15.18 Ortho-Para Ratio

As a monosubstituted benzene contains two *ortho* and one *para*-position, the ratio of the *o*- and *p*-isomers obtained must be 67 : 33 ; but it is never found to be so due to some factors which can be grouped mainly under two headings : (*i*) steric factor, and (*ii*) inductive effect of the group already present.

(*i*) **Steric factor :** It has been observed that larger the size of the group already present, the smaller will be percentage of the *o*-isomer formed, *e.g.*, the following results have been obtained on nitration.

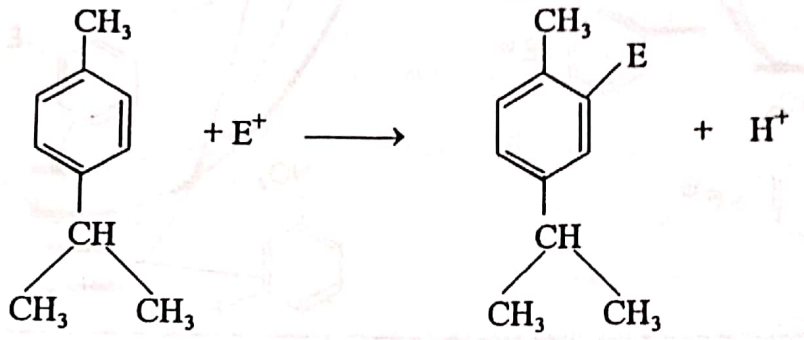
Name of the compound	% of ortho	% of para	*o*/*p* ratio
$C_6H_5.CH_3$	58.5	37.2	1.57
$C_6H_5.C_2H_5$	45	48.5	0.93
$C_6H_5.CH(CH_3)_2$	30	62.3	0.48
$C_6H_5.C(CH_3)_3$	15.8	72.7	0.22

The gradual decrease in *o* to *p* ratio is in consistant with the increasing size and thus, increasing steric hinderance of the substituent already present. In the case of *o*-substitution the steric interaction between the electrophile and the substituent already present on the ring raises the energy of the transition state, thus, making it less stable. This explains the increased proportion of the *o*-isomer in the *o*-, *p*-mixture when the

reaction in carried out at increasingly high temperatures. For example, nitration of acetanilide at 0°C gives almost exclusively the *p*-nitroacetanilide, and the amount of *o*-isomer increases with the rise in reaction temperature.

Other important example showing the role of steric effect in determining the *o/p* ratio is the halogenation of *ter*-butylbenzene. When *ter*-butylbenzene is chlorinated, significant amount of the *o*-isomer is formed (although main product is *p*-isomer), but when it is brominated, *o*-isomer is found to be almost negligible. This is consistant with the bulkier rize of the bromine molecule as compared to that of chlorine.

Similarly, we can explain why electrophilic substitution in *p*-cymene gives mainly the isomer having electrophile at the *o*-position to the methyl group, although from electronic considerations the substitution should take place at the position *ortho* to isopropyl group.



p-cymene

(*ii*) **Inductive effect :** However, it is seen that the steric factor is not only at work during the substitution reaction, *e.g.*, nitration of fluoro-, chloro-, and bromo-benzenes give following results [Sandin, 1947].

Name	ortho	para	*o/p* ratio
C_6H_5F	12.6	87.14	0.14
C_6H_5Cl	30.1	73.1	0.41
C_6H_5Br	37.1	62.5	0.59

