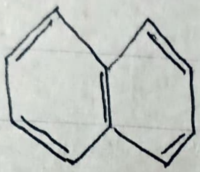
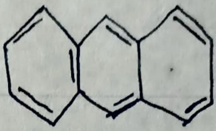
FUSED Polynuclear aromatic Hydrocarbons:

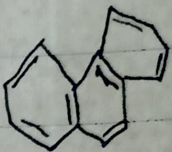
Fused or Condensed aromatic hydrocarbons Contains more than one ring and have two Carbons shared by two (or three) aromatic rings. The most important members of this Class are napthalenes, and anthracene.



Napthalene



Anthracene



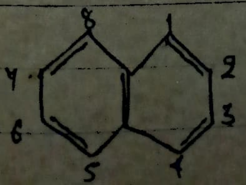
Phenathrene

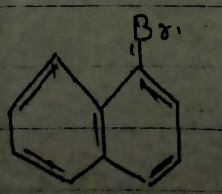
Naphthalene [NAPHTHALENE]

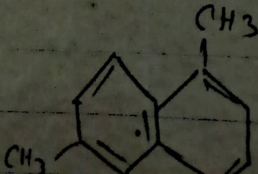
Naphthalene is the largest single constituent of Coal tar. It is obtained by chilling the middle oil fraction (b.p. 170 to 250°c). When crude napthalene Crystallises out. It is purified by washing successively with dilute Sulphuric acid (to remove basic impurities) and Sodium hydroxide (to remove acid impurities) and water. Finally the solid is sublimed or steam distilled to give pure napthalene.

Nomenclature of naphthalene derivatives →

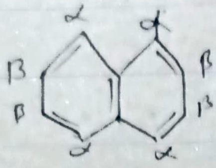
In naming derivatives of naphthalene, the numbering System shown below is used. The numbers selected to denote the position of a substituent on the naphthalene ring should be as small as possible.

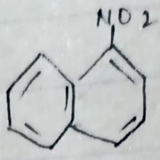


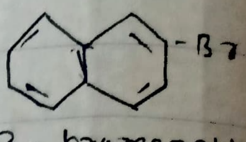




An alternative nomenclature system is occasionally used when there is only one substituent on the napthalene skeleton. This system uses Greek letters α (alpha) and β (beta) to designate the two possible orientations of the single substituent.







α- nitro napthalene, β- bromonapthalene

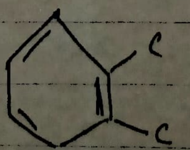
Structure of napthalene

(1) Classical Structure →

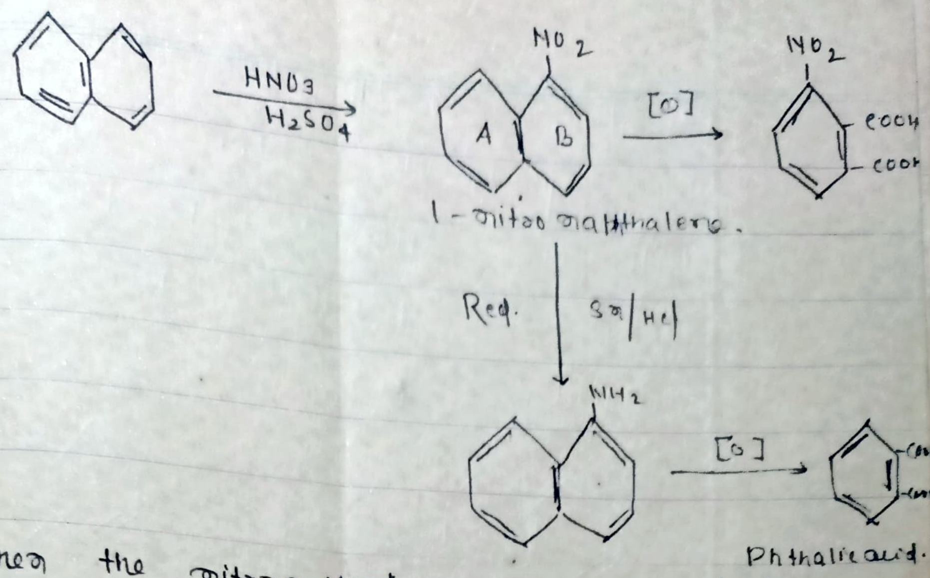
(i) Elemental analysis and molecular weight determinations shows that molecular formula of napthalene is $C_{10}H_8$.

(ii) Dipole moment of napthalene is zero. This indicates that napthalene molecule is symmetrical.

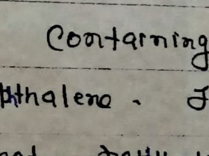
(iii) Oxidation - napthalene with Oxygen and V_2O_5 at 470°C yields Pthalic anhydride. This indicates the presence of a benzene ring with two ortho side chains in the molecule.



(iv). Nitration of napthalene produces a nitro napthalene which Oxidation yields 3-nitro pthalic acid. The presence of Nitro gr stablises the benzene ring to which it i attached (ring B).

