallised from benzene/light petroleum.

m.p. 120 - 121°.

yield 0·25 gm.

Analysis: $C_{17}H_{11}NO_3$ requires C = 73·6%; H = 4·0%.

found C = 73·7%; H = 4·2%.

I.R. Spectrum: 1245 cm^{-1} (m) ($-OCH_3$)

N.M.R. Spectrum: τ 1·8 - 2·85 (complex. 8 Aromatic protons)

τ 5·82 (singlet. 3 Methyl protons)

2,8-Dinitro-3-methoxy-fluoranthene:-

Fuming nitric acid (2 ml.) was added at room temperature with stirring to a solution of 2-nitro-3-methoxyfluoranthene (50 mg.) in glacial acetic acid (5 ml.). The stirring was

continued ½ hour longer and then the mixture was kept for 18 hours. The precipitate formed was filtered, washed with water and re-crystallised twice from toluene-1-methylnaphthalene.

m.p. 282 - 284°. (lit. 278 - 273°)

mixed m.p. 280 - 283°

Analysis: Calc. for $C_{17}H_{10}N_2O_5$: N = 8·7%

found: N = 8·8%.

2-Amino-3-methoxy-fluoranthene:-

3-Methoxy-2-nitro-fluoranthene (2·0 gm.) was dissolved in ethylacetate (50 ml.). Raney nickel (1 gm.) was added and the product was reduced with hydrogen at room temperature and pressure. After the theoretical amount of hydrogen had been absorbed, the mixture was filtered and the solvent was evaporated off. The product obtained was recrystallised from benzene/light petroleum.

m.p. 102 - 104°.

yield 1·5 gm.

Analysis: $C_{17}H_{13}NO$ requires C = 82·6%; H = 5·3%; N = 5·7%.

found C = 81·3%; H = 5·9%; N = 5·8%.

I.R. Spectrum: 3320, 3400 (w)(NH_2) (two bands) Nujol.

The attempted preparation of 2-bromo-3-methoxyfluoranthene:-

40% HBr (2 ml.) was added to 2-amino-3-methoxy-fluoranthene (0·1 gm.). The suspension was cooled to 5° and sodium nitrite (0·1 gm.) in 1 c.c. of water was added with stirring. The stirring was continued for ½ hour, but no clear solution was obtained. The suspension was added to freshly prepared cuprous bromide (0·3 gm.) and 40% HBr (5 ml.) solution, at 95°. After 15 minutes the

mixture was poured into water, and extracted with hot xylene (the product being insoluble in cold ether and benzene). The xylene extract was washed with 5% NaOH; 5% H_2SO_4 and then with water and dried evaporation of the solvent gave a reddish black product.

m.p. 200 - 320°

(2) 2-Amino-3-methoxy-fluoranthene (0·1 gm.) was dissolved in acetic acid (3 ml.) and 40% HBr (0·6 ml.) was added dropwise with stirring. Immediately a precipitate formed. This complex was cooled to 0° and sodium nitrite (0·040 gm.) in water (1 ml.) was added, and stirred for 1 hour. However no clear solution was obtained.

(3) The experiment was conducted as above, and after the addition of HBr the mixture was heated to 85° and cooled rapidly under tap water so as to give a fine suspension. Attempts to diazotise the suspension, however, were unsuccessful.

(4) The amine (0·1 gm.) was heated in acetic acid (5 ml.) cooled to 15° and added slowly into nitrosyl-sulphuric acid (1·5 ml.), made by suspending sodium nitrite (0·2 gm.) in conc. sulphuric acid. The directions of Hodgson and Walker, J.C.S. 1933, 1620, were then followed. The viscous diazonium solution was added gradually to freshly prepared cuprous bromide (0·5 gm.) in 38% HBr (10 ml.) at 40° and the temperature was gradually raised to 95° and maintained at this temperature for fifteen minutes. The mixture was poured into water, allowed to stand, and the precipitate obtained was filtered and dried. This was then extracted with hot

benzene, the volume reduced (10 ml.) and passed through a short column of alumina (2" x ½"). Evaporation of the benzene gave a red product (m.p. 150 - 350°) which could not be crystallised.

(5) 2-Amino-3-methoxyfluoranthene (0·2 gm.) was diazotised with sodium nitrite (0·15 gm.) at 15 - 20° by the procedure given on page 69 . The clear diazonium solution was added dropwise into a freshly prepared solution of cuprous bromide (0·5 gm.) and 40% HBr solution (10 ml.) at 60° and the temperature was gradually increased to 95°. It was stirred at that temperature for fifteen minutes. The mixture was allowed to cool and was diluted with water, and precipitate filtered off. The dried material was stirred with hot benzene and the insoluble product discarded. The benzene extract (20 ml.) was washed twice with conc. sulphuric acid, (4 ml. each time), then with water, 10% aqueous sodium carbonate (10 ml.), water, and dried (Na_2SO_4). Evaporation of the solvent gave only a trace of yellow solid.

m.p. 110 - 115°

Analysis: $C_{17}H_{11}BrO$ requires Br = 25·7%.

found Br = 28·45%.

Two more experiments at 60° and 35° were similarly conducted without any success.

Bromination of 3-methoxy-2-nitro-fluoranthene:-

3-Methoxy-2-nitrofluoranthene (1 gm.) was dissolved in glacial acetic acid (40 ml.). Bromine (1.80 gm.) in acetic acid (5 ml.) was added dropwise with stirring at 80 - 85°. A precipitate began to appear after 45 minutes. The stirring was continued for

one and a half hours at the same temperature. It was allowed to cool to room temperature and filtered. The precipitate (0·7 gm.) was crystallised twice from glacial acetic acid which gave light yellow needles of 8-bromo-3-methoxy-2-nitrofluoranthene.

m.p. 217 - 218°

yield 0·65 gm.

Analysis: $C_{17}H_{10}NO_3Br$ requires Br = 22·5%; N = 3·9%

found Br = 22·9%; N = 4·2%.

7-Bromo-2-acetylaminofluorene:-

7-Bromo-2-aminofluorene (1·13 gm.) was dissolved in benzene, and acetic anhydride (1 c.c.) was added dropwise with stirring, at room temperature. 7-Bromo-2-acetylaminofluorene was produced in quantitative yield.

m.p. 220°

yield 1·2 gm.

7-Bromo-3-nitro-2-acetylaminofluorene:-

The above acetyl derivative (1·2 gm.) was dissolved in hot glacial acetic acid (25 ml.). Conc. HNO_3 (d = 1·42; 1·2 c.c.) in 2 c.c. of glacial acetic acid was added at 70° with stirring. The temperature was raised to 75° and the mixture stirred at this temperature for fifteen minutes. The yellow precipitate (0·8 gm.) was filtered, washed with acetic acid and then with water, and recrystallised from glacial acetic acid.

m.p. 229-232°.

Analysis: $C_{15}H_{11}BrN_2O_3$

requires C = 51·8%; H = 3·2%; N = 8·1%; Br= 23·0%.

found C = 50·9%; H = 3·1%; N = 8·1%; Br= 21·8%.

I.R. Spectrum: $1695^{cm^{-1}}$ (C = O)(s) (Chloroform)

$1340^{cm^{-1}}$ (NO_2)(s) (Chloroform)

2-Amino-7-bromo-3-nitro-fluorene:-

The above acetyl-derivative (0·3 gm.) was boiled with 10 ml. of a mixture of acetic acid-water-sulphuric acid (1:1:1 by weight) for 1 hour. The mixture was poured into water. The red precipitate was filtered, washed with water and recrystallised from aqueous acetic acid in red needles.

m.p. 218 - 220°

yield 0·2 gm.

Analysis: $C_{13}H_9BrN_2O_2$

requires C = 51·1%; H = 2·9%; N = 9·2%; Br= 26·2%

found C = 50·55%; H = 2·6%; N = 9·4%; Br= 25·5%.

I.R. Spectrum: $3400^{cm^{-1}}$ (NH_2)(w) two bands

$1335^{cm^{-1}}$ (NO_2)(m).

Attempted preparation of 7-bromo-2-hydroxy-3-nitro-fluorene:-

(1) 2-Amino-7-bromo-3-nitrofluorene (0·3 gm.) was boiled under reflux with ethanol (30 ml.) and 10% NaOH (25 ml.) for 3½ hours. The dark reddish black solution was filtered and acidified. This was extracted with ether, after washing and evaporation of the solvent a reddish black product was obtained. The product was neither soluble in alkali nor in acid and did not melt below 350°.

(2) Another experiment was conducted where the period of boiling was 45 minutes. However the same results were obtained

7-Bromo-2-methoxy-fluorenone:-

7-Bromo-2-methoxy-fluorene (0·3 gm.) was refluxed with sodium dichromate (0·8 gm.) in glacial acetic acid (4 ml.) and water. After half an hour a further quantity of glacial acetic acid (4 ml.) was added and boiling continued for another $2\frac{1}{2}$ hours. the mixture was poured into water which gave a yellowish-orange precipitate. This was filtered. Recrystallisation from aqueous acetic acid gave orange coloured needles of the fluorenone.

m.p. 168 - 170°

Analysis: $C_{14}H_9BrO_2$ requires C = 58·4%; H = 3·2%; Br = 26·6%

found C = 57·6%; H = 3·8%; Br = 26·7%.

I.R. Spectrum: $1715^{cm^{-1}}$ (s) (C = O) (Chloroform)

$1300^{cm^{-1}}$ (s) (OCH_3) (Chloroform)

N.M.R. Spectrum: τ 2·3 - 3·2 (complex. 6 Armmatic protons)

τ 6·2 (singlet 3 methyl protons)

7-Bromo-2-methoxy-3-nitrofluorenone:-

7-Bromo-2-methoxy-9-fluorenone (0·1 gm.) was dissolved in glacial acetic acid (7 c.c.). Conc. HNO_3 (d. 1·42; 0·8 c.c.) was added dropwise at 70° and the temperature was increased to 80° and maintained for fifteen minutes. The precipitate formed was filtered, washed with water, and crystallised from glacial acetic acid which gave orange needles, of 7-bromo-2-methoxy-3-nitro-fluorenone.

m.p. 274 - 275°.

yield 0·05 gm.

Analysis: $C_{14}H_8BrNO_4$

requires C = 50·3%; H = 2·4%; N = 4·2%; Br = 23·95%

found C = 50·8%; H = 2·7%; N = 4·2%; Br = 23·95%.

Oxidation of 8-bromo-3-methoxy-2-nitrofluoranthene:-

8-Bromo-3-methoxy-2-nitrofluoranthene (0·5 gm.) was suspended in glacial acetic acid (38 ml.). To this chromic anhydride A.R. (0·7 gm.) in water (9 ml.) and glacial acetic acid (6 ml.) was added dropwise. During the addition the temperature of the oil bath was not allowed to exceed 115°. The mixture was boiled under reflux for two hours. A fresh quantity of chromic anhydride A.R. (1·0 gm.) in glacial acetic acid (80 ml.) was added dropwise and boiling continued for another three hours. Half of the glacial acetic acid was distilled off and the residual solution was poured into water (250 ml.) whereupon a precipitate appeared. It was filtered and washed thoroughly with water. The yellow precipitate thus obtained was boiled with aqueous sodium bicarbonate, filtered hot and the golden yellow alkaline extract was acidified with conc. HCl. The precipitate obtained was filtered, washed with water, dried and recrystallised from acetic acid.

m.p. 241 - 243°

yield = 0·3 gm.

Analysis: For 2-methoxy-3-nitro-7-bromo-9-oxo-fluorene-8-carboxylic acid

$C_{15}H_8BrNO_6$ requires C = 47·6%; H = 2·1%; Br = 21·2%; N = 3·7%.

found C = 54·6%; H = 2·9%; Br = 26·3%; N = 0·6%.

for 6-bromo-1-carboxy-fluorenone

$C_{14}H_7BrO_3$ requires C = 55·4%; H = 2·3%; Br = 26·4%.

found C = 54·6%; H = 2·9%; Br = 26·3%.

I.R. Spectrum: $1725^{cm^{-1}}$ (Ketonic; C = O)(s)(Chloroform)

$1685^{cm^{-1}}$ (Carbonyl; C = O)(s)

$1605^{cm^{-1}}$ (C = C)(s)

6-Bromo-1-carbomethoxy-fluorenone:-

The above acid (0·04 gm.), methanol (3 ml.) and 2 drops of conc. sulphuric acid were heated under reflux for 1 hour. The mixture was cooled, and poured into sodium bicarbonate solution. The product was extracted with ether, washed with water and dried. Evaporation of the solvent gave a yellow product which when twice recrystallised from methanol gave yellow needles of the methyl ester.

m.p. 125 - 127°.

mixed m.p. with authentic sample (125°) = 125°

I.R. Spectrum: $1710^{cm^{-1}}$ (ester; C = O)(s)(Chloroform)

$1690^{cm^{-1}}$ (carbonyl; C = O)

N.M.R. Spectrum: τ 2·2-2·8 (complex 6 Aromatic protons)

τ 6·0 (singlet 3 methyl protons)

Decarboxylation of 6-bromo-1-carboxy-fluorenone:-

The foregoing acid (70 mg.) was heated in quinoline (4 ml.) at a temperature of 210 - 215° in a metal bath for 45 minutes. The cooled solution was poured into dilute HCl and the product was extracted with benzene. The benzene solution was washed with water, sodium bicarbonate solution, water, dried and evaporated. The yellow crude product was chromatographed on a short column of alumina. The pale yellow band was eluted with benzene and after

evaporation of the solvent, the product was recrystallised from glacial acetic acid.

m.p. 161°

mixed m.p. 160 - 162° (with authentic 3-bromofluorenone)

I.R. Spectrum: $1710^{cm^{-1}}$ (Ketonic; C = O)(s) Chloroform

Attempted preparation of 2-acetamino-8-bromo-3-methoxy-fluoranthene:-

8-Bromo-3-methoxy-2-nitro-fluoranthene (60 mg.) was suspended in ethyl alcohol (20 ml.) and Raney nickel (0·5 gm.) was added. The reduction was done at ordinary temperature and pressure. After 4 hours, the catalyst was filtered off. Removal of ethanol gave a semi-oily product which could not be solidified. The product was dissolved in benzene (2 ml.) and a drop of acetic anhydride was added. After half an hour, the precipitate was filtered, washed with water, and recrystallised from benzene/light petroleum (100 - 120°).

m.p. 164 - 168°.

yield 16 m.g.

