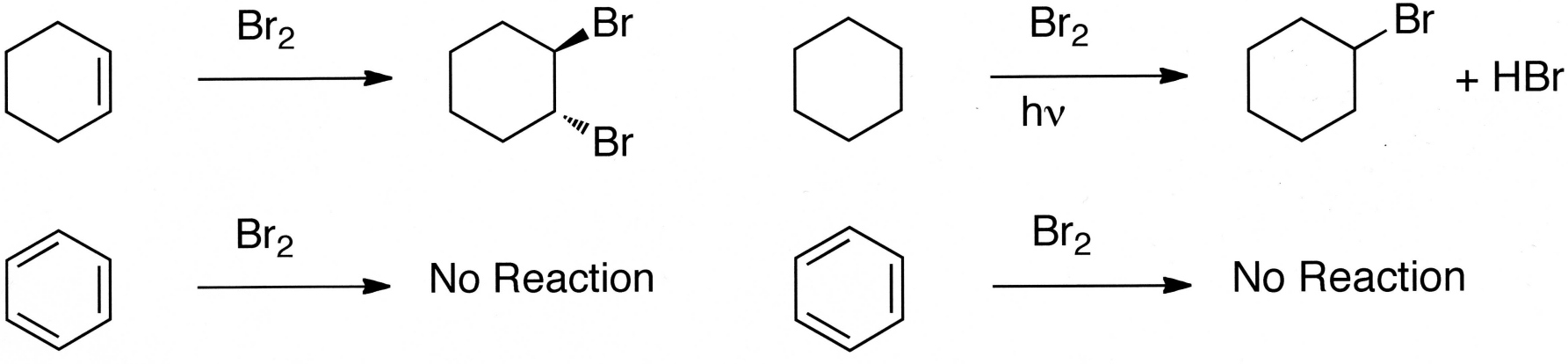
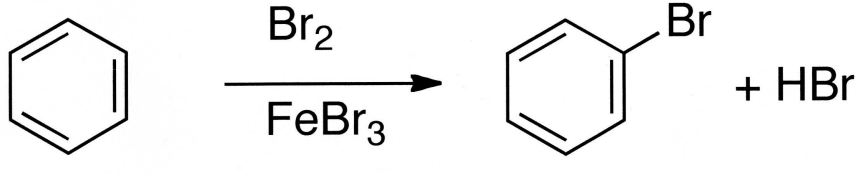
Electrophilic Aromatic Substitution

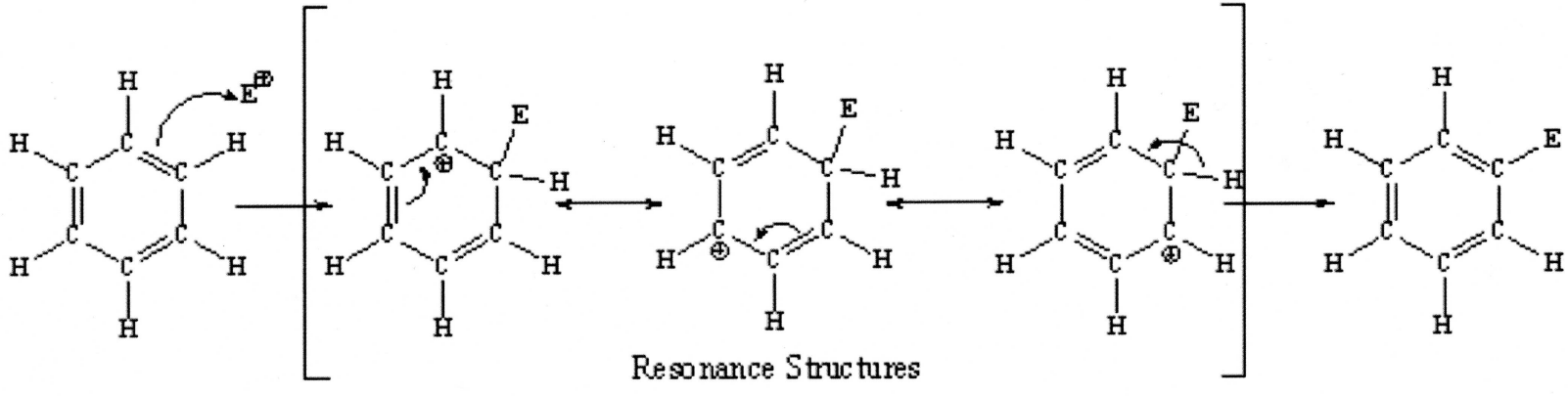
Benzene is remarkably stable and unreactive compared to alkenes and even alkanes



