

PART - 1

STUDIES IN ANTHRACENE DERIVATIVES

CHAPTER - 1  
GENERAL INTRODUCTION

## INTRODUCTION

## Chapter 1

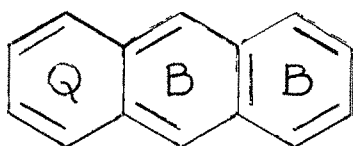
### GENERAL INTRODUCTION

Anthracene found in coaltar, is an important dye intermediate. In the form of its derivatives anthracene is widely distributed in nature. In the insect world it is in the form of kermesic, carmanic and laccaic acids. It is also distributed in the vegetable colouring matters as alizarin, chrysophanic acid, purpurin and emodin.

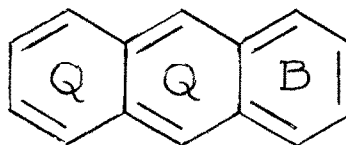
The reactivity of anthracene markedly differs from benzene and naphthalene. It is highly reactive compared to both of them, e.g. anthracene readily undergoes oxidation to anthraquinone and forms stable addition compounds with several reagents such as hydrogen, halogen etc. The meso position is the point of attack in all these reactions.

Anthracene is a tricyclic linear hydrocarbon with normal bond arrangement of an isolated benzene ring and hence no formulation of anthracene is possible. Structure (I) contains only one o-quinonoid ring, whereas, the alternate structure (II) has two o-quinonoid rings and hence on the

basis of the Fries rule (I) would be more stable. Chemical evidence indicates that the diquinonoid form (II) does not participate in the reactions of derivatives of the hydrocarbon.



I



II

The chemistry and the technology of anthracene compounds have been discussed by "Barnett(1)" and anthracene and its derivatives have been reviewed in detail in Elsevier's Encyclopaedia(2).

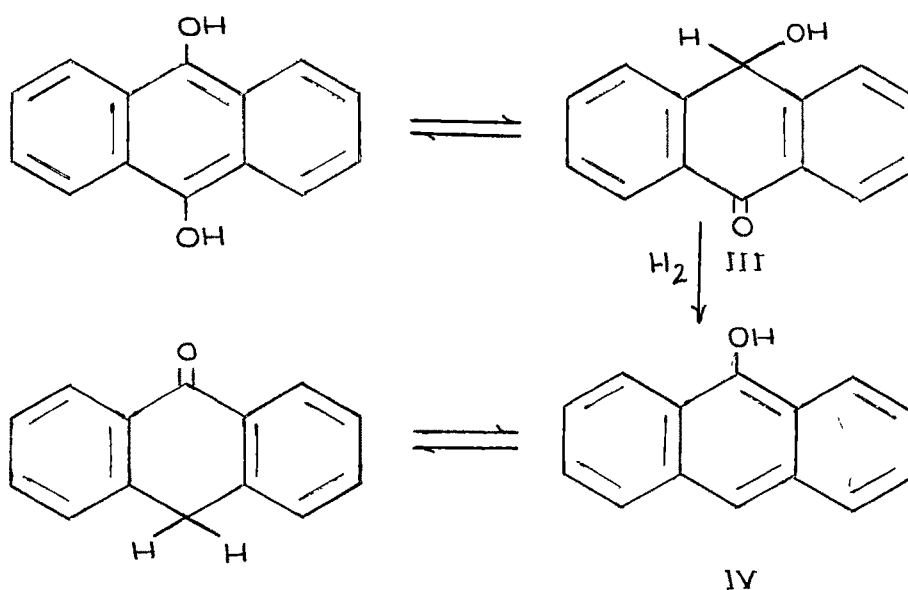
A few reactions on anthracene and hydroxyanthracene may now be described. These will indicate the pattern of addition and substitution in anthracene and the changes in this pattern with the introduction in the terminal ring. Further, these reactions illustrate the diversity of products obtained with changes in the reagents or reaction conditions.

## Reactions of Anthracene :

### 1. Oxidation:

Anthraquinone is formed when anthracene is oxidised with chromic acid in boiling acetic acid(3). This indicates the oxidation of both meso carbon atoms.

A Similar result is obtained when potassium dichromate or sodium dichromate in sulphuric acid(3-5) or hydrogen peroxide in acetic acid(6,7) or aqueous solutions of sodium chloride or sodium hypochlorite in <sup>the</sup> presence of trace of osmium tetroxide(8,9) are used. However, on oxidation with lead tetraacetate, manganese dioxide, cerium acetate or vanadium pentoxide in acetic acid solution, acetates of anthranol(IV) and oxanthrone(III) are formed(10). Halogenation in moist solvents also act as oxidising agents giving oxanthrone or 9-halogenoanthranes(11,12).



