Degree Part III chem (Hons)

Lec-no - 15

Paper - VII

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Topics : Polynuclear hydrocarbons

PHENANTHRENE

Occurance :- Phenanthrene occurs in the light oil fraction of coal-tar and in bone oil.

Isolation :- The light oil is dissolved in dil HCl which dissolves Pyridine and other basic substances. The acid layer is neutralised with NaOH and the liquid after fractionet to get phenanthrene.

STRUCTURE OF PHENANTHRENE

(i) From elementary analysis and molecular weight determination, the molecular formula of phenanthrene is $C_{14}H_{10}$

(ii) It shows typical properties and it undergoes nitration, sulphonation and Friedel Crafts reaction

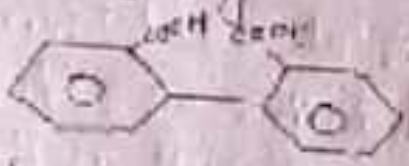
(iii) On oxidation with chromium trioxide in acetic acid produces a diketone

The presence of side chain would give $C_{14}H_8O_2$ rise to at least one carboxylic group. Since this does not form there is no side chain in phenanthrene. The compound $C_{14}H_8O_2$ gives a monoxide as well as dioxime. Therefore two carboxylic group is present in this product of oxidation. The diketonyl compound moreover condenses with ortho phenyl amine to give a cyclic

product, therefore two carbonyl groups are in adjacent position. Oxidation of above ~~dermatine~~ diketone gave rise to a dicarboxylic acid without loss of electron. This confirms the earlier conclusion that oxidation does not occurs in a ring. The dicarboxylic acid is called diphenic acid, on the carboxylation it gives diketone a compound of known structure.

The structure of diphenic acid obtained from oxidation of diphenine by placing a carboxyl group in appropriate position. Diphenic gives an anhydride which on further heating losses of carbon atoms. Such carboxylic group are placed in adjacent position on one ring, a diphenyl skelton, a phthalic acid type of compound can be obtained. This would give an anhydride but the anhydride would not loose carbon atom on further heating, therefore, in diphenic acid, the two carboxylic acid are not adjacent carbon atom on the same ring.

If the carboxylic group be present on the same ring be separated by 3, 4 and 5 carbon atom, anhydride formation would not taken place. Therefore two carboxylic groups in diphenic acid must be distributed over the two rings. Moreover there must be in such position that anhydride formation can possibly occur, the most reasonable places therefore are two ortho position to link joining the two benzene ring.



The diketone condenses the carbon atoms as diphenic acid and therefore must have same carbon skelton

Since this diketone is formed by oxidation occurring in a ring it follows that the phenanthrene condenses the carbon skelton

This accounts for 14 carbon atom by placing double bond as in the benzene ring. Thus we arrive at the bond structure of phenanthrene

According to this structure, there would be 5 mono substituted products. If the substituents are identical then 25 di substituted products are possible.

They predicted numbs completely with those experimentally obtained. The bond structure of phenanthrene can be written as following way

I

II

Among all these structures, structure II is one which odd rings ~~Benzene~~ Benzoid character. According to rule it would be the most stable structure. The large number of properties can be explained with this structure.

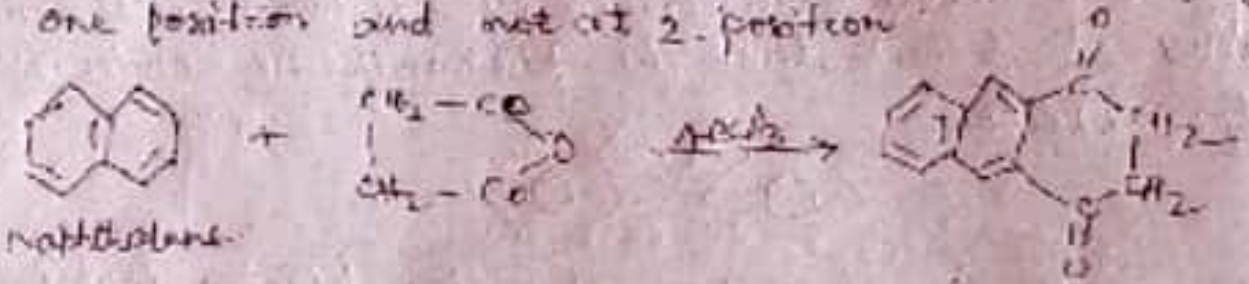
The structure II is confirmed by the following Syntheses :-

