BENZENE

(CHE-GE202)

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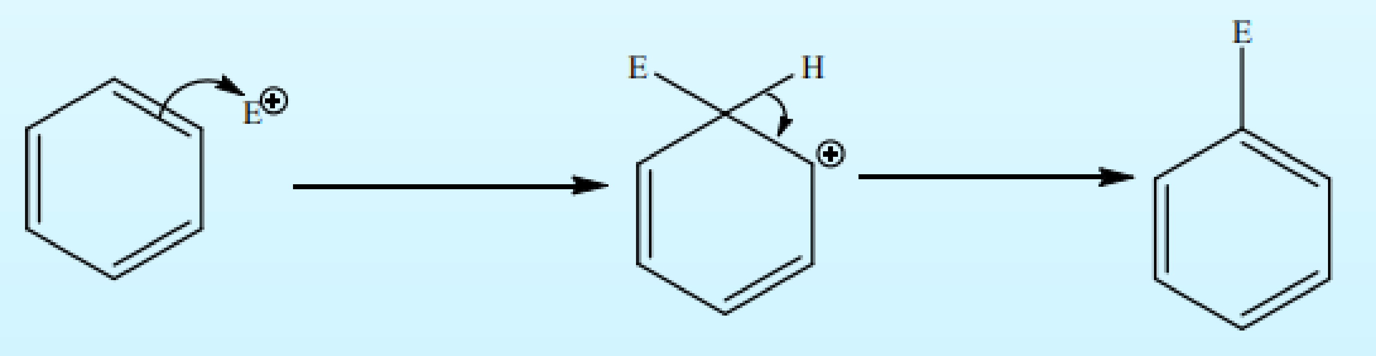
BENZENE

- BENZENE is a cyclic hydrocarbon with a chemical formula C_6H_6
- Each carbon atom in benzene is arranged in a six-membered ring and is bonded to only one hydrogen atom.
- According to molecular orbital theory for benzene structure, benzene ring involves the formation of three delocalized π – orbitals spanning all six carbon atoms, while the valence bond theory describes two stable resonance structures for the ring.
- Benzene is one of the most fundamental compounds used in the manufacturing of various plastics, resins, synthetic fibers, rubber lubricants, dyes, detergents, drugs, and pesticides. Benzene is found to exhibit a unique set of physical and chemical properties.

PROPERTIES OF BENZENE

- Benzene belongs to the family of aromatic hydrocarbons which are nonpolar molecules and are usually colorless liquids or solids with a characteristic aroma.
- **Benzene** is immiscible in water but soluble in organic solvents.
- It has an aromatic odour.
- It has a density of 0.87g cm^{-3}.
- **Benzene** has a moderate boiling point and a high melting point.
- **Benzene** shows resonance.
- It is highly inflammable and burns with a sooty flame.

Mechanism for general reaction of electrophilic subsitution of Benzene



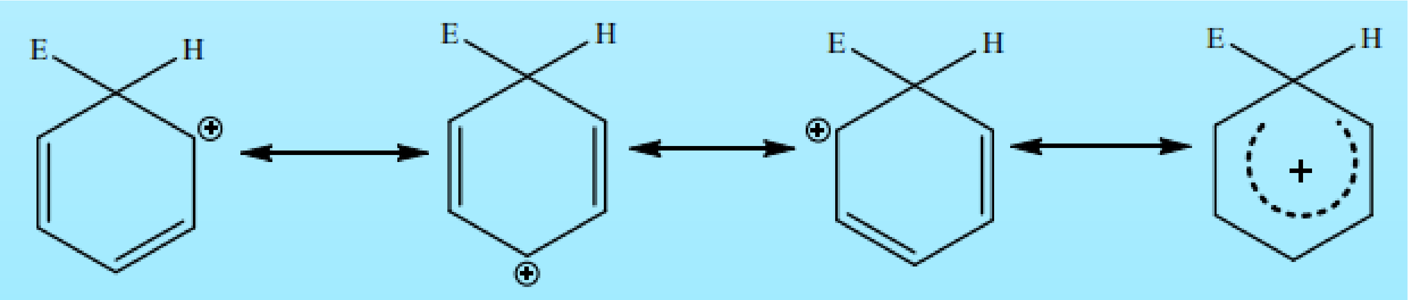
E+: electrophile

❑ Two step mechanism:

➢ First step is the rate determining involving interaction of the π 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**

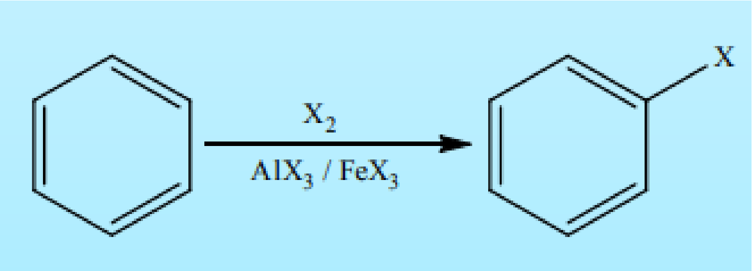
b) Nitration

c) Sulfonation

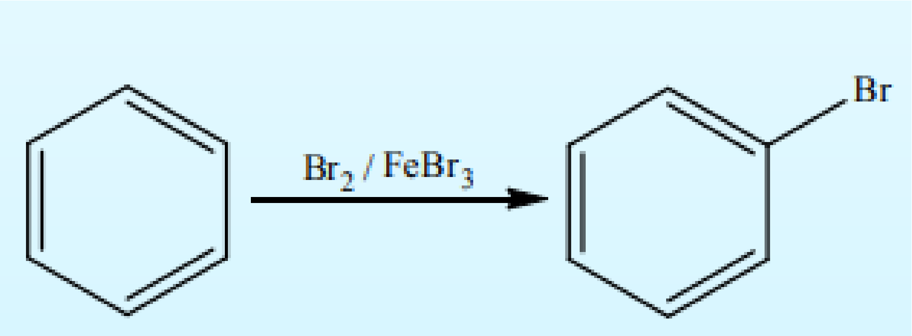
d) Friedel-Crafts alkylation and Friedel-Crafts acylation

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.
- ☐ X can be chlorine or bromine.
- ☐ Analogous reactions with iodine or fluorine are not synthetically useful because I_2 is too unreactive and F_2 reacts too violently.
- ☐ Iodination requires an acidic oxidizing agent, like nitric acid, which oxidizes the iodine to an iodonium ion.
- ☐ Reaction goes as follows:

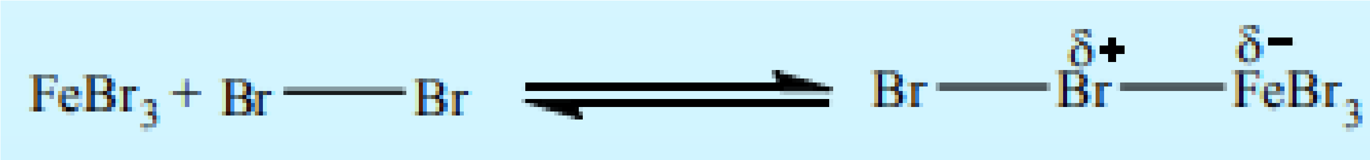


X: Bromine, Chlorine.



