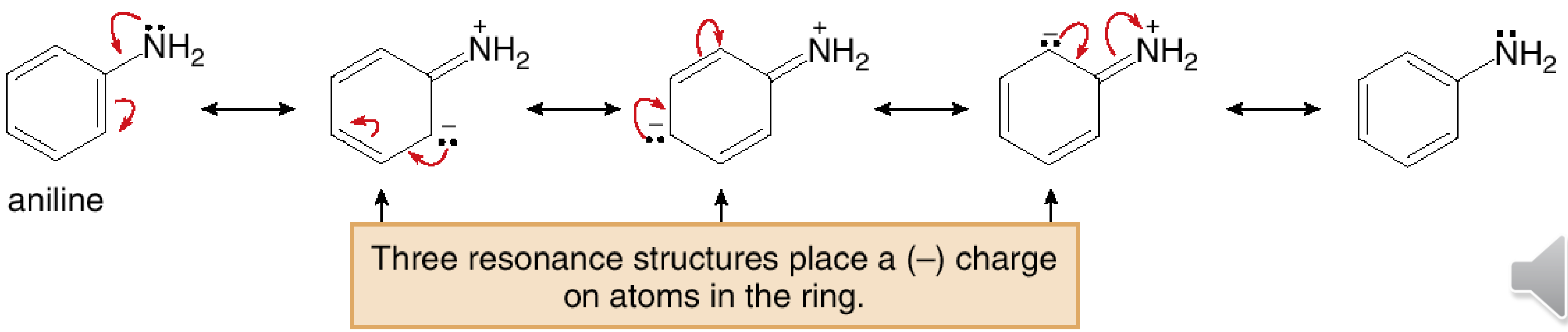
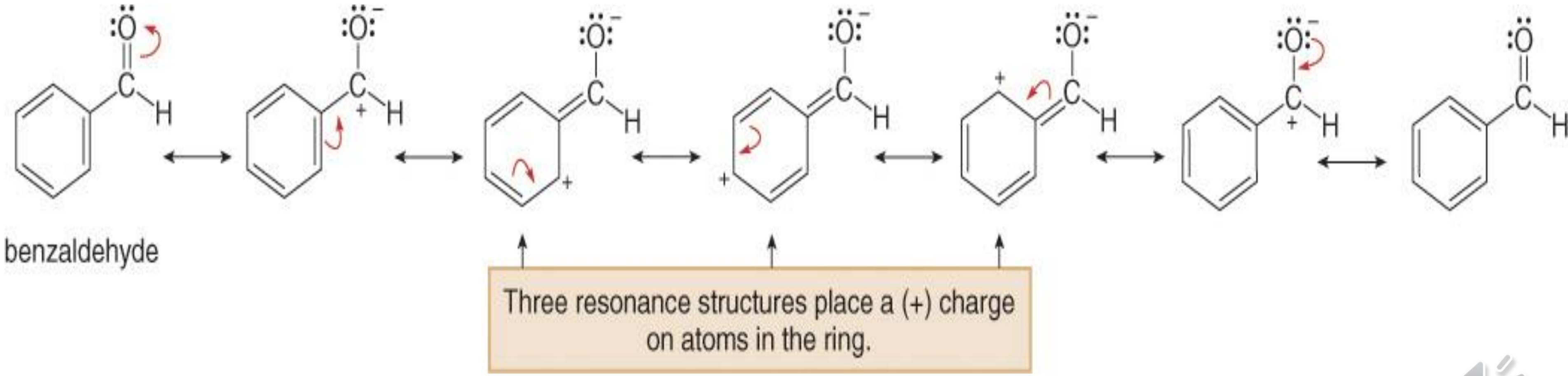
Resonance effects are only observed with substituents containing lone pairs or π bonds.

- A resonance effect is electron donating when resonance structures place a negative charge on carbons of the benzene ring.
- A resonance effect is electron withdrawing when resonance structures place a positive charge on carbons of the benzene ring.

