⑨ Diazonium Coupling →

$$\cancel{ArN_2}\ ArN_2^{\oplus} + Ar'H \rightarrow Ar-N=N-Ar' + \underline{H^{\oplus}}$$

⑩ Glattermen-Koch Rea^n -

(formylation of Aromatic Compounds by a mixture of. $\boxed{CO \text{ and } HCl}$

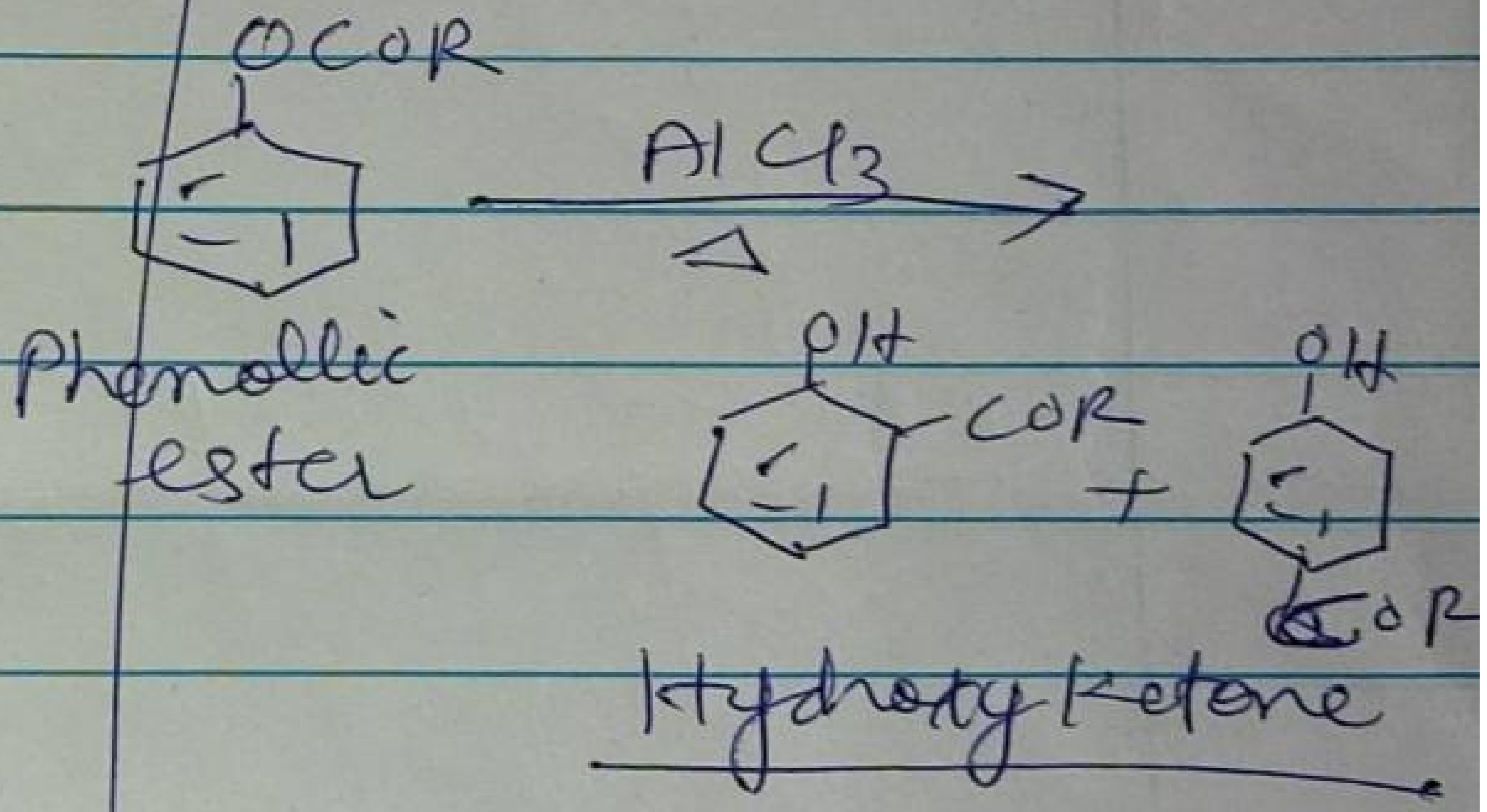
$$ArH + CO + HCl \xrightarrow[CuCl]{AlCl_3} ArCHO$$

⑪ Houben-~~Hoesch~~ Hoesch Rea^n

or Hoesch Rea^n

[friedel-crafts acylation with hydrogen chloride and Lewis acid catalyst.