## 2. Hydrogenation :

Hydrogenation of anthracene is much more easy than benzene or naphthalene. Initial product is 9,10-dihydroanthracene when a copper chromite catalyst is employed(13) or anthracene is reduced by sodium amalgam in boiling alcohol, sodium in amyl alcohol, hydrochloric acid and phosphorus at 160-70°C(3,14,15) or by calcium in alcohol(16). Continued hydrogenation, using nickel catalyst(17) affords first 1,2,3,4-tetrahydroanthracene and then 1,2,3,4,5,6,7,8-octahydroanthracene(18). A decahydroanthracene and three perhydroanthracenes,  $C_{14}H_{24}$  have also obtained(17,19,20).

## 3. Halogenation :

Anthracene readily undergoes addition reactions with halogens. Both substitution and addition occurs with fluorine, the product being perfluoroanthracene(21). With one mole of bromine in carbon disulphide cooled in freezing mixture, it forms the dibromide, 9,10-dibromo-9,10-dihydroanthracene(V). This compound decomposes even at room temperature and especially on warming, giving hydrobromic acid, 9-bromoanthracene(VI), anthracene and 9,10-dibromoanthracene(VII)(22). The later compound(VII) then undergoes addition with the formation of either 9,9, 10,10-tetrabromo-9,10-dihydroanthracene(VIII) or 1,2, 3,4, 9,10-hexabromo-

1,2, 3,4-tetrahydroanthracene(X) which may be obtained in stereoisomeric forms(11). Anthracene reacts similarly with chlorine. Low temperatures in chloroform or carbon tetrachloride favour the formation of (X) and high temperatures and benzene that of (XI). With excess of bromine in carbon disulphide without cooling 9,10-dibromoanthracene is obtained(VII)(3)(Chart 1). With bromine in moist 1,2-dioxane, 9-bromoanthracene(XII) and anthraquinone(XIII) are formed, but in dry dioxane if atmospheric moisture is excluded, 9,10-dibromoanthracene is obtained(12).

The substitution of halogen takes place initially on the meso positions, then in the 2- and 6- positions and finally in the other positions, such as 1- and 5. Similar results are obtained whether halogen is used alone or in presence of a carrier or a halogenating agent like sulphuryl chloride is used in nitrobenzene(24).

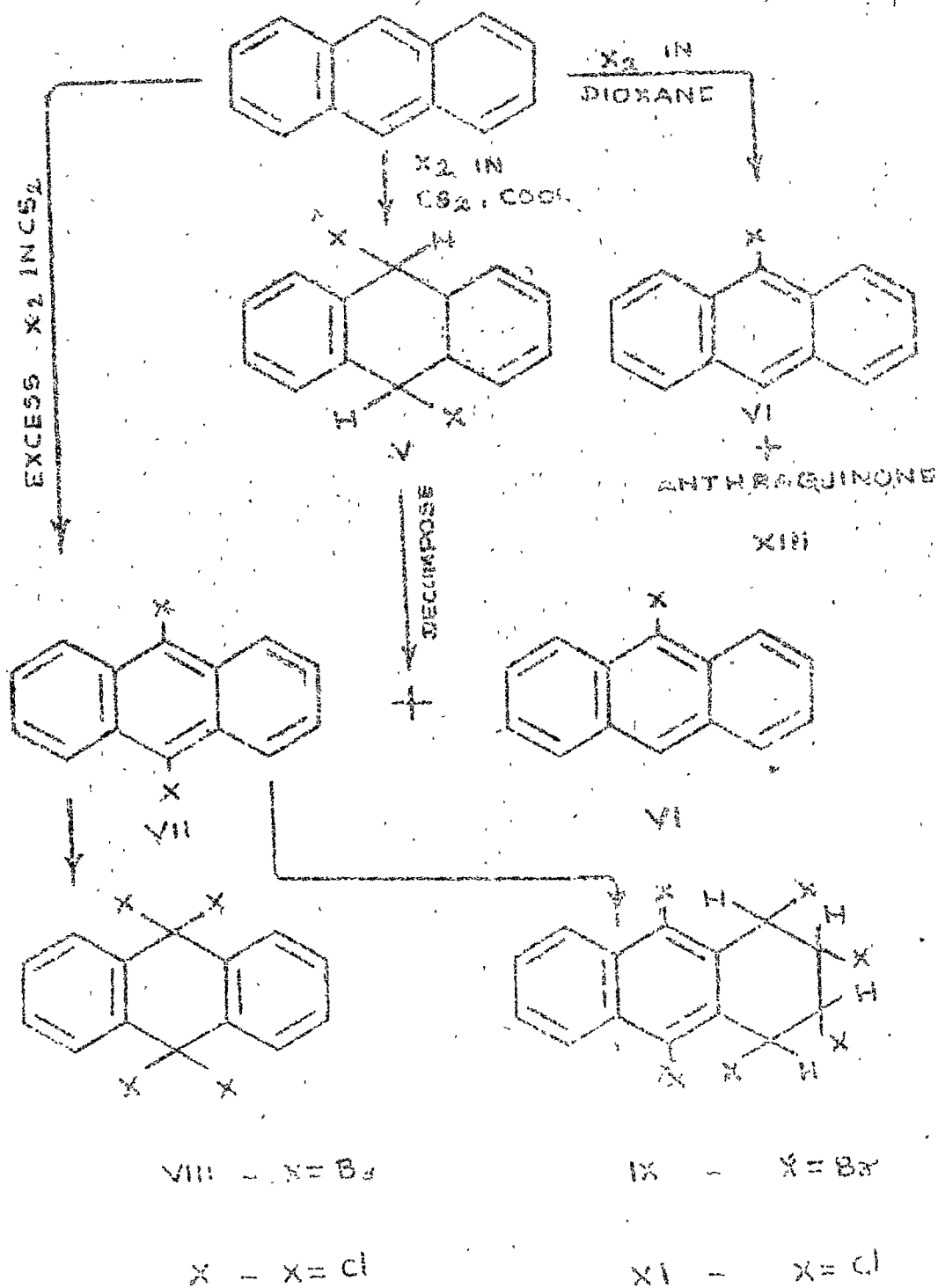
#### 4. Nitration :