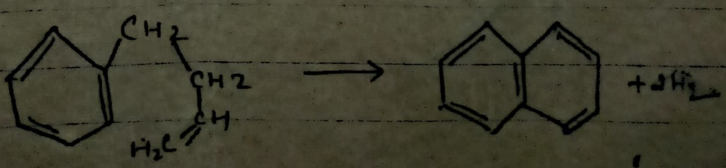


when the nitro naphthalene has reduced and Corresponding amino naphthalene oxidised, Phthalic acid was obtained. In Phthalic acid two -COOH groups are attached to benzene ring in ortho position. Results clearly indicate that benzene ring in the Phthalic acid obtained by oxidation of amino napthalene. It is not the same ring as that originally containing nitro group in nitro naphthalene. These experimental evidence show that naphthalene consists of two benzene ring fused in ortho position. This has been shown below.



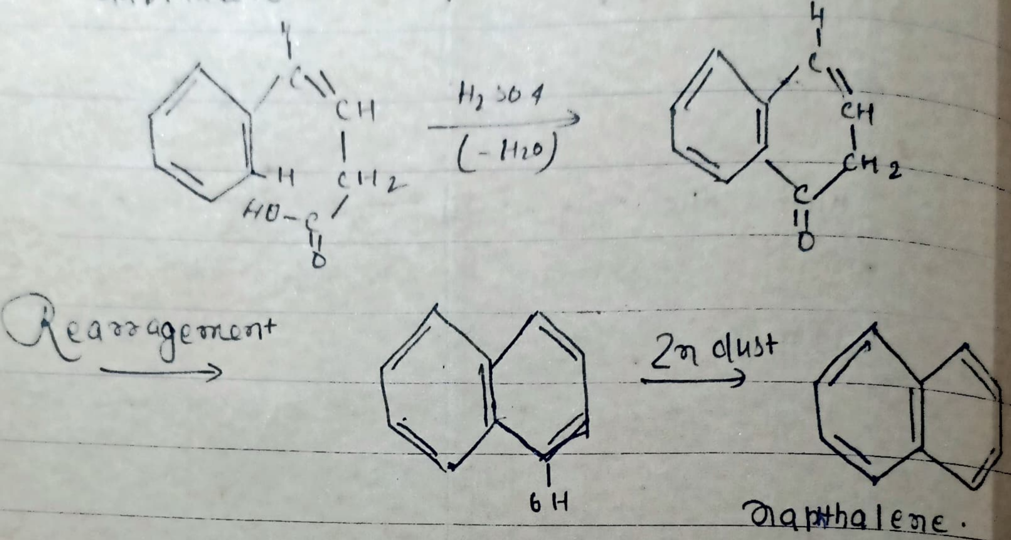
This structure of naphthalene has been confirmed by the following synthesis.

(i) when 4-phenyl-1-butene is passed over Calcium Oxide, naphthalene is formed.



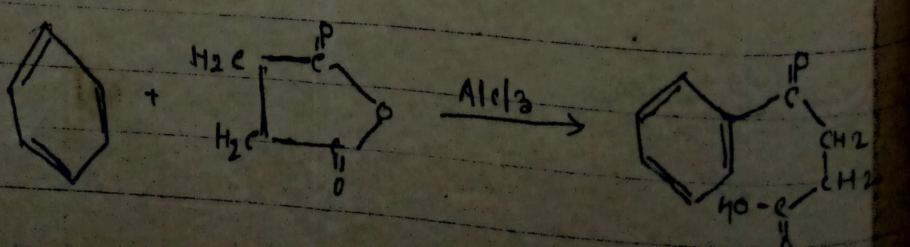
(2) From 4- Phenyl - 3-butenoic acid →

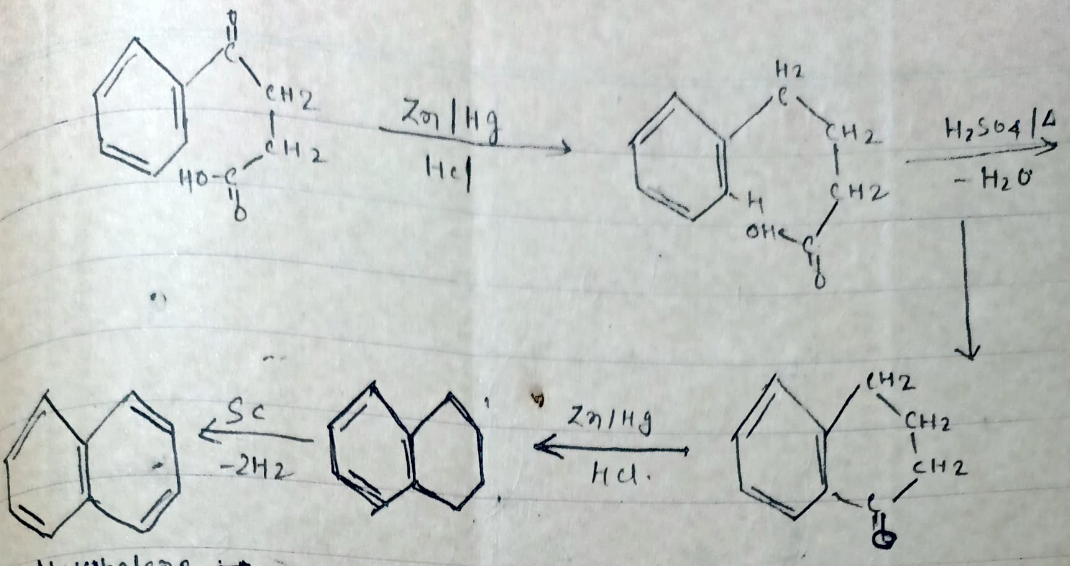
When 4- Phenyl - 3- butenoic acid is heated with Conc. Sulphuric acid, 1-napthol is formed This on distillation with Zn dust give napthalene.



