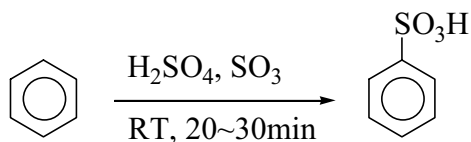
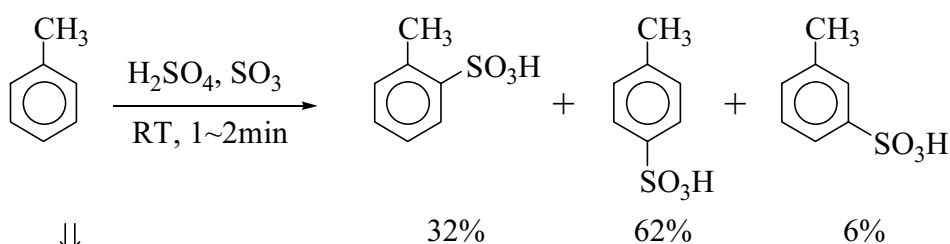


## Chapter 15

the  $\pi$  electrons in PhH are more tightly held than in olefin  $\Rightarrow$  loose enough to react with electrophile  $\Rightarrow$  electron source (act as a base)



$\Downarrow$   
 electrophilic substitution rxn rather than electrophilic addition rxn to maintain aromaticity

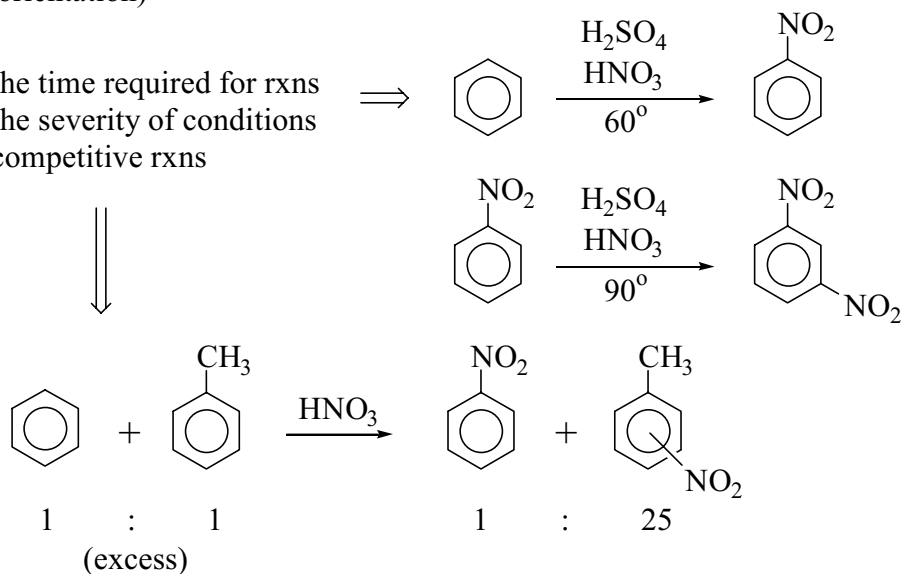


reactivity : activating group & deactivating group  
 orientation : ortho, para director & meta director

