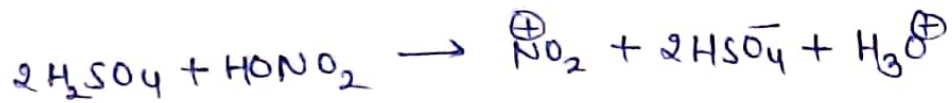


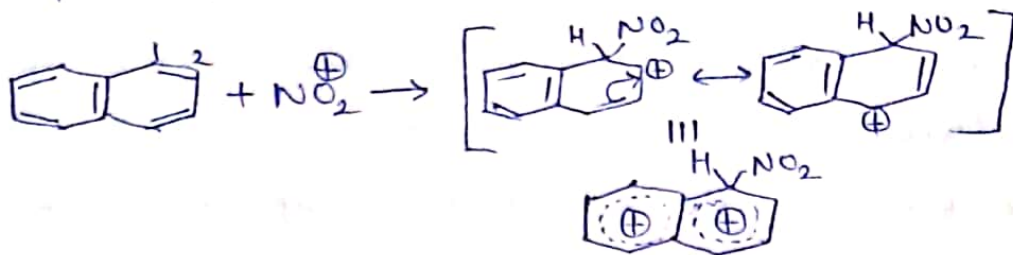
Mechanism:-

step 1. Generation of electrophile NO_2^+



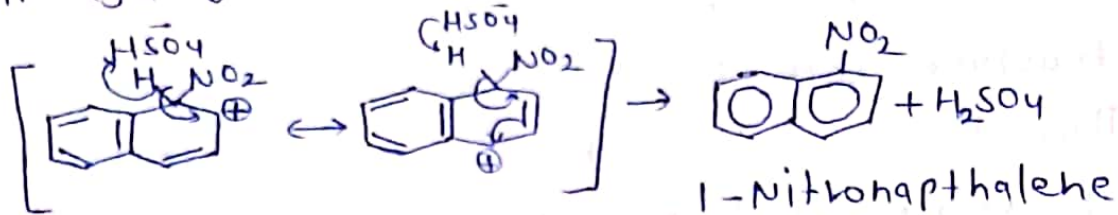
step-2. Nitronium ion attack on naphthalene

The electrophilic attack of naphthalene at C-1 position to form the resonance stabilised carbocation ion.



step-3. Elimination of hydrogen ion.

A hydrogen ion is eliminated to give 1-nitronaphthalene.

(2) Sulphonation Reaction:

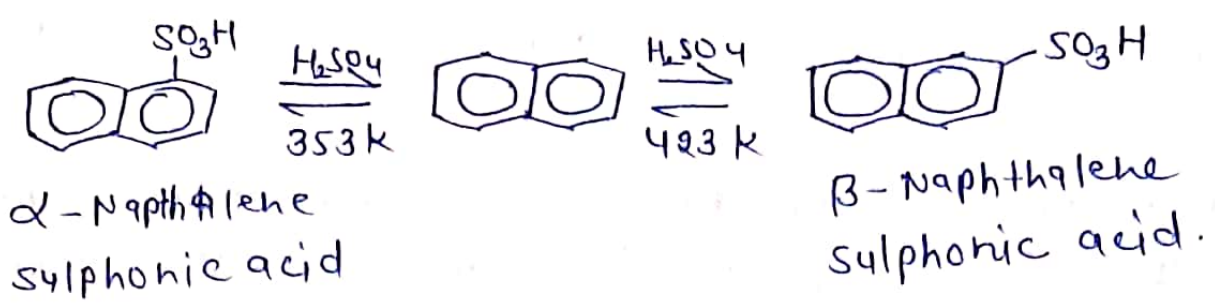
The sulphonation of naphthalene

is different from nitration and halogenation.

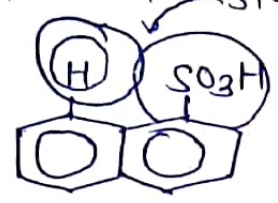
→ It is carried out with conc. H_2SO_4 at heating.

→ Temperature has a very important role to control this reaction.

