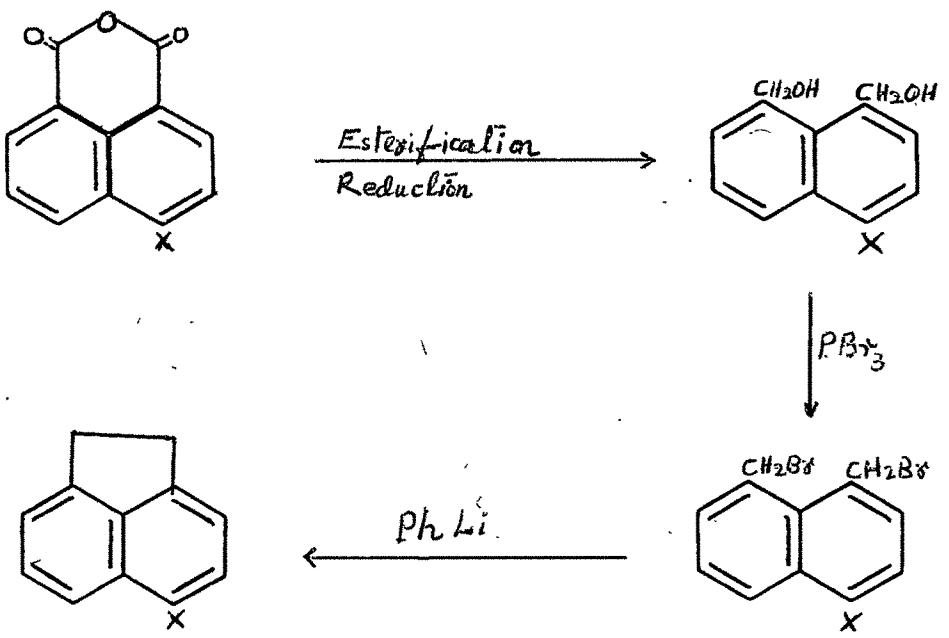
PART I

STUDIES IN ACENAPHTHENE DERIVATIVES

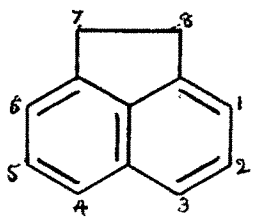
GENERAL INTRODUCTION

Acenaphthene, one of the constituents of the higher fraction obtained in the coal-tar distillation, finds a very useful application in the synthesis of vat-dyes belonging to the Ciba scarlet series. Coal-tar remains the main source of this hydrocarbon. It was Berthelot[1] who detected the presence of this three ring hydrocarbon in 1867 in Coal-tar. It has been isolated from coal-tar[2,3] and from petroleum tar.[4] Acenaphthene is also found in the "Stupp fat" formed in the early working up of the mercury ores of Indria[5]. It has been synthesised by passing acetylene with hydrogen through a porcelain tube heated to 600-800°[6,7]. Acenaphthene has been prepared though in low yield by passing propane through a chromium alloy steel tube heated to 800°[8], or by passing ethylene and benzene through a bright red hot porcelain tube[9]. 1-Ethylnaphthalene on bromination and treatment with potassium hydroxide gives acenaphthene[10]. Schonberg and Monbasher[11] condensed naphthalene with malonyl chloride and the product obtained was oxidised to perinaphthalene trione. This on heating with selenium in the presence of air at 250° gave acenaphthene quinone which was converted to acenaphthene through the semicarbazone. Bergmann and Szmuszkovicz[12] synthesised acenaphthene (Ia) and 5-bromo-acenaphthene (Ib) from the corresponding naphthalic anhydride through the following stages:

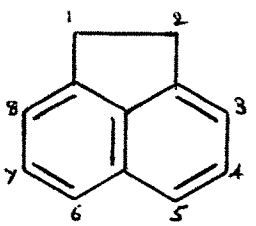


Ia – X = H
Ib – X = Br

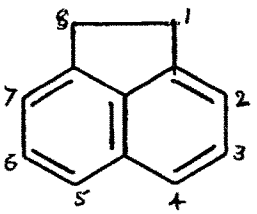
Three different systems of numbering are followed by various workers and journals. Richter system assigns number 1 to the carbon atom ortho to the methylene group (II). In Patterson ring index, the two methylene groups are numbered 1 and 2 (III). This is the system currently followed by chemical abstract. In this thesis also this system is followed. Morgan and Stanley[13] maintain that acenaphthene is structurally peri di-derivative of naphthalene. Therefore they have opted to number it as (IV).



II



III



IV

Physiological activity

Acenaphthene and its derivatives have been found to exhibit a wide range of physiological properties. Kostoff[14] observed chromosome duplication in germinating seed subjected to acenaphthene vapour. Chromosome doubling has also been observed in wheat and rye seeds when treated with 5-bromo-acenaphthene[15]. In this case, the roots remained short and thick, and tumour like swellings were observed. The overall growth of the seedlings was suppressed. 5-Chloro and 5-bromo acenaphthene have also been found to exhibit polyploid activity[16,17]. Carcinogenic activity is exhibited by acenaphthene-5-acetic acid[18]. Cameron and Garvin[19] obtained seeds from sterile oat plant when subjected to acenaphthene vapour. Gunter et al.[20] studied various aliphatic acids containing acenaphthyl group in the ω-position and all of them were found to possess choleretic activity comparable to that of cholic acid. 5-Amino-, 5-amino-6-chloro-, and 5-bromoacenaphthene were found to kill staphylococcus aureus, escherichia coli and tricopyton gypseum at 100 p.p.m.[21]. 5-Hydroxyacenaphthene has been shown to possess considerable <u>in vitro</u> activity on Candida[22].

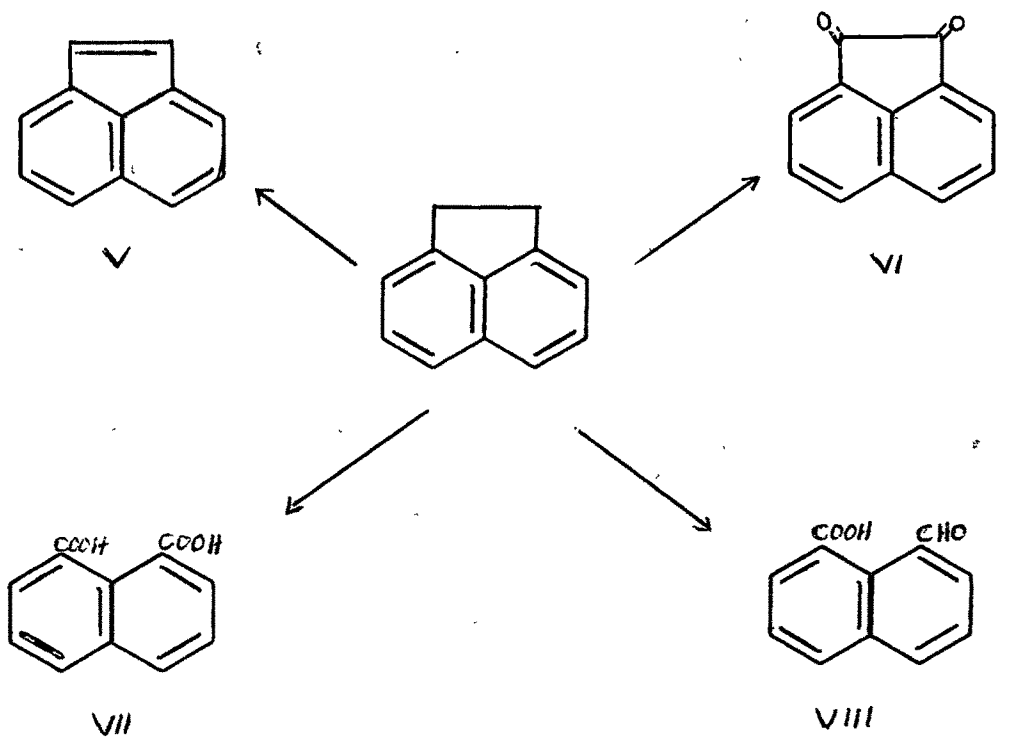
Other applications

3-Nitroacenaphthene has been shown to be a more powerful insecticide than lead arsenate[23]. Acenaphthene derivatives are potent antioxidants for fats, oils, fatty acids and petroleum products[24,25,26]. The complex formed between acenaphthene and T.N.T. is a good rodent repellent[27].

An important use of acenaphthene and acenaphthene quinone is in the vat dye industry.

Oxidation and dehydrogenation :

Dehydrogenation of acenaphthene takes place by passing its vapours mixed with carbon dioxide through a red hot quartz tube and acenaphthylene (V) is obtained[28,29]. Catalytic oxidation of acenaphthene by air gives various products. A mixture of acenaphthene quinone (VI), naphthalic acid (VII) and naphthaldehydic acid (VIII) are obtained by oxidising acenaphthene in the presence of vanadium oxide[30] while vanadium pentoxide and molybdenum trioxide on pumice stone gives naphthalic anhydride and maleic anhydride[31]. When vapour phase oxidation is carried out using vanadium pentoxide, ferric or copper vanadate or manganese dioxide, naphthalic acid is obtained[32]. Naphthalic anhydride has been obtained by oxidising acenaphthene by air under pressure in the presence of a little cobalt or manganese acetate[33].



Acenaphthene has been oxidised to 1-acetoxy acenaphthene by boiling the hydrocarbon with lead dioxide in acetic acid[34]. When acenaphthene is heated with lead dioxide to 180-200° under pressure fluorecyclene ($C_{48}H_{22}$) is obtained[35]. Oxidation of the hydrocarbon with dichromate and sulphuric acid gives naphthalic acid (VII)[36,37] and acenaphthene quinone (VI)[38]. Calcium permanganate in acetone oxidises acenaphthene to acenaphthene quinone (VI)[39] while in water-pyridine mixture potassium permanganate oxidises it to naphthalic acid (VIII)[40]. Acenaphthene quinone (VI) and naphthalic acid (VII) have been obtained by oxidation of the hydrocarbon with hydrogen peroxide in acetic acid[41]. Acenaphthylene, cis and trans acenaphthene glycol and acenaphthenone were reported to have been formed by the oxidation of the hydrocarbon with selenium dioxide[42]. Acenaphthenone has been formed in the oxidation of acenaphthene with chromic acid in acetic acid or with chromyl chloride in carbon tetrachloride[43]. Oxidation with periodic acid in acetic acid yields acenaphthene quinone[44].

Halogenation :

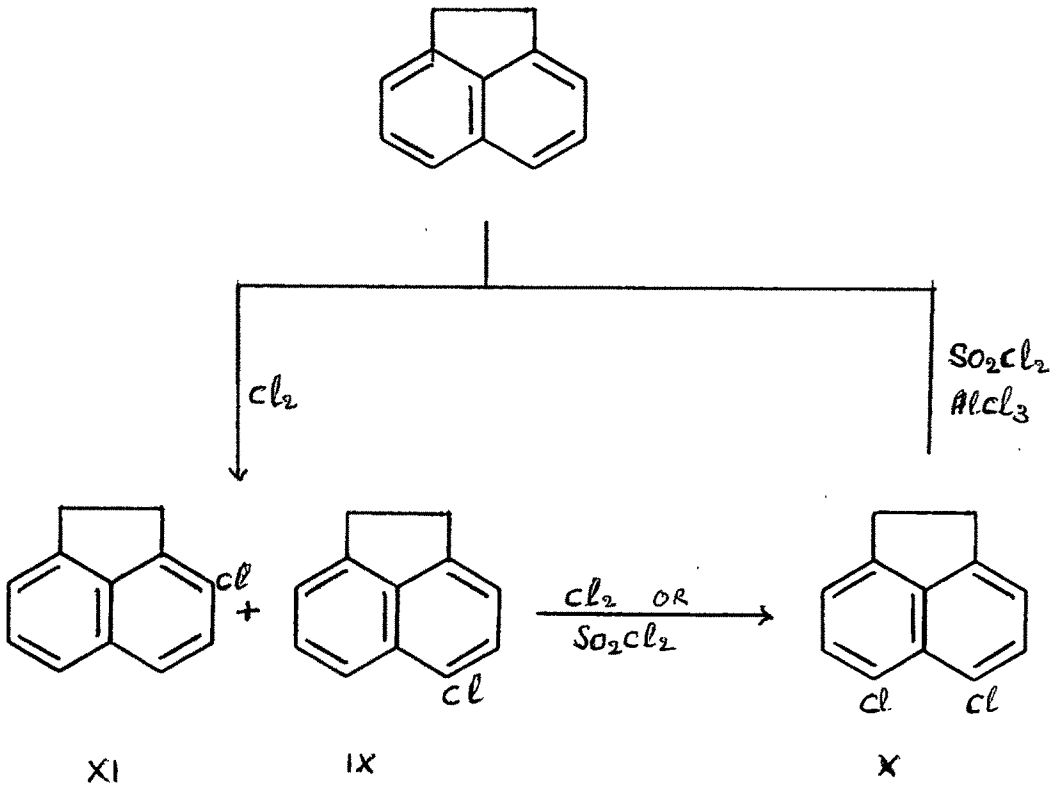
Many studies have been made on the halogenation of acenaphthene.

(a) Chlorination : All the possible mono chloroacenaphthenes have been prepared. Chlorination of acenaphthene dissolved in chloroform by elementary chlorine[45] or sulphuryl chloride[46] yields 5-chloro acenaphthene (IX). The orientation is established by comparing it with the compound obtained by the Sandmeyer reaction on diazotised 5-aminoacenaphthene[47]. Chlorination has

been carried out in solvents like methyl alcohol, ethyl alcohol and acetic acid and in the presence of a catalyst like iodine or antimony trichloride. Pillard and Favarger[48] obtained 5-chloroacenaphthene (IX) in good yield (82 %) by carrying out the chlorination in acetic acid or ethanol in the presence of a small quantity of iodine. Of the various solvents used, acetic acid and ethanol were found to give the best result. Goto and Nagai[49] chlorinated acenaphthene in the presence of metals like aluminium, zinc or iorn and obtained 5-chloroacenaphthene (IX). 5-Chloroacenaphthene under similar conditions yielded 5,6-dichloroacenaphthene (X). 5,6-Dichloroacenaphthene has also been prepared either by chlorinating acenaphthene with sulphuryl chloride in the presence of aluminium chloride[50] or through zinc catalysed chlorination of 5-chloroacenaphthene in acetic acid[51] or by chlorination of 5-chloroacenaphthene in chloroform with sulphuryl chloride[52]. Denisova et al.[53] has been successful in isolating both the 5- and the 3-chloroacenaphthene (XI) by chlorination of acenaphthene in methanol or 90 % acetic acid. Chlorination of 5-chloroacenaphthene has been studied in detail by Constantine et al.[54] who arrived at the conclusion that the second chlorine atom enters the 6-position. 5-Chloroacenaphthene has been shown to undergo isomerisation to a mixture of 5- and 3-chloro derivatives when its vapour mixed with carbon dioxide and hydrogen chloride is passed over alumino silicate at high temperature[55].

3-Chloro- and 3-bromoacenaphthene on further chlorination yields exclusively the 3,6-dichloro derivative[54]. Karishin[56] has described the preparation of 5-bromo-6-chloroacenaphthene by chlorinating 5-bromoacenaphthene with sulphuryl chloride in the

presence of ferric chloride at room temperature.

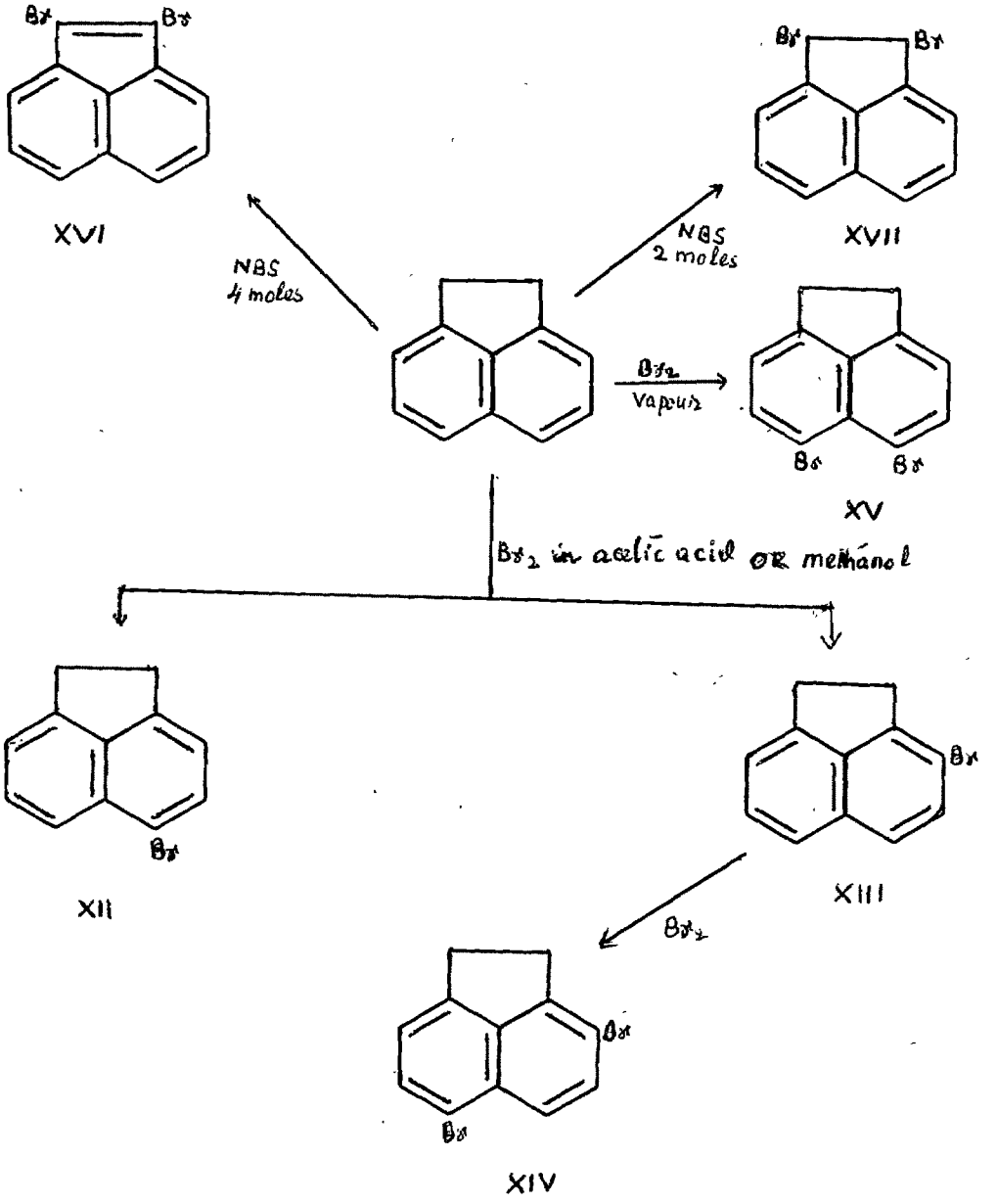


XI IX X

(b) Bromination : Blumenthal[57] reported the preparation of 5-bromoacenaphthene (XII) by the action of bromine on acenaphthene dissolved in ether. Later it was prepared by Graebe and Guinsbourg[58] by brominating acenaphthene in boiling chloroform. The structure was proved by converting it into 4-bromonaphthalene 1,8-dicarboxylic acid by oxidation. Excess of bromine in chloroform affords a dibromoacenaphthene tetrabromide for which no conclusive orientation is given[59]. Bromination of acenaphthene suspended in methanol or 90 % acetic acid gives a mixture of 3-bromo- (XIII) and 5-bromo-acenaphthene (XII)[53]. Lewis et al.[60] studied the bromination of acenaphthene in detail, using different solvents like acetic acid, pyridine and nitromethane and different brominating agents such as N-bromosuccinimide

in dimethyl formamide and acetyl bromide in carbon tetrachloride, iodine monobromide in carbon tetrachloride and hypobromous acid in dil. acetic acid and dioxan. In the last two instances the percentage of 3-bromo was higher ; but in all the cases 3-bromo was isolated, in yields ranging from 3.4 % to 32.4 % along with a higher percentage of the 5-isomer. Vorozhtsov and Tochilkin[55] synthesised 3- and 4-bromoacenaphthene by decomposing the corresponding diazonium salts with zinc halide. 3-Bromoacenaphthene on further bromination gives 3,6-dibromoacenaphthene[54]. Letsinger et al.[61] brominated acenaphthene by passing bromine vapour through the hydrocarbon dissolved in alcohol at its boiling point. 5,6-dibromoacenaphthene (XV) was isolated from the reaction mixture and the structure was established through NMR spectral data.

Trost and Brittelli[62] and Greene et al.[63] studied the bromination of acenaphthene with N-bromosuccinimide. They observed the formation of 1,2-dibromoacenaphthylene (XVI) when 4 moles of N-bromosuccinimide were used in carbon tetrachloride. By employing 2 moles of N-bromosuccinimide 1,2-dibromoacenaphthene (XVII) was obtained. This work was extended further by Ross, Finkelstein and Peterson[64]. They reported the formation of 1-bromoacenaphthene when 1 mole of N-bromosuccinimide was used in carbon tetrachloride, where as the use of dimethylformamide or propylene carbonate as a solvent gave 5-bromoacenaphthene. Buu-Hoi[65] reported the preparation of 5-bromoacenaphthene by the action of N-bromosuccinimide in carbon tetrachloride. 1,3-Dibromo-5,5-dimethylhydantoin and acenaphthene give 1-bromoacenaphthene[66].



(c) Iodination and Fluorination : Zakharova et al.[67] iodinated acenaphthene with iodine monochloride and obtained 5-iodo-, and 3,5-diiodoacenaphthene. There does not appear to be any other reference in the literature on the iodination of acenaphthene.

A survey of the literature also does not show any work on the direct fluorination of acenaphthene. Fluoro acenaphthenes

have however been prepared through the diazonium salts.

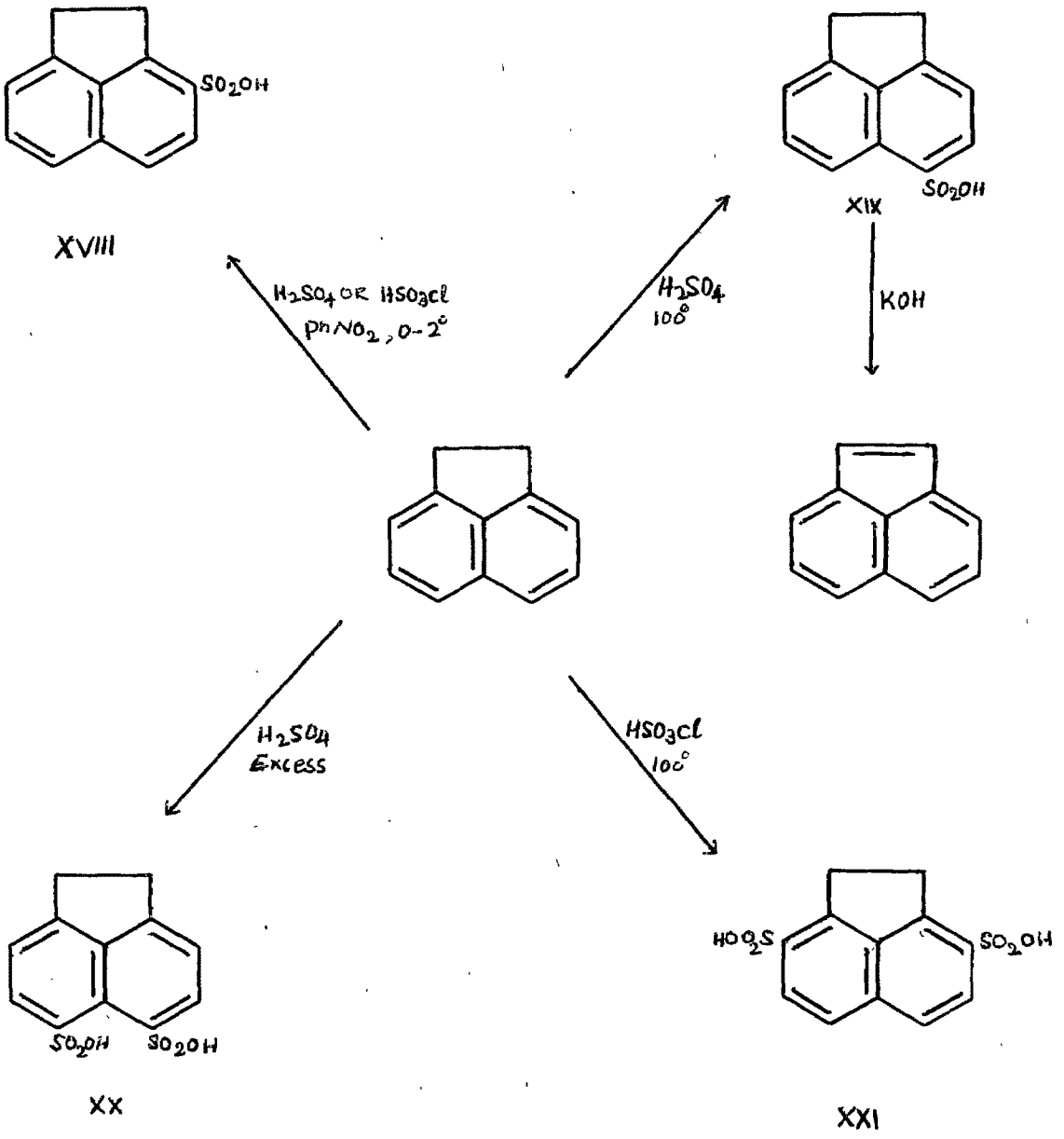
Sulphonation :

Acenaphthene behaves on sulphonation in the same way as naphthalene, substitution taking place in the α or 5-position at low temperature and at β or 3-position at higher temperature. Dziewonski et al.[68] subjected acenaphthene to sulphonation under various conditions and obtained 3- and 5-acenaphthene sulphonic acids (XVIII and XIX). Their orientation has been established by oxidising the sulphonic acids to naphthalic anhydride derivatives. and converting them to hydroxynaphthalic acids by potassium hydroxide fusion. Thus acenaphthene when heated on a water bath with conc. sulphuric acid yields acenaphthene-5-sulphonic acid[68,69] (XIX). This sulphonic acid on heating with potassium ferrocyanide or potassium cyanide gives acenaphthylene. Acenaphthene 3-sulphonic acid (XVIII) is obtained by the addition of sulphuric acid or chloro sulphonic acid to a solution of acenaphthene in nitrobenzene at 0-20^{0} [68].

