PART II

STUDIES IN FLUORENE DERIVATIVES

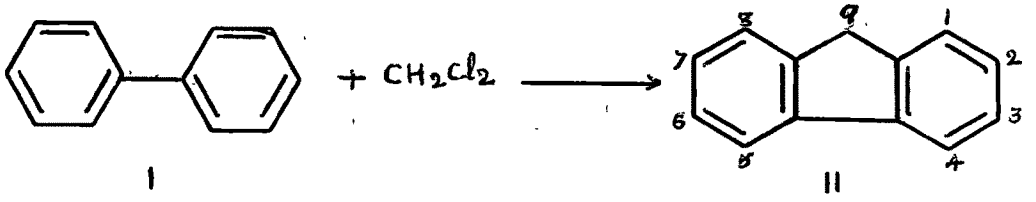
Fluorene was isolated by Berthelot[1] from the crude anthracene oil boiling between 300-310°. Later Barbier[2] improved Berthelot's method and obtained fluorene in large quantities.

Fluorenone can be obtained by the oxidation of fluorene by various oxidising agents or from phenanthraquinone. Fittig and Ostermayer[3] obtained fluorenone by the oxidation of phenanthraquinone and subsequent distillation of this acid with soda lime. Postovaski and Lugovkin[4] have shown that fluorene is converted to fluorenone in 5 % yield only by heating with selenium dioxide at 235°. Courtot[5] obtained fluorenone in quantitative yield by oxidising fluorene with potassium permanganate at room temperature. A convenient method for the preparation of fluorenone derivatives is to oxidise suitable fluorene derivatives by sodium dichromate in acetic acid[6]. Huntress, Herschburg and Cliff[6] carried out various studies on the conversion of diphenic acids into fluorenone derivatives.

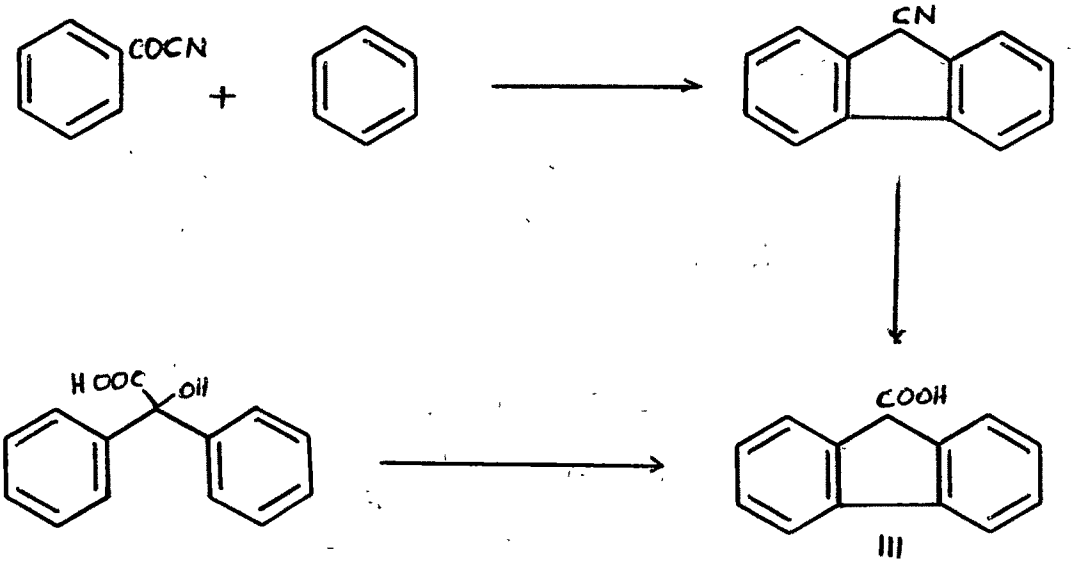
The synthesis of substituted fluorene and fluorenone can be attained either by direct substitution in fluorene or fluorenone or by converting properly substituted compounds into fluorene or fluorenone derivatives.

Synthesis of fluorene and fluorenone derivatives :

Adam[7] showed that biphenyl (I) and methylene dichloride under the conditions of Friedel-Crafts reaction gives fluorene (II).

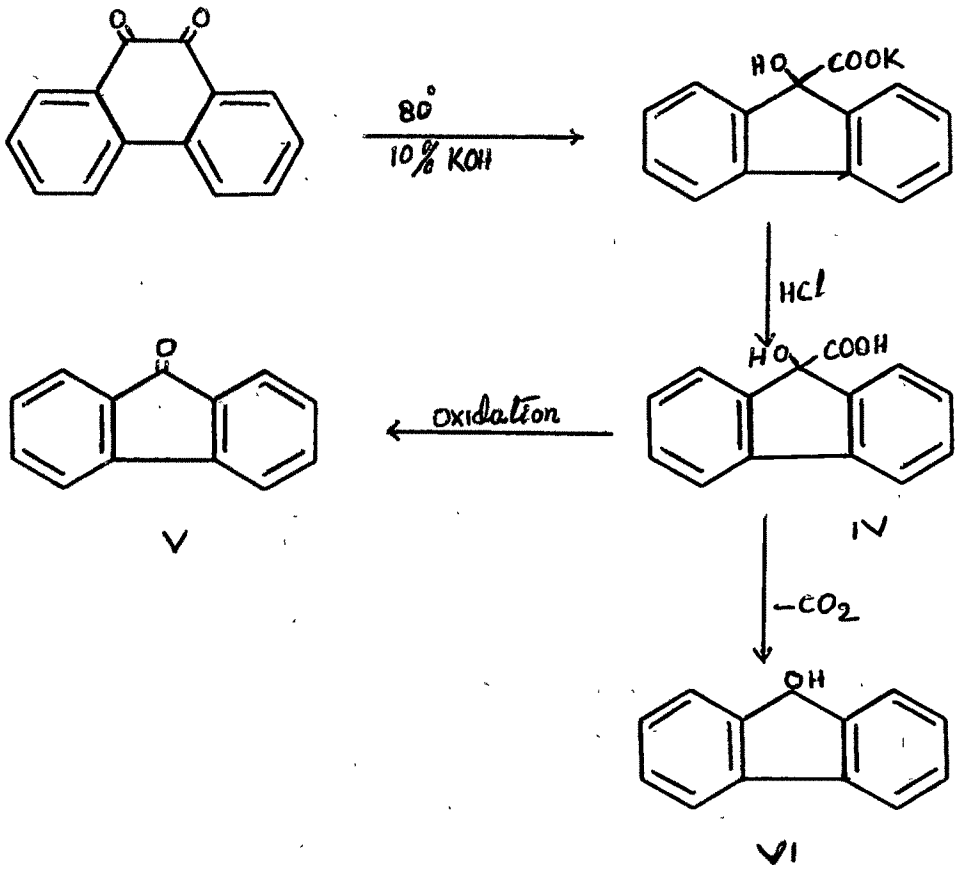


Delacre[8] recommended a general method for the preparation of fluorene derivatives in which benzene and ethyl trichloro acetate are heated with aluminium chloride. Vorlander[9,10] prepared fluorene 9-carboxylic acid (III) by condensing benzoyl cyanide with benzene in the presence of aluminium chloride and hydrolysing the product; or by substituting benzylic acid in place of benzoyl cyanide.

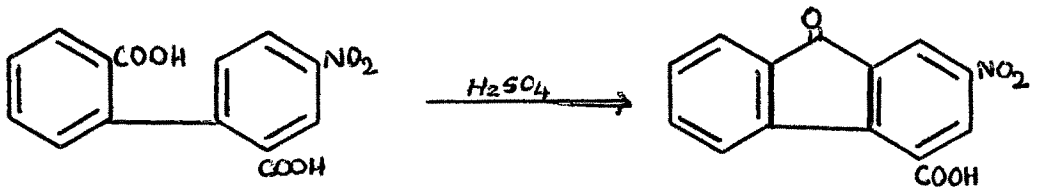


Synthesis of fluorene derivatives from phenanthraquinone derivatives affords a very reliable method because, the

orientation of the substituents are well established. Phenanthraquinone undergoes benzylic acid type of rearrangement giving 9-hydroxyfluorene-9-carboxylic acid (IV) which can be oxidised to fluorenone (V) or decarboxylated to 9-hydroxyfluorene (VI)[11,12,13]. Phenanthraquinone can directly be converted to fluorenone by alkaline potassium permanganate treatment[14].



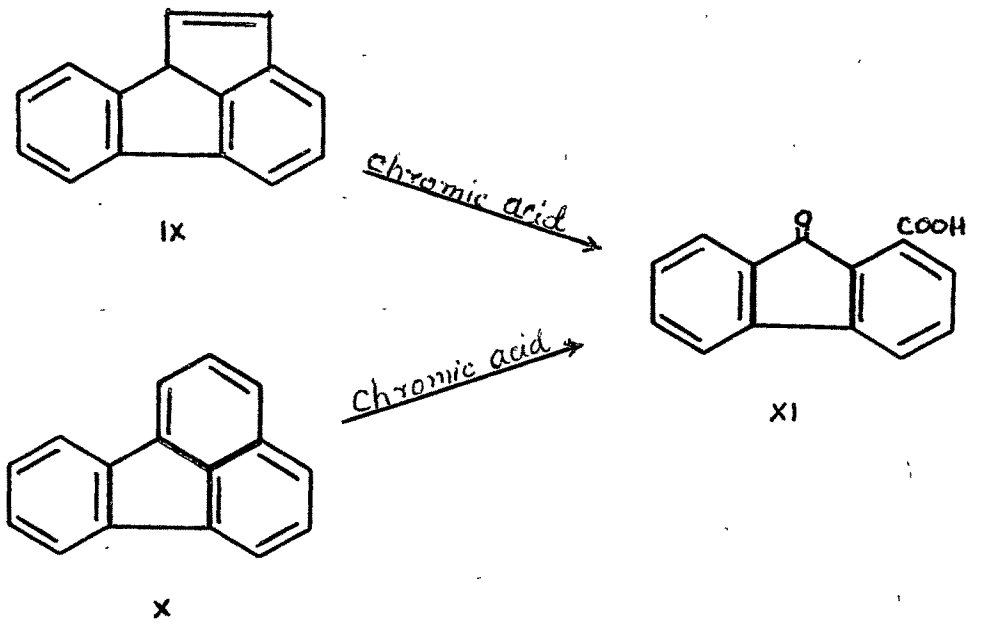
The cyclisation of diphenic acid derivatives can be achieved by heating them alone or with conc. sulphuric acid. Thus Moore and Huntress[15] prepared 2-nitrofluorenone-4-carboxylic acid (VIII) from 4-nitrodiphenic acid (VII).



VII VIII

Fluorenone derivatives can also be synthesised from o-halogen substituted benzophenone derivatives by heating with alkali. Montagne[16,17] obtained several derivatives of fluorenone by this method.

Diazotisation and internal coupling of o-amino benzophenone derivatives furnish fluorenone derivatives[18]. o,o'-Diaminobenzophenone gives 1-hydroxyfluorenone by this method[19]. Fluoranthrene (IX) and cholanthrene (X) on chromic acid oxidation gives fluorenone-1-carboxylic acid (XI)[20, 21, 22, 23]



IX XI

X

Condensation of fluorene with aldehydes :

The hydrogens of the methylene group in fluorene are highly reactive by virtue of the two phenyl groups. This is illustrated by the condensation of fluorene and its derivatives with aldehydes in the presence of sodium alkoxide and also by the ease with which these hydrogens are replaced by sodium or potassium. A large number of aromatic aldehydes have been condensed with fluorene and its derivatives[24,25].

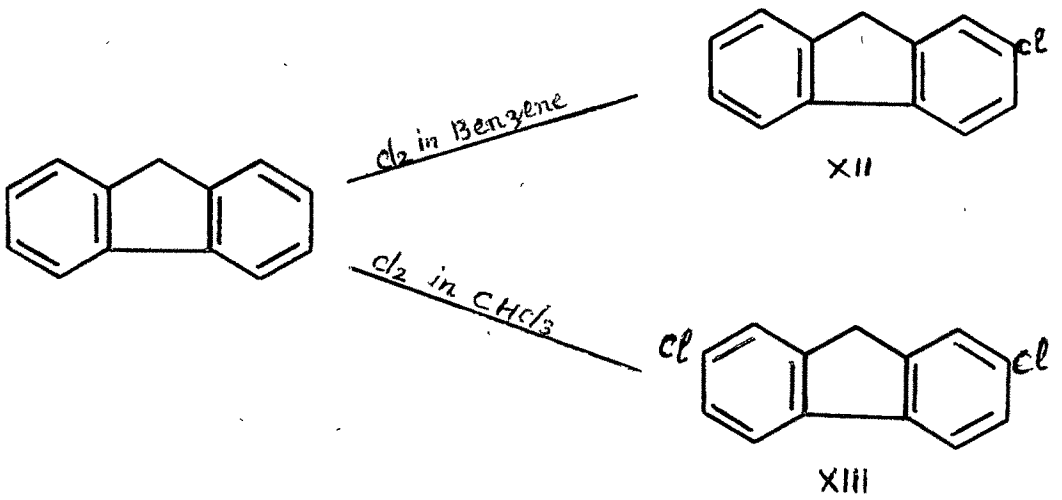
As a part of the present work ddals with substitution in fluorene and fluorenone derivatives some of the previous work on substitution in fluorene and fluorenone and some of their derivatives is discussed here to illustrate the pattern of substitution in these compounds and the types of studies made.

Substitution in fluorene and fluorenone :

Chlorination :

Hodgkinson and Matthews[26] carried out the chlorination of fluorene in dry chloroform and obtained 2,7-dichlorofluorene (XIII). Courtot and Vignati[27] later observed that chlorination of fluorene in chloroform by elementary chlorine at 0-5° gave a mixture of 2-chlorofluorene (XII) and 2,7-dichlorofluorene (XIII) and that the separation of these two was difficult. They could separate these two products only after oxidising them to the corresponding fluorenones. Buffle[28] obtained 2-chlorofluorene (XII) in good yield when he chlorinated the hydrocarbon in benzene at 80° using antimony pentachloride or iodine as catalyst. 2-chloro and 2,7-dichlorofluorene have been prepared through the Sandmayer reaction on diazotised

amino fluorenes[27,29]. Holm[30] prepared a trichloro fluorene by chlorinating fluorene in carbon disulphide. A pentachlorofluorene was prepared by Hodgkinson and Matthews[26] by the action of chlorine on fluorene dissolved in carbon tetrachloride and using iodine as a catalyst. The structures of these compounds have not been established.



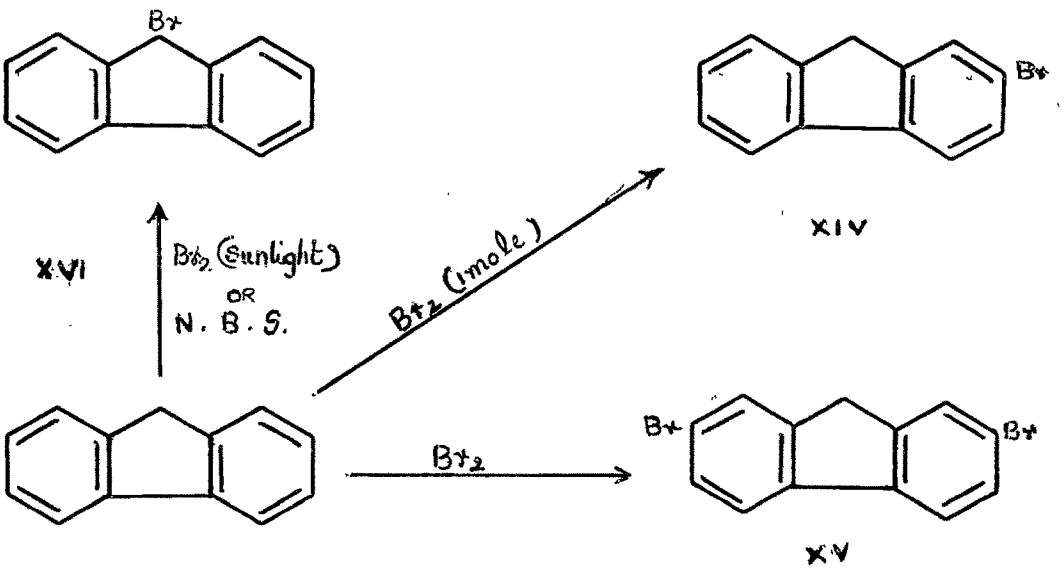
XIII

Varma and Subba Rao[31] carried out the chlorination of 2-bromoflurorene and obtained 2-bromo-7-chlorofluorene. The chlorination of 2-nitrofluorene gives 2-nitro-7-chlorofluorene as reported by Gutmann and Ray[32]. Streitwieser[33] obtained 2-chlorofluorene by the action of sulphuryl chloride on fluorene dissolved in dry ether. Greenhow, Harris and White[34] reported a hexachlorofluorene of unknown structure. Bell and Gibson[35] showed that the chlorination of 2-aminofluorene takes place at the 3-position.

Bromination :

Bromination of fluorene results in the formation of

2-bromofluorene (XIV) and 2,7-dibromofluorene (XV)[2,26,36-41]. The orientation of these compounds have been established either by synthesising them from suitable phenanthrene deriwatives or converting aminofluorenes of known orientation to bromofluorenes through the Sandmayer reaction. Sampey and Reid[42] carried out the bromination of fluorene in carbon tetrachloride in sunlight or mercury vapour lamp light and obtained 9-bromofluorene (XVI) in 64 % yield. The same compound has also been prepared by the action of N-bromosuccinimide on fluorene in carbon tetrachloride or benzene[43]. When this reaction was carried out in the presence of one mole of borom trifluoride, 2-bromofluorene (XIV) with a small amount of the 9-bromo derivative (XVI) was obtained. N-Bromosuccinimide and fluorene in propylene carbonate gives exclusively 2-bromofluorene (XIV).



Fluorene with 3-bromo-5,5-dimethyl hydantoin gives 9-bromofluorene[44], but the yields were improved when 1,3-dibromo-

5,5-dimethylhydantoin was employed[45]. Fluorene with dioxane bromide gives 2-bromofluorene. Two moles of the same reagent yields 2,7-dibromofluorene[46].

Bromination of 1-methyl fluorene gives 1-methyl-2-bromo fluorene[47]. Bromination of 2-aminofluorene in acetic acid gives 3-bromo-2-aminofluorene[48]. Bromination of 2-acetamidofluorene gives 7-bromo-2-acetamidofluorene and 3,7-dibromo-2-acetamido-fluorene, while 2-p-toluene sulphonamidofluorene gives 7-, 3- and 3,7-dibromo-2-p-toluenesulphonamidofluorene[49]. Courtot and Vignati[50] reported the formation of 2-nitro-7-bromo-fluorene in the bromination of 2-nitrofluorene, whereas Korezynski, Karlowska and Kierzek[51] reported the formation of 2-nitro-9-bromofluorene. Bromination of 9-bromofluorene gives 2,7,9-tribromofluorene[52].

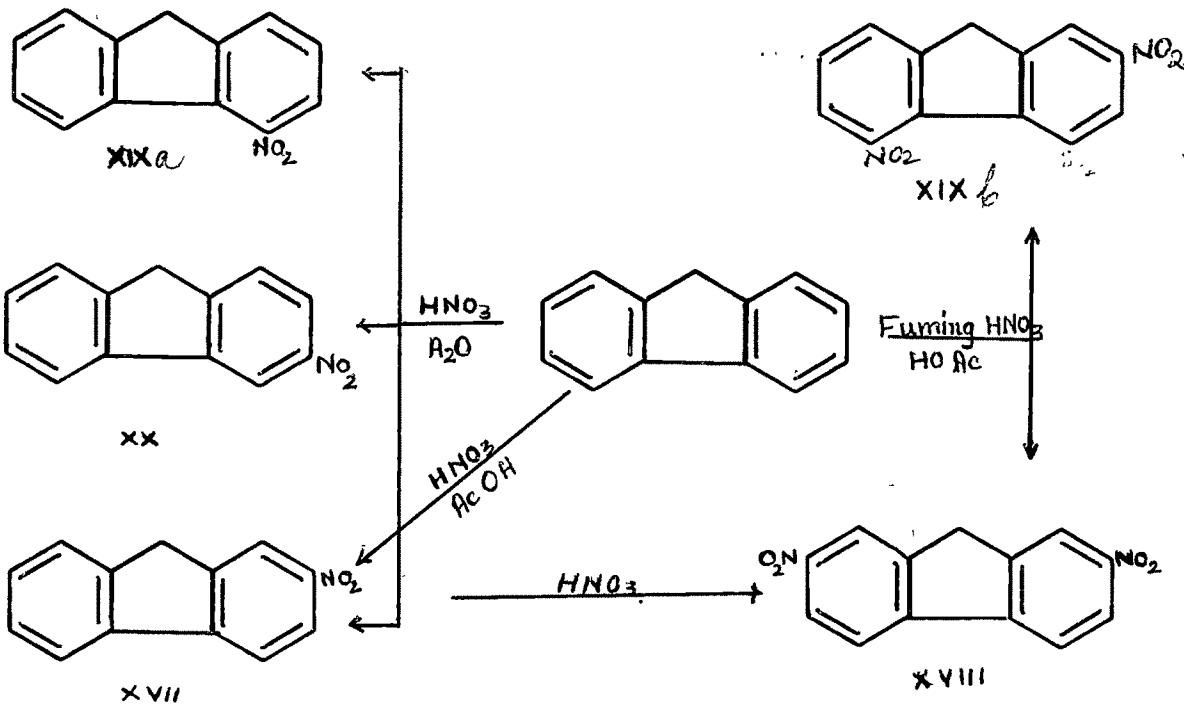
Bromination of 2-methoxyfluorene was carried out by Eckert and Langecker[53]. They reported the isolation of a dibromo and a tribromo 2-methoxyfluorene but the structures of these compounds are not established.

Iodination :

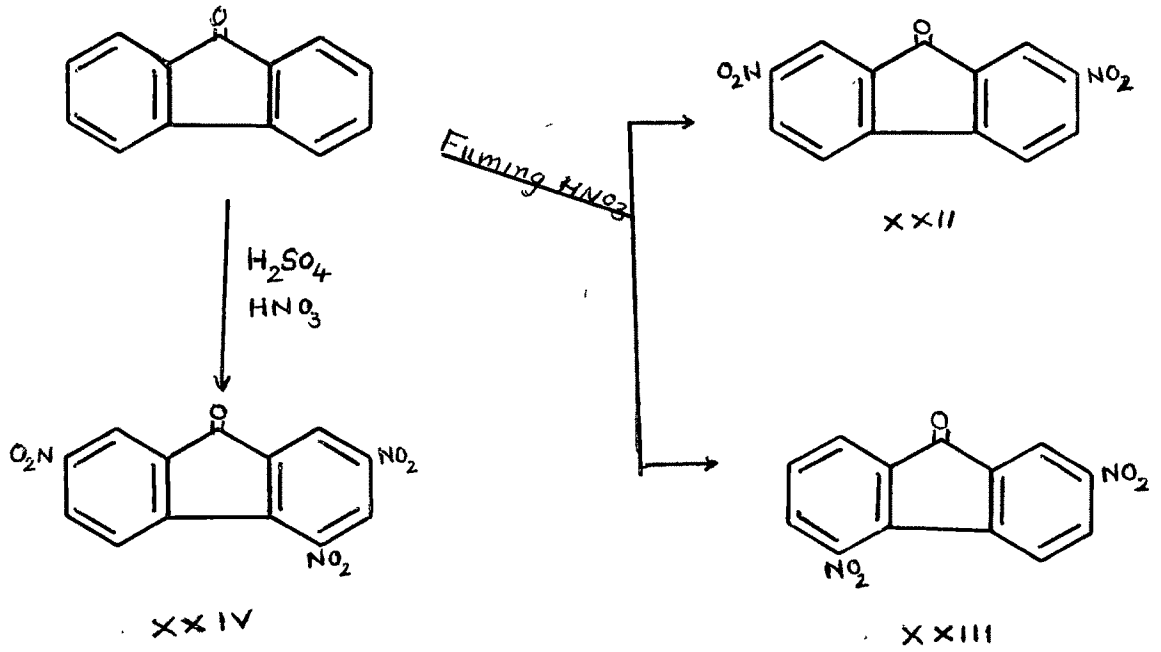
Iodofluorenes have been reported but they are prepared from the amino derivatives through the Sandmayer reaction. Varma and Subba Rao[31] refluxed 2-chlorofluorene in acetic acid with iodine and small amounts of a mixture of nitric acid and sulphuric acid and obtained 2-chloro-7-iodofluorene. A similar treatment of 2-bromofluorene gave 2-bromo-7-iodo-fluorene. Fluorene under similar conditions gave 2,7-diiodo-fluorene.

Nitration :

Nitration of fluorene and fluorenone has received the attention of many investigators. The first product of nitration of fluorene or fluorenone is the 2-nitro derivative[2,13,54-59] (XVII). The condition for mono nitration has been established by Kuhn[60]. Morgan and Thomason[58] carried out the nitration in acetic acid with fuming nitric acid and obtained 2,7-dinitrofluorene (XVIII) along with small amounts of the 2,5-isomer (XIX). The structures of these compounds are proved by synthesising them from suitably substituted phenanthraquinones. Langecker[61] obtained 2,7-dinitrofluorene (XVIII) along with an isomeric dinitrofluorene, the structure of which was not established. Dewar and Urch[62] obtained 2-nitrofluorene (XVII) along with the 3- (XX) and the 4-isomers (XXI) by carrying out the nitration in acetic anhydride. Monti, Martello and Valente[57] carried out the nitration of fluorene in solvents like ether, petroleum ether, benzene and acetic acid using nitrous fumes and obtained 2-nitrofluorene (XVII). These workers observed that when nitration was carried out in ligroin with liquid N_2O_4, 2-nitrofluorene (XVII) was formed whereas 2,7-dinitrofluorene (XVIII) was obtained when acetic acid was used as a solvent and the nitration is carried out at room temperature, at 90° 2,5-dinitrofluorene (XIX) was the main product. Schmidt, Retzlaff and Haid[63] obtained 2,3,6,7-tetranitrofluorene by carrying out the nitration with a mixture of sulphuric acid and nitric acid.



