CHAPTER - 2

SOME REACTIONS ON 1,5- AND 1,8- DIHYDROXYANTHRACENE

THEORETICAL

THEORETICAL

The Friedel-Crafts Reaction :

Price has defined the Friedel-Crafts reaction as " a process of uniting two or more organic molecules through the formation of carbon to carbon bonds under the influence of certain strongly acidic halide catalysts such as aluminium chloride, boron trifluoride, ferric chloride, zinc chloride, etc. ---------",(1). In general sense, today we consider Friedel-Crafts type reactions to be any substitution isomerisation, elimination, cracking, polymerisation, or addition reactions taking place under the catalytic effect of Lewis acid type acidic halides or proton acids. The different aspects of Friedel-Crafts reaction is are well covered by Olah(2).

The Friedel-Crafts ketone synthesis implies the introduction of an acetyl group into the aromatic nucleus by the action of an acetylating agent, usually an acyl halide, acid anhydride, ester or the acid itself, in the presence of a Friedel-Crafts catalyst

$$ArH + RCOCl \xrightarrow{AlCl_3} ArCOR + HX$$

$$ArH + (RCO)_2O \xrightarrow{AlCl_3} ArCOR + RCOOH$$

$$ArH + RCOOH \xrightarrow{BF_3} ArCOR + H_2O$$

$$ArH + RCOOR \xrightarrow{AlCl_3} ArCOR + R'OH$$

Friedel-Crafts acylation of aromatics is of considerable practical value owing to the importance of aryl ketones and aldehydes.

Friedel-Crafts acetylation of 1,5-dihydroxy-naphthalene with anhydrous aluminium chloride and acetyl chloride has been done by Kuriakose(3). 1,5-Dihydroxy-anthracene (I) on Friedel-Crafts acetylation with acetic anhydride at room temperature afforded 2,6-diacetyl-1,5-dihydroxyanthracene (II) in about 50% yield. The compound is giving s bluish violet colouration with alcoholic ferric chloride solution.

Under the same condition when 1,8-dihydroxyanthracene (III) was treated, 2,7-diacetyl-1,8-dihydroxyanthracene (IV) was obtained. (Chart 1).

The Fries Reaction :

The Fries reaction consists in the conversion of an ester of a phenol to an o- or p-hydroxyketones, or a mixture of both, by treatment with aluminium chloride.

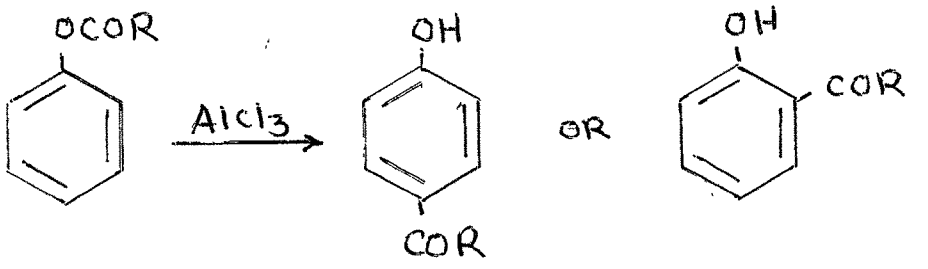
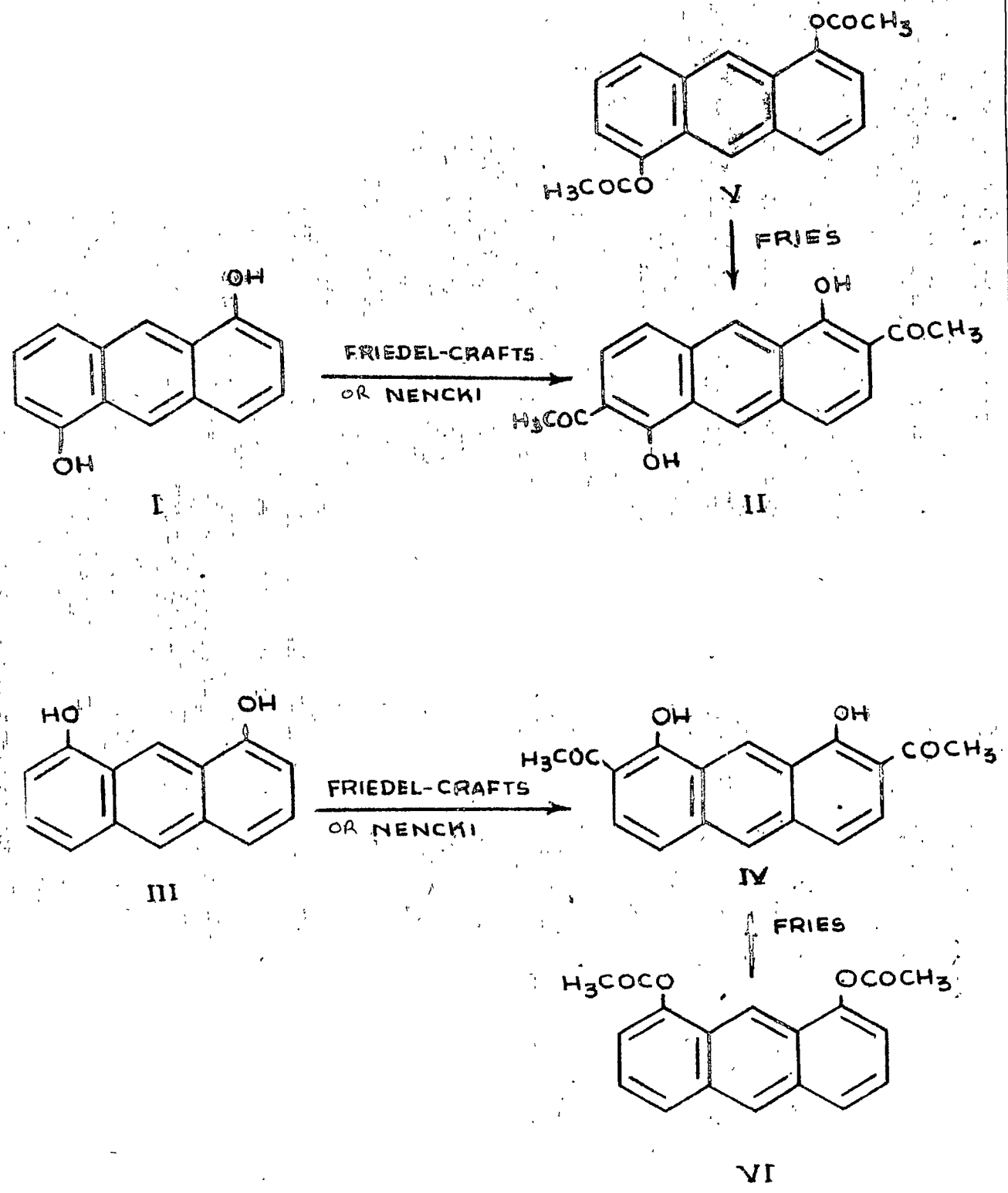


CHART-1


OCOCH3
H3COCO
V
FRIES
OH
OH
I
FRIEDEL-CRAFTS
OR NENCKI
OH
COCH3
H3COC
OH
II
HO
OH
III
FRIEDEL-CRAFTS
OR NENCKI
OH
OH
H3COC
COCH3
IV
FRIES
H3COCO
OCOCH3
VI

The details regarding this reaction is well reviewed by Bhatt(4) and others(5). The reaction mechanism has been evaluated by certain experimental facts(6). The structure of the phenyl ester determines whether or not a Fries reaction will take place. The reaction product o- or p-hydroxyketome is influenced by the structure of the ester, the temperature, the solvent, and the amount of aluminium chloride.

The temperature effect in the Fries reaction has been observed by m many workers(7,8). An important example of this is reported by Rosenmund, et. al. in which lower temperature (25°C) favours para product, while higher temperature (165°C) gives ortho product(8).

Fries rearrangement of 1,5-diacetoxynaphthalene is studied by Kuriakose(3). 1,5-Diacetoxynaphthalene on Fries rearrangement with anhydrous aluminium chloride without the use of any solvent gives an alkali soluble product.

When 1,5-diacetoxyanthracene(V) was subjected to Fries rearrangement under similar conditions, the product was characterized to be 2,6-diacetyl-1,5-dihydroxyanthracene for the following reasons :

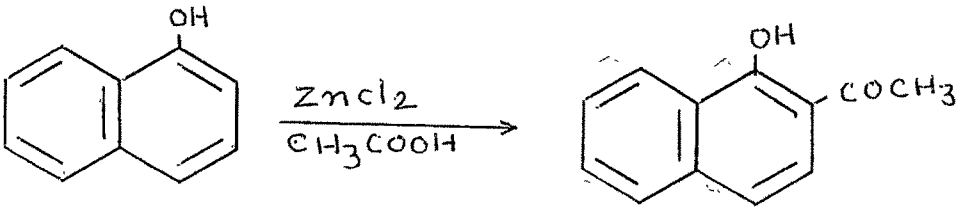
It gave a bluish violet colouration with alcoholic ferric chloride solution. The compound was mixed with product (II) obtained by Friedel-Crafts reaction and its

melting point was taken. No depression in melting point was observed. Also the U.V. and I.R. spectra of this compound superimpose on that of II.

Similarly 1,8-diacetoxyanthracene (VI) on Fries migration produced 2,7-diacetyl-1,5-dihydroxyanthracene. No depression in mixed melting point of this compound with (IV), shows its identity with IV. Further it was confirmed by superimposing its UV and I.R. spectra with IV.

Nencki Reaction :

The use of zinc chloride and an organic acid (acetic acid) for the nuclear acylation of phenol is generally known as Nencki reaction. Addition of acetic anhydride promotes the reaction. Witt and Brown synthesized 2-acetyl-1-naphthol by Nencki reaction(9). Using appropriate anhydride, Cheema and Venkataraman prepared a number of hydroxy ketones(10).



1,5- and 1,8-dihydroxyanthracene were subjected to Nencki acetylation when products II and IV were obtained respectively, in considerable good yield. (Chart 1).