But benzene is not completely unreactive - need Lewis acid catalyst



General Mechanism for Electrophilic Aromatic Substitution



an electrophile (E^+) is substituted for a hydrogen on the aromatic ring

the pi system of the benzene ring acts as the nucleophile

cation formed in the reaction is resonance stabilized but not aromatic

note that the postive charge is ortho and para to the electrophile

last step (loss of proton) is fast to regenerate the aromatic system

Electrophilic Aromatic Halogenation

MX_3 ($FeBr_3$, BCl_3, $AlCl_3$) is a Lewis Acid catalyst

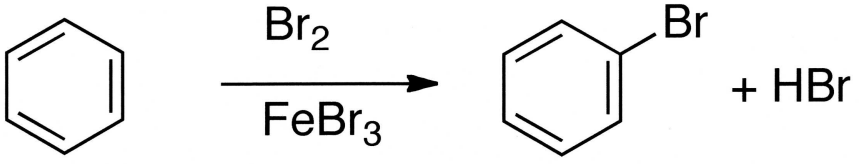
X_2 is the halogen, usually Cl_2 or Br_2

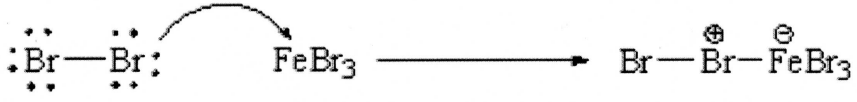
catalyst converts the halogen into a stronger electrophile

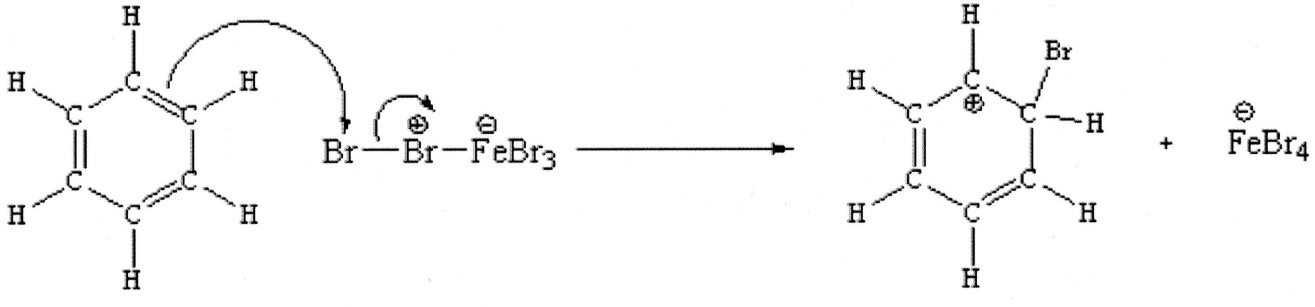
Lewis acid is substance that accepts a pair of electrons

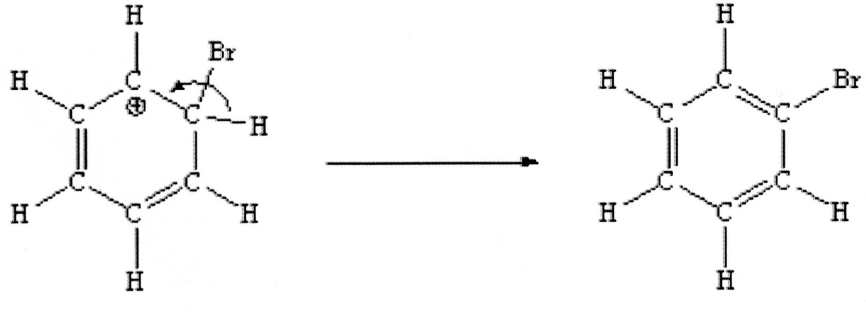
In halogenation the Lewis Acid catalyst is regenerated at the end