→ At low temperature (353K), the sulphonation takes place at α -position, while at high temp (423K), the sulphonation takes place at β -position.



(3) Halogenation steric hinderence



α -Naphthalene sulphonic acid



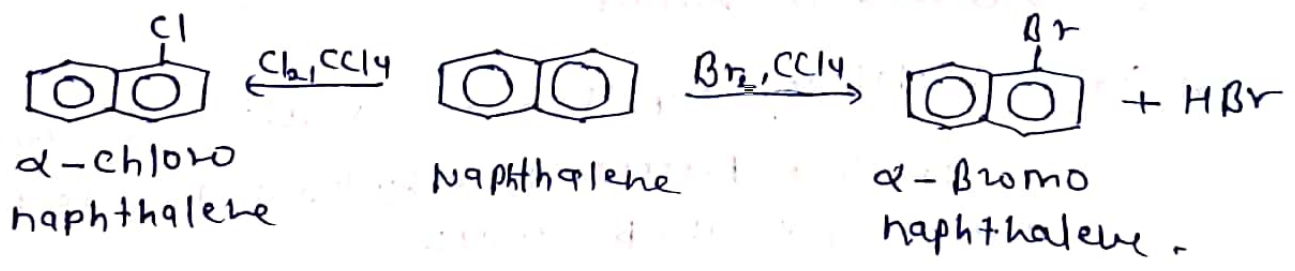
β -Naphthalene sulphonic acid

- more stable intermediate
- less stable pdt due to repulsion, p.e. \uparrow es
- kinetic control
- Require low energy

- less stable intermediate
- more stable product due to less repulsion p.e. \downarrow es.
- Thermodynamic control
- Require high energy.

(3) Halogenation Reaction

→ Chlorine and bromine dissolved in CCl_4 react with naphthalene to give α -halonaphthalene.
 → No halogen carrier such as ferric salt is needed as in halogenation of benzene. This shows that naphthalene is more reactive than benzene.



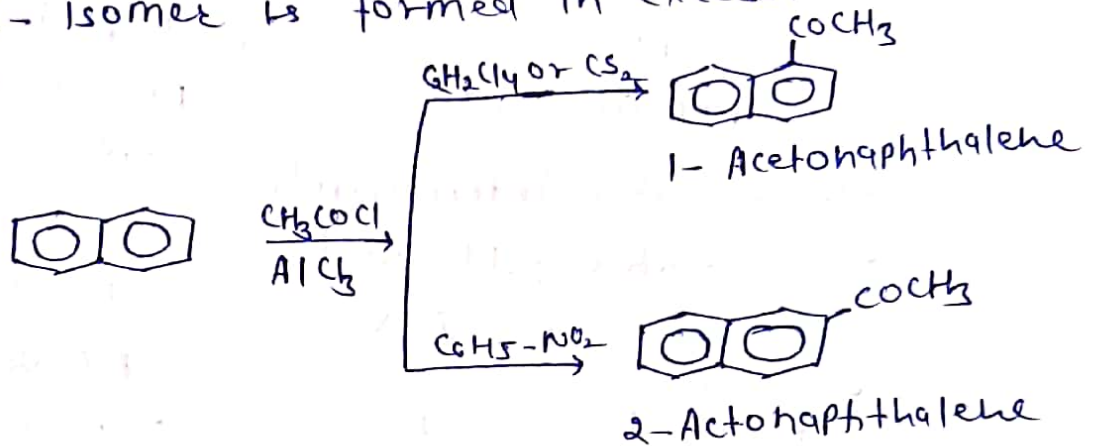
(4) Friedel-Craft's reaction:

Naphthalene can be acetylated with acetyl chloride in the presence of anhydrous aluminium chloride.

→ The nature of orientation i.e. the attack taking place at the α - or - β position is influenced by the nature (polarity) of the solvent.

→ In the non-polar solvents like CCl_4 , CS_2 , the acyl group is introduced at the α -position.

