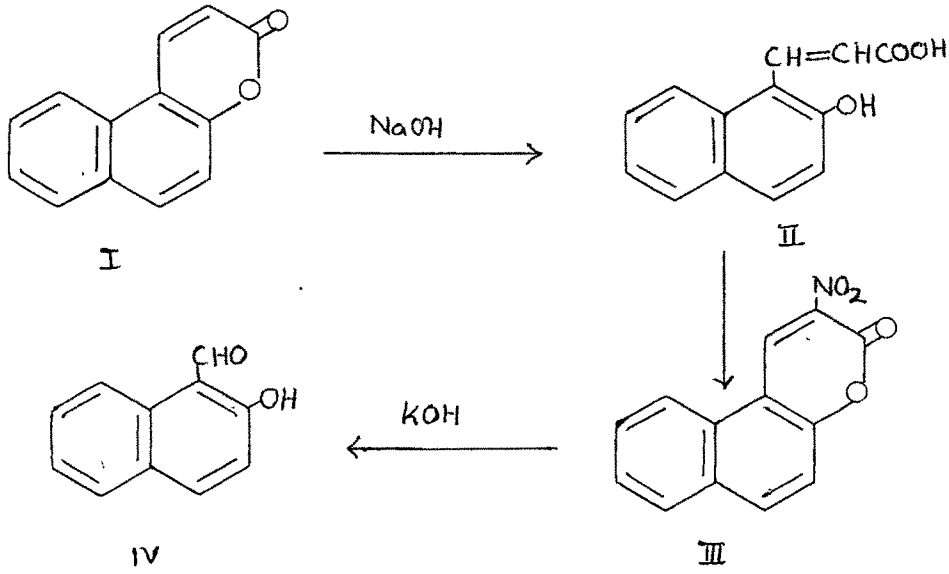
CHAPTER II

SOME REACTIONS ON HYDROXY NAPHTHO α-AND γ-PYRONES

Some reactions on hydroxy naphtho α-and γ-pyrones :

While a number of studies have been made on substitution in benzo-α-pyrone derivatives (coumarins) there have been very few studies on substitution in naphtho-α-pyrones (benzocoumarins) and their hydroxy derivatives. Before describing the present work some of the previous work on naphtho-α-pyrones and their hydroxy derivatives may be briefly reviewed here.

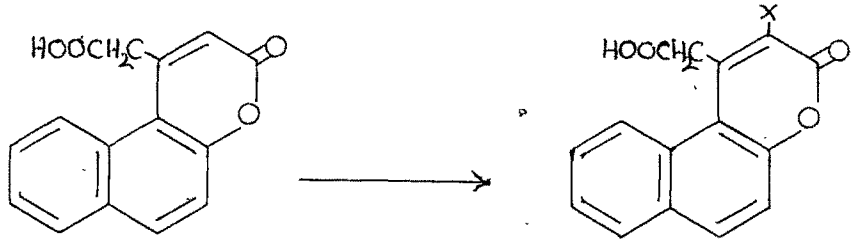
Nitration of naphtho (2,1:6',5')α-pyrone was studied by Dey and coworkers[1]. Direct nitration of this pyrone gave a mixture of different nitro derivatives, but they found that on nitration of the acid(II)derived from (I), 3'-nitro naphtho (2,1:6',5')α-pyrone (III) was obtained with simultaneous closure of the α-pyrone ring. They similarly prepared 3'-nitro derivative of 4'-methyl naphtho (2,1:6',5')α-pyrone by the nitration of the corresponding acid with fuming nitric acid in acetic anhydride. It was observed that when 3'-nitro derivative was treated with hot alkali the



pyrone ring was completely ruptured and 2-hydroxy-1-naphthaldehyde (IV) was quantitatively obtained.

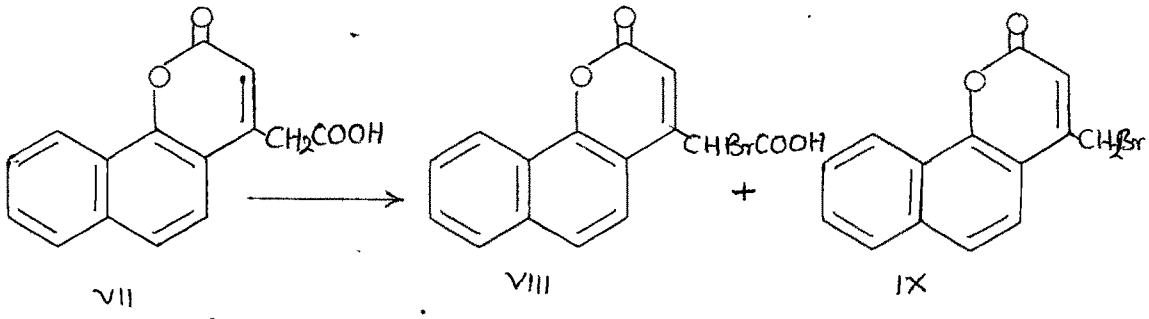
Goswami and Dasgupta[2] obtained 4-nitronaphtho (1,2:6',5') α-pyrone by the nitration of naphtho(1,2:6',5') α-pyrone with nitric acid in acetic acid.

Dey and Radhabai[3] found that naphtho (2,1:6',5') α-pyrone-4'-acetic acid (V) differs from coumarin-4-acetic acid as far as halogenation is concerned. It was not the hydrogen atom of the reactive methylene group but that attached to the carbon atom 3' which is replaced by halogen to give (VIa). Similarly bromination of naphtho(2,1:6',5') α-pyrone-4'-acetic acid gave the 3'-bromo derivative (VIb).



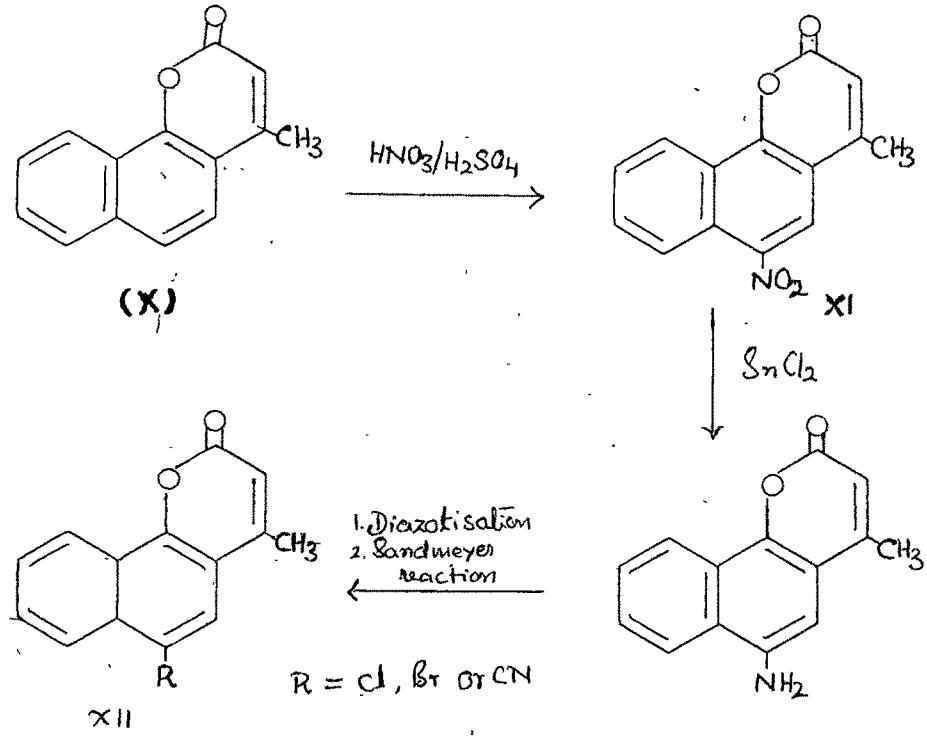
V VIa X = Cl VIb X = Br VI

It was interesting to note that naphtho(1,2:6',5') α-pyrone-4'-acetic acid (VII) behaved in a similar way as coumarin-4-acetic acid and gave on bromination the naphtho (1,2:6',5') α-pyrone-4'-bromoacetic acid (VIII) together with 4'-bromomethyl naphtho (1,2:6',5') α-pyrone (IX) by decarboxylation.



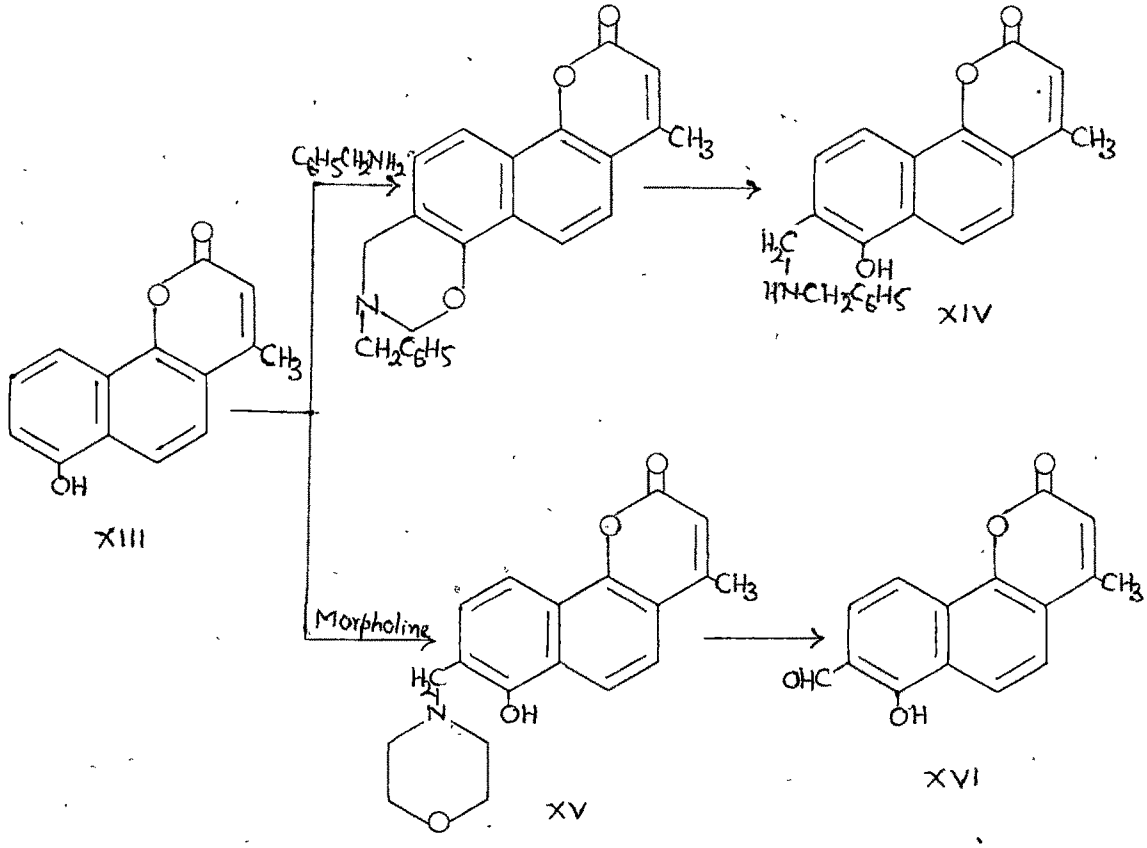
VII VIII IX

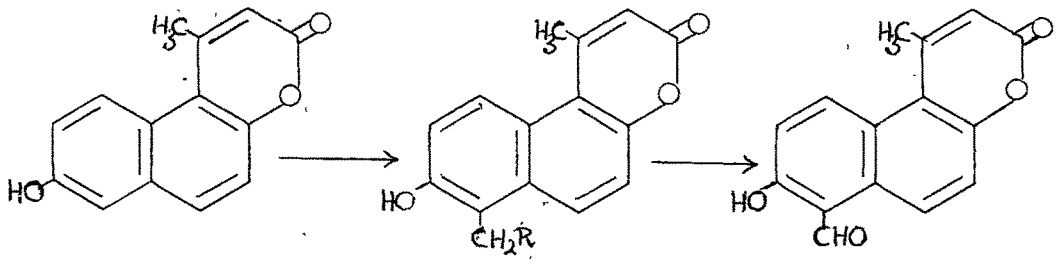
3'-Bromo-4-nitro-4'-methyl naphtho (1,2:6',5') α-pyrone was obtained on bromination of 4-nitro-4'-methyl naphtho (1,2:6',5') α-pyrone[4]. Nitration of 4'-methyl naphtho (1,2:6',5') α-pyrone (X) gave 4-nitro-4'-methyl naphtho (1,2:6',5') α-pyrone (XI)[5]. The above nitro derivative was converted to the corresponding amino derivative by reduction with stannous chloride. Dey and Dalal[6] obtained 4-chloro-, 4-bromo- and 4-cyano derivatives (XII) of 4'-methyl naphtho (1,2:6',5') α-pyrone from the corresponding amino derivative through diazotisation and Sandmeyer reaction.



