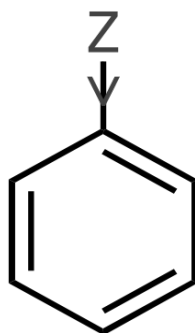
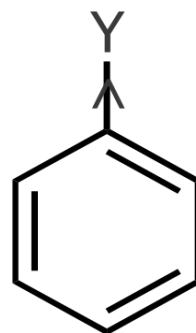


Reactions of Substituted Benzenes

- * In substituted benzene rings, each substituent affects the electron density in the benzene ring.

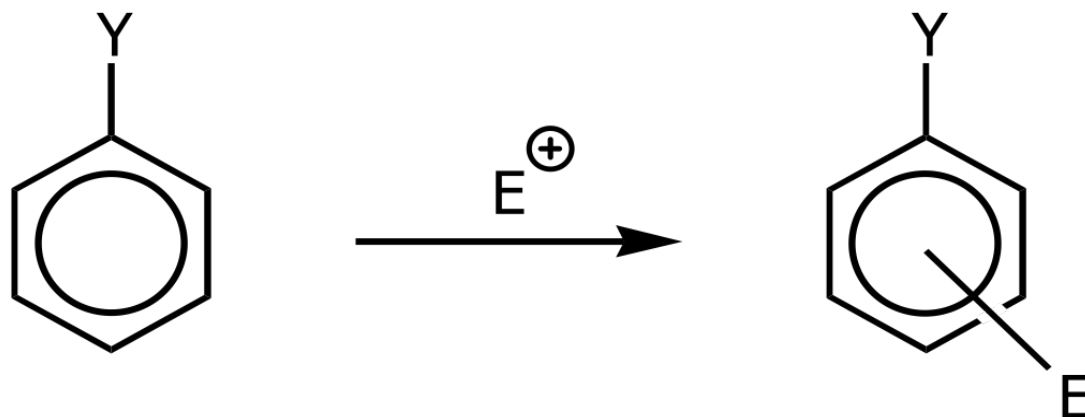


Ring is electron rich;
Ring reacts faster than
benzene with E^+

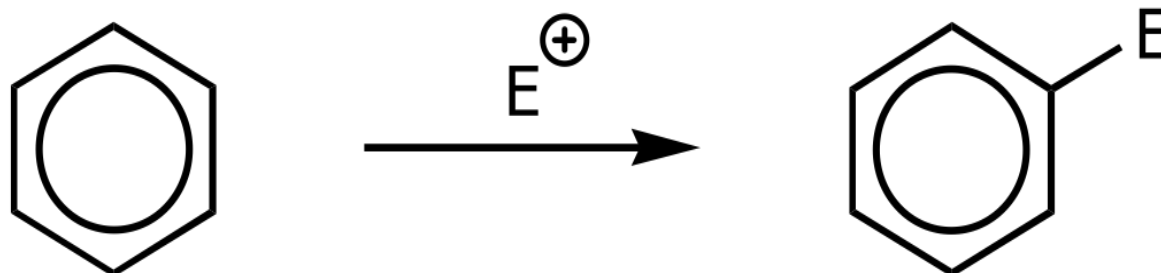


Ring is electron poor;
Ring reacts slower
than benzene with E^+

★ Rate of the reaction

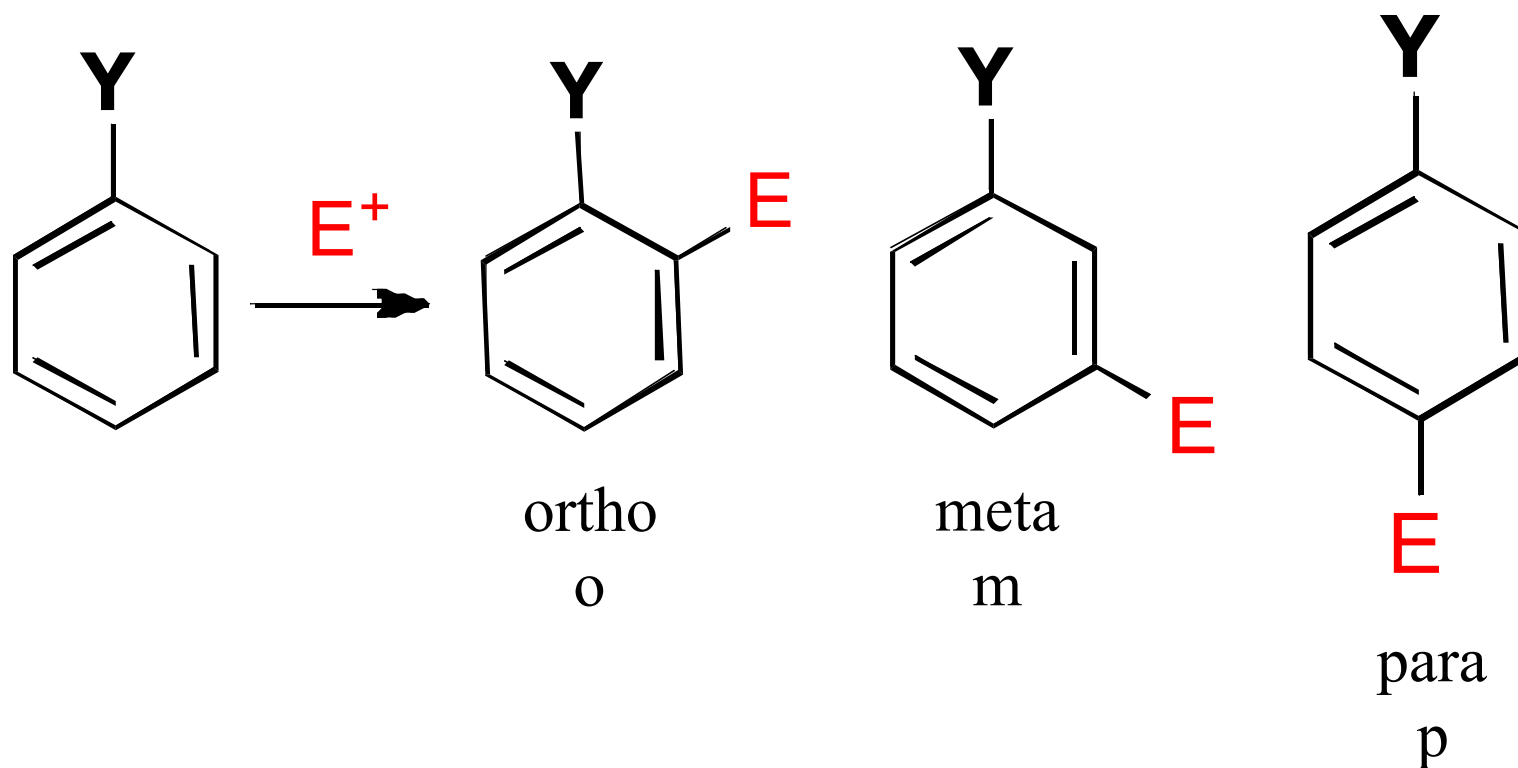


faster or slower than



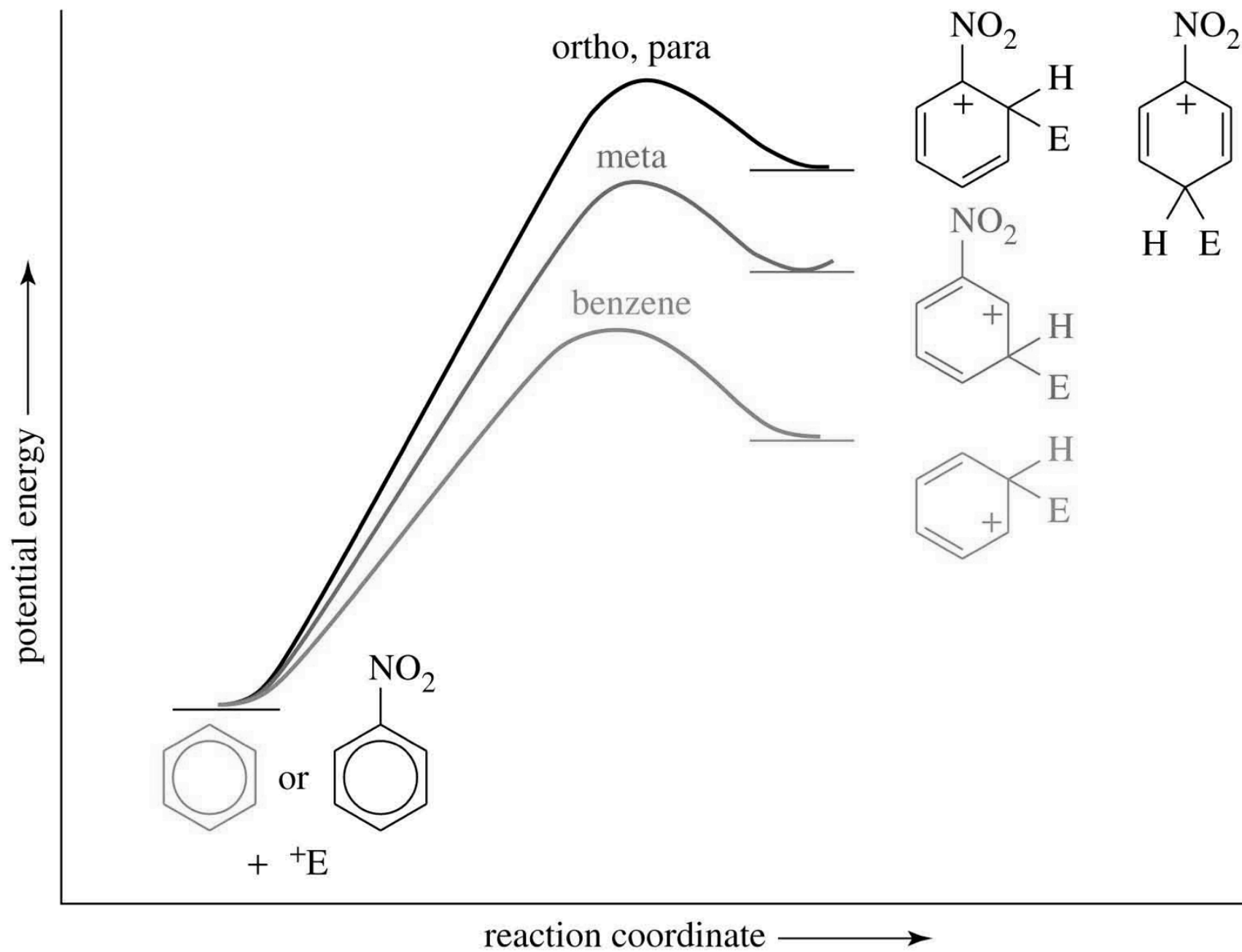
Y = EDG (electron-donating group) or
EWG (electron-withdrawing group)

★ Regiochemistry (course of electrophilic aromatic substitution)



Rate-determining-step:

aromatic ring π -electrons attacking the E^+

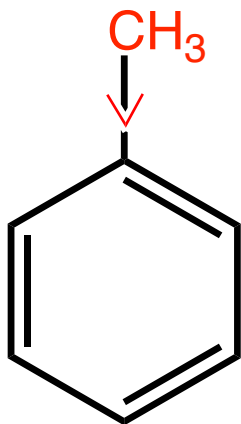


*Ortho/para directing and meta directing ability and activating and deactivating ability can be explained with two electronic effects

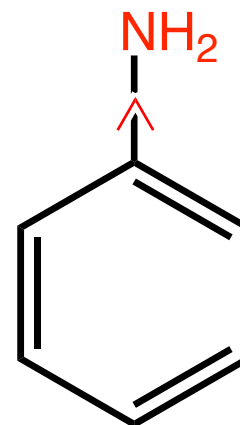
1. Inductive effect