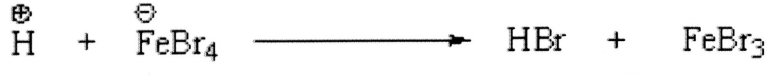
Electrophilic Aromatic Halogenation Mechanism





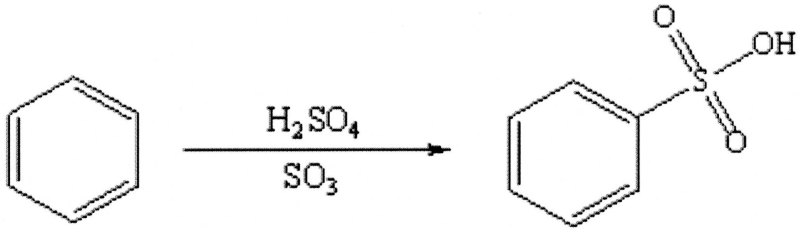


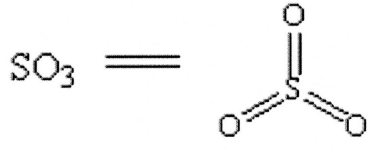




In halogenation the Lewis Acid catalyst is regenerated at the end

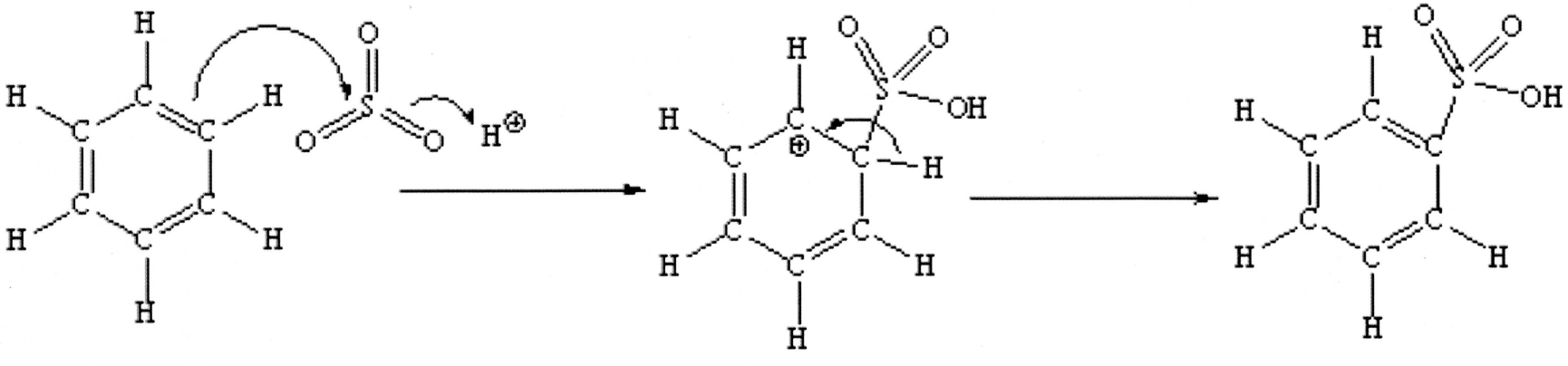
Sulfonation as Electrophilic Aromatic Substitution