(3) Haworth Synthesis → This involves the following 5 step.

Step (i) Benzene and Succinic anhydride are heated in the presence of AlCl3 and the Ketonic acid produced is reduced by Clemmensen method. The ring is closed by heating with Conc. H_2SO_4 and the product is reduced to tetrahydronapthalene by Clemmensen method. This compound is then dehydrogenated by heating with Selenium or Palladised - Charcoal.

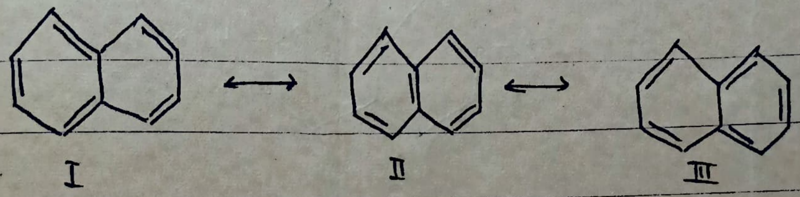




Naphthalene →

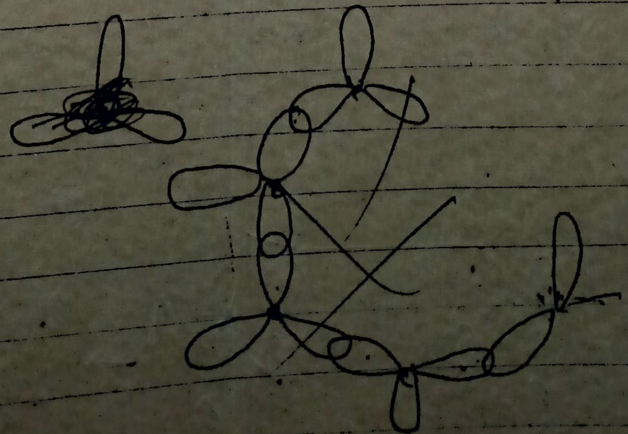
True - Structure of naphthalene ⟶

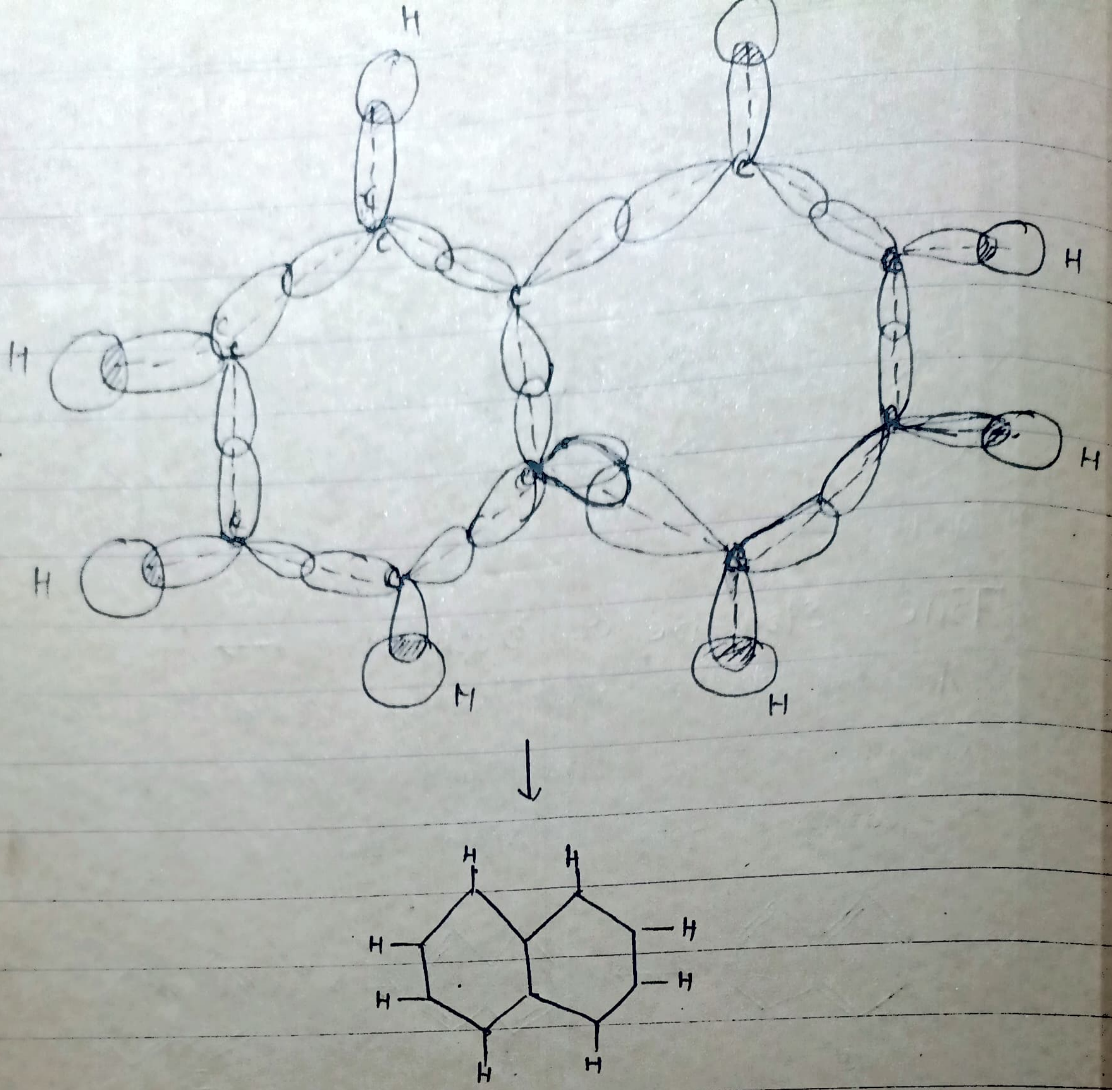
According to resonance theory, naphthalene is considered to be resonance hybrid of the following 3- canonical forms shown below.