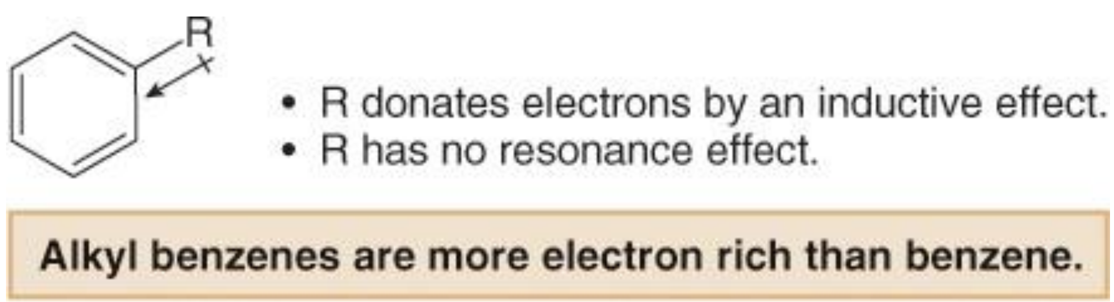
An electron-donating resonance effect is observed whenever an atom Z having a lone pair of electrons is directly bonded to a benzene ring.

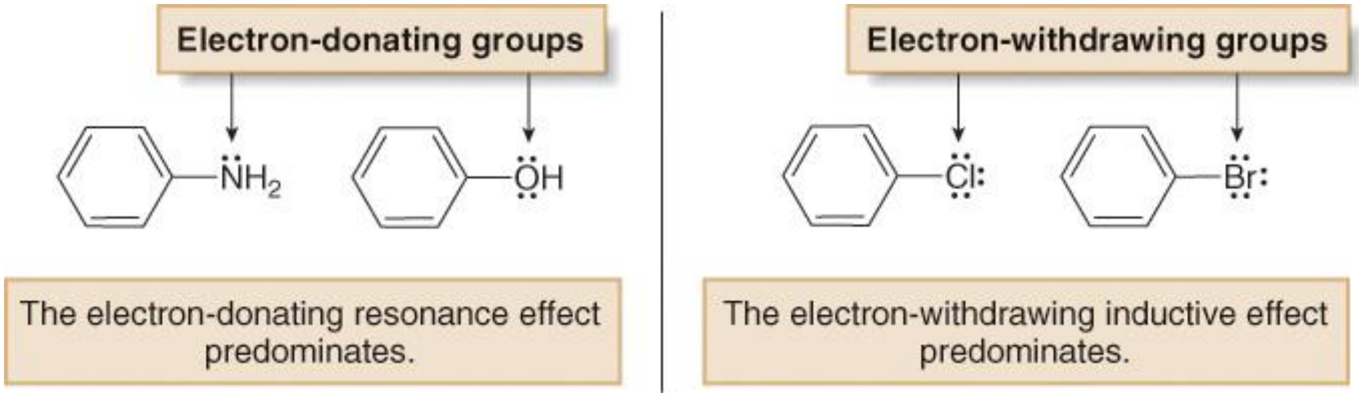


- An electron-withdrawing resonance effect is observed in substituted benzenes having the general structure C_6H_5-Y=Z, where Z is more electronegative than Y.
- Seven resonance structures can be drawn for benzaldehyde (C_6H_5CHO). Because three of them place a positive charge on a carbon atom of the benzene ring, the CHO group withdraws electrons from the benzene ring by a resonance effect.

