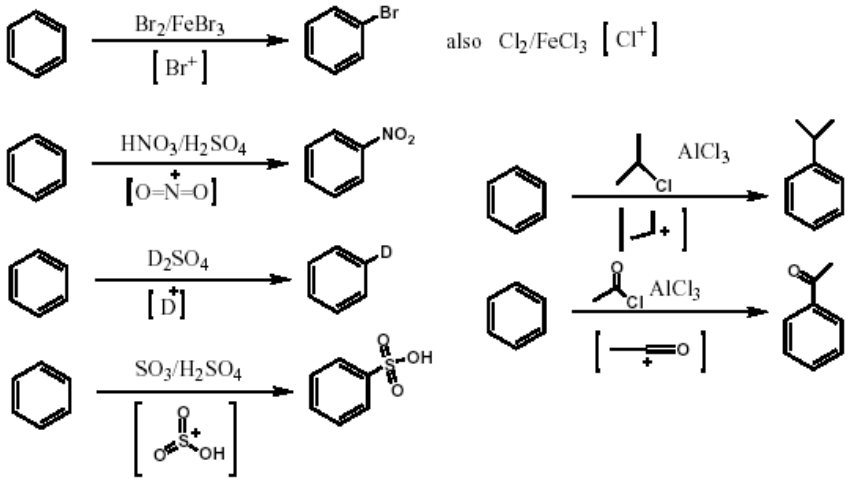
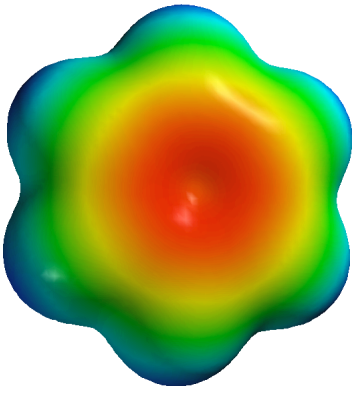
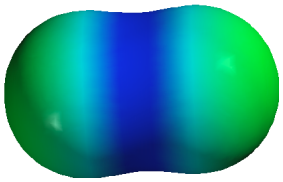
ELECTROPHILIC SPECIES IN EAS

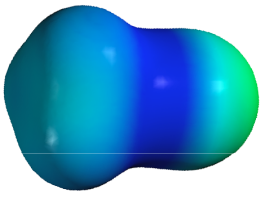




Benzene



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



Acylium $CH_3\overset{+}{C}=O$

Summary of Directing Effects

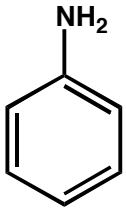
π Donors	σ Donors	Halogens	Carbonyls	Other
–NH$_2$ –OH –OR –NHCOCH$_3$	–R (alkyl) (aryl)	–F –Cl –Br –I	–C(=O)–R –C(=O)–OH –C(=O)–OR	–SO$_3$H –C≡N –NO$_2$ –$\overset{+}{N}$R$_3$
Ortho, Para-directing			*Meta-directing*	

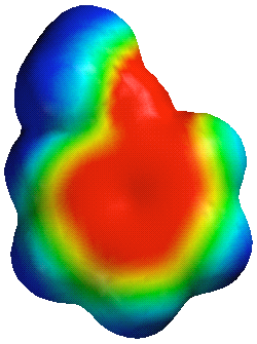
ACTIVATING ← → *DEACTIVATING*

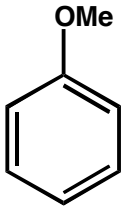
FOUR CATEGORIES:

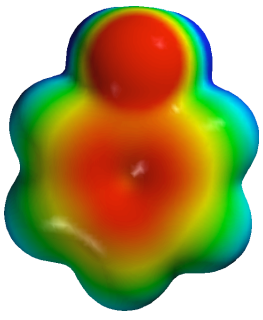
I. Strongly activating, ortho/para-directing (eg. -OMe, I, R)
II. Weakly activating, ortho/para-directing (eg. -CH$_3$I)
III. Weakly deactivating, ortho/para-directing (eg. -Cl, I, R)
IV. Deactivating, meta-directing (eg. -NO$_2$, I)