2. Resonance effect/Mesomeric Effect

* Inductive Effect (I) : Attracting or pushing of bonding electrons along the sigma bonds of the molecules.



Inductive e⁻ donation
(+I) effect

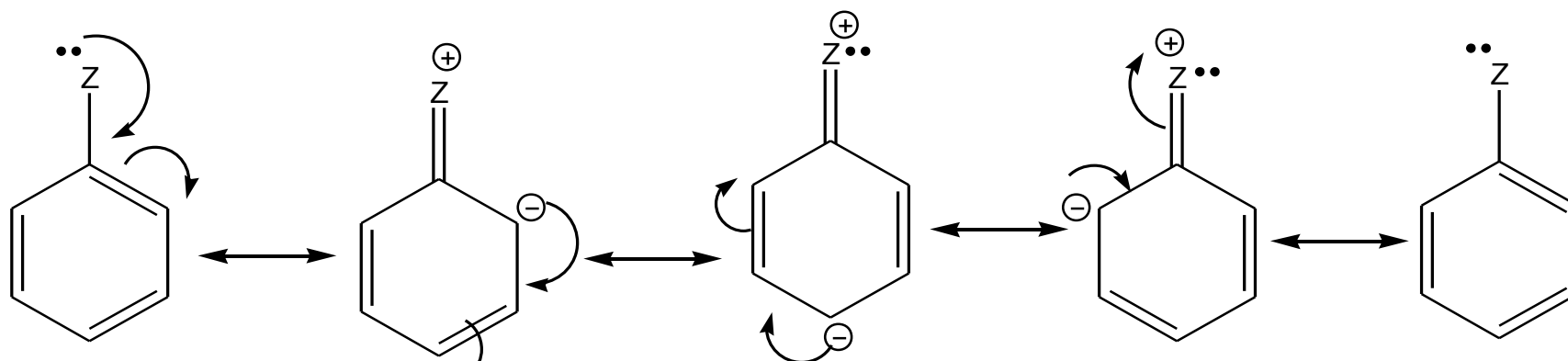


Inductive e⁻ withdrawing
(-I) effect

★ Resonance/Mesomeric Effect (M):

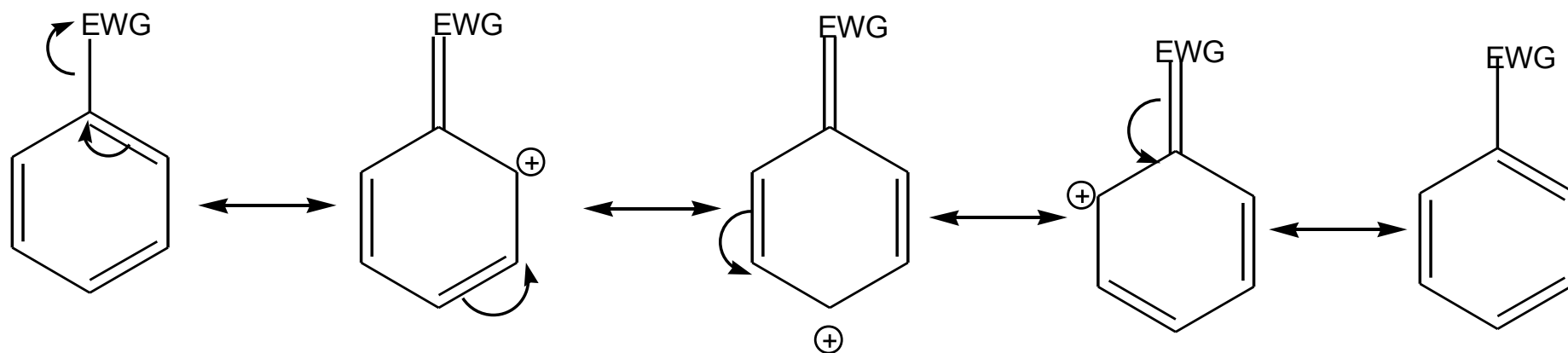
Movement of electrons through the pi bonds.
When non bonding electrons and pi electron are present resonance effect is observed

★ An electron donating (+M) resonance effect is observed whenever an atom Z having a lone pair of electrons which is directly bound to the benzene ring.



Eg : -OH, -NH₂, -OCH₃

* An electron withdrawing (-M) resonance effect is observed in substituted benzene having general structure $C_6H_5-Y=Z$ where, Z is more electronegative than Y.



Eg: $-NO_2$, $-COOH$, $-SO_3H$

★ To predict whether a substituted benzene is more or less electron rich than benzene itself, net balance of both the inductive and resonance effect should be considered.

