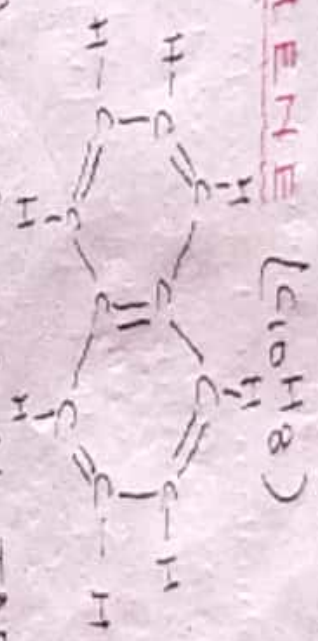


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NAPHTHALENE (C₁₀H₈)

OR



Preparation of Naphthalene from COAL-TAR :-

Naphthalene. It is fractionally distilled, the product collected in between 170 - 230°C is known as middle-oil which contains phenol, Naphthalene and cresol.

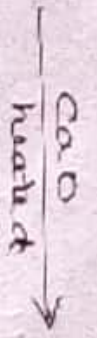
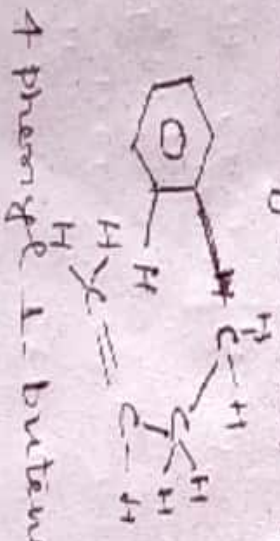
The middle oil fraction is cooled so that whole amount of naphthalene crystallises out.

It is separated by centrifuge machine. Then naphthalene is washed with NaOH solution so that adhering of phenol and cresol is removed as it is soluble in NaOH solution. It is collected by filtration and purified by recrystallisation in petroleum.

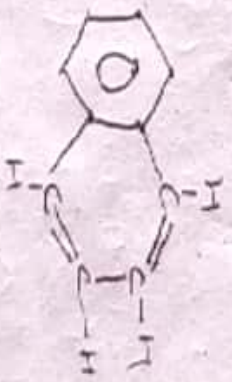
SYNTHETIC METHOD :-

1) From 1-phenyl-1-butene :-

It is cyclised to form naphthalene.



It is heated with CaO.



OR
naphthalene

Structure of Naphthalene

It is derived on the basis of following analysis and synthetic evidences.

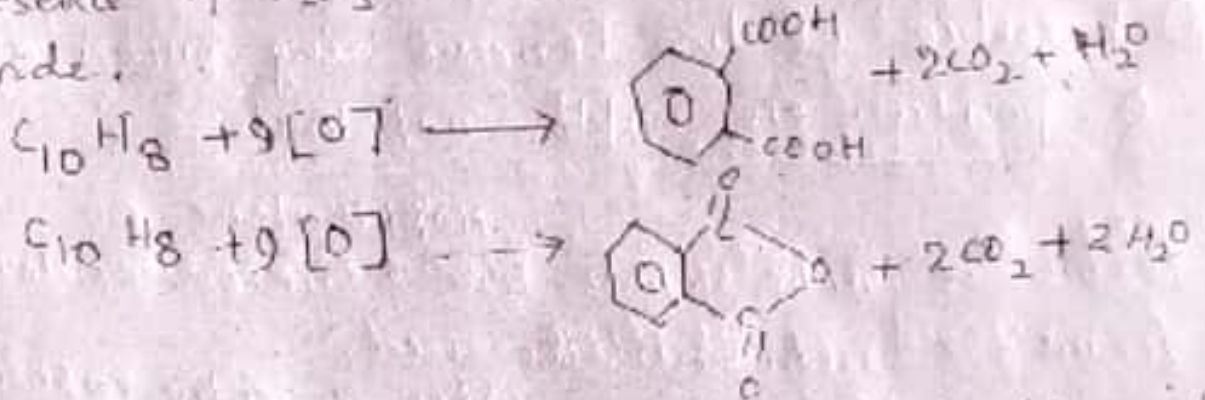
① Molecular Formula

From elementary analysis and molecular weight determination, the molecular formula of naphthalene is established as $C_{10}H_8$.

