M.Sc. II Semester
Sub- Chemistry
Paper-II (Organic Chemistry)

6.6 ORIENTATION AND REACTIVITY IN MONOSUBSTITUTED BENZENES

When a monosubstituted benzene undergoes an electrophilic substitution, the position taken up by the incoming group (the orientation) and the rate of the reaction (the reactivity) are determined by the substituent already present on the benzene ring. On this basis various substituents can be divided into three categories:

1. *Ortho, para*-directing and activating groups : If a group of this category is already present on the benzene ring then the incoming group is attached to the *ortho* and *para* positions. Furthermore, the benzene ring containing a group of this category is more reactive towards electrophilic substitution than benzene itself. This is called *activation* of the benzene ring.

Examples : $\overset{\ominus}{O}$, NR_2, NHR, NH_2, OH, OR, $NHCOR$, $OCOR$, SR alkyl and aryl.

2. *Meta*-directing and deactivating groups : If a group of this category is already present on the benzene ring then the incoming group is attached to the *meta* position. Furthermore, the benzene ring containing a group of this category is less reactive towards electrophilic substitution than benzene itself. This is called *deactivation* of benzene ring.

Examples : $\overset{\oplus}{N}R_3$, NO_2, CF_3, CN, SO_3H, CHO, COR, $COOH$, $COOR$, $CONH_2$, CCl_3 and $\overset{\oplus}{N}H_3$.

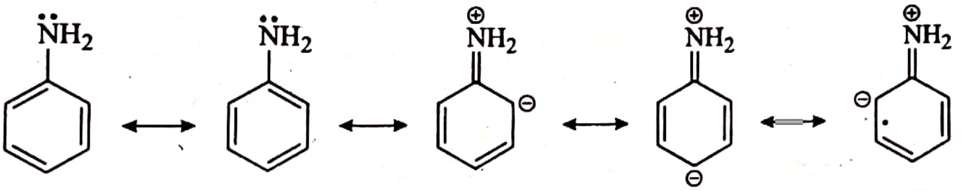
3. *Ortho, para*-directing and deactivating groups : Halogens (F, Cl, Br and I) are *ortho* and *para* directing but they deactivate the benzene ring for further electrophilc substitutions.

Explanation for Orientation and Reactivity

1. Explanation based on charge distribution :

Ortho, para-directing and activating groups :

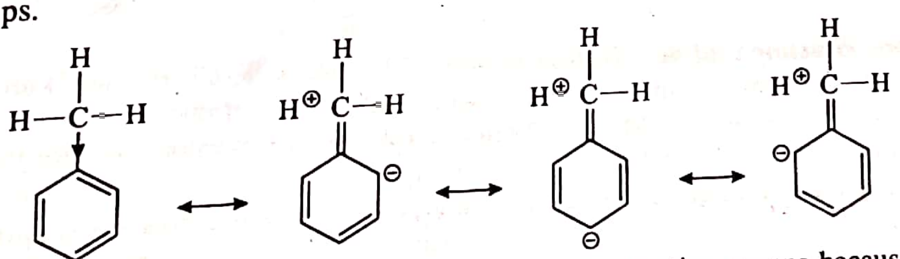
(a) When in a monosubstituted benzene ring the atom directly attached to the ring (the key atom) has a lone pair of electrons, the electron density on *ortho* and *para* position is increased through conjugation (*i.e.*, through $+R$ or $+$M effect) as shown in structures III–V.