(X) XI XII

paraformaldehyde afforded 5-hydroxy-6-morpholinomethyl (XV) and 6-hydroxy-5-morpholinomethyl(XVIII) derivatives, Both on treatment with hexamine were converted to the corresponding formyl derivatives (XVI) and (XXI). 6-Hydroxy-4'-methyl naphtho (2,1:6',5')α-pyrone (XVII) with dimethyl amine and paraformaldehyde in alcohol and with piperidine and paraformaldehyde gave 6-hydroxy-5-dimethyl aminomethyl(XIX) and 6-hydroxy-5-piperidinomethyl-4'-methyl naphtho(2,1:6',5') α-pyrone (XX). The structures of these mannich basis were ascertained on the basis of their conversion to 6-hydroxy-5-formyl-4'-methyl naphtho (2,1:6',5')α-pyrone (XXI) which was obtained directly from 6-hydroxy-4'-methyl naphtho (2,1:6',5')α-pyrone by reaction with hexamine and acetic acid.





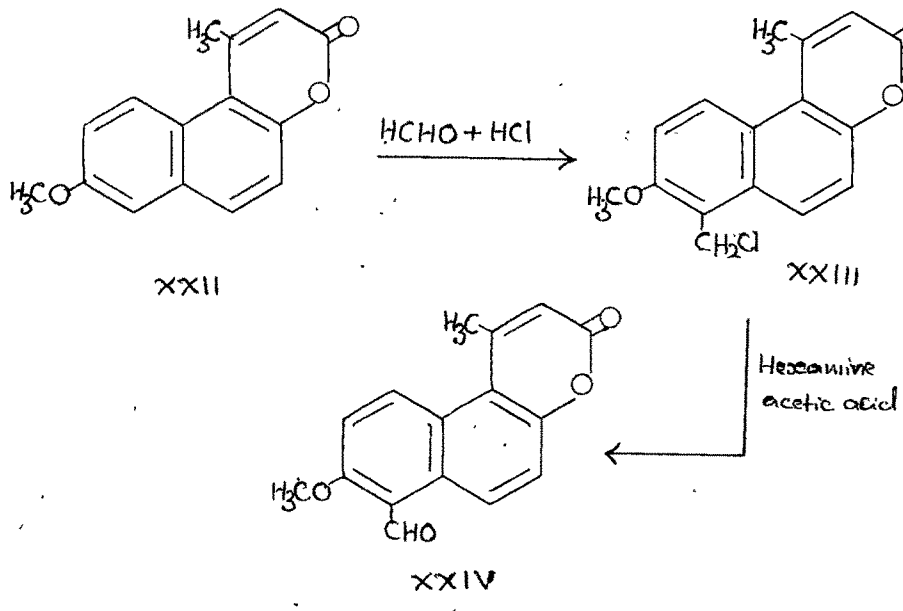
XXI

XVIII R = -N O

XIX R = -N(CH$_3$)$_2$

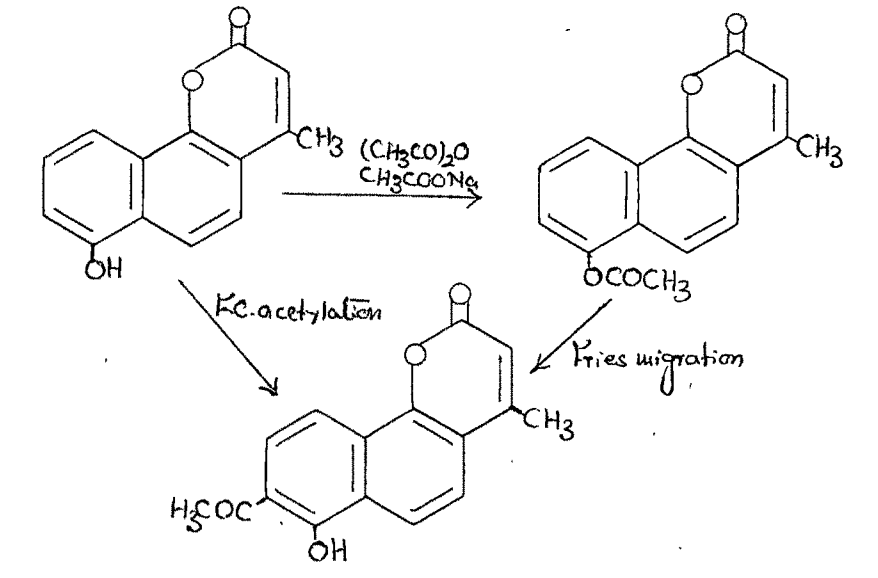
XX R = -N

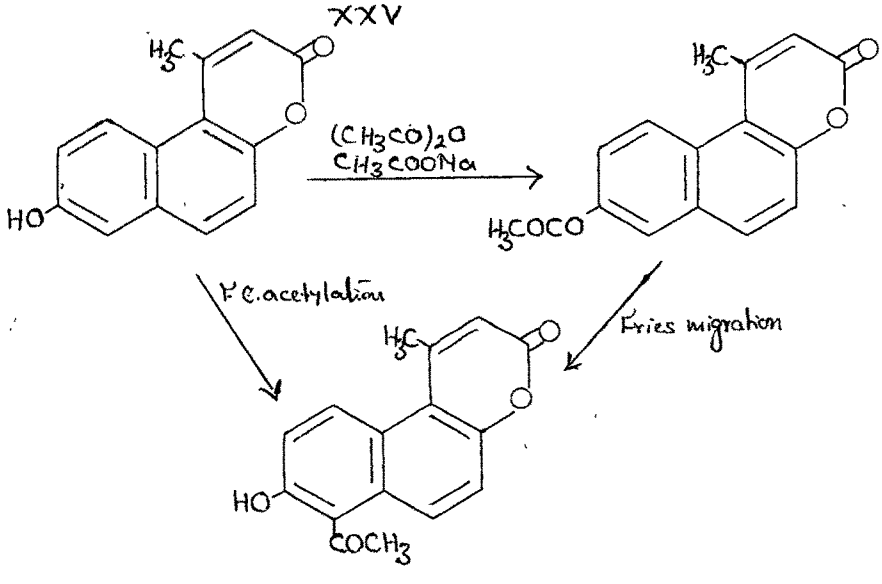
Chloromethylation of 6-methoxy-4'-methyl naphtho (2,1:6,5')α-pyrone (XXII) gave 6-methoxy-5-chloromethyl-4'-methyl naphtho (2,1:6,5')α-pyrone (XXIII) which on treatment with hexamine in acetic acid gave 6-methoxy-5-formyl-4'-methyl naphtho (2,1:6,5')α-pyrone (XXIV).



XXII XXIII XXIV

5-Hydroxy-4'-methyl naphtho (1,2:6',5')α-pyrone and 6-hydroxy-4'-methyl naphtho (2,1:6',5')α-pyrone on acetylation gave the corresponding acetoxy derivatives which on Fries migration afforded 5-hydroxy-6-acetyl-4'-methyl naphtho (1,2:6',5')α-pyrone (XXV) and 6-hydroxy-5-acetyl-4'-methyl naphtho (2,1:6',5')α-pyrone (XXVI). The same were obtained by Friedel-Craft's acetylation of the hydroxy naphtho-α-pyrones.

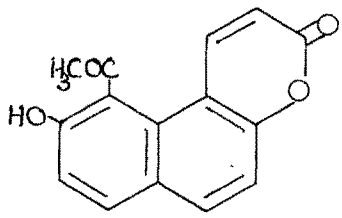




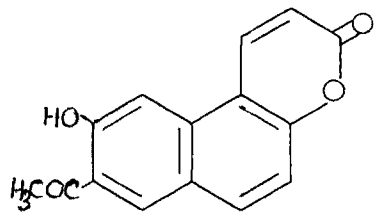
The present work deals with the building up of the γ-pyrone rings on 7-hydroxy-, 7-hydroxy-4'-methyl-, 5-hydroxy-4'-methyl naphtho α-pyrone and 5-hydroxy-2'-methyl naphtho γ-pyrone.

Synthesis of 7-hydroxy-6-acetyl naphtho(2,1:6',5') α-pyrone :

7-Acetoxy naphtho (2,1:6',5') α-pyrone prepared as described on p. 41 was subjected to Fries migration. The product obtained gave 2,4-dinitrophenyl hydrazone and a greenish brown colour with alcoholic ferric chloride. The product was very sparingly soluble in the usual solvents and its NMR spectrum therefore could not be taken. The acetyl derivative could have either of the structures i or ii.

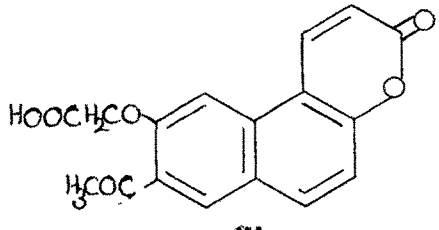


i



ii

The structure (ii) was assigned on the basis of the NMR spectrum of the acid (iii) obtained from it by its condensation with ethyl bromoacetate and hydrolysis of the ester obtained.



iii

The NMR spectrum showed two α-pyrone protons i.e. H-3' and H-4' at δ 6.57 and 8.9 respectively. The two singlets at δ 8.17 and 7.92 can be assigned to H-5 and H-8. Appearance of two singlets shows that the Fries migration takes place at 6-position in the naphthalene ring. The two doublets having coupling constant J of 9 Hz. at δ 8.15 and 7.86 can be assigned to H-4 and H-3 respectively. This shows that the acetyl derivative has the structure II.

Synthesis of naphtho(2,1:6',5')α-pyrono-2''-phenyl (7,6:6'',5'')γ-pyrone :

7-Hydroxy-6-acetyl(2,1:6',5')α-pyrone (XXVII) was converted into its benzoyloxy derivative (XXVIII) by treating with benzoyl chloride in pyridine. It was subjected to Baker-Venkataraman rearrangement in pyridine and powdered potassium hydroxide at room temperature. When the β-diketone (XXIX) was obtained. This on cyclisation with concentrated sulphuric acid by keeping overnight gave naphtho(2,1:6',5') α-pyrono-2-phenyl(7,6:6'',5'')γ-pyrone (XXX).

