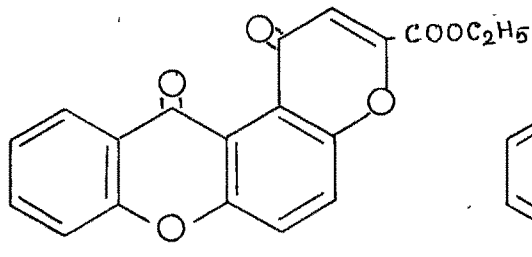
CHAPTER IV

SYNTHESIS OF PYRONO- AND FURANOXANTHONES

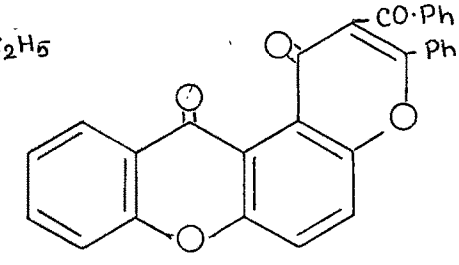
THEORETICAL

SYNTHESIS OF 4'-PYRONOXANTHONES

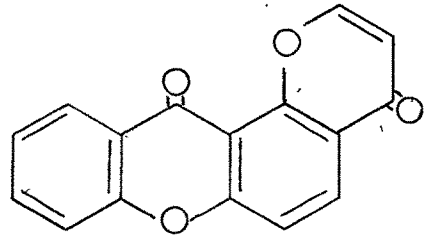
There are a few references available in the literature on the synthesis of 4'-pyronoxanthones. Lamb and Suschitzky[1] have prepared angular 4'-pyronoxanthones from 2-hydroxy-1-acetylxanthone. 2'-Carbethoxy-4'-pyrono(6',5':2,1) xanthone (I), was prepared by Claisen condensation of 2-hydroxy-1-acetylxanthone with diethyl oxalate and cyclisation of the condensed product in ethanol with hydrochloric acid. The 4'-pyronoxanthone (II) was prepared by the Kostanecki-Robinson benzoylation of 2-hydroxy-1-acetyl-xanthone. Davies et al.[2] have prepared the 4'-pyronoxanthone (III) by the Claisen condensation of 2-acetyl-1-hydroxyxanthone



(I)

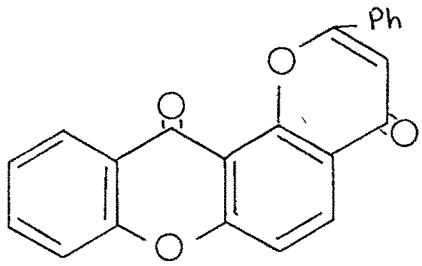


(II)



(III)

with diethyl oxalate. They report that the attempts to prepare 4'-pyrono derivatives through the condensation of ethyl acetate with 2-acetyl-1-hydroxyxanthone or by Kostanecki-Robinson acetylation of the ketone were unsuccessful. 2-Acetyl--1-hydroxyxanthone also did not condense with ethyl formate. Mustafa et al.[3] have prepared 1-hydroxy-2-cinnamoylxanthone by Friedel-Crafts cinnamoylation and subjected it to cyclo-dehydrogenation by selenium dioxide, which resulted in the 4'pyronoxanthone (IV). Da Re and others[4] have prepared the 4'-pyronoxanthone (V) from 3-hydroxy-4-propionylxanthone by Kostanecki-Robinson acetylation. They have also prepared 2'-phenyl-4'-pyrono(6',5':3,4)xanthone (VI), through the



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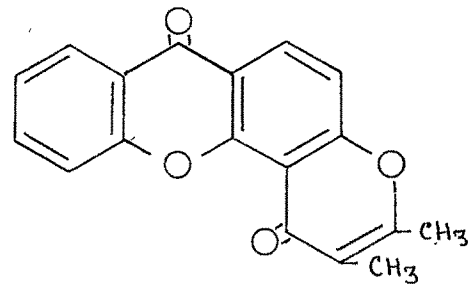

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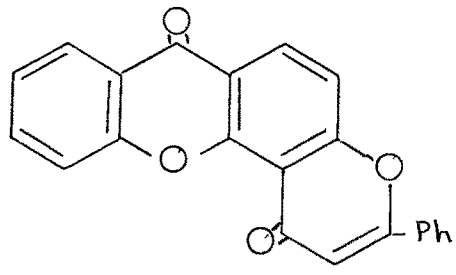


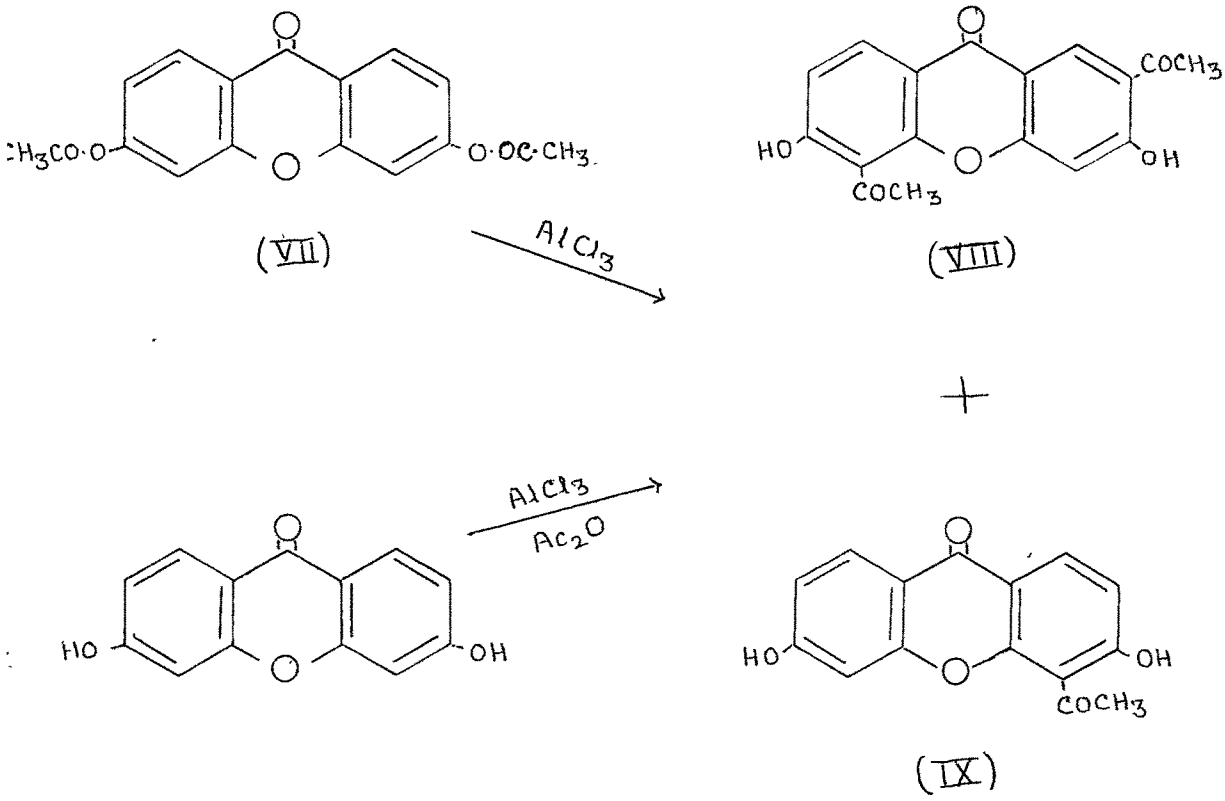
(VI)

styryl ketone obtained from 3-hydroxy-4-acetylxanthone and benzaldehyde. Cyclisation was effected by selenium dioxide.

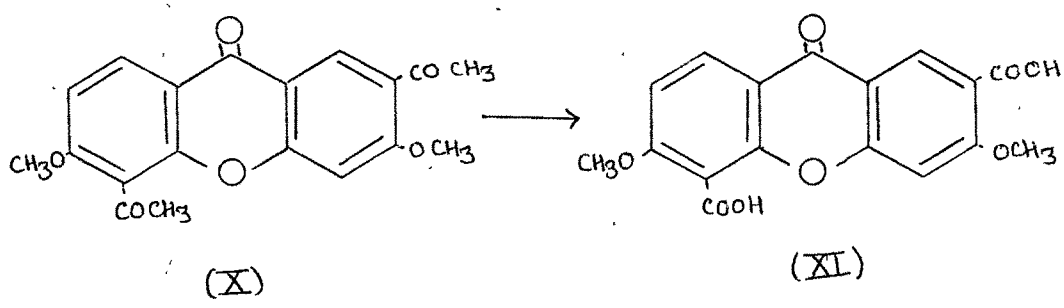
As the work done on the synthesis of 4'-pyrono-xanthones from various hydroxyxanthones has been meagre, it was thought of interest to study the synthesis of such compounds from various hydroxyxanthones.

Fries migration and Friedel-Crafts acetylation of 3,6-dihydroxyxanthone :

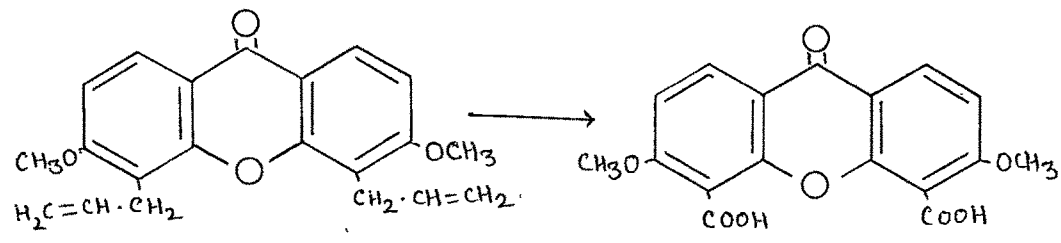
Fries migration and Friedel-Crafts acylation of xanthones have been reviewed in the Chapter I. As the o-hydroxyacetyl xanthones are the intermediates for the synthesis of 4'-pyronoxanthones, the work on Friedel-Crafts acetylation and Fries migration was undertaken. Literature survey showed that Lamb and Suschitzky[1] have reported the Fries rearrangement and Friedel-Crafts acetylation to be unsuccessful with 2-hydroxyxanthone. We repeated the work and found it to be so. Da Re et al.[4] have reported that the attempts to obtain 3,6-dihydroxy-4,5-diacetylxanthone either by Fries or Friedel-Crafts method were unsuccessful. We were, however, successful in getting a mixture of a diacetyl (VIII) alongwith a monoacetyl (IX) derivative, when 3,6-diacetoxy-xanthone (VII) was subjected to Fries rearrangement in the presence of aluminium chloride. The diacetyl derivative was obtained in a pure form after repeated crystallisations from nitrobenzene, while the monoacetyl derivative remained in the mother liquor. Acetylation of 3,6-dihydroxyxanthone by acetic anhydride in the presence of aluminium chloride at 140-60°



also gave a mixture containing the mono- and the diacetyl derivatives, but the yields were slightly inferior as the mixture contained original 3,6-dihydroxyxanthone also. The NMR spectrum of the diacetyl derivative could not be taken as the compound was very sparingly soluble in chloroform and dimethyl sulphoxide. It has, however, been assigned the unsymmetrical 3,6-dihydroxy-2,5-diacetylxanthone structure (VIII) tentatively. The diacetylxanthone cannot be 3,6-dihydroxy-4,5-diacetylxanthone as the dimethyl ether of the diacetyl derivative (X) on oxidation gave a dicarboxylic acid, m.p. 236°, which was different from the 3,6-dimethoxyxanthone-4,5-dicarboxylic acid (XIII), m.p. 282°, obtained by the oxidation of 3,6-dimethoxy-4,5-diallylxanthone (XII), the



(X) (XI)



(XII) (XIII)

structure of which was arrived at by its NMR spectrum in $CDCl_3$. The possibility of the other symmetrical structure 3,6-dihydroxy-2,7-diacetylxanthone may be ruled out as in the case of iodination, nitration and chloromethylation[4] the first electrophillic attack is on the 4-position. The structure of the monoacetylxanthone (IX) has been established on the basis of the NMR data as described later. Methylation of 3,6-dihydroxy-2,5-diacetylxanthone gave the dimethyl ether.

