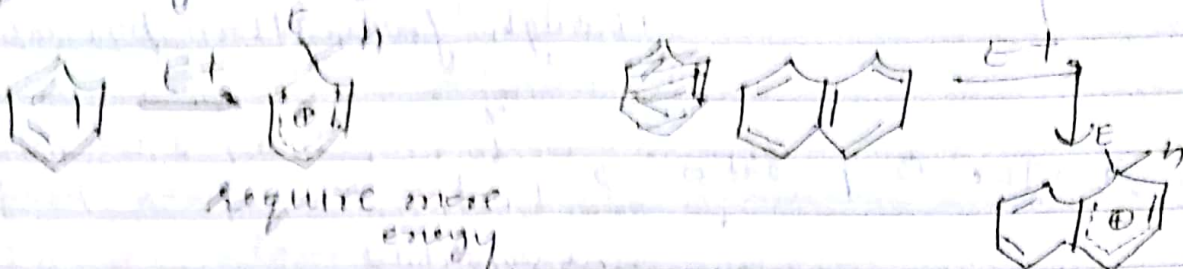


(A) Aromatic electrophilic substitution

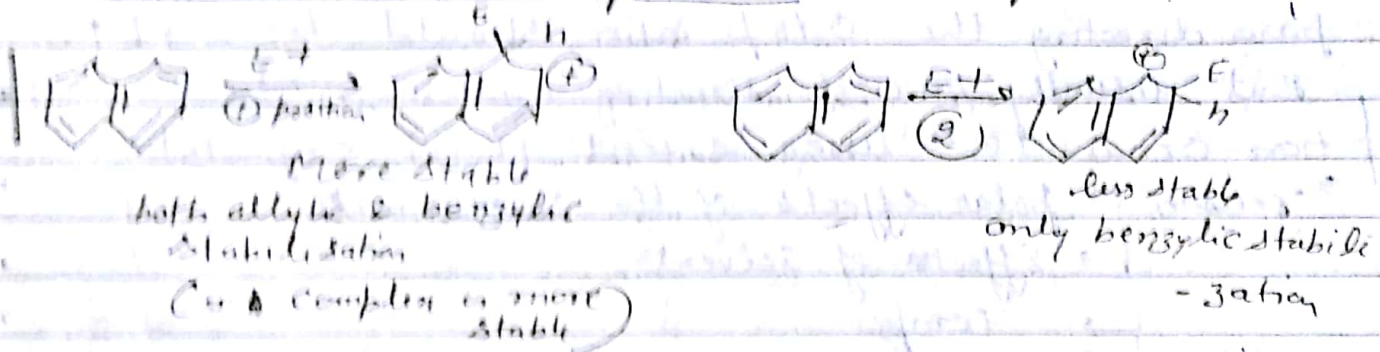
(2) Orientation in other ring systems ✓

↳ due to more extensive delocalization of charge in the corresponding arenium ion naphthalene is more reactive than benzene & electrophilic substitution is faster

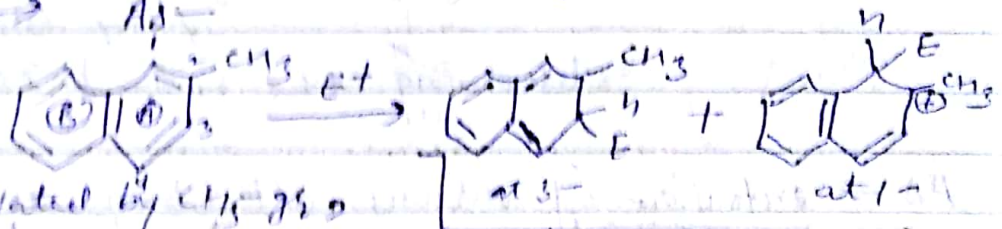
↳ Since consideration of the energy required for the formation of the intermediate arenium ions of polycyclic hydrocarbons, which is lower than that required for benzene