Anthracene is more readily oxidised when it is warmed with dilute nitric acid than it is nitrated, the reaction products are anthraquinone and nitroanthraquinones (3,25). When anthracene is treated with concentrated nitric acid, oxidation occurs with the formation of anthraquinone. 9,10-Dinitroanthracene(XII) together with anthraquinone(XIII)



## CHART - 1

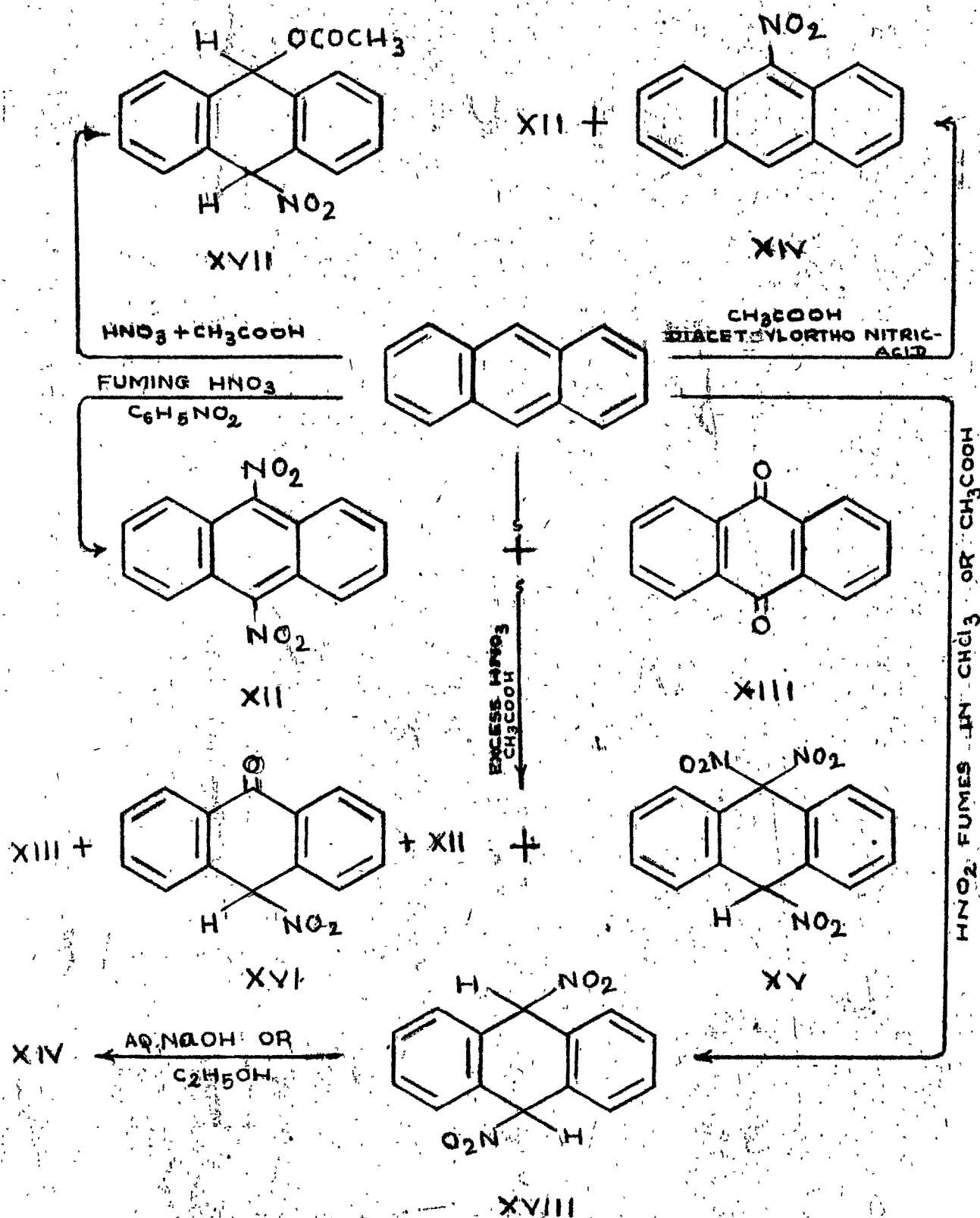
## HALOGENATION OF ANTHRACENE



are obtained when anthracene is added in a mixture of one part of fuming nitric acid (d.1.5) and two parts of nitrobenzene avoiding rise in temperature(26,27). 9-Nitro(XIV) and small amount of 9,10-dinitroanthracene are formed by nitration in acetic acid with diacetyl orthonitric acid at 20°C. When excess of nitric acid (d.1.4) diluted with acetic acid is used at 30-35°C, small amount of 9,10-dinitroanthracene, 9,9,10-trinitro-9,10-dihydroanthracene (XV) and 10-nitroanthrone(XVI) are formed together with some anthraquinone(27)(Chart 2). The acetate of 10-nitro-9,10-dihydroanthranol (XVII) is obtained by the addition of one mole of nitric acid to one mole of anthracene in acetic acid below 30°C. 9-Nitroanthracene can easily be obtained from the above acetate by the treatment with alkali(27-29), if however, the solution is refluxed 10,10'-bianthranyl is obtained(28,30). With two moles of nitric acid, first at 7-8°C then at 50-55°C, Turski obtained dinitro tetrahydro bianthranol(31). On treating anthracene in chloroform at 0°C, with excess of nitric acid (d.1.4), the nitrate of 10-nitro-9,10-dihydroanthranol is formed(30). By nitrating anthracene with the theoretical amount of pyridinium nitrate in pyridine, 9-nitroanthracene is formed together with small amount of 10-nitroanthracene and anthraquinone(32). By passing nitrous fumes into an anthracene suspension in acetic acid or chloroform, 9,10-dinitro-9,10-dihydroanthracene(XVIII) is

