

# Substitution reactions in Aromatic compounds

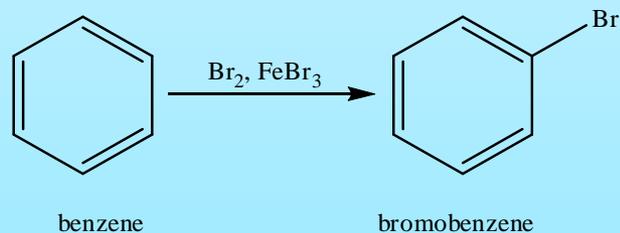
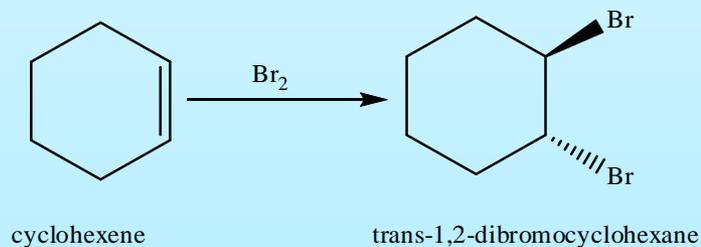
**Key words:** Aromatic electrophilic substitution, Directing effect, Friedel Crafts Reaction, Nitration, Sulfonation, Halogenation, Addition Elimination, Benzyne intermediate

# Introduction

- In this module, various substitution reactions are discussed. Classification based on the incoming group, as electrophilic and nucleophilic, is followed. Mechanism is described in detail and large number of general and specific examples are provided.

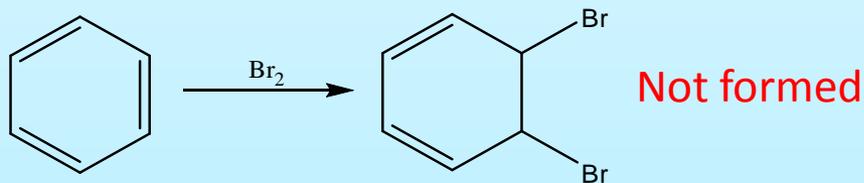
# Electrophilic substitution

- Aromatic compounds, unlike aliphatic compounds, undergo **substitution** in aromatic nucleus when treated with suitable electrophiles.
- Comparison of reaction between cyclohexene with bromine and that of benzene with bromine can explain this.



❑ Difference between this kind of behavior of benzene towards bromination originates from it being **aromatic**.

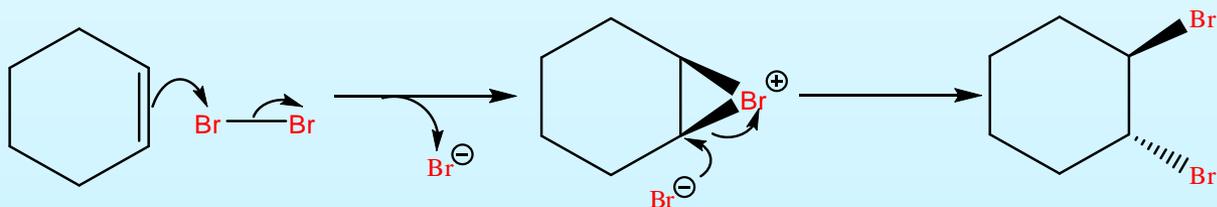
❑ If we assume a direct 1,2-addition of  $\text{Br}_2$  across one of the double bonds of benzene, the product obtained would be non-aromatic



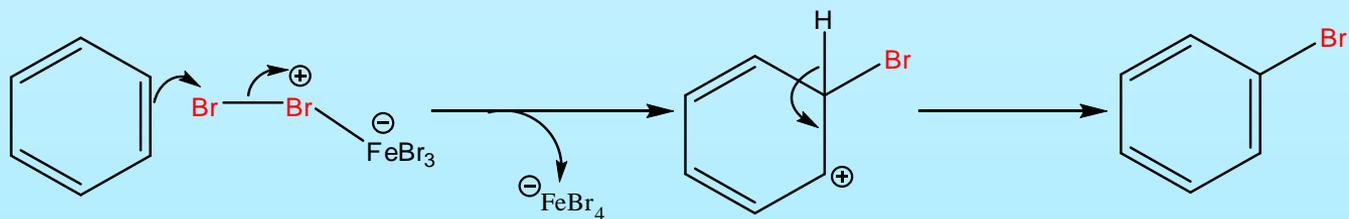
❑ Such a reaction is not favorable, thermodynamically.

❑ Its electrophilic substitution with bromine is only compatible in the presence of some strong **Lewis acid**, making bromine electrophilic.

□ Mechanism of addition to cyclohexene is as follows;

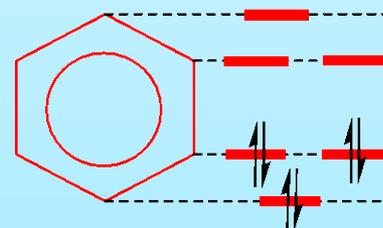
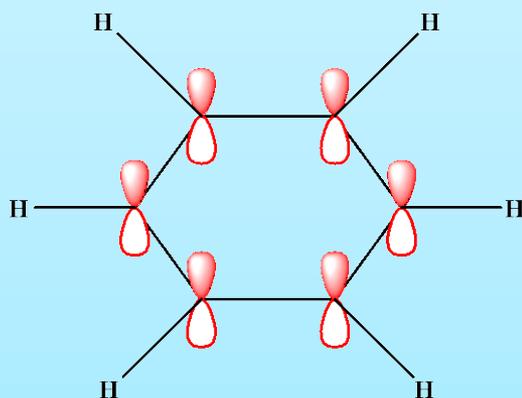


□ Whereas, mechanism of bromination in the presence of  $\text{FeBr}_3$  can be given as follows;  
[here bromine is made more electrophilic by its association with the Lewis acid]



□ Intermediate in both the reactions is cation. But, it is **bridged cation** in first while stable **arenium ion** (resonance stabilized) in the second case.

- ❑ First intermediate adds anion while second loses a proton so as to restore its aromatic character.
- ❑ This unusual behavior of benzene can be explained by taking into account its orbital interaction.
- ❑ Benzene is a planar molecule having six  $\pi$  electrons in three  $\pi$ -molecular orbitals. These are made up of overlap of six atomic p orbitals on carbon atom [for additional details refer to: molecular orbitals of common functional groups]



- ❑ These atomic orbitals are placed in such way that the molecule attains extra stability ( $140\text{KJmol}^{-1}$ ) than conjugated double bonds in aliphatic system.

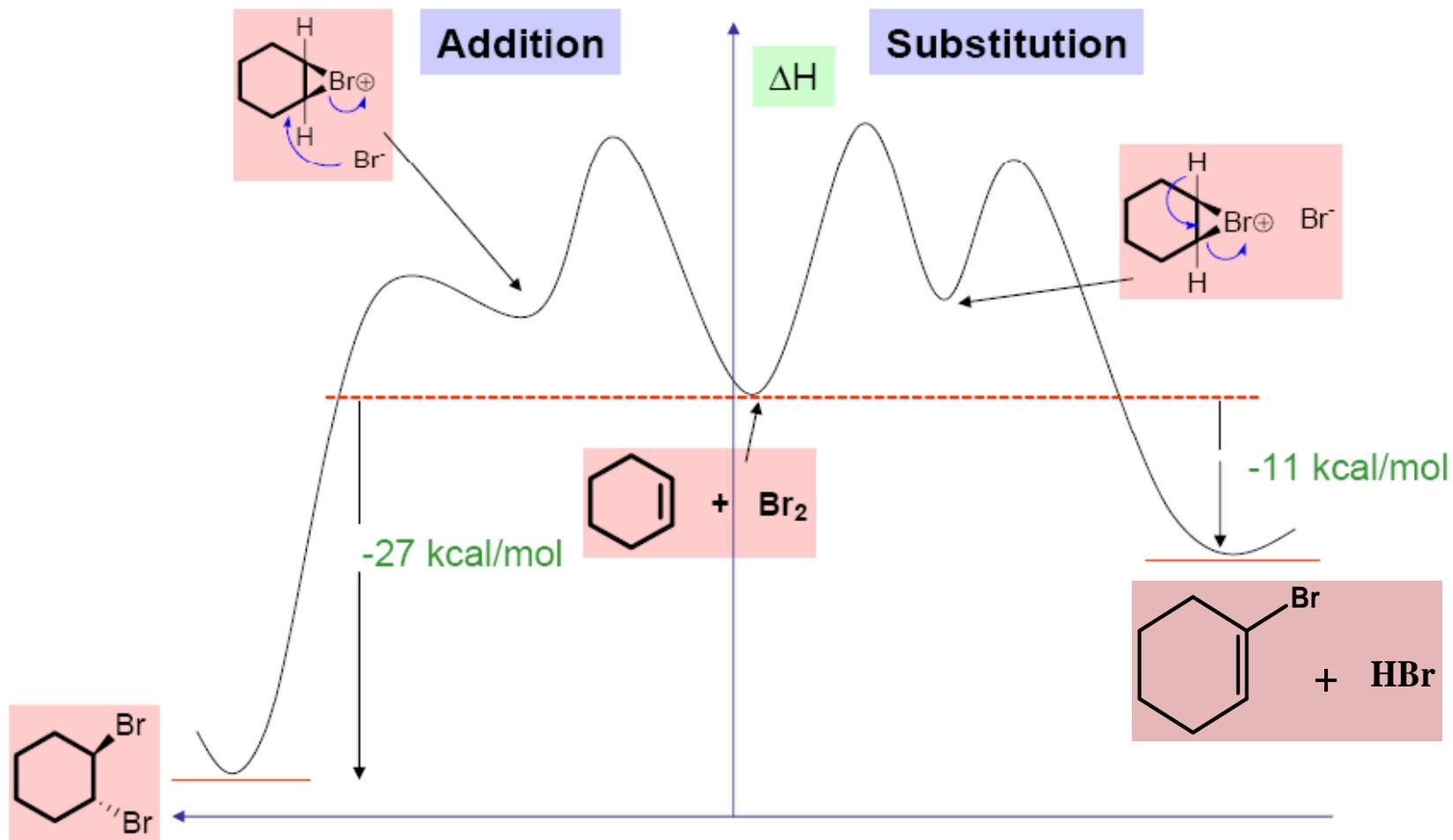
□ It is again indicated by shift of equivalent hydrogen in PMR spectrum ( $\delta_{\text{H}}$  7.2 ppm) showing presence of ring current and a fully delocalized  $\pi$  system.

□ The special reactivity of aromatic systems towards electrophile arises mainly from two factors:

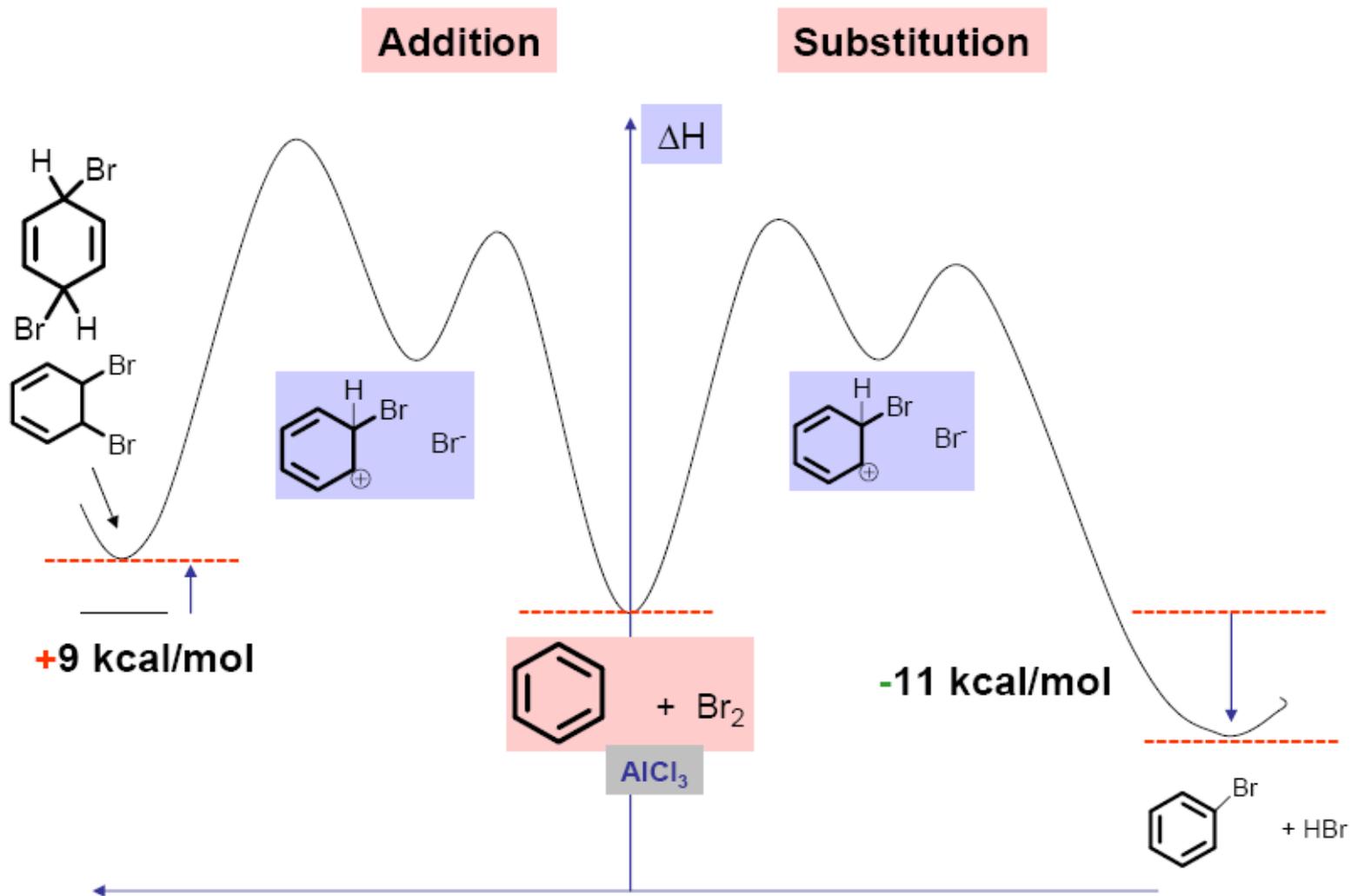
- a. presence of  $\pi$  electron density above and below the plane of the ring - making it nucleophilic.
- b. drive to regain the aromatic character by opting for substitution as opposed to a simple addition reaction.

□ It can be best explained by energy profile diagrams of two reactions:

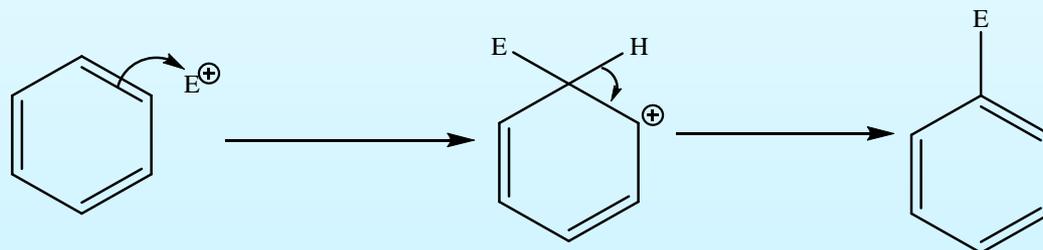
# Energy profile in the case of Olefins – Addition vs. Substitution



# Energy profile in the case of Benzene – Addition vs. Substitution



□ Mechanism for general reaction can be given as follows:

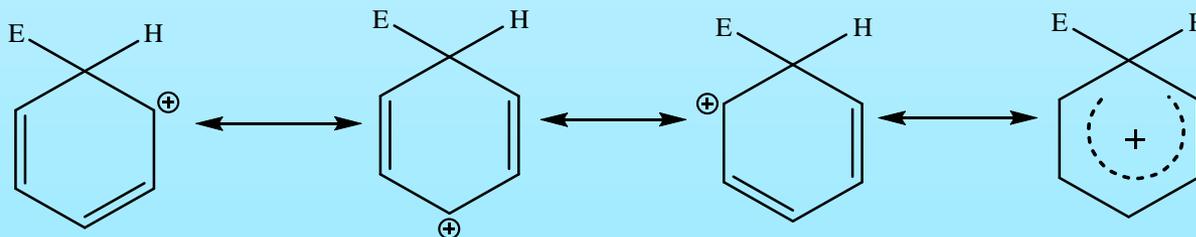


E<sup>+</sup>: electrophile

□ Two step mechanism:

- first step is the rate determining involving interaction of the  $\pi$  system with the electrophile to give a **benzenium ion** intermediate
- it undergoes a rapid **de-protonation** by the base in the second step to restore aromaticity