★ When considering -NH_2 , -OH :

Both (+M) effect and (-I) effect are present

But $(+M) > (-I)$

Therefore act as Electron donating O/P directors
(Activators)

★ When considering Halogens -X :

Both (+M) effect and (-I) effect are present

But $(-I) > (+M)$

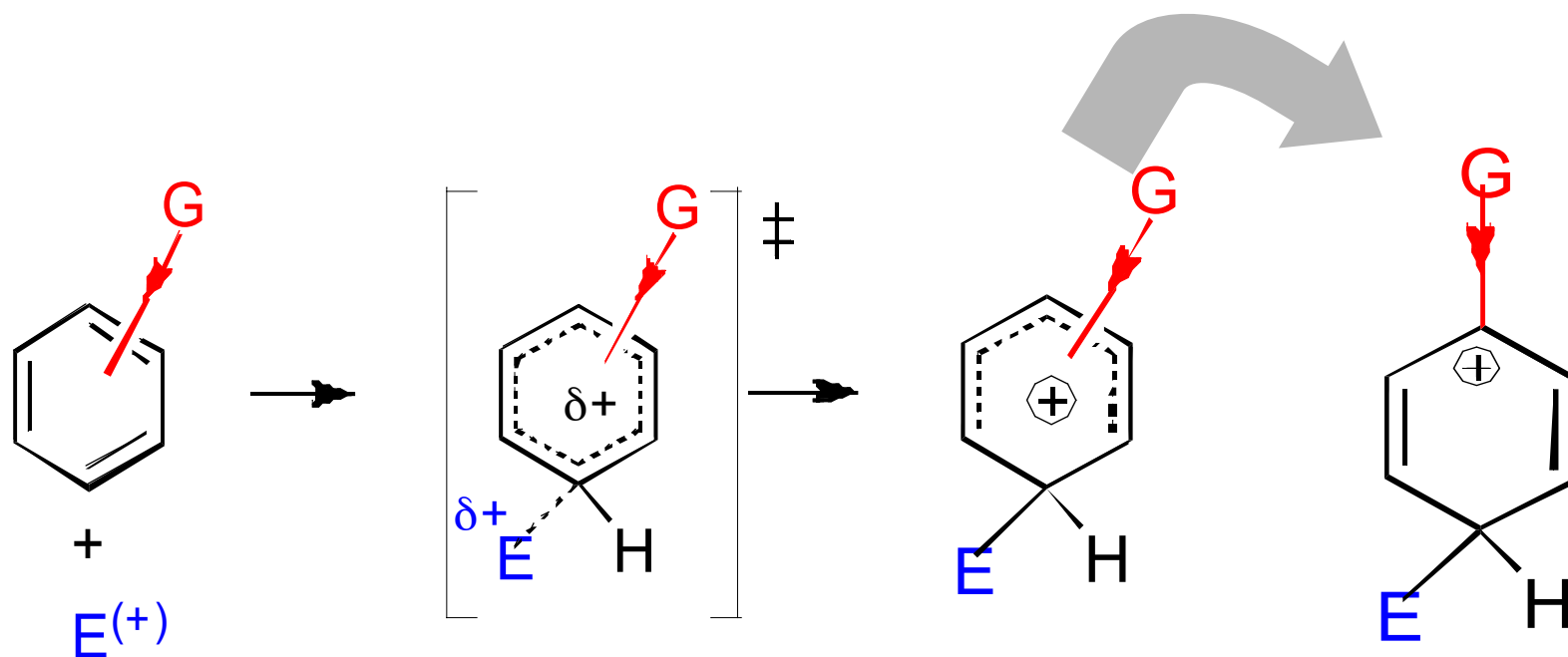
Therefore act as Electron withdrawing O/P
directors

(Deactivators)