Sulphonation of acenaphthene with excess of fuming or conc. sulphuric acid yields two disulphonic acids named α and β acids[68]. The α acid is assigned the 5,6-disulphonic acid structure (XX) and the β-acid is assigned the 3,8-or the 3,5-disulphonic acid structure. Acenaphthene with excess of chlorosulphonic acid at 100^{0} gives the 3,8-disulphonic acid only (XXI)[70].

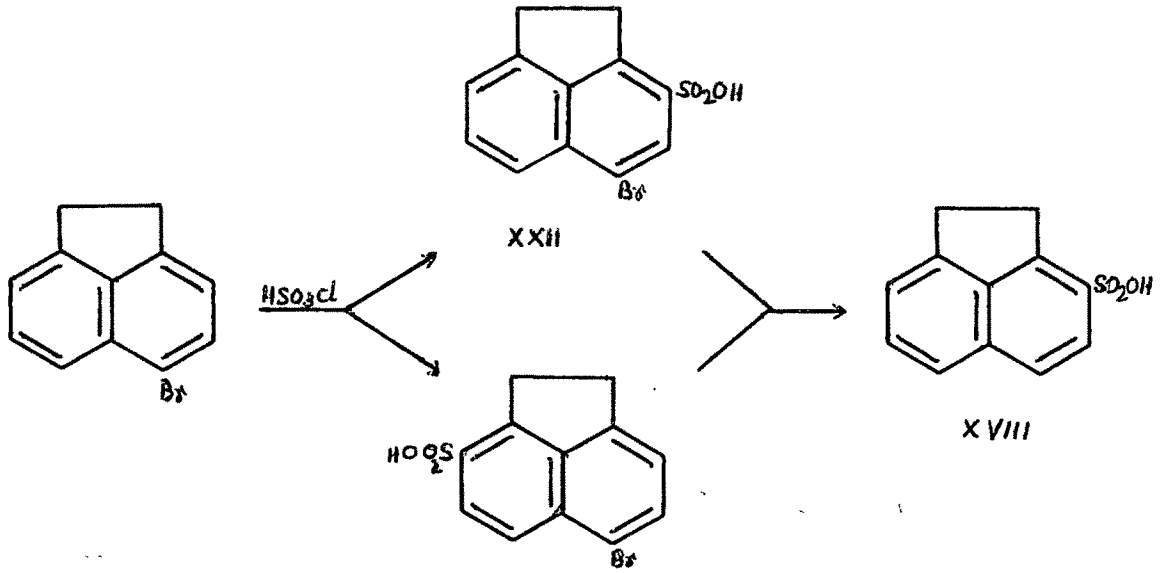
It is assumed that on heating with potassium hydroxide the sulphonic acid group migrates to 1-position and eliminates sulphurous acid giving acenaphthylene[70].

Acenaphthene-3-sulphonic acid along with small amounts of 3,3'-diacenaphthyl sulphone has been obtained by heating the hydrocarbon with chlorosulphonic acid to 125°[71].



Dziewonski[72,73] et al. isolated two sulphonic acids from the reaction of chlorosulphonic acid with 5-bromo acenaphthene. The structures were proved by removing the bromine by sodium amalgam in alcohol when the 3-sulphonic acid (XVIII) was

obtained from both. This clearly showed that the acids were 5-bromo acenaphthene 3-sulphonic acid (XXII) and 5-bromo acenaphthene 8-sulphonic acid (XXIII).



Nitration:

Nitration of acenaphthene and its derivatives have been studied in detail by several workers. The usual method of preparation of phenols namely preparing the sulphonic acid derivative and fusing it with potassium hydroxide, fails in the case of acenaphthene. When acenaphthene sulphonic acid is fused with potassium hydroxide acenaphthylene is obtained, irrespective of the position of the sulphonic acid group. Therefore the only route to hydroxyacenaphthene is through the diazonium salt. This has given an added interest to the work on the nitration of acenaphthene.

Nitration of acenaphthene was studied by Quincke[74] and Graebe and Guinsbourg[58]. In all cases 5-nitroacenaphthene (XXIV) was obtained. Its reduction furnished 5-aminoacenaphthene[75,76]. The acyl derivative of this compound nitrates in the ortho position as demonstrated by Sachs and Mosbach[75] who hydrolysed

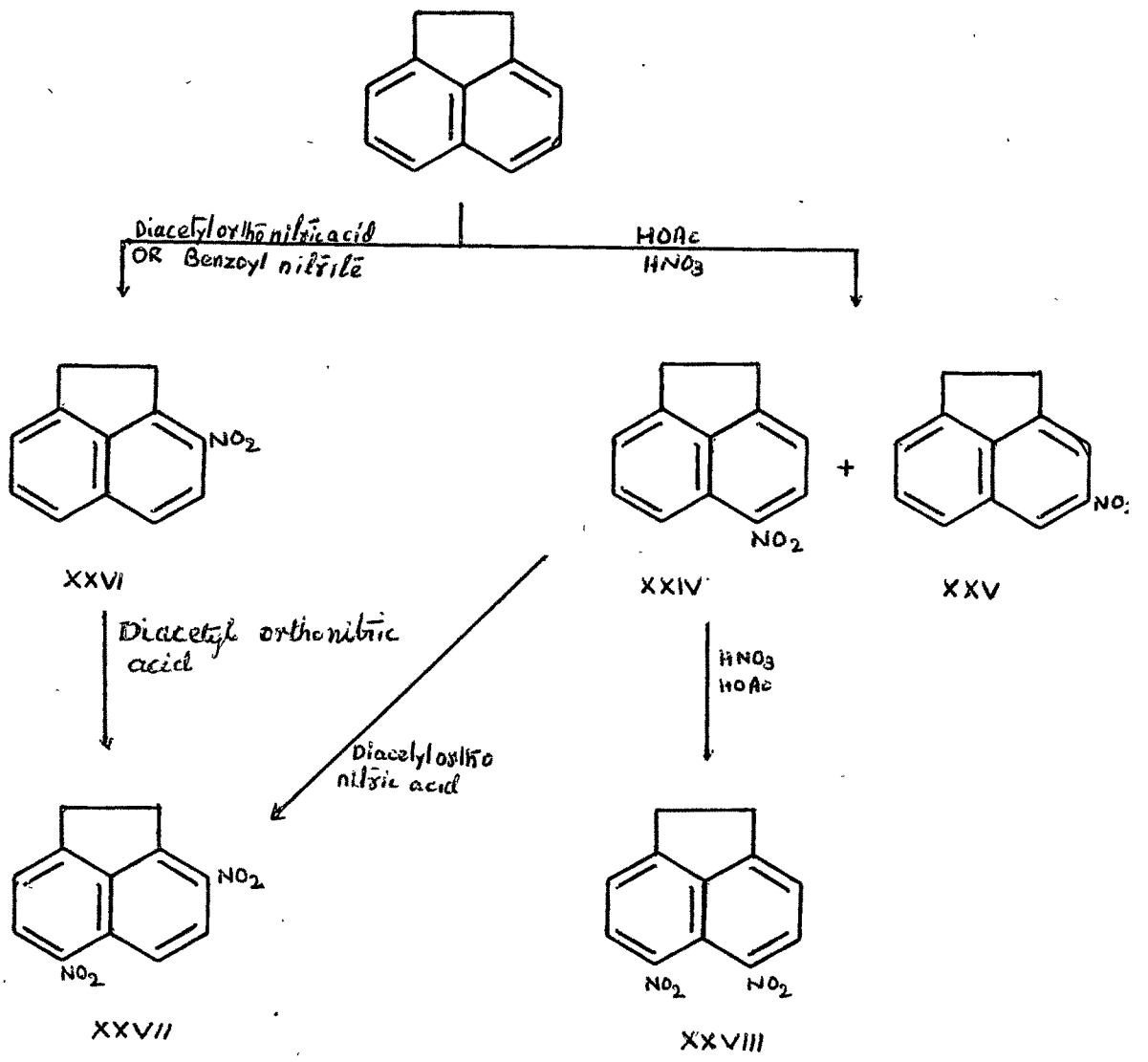
the nitro acylamino compound to 4-nitro-5-aminoacenaphthene. On reduction this furnished a diamino compound which was shown to be an o-diamino compound. It has been shown by Morgan and Stanley[77] that 5-formamido acenaphthene also undergoes nitration at the 4-position. The nitroformamido compound has been hydrolysed to 4-nitro-5-aminoacenaphthene. Usual methods for removing the amino group are reported to have failed. Therefore the amino derivative is converted to the iodo derivative through diazotisation and Sandmeyer reaction and this is reduced to 4-amino acenaphthene with tin and hydrochloric acid.

Nitration involving strong mineral acids and water invariably gives the 5-substituted product. The use of reagents avoiding these two leads to nitration at 3-position. Morgan and Sheasby[78] nitrated acenaphthene using benzoyl nitrate in petroleum ether at -10° and 3-nitroacenaphthene (XXVI) has been isolated as the sole reaction product. The same authors also carried out the nitration of acenaphthene with fuming nitric acid in excess of acetic anhydride at -5° and obtained a mixture of 3-nitroacenaphthene (XXVI) (65-70 %) and 5-nitroacenaphthene (XXIV) (30-35 %). Therefore Morgan and Sheasby[78] concluded that the first nitration product of acenaphthene is 3-nitro derivative which in the presence of water and mineral acids changes to the 5-isomer. This concept has been proved by heating 3-nitroacenaphthene with acetic acid containing a little nitric acid or sulphuric acid whereby obtaining 5-nitroacenaphthene. Morgan and Harrison[79] have shown that in the nitration of acenaphthene all the three possible isomers are

formed, though the 4-isomer (XXV) is formed in very small amount.

Nitration of acenaphthene with excess of nitric acid produces 5,6-dinitroacenaphthene[74,75,80] (XXVIII). Under anhydrous conditions, 3-nitroacenaphthene on further nitration gives mainly 3,6-dinitroacenaphthene (XXVII). This can also be obtained by nitrating 5-nitroacenaphthene with diacetyl ortho nitric acid.

The nitration of acenaphthene can be summarised as follows :



Acenaphthene has been found to undergo nitration in ether or petroleum ether at -10° to -15° with nitrous fumes to give 5-nitroacenaphthene. In acetic acid or benzene at 8-10°, 5,6-dinitroacenaphthene is formed[81]. 5-Chloro-6-nitroacenaphthene has been obtained by nitration of 5-chloro-acenaphthene[82,83]. Nitration of acenaphthene with zinc or copper nitrate in acetic anhydride at 30° gave 90 % 5-nitroacenaphthene and at -10° gave 70 % of the 3-nitro derivative[84].

Friedel-Crafts acylation and alkylation :

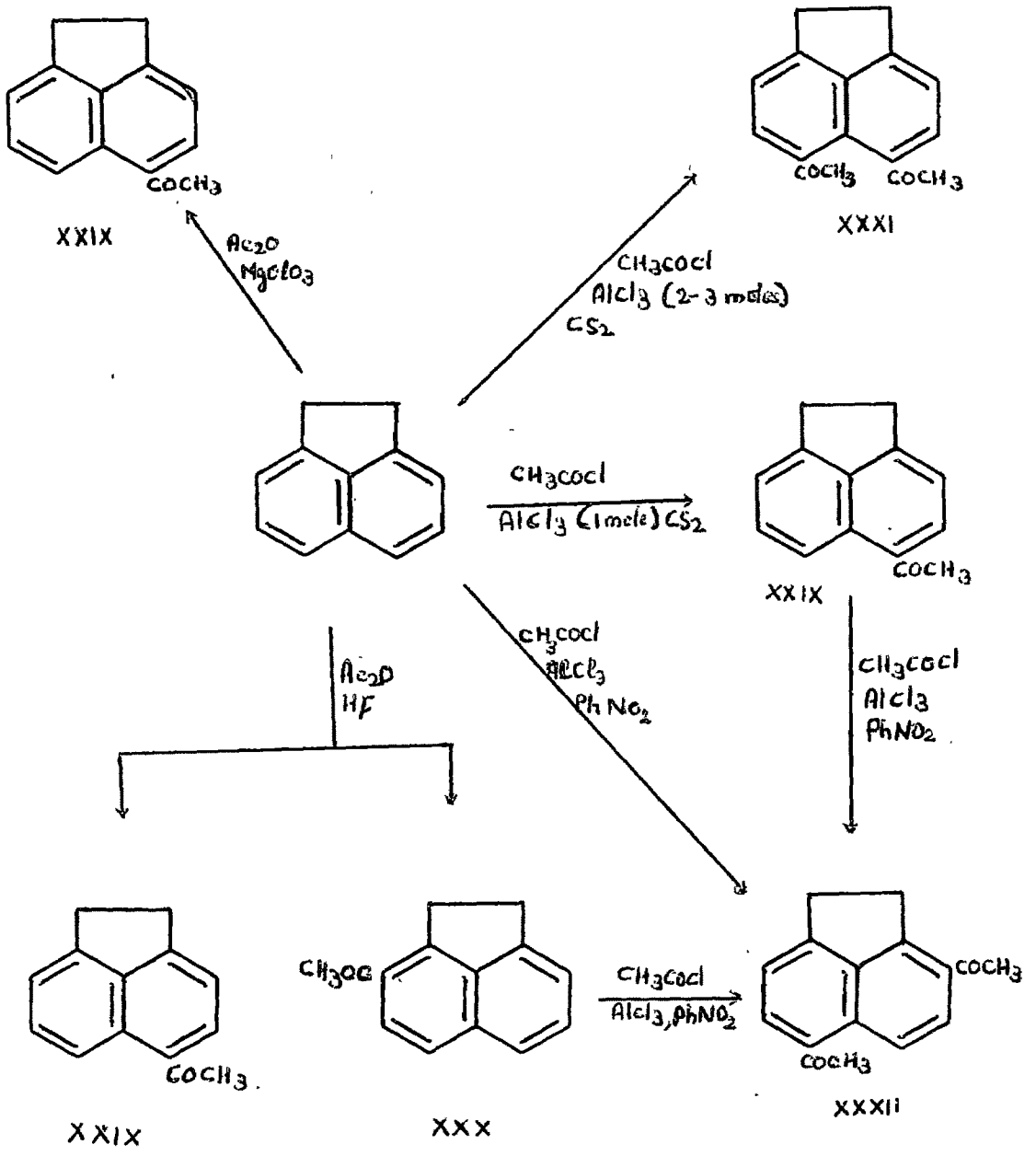
Acenaphthene in carbon disulphide and aromatic or aliphatic acid chloride in the presence of aluminium chloride gives 5-acylacenaphthene. Dziewonski and Reiss[85] obtained 5-acetyl acenaphthene (XXIX) by the action of acetyl chloride on acenaphthene in the presence of anhydrous aluminium chloride and without employing any solvent. Buu-Hoi et al.[86] synthesised the same compound by the addition of the complex obtained from aluminium chloride and acetyl chloride in carbon disulphide to a solution of acenaphthene in the same solvent at 0°. These workers extended this work by employing various acid chlorides such as caproyl, heptanoyl, decanoyl, hendecanoyl, lauroyl, myristoyl, palmitoyl and stearoyl. In all these cases 5-acylacenaphthenes have been isolated. By employing 2-3 moles of aluminium chloride and 3 moles of acetyl chloride, Anderson and Anderson[87] obtained 5,6-di-acetyl acenaphthene (XXXI) in 59 % yield. Formation of 3,6-diacetyl acenaphthene (XXXII) has been reported by Dashevski and Shamis[88] by the action of acetyl chloride on acenaphthene dissolved in nitrobenzene in the presence of

anhydrous aluminium chloride. The same diacetyl acenaphthene has been obtained by the acetylation of 3- and 5-acetyl-acenaphthene in the presence of aluminium chloride in nitrobenzene. These diacetyl compounds are oxidised to naphthalene tetracarboxylic acids. The same authors prepared 3,6-dipropionyl acenaphthene by the action of propionyl chloride on acenaphthene dissolved in ethylene dichloride in the presence of aluminium chloride at room temperature. The structure of this compound was proved in the following way. The dioxime obtained from the dipropionyl derivative was subjected to Beckmann rearrangement and the di-propionamido compound was hydrolysed to the diamine. This was found to be identical with the diamine of known orientation. Richter and Stocker[89] synthesised the 3,6-di-acetyl derivative (XXXII) and established the structure by converting its oxime through rearrangement to the corresponding diamine derivative. 3,6-Dibenzoyl derivative also has been prepared by the same workers. 5-Chloro acenaphthene when subjected to Friedel-Crafts acetylation has been found to give a mixture of 3-acetyl-6-chloro-, and 3-acetyl-5-chloroacenaphthene. 5-Bromoacenaphthene also gives the same result[90].

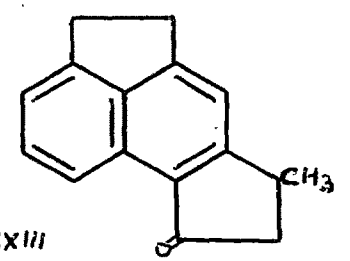
The condensation of acenaphthene and acetic anhydride has been investigated by Fieser and Hershberg[91]. By heating acenaphthene, acetic anhydride and hydrogen fluoride in a pressure vessel, they obtained 5-acetylacenaphthene in 37 % yield. Rozenberg et al.[92] effected the condensation with magnesium chlorate and obtained 5-acetyl derivative in 82 % yield. They extended the condensation by using other acid

chlorides and using chloric acid (5 %) instead of chlorate. Thus 5-propionyl-, 5-isopropionyl-, 5-valeryl-, 5-isovaleryl-, 5-caproyl- and 5-benzoylacenaphthene have been prepared in this way.

Some of the results obtained in the Friedel-Crafts acetylation of acenaphthene are summarised in the chart given below :

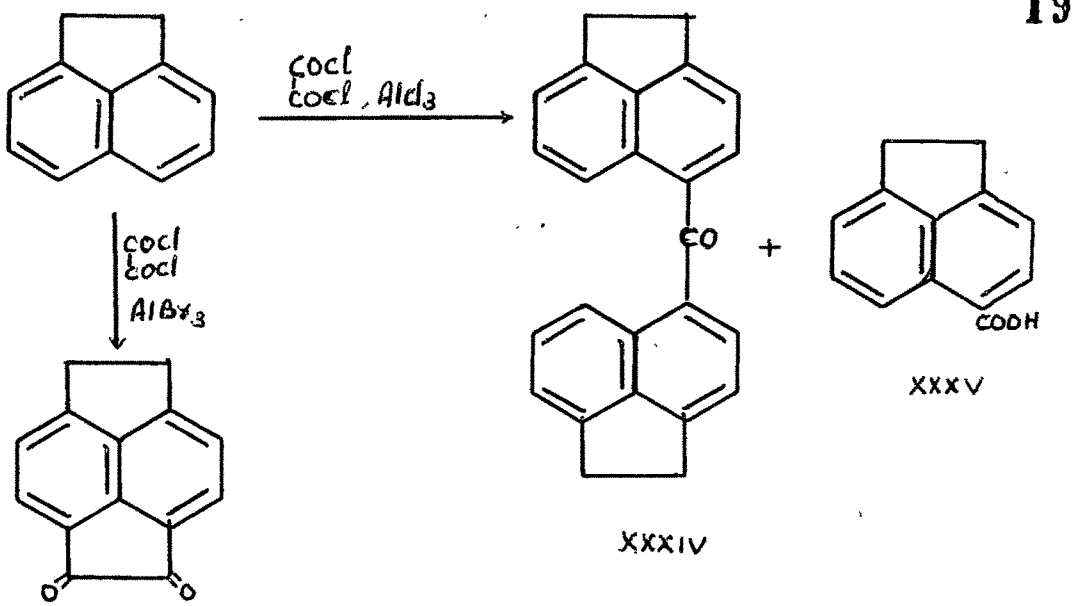


Fieser and Hershberg[93] extended the use of hydrogen fluoride as a condensing agent in the acylation of acenaphthene. Acenaphthene and acetic acid when kept at room temperature for three days with liquid hydrogen fluoride, gave a mixture of 3- and 5-acetylacenaphthene. 5-Benzoyl-acenaphthene was obtained from benzoic acid and acenaphthene in the presence of hydrogen fluoride in 2 1/2 hrs. in 60 % yield and no 3-isomer was obtained. Benzoyl chloride under these conditions gave 87 % yield of the 5-benzoyl derivative. Crotonic acid gave 1-methyl-3-keto-4,5-cyclopentane (XXXIII). This type of cyclisation has not been reported with naphthalene, phenanthrene and anthracene.



XXXIII

Acenaphthene condenses with oxalyl chloride in the presence of aluminium chloride to give di-5-acenaphthyl ketone (XXXIV) and acenaphthene 5-carboxylic acid (XXXV), however, when aluminium bromide is used as the condensing agent the 1,2-diketopyracene (XXXVI) is obtained[94].

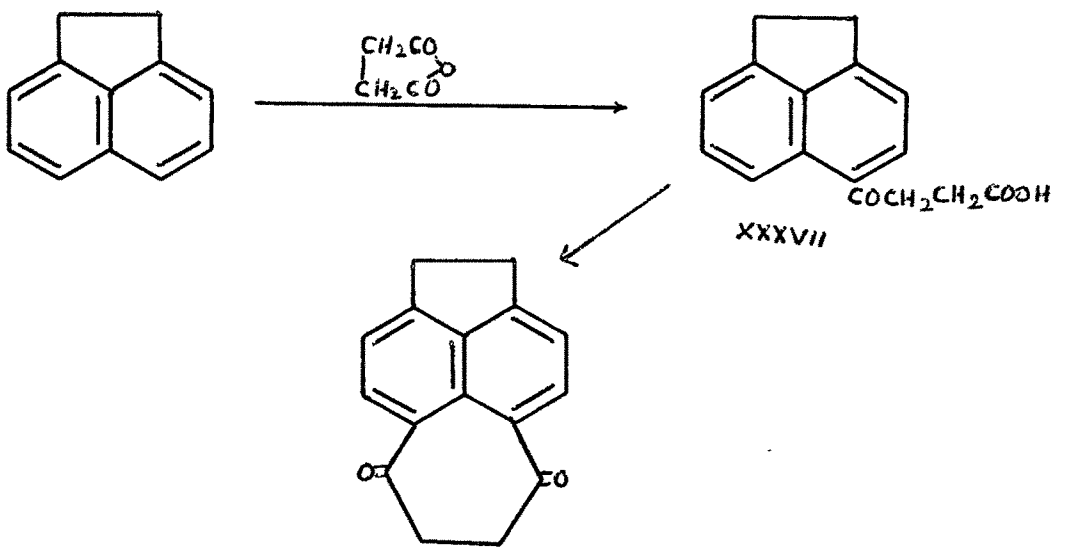


XXXIV

XXXV

XXXVI

Friedel-Crafts acylation with succinic anhydride presents an interesting feature. Fieser and Peters[95] studied this condensation and obtained β(5-acenaphthoyl) propionic acid (XXXVII). This acid was further cyclised by sodium chloride-aluminium chloride mixture to a seven membered ring (XXXVIII), which is quite unusual.



XXXVII

XXXVIII

Benzoylation of acenaphthene has been studied by a number of workers.

