

# HALOGENOALKANES

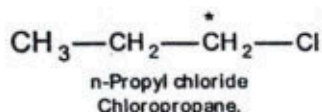
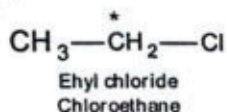
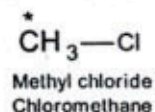
## Student Learning Outcomes (SLOs)

- Describe production of halogenoalkanes i.e. reaction of benzene with  $\text{Cl}_2$  and  $\text{Br}_2$  in the presence of catalyst.
- Compare the reactivity of halogenoalkane and halogenoarene using chloroethane and chlorobenzene as examples.
- Predict the major product(s) based on the reaction conditions and the molecular structure of the halogenoalkane.
- Analyze the mechanism and products of a reaction pathway involving a halogenoalkane, and use retro-synthesis to deduce the starting materials.
- Describe the  $\text{S}_\text{N}1$  and  $\text{S}_\text{N}2$  mechanisms of nucleophilic substitution in halogenoalkanes including the effects of alkyl groups.
- Identify that primary halogenoalkanes tend to react via the  $\text{S}_\text{N}2$  mechanism, tertiary halogenoalkanes via the  $\text{S}_\text{N}1$  mechanism, and secondary halogenoalkanes by a mixture of the two, depending on structure.
- Explain the different reactivities of halogenoalkanes (with particular reference to the relative strengths of the C-X bonds as exemplified by the reactions of halogenoalkanes with aqueous silver nitrate).

Halogenoalkanes also known as alkyl halides are compounds in which one hydrogen atom of alkanes has been replaced by a halogen atom. They are also known as halogen derivatives of alkanes. general formula of halogenoalkanes is R-X. The general formula of halogenoarenes is Ar-X, where Ar is an aryl or arene group.

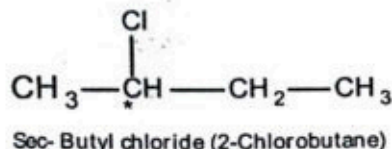
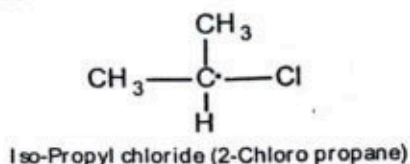
Recall that alkyl halides are classified into primary, secondary and tertiary alkyls halides.

- Alkyl halide in which halogen atom is attached with primary carbon are called primary alkyl halide. A primary carbon is a carbon that is bonded to only other carbon atom of none, as in case of methane.



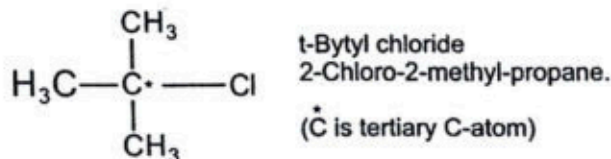
(C is primary carbon atom)

- Alkyl halides in which a halogen atom is attached to a secondary carbon atom is called secondary alkyl halide. Secondary carbon is carbon to which two alkyl groups are attached.



(C is secondary carbon atom)

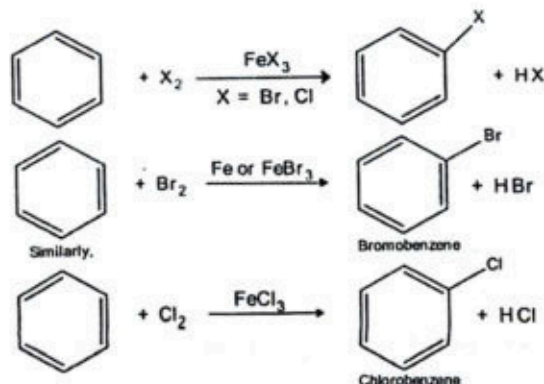
- Alkyl halides, in which a halogen atom is attached to a tertiary carbon are called tertiary alkyl halides. Tertiary carbon is carbon to which three alkyl groups are attached.



Alkyl halides have high melting and boiling points as compared to Alkanes.

## 9.1 Preparations of Halogenoarenes

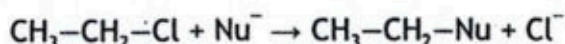
Halogenation of benzene occurs with halogens ( $X_2$ ) in the presence of Fe or Lewis acid catalyst  $\text{FeX}_3$ .