Effect of Electron Donating and Electron Withdrawing Groups

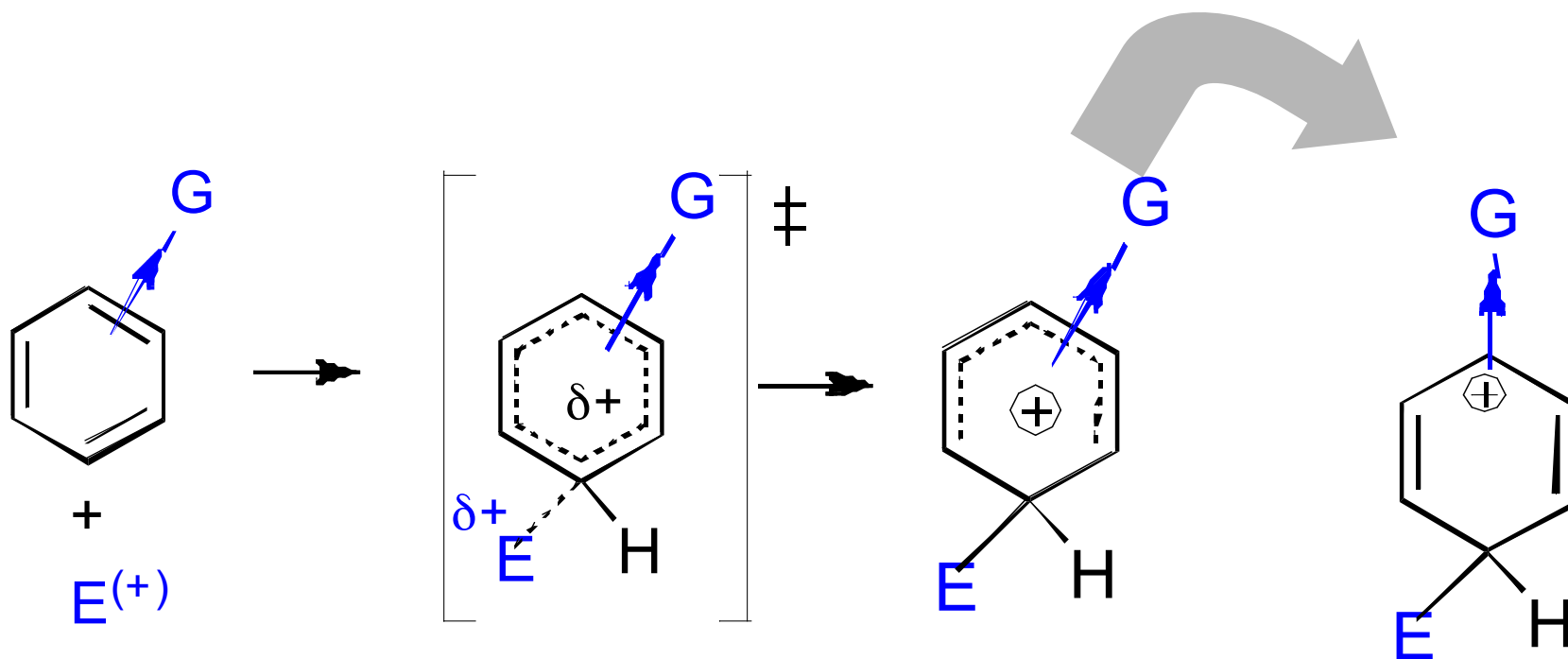
If G is **electron-donating** group

then reaction is **faster** than with benzene

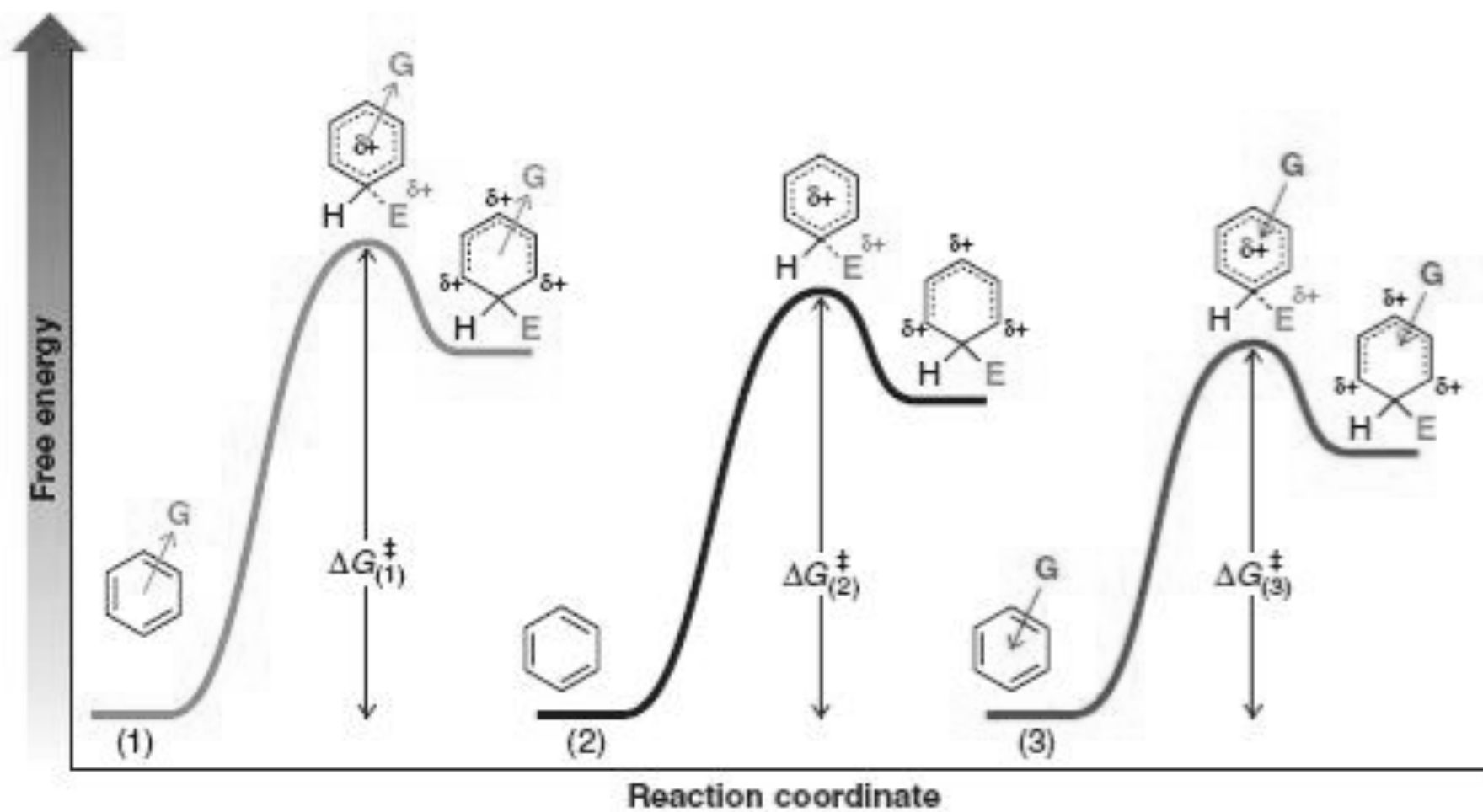


Transition state is
stabilized

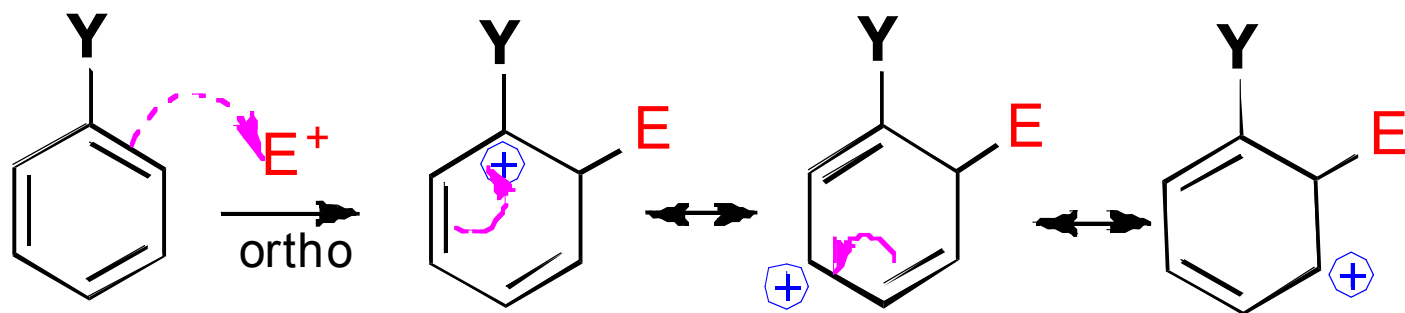
If G is an electron-withdrawing group,
then reaction is **slower** than with benzene



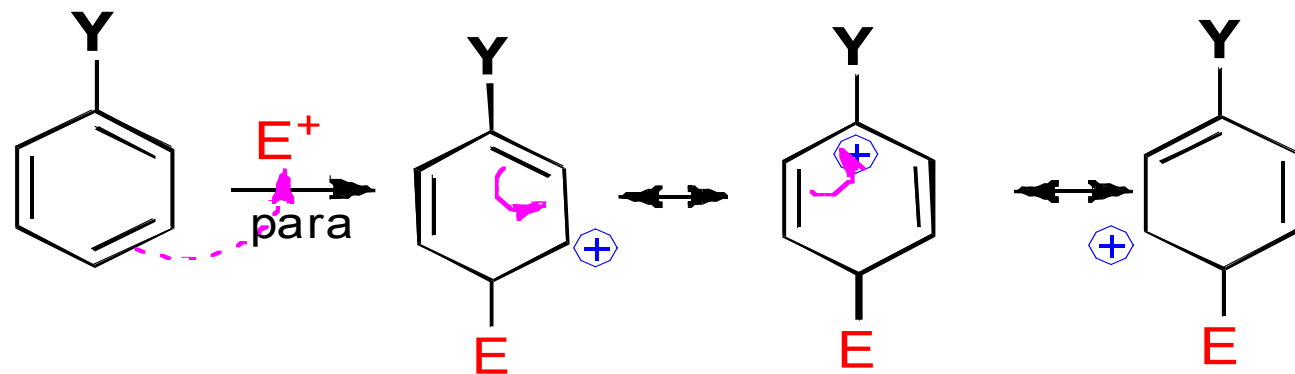
Transition state is
destabilized



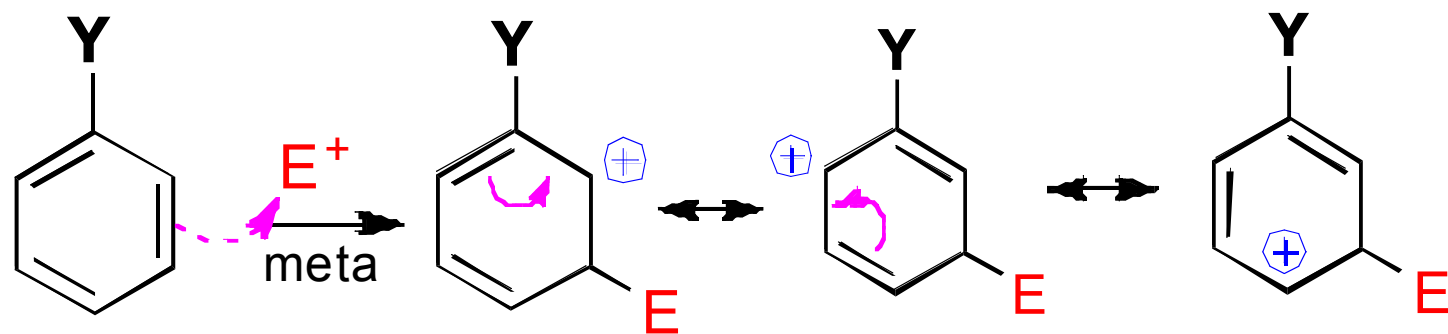
1.



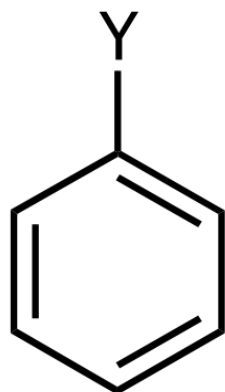
2.



3.