⑫ Fries Rearrangement —



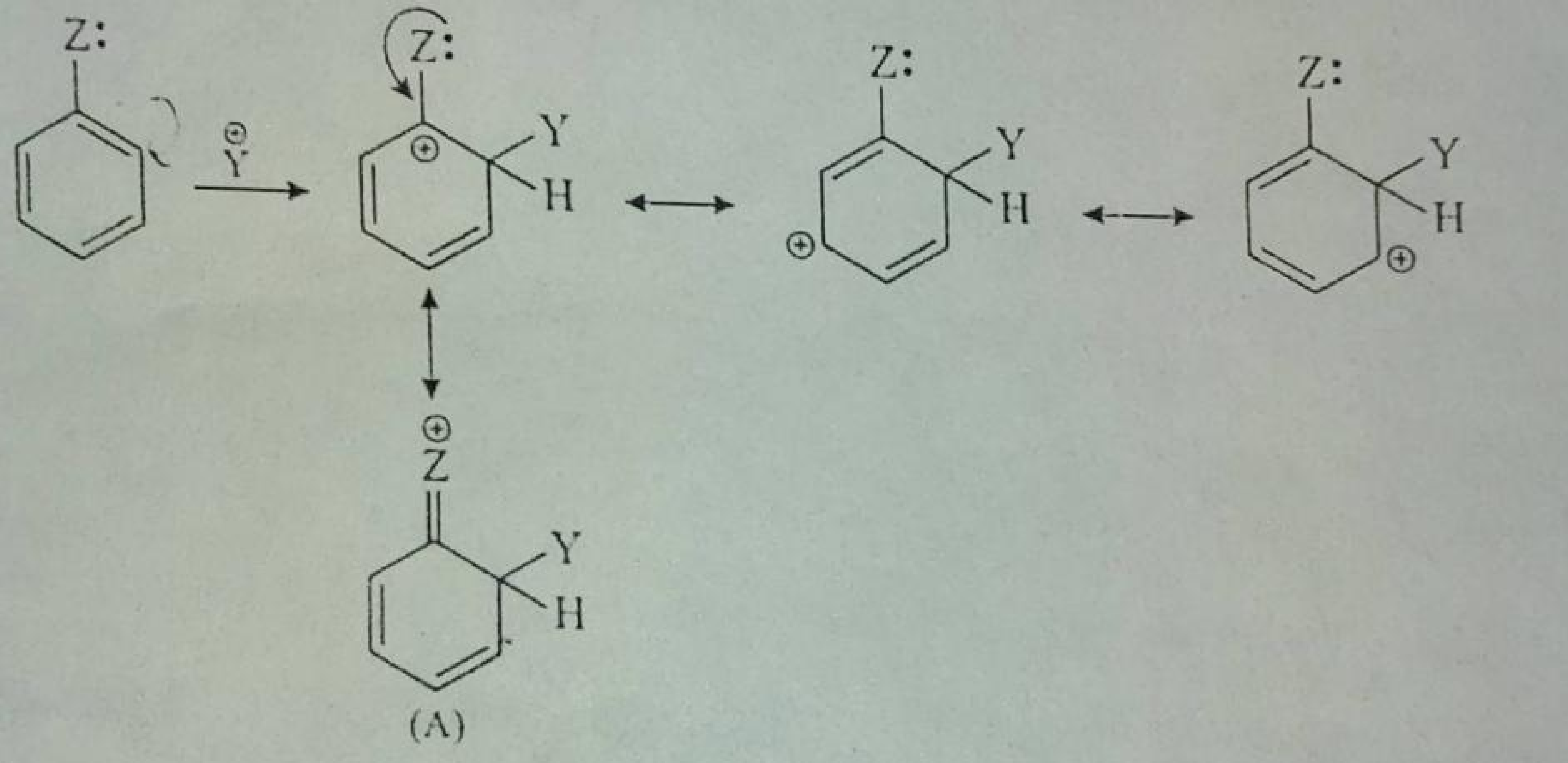
based on relative electronegativity. This is due to a size mismatch of the overlapping of the ring carbon and the p-orbital of the halogen because the overlap is maximum when the rlapping orbitals are of comparable size. Cl has $3p$, Br has $4p$ and I has $5p$ orbital, all of which have er size than the $2p$-orbital of carbon, thus there is poor overlap resulting in a very weak $+R$ effect. the other hand, F and carbon have $2p$-orbitals which are of comparable size, thus there is better overlap lting in greater $+R$ effect than that of Cl, Br, or I.

2. Explanation based on carbocation (Intermediate) stability : The effect of substituents on ntation and reactivity can be best explained by writing all the possible resonating structures of the ocation (arenium ion) intermediate for each of the three possible reaction courses, *i.e.*, for the attack p and *m*-positions, and comparing their stability.