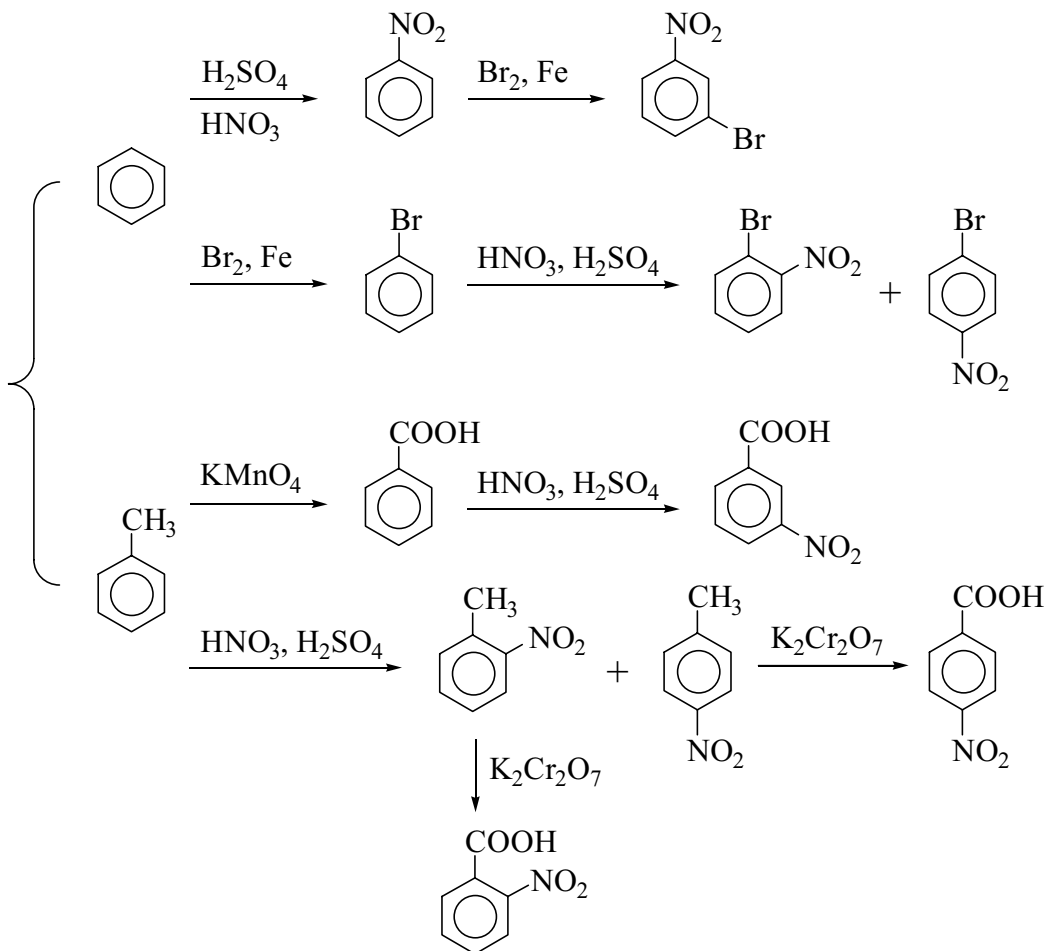
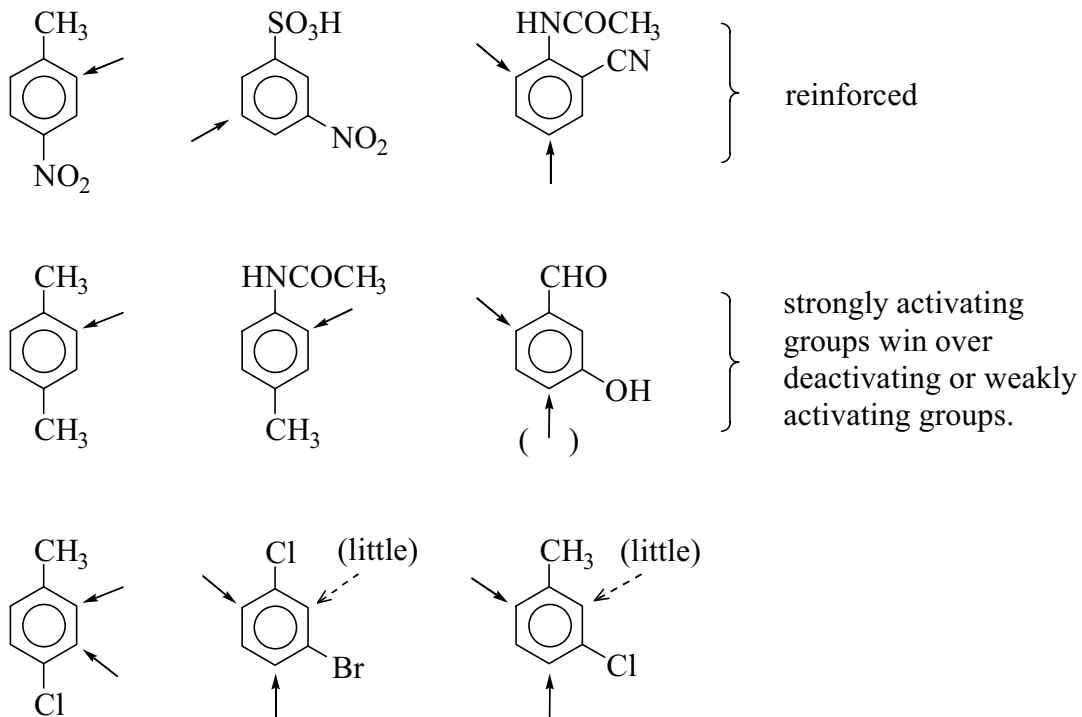
$\Downarrow$   
 CH<sub>3</sub> : activating group & ortho, para director