□ The benzenium ion formed exists in several **resonance** forms



□ Some common electrophilic aromatic substitution reactions are:

a) Halogenation

b) Nitration

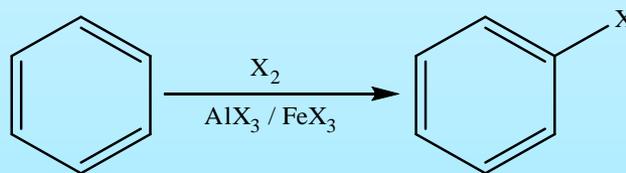
c) Sulfonation

d) Friedel-Crafts **alkylation** and Friedel-Crafts **acylation**

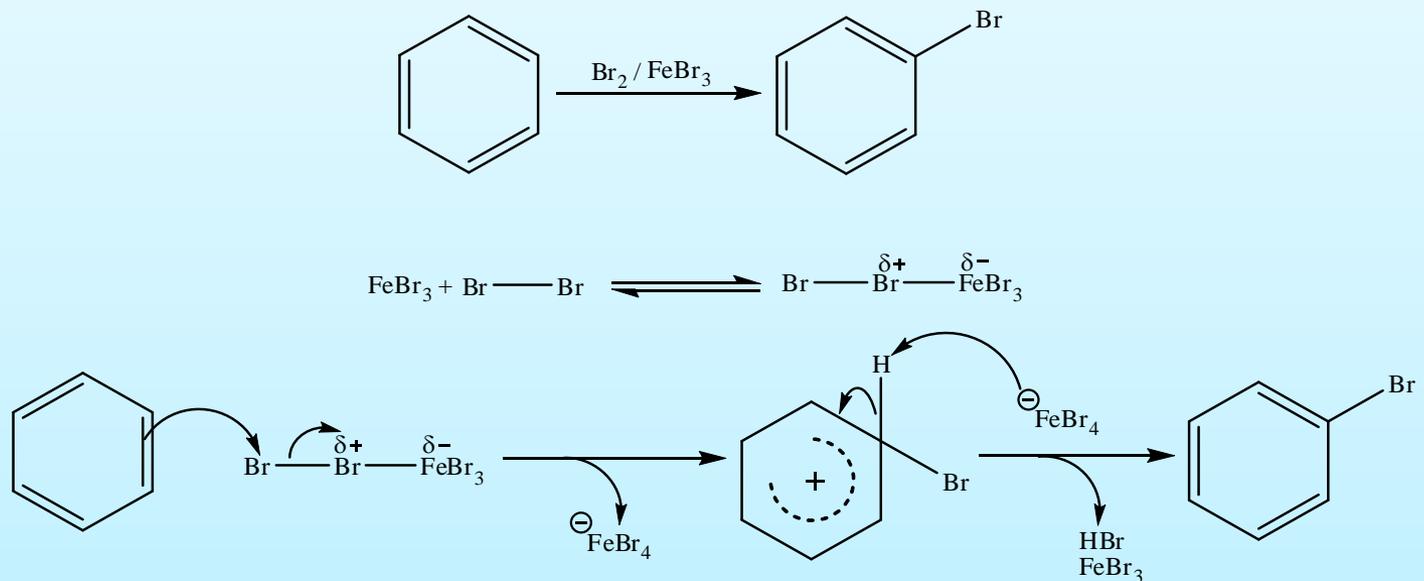
□ These differ only in the nature and mode of generation of electrophile, but in general follow the same two-step mechanism described above.

# Halogenation

- ❑ Reaction of halogens with aromatic compound in the presence of Lewis acid
- ❑ Electrophile is a halonium ion i.e. a cation of halogen ( $X^+$ )
- ❑ Main function of the Lewis acid is to polarize halogen-halogen bond
- ❑ Reaction goes as follows:



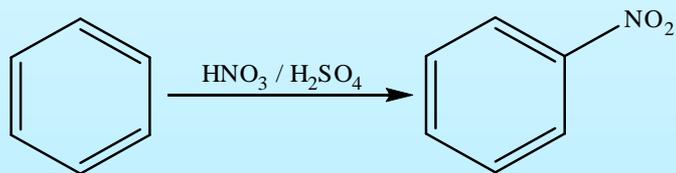
X: Bromine, Chlorine.



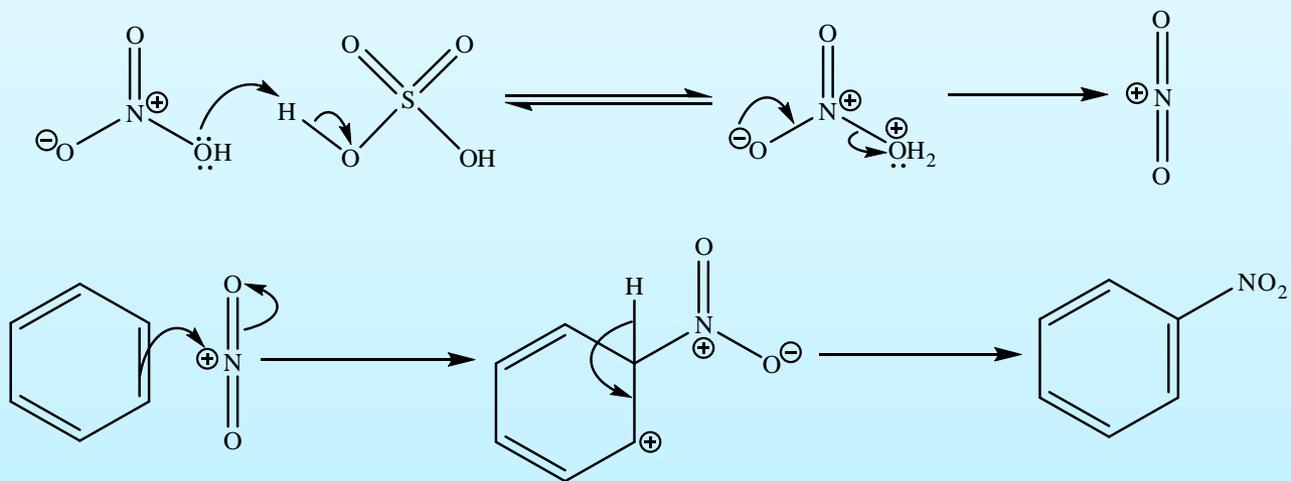
- ❑ X can be chlorine or bromine
- ❑ Analogous reactions with iodine or fluorine are not synthetically useful because  $\text{I}_2$  is too unreactive and  $\text{F}_2$  reacts too violently.
- ❑ Iodination requires an acidic oxidizing agent, like nitric acid, which oxidizes the iodine to an iodonium ion.

# Nitration

- ❑ Where a H atom attached to an aromatic ring is replaced by a  $\text{NO}_2$  group
- ❑ Reaction conditions are concentrated nitric and sulfuric acid at elevated temperature



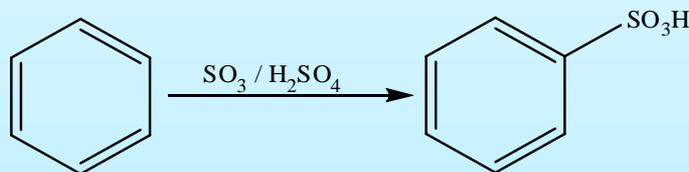
- ❑ Nitronium ion ( $\text{NO}_2^+$ ) is the electrophile that attacks the benzene ring
- ❑ Generation of the electrophile in nitration requires strong acid



- ❑ Mechanism is similar to that of typical aromatic electrophilic substitution
- ❑ Sulfuric acid is stronger and protonates nitric acid, which loses water molecule to give electrophile, nitronium ion.
- ❑ Introduction of nitro group in aromatic system is of particular significance because it provides general entry into aromatic nitrogen containing compounds

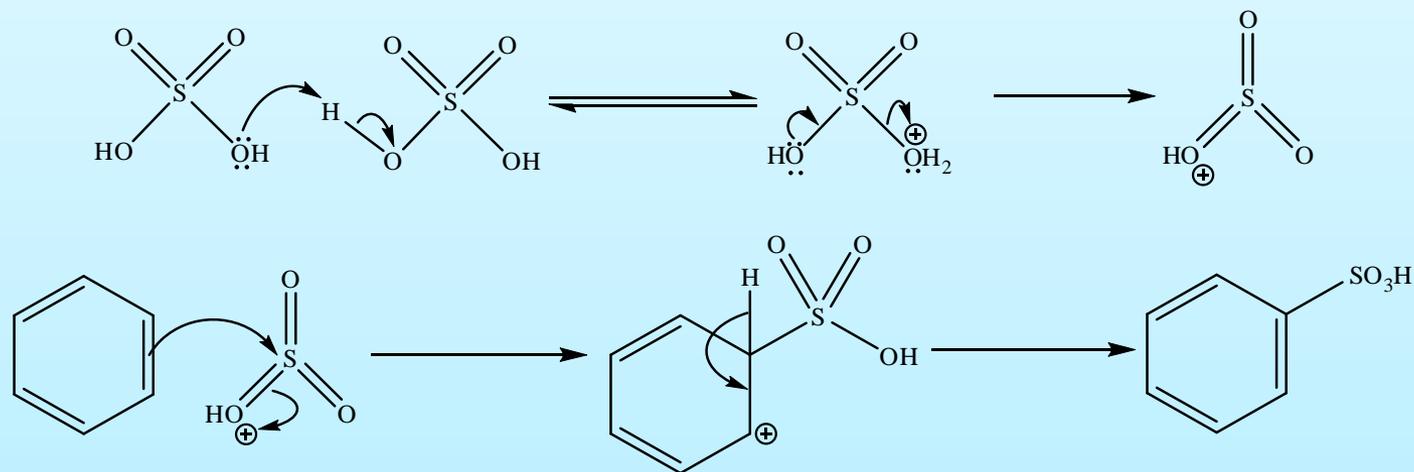
# Sulfonation

- Introduction of **sulfonic acid group** to aromatic system by treatment with concentrated sulfuric acid



- Sulfur trioxide,  $\text{SO}_3$ , in fuming sulfuric acid is the electrophile (This mixture is industrially known as **oleum**)
- Or benzene reacts slowly with sulfuric acid to give benzenesulfonic acid

Two molecules of sulfuric acid react to form electrophile and then reaction goes through general route



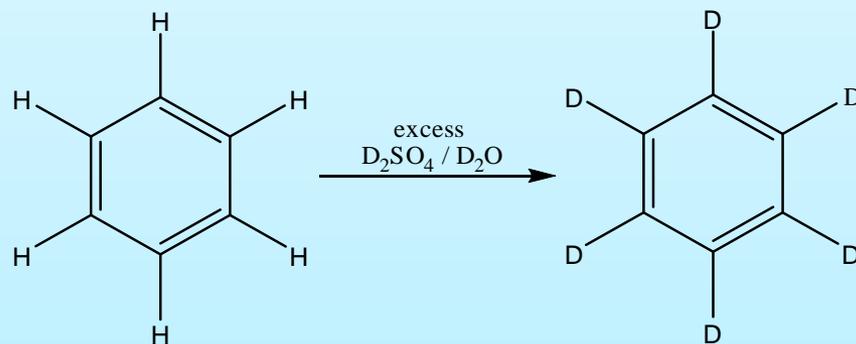
In the case of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  mixture,  $\text{SO}_3$  alone can act as electrophile instead of protonated  $\text{SO}_3$

Sulfonation, unlike other electrophilic substitution reactions, is reversible.

Sulfonic acid group can be removed by heating in dilute sulfuric acid.

❑ For reaction to proceed in the forward direction, it is necessary that water being generated in the reaction is continuously removed.

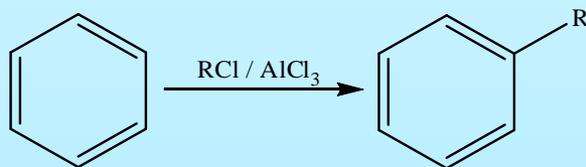
❑ Interestingly, this process is used to place deuterium in place of hydrogen in a benzene ring.



# Friedel-Crafts Reaction

## Alkylation

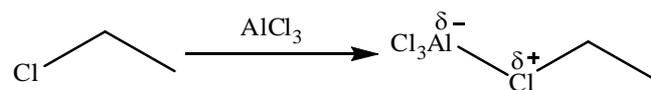
- ❑ Preparation of **alkyl benzenes** from **alkyl halides** and a **Lewis acid** (usually  $\text{AlCl}_3$ ).
- ❑ The **carbocation** is the electrophile
- ❑ The role of the anhydrous aluminum chloride is to generate a **stable carbocation complex**.



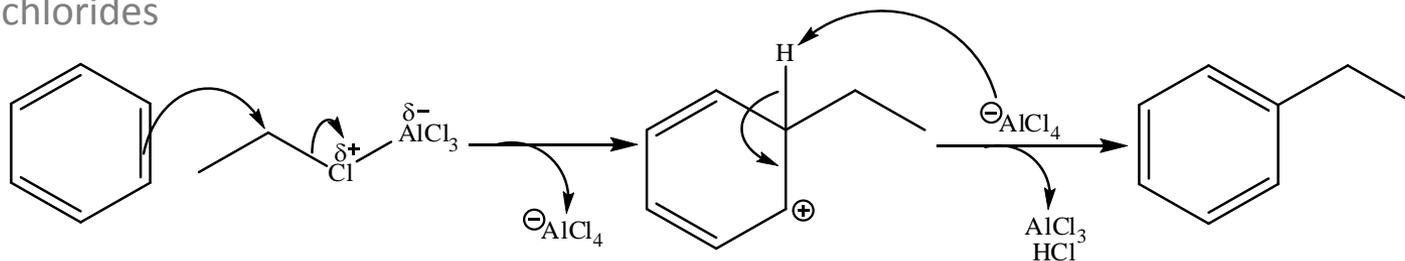
$\text{R-Cl}$ : alkyl chloride

- ❑ For  $\text{CH}_3\text{Cl}$  and  $1^\circ \text{RCl}$ , Lewis acid-base complex itself serves as electrophile.
- ❑ For  $2^\circ$  and  $3^\circ \text{RCl}$ , Lewis acid-base complex reacts further to furnish  $2^\circ$  and  $3^\circ$  carbocation respectively, due to the increased stability of such carbocations.

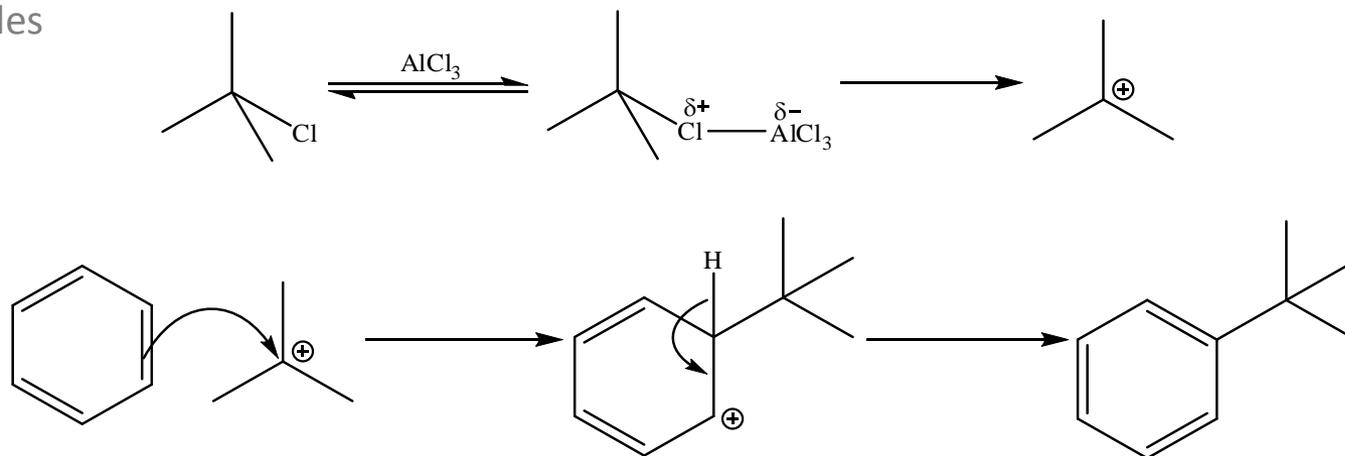
# Mechanism of alkylations

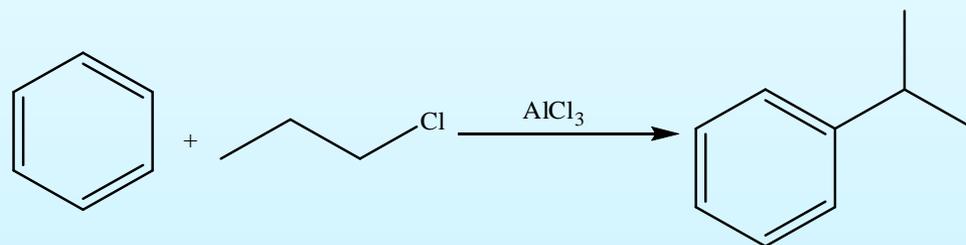


Primary alkyl chlorides



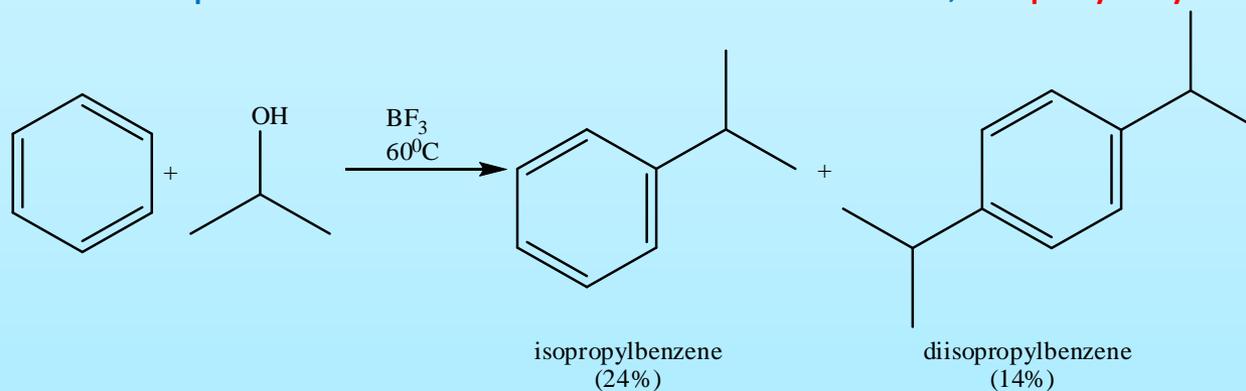
tert-alkyl chlorides





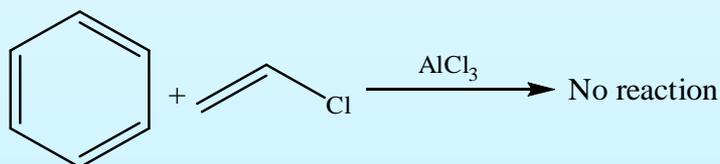
❑ **Carbocation rearrangement** is seen in case of alkyl halides [example above involves rearrangement of primary to secondary carbocation]

❑ The alkylbenzene product is more reactive than benzene, so **polyalkylation** occurs.