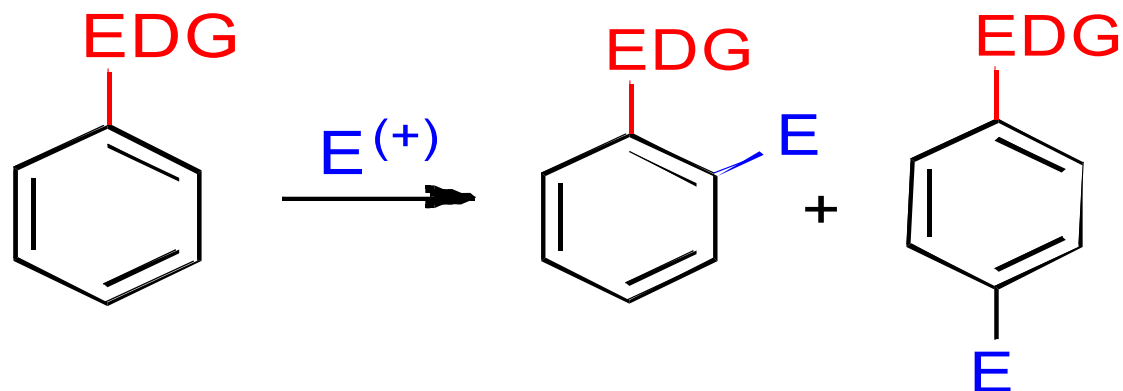


Classification of Substituents

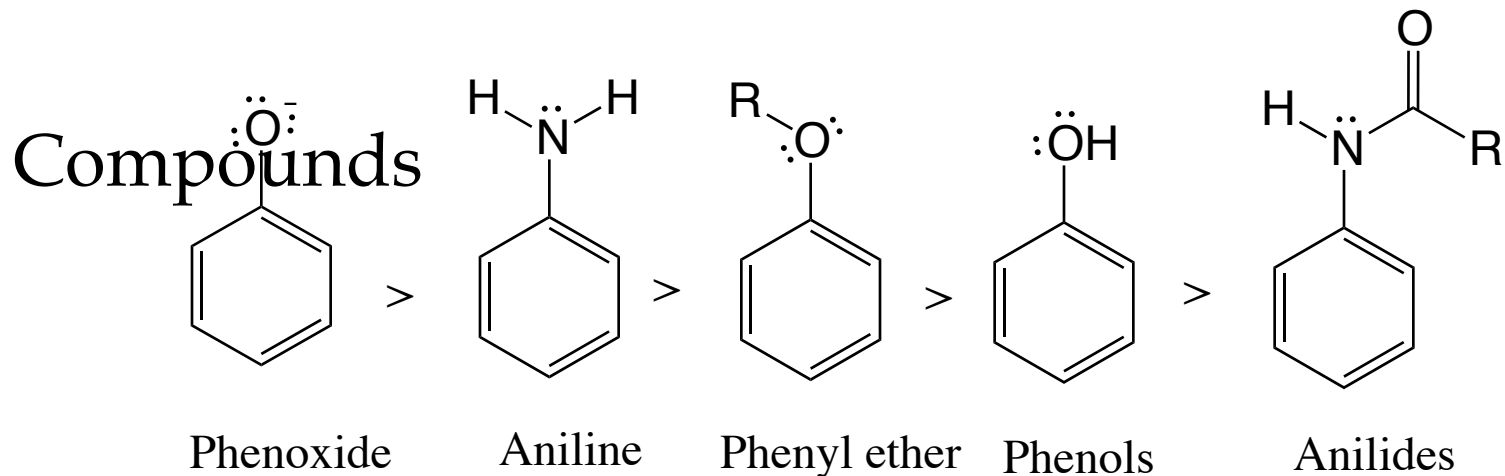
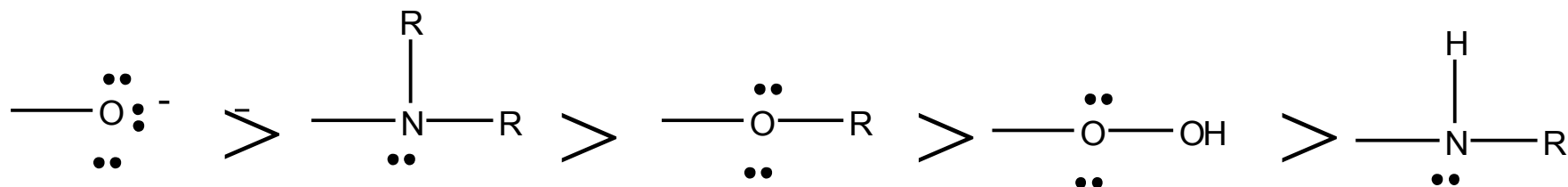


Y (EDG)	<i>reactivity</i>	<i>regiochemistry</i>
$-\text{NH}_2, -\text{NR}_2$ $-\text{OH}, -\text{O}^-$	Strongly activating	<i>o</i> -, <i>p</i> -directing
$-\text{NHCOR}$ $-\text{OR}$	Moderately activating	<i>o</i> -, <i>p</i> -directing
$-\text{R}$ (alkyl) $-\text{Ph}$	Weakly activating	<i>o</i> -, <i>p</i> -directing
Y (EWG)	<i>reactivity</i>	<i>regiochemistry</i>
$-\text{Halides}$ (F, Cl, Br, I)	Weakly deactivating	<i>o</i> -, <i>p</i> -directing
$-\text{COOR}, -\text{COR},$ $-\text{CHO}, -\text{COOH},$ $-\text{SO}_3\text{H}, -\text{CN}$	Moderately deactivating	<i>m</i> -directing
$-\text{CF}_3, -\text{CCl}_3,$ $-\text{NO}_2, -\text{NR}_3^+$	Strongly deactivating	<i>m</i> -directing

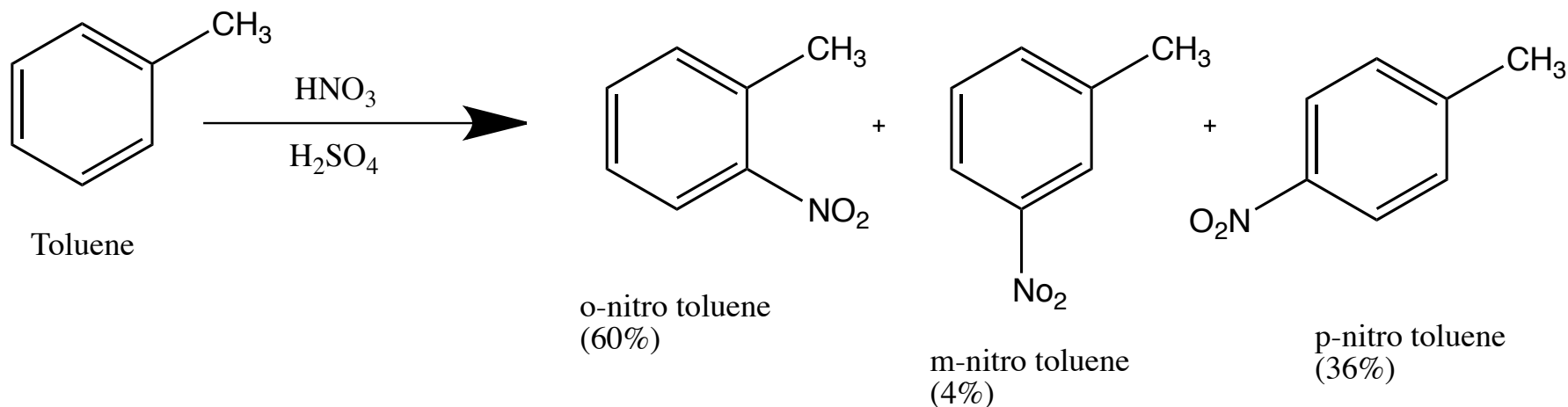
Ortho – Para Directing Groups (Activators)



Groups



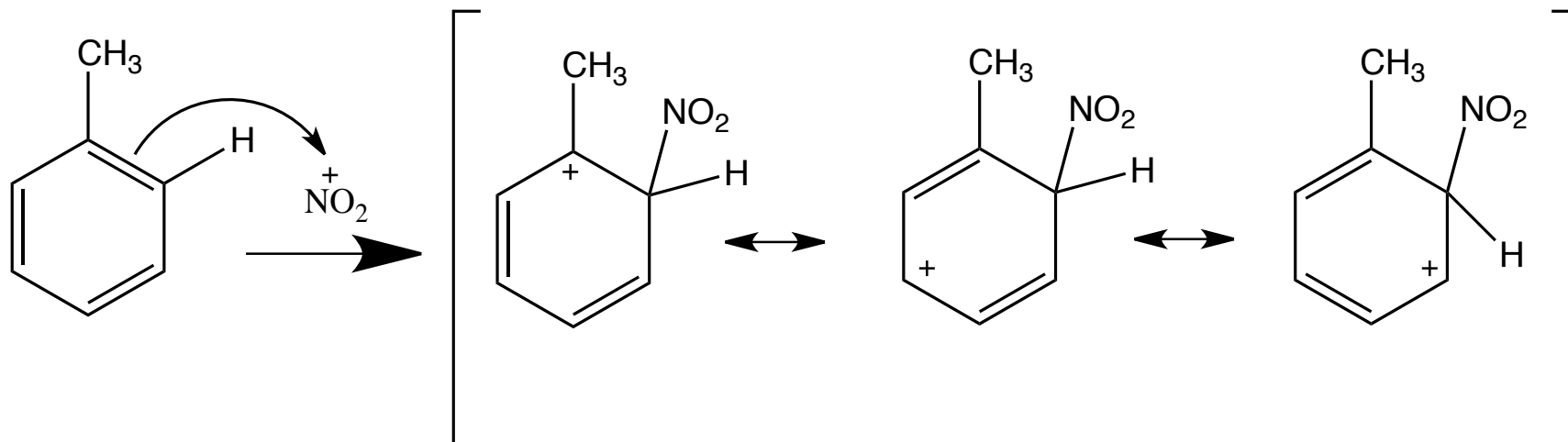
* Eg: Nitration of toluene



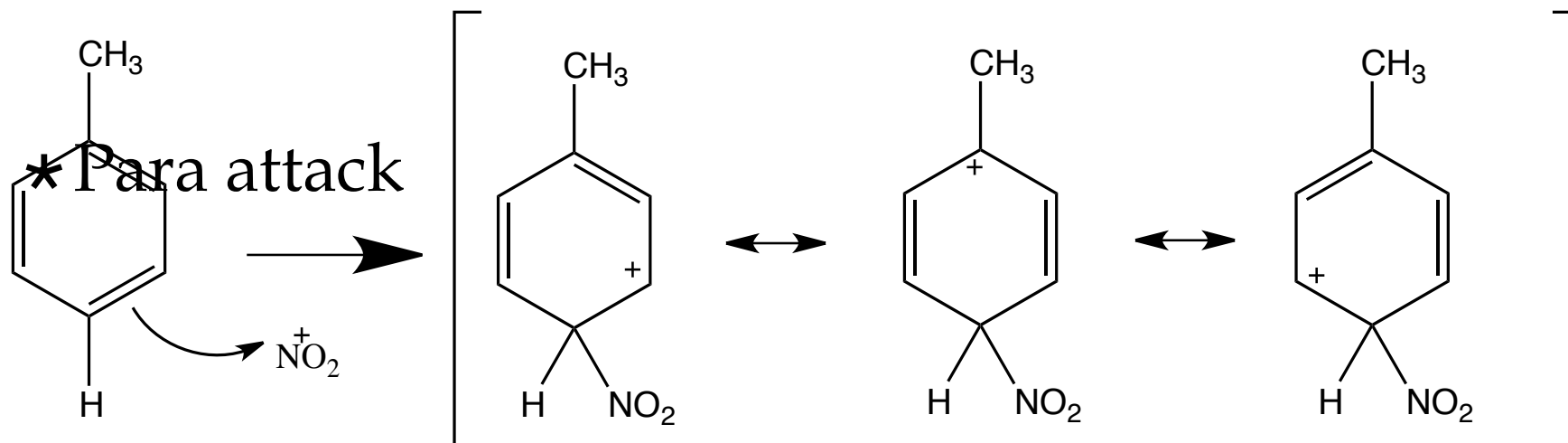
* Toluene reacts 25 times faster than benzene. The methyl group is an activator.