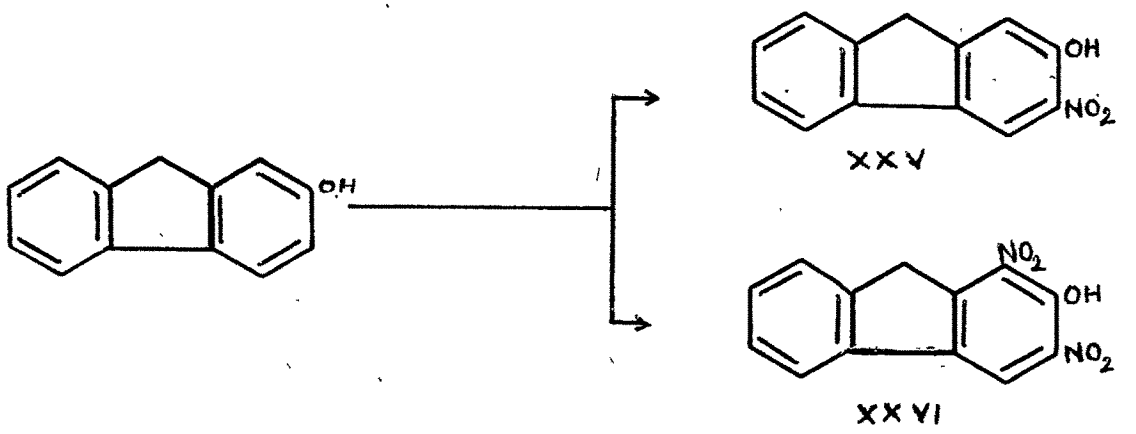
Nitration of fluorenone with fuming nitric acid gives a mixture of 2,7-dinitrofluorenone and 2,5-dinitrofluorenone.[64] Orchin and Woolfolk[65] obtained 2,4,7-trinitrofluorenone (XXIV) by the action of a mixture of nitric acid and sulphuric acid on fluorenone.

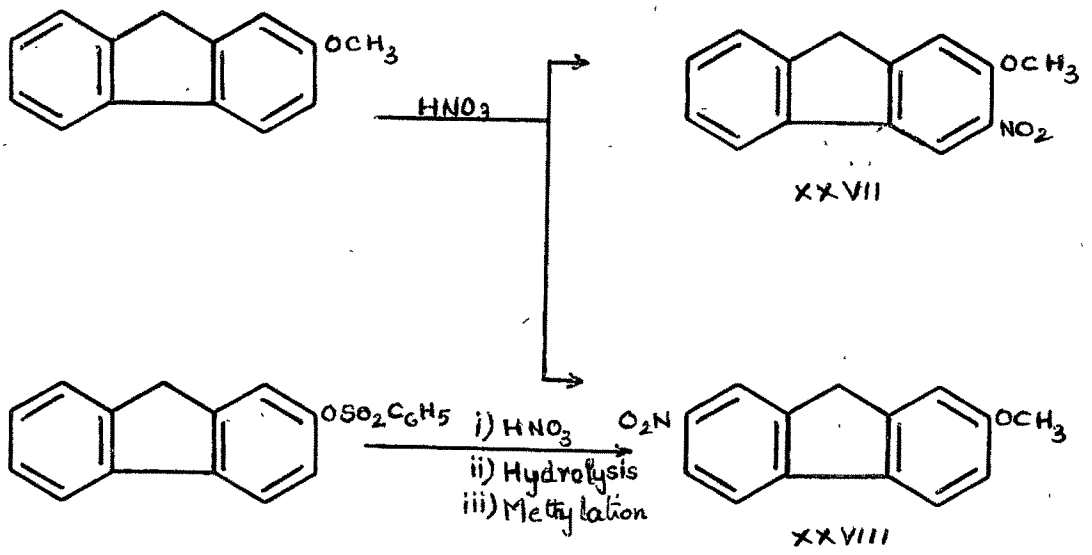


Both 2-benzyl and 2,7-dibenzylfluorene on nitration gave 2-benzyl-7-nitrofluorene[66]. Nitration takes place at the 7-position in the case of 2-bromo[50], 2-chloro[27], 2-iodo[67], 2-benzoyl[68], 2-methyl[69] and 4- and 2-carboxy-fluorene[70,71].

2-Acetamidofluorene on nitration gives 3-nitro derivative along with small amounts of the 7-isomer[53,72]. Nitration of 2,7-diacetamidofluorene gave the 3,6-dinitro derivative[73].

Nitration of 2-hydroxyfluorene gives 2-hydroxy-3-nitro (XXV) and 2-hydroxy-1,3-dinitro fluorene (XXVI) as shown by Ray and Hull[74] and Wiesburger[75]. 2-Methoxyfluorene in acetic acid gave a mixture of 2-methoxy-3-nitrofluorene (XXVII) and 2-methoxy-7-nitrofluorene (XXVIII)[76]. In the case of p-toluene sulphonate of 2-hydroxyfluorene, the nitro group enters only in the 7-position[77]. 1-Hydroxy fluorene on nitration in acetic acid with 1:1 nitric acid in the cold gave a mixture of 1-hydroxy-2-nitro and 1-hydroxy-4-nitro derivative ; whereas 3-hydroxyfluorene in acetic acid when nitrated with 1:1 nitric acid gave 3-hydroxy-2-nitro fluorene, with a small amount of the 2,4-dinitro derivative[78]. Nitration of 1,4-dimethoxyfluorenone gave 1,4-dimethoxy-2-nitrofluorenone[79].

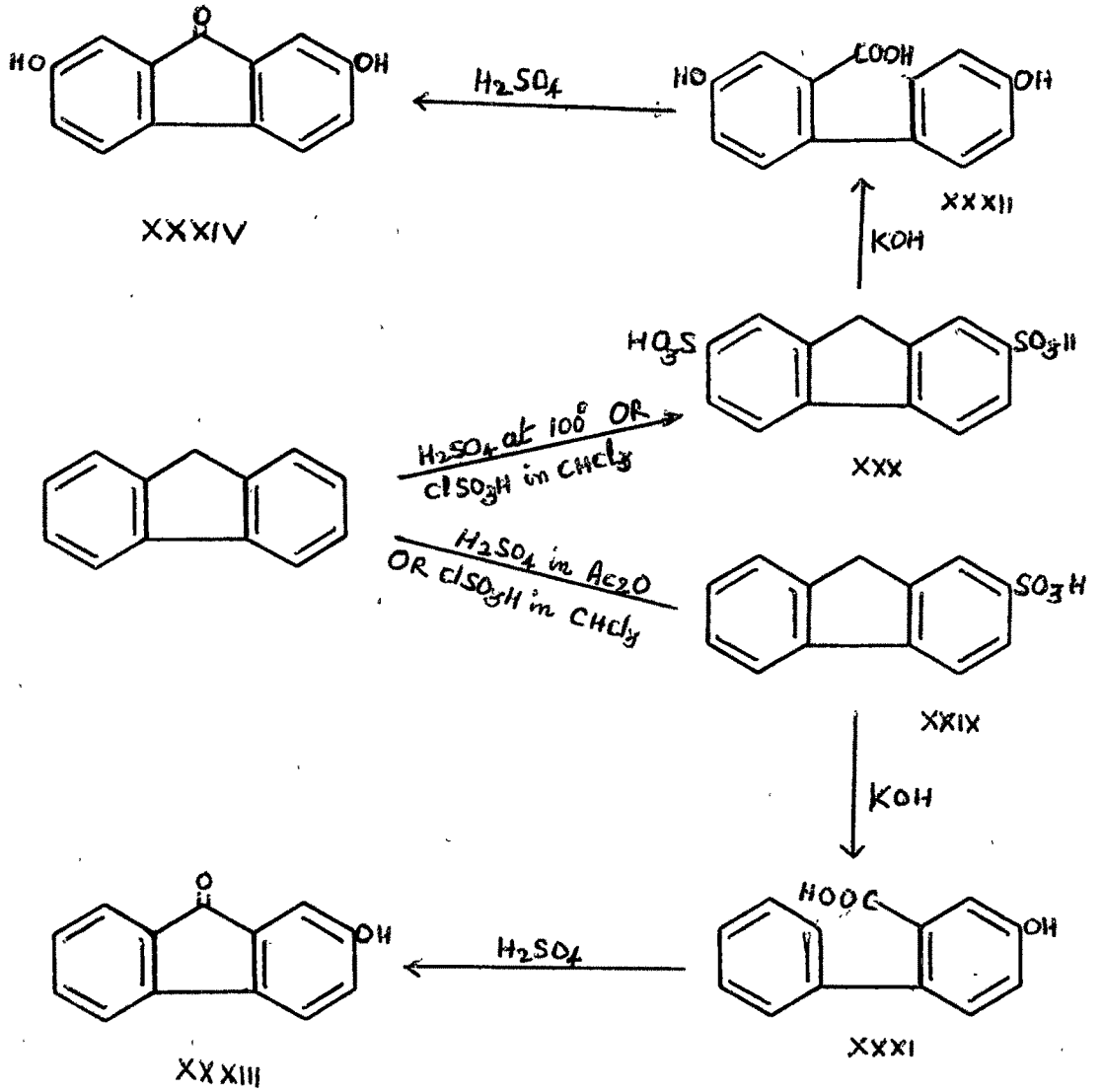




Sulphonation :

Action of sulphuric acid on fluorene leads to the substitution at the 2-position and further treatment leads to the 2,7-disubstitution. Sulphonation of the hydrocarbon with conc. sulphuric acid in acetic anhydride gives quantitative yield of fluorene 2-sulphonic acid[2,80] (XXIX). Fluorene with chlorosulphonic acid in chloroform gives fluorene 2-sulphonic acid, further sulphonation gives 2,7-disulphonic acid (XXX)[81]. The same disulphonic acid was obtained by Schmidt, Retzlaff and Haid[63] by heating fluorene with conc. sulphuric acid. The structures of fluorene sulphonic acid derivatives were proved by potassium hydroxide fusion. This breakes up the cyclopentane ring giving hydroxy-biphenyl carboxylic acids (XXXI and XXXII), which can be cyclised to hydroxyfluorenone derivatives (XXXIII and XXXIV) by conc. sulphuric acid or by zinc chloride[82]. Sulphonic acid group enters at the 7-position when 2-benzylfluorene[83], 2-nitrofluorene[84] and 2-aminofluorene[84] are treated with

sulphuric acid.



Friedel-Crafts acylation and alkylation :

In Friedel-Crafts acylation also the 2- and the 7-positions are favoured by the entering group. Dziewonski and Schnayder[85] condensed acetyl chloride with fluorene in the presence of anhydrous aluminium chloride in carbon disulphide and obtained 2-acetylfluorene (XXXV) and 2,7-diacetylfluorene (XXXVI). The constitution[5] of these compounds and in general of all the ketones obtained by Friedel-Crafts acylation of

fluorene, were established by the respective authors by preparing the oxime, rearranging to the acylaminofluorene and hydrolysing it to the amine. Dziewonski and Kleszcz[86] investigated this reaction in detail. According to their findings, at 5-10° 2-acetyl fluorene was the main product. At 20-25°, a mixture of 2,7-diacetylfluorene and 1,2-diacetylfluorene was obtained, the former one being the main product. At the boiling point of the solvent 1,2-diacetyl fluorene was the main product. These workers based the structure of this compound on the 1,2-diamino compound prepared by Diels, Schill and Tolson[72], but Eckert and Langecker[53] had shown that the diamino compound obtained by Diels was 2,3-diamino and therefore the 1,2-diacetylfluorene obtained by Dziewonski and Kleszcz[86] is 2,3-diacetylfluorene (XXXVII). Dziewonski and Schweiger[87] have reported the formation of 2-propionyl and 2,7-dipropionyl fluorene by the action of propionyl chloride and aluminium chloride on fluorene dissolved in carbon disulphide. Buu-Hoi *et al*[88,89] carried out the condensation of various aliphatic acid chlorides such as caproyl, heptanoyl, octanoyl, lauroyl and myristoyl with fluorene and obtained the 2-acylfluorenes. The same condensations were also carried out on fluorenone and 2-acylfluorenone derivatives were obtained.

Arene and Taylor[47] carried out the acetylation of 1-methylfluorene in carbon disulphide with acetyl chloride and aluminium chloride and obtained 1-methyl-7-acetylfluorene. 2-Methoxyfluorene on Friedel-Crafts acetylation in the presence of aluminium chloride in carbon disulphide

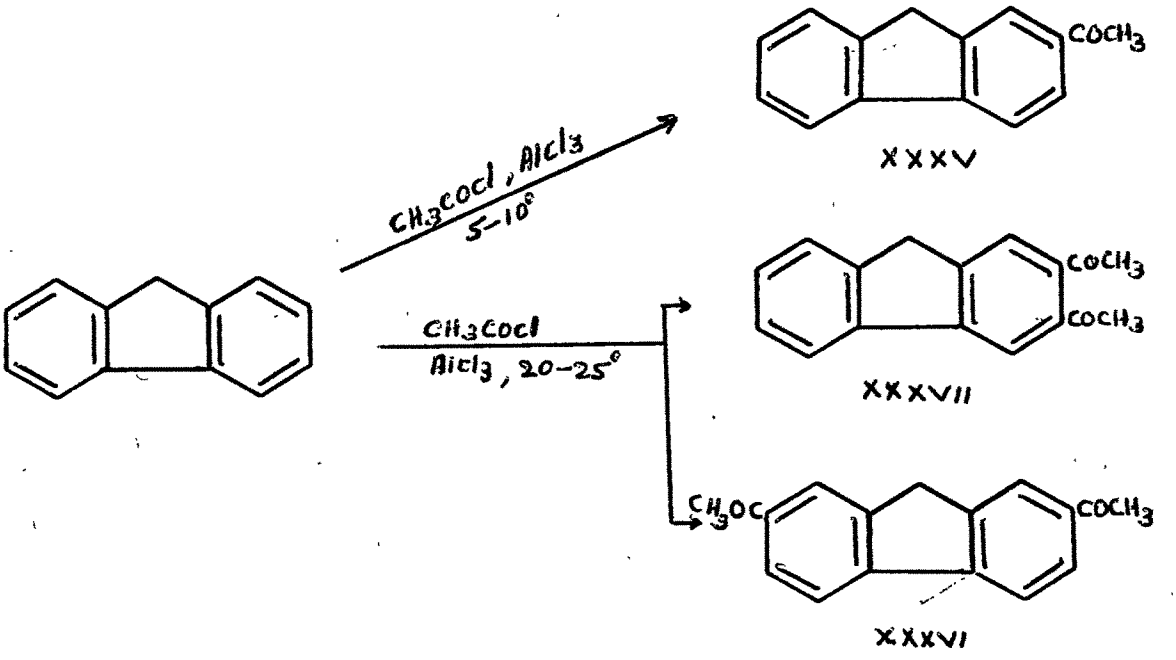
gives 2-methoxy-7-acetylfluorene[90]. Ross[91] observed that 2,7-di(chloracetyl) fluorene was formed when chloracetyl chloride reacted with fluorene in the presence of aluminium chloride in carbon disulphide. 2-Nitrofluorene on Friedel-Crafts acetylation with acetyl chloride and aluminium chloride in nitrobenzene gave 2-nitro-7-acetylfluorene[92].

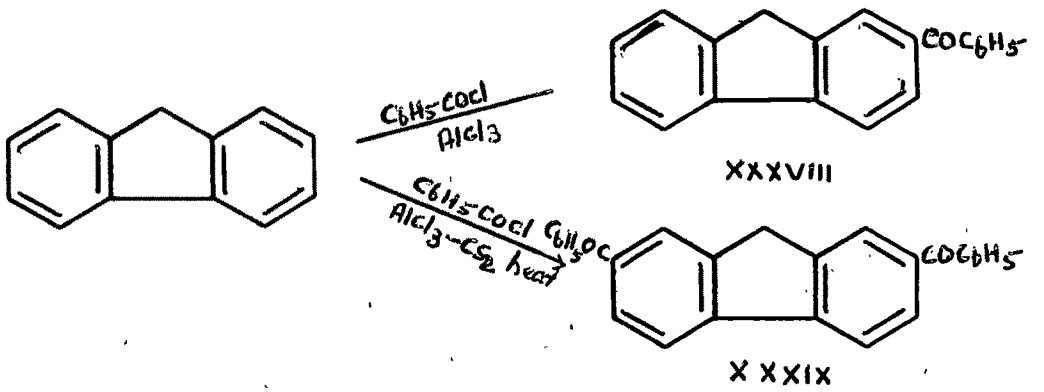
Benzoylation of fluorene with benzoyl chloride and aluminium chloride in carbon disulphide was carried out by Fortner[93] and obtained 2-benzoylfluorene (XXXVIII). Dziewonski and Obtulowicz[94] obtained 2-benzoylfluorene(XXXVIII) by the same reaction at room temperature but on refluxing the reaction mixture 2,7-dibenzoylfluorene (XXXIX) was obtained.

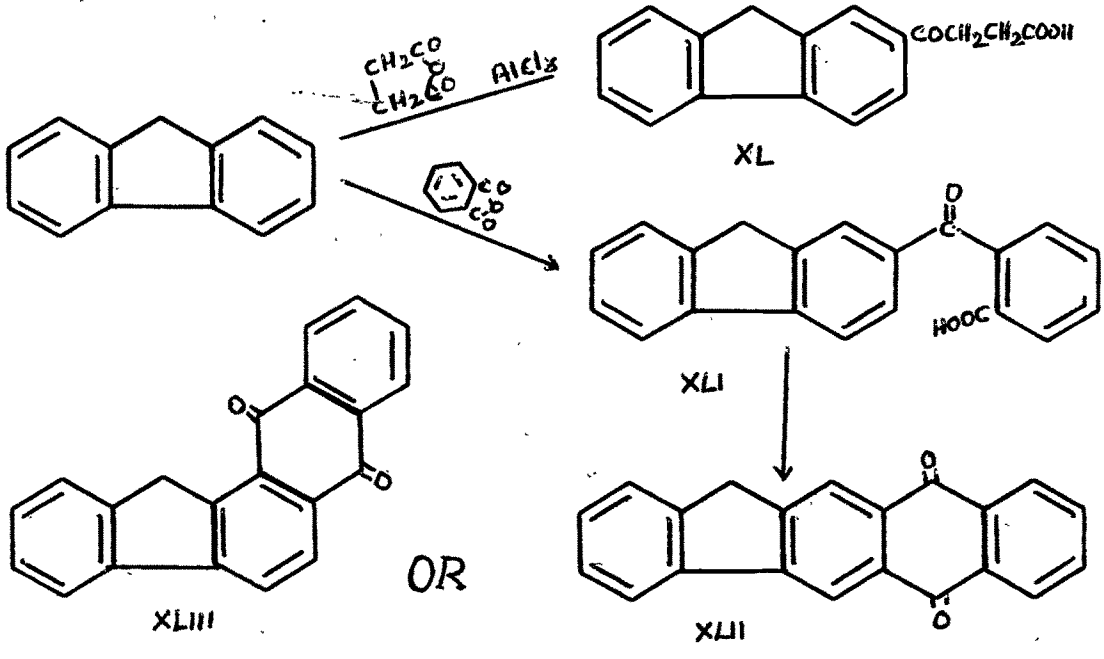
Succinoylation and phthaloylation of fluorene was studied by Koelsch[95] and Dansi and Sempronj[96]. The former reaction in benzene in the presence of aluminium chloride gave β-(2-fluorenoyl)propionic acid (XL), while the later reaction in carbon disulphide gave 2(o-carboxybenzoyl)fluorene (XLI) which cyclised on heating with potassium hydrogen sulphate to give phthaloyl fluorene[97] (XLII or XLIII). The structure of this compound is not established.

Fluorene when heated with benzene sulphonyl chloride or p-toluene sulphonyl chloride in the presence of stannic chloride gave the corresponding sulphones[98].

Friedel-Crafts acylation can be summarised as follows :

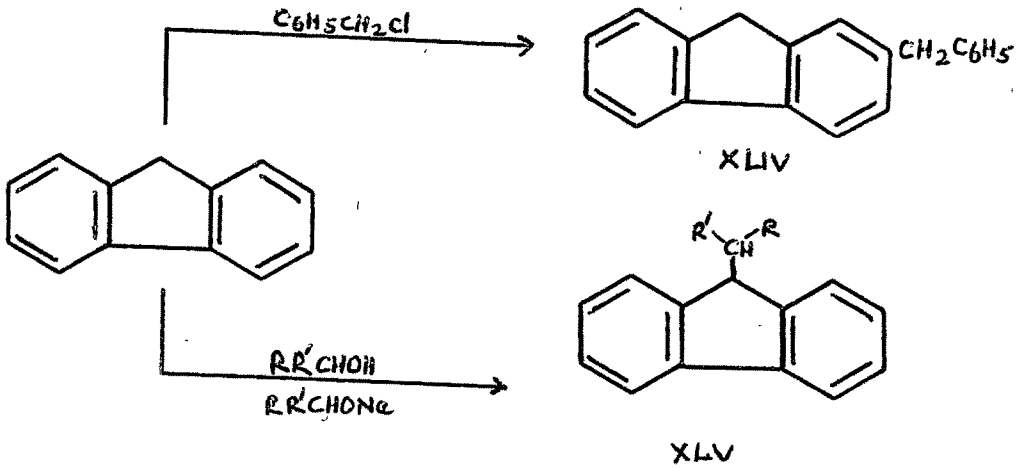

CH3COCl, AlCl3
5–10°
COCH3
XXXV
CH3COCl
AlCl3, 20–25°
COCH3
COCH3
XXXVII
CH3O
COCH3
XXXVI


C6H5-COCl
AlCl3
COC6H5
XXXVIII
C6H5-COCl C6H5O
AlCl3-CS2 heat
COC6H5
XXXIX


CH2CO
CH2CO
AlCl3
COCH2CH2COOH
XL
CO
CO
O
C
HOOC
XLI
O
O
XLIII
OR
O
O
XLII

Goldschmiedt[99] studied the benzylation of fluorene with benzyl chloride in the presence of zinc dust and obtained 2-benzylfluorene (XLIV). Later, Dzewonski and Reicher[83] have shown that the yield of 2-benzylfluorene could be improved by using zinc chloride or aluminium chloride as the condensing agent.

Schoen and Becker[100] have shown that alkylation of fluorene takes place at the 9-position when aliphatic primary alcohols are heated with fluorene in the presence of sodium salt of the alcohol. Sprinzak[101] prepared various 9-benzylfluorene derivatives by heating fluorene or substituted fluorene with benzyl alcohol in the presence of potassium hydroxide. Alkylation of fluorene with secondary alcohols in the presence of sodium alkoxide gave 9-alkylfluorene (XLV)[102]. Similar alkylation with glycols gave bis fluorenyl ethane.[103]



XLIV

XLV

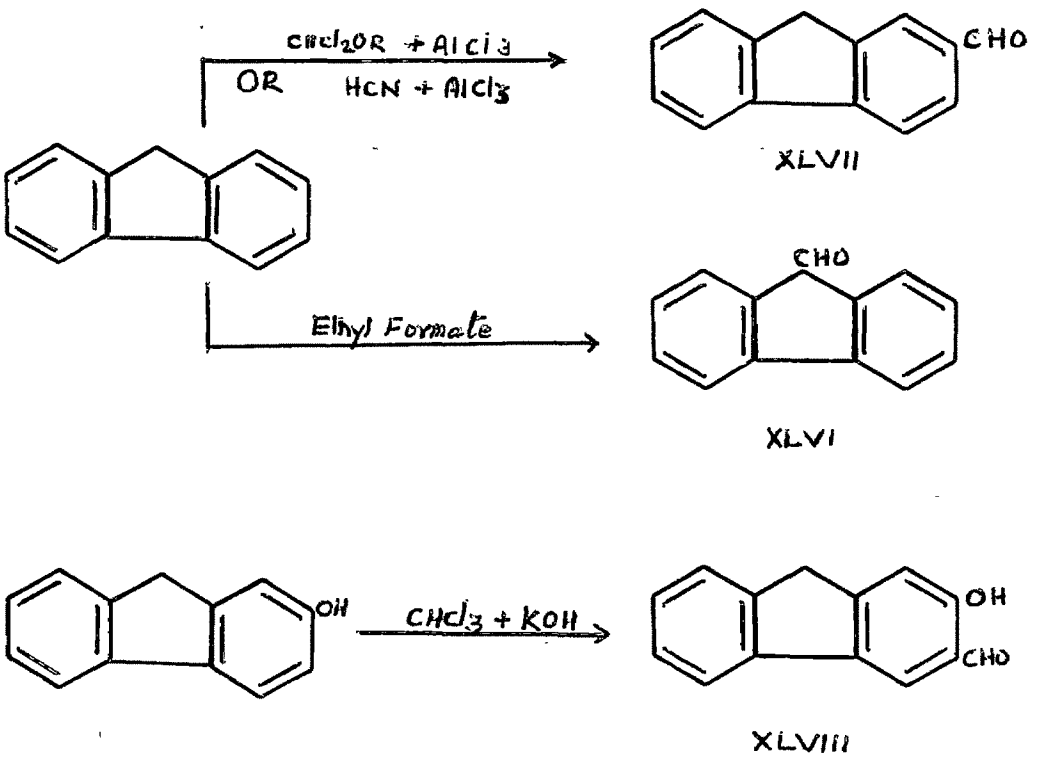
Alkylation of fluorene by the thermal decomposition of a mixture of fluorene and alkyl esters of benzene sulphonic acid gives all the possible isomeric mono alkyl fluorene

derivatives[104]. The alkylation with alcohols in the presence of aluminium chloride gives 1-, 2- and 3-alkyl fluorenes, the 3-isomer being the main product[104].