Analysis: $C_{19}H_{14}BrNO_2$ requires Br = 21·7%; N = 3·8%

found Br = 6·44%; N = 4·8%.

Obviously considerable hydrogenolysis had taken place.

2-Acetamino-8-bromo-3-methoxyfluoranthene:-

8-Bromo-3-methoxy-2-nitrofluoranthene (0·1 gm.), platinum oxide (50 mg.) and ethyl acetate (20 ml.) were placed in a hydrogenation flask. The reaction was carried out as before. The resultant product was acetylated in a similar manner, as in the previous case. 2-Acetamino-8-bromo-3-methoxyfluoranthene was

recrystallised from benzene/petroleum ether (100 - 120°).

m.p. 173 - 176°.

yield 40 mg.

Analysis: $C_{19}H_{14}BrNO_2$ requires Br = 21·7%; N = 3·8%.

found Br = 20·1%; N = 4·05%.

Attempted preparation of 2-amino-8-bromo-3-methoxy-fluoranthene:-

The reduction of the nitro-derivative (0·1 gm.) was done as in the above case. The semi-solid product was dissolved in the minimum of hot alcohol (1 c.c.), and a saturated solution of picric acid in alcohol (2 c.c.) was added. After half an hour, the product which separated out was collected (0·1 gm.) This was dissolved in benzene and passed through a column of alumina (6" x ½") using benzene as the eluent. The evaporation of the solvent gave a solid which melted over a range.

m.p. 112 - 118°.

No pure product could be obtained.

2-Amino-8-bromo-3-methoxy-fluoranthene:-

8-Bromo-3-methoxy-2-nitrofluoranthene (0·3 gm.), iron powder (0·3 gm.), 95% ethanol (13 ml.), water (7 ml.) and acetic acid (2 ml.) were refluxed together for six hours. The ethanol was distilled off and the residue was extracted three times with boiling benzene (50 ml.). The benzene extract was washed with water and dried (Na_2SO_4). The product obtained on evaporation of the solvent was recrystallised from benzene/light petroleum (1:1), which gave rectangular plates of the amine.

m.p. 127 - 129°.

yield 0·2 gm.

Analysis: $C_{17}H_{12}ONBr$

requires C = 62·6%; H = 3·7%; N = 4·2%; Br = 24·5%.

found C = 63·7%; H = 3·8%; N = 4·6%; Br = 23·9%.

I.R. Spectrum: $3350^{cm^{-1}}$ (NH_2)(m) two bands Chloroform

$1275^{cm^{-1}}$ (OCH_3)(m)

Attempted deamination of 2-amino-8-bromo-3-methoxy-fluoranthene:-

Sodium nitrite (0·05 gm.) was added with stirring, to a solution of conc. H_2SO_4 (3·5 ml.) and water (0·25 ml.) at room temperature. When all the sodium nitrite had dissolved the solution was cooled at -5°. Powdered 2-amino-8-bromo-3-methoxy-fluoranthene (0·070 gm.) was added in portions with vigorous stirring to the above solution. The temperature being maintained at -5°. Stirring was continued for one hour at this temperature. Pre-cooled hypophosphorous acid (4·8 ml.) was then added in ten minutes at 0°. The reaction mixture was kept standing for four days at 0 - 2°, in a cold storage. It was, then, diluted with water and the reddish precipitate was filtered. This was washed with water and dried, but was found to be insoluble in the usual solvents.

m.p. > 350°.

It was obviously not the desired compound .

(2) 2-Amino-8-bromo-3-methoxy-fluoranthene (0·1 gm.) was diazotised by the procedure given on page 69.

The clear diazonium solution was kept standing for four hours in ice water. The precipitate formed was filtered and added

gradually with hand stirring to methanol (10 ml.) containing water (1 ml.). The mixture was heated under reflux for eight hours. However, no product could be isolated.

8-Bromo-3-acetaminofluoranthene:-

3-Acetaminofluoranthene (0·6 gm.) was dissolved in a mixture of glacial acetic acid (20 ml.) and carbontetrachloride (10 ml.). The hot solution was filtered off to remove any insoluble product. Bromine (0·30 ml.) in acetic acid (2 ml.) was added dropwise at 50°. The mixture was stirred for 1½ hours at this temperature. The precipitate formed was filtered hot, washed with 10% $NaHSO_3$ (20 ml.), 10% NaOH (20 ml.) and then thoroughly with water. The product was crystallised from acetic acid and then from chlorobenzene.

m.p. 265 - 267°.

mixed m.p. with 2-bromo-3-acetaminofluoranthene 233 - 237°.

yield 0·32 gm.

Analysis: $C_{18}H_{12}NBrO$ requires Br = 23·6%

found Br = 23·4%.

It is noteworthy that when experiment was conducted by following the directions of Kaminska et al. mixture (m.p. 210 - 225°) was obtained.

3-Amino-8-bromo-fluoranthene:-

8-Bromo-3-acetaminofluoranthene (0·1 gm.), sodium hydroxide (0·2 gm.) in water (1 ml.) and ethylene glycol were refluxed together for one and a quarter hours. The resultant solution was poured into water (15 ml.). The precipitate formed was filtered

and recrystallised from aqueous ethanol.

m.p. 178 - 180° (lit. 186 - 187°)

yield 50 mg.

mixed m.p. with 3-amino-2-bromofluoranthene 155 - 160°.

Oxidation of 3-acetylamino-8-bromo-fluoranthene:-

Chromic anhydride (0·2 gm.) in water (0·5 ml.) and glacial acetic acid (1 ml.) were added dropwise to 3-acetylamino-8-bromo-fluoranthene (50 mg.) in glacial acetic acid (5 ml.), and the mixture was refluxed for eight hours. The volume was reduced to 3 ml. and poured into water (10 ml.). The precipitate was extracted with sodium carbonate solution and acidified. On standing over the weekend, a few crystals deposited. These were filtered, washed with water and dried.

m.p. 242 - 245°.

mixed m.p. with 6-bromofluorenone-1-carboxylic acid 243 - 246°.

Attempted preparation of 8-bromo-3-hydroxy-fluoranthene:-

3-Amino-8-bromo-fluoranthene (40 m.g) was dissolved in dry ether (10 ml.). 2 drops of conc. H_2SO_4 were added with stirring at room temperature. The precipitate formed was filtered dried and powdered.

The powdered salt was added in portions to a mixture of sulphuric acid (2 ml.) and acetic acid (2 ml.). It was diazotised with sodium nitrite (40 mg.) by following the procedure given on page 69 . The clear solution was added dropwise to a boiling 5% sulphuric acid, and heated for fifteen minutes longer; on cooling only tar formation was observed.

Fluorene-9-carboxylic acid:-

A. Campbell and Tucker, J.C.S., 1949, 2624.

5 gm. fluorene yielded 4·0 gm. fluorene-9-carboxylic acid.

m.p. 220 - 224°.

9-Carbomethoxy-fluorene:-

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

4 gm. Fluorene-9-carboxylic acid yielded 3·0 gm. of the methyl ester.

m.p. 64 - 66°.

β -9-Fluorenylpropionic acid:-

A. Campbell and Tucker, J.C.S. 1949, 2625.

5 gm. 9-Carbomethoxyfluorene yielded 4·1 gm. of the acid.

m.p. 141 - 145°.

N.M.R.:- τ 2·15 - 2·85 (complex 8-aromatic protons)

τ 5·85 - 6·0 (triplet 9H-1-proton)

τ 7·5 - 8·2 (4 methylene protons)

3-Oxo-1,2,3,10b-tetrahydrofluoranthene:-

John Craig, Thesis 1955, Edinburgh, p.68.

3 gm. of the acid yielded 2·2 gm. of the cyclised ketone.

m.p. 92 - 95°.

Attempted bromination of 3-oxo-1,2,3,10b-tetrahydrofluoranthene:-

Craig Thesis, Edinburgh 1955, p.85.

The ketone (0·2 gm.) in carbontetrachloride (10 ml.) when refluxed with N.B.S. (0·17 gm.) gave only tar.

Bromination of 3-oxo-1,2,3,10b-tetrahydrofluoranthene:-

3-Oxo-1,2,3,10b-tetrahydrofluoranthene (0·2 gm.) was dissolved in glacial acetic acid (6 ml.). Bromine (0·48 gm.) in glacial acetic acid (2 ml.) was added dropwise at 60°. The stirring was continued for one and a half hours. The solution was poured into water. The precipitate obtained was filtered, washed with water and recrystallised from acetic acid.

m.p. 149 - 151°.

yield 0·04 gm.

Analysis: $C_{16}H_{10}OBr_2$

requires C = 50·8%; H = 2·6%; Br = 42·3%.

found C = 51·0%; H = 2·7%; Br. = 38·4%.

The product is obviously a dibromo compound.

SECTION II

1-Iodo-4-methoxynaphthalene:-

This was prepared by the method of Stubbs and Tucker, J.C.S., 1954, 233.

1-Methoxy-naphthalene (2·0 gm.) gave 1-iodo-4-methoxy-naphthalene (2·2 gm.)

m.p. 50 - 51°.

Nitration of 1-iodo-4-methoxynaphthalene:-

Fuming nitric acid (8 c.c.) was added with stirring at room temperature to 1-iodo-4-methoxynaphthalene (1·0 gm.) in glacial acetic acid (10 ml.), and after 30 minutes the supernatant liquor was decanted from the black residue and poured into water. The precipitate was washed with aq. sodium thiosulphate and extracted with ether. Removal of the solvent gave a product most of which dissolved in boiling light petroleum. The cooled solution deposited 1-methoxy-2-4-dinitronaphthalene, yellow needles (from methanol).

m.p. 96 - 97°.

yield = 0·15 gm.

Analysis: $C_{11}H_8N_2O_5$

requires C = 53·2%; H = 3·25%; N = 11·3%.

found C = 53·7%; H = 3·5%; N = 11·4%.

I.R. Spectrum: $1355^{cm^{-1}}$ (m) (NO_2) Nujol

$1295^{cm^{-1}}$ (m) (OCH_3) Nujol

N.M.R. Spectrum: τ 1·2 - 2·3 (complex. 5 protons)

τ 5·8 (singlet 3 methyl protons)

1-Methoxy-4-nitro-naphthalene:-

Badder, El-Assal and Baghos, J.C.S., 1958, 986.

5·3 gm. of 1-methoxynaphthalene gave 4·0 gm. of 1-methoxy-4-nitro-naphthalene.

m.p. 81 - 82°.

1-Methoxy-2,4-dinitronaphthalene:-

1-Methoxy-4-nitronaphthalene (0·9 gm.) gave 0·6 gm.of 1-methoxy-2,4-dinitronaphthalene.

m.p. 97 - 98°.

mixed m.p. with the product obtained by nitration of 1-iodo-4-methoxynaphthalene 96 - 97°.

1,4-Dibromo-naphthalene:-

R.E. Bayer and E.J. O'Reilly, J. Org. Chem., 23, 311.

Naphthalene (6·4 gm.) gave 5·5 gm. of 1,4-dibromonaphthalene.

m.p. 80 - 81°.

1,4-Dibromo-5-nitronaphthalene:-

McLeish and Campbell, J.C.S., 1937, 1103.

1,4-Dibromonaphthalene (3·5 gm.) yielded 1,4-dibromo-5-nitro-naphthalene (1·5 gm.).

m.p. 115 - 116°.

Attempted dehalogenation of 1,4-dibromo-5-nitronaphthalene.

5-Amino-1,4-dibromonaphthalene:-

cf. Sandin and Evans, J.A.C.S., 61, 2916.

1,4-Dibromo-5-nitronaphthalene (0·6 gm.) was dissolved in a boiling mixture of glacial acetic acid (5 c.c.) and conc. HCl

(5 c.c.), and then stannous chloride (8 gm.) was added. The solution was refluxed for nine hours. The reaction mixture was treated with HCl, then cooled and the precipitate was filtered off and neutralised with sodium hydroxide solution (5%). The amine liberated and recrystallised from light petroleum (80 - 100°).

m.p. 99 - 100°.

Analysis: $C_{10}H_7Br_2N$ requires Br = 53·2%; N = 4·6%.

found Br = 54·8%; N = 4·9%.

I.R. Spectrum: $3430^{cm^{-1}}$, $3350^{cm^{-1}}$, (w), (NH_2) Nujol

Dehalogenation of 1-4-dibromo-5-nitronaphthalene:-

cf. W.T. Smith jr., J.A.C.S., 1949, 71, 2855.

1-4-Dibromo-5-nitronaphthalene (0·6 g), and benzoic acid (0·7 g.) were placed in a 25 ml. conical flask. It was heated to 150 - 200°. Copper powder (0·5 g.) was added in several portions over a period of five minutes and stirred with a hand stirrer. It was then allowed to cool. After the melt solidified the flask was placed in 100 ml. of 10% sodiumbicarbonate solution and the melt was digested until it was completely broken up and effervescence ceased. The liquid suspension was then filtered through a soxhlet thimble. The material in the thimble was then extracted in a soxhlet extractor with acetone (100 ml.), until no more colour was extracted. It was then cooled and filtered. The acetone was evaporated to give 1-bromo-5-nitro-naphthalene which was crystallised first from light petroleum and then from ethanol.

m.p. 122°.

yield 0·2 gm.

1-Bromo-5-nitronaphthalene:-

This was prepared by the method of Hannes Rubli, Ph.D. Thesis, Edinburgh, 1927, p.16.

1-Nitronaphthalene (2·13 gm.) gave 1-bromo-5-nitronaphthalene (1·6 gm.).

m.p. 122°.

mixed m.p. with the above product = 122° undepressed.

