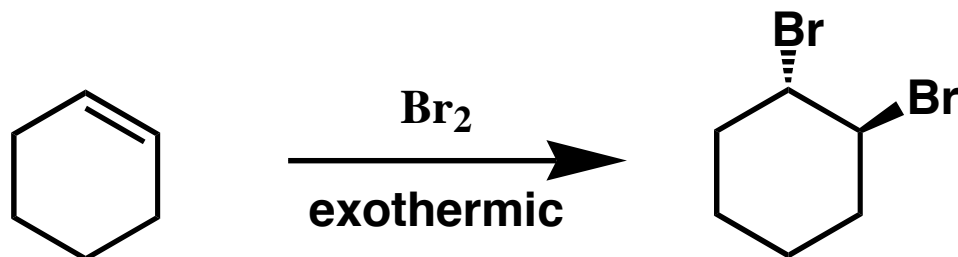


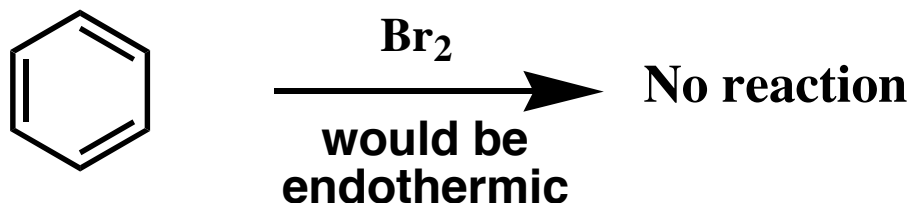
# EFFECT OF AROMATIC STABILIZATION ON REACTIONS OF BENZENE (and other aromatic compounds)

## ADDITION



**Bonds broken**  
 $\pi$  bond  
 (65 kcal/mol)  
 Br-Br  
 (50 kcal/mol)

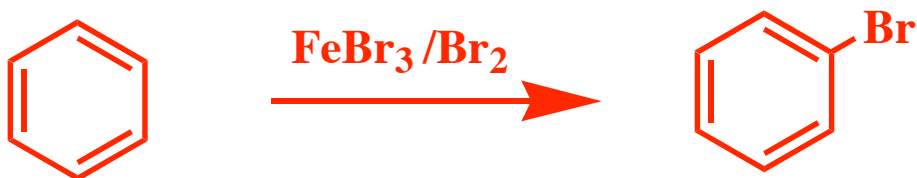
**Bonds made**  
 2 C-Br  
 (2 x 70 kcal/mol)



