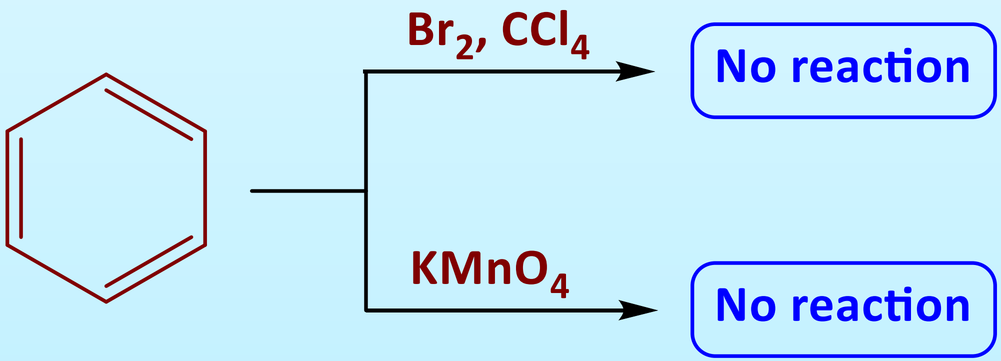
# Reaction of Benzene

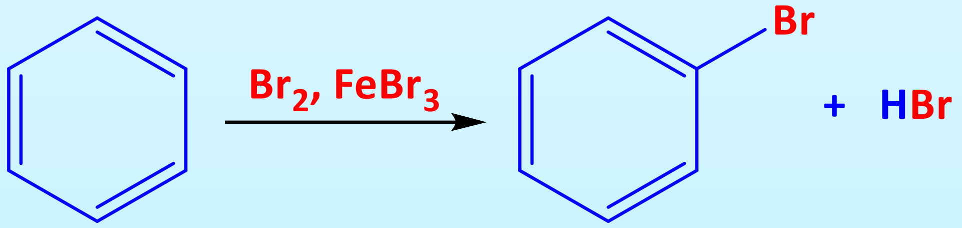
- By now, you would have noticed that because of the high concentration of double bonds in the ring, you would expect it to undergo many types of reactions such as hydrogenation, halogenation, oxidation, and adding water across the double bond
- Well! – benzene does none of that!!!
- When benzene is treated with bromine in $CCl_4$, or $KMnO_4$, no addition or oxidation takes place – this is strange!!!

# Reaction of Benzene




- So is benzene really inert to chemical reactions? – maybe not!
- Benzene does react with halogens but in the presence of a catalyst in the form of a Lewis acid such as ferric bromide ($FeBr_3$)

# Reaction of Benzene



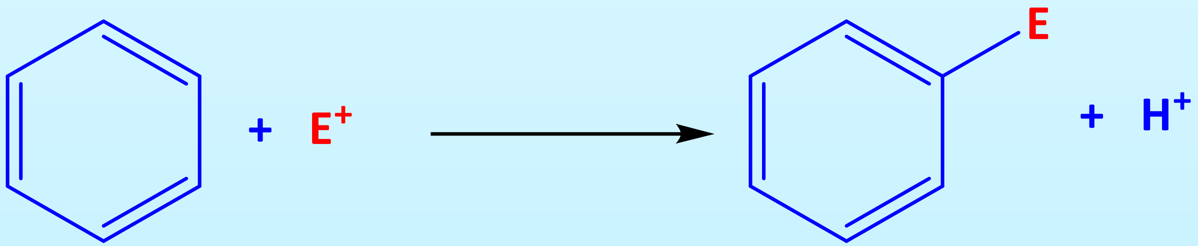

- The most interesting aspect of this reaction is that because of the three sets of double bonds, we would expect the addition of the bromine to occur across the double bonds
- Instead, a *substitution* reaction is observed in which the halogen replaces one of the aromatic hydrogen atoms

# Reaction of Benzene

- **This reaction is an example of the most common reaction involving aromatic compounds and this is *electrophilic aromatic substitution reactions***

- **Again, because of the high concentration of electrons in the ring system, the most favourable reagent it can accept is an electron-deficient species (an electrophile, $E^+$)**