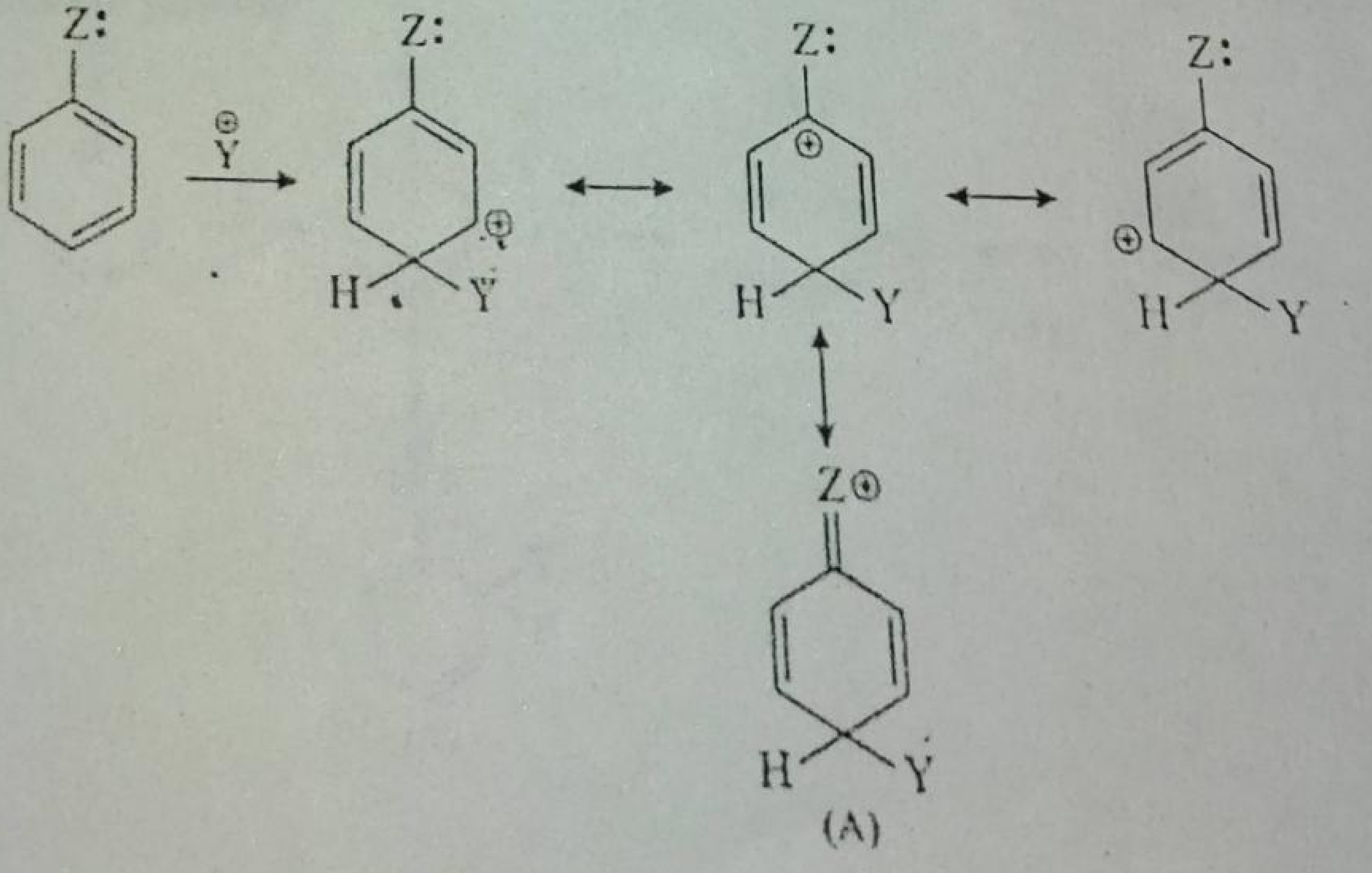
***Ortho*, *para*-directing and activating groups :**

(a) The groups containing a lone pair of electrons on the key atom stabilise the carbocation to a greater extent when the attack takes place at the *o* and *p*-positions as compared to the attack at the *m*-position. This is because for the attack at *ortho* and *para* positions an additional and particularly stable resonating structure (marked *A*) can be written in which all the atoms (except hydrogen) have a complete octet of electrons. Thus, the incoming electrophile is attached to the *o* and *p*-positions, *i.e.*, these groups are *o*-*p*-directing. Electron donation by such groups (Z) increases the rate of substitution compared to that in benzene itself, thus, these are activating groups.