Condensation of fluorene with cyclopentyl and cyclohexyl halides in the presence of aluminium chloride has been studied by Saidova and Sidorova[105]. When the condensation was carried out the in heptane with 0.5 mole of aluminium chloride at 20°, 40-50 % of 2-substituted fluorene was obtained along with small amount of the 3-isomer. When 1 mole of aluminium chloride was used and the reaction was carried out at 40-50°, 60 % of the 3-isomer was obtained. Ferric chloride, when used as the condensing agent in this reaction at 10-25°, gave 70 % of the 2-isomer and 15 % of the 3-isomer along with very small amounts of 1 and 4-isomers.

Formylation :

Brown and Bluestein[106] carried out the formylation of fluorene with ethyl formate in the presence of sodium or potassium ethoxide and obtained 9-formylfluorene (XLVI). Fluorene and dichloromethyl-alkyl ether in the presence of aluminium chloride give 2-formylfluorene (XLVII)[107]. Hinkel, Ayling and Beynon[108] prepared 2-formylfluorene (XLVII) by the action of hydrogen cyanide and hydrogen chloride on fluorene in the presence of anhydrous aluminium chloride. Formylation of 2-methoxyfluorene and 2-hydroxyfluorene was reported by Arene and Taylor[47] by the Riemer-Teimann method. They obtained 2-methoxy-3-formylfluorene and 2-hydroxy-3-formylfluorene (XLVIII) respectively.



XLVII

XLVI

XLVIII

Chloromethylation and Cyanoethylation :

Fluorene is chloromethylated in the 2-position with paraformaldehyde and hydrogen chloride in the presence of phosphoric acid[109]. Cyanoethylation of fluorene takes place at the 9-position[110].

Carboxylation :

2-Hydroxyfluorene on carboxylation by heating with carbon dioxide and alkali under pressure gives a mixture of 2-hydroxyfluorene-1-carboxylic acid and 2-hydroxyfluorene-3-carboxylic acid[111]. The same reaction on 3-hydroxyfluorene gives 3-hydroxyfluorene-2-carboxylic acid[112].

Metallation :

9-Fluorenyllithium is readily formed by the action of ethyllithium[113], phenyllithium[114] and butyllithium[115] on

fluorene. 9-Fluorenyl sodium was prepared by the reaction between fluorene and triphenyl methyl sodium[116] or by the action of sodamide on fluorene dissolved in ether[114] or by the action of amyl chloride and sodium on fluorene[117]. When fluorene is heated with potassium hydroxide to 280°, 9-fluorenyl potassium is formed[118]. Fluorene and ethyl magnesium bromide in xylene at 130° gives 9-fluorenyl magnesium bromide[113,119].

Fluorene when heated with mercuric acetate to 125-45° and then with alcoholic calcium chloride gives 3-fluorenyl mercuric chloride[120]. When the mixture is boiled in acetic acid 4-fluorenyl mercuric chloride is obtained[120].

Oxidation and dehydrogenation :

Fluorene and its derivatives can be oxidised to fluorenone derivatives. Phthalic acid is formed on further oxidation. Chromic acid or dichromate in acetic acid oxidises fluorene to fluorenone. When fluorene vapour mixed with air is passed over ferric vanadate fluorenone is obtained[121]. Oxidation of fluorene to fluorenone can also be brought about by potassium permanganate[122]. This oxidation by selenium dioxide is only to the extent of 5 %[4]. Fluorene when heated with 10 % nitric acid to 200° gives fluorenone[123].

Physiological actigities and other applications:

Wilson, DeEds and Cox[124] were the first to discover the carcinogenic properties of 2-aminofluorene and its derivativatives. Since them, a large number of fluorene derivatiges have been prepared and their carcinogenic activities tested. Bielschowsky[125] observed that 2-aminofluorene and its acetyl derivatives caused

mammary carcinomas in female rats and a mixture of 2-acetylaminofluorene with allylthiourea produced thyroid tumors. Armstrong and Bonser[126] found that bladder tumors were produced by these compounds in rats. Painting of the abdominal skin of rats with 2-acetylaminofluorene produces liver tumor[127]. Heiman and Meisel[128] observed that cysts and tumors of the salivary and parathyroid glands were produced in rats when they were fed with 2-acetylaminofluorene. 2-Aminofluorene and 2-acetylaminofluorene produces tumors of the bladder, thyroid, liver, breast, stomach, renal pelvis, female genitalia and external auditory canal even at as low a concentration as 0.004 %[129-134]. Horning[135] observed bronchogenic carcinoma when 2-acetylaminofluorene was injected in mice.

1,3-Dichloro-2-acetylaminofluorene, 7-bromo-2-acetylaminofluorene, 1,3,4-tribromo-2-acetylaminofluorene and similar compounds are shown to possess antitumour activity[136]. Aminoalkylesters of fluorene carboxylic acids were found to have local anesthetic activity and antispasmodic action[137-139].

Diethylaminoethylester of fluorene 9-carboxylic acid, when orally injected by a person with peptic ulcer caused relief of the epigastric pain[140].

2-Amino and 2-acetylaminofluorene are found to be active against tobacco and tomato horn-warm larvae[141].

Effective herbicidal compounds are obtained by preparing emulsion of fluorene compounds in oil or water[142].

2-Nitrofluorene and 2,7-dinitrofluorene are found to be useful as antioxidants in gasoline[143].

Present work.

The present work deals with the following studies on 2-hydroxyfluorene and 2-hydroxyfluorenone.

Section I deals with the synthesis of 2'-phenylfluoreno (2,1:6',5')γ-pyrone. 2-Hydroxy-1-acetylfluorene on condensation with benzaldehyde gave a styryl ketone which on cyclisation and dehydrogenation with selenium dioxide gave the above product. A similar series of reactions with anisaldehyde gave 2'-(p-methoxyphenyl)fluoreno(2,1:6',5')γ-pyrone. 9-Oxo derivatives of the above γ-pyrones are synthesised starting with 2-hydroxy -1-acetylfluorenone and going through the same sequence of reactions.

2-Hydroxy-1-acetylfluorene on Kostanecki-Robinson acetylation gave 2'-methyl-3'-acetylfluoreno(2,1:6',5')γ-pyrone. Similar benzoylation on 2-hydroxy-1-acetylfluorene and the Kostanecki-Robinson acetylation and benzoylation on 2-hydroxy -1-acetylfluorenone did not give the desired product. Attempts to synthesise fluoreno α-pyrones have been unsuccessful.

Section II describes the synthesis of fluoreno furan derivatives 2'-methylfluoreno(2,1:5',4')furan and 3'-methyl fluoreno(2,1:5',4')furan are synthesised from 2-hydroxy-1-acetylfluorene and 2-hydroxy-1-allylfluorene respectively. 2'-Methyl 9-oxofluoreno(2,1:5',4')furan, 3'-methyl 9-oxo-fluoreno(2,1:5',4')furan and 2'-phenyl 9-oxofluoreno(2,1:5',4') furan are synthesised from 2-hydroxy-1-acetyl-, 2-hydroxy -1-allyl-, and 2-hydroxy-1-benzoylfluorenones respectively.

In Section III bromination of 2-hydroxyfluorene and

2-hydroxyfluorenone and their methyl ethers has been described. Synthesis of a number of mono, di and tribromo derivatives has been achieved and the structures of these compounds have been established.

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SECTION I

SYNTHESIS OF SOME FLUORENO-γ-PYRONES AND 9-OXOFLUORENO-γ-PYRONES

SECTION I.

Synthesis of some fluoreno-γ-pyrones and 9-oxofluoreno-γ-pyrones :

A survey of the literature showed that attempts to build the α-pyrone and the γ-pyrone rings on fluorene or fluorenone nucleus are not known. α- And γ-pyrones occur in nature and possess diverse physiological activities. This aspect and the general methods for the synthesis of α- and γ-pyrones are described in part I, section I of this thesis. Attempts to prepare some fluoreno α- and γ-pyrones and their 9-oxo derivatives from 2-hydroxy fluorene and 2-hydroxy fluorenone are described here.

Synthesis of 2-hydroxyfluorene :

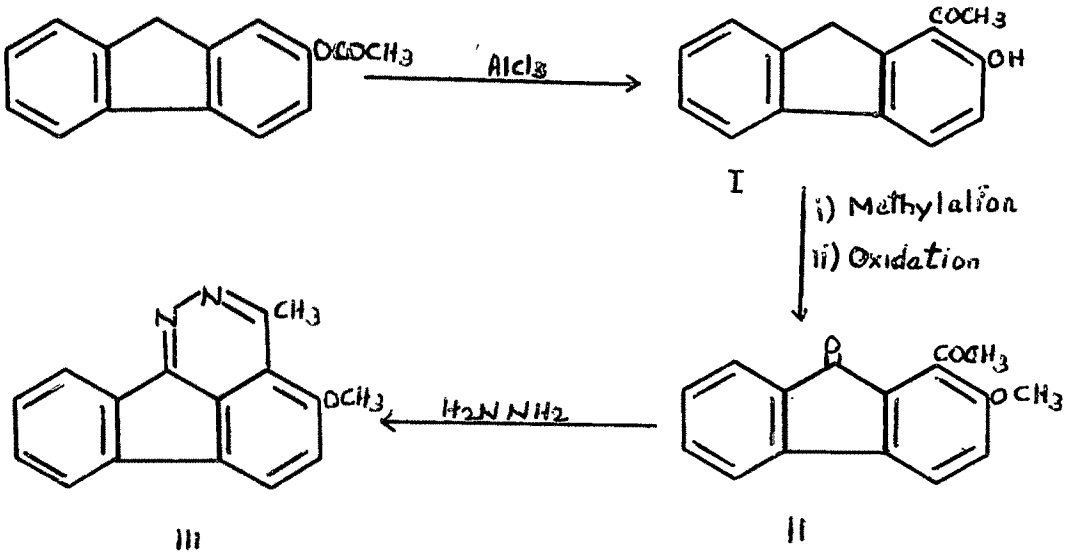
As the general method for preparing phenols viz. the fusion of the sulphonic acid with potassium hydroxide opens up the fluorene ring system giving biphenylcarboxylic acid derivatives, the route to hydroxyfluorene is generally through the nitro, amino and the diazonium salt.

Fluorene was nitrated with conc. nitric acid in glacial acetic acid according to Kuhn[1] and the 2-nitro fluorene was obtained. Reduction of the above nitro fluorene has been carried out by various workers using different reducing agents. In the present work it was obtained in over 90 % yield by the reduction of 2-nitro fluorene with sodium hydrosulphite.

The 2-amino derivative was converted into 2-hydroxy derivative according to Grey, Hartley and Ibbotson[2] through diazotisation.

2-Hydroxy-1-acetylfluorene :

This compound has already been prepared by Bergmann and Berlin[3] by the Fries rearrangement of 2-acetoxyfluorene. As a proof of the structure, these authors have shown that this compound does not form an oxime, which is a common feature of 2,6-substituted acetophenones. To determine the structure unequivocally the methyl ether of the compound was oxidised to the corresponding fluorenone derivative (II) by heating with sodium dichromate in acetic acid. The fluorenone derivative on heating with one mole of hydrazine hydrate in alcoholic solution gave a pyridazine derivative (III) as seen from the analytical data. Therefore 2-hydroxy-1-acetyl structure (I) is assigned to the hydroxy ketone.



Synthesis of 2'-phenylfluoreno(2,1:6',5')y-pyrone :

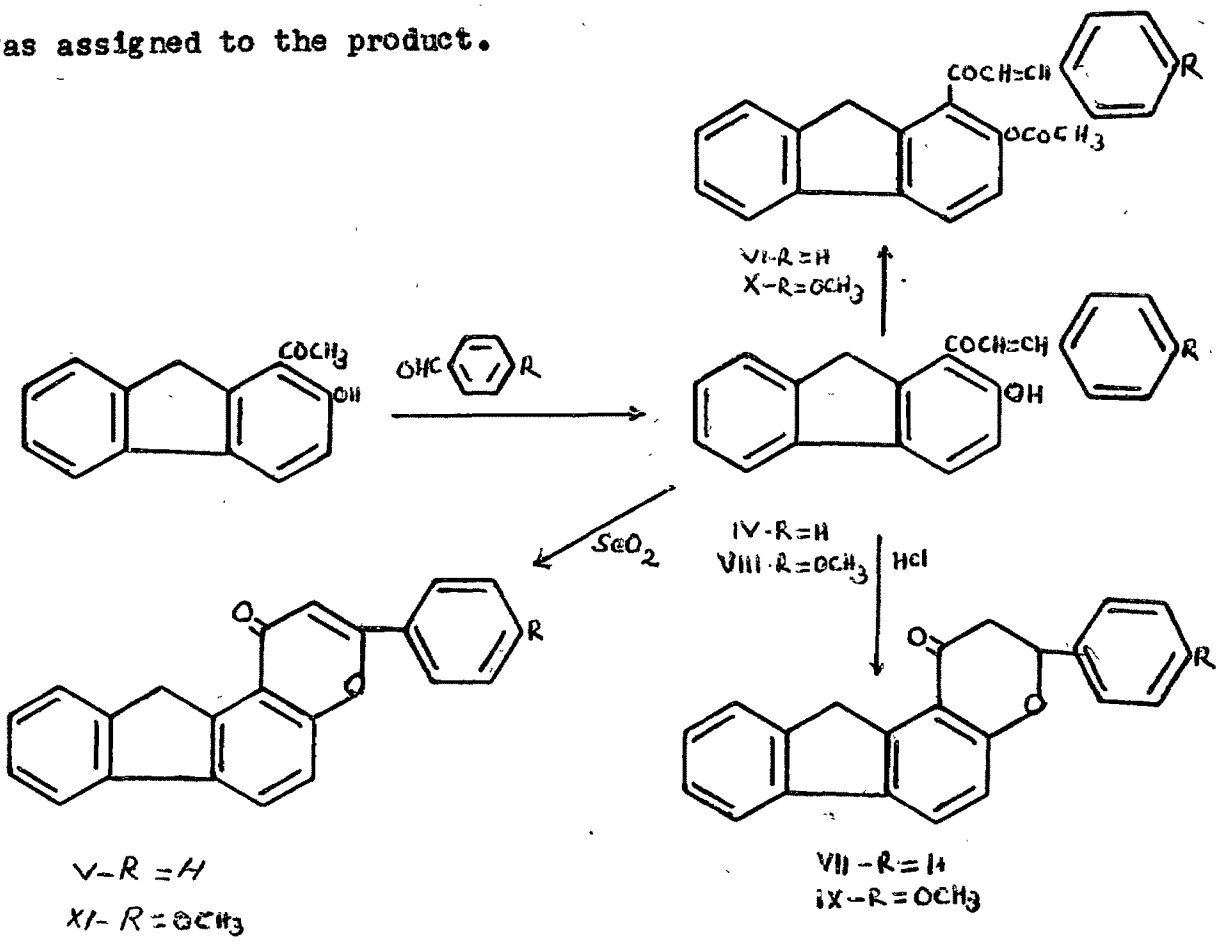
2-Hydroxy-1-acetylfluorene was condensed with benzaldehyde in the presence of alcoholic potassium hydroxide. The product obtained gave tests for a styryl ketone derivative such as

red colouration with conc. sulphuric acid and a yellow colour with a mixture of boric acid and citric acid in dry acetone (Wilson test[4]). Moreover it gave an acetyl derivative (VI) when refluxed with fused sodium acetate and acetic anhydride indicating that there was a free hydroxyl group and a greenish blue colour with alcoholic ferric chloride. Therefore 2-hydroxy--1-fluorenyl styryl ketone structure (IV) was assigned to this compound. This styryl ketone derivative on refluxing with alcoholic hydrochloric acid gave a product which did not give the Wilson test and did not give any colour with alcoholic ferric chloride. Therefore 2'-phenylfluoreno(2,1:6',5')pyran-4'-one structure (VII) was assigned to this compound. The fluorenyl styryl ketone derivative (IV) on refluxing with selenium dioxide in iso-amyl alcohol gave a product which analysed for 2'-phenylfluoreno(2,1:6',5')γ-pyrone (V). From the analysis result it is evident that the methylene group was not oxidised by selenium dioxide. Also Postovski and Lugovkin[5] have shown that conversion of fluorene to fluorenone by selenium dioxide even at 235° is only upto 5 %. Therefore 2'-phenylfluoreno (2,1:6',5')γ-pyrone structure (VII) was assigned to this compound.

Synthesis of 2'-(p-methoxyphenyl)fluoreno(2,1:6',5') γ-pyrone :

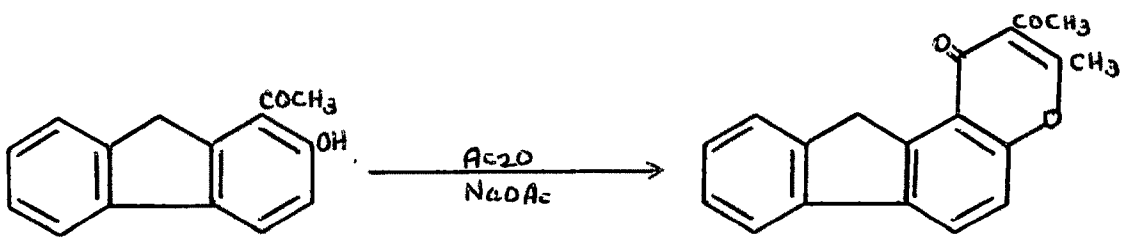
2-Hydroxy-1-acetylfluorene was condensed with anisaldehyde in the presence of alcoholic potassium hydroxide. The fluorenyl styryl ketone structure of the product was established by the formation of an acetyl derivative (X), a positive Wilson test, a deep red colouration with conc.

sulphuric acid and a greenish blue colouration with alcoholic ferric chloride. Therefore 2-hydroxy-1-fluorenyl p-methoxy styryl ketone structure (VIII) was assigned to this compound. On refluxing with alcoholic hydrochloric acid a product was obtained which did not give any colour with alcoholic ferric chloride or with a mixture of citric acid and boric acid in dry acetone. So the 2'-(p-methoxyphenyl)fluoreno(2,1:6',5') pyran-4'-one structure (IX) was assigned. On refluxing with selenium dioxide in iso-amyl alcohol it gave a product which analysed for 2'-(p-methoxyphenyl)fluoreno(2,1:6',5')γ-pyrone (XI). That the methylene group in position 9 was not oxidised was shown by the fact that the product was different from 2'-(p-methoxyphenyl)9-oxofluoreno(2,1:6',5')γ-pyrone prepared from 2-hydroxy-1-acetylfluorenone (p.161) and therefore 2'-(p-methoxyphenyl)fluoreno(2,1:6',5')γ-pyrone structure (XI) was assigned to the product.



Kostanecki-Robinson acetylation of 2-hydroxy-1-acetylfluorene : Synthesis of 2'-methyl-3'-acetylfluoreno (2,1:6',5')γ-pyrone :

2-Hydroxy-1-acetylfluorene on refluxing with fused sodium acetate and acetic anhydride gave a product which was insoluble in alkali. This compound analysed for the 3'-acetyl derivative of the desired γ-pyrone, and therefore 2'-methyl-3'-acetylfluoreno(2,1:6',5')γ-pyrone structure (XII) was assigned to this compound. The formation of 3-acyl chromone derivative in the Kostanecki-Robinson acylation is a common feature[6]. Attempts to remove the 3'-acetyl group did not succeed. When refluxed with sodium carbonate in alcohol, the original 2'-methyl-3'-acetyl fluoreno (2,1:6',5')γ-pyrone was recovered unchanged and when the hydrolysis was carried out with alcoholic sodium hydroxide 2-hydroxy-1-acetylfluorene was obtained. Bhullar and Venkataraman[7] have shown that it is sometimes difficult to remove the 3-acyl group from γ-pyrones.



XII

Attempted Kostanecki-Robinson benzoylation of 2-hydroxy-1-acetylfluorene :

2-Hydroxy-1-acetylfluorene, on heating with sodium benzoate and benzoic anhydride at 180° did not give the desired γ-pyrone. On decomposing the reaction mixture only a pasty mass was obtained from which no pure product could be isolated.

2-Hydroxy fluorenone :

2-Nitrofluorene was oxidised to 2-nitrofluorenone by sodium dichromate in acetic acid according to Diels[8]. Reduction of this compound was carried out by various workers using various reducing agents. In the present work 2-aminofluorenone was obtained in over 80 % yield by reducing 2-nitrofluorenone with sodium hydrosulphite in alcohol. 2-Aminofluorenone thus obtained was converted into the 2-hydroxyfluorenone by diazotisation and boiling with sulphuric acid according to Diels[8].

2-Hydroxy-1-acetylfluorenone :

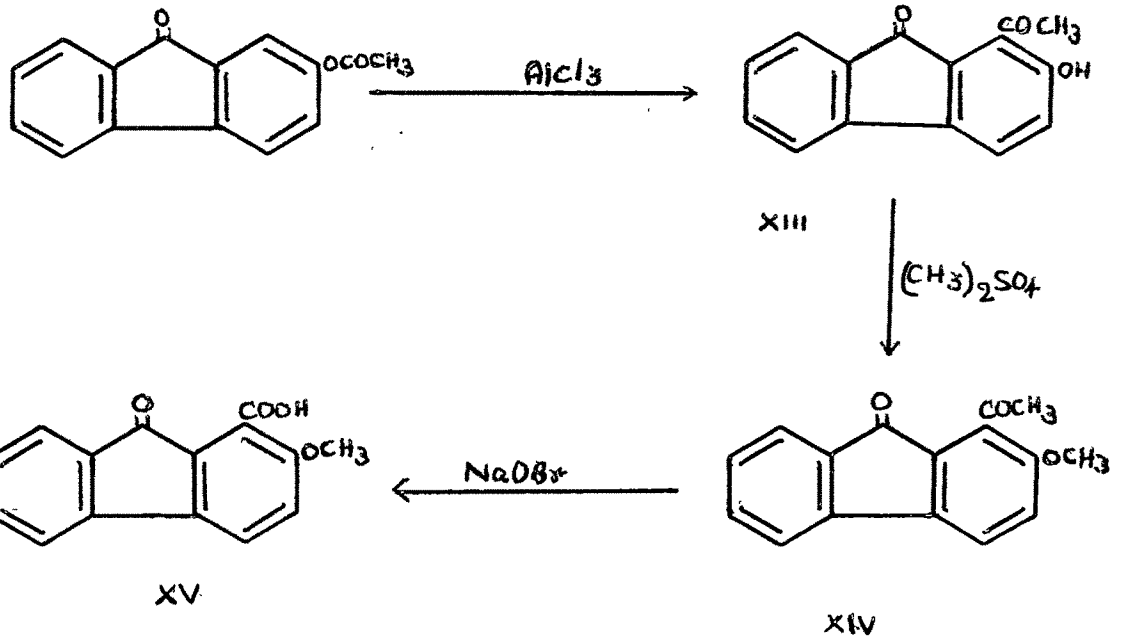
The Fries rearrangement of 2-acetoxyfluorenone has been studied by Bergmann and Berlin[3]. They reportdd the formation of two compounds. The first compound was obtained by heating at 80° a solution of 2-acetoxyfluorene in nitrobenzene in the presence of aluminium chloride. To this compound melting at 206° they assigned the 2-hydroxy-1-acetylfluorenone structure. The other compound was obtained by carrying out the reaction in nitrobenzene in the presence of anhydrous aluminium chloride at 115°. It melted at 249°.

According to them it analysed for $C_{15}H_{12}O_3$ while the molecular formula of 2-hydroxy-1-acetylfluorenone is $C_{15}H_{10}O_3$.

These workers based the structure of 2-hydroxy-1-acetylfluorenone on the formation of a pyridazine derivative by the action of hydrazine hydrate on the diketone. However the authors admitted that the analysis result of this pyridazine derivative did not agree with the calculated value. On calculation it was found that the analysis result came near to the calculated value of 2-hydroxyfluorenone-hydrazone. The m.p. of 2-hydroxyfluorenone hydrazone as reported by Gerhardt[9] is 201-2° and the m.p. of the pyridazine derivative reported by Bergamann and Berlin[3] is 197°. The m.p. of 2-hydroxy-1-acetylfluorenone reported by these workers also agrees with the m.p. of 2-hydroxyfluorenone. Moreover when the reaction was carried out according to Bergmann and Berlin[3] only 2-hydroxyfluorenone was obtained. Therefore it is to be assuemed that on subjecting 2-acetoxy fluorenone to Fries rearrangement at 80° in nitrobenzene and removing nitrobenzene with steam, only deacetylation takes place. The only data in favour of the formation of 2-hydroxy-1-acetylfluorenone is the analytical data.

In the present work 2-acetoxyfluorenone was subjected to Fries rearrangement without any solvent at 140-50°. On working up the reaction mixture, a compound which was soluble in sodium hydroxide was obtained. The melting point of this compound agreed with that of the second compound (m.p.249°) reported by Bergmann and Berlin[3]. To this compound 2-hydroxy-1-acetylfluorenone structure (XIII) was assigned by direct

comparison of its methyl ether (XIV) with 2-methoxy-1-acetyl fluorenone described earlier.



2-Methoxy-fluorenone-1-carboxylic acid :

2-Methoxy-1-acetylfluorenone dissolved in dioxane was added to a solution of sodium hypobromite and stirred at 40-50°. The product obtained on removal of the solvent and acidification gave effervescence with sodium bicarbonate solution. Therefore 2-methoxyfluorenone-1-carboxylic acid structure (XV) was assigned to this compound.