② Resemblance with benzene

→ Naphthalene gives (Presence of aromatic character) electrophilic substitution reaction, such as nitration, sulphonation, halogenation etc. like benzene. Therefore it is clear that naphthalene ~~possess~~ contains one or more than one benzene rings in its molecule.

③ Naphthalene on oxidation with acidified $KMnO_4$ forms phthalic acid; When it is oxidised with air in presence of V_2O_5 at $760^\circ C$ forms phthalic anhydride.



On the basis of the formation of phthalic acid or phthalic anhydride it is concluded that naphthalene molecule must contain a benzene ring associated with side chain at ortho-position.

④ Probable structural formula

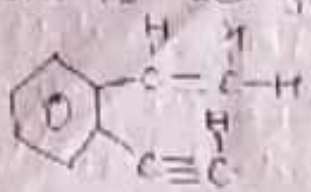
on the basis of above structural analytical evidences, probable structure

of Naphthalene may be written as

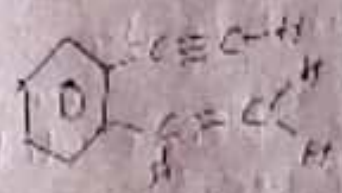


The side chain may be straight or cyclic.

The possible structure of naphthalene with straight side chain is as follows:



I



II

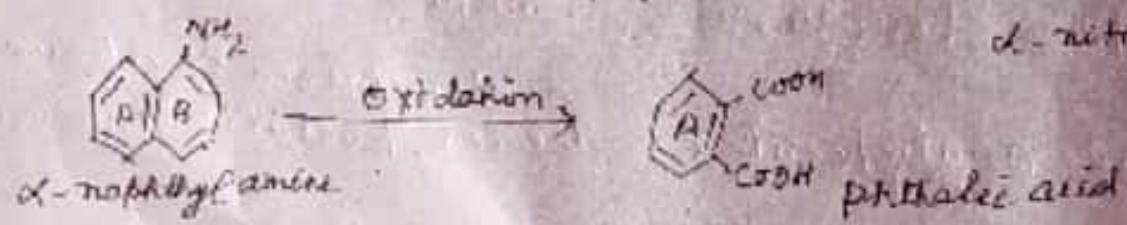
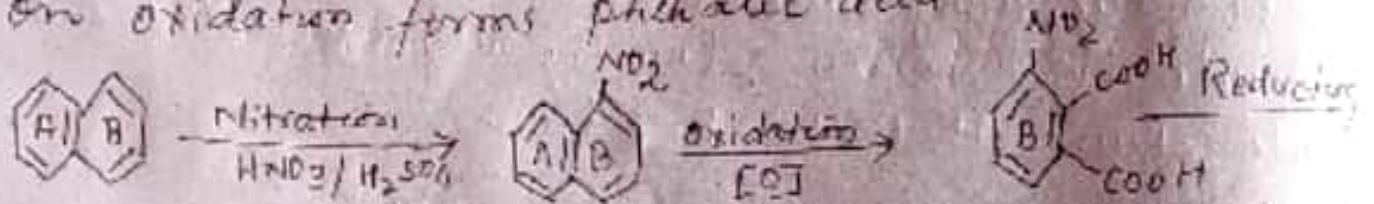
The Naphthalene is not highly unsaturated compound. It also oxidised to form carboxylic acid at 0-position. The above structure I and II represents highly unsaturation of naphthalene and they do not produce phthalic acid on oxidation. Therefore both the structure I and II are not possible according to above evidences.

In the side chain it may be cyclic chain which has been evidenced as follows.

⑤ Presence of two benzene ring fused at 0-position in naphthalene.

Naphthalene on nitration forms α -nitro naphthalene which on oxidation forms α -nitro phthalic acid.

When α -nitro naphthalene is reduced it forms α -naphthyl amine which on oxidation forms phthalic acid.



