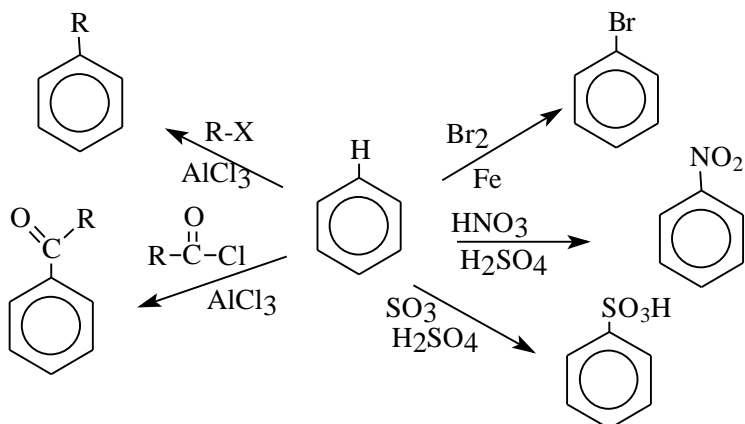


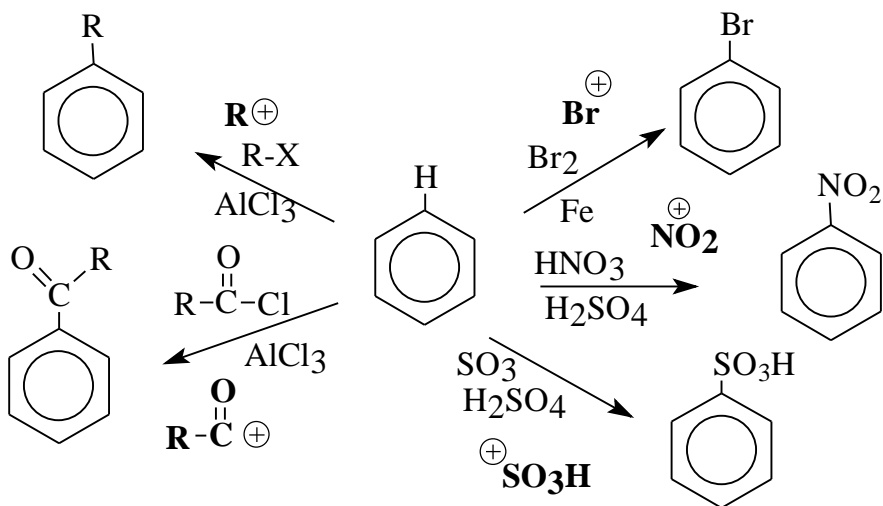
## Chapter 16 – Electrophilic Aromatic Substitution

Aromatic rings **do not** easily undergo addition reactions that would destroy the very stable pi bonding system.

Aromatic rings **do** undergo reactions are substituted for hydrogen atoms on the ring.

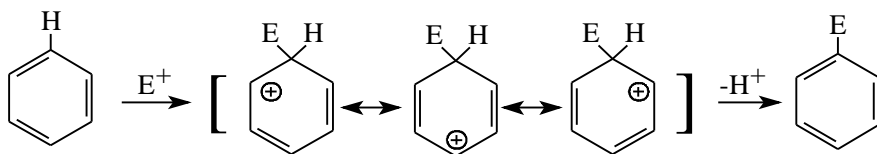


In each case the species that attacks the ring is an electrophile. That is, in most cases it is a positive ion as shown below.



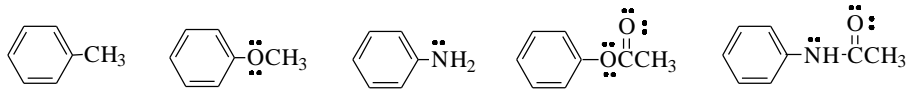
Mechanism of the reaction (cationic intermediate, resonance structures)

Remember that the positive charge is distributed to the positions ortho and para to the *point of attack of the electrophile*.