$\pi$  bond  
 Br-Br bond  
 also would lose AROMATIC STABILIZATION

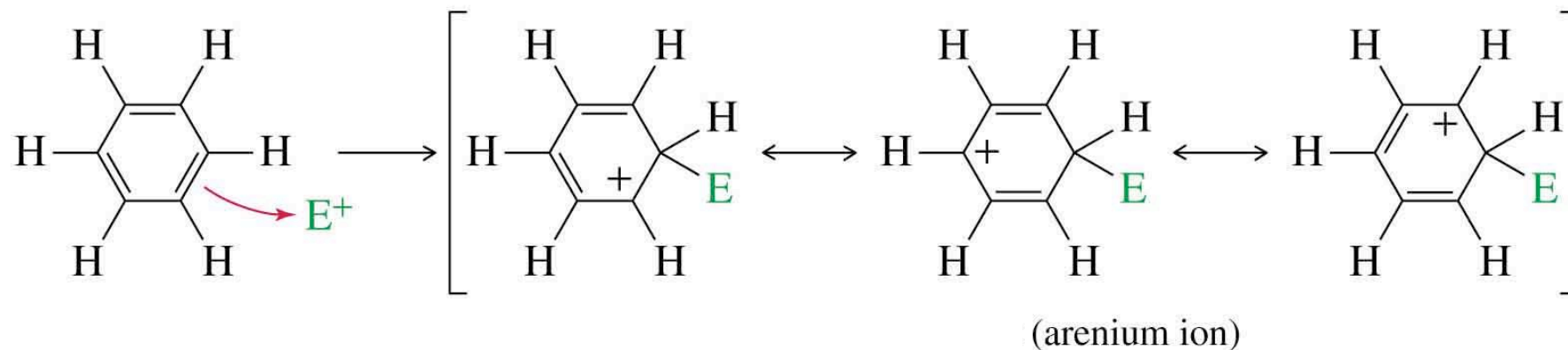
2 C-Br

## INSTEAD - SUBSTITUTION

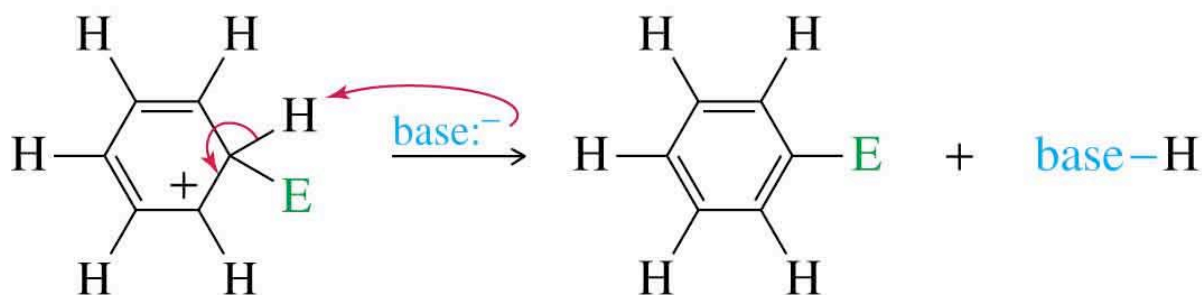


# Aromatic compounds like benzene undergo **SUBSTITUTION** Instead of **ADDITION**

*Step 1: Attack on the electrophile*

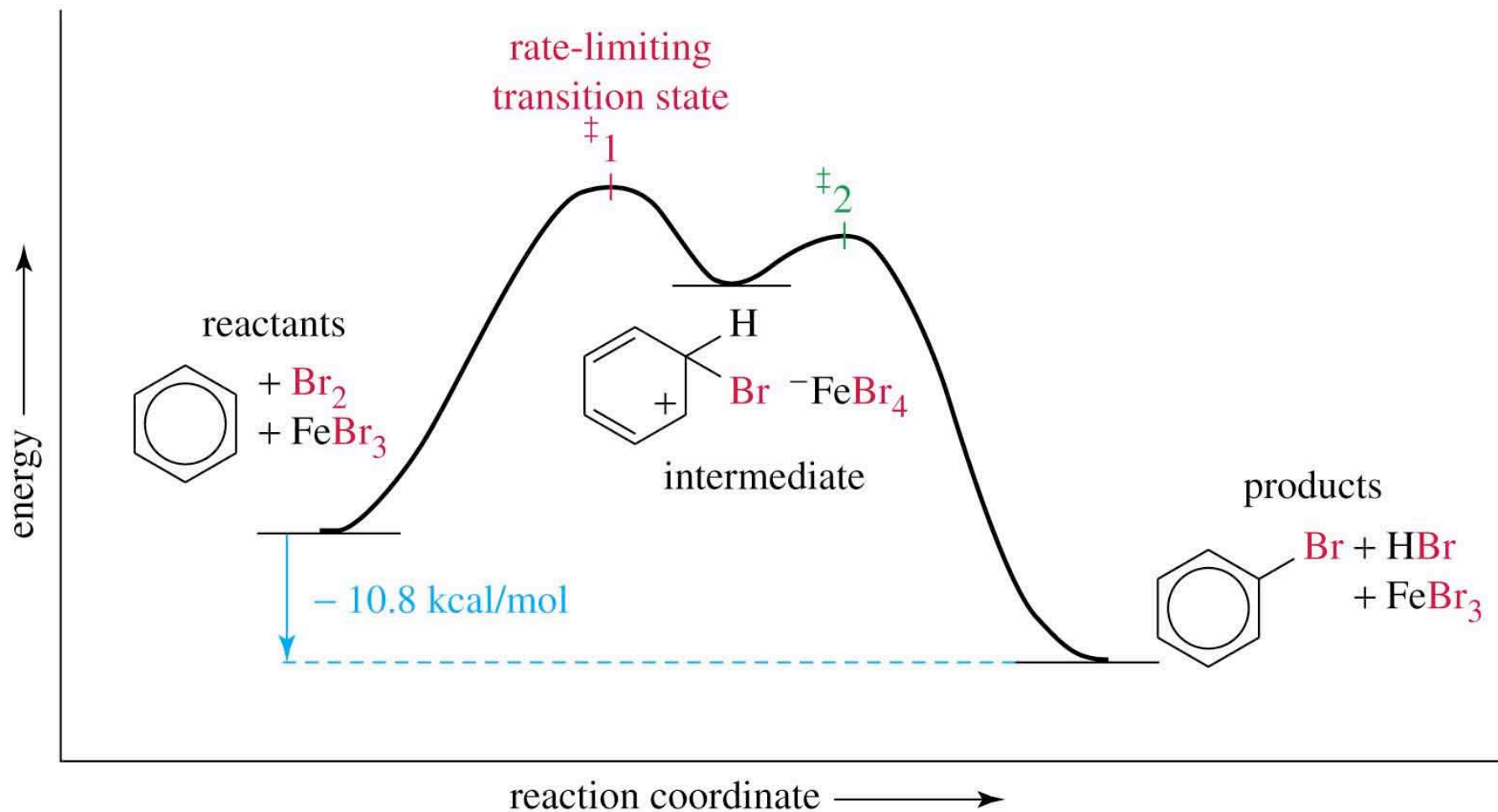


*Step 2: Loss of a proton gives the substitution product.*

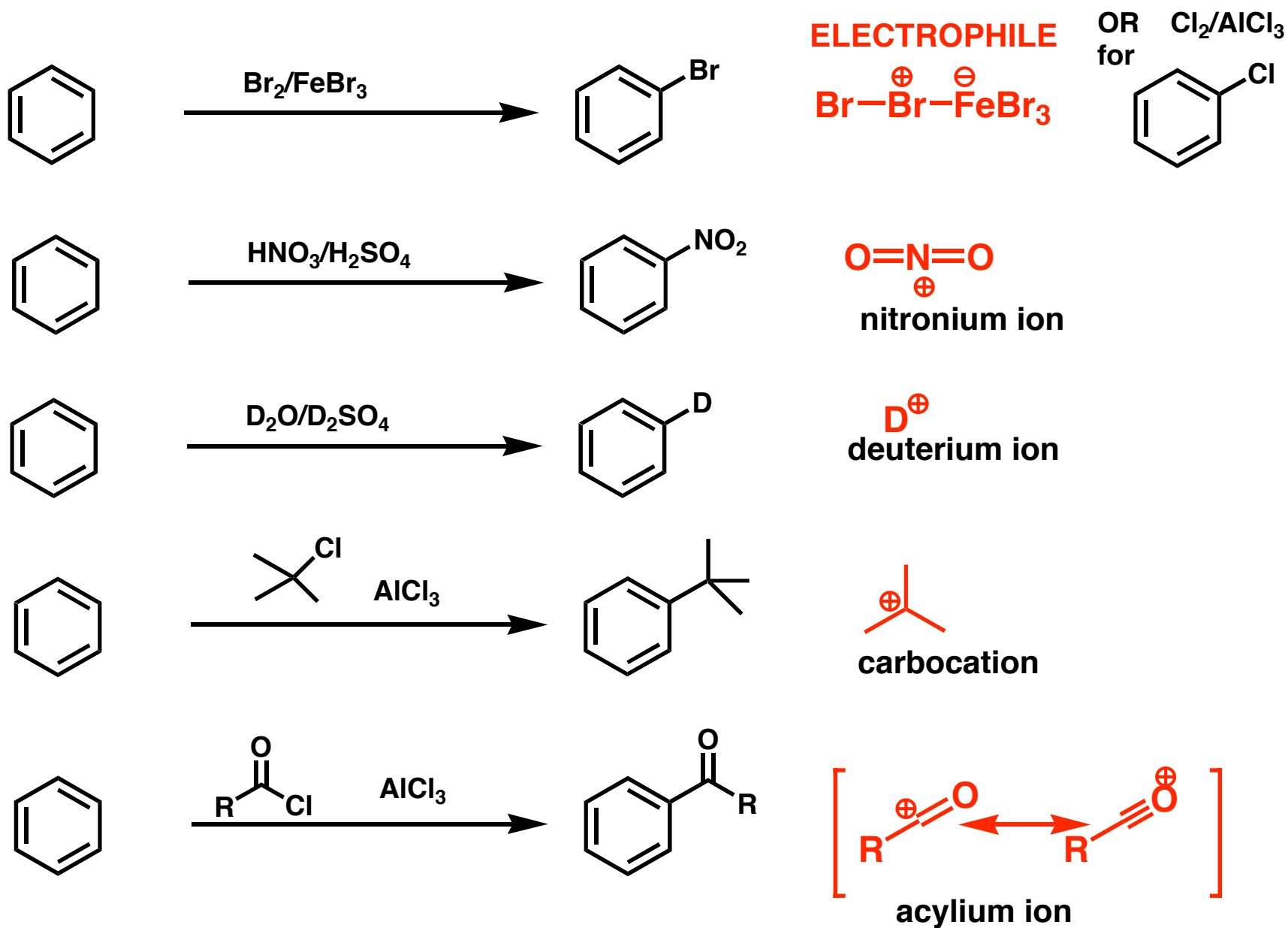


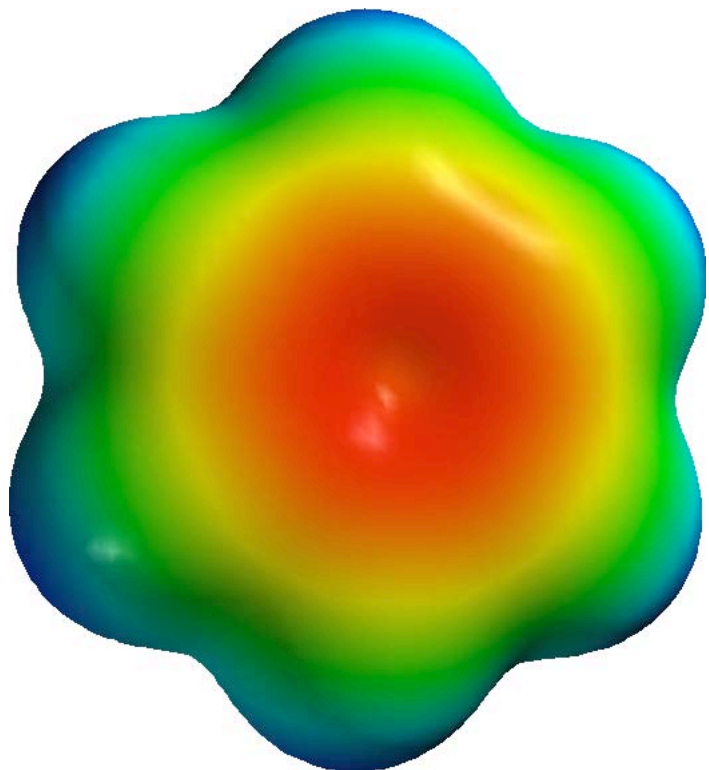
**For bromination  $E^+ = Br-Br + FeBr_3$**

# Energy Diagram for Bromination

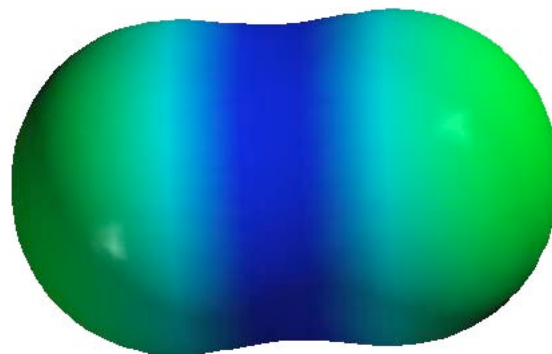


# ELECTROPHILIC SPECIES IN EAS

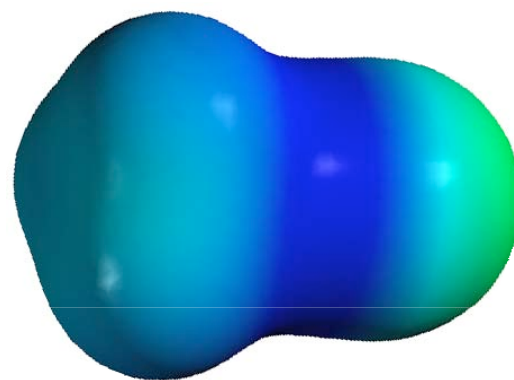




**Benzene**

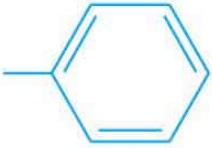


**Nitronium**  $\text{O}=\overset{+}{\text{N}}=\text{O}$



**Acylium**  $\text{CH}_3\overset{+}{\text{C}}=\text{O}$

# Summary of Directing Effects

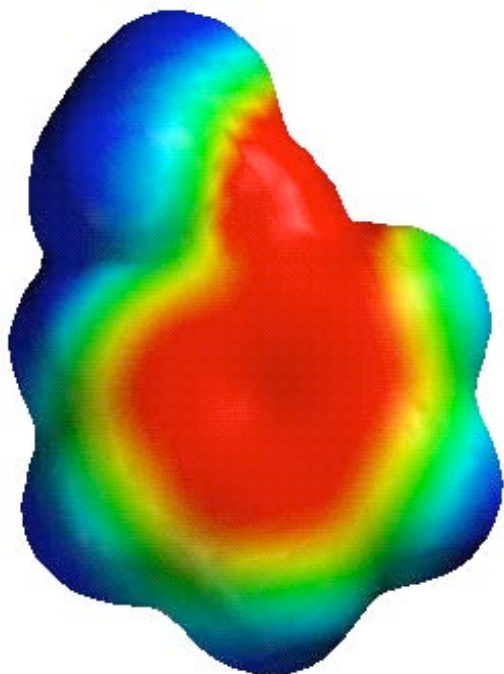
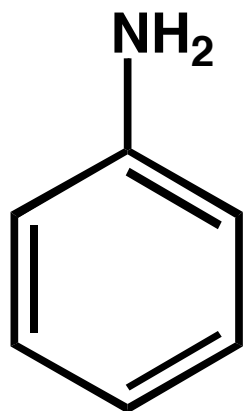