Attempted dehalogenation of 1-bromonaphthalene:-

The experiment was carried out exactly as in the case of 1,4-dibromo-5-nitronaphthalene (page 93). Benzoic acid (7 gm.) and 1-bromo-naphthalene (4·2 gm.) were heated together and copper powder (5 gm.) was added in several portions at a temperature of 150 - 200° over a period of five minutes. However unreacted 1-bromo-naphthalene (4·0 gm.) was obtained.

Phthalo-α-naphthylimide:-

This was prepared by the method of Hodgson and Crook, J.C.S., 1936, 1844.

1-Naphthylamine (43 gm.) gave phthalo-α-naphthylimide, which was crystallised from glacial acetic acid (50 gm.)

m.p. 180 - 181°.

Nitration of phthalo-α-naphthylimide:-

The above product (30 gm.) was nitrated with a mixture of fuming and conc. HNO_3 (1:1; 60 c.c.) to give a mixture of 4,5, or 8-nitro-phthalo-α-naphthylimides, 37 gm.

8-Nitro-1-naphthylamine:-

This was prepared by the method of Hodgson and Ratcliffe, J.C.S., 1949, 1315. The mixture of nitro-phthalo-1-naphthylimides gave 8-nitro-1-naphthylamine (5·5 g.)

m.p. 95 - 97°.

I.R. Spectrum: $3420^{cm^{-1}}$(w), $3370^{cm^{-1}}$(w) (NH_2) Nujol

$1348^{cm^{-1}}$(m) (NO_2) Nujol

8-Nitro-1-naphthylamine was also prepared by the method of Morgan and Jones, J. Soc. Chem. Ind., 1923, 42, 341T.

1-Naphthylamine (60 g.) gave 8-nitro-1-naphthylamine (3g.).

m.p. 96 - 97°.

1-Iodo-8-nitronaphthalene:-

This was prepared by the method of Hodgson and Crook, J.C.S., 1937, 571.

8-Nitro-1-naphthylamine (4·7 g.) gave 1-iodo-8-nitronaphthalene (3·5 g.).

m.p. 78°.

Dehalogenation of 1-iodo-8-nitronaphthalene:-

The experiment was conducted exactly as before (page 93). 1-iodo-8-natronaphthalene (0·5 g.) gave 1-nitronaphthalene (0·15g.).

m.p. 56°.

mixed m.p. with 1-nitronaphthalene 56° (undepressed).

Nitration of 1-bromo-naphthalene:-

1-Bromo-naphthalene (50g.) was nitrated with procedure of Kerkhof, Rec. trav. Chim. Pays-bas, 1932, 51, 739, 751, which gave

1-bromo-4,5-dinitro-naphthalene m.p. 167° (literature 167°) (15 g.). From the mother liquor 1-bromo-4-8-dinitronaphthalene m.p. 141° (literature 143°) (5g.) was obtained.

Dehalogenation of 1-bromo-4,5-dinitronaphthalene:-

Dehalogenation of 1-bromo-4,5-dinitronaphthalene (1·0g.) with benzoic acid and copper gave 1,8-dinitronaphthalene (0·3 g.), which crystallised from chloroform in yellow shining plates.

m.p. 171 - 172°.

mixed m.p. with 1,8-dinitronaphthalene 171 - 173°.

Dehalogenation of 1-bromo-4,8-dinitronaphthalene:-

Dehalogenation of 1-bromo-4,8-dinitronaphthalene (0·8 g.) gave 1,5-dinitronaphthalene (0·35 g.). The crude product was purified by sublimation and then crystallised from acetic acid which gave yellow needles (0·2 g.).

m.p. 216°.

mixed m.p. with 1,5-dinitronaphthalene 216°.

Attempted preparation of 1-chloro-4,8-dinitronaphthalene:-

1-Chloro-naphthalene (40·6 gm.) was nitrated with fuming nitric acid (d = 1·51, 83 ml.) by following the procedure of Bassilios, Saleem and Shawky, Rev. Trav. Chim. Pays-bas, 81, 209 to give 1-chloro-4,5-dinitronaphthalene, which was crystallised twice from glacial acetic acid (11·5 g.) m.p. 178 - 180°, m.p. lit. 180°.

The mother liquor on concentration gave a crude product (8 g.) m.p. 65 - 95°. The m.p. was over a range (100 - 120°) even after five recrystallisations from benzene/light petroleum (1:1).

In another attempt 1-chloro-naphthalene (5 g.) was added dropwise to fuming nitric acid (2·1 ml.) at 30°. The reaction was exothermic, and after the addition it was kept at 45 - 50° for 2½ hours. The experiment was further carried out as above which gave 1-chloro-4-5-dinitro-naphthalene (1·5 g., m.p. 179°). The mother liquor on concentration again gave a crude product m.p. 65 - 80°, and even repeated recrystallisation did not give the pure 1-chloro-4,8-dinitronaphthalene.

Preparation of 1-chloro-4-8-dinitronaphthalene:-

This was prepared by the method of Ullmann and Consonno, Ber. dt. Chem. Ges., 1902, 35, 2802.

1-Nitronaphthalene (20 g.) gave 1-chloro-8-nitronaphthalene (10 g.). This was recrystallised twice from a mixture of benzene and light petroleum (1:1).

m.p. obtained 92 - 93°.

m.p. literature 94°.

The 1-chloro-8-nitronaphthalene (5 g.), gave 1-chloro-4-8-dinitronaphthalene on further nitration with conc. nitric acid (sp. gr. 1·47, 25 c.c.). The product (3·5 g.) was crystallised from methanol/acetic acid mixture.

m.p. obtained 137 - 138°.

m.p. literature 138°.

Preparation of 1-methoxy-4,8-dinitronaphthalene:-

1-chloro-4,8-dinitronaphthalene (1g.) suspended in boiling methanol (25 ml.) was added (5 - 10 minutes) to 2% sodium methoxide (20 ml.). The liquid became red. This was refluxed

for 5½ hours and then was allowed to cool. On cooling 1-methoxy-4,8-dinitronaphthalene was deposited. The product was recrystallised from glacial acetic acid which gave light yellow needles.

m.p. 161 - 162°.

yield 0·55 g.

Analysis: $C_{11}H_8N_2O_5$

requires C = 53·2%; H = 3·25%; N = 11·3%.

found C = 53·4%; H = 3·15%; N = 11·5%.

I.R. Spectrum: $1342^{cm^{-1}}$ (m) (NO_2) Nujol

$1275^{cm^{-1}}$ (m) (OCH_3)

N.M.R. Spectrum: τ 1·0 - 3·1 (complex 5 aromatic protons)

τ 5·95 (singlet 3 methyl protons)

Attempted preparation of 2-nitro-fluorenone:-

Schultz., Ann., 203, 103.

Fluorenone (10 gm.) was added gradually with stirring to 50 ml. of fuming nitric acid which was cooled by ice-salt mixture. After one hour, the stirring was stopped and the solution was filtered off. The precipitate was washed with water and recrystallised from glacial acetic acid. Bright yellow needles possibly of 2,7-dinitrofluorenone were obtained.

m.p. 290°

yield 6 gm.

The filtrate was poured into water. The product was filtered, washed with water and recrystallised twice from the minimum quantity of glacial acetic acid, probably of 2,5-dinitro-fluorenone.

m.p. 238 - 240°

yield 1·0 gm.

The mother liquor was distilled off under reduced pressure. The crude yellow product was dissolved in benzene (15 ml.) and passed through a column of alumina (4" x 1") using benzene as solvent. Five fractions (each of 20 ml.) were collected.

1st	fraction on evaporation of solvent gave a product	m.p.200-225° (0·1 gm.)
2nd	" " " " " " " "	m.p. 212-227° (0·2 gm.)
3rd	" " " " " " " "	m.p. 210-220° (0·25 gm.)
4th	" " " " " " " "	m.p. 204-214° (0·15 gm.)
5th	" " " " " " " "	m.p. 175-210° (0·2 gm.)

Fractions 2,3 and 4 were collected and recrystallised three times from glacial acetic acid, which gave 2-nitro-fluorenone

m.p. 217 - 220°

yield (0·3 gm.)

mixed m.p. with 2-nitro-fluorenone 216 - 219°

2-Aminofluorenone:-

Arcus and Coombs, J.C.S., 1954, 3979.

2-Nitrofluorenone (25 gm.) gave permagnate coloured needles of 2-aminofluorenone (15 gm.)

m.p. 158 - 159°

I.R. Spectrum: $3350^{cm^{-1}}$(w), $3450^{cm^{-1}}$(w)(NH_2) Nujol

$1720^{cm^{-1}}$(s) (Ketonic; C = O)

2-Amino-3-bromo-fluorenone:-

Suzuki and Momoi, Chemical Society of Japan, 36, 1693, (1963).

2-Aminofluorenone (16 gm.) gave 2-amino-3-bromo-fluorenone (9·5 gm.)

m.p. 214° (lit., 215°).

3-Bromo-fluorenone:-

2-Amino-3-bromo-fluorenone (20 gm.) gave 3-bromo-fluorenone (10 gm.)

m.p. 160 - 162°

I.R. Spectrum: $1720^{cm^{-1}}$(s) (Ketonic; C = O) Nujol

3-Bromo-fluorene:-

Andrew. Ph.D. Thesis, Edinburgh, 1964, p.126.

3-Bromo-fluorenone (1·0 gm.) gave 3-bromo-fluorene (0·4 gm.)

m.p. 86 - 88°

I.R. Spectrum: No C = O peak.

N.M.R. Spectrum: τ 2·1 - 2·9 (complex 7 aromatic protons)

τ 6·2 (singlet 2 protons)

3-Bromo-9-fluorene-carboxylic acid:

Andrew. Thesis,Ph.D. Edinburgh, 1964, p.129.

Lithium (0·15 gm.), cut into small pieces, was dropped into anhydrous ether (6 ml.) in a nitrogen atmosphere. Bromobenzene (1·65 gm.) in ether (10 ml.) was added slowly, and the reaction started by warming. After 1 hour, most of the lithium had dissolved, and the reaction was completed by refluxing for 30 minutes. The mixture was filtered through a glass plug into an ethereal solution of 3-bromo-fluorene (2·0 gm.) to give a brown solution with evolution of heat. This was added carefully to a slurry of ether and solid carbondioxide, then left overnight to evaporate. The remaining solid was shaken with ether and water, and the layers separated. The ethereal layer was evaporated to leave a red oil containing biphenyl, and the aqueous layer on acidification yielded 3-bromo-9-carboxy-fluorene as colourless needles from aqueous alcohol.

m.p. 224 - 226°

yield 1·0 gm.

It must be stressed that the yield was variable.

The yield quoted above was the best obtained in five attempts.

Reformatsky Reaction:-

cf. Organic reactions. Vol. I. Page 2.

A solution of 3-bromo-fluorenone (2·66) and ethyl bromo-acetate (2·06) in dried benzene (30 c.c.) and dried toluene (25 c.c.) was placed in a 100 ml. dropping funnel in a 3-necked flask equipped with a mercury sealed stirrer and reflux condenser. In the flask was placed zinc foil (0·656) which had previously been washed with 2% HCl, water, ethanol, acetone, ether and dried at 100° in a vacuum oven. A few crystals of iodine were added, stirring was started, heat was applied by means of a water bath, and about 10 ml. of the solution run into the flask. A vigorous reaction started. The remainder of the mixture was now added through the dropping funnel at a rate designed to maintain gentle boiling. Stirring and heating were continued for two hours, during which most of the zinc dissolved. The mixture was cooled and the condensed product was decomposed with dil. H_2SO_4 (15%), sufficient to dissolve all the zinc hydroxide. The benzene-toluene layer was separated and dried over anhydrous sodium sulphate. The solvent was removed by distillation, which gave a light brown oil.

I.R. Spectrum: $3410^{cm^{-1}}$ (m) (OH) Chloroform

$1720^{cm^{-1}}$ (s) (C = O)

Ethyl 3-bromo-fluorenylidene acetate:-

The oil obtained in the previous experiment was refluxed with 98 - 100% formic acid (15 ml.) for 45 minutes. The formic acid

was removed by blowing air through the hot solution. The brownish oily residue was treated with light petroleum and successive fractions were obtained. On cooling a yellow product deposited. This on crystallisation from ethanol gave light yellow needles (0·8) of ethyl 3-bromo-fluorylidene acetate. The remaining mother liquor was dissolved in light petroleum-benzene mixture (1:2) and passed through a short column of alumina and eluted with light petroleum-benzene mixture (1:2). Evaporation of the solvent and recrystallisation from ethanol gave a further quantity of the ester (0·2 g.)

m.p. 126 - 127°

yield 1·0 gm.

Analysis: $C_{17}H_{13}BrO_2$

requires C = 62·0%; H = 4·0%; Br = 24·3%

found C = 62·0%; H = 4·1%; Br = 22·8%

I.R. Spectrum: $1700^{cm^{-1}}$ (s) (ester; C = O) Nujol

$1640^{cm^{-1}}$ (m) (C = C)

N.M.R. Spectrum: τ 1·2 - 2·8 (complex, 7 aromatic protons)

τ 3·4 (singlet, methine proton)

τ 5·65 (quartet, methylene protons J = 7c/s)

τ 8·65 (triplet 1 methyl proton J = 6 c/s)

3-Bromo-9-fluorenylidene-acetic acid:

The above unsaturated ester (0·1 gm.) was refluxed with a mixture of 2N sodium hydroxide (3 ml.) and methanol (3 ml.) for two hours. It was acidified after cooling. The product obtained was filtered, washed with water, and recrystallised

from aq. acetic acid and then from benzene.

m.p. 223 - 224°

yield 40 mg.

Analysis: $C_{15}H_9BrO_2$

requires C = 59·8%; H = 3·0%; Br = 26·6%.

found C = 60·4%; H = 3·8%; Br = 26·6%.

I.R. Spectrum: $1690^{cm^{-1}}$ (s) (Carbonyl C = O) Nujol

$1640^{cm^{-1}}$ (m) (C = C)

Attempted preparation of ethyl 3-bromo-fluorenylacetate:-

Ethyl 3-bromo-fluorenylidene acetate (0·4 gm.) was dissolved in hot ethanol (20 ml.) and cooled rapidly with shaking. The suspension with Raney nickel (0·4 gm.) was placed in the hydrogenation flask and reduction was done at room temperature and pressure. After four hours, Raney nickel was filtered off. Evaporation of the solvent gave an oil, which could not be solidified.