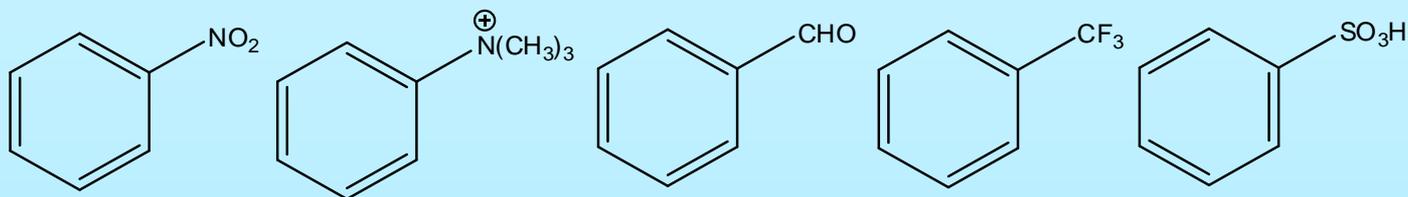


Alkyl group activates ring by +I effect for further substitution.

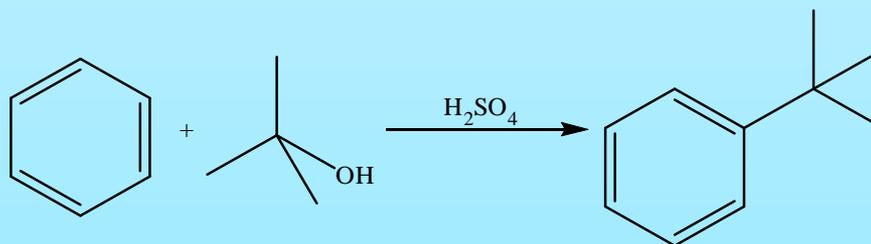
- ❑ Vinyl halides and aryl halides do not undergo Friedel-Crafts alkylation [cannot generate vinyl cations]



- ❑ Poor yields are obtained if powerful electron withdrawing group is present on aromatic nucleus (such as NO<sub>2</sub>, NR<sub>3</sub><sup>+</sup>, C=O)

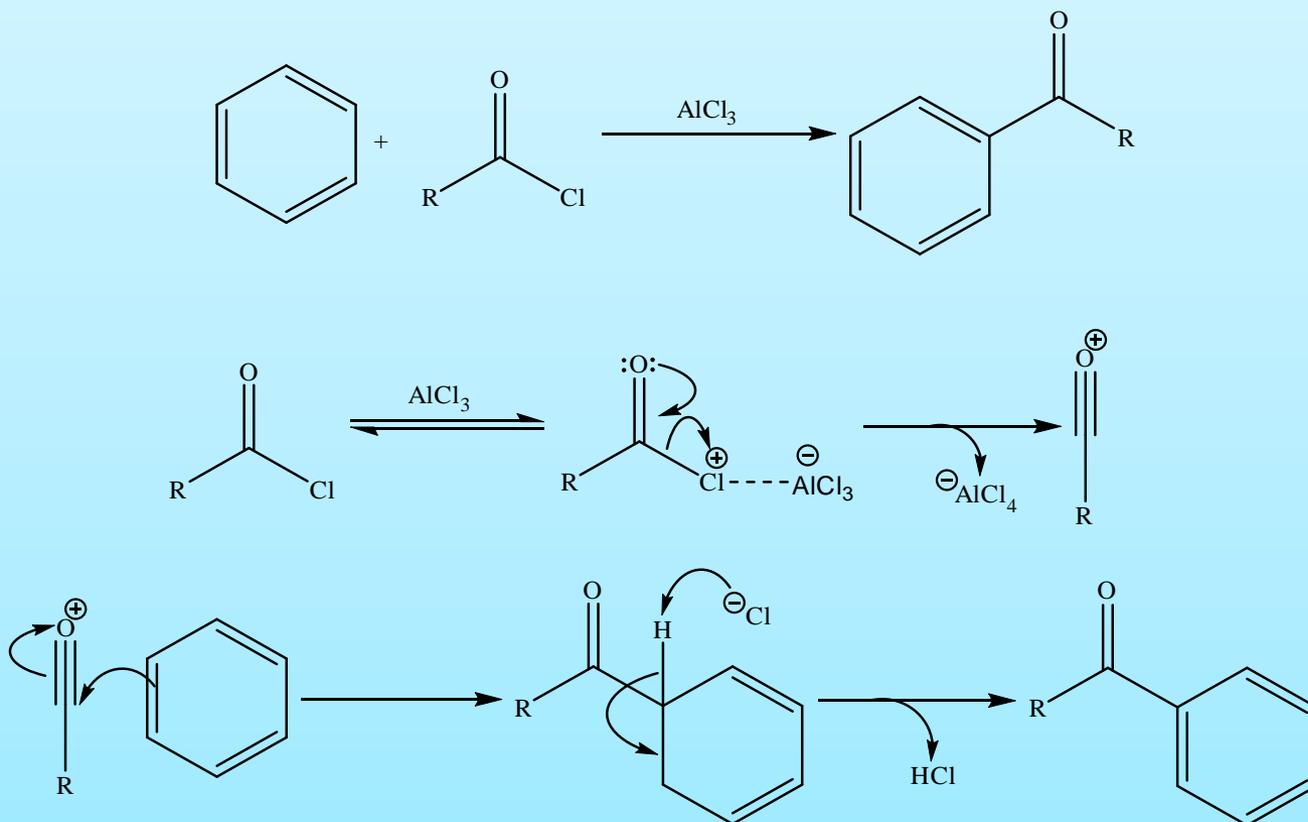


- ❑ Other sources of carbocation are alkenes + HF **or** alcohols + BF<sub>3</sub> **or** alcohol + H<sub>2</sub>SO<sub>4</sub>



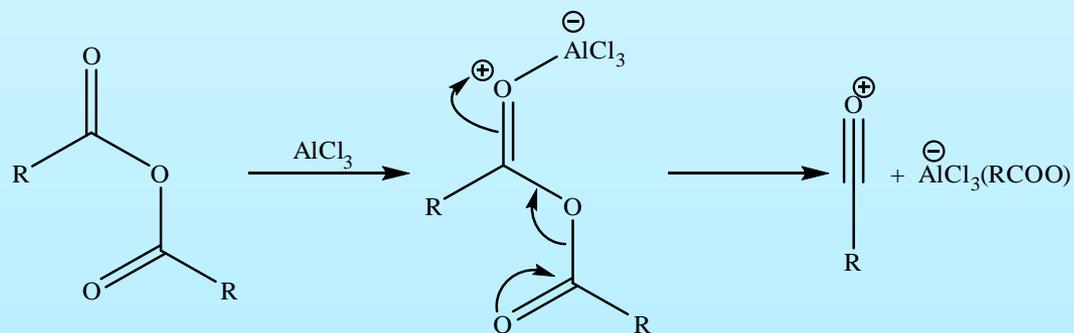
## Acylation

- ❑ Replacement of H in aromatic nucleus by an acyl group (R-C=O)
- ❑ Synthesis of aromatic ketones from acyl halides and a Lewis acid, usually AlCl<sub>3</sub>.
- ❑ Acylium ion is the electrophile



❑ In Friedel-Crafts acylation, no polysubstitution is seen, as carbonyl group is electron withdrawing and makes aromatic ring less electrophilic and  $\text{AlCl}_3$  forms complex with the carbonyl group, further preventing the reaction.

❑ The same result is obtained if an **acid anhydride** is used instead of an acid chloride.

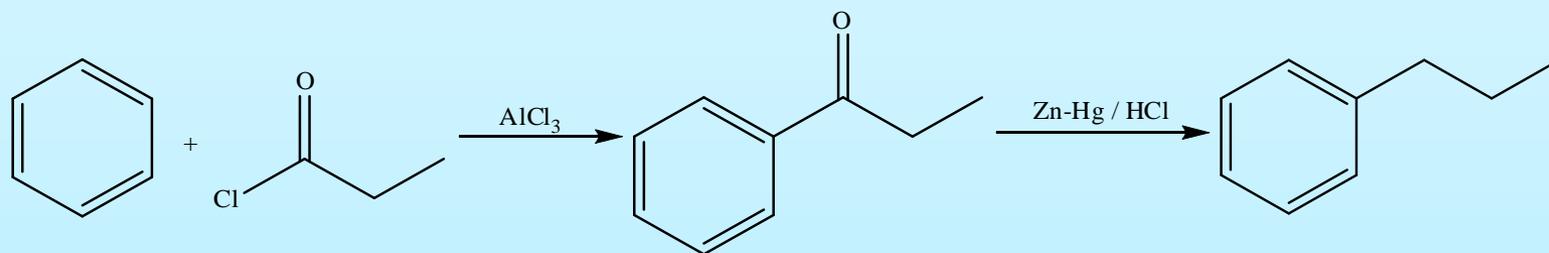


❑ The acylium ion intermediate is resonance stabilized and **does not rearrange** like a carbocation.

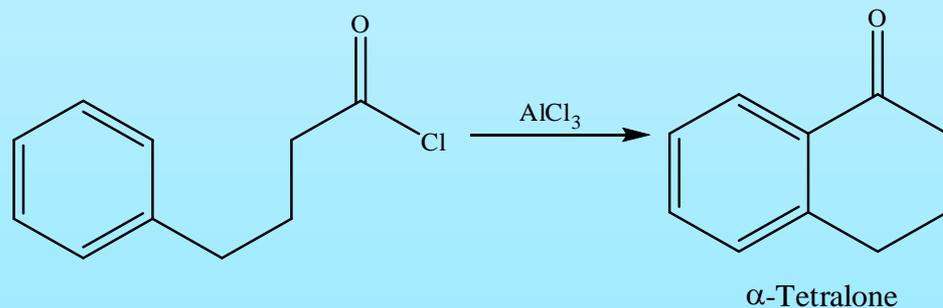
❑ Reaction can be used to prepare n-alkylbenzenes in two step process

i. Friedel-Crafts acylation

ii. Clemmensen's reduction



□ Starting materials that contain both benzene ring and an electrophile are capable of intramolecular Friedel-Crafts reactions.



# Reactivity in substituted aromatics

☐ Substituent groups on a benzene ring affect electrophilic aromatic substitution reactions in two ways:

## 1.Reactivity

- activate (faster than benzene)
- deactivate (slower than benzene)

## 2.Orientation

- ortho- & / or para- direction
- meta- direction

- If the aryl substituent **donates (releases) electrons** to the ring:
  - The **electron density of the ring will increase**, resulting in activation the ring.
  - The **free energy of activation will decrease**, as resulting **transition state** enjoys additional stabilization due to a more delocalized arenium ion.
  - Therefore, the **reaction rate is increased** relative to the rate on an unsubstituted aromatic ring.
  - The resulting resonance forms of the arenium ion favor the **substitution** of the second group at the **ortho/para positions**, i.e., positions 1, 4, 6 relative to the original group.

➤ Activation of ring by substituent can arise due to:

❖ Inductive effect

❖ Resonance effect

➤ Inductive effect is seen in the case of **alkyl** substitution

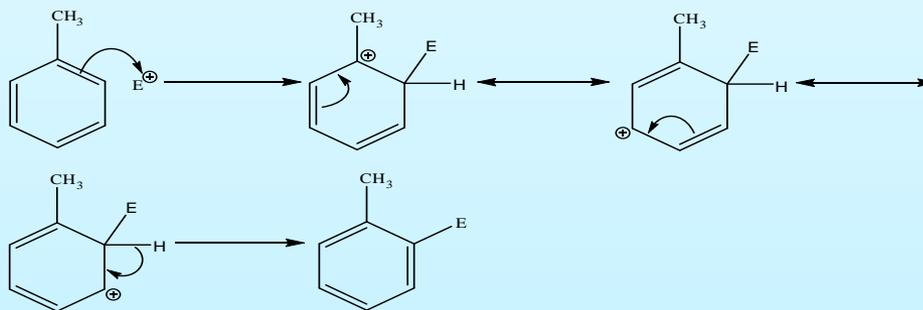
➤ Resonance effect is seen in the case of substituent having **lone pair** of electrons

Thus, alkyl groups stabilize the **sigma complex** by induction, **donating electron density** through the **sigma bond** and substituents with a lone pair of electrons stabilize the sigma complex by **resonance**.

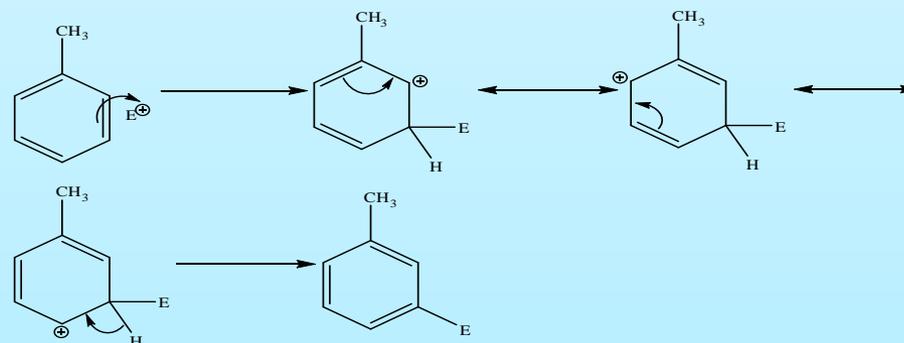
➤ eg. **alkyl**, **vinyl**, **phenyl**,  $\text{NH}_2$ , **NHR**,  $\text{NR}_2$ , **NHCOR**, **OH**, **OR** etc.

➤  $\text{-CH}_3$  group directs electrophilic attack ortho and para to itself because an electron-donating inductive effect stabilizes the carbocation intermediate.

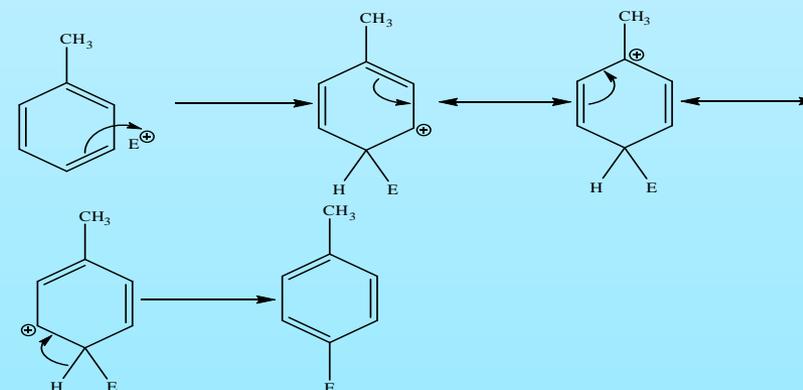
ortho attack



meta attack

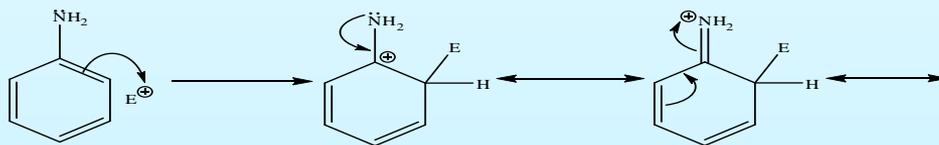


para attack

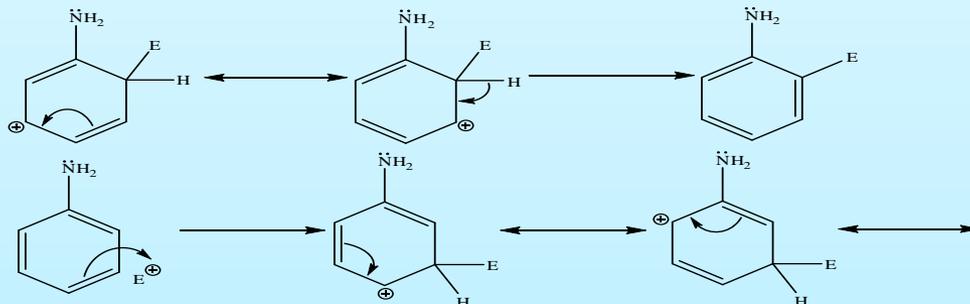


➤  $\text{NH}_2$  group directs electrophilic attack ortho and para to itself because the carbocation intermediate has additional resonance stabilization.