Orbital Structure of naphthalene ⟶

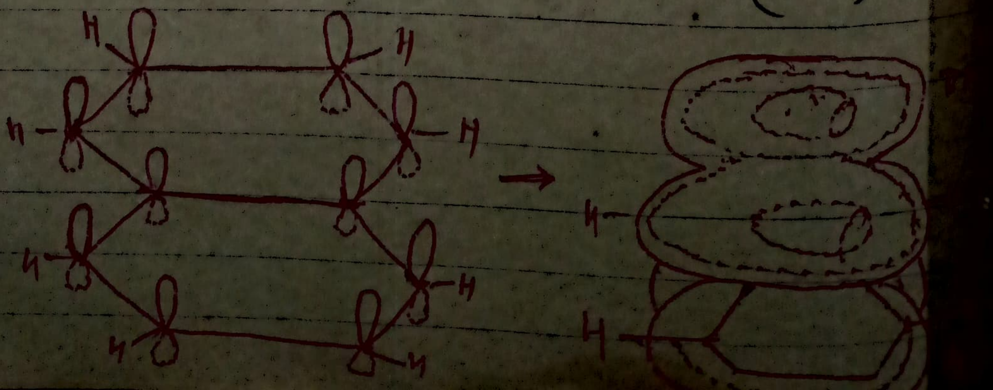
All ten Carbon atoms in napthalene are sp^2 hybridised the sp^2 hybrid orbitals overlap with each other and with s- orbital of 8 H- atoms forming C-C - and C-H, σ bonds. All the σ- bonds lie in one Plane. This has been ~~to~~ confirmed by X- ray diffraction studies.



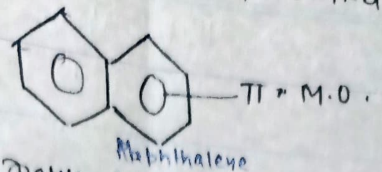


Formation of σ bonds in naphthalene -

These P- orbitals are perpendicular to plane containing σ- bonds. The lateral overlap of these P- orbitals produces a π. M.O. containing 10 electrons. One half of this π. M.O. lies above and another half lies below the plane of σ - bonds. Napthalene shows aromatic character because the resulting π. M.O. satisfies the Huckel's rule (n=2, 4n

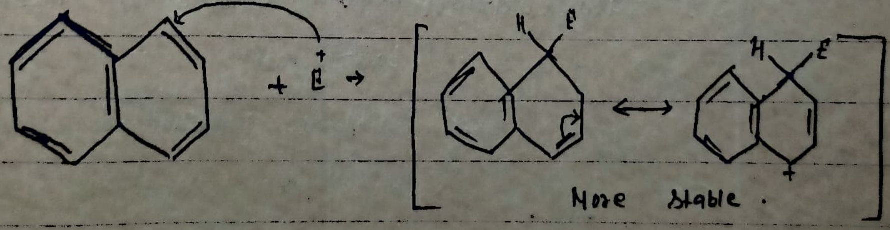


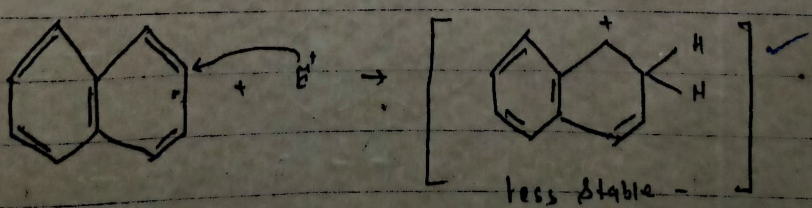
Naphthalene is now represented as



Properties of naphthalene → Naphthalene is a colourless crystalline solid. It melts at 82°c. and boils at 218°c. It is insoluble in water. but dissolves in ethanol, and ether. ~~and~~ It sublimes readily when warmed. Naphthalene has a characteristic "Moth ball" odour.