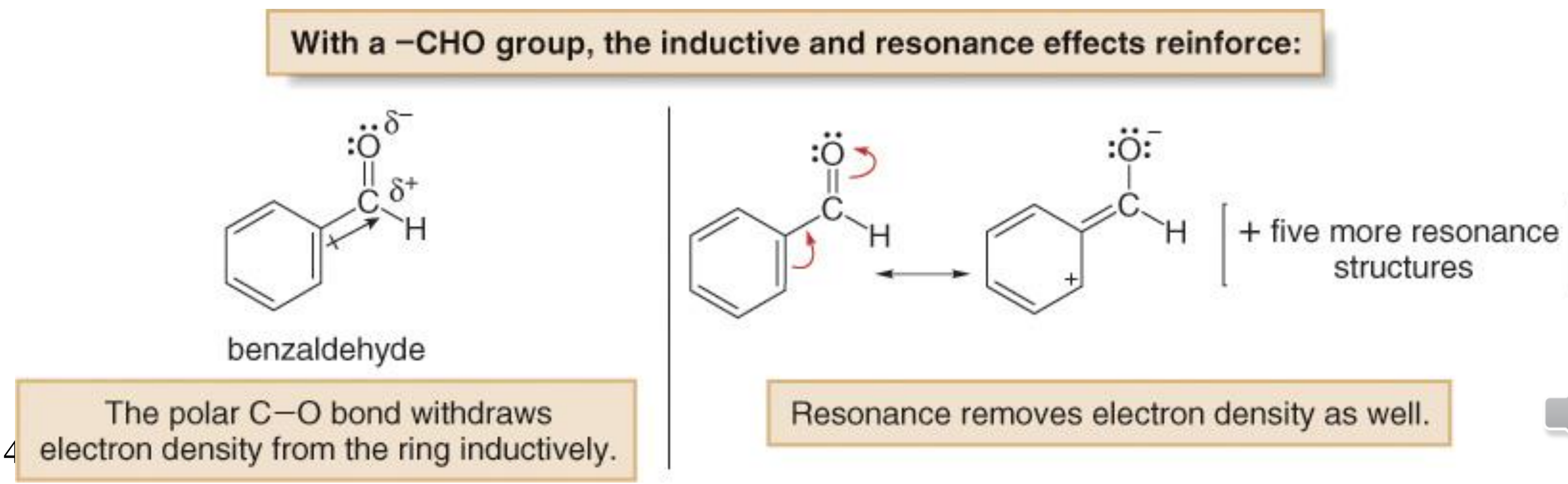


- To predict whether a substituted benzene is more or less electron rich than benzene itself, we must consider the net balance of both the inductive and resonance effects.
- For example, alkyl groups donate electrons by an inductive effect, but they have no resonance effect because they lack nonbonded electron pairs or π bonds.
- Thus, any alkyl-substituted benzene is more electron rich than benzene itself.





- **The inductive and resonance effects in compounds having the general structure C_6H_5-Y=Z (with Z more electronegative than Y) are both electron withdrawing.**

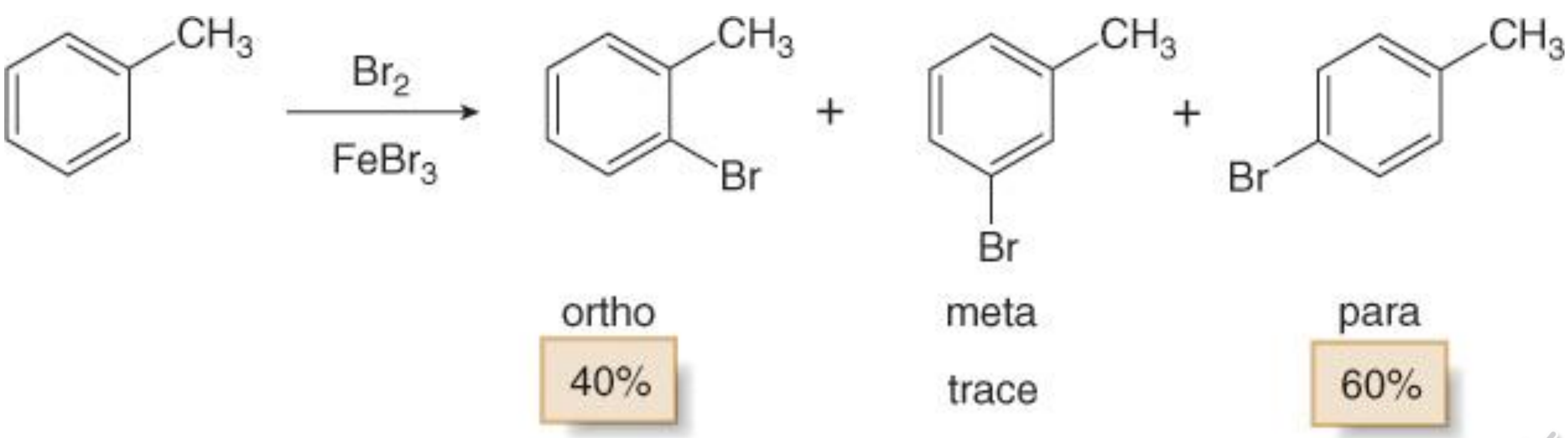


Electrophilic Aromatic Substitution and Substituted Benzenes.