I.R. showed two bands in thecarbonyl region 1725 cm^{-1} (lactonyl >C = O group) and 1630 cm^{-1} (γ-pyronyl>C=O)

Kostanecki-Robinson benzoylation of 7-hydroxy-6-acetyl naphtho (2,1:6',5')α-pyrone : Naphtho(2,1:6',5')α-pyrono-2''phenyl-3''-benzoyl(7,6:6'',5'')γ-pyrone :

7-Hydroxy-6-acetyl naphtho(2,1:6',5')α-pyrone when subjected to Kostanecki-Robinson benzoylation with benzoic anhydride and freshly fused sodium benzoate afforded a

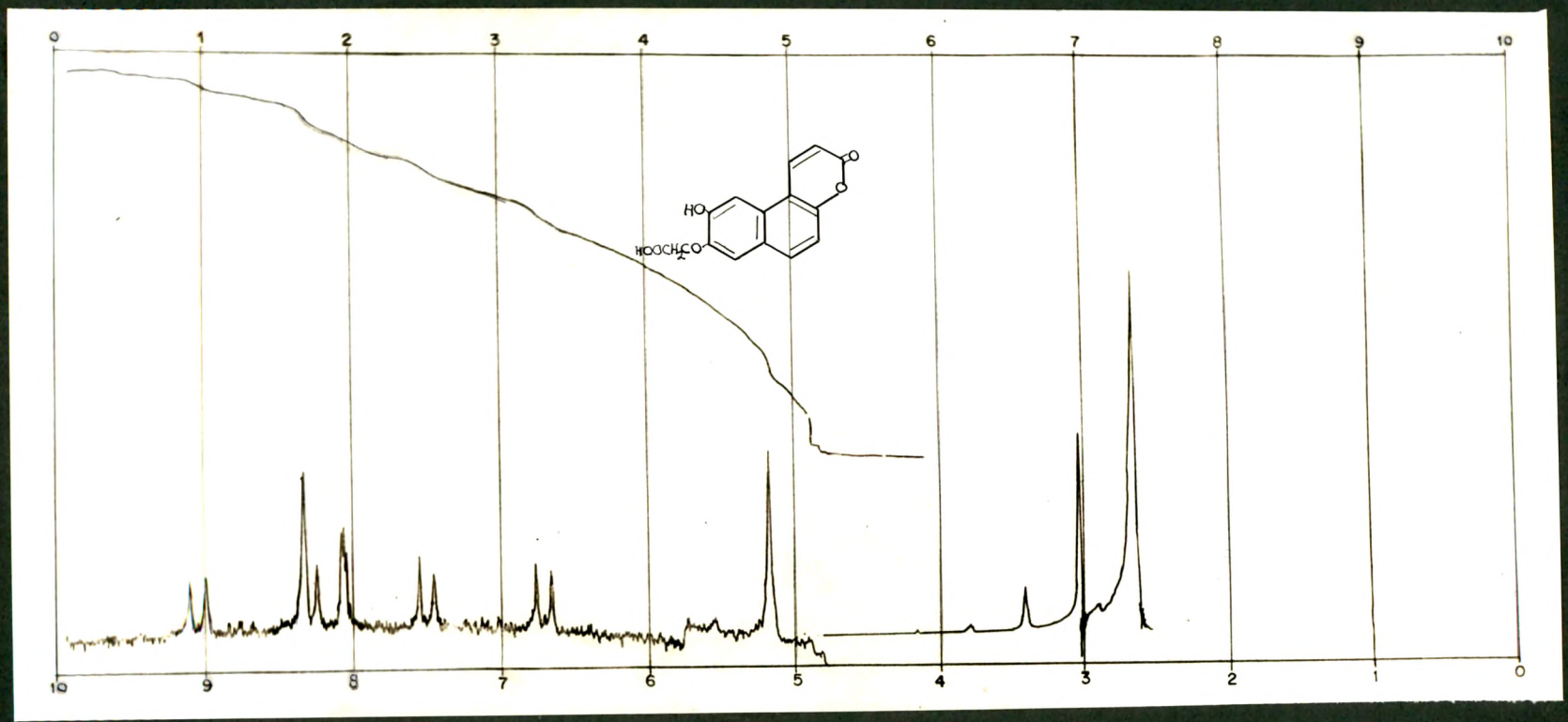


Fig. (iii) :- NMR spectrum of 7-carboxymethoxy-6-acetyl naphtho (2,1:6',5')α-pyrone. (DMSO)

compound to which naphtho(2,1:6',5')α-pyrono-2"-phenyl-3"-benzoyl(7,6:6",5")γ-pyrone (XXXI) structure was assigned. The compound was insoluble in dilute alkali and did not develop any colouration with alcoholic ferric chloride.

I.R.showed three bands in carbonyl region viz. 1725 cm^{-1} (lactonyl >C=O group) 1675 cm^{-1} (benzoyl group at position 3") and 1605 cm^{-1} (γ-pyronyl >C=O group).

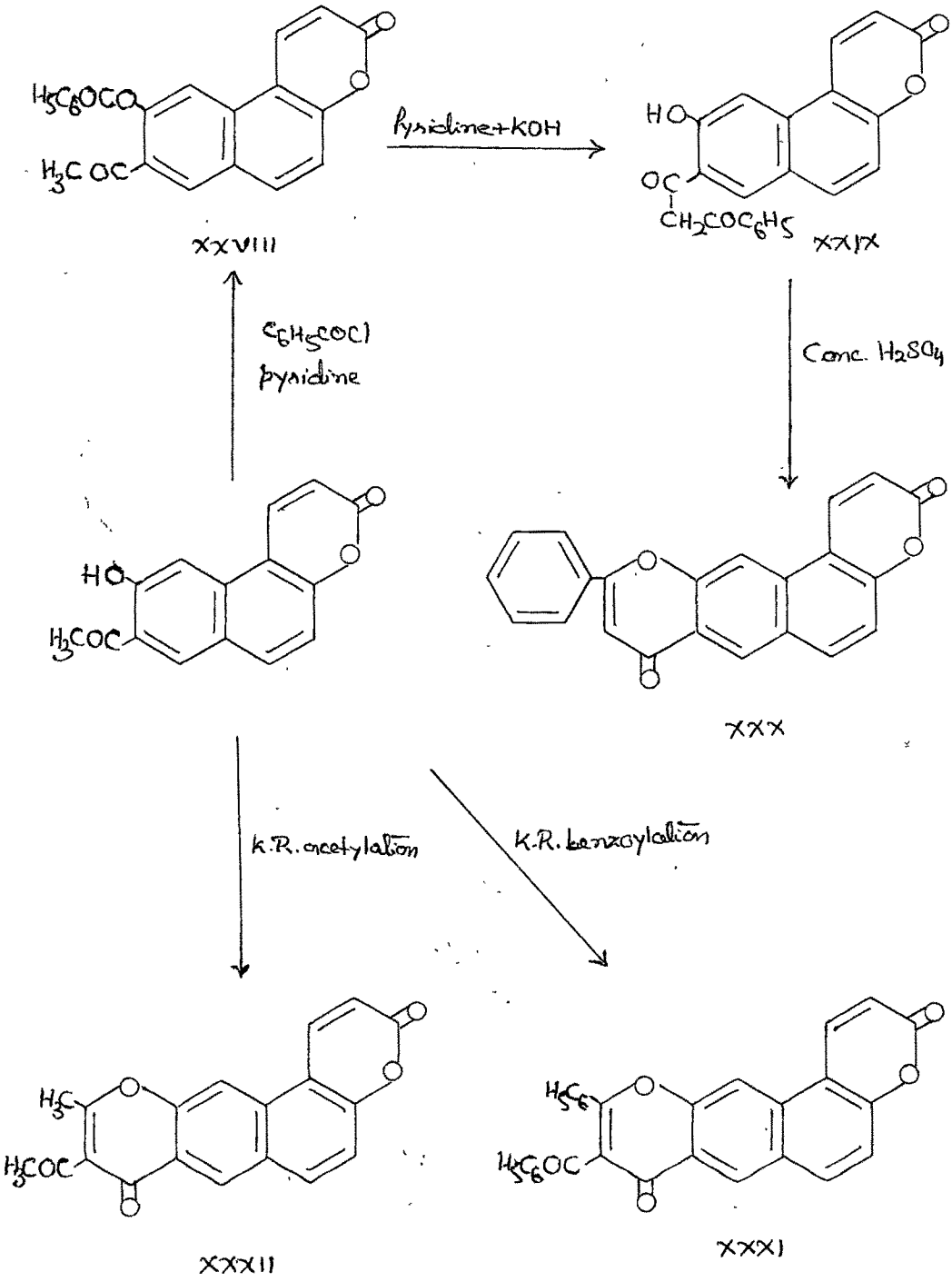
Kostanecki-Robinson acetylation of 7-hydroxy-6-acetyl naphtho (2,1:6',5')α-pyrone : Naphtho(2,1:6',5')α-pyrono-2",methyl-3"-acetyl(7,6:6",5")γ-pyrone :

Kostanecki-Robinson acetylation of 7-hydroxy-6-acetyl naphtho(2,1:6',5')α-pyrone with acetic anhydride and freshly fused sodium acetate gave an alkali insoluble compound which did not develop any colouration with alcoholic ferric chloride. The compound was assigned naphtho(2,1:6',5')α-pyrono-2"-methyl-3"-acetyl(7,6:6",5")γ-pyrone(XXXII) structure.

I.R.spectrum showed three bands 1720 cm^{-1} (lactonyl >C=O), 1630 cm^{-1} (γ-pyronyl >C=O group) and 1655 cm^{-1} (acetyl group at position 3").

Fries rearrangement of 7-acetoxy-4'-methyl naphtho (2,3:6',5')α-pyrone : 7-Hydroxy-8-acetyl-4'-methyl naphtho(2,3:6',5')α-pyrone :

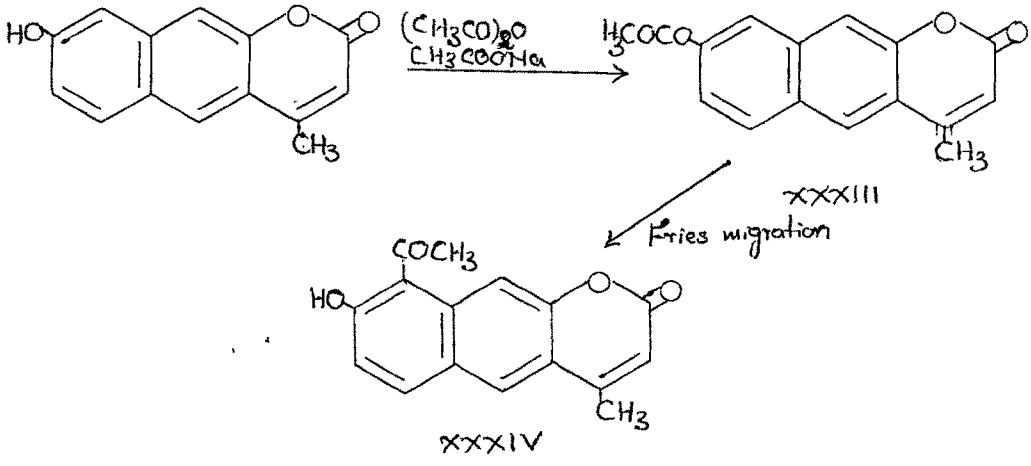
7-Acetoxy-4'-methyl naphtho(2,3:6',5')α-pyrone (XXXIII), prepared by acetylation of 7-hydroxy-4'-methyl


Pyridine+KOH
XXVIII
XXIX
C6H5COCl
pyridine
Conc. H2SO4
XXX
K.R. acetylation
K.R. benzoylation
XXXII
XXXI

naphtho(2,3:6',5')α-pyrone was heated with anhydrous aluminium chloride. The product obtained was soluble in alkali and gave a wine red colour with alcoholic ferric chloride and also gave a 2,4-dinitro phenylhydrazone. The structure assigned to this product was 7-hydroxy-8-acetyl naphtho (2,3:6',5')α-pyrone (XXXIV) on the basis of the NMR data.

The NMR spectrum of the above ketone shows two doublets and two singlets in the aromatic region, which proves that the $-COCH_3$ group must be at 8-position, as 6-acetyl derivative would have given four singlets. Again the fact that the singlet at δ 7.0 due to H-8 in the original α-pyrone has also disappeared which confirms that the $-COCH_3$ group must be at 8-position.

The singlets at δ 9.1 and 7.54 must be due to H-4 and H-1, while two doublets centred at δ 7.97 and 7.20 can be attributed to the protons at 5 and 6 positions respectively. The 3' proton appears at δ 6.29 as singlet. The methyl group in CH_3CO- appears slightly down field than the 4'-methyl group in the α-pyrone ring, the CH_3CO- being at δ 2.64 and CH_3 at δ 2.45 , both giving a three proton singlet.