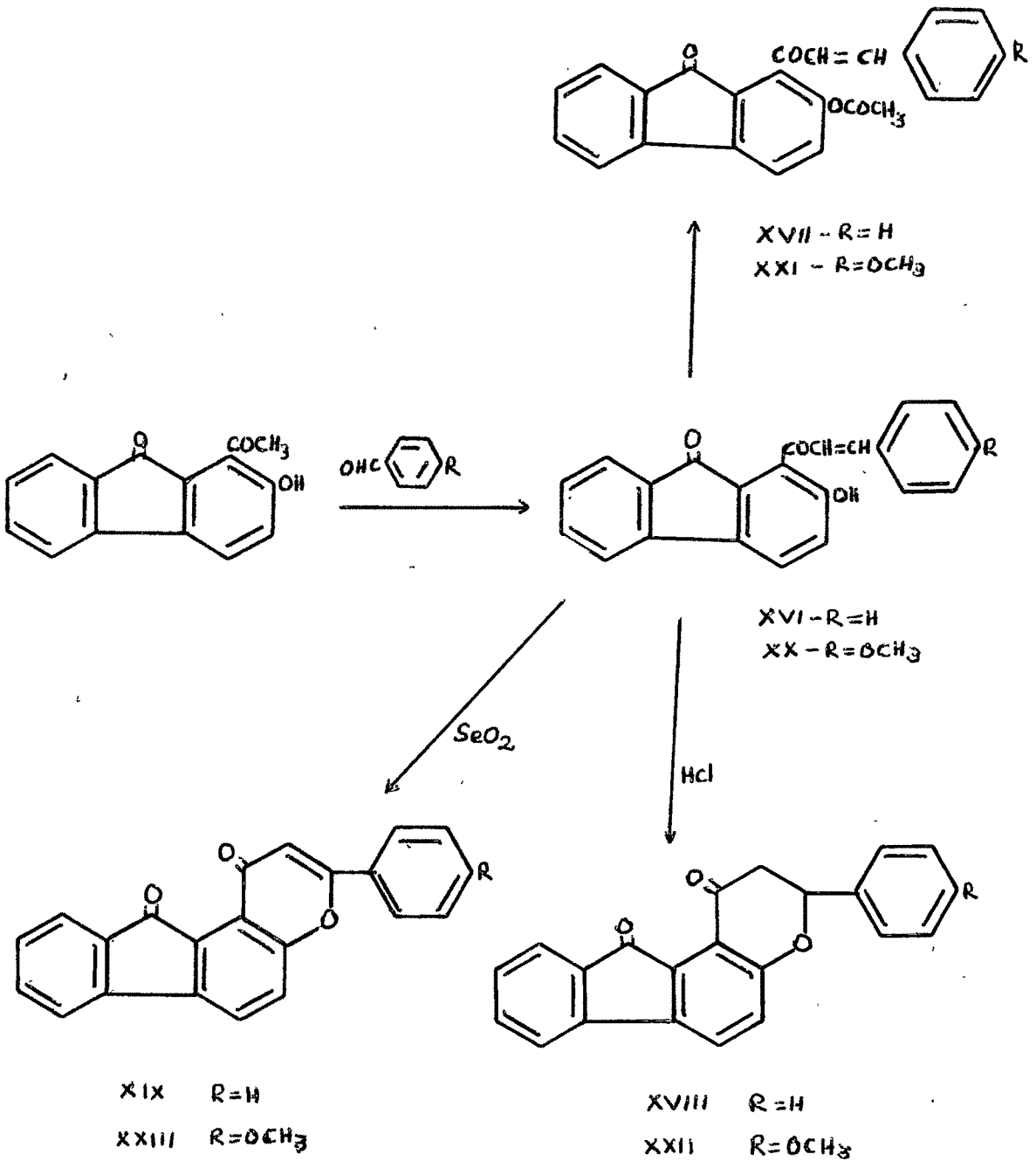
Synthesis of 2'-phenyl 9-oxofluoreno(2,1:6',5')γ-pyrone :

2-Hydroxy-1-acetylfluorenone was condensed with benzaldehyde in the presence of alcoholic potassium hydroxide. 2-Hydroxy-9-oxo-1-fluorenyl styryl ketone structure (XVI) was assigned to the product obtained because it gave an intense red colouration with concentrated sulphuric acid and answered the Wilson test. With alcoholic ferric chloride it gave a

reddish colouration. On refluxing with fused sodium acetate and acetic anhydride this compound gave an acetyl derivative (XVII). On refluxing with alcoholic hydrochloric acid a compound isomeric with the above styryl ketone was obtained to which 2'-phenyl-9-oxofluoreno(2,1:6',5')pyran-4'-one structure (XVIII) was assigned. The styryl ketone (XVI) on refluxing with selenium dioxide in iso-amyl alcohol gave a product to which 2'-phenyl-9-oxofluoreno(2,1:6',5')γ-pyrone structure (XIX) is assigned.

Synthesis of 2'-(p-methoxyphenyl)9-oxofluoreno(2,1:6',5') γ-pyrone :

2-Hydroxy-1-acetylfluorenone was condensed with anisaldehyde in the presence of alcoholic potassium hydroxide. The product gave an intense red colouration with conc. sulphuric acid and gave a positive Wilson test. With alcoholic ferric chloride it gave a reddish colour. When refluxed with acetic anhydride and fused sodium acetate it gave an acetyl derivative (XXI). On the basis of these tests 2-hydroxy-9-oxo-1-fluorenyl p-methoxystyryl ketone structure (XX) is assigned to the condensation product. On refluxing with alcoholic hydrochloric acid it gave an isomeric product to which 2'-(p-methoxyphenyl)-9-oxofluoreno (2,1:6',5') pyran-4'one structure (XXII) is assigned. The ketone (XX) on boiling with selenium dioxide in iso-amyl alcohol at 150° gave a compound to which 2'-(p-methoxyphenyl)-9-oxofluoreno (2,1:6',5')γ-pyrone structure (XXIII) is assigned.



XIX R=H

XXIII R=OCH3

XVIII R=H

XXII R=OCH3

Attempted Kostanecki-Robinson acetylation and benzoylation of 2-hydroxy-1-acetylfluorenone :

2-Hydroxy-1-acetylfluorenone was subjected to Kostanecki-Robinson acetylation. On decomposing the reaction mixture by pouring into ice only a pasty mass was obtained. Separation

of the product through column chromatography on alumina was tried but no pure products were obtained.

Kostanecki-Robinson benzoylation of the above ketone using benzoic anhydride and sodium benzoate was also attempted. The reaction mixture on decomposing with ice and on removing benzoic anhydride by petroleum ether and benzoic acid by sodium bicarbonate gave only an unworkable gum.

Attempted synthesis of fluoreno-a-pyrones :

Several attempts to prepare fluoreno-a-pyrones were made but were unsuccessful. 2-Hydroxyfluorene did not condense with ethyl acetoacetate in the presence of sulphuric acid either on keeping in the cold or on heating on a steam bath. Only the unreacted 2-hydroxyfluorene was recovered from the reaction mixture. The use of other condensing agents such as phosphorus pentoxide and aluminium chloride was tried but in these cases also no condensation took place.

Attempted formylation of 2-hydroxyfluorene :

The formylation of 2-hydroxyfluorene was attempted with a view to synthesis 2-hydroxy-1-formylfluorene which would be an intermediate for the synthesis of fluoreno-a-pyrone and also fluorenofuran.

The formylation was tried by various methods.2-Hydroxyfluorene on heating with hexamethylene tetramine in glacial acetic acid and decomposing the product with hydrochloric acid did not give the desired product, instead a polymeric product was obtained. The same reaction was tried in chloroform also. In this case only the unreacted 2-hydroxyfluorene was

recovered unchanged.

Formylation was tried by Gattermann reaction. When hydrogen chloride was passed through a solution of 2-hydroxyfluorene dissolved in dry ether in the presence of zinc cyanide no reaction took place and the 2-hydroxyfluorene was recovered unchanged. Addition of anhydrous aluminium chloride also did not give the desired formyl derivative.

Attempted chloromethylation of 2-hydroxyfluorene and its methyl ether :

The formylation being unsuccessful attempts to synthesise the formyl derivative through the chloromethyl derivative were made.

On passing hydrogen chloride through a solution of 2-hydroxyfluorene in glacial acetic acid containing paraformaldehyde, no chloromethyl compound was obtained. A solid separated, which on filtration turned into a paste. 2-Methoxyfluorene also gave the same result. Carrying out the reaction at lower temperature also did not improve the product.

Attempted synthesis of 9-oxofluoreno-a-pyrone :

Attempted condenstion of 2-hydroxyfluorenone with ethyl aceteacetate :

Attempts to condense 2-hydroxyfluorenone with ethyl acetoacetate in the presence of sulphuric acid gave only the unreacted product back. The condensation also did not take place in the presence of either phosphorus pentoxide or aluminium chloride.

Attempted formylation of 2-hydroxyfluorenone :

Attempts to formylate 2-hydroxyfluorenone with hexamethylene tetramine in glacial acetic acid or through Gattermann reaction did not succeed.

Attempted chloromethylation of 2-hydroxyfluorenone and its methyl ether :

Chloromethylation of 2-hydroxyfluorenone and its methyl ether did not succeed. Addition of zinc chloride or anhydrous aluminium chloride as a catalyst also did not give any chloromethyl derivative.

2-Hydroxyfluorene-3-aldehyde has been reported by Arene and Taylor[10] by the Riemer-Teimann reaction. The yield reported by the authors was only 5 % and it was found to be so by the present author. Therefore by this method enough of the formyl derivative could not be prepared to proceed further.

EXPERIMENTAL.

2-Aminofluorene :

2-Nitrofluorene, prepared according to Kuhn[1] (20 g.), was powdered well and refluxed with alcohol on a steam bath. It dissolved only partially. To this suspension water (100 ml.) and sodium hydrosulphite (50 g.) were added. Vigorous reaction took place and the nitrofluorene went in solution. It was refluxed for half an hour. The solvent was distilled off and the mixture was diluted with water. The solid obtained was filtered and washed with water. It was then crystallised from alcohol. M.P. 127-28°. Yield 95 %. Grey, Hartley and Ibbotson[2] gave m.p. 127.5°.

2-Hydroxyfluorene :

2-Aminofluorene was diazotised in acetic acid and the diazonium salt was hydrolysed with sulphuric acid according to Grey, Hartley and Ibbotson[2]. 2-Hydroxyfluorene obtained was purified by dissolving in warm sodium hydroxide and reprecipitating by hydrochloric acid. It was crystallised from dilute acetic acid. M.P. 170°. Grey, Hartley and Ibbotson[2] gave the m.p. 170.5°.

2-Hydroxy-1-acetylfluorene :

2-Hydroxyfluorene was acetylated and the product was subjected to Fries rearrangement according to Bergmann and Berlin[3].

2-Methoxy-1-acetylfluorene :

A mixture of 2-hydroxy-1-acetylfluorene (0.5 g.) in dry acetone (20 ml.), anhydrous potassium carbonate (1 g.) and

dimethyl sulphate (0.5 ml.) was refluxed on a steam bath for 4 hrs. The solvent was evaporated and the residue was diluted with water. The separated solid crystallised from dilute acetic acid in colourless needles (0.5 g.), m.p. 154°.

Analysis : Found : C, 80.67 ; H, 5.75 %.

$C_{16}H_{14}O_2$: requires : C, 80.67 ; H, 5.88 %.

Oxidation of 2-methoxy-1-acetylfluorene to 2-methoxy-1-acetylfluorenone :

The above compound (0.5 g.) was dissolved in acetic acid (20 ml.) and sodium dichromate (2 g.) was added. The mixture was refluxed on a sand bath for 1 hour. It was then cooled and diluted with water. The separated solid was crystallised from dilute acetic acid in yellow needles, (0.3 g.), m.p. 186°.

Analysis : Found : C, 75.94 ; H, 4.46 %.

$C_{16}H_{12}O_3$: requires : C, 76.19 ; H, 4.76 %.

The pyridazine derivative :

2-Methoxy-1-acetylfluorenone (1 g.) was dissolved in alcohol (150 ml.) by refluxing. Hydrazine hydrate (85 % :0.2 ml.) was added, and the mixture was refluxed on a steam bath for 8 hrs. The solvent was removed by distillation and the reaction mixture was diluted with water. The yellow solid obtained was crystallised from benzene in yellow crystals (0.5 g.), m.p. 238°.

Analysis : Found : N, 11.25 %.

$C_{16}H_{12}ON_2$: requires : N, 11.29 %.

Condensation of 2-hydroxy-1-acetylfluorene with benzaldehyde : Synthesis of 2-hydroxy-1-fluorenyl styryl ketone :

2-Hydroxy-1-acetylfluorene (1.5 g.) was dissolved in alcohol (100 ml.) by refluxing. The solution was then cooled well and potassium hydroxide (7 g. in 7 ml. of water) and benzaldehyde (1.5 ml.) were added. The mixture was kept at room temperature for 24 hrs. A dark red solution resulted. This was then diluted with cold water and acidified with conc. hydrochloric acid. The yellow solid obtained was filtered and crystallised from alcohol in yellow needles (0.6 g.), m.p. 182°.

Analysis : Found : C, 84.41 ; H, 5.42 %.

$C_{22}H_{16}O_2$: requires : C, 84.61 ; H, 5.23 %.

This compound gave a yellow colour with a mixture of boric acid and citric acid in dry acetone (Wilson test[4]) and greenish blue colour with alcoholic ferric chloride. With conc. sulphuric acid it gave a red colouration.

2-Acetoxy-1-fluorenyl styryl ketone :

The above ketone (0.5 g.) was mixed with freshly fused and powdered sodium acetate (1 g.) and acetic anhydride (2 ml.) and the mixture was refluxed on a sand bath for 1 hour. It was then poured on ice and kept overnight. The solid [illegible] crystallised from benzene-petroleum ether in light yellow needles (0.3 g.), m.p. 179°.

Analysis : Found : C, 81.25 ; H, 4.98 %.

$C_{24}H_{18}O_3$: requires : C, 81.36 ; H, 5.08 %.

2'-Phenylfluoreno(2,1:6',5')pyran-4'-one :

2-Hydroxy-1-fluorenyl styryl ketone (1 g.) was dissolved in alcohol (100 ml.) and conc. hydrochloric acid (10 ml.) was added. The mixture was refluxed on a steam bath for 36 hrs. The solvent was removed by distillation and the mixture was diluted with water. The solid obtained was crystallised from benzene-petroleum ether in colourless crystals (0.4 g.), m.p. 156°.

Analysis : Found : C, 84.78 ; H, 4.98 %.

$C_{22}H_{16}O_2$: requires : C, 84.61 ; H, 5.13 %.

2'-Phenylfluoreno(2,1:6',5')γ-pyrone :

2-Hydroxy-1-fluorenyl styryl ketone (1 g.) was dissolved in iso-amyl alcohol (20 ml.) and selenium dioxide (3 g.) was added. The mixture was heated in an oil bath at 140-50° for 15 hrs. It was then filtered hot and the solvent was removed by steam distillation. The yellow product obtained was crystallised from benzene-petroleum ether mixture in yellow needles (0.4 g.), m.p. 250°.

Analysis : Found : C, 85.29 ; H, 4.52 %.

$C_{22}H_{14}O_2$: requires : C, 85.15 ; H, 4.47 %.

Condensation of 2-hydroxy-1-acetylfluorene with anisaldehyde : 2-Hydroxy-1-fluorenyl p-methoxy styryl ketone :

2-Hydroxy-1-acetylfluorene (1.5 g.) was dissolved in alcohol (100 ml.) by heating. It was then cooled well and potassium hydroxide (8 g. in 8 ml. water) and anisaldehyde (1.5 ml.) were added. The mixture was kept overnight at

room temperature. The dark red solution obtained was then diluted with cold water and acidified with conc.hydrochloric acid with proper cooling. The yellow solid obtained was crystallised from benzene in yellow needles (0.8 g.), m.p.167°.

Analysis : Found : C, 80.87 ; H, 5.29 %.

$C_{23}H_{18}O_3$: requires : C, 80.70 ; H, 5.26 %.

This compound gave an intense red colouration with conc. sulphuric acid and a yellow colour with a mixture of citric acid and boric acid in dry acetone (Wilson test). With alcoholic ferric chloride a greenish blue colour was obtained.

2-Acetoxy-1-fluorenyl p-methoxy styryl ketone :

The above hydroxy ketone derivative (0.5 g.) was mixed with freshly fused sodium acetate (1 g.) and acetic anhydride (2 ml.) and the mixture was refluxed on a sand bath for 1 hour. It was then added to ice and kept overnight. The separated solid crystallised from benzene-petroleum ether mixture in light yellow needles (0.3 g.), m.p. 191°.

Analysis : Found : C, 28.60 ; H, 5.43 %.

$C_{25}H_{20}O_4$: requires : C, 78.12 ; H, 5.21 %.

2'(p-Methoxyphenyl)fluorene(2,1:6',5')pyran-4'-one :

2-Hydroxy-1-fluorenyl p-methoxy styryl ketone (1 g.) was dissolved in alcohol (100 ml.) and conc. hydrochloric acid (10 ml.) was added. The mixture was refluxed on a steam bath for 36 hrs. The solvent was then removed by distillation and the mixture was diluted with water. The

separated solid was crystallised from benzene-petroleum ether mixture in light yellow needles (0.4 g.), m.p. 187°.

Analysis : Found : C, 80.63 : H, 5.62 %.

$C_{23}H_{18}O_3$: requires : C, 80.70 ; H, 5.26 %.

2'(p-Methoxyphenyl)fluoreno(2,1:6',5')γ-pyrone :

2-Hydroxy-1-fluorenyl p-methoxy styryl ketone (1 g.) was dissolved in iso-amyl alcohol (20 ml.) and selenium dioxide (3 g.) was added. The mixture was then refluxed in an oil bath at 140-50° for 15 hrs. and then filtered hot. The solvent was then removed by steam distillation and the solid obtained crystallised from dilute acetic acid in yellow needles (0.3 g.), m.p. 253°.

Analysis : Found : C, 81.43 ; H, 4.76 %.

$C_{23}H_{16}O_3$: requires : C, 81.17 ; H, 4.70 %.

Kostanecki-Robinson acetylation of 2-hydroxy-1-acetylfluorene : 2'-Methyl-3'-acetylfluoreno(2,1:6',5')γ-pyrone :

2-Hydroxy-1-acetylfluorene (1.5 g.) was mixed well with freshly fused sodium acetate (3 g.) and acetic anhydride (3 ml.) was added. The mixture was heated in an oil bath at 180-90° for 10 hrs. It was then added to ice and kept overnight. The separated solid was crystallised from dilute acetic acid in yellow needles (0.6 g.), m.p. 242°.

Analysis : Found : C, 78.41 ; H, 5.00 %.

$C_{19}H_{14}O_3$: requires : C, 78.61 ; H, 4.83 %.

Attempted deacetylation of 2'-methyl-3'-acetylfluoreno(2,1:6',5')γ-pyrone :

The above γ-pyrone derivative (0.5 g.) was dissolved in alcohol (50 ml.) and anhydrous sodium carbonate (1 g.) was added. The mixture was refluxed on a steam bath for 8 hrs. The solvent was removed by distillation and the mixture was then diluted with water. The solid obtained was crystallised from dilute acetic acid, M.p. and mixed m.p. with 2'-methyl-3'-acetylfluoreno(2,1:6',5')γ-pyrone was 242°.

The deacetylation was attempted with sodium hydroxide in alcohol. The product obtained on working up as above was found to be 2-hydroxy-1-acetylfluorene. M.P. and mixed m.p. with an authentic sample was 159°.

Attempted Kostanecki-Robinson benzoylation of 2-hydroxy-1-acetyl fluorene :

2-Hydroxy-1-acetylfluorene (1 g.) was mixed with anhydrous sodium benzoate (2 g.) and benzoic anhydride (3 g.) and the mixture was heated in an oil bath at 180-90° for 10 hrs. The mixture was then added to ice and boiled with water to remove the unreacted benzoic anhydride and sodium benzoate. The product left behind was a pasty mass. It was washed with sodium bicarbonate to remove the benzoic acid. The dried mass was dissolved in benzene and chromatographed through an alumina column. It was then eluted successively with petroleum ether, benzene petroleum ether mixture and benzene. On removing the solvents no pure product was obtained.

Attempted condensation of 2-hydroxyfluorene with ethyl aceto acetate :

2-Hydroxyfluorene (1 g.) was mixed with ethyl aceto-

acetate (1 ml.) and sulphuric acid (20 ml.; 80 %) was added. The mixture was kept at room temperature for 24 hrs. It was then added to ice. The separated solid on crystallisation from dilute acetic acid gave m.p. 170°. Mixed m.p. with a sample of 2-hydroxyfluorene was not depressed.

Attempted formylation of 2-hydroxyfluorene :

(a) 2-Hydroxyfluorene (1 g.) was dissolved in glacial acetic acid (20 ml.) and hexamethylene tetramine (2 g.) was added. The mixture was heated on a steam bath for 4 hrs. Hydrochloric acid (5 ml.; 1:1) was added and the heating was continued for 30 minutes. It was then added to water and the separated solid was filtered. A pasty mass resulted. It was then dried and dissolved in chloroform and chromatographed through alumina. The column was eluted successively with petroleum ether, benzene and chloroform. On evaporating the benzene fraction, a pasty mass was obtained which gave a greenish blue colour with alcoholic ferric chloride, but on crystallisation no pure product was obtained. On evaporating other fractions no solid was obtained.

(b) 2-Hydroxyfluorene (1 g.) was dissolved in dry ether (100 ml.). Anhydrous aluminium chloride (1 g.) and zinc cyanide (1 g.) were added. Dry hydrogen chloride was passed through the solution for 6 hrs. The solvent was removed and the product was crystallised from dilute acetic acid. It was found on direct comparison to be 2-hydroxyfluorene.

Attempted chloromethylation of 2-hydroxyfluorene and its methyl ether :

Paraformaldehyde (0.3 g.) was suspended in glacial

acetic acid (20 ml.) and dry hydrogen chloride was passed till a clear solution was obtained. 2-Hydroxyfluorene (1 g.) was added and hydrogen chloride was passed for further 3 hrs. A solid separated. On filtration it turned into a paste. It was then dissolved in dry benzene and passed through an alumina column. On eluting the column with petroleum ether and then with benzene and evaporating the solvents no pure product was obtained.

The same reaction was carried out with 2-methoxy-fluorene under identical condition. Here again, the separated solid on filtration turned into a paste from which no pure product could be isolated.

Synthesis of 2-aminofluorenone :

2-Nitrofluorenone (20 g.) prepared according to Diels[8] was powdered well and boiled with alcohol (200 ml.). To this suspension water (100 ml.) and sodium hydrosulphite (50 g.) were added. Vigorous reaction took place and most of the nitro compound went in solution. It was then refluxed for half an hour. The nitro fluorenone dissolved and a dark red solution was obtained. The solvent was removed by distillation and the mixture was diluted with water. Conc. hydrochloric acid (100 ml.) was added and the solution was heated to boiling and filtered hot. This was repeated three times. The combined filtrate was made alkaline by liquor ammonia and the dark red solid obtained was crystallised from alcohol in dark red flakes (15 g.)m.p. 163°. Diels[8] gave m.p. 163°.

Synthesis of 2-hydroxyfluorenone :

2-Aminofluorenone was diazotised in acetic acid in the presence of sulphuric acid according to Diels[8] and the diazonium sulphate was decomposed by boiling with sulphuric acid. The product obtained gave m.p. 210°. Diels[8] gave m.p. 210-11°.

2-Acetoxyfluorenone :

2-Hydroxyfluorenone was acetylated according to Bergmann and Berlin[3] and the product was crystallised from acetic acid in yellow flakes, m.p. 157°. Bergmann and Berlin[3] gave the m.p. 157°.

2-Hydroxy-1-acetylfluorenone :

2-Acetoxyfluorenone (2 g.) was powdered well and mixed with anhydrous aluminium chloride (2 g.) and the mixture was heated in an oil bath at 140-50° for 4 hrs. It was then cooled and decomposed by adding ice and hydrochloric acid. The separated solid was filtered and dissolved in cold sodium hydroxide. It was again filtered and the filtrate was acidified with conc. hydrochloric acid. The separated solid was crystallised from acetic acid in brown needles (0.8 g.), m.p. 249°.

Analysis : Found : C, 74.87 ; H, 4.16 %.

$C_{15}H_{10}O_3$: requires : C, 75.11 ; H, 4.20 %.

This compound gave a red colouration with alcoholic ferric chloride.

2-Methoxy-1-acetylfluorenone :

The above ketone (0.5 g.) in dry acetone (20 ml.) was refluxed with anhydrous potassium carbonate (1 g.) and

dimethyl sulphate (0.5 ml.) on a steam bath for 3 hrs. The solvent was then allowed to evaporate and the residue was diluted with water. The separated solid crystallised from dilute acetic acid in yellow needles (0.4 g.), m.p. 186°. Mixed m.p. of this compound with 2-methoxy-1-acetylfluorenone obtained by the oxidation of 2-methoxy-1-acetylfluorene described earlier was not depressed.

2-Methoxyfluorenone-1-carboxylic acid :

2-Methoxy-1-acetyl fluorenone (1 g.) was dissolved in dioxane. This solution was slowly added to a solution of sodium hypobromite (prepared from 3 g. of sodium hydroxide and 3 g. of bromine) with constant stirring. This solution was stirred at 40-50° for 8 hrs. The excess of hypobromite was destroyed by adding sodium sulphite and then boiled to remove the dioxane. It was filtered and the filtrate was acidified with conc. hydrochloric acid with cooling. The solid obtained was further purified by extraction with sodium bicarbonate and finally crystallised from dilute acetic acid in yellow flakes (0.4 g.) m.p. 241°.

Analysis : Found : C, 70.79 ; H, 3.62 %.

$C_{15}H_{10}O_4$: requires : C, 70.87 ; H, 3.93 %.

Condensation of 2-hydroxy-1-acetylfluorenone with benzaldehyde : 2-Hydroxy-9-oxo-1-fluorenyl styryl ketone :

2-Hydroxy-1-acetylfluorenone (1 g.) was dissolved in hot alcohol (100 ml.). The solution was cooled and potassium hydroxide (5 g. in 5 ml. water) and then benzaldehyde (1 ml.) were added and the mixture left

overnight at room temperature. The dark red solution obtained was then diluted with water and acidified with conc. hydrochloric acid with cooling. The separated solid crystallised from xylene in red prisms (0.4 g.), m.p. 234°.