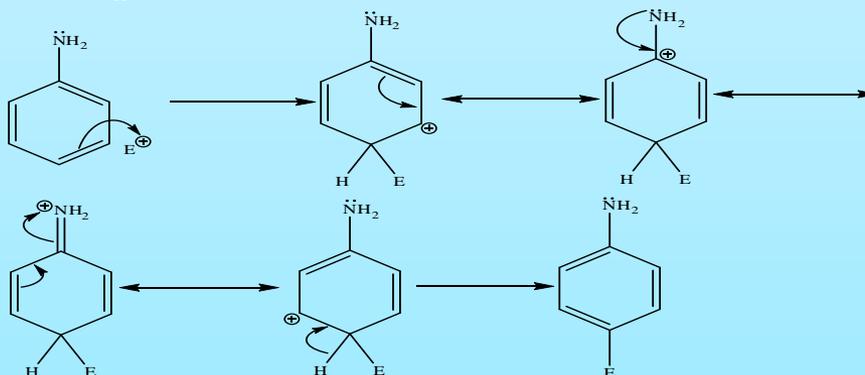
ortho attack



meta attack

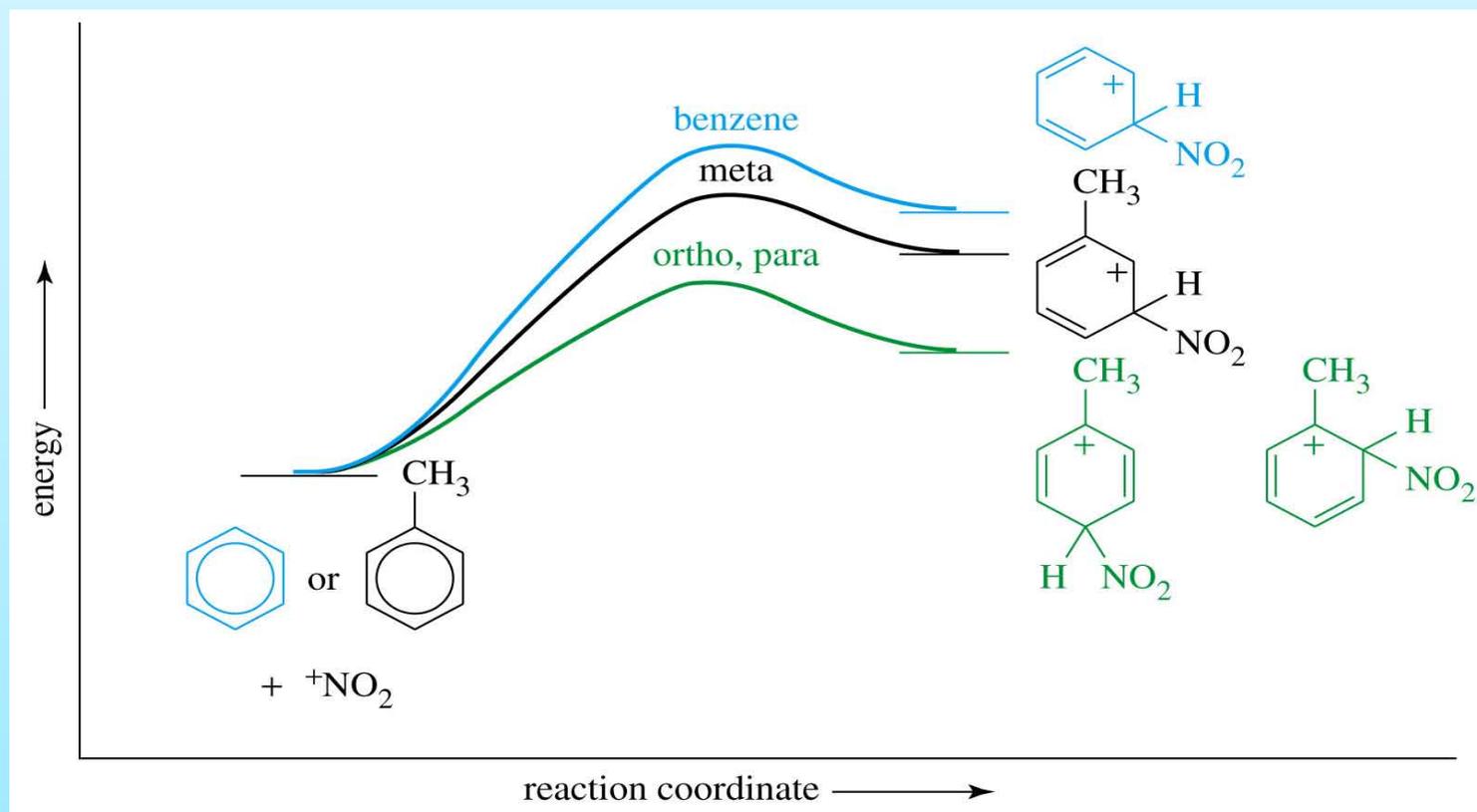


para attack

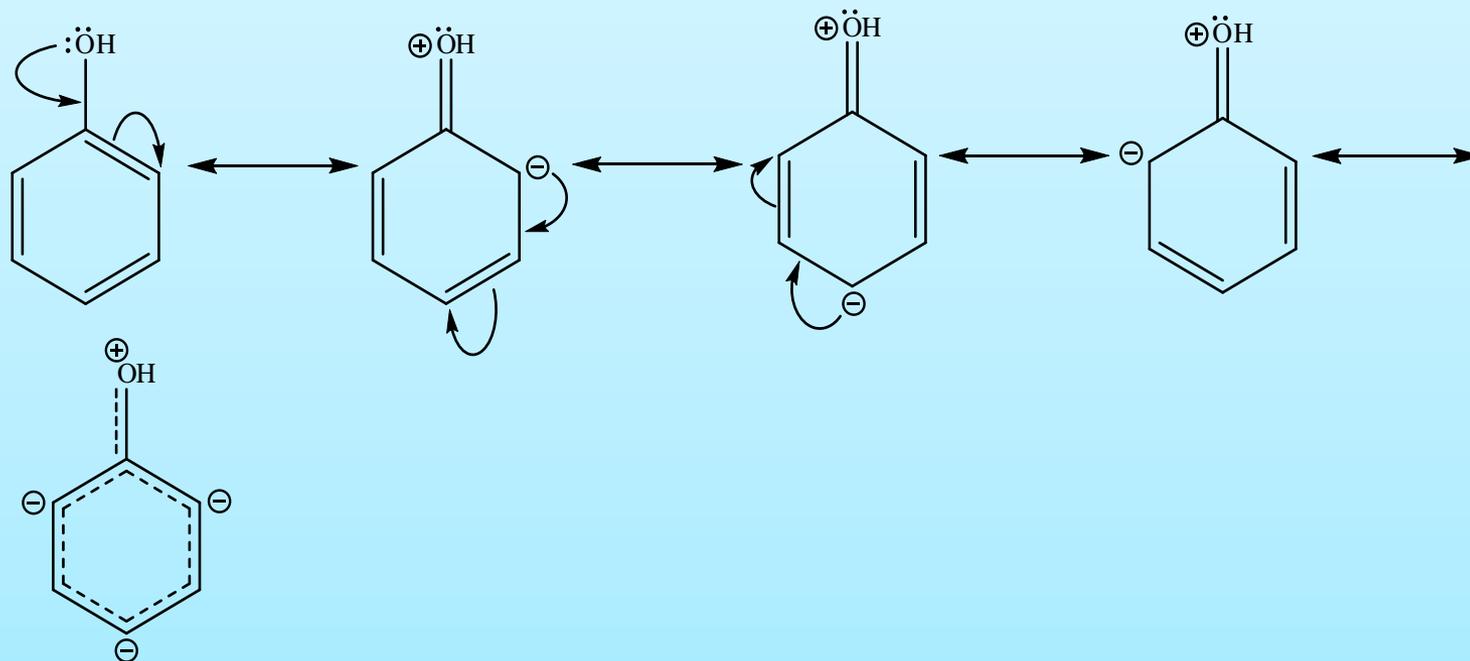


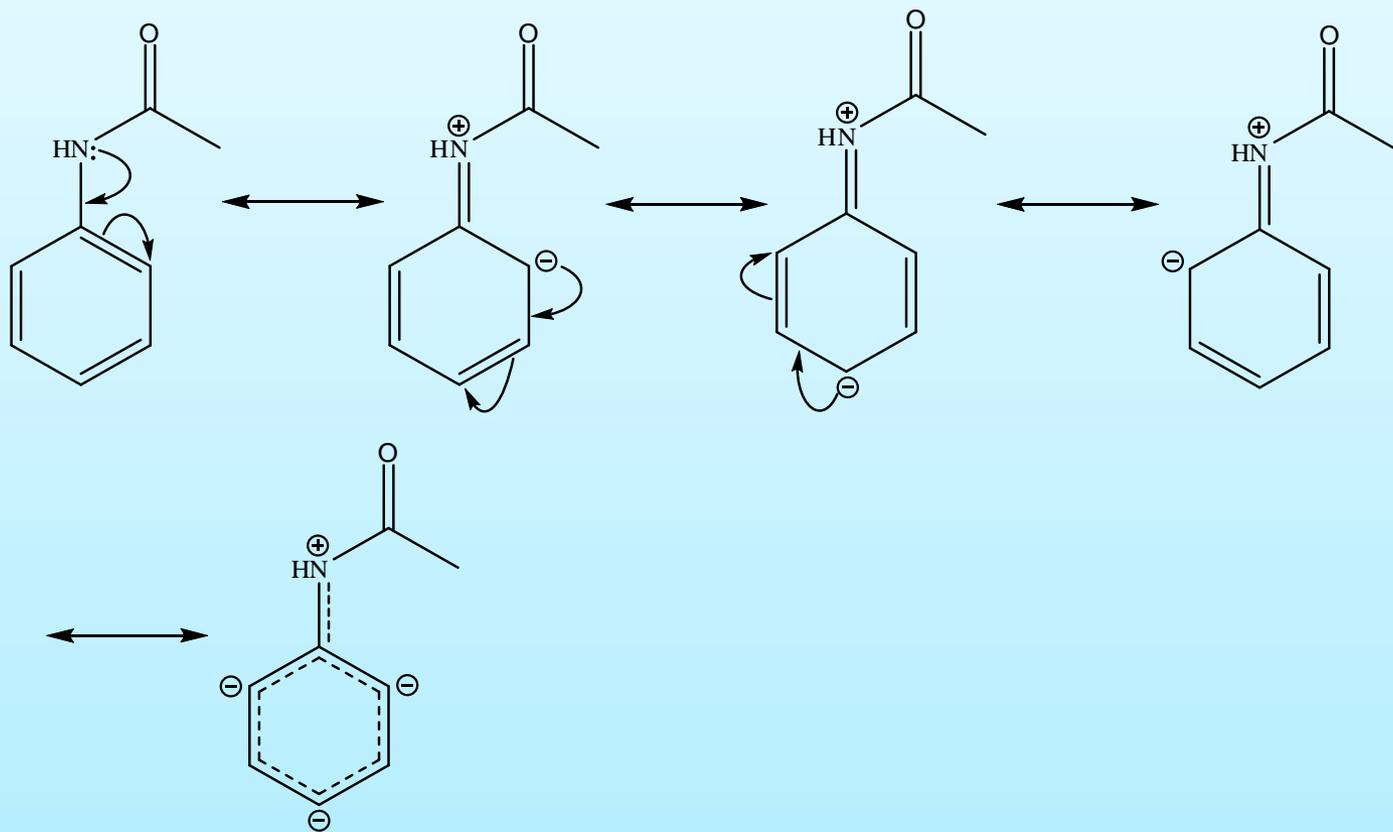
➤ Comparison of the resonance structures involved in electrophilic aromatic substitution of toluene and aniline, it becomes clear that when the electrophile attacks at the ortho and para positions, the resulting arenium ion is more stabilized due to electron donation through inductive and resonance effect.

➤ It can be explained graphically as follows



➤ Similar effect can be explained using the resonance structures of **phenol** and **acetanilide** as representative examples to identify the preferred site of attack for the incoming electrophile





- If the substituents **withdraws (accepts) electrons** from the ring:
  - The **electron density of the ring decreases** leading to deactivation the ring.
  - **Energy of the transition state thereby increases and** leads to the formation of less stable delocalized arenium ion.
  - Therefore, the **reaction rate decreases** relative to the rate on an unsubstituted aromatic ring.
  - The resulting resonance forms of the arenium ion favor **substitution** of the second group at the **meta position**, i.e., position 3 relative to the original group.

➤ Deactivation of the aryl ring can be attributed due to:

❖ Inductive effect

❖ Resonance effect

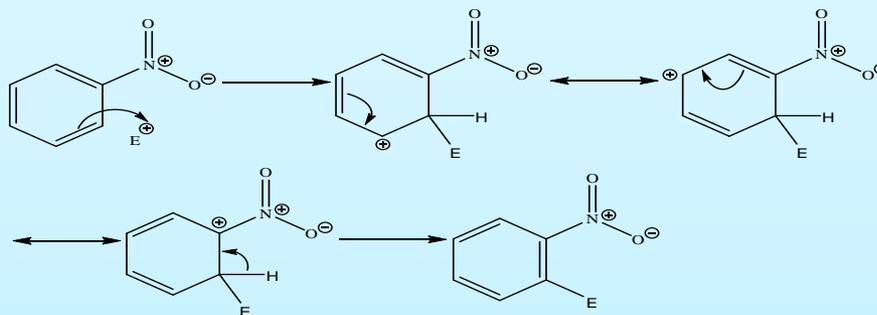
➤ The atom attached to the aromatic ring will have a partial positive charge.

➤ Electron density is withdrawn inductively through the sigma bond, so the ring is less electron-rich than benzene.

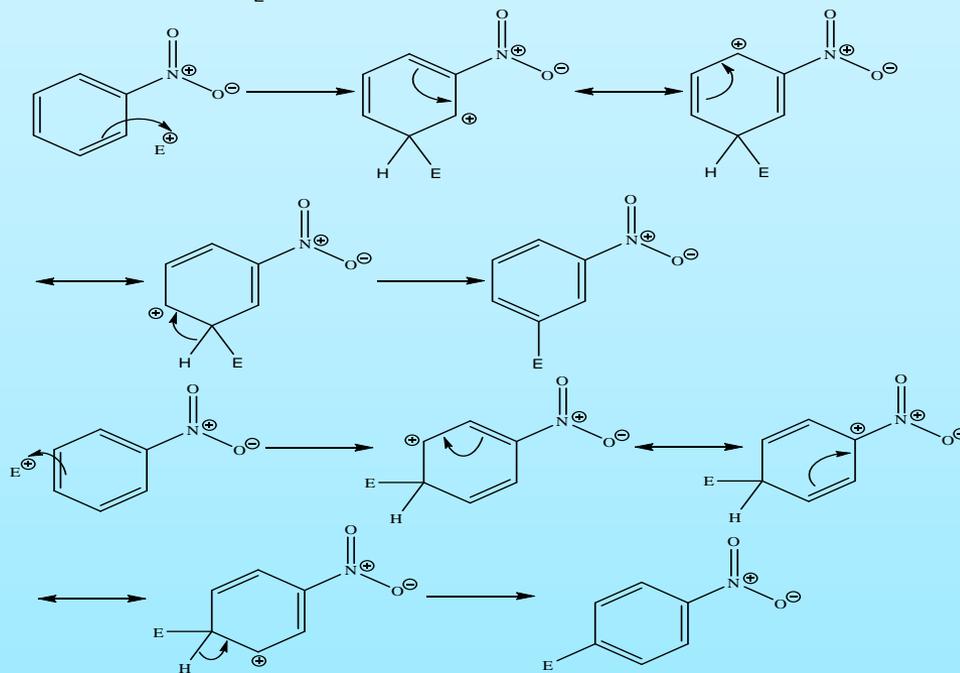
➤ eg. CHO, COR, COOH, COOR, NH<sub>3</sub><sup>+</sup>, NR<sub>3</sub><sup>+</sup>, CF<sub>3</sub>, CN, NO<sub>2</sub>, SO<sub>3</sub>H etc.