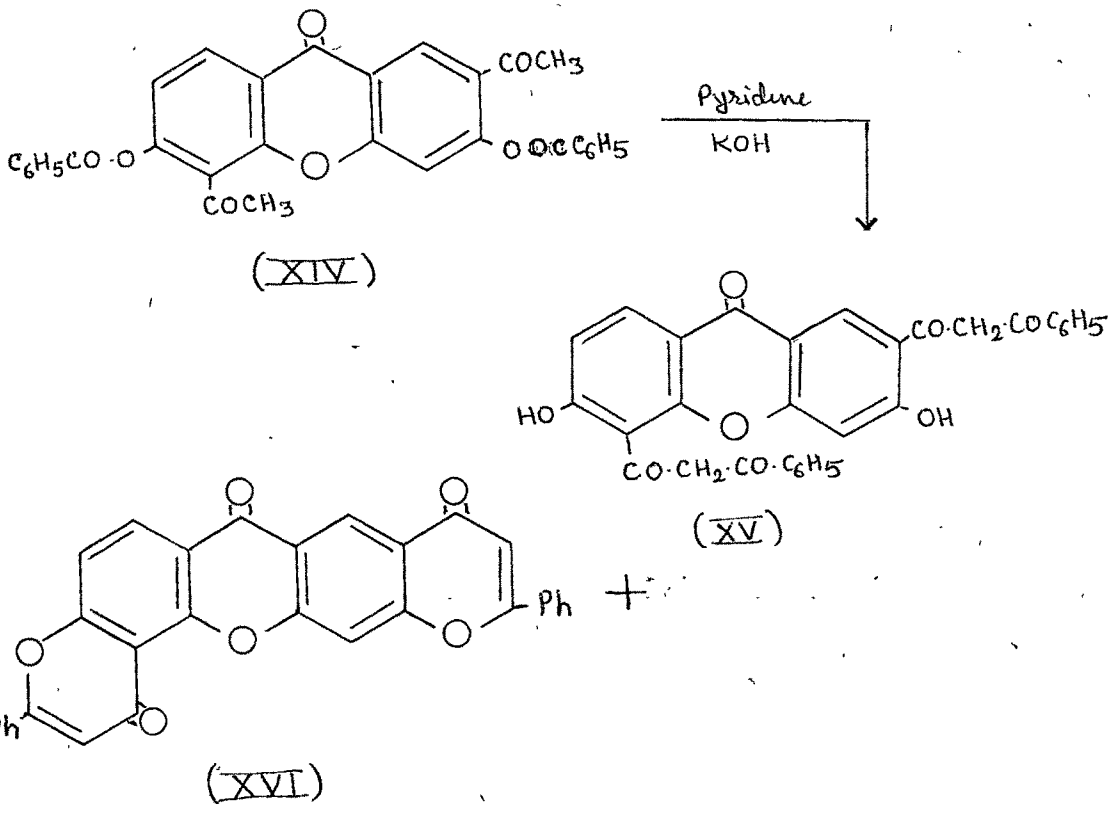
Oxidation of 3,6-dimethoxy-2,5-diacetylxanthone

Attempts to oxidise the diacetyl derivative by sodium hypobromite were unsuccessful. It resulted in the bromination of the compound. Lamb and Suschitzky[1] have also reported such bromination rather than the oxidation

in the case of 2-hydroxy-1-acetylxanthone. Dakin oxidation of the diacetyl also failed. The Dakin oxidation in the case of 2-hydroxy-1-acetylxanthone gave the original product. In the case of 1,3-dihydroxy-2-acetylxathone , however, Agasimundin and Rajagopal[5] found that the Dakin oxidation resulted in 1,2,3-trihydroxyxanthone. Finally the dimethyl ether of 3,6-dihydroxy-2,5-diacetylxanthone (X) was subjected to alkaline potassium permanganate oxidation, when it gave the 3,6-dimethoxyxanthone-2,5-dicarboxylic acid (XI).

Synthesis of 2',2''-diphenyl-4'-pyrono(6',5':3,2) and 4''-pyrono(6'',5'':6,5)xanthone

This ~~di~~pyronoxanthone was synthesised by Baker-Venkataraman transformation. 3,6-Dihydroxy-2,5-diacetylxanthone was treated with benzoyl chloride in pyridine, when it gave 3,6-dibenzoyloxy-2,5-diacetylxanthone. When the dibenzoyloxy derivative was treated with potassium hydroxide in dry pyridine at 150° and poured in [illegible] ice-cold hydrochloric acid, it gave a white solid. This solid was found to be a mixture of ~~di~~pyronoxanthone (XVI) and the β-diketone (XV). This mixture was crystallised from acetic acid when white crystals separated, which were of the ~~di~~pyronoxanthone (XVI). The mother liquor on dilution gave the β-diketone (XV). The flavone was insoluble in alkali, while the β-diketone was going slowly in alkali and gave brown colouration with alcoholic ferric chloride. This β-diketone could be cyclised further to the dipyronoxanthone with a little sulphuric acid in acetic acid.



(XIV)

(XV)

(XVI)

Fries migration of 3-acetoxy-6-methoxyxanthone.

3-Hydroxy-6-methoxyxanthone prepared as described in Chapter II gave 3-acetoxy-6-methoxyxanthone (XVII) on treatment with acetic anhydride in pyridine. This was subjected to Fries migration by baking with aluminium chloride at 140-60°. This resulted in a compound which on analysed for 3,6-dihydroxymonoacetylxanthone, indicating that both the Fries migration and demethylation have taken place simultaneously. It gave a dimethyl ether on methylation, and a diacetate derivative on acetylation. The structure of the monoacetyl was arrived at from the NMR (Fig.1) of its dimethoxy derivative in $CDCl_3$. The NMR spectrum shows two doublets at δ 8.35 and δ 8.2 for the two peri protons H-1

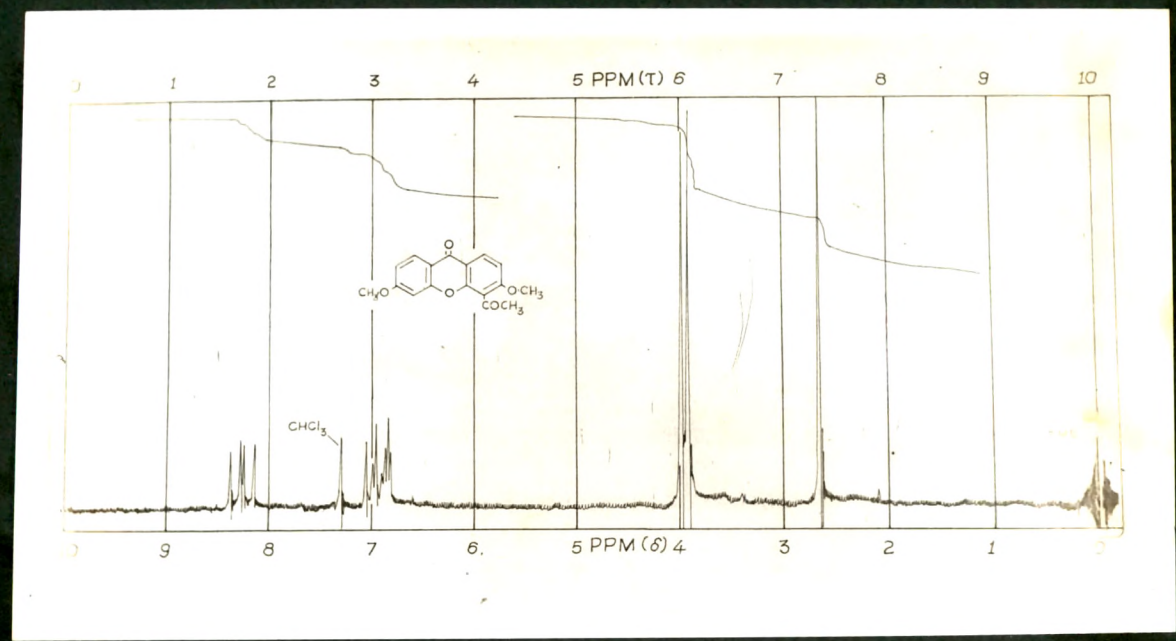
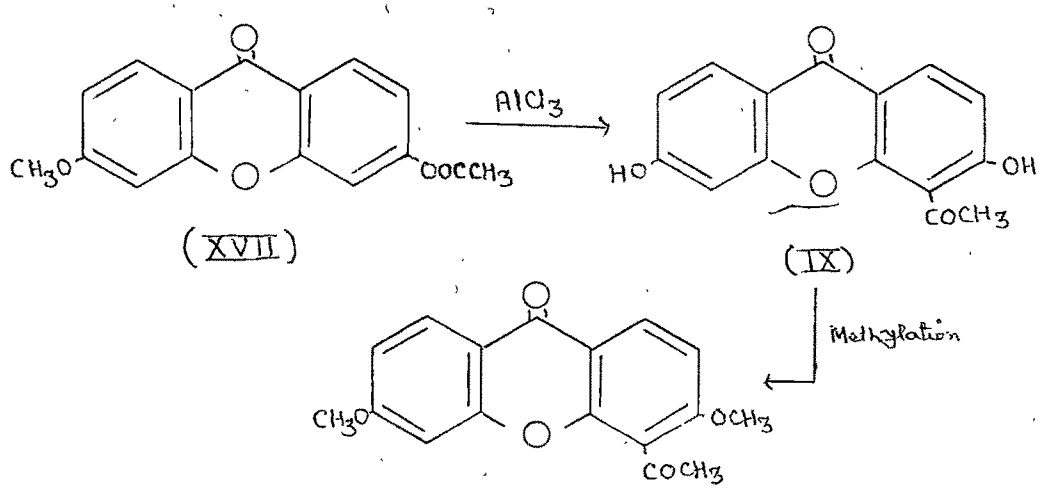


Fig. 1 : NMR spectrum of 3,6-dimethoxy-4-acetylxanthone (XVIII) in $CDCl_3$ (90 MHz).



(XVII) (IX) (XVIII)

and H-8. Thus it indicates that the protons H-2 and H-7 which are ortho to the peri protons are not substituted. The acetyl group thus has migrated to the 4-position and not to the 2-position. The acetyl group appeared at δ 2.65 as three-proton singlet, while the two methoxy groups appeared at δ 4.0 and δ 3.9 as three-proton singlets. The other aromatic protons appeared as a multiplet between δ 7.1 and δ 6.8. The signal at δ 7.3 is due to the chloroform impurity. Thus the NMR data favours 3,6-dimethoxy-4-acetylxanthone structure (XVIII). This monoacetyl derivative was found to be the same as the monoacetyl-xanthone (IX) obtained along with diacetyl from 3,6-diacetoxy-xanthone by Fries migration.