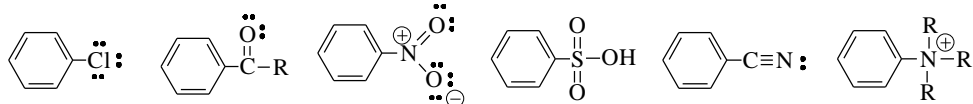


## Substituent Effects

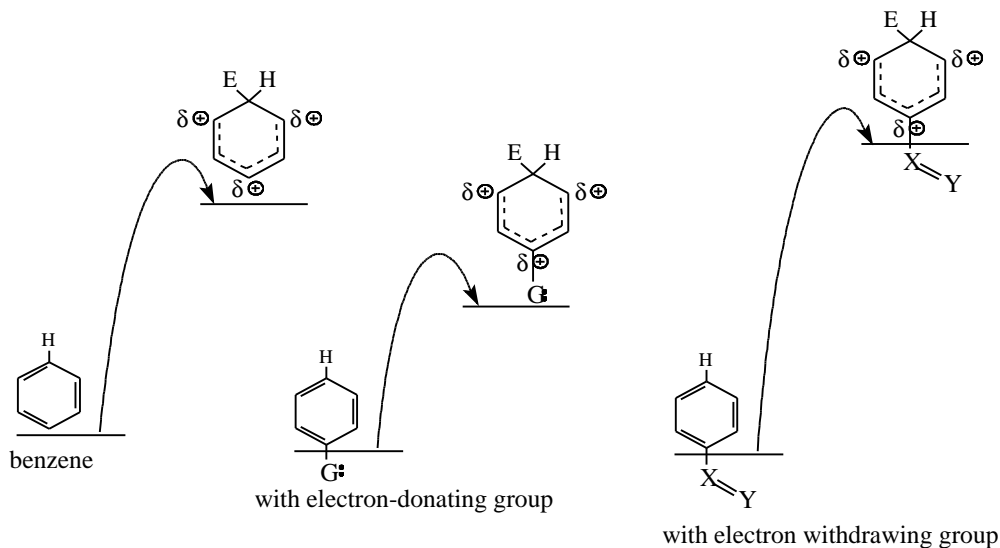
activating groups: electron donating



deactivating groups: electron withdrawing

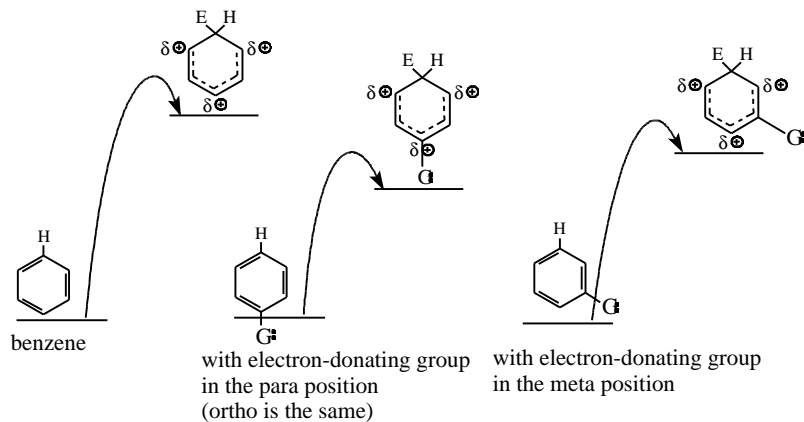


Since electron donating groups absorb some of the positive charge off the ring, they produce lower energy carbocations that are formed faster than the cation from benzene. Electron withdrawing groups have the opposite effect so they cause the reactions to go slower than with benzene.