Attempted preparation of 3-bromo-fluorene-9-acetic acid:-

The oil obtained in the previous experiment was refluxed with a mixture of 2N sodium hydroxide (3 ml.) and methanol (3 ml.) for two hours. Acidification gave a solid (50 mg.) with a wide range of melting point (100 - 125°). Various attempts to obtain a pure product were unsuccessful.

Attempted preparation of Ethyl (3-bromo-9-fluorenylidene)-cyano-acetate:-

Ethyl cyanoacetate (1·4 gm.), 3-bromofluorenone (2·6 gm.),

acetic acid (0·5 g.) and benzene (5 ml.) were placed in a flask attached to a Dean and Stark apparatus. The mixture was vigorously refluxed and ammonium acetate (0·3 g.) was added in small portions (50 mg.) every 3 hours. After refluxing for 24 hours, the mixture was allowed to cool, washed with water and after being dried, the solvent was distilled off. The remaining product which contained some black impurity was extracted with light petroleum. A yellow product m.p. 150° was deposited (1·8 g.). This when crystallised with benzene gave yellow needles, m.p. 158 - 160°. Mixed m.p. with 3-bromo-fluorenone was undepressed (158 - 160°). Two more experiments were conducted. In the first after 24 hours, an equal amount of catalyst was added portionwise and the mixture refluxed for 46 hours, while in the second the catalyst was added twice and the mixture boiled for 66 hours. Tar formation was observed in both cases and unreacted 3-bromo-fluorenone was recovered (as identified by mixed m.p.) in variable quantity.

3-Bromo-9-fluorenyldicyanoethylene:-

Malononitrile (0·4 gm.) in absolute alcohol (5 c.c.) was added dropwise to a boiling mixture of 3-bromo-fluorenone (1·3 gm.) in absolute alcohol (60 ml.), containing diethylamine (0·2 ml.) (which had been distilled over metallic sodium). The mixture was refluxed over night. On cooling, orange crystals of the dicyano-compound were filtered, washed with alcohol, and recrystallised from acetic acid.

m.p. 210 - 211°

yield 1·3 gm.

Analysis: $C_{16}H_7BrN_2$

requires N = 9·1%; Br = 26·1%.

found N = 9·3%; Br = 26·2%.

I.R. Spectrum: $2230^{cm^{-1}}$ (w) (C = N) Nujol

Hydrolysis of 3-bromo-9-fluorenyldicyanoethylene:-

3-Bromo-9-fluorenyldicyanoethylene (1·3 gm.) was refluxed with concentrated hydrochloric acid (70 c.c.) for 12 hours. It was poured onto ice and then extracted with ether. Removal of the solvent gave the original product.

m.p. 210 - 211°

mixed m.p. 210 - 211°

(2) A mixture of 3-bromo-fluorenylidenedicyano-ethylene (0·26 g.) and phosphoric acid (15 c.c.) was refluxed for 6 hours. It was poured into cold water and extracted with ether. Removal of ether gave a tar.

(3) A mixture of 3-bromo-fluorenylidenedicyanoethylene (0·26 g.) and 20 c.c. of a water-sulphuricacid-glacial acetic acid mixture (1:1:1) was boiled under reflux for 6 hours. The mixture was then poured into cold water (80 c.c.). The resulting precipitate was proved to be unchanged product.

m.p. 210 - 211°

mixed m.p. 210 - 211°

(4) The dinitrile (0·52 g.) suspended in ethanol (10 c.c.) and potassium hydroxide (0·55) in water (10 c.c.) was boiled for 12 hours. The solution was poured into water. The precipitate deposited was filtered, then dissolved in ether and extracted three times with sodiumbicarbonate solution. The principal filtrate and sodiumbicarbonate extracts on acidification gave a very small amount of acid (20 mg.) after standing over night. The ether layer was washed with water, dried and removal of solvent gave a yellow product, 3-bromofluorenone (0·25 gm.)

m.p. 150 - 155°

Two recrystallisations from benzene raised the m.p. to 157 - 158°.

Mixed m.p. with a sample of 3-bromofluorenone 156 - 158°.

(5) The hydrolysis (and attendant decarboxylation) was finally achieved when 3-bromo-fluorenyldicyanoethylene (1·5 gm.) was boiled under reflux in a mixture of hydriodic acid (S.G. 1·92) (15 ml.) and glacial acetic acid (15 c.c.) for 12 hours. The dark coloured solution was poured into an excess of sulphurous acid. The product obtained was dissolved in sodiumbicarbonate solution, filtered and reacidified. The crude 3-bromo-fluorene-9-acetic acid was recrystallised from benzene-light petroleum in colourless needles.

m.p. 137 - 139°

yield 0·45 gm.

Analysis: $C_{16}H_{11}BrO_2$

requires C = 59·4%; H = 3·6.; Br = 26·4%.

found C = 60·3%; H = 3·8%; Br = 25·5%.

I.R. Spectrum: $1682^{cm^{-1}}$ (s) (Carbonyl C = O) Nujol

N.M.R. Spectrum: τ 2·1 - 2·9 (complex 7 aromatic protons)

τ 5·65 (triplet 9-H proton J = 7 c/s)

τ 7·25 (doublet 2-methylene protons J = 9 c/s)

Preparation of 3,9-dibromo fluorene:-

Bachmann and Sheehan, J.A.C.S., 62, 2689.

3-Bromofluorene (1·3 g.) was refluxed in dry carbon tetrachloride (15 ml.) with N-bromo-succinimide (1·2 g.) over night. The succinimide floated over the surface was filtered off after cooling. The quantity of the solvent was reduced to half (8 c.c.) and was passed through a short column (3" x ½") of alumina with carbon tetrachloride as the eluent. The solvent was then evaporated off and the product obtained was crystallised twice from light petroleum which gave colourless fine needles of 3,9-dibromofluorene.

m.p. 135 - 136°

yield 0·9 gm.

Analysis: $C_{13}H_8Br_2$ requires Br = 49·4%

found Br = 48·4%

N.M.R. Spectrum: τ 2·2 - 2·8 (complex 7 aromatic protons)

τ 4·1 (singlet 9-H-proton)

Preparation of 3-bromo-9-fluorenylacetic acid:-

cf. Bachmann and Sheehan, J.A.C.S., 62, 2689.

Sodium (0·08 gm.) was dissolved in absolute ethyl alcohol

(6 ml.). Diethyl malonate (1 c.c.) was added dropwise to this solution, and the mixture was cooled to 5°. 3,9-Dibromofluorene (0·4 gm.) in benzene (3 c.c.) was added drop by drop to the chilled sodio-malonic ester solution in an atmosphere of nitrogen, and the mixture was refluxed for one and a half hours. Sodium bromide which precipitated was removed by filtration. The solvents were distilled off and the residual ester was hydrolysed with 40% aqueous potassium hydroxide solution. It was then acidified. Extracted with ether, washed with water and after being dried (Na_2SO_4), ether was distilled off. The residual product was heated at 200° for half an hour and after being cooled was extracted with sodiumbicarbonate solution. On acidification an oil was obtained, which on standing over the week-end became solid. 3-Bromofluorenyl acetic acid crystallised from light petroleum-benzene.

m.p. 137 - 140°

yield 0·04 gm.

Analysis: $C_{15}H_{11}BrO_2$

requires C = 59·4%; H = 3·6%; Br = 26·4%

found C = 60·6%; H = 4·0%; Br = 25·2%.

The method is obviously not of preparative value.

Preparation of 3-bromo-9-formylfluorene:-

cf. Von and Wagner. J. Org. Chem., 2, 155.

A mixture of 3-bromofluorene (1·3 g.), dry ether (6 ml.), ethyl formate (0·4 g.) and potassium methoxide (0·4 g.), (prepared from 0·2 g. of potassium) was heated under reflux on

a water bath, for 4 hours. The cooled mixture was extracted with water (10 ml.). The water extract was shaken with several small portions of ether and the aq. layer was then acidified with dilute sulphuric acid. The oil which separated was extracted in ether and was then washed with dilute sodium bicarbonate solution, then with water and dried. Evaporation of ether gave an oil (0·3 gm.), probably impure formyl-derivative.

I.R. Spectrum: $1705^{cm^{-1}}$ (s) (Aldehyde C = O) oil

Preparation of β-(3-bromo-9-fluorenyl)-acrylic acid:-

The above oil (0·3 gm.), malonic acid (0·15 gm.) and freshly distilled pyridine were heated together on a water bath over night. After cooling, the mixture was dissolved in ether and the ether layer was washed with water, then extracted with sodium carbonate solution. Acidification gave an oil. Various attempts to solidify by trituration with solvents failed. The oil was kept in cold storage for three weeks, and the few crystals formed were scratched, washed with light petroleum.

m.p. 113 - 114°

yield - very poor

Analysis: $C_{16}H_{11}BrO_2$

requires C = 60·9%; H = 3·5%; Br = 25·4%.

found C = 60·3%; H = 3·3%; -

I.R. Spectrum: $1700^{cm^{-1}}$ (s) (Carbonyl C = O) Nujol

3-Bromo-9-fluorene-carboxylic acid:-

Clean lithium (0·6 gm.) was cut into small pieces and dropped rapidly into anhydrous ether (40 ml.) in a nitrogen atmosphere. Bromobenzene (4 ml.) in ether (10 ml.) was placed in a dropping funnel. 2 ml. of this mixture was added to the reaction flask and the reaction was started by warming and stirring. The remaining solution was added dropwise to maintain gentle boiling. Boiling was continued for one hour and more anhydrous ether was added, during the boiling, from time to time to maintain the original volume. During the reaction most of the lithium had dissolved. The unreacted lithium (0·1 gm.) was removed by filtration through a cotton plug. The filtered solution was then added gradually to a solution of 3-bromofluorene (6·6 gm.) in anhydrous ether (200 ml.). It was stirred for ten minutes at room temperature under nitrogen. The nitrogen flow was stopped and carbon dioxide from a cylinder was passed first through conc. sulphuric acid and then into the ethereal solution of 9-lithio-3-bromo-fluorene for ten to fifteen minutes. It was then left over night to evaporate. The remaining solid obtained was shaken with a mixture of water and ether (2:1; 100 ml.). The layers were separated. The aqueous layer on acidification with dil. hydrochloric acid gave 3-bromo-9-fluorene-carboxylic acid. This was filtered, washed with water and dried.

m.p. 226 - 229°

yield 5·0 gm.

I.R. Spectrum: $1695^{cm^{-1}}$ (s) (Carbonyl C = O) Nujol

3-Bromo-9-Carbomethoxy-fluorene:-

3-Bromo-9-fluorene-carboxylic acid (6 gm.) was suspended in dry methanol (30 ml.). Dry hydrogen chloride was passed until a clear solution was obtained (fifteen minutes). It was set aside for 3 hours. Crystals formed, were filtered, washed with water and crystallised from methanol (4·0 gm.).

The mother liquor was poured into water. The product obtained, after standing over night, was recrystallised from methanol which gave a further amount of 3-bromo-9-carbomethoxyfluorene (0·4 gm.)

m.p. 102 - 104°

yield 4·4 gm.

I.R. Spectrum: $1720^{cm^{-1}}$ (s) (Ester C = O) Nujol

N.M.R. Spectrum: τ 2·1 - 2·9 (complex 7 aromatic protons)

τ 5·3 (singlet 9-H proton)

τ 6·4 (singlet 3-methyl protons)

3-Bromo-9-carbomethoxy-9(2-cyanoethyl)-fluorene:-

3-Bromo-9-carbomethoxyfluorene (0·5 gm.) was dissolved in dioxan (2·5 ml.) and trimethylbenzylammonium hydroxide (0·1 ml.) and acrylonitrile (0·2 ml.) were added separately dropwise to the stirred solution, at 35 - 40°. Stirring was continued for one hour at this temperature and then for two hours at room temperature. It was then poured into water (20 ml.). One ml. of 20% HCl was added. The resulting oil after standing for about three hours became solid. The cyano-ester was filtered, washed with water and recrystallised from methanol.

m.p. 114 - 115°

yield 0·42 gm.

I.R. Spectrum: $2240^{cm^{-1}}$ (m) (C ≡ N) ($CHCl_3$)

$1718^{cm^{-1}}$ (s) (Ester C = O)

N.M.R. Spectrum: τ 2·0 - 2·7 (complex 7 aromatic protons)

τ 6·4 (singlet 3-methyl protons)

τ 7·23 (triplet 2 methylene protons J = 8-9 c/s)

τ 8·32 (triplet 2 methylene protons J = 8-9 c/s)

3-Bromo-9-(2-carboxyethyl)-fluorene:-

H. Andrew, Thesis, Edinburgh, 1964.

The above cyano-ester (2·0 gm.) gave 3-bromo-9-(2-carboxyethyl)-fluorene (1·2 gm.)

m.p. 159 - 160° (lit. 160 - 161°)

I.R. Spectrum: $1705^{cm^{-1}}$ (s) (Carbonyl C = O) Nujol

N.M.R. Spectrum: τ 2·1 - 2·8 (complex 7 aromatic protons)

τ 5·85 - 6·05 (triplet 9-H proton)

τ 7·55 (m 2 methylene protons J = 1 c/s)

τ 7·95 (m 2 methylene protons J = 1 c/s)

8-Bromo-1,2,3,10b-tetrahydro-3-oxo-fluoranthene:-

H. Andrew, Thesis, Edinburgh, 1964.

(1) The previous acid (1·0 gm.) with HF gave 8-bromo-1,2,3,10b-tetrahydro-3-oxo-fluoranthene.

m.p. 171 - 172° (Lit. 173 - 174°)

yield 0·25 gm.