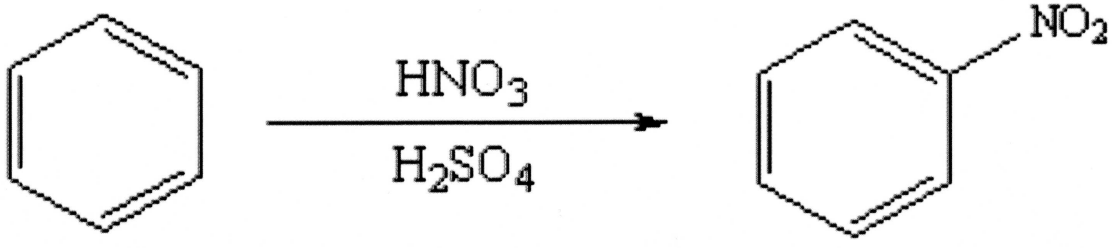


In this reaction, SO_3 is the electrophile

Mechanism:

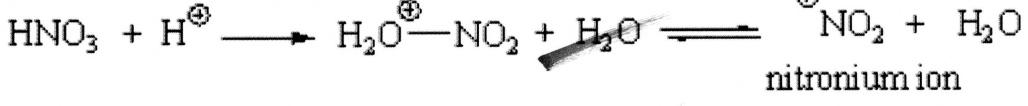


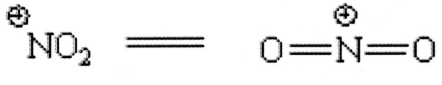
Nitration as Electrophilic Aromatic Substitution

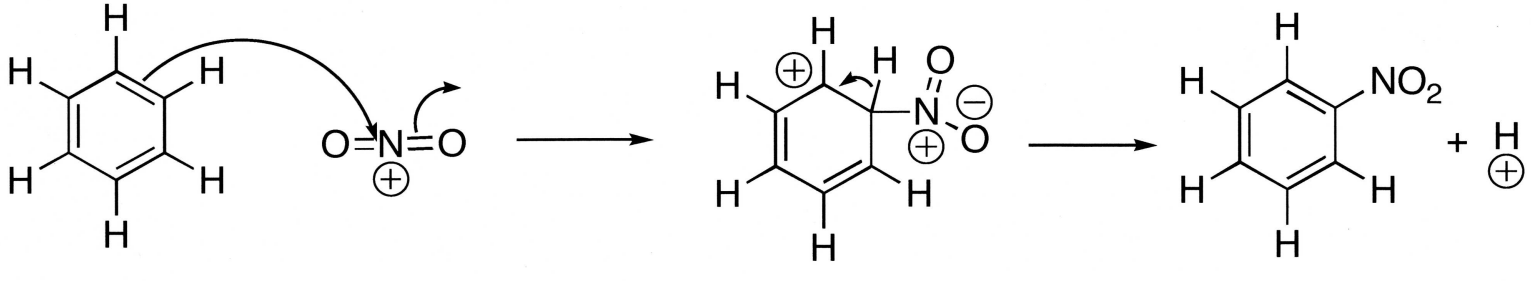


In this reaction, NO_2^+ is the electrophile

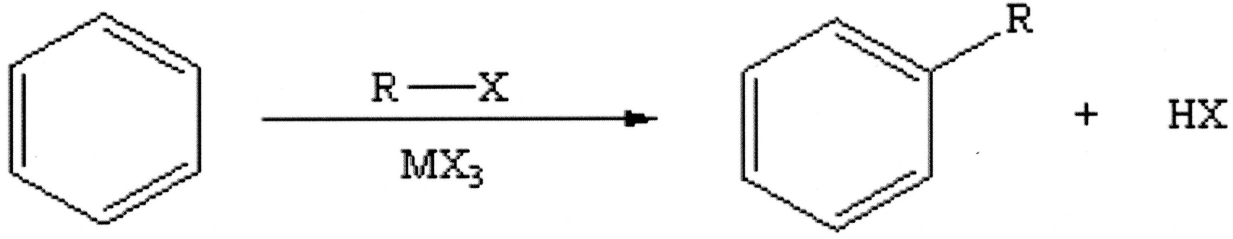
Mechanism:







Alkylation (Friedel Crafts) as Electrophilic Aromatic Substitution

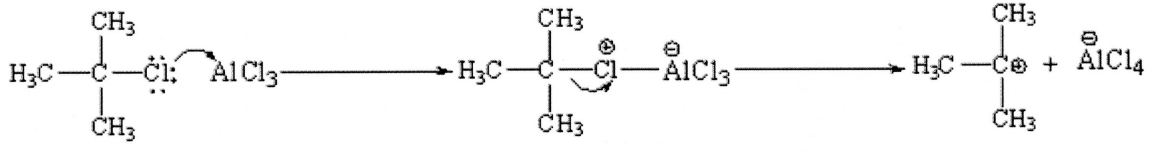


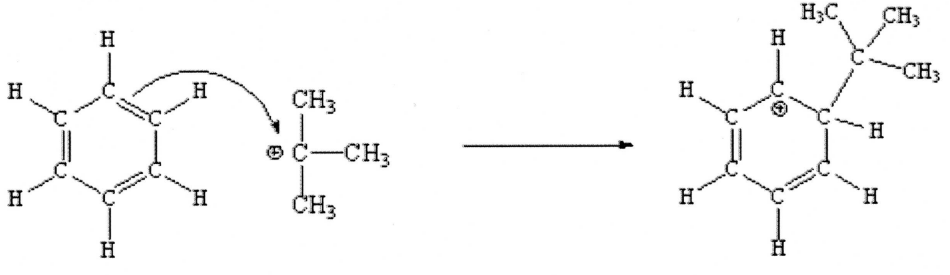
Where R = alkyl (methyl, ethyl, isopropyl, *tert*-butyl, etc)

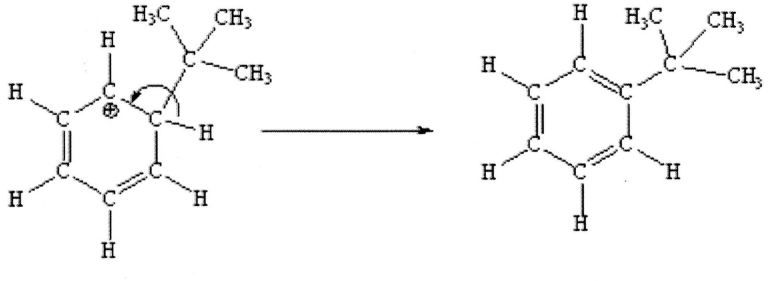
X = halogen: Cl, Br, I

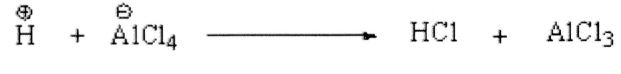
MX_3 = Lewis acid: e.g. BCl_3, $FeCl_3$, $AlCl_3$

Mechanism:



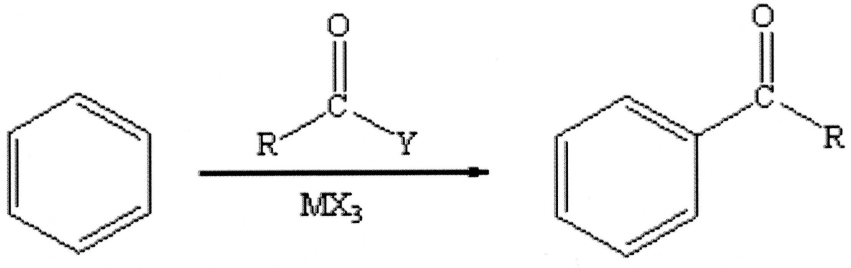




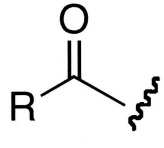


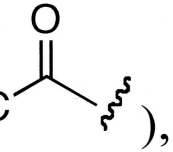
In this reaction, R^+ is the electrophile

Acylation (Friedel Crafts) as Electrophilic Aromatic Substitution



Y = halogen (Cl, Br, and I), or OCOR (carboxylate part of anhydride)