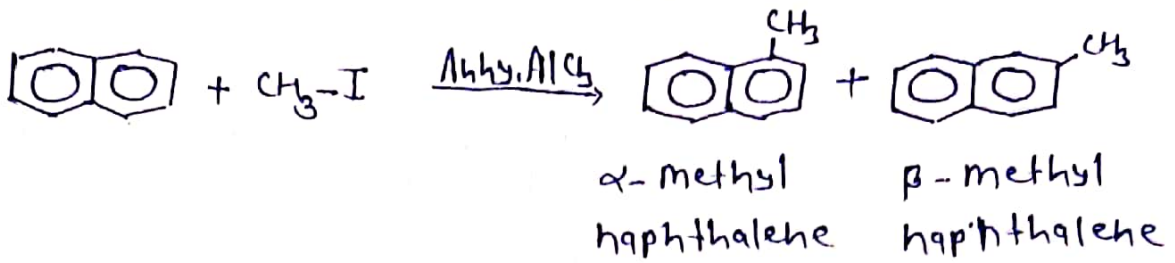
→ While when nitrobenzene (a polar solvent) is used as solvent, β -isomer is formed in excess.



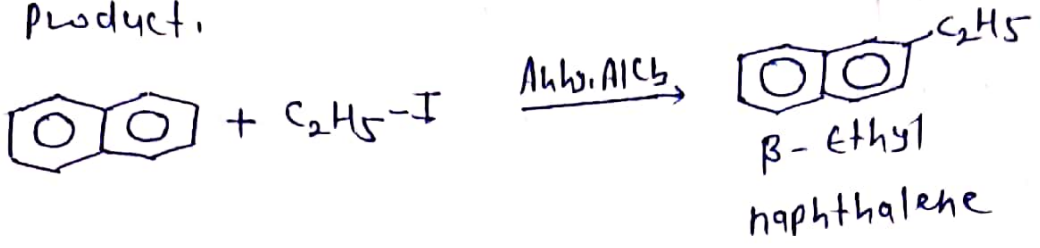
The β -directing influence in the presence of nitrobenzene solvent is explained on the basis of steric factors. It is ~~believed~~ believed that nitrobenzene forms a complex with CH_3COCl and AlCl_3 . The complex is bulky in size and therefore cannot attack at α -position. It attacks the β -position as is less crowded in nature.

(5) Friedel-Craft's Alkylation: Naphthalene on reaction with methyl iodide in presence of anhydrous AlCl_3 to give as mixture of α - and β isomers.

(21)

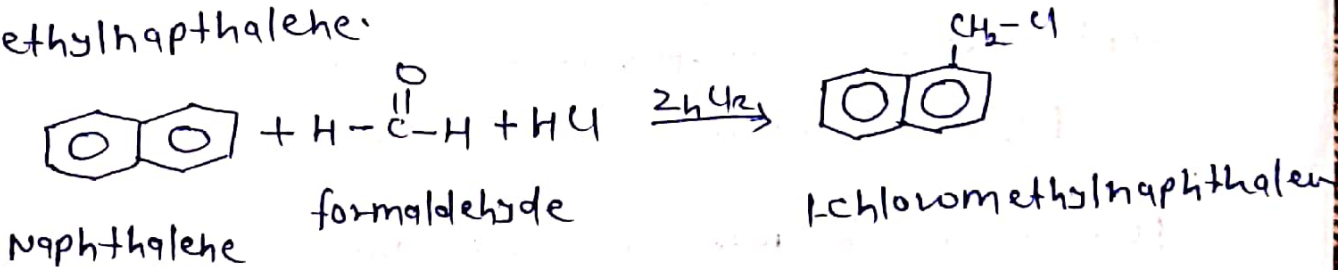


→ If the alkylation carried with ethyl iodide, only the β -isomer is formed as the product.



→ The prod formation can be explained on the basis of steric factors. The ethyl group being bigger in size as compared to the methyl group, it prefers to attack the β -position as it is less sterically hindered than the α -position.

(c) Chloromethylation: Naphthalene reacts with formaldehyde and HCl in the presence of ZnCl_2 to give 1-chloromethylnaphthalene.



ArSE² in substituted Naphthalene