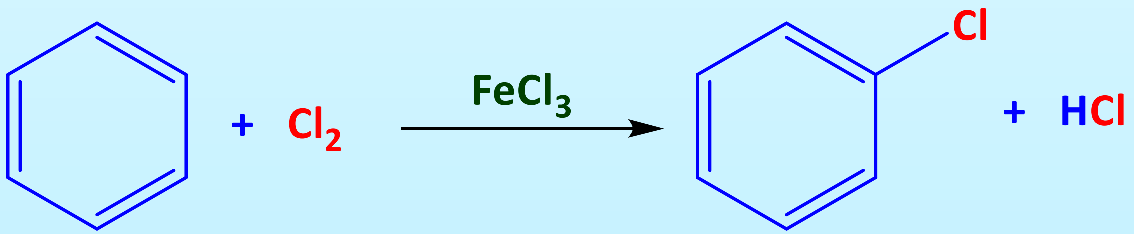
# Reaction of Benzene



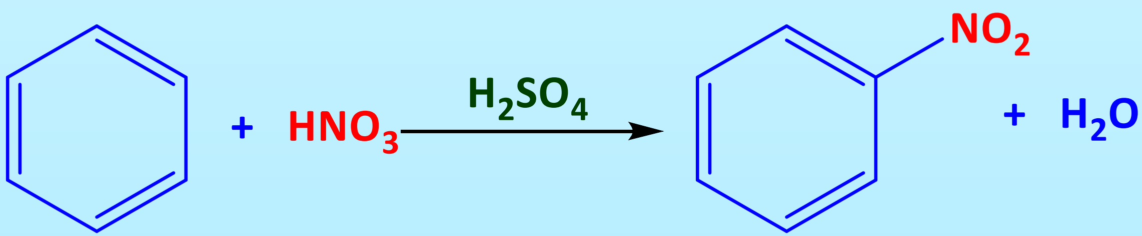

- **Given below are some of the most common electrophilic aromatic substitution reactions – halogenation, nitration, sulfonation, acylation and alkylation**
- **In the examples givens R – alkyl group, X – halogen atom**