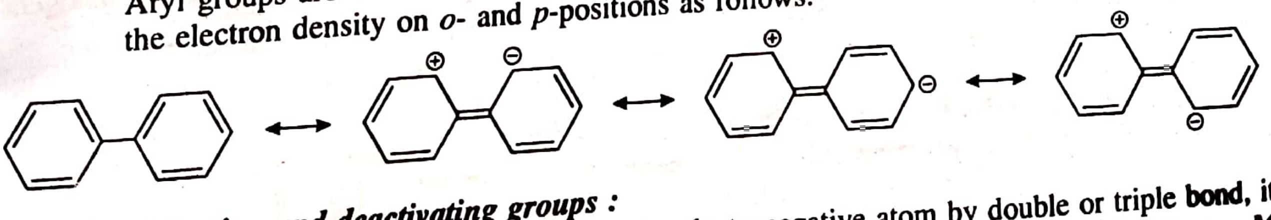
(I) (II) (III) (IV) (V)

Thus, the incoming electrophile is attached to these positions, *i.e.*, *ortho* and *para* positions. The electron density on *ortho* and *para* positions is increased, hence, the overall electron density on the benzene ring is also increased resulting in the activation of the ring, *i.e.*, further electrophilic substitution is facilitated by the presence of an *ortho* and *para* directing group (except halogens).

(b) In the case of alkyl groups the electron density on *ortho* and *para* positions is increased by $+I$ and/or hyperconjugative effect. Thus, they are *ortho* and *para* directing and activating groups.

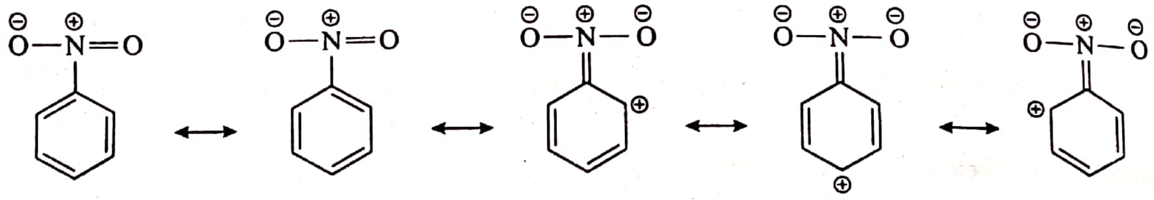


Aryl groups are also *ortho* and *para* directing and activating groups because they increase the electron density on *o*- and *p*-positions as follows:



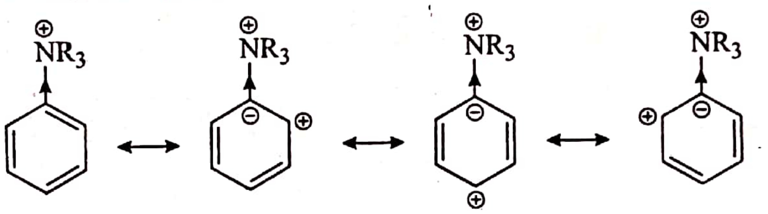
Meta-directing and deactivating groups :

(a) When the key atom is attached to a more electronegative atom by double or triple **bond, it** attracts electrons from *o*- and *p*-positions through conjugation (*i.e.*, through $-R$ or $-M$ effect) as shown in structures VIII–X, thus, *m*-positions have a relatively high **electron** density. Therefore, the incoming electrophile is attached to *m*-positions. Since the **electron** density on *o* and *p* positions is decreased, the overall electron density on the **benzene ring** is also decreased resulting in the deactivation of the ring, *i.e.*, further **electrophilic** substitution is made more difficult by the presence of a *m*-directing group.

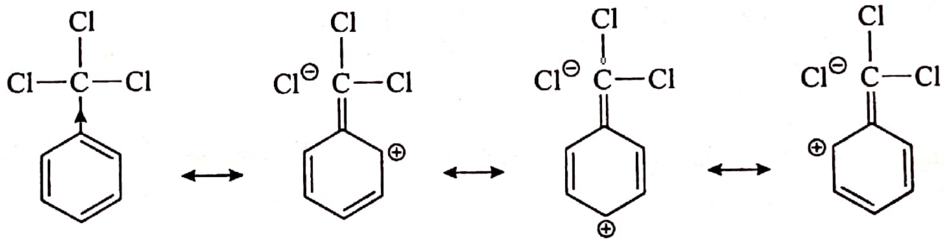


(VI) (VII) (VIII) (IX) (X)