➤ With the  $\text{NO}_2$  group (and all meta directors) meta attack occurs because attack at the ortho and para positions gives a destabilized arenium ion intermediate as shown below.

ortho attack



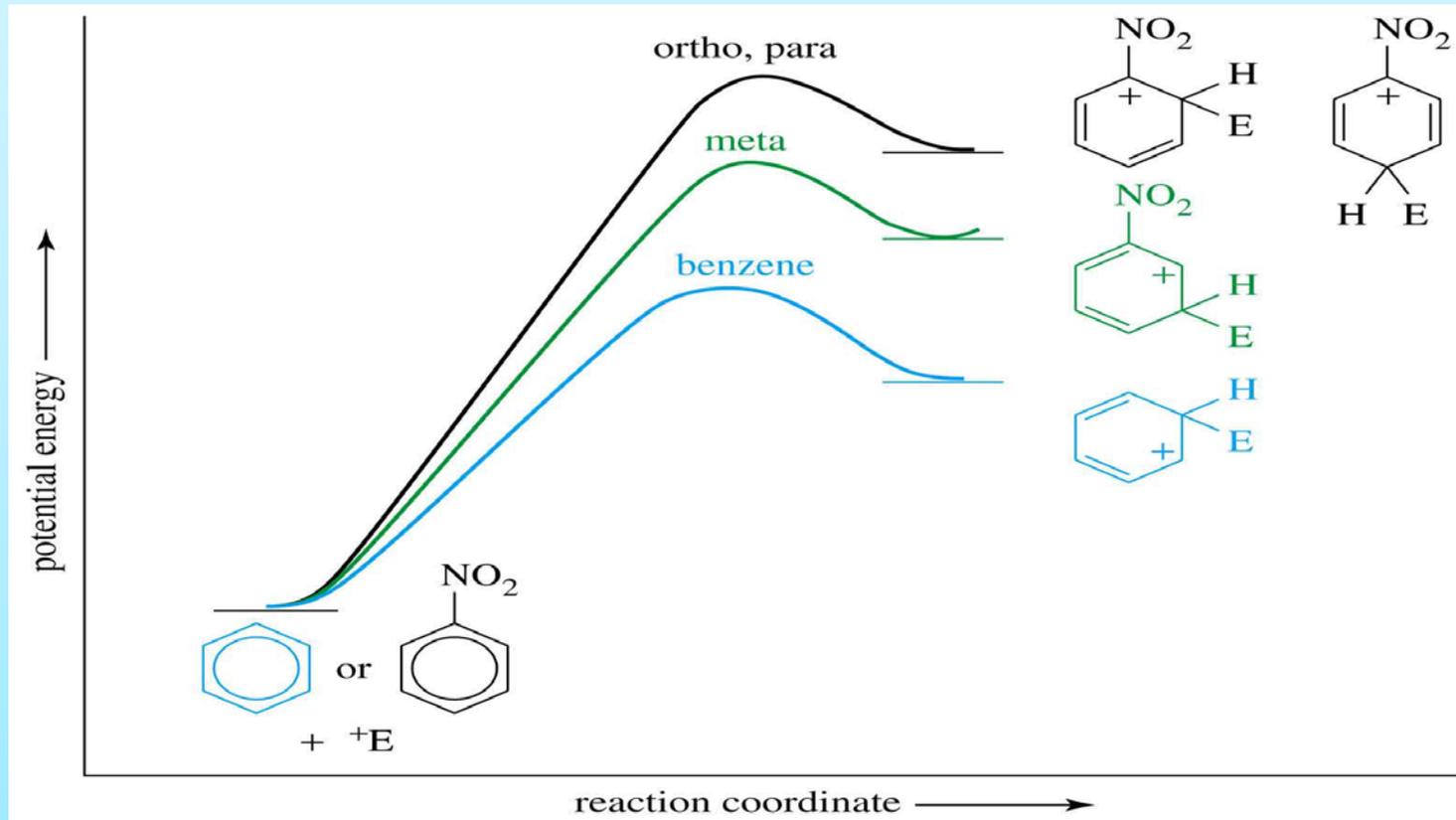
meta attack



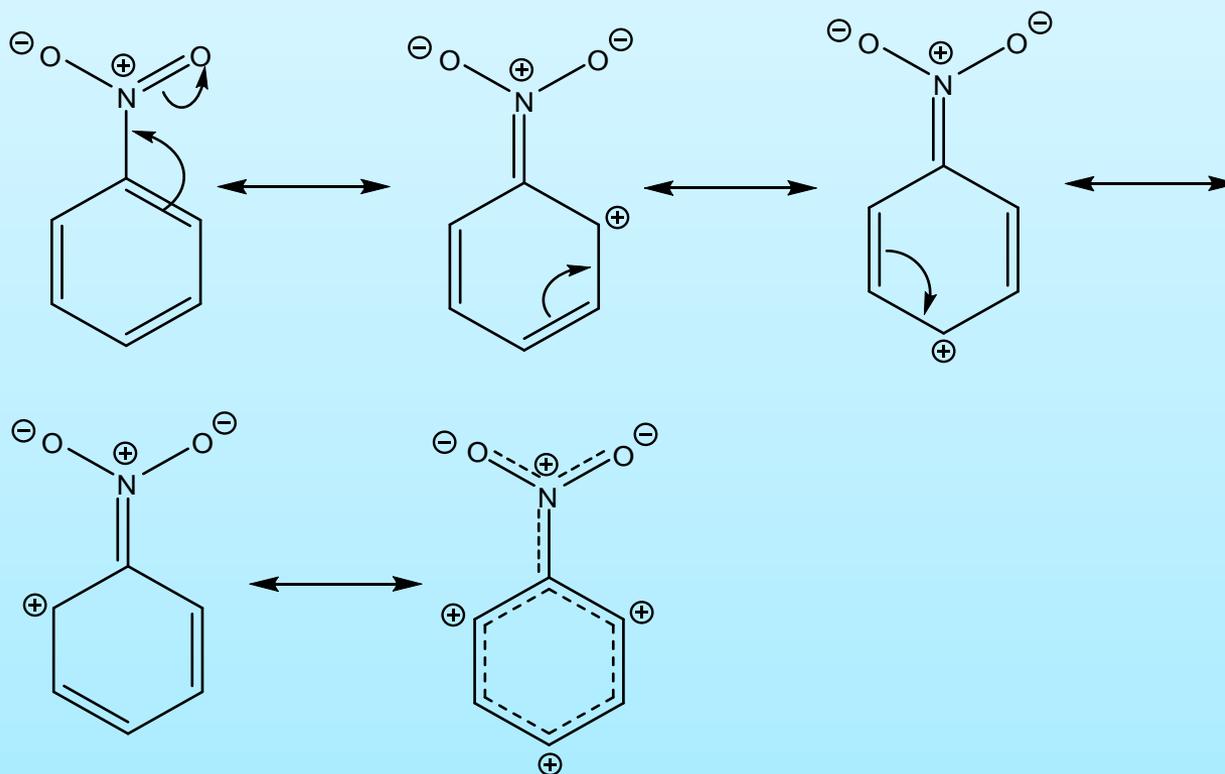
para attack

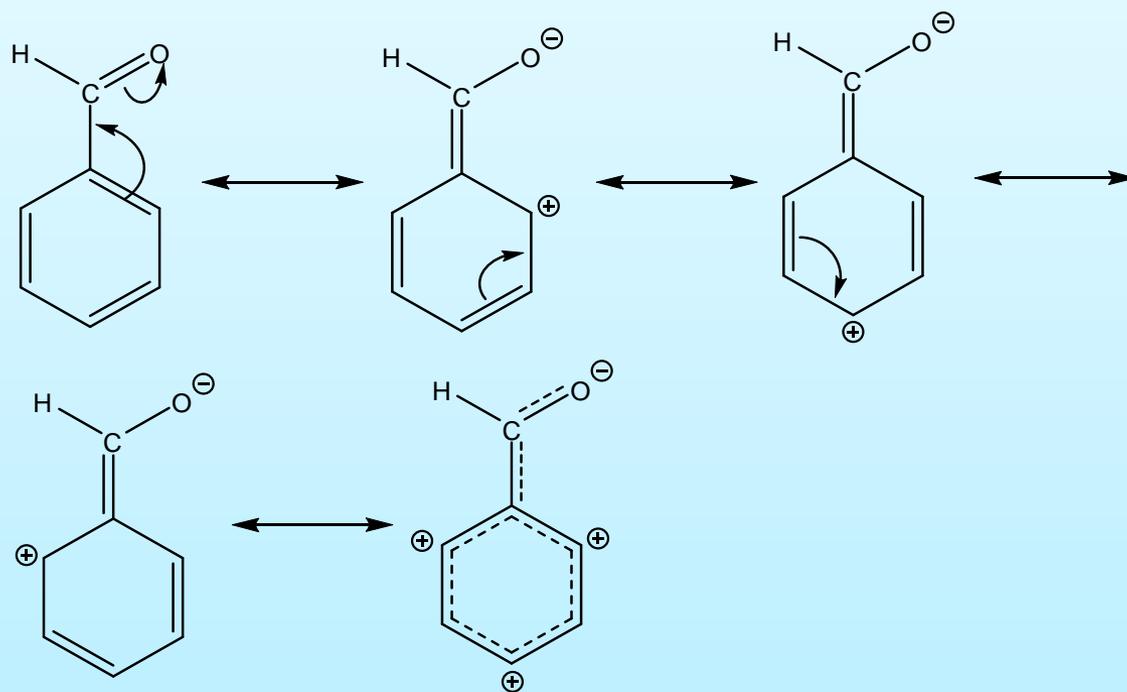
➤ Comparison of the resonance structures involved in electrophilic aromatic substitution of nitrobenzene, it becomes clear that when the attack is at the ortho and para positions the resulting arenium ion is more destabilized than when the attack occurs at the meta position.

➤ It can be explained graphically as follows



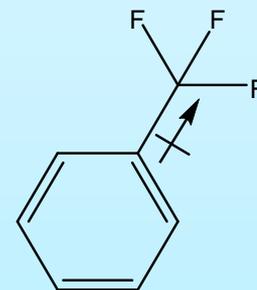
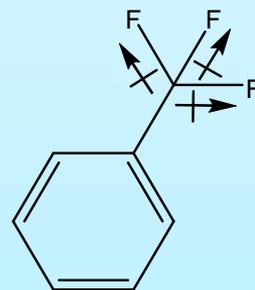
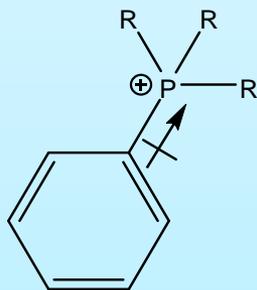
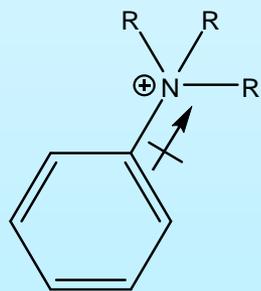
➤ The resonance structures of nitrobenzene and benzaldehyde are given below.





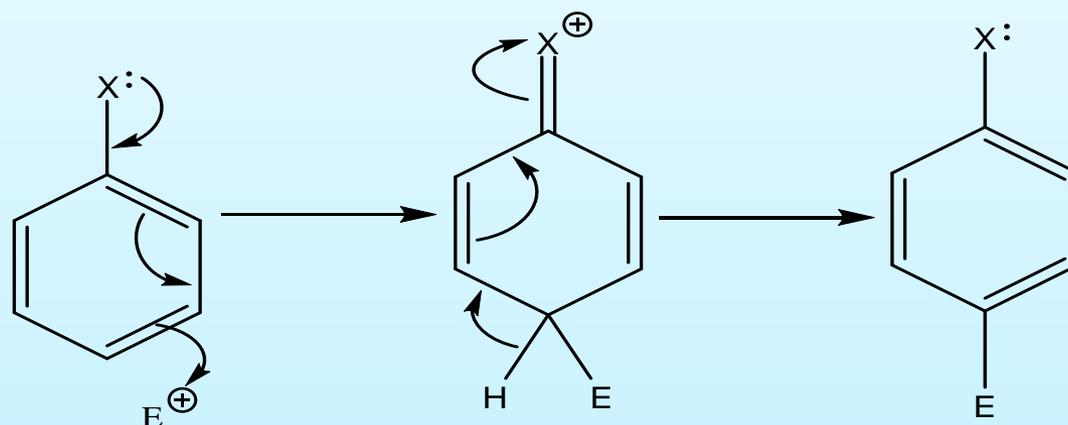
➤ **electron density** at the **ortho and para** positions, relative to  $\text{NO}_2$  and  $\text{CHO}$  is **less** as compared to that at the meta position, making these positions **less electrophilic**.

➤ Substituents like,  $\text{NR}_3^+$ ,  $\text{PR}_3^+$ ,  $\text{CF}_3$  will exert **electronic effect** on benzene ring, **polarizing Ar-Z bond** because of electronegativity of Z.

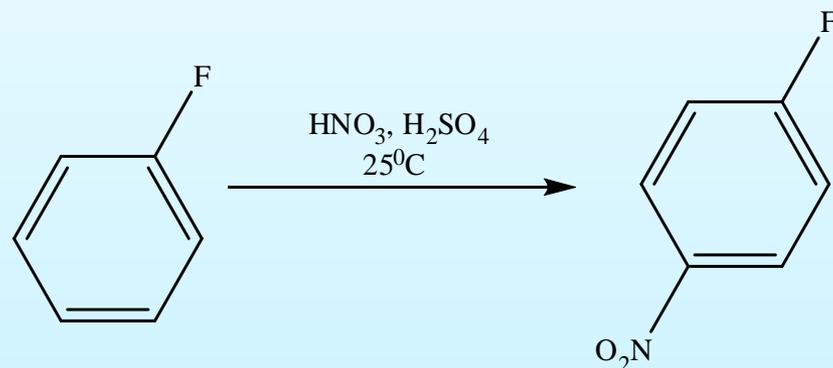


**Halogens** provide a peculiar effect when attached to an aromatic nucleus.

- They are **ortho / para directors** with **deactivating** effect.
- This is because they are highly **electronegative** elements and therefore inductively pull the electron density towards it through sigma bonds.
- But halogens have **lone pairs of electrons** that can stabilize the sigma complex by resonance.
- There are two aspects to this behavior, one is **orbital size** containing lone pair of electrons and other is **electronegativity**.

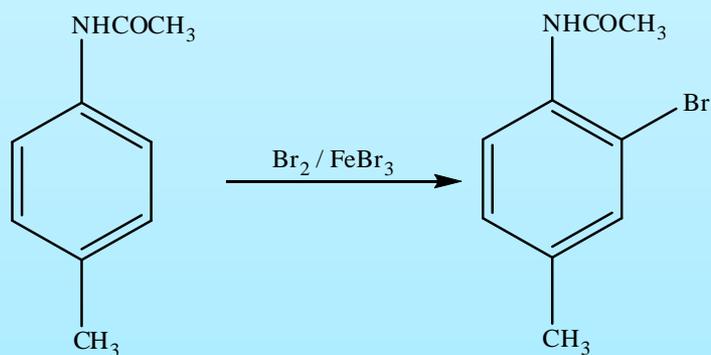


- For Cl, Br and I, there is size mismatch and **poor overlap of orbitals** of 2p of carbon and 3p, 4p and 5p of Cl, Br and I, respectively.
- F 2p orbitals are of similar size to that of C 2p, but F is far much electronegative, hence F 2p is much **lower in energy** than C.
- On inspection of reactivity of fluoroarenes, it is seen that the para position is much favored over other positions.



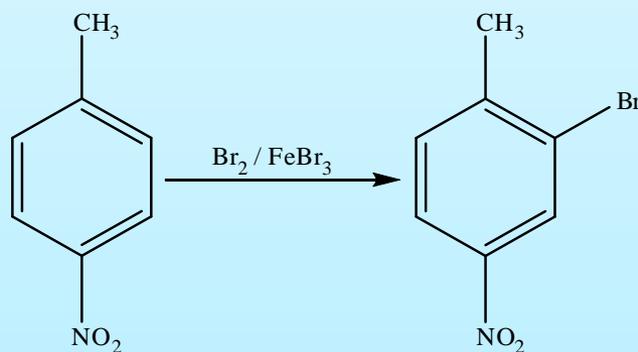
□ When more than one substituent is present in aromatic nucleus, then, position of the incoming group is determined by

➤ most strongly activating substituent for the incoming group



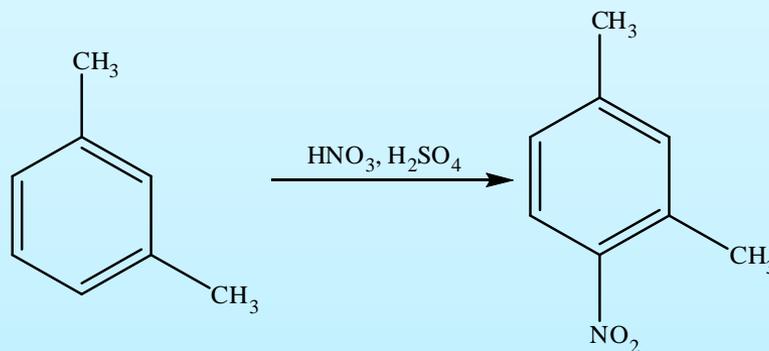
In this reaction  $\text{NHCOCH}_3$  is powerful activator than  $\text{CH}_3$ , hence, substitution occurs ortho to this group, than less activating  $\text{CH}_3$  group

- When the directing effects of two groups reinforce, the new substituent is attached to the position directed by both groups.



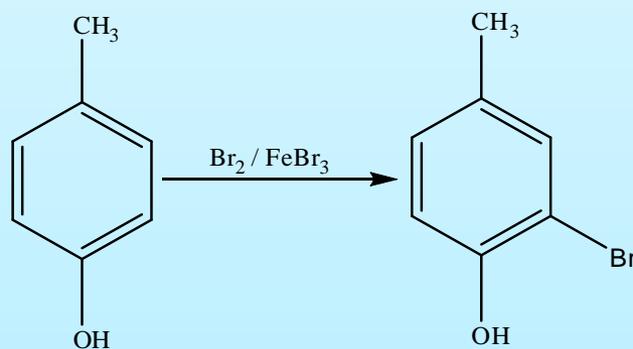
- In bromination of p-nitrotoluene, incoming Br group attaches ortho to CH<sub>3</sub> and meta to NO<sub>2</sub> group as, CH<sub>3</sub> is o /p-directing and NO<sub>2</sub> is meta directing

➤ There will be little or no substitution between groups that are meta to each other.