(2) 3-Bromo-9(2-carboxyethyl)-fluorene (1·0 gm.) and poly-phosphoric acid (25 gm.) were heated at 100° on a water bath for

one hour. The mixture was then heated for 20 minutes at 150 - 155° with occasional shaking. It was then poured into water and extracted with ether. The ether layer was washed with water, then twice with 10% aqueous sodium bicarbonate solution (50 ml.). Acidification of the aqueous layer gave a little acid (50 mg.). The ether layer was washed with water, dried (Na_2SO_4) and evaporated. The product obtained was dissolved in benzene and passed through a column of alumina (12" x 1"). Benzene was used as solvent and 20 fractions each of 10 ml. were collected. The first three dark yellow coloured fractions gave a minute quantity of oil. From the next two fractions a yellow product m.p. 140 - 155° (0·1 gm.) was obtained. Fractions from six to nine were pale yellow. Removal of the solvent gave a pale yellow product m.p. 160 - 163° (0·25 gm.). The remaining fractions (10 - 20) were almost colourless in visible light but gave a yellow fluorescence under U.V. light. Evaporation of benzene gave a dirty white product m.p. 165 - 167° (0·35 gm.)

The last two products (0·6 gm.) were combined and recrystallised from aqueous methanol, as colourless needles.

m.p. 167 - 169°

mixed m.p. with the above 168 - 169°

Yield 0·5 gm.

I.R. Spectrum: $1685^{cm^{-1}}$ (s) (Carboxyl C = O) Nujol

Preparation of substituted fluoranthene by aromatisation of cyclic ketones

Attempted preparation of benzo cyclohexenyl acetate:-

Cf. Edwards and Narashima Roa, J. Org. Chem., 1966, 31, 324.

(1) Tetralone (1 gm.) was dissolved in 100 ml. of reagent B (80 ml. of absolute ethyl acetate was added to 0·1 ml. of 72% perchloric acid and 9·6 ml. of acetic anhydride and the solution was made to 100 ml. with ethyl acetate). The solution was allowed to stand for ½ hour at room temperature, then washed with sodium bicarbonate solution, dried. Evaporation of the solvent gave the unchanged ketone almost quantitatively.

Cf. Hartshorn and Jones, J.C.S. 1962, 1316.

(2) Tetralone (5 c.c.) in carbontetrachloride (42 ml.) was treated with acetic anhydride (4 c.c.) and 66% aqueous perchloric acid (0·1 ml.) and the mixture was kept at room temperature for 24 hours. It was then diluted with ether (200 ml.), washed with sodium bicarbonate, water, brine and dried. Evaporation of solvent gave the starting material.

Cf. Berkoz, Chavez and Djerassi, J.C.S., 1962, 1327.

(3) An ice cold mixture of acetic anhydride (12 ml.) and 72% perchloric acid (20 drops) was added to tetralone (2·5 c.c.) dissolved in a mixture of benzene (80 ml.) and carbon tetrachloride (30 ml.). After standing for four hours at room temperature, ice water was added followed by more carbon tetrachloride, then the mixture was washed with water and worked up as in the previous case.

However the I.R. Spectrum indicated a weak peak of acetate at ν_{max} $1760^{cm^{-1}}$

No better results were obtained when the previous mixture was kept for 24 hours or heated at 45 - 50° for four hours.

Improved preparation of benzo cyclo hexenyl acetate:-

cf. Barton et al. J.C.S., 1954, 747.

A solution of tetralone (2·5 ml.) acetic anhydride (35 ml.) and toluene-p-sulphonic acid (2·5 gm.) was slowly distilled through a short column in four hours. Additional acetic anhydride (40 ml.) was added in portions from time to time during this distillation, the final volume being 20 ml. Most of the acetic anhydride was then removed under reduced pressure on a water bath. The residue was dissolved in ether, filtered, washed with 5% ice cold sodium hydroxide solution then water and dried. Evaporation of the solvent gave an oil. I.R. and G.L.C. suggested the formation of about 35% enol-acetate.

I.R. Spectrum: $1760^{cm^{-1}}$ (s) (Acetate; C = O) Oil

$1680^{cm^{-1}}$ (s), (Ketonic; C = O)

G.L.C. Analysis on a 6 ft. 15% P.E.G.A. column at 150° using N_2 as carrier gas at 15 lb. per sq. inch indicated 35% conversion.

Acetoxy-1-naphthol:-

The above mixture (2·5 gm.), chloranil (2 gm.) and sulphur free xylene (60 ml.) were boiled under reflux for 16 hours. After cooling the solution was decanted, diluted with ether (100 ml.)

washed with 5% sodium hydroxide solution, water and dried. Evaporation of the solvent gave an oil.

I.R. Spectrum: $1750^{cm^{-1}}$ (Acetate: C = O) (s) Oil
$1680^{cm^{-1}}$ (Ketonic; C = O) (s)

α -naphthol:-

The above mixture was heated with sodium hydroxide solution (10 ml.) and methanol (30 ml.) for four hours. The solution was concentrated to a small volume (10 ml.) After cooling a mixture of ether (50 ml.) and 2% sodium hydroxide (20 ml.) were added. The layers were separated. Acidification of the aqueous layer gave crude α -naphthol in small yield. This was purified by sublimation.

m.p. 95 - 96°.

mixed m.p. with α -naphthol 95 - 96°.

1,10b-dihydro-fluoranthene-3-acetate:-

3-oxo-1,2,3,10b-tetrahydrofluoranthene (0·9 gm.), acetic anhydride (30 ml.) and toluene-p-sulphonic acid (1 gm.) were distilled slowly through a column (10") for four hours. Additional acetic anhydride (50 ml.) was added from time to time during this distillation. Working up as before (page 116) gave an oil.

I.R. Spectrum: $1750^{cm^{-1}}$ (s) (Acetate; C = O) Oil
$1690^{cm^{-1}}$ (m) (Ketonic; C = O)
$1225^{cm^{-1}}$ (s)

Fluoranthene-3-acetate:-

The oil (1·0 gm.) was boiled with chloranil (1·0 gm.) and sulphur-free xylene for 16 hours. The experiment was further carried out as in the previous case (page 116) to yield a viscous oil.

I.R. Spectrum: $1750^{cm^{-1}}$ (s) (Acetate; C = O) Chloroform
$1690^{cm^{-1}}$ (m) (Ketonic; C = O)
$1220^{cm^{-1}}$

3-Hydroxy-fluoranthene:-

The dark red gum obtained in the previous experiment was hydrolysed with 10% NaOH(10 ml.) and methyl alcohol (30 ml.) by boiling under reflux for four hours. The experiment was worked up as in the previous case. Acidification of the aqueous layer gave yellow needles (0·25 gm.) m.p. 184 - 186°. A sample was recrystallised from methanol and the m.p. raised to 187 - 189°.

mixed m.p. with 3-hydroxy-fluoranthene 188 - 189°.

I.R. Spectrum: $3250^{cm^{-1}}$ (w) (OH) Nujol

8-Bromo-1,2-dihydro-fluoranthene-3-acetate:-

8-Bromo-3-oxo-1,2,3,10b-tetrahydrofluoranthene (0·9 gm.), toluene-p-sulphonic acid (1 gm.) and acetic anhydride (50 ml.) were distilled slowly through a column. By means of the method described above the enol-acetate was obtained as a red oil.

I.R. Spectrum: $1750^{cm^{-1}}$ (s) (Acetate; C = O) oil
$1695^{cm^{-1}}$ (m) (Ketonic; C = O)
$1220^{cm^{-1}}$

8-Bromo-fluoranthene-3-acetate:-

The reddish oil mixture (1 gm.), chloranil (1·0 gm.) and sulphur free xylene (25 ml.) were refluxed together for 16 hours to give the acetate as a semi-solid, which was not further purified.

I.R. Spectrum: $1750^{cm^{-1}}$ (s) (Acetate; C = O) Nujol
$1695^{cm^{-1}}$ (m) (Ketonic; C = O)
$1220^{cm^{-1}}$

8-Bromo-3-hydroxy-fluoranthene:-

The previous mixture (0·4 gm.), 10% NaOH (5 ml.) and methanol (15 ml.) were refluxed for four hours. The phenol was finally isolated as a pale yellow compound.

m.p. 182 - 188°

yield 0·07 gm.

Resolidified and melted > 350°

8-Bromo-3-methoxy-fluoranthene:-

To 8-bromo-3-hydroxy-fluoranthene (0·07 gm.) dissolved in chlorobenzene (10 ml.), anhydrous potassium carbonate (0·4 gm.) and dimethyl sulphate (1 ml.) were added. The mixture was refluxed for 1 hour, and filtered hot. The potassium carbonate residue was washed with a little hot chlorobenzene. This was cooled and diluted with ether (30 ml.) and washed with 5% sodium hydroxide solution (20 ml.), water and dried and the solvent was removed. The residue obtained was dissolved in benzene and passed through a short column of alumina using benzene as the

elute. Removal of the solvent gave a yellow product.

Crystallisation from methanol-acetic acid, or benzene-petroleum ether was not successful.

m.p. 168 - 173°

yield 30 mg.

Analysis: $C_{17}H_{11}BrO$

requires C = 65·6%; H = 3·5%; Br = 25·7%.

found C = 67·9%; H = 4·4%; Br = 22·75%.

I.R. Spectrum: $1270^{cm^{-1}}$ (m) $CHCl_3$ (OCH_3)

Obviously this contained some impurity.

8-Bromo-3-hydroxy-fluoranthene:-

8-Bromo-3-oxo-1,2,3,10b-tetrahydrofluoranthene (0·1 gm.) was dissolved in nitrobenzene (10 ml.) and two crystals of iodine added. The solution was boiled for fifteen minutes, cooled and the reagent removed by steam distillation. The solid residue in the distillation flask was collected and dried. It was dissolved in 2% NaOH and after filtration was reacidified.

m.p. 186 - 190°

yield 50 mg.

I.R. Spectrum: $3230^{cm^{-1}}$ (m) (OH) $CHCl_3$

8-Bromo-3-methoxy-fluoranthene:-

The crude material from the previous experiment (0·050 gm.), chlorobenzene (10 ml.) anhydrous potassium carbonate (0·5 gm.) and dimethyl sulphate (1 ml.) were heated under reflux for three hours. The experiment was further carried out as in the previous

case. Removal of the solvent gave 8-bromo-3-methoxyfluoranthene as a pale yellow product. This was recrystallised twice from acetic acid which gave light brownish yellow needles.

m.p. 173 - 175°

yield 0·020 gm.

Analysis: $C_{17}H_{11}BrO$

requires C = 65·6%; H = 3·5%; Br = 25·7%.

found C = 66·3%; H = 4·4%; Br = 25·7%.

I.R. Spectrum: $1270^{cm^{-1}}$ (m) (OMe) $CHCl_3$

2,8-Dibromo-3-methoxy-fluoranthene:-

8-Bromo-3-methoxy-fluoranthene (6 mg.) was dissolved in glacial acetic acid (0·2 ml.). Bromine (3 mg.) in acetic acid (0·1 ml.) was added. The mixture was heated for ½ hour at 60°. The few crystals separated out were scratched.

m.p. 160 - 162°

mixed m.p. with the authentic sample of 2,8-dibromo-3-methoxy-fluoranthene (m.p. 165 - 167°) = 160 - 162°.

SECTION III Part 2.

2-Bromo-fluorene:-

Gilmore. Ph.D. Thesis, 1940.

Fluorene (75 g.) on bromination in chloroform at 0° gave 2-bromo-fluorene. The crude product was recrystallised repeatedly (five times) from 85% ethanol.

m.p. 102 - 104°

yield 60 gm.

2-Bromo-7-nitro-fluorene:-

N. Campbell and Temple, J.C.S., 1957, 207.

2-Bromo-fluorene (60 g.) on nitration gave 2-bromo-7-nitro-fluorene, and the product was twice recrystallised from glacial acetic acid.

yield 32 gm. (45%)

m.p. 235 - 236°

lit. m.p. 236°

7-Amino-2-bromo-fluorene:-

S. Berkovic Israel J. Chemistry I, 1 (1963).

A mixture of 2-bromo-7-nitrofluorene (32 gm.), 80% ethanol (800 ml.), calcium chloride (9·0 g.) in water (20 ml.) and zinc dust (300 g.) was refluxed with stirring for 3½ hours. It was then filtered and the zinc dust residue was washed with a little hot ethanol and the filtrate was added to 4 litres of water. The white precipitate of the amine obtained was filtered and dried. This was sufficiently pure for the next stage.

m.p. 138 - 140°

yield 21 gm. (75 %)

A sample was recrystallised from ethanol

m.p. 140°.

lit. m.p. 140°

2-Bromo-7-hydroxy-fluorene:-

cf. Charlesworth and Blackburn, Cana. J. Chem., 42, 354.

7-Amino-2-bromo-fluorene (0·5 g.) was stirred in dried ether (75 ml.). Then conc. H_2SO_4 (0·20 ml.) was added with stirring. The amine sulphate was filtered off, allowed to dry and finely ground. The salt was added gradually to a stirred solution of conc. H_2SO_4 (19 ml.) and glacial acetic acid (19 ml.) with gentle warming to 60°. The solution was cooled to room temperature and then 40 c.c. of ice-water was added rapidly with stirring. The finally divided salt was diazotised at 15-20° by the addition of sodium nitrite (0·4 gm.) in water (3 ml.) and after stirring for five minutes it was filtered. This diazonium solution was added dropwise with stirring to a boiling 5% sulphuric acid solution (100 ml.). Heating and stirring were continued for another 10 minutes, and the solution then cooled. Reddish brown crystals of 2-bromo-7-hydroxy-fluorene (0·25 gm.) were obtained, and were recrystallised from benzene/light petroleum.

m.p. 172 - 175°

Analysis: $C_{13}H_9BrO$

requires C = 59·8%; H = 3·5%; Br = 30·7%

found C = 59·6%; H = 3·7%; Br = 29·4%

I.R. Spectrum: $3240^{cm^{-1}}$ (m) (OH) Nujol

(2) cf. Hodgson and Walker, J.C.S. 1933, 1620.