## CHART-2

## NITRATION OF ANTHRACENE



formed which with warm aqueous sodium hydroxide or cold pyridine and alcohol, readily gives 9-nitroanthracene(27) (Chart 2).

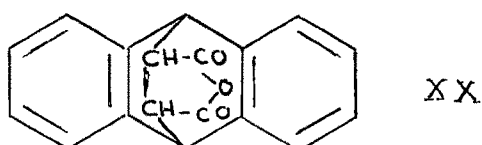
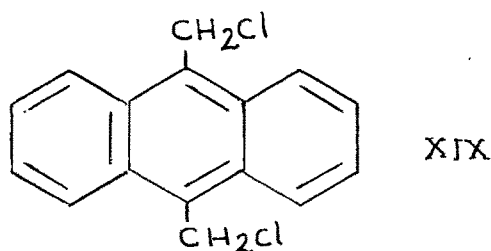
#### 5. Sulphonation :

A mixture of anthracene 1- and 2-sulphonic acids is produced when anthracene is sulphonated in acetic acid with oleum or with chloro sulphonic acid(33,34). Anthracene-1-sulphonic<sup>acid</sup> is almost exclusively formed when anthracene is sulphonated with pyridinium anhydrosulphate in basic or neutral solution(33). Anthracene-1,5 and 1,8-disulphonic acids are obtained when anthracene is sulphonated using sulphuric acid on water-bath(35). At higher temperatures (150°C) anthracene 2,6 and 2,7-disulphonic acids are formed(36). With sulphur dichloride at room temperature anthracene gives anthracene-9-dithiochloride  $C_{14}H_9S_2Cl$ (37), but on heating with sulphur dichloride in benzene 9,10-dichloroanthracene is obtained(38).

#### 6. Alkylation and Acylation :

Anthracene condenses with benzoyl chloride in nitrobenzene without catalyst to give 9-benzoylanthracene(39). In presence of anhydrous aluminium chloride in addition to this compound 1- and 2-benzoylanthracenes and 9,10-dibenzoylanthracenes are formed in small yield(40-42). Acetyl chloride readily affords 9-acetylanthracene(43). By the interaction of