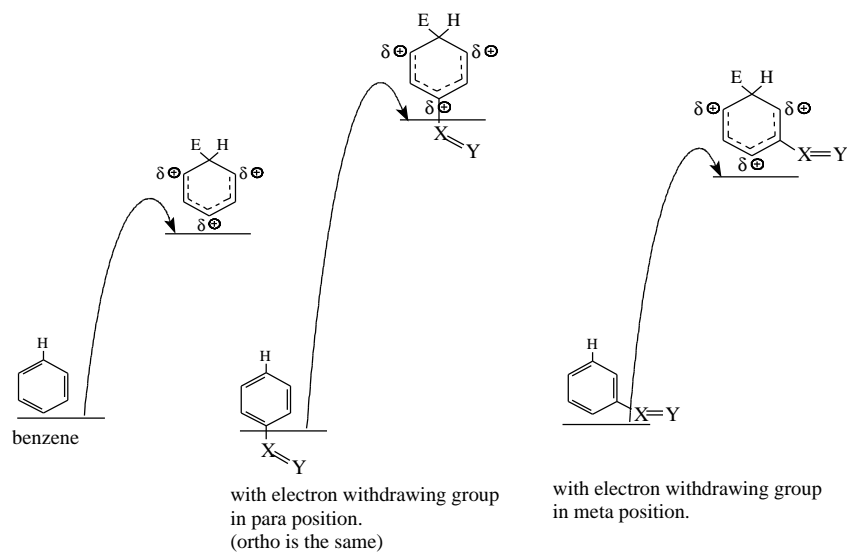


## DIRECTING EFFECTS:

1 Activating groups are generally ortho/para directing. This is because for these transition states they will be donating electron density directly *into* one of the positively charged sites on the benzene ring making those transition states lower in energy.

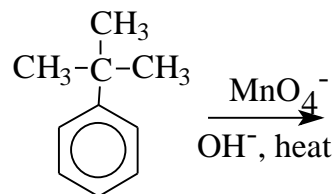
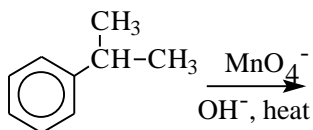
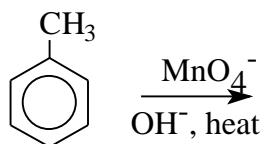
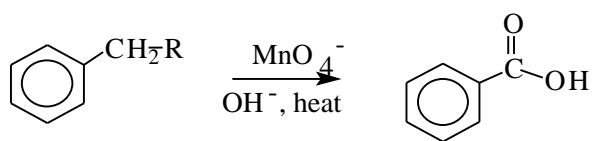


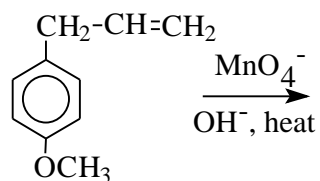
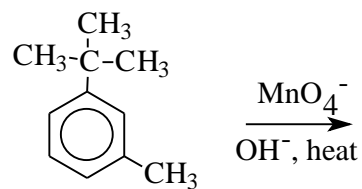
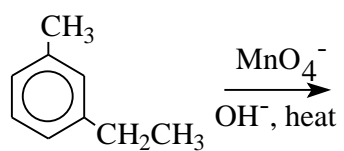
Deactivating groups are generally meta directing. This is because in the transition states for ortho/para attack they are withdrawing electron density directly *from* one of the positively charged sites on the benzene ring making those transition states higher in energy.