(1) Haworth - synthesis :-

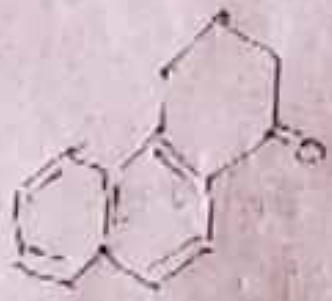
Naphthalene

Condenses with Succinic anhydride ~~enters~~ in the two position. They also give phenanthrene and not anthracene because the ring closes at

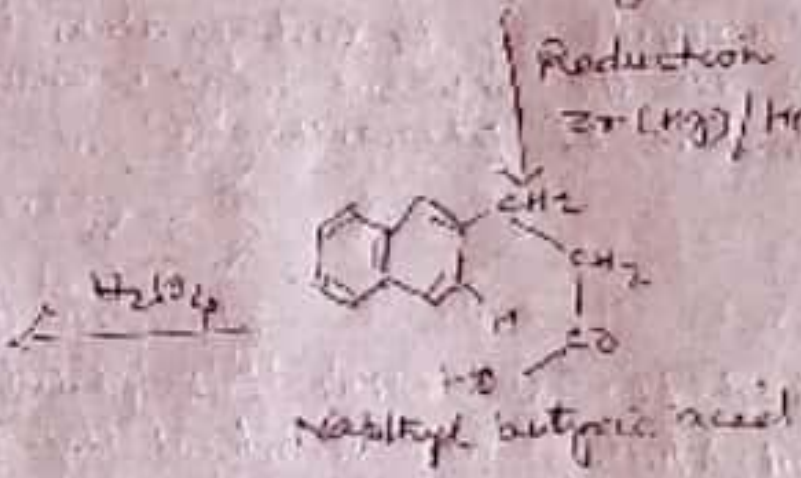
one position and not at 2. position



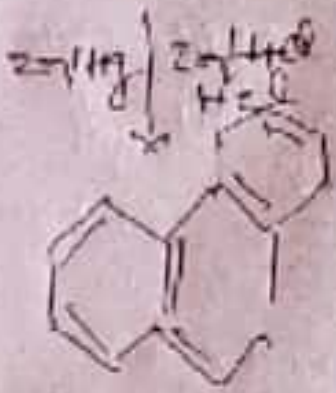
Naphthalene

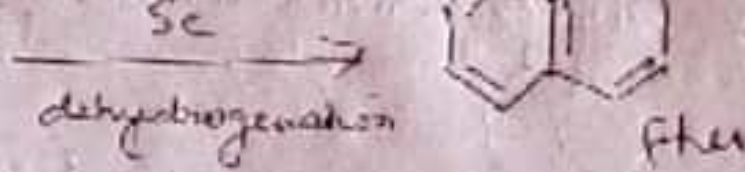


Kelein



Naphthyl butyric acid

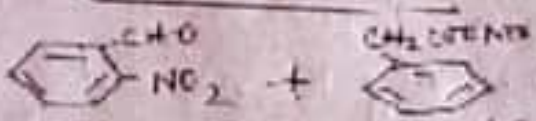




dehydrogenation

Phenanthrene

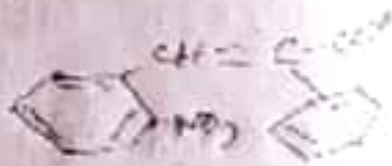
(2) Perkin's Method



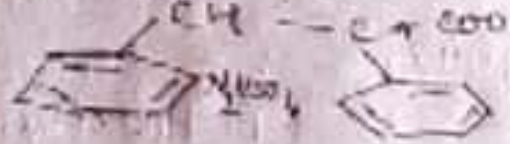
O-Nitrobenzaldehyde

sodium phenyl acetate

(Perkin's)



Phenanthrene 9 carboxylic acid



Phenanthrene