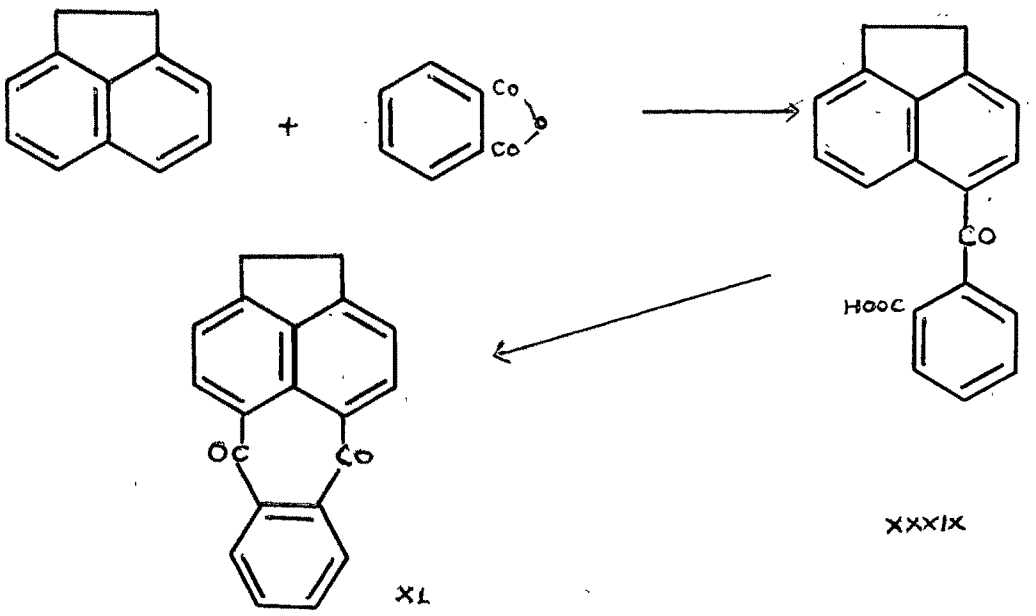
Dziewonski and Rychlik[96] reported the formation of only 5-benzoylacenaphthene by using zinc chloride as a condensing agent. Ju-Hua Chu[97] has increased the yield of 5-benzoylacenaphthene by using aluminium chloride in nitrobenzene. Azatyan[98] carried out the condensation by heating acenaphthene and benzoyl chloride in the presence of catalytic amount of aluminium powder without any solvent and obtained the same compound in 68 % yield. Rozenberg et al.[92] employed chloric acid as a condensing agent and obtained 34 % yield of 5-benzoylacenaphthene. Richter and Stocker[89] carried out benzoylation in nitrobenzene using aluminium chloride as catalyst and obtained 3,6-dibenzoylacenaphthene. The orientation of this compound was established by the Beckmann rearrangement of its ketoxime to a diamino derivative of known orientation. Tsukarvanik et al.[99] obtained 5-benzoylacenaphthene in 82 % yield by the action of benzoyl chloride on acenaphthene in the presence of very small amounts of iron as catalyst.

Phenyl acetic acid on condensation with acenaphthene in the presence of hydrogen fluoride gave 5-phenylacetyl-acenaphthene with traces of the 3-isomer[100]. Buu-Hoi and Royer[101] obtained the same compound by condensing phenyl-acetylchloride with acenaphthene in carbon disulphide in the presence of aluminium chloride.

Freund and Fleischer[102] have reported that in the reaction of acenaphthene with dimethyl malonyl chloride, two substances are formed. They assigned the 5,6-acenaphthene

dimethyl indan-dione and isoacenaphthene dimethyl indan-dione structures to these compounds without giving any proof.

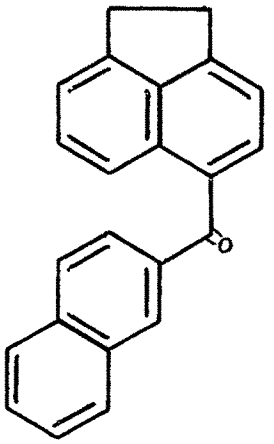
Phthaloylation and naphthoylation of acenaphthene has been studied by Peters and Rowe[103] and Buckley[104]. Acenaphthene, phthalic anhydride and aluminium chloride in benzene at room temperature gives 5(o-carboxybenzoyl)-acenaphthene (XXXIX) which has been further cyclised by heating with sodium chloride-aluminium chloride mixture for 3 hrs. at 135° to get 5,6-phthaloyl acenaphthene (XL).



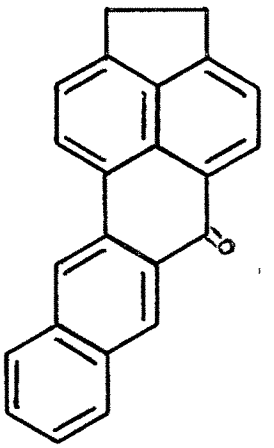
XXXIX

XL

Acenaphthene and 2-naphthoylchloride in the presence of 2.5 moles of aluminium chloride gives naphthylacenaphthyl ketone (XLI) while with 5 moles of aluminium chloride intramolecular cyclisation is found to take place to give (XLII).



XLI



XLII

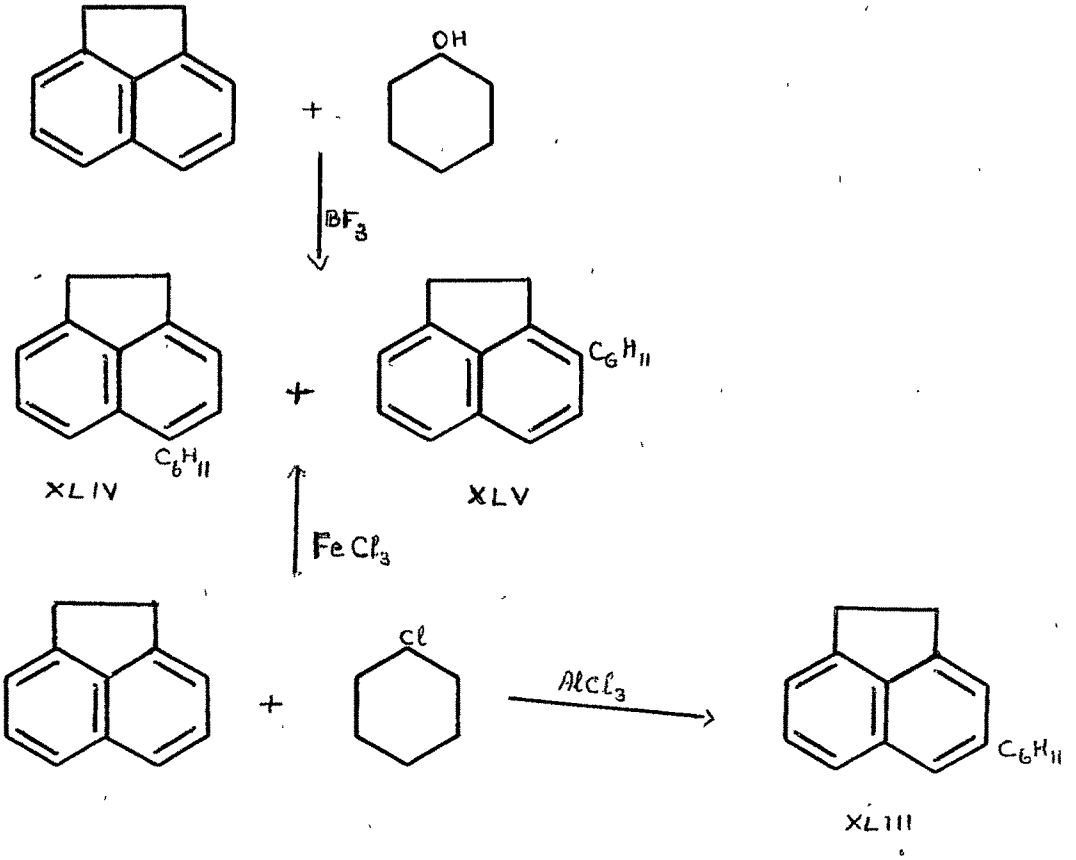
Acylation of acenaphthene with chloracetic acid in chloroform in the presence of aluminium chloride gives a mixture of 3-chloracetyl and 5-chloracetylacenaphthene[105] in which the latter predominates, whereas the isolation of only 5-chloracetylacenaphthene has been reported by Sych[106] by carrying out the reaction in carbon disulphide. Nightingale and Brooker[107] carried out the condensation of 5-haloacenaphthene with benzoyl chloride and acetyl chloride in the presence of aluminium chloride and obtained 3-acyl-5-halo- and 3-acyl-6-halo-acenaphthenes, the orientation being established through spectral studies.

Friedel-Crafts alkylation has been extensively studied by various workers.

Mayer and Kaufmann[108] prepared 5-ethylacenaphthene from ethyl bromide and acenaphthene in the presence of aluminium chloride. Later, Nurnsten and Peters[109] proved it to be 4-ethylacenaphthene. Peters[110] reported the preparation of 5-tert-butyl- and 5,6-di-tert-butyl-acenaphthene from acenaphthene and tert-butyl chloride in

the presence of aluminium chloride, but Nurnsten and Peters[111] have shown them to be 4-tert-butyl- and 4,7-di-tert-butyl-acenaphthene by converting them to naphthalic acid derivatives. The preparation of mono, di and tri n-butyl-acenaphthenes has been described by Akhmedov and Khalilov[112]. Dziewonski and Rychlik[96] prepared 5-benzylacenaphthene by heating benzyl chloride, acenaphthene and zinc chloride.

Cyclohexylation and cyclopentylation of acenaphthene has also been studied in detail by Sidorova and Saidova[113,114]. Acenaphthene, cyclohexyl chloride and excess aluminium chloride in heptane when heated to 40-50° gave 4-cyclohexyl-acenaphthene (XLIII). They also obtained a mixture of 5- and 3-cyclohexyl acenaphthene (XLIV and XLV) by saturating acenaphthene in cyclohexanol with boron trifluoride. When acenaphthene and cyclohexylchloride in heptane is heated to 115° with ferric chloride 3-, and 5-isomers are formed.



5- and 3-Cyclopentylacenaphthene have been isolated[114] from the reaction of acenaphthene, cyclopentyl chloride and copper powder after heating for 3 hrs. at 150-60°. The same reaction proceeds in heptane and with equimolar amounts of acenaphthene, cyclopentyl chloride and aluminium chloride at 40° giving 4-cyclopentyl acenaphthene. These workers observed that all the three mono cyclopentyl derivatives are formed by reducing the amount of aluminium chloride to 0.3 mole and time to 5 minutes. Cyclopentanol when heated with acenaphthene and aluminium chloride gives 40 % yield of 5-cyclopentyl-acenaphthene. The structure of these compounds have been established by converting them to carboxy naphthalic anhydride by oxidation.

Cairns and Hickinbottom[115] observed the migration of the 5-alkyl substituent such as tert-butyl to the 4-position on boiling it with aluminium chloride in carbon disulphide. These workers carried out the alkylation of acenaphthene by the thermal decomposition of alkyl benzene sulphonates. When ethyl benzenesulphonate, isopropyl benzenesulphonate, sec. butyl benzenesulphonate and cyclohexyl benzenesulphonate were used the 3-, 4- and 5-monoalkylacenaphthenes were isolated.

Alkylation of acenaphthene by olefines in the presence of sulphuric acid has been studied by Akhmedov and Khalilov[112] and Akhmedov[116]. Thus acenaphthene, amylene and sulphuric acid gave mono, di and triamylacenaphthene. But the exact orientation of these compounds has not been given. Similarly decalene and isobutylene gave a mixture of mono, di and tri substituted derivative.

1-Vinyl and 1,2-divinyl acenaphthene have been

prepared by Levchenko and Suprun[117] by the action of acetylene on acenaphthene dissolved in benzene in the presence of alkali.

Formylation :

Hinkel et al.[118] formylated acenaphthene with hydrogen cyanide in tetrachloroethane at 80° in the presence of aluminium chloride and obtained 5-formylacenaphthene. 3-Formylacenaphthene has been obtained by formylation with s-triazine[119].

Substitution in hydroxyacenaphthenes :

Though considerable work has been done on substitution in simple acenaphthene, studies on substitution in hydroxy-acenaphthenes are comparatively very few. Rapoport et al.[120] obtained 5-hydroxy-4-piperidinomethylacenaphthene by heating 5-hydroxyacenaphthene and methylene bis piperidine. 5-Hydroxy-acenaphthene when treated with sodium nitrite gives 4-nitroso-5-hydroxy acenaphthene[121]. 5-Hydroxy-4-chloroacenaphthene has been obtained by chlorinating 5-hydroxyacenaphthene in chloroform with sulphuryl chloride at 0°[120]. Coupling takes place in the 4-position in 5-hydroxyacenaphthene. Thus 5-hydroxy-acenaphthene, when coupled with diazotised 2-aminobenzothiazole or 2-aminothiazole gives 5-hydroxy-4-(2-benzothiazolyl azo) acenaphthene and 5-hydroxy-4(2-thiazolyl azo)acenaphthene[122]. Coupling with diazotised aniline derivative takes place invariably in the 4-position as shown by various workers[123,124]. 5-Acetoxyacenaphthene when stirred in nitrobenzene with aluminium chloride at room temperature gives 5-hydroxy-4-acetylacenaphthene in 75 % yield[125].

Present work.

The present work deals with the following studies on 5-hydroxyacenaphthene.

Section I deals with the building up of α- and γ-pyrone rings on acenaphthene ring system. Synthesis of acenaphtho (5,4:6',5')α-pyrone was achieved from 5-hydroxy-4-formyl acenaphthene by Perkin and Knoevenagel condensations. It's 4'-methyl and 4'-phenyl derivatives are synthesised by the Pechmann condensation of ethyl acetoacetate and ethyl benzoyl acetate with 5-hydroxyacenaphthene. Kostanecki-Robinson acetylation and benzoylation of 5-hydroxy-4-acetyl acenaphthene gave 2'-methylacenaphtho(5,4:6',5')γ-pyrone and 2'-phenyl-3'-benzoylacenaphtho(5,4:6',5')γ-pyrone respectively. Synthesis of 2'-phenyl and 2'-p-methoxypheryl acenaphtho(5,4:6',5')γ-pyrones is achieved by the condensation of 5-hydroxy-4-acetylacenaphthene with benzaldehyde and anisaldehyde respectively and subsequent cyclisation and dehydrogenation of the styryl ketones obtained.

A γ-pyrone derivative with acenaphthyl group at the 2-position is obtained from 5-methoxy-4-formyl acenaphthene through condensation with o-hydroxyacetophenone and cyclisation and dehydrogenation of the intermediate β(5-methoxy-4-acenaphthyl)vinyl o-hydroxy phenyl ketone.

Section II deals with the synthesis of some acenaphthofurans. Acenaphtho(5,4:5',4')furan is synthesised from 5-hydroxy-4-formylacenaphthene by condensing it with ethyl bromoacetate and subsequent hydralysis and cyclisation of the intermediate 5-carbethoxymethoxy-4-formylacenaphthene.

By a similar series of reactions 3'-methyl and 3'-pheryl derivatives of the above furan are synthesised starting with 5-hydroxy-4-acetyl and 5-hydroxy-4-benzoyl acenaphthenes.

Section III deals with the synthesis of some Mannich bases from 5-hydroxyacenaphthene, paraformaldehyde and secondary and primary amines.

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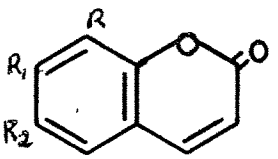
SECTION I

SYNTHESIS OF SOME ACENAPHTHO α- AND γ-PYRONES

SECTION I.

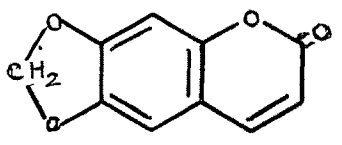
Synthesis of some acenaphtho α-and γ-pyrones :

Benzo α-and γ-pyrone derivatives such as coumarins, chromones and flavones occur in nature, generally in the form of glucosides or associated with tannins or are found in the uncombined state. Coumarin, the parent substance of the benzo-α-pyrone group was first isolated from tonka-beans. Aesculetin (I), scopoletin (II), daphnetin (III), fraxetin (IV), umbelliferon (V), are a few of the simpler members isolated from plants[1].

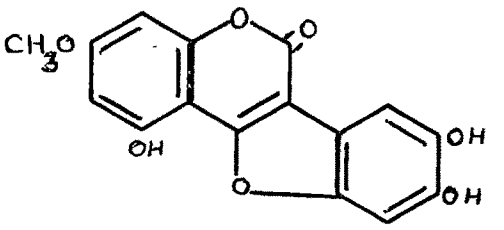


	R	R_1	R_2
I Aesculetin	H	OH	OH
II Scopoletin	H	OH	OCH_3
III Daphnetin	OH	OH	H
IV Fraxetin	OH	OH	OCH_3
V Umbelliferon	H	OH	H

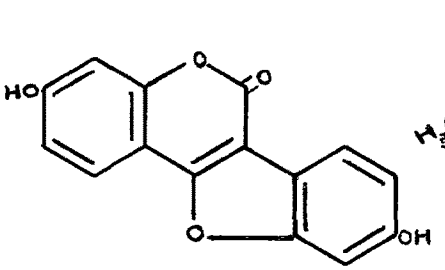
In recent years more complex compounds having the coumarin ring system have been isolated. Ayapin (VI), Wedelolactone (VII), Coumestrol (VIII), Robustic acid (IX), Scandenin (X) and Novobiocin (XI) are a few examples.



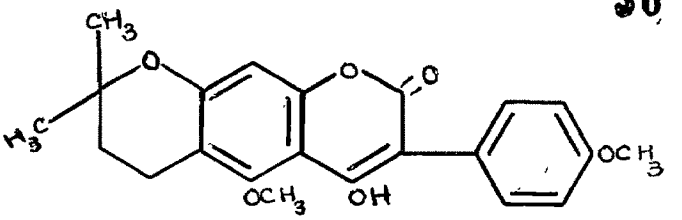
VI



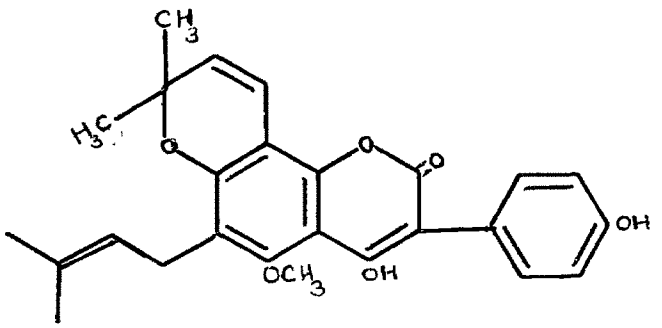
VII



VIII



IX



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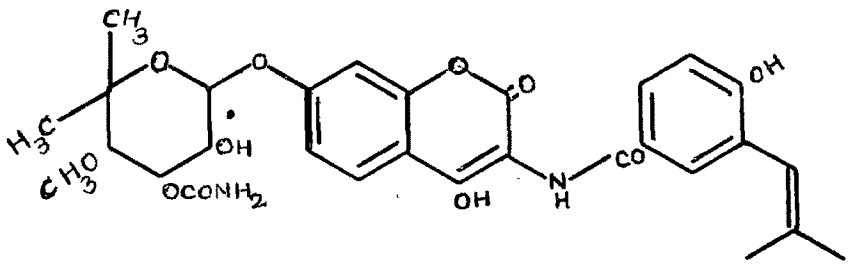
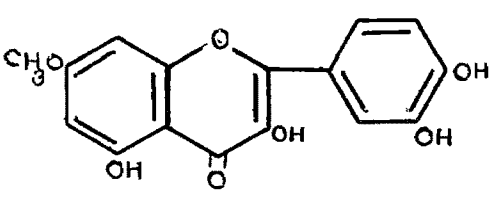


XI

Many γ-pyrone derivatives are also found to occur in nature. Rhamnetin (XII), Calycopterin (XIII), Gossypetin (XIV), Quercetin (XV) and Rutin (XV. R = Rutinoside) are some of the γ-pyrone derivative found in nature.



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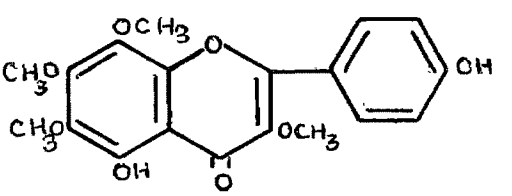

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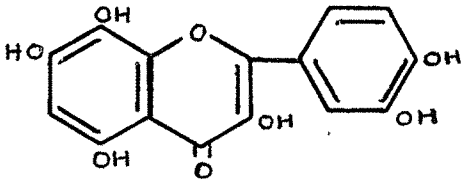
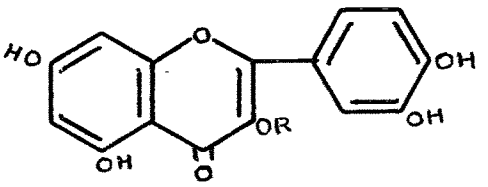


XIV

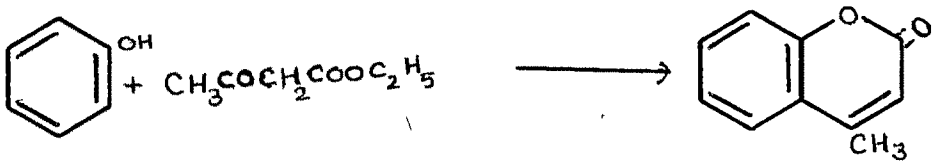


XV

As the present work deals with the building up of the α-and γ-pyrone rings on one of the aromatic rings of acenaphthene, some of the important methods of building up these rings are mentioned here.

Methods for the synthesis of benzo-α-pyrone derivatives :

One of the well known methods of coumarin synthesis is the Pechmann method[2], which consists in the condensation of phenols with β-ketonic esters in the presence of condensing agents like sulphuric acid, phosphorus pentoxide, aluminium chloride, etc.



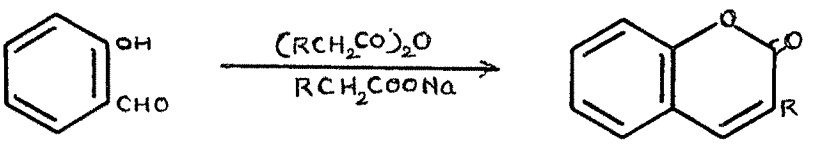
This reaction has been reviewed by Sethna and Phadke[3]. The use of sulphuric acid as the condensing agent always leads to the formation of α-pyrones. Those phenols which do not condense in the presence of sulphuric acid or form coumarins in low yield give γ-pyrones when phosphorus pentoxide is employed as the condensing agent.

Mentzer et al.[4] found that if a phenol was heated with β-ketonic ester at a high temperature without any condensing agent chromones are formed instead of coumarins. Later,

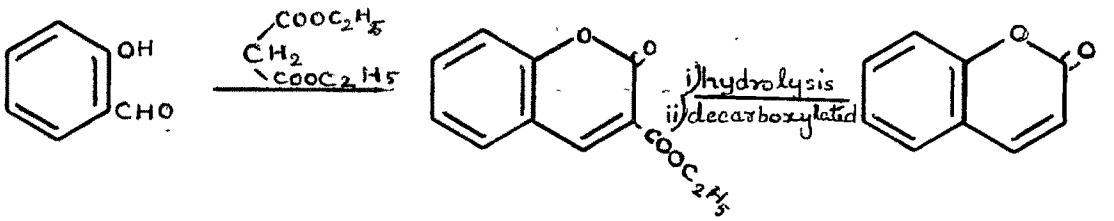
Desai, Trivedi and Sethna[5] observed that the reaction is more rapid and better products are obtained if diphenyl ether is used as a solvent and the reaction mixture refluxed with a short condenser to remove the water formed.

Besides these, other condensing agents such as anhydrous aluminium chloride, phosphorus oxychloride, hydrogen chloride, etc. are used as condensing agents.

Another method which is equally important is the Perkin acylation which consists in heating an ortho hydroxy aldehyde with an acid anhydride and its sodium salt[6].



A method developed by Knoevenagel[7] is the condensation of o-hydroxy aldehydes with diethyl malonate and the coumarin-3-carboxylate formed is then hydrolysed and decarboxylated.

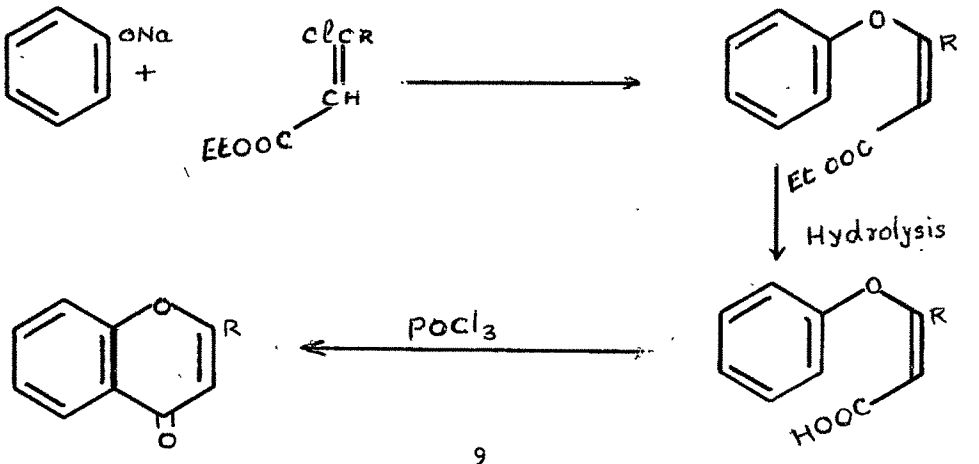


Besides these methods which have been used in the course of this work there are other methods available for the preparation of coumarins and these are enumerated in several reviews[33,34].