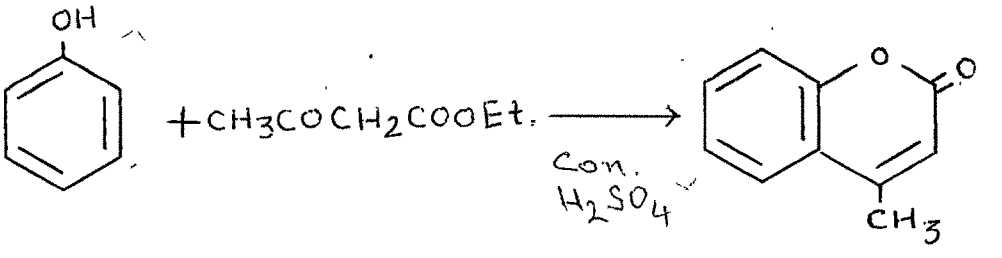
The yield of derivatives III and IV by the above three reactions is in following decreasing order :

Nencki > Friedel-Crafts > Fries

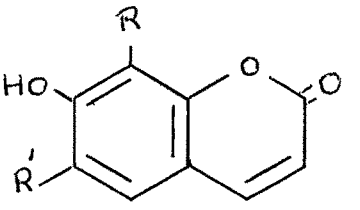
55% > 50% > 45%

The Pechmann Condensation :

The Pechmann condensation(11) is an important method for preparing coumarins, since it proceeds from very simple starting materials and gives good yield of coumarins. It consists in the condensation of phenol with β-ketonic ester in the presence of condens agents such as concentrated sulphuric acid (11) phosphorus pentoxide(12), phosphorus oxychloride(13) and anhydrous aluminium chloride(14). The other condensing agents such as sodium ethoxide, boric anhydride, sodium acetate, ferric chloride, stannic chloride, titanium chloride and thionyl chloride have been found to be useful only for the condensation of reactive phenols with β-ketonic esters(15).



Coumarins without substituents in the pyrone ring can be synthesized by condensing phenols with malic acid in the presence of conc. sulphuric acid(16). Various aspects of this reaction have been reviewed by Sethna and Phadke(17). The use of sulphuric acid as the condensing agent leads to the formation of Coumarins except in a very few cases where chromones are also formed(17). Those phenols which are reactive and give good yields of coumarins with sulphuric acid, invariably give coumarins with phosphorous pentoxide as the condensing agent(18) and phenols which do not condense in the presence of sulphuric acid or form coumarins in low yield give chromones when phosphorous pentoxide is employed as the condensing agent. Mentzer et. al.(19) found that if a phenol is heated with a β-ketonic ester at a high temperature without any condensing agent chromones are formed instead of coumarin. Later, Desai, Trivedi and Sethna(20) found that the reaction is more rapid and better products are obtained if diphenyl ether is used as a solvent and the reaction mixture refluxed with a short condenser to remove the water formed. Benzo-α-pyrone known as coumarins are found to be widely distributed in the plant kingdom in grass, orchids, legumes and citrus fruits either in the free state or in the combined state. Umbelliferon(i), aesculetin (ii), scopoletin(iii), daphnetin(iv) and fraxetin(v) are few of the simple coumarins occuring in nature(21).

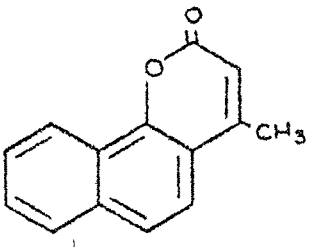


I

		R	R'
Umbelliferon	(i)	H	H
Aesculetin	(ii)	H	OH
Scopoletin	(iii)	H	OCH_3
Daphnetin	(iv)	OH	H
Fraxetin	(v)	OH	OCH_3

Robinson and Weygand(22) obtained 5-hydroxynaphtho (1,2; 6';5')α-pyrone(vi) by the Pechmann condensation of 1,5-dihydroxynaphthalene with ethyl acetoacetate. Kuriakose obtained some α and γ naphthodipyrones from 2,6 2,7 and 1,5-dihydroxynaphthalene(3). Sethna et. al.(44). synthesized some anthra α and γ pyrone(vii-xiii) from 1-hydroxyanthracene and 2-hydroxyanthracene (Chart 2).

CHART-2



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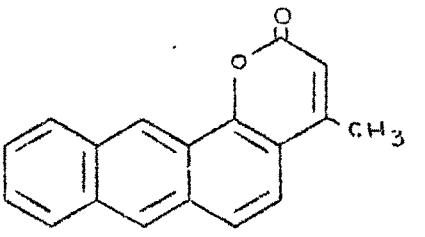

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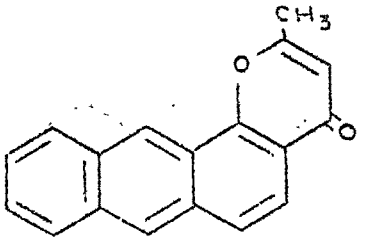
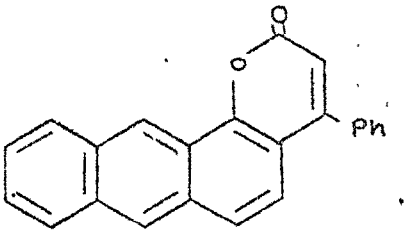


viii



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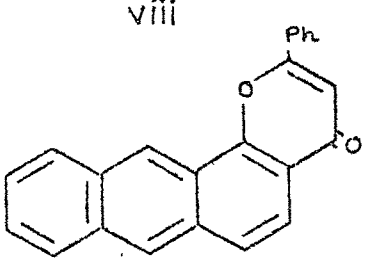

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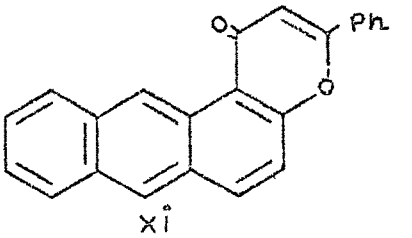

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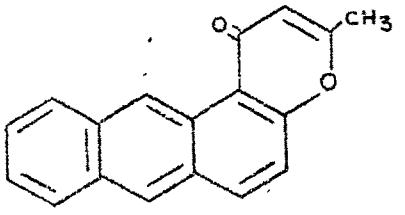
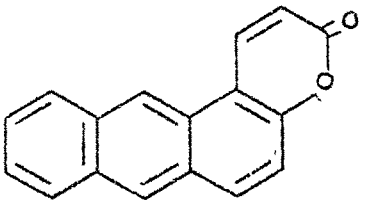


xii

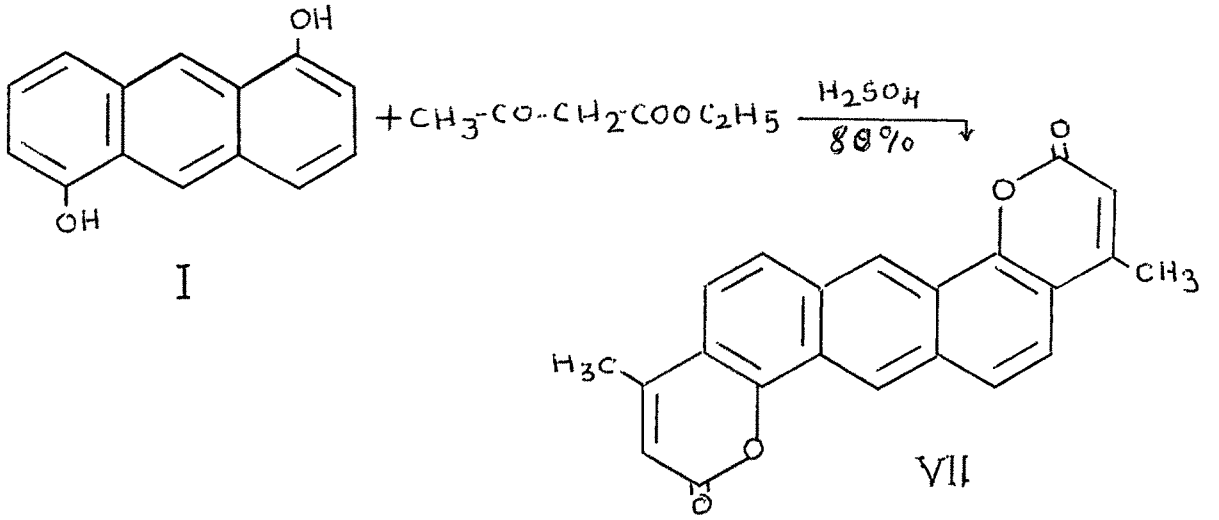


xiii

This appears to be the only synthesis of anthrapyrone derivatives reported so far. It was therefore, thought of interest to study the synthesis of ∝-dipyrone derivatives from 1,5 and 1,8-dihydroxyanthracene by Pechmann condensation, with ethyl acetoacetate.

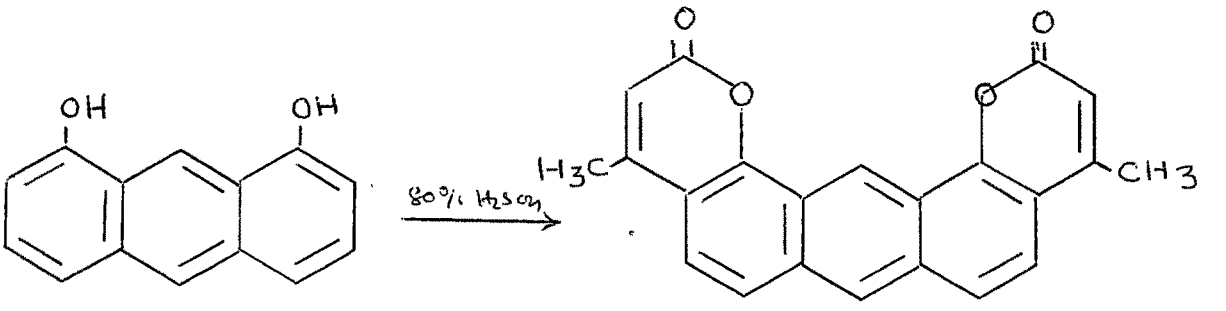
Pechmann Condensation of 1,5-dihydroxyanthracene with ethyl acetoacetate :

When 1,5-dihydroxyanthracene(I) was condensed with ethyl acetoacetate in the presence of sulphuric acid (80%), a product(VII) was obtained in good yield. It was insoluble in cold sodium hydroxide solution. On heating with alkali and dimethyl sulphate in acetone solution on a steam bath it gave an unsaturated acid as seen by decolourisation of dilute bromine water and potassium permanganate solution. The formation of such an unsaturated acid is a diagnostic test for coumarin derivative(23). 4',4"-Dimethyl-1,2; 5,6-anthra-∝-dipyrone(VII) has been assigned the structure based on analytical data and spectroscopic analysis.