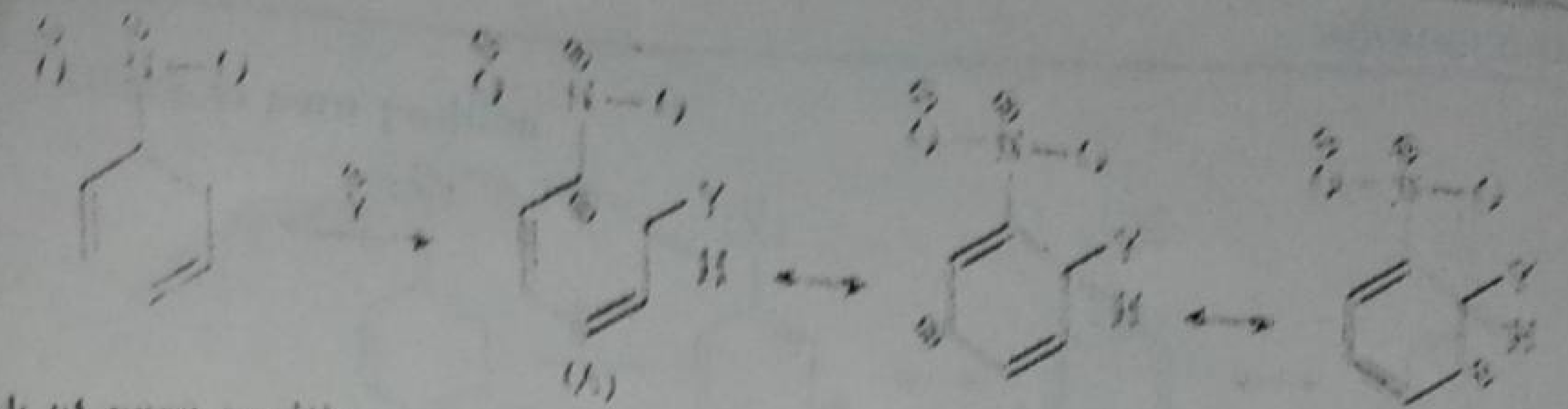
Attack at *ortho* position



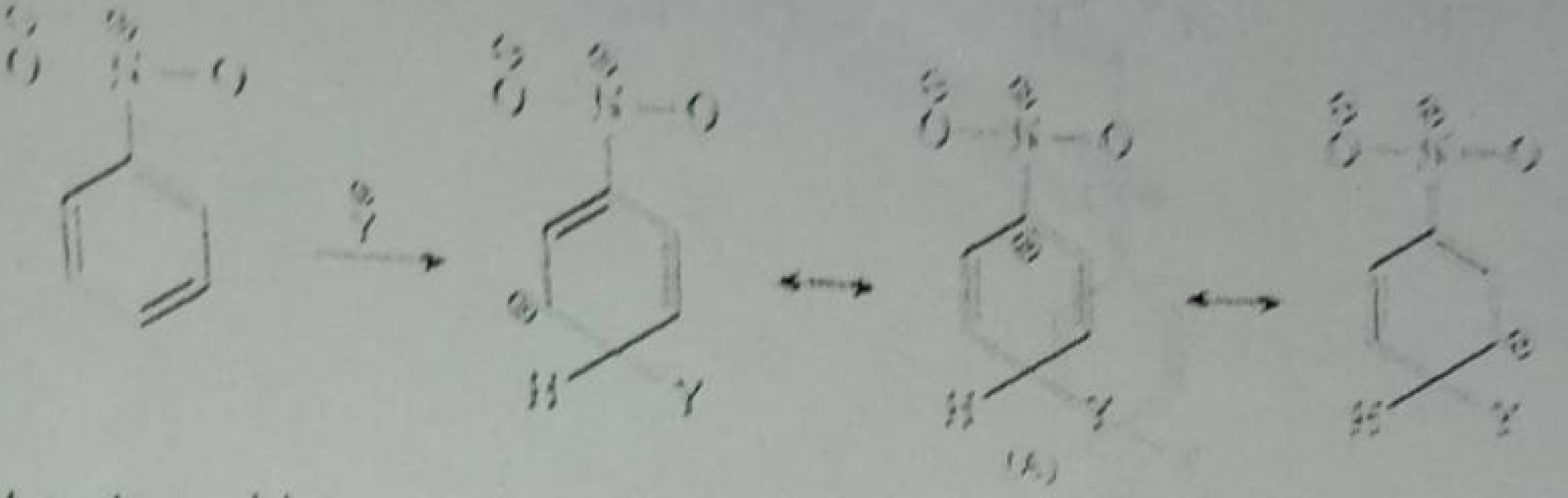
Attack a *p*-postion



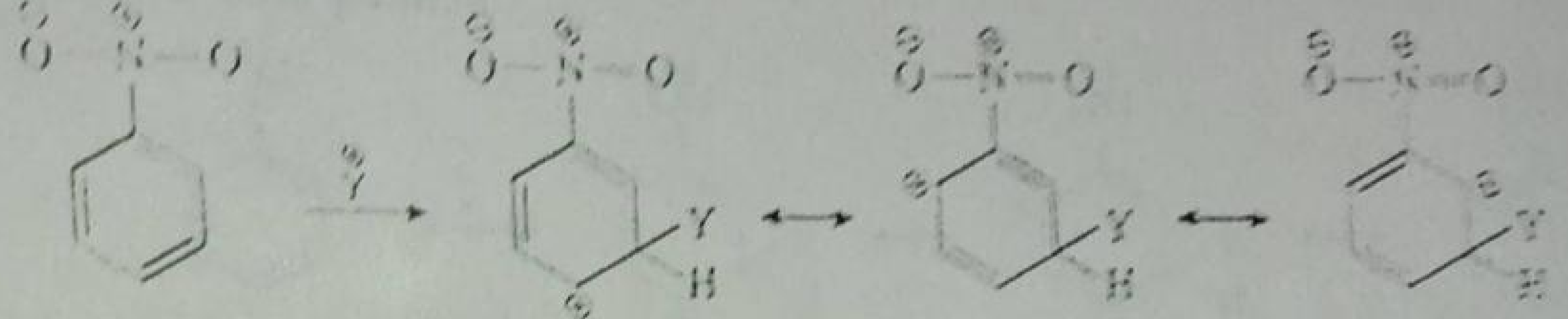
Attack at *ortho* position



Attack at *para* position



Attack at *meta* position

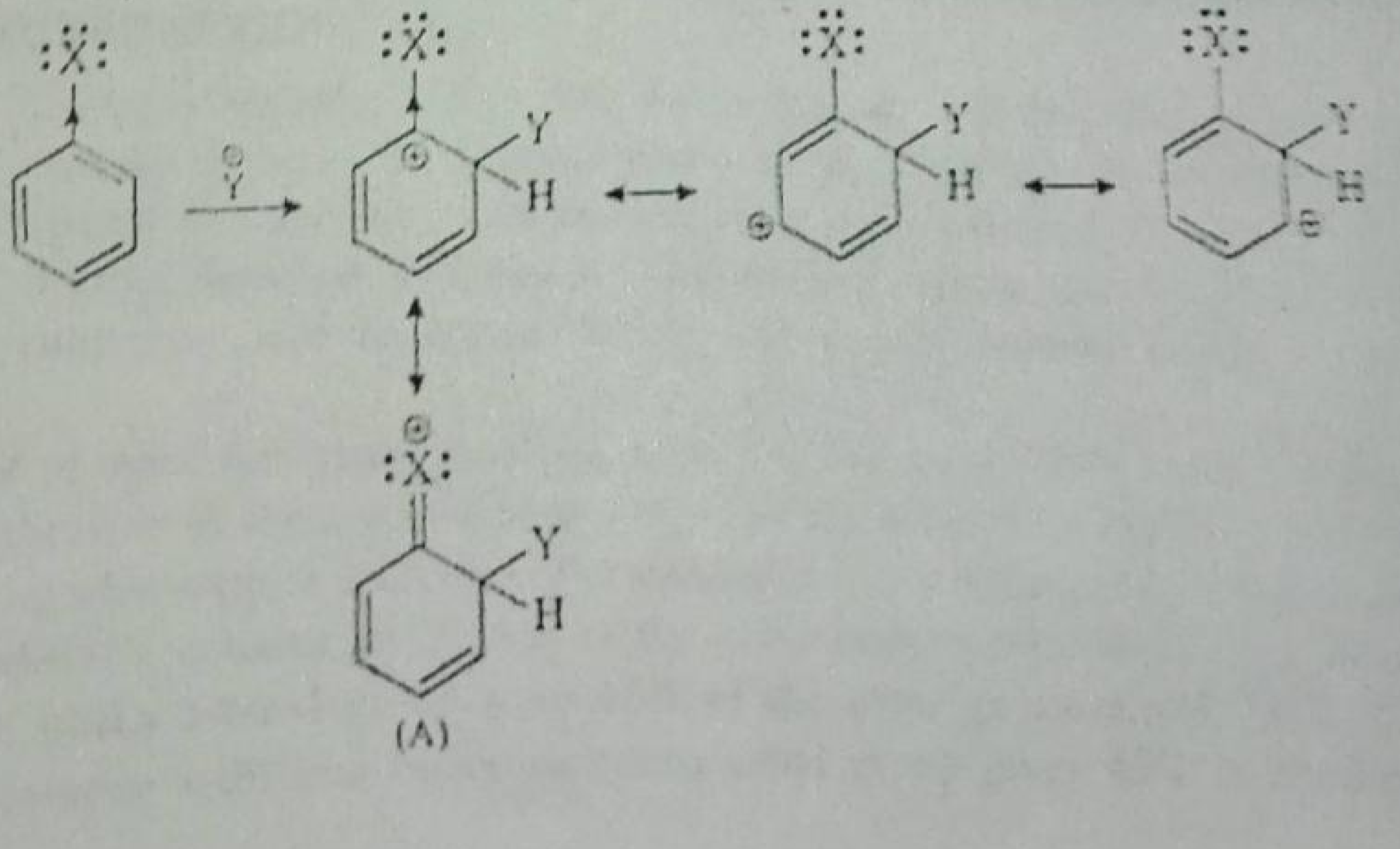


In the case of *ortho* and *para* attacks the resonating structures marked A are particularly unstable because the charge intensification in these is maximum due to the presence of the electron-withdrawing group on the carbon carrying the positive charge. No such unstable structure is possible in the case of *m*-attack. In other words, the carbocation intermdiate formed in *ortho* and *para* attack are destabilised to a greater extent than that in *meta* attack. Thus, *meta* substitution is preferred to *ortho* and *para* substitution in nitrobenzene.