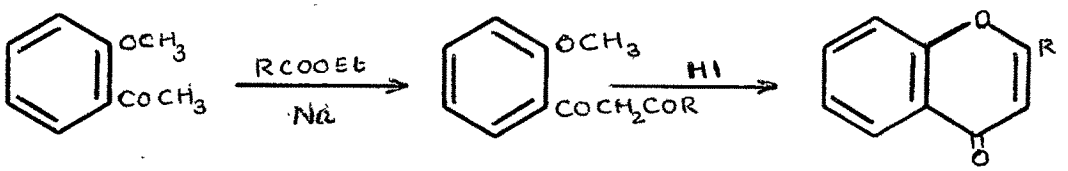
Methods for the synthesis of benzo-γ-pyrones derivatives :

Reuhemann and Stapleton[8] condensed sodium phenolate with ethylchlorofumarate. The intermediate acid obtained cyclised on treatment with condensing agents like sulphuric acid,

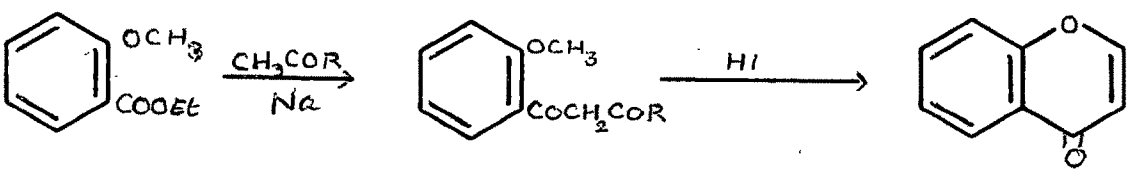
phosphorus oxychloride or aluminium chloride to give chromones.



Kostanecki and Tambor[9] developed a method which has been of great synthetical importance. He condensed esters of aromatic or aliphatic acids with o-methoxyacetophenones and the β-diketone obtained was cyclised by heating with hydriodic acid.

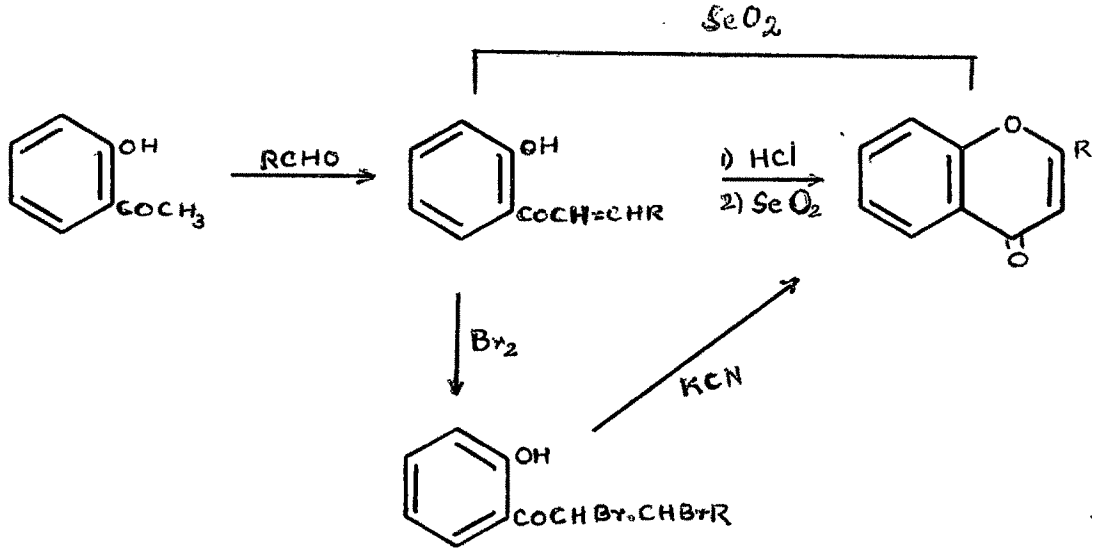


A variation of this method, developed by Kostanecki and Bloch[10] consists in condensation an o-methoxy ester with a ketone. The β-diketone formed is then converted into γ-pyrone by heating with hydriodic acid.

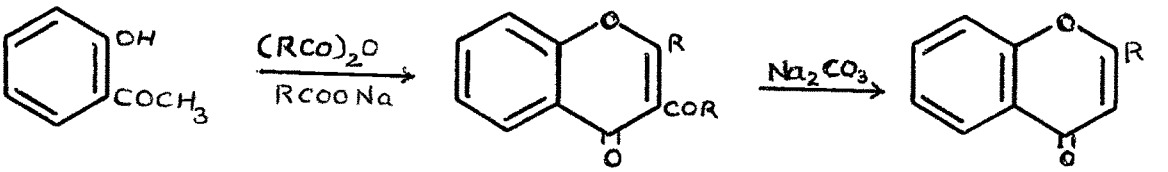


Though, the credit for the development of these methods for the synthesis of γ-pyrones goes to Kostanecki, the synthesis of β-diketones was first achieved by Claisen[11].

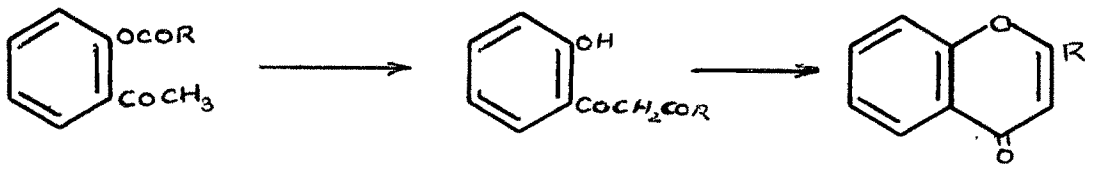
Another method also due to Kostanecki[12] consists in condensing o-hydroxy acetophenones with aldehydes. This gives rise to chalcones which can be cyclised either by boiling with alcoholic hydrochloric acid[13,14] and the flavanone obtained can then be dehydrogenated with selenium dioxide, or as has been found by Hutchins and Wheeler[15], it can be converted into chalcone dibromide which on treatment with alcoholic potassium cyanide can be converted into a flavone.



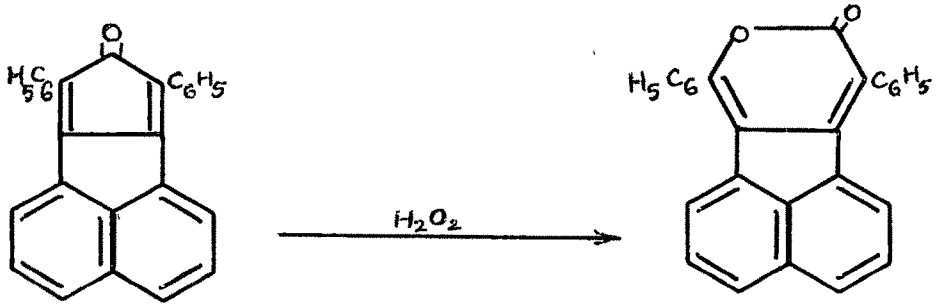
Kostanecki-Robinson acylation[16,17] affords an important route to γ-pyrones. In this method an o-hydroxyketone is refluxed with an acid anhydride and its sodium salt.



Baker[18] and Venkataraman[19] developed yet another method for the synthesis of γ-pyrones in which an ω-aryloxyacetophenone is rearranged in the presence of sodamide or potassium carbonate or according to a recent modification by Looker[20] with pyridine and potassium hydroxide. The β-diketone is then cyclised with a mineral acid.

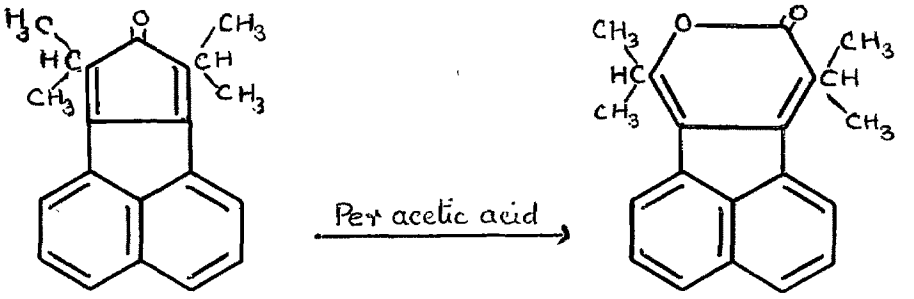


Though a large number of benzo- and naphtho- α- and γ-pyrone derivatives have been synthesised, practically no work has been done on building up of an α- or γ-pyrone ring on acenaphthene nucleus. Dilthey, Henkels and Leonhard[21] reported the preparation of an α-pyrone derivative of acenaphthene. These workers treated acecyclone (XVI) in acetic acid with hydrogen peroxide and obtained (XVII).



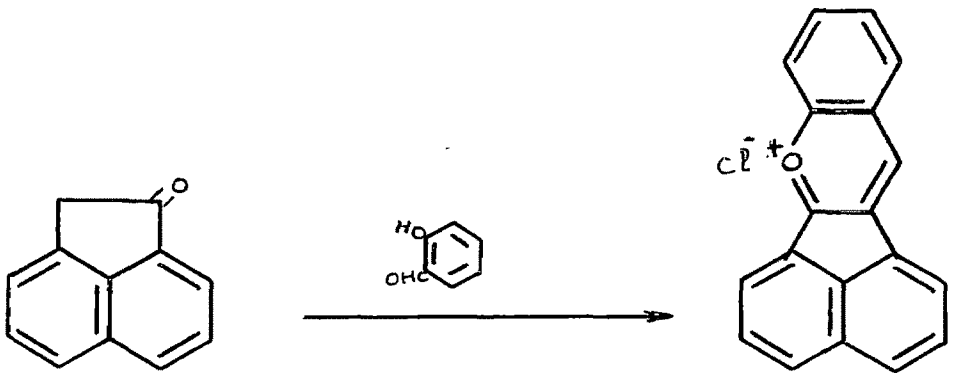
XVI XVII

Allen and VamAllen[22] similarly oxidised acenaphtho-(1,2:5',4'),2',5' -diisopropyl cyclopentan-1-one (XVIII) with peracetic acid and obtained acenaphtho (1,2:5',4'),3',6'-di-isopropyl-α-pyrone (XIX).



XVIII XIX

Sircar and Rajagopalan[23] synthesised various acenaphtho-benzopyrilium chlorides (XXI) by condensing acenaphthenone (XX) with aldehydes such as salicylaldehyde.



XX XXI

The present work deals with the synthesis of some acenaphtho α- and γ-pyrones. As no work appears to have been done on the building up of the α- and γ-pyrone rings on one of the aromatic rings of acenaphthene, it was thought of interest to

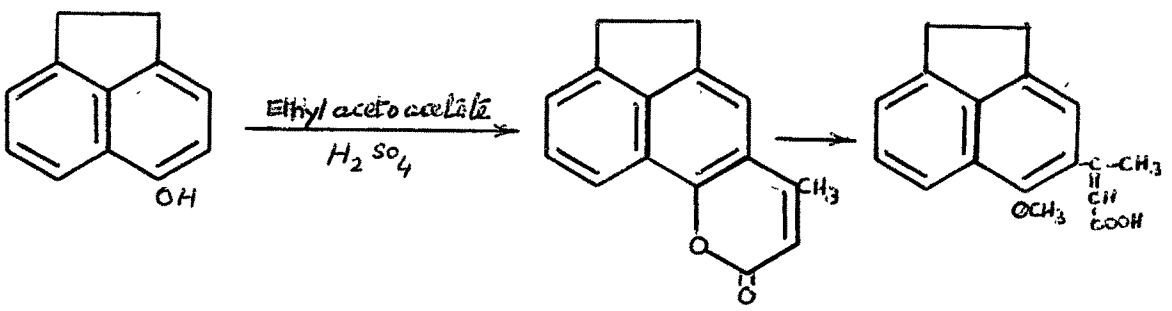
synthesise such oxygen heterocyclic compounds by some of the known methods described earlier.

Pechmann condensation of 5-hydroxyacenaphthene with ethyl acetoacetate. Synthesis of 4'-methylacenaphtho(5,4:6',5')α-pyrone :

5-Hydroxyacenaphthene on Pechmann condensation with ethyl acetoacetate in the presence of sulphuric acid (80 %) gave a product which was insoluble in dilute alkali and gave fluorescence with conc. sulphuric acid. It has been assigned the 4'-methylacenaphtho(5,4:6',5')α-pyrone structure(XXII) for the following reasons.

(a) On treatment with alkali and dimethyl sulphate on a steam bath, it gave an unsaturated acid (XXIII) as seen by decolourisation of bromine water and potassium permanganate. The formation of such an unsaturated acid is a diagnostic test for benzo-α-pyrone derivatives.[24]

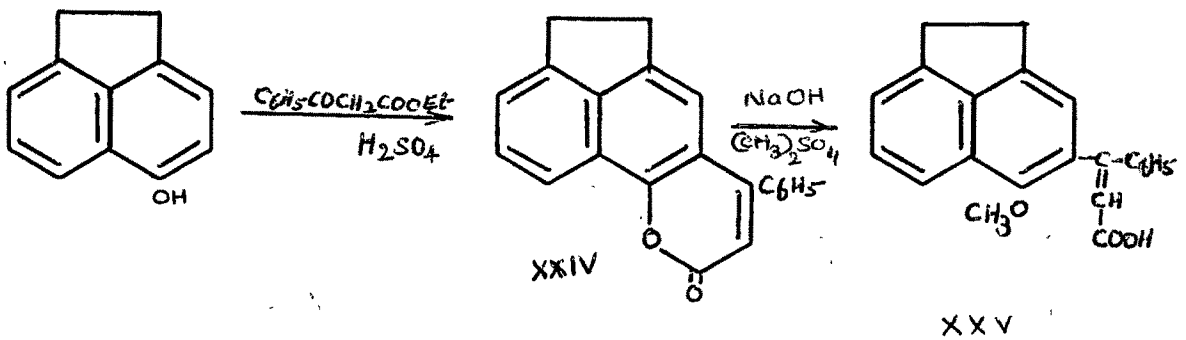
(b) As will be seen in the following section (p.85) the product can be brominated to a 3'-bromo derivative which on alkaline hydrolysis gave 3'-methylacenaphtho-(5,4:5',4') furan-2'-carboxylic acid which is a characteristic reaction of 3-bromo coumarins.



XXII XXIII

Pechmann condensation of 5-hydroxyacenaphthene with ethyl benzoylacetate : Synthesis of 4'-phenylacenaphtho (5,4:6',5')α-pyrone :

5-Hydroxyacenaphthene on condensation with ethyl benzoylacetate in the presence of 80 % sulphuric acid gave a product which was insoluble in dilute alkali. This compound also gave intense green fluorescence with conc. sulphuric acid. On heating with alkali and dimethyl sulphate, it gave an unsaturated acid (XXV) and therefore 4'-phenylacenaphtho-(5,4:6',5')α-pyrone structure (XXIV) has been assigned to it.



Synthesis of acenaphtho(5,4:6',5')α-pyrone :

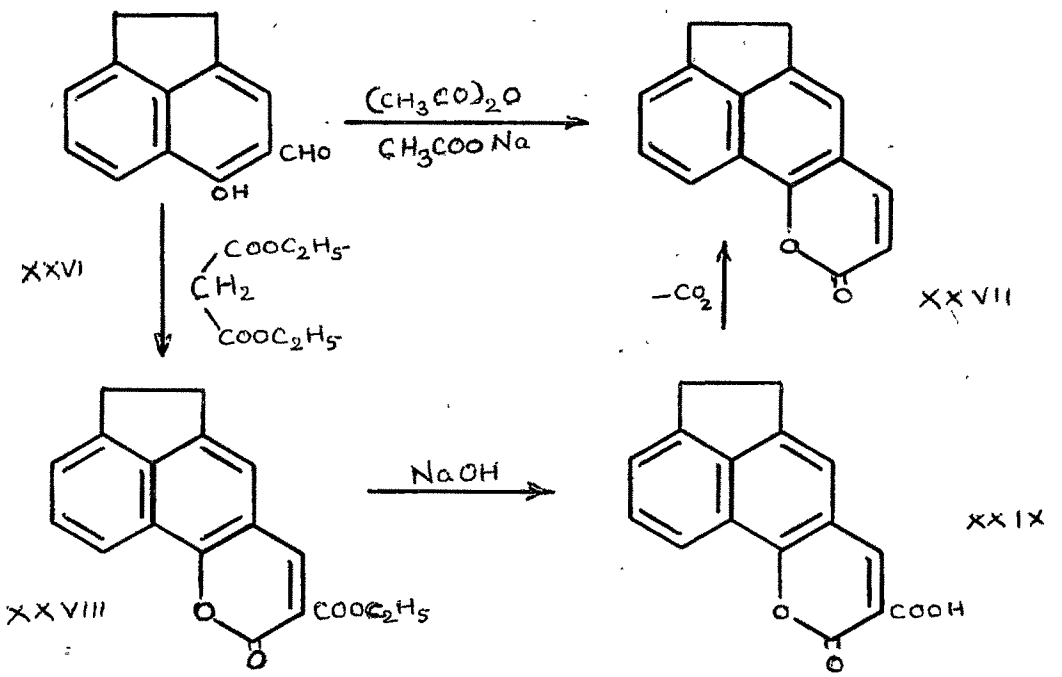
(a) Perkin acylation of 5-hydroxy-4-formylacenaphthene :

5-Hydroxy-4-formylacenaphthene required as an intermediate for the synthesis of the above compound, was prepared as follows :

5-Hydroxyacenaphthene was heated with hexamethylene tetramine in glacial acetic acid. On decomposing the complex product formed with hydrochloric acid, a hydroxy formyl derivative was obtained which gave a blue colour with alcoholic ferric chloride. This formyl derivative underwent

Perkin acylation and Knovenagel condensation (described below) to give α-pyrone derivatives. Since there is only one ortho position free to the hydroxy group, the 5-hydroxy-4-formyl-acenaphthene structure (XXVI) is assigned to it.

5-Hydroxy-4-formylacenaphthene on heating with acetic anhydride and sodium acetate gave a compound which was insoluble in alkali and which did not give the test for an aldehyde. It gave an intense green fluorescence with conc. sulphuric acid and therefore acenaphtho(5,4:6',5')α-pyrone structure (XXVII) is assigned to this compound.



(b) Knovenagel condensation of 5-hydroxy-4-formyl-acenaphthene with diethyl malonate :

5-Hydroxy-4-formylacenaphthene on Knovenagel condensation with diethyl malonate in the presence of pyridine gave a product which was found to be insoluble in dilute alkali in the cold. and did not give any colour with alcoholic ferric chloride. Ethyl acenaphtho(5,4:6',5')α-pyrone-3-carboxylate

structure (XXVIII) was assigned to this compound. It was hydrolysed to the corresponding acid (XXIX) which on decarboxylation by heating in quinoline with copper powder gave acenaphtho(5,4:6',5')α-pyrone (XXVII) described above.

Synthesis of acenaphtho-γ-pyrones :

Synthesis of 2'-methylacenaphtho(5,4:6',5')γ-pyrone :

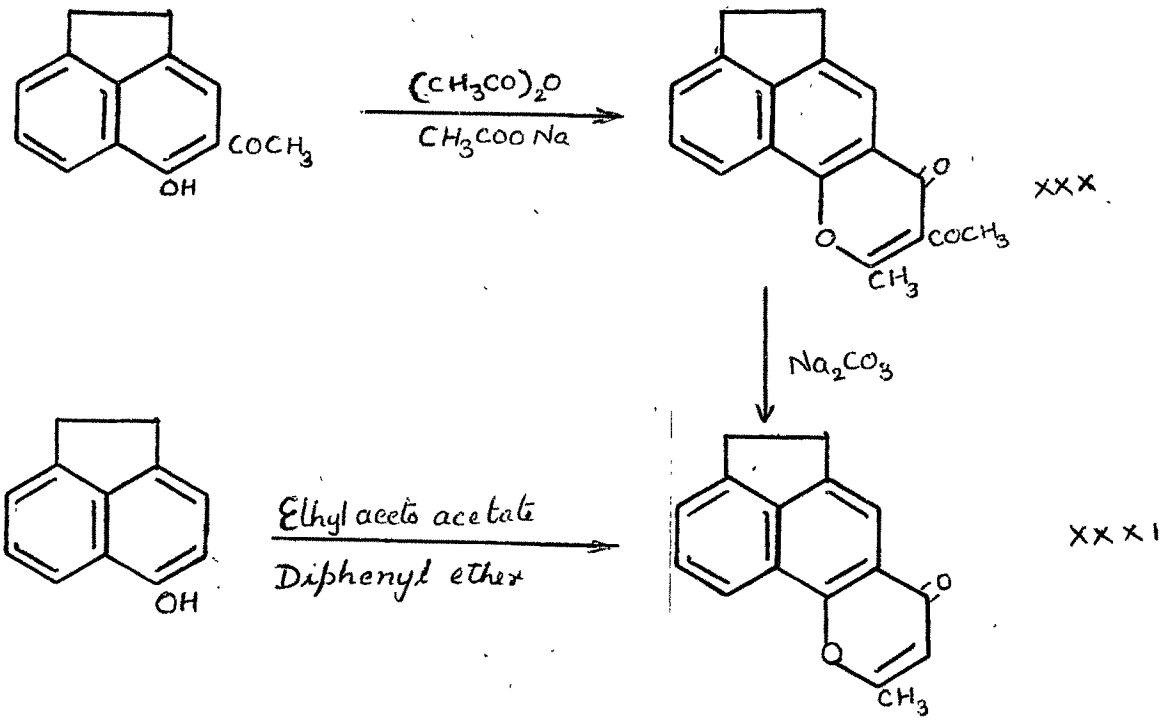
(a) Kostanecki-Robinson acetylation of 5-hydroxy-4-acetylacenaphthene :

5-Hydroxy-4-acetylacenaphthene was obtained by the Fries rearrangement of 5-acetoxyacenaphthene according to Richter and Feist[25]. On heating in an oil bath at 180° with acetic anhydride and fused sodium acetate it gave a product which was found to be insoluble in cold alkali. This analysed for the acetyl derivative of the desired γ-pyrone. This compound was further deacetylated by boiling in absolute alcohol with anhydrous sodium carbonate. The condensation product was assigned 2'-methyl-3'-acetylacenaphtho(5,4:6',5') γ-pyrone (XXX) and the deacetylated product 2'-methylacenaphtho (5,4:6',5')γ-pyrone structure (XXXI).

(b) Condensation of 5-hydroxyacenaphthene with ethyl acetoacetate in diphenyl ether :

5-Hydroxyacenaphthene on refluxing with ethyl aceto-acetate in diphenyl ether and on removing the diphenyl ether with steam, gave a product which was found to be insoluble in alkali. This was found to be different from the Pechmann condensation product with ethyl acetoacetate described before. Mixed melting point of this sample with 2'-methylacenaphtho (5,4:6',5')γ-pyrone obtained by the Kostanecki-Robinson

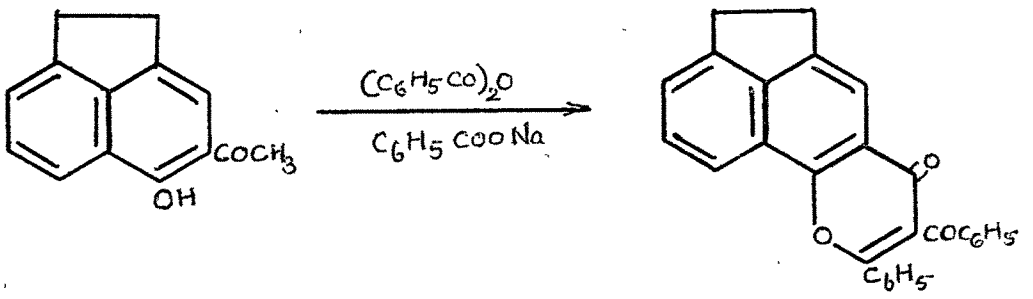
acetylation was not depressed.



Synthesis of 2¹-phenyl-3¹-benzoylacenaphtho(5,4:6',5')y-pyrone: Kostanecki-Robinson benzoylation of 5-hydroxy-4-acetyl-acenaphthene :

5-Hydroxy-4-acetylacenaphthene on heating with benzoic anhydride and sodium benzoate at 180° gave a compound which was found to be insoluble in sodium hydroxide. It analysed for 2¹-phenyl-3¹-benzoylacenaphtho(5,4:6',5')y-pyrone (XXXII). This compound however, resisted all attempts to hydrolyse the 3¹-benzoyl group. When refluxed in alcohol with anhydrous sodium carbonate the original 2¹-phenyl-3¹-benzoyl acenaphtho(5,4:6',5')-y-pyrone was recovered unchanged and on boiling with alcoholic sodium hydroxide 5-hydroxy-4-acetylacenaphthene was obtained. The formation of C-acyl derivatives in the Kostanecki-Robinson acylation is a normal feature[26] and it is sometimes difficult

to remove the 3-benzoyl group from the γ-pyrone derivative formed[27].