7-Amino-2-bromo-fluorene (0·5 gm.) was boiled in boiling acetic acid (16 ml.), and cooled rapidly to room temperature. The suspension was added gradually to nitrosyl sulphuric acid (2 c.c.) with stirring at about 15°C. The viscous solution thus obtained was filtered and then added gradually to boiling 5% H_2SO_4 (100 ml.). On cooling a dark red semi-solid product, insoluble in alkali, was obtained.

(3) cf. Craig, Ph.D. Thesis, Edinburgh, 1955, p.154.

Ice (100 gm.) was added to a solution of 7-amino-2-bromo-fluorene (0·5 gm.) in conc. H_2SO_4 (25 ml.), then a solution of sodium nitrite (0·18 gm.) in water (13 ml.) dropwise with stirring. The mixture was stirred for 45 minutes longer and then added over a period of 25 minutes to a boiling mixture of conc. H_2SO_4 (5 ml.) and water (250 ml.). The mixture was cooled, filtered, to give a reddish brown product. Attempts to recrystallise or to purify it met with no success.

m.p. 140 - 200°

cf. J. Weisburger and Elizabeth Weisburger, 1954, 758.

7-Amino-2-bromo-fluorene (5·4 g.) dissolved in glacial acetic acid was heated to 60°. At this temperature 10N H_2SO_4 (14 ml.) was added dropwise with stirring, the temperature being maintained 60 - 65°. Five minutes after the addition, the mixture was cooled

to 10°. A solution of $NaNO_2$ (1·7 g.) in 5 ml. of water was added dropwise at this temperature and stirred for 1 hour at 8 - 10°. During this period, the dirty green diazonium solution gave way to a yellow suspension. Urea (0·44 g.) in water (4 ml.) and cold 2·5N sulphuric acid (48 ml.) were added rapidly and stirring continued for another ten to fifteen minutes at the same temperature.

The suspension was added in portions over half an hour to a boiling, stirred mixture of xylene (36 ml.), (to prevent tar formation) and 2·1N sulphuric acid (144 ml.). After the addition the mixture was boiled and stirred for another 30 minutes and then allowed to cool. The reddish brown product (3·5 gm.) was filtered, washed thoroughly with water, dried and recrystallised from benzene-light petroleum in light brown needles.

m.p. 173 - 175°

yield 3·1 gm. (61%)

Mixed m.p. with 2-bromo-7-hydroxy-fluorene prepared by the 1st method = 172 - 174°.

2-Bromo-7-methoxy-fluorene:-

Anhydrous potassium carbonate (50 gm.) was added to a solution of 2-bromo-7-hydroxy-fluorene (5·0 gm.) in sulphur-free xylene (250 ml.). Dimethyl sulphate (40 c.c.) was then added with gentle stirring to this mixture, and the mixture was heated under reflux with gentle stirring. After two hours a fresh quantity of anhydrous potassium carbonate (20 gm.) and dimethyl sulphate (20 c.c.) was added and the solution was boiled with stirring for another hour. This was filtered hot after approximately three-quarters of the

solvent had been removed under reduced pressure. The potassium carbonate residue was pressed hard and washed three times with a little xylene. The filtrate and washings (70 ml.) were passed through a column of alumina (10" x 2") using benzene as solvent. A pale yellow band developed and came down smoothly. Removal of the solvent gave a red oil which solidified to a colourless product on cooling (3·5 g.).

The potassium carbonate residue was dissolved in water and the solution was extracted with ether. After being dried (Na_2SO_4), the ether was distilled off. The product was dissolved in benzene and passed through a short column of alumina (2" x ½") using benzene as solvent. Removal of benzene gave a further quantity (0·5 g.) of the product. The combined 2-bromo-7-methoxy-fluorene (4·0 g.) was recrystallised from ethanol (3·5 gm.).

m.p. 108 - 110° colourless needles.

yield 3·5 gm. (66%)

Analysis: $C_{14}H_{11}BrO$

requires C = 61·0%; H = 4·0%; Br = 29·1%.

found C = 60·7%; H = 4·0%; Br = 28·7%.

I.R. Spectrum: 1290 cm^{-1} (s) (OCH_3) Chloroform

N.M.R. Spectrum: τ 2·49 - 3·33 (complex 6 aromatic protons)

τ 6·19 (singlet 3 methonyl protons)

τ 6·35 (singlet 2 protons)

2-Bromo-7-methoxy-9-fluorene-carboxylic acid:-

The experiment was conducted exactly as in the case of 3-bromo-9-fluorene-carboxylic acid (page 111).

Phenyllithium was prepared from lithium (1·0 gm.) and bromobenzene (6 ml.) in ether (8 ml.). The unreacted lithium (0·12 gm.) was removed by filtration through a cotton plug. This filtrate was then added gradually to a solution of 2-bromo-7-methoxyfluorene (10·4 gm.) in anhydrous ether (300 ml.). After stirring for about 10 minutes, dried carbon dioxide gas was bubbled through the solution, and the solution was then worked up as in the previous case.

Acidification of the aqueous layer gave 2-bromo-7-methoxyfluorene-9-carboxylic acid.

yield 7·8 gm. (62%).

A sample was recrystallised from aqueous ethanol.

m.p. 216 - 218°.

Analysis: $C_{15}H_{11}BrO_3$

requires C = 56·4%; H = 3·45%; Br = 25·1%

found C = 55·8%; H = 3·4%; Br = 24·2%.

I.R. Spectrum: $1680^{cm^{-1}}$ (s) (Carbonyl; C = O) Nujol

$1270^{cm^{-1}}$ (m) (OCH_3)

2-Bromo-7-methoxy-9-carbomethoxy-fluorene:-

The acid (7·5 gm.) was suspended in anhydrous methanol (250 ml.) and dry HCl gas was passed till a clear solution was obtained (15 minutes). This was allowed to stand over night and then cooled. Cream coloured beautiful crystals were filtered. The filtrate on dilution with water gave a further quantity (0·5 gm.) of the ester. The combined products were recrystallised from methanol.

m.p. 126 - 127°.

yield 5·8 gm. (73%)

Analysis: $C_{16}H_{13}BrO_3$

requires C = 57·6%; H = 3·9%; Br = 24·1%

found C = 56·5%; H = 3·4%; Br = 24·4%

I.R. Spectrum: $1715^{cm^{-1}}$ (s) (Ester; C = O) Chloroform

$1280^{cm^{-1}}$ (m) (OCH_3)

N.M.R. Spectrum: τ 2·25 - 3·2 (complex 6 aromatic protons)

τ 5·25 (singlet 9-H 1-proton)

τ 6·2 (singlet 3-methoxy protons)

τ 6·3 (singlet 3-methyl protons)

2-Bromo-7-methoxy-9-carbomethoxy-9-(2-cyanoethyl)-fluorene:-

The above ester (4·0 gm.) was dissolved in dioxan (28 ml.). Trimethylbenzylammonium hydroxide (0·5 ml.) and acrylonitrile (1·1 ml.) were added at 35 - 40°. The experiment was then carried out as previously (page 112). Recrystallisation from acetic acid gave colourless long needles of the ester nitrile,

m.p. 162 - 163°

yield 3·4 gm. (74%)

Analysis: $C_{19}H_{16}BrNO_3$

requires C = 59·1%; H = 4·1%; Br = 20·7%; N = 3·6%

found C = 58·4%; H = 4·1%; Br = 20·1%; N = 3·4%.

I.R. Spectrum: $2220^{cm^{-1}}$ (w) (C ≡ N) Chloroform

$1715^{cm^{-1}}$ (s) (C = O)

$1290^{cm^{-1}}$ (m) (OCH_3)

N.M.R. Spectrum: τ 2·3 - 3·1 (complex 6 aromatic protons)

τ 6·1 (singlet 3 methoxy protons)

τ 6·35 (singlet 3 methyl protons)

τ 7·25 (triplet 2 methylene protons J = 6 - 7 c/s)

τ 8·35 (triplet 2 methylene protons J = 6 - 7 c/s)

2-Bromo-7-methoxy-~~9-carbomethoxy~~-9,9-di(2-cyanoethyl)-fluorene:- N

(1) 2-Bromo-7-methoxy-9-carbomethoxy-fluorene (1·0 gm.) was dissolved in dioxan (6 ml.). Then triton B 40% (2·5 ml.) and acrylonitrile (2 ml.) were added at 35° - 40°. The experiment was further carried out as above. The dicyano-compound obtained was recrystallised from glacial acetic acid and then from benzene/light petroleum.

m.p. 218 - 220°

yield 0·7 gm.

Analysis: $C_{20}H_{17}BrN_2O$

requires N = 7·35% Found N = 7·34%.

The filtrates were evaporated to give a dirty white product (m.p. 140 - 200°), which could not be purified.

I.R. Spectrum: $2240^{cm^{-1}}$ (s) (C ≡ N) Chloroform

No peak at $1715^{cm^{-1}}$

$1290^{cm^{-1}}$ (m) (OCH_3)

N.M.R. Spectrum: τ 2·3 - 3·2 (complex 6 aromatic protons)

τ 6·15 (singlet 3-methoxyl protons)

τ 7·6 (triplet 4 methylene protons J = 6-7 c/s)

τ 8·4 (triplet 4 methylene protons J = 6 - 7 c/s)

Hydrolysis of 2-bromo-7-methoxy-9,9-(di-2-cyanoethyl)-fluorene:-

The above di-nitrile (0·2 gm.) was hydrolysed by heating a mixture of glacial acetic acid-water-sulphuric acid 1:1:1, by weight (15 ml.), for five hours. This was poured into water (30 ml.) and extracted with ether. The ether was washed twice with water, and shaken with aqueous sodium bicarbonate solution. The acid, obtained by acidification of the aqueous layer, was filtered, dried and recrystallised from aqueous ethanol

m.p. 272 - 275°

yield 0·12 gm.

Analysis: $C_{20}H_{19}BrO_5$ requires C = 57·0%; H = 4·53%

found C = 56·1%; H = 4·55%

I.R. Spectrum: $1705^{cm^{-1}}$ (s) (Carbonyl; C = O) Chloroform

$1290^{cm^{-1}}$ (m) (OCH_3)

(2) 9-Carbomethoxy-fluorene (1·0 gm.) was dissolved in dioxan (6 ml.). Benzyl trimethylammonium hydroxide 40% (2·5 c.c.) and acrylonitrile (2·0 c.c.) were added all at once at 35 - 40°. The experiment was further carried out as in previous cases (page 112). The product obtained was recrystallised from ethanol which gave colourless needles.

m.p. 119°

Literature m.p. of 9,9-(di-2-cyanoethyl)-fluorene. 121°.

Analysis: $C_{20}H_{16}N_2$ requires N = 10·7%

found N = 10·3%

I.R. Spectrum: $2230^{cm^{-1}}$ (s) (C ≡ N) Chloroform

No peak at $1725^{cm^{-1}}$

N.M.R. Spectrum: τ 2·15 - 2·65 (complex 8 aromatic protons)

τ 7·52 (triplet 4 methylene protons J = 6 c/s)

τ 8·52 (triplet 4 methylene protons J = 6 c/s)

Reaction of acrylonitrile with 9-carbomethoxy-9-(2-cyanoethyl)-fluorene:-

9-Carbomethoxy-9-(2-cyanoethyl)-fluorene (0·1 gm.) was dissolved in dioxan (2·5 ml.). Benzyltrimethylammonium hydroxide (40%) (0·5 ml.) and acrylonitrile (0·5 ml.) were added separately at 38°. The experiment was further carried out as in previous cases. After two recrystallisations from ethanol colourless needles were obtained.

m.p. 119°.

mixed m.p. with 9,9-(di-2-cyanoethyl)-fluorene 118 - 119°.

I.R. Spectrum: Identical to the previous case.

N.M.R. Spectrum: τ 2·15 - 2·65 (complex 8 aromatic protons)

τ 7·52 (triplet 4 methylene protons J = 6 c/s)

τ 8·52 (triplet 4 methylene protons J = 6 c/s)

2-Bromo-7-methoxy-9-(2-carboxyethyl)-fluorene-9-carboxylic acid:-

2-Bromo-7-methoxy-9-carbomethoxy-9-(2-(cyanoethyl)-fluorene (1·6 gm.) was refluxed with a mixture of acetic acid-sulphuric acid-water (30 ml.) 2:1:1 by weight for six hours. This was poured into water (60 ml.) and kept overnight. The product was filtered, washed with water and crystallised from aqueous ethanol.

m.p. 206 - 209°

yield 1·5 gm.

Analysis: $C_{18}H_{15}BrO_5$

requires C = 55·2%; H = 3·8%; Br = 20·4%.

found C = 55·1%; H = 4·25%; Br = 19·4%

I.R. Spectrum: $1710^{cm^{-1}}$ (s) (Carbonylic C = O) Chloroform

$1290^{cm^{-1}}$ (m) (OCH_3)

Attempted decarboxylation[b] 2-bromo-7-methoxy-9-(2-carboxyethyl)-fluorene-9-carboxylic acid:-

(1) The above acid (0·2 gm.) was heated under reflux in methanol (10 ml.) with 5% sodium hydroxide (3 ml.) for 1 hour. It was poured into water (20 ml.) and acidified which gave an oil. Various attempts to solidify this did not meet with success.

(2) cf. Craig, Thesis, Edinburgh, 1955, 145.

The diacid (0·3) was dissolved in saturated sodium carbonate solution (18 ml.) and the solution was heated under reflux for 20 minutes. Acidification with concentrated hydrochloric acid gave a semi-solid, m.p. 45 - 65° contaminated with oil. Various attempts to purify it failed.

Similarly another attempt with sodiumbicarbonate under the same conditions failed.

Decarboxylation of 9-carboxy-9-(2-carboxyethyl)-fluorene:-

9-Carboxy-9-(2-carboxyethyl)-fluorene (0·2 gm.) was heated with pyridine (1 ml.) and a trace of copper at 230 - 240° for ten minutes. This was poured into water (10 ml.). Ether (20 ml.)

was added and the mixture was filtered to remove the copper powder. The ethereal layer was separated from the aqueous layers, and evaporated to dryness. The crude product was recrystallised from ethanol.

m.p. 137 - 139°

yield 0·05 gm.