~~Nitro group~~ Amino group accelerates the oxidation of such benzene ring at which it is attached. It is due to fact that amino group is electron donating group. on the basis of the formation nitro phthalic acid and phthalic acid as above, it is confirmed that Naphthalene molecule contains two benzene ring fused at 0-position, therefore the structure of naphthalene is as follows:-



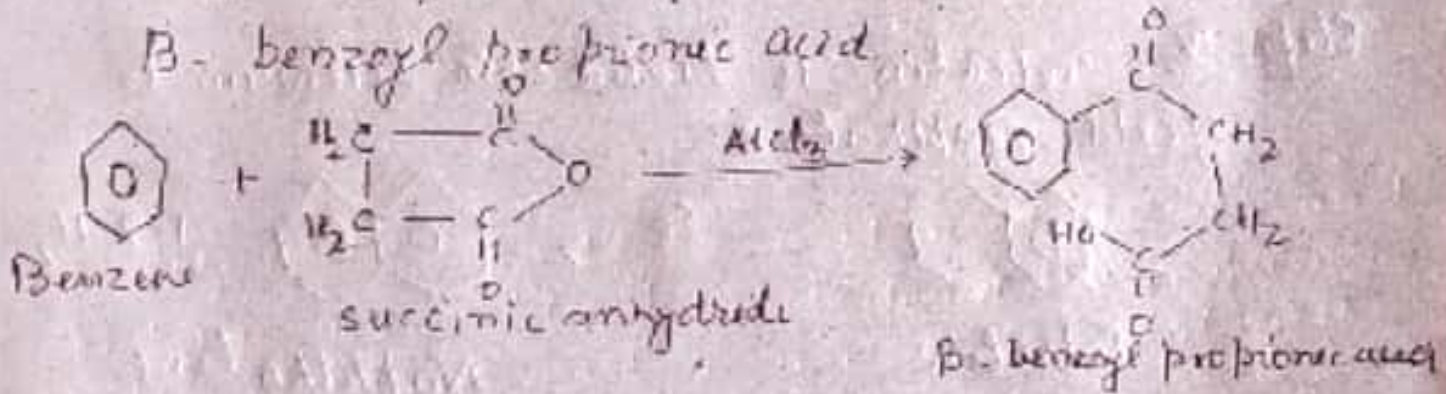
⑥ SYNTHESIS :- The above structure of naphthalene is confirmed from its synthesis as follows.

HAWORTH SYNTHESIS :

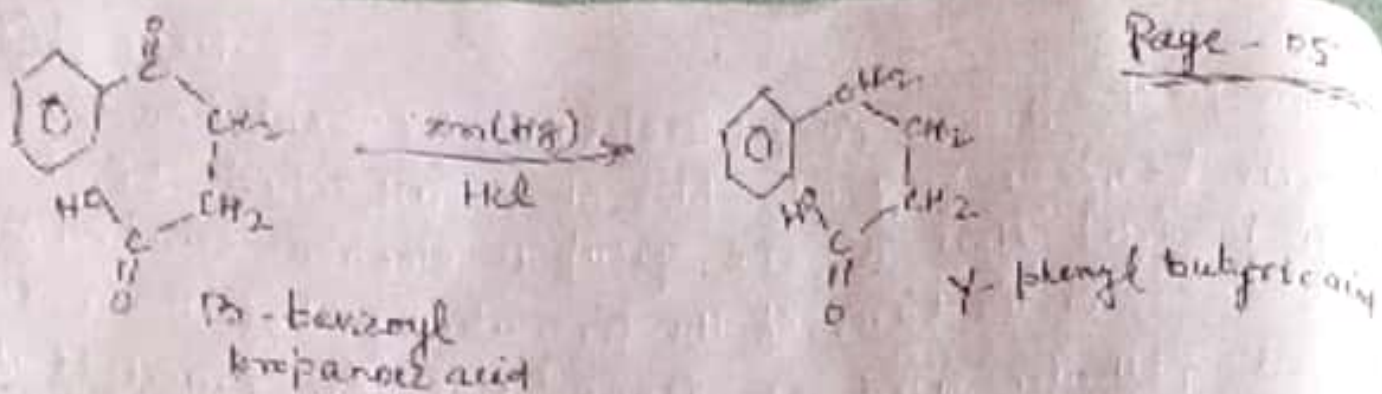
This involves the following five steps

Step-I Benzene and succinic anhydride are heated in the presence of Aluminium chloride to form