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

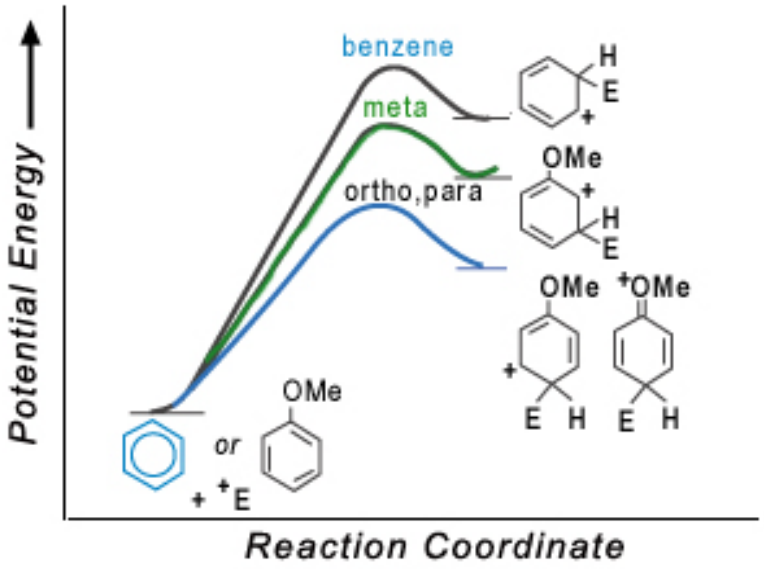
Aniline 



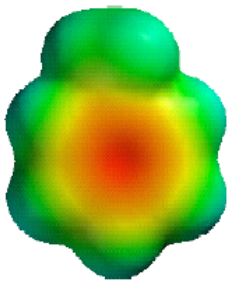
Anisole 

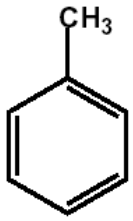


I. Strongly activating, ortho/para directing (eg. -OMe, inductive, resonance)

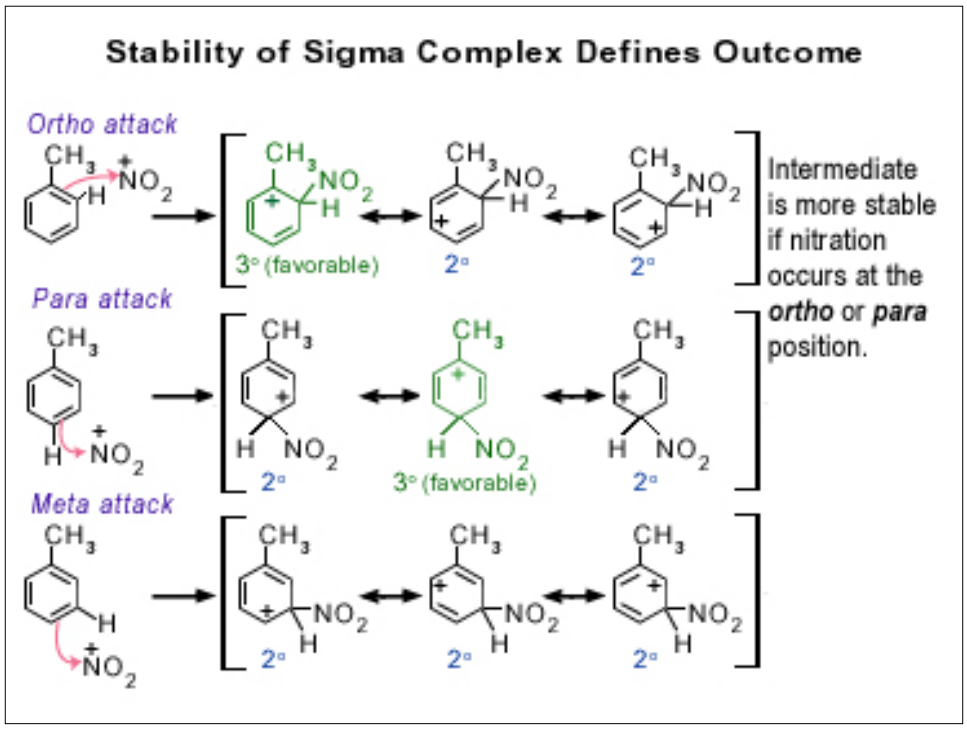


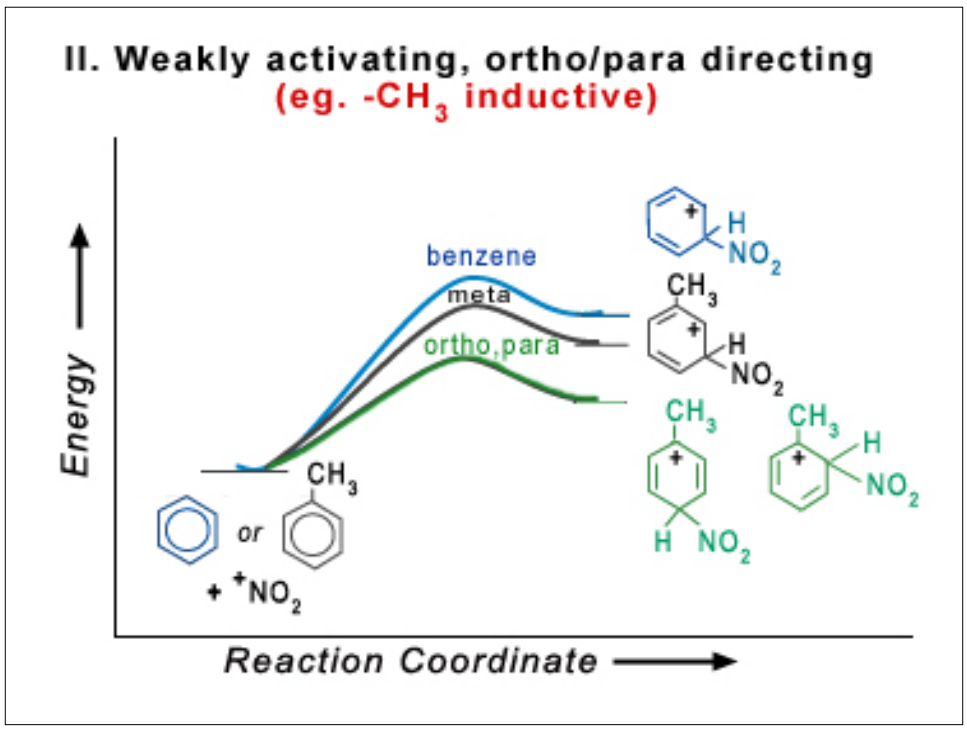
II. Weakly activating, ortho/para directing (eg. -CH_3 inductive)



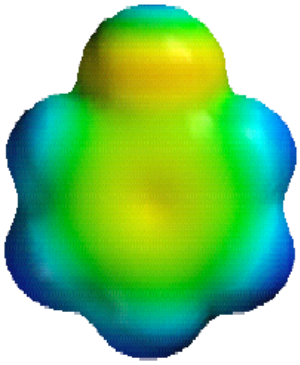


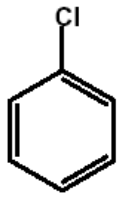
Toluene


Stability of Sigma Complex Defines Outcome
Ortho attack
3° (favorable)
2°
2°
Intermediate is more stable if nitration occurs at the ortho or para position.
Para attack
2°
3° (favorable)
2°
Meta attack
2°
2°
2°