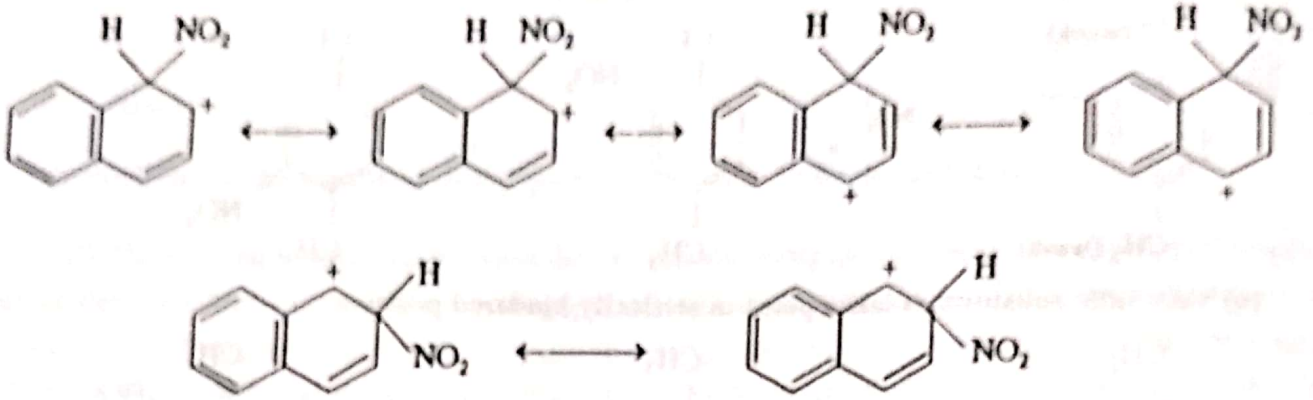
So if steric effect is the only governing factor then the *o/p* ratio must have fallen from fluorine to bromine as the size of the halogen increases from fluorine to bromine, but it is actually reverse in the table. This is explained by the fact that electron-withdrawing inductive effect influences the adjacent *ortho*-positions much powerfully than the more distant *para*-position. And as the inductive effect falls from fluorine to bromine, the percentage of ortho substitution must increase from fluorine to bromine and actually it is so as given in the above table.

Other factors governing the *o/p* ratio are temperature and solvent. The effect of temperature on the *o/p* ratio can be judged by the following data on sulphonation of toluene at 0° and 100°C.

15.19 Electrophilic Substitution of Other Aromatic Species

Uptil now we discussed the electrophilic substitution reaction in the benzene nucleus but now we will discuss the substitution reactions in other nuclei especially naphthalene and pyridine.

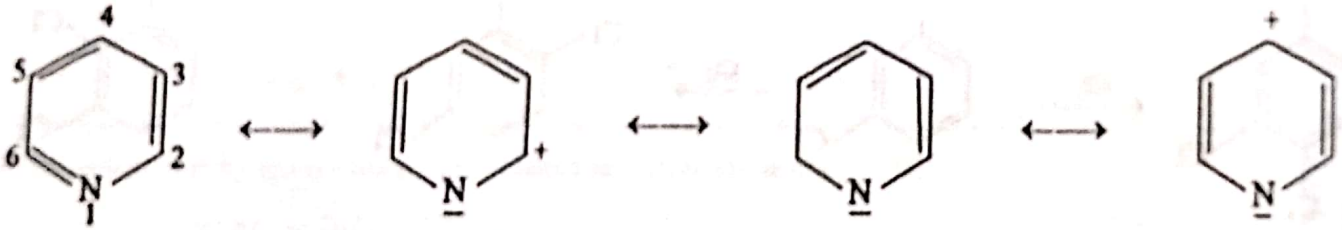
In naphthalene electrophilic substitution takes place, preferentially at α- rather than the β-position. It is explained on the basis of stabilities of their transition states (intermediate carbonium ions). As we shall see below the intermediate carbonium ion of the α-substituted naphthalene can stabilise itself by four resonating structures whereas in the case of β-substituted naphthalene only two such structures are possible.



Note that here we are considering only important contributing structures in which one benzene ring is retained.

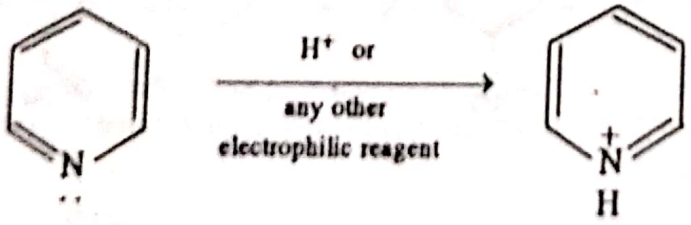
It must be noted that as there are more possibilities for delocalisation of charge in monosubstituted naphthalene intermediate than that of monosubstituted benzene, the naphthalene will undergo more readily electrophilic attack than benzene.