The same product was obtained when 1,5-dihydroxyanthracene was condensed with ethyl acetoacetate using phosphorus pentoxide as condensing agent (Simonis reaction).

Similarly 1,8-dihydroxyanthracene(III) on condensation with ethyl acetoacetate in the presence of 80% sulphuric acid under the same conditions gave compound(VIII). An unsaturated acid was obtained on heating with alkali and dimethyl sulphate in acetone solution on steam bath. The compound(VIII) has been assigned the structure 4',4"-dimethyl-1,2,7,8-anthra-α-dipyrone based on analytical data and spectroscopic analysis.

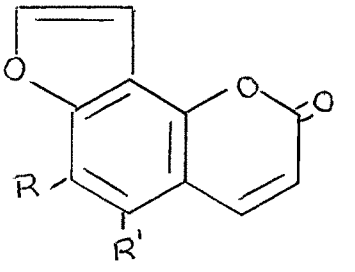


III VIII

Synthesis of Bibenzofurans from 1,5 and 1,8-dihydroxy Anthracene :

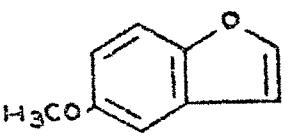
Eventhough a large number of benzofuran derivatives have been synthesized the synthesis of anthrafurans have been comparatively fewer. Numerous derivatives of benzofurans have been isolated from various plants. Some of these may be mentioned here, 5-methoxybenzofuran(xiv) cuparin(xv), pongamol(xvi), egonol(xvii) and griseofulvin(xviii) and khellin(xix) are a few of the simple benzofuran derivatives occuring in nature.(Chart 3).

A large number of furocoumarins have also been isolated from plants, for example, angelicin(xx), pimpinellin(xxi), psoralene(xxii), bergapten(xxiii), xanthotoxin(xxiv), isopimpinellin(xxv) and oreoselone (xxvi).

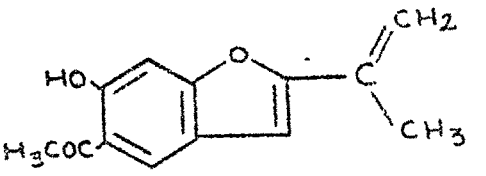


	R	R'
xx Angelicin	H	H
xxi Pimpinellin	OCH_3	OCH_3

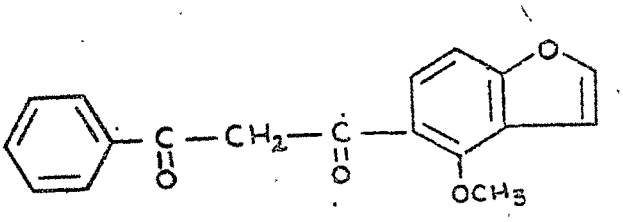
CHART-3



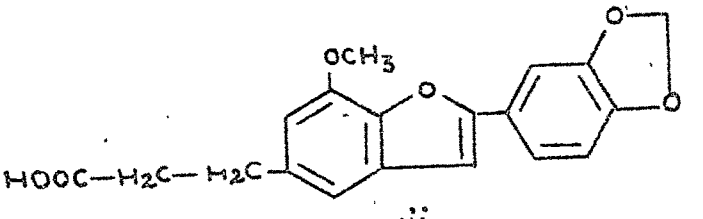
xiv



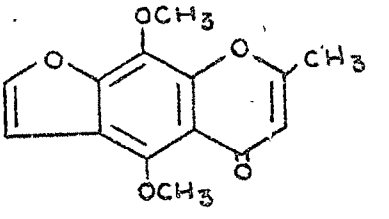
XV



xvi



xvii



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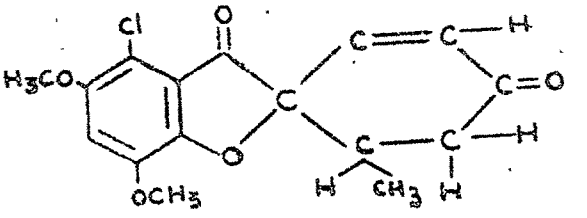
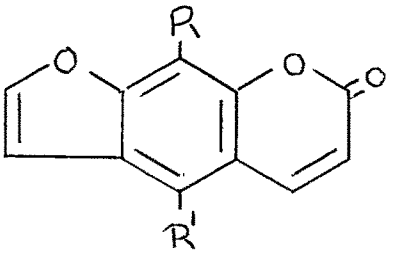
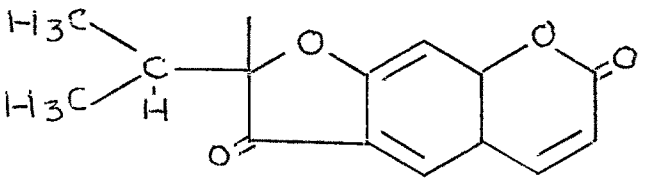


xviii

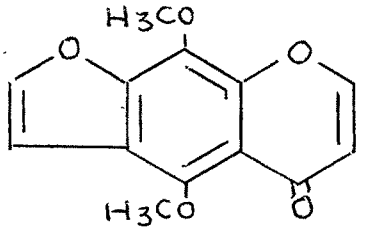


		R	R'
xxii	Psoralene	H	H
xxiii	Bergapten	H	OCH_3
xiv	Xanthotoxin	OCH_3	H
xxv	Isopimpinellin	OCH_3	OCH_3

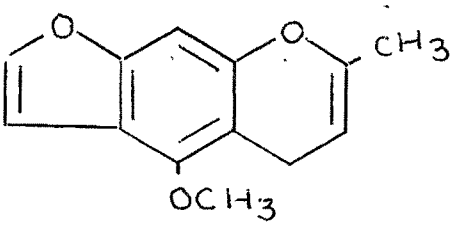


xxvi

Khellin(xxvii) and visnagin(xxviii) are the naturally occuring molecules of the furochromone group and karajin(xix) is an example of a naturally occuring furoflavones



xxvii



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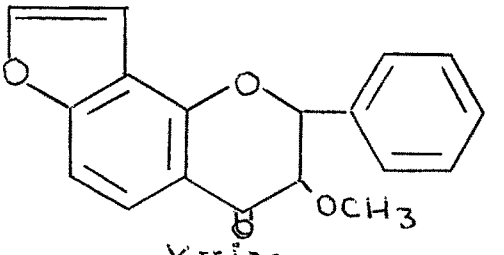
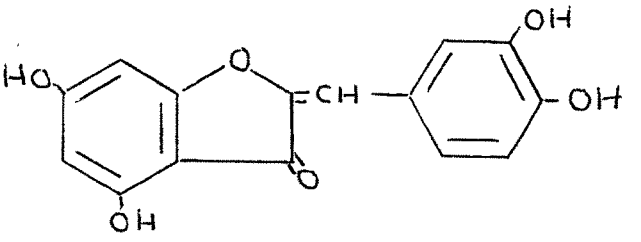
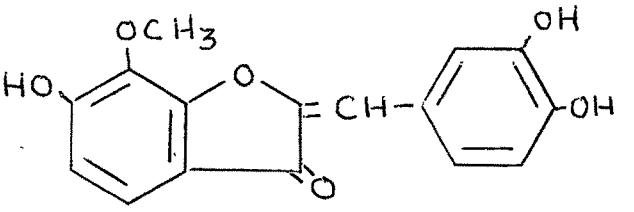


xxix

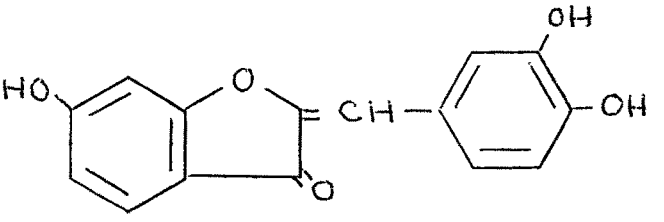
Still another group of benzofuran derivatives are the aurones. They are glycosides of hydroxylated benzylidine coumaranones. Aureusidin(xxx) leptosidin(xxxi) and sulpuretin(xxxii) are a few members of this group.



XXX



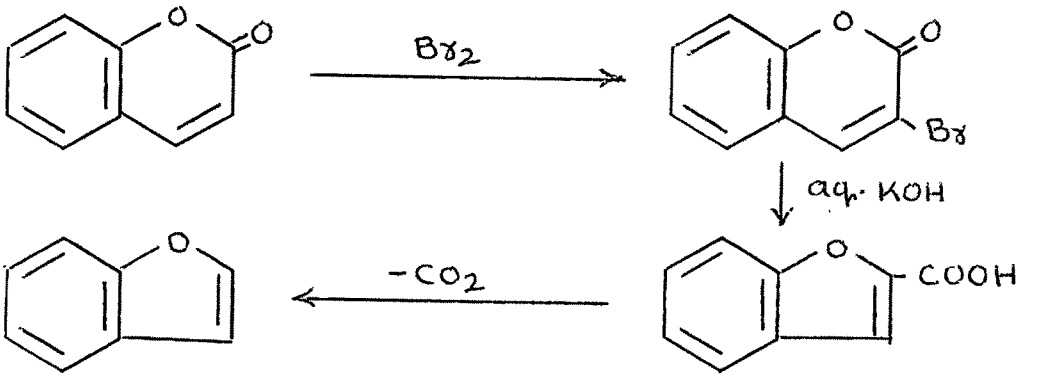
XXXI



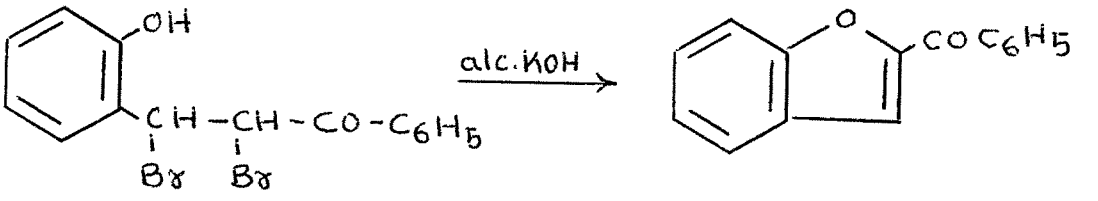
XXXII

Some of the important general methods of the synthesis of benzofuran derivatives may be briefly described here as they illustrate the different ways in which a furan ring can be built up on an aromatic nucleus.