$\Downarrow$   
 Table 15.1 (orientation)

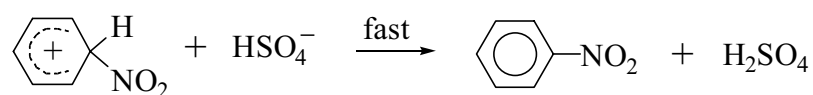
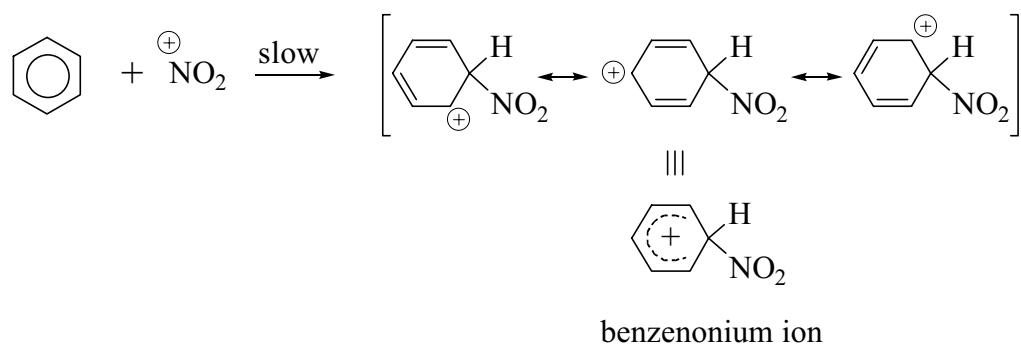
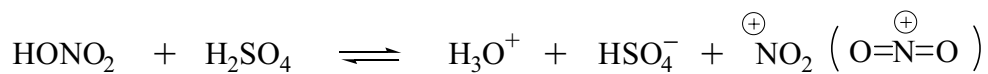
$\Downarrow$   
 reactivity : the time required for rxns  
 the severity of conditions  
 competitive rxns



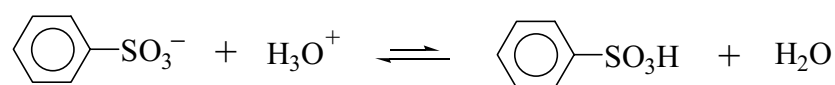
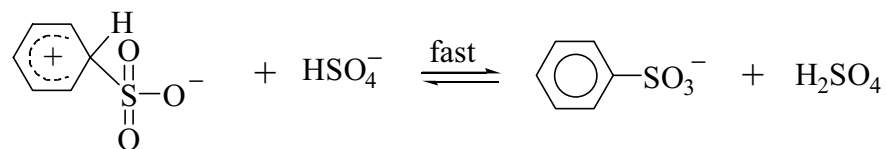
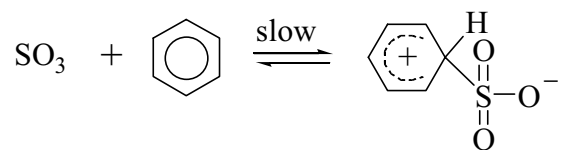
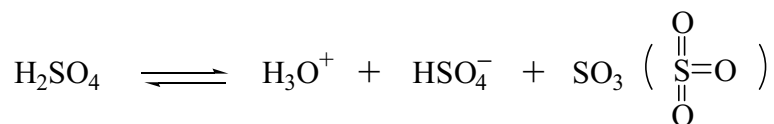
$\Downarrow$   
 Table 15.3



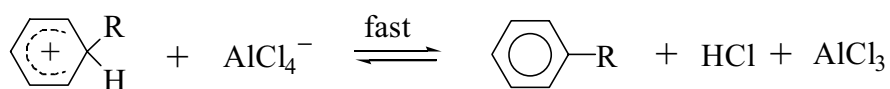
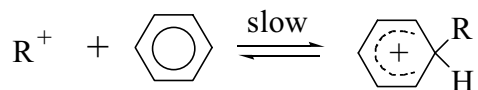
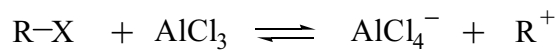
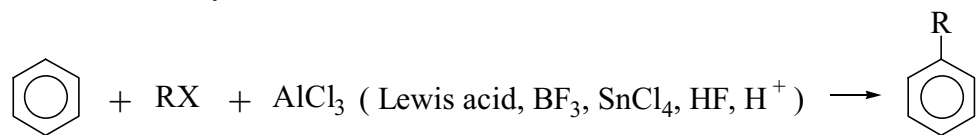
## Nitration