XXXII

Synthesis of 2'-phenylacenaphtho(5,4:6',5')γ-pyrone : Condensation of 5-hydroxy-4-acetylacenaphthene with benzaldehyde :

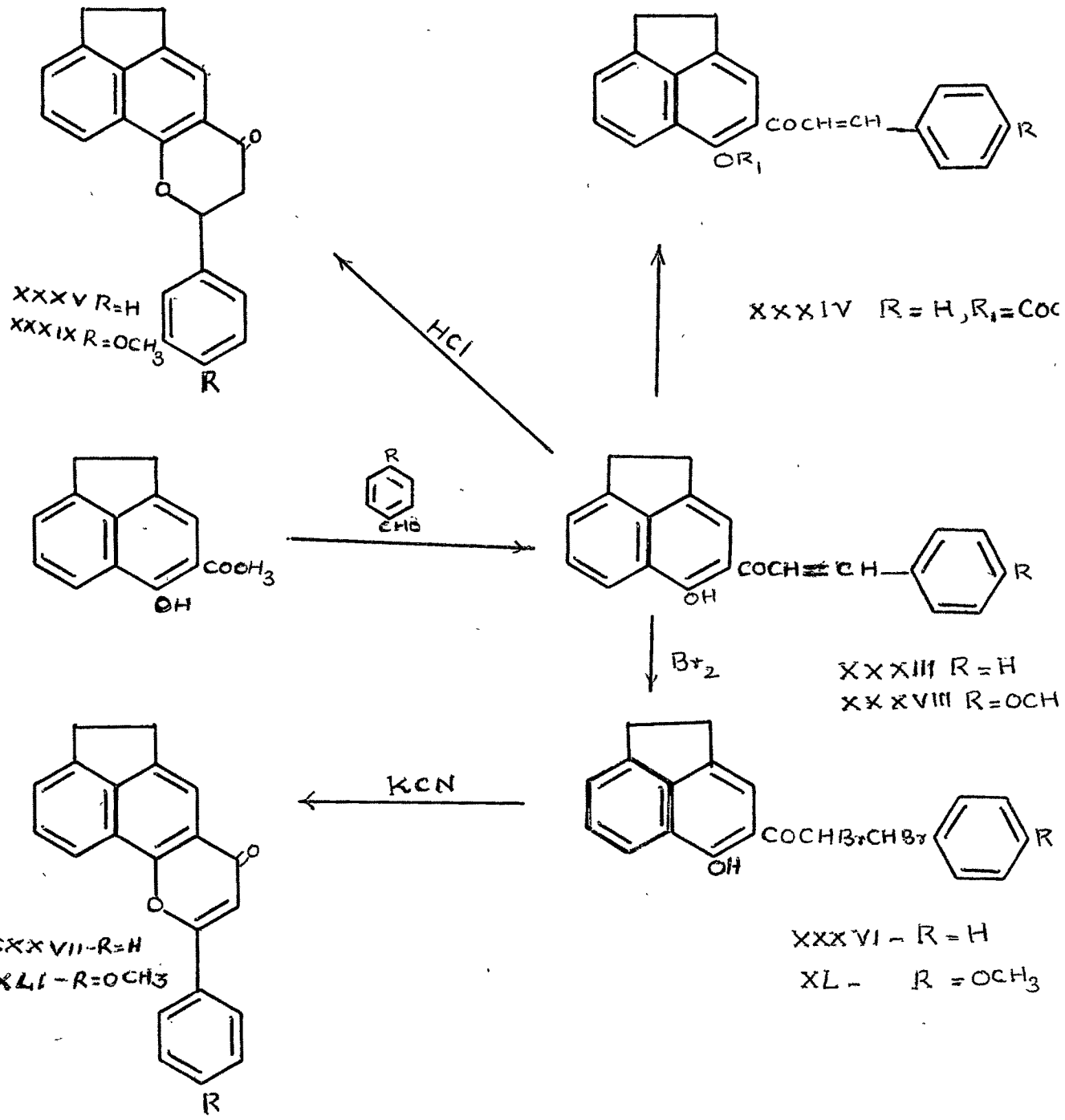
5-Hydroxy-4-acetylacenaphthene was condensed with benzaldehyde in the presence of alcoholic potassium hydroxide. The red product obtained gave tests for a chalcone such as red colouration with conc. sulphuric acid and yellow colouration with a mixture of citric acid and boric acid in dry acetone (Wilson test[28]), which is characteristic test for a chalcone derivatives. Moreover it gave an acetyl derivative (XXXIV) when refluxed with acetic anhydride and fused sodium acetate. On refluxing with alcoholic hydrochloric acid a product isomeric with the acenaphthyl styryl ketone was obtained to which 2'phenyl acenaphtho(5,4:6',5')-pyran-4'-one structure (XXXV) was assigned. 5-Hydroxy-4-acenaphthyl-

styryl ketone structure (XXXIII) was therefore assigned to the ketone. The acenaphthyl styryl ketone on refluxing with selenium dioxide in iso-amyl alcohol and subsequent removal of the solvent gave a pasty mass from which no pure product could be isolated. Acenaphthene itself has been shown to give various oxidation products with selenium dioxide[29]. In order to get the desired y-pyrone derivative, the acenaphthyl styryl ketone was therefore brominated with exactly one mole of bromine. The product obtained analysed for a dibromo compound . On boiling with alcoholic potassium cyanide, a compound free from bromine was obtained and therefore the structure 5-hydroxy-4-acenaphthyl-styryl ketone-α-β-dibromide (XXXVI) was assigned to the bromo compound and 2'-phenylacenaphtho(5,4:6',5')y-pyrone was assigned to the final compound (XXXVII).

Synthesis of 2'-(p-methoxyphenyl)acenaphtho(5,4:6',5') y-pyrone : Condensation of 5-hydroxy-4-acetylacenaphthene with anisaldehyde :

5-Hydroxy-4-acetylacenaphthene was condensed with anisaldehyde in the presence of alcoholic potassium hydroxide. The acenaphthyl styryl ketone structure (XXXVIII) of the product was established by the formation of a dimethoxy derivative and a positive Wilson test[28] and a deep red colouration produced with conc. sulphuric acid. On refluxing with alcoholic hydrochloric acid a yellow product isomeric with the acenaphthyl styryl ketone was obtained to which 2'(p-methoxyphenyl)acenaphtho(5,4:6',5')pyran-4'-one structure (XXXIX) was assigned. The ketone (XXXVIII) on refluxing with

selenium dioxide in iso-amyl alcohol did not give any pure product. It however gave a dibromide on treatment with one mole of bromine. This dibromide (XL) was cyclised to 2'(p-methoxy-phenyl)acenaphtho(5,4:6',5')γ-pyrone (XLI) on treatment with alcoholic potassium cyanide.

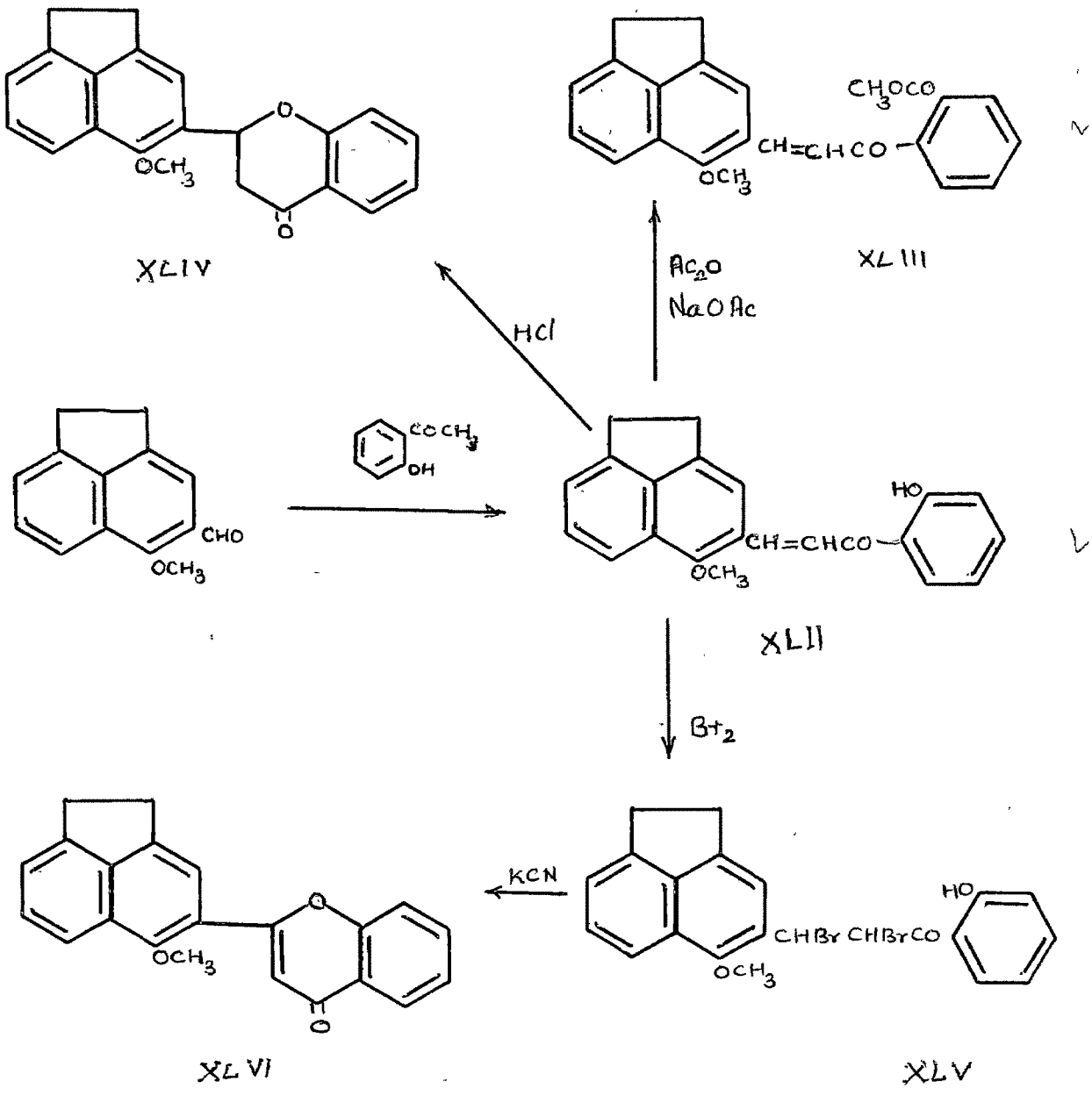


Synthesis of 2(5-methoxy-4-acenaphthyl)benzo-γ-pyrone :-

Condensation of 5-methoxy-4-formylacenaphthene with o-hydroxyacetophenone : β-(5-methoxy-4-acenaphthyl) vinyl-o-hydroxyphenyl ketone :

5-Methoxy-4-formylacenaphthene, described earlier, on condensation with o-hydroxyacetophenone in the presence of alcoholic potassium hydroxide gave a compound to which β-(5-methoxy-4-acenaphthyl)vinyl-o-hydroxyphenyl ketone structure (XLII) was assigned as it gave the Wilson test[28] and a red colour with conc. sulphuric acid. It also gave an acetyl derivative (XLIII). This compound on boiling with alcoholic hydrochlorid acid gave a light yellow product which on analysis was found to be isomeric with the ketone (XLII) and 2(5-methoxy-4-acenaphthyl)benzo-γ-pyran-4-one structure (XLIV) was assigned to this compound. Boiling the ketone (XLII) with selenium dioxide in iso-amyl alcohol did not give any pure product. Therefore the ketone (XLII) was brominated with one mole of bromine and the dibromide (XLV) obtained was cyclised with alcoholic potassium cyanide. The structure 2(5-methoxy-4-acenaphthyl)benzo-γ-pyrone (XLVI) was assigned to this compound.

This is the first example of a benzo-γ-pyrone derivative with an acenaphthyl substituent in the 2-position.



Attempted Pechmann condensation of 3-hydroxyacenaphthene with ethyl acetoacetate :

3-Hydroxyacenaphthene prepared according to Morgan and Harrison[30] on condensation with ethyl acetoacetate in the presence of sulphuric acid did not undergo any reaction and

the unreacted 3-hydroxyacenaphthene was recovered. The condensation could not be affected with other condensing agents like zinc chloride, aluminium chloride or phosphorus pentoxide.

Fries rearrangement of 3-acetoxyacenaphthene :

3-Acetoxyacenaphthene prepared by the acetylation of 3-hydroxyacenaphthene when subjected to Fries rearrangement in carbon disulphide in the presence of aluminium chloride gave a product which was soluble in sodium hydroxide and also gave the test for a ketone, but it did not give any colour with alcoholic ferric chloride. Therefore it was not the required 3-hydroxy-4-acetylacenaphthene. Its structure has so far not been elucidated and further work is in progress.

Attempted formylation of 3-hydroxyacenaphthene :

3-Hydroxyacenaphthene on boiling with hexamethylene tetramine in glacial acetic acid and decomposing the mixture with hydrochloric acid did not give any aldehyde. The unreacted 3-hydroxyacenaphthene was recovered unchanged.

EXPERIMENTAL

5-Hydroxyacenaphthene :

Acenaphthene was nitrated in glacial acetic acid according to Okazaki et al.[31] Of the various reagents employed for the reduction of the nitro compound, it was found that sodium dithionite in alcohol was the best[31]. 5-Aminoacenaphthene thus obtained was converted into 5-hydroxyacenaphthene in 70 % yield by heating with 10 % sulphuric acid (w/v) at 190-200° for 8 hrs. in an autoclave[31], m.p.125°. Rapoport et al.[32] gave m.p. 125-26°.

Pechmann condensation of 5-hydroxyacenaphthene with ethyl acetoacetate : 4'-methylacenaphtho(5,4:6',5') α-pyrone :

5-Hydroxyacenaphthene (1 g.) and ethyl acetoacetate (1 ml) were mixed together and sulphuric acid (80 % ; 20 ml.) was added with cooling and shaking. The reaction mixture was kept overnight at room temperature and was then poured on ice. The solid obtained was filtered and washed with cold dilute sodium hydroxide and then with water. It crystallised from benzene in colourless needles (0.5 g.), m.p. 218°.

Analysis : Found : C, 80.87 ; H, 5.11 %.

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

β-Methyl-β(5-methoxy-4-acenaphthyl)acrylic acid :

The above α-pyrone (1 g.) was dissolved in a hot mixture of acetone (100 ml.) and sodium hydroxide (10 %; 20 ml.) and to this solution dimethyl sulphate (2 ml) was added drop by drop with shaking. More sodium hydroxide and dimethyl sulphate were added with shaking and finally the

mixture was heated on a steam bath for 30 minutes after making the solution distinctly alkaline. The separated solid on acidification was filtered and purified by extraction with sodium bicarbonate solution. The acid on crystallisation from benzene-petroleum ether mixture gave m.p. 177°. Yield 0.4 g.

Analysis	: Found	: C, 75.99 ; H, 5.67 %.
$C_{17}H_{16}O_3$	: requires	: C, 76.12 ; H, 5.97 %.

Condensation of 5-hydroxyacenaphthene with ethyl benzoyl-acetate : 4'-Phenylacenaphtho(5,4:6',5')α-pyrone :

5-Hydroxyacenaphthene (1 g.) and ethyl benzoyl acetate (1 ml.) were mixed well and sulphuric acid (80 % ; 30 ml.) was added with external cooling. The mixture was kept at room temperature for 48 hrs. and then added to ice. The solid obtained was crystallised from acetic acid, M.p.208°. Yield 0.3 g.

Analysis	: Found	: C, 84.13 ; H, 4.60 %.
$C_{21}H_{14}O_2$	: requires	: C, 84.57 ; H, 4.69 %.

β-Phenyl-β(5-methoxy-4-acenaphthyl)acrylic acid :

The above α-pyrone (1 g.) was dissolved in a mixture of acetone (40 ml.) and sodium hydroxide (20 ml.; 5 %) with heating. Dimethyl sulphate (2 ml.) was added slowly and the mixture was shaken vigorously. More alkali and dimethyl sulphate were added and the mixture was heated on a steam bath for half an hour after making the solution distinctly alkaline. Dilute hydrochloric acid was added and the acid separated was further purified by extraction with sodium bicarbonate solution and finally crystallised from benzene-

petroleum ether mixture in pale yellow crystals (0.4 g.), m.p. 137°.

Analysis : Found : C, 80.22 ; H, 5.87 %.

$C_{22}H_{18}O_3$: requires : C, 80.00 ; H, 5.45 %.

5-Hydroxy-4-formylacenaphthene :

5-Hydroxyacenaphthene (1.7 g.) was dissolved in glacial acetic acid (50 ml.) and hexamethylene tetramine (5 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 another half an hour. On cooling, yellow needles separated. These were recrystallised from dilute alcohol in light yellow needles (1.7 g.), m.p. 95°.

Analysis : Found : C, 78.87 ; H, 5.17 %.

$C_{13}H_{10}O_2$: requires : C, 78.77 ; H, 5.05 %.

The compound gave blue colour with alcoholic ferric chloride when dissolved in alcohol and an intense red colouration with conc. sulphuric acid.

The 2,4-dinitro phenylhydrazone :

This was prepared by mixing a solution of the aldehyde in glacial acetic acid and a solution of 2,4-dinitrophenyl-hydrazine in glacial acetic acid and adding a drop of conc. hydrochloric acid. A red product separated out immediately. It was crystallised from nitrobenzene, m.p. 284° (decomp.)

Analysis : Found : N, 14.81 %.

$C_{19}H_{14}O_5N_4$: requires : N, 14.54 %.

5-Methoxy-4-formylacenaphthene :

5-Hydroxy-4-formylacenaphthene (2 g.) was dissolved in

dry acetone (20 ml.) and anhydrous potassium carbonate (5 g.) was added. Dimethyl sulphate (2 ml.) was added with shaking. The mixture was heated on a water bath under reflux for 5 hrs. The acetone was evaporated and the reaction mixture was added to water. The separated solid crystallised from dilute alcohol in light yellow needles (1.8 g.), m.p. 99°.

Analysis : Found : C, 78.76 ; H, 5.54 %.

$C_{14}H_{12}O_2$: requires : C, 79.25 ; H, 5.66 %.

Perkin acetylation of 5-hydroxy-4-formylacenaphthene : Acenaphtho(5,4:6',5')α-pyrone :

5-Hydroxy-4-formylacenaphthene (1 g.) was mixed with acetic anhydride (5 ml.) and fused sodium acetate (1.5 g.) and the mixture was refluxed in an oil bath at 170-80° for 15 hrs. It was then poured on ice and kept overnight. The solid that separated was filtered and crystallised from dilute alcohol in yellow needles (0.4 g.), m.p. 166-67°.

Analysis : Found : C, 80.74 ; H, 4.27 %.

$C_{15}H_{10}O_2$: requires : C, 81.08 ; H, 4.50 %.

Condensation of 5-hydroxy-4-formylacenaphthene with diethylmalonate : Ethyl acenaphtho(5,4:6',5')α-pyrone-3'-carboxylate :

A mixture of 5-hydroxy-4-formylacenaphthene (1 g.), diethylmalonate (1 ml.) and a few drops of piperidine was kept at room temperature for 24 hrs. The reaction mixture was then treated with ice and hydrochloric acid and the solid which separated was filtered and crystallised from

benzene in golden yellow needles (0.6 g.),m.p. 205°.

Analysis : Found : C, 73.44 ; H, 4.49 %.

$C_{18}H_{14}O_4$: requires : C, 73.48 ; H, 4.76 %.

Acenaphtho(5,4:6',5')α-pyrone-3'-carboxylic acid :

The above ester (0.8 g.) was heated with sodium hydroxide solution (25 ml.; 5 %) over a steam bath for 3 hrs. It was cooled and acidified with hydrochloric acid with cooling. The product was further purified by sodium bicarbonate treatment. The acid was crystallised from benzene in greenish yellow needles (0.5 g.), m.p. 236° (effer.)

This acid was observed to give green fluorescence when dissolved in benzene or alcohol and a deep red colour with conc. sulphuric acid.

Analysis : Found : C, 72.14 ; H, 3.70 %.

$C_{16}H_{10}O_4$: requires : C, 72.18 ; H, 3.75 %.

Acenaphtho(5,4:6',5')α-pyrone :

The above acid (0.5 g.) was dissolved in quinoline (5 ml.) and a pinch of copper powder was added. The mixture was refluxed on a sand bath for one hour and then poured in 1:1 hydrochloric acid. The product that sepa rated one keeping the reaction mixture overnight crystallised from dilute alcohol in yellow needles (0.3 g.), m.p. 166-67°.

The mixed m.p. of the compound with acenaphtho(5,4:6',5') α-pyrone obtained through the Perkin acetylation was not depressed.

Kostanecki-Robinson acetylation of 5-hydroxy-4-acetyl-acenaphthene : 2'-Methyl-3'-acetylacenaphtho(5,4:6',5') γ-pyrone :

5-Hydroxy-4-acetylacenaphthene (1.5 g.) was thoroughly mixed with freshly fused sodium acetate (3 g.) and acetic anhydride (6 ml.) and the mixture was heated in an oil bath at 180-90° for 15 hrs. The reaction mixture was then cooled and poured on ice and kept overnight. The solid which separated was filtered and crystallised from alcohol in shining flakes (0.4 g.), m.p. 212°.

Analysis : Found : C, 78.09 ; H, 4.98 %.
$C_{18}H_{14}O_3$: requires : C, 77.71 ; H, 5.03 %.

2'-Methylacenaphtho(5,4:6',5')γ-pyrone :

The above γ-pyrone (0.5 g.) was dissolved in alcohol (25 ml.) and anhydrous sodium carbonate (3 g.) was added. The mixture was heated on a steam bath under reflux for 3 hrs. The solvent was removed by distillation and the mixture was diluted with water. The product obtained crystallised from alcohol in light yellow needles (0.15 g.), m.p. 225-26°.

Analysis : Found : C, 81.01 ; H, 5.24 %.
$C_{16}H_{12}O_2$: requires : C, 81.36 ; H, 5.08 %.

Condensation of 5-hydroxyacenaphthene with ethyl acetoacetate in diphenyl ether : 2'-Methylacenaphtho (5,4:6',5')γ-pyrone :

5-Hydroxyacenaphthene (1 g.) was mixed with ethyl acetoacetate (1 ml.) and diphenyl ether (10 ml.). The mixture was taken in a test tube and boiled for 2 hrs. over a small flame with a short air condenser, so that the water formed was removed. The solvent was then removed by steam

distillation. The solid obtained on cooling crystallised from alcohol in light yellow needles (0.7 g.), m.p. 225-26°.

The mixed m.p. of the above compound with 2'-methyl-acenaphtho(5,4:6',5')γ-pyrone, prepared through Kostanecki-Robinson acetylation as described above, was not depressed.

Kostanecki-Robinson benzoylation of 5-hydroxy-4-acetylacenaphthene : Synthesis of 2'-phenyl-3'-benzoyl-acenaphtho(5,4:6',5')γ-pyrone :

5-Hydroxy-4-acetylacenaphthene (2 g.) was mixed with sodium benzoate (3 g.) and benzoic anhydride (6 g.) and heated on an oil bath at 180-90° for 15 hrs. The mixture was then poured on ice and kept overnight. The pasty mass obtained was repeatedly boiled with water to remove the sodium benzoate and unreated benzoic anhydride. The solid obtained was crystallised from acetic acid in yellow flakes (0.8 g.), m.p. 261°.

Analysis : Found : C, 83.65 ; H, 4.63 %.

$C_{28}H_{18}O_3$: requires : C, 83.50 ; H, 4.47 %.

Attempted hydrolysis of 2'-phenyl-3'-benzoylacenaphtho(5,4:6',5')γ-pyrone :

The above γ-pyrone (0.8 g.) was dissolved in alcohol and anhydrous sodium carbonate (3 g.) was added and the mixture was refluxed on a steam bath for 6 hrs. The solvent was removed and the mixture was diluted with water. The solid obtained was crystallised from acetic acid. Mixed m.p. of the product with 2'-phenyl-3'-benzoylacenaphtho(5,4:6',5') γ-pyrone was not depressed.

2'-Phenyl-3'-benzoylacenaphtho(5,4:6',5')γ-pyrone (0.5 g.) was refluxed with alcohol (40 ml.) and sodium hydroxide solution (20 ml. ; 5 %) on a steam bath for 4 hrs. The solvent was removed and the mixture was added to water. The solution was made acidic with dilute hydrochloric acid. The product crystallised from alcohol and was found to be 5-hydroxy-4-acetylacenaphthene.

Condensation of 5-hydroxy-4-acetylacenaphthene with benzaldehyde : 5-Hydroxy-4-acenaphthyl styryl ketone :

5-Hydroxy-4-acetylacenaphthene (2 g.) was dissolved in alcohol (40 ml.) and benzaldehyde (3 ml.) and potassium hydroxide (10 g. in 10 ml. water) were added. The mixture was kept at room temperature for 48 hrs. It was then diluted and acidified with dilute hydrochloric acid with cooling. The solid obtained was filtered and crystallised from petroleum ether in red prisms (1.1 g.), m.p. 181°.

Analysis : Found : C, 83.88 ; H, 5.41 %.

$C_{21}H_{16}O_2$: requires : C, 84.01 ; H, 5.33 %.

This compound gave deep red colouration with conc. sulphuric acid and a positive Wilson test[28]. With alcoholic ferric chloride it gave a blue colour.

5-Acetoxy-4-acenaphthyl styryl ketone :

The above ketone (0.8 g.) was mixed with freshly fused sodium acetate (1.5 g.) and acetic anhydride (2 ml.) and refluxed on a sand bath for an hour. It was then poured on ice and left overnight. The solid obtained crystallised

from petroleum ether in yellow crystals (0.6 g.), m.p.108°.

Analysis : Found : C, 80.96 ; H, 5.08 %.

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

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

5-Hydroxy-4-acenaphthyl-styryl ketone (1 g.) was dissolved in alcohol (75 ml.) and hydrochloric acid (5 ml.) was added. The mixture was refluxed on a steam bath for 48 hrs. The solvent was removed and the mixture was diluted with water. The solid obtained was filtered and crystallised from alcohol in yellow needles (0.6 g.), m.p. 154°.