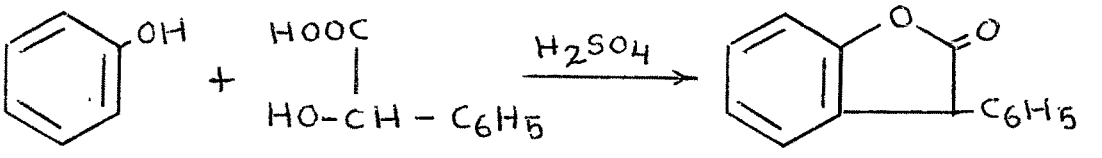
1. The classical synthesis of benzofuran involves bromination of coumarin and treatment of the resulting 3-bromocoumarin with alkali to get (benzofuran-2-carboxylic acid) coumarilic acid which on decarboxylation gives benzofuran(24,25).



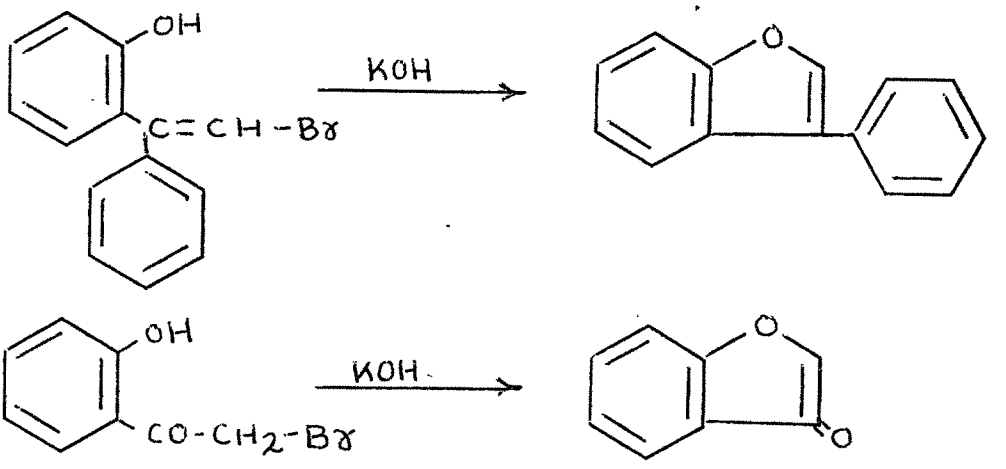
2. Synthesis of a benzofuran derivative can be accomplished from the dibromide of a chalcone(26) as follows;



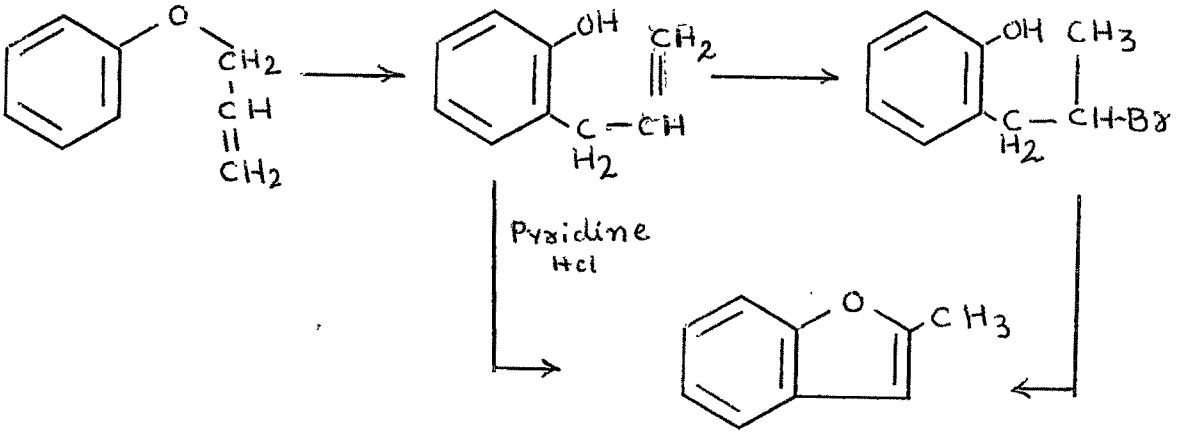
3. ∝-Hydroxyphenyl acetic acids readily undergo ring closure with phenol in presence of sulphuric acid to yield furan derivatives(27-29). Thus when mandelic acid is condensed with phenol, 3-phenylcoumaran-2-one is formed.



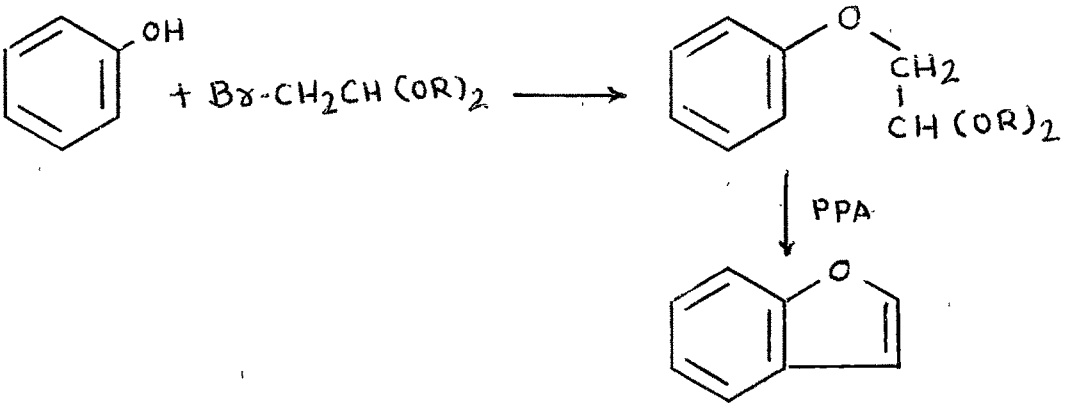
4. A related synthesis involves the action of alkali on o-hydroxy-B-halostyrene(30), 3-phenylbenzofuran can be prepared in this way and if o-hydroxybromoacetophenone is used, 3-coumaranone results(31).



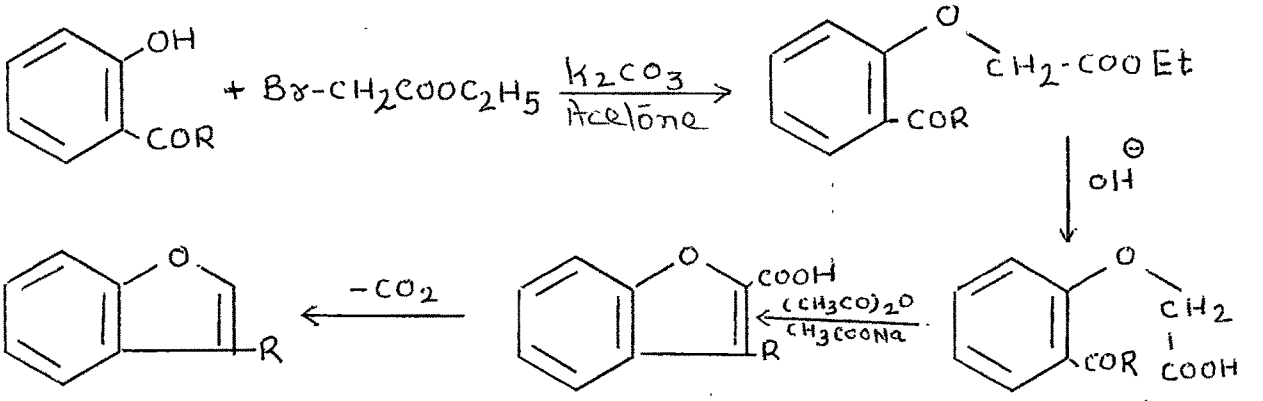
5. Benzofuran can be obtained by the catalytic cyclodehydrogenation of o-ethylphenol(32), and 2,3-benzofurans can be prepared by the cyclisation of o-allylphenols on heating with hydrobromic acid or with pyridine hydrochloride(33-36).



6. Sulphuric acid, anhydrous zinc chloride or polyphosphoric acid are effective reagents for the ring closure of phenoxy carbonyl(37-40) compounds.

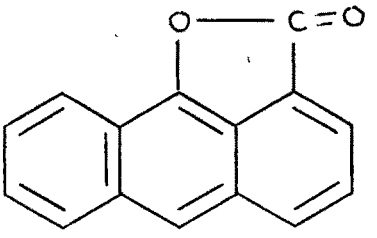


7. A method which is extensively used for the synthesis of furan derivatives consists in the condensation of bromoacetic ester with an o-hydroxy aldehyde or an o-hydroxyketone and subsequent hydrolysis and cyclisation of phenoxy acetic acid derivative formed with sodium acetate and acetic anhydride.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

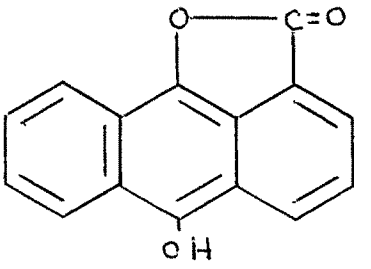


A very large number of benzofuran derivatives have been synthesized. Furan ring has also been built up on the naphthalene ring system and a number of simple as well as substituted naphtho-furan have been synthesized(3).

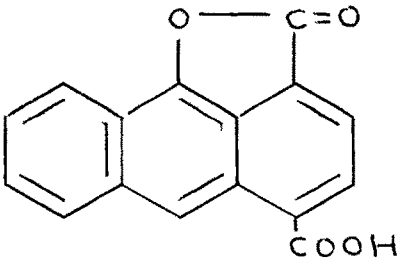
A few anthrafuran-2-ones, such as 2H-anthra (9,1-bc) furan2-one(41)(xxxiii), 2H-anthra (9,1-bc) furan-2-one-6-hydroxy(xxxiv)(42), 2H-anthra (9,1-bc) furan-2-one-5-carboxylic acid(xxxv), and 2H-anthra (9,1-bc) furan-2-one-7-carboxylic acid(xxxvi)(43) have been reported. 3-Methyl-anthra (1,2-b) furan, 1-methylanthra (2,1-b) furan and anthra (2,1-b) furan have been synthesized by Shah and Sethna(44,45).