Analysis	: Found	: C, 81.12 ; H, 4.31 %.
$C_{22}H_{14}O_3$	: requires	: C, 80.98 ; H, 4.29 %.

This compound gave an intense red colouration with conc. sulphuric acid and a positive Wilson test. It also gave a reddish colouration with alcoholic ferric chloride.

2-Acetoxy-9-oxo-1-fluorenyl styryl ketone :

The above ketone (0.5 g.) was mixed with freshly fused sodium acetate (1 g.) and acetic anhydride (2 ml.) and refluxed on a sand bath for 1 hour. It was then added to ice and kept overnight. The separated solid was then crystallised from acetic acid in yellow needles (0.3 g.), m.p. 169°.

Analysis	: Found	: C, 78.43 ; H, 4.08 %.
$C_{24}H_{16}O_4$	: requires	: C, 78.27 ; H, 4.34 %.

2-Phenyl 9-oxofluoreno(2,1:6,5)pyran-4-one :

2-Hydroxy-9-oxo-1-fluorenyl styryl ketone (1 g.) was dissolved in alcohol (150 ml.) and hydrochloric acid (15 ml.) was added. The mixture was refluxed on a steam bath for 48 hrs. The solvent was removed by distillation and water was added. The separated solid was crystallised from benzene in yellow needles (0.6 g.), m.p. 192°.

Analysis	: Found	: C, 81.16 ; H, 4.29 %.
$C_{22}H_{14}O_3$	: requires	: C, 80.98 ; H, 4.29 %.

2'-Phenyl 9-oxofluoreno(2,1:6',5')γ-pyrone :

2-Hydroxy-9-oxo-1-fluorenyl styryl ketone (1 g.) was dissolved in iso-amyl alcohol (50 ml.) and selenium dioxide (3 g.) was added. The mixture was refluxed in an oil bath at 140-50° for 15 hrs. It was then filtered hot and the solvent was then removed by steam distillation. The solid obtained was crystallised from xylene in orange prisms (0.3 g.), m.p. 284°.

Analysis : Found : C, 81.17 ; H, 3.84 %.

$C_{22}H_{12}O_3$: requires : C, 81.47 ; H, 3.70 %.

Condensation of 2-hydroxy-1-acetylfluorenone with anisaldehyde : 2-Hydroxy-9-oxo-1-fluorenyl p-methoxy styryl ketone :

2-Hydroxy-1-acetylfluorenone (1 g.) was dissolved in alcohol (100 ml.) by heating. The solution was cooled and potassium hydroxide (5 g. in 5 ml. water) and anisaldehyde (1 ml.) were added. The mixture was left at room temperature for 24 hrs. The dark-red solution obtained was then diluted with cold water and acidified with conc. hydrochloric acid with cooling. The solid obtained was crystallised from xylene in red prisms (0.4 g.), m.p. 238°.

Analysis : Found : C, 77.23 ; H, 4.67 %.

$C_{23}H_{16}O_4$: requires : C, 77.54 ; H, 4.49 %.

This compound gave an intense red colouration with conc. sulphuric acid and a positive Wilson test. With alcoholic ferric chloride it gave a red colour.

2-Acetoxy-9-oxo-1-fluorenyl p-methoxystyryl ketone :

The above ketone (0.5 g.) was mixed with freshly fused sodium acetate (1 g.) and acetic anhydride (2 ml.) and the mixture refluxed on a sand bath for 1 hour. It was then cooled and added to ice and left overnight. The separated solid was crystallised from benzene in orange needles (0.3 g.), m.p. 174°.

Analysis : Found : C, 75.61 ; H, 4.45 %.

$C_{25}H_{18}O_5$: requires : C, 75.37 ; H, 4.52 %.

2'-(p-Methoxyphenyl)9-oxofluoreno(2,1:6,5')pyran-4'-one :

2-Hydroxy-9-oxo-1-fluorenyl p-methoxystyryl ketone (1 g.) was dissolved in alcohol (200 ml.) and conc. hydrochloric acid (20 ml.) was added. The mixture was then refluxed on a steam bath for 48 hrs. The solvent was then distilled and the mixture was diluted with water. The solid obtained was crystallised from benzene in orange prisms (0.4 g.), m.p. 216°.

Analysis : Found : C, 77.39; H, 4.53 %.

$C_{23}H_{16}O_4$: requires : C, 77.54; H, 4.49 %.

2'(p-Methoxyphenyl)9-oxofluoreno(2,1:6,5')γ-pyrone :

2-Hydroxy-9-oxo-1-fluorenyl p-methoxystyryl ketone (1 g.) was dissolved in iso-amyl alcohol (50 ml.) and selenium dioxide (3 g.) was added. The mixture was then refluxed in an oil bath at 140-50° for 15 hrs. It was then filtered hot and the solvent was removed by steam distillation. The separated solid was crystallised from

xylene in orange cubes (0.3 g.), m.p. 296°.

Analysis	: Found	: C, 78.21 ; H, 3.50 %.
$C_{23}H_{14}O_4$	: requires	: C, 77.96 ; H, 3.95 %.

Attempted Kostanecki-Robinson acetylation and benzoylation of 2-hydroxy-1-acetylfluorenone :

2-Hydroxy-1-acetylfluorenone (1 g.) was mixed with freshly fused powdered sodium acetate (2 g.) and acetic anhydride (3 ml.) was added. The mixture was heated in an oil bath for 10 hrs. at 180-90°. The mixture was then added to ice. A pasty mass was obtained from which no pure product could be isolated.

Kostanecki-Robinson benzoylation also was tried in a similar way. The product obtained on decomposing the reaction mixture with ice was again a pasty mass from which no pure product could be isolated.

Attempted condensation of 2-hydroxyfluorenone with ethyl acetoacetate :

2-Hydroxyfluorenone (1 g.) was mixed with ethyl acetoacetate (1 ml.) and sulphuric acid (20 ml.; 80 %) and the mixture was kept overnight. It was then added to ice and the solid obtained was crystallised from dilute acetic acid in red needles. It was soluble in dilute sodium hydroxide. Mixed m.p. with 2-hydroxyfluorenone was not depressed.

The same condensation was tried with phosphorus pentoxide as a condensing agent in the place of sulphuric acid. In this case also 2-hydroxyfluorenone was the only

product isolated from the reaction mixture.

Attempted formylation of 2-hydroxyfluorenone :

2-Hydroxyfluorenone (1 g.) was dissolved in acetic acid (50 ml.) and hexamethylene tetramine (3 g.) was added. The mixture was heated on a steam bath for 4 hrs. Hydrochloric acid (10 ml. ; 1:1) was added and the heating was continued for half an hour. It was then diluted and the solid obtained was crystallised from dilute acetic acid, m.p. 210°. Mixed m.p. with 2-hydroxyfluorenone was not depressed.

2-Hydroxyfluorenone (0.5 g.) was dissolved in dry ether (150 ml.) and zinc cyanide (0.5 g.) was added. Dry hydrogen chloride was passed through this solution for 4 hrs. The solvent was then evaporated and the solid obtained was washed with water and boiled with hydrochloric acid. The red product obtained was crystallised from dilute acetic acid, m.p. 210°. Mixed m.p. with 2-hydroxyfluorenone was not depressed.

Attempted chloromethylation of 2-hydroxyfluorenone and its methyl ether :

Paraformaldehyde (0.3 g.) was suspended in glacial acetic acid (25 ml.) and dry hydrogen chloride was passed till a clear solution was obtained. 2-Hydroxyfluorenone (1 g.) was added and hydrogen chloride was passed for 4 hrs. The solid obtained on dilution when crystallised from dilute acetic acid gave m.p. 210°. Mixed m.p. with 2-hydroxyfluorenone was not depressed.

The same reaction was carried out with 2-methoxy fluorenone. In this case also 2-methoxyfluorenone was recovered from the reaction mixture.

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SECTION II

SYNTHESIS OF FLUORENOFURAN DERIVATIVES

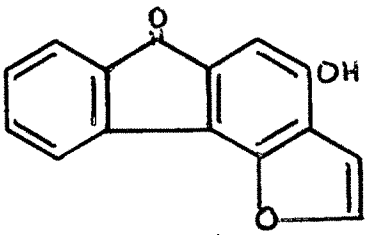
SECTION II.

Synthesis of fluorenofuran derivatives :

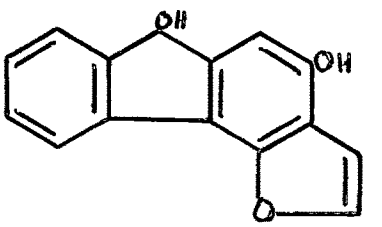
Many furan derivatives occur in nature. A large number of furan derivative, especially benzofuran derivatives and naphtho furan derivatives have been synthesised. Various methods which are employed in the synthesis of furan derivatives are summarised in Part I Section II of this thesis.

Very few furan derivatives in which the furan ring is fused to the fluorene ring system are known. Those which are known are prepared by building up the fluorene ring system on a suitable furan derivative.

Fluoreno furan derivatives are found to be useful in photography. Grey, black or brown images are formed on a photographic plate when 2-hydroxy-9-oxofluoreno(4,3:5',4') furan (I) is used as a colour coupler. When 2,9-dihydroxy-fluoreno(4,3:5',4')furan (II) is used olive green colours are obtained.[1]



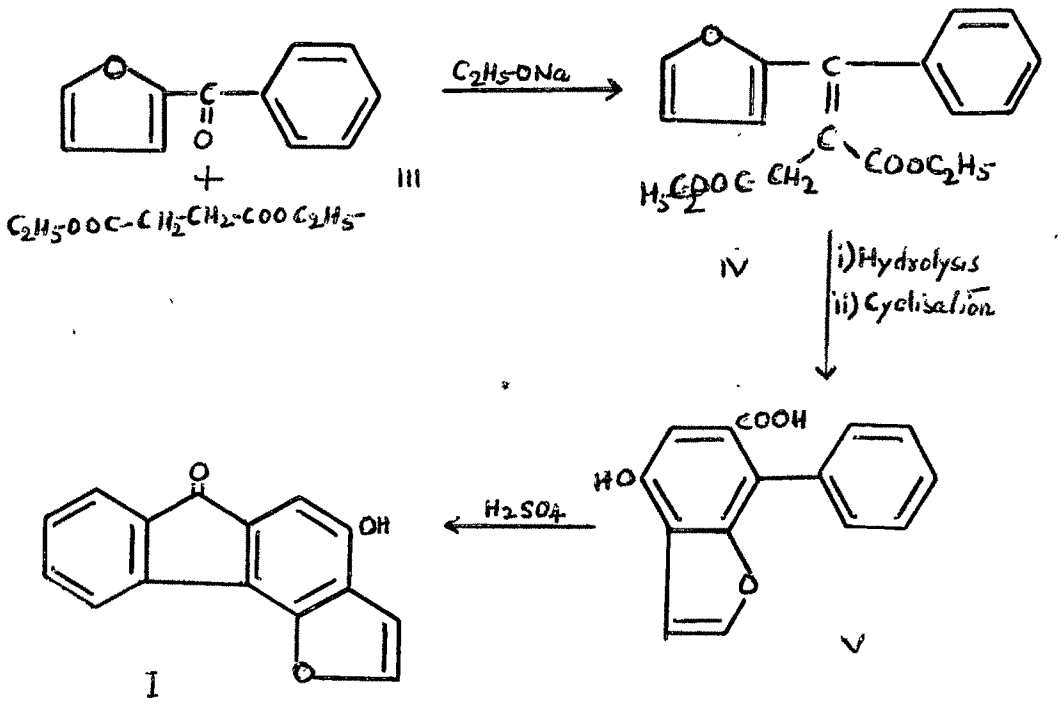
I



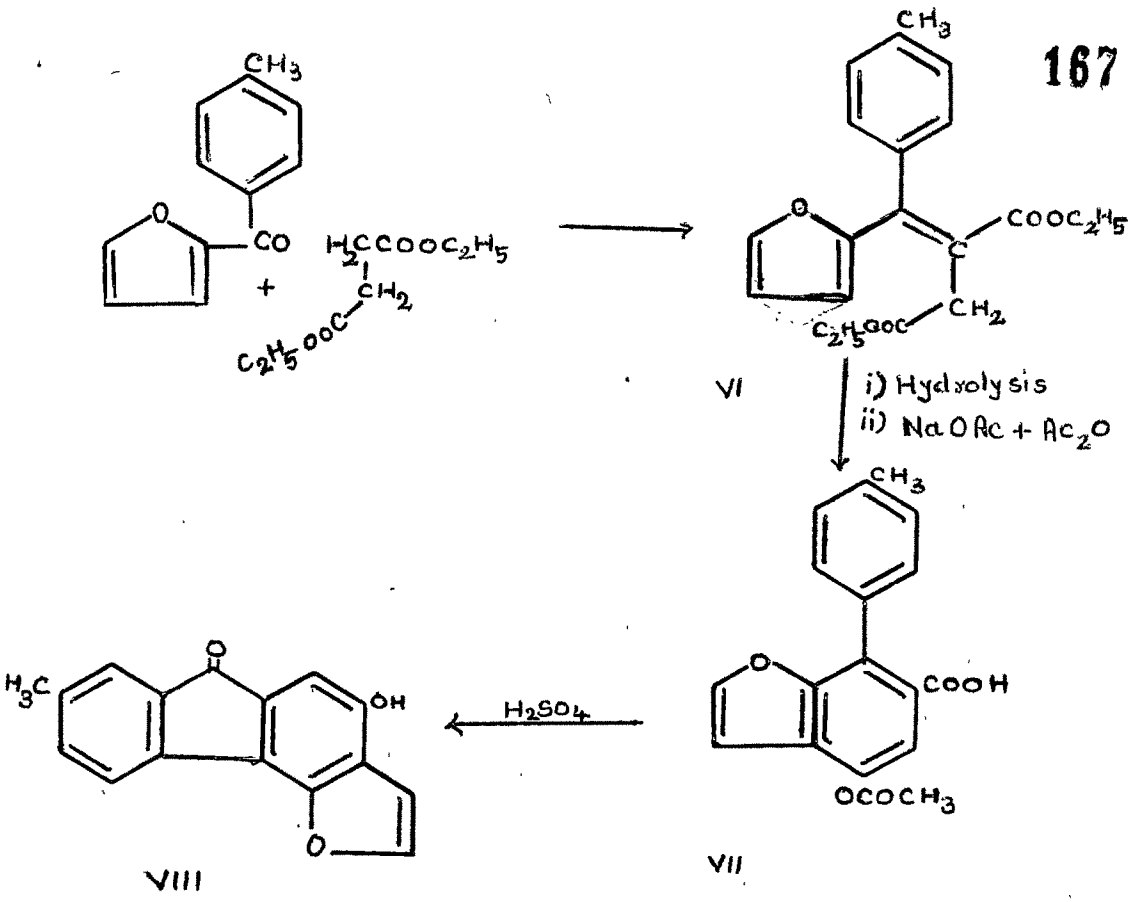
II

The fluorenofuran (I) was synthesised by condensing 2-furyl-phenyl ketone (III) with succinic ester in the presence of sodium ethoxide. The product[(V)] obtained was

hydrolysed to the acid and cyclised to a benzofuran derivative (V). When this was treated with conc. sulphuric acid at room temperature 2-hydroxy-9-oxo-fluoreno(4,3:5',4') furan (I) was obtained[2]. On reduction it gave the 2,9-dihydroxy derivative (II).



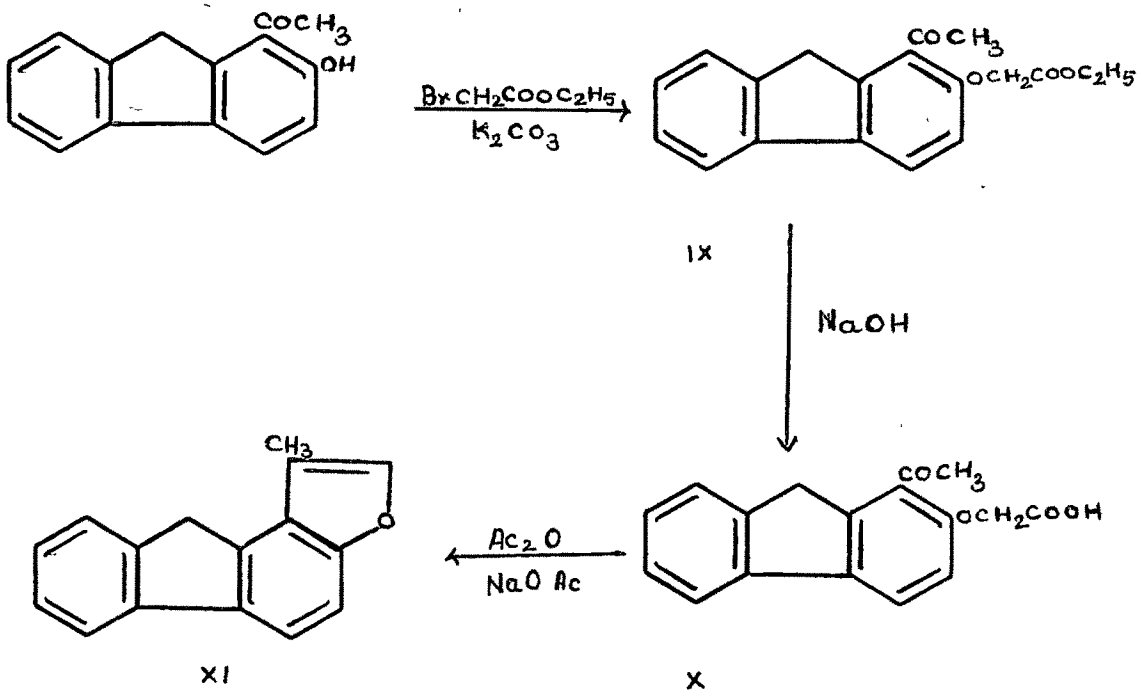
Borsche and Leditschke[3] synthesised 2-hydroxy-7-methyl-9-oxo-fluoreno(4,3:5',4')furan (VIII) in an identical manner, starting with 2-furyl 4-tolyl ketone . This was condensed with ethyl succinate and the product (VI) was hydrolysed and cyclised with acetic anhydride and sodium acetate. The product 7(4-methylphenyl)-4-acetoxy benzofuran 6-carboxylic acid (VII) was deacetylated and cyclised with conc. sulphuric acid to the fluorenofuran (VIII)



No other fluoreno furan derivatives seem to have been synthesised so far. It was therefore thought of interest to synthesise some fluorenofurans.

Synthesis of 3'-methylfluoreno(2,1:5',4')furan :

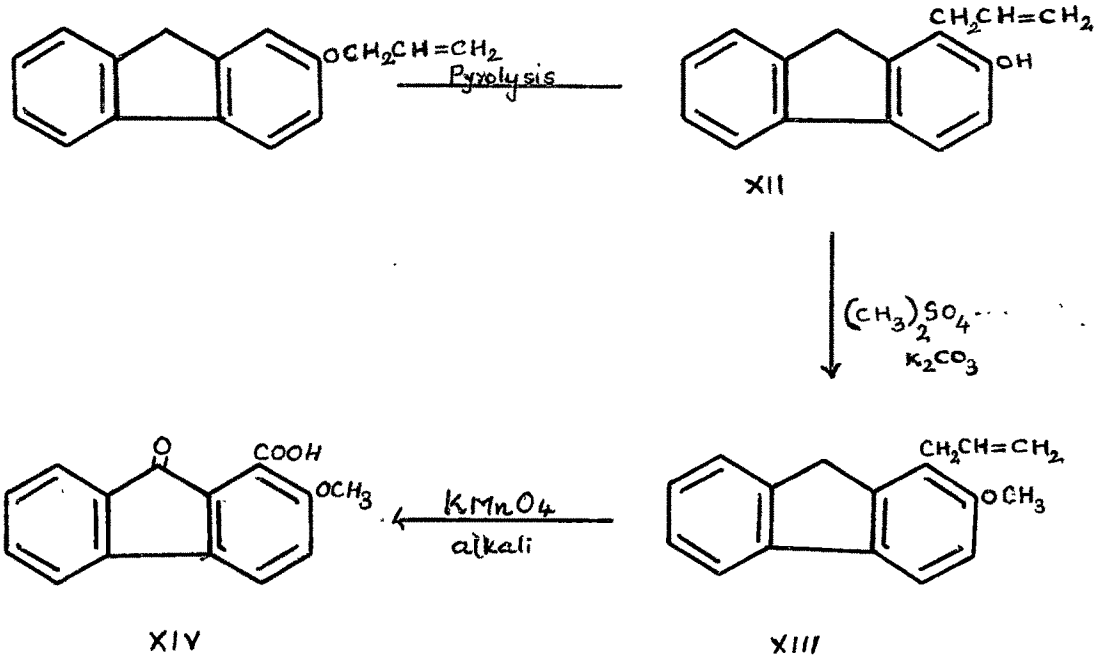
2-Hydroxy-1-acetylfluorene when refluxed in dry acetone with ethyl bromoacetate in the presence of anhydrous potassium carbonate gave 2-carboxymethoxy-1-acetylfluorene (IX). This ester on heating with sodium hydroxide gave the corresponding acid (X). The acid when refluxed with freshly fused sodium acetate and acetic anhydride gave 3'-methyl-fluoreno(2,1:5',4')furan (XI).



2-Hydroxy-1-allyl fluorene :

2-Allyloxyfluorene was subjected to pyrolysis according to Lothrop[4]. Out of the two products reported, only the one melting at 111° could be obtained in a workable quantity. Lothrop[4] assigned 2-hydroxy-1-allylfluorene structure to this compound without giving a conclusive proof for the structure. In the present work the structure was established in the following way. The hydroxy-allyl compound was methylated by refluxing with dimethyl sulphate in dry acetone in the presence of anhydrous potassium carbonate. The methoxy allyl compound (XIII) was heated with alkaline potassium permanganate at 50-60° on a water bath. The solution was filtered and the filtrate was acidified. The separated solid was found to be identical with 2-methoxy-fluorenone-1-carboxylic acid (XIV) described in Section I,

page 158. Therefore 2-hydroxy-1-allyl fluorene structure (XII) has been assigned to the compound.

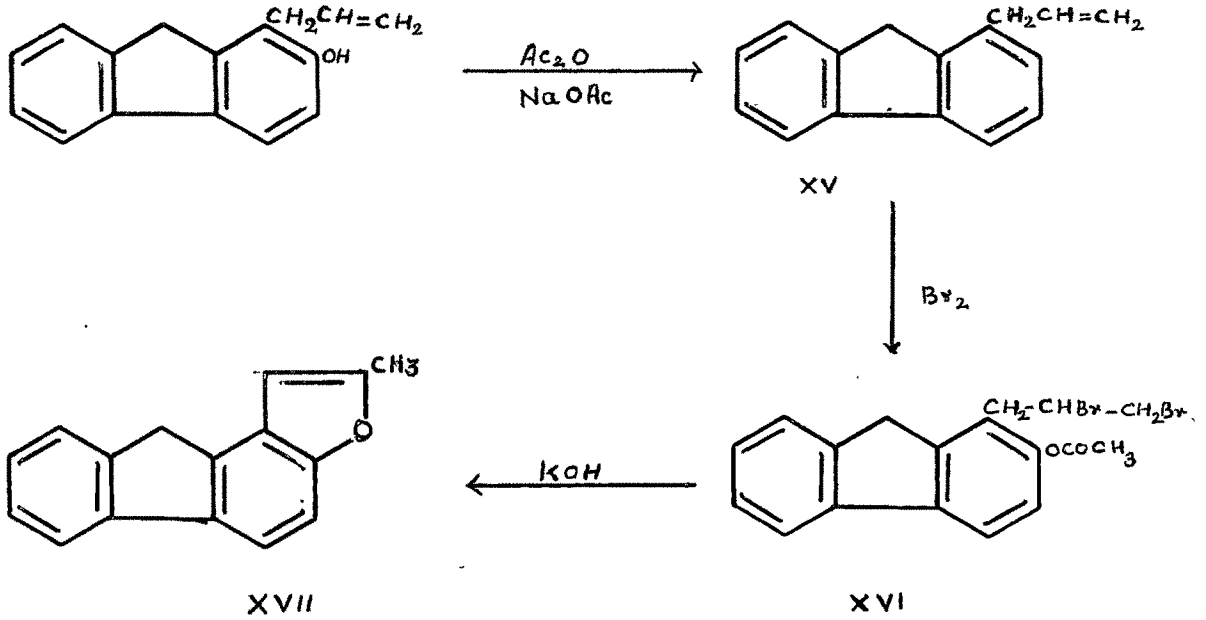


Synthesis of 2'-methylfluoreno(2,1:5',4')furan :

Attempts to cyclise 2-hydroxy-1-allylfluorene with sulphuric acid to 2'-methylfluoreno(2,1:5',4')2',3'-dihydrofuran did not give a pure product. Therefore 2-hydroxy-1-allylfluorene was converted into 2'-methylfluoreno(2,1:5',4') furan by Kaufmann's method[5] as follows :

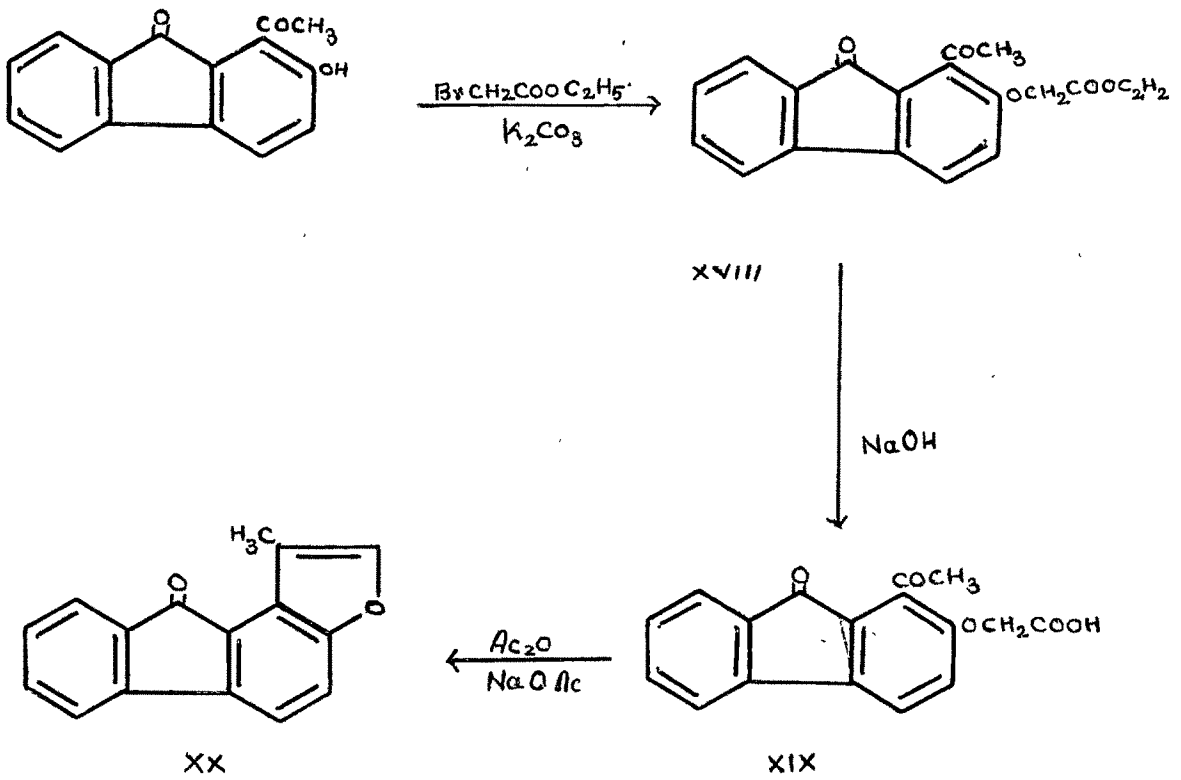
2-Hydroxy-1-allylfluofene was refluxed with acetic anhydride and fused sodium acetate to get 2-acetoxy-1-allylfluorene (XV). This acetoxy derivative was brominated in acetic acid with exactly one mole of bromine when a product separated immediately. This analysed for a dibromo derivative. 2-Acetoxy-1-allylfluorene dibromide structure (XVI) was assigned to this compound. The dibromide on

refluxing with alcoholic potassium hydroxide gave a halogen free compound insoluble in sodium hydroxide. 2'-Methyl-fluoreno(2,1:5',4')furan (XVII) structure is assigned to this compound.