$\pi$ Donors	$\sigma$ Donors	Halogens	Carbonyls	Other
$-\ddot{\text{N}}\text{H}_2$ $-\ddot{\text{O}}\text{H}$ $-\ddot{\text{O}}\text{R}$ $-\ddot{\text{N}}\text{HCOCH}_3$	$-\text{R}$ (alkyl)  (aryl)	$-\text{F}$ $-\text{Cl}$ $-\text{Br}$ $-\text{I}$	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{R} \end{array}$ $\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{OH} \end{array}$ $\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{OR} \end{array}$	$-\text{SO}_3\text{H}$ $-\text{C}\equiv\text{N}$ $-\text{NO}_2$ $-\text{NR}_3^+$
ortho, para-directing		meta-directing		
ACTIVATING		DEACTIVATING		

## Four categories:

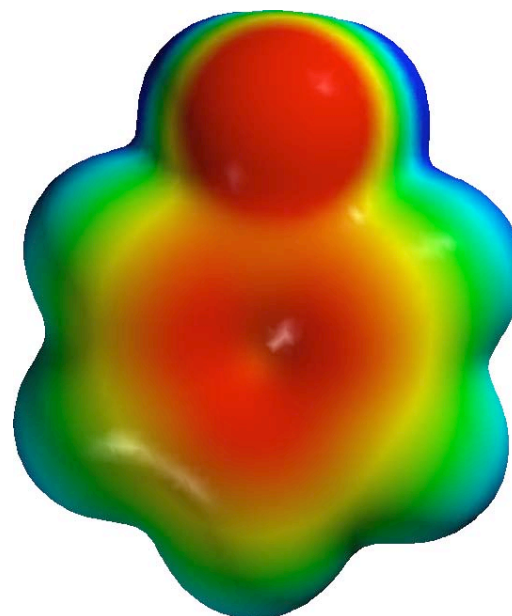
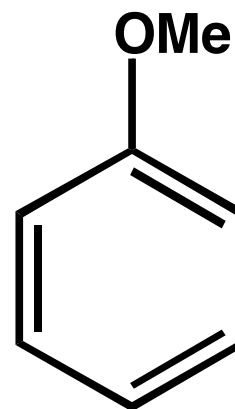
- I. Strongly activating, ortho/para directing (eg. -OMe)
- II. Weakly activating, ortho/para directing (eg. -CH<sub>3</sub>)
- III. Weakly deactivating, ortho/para directing (eg. -Cl,)
- IV. Deactivating, meta directing (eg. -NO<sub>2</sub>)