II. Weakly activating, ortho/para directing
(eg. -CH3 inductive)
Energy
benzene
meta
ortho,para
or
Reaction Coordinate

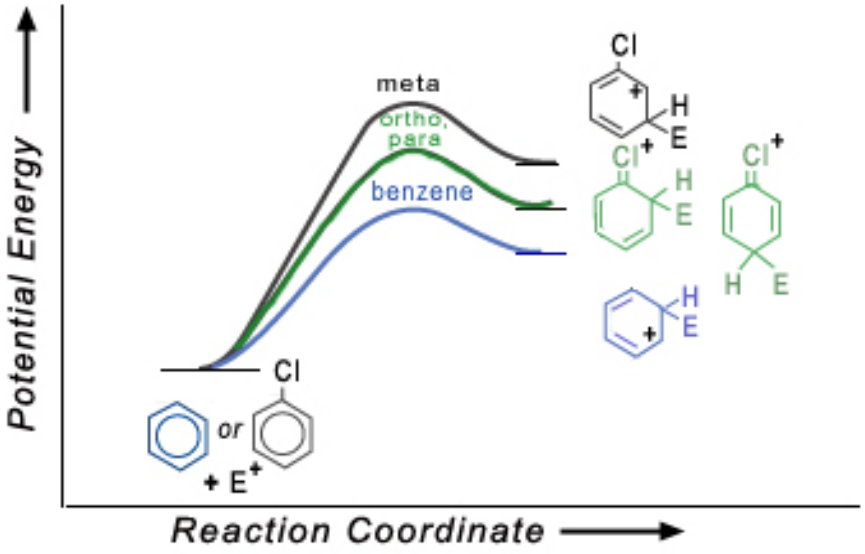
III. Weakly deactivating, ortho/para directing
(eg. -Cl, Inductive/Resonance)



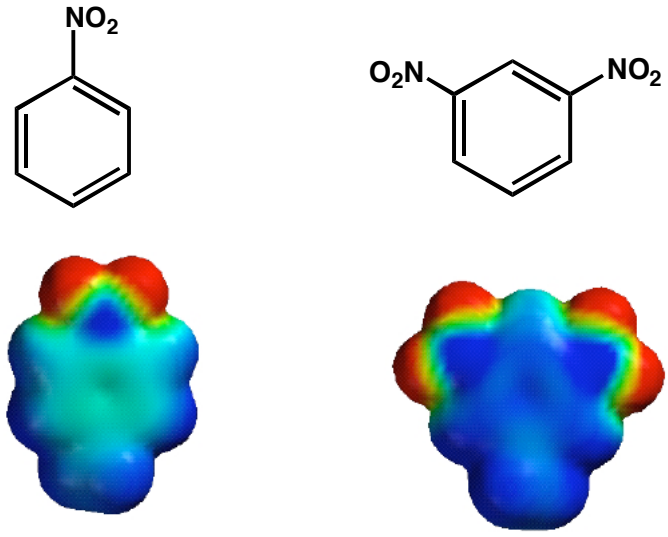


Chlorobenzene

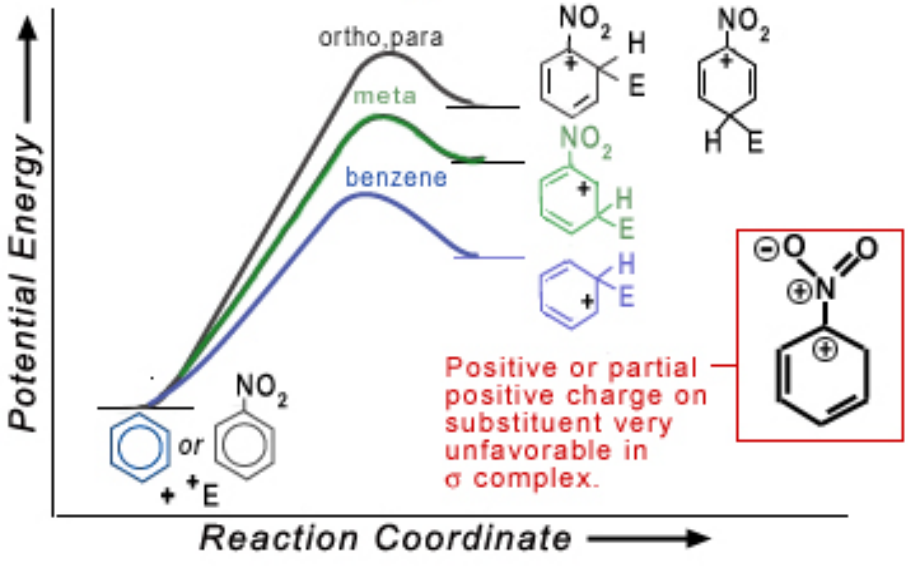
III. Weakly deactivating, ortho/para directing
(eg. -Cl, inductive/resonance)