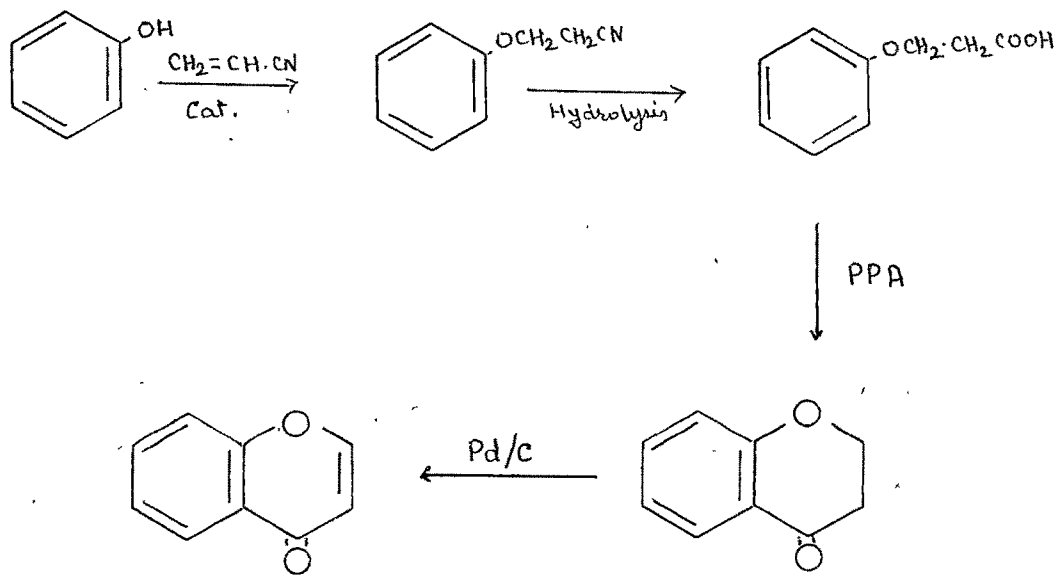
Attempted Baker-Venkataraman transformation of 3-benzoyloxy-4-acetylxanthone

3-Hydroxy-4-acetylxanthone has been prepared by Puranik and Rajagopal[6] by Friedel-Crafts acetylation of 3-hydroxyxanthone. We tried Fries migration of 3-acetoxy-xanthone with aluminium chloride at 140-60° when the same product was obtained in good yield. 3-Benzoyloxy-4-acetyl-

xanthone was prepared by the action of benzoyl chloride in pyridine on 3-hydroxy-4-acetylxanthone. This was taken in dry pyridine and treated with dry potassium hydroxide at 150° when 3-hydroxy-4-acetylxanthone was obtained instead of the β-diketone.

CYANOETHYLATION OF XANTHONES

Cyanoethylation of xanthones has also not been reported in the literature so far, so it was thought of interest to study the cyanoethylation of xanthones. Cyanoethylation is a good method for preparing 4'-pyrones which are unsubstituted in the heterocyclic ring. The method can be illustrated by the example of synthesis of a simple 4'-pyrone (XIX) as follows :-



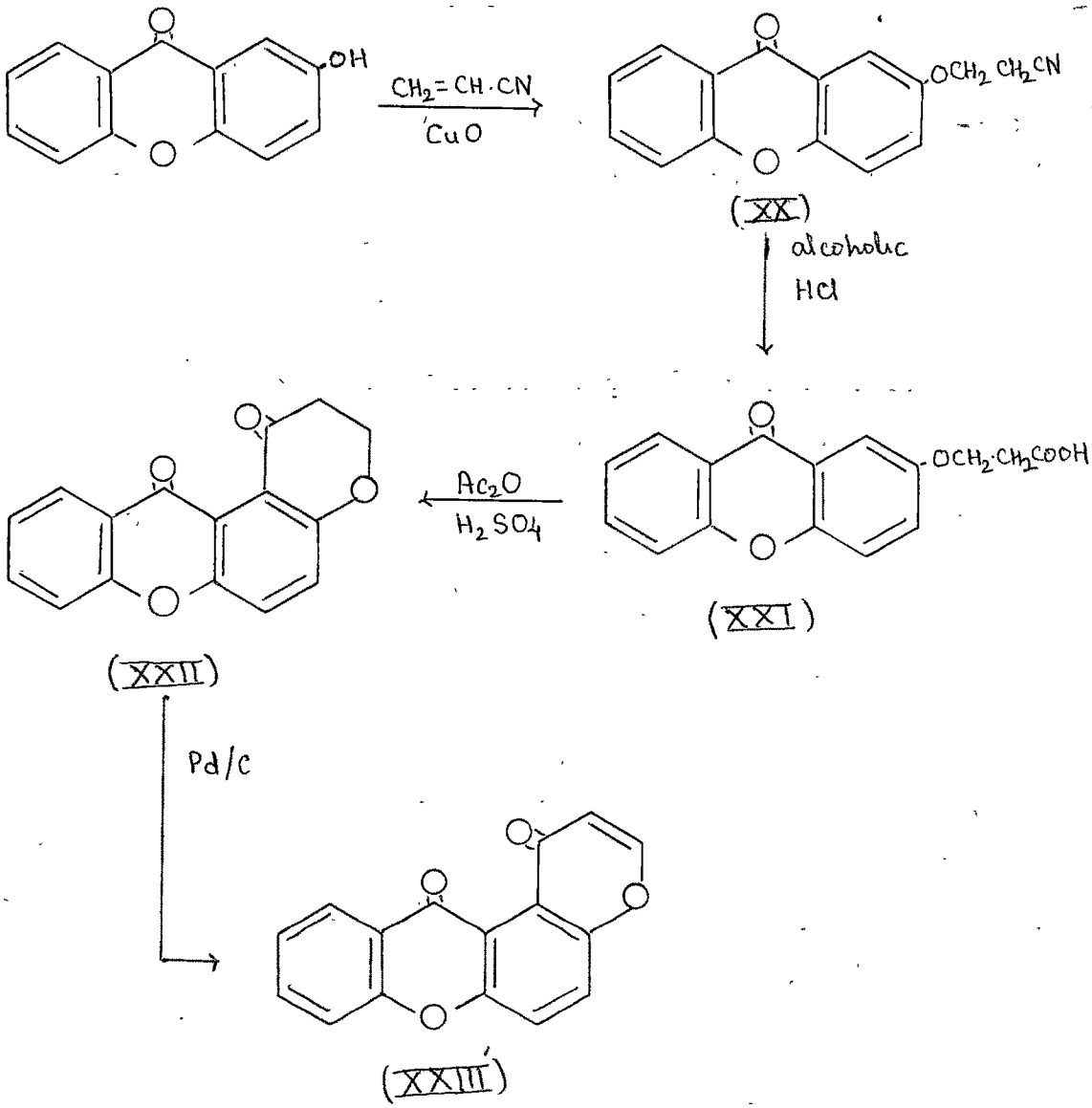
(XIX)

It was thought of interest to study the cyanoethylation of some hydroxyxanthones. In this work it has been observed that cupric oxide is the best catalyst. Other catalysts such as sodium hydroxide solution (5-10 %), Triton-B and pyridine did not give good yields, moreover a lot of polymeric product was formed. Cyanoethylation worked well with 3-hydroxy- and 2-hydroxyxanthone. The other xanthones 3,6-dihydroxy- and 3-hydroxy-6-methoxy- did not give the β-cyanoethoxyxanthones. Cyclisation of β-carboxyethoxyxanthones posed a problem as polyphosphoric acid and conc. sulphuric acid did not work, but a mixture of acetic anhydride and sulphuric acid at 80-90° cyclised the acid to 4'-pyranoxanthones in about 10-15 min.

Synthesis of 4'-pyrono(6',5' : 2,1)xanthone

2-Hydroxyxanthone was refluxed in acrylonitrile with powdered cupric oxide as catalyst for about 30 hr., when 2-(β-cyanoethoxy)xanthone (XX) was obtained. This was hydrolysed by refluxing with alcoholic hydrochloric acid to 2-(β-carboxyethoxy)xanthone (XXI). Cyclisation of this acid could not be effected by either polyphosphoric acid at 100° or by sulphuric acid at room temperature. However, it could be cyclised by heating it in acetic anhydride with a little sulphuric acid at 80-90° for 20 min. to 4'-pyrano-(6',5' : 2,1)xanthone (XXII). Prolonged heating or heating at higher temperature gave a sulphonated product. As the cyclisation proceeds the original greenish-yellow fluorscence fades and the solution assumes a light brown colour. The

product obtained on pouring on ice was washed with sodium bicarbonate solution to remove the unreacted acid and then crystallised. The structure was established on the basis of the NMR (Fig. 2) of the cyclised product in $CDCl_3$. The NMR spectrum shows a one-proton doublet at δ 8.3 with $J = 9Hz$, which is characteristic of peri proton, showing



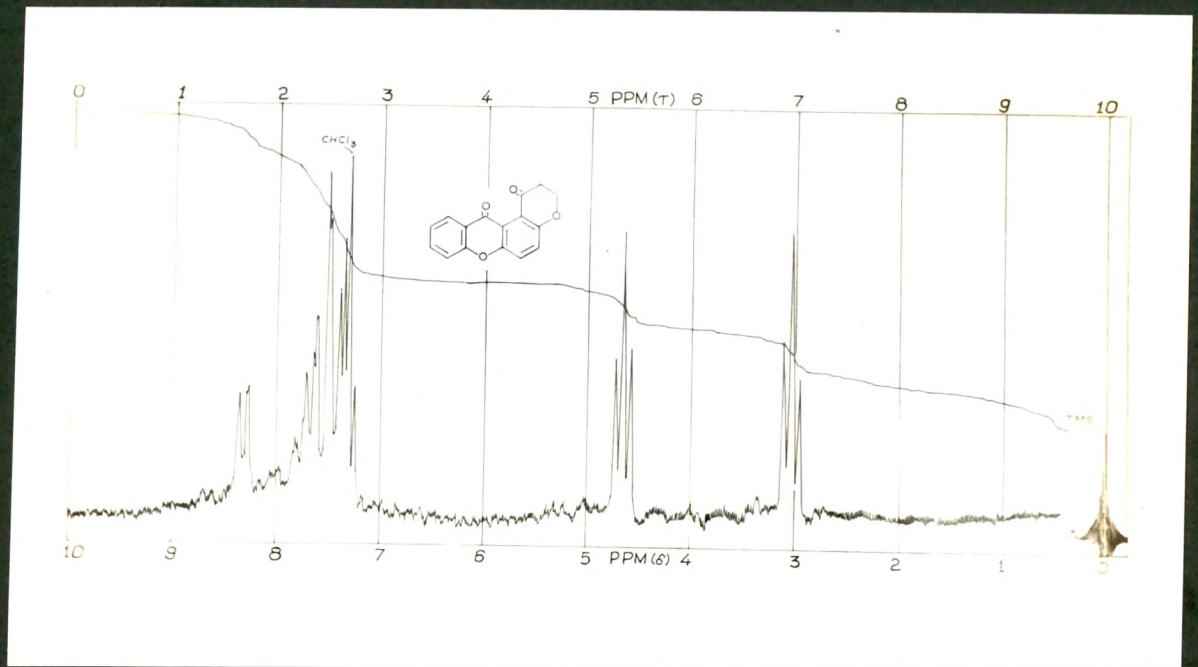


Fig. 2 : NMR spectrum of 4'-pyrano(6',5' : 2,1)xanthone (XXII) in $CDCl_3$ (90 MHz).