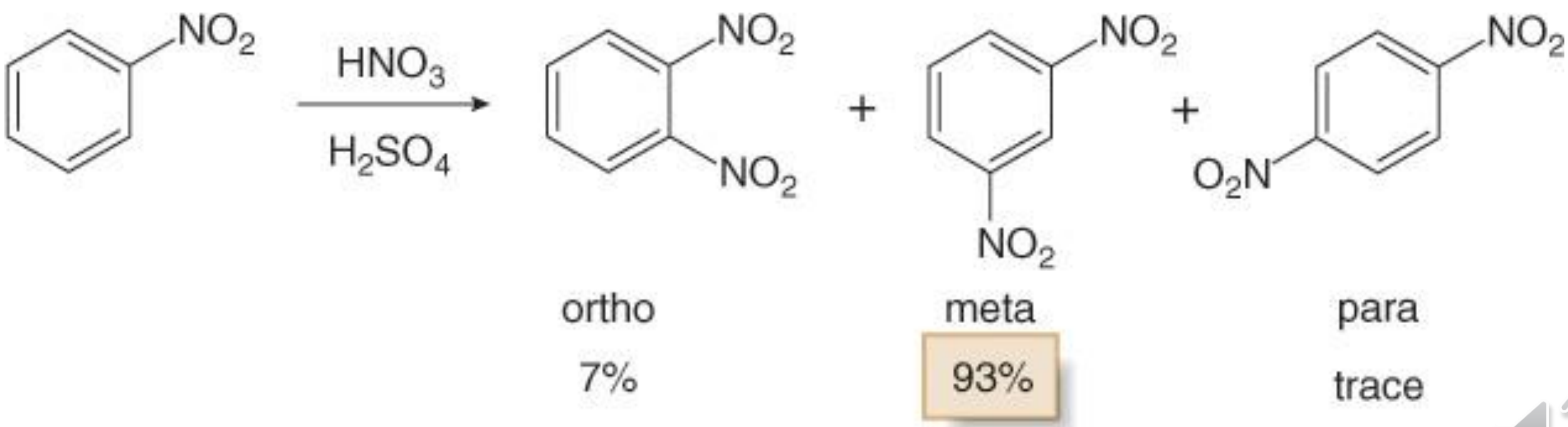
- Electrophilic aromatic substitution is a general reaction of all aromatic compounds, including polycyclic aromatic hydrocarbons, heterocycles, and substituted benzene derivatives.
- A substituent affects two aspects of the electrophilic aromatic substitution reaction:

1. **The rate of the reaction**—A substituted benzene reacts faster or slower than benzene itself.
2. **The orientation**—The new group is located either ortho, meta, or para to the existing substituent. The identity of the first substituent determines the position of the second incoming substituent.

- **Consider toluene—Toluene reacts faster than benzene in all substitution reactions.**
- **The electron-donating CH_3 group activates the benzene ring to electrophilic attack.**
- **Ortho and para products predominate.**
- **The CH_3 group is called an ortho, para director.**



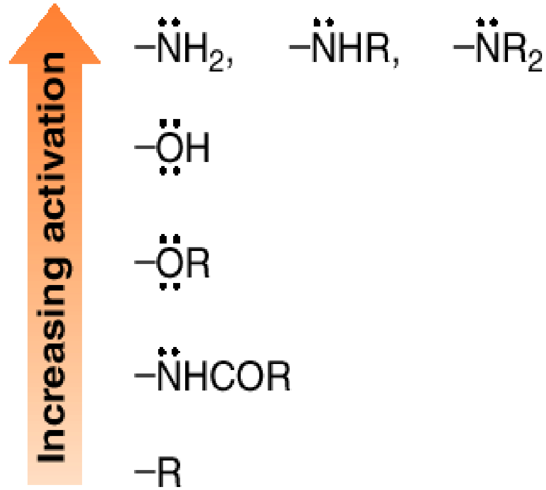
- Consider nitrobenzene—It reacts more slowly than benzene in all substitution reactions.
- The electron-withdrawing NO_2 group deactivates the benzene ring to electrophilic attack.
- The meta product predominates.
- The NO_2 group is called a **meta director**.



All substituents can be divided into three general types:

[1] ortho, para directors and activators

- **Substituents that *activate* a benzene ring and direct substitution ortho and para.**



General structure

−R or −Z:

[2] ortho, para deactivators

- **Substituents that *deactivate* a benzene ring and direct substitution ortho and para.**

$-\ddot{\underset{\cdot\cdot}{F}}:$ $-\ddot{\underset{\cdot\cdot}{Cl}}:$ $-\ddot{\underset{\cdot\cdot}{Br}}:$ $-\ddot{\underset{\cdot\cdot}{I}}:$

[3] meta directors

- **Substituents that direct substitution meta.**
- **All meta directors *deactivate* the ring.**

Increasing deactivation ↓

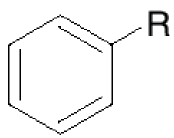
- $-CHO$
- $-COR$
- $-COOR$
- $-COOH$
- $-CN$
- $-SO_3H$
- $-NO_2$
- $-\overset{+}{N}R_3$

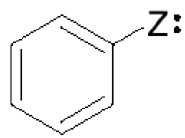
General structure

$-Y$ (δ^+ or $+$)

- **Keep in mind that halogens are in a class by themselves.**
- **Also note that:**

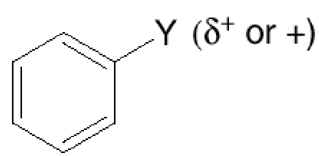
- All ortho, para directors are R groups or have a nonbonded electron pair on the atom bonded to the benzene ring.