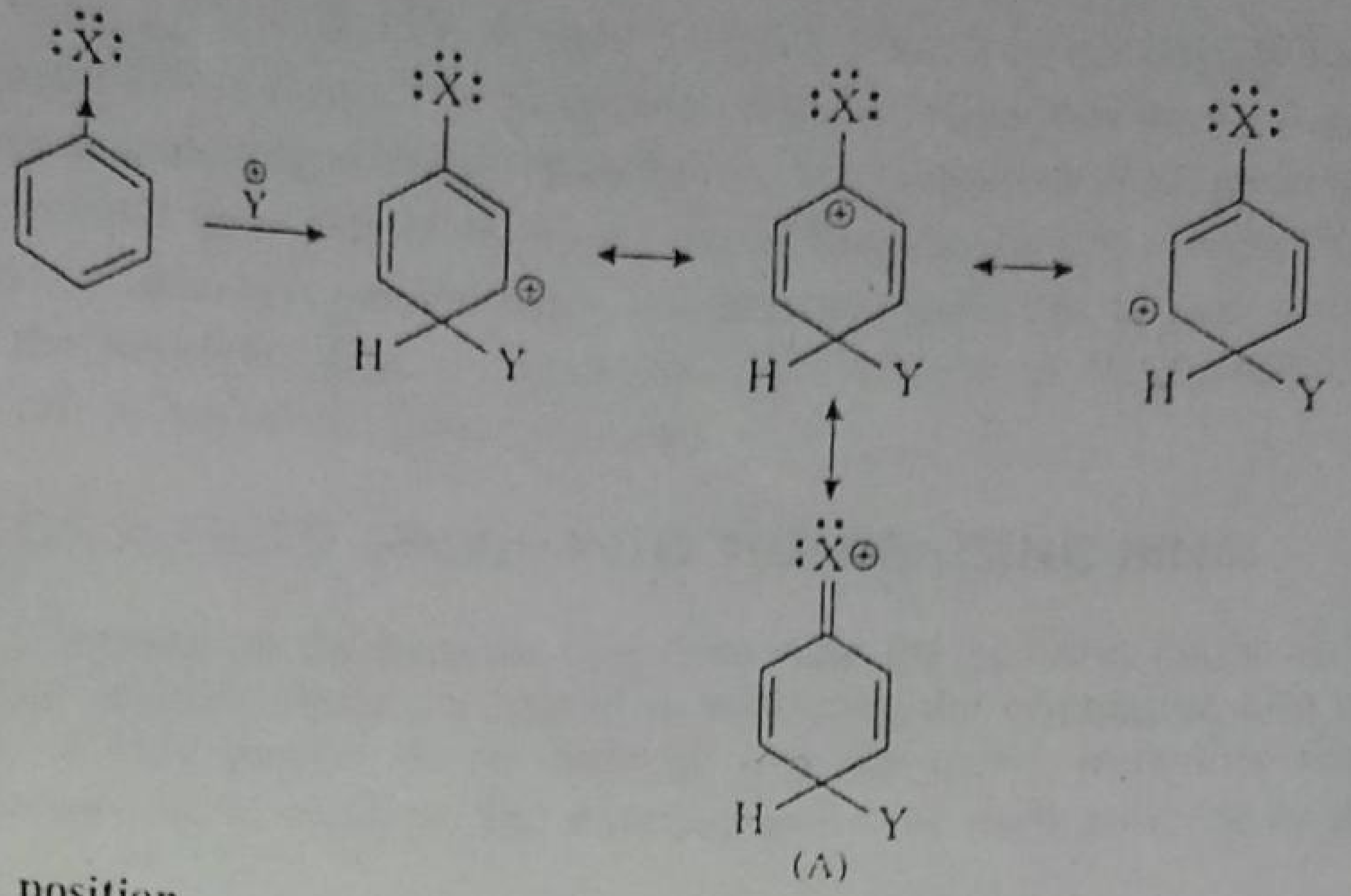
Similarly, the *meta* directing and deactivating nature of the other groups of this category can be explained.

***Ortho, para*-directing and deactivating groups** : Halogens (F, Cl, Br and I) belong to this category. These are *o*-*p*-directing but deactivate the benzene ring toward electrophilic substitution. This exceptional behaviour can be explained on the basis of inductive and resonance effects of halogens.