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that the other (C - 1) peri-position is blocked. The cyclisation resulting in 3-position would have given an additional one-proton singlet near δ 8.3. The protons at C-3' and C-2' appeared as triplets at δ 3.0 and δ 4.5 respectively. The other aromatic protons appeared as multiplet between δ 7.2 to 7.8. The chloroform impurity signal is at δ 7.3.

The 4'-pyranoxanthone was dehydrogenated to 4'-pyrono(6',5' : 2,1)xanthone (XXIII), by palladised charcoal by refluxing in diphenyl ether for 10 hr. The compound separated on cooling. The pyranoxanthone showed the carbonyl band at 1690 $cm.^{-1}$, while the pyronoxanthone showed the carbonyl band at 1650 $cm.^{-1}$. The shifting of the carbonyl band to the lower frequency is in agreement with the aromatisation of the pyranoxanthone.

Sunthesis of 4'-pyrano(6',5' : 3,4)xanthone

3-Hydroxyxanthone was refluxed in acrylonitrile in the presence of powdered cupric oxide which resulted in 3-(β-cyanoethoxy)xanthone (XXIV).

The above cyanoethoxyxanthone was hydrolysed by alcoholic hydrochloric acid to give 3-(β-carboxyethoxy)-xanthone (XXV). The acid was cyclised to the pyran derivative (XXVI) by acetic anhydride and sulphuric acid mixture. That the acid cyclised in the 4-position only was confirmed by the NMR (Fig. 3) of this pyranoxanthone in trifluoroacetic acid. The NMR spectrum showed two doublets with coupling constant of 9Hz at δ 8.28 and δ 8.08 in the

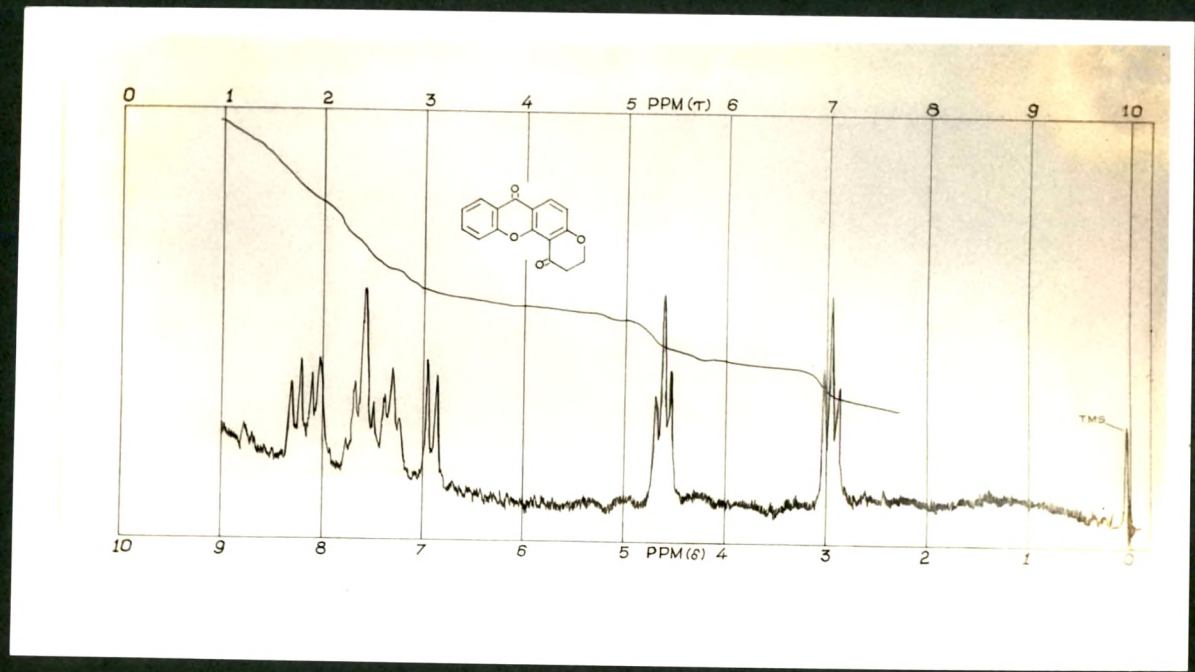
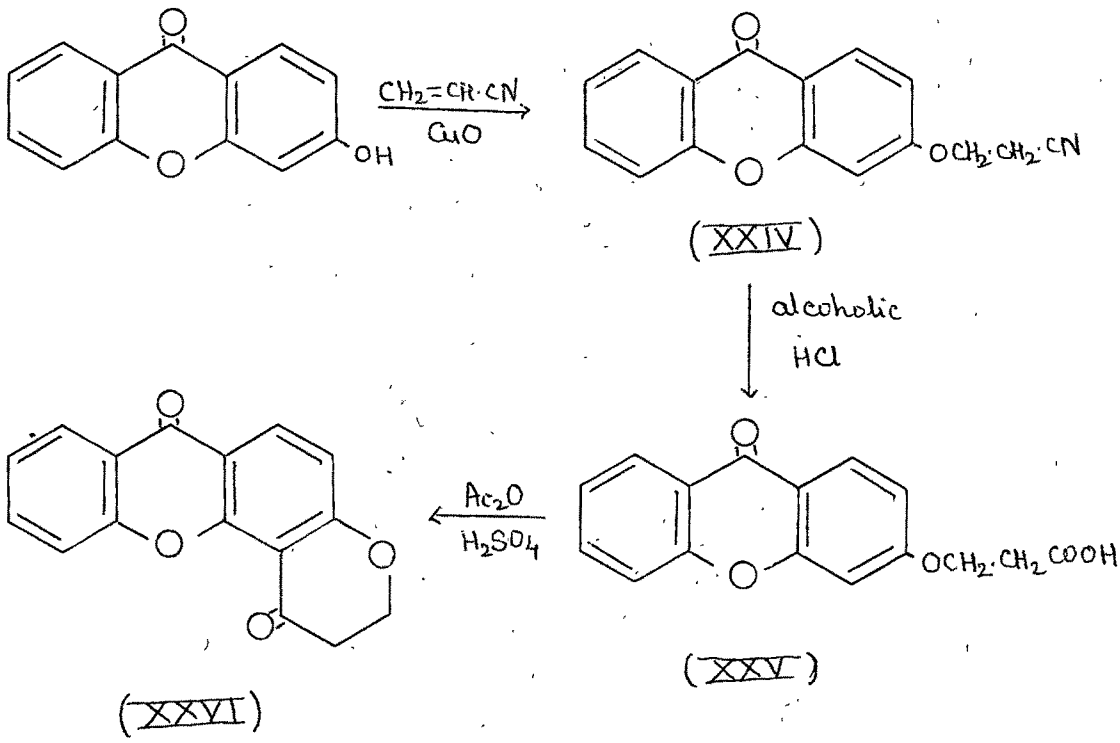


Fig. 3 : NMR spectrum of 4'-pyrano(6',5' : 3,4)xanthone (XXVI) in CF_3COOH) (90 MHz).



peri-proton region due to H-1 and H-8 respectively. The proton H-2 appeared as a doublet in the up field region at δ 6.92 (J = 9Hz), as being ortho to the ring oxygen. The other aromatic protons appeared as a multiplet as in the region between δ 7.3-7.8. The aliphatic protons at C-2' and C-3' appeared as two-proton triplets at δ 4.6 and δ 2.95 respectively. The IR spectrum of this compound showed the xanthone carbonyl band at 1655 $cm.^{-1}$ and the band at 1690 $cm.^{-1}$ which is characteristic of cyclic aliphatic-aromatic ketone.

Dehydrogenation of this pyranoxanthone was, however, not successful as it gave the unreacted compound back.

Attempted cyanoethylation

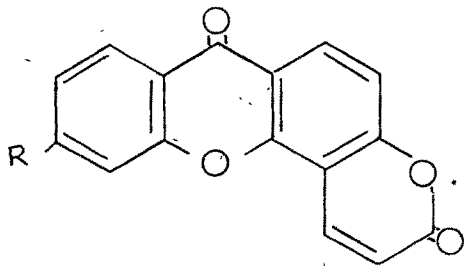
3,6-Dihydroxyxanthone did not react with acrylonitrile in the presence of either 5-10 % sodium hydroxide solution or Triton-B or pyridine. In one attempt the xanthone was dissolved in dimethyl formamide and refluxed with cupric oxide as a catalyst with acrylonitrile. This gave the hydroxyxanthone back showing that no condensation with acrylonitrile has taken place. Excess of acrylonitrile alone in the presence of cupric oxide also did not work. In almost all cases the polymerisation of acrylonitrile occurred excessively and the unreacted xanthone was recovered back.

Similarly, 3-hydroxy-6-methoxyxanthone failed to condense with acrylonitrile under the conditions described above.

ATTEMPTED SYNTHESIS OF 2'-PYRONOXANTHONES

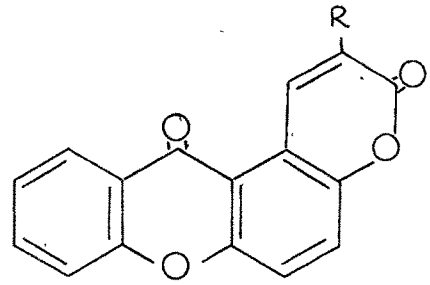
2'-Pyronoxanthones have so far not been found in nature. Some of them have, however, been prepared synthetically. Puranik and Rajagopal prepared 2'-pyronoxanthones (XXVII) and (XXVIIa) by Perkin reaction on 3-hydroxy-4-formyl-[7] and 3-hydroxy-4-formyl-6-methylxanthone[8] respectively. Similarly, the 2'-pyronoxanthones (XXVIII) and (XXVIIIa) were synthesised by the Perkin reaction on 2-hydroxy-1-formylxanthone.[16]

Scheinmann et al.[9] have reported that the condensation of 1-hydroxyxanthone with ethyl acetoacetate under the conditions of either Pechmann reaction or Simonis



(XXVII) ; R = H

(XXVII a) ; R = CH_3



(XXVIII) ; R = H

(XXVIII a) ; R = CH_3

reaction was unsuccessful.

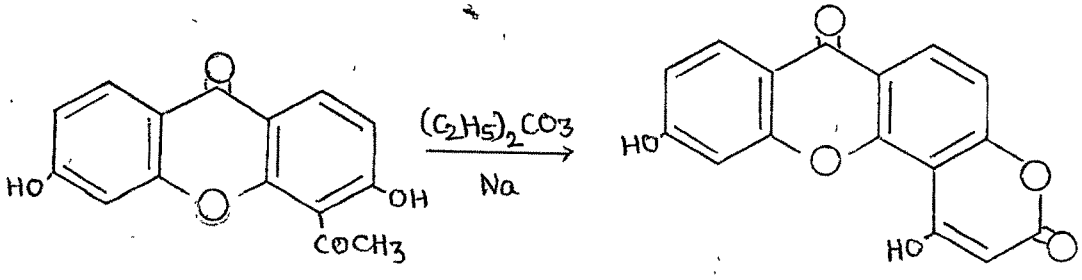
In the present investigation also xanthones such as 2-hydroxy-, 3-hydroxy- and 3,6-dihydroxyxanthones were subjected to Pechmann condensation with ethyl acetoacetate using different condensing agents like 80 % sulphuric acid at 0-5°, conc. sulphuric acid at room temperature, increasing the time period from 1 to 48 hr. (in the case of 3-hydroxy-xanthone 80 hr.), but no condensation occurred and always the unchanged xanthone was recovered.