anthracene with anhydrous aluminium chloride, two moles of hydrocyanic acid and dry hydrochloric acid in chlorobenzene at 70°C anthracene-9-aldehyde is obtained(44). It can also be obtained by treating the hydrocarbon with methyl formanilide and phosphorus oxychloride in o-dichlorobenzene(45). In presence of anhydrous aluminium chloride, cyanogen bromide gives the 9-cyanoanthracene(46). By heating anthracene with phosgene at 180-200°C or preferably with oxalyl chloride at 160°C, the chloride of anthracene-9-carboxylic acid is obtained(47,48). At higher temperatures, this chloride is converted into the chloride of 10-chloroanthracene-9-carboxylic acid and into 9,10-dichloroanthracene(49). With oxalyl chloride in presence of anhydrous aluminium chloride in carbon disulphide, 1,9-oxalylanthracene and 9-anthroic acid chloride are formed(48). With malonyl chloride in presence of anhydrous aluminium chloride 1,9-malonylanthracene(50), and with dimethyl and diethyl malonyl chloride 2,3 (or 1,2)-dimethyl or diethyl malonyl anthracene are obtained(51). With succinic anhydride in nitrobenzene  $\beta$ -(2-anthronyl) propionic acid is formed in small amount(52). It gives o-(9-anthronyl) benzoic acid with phthalic anhydride and anhydrous aluminium chloride in benzene(53). 9,10-bis(chloromethyl)-anthracene(XIX) is formed on the meso atoms on subjecting to chloromethylation(54).

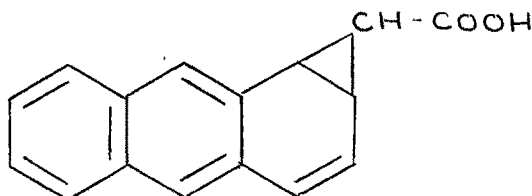


7. Diels-Alder diene Reaction :

Addition occurs across the meso positions when anthracene and maleic anhydride are heated together in xylene, with the formation of cis-9,10-dihydroanthracene-9,10-endo succinic anhydride (XX) (55-57). Fumaric acid reacts more slowly giving the corresponding trans-acid (58).

8. Action of ethyl diazoacetate and osmium tetroxide :

The reagents employed in the above reactions react with the most reactive centres in the anthracene molecule. There are two reagents, however, which undergo addition to the most reactive bonds, namely, esters of diazoacetic acid, which add across the 1,2 bond and giving 1,2-dihydroanthra-1,2-yelneacetic acid (XXI) (59), osmium tetroxide reacts with the 1,2- bond and the 3,4-bond giving 1,2,3,4,-tetrahydroxy-1,2,3,4-tetrahydroanthracene (60).



XX1

### Reactions of Hydroxyanthracene :

#### 1. Oxidation :

When a solution of 1-hydroxyanthracene in alkali is allowed to expose to air for sometime it gets oxidized and a bluish black product begins to separate(61). 1 or 2-acetoxyanthracene is oxidized by chromic acid in hot acetic acid solution to 1 or 2-acetoxyanthraquinone(62).

2-hydroxyanthracene is oxidized by ferric chloride to 3,3'-dihydroxy-10,10'-bianthrone and the hydroxydianthrone oxide(63,64,65).

#### 2. Reduction :

When 1 or 2-hydroxyanthracene is reduced with sodium metal in absolute alcohol, 9,10-dihydro 1 or 2-hydroxyanthracene is obtained(66). 9,10-Dihydro-1-hydroxyanthracene, 1-keto-1,2,3,4-tetrahydroanthracene and 9,10-dihydroxyanthracene, 1,2,3,4-tetrahydro-2-hydroxyanthracene are formed respectively on reduction of 1- and 2-hydroxyanthracene with

one mole of hydrogen in an autoclave in presence of nickel salt(66-68). 2-Hydroxyanthracene, when hydrogenated in alcohol over copper chromite at 200°/122 atmos. gives an easily separable mixture of 9,10-dihydro-2-hydroxyanthracene and 1,2,3,4-tetrahydro-2-hydroxyanthracene(69).

### 3. Halogenation :

1-Hydroxyanthracene is found to react with two moles of bromine, one in the 9 or 10- position and the other in the ortho position to the hydroxyl group(70).

2-Acetoxyanthracene in polychlorobenzene solution when treated with chlorine in acetic acid at 5.7°C for one hour and then stirred for two hours at room temperature gives a mixture of 9,10-dichloro and 9-chloro-2-acetoxyanthracene which on hydrolysis gives 9,10-dichloro-2-hydroxyanthracene and 9-chloro-2-hydroxyanthracene respectively(71).

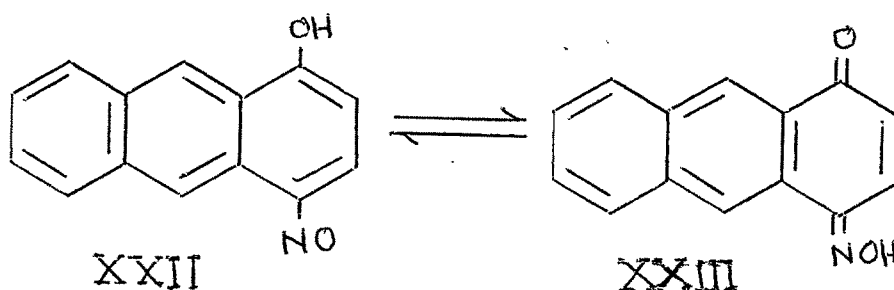
2-Hydroxyanthracene when brominated in cold acetic acid ~~it~~ undergoes both oxidation and bromination to give 2-hydroxy-1,1'-bianthranyl 9,2'-oxide, 1,10-dibromo-2-hydroxyanthracene and 1,9-dibromo-2-hydroxyanthracene isolated only as the acetyl derivative. 2-Acetoxyanthracene with bromine in cold glacial acetic acid gives the 9-bromo-2-hydroxyanthracene(72).