Analysis : Found : C, 84.12 ; H, 5.17 %.

$C_{21}H_{16}O_2$: requires : C, 84.01 ; H, 5.33 %.

This compound did not answer Wilson test and gave no colour with alcoholic ferric chloride.

5-Hydroxy-4-acenaphthyl-styryl ketone dibromide :

5-Hydroxy-4-acenaphthyl-styryl ketone (1 g.) was dissolved in chloroform (15 ml.) and bromine (0.5 g.) dissolved in chloroform (5 ml.) was added at 10-15° drop by drop with constant stirring. After the addition, the solution was kept at 10-15° for 2 hrs. The solvent was allowed to evaporate and the residue was crystallised from benzene-petroleum ether in yellow needles (0.8 g.), m.p. 112°.

Analysis : Found : Br, 34.91 %.

$C_{21}H_{16}O_2Br_2$: requires : Br, 34.77 %.

2-Phenylacenaphtho(5,4:6',5')γ-pyrone :

The above ketone dibromide (1 g.) was dissolved in alcohol (75 ml.) and potassium cyanide (1.5 g.) was added.

The mixture was heated under reflux over a steam bath for 1 hour. The solvent was removed and the mixture was diluted with water. The solid obtained was crystallised from benzene in yellow crystals (0.4 g.), m.p. 256°.

Analysis	: Found	: C, 84.22	; H, 4.69 %.
$C_{21}H_{14}O_2$	: requires	: C, 84.57	; H, 4.70 %.

Condensation of 5-hydroxy-4-acetylacenaphthene with anisaldehyde : 5-Hydroxy-4-acenaphthyl(p-methoxy styryl) ketone :

A mixture of 5-hydroxy-4-acetylacenaphthene (1 g.), anisaldehyde (1 ml.) and potassium hydroxide (5 g.in 5 ml. water) in alcohol (50 ml) was kept at room temperature for 48 hrs. The solution turned dark red in colour. Some ice cold water was added and the solution was acidified with hydrochloric acid. The separated solid was filtered and washed several times with sodium bicarbonate. The residue was crystallised from benzene in red prisms (0.4 g.), m.p.157°.

Analysis	: Found	: C, 80.13	; H, 5.42 %
$C_{22}H_{18}O_3$	: requires	: C, 80.00	; H, 5.45 %.

It gave a positive Wilson test and a deep red colour with conc. sulphuric acid. With alcoholic ferric chloride it gave a blue colour.

5-Methoxy-4-acenaphthyl(p-methoxy styryl)ketone :

The above ketone (0.5 g.) was refluxed with anhydrous potassium carbonate (1.5 g.) and dimethyl sulphate (0.8 ml.) in acetone (30 ml.) on a steam bath for 3 hrs. The solvent was removed and the reaction mixture was diluted with water.

The product crystallised from alcohol in yellow needles (0.3 g.), m.p. 142°.

Analysis : Found : C, 80.68 ; H, 6.12 %.

$C_{23}H_{20}O_3$: requires : C, 80.23 ; H, 5.81 %.

2'(p-Methoxy phenyl)acenaphtho(5,4:6',5')γ-pyran-4'-one :

5-Hydroxy-4-acenaphthyl(p-methoxy styryl)ketone (1 g.) was refluxed in alcohol (75 ml.) containing hydrochloric acid (5 ml.) for 36 hrs. on a steam bath. The solvent was removed by distillation and the mixture was diluted with water. The product that separated crystallised from petroleum ether in yellow needles (0.3 g.), m.p. 152°.

Analysis : Found : C, 79.64 ; H, 5.29 %.

$C_{22}H_{18}O_3$: requires : C, 80.00 ; H, 5.45 %.

Mixed m.p. of the compound with the ketone was depressed by 18°. This compound did not give the Wilson test.

5-Hydroxy-4-acenaphthyl(p-methoxy styryl)ketone dibromide:

5-Hydroxy-4-acenaphthyl(p-methoxy styryl)ketone (1.1 g.) was dissolved in chloroform (15 ml.) and bromine (0.5 g.) in chloroform (5 ml.) was added dropwise at 10-15° with stirring. The mixture was kept at 10-15° for 2 hrs. The product obtained on removal of the solvent was crystallised from petroleum ether in yellow needles (0.9 g.), m.p. 155°.

Analysis : Found : Br, 32.60 %.

$C_{22}H_{18}O_3Br_2$: requires : Br, 32.65 %.

2'(p-Methoxy phenyl)acenaphtho(5,4:6',5')γ-pyrone :

The above dibromide (1 g.) and potassium cyanide (2 g.) in alcohol (50 ml.) were refluxed for 1 hour on a steam

bath. The solvent was distilled off and the mixture was diluted with water. The solid obtained crystallised from benzene in yellow prisms (0.7 g.), m.p. 242°.

Analysis	: Found	: C, 80.50 ; H, 4.98 %.
$C_{22}H_{16}O_3$	: requires	: C, 80.48 ; H, 4.87 %.

Synthesis of 2'(5-methoxy-4-acenaphthyl)benzo-γ-pyrone : Condensation of 5-methoxy-4-formylacenaphthene with o-hydroxyacetophenone : β-(5-methoxyacenaphthyl)vinyl-o-hydroxyphenyl ketone :

A mixture of 5-methoxy-4-formylacenaphthene (1 g.), o-hydroxyacetophenone (0.6 ml.) and potassium hydroxide (5 g. in 5 ml. water) in alcohol (50 ml.) was kept at room temperature for two days. The solution became deep red in colour. It was then diluted and acidified with conc. hydrochloric acid with proper cooling. The solid obtained was filtered and crystallised from benzene in yellow needles (1.1 g.), m.p. 164°.

Analysis	: Found	: C, 80.50 ; H, 5.70 %.
$C_{22}H_{18}O_3$	: requires	: C, 80.00 ; H, 5.45 %.

The compound gave a positive Wilson test and a deep red colouration with conc. sulphuric acid. With alcoholic ferric chloride it gave a brown colour.

β(5-Methoxy-4-acenaphthyl)vinyl-o-acetoxy phenyl ketone :

The above ketone (0.5 g.) was dissolved in acetic anhydride (3 ml.) and freshly fused sodium acetate (1 g.) was added. The mixture was refluxed on a sand bath for 1.5 hrs. It was then poured on ice and the solid obtained was

crystallised from petroleum ether in light yellow needles (0.4 g.), m.p. 98°.

Analysis	: Found	: C, 77.66 ; H, 5.66 %.
$C_{24}H_{20}O_4$	: requires	: C, 77.41 ; H, 5.37 %.

2'(5-Methoxy-4-acenaphthyl)benzo--pyran-4'-one :

β(5-Methoxy-4-acenaphthyl)vinyl p-hydroxyphenyl ketone (1 g.) was dissolved in alcohol (75 ml.) and concentrated hydrochloric acid (5 ml.) was added. The mixture was refluxed on a steam bath for 48 hrs. The solvent was removed by distillation and the mixture was diluted with water. The solid obtained was crystallised from alcohol in light yellow needles (0.6 g.), m.p. 148°.

Analysis	: Found	: C, 80.22 ; H, 5.17 %.
$C_{22}H_{18}O_3$	: requires	: C, 80.00 ; H, 5.45 %.

This compound did not give the Wilson test and gave no colour with alcoholic ferric chloride.

β(5-Methoxy-4-acenaphthyl)α-β-dibromo ethyl o-hydroxyphenyl ketone :

β(5-Methoxy-4-acenaphthyl)vinyl o-hydroxyphenyl ketone (1.1 g.) was dissolved in chloroform (15 ml.) and bromine (0.5 g.) in chloroform (5 ml.) was added dropwise at 10-15° with stirring. After completing the addition the mixture was stirred for 2 hrs. The solvent was allowed to evaporate and the residue was crystallised from benzene-petroleum ether in light yellow needles (0.9 g.), m.p. 153°.

Analysis	: Found	: Br, 32.60 %.
$C_{22}H_{18}O_3Br_2$	: requires	: Br, 32.65 %.

2'(5-Methoxy-4-acenaphthyl)benzo-γ-pyrone :

The above dibromide (1.5 g.) was dissolved in alcohol (100 ml.) and potassium cyanide (3 g.) was added. The mixture was heated on a steam bath for 1 hour. The solvent was removed and the residue was diluted with water. The solid obtained was crystallised from alcohol in light yellow needles, (0.9 g.), m.p. 152°.

Analysis	: Found	: C, 80.28 ; H, 4.98 %.
$C_{22}H_{16}O_3$	: Requires	: C, 80.48 ; H, 4.87 %.

Preparation of 3-hydroxyacenaphthene :

Acenaphthene was nitrated in large excess of acetic anhydride using diacetyl ortho nitric acid according to Morgan and Harrison[30] and 3-nitroacenaphthene was obtained. This was reduced to 3-amino derivative by aluminium amalgam and converted to 3-hydroxyacenaphthene by diazotisation and boiling with sulphuric acid, m.p. 151°. Morgan and Harrison[30] gave the m.p. 151°.

3-Acetoxyacenaphthene :

3-Hydroxyacenaphthene (1.5 g.) was dissolved in sodium hydroxide (25 ml.; 10 %) and a few pieces of ice were added. Acetic anhydride (2 ml.) was added slowly with vigorous stirring. The separated solid was filtered, washed with dilute sodium hydroxide and crystallised from dilute alcohol (1.3 g.), m.p. 57°.

Analysis	: Found	: C, 79.51 ; H, 5.63 %.
$C_{14}H_{12}O_2$	: requires	: C, 79.25 ; H, 5.66 %.

3-Hydroxy-?-acetylacenaphthene :

The above 3-acetoxyacenaphthene (1 g.) was dissolved in dry carbon disulphide (25 ml.) and anhydrous aluminium chloride (2 g.) was added with cooling. The mixture was heated on a water bath under reflux for 6 hrs. The clear solvent was decanted out and the pasty mass was decomposed by adding ice and hydrochloric acid. The yellow solid was filtered and crystallised from alcohol in yellow flakes (0.6 g.), m.p. 185°. It did not give any colour with alcoholic ferric chloride.

Analysis : Found : C, 79.38 ; H, 5.65 %.

$C_{14}H_{12}O_2$: requires : C, 79.25 ; H, 5.66 %.

2,4-Dinitrophenylhydrazone :

The above ketone was dissolved in acetic acid and a solution of 2,4-dinitrophenylhydrazine in acetic acid was added. The separated solid was filtered and crystallised from nitrobenzene, m.p. 267° (decomp.).

Analysis : Found : N, 13.86 %.

$C_{20}H_{16}O_5N_4$: requires : N, 14.29 %.

3-Methoxy-?-acetylacenaphthene :

3-Hydroxy-?-acetylacenaphthene (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 4 hrs. The solvent was then removed and water was added. The solid was crystallised from alcohol in colourless needles (0.3 g.), m.p. 114°.

Analysis : Found : C, 79.45 ; H, 5.99 %.

$C_{15}H_{14}O_2$: requires : C, 79.66 ; H, 6.19 %.

Attempted formylation of 3-hydroxyacenaphthene :

3-Hydroxyacenaphthene (1 g.) was dissolved in glacial acetic acid (20 ml.) and hexamethylene tetramine (3 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 more. The solution was diluted and the solid was crystallised from dilute alcohol. Mixed m.p. with 3-hydroxyacenaphthene was not depressed.

Attempted Pechmann condensation of 3-hydroxyacenaphthene with ethyl acetoacetate :

To a mixture of 3-hydroxyacenaphthene (1g.) and ethyl acetoacetate (1.5 ml.), sulphuric acid (80 % ; 20 ml.) was added with cooling and the mixture was kept for 24 hrs. at room temperature. It was then poured on ice and the separated solid was crystallised from dilute alcohol. The product was soluble in sodium hydroxide and the mixed m.p. with 3-hydroxyacenaphthene was not depressed.

3-Hydroxyacenaphthene was also recovered unchanged, when aluminium chloride or phosphorus pentoxide was used as the condensing agents.

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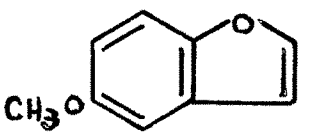
SECTION II

SYNTHESIS OF SOME ACENAPHTHOFURANS

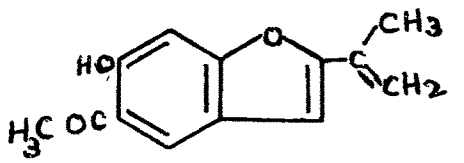
SECTION - II

Synthesis of some acenaphthofurnas :

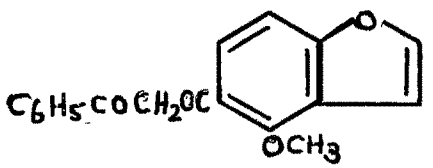
A large number of furan derivatives are present in plants. 5-Methoxybenzofurna (I), Euparin (II), Pongamol (III), and Egonol (IV) are a few of the simple benzofuran derivatives found in nature.



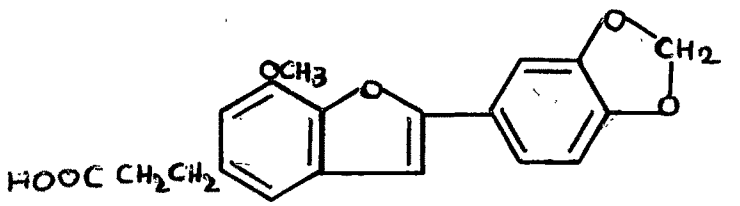
I



II

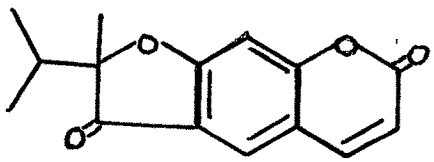


III

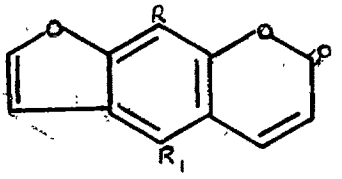


IV

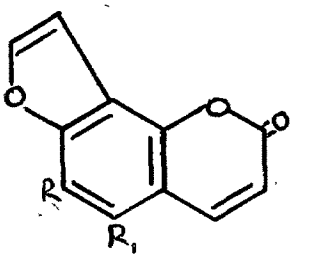
Another group of interesting naturally occuring furan derivatives are the furocoumarins. Oreoselone (V), Angelicin (VI), Bergapten (VII), Xanthotoxin (VIII), Pimpinellin (IX), iso-Pimpinellin (X) and Psoralene (XI) are a few members belonging to this group.



(V) Oreoselone

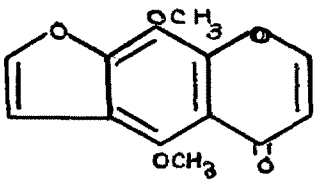


	R	R_1
VII. Bergapten	H	OCH_3
VIII. Xanthotoxin	OCH_3	H
X. iso-Pimpinellin	OCH_3	OCH_3
XI. Psoralene	H	H

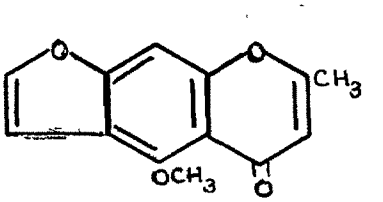


	R	R_1
VI. Angelicin	H	H
IX. Pimpinellin	OCH_3	OCH_3

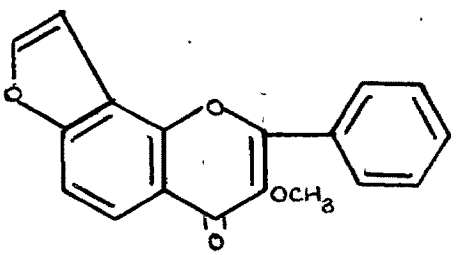
Khellin (XII) and Visnagin (XIII) are examples of naturally occurring furochromones and Karanjin (XIV) is an example of a naturally occurring furoflavone.



XII



XIII

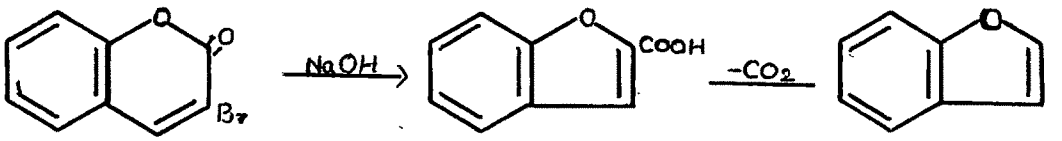


XIV

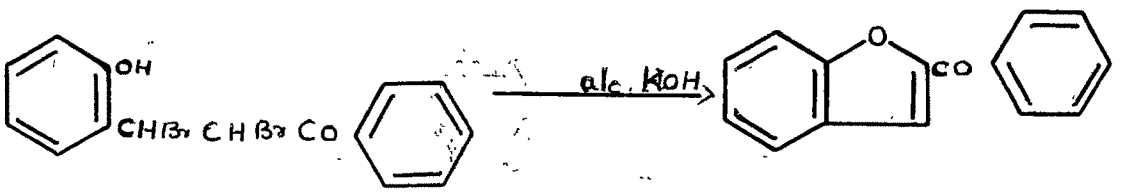
Some of the general methods available for the synthesis

of benzofuran derivatives are described below :-

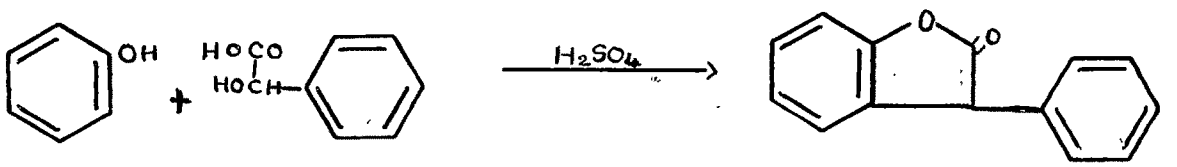
When 3-halocoumarins are heated with alkali a coumarilic acid derivative is obtained which can be easily decarboxylated to a furan derivative.



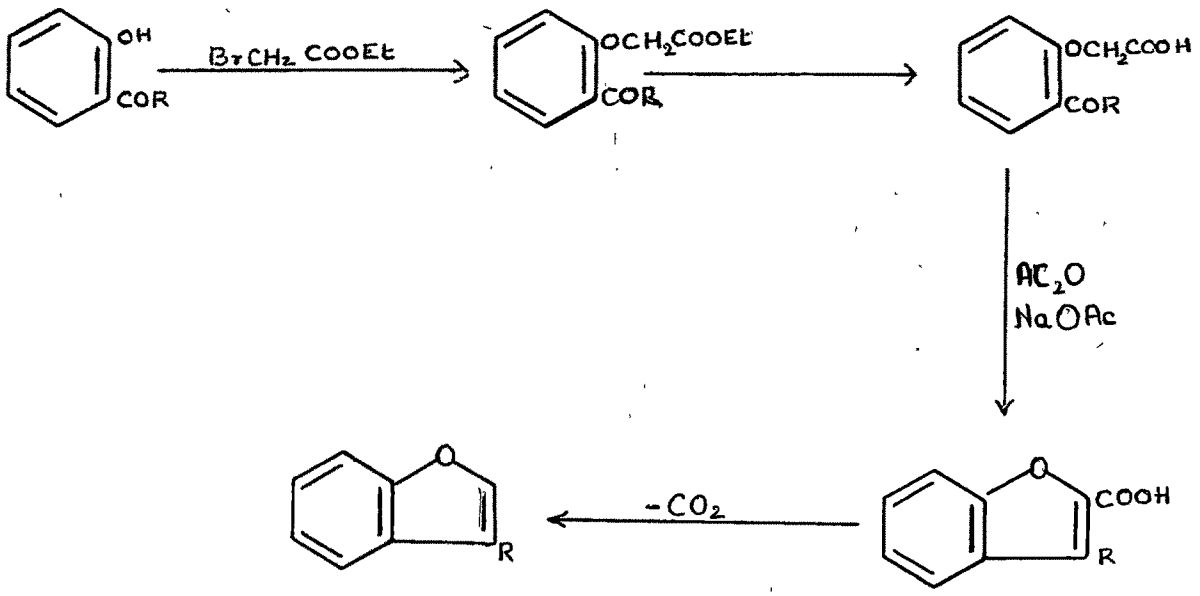
Synthesis of a benzofuran derivative can be accomplished from the dibromide of a chalcone[1] by treatment with alcoholic potassium hydroxide.



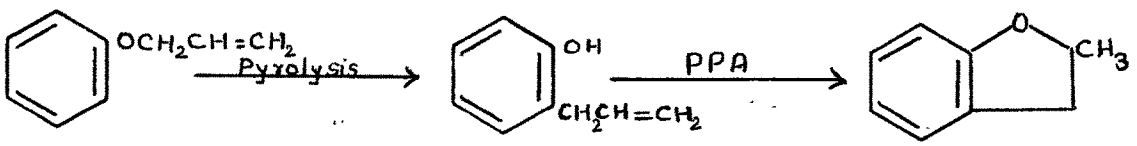
α-Hydroxy phenylacetic acid readily undergoes ring closure with sulphuric acid to yield a furan derivative[2,3,4]. Thus when mandelic acid is condensed with phenol 3-phenyl-coumaran-2-one is formed.



A method which is extensively used for the synthesis of furan derivatives consists in the condensation of bromo acetic ester with an o-hydroxyaldehyde or an o-hydroxyketone and subsequent hydrolysis and cyclisation of the phenoxy acetic acid derivative formed with sodium acetate and acetic anhydride. Simultaneous decarboxylation has been observed in many cases.

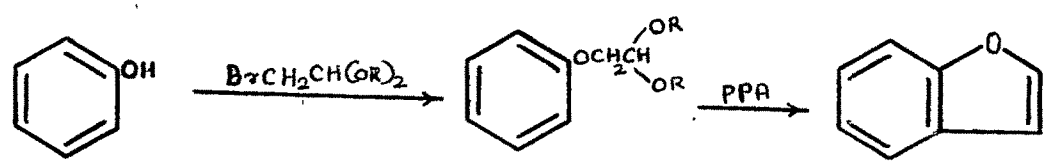


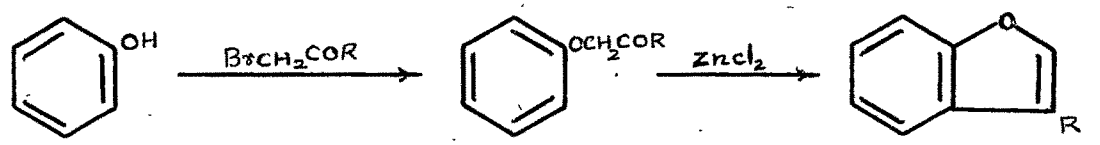
2,3-Dihydrofurans are formed from o-allyl phenols as follows[5,6,7]:-



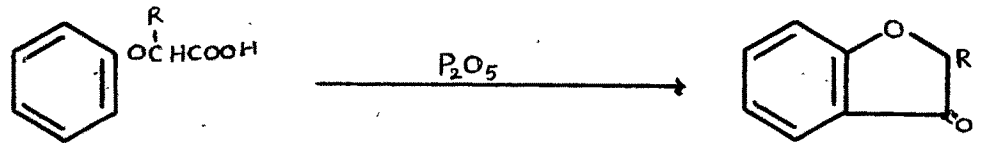
Ring closure of phenoxy carbonyl compounds or their acetals can be effected with the help of reagents like conc. sulphuric acid, anhydrous zinc chloride or polyphosphoric

acid to get the furan derivative.[8,9,10,11]

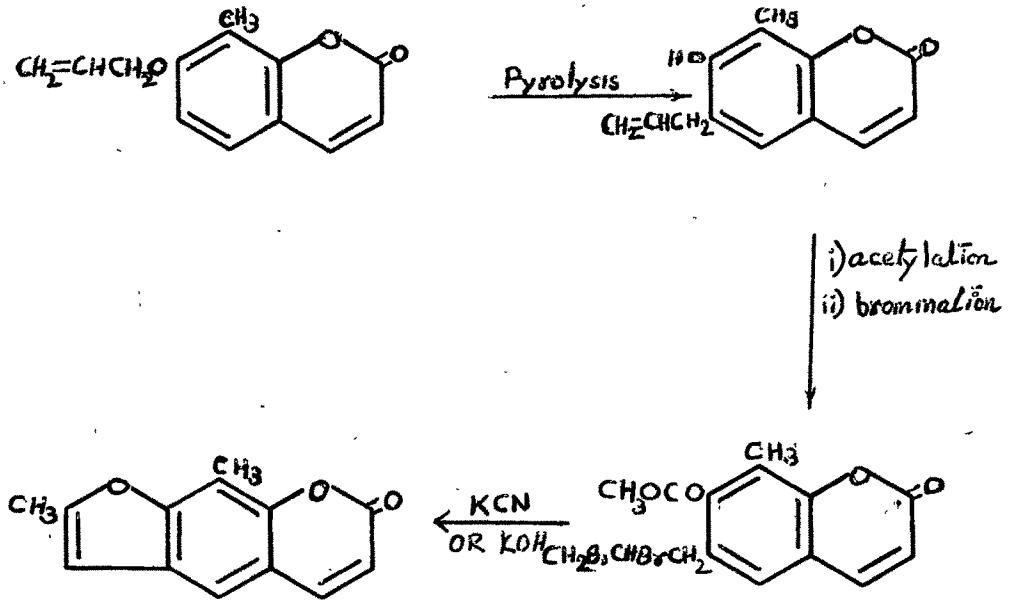




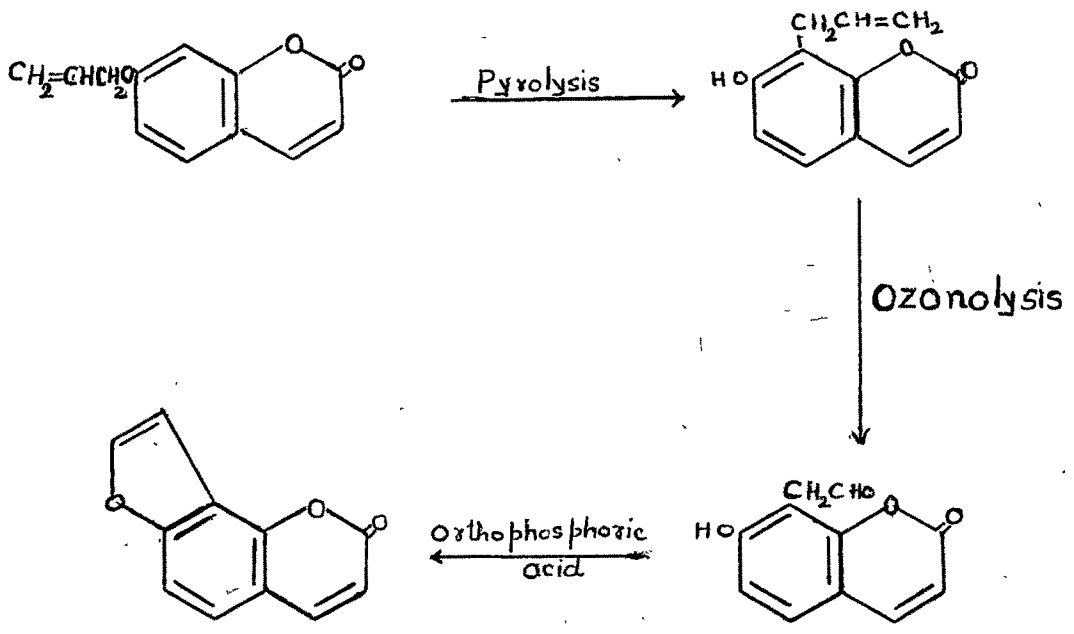
Phenoxy acetic acids undergo similar cyclisations when treated with phosphorus pentoxide to yield coumaran-3-one[12,13,14].