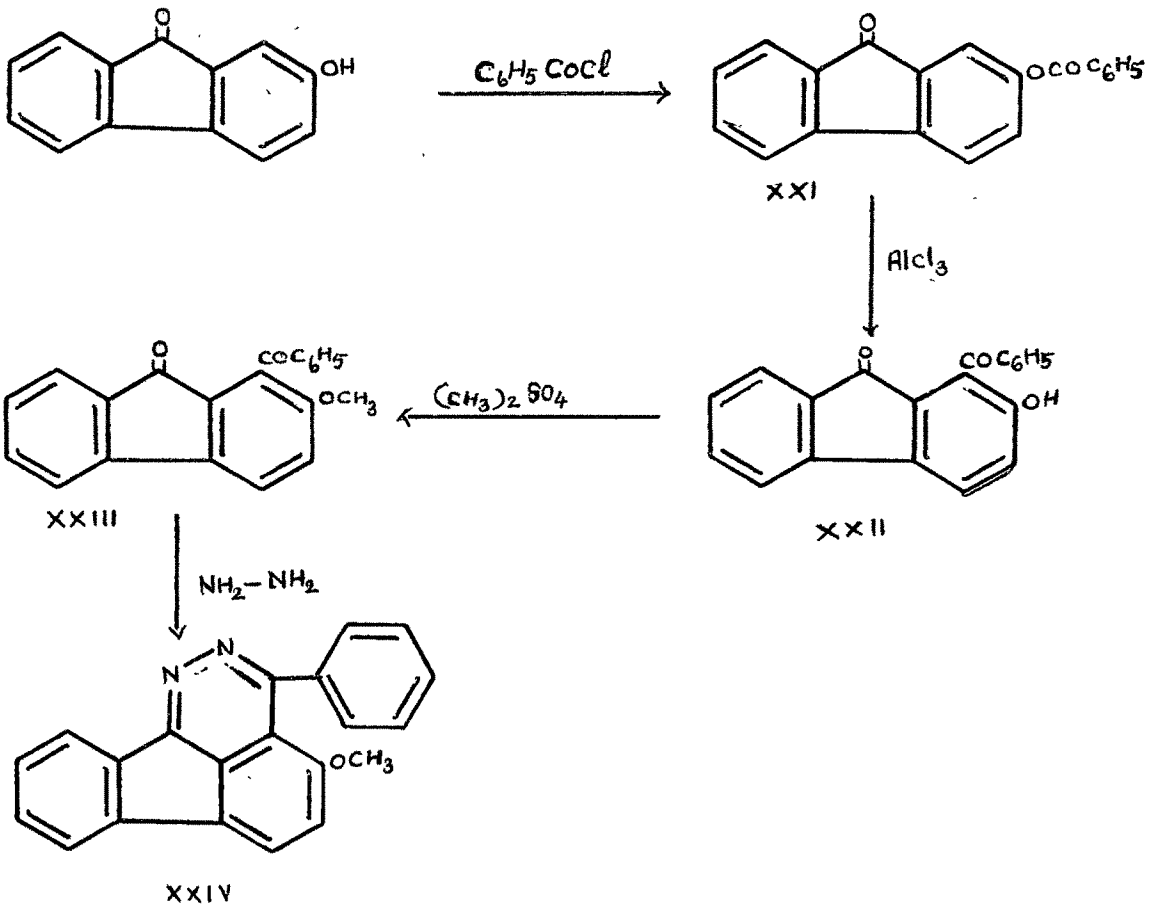
Synthesis of 3'-methyl-9-oxofluoreno(2,1:5',4')furan :

2-Hydroxy-1-acetylfluorenone on condensation with ethyl bromoacetate in the presence of anhydrous potassium carbonate in dry acetone gave 2-carbethoxymethoxy-1-acetyl-fluorenone (XVIII). On heating with sodium hydroxide on a steam bath it gave the corresponding acid : 2-carboxy-methoxy-1-acetylfluorenone (XIX). This acid on boiling with acetic anhydride and freshly fused sodium acetate gave a compound which was insoluble in alkali. 3'-Methyl-9-oxofluoreno(2,1:5',4')furan structure (XX) was assigned to it.



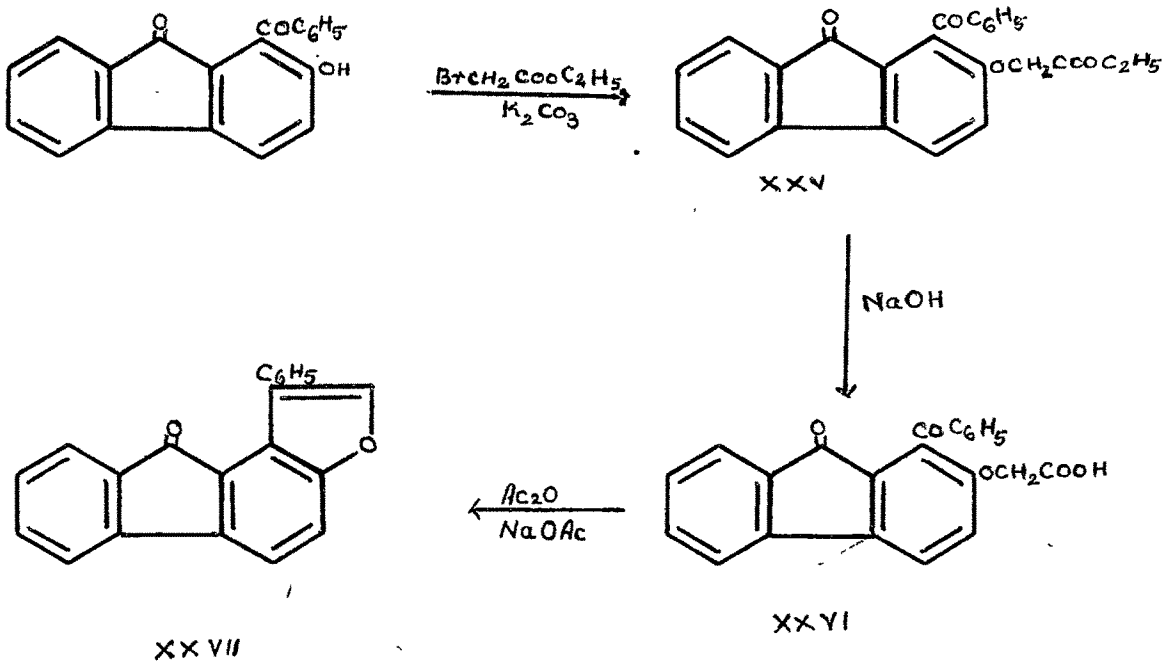
2-Hydroxy-1-benzoylfluorenone :

2-Hydroxyfluorenone when dissolved in sodium hydroxide and shaken with benzoyl chloride gave a product which was insoluble in alkali. This benzoyloxy compound (XXI) was subjected to Fries rearrangement by heating with aluminium chloride and an alkali soluble compound was obtained. This compound gave a red colour with ferric chloride showing its ortho hydroxy carbonyl structure. The product was methylated, and the methyl ether (XXIII) on refluxing with one mole of hydrazine hydrate in alcohol gave a product which analysed for the pyridazine derivative (XXIV). Therefore 2-hydroxy-1-benzoylfluorenone structure (XXII) is assigned to the hydroxy ketone and 2-methoxy-1-benzoylfluorenone structure (XXIII) is assigned to the methyl ether.



3'-Phenyl-9-oxofluoreno(2,1:5',4')furan :

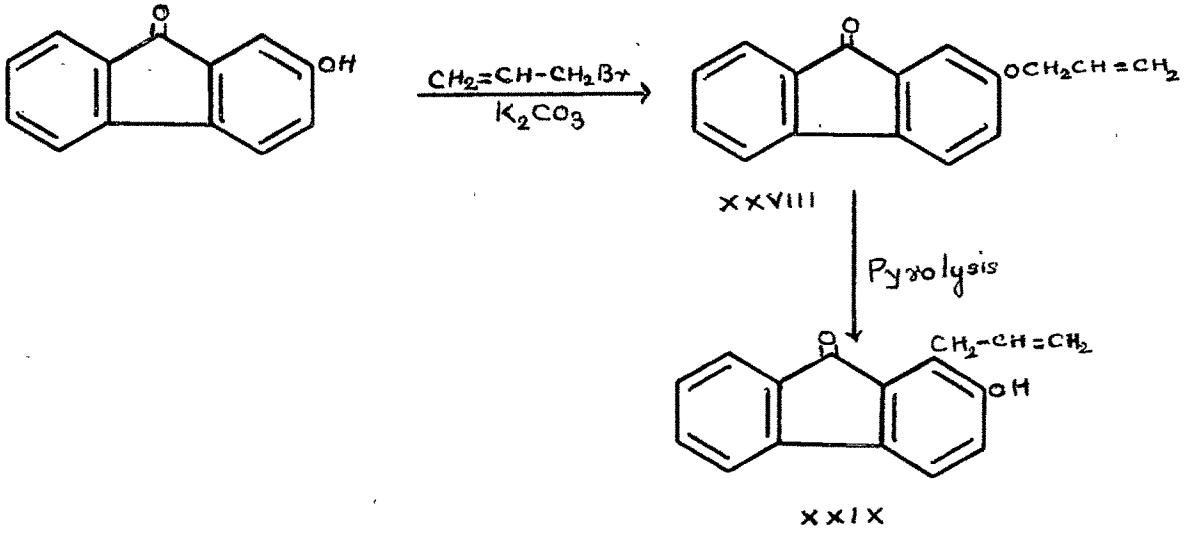
2-Hydroxy-1-benzoylfluorenone when refluxed with ethyl bromoacetate in the presence of anhydrous potassium carbonate in dry acetone gave 2-carbethoxymethoxy-1-benzoyl fluorenone (XXV). This was hydrolysed by heating with sodium hydroxide to 2-carboxymethoxy-1-benzoylfluorenone (XXVI). This was heated with freshly fused sodium acetate and acetic anhydride and 3'-phenyl-9-oxofluoreno(2,1:5',4')furan (XXVII) was obtained.



2-Hydroxy-1-allylfluorenone :

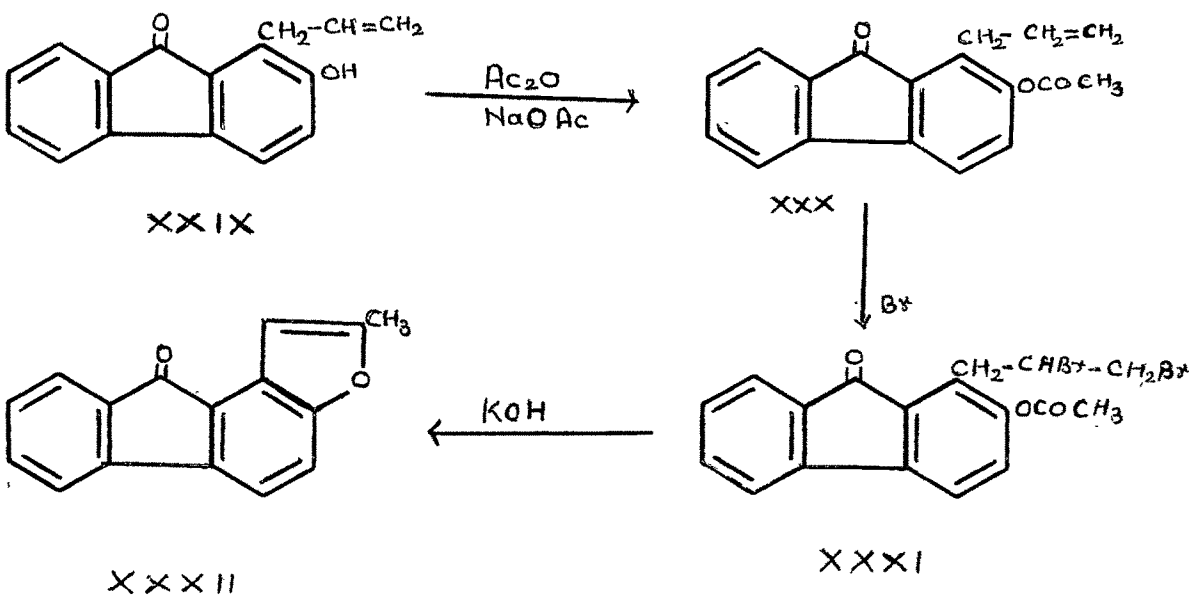
2-Hydroxyfluorenone was refluxed with allyl bromide in the presence of anhydrous potassium carbonate in dry acetone to get 2-allyloxyfluorenone (XXVIII). When this was heated alone to 230-35°; an alkali soluble product was obtained to which 2-hydroxy-1-allylfluorenone structure (XXIX) is assigned on the basis of the following observation :-

The furan derivative (XXXII) obtained from this hydroxy allyl fluorenone was reduced with hydrazine hydrate and potassim hydroxide by heating in ethoxy ethanol. The product obtained was found to be identical with 2'-methylfluoreno (2,1:5',4')furan described on page 170 .



2'Methyl-9-oxofluoreno(2,1:5',4')furan :

2-Hydroxy-1-allylfluorenone (XXIX) was acetylated by boiling with sodium acetate and acetic anhydride. The 2-acetoxy-1-allyl-fluorenone (XXX) was treated with exactly one mole of bromine in acetic acid solution. The product obtained analysed for a dibromo derivative and therefore 2-acetoxy-1-allyfluorenone dibromide structure (XXXI) was assigned to this compound. The dibromide on refluxing in alcohol with potassium hydroxide gave a compound free from bromine and to this compound 2'-methyl-9-oxofluoreno (2,1:5',4')furan structure (XXXII) is given.



EXPERIMENTAL.

Synthesis of 2-carbethoxymethoxy-1-acetylfluorene :

2-Hydroxyl-1-acetylfluorene (1 g.) was dissolved in dry acetone (40 ml.) and anhydrous potassium carbonate (2 g.) was added. Ethyl bromoacetate (1 ml.) was added and the mixture was refluxed on a water bath for 4 hrs. The solvent was then removed and the residue was added to water. The separated solid was crystallised from petroleum ether-benzene mixture in colourless needles (0.8 g.), m.p. 147°.

Analysis : Found : C, 73.06 ; H, 5.72 %.

$C_{19}H_{18}O_4$: requires : C, 73.53 ; H, 5.80 %.

2-Carboxymethoxy-1-acetylfluorene :

The above ester (1 g.) was powdered well and sodium hydroxide (5 % ; 25 ml.) was added. The mixture was heated on a steam bath till it dissolved (2 hrs.). It was then filtered and the filtrate was acidified with conc.hydrochloric acid. The separated solid was further purified by sodium bicarbonate treatment. The acid thus obtained crystallised from ethyl acetate in colourless cubes (0.4 g.), m.p.194°.

Analysis : Found : C, 71.98 ; H, 4.72 %.

$C_{17}H_{14}O_4$: requires : C, 72.35 ; H, 4.96 %.

3'-Methylfluoreno(2,1:5',4')furan :

The above acid (0.5 g.) was mixed with freshly fused and powdered sodium acetate (1.5 g.) and acetic anhydride (2 ml.). The mixture was refluxed on a sand bath for one and half hours. It was then cooled, added to ice and left overnight. The separated solid was filtered, washed with

sodium bicarbonate and then with water. It crystallised from dilute alcohol in colourless flakes (0.3 g.), m.p. 114°.

Analysis : Found : C, 87.02 ; H, 5.31 %.

$C_{16}H_{12}O$: requires : C, 87.28 ; H, 5.45 %.

Synthesis of 2-hydroxy-1-allylfluorene :

2-Allyloxyfluorene[4] (1 g.) was heated in an oil bath at 230-35° for 5 minutes. It was then cooled and extracted several times with hot petroleum ether. The solvent was then evaporated and the solid was crystallised from petroleum ether in light brown needles (0.3 g.), m.p. 111°. Lothrop[4] gave m.p. 111-12°.

2-Methoxy-1-allylfluorene :

The above compound (1 g.) was dissolved in dry acetone (50 ml.). Anhydrous potassium carbonate (2 g.) and dimethyl sulphate (1 ml.) were added and the mixture was refluxed on a water bath for 2 hrs. The solvent was removed and the reaction mixture was added to water. The separated solid crystallised from petroleum ether in colourless flakes (0.8 g.), m.p. 58°.

Analysis : Found : C, 86.56 ; H, 6.79 %.

$C_{17}H_{16}O$: requires : C, 86.44 ; H, 6.78 %.

2-Methoxyfluorenone-1-carboxylic acid :

2-Methoxy-1-allylfluorene (1 g.) was finely powdered and sodium hydroxide (25 ml. ; 5 %.) was added. Potassium permanganate (1 g.) dissolved in water was added and the mixture was heated on a water bath at 50-60° for 15 hrs.

It was filtered and the filtrate was decolourised by the addition of sodium sulphite, and acidified with dilute hydrochloric acid. The separated solid was filtered and crystallised from dilue acetic acid in yellow flakes (o.2 g.), m.p. 241°. Mixed m.p. of the compound with 2-methoxyfluorenone-1-carboxylic acid described on page 158 was not depressed.

2-Acetoxy-1-allylfluorene :

2-Hydroxy-1-allylfluorene (0.5 g.) was mixed well with freshly fused powdered sodium acetate (1 g.) and acetic anhydride (2 ml.) and the mixture was refluxed on a sand bath for half an hour. The mixture was then cooled and added to ice and kept overnight. The separated solid was then crystallised from petroleum ether in colourless cubes (0.4 g.), m.p. 84°.

Analysis	: Found	: C, 81.83 ; H, 6.32 %.
$C_{18}H_{16}O_2$	: requires	: C, 81.83 : H, 6.06 %.

2-Acetoxy-1-allylfluorene dibromide :

2-Acetoxy-1-allylfluorene (1 g.) was dissolved in glacial acetic acid (10 ml.). It was then cooled to 15-20°. Bromine (0.6 g.) in acetic acid (5 ml.) was added dropwise with constant stirring. The product separated immediately. It was stirred at 15-20° for one hour and then filtered. The residue was crystallised from petroleum ether in colourless needles (1 g.), m.p. 153°.

Analysis	: Found	: C,50.94 ; H,3.77 ; Br,37.71 %.
$C_{18}H_{16}O_2Br_2$	: requires	: C,50.77 ; H,3.58 ; Br,37.75 %.

2'-Methylfluoreno(2,1:5',4')furan :

2-Acetoxy-1-allylfluorene dibromide (1 g.) was dissolved in alcohol (50 ml.) and potassium hydroxide (1.5 g.) in alcohol (15 ml.) was added. The mixture was refluxed on a steam bath for 3 hrs. The solvent was then distilled off and the residue was diluted with water. The separated solid was crystallised from alcohol in colourless needles (0.4 g.), m.p. 148°.

Analysis : Found : C, 87.16 ; H, 5.47 %.

$C_{16}H_{12}O$: requires : C, 87.28 ; H, 5.45 %.

Synthesis of 2'-methyl-9-oxofluoreno(2,1:5',4')furan :

2-Carbethoxymethoxy-1-acetylfluorenone :

2-Hydroxy-1-acetylfluorenone (1 g.) was dissolved in dry acetone (50 ml.) and anhydrous potassium carbonate (2 g.) was added. Ethylbromoacetate (1 ml.) was added and the mixture was refluxed on a steam bath for 4 hrs. The solvent was then removed and the residue was added to water. The separated solid was filtered and washed with dilute sodium hydroxide. The solid crystallised from dilute acetic acid in yellow needles (0.9 g.), m.p. 172°.

Analysis : Found : C, 70.73 ; H, 5.40 %.

$C_{19}H_{16}O_5$: requires : C, 70.37 ; H, 4.94 %.

2-Carboxymethoxy-1-acetylfluorenone :

The above ester (1 g.) was powdered well and sodium hydroxide (5 % ; 25 ml.) was added. The mixture was heated on a steam bath for 4 hrs. It was then filtered and the filtrate was acidified with conc. hydrochloric acid. The

separated solid was further extracted with sodium bicarbonate. The product obtained on acidification of the sodium bicarbonate extract crystallised from acetic acid in brown cubes (0.4 g.), m.p. 252° (decomp.).

Analysis : Found : C,68.87 ; H, 4.16 %.

$C_{17}H_{12}O_5$: requires : C, 68.92 ; H, 4.05 %.

3'-Methyl-9-oxofluoreno(2,1:5',4')furan :

The above acid (1 g.) was refluxed with freshly fused and powdered sodium acetate (2 g.) and acetic anhydride (2 ml.) for 2 hrs. It was cooled and then added to ice. The separated solid was filtered and washed with sodium bicarbonate solution The residue crystallised from dilute alcohol in yellow needles (0.3 g.), m.p. 136°.

Analysis : Found : C, 81.77 ; H, 4.13 %.

$C_{17}H_{12}O_2$: requires : C, 82.06 ; H, 4.27 %.

2-Benzoyloxyfluorenone :

2-Hydroxyfluorenone (1 g.) was dissolved in sodium hydroxide (10 % ; 25 ml.) and crushed ice was added. Benzoyl chloride (1 ml.) was then added and the solution was shaken vigourously for ten minutes. The separated solid was filtered and the residue washed with dilute sodium hydroxide and then with water. The residue was crystallised from acetic acid in yellow flakes (0.9 g.), m.p. 174°.

Analysis :Found : C, 79.63 ; H, 3.87 %.

$C_{20}H_{12}O_3$:requires : C, 80.00 ; H, 4.00 %.

2-Hydroxy-1-benzoylfluorenone :

2-Benzoyloxyfluorenone (2 g.) was powdered well and

mixed with anhydrous aluminium chloride (2 g.). The mixture was heated in an oil bath at 140-50° for 4 hrs. It was then cooled and crushed ice and conc. hydrochloric acid were added and the reaction mixture left overnight and filtered. The residue was purified by extracting with sodium hydroxide solution. The product obtained on acidification of the sodium hydroxide solution with conc. hydrochloric acid crystallised from acetic acid in brown needles (0.6 g.), m.p. 171°.

Analysis : Found : C, 79.88 ; H, 3.51 %.

$C_{20}H_{12}O_3$: requires : C, 80.00 ; H, 4.00 %.

This compound gave a red colouration with alcoholic ferric chloride.

2-Methoxy-1-benzoylfluorenone :

The above hydroxy ketone (0.5 g.) was refluxed in dry acetone (50 ml.) with anhydrous potassium carbonate (1 g.) and dimethyl sulphate (0.5 ml.) for 4 hrs. The solvent was then removed and the residue was added to water. The separated solid was washed with dilute sodium hydroxide and then with water. It crystallised from dilute acetic acid in orange needles (0.4 g.), m.p. 212°.

Analysis : Found : C, 79.76 ; H, 4.22 %.

$C_{21}H_{14}O_3$: requires : C, 80.26 ; H, 4.45 %.

The pyridazine derivative :

2-Methoxy-1-benzoylfluorenone (1 g.) was dissolved in alcohol (100 ml.) and hydrazine hydrate (0.2 ml.) was added. The mixture was refluxed on a water bath for 8 hrs. The solvent was then removed and the residue was diluted with

water. The solid obtained was crystallised from benzene-petroleum ether in yellow needles (0.4 g.), m.p. 208°.

Analysis	: Found	:	N, 8.95 %.
$C_{21}H_{14}ON_2$	: requires	:	N, 9.03 %.