# Reaction of Benzene

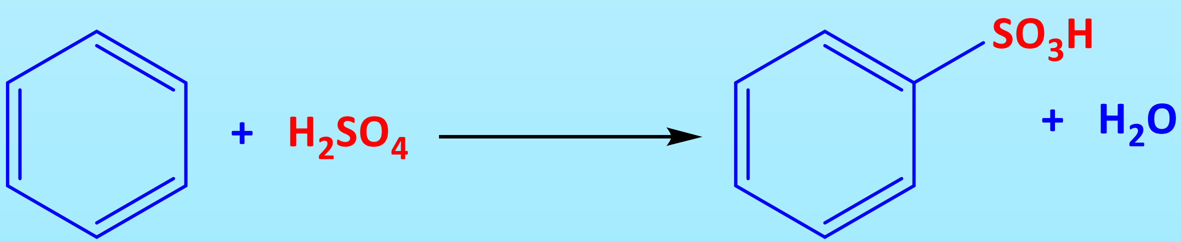
**Halogenation:**



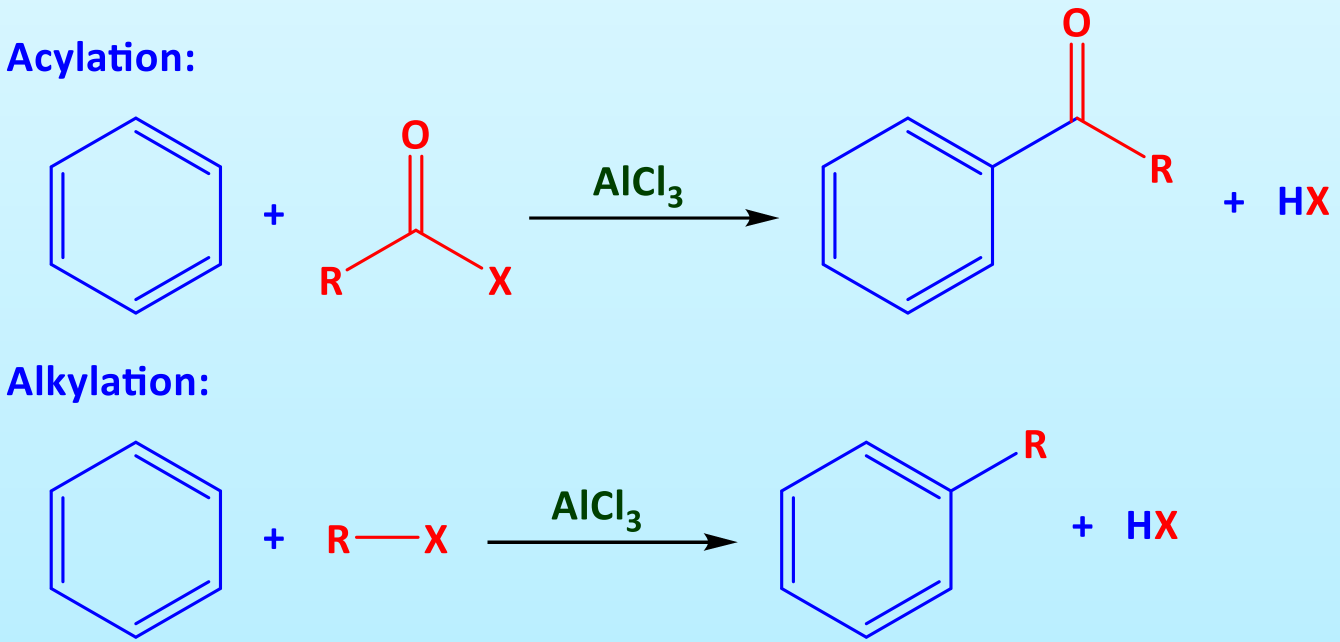

**Nitration:**




**Sulfonation:**



# Reaction of Benzene




- **In all these reactions, the initial step involves the preparation of the electrophile, $E^+$, an electron-deficient species**

# Reaction of Benzene

- **The electrophile must be capable of accepting a pair of electrons from the nucleophile – what is the nucleophile here?**
- **Once it is formed then the electrophilic substitution reaction can proceed:**

$$\mathrm{E{-}A} \;+\; \mathrm{LA} \longrightarrow \underset{\textit{electrophile}}{\mathrm{E^{+}}} \;+\; \mathrm{[A\text{-}LA]\text{-}}$$

- **The electrophile has to be positive enough in order for the reaction to happen…**

# Mechanism

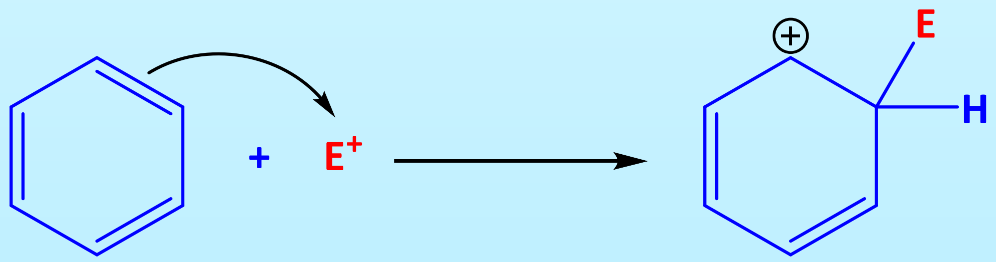
- To help you understand what goes on between the steps in the halogenation process, look over the following steps below.