### 4. Nitrosation :

1-Hydroxyanthracene on boiling in aqueous alcohol with sodium nitrite in presence of zinc chloride gives the



zinc salt of 2-nitroso-1-hydroxyanthracene and 4-nitroso-1-hydroxyanthracene(73). This nitroso compound is tautomeric and may be ~~regarded~~<sup>regarded</sup> as the monoxime of 1,4-anthraquinone (XXI, XXIII).



Under the similar condition 2-hydroxyanthracene gives 1-nitroso-2-hydroxyanthracene(74).

#### 5. Miscellaneous Reactions :

When benzene diazonium chloride is coupled with an alcoholic solution of 1-hydroxyanthracene ~~the~~ benzenazo-1-hydroxyanthracene is obtained(75,76).

1-Benzenazo-2-hydroxyanthracene is also obtained under similar condition with 2-hydroxyanthracene(77).

1 or 2-Hydroxyanthracene on formylation in sodium dried ether with zinc cyanide and dry HCl gas gives 4-formyl-1-hydroxyanthracene or 1-formyl-2-hydroxyanthracene respectively(78,79).

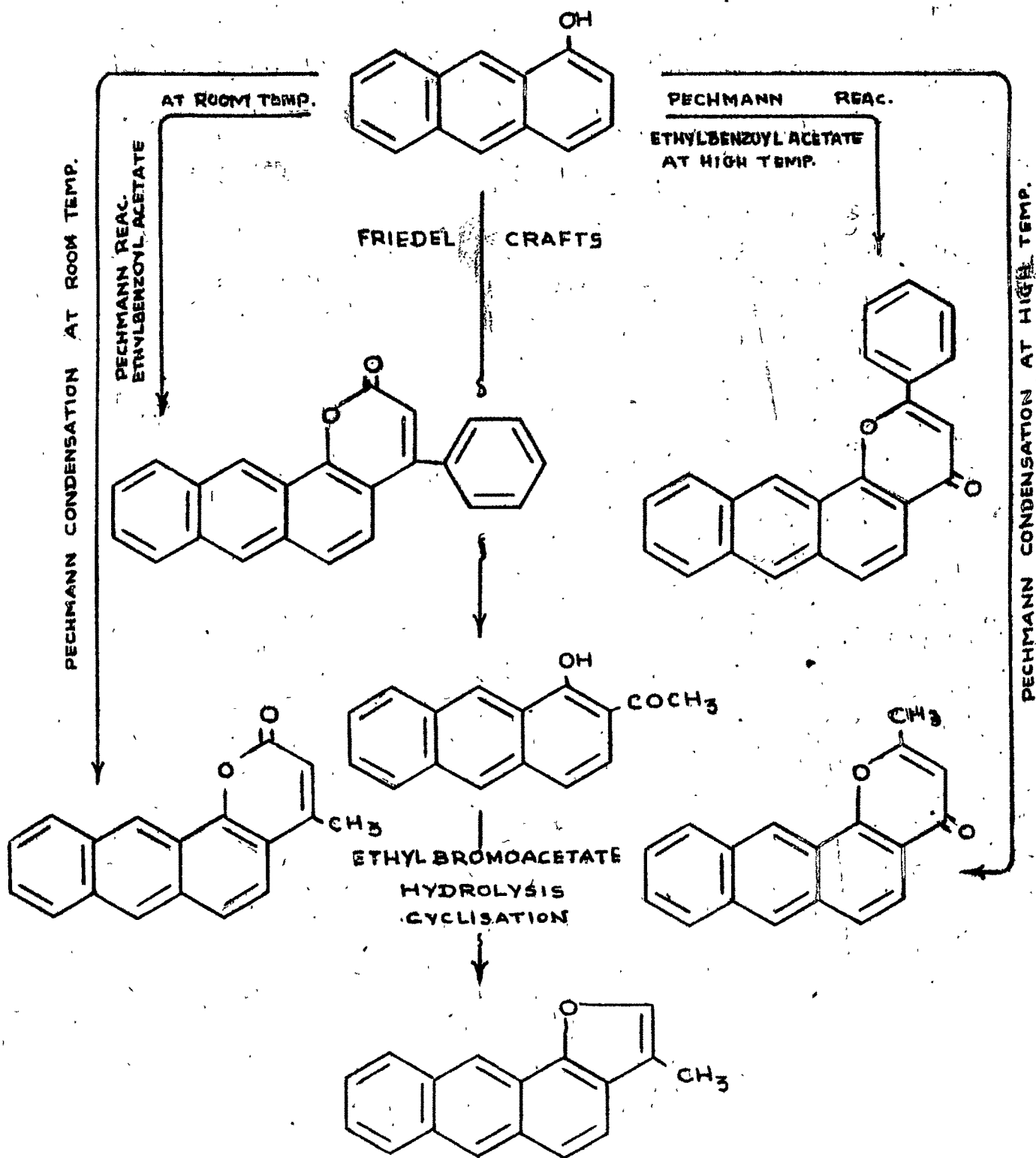
On Friedel-Crafts acetylation of 1 and 2-hydroxyanthracene with acetic anhydride in nitrobenzene both