Literature m.p. of -fluorene-9-propionic acid 141°.

Decarboxylation of 2-methoxy-7-bromo-9-carboxy-9-(2-carboxyethyl)-fluorene:-

The above acid (0·1 gm.), with pyridine (½ ml.) and a trace of copper were heated together at 220 - 230° for 10 minutes. This gave a product which was crystallised from aqueous methanol, which gave colourless needles of 2-methoxy-7-bromo-9-(2-carboxy-ethyl)-fluorene.

m.p. 104 - 106°

yield 15 mg.

Improved preparation of 2-bromo-7-methoxy-9-(2-carboxyethyl)-fluorene:-

2-Bromo-7-methoxy-9-carbomethoxy-9-(2-carboethyl)-fluorene (2·5 gm.) in 2-methoxy ethanol (35 ml.) and KOH (10 gm.) in water (20 ml.) were refluxed gently in a current of nitrogen, for forty minutes. A mixture of 2-methoxyethanol and water 1:1 by volume (10 ml.) was added in portions to maintain the volume. The mixture was poured into water (100 ml.), and acidified. This yielded an oily precipitate of the propionic acid which soon solidified, and crystallised from aqueous methanol as colourless neelds

m.p. 105 - 107°

yield 1·4 gm.

Analysis: $C_{17}H_{15}BrO_3$

requires C = 58·8%; H = 4·3%; Br = 23·0%

found C = 58·7%; H = 4·3%; Br = 22·2%

I.R. Spectrum: $1700^{cm^{-1}}$ (s) (Carbonyl; C = O) Nujol

N.M.R. Spectrum: τ 2·3 - 3·25 (complex 6 aromatic protons)

τ 5·90 (triplet 9-H 1-proton)

τ 6·15 (singlet 3-methyl protons)

τ 7·3 - 8·4 (multiplet 4-methylene protons)

It is noteworthy that when the above experiment was carried out without nitrogen atmosphere, an oil was obtained which could not be purified.

Action of benzyltrimethylammonium hydroxide on 2-methoxy-9-fluorene-carboxylic acid:-

2-Methoxy-9-fluorene-carboxylic acid (0·1 gm.) was dissolved in dioxan (2·5 ml.) and Triton B 40% (0·6 ml.) was added at 40 - 45° all at once with stirring. The experiment was further carried out as in the previous case (p.112). The crude product (m.p. 68 - 72°) was recrystallised from ethanol.

m.p. 73 - 75°

mixed m.p. with 2-methoxyfluorenone = 74°

yield 60 mg.

No original acid recovered

I.R. Spectrum: $1710^{cm^{-1}}$ (s) (Ketonic; C = O) Chloroform

$1290^{cm^{-1}}$ (s) (OCH_3)

Action of benzyltrimethylammonium hydroxide on 3-bromo-9-fluorene-carboxylic acid:-

The experiment was carried out exactly as in the previous cases. 3-Bromo-9-fluorene-carboxylic acid (0·1 gm.) gave 3-bromo-fluorenone (60 mg.)

m.p. 159 - 161°

mixed m.p. with 3-bromo-fluorenone 158 - 161°

No original acid was recovered.

I.R. Spectrum: $1710^{cm^{-1}}$ (s) (Ketonic; C = O) Chloroform
$1298^{cm^{-1}}$ (s) (OCH_3)

Action of benzyltrimethylammonium hydroxide on 2-bromo-7-methoxy-9-fluorene-carboxylic acid:-

2-Bromo-7-methoxy-9-fluorene-carboxylic acid (0·1 gm.) was dissolved in dioxan (2·5 ml.) and Triton B 40% (0·6 ml.) was added with stirring at 40° all at once. The stirring was continued for 1 hour at 45 - 50° and then the water bath was allowed to cool to room temperature. Stirring was continued for another two hours. The solution was poured into diluted 2% HCl (10 ml.). The orange precipitate was filtered, washed with water and then shaken with warm sodium bicarbonate solution, again washed with water, dried, and recrystallised from glacial acetic acid which gave long orange coloured needles.

m.p. 168 - 169°

yield 80 mg.

mixed m.p. with 2-bromo-7-methoxyfluorenone 167 - 168°.

I.R. Spectrum: $1720^{cm^{-1}}$ (s) (Ketonic; C = O) Chloroform

$1295^{cm^{-1}}$ (s) (OCH_3)

Action of Triton B on 9-fluorene-carboxylic acid:-

The experiment was done as in the previous cases. 9-Fluorene-carboxylic acid (0·1 gm.) gave impure fluorenone (50 mg.) m.p. 65 - 75°, raised to 79 - 81° after three recrystallisations. Yield 10mg.

m.p. 79 - 81°

mixed m.p. with fluorenone 78 - 80°

I.R. Spectrum: $1710^{cm^{-1}}$ (s) (Ketonic; C = O) Chloroform

9-Fluorene-carboxylic acid recovered (25 mg.)

m.p. 221 - 223° (mixed m.p. undepressed)

Action of Triton B on fluorene:-

Fluorene (0·2 gm.) was treated with Triton B 40% as in the previous cases. The pale yellow product (m.p. 80 - 100°) was dissolved in benzene and passed through a short column of alumina. The first three colourless fractions each of 20 ml. were collected together. On evaporation of the solvent crude fluorene (m.p. 102 - 106°) was obtained, which was recrystallised from ethanol.

m.p. 108 - 112°.

mixed m.p. with fluorene 110 - 112°

yield 0·12 gm.

The last fourth fraction which was yellow in colour gave a yellow product (20 mg.)

m.p. 70-130°

Action of benzyltrimethylammonium hydroxide on 2-methoxy-9-fluorene-carboxylic acid under nitrogen:-

The whole apparatus was flushed initially with nitrogen. 2-Methoxy-fluorene-9-carboxylic acid (0·1 gm.) was dissolved in dioxan (3 ml.) and Triton B (0·6 ml.) was added. The experiment was conducted further as in a previous case (page 134) under nitrogen. The solution was then poured into 2% HCl (10 ml.). The suspension was allowed to stand overnight, filtered, washed with water. The product obtained was shaken with a warm solution of sodium bicarbonate, which on acidification gave 2-methoxy-9-fluorene-carboxylic acid.

m.p. 184 - 185°

mixed m.p. with 2-methoxy-9-fluorene-carboxylic acid 183-185°.

yield 60 mg.

Action of benzyltrimethylammonium hydroxide on 9-fluorene-carboxylic acid under nitrogen:-

The experiment was conducted exactly as in the previous case. From 0·2 gm. 9-fluorene-carboxylic, 0·13 gm. of the original acid recovered.

m.p. 216 - 220°

mixed m.p. 217 - 222°

Attempted preparation of 9-bromo-4-methoxy 1,2,3,10b-tetrahydro-3-oxo-fluoranthene:-

(1) 2-Bromo-7-methoxy-9-(2-carboxyethyl)-fluorene (0·2 gm.) was heated with PPA (3 gm.) on a boiling water bath for 1 hour. Then

it was heated for twenty minutes at 150 - 160°. The product was poured into water (15 ml.). The reddish brown precipitate thus obtained was filtered, washed with water, $NaHCO_3$, water and dried. Attempts to recrystallise did not meet with success.

m.p. 250 - 340°

(2) When the acid (0·1 gm.) was heated at 100° for ½ hour and poured into water, the starting material was recovered (60 mg.)

m.p. 100 - 104°.

mixed m.p. 100 - 103°.

2-Hydroxy-fluorene:- (cf. p.124)

2-Amino-fluorene (20 gm.) gave 2-hydroxy-fluorene (10·5 gm.)

m.p. 170°

Literature m.p. 169 - 171°

I.R. Spectrum: $3270^{cm^{-1}}$ (m) (OH) Chloroform

2-Methoxy-fluorene:- (cf. p.125)

2-Hydroxy-fluorene (10·0 gm.) gave 2-methoxy fluorene (8·5 gm.).

m.p. 106 - 108°

Literature m.p. 109°

I.R. Spectrum: $1280^{cm^{-1}}$ (m) (OCH_3) Chloroform

2-Methoxy-9-fluorene-carboxylic acid: (cf. p.111)

Phenyllithium was prepared from lithium (0·8 gm.) and bromobenzene (4 ml.) in ether (6 ml.). The unreacted lithium (0·2 gm.) was removed by filtration through a cotton plug. This was then added gradually to a solution of 2-methoxy-fluorene (8 gm.) in

anhydrous ether (200 ml.). After stirring for about 10 minutes at room temperature, dried carbon dioxide gas was bubbled through the solution, which was then worked as in previous cases. Acidification of the aqueous layer gave 2-methoxy-fluorene-9-carboxylic acid. This was recrystallised from aqueous methanol in colourless needles.

m.p. 184 - 185°

yield 4·3 gm.

Analysis: $C_{15}H_{12}O_3$ requires C = 75·0%; H = 5·0%

found C = 74·8%; H = 5·25%.

I.R. Spectrum: $1710^{cm^{-1}}$ (s) (C = O) Chloroform

N.M.R. Spectrum: τ 2·15 - 3·15 (complex 7 aromatic protons)

τ 5·2 (singlet 9-H 1-proton)

τ 6·15 (singlet 3-methyl proton)

2-Methoxy-9-carbomethoxy-fluorene:-

A mixture of 2-methoxy-fluorene-9-carboxylic acid (3·8 gm.), methanol (35 ml.), and conc. H_2SO_4 (1·0 ml.) was heated under reflux for three hours. Then half of the methanol was distilled off and the cooled solution was poured into water. It was extracted with ether, washed with water, sodium bicarbonate solution (twice; no acid recovered) and then with water and finally dried over anhydrous sodium sulphate. Removal of the solvent gave the ester as a pale yellow viscous oil

yield 3·4 gm.

I.R. Spectrum: $1725^{cm^{-1}}$ (s) Oil in Chloroform

$1285^{cm^{-1}}$ (m) (OCH_3)

2-Methoxy-9-carbomethoxy-9-(2-cyanoethyl)-fluorene:- (cf. p.112)

The above ester (3·4 gm.) was dissolved in dioxan (12 ml.). Triton B 40% (0·15 ml.) and acrylonitrile (0·75 gm.) were added at 40°. The resulting cyano-ester was recrystallised from ethanol.

m.p. 119 - 120°

yield 3·0 gm.

Analysis: $C_{19}H_{17}NO_3$

requires C = 74·3%; H = 5·5%; N = 4·5%

found C = 74·6%; H = 5·78%; N = 4·3%

N.M.R. Spectrum: τ 2·25 - 3·15 (complex 7 aromatic protons)

τ 6·15 (singlet 3-methyl protons)

τ 6·45 (singlet 3-methyl protons)

τ 7·25 (triplet 2-methylene protons J = 7 - 8 c/s)

8·38 (triplet 2-methylene protons J = 7-8 c/s)

I.R. Spectrum: $2240^{cm^{-1}}$ (m) (C ≡ N) Chloroform

$1725^{cm^{-1}}$ (s) (Ester; C = O)

$1285^{cm^{-1}}$ (m) (OCH_3)

2-Methoxy-9-carboxyethyl-9-fluorene-carboxylic acid:-

2-Methoxy-9-carbomethoxy-9-(2-cyanoethyl)-fluorene (0·2 gm.) was heated under reflux with a mixture of acetic acid-sulphuric acid-water (15 ml.) 1:1:1 by weight for three hours. The mixture was then poured into water, and extracted with ether. The ether layer was washed with water and extracted with aqueous sodium bicarbonate solution. This was acidified and the product was

allowed to stand overnight. The crystals obtained were filtered, washed with water and dried, m.p. 194 - 197°.

Analysis: $C_{18}H_{16}O_5$ requires C = 69·2%; H = 5·12%

found C = 67·5%; H = 5·14%

I.R. Spectrum: $1718^{cm^{-1}}$ (s) (Carbonyl; C = O) Nujol

2-Methoxy-9-(2-carboxyethyl)-fluorene:-

2-Methoxy-9-carbomethoxy-9-(2-cyanoethyl)-fluorene (0·6 gm.), 2-methoxy-ethanol (12 c.c.) and 10N KOH (3 ml.) were gently refluxed under nitrogen for 20 minutes. The solution was then poured into water (30 ml.), and acidified. The precipitate obtained was washed with water, dried and recrystallised from aqueous methanol which gave rhombic crystals.

m.p. 139 - 140°

Analysis: $C_{17}H_{16}O_3$ requires C = 76·1%; H = 6·0%

found C = 76·8%; H = 6·0%.

I.R. Spectrum: $1705^{cm^{-1}}$ (s) (Carbonyl; C = O) Chloroform

$1280^{cm^{-1}}$ (m) (OCH_3)

N.M.R. Spectrum: τ 2·2 - 3·2 (complex 7 aromatic protons)

τ 5·97 (triplet 9-H-1 proton J = 6 c/s)

τ 6·15 (singlet 3 methoxyl protons)

τ 7·68 (Multiplet 2-methylene protons)

τ 8·05 (multiplet 2 methylene protons)

4-Methoxy-1,2,3,10b-tetrahydro-3-oxo-fluoranthene:-

(1) 2-Methoxy-9-(2-carboxyethyl)-fluorene (0·1 gm.) and PPA (2 gm.) were heated together for 1 hour at 100° on a steam bath. Then the mixture was heated at 150 - 160° for 20 minutes and poured into water (20 ml.). This was extracted twice with chloroform, washed twice with water, then twice with 3% NaOH, and several times with water. The chloroform layer was dried over anhydrous sodium sulphate and evaporated off. The resultant reddish brown gum could not be crystallised.

(2) 2-Methoxy-9-(2-carboxyethyl)-fluorene (0·1 gm.) was dissolved in benzene (3 ml.) and thionyl chloride (0·2 ml.) was added. The mixture was allowed to stand at room temperature for two hours, and the solvent and excess of thionyl chloride were removed under reduced pressure on a water bath at 50°. A fresh quantity of benzene (1 ml.) was added and removed by means of a water pump. The process was repeated twice to remove any trace of thionyl chloride.