**I. Strongly activating, ortho/para directing (LP electrons)**  
**(eg. -OMe, Inductive and Resonance effects)**

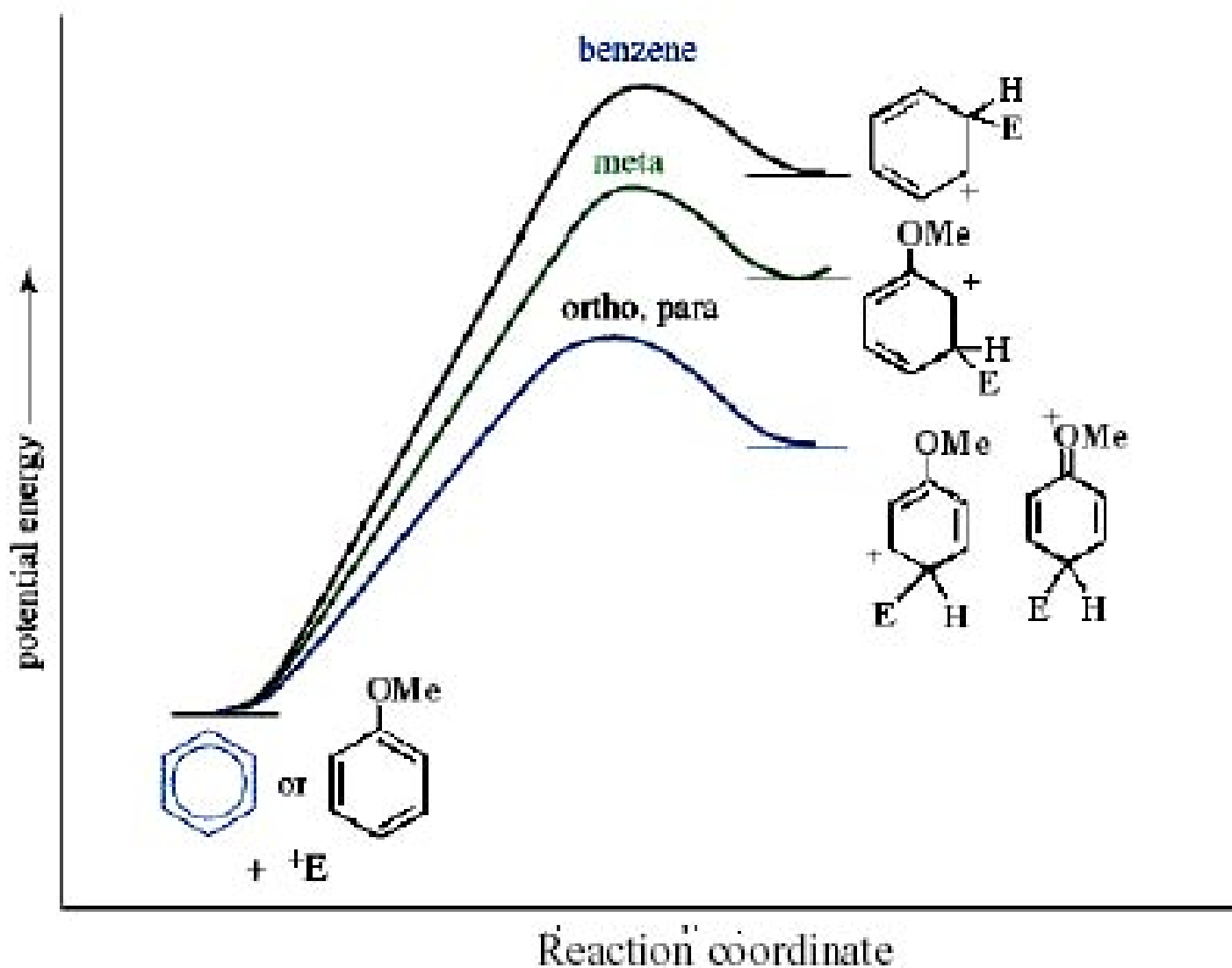
**Aniline**



**Anisole**

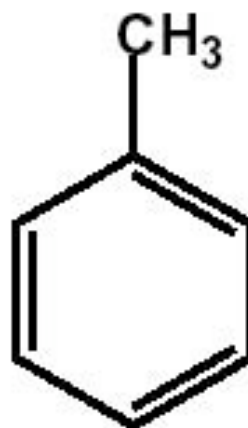
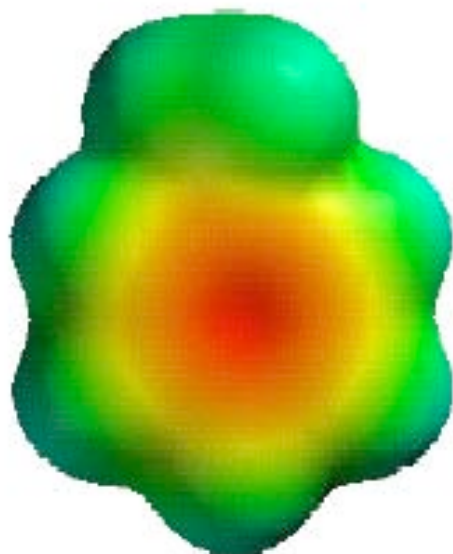


# I. Strongly activating, ortho/para directing (eg. -OMe, Consider inductive and resonance effects)





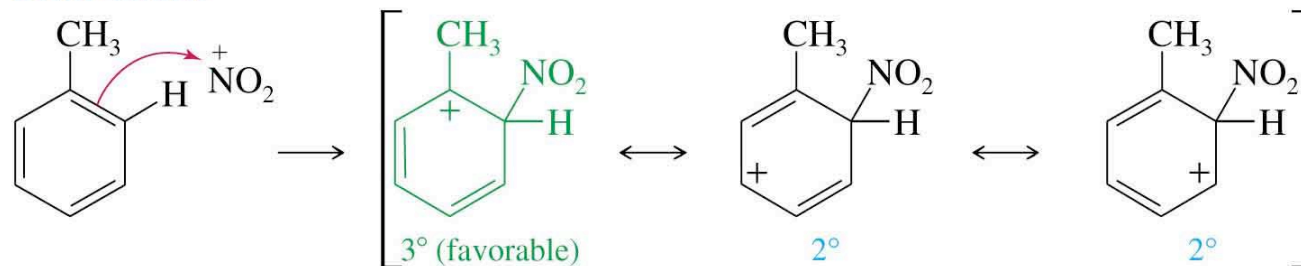
**II. Weakly activating, ortho/para directing**  
**(eg. -CH<sub>3</sub> Consider inductive effects)**



**Toluene**

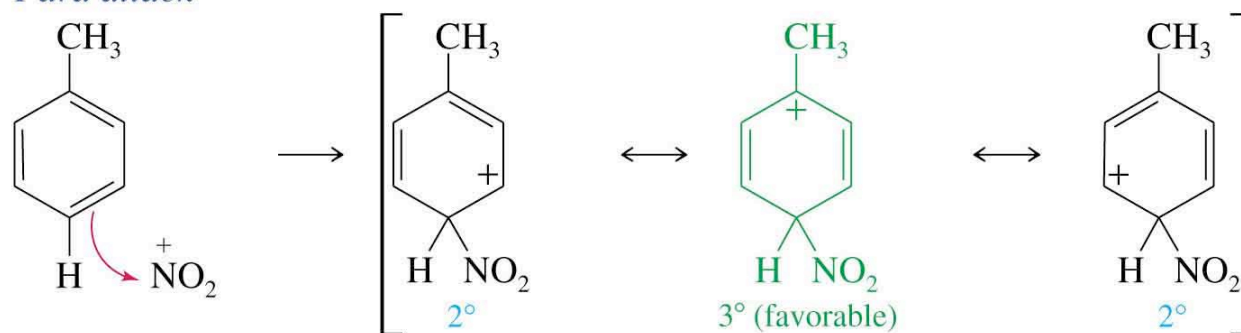
# Stability of Intermediate defines outcome