Condensation of ethylacetoacetate with 3,6-dihydroxyxanthone at 120° with a few drops of sulphuric acid gave some alkali insoluble product. This was a mixture of three components. One component was alcohol insoluble and was giving positive test for sulphur, showing that sulphonation had taken place. The alcohol soluble portion was treated with petroleum ether (40-60°) and filtered hot. This fraction gave an oily material, alkali insoluble, giving no colour with ferric chloride. The petroleum ether insoluble and alkali insoluble brown powder, however, did not give the elemental analysis conforming to the di-2'-pyrone. The

carbon percentage was high by about 11 % than that required for the di-2'-pyrone.

The condensation of ethyl acetaacetate with 2-hydroxy-, 3-hydroxy- and 3,6-dihydroxyxanthone in diphenyl ether[10] gave the unreacted xanthone back. In the presence of aluminium chloride also condensation did not take place. Similarly, the condensation between 3-hydroxy-xanthone and ethylacetoacetate in alcohol by passing hydrochloric acid gas, as reported by Buu Hoi[11] also did not succeed.

As the attempt to build up a 2'-pyrone ring by Pechmann method was a failure, it was thought of interest to synthesise 4'-hydroxy-2'-pyrones starting with the o-hydroxyacetylxanthones. Thus 3,6-dihydroxy-4-acetylxanthone on treatment with diethylcarbonate in the presence of pulverised sodium gave a bicarbonate soluble product to which 4',6-dihydroxy-2'-pyrono(6',5' : 3,4)xanthone (XXIX) structure has been assigned.

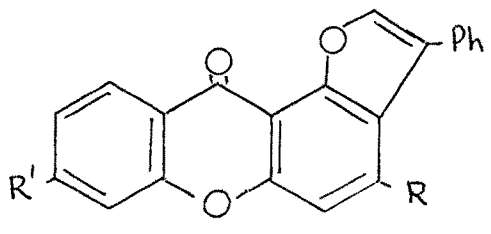


(IX) (XXIX)

SYNTHESIS OF FURANOXANTHONES

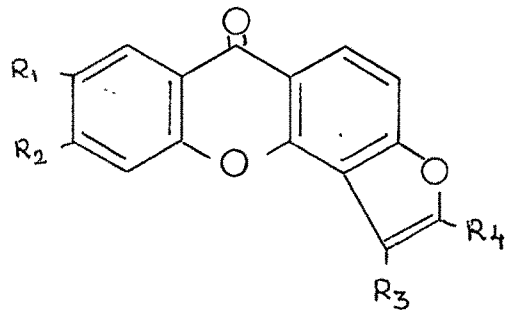
Many 2'-methyl-, 3'-methyl- and simple furanoxanthones have been synthesised so far from the corresponding o-hydroxyallyl-, o-hydroxyacetyl- and o-hydroxyformylxanthone intermediates, which have been reviewed in the Chapter I. It will be worth mentioning here about some of the new methods used for synthesising the furanoxanthones.

2'-Phenyl- and 3'-phenyl substituted xanthones have also been reported in the literature. 3-Methyl-3'-phenylfurano(5',4' : 1,2)xanthone (XXX) and 3,6-dimethyl-3'-phenylfurano(5',4' : 1,2)xanthone (XXXI) have been prepared by Angadiyavar and Rajagopal[12] from the corresponding 1-hydroxy-2-benzoylxanthones. Angadiyavar and Rajagopal[13] have also prepared 3'-phenylfurano(5',4' : 3,4)xanthone (XXXII), 6-methyl-3'-phenylfurano(5',4' :3,4)xanthone (XXXIII), 7-methyl-3'-phenylfurano(5',4' : 3,4)xanthone (XXXIV) and their 2'-phenyl- isomers (XXXV), (XXXVI) and (XXXVII) by cyclising the corresponding 3-phenacyloxyxanthones with



(XXX) $R=CH_3$; $R'=H$

(XXXI) $R=R'=CH_3$



(XXXII) $R_1=R_2=H$; $R_3=Ph$; $R_4=H$

(XXXIII) $R_1=H$; $R_2=CH_3$; $R_3=Ph$; $R_4=H$

(XXXIV) $R_1=CH_3$; $R_2=H$; $R_3=Ph$; $R_4=H$

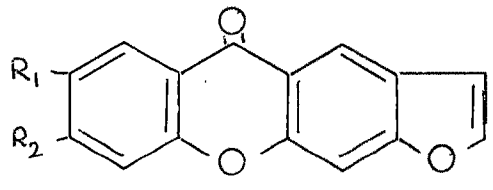
(XXXV) $R_1=R_2=H$; $R_3=H$; $R_4=Ph$

(XXXVI) $R_1=H$; $R_2=CH_3$; $R_3=H$; $R_4=Ph$

(XXXVII) $R_1=CH_3$; $R_2=R_3=H$; $R_4=Ph$

polyphosphoric acid[14] at 130° and at 170°, when the lower temperature favoured the 3'-phenyl- isomer, while the higher temperature gave the 2'-phenyl- isomer.

Linear furanoxanthones having no substituents in the furano ring such as (XXXVIII), (XXXIX) and (XL) have been synthesised by Angadiyavar and Rajagopal[15] starting with



(XXXVIII) $R_1=R_2=H$

(XXXIX) $R_1=CH_3$; $R_2=H$

(XL) $R_1=H$; $R_2=CH_3$

the condensation of 6-hydroxycoumaran with the appropriate o-chlorobenzoic acids.

In the literature no difuranoxanthones have been reported. Hence it was thought of interest to study the synthesis of a difuranoxanthone.

Synthesis of 2',2"-dimethyldifurano(5',4' : 3,4) and (5",4" : 6,5)xanthone

3,6-Dihydroxyxanthone on allylation with allyl bromide in the presence of potassium carbonate in dry acetone gave 3,6-diallyloxyxanthone (XLI). This xanthone was subjected to the Claisen rearrangement in dimethyl aniline, when it gave 3,6-dihydroxy-4,5-diallylxanthone (XLII). The structure was arrived at on the basis of the NMR spectrum (Fig. 4) of its dimethoxy derivative (XII) which is soluble in $CDCl_3$. The NMR spectrum showed two two-proton doublets at δ 8.2 and δ 7.0, confirming the symmetrical structure 3,6-dimethoxy-4,5-diallylxanthone. The low field doublets can be assigned to the two peri-protons H-1 and H-8. The up field doublet can be attributed to H-2 and H-7. The two methyl protons of the two methoxy groups appeared as a six-proton singlet at δ 4.0. Multiplet near δ 6.0 (=CH), another multiplet near δ 5.1 ($=CH_2$) and a doublet at δ 3.8 ($-CH_2$) are the protons of the two allyl groups. The structure 3,6-dimethoxy-2,7-diallylxanthone would have given two two-proton singlets in the aromatic region while the unsymmetrical structure would have given two singlets and two doublets in

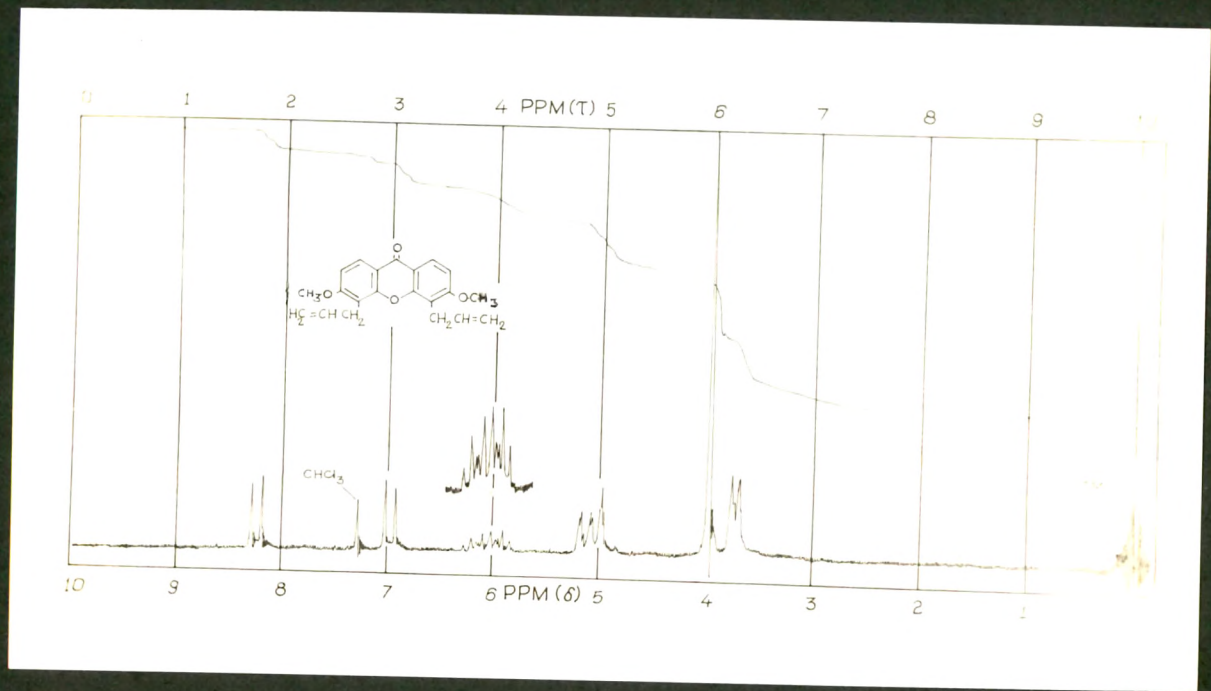
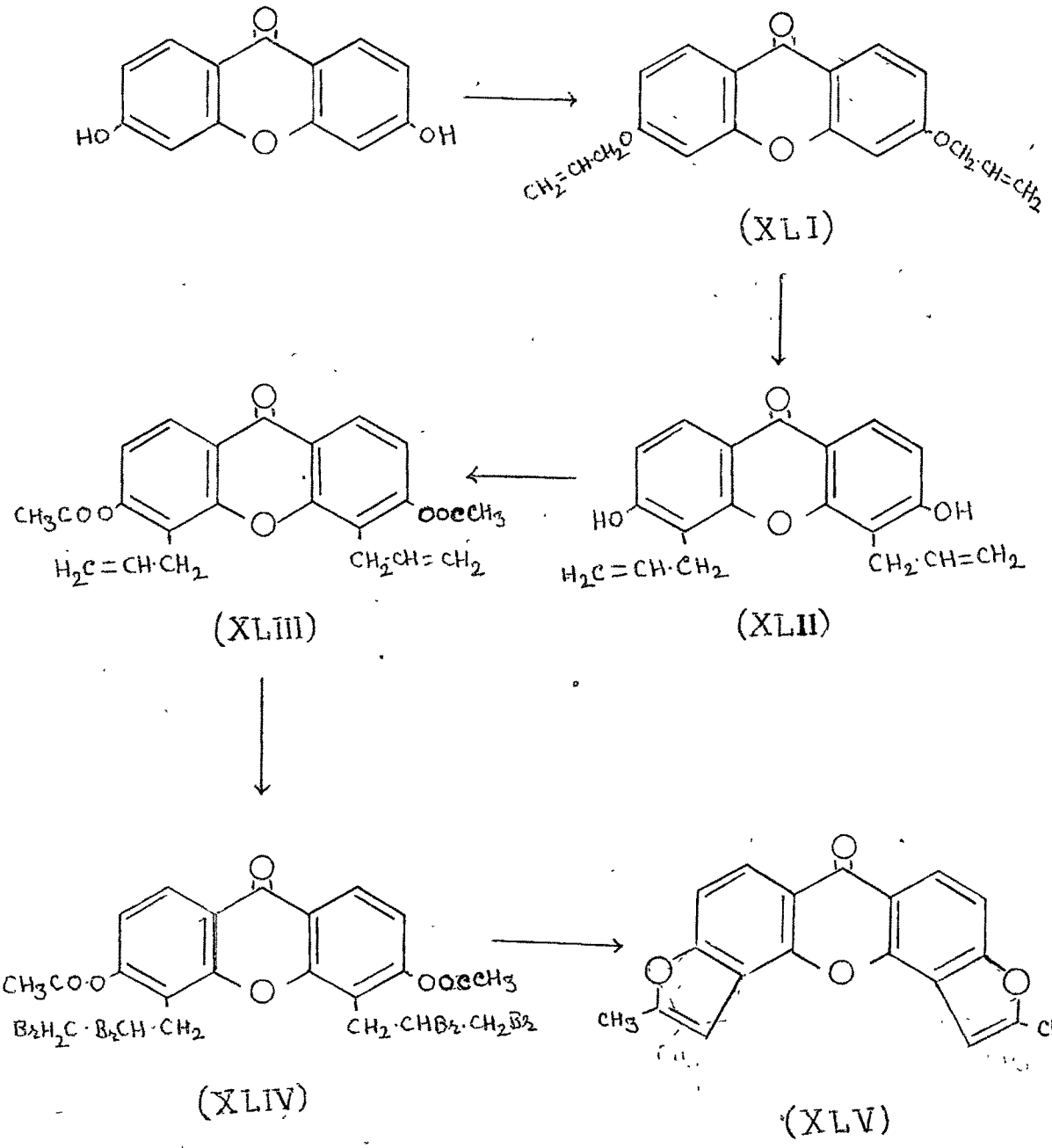