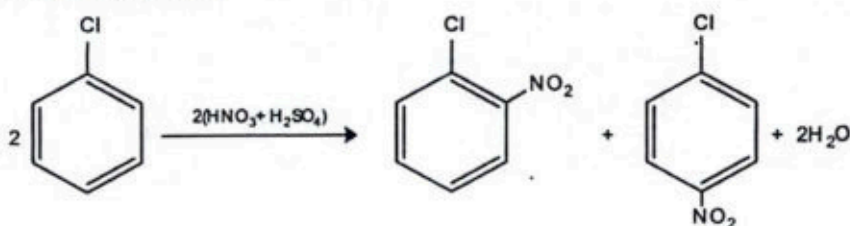
## 9.2 Reactivity of Halogenoalkanes

The strength of the C—X bond is an important factor that determines the reactivity of alkyl halides and aryl halides. The alkyl halide molecule is polarized due to the higher electronegativity of halogens compared to C. Thus, carbon receives a partial positive charge, while the halogens receive a partial negative charge. The halogen becomes nucleophilic in nature, which can be replaced by another nucleophile for example, chloroethane can undergo a nucleophilic substitution reaction. In this reaction, the nucleophile attacks the carbon atom that is attached to the chlorine atom. This results in the replacement of chlorine by a nucleophile.



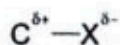
In chlorobenzene, the lone pair of electrons on chlorine atoms are delocalized over the ring, giving the C—Cl bond the character of a partial double bond. Therefore, the C—Cl bond is more difficult to break. Thus, the chlorine atom cannot be replaced by a nucleophile. Chlorine increases the ring electron density due to resonance. Thus, chlorobenzene undergoes an electrophilic substitution reaction. In this reaction, one of the hydrogen atoms of benzene in the ortho and para position is replaced by an electrophile.

For example, nitration of chlorobenzene gives a mixture of o-nitrochloro-benzene and p-nitrochloro-benzene is obtained.



## 9.3 Reactions of Halogenoalkanes or Alkyl Halides

In an alkyl halide molecule, the carbon-halogen bond is polarized due to the more electronegative nature of halogen than carbon. So, halogen atoms induce dipolar character in carbon-halogen bonds. The electron density is drawn more towards halogen atom. As a result, the halogen atom acquires a partial negative charge and carbon atom partial positive charge. This is called the inductive effect.



This polar character of the C—X bond is responsible for characteristic chemical reactions of alkyl halides.

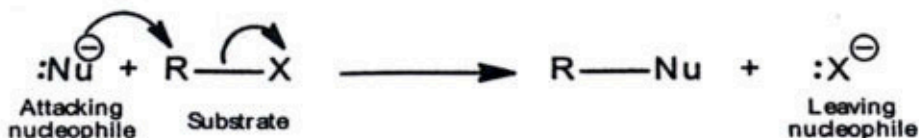
Alkyl halides undergo two types of reactions

- Nucleophilic substitution reactions (S<sub>N</sub> Reactions)
- Elimination reaction

### 9.3.1 Nucleophilic substitution (SN) reactions of Alkyl halides

The reaction in which a halogen atom of an alkyl halide is substituted or replaced by a strong nucleophile is known as the nucleophilic substitution reaction. The general representation of such reactions is given below.

These reactions are called the nucleophilic substitution or SN reactions.



Substrate, nucleophile and Leaving Group

Substrate Molecule

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

Nucleophile

It is species having lone pair of electrons and donate a pair of electrons to electrophilic carbon of alkyl halide. (It may be neutral or negatively charge).

Examples of Nucleophiles

|                                  |                       |                             |              |
|----------------------------------|-----------------------|-----------------------------|--------------|
| $\text{HO}^-$                    | Hydroxide ion         | $\text{NH}_2^-$             | Amino group  |
| $\text{C}_2\text{H}_5\text{O}^-$ | Ethoxide ion          | $\text{Cl}^-$               | Chloride ion |
| $\text{HS}^-$                    | Hydrogen sulphide ion | $\text{Br}^-$               | Bromide ion  |
| $\text{SCN}^-$                   | Thio cyanate ion      | $\ddot{\text{N}}\text{H}_3$ | Ammonia      |
| $\text{H}_2\ddot{\text{O}}:$     | Water                 |                             |              |

Leaving Group (LG)

The halogen of alkyl halide is called the leaving group. The leaving group is also a nucleophile. It departs with an unshared pair of electrons. The incoming nucleophile must be stronger than the departing ones,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{HSO}_4^-$  are good leaving groups. Poor leaving groups are  $\text{OH}^-$ ,  $\text{OR}$  and  $\text{NH}_2^-$ , Iodide ion is a good nucleophile as well as a good leaving group.