*Ortho attack*



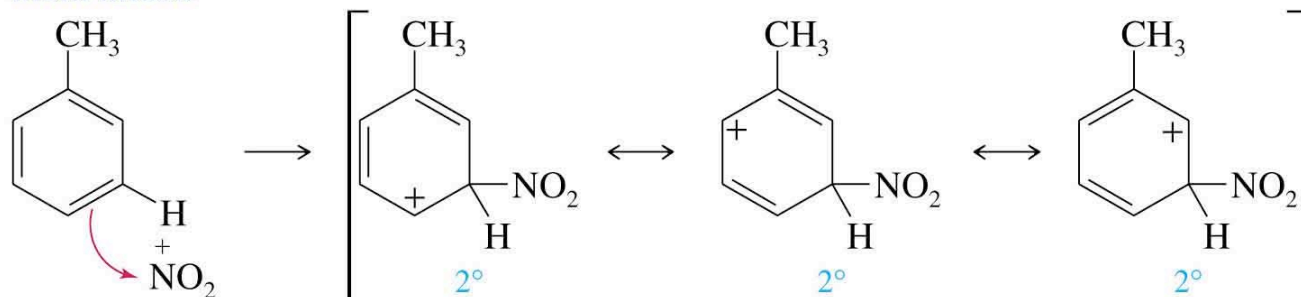
**Intermediate is more stable if nitration occurs at the *ortho* or *para* position.**

*Para attack*

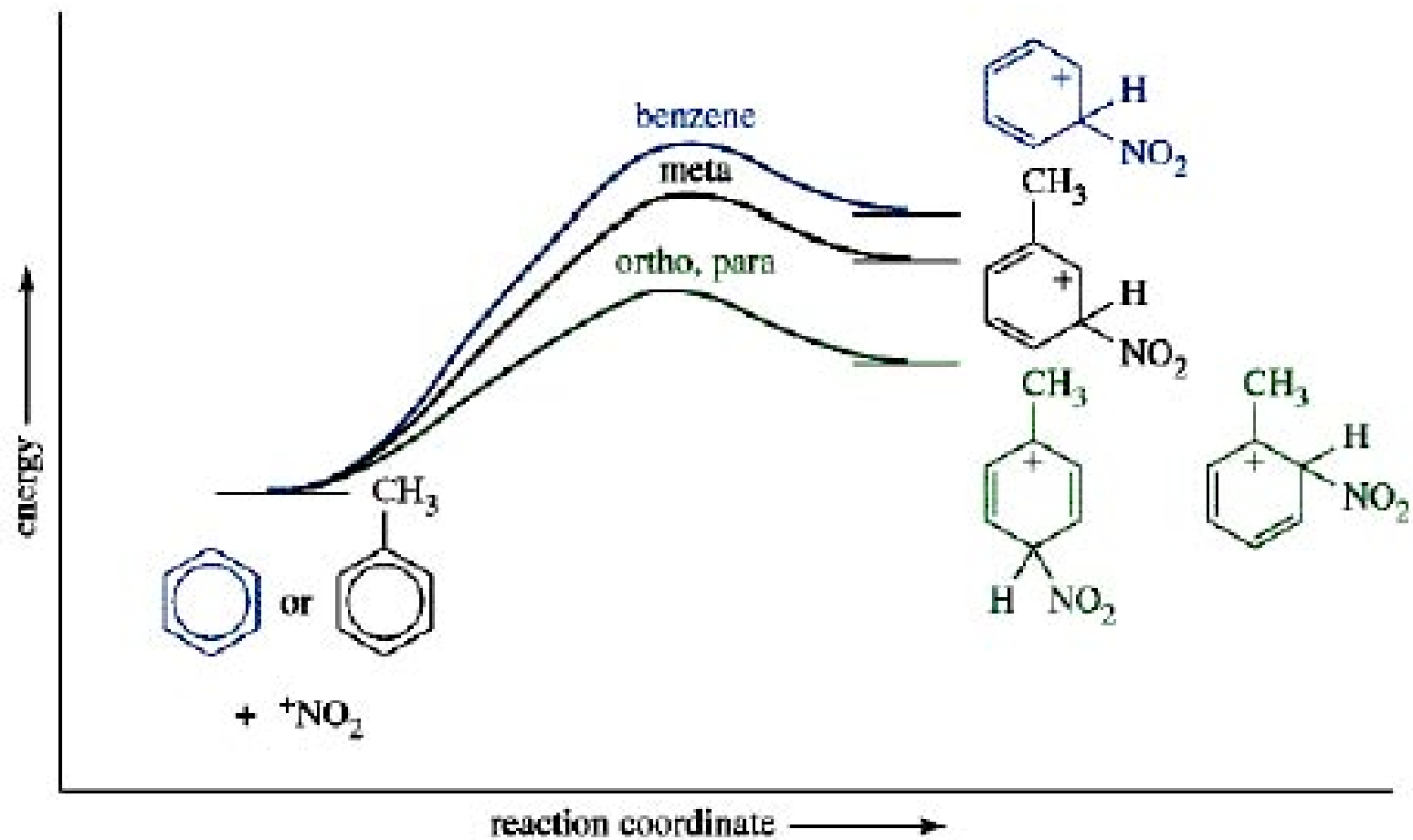


**Carbocation stability!**

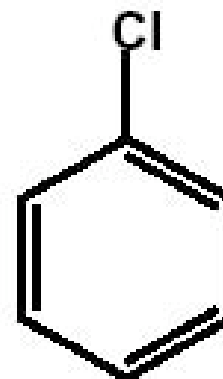
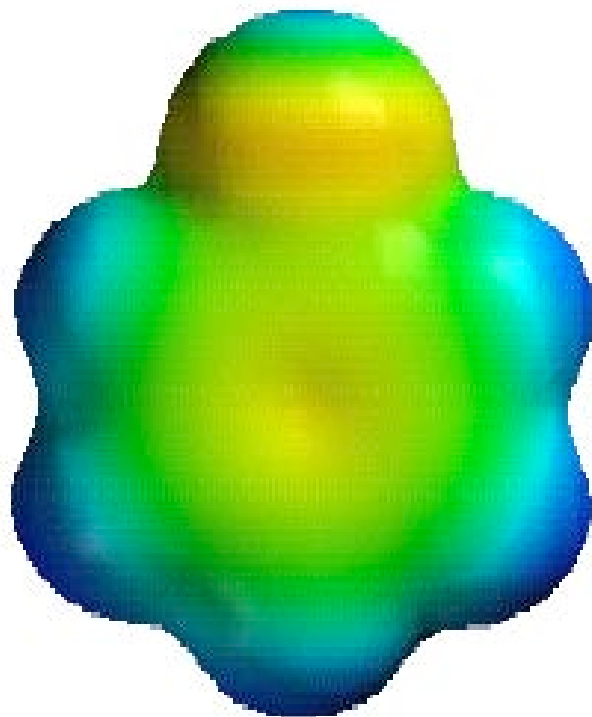
*Meta attack*