Fig. 4 : NMR spectrum of 3,6-dimethoxy-4,5-diallylxanthone (XII) in $CDCl_3$ (90 MHz).

the aromatic region.

3,6-Dihydroxy-4,5-diallylxanthone on acetylation gave 3,6-diacetoxy-4,5-diallylxanthone (XLIII) which was



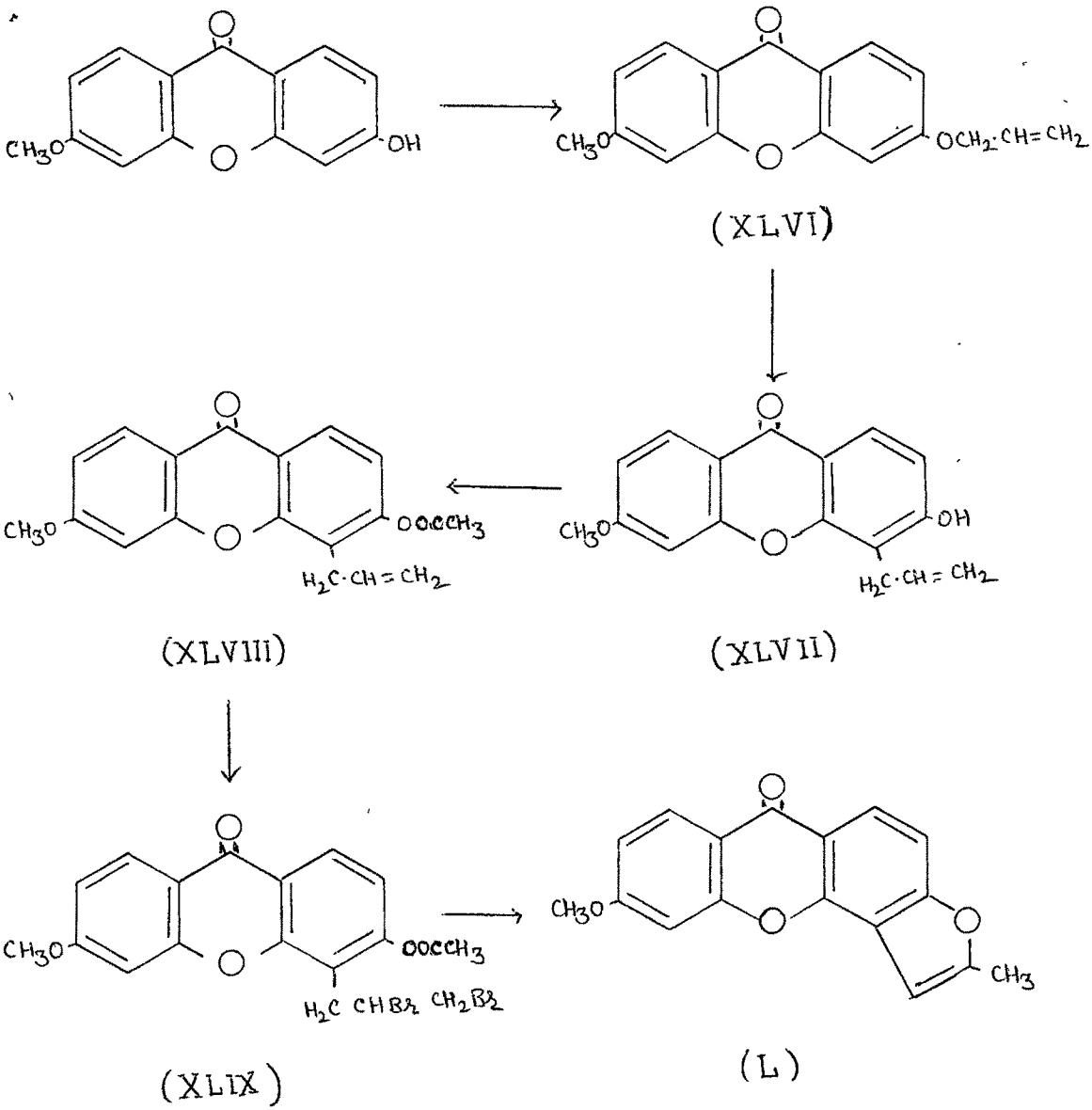
brominated with two mole amount of bromine in acetic acid when it gave 3,6-diacetoxy-4,5-bis(2',3'-dibromopropyl)-xanthone (XLIV). This on refluxing with potassium hydroxide in absolute alcohol gave 2',2"-dimethyldifurano(5',4' : 3,4) and (5",4" : 6,5)xanthone (XLV).

Oxidation of 3,6-dimethoxy-4,5-diallylxanthone

3,6-Dimethoxy-4,5-diallylxanthone (XII) was obtained by methylation of 3,6-dihydroxy-4,5-diallylxanthone. The oxidation of this dimethyl ether with potassium permanganate in acetone resulted in 3,6-dimethoxyxanthone-4,5-dicarboxylic acid (XIII). This has been found to be a good method of getting xanthonecarboxylic acids as the hydrolysis of the cyanoxanthones does not succeed as seen earlier.

Synthesis of 6-methoxy-2'-methylfurano(5',4' : 3,4)-xanthone

To synthesise the above furanoxanthone, 3-hydroxy--6-methhoxyxanthone was treated with allyl bromide in acetone in the presence of potassium carbonate, when 3-allyloxy-6--methoxyxanthone (XLVI) was obtained. This on migration in dimethyl aniline gave a product to which 3-hydroxy-4-allyl--6-methoxyxanthone structure (XLVII) has been assigned on the basis of the NMR data. The NMR of this compound was taken in dimethyl sulphoxide in only aromatic region. The two doublets in the peri-proton region at δ 8.16 and δ 8.05 indicate that 2- and 7-position are not occupied. The situation is possible only when the allyl group migrates to the 4-position. Both the doublets have the J value of 9Hz.



On acetylation of 3-hydroxy-4-allyl-6-methoxy-xanthone, the 3-acetoxy derivative (XLVIII) was obtained. This was brominated to get 3-acetoxy-4-(2',3'-dibromopropyl)-xanthone (XLIX), which on treatment with alcoholic potassium hydroxide gave 6-methoxy-2'-methylfurano(5',4' : 3,4)-xanthone (L).

EXPERIMENTAL

SYNTHESIS OF 4'-PYRONOXANTHONES

Fries migration of 3,6-diacetoxyxanthone : 3,6-Dihydroxy--2,5-diacetylxanthone :

3,6-Diacetoxyxanthone (1.0 g.) and aluminium chloride (2.0 g.) were powdered together and kept in an oil bath for 2 hr. at 140° for half an hour. The temperature was then raised to 160° and maintained for 1 1/2 hr. more. The product obtained after addition of cold hydrochloric acid was taken up in hot nitrobenzene. The separated yellow powder was repeatedly crystallised from nitrobenzene, when it gave yellow buds (0.16 g.), m.p. 336-38°. It showed a reddish-brown colouration with alcoholic ferric chloride.

Analysis : Found : C, 65.22 ; H, 3.68 %

$C_{17}H_{12}O_6$ requires : C, 65.37 ; H, 3.85 %.

3,6-Dihydroxy-4-acetylxanthone :

The product obtained after removal of nitrobenzene by steam distilling the mother liquor was crystallised from nitrobenzene and the separated product, which was found to be the impure diacetylxanthone discarded. The filtrate on dilution with petroleum ether (40-60°) gave a product which came out from acetic acid as a grey powder (0.07 g.), m.p. 343-45°. This also showed brown colouration with alcoholic ferric chloride.

Analysis : Found : C, 67.16 ; H, 4.16 %

$C_{15}H_{10}O_5$ requires : C, 66.66 ; H, 3.70 %.

Friedel-Crafts acetylation of 3,6-dihydroxyxanthone :

3,6-Dihydroxyxanthone (1.0 g.), aluminium chloride (2.0 g.) and acetic anhydride (2 ml.) were heated at 160° for 2 hr. After adding cold hydrochloric acid the product obtained was extracted in hot nitrobenzene and processed as described earlier, when 3,6-dihydroxy-2,5-diacetylxanthone (0.15 g.) and 3,6-dihydroxy-4-acetylxanthone (0.6 g.) were obtained. The material insoluble in nitrobenzene contained the unreacted 3,6-dihydroxyxanthone.

3,6-Dimethoxy-2,5-diacetylxanthone :

3,6-Dihydroxy-2,5-diacetylxanthone (0.1 g.) and dimethyl sulphate (0.2 ml.) in acetone (30 ml.) were refluxed for 2 hr. in the presence of anhydrous potassium carbonate and the dimethyl ether obtained was crystallised from aqueous acetic acid in light brown needles (0.09 g.), m.p. 287°.

IR in nujol : 1690 $cm.^{-1}$ ($-COCH_3$) ; 1650 $cm.^{-1}$ ($>CO$).

Analysis : Found : C, 67.35 ; H, 4.39 %

$C_{19}H_{16}O_6$ requires : C, 67.05 ; H, 4.70 %.

3,6-Diacetoxy-2,5-diacetylxanthone :

3,6-Dihydroxy-2,5-diacetylxanthone (0.5 g.) in pyridine (8 ml.), when heated with acetic anhydride (1 ml.) in water bath for 1 hr. gave a product which crystallised from aqueous alcohol in white needles (0.4 g.), m.p. 144-46°.