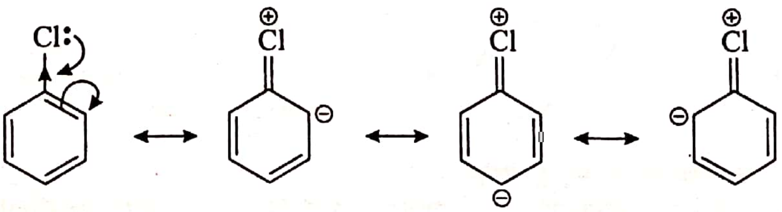
(b) The *m*-orienting and deactivating groups having a positively charged key atom (*e.g.*, $\overset{\oplus}{N}R_3$, $\overset{\oplus}{N}H_3$, etc.) also attract electrons from the *o*- and *p*-positions through strong inductive effect (—I effect), for example :



The *m*-directing and deactivating nature of CCl_3 group is due to electron attraction from the *o* and *p*-positions through —I as well as hyperconjugative effect.



Ortho, para directing and deactivating groups : Halogens (F, Cl, Br and I) are *o*-*p*-directing but they deactivate the benzene ring for further electrophilic substitutions. This is because there are two opposing effects, *i.e.*, $+R$ (or $+M$) and $-I$ effects. They are deactivators because they inductively withdraw electrons from the ring more strongly than they donate electrons by resonance. All the ring positions are deactivated by inductive electron withdrawal, but this deactivation is partially made up for at the *ortho* and *para* positions by electron donation by resonance. Because the *meta* position cannot benefit from resonance electron donation, it is the most deactivated position. Thus, the halogens are *ortho/para* directors and deactivators.



The order of reactivity of various halobenzenes is:

$$PhF > PhCl \approx PhBr > PhI$$

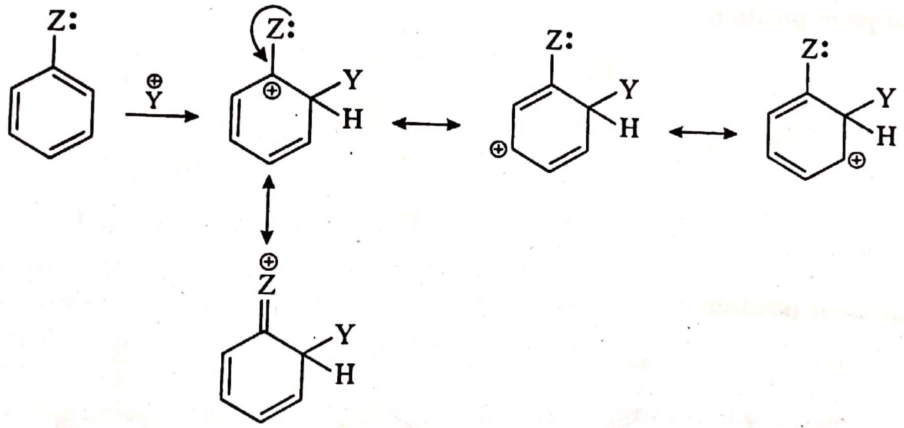
On the basis of —I effect $(F > Cl > Br > I)$ and $+R$ effect $(F < Cl < Br < I)$ one might have **expected** the reverse of the above order of reactivity. It is clear that here the resonance effect does not **follow the expected order** based on relative electronegativity. This is due to a size mismatch of the **overlapping 2*p*-orbital** of the ring carbon and the *p*-orbital of the halogen because the overlap is maximum when the overlapping orbitals are of comparable size. Cl has 3*p*, Br has 4*p* and I has 5*p* orbital, all of which have larger size than the 2*p*-orbital of carbon, thus there is poor overlap resulting in a very weak + *R* effect. On the other hand, F and carbon have 2*p*-orbitals which are of comparable size, thus there is better overlap resulting in greater + *R* effect than that of Cl, Br, or I.