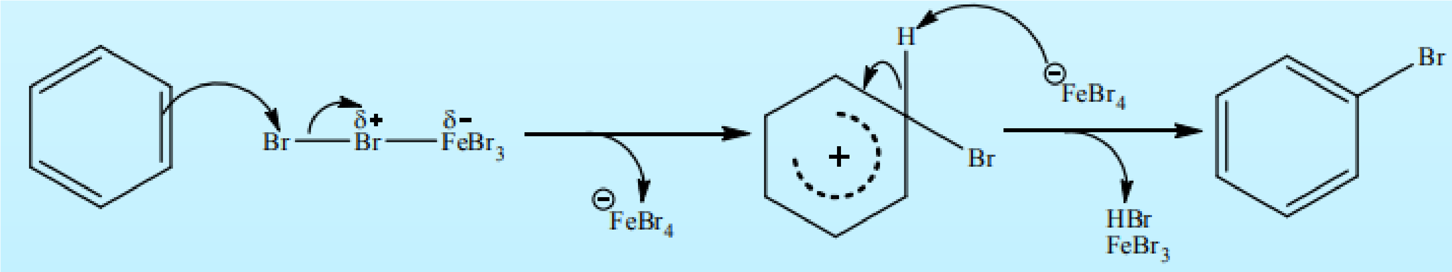
Mechanism

Step 1:



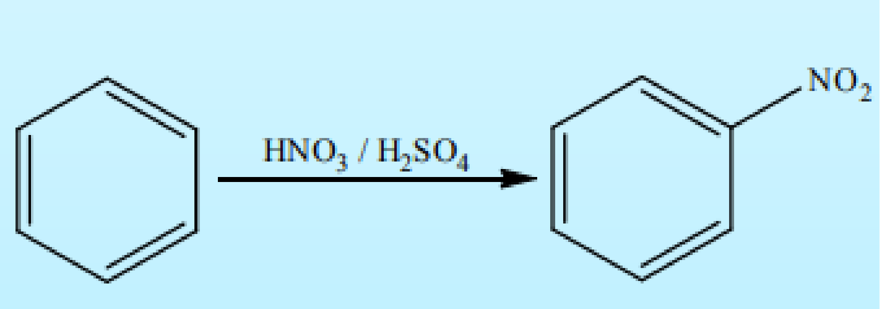
$$FeBr_3 + Br{-}Br \rightleftharpoons Br{-}\overset{\delta+}{Br}{-}\overset{\delta-}{FeBr_3}$$

Step 2:



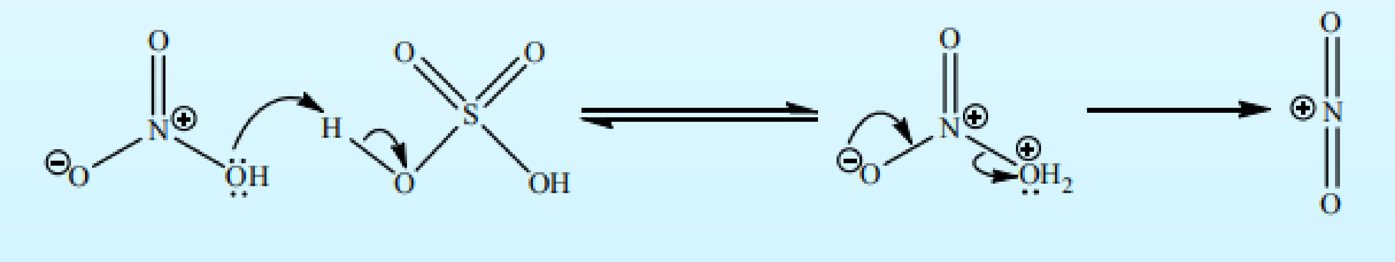
Nitration

- Where a H atom attached to an aromatic ring is replaced by a NO2 group
- Reaction conditions are concentrated nitric and sulfuric acid at elevated temperature.
- Nitronium ion (NO_2^+) is the electrophile that attacks the benzene ring.
- Generation of the electrophile in nitration requires strong acid.
- 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.