* The rate of the reaction can be explained considering the stability of sigma intermediate formed at each attack.

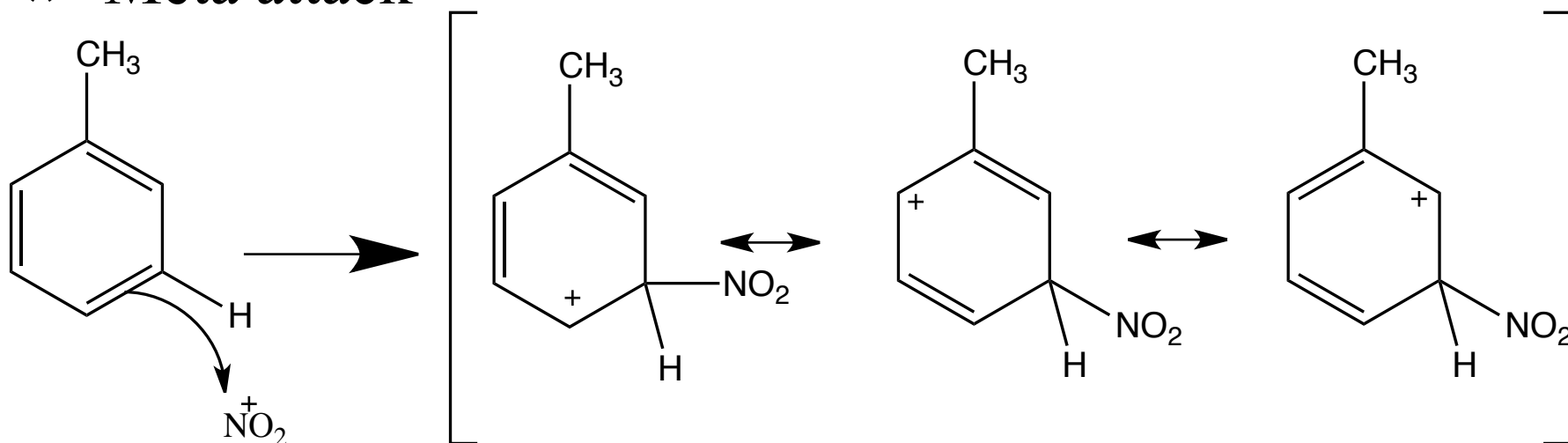
* Ortho attack



* Para attack

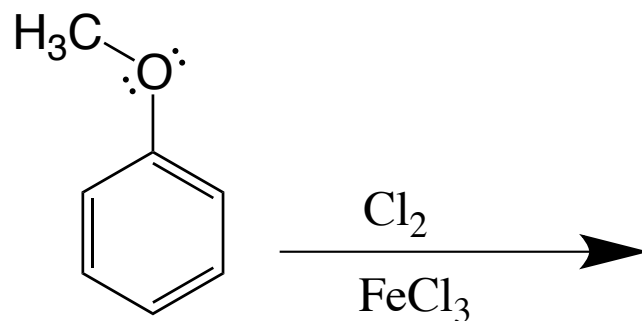


★ Meta attack

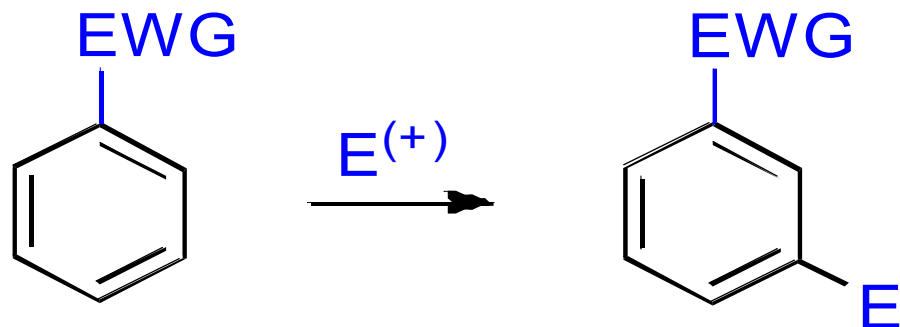


★ Intermediate is more stable if nitration occurs at the ortho or para position than meta position.

★ Write down the mechanism for the following reaction?



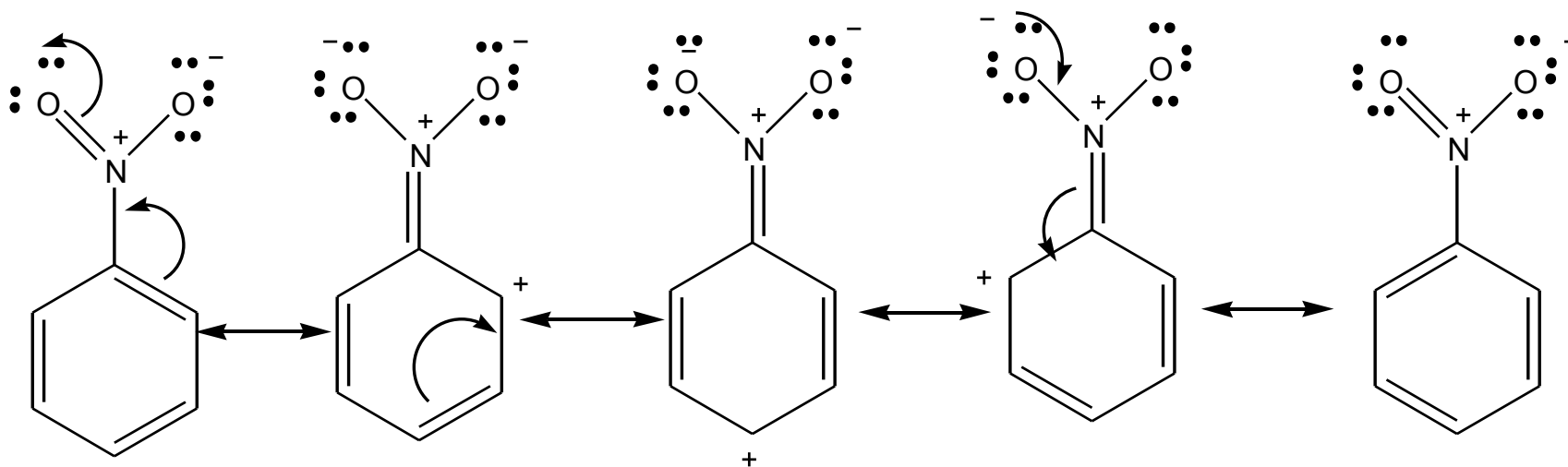
Meta Directing Groups (Deactivators)



Groups :

$-\text{COOR}$, $-\text{COR}$, $-\text{CHO}$, $-\text{CF}_3$, $-\text{NO}_2$, $-\text{CN}$ etc