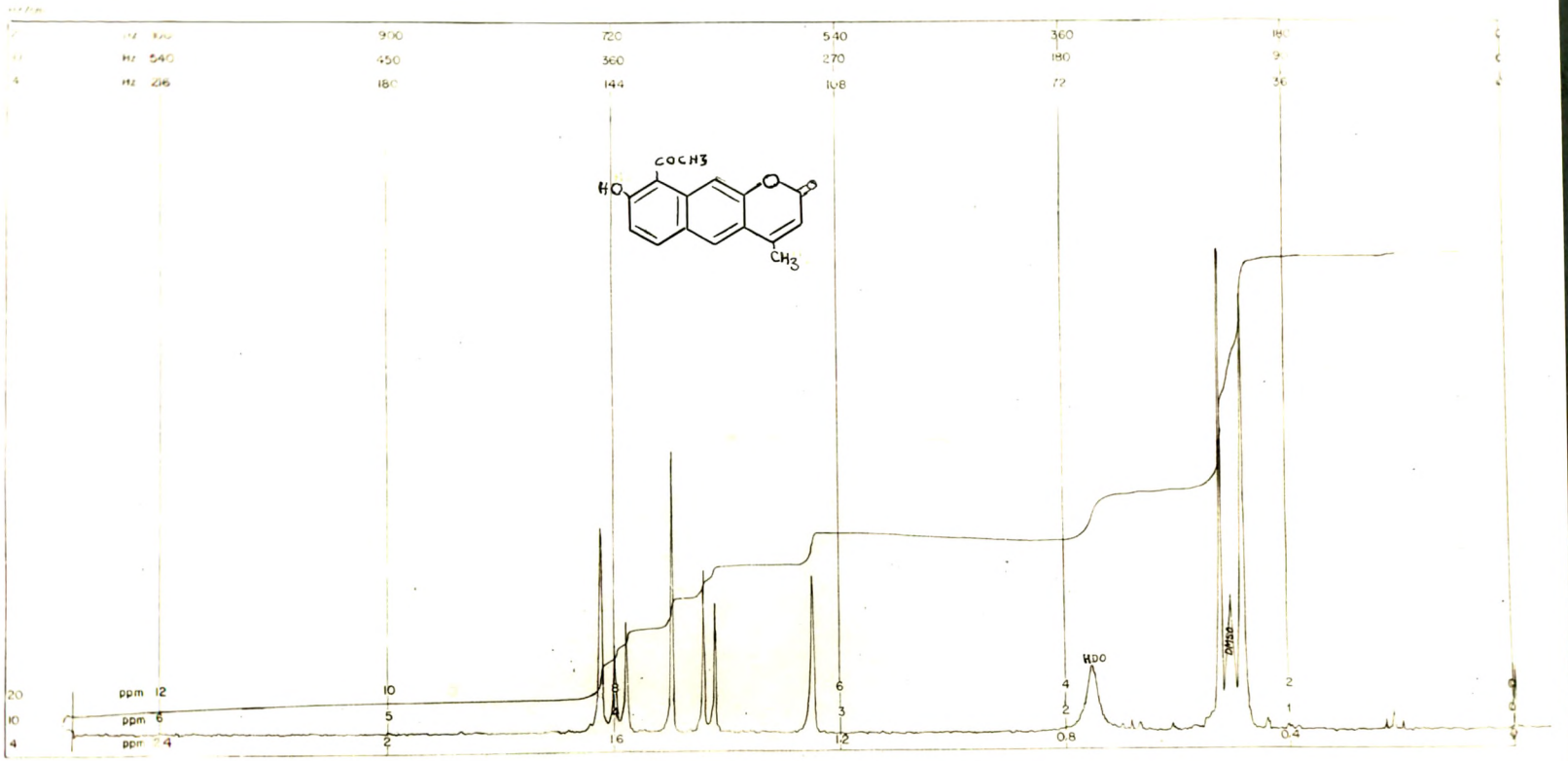
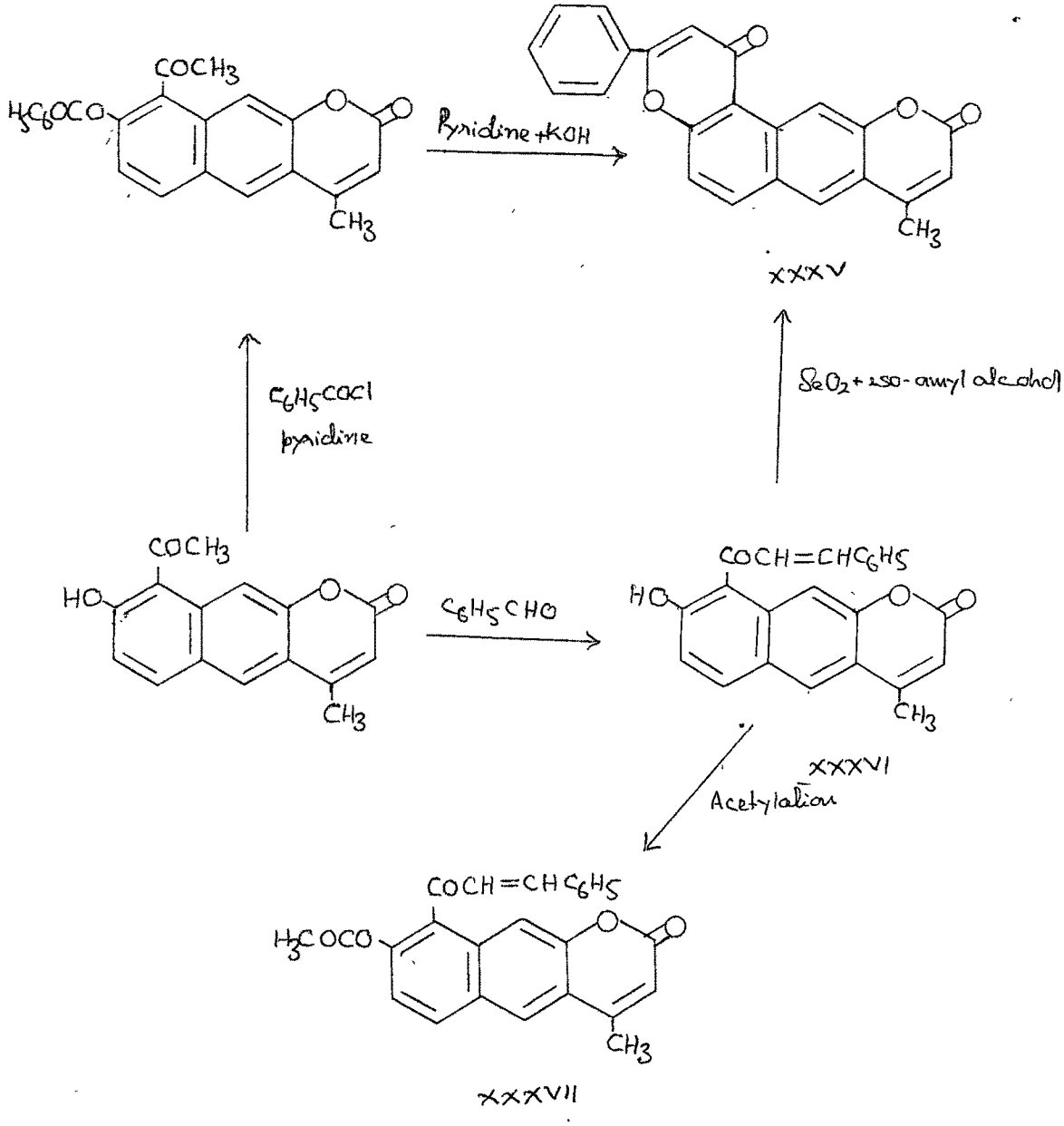


Fig. (XXXIV) :- NMR spectrum of 7-hydroxy-8-acetyl naphtho(2,3:6,5')a-pyrone. (DMSO)

Synthesis of 4'methyl naphtho(2,3:6',5')α-pyrono-2"-phenyl(7,8:6",5")γ-pyrone :

7-Hydroxy-8-acetyl-4'methyl naphtho(2,3:6',5') α-pyrone was converted into its benzoyl derivative with benzoyl chloride in pyridine. This in presence of pyridine and powdered potassium hydroxide at room temperature gave a product which was found insoluble in dilute alkali but was different from the original benzoyl derivative. It did not give any colouration with alcoholic ferric chloride. The compound was found to be the cyclised product to which 4'methyl naphtho(2,3:6',5')α-pyrono-2"-phenyl(7,8:6",5")γ-pyrone structure (XXXV) was assigned.

The same compound has also been synthesised through another route. 7-Hydroxy-8-acetyl-4'methyl naphtho (2,3:6',5')α-pyrone on condensation with benzaldehyde in the presence of alkali gave 7-hydroxy-8-cinnamoyl-4'-methyl naphtho (2,3:6',5')α-pyrone (XXXVI). It gave tests for a styryl ketone derivative viz. red colouration with conc. sulphuric acid and a positive Wilson test. It gave an acetoxy derivative (XXXVII) when refluxed with acetic anhydride and sodium acetate indicating that the hydroxyl group was free. 7-Hydroxy-8-cinnamoyl derivative on cyclisation and dehydrogenation with selenium dioxide in iso-amyl alcohol gave a product which did not give any colouration with sulphuric acid. 4'Methyl naphtho(2,3:6',5')α-pyrono-2"-phenyl (7,8:6",5")γ-pyrone structure is assigned to the product.

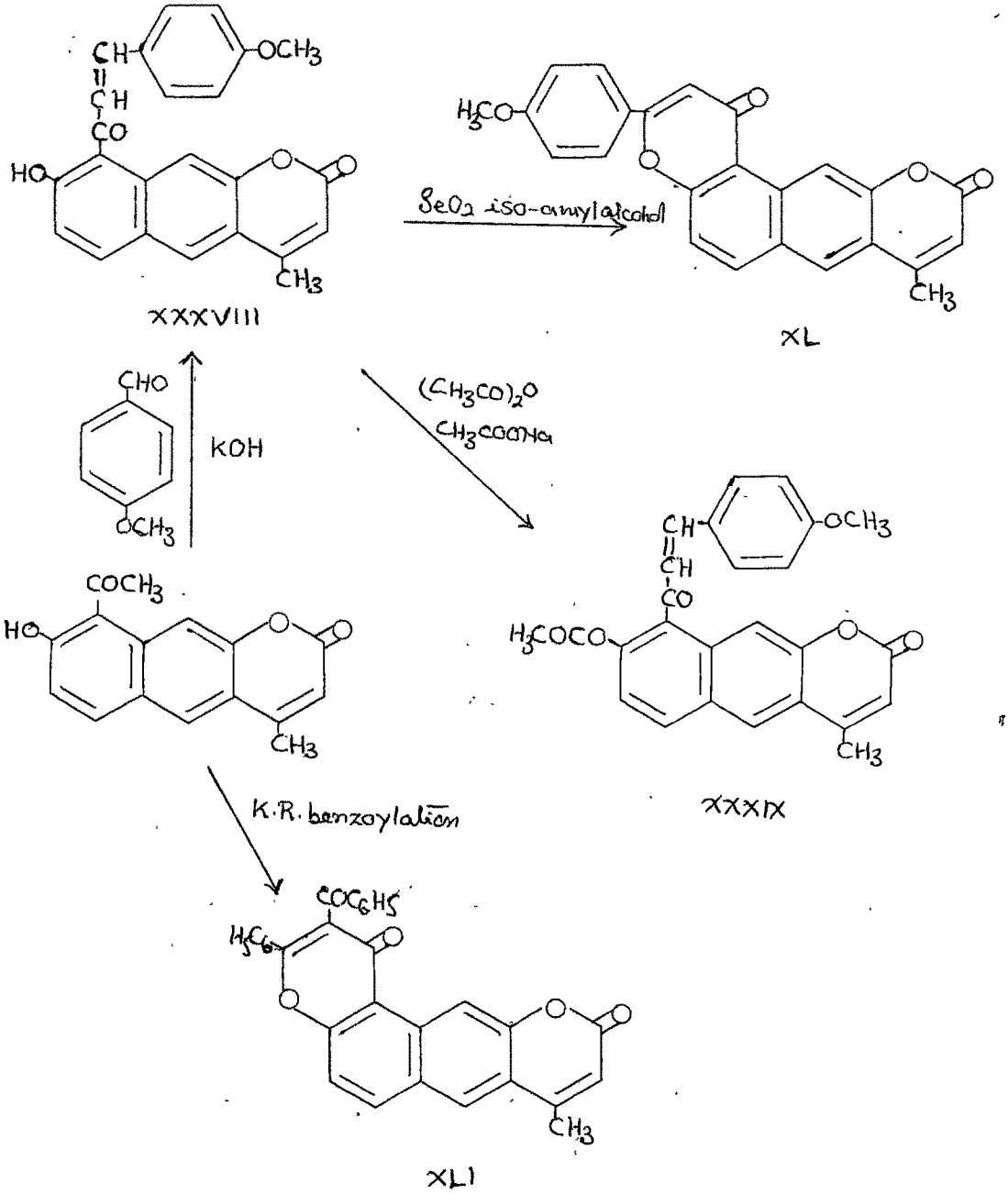

COCH3
H5C6OCO
CH3
Pyridine+KOH
XXXV
C6H5COCl
pyridine
SeO2+iso-amyl alcohol
COCH3
HO
CH3
C6H5CHO
COCH=CHC6H5
HO
CH3
XXXVI
Acetylation
COCH=CHC6H5
H3COCO
CH3
XXXVII