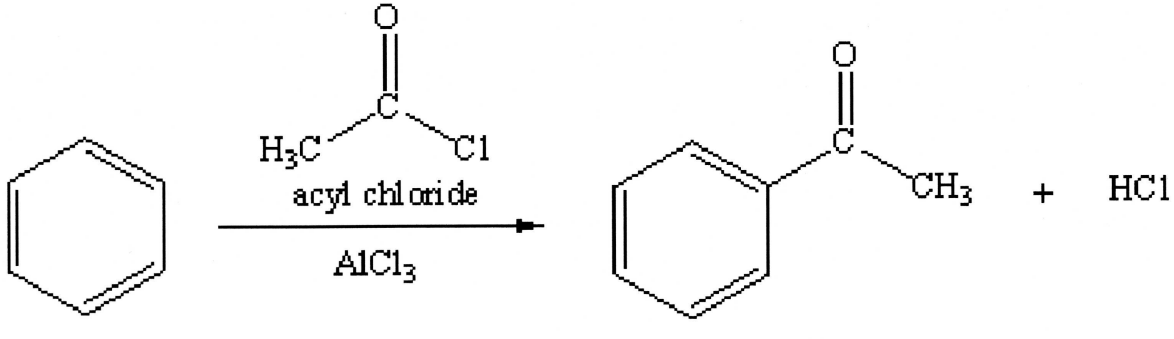
An acyl group = 

. When R=CH_3, the group is called acetyl (

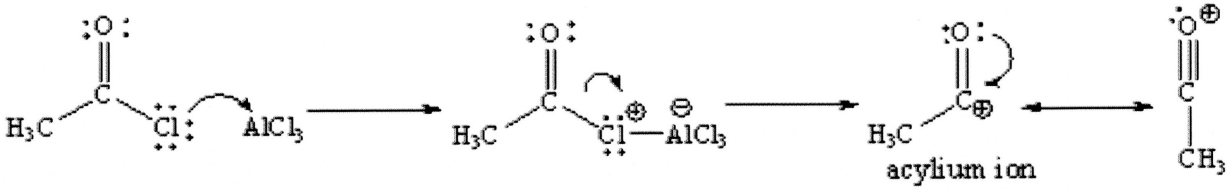
),

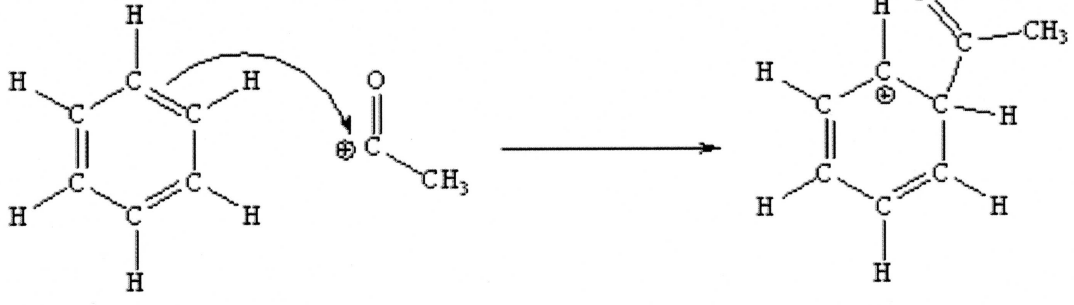
Example:

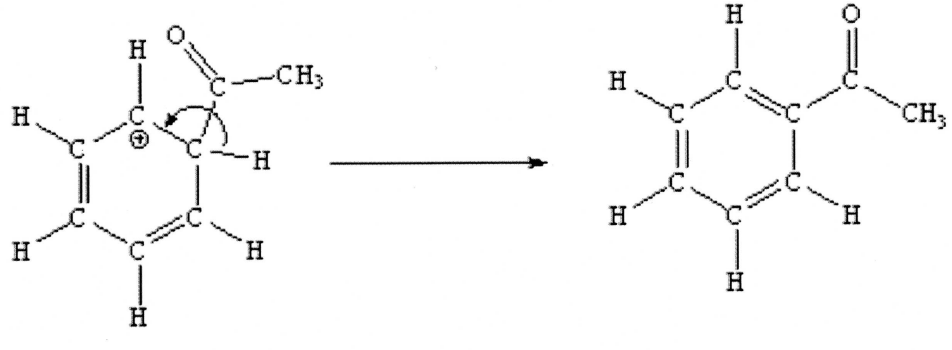
In this reaction, RCO^+ is the electrophile