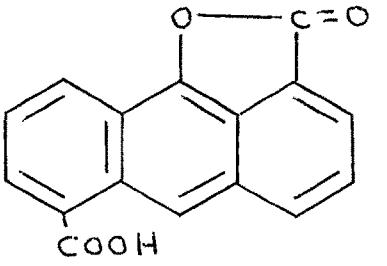
XXXiii



XXXiv

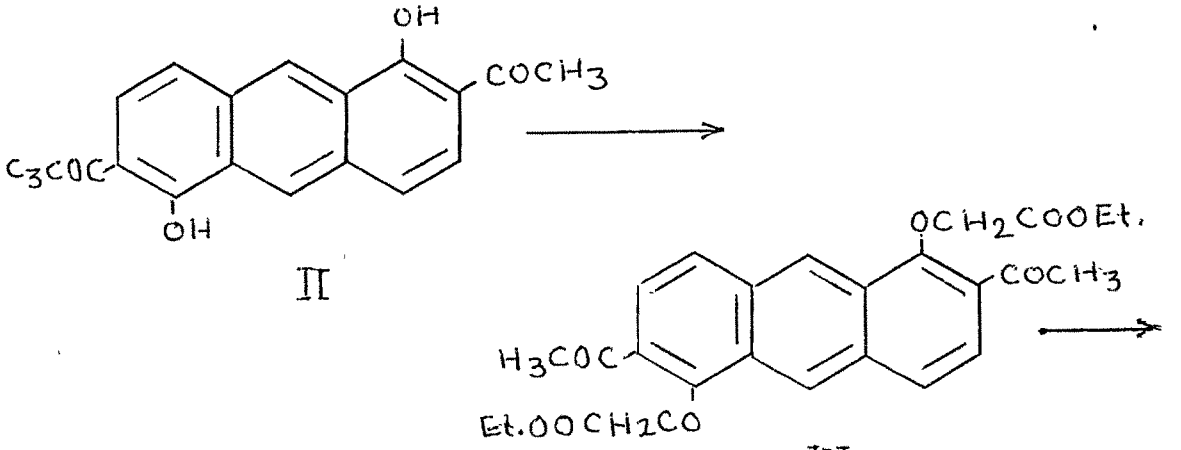


XXXV



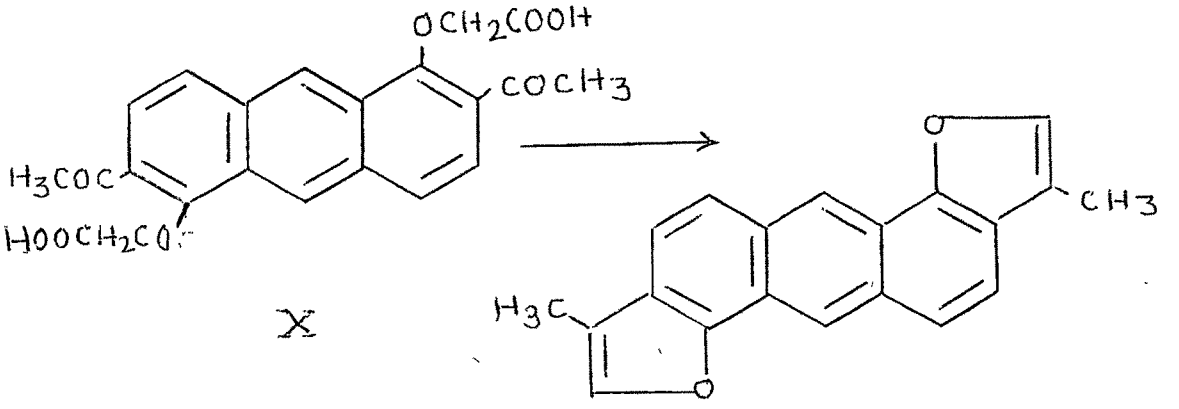
XXXVi

Synthesis of 3', 3"-Dimethyl-anthra(1,2b; 5,6b')bifuran: 2,6-Diacetyl-1,5-dihydroxyanthracene(II) was condensed with ethyl bromoacetate in boiling acetone in presence of anhydrous potassium carbonate when 2,6-diacetyl-1,5-dicarbethoxy-methoxy)anthracene(IX) was obtained. This ester was hydrolysed by treatment with alkali to 2,6-diacetyl-1,5-dicarboxymethoxy)anthracene(X). The cyclisation of this acid was effected by refluxing it with acetic anhydride and freshly fused and powdered sodium acetate and 3',3"-dimethylanthra(1,2b; 5,6b')difuran(XI) was obtained.



II

IX

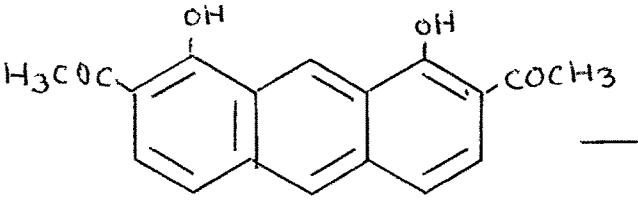


X

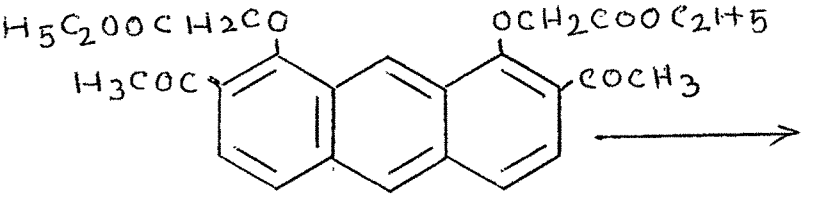
XI

Synthesis of 3',3"-dimethylanthra (1,2b; 7,8d')bifuran:

Similarly 2,7-diacetyl-1,8-dihydroxyanthracene(IV) on condensation with ethylbromoacetate, under the same conditions, gave 2,7-diacetyl-1,8-di(carbethoxymethoxy) anthracene(XII). The ester was hydrolysed with alkali to 2,7-diacetyl-1.8-di(carboxymethoxy)anthracene(XIII). 3',3"-dimethylanthra(1,2b; 7,8d')bifuran(XIV) was obtained on heating the acid(XIII) with sodium acetate and acetic anhydride.



IV



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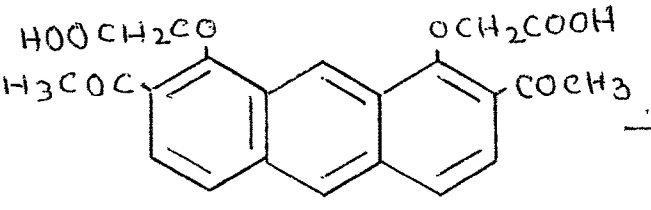
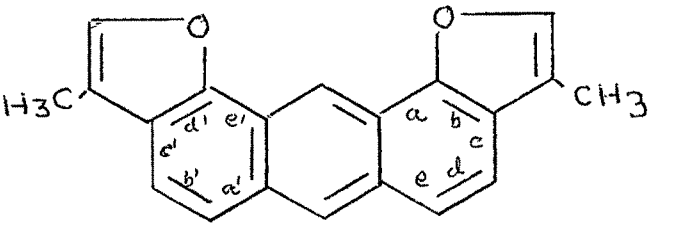


XIII



XIV

Spectroscopic Analysis :

Ultraviolet Spectra :

The ultraviolet spectra of dihydroxy anthracene derivatives are given in Table 2. These spectra were scanned in alcohol as a solvent except the compound VII and VIII, which were scanned in chloroform since they are insoluble in alcohol, using Beckmann DU-2 Spectrophotometer. Generally a very sharp peak (λmax) is located around 255 nm. The compounds II, IV, VII and VIII have another peak around 300 nm.

The anthracene absorbs at 221, 256, 375 nm(46). In all the compounds peak around 255 may be corresponding to the absorption peak of anthracene. Coumarin shows two absorption bands in the region 250 to 330 nm(47-51). The first absorption band of medium intensity is observed in the region 300 to 330 nm with a maximum at 311 (log E 3.72) nm, which is attributed to the presence of the C=C-C=O group in the pyrone ring of coumarin. The second absorption band of comparatively higher intensity is observed in the region 250 to 300 nm with a maximum at 274 nm (log E 4.03), which is due to benzenoid absorption(52). In compounds VII and VIII (bipyrones) the peaks at 310 and 313 respectively can be attributed due to C=C-C=O group of pyrone ring and in compounds II and IV at 302 and 292 due to the same group.

Infra Red Spectra :

The i.r. spectra were taken in the nujol mull using Perkin Elemer i.r. spectrophotometer.

Ketonic C=O and C=C :

The unsaturated ketonic vibrations due to C=O and C=C are are absorbed in the region around 1693 and 1621 cm^{-1} respectively(53). In the compounds II, IV, X and XIII studied here. the carbonyl frequency is assigned at 1715 to 1730 cm^{-1}, while the C=C band assigned at 1620, except in the compound II, which is at 1545, which may be due to different position of carbonyl group.

C=O Stretching Vibrations in Pyrones :

The ester carbonyl group of δ-lactones occurs in the same position as in open chain compounds. This is parallel to the case of cyclic ketones, and is to be attributed to the lack of strain in rings of this size. This correlation is quoted by Rasmussen and Brattain(54) and have given a value at 1738 cm^{-1}. Jones et. al. (55-57) have confirmed this correlation in a number of steroid δ-lactones and it has also been found to hold good for a number of six membered ring lactoes by Grove and Willis(58). Korte and his co-workers have also reported in the range 1715 to 1730 cm^{-1} for such $\alpha\beta$ six membered unsaturated C=O group(59). In the compounds VII and VIII this band is located at 1730 cm^{-1}, with the confirmity of the reported values.

C-O-C Stretching Vibrations :

A strong band is found in the range 1015 to 1035 cm^{-1} due to stretching vibration at C-O-C ether linkage in compounds X, XI and XIII and XIV. Generally compounds having the furan linkage, these frequencies are in the range 1015 to 1035 cm^{-1} (60).

Nuclear Magnetic Resonance Spectra :

As these derivatives are only sparingly soluble in the usual solvents, the NMR spectra could not be obtained.