Synthesis of 4'-methyl naphtho (2,3:6,5')α-pyrono-2"(p-methoxy phenyl)(7,8:6",5")γ-pyrone :

7-Hydroxy-8-acetyl-4'-methyl naphtho(2,3:6,5') α-pyrone was condensed with anisaldehyde in the presence of alcoholic potassium hydroxide solution. The yellow product obtained on acidification gave a red colour with concentrated sulphuric acid and a positive Wilson test[9]. 7-Hydroxy-8-(p-methoxy cinnamoyl)-4'-methyl naphtho (2,3:6,5')α-pyrone (XXXVIII) structure has been assigned to this compound. It gave an acetoxy derivative (XXXIX) on refluxing with acetic anhydride and sodium acetate indicating that the hydroxy group was free. The above cinnamoyl ketone was then cyclised to 4'-methyl naphtho (2,3:6,5')α-pyrono-2"(p-methoxy phenyl)(7,8:6",5")γ-pyrone (XL) by refluxing with selenium dioxide in iso-amyl alcohol for 20 hr.

Kostanecki-Robinson benzoylation of 7-hydroxy-8-acetyl-4'-methyl naphtho(2,3:6,5')α-pyrone : 4'-Methyl naphtho(2,3:6,5')α-pyrono-2"-phenyl-3"-benzoyl (7,8:6",5")γ-pyrone :

7-Hydroxy-8-acetyl-4'-methyl naphtho(2,3:6,5') α-pyrone when subjected to Kostanecki-Robinson benzoylation with benzoic anhydride and freshly fused sodium benzoate gave the product which was insoluble in dilute alkali and did not give any colouration with alcoholic ferric chloride. It analysed for $C_{30}H_{18}O_5$ and the 4'-methyl naphtho(2,3:6,5') α-pyrono-2"-phenyl-3"-benzoyl(7,8:6",5")γ-pyrone(XLI)

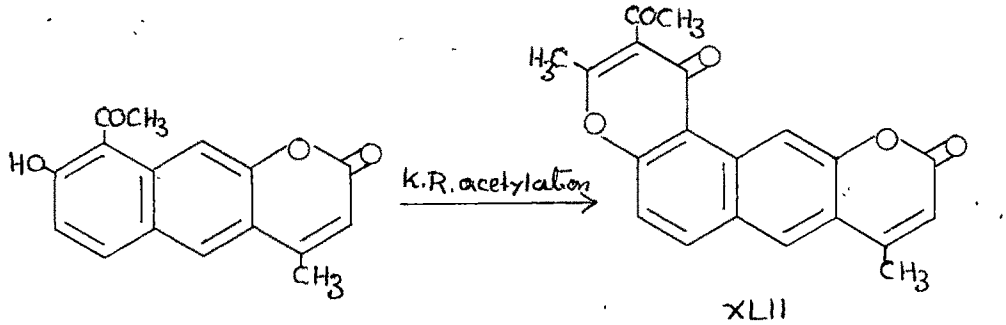

OCH3
CH
CH
CO
HO
CH3
XXXVIII
H3CO
SeO2 iso-amylalcohol
XL
CHO
KOH
OCH3
(CH3CO)2O
CH3COONa
COCH3
HO
CH3
OCH3
CH
CH
CO
H3COCO
CH3
XXXIX
K.R. benzoylation
COC6H5
H5C6
CH3
XLI

structure has been assigned to this product. Debenzoylation of this product with alcoholic potassium hydroxide did not succeed.

Synthesis of 4'-methyl naphtho(2,3:6',5')α-pyrono-2"-methyl-3"-acetyl(7,8:6",5")γ-pyrone :

7-Hydroxy-8-acetyl-4'-methyl naphtho(2,3:6',5') α-pyrone on Kostanecki-Robinson acetylation with acetic anhydride and freshly fused sodium acetate gave an alkali insoluble product. 4'-Methyl naphtho(2,3:6',5')α-pyrono-2"-methyl-3"-acetyl(7,8:6",5")γ-pyrone structure (XLII) is assigned to the product.

The I.R. showed three bands in carbonyl region viz. 1720 cm^{-1} (lactonyl >C=O group), 1680 cm^{-1} (acetyl group at 3" position) and 1635 cm^{-1} (γ-pyronyl >C=O group)

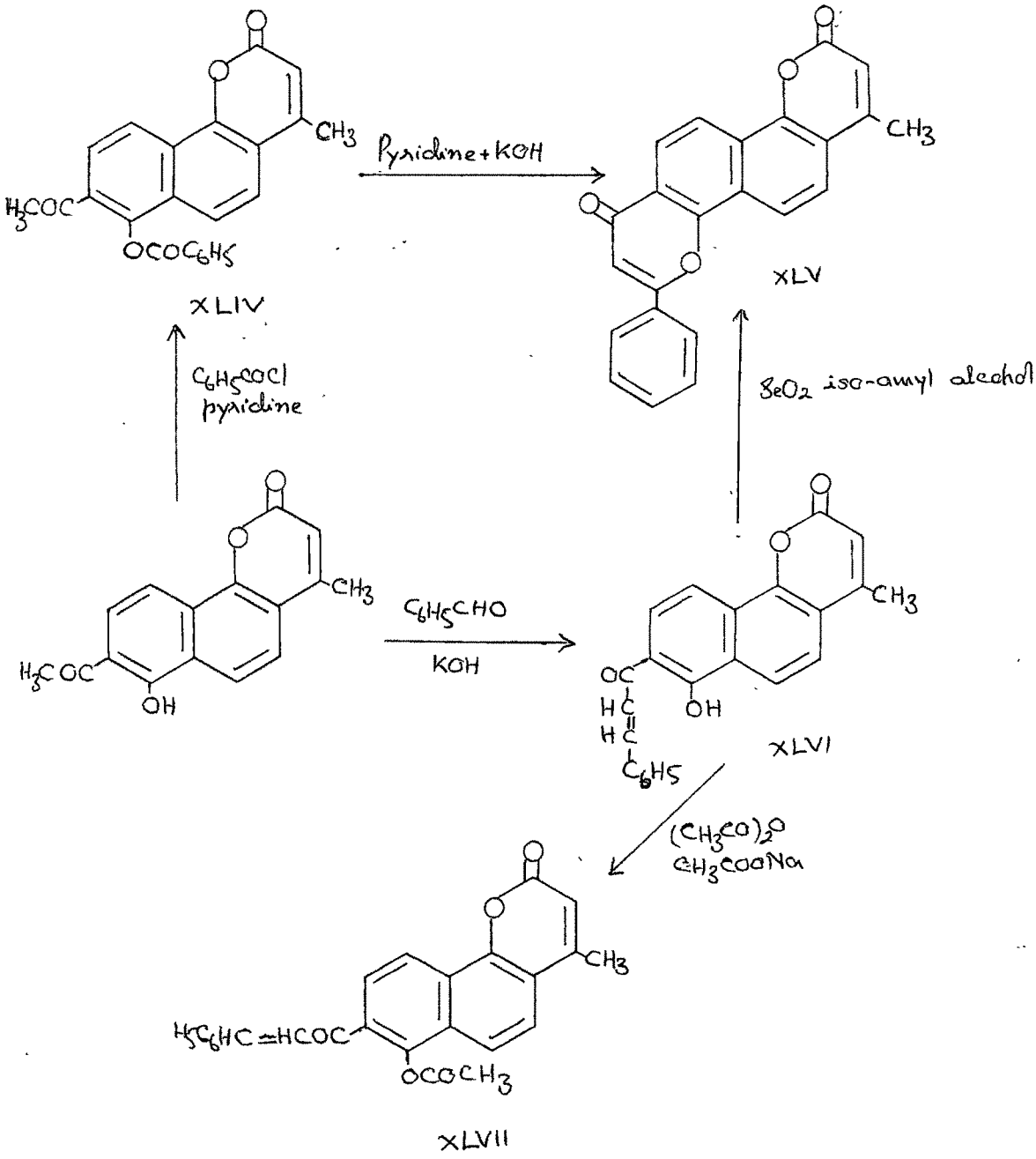


XLII

Synthesis of 4'-methyl naphtho(1,2:6,5')α-pyrono-2"-phenyl(5,6:6",5")γ-pyrone :

5-Hydroxy-6-acetyl-4'-methyl naphtho(1,2:6,5') α-pyrone (XLIII) prepared according to Mehta[8] was benzoylated with benzoyl chloride in pyridine. The benzoyl derivative (XLIV) was then subjected to Baker-Venkataraman rearrangement in the presence of pyridine and powdered potassium hydroxide. On working up as usual it affofded directly the cyclised product which was assigned 4'-methyl naphtho(1,2:6,5') α-pyrono-2"-phenyl(5,6:6",5")γ-pyrone (XLV). The structure of γ-pyrone derivative was also synthesised by condensing 5-hydroxy-6-acetyl-4-methyl naphtho(1,2:6,5')α-pyrone with benzaldehyde in the presence of potassium hydroxide, which resulted in 6-cinnamoyl-5-hydroxy-4'-methyl naphtho(1,2:6,5')α-pyrone (XLVI). It gave tests for a styryl ketone derivative viz. red colouration with concentrated sulphuric acid and positive Wilson test. It gave an acetoxy derivative (XLVII) with acetic anhydride and sodium acetate indicating that the hydroxy group was free. The 6-cinnamoyl derivative on cyclisation with selenium dioxide in iso-amyl alcohol gave product (XLV) which did not give any colouration with sulphuric acid.