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

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

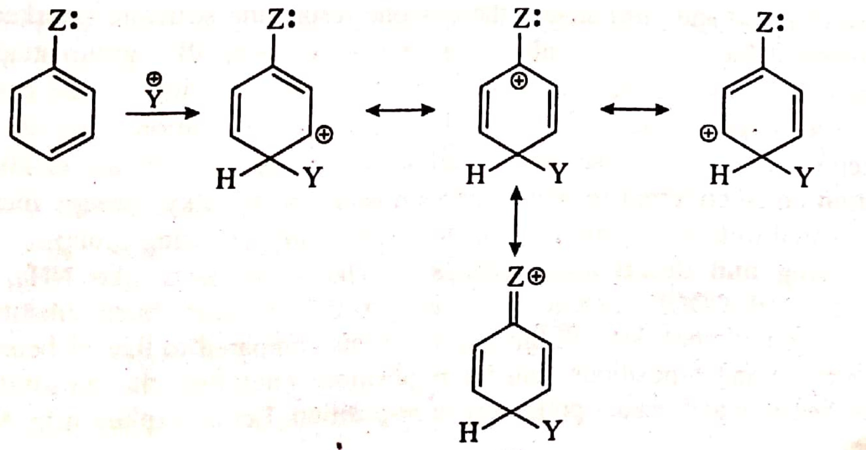
(a) The groups containing a lone pair of electrons on the key atom stabilise the carbocation to a greater extent when the attack takes place at the *o* and *p*-positions as compared to the attack at the *m*-position. This is because for the attack at *ortho* and *para* positions an additional and particularly 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



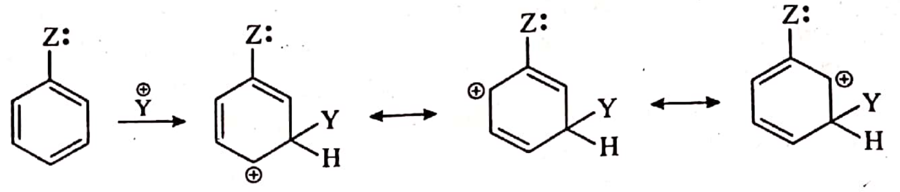
(A)

Attack at *p*-postion



(A)

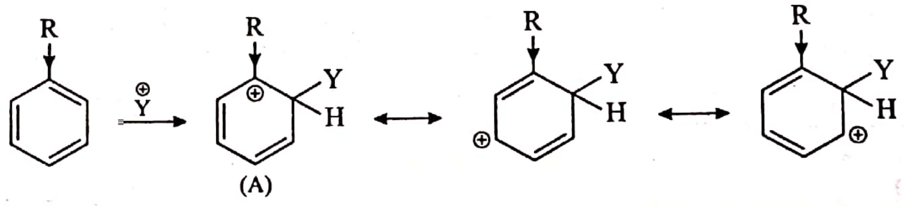
Attack at *m*-position



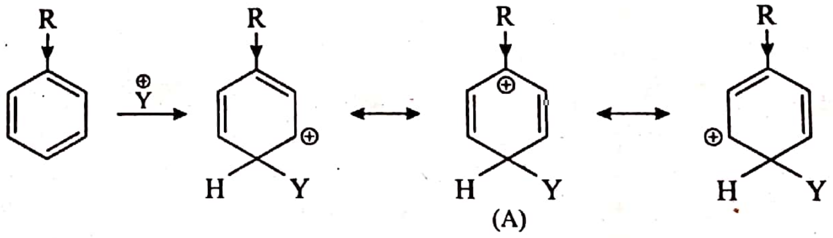
$(Z = \overset{\ominus}{:\ddot{O}:}, \ddot{N}R_2\ \ddot{N}HR, \ddot{N}R_2, \ddot{O}H, \ddot{O}R, \ddot{N}HCOR, \ddot{O}COR$ and $\ddot{S}R)$

(b) In the case of alkyl groups the following resonating structures can be written:

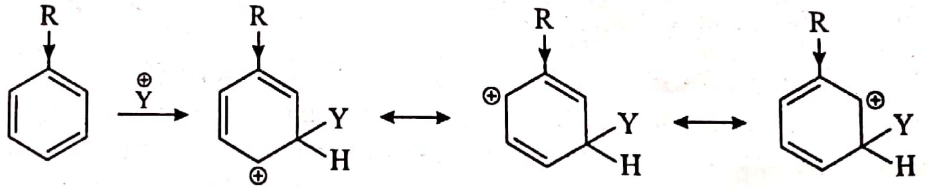
Attack at *ortho* position



Attack at *para* position



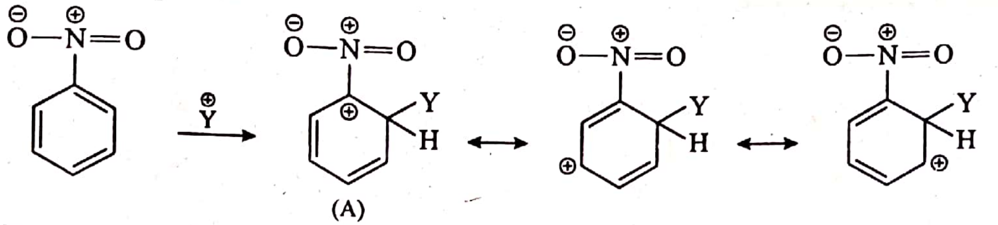
Attack at *meta* position



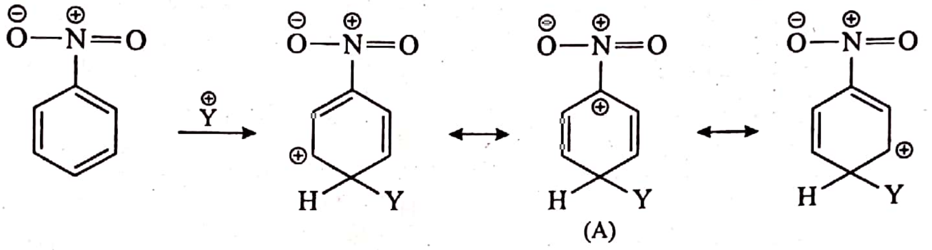
In the case of *ortho* and *para* attacks there is one resonating structure (marked *A*) in each case which is particularly stable because it contains the electron-releasing alkyl group attached to the carbon carrying the positive charge. No such resonating structure can be written in the case of *meta* attack. Furthermore, the resonating structures marked *A* are tertiary carbocations, and are more stable than rest of the structures which are all secondary carbocations. Thus, in the case of alkylbenzenes *ortho* and *para* substitution is preferred to *meta*. Electron donation by alkyl groups increases the rate of substitution compared to that in benzene itself, thus, these are activating groups.

***Meta* directing and deactivating groups :** The substituents like $\overset{\oplus}{N}H_3$, $\overset{\oplus}{N}R_3$, NO_2, CF_3, CN, SO_3H, CHO, COR, COOH, COOR, etc. belong to this category. Such substituents are strongly electron withdrawing and deactivate all the ring positions compared to that of benzene, but are more deactivating for the *o* and *p*-positions than for *m*-position. Therefore, the substitution takes place at slower rate than benzene and occurs preferably at *m*-position. Let us explain it by taking the example of nitrobenzene:

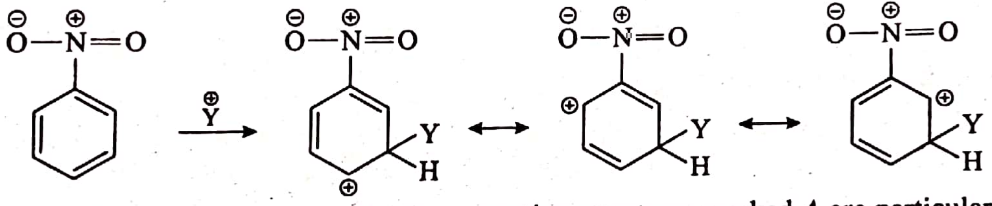
Attack at *ortho* position



Attack at *para* position



Attack at *meta* position

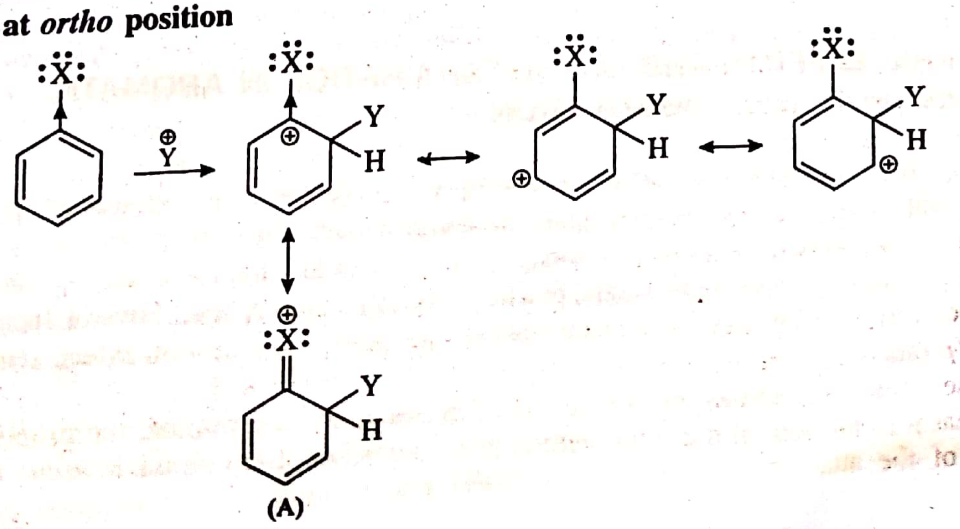


In the case of *ortho* and *para* attacks the resonating structures marked *A* are particularly unstable because the charge intensification in these is maximum due to the presence of the electron-withdrawing group on the carbon carrying the positive charge. No such unstable structure is possible in the 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.

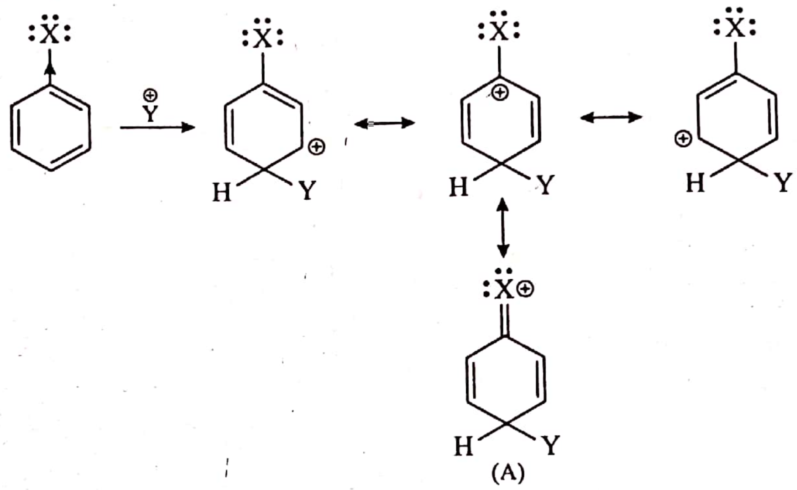
Similarly, the *meta* directing and deactivating nature of the other groups of this category can be explained.

***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.

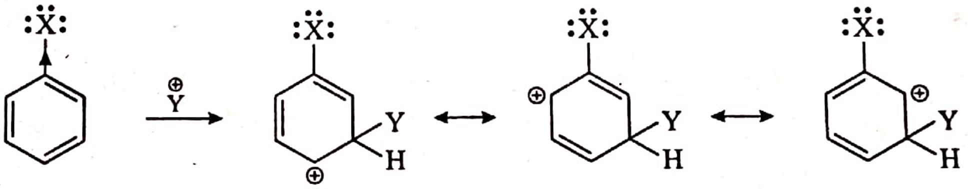
Attack at *ortho* position



Attack at *para* position



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.

By

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