Condensation of 2-hydroxy-1-benzoylfluorenone with ethyl bromoagetate : 2-Carbethoxymethoxy-1-benzoyl fluofenone :

2-Hydroxy-1-benzoylfluoeenone (1 g.) was dissolved in dry acetone (100 ml.) and anhydrous potassium carbonate (2 g.) was added. Ethyl bromoacetate (1 ml.) was added and the mixture was refluxed on a water bath for 6 hrs. The solvent was then evaporated and the residue was added to water. The separated solid was filtered and washed with cold dilute sodium hydroxide and water. It was then crystallised from dilute acetic acid in yellow needles (0.8 g.), m.p. 177-78°.

Analysis	: Found	: C, 74.69 ; H, 4.94 %.
$C_{24}H_{18}O_5$	: requires	: C, 74.61 ; H, 4.63 %.

2-Carboxymethoxy-1-benzoylfluorenone :

The above ester (2 g.) was powdered well and sodium hydroxide (10 %; 50 ml.) was added. The mixture was heated on a steam bath with shaking for 2 hrs. The solution was filtered and the filtrate was acidified with conc. hydrochloric acid. The precipitated acid was further purified by extracting it with sodium bicarbonate. It

crystallised from acetic acid in brown needles (0.9 g.), m.p. 226° (decomp.).

Analysis : Found : C, 73.59 ; H, 4.03 %.

$C_{22}H_{14}O_5$: requires : C, 73.74 ; H, 3.91 %.

3'-Phenyl-9-oxofluoreno(2,1:5,4')furan :

2-Carboxymethoxy-1-benzoylfluorenone (1 g.) was refluxed with freshly fused sodium acetate (2 g.) and acetic anhydride (2 ml.) on a sand bath for 1 hour. It was then poured on ice and left overnight. The separated solid was filtered and washed with sodium bicarbonate solution. The residue crystallised from alcohol in yellow needles (0.3 g.), m.p. 152°.

Analysis : Found : C, 85.12 ; H, 4.18 %.

$C_{21}H_{12}O_2$: requires : C, 85.13 ; H, 4.05 %.

2-Allyloxyfluorenone :

2-Hydroxyfluorenone (2 g.) was dissolved in dry acetone (100 ml.) and anhydrous potassium carbonate (4 g.) was added. Allyl bromide (2 ml.) was added and the mixture was refluxed on a water bath for 15 hrs. The solvent was then evaporated and the residue was added to water. The separated solid was filtered and washed with dilute sodium hydroxide and then with water. The residue obtained was crystallised from alcohol in golden yellow needles (1.5 g.), m.p. 78°.

Analysis : Found : C, 81.66 ; H, 5.37 %.

$C_{16}H_{12}O_2$: requires : C, 81.36 ; H, 5.08 %.

2-Hydroxy-1-allylfluorenone :

2-Allyloxyfluorenone (1 g.) was powdered well and

heated in an oil bath at 230-35° for 5 minutes. It was then cooled and the solid was dissolved in ether. The ether solution was extracted twice with 25 c.c. of 10 %. sodium hydroxide solution. The alkali layer was separated and acidified with conc. hydrochloric acid with proper cooling. The separated solid crystallised from dilute alcohol in red needles (0.5 g.), m.p. 139°.

Analysis : Found : C, 81.39 ; H, 5.27 %.

$C_{16}H_{12}O_2$: requires : C, 81.36 ; H, 5.08 %.

2-Acetoxy-1-allylfluofenone :

2-Hydroxy-1-allylfluorenone (1 g.) was refluxed with freshly fused sodium acetate and acetic anhydride on a sand bath for 1 hour. It was then cooled and added to ice and left overnight. The separated solid crystallised from benzene-petroleum ether mixture. M.P. 129°. Yield 0.9 g.

Analysis : Found : C, 78.00 ; H, 5.24 %.

$C_{18}H_{14}O_3$: requires : C, 78.27 ; H, 5.07 %,

2-Acetoxy-1-allylfluorenone dibromide :

2-Acetoxy-1-allylfluofenone (1 g.) was dissolved in glacial acetic acid (20 ml.) and cooled to 15-20°. Bromine (0.5 g.) in glacial acetic acid (5 ml.) was added dropwise with constant stirring. A yellow solid separated immediately. The mixture was stirred at 15-20° for 1 hour and filtered. The residue was crystallised from benzene in yellow needles (1.1 g.), m.p. 193°.

Analysis : Found : C, 49.53; H,3.00; Br,36.93 %.

$C_{18}H_{14}O_3Br_2$: requires : C, 49.32; H,3.33; Br,36.53 %.

2'-Methyl-9-oxofluoreno(2,1:5',4')furan :

The above dibromide (1 g.) was dissolved in alcohol (75 ml.) and potassium hydroxide (1.5 g.) in alcohol (25 ml.) was added. The mixture was refluxed on a steam bath for 3 hrs. The solvent was distilled off and the residue was diluted with water. The separated solid was crystallised from dilute alcohol in yellow needles (0.3 g.), m.p. 143°.

Analysis : Found : C, 82.13 ; H, 4.17 %.

$C_{16}H_{10}O_2$: requires : C, 82.06 ; H, 4.27 %.

2'-Methylfluoreno(2,1:5',4')furan :

2'-Methyl-9-oxofluoreno(2,1:5',4')furan (0.5 g.) was dissolved in ethoxy ethanol (25 ml.) and hydrazine hydrate (85 %; 2 ml.) was added. The mixture was refluxed on a sand bath for 1 hour. Potassium hydroxide (2 g.) was added and the mixture was refluxed on a sand bath for 6 hrs. It was cooled and added to water. The separated solid was filtered and crystallised from dilute alcohol in colourless needles (0.2 g.), m.p. 148°. Mixed m.p. with 2'-methyl-fluoreno(2,1:5',4')furan was not depressed.

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2. E. B. Knott, J.Chem.Soc., 189 (1945).

3. W. Borsche and H. Leditschke, Ann., 529, 108 (1937).

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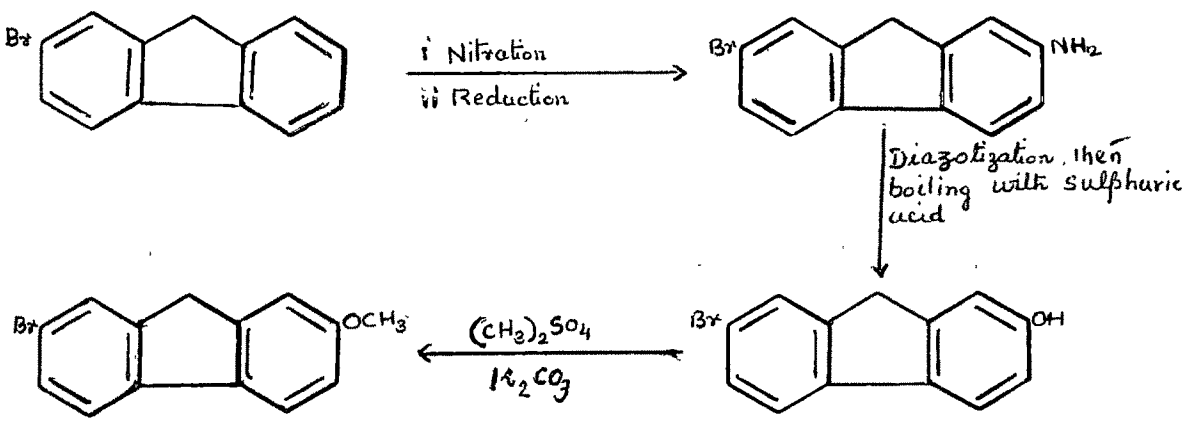
SECTION III

BROMINATION OF 2-HYDROXYFLUORENE, 2-HYDROXYFLUORENONE AND THEIR METHYL ETHERS

Bromination of 2-hydroxyfluorene, 2-hydroxyfluorenone and their methyl ethers :

Bromination of simple fluorene and some of its derivatives has been studied and this has been discussed in the general introduction. Bromination of hydroxyfluorenes and hydroxyfluorenones has however not been systematically studied. Eckett and Langecker[1] carried out the bromination of 2-methoxyfluorene in acetic acid. They reported the formation of a dibromo 2-methoxyfluorene and a tribromo 2-methoxyfluorene. The structures of these derivatives have not been established. A tribromo derivative of 2-methoxy-fluorenone was prepared by these workers by oxidising the above methoxy-tribromofluorene with sodium dichromate in acetic acid. A hydroxy tribromo fluorenone also of unkrown structure was prepared by the same workers by brominating 2-aminofluorenone and converting the amino group to hydroxy through diazotisation. 2-Methoxy-7-bromofluorene has been prepared by Campbell and Hasan[2] through the following sequence of reactions.

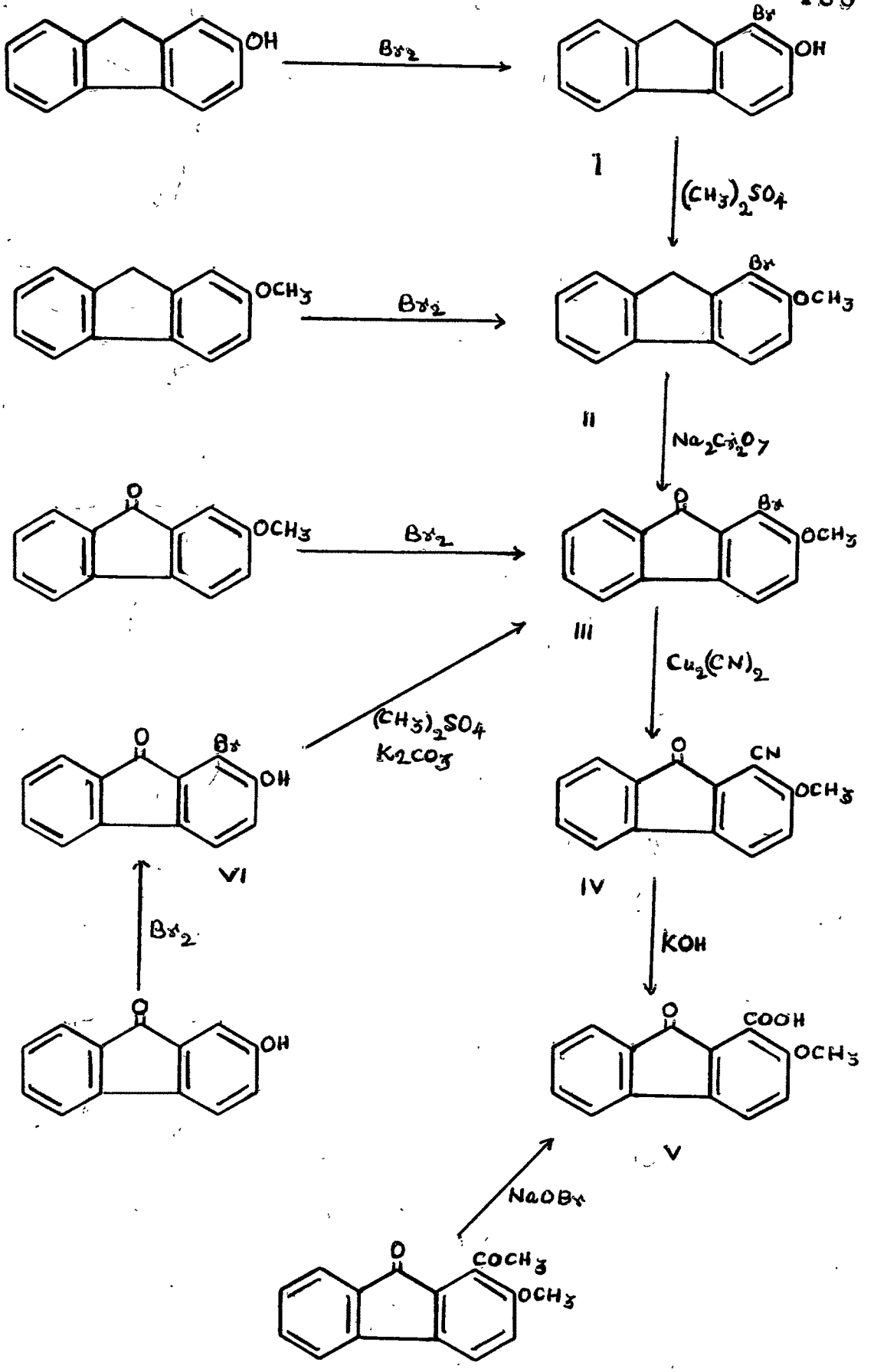


Other bromo derivatives of 2-hydroxyfluorene and 2-hydroxyfluorenone and their methyl ethers have not been reported . It was therefore thought of interest to study systematically the bromination of 2-hydroxyfluorene and 2-hydroxyfluorenone and their methyl ethers.

Bromination of 2-hydroxyfluorene and 2-hydroxyfluorenone and their methyl ethers with one mole of bromine :

2-Hydroxyfluorene dissolved in acetic acid was treated with exactly one mole of bromine in glacial acetic acid. On keeping the reaction mixture overnight a product separated which analysed for a mono bromo derivative. It has been assigned 2-hydroxy-1-bromofluorene structure (I) because it could be converted into 2-methoxyfluorenone-1-carboxylic acid through the following sequence of reactions :

The methyl ether of the monobromo compound (II) was prepared and oxidised by boiling with sodium dichromate in glacial acetic acid to the corresponding fluorenone derivative (III). This on boiling with cuprous cyanide in dimethyl formamide gave the cyano derivative (IV) which on refluxing with potassium hydroxide in alcohol gave an acid which was found on direct comparison to be identical with 2-methoxyfluorenone-1-carboxylic acid (V) prepared by the haloform reaction on 2-methoxy-1-acetyl fluorenone as described earlier (p.158).


OH
Br2
Br
OH
1
(CH3)2SO4
OCH3
Br2
Br
OCH3
II
Na2Cr2O7
O
OCH3
Br2
O
Br
OCH3
III
Cu2(CN)2
(CH3)2SO4
K2CO3
O
Br
OH
VI
O
CN
OCH3
IV
Br2
KOH
O
OH
O
COOH
OCH3
V
NaOBr
O
COCH3
OCH3

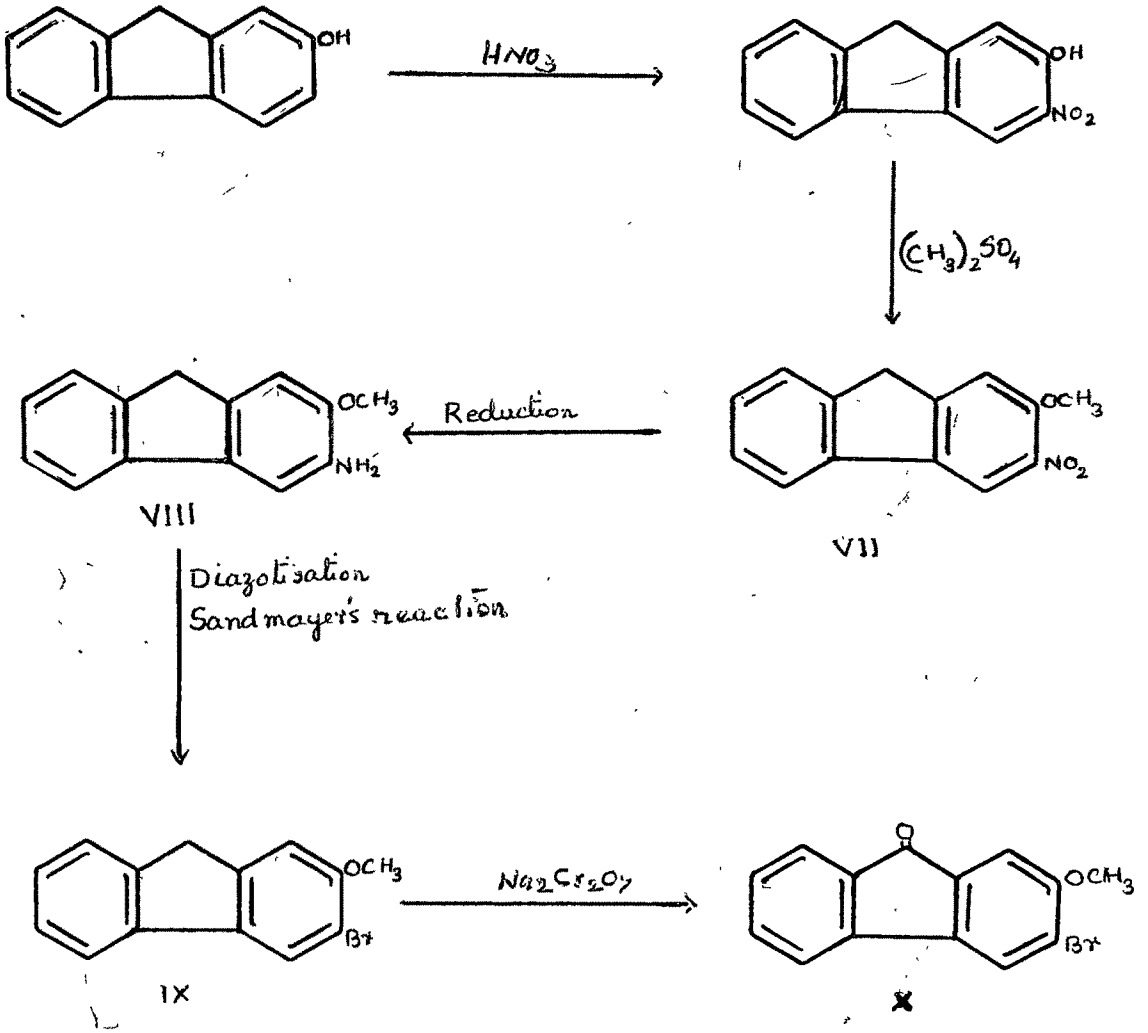
2-Methoxyfluorene, on bromination with one mole of bromine in acetic acid gave 2-methoxy-1-bromofluorene (II) as seen by direct comparison with the methyl ether of 2-hydroxy-1-bromo fluorene described above.

2-Hydroxyfluorenone, on similar bromination with one mole of bromine gave a mono bromo derivative to which 2-hydroxy-1-bromofluorenone structure (VI) has been assigned because the methyl ether of this compound was identical with 2-methoxy-1-bromofluorenone obtained by the oxidation of 2-methoxy-1-bromofluorene. 2-Methoxyfluorenone also with one mole of bromine gave 2-methoxy-1-bromofluorenone.

2-Methoxy-3-bromofluorene and 2-methoxy-3-bromo fluorenone :

2-Hydroxyfluorene was nitrated according to Ray and Hull[4]. These authors assigned 2-hydroxy-3-nitrofluorene structure to the product formed because the compound could also be obtained from the known 2-amino-3-nitrofluorene through diazotisation. The methyl ether (VII) of the hydroxy nitro compound was reduced with sodium hydrosulphite in alcohol to 2-methoxy-3-aminofluorene (VIII). This was diazotised in hydrobromic acid and boiled with a solution of cuprous bromide in hydrobromic acid. 2-Methoxy-3-bromofluorene structure (IX) is assigned to the product obtained.

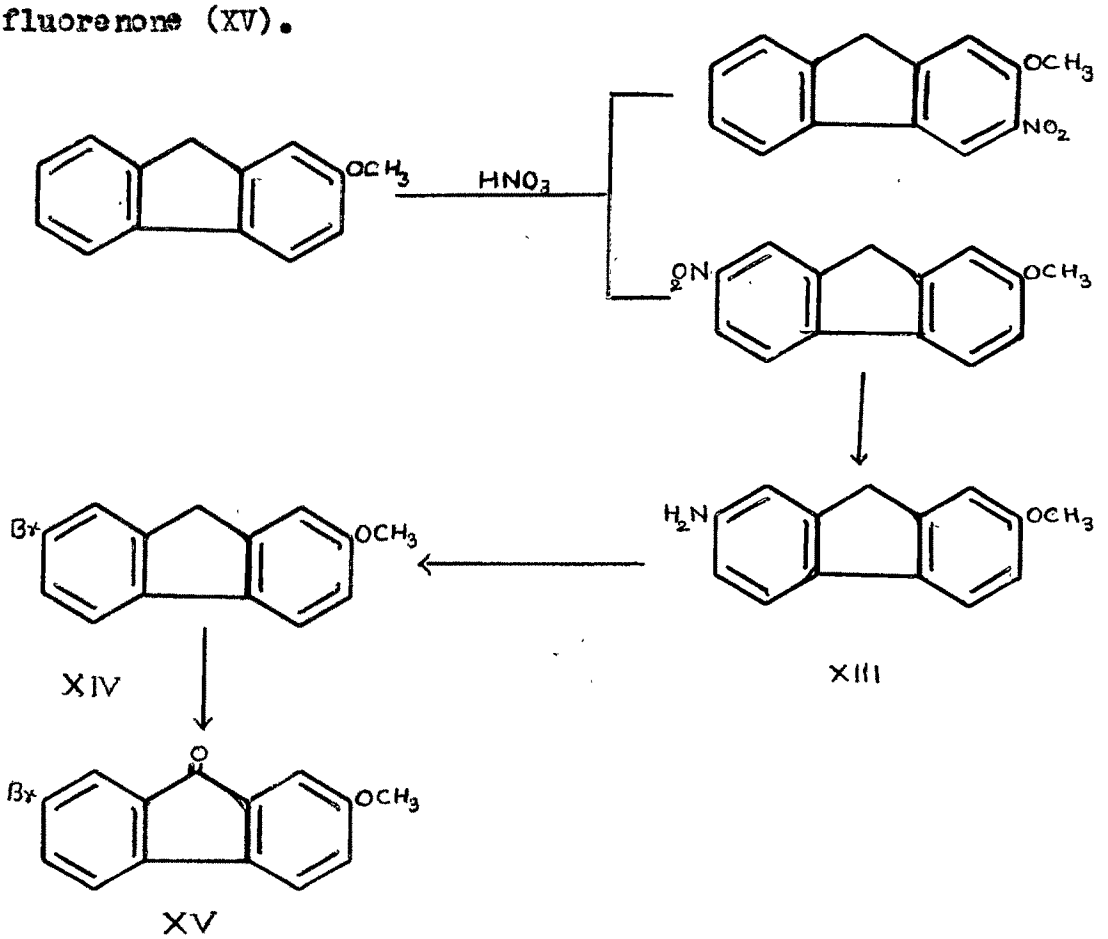
2-Methoxy-3-bromofluorene was oxidised with sodium dichromate in glacial acetic acid to 2-methoxy-3-bromo-fluorenone (X).



<u>2-Methoxy-7-bromofluorene and 2-methoxy-7-bromofluorenone</u> :

2-Methoxyfluorene was nitrated according to Ishikawa and Okazaki[3]. These workers reported the formation of two derivatives : 2-methoxy-7-nitrofluorene and 2-methoxy-3-nitrofluorene. 2-Methoxy-7-nitrofluorene structure was assigned to this compound as it was found to be identical with the compound prepared earlier from 2,7-dinitrofluorene through partial reduction, diazotisation and methylation

of the hydroxy compound. 2-Methoxy-7-nitrofluorene thus obtained was reduced to 2-methoxy-7-aminofluorene (XIII) which was diazotised in the presence of hydrobromic acid. On boiling the diazonium bromide with copper powder a bromo compound was obtained to which 2-methoxy-7-bromofluorene structure (XIV) is assigned. This has been prepared previously by Campbell and Hasan[2] by a different route as shown on page 186 . This was oxidised with sodium dichromate in glacial acetic acid to 2-methoxy-7-bromofluorenone (XV).



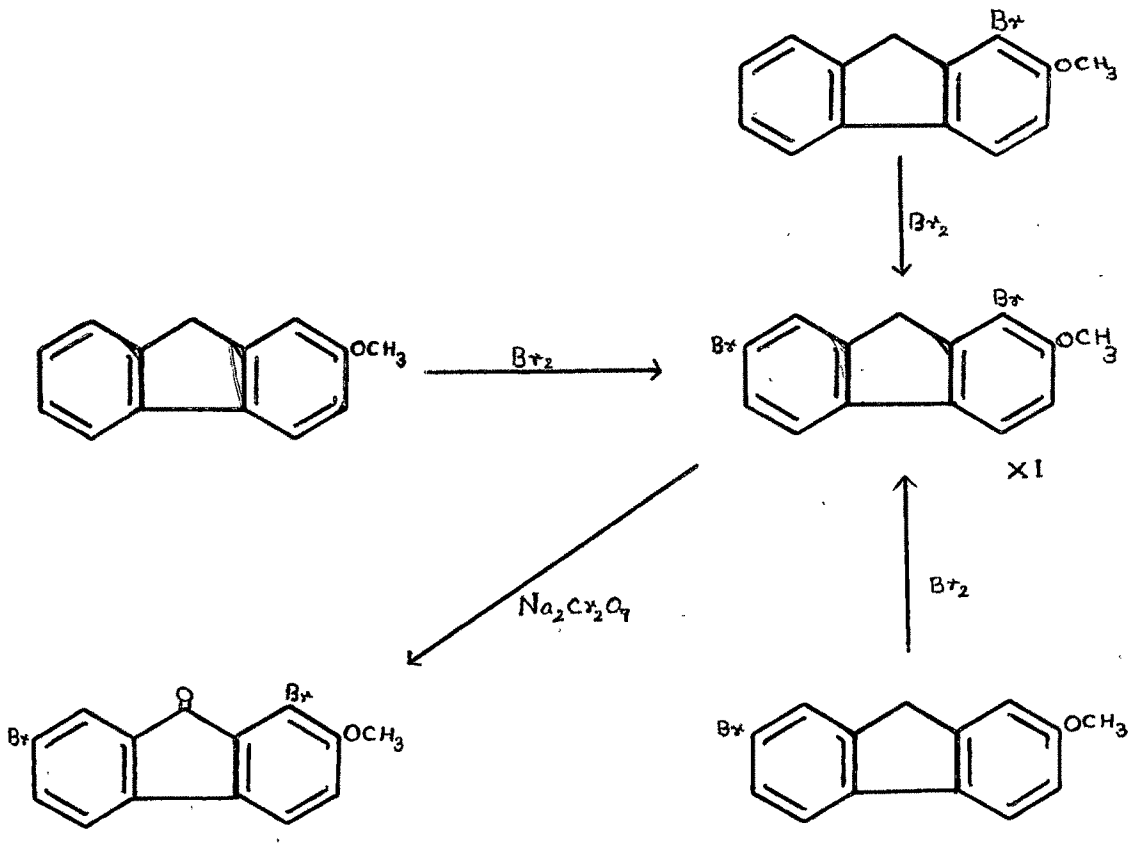
2-Methoxy-1,7-dibromofluorene and 2-methoxy-1,7-dibromofluorenone :

2-Methoxyfluorene was dissolved in chloroform and stirred with two moles of bromine also dissolved in the

same solvent. On removing chloroform a product was obtained which analysed for a dibromo derivative. 2-Methoxy-1,7-dibromofluorene structure (XI) is assigned to the compound as the same compound was obtained when 2-methoxy-1-bromofluorene and 2-methoxy-7-bromofluorene were treated with one mole of bromine in chloroform solution.