I.R. showed two bands in the carbonyl region viz. 1730 cm^{-1} (lactonyl >C=O group) and 1640 cm^{-1} (γ-pyronyl >C=O)

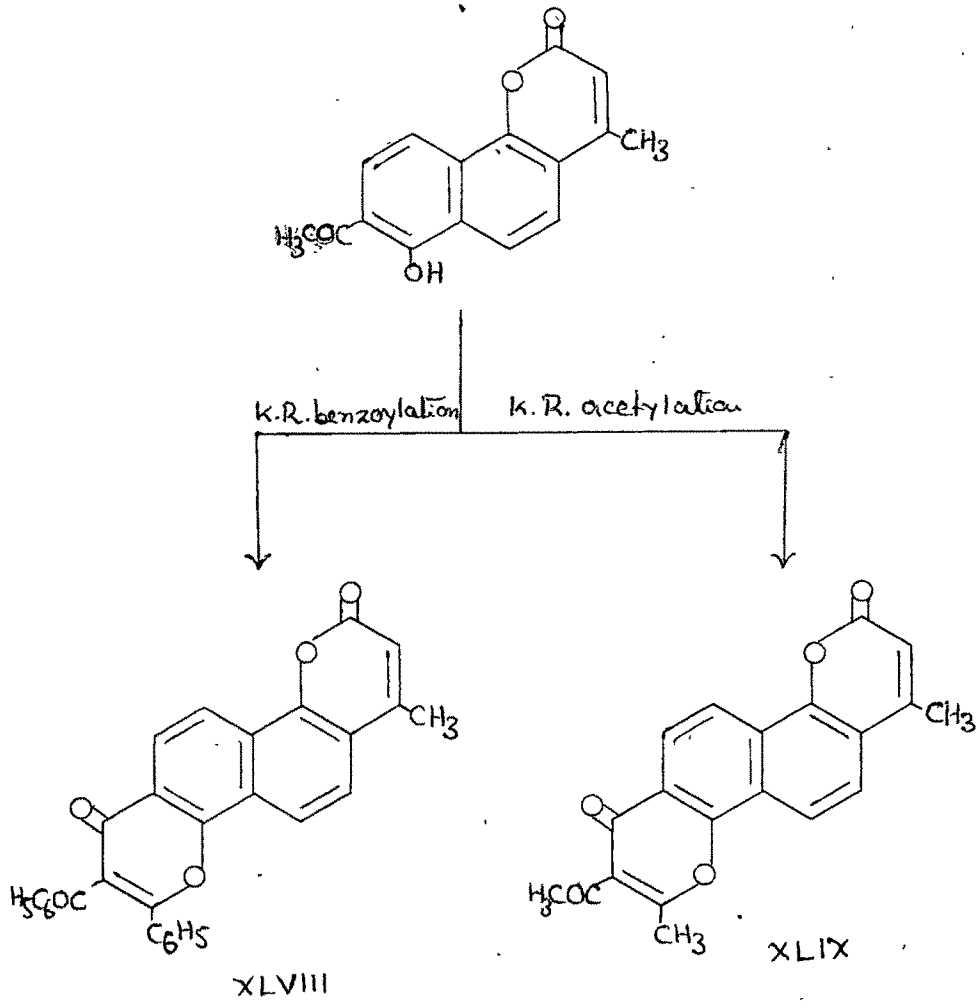

Pyridine+KOH
XLIV
XLV
C6H5COCl
pyridine
SeO2 iso-amyl alcohol
C6H5CHO
KOH
XLVI
(CH3CO)2O
CH3COONa
XLVII

Synthesis of 4'-methyl naphtho(1,2:6,5')α-pyrono-2"-phenyl-3"-benzoyl(5,6:6",5")γ-pyrone and 4'-methyl naphtho(1,2:6,5')α-pyrono-2"-methyl-3"-acetyl(5,6:6",5") γ-pyrone :

5-Hydroxy-6-acetyl-4'-methyl(1,2:6,5')α-pyrone when subjected to Kostanecki-Robinson benzoylation with benzoic anhydride and freshly fused sodium benzoate at 190-200° yielded a product which was insoluble in sodium hydroxide and did not give any colouration with alcoholic ferric chloride. It analysed for $C_{30}H_{18}O_5$. 4'-Methyl naphtho (1,2:6,5')α-pyrono-2"-phenyl-3"-benzoyl(5,6:6",5")γ-pyrone (XLVIII) structure has been assigned to the product. Its I.R.showed three bands in the carbonyl region viz. 1730 cm^{-1} (lactonyl >C=0 group) 1670 cm^{-1} (benzoyl group at position 3") and 1635 cm^{-1} (γ-pyronyl >C=0 group)

Similarly when the above o-hydroxy acetyl derivative was subjected to Kostanecki-Robinson acetylation with freshly fused sodium acetate and acetic anhydride at 170-80° yielded a product which was insoluble in dilute alkali and did not give any colouration with ferric chloride. It analysed for $C_{20}H_{14}O_5$. 4'-Methyl naphtho(1,2:6,5') α-pyrono-2"-methyl-3"-acetyl(5,6:6",5")γ-pyrone (XLIX) structure has been assigned to this product.

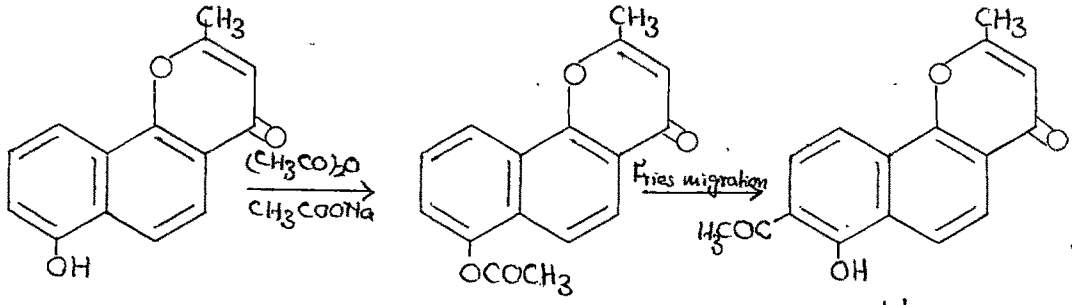
The I.R.showed three bands in the carbonyl region viz. 1755 cm^{-1} (lactonyl >C=0 group) 1690 cm^{-1} (acetyl group at position 3") and 1650 cm^{-1} (γ-pyronyl >C=0 group)



Fries rearrangement of 5-acetoxy-2'methyl naphtho (1,2:6,5')γ-pyrone : 5-Hydroxy-6-acetyl-2'methyl naphtho(1,2:6,5')γ-pyrone :

5-Acetoxy-2'methyl naphtho(1,2:6,5')γ-pyrone(L) prepared by acetylation of 5-hydroxy-2'methyl(1,2:6,5') γ-pyrone was subjected to Fries rearrangemant in the presence of anhydrous aluminium chloride. The yellow product obtained gave a green colour with alcoholic ferric chloride and was soluble in alkali. The structure assigned to this was 5-hydroxy-6-acetyl-2'methyl naphtho(1,2:6,5')γ-pyrone(LI).

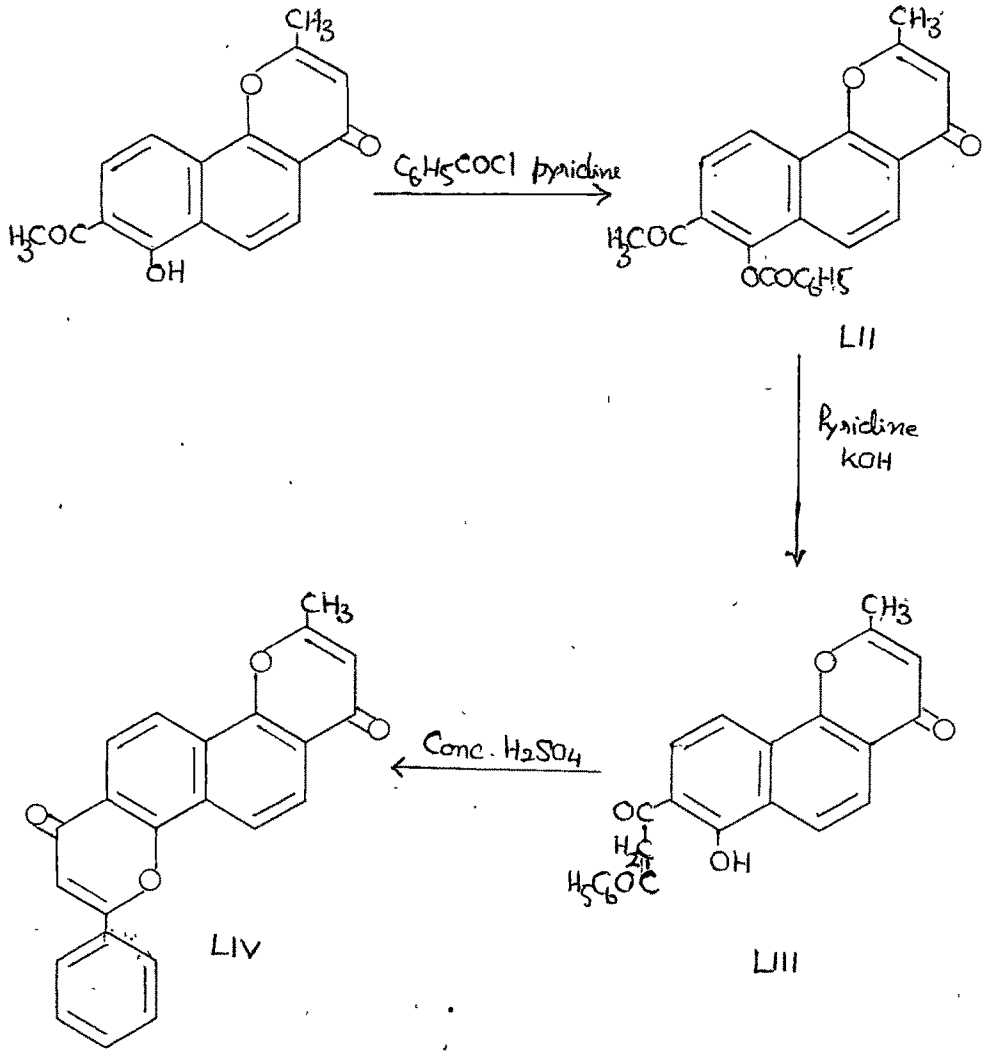
The ortho position of the acetyl group to the hydroxyl group has also been shown by the formation of the γ-pyrone derivatives as described below.



L LI

Synthesis of 2'-methyl-2"-phenyl naphtho(1,2:6,5') and 5,6:6",5")di-γ-pyrone :

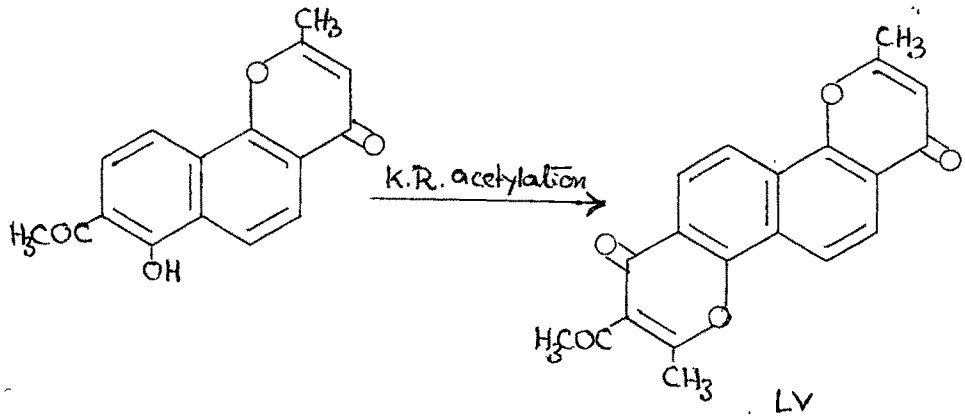
5-Hydroxy-6-acetyl-2'-methyl naphtho(1,2:6,5') γ-pyrone was refluxed with benzoyl chloride in pyridine when 6-acetyl-5-benzoyloxy-2'-methyl naphtho(1,2:6,5') γ-pyrone (LII) was obtained. This in presence of pyridine and powdered potassium hydroxide at room temperature gave the β-diketone derivative (LIII), which on cyclisation with conc.sulphuric acid by keeping overnight at room temperature gave a compound which was insoluble in dilute alkali. 2'-Methyl-2"-phenyl naphtho(1,2:6,5') and 5,6:6",5")di-γ-pyrone (LIV) structure has been assigned to this product.