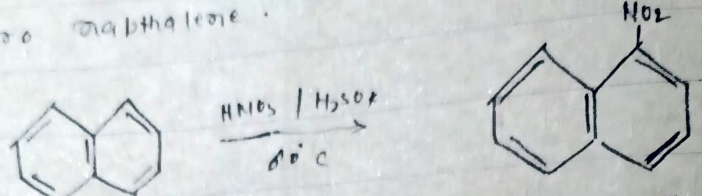
Chemical Properties → Naphthalene like benzene. undergoes electrophilic substitution reaction. Substitution primarily occurs at c-1 (α-Position) This can understood if we examine the intermediate carbonium ion. Two resonance forms can be written for the intermediate carbonium ion, obtained from attack C-1 (α-Position) where as only one such form is possible. for substitution at c=2





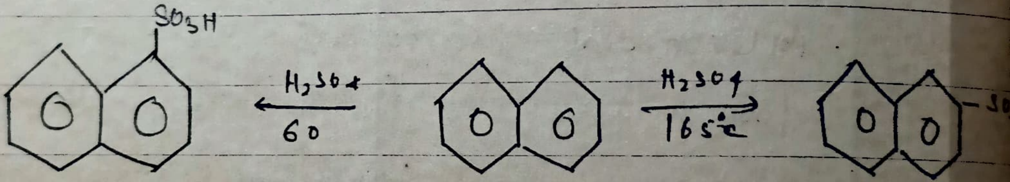
Consequently the former intermediate is much more stable than latter. Substitution at C-2 (β-Position) occurs only when the reactions are carried out at high temp.

(i) Nitoation → Napthalene undergoes nitration with Conc. HNO_3 and Con. H_2SO_4 to give 1- nitro napthalene.



α - nitro napthalene.

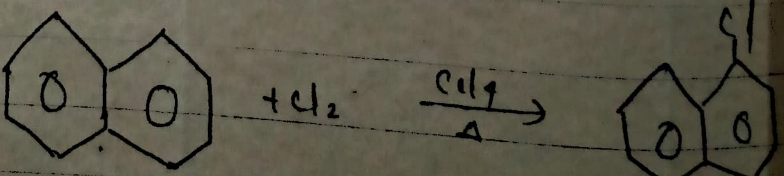
(2) Sulphonation → Napthalene undergoes sulphonation with Conc. H_2SO_4 at 60°C to give α- napthalene sulphonic acid, If reaction is carred out at 165°C 2- napthalene sulphonic acid is obtained.



α - napthalene sulphonic acid

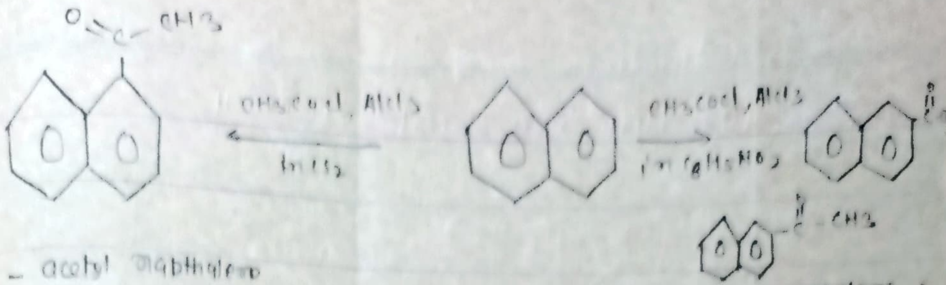
β - napthalene sulphonic acid.

(3) Halogenation → Napthalene undergoes chlorination or bromination in boiling CCl_4 to give α- Chloro- napthalene. unlike Benzene no Lewis Catlyst is required.



(4) Friedel Craft - acylation →

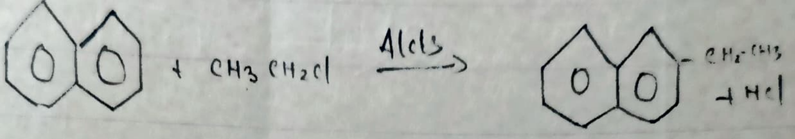
Napthalene undergoes acylation with acetyl chlo and $AlCl_3$ in CS_2 to give 1- acetyl- napthale when nitrobenzene is used as, 2- actyl napthale is obtained.



1 - acetyl napthalene

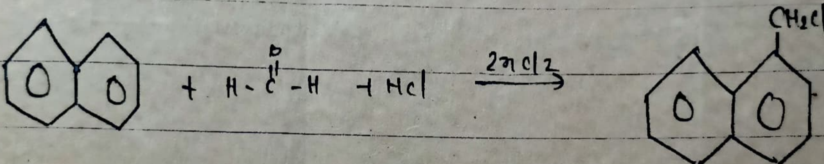
β- acetyl napthalene.

(5) Friedel- Craft - Alkylation → Napthalene undergoes alkylation with alkyl halides (and CH_3X) in the presence of $AlCl_3$ to give 2- alkyl napthalene.