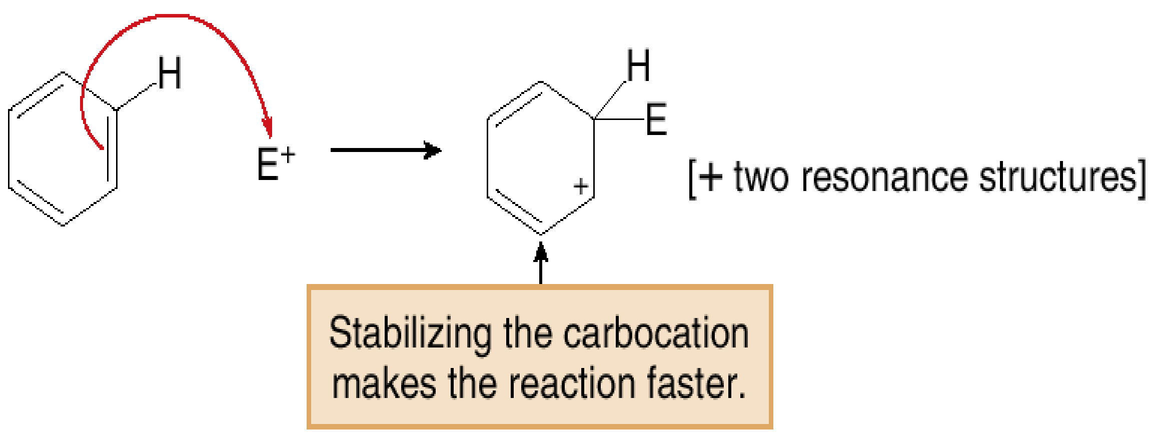
Z = N or O ---→ The ring is **activated.**
Z = halogen –→ The ring is **deactivated.**

- All meta directors have a full or partial positive charge on the atom bonded to the benzene ring.



- **To understand how substituents activate or deactivate the ring, we must consider the first step in electrophilic aromatic substitution.**
- **The first step involves addition of the electrophile (E^+) to form a resonance stabilized carbocation.**
- **The Hammond postulate makes it possible to predict the relative rate of the reaction by looking at the stability of the carbocation intermediate.**

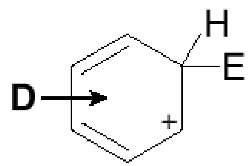
- The more stable the carbocation, the lower in energy the transition state that forms it, and the faster the reaction.



• The principles of inductive effects and resonance effects can now be used to predict carbocation stability.

- Electron-donating groups stabilize the carbocation, making the reaction faster.
- Electron-withdrawing groups destabilize the carbocation, making the reaction slower.