Analysis : Found : C, 63.43 ; H, 4.48 %

$C_{21}H_{18}O_8$ requires : C, 63.31 ; H, 4.52 %.

3,6-Dimethoxyxanthone-2,5-dicarboxylic acid :

3,6-Dimethoxy-2,5-diacetylxanthone (0.5 g.) was

taken in sodium hydroxide solution (90 % ; 5 ml.) and heated on a steam bath by adding potassium permanganate (1.0 g.) portion-wise during half an hour. The mixture was acidified with sulphuric acid and after chemical purification the acid was crystallised from aqueous acetic acid in white needles, (0.06 g.), m.p. 234-36°. IR in nujol : 1715 $cm.^{-1}$ (-COOH) ; 1655 $cm.^{-1}$ (>CO).

Analysis : Found : C, 59.26 ; H, 3.81 %

$C_{17}H_{12}O_8$ requires : C, 59.29 ; H, 3.49 %.

Synthesis of 2',2"-diphenyl-4'-pyrono(6',5' : 3,2) and 4"-pyrono(6",5" : 6,5)xanthone :

3,6-Dibenzoyloxy-2,5-diacetylxanthone :

3,6-Dihydroxy-2,5-diacetylxanthone (1.0 g.) was dissolved in pyridine (10 ml.) and treated with benzoyl chloride (2 ml.). After heating the mixture on a steam bath at 60° for 2 hr. it was poured in ice cold hydrochloric acid when a pasty product was obtained. The product was washed with dilute hydrochloric acid, sodium bicarbonate solution and then with water. When crystallised from aqueous acetic acid it gave white needles (0.8 g.), m.p. 185-87°.

Analysis : Found : C, 71.53 ; H, 3.97 %

$C_{31}H_{20}O_8$ requires : C, 71.53 ; H, 3.85 %.

Baker-Venkataraman transformation of 3,6-dibenzoyloxy-2,5-diacetylxanthone : 2',2"-Diphenyl-4'-pyrono(6',5' : 3,2)-and 4"-pyrono(6",5": 6,5)xanthone :

3,6-Dibenzoyloxy-2,5-diacetylxanthone (0.8 g.) was dissolved in dry pyridine (6 ml.). After adding powdered dry

potassium hydroxide (0.8 g.) to the solution it was heated at 150° for half an hour with occasional shaking and left overnight. The reaction mixture was poured into ice cold hydrochloric acid (20 % ; 50 ml.) and the solid collected. This was taken in acetic acid (15 ml.) and kept in a refrigerator, when white needles (0.12 g.) of dipyrano-xanthone separated, which decomposed above 375°. IR in nujol : 1645 $cm.^{-1}$ (4'-pyrono >CO) ; 1615 $cm.^{-1}$ (xanthone >CO).

Analysis : Found : C, 76.50 ; H, 3.43 %

$C_{31}H_{16}O_6$ requires : C, 76.86 ; H, 3.31 %.

3,6-Dihydroxy-2,5-di(benzoylacetyl)xanthone :

The acetic acid mother liquor from the above experiment when heated and diluted with water till it became hazy, gave on cooling white needles (0.26 g.) of the β-diketone. M.p. 216-18°. It showed light brown colouration with alcoholic ferric chloride.

Analysis : Found : C, 71.11 ; H, 3.55 %

$C_{31}H_{20}O_8$ requires : C, 71.53 ; H, 3.85 %.

Cyclisation of 3,6-dihydroxy-2,5-di(benzoylacetyl)xanthone :

The β-diketone (0.2 g.) in freshly distilled acetic acid (15 ml.) was heated with sulphuric acid (0.5 ml.) on a steam bath for 2 hr. and the reaction mixture was poured over ice. It gave the some alkali insoluble dipyranoxanthone as described above.

3-Acetoxy-6-methoxyxanthone :

When 3-hydroxy-6-methoxyxanthone (0.5 g.) in pyridine (5 ml.) was heated with acetic anhydride (1 ml.) and the reaction mixture poured in ice cold hydrochloric acid, a product was obtained which crystallised from alcohol in white needles (0.4 g.), m.p. 164°.

Analysis : Found : C, 67.20 ; H, 3.79 %

$C_{16}H_{12}O_5$ requires : C, 67.60 ; H, 4.25 %.

Fries migration of 3-acetoxy-6-methoxyxanthone : 3,6-Dihydroxy-4-acetylxanthone :

3-Acetoxy-6-methoxyxanthone (1.0 g.) and anhydrous aluminium chloride (2.0 g.) were heated in an oil bath at 120° for 15 min. and then at 160° for 2 hr. The product after working up came down from acetic acid as a grey powder (0.6 g.), m.p. 343-45°. This was identical with the monoacetylxanthone obtained from 3,6-diacetoxyxanthone by Fries migration along with the diacetylxanthone.

The dimethyl ether :

3,6-Dihydroxy-4-acetylxanthone (0.5 g.) and dimethyl sulphate (1 ml.) in acetone (50 ml.) were refluxed in the presence of anhydrous potassium carbonate (1.0 g.), when an alkali insoluble product was obtained which crystallised from aqueous acetic acid in white needles (0.48 g.), m.p. 208-10°.

Analysis : Found : C, 68.45 ; H, 4.60 %.

$C_{17}H_{14}O_5$ requires : C, 68.45 ; H, 4.69 %.

Fries migration of 3-acetoxyxanthone : 3-Hydroxy-4-acetylxanthone :

3-Acetoxyxanthone (1.0 g.) and anhydrous aluminium chloride (2.0 g.) were mixed thoroughly and heated in an oil bath between 140-60° for 2 hr. After working up, the product crystallised from aqueous alcohol in yellow needles (0.7 g.), m.p. 205-06°. This was identical with the xanthone obtained according to Puranik and Rajagopal[6].

3-Benzoylation of 3-hydroxy-4-acetylxanthone (1.0 g.) in pyridine (10 ml.) with benzoyl chloride (1 ml.) gave an alkali insoluble product which crystallised from alcohol in brown needles (0.9 g.), m.p. 183°.

Analysis : Found : C, 74.08 ; H, 4.09 %

$C_{22}H_{14}O_5$ requires : C, 73.74 ; H, 3.94 %.

Attempted Baker-Venkataraman transformation of 3-benxoyloxy-4-acetylxanthone :

3-Benzoyloxy-4-acetylxanthone (1.0 g.) dissolved in dry pyridine (10 ml.) was treated with powdered potassium hydroxide (1.0 g.) at 150° for half an hour and the reaction mixture then poured in icecold hydrochloric acid, when an alkali soluble product was obtained. This was found to be the 3-hydroxy-4-acetylxanthone.

CYANOETHYLATION OF XANTHONES

Synthesis of 4'-pyrono(6',5' : 2,1)xanthone :

2-(β-Cyanoethoxy)xanthone :

A mixture of 2-hydroxyxanthone (1.0 g.), cupric

oxide (0.2 g.) and acrylonitrile (50 ml.) was refluxed on a sand bath for 50 hr. The unreacted acrylonitrile was removed under vacuum and the mixture was extracted in chloroform. The chloroform extract was washed with dilute alkali and the solvent was removed. The product obtained thus crystallised from aqueous acetic acid in white needles (0.2 g.) m.p. 176-77°.

Analysis : Found : C, 72.36 ; H, 4.22 ; N, 4.84 %

$C_{16}H_{11}O_3N$ requires : C, 72.45 ; H, 4.15 ; N, 5.28 %.

2-(β-Carboxyethoxy)xanthone :

2-(β-Cyanoethoxy)xanthone (1.0 g.) in alcohol (50 ml.) was refluxed with conc. hydrochloric acid (15 ml.) for 50 hr., adding hydrochloric acid (10 ml.) after every 8 hr., yellowish needles separated on cooling. The solvent was removed and the separated product was collected. This after chemical purification was crystallised from aqueous acetic acid in white needles (0.5 g.), m.p. 200-03°.

IR in nujol : 1740 $cm.^{-1}$ (-COOH) ; 1650 $cm.^{-1}$ (>CO).

Analysis : Found : C, 67.42 ; H, 4.23 %

$C_{16}H_{12}O_5$ requires : C, 67.60 ; H, 4.22 %.

4'-Pyrano(6',5' :2,1)xanthone :

2-(β-Carboxyethoxy)xanthone (0.5 g.) was dissolved in acetic anhydride (5 ml.) by warming. The solution was cooled and then conc. sulphuric acid (0.5 ml.) was added. The reaction mixture was heated on a steam bath at 80-90° for 20 min., when the original greenish-yellow fluorescence disappeared and the solution turned light brown. This was

left overnight. Next day after pouring over ice it gave a pasty mass, which was treated with sodium bicarbonate to remove the unreacted acid and the solid obtained was crystallised from alcohol in yellow needles (0.38 g.), m.p. 195°. IR in nujol : 1690 $cm.^{-1}$ (pyrano >CO) ; 1655 $cm.^{-1}$ (xanthone >CO).

Analysis : Found : C, 71.76 ; H, 3.81 %

$C_{16}H_{10}O_4$ requires : C, 72.18 ; H, 3.79 %.

Dehydrogenation of 4'-pyrano(6',5' : 2,1)xanthone : 4'-Pyrono(6',5' : 2,1)xanthone :

The pyranoxanthone (0.3 g.) was refluxed in diphenyl ether (5 ml.) in the presence of palladised charcoal (0.25 g.) for 8 hr. The solution was filtered hot and the separated product crystallised from acetic acid in yellow needles (0.08 g.), m.p. 230°. IR in nujol : 1650 $cm.^{-1}$ (pyrono >CO) ; 1640 $cm.^{-1}$ (xanthone >CO).

Analysis : Found : C, 73.18 ; H, 3.46 %

$C_{16}H_8O_4$ requires : C, 72.73 ; H, 3.05 %.

Synthesis of 4'-pyrano(6',5' : 3,4)xanthone :

3-(β-Cyanoethoxy)xanthone :

A mixture of 3-hydroxyxanthone (1.0 g.) and acrylonitrile (50 ml.) was refluxed for 50 hr. in the presence powdered cupric oxide (0.2 g.). After removing acrylonitrile the product was extracted with chloroform and the extract was washed with dilute sodium hydroxide solution. The compound obtained after removal of chloroform crystallised

from acetic acid in white needles (0.25 g.), m.p. 173-75°.
Analysis : Found : : C, 72.64 ; H, 4.41 ; N, 5.29 %.
$C_{16}H_{11}O_3N$ requires : C, 72.45 ; H, 4.15 ; N, 5.28 %.

3-(β-Carboxyethoxy)xanthone :

When 3-(β-cyanoethoxyxanthone (1.0 g.) was refluxed in alcohol (50 ml.) in the presence of conc. hydrochloric acid (15 ml.) for 50 hr. tiny needles of the acid separated. After removing alcohol, the solid was collected and taken in sodium bicarbonate solution. The filtrate on acidification gave a solid which crystallised from alcohol in white needles (0.35 g.), m.p. 138-40°.
IR in nujol : 1725 $cm.^{-1}$ (-COOH) ; 1620 $cm.^{-1}$ (>CO).
Analysis : Found : C, 67.10 ; H, 4.30 %
$C_{16}H_{12}O_5$ requires : C, 67.60 ; H, 4.22 %.