↳ E^+ substitution in naphthalene \rightarrow on 1-position



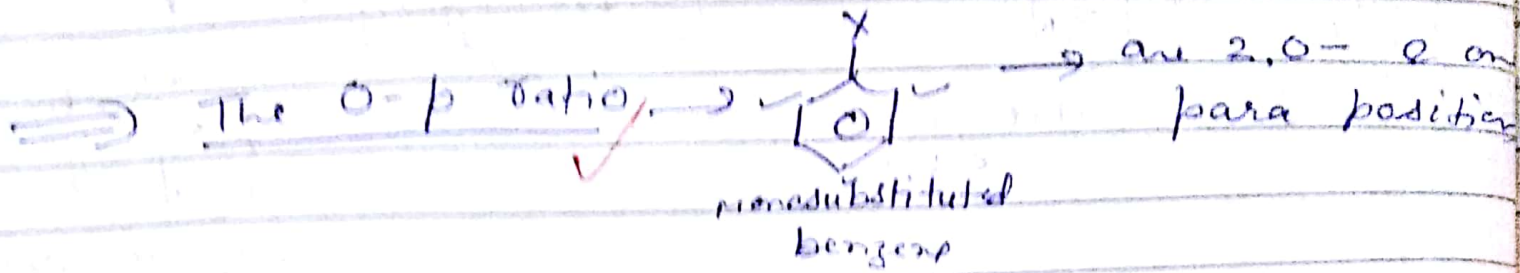
↳ E^+ substitution, when fused ring systems have substituents \rightarrow



ring A is activated by CH_3 gr.

ring B is not. So we expect substitution in ring A.

↳ so CH_3 gr. activates the position o- to itself (1,2) (1,3) but not position 4, which is m- to it.



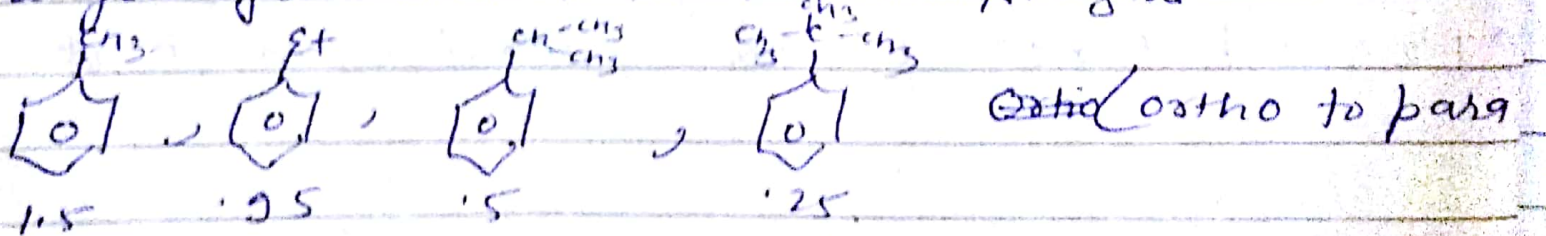
\rightarrow so it is expected that if the substituent is para directing the o to p ratio should be 2:1.

But usually in o,p-directing systems, the o-substitution occurs to a lesser extent than expected.

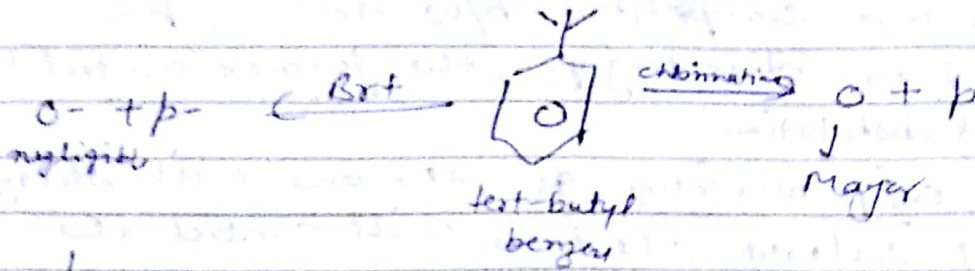
- \rightarrow reason \rightarrow polar effects of the substituents
- \rightarrow Effects of solvent
 - \rightarrow Temp
 - \rightarrow Size of the substituents
 - \rightarrow entering gr (steric factor)
 - \downarrow play dominant role in determining the o to p ratio.

As - variation of various alkylbenzenes \rightarrow

o-to p-ratio decreases gradually from 1.5 to ~25 as one goes from toluene to tert-butylbenzene.



(Ans) → In case of o-substitution, the steric interaction between the electrophile & the g_2 already present on the ring raises the energy of the T.S, thus making it less stable, ΔH^\ddagger increases; why the proportion of o-isomer in the o-p mixture increases if the reaction is carried out at higher temp. i.e. temp \uparrow increase \rightarrow ΔH^\ddagger o-isomer increases \rightarrow ΔH^\ddagger p-isomer.



↳ since ~~Br₂~~ Bromine molecule is bulkier than chlorine.

↳ when substituent already present has a pair of non-bonding e^- → then a different situation arise. Here electronic factors now dominate, & by which the amount of p-isomer increase.