EXPERIMENTAL

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

1. Preparation of 1,5-dihydroxyanthracene :

Disodium salt of anthracene 1,5-disulphonic acid was prepared from anthracene according to Liebermann(61) with minor modifications as follows :

Anthracene (5.0g) was powdered and added in small portions to (80%, 10 ml) sulphuric acid contained in a three necked round bottom flask. The reaction mixture was mechanically stirred for 6 hours at 65-70°C. The reaction proceeded slowly and ultimately the reaction mixture became olive green paste. This was then poured into water (1 litre) and the unreacted anthracene was filtered off and the filtrate after making alkaline with sodium hydroxide solution (40%) was evaporated to half of its volume and allowed to cool, when the solid separated mainly consisted of disodium anthracene 1,5-disulphonate. This was then recrystallized from water in the form of yellowish green micro needles. (Yield 40%).

The disodium anthracene 1,5-disulphonate on fusion with alkali according to Lampe(62) with minor modification gave 1,5-dihydroxyanthracene, as follows:

Potassium hydroxide (35g) was taken in a nickel crucible and heated in Muffle furnace to about 200-220°C. When alkali

was fused, disodiumanthracene 1,5-disulphonate (5g) was then added to the molten alkali in small portions with stirring and the temperature was then gradually raised and maintained at 290°C for 6 hours. The fusion mixture was then cooled and cake was taken out from crucible and dissolved in ice water (1 litre). The alkaline solution was then acidified with cold concentrated hydrochloric acid when light greenish yellow precipitate of 1,5-dihydroxy-anthracene was obtained, and was crystallized from dilute alcohol in yellow needles m.p. 265 d. (reported m.p.265 d).

2. Synthesis of 2,6-diacetyl-1,5-dihydroxyanthracene :

(a) Friedle Craft Acetylation of 1,5-Dihydroxy Anthracene:

A solution of 1,5-dihydroxyanthracene (2.1g) and acetic anhydride (3.0ml) in nitrobenzene (15ml) was mixed with a solution of anhydrous aluminium chloride (5.3g) in nitrobenzene (35ml) and the reaction mixture was kept for 72 hours at room temperature protecting it from moisture. It was then treated with ice and hydrochloric acid (50ml HCl + 200g ice) and the nitrobenzene was steam distilled. The black product obtained was extracted with 10% alkali. The product obtained on acidification of the alkaline extracts crystallized from chloroform in yellowish brown needles m.p.167°C. It gave bluish violet colouration with alcoholic

ferric chloride solution. The yield and analytical data are recorded in Table 1.

The same ketone was obtained when the reaction mixture was taken as above and heated on steam bath for 3 hours instead of keeping at room temperature for 72 hours. m.p. 167°C. It gave bluish violet colouration with alcoholic ferric chloride.

(b) Fries Rearrangement of 1,5-Diacetoxyanthracene :

1,5-Diacetoxyanthracene was prepared according to the method of Dienel(63) using pyridine and acetic anhydride as follow :

Preparation of 1,5-diacetoxyanthracene :

1,5-Dihydroxyanthracene (2g) was dissolved in acetic anhydride (30ml) and pyridine (1.5ml) was added to it and the reaction mixture kept for 24 hours at room temperature protecting it from moisture using guard tube. The product obtained on pouring the mixture in cold water was crystallized from alcohol in light brown needles m.p. 198°C (reported m.p. 198°C (yield 40%).

A mixture of 1,5-diacetoxyanthracene (1.5g) and anhydrous aluminium chloride (2.7g) was heated in an oil bath at 140°C for 3 hours. The reaction mixture was then treated with ice and hydrochloric acid and the product obtained was extracted with ether. The ethereal layer was extracted repeatedly with 10% alkali. The product obtained

on acidification of the alkaline extract was crystallized from dilute acetic acid in yellowish brown needles. m.p. 167°C and mixed m.p. with 2,6-diacetyl-1,5-dihydroxy-anthracene was not depressed(yield 50%).

(c) Nencki Reaction on 1,5-Dihydroxyanthracene :

Anhydrous zinc chloride (10g) was powdered and dissolved in glacial acetic acid (15ml) by heating and the solution was allowed to cool at room temperature. 1,5-Dihydroxyanthracene (1g) was added to it and the reaction mixture was refluxed on sand bath for one hour protecting it from moisture. It was left at room temperature for about 2 hours and then added to 1:1 hydrochloric acid (150ml). The green coloured solid which separated, on crystallisation from alcohol, gave greenish yellow needles m.p. 167°C.The mixed melting point with 2,6-diacetyl-1,5-dihydroxyanthracene obtained before by the Friedel-Crafts acetylation of 1,5-dihydroxyanthracene was not depressed (yield 55%).

3. Preparation of 1,8-Dihydroxyanthracene :

Disodium salt of anthracene 1,8-disulphonic acid was prepared from anthracene according to the method of Libermann(1) with a little modification.

Anthracene (5g) was dried and powdered and added in small portions in (90% 10ml) sulphuric acid. The reaction mixture was mechanically stirred for 6 hours at 65-75°C. The

reaction proceeded slowly and ultimately the reaction mixture became olive green paste. This was poured into water (1 litre) when dark green solution was obtained, this was then filtered to remove unreacted anthracene The filtrate after making alkaline with sodium hydroxide solution (40%) was evaporated to half of its volume and allowed to cool, when the solid separated mainly consisted of disodiumanthracene 1,8-disulphonate. This was then recrystallized from water in the form of yellowish needles (yield 40%).

The disodiumanthracene 1,8-disulphonate on fusion with alkali according to the method of Lampe(2) with minor modification gave 1,5-dihydroxyanthracene as follow :

Potassium hydroxide (35g) was taken in a nickel crucible and heated in Muffle furnace to about 200-220°C when alkali was fused. Disodiumanthracene 1,8-disulphonate (5g) was then added to the molten alkali in small portion with stirring and the temperature was then gradually raised and maintained at 290°C for 6 hours. The molten fusion mixture was then poured on crushed ice (1 kg) with continuously stirring. The alkaline solution was then acidified with cold concentrated hydrochloric acid when light yellow precipitate of 1,8-dihydroxyanthracene was obtained which was repeatedly extracted with ether. Residue obtained after evaporating ether was crystallized from alcohol in yellow needles m. p. 224 d. (reported m. p. 225 d).

4. Synthesis of 2,7-Diacetyl-1,8-Dihydroxyanthracene :

(a) Friedel Crafts Acetylation of 1,8-Dihydroxy-Anthracene :

A solution of 1,8-dihydroxyanthracene (2.1g) and acetic anhydride (3ml) in nitrobenzene (15ml) was mixed with a solution of anhydrous aluminium chloride (5.3g) in nitrobenzene (35ml) and the reaction mixture was kept for 72 hours at room temperature protecting it from moisture. It was then treated with ice and hydrochloric acid and the nitrobenzene was steam distilled. The black product obtained was extracted with sodium hydroxide solution (10%). The product obtained on acidification of the alkaline extract was crystallized from chloroform in light brown needles m.p. 271°C. It gave bluish violet colouration with alcoholic ferric chloride solution. The yield and analytical data are recorded in Table 1.

(b) Fries Rearrangement of 1,8-Diacetoxyanthracene :

Diacetyl derivative of 1,8-dihydroxyanthracene was prepared according to the method of Dienel(3) as follow :

1,8-Dihydroxyanthracene (2g) was dissolved in acetic anhydride (30ml) and pyridine (1.5ml) was added to it and the reaction mixture was kept for 24 hours at room temperature protecting it from moisture using guard tube. The product obtained on pouring the mixture in cold water was crystallized from alcohol in light brown needles. m.p. 184°C (reported m. p. 184°C).

A mixture of 1,8-diacetoxyanthracene (1.5g) and anhydrous aluminium chloride (2.7g) was heated in an oil bath at 140 °C for 3 hours. The reaction mixture was then treated with ice and hydrochloric acid and the product obtained was extracted with ether. The etherial layer was extracted repeatedly with 10% sodium hydroxide solution. The product obtained on acidification of the alkaline extract was crystallized from dilute acetic acid in yellowish brown needles, m.p.271°C and mixed m.p.with 2,7-diacetyl-1,8-dihydroxyanthracene was not depressed (yield 40%).

(c) Nencki Reaction on 1,8-Dihydroxyanthracene :

Anhydrous zinc chloride (10g) was powdered and dissolved in glacial acetic acid (15ml) by heating and the solution was allowed to cool at room temperature. 1,8-Dihydroxyanthracene (1.0g) was added to it and the reaction mixture was refluxed on sand-bath for 1 hour protecting it from moisture. It was left at room temperature for about 2 hours and then added to hydrochloric acid (1:1, 150ml). The green colour solid which separated on crystallization from alcohol, gave greenish yellow needles. m.p.271°C. The mixed melting point with 2,7-diacetyl-1,8-dihydroxy anthracene obtained above by Friedel-Crafts acetylation of 1,8-dihydroxyanthracene was not depressed. (yield 55%).

Pechmann Reaction on 1,5-Dihydroxyanthracene :

5. Preparation of 4'-4"-Dimethyl-1,2,5,6-Anthra-α-dipyrone:

(a) With sulphuric acid as the condensing agent:

1,5-Dihydroxyanthracene (1g) and ethyl acetoacetate (1.5ml) were mixed together and sulphuric acid (80% 25ml) was added gradually with shaking and external cooling. The reaction mixture was kept in refrigerator for 24 hours and then poured on crushed ice (100g). The solid separated was filtered and washed with 5% sodium hydroxide solution and was crystallized from chloroform when yellow plates were obtained m.p. > 335.0°C. Yield and analytical data are given in Table 1.

(b) With the phosphorus pentoxide as the condensing agent:

To a mixture of 1,5-dihydroxyanthracene (0.5g) and ethyl acetate (0.7ml), phosphorus pentoxide (2g) was gradually added with stirring. The reaction mixture protected from moisture, was then heated on a steam bath for one and half hour. Crushed ice was then added and the residue taken up in ether. The etherial layer was repeatedly washed with alkali(2%) followed by water. The residue obtained after evaporating ether was crystallized from nitrobenzene in yellow plates. m.p. > 335°C.

6. Pechmann Reaction on 1,8-Dihydroxyanthracene : Preparation of 4'-4"-Dimethyl-1,2; 7,8-Anthra-α-Dipyrone :

(a) With sulphuric acid as the condensing agent :

1,8-Dihydroxyanthracene (1g) and ethyl acetoacetate (1.5ml) were mixed together and sulphuric acid (80%, 25ml) was added gradually with shaking and cooling externally. The reaction mixture was kept in refrigerator for 24 hours and then poured on crushed ice. The solid separated was filtered, washed with 5% sodium hydroxide solution followed by water and crystallized from chloroform when bright yellow plates were obtained. m.p.$>$350°C. Yield and elemental analysis are given in Table 1.