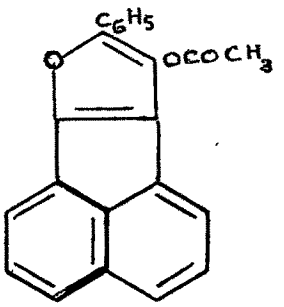
Kaufmann[15] developed a versatile method for the synthesis of furan derivatives from o-hydroxy allyl derivatives. It can be illustrated with the synthesis of a psoralene derivative.



Aneja, Mukerjee and Seshadri[16] in the course of their work on the synthesis of furocoumarins developed another method for the synthesis of furan derivatives. They subjected the o-hydroxy allyl derivative to ozonolysis and cyclised the o-hydroxyacetaldehyde derivative obtained with ortho phosphoric acid.



When the present work was started there was only one reference in the literature on the synthesis of an acenaphthofuran viz. that of Sircar and Chowdhary[17] who synthesised 2'-phenyl-3'-acetoxyacenaphtho(1,2:5',4')furan (XV) by heating acenaphthene quinone, acetophenone and acetic anhydride in the presence of a little conc. sulphuric acid at 50° for 40 hrs. and then at 75-80° for ½ 1 hour.



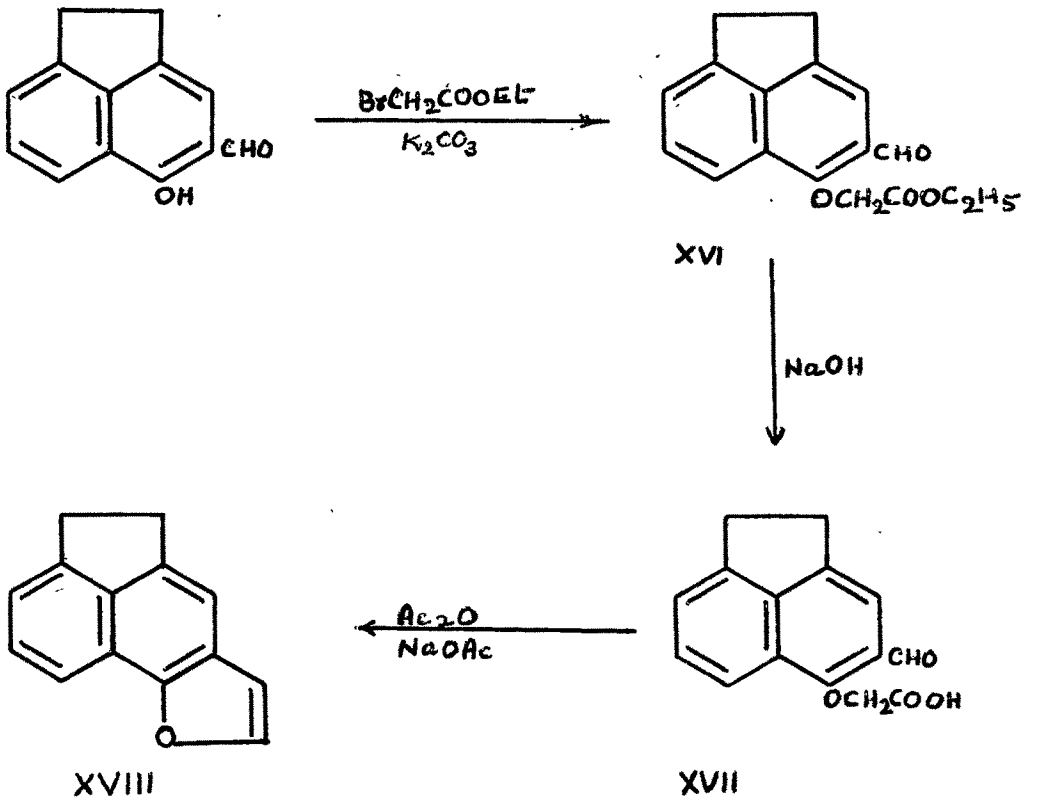
XV

No acenaphtho furan derivative with the furan ring built on one of the aromatic rings was known. It was therefore thought of interest to synthesise such compounds.

Synthesis of acenaphtho(5,4:5',4')furan :

5-Hydroxy-4-formylacenaphthene was synthesised as given on page 56 and was condensed with ethylbromoacetate in the presence of anhydrous potassium carbonate. The 4-formyl-5-carbethoxymethoxyacenaphthene (XVI) obtained was hydrolysed with sodium hydroxide to 4-formyl-5-carboxymethoxyacenaphthene (XVII). This was refluxed with freshly fused sodium acetate and acetic anhydride to get acenaphtho(5,4:5',4')furan (XVIII),

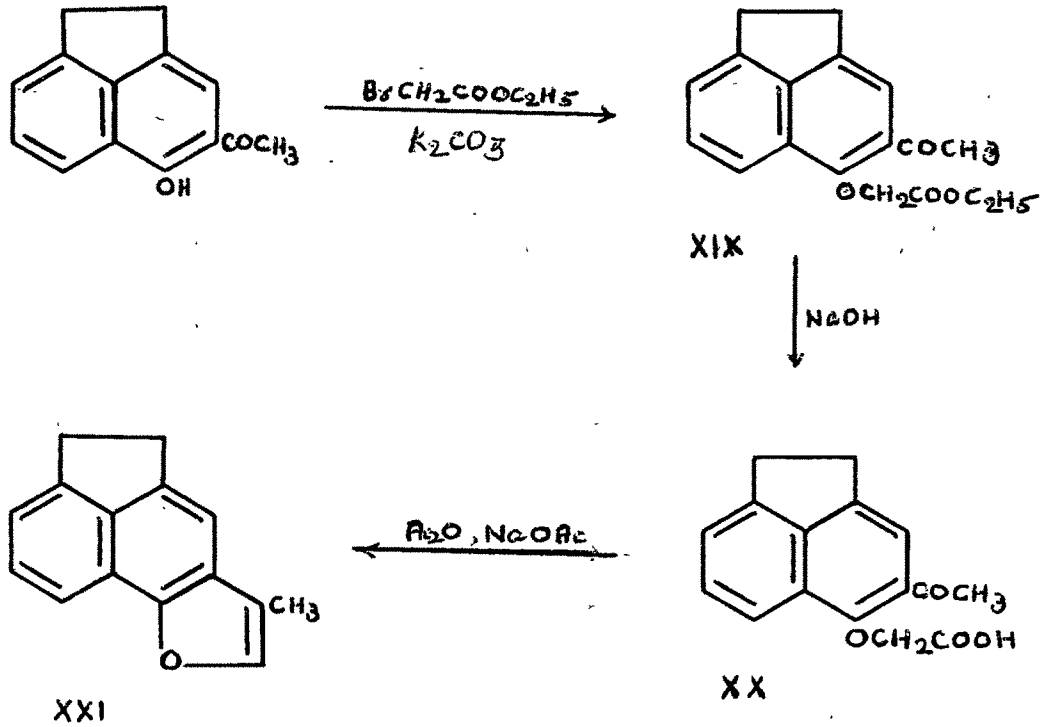
the decarboxylation taking place along with the cyclisation.



Synthesis of 3'-methylacenaphtho(5,4:5',4')furan :

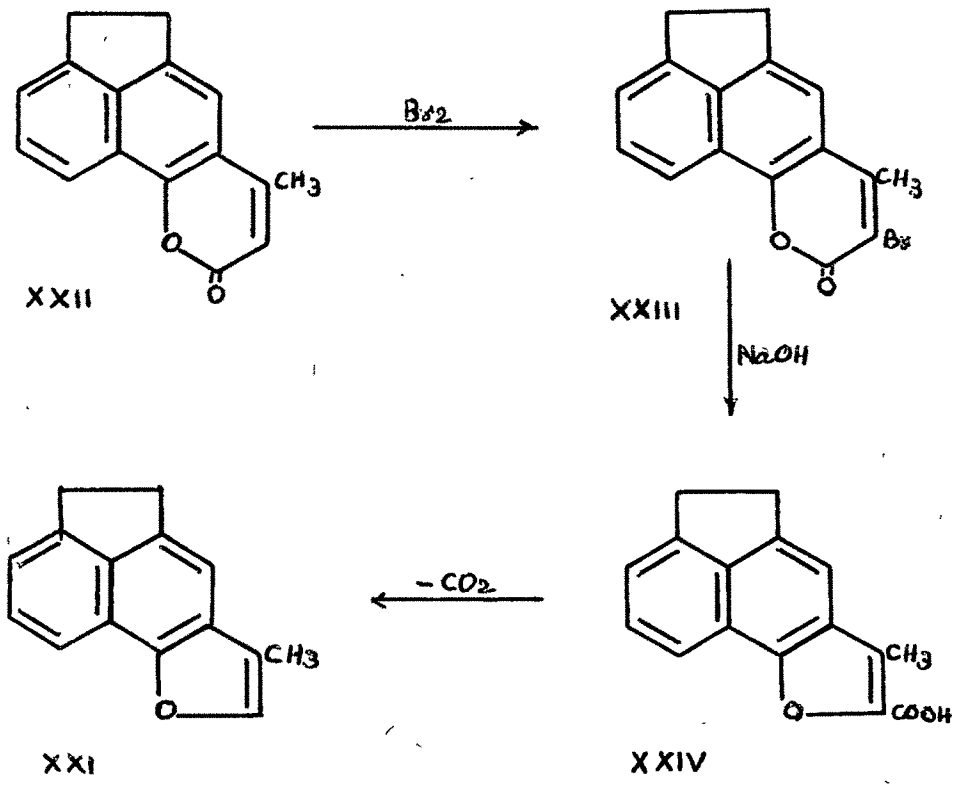
(A) From 5-hydroxy-4-acetylacenaphthene :

5-Hydroxy-4-acetylacenaphthene prepared by the Fries rearrangement of 5-acetoxyacenaphthene according to Richter and Feist[18] was condensed with ethyl bromoacetate in boiling acetone in the presence of anhydrous potassium carbonate when 4-acetyl-5-carbethoxymethoxyacenaphthene (XIX) was obtained. This was hydrolysed by boiling with sodium hydroxide to 4-acetyl-5-carboxymethoxy acenaphthene (XX). On boiling with freshly fused sodium acetate and acetic anhydride, the acid gave 3'-methyl acenaphtho(5,4:5',4')furan (XXI).



(B) From 4'-methylacenaphtho(5,4:6',5')α-pyrone :

4'-Methylacenaphtho(5,4:6',5')α-pyrone (XXII) obtained by the Pechmann condensation of 5-hydroxyacenaphthene with ethyl acetaacetate as described on page 54 was brominated in acetic acid. The monobromo derivative obtained on heating with sodium hydroxide on a steam bath gave an acid which did not contain any bromine. The acid on decarboxylation by heating in quinoline with copper powder gave a product which was identical with 3'-methylacenaphtho(5,4:5',4')furan described above. The bromo compound has therefore been assigned 4'-methyl-3'-bromoacenaphtho(5,4:6',5')α-pyrone structure (XXIII) and the acid is assigned the 3'-methylacenaphtho(5,4:5',4')furan-2'-carboxylic acid structure (XXIV).

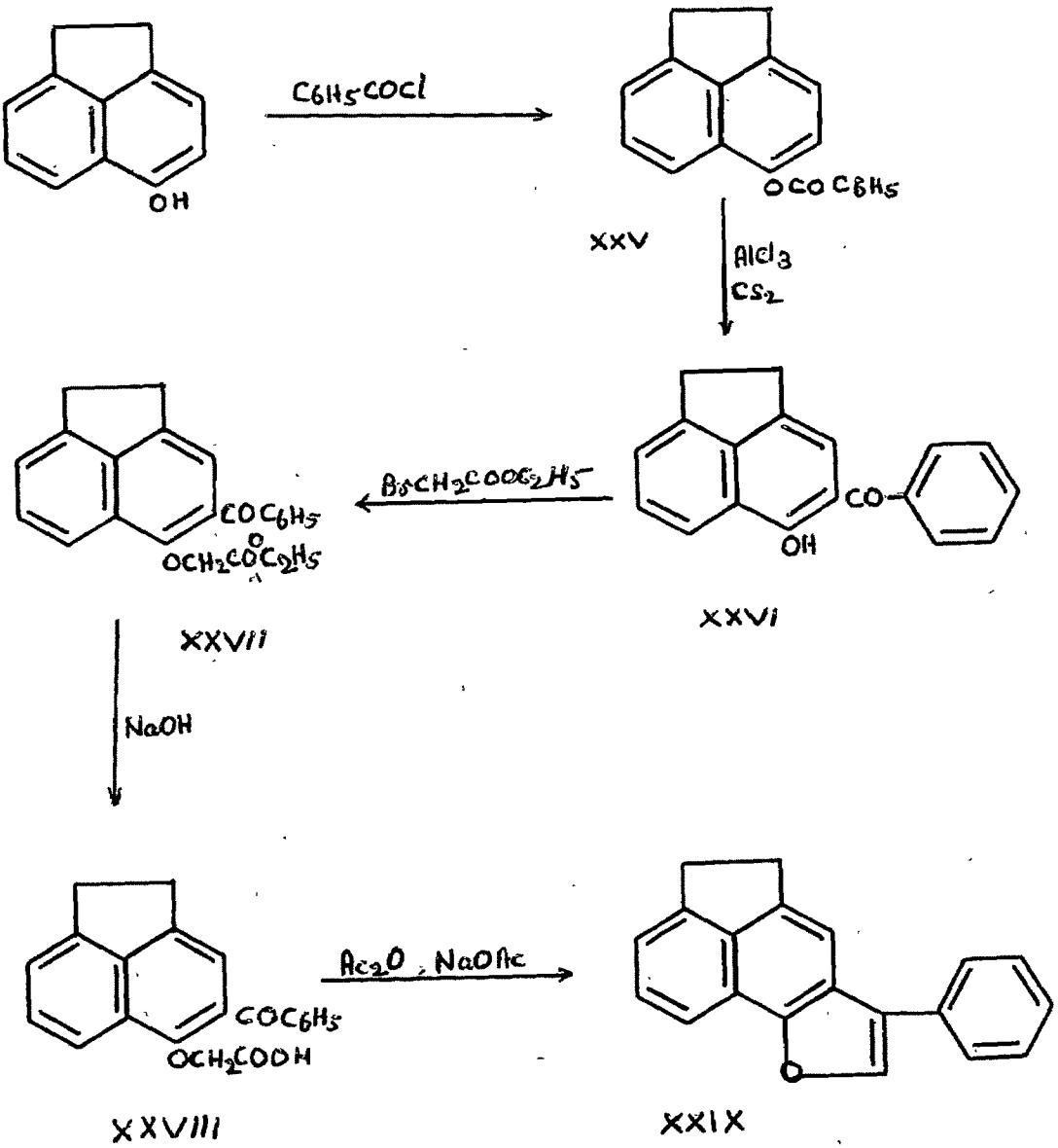


Synthesis of 3'-phenylacenaphtho(5,4:5',4')furan :

5-Hydroxyacenaphthene was dissolved in 2N sodium hydroxide and benzoylated by shaking with benzoyl chloride. The 5-benzoyloxyacenaphthene (XXV) thus obtained was subjected to Fries rearrangement in carbon disulphide in the presence of anhydrous aluminium chloride. On removing carbon disulphide, the 5-hydroxy-4-benzoylacenaphthene (XXVI) was obtained. The 5-hydroxy-4-benzoyl structure was assigned to the ketone because (1) it gave a blue colour with alcoholic ferric chloride, (2) it underwent cyclisation to give the furan derivative and (3) in analogy with the Fries rearrangement of the 5-acetoxy derivative.

5-Hydroxy-4-benzoylacenaphthene was condensed with

ethylbromoacetate in the presence of anhydrous potassium carbonate in dry acetone when 4-benzoyl-5-carbethoxymethoxy acenaphthene was obtained (XXVII). This was hydrolysed by heating with alcoholic sodium hydroxide to the corresponding acid- 4-benzoyl-5-carboxymethoxyacenaphthene (XXVIII) which was cyclised by refluxing with freshly fused sodium acetate and acetic anhydride to 3'-phenylacenaphtho(5,4:5',4')furan(XXIX).



EXPERIMENTAL.

Condensation of 5-hydroxy-4-formylacenaphthene with ethyl bromoacetate : 4-Formyl-5-carbethoxymethoxy-acenaphthene :

5-Hydroxy-4-formylacenaphthene (1 g.) prepared as given on page 56 was dissolved in dry acetone (25 ml.) and anhydrous potassium carbonate (2 g.) was added. To this solution ethyl bromoacetate (1 ml.) was added and the mixture was heated under reflux on a steam bath for 8 hrs. The solvent was evaporated and the mixture was added to water. The solid which separated was filtered and crystallised from petroleum ether in colourless flakes (1 g.), m.p. 79-80°.

Analysis	: Found	: C, 72.18 ; H, 5.78 %.
$C_{17}H_{16}O_4$	: requires	: C, 71.83 ; H, 5.63 %.

4-Formyl-5-carboxymethoxyacenaphthene :

The above ester (1 g.) was heated with sodium hydroxide (25 ml.; 5 %) on a steam bath for 3 hrs. A clear solution was obtained. This was acidified and the solid was further purified by sodium bicarbonate treatment. The acid obtained was finally crystallised from benzene in colourless needles (0.6 g.), m.p. 172°.

Analysis	: Found	: C, 70.54 ; H, 4.79 %.
$C_{15}H_{12}O_4$	: requires	: C, 70.33 ; H, 4.68 %.

Acenaphtho(5,4:5',4')furan :

The above acid (1 g.) was mixed with acetic anhydride (10 ml.) and freshly fused and powdered sodium acetate (1.5 g.)

and refluxed gently on a sand bath for 1 hour. The reaction mixture was then poured on ice and the product which separated was filtered and washed with sodium bicarbonate and finally crystallised from aqueous alcohol in colourless flakes (0.5 g.) , m.p. 48°.

Analysis	: Found	: C, 87.07 ; H, 4.77 %.
$C_{14}H_{10}O$	: requires	: C, 86.60 ; H, 5.18 %.

Condensation of 5-hydroxy-4-acetylacenaphthene with ethyl bromoacetate : 4-Acetyl-5-carbethoxymethoxy acenaphthene :

5-Hydroxy-4-acetylacenaphthene (2 g.) was dissolved in dry acetone (25 ml.). To this ethyl bromoacetate (1.8 g.) and anhydrous potassium carbonate (2 g.) were added and the mixture was refluxed on a steam bath for 3 hrs. The solvent was then removed and the reaction mixture was added to water. The separated solid was filtered and crystallised from petroleum ether in colourless needles (1.5 g.), m.p. 74°.

Analysis	: Found	: C, 72.13 ; H, 5.98 %.
$C_{18}H_{18}O_4$	: requires	: C, 72.47 ; H, 6.04 %.

4-Acetyl-5-carboxymethoxyacenaphthene :

The above ester (1 g.) was heated with sodium hydroxide solution (20 ml. ; 10 %) on a steam bath till a clear solution was obtained (3 hrs.). It was carefully acidified with dilute hydrochloric acid. The product was filtered and purified by sodium bicarbonate treatment. The acid was

finally crystallised from benzene in colourless needles (0.6 g.), m.p. 168°.

Analysis	: Found	: C, 71.41 ; H, 4.83 %.
$C_{16}H_{14}O_4$	: requires	: C, 71.11 ; H, 5.18 %.

3'-Methylacenaphtho(5,4:5',4')furan :

A mixture of 4-acetyl-5-carboxymethoxyacenaphthene (1 g.), acetic anhydride (4 ml.) and freshly fused sodium acetate (1 g.) was refluxed gently on a sand bath for 3 hrs. The reaction mixture was then poured on ice and the solid was filtered and washed with sodium bicarbonate solution. It was finally crystallised from dilute alcohol in colourless flakes (0.5 g.), m.p. 57-58°.

Analysis	: Found	: C, 86.28 ; H, 5.60 %.
$C_{15}H_{20}O$	: requires	: C, 86.54 ; H, 5.76 %.

Synthesis of 3'-methylacenaphtho(5,4:5',4')furan from 4'-methylacenaphtho(5,4:6',5')α-pyrone :

4'-Methyl-3'-bromoacenaphtho(5,4:6',5')α-pyrone :

4'-Methylacenaphtho(5,4:6',5')α-pyrone described on page54 (1 g.) was dissolved in glacial acetic acid (100 ml.). The solution was cooled and bromine in acetic acid (7 ml.; 10 %) was added dropwise with constant stirring. The mixture was allowed to stand for 3 hrs. The separated solid on pouring it into water was filtered and crystallised from glacial acetic acid in colourless needles (1.0 g.), m.p.298° (decomp.).

Analysis	: Found	: Br, 25.64 %.
$C_{16}H_{11}O_2Br$	: requires	: Br, 25.40 %.

3'-Methylacenaphtho(5,4:5',4')furan-2'-carboxylic acid :

The above-bromo-α-pyrone (2 g.) was refluxed with sodium hydroxide (25 ml.; 10 %) till the solution became clear (8 hrs.). It was filtered and the filtrate was cooled by adding ice and the solid obtained on acidification with hydrochloric acid was purified through sodium bicarbonate treatment and then crystallised from toluene as colourless small needles (0.3 g.), m.p. 247°.

Analysis	: Found	: C, 75.74 ; H, 4.89 %.
$C_{16}H_{12}O_3$	: requires	: C, 76.19 ; H, 4.76 %.

3'-Methylacenaphtho(5,4:5',4')furan :

The above acid (0.5 g.) was dissolved in quinoline (5 ml.) and copper bronze (0.2 g.) was added. The mixture was then refluxed on a sand bath for half an hour. It was cooled and poured in cold dilute hydrochloric acid. The solution was extracted with ether (100 ml.) and the solid obtained on removal of ether was washed thoroughly with sodium bicarbonate solution. The residue was crystallised from dilute alcohol (0.15 g.), m.p. 57-58°. Mixed m.p. of this sample with 3'-methylacenaphtho(5,4:5',4')furan prepared from 5-hydroxy-4-acetylacenaphthene was not depressed.

Synthesis of 3'-phenylacenaphtho(5,4:5',4')furan :

5-Benzoyloxyacenaphthene :

5-Hydroxyacenaphthene (1 g.) was dissolved in sodium hydroxide (25 ml.; 10 %) and crushed ice was added. To this benzoyl chloride (1 ml.) was added and the flask was corked and shaken well for 15 minutes. The solid was filtered

and crystallised from alcohol in colourless flakes (1.2 g.), m.p. 105°.

Analysis	: Found	: C, 83.12 ; H, 4.86 %.
$C_{19}H_{14}O_2$	: requires	: C, 83.20 ; H, 5.10 %.

4-Benzoyl-5-hydroxyacenaphthene :

5-Benzoyloxyacenaphthene (1 g.) was added in small portions to anhydrous aluminium chloride (2 g.) dissolved in carbon disulphide (100 ml.). After completing the addition the mixture was heated on a water bath under reflux for 4 hrs. The clear solvent was then decanted and the pasty mass was decomposed by adding ice and hydrochloric acid (10 ml.). It was left overnight and the separated solid was purified through sodium hydroxide treatment. It crystallised from petroleum ether as red prisms (0.8 g.), m.p. 126°.