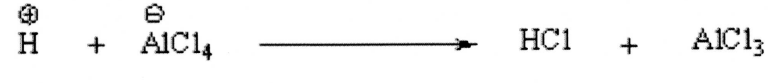


Acylation (Friedel Crafts) Mechanism:









Electrophilic Aromatic Substitution for Substituted Benzenes (see handout)

Substituents already present on the benzene ring determine:

the **position** of reaction and

the **reactivity** of the system

Resonance and Inductive Effects

A substituent can **donate** or **withdraw** electrons from the aromatic ring in 2 ways:
by inductive effects and by resonance effects

Resonance Effect:

* Through pi (double bond) system (due to conjugation)
* Strong effect
* Can be e-donating (ortho-para directing) or withdrawing (meta directing)

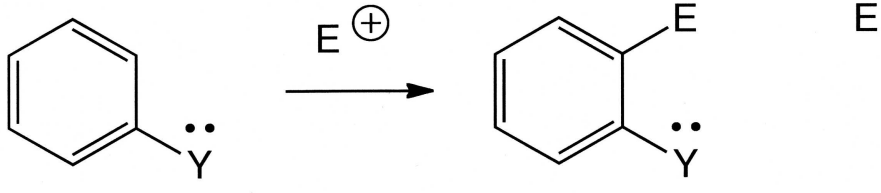
Inductive Effect:

* Through sigma (single bond) system (due to electronegativity of atoms)
* Weaker effect
* Can be e-donating (ortho-para directing) or withdrawing (meta directing)

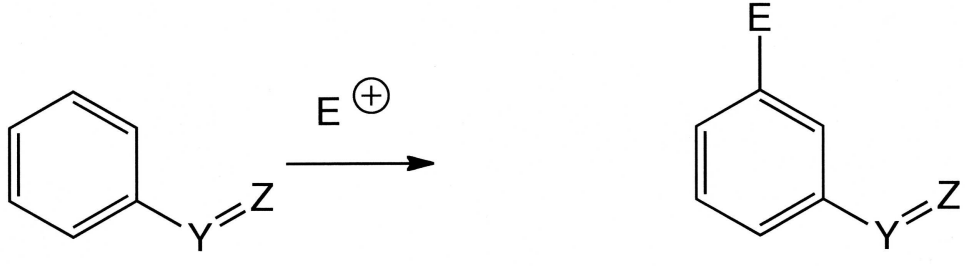
How to determine position & reactivity

Substituents already present on the benzene ring determine:

the **position** of reaction and the **reactivity** of the system



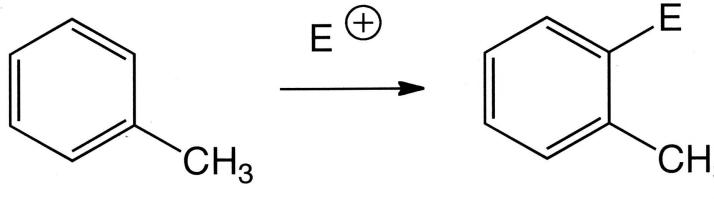
ortho-para
activating



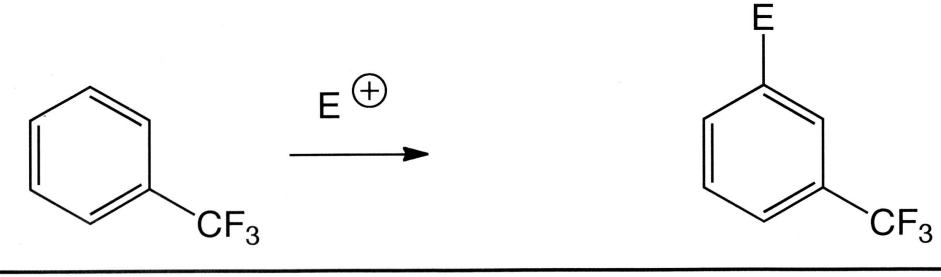
meta
deactivating

resonance

strong



ortho-para
activating



meta
deactivating

inductive

weak