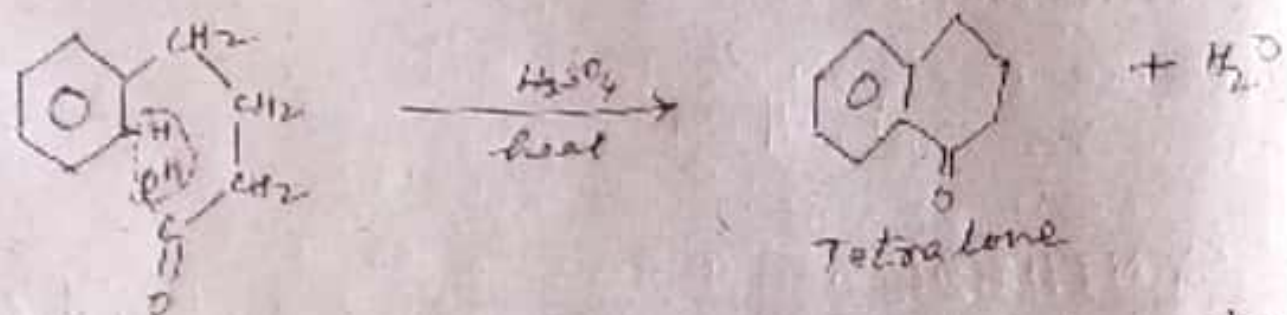
B-benzoyl propionic acid



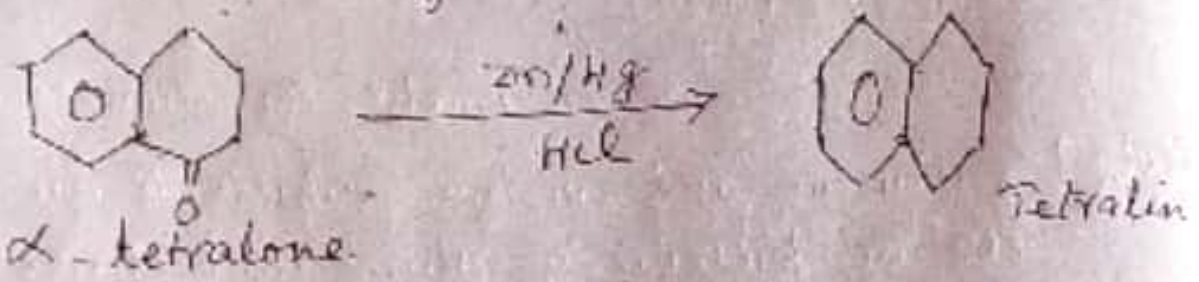
Step-II : B-benzoyl propionic acid is treated with amalgamated zinc in the presence of HCl to give γ-phenyl butyric acid.



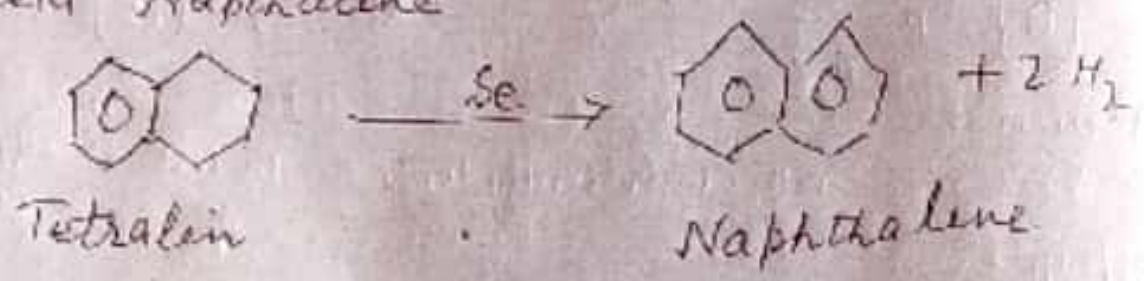
Step III γ -phenyl butyric acid is heated with conc. H_2SO_4 to form α -tetralone (Ring closure reaction)



Step-IV α -tetralone is heated with amalgamated zinc and HCl to give tetralin



Step-IV Tetralin is heated with selenium to yield naphthalene



————— α —————