Kostanecki-Robinson acetylation of 5-hydroxy-6-acetyl-2'methyl naphtho(1,2:6',5')γ-pyrone :

5-Hydroxy-6-acetyl-2'methyl naphtho(1,2:6',5') γ-pyrone when refluxed with acetic anhydride and freshly fused sodium acetate for 10 hr. at 170-80° afforded a product which was insoluble in dilute alkali and did not

give any colouration with alcoholic ferric chloride. It analysed for $C_{20}H_{14}O_5$. 2',2''-Dimethyl-3''-acetyl naphtho (1,2:6',5' and 5,6:6'',5'')di-γ-pyrone (LV), structure has been assigned to this product. Its I.R.spectrum showed two strong bands in the carbonyl region one at 1640 cm^{-1} (γ-pyronyl >C=O group) and the other at 1680 cm^{-1} (acetyl group at position 3'').



LV

EXPERIMENTAL

Fries rearrangement of 7-acetoxy naphtho(2,1:6',5') α-pyrone : 7-Hydroxy-6-acetyl naphtho (2,1:6',5') α-pyrone :

An intimate mixture of 7-acetoxy naphtho(2,1:6',5') α-pyrone (prepared as described on p.41.) (2 g.) and anhydrous aluminium chloride (5 g.) was heated in an oil bath at 140° for 3 hr. The reaction mixture was decomposed with ice cold hydrochloric acid. The yellow product obtained was taken in sodium hydroxide. The solid obtained on acidification was crystallised from xylene. M.P.278°. Yield 1.1 g.It gave a greenish brown colour with alcoholic ferric chloride.

Analysis : Found : C, 71.01 ; H, 3.71 %.

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

The 2,4-dinitro phenylhydrazone :

The above ketone was heated with a solution of 2,4-dinitro phenylhydrazine hydrochloride in alcohol and the separated red product was filtered and crystallised from dimethyl formamide. It gave m.p.293-4°.

Analysis : Found : N, 12.49 %.

$C_{21}H_{14}O_4N_4$ requires : N, 12.90 %.

Synthesis of 7-benzoyloxy-6-acetyl naphtho(2,1:6',5') α-pyrone :

7-Hydroxy-6-acetyl naphtho (2,1:6',5') α-pyrone (1 g.) was dissolved in pyridine (15 ml.) and benzoyl chloride (1 ml.) was added. The reaction mixture after

keeping for 2 hr. at room temperature was poured in ice cold hydrochloric acid. The pasty mass obtained was then washed with sodium bicarbonate solution and water to remove benzoic acid formed. The solid obtained was crystallised from acetic acid. M.P.225°. Yield 0.6 g.

Analysis : Found : C, 73.26 ; H, 3.50 %.

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

7-Hydroxy-6-(ω-benzoylacetyl)naphtho(2,1:6,5')α-pyrone :

The above benzoyloxy derivative (1 g.) was dissolved in pyridine (20 ml.) and powdered potassium hydroxide (4 g.) was added. The reaction mixture after keeping for 4 hr. at room temperature was poured in ice cold hydrochloric acid. The separated product was crystallised from alcohol. M.P. 275°. Yield 0.6 g.

Analysis : Found : C, 74.04 ; H, 4.10 %.

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

Cyclisation: Naphtho(2,1:6,5')α-pyrono-2''-phenyl (7,8:6'',5'')α-pyrone :

The above β-diketone (0.5 g.) was mixed with concentrated sulphuric acid (5 ml.) and kept at room temperature overnight. The product obtained on pouring the reaction mixture in ice cold water was washed with dilute alkali and water. It crystallised from dimethyl formamide in greenish needles (0.25 g.). M.P.338°.

Analysis : Found : C, 77.18 ; H, 3.38 %.

$C_{22}H_{12}O_4$ requires : C, 77.64 ; H, 3.53 %.

Kostanecki-Robinson benzoylation of 7-hydroxy-6-acetyl naphtho(2,1:6',5')α-pyrone : Naphtho(2,1:6',5')α-pyrono-2''-phenyl-3''-benzoyl(7,6:6'',5'')γ-pyrone :

A mixture of 7-hydroxy-6-acetyl naphtho(2,1:6',5')α-pyrone (1.5 g.), benzoic anhydride (5 g.) and freshly fused sodium benzoate (4 g.) was heated at 200° in an oil bath for 10 hr. The reaction mixture was kept with dilute sodium hydroxide solution for 30 minutes. The insoluble compound was filtered and washed with water. It crystallised from dimethyl formamide in light green tiny needles(0.7 g.). M.P.348.°

Analysis : Found : C, 78.25 ; H, 4.04 %.

$C_{29}H_{16}O_5$ requires : C, 78.38 ; H, 3.60 %.

Kostanecki-Robinson acetylation of 7-hydroxy-6-acetyl naphtho(2,1:6',5')α-pyrone : Naphtho(2,1:6',5')α-pyrono-2''-methyl-3''-acetyl(7,6:6'',5'')γ-pyrone :

7-Hydroxy-6-acetyl naphtho(2,1:6',5')α-pyrone (1 g.) was refluxed with freshly fused sodium acetate (3 g.) and acetic anhydride (8 ml.) in an oil bath at 190° for 10 hr. The reaction mixture was then poured into ice cold water and the separated solid was washed with dilute alkali to remove unreacted product and dried. It was dissolved in chloroform and the solution was run over a short column of alumina. The product was eluted with chloroform. After the removal of the solvent, the solid

obtained was crystallised from xylene. M.P.315°. Yield 0.4 g.

Analysis : Found : C, 71.19 ; H, 3.70 %.

$C_{19}H_{12}O_5$ requires : C, 71.25 ; H, 3.75 %.

Fries rearrangement of 7-acetoxy-4'-methyl naphtho (2,3:6',5')α-pyrone : 7-Hydroxy-8-acetyl-4'-methyl naphtho(2,3:6',5')α-pyrone :

Acetylation :

7-Hydroxy-4'-methyl naphtho(2,3:6',5')α-pyrone (2 g.) was refluxed with acetic anhydride(10 ml.) and freshly fused sodium acetate (4 g.) for 1 1/2 hr. The reaction mixture was poured in cold water. The separated solid was dried and crystallised from xylene in colourless needles (1.5 g.), m.p.204°.

Analysis : Found : C, 71.66 ; H, 4.66 %.

$C_{16}H_{12}O_4$ requires : C, 71.64 ; H, 4.47 %.

The above acetoxy derivative (2 g.) was intimately mixed with anhydrous aluminium chloride(5 g.) and the mixture was heated in an oil bath at 140° for 3 hr. The reaction mixture was decomposed with ice cold hydrochloric acid. The product crystallised from alcohol in yellow needles (1.2 g.). M.P.236°. It gave wine red colour with alcoholic ferric chloride.

Analysis : Found : C, 71.31 ; H, 4.47 %.

$C_{16}H_{12}O_4$ requires : C, 71.64 ; H, 4.47 %.

The 2,4-dinitro phenylhydrazone :-

It was prepared from the above ketone as usual and crystallised from dimethyl formamide in fine orange needles, m.p.315°(decomp.)

Analysis : Found : N, 12.69 %.

$C_{22}H_{16}O_7N_4$ requires : N, 12.50 %.

7-Benzoyloxy-8-acetyl-4'-methyl naphtho(2,3:6',5') α-pyrone :

To a solution of 7-hydroxy-8-acetyl-4'-methyl naphtho(2,3:6',5')α-pyrone(1 g.) in pyridine, benzoyl chloride (1.5 ml.) was added. The reaction mixture was kept for 2 hr. at room temperature. The product obtained on decomposition was washed with sodium bicarbonate solution and water. It crystallised from acetic acid, m.p.225°. Yield 0.6 g.

Analysis : Found : C, 74.30 ; H, 3.98 %.

$C_{23}H_{16}O_5$ requires : C, 74.20 ; H, 4.30 %.

4'-Methyl naphtho(2,3:6',5')α-pyrono- 2''-phenyl (7,8:6'',5'')γ-pyrone :

The above benzoyloxy derivative(1 g.) was dissolved in pyridine (20 ml.) and powdered potassium hydroxide(4 g.) was added with stirring. The reaction mixture after keeping for 4 hr. at room temperature was poured in ice cold hydrochloric acid. The product obtained crystallised from dimethyl formamide. It was insoluble in alkali, m.p.357°.

Yield 0.4 g. It was almost insoluble in most of the common organic solvents.

Analysis : Found : C, 78.20 ; H, 3.93 %.

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

7-Hydroxy-8-cinnamoyl-4'-methyl naphtho(2,3:6,5') α-pyrone :

To a mixture of 7-hydroxy-8-acetyl-4'-methyl naphtho(2,3:6,5')α-pyrone (1 g.) and benzaldehyde (1 ml.) in alcohol (100 ml.), potassium hydroxide (5 g. in 5 ml.water) was added and the reaction mixture was kept overnight. The mixture after dilution with ice cold water and acidification with conc.hydrochloric acid gave a product which was washed with sodium bicarbonate and water. The solid obtained was sparingly soluble in all solvents. It crystallised from dimethyl formamide in fine yellow plates(0.5 g.), m.p.306°.

It gave yellow colouration with dry acetone solution of citric acid-boric acid mixture.

Analysis : Found : C, 77.18 ; H, 4.26 %.

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

The acetyl derivative :

The above cinnamoyl derivative (0.3 g.) was refluxed with acetic anhydride (3 ml.) and fused sodium acetate (1 g.) for an hour. The product separated on pouring the reaction mixture in ice cold water crystallised from alcohol in light yellow crystals(0.2 g.), m.p.212°.

Analysis : Found : C, 75.26 ; H, 4.50 %.

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

4'Methyl naphtho(2,3:6',5')α-pyrono-2"-phenyl(7,8:6",5") γ-pyrone :

7-Hydroxy-8-cinnamoyl-4'methyl naphtho(2,3:6',5') α-pyrone (0.5 g.) was dissolved in dry iso-amyl alcohol (50 ml.) by refluxing and selenium dioxide(3 g.) was added. The mixture was refluxed in an oil bath at 135-40° for 24 hr. It was filtered hot. The separated product was crystallised from dimethyl formamide. M.P. and mixed m.p. with 4'methyl naphtho(2,3:6',5')α-pyrono-2"-phenyl(7,8:6",5") γ-pyrone prepared by Baker-Venkataraman transformation method was 357°.

7-Hydroxy-8-(p-methoxy cinnamoyl)-4'methyl naphtho (2,3:6',5')α-pyrone :

To a mixture of 7-hydroxy-8-acetyl-4'methyl (2,3:6',5')α-pyrone (1 g.) and anisaldehyde (1 ml.) in alcohol (100 ml.), potassium hydroxide (5 g. in 5 ml.water) was added and the reaction mixture was left overnight. The mixture after dilution with ice cold water and acidification with conc.hydrochloric acid gave a product which was taken in alkali after filtration and washing with bicarbonate solution. The yellow compound obtained on acidification of alkaline solution was crystallised from xylene. Yield 0.5 g. M.P. 265°. It gave a red colour with conc.sulphuric acid and yellow colouration with dry acetone solution of citric acid-boric acid mixture.

Analysis : Found : C, 74.15 ; H, 4.47 %.

$C_{24}H_{18}O_5$ requires : C, 74.61 ; H, 4.66 %.

7-Acetoxy-8-(p-methoxycinnamoyl)-4'methyl naphtho (2,3:6',5')α-pyrone :

7-Hydroxy-8-(p-methoxycinnamoyl)-4'methyl naphtho (2,3:6',5')α-pyrone (0.2 g.) was refluxed with (1.5 ml.) acetic anhydride and fused sodium acetate for an hour. The product obtained on pouring the reaction mixture in cold water crystallised from alcohol, m.p.205°.

Analysis : Found : C, 72.41 ; H, 4.38 %.

$C_{26}H_{20}O_6$ requires : C, 72.90 ; H, 4.67 %.

4'Methyl naphtho(2,3:6',5')α-pyrono-2''-(p-methoxy phenyl) (7,8:6'',5'')γ-pyrone :

7-Hydroxy-8-(p-methoxycinnamoyl)-4'methyl naphtho (2,3:6',5')α-pyrone (0.5 g.) was refluxed in dry iso-amyl alcohol(50 ml.) with selenium dioxide (3 g.) at 135-40° in an oil bath for 24 hr. It was filtered hot. The separated product was crystallised from dimethyl formamide in yellow crystalline product, m.p.348-50°. Yield 0.2 g.