at room temperature and on steam-bath, 2-acetyl-1-hydroxyanthracene and 1-acetyl-2-hydroxyanthracene are obtained(78,79).

When 1-hydroxyanthracene and 2-hydroxyanthracene are subjected to Nencki acetylation by using anhydrous zinc chloride and glacial acetic acid as well as when 1- or 2-acetoxyanthracene are subjected to Fries rearrangement, 2- and 1-acetyl derivatives are obtained which are similar to those obtained in Friedel-Crafts acetylation(78,79).

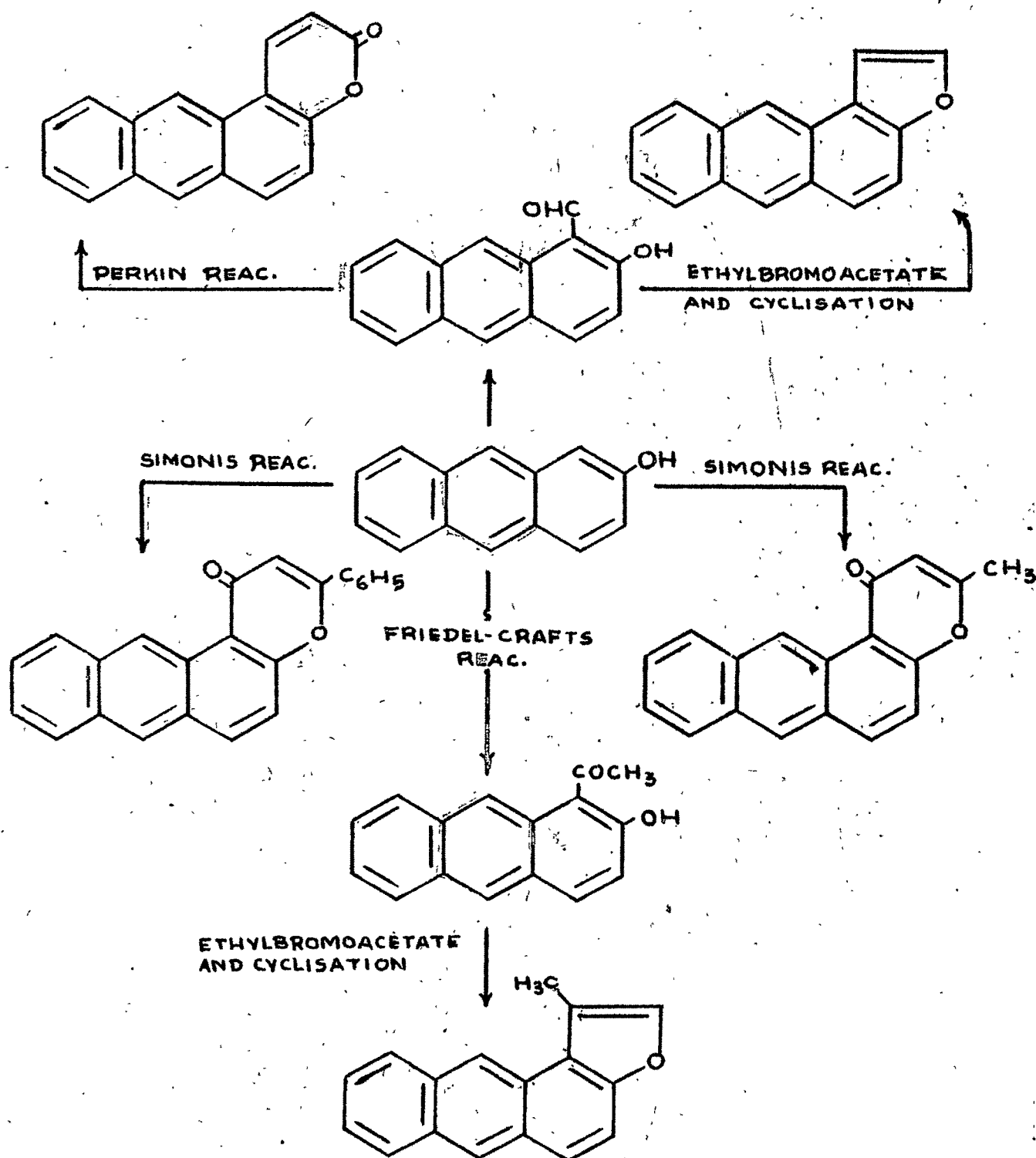
Sethna et. al. synthesized some heterocyclic compounds e.g. 4'-methyl 1,2-anthra-a-pyrone, 2'-methyl 1,2-anthra- $\gamma$ -pyrone, 3-methylanthra-(1,2-b) furan, 1-methylanthra (2,1-b) furan and anthra-(2,1-b) furan and other furans and pyrones which are summarized in Chart 3 and 4(80,81). Some work has been done on the substitution in dihydroxy anthracene with a view to find out whether the bonds in anthracene derivatives are rigid or labile. To test the conclusion that (XXIV) is the preferred structure for anthracene, which was derived from purely theoretical considerations, Fries studied bromination of 2,6-dihydroxyanthracene(82). If the bond structure of this compound is (XXV), the bromine atoms would be directed to the two enolic ortho positions, 1 and 5, while the alternate structure(XXVI) would lead to 3,5-substitution. It was found that bromination occurs