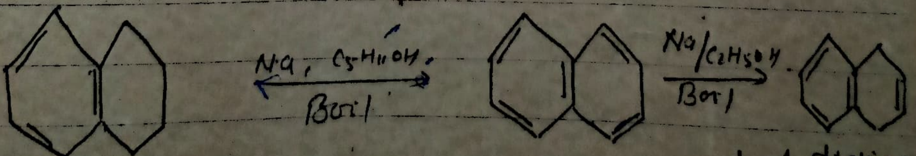


2- ethyl napthalene. -

(6) Chloro methylation → Napthalene reacts with HCHO and HCl to give 1- Chloro methyl napthalene.

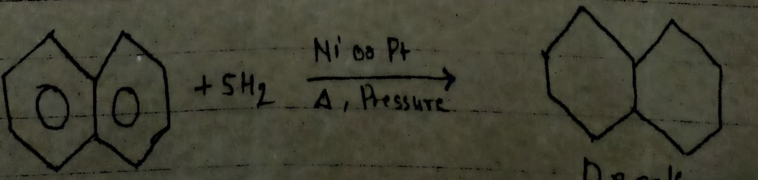


(7) Reduction → Napthalene undergoes reduction more readily than benzene, with Na and C_2H_5OH. It gives 1,4-dialine or 1,4.- dihydro napthalene with Na and isopentanol (B.P-138c). it gives tetraline or, 1,2,3-4, tetrahydro napthalene.



1 - 4, dialine

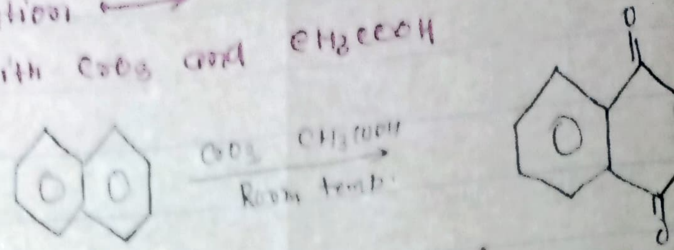
Catlytic hydrogenation - hydrogenates both the rings -



Decaline.

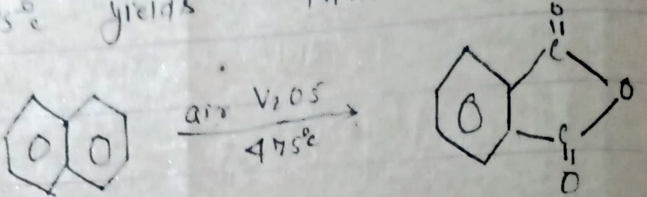
Oxidation →

(a) With CrO_3 and CH_3COOH



1, 4. naphthaquinone

Oxidation of naphthalene with air and V_2O_5 at 475°C yields Phthalic anhydride.



Phthalic anhydride.

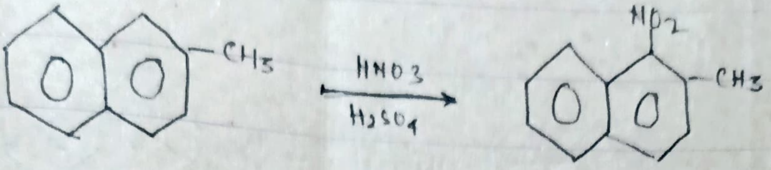
Uses → It is used as "moth balls" to protect woolen goods. It is used for increasing the illuminating power of coal gas. It is used in manufacturing Phthalic anhydride, 2-napthol, dyes and several insecticides.

Substitution in naphthalene derivatives :→

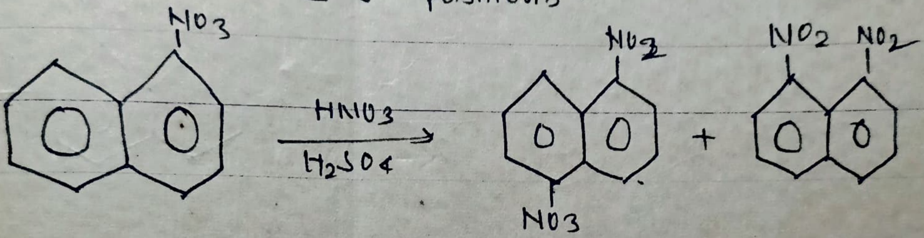
The introduction of a second substituent into naphthalene ring follows essentially same rules as for Benzene. The nature of the group already presents determines the position of entering group.

Rule (i) If the first group is o.p. di (e.g. $-OH$, $-NH_2$, $-CH_3$) and is located at C it will direct the incoming group to the C-2 or C-4, positions.

Rule - 2 → If first group is o.p. directing and is located at C-2, it will direct the incoming to the C-1 Position.



Rule - 3 → If first group is meta directing (eg - –COOH, –SO3H) and is located at C-1, or C-2 it will direct the incoming group to the C-5 or C-8 positions.

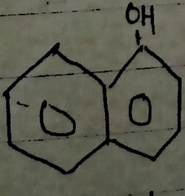


Above rules do not always hold in Sulphonation

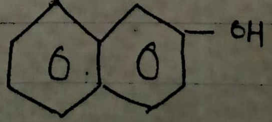
Naphthols -

Naphthols → The hydroxy derivatives of naphthalene are Called naphthols.

Two hydroxy derivatives of naphthalene are Known. One is Called α-napthol and other is β-naphthol.