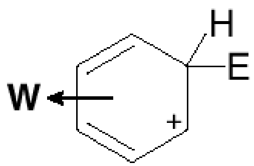
D = electron-donor group



more stable carbocation

Substitution is **faster**.
The ring is **activated.**

W = electron-withdrawing group

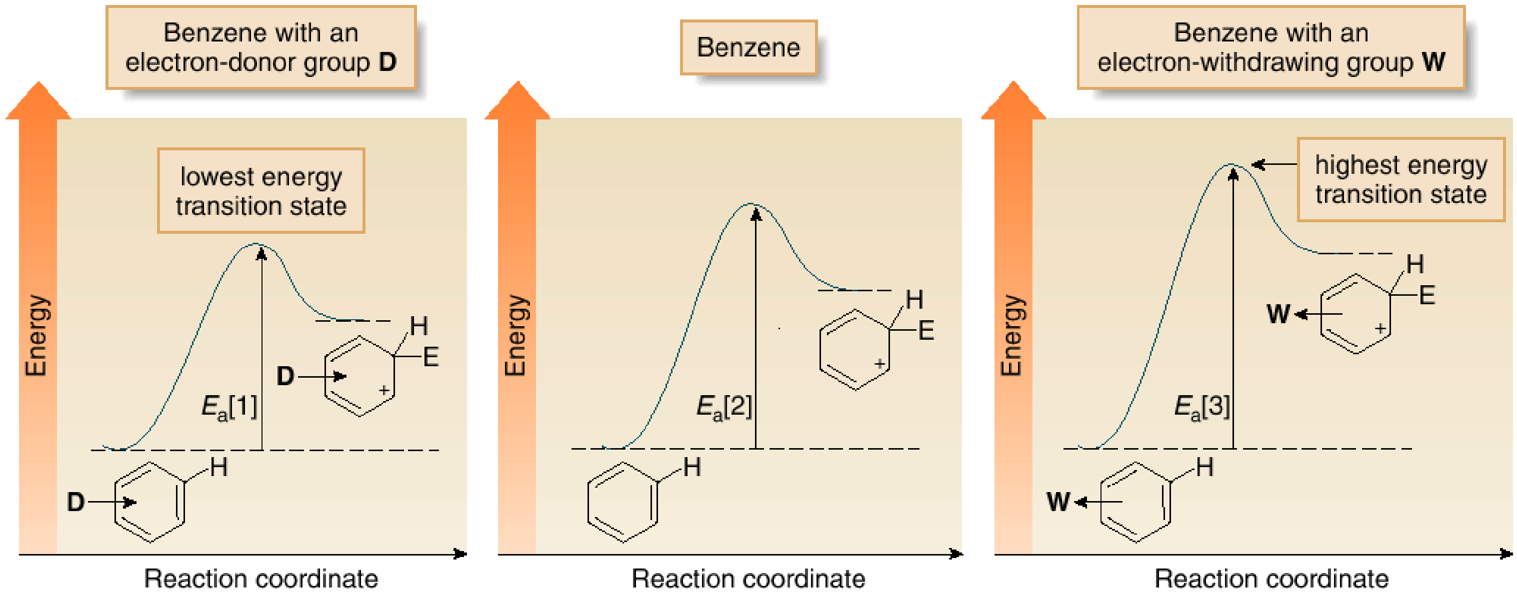


less stable carbocation

Substitution is **slower.**
The ring is **deactivated.**

- In other words, electron-donating groups activate a benzene ring and electron-withdrawing groups deactivate a benzene ring towards electrophilic attack.

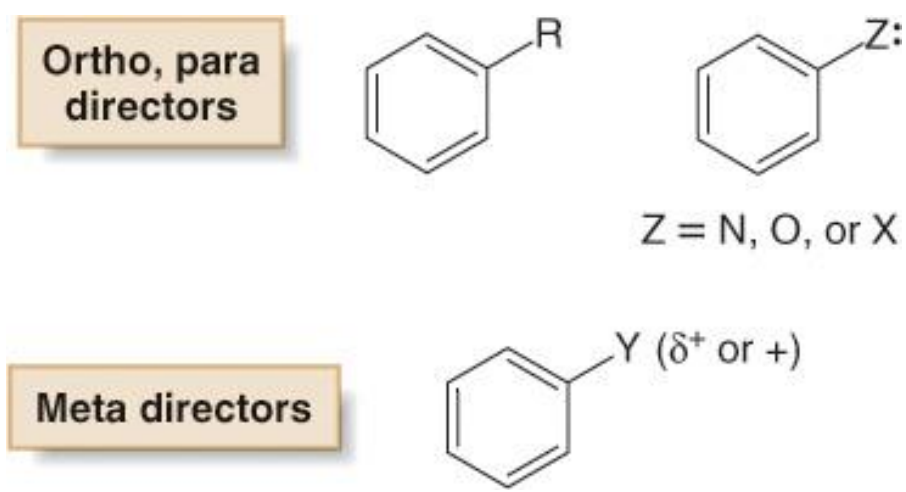
The energy diagrams below illustrate the effect of electron-withdrawing and electron-donating groups on the transition state energy of the rate-determining step.



- Electron-donor groups **D** stabilize the carbocation intermediate, lower the energy of the transition state, and increase the rate of reaction.
- Electron-withdrawing groups **W** destabilize the carbocation intermediate, raise the energy of the transition state, and decrease the rate of reaction.

Orientation Effects in Substituted Benzenes

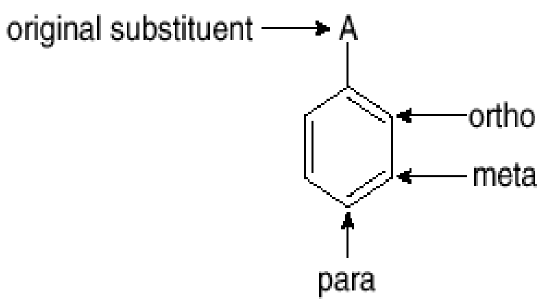
- There are two general types of ortho, para directors and one general type of meta director.
- All ortho, para directors are R groups or have a nonbonded electron pair on the atom bonded to the benzene ring.
- All meta directors have a full or partial positive charge on the atom bonded to the benzene ring.