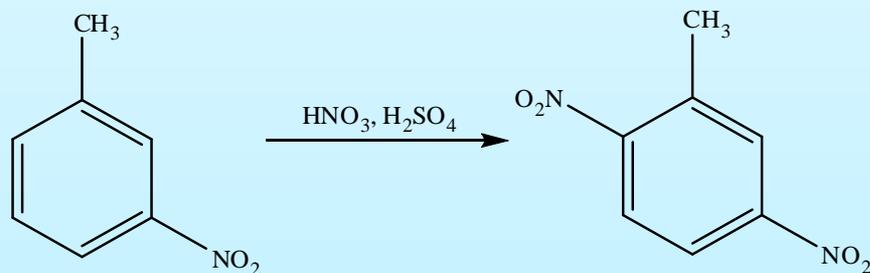
▪ In nitration of m-xylene, NO<sub>2</sub> group is substituted ortho to one CH<sub>3</sub> while it is para to the other CH<sub>3</sub> group, rather than at position 2, to avoid crowding

➤ For substituents with opposite effects, the resonance effect overrides all other effects.

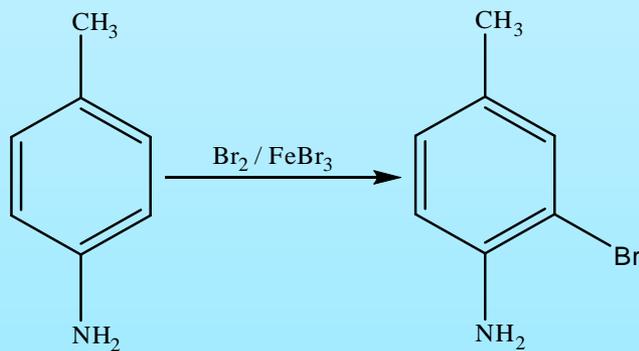


- In bromination of p-cresol, Br is substituted at position ortho to OH than at ortho to CH<sub>3</sub>, as OH is powerful activator due to resonance

➤ donor substituent overpowers an acceptor substituent



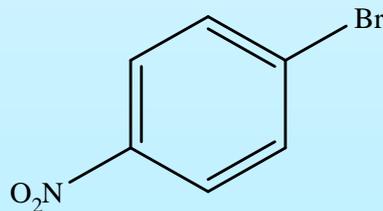
➤ resonance donor substituent overpowers a hyperconjugative donor substituent



❑ Course of reaction is determined by taking all these facts into consideration.

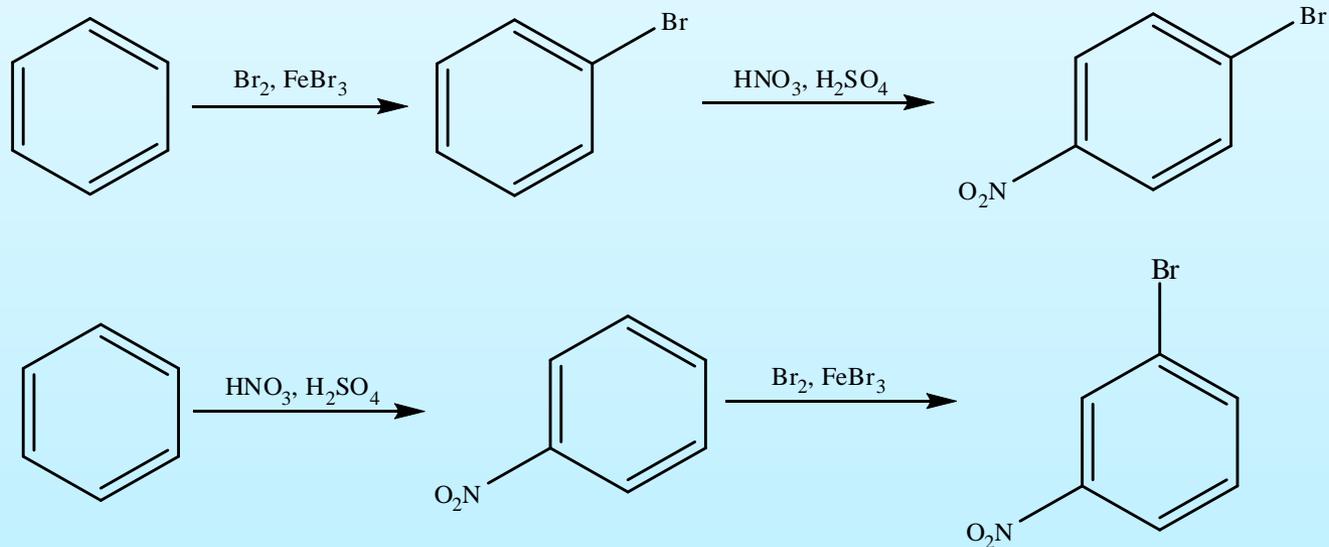
➤ In syntheses of disubstituted benzene derivatives, **order of addition of reagents** are important

➤ Let us consider, **syntheses of p-nitrobromobenzene**



➤ It can be synthesized in two ways,

- **first bromination** followed by nitration
- **first nitration** followed by bromination



- In the first case, Br present on benzene ring directs  $\text{NO}_2$  group to para position and required product is obtained
- whereas, in the second case,  $\text{NO}_2$  group directs Br to meta position and unwanted product is obtained

# Summary of directing effects of substituents in electrophilic aromatic substitution

## ortho / para directing

✓ **strongly activating**

$-O^-$ ,  $-NR_2$ ,  $-NHR$ ,  $-NH_2$ ,  $-OH$

✓ **moderately activating**

$-NHCOCH_3$ ,  $-NHCOR$ ,  $-OCH_3$ ,  $-OR$

✓ **weakly activating**

$-OCOR$ , Me, Et, alkyl, phenyl,  $-CH=CR_2$

✓ **weakly deactivating**

$-F$ ,  $-Cl$ ,  $-Br$ ,  $-I$

## meta directing

✓ **strongly deactivating**

$-NO_2$ ,  $-NR_3^+$ ,  $-PR_3^+$ ,  $-CF_3$ ,  $-CCl_3$

✓ **moderately deactivating**

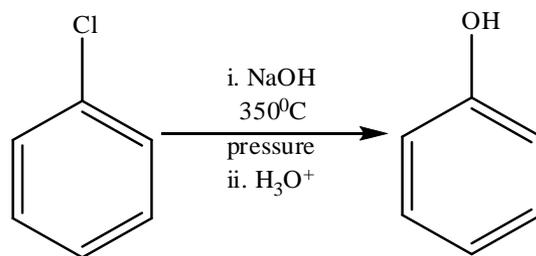
$-CN$ ,  $-SO_3H$ ,  $-COOH$ ,  $-CONH_2$

$-COCl$ ,  $-COOR$ ,  $-COR$ ,  $-CHO$

# Nucleophilic substitution

☐ Nucleophilic substitution in an aromatic compound though not common, can be observed in many aromatic systems, which has even found industrial importance.

☐ Example is industrial synthesis of phenol from chlorobenzene by Dow's process.



Reaction does not go through simple S<sub>N</sub>2 or S<sub>N</sub>1 mechanism.

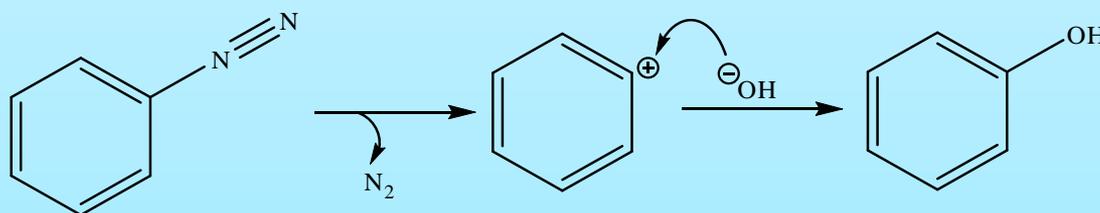
☐ S<sub>N</sub>2 is not possible because carbon atom is sp<sup>2</sup> hybridized and bromine is in same plane as that of carbon.

☐ Due to this hydroxyl can not attack from back side of C-Br bond as is required in S<sub>N</sub>2 reaction.

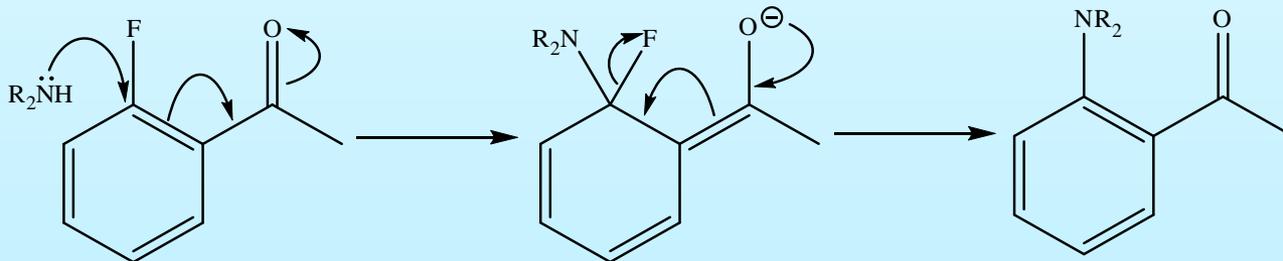
❑  $S_N1$  is possible in some cases but is unfavorable because the aryl cation formed will be planar but will not contain empty p orbital. Instead it will have **filled p orbital** as it is part of the aromatic system.

❑ Also, **C-X bonds of aryl halides are shorter and stronger** than those of aliphatic halides because of the hybridized state and the resonance, hence, **ionization to form a cation is a high energy process**.

❑ Such a mechanism is observed only with leaving group such as gaseous nitrogen.



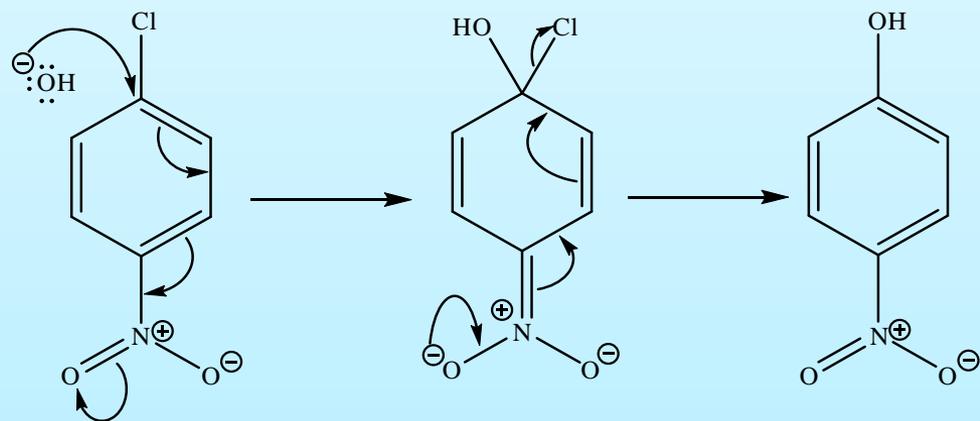
❑ Instead, reaction proceeds through a different mechanism altogether- **addition-elimination mechanism**.



❑ Nucleophile first adds to the aromatic system and then **elimination of the leaving group** provides the product.

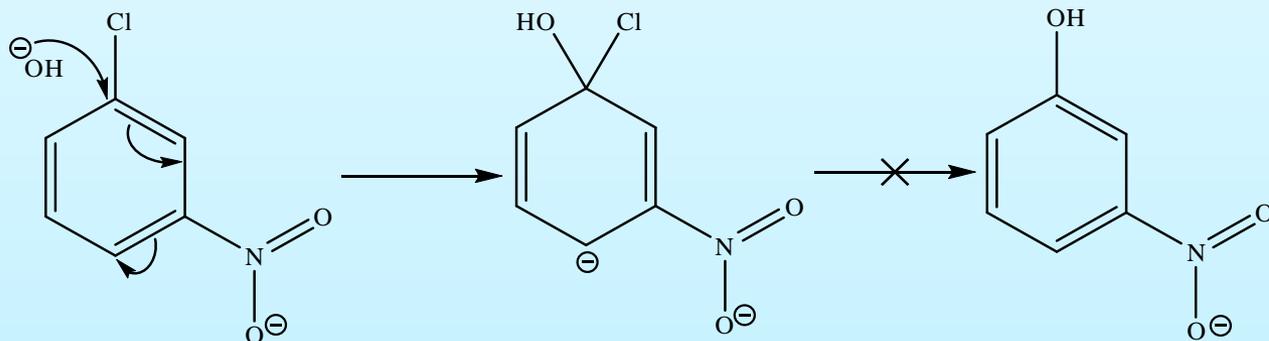
❑ The reaction is best observed in substrates having **anion stabilizing group** such as NO<sub>2</sub> or CHO etc., when present at the ortho and para positions with respect to the leaving group.

□ Nucleophilic substitution in 4-nitrochlorobenzene.



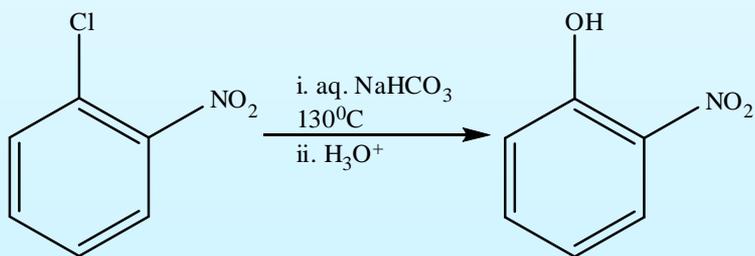
□ Negative charge can be pushed through the aromatic ring if an electron withdrawing group is present at the ortho or para position.

❑ Such an assistance can not be seen when an electron withdrawing group is at the meta position.

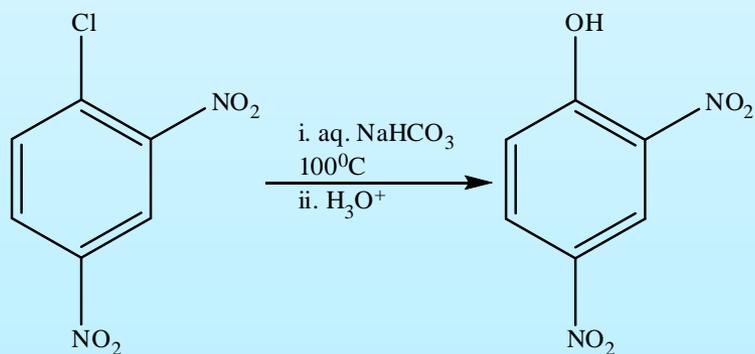


❑ The number of electron withdrawing groups present in the aromatic nucleus also affect the course of reaction, as can be shown in following reactions.

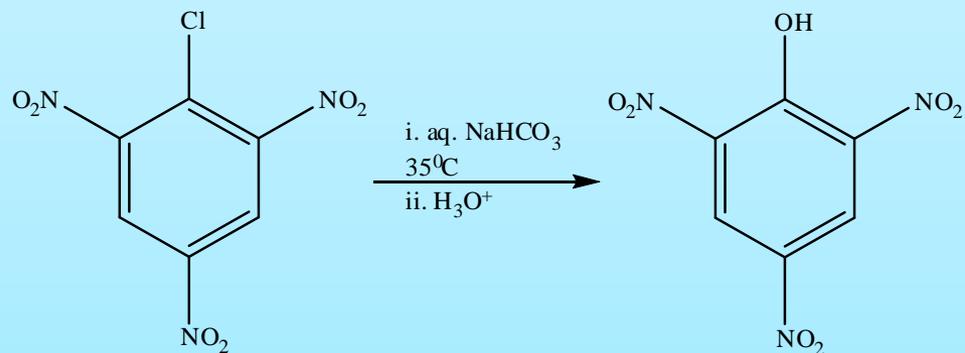
❑ o-nitrochlorobenzene requires higher temperature as compared to 2,4-dinitrochlorobenzene and 2,4,6-trinitrochlorobenzene which can easily be converted to phenol at  $35^\circ\text{C}$ .



rate:  $7 \times 10^{10}$



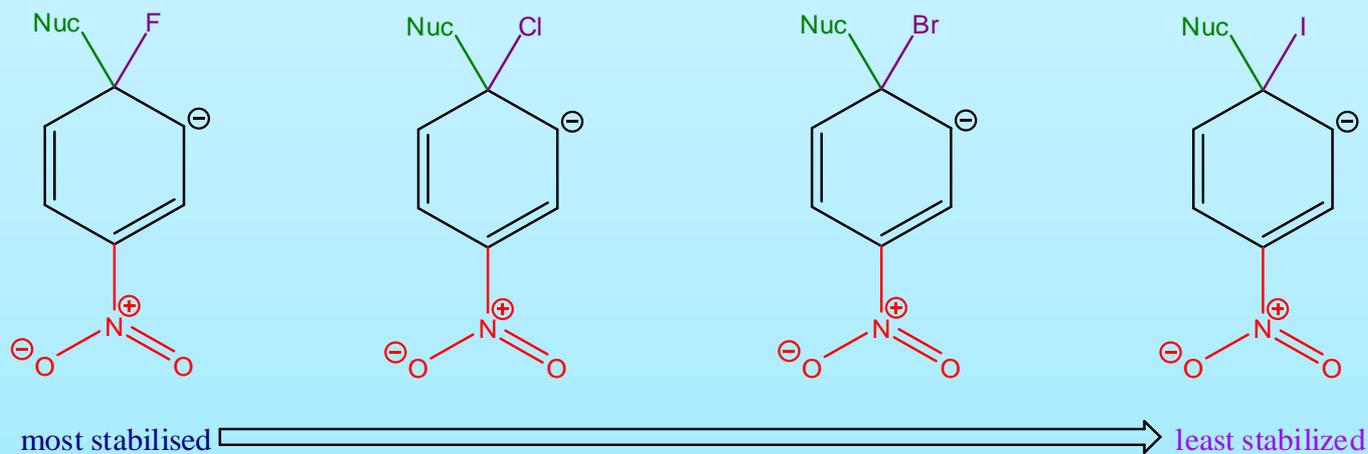
rate:  $2.4 \times 10^{15}$



rate: too fast to measure

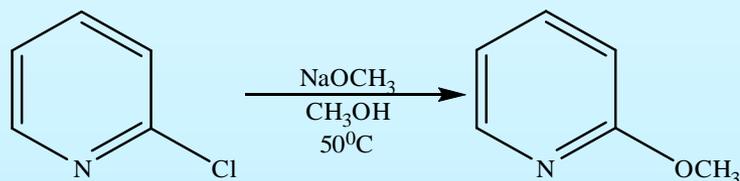
Pay attention to the temperature employed in each of these reactions

- ❑ C-X bond breaking occurs after the rate-determining step in the reaction.
- ❑ Carbanion formed after the nucleophilic attack, is most stable in the case of fluorobenzene and is the least stable for iodobenzene.
- ❑ F being most electronegative stabilizes the negative charge in the intermediate carbanion.