Mechanism

Step 1:



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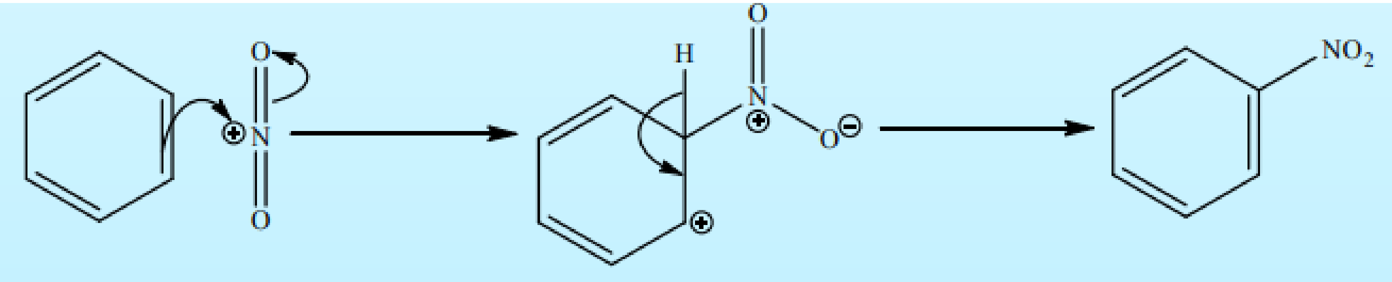
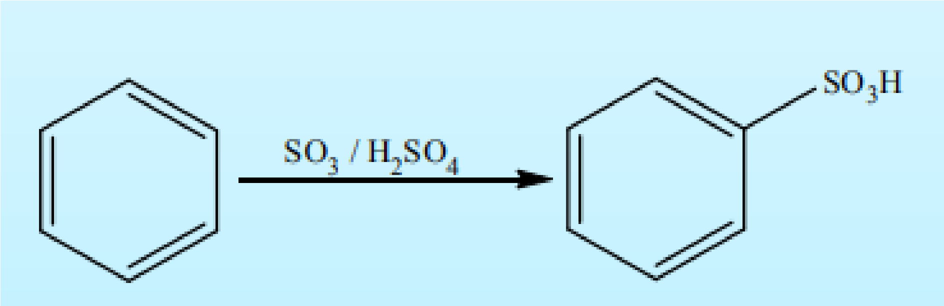


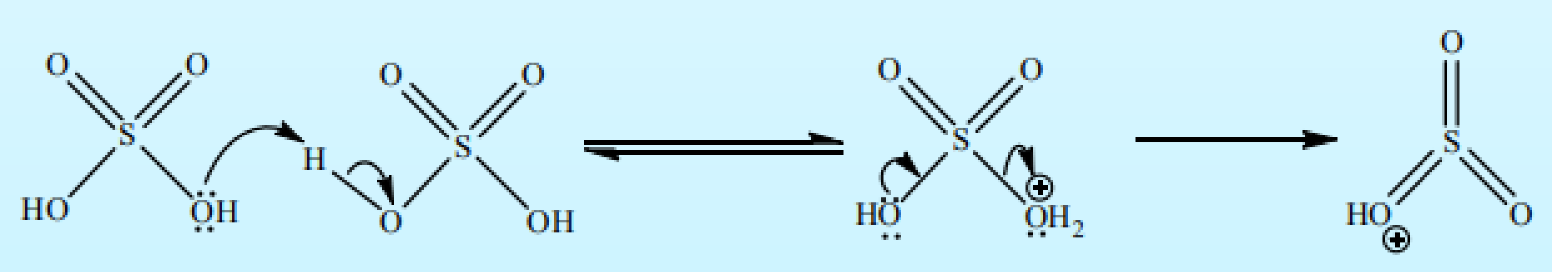
Sulfonation

- Introduction of sulfonic acid group to aromatic system by treatment with concentrated sulfuric acid.
- Sulfur trioxide, SO_3, in fuming sulfuric acid is the electrophile.
- 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 SO_3 and H_2SO_4 mixture, SO_3 alone can act as electrophile instead of protonated 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.