## II. Weakly activating, ortho/para directing (eg. $-\text{CH}_3$ inductive)

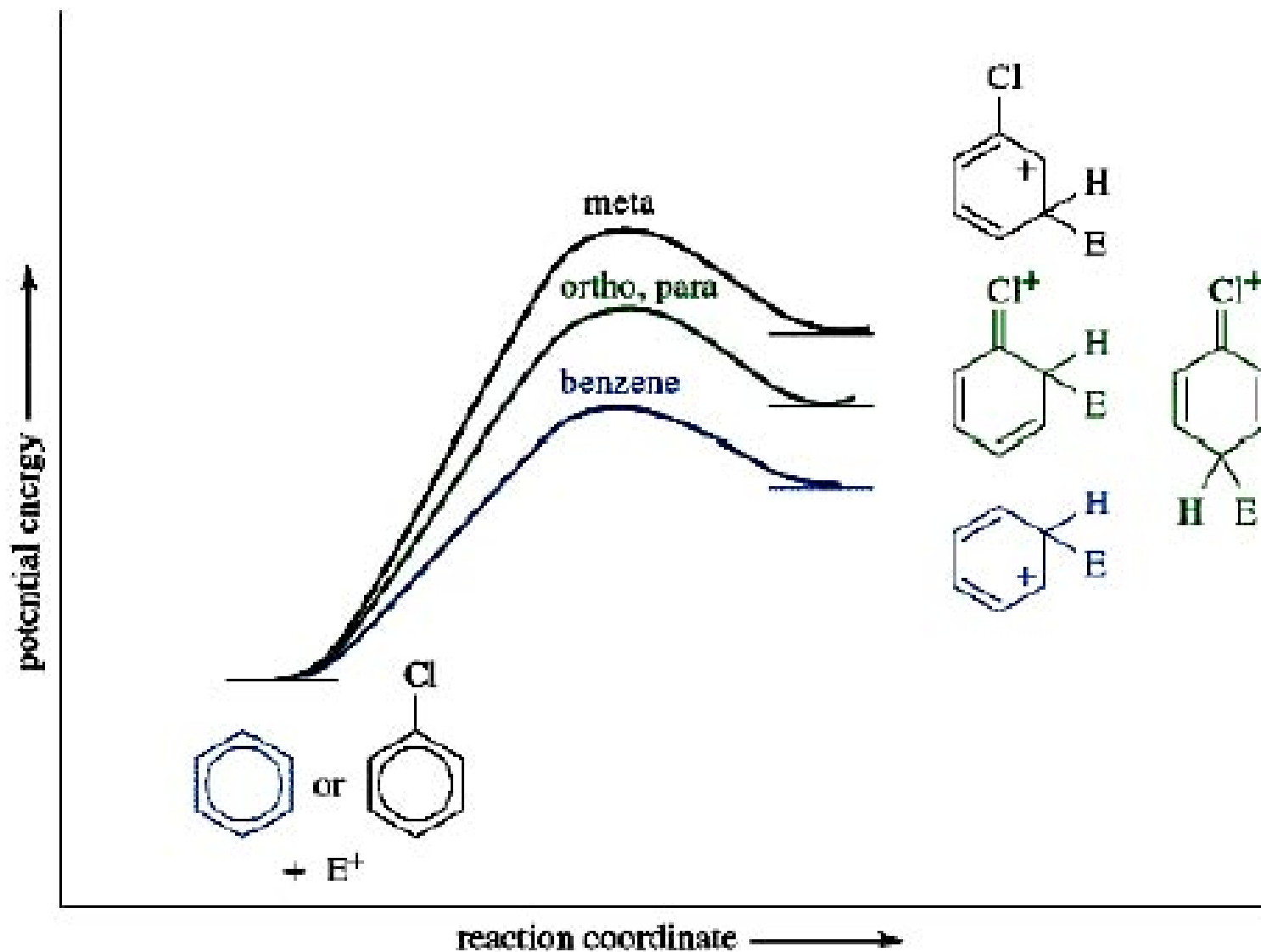


**III. Weakly deactivating, ortho/para directing  
(eg. -Cl, Inductive/Resonance)**

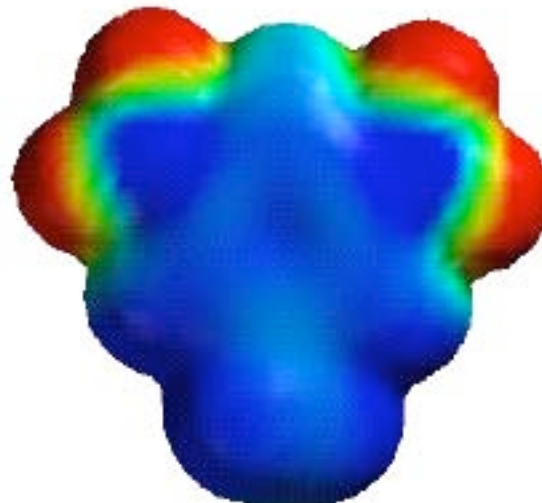
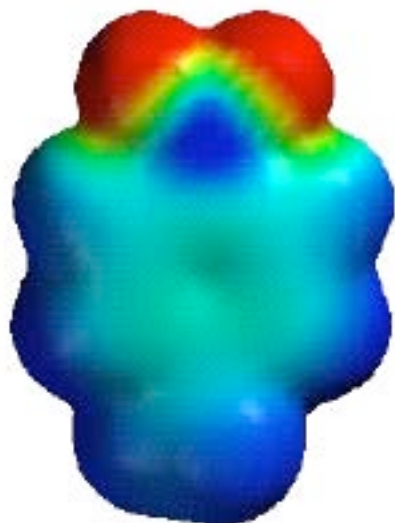
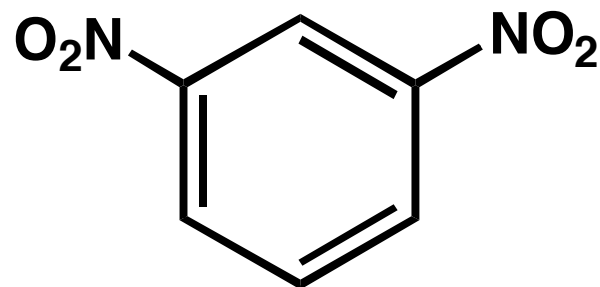
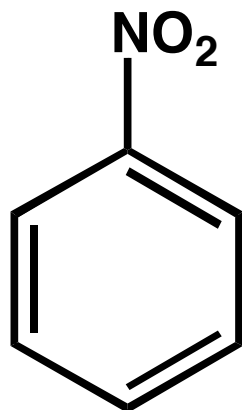