Attack at *ortho* position

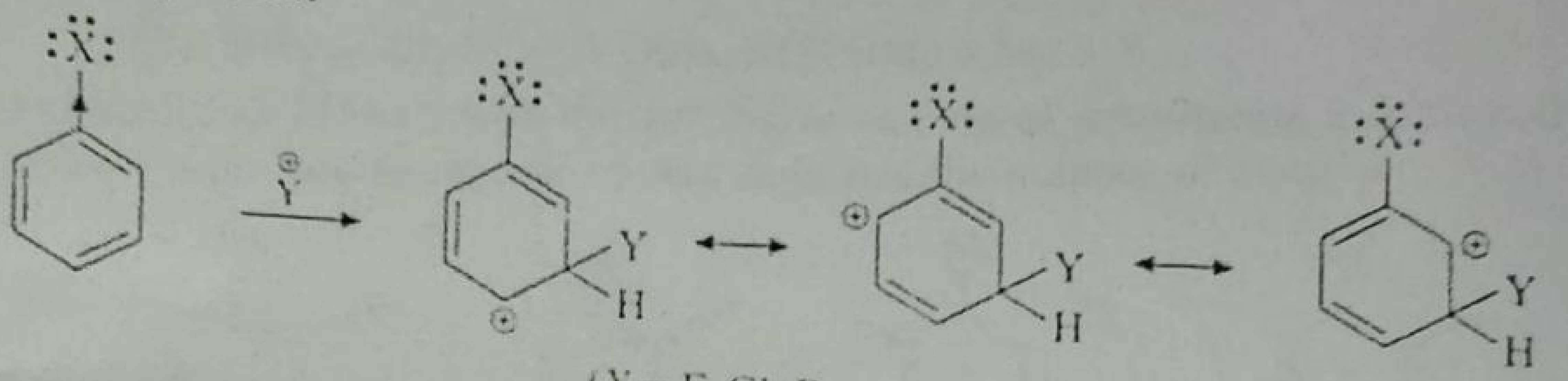


Attack at *para* position



(A)

Attack at *meta* position



(X = F, Cl, Br, or I)

In the case of *ortho* and *para* attacks there is one resonating structure (marked *A*) in each case which is comparatively more stable because in this structure all the atoms (except hydrogen) have a complete octet of electrons. No such structure of comparable stability is possible in the case of *meta* attack. Thus, halobenzenes undergo electrophilic substitution at *ortho* and *para* positions in preference to *meta* position.

Although *ortho* and *para* positions are activated as shown above, the strong electron-withdrawing inductive (− I) effect of halogens intensifies the positive charge on carbocation and destabilises it. The strong − I effect (− I > + *R*) causes net electron withdrawal and hence, deactivation of the ring for electrophilic substitution. Thus, reactivity is controlled by the stronger inductive effect, while the weaker resonance effect controls the orientation.

6.7 STERIC EFFECTS AND *ORTHO/PARA* RATIOS IN AROMATIC ELECTROPHILIC SUBSTITUTION

When a monosubstituted benzene containing an *o-p*-directing group undergoes electrophilic substitution, mainly *o*- and *p*-substituted products are obtained. Since, there are two *ortho* positions available compared to only one *para* position, it may be expected that the *o* and *p*-isomers should be formed in 2 : 1 ratio. However, in actual practice this *o*/*p* ratio is less. Several factors like steric hindrance, polar effect (inductive and resonance) of the substituent, solvent effect, temperature, etc. affect the *o*-*p* ratio.

Because of steric hindrance involved in the T.S. for *ortho* substitution, the proportion of *ortho* isomer decreases as the size of the *o-p*-directing group already present on the benzene ring increases, or the size of the attacking electrophile increases. For example, in the nitration of toluene and *t*-butylbenzene under the same conditions, toluene gave 58% of the *ortho* compound and 37% of the *para*, whereas the latter with the more bulky *t*-butyl group gave 16% of the *ortho* product and 73% of the *para*. Similarly, the alkylation of toluene with less bulky incoming ethyl group gives 45% of the *ortho* compound and 25%

of the para, whereas if the more bulky t-butyl group is incoming group then 0% of the *ortho* and 94% of the para products are obtained.

Another important factor which affects the *o*/*p* ratio is the inductive effect. For example, nitration of the halobenzenes gave *ortho* products as follows:

PhF 12%, PhCl, 30%, PhBr, 38%; PHI 41%. It should be noted that this is opposite to what would be predicted on the basis of steric effect alone. This is because fluorine which has the strongest – I effect of the four halogens has greater deactivating effect at the *ortho* position compared to the *para* than chlorine, and the effect of chlorine is greater than that of bromine, which has greater effect than that of iodine. Thus, in electrophilic substitution, amongst halobenzenes, iodobenzene gives the largest amount of *ortho* product and fluorobenzene the smallest. This indicates that in the case of halobenzenes —I effect predominates over the steric effect in governing the *o*/*p* ratio.