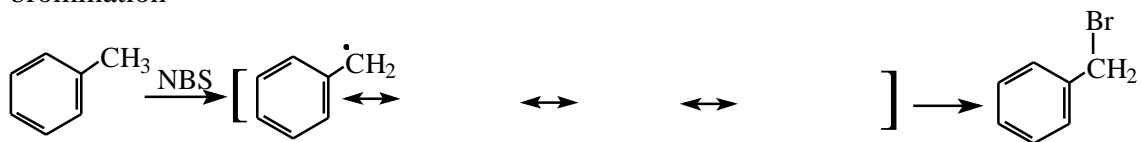
## SIDE-CHAIN REACTIONS

### A. Oxidation

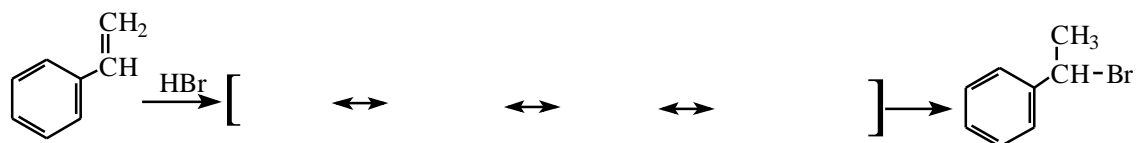




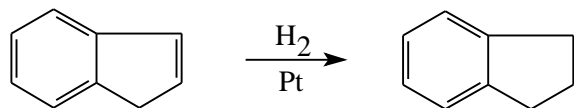
### B. Benzylic bromination



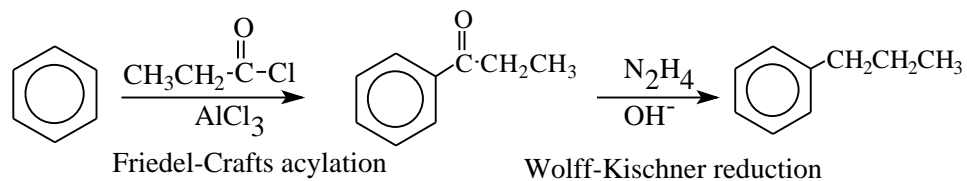
### C. Alkene addition



### D. Alkene Reduction

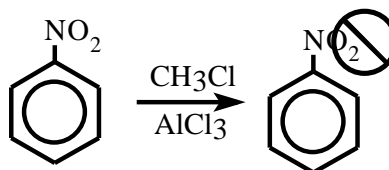


### E. Ketone Reduction



Limitations of the Friedel-Crafts Reaction:

- The reaction does not happen if there are strong deactivating groups attached to the ring.

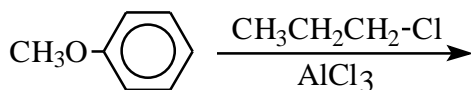
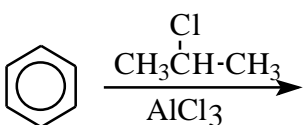
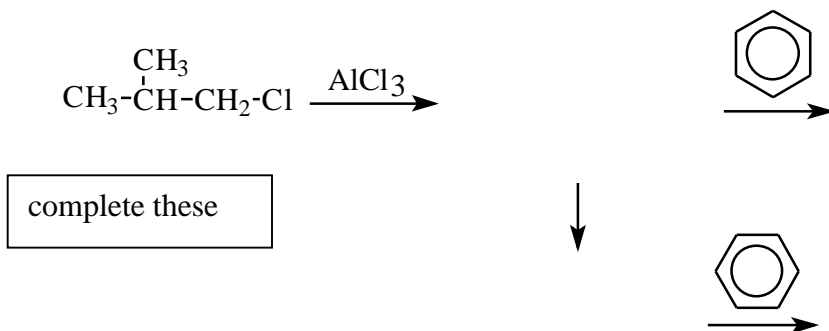


- Since alkyl groups are activating groups the product is more reactive than the reactant so the reaction is difficult to stop after one step.

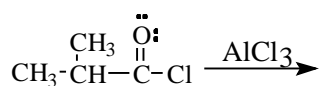


To maximize the yield of the monosubstitution product you must add a large excess of benzene.

- Since the intermediates that attack the ring are carbocations they often rearrange.



So how could you make isobutylbenzene?



Propose sequences of reactions by which each of the following can be synthesized in good yield.