(b)With phosphorus pentoxide as the condensing agent :

To a mixture of 1,8-dihydroxyanthracene (0.5g) and ethyl acetoacetate (0.7ml), phosphorus pentoxide (2g) was gradually added with stirring. The reaction mixture protected from moisture, was then heated on a steam bath. After one and half hour crushed ice was added into the flask and the residue taken up in ether. The etherial layer was repeatedly washed with sodium hydroxide solution (2%) followed by water. The ether was evaporated and the residue obtained was crystallized from nitrobenzene in bright yellow plates m.p.$>$ 350°C.

7. Synthesis of (3',3"-Dimethyl-anthra 1,2-b; 5,6-b') difuran :

(a) Condensation of 2,6-diacetyl 1,5-dihydroxyanthracene with ethylbromoacetate :

1,5-Diethyl-2,6-diacetyl-1,5-anthraxyacetate :

A mixture of 2,6-diacetyl 1,5-dihydroxyanthracene (0.5g), ethylbromo acetate (1ml) and anhydrous potassium carbonate (3g) was refluxed in dry acetone (50ml) for 4 hours on steam bath. The solution was then filtered hot and the oily residue obtained on removal of acetone was taken in excess of water and left overnight. The product obtained after removal of water was crystallized from dilute alcohol in yellow needles. m.p. 97°C. Yield and analytical data are given in Table 1.

(b) 2,6-Diacetyl 1,5-dianthroxy acetic acid :

The above ester (0.5g) was heated with sodium hydroxide solution (10% 20ml) on a steam bath till the ester dissolved. The solution was then filtered hot and the product obtained on acidification with dilute hydrochloric acid, was crystallized from dilute alcohol in yellow needles. m.p., 184°C yield etc are given in Table 1.

(c) 3'.3"-Dimethylanthra(1,2-b; 5,6-d')difuran :

A mixture of 2,6-diacetyl 1,5-dianthroxy acetic acid (0.5g) acetic anhydride (6ml) and freshly fused sodium acetate (1.5g) was refluxed for 30 minutes. The reaction mixture was

then poured in cold water and left overnight. The product separated was crystallized from dilute alcohol in brown yellow plates m.p. 143°C, yield and analytical data are given in Table 1.

8. Synthesis of 3',3"-Dimethylanthra(1,2-b; 7,8-d') difurans :

(a) Condensation of 2,7-diacetyl 1,8-dihydroxyanthracene with ethylbromo acetate :

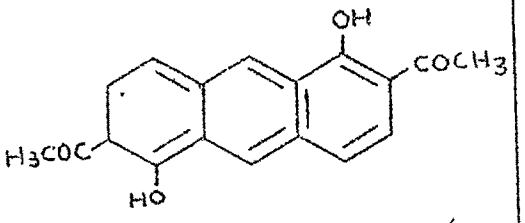
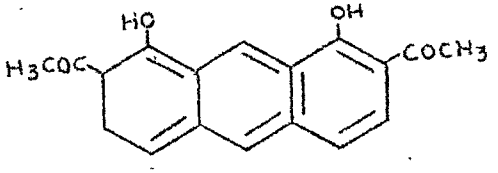
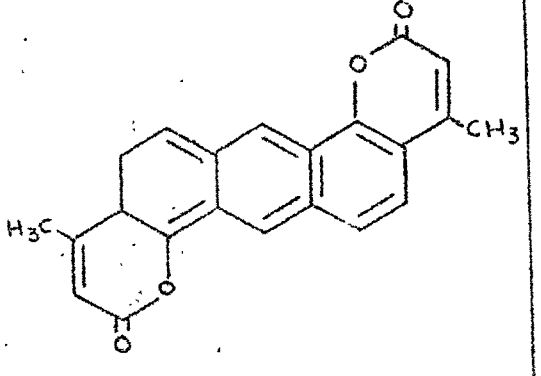
A mixture of 2,7-diacetyl 1,8-dihydroxyanthracene (0.5g) ethylbromo acetate (1ml) and anhydrous potassium carbonate (3g) was refluxed in dry acetone (50ml) for 4 hours. The solution was then filtered hot and the oily residue obtained on removal of acetone was taken in excess of water and left overnight. The residue after decanting water was crystallized from dilute alcohol in yellow needles m.p. 127°C, Yield and analytical data are given in Table 1.

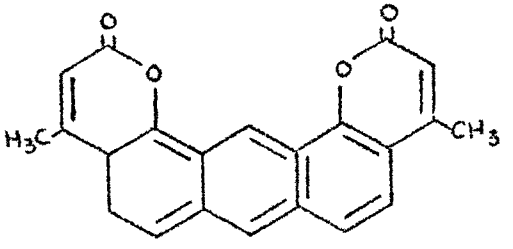
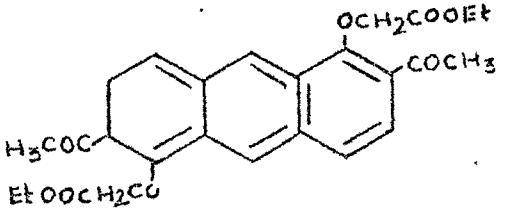
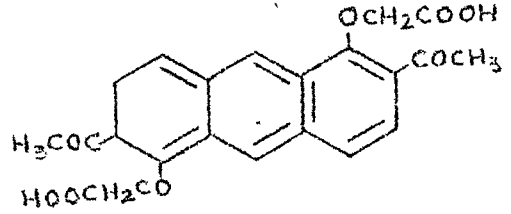
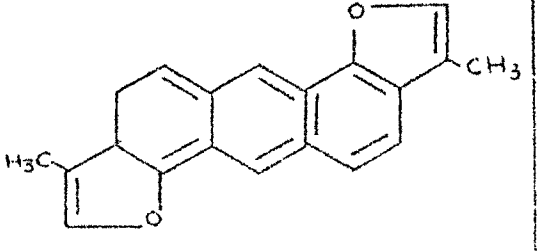
(b) 2,7-Diacetyl 1,8-dianthroxy acetic acid :

The above ester (0.5g) was heated with sodium hydroxide solution (10% 20ml) on a steam bath till the ester was dissolved. The solution was then filtered hot and the product obtained on acidification with dilute hydrochloric acid was crystallized from dilute alcohol in yellow needles, m.p. 118°C, Yield and analytical data are given in Table 1.

(c) 3',3"-Dimethylanthra 1,2b, 7,8d' bifuran :

A mixture of 2,7-diacetyl 1,8-dianthroxy acetic acid (0.5g) acetic anhydride (6ml) and freshly fused sodium acetate (1.5g) was refluxed for 30 minutes. The reaction mixture was then poured in cold water and left overnight. The product separated was crystallized from dilute alcohol in yellowish brown plates m.p. 149°C, Yield and analytical data are given in Table 1.

Name	Constitution	Derivative number
2,6-Diacetyl-1,5-dihydroxyanthracene		II
2,7-Diacetyl-1,8-dihydroxyanthracene		IV
4'-4"-Dimethyl-1,2,5,6-anthra-α-dipyrone		VII

Name	Constitution	Derivative number
4'-4"-Dimethyl-1,2,7,8-anthra-α-dipyrone		VIII
2,6-Diacetyl- 1,5-di(carbethoxymethoxy)-anthracene		IX
2,6-Diacetyl-1,5-di(carboxymethoxy)-anthracene		X
3'-3"-Dimethylanthra(1,2-b; 5,6-b')difuran		XI

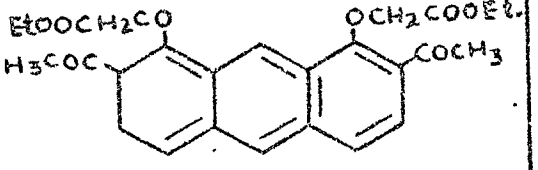
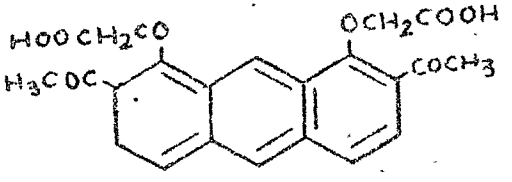
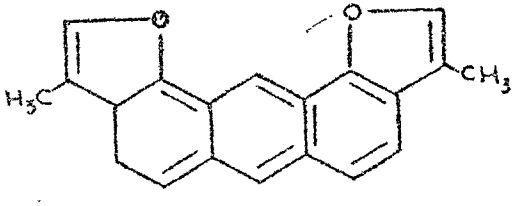
Name	Constitution	Derivative number
2,7-Diacetyl-1,8-di(carbethoxymethoxy)-anthracene		XII
2,7-Diacetyl-1,8-di(carboxymethoxy)-anthracene		XIII
3'-3"-Dimethylanthra(1,2-b; 7,8-b')difuran		XIV

Table 1

Melting Point and Analytical Data of Dihydroxyanthracene Derivatives

NO.	Derivative number	M.P. in °C	% Yield	Mol. formula	Elemental Analysis			
					Found		Required	
					% C	% H	% C	% H
1.	2.	3.	4.	5.	6.	7.	8.	9.
1.	II	167	55	$C_{18}H_{14}O_4$	73.34	4.630	73.46	4.761
2.	IV	271	55	$C_{18}H_{14}O_4$	73.91	4.647	73.46	4.761
3.	VII	360	60	$C_{22}H_{14}O_4$	76.74	3.699	77.19	4.093
4.	VIII	360	60	$C_{22}H_{14}O_4$	77.25	4.109	77.19	4.093
5.	IX	97	63	$C_{26}H_{26}O_8$	66.76	5.393	66.95	5.579

Table 1 (cont.)