IV. Deactivating, meta directing (eg. -NO_2, inductive)

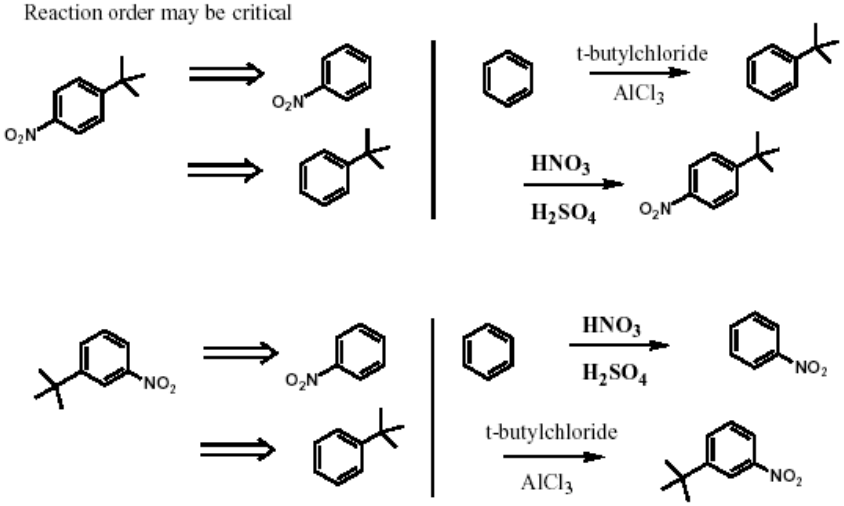


IV. Deactivating, meta directing (eg. -NO_2, inductive)

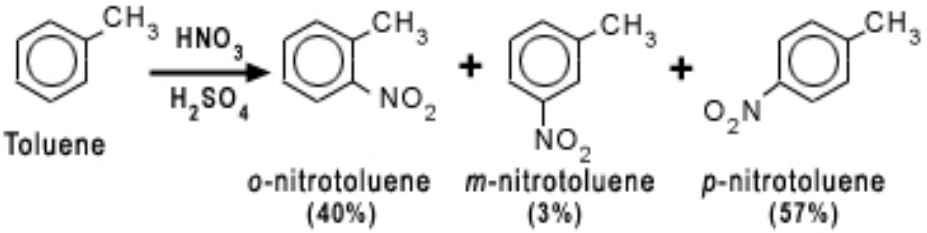


SYNTHETIC STRATEGIES WITH AROMATIC COMPOUNDS

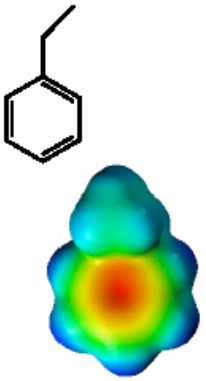
Reaction order may be critical



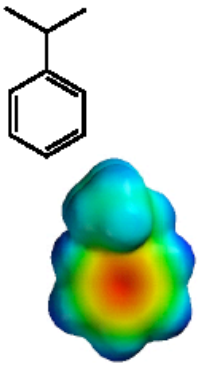
Steric Effects in Electrophilic Aromatic Substitution



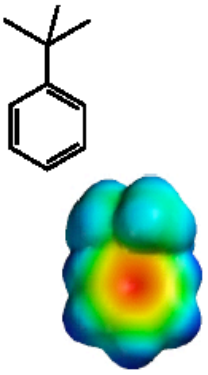
STERIC EFFECTS IN ELECTROPHILIC AROMATIC SUBSTITUTION
Reaction with $Br_2/FeBr_3$ to afford monobrominated derivative
Statistically 66%ortho/33%para)



Ortho 45%
Meta 7%
Para 48%



Ortho 30%
Meta 8%
Para 62%



Ortho 16%
Meta 11%
Para 73%