**Chlorobenzene**

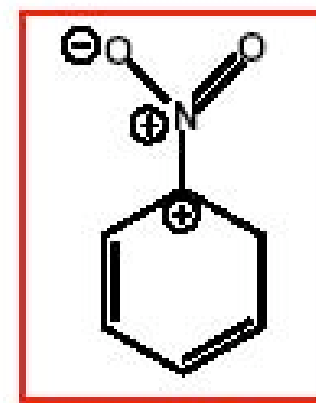
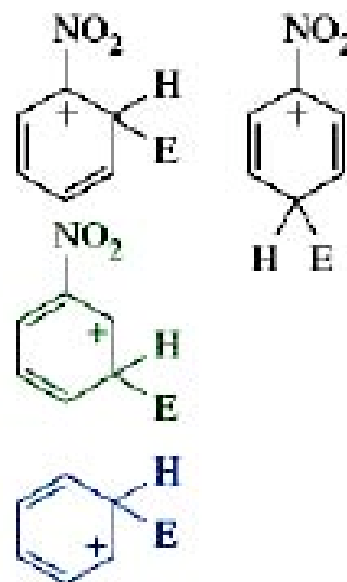
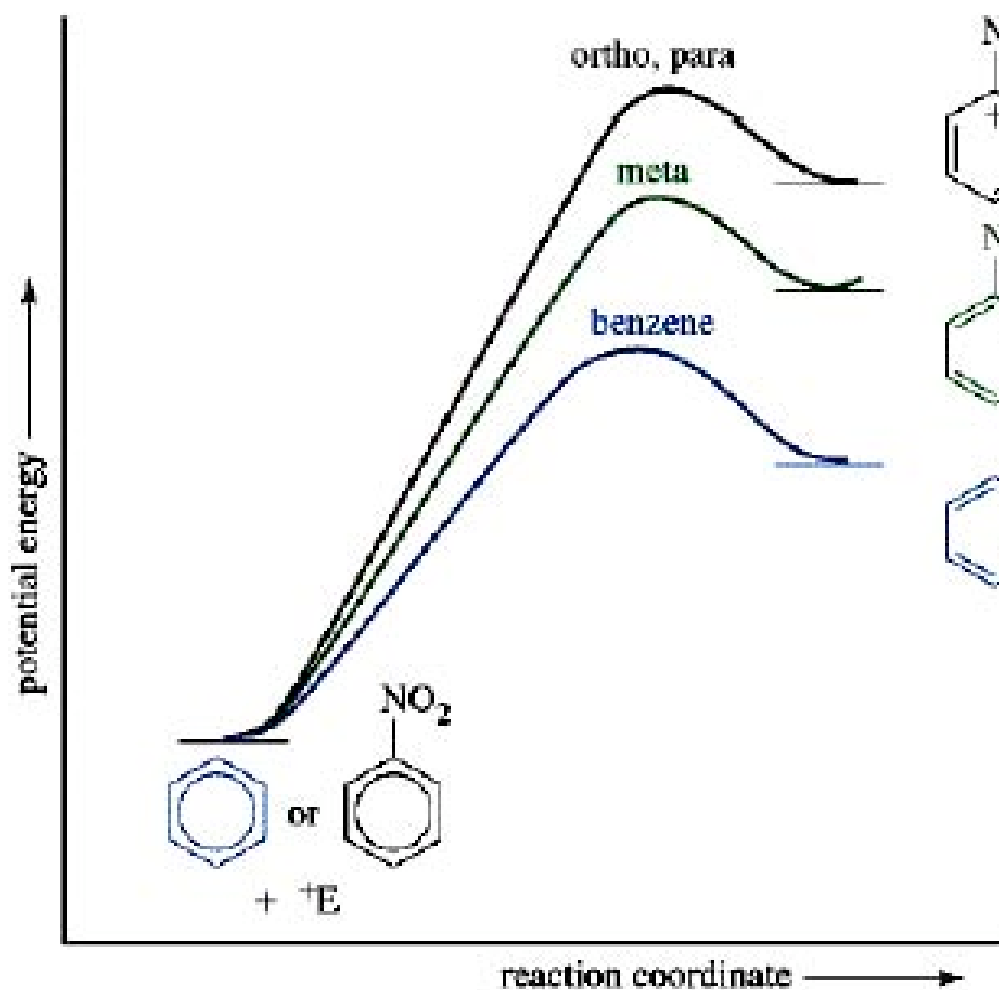
### III. Weakly deactivating, ortho/para directing (eg. -Cl, Consider inductive and resonance effects)



#### IV. Deactivating, meta directing (eg. $\text{-NO}_2$ , inductive effects)



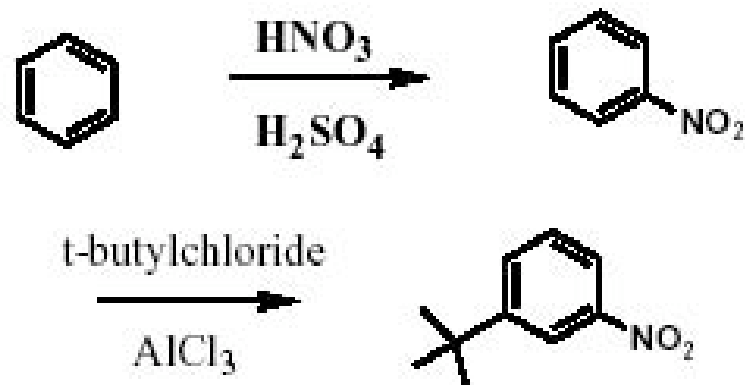
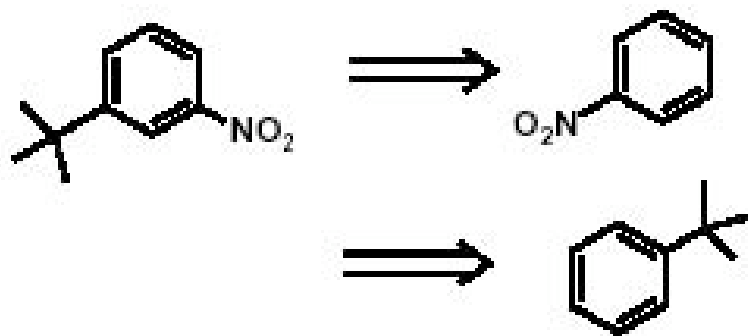
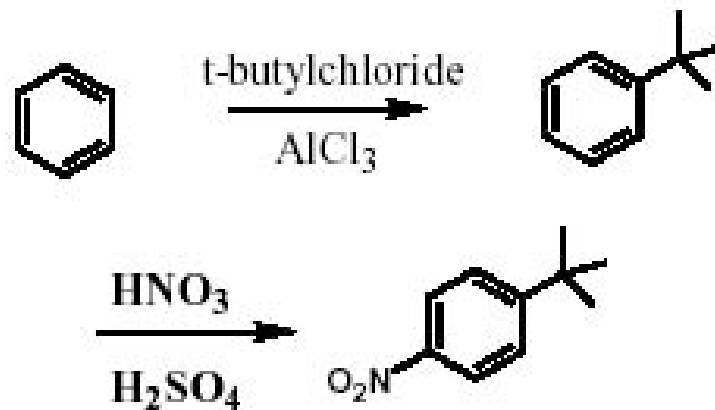
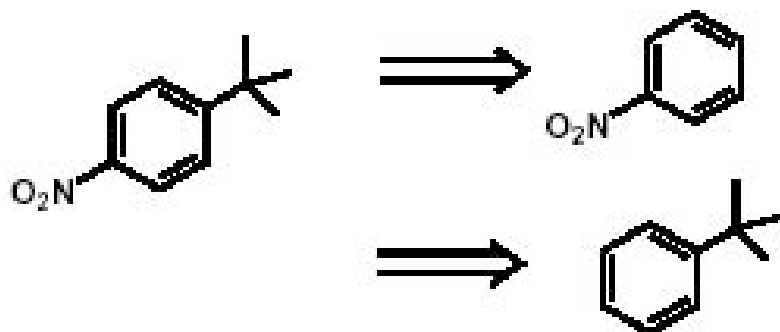
## IV. Deactivating, meta directing (eg. $-\text{NO}_2$ , inductive)