To evaluate the effects of a given substituent, we can use the following stepwise procedure:

How To Determine the Directing Effects of a Particular Substituent

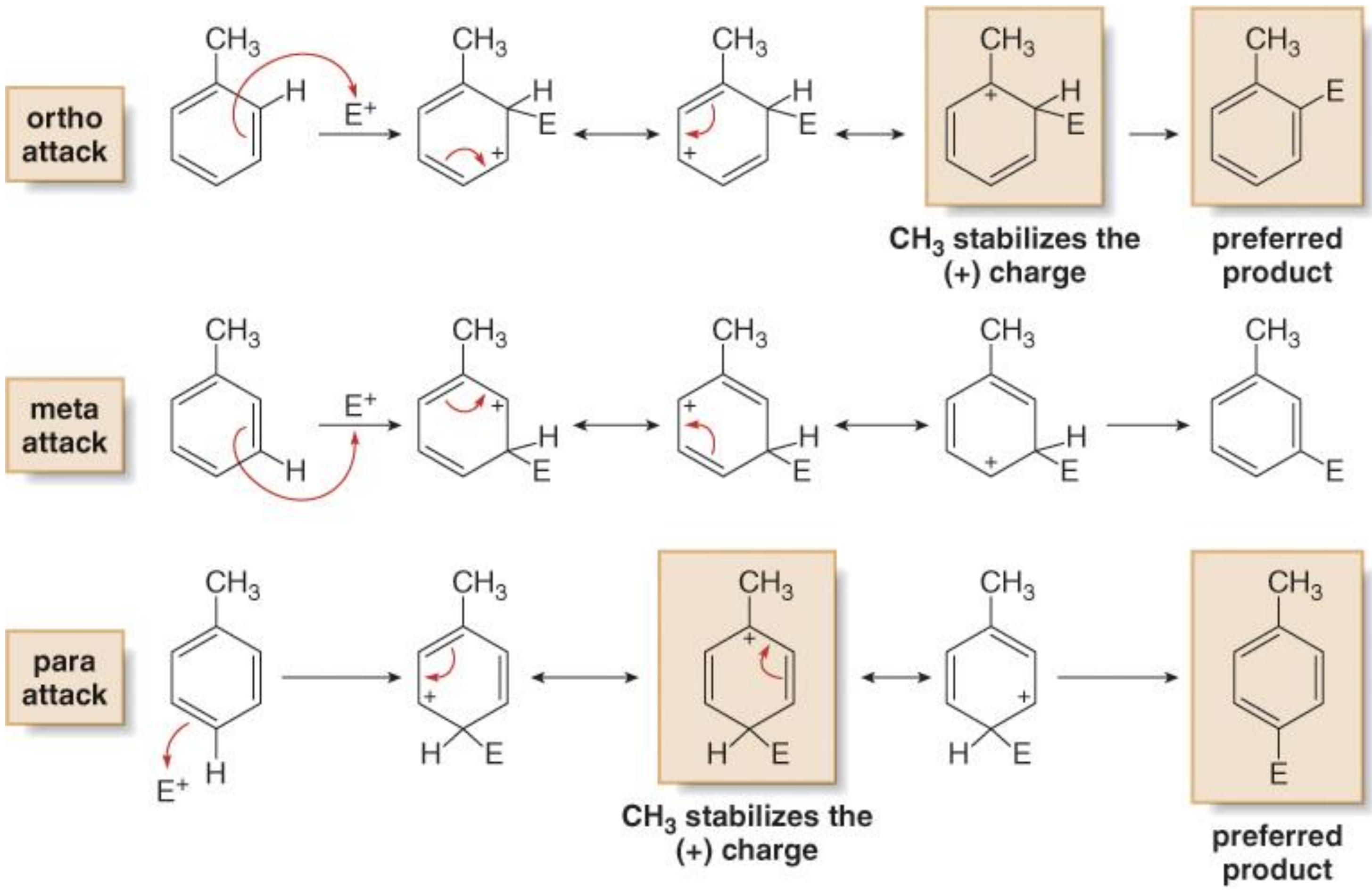
Step [1] Draw all resonance structures for the carbocation formed from attack of an electrophile E^+ at the ortho, meta, and para positions of a substituted benzene (C_6H_5-A).