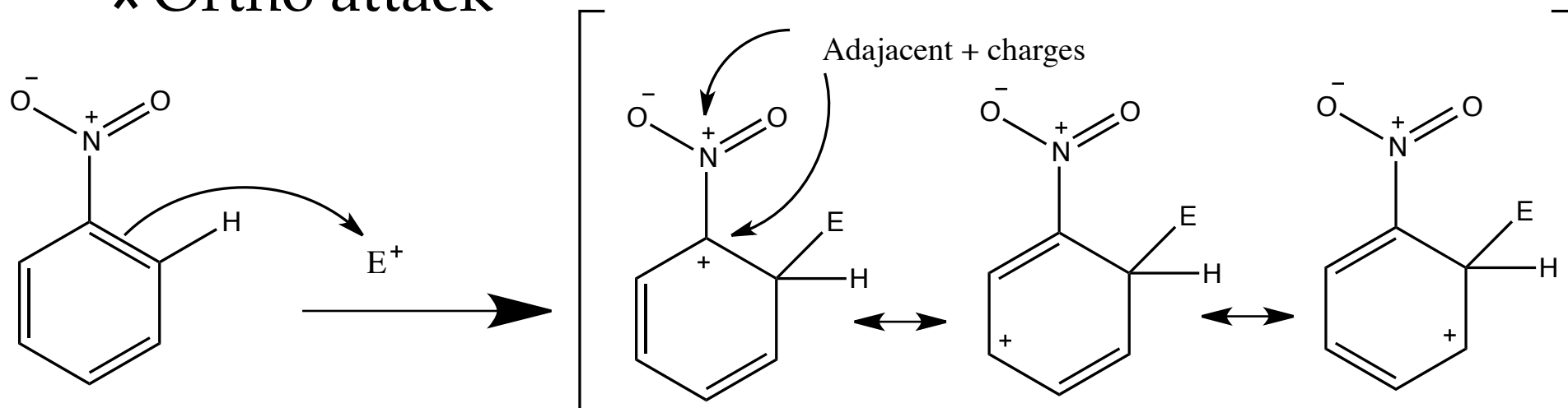
Write down the electron withdrawing effect by resonance on benzene by $-\text{NO}_2$ group



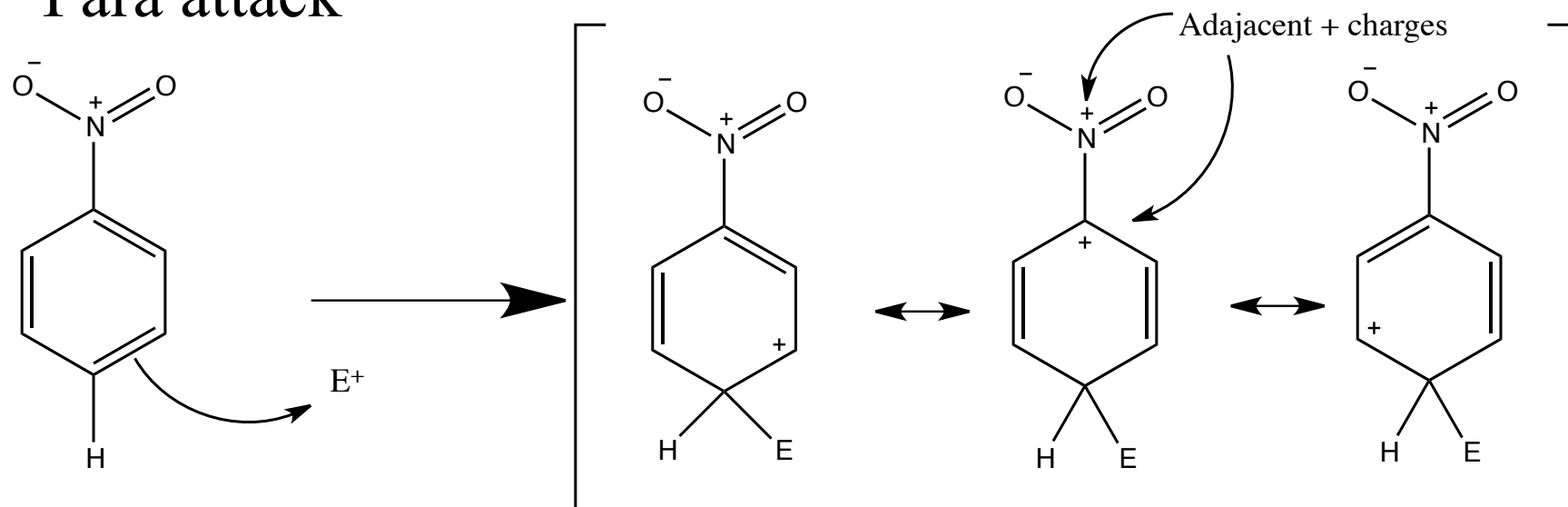
✱ Electrophilic substitution reactions for nitrobenzene are 100,000 times slower than for benzene.

✱ Formation of meta product can be further explained considering the stability of intermediate cation in each state