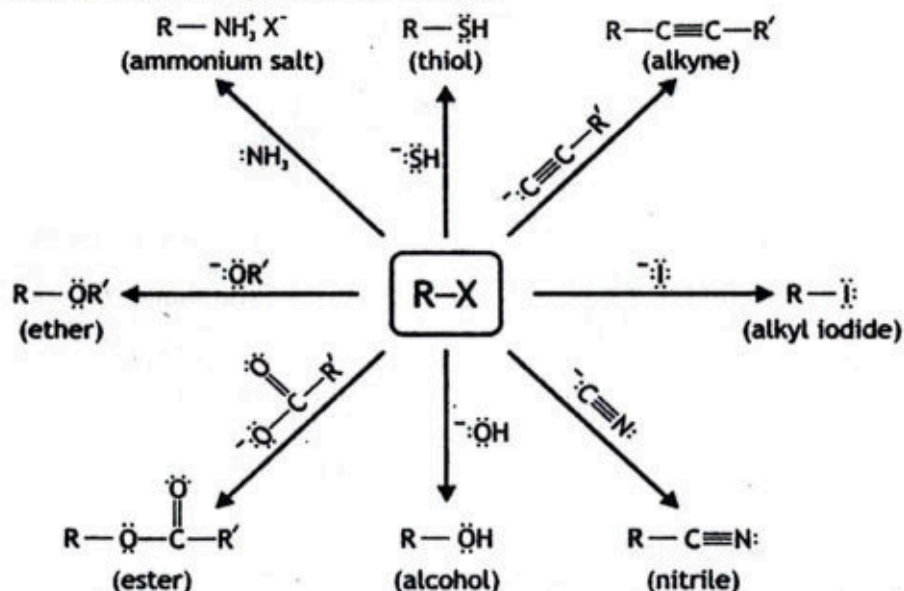
There are two fundamental events in a nucleophilic substitution reaction:

1. Breaking of the  $\delta$  bond between carbon and halogen.
2. Formation of the new  $\delta$  bond between carbon and the attacking nucleophile.

The substitution reaction is greatly influenced by the nature of the attacking nucleophile, the substrate, and the leaving group. In primary or secondary alkyl halides, attack by the incoming nucleophile and displacement of the leaving group occurs in one step, but in bulky tertiary alkyl halides, attack by the incoming nucleophile and displacement of the leaving group occurs in two steps. Thus, these substitution reactions follow two different mechanisms known as  $\text{SN}_1$  and  $\text{SN}_2$  reactions.



## Examples of Nucleophilic Substitution Reactions



## Carbocations and their Stability

## Carbocation

A carbon atom that is attached to three atoms or a group of atoms and possesses a unit positive charge is known as carbocation.

## Stability

The general stability order of simple alkyl carbocations is:

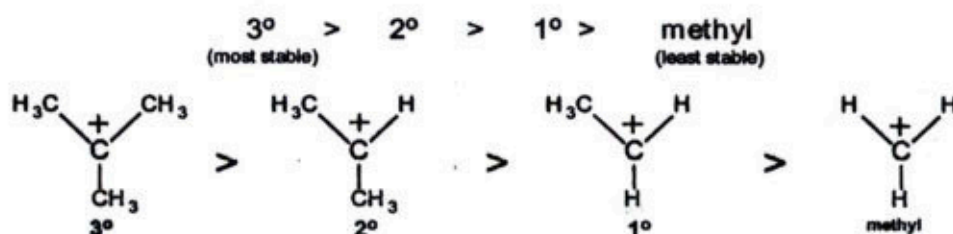


Fig. 9.1 Stability order of carbocations

This is because alkyl groups are weak electron-donating due to hyperconjugation and inductive effects. The stability order of carbocation increases with an increase in alkyl groups.

 $\text{SN}_1$  Mechanism

$\text{SN}_1$  is a unimolecular nucleophilic substitution reaction.

It is two step reaction mechanism in which the substrate  $\text{R-X}$  first ionizes reversibly into Carbonium ion ( $\text{R}^+$ ) and  $\text{X}^-$  ions. This is a slow and rate determining step.



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**Reaction with aqueous silver nitrate:** When a haloalkane reacts with aqueous silver nitrate ( $\text{AgNO}_3$ ), the silver ion ( $\text{Ag}^+$ ) in the solution is exchanged with the halide ion ( $\text{X}^-$ ) in the haloalkane. A precipitate of silver halide is formed. Alkyl fluoride does not react readily with  $\text{AgNO}_3$  because  $\text{C}-\text{F}$  is strong, so fluoride ion is not displaced.



Where  $\text{X}$  is =  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$

The colour of the precipitate depends on the halogens present.

**AgCl:** White precipitate which is soluble in  $\text{NH}_4\text{OH}$  solution.

**AgBr:** Cream coloured precipitate which is partially soluble  $\text{NH}_4\text{OH}$  solution.

**AgI:** Yellow precipitate which is insoluble in  $\text{NH}_4\text{OH}$  solution.

## 9.6 Alkyl Halides and Retrosynthesis

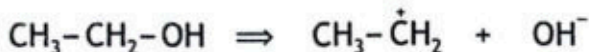
Alkylhalides are good starting materials to produce a verity of organic compounds. You can break down the analysis of a reaction pathway involving halogenoalkane. Consider the reaction between a haloalkane and a nucleophile. The mechanism involves the nucleophile attacking the carbon bonded to the halogen atom and the halogen departs.