4'-Pyrano(6',5' : 3,4)xanthone :

3-(β-Carboxyethoxy)xanthone (0.5 g.) was dissolved in acetic anhydride (5 ml.) by warming. After cooling the solution, conc. sulphuric acid (0.5 ml.) was added to it and the solution heated on a steam bath for 25 min. The solid separating after pouring the reaction mixture over ice, was treated with sodium bicarbonate solution and the insoluble solid collected. This was taken in chloroform and passed through a short column of silica gel. The solid obtained thus crystallised from aqueous acetic acid in light yellow needles (0.18 g.), m.p. 242-43°. IR in nujol : 1690 $cm.^{-1}$ (pyrano >CO) ; 1655 $cm.^{-1}$ (xanthone >CO).

Analysis : Found : C, 72.30 ; H, 3.96 %

$C_{16}H_{10}O_4$ requires : C, 72.18 ; H, 2.79 %.

Attempted dehydrogenation of 4'-pyrano(6',5' :3,4)xanthone :

The pyranoxanthone (0.2 g.) in diphenyl ether (4 ml.) was refluxed with palladised charcoal (0.2 g.) for 10 hr. and filtered hot. The solution on dilution with petroleum ether (40-60°) gave a product which was found to be the original pyranoxanthone.

Attempted cyanoethylation of 3,6-dihydroxyxanthone :

When 3,6-dihydroxyxanthone (0.8 g.) was refluxed with acrylonitrile (25 ml.) in the presence of sodium hydroxide solution (5 % ; 10 ml.) for about 60 hr., it gave an alkali insoluble product along with a polymeric product. This was extracted in chloroform and then crystallised from aqueous alcohol in light brown buds (0.09 g.), m.p. 255-58°. This, however, showed nitrogen in very low percentage.

Analysis : Found : N, 2.68 %

$C_{19}H_{14}O_4N_2$ requires : N, 8.92 %.

The same product resulted when more concentrated sodium hydroxide solution (10 %) was used.

When powdered 3,6-dihydroxyxanthone (0.5 g.) and acrylonitrile (50 ml.) were refluxed in the presence of Triton-B (0.5 ml.) for 15 hr., no reaction occurred.

Use of pyridine (3 ml.) instead of Triton-B also did not work.

When 3,6-dihydroxyxanthone (0.5 g.) in dimethyl formamide (15 ml.) and acrylonitrile (25 ml.) were refluxed

in the presence of cupric oxide (0.2 g.) no condensation occurred. The unreacted product was associated with a lot of polymeric product.

Attempted cyanoethylation of 3-hydroxy-6-methoxyxanthone :

Under the above conditions of reaction acrylonitrile did not condense with 3-hydroxy-6-methoxyxanthone.

In all the cases the polymeric product resulted which was insoluble in alkali and in solvents like chloroform, ether and benzene.

ATTEMPTED SYNTHESIS OF 2'-PYRONOXANTHONES

Attempted Pechmann reaction on hydroxyxanthones :

To a mixture of 2-hydroxyxanthone (1.0 g.) and ethyl acetoacetate (1.8 ml.) was added sulphuric acid (80 % ; 10 ml.) between 0-5° and the reaction mixture was left overnight. The product obtained on pouring the reaction mixture in water was found to be the original 2-hydroxyxanthone.

Increase in the period of time (48 hr.) also did not work.

Use of conc. sulphuric acid (3 ml.) also gave the unchanged product.

3-Hydroxyxanthone and 3,6-dihydroxyxanthone also did not condense with ethyl acetoacetate in the presence of conc. sulphuric acid under the above conditions.

On refluxing 2-hydroxyxanthone (1.0 g.) and ethyl acetoacetate (1.8 ml.) in diphenyl ether (4 ml.) for 3 hr.

no condensation occurred and the original 2-hydroxyxanthone was obtained back.

Similarly, ethyl acetoacetate did not condense with 3-hydroxyxanthone and 3,6-dihydroxyxanthone under the conditions mentioned above.

When powdered aluminium chloride (0.8 g.), ethyl acetoacetate (1.8 ml.) and 2-hydroxyxanthone (1.0 g.) were mixed and left overnight, no reaction occurred.

4',6-Dihydroxy-2'-pyrono(6',5' : 3,4)xanthone :

A mixture of 3,6-dihydroxy-4-acetylxanthone (1.0 g.), diethyl carbonate (25 ml.) and pulverised sodium (2.5 g.) was refluxed on a steam bath for 6 hr. The reaction mixture was poured in cold water and excess of diethyl carbonate removed by extraction with ether. The product obtained after acidification was taken in sodium bicarbonate solution, filtered and acidified again. The product crystallised from aqueous alcohol as brown powder (0.17 g.), m.p. 198-200° (decomp.).

Analysis : Found : C, 64.53 ; H, 2.97 %

$C_{16}H_8O_6$ requires : C, 64.87 ; H, 2.72 %.

SYNTHESIS OF FURANOXANTHONES

Synthesis of 2',2"-dimethyldifurano(5',4' : 3,4) and (5",4" : 6,5)xanthone :

3,6-Diallyloxyxanthone :

A mixture of 3,6-dihydroxyxanthone (1.0 g.) and allyl bromide (2 ml.) in acetone (70 ml.) was refluxed for 4 hr. in the presence of anhydrous potassium carbonate (2.0 g.).

The alkali insoluble product obtained crystallised from alcohol, in yellow needles (1.1 g.), m.p. 140°.

Analysis : Found : C, 72.61 ; H, 5.13 %

$C_{19}H_{16}O_4$ requires : C, 72.23 ; H, 5.56 %.

3,6-Dihydroxy-4,5-diallylxanthone :

3,6-Diallyloxyxanthone (1.0 g.) was refluxed in dimethyl aniline (8 ml.) for 4 hr. and reaction mixture was poured in ice cold hydrochloric acid. The product obtained was taken in sodium hydroxide solution and filtered and the filtrate acidified gave a solid which crystallised from aqueous alcohol in white buds (0.7 g.), m.p. 300°.

Analysis : Found : C, 71.96 ; H, 5.55 %

$C_{19}H_{16}O_4$ requires : C, 72.23 ; H, 5.56 %.

3,6-Diacetoxy-4,5-diallylxanthone :

3,6-Dihydroxy-4,5-diallylxanthone (1.0 g.) was dissolved in pyridine (10 ml.) and treated with acetic anhydride (2 ml.) on a steam bath for 2 hr. The product obtained on pouring the reaction mixture in cold hydrochloric acid crystallised from acetic acid in white needles (1.1 g.), m.p. 165-66°.

Analysis : Found : C, 70.53 ; H, 4.74 %

$C_{23}H_{20}O_6$ requires : C, 70.40 ; H, 5.10 %.

3,6-Diacetoxy-4,5-bis(2',3'-dibromopropyl)xanthone :

3,6-Diacetoxy-4,5-diallylxanthone (0.8 g.) in acetic acid (40 ml.) was treated with bromine solution in acetic acid (3 % ; 27 ml.) with constant stirring. The

solution was diluted and the separated product crystallised from acetic acid (1.1 g.), m.p. 170°.

Analysis : Found : Br, 45.40 %

$C_{23}H_{20}O_6Br_4$ requires : Br, 44.94 %.

2',2"-Dimethyldifurano(5',4' : 3,4) and (5",4" : 6,5)xanthone :

3,6-Diacetoxy-4,5-bis(2',3'-dibromopropyl)xanthone (1.0 g.) was refluxed in absolute alcohol (40 ml.) in the presence of potassium hydroxide (0.5 g.) for 6 hr. The product obtained after removing alcohol crystallised from acetic acid in white needles (0.7 g.), m.p. 273°. IR in nujol : 1630 $cm.^{-1}$ (>CO) ; 915 $cm.^{-1}$ (furan ring breathing).

Analysis : Found : C, 74.99 ; H, 3.80 %

$C_{19}H_{12}O_4$ requires : C, 74.99 ; H, 3.97 %.

Oxidation of 3,6-dimethoxy-4,5-diallylxanthone : 3,6-Dimethoxyxanthone-4,5-dicarboxylic acid :

3,6-Dihydroxy-4,5-diallylxanthone was methylated with dimethyl sulphate in acetone in the presence of anhydrous potassium carbonate as usual. The dimethyl ether crystallised from aqueous alcohol in white needles. M.p. 162-64°.

Analysis : Found : C, 74.91 ; H, 5.95 %

$C_{21}H_{20}O_4$ requires : C, 75.00 ; H, 5.95 %.

The above dimethyl ether (0.5 g.) and potassium permanganate (0.5 g.) in acetone (40 ml.) was refluxed for 15 hr., fresh quantity of potassium permanganate (0.5 g.) being added after every 5 hr. The acetone was removed and

and the solution was treated with dilute sulphuric acid. The separated solid was taken up in sodium bicarbonate. The product which separated on acidification crystallised from acetic acid in white needles (0.35 g.), m.p. 282-84°. IR in nujol : 1705 $cm.^{-1}$ (-COOH) ; 1630 $cm.^{-1}$ (>CO).

The m.p. of this acid with 3,6-dimethoxyxanthone-2,5-dicarboxylic acid was depressed by 30°.

Analysis : Found : C, 59.79 ; H, 3.93 %

$C_{17}H_{12}O_8$ requires : C, 59.29 ; H, 3.49 %.

Synthesis of 6-methoxy-2'-methylfurano(5',4' : 3,4)xanthone :

3-Allyloxy-6-methoxyxanthone :

A mixture of 3-hydroxy-6-methoxyxanthone (1.0 g.), allyl bromide (1 ml.) and acetone (50 ml.) was refluxed for 4 hr. in the presence of anhydrous potassium carbonate (2.0 g.). The alkali insoluble product obtained crystallised from aqueous alcohol in white needles (0.9 g.), m.p. 148°.

Analysis : Found : C, 70.76 ; H, 5.22 %

$C_{17}H_{14}O_4$ requires : C, 70.53 ; H, 4.97 %.

3-Hydroxy-4-allyl-6-methoxyxanthone :

3-Allyloxy-6-methoxyxanthone (1.0 g.) was refluxed in dimethyl aniline (8 ml.) for 4 hr. and poured into cold hydrochloric acid (50 % ; 50 ml.). The separated product was taken in alkali and filtered. Acidification of this filtrate gave a solid which crystallised from aqueous acetic acid in white buds (0.8 g.), m.p. 246-48°.

Analysis : Found : C, 70.13 ; H, 4.80 %

$C_{19}H_{16}O_5$ requires : C, 70.36 ; H, 4.98 %.

3-Acetoxy-6-methoxy-4(2',3'-dibromopropyl)xanthone :

3-Acetoxy-4-allyl-6-methoxyxanthone (0.8 g.) in acetic acid (30 ml.) was treated with bromine in acetic acid (3 % ; 14 ml.) with constant stirring. The solution was diluted and the separated product crystallised from acetic acid in white needles (0.6 g.), m.p. 156-58°.

Analysis : Found : Br, 33.48 %

$C_{19}H_{16}O_5Br_2$ requires : Br, 33.06 %.

6-Methoxy-2'-methylfurano(5',4' : 3,4)xanthone :

3-Acetoxy-6-methoxy-4-(2',3'-dibromopropyl)-xanthone (0.5 g.) when refluxed in absolute alcohol (25 ml.) in the presence of potassium hydroxide (0.2 g.) for 6 hr. gave a white solid which crystallised from aqueous acetic acid in white needles (0.3 g.), m.p. 178-80°. IR in nujol : 1635 $cm.^{-1}$ (>CO) ; 920 $cm.^{-1}$ (furan ring breathing).

Analysis : Found : C, 72.53 ; H, 4.08 %

$C_{17}H_{12}O_4$ requires: C, 72.85 ; H, 4.25 %.

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