2-Methoxy dibromofluorene on boiling with sodium dichromate in acetic acid gave a product to which 2-methoxy-1,7-dibromofluorenone structure (XII) has been assigned.

The methoxy dibromofluorene obtained by Eckert and Langecker[1] by brominating 2-methoxyfluorene in acetic acid seems to be a different one, because the m.p. of their compound (121°) is different from the m.p. of 2-methoxy-1,7-dibromofluorene (143°) obtained in the present work.

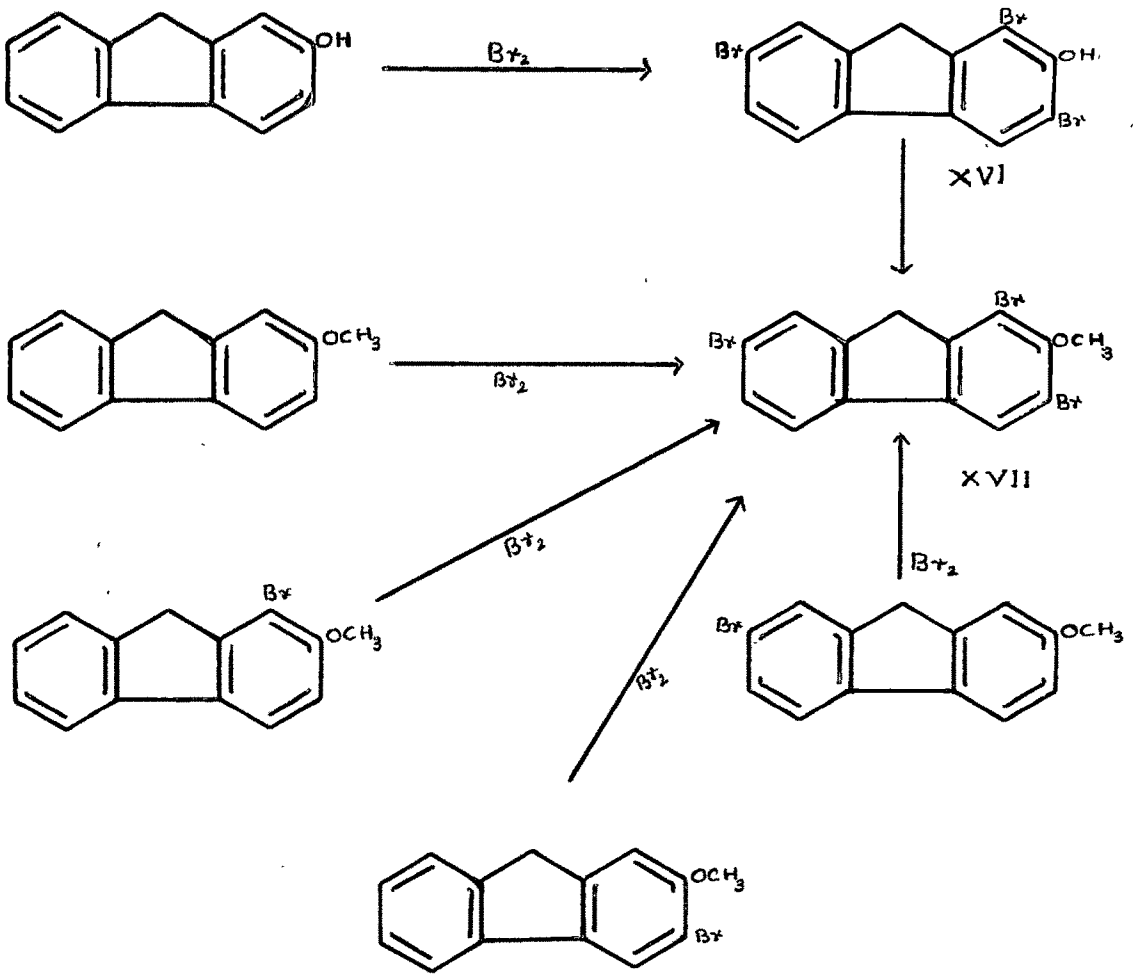


XI

XII

2-Hydroxy-1,3,7-tribromofluorene and its methyl ether:

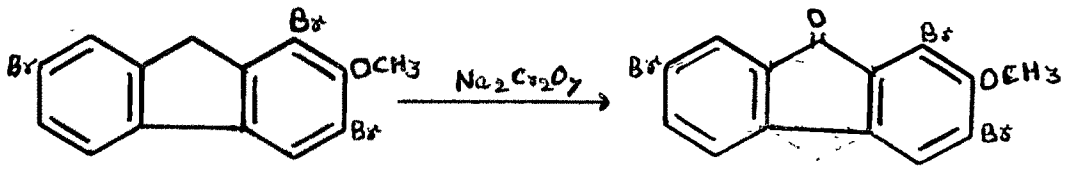
2-Hydroxyfluorene dissolved in acetic acid was treated with excess of bromine in acetic acid. A product separated out immediately, which on analysis was found to be a tribromo derivative (XVI). 2-Methoxyfluorene on treatment with excess of bromine in glacial acetic acid gave a tribromo derivative which was identical with the methyl ether of 2-hydroxy tribromo fluorene. 2-Methoxy-1,3,7- tribromofluorene structure (XVII) has been assigned to this product as the same tribromo derivative was obtained when 2-methoxy-1-bromofluorene or 2-methoxy-3-bromofluorene or 2-methoxy-7-bromofluorene was treated with excess of bromine.



The methoxy tribromofluorene reported by Eckert and Langecker[1] seems to be the same compound because the m.p. reported by them (188°) agrees with the m.p. of the compound described above.

2-Methoxy-1,3,7-tribromofluorenone :

2-Methoxy-1,3,7-tribromofluorene obtained by the bromination of 2-methoxyfluorene as described above was refluxed with sodium dichromate in acetic acid solution. The solid obtained on cooling analysed for the corresponding fluorenone derivative and had the m.p. 268°. Therefore 2-methoxy-1,3,7-tribromofluorenone structure (XVIII) is assigned to this compound.



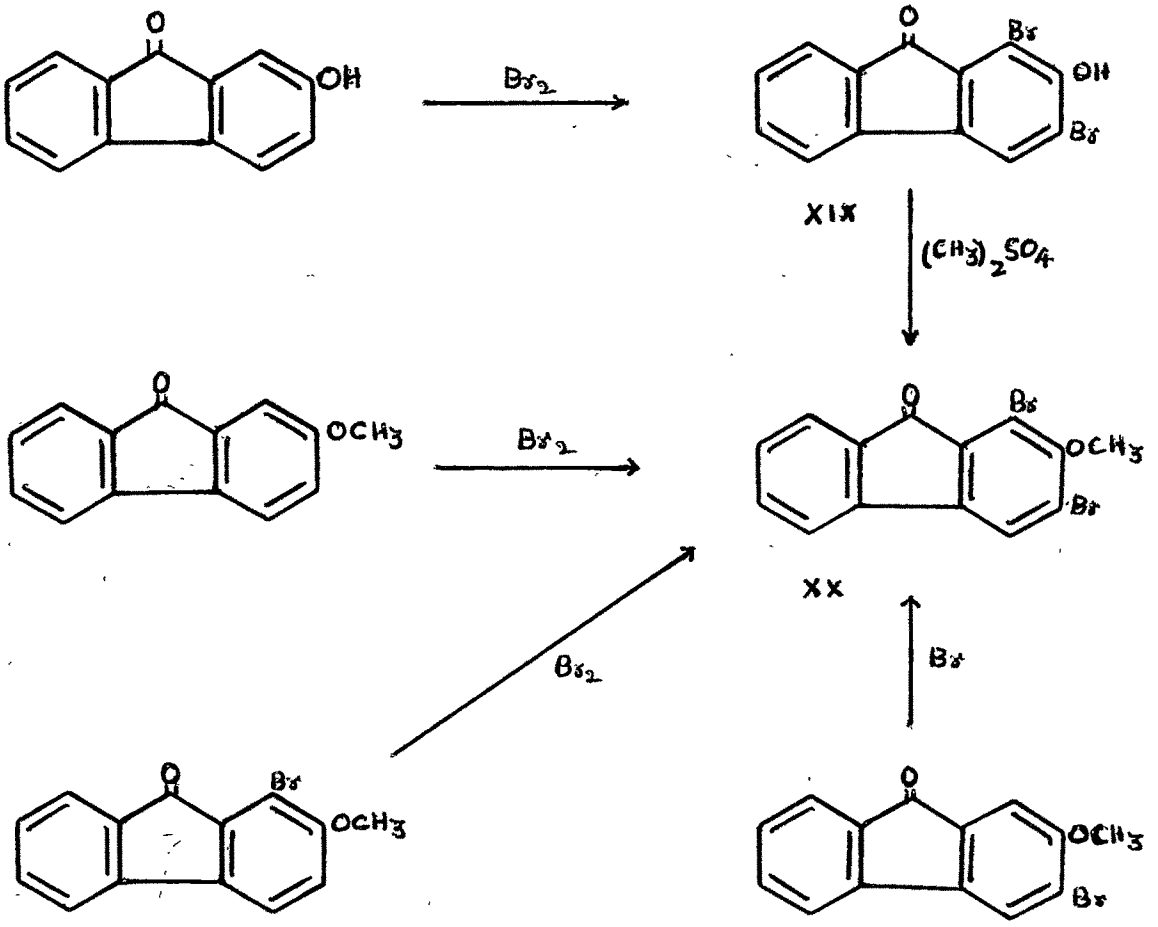
XVIII

The methoxy tribromo fluorenone reported by Eckert and Langecker[1] has the m.p. 268°.

Bromination of 2-hydroxyfluorenone and its methyl ether with excess of bromine : 2-Hydroxy-1,3-dibromo fluorenone and its methyl ether :

2-Hydroxyfluorenone dissolved in acetic acid was treated with excess of bromine in acetic acid solution. The product that separated immediately analysed for a dibromo derivative. 2-Methoxyfluorenone also on a similar bromination with excess of bromine gave a product which was identical with the methyl

ether of 2-hydroxy dibromofluorenone. 2-Methoxy-1,3-dibromo-fluorenone structure (XX) has been assigned to this compound as the same product was obtained on further bromination of 2-methoxy-1-bromofluorenone and 2-methoxy-3-bromofluorenone. Therefore 2-hydroxy-1,3-dibromofluorenone structure (XIX) has been assigned to the bromo product from 2-hydroxy-fluorenone.



EXPERIMENTAL.

2-Hydroxy-1-bromofluorene :

2-Hydroxyfluorene (1 g.) was dissolved in acetic acid (5 ml.) and bromine (0.8 g.) dissolved in acetic acid (2 ml.) was added dropwise with stirring. The mixture was left overnight. The separated solid was filtered and crystallised from alcohol in colourless needles (0.9 g.), m.p. 159°.

Analysis	: Found	: Br, 30.99 %
$C_{13}H_9OBr$	: requires	: Br, 31.41 %.

2-Methoxy-1-bromofluorene :

The above compound (0.5 g.) dissolved in dry acetone (20 ml.) was refluxed with anhydrous potassium carbonate (1 g.) and dimethyl sulphate (0.5 ml.) on a steam bath for 3 hrs. The solvent was then removed and the reaction mixture was diluted with water. The solid obtained was crystallised from acetic acid in colourless needles (0.3 g.), m.p. 146°.

The same product was obtained when 2-methoxyfluorene (1 g.) was dissolved in glacial acetic acid (5 ml.) and bromine (0.7 g.) in glacial acetic acid (2 ml.) was added dropwise with stirring and the solution was kept overnight.

Analysis	: Found	: Br, 29.52 %.
$C_{14}H_{11}OBr$	: requires	: Br, 29.13 %.

2-Methoxy-1-cyanofluorene :

The above compound (1 g.) was dissolved in dimethyl formamide (15 ml.) and cuprous cyanide (1.5 g.) was added. The mixture was refluxed on a sand bath for 2 hrs. It was then filtered hot and the filtrate was diluted with water.

The separated solid was filtered and washed with ammonium hydroxide and then with water. The residue obtained crystallised from benzene-petroleum ether in colourless cubes (0.6 g.), m.p. 174°.

Analysis : Found : C, 81.37; H, 4.77; N, 6.15 %.

$C_{15}H_{11}ON$: requires : C, 81.45 ; H, 4.97; N, 6.33 %.

2-Methoxy-1-bromofluorenone :

2-Methoxy-1-bromofluorene (0.5 g.) was dissolved in glacial acetic acid (15 ml.) and sodium dichromate (1.5 g.) was added. The mixture was heated under reflux on a sand bath for 1 hour. It was then cooled and diluted with water. The separated solid was filtered and crystallised from glacial acetic acid in yellow needles (0.3 g.), m.p. 208°.

Analysis : Found : Br, 27.65 %.

$C_{14}H_9O_2Br$: requires : Br, 27.65 %.

2-Hydroxy-1-bromofluorenone :

2-Hydroxyfluorenone (1 g.) was dissolved in glacial acetic acid (20 ml.) and bromine (0.7 g.) in acetic acid (5 ml.) was added dropwise with stirring. The mixture was kept overnight and the yellow solid which separated out was filtered and crystallised from toluene in yellow needles (0.8 g.), m.p. 217°.

Analysis : Found : Br, 28.86 %.

$C_{13}H_7O_2Br$: requires : Br, 29.02 %.

2-Methoxy-1-bromofluorenone :

The above hydroxy bromo fluorenone (0.5 g.) was refluxed in dry acetone (20 ml.) with anhydrous potassium carbonate (1 g.) and dimethyl sulphate (0.5 ml.) on a steam bath for

3 hrs. The solvent was then removed and the reaction mixture was diluted with water. The separated solid crystallised from glacial acetic acid in yellow needles (0.4 g.), m.p. 208°. Mixed m.p. with 2-methoxy-1-bromofluorenone obtained by the oxidation of 2-methoxy-1-bromofluorene was not depressed.

The same compound was also obtained when a solution of bromine (0.7 g.) in glacial acetic acid (5 ml.) was added dropwise to 2-methoxyfluorenone (1 g.) dissolved in glacial acetic acid (10 ml.) and the reaction mixture kept overnight and worked up as before.

2-Methoxy-1-cyanofluorenone :

The above bromo compound (1 g.) was dissolved in hot dimethyl formamide (20 ml.) and cuprous cyanide (1 g.) was added. The mixture was refluxed on a sand bath for 2 hrs. It was then filtered hot and the filtrate was diluted with water. The separated solid was filtered and washed with ammonium hydroxide solution and then with water. It crystallised from toluene in golden yellow needles (0.6 g.), m.p. 292°.

Analysis : Found : C, 76.54 ; H, 3.55 ; N, 5.46 %.
$C_{15}H_9O_2N$: requires : C, 76.60 ; H, 3.82 ; N, 5.68 %.

2-Methoxyfluorenone-1-carboxylic acid :

2-Methoxy-1-cyanofluorenone (1 g.) in alcohol (100 ml.) was refluxed with potassium hydroxide (4 g. in 10 ml. water) on a steam bath for 8 hrs. The solvent was then removed and the reaction mixture was diluted with water. It was filtered and the filtrate was acidified with conc. hydrochloric acid with external cooling. The acid obtained was further

purified by extraction with sodium bicarbonate solution. The product obtained on acidification of the bicarbonate solution crystallised from dilute acetic acid in yellow flakes (0.3 g.), m.p. 241°. Mixed m.p. with 2-methoxy-fluorenone-1-carboxylic acid prepared from 2-methoxy-1-acetylfluorenone, as described on page 158 was not depressed.

2-Methoxy-7-aminofluorene :

2-Methoxy-7-nitrofluorene prepared according to Ishikawa and Okazaki[3] (2 g.) was powdered well and boiled with alcohol (20 ml.). To this hot solution water (10 ml.) and sodium hydrosulphite (5 g.) were added and the mixture was refluxed on a steam bath for 2 hrs. The solvent was then removed and the reaction mixture was diluted with water. The solid obtained was filtered and crystallised from alcohol in colourless flakes (1.2 g.), m.p. 203°. Ishikawa and Okazaki[3] gave the m.p. 204°.

2-Methoxy-7-bromofluorene :

The above amino fluorene (1.5 g.) was dissolved in acetic acid (15 ml.) and hydrobromic acid (3 ml.) was added. The solution was cooled to 0-3° and then diazotised by adding dropwise a solution of sodium nitrite (0.6 g.) in water (5 ml.). The solution was kept at 0-3° for 1 hour. Copper powder (0.5 g.) was added and the solution was heated slowly to boiling and then filtered hot. The filtrate was cooled and diluted with water. The separated solid was filtered and crystallised from petroleum ether in yellow cubes (0.3 g.), m.p. 109°. Campbell and Hasan[2] gave m.p. 108-110°.

2-Methoxy-7-bromofluorenone :

The above bromo compound (1 g.) was dissolved in glacial acetic acid (20 ml.) and sodium dichromate (3 g.) was added. The mixture was refluxed on a sand bath for one hour. It was then cooled and diluted with water. The separated solid was crystallised from dilute acetic acid in red needles (0.9 g.), m.p. 147°.

Analysis : Found : Br, 27.58 %.

$C_{14}H_9O_2Br$: requires : Br, 27.65 %.

2-Methoxy-3-nitrofluorene :

2-Hydroxy-3-nitrofluorene (1 g.), prepared according to Ray and Hull[4] was refluxed in acetone (30 ml.) with anhydrous potassium carbonate (2 g.) and dimethyl sulphate (1 ml.) on a steam bath for 3 hrs. The solvent was then removed and the mixture was then diluted with water. The separated solid was crystallised from acetic acid in yellow needles, m.p. 190°. Ishikawa and Okazaki[3] gave m.p. 190-91°.

2-Methoxy-3-aminofluorene :

2-Methoxy-3-nitrofluorene (1 g.) was powdered well and refluxed with alcohol (25 ml.). Sodium hydrosulphite (2.5 g.) and water (10 ml.) were added and the mixture was refluxed for 2 hrs. The solvent was removed and the reaction mixture was diluted with water. The separated solid crystallised from alcohol in colourless needles (0.6 g.), m.p. 189°. Ishikawa and Okazaki[3] gave m.p. 190°.

2-Methoxy-3-bromofluorene :

2-Methoxy-3-aminofluorene (1.5 g.) was dissolved in acetic acid (20 ml.) and hydrobromic acid (3 ml.) was added. The solution was cooled to 0-3° and sodium nitrite (0.8 g.)

in water (10 ml.) was added dropwise with stirring. The solution was kept at this temperature for 2 hrs. It was then added slowly to a boiling solution of cuprous bromide (prepared from 3 g. of copper sulphate) in hydrobromic acid (10 ml.). The solution was boiled for 10 minutes and then filtered hot. The filtrate was diluted with water. The separated solid was filtered and crystallised from dilute acetic acid in yellow needles (0.3 g.), m.p. 184°.

Analysis	: Found	: Br, 28.98 %.
$C_{14}H_{10}OBr$	: requires	: Br, 29.13 %.

2-Methoxy-3-bromofluorenone :

2-Methoxy-3-bromofluorene (0.5 g.) was dissolved in glacial acetic acid (20 ml.) and sodium dichromate (1.5 g.) was added. The mixture was refluxed for 1 hour. It was then diluted with water and the separated solid was crystallised from acetic acid in orange needles (0.3 g.), m.p. 196°.

Analysis	: Found	: Br, 27.64 %.
$C_{14}H_9O_2Br$	: requires	: Br, 27.65 %.

7-Methoxy-1,7-dibromofluorene :

2-Methoxyfluorene (1 g.) was dissolved in chloroform (10 ml.) and bromine (1.5 g.) dissolved in chloroform (5 ml.) was added dropwise with stirring. The solvent was then removed and the residue obtained was crystallised from acetic acid in colourless needles (0.8 g.), m.p. 143°.

Analysis	: Found	: Br, 44.79 %.
$C_{14}H_{10}OBr_2$	: requires	: Br, 45.16 %.

The same compound was obtained on adding a solution of bromine (0.7 g.) in chloroform (5 ml.) to a solution of 2-methoxy-1-bromofluorene (1 g.) in chloroform (10 ml.) and

evaporating the solvent. Yield 0.4 g.

The same compound was also obtained when 2-methoxy-7-bromofluorene (1 g.) dissolved in chloroform (10 ml.) was treated with bromine (0.7 g.) in chloroform (5 ml.) and the reaction mixture worked up as above. Yield 0.8 g.

2-Methoxy-1,7-dibromofluorenone :

2-Methoxy-1,7-dibromofluorene (1 g.) was refluxed in acetic acid (20 ml.) with sodium dichromate (3 g.) on a sand bath for 1 hour. It was then cooled. The separated solid was crystallised from glacial acetic acid in orange needles (0.8 g.), m.p. 237°.

Analysis	: Found	: Br, 43.22 %.
$C_{14}H_8O_2Br_2$	: requires	: Br, 43.45 %.

2-Hydroxy-1,3,7-tribromofluorene :

2-Hydroxyfluorene (1 g.) was dissolved in glacial acetic acid (10 ml.). Bromine (4 g.) dissolved in acetic acid (10 ml.) was added dropwise with constant stirring. The solid that separated immediately was filtered and crystallised from benzene in solourless needles (1.8 g.), m.p. 190°.

Analysis	: Found	: Br, 57.62 %.
$C_{13}H_7OBr_3$	: requires	: Br, 57.20 %.

2-Methoxy-1,3,7-tribromofluorene :

The above tribromo compound (0.5 g.) was refluxed in dry acetone (20 ml.) with anhydrous potassium carbonate (1 g.) and dimethyl sulphate (0.5 ml.) on a steam bath for 3 hrs. The solvent was then evaporated and the reaction mixture was diluted with water. The separated solid was filtered

and crystallised from acetic acid in colourless needles (0.2 g.), m.p. 193°.

Analysis : Found : Br, 55.40 %.

$C_{14}H_9OBr_3$: requires : Br, 55.39 %.

The same product was obtained when :

i) 2-Methoxyfluorene (1 g.) was dissolved in glacial acetic acid (10 ml.) and bromine (3 g.) in glacial acetic acid (10 ml.) was added dropwise with stirring, and the reaction mixture was worked up as before.

ii) 2-Methoxy-1-bromofluorene (1 g.) was dissolved in acetic acid (10 ml.) and bromine in acetic acid (10 %; 15 ml.) was added slowly with stirring and the reaction mixture worked up as before.

iii) 2-Methoxy-3-bromofluorene (0.5 g.) was dissolved in acetic acid and bromine (1 g.) in acetic acid (5 ml.) was added dropwise with shaking and the reaction mixture was worked up as before.

iv) 2-Methoxy-7-bromofluorene (0.3 g.) was dissolved in glacial acetic acid (5 ml.) and bromine (0.6 g.) in acetic acid (5 ml.) was added with stirring and the separated solid crystallised from acetic acid.

2-Hydroxy-1,3-dibromofluorenone :

2-Hydroxyfluorenone (1 g.) was dissolved in acetic acid (20 ml.) and a solution of bromine in acetic acid (20 %; 20 ml.) was added dropwise with constant stirring. The solid that separated immediately was crystallised from

acetic acid in golden yellow needles (1.2 g.), m.p.237°.

Analysis : Found : Br, 45.04 %.

$C_{13}H_6O_2Br_2$: requires : Br, 45.16 %.

2-Methoxy-1,3-dibromofluorenone :

2-Hydroxy-1,3-dibromofluorenone (0.5 g.) in dry acetone (40 ml.) was refluxed with anhydrous potassium carbonate (1 g.) and dimethyl sulphate (0.5 ml.) on a steam bath for 4 hrs. The solvent was then evaporated and the reaction mixture was diluted with water. The separated solid was crystallised from acetic acid in yellow needles (0.4 g.), m.p. 191°.

Analysis : Found : Br, 43.00 %.

$C_{14}H_8O_2Br_2$: requires : Br, 43.45 %.

The same compound was obtained when :

i) 2-Methoxyfluorenone (1 g.) was dissolved in glacial acetic acid (15 ml.) and bromine (2 g.) in acetic acid was added dropwise.

ii) 2-Methoxy-1-bromofluorenone (1 g.) was dissolved in acetic acid (20 ml.) and bromine (1 g.) in acetic acid (5 ml.) was added dropwise and the reaction mixture worked up as above.

iii) 2-Methoxy-3-bromofluorenone (0.5 g.) was dissolved in acetic acid (20 ml.) and bromine (0.5 g.) in acetic acid (5 ml.) was added slowly with stirring.

2-Methoxy-1,3,7-tribromofluorenone :

2-Methoxy-1,3,7-tribromofluorene (1 g.) was dissolved in acetic acid (20 ml.) and sodium dichromate (3 g.) was

added. The mixture was refluxed on a sand bath for one hour. It was then diluted with water. The separated solid was crystallised from glacial acetic acid in golden yellow needles (0.8 g.), m.p. 268°.

Analysis	: Found	: Br, 53.63 %.
$C_{14}H_7O_2Br_3$	: requires	: Br, 53.67 %.

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