**Step 1:**

- The electrophile takes two electrons of the 6-electron $\pi$ system to form a sigma bond to one of the carbon atoms of the benzene ring to form an arenium ion

# Mechanism

- **When this occurs, the aromaticity (or ring stability) is temporarily destroyed**



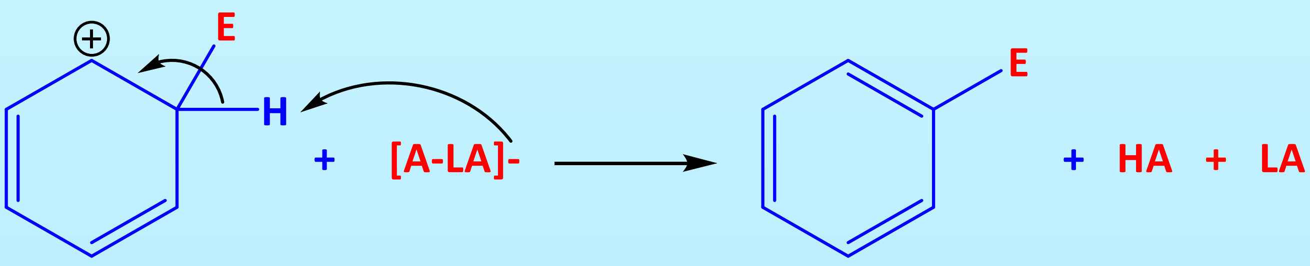

*aromaticity is destroyed temporarily*

## Step 2:

- **The proton on the *sp*$^3$-hybridized carbon atom on the ring is removed by the base ([A-LA]$^-$) that is present**

# Mechanism

- **The electrons for the C-H bond are then used to make π bond again and in doing so, restores the aromaticity of the ring**

