

## Naphthalene



(15)

m. f. -  $C_{10}H_8$

→ It is the simplest polycyclic aromatic hydrocarbon and a white crystalline solid with a characteristic odor that is detectable at concentrations as low as 0.08 ppm by mass.

→ It is aromatic hydrocarbon, naphthalene's structure consists of a fused pair of benzene rings. It is

best known as the main ingredient of mothballs

→ It is insoluble in water but readily dissolves in alcohol and benzene.

→ It is highly volatile and sublimates on heating

### Reactions of Naphthalene

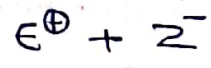
→ Since naphthalene is aromatic hydrocarbon, it is expected to take part in electrophilic substitution reaction as in benzene.

→ The electrophilic substitution is expected to complete

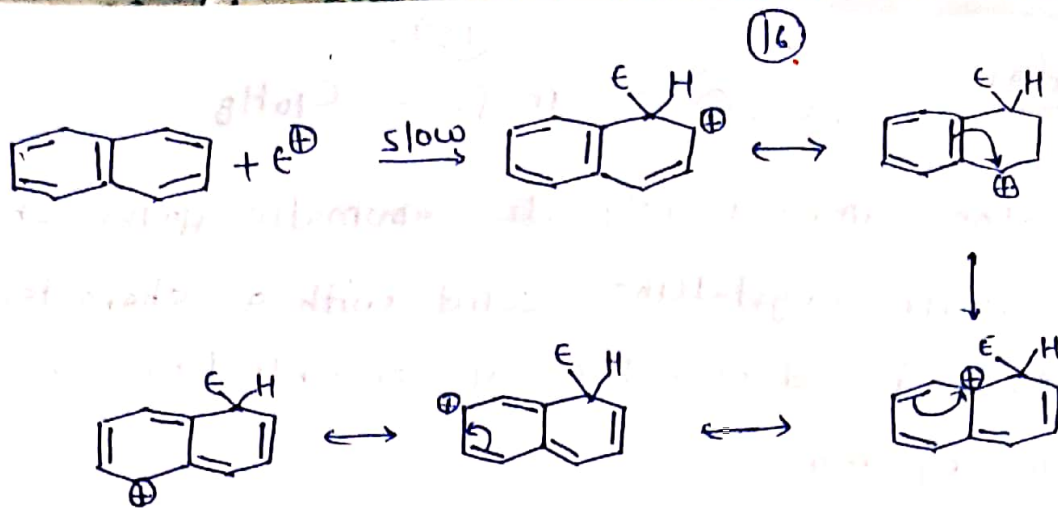
in two steps:

step 1: The electrophile ( $E^+$ ) is generated  $\subseteq$  attack on

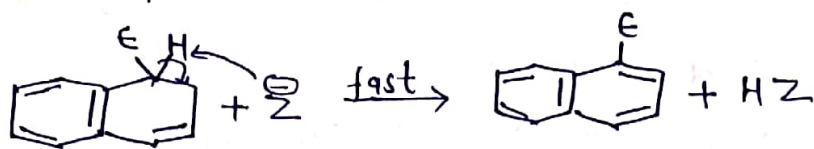
one of the  $\alpha$ -position in any of the two condensed rings to generate a carbocation  $\subseteq$  gets resonance stabilized. This is the rate determining or slow step.



Electrophile



Step-2: In the second step, the carbocation loses a proton to the nucleophile  $Z^-$  ion in fast step to form the desired product.



mono substituted pldt.

### Orientation in monosubstitution:

Although the electrophilic substitution in naphthalene can take place at both  $\alpha$ - and  $\beta$ -positions but monosubstitution actually occurs at  $\alpha$ -position why?

This can be explained by comparing the relative stabilities of the different cations  $\ominus$  are formed when the electrophile attacks takes place at the  $\alpha$  and  $\beta$  position respectively.

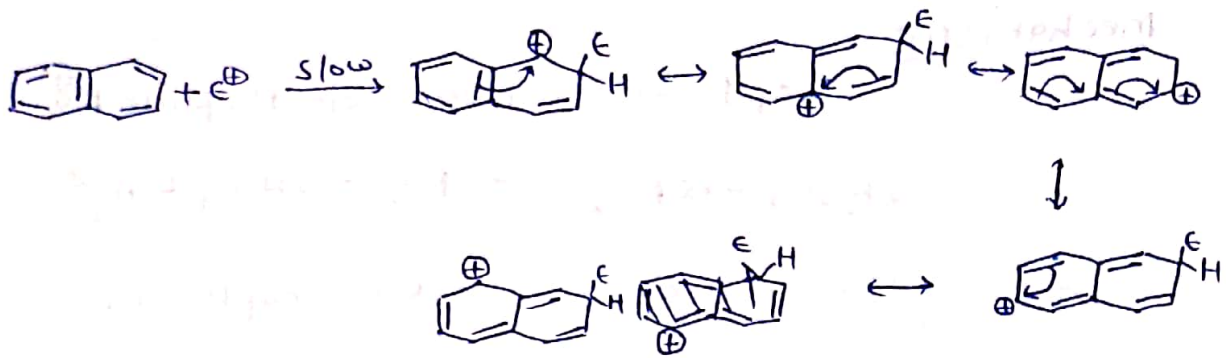
(i) Attack at  $\alpha$ -position: When the electrophile attack takes place at  $\alpha$ -position, there are five possible contributing structures for the carbocation  $\ominus$  shown earlier.

$\beta$   $\alpha$ -attack resonance structure discussed earlier

(ii) Attack at  $\beta$ -position: similarly, when the electrophile attack takes place at  $\beta$ -position, there are five possible contributing

(17)

structures for the carbocation.



A comparison of these contributing structure formed when the electrophile attack occurs at the  $\alpha$  and  $\beta$  position.

→ In case of attack at  $\alpha$ -position, two out of five contributing structures have one benzene ring intact which contribute more towards the hybrid as compared to the three other

→ In case of attack at  $\beta$ -position, only one benzene out of the five contributing resonance structure have ~~one~~ intact, while in the remaining four contributing structure both the rings gets destroyed.

→ Thus the resonance hybrid is more stabilised in case of attack at  $\alpha$ -position than in case of  $\beta$ -position.

→ In other words, the electrophilic attack occurs at the  $\alpha$ -position in the monosubstitution reaction of Naphthalene.

(1) Nitration - Naphthalene undergoes nitration with nitrating mixture consisting of conc.  $HNO_3$  and conc.  $H_2SO_4$  at 325 K temperature give nitro naphthalene as the product.