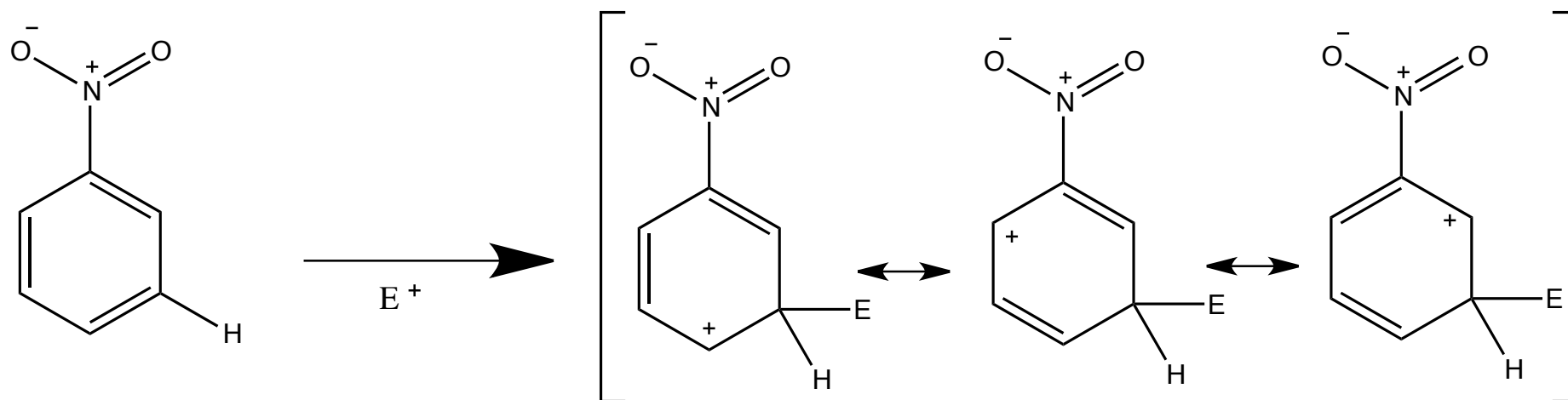
✱ Ortho attack



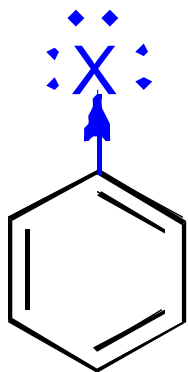
* Para attack



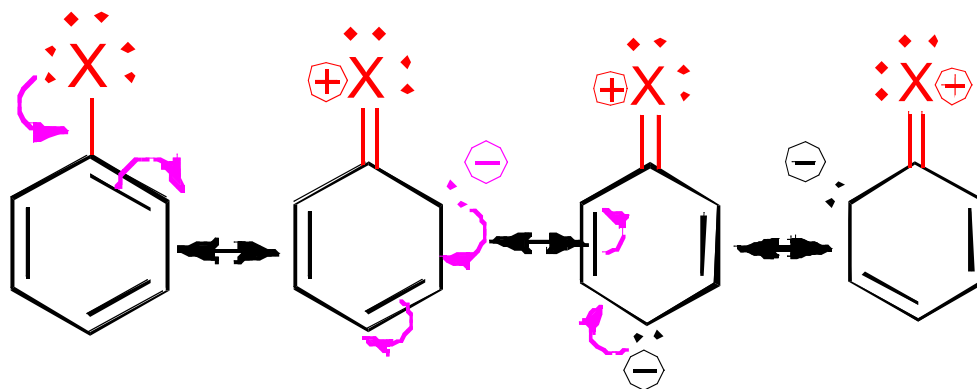
* Meta attack



halogens, two opposing effects



negative inductive
effect

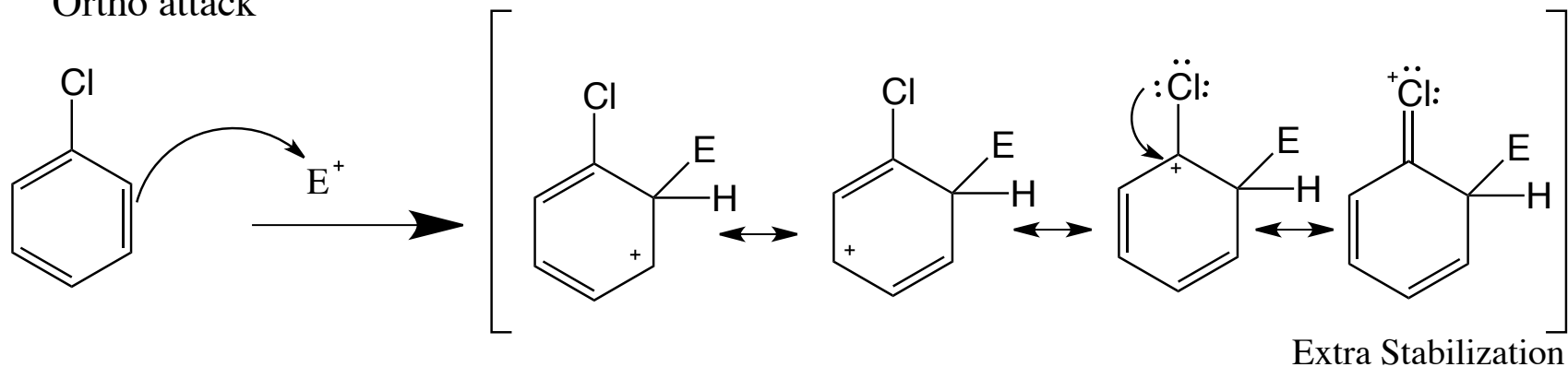


positive resonance effect

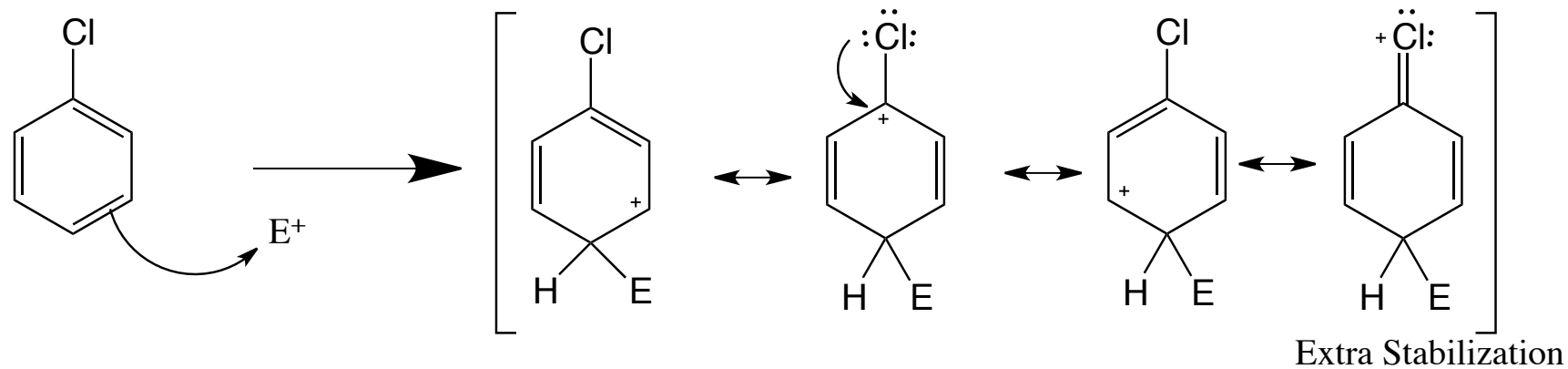
halogens - weak deactivating

negative inductive effect > positive resonance

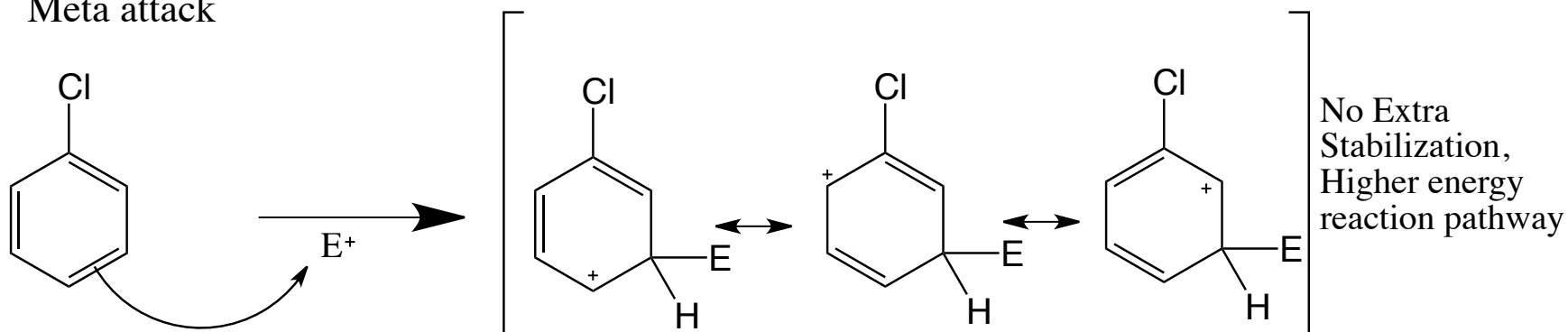
*** But they are O/P directors**
 Ortho attack



Para attack

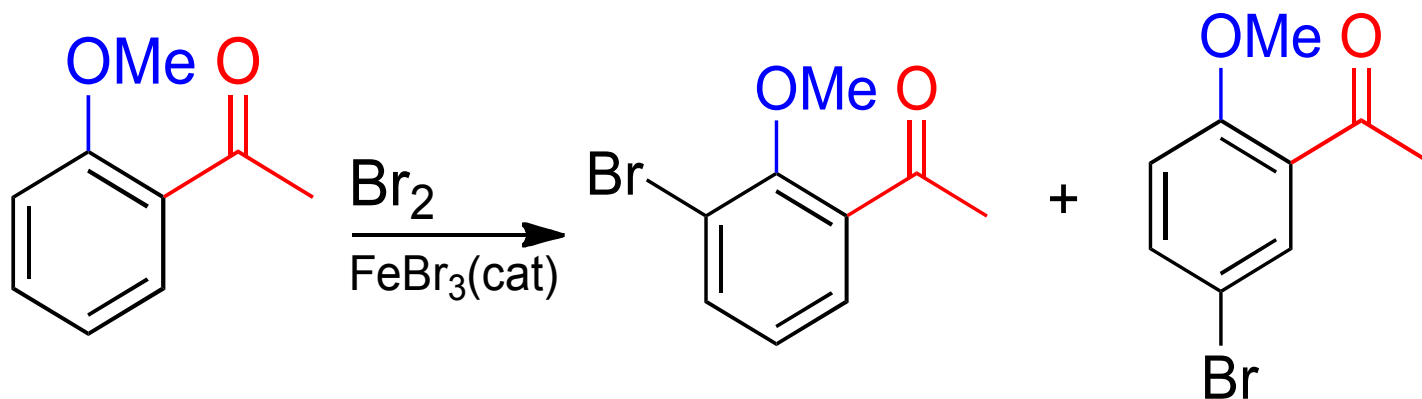


Meta attack

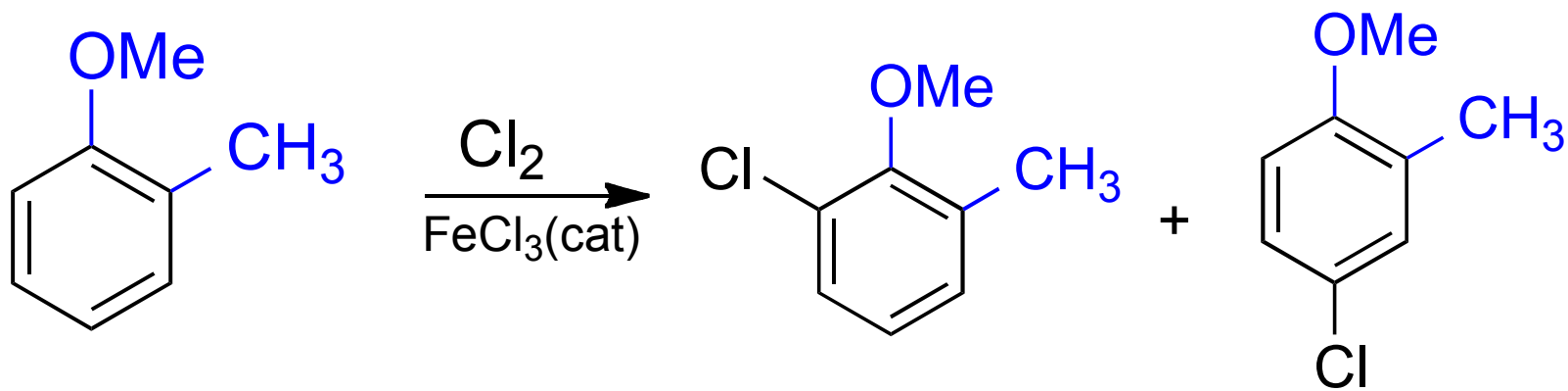


Third Substitution of Aromatic Compounds

- ★ Activating O/P directors are stronger than the m directing deactivators.



- ★ When two EDGs are present directing controls by stronger groups



★ The alkyl groups and halides show intermediate effects on 3rd substitution.

★ No substitution occurs between two meta substituents due to the steric effects.