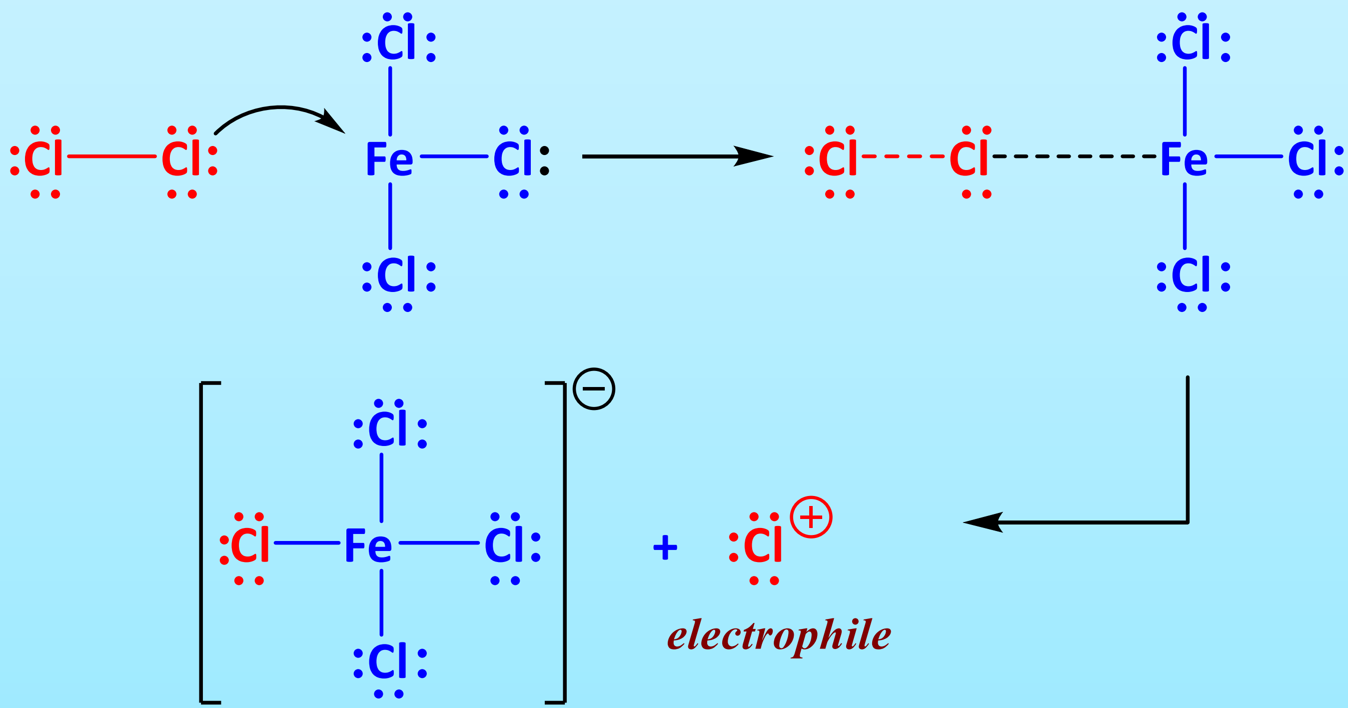



*aromaticity is restored*

- **Now let us look at the halogenation substitution of benzene – in particular, the chlorination of benzene**

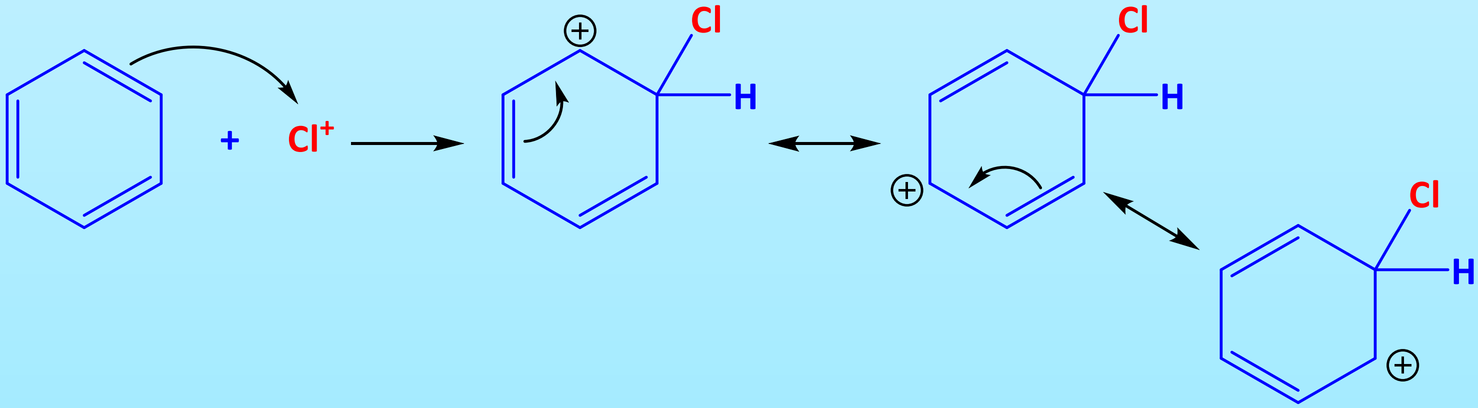
# Mechanism

- The initial reaction is between the chlorine molecule ($Cl_2$) and the ferric chloride ($FeCl_3$) which produces an iron complex $FeCl_4^-$ and $Cl^+$ [ the $Cl^+$ is the electrophile here]