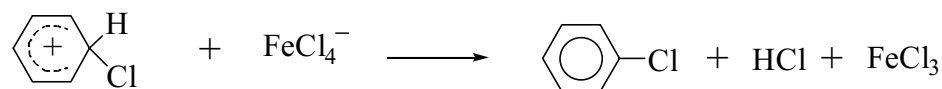
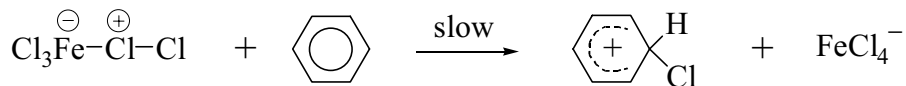
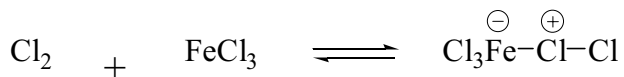
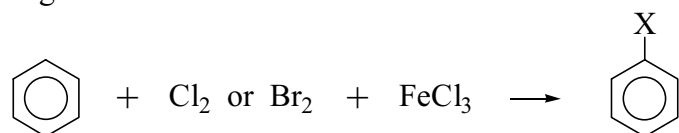
## Sulfonation



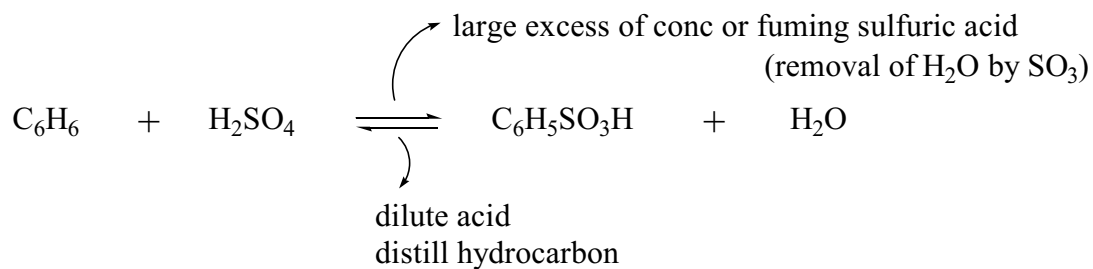
### Friedel-Crafts alkylation

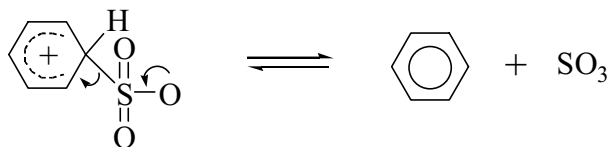
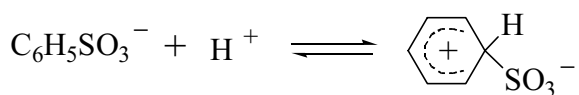


### Halogenation

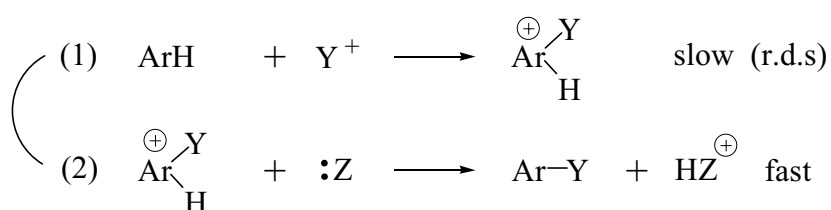


highly reactive aromatic compds react with halogen without Lewis acid.

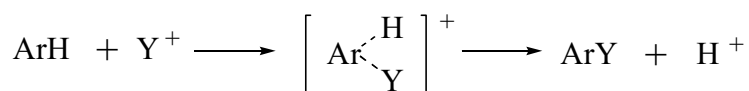




General mechanism of electrophilic aromatic substitution



not

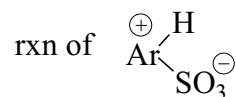


for nitration, bromination, Friedel-Crafts alkylation  $\Rightarrow$  no significant isotope effect