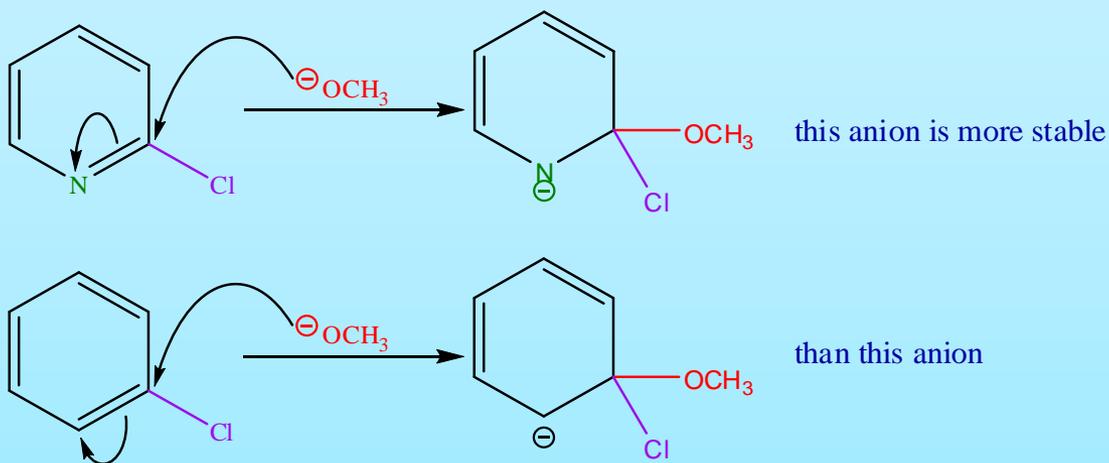


❑ Nucleophilic substitution in heteroaromatic compounds takes place much faster than in aromatic compounds.

❑ 2-Chloropyridine reacts 230,000,000 times faster than chlorobenzene under similar conditions.

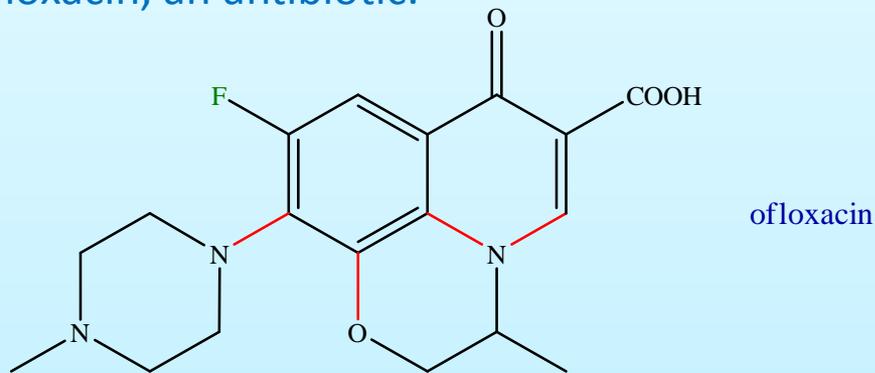


❑ Nitrogen is more electronegative than carbon and stabilizes the anion formed and increases rate at which it is formed.

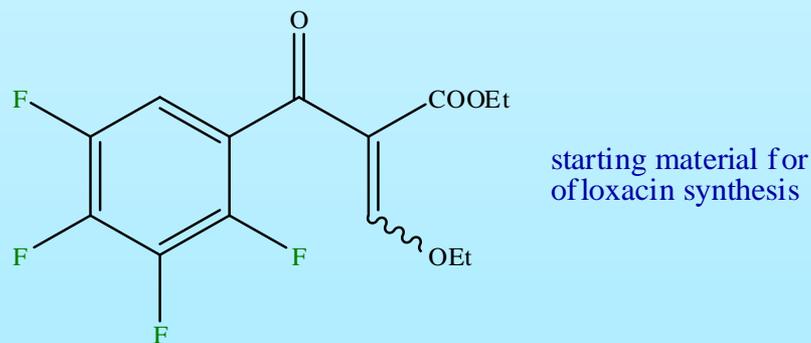


## ❑ Synthetic application of aromatic nucleophilic substitution

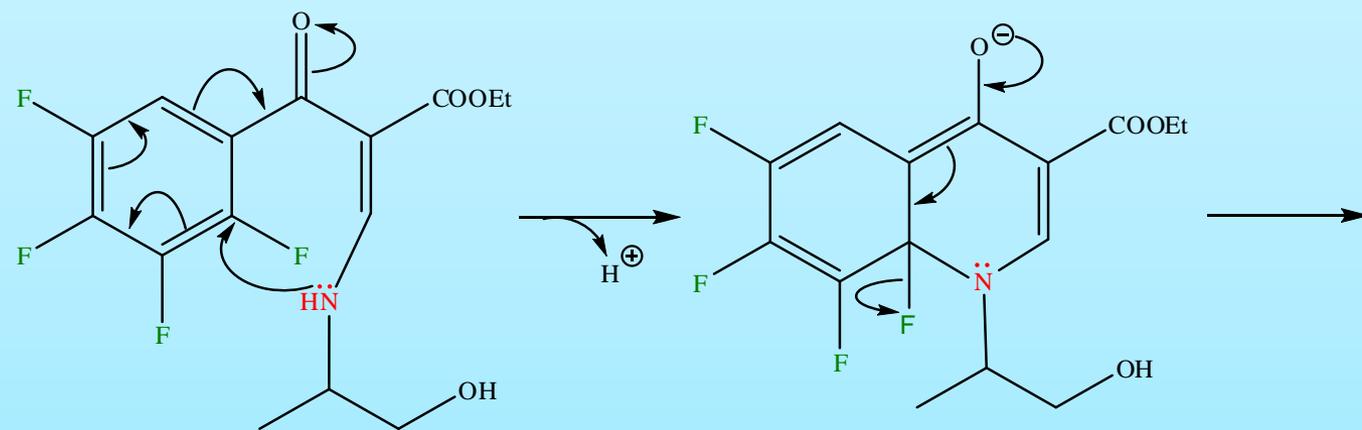
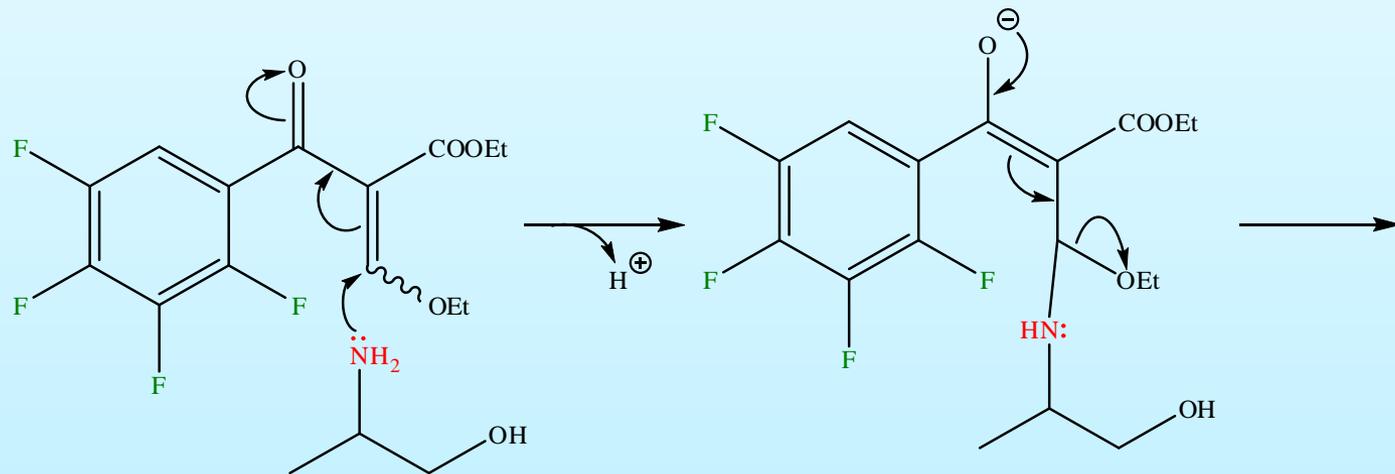
### (1) Syntheses of ofloxacin, an antibiotic.

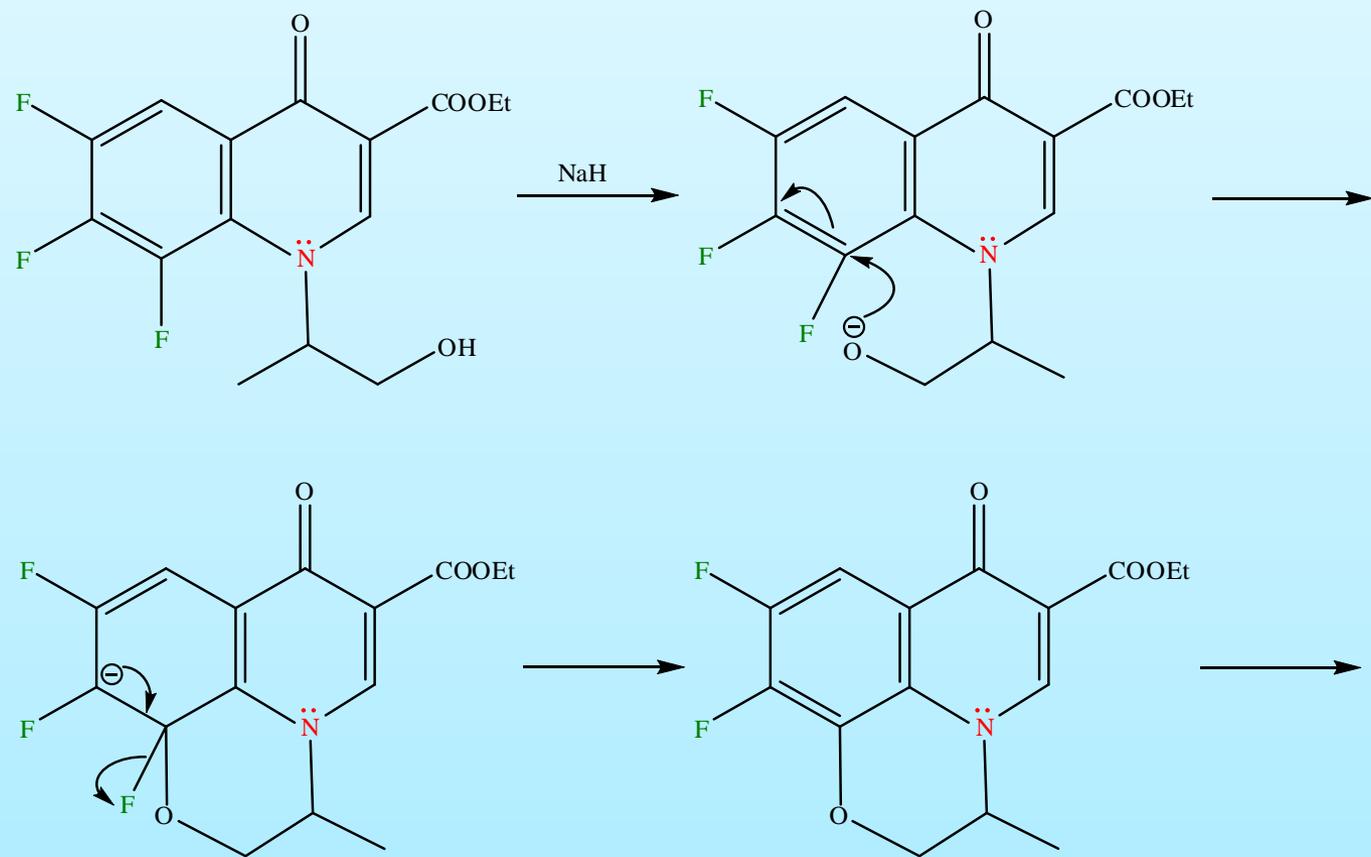


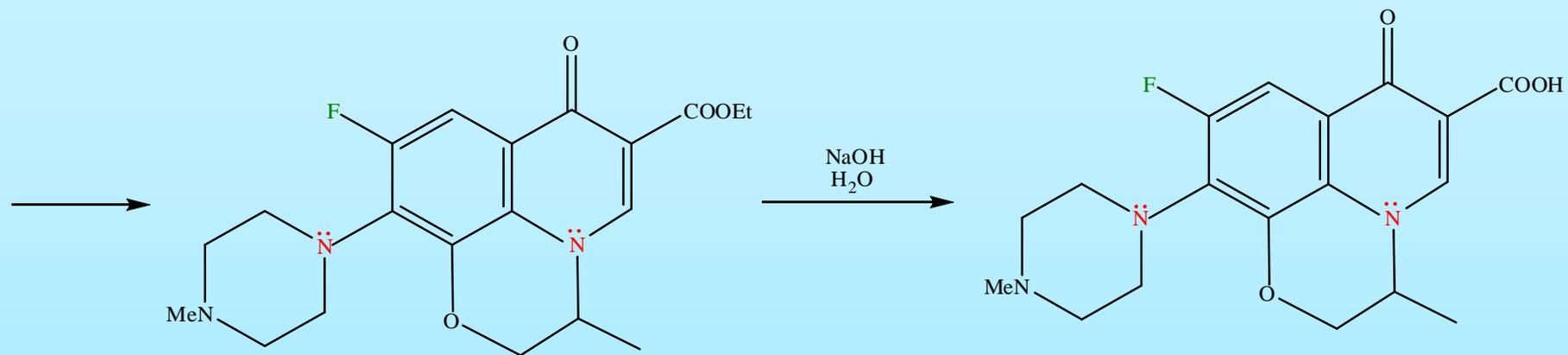
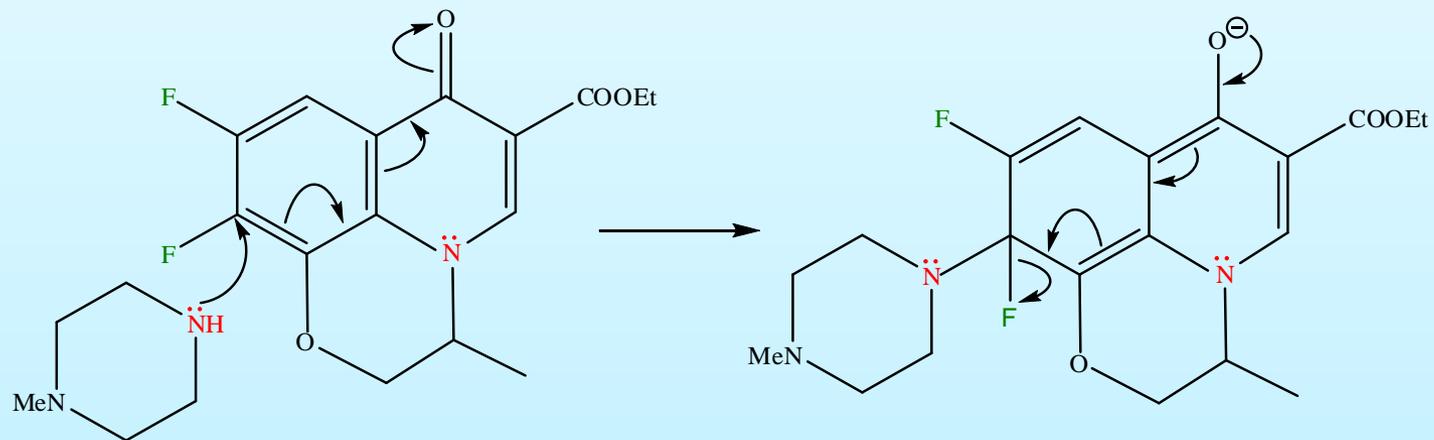
### ❑ It is synthesized from following starting material, containing four fluorine atoms.