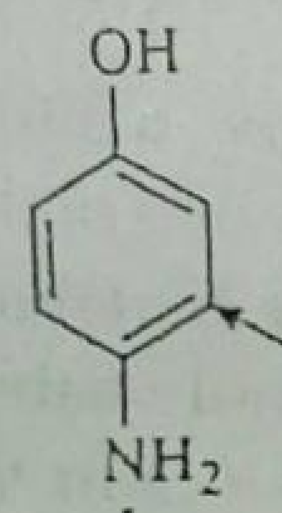
6.8 INTRODUCTION OF A THIRD GROUP INTO THE BENZENE RING

The two groups already present on the benzene ring determine the position taken up by the third incoming group. The following generalisations are helpful in predicting the orientation and reactivity:

(i) When both groups already present on the benzene ring are *ortho*, *para*-directing, the more powerful group controls the orientation. The directing power of each group is in the following order :

$$\overset{\ominus}{O} > NH_2 > NR_2 > OH > OMe, NHCOMe > Me > X$$

This has been illustrated below where the qualitative amount of substitution is indicated by the number of arrow heads, and the number below indicates the number of isomers :



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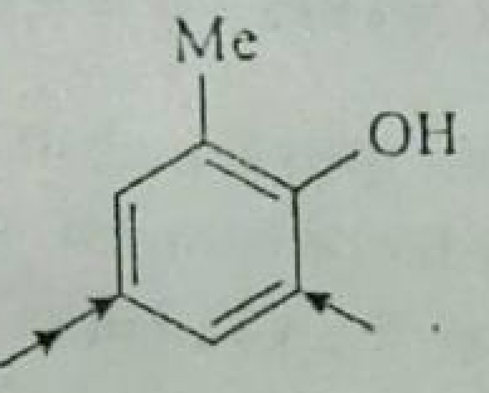

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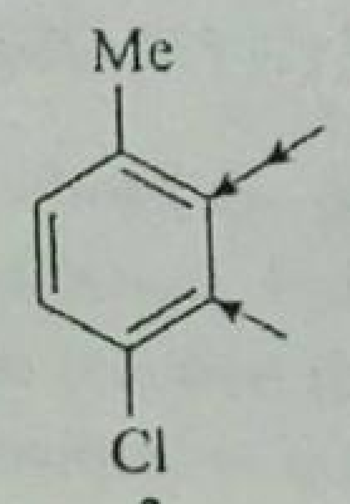

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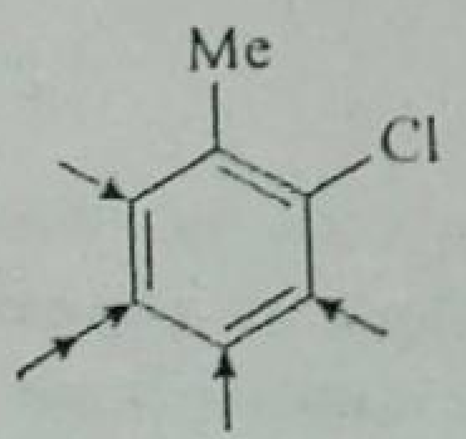

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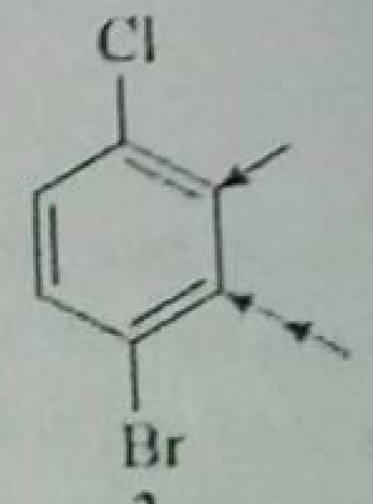

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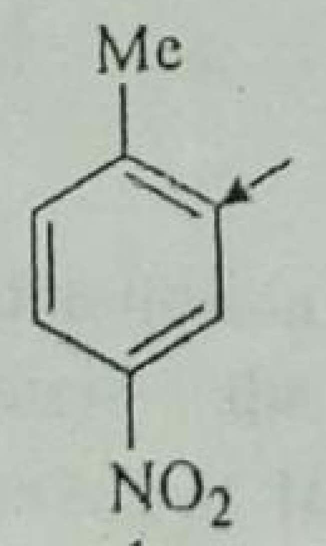
(ii) When both groups are *meta* directing, it is difficult to introduce a third group. The following is the general order of directing power of each group, and it is the less powerful group which controls the orientation.

$$Me_3\overset{\oplus}{N} > NO_2 > CN > SO_3H > CHO > COMe > COOH$$

(iii) When one group is *ortho*, *para*-directing and the other is *meta*-directing, but the orientations reinforce each other, the third group enters almost entirely to one position.



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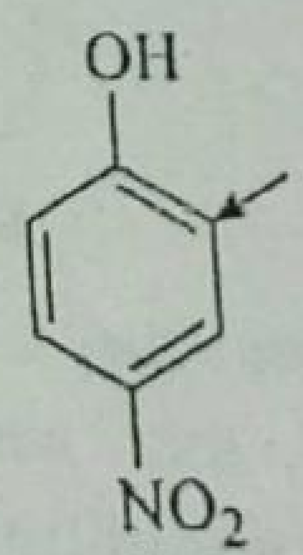

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(iv) When one group is *o*-*p*-directing and the other is *m*-directing, the *o*-*p*-directing group takes precedence over the *m*-directing group. Between the *o*- and *p*-orientations, the *p*-orientation is preferred as far as possible.