Although pyridine, like benzene, has six π electrons (one is supplied by nitrogen) in delocalised π orbital, yet it, unlike benzene, does not undergo electrophilic substitution very easily. It is explained by the fact that due to the presence of more electronegative element nitrogen, the electrons are displaced towards it and thus, the following structures contribute more to the pyridine structure.



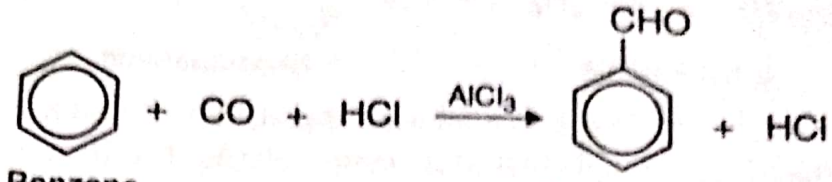
Thus, the presence of nitrogen in the pyridine ring deactivates the ring and hence, electrophilic substitution takes place in 3 and 5 (β-) positions. Moreover, deactivation of the ring also explains why pyridine is less reactive towards electrophilic reagent than benzene.

Moreover, deactivation of the pyridine nucleus is further increased on electrophilic attack, because during electrophilic attack nitrogen atom develops a positive charge either by protonation or by the direct attack of the reagent. Thus, the nitrogen atom withdraws electrons more strongly and further hinders electrophilic substitution.



Benzaldehyde

(5) By Gattermann-Koch Synthesis. This involves the treatment of benzene with carbon monoxide and hydrogen chloride in the presence of $AlCl_3$ catalyst.



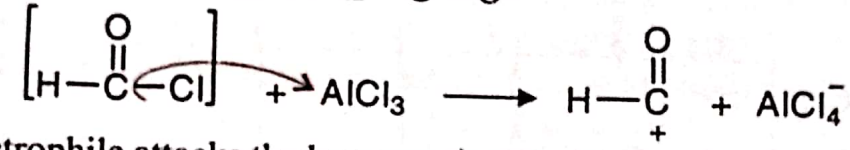
Benzene Benzaldehyde

MECHANISM. The above reaction is similar to the Friedel-Crafts reaction.

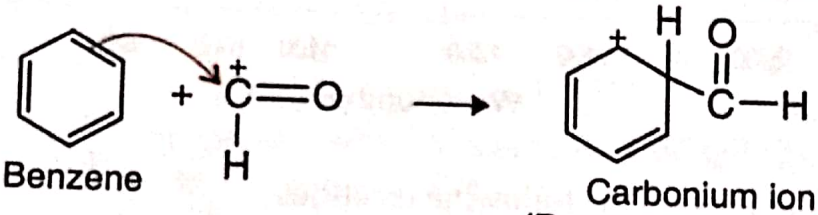
Step 1. Carbon monoxide and hydrogen chloride react to form unstable formyl chloride.

Formyl chloride

Step 2. Formation of the electrophile $H-\overset{+}{C}=O$.

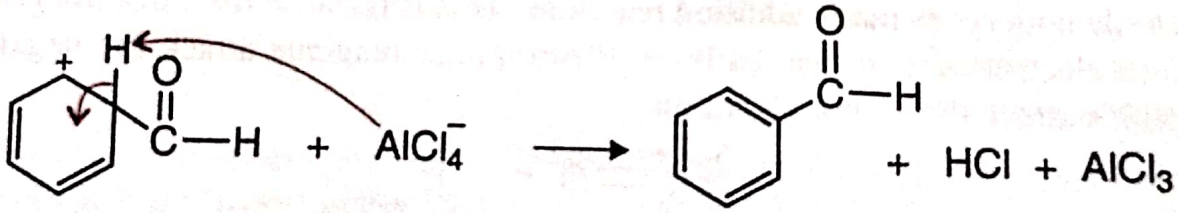


Step 3. The electrophile attacks the benzene ring to give a carbonium ion.



Benzene Carbonium ion (Resonance stabilized)

Step 4. Removal of proton gives benzaldehyde.



Benzaldehyde

(6) Stephen's Reaction. Benzonitrile