1.	2.	3.	4.	5.	6.	7.	8.	9.
6.	X	189	50	$C_{22}H_{18}O_8$	64.01	4.121	64.39	4.390
7.	XI	143	50	$C_{20}H_{14}O_2$	83.71	4.503	83.91	4.895
8.	XII	127	63	$C_{26}H_{26}O_8$	66.64	5.209	66.95	5.579
9.	XIII	118(d)	50	$C_{22}H_{18}O_8$	64.01	4.121	64.39	4.390
10.	XIV	149	50	$C_{20}H_{14}O_2$	83.88	4.714	83.91	4.895

Table 2

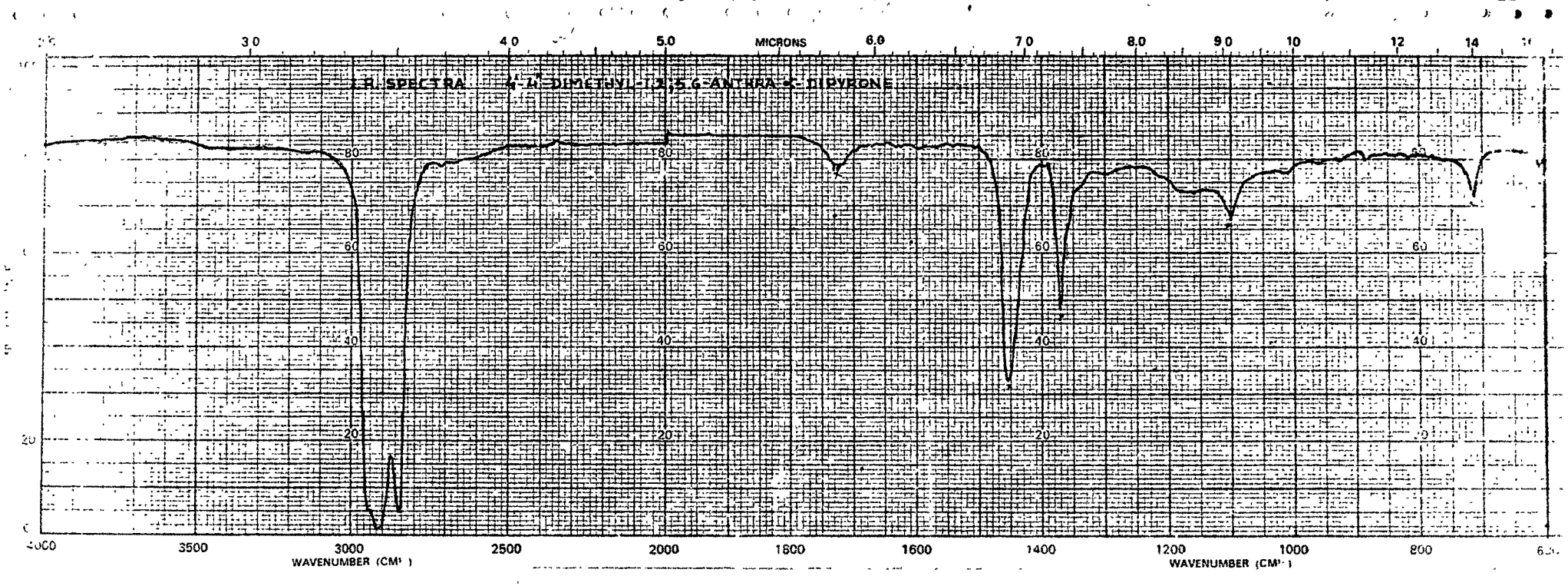
Ultraviolet Spectra of Dihydroxyanthracene Derivatives

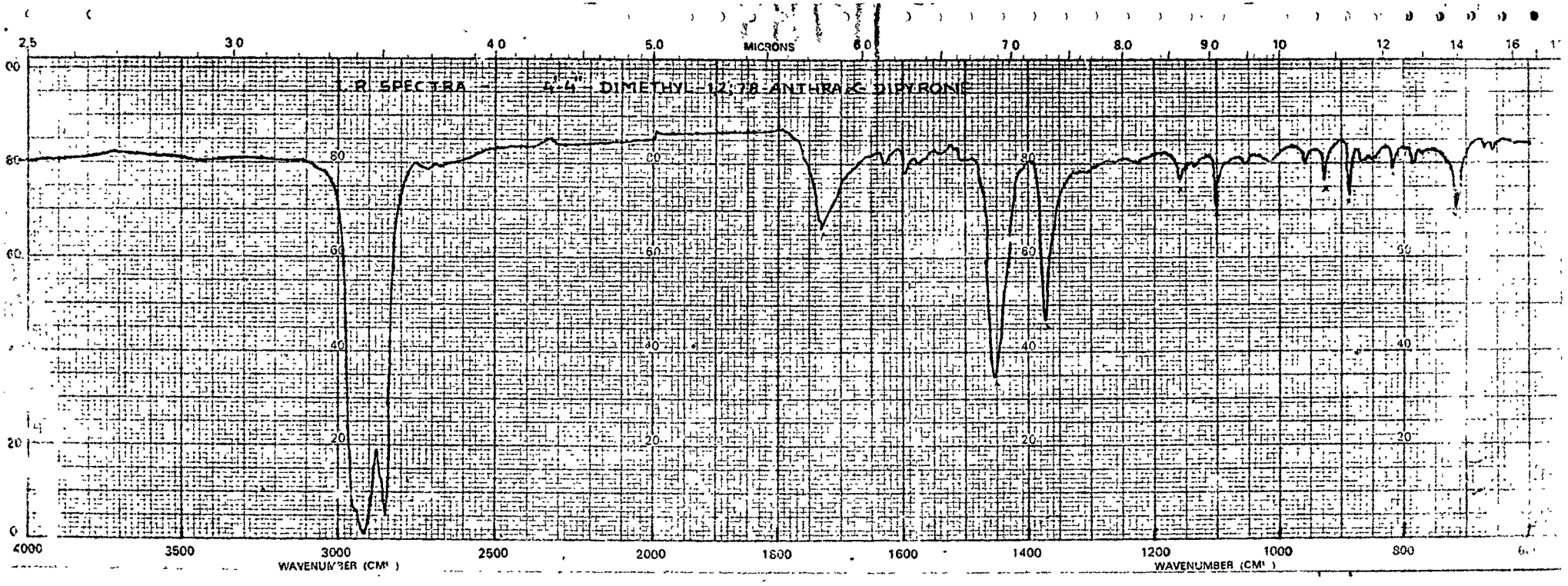
No.	Derivative number	λmax in nm	E max x 10^3
1.	II	256, 302	2.126, 1.725
2.	IV	262, 292	1.94 , 1.75
3.	VII	257, 310, 317, 326, 340	6.0, 2.92, 3.30, 3.04, 2.75
4.	VII	265, 313, 325, 342	6.5 , 4.2 , 4.1 , 4.0
5.	X	252	8.750
6.	XI	260	6.750
7.	XIII	258	8.550
8.	XIV	254	8.250

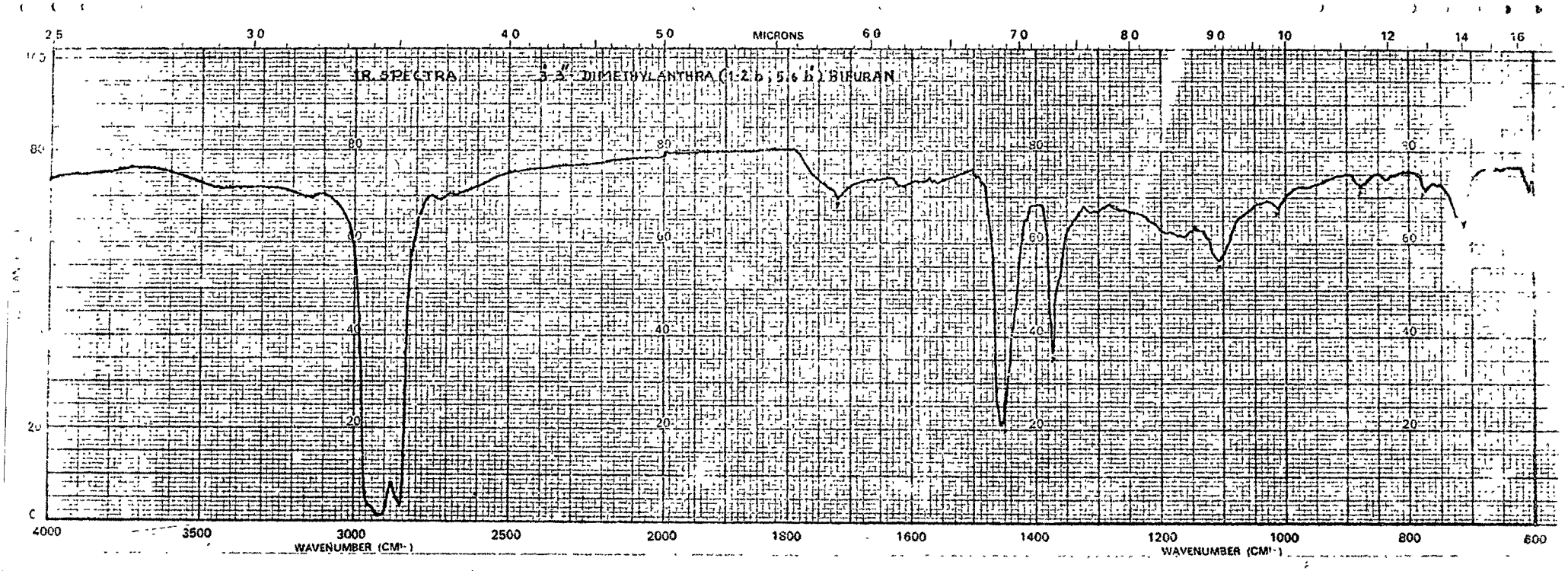
Table 3

Infra Red Spectra of Dihydroxyanthracene Derivatives

No.	Derivative number	Characteristic Frequencies in cm^{-1}			
		ν C = O	νC = C	νC = O (pyrone)	νC - ϕ - C
1.	II	1720	1545	-	-
2.	IV	1720	1625	-	-
3.	VII	-	-	1730	-
4.	VIII	-	-	1730	-
5.	X	1715	1620	-	1020
6.	XI	-	-	-	1015
7.	XIII	1720	1620	-	1015
8.	XIV	-	-	-	1035


I.R. SPECTRA 4-4' DIMETHYL-1,2,5,6-ANTHRA-C- DIPYRONE
3.0
4.0
5.0
MICRONS
6.0
7.0
8.0
9.0
10
12
14
80
60
40
20
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)
WAVENUMBER (CM⁻¹)


I.R SPECTRA — 4-4"- DIMETHYL-1,2,7,8-ANTHRA-α-DIPYRONE
2.5
3.0
4.0
5.0
MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)
WAVENUMBER (CM⁻¹)


IR SPECTRA
3,4' DIMETHYLANTHRA (1,2 b ; 5,6 b') BIURAN
MICRONS
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
WAVENUMBER (CM⁻¹)
WAVENUMBER (CM⁻¹)

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