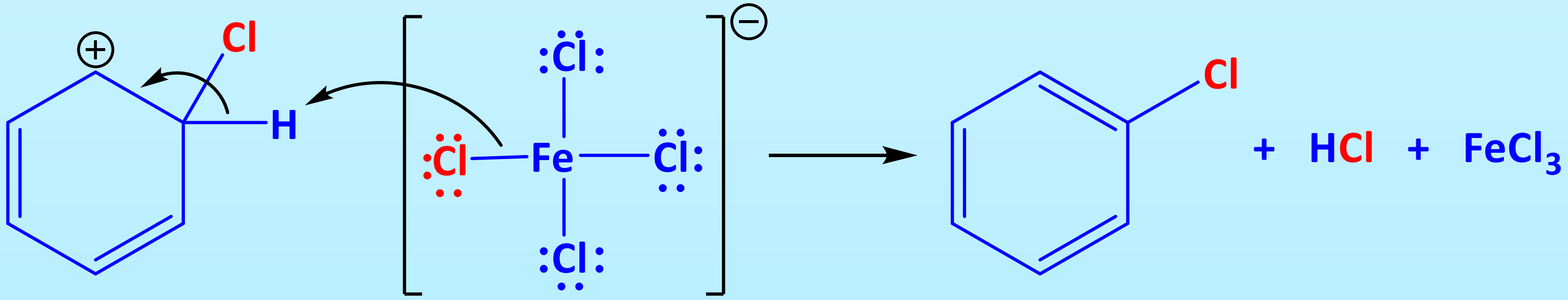
# Mechanism

- Once the electrophile is produced, it will then react with the benzene ring
- The chloronium ion [$Cl^+$] reacts with the $\pi$ electrons of the aromatic ring to produce a resonance-stabilized cation intermediate



# Mechanism

- The negatively charged iron complex then abstracts a proton from the cation intermediate and regenerates the aromatic character of the ring




- The overall reaction is therefore a substitution reaction because chlorine substitutes a hydrogen atom on the aromatic ring

# Mechanism

- **It is called electrophilic because the incoming species is positively charged ($Cl^+$) and the outgoing species ($H^+$) is positively charged as well**

- **You have seen that the different reactions have different electrophiles ($Cl^+$, $NO_2^+$, $R\text{-}CO^+$, $HSO_3^+$ etc.) but the mechanism by which the electrophile is introduced onto the ring is exactly the same**

# Haloalkanes

# Haloalkanes

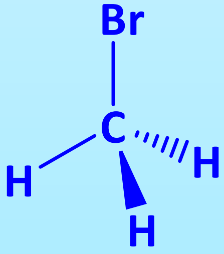
- **Haloalkanes are compounds that contain a halogen atom covalently bonded to an *sp*$^3$ hybridized carbon atom.**
- **They are also referred to as alkyl halides and have the general formula of R–X where R is an alkyl residue while –X is –F, –Cl, –Br or –I.**
- **Alkyl halides are classified as primary (1$^o$), secondary (2$^o$) or tertiary (3$^o$)**
- **This classification is based on the carbon atom to which the halogen is directly attached**

# Haloalkanes

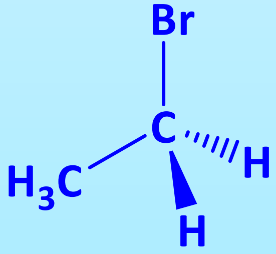
- If the carbon atom that bears the halogen is attached  to only one carbon, then the carbon atom is said to be a primary carbon atom and the alkyl halide is classified as a primary alkyl halide
- If the carbon atom that bears the halogen is itself attached  to two other carbon, then the carbon atom is said to be a secondary carbon atom and the alkyl halide is classified as a secondary alkyl halide

# Haloalkanes

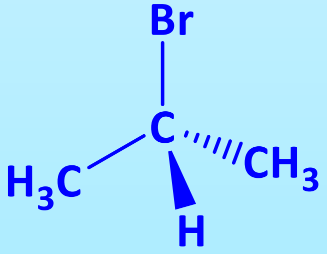
- If the carbon atom that bears the halogen is attached to three other carbon atoms, then the carbon atom is said to be a tertiary carbon atom and the alkyl halide is classified as a tertiary alkyl halide



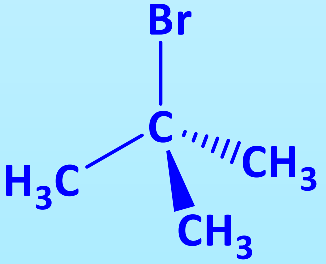
bromomethane
(1°)



bromoethane
(1°)



2-bromopropane
(2°)

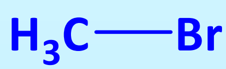


2-bromo-2-methylpropane
(3°)

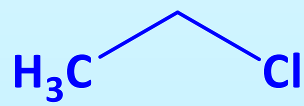
# Haloalkanes

- The IUPAC naming system is very similar to the rules used in the naming of alkanes.
- Longest continuous carbon chain adopts the parent compound name
- The halogen is expressed as a substituent on the chain and indicated as the prefixes fluoro-, chloro-, bromo- or iodo and are listed in alphabetical order along with the other substituents