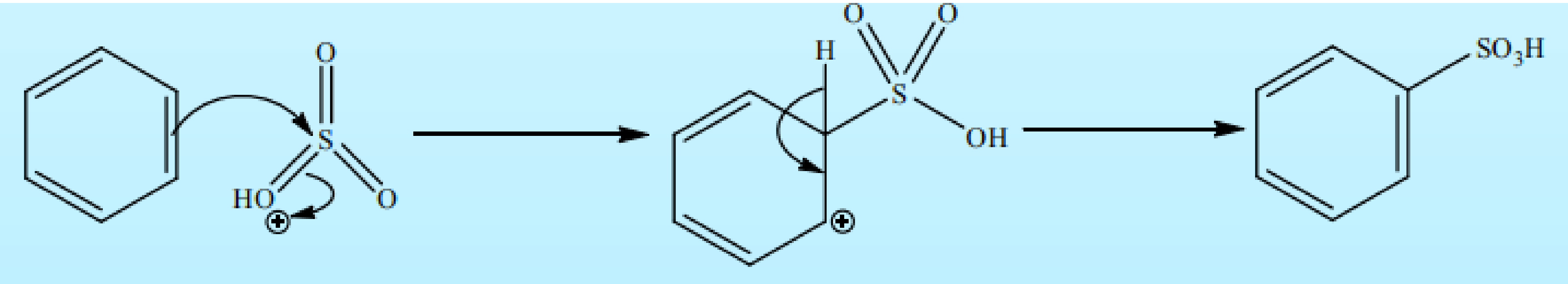


Mechanism

Step 1:

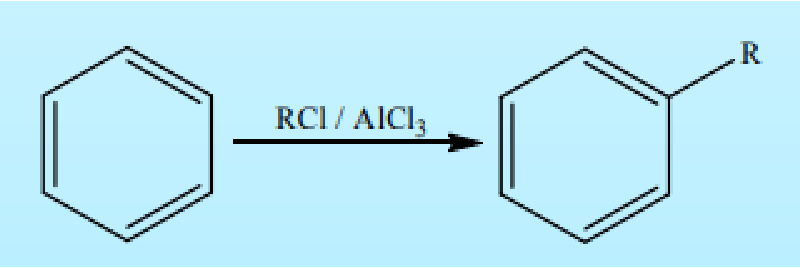


Step 2:



Friedel-Crafts Alkylation Reaction

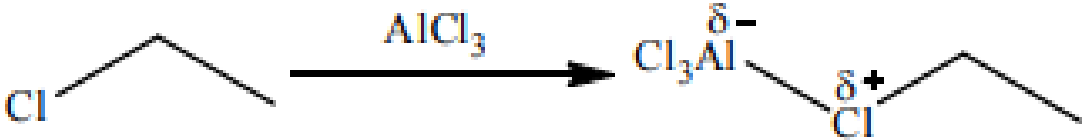
- ❑ Preparation of alkyl benzenes from alkyl halides and a Lewis acid (usually $AlCl_3$).
- ❑ The carbocation is the electrophile
- ❑ The role of the anhydrous aluminum chloride is to generate a stable carbocation complex.
- ❑ For CH_3Cl and 1° RCl, Lewis acid-base complex itself serves as electrophile.
- ❑ For 2° and 3° RCl, Lewis acid-base complex reacts further to furnish 2° and 3° carbocation respectively, due to the increased stability of such carbocations