$\Downarrow$

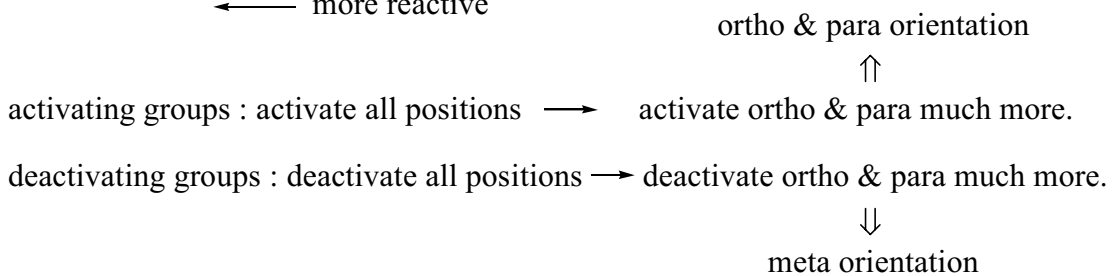
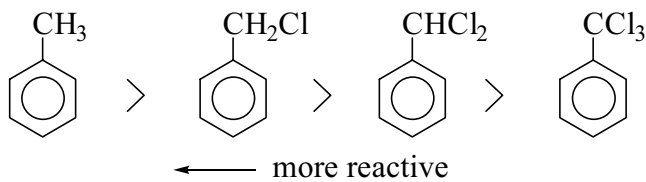
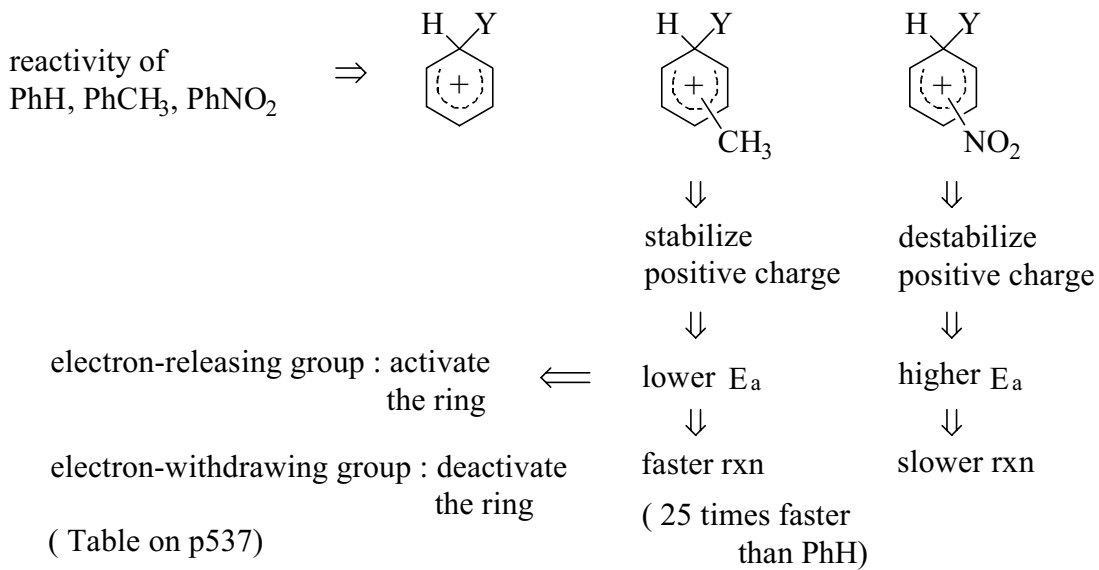
Fig 15.2  $\Leftarrow$  step(1) is r.d.s.  $\Leftarrow$  not one step reaction  $\Leftarrow$  C-H bond breaking is not r.d.s.  $\Leftarrow$  step(2) is fast

for sulfonation,  $k_{\text{H}}/k_{\text{D}} \approx 2 \Rightarrow$  comparable  $E_a$  of forward and reverse