Positive or partial positive charge on substituent very unfavorable in  $\sigma$  complex

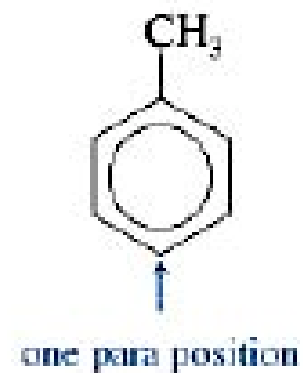
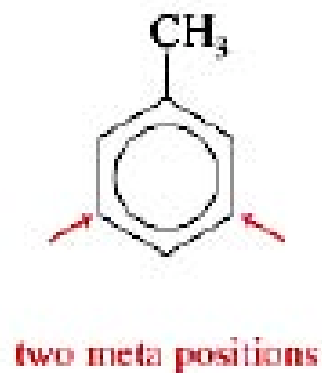
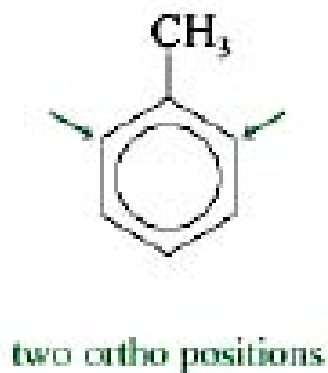
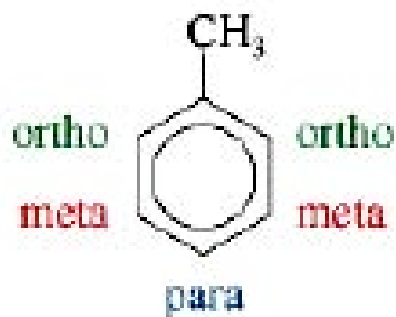
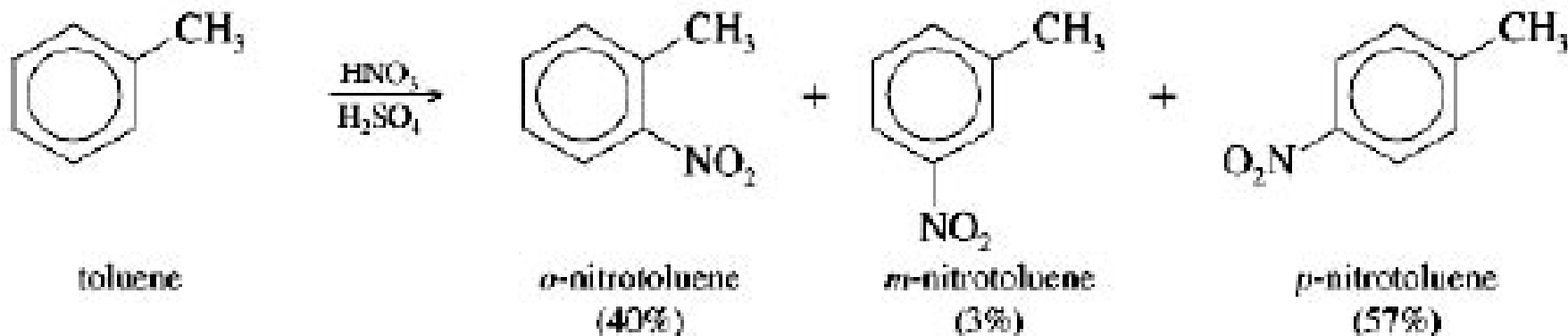
# SYNTHETIC STRATEGIES WITH AROMATIC COMPOUNDS

Reaction order may be critical





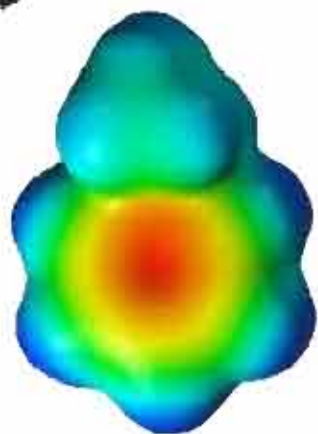
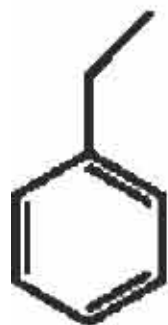
# STERIC EFFECTS IN ELECTROPHILIC AROMATIC SUBSTITUTION



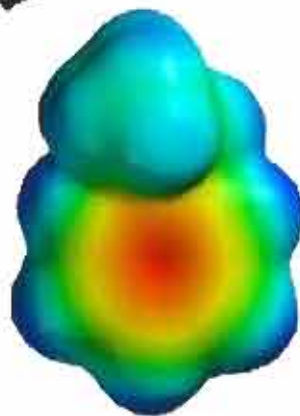
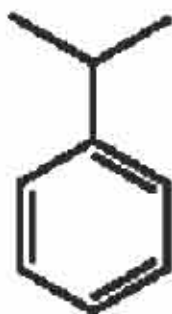
## STERIC EFFECTS IN ELECTROPHILIC AROMATIC SUBSTITUTION

Reaction with  $\text{Br}_2/\text{FeBr}_3$  to afford monobrominated derivative

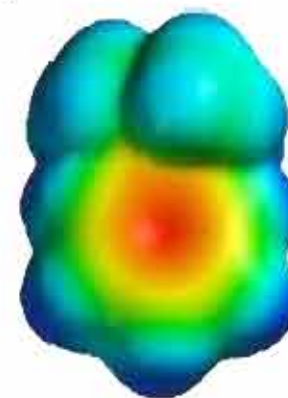
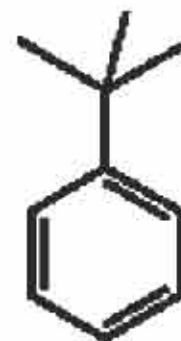
Statistically 66%ortho/33%para)



**Ortho 45%**  
**Meta 7%**  
**Para 48%**



**Ortho 30%**  
**Meta 8%**  
**Para 62%**



**Ortho 16%**  
**Meta 11%**  
**Para 73%**