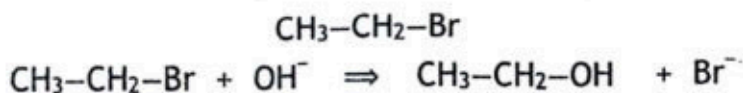
Let's perform retro-synthesis to deduce the starting materials. For this, we work backwards from the product  $\text{R-Nu}$  to identify the starting materials. For this purpose you can consider the following reaction.



The starting material for this reaction is a haloalkane which could give the same product. Suppose you want to prepare ethyl alcohol. To find the starting compound, work backwards from ethyl alcohol.



So, starting material for this reaction is:



### KEY POINTS

- Halogenoalkanes, also known as alkyl halides are compounds in which one hydrogen atom of alkanes has been replaced by a halogen atom.
- Halogenation of benzene occurs with halogens ( $\text{X}_2$ ) in the presence of  $\text{Fe}$  or Lewis acid catalyst  $\text{FeX}_3$ .
- The alkyl halide molecule is polarized due to the higher electronegativity of halogens compared to  $\text{C}$ .
- In chlorobenzene, the lone-pair of electrons on chlorine atoms is delocalized over the ring, giving the  $\text{C}-\text{Cl}$  bond the character of a partial double bond.
- The reactions in which the halogen atom of an alkyl halide is substituted or replaced by a strong nucleophile are known as nucleophilic substitution reactions.

- A carbon atom that is attached to three atoms or a group of atoms and possesses a unit positive charge is known as carbocation.

The general stability order of simple alkyl carbocations is:



- $\text{S}_\text{N}1$  is two-step reaction mechanism in which the substrate  $\text{R-X}$  first ionizes reversibly into Carbonium ion ( $\text{R}^+$ ) and  $\text{X}^-$  ions.
- $\text{S}_\text{N}2$  is a Bimolecular nucleophilic substitution reaction that occurs in a single step.
- A common test to assess the reactivity of haloalkanes is their reaction with aqueous silver nitrate ( $\text{AgNO}_3$ ).
- Alkyl halides are good starting materials to produce a variety of organic compounds.

## EXERCISE

### 1. Multiple Choice Questions (MCQs)

- i. Which catalyst is commonly used in the halogenation of benzene with  $\text{Cl}_2$  or  $\text{Br}_2$ ?  
 a)  $\text{H}_2\text{SO}_4$                       b)  $\text{FeCl}_3$                       c)  $\text{AlCl}_3$                       d)  $\text{NaOH}$
- ii. In the reaction of benzene with  $\text{Cl}_2$  in the presence of a catalyst, the product is:  
 a) Chloromethane                      b) Chlorobenzene  
 c) Dichloromethane                      d) Benzyl chloride
- iii. What is the major product of the reaction between benzene and  $\text{Br}_2$  with  $\text{FeBr}_3$  as a catalyst?  
 a) Benzene bromide                      b) Bromobenzene  
 c) Dibromobenzene                      d) Bromomethane
- iv. Which mechanism do primary halogenoalkanes typically follow in nucleophilic substitution reactions?  
 a)  $\text{S}_\text{N}1$                       b)  $\text{S}_\text{N}2$                       c)  $\text{S}_\text{N}1$  and  $\text{S}_\text{N}2$  both                      d) None of these
- v. What type of bond is broken in the nucleophilic substitution reaction of a halogenoalkane?  
 a)  $\text{C-H}$                       b)  $\text{C-O}$                       c)  $\text{C-X}$  (where X is a halogen)                      d)  $\text{C-C}$
- vi. Which factor does NOT significantly affect the rate of  $\text{S}_\text{N}1$  reactions?  
 a) Stability of the carbocation                      b) Solvent polarity  
 c) Strength of the nucleophile                      d) Leaving group ability
- vii. Which halogenoalkane is more reactive in an  $\text{S}_\text{N}2$  reaction?  
 a) Chloromethane    b) Chlorobenzene    c) Chloroethane    d) All of these
- viii. The  $\text{C-Cl}$  bond in chlorobenzene is less reactive towards nucleophilic substitution because:  
 a) The  $\text{C-Cl}$  bond is too strong                      b) The phenyl ring stabilizes the chlorine  
 c) Resonance effect makes the bond partially double  
 d) Steric hindrance from the benzene ring