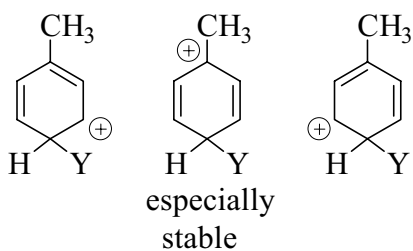
$\Downarrow$

Fig 15.3

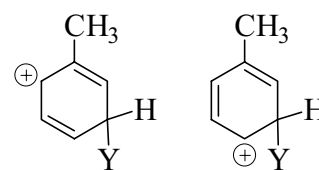


<for toluene>

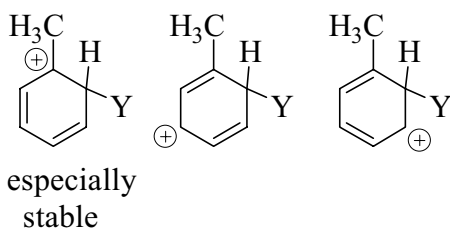
para attack



meta attack

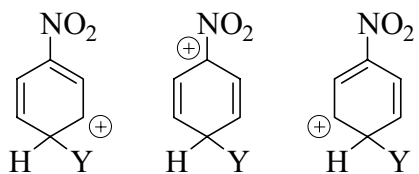


ortho attack



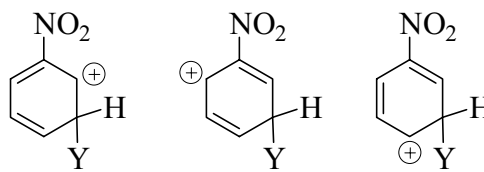
<for nitrobenzene>

para attack

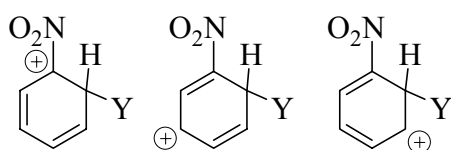


especially  
unstable

meta attack



ortho attack



especially  
unstable

PhNRR', PhOR : N and O show electron-withdrawing inductive effects

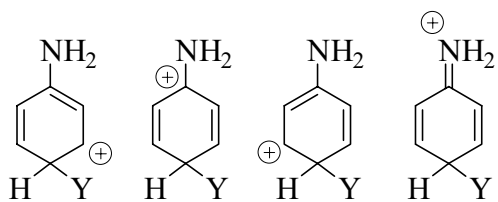
but electron-donating resonance effect  $\Rightarrow$  strong activator

$\downarrow$

much more reactive than benzene

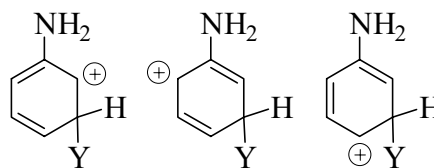
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para

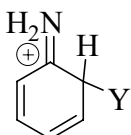


especially  
stable  
(complete octet)

meta

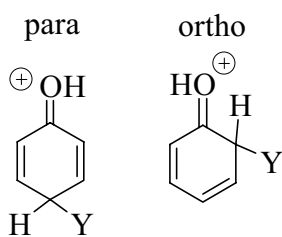


ortho

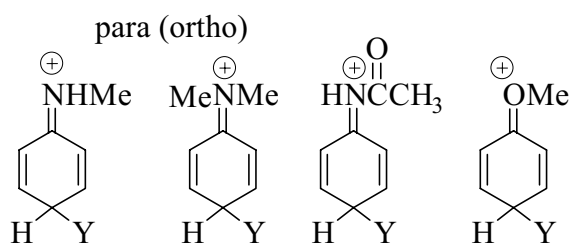


especially  
stable  
(complete octet)

<phenol>



<others>

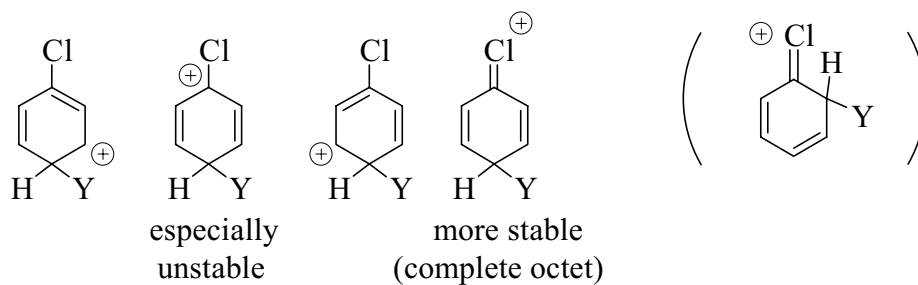


Ph-X : X  $\Rightarrow$  deactivate  $\implies$  electron - withdrawing  $\Rightarrow$  by inductive effect

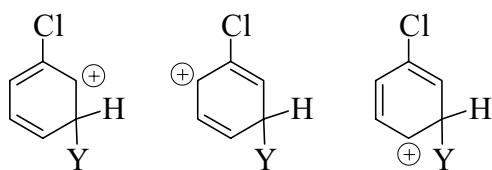
para, ortho orientation  $\Rightarrow$  electron - donating  $\Rightarrow$  by resonance effect

<chlorobenzene>

para (ortho)



meta



<naphthalene>