SOME DERIVATIVES OF 1-HYDROXYANTHRACENE

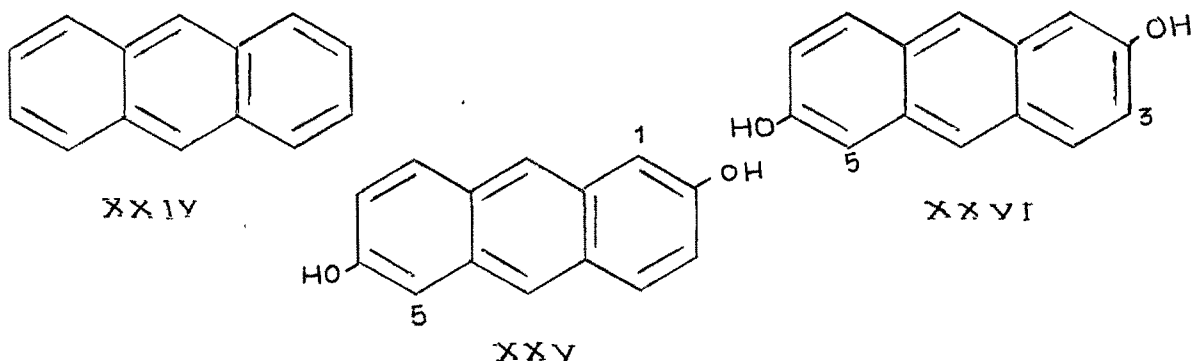


## CHART-4

## SOME DERIVATIVES OF 2-HYDROXYANTHRACENE



at the 1 and 5- positions, as predicted for a substance of the structure(XXIV).



In the attempt to substantiate the views of Fries by providing more conclusive evidence, Fieser and Lothrop(83) subjected 1,5-dimethyl and 1,5-diallyl derivatives of 2,6-dihydroxyanthracene to further reactions. These substances were investigated for their ability to couple with diazotized amines. The structure(XXV) for such a compound would permit no reaction, since both of the normal ortho positions are blocked by alkyl groups, but if the substance can exist to any appreciable extent in the form with the bond structure(XXVI ) coupling should occur at the available ortho position C<sub>3</sub>, for this is connected to the hydroxylated carbon atom by an enolic double bond. There was in no case any indication of a reaction and consequently it is concluded that the substances exist entirely in the forms corresponding to(XXV) and that tautomerization is negligible.

According to modern concept, there is resonance in these molecules, with the predominant contribution by the structure(XXV) suggested by Fries and Fieser.

### Present Work

A perusal of the literature on substitution in hydroxynaphthalene and hydroxyanthracene reveals that eventhough, extensive studies have been made on  $\alpha$  and  $\beta$ -naphthols,  $\alpha$  and  $\beta$ -hydroxyanthracenes and dihydroxynaphthalenes, the studies on dihydroxyanthracenes have been comparatively fewer. It was therefore thought of interest to synthesize diketones by means of Friedel-Crafts, Fries and Nencki reactions, and  $\alpha$ -dipyrones by Pechmann reaction and difurans from 1,5 and 1,8-dihydroxyanthracene. This work has been described in chapter II.

The azo dyes based on anthracene are not studied in much detail. It was thought of interest to utilize hydroxyanthracene derivatives as azoic coupling components and to synthesize azo dyes based on 1-hydroxyanthracene.

Chapter III, deals with the synthesis of different anthracene derivatives and their impregnation on cotton fibres and then the development of these components with number of substituted phenyl diazonium chloride solution. The dyed fibres are evaluated for their shades and fastness properties.

Chapter IV deals with the synthesis of number of azo dyes based on 1-hydroxyanthracene by reacting it with

different diazotized substituted arylamines, Visible spectra, I. R. Spectra and Fluorescence spectra of these arylazo derivatives of 1-hydroxyanthracene have been studied.



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