Analysis : Found : C, 74.59 ; H, 3.90 %.

$C_{24}H_{16}O_5$ requires : C, 75.00 ; H, 4.16 %.

Kostanecki-Robinson benzoylation of 7-hydroxy-8-acetyl-4'methyl naphtho(2,3:6',5')α-pyrone : 4'Methyl naphtho(2,3:6',5')α-pyrono-2''-phenyl-3''-benzoyl (7,8:6'',5'')γ-pyrone :

A mixture of 7-hydroxy-8-acetyl-4'methyl naphtho (2,3:6',5')α-pyrone (1 g.), benzoic anhydride (5 g.) and

freshly fused sodium benzoate (4 g.) was heated at 200° in an oil bath for 12 hr. After cooling, the reaction mixture was kept in dilute sodium hydroxide solution for some time and insoluble product obtained was filtered and washed with water. The product obtained was crystallised from xylene, m.p.282°. Yield 0.4 g.

Analysis : Found : C, 78.79 ; H, 3.79 %.

$C_{30}H_{18}O_5$ requires : C, 78.59 ; H, 3.93 %.

Attempted debenzoylation :

The above 4'-methyl naphtho(2,3:6',5')α-pyrono-2''-phenyl-3''-benzoyl(7,8: 6'',5'')γ-pyrone (0.3 g.) was refluxed with alcoholic potassium hydroxide solution (10 ml. 10 %) for 1 1/2 hr. The product obtained on acidification of the reaction mixture crystallised from xylene, m.p.280°. Mixed m.p. with the original product was not depressed.

Kostanecki-Robinson acetylation of 7-hydroxy-8-acetyl-4'-methyl naphtho(2,3:6',5')α-pyrone : 4'-Methyl naphtho(2,3:6',5')α-pyrono-2''-methyl-3''-acetyl(7,8:6'',5'')γ-pyrone :

7-Hydroxy-8-acetyl-4'-methyl naphtho(2,3:6',5')α-pyrone (1 g.) was refluxed with acetic anhydride(7 ml.) and fused sodium acetate (3 g.) at 180° for 12 hr. The product obtained after working up as usual crystallised from diphenyl ether. M.P.above 335°. Yield 0.4 g.

Analysis : Found : C, 71.80 ; H, 4.14 %.

$C_{20}H_{14}O_5$ requires : C, 71.86 ; H, 4.19 %.

5-Benzoyloxy-6-acetyl-4'-methyl naphtho(1,2:6',5') α-pyrone :

5-Hydroxy-6-acetyl-4'-methyl naphtho(1,2:6',5') α-pyrone (1 g.) dissolved in pyridine (15 ml.) and a few drops of piperidine were added to it. After adding benzoyl chloride (1.5 ml.), the reaction mixture was left for 2 hr. at room temperature with occasional shaking. On working up as usual, the product obtained was crystallised from acetic acid in fine yellow needles (0.6 g.). M.P.185°.

Analysis : Found : C, 74.48 ; H, 4.40 %.

$C_{23}H_{16}O_5$ requires : C, 74.20 ; H, 4.30 %.

4'-Methyl naphtho(1,2:6',5')α-pyrono-2''-phenyl (5,6:6'',5'')γ-pyrone :

5-Benzoyloxy-6-acetyl-4'-methyl naphtho(1,2:6',5') α-pyrone (1 g.) was dissolved in pyridine (20 ml.) and powdered potassium hydroxide (4 g.) was added with stirring. The reaction mixture after keeping for 4 hr. at room temperature was poured in ice cold hydrochloric acid. The product obtained was treated with sodium bicarbonate and then with sodium hydroxide solution. The product obtained was insoluble in sodium hydroxide. It was crystallised from dimethyl formamide in cream coloured needles(0.4 g.). M.P.310°.

Analysis : Found : C, 77.80 ; H, 3.87 %.

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

Synthesis of 5-hydroxy-6-cinnamoyl-4'-methyl naphtho (1,2:6,5')α-pyrone :

To a mixture of 5-hydroxy-6-acetyl-4'-methyl naphtho(1,2:6,5')α-pyrone (1 g.) and benzaldehyde (1 ml.) in alcohol (100 ml.), potassium hydroxide (5 g. in 5 ml. water) was added in a lot and the reaction mixture was kept overnight. The mixture after dilution with ice cold water and acidification with concentrated hydrochloric acid gave a product which after washing with sodium bicarbonate solution and water was crystallised from acetic acid, m.p. 261°. Yield 0.6 g. It gave a dark red colour with concentrated sulphuric acid.

Analysis : Found : C, 77.23 ; H, 4.77 %.

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

5-Acetoxy-6-cinnamoyl-4'-methyl naphtho(1,2:6,5') α-pyrone :

5-Hydroxy-6-cinnamoyl-4'-methyl naphtho(1,2:6,5') α-pyrone (0.3 g.) was refluxed with acetic anhydride(1.5 ml.) and fused sodium acetate (1 g.) for an hour. After pouring the reaction mixture in ice cold water the product obtained was crystallised from dimethyl formamide in light yellow flat plates. M.P.229°.

Analysis : Found : C, 75.39 ; H, 4.97 %.

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

4'-Methyl naphtho(1,2:6',5')α-pyrono-2''-phenyl (5,6:6'',5'')γ-pyrone :

5-Hydroxy-6-cinnamoyl-4'-methyl naphtho (1,2:6',5')α-pyrone (0.5 g.) was dissolved in dry iso-amyl alcohol (75 ml.) by refluxing and selenium dioxide(3 g.) was added. The mixture was refluxed in an oil bath at 135-40° for 20 hr. It was filtered hot. The separated product was crystallised from dimethyl formamide in cream coloured needles. M.P. and mixed m.p.with 4'-methyl naphtho (1,2:6',5')α-pyrone-2 -phenyl(5,6: 6 ,5)described above was 310°.

Kostanecki-Robinson benzoylation of 5-hydroxy-6-acetyl-4'-methyl naphtho(1,2:6',5')α-pyrone : 4'-Methyl naphtho(1,2:6',5')α-pyrono-2''-phenyl-3''-benzoyl (5,6 : 6'',5'')γ-pyrone:

An intimate mixture of 5-hydroxy-6-acetyl-4'-methyl naphtho(1,2:6',5')α-pyrone (1 g.), benzoic anhydride(5 g.) and freshly fused sodium benzoate (3 g.) was heated in an oil bath at 200° for 12 hr. The reaction mixture was taken in sodium bicarbonate solution to remove benzoic acid formed. The solid obtained after washing with dilute sodium hydroxide and water was crystallised from dimethyl formamide m.p.320-24°. Yield 0.4 g.

Analysis : Found : C, 78.10 ; H, 4.00 %.

$C_{30}H_{18}O_5$ requires : C, 78.59 ; H, 3.93 %.

Kostanecki-Robinson acetylation of 5-hydroxy-6-acetyl-4'methyl naphtho(1,2:6',5')α-pyrone : 4'-Methyl naphtho(1,2:6',5')α-pyrono-2''-methyl-3''-acetyl (5,6:6'',5'')γ-pyrone :

5-Hydroxy-6-acetyl-4'methyl naphtho(1,2:6',5') α-pyrone (1 g.) was refluxed with acetic anhydride(7 ml.) and freshly fused sodium acetate (3 g.) at 180-90° in an oil bath for 10 hr. The reaction mixture was then poured in cold water. The separated solid was washed with dilute sodium hydroxide solution then with water. It crystallised from dimethyl formamide, m.p. 297-98°. Yield 0.4 g.

Analysis : Found : C, 71.68 ; H, 4.66 %.

$C_{20}H_{14}O_5$ requires : C, 71.86 ; H, 4.19 %.

5-Acetoxy-2'methyl naphtho(1,2:6',5')γ-pyrone :

5-Hydroxy-2'methyl naphtho(1,2:6',5')γ-pyrone (2 g.) was refluxed with acetic anhydride (10 ml.) and fused sodium acetate (5 g.) for 1 1/2 hr. The reaction mixture was then poured in ice cold water, after filtration, it crystallised from alcohol in light brown needles(1.6 g.). M.P.193°.

Analysis : Found : C, 71.31 ; H, 4.56 %.

$C_{16}H_{12}O_4$ requires : C, 71.64 ; H, 4.47 %.

Fries rearrangement of 5-acetoxy-2'methyl naphtho (1,2:6',5')γ-pyrone : 5-Hydroxy-6-acetyl-2'methyl naphtho(1,2:6',5')γ-pyrone :

An intimate mixture of 5-acetoxy-4'methyl naphtho

(1,2:6',5')γ-pyrone (2 g.) and anhydrous aluminium chloride (5 g.) was heated in an oil bath for 3 hr. The reaction mixture was decomposed as usual with ice cold hydrochloric acid (1:1). The solid obtained was taken in sodium hydroxide solution. The yellow product which separated on acidification crystallised from xylene in fine yellow wooly needles(0.8 g.) m.p.275-6°. It gave a green colour with alcoholic ferric chloride.

Analysis : Found : C, 71.37 ; H, 4.65 %.

$C_{16}H_{12}O_4$ requires : C, 71.64 ; H, 4.47 %.

Synthesis of 5-benzoyloxy-6-acetyl-2'methyl naphtho (1,2:6',5')γ-pyrone :

A mixture of 5-hydroxy-6-acetyl-2'methyl naphtho (1,2:6',5')γ-pyrone (2.0 g.) in pyridine (25 ml.), a few drops of piperidine and benzoyl chloride (4 ml.) was refluxed on a steam bath for 2 hr. The reaction mixture was then poured in ice cold hydrochloric acid (1:1). The pasty mass which separated was treated with sodium bicarbonate solution followed by water. The separated solid crystallised from benzene in light yellow thick needles(1.1 g.). M.P.211°.

Analysis : Found : C, 73.87 ; H, 4.27 %.

$C_{23}H_{16}O_5$ requires : C, 74.20 ; H, 4.30 %.

5-Hydroxy-6(ω-benzoyl acetyl)-2'methyl naphtho (1,2:6',5')γ-pyrone :

5-Benzoyloxy-6-acetyl-2'methyl naphtho(1,2:6',5') γ-pyrone (1 g.) was dissolved in pyridine (20 ml.) and

powdered potassium hydroxide (4 g.) was added. The reaction mixture after keeping for 4 hr. at room temperature was poured in ice cold hydrochloric acid. The product obtained was taken in sodium hydroxide. Acidification of this resulted in a yellow product crystallised from acetic acid. M.P.244°. Yield 0.6 g.

Analysis : Found : C, 73.77 ; H, 4.53 %.

$C_{23}H_{16}O_5$ requires : C, 74.20 ; H, 4.30 %.

Cyclisation: 2'-Methyl-2''-phenyl naphtho(1,2:6,5' and 5,6: 6'',5'')di-γ-pyrone :

The above β-diketone (0.5 g.) was mixed with concentrated sulphuric acid (5 ml.) and kept overnight at room temperature. The product obtained on pouring the reaction mixture in ice cold water was washed with dilute alkali. It crystallised from xylene. M.P.330°.Yield 0.25 g.

Analysis : Found : C, 78.00 ; H, 4.33 %.

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

Kostanecki-Robinson acetylation of 5-hydroxy-6-acetyl 2'-methyl naphtho(1,2:6,5')γ-pyrone : 2',2''-Dimethyl-3''-acetyl naphtho(1,2:6,5' and 5,6:6'',5'')di-γ-pyrone :

5-Hydroxy-6-acetyl-2'-methyl naphtho(1,2:6,5') γ-pyrone(1 g.) was dissolved in acetic anhydride(8 ml.) and refluxed with freshly fused sodium acetate(3 g.) at 180° in an oil bath for 12 hr. The reaction mixture was poured in cold water.The separated product was washed with dilute alkali and water.It crystallised from acetic acid,m.p. 302°.

Yield 0.5 g.

Analysis : Found : C, 71.45 ; H, 4.64 %.

$C_{20}H_{14}O_5$ requires : C, 71.86 ; H, 4.19 %.

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