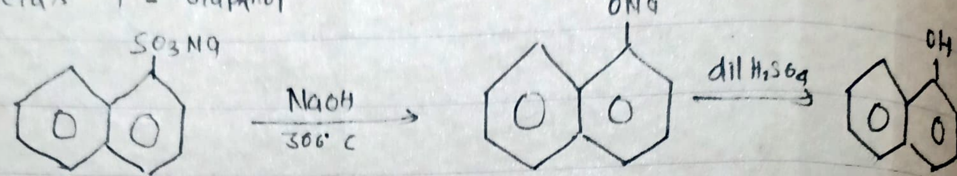
1 naphthol
(α- naphthol)



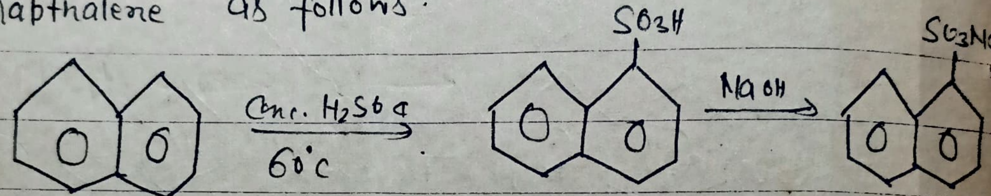
2 - naphthol
β - naphthol

α - naphthol → α - naphthol may be prepared by any of the following way:

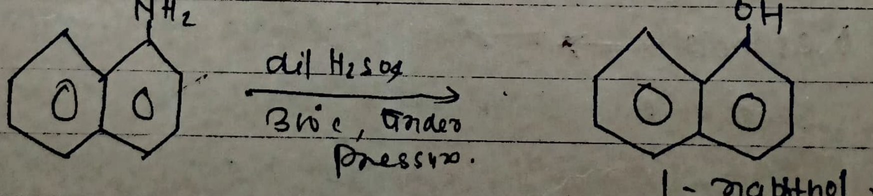
(1) From Sodium 1-naphthalene Sulphonate → When Sodium 1-naphthalene Sulphonate is fused with NaOH Sodium 1-naphthoxide is obtained at on treatment with dil Sulphuric acid yields 1-naphthol.



Sodium-1-naphthalene Sulphonate used in the above reaction may be obtained from naphthalene as follows.

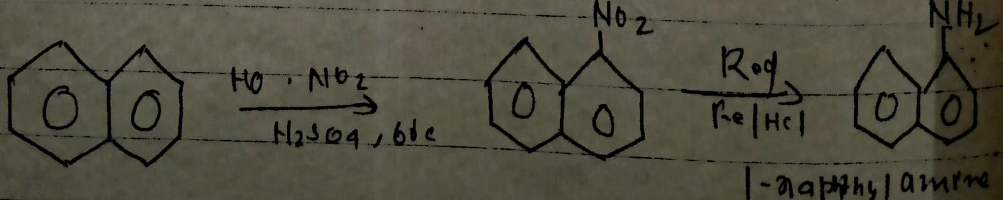


② From-1-naphthylamine ⟶ When 1-naphthyl amine is heated with dil H_2SO_4 at 306°c under pressure 1-naphthol is formed.



1-naphthol.

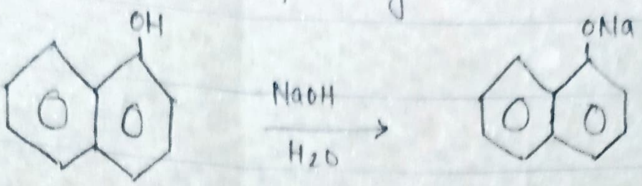
1 naphthylamine used in the above reaction may be obtained from 1-naphthalene as shown below.



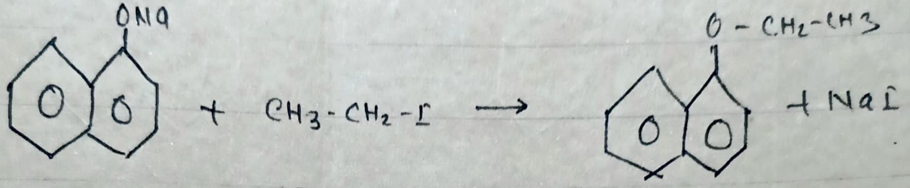
1-naphthylamine

Properties → It is Colourless Solid m.p. 94°c, It is Slightly Soluble in water but dissolves readily in ethanol and ether.

Chemical Propertries → (1) It is weakly acidic and dissolves in NaOH forming Sodium · 1 napthoxide.

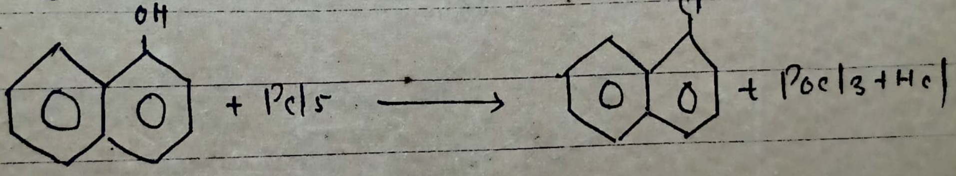


When Sodium · 1 napthoxide is heated with alkyl halide, the corresponding ethers are formed.