R-Cl: alkyl chloride

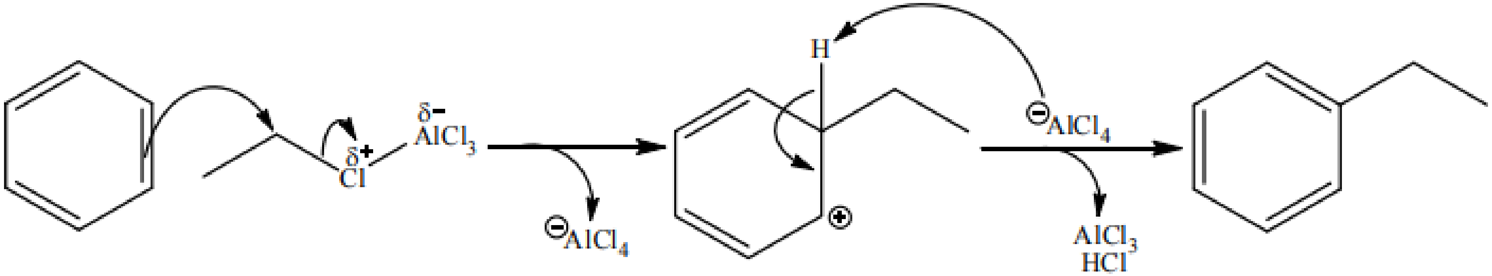
Mechanism

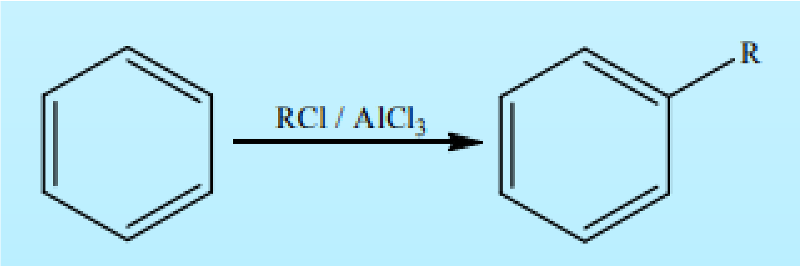
Step 1:



Primary alkyl chlorides

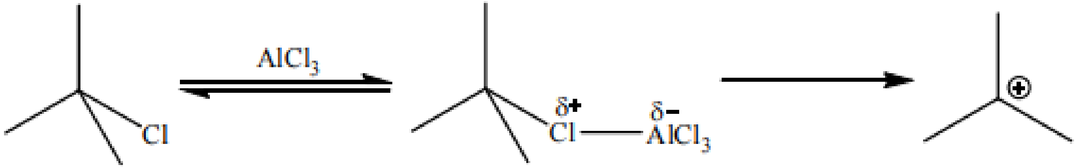
Step 2:



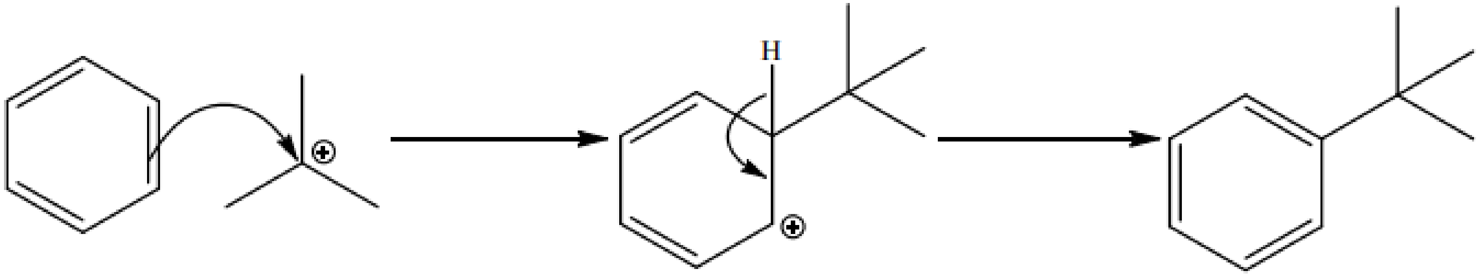


Mechanism

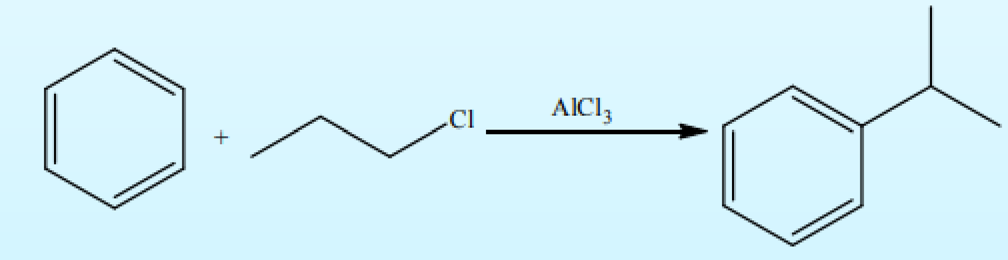
Step 1: tert-alkyl chlorides



Step 2:

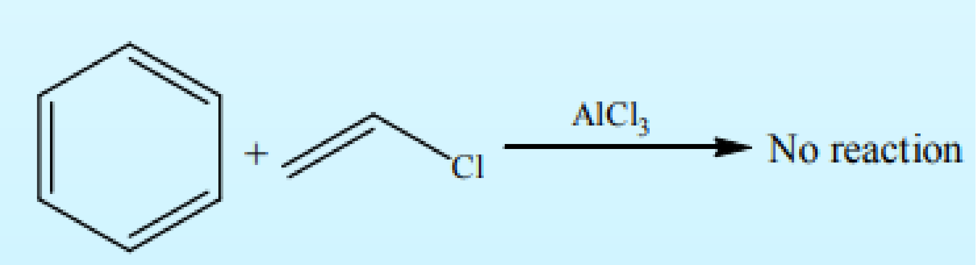


❑ **Carbocation rearrangement** is seen in case of alkyl halides [example above involves rearrangement of primary to secondary carbocation].



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

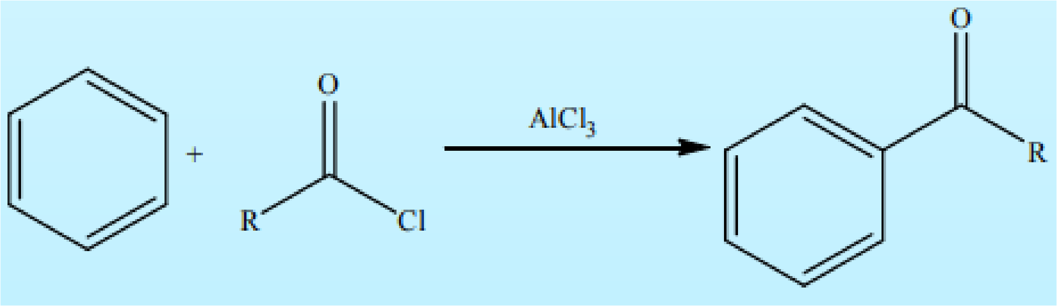
❑Vinyl halides and aryl halides do not undergo Friedel-Crafts alkylation [cannot generate vinyl cations].



❑Poor yields are obtained if powerful electron withdrawing group is present on aromatic nucleus (such as NO_2, NR_3^+, C=O)

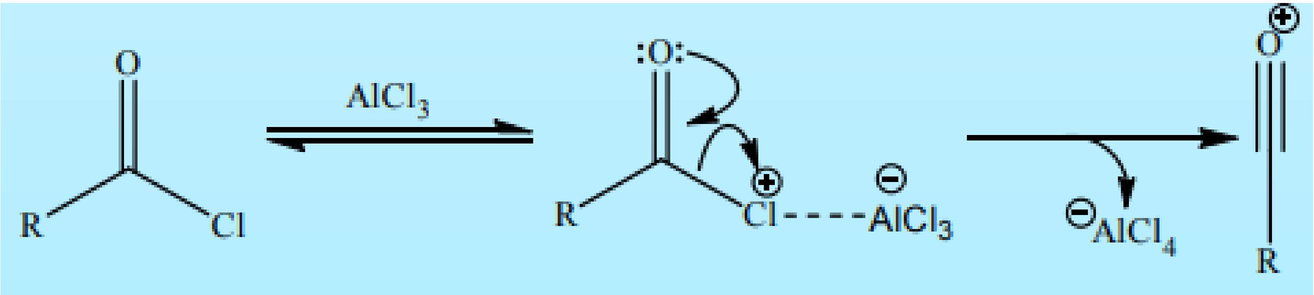
Friedel-Crafts Acylation Reaction

- 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 $AlCl_3$.
- Acylium ion is the electrophile.
- The acylium ion intermediate is resonance stabilized and does not rearrange like a carbocation.
- In Friedel-Crafts acylation, no polysubstitution is seen, as carbonyl group is electron withdrawing and makes aromatic ring less electrophilic and $AlCl_3$ forms complex with the carbonyl group, further preventing the reaction.