❑ Reaction involves nucleophilic substitution of fluorine atoms. Steps involved are as follows.



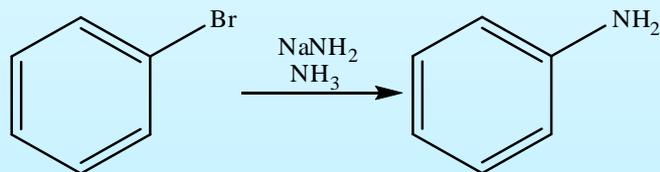




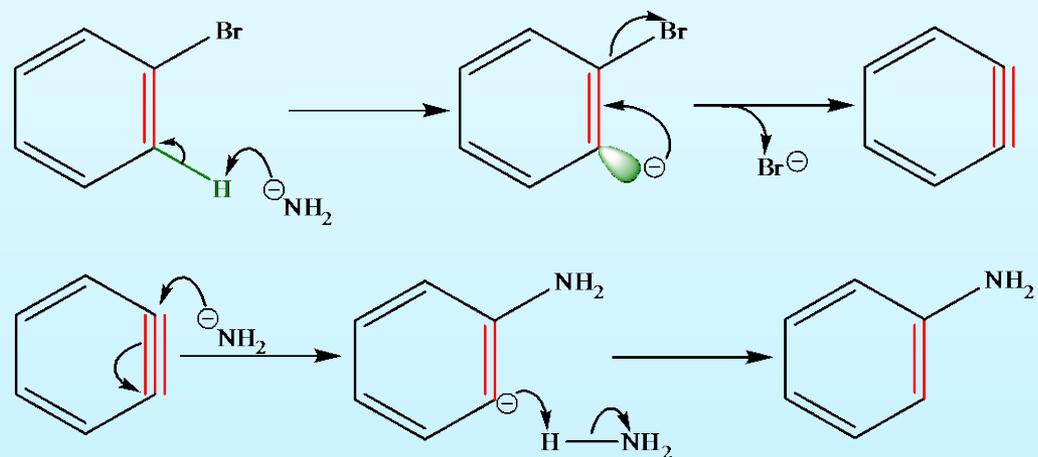
ofloxacin

# Benzyne mechanism

- ❑ Bromobenzene reacts with a strong base such as sodium amide in liquid ammonia to give aniline through nucleophilic substitution reaction.

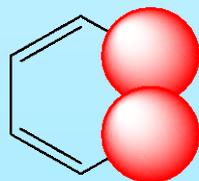


- ❑ Reaction goes through different mechanism than stated earlier.
- ❑ It involves formation of a **benzyne intermediate** hence name benzyne mechanism.
- ❑ It is **reverse of normal addition-elimination mechanism**.
- ❑ Sometimes it is called **elimination-addition mechanism**.

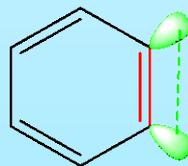


- ❑ In the first step, the *ortho* proton is removed by the action of a strong base to furnish a carbanion.
- ❑ This anion then loses the bromide ion to give a highly reactive benzyne intermediate.
- ❑ This benzyne intermediate then reacts with the nucleophile to give the product. In the above example amide ion acts as a nucleophile.
- ❑ Strong bases such as amide ions, oxyanions, carbanion are required for the reaction to go forward.

- ❑ Due to the presence of electronegative bromine, **ortho proton is relatively more acidic**, resulting in its removal by the base.
- ❑ Benzyne intermediate is formed from this carbanion by **syn-periplanar elimination** of the bromide ion.
- ❑ Benzyne intermediate appears like an **alkyne in its representation with triple bond in the benzene ring**. However, this triple bond is not like an usual triple bond as its is formed by the lateral **overlap between two  $sp^2$  hybridized orbitals outside the ring**.

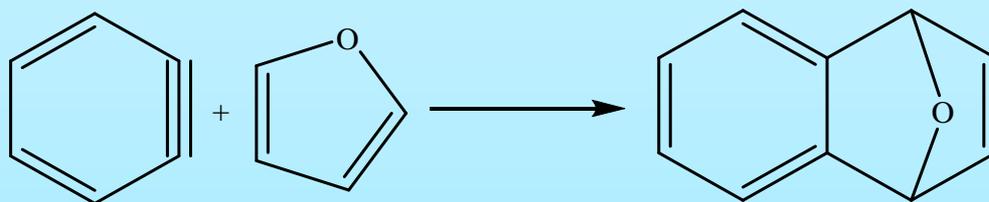


normal  $\pi$  bond  
two p orbitals inside ring



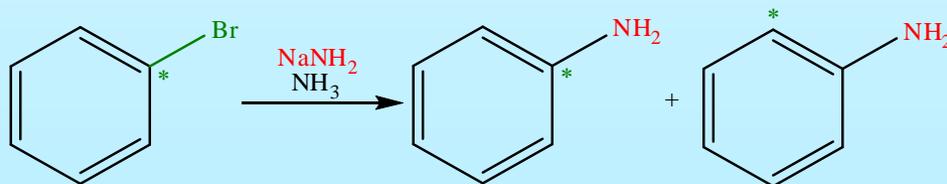
abnormal  $\pi$  bond  
two  $sp^2$  orbitals outside ring

- ❑ This external  $\pi$  bond is weak, making benzyne intermediate unstable and highly reactive.
- ❑ It can not be isolated but it can be **trapped** in order to detect its presence as an intermediate.
- ❑ Reaction such as Diels-Alder reaction (as shown below) can be used to trap this intermediate.



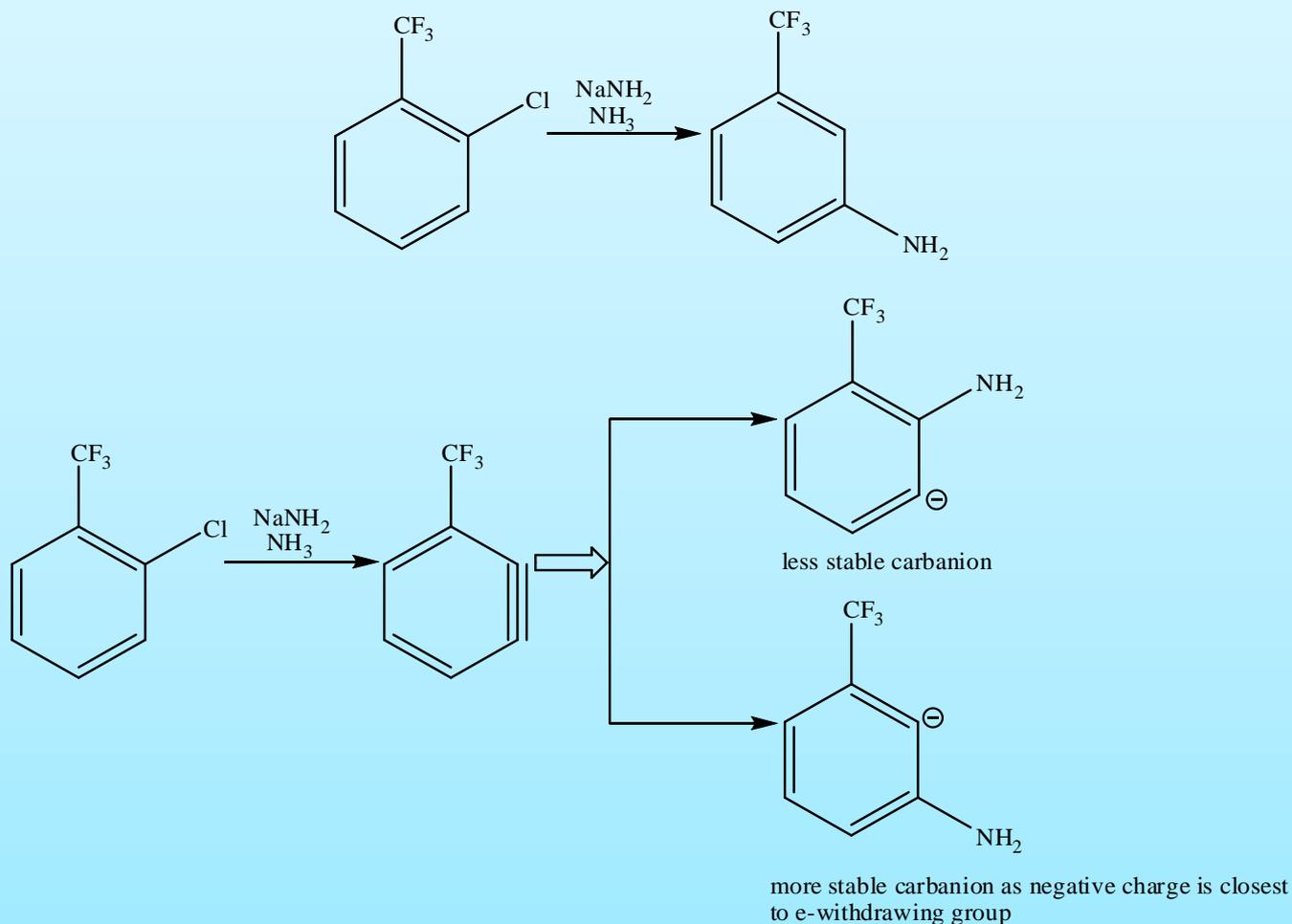
❑ First major evidence for the presence of benzyne intermediate was given by J. D. Roberts in 1953.

❑ He showed that  $^{14}\text{C}$  labeled bromobenzene on treatment with amide in liquid ammonia gives aniline in which  $^{14}\text{C}$  label is equally distributed in two positions.

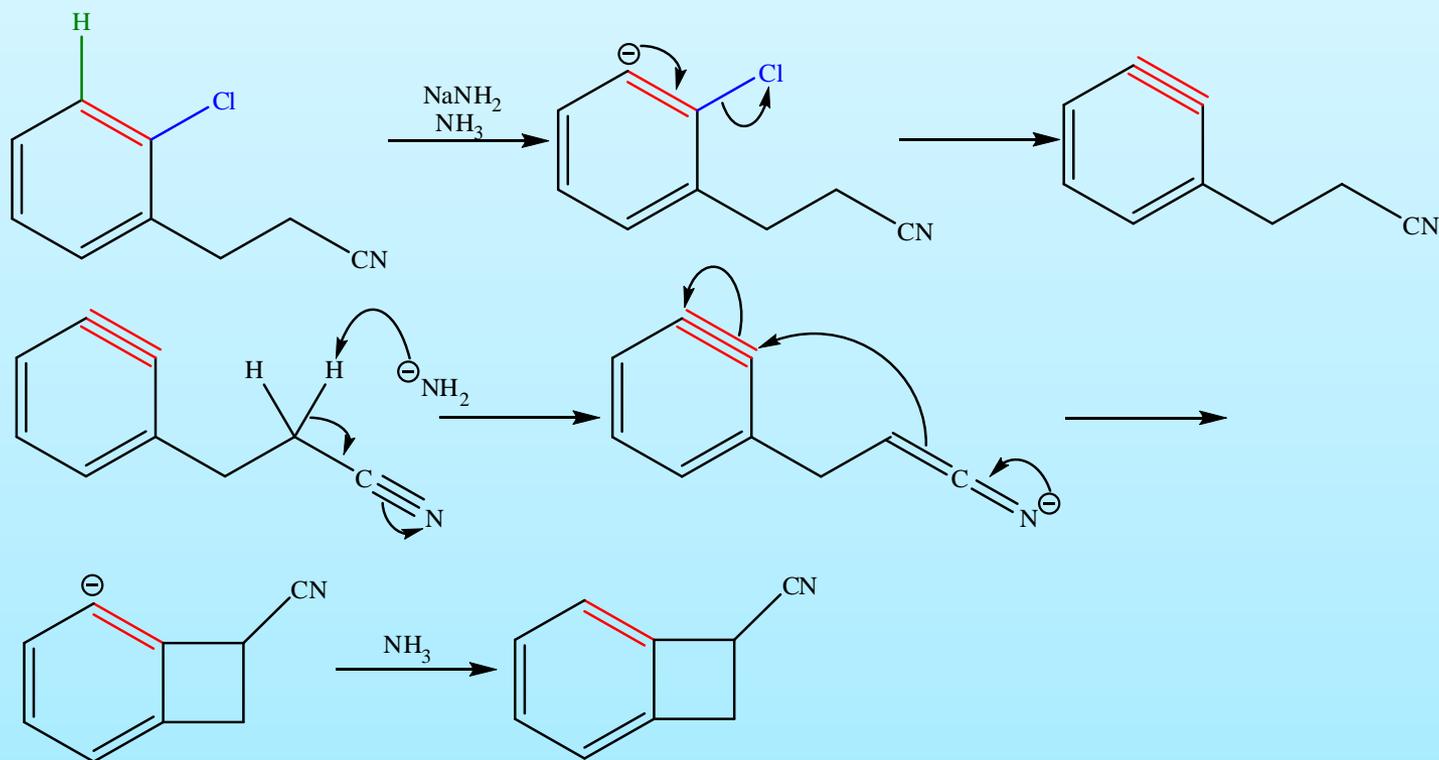


❑ Benzyne is a **symmetrical intermediate**. For this reason probability of formation of both products is equal. But, when aromatic nucleus has more than one substituent then product formed will be depending upon existing group.

Formation of exclusively m-(trifluoromethyl)aniline from o-(trifluoromethyl)chlorobenzene can be explained by taking into consideration the carbanion formed after the addition of the nucleophile to benzyne.

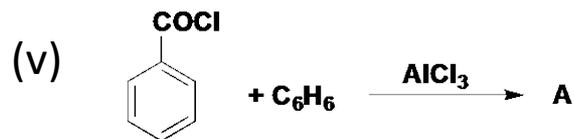
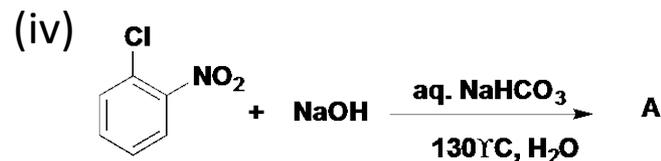
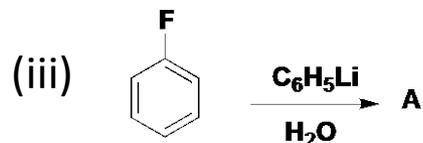
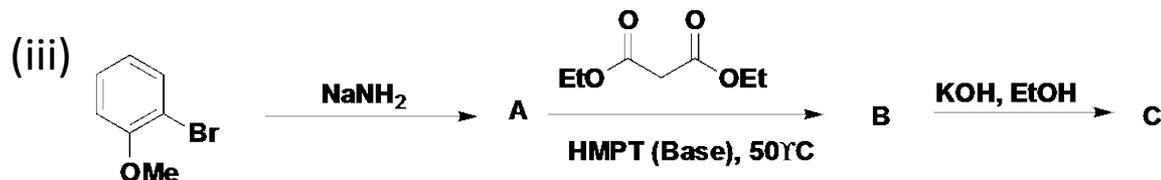
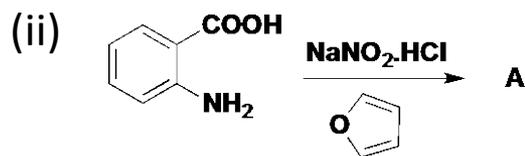
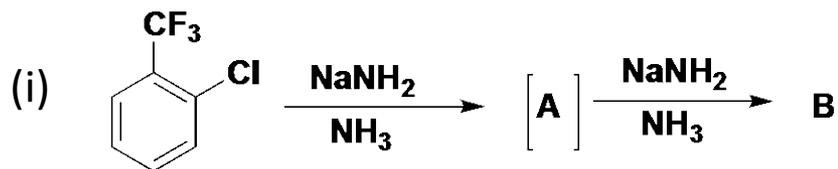


□ In intramolecular attack of nucleophiles, selectivity is not an issue. It simply gives one cyclization product with the nearer end of the triple bond.



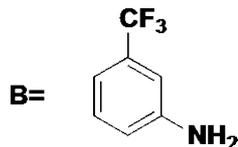
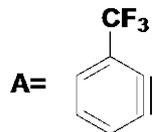
# Practice problems

(1) Identify the unknowns in the following equations



# Answers

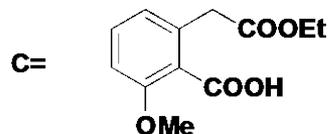
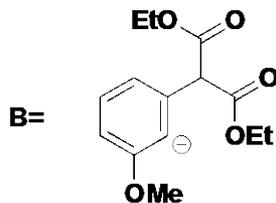
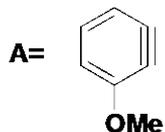
(1) (i)



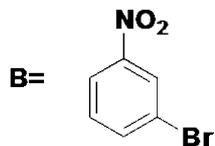
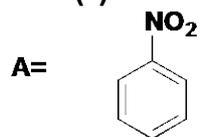
(ii)



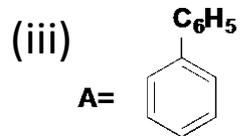
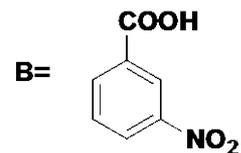
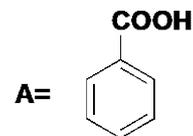
(iii)



(2) (i)



(ii)



(iv)