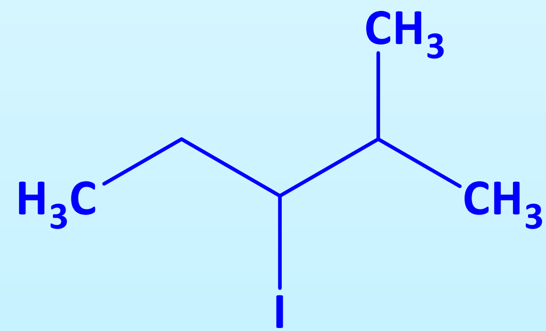
# Haloalkanes



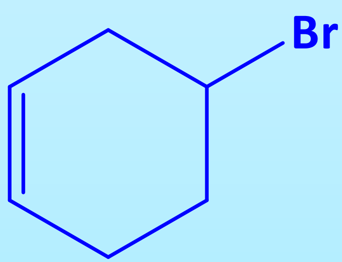

**bromomethane**



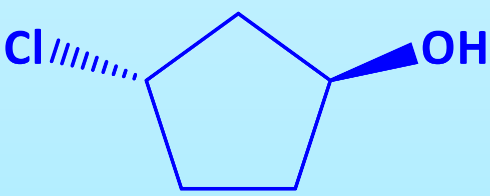

**chloroethane**




**3-iodo-2-methylpentane**




**4-bromocyclohexene**




***trans*-3-chlorocyclopentanol**

# Reactions of Haloalkanes

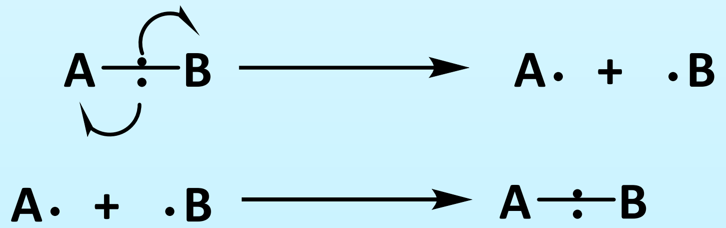
- **An important feature of chemistry is the chemical changes that convert one substance to another, i.e. old molecules are changed to new ones**
- **In the chemical sense, this means existing bonds are broken and new ones are formed**
- **In organic chemistry, this means breaking and forming covalent bonds**
- **So the question is: what happens to the two or more electrons that hold bonding atoms together during this process?**

# Reactions of Haloalkanes

- **As we saw earlier, organic reactions proceed primarily via two mechanisms – *free radical processes* (homolytic reaction) and *ionic processes* (heterolytic reaction)**
- **In free radical processes, the reaction involves homolytic cleavage and the formation of bonds**
- **Here the two electrons holding the atoms together are equally shared by the fragments when the bond breaks or the two fragments equally share one electron each to form the product.**

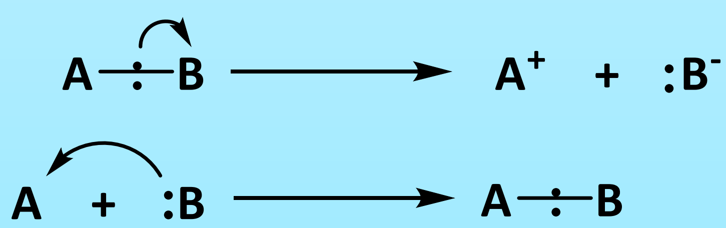
# Reactions of Haloalkanes

**Homolytic reactions:**




- **For the heterolytic (ionic) reactions, the two electrons in the bond are given to just one fragment or donated from just one of the fragments to form the product**

**Heterolytic reactions:**



# Reactions of Haloalkanes

- **To deal with the nucleophiles and electrophiles substitution, we have to explore more into the family of haloalkanes**
- **Haloalkanes are a very important family of compounds because they can be used to prepare a great number of compounds used in organic synthesis.**
- **They are used to determine a chemical reaction – i.e. *what* happens, *where* it happens, and *whether* it happens**