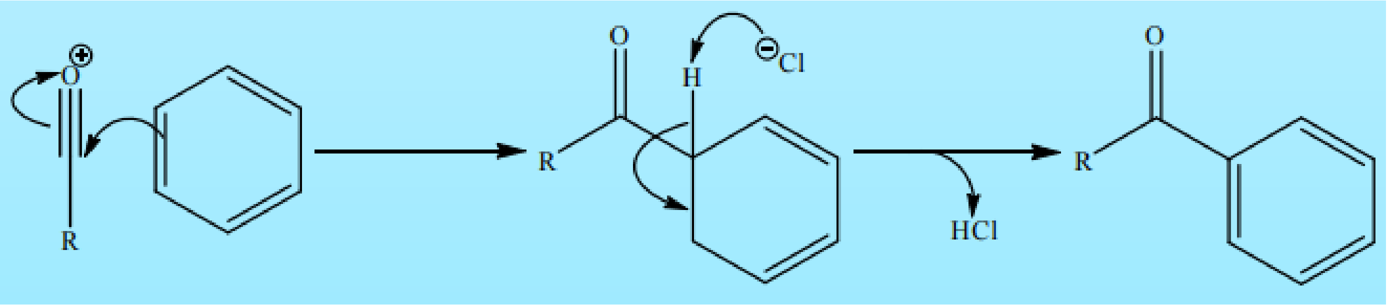


Mechanism

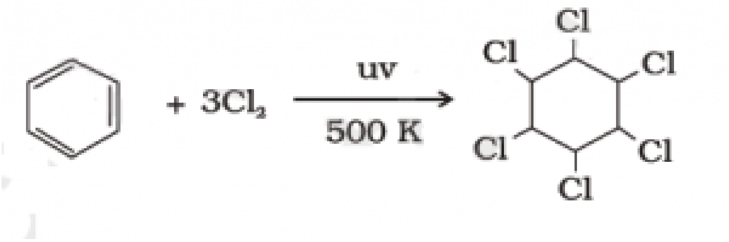
Step 1:



Step 2:



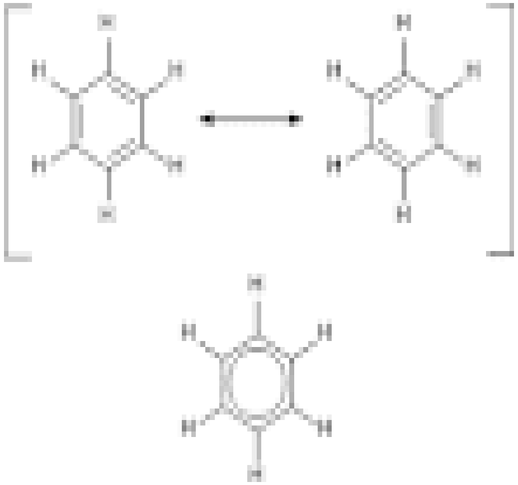
<u>Addition reactions</u>: Addition of chlorine in the presence of ultraviolet light produces benzene hexachloride better known as gammaxene.



Combustion of benzene: Upon combustion of benzene, benzene burns with a sooty flame along with the evolution of CO_2 gas.

- $C_6H_6 + O_2 \rightarrow CO_2 + H_2O$

STRUCTURE OF BENZENE



- **Benzene** has two **resonance structures**, showing the placements of the bonds. Another example of **resonance** is ozone.
- The difference between the two resonance **structures** is the location of double bond
- Although there are three π bonds in the **structure** of **benzene**, there is actually **resonance**, or electron delocalization.
- This means that the electrons are not localised in π bonds between two specific carbons, but distributed throughout the ring. This is one of the most important characteristics of an aromatic system.