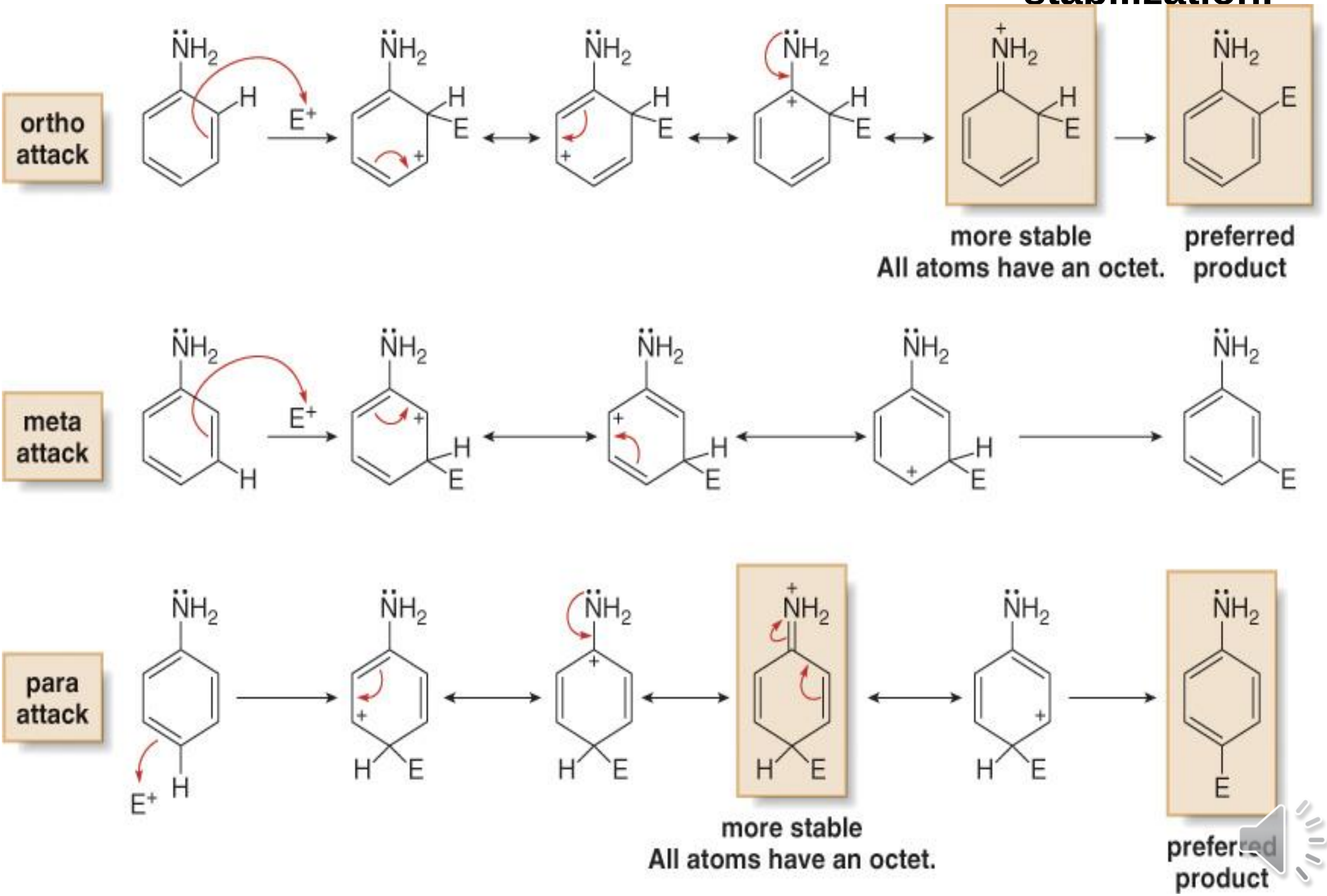
- There are at least three resonance structures for each site of reaction.
- Each resonance structure places a positive charge ortho or para to the new C – E bond.

Step [2] Evaluate the stability of the intermediate resonance structures. The electrophile attacks at those positions that give the most stable carbocation.

- A CH_3 group directs electrophilic attack ortho and para to itself because an electron-donating inductive effect stabilizes the carbocation intermediate.



An NH_2 group directs electrophilic attack ortho and para to itself because the carbocation intermediate has additional resonance stabilization.



With the NO_2 group (and all meta directors) meta attack occurs because attack at the ortho and para position gives a destabilized carbocation intermediate.