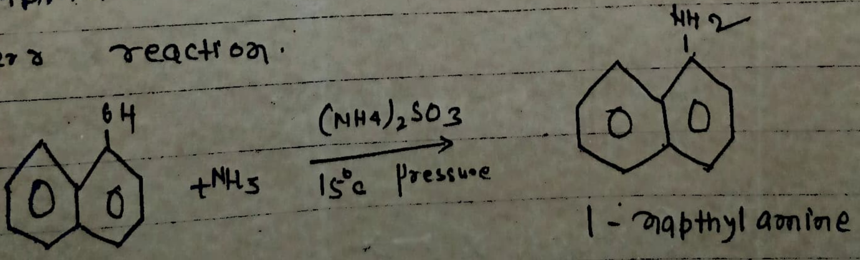


ethyl -1 napthyl ether :

(2) With Pcl5 → 1-napthol reacts with Pcl5 forming 1-Chloronapthalene.

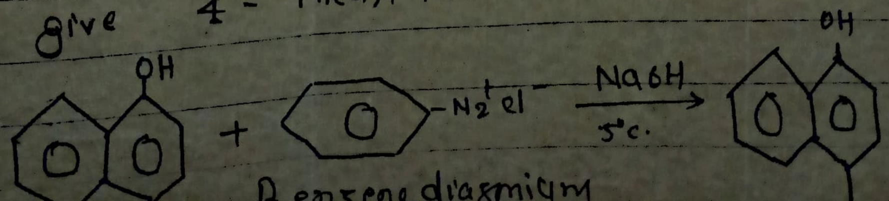


(3) Bucherer reaction → Reversible conversion 1-napthol into 1-napthyl amine is called Bucherer reaction.



1-napthyl amine

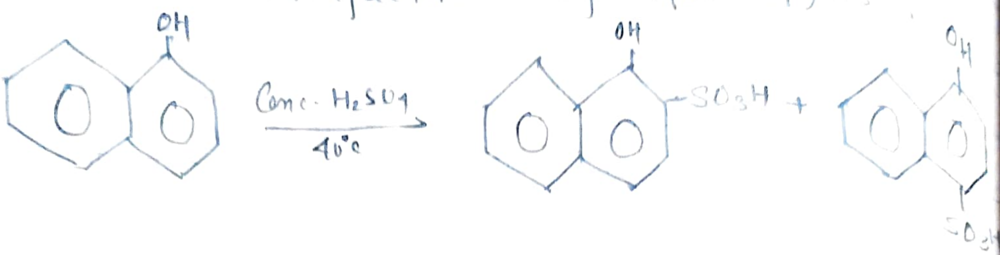
(4) Azo-Coupling → 1-napthol reacts benzene diazonium chloride in a weakly alkaline Solution to give 4-Phenyl Azo-1-napthol.



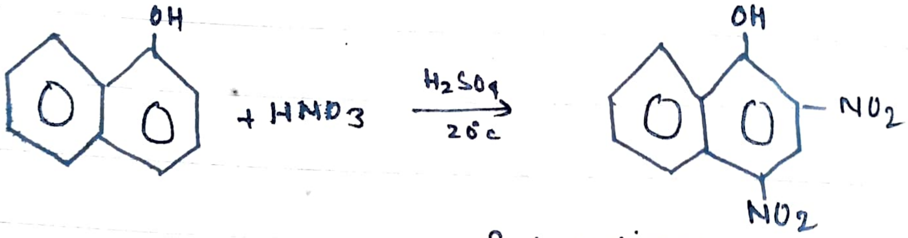
Benzene diazmium

(5) Sulphonation → 1- naphthol reacts with Conc. H_2SO_4 at 40°c to yield a mixture of 1- napthol - 2 sulphonic acid (Schaeffer's acid) and 1- naphthol 4 sulphonic ac

Both these sulphonic acids are used in the manufacture of Azo - dyes.



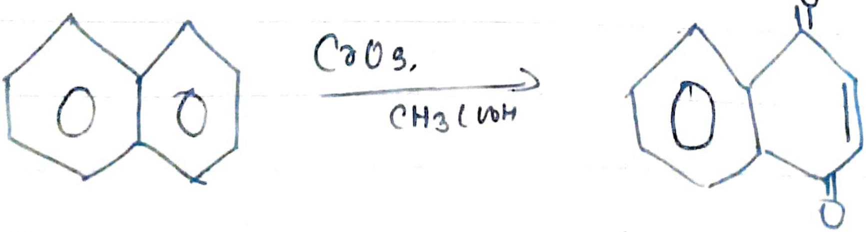
(6) Nitration → 1 - naphthol reacts with Conc. HNO_3 and conc. H_2SO_4 at 20°c to give 2,4. - dinitro - napthol.



2,4, dinitro -1 - naphtho

Sodium salt of 2,4 - dinitro -1 naphthol is known as mastius yellow. It is used as a dye for wool and silk.

(7) Oxidation → It is oxidised by chromi trioxide in acetic acids ~~in~~ to 1,4 - napthaqui



~~1- napthol~~.

1, 4 - napthaquinone