Analysis	: Found	: C, 83.70 ; H, 4.85 %.
$C_{19}H_{14}O_2$	: requires	: C, 83.20 ; H, 5.10 %.

It gave a blue colour with alcoholic ferric chloride and red colour with conc. sulphuric acid.

Condensation of 4-benzoyl-5-hydroxyacenaphthene with ethylbromoacetate : 4-Benzoyl-5-carbethoxymethoxy acenaphthene :

5-Hydroxy-4-benzoylacenaphthene (2 g.) dissolved in dry acetone (20 ml.) was refluxed with ethyl bromoacetate (2 ml.) and anhydrous potassium carbonate (4 g.) on a steam bath for 4 hrs. The solvent was then removed and the reaction mixture was added to water. The solid obtained was filtered

and washed with cold dilute sodium hydroxide to remove any unreacted compound. The residue was crystallised from petroleum ether in light yellow flakes (1.5 g.), m.p.126°.

Analysis	: Found	: C, 76.30 ; H, 5.42 %.
$C_{23}H_{20}O_4$	: requires	: C, 76.67 ; H, 5.55 %.

4-Benzoyl-5-carboxymethoxyacenaphthene :

The above ester (1 g.) was heated under reflux with alcoholic sodium hydroxide (30 ml. ; 5 %) on a steam bath for 3 hrs. The alcohol was evaporated and the residue was diluted with water. It was filtered and the filtrate was acidified with hydrochloric acid. The solid obtained was further purified through sodium bicarbonate treatment. The acid so obtained was crystallised from benzene in cubes (0.5 g.), m.p. 174°.

Analysis	: Found	: C, 75.82 ; H, 4.66 %.
$C_{21}H_{16}O_4$	: requires	: C, 75.91 ; H, 4.81 %.

3'-Phenylacenaphtho(5,4:5',4')furan :

The above acid (0.5 g.) was mixed with freshly fused and powdered sodium acetate (1 g.) and acetic anhydride (3 ml.) and refluxed gently on a sand bath for 2 hrs. The mixture was then added to ice and stirred well to decompose the acetic anhydride. The separated solid was filtered and washed with sodium bicarbonate solution and then with water. The residue was crystallised from alcohol in golden yellow needles, (0.2 g.), m.p. 88°.

Analysis	: Found	: C, 88.78 ; H, 5.26 %.
$C_{20}H_{14}O$	: requires	: C, 88.88 ; H, 5.18 %.

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SECTION III

MANNICH REACTION ON 5-HYDROXYACENAPHTHENE

SECTION III.

Mannich reaction on 5-hydroxyacenaphthene

The essential feature of the Mannich reaction is the replacement of an active hydrogen atom by an aminomethyl or substituted aminomethyl group in a compound containing atleast one reactive hydrogen atom.

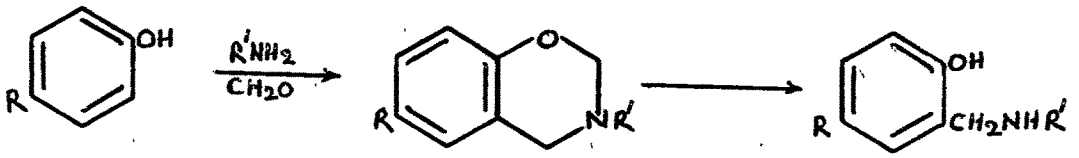
$$BH + CH_2O + NHRR' \longrightarrow B.CH_2\ NRR'$$

Alcohol and acetic acid have been generally used as solvents. If aqueous formaldehyde is used, the condensation can also be carried out without organic solvents. Burke and coworkers[1] used dioxane as solvent with very good results. They employed catalytic quantity of alcoholic potassium hydroxide to effect the depolymerisation of paraformaldehyde.

Phenols, ketones, aldehydes, acids, esters, nitro compounds and heterocyclic ring systems containing either oxygen, nitrogen or sulphur are found to undergo the reaction.

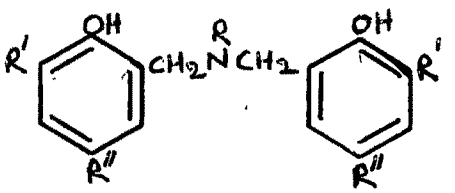
Decombe[2] has proved that in Mannich reaction of a phenol with formaldehyde and secondary amines, the resulting dialkyl aminomethyl group enters ortho or para position or both and that in no case it attaches to oxygen of the hydroxy group. Burke[3] showed that the condensation of equimolecular quantities of para substituted phenols with formaldehyde and primary amines gave alkylaminomethyl p- substituted phenols. When the reaction was carried out using phenol, formaldehyde and primary amine in the molar ratio 1:2:1 respectively the formation of a substituted benzoxazine (I), a new series of compounds took place. The benzoxazine

derivative on heating with hydrochloric acid in alcoholic solution decomposes readily to give the corresponding 2-alkylaminomethyl-p-substituted phenol.



I

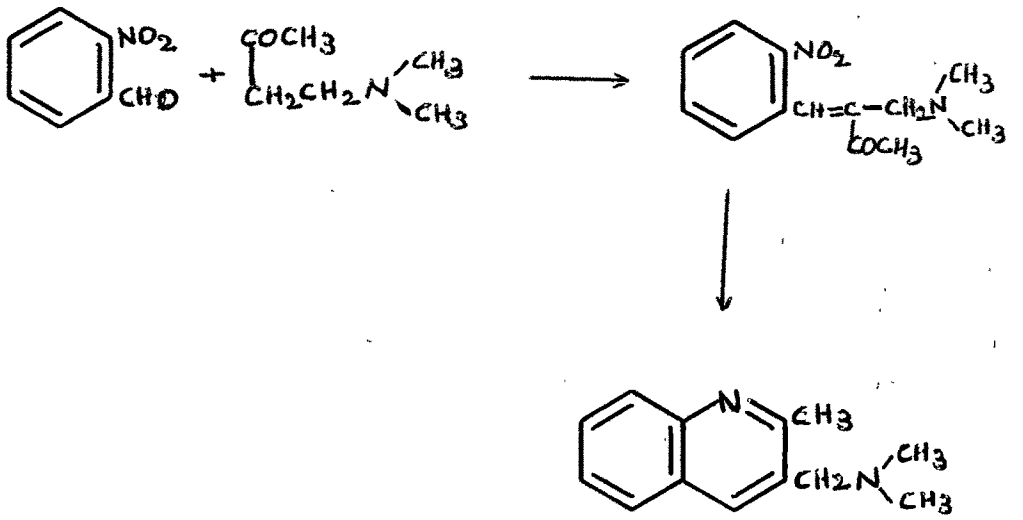
The same authors also showed that a third kind of product, N,N-bis-(2-hydroxy benzyl)alkylamine (II) could be directly obtained in the reaction of certain ortho, para substituted phenols with paraformaldehyde and primary amines.[4] When polyhydroxy phenols were condensed with formaldehyde and primary amines poly-1,2-benzoxazines were formed[5].



II

Mannich reaction has proved to be an important tool in the field of synthetic organic chemistry. The resulting products of the Mannich reaction may be further transformed into a variety of compounds. The most important characteristic property of many of the products obtained in the Mannich reaction, especially those derived from secondary amines, is the decomposition into the amines and unsaturated compounds when subjected to heat or steam distillation.

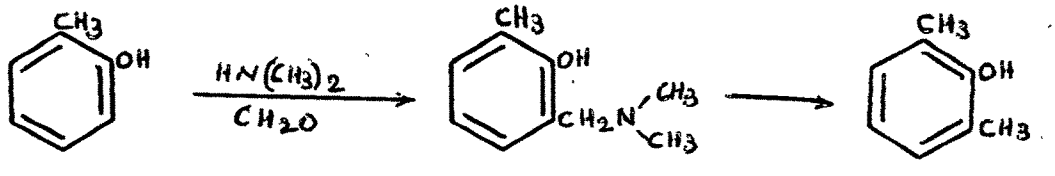
Mannich et al.[6] found that β-dimethylaminomethyl ketone and o-nitrobenzaldehyde reacted to give a product, which on reduction lost water to form a substituted quinoline (III).



III

The β-substituted amino ketones or aldehydes have been reduced to the corresponding γ-substituted amino alcohols. Many such amino alcohols in the form of their esters, especially the benzoates and p-aminobenzoates, have been widely used as local anaesthetics.

Caldwell and Thompson[7] have developed a new method of nuclear methylation of phenols by reducing the Mannich base, which can be illustrated by the preparation of 2,6-xylenol (IV).



IV

Mannich bases have been found to be of importance in the preparation of aldehydes. It was observed by Snyder[8] *et al.* that when Mannich bases in acetic acid are treated with hexamethylene tetramine the intermediate quaternary salt decomposed to an aldehyde. The intermediate quaternary ammonium salts were of the type encountered in Sommelet reaction[9].

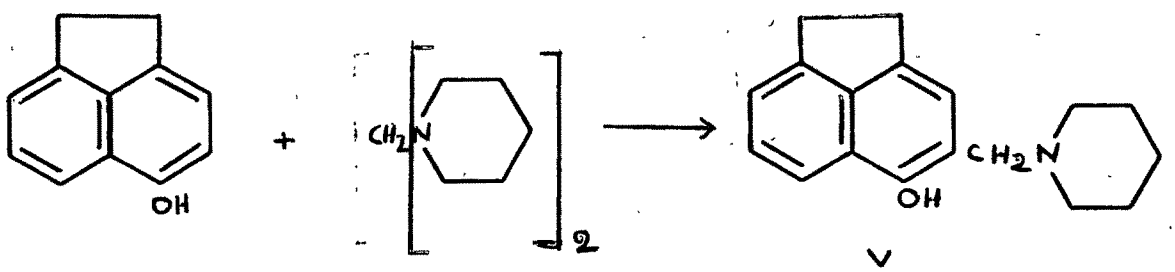
$$R.CH_2\ N(CH_3)_2 + (CH_2)_6N_4 + CH_3\ COOH \longrightarrow$$

$$(CH_3)_2\ NH + R.\ CH_2\ N(CH_2)_6\ \overset{+}{N}_3 + CH_3\ \overset{-}{COO}$$

$$R.\ CH_2\ \overset{+}{N}.\ (CH_2)_6\ N_3 \longrightarrow R.\ CHO$$

Mannich reaction on acenaphthene derivatives :

There appears to be only one reference in the literature on the Mannich reaction on a acenaphthene derivative. Rapoport et al.[10] refluxed 5-hydroxyacenaphthene with methylene bis-piperidine and obtained 5-hydroxy-4-piperidine-methyl acenaphthene (V).



V

The present work deals with the synthesis of Mannich bases from 5-hydroxy acenaphthene and primary and secondary amines.

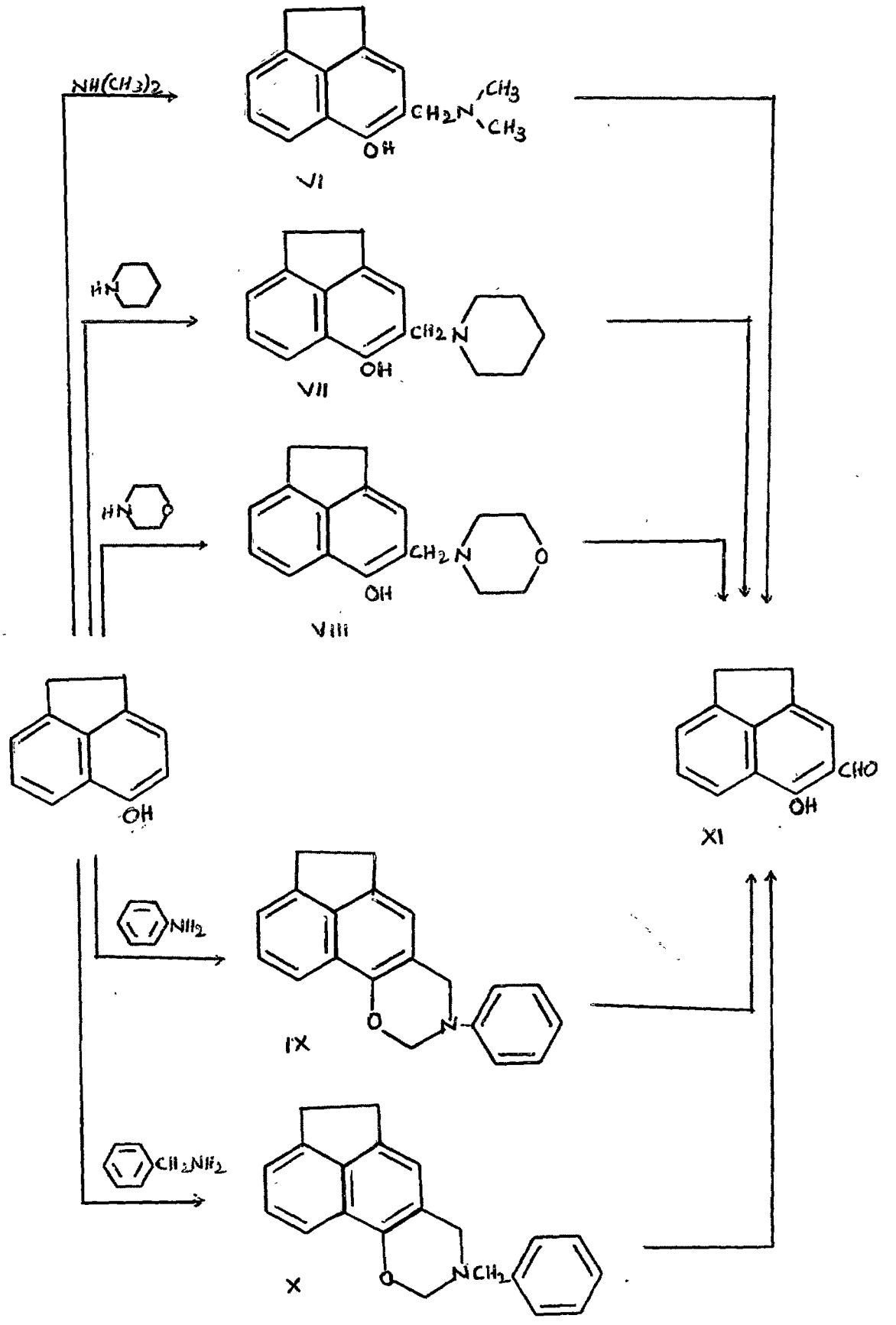
Mannich reaction on 5-hydroxy acenaphthene with (a) dimethylamine, (b) piperidine, (c) morpholine, (d) aniline and (e) benzylamine :

(a) 5-Hydroxy acenaphthene on condensation with paraformaldehyde and dimethylamine in equimolecular proportion gave a compound which was found to be soluble in hydrochloric acid and in sodium hydroxide solution. To this compound 5-hydroxy-4-dimethylaminomethyl structure (VI) has been assigned because on treatment with hexamethylene tetramine it gave 5-hydroxy-4-formylacenaphthene (XI) which has been synthesised by direct formylation of 5-hydroxy acenaphthene and has been described earlier (p.56).

(b) 5-Hydroxy acenaphthene, paraformaldehyde and piperidine when mixed in equimolecular proportion furnished a compound which was soluble in alkali and in mineral acids. 5-Hydroxy-4-piperidinemethyl structure (VII) has been assigned to this compound because on treatment with hexamethylene tetramine in acetic acid, it gave 5-hydroxy-4-formyl acenaphthene (XI).

The same compound has been previously prepared by Rapoport et al.[10] by the action of methylene-bis-piperidine on 5-hydroxy acenaphthene as stated before.

(c) 5-Hydroxy acenaphthene with paraformaldehyde and morpholine gave a compound which was soluble both in mineral acids and in alkali. 5-Hydroxy-4-morpholinomethyl structure (VIII) has been assigned as it afforded 5-hydroxy-4-formyl acenaphthene on treatment with hexamethylene tetramine in glacial acetic acid.


NH(CH3)2
CH2N
CH3
CH3
OH
VI
HN
CH2N
OH
VII
HN
O
CH2N
O
OH
VIII
OH
CHO
OH
XI
NH2
O
N
IX
CH2NH2
O
NCH2
X

(d) 5-Hydroxy acenaphthene on treatment with paraformaldehyde and anilins in the molecular ratio 1:2:1 yielded a product to which 2'H-3'-phenyl 3',4'-dihydro 1',3'-oxazino(6',5':5,4) acenaphthene structure (IX) has been assigned. The product was insoluble in both alkali and in minerals acids. It however, coult not be hydrolysed to 5-hydroxy-4-phenylaminomethyl acenaphthene on boiling with hydrochloric acid and only unchanged product was recovered but on boiling with hexamethylene tetramine in glacial acetic acid it was directly converted into 5-hydroxy-4-formyl acenaphthene (XI).

(e) 5-Hydroxy acenaphthene when mixed with benzylamine and paraformaldehyde in the ratio 1:1:2 gave a compound which was insoluble in acid and in alkali. To this 2'H-3'-benzyl-3',4'-dihydro-1',3'-oxazino(6',5':5,4)acenaphthene structure (X) has been assigned because this compound was converted into 5-hydroxy-4-formyl acenaphthene by boiling with hexamethylene tetramine in glacial acetic acid. It could not be converted into 5-hydroxy-4-benzylaminomethyl acenaphthene by boiling with conc. hydrochloric acid. Only unchanged product was recovered.

Attempted Mannich reaction on 3-hydroxy acenaphthene :

Mannich reaction on 3-hydroxy acenaphthene was tried with dimethylamine, piperidine, morpholine, aniline and benzylamine. 3-Hydroxy acenaphthene, paraformaldehyde and each of the above amine in alcohol was heated on a boiling water bath for 4 hrs. On working up the mixture only unreacted 3-hydroxy acenaphthene could be recovered.

Attempted chloromethylation of 5-hydroxyacenaphthene and its methyl ether :

5-Hydroxy acenaphthene on chloromethylation with paraformaldehyde and dry hydrogen chloride gas in dioxane or in glacial acetic acid at room temperature or at 5° gave only a polymeric product from which no pure chloromethyl derivative could be isolated. 5-Methoxy acenaphthene also on a similar reaction gave only a polymeric product.

Attempted chloromethylation of 3-hydroxy acenaphthene and its methyl ether :

Chloromethylation of 3-hydroxy and 3-methoxy acenaphthene was carried out using different solvents like dioxane, acetic acid, etc. and at different temperatures. In all the trials only a polymerised product could be obtained from which no pure product could be isolated.

EXPERIMENTAL.

Mannich reaction on 5-hydroxy acenaphthene with paraformaldehyde and (a) dimethylamine, (b) piperidine, (c) morpholine, (d) aniline and (e) benzylamine :

(a) 5-Hydroxy-4-dimethylaminomethyl acenaphthene :

Paraformaldehyde (0.18 g.) was depolymerised by boiling with alcohol (5 ml.) containing a very small piece of potassium hydroxide. 5-Hydroxy acenaphthene (1 g.) was dissolved in alcohol (10 ml.) and dimethylamine (0.4 ml.) was added. To this solution, the paraformaldehyde solution was added. The product which separated out immediately was filtered and crystallised from petroleum ether in colourless needles (1.1 g.), m.p. 100°.

Analysis : Found : C, 79.28 ; H, 7.55 ; N, 5.99 %.

$C_{15}H_{17}ON$: requires : C, 79.30 ; H, 7.48 ; N, 6.16 %.

The above Mannich base (0.5 g.) and hexamethylene tetramine (1 g.) in glacial acetic acid (10 ml.) were heated on a boiling water bath for 3 hrs. Hydrochloric acid (5 ml.; 1:1) was added and the heating was continued for 30 mimutes. The product which separated on cooling was crystallised from dilute alcohol in colourless long needles (0.3 g.), m.p. 95°. Mixed melting point with 5-hydroxy-4-formyl acenaphthene reported earlier (p.56) was not depressed.

(b) 5-Hydroxy-4-piperidinemethyl acenaphthene :

The above reaction was carried out with piperidine (0.5 ml.) as the amine. The product which separated out

on working up as before crystallised from petroleum ether in colourless needles (1.2 g.), m.p. 77°.

Analysis : Found : C, 80.67 ; H, 7.72 ; N, 5.68 %.

$C_{18}H_{12}ON$: requires : C, 80.91 ; H, 7.86 ; N, 5.24 %.

The above Mannich base on heating with hexamethylene tetramine in glacial acetic acid and working up as before afforded 5-hydroxy-4-formyl acenaphthene.

(c) 5-Hydroxy-4-morpholinomethyl acenaphthene :

Paraformaldehyde (0.18 g.) and a very small piece of potassium hydroxide, 5-hydroxy acenaphthene (1 g.) and morpholine (0.6 ml.) were reacted in alcohol as before. The product that separated after 4 hrs. was filtered and crystallised from petroleum ether in colourless needles (1.1 g.) m.p. 95°.

Analysis : Found : C, 76.36 ; H, 7.03 ; N, 5.62 %.

$C_{17}H_{19}O_2N$: requires : C, 75.82 ; H, 7.06 ; N, 5.20 %.

The above Mannich base on heating with hexamethylene tetramine in glacial acetic acid and working up as above afforded 5-hydroxy-4-formyl acenaphthene.

(d) 2'-H-3'-Phenyl-3',4'-dihydro-1',3'-oxazino(6',5':5,4) acenaphthene :

Paraformaldehyde (0.3 g.) depolymerised by boiling in alcohol with a small amount of potassium hydroxide was reacted with a mixture of aniline (0.5 ml.) and 5-hydroxy acenaphthene (1 g.) in alcohol (10 ml.). The solution on keeping overnight gave a solid which was crystallised from petroleum ether in colourless flakes (0.8 g.). The product was found to be

insoluble in cold sodium hydroxide solution, m.p. 104°.

Analysis : Found : C, 83.95 ; H, 6.21 ; N, 5.08 %.

$C_{20}H_{17}ON$: requires : C, 83.62 ; H, 5.92 ; N, 4.87 %.

The above oxazino derivative was unaffected by boiling with hydrochloric acid in alcohol even after refluxing for 6 hrs.

The above oxazino derivative (0.5 g.) was dissolved in glacial acetic acid (10 ml.) and hexamethylene tetramine (2 g.) was added. The mixture was heated on a water bath for 3 hrs. Hydrochloric acid (5 ml.; 1:1) was added and the heating was continued for 30 minutes more. The crystalline product which separated on cooling was filtered and recrystallised from dilute alcohol (0.3 g.), m.p. 95°. Mixed m.p. with 5-hydroxy-4-formyl acenaphthene was not depressed.

(e) 2'-H-3'-benzyl-3',4'-dihydro-1',3'-oxazino(6',5':5,4) acenaphthene :

Paraformaldehyde (0.3 g.) was dissolved in alcohol by boiling along with a little potassium hydroxide and the solution was reacted with benzyl amine (0.7 ml.) and 5-hydroxy acenaphthene (1 g.) in alcohol (10 ml.) by keeping overnight. The separated solid crystallised from petroleum ether in colourless needles (0.7 g.), m.p. 118°.

Analysis : Found : C, 83.19 ; H, 6.36 ; N, 4.65 %.

$C_{21}H_{19}ON$: requires : C, 83.71 ; H, 6.31 ; N, 4.65 %.

The above oxazino compound on boiling with alcoholic hydrochloric acid for 6 hrs. on a water bath remained unchanged.

The oxazino derivative, however, on heating with

hexamethylene tetramine in glacial acetic acid and working up as above gave 5-hydroxy-4-formyl acenaphthene.

Attempted Mannich reaction on 3-hydroxy acenaphthene :

Paraformaldehyde (0.18 g.) in alcohol (5 ml.) with a very small amount of potassium hydroxide was added to dimethylamine (0.5 ml.) and 3-hydroxy acenaphthene[18] prepared according to Morgan and Harrison[11] in alcohol (10 ml.). No solid material separated out even after keeping the mixture overnight. The alcohol was removed and the residue on crystallisation was found to be the original 3-hydroxyacenaphthene.

Only unreacted 3-hydroxy acenaphthene could be isolated even after heating the reaction mixture on a steam bath for 4 hrs. Piperidine, morpholine and their hydrochlorides were also tried in this reaction, but no Mannich bases could be isolated.

Attempted chloromethylation of 5-hydroxy acenaphthene and its methyl ester :

Paraformaldehyde (0.12 g.) was suspended in glacial acetic acid (20 ml.) and dry hydrogen chloride gas was passed at room temperature till the solution became clear. 5-Hydroxy acenaphthene (1 g.) was added and dry hydrogen chloride gas was passed for 3 hrs. when a solid precipitated out. It was left overnight and filtered. No pure product could be obtained from this solid.

Similar type of compounds were obtained when the reaction was carried out at low temperature. 5-Methoxy acenaphthene also gave a similar product under different set of conditions. The use of dioxan as a solvent in the above two cases did not

improve the product.

Attempted chloromethylation of 3-hydroxy acenaphthene and its methyl ester :

When the above reaction was repeated with 3-hydroxy acenaphthene similar results were obtained.

The same result was obtained when 3-methoxy acenaphthene was used. Use of dioxan as a solvent or carrying out the reaction at lower temperature did not impeove the product.

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