The acid chloride in 2 c.c. of benzene was cooled in a freezing mixture until the benzene began to crystallise then removed from the cooling bath and treated rapidly with a chilled solution of stannic chloride (0·2 ml.) in 1 ml. of benzene. The mixture was swirled and a red slurry was obtained. After keeping for ten minutes, the mixture was poured into ice, and 5 c.c. of ether and 5 c.c. of 10% HCl were added. The product dissolved in the ether and then ether (10 ml.) was added The ether layer was washed three times with 10% HCl, water, $NaHCO_3$ solution and several times

with water, dried and evaporated off. The product obtained was recrystallised from aqueous methanol and then from benzene/light petroleum (100 - 120) which gave rectangular prisms of 4-methoxy-1,2,3,10b-tetrahydro-3-oxo-fluoranthene.

m.p. 124 - 125°

yield 25 mg.

Analysis: $C_{17}H_{13}O_2$ requires C = 81·6%; H = 5·6%.

found C = 81·9%; H = 6·2%.

I.R. Spectrum: $1685^{cm^{-1}}$ (s) (Ketonic; C = O) Chloroform

9-Bromo-4-methoxy-1,2,3,10b-tetrahydro-3-oxo-fluoranthene:-

2-Bromo-7-methoxy-9-(2-carboxyethyl)-fluorene (0·5 gm.) was dissolved in anhydrous ether (5 c.c.) and then to the cold solution thionyl chloride (0·5 ml.) and a trace of pyridine were added. The solution was kept at room temperature for 3 hours with occasional shaking, and then heated under reflux gently on a water bath for ten minutes. The thionyl chloride and ether were removed at 35° under reduced pressure (water bath). Dry benzene (2 c.c.) was added and distilled off under reduced pressure. The process was once repeated. The acid chloride obtained was dissolved in benzene (3 c.c.), and cooled in an ice-salt mixture. When the benzene began to crystallise it was removed from the cooling bath and added rapidly with shaking to a chilled solution of stannic chloride (0·35 c.c.) in benzene (3 c.c.). Immediately a red colour complex formed. This was placed in ice water for ½ hour and then at room temperature for 2 hours and poured into water. This was worked up as before. The cyclised ketone was recrystallised twice from

methanol/acetic acid which gave colourless needles.

m.p. 168 - 169°

yield 0·25 gm.

Analysis: $C_{17}H_{13}BrO_2$

requires C = 62·1%; H = 4·0%; Br = 24·2%

found C = 62·4%; H = 4·2%; Br = 22·7%

I.R. Spectrum: $1680^{cm^{-1}}$ (s) (C = O) Chloroform

$1600^{cm^{-1}}$ (s) (C = C)

$1280^{cm^{-1}}$ (m) (OCH_3)

$970^{cm^{-1}}$ (s)

9-Bromo-4-methoxy-1,2,3,10b-tetrahydro-3-hydroxy-fluoranthene:-

The above ketone (0·16 gm.) was suspended in methanol (8 ml.). Sodium-borohydride (50 mg.) was added in portions with vigorous stirring at 15 - 20°. The stirring was continued for 1 hour and during which a clear colourless solution formed. This was poured into water (20 ml.). 10% HCl (2 c.c.) was added. The product was deposited after keeping the solution for 3 hours in ice-water. It was filtered, washed with water and dried. Recrystallised from aqueous methanol which gave plates.

m.p. 135 - 137°

yield 0·11 gm.

I.R. Spectrum: $3520^{cm^{-1}}$ (m) (OH) Chloroform

$1280^{cm^{-1}}$ (m) (OCH_3)

Analysis: $C_{17}H_{15}BrO_2$ requires C = 61·6%; H = 4·6%.

found C = 62·5%; H = 5·0%.

9-Bromo-4-methoxy-1,10b-dihydro-fluoranthene:-

9-Bromo-4-methoxy-1,2,3,10b-tetrahydro-3-hydroxy-fluoranthene (90 mg.) and 98% formic acid (1·5 ml.) were heated on a steam bath for ½ hour. The milky solution formed, was poured into water (10 ml.). This was extracted with ether, washed with water and dried. Removal of solvent gave a pale yellow product.

m.p. 120 - 124°

yield 45 mg.

Attempted preparation of 8-bromo-3-methoxy-fluoranthene:-

The above di-hydro product (45 mg.) was heated under reflux with chloranil (60 mg.) in sulphur free xylene (4 ml.) for 3 hours. It was allowed to cool. The solution was filtered, diluted with ether and shaken twice with 2% NaOH (10 c.c.). The ether extract was washed with water and dried. Removal of solvent gave a yellow product (30 mg.). This was dissolved in benzene and passed through a short column of alumina using benzene as the solvent. A pale yellow band developed and came down smoothly. Benzene was distilled off. The pale yellow product (20 mg.) was heated with acetic acid, and the insoluble portion was filtered off. The m.p. of this was found 195 - 200°. The acetic acid filtrate did not give any crystallised product. Evaporation of the solvent gave a crude product (5 mg.) m.p. 164 - 170°, suggesting that it is impure 8-bromo-3-methoxy-fluoranthene.

I.R. Spectrum: $1690^{cm^{-1}}$ (Carbonyl; C = O), (w), Chloroform

$1290^{cm^{-1}}$ (OCH_3) (m).

Miscellaneous Experiments

Wilshire (170) prepared 1-hydroxy-2-nitro-1,2,3,10b-tetrahydrofluoranthene. The work was repeated and the assigned structure was confirmed by its I.R. Spectrum.

1,2,3,10b-tetrahydrofluoranthene:-

Wilshire, Ph.D. Thesis, 1952, p.100.

Fluoranthene (50 gm.) with 5% sodium amalgam gave 1,2,3,10b-tetrahydrofluoranthene (42.0 gm.).

m.p. 75 - 77°

Sodium amalgam was prepared by following the directions of Hollemann (171) It may be pointed out that the method for the preparation of sodium amalgam given by Fiser (172) when attempted produced an explosion,

2-Nitro-1-hydroxy-1,2,3,10b-tetrahydrofluoranthene:-

Wilshire, Ph.D. Thesis, 1952, p.101.

1,2,3,10b-tetrahydrofluoranthene (20 gm.) gave 2-nitro-1-hydroxy-1,2,3,10b-tetrahydrofluoranthene

m.p. 192 - 193°

I.R. Spectrum: $3250^{cm^{-1}}$ (m) (OH) Nujol

$1560^{cm^{-1}}$ (s) (NO_2)

3,6-Dimethyl-fluoranone was prepared for the study of its I.R. Spectrum.

3-Bromo-4-aminotoluene:-

Gennady M. Kosolapoff, J.A.C.S., 75, 3596.

p-Toluidine (21·4 gm.) gave 3-bromo-4-amino-toluene (19·8 gm.)

B.p. 142 - 145/22 mm.

2-Bromo-4-methylbenzonitrile:-

Lindemann and Pabst, Ann. 462, 39.

3-Bromo-4-aminotoluene (19·5 gm.) gave 2-bromo-4-methyl-benzonitrile (10·0 gm.)

m.p. 50°

Attempted preparation of 3,3'-dimethyl-diphenyl-6,6'-dinitrile:-

2-Bromo-4-methylbenzonitrile (2·5 gm.) was refluxed with copper bronze (4 gm.) in dimethylformamide (25 ml.) for three hours. It was filtered and poured into water. The sticky gum like product was dissolved in benzene and passed through a column of alumina. Evaporation of the solvent gave the starting material.

m.p. 50°

mixed m.p. with the original product 48 - 50°.

3-Nitro-p-toluidine:-

Nolting and Collin, Ber, 17, 263.

p-Toluidine (10 gm.) gave 3-nitro-p-toluidine (8 gm.).

m.p. 114°.

3-Nitro-4-tolunitrile:-

Mayer and Günther, Ber, 63, 1458 (1930).

3-Nitro-toluidine (15·2 gm.) gave 3-nitro-4-tolunitrile (7·5 gm.).

m.p. 105°.

2-Amino-4-methyl-benzoic acid:-

Mayer and Günther, loc. cit.

The above nitrile (5 gm.) gave 4-methyl-2-amino-benzoic acid (3·0 gm.).

m.p. 175°.

5,5'-dimethyl-diphenyl-2,2'-diacid:-

Chardonnens and Würmli, Hel. Chem. Acta, 29, 922.

2-Amino-4-methyl-benzoic acid (5 gm.) gave 5,5'-dimethyl-diphenyl-2,2'-diacid (2·5 gm.).

m.p. 230°

Attempted preparation of 3,6-dimethylfluorenone:-

Chardonnens and Würmli, loc. cit.

5,5'-dimethyl-diphenyl-2,2'-diacid (2·0 gm.) was heated with calcium oxide (5 gm.) at 350°. After 2 hours the temperature was raised to 450°, and kept for ½ hour. After cooling the product was poured into water. Ether extraction was unsuccessful and the product melted over a wide range.

m.p. 250 ÷ 350°.

4-Methyl-2-tosylamino-benzoic acid:-

Chardonnens and Würmli, loc. cit.

2-Amino-4-methyl-benzoic acid (4 gm.) gave 4-methyl-2-tosylamino-benzoic acid (4·5 gm.).

m.p. 201°.

4,4'-dimethyl-2-aminobenzophenone:-

Chardonnens and Würmli, loc.cit.

4-Methyl-2-tosylamino-benzoic acid (2·0 gm.) gave 4,4'-dimethyl-2-aminobenzophenone (0·6 gm.).

m.p. 117°.

3,6-dimethyl-fluorenone:-

Chardonnens and Würmli, loc. cit.

Dimethyl-amino-benzophenone (0·6 gm.) gave 3,6-dimethyl-fluorenone. The crude product was steam distilled and recrystallised from acetic acid.

yield 0·05 gm.

m.p. 118°

I.R. Spectrum: $1705^{cm^{-1}}$ (s) (C = O) Nujol

$1610^{cm^{-1}}$ (s) (C = C)

$858^{cm^{-1}}$ (s) (1,2,4 substitution)

$780^{cm^{-1}}$ (s)

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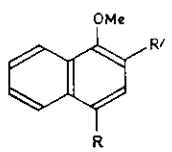
Reactivity of 1-Halogenonitronaphthalenes

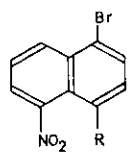
By Neil Campbell and Naim Masood Hasan

Department of Chemistry, University of Edinburgh

Nitration of 1-iodo-4-methoxynaphthalene (I, R = I, R′ = H) by fuming nitric acid in acetic acid is accompanied by the elimination of the iodine to give 1-methoxy-2,4-dinitronaphthalene (I, R = R′ = NO_2). Other instances of the liberation of iodine during nitration have been observed in iodobenzene derivatives[1] and iodonaphthalene derivatives[2,3] but with certain exceptions[4] the products have not been identified.



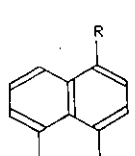
(I)



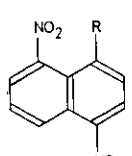
(II)

It was of interest to prepare the isomeric 1-methoxy-4,8-dinitronaphthalene (IV, R = OMe) and this was done by taking advantage of the activating influence of the nitro-groups in 1-chloro-4,8-dinitronaphthalene[5] to convert it into the desired compound by means of methanol and sodium methoxide. It is probable that both groups activate the chlorine and we have now found other examples of the effect of the 8-nitro group on a halogen atom in the 1-position of the naphthalene molecule.[2,6] An example is 1,4-dibromo-5-nitronaphthalene (II, R = Br)[7,8] which with copper bronze and benzoic acid[9] gives 1-bromo-5-nitronaphthalene (II, R = H), m.p. 122°, while 1-iodo-8-nitronaphthalene with the same reagent yields 1-nitronaphthalene, m.p. 56–57°. It is noteworthy that 1-bromo-8-nitronaphthalene does not exhibit the reactivity towards piperidine shown by 1-bromo-2-nitronaphthalene.[8]

The nitration of 1-bromonaphthalene yields mainly 1-bromo-4,5-dinitronaphthalene (III, R = Br) along with the 4,8-dinitro isomer (IV, R = Br),[10] which with copper and benzoic acid yield respectively 1-8,dinitronaphthalene (III, R = H), m.p. 171°, and 1.5-dinitronaphthalene (IV, R = H), m.p. 216°, with sublimation. It may be pointed out that the structure of 1-bromo-4,8-dinitronaphthalene has never been rigidly established and its implicit acceptance rests on a statement in Beilstein's *Handbuch der Organischen Chemie*, V, 562. The above reaction provides a simple and unambiguous confirmation of the structure of this compound.



(III)



(IV)

Fuming nitric acid (8 c.c.) was added with stirring at room temperature to 1-iodo-4-methoxynaphthalene[11] (1 g.) in acetic acid (10 ml.) and after 30 minutes the supernatant liquor was decanted from the black residue and poured into water. The precipitate was washed with sodium thiosulphate and extracted with ether. Removal of the solvent gave a product, most of which dissolved in boiling light petroleum (b.p. 60–80°). The cooled solution deposited 1-methoxy-2,4-dinitronaphthalene, yellow needles (from methanol) (0·15 g.), m.p. 96–97°, not depressed when admixed with an authentic sample prepared by nitrating 1-methoxy-4-nitronaphthalene[12] with fuming nitric acid in acetic acid (Found: C, 53·7; H, 3·5; N, 11·4. Calc. for $C_{11}H_8N_2O_5$: C, 53·2; H, 3·25; N, 11·3%).

1-Chloro-4,8-dinitronaphthalene (1 g.) suspended in boiling methanol (25 ml.) was added (5–10 min.) to 2% sodium methoxide (20 ml.) and the red solution was boiled (5·5 hr). On cooling 1-methoxy-4,8-dinitronaphthalene was deposited, light yellow needles (from acetic acid), m.p. 161–162° (Found: C, 53·4; H, 3·15; N, 11·5. $C_{11}H_8N_2O_5$ requires C, 53·2; H, 3·25; N, 11·3%).

The other products reported above were identified by lack of m.p. depression when admixed with authentic samples.

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